THE UNIVERSITY OF HULL

The Determination of the Core Structure and Core Surfactant Interface in Overbased Detergents.

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by

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Abstract

Overbased detergents are oil additives, which are included in oil to neutralise the acids that are generated as by-products during the combustion process within an engine. These overbased detergents have been investigated on an atomic scale by the preparation and characterisation of pure model complexes with relevant metal ions and ligands. Group 2 metal ion complexes have been prepared with sulfurised alkylphenol ligands from a range of conditions. The complexes prepared from methanol have shown that calcium cations and strontium cations give isostructural complexes and that the alkyl chain has a minimal effect on the structures of the complexes. In the solid state, the complexes all have the formula $M_2L_2.6MeOH$. Calix[8]arene complexes have been prepared, including a mixed metal ion complex with an ion-channel structure. Three calcium cation complexes have been prepared with calix[8]arene ligands, where two of the complexes are mimics for the precursors for overbased detergents as they contain calcium hydroxide cores. One of the complexes has a tetranuclear $Ca_4(OH)_4$ core and has shown that the conversion of the calcium hydroxide core to the calcium carbonate core in an overbased detergent is a facile reaction. The second precursor mimic contains a decanuclear calcium cation core and has the formula $(Ca^{2+})_{10}(\mathbf{BC8}^{5-})_2(OH^-)_8(OMe^-)_2(DMF)_{10}.5DMF$. An unusual monodentate carboxylic acid complex with calcium has been prepared which utilised ligand design to achieve the desired monodentate coordination. Finally, a novel complex containing calcium cations and carbonate anions has been prepared, which has the formula $Ca_{10}(\mathbf{M2}^{2-})_8(CO_3^{2-})_2(\mathbf{DMPD})_4(MeOH)_4.8acetone$. This complex contains μ_6-CO_3^{2-} anions and can be considered to be a model for overbased detergents.

Dedication

This thesis is dedicated to Mrs Anne Waller to say thank you for the 'brains' and to help her in her battle against cancer. Thank you Great Aunt Anne!

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There are many people who deserve my thanks and sorry if you're not on the list, I'll thank you personally some other time (the list could only be so long). For my acknowledgements, I've split people up into five random groups; financial, supervisors, technical, university and miscellaneous.

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Notes

All of the single crystal x-ray structures have been solved by Dr. J. D. Crane, except for the initial solution for the tetrabutylammonium cation salt with **IC8**, which was done by Jens Richter and Stefan Menzer (Stoe) and two of the calcium cation complexes (the calcium cation complex with **IC8** and the first calcium cation complex with **BC8**), which were solved by Dr. Andres Goeta at Durham University.

All of the crystal structures shown are as ORTEP views, using the Ortep32 programme. Carbon is represented in grey, hydrogen in black spheres, nitrogen in light blue, sulfur in yellow, oxygen in red, metal cation (or Group 2 metal cation in mixed metal ion complexes) in green, other metal cation in blue, silicon in pink and phosphorus in orange.

The bond lengths and bond angles for the crystal structures given in this thesis do not include error values, these are available in the appendices.

The p-*tert*-butylcalix[8]arene used in the preparation of complexes was prepared by Dr. N. P. Clague.

Abbreviations

Abbreviation	**Full Name**
A2	2,2'-Thiobis-(4-*tert*-amylphenol)
ACHM	2-[(Adamantane-1-carbonyl)-amino]-5-methylbenzoic acid
ACM	2-[(Adamantane-1-carbonyl)-amino]-6-methylbenzoic acid
B2	2,2'-Thiobis-(4-*tert*-butylphenol)
BC8	para-*tert*-Butylcalix[8]arene
BHPD	1,4-Bis-(2-hydroxyethyl)-piperazine-2,3-dione
Bu_4N^+	Tetrabutylammonium cation
CN	Coordination number
DBPD	1,4-Di-*tert*-butylpiperazine-2,3-dione
DCM	Dichloromethane
DEF	*N,N*-Diethylformamide
DHB2	2,2'-Thiobis-(4-*tert*-butylcatechol)
DMF	*N,N*-Dimethylformamide
DMI	1,3-Dimethylimidazolidinone
DMPD	1,4-Dimethylpiperazine-2,3-dione
DMSO	Dimethylsulfoxide
DOM2	2,2'-Sulfonylbis-(4-methylphenol)
DTMC	2,6-Bis-(2,2-dimethylpropionylamino)-benzoic acid
EG	Ethylene glycol
EXAFS	Extended x-ray absorption fine structure spectroscopy
I2	2,2'-Thiobis-(4-isopropylphenol)
IC8	para-Isopropylcalix[8]arene
IR	Infrared
KOH	Potassium hydroxide
M2	2,2'-Thiobis-(4-methylphenol)
MeOH	Methanol
MOM2	2,2'-Sulfinylbis-(4-methylphenol)
MS	Mass spectrometry
NMR	Nuclear Magnetic Resonance
O2	2,2'-Thiobis-(4-*tert*-octylphenol)
SAP	Sulfurised alkylphenol
THF	Tetrahydrofuran
TMCHM	2-(2,2-Dimethylpropionylamino)-5-methylbenzoic acid
TMCM	2-(2,2-Dimethylpropionylamino)-6-methylbenzoic acid

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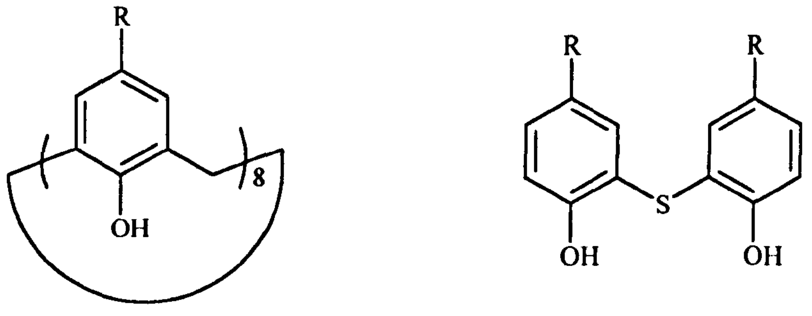
Chapter 1

Introduction

1.1. Introduction to the Project

The aim of this project was to understand the interactions that occur on an atomic scale within overbased detergents. This involved understanding the cores of overbased detergents and the interactions of the core with the polar head-groups of the surfactant molecules. To accomplish the aims of the project, pure model complexes have been prepared and characterised, based upon overbased detergent systems. The complexes that have been prepared have used relevant metal cations and ligands that are the same as the surfactant molecules used in overbased detergents, except with shorter alkyl chains. The shorter alkyl chains confer improved polar solvent solubility on the ligands and improve the crystallinity of the complexes prepared with the ligands. The surfactant molecules, which have been used as ligands in this study, are shown below (figure 1).



Calix[8]arene

Sulfurised alkylphenol

Figure 1. The ligands used in this study, where R indicates an alkyl chain.

These surfactant molecules are used in the preparation of commercial overbased detergents.[1-10] Co-surfactants used in the preparation of overbased detergents, such as ethylene glycol and carboxylic acids, have also been investigated.[1, 6, 10]

Group 1 and Group 2 metal cations have been used in the preparation of complexes, in particular Group 2 metal cations and especially calcium cations, as they are the most relevant.[7, 11]

The complexes, once prepared, have been characterised to determine their structures in the solid state and in solution. The solid state structural analysis has predominantly involved single crystal x-ray diffraction, with supporting information gained from elemental analysis and infrared (IR) spectroscopy. For the solution state structural analysis, nuclear magnetic resonance (NMR) spectroscopy has been the main method utilised, though mass spectrometry (MS) has also been used.

The information acquired from the complexes that have been prepared has been compared to the limited data known about overbased detergents[7, 12] to create hypotheses about overbased detergents on an atomic scale. This information can potentially be used to develop improved overbased detergents.

1.2. Overbased Detergents

The combustion process within an engine can generate organic acids and inorganic acids such as hydrochloric acid, nitric acid and sulfuric acid.[1, 13] For fuel containing high levels of sulfur, such as marine fuel, which can contain up to 5% of sulfur, the generation of sulfuric acid is a significant problem.[7, 13, 14] These acids, if not neutralised, can corrode the engine, leading to reduced lifetime and efficiency.[7] Overbased detergents are oil additives, which are included in oil to neutralise the acidic materials and thus protect the engine from degradation.[5, 15] These overbased detergents consist of a basic mineral core, which, as the core is insoluble in oil, is coordinated to surfactant molecules to create an oil soluble reverse micelle.[7, 13, 16] The most common core material is calcium carbonate, though other metal cations can be used or incorporated, such as magnesium, barium, sodium, potassium and zinc.[3, 7, 11] The surfactant molecules include sulfurised alkylphenols, calixarenes, salicylic acids and sulfonic acids, where the choice of surfactant is determined by factors such as cost, ability to stabilise large cores and additional additive benefits such as antioxidancy and dispersancy.[3, 5, 10] Co-surfactants can also be used, such as carboxylic acids.[1] A schematic diagram of an overbased detergent reverse micelle is shown below (figure 2).

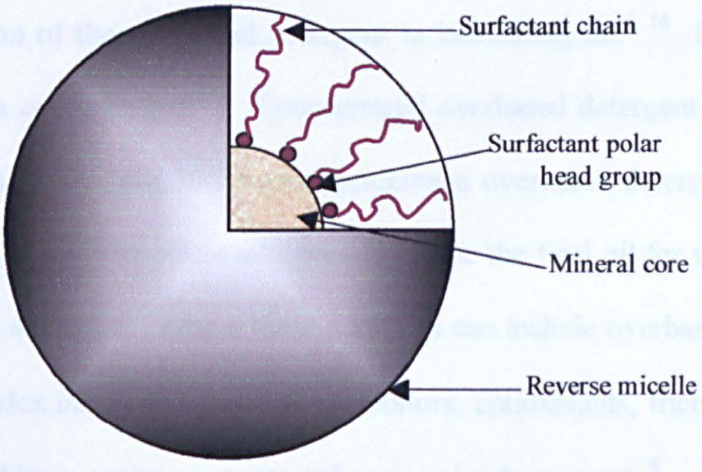
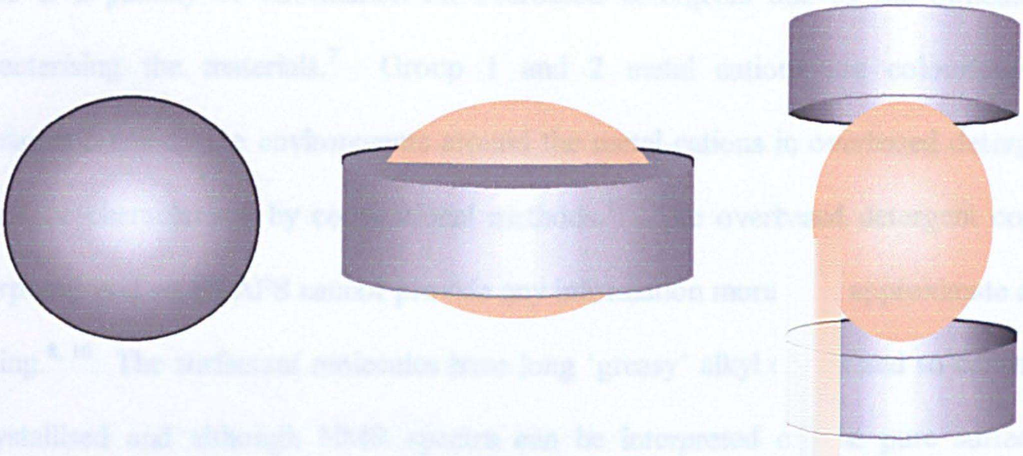


Figure 2. Schematic diagram of an overbased detergent micelle.

A normal calcium carbonate core consists of amorphous calcium carbonate and has a diameter of approximately 1.25nm.[8] The core contains approximately ten to sixteen calcium carbonate units, where the number of units is determined by the preparation method and surfactant molecules.[7, 8] Typical overbased detergents have diameters of 2-5nm.[10] The basicity of the overbased detergents is measured as total base number, which compares the basicity of the overbased detergent to potassium hydroxide.[11] Total base numbers of up to 500 can be achieved in overbased detergents,[7] which can be compared to the total base number of calcium carbonate which is 1122.[10] The term 'overbased' comes from the fact that overbased detergents contain a stoichiometric excess of calcium ions to molecules of surfactant.[4, 8, 14] Overbased detergents are believed to neutralise acids by base transfer from the overbased detergent micelle into the acid droplet.[13, 16] Although overbased detergents are classed as reverse micelles, they are not true classical micelles in that the rate of surfactant exchange is negligible.[9, 14]

Overbased detergents are prepared by a relatively simple route. Surfactant and co-surfactant (if used) are mixed in lubricating oil and then solvent and calcium hydroxide are added to give a colloidal mixture. The mixture is stirred at elevated temperatures before carbon dioxide is added. The solvent is then removed and the sediment filtered off to give a solution of the overbased detergent in lubricating oil.[1, 16] Stearic acid is commonly used as a co-surfactant.[1, 6] Concentrated overbased detergent solutions can be generated by this route, with 50-70 mass percentage overbased detergent in the oil, which can be added along with other additives to create the final oil for use.[5] Modern oils contain 10-20% additives,[15] where these additives can include overbased detergents (*op cit*), viscosity index improvers, corrosion inhibitors, antioxidants, friction modifiers, dispersants, rust inhibitors, antiwear agents and pour point depressants.[5]

Molecular modelling of overbased detergents has provided information about the shapes of overbased detergents, which has shown that the shape is dependent on the surfactant.[7, 9, 10, 14] The diagram below (figure 3) shows the shapes of overbased detergents with sulfonic acid, salicylic acid, sulfurised alkylphenol and calix[6]arene surfactant molecules.



Sulfonic acid and salicylic acid overbased detergent micelles

Sulfurised alkylphenol overbased detergent micelle

Calix[6]arene overbased detergent micelle

Figure 3. Schematic diagram of the shapes of overbased detergents with a range of surfactant groups.

Sulfonic acid and salicylic acid overbased detergents are spherical, whereas sulfurised alkylphenol overbased detergents are oblate spheroid and calix[6]arene overbased detergents are prolate spheroid.[7, 10] The cores within the particles are also only spherical for sulfonic acid and salicylic acid overbased detergents.[7, 9, 10] The non-spherical nature of the sulfurised alkylphenol overbased detergents results in the micelles aggregating in solution.[9] With co-surfactants included in the overbased detergents though, all of the surfactant molecules give spherical particles.[10] The shapes of overbased detergents with calix[8]arene surfactant molecules have not been characterised, though these probably possess the same shape as the calix[6]arene overbased detergents. Calix[8]arene surfactant molecules are used in commercial overbased detergents in preference to calix[6]arene surfactant molecules as larger cores can be stabilised and a smaller amount of sediment is generated in the overbasing process.[6] Calixarene surfactant systems are replacing traditional sulfonic acid and sulfurised alkylphenol overbased detergent systems due to international legislation, which is reducing the percentage of sulfur that can be included within oils.[1, 2, 6]

There is a paucity of information on overbased detergents due to the difficulty in characterising the materials.[7] Group 1 and 2 metal cations are colourless and diamagnetic and so the environments around the metal cations in overbased detergents cannot be characterised by conventional methods.[17] The overbased detergent core is amorphous and so EXAFS cannot provide any information more than approximate atom spacing.[8, 10] The surfactant molecules have long 'greasy' alkyl chains and so cannot be recrystallised and although NMR spectra can be interpreted on the pure surfactant molecules, overbased detergents give complicated, noisy spectra with very poor resolution.[8] Molecular modelling can provide theoretical information and physical chemical techniques, such as Langmuir trough measurements, can provide information about the shape and size of the micelles, though none of these methods can define overbased detergents on an atomic scale. This study aims to address this area of investigation.

1.3. Group 2 Element Chemistry

The *s*-block of the periodic table contains the Group 1 and Group 2 elements, where Group 1 elements are known as alkali metals and Group 2 elements are known as the alkaline earth metals. The Group 2 metals are beryllium, magnesium, calcium, strontium, barium and radium, though beryllium has different properties to the other members of the Group and radium is radioactive. The Group 2 metal cations relevant to this work are magnesium, calcium, strontium and barium and henceforth 'Group 2' will refer to these elements.

In general, the Group 2 metal cations are divalent, electropositive, hard, Lewis acids and prefer coordination to hard donors such as oxygen and nitrogen.[18] The heavier Group 2 metal cations (calcium, strontium and barium) form predominantly ionic compounds, whereas magnesium cation compounds tend to have more covalent character.[18, 19] The ionic nature of the heavier Group 2 metal cations is the same as the Group 1 metal cations. The heavier Group 2 metal cations also behave similarly to divalent lanthanide metal cations, such as europium, samarium and ytterbium, in complexes.[19-22] The table below (table 1) summarises some of the general information about Group 2 metal cations.

	Magnesium	**Calcium**	**Strontium**	**Barium**
Atomic radius (Å)[18]	1.60	1.97	2.15	2.24
Ionic radius (for CN 6) (Å)[18]	0.72	1.00	1.16	1.36
Normal CN range	4-8	5-10	6-10	6-12
Preferred CN[23]	6	6 or 8	6 or 8	6 or 8
Biologically[24]	Essential	Essential	Trace element	Trace element
Natural abundance[25]	2.10%	3.63%	42ppm	39ppm
Number of naturally occurring isotopes[26]	3	6	4	7

Table 1. Table to summarise some general properties of Group 2 elements, where CN refers to coordination number.

Magnesium cations most often form octahedral six coordinate complexes, whereas the heavier Group 2 metal cations form complexes with ranges of geometries and coordination numbers.[27-29] Very low coordination number complexes have been characterised for all of the heavier Group 2 metal cations, including barium cation complexes where the barium cations have coordination numbers of three, four and five.[30-34] The structure of the three coordinate barium cation complex is shown below (figure 4).[30]

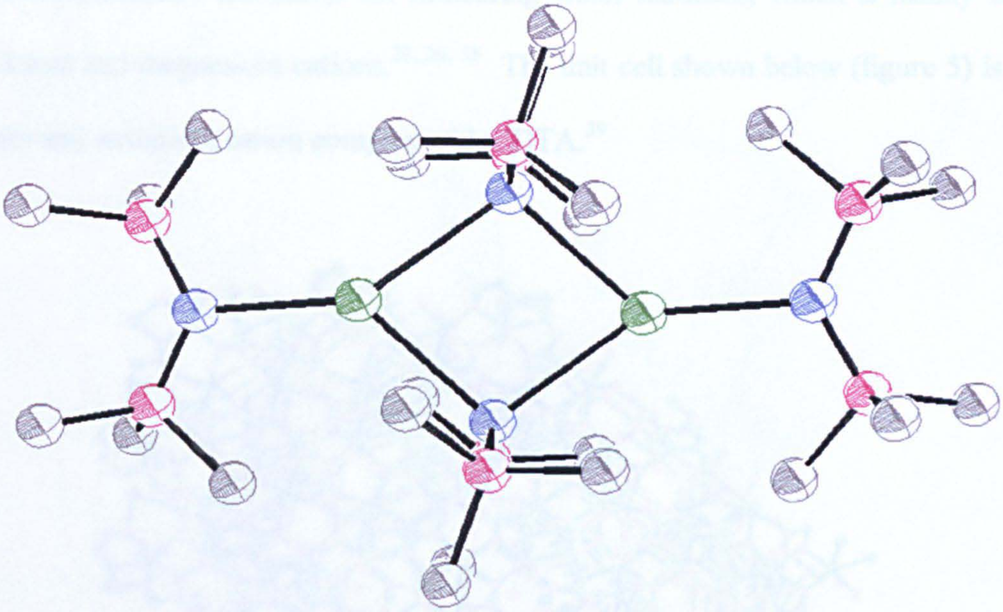


Figure 4. A barium cation complex, bis-(μ-2-bis-(trimethylphenylsilyl)-amido)-barium, where the barium cations (shown in green) have a coordination number of three.

For the low coordination number complexes, large, bulky ligands are usually used. The characterisation of complexes with the heavier Group 2 metal cations possessing very low and high coordination numbers shows the structural versatility of the cations.[26, 34]

The Group 2 metal cations prefer complexation to polydentate ligands, such as crown ethers and polycarboxylic acids.[18] For magnesium, this complexation is usually as a second sphere interaction due to the high affinity of magnesium cations for water molecules.[27] Magnesium cations most often form hexaaqua cationic units, which interact with ligands *via* hydrogen-bonding. The heavier Group 2 metal cations coordinate directly to ligands, most often to oxygen atoms. Solvent molecules, such as water molecules, fill the coordination spheres of the heavier Group 2 metal cations and in general are not coordinated in preference to ligand hard donor atoms. The predilection for polydentate ligands enables the concentrations of Group 2 metal cations in solution to be measured. For example ethylenediaminetetraacetic acid (EDTA) titration experiments are useful for measuring water hardness, which is mainly caused by calcium and magnesium cations.[23, 26, 35] The unit cell shown below (figure 5) is for a calcium and strontium cation complex with EDTA.[39]

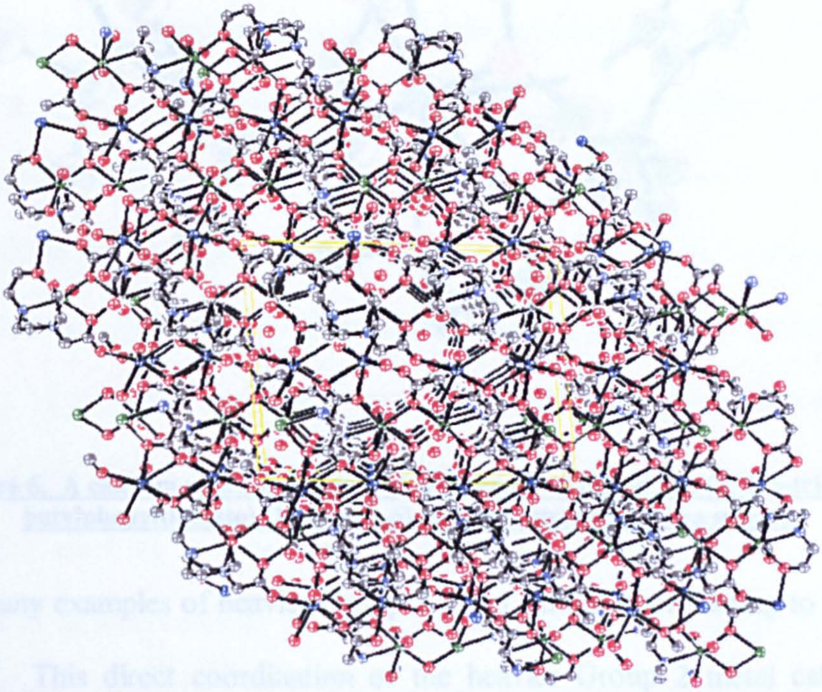


Figure 5. Unit cell of a calcium and strontium cation complex with EDTA, where calcium cations are represented in green and strontium cations are represented in blue.

The structure above (figure 5) shows extensive bridging between the ligand molecules and the metal cations. The structure shown below (figure 6) is a calcium cation complex with a crown ether ligand.[40]

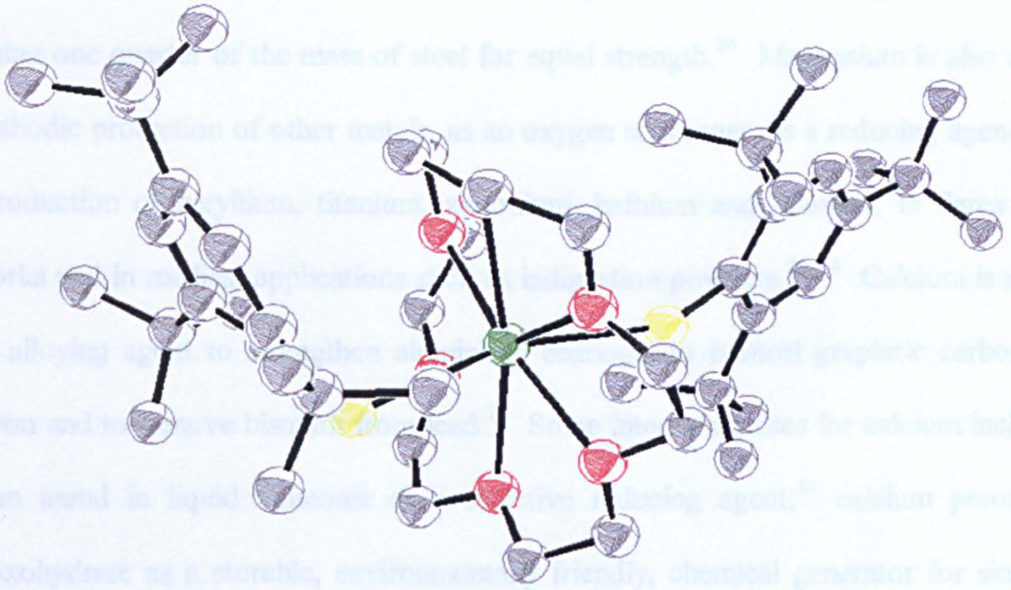


Figure 6. A calcium cation complex with a 18-crown-6 ligand, bis-(2, 4, 6-tri-*tert*-butylphenylthiolato)-(18-crown-6)-calcium tetrahydrofuran solvate.

There are many examples of heavier Group 2 metal cations coordinating to crown ether ligands.[41, 42] This direct coordination of the heavier Group 2 metal cations to the optimum number of the donor atoms in a ligand causes the large range in coordination numbers and geometries that are observed for these metal cations.

Group 2 elements, in particular strontium and barium, are very important elements in the preparation of high temperature superconductors and electronic materials.[34, 43-46] The first continuous wave operation blue-green laser diode which worked at ambient temperature was ZnMgSSe.[43] Other electronic materials containing Group 2 metal cations include BaO-TiO$_2$ compounds, YBa$_2$Cu$_3$O$_{7-x}$, SrSiCe and Ba$_{1-x}$Sr$_x$TiO$_3$.[47, 48] These materials are usually produced by vapour deposition techniques (MOCVD), where the formation of the necessary volatile, soluble, precursors has attracted much recent attention.[47-51]

Magnesium is used in the construction industry, such as in aircraft, as it is the lightest construction metal.[22, 52] The low density of magnesium results in magnesium alloys weighing one quarter of the mass of steel for equal strength.[26] Magnesium is also used for cathodic protection of other metals, as an oxygen scavenger, as a reducing agent for the production of beryllium, titanium, zirconium, hafnium and uranium, in flares and fireworks and in medical applications such as indigestion powders.[26, 34] Calcium is used as an alloying agent to strengthen aluminium bearings, to control graphitic carbon in cast-iron and to remove bismuth from lead.[26] Some interesting uses for calcium include calcium metal in liquid ammonia as a selective reducing agent,[53] calcium peroxide diperoxohydrate as a storable, environmentally friendly, chemical generator for singlet oxygen[54] and ^{48}Ca used in conjunction with $^{244 \text{ or } 242}$Pu to prepare element [114].[55] A nickel and barium alloy is used for spark plug wire as it has high emissivity.[26] Barium sulfate is also used as a non-toxic imaging agent for diagnosing gastrointestinal conditions such as ulcers due to its insolubility and opacity to x-rays.[56] The uses for barium are limited by its high toxicity in compounds which are soluble.[34] There are very few references to uses for strontium.

Strontium (^{90}Sr) has a half life of 29 years and along with $^{137 \text{ and } 135}$Cs is one of the long-life β/γ emitters, which if present, cause nuclear waste to be classified as high activity liquid waste.[57] High activity nuclear waste has to be cooled for at least ten years and disposed of in geological formations after embedding.[57, 58] It is believed that ^{90}Sr contamination, such as would be caused by a nuclear energy plant disaster, would result in ^{90}Sr getting into grass, then milk and then bones, which would have a serious long term impact due to the similarity of strontium to calcium.[34] To declassify the waste, it is necessary to remove the strontium and caesium, which can then have alternative uses, for example ^{90}Sr can be used for continuous electrical power.[58] The method for removal of the elements has to be selective due to the high concentrations of sodium in the waste[59] and recently research has focussed on derivatised calixarenes for selective extraction.[57-60]

In Nature, calcium and magnesium are essential elements, though they do have different roles.[61-63] Magnesium is important in DNA, protein synthesis, enzyme activation, nerve impulse transmissions, muscle contractions and metabolism of carbohydrates.[64] Magnesium is the metal cation in chlorophyll, which enables green plants to carry out photosynthesis.[26] The structure of chlorophyll a is shown below (figure 7).[34]

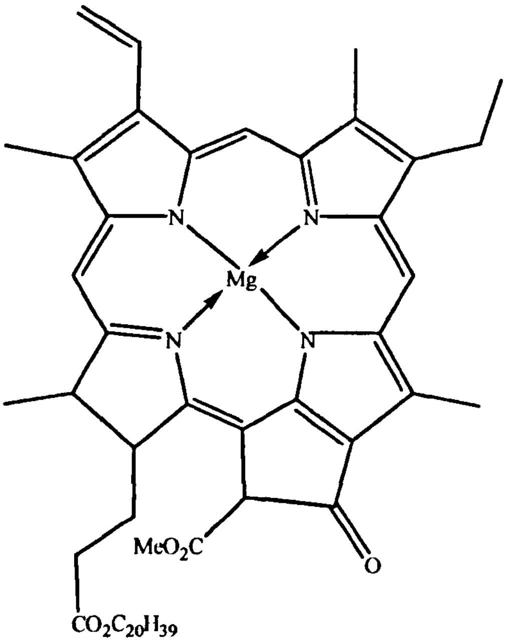


Figure 7. Schematic diagram of chlorophyll a.

Calcium is important in biological structure, maintaining heart rhythm, hormone messaging, muscle triggering, initiating blood clots and protein stabilisation.[18, 26] Calcium is the most prominent metal in structural biology and in higher animals is the most abundant inorganic element.[24, 35] Dry human matter consists of approximately 4.8% calcium.[35] Magnesium and calcium cations tend to form complexes in biology with carboxylic acid residues and with water molecules,[28] where the magnesium cations have a coordination number of six and the calcium cations tend to have a range of coordination numbers with seven and eight being most common.[33, 62] Strontium is an antagonist for calcium cations and so can accumulate in bones and teeth[37, 61] and barium is an antagonist for potassium[61]. Barium forms compounds which can be toxic to mammals if soluble and causes typical heavy metal poisoning.[34, 38]

Magnesium is found naturally in many ores such as magnesite, dolomite, kieserite and carnallite and also in seawater as magnesium chloride.[36] Magnesium is the eighth most abundant metal in the Earth's crust, though calcium is more abundant, where it is the most common metallic element in the Earth's crust and the third most common metallic element overall, after aluminium and iron.[22, 26, 35, 36] The most widespread mineral forms of calcium are calcite and gypsum. Calcium is found in high concentrations in natural water and seawater, where in natural water, the concentration of calcium cations dictates the hardness of the water and can constitute up to 25% of the dissolved solid.[35] Strontium is the least abundant of the Group 2 elements, with the Earth's crust only containing 0.02-0.03%.[37] This makes strontium the fifteenth most abundant element.[26] The two main ores which contain strontium are celestite and strontianite, though strontium is also found in seawater.[37] Barium is slightly more abundant in the Earth's crust than strontium, though is present in significantly lower concentrations in seawater than strontium.[38] Barium is the fourteenth most abundant element.[26] The main mineral source of barium is barite.[38]

The organometallic chemistry of Group 2 metal cations is largely limited to magnesium, where Grignard compounds (RMgX) are very important compounds in organic chemical synthesis.[65] Magnesium has some covalent character, which assists in the formation of organometallic compounds. The progress of development of heavier Group 2 metal cation organometallic chemistry has been hampered by the low reactivity of the cations, the high reactivity of the products and the low solubilities of the cations and products.[66, 67] Some heavier Group 2 organometallic compounds have been prepared and have found uses, including an allyl barium compound for selective catalysis,[68] benzyl calcium and benzyl strontium compounds as living initiators for styrene polymerisation[69, 70] and aryloxide and alkoxide barium compounds for organometallic vapour deposition[50]. The structure of the first structurally characterised heavy Group 2 metal organometallic complex is shown below (figure 8).[50, 66, 71]

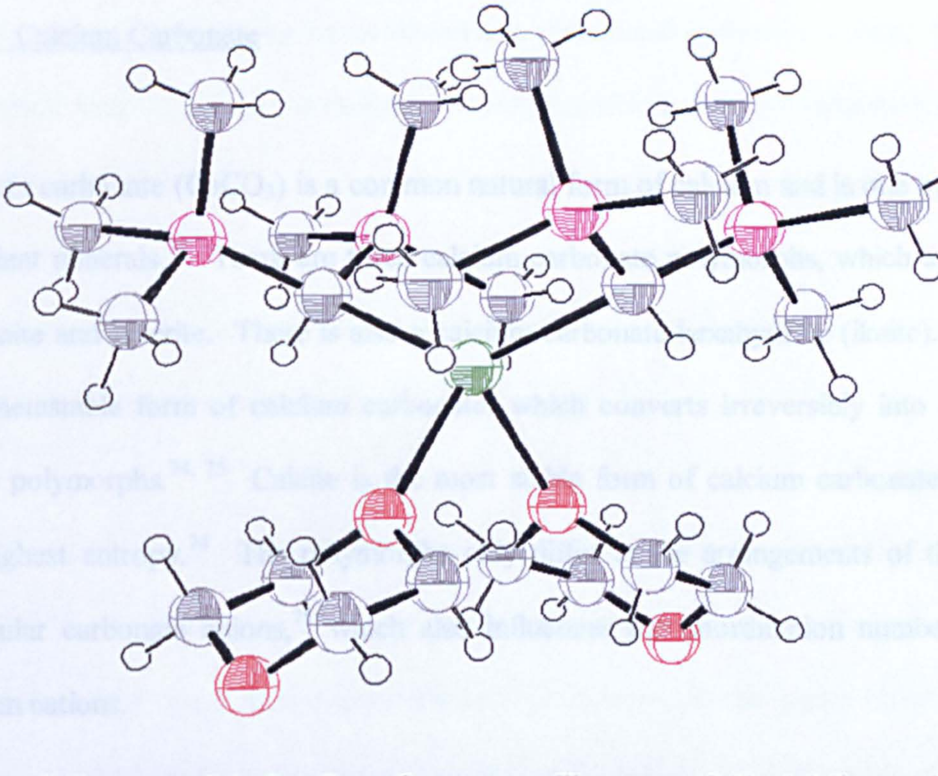


Figure 8. Structure of the first Group 2 organometallic compound, bis-(1,4-dioxane)-bis-(bis-(trimethylsilyl)-methyl)-calcium, where silicon is shown in pink.

This compound contains a tetrahedral calcium cation and has the formula $[CaR_2(1,4\text{-dioxane})_2]$, where R refers to $CH(SiMe_3)_2$.[71] The organocalcium compound $[Ca(C_5H_5)_2]$ is structurally unique and includes the first structurally characterised example of η^1, η^3 and η^5-C_5H_5 within a compound.[26, 72] An interesting triple-decker organobarium cation complex has been prepared by Sitzmann *et al.*[73] The triple-decker sandwich structure of the complex is a common structural motif in transition metal chemistry, though is quite novel for Group 2 metal cations.[73]

Although there are many uses for Group 2 elements and their complexes, in general Group 2 elements are less well studied than transition metals due to difficulties in characterising the products and the colourless nature of the complexes.[17]

1.3.1. Calcium Carbonate

Calcium carbonate ($CaCO_3$) is a common natural form of calcium and is one of the most abundant minerals.[74] There are three calcium carbonate polymorphs, which are calcite, aragonite and vaterite. There is also a calcium carbonate hexahydrate (ikaite). Vaterite is a metastable form of calcium carbonate, which converts irreversibly into the other stable polymorphs.[74, 75] Calcite is the most stable form of calcium carbonate as it has the highest entropy.[74] The polymorphs only differ in the arrangements of the ideally triangular carbonate anions,[75] which also influences the coordination numbers of the calcium cations.

Calcite contains calcium cations with a coordination number of six and calcium cation to oxygen atoms distances of 2.37Å. The structure of calcite is isomorphous with magnesite (magnesium carbonate).[76] Calcite is the most stable and most common form of calcium carbonate.[74, 77]

Aragonite contains calcium cations with a coordination number of nine and slightly longer calcium cation to oxygen atom distances (2.49Å) than in calcite. The structure of aragonite is isomorphous with strontianite (strontium carbonate) and witherite (barium carbonate).[76] Strontium carbonate and barium carbonate do not have other polymorphs, unlike calcium carbonate.[78]

Vaterite does not have a fixed structure as the carbonate anions are disordered over several possible orientations. The calcium cations are usually six coordinate, which is the same as the coordination number for the calcium cations in calcite. The structure of vaterite has the same layering system in the solid state as the other calcium carbonate polymorphs, with alternating layers of calcium cations and carbonate anions. Vaterite is the kinetic form of calcium carbonate,[74] which transforms into the other polymorphs in the presence of water.[75]

The polymorphs can be differentiated by powder x-ray diffraction, single crystal x-ray diffraction, IR spectroscopy and Raman spectroscopy.[79]

Calcium carbonate is the most abundant mineral in nature.[80] Calcium carbonate is essential for the structure of many animals, including coral and seashells.[26] Calcium carbonate is also used in the glass industry, in cement, in the paper industry, as an antacid, in toothpaste, in structural engineering as a filler for fabrication of polymer composite materials and for improving the mechanical properties of polymers.[23, 26, 79] Calcite is found naturally in compounds such as Iceland spar, limestone, marble, stalagmites, stalactites, coral and pearl.[26, 35] Aragonite is the form of calcium carbonate upon which the Bahamas, the Florida Keys and the Red Sea Basin sit.[26] Vaterite is known to be present in gallstones, sediments, fishotoliths and mollusc shells.[75] Amorphous calcium carbonate normally exists in biology as a precursor for calcite or aragonite, though in the presence of suitable macrocycles/biopolymers and metal ions, amorphous calcium carbonate can be stabilised.[77, 80-86] Some creatures have amorphous calcium carbonate in their skeletons, such as cysoliths in certain plant's leaves and in the exoskeletons of crustaceans.[77] Sea urchins use constrained environments to cause crystalline calcium carbonate (calcite) to adopt unusual shapes, such as curves, when it forms from amorphous calcium carbonate.[81]

Dolomite is a mixed metal ion carbonate compound consisting of $[MgCa(CO_3)_2]$. The Dolomites in Italy consist predominately of dolomite (hence the name), making dolomite a common and important Group 2 metal compound.[26]

Overbased detergents usually include calcium carbonate cores, mainly for financial reasons. In these cores, the calcium carbonate is amorphous,[8, 14] though it may possess some structure to enable the calcium cations to coordinate to the surfactant molecules[7].

1.4. Sulfurised Alkylphenol Molecules

Sulfurised alkylphenol molecules are diphenol molecules where the two phenolic units are linked by a sulfur bridge. Below (figure 9) is a schematic diagram of a sulfurised alkylphenol molecule.

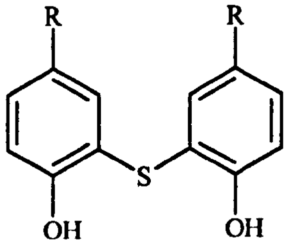


Figure 9. Schematic diagram of a sulfurised alkylphenol molecule.

The 'R' group is usually alkyl. The sulfur atom may be derivatised to sulfinyl or sulfonyl or may even be a disulfur bridge.[87-91] Sulfurised alkylphenol molecules may also consist of more than two phenolic units, such as three or four phenolic units, all linked by sulfur bridges.[92, 93] These alternative structures can be seen schematically below (figure 10).

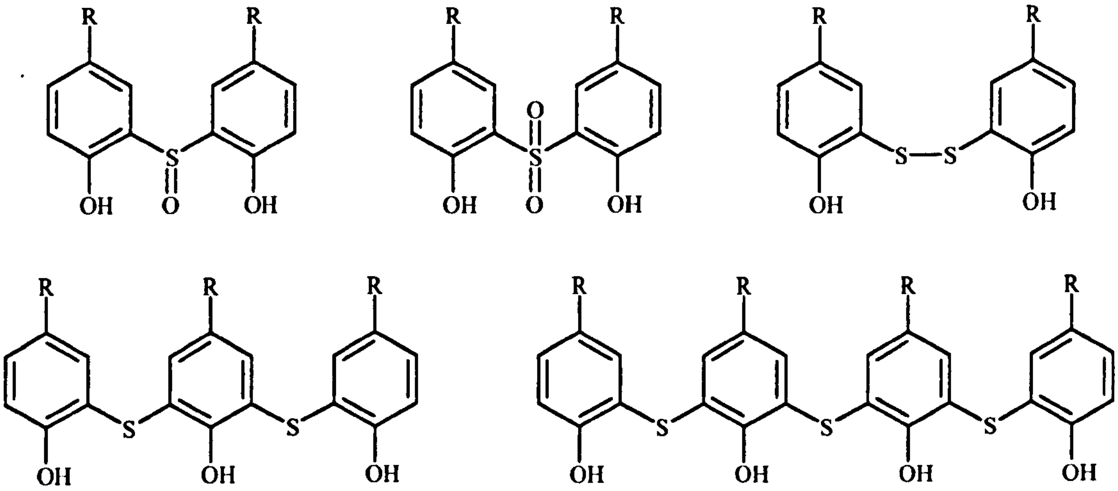


Figure 10. Schematic diagram of some alternative sulfurised alkylphenol molecules.

The number of structurally characterised sulfurised alkylphenol molecules is small, as is the number of structurally characterised sulfurised alkylphenol complexes.[41] Most of the complexes that have been characterised are with transition metals.

There are few published uses for sulfurised alkylphenol molecules, other than as surfactants for overbased detergents, though one potential use is for a nickel cation complex with a sulfurised alkylphenol ligand which has been shown to effectively quench the excited state of diethyl ketone and thus protect materials from photooxidation initiated by aliphatic carbonyl compounds.[94]

Sulfurised alkylphenol molecules are used in overbased detergents, where the alkyl chain is usually dodecyl.[8] This long alkyl chain is sufficient to dissolve the overbased detergents with sulfurised alkylphenol surfactant molecules in oil. Sulfurised alkylphenol molecules have an added advantage of providing some antioxidancy benefits to oil.[4] Unfortunately, sulfurised alkylphenol molecules can decompose to give hydrogen sulfide, which is an environmental pollutant and hence sulfurised alkylphenol overbased detergents are being phased out of use.[1, 6]

1.5. Calixarene Molecules

Calixarene molecules (or $[1_n]$metacyclophanes) are cyclic molecules consisting of phenolic units bridged by methylene groups. The general structure is shown schematically below (figure 11).

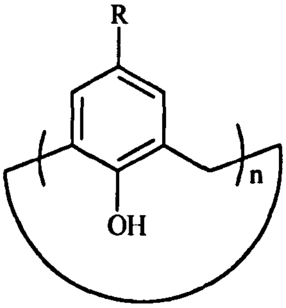


Figure 11. Schematic diagram of a calixarene molecule.

The 'R' group is normally alkyl and the number of repeating units, 'n', covers the range from three up to approximately twenty, though this range is frequently being extended.[95, 96] The number of phenolic units is included in the name of the calixarene as calix[n]arene, where the value in the place of 'n' signifies the number.

Calixarenes were first discovered by von Baeyer in the 1870s, though were not isolated until the 1940s.[97] Originally, the products from the reaction of phenol with formaldehyde were thought to be conformational isomers of a cyclic tetramer (calix[4]arene) and it was many years before the products were characterised as cyclic oligomers with various ring sizes, mainly tetramer, hexamer and octamer.[98] The name 'calixarene' was coined by Gutsche in 1975, due to the similarity of the molecules, in particular the calix[4]arenes, to a vase, or *calix* in Greek.[99] Since the full characterisation of the products, synthetic routes have been developed to prepare the molecules in high and pure yields.[96, 98, 100, 101] Calixarenes are in general well researched due the factors such as their cavity, which makes then ideal host molecules, they are reasonably cheap to prepare and derivatisation is relatively simple.[102]

Calixarenes have found many uses including as accelerators for instant adhesives, stationary phases for field effect transistors, ion scavengers in electronic devices,[97] ion selective electrodes,[97, 103] liquid chromatography,[97, 104] liquid crystals,[105] purification of C_{60},[102, 106] catalysis[107] and purification of liquid petroleum gas[108, 109].

Calixarenes are large flexible molecules, especially the larger calixarenes than calix[4]arene. This flexibility can be reduced by using large bulky alkyl chains, which stops rotation around the methylene bridges and has been a useful strategy for preparing calix[4]arene ligands with fixed 'cone' conformations.[97, 102, 110-112] Calixarene molecules cannot be planar and so many conformations of the ring structures are observed.[97] Most research focuses on calix[4]arenes due to their reduced number of conformations, smaller cavity and simpler characterisation.[95, 113] The cavity within a calix[4]arene molecule is ideally sized to be a host for metal cations such as sodium and calcium, where the radius of the cavity is equal or just slightly larger than the radius of the cation for selection.[97, 102, 110] Calix[6]arenes and then calix[8]arenes are the next most studied calixarene molecules.[95] Some research is carried out on larger calixarenes, such as calix[10]arene,[114] calix[12]arene and calix[16]arene,[115, 116] and synthetic routes exist for calixarene molecules as large as calix[20]arene.[96]

The structure of the first calix[8]arene complex is shown below (figure 12).[117] This complex contains two titanium (IV) cations coordinated to the calixarene molecule.

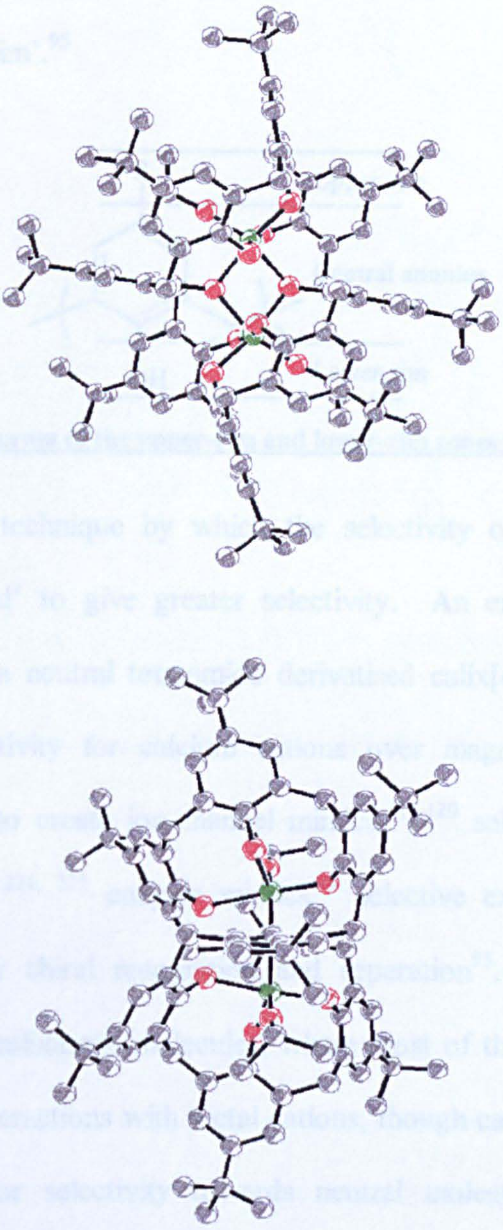


Figure 12. Two views of the first structurally characterised calix[8]arene complex, sodium-(μ-2, 5, 11, 17, 23, 29, 35, 41, 47-octa-*tert*-butyl-49-hydroxy-50, 51, 52, 53, 54, 55, 56-heptaoxycalix[8]arene)-bis-(isopropoxy-titanium (IV)), where a solvent molecule and a co-cation have been deleted for clarity. Hydrogen atoms are not shown.

The complex contains two metal cations coordinated to one calixarene ring. The calix[8]arene ring has twisted to coordinate to the metal cations, almost to give two calix[4]arene coordination environments.

Calixarene molecules can be derivatised at the 'upper-rim' and at the 'lower-rim', where 'upper-rim' refers to the alkyl chain and 'lower-rim' refers to the hydroxide.[95, 102, 111] Lower-rim derivatisation is most common. The diagram below (figure 13) defines 'upper-rim' and 'lower-rim'.[95]

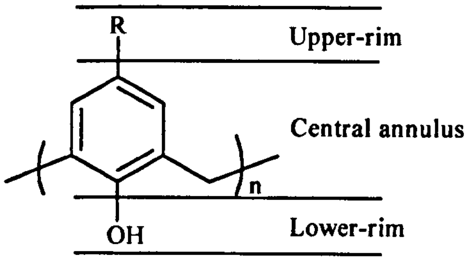


Figure 13. Schematic diagram of the upper-rim and lower-rim zones on a calixarene molecule.

Derivatisation offers a technique by which the selectivity of the parent calixarene molecules can be 'tuned' to give greater selectivity. An example of the potential selectivity is shown by a neutral tetraamide derivatised calix[4]arene molecule which exhibits over 10^7 selectivity for calcium cations over magnesium cations.[97] The selectivity can be used to create ion-channel mimics,[118-120] selective liquid membrane carriers/ion transport,[60, 221, 222] enzyme mimics,[98] selective extractants,[57-59, 97, 123-128] sensors[17, 97, 103] and for chiral recognition and separation[95]. There are numerous examples of derivatised calixarene molecules, where most of the derivatives have been designed for selective interactions with metal cations, though calixarene molecules have also been derivatised for selectivity towards neutral molecules and even anionic species.[129-131] The volume of published work on derivatised calixarene molecules and their complexes far surpasses the amount of literature on the parent calixarene molecules and their complexes. The majority of the literature concerns derivatised calix[4]arene molecules (for example[103, 110-112, 118, 125, 131-144]). Selective hosts for Group 1 metal cations are most common,[59, 110, 118, 121, 122, 125, 127, 134, 136-139, 144, 145] with fewer examples for Group 2 metal cations[17, 59, 60, 126, 140-142] and Lanthanide cations[120, 135, 143].

Below (figure 14) are the schematic diagrams of two of the dervisatised calixarene molecules, which are selective hosts for calcium cations.[17, 140]

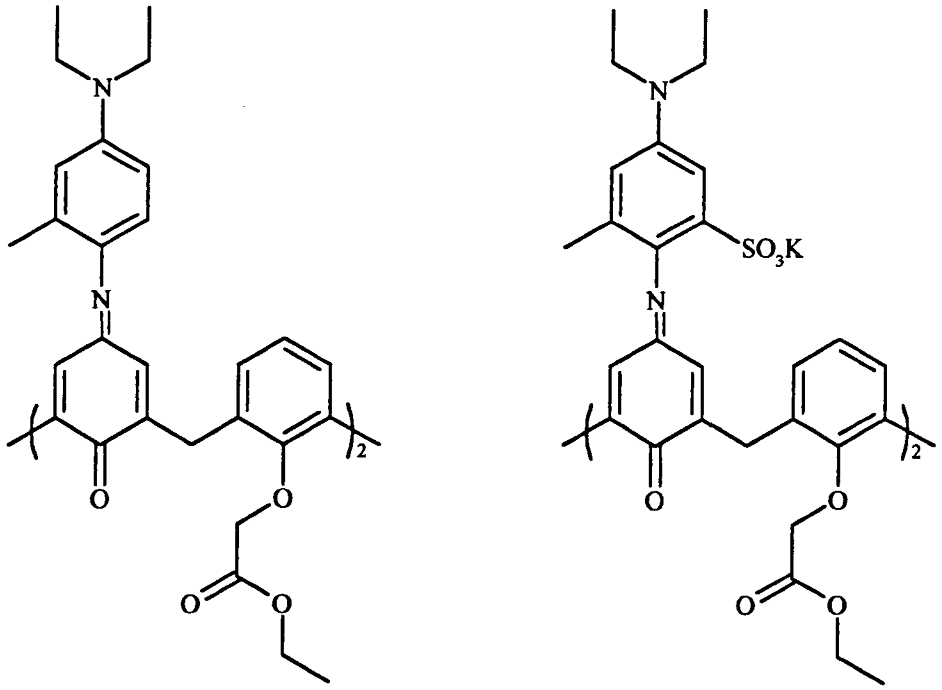


Figure 14. Schematic diagrams of two selective calix[4]arene molecules for calcium cations.

These selective hosts for calcium cations are chromogenic molecules, which enable calcium cation concentrations to be measured in solution. The SO_3K group on the second molecule enables the molecule to be water soluble and so has potential for measuring the concentration of free calcium in physiological samples, such as blood.[17] The molecule exhibits a bathochromic shift upon complexation to calcium cations and detects calcium cations over a range which includes the range for calcium cations in physiological systems (the physiological calcium cation concentration covers the range 1-2mM). The molecule shown below (figure 15) is used commercially for analysing the sodium concentration in blood.[95]

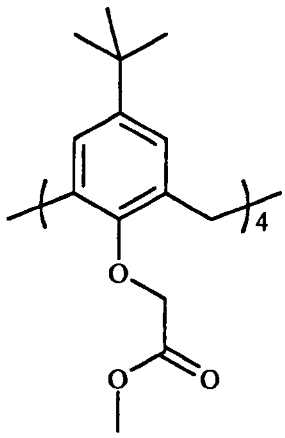


Figure 15. A commercial calix[4]arene molecule for sensing the concentration of sodium cations in blood.

The molecule can be seen to be quite simple, with only a lower-rim derivatisation of p-*tert*-butylcalix[4]arene affording a commercially useful molecule.

A nice example of the use of calixarene selectivity is given by the selectivity of calixarene molecules for buckminsterfullerene C_{60}.[102, 106, 132] p-Phenylcalix[5]arene does not coordinate to C_{70}, only to C_{60} and hence is highly selective.[106] A calix[8]arene molecule (p-*tert*-butylcalix[8]arene) coordinates to C_{60} to give 99.8% purity C_{60} from carbon soot.[102] These calixarene molecules allow C_{60} to be isolated from carbon soot in high purities and high recoveries, using significantly cheaper methods than currently required.[102] Using slightly different alkyl chains, the selectivity of the calixarene molecules can be changed to become highly selective for other fullerenes, such as C_{70}.[132] The diagram below (figure 16) shows the selective calix[5]arene molecule.[106]

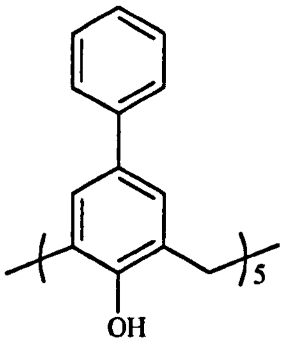
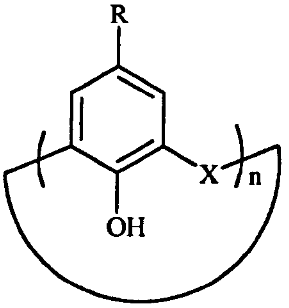


Figure 16. p-Phenylcalix[8]arene, which selectively coordinates to C_{60}.

It can be seen that calixarene molecules are very versatile and can be used for selective coordination.

Calixarene molecules have been prepared with alternative bridging groups between the phenolic units, such as sulfur, nitrogen and oxygen, see diagram below (figure 17).[124, 146-155]



X = S, SO, SO_2, NH, O

Figure 17. Schematic diagram of alternative calixarene molecules.

Sulfur as the bridging atom is the most common.[124, 146, 147, 149-155] The alternative calixarene molecules can be more selective for certain metal cations, such as softer cations if the bridging atom is sulfur. This enables calixarene molecules to become selective hosts for transition metals as apposed to Group 1 and 2 metals.[146, 153]

Overbased detergents with calix[8]arene surfactant molecules have advantages over the traditional overbased detergent surfactant molecules. For example, calix[8]arene surfactant molecules can stabilise large cores, they can provide some antioxidancy, they have good compatibility with other additives, they are slightly water tolerant and they include no sulfur.[156]

Chapter 2

Sulfurised Alkylphenol Complexes

2.1. Introduction

Sulfurised alkylphenol molecules are used commercially as overbased detergent surfactants. The diagram below (figure 18) shows the structure of the sulfurised alkylphenol molecule which is used as an overbased detergent surfactant.[8]

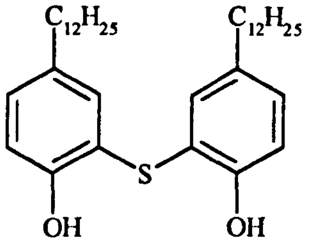
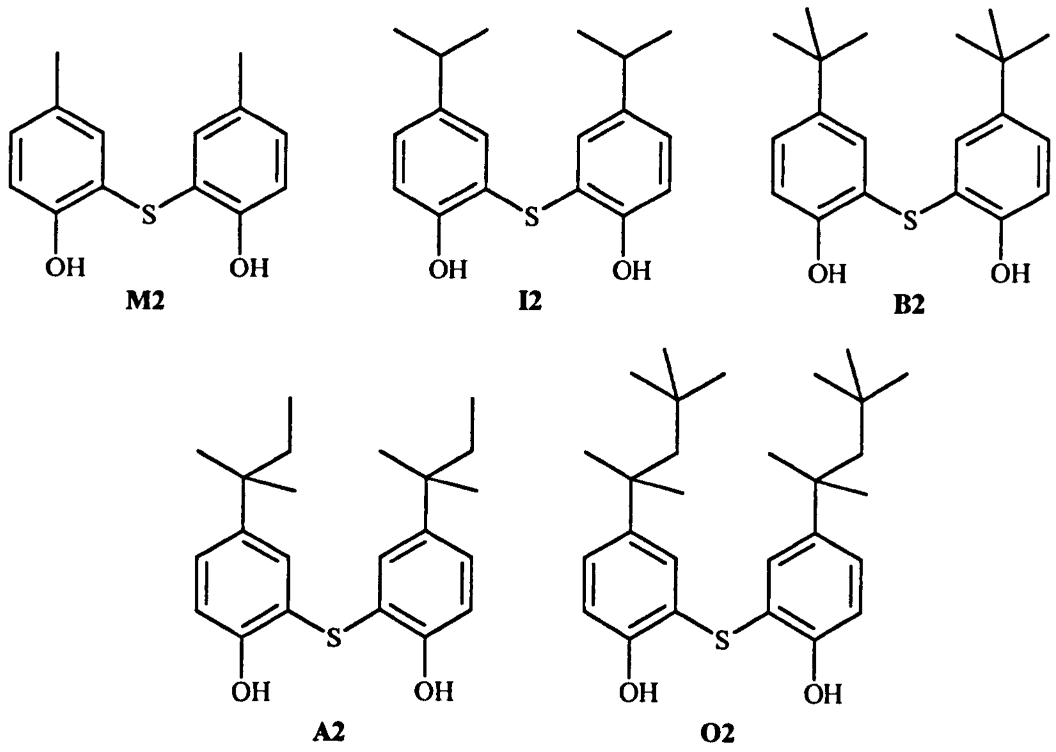


Figure 18. Schematic diagram of the sulfurised alkylphenol molecule used as a surfactant in overbased detergents, where the alkyl group is dodecyl.

The long alkyl chain (dodecyl) makes the surfactant molecule soluble in oil. The sulfurised alkylphenol ligands used in the preparation of complexes in this study are the same as the sulfurised alkylphenol surfactant molecules used in the preparation of overbased detergents, except that the ligands used for complexes have shorter alkyl chains (methyl to *tert*-octyl). The shorter alkyl chains improve the polar solvent solubility and crystallinity of the compounds. Increased polar solvent solubility reduces the technical difficulties associated with the preparation of complexes and simplifies the isolation of the complexes. The increased crystallinity of the molecules caused by the reduction of the long 'greasy' chains of the surfactant molecules aids the characterisation of the complexes, as single crystal x-ray diffraction can be used on many crystalline samples. Single crystal x-ray diffraction is a relatively simple technique for characterising the structure of crystalline materials, which does not suffer from the ambiguity of methods such as ^{1}H NMR spectroscopy.[157] As the alkyl chain does not participate in coordination to metal cations, the reduction in the chain length will not significantly affect the coordination of the sulfurised alkylphenol molecules. By the characterisation of model complexes with sulfurised alkylphenol ligands, it should be possible to deduce some of the characteristics of the coordination of surfactant sulfurised alkylphenol molecules to the metal cations in the overbased detergent core.

2.2. Sulfurised Alkylphenol Ligands

Sulfurised alkylphenol molecules consist of two phenolic rings connected by a sulfur bridge. The phenolic rings have an alkyl substituent *para* to the hydroxy group and the alkyl groups that have been used are methyl, isopropyl, *tert*-butyl, *tert*-amyl and *tert*-octyl. The sulfur atom is *ortho* to the hydroxy group. A schematic diagram of the sulfurised alkylphenol molecules used to prepare complexes can be seen below (figure 19).



M2 I2 B2

A2 O2

Figure 19. Sulfurised alkylphenol molecules synthesised and used in this study with their code names.

The codes used for each of the sulfurised alkylphenol molecules are shown in figure 19. The letter relates to the alkyl groups on the sulfurised alkylphenol molecules and the 2 relates to the molecules consisting of two phenolic rings. For the letter used to describe the alkyl groups; M is for methyl, I is for isopropyl, B is for *tert*-butyl, A is for *tert*-amyl and O is for *tert*-octyl. The table below shows the full names for the molecules with their codes (table 2).

Code	Name
M2	2,2'-Thiobis-(4-methylphenol)
I2	2,2'-Thiobis-(4-isopropylphenol)
B2	2,2'-Thiobis-(4-*tert*-butylphenol)
A2	2,2'-Thiobis-(4-*tert*-amylphenol)
O2	2,2'-Thiobis-(4-*tert*-octylphenol)

Table 2. Table summarising the names and codes for the sulfurised alkylphenol molecules.

It can be seen in the diagram above (figure 19) that the sulfurised alkylphenol molecules can coordinate to metal ions *via* two phenolic oxygen atoms and *via* the sulfur atom, though as Group 2 metal ions are 'hard', strong coordination *via* the sulfur atom is unlikely.[18]

Sulfurised alkylphenol molecules are prepared by the reaction of sulfur dichloride with the appropriate phenol.[92] The proposed mechanism for the reaction can be seen below (figure 20).

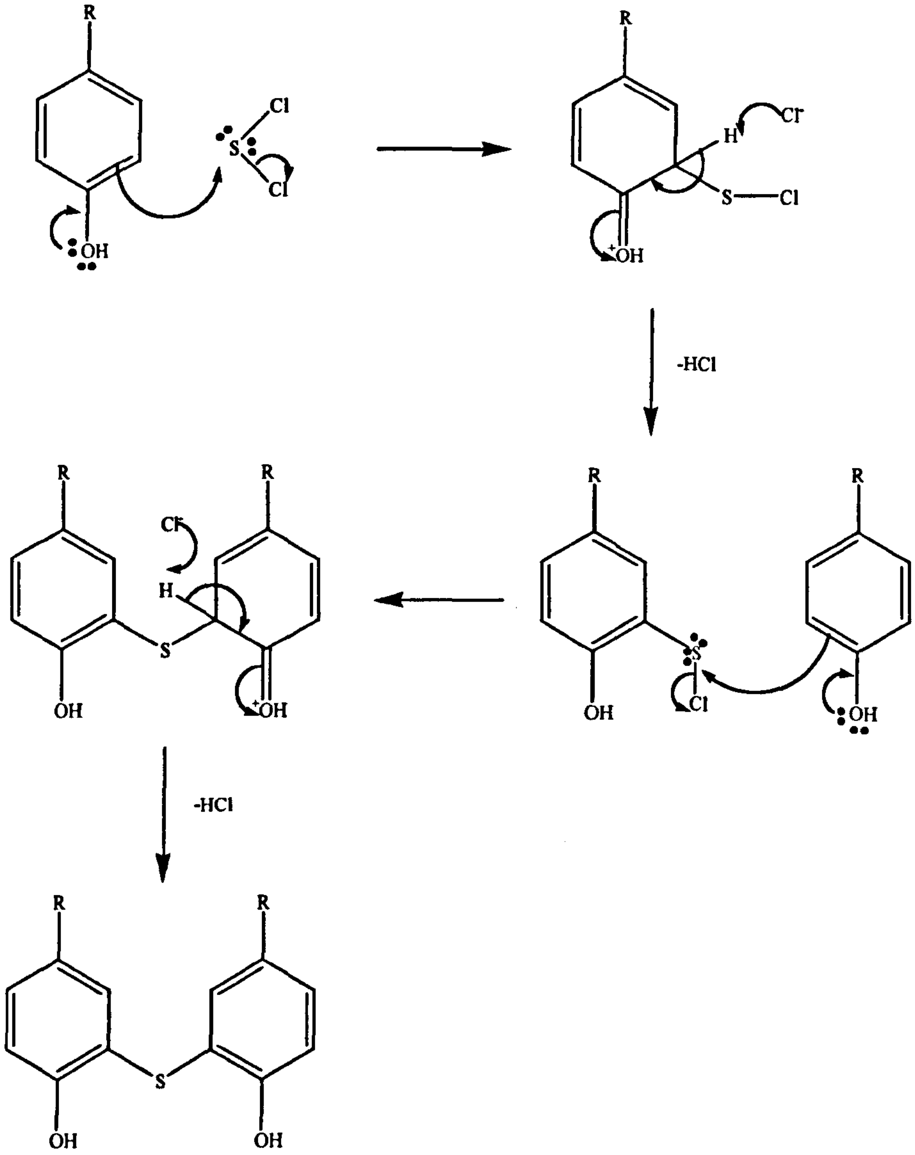


Figure 20. Schematic representation of the proposed mechanism for the preparation of sulfurised alkylphenol molecules.

M2 (**1**) has been prepared in a 33% yield, **I2** (**2**) has been prepared in a 46% yield, **B2** (**3**) has been prepared in an 8% yield, **A2** (**4**) has been prepared in a 5% yield and **O2**

(5) has been prepared in a 49% yield. The moderate yield for **M2**, **I2** and **O2** is probably due to the preparation of by-products such as larger sulfur atom bridged phenol oligomers (for example molecules consisting of three or four phenolic units) and molecules with di-sulfur bridges,[89] and the difficulty in isolating the products from the oil that is generated. For example, **I2** and **O2** are slightly soluble in *n*-pentane and so cooling is required to precipitate out the product. The yield for **O2** is the highest yield achieved for the sulfurised alkylphenol molecules, though the product obtained was the only sulfurised alkylphenol product which was not completely pure. **O2** was not recrystallised as the loss of product would have been greater than the relative benefit of having completely pure **O2**. **B2** and **A2** were prepared in much lower yields due to problems in isolating the products. For the isolation of **B2** it was found necessary to prepare the lithium salt and then obtain pure **B2** from this salt. For the isolation of **A2** it was found necessary to use a combination of cooling and decanting.

All of the sulfurised alkylphenol molecules give simple ^{1}H NMR (d_6-acetone) spectra, which show that the two phenolic units within each molecule are equivalent. The phenolic hydrogen signal is always broad, probably due to interaction of the hydrogen atoms with the other phenolic oxygen atoms and with the solvent *via* hydrogen bonding. The short chain alkyl group on the sulfurised alkylphenol molecules has resulted in molecules which can be dissolved in solvents as polar as methanol, though for the molecules with the longer alkyl groups, such as **O2**, warming and/or the addition of base is required to fully dissolve the molecule.

2.3. Sulfurised Alkylphenol Complexes Prepared from Methanol Solution

2.3.1. Introduction

Complexes with sulfurised alkylphenol ligands and magnesium, calcium, strontium and zinc metal ions have been prepared from methanol. Zinc cations were used to prepare complexes as zinc is a divalent metal ion, which was hoped to give crystalline complexes that would be suitable for single crystal x-ray diffraction, though unfortunately all of the crystalline complexes that were obtained with zinc cations were unsuitable for single crystal x-ray diffraction. Zinc cations form more stable complexes than Group 2 metal cations and the zinc cation has a similar ionic radius to the magnesium cation.[18, 158] Attempts were made to prepare crystalline complexes with Group 1 metal ions, though all of the reactions were unsuccessful resulting in no isolated Group 1 metal ion complexes with sulfurised alkylphenol ligands. The scheme shown below (figure 21) represents the general procedure used for the preparation of sulfurised alkylphenol complexes from methanol.

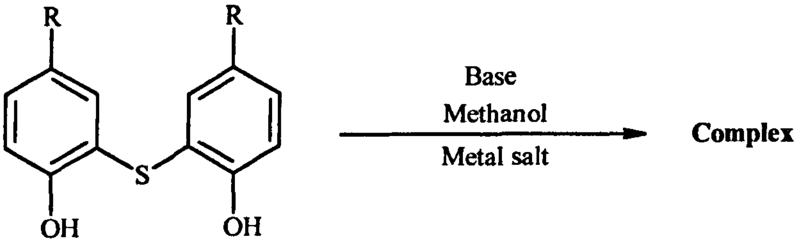


Figure 21. Schematic diagram of the general procedure used to prepare sulfurised alkylphenol complexes from methanol.

In general, the sulfurised alkylphenol ligand was dissolved in methanol with base and then metal salt was added to this solution. The bases that were used were potassium hydroxide and tetrabutylammonium hydroxide. Tetrabutylammonium hydroxide is used as a solution in methanol and so solubility is not an issue and as the molecule is organic, it is visible on ^{1}H NMR spectra, which allows the purity of products prepared with this base to be assessed. Potassium hydroxide is slow to dissolve in methanol and cannot be seen on ^{1}H NMR spectra. All of the solutions of the deprotonated sulfurised alkylphenol ligands in methanol were yellow, where **I2** gave the faintest yellow coloration and **M2** gave the brightest yellow coloration. The method of addition of the metal salt to the solution dictated the crystallinity of the final complex. When the metal salt was added as a solid or was added carefully as a solution in methanol, and in both cases if the solution was left undisturbed, then crystalline products could be isolated. The crystallinity of the product was also found to be affected by the concentration of the reagents in the methanol solution. For maximum yields, the solutions were stirred, which gave powder products. The powder products were shown to be the same as the crystalline products by ^{1}H NMR spectroscopy. The metal salts were found to have little influence on the complexes that were prepared. For calcium cation complexes, the metal salt was found to slightly affect the degree of crystallinity of the product. For all of the metal ions, the metal salt that was used was chosen was usually determined by the quality of the metal salt and the solubility of the metal salt in methanol. For example, calcium nitrate absorbs moisture from the atmosphere faster than calcium bromide and so calcium nitrate is usually 'wet' which results in technical difficulties in handling calcium nitrate and in water being introduced into the reaction mixture. Group 2 metal ion hydroxides could not be used as they are completely insoluble in methanol. The purest calcium complexes were prepared when a co-ligand was added to the reaction mixture, for example, when pivalic acid (trimethylacetic acid) was added (**6**, **7**). As the level of solvation of the products is unknown, the percentage yields have been calculated assuming no solvation, therefore, some of the percentage yields may be artificially high. The preparation of complexes from methanol was found to give reproducible results and the products were found to be the same, independent of the actual synthesis route.

The analysis of the complexes that have been prepared will be discussed starting with solid state analyses and their trends, then solution state analyses. Infrared spectroscopy was used as a solid state analysis method, though it will not be discussed in detail as it was only used as a finger-print method, as it was found that complexes had characteristically different infrared spectra to the ligands.

2.3.2. Solid State Structures of Sulfurised Alkylphenol Complexes Prepared from Methanol

Elemental analysis has been used to study the solid state structures of crystalline sulfurised alkylphenol complexes. Unfortunately, the crystalline complexes rapidly change into powder once removed from the solvent, which is accompanied by desolvation, solvent exchange with atmospheric moisture and occasionally decomposition, so this makes reliable analysis by elemental analysis difficult. It has also been observed that the percentage of carbon value is usually low. This may be due to the formation of stable metal carbonates during decomposition.[44] To overcome some of the difficulties, a catalyst has been used (V_2O_5). As the change into powder from a crystalline complex is accompanied by desolvation, this makes the choice of a standard and the interpretation of the results difficult, especially as coordinated methanol molecules which are lost on exposure to air are often replaced by water from the air.[124] Difficulties with obtaining valid elemental analysis data have been reported by many groups working with complexes including highly solvated metal cations and have been observed for all of the Group 2 metal cation complexes discussed in this thesis.[44, 46, 73] Decomposition is commonly observed for the calix[8]arene complexes. For sulfurised alkylphenol complexes, the results for elemental analyses shown in the Experimental

Chapter show that only Ca**M2** has a result which agrees with the solid state structure, the other complexes show that water molecules have replaced methanol molecules. All of the results do show, however, that there are three solvent molecules to one metal cation.

2.3.2.1. Calcium Cation Complex with **M2** (CaM2) (8)

A crystalline complex of calcium cations with **M2** ligands was grown from methanol. The complex consists of two **M2** ligands, each with –2 charge, two calcium cations and six methanol molecules. The two calcium cations are equivalent with a coordination number of six and distorted octahedral (trigonal distortion) geometry. Each calcium cation is coordinated to one terminally bound **M2** oxygen atom, two bridging **M2** oxygen atoms and three methanol molecule oxygen atoms.

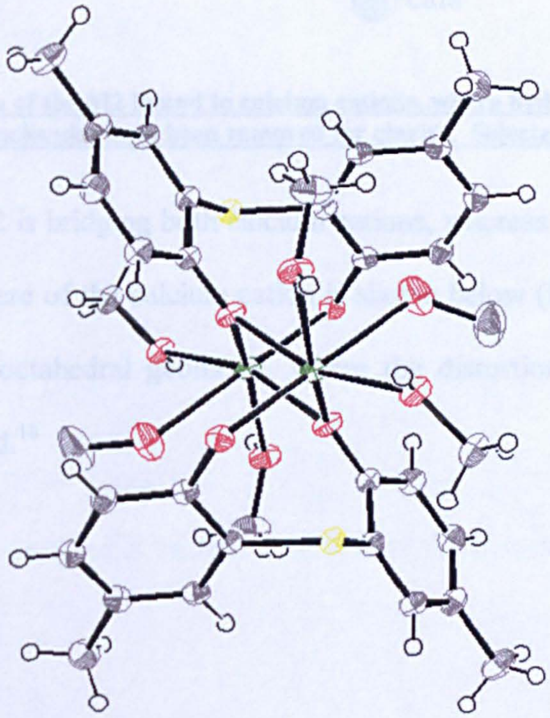


Figure 22. Structure of the calcium cation complex with M2 prepared from methanol, $(Ca^{2+})_2(M2^{2-})_2.6MeOH$.

The hydrogen atoms on two of the methanol ligands have not been found due to disorder around the methanol molecule oxygen and carbon atoms. The **M2** ligand oxygen atoms can be seen to coordinate to the calcium cations in two ways: terminally and bridging. This is shown more clearly in the diagram below (figure 23).

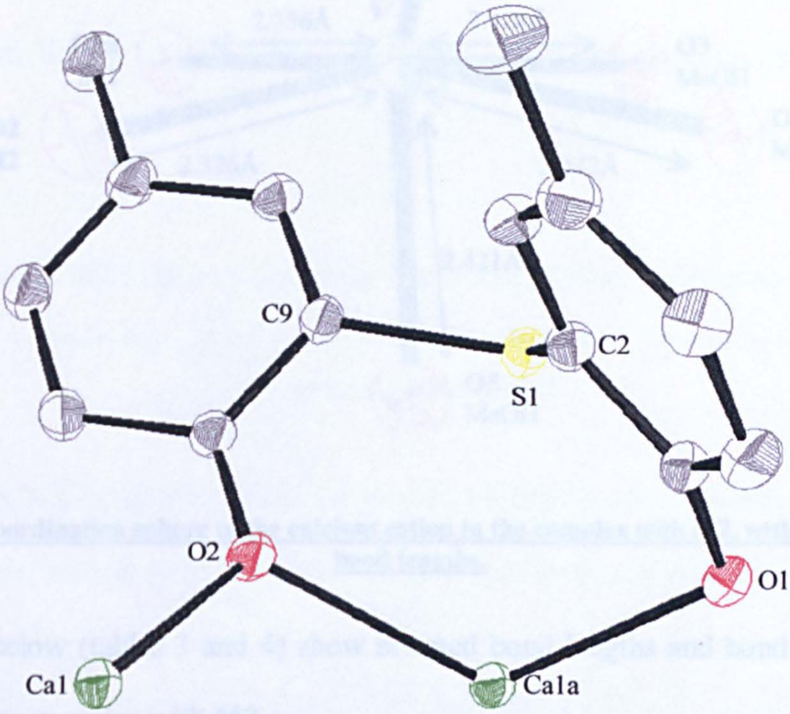


Figure 23. Coordination of the M2 ligand to calcium cations, where hydrogen atoms, the other M2 ligand and methanol molecules have been removed for clarity. Selected atom labels are shown.

It can be seen that O2 is bridging both calcium cations, whereas O1 is terminally bound. The coordination sphere of the calcium cation is shown below (figure 24). The calcium cation has distorted octahedral geometry, where the distortion is caused by the bite angle of the **M2** ligand.[18]

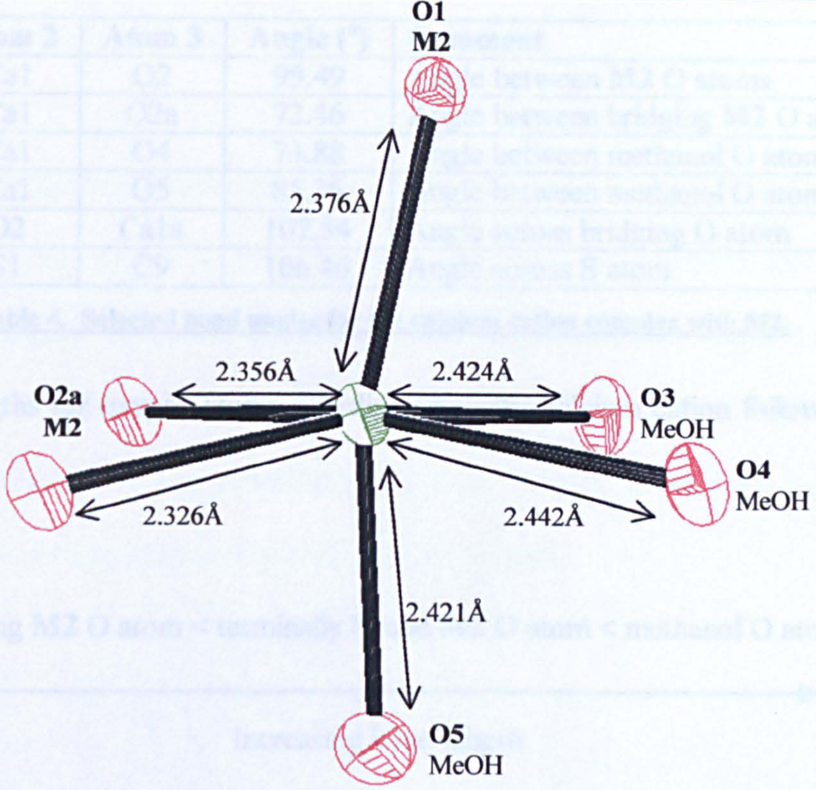


Figure 24. Coordination sphere of the calcium cation in the complex with M2, with atom labels and bond lengths.

The tables below (tables 3 and 4) show selected bond lengths and bond angles for the calcium cation complex with **M2**.

Atom 1	Atom 2	Bond length (Å)	Comment
Ca1	O1	2.376	Ca cation to terminal **M2** O atom bond
Ca1	O2	2.326	Ca cation to bridging **M2** O atom bond
Ca1	O2a	2.356	Ca cation to bridging **M2** O atom bond
Ca1	O3	2.424	Ca cation to methanol O atom bond
Ca1	O4	2.442	Ca cation to methanol O atom bond
Ca1	O5	2.421	Ca cation to methanol O atom bond
Ca1	S1	3.064	No interaction
Ca1	Ca1a	3.777	Interatomic distance
O1	O2	3.905	Interatomic distance

Table 3. Selected bond lengths for the calcium cation complex with M2.

Atom 1	**Atom 2**	**Atom 3**	**Angle (°)**	**Comment**
O1	Ca1	O2	99.49	Angle between **M2** O atoms
O2	Ca1	O2a	72.46	Angle between bridging **M2** O atoms
O3	Ca1	O4	73.88	Angle between methanol O atoms
O3	Ca1	O5	85.36	Angle between methanol O atoms
Ca1	O2	Ca1a	107.54	Angle across bridging O atom
C2	S1	C9	106.46	Angle across S atom

Table 4. Selected bond angles for the calcium cation complex with M2.

The bond lengths for oxygen atoms coordinated to the calcium cation follow the trend shown below.

Bridging **M2** O atom < terminally bound **M2** O atom < methanol O atom

→

Increasing bond length

The bridging **M2** oxygen atom can be seen to be slightly closer to one calcium cation than the other, though even the longer bond is shorter than the bond to the terminally bound **M2** oxygen atom. The methanol molecules fill the coordination sphere of the calcium cation by fitting into the space unoccupied by **M2** oxygen atoms and all of the methanol oxygen atom bond lengths to the calcium cation are very similar. The sulfur atom is too far away from the calcium cation for a bond to exist as the distance is over 3Å (3.064Å). The bond angles around the calcium cation show that the calcium cation geometry is distorted from octahedral. This is probably due to the **M2** ligand, where the angle between bridging **M2** oxygen atoms across the calcium cation is less than 90° and the angle between bridging and non-bridging **M2** oxygen atoms is more than 90°, thus the calcium cation geometry is distorted.

2.3.2.2. Strontium Cation Complex with **M2** (Sr**M2**) (9)

A crystalline complex of strontium cations with **M2** was grown from methanol. The complex consists of two **M2** ligands, each with –2 charge, two strontium cations and six methanol molecules. The two strontium cations are equivalent with a coordination number of six and distorted octahedral (trigonal distortion) geometry. Each strontium cation is coordinated to one terminally bound **M2** oxygen atom, two bridging **M2** oxygen atoms and three methanol molecule oxygen atoms.

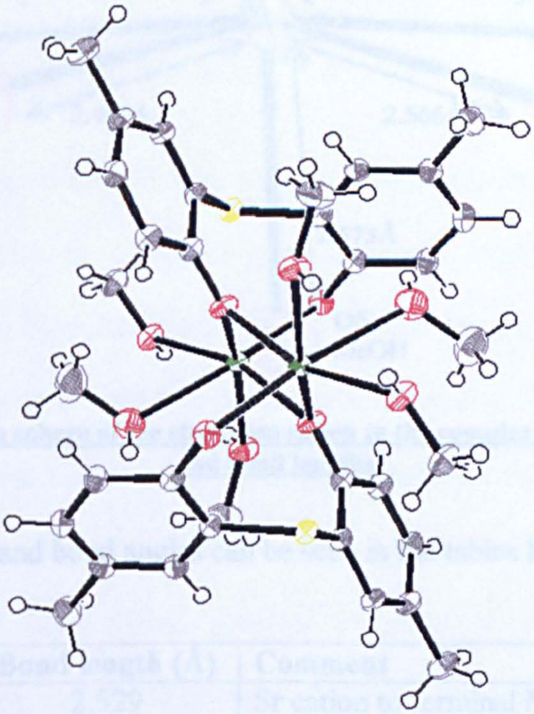


Figure 25. Structure of the strontium cation complex with M2 prepared from methanol, $(Sr^{2+})_2(M2^{2-})_2.6MeOH$.

The two binding modes of the **M2** ligand to strontium cations can be seen in the above diagram (figure 25). One **M2** oxygen atom binds terminally to a strontium cation and the other oxygen atom binds by bridging both strontium cations. The **M2** ligand twists around the sulfur bridge (C1-S1-C4) to accommodate this method of coordination.

The coordination sphere for the strontium cation within the complex can be seen below with bond lengths (figure 26), where both strontium cations in the molecule are equivalent. The strontium cation can be seen to be distorted from octahedral geometry.

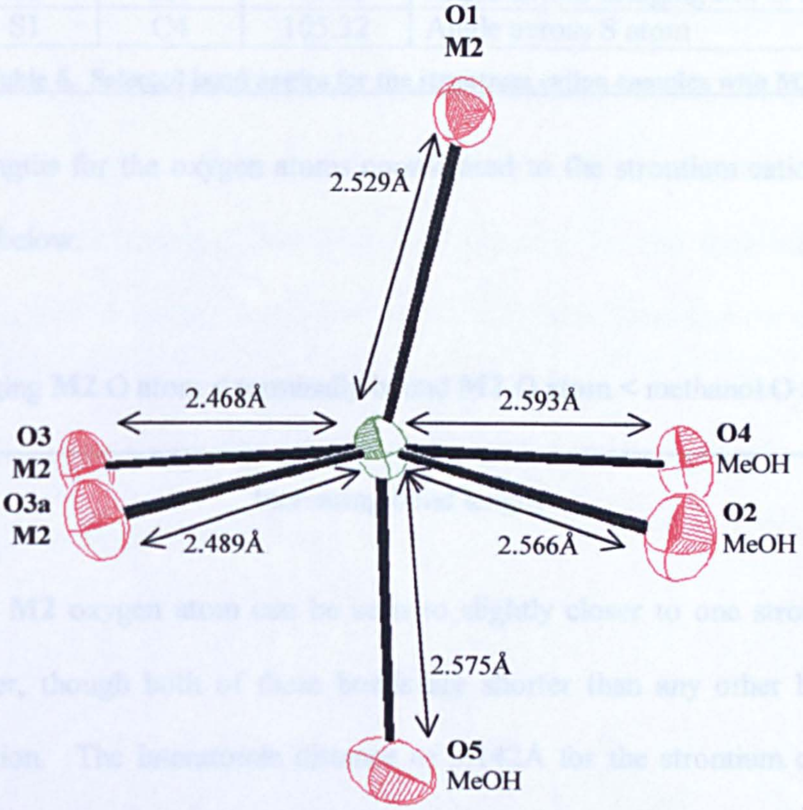


Figure 26. Coordination sphere of the strontium cation in the complex with M2, with atom labels and bond lengths.

Selected bond lengths and bond angles can be seen in the tables below (tables 5 and 6).

Atom 1	Atom 2	Bond length (Å)	Comment
Sr1	O1	2.529	Sr cation to terminal **M2** O atom bond
Sr1	O2	2.566	Sr cation to methanol O atom bond
Sr1	O3	2.468	Sr cation to bridging **M2** O atom bond
Sr1	O3a	2.489	Sr cation to bridging **M2** O atom bond
Sr1	O4	2.593	Sr cation to methanol O atom bond
Sr1	O5	2.575	Sr cation to methanol O atom bond
Sr1	S1	3.142	No interaction
Sr1	Sr1	3.998	Interatomic distance
O1	O3	4.097	Interatomic distance

Table 5. Selected bond lengths for the strontium cation complex with M2.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O1	Sr1	O3	102.30	Angle between **M2** O atoms
O2	Sr1	O4	72.76	Angle between methanol O atoms
O2	Sr1	O5	86.03	Angle between methanol O atoms
O3	Sr1	O3a	72.47	Angle between bridging **M2** O atoms
Sr1	O3	Sr1	107.53	Angle across bridging **M2** O atom
C1	S1	C4	105.32	Angle across S atom

Table 6. Selected bond angles for the strontium cation complex with M2.

The bond lengths for the oxygen atoms coordinated to the strontium cation follow the trend shown below.

Bridging **M2** O atom < terminally bound **M2** O atom < methanol O atom

$\longrightarrow$

Increasing bond length

The bridging **M2** oxygen atom can be seen to slightly closer to one strontium cation than the other, though both of these bonds are shorter than any other bonds to the strontium cation. The interatomic distance of 3.142Å for the strontium cation to the sulfur atom is too long for a bond to exist between the atoms. The interatomic distances between the two strontium cations and between the **M2** molecule oxygen atoms are very similar, showing that the **M2** ligand twists to bring its oxygen atoms closer together and therefore improve the ability of the ligand to coordinate through both of its oxygen atoms. The twist is also evident from the angle across the sulfur atom (105.32°). The angles between the oxygen atoms coordinated to the strontium cation show that the geometry around the strontium cation is distorted from octahedral.

The complex can be seen to be almost identical to the calcium cation complex with **M2** (**8**). The differences in bond lengths and bond angles between the two complexes can be attributed to the larger size of the strontium cation.

2.3.2.3. Strontium Cation Complex with **I2** (SrI2) (**10**)

A crystalline complex of strontium cations with **I2** was grown from methanol. The complex consists of two **I2** ligands, each with –2 charge, two strontium cations and six methanol molecules. The two strontium cations within the complex are not equivalent, though are very similar. Both strontium cations are six coordinate with distorted octahedral geometry (trigonal distortion), coordinating to one terminally bound **I2** oxygen atom, two bridging **I2** oxygen atoms and three methanol molecule oxygen atoms. There are two free methanol molecules in the lattice. The crystals were of low quality and so one methanol molecule and two isopropyl groups are distorted and not all of the hydrogen atoms have been found.

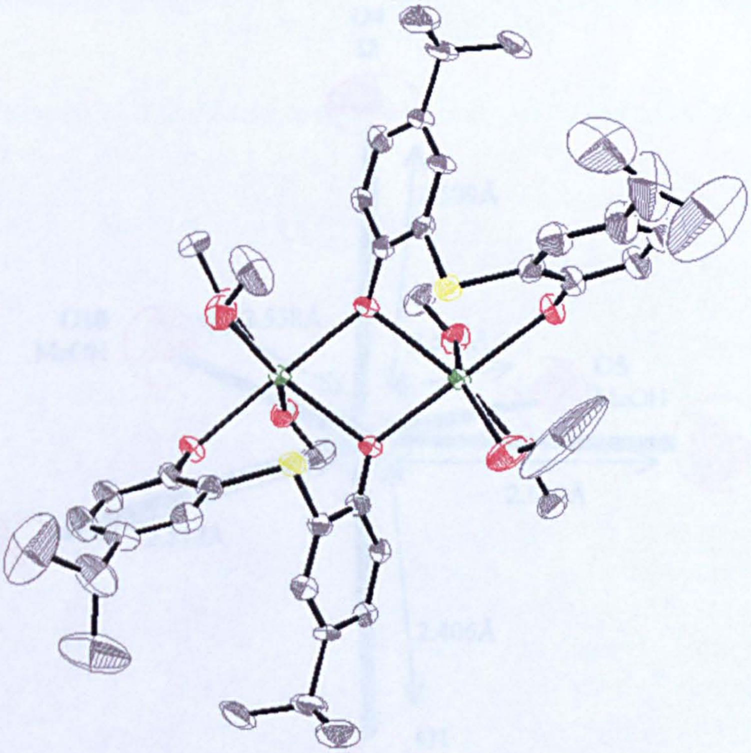


Figure 27. Structure of the strontium cation complex with I2 prepared from methanol, $(Sr^{2+})_2(I2^{2-})_2.6MeOH$, where the two free methanol molecules in the lattice and the hydrogen atoms have been removed for clarity.

The coordination spheres for the two strontium cations within the complex can be seen below (figure 28).

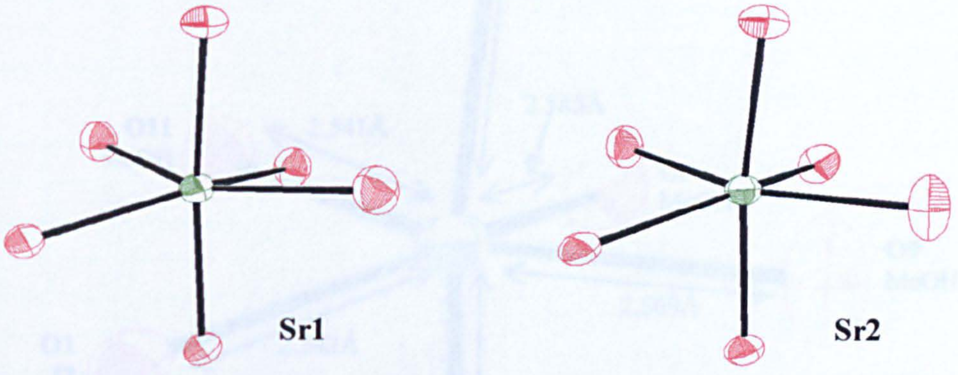


Figure 28. The coordination spheres around the two strontium cations in the complex with I2.

The two strontium cations within the complex can be seen to be very similar. The diagrams below (figure 29 and figure 30) show the bond lengths to the coordinated oxygen atoms for each of the strontium cations.

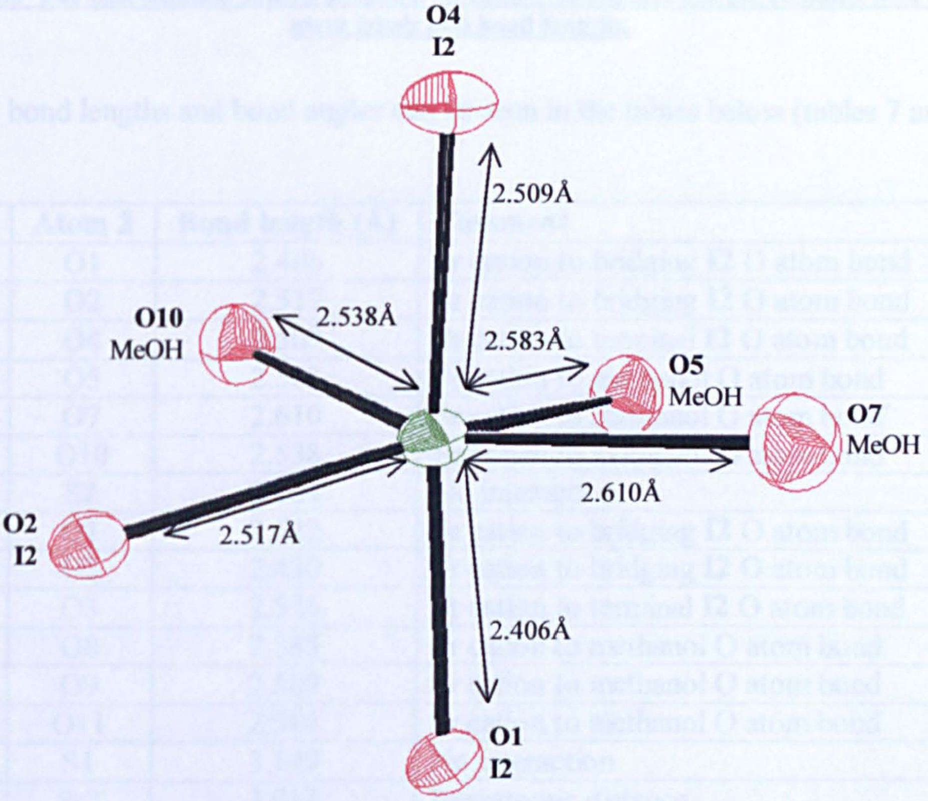


Figure 29. The coordination sphere around a strontium cation (Sr1) in the complex with I2, with atom labels and bond lengths.

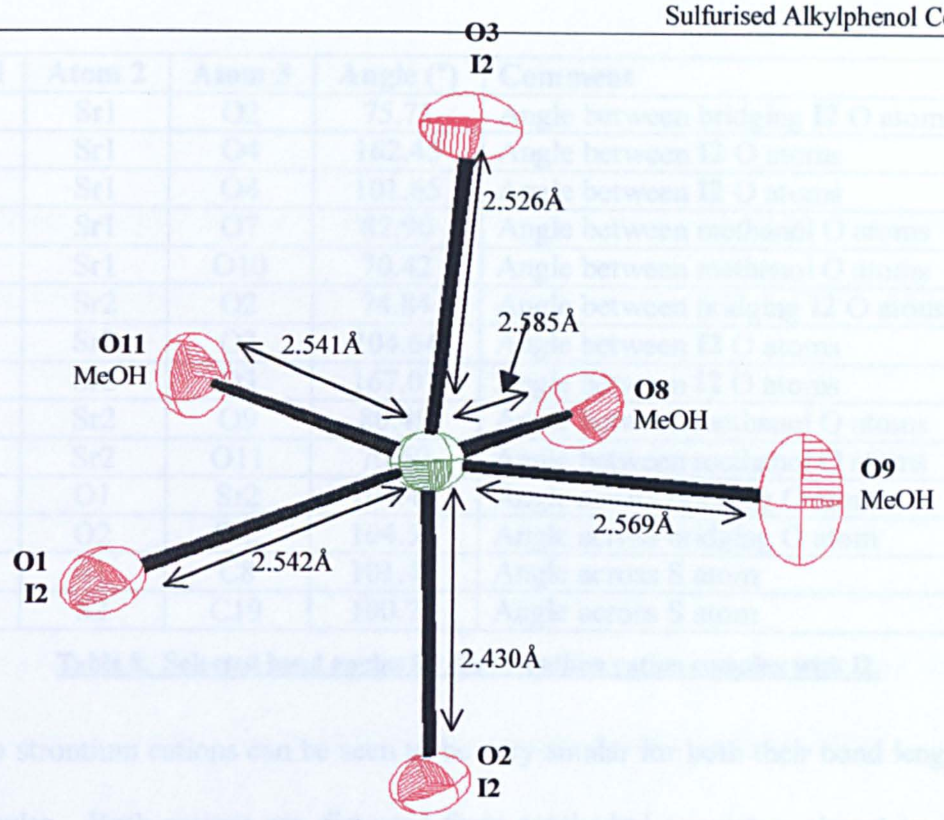


Figure 30. The coordination sphere around a strontium cation (Sr2) in the complex with I2, with atom labels and bond lengths.

Selected bond lengths and bond angles can be seen in the tables below (tables 7 and 8).

Atom 1	Atom 2	Bond length (Å)	Comment
Sr1	O1	2.406	Sr cation to bridging **I2** O atom bond
Sr1	O2	2.517	Sr cation to bridging **I2** O atom bond
Sr1	O4	2.509	Sr cation to terminal **I2** O atom bond
Sr1	O5	2.583	Sr cation to methanol O atom bond
Sr1	O7	2.610	Sr cation to methanol O atom bond
Sr1	O10	2.538	Sr cation to methanol O atom bond
Sr1	S2	3.164	No interaction
Sr2	O1	2.542	Sr cation to bridging **I2** O atom bond
Sr2	O2	2.430	Sr cation to bridging **I2** O atom bond
Sr2	O3	2.526	Sr cation to terminal **I2** O atom bond
Sr2	O8	2.585	Sr cation to methanol O atom bond
Sr2	O9	2.569	Sr cation to methanol O atom bond
Sr2	O11	2.541	Sr cation to methanol O atom bond
Sr2	S1	3.149	No interaction
Sr1	Sr2	3.913	Interatomic distance
O1	O3	4.011	Interatomic distance
O2	O4	3.896	Interatomic distance

Table 7. Selected bond lengths for the strontium cation complex with I2.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O1	Sr1	O2	75.71	Angle between bridging **I2** O atoms
O1	Sr1	O4	162.45	Angle between **I2** O atoms
O2	Sr1	O4	101.65	Angle between **I2** O atoms
O5	Sr1	O7	82.90	Angle between methanol O atoms
O5	Sr1	O10	70.42	Angle between methanol O atoms
O1	Sr2	O2	74.84	Angle between bridging **I2** O atoms
O1	Sr2	O3	104.64	Angle between **I2** O atoms
O2	Sr2	O3	167.01	Angle between **I2** O atoms
O8	Sr2	O9	80.49	Angle between methanol O atoms
O8	Sr2	O11	70.69	Angle between methanol O atoms
Sr1	O1	Sr2	104.49	Angle across bridging O atom
Sr1	O2	Sr2	104.53	Angle across bridging O atom
C1	S1	C8	101.45	Angle across S atom
C2	S2	C19	100.76	Angle across S atom

Table 8. Selected bond angles for the strontium cation complex with I2.

The two strontium cations can be seen to be very similar for both their bond lengths and bond angles. Both cations are distorted from octahedral geometry, almost to trigonal prismatic geometry. The trend for bond lengths of oxygen atoms coordinated to the strontium cations can be seen below.

1 of the bridging **I2** O atoms < terminally bound **I2** O atom < 2nd bridging **I2** O atom < methanol O atoms

→

Increasing bond length

The longer of the two bonds from the bridging **I2** oxygen atoms to the strontium cations can be seen to be longer than the bonds between the terminally bound **I2** oxygen atoms and the strontium cation in this complex. The interatomic distance between the strontium cations is very similar to the interatomic distances between the **I2** oxygen atoms of each **I2** molecule, which, along with the bond angle across the sulfur atoms, shows that the **I2** ligand twists to coordinate to the two strontium cations. The interatomic distance between the sulfur atoms and the strontium cations shows that there is no bond as the distance is too large.

2.3.2.4. Strontium Cation Complex with **O2** (Sr**O2**) (**11**)

A crystalline complex of strontium cations with **O2** was grown from methanol. The structure contains two molecules, where each molecule contains two **O2** ligands, each with –2 charge, two strontium cations and six methanol molecules. The two strontium cations within each molecule are equivalent, but not equivalent to the strontium cations within the other molecule (though they are very similar). All of the strontium cations are six coordinate with distorted trigonal prismatic geometry, coordinating to one terminally bound **O2** oxygen atom, two bridging **O2** oxygen atoms and three methanol molecule oxygen atoms. There are two free methanol molecules in the lattice.

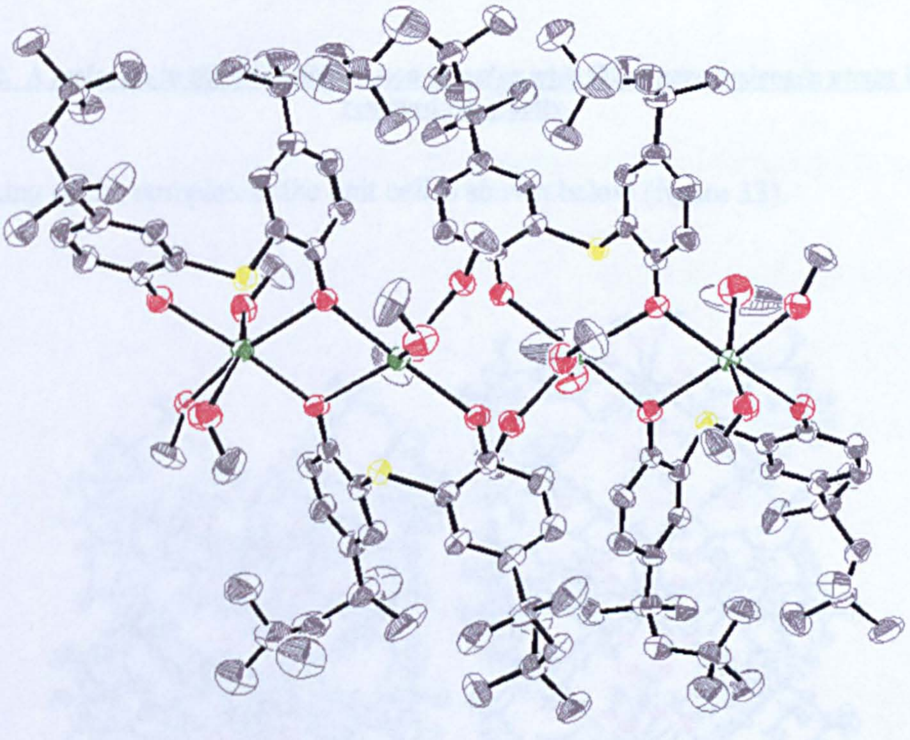


Figure 31. Structure of the strontium cation complex with O2 prepared from methanol, $(Sr^{2+})_2(O2^{2-})_2$.6MeOH, where two free methanol molecules from the lattice and the hydrogen atoms have been removed for clarity.

It can be seen that the two molecules within the complex are very similar. The coordination of the **O2** ligands to the strontium cations within one molecule in the complex is shown below (figure 32).

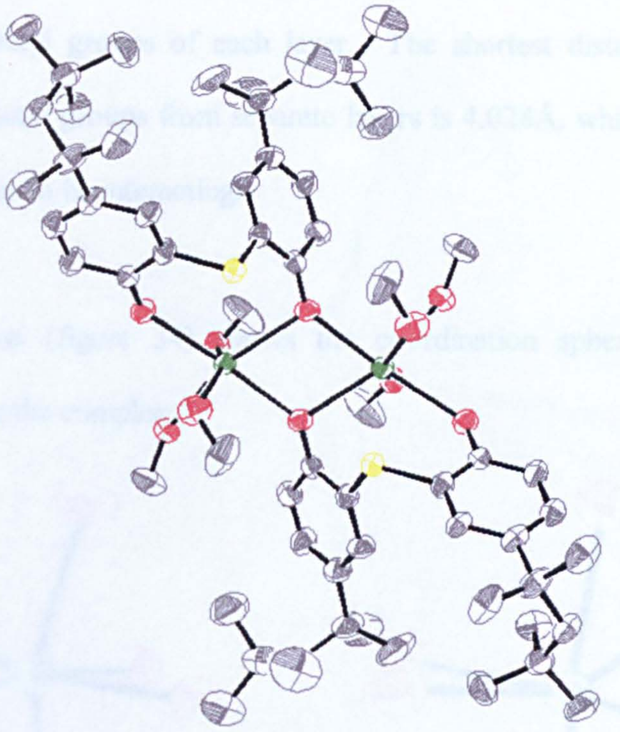


Figure 32. A molecule in the strontium cation complex with O2, where hydrogen atoms have been removed for clarity.

The packing of the complex in the unit cell is shown below (figure 33).

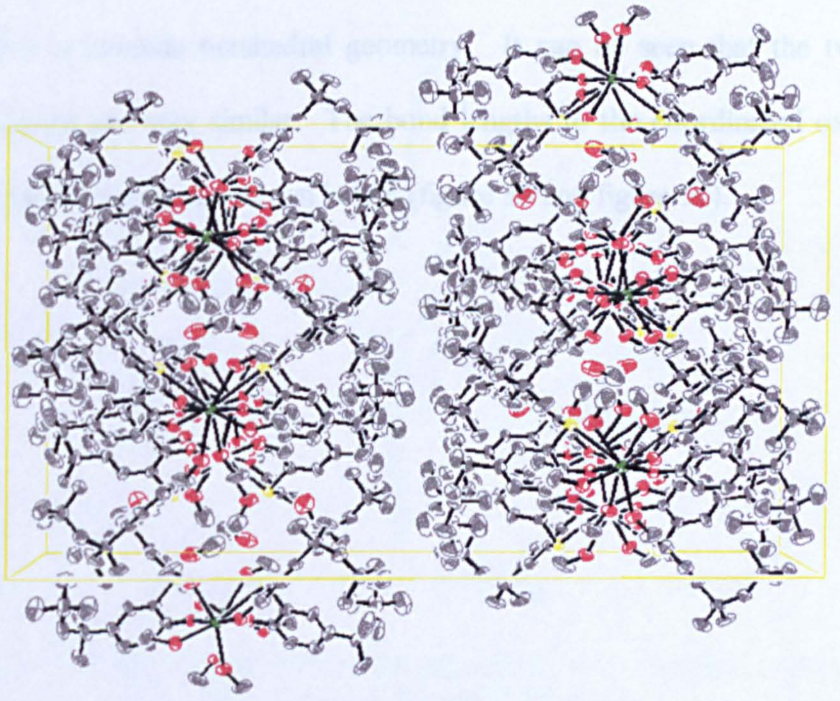


Figure 33. Unit cell of the strontium cation complex with O2.

The unit cell shows that the complex forms lamellar bilayers, where there is space between the *tert*-octyl groups of each layer. The shortest distance between carbon atoms of the *tert*-octyl groups from separate layers is 4.028Å, which is clearly too long for the carbon atoms to be interacting.

The diagram below (figure 34) shows the coordination spheres around the two strontium cations in the complex.

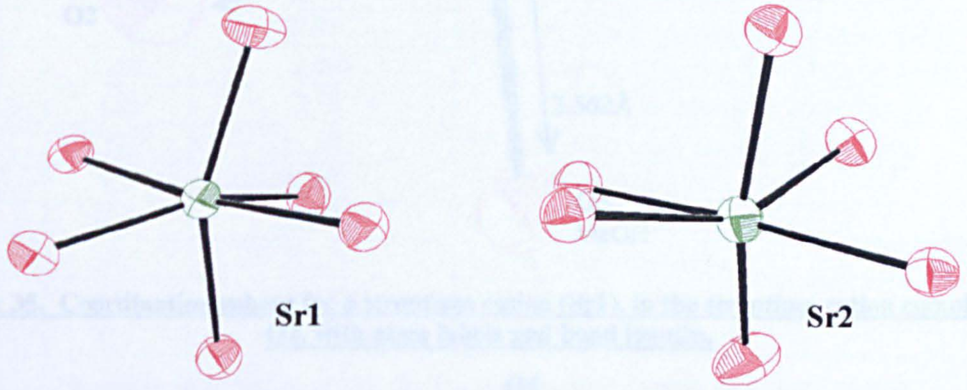


Figure 34. The coordination spheres for the strontium cations in the strontium cation complex with O2.

The two different strontium cations have distorted trigonal prismatic geometry, where the distortion is towards octahedral geometry. It can be seen that the two different strontium cations are very similar. The bond lengths to the coordinated oxygen atoms for each strontium cation are shown below (figure 35 and figure 36).

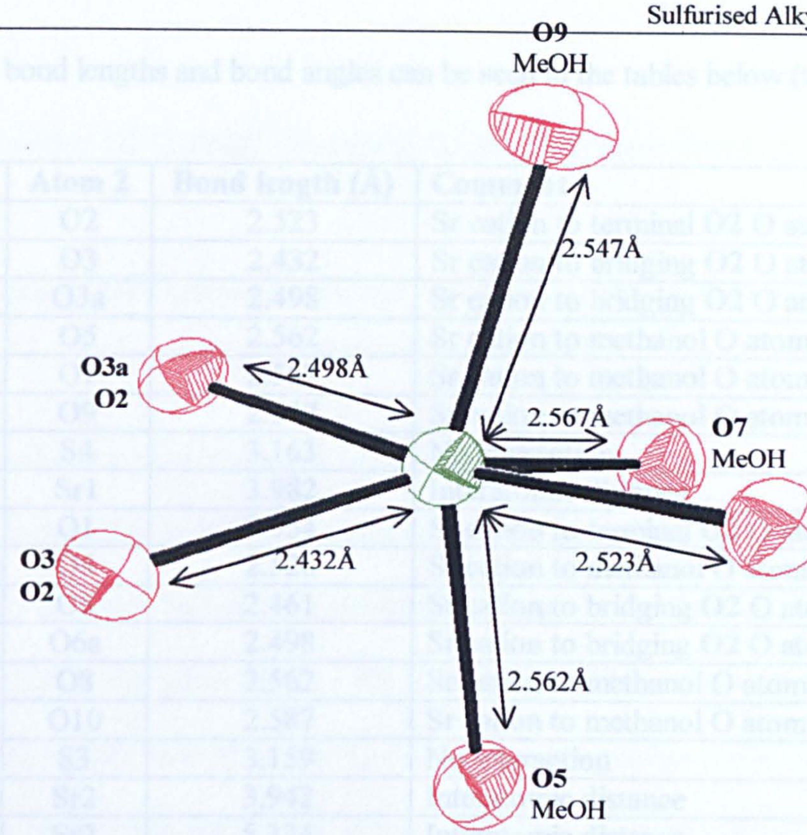


Figure 35. Coordination sphere for a strontium cation (Sr1), in the strontium cation complex with O2, with atom labels and bond lengths.

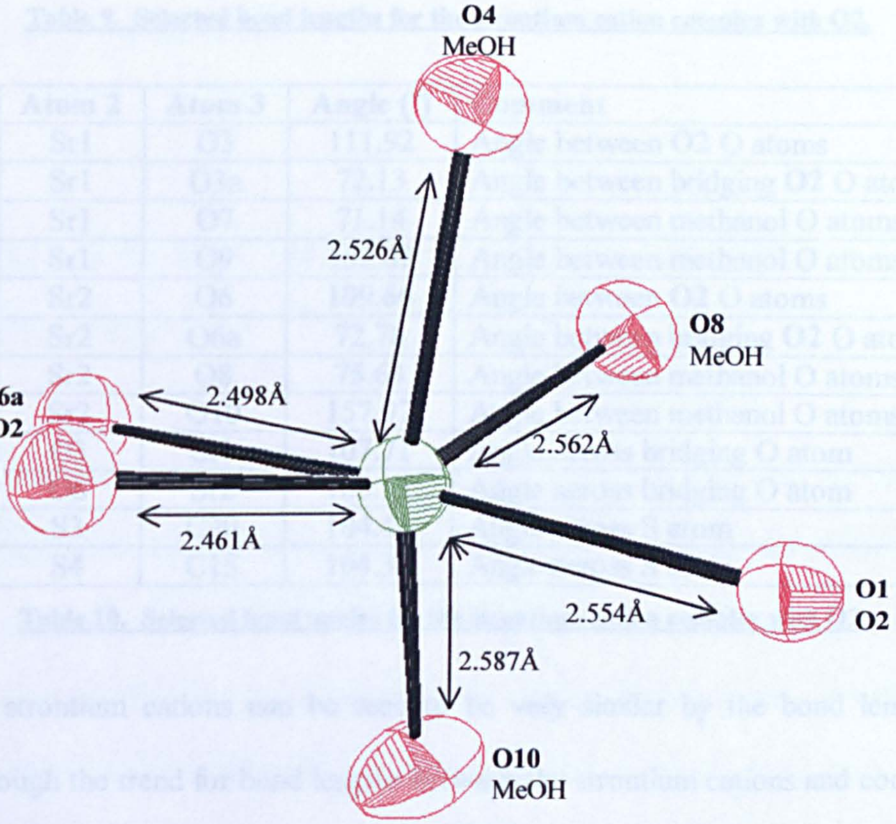


Figure 36. Coordination sphere for a strontium cation (Sr2), in the strontium cation complex with O2, with atom labels and bond lengths.

Selected bond lengths and bond angles can be seen in the tables below (tables 9 and 10).

Atom 1	Atom 2	Bond length (Å)	Comment
Sr1	O2	2.523	Sr cation to terminal **O2** O atom bond
Sr1	O3	2.432	Sr cation to bridging **O2** O atom bond
Sr1	O3a	2.498	Sr cation to bridging **O2** O atom bond
Sr1	O5	2.562	Sr cation to methanol O atom bond
Sr1	O7	2.567	Sr cation to methanol O atom bond
Sr1	O9	2.547	Sr cation to methanol O atom bond
Sr1	S4	3.163	No interaction
Sr1	Sr1	3.982	Interatomic distance
Sr2	O1	2.554	Sr cation to terminal **O2** O atom bond
Sr2	O4	2.526	Sr cation to methanol O atom bond
Sr2	O6	2.461	Sr cation to bridging **O2** O atom bond
Sr2	O6a	2.498	Sr cation to bridging **O2** O atom bond
Sr2	O8	2.562	Sr cation to methanol O atom bond
Sr2	O10	2.587	Sr cation to methanol O atom bond
Sr2	S3	3.159	No interaction
Sr2	Sr2	3.942	Interatomic distance
Sr1	Sr2	5.334	Interatomic distance
O1	O6	4.129	Interatomic distance
O2	O3	4.161	Interatomic distance

Table 9. Selected bond lengths for the strontium cation complex with O2.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O2	Sr1	O3	111.92	Angle between **O2** O atoms
O3	Sr1	O3a	72.13	Angle between bridging **O2** O atoms
O5	Sr1	O7	71.14	Angle between methanol O atoms
O5	Sr1	O9	152.02	Angle between methanol O atoms
O1	Sr2	O6	109.66	Angle between **O2** O atoms
O6	Sr2	O6a	72.78	Angle between bridging **O2** O atoms
O4	Sr2	O8	75.63	Angle between methanol O atoms
O4	Sr2	O10	157.97	Angle between methanol O atoms
Sr1	O3	Sr1	107.71	Angle across bridging O atom
Sr2	O6	Sr2	105.32	Angle across bridging O atom
C4	S3	C20	104.46	Angle across S atom
C8	S4	C15	104.30	Angle across S atom

Table 10. Selected bond angles for the strontium cation complex with O2.

The two strontium cations can be seen to be very similar by the bond lengths and angles, though the trend for bond lengths between the strontium cations and coordinated oxygen atoms is slightly different, as shown below.

Sr1

Bridging **O2** O atoms < terminally bound **O2** O atom < methanol O atoms

Sr2

Bridging **O2** O atoms < terminally bound **O2** O atom ≤ methanol O atoms

$$\xrightarrow[\text{Increasing bond length}]{\hspace{4cm}}$$

Neither molecules have strontium to sulfur bonds as the interatomic distances are too large. The interatomic distances between the **O2** oxygen atoms are very close to the interatomic distances between the strontium cations in each molecule, which, along with the angle across the sulfur atoms (which are very similar in the two molecules), show that the **O2** ligands twist about the C-S-C bond to coordinate to the strontium cations. The distances between the oxygen atoms of the two molecules are all longer than 3Å, suggesting that the two molecules are not held together by hydrogen-bonding and therefore just by packing effects.

2.3.3. Trends in the Solid State Structures of the Sulfurised Alkylphenol Complexes Prepared from Methanol

The sulfurised alkylphenol complexes **CaM2 (8)**, **SrM2 (9)**, **SrI2 (10)** and **SrO2 (11)** prepared from methanol all have very similar solid state structures. All of the sulfurised alkylphenol ligands coordinate to the metal cations with the same bonding motif, all of the complexes are dinuclear and all of the metal ions are six coordinate, coordinating to one terminally bound sulfurised alkylphenol ligand oxygen atom, two bridging sulfurised alkylphenol ligand oxygen atoms and three methanol molecule oxygen atoms. The coordination of the sulfurised alkylphenol ligands to the metal ions is shown schematically below (figure 37).

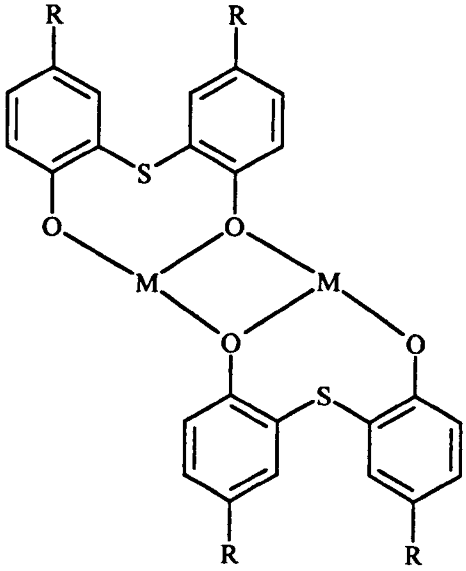
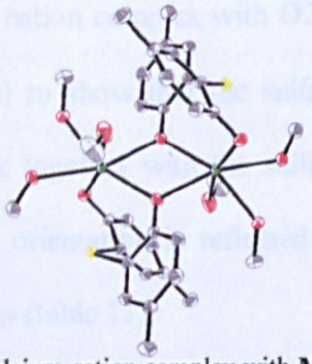


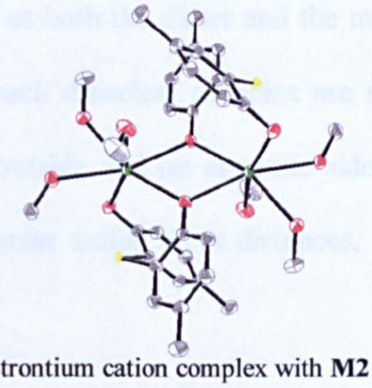
Figure 37. Coordination mode of sulfurised alkylphenol molecules to metal ions (M) in complexes prepared from methanol, where R = methyl, isopropyl and *tert*-octyl and M = calcium and strontium cations.

The calcium cation complex with **M2** and the strontium cation complex with **M2** are almost identical, with the only difference being in slightly longer bond lengths and slightly different bond angles for the strontium cation complex, which is due to the strontium cation having a larger ionic radius than the calcium cation (the strontium cation ionic radius is 1.12Å as opposed to the calcium cation ionic radius of 0.99Å).[69] The characterisation of isostructural calcium cation and strontium cation complexes is not unusual,[24, 61, 64, 69] though is counterintuitive, and for this study is very important as the other crystalline calcium cation complexes with sulfurised alkylphenol ligands were all unsuitable for single crystal x-ray diffraction. With the solid state structures of the calcium cation and strontium cation complexes with **M2** being isostructural and the solution structures of the calcium cation complexes with **M2** and with **I2** being identical, it is reasonable to assume that all of the calcium cation complexes with sulfurised alkylphenol ligands prepared from methanol will be isostructural to the strontium cation complexes, and hence that the bonding motif of the sulfurised alkylphenol ligands and the coordination numbers of the cations will all be the same.

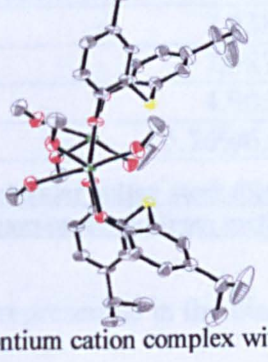
There are small differences between all of the complexes prepared from methanol, of which the two main differences are in the coordination geometries of the metal ions and the orientation of the sulfurised alkylphenol ligands, where both of these differences relate directly to the length of the alkyl chain of the sulfurised alkylphenol ligands. It has been shown that as the alkyl chain on the sulfurised alkylphenol ligand increases, the coordination geometry around the metal ions goes from trigonally distorted octahedral to octahedrally distorted trigonal prismatic geometry. This change is very small. The change in the orientation of the sulfurised alkylphenol ligands is a larger difference, though it does not affect the bonding motif of the ligands. The structures of the complexes show that as the alkyl chain is increased from methyl to isopropyl, the sulfur atoms in the two sulfurised alkylphenol ligands go from being on opposite sides of the molecule to being on the same side of the molecule. As the alkyl chain length is increased to *tert*-octyl, the sulfur atoms remain on the same side of the molecule. The side views of the complexes below show this feature (figure 38).



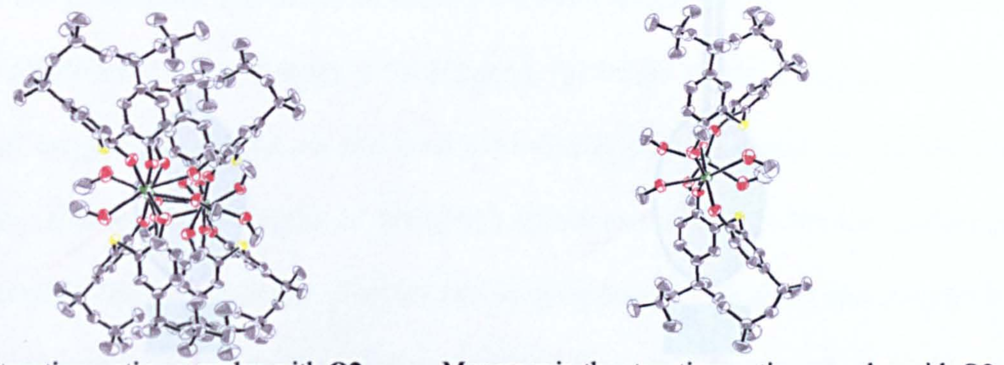
Calcium cation complex with **M2**



Strontium cation complex with **M2**



Strontium cation complex with **I2**



Strontium cation complex with **O2** Monomer in the strontium cation complex with **O2**

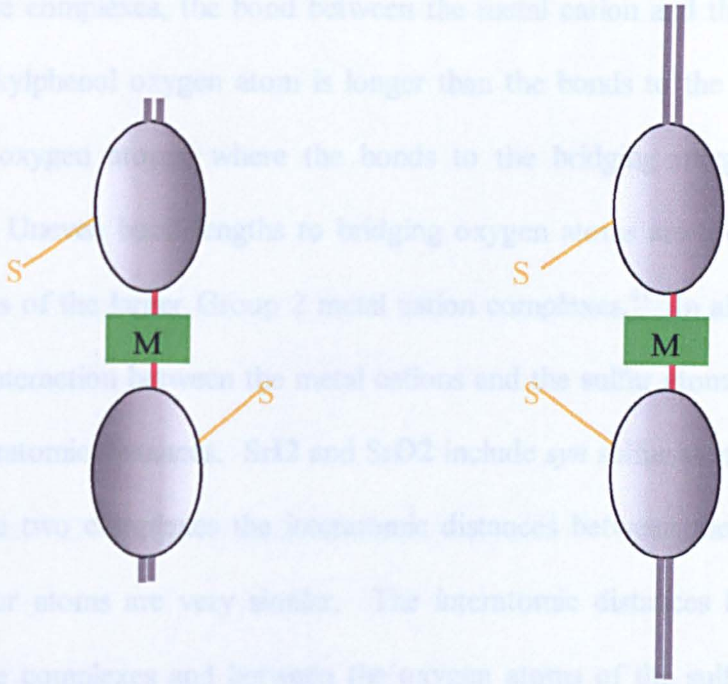
Figure 38. Side views of the sulfurised alkylphenol complexes prepared from methanol, where the dimer and monomer for the strontium cation complex with O2 have been shown for clarity.

The side views clearly show the change in the orientation of the sulfur atoms, where the **M2** complexes can be described as having *anti* sulfur atoms and the **I2** and **O2** complexes can be described as having *syn* sulfur atoms. As Sr**O2** has the same *syn* configuration as Sr**I2** and both Ca**M2** and Sr**M2** have *anti* sulfur atoms, this shows that the trend is not simply an anomaly in one structure. The different orientation of the sulfur atoms on increasing the alkyl chain length may be due to packing effects on the molecules, for example as the longer alkyl chains start to influence the packing. The strontium cation complex with **O2** has been shown as both the dimer and the monomer (figure 38) to show that the sulfur atoms within each dinuclear complex are *syn,* but these pack together with the sulfur atoms on the outside and on opposite sides. The change in orientation is reflected in the intramolecular sulfur atom distances, see the table below (table 11).

Complex	Sulfur atom to sulfur atom intramolecular distance (Å)
CaM2	7.438
SrM2	7.587
SrI2	4.905
SrO2	5.769/6.063

Table 11. Table comparing intramolecular sulfur atom distances in the sulfurised alkylphenol complexes prepared from methanol.

This trend has been schematically represented in the diagram below (figure 39).



Sulfurised alkylphenol molecules with short (methyl) alkyl chains

Sulfurised alkylphenol molecules with longer alkyl chains

Figure 39. Schematic diagram of the change in orientation of the sulfur atoms with increasing alkyl chain length within the sulfurised alkylphenol complexes prepared from methanol.

The table below (table 12) compares some of the bond lengths and bond angles for the complexes, where it must be noted that the strontium cation complex with **I2** structure is not completely refined due to the low quality of the crystals and therefore there is a greater error associated with all of the values for this complex.

Bond	CaM2	SrM2	SrI2	SrO2
Metal cation to terminally bound O atom bond (Å)	2.376	2.529	2.509/2.526	2.523/2.554
Metal cation to bridging O atom bond (Å)	2.326/2.356	2.468/2.489	2.406/2.517/ 2.430/2.542	2.432/2.498/ 2.461/2.498
Metal cation to S atom distance (no interaction) (Å)	3.064	3.142	3.164/3.149	3.163/3.159
Metal cation to methanol O atom bond range (Å)	2.421-2.442	2.566-2.593	2.538-2.610	2.526-2.587
Metal cation to metal cation distance (Å)	3.777	3.998	3.913	3.982/3.942
SAP oxygen atom to oxygen atom distance (Å)	3.905	4.097	4.011/3.896	4.129/4.161
Carbon to sulfur to carbon atom bond angle (°)	106.46	105.32	101.45/100.76	104.46/104.30

Table 12. Table comparing the data for the sulfurised alkylphenol complexes prepared from methanol.

For all of the complexes, the bond between the metal cation and the terminally bound sulfurised alkylphenol oxygen atom is longer than the bonds to the bridging sulfurised alkylphenol oxygen atoms, where the bonds to the bridging oxygen atoms are not equidistant. Uneven bond lengths to bridging oxygen atoms are a common feature in the structures of the larger Group 2 metal cation complexes.[41] In all of the complexes there is no interaction between the metal cations and the sulfur atoms, which is seen by the long interatomic distances. **SrI2** and **SrO2** include *syn* sulfur atoms in the molecules and for these two complexes the interatomic distances between the strontium cations and the sulfur atoms are very similar. The interatomic distances between the metal cations in the complexes and between the oxygen atoms of the sulfurised alkylphenol ligands are very close, where the interatomic oxygen atom distance is always slightly longer than the intercationic distance. This shows that the sulfurised alkylphenol ligands are able to twist to provide preferable coordination bond lengths and angles for the oxygen atoms. The twist is reflected by the bond angles across the sulfur atoms, which are all very similar, except for **SrI2**, and show that the change in the orientation of the sulfur atoms within the molecules on increasing the lengths of the alkyl chains does not effect the bond angles within the ligands. As discussed above, the bond lengths in the calcium cation complex with **M2** and the corresponding bond lengths in the strontium cation complex with **M2** are all shorter in the calcium cation complex, due to the smaller size of the calcium cation. For all of the complexes, the bonds between the metal cations and the methanol molecule oxygen atoms are the longest of the bonds to the metal cations. This shows that the complexes are very similar.

A search on the Cambridge Structural Database has shown that there are no published structures of complexes of sulfurised alkylphenol ligands with Group 2 metal ions.[41]

For a comparison of these structures to relevant structures from the database see section 2.7.2.

2.3.4. Solution Structure Studies on the Sulfurised Alkylphenol Complexes Prepared from Methanol Solutions

2.3.4.1. Nuclear Magnetic Resonance Spectroscopy (NMR Spectroscopy)

^{1}H NMR spectroscopy is an analytical method for characterising products in solution. The technique shows the hydrogen atoms that are present within a product, which can be used to identify the organic species that are present in the product, the symmetry of the organic species and the specific environment around each hydrogen atom. Free ligands usually have simple ^{1}H NMR spectra, as the molecules are able to move freely in solution.[22] For flexible molecules, such as calix[8]arenes, the ^{1}H NMR spectra of the free ligand is an average of all of the possible conformations of the molecule and so, for example, only one aromatic proton peak is obtained. Sulfurised alkylphenol molecules have sharp ^{1}H NMR spectra, where the aromatic and alkyl hydrogen atoms can be easily identified. The peak for the phenolic hydroxide hydrogen atom is often broad as the atom tends to be involved in hydrogen-bonding, which makes its environment less well defined. Broad peaks tend to underintegrate, which can cause difficulties in determining relative numbers of hydrogen atoms from NMR spectra. When complexes are formed, the flexibility of the ligand is usually restricted, which causes some or all of the hydrogen atoms to become inequivalent. This shows the symmetry of the complex and can give information about the way in which the ligand has coordinated to the metal ions. If the ligand has become deprotonated by complexation, this can be identified by peak integrations. When salts are formed, the ligand hydrogen atoms do not appear significantly different to the free ligand, though the peaks are usually slightly shifted and deprotonation of the ligand can be seen by reduced peak intensities. Hydrogen-bonding can be observed under some conditions by broad NH or OH peaks and these peaks shifting downfield,[159] where the shift of the peak can indicate the strength of the hydrogen-bond (a larger shift equates to a stronger hydrogen-bond).[83, 160] ^{1}H NMR spectra are affected by the ^{1}H NMR solvents that are used to dissolve the sample, where the commonly used solvents have been; d_6-acetone, d_1-chloroform ($CDCl_3$), d_2-dichloromethane (CD_2Cl_2), d_6-dimethylsulfoxide (d_6-DMSO), d_3-acetonitrile and d_4-methanol. The more polar solvents tend to show hydrogen-bonding, though many of the ligands have low solubilities in polar solvents. DMSO is an excellent solvent for dissolving many materials, though DMSO can be considered to be a hydrogen-bond disrupting solvent[83] and so simple spectra are usually obtained with this solvent. For sulfurised alkylphenol complexes, acetone is the preferred solvent as this solvent allows solution structures to be observed, though the choice of solvent is always determined by solubility of the product. It has been observed that the more crystalline a complex is, the less soluble the complex is and so more solubilising and less polar solvents tend to have to be used, which results in spectra with lower information value.

^{13}C NMR spectroscopy is not as useful as ^{1}H NMR spectroscopy as the natural abundance of ^{13}C carbon is only 1.11%, whereas the natural abundance of ^{1}H hydrogen is 99.99%.[159] This leads to very little ^{13}C carbon in a product, which makes ^{13}C NMR spectra weak and results in no coupling between carbon atoms. ^{13}C NMR spectra, therefore, have low use as a solitary method for characterising a product, but are useful as supporting material for ^{1}H NMR spectra.

2D COSY (two dimensional correlation spectroscopy) spectroscopy is a useful method for deconvoluting complicated ^{1}H NMR spectra. By this method, the normal ^{1}H NMR spectrum is seen along the diagonal and off-diagonal signals show protons which are coupled are to each other.[161] This allows protons within one structural unit to be identified, which is especially useful for complexes which form clusters in solution.

The solution structures of the main sulfurised alkylphenol complexes that have been prepared from methanol solution (as determined by NMR spectroscopy) will be discussed in turn below.

2.3.4.1.1. Magnesium Cation Complex with M2 (MgM2)

The magnesium cation complex with **M2** gives a complicated ^{1}H NMR spectrum, independent of the reagents used in the preparation of the complex and the deuterated solvent used for the analysis of the complex. ^{1}H NMR spectra have been obtained for Mg**M2** in d_6-acetone, d_6-DMSO and $CDCl_3$. All of the spectra show peaks for deprotonated **M2** and peaks for a clustered complex. The ^{1}H NMR spectrum for the Mg**M2** complex in d_6-DMSO shows clustered Mg**M2**, which is unusual as deuterated DMSO ^{1}H NMR spectra usually resemble salt ^{1}H NMR spectra in being very simple and often broad. The spectrum shows four different clustered aromatic protons for each type of proton on the aromatic ring, hence the solution structure of clustered Mg**M2** is possibly tetranuclear in DMSO. The peaks for deprotonated **M2** are larger than the peaks for the clustered complex. In the other deuterated solvents (d_6-acetone and $CDCl_3$), the clustered aromatic protons are not as easy to identify as they are broader and more overlapped, though they all show a tetranuclear clustered complex.

From the ^{1}H NMR spectra it is not possible to determine if the complex is actually a mixture of an **M2** salt with MgM**2** complex or if the complex displays fluxional behaviour in solution.[161] As the crystalline MgM**2** complex was found to be unsuitable for single crystal x-ray diffraction, the solid state structure of the complex is unknown, therefore it is difficult to determine if the complex is really a mixture or not.

2.3.4.1.2. Calcium Cation Complex with M2 (CaM2)

The complex of calcium cations with **M2** dissolves in acetone and so d_6-acetone was used for all of the ^{1}H NMR spectroscopy studies on the complex. This complex exhibits a complicated solution structure, which is different to the solid state structure of the complex. The ^{1}H NMR spectra of the complex always include peaks for water and methanol, where the water may be from air or from the acetone. Occasionally tetrabutylammonium cations are observed as an impurity in the complex. The cleanest complex was prepared in the presence of pivalic acid (6), where the spectrum contains no pivalic acid, free **M2** or tetrabutylammonium cations. There is very little variation between all of the spectra obtained for CaM**2**, where the spectra obtained are independent of whether the complex was crystalline or powder or prepared in the presence of another potential ligand such as pivalic acid or **DMPD (25)**. The ^{1}H NMR (d_6-acetone) spectrum for CaM**2** can be seen below (figure 40).

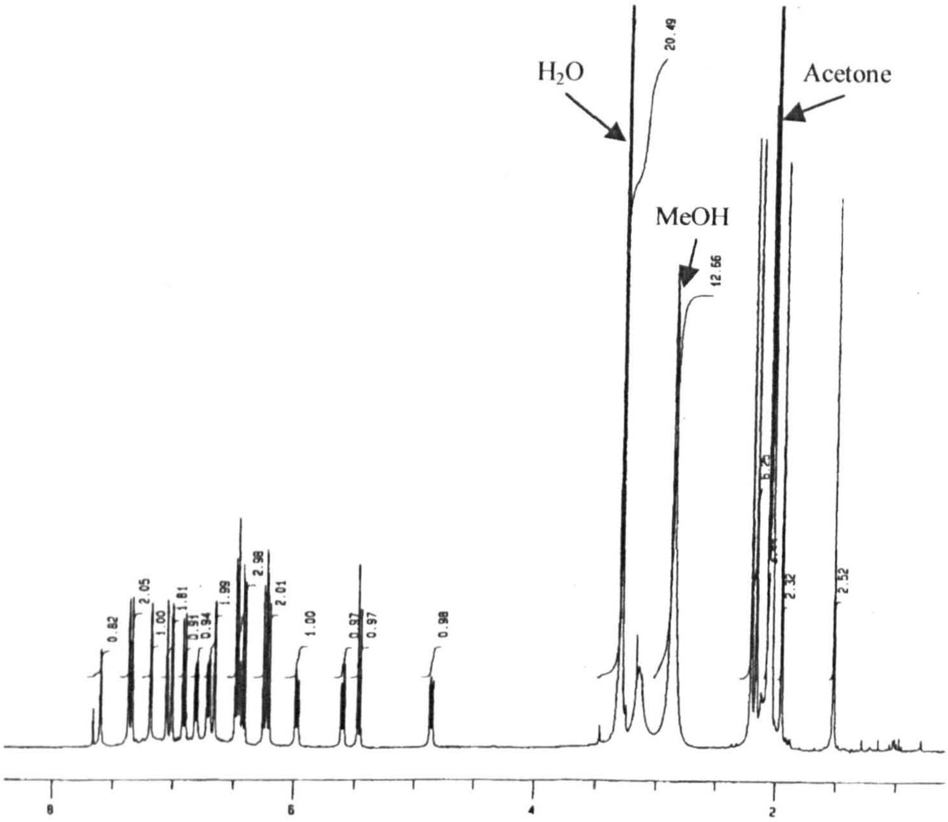


Figure 40. ^{1}H NMR (d$_6$-acetone) spectrum for the calcium cation complex with M2 prepared from methanol.

The above ^{1}H NMR spectrum (figure 40) contains eighteen aromatic proton peaks, over the range 7.37-4.85ppm, and six methyl proton peaks. These peaks are for **M2** in the complex and it can be seen that the aromatic protons cover a very wide range. The eighteen aromatic proton peaks are for three different aromatic protons with six peaks for each proton. In the above spectrum, there is no evidence for phenolic hydroxide protons and so the **M2** ligand is fully deprotonated (-2 charge). There are also peaks for methanol, water and acetone. There are many possible solution structures which the complex may possess though it can be assumed that the solution structure will be related to the solid state structure and will thus probably possess at least inversion symmetry. Therefore on the basis of eighteen aromatic proton and six methyl proton peaks, it can be proposed that the complex forms hexanuclear clusters in solution (as $(Ca^{2+})_2(\mathbf{M2}^{2-})_6$.solvent), with six $\mathbf{M2}^{2-}$ ligands, which to be charge-balanced, must be coordinated to six calcium cations. This is the simplest option for the solution structure of the complex. It is possible that the complex could form trinuclear clusters in solution (as $(Ca^{2+})_3(\mathbf{M2}^{2-})_3$.solvent), where the two phenolic units of the sulfurised alkylphenol ligands are inequivalent, though this is less probable than hexanuclear clusters as it required a significant change in the structure of the complex. Larger complexes, such as with twelve calcium cations and twelve **M2** ligands, are possible though this cannot be determined by NMR spectroscopy. The aromatic region of the ^1H NMR spectrum can be seen below (figure 42). The labels shown for each peak come from information gained from the 2D COSY NMR (d_6-acetone) spectrum of the complex, where A, B and C are the three different aromatic protons (see figure 41) and the number relates to protons which are coupled to each other. Thus A1, B1 and C1 are coupled to each other.

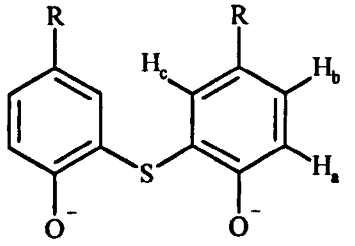


Figure 41. Schematic diagram of a sulfurised alkylphenol molecule with the labels for the aromatic protons.

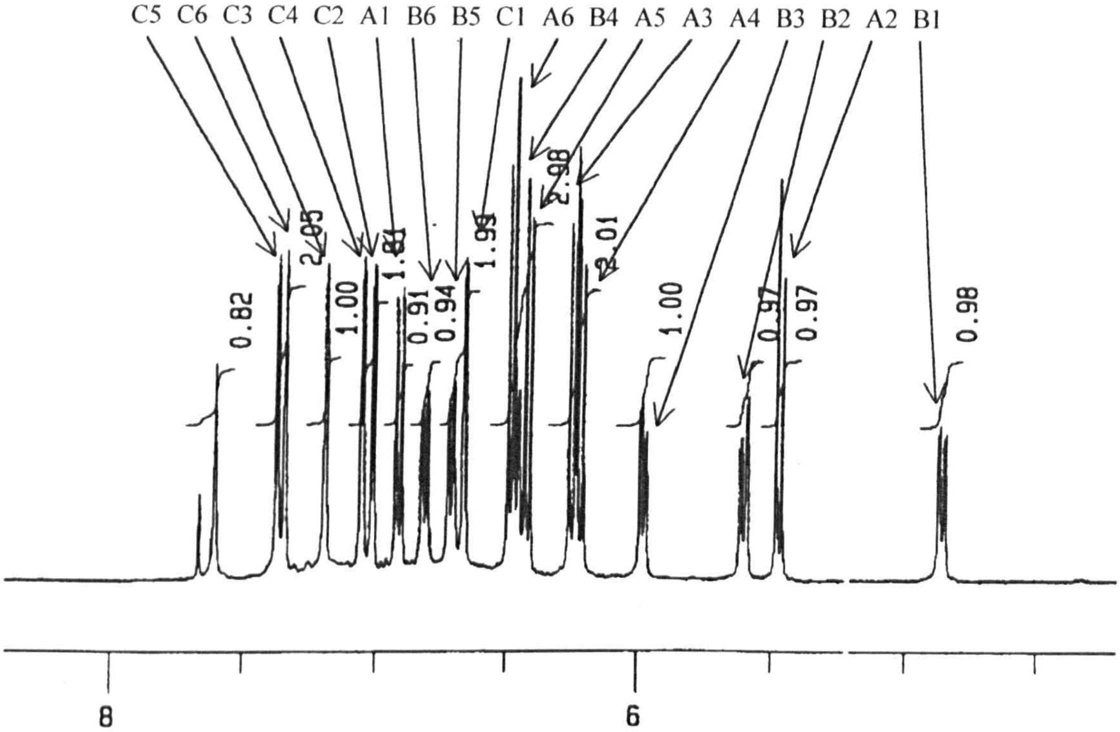


Figure 42. Aromatic region for the ^{1}H NMR (d_6-acetone) spectrum for the calcium cation complex with M2. Peak labels have been obtained from the 2D COSY NMR (d_6-acetone) spectrum for the complex, where A, B and C relate to the three different aromatic protons.

The ^{13}C NMR (d_6-acetone) spectrum of the complex also suggests a hexanuclear system.

It has not been possible to characterise the peaks at 7.66 and 7.60ppm, which are present on all of the ^{1}H NMR spectra of Ca**M2**, always in a similar ratio to the aromatic proton peaks. Their total intensity is equivalent to approximately one aromatic proton in the cluster.

Over time in air the isolated solid complex changes. At first, a crystalline complex will change to a powder (within five minutes) and then the powder slowly changes colour, going from pale yellow to pale brown over a period of approximately one year. The complex in solution remains stable indefinitely. The change in appearance of the isolated complex is reflected by a change in the ^{1}H NMR spectrum. Crystalline samples and fresh powder samples have the same ^{1}H NMR spectra, but as the powder ages, the

^{1}H NMR spectrum shows decomposition. The ^{1}H NMR spectrum of an 'old' Ca**M2** sample can be seen below (figure 43).

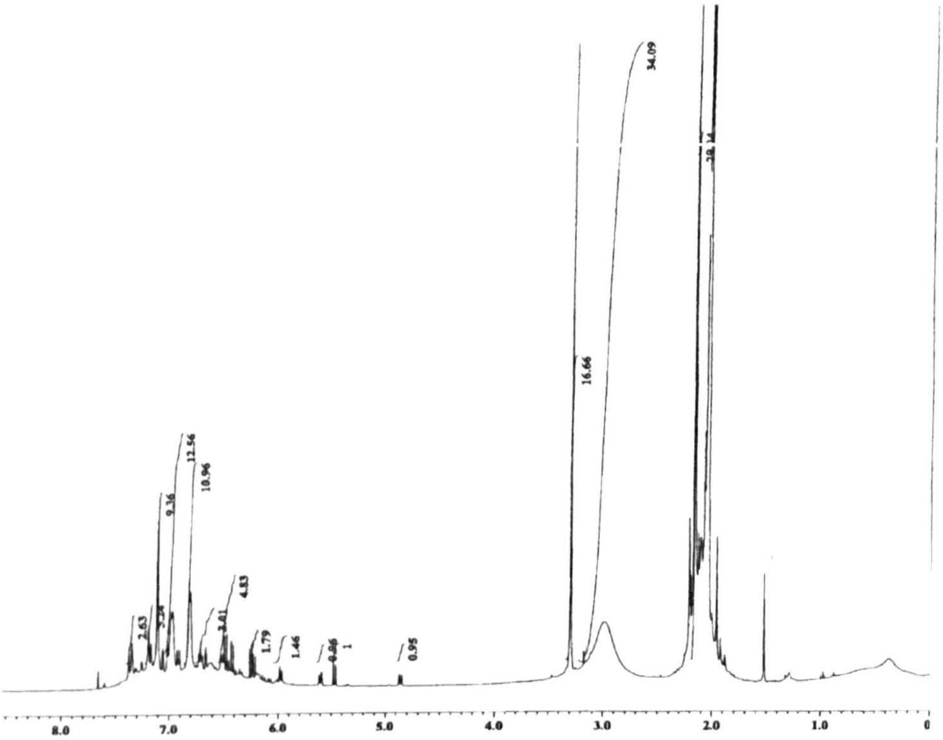


Figure 43. ^{1}H NMR (d_6-acetone) spectrum for 'old' CaM2.

The spectrum clearly shows that the complex has decomposed, possibly due to loss of coordinated methanol molecules. The water peak is not large, suggesting that the methanol molecules have not been replaced by water molecules from the air, but that the complex has decomposed to **M2** and a stable calcium compound, such as calcium carbonate or calcium hydroxide. The level of decomposition is not high considering that the complex has been in air for over one year.

2.3.4.1.3. Calcium Cation Complex with **I2** (Ca**I2**)

The ^{1}H NMR (d_6-acetone) spectrum for the calcium cation complex with **I2** is very similar to the Ca**M2** spectrum. As for Ca**M2**, the spectrum contains eighteen aromatic proton peaks over a large range, no phenolic proton peaks and peaks for methanol, water and acetone. The isopropyl alkyl group can be seen by six multiplet peaks for CH and twelve doublet peaks for CH_3. The ^1H NMR spectrum for **CaI2** can be seen below (figure 44).

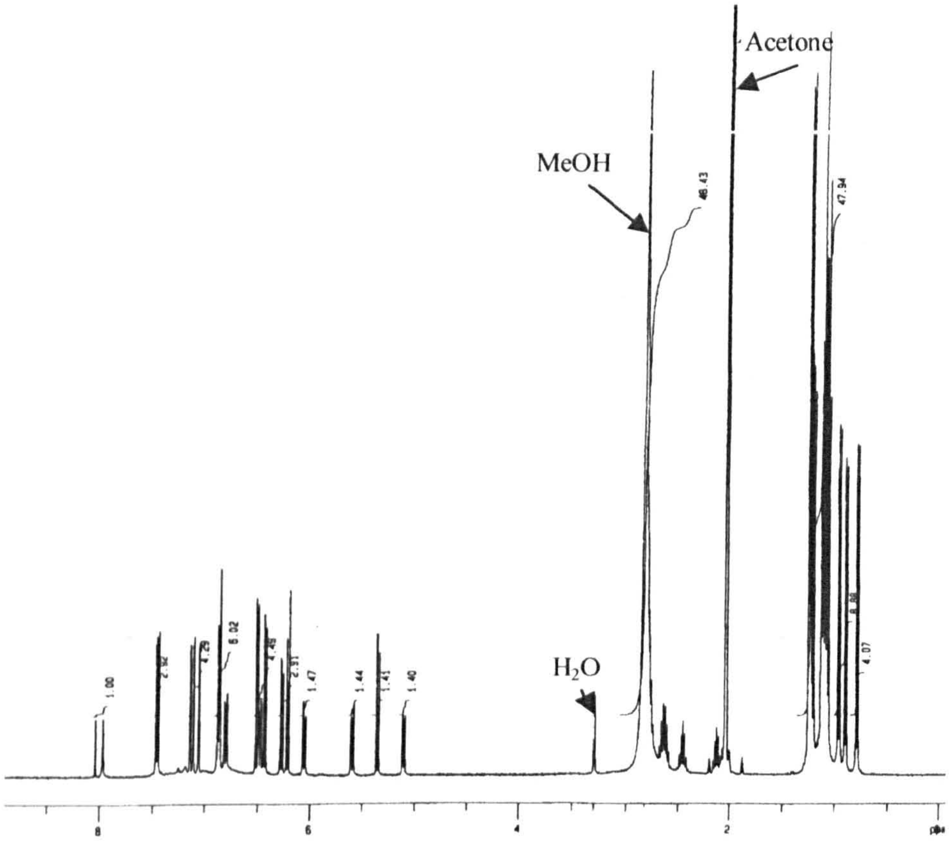


Figure 44. ^1H NMR (d_6-acetone) spectrum for the calcium cation complex with I2 prepared from methanol.

The spectrum is clearly very similar to the spectrum for Ca**M2** (figure 40) and shows that Ca**I2** probably forms hexanuclear clusters in solution. The reduced polarity of the CH_3 groups in **I2**, as apposed to **M2**, is shown by the CH_3 proton peaks in Ca**I2** occurring at a lower ppm. This results in the CH_3 proton peaks no longer overlapping with the acetone solvent peak, though instead the CH proton peaks can be seen to overlap with the water solvent peak. The hexanuclear nature of the complex in solution is supported by the ^{13}C NMR spectrum for the complex, which also shows that every carbon within one aromatic ring is inequivalent.

The 2D COSY NMR spectrum of Ca**I2** is shown below (figure 45). The 2D COSY spectrum for Ca**M2** is analogous to the one shown below (figure 45), except that the Ca**M2** spectrum shows a slightly greater level of decomposition.

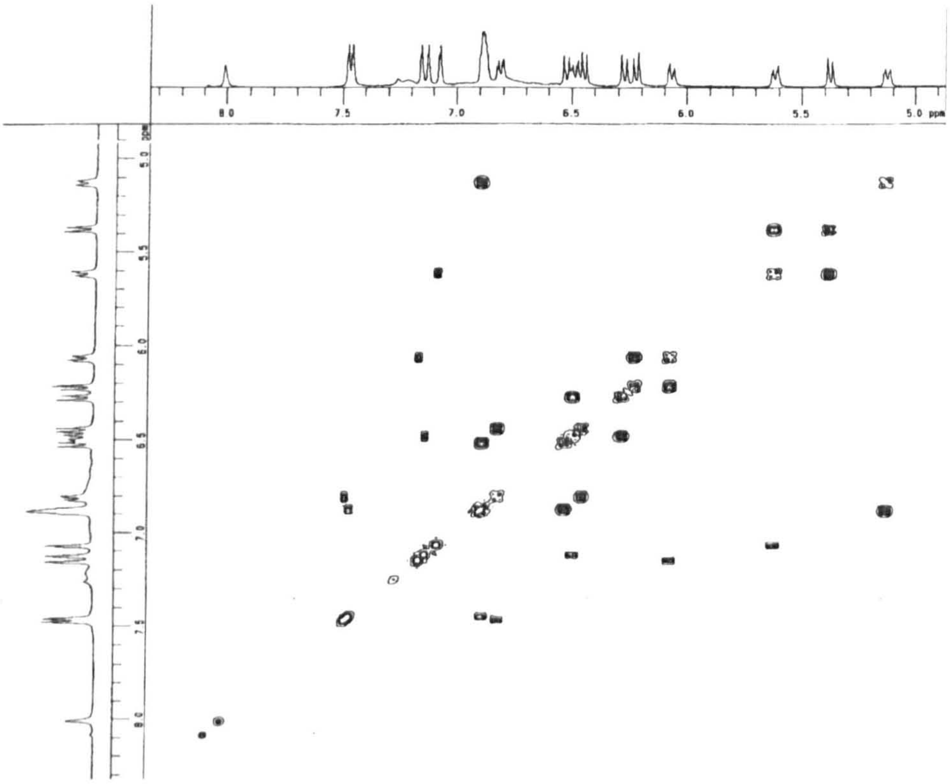


Figure 45. 2D COSY NMR (d_6-acetone) spectrum for the calcium cation complex with I2.

The assigned Ca**I2** ^{1}H NMR spectrum aromatic region can be seen below (figure 46), where the assignments have been obtained from the 2D COSY NMR spectrum.

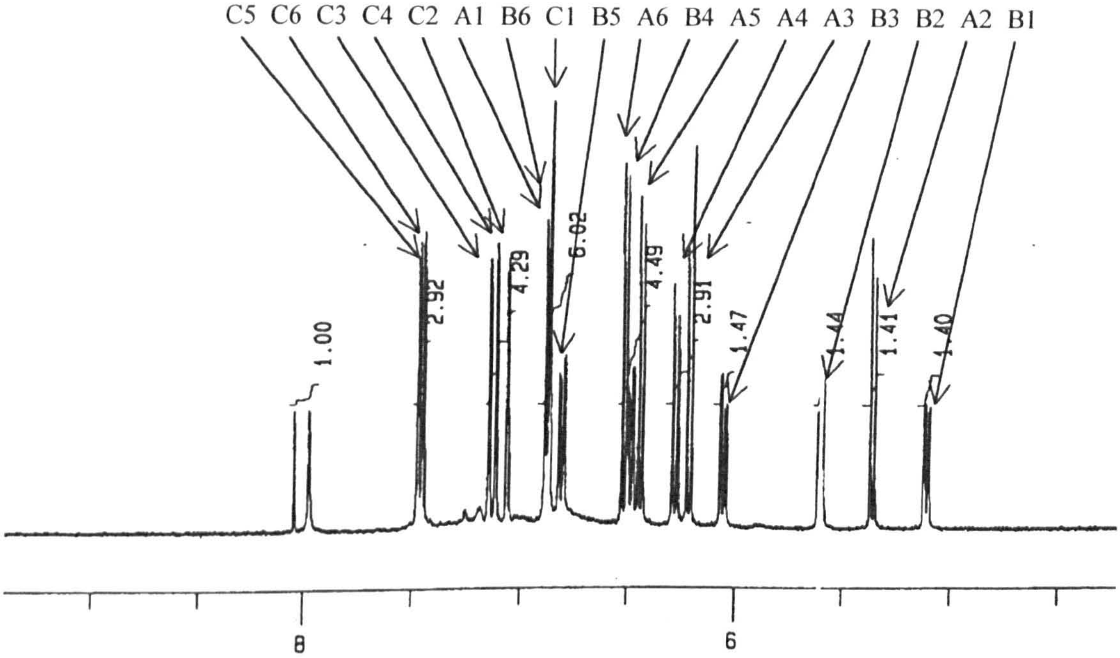


Figure 46. Aromatic region of the ^{1}H NMR (d_6-acetone) spectrum for the calcium cation complex with I2. Peak labels have been obtained from the 2D COSY NMR (d_6-acetone) spectrum for the complex, where A, B and C relate to the three different aromatic protons.

The assigned Ca**I2** NMR spectrum shows how comparable Ca**M2** and Ca**I2** are in solution.

It is clear that Ca**M2** and Ca**I2** have the same structures in solution and so it is reasonable to assume that they both have the same structure in the solid state, especially as all of the strontium cation complexes with sulfurised alkylphenol ligands have the same structure in the solid state (with only the slight difference between all of the complexes being in the orientation of the sulfur atoms in the complex). It is useful that NMR spectroscopy has been able to show that Ca**M2** and Ca**I2** have the same structures, as the crystalline form of Ca**I2** is unsuitable for single crystal x-ray diffraction due to the crystals being too small. This comparison between the Ca**M2** and Ca**I2** NMR spectra also suggests that all of the strontium cation complexes with sulfurised alkylphenol ligands will have the same solution structures in a specific solvent, which is useful as the ^{1}H NMR spectra for strontium cation complexes are always broad and often have to be collected in lower polarity solvents than d_6-acetone and hence have lower information content about the solution structure of the complex (see discussion of strontium cation complexes below).

2.3.4.1.4. Calcium Cation Complex with **O2** (CaO2)

The ^{1}H NMR (d_6-acetone) spectrum of a calcium cation complex with **O2** was collected and was found to be pure. The ^{1}H NMR spectrum shows that the complex in solution is clustered, though the solution species is not easy to determine. The aromatic region of the ^{1}H NMR spectrum shows that the solution structure of **CaO2** is not simply hexanuclear, but is more complicated. The peaks are broad suggesting that the complex has a fluxional solution structure. The ^{1}H NMR spectrum of **CaO2** in $CDCl_3$ is exceptionally broad, therefore the complex can be taken to be very fluxional in chloroform solution. It has not been possible to characterise **CaO2** in the solid state as the crystalline complex is unsuitable for single crystal x-ray diffraction (the crystals are too small and intergrown) and the results from elemental analysis have not been interpretable.

2.3.4.1.5. Strontium Cation Complex with **M2** (SrM2)

The solid state structure of the strontium cation complex with **M2** is known and it is a dinuclear complex isostructural with **CaM2**. Unfortunately strontium cation complexes do not give useful NMR spectra as they are always broad (see section 3.6.4. for a more indepth discussion of this problem). The ^{1}H NMR (d_6-DMSO) spectrum of crystalline **SrM2** was collected and the spectrum was broad and hence does not show if the complex is clustered in solution. Deuterated DMSO was used as the solvent as the complex was insoluble in acetone, which means that the ^{1}H NMR spectrum can only be expected to provide information on the organic species present in the product and not give any solution structure information. From the ^{1}H NMR spectrum it is possible to identify **M2** as the only organic ligand in the product and that the **M2** is deprotonated. As the **M2** molecule is deprotonated and the product does not contain an organic cation (such as tetrabutylammonium) then it can be presumed that the NMR spectrum is for a pure complex of strontium cations with **M2**.

2.3.4.1.6. Strontium Cation Complex with I2 (SrI2)

The ^{1}H NMR (d_6-acetone) spectrum of a crystalline strontium cation complex with **I2** was collected. The crystalline complex was also sampled for single crystal x-ray diffraction and so the solid state structure of the sample is known (**8**). The ^{1}H NMR spectrum shows some clustering which is unusual for strontium cation complexes as they rarely show anything other than broad peaks with no fine structure. The complex had low solubility, which caused a large acetone peak to be present on the spectrum and some noise. The acetone peak is due to proton exchange between water and the deuterated solvent, resulting in the deuterated solvent becoming non-deuterated and therefore showing on the ^{1}H NMR spectrum. As the complex had to be left for a long period of time for enough to dissolve for an NMR spectrum to be collected there has been significant proton exchange and hence the acetone peak is large. The complex is slightly impure with tetrabutylammonium cations (observed as peaks at 3.45, 1.80, 1.45 and 0.95ppm). The aromatic region of the spectrum shows three main peaks with many smaller peaks. This may be because the complex is clustered in solution (like **CaM2** and **CaI2**), but is fluxional, where the rate of exchange is almost too fast for the NMR timescale and so the main peaks are the time-averaged peaks for the clustered complex.

The achievement of a clustered strontium cation complex supports the hypothesis that calcium cation complexes and strontium cation complexes with sulfurised alkylphenol ligands which are prepared from methanol solution are isostructural in the solid state and in solution.

2.3.4.1.7. Strontium Cation Complex with **O2** (SrO2)

The ^1H NMR (d_6-acetone) spectrum of a strontium cation complex with **O2** was collected and shows that the complex was very pure. It is unusual for an **O2** complex to dissolve in acetone, though the ^1H NMR does show that the sample had low solubility in acetone. The ^1H NMR spectrum is broad, where the sharpest peak is for methanol. Although the spectrum is broad, there is some evidence that the complex is clustered in solution, especially by the aromatic region of the ^1H NMR spectrum. The aromatic region shows some fine structure to the broad aromatic proton peaks. This suggests that the complex is clustered in solution, but is fluxional, with the rate of fluxional behaviour similar to than the NMR timescale, resulting in a time-averaged, broad spectrum.

2.3.4.1.8. Zinc Cation Complex with **M2** (ZnM2)

The ^1H NMR (d_6-acetone) spectrum of a zinc cation complex with **M2** was collected and it is complicated. The product contains methanol, but no water. The complex contains no tetrabutylammonium cations and so is probably pure. The peaks for the methyl groups of the **M2** ligand are completely overlapped with the acetone peak and the aromatic region is broad and overlapped. The larger aromatic proton peaks represent deprotonated **M2**, though it is not clear if the product is a mixture of **M2** salt and clustered Zn**M2** or fluxional Zn**M2** complex. It is probable, as for Mg**M2**, Ca**O2**, Sr**I2** and Sr**O2**, that the complex is simply fluxional, especially as the spectrum shows no tetrabutylammonium cations which could form a salt with **M2**. None of the zinc cation complexes with sulfurised alkylphenol ligands gave crystalline products which were suitable for single crystal x-ray diffraction and so the solution structures cannot be compared to the solid state structures.

2.3.4.1.9. Zinc Cation Complex with I2 (ZnI2)

The ^1H NMR (d_6-acetone) spectrum for a zinc cation complex with **I2** can be seen below (figure 47).

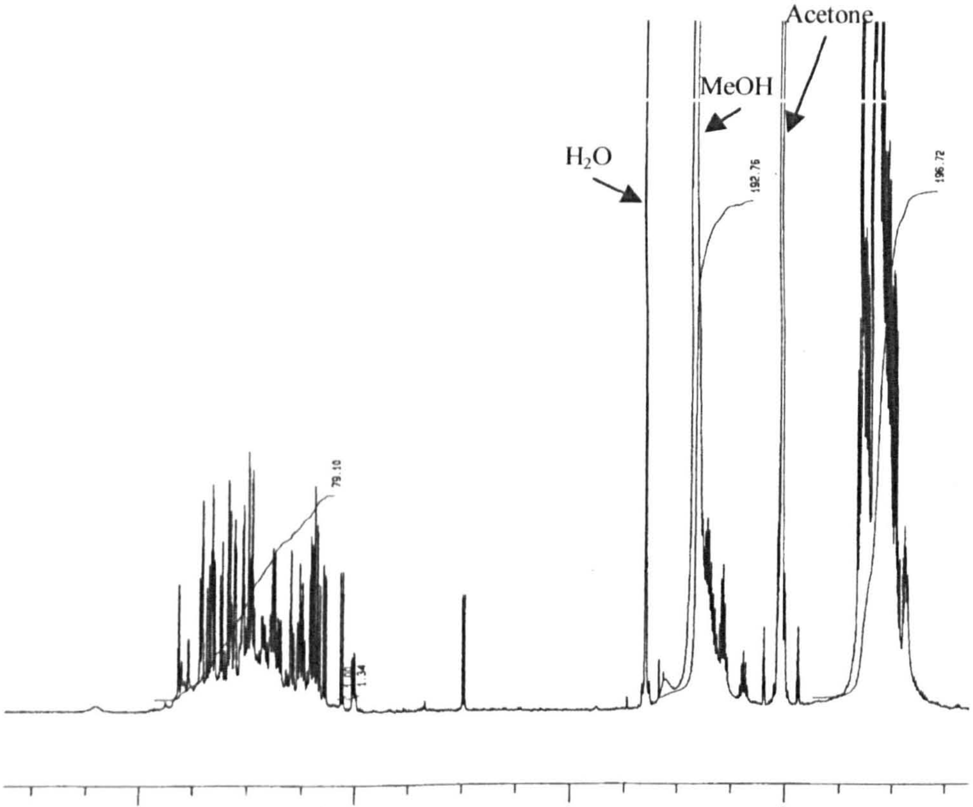


Figure 47. ^1H NMR (d_6-acetone) spectrum for the zinc cation complex with I2 prepared from methanol.

The complex is clearly clustered in solution, with at least twelve different ligand proton environments, suggesting at least a nuclearity of twelve. This gives this complex the largest solution structure of all of the sulfurised alkylphenol complexes that have been characterised.

2.3.4.1.10. Zinc Cation Complex with **B2** (**ZnB2**)

The zinc cation complex with **B2** has a very unclear ^{1}H NMR (d_6-acetone) spectrum as the spectrum is broad and as there are nine *tert*-butyl protons to one aromatic proton, the aromatic region has a low overall intensity. The spectrum shows that the complex is clustered in solution, but no other information, such as the aggregation number, can be gained from it.

2.3.4.1.11. Zinc Cation Complex with **O2** (**ZnO2**)

The ^{1}H NMR spectrum for the zinc cation complex with **O2** was collected in d_6-acetone and $CDCl_3$. The spectrum for the complex in d_6-acetone is very broad and unclear, whereas the spectrum for the complex in $CDCl_3$ is sharper. The spectrum in $CDCl_3$ shows that the complex in solution is clustered with a low aggregation number. The number of **O2** ligands per cluster cannot be determined exactly as the spectrum is slightly broad and the chloroform peak overlaps with some of the aromatic proton peaks.

2.3.4.2. Mass Spectrometry (MS)

The results from the NMR spectroscopy study and single crystal x-ray diffraction analysis show that sulfurised alkylphenol complexes prepared from methanol have different solid state structures to solution state structures. To attempt to conclusively determine the solution structures of the sulfurised alkylphenol complexes, mass spectrometry was used. Calcium complexes and zinc complexes were analysed by MS using a range of techniques. For all of the complexes, acetone was used as the solvent as this solvent had yielded the most information by ^{1}H NMR spectroscopy. Zn**M2**, Zn**I2**, Zn**B2** and Ca**I2** were analysed by positive ion electrospray MS. The spectrum obtained for Zn**M2** can be seen below (figure 48).

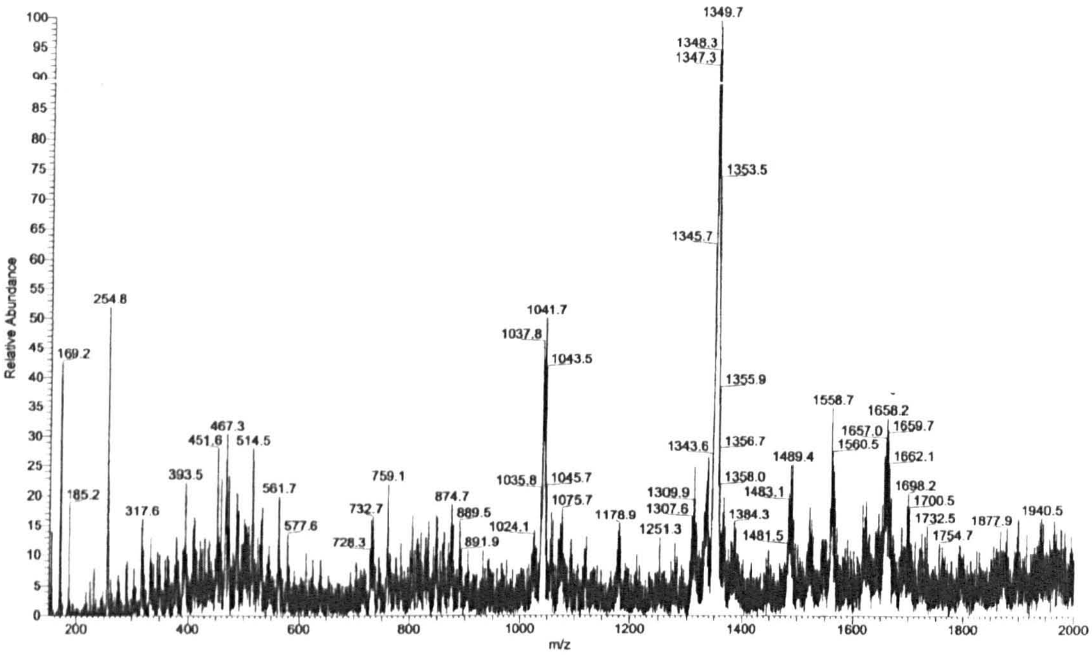


Figure 48. Positive ion electrospray mass spectrometry mass spectrum for the zinc cation complex with M2 prepared from methanol.

The spectrum above is representative of the spectra obtained for the other complexes. It is clear that the spectrum has little use. The only information that could be gained from the MS spectra was that the complexes were clustered in acetone solution, where the difference between the larger peaks is usually equivalent to the loss of one mononuclear unit. A more indepth study was undertaken by the EPSRC Mass Spectrometry Service Centre, Swansea, to discover if there was a condition under which useful MS data could be obtained. Two techniques were assessed for Ca**M2** and Ca**I2** samples, which had exhibited clustered clean ^{1}H NMR spectra. Low resolution electrospray MS was carried out using a range of spray and cone voltages and low resolution fast atom bombardment (LSIMS) was carried out using a range of NOBA matrices. The spectra show that both of the complexes are clustered in solution, but cannot be used to determine the aggregation number.

The MS spectra obtained on the sulfurised alkylphenol complexes with a range of techniques show that the complexes are clustered in solution, but the aggregation numbers cannot be determined, even with 'soft' techniques such as electrospray.[159] This shows that the complexes are too fragile to be analysed by MS and therefore NMR spectroscopy is the only useful source of information on the solution structures of the complexes. The high fragility of the complexes may be due to the complexes forming clustered complexes in solution where the clusters are formed by hydrogen-bonding, which is too weak to be observed by MS.

2.3.4.3. Solution Structure Study Summary

Sulfurised alkylphenol complexes have been characterised in solution by ^{1}H NMR spectroscopy. All of the complexes appear to have different solution structures to solid state structures. The calcium cation complexes with **M2** and **I2** have given the cleanest ^{1}H NMR spectra as these complexes do not have fluxional behaviour in solution as observed for the other complexes. **CaM2** and **CaI2** have hexanuclear structures in solution. It has been found that the solvent has a significant effect on the solution structure of the complex. Clustered complexes are most often observed in deuterated acetone solution, though clustered complexes of **MgM2**, **CaO2**, **SrM2** and **ZnO2** have been observed in solvents other than d_6-acetone. It has been found that the morphology of the product affects the solubility of the product, but does not affect the ^{1}H NMR spectrum. Mass spectrometry was found to be of no use in the characterisation of sulfurised alkylphenol complexes in solution as the complexes are too fragile.

2.3.5. Summary

Sulfurised alkylphenol complexes have been reproducibly prepared from methanol solutions in good yields. Crystalline complexes CaM2 (8), SrM2 (9), SrI2 (10) and SrO2 (11) have been characterised in the solid state by single crystal x-ray diffraction. This has shown that the calcium and strontium complexes are isostructural and that all of the strontium cation complexes are the same, except for a change in the orientation of the sulfur atoms. The coordination mode of the sulfurised alkylphenol molecules is the same for all of the complexes and is different to any coordination mode observed in the literature. All of the complexes are dinuclear in the solid state, though it has been shown by ^{1}H NMR spectroscopy that in solution the complexes have different structures, usually with higher aggregation numbers. Solution studies have shown that the complexes have the same structure, independent of crystallinity or the metal salt used in the preparation. Elemental analysis and mass spectrometry have shown that the complexes are fragile.

2.4. Sulfurised Alkylphenol Complexes Prepared from Acetone and Water Solution

2.4.1. Introduction

Sulfurised alkylphenol complexes have been prepared from acetone and water solutions. As single crystal x-ray diffraction is the most useful analytical tool for understanding the complexes that have been prepared, time was not spent on characterising products which were unsuitable for single crystal x-ray diffraction. The general preparation method gave several crystalline complexes, of which four were analysed by single crystal x-ray diffraction. Most of the other crystalline products were unsuitable for single crystal x-ray diffraction, for example, due to being too small crystals or twinned. **I2** often results in fine needle crystals, independent of the solvents used in the preparation, and this form of crystalline product is not suited to single crystal x-ray diffraction. For the preparation, deprotonated ligand solution was added to the metal salt in water. Water was used as the main solvent as the products should not be soluble in water, with acetone used to dissolve the ligand so it could react to form a complex. All of the reactions used slow diffusion of the deprotonated ligand into the metal salt solution to aim for crystalline products.

The solid state structures of the complexes analysed by single crystal x-ray diffraction will be discussed before their solution state structures. The reactions that did not give crystalline complexes analysed by single crystal x-ray diffraction will not be discussed.

2.4.2. Solid State Structures of Sulfurised Alkylphenol Complexes Prepared from Acetone and Water Solutions

The solid state structures of Sr**B2** and Ba**B2** have been supported by elemental analysis data, using V_2O_5 as a catalyst. Not enough crystalline Mg**M2** could be isolated for elemental analysis and no result could be interpreted from the data obtained on Ba**I2**.

2.4.2.1. Magnesium Cation Complex with **M2** (Mg**M2**) (**12**)

A crystalline magnesium cation complex with **M2** was grown from acetone and water solution. The complex consists of the **M2** ligand, with –2 charge, a magnesium cation and water molecules. The **M2** ligand coordinates to the magnesium cation *via* both oxygen atoms and very weakly through the sulfur atom. Unlike the complexes prepared from methanol, the **M2** ligand does not bridge two metal ions. The magnesium cation is five coordinate with slightly distorted square based pyramidal geometry.

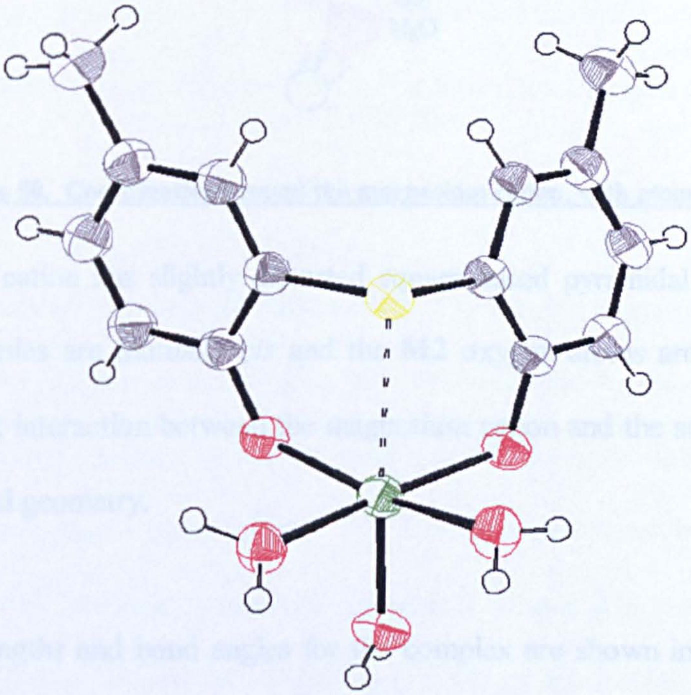


Figure 49. Structure of the magnesium cation complex with M2 prepared from acetone/water, MgM2.3H$_2$O, where one free acetone molecule and two free water molecules have been deleted from the lattice. The interaction between the sulfur atom and the magnesium cation is represented by a dashed line.

The structure of the magnesium cation complex with **M2** can be seen above (figure 49). The interaction between the magnesium cation and the sulfur atom has been represented by a dashed line as the bond is very weak. The coordination sphere around the magnesium cation can be seen below (figure 50).

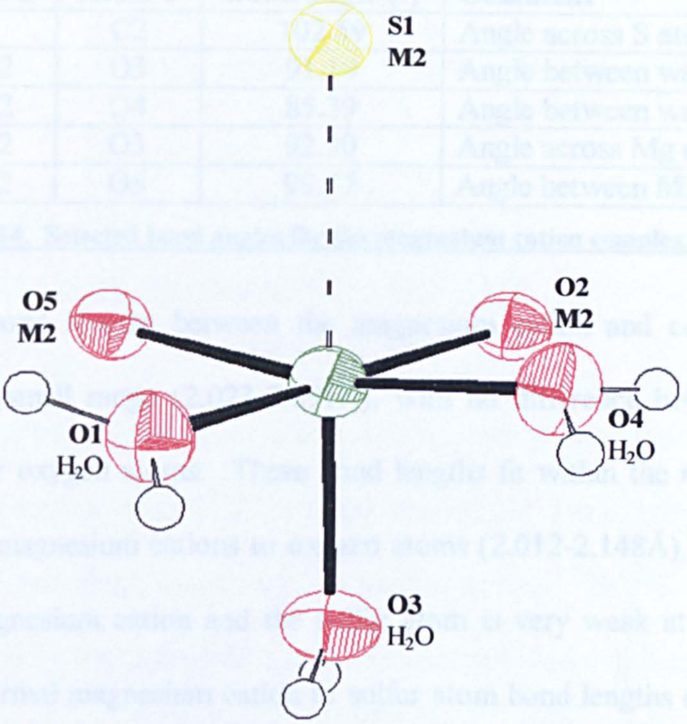


Figure 50. Coordination around the magnesium cation, with atom labels.

The magnesium cation has slightly distorted square based pyramidal geometry, where the water molecules are mutually *cis* and the **M2** oxygen atoms are also *cis* to each other. The weak interaction between the magnesium cation and the sulfur atom creates a quasi-octahedral geometry.

Selected bond lengths and bond angles for the complex are shown in the tables below (tables 13 and 14).

Atom 1	Atom 2	Bond length (Å)	Comment
Mg2	S1	2.712	Very weak interaction
Mg2	O1	2.056	Mg cation to water O atom bond
Mg2	O2	2.023	Mg cation to **M2** O atom bond
Mg2	O3	2.042	Mg cation to water O atom bond
Mg2	O4	2.091	Mg cation to water O atom bond
Mg2	O5	2.044	Mg cation to **M2** O atom bond

Table 13. Selected bond lengths for the magnesium cation complex with M2.

Atom 1	Atom 2	Atom 3	Bond angle (°)	Comment
C1	S1	C2	102.59	Angle across S atom
O1	Mg2	O3	91.19	Angle between water O atoms
O1	Mg2	O4	85.39	Angle between water O atoms
O2	Mg2	O3	92.30	Angle across Mg cation
O2	Mg2	O5	99.47	Angle between **M2** O atoms

Table 14. Selected bond angles for the magnesium cation complex with M2.

The range of bond lengths between the magnesium cation and coordinated oxygen atoms covers a small range (2.023-2.091Å), with no difference between **M2** oxygen atoms and water oxygen atoms. These bond lengths fit within the range expected for coordination of magnesium cations to oxygen atoms (2.012-2.148Å).[41] The interaction between the magnesium cation and the sulfur atom is very weak at 2.712Å, which is shown by the normal magnesium cation to sulfur atom bond lengths covering the range 2.348-2.690Å.[41]

The above complex is very unusual for magnesium in that the magnesium cation is only coordinated to five oxygen atoms.[29] This has been enforced by the **M2** ligand, where the magnesium cation has been forced to weakly coordinate to the sulfur atom to obtain its preferred coordination number of six,[28, 29, 162] though the interaction is weak due to the shape of the **M2** molecule. Normally magnesium cations prefer coordination to six water molecule oxygen atoms, as $[Mg(OH_2)_6]^{2+}$, where the interactions with ligands occur in the second coordination sphere for the magnesium cation.[24, 27, 162] This coordination motif is observed most often for magnesium cation complexes including those in nature.[28] For the magnesium cation to have accepted less favourable coordination conditions, such as coordination to only five oxygen atoms, the oxygen atoms on the **M2** ligand must be preferable to the magnesium cation over water molecule oxygen atoms, of which there was an excess available to the magnesium cation by the preparation method of the complex. Normally anhydrous conditions are required to avoid $[Mg(OH_2)_6]^{2+}$ formation.[162] The bond lengths for the magnesium cation to the oxygen atoms in the complex are reasonably short, which shows that the magnesium cation is strongly bound and therefore is not within an unfavourable environment.

2.4.2.2. Strontium Cation Complex with **B2** (SrB2) (13)

A crystalline complex of strontium cations with **B2** was grown from acetone and water solution. The complex consists of a deprotonated **B2** ligand, with –2 charge, one strontium cation and seven coordinated water molecules. The –2 charge on the **B2** ligand is stabilised by hydrogen-bonding to coordinated water molecules and as the **B2** ligand is not bound to the strontium cation, the complex is actually a salt. The strontium cation is eight coordinate, with antiprismatic geometry, coordinated to eight water molecule oxygen atoms, of which two water molecule oxygen atoms bridge to a second strontium cation. All of the strontium cations within the salt are equivalent. The asymmetric unit of the complex is shown below (figure 51).

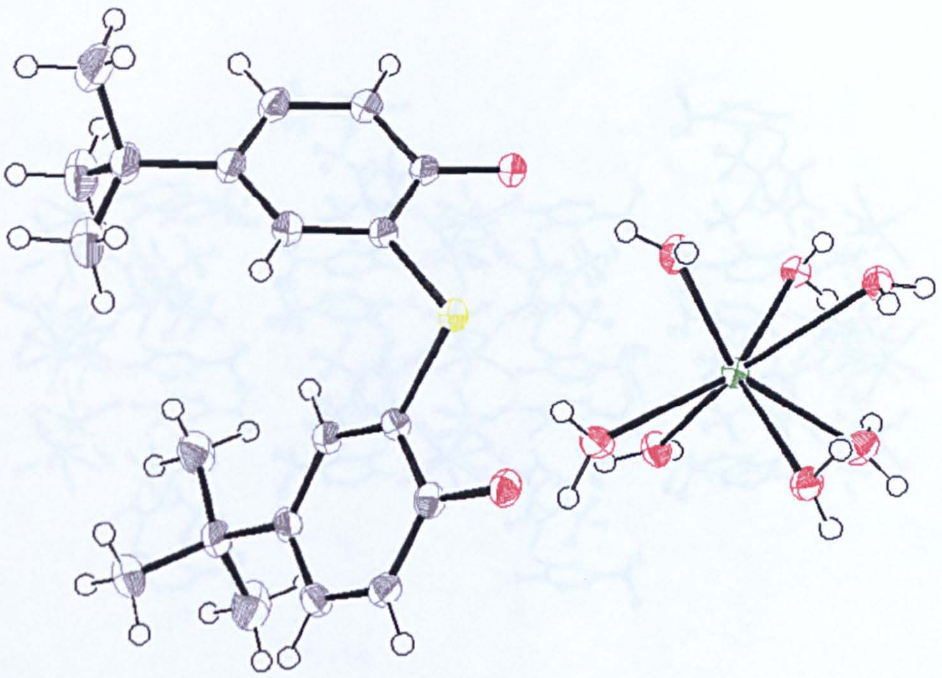


Figure 51. Asymmetric unit of the strontium cation salt with B2, $(Sr^{2+})(B2^{2-}).7H_2O$, prepared from acetone/water.

In the asymmetric unit of the salt (figure 51) it can be seen that the **B2** ligand is not coordinated directly to the strontium cation. The hydrogen atoms in the water molecules orientate towards the **B2** ligand oxygen atoms to stabilise the –1 charge on each of these oxygen atoms *via* hydrogen-bonding. The hydrogen-bonding and bridging water molecule oxygen atoms create a 2D polymeric structure, as shown by the unit cell below (figure 52).

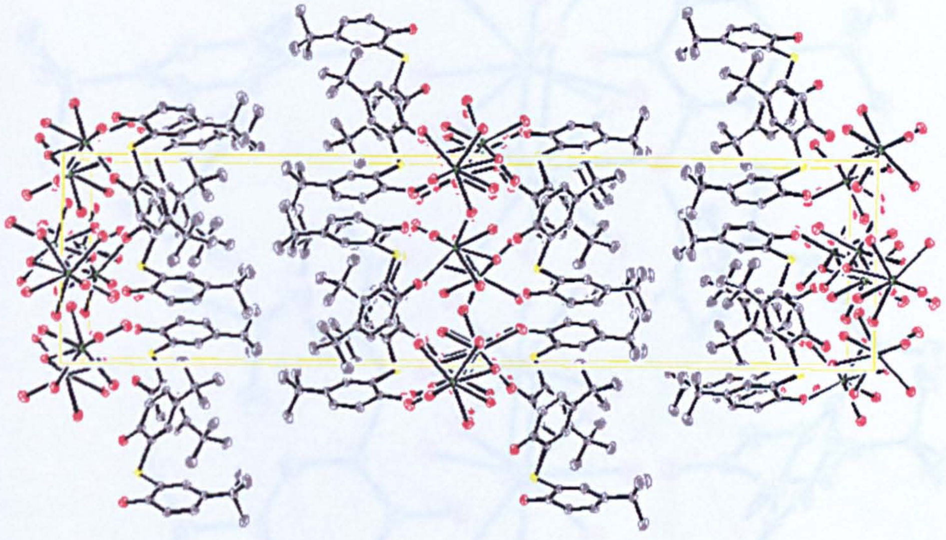


Figure 52. Unit cell of the strontium cation salt with B2, where the hydrogen atoms have been removed for clarity.

The unit cell of the salt shows that the salt has a bilayer structure, where rows of hydrated strontium cations sit within rows of **B2** ligands. The *tert*-butyl groups of the **B2** ligands form the edge of each layer and there is space between the *tert*-butyl groups of each layer.

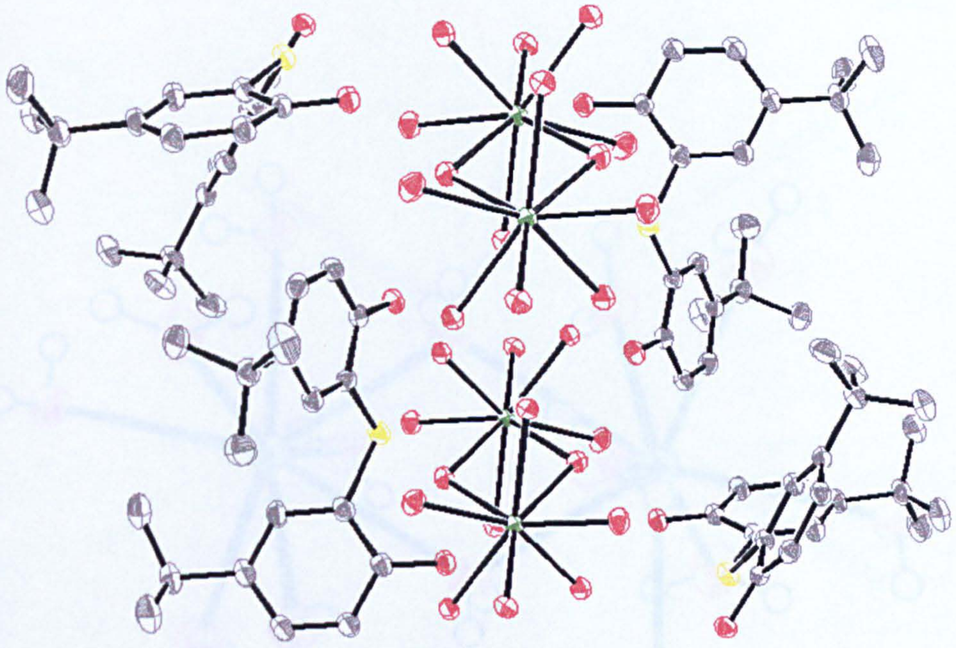


Figure 53. Section of the layer structure within the strontium cation salt with B2, where the hydrogen atoms have been removed for clarity.

A section of the unit cell shows how the layer structure within the salt is built up (figure 53). The strontium cations are arranged into pairs of hydrated strontium cations that are bridged by two water molecule oxygen atoms. There is one **B2** ligand per strontium cation, though they are not directly bound. The **B2** ligands are hydrogen-bonded to water molecules, where half of the **B2** ligands are orientated at 90° to the other **B2** ligands. The orientation and positioning of the **B2** ligands is probably caused by packing effects, where the oxygen atoms of the **B2** ligands are too far apart to coordinate to a pair of strontium cations and hence some **B2** ligands are forced to sit at 90° to the angle of the other **B2** ligands.

The diagram below shows the environment around a pair of strontium cations in the salt (figure 54).

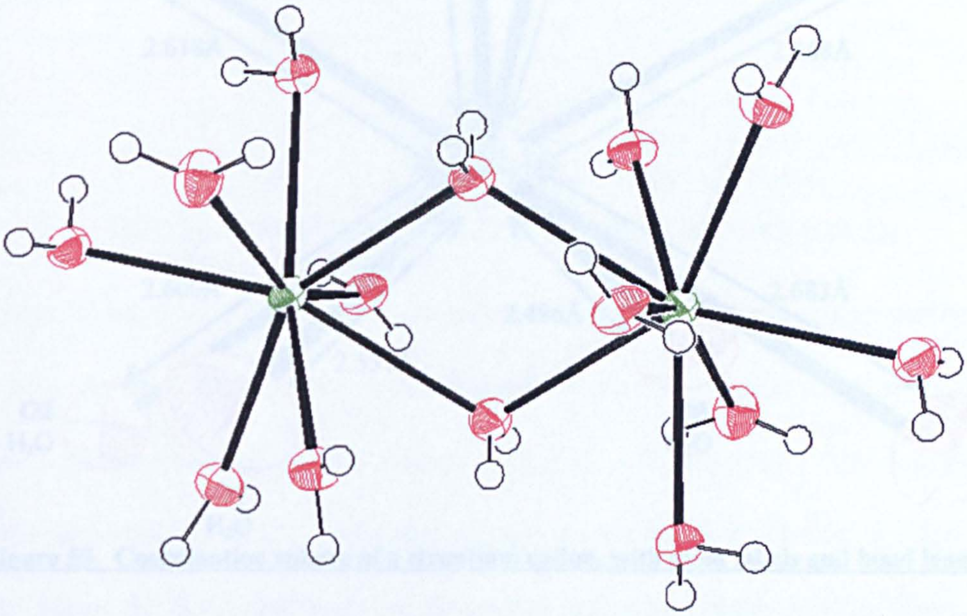


Figure 54. Coordination spheres of two strontium cations bridged by water molecule oxygen atoms.

The diagram below (figure 55) shows the coordination sphere around one strontium cation in the salt, where all of the strontium cations in the salt are equivalent.

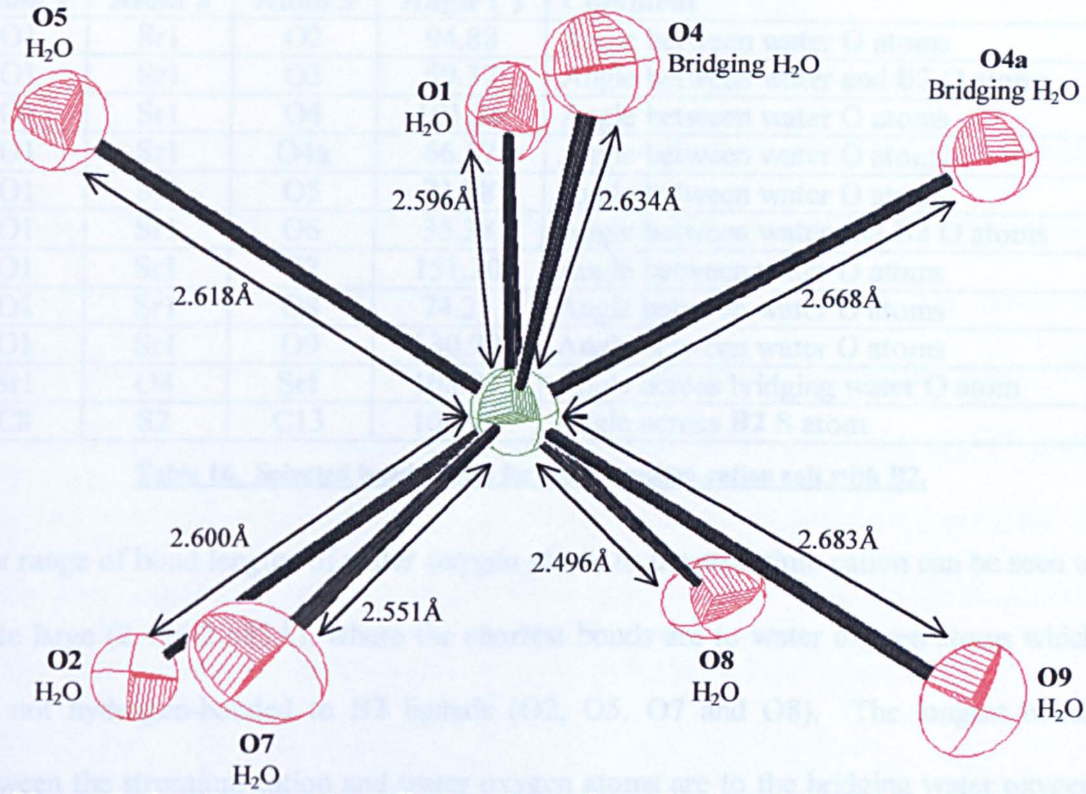


Figure 55. Coordination sphere of a strontium cation, with atom labels and bond lengths.

Selected bond lengths and bond angles can be seen in the tables below (tables 15 and 16).

Atom 1	Atom 2	Length (Å)	Comment
Sr1	O1	2.596	Sr cation to water O atom
Sr1	O2	2.600	Sr cation to water O atom
Sr1	O3	5.451	Sr cation to **B2** O atom – no interaction
Sr1	O4	2.634	Sr cation to bridging water O atom
Sr1	O4a	2.668	Sr cation to bridging water O atom
Sr1	O5	2.618	Sr cation to water O atom
Sr1	O6	4.550	Sr cation to **B2** O atom – no interaction
Sr1	O7	2.551	Sr cation to water O atom
Sr1	O8	2.496	Sr cation to water O atom
Sr1	O9	2.683	Sr cation to water O atom
Sr1	Sr1	4.314	Sr cation to Sr cation within a pair
Sr1	Sr1	5.830	Sr cation to nearest Sr cation of another pair
O3	O6	5.649	Interatomic distance between **B2** O atoms
O3	O9	2.727	Hydrogen-bond
O6	O1	2.863	Hydrogen-bond
O6	O4a	2.692	Hydrogen-bond

Table 15. Selected bond lengths for the strontium cation salt with B2.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O1	Sr1	O2	94.88	Angle between water O atoms
O1	Sr1	O3	59.37	Angle between water and **B2** O atoms
O1	Sr1	O4	101.36	Angle between water O atoms
O1	Sr1	O4a	66.57	Angle between water O atoms
O1	Sr1	O5	71.98	Angle between water O atoms
O1	Sr1	O6	35.38	Angle between water and **B2** O atoms
O1	Sr1	O7	151.20	Angle between water O atoms
O1	Sr1	O8	74.21	Angle between water O atoms
O1	Sr1	O9	130.99	Angle between water O atoms
Sr1	O4	Sr1	108.91	Angle across bridging water O atom
C8	S2	C13	104.95	Angle across **B2** S atom

Table 16. Selected bond angles for the strontium cation salt with B2.

The range of bond lengths of water oxygen atoms to the strontium cation can be seen to quite large (2.496-2.683Å), where the shortest bonds are to water oxygen atoms which are not hydrogen-bonded to **B2** ligands (O2, O5, O7 and O8). The longest bonds between the strontium cation and water oxygen atoms are to the bridging water oxygen atoms. All of the bonds between the strontium cation and water oxygen atoms, except the bond between the strontium cation and water oxygen atom O8, are within the normal range for these types of bonds, where strontium cation to water oxygen atom bonds normally cover the range 2.504-2.702Å and bonds between strontium cations and bridging water molecule oxygen atoms (bridging between two strontium cations) cover the range 2.601-2.811Å.[41] The bond between the strontium cation and the water oxygen atom O8 can be seen to be slightly shorter than the normal range. The interatomic distances between the strontium cation and the **B2** oxygen atoms show that there is no interaction between the strontium cations and the **B2** molecules. The **B2** ligands are hydrogen-bonded to some of the water molecules that are coordinated to the strontium cations, as shown by interatomic distances of less than 2.9Å. The angles around the strontium cations show that the strontium cation geometry is distorted antiprismatic.

2.4.2.3. Barium Cation Complex with **I2** (BaI2) (14)

A crystalline complex of barium cations with **I2** was grown from acetone and water solution. The complex consists of two **I2** ligands, one barium cation, one acetone molecule and three water molecules. One of the **I2** molecules is a free neutral **I2** molecule and the other has a –2 charge and is coordinated to the barium cation. The barium cation is nine coordinate, coordinating to one **I2** oxygen atom, one **I2** sulfur atom, one acetone oxygen atom and six bridging water molecules oxygen atoms, of which three bridge to one other barium cation and the other three bridge to another barium cation. The asymmetric unit of the complex is shown below (figure 56).

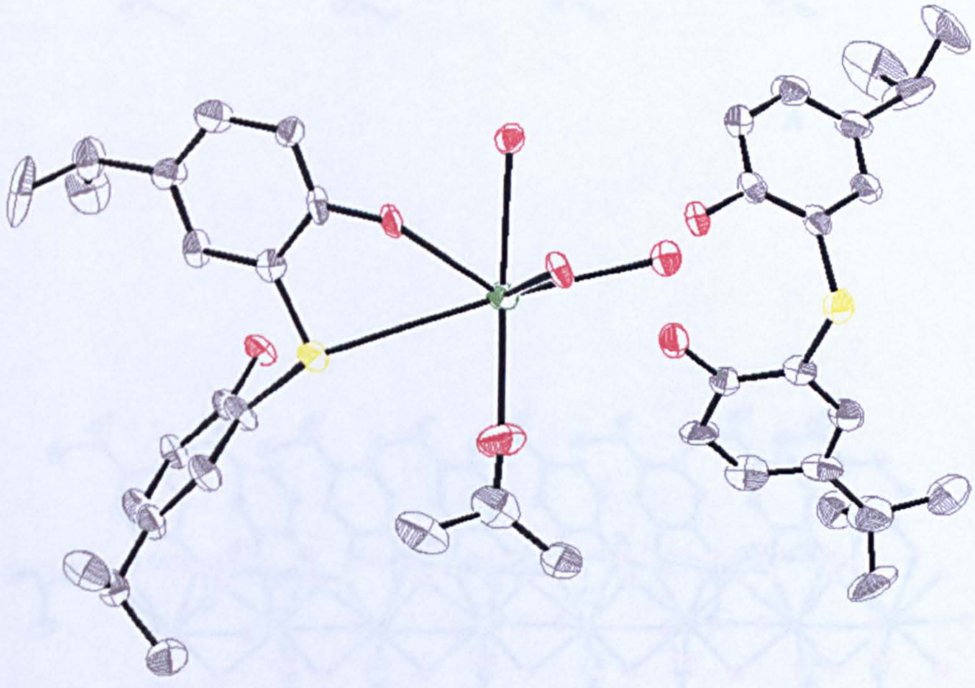


Figure 56. Asymmetric unit of the barium cation complex with I2, BaI2.3H_2O.acetone.I2, prepared from acetone/water, where the hydrogen atoms have been removed for clarity.

The complex consists of 1D polymeric chains of hydrated barium cations coordinated to **I2** ligands, all connected by bridging water molecules and hydrogen-bonding. The free **I2** molecule is bound by hydrogen-bonding to two bridging water molecules.

Coordinated **I2** ligands outnumber free **I2** molecules in the unit cell, with approximately one free **I2** ligand per eighteen coordinated **I2** molecules. A polymeric chain is shown in the diagram below (figure 57).

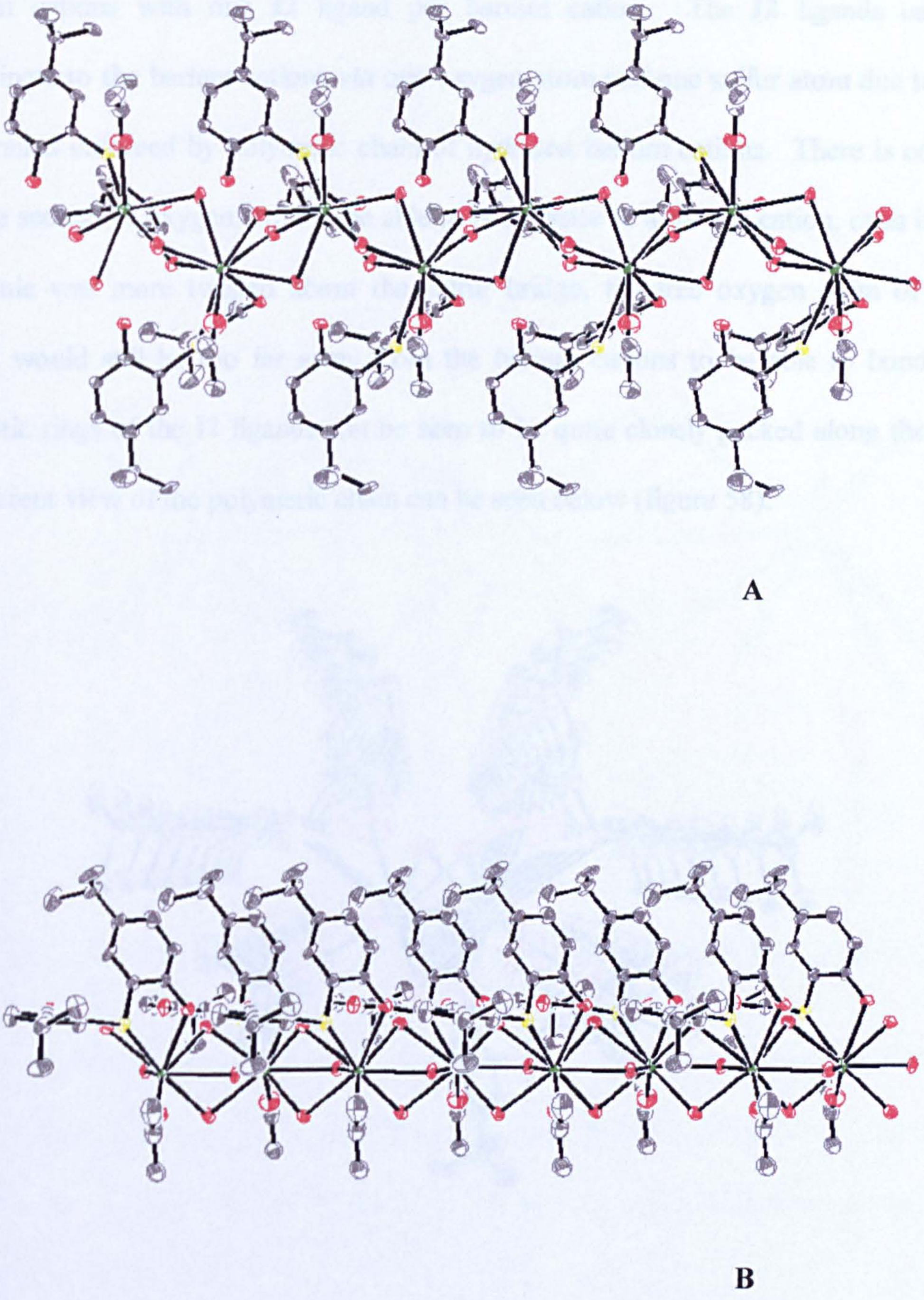


Figure 57. Two views (A and B) of a polymeric chain in the barium cation complex with I2. Hydrogen atoms and the free I2 molecule have been removed for clarity.

The above diagram (figure 57) shows a polymeric chain in the barium cation complex with **I2**, where diagram B is diagram A rotated around the direction of the chain. The diagram shows that all of the water molecules in the complex bridge between barium cations. The **I2** ligands coordinate *via* one oxygen atom and one sulfur atom to the barium cations with one **I2** ligand per barium cation. The **I2** ligands can only coordinate to the barium cations *via* one oxygen atom and one sulfur atom due to steric constraints enforced by polymeric chain of hydrated barium cations. There is no space for the second **I2** oxygen atom to be able to coordinate to a barium cation, even if the **I2** molecule was more twisted about the sulfur bridge, the free oxygen atom of the **I2** ligand would still be too far away from the barium cations to be able to bond. The aromatic rings of the **I2** ligands can be seen to be quite closely packed along the chain. A different view of the polymeric chain can be seen below (figure 58).

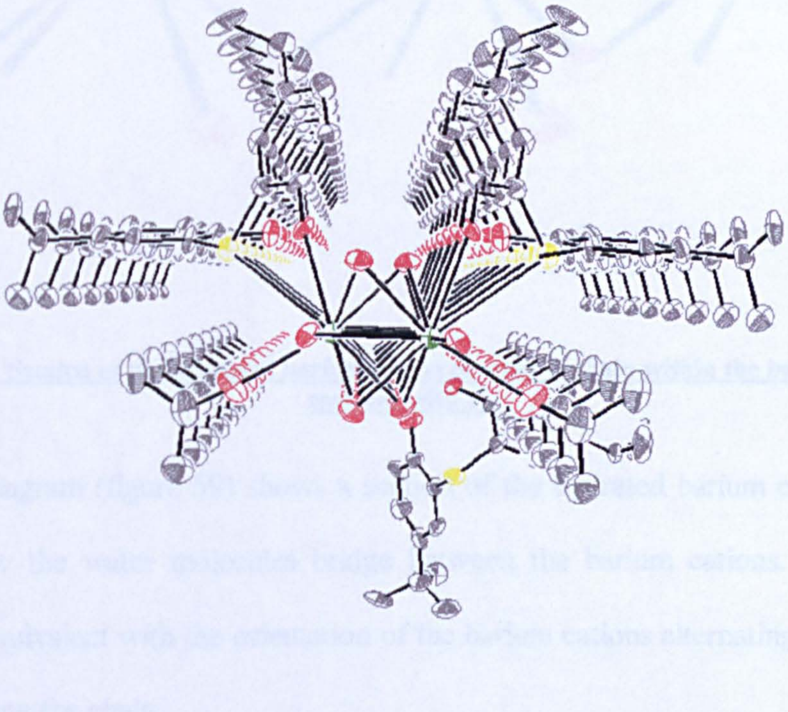


Figure 58. The 'end-on' view of a polymeric chain in the barium cation complex with I2, where hydrogen atoms have been removed for clarity.

The above diagram (figure 58) shows the 'end-on' view of a polymeric chain in the barium cation complex with **I2**. The hydrated barium cations sit within a channel that is surrounded by **I2** ligands and acetone molecules. Within the chain, the acetone molecules and the **I2** ligands form rows, where the rows are too separated for the acetone molecules and the **I2** ligands to be interacting. The free **I2** molecule can be seen and it is clear that this molecule has no effect on the chain, though this molecule may have some influence on the packing of the chains in the unit cell. The diagram below shows a section of the chain of hydrated barium cations in the complex (figure 59).

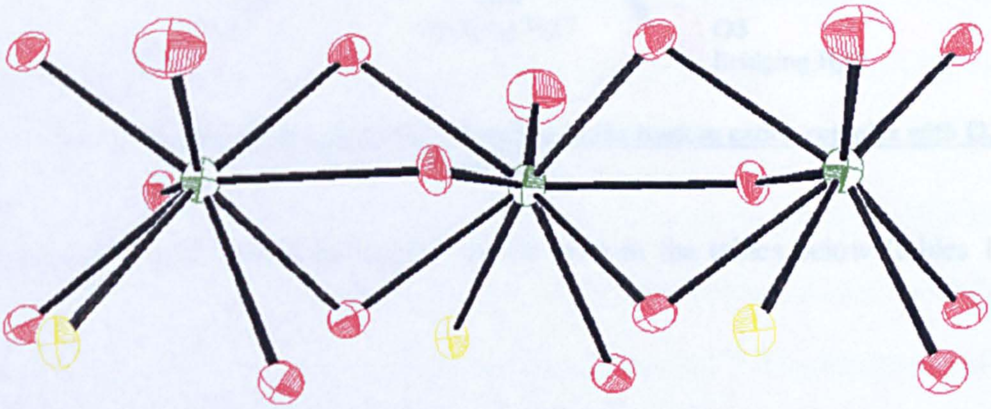


Figure 59. Section of the hydrated barium cation polymeric chain within the barium cation complex with I2.

The above diagram (figure 59) shows a section of the hydrated barium cation chain to illustrate how the water molecules bridge between the barium cations. The barium cations are equivalent with the orientation of the barium cations alternating between two directions along the chain.

The diagram below (figure 60) shows the coordination sphere around the barium cation within the complex (with atom labels).

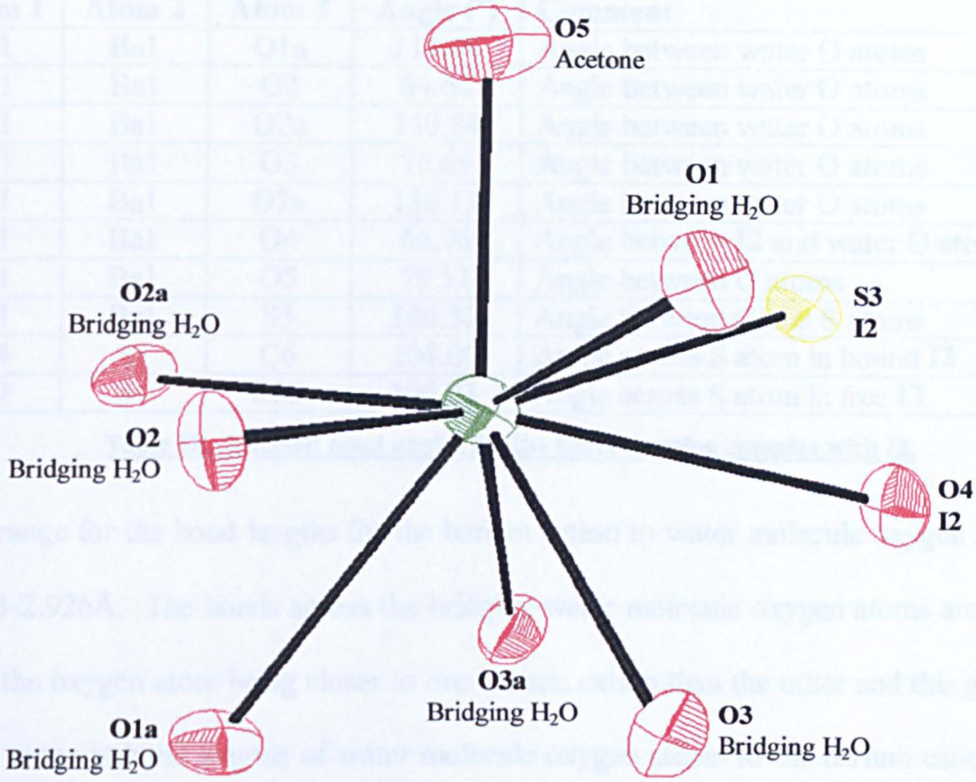


Figure 60. Coordination sphere of the barium cation in the barium cation complex with I2, with atom labels.

Selected bond lengths and bond angles can be seen in the tables below (tables 17 and 18).

Atom 1	Atom 2	Length (Å)	Comment
Ba1	O1	2.785	Ba cation to bridging water O atom bond
Ba1	O1a	2.926	Ba cation to bridging water O atom bond
Ba1	O2	2.773	Ba cation to bridging water O atom bond
Ba1	O2a	2.881	Ba cation to bridging water O atom bond
Ba1	O3	2.815	Ba cation to bridging water O atom bond
Ba1	O3a	2.860	Ba cation to bridging water O atom bond
Ba1	O4	2.811	Ba cation to **I2** O atom
Ba1	O5	2.691	Ba cation to acetone O atom
Ba1	S3	3.458	Ba cation to **I2** S atom
Ba1	Ba1	4.291	Interatomic distance
O4	O8	5.076	Interatomic distance within bound **I2**
O4	O3	2.613	Hydrogen-bond between **I2** and water O atoms
O8	O1a	2.787	Hydrogen-bond between **I2** and water O atoms
O8	O4a	2.481	Intermolecular hydrogen-bond (**I2** O atoms)
O2	O6	2.587	Hydrogen-bond (free **I2** O atom to water O atom)
O2	O7	2.641	Hydrogen-bond (free **I2** O atom to water O atom)
O6	O7	2.499	Intramolecular hydrogen-bond

Table 17. Selected bond lengths for the barium cation complex with I2.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O1	Ba1	O1a	119.48	Angle between water O atoms
O1	Ba1	O2	64.61	Angle between water O atoms
O1	Ba1	O2a	140.84	Angle between water O atoms
O1	Ba1	O3	76.69	Angle between water O atoms
O1	Ba1	O3a	132.13	Angle between water O atoms
O1	Ba1	O4	66.76	Angle between **I2** and water O atoms
O1	Ba1	O5	79.51	Angle between O atoms
O1	Ba1	S3	100.30	Angle between O and S atoms
C4	S3	C6	104.00	Angle across S atom in bound **I2**
C7	S4	C23	106.23	Angle across S atom in free **I2**

Table 18. Selected bond angles for the barium cation complex with I2.

The range for the bond lengths for the barium cation to water molecule oxygen atoms is 2.773-2.926Å. The bonds across the bridging water molecule oxygen atoms are uneven with the oxygen atom being closer to one barium cation than the other and this gives the wide range in bond lengths of water molecule oxygen atoms to the barium cation. The bond lengths fit within the normal range of barium cation to bridging water molecule oxygen atom bond lengths of 2.711-3.019Å, where the water molecules bridge between barium cations.[41] It has been observed that bridging water molecules normally have unequal bonds to the metal ions, as observed in this complex.[41] The shortest bond to the barium cation is to the acetone oxygen atom. The **I2** ligand coordinates to the barium cation *via* one oxygen atom and the sulfur atom, where the barium cation to oxygen atom bond length is within the range of bond lengths of the barium cation to water oxygen atoms and the bond length to the sulfur atom is within the range for barium cation to sulfur atom bond lengths (3.014-3.611Å).[41] The free oxygen atom on the bound **I2** ligand is hydrogen-bonded to one bridging water oxygen atom (O1a) and to a neighbouring **I2** ligand oxygen atom (O4a). The free **I2** molecule is hydrogen-bonded to a water molecule oxygen atom (O2) *via* both of its oxygen atoms (O6 and O7). The two oxygen atoms within the free **I2** molecule are also hydrogen-bonded to each other. The bound **I2** ligand is very different to the free **I2** molecule, which is shown by the hydrogen-bonding of these molecules, the O-O intramolecular distance and the angle across the sulfur atom. The O-O intramolecular distance in the free **I2** molecule is very short (2.499Å) as the two oxygen atoms are connected by a hydrogen-bond, whereas in the bound **I2** ligand this distance is large (5.076Å). The packing of the coordinated **I2** molecules within the complex and the hydrogen-bonding within the complex cause the angle across the sulfur atom to be different for the two **I2** molecules.

2.4.2.4. Barium Cation Complex with B2 (BaB2) (15)

A crystalline complex of barium cations with **B2** was grown from acetone and water solution. The asymmetric unit of the complex consists of two **B2** ligands, with –2 charge, two barium cations and twelve water molecules. One **B2** ligand coordinates to a barium cation *via* one oxygen atom, whereas the other **B2** ligand coordinates *via* one oxygen atom and one sulfur atom. The –1 charge on the uncoordinated **B2** oxygen atom is stabilised by hydrogen-bonding to water molecules. One barium cation (Ba1) is ten coordinate, coordinating to one **B2** oxygen atom, two bridging water molecule oxygen atoms (Ba1-Ba2), one bridging water molecule oxygen atom (Ba1-Ba2-2) and six non-bridging water molecule oxygen atoms. The other barium cation (Ba2) is nine coordinate, coordinating to one **B2** oxygen atom, one **B2** sulfur atom, two bridging water molecule oxygen atoms (Ba1-Ba2), two bridging water molecule oxygen atoms (Ba2-Ba2), one bridging water molecule oxygen atom (Ba2-Ba1-2) and two non-bridging water molecule oxygen atoms. The complex has a layer structure, which is held together by water molecule oxygen atoms that bridge between barium cations and hydrogen-bonding. There are six free water molecules in the lattice. The asymmetric unit of the complex is shown below (figure 61).

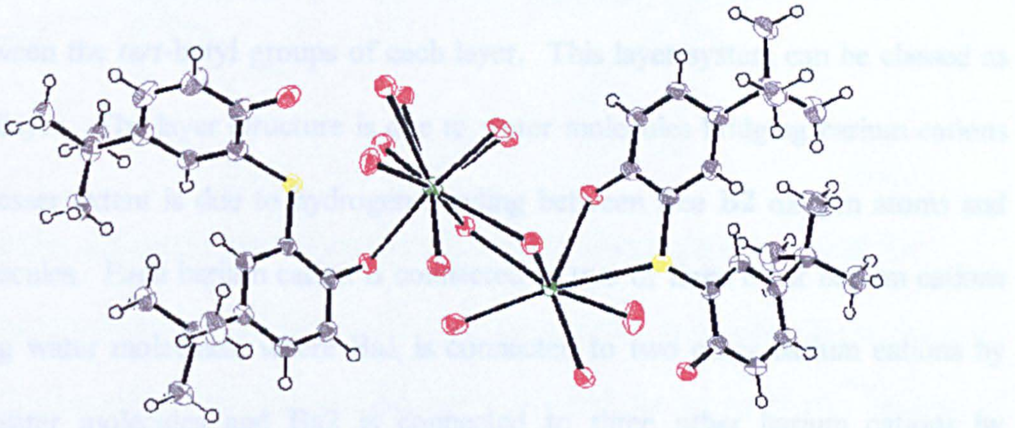


Figure 61. Structure of the asymmetric unit of the barium cation complex with B2, (Ba^{2+})$_2$(B2^{2-})$_2$.12H$_2$O, prepared from acetone/water, where the free lattice water molecules have been removed for clarity.

The complex has a layer structure, which is shown in the diagram below (figure 62).

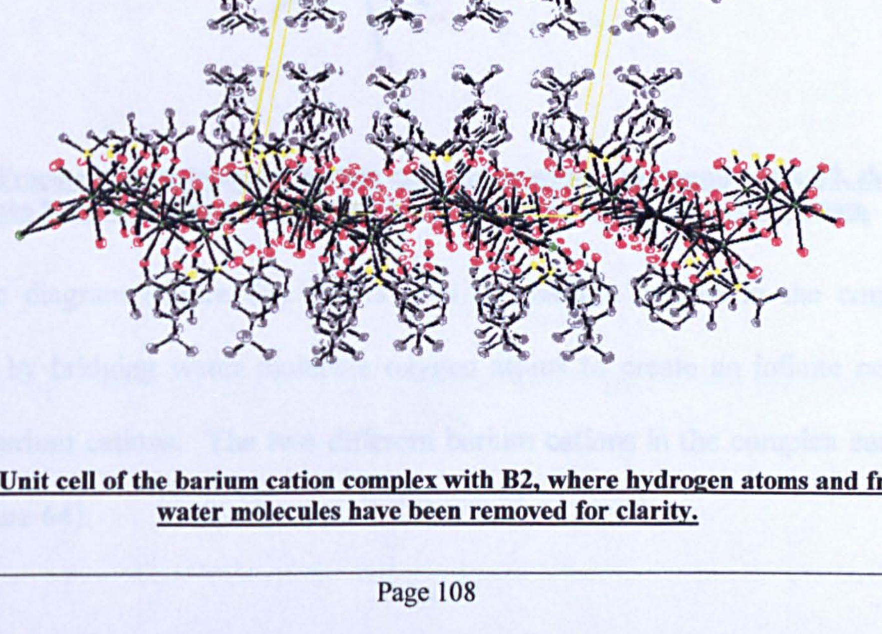


Figure 62. Unit cell of the barium cation complex with B2, where hydrogen atoms and free lattice water molecules have been removed for clarity.

The unit cell of the complex shows the layer structure, where each layer consists of hydrated barium cations with **B2** molecules sitting in rows above and below the hydrated barium cations. *tert*-Butyl groups form the edge of each layer and there is space between the *tert*-butyl groups of each layer. This layer system can be classed as lamellar bilayer. The layer structure is due to water molecules bridging barium cations and to a lesser extent is due to hydrogen-bonding between free **B2** oxygen atoms and water molecules. Each barium cation is connected to two or three other barium cations by bridging water molecules, where Ba1 is connected to two other barium cations by bridging water molecules and Ba2 is connected to three other barium cations by bridging water molecules (see below in figure 63).

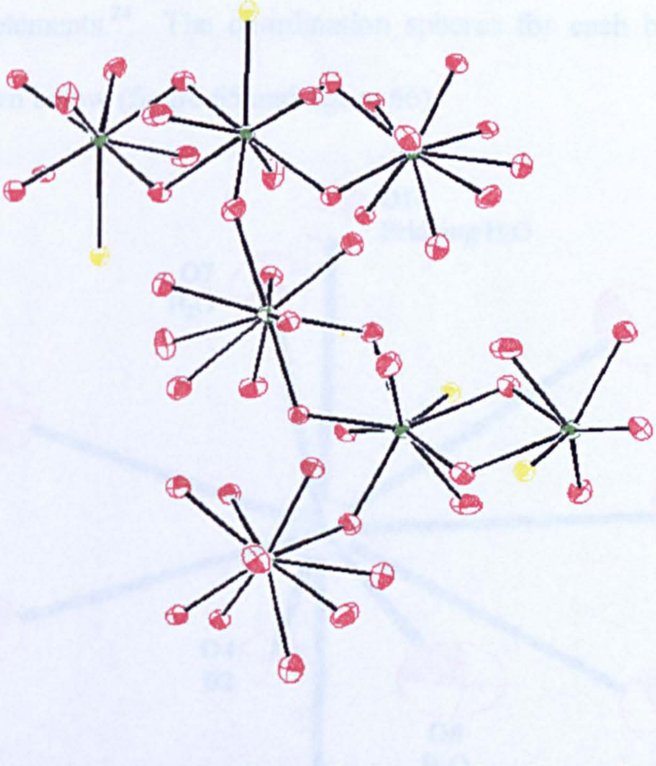


Figure 63. Fragment of the hydrated barium cation layer within the complex with B2, showing how the barium cations are connected by bridging water molecule oxygen atoms.

The above diagram (figure 63) shows how the barium cations in the complex are connected by bridging water molecule oxygen atoms to create an infinite network of hydrated barium cations. The two different barium cations in the complex can be seen below (figure 64).

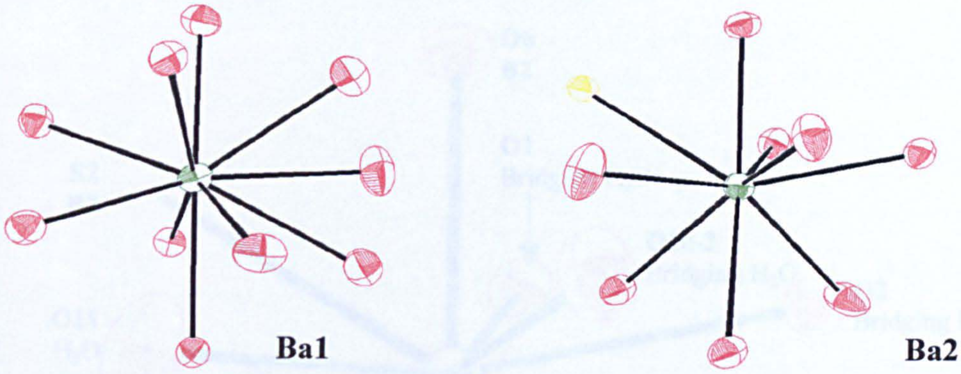


Figure 64. The coordination spheres for the barium cations in the complex with B2.

Both barium cations have large coordination numbers, which is possible due to the large size of the barium cation (the barium ionic radius is 1.36Å for a coordination number of 6[18]). The barium cation, Ba2, coordinates to a sulfur atom despite Group 2 elements preferring hard-donors, because the barium cation is larger and therefore softer than the other Group 2 elements.[24] The coordination spheres for each barium cation in the complex are shown below (figure 65 and figure 66).

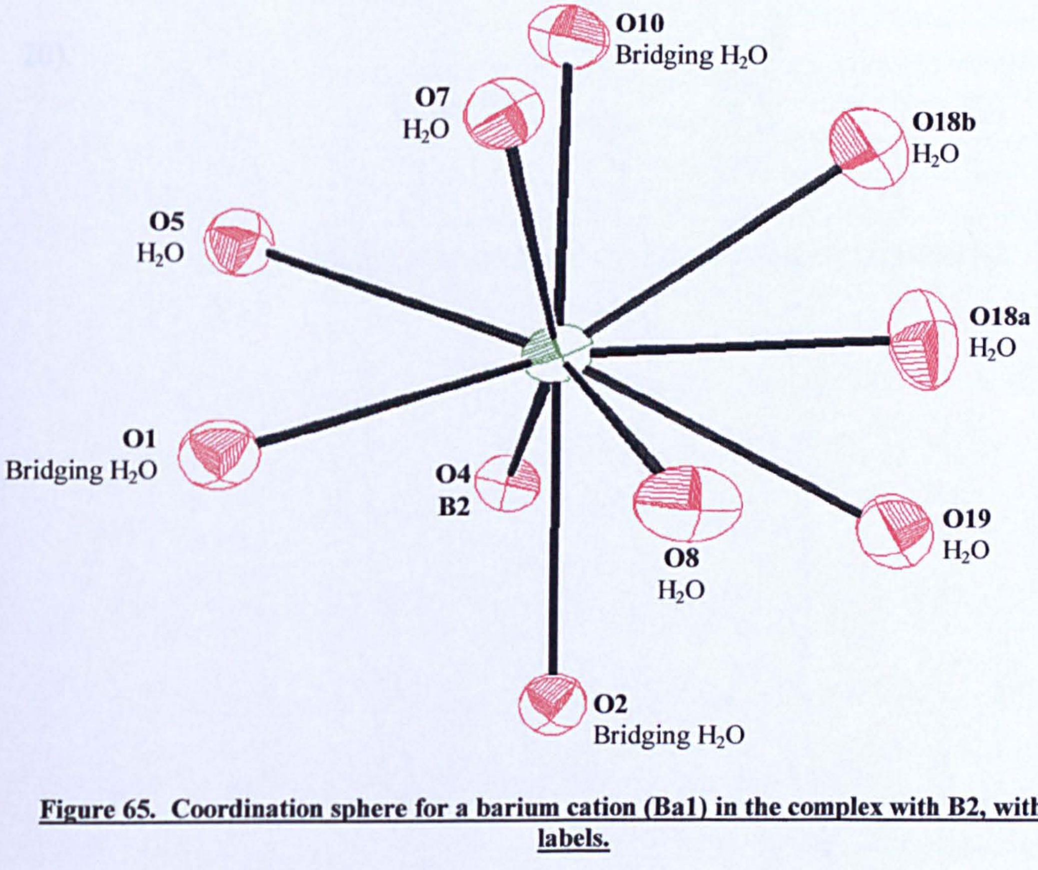


Figure 65. Coordination sphere for a barium cation (Ba1) in the complex with B2, with atom labels.

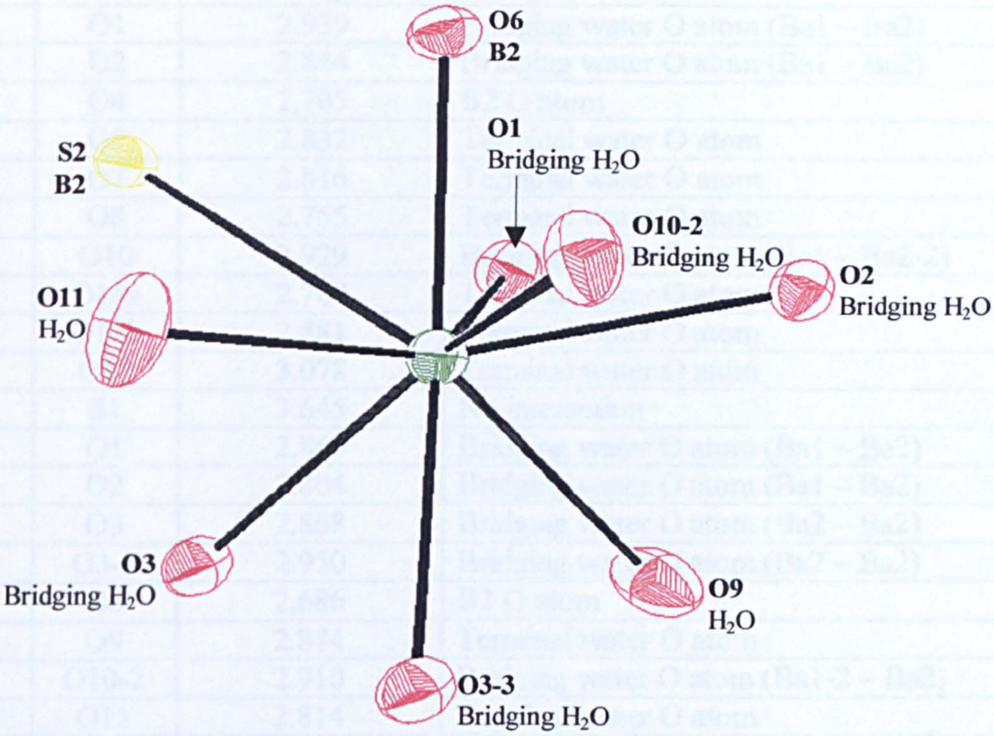


Figure 66. Coordination sphere for a barium cation (Ba2) in the complex with B2, with atom labels.

Selected bond lengths and bond angles can be seen in the tables below (tables 19 and 20).

Atom 1	Atom 2	Bond length (Å)	Comment
Ba1	O1	2.939	Bridging water O atom (Ba1 – Ba2)
Ba1	O2	2.844	Bridging water O atom (Ba1 – Ba2)
Ba1	O4	2.705	**B2** O atom
Ba1	O5	2.832	Terminal water O atom
Ba1	O7	2.816	Terminal water O atom
Ba1	O8	2.755	Terminal water O atom
Ba1	O10	2.929	Bridging water O atom (Ba1 – Ba2-2)
Ba1	O18a	2.760	Terminal water O atom
Ba1	O18b	2.881	Terminal water O atom
Ba1	O19	3.078	Terminal water O atom
Ba1	S1	3.645	No interaction
Ba2	O1	2.865	Bridging water O atom (Ba1 – Ba2)
Ba2	O2	2.804	Bridging water O atom (Ba1 – Ba2)
Ba2	O3	2.868	Bridging water O atom (Ba2 – Ba2)
Ba2	O3-3	2.950	Bridging water O atom (Ba2 – Ba2)
Ba2	O6	2.686	**B2** O atom
Ba2	O9	2.874	Terminal water O atom
Ba2	O10-2	2.910	Bridging water O atom (Ba1-2 – Ba2)
Ba2	O11	2.814	Terminal water O atom
Ba2	S2	3.437	**B2** S atom
Ba1	Ba1	6.752	Interatomic distance
Ba1	Ba2	4.616	Interatomic distance
Ba2	Ba2	4.785	Interatomic distance
O4	O13	5.358	Interatomic distance
O6	O12	5.467	Interatomic distance
O4-4	O14-3	2.673	Hydrogen-bond
O9	O17b-2	2.538	Hydrogen-bond
O11-2	O13	2.700	Hydrogen-bond
O12-2	O16-3	2.653	Hydrogen-bond
O17a-2	O18a-2	2.876	Hydrogen-bond

Table 19. Selected bond lengths for the barium cation complex with B2.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O1	Ba1	O2	71.33	Angle between bridging water O atoms
O1	Ba1	O4	102.78	Angle between **B2** and water O atoms
O1	Ba1	O5	61.03	Angle between water O atoms
O1	Ba1	O7	70.09	Angle between water O atoms
O1	Ba1	O8	73.86	Angle between water O atoms
O1	Ba1	O10	116.97	Angle between bridging water O atoms
O1	Ba1	O18a	137.27	Angle between water O atoms
O1	Ba1	O18b	141.10	Angle between water O atoms
O1	Ba1	O19	131.74	Angle between water O atoms
O1	Ba2	O2	73.01	Angle between bridging water O atoms
O1	Ba2	O3	85.23	Angle between bridging water O atoms
O1	Ba2	O3-3	136.26	Angle between bridging water O atoms
O1	Ba2	O6	68.39	Angle between **B2** and water O atoms
O1	Ba2	O9	70.01	Angle between water O atoms
O1	Ba2	O10-2	135.93	Angle between bridging water O atoms
O1	Ba2	O11	138.05	Angle between water O atoms
O1	Ba2	S2	65.33	Angle between O and S atoms
Ba1	O1	Ba2	105.36	Angle across bridging water O atom
Ba1	O2	Ba2	109.62	Angle across bridging water O atom
Ba2	O3	Ba2	110.65	Angle across bridging water O atom
Ba1	O10	Ba2-2	130.86	Angle across bridging water O atom
C3	S1	C4	103.50	Angle across S atom
C9	S2	C14	103.05	Angle across S atom

Table 20. Selected bond angles for the barium cation complex with B2.

The trend for oxygen atoms coordinated to the barium cations is shown below.

Ba1

B2 O atom < water O atom ≤ bridging water O atom

Ba2

B2 O atom < water O atom ≈ bridging water O atom

Increasing bond length →

The range of bond lengths to the oxygen atoms coordinated to Ba1 is 2.705-3.078Å and to Ba2 is 2.686-2.950Å. The smaller bond lengths for Ba2 can be ascribed to the lower coordination number for this barium cation as apposed to Ba1.[31, 33, 44] The barium cation to water molecule oxygen atom bond lengths fit within the range found in the literature,[41] where the barium cation to terminally bound water molecule oxygen atom range is 2.678-3.071Å and the barium cation to bridging water molecule oxygen atom range is 2.711-3.019Å. It can be seen that when the water molecule oxygen atoms bridge two barium cations that the bonds are slightly longer, as observed in this complex. The interatomic distance between Ba1 and S1 is marginally too long to be a bond. The normal range of bond lengths between barium cations and sulfur atoms is 3.014-3.611Å.[41] The shortest bonds to the barium cations are with the **B2** oxygen atoms. The **B2** molecules are twisted around the C-S-C bond, possibly to enable the free **B2** oxygen atoms to hydrogen-bond to water molecules. The extensive hydrogen-bonding network can be seen by the set of O-O interatomic distances that are less than 3Å, where the hydrogen-bonding network includes hydrogen-bonding between water molecules as well as between water molecules and **B2** oxygen atoms.

2.4.3. Trends in the Solid State Structures of the Sulfurised Alkylphenol Complexes Prepared from Acetone and Water

The structures of four complexes prepared from acetone and water solution have been determined. The magnesium cation complex with **M2** **(12)** shows that **M2** is a good ligand for magnesium cations, which can compete with water molecules for coordination directly to the metal cation. This is unusual, as magnesium cations normally form hexaaqua cationic units whenever water is available, as it was, in excess, in the preparation of the magnesium cation complex with **M2**. The structures of the strontium cation complex with **B2** **(13)**, the barium cation complex with **I2** **(14)** and the barium cation complex with **B2** **(15)** show that the larger Group 2 metal cations prefer coordination to water molecules over coordination to sulfurised alkylphenol ligands, especially strontium cations. The strontium cation complex with **B2** has the strontium cations as hydrated cationic units, which are only hydrogen-bonded to the **B2** ligands. The strontium and barium cation complexes all contain hydrated metal cations with water molecule oxygen atoms bridging between the metal cations. The unit cells for the strontium cation complex with **B2** and the barium cation complex with **B2** are very similar, despite the different coordination modes of the **B2** ligands to the metal cations in the complexes. It can be seen that the magnesium cation complex with **M2** and the strontium cation complex with **B2** are both counterintuitive, where the observed structures are converse to what would be expected (allowing for different coordination numbers).

2.4.4. Solution Structure Studies of the Sulfurised Alkylphenol Complexes Prepared from Acetone and Water Solutions

The ^{1}H NMR spectra of the complexes characterised by single crystal x-ray diffraction are discussed below. ^{1}H NMR spectroscopy was the only form of solution state characterisation carried out on the complexes prepared from acetone and water solution as mass spectrometry had been found to be unsuitable for sulfurised alkylphenol complexes (see 2.3.4.).

2.4.4.1. Magnesium Cation Complex with M2 (MgM2)

The yield of crystalline magnesium cation complex with **M2** was very low and the major product was a brown powder. A sample of crystalline solid and powder was analysed by ^{1}H NMR (d_6-DMSO) spectroscopy, where the sample contained both powder and crystals due to difficulties in obtaining a pure sample of a single morphology. The ^{1}H NMR spectrum is very broad and there is a very large peak for water. The water peak in the spectrum will be mainly from the complex, where there are three water molecules to one **M2** ligand, and possibly some from the deuterated solvent. The spectrum has an uneven baseline, possibly indicating that the complex is clustered in solution, with the main peaks showing the presence of deprotonated **M2**. As deuterated DMSO was the solvent, a broad 'salt-like' spectrum was to be expected. Although the peaks are broad, only one set of major peaks can be seen, which indicates that the two morphologies are the same complex.

2.4.4.2. Strontium Cation Complex with **B2** (Sr**B2**)

The ^{1}H NMR (d_6-DMSO) spectrum of the strontium cation complex with **B2** is very broad. As described earlier for the solution structure of the strontium cation complexes with sulfurised alkylphenol ligands prepared from methanol and as will be discussed later in the calixarene complexes chapter (see section 3.6.4.), strontium cation complexes usually give broad ^{1}H NMR spectra and so the broadness of the spectrum for Sr**B2** is indicative of a strontium cation complex. The spectrum shows deprotonated **B2**, plus peaks for water, DMSO and acetone, where the acetone peak is small and the DMSO peak is due to proton exchange between the complex and the deuterated DMSO solvent. The broadest peak is at approximately 6.4ppm and this shows the degree of the broad nature of strontium cation complex ^{1}H NMR spectra. Although the spectrum shows that the product contains deprotonated **B2**, no more information about the solution structure of Sr**B2** can be obtained from it.

2.4.4.3. Barium Cation Complex with I2 (BaI2)

The crystalline barium cation complex with **I2** was analysed by ^1H NMR spectroscopy, using d_6-acetone as the deuterated solvent. Although d_6-acetone usually shows the fine structure within sulfurised alkylphenol complexes, the ^1H NMR spectrum for **BaI2** shows mainly deprotonated **I2**. There is some evidence for the solution containing a clustered complex by small peaks, barely visible above the baseline. These small peaks indicate that the complex may be clustered in solution, possibly a hexanuclear cluster by the six small doublets observed upfield of the main isopropyl CH_3 doublet. This may indicate that the complex has fluxional behaviour in solution. The deprotonated **I2** peaks are shifted relative to the **I2** ^1H NMR (d_6-acetone) spectrum, where the isopropyl peaks are shifted by only a small amount upfield and the aromatic proton peaks are shifted by a greater amount. The change in the positions of the protons in **BaI2** relative to the free **I2** ligand can be seen in the table below (table 21).

Peak assignment/ppm	OH	Ph	Ph	Ph	CH	CH_3
I2 proton peaks/ppm	8.39	7.15	7.08	7.06	2.76	1.13
BaI2 proton peaks/ppm	N/A	7.22	6.94	6.77	2.71	1.12
Shift/ppm	N/A	0.07	0.14	0.39	0.05	0.01

Table 21. Table comparing the ^1H NMR (d_6-acetone) spectra for free I2 and BaI2 complex.

It can be seen from the above table (table 21) that the aromatic protons are significantly affected by the complex formation. The water peak in the spectrum for the complex gives a ratio of water to **I2** of six water molecules to one **I2** molecule, which is higher than the ratio for the complex in the solid state, but can be explained by d_6-acetone usually being slightly 'wet'. There are two overlapped acetone peaks on the ^1H NMR spectrum of the complex, where one peak relates to the acetone molecules coordinated to the barium cations in the complex, though the ratio is not known as the peak which relates to the coordinated acetone molecule cannot be easily identified and the two peaks are too overlapped.

2.4.4.4. Barium Cation Complex with B2 (BaB2)

The ^{1}H NMR (d_6-acetone) spectrum of the barium cation complex with **B2** shows mainly a broad spectrum for deprotonated **B2** along with a small percentage of clustered complex. The spectrum is similar to the spectrum for Ba**I2**, except that it is broader. The peaks for the clustered complex are too overlapped with the peaks for deprotonated **B2** for the aggregation number of the complex in solution to be calculated. The spectrum shows that, as with Ba**I2**, the complex probably has fluxional behaviour in solution. As for Ba**I2**, the aromatic protons are the most shifted relative to the peaks for the free **B2** molecule. The acetone peak is broad and so it is not possible to see if it consists of two overlapped peaks.

2.4.4.5. Solution Structure Study Summary

The solution structures of the complexes prepared from acetone and water solutions show that the complexes have fluxional behaviour in solution. The ^{1}H NMR spectra tend to be broad for all of the complexes and show mainly deprotonated ligand. The complexes are probably all clustered in solution, though by ^{1}H NMR spectroscopy it has not been possible to determine the structures of the complexes in solution.

2.4.5. Summary

Crystalline sulfurised alkylphenol complexes have been prepared from acetone and water solutions and of these, **MgM2** (**12**), **SrB2** (**13**), **BaI2** (**14**) and **BaB2** (**15**) have been characterised in the solid state by single crystal x-ray diffraction. **MgM2** has a mononuclear structure and is interesting because it shows the **M2** is a good ligand for magnesium cations as the **M2** ligand is coordinated to the magnesium cation in the first coordination sphere for the cation. The strontium and barium cation complexes show the high affinities of these cations for water as a ligand (opposite trend to the magnesium cation complex with **M2** prepared from the same conditions). In the case of the strontium cation complex with **B2**, the strontium cation is only coordinated to the **B2** ligands in the second coordination sphere of the cation, making the complex a 'salt'. The relative 'softness' of barium cations when compared with the other Group 2 metal cations is shown by barium cations coordinating to the sulfur atoms of the sulfurised alkylphenol ligands. Studies of the complexes in solution by ^{1}H NMR spectroscopy has shown that the complexes are clustered in solution, but have fluxional behaviour.

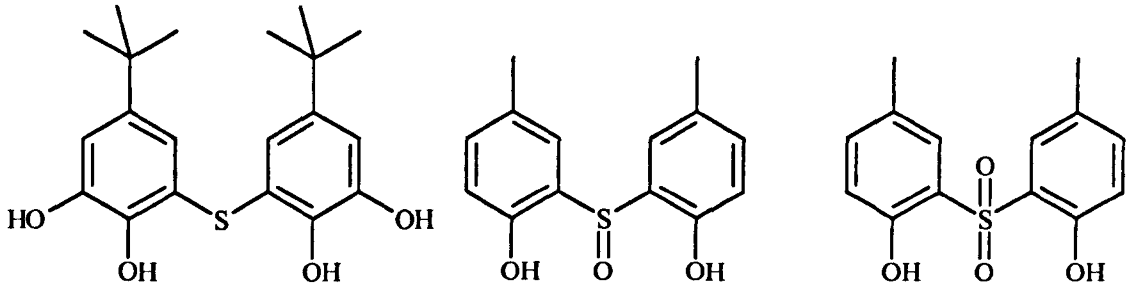
2.5. Sulfurised Alkylphenol Complexes Prepared from Acetonitrile and Water Solution

Crystalline complexes of sulfurised alkylphenol ligands with magnesium, strontium and barium cations were prepared from acetonitrile and water solutions, though all of the complexes were found to be unsuitable for single crystal x-ray diffraction analysis. Due to the unsuitability of the complexes for single crystal x-ray diffraction, the complexes were not analysed by any other analytical method.

2.6. Alternative Sulfurised Alkylphenol Ligands

2.6.1. Introduction

A selection of alternative sulfurised alkylphenol ligands were synthesised. Schematic views of the ligands can be seen below (figure 67).



DHB2 **MOM2** **DOM2**

Figure 67. Schematic diagram of the molecules studied as alternatives to the parent sulfurised alkylphenol molecules.

The codes for the ligands are created by prefixing two letters relating to the difference between the alternative ligand and the parent ligand onto the code for the parent ligand. Thus, **MOM2** contains a mono-oxo group on the parent **M2** ligand, **DOM2** contains a di-oxo group on the parent **M2** ligand and **DHB2** contains di-hydroxy groups as apposed to one hydroxy group on the parent **B2** ligand. For the full names of the molecules see the table below (table 22).

Code	Name
DHB2	2,2'-Thiobis-(4-*tert*-butylcatechol)
MOM2	2,2'-Sulfinylbis-(4-methylphenol)
DOM2	2,2'-Sulfonylbis-(4-methylphenol)

Table 22. Table summarising the names and codes for the alternative sulfurised alkylphenol molecules.

DHB2 (**16**) was prepared by the same route as the parent sulfurised alkylphenol molecules. The yield of 35% crude product is higher than the yield for **B2**. Crystalline **DHB2** was prepared by dissolving the crude **DHB2** in warm petroleum ether (40-60°), using the minimum volume of acetone to fully dissolve the crude material and then rapidly cooling the solution.

MOM2 (17) was prepared serendipitously. A crystalline product was obtained from the attempted preparation of a calcium cation complex with **M2** from THF and water solution and the structure of the crystalline solid showed that **MOM2** had actually been formed. The single oxidation of organic sulfur atoms if difficult and usually requires indirect methods[91] and this method achieved a single step oxidation to give pure, crystalline **MOM2**, though in a very low yield. The low yield has made it impossible to obtain enough **MOM2** for any other form of analysis other than single crystal x-ray diffraction or for the preparation of complexes and the reaction was not repeated as it probably occurred *via* the formation of peroxide from the THF, where such a peroxide is highly explosive. A suggested mechanism for the reaction is shown below (figure 68).

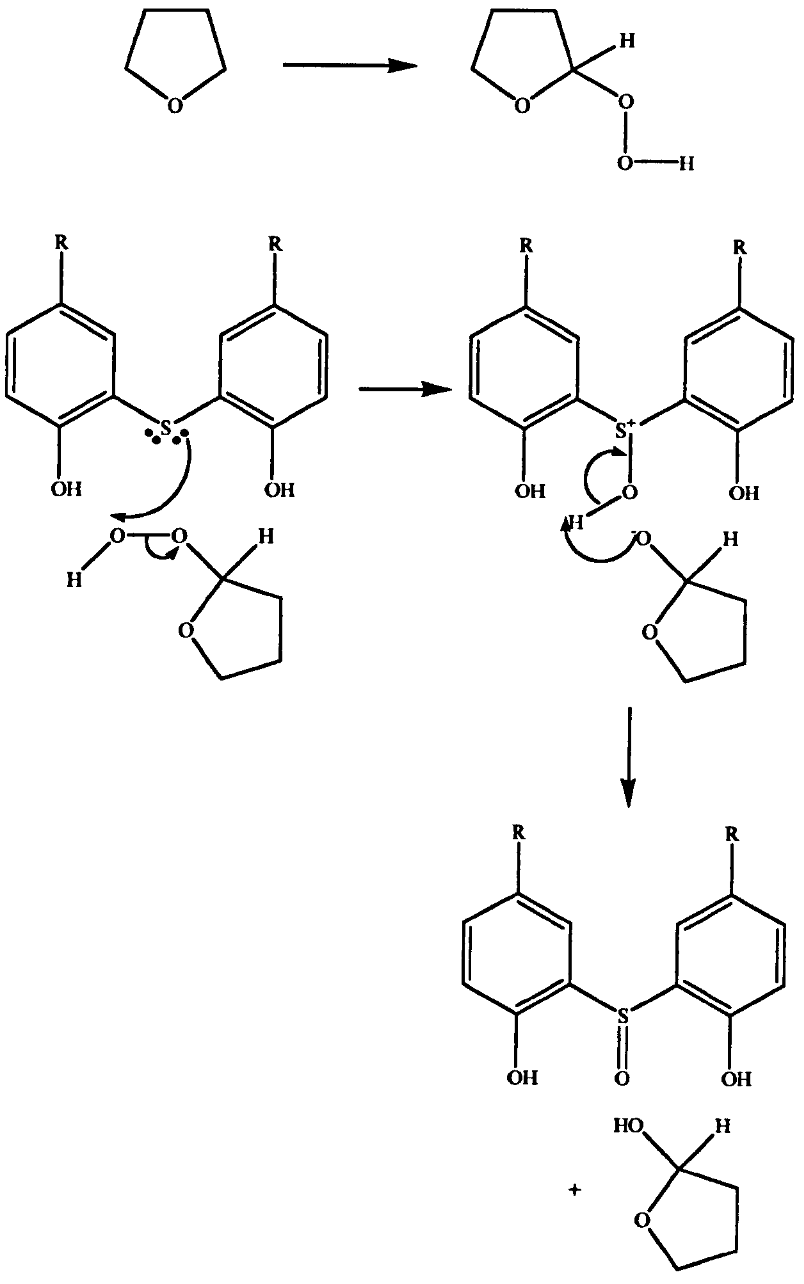


Figure 68. Proposed mechanism for the formation of MOM2, where the most likely peroxide form of THF is shown.

The use of peroxide to singly oxidise sulfur atoms within organic compounds is known to be rate enhanced by the presence of protic solvents, with the effect of the protic solvent being directly linked to the concentration of the protic solvent and the effect following the order:[163]

$$\text{AcOH} > H_2O > D_2O > \text{MeOH} > {}^{i}\text{PrOH} > {}^{t}\text{BuOH}.$$

The protic solvents increase the rate constant for the reaction by hydrogen-bonding to the intermediates formed during the reaction. This shows that the oxidation of **M2** to **MOM2** required the decomposition of THF to peroxide and was probably aided by the presence of water.

The oxygen atom bound to the sulfur atom should make **MOM2** a better ligand for 'hard' metal ions than the parent **M2** ligand, by making the ligand capable of coordination to metal ions *via* two phenolic oxygen atoms and one neutral sulfoxide oxygen atom.[163] For more **MOM2** to be prepared, an alternative route would have to be devised.

DOM2 (18) was prepared by the literature method.[87, 88, 90, 91] The reaction uses hydrogen peroxide, in the presence of acetic acid, to oxidise the sulfur atom of **M2** to a sulfone group. The product was recrystallised to give crystals suitable for single crystal x-ray diffraction by dissolving the **DOM2** in acetone and adding water to the solution.

2.6.2. Solid State Structures of the Alternative Sulfurised Alkylphenol Ligands

The alternative ligands to the parent sulfurised alkylphenol ligands have been characterised in the solid state by single crystal x-ray diffraction. ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis data show agreement with the structures determined by single crystal x-ray diffraction for **DHB2** and **DOM2**. Not enough **MOM2** could be prepared for other forms of analysis to be used other than single crystal x-ray diffraction.

2.6.2.1. Structure of 2,2'-Thiobis-(4-*tert*-butylcatechol) (**DHB2**) (**16**)

Crystalline **DHB2** was grown from warm petroleum ether (40-60°) and acetone solution by rapid cooling. The crystals consist of the **DHB2** molecule and one acetone molecule. The acetone molecule is bound to the **DHB2** molecule by hydrogen-bonding between the acetone molecule oxygen atom and one **DHB2** hydroxy group.

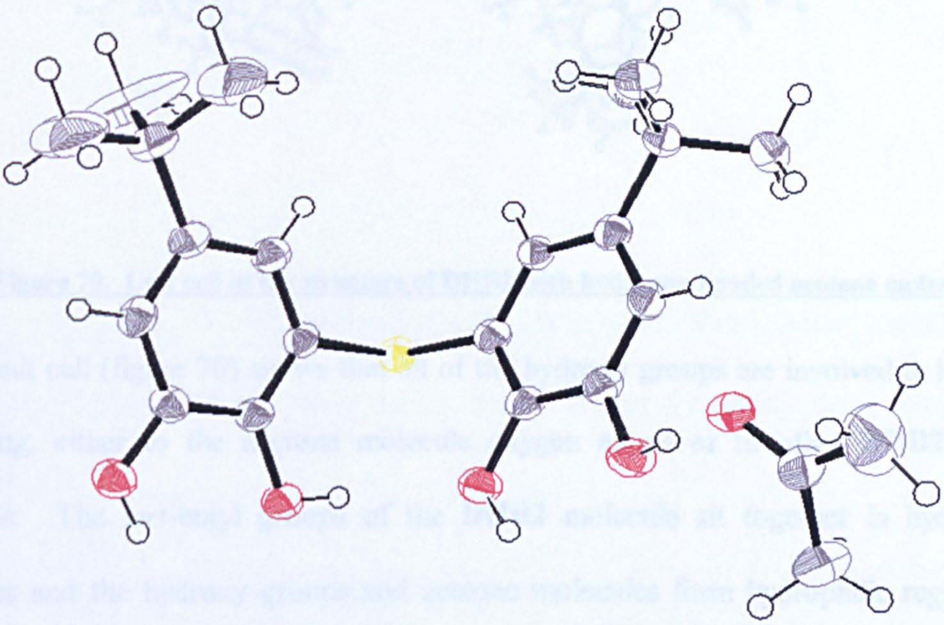


Figure 69. Structure of DHB2 with the co-crystallised acetone molecule, DHB2.acetone.

The four hydroxy groups on the ligand can be clearly seen, as can the orientation of one hydroxy group towards the acetone molecule oxygen atom. The packing of the molecules in the solid state (see below in figure 70) shows why the hydrogen atoms on the hydroxy groups are all directed towards the right.

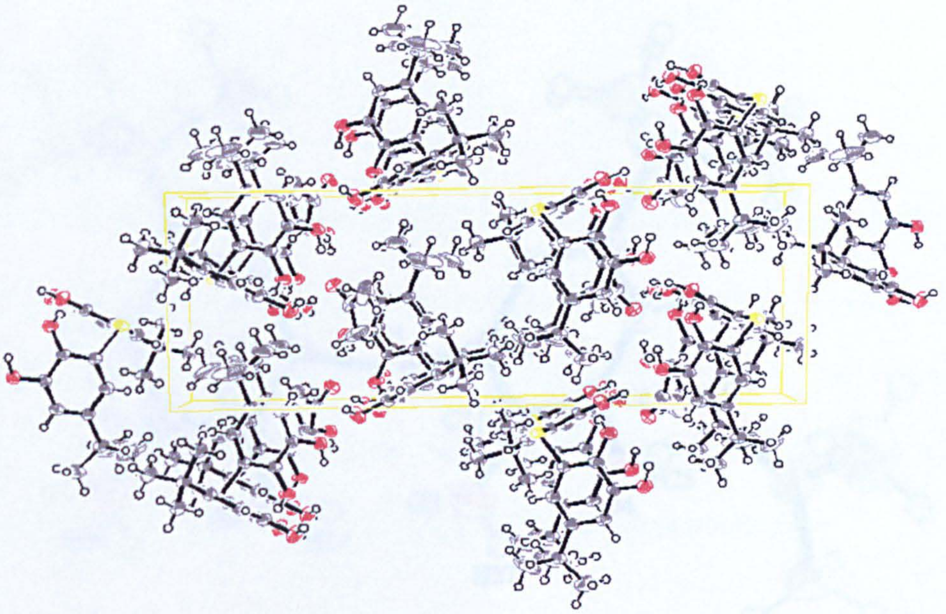


Figure 70. Unit cell of the structure of DHB2 with hydrogen-bonded acetone molecules.

The unit cell (figure 70) shows that all of the hydroxy groups are involved in hydrogen-bonding, either to the acetone molecule oxygen atoms or to other **DHB2** hydroxy groups. The *tert*-butyl groups of the **DHB2** molecule sit together in hydrophobic regions and the hydroxy groups and acetone molecules form hydrophilic regions with extensive hydrogen-bonding. The unit cell also shows that within each **DHB2** molecule, one aromatic ring is directed at approximately 90° to the other aromatic ring.

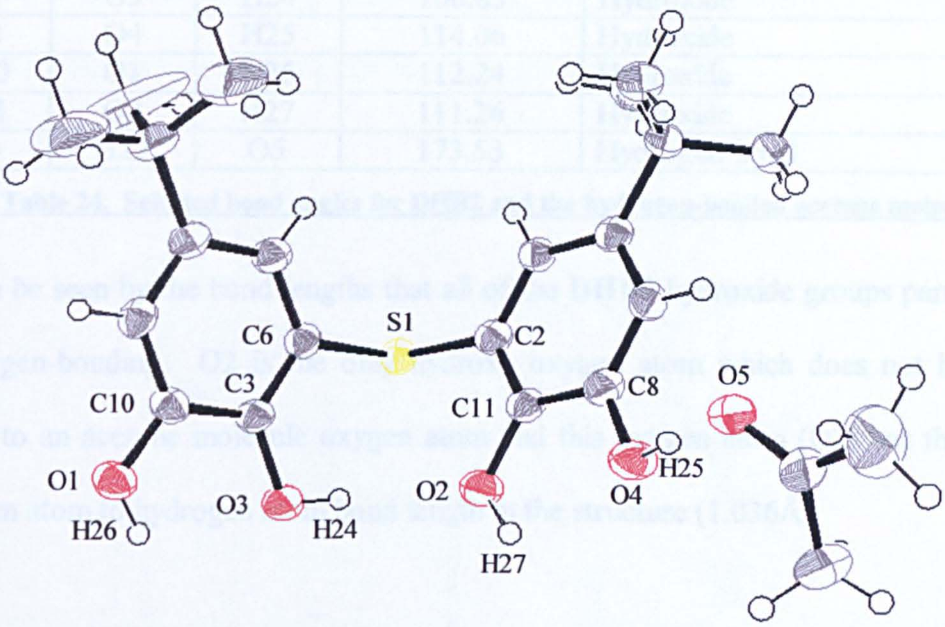


Figure 71. The DHB2 molecule and acetone molecule with selected atom labels.

Selected bond lengths and bond angles can be seen in the tables below (tables 23 and 24).

Atom 1	Atom 2	Bond length (Å)	Comment
S1	C2	1.783	S atom to C atom bond
S1	C6	1.794	S atom to C atom bond
O1	H26	0.884	Hydroxide bond
O1	O2a	2.784	Intermolecular hydrogen-bond
O1	O5	2.750	Intermolecular hydrogen-bond
O2	H27	1.036	Hydroxide bond
O2	O3	2.908	Weak intramolecular hydrogen-bond
O2	O5	5.339	No interaction
O3	H24	0.839	Hydroxide bond
O3	O5	2.891	Intermolecular hydrogen-bond
O4	H25	0.944	Hydroxide bond
O4	O5	2.782	Intermolecular hydrogen-bond
O5	H25	1.842	Intermolecular hydrogen-bond

Table 23. Selected bond lengths for DHB2 and the hydrogen-bonded acetone molecule

Atom 1	Atom 2	Atom 3	Bond angle (°)	Comment
C2	S1	C6	100.94	Angles across S atom
C3	O3	H24	106.83	Hydroxide
C8	O4	H25	114.06	Hydroxide
C10	O1	H26	112.24	Hydroxide
C11	O2	H27	111.26	Hydroxide
O4	H25	O5	173.53	Hydrogen-bond

Table 24. Selected bond angles for DHB2 and the hydrogen-bonded acetone molecule.

It can be seen by the bond lengths that all of the **DHB2** hydroxide groups participate in hydrogen-bonding. O2 is the only hydroxy oxygen atom which does not hydrogen-bond to an acetone molecule oxygen atom and this oxygen atom (O2) has the longest oxygen atom to hydrogen atom bond length in the structure (1.036Å).

2.6.2.2. Structure of 2,2'-Sulfinylbis-(4-methylphenol) (MOM2) (17)

Crystalline **MOM2** was grown from THF and water solution. In **MOM2** there is a single oxygen atom on the sulfur atom. No solvent molecules co-crystallised with the **MOM2** molecule.

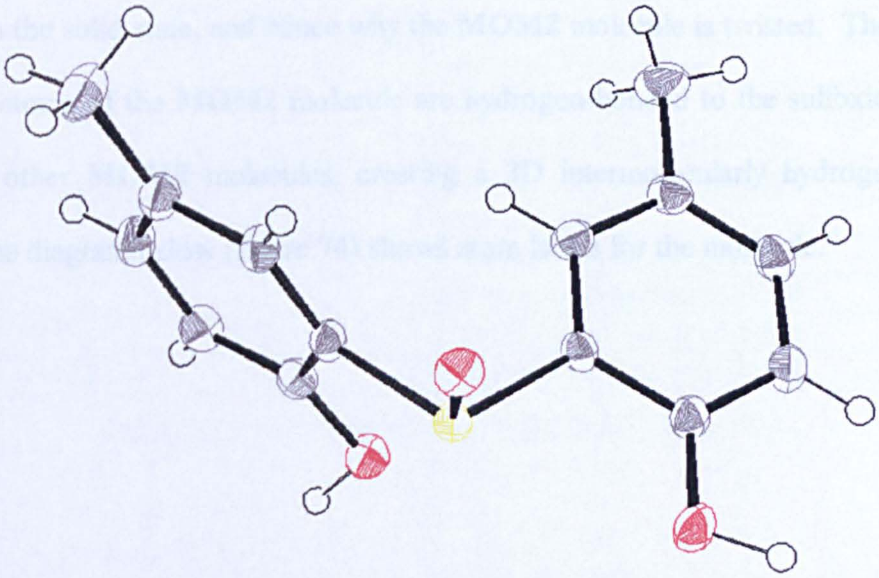


Figure 72. Structure of the MOM2 molecule.

The **MOM2** molecule can be seen to be twisted and the phenolic hydrogen atoms can be seen to be orientated away from the rings, this is due to hydrogen-bonding between **MOM2** molecules, as shown in the diagram below (figure 73).

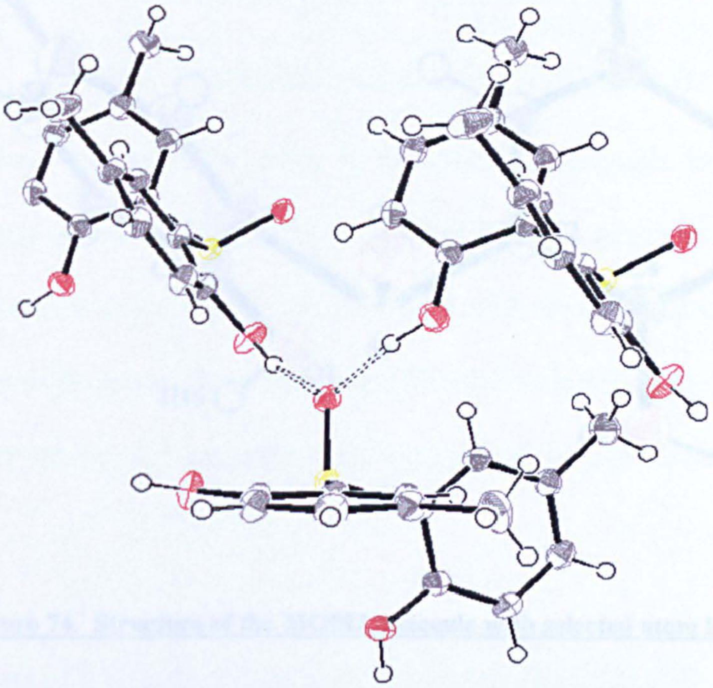


Figure 73. Interaction between MOM2 molecules in the solid state, where dashed lines represent hydrogen-bonds.

The above view (figure 73) shows that **MOM2** molecules interact *via* hydrogen-bonding in the solid state, and hence why the **MOM2** molecule is twisted. The phenolic hydrogen atoms of the **MOM2** molecule are hydrogen-bonded to the sulfoxide oxygen atoms of other **MOM2** molecules, creating a 3D intermolecularly hydrogen-bonded lattice. The diagram below (figure 74) shows atom labels for the molecule.

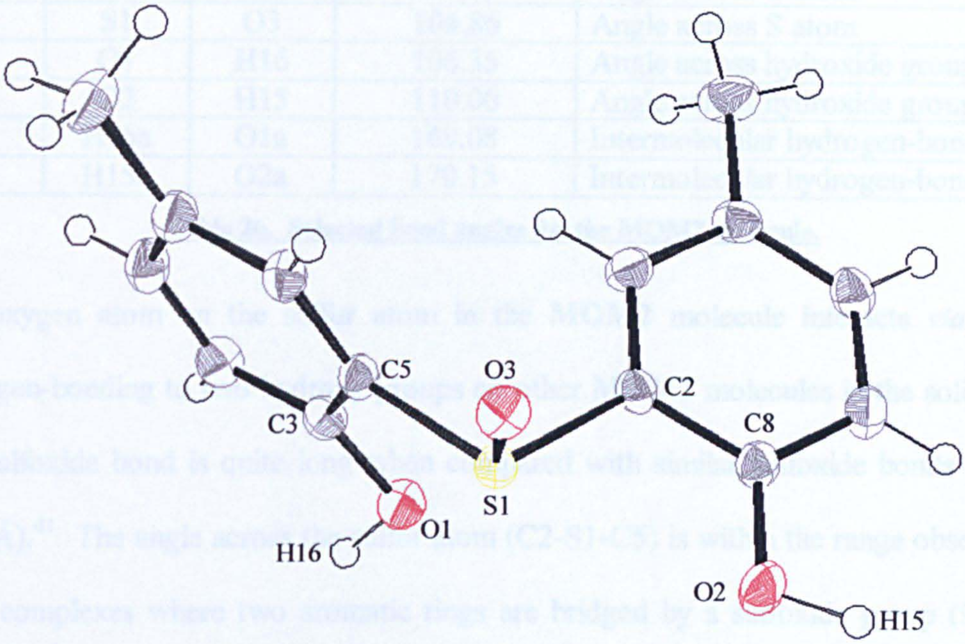


Figure 74. Structure of the MOM2 molecule with selected atom labels.

Selected bond lengths and bond angles can be seen in the tables below (tables 25 and 26).

Atom 1	Atom 2	Bond length (Å)	Comment
S1	C2	1.779	S atom to C atom bond
S1	C5	1.781	S atom to C atom bond
S1	O3	1.533	S atom to O atom bond
O1	H16	1.018	Hydroxide bond
O1	O3	4.338	No intramolecular interaction
O1	O3a	2.671	Intermolecular hydrogen-bond
O2	H15	0.963	Hydroxide bond
O2	O3	3.383	No intramolecular interaction
O2	O3a	2.655	Intermolecular hydrogen-bond
O3	H15a	1.701	Intermolecular hydrogen-bond
O3	H16a	1.665	Intermolecular hydrogen-bond

Table 25. Selected bond lengths for the MOM2 molecule.

Atom 1	Atom 2	Atom 3	Bond angle (°)	Comment
C2	S1	C5	101.03	Angle across S atom
C2	S1	O3	105.57	Angle across S atom
C5	S1	O3	104.86	Angle across S atom
C3	O1	H16	106.35	Angle across hydroxide group
C8	O2	H15	110.00	Angle across hydroxide group
O3	H16a	O1a	169.08	Intermolecular hydrogen-bond
O3	H15a	O2a	170.15	Intermolecular hydrogen-bond

Table 26. Selected bond angles for the MOM2 molecule.

The oxygen atom on the sulfur atom in the **MOM2** molecule interacts *via* strong hydrogen-bonding to two hydroxy groups on other **MOM2** molecules in the solid state. The sulfoxide bond is quite long when compared with similar sulfoxide bonds (1.428-1.510Å).[41] The angle across the sulfur atom (C2-S1-C5) is within the range observed in other complexes where two aromatic rings are bridged by a sulfoxide group (95.711-103.674°.[41]

2.6.2.3. Structure of 2,2'-Sulfonylbis-(4-methylphenol) (DOM2) (18)

Crystalline **DOM2** was grown from acetone and water solution. In **DOM2** there are two oxygen atoms bound to the sulfur atom. No solvent molecules co-crystallised with the **DOM2** molecule.

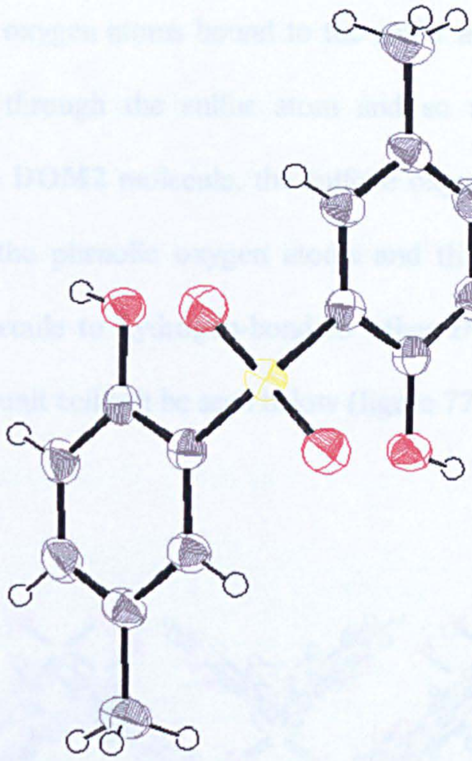


Figure 75. Structure of the DOM2 molecule.

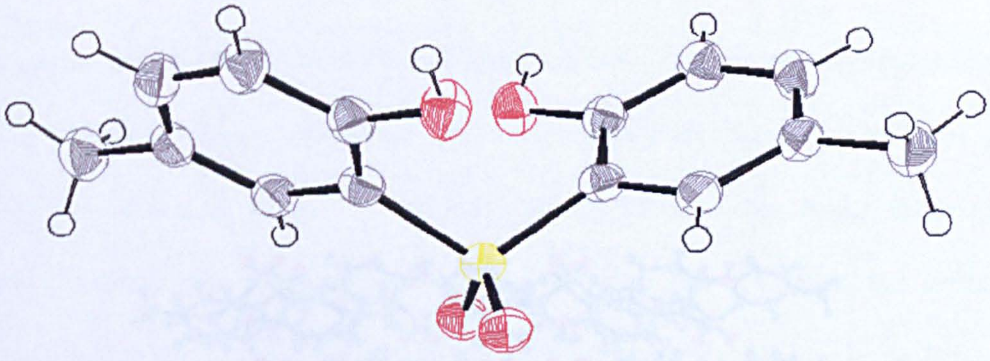


Figure 76. Structure of the DOM2 molecule.

The above two views (figure 75 and figure 76) of the **DOM2** molecule show that the molecule contains two oxygen atoms bound to the sulfur atom. The molecule contains an axis of symmetry through the sulfur atom and so the two phenolic rings are equivalent. Within the **DOM2** molecule, the sulfone oxygen atoms are directed in the opposite direction to the phenolic oxygen atoms and this orientation of the oxygen atoms enables the molecule to hydrogen-bond to other **DOM2** molecules in the unit cell. Two views of the unit cell can be seen below (figure 77).

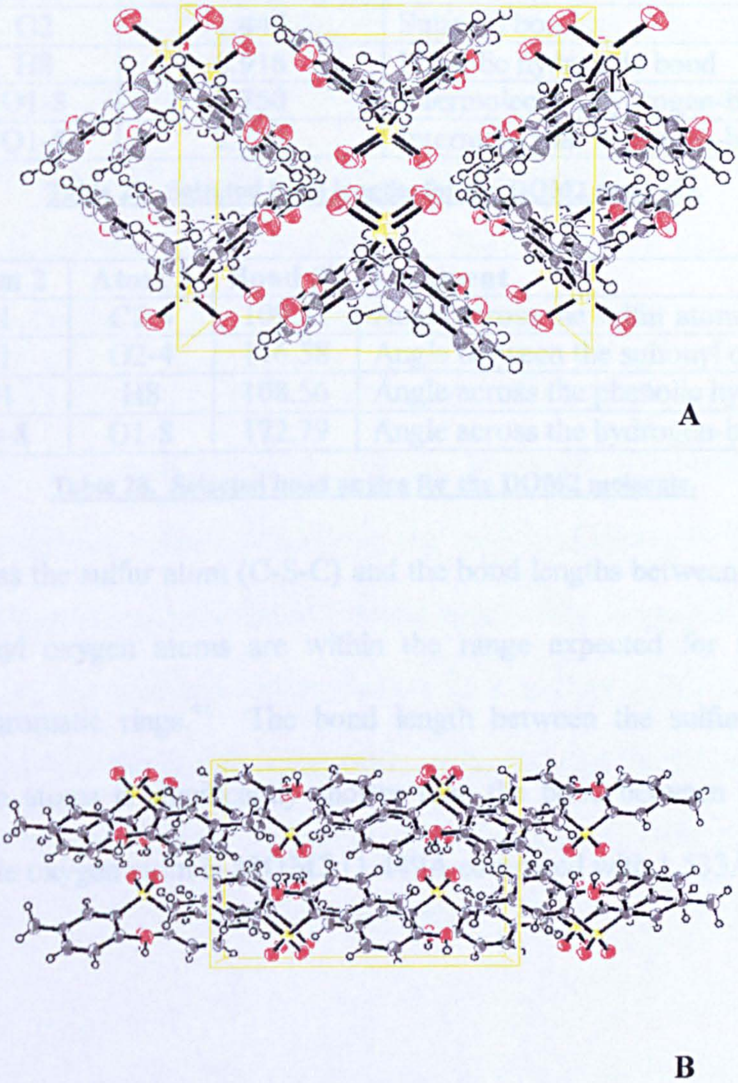


Figure 77. Two views of the unit cell for DOM2, where view A is the 'end-on' view and view B is the 'side' view.

The two views of the unit cell (figure 77) show that the **DOM2** molecules pack to enable the phenolic oxygen atoms to intermolecularly hydrogen-bond to sulfonyl oxygen atoms. The hydrogen-bonds are observed by interatomic distances of 2.750Å between oxygen atoms. These hydrogen-bonds are medium in strength and longer than the intermolecular hydrogen-bonds observed for **MOM2** (**17**).

Selected bond lengths and bond angles for the **DOM2** molecule can be seen in the tables below (tables 27 and 28).

Atom 1	**Atom 2**	**Bond length (Å)**	**Comment**
S1	02	1.449	Sulfonyl bond
01	H8	0.918	Phenolic hydroxide bond
02-2	01-8	2.750	Intermolecular hydrogen-bond
02-3	01-5	2.750	Intermolecular hydrogen-bond

Table 27. Selected bond lengths for the DOM2 molecule.

Atom 1	**Atom 2**	**Atom 3**	**Bond (°)**	**Comment**
C2	S1	C2-4	109.82	Angle across the sulfur atom
02	S1	02-4	116.58	Angle between the sulfonyl oxygen atoms
C1	01	H8	108.56	Angle across the phenolic hydroxide bond
02-2	H8-8	01-8	172.79	Angle across the hydrogen-bond

Table 28. Selected bond angles for the DOM2 molecule.

The angle across the sulfur atom (C-S-C) and the bond lengths between the sulfur atom and the sulfonyl oxygen atoms are within the range expected for sulfonyl groups bridging two aromatic rings.[41] The bond length between the sulfur atom and the sulfonyl oxygen atoms is significantly shorter than the bond between the sulfur atom and the sulfoxide oxygen atom in **MOM2** (1.449Å compared with 1.533Å in **MOM2**).

2.6.3. Preparation of Complexes with the Alternative Sulfurised Alkylphenol Ligands

2.6.3.1. Complexes with 2,2'-Thiobis-(4-*tert*-butylcatechol) (**DHB2**)

A range of methods were used to attempt to prepare crystalline complexes with **DHB2**. It was observed that reactions of deprotonated **DHB2** with the larger Group 2 metal ions (calcium, strontium and barium cations) gave intense dark inky-blue solutions. To investigate the effect of metal ion on solutions of the deprotonated **DHB2** molecule, a study was carried out which showed that only the larger Group 2 metal ions gave the intense dark blue solutions, though some other metal ions gave other intensely coloured solutions. It was also found that the intense dark inky-blue colouration was independent of the larger Group 2 metal ion salt that was used, the solvent or the base that was used to deprotonate the **DHB2** ligand. For example, for the reaction with calcium cations, dark inky-blue coloration was obtained with calcium metal granules, calcium hydroxide, calcium chloride, calcium bromide and calcium nitrate and with bases such as triethylamine, potassium hydroxide, calcium hydroxide and tetrabutylammonium hydroxide. The intense colours obtained in the study and especially the formation of brightly coloured solutions with Group 2 metal ions (where in general, Group 2 metal ion complexes are not coloured and any colour in a product which includes Group 2 metal ions comes from the ligand or impurities) indicated that the **DHB2** molecule was capable of forming quinone-type structures when complexed.[164] The possible quinone-type structures are shown schematically below (figure 78).

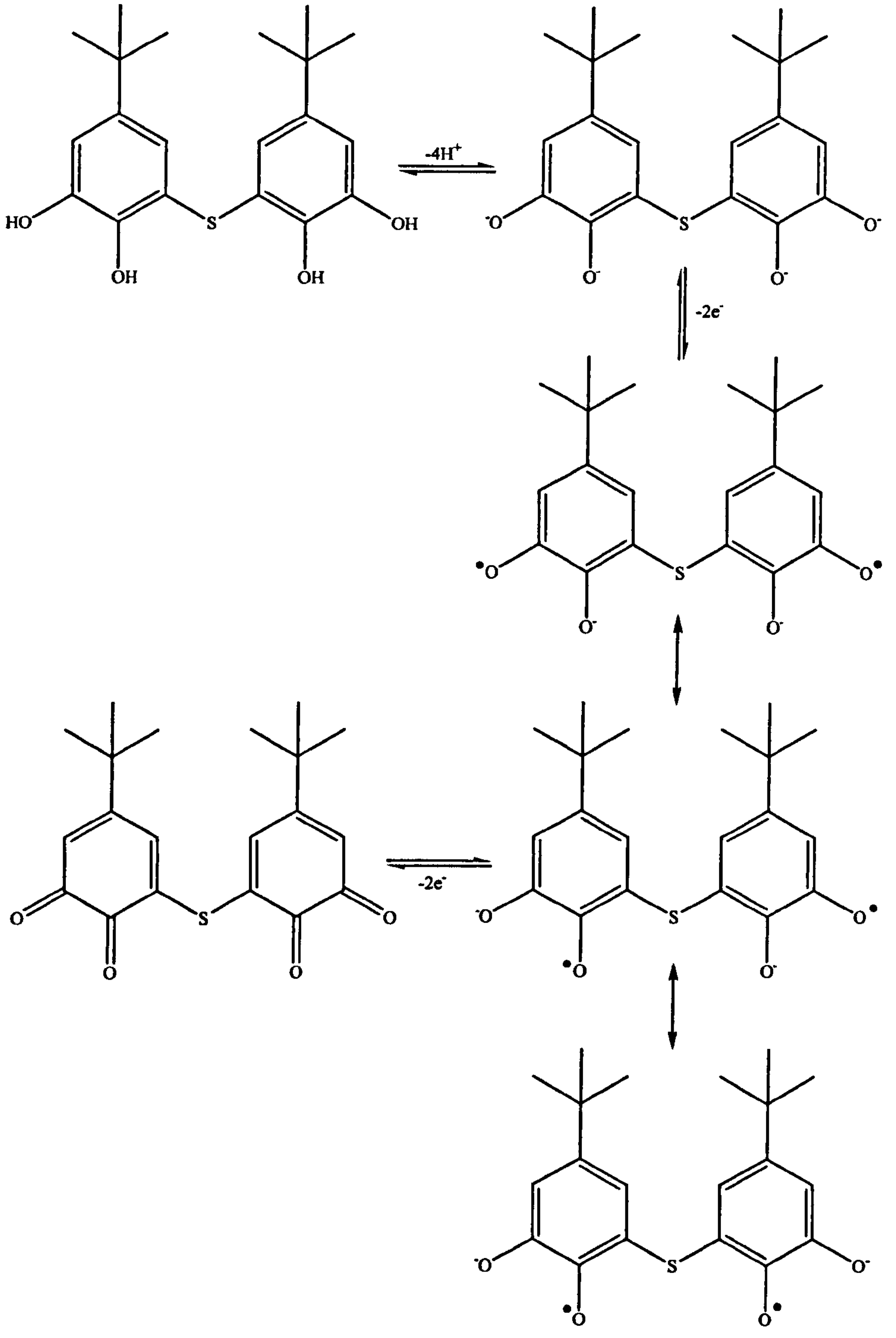


Figure 78. Schematic diagram of the potential quinone versions of DHB2.

For the above mechanism (figure 78), it has been assumed that all four hydroxy protons have been removed in one step and that electrons have been lost in pairs. The resonance structures for the loss of less than four protons and for the loss of single electrons can be inferred from the structures shown above. For quinones, the above forms are highly coloured, except for the hydro-quinone form of which the **DHB2** molecule is analogous.

For **DHB2**, intense coloration is only observed when the ligand is coordinated to metal cations, probably as the half oxidised or fully oxidised forms.

The quinone-type structure of **DHB2** was supported by ^{1}H NMR spectroscopy. The ^{1}H NMR (d_6-acetone) spectrum of **DHB2** was collected and then a pellet of potassium hydroxide was added to the solution (with a small volume of d_1-methanol to make the potassium hydroxide pellet more soluble). This caused the solution to become an intense dark red colour. The ^{1}H NMR spectrum of the solution was not the expected spectrum for deprotonated **DHB2**. The aromatic regions of the ^{1}H NMR spectra for **DHB2** and for **DHB2** plus potassium hydroxide can be seen below (figure 79).

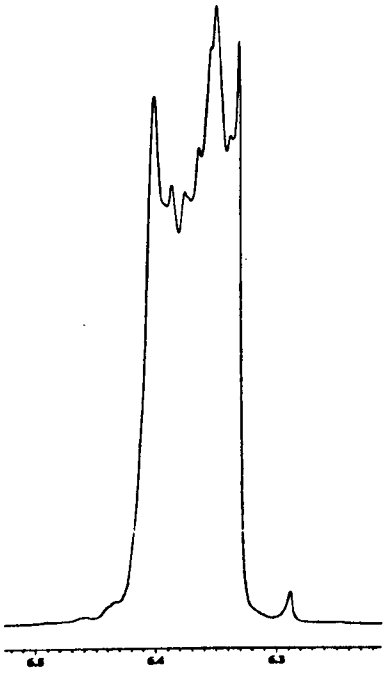


Figure 79. Aromatic region of the ^{1}H NMR (d_6-acetone) spectrum of DHB2 plus KOH.

It is clear that the aromatic protons have been significantly affected by the addition of potassium hydroxide. Unfortunately the dark inky-blue solutions could not be analysed by ^{1}H NMR spectroscopy as the solutions contained precipitate. When the dark blue solid was filtered off it was found to be an intractable solid, insoluble in all useful ^{1}H NMR deuterated solvents and so a ^{1}H NMR spectrum of the blue solid could not be obtained either. Crystalline samples of the intense dark ink blue solid could not be prepared as the solid forms too quickly. Over time it was discovered that the dark blue solution changed to an orange/brown solution with orange/brown solid precipitating out of the solution.

A crystalline complex with **DHB2** was prepared with nickel metal ions, though unfortunately the crystals were found to be unsuitable for single crystal x-ray diffraction (too small) and ^{1}H NMR spectroscopy on the crystals was not carried out due to the nickel (II) metal ions probably being paramagnetic.

This study shows that **DHB2** probably readily forms quinone-type structures when deprotonated, though no crystalline complexes suitable for single crystal x-ray diffraction have been prepared to confirm this.

2.6.3.2. Complexes with 2,2'-Sulfonylbis-(4-methylphenol) (DOM2)

A series of reactions with **DOM2** have been carried out, of which only one reaction has given a product as yet. **DOM2** appears to be more soluble than **M2** in polar solvents and therefore is slower to precipitate out of solutions as a complex. The reaction that gave product was by ammonia gas diffusion into a methanol solution containing calcium cations and **DOM2**, which gave both crystalline and non-crystalline products. Unfortunately, the crystal structure has not yet been determined. As **DOM2** contains two extra oxygen atoms over **M2**, it may be a better ligand for 'hard' metal ions, therefore **DOM2** should form interesting complexes, possibly even with Group 1 metal ions, though as no complexes with **DOM2** have been characterised, its coordination to metal ions remains unknown.

2.6.4. Summary

Derivatised sulfurised alkylphenol molecules have been prepared and characterised by single crystal x-ray diffraction. As yet, no crystalline complexes have been prepared and characterised for these ligands, though it has been shown that **DHB2** has interesting semiquinone/quinone-type behaviour. These ligands are not directly useful for understanding overbased detergents as they do not resemble any overbased detergent surfactants, though they present a route to understand how overbased detergent surfactants may interact with the core and therefore how overbased detergent surfactants may be improved.

2.7. Comparisons between Sulfurised Alkylphenol Ligands, Their Complexes and Literature Systems

The table below (table 29) summarises all of the data from the Cambridge Structural Database and this study for sulfurised alkylphenol ligands and complexes.[41]

Ligand/ Complex	Metal ion	Binding mode	C - S - C angle (°)	O - O distance (Å)	S - O bond (Å)	M - O bond (Å)	M - S bond (Å)	M - M distance (Å)
M2[165]			102.9	2.73				
DHB2			100.93	2.740/ 2.908/ 2.691				
a[166]			99.74	2.862				
b[167]			105.48	4.825				
c[168]			104.21	3.893				
MOM2			101.03	4.449	1.533			
d[169]			98.52	5.440	1.510			
e[90]			99.98	5.425	1.519			
DOM2			109.82	4.455	1.449/ 1.449			
f[170]			102.70	4.422	1.446/ 1.441			
MgM2	Mg	B	102.59	3.103		2.044/ 2.023		
CaM2	Ca	A	106.46	3.905		2.356/ 2.376		3.777
SrM2	Sr	A	105.33	4.097		2.489/ 2.529		3.998
SrI2	Sr	A	100.76	3.896		2.509/ 2.517		3.193
			101.45	4.011		2.526/ 2.542		
SrB2	Sr	H	104.95	5.649				4.314
SrO2	Sr	A	104.30	4.161		2.523/ 2.498		3.982
			104.46	4.129		2.498/ 2.554		3.942
BaI2	Ba	E	104.00	5.076		2.811	3.458	4.291
		none	106.23	2.499				
BaB2	Ba	I	103.50	5.358		2.705		4.616
			103.05	5.467		2.686	3.437	
g[171]	Co	F	101.88	3.129		2.070/ 2.047		
			102.01	3.112		2.034/ 2.027	2.468	
h[172]	V	D	102.26	2.713		1.829/ 1.845		3.194
i[172]	V	D	105.63	2.755		1.838/ 1.861		3.161

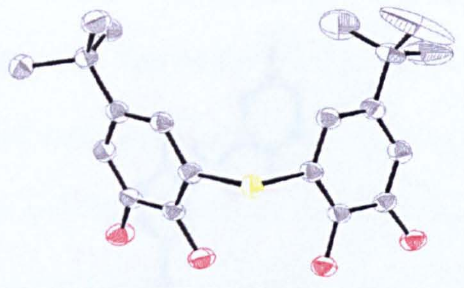
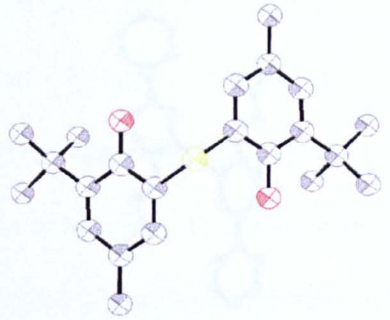
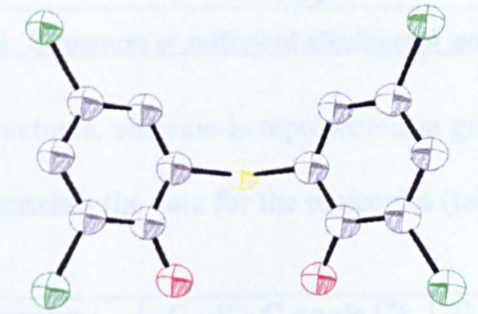
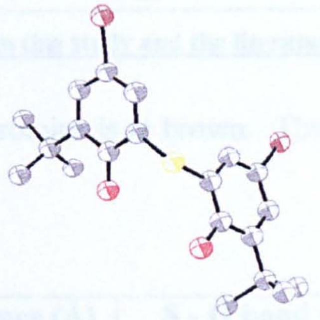
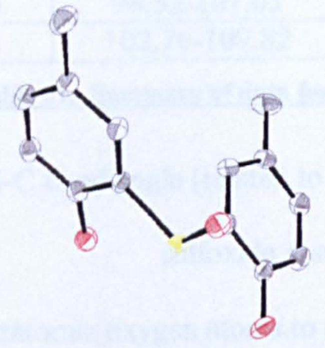
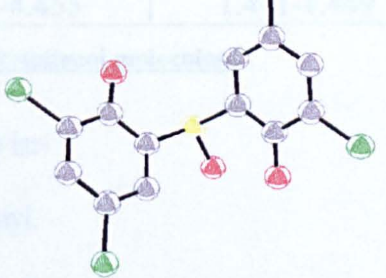
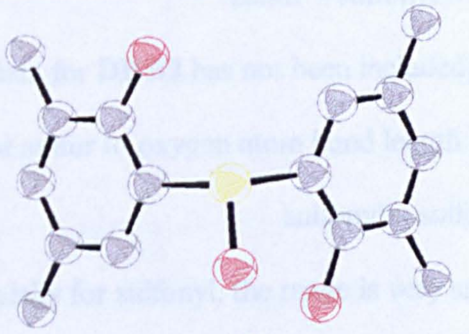
j[173]	W	C	102.64	2.725		1.930/1.945	2.638	
k[173]	W	B	101.11	2.796		2.053/1.912		
l[173]	W	C	103.96	2.799		1.941/2.019	2.627	
m[174]	W	K	101.54	2.571		1.869/1.901		3.697/3.691/3.682
			103.96	2.739		1.873/2.024		
			104.91	2.824		1.844/1.988		
n[175]	Ti	B	107.33	3.092		1.827/1.828		
o[176]	Ti	D	100.93	2.728		1.878/1.899		3.243
p[177]	Ti	D	100.97	2.730		1.885/1.899		3.238
q[177]	Ti	C	103.33	2.836		1.832/1.879	2.704	
r[178]	Ge	G	105.11	2.783		1.799/1.862		
s[179]	Cu	C	111.84	3.674		1.895/1.890	2.290	
t[180]	Cu	J	102.34	3.125		1.924	2.484	
			104.90	3.100		1.934	2.480	
	Li					1.924		4.389
						1.966		
u[172]	V	L	102.61	4.607	1.566	1.888	2.050	
			100.39	2.686	1.512	1.850/1.861		
v[181]	Ti	M	103.50	2.695	1.490	1.933/1.898	2.149	3.217
w[182]	Pyridine	H	108.50	3.062	1.424/1.439			

Table 29. Table to summarise the data for sulfurised alkylphenol ligands and complexes.

The sulfurised alkylphenol ligands are compared below and then the complexes.

2.7.1. Sulfurised Alkylphenol Ligands

The table above (table 29) shows all of the data for sulfurised alkylphenol molecules where the crystal structures are known. It can be seen that there are very few known structures for this class of molecule. The structures of all of the ligands, except **M2**,[165] are shown below (table 30).

Sulfur bridge	 **DHB2 (16)**	 ref.[167]
	 ref.[166]	 ref.[168]
Sulfinyl bridge	 **MOM2 (17)**	 ref.[169]
	 ref.[90]	

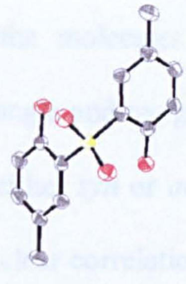
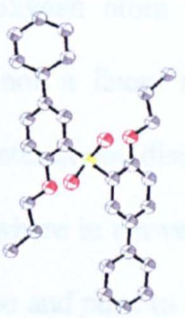
Sulfonyl bridge	 **DOM2 (18)**	 ref.[170]

Table 30. Structures of sulfurised alkylphenol molecules from this study and the literature.

For the structures, chlorine is represented in green and bromine is in brown. The table below summarises the data for the molecules (table 31).

Sulfur group	C - S - C angle (^{o})	O - O distance (Å)	S - O bond (Å)
Sulfur (S)	99.74-105.48	2.730-4.825	N/A
Sulfoxide (SO)	98.52-101.03	4.449-5.440	1.510-1.533
Sulfonyl (SO_2)	102.70-109.82	4.422-4.455	1.441-1.449

Table 31. Summary of data for sulfurised alkylphenol molecules.

The trend for C-S-C bond angle (related to sulfur atom) is:-

sulfoxide < sulfur < sulfonyl.

The trend for interatomic oxygen atoms to oxygen atom distance is:-

sulfur < sulfonyl < sulfoxide,

(where the data for **DHB2** has not been included).

The trend for sulfur to oxygen atom bond length is:-

sulfonyl < sulfoxide,

where, especially for sulfonyl, the range is very small.

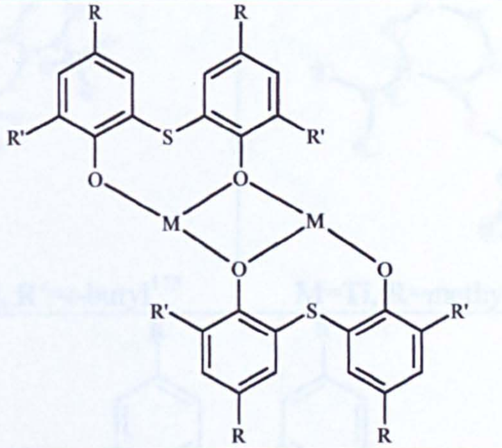
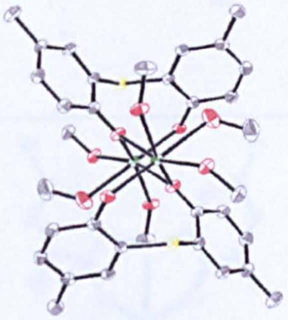
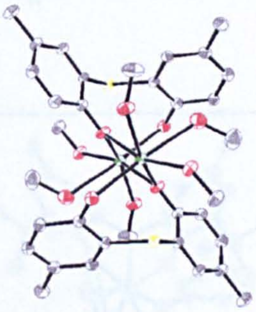
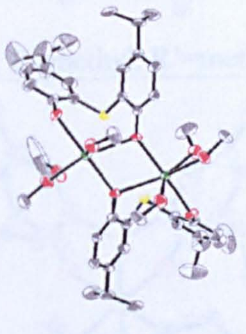
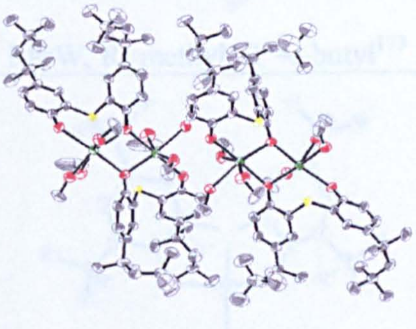
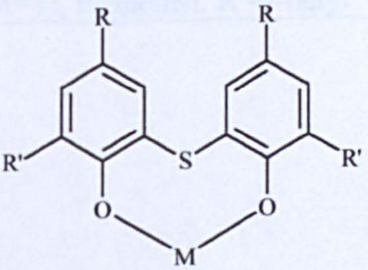
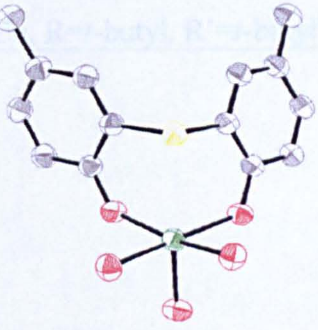
These results (C-S-C bond angle and S-O bond length) are comparable to molecules with sulfur atoms bridging diphenyl molecules[41] and so the phenolic oxygen atom does not greatly affect the structure of the molecules.

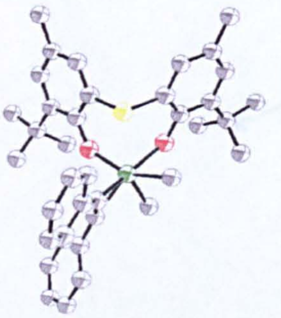
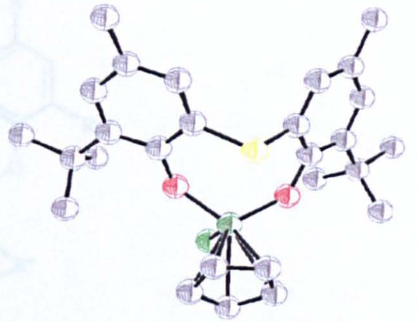
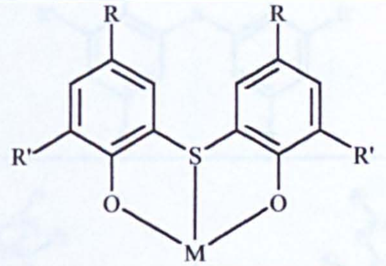
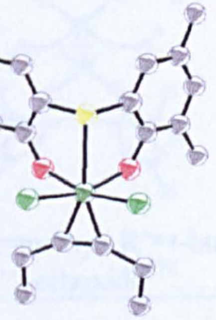
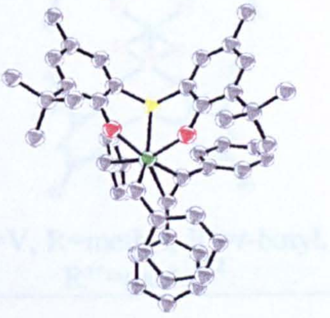
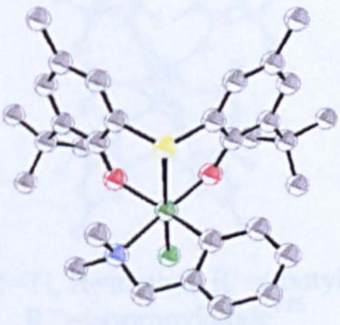
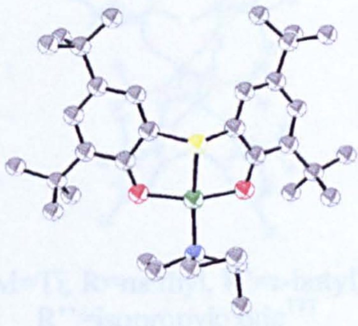
The ranges in C-S-C bond angles and oxygen atom to oxygen atom interatomic distances show that the molecules are flexible. There is not a linear relationship between C-S-C bond angle and oxygen atom to oxygen atom interatomic distance as the oxygen atoms can be either *syn* or *anti* to each other or somewhere in between *syn* and *anti*. There is also no clear correlation between the groups *ortho* and *para* to the oxygen atoms and the distance between the oxygen atoms. For molecules bridged by a sulfur atom, the range of oxygen atom to oxygen atom interatomic distances is the largest. Packing effects and hydrogen-bonding probably have the greatest influence on the shapes of the molecules.

It can be seen that **DHB2, MOM2** and **DOM2** compare well to similar molecules from the literature.

2.7.2. Sulfurised Alkylphenol Complexes

The table (table 29) contains data for almost all of the known complexes with sulfurised alkylphenol ligands.[41] The table does not include any molecules where the phenolic oxygen atoms are derivatised. It can be seen that there are no Group 2 metal ion complexes known other than the ones presented in this chapter. There is only one complex which includes Group 1 metal ions and this is a mixed metal ions complex with copper cations.[180, 183] The table below (table 32) shows the structures of the complexes, where the complexes have been sorted by binding mode. Schematic diagrams of the binding modes are also shown in the table.

<table>
<tr><th>Binding mode</th><th colspan="2"></th></tr>
<tr><td rowspan="3">A</td><td colspan="2"> </td></tr>
<tr><td>
CaM2 (8)
M=Ca, R=methyl, R'=H</td><td>
SrM2 (9)
M=Sr, R=methyl, R'=H</td></tr>
<tr><td>
SrI2 (10)
M=Sr, R=isopropyl, R'=H</td><td>
SrO2 (11)
M=Sr, R=<i>t</i>-octyl, R'=H</td></tr>
<tr><td>B</td><td> </td><td>
MgM2 (12)
M=Mg, R=methyl, R'=H</td></tr>
</table>

	 M=W, R=methyl, R'=*t*-butyl[173]	 M=Ti, R=methyl, R'=*t*-butyl[175]
C	 	
	 M=W, R=methyl, R'=methyl[173]	 M=W, R=methyl, R'=*t*-butyl[173]
	 M=Ti, R=methyl, R'=*t*-butyl[177]	 M=Cu, R=*t*-butyl, R'=*t*-butyl[179]

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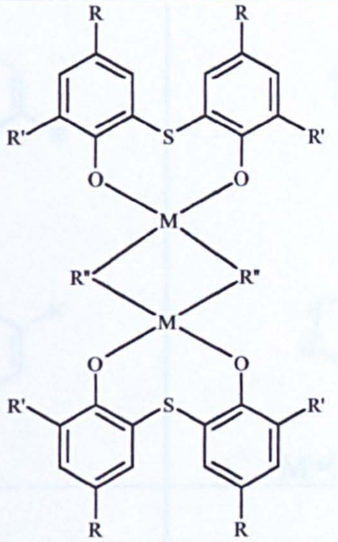
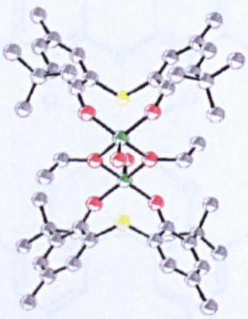
<tr><td rowspan="3">D</td><td colspan="2"> </td></tr>
<tr><td>
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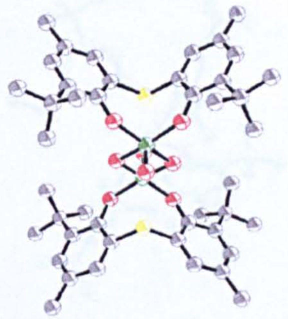
R''=ethoxide[172]</td><td>
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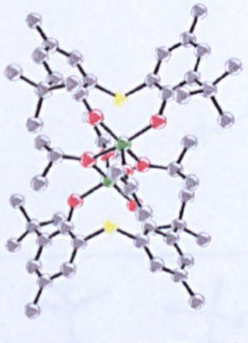
<tr><td>
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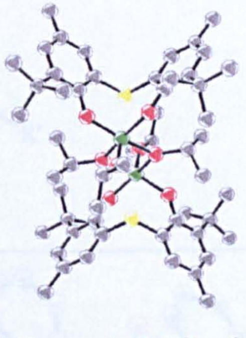
R''=isopropyloxide[176]</td><td>
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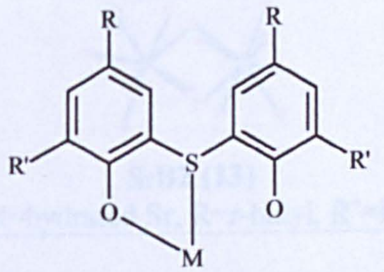
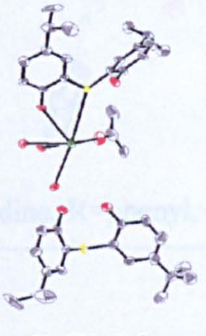
R''=isopropyloxide[177]</td></tr>
<tr><td>E</td><td> </td><td>
BaI2 (14)
M=Ba, R=isopropyl, R'=H</td></tr>
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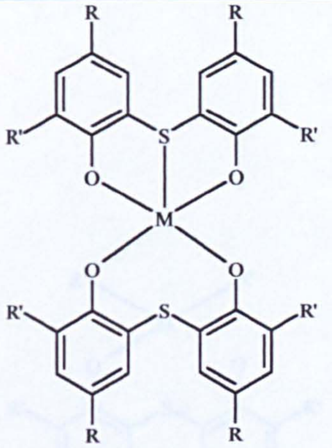
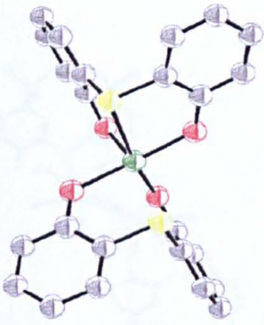
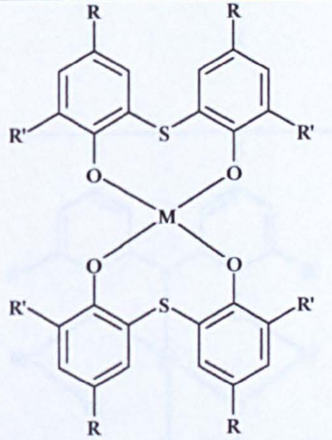
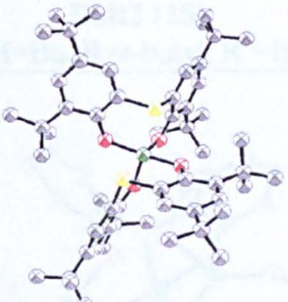
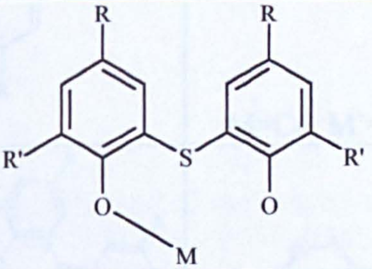
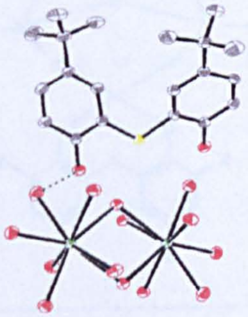
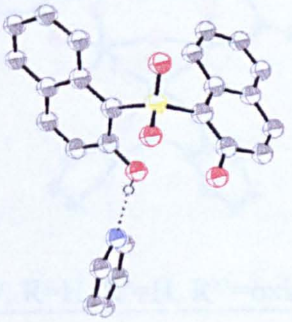
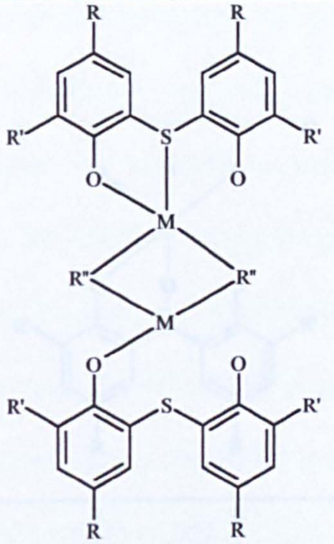
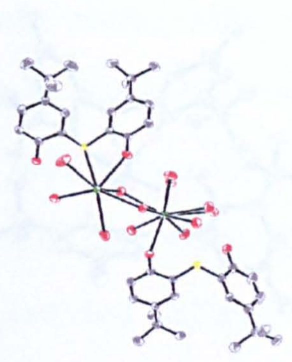
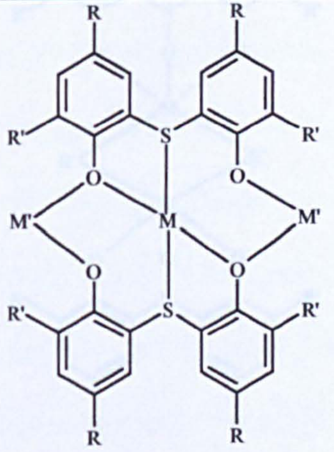
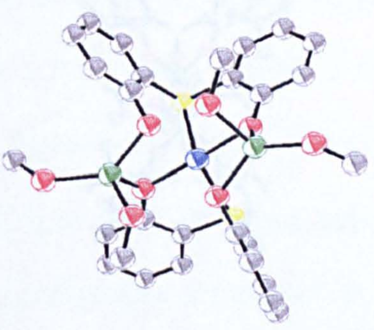
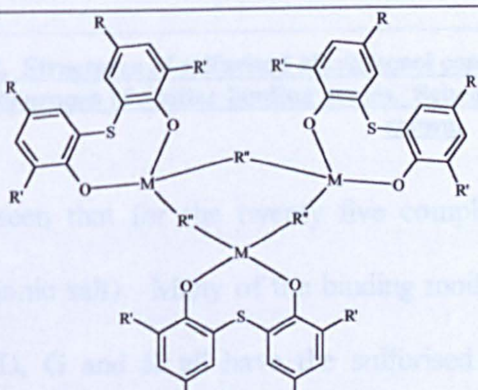
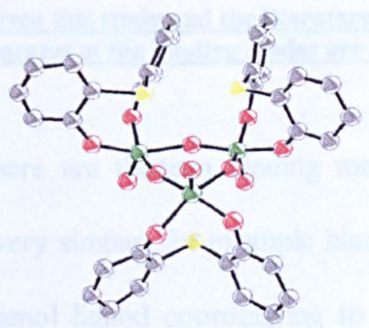
F		 M=Co, R=H, R'=H[171]
G		 M=Ge, R=*t*-butyl, R'=*t*-butyl[178]
H		
	 **SrB2 (13)** M=hydrated Sr, R=*t*-butyl, R'=H	 'M'=pyridine, R=phenyl, R'=H[182]

I		BaB2 (15) M=Ba, R=*t*-butyl, R'=H
J		M=Cu, M'=Li, R=H, R'=H[180, 184]
K		M=W, R=H, R'=H, R''=oxide[174]

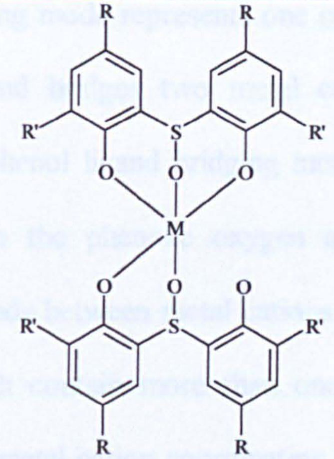
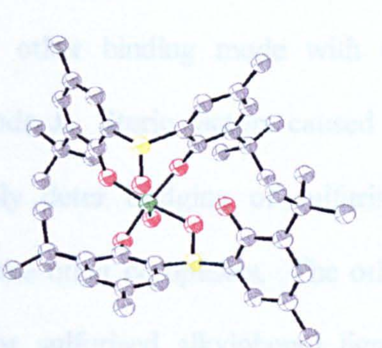
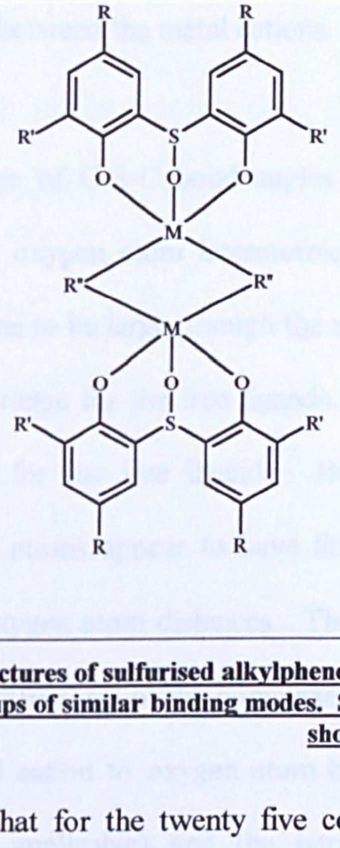
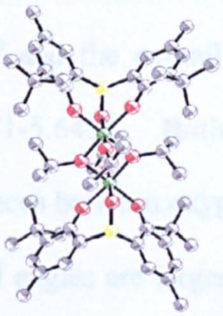
L		 M=V, R=methyl, R'=*t*-butyl[172]
M		 M=Ti, R=methyl, R'=*t*-butyl, R''=isopropyloxide[181]

Table 32. Structures of sulfurised alkylphenol complexes from this study and the literature arranged into groups of similar binding modes. Schematic diagrams of the binding modes are also shown.

It can be seen that for the twenty five complexes, there are thirteen binding modes (including ionic salt). Many of the binding modes are very similar, for example binding modes B, D, G and K all have the sulfurised alkylphenol ligand coordinating to the metal ions through the oxygen atoms. The difference between B, D, G and K is in the number of metal ions and ligands. As can be expected, the binding mode is affected by the metal ion, where the softer metal ions coordinate to the sulfur atom, sometimes in preference to one of the oxygen atoms, for example binding mode J and the binding modes for the barium cation complexes. The binding mode observed for the sulfurised alkylphenol complexes prepared from methanol is not observed for any other complex, where this binding mode represents one of the two binding modes where the sulfurised alkylphenol ligand bridges two metal cations. The other binding mode with the sulfurised alkylphenol ligand bridging metal ions is mode J. Steric factors caused by groups *ortho* to the phenolic oxygen atoms probably deter bridging of sulfurised alkylphenol ligands between metal cations for most of the other complexes. The other complexes which contain more than one metal ion or sulfurised alkylphenol ligand either have one metal cation coordinating to two sulfurised alkylphenol ligands or have bridging groups between the metal cations.

The overall range of C-S-C bond angles is 100.76-111.84° and the overall range of oxygen atom to oxygen atom interatomic distances is 2.571-5.649Å. Both of these ranges can be seen to be large, though the range for the distances between oxygen atoms is similar to the range for the free ligands. The C-S-C bond angles are larger than the angles observed for the free ligands. Binding mode and groups *ortho/para* to the phenolic oxygen atoms appear to have little influence of the C-S-C bond angles and intramolecular oxygen atom distances. The metal cations themselves have the greatest influence on the structures of the complexes. There is a clear correlation between metal cation, the metal cation to oxygen atom bond length, the metal cation to sulfur atom bond length (if applicable) and the intramolecular oxygen atom to oxygen atom distance. The metal cation appears to affect the complex by its coordination number, softness and especially by its ionic radius. The larger ionic radii metal cations, for example barium, have the longest bond lengths to oxygen atoms and to sulfur atoms and the largest oxygen atom to oxygen atom distances. The sulfurised alkylphenol ligands twist about the C-S-C bond to provide an optimal shape to coordinate to the metal cations, which shows how flexible the ligands are. The intercation distances in the complexes cover the range 3.161-4.616Å, where the distance appears to be independent of the actual metal cations.

The sulfurised alkylphenol complexes discussed in this chapter can be seen to show novel binding modes as compared to complexes with similar ligands in the literature, but do show comparable trends in bond lengths and angles.

2.8. Discussion on the Coordination of Sulfurised Alkylphenol Molecules to the Core in Overbased Detergents

A selection of sulfurised alkylphenol complexes have been characterised in the solid state and in solution. Most of the solution state structures have been ambiguous and so for understanding overbased detergents with sulfurised alkylphenol surfactants, it is necessary to look at the solid state structures of the complexes that have been prepared as models. Overbased detergents with sulfurised alkylphenol surfactants are usually prepared from solvents, where the solvent is removed after the formation of the overbased detergent. These solvents include ethylene glycol, 2-ethylhexanol and methanol and toluene mixture.[1, 4] Methanol and water have also been shown to be good promoters for the formation of overbased detergents in small volumes.[5] Therefore the complexes prepared from methanol solution can be seen to be relevant. Of the complexes prepared from acetone and water solutions, **SrB2**, **BaI2** and **BaB2** are not particularly relevant as they contain significant quantities of water and polymeric chains of hydrated metal cations. Thus, in order to understand the coordination of sulfurised alkylphenol surfactant molecules to an overbased detergent core, the complexes **CaM2**, **SrM2**, **SrI2**, **SrO2** and **MgM2** will be mainly used.

Below are sections of two of the sulfurised alkylphenol complexes (figure 80).

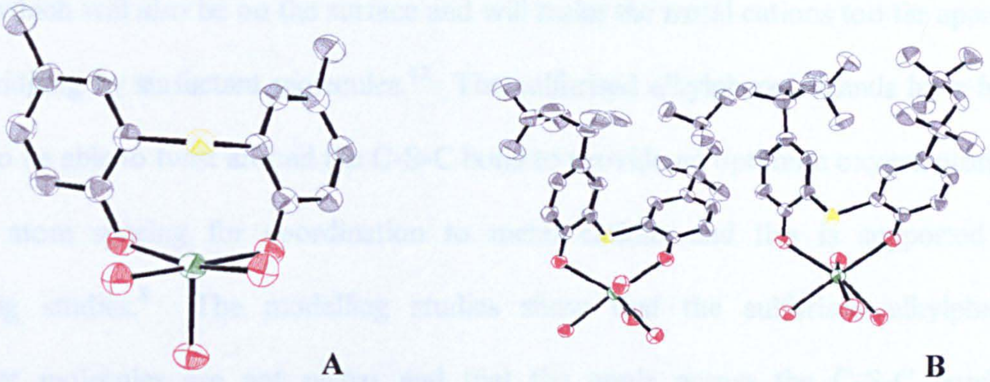


Figure 80. Sections of structures of sulfurised alkylphenol complexes, where A is the magnesium cation complex with M2 (12) and B is the strontium cation complex with O2 (11). Hydrogen atoms and methanol molecule carbon atoms have been removed for clarity.

The above two structures (figure 80) show that the sulfurised alkylphenol molecules probably coordinate to a core in discrete units. The magnesium cation complex with **M2** (**12**) shows that the oxygen atoms of the sulfurised alkylphenol surfactant molecules will be included within the surface of the core, which is supported by molecular dynamic studies.[7, 9, 10] The section of the strontium cation complex with **O2** (**11**) shows that with longer alkyl chains, it is sterically difficult for sulfurised alkylphenol molecules to be close enough to each other to allow the sulfurised alkylphenol molecules to bridge more than two metal ions. This complex also suggests that the sulfur atoms of the sulfurised alkylphenol molecules will alternate in direction along a row. The complexes prepared from methanol all have bridging sulfurised alkylphenol ligands, where the sulfurised alkylphenol ligands bridge two metal cations (see a section of the calcium cation complex with **M2** (**8**) below, figure 81). This may be possible on the surface of the overbased detergent core, though it is probable that if this coordination motif is observed, it will exist as well-separated discrete units so that there is enough space for the alkyl chains of the surfactant molecules. It is more likely that discrete units of one sulfurised alkylphenol molecule to one metal cation is observed, due to the steric factors caused by the alkyl chains of the surfactant molecules that have already been discussed, but also due to the spacing of the metal cations. The metal cations on the surface of the core will be coordinated to carbonate anions and hydroxide anions, which will also be on the surface and will make the metal cations too far apart to allow bridging by surfactant molecules.[12] The sulfurised alkylphenol ligands have been shown to be able to twist around the C-S-C bond to provide an optimum oxygen atom to oxygen atom spacing for coordination to metal cations and this is supported by modelling studies.[8] The modelling studies show that the sulfurised alkylphenol surfactant molecules are not planar and that the angle across the C-S-C bond is dependant on factors such as core size and solvent, though not on alkyl chain length. On increasing the alkyl chain upto C_{12} in length, the angle across the C-S-C bond was found to vary by less than 1°.

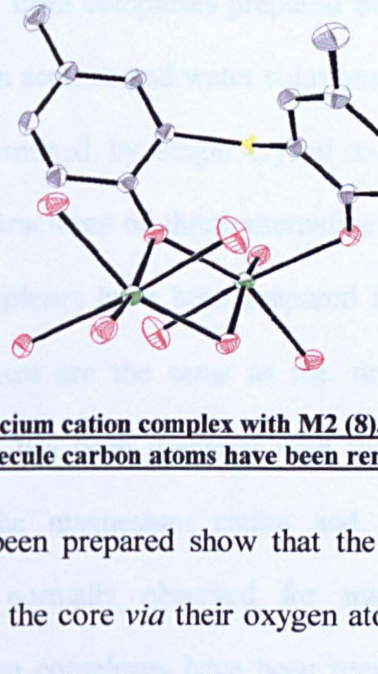


Figure 81. Section of the calcium cation complex with M2 (8), where hydrogen atoms and the methanol molecule carbon atoms have been removed for clarity.

The complexes that have been prepared show that the sulfurised alkylphenol ligands probably only coordinate to the core *via* their oxygen atoms and not through the sulfur atoms (unless the core contains barium cations) and that any uncoordinated sulfurised alkylphenol molecule oxygen atoms will be hydrogen-bonded, either with other sulfurised alkylphenol molecules or with hydroxide anions on the surface of the core. No interaction between the sulfur atoms of the surfactant molecules and the core calcium cations is supported by molecular dynamic studies, which suggests that the sulfur atoms are too far away from the calcium cations to be coordinated.[7]

In summary, sulfurised alkylphenol surfactant molecules probably coordinate to an overbased detergent core *via* their oxygen atoms in discrete units of one sulfurised alkylphenol molecule to one metal cation, with hydrogen-bonding and the inclusion of the oxygen atoms of the sulfurised alkylphenol molecules into the core surface ensuring that the overbased detergent micelles are stable with negligible surfactant exchange.[9]

2.9. Conclusion

Sulfurised alkylphenol complexes have been prepared from a range of solvents, where the most results have come from complexes prepared from methanol solution, followed by complexes prepared from acetone and water solutions. The structures of eight of the complexes have been determined by single crystal x-ray diffraction and have been presented along with the structures of three alternative sulfurised alkylphenol ligands. Isostructural dinuclear complexes have been prepared from methanol solution, where the calcium cation complexes are the same as the strontium cation complexes. A magnesium cation complex has been prepared with the sulfurised alkylphenol ligand coordinating directly to the magnesium cation and not to a hydrated hexaaqua magnesium cation as is normally observed for magnesium cation complexes.[24] Strontium and barium cation complexes have been prepared from acetone and water solutions where all three of the complexes have hydrated metal cations forming polymeric chains. All of the complexes are unusual as there are no precedents in the literature for Group 2 metal cation complexes with sulfurised alkylphenol ligands. Unfortunately no Group 1 cation complexes have been prepared to compare Group 1 and 2 metal cations. The complexes that have been prepared have been characterised in solution as well as the solid state and have shown that in solution they all have different structures to the solid state structures. Calcium cation complexes with **M2** and **I2** prepared from methanol solution have been shown to form hexanuclear clusters in solution. Mass spectrometry and elemental analysis have been shown to have little use in characterising sulfurised alkylphenol complexes.

Alternative ligands to the parent sulfurised alkylphenol ligands have been prepared and characterised. Unfortunately no complexes have been fully characterised with these ligands as yet. It has been shown that **DHB2** forms quinone-type structures when deprotonated. These ligands are not directly relevant to understanding overbased detergents, but are interesting and may show how to improve overbased detergents.

Chapter 3

Calix[8]arene Complexes

3.1. Introduction

Calixarenes are cyclic polyphenol molecules where each phenolic group is linked by a methylene bridge.[99]

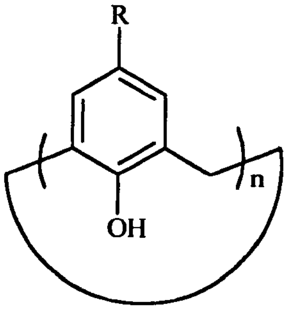


Figure 82. Schematic diagram of the calixarene molecule.

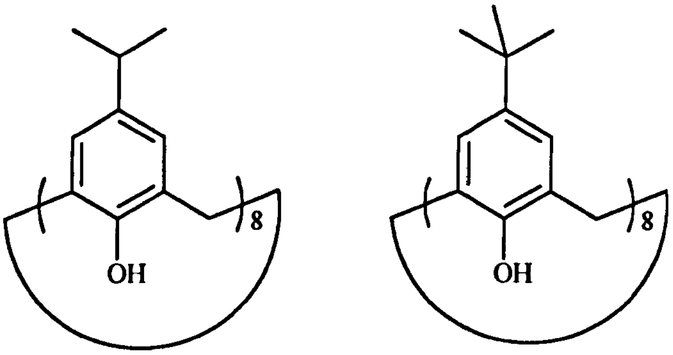
The ring size, n, can range from n = three to n = twenty and the R group is typically an alkyl group.

Calixarenes with ring sizes of four, six or eight are normally synthesised by a base-induced condensation reaction,[184-186] where the choice of base (Group 1 metal hydroxide) dictates the calixarene ring size by a templating effect. This method yields both high purity and a high yield of the chosen ring size. Larger (n > eight) or odd-numbered ring size calixarenes are prepared by the acid-catalysed route or stepwise approach, which usually yield mixtures.[96, 101, 187, 188]

The calixarene used in overbased detergents is p-dodecylcalix[8]arene, which has $C_{12}H_{25}$ as the alkyl chain.[1, 6] For the preparation of complexes, shorter alkyl chains have been used, which confers improved polar solvent solubility on the calixarene and ameliorates the likelihood of crystalline complexes being prepared, which can then be analysed by single crystal x-ray diffraction. The calix[8]arenes that have been used as ligands for the preparation of complexes have been p-isopropylcalix[8]arene and p-*tert*-butylcalix[8]arene, where the p-*tert*-butylcalix[8]arene used was kindly donated by Dr. Clague.[165]

3.2. Calix[8]arene Ligands

The two calix[8]arene molecules which have been used as ligands have been p-isopropylcalix[8]arene (**IC8**) and p-*tert*-butylcalix[8]arene (**BC8**). The diagram below (figure 83) shows schematic representations of these molecules.



IC8 **BC8**

Figure 83. Schematic diagrams of p-isopropylcalix[8]arene (IC8) and p-*tert*-butylcalix[8]arene (BC8) molecules.

The two molecules have short alkyl chains to improve their polar solvent solubility and crystallinity, though due to the large size of the molecules, they both have low solubilities in polar solvents. For example, **IC8** dissolves in methanol only by the addition of a base and **BC8** is completely insoluble in methanol, even with the addition of base. As the phenolic hydrogen atoms are able to form strong hydrogen-bonds with their neighbouring phenolic oxygen atoms, the ligands are able to stabilise any small charge introduced by partial deprotonation.[96, 100, 189] Larger charges, such as more than

–4, are not as easy to stabilise by hydrogen-bonding and therefore are more difficult to achieve.[190]

IC8 (**19**) was prepared by the route shown below (figure 84).

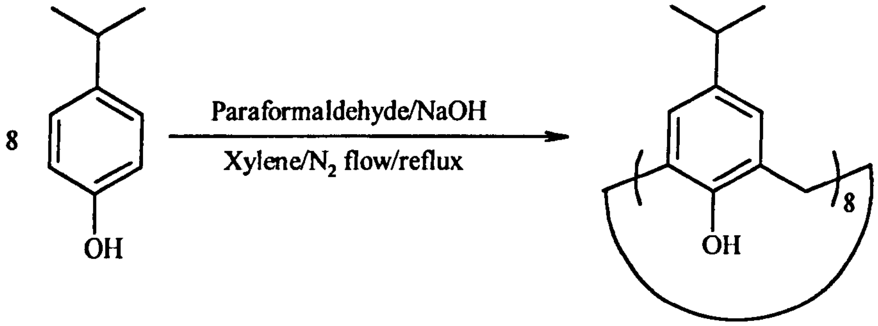


Figure 84. Preparation method for IC8.

The synthesis method uses base catalysis to catalyse the condensation reaction of paraformaldehyde with the desired phenol, where the water is collected *via* a Dean-Stark water collector so that the water does not inhibit the reaction. The ring size is determined by a template effect, where sodium cations template a ring size of eight phenolic units.[184, 191] For **IC8**, the maximum yield that was achieved was 52%. It was observed that a longer reflux time resulted in a higher yield (50% versus 37% yield for four hours versus three hours respectively), but a less pure product. It was found that the most convenient method for the removal of impurities was by washing the crude product with boiling methanol, in which only **IC8** is insoluble. The quantity of impurities was also found to be kept to a minimum by ensuring large volumes of xylene were used. It has been shown that p-*tert*-butylcalixarenes give the highest percentage yields,[187, 192] where the maximum yield for the preparation of **BC8** is 80%.[193] p-Isopropylcalixarenes give lower percentage yields (and have been studied less than their *tert*-butyl analogues), where the highest literature yield for **IC8** is 42%.[194] The method used to prepare **IC8** in this work gave a higher yield than the maximum yield described in the literature. The preparation method is not highly reproducible for percentage yields,[100] which may partly explain the higher yield obtained in this study.

Due to the size of the rings in calix[8]arenes and the rotationally flexible nature of these molecules, there are many possible conformations.[95, 195] For **IC8** and **BC8**, there are sixteen possible up/down conformations, plus many more conformations where one or more of the phenolic units aim 'out'.[194] **BC8** has a preferred pleated loop conformation, especially in solution,[96, 196, 197] which is a conformation where the phenolic units alternate between 'aiming' up and 'aiming' down. This regular up/down conformation of the phenolic units enables to oxygen atoms to hydrogen-bond, which stabilises the conformation.[187] As the calix[8]arene molecules are very flexible, the conformation can vary depending on the inclusion of guests within the ring or the formation of complexes.[197] The ability of these molecules to adopt a large number of potential conformations has hindered the research carried out on these molecules, with calix[4]arenes and calix[6]arenes studied more due to the reduced number of possible conformations (four for p-*tert*-butylcalix[4]arene[187, 198]) and the ease with which the conformations can be controlled relative to calix[8]arenes and the larger calixarene molecules.

The solution structure of **IC8** was determined by ^1H NMR spectroscopy, which showed that **IC8** is conformationally flexible in solution. The degree of flexibility is shown by one phenolic proton peak and two broad alkyl proton peaks. The two alkyl peaks show that there is some rigidity in the ring, though as they are broad this indicates flexibility. ^{13}C NMR spectroscopy and mass spectrometry support these findings. The data for ^1H NMR ($CDCl_3$) spectroscopy agrees with the data for **IC8** in the literature.[199]

3.3. Preparation of Calix[8]arene Complexes

A wide range of conditions where used to attempt to prepare crystalline complexes with **IC8** and with **BC8**. Crystalline complexes were aimed for so that single crystal x-ray diffraction could be used to characterise the complexes. This was due to the lower ambiguity of single crystal x-ray diffraction to characterise structures of complexes compared with most other techniques.[157] The low solubilities of the calix[8]arenes often hindered the achievement of satisfactory ^1H NMR spectra, but wherever possible NMR spectroscopy was used to obtain information on the solution structure, complementary to the solid state. Infrared spectroscopy was found to be of little use as KBr discs could rarely be prepared due to the complexes usually remaining 'damp', even after vacuum drying, and the low quantitative use of the method for understanding the complexes.

In general, complexes were prepared by dissolving the calix[8]arene in a solvent with a base and then adding a solution of the metal salt in a solvent. The metal salt was usually dissolved in a different solvent due to the very different solubilities of the calix[8]arenes compared with the metal salts. **IC8** and **BC8** were found to have low solubilities in polar solvents, whereas the metal salts were found to be soluble only in polar solvents. The base which was most often used to deprotonate the calix[8]arene was tetrabutylammonium hydroxide, due to it being available as a solution in methanol, and hence not requiring dissolution, and due to its easy identification by ^1H NMR spectroscopy. Potassium hydroxide was sometimes used, though it has low solubility in solvents other than water, which was normally avoided. Other bases were tried, but with low success rates. Normally the reactions were carried out under a nitrogen flow to avoid carbon dioxide getting into the reaction, as the complexes were found to be very reactive towards carbon dioxide, leading to decomposition (see 5.2.). For most of the reactions, calcium cation salts were used, as calcium cation complexes are the most relevant for understanding overbased detergents, though reactions were carried out with other Group 1 and 2 metal ions.

The complexes that have been prepared have been divided into three main groupings; salts, calcium cation complexes and strontium cation complexes, and these will be discussed below.

3.4. Calix[8]arene Salts

3.4.1. Introduction

Salts are materials consisting of cations and calix[8]arene anions, where the cations are weakly bound to the anion. The salts may only be observed in solution, due to dissociation, or may also exist in the solid state, where the cations and anions interact by weak forces such as hydrogen-bonds. Calix[8]arene salt products can be divided into two groups; inorganic salts and organic salts. Inorganic calix[8]arene salts have been prepared with sodium, potassium, magnesium, zinc and calcium metal ions. It is not known what the solid state structure of the inorganic salts is, only that in solution the calixarene ring is partly deprotonated and has high symmetry. This indicates the presence of a fluxional calixarene anion in solution and therefore any cations present must be coordinated weakly, if at all. Inorganic salts are often seen when d_6-DMSO is the ^1H NMR spectroscopy solvent as DMSO is a good solvent which can disrupt hydrogen-bonding in a complex.[83] Organic salts contain the tetrabutylammonium cation and no metal ions. Organic salts have been prepared from reaction mixtures containing lithium, sodium, magnesium, strontium and calcium cations, with **IC8** and **BC8**. In methanol, the organic salt readily precipitates out of solution if the calixarene is **IC8**. This limits the level of deprotonation of **IC8** that can be achieved with tetrabutylammonium hydroxide in methanol. **BC8** is not soluble in methanol and so this behaviour is not observed for **BC8**. Crystalline organic calix[8]arene salts have been prepared and one has been characterised by single crystal x-ray diffraction.

3.4.2. Inorganic Calix[8]arene Salts

Group 1 metal ion salts with **BC8** have been prepared from the reactions of **BC8** with sodium hydroxide or with potassium hydroxide in *N,N*-dimethylformamide (DMF). The ^{1}H NMR spectra of the products show the presence of a high symmetry, partially deprotonated calix[8]arene ring plus water and DMF. It is not clear whether the complex contains water or DMF or if the product was 'damp'. The same reaction was carried out with lithium hydroxide, but the product was insoluble in all of the available deuterated solvents and so no ^{1}H NMR spectrum is available for the product. The IR spectrum indicates that the product contains deprotonated calixarene and so it likely that the NMR spectrum would be similar to the spectra obtained for sodium and potassium cations.

The solvent mixture of methanol and 1,3-dimethylimidazolidinone (DMI) was used to prepare calcium ion complexes with calixarenes (see 5.3.2.). When this solvent mixture was used for reactions involving magnesium cations or zinc cations, the products were found by ^{1}H NMR (d_6-DMSO) spectroscopy to be inorganic salts. As the deuterated solvent was d_6-DMSO, the appearance of solution salt structures was to be expected. The use of ^{1}H NMR spectroscopy to predict the number of metal cations in the salt is not usually possible as the phenolic proton peak is usually very broad and so underintegrates. The products were insoluble in all other useful ^{1}H NMR spectroscopy solvents and so solvents such as deuterated dichloromethane (DCM) or deuterated acetone could not be used to observe any hydrogen bonding or symmetry in the salts. As the products were powders, single crystal x-ray diffraction could not be used to identify the solid state structure to ascertain if the salts were really complexes.

A calcium cation complex with **BC8** that had been prepared from DMI (**20**) (see 5.3.2.) and was found by ^{1}H NMR (CD_2Cl_2) spectroscopy to be impure was recrystallised from DCM and DMI to give a crystalline material. ^{1}H NMR (CD_2Cl_2) spectroscopy on the crystals (see below in figure 85) indicated that the product was an inorganic calixarene salt in solution.

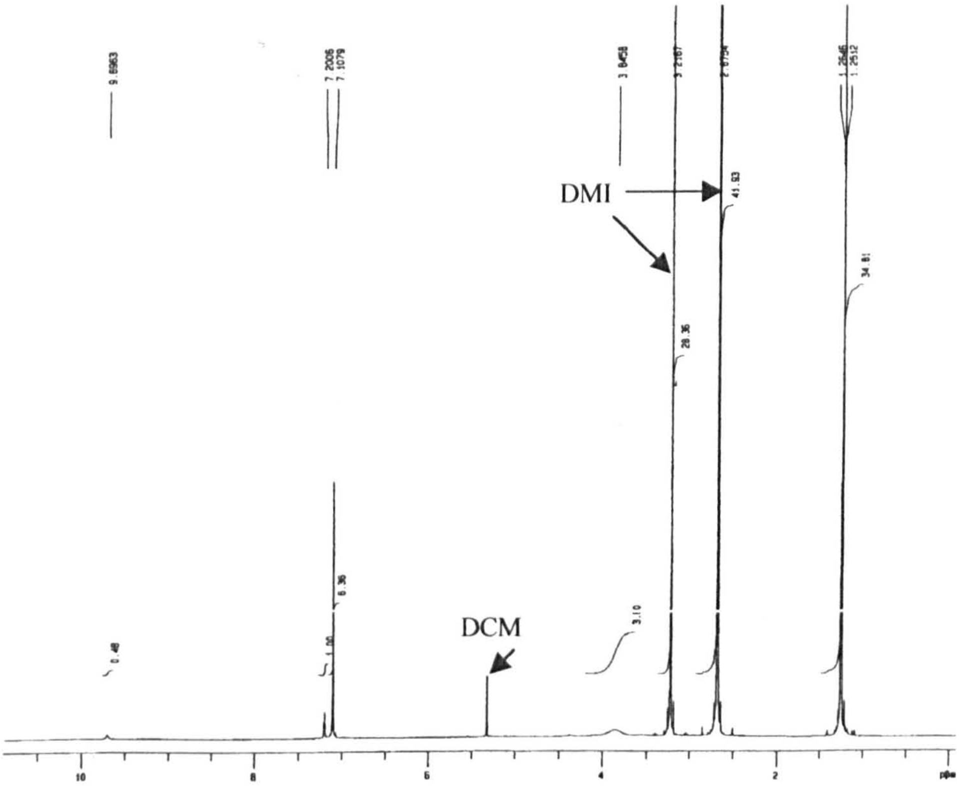


Figure 85. Calcium cation inorganic salt with BC8 ^{1}H NMR (CD_2Cl_2) spectrum

Significant levels of DMI can be seen to be in the crystals, possibly filling the available coordination sites around the calcium ions. The original product before recrystallisation had not included any of the above salt. The crystals may have the same structure in the solid state as the calcium ion complex with **IC8** (see 3.5.), except with DMI replacing the DMF molecules. Repeating the recrystallisation yielded the same inorganic calixarene salt product. Unfortunately the crystals were found to be unsuitable for single crystal x-ray diffraction.

3.4.3. Organic Calix[8]arene Salts

Tetrabutylammonium cation salts of **IC8** and **BC8** have been prepared from a range of solvents in the presence of a range of metal ions. The salt with **IC8** can be readily prepared from methanol by simply adding tetrabutylammonium hydroxide to **IC8** in methanol. **IC8** is observed to dissolve after the addition of at least two equivalents of tetrabutylammonium hydroxide to **IC8** and then reprecipitate out as the salt immediately after the solution has become clear, even without mixing. The salt can then be reacted with metal ions to give a complex, though the level of deprotonation is limited to H_6L^{2-}. The salt with **BC8** does not precipitate out spontaneously from any solvent unless metal ions have been added. **BC8** organic salts are most easily obtained from diethyl ether. A **BC8** organic salt was obtained from diethyl ether under nitrogen by dissolving **BC8** in diethyl ether and then adding tetrabutylammonium hydroxide to the solution. The solvent was then removed under vacuum and the solid recrystallised with clean diethyl ether to yield crystals. The integration on the ^1H NMR ($CDCl_3$) spectrum is not in the expected ratio of two tetrabutylammonium cations to one calixarene, probably because the crystals were impure with tetrabutylammonium hydroxide. **BC8**, even after the addition of tetrabutylammonium hydroxide, is insoluble in methanol and hence organic salts of **BC8** have not been obtained from methanol alone. Below is the ^{1}H NMR (CDCl$_3$) spectrum (figure 86) of the tetrabutylammonium cation salt with **IC8** (**21**). This salt was prepared from methanol with sodium ions in the reaction mixture.

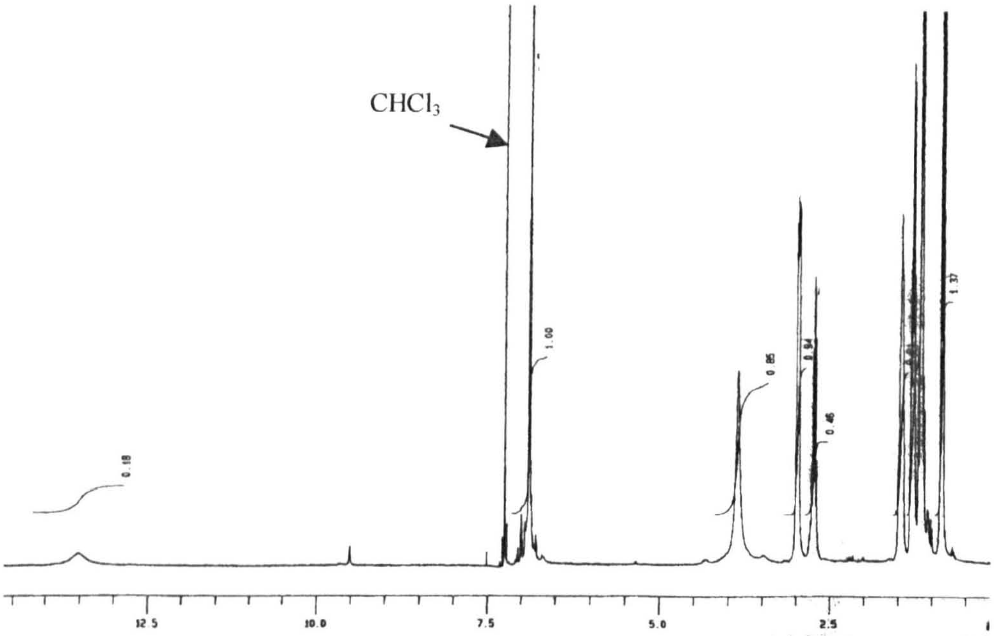


Figure 86. ^{1}H NMR (CDCl$_3$) spectrum of an organic salt with IC8, [Bu$_4$N$^+$]$_2$[H$_6$L^{2-}].

The above crystals were prepared from methanol, though the ^{1}H NMR spectrum shows none of the solvent was incorporated into the crystals, even within the lattice. The phenolic proton peak of the calixarene at 6.9ppm can be seen to be a singlet, as can the alkyl proton peak at 3.87ppm, which shows that the calixarene has high symmetry and therefore is probably a salt rather than a complex. The four peaks for the tetrabutylammonium cation are clearly visible and give a ratio of two tetrabutylammonium cations to one calixarene. The crystals were analysed by single crystal x-ray diffraction to give the structure discussed below.

3.4.3.1. Structure of the Tetrabutylammonium Cation Salt with **IC8** (21)

A crystalline salt of **IC8** with tetrabutylammonium cations was prepared from methanol in the presence of sodium ions. No sodium cations are present in the salt. The salt consists of one calixarene ring, with –2 charge and pleated loop conformation, and two tetrabutylammonium cations.

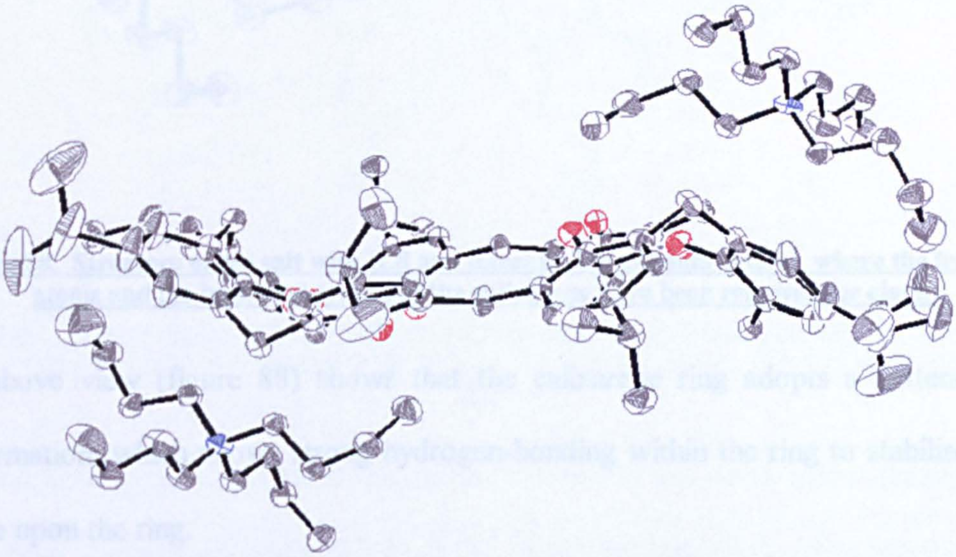


Figure 87. Structure of the IC8 salt with tetrabutylammonium cations, $[Bu_4N^+]_2[H_6L^{2-}]$. Hydrogen atoms have been removed for clarity.

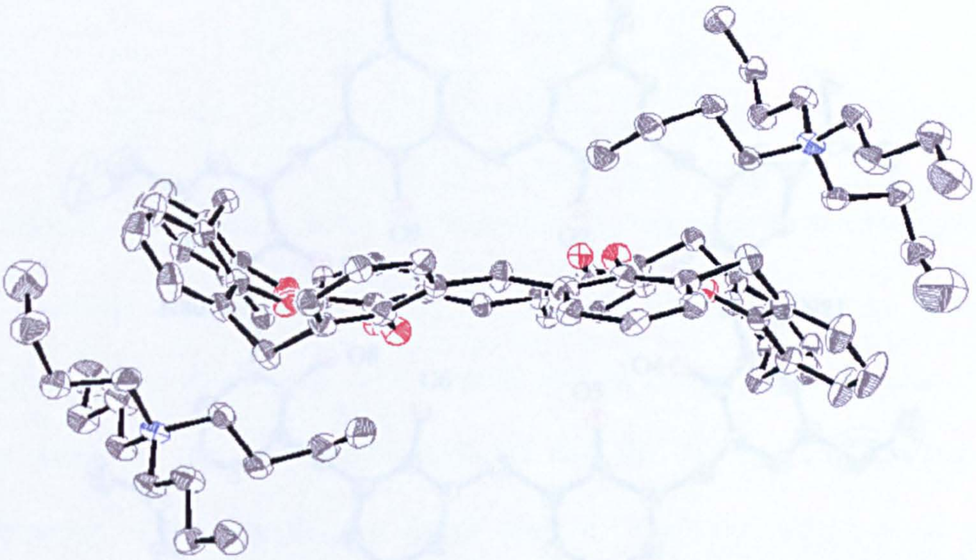


Figure 88. Structure of the salt with IC8 and tetrabutylammonium cations, where the hydrogen atoms and the isopropyl groups of the calixarene have been removed for clarity.

The above view (figure 88) shows that the calixarene ring adopts a flattened chair conformation, which allows strong hydrogen-bonding within the ring to stabilise the –2 charge upon the ring.

The view of the salt below shows selected atom labels (figure 89).

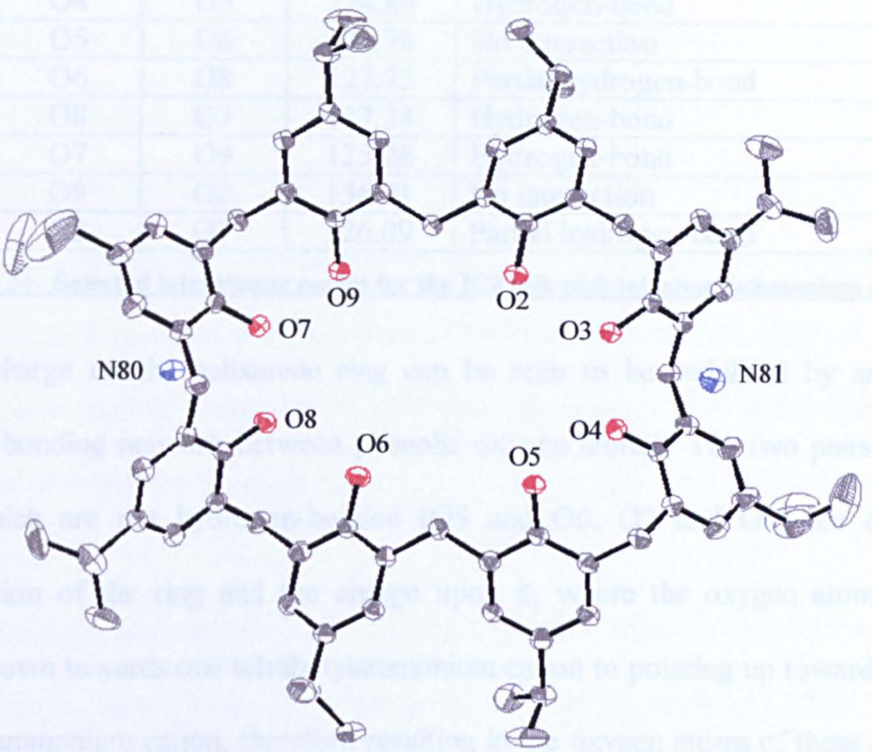


Figure 89. View of the salt with IC8 and tetrabutylammonium cations, where the hydrogen atoms and the *n*-butyl groups of the cations have been removed for clarity. Selected atom labels are shown.

Selected bond lengths and bond angles can be seen in the tables below (tables 33 and 34), where the order is clockwise from O2 for the interatomic oxygen atom distances and for the interatomic angles.

Atom 1	Atom 2	Bond length (Å)	Comment
O2	O3	2.548	Hydrogen-bond
O3	O4	2.473	Hydrogen-bond
O4	O5	2.783	Hydrogen-bond
O5	O6	4.855	No interaction
O6	O8	2.545	Hydrogen-bond
O8	O7	2.471	Hydrogen-bond
O7	O9	2.790	Hydrogen-bond
O9	O2	4.893	No interaction

Table 33. Selected interatomic distances for the IC8 salt with tetrabutylammonium cations.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O2	O3	O4	118.22	Hydrogen-bond
O3	O4	O5	124.80	Hydrogen-bond
O4	O5	O6	136.78	No interaction
O5	O6	O8	127.75	Partial hydrogen-bond
O6	O8	O7	117.34	Hydrogen-bond
O8	O7	O9	125.26	Hydrogen-bond
O7	O9	O2	136.91	No interaction
O9	O2	O3	126.09	Partial hydrogen-bond

Table 34. Selected interatomic angles for the IC8 salt with tetrabutylammonium cations.

The –2 charge on the calixarene ring can be seen to be stabilised by an extensive hydrogen-bonding network between phenolic oxygen atoms. The two pairs of oxygen atoms which are not hydrogen-bonded (O5 and O6, O2 and O9) are due to the conformation of the ring and the charge upon it, where the oxygen atoms go from pointing down towards one tetrabutylammonium cation to pointing up towards the other tetrabutylammonium cation, therefore resulting in the oxygen atoms of these pairs being too far apart to participate in hydrogen-bonding with each other and repelling each other. The interatomic distances between the nitrogen atoms of the cations and the nearest oxygen atoms of the calixarene ring (4.284-4.471Å) compare well with the distances given for tetraalkylammonium cation salts with p-*tert*-butylcalix[4]arene and p-*tert*-butylcalix[6]arene molecules of approximately 4Å.[130] The salt with **BC8** and tetrabutylammonium cations has been reported in the literature, though the structure of the salt was not given.[130]

3.4.4. Summary on Calix[8]arene Salts

There are two types of salts with calix[8]arene molecules that have been formed, which have been classified as inorganic and organic salts. Inorganic salts have been prepared with sodium, potassium, zinc, magnesium and calcium and probably lithium metal ions.

Salts with Group 1 metal ions are observed in solution due to the high lability of Group 1 metal ions. For all of the inorganic salts, the solution structure is probably not the same as the solid state structure, with the possible exception of the calcium ion salt. The inorganic salts with zinc and magnesium ions were only soluble in d_6-DMSO for ^{1}H NMR spectroscopy and so the observed salt structure was expected. For all of the inorganic salts, it is necessary to obtain crystalline samples for single crystal x-ray diffraction to be used to determine the solid state structure, which would show whether the salts are complexes in the solid state.

Organic salts are salts of the calix[8]arene molecule with the tetrabutylammonium cation. These have been prepared from solutions containing lithium, sodium, magnesium, strontium and calcium ions. Organic salts contain no metal ions and can be prepared with **IC8** or **BC8**. The structure of a crystalline organic salt with **IC8** has been determined by single crystal x-ray diffraction (**21**), which showed that the salt had the formula of $[Bu_4N^+]_2[H_6L^{2-}]$. The formula agrees with the solution formula calculated from ^{1}H NMR spectra. In the solid state structure, the tetrabutylammonium cations can be seen to be weakly interacting with the calixarene ring.

3.5. Calcium Cation Calix[8]arene Complexes

3.5.1. Introduction

A range of calcium cation complexes have been prepared, of which two are discussed later (chapter 5, sections 5.2. and 5.3.). As single crystal x-ray diffraction is the most useful analytical method for understanding calcium cation complexes, only crystalline complexes characterised by single crystal x-ray diffraction will be discussed. In this section, one calcium cation complex will be described.

A calcium cation complex with **IC8** has been prepared under a range of conditions. The complex has been prepared from DMF, diethyl ether plus six mole equivalents of DMF to **IC8** and from methanol plus six mole equivalents of DMF to **IC8**, from calcium chloride, calcium bromide and calcium hydroxide and with tetrabutylammonium hydroxide and with calcium hydroxide as the base. Organic salt preparation was avoided by adding the metal salt as soon as the deprotonated calixarene solution became clear. The common theme to all of the complexes appears to be the addition of DMF, even in limited quantities. The ^{1}H NMR ($CDCl_3$ or CD_2Cl_2) spectra of all of the products are identical, where the minor differences in peak positions (+/- 0.1ppm) can be ascribed to the effect of impurities. The ^{1}H NMR spectrum of the complex is discussed in more detail later (section 3.5.3.). One of the products was crystalline and the crystal structure was determined on this product.

3.5.2. Solid State Structure of a Calcium Cation Complex with IC8 (22)

A crystalline complex of calcium with **IC8** was grown from DMF. The complex consists of one calixarene ring and two coordinated calcium cations and has the formula $Ca_2(\mathbf{IC8}^{4-})$.8DMF, where the **IC8** molecule and DMF molecules fill the coordination spheres of the calcium cations. The calixarene ring has a –4 charge and a chair conformation with one calcium cation sitting above the centre and one sitting below the centre of the calixarene anion. The two calcium cations are related by a crystallographic inversion centre. The –4 charge is stabilised by hydrogen-bonding between the oxygen atoms of the calixarene ring, where three oxygen atoms 'share' two hydrogen atoms at each end of the calixarene ring. The calcium cations are equivalent with slightly distorted octahedral geometry. Each calcium cation is six coordinate, coordinating to two bridging calixarene oxygen atoms (O41) and four DMF molecule oxygen atoms (O51, O61, O71 and O81). There is one free DMF molecule within the lattice. The structure of the complex can be seen below (figure 90 and figure 91).

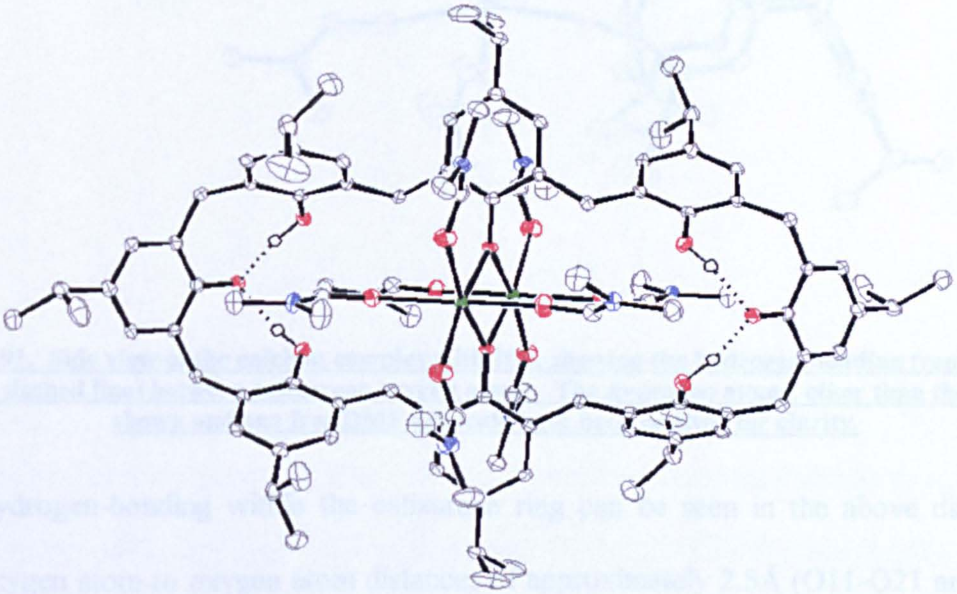


Figure 90. Structure of the calcium complex with IC8, $(Ca^{2+})_2(IC8^{4-})$.8DMF, showing the hydrogen-bonding (represented by a dashed line) between calixarene oxygen atoms. The hydrogen atoms, other than the ones shown and one free DMF molecule have been omitted for clarity.

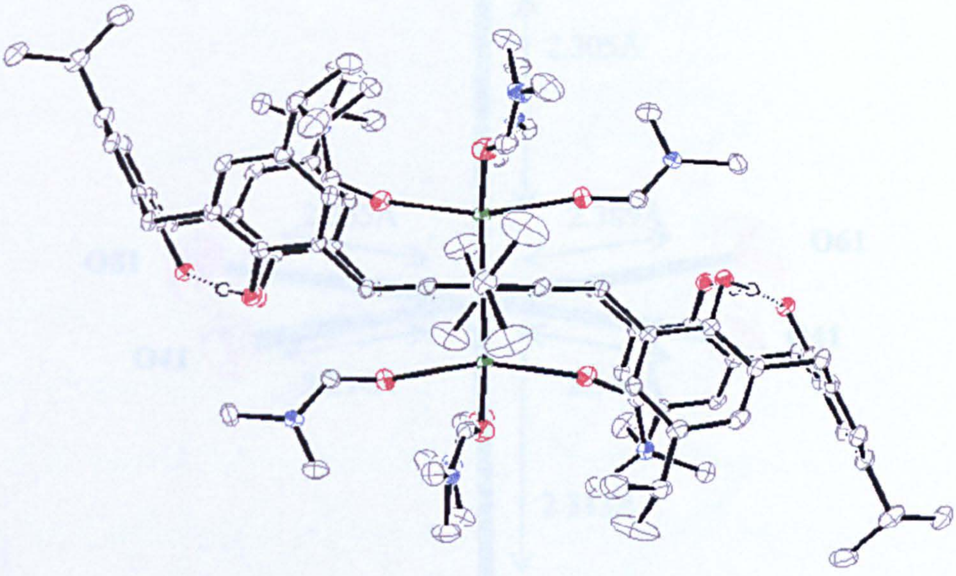


Figure 91. Side view of the calcium complex with IC8, showing the hydrogen bonding (represented by a dashed line) between calixarene oxygen atoms. The hydrogen atoms, other than the ones shown and one free DMF molecule have been omitted for clarity.

The hydrogen-bonding within the calixarene ring can be seen in the above diagrams. The oxygen atom to oxygen atom distances of approximately 2.5Å (O11-O21 and O21-O31), plus the orientation of the hydrogen atoms (H11 and H31a) towards the deprotonated oxygen atoms (O21), supports the existence of hydrogen-bonds. These hydrogen-bonds can be considered to be strong hydrogen-bonds.[191, 200, 201]

The slightly distorted octahedral geometry around the calcium cation can be seen in the diagram below (figure 92) with the bond lengths to the coordinated oxygen atoms.

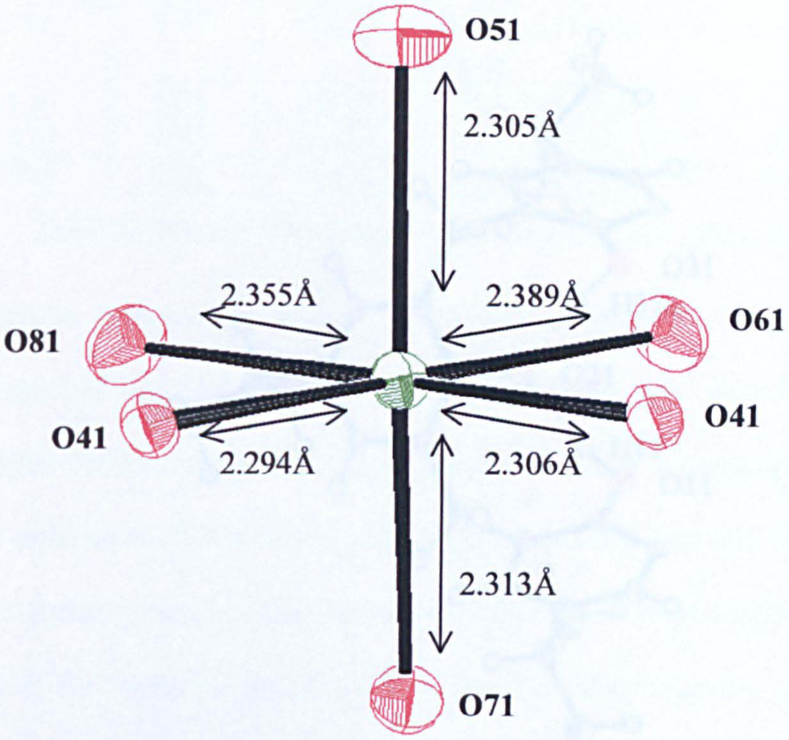


Figure 92. Coordination of the calcium cation with oxygen atoms, showing atom labels and selected bond lengths.

The diagram above (figure 92) shows the coordination around the calcium cation within the complex. O41 represents the bridging phenolic oxygen atoms, which bridge the two calcium cations. O51, O61, O71 and O81 represent the oxygen atoms of coordinated DMF molecules.

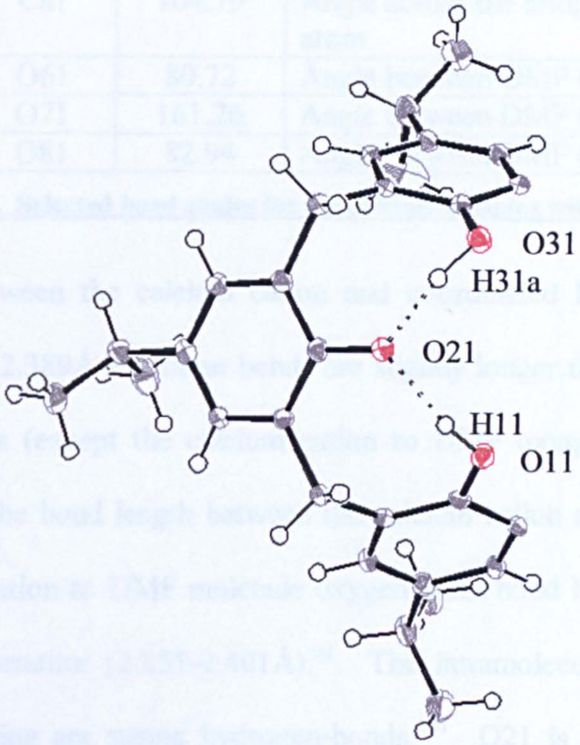


Figure 93. Section of the calixarene ring showing the hydrogen-bonding (represented by a dashed line) with atom labels.

The diagram above (figure 93) shows a section of the calixarene ring, showing the hydrogen-bonds to the deprotonated central oxygen atom. Selected bond lengths and bond angles for the complex can be seen in the tables below (tables 35 and 36).

Atom 1	Atom 2	Bond Length (Å)	Comment
Ca1	O41	2.2942	Ca to bridging calixarene O atom bond
Ca1	O41	2.3060	Ca to bridging calixarene O atom bond
Ca1	O51	2.3046	Ca to DMF O atom bond
Ca1	O61	2.3890	Ca to DMF O bond atom
Ca1	O71	2.3126	Ca to DMF O bond atom
Ca1	O81	2.3550	Ca to DMF O bond atom
Ca1	Ca1	3.6445	Ca cation to Ca cation distance
O11	O21	2.577	Calixarene O to calixarene O distance, linked by strong H-bonding
O31	O21	2.525	Calixarene O to calixarene O distance, linked by strong H-bonding
O11	H11	0.877	Calixarene O atom to H atom bond
O31	H31a	0.980	Calixarene O atom to H atom bond
O21	H11	1.714	Hydrogen bond
O21	H31a	1.556	Hydrogen bond

Table 35. Selected bond lengths for the calcium complex with IC8.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
Ca1	O41	Ca1	104.79	Angle across the bridging calixarene O atom
O51	Ca1	O61	80.72	Angle between DMF O atoms
O51	Ca1	O71	161.26	Angle between DMF O atoms
O51	Ca1	O81	82.94	Angle between DMF O atoms

Table 36. Selected bond angles for the calcium complex with IC8.

The bond lengths between the calcium cation and coordinated DMF oxygen atoms cover the range 2.305-2.389Å and these bonds are slightly longer than the bonds to the phenolic oxygen atoms (except the calcium cation to DMF oxygen atom O51 bond, which is the same as the bond length between the calcium cation and phenolic oxygen atom). The calcium cation to DMF molecule oxygen atom bond lengths fit within the range found in the literature (2.255-2.401Å).[41] The intramolecular hydrogen-bonds within the calixarene ring are strong hydrogen-bonds.[201] O21 is a double hydrogen-bond acceptor oxygen atom in that it accepts hydrogen atoms from two other oxygen atoms. O11 and O31 are both hydrogen-bond donor oxygen atoms.

3.5.3. Solution Structure Studies on the Calcium Cation Complex with IC8

The solution structure of the complex described above is different to the solid state structure. Unlike the differences between the solid state and solution state structures of the sulfurised alkylphenol complexes which was due to aggregation size, this complex has a completely different structure in solution. The complete ^{1}H NMR (CD_2Cl_2) spectrum of the complex can be seen below (figure 94). The ^{1}H NMR spectrum is for the complex that was characterised by single crystal x-ray diffraction, though all of the other complexes prepared from solutions including DMF have the same spectra.

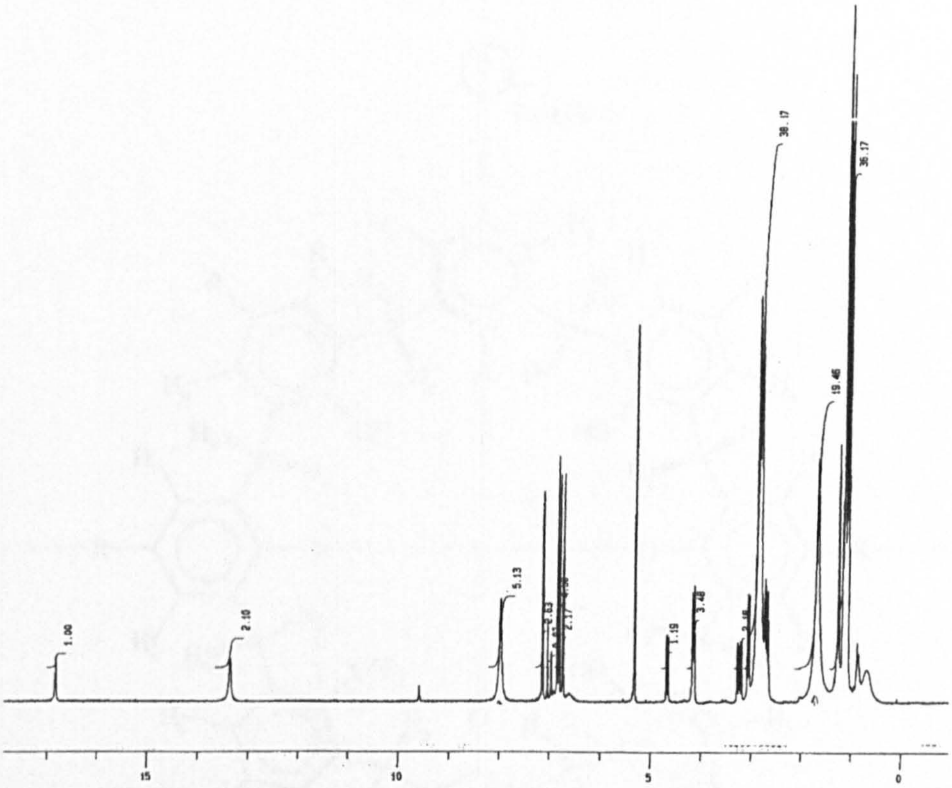


Figure 94. ^{1}H NMR (CD_2Cl_2) spectrum for the calcium cation complex with IC8.

The ^{1}H NMR spectrum contains four aromatic proton peaks (as doublets) and six peaks (as doublets) relating to the protons of the alkyl bridges in the calixarene molecule. The six alkyl proton peaks consist of two peaks with double the intensity of the other four peaks. This suggests that the complex cannot have the same symmetry in solution as in the solid state (which is local C_{2h} symmetry). Peaks for DMF can be seen at approximately 8ppm and two overlapped peaks at approximately 2.9ppm. There are two peaks downfield[159] of the aromatic proton peaks and these peaks are due to hydroxide (see 5.2.4.), though the complex does not include hydroxide anions or even water.

The diagram below shows a calixarene ring with C_{2h} symmetry (figure 95).

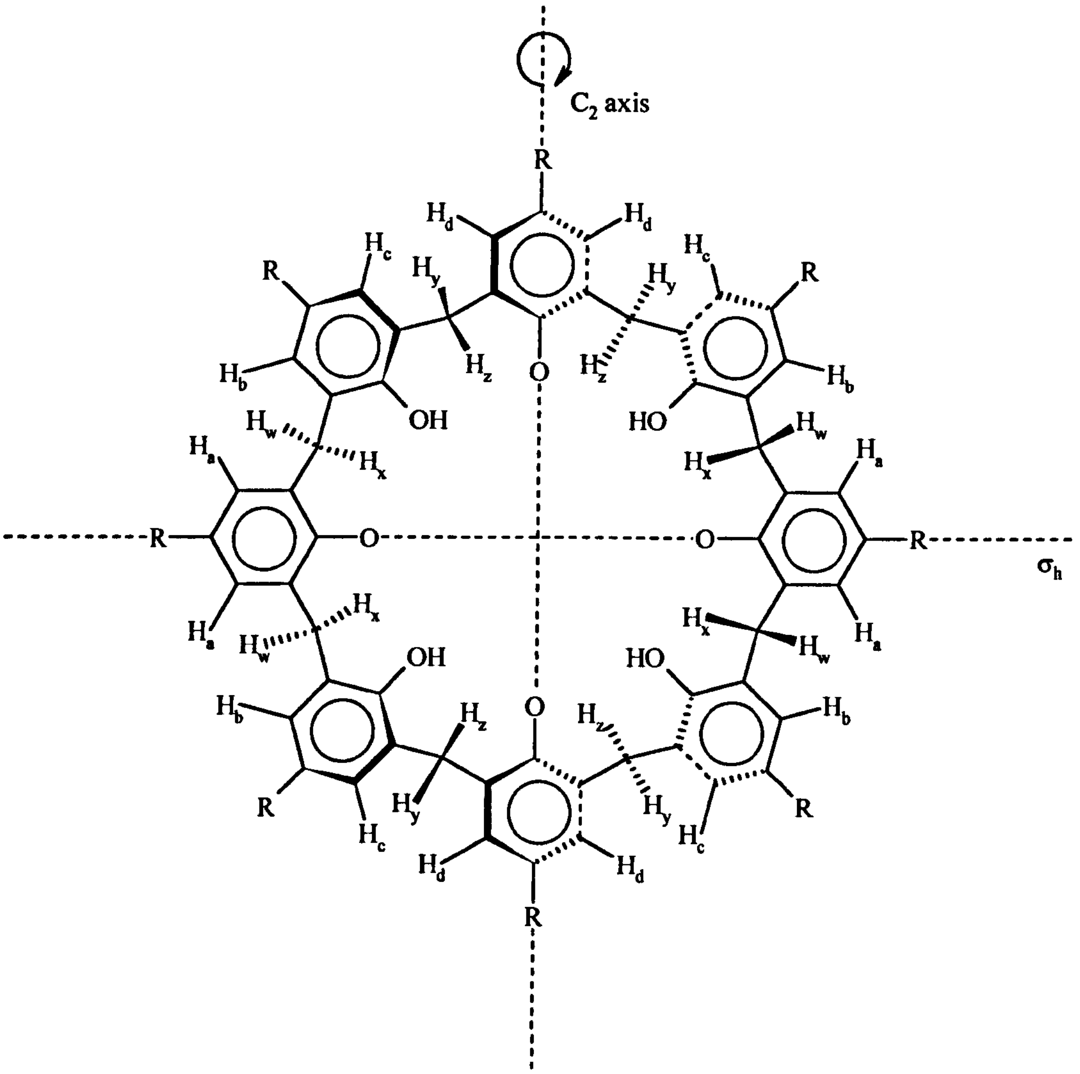


Figure 95. Schematic diagram of a calixarene ring with C_{2h} symmetry.

The diagram shows that the ^{1}H NMR spectrum of a calixarene ring with local C_{2h} symmetry would have four aromatic proton peaks, where two of the peaks would be doublets and two of the peaks would be singlets, and would have four alkyl proton peaks, all as doublets. The ^{1}H NMR spectra that have been obtained on the calcium cations complexes with **IC8** show that the complexes do not have C_{2h} symmetry in solution, but indicates that they have probable local C_{2v} symmetry, where the diagram below shows a calixarene ring with this symmetry (figure 96).

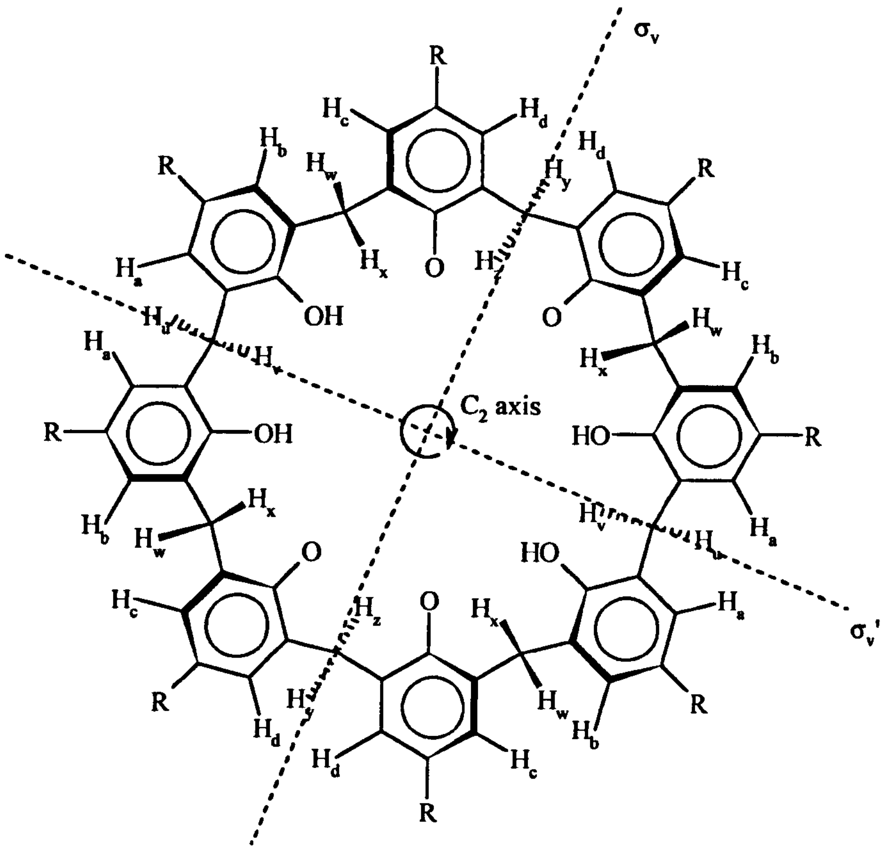


Figure 96. Schematic diagram of a calixarene ring with C_{2v} symmetry.

A calixarene ring with C_{2v} symmetry in solution would give ^1H NMR spectra with four aromatic proton peaks (as doublets) and six alkyl proton peaks (all as doublets) with two peaks having double the intensity of the other four peaks. Thus the calcium cation complexes with **IC8** have local C_{2v} symmetry in solution. C_{2v} symmetry relates to the calixarene ring having pleated loop conformation and C_{2h} symmetry relates to chair conformation. The change in conformation from C_{2h} symmetry to C_{2v} symmetry requires half of the alkyl bridges within the calixarene molecule to twist.

The ^{13}C NMR (CD_2Cl_2) spectrum of the complex is very similar to the ^{13}C NMR (CD_2Cl_2) spectrum for free **IC8** and does not show any of the complicated structure observed by ^1H NMR spectroscopy, even though the deuterated solvent and complex were the same for both forms of spectroscopy. The table below (table 37) compares the

^{13}C NMR spectrum peak positions of the complex to those for **IC8**, where the ^{13}C NMR spectra were collected on deuterated DCM solutions.

	DMF	Ph	Ph	Ph	Ph	DMF	CH_2	CH	DMF	CH_3
Complex	162.59	147.11	143.27	129.52	126.73	36.55	33.68	32.27	30.05	24.32
IC8	N/A	147.10	143.24	129.51	126.72	N/A	33.68	32.25	N/A	24.31

Table 37. Table comparing the ^{13}C NMR (CD_2Cl_2) spectra for the calcium cation complex with IC8 versus free IC8.

The complex can be seen to have a very similar ^{13}C NMR spectrum to the parent **IC8** ^{13}C NMR spectrum.

3.5.4. Summary on Calcium Cation Complexes with Calix[8]arene Ligands

Calcium cation complexes with **IC8** have been prepared from a range of conditions, where the common factor is DMF. All of the complexes have the same ^{1}H NMR spectrum, which shows that the complex has local C_{2v} symmetry in solution. The solid state structure of one of the complexes shows that the calixarene has local C_{2h} symmetry in the solid state. In the solid state, **IC8** is coordinated to two calcium cations, which are related by symmetry. The calcium cations are equivalent and are coordinated to two bridging phenolic oxygen atoms and four DMF molecule oxygen atoms. It is presumed that all of the complexes have the same symmetry in the solid state and all undergo a change to C_{2v} symmetry in solution, though at present this cannot be proven.

3.6. Strontium Cation Calix[8]arene Complexes

3.6.1. Introduction

Strontium cation complexes with **IC8** and **BC8** have been prepared under a range of conditions. Several of the reactions gave crystalline products, though unfortunately most were unsuitable for single crystal x-ray diffraction, usually due to the crystals having low stability and decomposing to powder when disturbed. Two crystalline products were analysed by single crystal x-ray diffraction and these were found to both have the same structure. The structure shows that the complex contains strontium cations, but also potassium cations as a mixed metal ion complex.

3.6.2. Solid State Structure of the Strontium Cation and Potassium Cation Complex with IC8 (23)

A crystalline complex of strontium and potassium cations with **IC8** has been grown from ethylene glycol/water/acetone solution and from water/acetone solution (in the presence of **TMCM**, **(31)**). The structures of the two complexes are equivalent, though the crystals formed from ethylene glycol/water/acetone solution were of lower quality and most of the crystals were twinned. In the structure from ethylene glycol/water/acetone solution, there is some evidence for ethylene glycol occasionally taking the place of two of the coordinated water molecules. The structure that will be discussed below is the one prepared from water/acetone solution. Although **TMCM** was included in the reaction mixture for this complex, there is no evidence for **TMCM** in the product.

The complex of strontium and potassium with **IC8** is a mixed metal ion complex consisting of an asymmetric unit containing one strontium cation, one potassium cation, one **IC8** calixarene ring with –3 charge, acetone molecules (coordinated and free lattice molecules) and coordinated water molecules, giving a formula of SrK(**IC8**$^{3-}$).2acetone.7H_2O. The **IC8** calixarene ring is coordinated to one strontium cation and one potassium cation to give the ring a –3 charge, which is stabilised by hydrogen-bonding of phenolic hydrogen atoms. The calixarene ring has a pleated loop conformation. The strontium and potassium metal cations are both seven coordinate with distorted capped trigonal prismatic geometry. Both cations are coordinated to one calixarene oxygen atom, one bridging calixarene oxygen atom, which is coordinated to both cations, one acetone oxygen atom and four water oxygen atoms, where one water bridges the two cations. For the potassium cation, two of the coordinated water molecules bridge two potassium cations. For the strontium cation, none of the coordinated molecules bridge between two strontium cations, though at least one coordinated water molecule interacts with another water molecule coordinated to another strontium cation *via* hydrogen-bonding (O-O distance <3Å). There are two free acetone molecules in the lattice per calixarene ring. The asymmetric unit of the complex is shown below (figure 97).

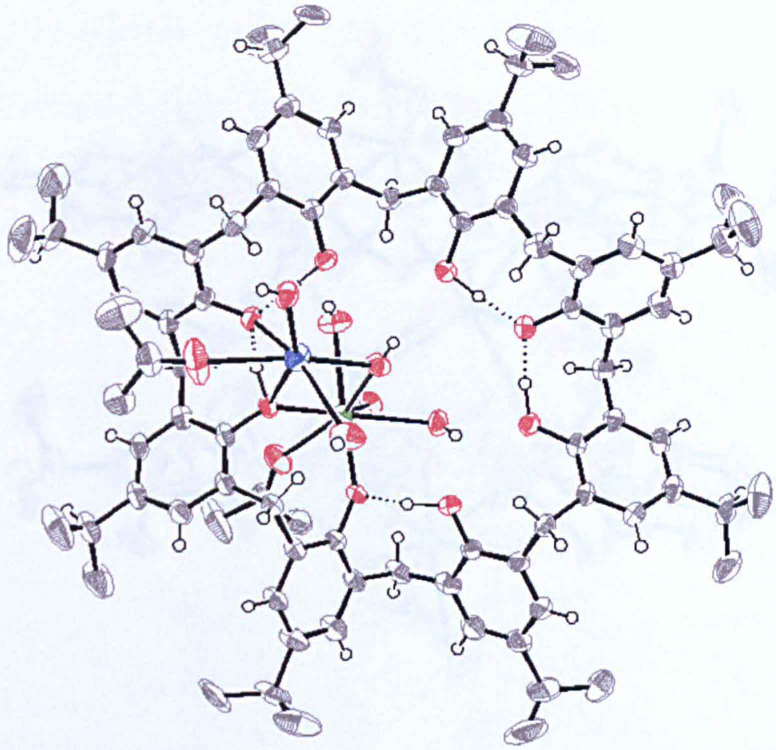


Figure 97. Structure of the asymmetric unit in the strontium and potassium complex with IC8, (Sr^{2+})(K^{+})($IC8^{3-}$).2acetone.7H_2O, where the strontium cation is shown in green and the potassium cation is shown in blue. The hydrogen-bonding between phenolic oxygen atoms is shown by a dashed line. The free lattice acetone molecules have been removed for clarity.

The complex has a layer structure, where the layers are linked by water molecules bridging between pairs of potassium cations and hydrogen-bonded water molecules, which are coordinated to strontium cations. The metal ions sit within the central cavity of the calixarene rings in an ion channel type of structure,[202] where the calixarene rings are all equivalent and sit perfectly over each other, creating the channel. The two views of the complex shown below (figure 98 and figure 99) illustrate the ion channel structure of the complex.

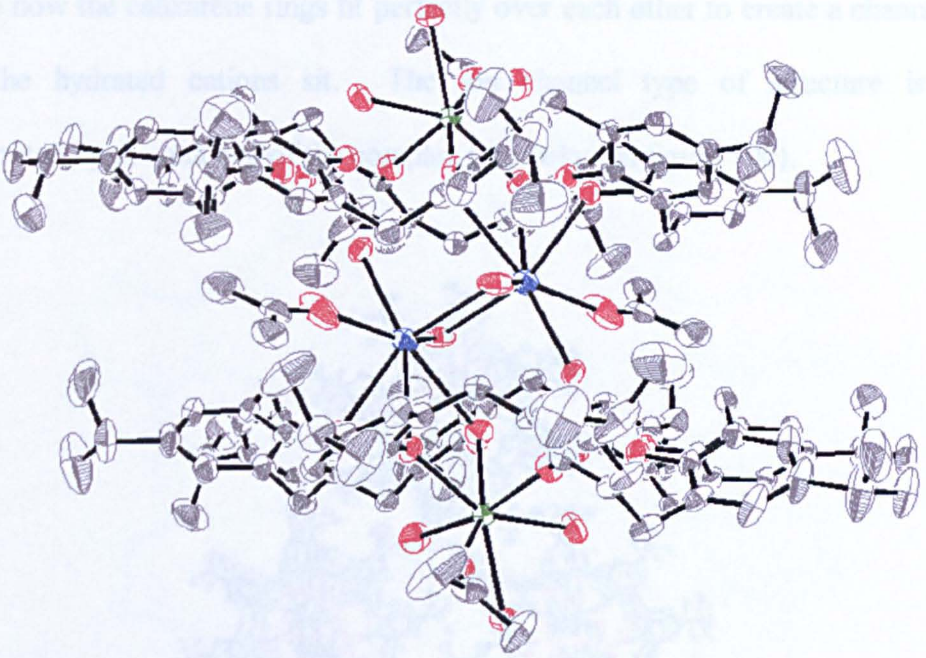


Figure 98. Side view of the strontium and potassium complex with IC8, showing two asymmetric units to illustrate the layering within the structure. Hydrogen atoms and free lattice acetone molecules have been removed for clarity.

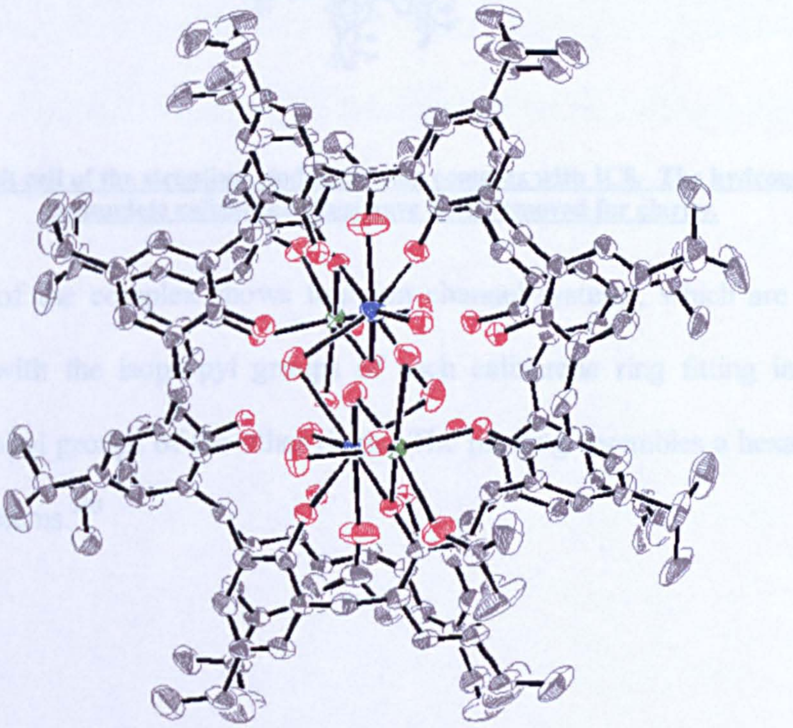


Figure 99. Top view of the strontium and potassium complex with IC8, showing two layers to illustrate how the cations sit in the central cavity of the calixarene rings. Hydrogen atoms and free lattice acetone molecules have been removed for clarity.

The above two views (figures 98 and 99) of the complex show two calixarene rings to illustrate how the calixarene rings fit perfectly over each other to create a channel within which the hydrated cations sit. The ion channel type of structure is further demonstrated by the unit cell of the complex (see below in figure 100).

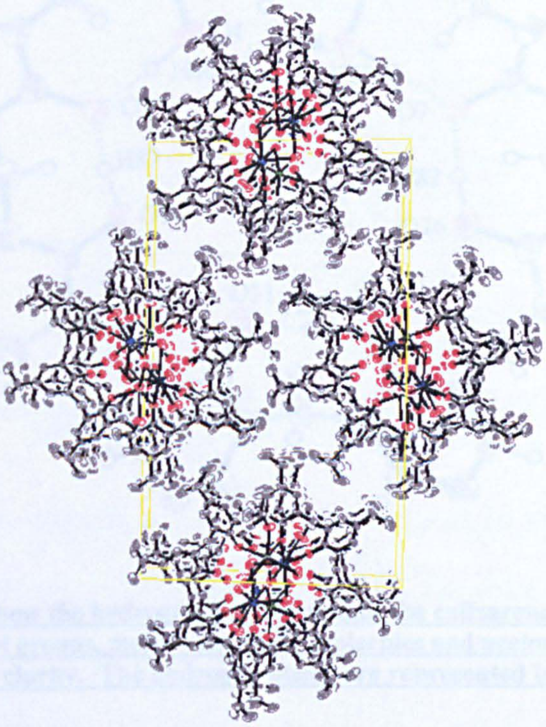


Figure 100. Unit cell of the strontium and potassium complex with IC8. The hydrogen atoms and incomplete calixarene rings have been removed for clarity.

The unit cell of the complex shows four ion channel systems, which are packed like 'cog-wheels' with the isopropyl groups of each calixarene ring fitting into the gaps between isopropyl groups of the other rings. The packing resembles a hexagonal phase for micellar systems.[203]

The –3 charge on the calixarene ring is stabilised by hydrogen-bonding, as shown by the diagram below (figure 101).

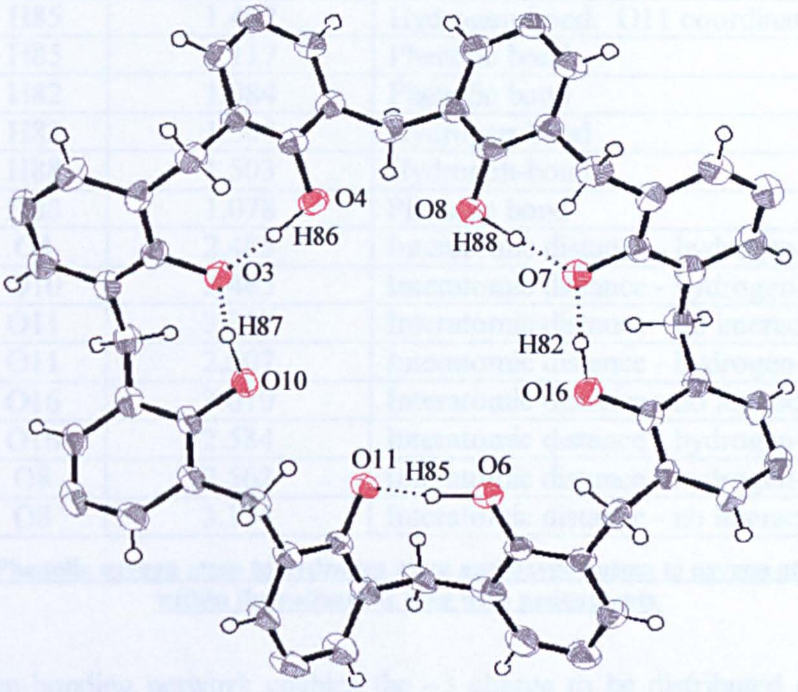


Figure 101. View to show the hydrogen-bonding within the calixarene ring with selected atom labels. The isopropyl groups, metal ions, water molecules and acetone molecules have been removed for clarity. The hydrogen-bonds are represented by dashed lines.

The table below (table 38) contains the bond lengths for the hydrogen-bonds shown in the above diagram. The order is given in an anticlockwise direction starting from O4.

Atom 1	Atom 2	Bond length (Å)	Comment
O4	H86	1.060	Phenolic bond
O3	H86	1.427	Hydrogen-bond. O3 coordinated to K
O3	H87	1.345	Hydrogen-bond
O10	H87	1.108	Bond. O10 bridges Sr and K cations
O11	H85	1.402	Hydrogen-bond. O11 coordinated to Sr
O6	H85	1.117	Phenolic bond
O16	H82	1.084	Phenolic bond
O7	H82	1.504	Hydrogen-bond
O7	H88	1.503	Hydrogen-bond
O8	H88	1.078	Phenolic bond
O3	O4	2.485	Interatomic distance - hydrogen-bond
O3	O10	2.485	Interatomic distance - hydrogen-bond
O10	O11	3.357	Interatomic distance - no interaction
O6	O11	2.507	Interatomic distance - hydrogen-bond
O6	O16	3.010	Interatomic distance - no interaction
O7	O16	2.584	Interatomic distance - hydrogen-bond
O7	O8	2.562	Interatomic distance - hydrogen-bond
O4	O8	3.174	Interatomic distance - no interaction

Table 38. Phenolic oxygen atom to hydrogen atom and oxygen atom to oxygen atom distances within the calixarene ring with assignments.

The hydrogen-bonding network enables the –3 charge to be distributed evenly around the ring, where all of the hydrogen-bonds can be classified as strong.[200, 201] The hydrogen-bonding network contains two oxygen atoms which are double acceptor oxygen atoms, one single acceptor oxygen atom and five donor oxygen atoms.

The coordination sphere around the strontium cation is shown below (figure 102), with atom labels.

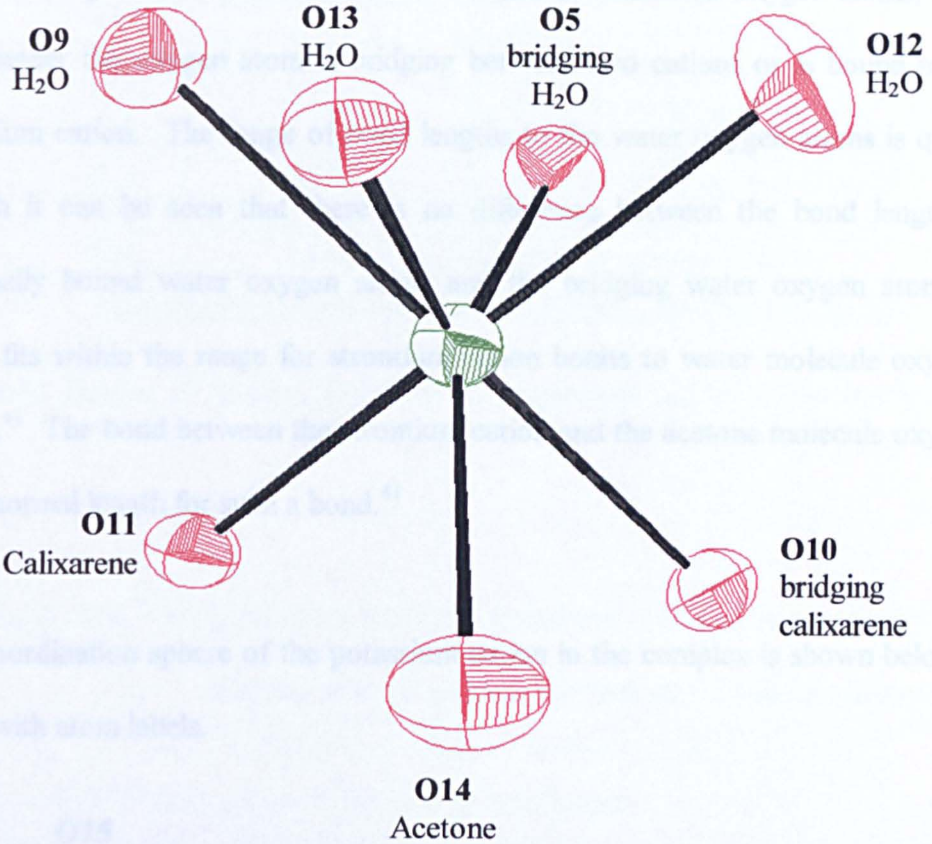


Figure 102. Coordination sphere around the strontium cation in the mixed metal ion complex with IC8, showing atom labels.

The bond lengths for the coordinated oxygen atoms to the strontium cation can be seen in the table below (table 39).

Atom 1	Atom 2	Bond length (Å)	Comment
Sr1	O5	2.608	Sr cation to bridging H_2O O atom
Sr1	O9	2.595	Sr cation to H_2O O atom
Sr1	O10	2.552	Sr cation to bridging calixarene O atom
Sr1	O11	2.399	Sr cation to calixarene O atom
Sr1	O12	2.567	Sr cation to H_2O O atom
Sr1	O13	2.618	Sr cation to H_2O O atom
Sr1	O14	2.520	Sr cation to acetone O atom

Table 39. Bond lengths for the strontium cation coordination sphere.

The strontium cation to oxygen atom bond lengths follow the order;
Calixarene O atom < acetone O atom < bridging calixarene O atom < water O atom.

$\longrightarrow$
Increasing bond length

There is a significant difference in bond lengths to calixarene oxygen atoms, depending on whether the oxygen atom is bridging between two cations or is bound to only the strontium cation. The range of bond lengths to the water oxygen atoms is quite large, though it can be seen that there is no difference between the bond lengths to the terminally bound water oxygen atoms and the bridging water oxygen atom and the range fits within the range for strontium cation bonds to water molecule oxygen atom bonds.[41] The bond between the strontium cation and the acetone molecule oxygen atom has a normal length for such a bond.[41]

The coordination sphere of the potassium cation in the complex is shown below (figure 103), with atom labels.

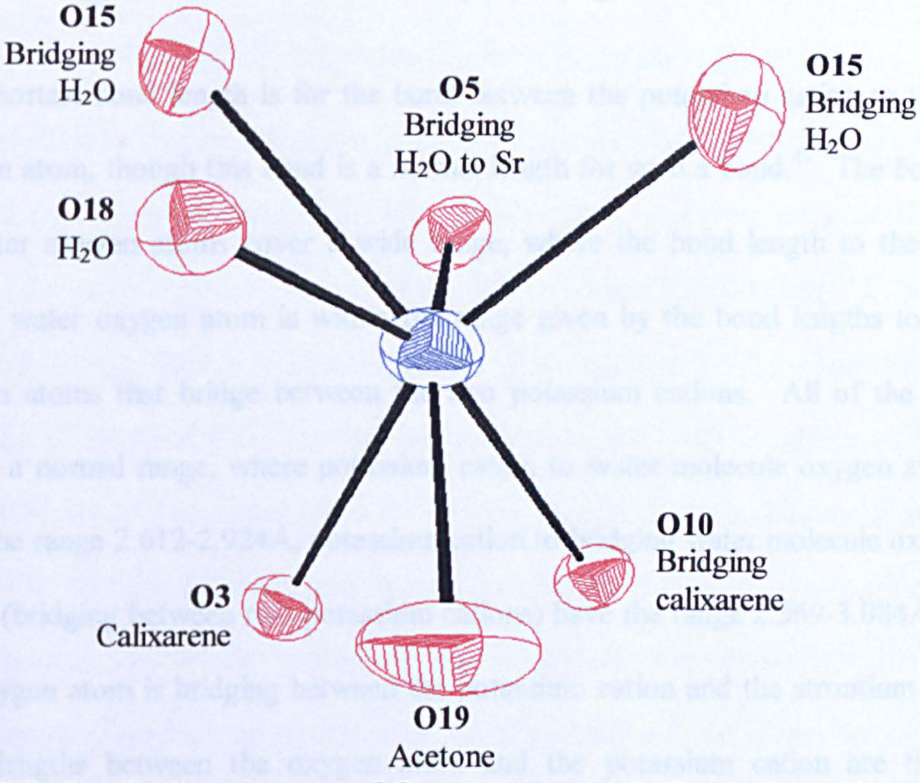


Figure 103. Coordination sphere around the potassium cation in the mixed metal ion complex with IC8, showing atom labels.

The bond lengths for the coordinated oxygen atoms to the potassium cation can be seen in the table below (table 40).

Atom 1	**Atom 2**	**Bond length (Å)**	**Comment**
K2	O3	2.753	K cation to calixarene O atom
K2	O5	3.063	K cation to bridging H_2O O atom (to Sr)
K2	O10	3.120	K cation to bridging calixarene O atom
K2	O15	2.706	K cation to bridging H_2O O atom
K2	O15	2.894	K cation to bridging H_2O O atom
K2	O18	2.836	K cation to H_2O O atom
K2	O19	2.640	K cation to acetone O atom

Table 40. Bond lengths for the potassium cation coordination sphere.

The bond lengths of oxygen atoms to the potassium cation follow the trend shown below.

Acetone O atom < bridging water O atom ≤ calixarene O atom ≤ water O atom <

bridging water O atom (to Sr cation) < bridging calixarene O atom

$\longrightarrow$

Increasing bond length

The shortest bond length is for the bond between the potassium cation to the acetone oxygen atom, though this bond is a normal length for such a bond.[41] The bond lengths to water oxygen atoms cover a wide range, where the bond length to the terminally bound water oxygen atom is within the range given by the bond lengths to the water oxygen atoms that bridge between the two potassium cations. All of the bonds are within a normal range, where potassium cation to water molecule oxygen atom bonds have the range 2.612-2.924Å, potassium cation to bridging water molecule oxygen atom bonds (bridging between two potassium cations) have the range 2.569-3.084Å.[41] When the oxygen atom is bridging between the potassium cation and the strontium cation the bond lengths between the oxygen atom and the potassium cation are the longest observed for the potassium cation and are almost too long to be considered bonds. The bridging water molecule oxygen atom between the potassium cation and the strontium cation is unique as no other examples of water bridging between these two metal ions have been found, though bridging water molecules themselves are not unusual.

The complex may involve weak potassium cation to calixarene π interactions, as the complex contains potassium cation to calixarene ring aromatic ring distances of 3.736Å and 3.896Å. These are slightly longer than the distances shown to be due to cation-π interactions (approximately 3.168-3.582Å).[119] If the complex contains cation-π interactions then this has probably influenced the structure of the complex and probably gives the complex extra stability.[191]

The table below (table 41) shows the intercationic distances for juxtaposed metal cations within the complex.

Atom 1	Atom 2	Distance (Å)
Sr1	Sr1	6.044
K2	K2	3.910
Sr1	K2	4.712

Table 41. Shortest distances between the cations in the complex.

The interatomic distance between potassium cations is short because the cations are bridged by two water oxygen atoms. The distance is normal for potassium cations bridged by water molecule oxygen atoms (normal range 3.789-4.658Å[41]). This bond is too long, though, for the cations themselves to be interacting. The distance between the potassium cation and the strontium cation is also reasonably short due to the cations being bridged by one water molecule oxygen atom and one calixarene ligand oxygen atom. The shortest distance between strontium cations is 6.044Å, which is long because no oxygen atoms bridge between strontium cations and only one water molecule coordinated to each strontium cation is linked by hydrogen-bonding. An oxygen atom to oxygen atom distance of 2.893Å is the shortest distance between oxygen atoms coordinated to two different strontium cations and this is quite long for a hydrogen-bond, indicating that the bond is weak.

Selected bond angles for the complex can be seen in the table below (table 42).

Atom 1	**Atom 2**	**Atom 3**	**Angle (°)**	**Comment**
Sr1	O5	K2	112.12	Angle across bridging H_2O O atom
K2	O15	K2	88.50	Angle across bridging H_2O O atom
O5	Sr1	O9	79.28	Angle between H_2O O atoms
O5	Sr1	O12	72.18	Angle between H_2O O atoms
O5	Sr1	O13	127.45	Angle between H_2O O atoms
O5	Sr1	O14	152.76	Angle between H_2O and acetone O atoms
O10	Sr1	O11	85.34	Angle between calixarene O atoms
O3	K2	O10	48.56	Angle between calixarene O atoms
O5	K2	O19	146.70	Angle between H_2O and acetone O atoms
O15	K2	O15	91.50	Angle between H_2O O atoms
O15	K2	O18	92.12	Angle between H_2O O atoms

Table 42. Selected bond angles for the strontium and potassium complex with IC8.

The bond angles show that both metal cations have similar coordination geometries. For both cations, the coordination to calixarene oxygen atoms is *cis*, which is determined by the calixarene anions coordinating to the metal cations *via* neighbouring oxygen atoms. The coordinated water molecules are all together and for both cations are *trans* to the coordinated acetone molecule.

3.6.3. Solution State Structure of the Strontium Cation and Potassium Cation Complex with IC8

The ^1H NMR ($CDCl_3$) spectrum of the mixed metal ion complex with **IC8** is very broad and therefore is not useful for characterising the solution state structure of the complex. The following section discusses the ^1H NMR spectra for strontium cation complexes. The complex is too large and probably too fragile to be analysed by mass spectrometry.

3.6.4. Solution State Structure Studies on Strontium Cation Complexes by ^{1}H NMR Spectroscopy

All of the ^{1}H NMR spectra that have been obtained on strontium cation complexes have had very broad peaks and therefore have been of little quantitative use. The broadness may be due to fluxional behaviour, where in solution the structure of the complex may change to either several similar complexes or by flexibility of the complex in solution, or perform continuous ligand exchange, all of which is fast compared to the NMR timescale.[64, 161, 200, 204] The attainment of a broad spectrum has qualitative use in being indicative of strontium cation complex formation, but cannot be used to determine the symmetry of the species present in the complex or even the nature of the complex. To illustrate this point, the ^{1}H NMR spectrum ($CDCl_3$) of the crystalline product obtained from a reaction mixture containing strontium bromide, **IC8**, pivalic acid and tetrabutylammonium hydroxide in methanol (**24**) is shown below (figure 104).

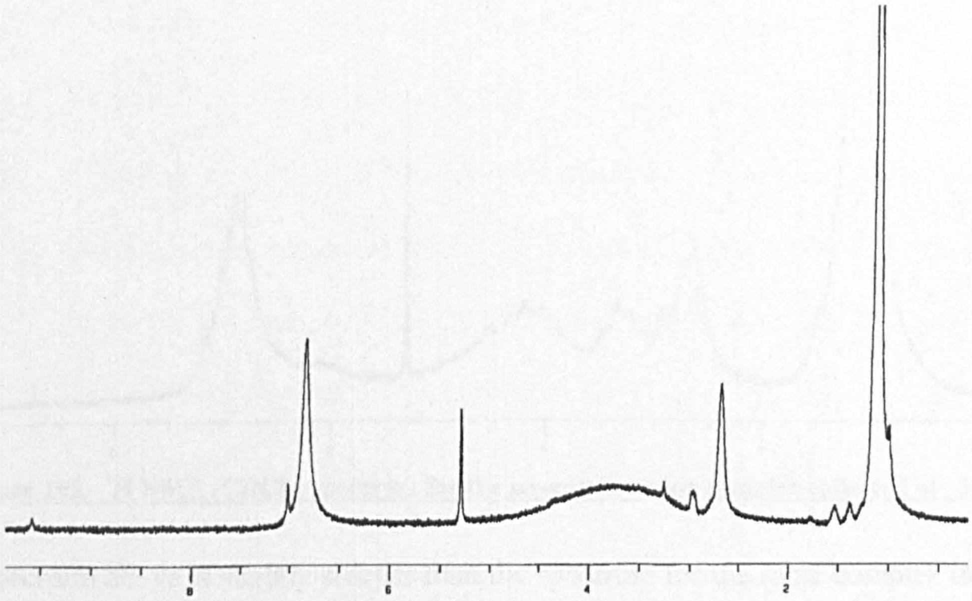


Figure 104. ^{1}H NMR ($CDCl_3$) spectrum of a strontium cation complex collected at 20°C.

The above spectrum can be seen to be very broad. The complex probably contains **IC8**, as determined by peaks at approximately 7, 4 and 1ppm, though any other organic species that may be present in the complex cannot be identified. This spectrum is characteristic of all of the strontium cation complex ^{1}H NMR spectra that have been obtained with ligands such as sulfurised alkylphenols and calix[8]arenes. In the above spectrum, it is not possible to determine if the complex contains pivalic acid or tetrabutylammonium hydroxide. To investigate whether the broadness was due to fluxional behaviour, variable temperature ^{1}H NMR spectra were collected at 20, 0, -10, -30 and -50°C. With reducing the temperature at which the spectrum was collected, the spectrum gets slightly sharper. The spectrum that was collected at -50°C can be seen below (figure 105).

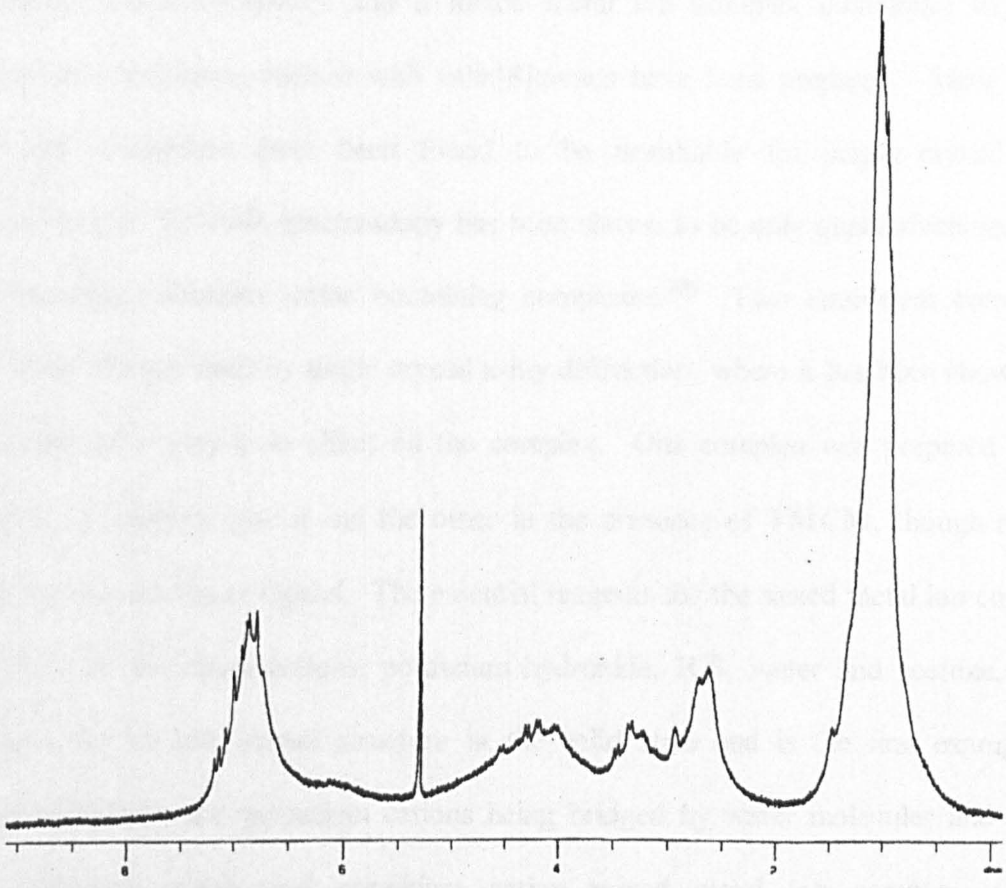


Figure 105. ^{1}H NMR ($CDCl_3$) spectrum for the strontium cation complex collected at –50°C.

The spectrum above is slightly sharper than the spectrum for the same complex that was collected at 20°C, but is still too broad to be quantitatively useful. The spectrum does show some fine structure and so the crystalline product is a complex, though the species present still cannot be identified. This problem with strontium cation complex ^{1}H NMR spectra limits the usefulness of NMR spectroscopy for products containing strontium cations and therefore means that single crystal x-ray diffraction is an essential analytical method for characterising strontium cation containing products. Unfortunately the above crystalline complex was unsuitable for single crystal x-ray diffraction due to the crystals being too unstable and so it has not been possible to characterise the product.

3.6.5. Summary on Strontium Cation Complexes with Calix[8]arene Ligands

Strontium cation complexes and a mixed metal ion complex containing strontium cations and potassium cations with calix[8]arenes have been prepared. Most of the crystalline complexes have been found to be unsuitable for single crystal x-ray diffraction and ^{1}H NMR spectroscopy has been shown to be only qualitatively useful in characterising strontium cation containing complexes.[200] Two equivalent complexes have been characterised by single crystal x-ray diffraction, where it has been shown that co-ligands have very little effect on the complex. One complex was prepared in the presence of ethylene glycol and the other in the presence of **TMCM**, though neither complex includes the co-ligand. The essential reagents for the mixed metal ion complex appear to be strontium cations, potassium hydroxide, **IC8**, water and acetone. The complex has an ion-channel structure in the solid state and is the first example of strontium cations and potassium cations being bridged by water molecules and is the first strontium cation and potassium cation mixed metal ion complex with a calix[8]arene ligand.

3.7. Comparisons between the Calix[8]arene Complexes and Calix[8]arene Complexes in the Literature

A search of the Cambridge Crystallographic Database showed that there are twenty two crystal structures known for metal cation complexes with non-derivatised calix[8]arene ligands,[205] of which most of the structures are with lanthanide metal cations.[41] The complexes evince a wide range of conformations for the calix[8]arene ligands, including complexes where the calixarene molecule folds around the metal cations[195] and a complex where the calixarene has a 'tub-shape'[191]. For the complexes it is most common for there to be two metal cations per calix[8]arene ligand, with the second most common ratio being one metal cation to one calix[8]arene ligand. There is only one calcium cation complex,[21] in which there is one calcium cation coordinated to one **BC8** ligand. The structure of the complex can be seen below (figure 106).

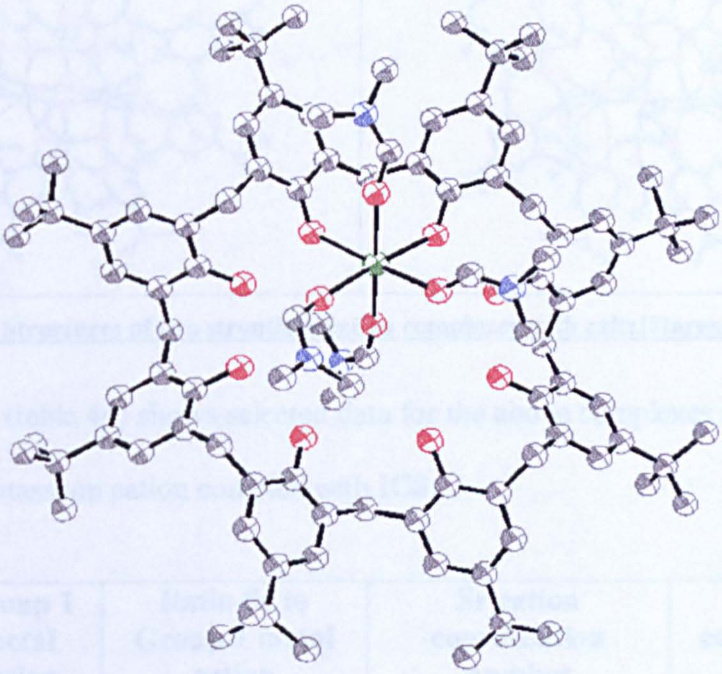


Figure 106. Calcium cation complex with BC8.[21]

The table below (table 43) compares some of the data for the calcium cation complex with **IC8 (22)** to the above complex.[21]

Complex	Ca cation coordination number	Ca to calix[8]arene O atom (Å)	Ca to DMF O atom range (Å)
22	6	2.294, 2.306	2.305-2.389
A[21]	6	2.269, 2.317	2.279-2.357

Table 43. Comparisons between calcium cation complexes with calix[8]arene ligands from this study and the literature.

The environments around the calcium cations in the two complexes can be seen to be very similar.

There are two strontium cation complexes,[206] where both of the complexes are mixed metal ion complexes, though neither of the complexes have ion-channel structures. Both of the complexes contain strontium cations and lithium cations. The structures of the two complexes are shown below (figure 107), where the lithium cations are represented in blue.

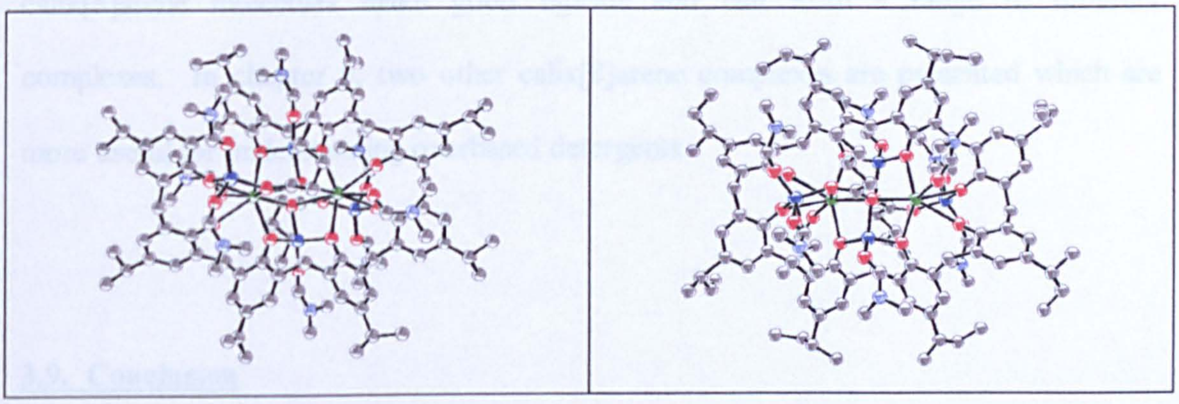


Figure 107. Structures of two strontium cation complexes with calix[8]arene ligands.[206]

The table below (table 44) shows selected data for the above complexes compared to the strontium and potassium cation complex with **IC8**.

Complex	Group 1 metal cation	Ratio Sr to Group 1 metal cation	Sr cation coordination number	Sr to calix[8]arene O atom (Å)
23	K	1:1	7	2.399-2.552
A[206]	Li	1:2	8	2.447-2.828
B[206]	Li	1:2	8	2.451-2.886

Table 44. Comparisons between the strontium cation complexes with calix[8]arene ligands from this study and the literature.

The two strontium and lithium cation complexes are very similar. In the strontium and potassium cation complex (**23**), the bonds between the calix[8]arene ligand and the strontium cations are shorter and cover a smaller range than in the other two complexes. The reduced ratio of the Group 1 metal cations to strontium cations may be due to the larger size of the potassium cation in the strontium and potassium cation complex.

3.8. Discussion on the Coordination of Calix[8]arene Molecules to the Core in Overbased Detergents

The complexes and salts that have been presented in this chapter have very little use as far as understanding overbased detergents is concerned. It has been seen that calix[8]arene molecules make good ligands and can form a range of different complexes. In chapter 5, two other calix[8]arene complexes are presented which are more useful for understanding overbased detergents.

3.9. Conclusion

A wide range of calix[8]arene complexes have been prepared of which the structures of three calix[8]arene 'complexes' (one was a salt) have been presented. All three of the materials which have been characterised in the solid state by single crystal x-ray diffraction have **IC8** as the calixarene ligand. Inorganic salts and organic salts have been described and the crystal structure of the organic salt presented (**21**). The structures of the inorganic salts are unknown and therefore some of the 'salts' may actually be complexes in the solid state. A calcium cation complex has been presented

(22), where the complex has a very different solid state structure to its solution state structure. A mixed metal ion complex containing strontium cations and potassium cations has been presented **(23)**, which has an interesting ion-channel structure in the solid state. The characterisation of strontium cation complexes by ^{1}H NMR spectroscopy has been discussed, which has shown that ^{1}H NMR spectra for strontium cation complexes are always broad and therefore the broadness itself is indicative of strontium cation complex formation. This broadness effect has been observed with ligands such as calix[8]arenes and sulfurised alkylphenols.

Chapter 4

Co-Ligands

4.1. Introduction

The overbasing process is represented schematically below (figure 108).[1,2,6]

$$\begin{array}{c}\text{Surfactant}\\ \text{Solvent}\\ \text{Optional - lubricating oil}\end{array} \xrightarrow[\text{B) Carbon dioxide}]{\begin{array}{l}\text{A) Basic Group 2 metal compound}\\ \quad\text{Optional - co-surfactant}\\ \quad\text{Optional - catalyst}\end{array}} \text{Overbased Detergent}$$

Where: -
Surfactant – for example, calix[8]arene, sulfurised alkylphenol
Solvent – for example, ethylene glycol, ethylene glycol/2-ethylhexanol, methanol/toluene
Basic Group 2 metal compound – for example, calcium hydroxide
Co-surfactant – for example, long chain carboxylic acid
Catalyst – for example, calcium acetate.

Figure 108. Schematic representation of the overbasing process.

For the preparation of overbased detergents with calix[8]arene surfactant molecules, co-surfactants are necessary to give large cores.[6] Catalysts are often used in the preparation of sulfurised alkylphenol overbased detergents.[1]

In order to understand overbased detergents, it is important to investigate the roles of the solvents and the co-surfactants, as well as the metal cations and the surfactants. The potential role of methanol has been investigated by the preparation of complexes from this solvent. This has shown that methanol is a good ligand for Group 2 metal ions and can fill coordination spheres for these cations in complexes. Ethylene glycol has been used as a solvent, though no complexes have been formed from it that have been characterisable. Toluene and 2-ethylhexanol have not been used as they are too non-polar and so it will not be possible to prepare complexes from them. Reactions have been carried out where carboxylic acids have been added along with calix[8]arenes and sulfurised alkylphenol ligands, though no mixed ligand complexes have been characterised. Thus solvents and co-surfactants must be investigated as individual entities.

Ethylene glycol is the most relevant solvent to be studied, though ethylene glycol is a viscous liquid which is difficult to add accurately and tends to form a coating on products. Therefore, to investigate ethylene glycol, structural mimics for ethylene glycol have been used.

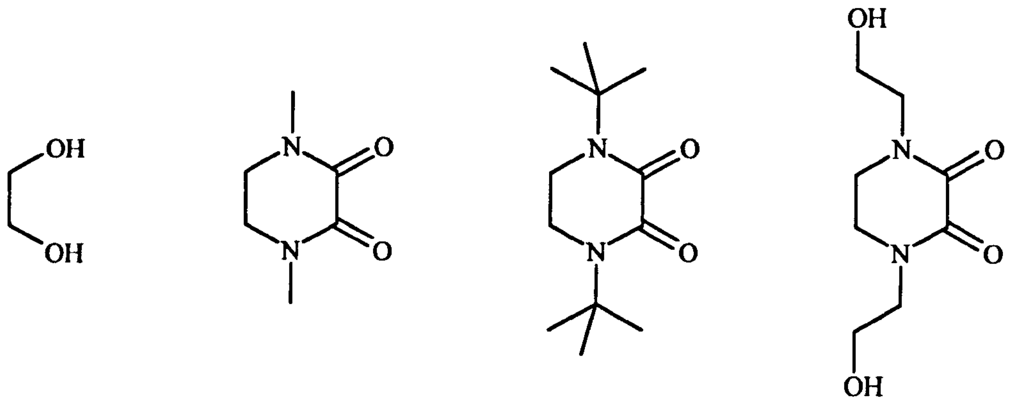
The co-surfactants used in the overbasing process tend to be long chain carboxylic acids, where the most commonly used carboxylic acid is stearic acid.[1] Stearic acid is a long chain unbranched carboxylic acid. Alternative carboxylic acids have been used to investigate the many potential modes of coordination of stearic acid to a core. The alternative carboxylic acids have shorter alkyl chains than stearic acid to improve polar solvent solubility and increase the crystallinity of the complexes.

For this chapter, ethylene glycol mimics and carboxylic acids will be discussed separately as they are unlikely to have comparable roles in the preparation of overbased detergents and are very different molecules. For example, ethylene glycol aids the preparation of large cores, though is not included in the final product, whereas carboxylic acids are included in the final product.[207]

4.2. Ethylene Glycol Mimics

4.2.1. Introduction

As mentioned above, ethylene glycol is a viscous liquid, which is difficult to add accurately and to remove from products where it tends to coat the product. To understand the role of ethylene glycol in the preparation of overbased detergents, mimics for ethylene glycol were used. The diagram below (figure 109) shows the mimics which were prepared and the ethylene glycol molecule for comparison.



Ethylene glycol **DMPD** **DBPD** **BHPD**

Figure 109. Ethylene glycol and the molecules designed as mimics for it.

The common theme for all of the molecules is the O-C-C-O unit, where in the mimics this unit is designed to coordinate as a neutral molecule to metal ions. The enforced neutral coordination mode of the mimics was included to simplify characterisation of the complexes and also enable the ligands to form simple mixed ligand complexes with other ligands such as calix[8]arenes. Although ethylene glycol contains two hydroxy groups, the complexes of ethylene glycol with strontium cations and with barium cations have ethylene glycol as a neutral ligand and so it is not unreasonable to make the mimics neutral.[208-210] Also, as ethylene glycol is used as a solvent in the preparation of overbased detergents, it is unlikely to be charged. The mimics have a fixed environment for the O-C-C-O unit, where in ethylene glycol this unit is free to rotate. This was done to simplify characterisation by single crystal x-ray diffraction. All of the mimics contain two amide groups, which was included so that the mimics could also potentially mimic *N,N*-dimethylformamide (DMF), which is a toxic, viscous solvent, but is very good at coordinating to calcium cations, as observed by the calcium cation complex with a calix[8]arene ligand shown in the last chapter (**22**). The mimics should be better ligands for calcium cations than DMF as they include two amide functions as apposed to one in the DMF molecule. All of the mimics are solids, which provides a clear advantage over ethylene glycol (and DMF), in that the mimics can be added accurately and are unlikely to coat products.

The codes and names of the mimic molecules are shown in the table below (table 45).

Code	Name
DMPD	1,4-Dimethylpiperazine-2,3-dione
DBPD	1,4-Di-*tert*-butylpiperazine-2,3-dione
BHPD	1,4-Bis-(2-hydroxyethyl)-piperazine-2,3-dione

Table 45. Codes and names of the ethylene glycol mimic molecules.

The preparation of the mimic molecules will be discussed before two complexes with mimic ligands are presented.

4.2.2. Preparation of the Ethylene Glycol Mimic Molecules

DMPD (**25**) was prepared by the method described in the literature.[211, 212] This method gave 93% yield of pure **DMPD**, where the analysis of the compound agreed with the analysis in the literature. The preparation method gives crystalline **DMPD**, though the solid is unsuitable for single crystal x-ray diffraction, therefore the structure of **DMPD** is unknown.[41]

DBPD (26) could not be prepared by the same method as **DMPD**. A similar route was used, where oxalyl chloride was used to complete the ring. This method gave a 33% yield, which compares well to the literature yield of 35%,[213] where toluene was used as the solvent. Although two routes for the preparation of **DBPD** are known in the literature,[213, 214] the structure of the compound is unknown.

BHPD (27) was prepared by the same method as **DMPD**, except with different solvents. The method was found to be not very reproducible. The highest yield that was achieved was 41%. There are no references to **BHPD** in the literature and so **BHPD** is a new molecule.

4.2.3. Preparation of Complexes with the Ethylene Glycol Mimic Molecules

Crystalline complexes of the mimics were prepared to check the mode of coordination of the mimics to metal cations to ensure that they coordinated *via* the two oxygen atoms of the O-C-C-O unit. It was necessary to prepare crystalline complexes as ^{1}H NMR spectroscopy could not conclusively provide the information required. Crystalline Group 2 metal ion complexes with **DMPD** and **DBPD** could not be prepared and as copper (II) cations form more stable complexes than Group 2 metal cations, copper (II) cation complexes were prepared.[18] The copper (II) cation complexes of **DMPD** and **DBPD** are discussed below. A crystalline copper (II) complex with **BHPD** could not be prepared, though it was not necessary with the structures of the **DMPD** and **DBPD** complexes being known. A crystalline calcium cation complex with **BHPD** was prepared, though the structure has not as yet been characterised. The increase in the alkyl chain from methyl in **DMPD** to *tert*-butyl in **DBPD** resulted in different solvents being required to prepare crystalline complexes. The **DMPD** complex was prepared from methanol and the **DBPD** complex was prepared from ethanol, where powders were obtained if the solvents were used the other way around.

4.2.3.1. Structure of the Copper (II) Cation Complex with **DMPD** (**CuDMPD**) (**28**)

A bright green crystalline complex of a copper (II) cation with the **DMPD** ligand was grown from methanol. The complex consists of the **DMPD** ligand, a copper (II) cation and two chloride anions. Within the asymmetric unit, the copper cation is four coordinate with distorted square planar geometry, coordinating to the two oxygen atoms of the **DMPD** ligand and two chloride anions. The complex, though, is a dimer, where the copper cation is weakly coordinated to an oxygen atom of another monomer, giving the copper cation a pseudo coordination number of five and quasi-distorted square pyramidal geometry. The **DMPD** ligand is neutral. The asymmetric unit of the complex can be seen below (figure 110).

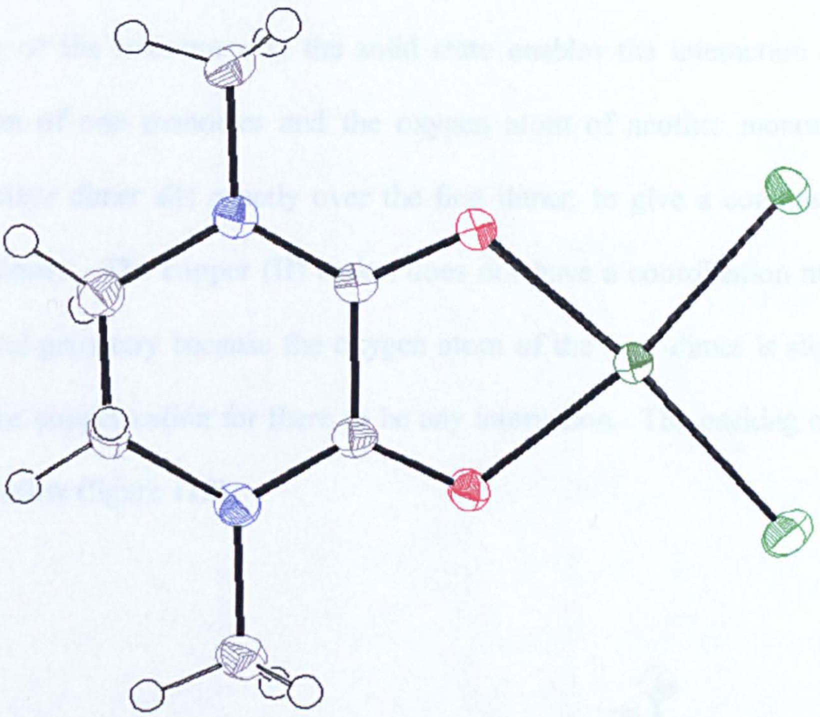


Figure 110. The asymmetric unit of the complex of a copper (II) cation with DMPD, (Cu^{2+})(Cl^-)$_2$(DMPD), grown from methanol. The copper cation is represented in dark green and the chloride anions are represented in bright green.

The diagram of the dimer is shown below (figure 111).

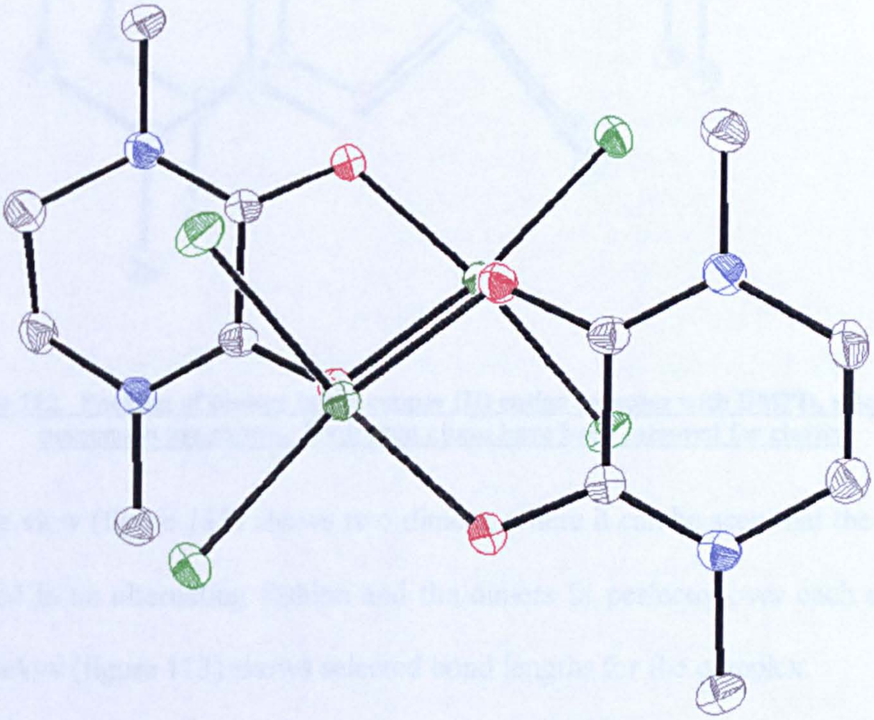


Figure 111. The dimer for the copper cation complex with DMPD. Hydrogen atoms have been removed for clarity.

In the dimer, the copper cations interact with an oxygen atom of the other monomer. The packing of the monomers in the solid state enables the interaction between the copper cation of one monomer and the oxygen atom of another monomer. In the packing, another dimer sits exactly over the first dimer, to give a continuous stack of alternating dimers. The copper (II) cation does not have a coordination number of six and octahedral geometry because the oxygen atom of the next dimer is slightly too far away from the copper cation for there to be any interaction. The packing of the dimers can be seen below (figure 112).

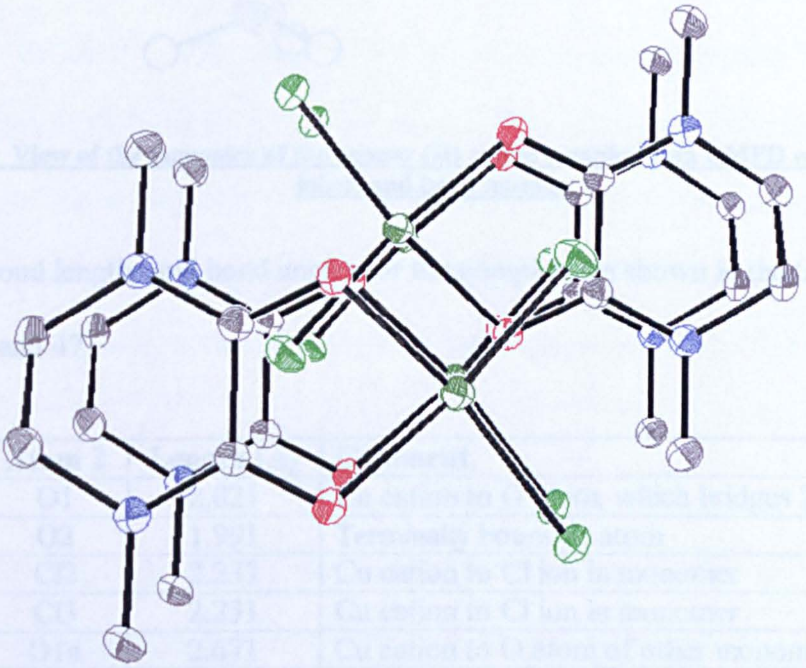


Figure 112. Packing of dimers in the copper (II) cation complex with DMPD, where four monomers are shown. Hydrogen atoms have been removed for clarity.

The above view (figure 112) shows two dimers, where it can be seen that the monomers are stacked in an alternating fashion and the dimers fit perfectly over each other. The diagram below (figure 113) shows selected bond lengths for the complex.

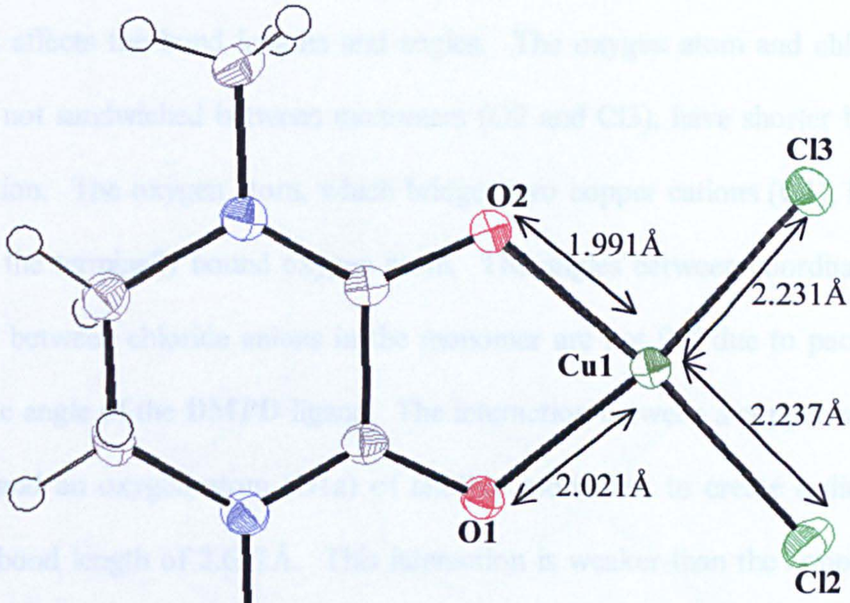


Figure 113. View of the monomer of the copper (II) cation complex with DMPD with selected atom labels and bond lengths.

Selected bond lengths and bond angles for the complex are shown in the tables below (tables 46 and 47).

Atom 1	Atom 2	Length (Å)	Comment
Cu1	O1	2.021	Cu cation to O atom, which bridges 2 Cu cations
Cu1	O2	1.991	Terminally bound O atom
Cu1	Cl2	2.237	Cu cation to Cl ion in monomer
Cu1	Cl3	2.231	Cu cation to Cl ion in monomer
Cu1	O1a	2.671	Cu cation to O atom of other monomer in dimer
Cu1	O1b	3.970	Cu cation to nearest O atom of another dimer

Table 46. Selected bond angles for the copper (II) cation complex with DMPD.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O1	Cu1	Cl2	91.61	Angle across Cu cation
O1	Cu1	O2	81.59	Angle between monomer O atoms
O1	Cu1	O1a	79.85	Angle between bridging O atoms
O1	Cu1	O1b	102.04	Angle between monomer O atoms
O1a	Cu1	O1b	145.95	Angle across Cu cation
O2	Cu1	Cl3	88.69	Angle across Cu cation
Cl2	Cu1	Cl3	98.47	Angle between Cl anions

Table 47. Selected bond angles for the copper (II) cation complex with DMPD.

The packing of the complex in the solid state and the interaction between pairs of monomers affects the bond lengths and angles. The oxygen atom and chloride anion, which are not sandwiched between monomers (O2 and Cl3), have shorter bonds to the copper cation. The oxygen atom, which bridges two copper cations (O1), has a longer bond than the terminally bound oxygen atom. The angles between coordinated oxygen atoms and between chloride anions in the monomer are not 90° due to packing effects and the bite angle of the **DMPD** ligand. The interaction between a copper cation of one monomer and an oxygen atom (O1a) of another monomer, to create a dimer, can be seen by a bond length of 2.671Å. This interaction is weaker than the copper cation to oxygen atom interactions within the monomer. The next nearest oxygen atom (O1b) to the copper cation is too far away for the atoms to be interacting (3.970Å) and so the copper cation in the complex is five coordinate. The differences in bond lengths and the deviations of the angles from 90° in the monomer results in the copper cation having distorted square planar geometry. The **DMPD** ligand itself is twisted and so is not planar, which also effects the coordination around the copper cation *via* the two oxygen atoms.

The **DMPD** ligand can be seen to coordinate to the copper cation *via* its two oxygen atoms, with no interaction between the copper cation and the **DMPD** nitrogen atoms.

4.2.3.2. Structure of the Copper (II) Cation Complex with **DBPD** (**CuDBPD**) (**29**)

A dark green crystalline complex of a copper (II) cation and the **DBPD** ligand was grown from ethanol. The complex consists of one copper (II) cation, one **DBPD** ligand and two chloride anions. The **DBPD** ligand is neutral. The copper cation is four coordinate, coordinating to the two oxygen atoms of the **DBPD** ligand and two chloride anions to give a slightly distorted square planar geometry. There is an axis of symmetry through the copper cation.

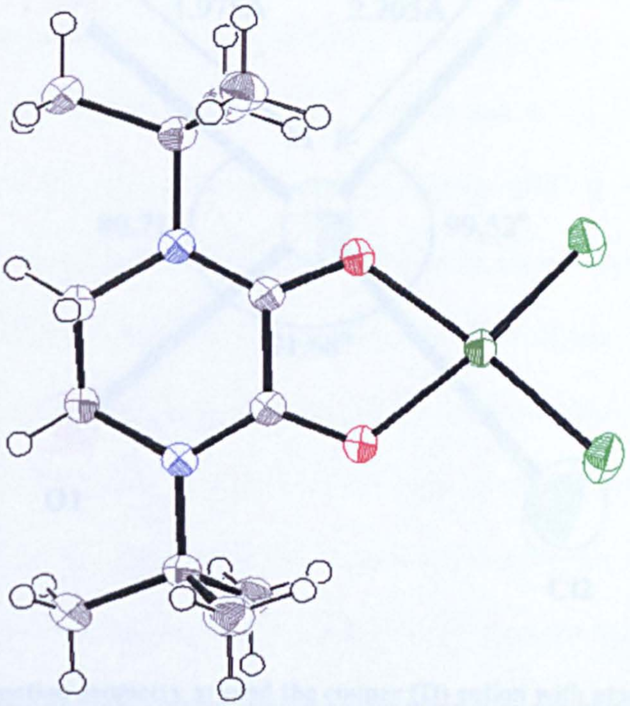
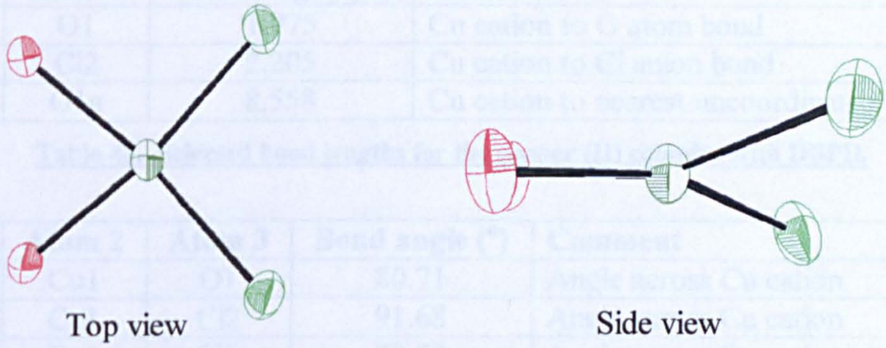


Figure 114. Structure of the copper (II) cation complex with DBPD, (Cu^{2+})(Cl$^-$)$_2$(DBPD), grown from ethanol.

The coordination geometry for the copper cation can be seen below (figure 115).



Top view

Side view

Figure 115. Coordination geometry around the copper (II) cation.

The coordination geometry around the copper cation shows that the copper cation is in a distorted square planar geometry. Selected bond lengths and angles are shown in the diagram below (figure 116).

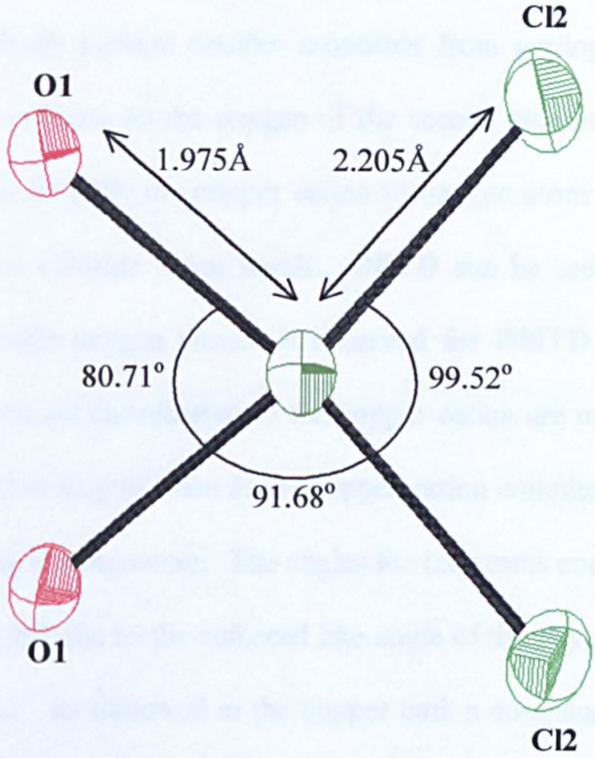


Figure 116. Coordination geometry around the copper (II) cation with atom labels and selected bond lengths and angles.

Selected bond lengths and bond angles for the complex can be seen in the tables below (tables 48 and 49).

Atom 1	Atom 2	Bond length (Å)	Comment
Cu1	O1	1.975	Cu cation to O atom bond
Cu1	Cl2	2.205	Cu cation to Cl anion bond
Cu1	O1a	8.558	Cu cation to nearest uncoordinated O atom

Table 48. Selected bond lengths for the copper (II) complex with DBPD.

Atom 1	Atom 2	Atom 3	Bond angle (°)	Comment
O1	Cu1	O1	80.71	Angle across Cu cation
O1	Cu1	Cl2	91.68	Angle across Cu cation
Cl2	Cu1	Cl2	99.52	Angle across Cu cation

Table 49. Selected bond angles for the copper (II) complex with DBPD.

Unlike the copper cation complex with **DMPD (28)**, this complex is not a dimer. The copper cation to nearest oxygen atom of another monomer distance of 8.558Å proves that the complex is not a dimer, as the distance is too large for there to be any interaction. The complex probably exists as a monomer due to the bulky *tert*-butyl groups, which sterically prevent another monomer from getting close enough for the copper cation to coordinate to the oxygen of the second monomer. As for the copper cation complex with **DMPD**, the copper cation to oxygen atom bonds are shorter than the copper cation to chloride anion bonds. **DBPD** can be seen to coordinate to the copper cation *via* both oxygen atoms as observed for **DMPD** coordination. In this complex, all of the atoms coordinated to the copper cation are more strongly bound, as shown by shorter bond lengths, than in the copper cation complex with **DMPD**. This is because this complex is a monomer. The angles for the atoms coordinated to the copper cation deviate from 90° due to the enforced bite angle of the oxygen atoms as controlled by the **DBPD** ligand. As observed in the copper cation complex with **DMPD**, there is no interaction between the copper cation and the nitrogen atoms in the **DBPD** ligand.

4.2.3.3. Comparisons between the Copper Cation Complexes and with Copper Cation Complexes with Ethylene Glycol

Two similar copper cation complexes with ethylene glycol are known, where the difference between the complexes is in the co-crystallised material (for one complex there is a proton and an oxygen atom in the asymmetric unit, possibly from a water molecule). Both of the complexes have two chloride anions coordinated to the copper cation and so can be directly compared with the copper cation complexes with **DMPD** and with **DBPD**. The structure of one of the complexes can be seen below (figure 117).[215]

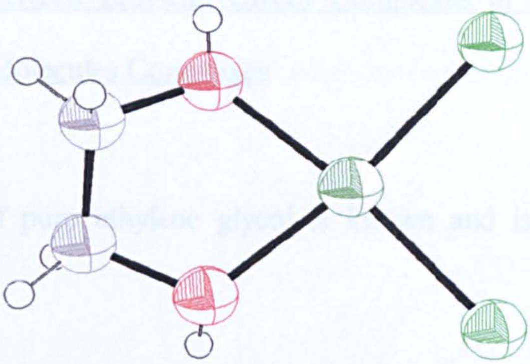


Figure 117. Structure of the copper cation complex with ethylene glycol, with chloride anions.

The table below (table 50) compares the data for the copper cation complexes.

Complex	Cu-O bond length (Å)	Cu-Cl bond length (Å)	O-O distance (Å)
$CuEG(Cl)_2$[214]	1.968/2.004	2.235/2.267	2.550
$CuEG(Cl)_2$[214]	1.958/1.997	2.233/2.235	2.518
Cu**DMPD**$(Cl)_2$	1.991/2.021	2.231/2.237	2.621
Cu**DBPD**$(Cl)_2$	1.975/1.975	2.205/2.205	2.557

Table 50. Summary of data for copper cation complexes with ethylene glycol and with the mimics for ethylene glycol, where EG represents ethylene glycol.

It can be seen that the bond lengths and interatomic distances are very similar and that **DMPD** and **DBPD** can be considered to be mimics for neutral ethylene glycol complexes with copper cations.

4.2.3.4. Solution State Studies on the Copper (II) Cation Complexes

^{1}H NMR spectroscopy could not be used on the two copper cation complexes as copper (II) is paramagnetic. Mass spectrometry was used which showed that in solution the complexes aggregate. The dimeric nature of the copper cation complex with **DMPD** was shown by the presence of peaks above the molecule weight of the monomer.

4.2.4. Comparisons between Ethylene Glycol Complexes in the Literature and the Ethylene Glycol Mimic Molecules Complexes

The crystal structure of pure ethylene glycol is known and is shown below (figure 118).[216]

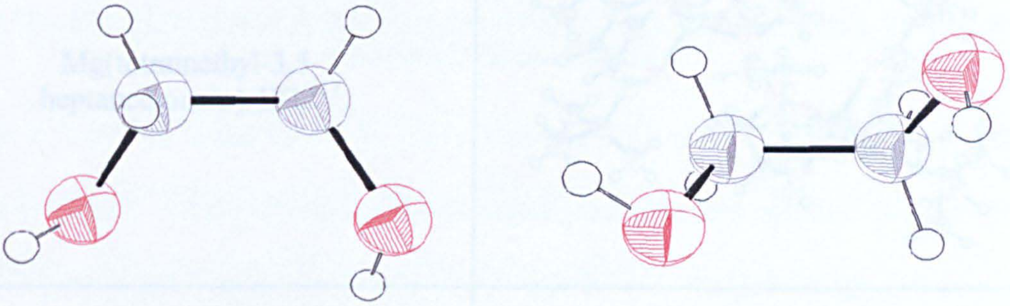
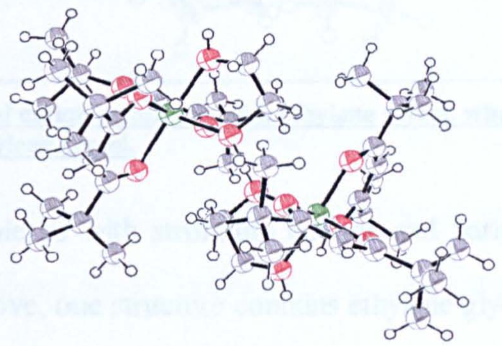
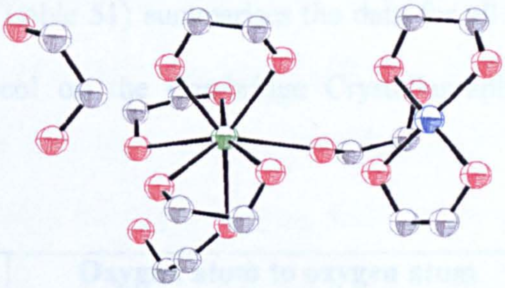
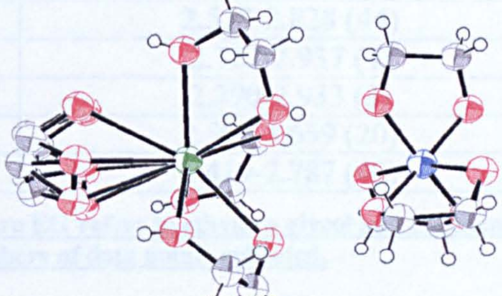
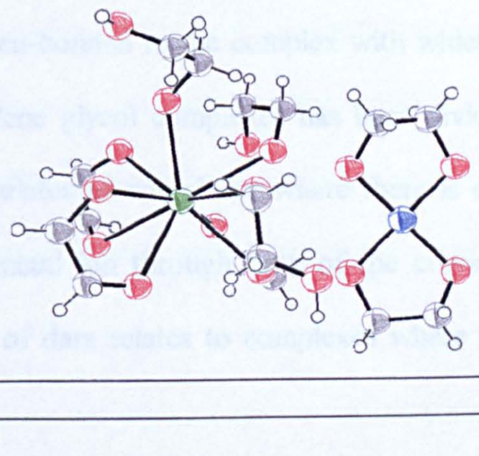


Figure 118. Two views of the ethylene glycol molecule.

The ethylene glycol molecule is twisted, with the oxygen atom to oxygen atom intramolecular distance being 2.903Å. The ethylene glycol molecules in the unit cell interact by hydrogen-bonding, with one intermolecular distance being 2.730Å. The crystal structures of ethylene glycol complexes are known with a range of metal ions. There are also many crystal structures (more than fifteen), which include ethylene glycol as a co-crystallised solvent. In the complexes where ethylene glycol is a co-crystallised solvent, the ethylene glycol molecules are often hydrogen-bonded to the complex. No ethylene glycol complexes with calcium cations are known, though complexes with magnesium cations, strontium cations and barium cations are known. The strontium cation and barium cation complexes contain other metal ions, where the Group 2 metal cation forms a cationic unit with ethylene glycol and the other metal ion forms the anionic unit in all except one complex. There is only one magnesium cation complex with ethylene glycol and this complex has ethylene glycol as a co-ligand which is unusual as not many complexes including ethylene glycol have the ethylene glycol as a co-ligand, it is usually the main ligand or not coordinated to the metal ion. The structures of some of the Group 2 metal ion complexes with ethylene glycol are shown below (figure 119).

Complex	**Structure**
Mg(tetramethyl-3,5-heptanedionato)$_2$EG.[217]	
$[Sr(EG)_5]^{2+}[Cu(EG)_2]^{2-}$.EG, where the strontium cation is green. The positions of the hydrogen atoms are unavailable.[208]	
$[Ba(EG)_4]^{2+}[Ti(EG)_3]^{2-}$, where the barium cation is green. One EG molecule is disordered.[210]	
$[Ba(EG)_8]^{2+}[Cu(EG)_2]^{2-}$, where the barium cation is green.[209]	

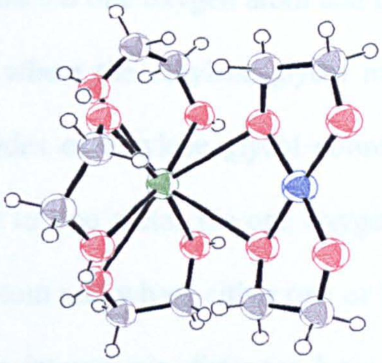
$BaCu(EG)_5$, where the barium cation is green.[209]	

Figure 119. Structures of some of the Group 2 metal cation complexes with ethylene glycol, where EG refers to ethylene glycol.

The most common metal cation in the complexes with strontium cations and barium cations is copper. Of the structures shown above, one structure contains ethylene glycol as a bridging ligand, where ethylene glycol anions (-2 charge) bridge between two juxtaposed metal cations.[209] The table below (table 51) summarises the data for all of the structures which contained ethylene glycol on the Cambridge Crystallographic Database.[41]

Form of ethylene glycol	Oxygen atom to oxygen atom distance (Å)
Pure	2.903 (1)
Co-crystallised	2.725-3.691 (28)
Complex (EG coordinating *via* 2 O atoms)	2.518-2.828 (44)
Complex (EG coordinating *via* 1 O atom)	2.722-2.937 (4)
Complex with bridging EG	2.790-2.933 (3)
Complex with charged, EG^-	2.566-3.659 (20)
Complex with charged, EG^{-2}	2.419-2.787 (40)

Table 51. Summary of data on ethylene glycol, where EG refers to ethylene glycol and the number in parentheses relates to the numbers of data points collected.

The longer interatomic oxygen atom distances for co-crystallised ethylene glycol are usually for where the ethylene glycol is hydrogen-bonded to the complex with which it has co-crystallised. The data for neutral ethylene glycol complexes has been divided into three groups; where the first set of data relates to complexes where there is one ethylene glycol molecule coordinated to one metal ion through both of the ethylene glycol molecule oxygen atoms, the second set of data relates to complexes where the ethylene glycol molecule coordinates to the metal ion *via* one oxygen atom and the final set of data relates to ethylene glycol complexes where the ethylene glycol molecule bridges between metal cations. The bridging modes of ethylene glycol coordination include one ethylene glycol molecule coordinating to one metal *via* one oxygen atom and to another metal cation *via* the other oxygen atom and where either one or both of the oxygen atoms bridge two metal cations. The interatomic distances between the oxygen atoms are shortest when the ethylene glycol molecule coordinates to a metal cation *via* both of the oxygen atoms. The range is mainly caused by the range in metal ionic radii, where the largest interatomic distances are for larger metal cations. When the ethylene glycol is coordinated *via* one oxygen atom or is bridging metal cations, the interatomic distances are longer. Structures in which ethylene glycol has a –2 charge appear to be more common than those within which ethylene glycol with a –1 charge. For ethylene glycol with a –1 charge, most of the complexes have the ethylene glycol anion coordinating to the metal cation *via* both of the oxygen atoms, with the second most common coordination mode being where the ethylene glycol anion coordinates to the metal cation *via* the charged oxygen atom, with the hydroxy oxygen atom uncoordinated. The bond between the metal cation and the charged oxygen atom is shorter than the bond between the metal cation and the hydroxy oxygen atom when both oxygen atoms are coordinated to a metal cation. For ethylene glycol with a –2 charge, the range of interatomic distances is small. The vast majority of complexes have the ethylene glycol anion (-2 charge) coordinating to a metal cation *via* both of the oxygen atoms and this gives a similar range of interatomic distances to neutral ethylene glycol coordinating to a metal cation *via* both oxygen atoms. The longer interatomic distances occur when the ethylene glycol anion coordinates in a bridging mode to two metal cations. One ethylene glycol anion complex has an ethylene glycol anion coordinating to four metal cations.[218] The large range in interatomic distances shows how flexible the ethylene glycol molecule is and the versatility of the molecule as a ligand.

Although there are no known calcium cation complexes with ethylene glycol, there are complexes with similar molecules, see diagram below (figure 120).[41]

Figure 120. Calcium cation complexes with ligands that are similar to ethylene glycol.

For these complexes, the range of calcium cation to oxygen atom bond lengths is 2.350-2.571Å, which is within the normal range for calcium cation to oxygen atom bond lengths.[41] The range is similar to the range of bond lengths observed for calcium cations coordinated to polyethylene glycol ligands (2.384-2.558Å[41]).

4.2.5. Discussion on the Role of Ethylene Glycol Molecules in the Preparation of Overbased Detergents

As ethylene glycol is not included in the final overbased detergent products, though does improve the size of cores that can be produced, its role on an atomic scale is difficult to ascertain. It is probable that ethylene glycol coordinates to the calcium hydroxide core in the precursor to the overbased system and is released when the core is converted to calcium carbonate. Ethylene glycol may also stabilise the calcium hydroxide precursor by hydrogen-bonding to surfactant molecules. It has been shown that ethylene glycol is a flexible molecule, which can change its shape to coordinate to metal ions, where the most common conformations of neutral ethylene glycol in complexes are shown below (figure 121).

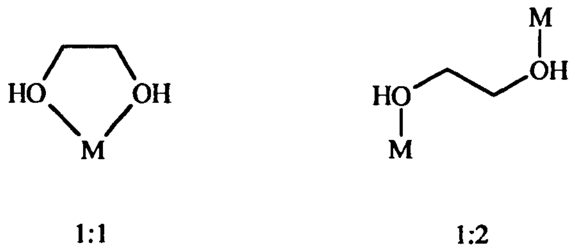


Figure 121. Most common coordination modes of ethylene glycol to metal ions.

The one ethylene glycol to one metal ion conformation is the most commonly observed conformation of the two shown. The large flexibility of the ethylene glycol molecule and its small size may enable it to complete the coordination spheres of calcium cations, which are coordinatively unsatisfied on the surface of the calcium hydroxide core.[11] This coordination may be either as the 1:1 system or bridging as in the 1:2 system. The two hydroxy groups per ethylene glycol molecule will make the molecule excellent for hydrogen-bonding and therefore ethylene glycol probably stabilises larger calcium hydroxide cores before the carbonation step.

4.2.6. Ethylene Glycol Mimics Summary

Mimics for ethylene glycol have been prepared which have been shown to coordinate in a similar way to ethylene glycol to metal ions. These mimics are solids with more fixed structures than ethylene glycol and therefore are easier to use in reactions and characterise in products than ethylene glycol. The mimics can also be considered to be alternatives to DMF as a co-ligand.

4.3. Carboxylic Acids

4.3.1. Introduction

Stearic acid is commonly used in the preparation of overbased detergents, especially with calix[8]arenes, as it enables larger cores to be prepared.[6] Upto 40% w/w stearic acid is included in some overbased detergents.[6] The structure of the stearic acid molecule is shown below (figure 122).

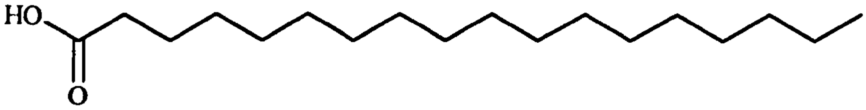


Figure 122. Stearic acid molecule.

Thus to understand overbased detergents, it is important to understand how stearic acid coordinates to the core.

There are three coordination modes of carboxylic acids to Group 2 metal ions and these are represented below (figure 123).

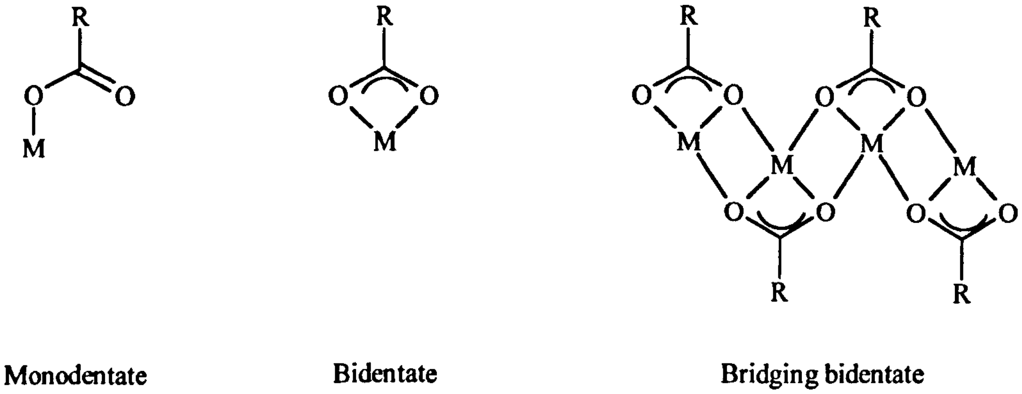
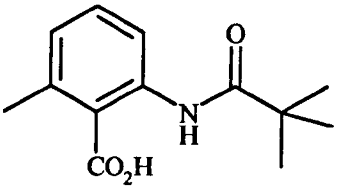


Figure 123. Coordination modes of carboxylic acid ligands to Group 2 metal ions.

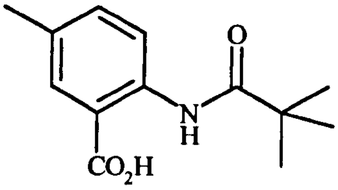
Bridging bidentate coordination is the most commonly observed coordination mode, followed by bidentate.[41] Bridging bidentate complexes are usually intractable, insoluble lattices and therefore are difficult to characterise. Unfortunately bridging bidentate complexes are formed with simple carboxylic acids and so a calcium cation complex with stearic acid would probably be bridging bidentate. This is not useful in understanding overbased detergents as extensive bridging bidentate lattices cannot be formed over a core. Therefore to understand overbased detergents, complexes with the other two coordination modes must be investigated. Bidentate coordination has been shown to be more stable than monodentate coordination for calcium cations and magnesium cations.[219] Theoretically, monodentate complexes will have a shorter bond from the oxygen atom to the metal cation, but the bond will be less strong than in bidentate complexes.[220] Monodentate complexes are unusual and are really only observed in proteins,[41] where the free carboxylic acid oxygen atom is hydrogen-bonded to give the complex stability.[219-222] To get monodentate carboxylic acid complexes it is necessary to design bulky ligands, which are able to hydrogen-bond.[220] In this section, novel carboxylic acid molecules will be introduced which have been designed for monodentate and bidentate coordination to Group 2 metal ions.

4.3.2. Carboxylic Acid Ligands

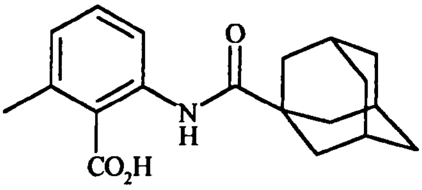
It has been shown that by carefully designing ligands with advantageous and controlled hydrogen-bonding that the coordination mode of the ligand can be influenced.[84, 160, 221, 223-226] In general, amido groups are employed to provide conformational restriction to the structure of the ligand and hydrogen-bond to free oxygen atoms and steric bulk is used to stop polymerisation.[160, 221, 225] Using this theory, the ligands below (figure 124) were designed and prepared.



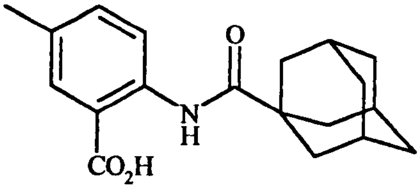
TMCM



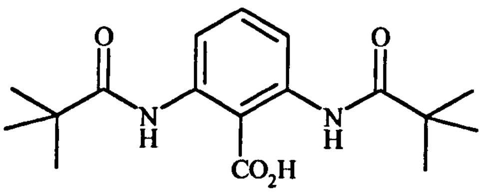
TMCHM



ACM



ACHM



DTMC

Figure 124. Novel carboxylic acid ligands synthesised and used in this study.

DTMC was designed for monodentate coordination, where the amido groups were included to hydrogen-bond to the free oxygen atom and reduce the flexibility of the ligand and the *tert*-butyl groups were included to hinder polymerisation. **ACM** and **TMCM** were designed with reduced bulk for either monodentate or bidentate coordination modes and **ACHM** and **TMCHM** were designed with even less bulk for bidentate coordination. 2-acetamidobenzoic acid was also purchased to give an even less bulky ligand.

The table below shows the codes and names for the ligands (table 52).

Code	Name
DTMC	2,6-Bis-(2,2-dimethylpropionylamino)-benzoic acid
TMCM	2-(2,2-Dimethylpropionylamino)-6-methylbenzoic acid
TMCHM	2-(2,2-Dimethylpropionylamino)-5-methylbenzoic acid
ACM	2-[(Adamantane-1-carbonyl)-amino]-6-methylbenzoic acid
ACHM	2-[(Adamantane-1-carbonyl)-amino]-5-methylbenzoic acid

Table 52. Codes and names of the carboxylic acid molecules.

The preparation of the ligands will be discussed before the structures of two complexes are presented.

4.3.3. Preparation of the Carboxylic Acid Ligands

DTMC (30) was prepared by pivaloylation of the amine groups of 2,6-diaminotoluene and the oxidation of the methyl group to a carboxylic acid group. The pivaloylation step gave a good yield (86%) of product. Due to the insolubility of the pivaloylated product in water, low yields (41%) were only achieved for the oxidation step, which required water as the solvent. Alternative routes were assessed, such as using dicyclohexyl-18-crown-6 to give a non-polar solvent soluble form of potassium permanganate,[227, 228] but these were found to give lower yields. The preparation scheme can be seen below (figure 125).

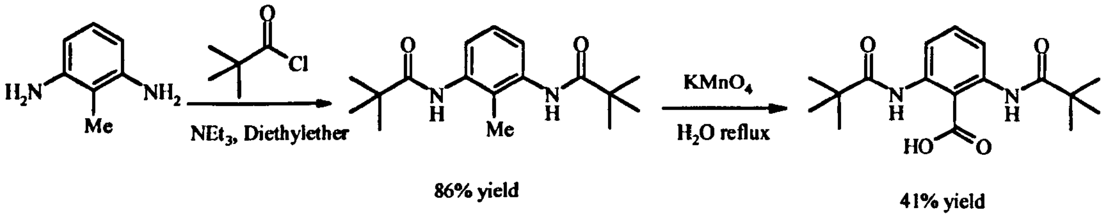


Figure 125. Synthesis of 2,6-bis-(2,2-dimethylpropionylamino)-benzoic acid

The other carboxylic acids were prepared from of 2-amino-6-methylbenzoic acid for **TMCM (31)** and **ACM (32)** and from of 2-amino-5-methylbenzoic acid for **TMCHM (33)** and **ACHM (34)**. The general scheme can be seen below (figure 126).

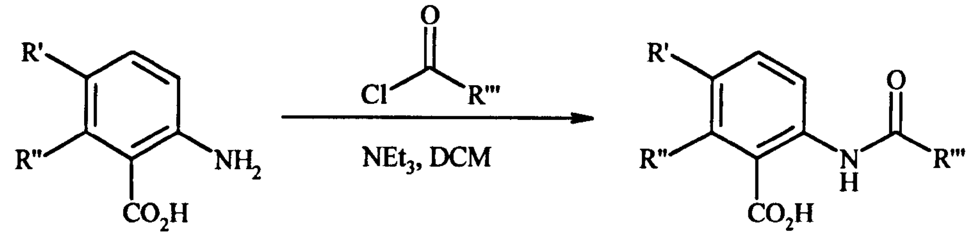


Figure 126. General preparation of the carboxylic acid ligands TMCM, TMCHM, ACM and ACHM.

TMCM was prepared in a 33% yield, which was lower than the yield for **TMCHM** (78%) and **ACHM** (79%). This was due to the method used to remove by-products. For **TMCM** the by-products were removed by extraction into water, into which the product was also slightly soluble. For **TMCHM** and **ACHM**, the by-products were removed by filtration and so the loss of product into water was eliminated without the purity of the product being affected. The yield of **ACM** was very low (2%) as the main product was a rearrangement product, with the structure shown below (figure 127). The structure of the main product was determined by single crystal x-ray diffraction.

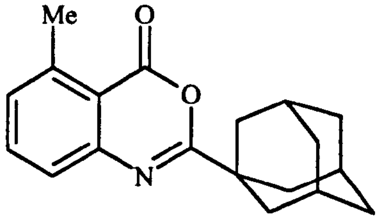


Figure 127. Main product from the preparation of ACM.

The main product is clearly not **ACM**.

All of the ligands are new and represent a novel area of research. **DTMC** is the most interesting ligand as it is much simpler than the ligand used by Tolman *et al.* to give monodentate complexes.[226] The ligand used by Tolman *et al.* ($BmtCO_2H$, where Bmt is 4-*tert*-butyl-2,6-bis-[(2,2'',6,6''-tetramethyl-*m*-terphenyl-2'-yl)-methyl]phenyl) utilised three aromatic rings on each side of the carboxylic acid function to control the coordination mode of the metal cations (iron (II), cobalt (II) and copper (II)).

4.3.4. Preparation of Carboxylic Acid Complexes

Two carboxylic acid complexes have been characterised by single crystal x-ray diffraction and both of these complexes have **DTMC** as the ligand. These 'complexes' (one is actually a salt) were prepared by allowing ammonia gas to diffuse slowly into a solution of the ligand and metal salt in methanol. The ammonia gas was generated from aqueous ammonia solution. The method is similar to the method used by Murugavel *et al.*,[61] except that this method uses ammonia gas rather than ammonia aqueous solution to deprotonate the ligand. The ammonium cation salt with **DTMC** was grown in the presence of metal ions including calcium cations, cobalt cations, copper cations, zinc cations, nickel cations and lithium cations, where the salt was usually the main product. In the case of calcium cations, a calcium cation complex was the main product, with the ammonium cation salt being the minor product. The structures of the ammonium cation salt and the calcium cation complex are discussed below. Many other methods were attempted to prepare crystalline complexes with the carboxylic acids, though in general the crystalline product that was produced was found to be unsuitable for single crystal x-ray diffraction, usually due to the crystals being too small. Unfortunately, therefore, the binding modes of the carboxylic acid ligands other than **DTMC** to Group 2 metal ions are unknown.

4.3.4.1. Structure of an Ammonium Cation Salt with **DTMC** (35)

A crystalline salt of ammonia with **DTMC** was grown from methanol by ammonia gas diffusion into solutions containing **DTMC** with or without metal ions. The salt consists of the **DTMC** ligand with –1 charge and an ammonium cation. The salt is held together by a hydrogen-bond between the anion and cation.

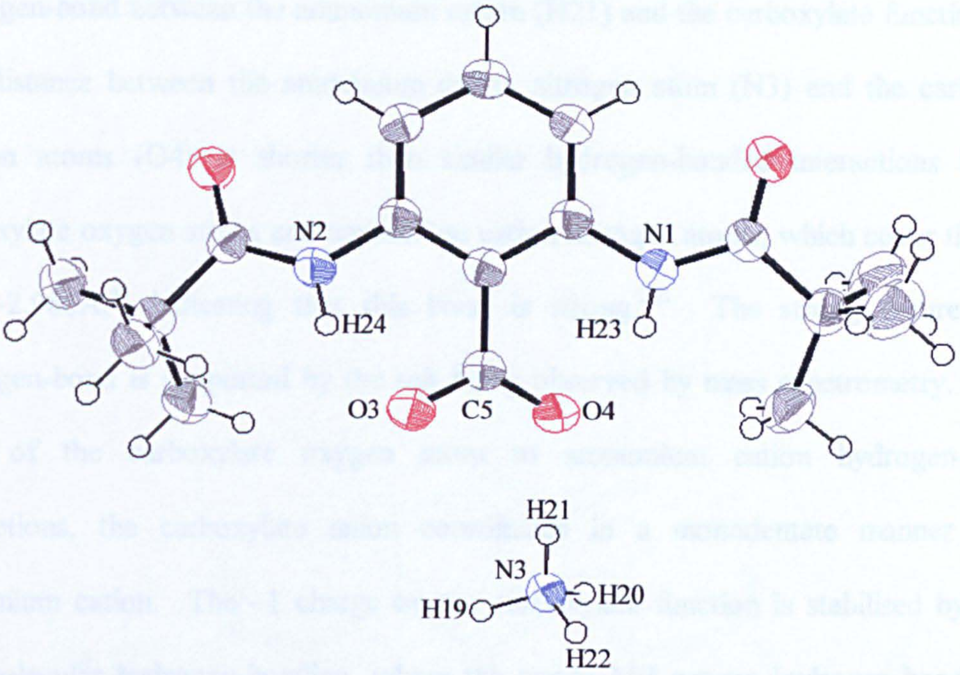


Figure 128. Salt of ammonium cation with DTMC$^-$, (NH^{4+})(DTMC$^-$), with selected atom labels.

Selected bond lengths and angles can be seen in the tables below (tables 53 and 54).

Atom 1	Atom 2	Bond length (Å)	Comment
N3	H19	0.987	Ammonium bond
N3	H20	0.979	Ammonium bond
N3	H21	0.919	Ammonium bond
N3	H22	0.924	Ammonium bond
O3	H21	2.841	No interaction
O3	N2	2.569	Hydrogen-bond
O4	N1	2.565	Hydrogen-bond
O4	H21	1.813	Hydrogen-bond
O4	N3	2.715	Hydrogen-bond
H23	O4	1.802	Hydrogen-bond
H24	O3	1.746	Hydrogen-bond

Table 53. Selected bond lengths for the ammonium cation salt with DTMC.

Atom 1	Atom 2	Atom 3	Bond angle (°)	Comment
O3	C5	O4	122.05	Angle across carboxylate group
O4	H21	N3	166.53	Angle to ammonium cation
H19	N3	H20	113.71	Angle within ammonium cation
H19	N3	H21	108.79	Angle within ammonium cation
H19	N3	H22	104.14	Angle within ammonium cation

Table 54. Selected bond angles for the ammonium cation salt with DTMC.

From the bond lengths and angles it can be seen that the salt is held together by a hydrogen-bond between the ammonium cation (H21) and the carboxylate function (O4). The distance between the ammonium cation nitrogen atom (N3) and the carboxylate oxygen atoms (O4) is shorter than similar hydrogen-bonded interactions between carboxylate oxygen atoms and ammonium cation nitrogen atoms, which cover the range 2.762-2.986Å,[41] indicating that this bond is strong.[201] The strong nature of the hydrogen-bond is supported by the salt being observed by mass spectrometry. As for most of the carboxylate oxygen atom to ammonium cation hydrogen-bonded interactions, the carboxylate anion coordinates in a monodentate manner to the ammonium cation. The –1 charge on the carboxylate function is stabilised by strong intramolecular hydrogen-bonding, where the amido NH groups hydrogen-bond to the carboxylate oxygen atoms, as shown by the O3-N2 interatomic distance of 2.569Å and the O4-N1 interatomic distance of 2.565Å. The hydrogen atoms within the ammonium cation are not all equivalent as shown by the range of 0.919-0.987Å for nitrogen atom to hydrogen atom bond lengths and by the angles deviating from a tetrahedral arrangement. The shortest nitrogen atom to hydrogen atom bond length within the cation is observed for the hydrogen atom H21, which is hydrogen-bonded to the carboxylate oxygen atom O4.

4.3.4.2. Structure of a Calcium Cation Complex with **DTMC** (CaDTMC) (36)

A crystalline complex of **DTMC** with a calcium cation was grown from methanol. The asymmetric unit of the complex consists of a calcium cation coordinated to the **DTMC** ligand. The **DTMC** ligand has –1 charge and is coordinated to the calcium cation in a monodentate binding mode. The calcium cation is six coordinate with a slightly distorted octahedral geometry. The coordination sphere of the calcium cation is filled by coordination to two **DTMC** monodentate carboxylate oxygen atoms (*cis* to each other), two **DTMC** amido oxygen atoms (*cis* to each other) and two water oxygen atoms (*trans* to each other). The –1 charge on the **DTMC** ligand is stabilised by intramolecular hydrogen-bonding. The asymmetric unit of the complex is shown below (figure 129).

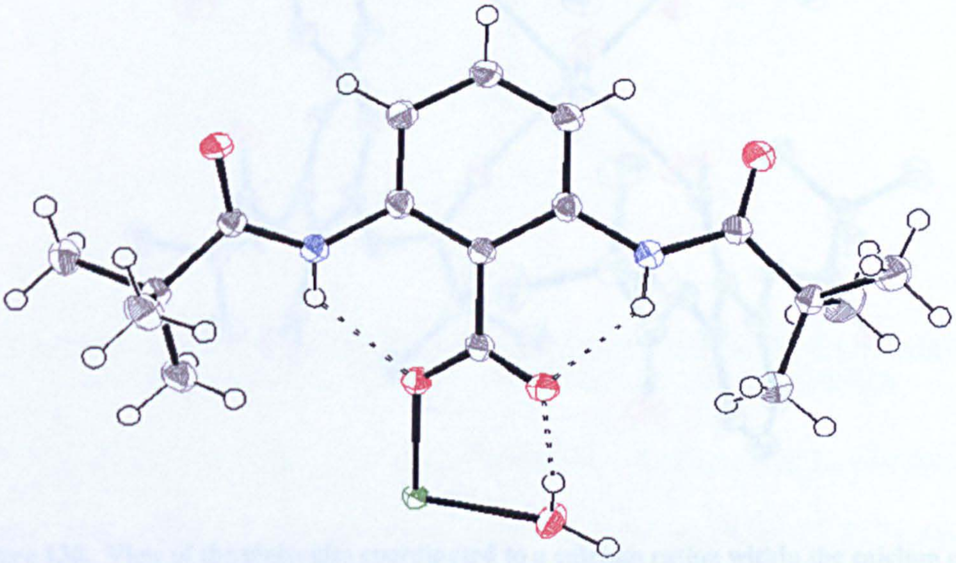


Figure 129. Structure of the asymmetric unit of the calcium cation complex with DTMC, (Ca^{2+})(DTMC$^-$)$_2$(H$_2$O)$_2$(DTMC)$_2$. The dashed lines represent the hydrogen-bonds within the complex.

The coordination of the calcium cation to the carboxylate group clearly shows that the calcium cation has coordinated in a monodentate coordination mode. The calcium cation is too far away from the other carboxylate oxygen atom for the calcium cation to be coordinated in a bidentate coordination mode (Ca1-O3 3.721Å). The –1 charge on the **DTMC** molecule is stabilised by intramolecular hydrogen-bonding between the carboxylate group and the amido NH groups and intermolecular hydrogen-bonding between the water molecule and the uncoordinated carboxylate oxygen atom. The complete coordination around the calcium cation is shown in the diagram below (figure 130).

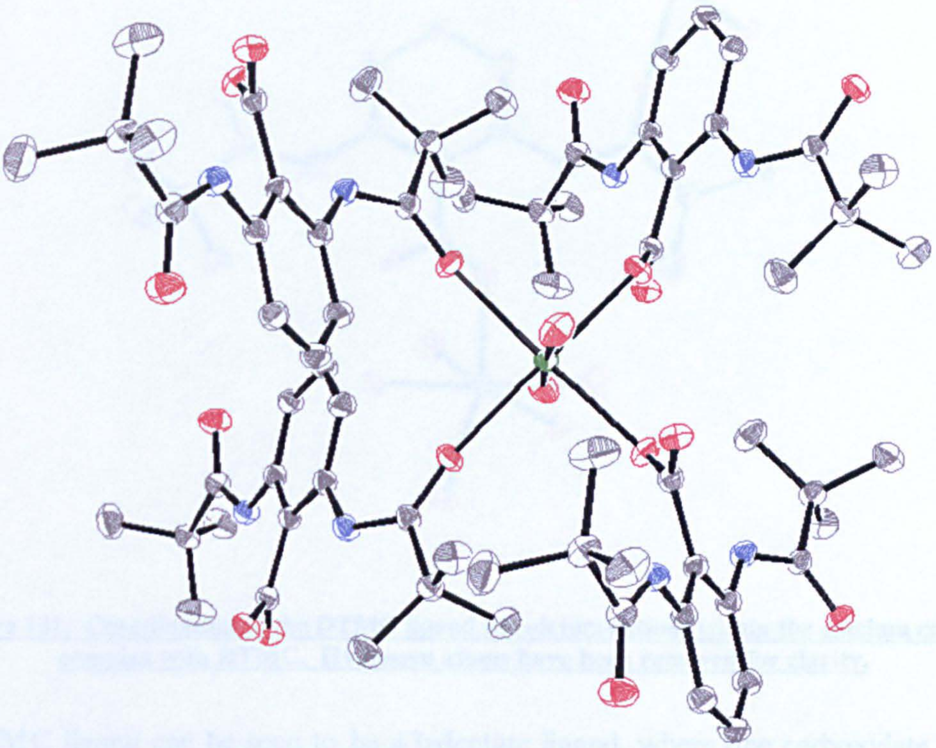


Figure 130. View of the molecules coordinated to a calcium cation within the calcium cation complex with DTMC. Hydrogen atoms have been removed for clarity.

The full coordination around the calcium cation is shown in the above diagram (figure 130). The ligands can be seen to be bulky, which enforces the monodentate binding mode of the carboxylate group. It is surprising that the calcium cation chooses to coordinate to the amido groups of two **DTMC** molecules rather than to, for example, more water molecules. This amido oxygen atom coordination appears to be sterically unfavourable, but preferable to the calcium cation. The coordination of the **DTMC** ligand to calcium cations can be seen below (figure 131).

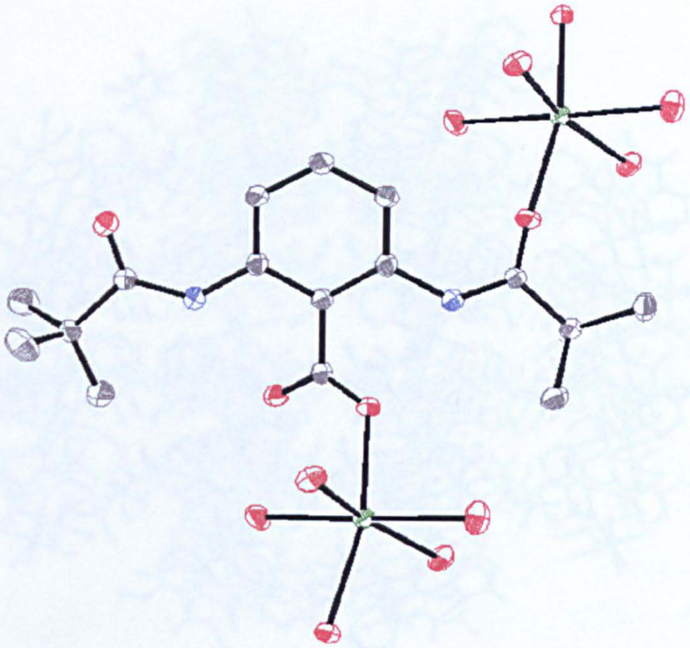


Figure 131. Coordination of the DTMC ligand to calcium cations within the calcium cation complex with DTMC. Hydrogen atoms have been removed for clarity.

The **DTMC** ligand can be seen to be a bidentate ligand, where one carboxylate oxygen atom and one amido oxygen atom coordinate to calcium cations. Only one amido oxygen atom coordinates to a calcium cation, which along with the monodentate nature of the carboxylate group causes the ligand to be slightly twisted and so not planar. Steric and packing factors may cause the ligand to be able to coordinate to calcium cations through only one amido oxygen atom. The coordination of the ligand to calcium cations can be described by Harris notation as $[2.1_1.1_2]$.[229, 230] The packing of the complex in the unit cell can be seen below (figure 132).

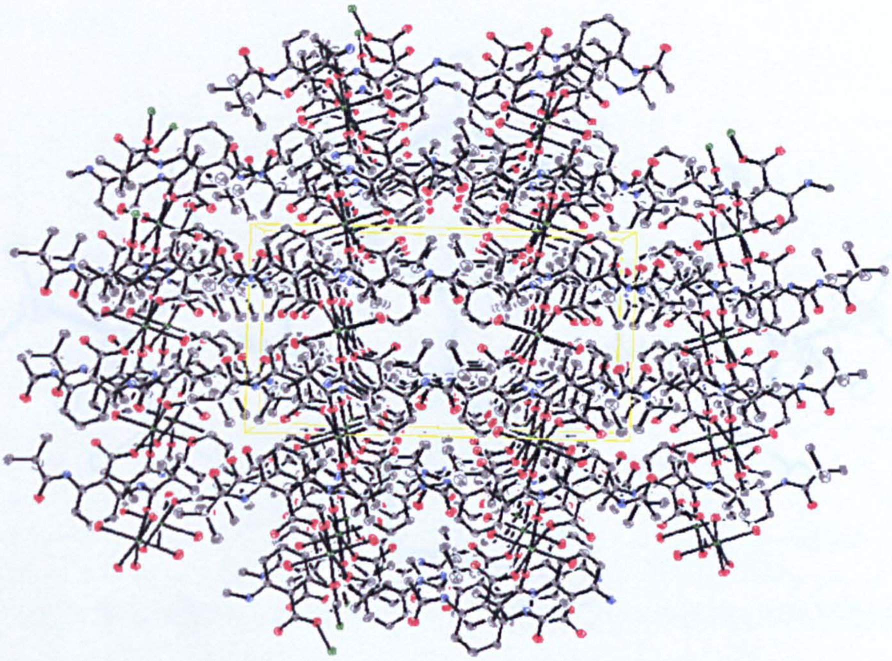


Figure 132. Unit cell for the calcium cation complex with DTMC. Hydrogen atoms have been removed for clarity.

The unit cell of the complex shows that the complex packs as layers of **DTMC** ligands with the calcium cations intercalating between the layers. This layering is similar to the layering for calcium cation complexes with dicarboxylates.[45]

The two diagrams below (figure 133 and figure 134) show selected atom labels for the complex.

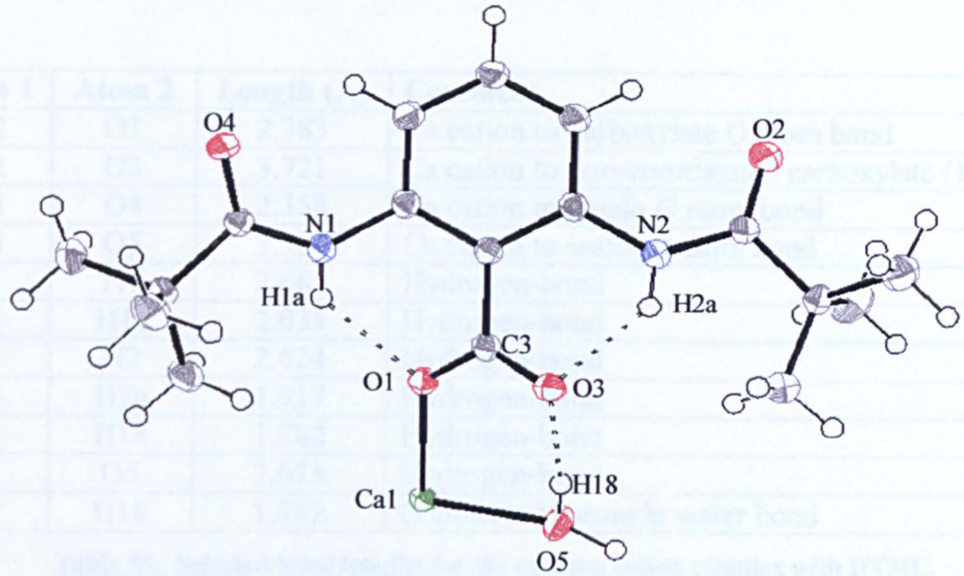


Figure 133. Asymmetric unit in the calcium cation complex with DTMC, with selected atom labels.

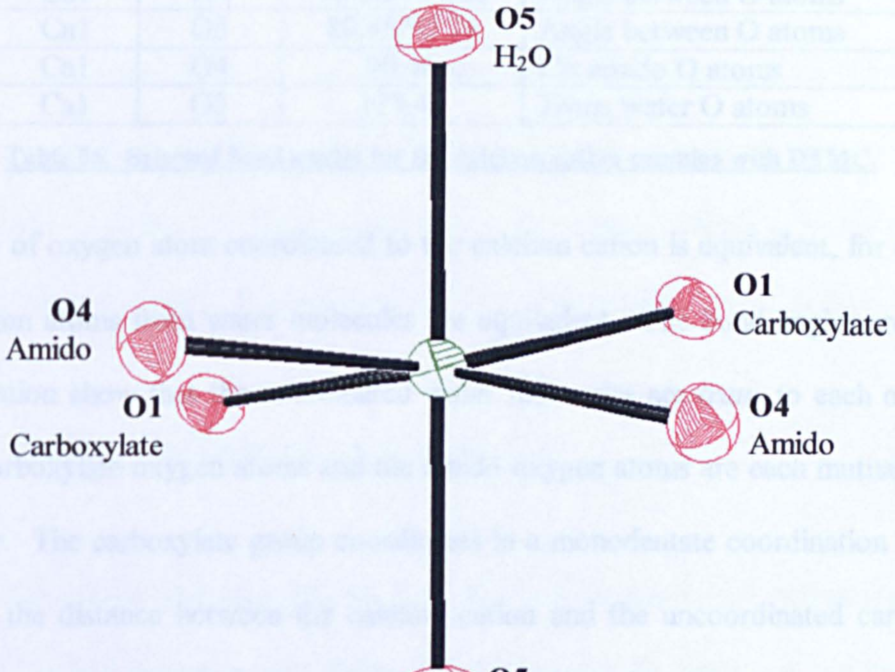


Figure 134. Coordination sphere for the calcium cation within the calcium cation complex with DTMC, with atom labels.

The calcium cation has slightly distorted octahedral geometry.

Selected bond lengths and bond angles for the complex are shown in the tables below (tables 55 and 56).

Atom 1	Atom 2	Length (Å)	Comment
Ca1	O1	2.383	Ca cation to carboxylate O atom bond
Ca1	O3	3.721	Ca cation to non-coordinated carboxylate O atom
Ca1	O4	2.358	Ca cation to amido O atom bond
Ca1	O5	2.337	Ca cation to water O atom bond
O1	N1	2.685	Hydrogen-bond
O1	H1a	2.035	Hydrogen-bond
O3	N2	2.624	Hydrogen-bond
O3	H2a	1.917	Hydrogen-bond
O3	H18	1.782	Hydrogen-bond
O3	O5	2.673	Hydrogen-bond
O5	H18	1.782	O atom to H atom in water bond

Table 55. Selected bond lengths for the calcium cation complex with DTMC.

Atom 1	Atom 2	Atom 3	Bond angle (°)	Comment
O1	C3	O3	124.09	Angle across carboxylate group
O1	Ca1	O1	93.07	*Cis* carboxylate O atoms
O1	Ca1	O4	90.26/164.66	Angle between O atoms
O1	Ca1	O5	80.45/97.74	Angle between O atoms
O4	Ca1	O4	90.46	*Cis* amido O atoms
O5	Ca1	O5	177.40	*Trans* water O atoms

Table 56. Selected bond angles for the calcium cation complex with DTMC.

Each type of oxygen atom coordinated to the calcium cation is equivalent, for example, both oxygen atoms from water molecules are equivalent. The bond angles around the calcium cation show that the coordinated water molecules are *trans* to each other and that the carboxylate oxygen atoms and the amido oxygen atoms are each mutually *cis* to each other. The carboxylate group coordinates in a monodentate coordination mode as shown by the distance between the calcium cation and the uncoordinated carboxylate oxygen atom being too long for a bond to exist (3.721Å). The bond length to the calcium cation from the carboxylic acid oxygen atom is very close to the average bond length observed for all calcium cations coordinated to carboxylic acid oxygen atoms of 2.42Å.[231] The calcium cation is six coordinate, where the bond lengths to the calcium cation follow the trend shown below.

Water oxygen atom < amido oxygen atom < carboxylate oxygen atom

$\longrightarrow$

Increasing bond length of oxygen atom to calcium cation

The range of bond lengths to the calcium cation is small (2.337-2.383Å). The bond length to the water molecule oxygen atom is within the range expected for calcium cation coordination to water oxygen atoms, though is reasonably short (2.337Å compared to normal range of 2.278-2.536Å).[41] The charge on the **DTMC** ligand can be seen to be stabilised by hydrogen-bonding, where the carboxylate oxygen atoms are hydrogen-bonded to the amido NH groups and the uncoordinated carboxylate oxygen atom is hydrogen-bonded to a water molecule.

4.3.4.3. Solution State Studies on the Carboxylic Acid Complexes

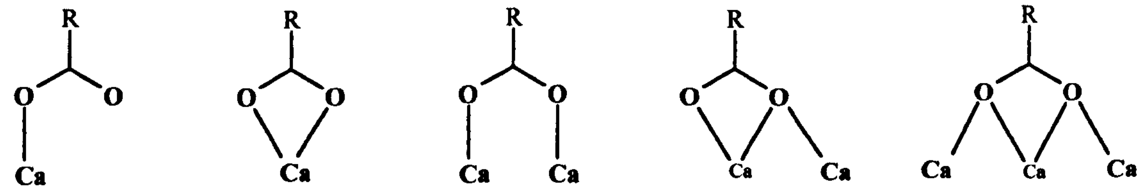
The ammonium cation salt with **DTMC** was characterised in solution by ^{1}H NMR (d_6-DMSO) spectroscopy and mass spectrometry, which all showed that the salt has the same structure in solution as in the solid state. The calcium cation complex could not be properly characterised in solution as it was impure with the ammonium cation salt.

4.3.4.4. Summary of the Carboxylic Acid Complexes

An ammonium cation salt with **DTMC (35)** has been characterised, which shows that the **DTMC** ligand possesses the shape it was designed to have. A calcium cation complex with **DTMC (36)** has been characterised within which the **DTMC** ligand coordinates to the calcium cation through the carboxylic acid function in a monodentate coordination mode. The calcium cation complex is interesting as monodentate calcium cation complexes with carboxylic acid ligands are unusual.

4.3.6. Comparisons between Calcium Cation Carboxylic Acid Complexes in the Literature and the Calcium Cation Complex with **DTMC**

The coordination modes of carboxylic acid ligands to calcium cations is shown below (figure 135) with the names that will be used henceforth for the modes.



Monodentate Bidentate Bridging monodentate Bridging bidentate

Figure 135. Coordination modes of carboxylic acid ligands to calcium cations.

For bridging bidentate mode, there are two options; where in the first only one oxygen atom bridges two calcium cations and in the second both oxygen atoms bridge calcium cations. Below is a table (table 57) of data for carboxylic acid complexes with calcium cations, where the bond angles across the carboxylate group, the bond lengths to the calcium cations and the interatomic calcium cation distances are shown. The data was collected from the Cambridge Crystallographic Database and is a representative survey of the complexes where calcium cations are coordinated to carboxylic acid ligands.[41] For the table of data, bridging bidentate refers only to the calcium cations which are bridged and not to the bidentate-coordinated calcium cation. This is shown by the calcium cations in the above diagram in bold (figure 135). The survey does not include any mixed metal ion complexes or crown complexes.

Bond	**Range**
Bridging monodentate carboxylate O-C-O bond angle (°)	115.19-127.39
Bidentate/bridging bidentate carboxylate O-C-O bond angle (°)	117.40-124.01
Monodentate Ca-O bond length (Å)	2.272-2.449
Bidentate Ca-O bond length (Å)	2.373-2.823
Bridging monodentate Ca-O bond length (Å)	2.318-2.497
Bridging bidentate Ca-O bond length (Å)	2.317-2.489
Bridging monodentate Ca-Ca distance (Å)	3.712-4.699
Bridging bidentate Ca-Ca- distance (Å)	3.612-4.506

Table 57. Summary of data on calcium cation complexes with carboxylic acid ligands.

It can be seen that the angle across the carboxylate group is not affected by the coordination mode, though the range is greater for monodentate coordination. Calcium cations coordinated by carboxylate oxygen atoms which are coordinated to other calcium cations have shorter bonds than monodentate and bidentate coordinated calcium cations, this is shown schematically below (figure 136). As would be expected, calcium cations that are bridged across a bridging monodentate carboxylate group are further apart than calcium cations bridged by bidentate carboxylate groups.

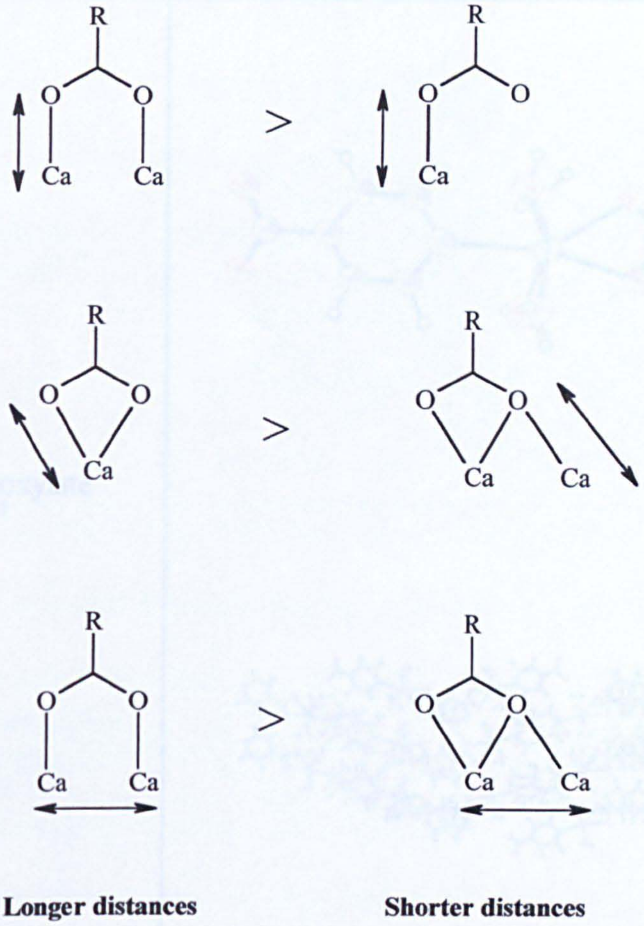
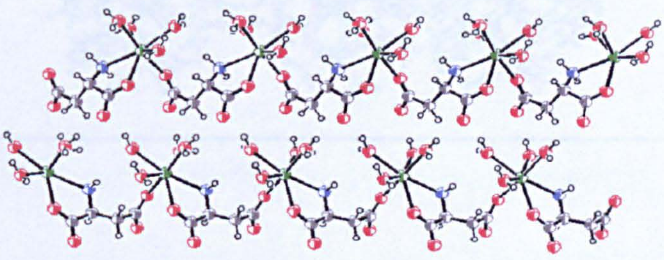
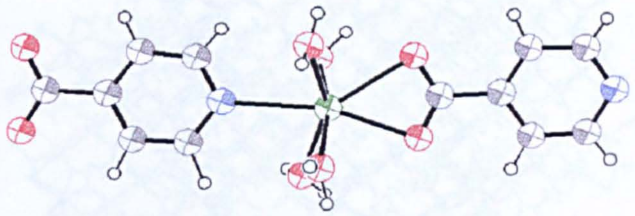
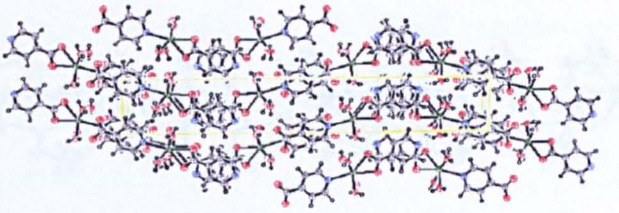
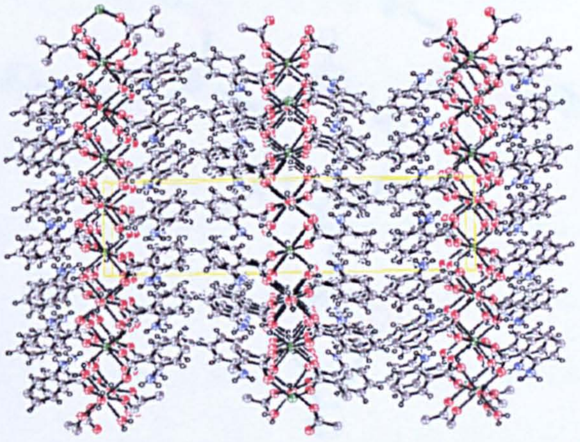


Figure 136. Schematic representation of the trends in bond lengths.

The diagrams below (figure 137) show a range of the coordination modes discussed above.

Bonding description	Structure
Monodentate carboxylate group[232]	

Bidentate carboxylate group[233]	 
Bridging monodentate carboxylate group[234]	

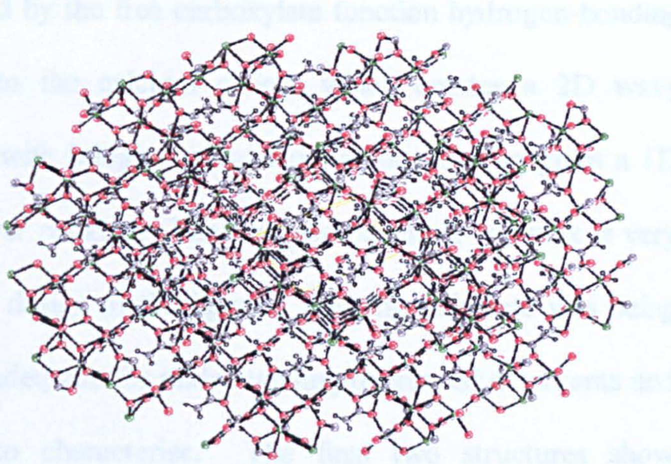
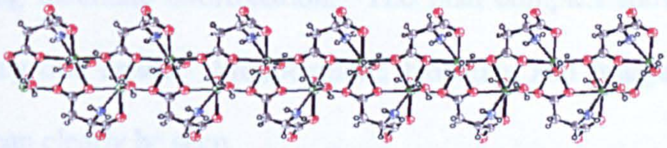
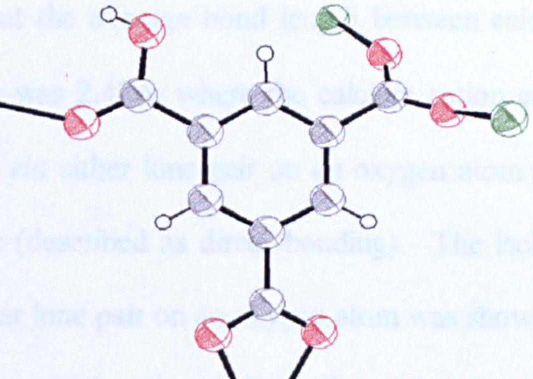
Bridging bidentate carboxylate group[235]	
Monodentate and bridging bidentate carboxylate groups[232]	
Monodentate, bidentate and bridging bidentate carboxylate groups[236]	

Figure 137. Examples of the coordination modes of carboxylic acid ligand to calcium cations.

The above views (figure 137) show a range of interesting features. The monodentate complex contains a ligand with two carboxylate groups which enables it to form a 1D polymeric chain. The bidentate complex is simple, with two ligands to one calcium cation, despite the ability of the ligand to coordinate to more than one calcium cation.

This coordination mode is stabilised by the free carboxylate function hydrogen-bonding to water molecules coordinated to the calcium cation, which creates a 2D wavy polymeric network. The complex with bridging monodentate coordination gives a 1D polymeric chain, with lamellar bilayer packing. The bridging bidentate complex is very complicated and shows why in the design of the ligands, bridging bidentate was being avoided. The complex is clearly inadequate for understanding overbased detergents and would have been very difficult to characterise. The final two structures show complexes with more than one coordination mode present. The first structure shows both monodentate coordination and bridging bidentate coordination. This complex gives a nice illustration of bridging bidentate coordination. The final complex shows three coordination modes with only one ligand. Monodentate, bidentate and bridging monodentate coordination modes can clearly be seen.

This research agrees with a review of carboxylic acid complexes carried out by Carrell *et al.* in 1988.[231] The review showed that the average bond length between calcium cations and carboxylic acid oxygen atoms was 2.42Å, where the calcium cation could coordinate to the carboxylic acid function *via* either lone pair on an oxygen atom (*syn* and *anti*) or to both of the oxygen atoms (described as direct bonding). The lack of preference of calcium cations for a particular lone pair on an oxygen atom was shown to be very unusual when compared to other metal cations. For all metal cations the percentage of data points for each coordination site was found to be 63.9% *syn*, 22.7% *anti* and 14.4% direct, whereas for calcium cations the percentages were 31.6% *syn*, 34.2% *anti* and 34.2% direct. Magnesium cations were found to preferentially coordinate *via* the *anti* lone pair whereas strontium cations and barium cations coordinated *via* the *syn* lone pair.

In the calcium cation complex with **DTMC** the bond between the calcium cation and the monodentate carboxylate oxygen atom is short compared to other monodentate bonds, though the angle across the carboxylate group is within the normal range.

4.3.7. Discussion on the Role of Carboxylic Acid Molecules in the Preparation of Overbased Detergents

The interaction of stearic acid to an overbased detergent core cannot be determined empirically, though by a combination of computer modelling studies[10] and the preparation and characterisation of complexes, the coordination mode/s can be estimated. Extensive bridging bidentate coordination is unlikely as the calcium cations on the surface of the core are too well separated and the coordination mode would bring the alkyl chains of the carboxylic acid too close together to be acceptable. Bidentate coordination, monodentate coordination or bridging monodentate coordination is most likely. Bidentate coordination would fill two coordination sites for the calcium cations and would be preferred by the calcium cations to monodentate coordination.[219] Monodentate coordination could be stabilised by hydroxide groups on the surface of the core, with which the acid could hydrogen-bond.[12] Bridging monodentate coordination is a strong possibility as this mode allows calcium cations to be more separated than bridging bidentate and as there is one ligand to two calcium cations, there would not be crowding problems for the carboxylic acid alkyl chain. It is probable that more than one coordination mode is observed and that the mode may change depending on conditions.[7, 10]

4.3.8. Carboxylic Acid Molecules Summary

A set of novel carboxylic acid ligands has been prepared and the calcium cation complex with one of the ligands characterised. The ligands use hydrogen-bonding and steric bulk to influence the coordination modes of the ligand to Group 2 metal ions. **DTMC** was designed for monodentate coordination and the calcium cation complex shows that monodentate coordination was achieved. This is exciting as monodentate coordination to calcium cations is rare.

4.4. Conclusion

The overbasing process has been investigated by the study of the potential roles of ethylene glycol and carboxylic acids. For ethylene glycol, mimics for ethylene glycol were prepared. The copper cation complexes of the mimics show that the mimics are realistic mimics for ethylene glycol. For carboxylic acids, novel carboxylic acid ligands have been prepared. A carboxylic acid ligand designed for monodentate coordination to Group 2 metal ions was prepared and the calcium cation complex characterised, which shows that the ligand coordinates in a monodentate mode.

Chapter 5

Overbased Systems

5.1. Introduction

In order to help understand overbased detergents on an atomic scale, models for overbased detergents have been prepared and characterised. These models allow the interaction between the surfactant molecules and the core metal cations to be investigated. Overbased detergents usually contain calcium carbonate cores, which are formed from calcium hydroxide cores by carbonation. Overbased detergent cores consist of approximately sixteen calcium cations, depending on the size of the core.[8] The complexes which have been presented so far have been simple models with one or two metal ions per complex. These complexes have supplied information about the potential coordination of the surfactant molecules to individual metal ions. To better understand overbased detergents, it is necessary to prepare and characterise more complicated complexes, with more than one or two metal ions, preferably in a 'core'. These complexes would be superior models for overbased detergents and if the core was calcium hydroxide, they could allow the overbasing process to be investigated to understand how calcium carbonate cores are formed from calcium hydroxide cores. Three complexes have been prepared which contain 'cores' and therefore are models for overbased detergents. These complexes will be discussed in this chapter. Two of the complexes contain calcium hydroxide 'cores' and the other complex contains a calcium carbonate 'core'. All three complexes have calcium cations as the metal ions.

5.2. Calcium Cation Complex with p-*tert*-Butylcalix[8]arene (One)

5.2.1. Introduction

In the calix[8]arene complexes chapter (chapter 3), two calix[8]arene complexes were presented, where each contained two metal ions per complex and p-isopropylcalix[8]arene. Neither of the complexes contained any sort of 'core'. In this section, a p-*tert*-butylcalix[8]arene (**BC8**) complex will be presented, which contains a calcium hydroxide core. This core is probably the smallest 'core' that can be achieved as it contains only four calcium cations and four hydroxide anions.

5.2.2. Preparation of the Calcium Cation Complex with BC8

A calcium cation complex with **BC8** was prepared from diethyl ether with six mole equivalents of DMF to **BC8**. The complex was also prepared from methanol and DMF, where a larger volume of DMF was used (0.5ml). The larger volume of DMF was added to dissolve the **BC8** in the basic methanol solution. Even with 0.5ml DMF, the calix[8]arene did not dissolve and so after addition of the metal salt, the solution was agitated in a sonic bath, which did give a clear solution briefly, before the product began to precipitate out of the solution. The yield from methanol (64%) was lower than from diethyl ether (73%), though the product was purer as all of the reagents dissolved, unlike in diethyl ether in which simple calcium salts are almost completely insoluble. The reactions were found to be reproducible. Both methods yielded powder products, which were found by ^{1}H NMR spectroscopy ($CDCl_3$ or CD_2Cl_2) to be identical. Recrystallisation from dichloromethane and diethyl ether gave a crystalline product, which by ^1H NMR ($CDCl_3$ or CD_2Cl_2) spectroscopy was found to be the same as the powder product. The crystalline complex was analysed by single crystal x-ray diffraction and the structure is discussed below.

The complex contains a tetracalcium cation core with four hydroxide anions, where the core is sandwiched between two calix[8]arene anions. Therefore this complex has an overbased detergent precursor core.

5.2.3. Solid State Structure of the Calcium Cation Complex with BC8 (37)

A crystalline complex of calcium cations with **BC8** was grown from DCM and diethyl ether solution. The complex consists of two calixarene rings, four calcium cations, six DMF molecules and four hydroxide anions to give the formula $(Ca^{2+})_4(OH^-)_4(\mathbf{BC8}^{2-})_2$.6DMF. There are also some DCM and diethyl ether molecules in the lattice. The complex has a calcium hydroxide core, which is sandwiched between two calixarene rings. The calixarene rings have a pleated loop conformation and –2 charge, which is stabilised by hydrogen-bonding between calixarene oxygen atoms. The core of the complex is a pseudo endcapped cubane cluster[237] consisting of four calcium cations, four bridging hydroxide anions (μ_3-OH) and capped by two bridging DMF molecule oxygen atoms. Each calcium cation is seven coordinate with capped trigonal prismatic geometry. All of the calcium cations are coordinated to two calixarene ligand oxygen atoms, three bridging hydroxide anions, one terminally bound DMF molecule oxygen atom and one bridging DMF molecule oxygen atom. The complex is not fully refined and so all of the hydrogen atoms have not as yet been characterised.

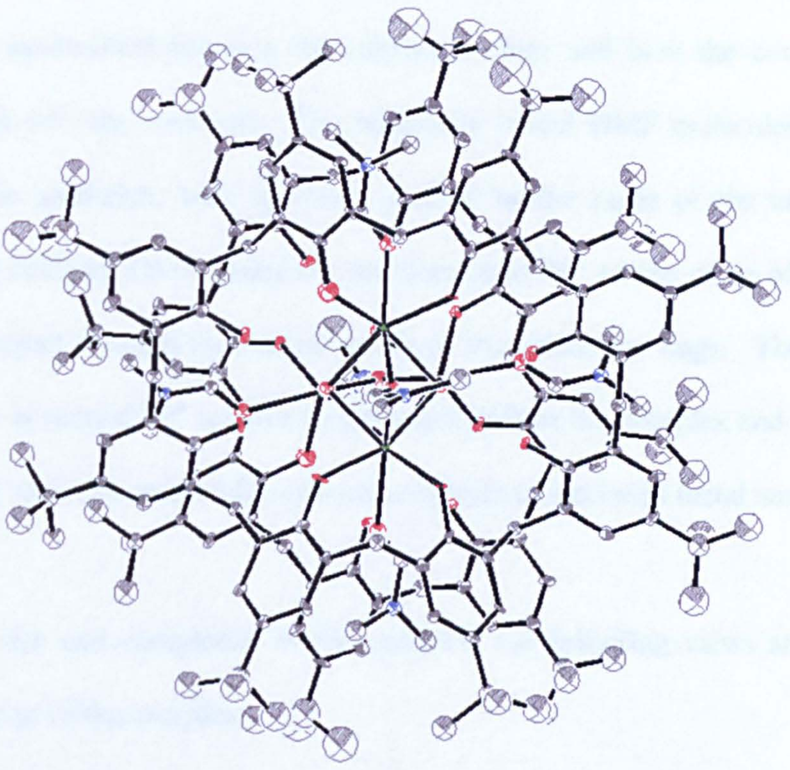


Figure 138. Structure of the calcium complex with BC8 with a calcium hydroxide core (hydrogen atoms and free lattice molecules have been omitted for clarity), $(Ca^{2+})_4(OH^-)_4(BC8^{2-})_2$.6DMF.

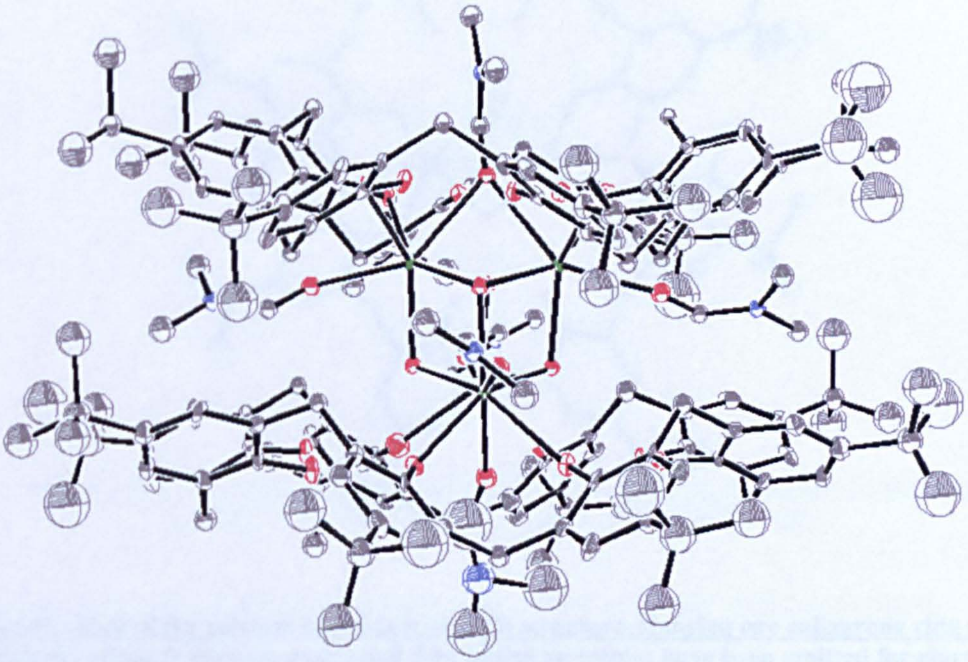


Figure 139. Side view of the calcium complex with BC8 (hydrogen atoms and free lattice molecules have been omitted for clarity).

The above diagram (figure 139) shows the side view of the complex to illustrate how the core is sandwiched between the calixarene rings and how the coordinated DMF molecules fit into the structure. The terminally bound DMF molecules sit within the centre of the sandwich, with the core, parallel to the plane of the calixarene rings, whereas the bridging DMF molecules are orientated 90° to the plane of the calixarene rings and project through the central cavity of the calixarene rings. The lower half of the complex is rotated 90° relative to the upper half of the complex and the two halves are identical. It is not unusual for calixarene ligands to sandwich metal ions.[123, 155]

Due to the size and complexity of the complex, the following views and descriptions explain sections of the complex.

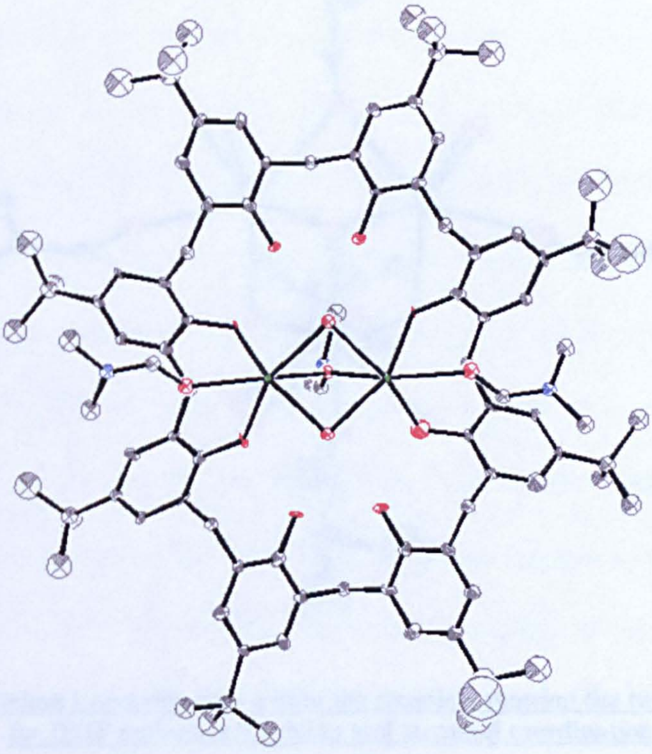


Figure 140. Half of the calcium complex with BC8 structure, showing one calixarene ring and two calcium cations (hydrogen atoms and free lattice molecules have been omitted for clarity).

The above view (figure 140) shows half of the complex to illustrate the coordination of the calixarene ring to the calcium cations. The calixarene ring coordinates to each calcium cation through two neighbouring oxygen atoms and coordinates to both calcium cations using the most separated oxygen atoms in the ring (opposite sides of the ring). The bridging of the calcium cations by core hydroxide anions and DMF molecules causes the ring to adopt a pleated loop conformation. This conformation is one of the most common conformations for calix[8]arenes and is the conformation of free **BC8** in solution.[96, 196, 197] The charge on the ring is stabilised by strong hydrogen bonding between the uncoordinated oxygen atoms,[201] as observed by oxygen atom to oxygen atom distances of 2.434-2.683Å.

The core of the complex with DMF molecules included can be seen below (figure 141).

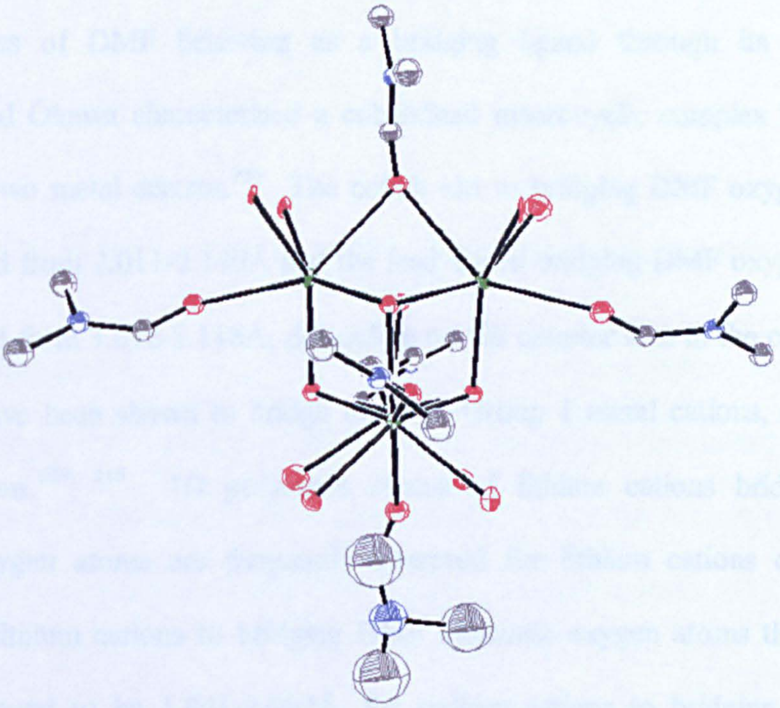


Figure 141. The calcium hydroxide core within the complex, showing the two coordination modes for DMF molecules (bridging and terminal coordination).

The above view (figure 141) shows the core of the complex with the coordinated DMF molecules. The bridging DMF molecules at the top and bottom of the core can be seen. The bond lengths of the bridging DMF oxygen atoms to the calcium cations are all similar (2.586-2.631Å) and are within the normal range for calcium cation to oxygen atom bond lengths, though are long when compared to calcium cation to DMF molecule oxygen atom bond lengths. For calcium cations coordinated to DMF molecule oxygen atoms the bond length range was found to be 2.255-2.401Å.[41] The bonds between the calcium cations and the DMF oxygen atoms are shorter for the terminally bound DMF molecules than the bridging DMF molecules, where the terminally bound DMF molecule bond lengths to the calcium cations fit within the normal range. The longer bond lengths for the bridging DMF molecules may be partly due to steric constraints, because the calcium cations are also bridged by hydroxide oxygen atoms and so cannot physically get closer together, plus the DMF oxygen atoms will be repelled by the hydroxide oxygen atoms. This is the first example of DMF bridging calcium cations (no hits in 264000 entries on the Cambridge Crystallographic Database[41]). There are few examples of DMF behaving as a bridging ligand through its oxygen atom. Furutachi and Ōkawa characterised a cobalt/lead macrocyclic complex in which DMF bridges the two metal centres.[238] The cobalt ion to bridging DMF oxygen atom bond length ranged from 2.011-2.140Å and the lead ion to bridging DMF oxygen atom bond length ranged from 3.072-3.116Å, depending on the counter ions in the complex. DMF molecules have been shown to bridge between Group 1 metal cations, especially with lithium cations.[239, 240] 1D polymeric chains of lithium cations bridged by DMF molecule oxygen atoms are frequently observed for lithium cations coordinated to DMF. For lithium cations to bridging DMF molecule oxygen atoms the bond length range was found to be 1.941-2.067Å, for sodium cations to bridging DMF oxygen atoms the bond length range was 2.294-2.420Å and for potassium cations to bridging DMF molecule oxygen atoms the bond length range was 2.757-2.801Å. The bond lengths for the bridging DMF molecules in the calcium cation complex with **BC8** are in a similar range to the bond lengths to potassium cations. There are no examples of DMF molecules bridging Group 2 metal cations.

The core of the complex can be seen below (figure 142), where the oxygen atoms from the ligands have been included.

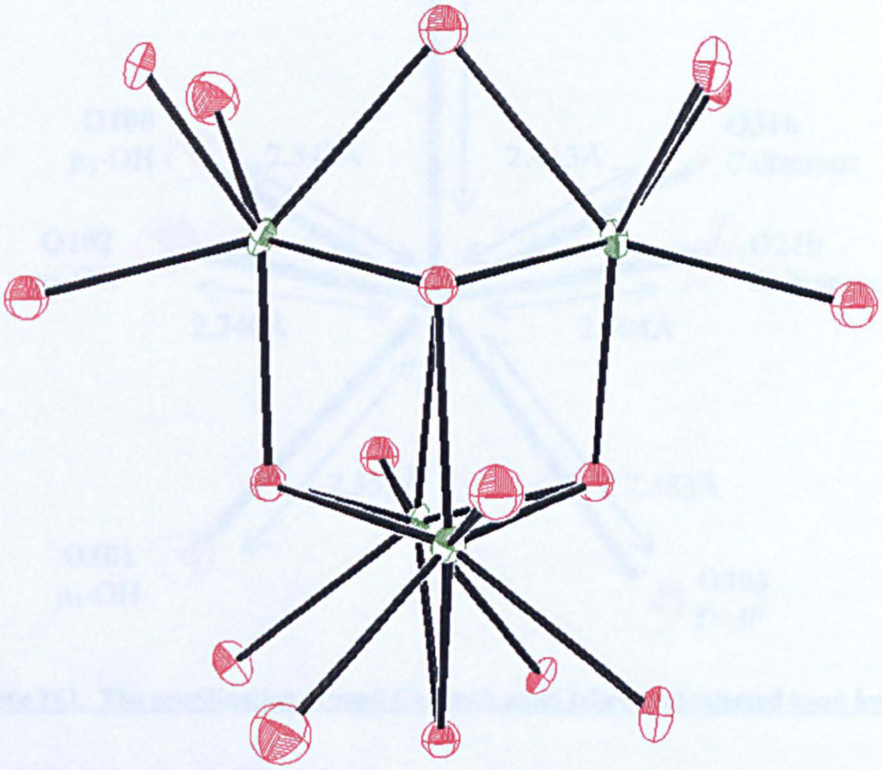


Figure 142. The calcium hydroxide core within the complex, showing only calcium cations and oxygen atoms.

The above diagram (figure 142) shows the core of the complex to show that it is a pseudo endcapped cubane cluster. All of the oxygen atoms coordinated to the calcium cations are shown. The coordination sphere around one of the calcium cations (Ca1) in the complex is shown in more detail below with bond lengths (figure 143).

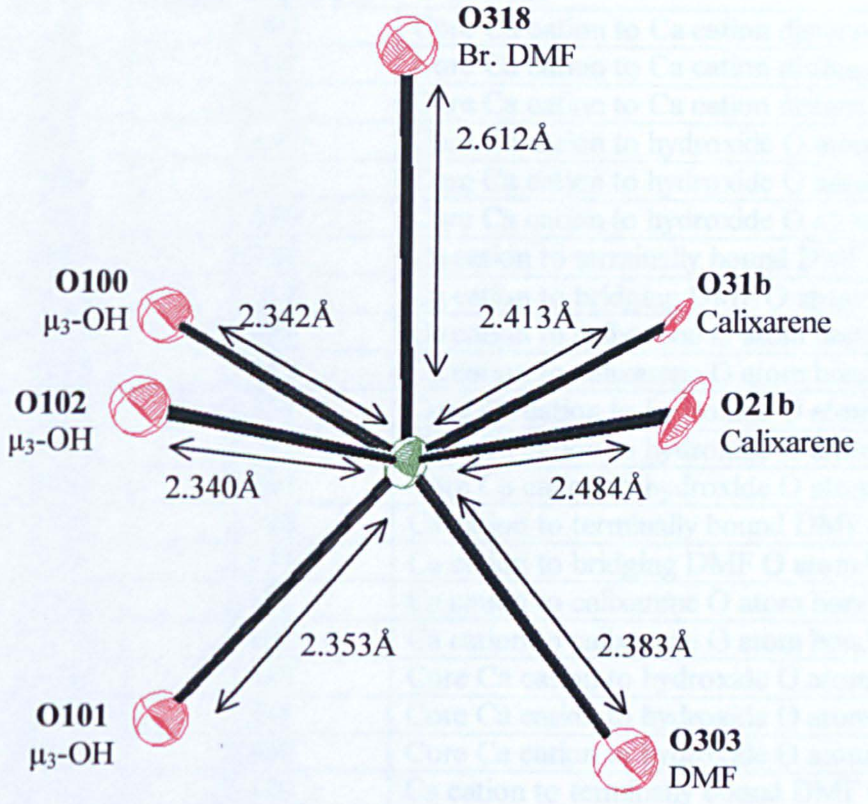


Figure 143. The coordination around Ca1 with atom labels and selected bond lengths.

The above diagram (figure 143) shows the coordination sphere around Ca1. Ca2, Ca3 and Ca4 have the same coordination geometry and similar bond lengths to coordinated oxygen atoms.

Selected bond lengths and angles can be seen in the tables below (table 58 and 59).

Atom 1	**Atom 2**	**Bond length (Å)**	**Comment**
Ca1	Ca2	3.607	Core Ca cation to Ca cation distance
Ca1	Ca3	3.347	Core Ca cation to Ca cation distance
Ca1	Ca4	3.776	Core Ca cation to Ca cation distance
Ca1	O100	2.342	Core Ca cation to hydroxide O atom bond
Ca1	O101	2.353	Core Ca cation to hydroxide O atom bond
Ca1	O102	2.340	Core Ca cation to hydroxide O atom bond
Ca1	0303	2.383	Ca cation to terminally bound DMF O atom
Ca1	O318	2.612	Ca cation to bridging DMF O atom bond
Ca1	O21b	2.484	Ca cation to calixarene O atom bond
Ca1	O31b	2.413	Ca cation to calixarene O atom bond
Ca2	O101	2.357	Core Ca cation to hydroxide O atom bond
Ca2	O102	2.347	Core Ca cation to hydroxide O atom bond
Ca2	O103	2.364	Core Ca cation to hydroxide O atom bond
Ca2	O309	2.386	Ca cation to terminally bound DMF O atom
Ca2	O315	2.631	Ca cation to bridging DMF O atom bond
Ca2	O21a	2.391	Ca cation to calixarene O atom bond
Ca2	O31a	2.462	Ca cation to calixarene O atom bond
Ca3	O100	2.339	Core Ca cation to hydroxide O atom bond
Ca3	O102	2.358	Core Ca cation to hydroxide O atom bond
Ca3	O103	2.349	Core Ca cation to hydroxide O atom bond
Ca3	O312	2.388	Ca cation to terminally bound DMF O atom
Ca3	O318	2.607	Ca cation to bridging DMF O atom bond
Ca3	O61b	2.430	Ca cation to calixarene O atom bond
Ca3	O71b	2.419	Ca cation to calixarene O atom bond
Ca4	O100	2.344	Core Ca cation to hydroxide O atom bond
Ca4	O101	2.346	Core Ca cation to hydroxide O atom bond
Ca4	O103	2.335	Core Ca cation to hydroxide O atom bond
Ca4	O306	2.372	Ca cation to terminally bound DMF O atom
Ca4	O315	2.586	Ca cation to bridging DMF O atom bond
Ca4	O61a	2.412	Ca cation to calixarene O atom bond
Ca4	O71a	2.493	Ca cation to calixarene O atom bond

Table 58. Selected bond lengths for the calcium complex with BC8.

Atom 1	**Atom 2**	**Atom 3**	**Angle (°)**	**Comment**
Ca1	O318	Ca3	79.99	Angle across bridging DMF O atom
Ca2	O315	Ca4	80.42	Angle across bridging DMF O atom
O100	Ca1	O101	72.76	Angle between core hydroxide O atoms
O100	Ca1	O102	84.07	Angle between core hydroxide O atoms
O101	Ca2	O102	78.87	Angle between core hydroxide O atoms
O101	Ca2	O103	83.13	Angle between core hydroxide O atoms
O100	Ca3	O102	83.33	Angle between core hydroxide O atoms
O100	Ca3	O103	77.50	Angle between core hydroxide O atoms
O100	Ca4	O101	72.85	Angle between core hydroxide O atoms
O100	Ca4	O103	77.67	Angle between core hydroxide O atoms

Table 59. Selected bond angles for the calcium complex with BC8.

The table below (table 60) summarises the trend for bond lengths of calcium cations to coordinated oxygen atoms

Bond	Bond length range	Trend
Ca cation to core hydroxide O atom	2.335-2.364Å	↓ Increasing bond length
Ca cation to terminally bound DMF O atom	2.372-2.388Å	
Ca cation to calixarene O atom	2.391-2.493Å	
Ca cation to bridging DMF O atom	2.586-2.631Å	

Table 60. Summary of bond length trends for the calcium complex with BC8.

It can be seen that the bonds between the calcium cations and the core hydroxide oxygen atoms are the shortest bonds and that the bonds to the bridging DMF molecules oxygen atoms are the longest bonds, though none of these bonds are exceptionally short or long.[29]

By the bond angles and bond lengths it can be seen that the calcium cations are in almost equivalent environments.

The range of distances between calcium cations in the core shows that the core is not a perfect cube. The core is closer to rectangular with the longest side being perpendicular to the plane of the calixarene rings. The bond angles for the core also show that the core is slightly twisted, probably due to coordination of the calcium cations to the bridging DMF molecules, causing the calcium cations to be 'pulled' towards the DMF oxygen atoms and the core hydroxide oxygen atoms to be 'repelled' away from the DMF oxygen atoms. A selection of bond lengths and angles are shown on the diagram below (figure 144) to illustrate the slight elongation of the core and the twist.

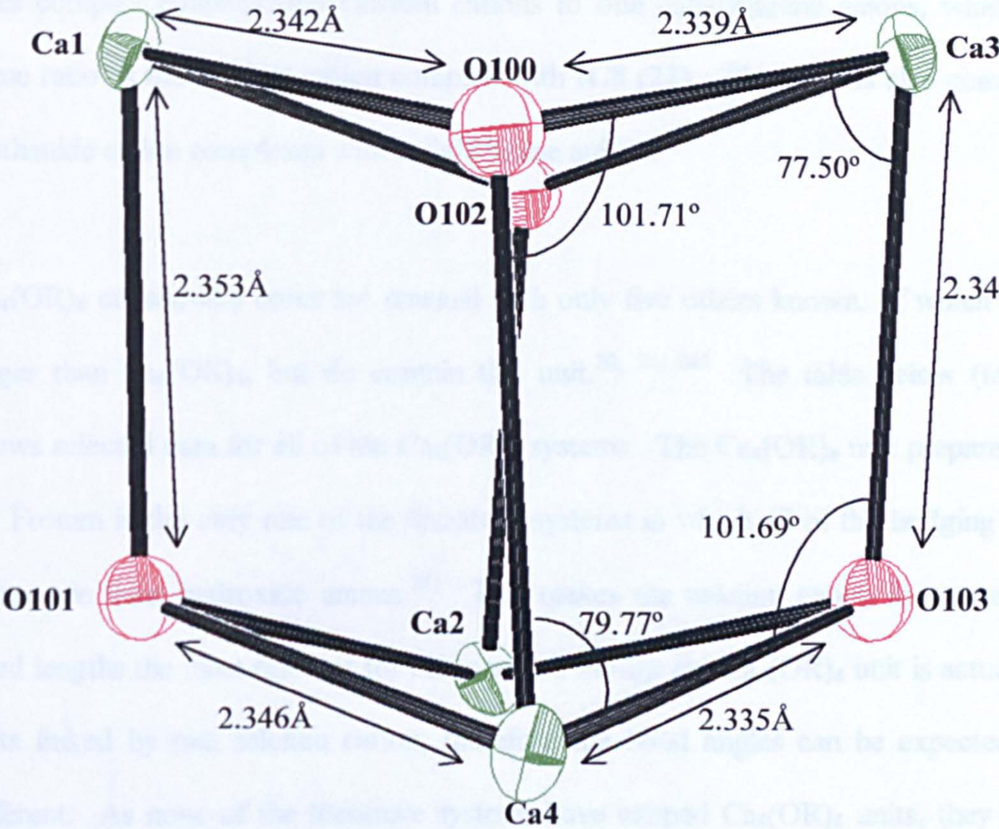


Figure 144. Calcium hydroxide core, showing atom labels and selected bond lengths and angles.

The twist in the core can be seen by the O-Ca-O angles being significantly smaller than the corresponding Ca-O-Ca angles. In a cube these angles would all be 90°. The elongation of the core in the direction perpendicular to the plane of the calixarene rings can be seen by the Ca1-O101 and Ca3-O103 bonds being longer than the Ca1-O100, Ca3-O100, Ca4-O101 and Ca4-O103 bonds, where one calixarene ring is above Ca1, Ca3, O100 and O102, and the other calixarene ring is below Ca2, Ca4, O101 and O103. In a comparison of cubane cores with various metal cations by Turova *et al.*,[49] it was shown that O-M-O bond angles are always smaller than M-O-M bond angles, which is the same trend as observed in this complex. For a magnesium cation cubane core the Mg-O-Mg bond angles were in the range 92.9-101.4° and the O-Mg-O bond angles were in the range 78.4-85.5°.[49]

This complex contains two calcium cations to one calix[8]arene anions, which is the same ratio as the calcium cation complex with **IC8** (**22**). This ratio is also common for lanthanide cation complexes with calix[8]arene anions.[196]

$Ca_4(OR)_4$ cubane-like cores are unusual with only five others known, of which two are larger than $Ca_4(OR)_4$, but do contain this unit.[20, 241-245] The table below (table 61) shows selected data for all of the $Ca_4(OR)_4$ systems. The $Ca_4(OR)_4$ unit prepared by K. M. Fromm is the only one of the literature systems in which all of the bridging oxygen atoms are from hydroxide anions.[241] This makes the calcium cation to oxygen atom bond lengths the most relevant for comparison, though the $Ca_4(OR)_4$ unit is actually two units linked by one calcium cation, therefore the bond angles can be expected to be different. As none of the literature systems have capped $Ca_4(OR)_4$ units, they are not completely comparable.

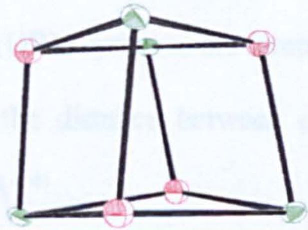
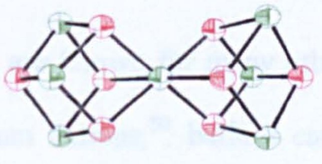
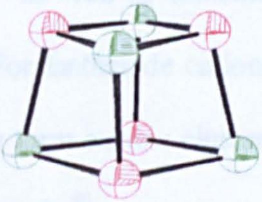
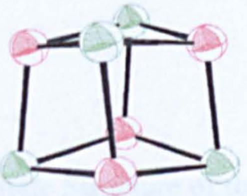
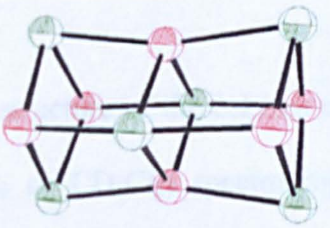
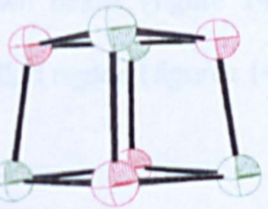
Reference	$Ca_4(OR)_4$	Ca-O (Å)[a]	Ca-O-Ca (°)[b]	Ca-Ca (Å)[c]
37		2.335-2.364	91.57-106.97	3.347-3.776
A[241d]		2.311-2.388	98.41-102.06	3.553-3.592
B[20]		2.366-2.399	95.58-108.38	3.530-3.837
C[242]		2.346-2.429	96.23-103.18	3.556-3.753
D[243d]		2.312-3.364[e] 2.407-2.529[f]	93.94-99.76	3.580-3.609
E[244]		2.329-3.368	96.74-101.80	3.507-3.640

Table 61. Crystal data for $Ca_4(OR)_4$ containing complexes. [a]Calcium cation to oxygen atoms bond lengths. [b]Calcium cation-oxygen atom-calcium cation bond angle. [c]Interatomic distance between calcium cations. [d]Data for a single $Ca_4(OR)_4$ unit. [e]Bridging ethanol molecule oxygen atoms. [f]Bridging hydroxide anion oxygen atoms.

The $Ca_4(OR)_4$ core in the calcium cation complex with **BC8** has the widest range of bond angles and interatomic calcium cation distances of all of the $Ca_4(OR)_4$ systems, suggesting that the core is the most distorted. Only the range of interatomic calcium cation to calcium cation distances fit within the range given by the other systems. For all of the $Ca_4(OR)_4$ systems, the interatomic calcium cation to calcium cation distance is smaller than the distance between calcium cations simply bridged by oxygen atoms (3.656-3.992Å).[41]

Cubane cores are known for many other metal cations, including magnesium cations,[20, 49, 204] strontium cations,[50] barium cations,[20, 50] Group 1 metal cations,[49] lanthanide cations[20, 246, 247] as well as transition metal cations for which the term 'cubane' was coined.[237, 248] For lanthanide cations, the cubane cluster is a common structural motif. Group 1 cations form cubane clusters more often than Group 2 metal cations, especially with alkoxide ligands.[50]

5.2.4. Solution State Structure of the Calcium Cation Complex with BC8

The solution structure of the calcium cation complex with **BC8** was determined by ^1H NMR ($CDCl_3$ or CD_2Cl_2) spectroscopy. The ^1H NMR (CD_2Cl_2) spectrum of the complex is shown below (figure 145), followed by expanded views of the aromatic region and the alkyl region (figures 146 and 147).

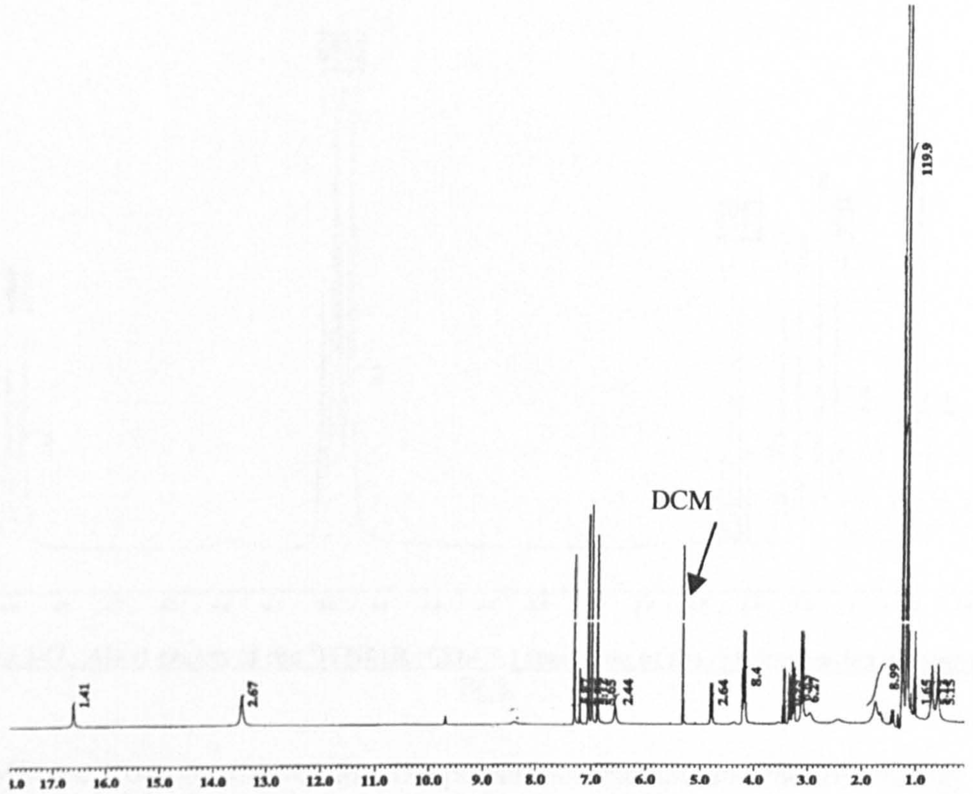


Figure 145. ¹H NMR (CD_2Cl_2) spectrum of the calcium cation complex with BC8.

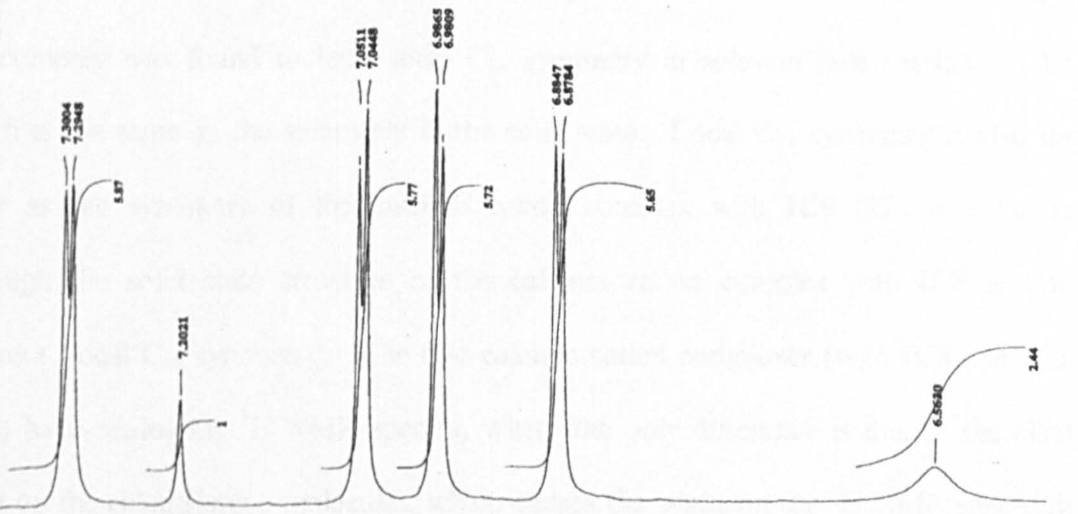


Figure 146. Aromatic region of the ¹H NMR (CD_2Cl_2) spectrum of the calcium cation complex with BC8.

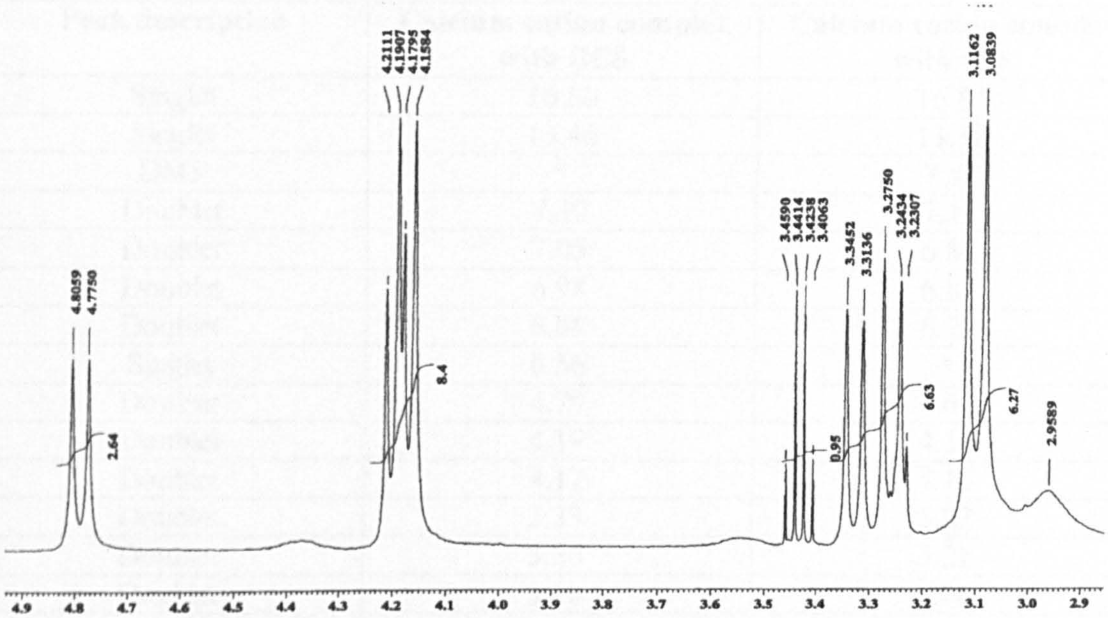


Figure 147. Alkyl region of the ^1H NMR (CD_2Cl_2) spectrum of the calcium cation complex with BC8.

^1H NMR spectroscopy showed that the preparation method and the morphology of the complex did not affect the structure of the complex in solution. The calixarene ring in the complex was found to have local C_{2v} symmetry in solution (see section 3.5.3.), which is the same as the symmetry in the solid state. Local C_{2v} symmetry is also the same as the symmetry of the calcium cation complex with **IC8** (**22**) in solution, although the solid state structure of the calcium cation complex with **IC8** is very different (local C_{2h} symmetry). The two calcium cation complexes (with **IC8** and with **BC8**) have analogous ^1H NMR spectra, where the only difference is due to the alkyl chain on the calix[8]arene molecules, which causes the peaks on the ^1H NMR spectrum for the calcium cation complex with **IC8** to be shifted slightly upfield relative to the **BC8** complex.[159] The table below (table 62) compares the peak positions for the two complexes.

Peak description	Calcium cation complex with BC8	Calcium cation complex with IC8
Singlet	16.60	16.84
Singlet	13.46	13.38
DMF	*	7.89
Doublet	7.30	7.14
Doublet	7.05	6.84
Doublet	6.98	6.81
Doublet	6.88	6.73
Singlet	6.56	*
Doublet	4.79	4.66
Doublet	4.19	4.18
Doublet	4.17	4.16
Doublet	3.33	3.27
Doublet	3.26	3.21
Doublet	3.10	3.06
DMF	*	2.90
DMF	*	2.84
Multiplet	**	2.69
Singlet	1.25	**
Singlet	1.18	**
Overlapped peaks	**	1.19-1.07

Table 62. Comparison between the two C_{2v} ^1H NMR (CD_2Cl_2) spectra, where * indicates that the peak is too small to obtain an accurate position and ** indicates that the peak is not relevant for that complex.

It can be seen that the calcium cation complex with BC8 has very small peaks for DMF, whereas the other calcium cation complex has larger peaks. This is to be expected from the crystal structures of the complexes where the calcium cation complex with IC8 has significantly more DMF in it than the other complex.

For the calcium cation complex with BC8, the local C_{2v} symmetry ^1H NMR spectrum contains four aromatic proton doublets, six alkyl proton doublets (which are often overlapped) and peaks for the *tert*-butyl group (two singlets), plus peaks for DMF (where the peaks at approximately 3ppm are often overlapped to give a broad singlet). There are also three extra peaks at approximately 16.6, 13.5 and 6.6ppm, which always occur in the same ratio and intensity relative to the other peaks, for example, relative to the aromatic proton peaks. These peaks are potentially either due to the CH group of bound DMF molecules or hydroxide protons within the complex. Firstly, it was investigated whether the peaks were due to bound DMF by preparing a calcium cation complex with **BC8** from diethyl ether plus six mole equivalents of deuterated DMF to **BC8**. The method was the same as the method by which the calcium cation complex with **BC8** was prepared in the highest yield. If the peaks were due to bound DMF then in the spectrum of the complex containing deuterated DMF the peaks should have lower intensity or even not be present. The ^{1}H NMR spectrum of the complex that was prepared showed no change in the peaks and so the peaks could not be due to bound DMF, therefore were due to hydroxide protons. The peaks were confirmed as hydroxide proton peaks by mixing a calcium cation complex with **BC8** in DCM with d_1-methanol (CH_3OD) and monitoring the level of hydroxide proton exchange by ^{1}H NMR spectroscopy. After the first treatment with d_1-methanol, the peaks at 13.5 and 6.6ppm reduced in intensity relative to C_{2v} symmetry calix[8]arene protons (the intensity approximately halved), but the peak at 16.6ppm remained unchanged. This indicated that the protons shown by the peak at 16.6ppm were more strongly bound than the protons shown by the peaks at 13.5 and 6.6ppm. After the second treatment with d_1-methanol, the peak at 16.6ppm also reduced in intensity. Decomposition of the complex to **BC8** was observed with each treatment. The experiment showed that the 'unknown' peaks were due to hydroxide protons, where the peaks at 13.5 and 6.6ppm probably represented calix[8]arene hydroxy protons and the peak at 16.6ppm represented core hydroxide protons. The relative intensities of the peaks also support these assignments. The table below (table 63) shows the assignments for all of the peaks in the calcium cation complex with **BC8** ^{1}H NMR (CD_2Cl_2) spectrum.

Peak (ppm) (1 d.p.)	Splitting	Assignment
16.6	(1H) Singlet	Core hydroxide proton
13.5	(2H) Singlet	Calixarene hydroxide proton
approx. 8.0	Singlet	DMF
7.3	(4H) Doublet	Aromatic calixarene proton
7.1	(4H) Doublet	Aromatic calixarene proton
7.0	(4H) Doublet	Aromatic calixarene proton
6.9	(4H) Doublet	Aromatic calixarene proton
6.6	(2H) Singlet	Calixarene hydroxide proton
4.8	(2H) Doublet	Alkyl calixarene proton
4.2	(2H) Doublet	Alkyl calixarene proton
4.2	(4H) Doublet	Alkyl calixarene proton
3.3	(2H) Doublet	Alkyl calixarene proton
3.3	(2H) Doublet	Alkyl calixarene proton
3.1	(4H) Doublet	Alkyl calixarene proton
approx. 3.0	Singlet	DMF
approx. 3.0	Singlet	DMF
1.3	(36H) Singlet	*t*-butyl calixarene proton
1.2	(36H) Singlet	*t*-butyl calixarene proton

Table 63. Assignments for the ^{1}H NMR (CD_2Cl_2) spectrum for the calcium cation complex with BC8.

For the spectrum in deuterated chloroform the peaks occur in the same intensities in slightly shifted positions.

When the calcium cation complex with **BC8** is dissolved, such as for ^{1}H NMR spectroscopy, there is some decomposition to **BC8**, even if the complex is dissolved under nitrogen. A sample of the calcium cation complex with **BC8** was dissolved in dichloromethane and then the solvent was removed. The sample was then analysed by ^{1}H NMR (CD_2Cl_2) spectroscopy which showed that the some of the complex had decomposed to **BC8**, and that the level of **BC8** in the sample was greater than before treatment with DCM. This study showed that the presence of free calix[8]arene in ^{1}H NMR spectra of calixarene complexes was due to decomposition caused by dissolving the complex and not by the complexes being impure.

The ^{13}C NMR (CD_2Cl_2) spectrum of the calcium cation complex with **BC8** supports the local C_{2v} symmetry designation. The ^{13}C NMR (CD_2Cl_2) spectrum of the calcium cation complex with **IC8** is not similar to the ^{13}C NMR spectrum of the calcium cation complex with **BC8**, despite the similarity between the ^{1}H NMR spectra. It is not known why the ^{13}C NMR spectra would be antilogous when the ^{1}H NMR spectra are so alike, though this does offer a method for identifying if the complex has constant C_{2v} symmetry or variable symmetry (such as whether the complex is in the solid state or in solution) as for the calcium cation complex with **IC8**.

The 2D COSY NMR (CD_2Cl_2) spectrum was collected on the calcium cation complex with **BC8**. The spectrum confirms the solution C_{2v} symmetry designation.

The calcium cation complex with **BC8** can be seen to have the same symmetry in solution as in the solid state, which is unusual when compared with all of the other calix[8]arene and sulfurised alkylphenol complexes.

5.2.5. Solution State Study on the Calcium Cation Complex with BC8 – The Effect of Co-solvents on the ^{1}H NMR Spectrum

It has been shown that the calix[8]arene ring in complexes with calcium cations prepared from solutions containing DMF has local C_{2v} symmetry in solution, even when the solid state symmetry is not C_{2v}, as in the case of the calcium cation complex with **IC8**. A study was undertaken to investigate the solution symmetry of the calcium cation complex with **BC8** to establish which solvents affected the symmetry of the complex and to see if local C_{2v} symmetry could be converted to local C_{2h} symmetry to determine if the two calcium cation calix[8]arene complexes were inteconvertible. As the differences between the solid state structures of the two calcium cations were in the levels of DMF and hydroxide, it was envisaged that the C_{2v} symmetry complex could be converted to the C_{2h} symmetry complex in solution by adding DMF, which could drive the equilibrium (if present) to the C_{2h} symmetry complex. Other solvents than DMF were also assessed, where ethylene glycol and methanol were added to solutions of the calcium cation complex with **BC8** to understand the role of solvents in the overbasing process and **DMPD** was tested to compare its coordinating ability to DMF (see chapter 4).

The effect of the solvents on the solution state of the calcium cation complex with **BC8** will be discussed in the order of DMF, then ethylene glycol and methanol and then finally **DMPD**.

5.2.5.1. Effect of *N,N*-Dimethylformamide on the Symmetry of the Calcium Cation Complex with BC8 in Solution

As briefly mentioned above, the solid state structure of the calcium cation complex with **BC8** contains DMF and hydroxide groups coordinated to the calcium ions whereas the solid state structure of the calcium cation complex with **IC8** has only DMF molecules as a co-ligand. The ratio of DMF to calix[8]arene in the calcium cation complex with **BC8** is three DMF molecules to one **BC8** anion, whereas in the calcium cation complex with **IC8** the level of DMF is significantly higher giving a ratio of DMF to calix[8]arene of eight DMF molecules to one **IC8** anion. The calixarene rings in these complexes both have local C_{2v} symmetry in solution. The possible interconversion of the two complexes is shown schematically below (figure 148).

$$C_{2v} \underset{^{-}OH}{\overset{DMF}{\rightleftharpoons}} C_{2h}$$

Figure 148. Proposed interconversion of C_{2v} symmetry with C_{2h} symmetry.

It was proposed that by adding DMF to the calcium cation complex with **BC8**, that local C_{2h} symmetry could possibly be observed, which would show that the two solid state calcium cation calix[8]arene complex structures are interconvertible. The opposite route of converting local C_{2h} symmetry to local C_{2v} symmetry was not tested as C_{2h} symmetry is not observed in solution and it would be technically difficult to add hydroxide. To gauge if the calcium cation complex with **BC8** in solution was sensitive to the levels of available DMF, a few drops of deuterated DMF were added to a solution of the complex in deuterated chloroform. Deuterated solvents were utilised so that ^1H NMR spectroscopy could be used to monitor any changes to the complex. Below is the aromatic region of the ^1H NMR spectrum that was obtained upon addition of deuterated DMF to the complex in solution (figure 149).

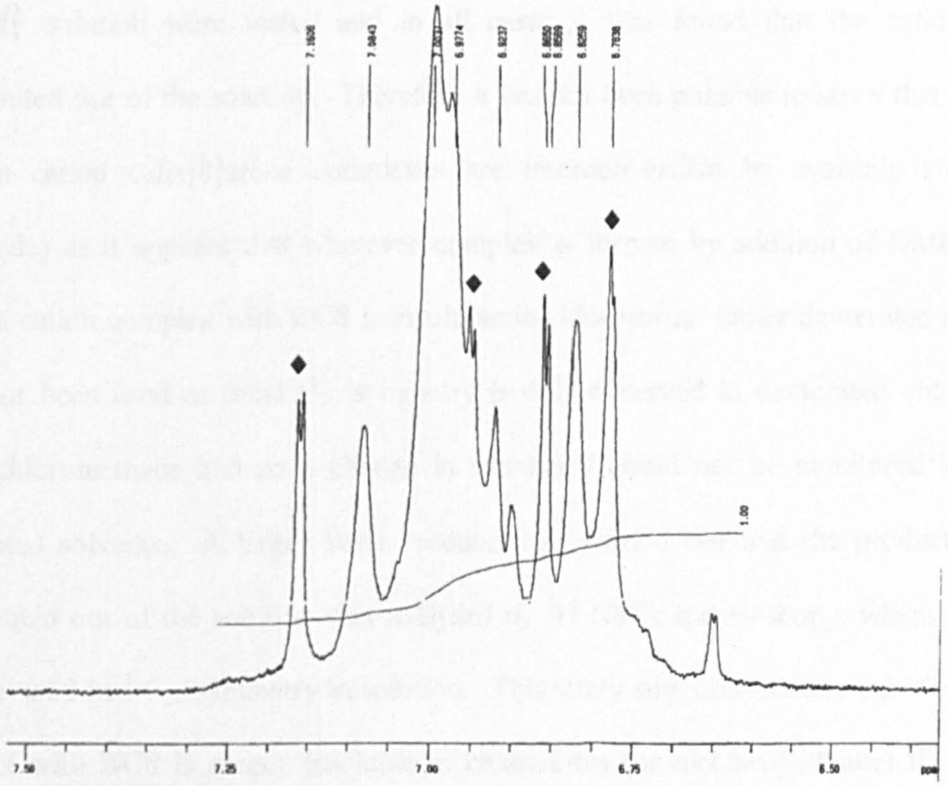


Figure 149. ^1H NMR ($CDCl_3$) spectrum aromatic region for the calcium cation complex with BC8 plus deuterated DMF.

The ^{1}H NMR spectrum shows a mixture, where the broad singlet is due to decomposition of the complex to **BC8** and the peaks at approximately 7.16, 6.90, 6.85 and 6.78ppm (◆) represent the C_{2v} symmetry calixarene within the complex. Other peaks can be seen which are due to a change of local C_{2v} symmetry to another symmetry, caused by the addition of DMF. The mixture may contain a calixarene ring with local C_{2h} symmetry (as would be observed by two singlets and two doublets with equal intensity), though it is difficult to be certain.

To investigate the change from C_{2v} symmetry quantitatively, aliquots containing very low concentrations of DMF were added to the calcium cation complex with **BC8** in deuterated chloroform and the ^{1}H NMR spectrum monitored after each addition. Very small quantities of DMF sharpened up the NMR spectrum, especially for the alkyl proton peaks. Unfortunately it was found that continuing to add aliquots of the DMF containing solution caused solid to precipitate out of the solution. Other concentrations of DMF solution were tested and in all cases it was found that the solid readily precipitated out of the solution. Therefore it has not been possible to show that the two calcium cation calix[8]arene complexes are interconvertible by available DMF (or hydroxide) as it appears that whatever complex is formed by addition of DMF to the calcium cation complex with **BC8** is insoluble in chloroform. Other deuterated solvents have not been used as local C_{2v} symmetry is only observed in deuterated chloroform and dichloromethane and so a change in symmetry could not be monitored in other deuterated solvents. A larger scale reaction was carried out and the product which precipitated out of the solution was analysed by ^{1}H NMR spectroscopy, which showed that the solid had C_{2v} symmetry in solution. This study suggests that the calcium cation complex with **BC8** is simply insoluble in chloroform (or dichloromethane) if DMF is present above a low concentration. The attainment of the mixed symmetry ^{1}H NMR spectrum was probably enabled by a very small time delay between the addition of DMF and the analysis of the solution, which 'caught' the solution before solid could precipitate out of the solution. This spectrum does show that the solution state of the calcium cation complex with **BC8** is sensitive to solvents that are present and that possibly the two calcium cation calix[8]arene complexes are interconvertible.

5.2.5.2. Effect of Ethylene Glycol and Methanol on the Symmetry of the Calcium Cation Complex with BC8 in Solution

As shown above, addition of DMF to a solution of calcium cation complex with **BC8** affects the symmetry of the complex within the solution. To investigate whether other solvents could also have an effect on the C_{2v} symmetry of the complex, ethylene glycol and methanol were added as low concentration aliquots to a solution of the calcium cation complex with **BC8** in deuterated chloroform by the same method used for additions of DMF aliquots.

Ethylene glycol is used in the overbasing process as it has been found to improve the efficiency of the process, but the role of ethylene glycol is not known (see chapter 4). Therefore the effect of ethylene glycol on the calcium cation complex with **BC8** with a calcium hydroxide core was assessed to study the purpose of ethylene glycol in the overbasing process. After addition of three drops of ethylene glycol-containing solvent solution to the calcium cation complex with **BC8** in deuterated chloroform the ^1H NMR spectrum was seen to refine, as was observed for DMF. After addition of six drops, the spectrum became less resolved. A small impurity of the tetrabutylammonium cation in the calcium cation complex with **BC8** solid product used, observed at 3.4ppm, shifted with addition of six drops of ethylene glycol-containing solvent solution, probably to become overlapped by the calcium cation complex alkyl proton doublet at 3.2ppm. It was observed that ethylene glycol appears to have the greatest influence on impurities in the complex rather than the complex itself.

Methanol was selected as complexes prepared from methanol as the main solvent (without any DMF) are either salts or mixtures containing a small quantity of a low symmetry complex (local C_1 symmetry) and as methanol is sometimes used as a solvent in the overbasing process. It was found that addition of a few drops of d_1-methanol-containing solvent solution resolved the ^{1}H NMR spectrum of the C_{2v} symmetry complex. This is the same as the effect observed for small concentration additions of DMF and for ethylene glycol.

This study has shown that small concentration additions of solvents to the calcium cation complex with **BC8** in solution refines the ^{1}H NMR spectrum of the complex. Larger concentrations were not assessed due to the problems observed with DMF additions and the lack of effect of the small concentration additions.

5.2.5.3. Effect of DMPD on the Symmetry of the Calcium Cation Complex with BC8 in Solution

DMPD was introduced in chapter 4 as a mimic for ethylene glycol and as a potential alternative to DMF. A rough test on the effect of **DMPD** on the calcium cation complex with **BC8** was carried out to see if **DMPD** gave the same effects as the other solvents tested. A very small quantity of **DMPD** was added to a solution of the calcium cation complex with **BC8** in deuterated chloroform and the ^{1}H NMR spectrum of the solution was collected. The spectrum is broader than the spectrum for the complex without the addition of **DMPD**. The level of **DMPD** in the solution is very low as the peaks for **DMPD** (two singlets at approximately 3.53 and 3.06ppm with a ratio of 2:3) can only just be identified. More **DMPD** was added to the solution (approximately equivalent mass to calcium cation complex with **BC8**) and the ^{1}H NMR spectrum was collected. The aromatic region for the spectrum can be seen below (figure 150).

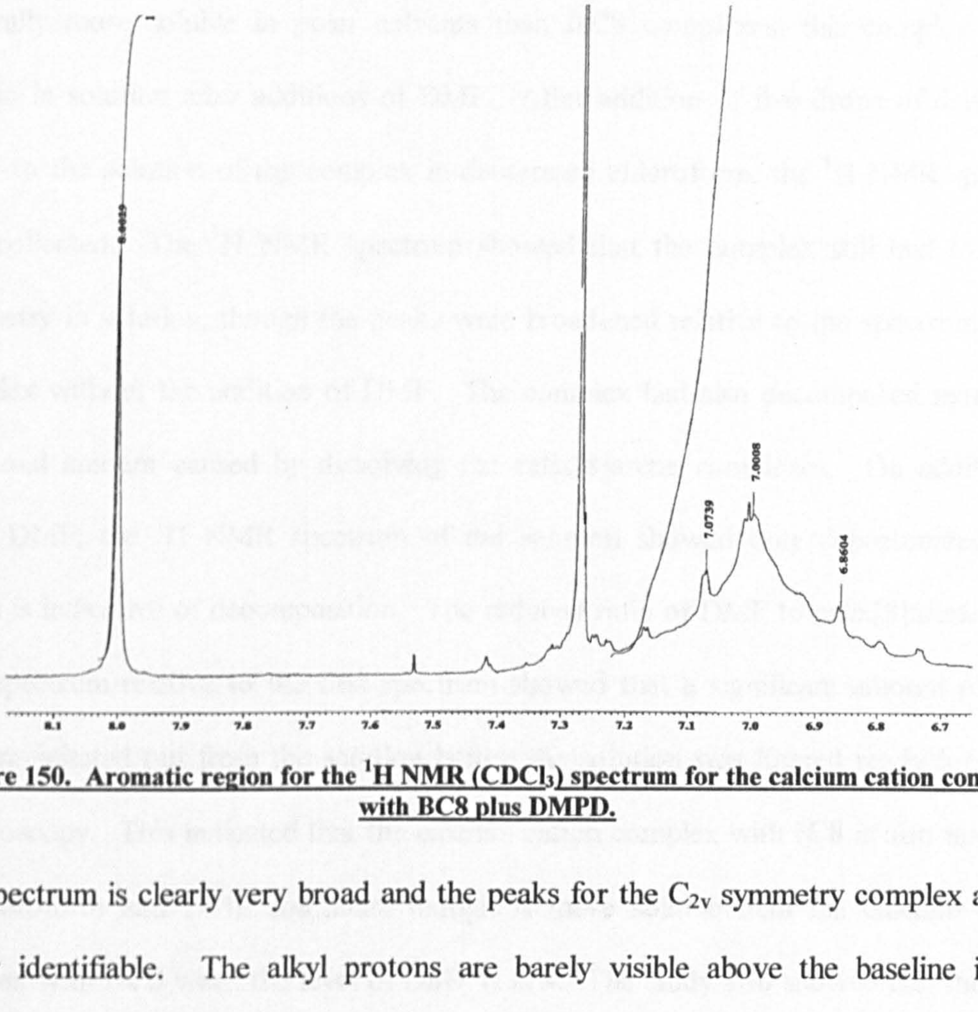


Figure 150. Aromatic region for the ^{1}H NMR ($CDCl_3$) spectrum for the calcium cation complex with BC8 plus DMPD.

The spectrum is clearly very broad and the peaks for the C_{2v} symmetry complex are no longer identifiable. The alkyl protons are barely visible above the baseline in the spectrum. On addition of more **DMPD** to the solution, the ^{1}H NMR spectrum of the solution becomes very broad and 'salt-like'.

It can be seen that **DMPD** has the greatest effect on the solution symmetry of the calcium cation complex with **BC8**, though as the additions of **DMPD** make the spectrum broader, the effect cannot be quantified to give symmetry information. Unlike DMF, additions of **DMPD** does not cause solid to precipitate out from the solution.

5.2.5.4. Effect of *N,N*-Dimethylformamide on the Symmetry of the Calcium Cation Complex with IC8 in Solution

To complete the study, the effect of DMF on a calcium cation complex with **IC8** (**22**), which had local C_{2v} symmetry in solution was assessed. As **IC8** complexes are generally more soluble in polar solvents than **BC8** complexes, this complex should remain in solution after additions of DMF. After addition of five drops of deuterated DMF to the solution of the complex in deuterated chloroform, the ^1H NMR spectrum was collected. The ^1H NMR spectrum showed that the complex still had local C_{2v} symmetry in solution, though the peaks were broadened relative to the spectrum of the complex without the addition of DMF. The complex had also decomposed more than the usual amount caused by dissolving the calix[8]arene complexes. On addition of more DMF, the ^1H NMR spectrum of the solution showed only deprotonated **IC8**, which is indicative of decomposition. The reduced ratio of DMF to calix[8]arene in the final spectrum relative to the first spectrum showed that a significant amount of solid had precipitated out from the solution before the solution was filtered ready for NMR spectroscopy. This indicated that the calcium cation complex with **IC8** is also insoluble in chloroform and DMF solutions, though is more soluble than the calcium cation complex with **BC8** when the level of DMF is low. The study also showed that the local C_{2v} symmetry solution structure of the complex was sensitive to DMF, leading to decomposition rather than a change in symmetry.

5.2.5.5. Summary on the Effect of Co-solvents on the Calcium Cation Complex with BC8 in Solution

Overall, the solution state of the calcium cation complex with **BC8** has been shown to be stable to small concentrations of other solvents. Additions of larger concentrations of solvents, such as DMF, usually cause the complex to become insoluble and precipitate out from the solution. It has been shown that DMF and **DMPD** can cause the symmetry of the complex in solution to change from local C_{2v} symmetry. The calcium cation complex with **IC8** has been shown to decompose in the presence of excess DMF.

5.2.6. Effect of Carbon Dioxide on the Calcium Cation Complex with BC8

The calcium cation complex with **BC8** had been prepared under a nitrogen atmosphere to ensure that carbon dioxide did not get into the reaction mixture. This was done so that calcium hydroxide cores could be obtained and then the effect of carbon dioxide upon these cores could be investigated. Carbon dioxide is included in the overbasing process to create a calcium carbonate core in the overbased detergent product from the calcium hydroxide precursor core. The carbon dioxide is blown through a solution containing the overbased detergent precursor and the calcium hydroxide core is 'carbonated'.[5] As the calcium cation complex with **BC8** has a calcium hydroxide core, the effect of carbon dioxide upon this complex was investigated. It was anticipated that with the small size of the core ($Ca_4(OH)_4$), understanding the effect of the carbon dioxide would be simplified. As the calcium cation complex with **BC8** has the same structure in the solid state and in solution (which is very unusual amongst the complexes discussed up to this point), the reaction of the complex with carbon dioxide could be monitored by ^{1}H NMR spectroscopy. Any changes to the symmetry of the complex in solution could be taken to be changes to the solid state symmetry of the complex. Carbon dioxide gas and bis-(4-nitrophenyl)-carbonate have been used as sources of carbonate in this study. Bis-(4-nitrophenyl)-carbonate was used as it offers a route by which controllable quantities of carbonate relative to the calcium cation complex with **BC8** can be added, it is less reactive than carbon dioxide gas and the reaction can also be followed colorimetrically. The reactions with the two sources of carbonate are discussed below.

5.2.6.1. Carbon Dioxide Gas

When a solution of the calcium cation complex with **BC8** in deuterated DCM was left under an atmosphere of carbon dioxide gas, solid precipitated from the solution. The solid was found to be calcium carbonate (calcite, by IR spectroscopy) with only **BC8** remaining in the solution. This indicated that the complex was reactive towards carbon dioxide. By controlling the amount of carbon dioxide above the solution it was observed that even by using the minimum volume of carbon dioxide that could be added, this still caused rapid precipitation of calcium carbonate from the solution. Using carbon dioxide gas it was not possible to add very small, known amounts of carbon dioxide to a solution or go below a certain molarity of carbon dioxide, therefore, a less reactive source of carbonate was used; bis-(4-nitrophenyl)-carbonate.

5.2.6.2. Bis-(4-nitrophenyl)-carbonate

Bis-(4-nitrophenyl)-carbonate was tested as a source of carbonate that could be added to a solution in known quantities. Bis-(4-nitrophenyl)-carbonate is a very reactive molecule towards nucleophiles such as water or hydroxide. There is a large δ+ on the carbonate carbon atom due to the electron withdrawing nature of the phenyl rings, which is reduced if the carbon atom can become tetrahedral instead of planar, at the expense of losing the double bond to the oxygen atom. The scheme for the generation of the carbonate anion from bis-(4-nitrophenyl)-carbonate is shown below (figure 151).

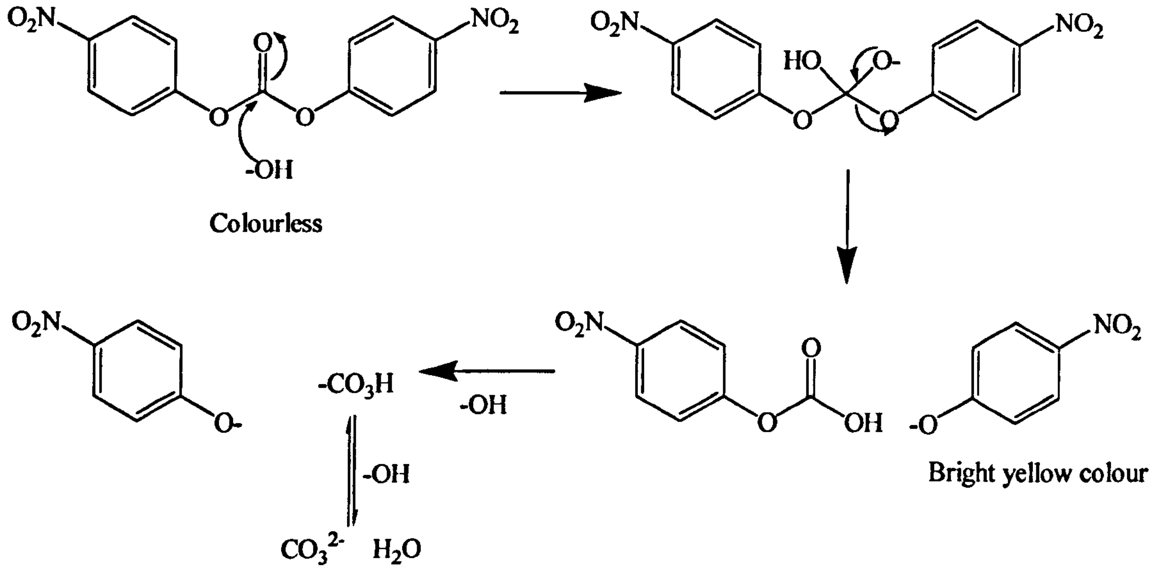


Figure 151. Mechanism of attack of a nucleophile (OH-) on bis(4-nitrophenyl)carbonate.

The double bond to the oxygen is then regained by the loss of the leaving group, p-nitrophenate, identified by a bright yellow colour. This enables alternative analytical methods to be used to monitor the progression of the reaction, such as colorimetric methods. The molecule can then react further to yield the carbonate anion. Bis-(4-nitrophenyl)-carbonate was therefore chosen as a reactive source of carbonate which could be added in known quantities (as a standard solution in $CDCl_3$) to the calcium cation complex with **BC8** in solution.

^{1}H NMR ($CDCl_3$) spectra collected on solutions of the calcium cation complex with **BC8** with one mole equivalent of bis-(4-nitrophenyl)-carbonate to complex added, even after the addition of deuterated DMF to stabilise the solution, showed that the complex had reacted with the source of carbonate to yield free **BC8**$^{x-}$. As soon as the bis-(4-nitrophenyl)-carbonate solution was added, the solution developed a bright yellow colouring indicative of the loss of the p-nitrophenolate leaving group. This showed that the reaction of the complex with this source of carbonate is very fast. The reaction was found to be too fast to be monitored by ^{1}H NMR spectroscopy.

5.2.6.3. Summary of Reactivity of the Calcium Cation Complex with BC8 with Carbon Dioxide

It has been shown that the calcium cation complex with **BC8** is very reactive towards carbon dioxide leading to rapid decomposition to **BC8** and calcium carbonate. It has not been possible to isolate any of the intermediates formed before decomposition due to the speed of decomposition. This study shows that the conversion of the calcium hydroxide core overbased detergent precursor to a calcium carbonate core overbased detergent is a very facile reaction.

The findings of this study are supported by the observations that whenever the complex is dissolved, some decomposition is observed (see 5.2.4.) and the observations from elemental analysis. Analytical data from elemental analysis on the percentage composition of carbon, hydrogen and nitrogen in the solid complex always shows decomposition. These observations are probably related to the exposure of the samples to atmospheric carbon dioxide.

5.2.7. Summary

A calcium cation complex with **BC8** has been prepared which has a calcium hydroxide core. This complex may be considered to be a model for the overbased detergent precursor with a calcium hydroxide core. The calixarene in the complex has local C_{2v} symmetry in the solid state and in solution, where the solution structure is little affected by the addition of small volumes of coordinating solvents. DMF and **DMPD** have been shown to have the greatest effect on the solution state of the complex. The overbasing process has been investigated on the complex, which has shown that the carbonation of a calcium hydroxide core to a calcium carbonate core (albeit unstable) is a very facile reaction.

5.3. Calcium Cation Complex with p-*tert*-Butylcalix[8]arene (Two)

5.3.1. Introduction

During this work it was frequently observed that products from reactions of the calix[8]arene molecules with calcium cations were mixtures by ^1H NMR spectroscopy, where the mixture contained mainly either free calixarene or calixarene salt plus a small quantity of a low symmetry calixarene complex. This complex had very low local C_1 symmetry and when the mixture was recrystallised, either pure calixarene or inorganic calixarene salt (see section 3.4.2.) was obtained.

In this section, these low symmetry complexes will be discussed, starting with the conditions which have generated this complex as a co-product and then moving on to present the structure of a low symmetry complex.

5.3.2. Preparation of Mixtures Containing a Low Symmetry Calix[8]arene Complex

Reactions of **BC8** or **IC8** with a calcium salt under a range of conditions gave either calix[8]arene or the calix[8]arene organic salt, plus a small quantity of a low symmetry complex. The solvents which gave a mixture are shown in the table below (table 64) along with the major product.

Calix[8]arene	Solvent/s	Major product
IC8	Methanol and DMI	**IC8**
BC8	Methanol	Organic salt
BC8	DMI	Organic salt
BC8	Methanol/DMI	**BC8**
BC8	Methanol/DEF	**BC8**
BC8	Diethyl ether/DEF	**BC8**

Table 64. Reactions which gave the low symmetry complex in a very low yield, where DMI is 1,3-dimethylimidazolidinone, DMF is *N,N*-dimethylformamide and DEF is *N,N*-diethylformamide.

It can be seen that only one solvent mixture gave a low symmetry complex with **IC8**, which is due to the increased polar solvent solubility of **IC8** when compared to **BC8**, resulting in products rarely precipitating from solutions when the calix[8]arene ligand was **IC8**. DMI and DEF were tested as these solvents are alternatives to DMF. DMI has a more fixed structure than DMF, which simplifies structure determinations by single crystal x-ray diffraction, and is less harmful. DEF is simply DMF with ethyl rather than methyl groups bound to the nitrogen atom of the molecule. Intuitively, the products from methanol and DEF and from diethyl ether and DEF, where DEF was used as six mole equivalents to calixarene, should have been very similar to the calcium cation complex with **BC8** discussed above (**37**). The reaction from methanol and DMI solution with **BC8** was repeated with twenty mole equivalents of calcium cations to calixarene (rather than the normal ratio of four to six mole equivalents of calcium cations to calixarene) to investigate if the low symmetry complex was being formed in a low yield due to a lack of available calcium cations and this reaction gave the same product as for the lower concentration of calcium cations. The aromatic regions of the ^{1}H NMR spectra for two of the products are shown below (figures 152 and 153).

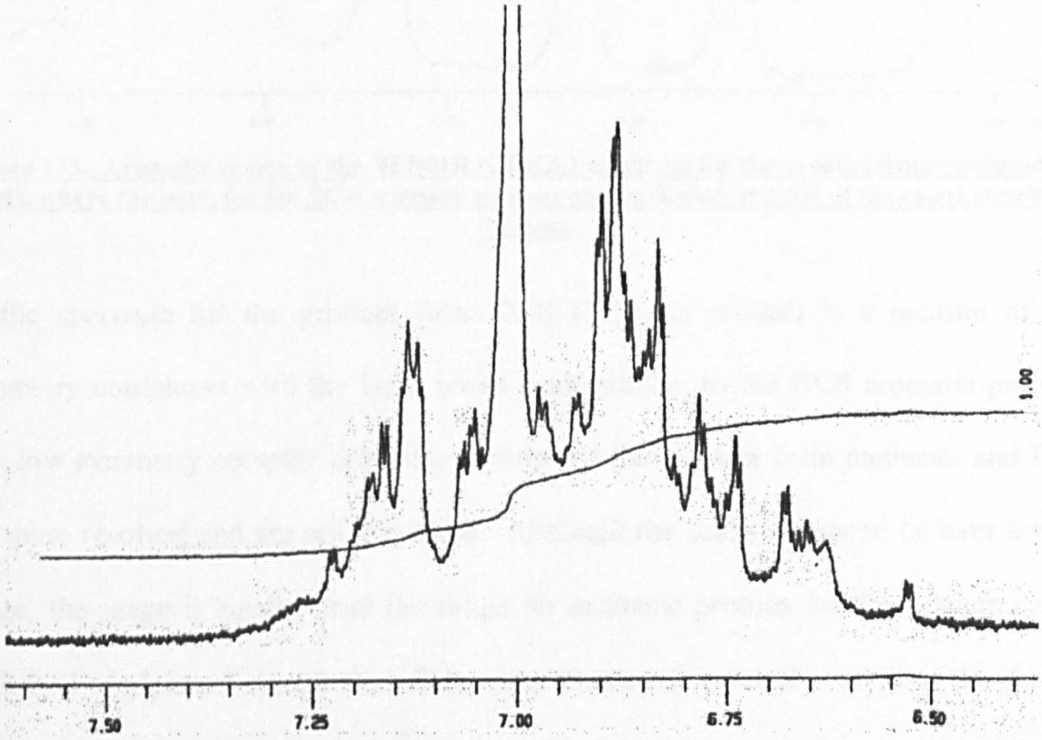


Figure 152. ^{1}H NMR (CD_2Cl_2) spectrum aromatic region for the calcium cation complex with BC8 prepared from DMI, where the major product was an organic salt with BC8 (20).

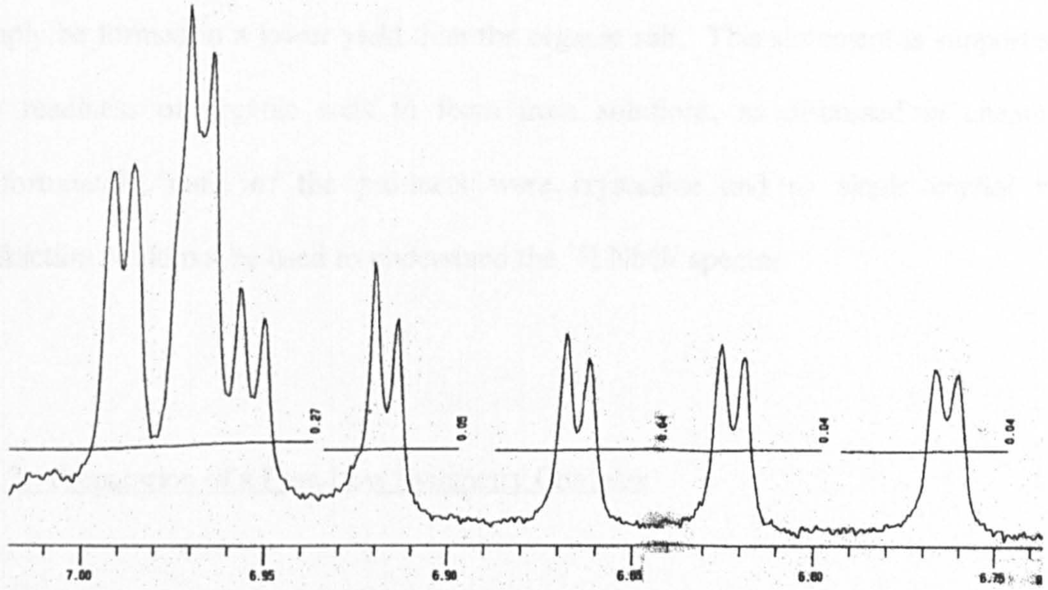


Figure 153. Aromatic region of the ^{1}H NMR (CD_2Cl_2) spectrum for the product from methanol and DMI, where the peak for the BC8 aromatic protons occurs slightly outside of the range shown, at 7.2ppm.

In the spectrum for the product from DMI (**20**), the product is a mixture of low symmetry complexes with the large broad peak relating to the **BC8** aromatic protons. The low symmetry complex aromatic protons for the product from methanol and DMI are more resolved and are not a mixture. Although the peaks appear to be over a wide range, the range is smaller than the range for aromatic protons for the calcium cation sulfurised alkylphenol complexes. These spectra are representative of all of the spectra obtained on the low symmetry complexes where they are present as a mixture in the product with calix[8]arene or calix[8]arene salt. The deuterated solvent used to analyse the samples has been found to have little effect on the spectrum, though for most of the products, only one or two deuterated solvents could be used to dissolve the product due to the low solubilities of calix[8]arene products. For all of the ^{1}H NMR spectra obtained, the low symmetry complex is present in a very small quantity in the product. It is possible that the products where free calix[8]arene is the major product, may actually be fluxional in solution and time averaging to show mainly calix[8]arene or that the product is decomposing when it is isolated to give mainly free calix[8]arene. For the products with organic calixarene salt as the major product, these complexes may simply be formed in a lower yield than the organic salt. This statement is supported by the readiness of organic salts to form from solutions, as discussed in chapter 3. Unfortunately, none of the products were crystalline and so single crystal x-ray diffraction could not be used to understand the ^1H NMR spectra.

5.3.3. Preparation of a Pure Low Symmetry Complex

Calcium cation complexes with calix[8]arene molecules from DMF (or mixtures containing DMF) have so far all had local C_{2v} symmetry in solution. A study to see if the order of addition of reagents could have an impact on the final product that was formed was carried out by adding tetrabutylammonium hydroxide last to a reaction mixture. Tetrabutylammonium hydroxide solution (1.0M in methanol) was added dropwise to a mixture containing **BC8** and calcium ions (from calcium bromide) in DMF. Approximately one drop of tetrabutylammonium hydroxide caused all of the **BC8** to dissolve, which is unsurprising as **BC8** will dissolve slowly in DMF without tetrabutylammonium hydroxide or any other basic material if sufficient time is allowed. After the addition of approximately 1.15ml of tetrabutylammonium hydroxide (which equates to seven or eight equivalents of tetrabutylammonium hydroxide to **BC8**), the solution developed a slight turbidity, which did not disappear on continued stirring. It is likely that the turbidity was due to a small amount of precipitated calcium hydroxide, which had formed with the high concentrations of hydroxide in the solution. Masses of white needles formed from the solution over the two days and smaller crystals formed from the solution over the following weeks in a lower quantity. The ^1H NMR (CD_2Cl_2) spectrum of the product from the reaction indicated that the product was a mixture of at least two low symmetry complexes. It is probable that the needle-like crystalline product was the kinetic product and the smaller crystalline product was the thermodynamic product. It was not possible to sample one type of crystalline material and so the ^{1}H NMR spectrum could not be deconvoluted. The main crystalline product was found to be unsuitable for single crystal x-ray diffraction.

The reaction was repeated with tetrabutylammonium hydroxide added to the point just before the formation of turbidity. Within one day, powder and a crystalline material had formed from the solution, where at first there was more powder present than crystalline material and over time the powder disappeared to leave only crystalline material (over one week). As for the first reaction, it appeared that two products were formed, where the powder was the kinetic product and the crystalline material was the thermodynamic product. Once only crystalline material was present, single crystal x-ray diffraction and NMR spectroscopy (^{1}H NMR, ^{13}C NMR and 2D COSY spectroscopy) were performed on the crystals. These results showed that a pure low symmetry calcium cation complex with **BC8** had been prepared. The solid state structure and the solution state structure of the complex are discussed below. The complex is very interesting as it has a larger calcium hydroxide core than the calcium cation complex with **BC8** discussed above.

The complex that has been characterised has a decacalcium cation core, which is unusual. This complex was formed under more basic conditions than the calcium cation complex with **BC8** with a tetracalcium cation core (**37**), which suggests that in the presence of excess hydroxide anions a decacalcium cation core is formed. It may be that a tetracalcium cation core is formed under slightly basic conditions and then as the basicity is increased, the complex that forms has a decacalcium core. When the basicity is further increased, calcium hydroxide is formed, which precipitates out from the solution (hence the turbidity observed for the first attempt to prepare the pure low symmetry complex).

5.3.4. Solid State Structure of the Calcium Cation Complex with BC8 (38)

A crystalline complex of calcium cations with **BC8** was grown from DMF solution. The complex consists of two calixarene rings, ten calcium cations, eight hydroxide anions, two methoxide anions and ten DMF molecules, with five free DMF molecules in the lattice, to give the formula $(Ca^{2+})_{10}(\mathbf{BC8}^{5-})_2(OH^-)_8(OMe^-)_2(DMF)_{10}.5DMF$. The complex has a calcium hydroxide core, which is sandwiched between two **BC8** calixarene rings each with –5 charge. The calixarene rings are equivalent and have local C_1 symmetry with no easily identifiable conformation type. The –5 charge on the calixarene rings is stabilised by intramolecular hydrogen-bonding between phenolic oxygen atoms. The core of the complex is a calcium hydroxide core, consisting of ten calcium cations with six different calcium cation environments and fourteen oxygen atoms, where the oxygen atoms are from eight bridging hydroxide anions, four calixarene oxygen atoms and two methoxide anions (μ_3-OMe). The core is coordinated to ten DMF molecules and two calixarene rings, where all of the oxygen atoms in the two calixarene rings are coordinated to calcium cations. The complex is quite disordered at the periphery as can be seen by the large size of some of the outermost atoms in the structure.

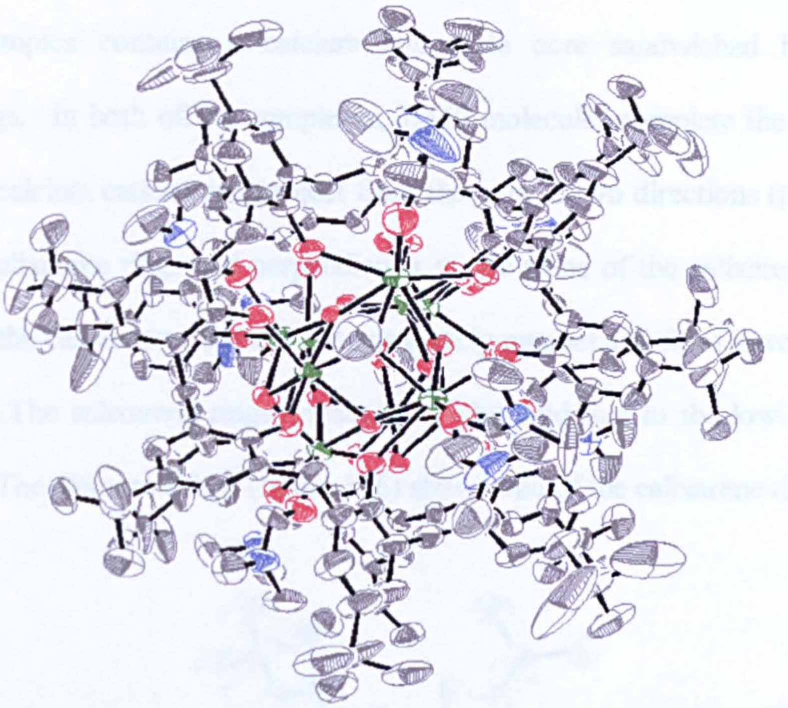


Figure 154. Structure of the calcium cation complex with BC8, $(Ca^{2+})_{10}(BC8^{5-})_2(OH^-)_8(OMe^-)_2(DMF)_{10}.5DMF$, where the hydrogen atoms and the free DMF molecules have been removed for clarity.

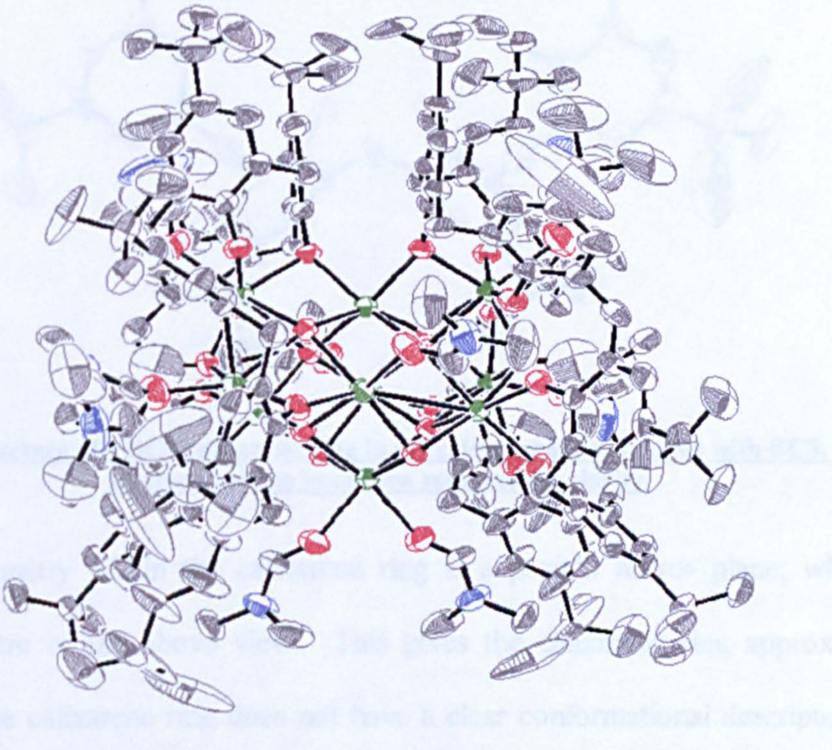


Figure 155. Side view of the calcium cation complex with BC8, where the hydrogen atoms and the free DMF molecules have been removed for clarity.

As for the other calcium cation complex with **BC8** that had a calcium hydroxide core (**37**), this complex contains a calcium hydroxide core sandwiched between two calixarene rings. In both of the complexes, DMF molecules complete the coordination sphere of the calcium cations and project from the core in two directions (parallel to the plane of the calixarene rings and perpendicular to the plane of the calixarene rings). In this complex, the calixarene rings are not completely parallel and form a wedge shape to the complex. The calixarene rings appear quite cluttered due to the low symmetry of the complex. The diagram below (figure 156) shows one of the calixarene rings.

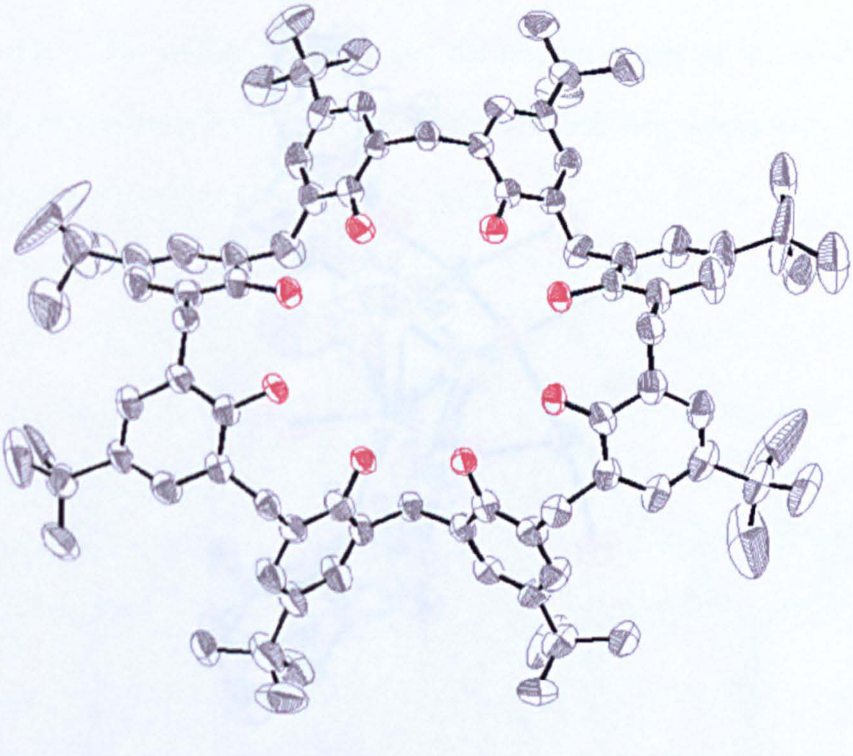


Figure 156. Structure of a BC8 calixarene ring in the calcium cation complex with BC8, where the hydrogen atoms have been removed for clarity.

The only symmetry within the calixarene ring is a pseudo mirror plane, which runs down the centre of the above view. This gives the calixarene ring approximate C_s symmetry. The calixarene ring does not have a clear conformational descriptor. Most of the calixarene ring has pleated loop conformation, though two phenolic units within the ring spoil this conformation by orientating in the opposite direction to the pleated loop (the bottom two phenolic units in the above view). The best conformation descriptor that can be given is pinched pleated loop conformation, though this description is clearly inadequate in describing the shape of the calixarene ring.

The shape of the calixarene ring allows the oxygen atoms of the phenolic units to point in approximately the same direction, towards the core, where the core is partially included within the central cavity of the calixarene ring. This is shown more clearly in the diagram below (figure 157).

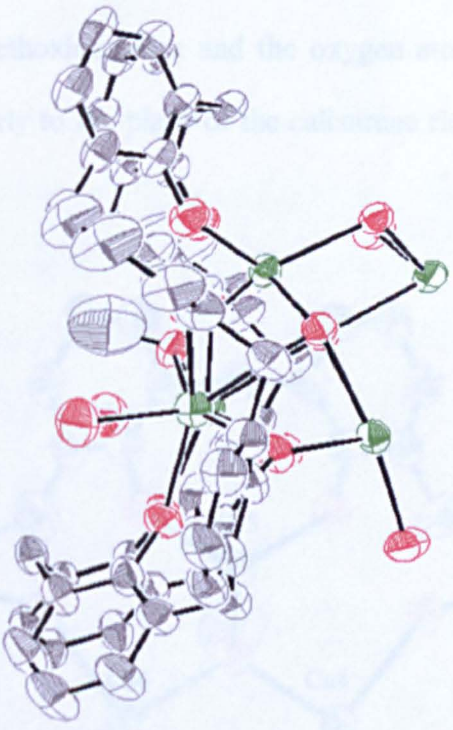


Figure 157. Side view of the asymmetric unit of the calcium cation complex with BC8, where the *tert*-butyl groups, the hydrogen atoms, the DMF molecules (except the oxygen atoms) and the free DMF molecules have been removed for clarity.

The core of the complex is mainly sandwiched between the two calixarene rings, though (as shown in the above view) some of the core can be seen to be included within the central cavity of the calixarene. This is very different to the other calixarene complex with a calcium hydroxide core (**37**), where the core was not included in the cavities of the calixarene rings and only one DMF molecule sat within each calixarene ring cavity.

In the other calcium hydroxide complex (**37**), the calixarene ring was able to avoid including the core by only coordinating to the core *via* four phenolic oxygen atoms, which enabled the calixarene ring to adopt its preferred pleated loop conformation[96, 196, 197] and keep the calcium cations and hydroxide anions out of the hydrophobic central cavity. In this complex, the calixarene ring coordinates to the core *via* all eight of its phenolic oxygen atoms (as shown below in figure 158), which forces the core to partially sit within the cavity. Molecular dynamics calculations have shown that overbased detergents cores with calixarene surfactant molecules are probably partially included within the calixarene cavity and so the decacalcium cation complex is a good model for this.[7] The methoxide anion and the oxygen atoms of the DMF molecules which point perpendicularly to the plane of the calixarene ring can be seen in the above diagram (figure 157).

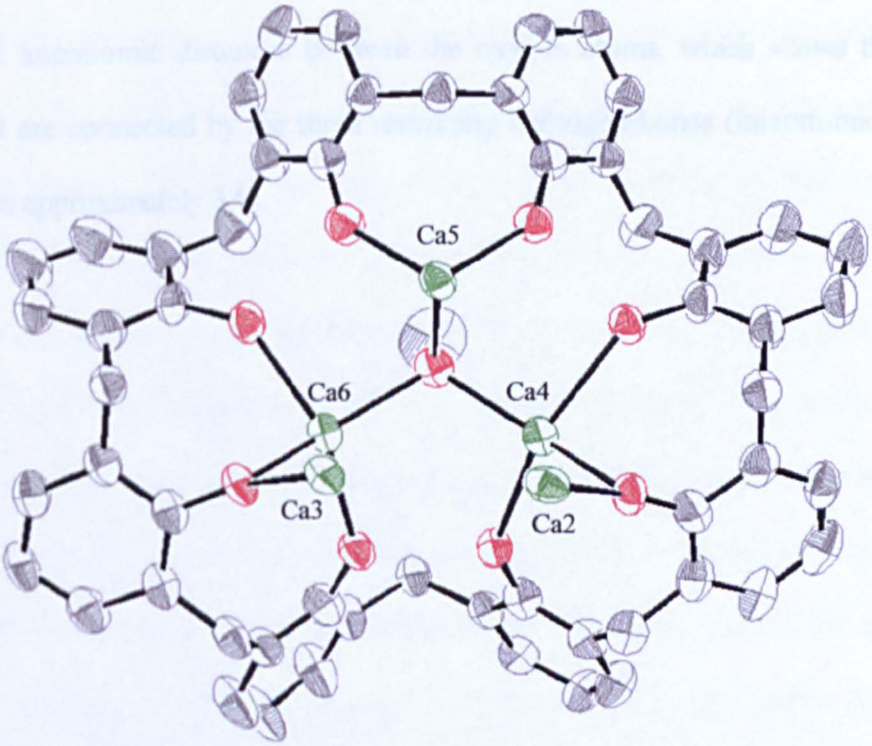


Figure 158. View of the coordination of the calixarene ring to the calcium cations, where the hydrogen atoms and *tert*-butyl groups have been removed for clarity. The methoxide anion has been included.

The above diagram (figure 158) shows one calixarene ring from the complex with all of the bonds from that ring to the calcium cations of the core. A methoxide anion has also been included in the view above. It can be seen that every phenolic oxygen atom is coordinated to at least one calcium cation. Two of the phenolic oxygen atoms bridge two calcium cations (O1 and O13, μ_2-O), where one of the calcium cations is terminally bound to the calixarene ring (Ca2 and Ca3), one calcium cation bridges two phenolic oxygen atoms (Ca5) and two calcium cations bridge three phenolic oxygen atoms (Ca4 and Ca6). Overall, this results in one calixarene ring coordinating to five calcium cations.

The calixarene ring has a –5 charge on it, therefore five of the phenolic hydrogen atoms have been removed. This charge-balances the complex. The –5 charge is stabilised by hydrogen-bonding between phenolic oxygen atoms and the diagram below (figure 159) shows the interatomic distances between the oxygen atoms, which shows the oxygen atoms that are connected by the three remaining hydrogen-bonds (interatomic distances of less than approximately 3Å).

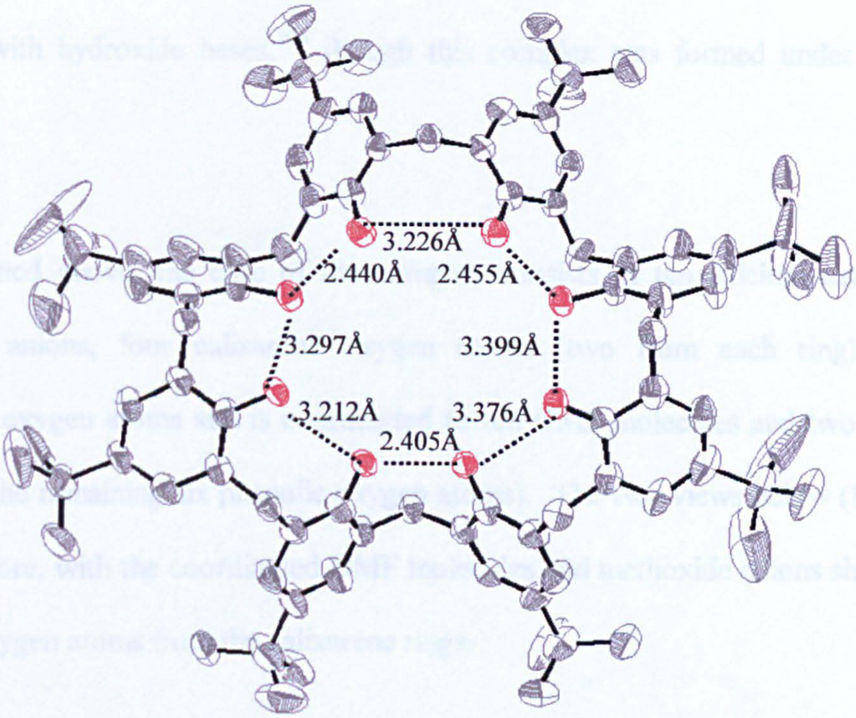


Figure 159. One calixarene ring from the calcium cation complex with BC8, showing interatomic distances between phenolic oxygen atoms.

The above diagram (figure 159) shows that three of the interatomic distances between phenolic oxygen atoms are small enough for hydrogen-bonding to be occurring between the oxygen atoms. The distances infer strong hydrogen-bonding as they are less than 2.5Å.[200, 201] The remaining charge is stabilised by two of the phenolic oxygen atoms being included within the core of the complex (O1 and O13). The phenolic hydrogen atoms have not been characterised and so the exact positions of the phenolic hydrogen atoms is unproven, but can be inferred from the oxygen atom to oxygen atom distances. The two phenolic oxygen atoms which are not involved in hydrogen-bonding within the ring are O1 and O13, which are the oxygen atoms that are included in the core of the complex. O1 has the shortest phenolic carbon atom to oxygen atom bond length (1.319Å) for all of the phenolic units, where the range for the other phenolic carbon atoms to oxygen atoms is 1.352-1.397Å.

A charge of –5 is high for calix[8]arenes, as –4 is normally the maximum that can be achieved with hydroxide bases,[190] though this complex was formed under very basic conditions.

As mentioned above, the core of the complex consists of ten calcium cations, eight hydroxide anions, four calixarene oxygen atoms (two from each ring) and two methoxide oxygen atoms and is coordinated to ten DMF molecules and two calixarene rings (*via* the remaining six phenolic oxygen atoms). The two views below (figure 160) show the core, with the coordinated DMF molecules and methoxide anions shown along with the oxygen atoms from the calixarene rings.

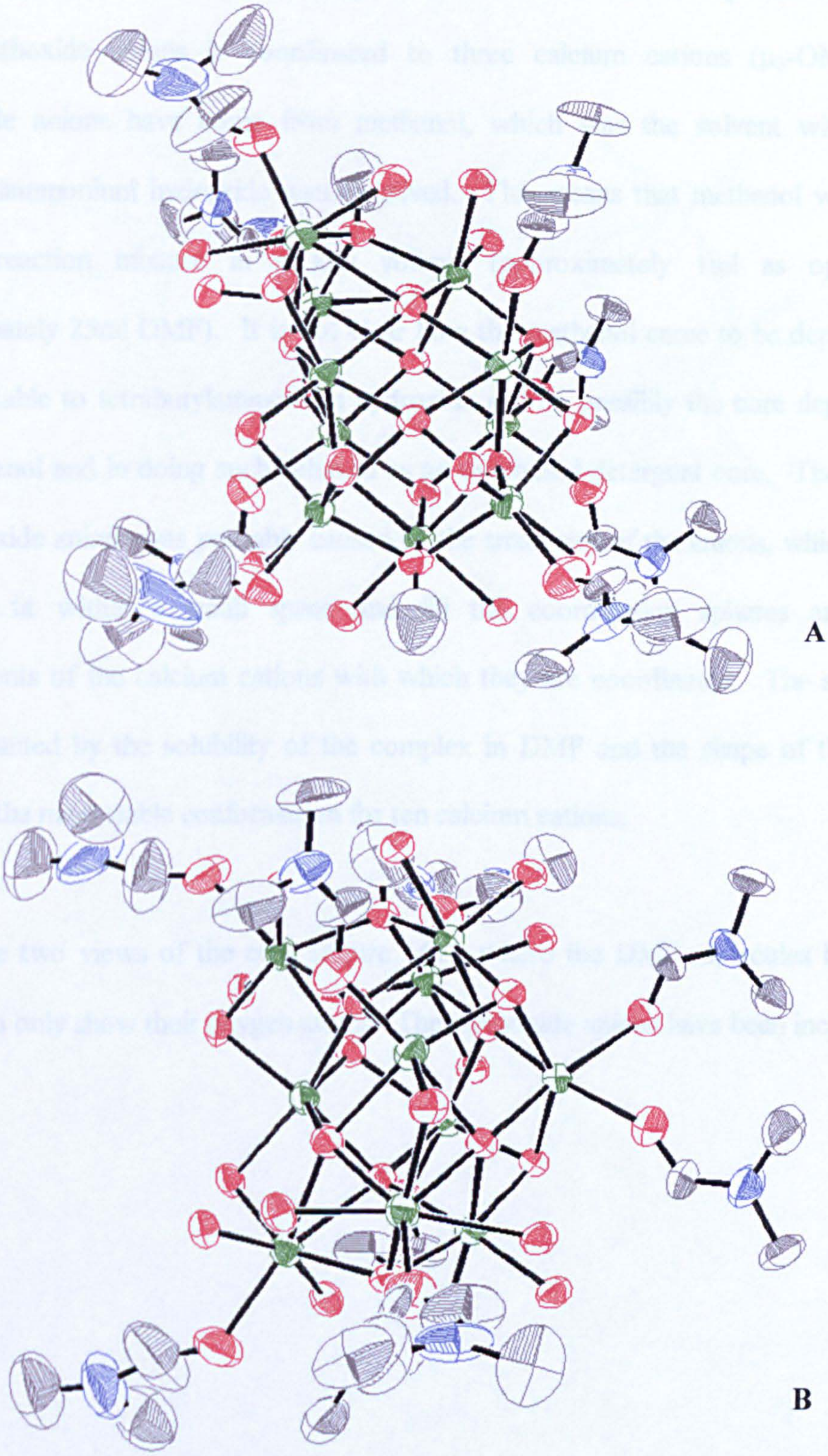


Figure 160. Structure of the core of the calcium cation complex with BC8 with the coordinated DMF molecules. Hydrogen atoms have been removed for clarity.

Four of the coordinated DMF molecules sit within the calixarene sandwich, whereas the other DMF molecules sit within the cavities of the calixarene rings with three DMF molecules within each calixarene ring. The methoxide anions 'cap' the core, where each methoxide anions is coordinated to three calcium cations (μ_3-OMe). The methoxide anions have come from methanol, which was the solvent within which tetrabutylammonium hydroxide was dissolved. This means that methanol was present in the reaction mixture in a low volume (approximately 1ml as opposed to approximately 25ml DMF). It is not clear how the methanol came to be deprotonated, as it is stable to tetrabutylammonium hydroxide and so possibly the core deprotonated the methanol and in doing such behaved as an overbased detergent core. The inclusion of methoxide anions was probably caused by the small size of the anions, which enabled them to fit within a small space and fill the coordination spheres and charge requirements of the calcium cations with which they are coordinated. The size of the core is limited by the solubility of the complex in DMF and the shape of the core is probably the most stable conformation for ten calcium cations.

Below are two views of the core (figure 161), where the DMF molecules have been reduced to only show their oxygen atoms. The methoxide anions have been included.

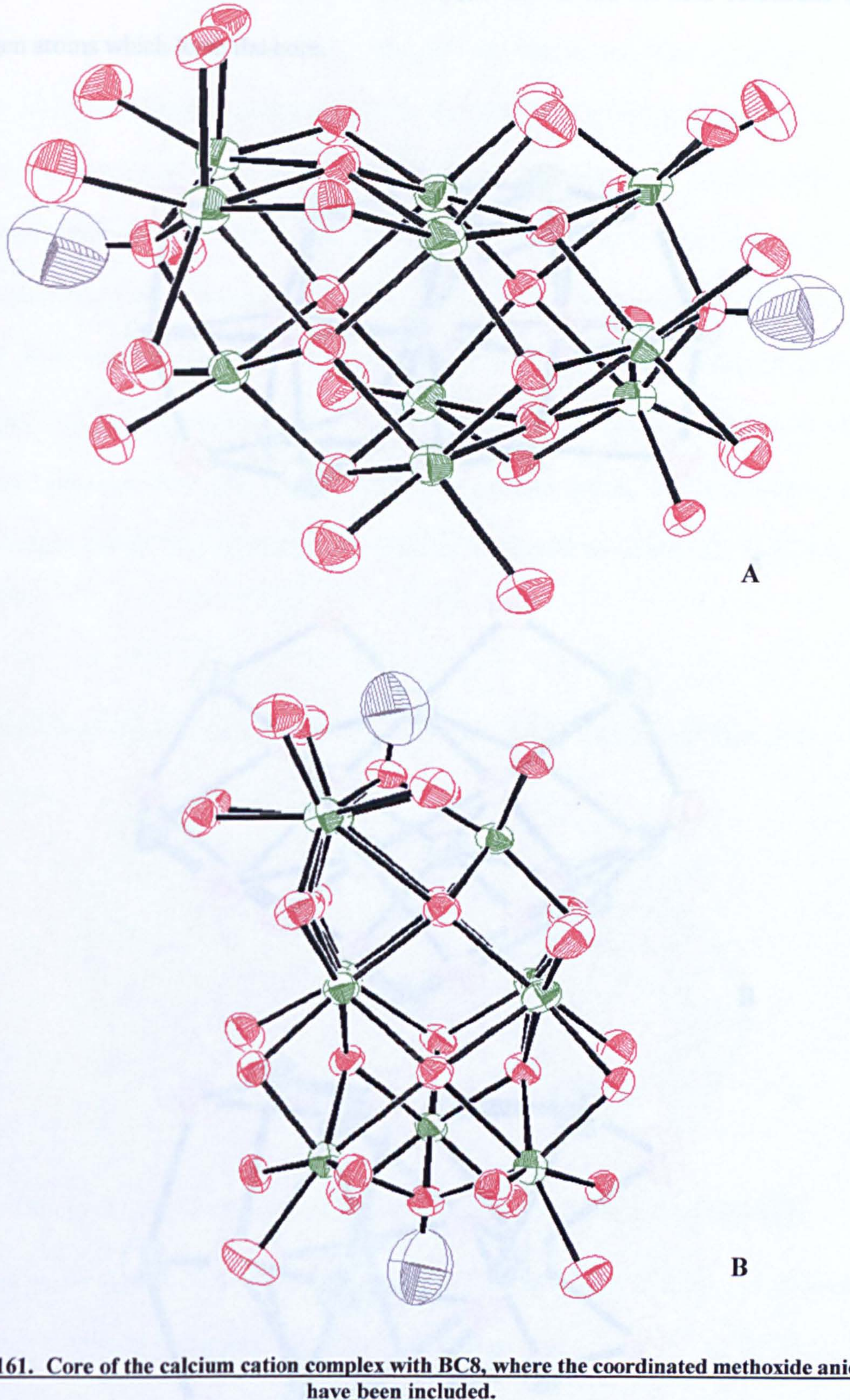


Figure 161. Core of the calcium cation complex with BC8, where the coordinated methoxide anions have been included.

The core consists of alternating layers of calcium cations and layers of oxygen atoms. The three views of the core below (figure 162) show the calcium cations, the hydroxide anion oxygen atoms, the methoxide anion oxygen atoms and the four calixarene ligand oxygen atoms which form the core.

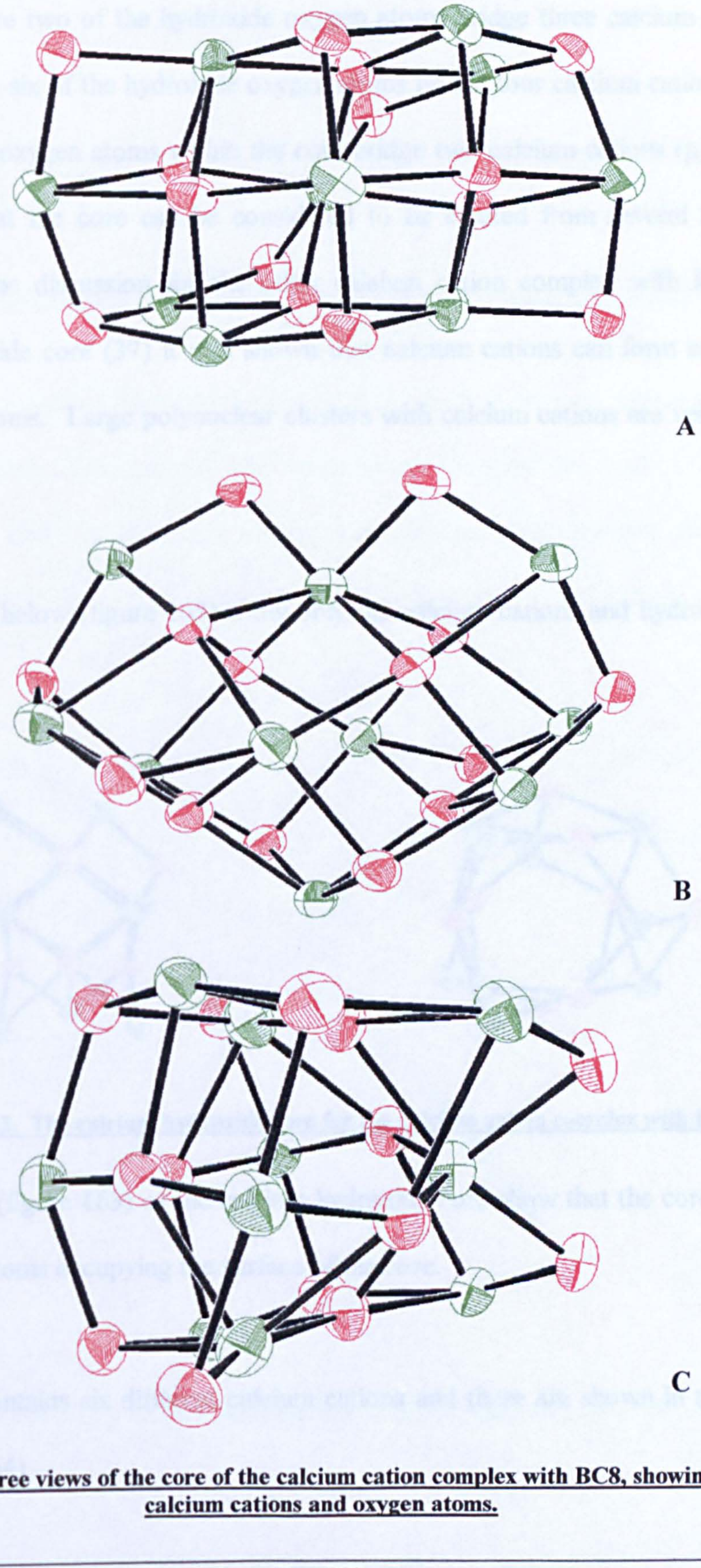


Figure 162. Three views of the core of the calcium cation complex with BC8, showing only the calcium cations and oxygen atoms.

The above views (figure 162) of the core show the core from three different angles. The views show that the core consists of ten calcium cations and fourteen oxygen atoms. There are two different coordination modes for the hydroxide oxygen atoms in the core, which are where two of the hydroxide oxygen atoms bridge three calcium cations (μ_3-OH) and where six of the hydroxide oxygen atoms bridge four calcium cations (μ_4-OH). The calixarene oxygen atoms within the core bridge two calcium cations (μ_2-OR). The views show that the core can be considered to be created from several face-sharing cubanes. In the discussion for the other calcium cation complex with **BC8** with a calcium hydroxide core (**37**) it was shown that calcium cations can form cubane cores with oxygen atoms. Large polynuclear clusters with calcium cations are very rare.[20, 41, 51, 241-245]

The two views below (figure 163) show only the calcium cations and hydroxide anions of the core.

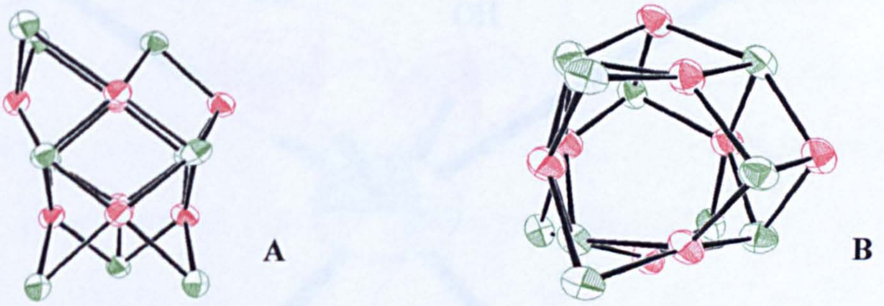


Figure 163. The calcium hydroxide core for the calcium cation complex with BC8.

The two views (figure 163) of the calcium hydroxide core show that the core is hollow, with all of the atoms occupying the surface of the core.

The complex contains six different calcium cations and these are shown in the diagram below (figure 164).

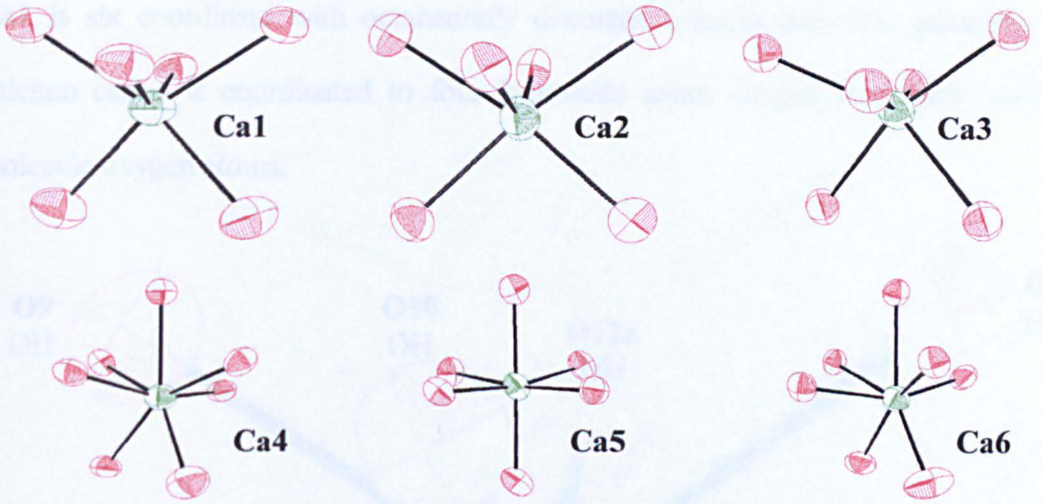


Figure 164. Diagrams of the six different calcium cation environments in the calcium cation complex with BC8.

As the complex contains ten calcium cations, there are two calcium cations of type Ca2, Ca4, Ca5 and Ca6. The complex only contains one Ca1 and one Ca3. It can be seen that Ca1, Ca2 and Ca3 are very similar and Ca4 and Ca6 are very similar. The coordination sphere for each calcium cation will be discussed in turn below.

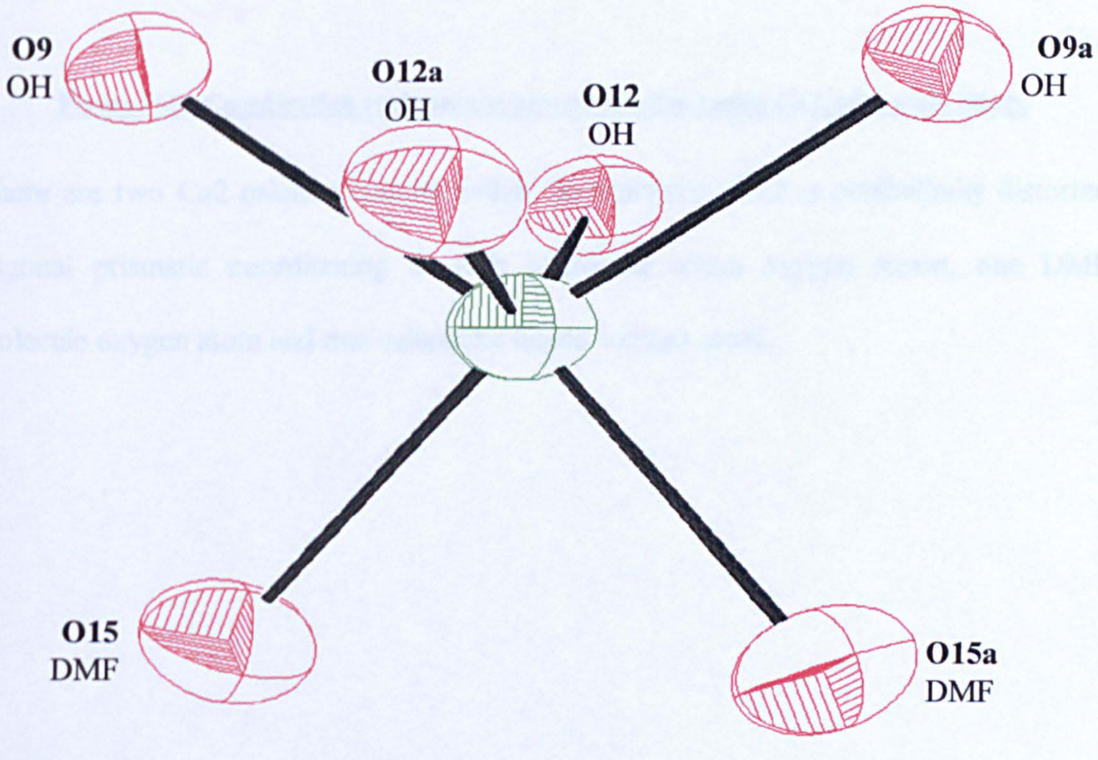


Figure 165. Coordination environment around calcium cation Ca1, with atom labels.

Ca1 is six coordinate with octahedrally distorted trigonal prismatic geometry. The calcium cation is coordinated to four hydroxide anion oxygen atoms and two DMF molecule oxygen atoms.

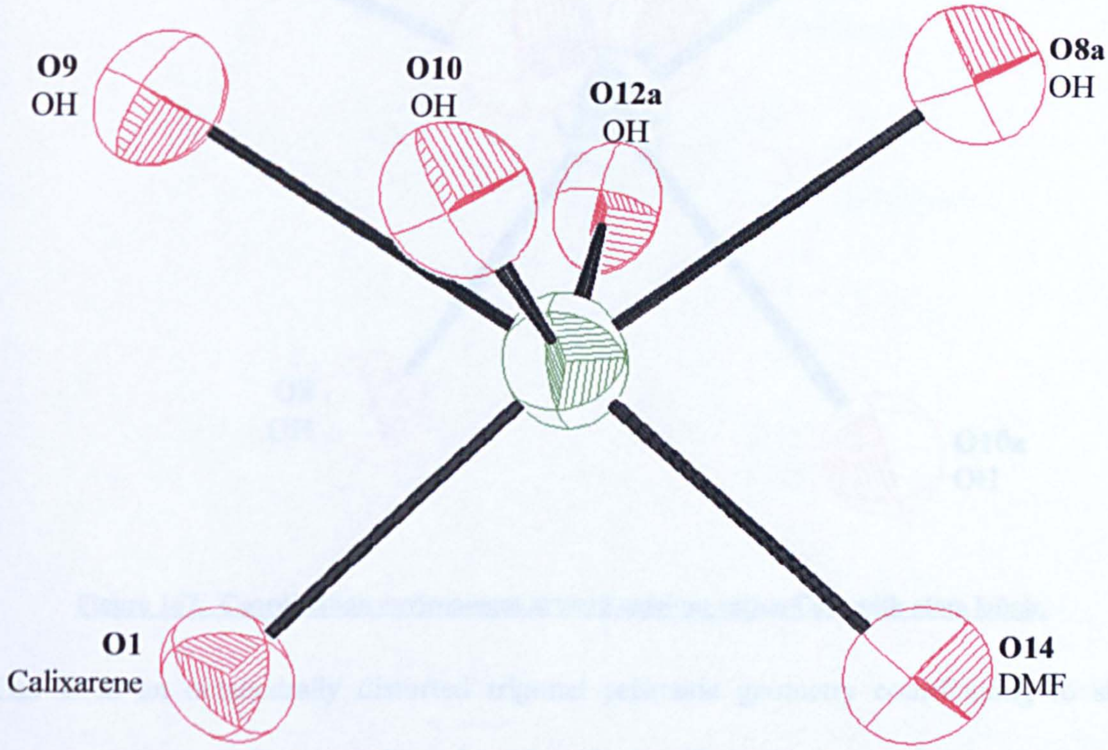


Figure 166. Coordination environment around calcium cation Ca2, with atom labels.

There are two Ca2 calcium cations within the complex. Ca2 is octahedrally distorted trigonal prismatic coordinating to four hydroxide anion oxygen atoms, one DMF molecule oxygen atom and one calixarene ligand oxygen atom.

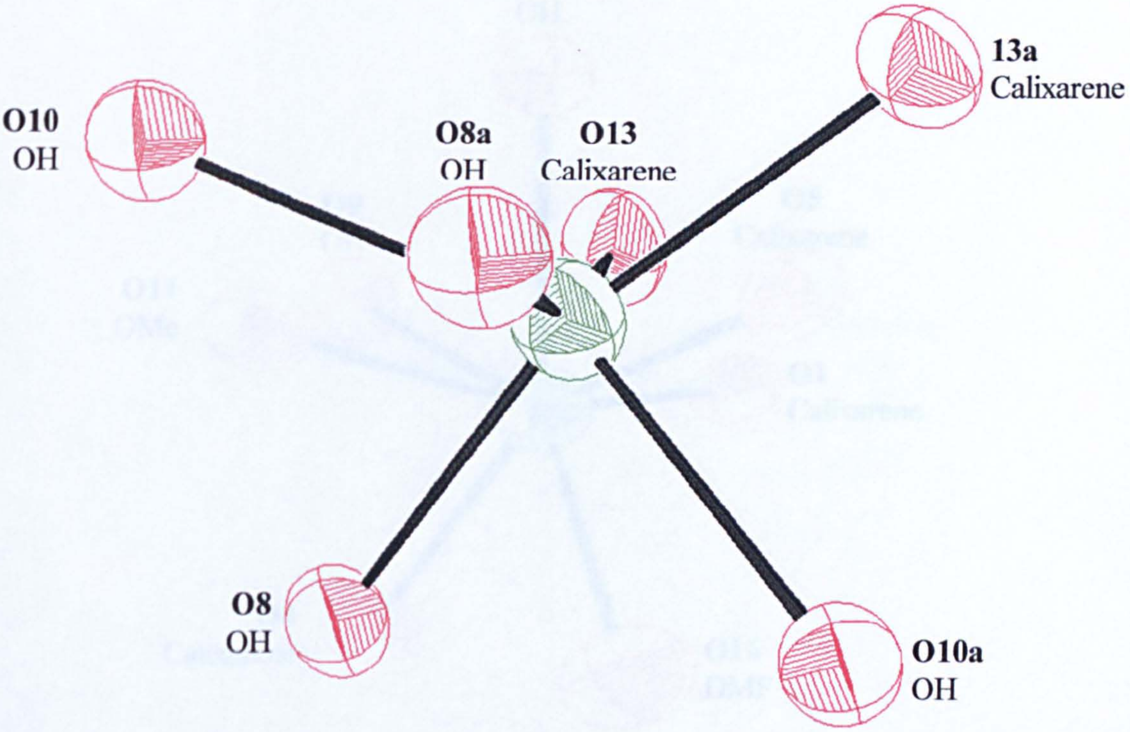


Figure 167. Coordination environment around calcium cation Ca3, with atom labels.

Ca3 is in an octahedrally distorted trigonal prismatic geometry coordinating to six oxygen atoms. Ca3 is coordinated to four hydroxide anion oxygen atoms and two calixarene ligand oxygen atoms.

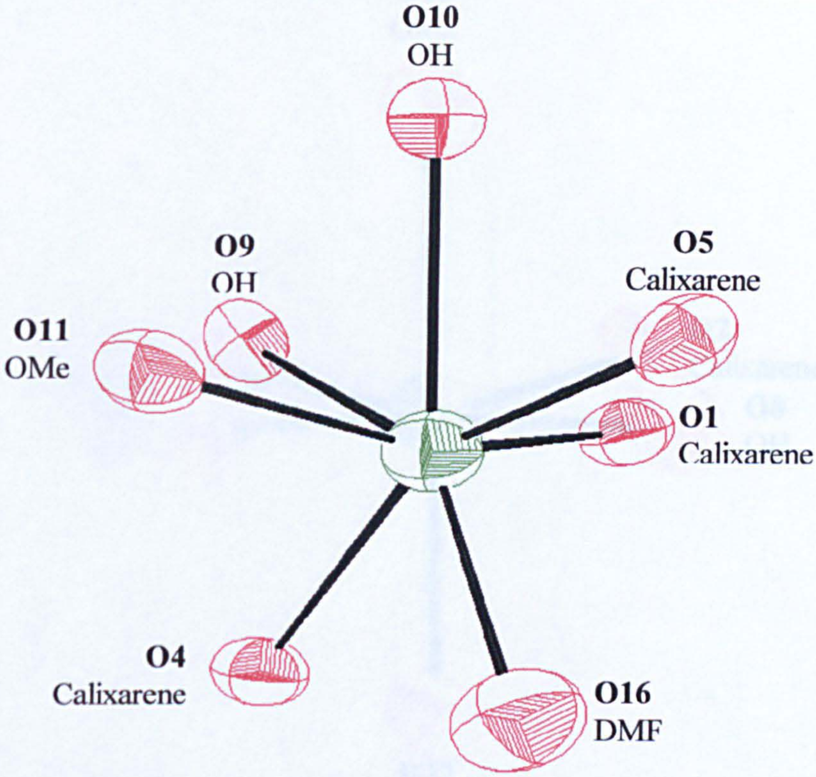


Figure 168. Coordination environment around calcium cation Ca4, with atom labels.

There are two Ca4 calcium cations within the complex. Ca4 is in a capped trigonal prismatic geometry, slightly distorted towards pentagonal bipyramidal geometry, coordinating to seven oxygen atoms. Ca4 is coordinated to two hydroxide anion oxygen atoms, three calixarene ligand oxygen atoms, one methoxide anion oxygen atom and one DMF molecule oxygen atom.

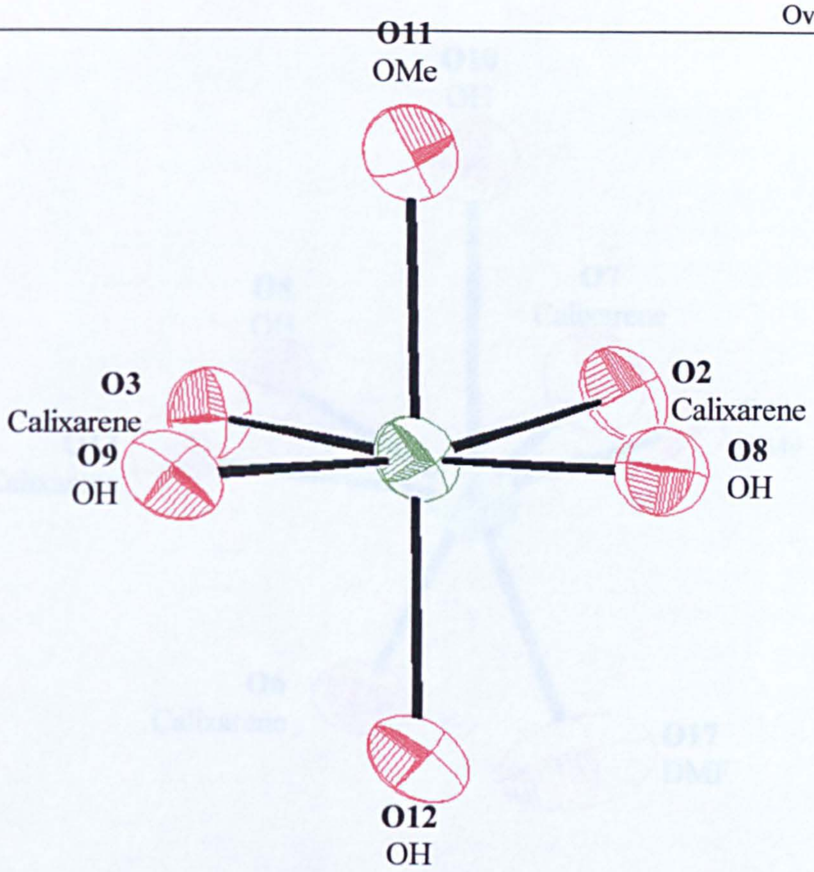


Figure 169. Coordination environment around calcium cation Ca5, with atom labels.

There are two Ca5 calcium cations within the complex. Ca5 is in an octahedral geometry coordinating to six oxygen atoms. Ca5 is coordinated to three hydroxide anion oxygen atoms, one methoxide anion oxygen atom and two calixarene ligand oxygen atoms.

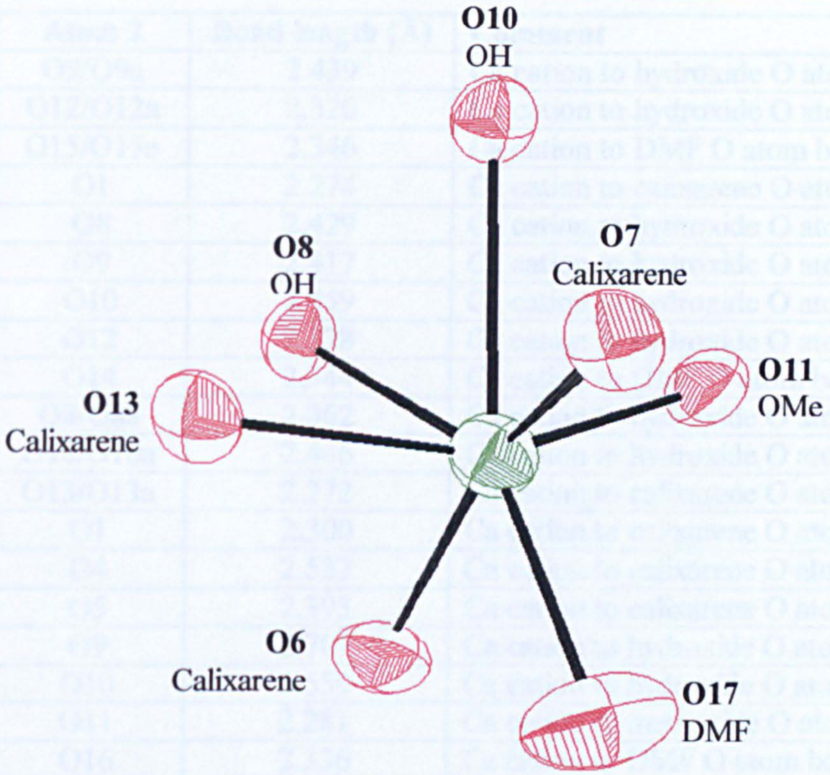


Figure 170. Coordination environment around calcium cation Ca6, with atom labels.

There are two Ca6 calcium cations within the complex. Ca6 is in a slightly distorted capped trigonal prismatic geometry (distortion towards pentagonal bipyramidal geometry), coordinating to seven oxygen atoms. Ca6 is coordinated to two hydroxide anion oxygen atoms, one methoxide anion oxygen atom, three calixarene ligand oxygen atoms and one DMF molecule oxygen atom.

The tables below show selected bond lengths and bond angles for the complex (tables 65 and 66).

Atom 1	Atom 2	Bond length (Å)	Comment
Ca1	O9/O9a	2.439	Ca cation to hydroxide O atom bond
Ca1	O12/O12a	2.320	Ca cation to hydroxide O atom bond
Ca1	O15/O15a	2.346	Ca cation to DMF O atom bond
Ca2	O1	2.274	Ca cation to calixarene O atom bond
Ca2	O8	2.429	Ca cation to hydroxide O atom bond
Ca2	O9	2.417	Ca cation to hydroxide O atom bond
Ca2	O10	2.459	Ca cation to hydroxide O atom bond
Ca2	O12	2.378	Ca cation to hydroxide O atom bond
Ca2	O14	2.344	Ca cation to DMF O atom bond
Ca3	O8/O8a	2.362	Ca cation to hydroxide O atom bond
Ca3	O10/O10a	2.446	Ca cation to hydroxide O atom bond
Ca3	O13/O13a	2.272	Ca cation to calixarene O atom bond
Ca4	O1	2.300	Ca cation to calixarene O atom bond
Ca4	O4	2.537	Ca cation to calixarene O atom bond
Ca4	O5	2.395	Ca cation to calixarene O atom bond
Ca4	O9	2.707	Ca cation to hydroxide O atom bond
Ca4	O10	2.559	Ca cation to hydroxide O atom bond
Ca4	O11	2.281	Ca cation to methoxide O atom bond
Ca4	O16	2.336	Ca cation to DMF O atom bond
Ca5	O2	2.332	Ca cation to calixarene O atom bond
Ca5	O3	2.329	Ca cation to calixarene O atom bond
Ca5	O8	2.330	Ca cation to hydroxide O atom bond
Ca5	O9	2.355	Ca cation to hydroxide O atom bond
Ca5	O11	2.385	Ca cation to methoxide O atom bond
Ca5	O12	2.349	Ca cation to hydroxide O atom bond
Ca6	O6	2.470	Ca cation to calixarene O atom bond
Ca6	O7	2.368	Ca cation to calixarene O atom bond
Ca6	O8	2.805	Ca cation to hydroxide O atom bond
Ca6	O10	2.653	Ca cation to hydroxide O atom bond
Ca6	O11	2.282	Ca cation to methoxide O atom bond
Ca6	O13	2.240	Ca cation to calixarene O atom bond
Ca6	O17	2.356	Ca cation to DMF O atom bond
Ca1	Ca2	3.607	Intercationic distance
Ca1	Ca3	4.963	Intercationic distance
Ca1	Ca4	5.135	Intercationic distance
Ca1	Ca5	3.590	Intercationic distance
Ca1	Ca6	6.314	Intercationic distance

Table 65. Selected bond lengths for the calcium cation complex with BC8.

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O9	Ca1	O9a	110.58	Angle between hydroxide O atoms
O9	Ca1	O12	80.26	Angle between hydroxide O atoms
O9	Ca1	O12a	80.46	Angle between hydroxide O atoms
O9	Ca1	O15	165.08	Angle between hydroxide/DMF O atoms
O9	Ca1	O15a	83.23	Angle between hydroxide/DMF O atoms
O1	Ca2	O8	162.76	Angle between calixarene and hydroxide O atoms
O1	Ca2	O9	80.66	Angle between calixarene and hydroxide O atoms
O1	Ca2	O10	86.63	Angle between calixarene and hydroxide O atoms
O1	Ca2	O12	117.96	Angle between calixarene and hydroxide O atoms
O1	Ca2	O14	89.57	Angle between calixarene/DMF O atoms
O8	Ca3	O8a	113.10	Angle between hydroxide O atoms
O8	Ca3	O10	78.54	Angle between hydroxide O atoms
O8	Ca3	O10a	83.25	Angle between hydroxide O atoms
O8	Ca3	O13	80.27	Angle between hydroxide and calixarene O atoms
O8	Ca3	O13a	161.08	Angle between hydroxide and calixarene O atoms
O1	Ca4	O4	89.15	Angle between calixarene O atoms
O1	Ca4	O5	91.92	Angle between calixarene O atoms
O1	Ca4	O9	74.19	Angle between calixarene and hydroxide O atoms
O1	Ca4	O10	83.75	Angle between calixarene and hydroxide O atoms
O1	Ca4	O11	153.06	Angle between calixarene and methoxide O atoms
O1	Ca4	O16	105.50	Angle between calixarene/DMF O atoms
O2	Ca5	O3	87.60	Angle between calixarene O atoms
O2	Ca5	O8	90.49	Angle between calixarene and hydroxide O atoms
O2	Ca5	O9	169.34	Angle between calixarene and hydroxide O atoms
O2	Ca5	O11	82.41	Angle between calixarene and methoxide O atoms
O2	Ca5	O12	108.77	Angle between calixarene and hydroxide O atoms
O6	Ca6	O7	156.08	Angle between calixarene O atoms
O6	Ca6	O8	64.86	Angle between calixarene and hydroxide O atoms
O6	Ca6	O10	132.15	Angle between calixarene and hydroxide O atoms
O6	Ca6	O11	90.48	Angle between calixarene and methoxide O atoms
O6	Ca6	O13	88.69	Angle between calixarene O atoms
O6	Ca6	O17	78.18	Angle between calixarene/DMF O atoms

Table 66. Selected bond angles for the calcium cation complex with BC8.

All of the calcium cations have slightly distorted geometries with a large range in the bond lengths to coordinated oxygen atoms, especially to core hydroxide anion oxygen atoms and calixarene ligand oxygen atoms. If the shortest bond lengths are considered then the trend for ligands is as shown below.

Calixarene O atom < methoxide O atom < hydroxide O atom < DMF O atom.

$$\xrightarrow[\text{Increasing bond length}]{\hspace{12em}}$$

The wide range in bond lengths to calixarene ligand oxygen atoms (2.240-2.537Å) means that the range covers the range for bond lengths to methoxide anion oxygen atoms (2.281-2.385Å). The range in bond lengths to hydroxide anion oxygen atoms (2.320-2.805Å) covers the range for bond lengths to DMF molecule oxygen atoms (2.336-2.356Å). There appears to be no definitive reason for the wide ranges in bond lengths observed. The bond lengths to the DMF molecule oxygen atoms are within the range observed in the literature.[41] There are three references in the literature for complexes containing calcium coordinated to methoxide anions,[250] though none of these complexes have crystallographic data available and so it not possible to compare the bond lengths observed in this complex. The interatomic distances between the calcium cations shows that the core is not square/circular, but is elongated.

A search of the Cambridge Crystallographic Database showed that for polynuclear calcium cation cores within complexes a tetracalcium cation core is the most common, with three complexes known.[20, 41, 245] One complex had a hexacalcium cation core,[243] one complex had heptacalcium cation core[241] and one complex had an octacalcium cation core[224]. There were no references to crystalline complexes with cores larger than eight calcium cations. Buhro *et al.* describe a calcium cation complex including nine calcium cations,[51] but the structure of the complex could not be found on the crystallographic database[41]. The complex with eight calcium cations has the calcium cations in a ring.[224] The whole complex and the core of the complex are shown below (figures 171 and 172).

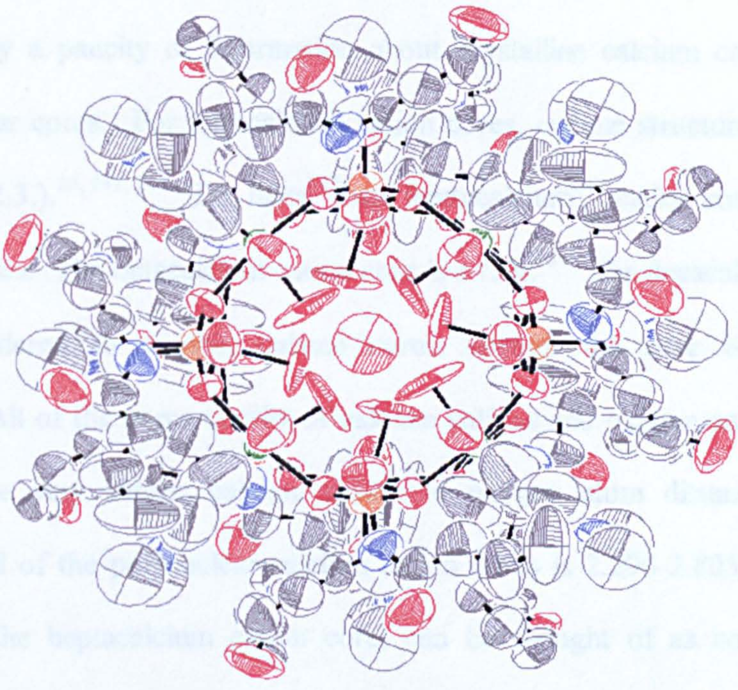


Figure 171. Calcium cation complex containing eight calcium cations, $[Ca_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8(O{=}CHNMe_2)_8(H_2O)_{12}]$, where the hydrogen atoms have been removed for clarity.[224]

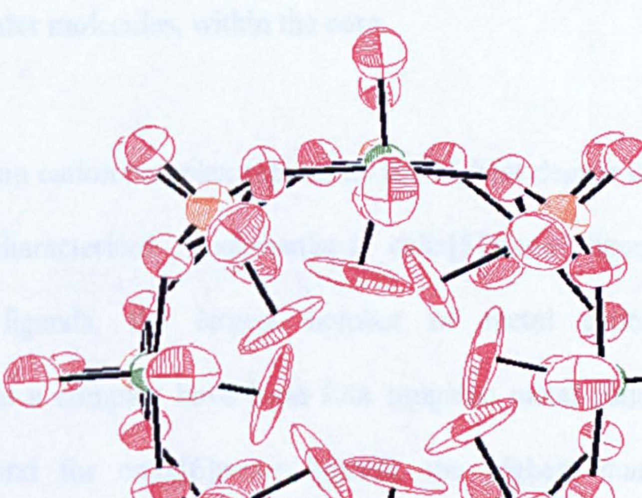


Figure 172. Core of the above calcium cation complex.[224]

The complex with eight calcium cations has the calcium cations in a ring, where there are only two different calcium cations, both of which are seven coordinate. The calcium cations are separated by 3.705Å and 3.721Å around the ring.

There is clearly a paucity of information about crystalline calcium cation complexes with polynuclear cores. For tetracalcium cation cores, cubane structures are observed (see section 5.2.3.).[20, 242, 245] The hexa[243] and heptacalcium[241] cation cores both contain cubane structures. The octacalcium cation core is a ring.[224] The decacalium cation core may be considered to contain cubane cores, though the core is clearly more complicated. All of the cores consist of calcium cations and oxygen anions, where the complexes have very similar calcium cation to oxygen atom distances (the range observed for all of the polynuclear calcium cation cores is 2.296-2.805Å). All of the cores, except the heptacalcium cation core, can be thought of as hollow, with the calcium cations and oxygen anions covering the surface of the core. The hollow core in the octacalcium cation complex is shown by the inclusion of two oxygen atoms, probably as water molecules, within the core.

The decacalcium cation complex represents the highest degree of metallation known for structurally characterised underivatised calix[8]arene ligand complexes. For calix[8]arene ligands, the largest number of metal cations which have been characterised in a complex have been four tungsten metal cations coordinated to one **BC8** ligand and for calix[6]arene ligands, the highest number of metal cations coordinated have been five aluminium cations.[251] One or two metal cations per complex are most commonly observed.[41, 205] Despite the similarities of complexes of the larger Group 2 metal cations to divalent lanthanide metal cations, the largest number of f-block metal cations in a structurally characterised calix[8]arene complex is two.[205]

A complex containing eight lithium cations coordinated to a calix[8]arene ligand has been reported, though the crystal structure of the complex was not given and the evidence was weak.[189]

5.3.5. Solution State Structure of the Calcium Cation Complex with **BC8**

The ^{1}H NMR spectrum of the calcium cation complex with **BC8** with the decacalcium cation core is shown below in deuterated DMSO (figure 173) and the aromatic region of the ^{1}H NMR spectrum of the complex in deuterated DCM is shown underneath (figure 174).

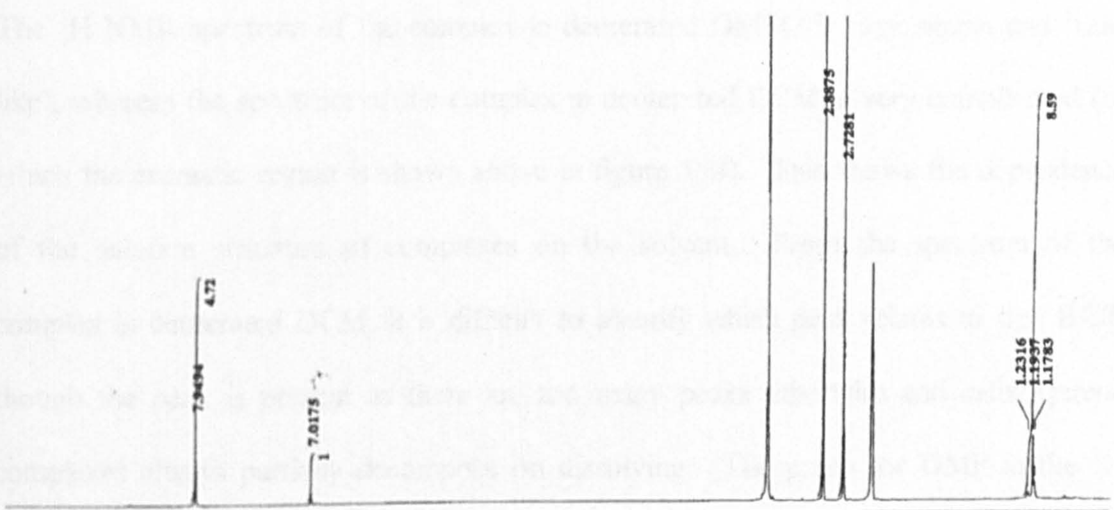


Figure 173. ^{1}H NMR (d$_6$-DMSO) spectrum of the calcium cation complex with BC8.

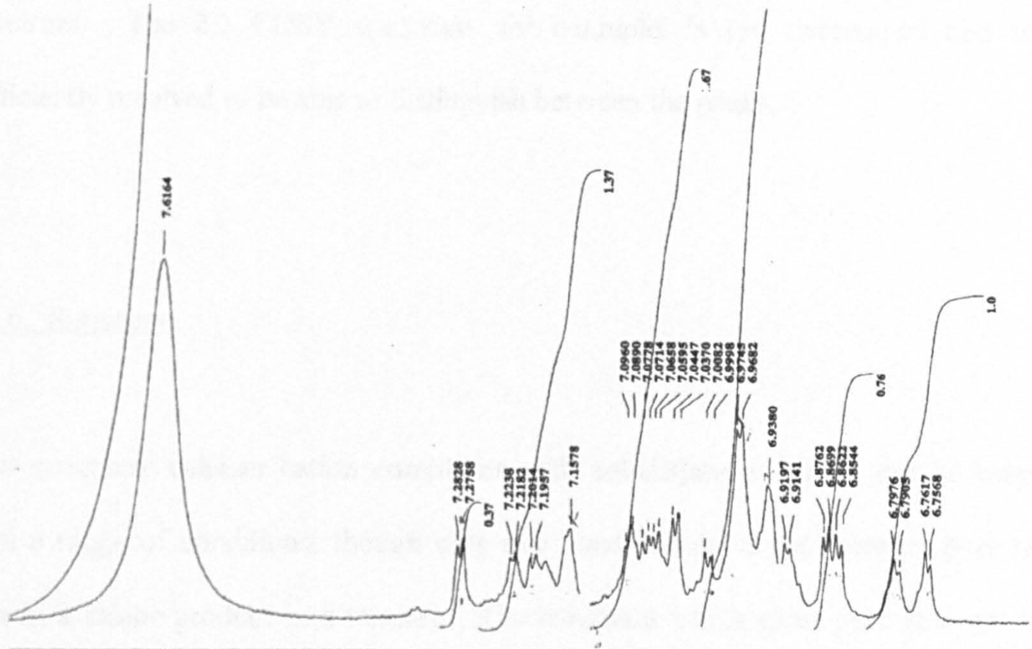


Figure 174. Aromatic region of the ^1H NMR (CD_2Cl_2) spectrum for the calcium cation complex with BC8.

The ^1H NMR spectrum of the complex in deuterated DMSO is very simple and 'salt-like', whereas the spectrum of the complex in deuterated DCM is very complicated (of which the aromatic region is shown above in figure 174). This shows the dependence of the solution structure of complexes on the solvent. From the spectrum of the complex in deuterated DCM, it is difficult to identify which peak relates to free **BC8**, though the peak is present as there are too many peaks otherwise and calix[8]arene complexes always partially decompose on dissolving. The peaks for DMF in the ^1H NMR (CD_2Cl_2) spectrum are significantly shifted relative to the positions for free DMF (the CH peak is shifted by approximately 0.5ppm upfield) showing that the DMF is not exchanging (one sharp peak). The spectrum shows that the product is probably pure and that it has local C_1 symmetry, though no other information can be gained from it, as it is too complicated. The ^{13}C NMR (CD_2Cl_2) spectrum and the 2D COSY NMR (CD_2Cl_2) spectrum on the complex are equally complicated, which although they support the local C_1 symmetry label, they do not assist in understanding the ^1H NMR spectrum. The 2D COSY spectrum, for example, is too overlapped and so not sufficiently resolved to be able to distinguish between the peaks.

5.3.6. Summary

Low symmetry calcium cation complexes with calix[8]arene ligands can be prepared from a range of conditions, though only one condition gives the complex pure rather than as a minor product in a mixture. The condition which gives pure low symmetry complex actually gives two pure low symmetry complexes where one complex is the kinetic product and over time this complex is replaced by the thermodynamic product. The structure of the thermodynamic product has been determined which shows that the complex has a decacalcium cation core. The core is a calcium hydroxide core, which can therefore be considered to be a model for the precursor in the preparation of overbased detergents. Within the complex, there are methoxide anions, which have formed from the small volume of methanol in the reaction mixture. The structure of the complex in solution shows that the complex has very low symmetry, though the solution structure is sensitive to the solvent in which the complex is dissolved. It is not known if all of the low symmetry complexes have the structure of the complex analysed by single crystal x-ray diffraction.

5.4. Calcium Cation Complex with a Calcium Carbonate Core

5.4.1. Introduction

To understand overbased detergents, the ultimate model complex would have a calcium carbonate core. It has been shown that converting calcium hydroxide cores to stable calcium carbonate cores (see above, section 5.2.6.) is not yet possible, as the reaction is too fast and leads to decomposition of the complex. Calcium carbonate does not form molecular complexes in general; there are no known complexes containing calcium cations and carbonate anions. Two magnesium cation and carbonate anion core complexes are known,[204, 263] plus one mixed metal cation complex which includes barium cations and carbonate anions, though in the structure of this complex it is difficult to determine if the carbonate anions are coordinated to the barium cations[264]. The structures of the two magnesium cation complexes can be seen below (figure 175).

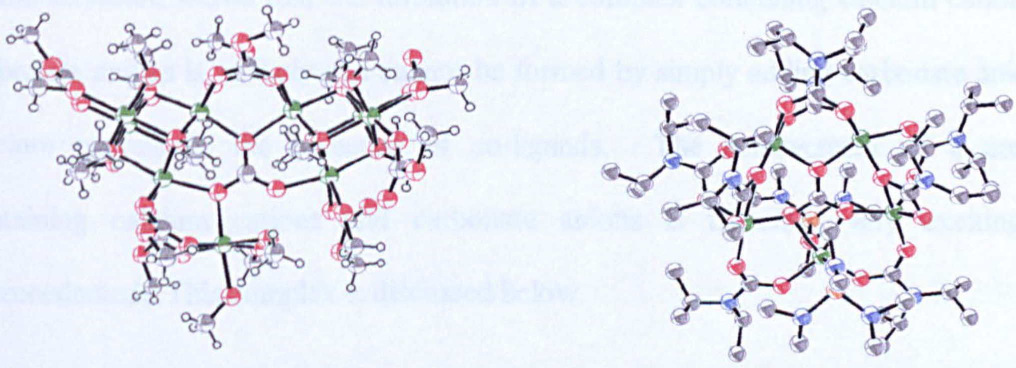


Figure 175. Structures of two magnesium cation complexes with magnesium cations coordinated to carbonate anions. The hydrogen atoms have been eliminated from the second structure for clarity.

In both of the complexes there is a single carbonate (μ_5-CO_3) anion, which is in the centre of the complex. In the second complex,[263] the carbonate anion is coordinated to all of the magnesium cations in the complex, whereas in the first complex, four magnesium cations are not coordinated to the carbonate anion,[204] though these cations do form two cubane Mg_4O_4 clusters with coordinated magnesium cations. The analogous calcium cation complex of the first magnesium cation complex could not be recrystallised and so the structure is unknown (as is whether it contained calcium cations coordinated to carbonate anions).[204]

The only structures for calcium cations and carbonate anions are for the calcium carbonate polymorphs and mixed metal ion carbonates, for example calcium magnesium carbonate.[41] It has been shown that calcium carbonate can be grown on polymeric or macrocyclic molecules, but the nature of the interaction of the organic material with the crystalline calcium carbonate is not known on an atomic scale.[75, 77, 79, 82-86] The research on the growth of calcium carbonate on organic materials has shown that the calcium cations probably coordinate to acidic sites of the organic material and then bind to carbonate anions[84] and that crystalline calcium carbonate detaches from the organic medium by the action of water on the material[83]. The organic material has been shown to affect the morphology of the calcium carbonate which is formed. The study of the literature shows that the formation of a complex containing calcium cations and carbonate anions is unlikely and cannot be formed by simply adding carbonate anions to calcium cations in the presence of co-ligands. The achievement of a complex containing calcium cations and carbonate anions is therefore very exciting and unprecedented. This complex is discussed below.

5.4.2. Preparation of the Calcium Cation Complex with a Calcium Carbonate Core

The calcium cation complex with a calcium carbonate core was prepared by serendipitous assembly.[229] It had been observed that adding **DMPD (25)** to a solution of the calcium cation complex with **M2** (see section 2.3.) in acetone caused a solid to precipitate out from the solution. As the calcium cation complex with **M2** (**CaM2**) is completely soluble in acetone and **DMPD** is slowly soluble in acetone, the solid was a new material and not starting material. ^{1}H NMR (d_6-DMSO) spectroscopy showed that the solid included **DMPD** and **M2**, but was very broad and so no more information could be gained from the spectrum. The reaction was repeated under controlled conditions, where the **DMPD** solution in acetone was allowed to slowly diffuse into the **CaM2** solution in acetone, to promote the probability of crystalline product formation. Approximately 1ml of methanol was added accidentally to the solution, though no immediate effect was observed and so the experiment was not abandoned. Within one day, crystalline product had grown from the solution and single crystal x-ray diffraction was performed on the crystals. Single crystal x-ray diffraction showed that the **CaM2** complex had reacted with the **DMPD** ligand to give a new complex. Excitingly, the new complex contained carbonate anions coordinated to the calcium cations, even though no source of carbonate had been added to the reaction mixture. The complex also contained methanol molecules coordinated to the calcium cations and included ten calcium cations. Furthermore, the complex is an example of a mixed ligand calcium cation complex, which is rare.[265] The structure of the complex is discussed below. As a small volume of methanol had been added accidentally, the reaction was repeated without any methanol added and this reaction yielded a powder product. Therefore the addition of methanol was beneficial to crystalline complex formation. The reaction was repeated several times, using the conditions which gave crystalline material, to discover if the reaction was reproducible, especially with the source of carbonate being unknown. It was found that the reaction was repeatable as long as the **CaM2** complex which was used was 'old'. When freshly prepared **CaM2** complex (yellow crystalline material) was used in the preparation of the calcium cation complex with a calcium carbonate core, powder product was obtained. It was found necessary to use **CaM2** which was over one year old and pale brown in colour, with a ^{1}H NMR spectrum which showed some decomposition of the **CaM2** complex (see section 2.3.4.1.2.), to obtain a pure crystalline product. Vacuum dried, 'newer' **CaM2** could be used to gain crystalline product, though the vacuum dried **CaM2** always gave a mixture of powder and crystalline product. Alternative reactions where assessed, such as substituting the strontium cation complex with **M2** for **CaM2**, substituting the calcium cation complex with **I2** for **CaM2** or substituting **DBPD** for **DMPD**, though none of these reactions have given a crystalline product. In fact, no product has been obtained as yet from any of the alternative reactions, except the one with the calcium cation complex with **I2**, which gave an instant powder product upon addition of the calcium cation complex with **I2** solution to the **DMPD** solution.

The source of carbonate in the complex is unknown, especially as the reaction is repeatable. The carbonate possibly was present as an impurity in the acetone, though the same acetone solution has not been used for all of the reactions and for the acetone solvent to be the source of carbonate, carbonate must be an impurity in all acetone solutions, probably at a significant level, which would be known. Thus acetone as the source of carbonate is unlikely. The other potential source of carbonate could be from carbon dioxide in the air, which would make the reaction an 'overbasing' reaction. The reaction was not successfully carried out under an inert atmosphere due to technical difficulties and so it is not possible to define if the carbonate source was air, though there is no other logical source of the carbonate in the complex. The presence of carbonate in the complex coordinated to calcium cations shows that **M2** and **DMPD** are good ligands for overbased core formation. This is because calcium carbonate usually precipitates out of solutions as soon as it is formed, thus **M2** and **DMPD** must be good enough ligands to hold calcium carbonate in solution for long enough for the complex to form and to successfully compete with the carbonate anions for coordination sites on the calcium cations.

The complex contains a decacalcium cation core, which is unusual, as discussed earlier (section 5.3.4.). The core is not as compact as the cores for the two calix[8]arene complexes discussed in this chapter, though it is still a core. The calcium cations in the core form a ring shape, which can be compared to the octacalcium cation complex prepared by Onoda *et al.*[224]

Although all of the sulfurised alkylphenol complexes shown in chapter 2 were prepared in air and not under nitrogen and hence are not 'sensitive' to carbon dioxide, it can be seen that by this complex that in the presence of suitable solvents and co-ligands, overbased materials are readily formed with sulfurised alkylphenol ligands.

5.4.3. Solid State Structure of the Calcium Cation Complex with a Calcium Carbonate Core (39)

A crystalline complex containing calcium carbonate was grown from acetone and methanol solution. The complex has the formula $Ca_{10}(M2^{2-})_8(CO_3^{2-})_2(DMPD)_4(MeOH)_4$.8acetone and so consists of ten calcium cations, eight **M2** ligands, two carbonate anions, four **DMPD** ligands, four methanol molecules and eight free acetone molecules in the lattice. There are three different calcium cation environments in the complex. The first calcium cation environment (Ca1) is six coordinate with distorted octahedral geometry, coordinating to two methanol molecule oxygen atoms, two carbonate anion oxygen atoms and two **M2** oxygen atoms. There are two calcium cations in the complex in this environment. The second calcium cation environment (Ca2) is eight coordinate, coordinating to two **M2** ligands *via* both oxygen atoms and the sulfur atom and to one carbonate anion *via* two of the carbonate oxygen atoms. There are four calcium cations in this environment. The third calcium cation environment (Ca4) is seven coordinate with capped trigonal prismatic geometry, coordinating to one carbonate anion, one **DMPD** ligand *via* both of its oxygen atoms, and four **M2** oxygen atoms. There are four calcium cations in this environment, though due to two disordered (doubled) **DMPD** molecules in the complex, two of the calcium cations are not completely equivalent to the other two calcium cations. For this discussion, bond lengths and angles to the calcium cations without disordered **DMPD** ligands will be used. The percentage occupancy for the doubled **DMPD** molecules is 50% in each position, where one of each of the doubled **DMPD** molecules has been deleted from the views below for clarity.

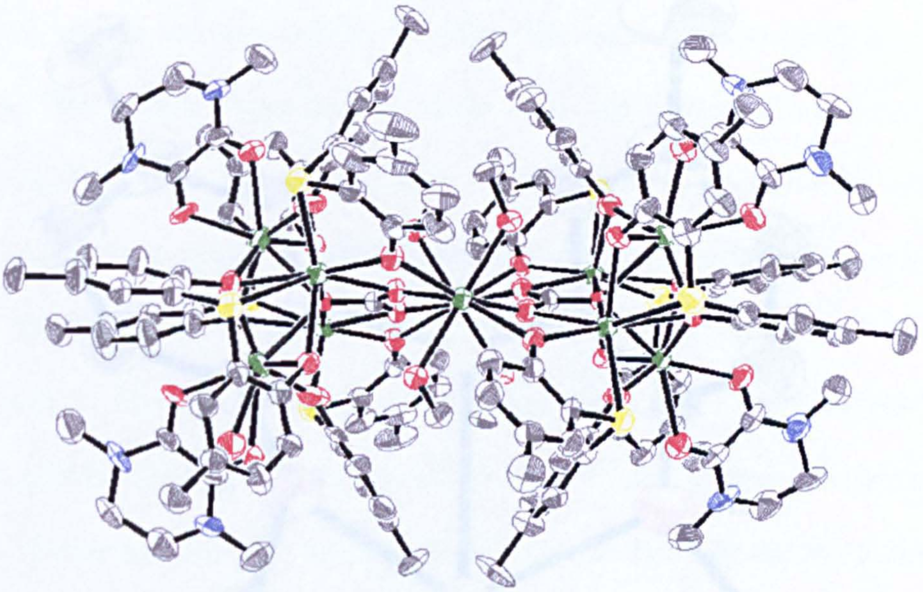


Figure 176. Structure of the complex containing calcium cations and carbonate anions, $Ca_{10}(M2^{2-})_8(CO_3^{2-})_2(DMPD)_4(MeOH)_4$.8acetone, where the free acetone molecules and the hydrogen atoms have been removed for clarity.

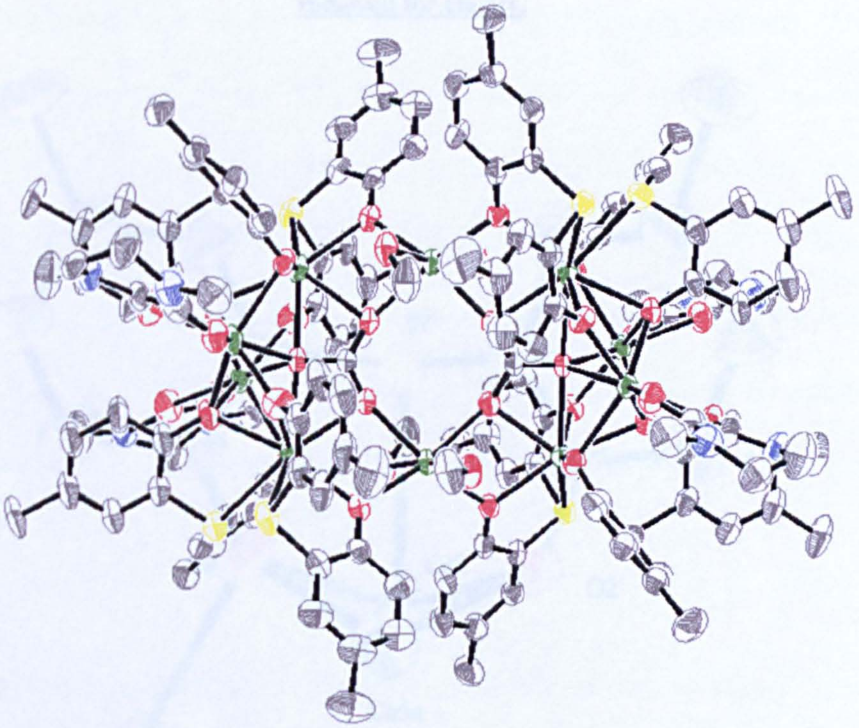


Figure 177. Structure of the complex containing calcium cations and carbonate anions, where the free acetone molecules and the hydrogen atoms have been removed for clarity.

Within the complex, the **M2** ligands coordinate to calcium cations in two different ways, as shown below (figure 178 and 179).

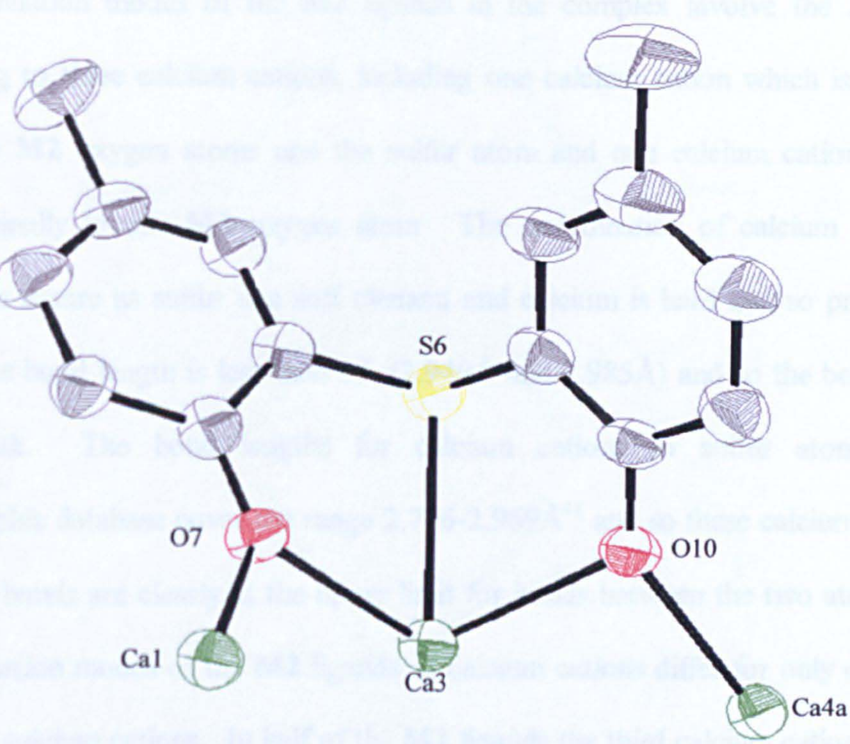


Figure 178. View of the coordination of one M2 ligand to calcium cations in the complex containing calcium cations and carbonate anions, with selected atom labels. Hydrogen atoms have been removed for clarity.

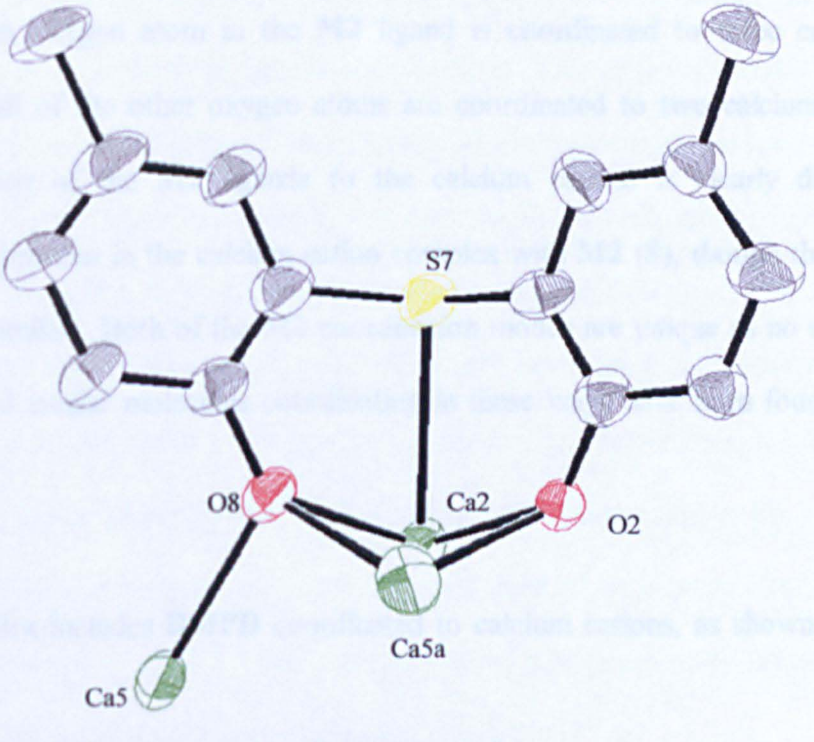


Figure 179. View of the coordination of one M2 ligand to calcium cations in the complex containing calcium cations and carbonate anions, with selected atom labels. Hydrogen atoms have been removed for clarity.

Both coordination modes of the **M2** ligands in the complex involve the **M2** ligand coordinating to three calcium cations, including one calcium cation which is bound by both of the **M2** oxygen atoms and the sulfur atom and one calcium cation which is bound terminally to one **M2** oxygen atom. The coordination of calcium cations to sulfur atoms is rare as sulfur is a soft element and calcium is hard and so prefers hard donors. The bond length is less than 3Å (2.940Å and 2.985Å) and so the bond is real, though weak. The bond lengths for calcium cations to sulfur atoms in the crystallographic database cover the range 2.776-2.969Å[41] and so these calcium cation to sulfur atom bonds are clearly at the upper limit for bonds between the two atoms. The two coordination modes of the **M2** ligands to calcium cations differ for only one of the coordinated calcium cations. In half of the **M2** ligands the third calcium cation is bound in a terminal mode to one **M2** oxygen atom, whereas in the other half of the **M2** ligands, the third calcium cation is coordinated to both of the **M2** oxygen atoms. In the latter mode, one oxygen atom in the **M2** ligand is coordinated to three calcium cations, whereas all of the other oxygen atoms are coordinated to two calcium cations. The coordination of the **M2** ligands to the calcium cations is clearly different to the coordination seen in the calcium cation complex with **M2** (**8**), though the bond lengths are very similar. Both of the **M2** coordination modes are unique as no other examples of **M2** and similar molecules coordinating in these ways have been found (see section 2.7.2.)[41]

The complex includes **DMPD** coordinated to calcium cations, as shown below (figure 180).

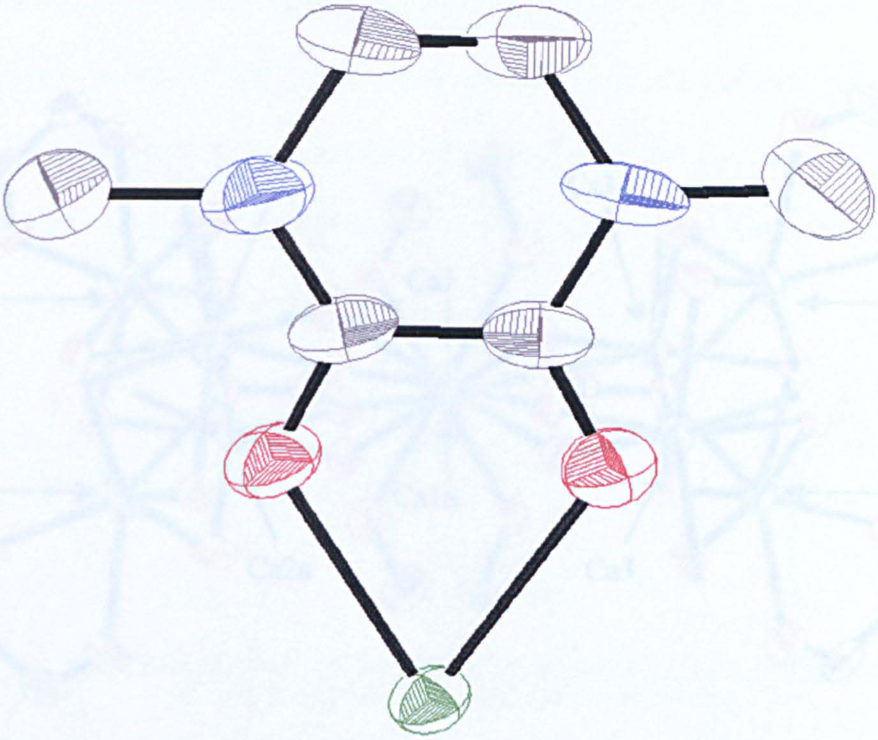


Figure 180. Coordination of a DMPD ligand to a calcium cation in the complex containing calcium cations and carbonate anions. Hydrogen atoms have been removed for clarity.

The coordination mode of the **DMPD** ligands to the calcium cations can be seen above (figure 180). The **DMPD** ligands coordinate to the calcium cations *via* both oxygen atoms, with one **DMPD** ligand coordinating to one calcium cation (no bridging oxygen atoms). The coordination mode is the same as the coordination mode of **DMPD** to copper cations (**28**). **DMPD** was designed as a mimic for ethylene glycol and the above coordination shows how ethylene glycol could coordinate to calcium cations. The interatomic oxygen atom to oxygen atom distance in the complex is 2.609Å, which is within the range observed for ethylene glycol complexes where the ethylene glycol ligand coordinates as a neutral ligand through both of its oxygen atoms to one metal cation (see section 4.2.4.). No calcium cation complexes with ethylene glycol are known and so accurate comparisons cannot be made.[41]

The core of the complex can be seen below (figure 181), where the calcium cations have been labelled.

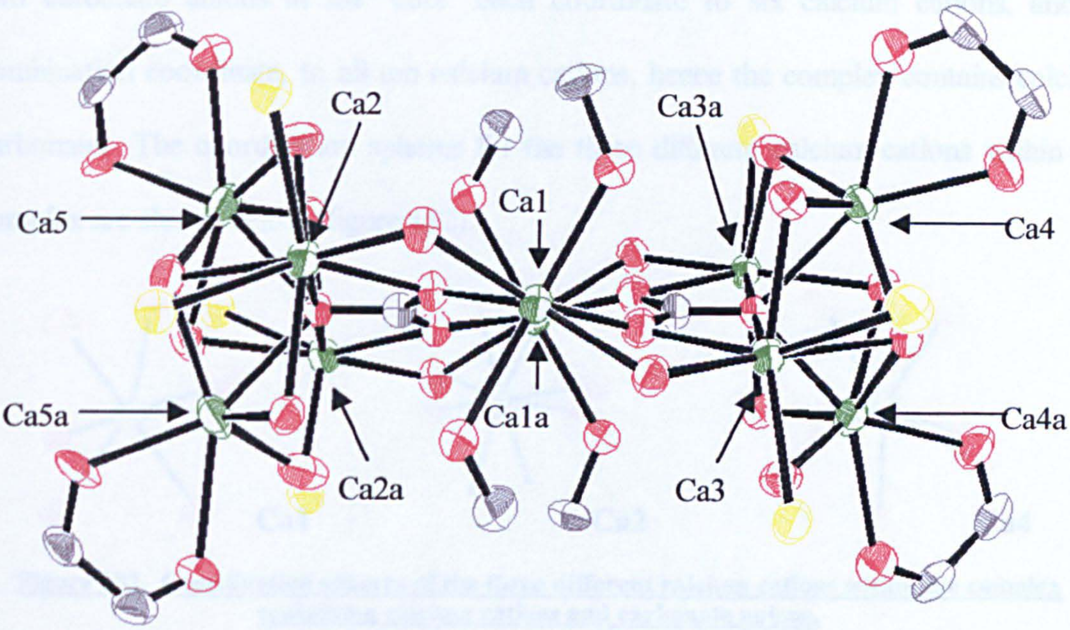


Figure 181. Core of the complex containing calcium cations and carbonate anions, where the free acetone molecules and hydrogen atoms have been removed and the M2 ligands and DMPD molecules have been reduced for clarity.

The above diagram (figure 181) shows the 'core' of the complex, to illustrate the calcium cations and carbonate anions. The **DMPD** ligands have been reduced to show how they can be considered to be mimics for ethylene glycol and so how ethylene glycol could coordinate to calcium cations in the preparation of overbased detergents. The four methanol molecules within the complex can be seen, coordinated to the central two calcium cations (Ca1). A small volume of methanol is required for the crystalline complex to form and it can be seen that the methanol molecules are the correct size to fill a space in the complex and ensure that the central calcium cations attain an acceptable coordination number. Calcium cations tend to form complexes with coordination numbers between six and nine, where smaller and larger coordination numbers are known and a coordination number of eight is preferred.[29, 33, 51] The above diagram also shows the coordination of four calcium cations (Ca2/Ca3) to sulfur atoms and the coordination of four calcium cations (Ca4/Ca5) to **DMPD** oxygen atoms. The two carbonate anions in the 'core' each coordinate to six calcium cations, and in combination coordinate, to all ten calcium cations, hence the complex contains calcium carbonate. The coordination spheres for the three different calcium cations within the complex are shown below (figure 182).

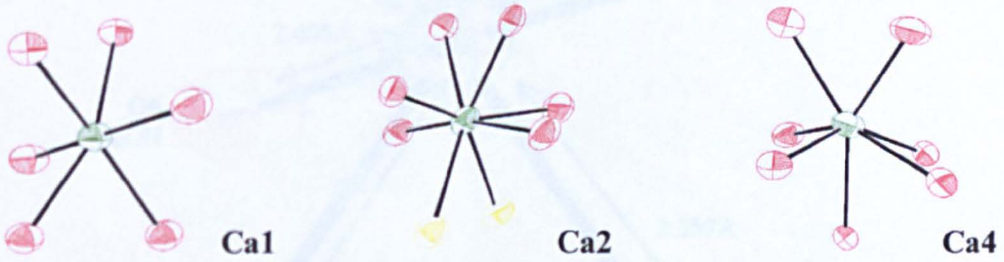


Figure 182. Coordination spheres of the three different calcium cations within the complex containing calcium cations and carbonate anions.

The three calcium cations are clearly different in the complex. Due to the disorder of two **DMPD** molecules in the complex, two other calcium cations exist, Ca3 and Ca5, where Ca3 is the same as Ca2 and Ca5 is the same as Ca4. The **DMPD** disorder results in very slightly different bond lengths and angles for Ca3 as compared to Ca2 and for Ca5 as compared to Ca4. It is interesting to note that the complex contains three different coordination numbers for the three different calcium cations (coordination numbers of six, seven and eight). Overall the bond lengths to the calcium cations have the range 2.302-2.985Å, where the longest bonds are to the sulfur atoms. The coordination sphere for each calcium cation in the complex is shown below (figures 183 to 185) with bond lengths.

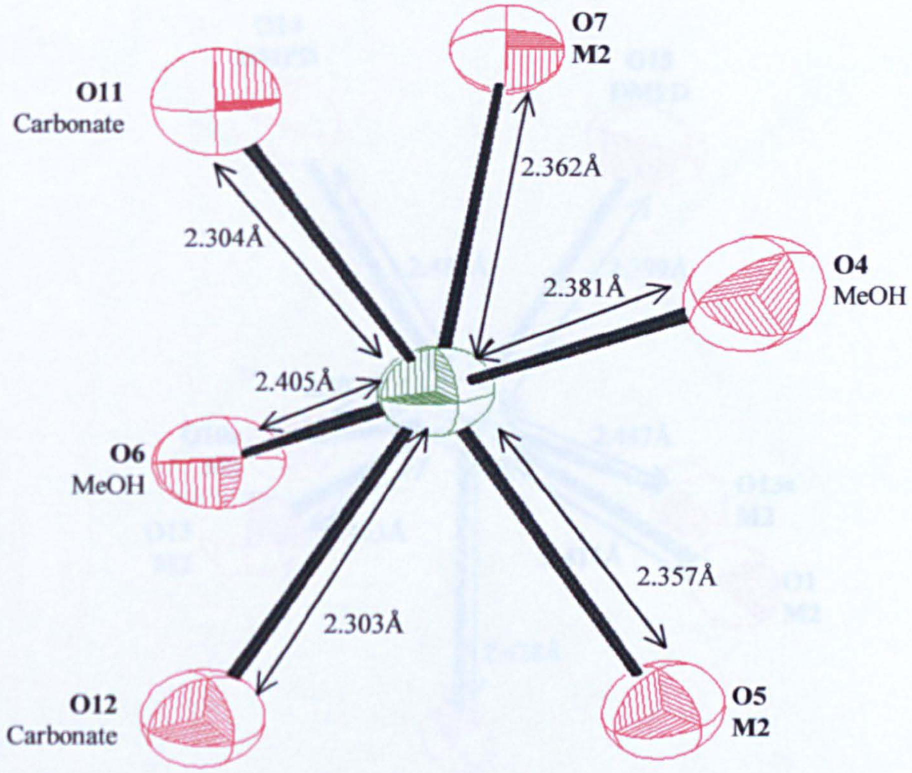


Figure 183. Coordination sphere of a calcium cation (Ca1) from the complex containing calcium cations and carbonate anions, with atom labels and bond lengths.

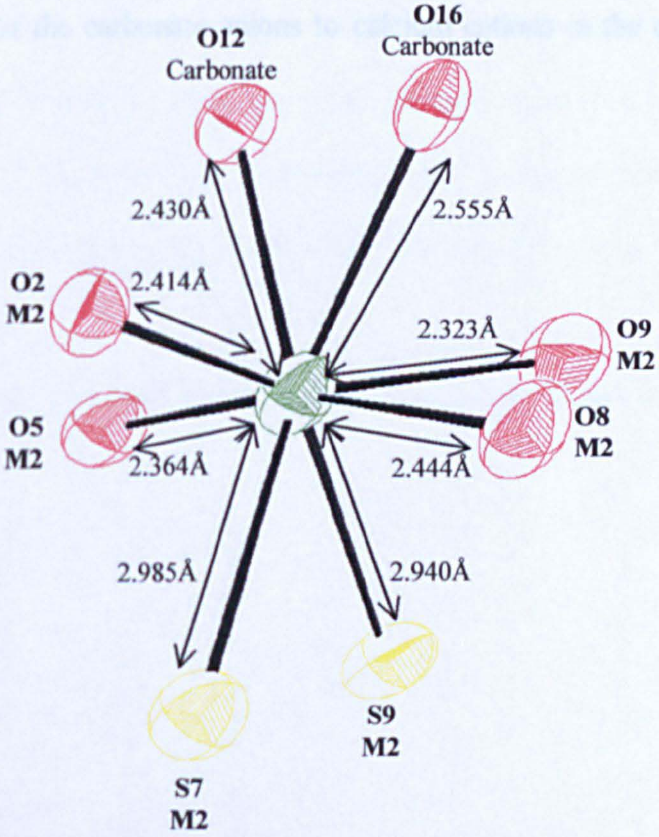


Figure 184. Coordination sphere of a calcium cation (Ca2) from the complex containing calcium cations and carbonate anions, with atom labels and bond lengths.

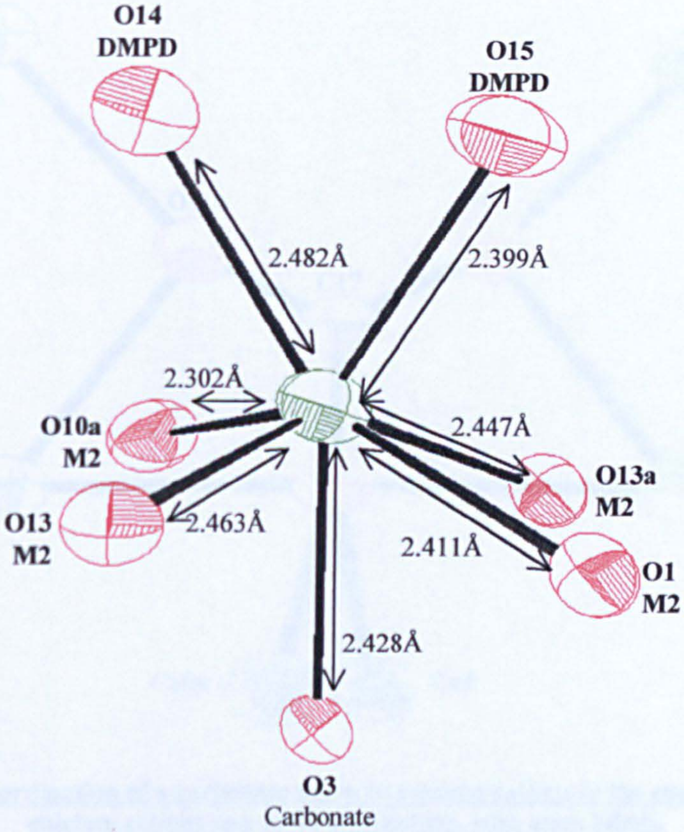


Figure 185. Coordination sphere of a calcium cation (Ca4) from the complex containing calcium cations and carbonate anions, with atom labels and bond lengths.

The coordination of the carbonate anions to calcium cations in the complex is shown below (figure 186).

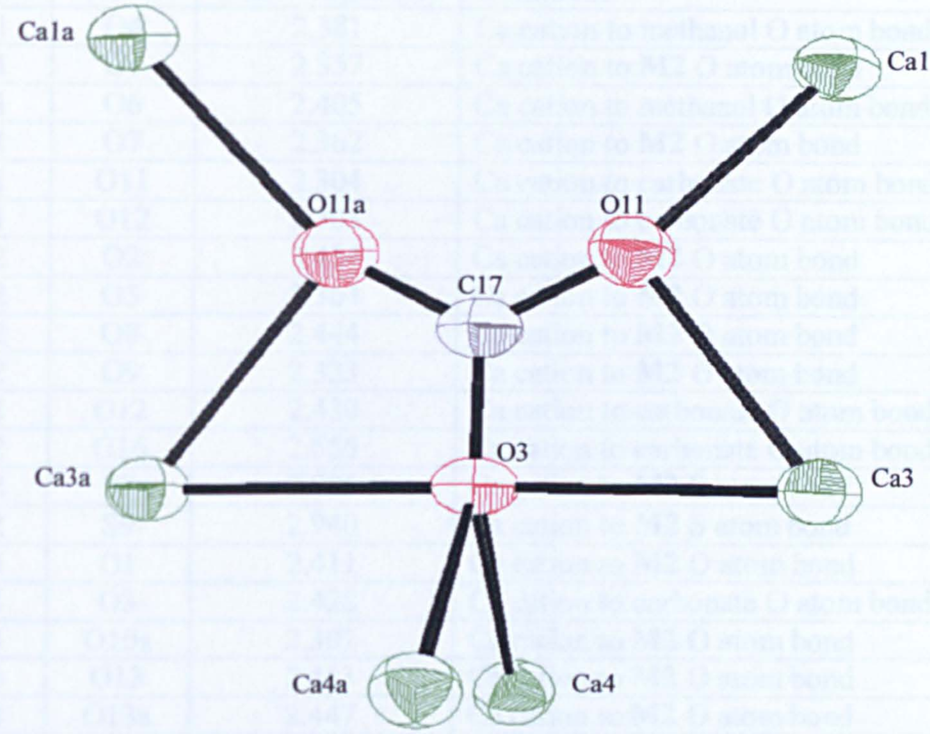


Figure 186. Coordination of a carbonate anion to calcium cations in the complex containing calcium cations and carbonate anions, with atom labels.

The carbonate anions coordinate to calcium cations *via* two modes: terminally and bridging. Both of the carbonate anions coordinate in the same way to the calcium cations. The bond lengths for carbonate anion oxygen atoms to calcium cations have the range 2.303-2.555Å, where the longest bonds are to the calcium cations that are bridged by one carbonate anion (Ca2/Ca3). The carbonate anion is μ_6-CO_3.

Selected bond lengths and bond angles for the complex are shown in the tables below (tables 67 and 68).

Atom 1	Atom 2	Bond length (Å)	Comment
Ca1	O4	2.381	Ca cation to methanol O atom bond
Ca1	O5	2.357	Ca cation to M2 O atom bond
Ca1	O6	2.405	Ca cation to methanol O atom bond
Ca1	O7	2.362	Ca cation to M2 O atom bond
Ca1	O11	2.304	Ca cation to carbonate O atom bond
Ca1	O12	2.303	Ca cation to carbonate O atom bond
Ca2	O2	2.414	Ca cation to M2 O atom bond
Ca2	O5	2.364	Ca cation to M2 O atom bond
Ca2	O8	2.444	Ca cation to M2 O atom bond
Ca2	O9	2.323	Ca cation to M2 O atom bond
Ca2	O12	2.430	Ca cation to carbonate O atom bond
Ca2	O16	2.555	Ca cation to carbonate O atom bond
Ca2	S7	2.985	Ca cation to M2 S atom bond
Ca2	S9	2.940	Ca cation to M2 S atom bond
Ca4	O1	2.411	Ca cation to M2 O atom bond
Ca4	O3	2.428	Ca cation to carbonate O atom bond
Ca4	O10a	2.302	Ca cation to M2 O atom bond
Ca4	O13	2.463	Ca cation to M2 O atom bond
Ca4	O13a	2.447	Ca cation to M2 O atom bond
Ca4	O14	2.482	Ca cation to DMPD O atom bond
Ca4	O15	2.399	Ca cation to DMPD O atom bond
Ca1	Ca2	3.665	Interatomic distance
Ca1	Ca4	5.847	Interatomic distance
C10	O12	1.239	Carbonate bond length
C10	O12a	1.239	Carbonate bond length
C10	O16	1.331	Carbonate bond length
C17	O3	1.287	Carbonate bond length
C17	O11	1.280	Carbonate bond length
C17	O11a	1.280	Carbonate bond length
O2	O8	3.096	Interatomic distance for M2 ligand
O5	O9	3.739	Interatomic distance for M2 ligand

Table 67. Selected bond lengths for the complex containing calcium cations and carbonate anions

Atom 1	Atom 2	Atom 3	Angle (°)	Comment
O4	Ca1	O5	85.94	Methanol O atom to M2 O atom
O4	Ca1	O6	171.05	Methanol O atom to methanol O atom
O4	Ca1	O7	90.83	Methanol O atom to M2 O atom
O4	Ca1	O11	79.84	Methanol O atom to carbonate O atom
O4	Ca1	O12	107.94	Methanol O atom to carbonate O atom
O2	Ca2	O5	103.01	M2 O atom to M2 O atom
O2	Ca2	O8	79.18	M2 O atom to M2 O atom
O2	Ca2	O9	145.66	M2 O atom to M2 O atom
O2	Ca2	O12	84.88	M2 O atom to carbonate O atom
O2	Ca2	O16	75.23	M2 O atom to Carbonate O atom
O2	Ca2	S7	88.33	M2 O atom to M2 S atom
O2	Ca2	S9	142.03	M2 O atom to M2 S atom
O1	Ca4	O3	78.11	M2 O atom to carbonate O atom
O1	Ca4	O10a	108.50	M2 O atom to M2 O atom
O1	Ca4	O13	78.18	M2 O atom to M2 O atom
O1	Ca4	O13a	144.39	M2 O atom to M2 O atom
O1	Ca4	O14	92.08	M2 O atom to DMPD O atom
O1	Ca4	O15	101.44	M2 O atom to DMPD O atom
O3	C17	O11	118.85	Angle across carbonate C atom
O12	C10	O16	116.85	Angle across carbonate C atom
C16	S7	C23	104.21	Angle across S atom in M2
C8	S9	C19	101.29	Angle across S atom in M2

Table 68. Selected bond angles for the complex containing calcium cations and carbonate anions.

The trends for bond lengths for each of the calcium cations can be seen below.

Ca1

Carbonate O atom < M2 O atom < methanol O atom

Ca2

M2 O atom < carbonate O atom < M2 S atom

Ca4

No clear trend

Increasing bond length →

The carbonate oxygen atom bonds to Ca2 are longer than the bonds for Ca1 and Ca4 and are longer than the bonds to the M2 oxygen atom. Ca2 bonds to two oxygen atoms within one carbonate anion, which causes steric strain, whereas Ca1 bonds to two oxygen atoms from two different carbonate anions and Ca4 is coordinated to only one carbonate anion oxygen atom. For Ca4 there is no trend in bond lengths though the shortest bond is to an M2 oxygen atom and the longest bond is to a DMPD oxygen atom. The two carbonate anions in the complex are not equivalent, but are very similar by intramolecular bond lengths and angles. The bonds between the carbonate anion oxygen atoms and the calcium cations are similar in length to the bond lengths observed in the calcium carbonate polymorphs[74] and the bond lengths in the overbased detergent core (determined by EXAFS)[8] of approximately 2.4Å. The two different **M2** ligands can be seen by the different O-O interatomic distances and C-S-C bond angles, where the shortest interatomic O-O distance and largest C-S-C bond angle belong to the **M2** ligand which contains one oxygen atoms which coordinates to three calcium cations.

The solid state structure of the complex is supported by elemental analysis data, where the elemental analysis data shows the decomposition product of the complex rather than the actual complex itself.

5.4.4. Solution State Structure of the Calcium Cation Complex with a Calcium Carbonate Core

The ^1H NMR (d_6-DMSO) spectrum of the calcium cation complex with a calcium carbonate core was collected. The spectrum is very broad, especially the peaks for **M2**. The spectrum was collected in deuterated DMSO as the complex was insoluble in all of the other useful ^1H NMR solvents. ^1H NMR spectroscopy is therefore not a worthwhile technique for understanding the structure of the complex in solution.

5.4.5. Summary

A crystalline mixed ligand complex containing ten calcium cations and carbonate anions has been prepared and characterised. This complex contains many unusual characteristics. The complex has a calcium carbonate core, where the carbonate anions were not added to the reaction mixture and therefore probably came from carbon dioxide in the air, making the reaction an 'overbasing' reaction. The characterisation of calcium cations coordinated to carbonate anions within a complex is unknown and thus this complex is unprecedented. The complex contains **DMPD** which coordinates to calcium cations in the same way as ethylene glycol molecules coordinate to many metal cations, showing that **DMPD** can be considered to be a mimic for ethylene glycol. The complex has a decacalcium cation core, which makes it very unusual. The ten calcium cations are distributed very differently to the ten calcium cations in the calcium cation complex with **BC8** discussed above (**38**). Overall this complex can be considered to be a model for overbased detergents.

5.5. Discussion on the Interaction Between Overbased Detergent Surfactant Molecules and the Overbased Detergent Core

The model complexes that have been prepared and information from the literature can be used to gain some insight into the interaction of overbased detergent surfactant molecules with the overbased detergent calcium carbonate core on an atomic scale. The core is classed as amorphous calcium carbonate,[8, 10] though it probably contains some internal structure and a percentage of water molecules or hydroxide anions,[12] where the water molecules or hydroxide anions are probably included within the core surface, rather than coordinated onto the calcium cations on the surface.[10, 74] The carbonate anions within the core may coordinate to up to six calcium cations, by each oxygen atom bridging two calcium cations.[8] The surfactant molecules coordinate to the core, where the oxygen atoms of the surfactant molecules are probably included within the surface of the core.[7, 9, 10] Sulfurised alkylphenol surfactant molecule oxygen atoms are included to a greater extent into the core than calixarene surfactant molecule oxygen atoms, where the calixarene surfactant oxygen atoms are included in the surface of the core within hydrogen-bonding distance of non-coordinated oxygen atoms.[7] For the sulfurised alkylphenol overbased detergent systems, it has been calculated that calcium cations can be up to approximately 6.8Å from the centre of the core and sulfurised alkylphenol surfactant molecule oxygen atoms can be a maximum of approximately 7.3Å from the centre of the core, showing that most of the sulfurised alkylphenol surfactant molecule oxygen atoms are probably within the surface of the core with the calcium cations.[7] The difference in maximum distances may be due to either a few of the sulfurised alkylphenol surfactant molecule oxygen atoms being uncoordinated to the core or due to the non-spherical nature of sulfurised alkylphenol overbased detergent micelles.[7, 9, 10] For calixarene overbased detergents, modelling has shown that the core may be partially included within the cavity of the calixarene ring,[7] which agrees with the findings shown by the decacalcium cation complex with **BC8** (**38**). This makes the area surrounding the core quite hydrophobic and hence why water molecules or hydroxide anions are probably included within the surface of the core. The hydrophobicity of the area surrounding the core surface will repel water molecules and will therefore stop precipitation of calcium carbonate, which requires water molecules to separate the calcium carbonate from the organic species.[83] Organic materials have been shown to inhibit crystalline calcium carbonate formation by blocking all of the possible growth sites,[85] hence the surfactant molecules must coordinate to all of the calcium cations on the surface of the core and thus are able to stabilise the amorphous calcium carbonate core indefinitely. The coordination spheres of calcium cations are therefore filled by coordination to the core carbonate anions, the surfactant molecules and, if possible, to other small molecules.[8] This explains why larger cores for calix[8]arene overbased detergents require co-surfactants such as stearic acid, as the calix[8]arene surfactant molecules cannot coordinate to all of the calcium cations. Stearic acid is a 'narrow' molecule, which can fit in small spaces to coordinate to coordinatively unsatisfied calcium cations.[10] This also suggests that the coordination mode of stearic acid will be monodentate or bidentate and not bridging bidentate. Surfactant molecules which are flexible, such as calix[8]arene molecules and sulfurised alkylphenol molecules will be very good at ensuring that all of the calcium cations on the surface of the core are fully coordinated as they are able to adapt their shape to match the calcium cation spacings on the surface. For calix[8]arene molecules, this is done by the conformation of the ligand changing, whereas for sulfurised alkylphenol molecules, the molecule twists around the C-S-C bond to provide optimal O-O spacing. These ligands have been shown to be capable of stabilising large model cores (**38** and **39**), which shows that they are good ligands for calcium cations and for overbased detergents. Co-operative interactions between the alkyl chains of the surfactant molecules will allow the surfactant molecules to close pack if necessary.[10] The core of the decacalcium cation complex with **BC8** shows that all of the cations and anions in the core are probably on the surface of the core, with none in the centre of the core.

5.6. Conclusion

Model complexes for overbased detergent precursors and overbased detergents have been prepared and characterised. Two overbased detergent precursor model complexes have been synthesised with calix[8]arene ligands, where one model complex had a tetracalcium cation core (**37**) and the other had a decacalcium cation core (**38**). The tetracalcium cation complex was shown to be very reactive towards carbon dioxide. The overbased detergent model complex (**39**), which has a calcium carbonate core, has sulfurised alkylphenol and ethylene glycol mimic molecules as ligands. This complex was prepared serendipitously. It is probable that overbased detergent models with calix[8]arene ligands will be difficult to prepare due to the low solubility of calix[8]arene ligands in polar solvents and the high reactivity of the complexes toward carbon dioxide. Sulfurised alkylphenol complexes have been shown to be less reactive towards carbon dioxide, which shows why overbased detergents prepared with these surfactant molecules often require catalysts. The only ligand type which has not been included in a model complex has been a carboxylic acid. Two of the model complexes contain ten calcium cations, which is very unusual and shows the ability of the ligands to stabilise large polynuclear cores. The solution structures of the complexes have been shown to be affected by solvents. All three of the complexes are unprecedented and very interesting.

Chapter 6

Experimental

Equipment

Infrared spectra were obtained on a Perkin Elmer Paragon 100 FT-IR spectrometer using potassium bromide discs. NMR spectra (^1H, ^{13}C, 2D COSY) were obtained on a Jeol JNM-LA400 NMR spectrometer. Elemental analyses were obtained on a Fisons EA1108 CHN analyser. Crystal structures were obtained on a Stoe IPDSII Image Plate diffractometer, except for the structures determined at Durham University by Dr. A. Goeta, which were obtained on a Bruker Smart CCD diffractometer.

Chemicals

Chemicals and solvents were used as purchased, except for THF and diethyl ether, which were dried before use. para-*tert*-Butylcalix[8]arene was kindly donated by Dr. N. Clague.

2. Sulfurised Alkylphenol Complexes

2.2. Sulfurised Alkylphenol Ligands

2,2'-Thiobis-(4-methylphenol) (M2) (1)

para-Cresol (20.00g, 0.18mol) was stirred and cooled to 0°C in DCM (100ml). Sulfur dichloride (9.52g, 0.09mol in 10ml DCM) was added slowly to give a yellow solution. The solution was allowed to warm slowly to ambient temperature. After approx. 16h, the solvent was removed to give an oil. The product was obtained from the oil by precipitation from 4:1 petroleum ether (60-80°)/toluene solution. The solid was filtered off and washed with 4:1 petroleum ether (60-80°)/toluene solution. Yield = 7.62g (33%). ^{1}H NMR (d_6-acetone) spectroscopy and IR spectroscopy were used to show that the product was pure. **M2** was recrystallised from toluene/*n*-pentane solution. ^{1}H NMR (400MHz, d_6-acetone) δ8.39 (br. s, 1H, OH), 7.10 (s, 1H, Ph), 6.98 (d, 1H, Ph), 6.81 (d, 1H, Ph) and 2.16 (s, 3H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ155.75 (s, Ph), 135.48 (s, Ph), 131.76 (s, Ph), 130.93 (s, Ph), 121.14 (s, Ph), 116.64 (s, Ph) and 20.80 (s, CH_3). Calc. for $C_{14}H_{14}SO_2$: C, 68.27; H, 5.73; S, 13.02%. Found: C, 68.58; H, 5.72; S, 13.30%. *m/z* 246 (M^+), 139 ($M-C_7H_6O$), 108 ($M-C_7H_6SO$).

2,2'-Thiobis-(4-isopropylphenol) (I2) (2)

4-Isopropylphenol (20.00g, 0.15mol) was stirred and cooled to 0°C in DCM (100ml). Sulfur dichloride (7.56g, 0.07mol in 20ml DCM) was added slowly to give a yellow solution. The solution was allowed to warm slowly to ambient temperature. After approx. 16h, the solvent was removed to give an oil. The product was obtained from the oil by agitation of the oil in a sonic bath in *n*-pentane until the oil dissolved and then rapid cooling. The solid was cold filtered off and washed with cold *n*-pentane. Yield = 10.23g (46%). ^{1}H NMR (d_6-acetone) spectroscopy and IR spectroscopy were used to show that the product was pure. ^{1}H NMR (400MHz, d_6-acetone) δ8.39 (br. s, 1H, OH), 7.15 (s, 1H, Ph), 7.08 (d, 1H, Ph), 7.06 (d, 1H, Ph), 2.76 (m, 1H, CH) and 1.13 (d, 3H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ155.45 (s, Ph), 141.77 (s, Ph), 132.37 (s, Ph), 128.54 (s, Ph), 120.69 (s, Ph), 116.14 (s, Ph), 33.86 (s, CH) and 24.39 (s, CH_3). Calc. for $C_{18}H_{22}SO_2$: C, 71.49; H, 7.33; S, 10.60%. Found: C, 71.26; H, 7.42; S, 10.50%. *m/z* 302 (M^+), 287 (M-OH), 245 (M-C_3H_7O), 136 (M-$C_9H_{11}SO$).

2,2'-Thiobis-(4-*tert*-butylphenol) (B2) (3)

4-*tert*-Butylphenol (5.00g, 33.0mmol) was stirred and cooled to 0°C in DCM (100ml). Sulfur dichloride (1.71g, 16.60mmol) was added slowly to give a yellow solution. The solution was allowed to warm slowly to ambient temperature. After approx. 16h, the solvent was removed to give an oil. The oil was stirred in water and an excess of LiOH was added. The yellow solid that precipitated out from the solution was filtered off. The solid was stirred in water and conc. HCl was added dropwise until the solution was acidic. The product was extracted into diethyl ether, dried over $MgSO_4$ and then the solvent was removed to give an oil. *n*-Pentane was added to the oil and the solution was cooled. The solid that precipitated out from the solution was filtered off and washed with cold *n*-pentane. Yield = 0.42g (8%). ^{1}H NMR (d_6-acetone) spectroscopy and IR spectroscopy were used to show that the product was pure. ^{1}H NMR (400MHz, d_6-acetone) δ8.40 (br. s, 1H, OH), 7.30 (s, 1H, Ph), 7.22 (d, 1H, Ph), 6.86 (d, 1H, Ph) and 1.21 (s, 9H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ155.58 (s, Ph), 144.51 (s, Ph), 131.94 (s, Ph), 127.92 (s, Ph), 120.92 (s, Ph), 116.31 (s, Ph), 35.05 (s, $C(CH_3)_3$) and 32.16 (s, CH_3).

2,2'-Thiobis-(4-*tert*-amylphenol) (A2) (4)

4-*tert*-Amylphenol (10.00g, 61.0mmol) was stirred and cooled to 0°C in DCM (100ml). Sulfur dichloride (3.14g, 30.49mmol in 20ml DCM) was added slowly to give a yellow solution. The solution was allowed to warm slowly to ambient temperature. After approx 16h, the solvent was removed to give an oil. The product was precipitated out from the oil by dissolving the oil in *n*-pentane and then rapidly cooling. The *n*-pentane was decanted off from the solid that precipitated out and clean, cold *n*-pentane was added and the solution re-cooled. The crystals that formed from the solution were filtered off. Yield = 0.56g (5%). ^1H NMR (d_6-acetone) spectroscopy and IR spectroscopy were used to show that the product was pure. ^1H NMR (400MHz, d_6-acetone) δ8.33 (br. s, 1H, OH), 7.21 (s, 1H, Ph), 7.16 (d, 1H, Ph), 6.86 (d, 1H, Ph), 1.54 (q, 2H, CH_2), 1.17 (s, 6H, CH_3) and 0.60 (t, 3H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ155.46 (s, Ph), 142.58 (s, Ph), 132.48 (s, Ph), 128.54 (s, Ph), 120.89 (s, Ph), 116.24 (s, Ph), 38.34 (s, $C(CH_3)_2$), 37.82 (s, CH_2), 29.35 (s, CH_3) and 9.87 (s, CH_3). Calc. for $C_{22}H_{30}SO_2$: C, 73.70; H, 8.43; S, 8.94%. Found: C, 73.77; H, 8.53; S, 8.99%. *m/z* 358 (M^+), 329 ($M-C_2H_5$), 259 ($M-C_7H_{15}$) and 150 ($M-C_{12}H_{16}SO$).

2,2'-Thiobis-(4-*tert*-octylphenol) (O2) (5)

4-*tert*-Octylphenol (20.00g, 0.10mol) was stirred and cooled to 0°C in DCM (150ml). Sulfur dichloride (4.99g, 0.05mol in 10ml DCM) was added slowly to give a yellow solution. The solution was allowed to warm slowly to ambient temperature. After approx. 16h, the solvent was removed to give an oil. The oil was dissolved in minimum *n*-pentane with warming and then rapidly cooled to precipitate out the product, which was cold filtered off and washed with cold *n*-pentane. Yield = 10.61g (49%). ^{1}H NMR (d_6-acetone) spectroscopy and IR spectroscopy were used to show that the product was slightly impure **O2**. **O2** was recrystallised from water and methanol to give crystalline **O2**. ^{1}H NMR (400MHz, d_6-acetone) δ8.31 (br. s, 1H, OH), 7.25 (s, 1H, Ph), 7.19 (d, 1H, Ph), 6.82 (d, 1H, Ph), 1.63 (s, 2H, CH_2), 1.23 (s, 6H, CH_3) and 0.65 (s, 9H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ155.44 (s, Ph), 143.24 (s, Ph), 132.70 (s, Ph), 128.83 (s, Ph), 120.62 (s, Ph), 116.04 (s, Ph), 57.73 (s, $C(CH_3)_2$), 39.00 (s, CH_2), 33.31 (s, $C(CH_3)_3$), 32.69 (s, CH_3) and 32.58 (s, CH_3). *m/z* 442 (M^+), 371 ($M-C_5H_6$), 259 ($M-C_{13}H_{27}$).

2.3. Sulfurised Alkylphenol Complexes Prepared from Methanol Solution

Method 1

Sulfurised alkylphenol (SAP, 1.00g) was stirred into a solution of KOH (2 mole equivalents to SAP) in methanol (approx. 45ml) to give a yellow solution. Metal salt ($CaBr_2$ or $ZnCl_2$, 1 mole equivalent to SAP), predissolved in a small volume of methanol (<5ml), was stirred into the deprotonated SAP solution. After approx. 16h, the solid that had precipitated out from the solution was filtered off. ^{1}H NMR spectroscopy and IR spectroscopy were used to show that the products were complexes. **CaM2** yield = 0.88g (77%). **CaI2** yield = 0.74g (66%). **CaO2** yield = 0.58g (53%). **ZnM2** yield = 0.94g (75%). **ZnI2** yield = 1.16g (96%). **ZnB2** yield = 0.93g (86%).

Method 2

Sulfurised alkylphenol (approx. 0.50g) was dissolved in methanol (approx. 20ml) with the addition of tetrabutylammonium hydroxide (1M solution in methanol, 2 moles equivalent to SAP) to give a yellow solution. Metal salt ($MgBr_2$, $MgCl_2$, $Mg(NO_3)_2$, $CaBr_2$, $CaCl_2$, $Ca(NO_3)_2$, $SrBr_2$, $Sr(NO_3)_2$ or $ZnCl_2$, 1 mole equivalent to SAP), predissolved in a small volume of methanol, was added. For maximum yields, the solution was stirred after the addition of metal salt solution. For crystalline products, the metal salt solution was added carefully and the solution was not mixed after the addition.

MgM2 prepared using $MgBr_2$. A crystalline product was formed after cooling the solution for 1 day, which was shown by IR spectroscopy and ^1H NMR (d_6-acetone) spectroscopy to be a complex. The crystals were found to be unsuitable for single crystal x-ray diffraction. Yield of crystalline complex = 0.59g (100%).

MgM2 prepared using $MgCl_2$. A crystalline product was formed within 1 day. The crystals were found to be unsuitable for single crystal x-ray diffraction.

MgM2 prepared using $Mg(NO_3)_2$. A crystalline product was formed by cooling the solution for more than 1 day. IR spectroscopy and ^1H NMR (d^6-acetone) spectroscopy showed that the crystalline product was a mixture containing **M2** and **MgM2** clustered complex. The crystals were found to be unsuitable for single crystal x-ray diffraction. ^1H NMR (400MHz, d_6-acetone) δ7.43-5.90 (Ph) and 2.17-1.87 (CH_3).

CaM2 prepared using $CaBr_2$. Yield = 0.58g (100%). A crystalline product was formed within 1 day. IR spectroscopy, ^1H NMR (d_6-acetone) spectroscopy and single crystal x-ray diffraction showed that the product was a complex.

CaM2 prepared using $CaCl_2$. Yield = 0.56g (73%). IR spectroscopy and ^1H NMR (d_6-acetone) spectroscopy were used to show that the product was a complex.

CaM2 prepared using $Ca(NO_3)_2$. Yield = 0.64g (83%). IR spectroscopy and ^1H NMR (d_6-acetone) spectroscopy were used to show that the product was a complex.

CaI2 prepared using $CaBr_2$. Yield = 0.22g (41%). A crystalline product was formed within 1 day, which was shown by IR spectroscopy and ^1H NMR (d_6-acetone) spectroscopy to be a complex. The crystals were found to be unsuitable for single crystal x-ray diffraction.

SrM2 prepared using $SrBr_2$. Yield = 0.55g (82%). IR spectroscopy and ^1H NMR (d_6-DMSO) spectroscopy were used to show that the product was a complex.

SrM2 prepared using $Sr(NO_3)_2$. A crystalline product was formed within 1 day.

SrI2 (10) prepared using $SrBr_2$. A crystalline product was formed within 1 day, which was shown by IR spectroscopy, ^1H NMR (d_6-acetone) spectroscopy and single crystal x-ray diffraction to be a complex.

SrO2 prepared using $SrBr_2$. Yield = 0.17g (28%). A crystalline product was formed within 1 week, which was shown by IR spectroscopy and ^{1}H NMR (d_6-acetone) spectroscopy to be a complex.

ZnM2 prepared using $ZnCl_2$. A crystalline product was formed within 1 week, which was shown by IR spectroscopy and ^{1}H NMR ($CDCl_3$) spectroscopy to be a complex. The crystals were found to be unsuitable for single crystal x-ray diffraction.

ZnO2 prepared using $ZnCl_2$. Yield = 0.39g (68%). IR spectroscopy and ^{1}H NMR ($CDCl_3$) spectroscopy were used to show that the product was a complex.

Method 3 **(8, 9, 11)**

Sulfurised alkylphenol (**M2** or **O2**, 0.05-0.20g) was dissolved in methanol (approx. 15ml) with the addition of tetrabutylammonium hydroxide (1M solution in methanol, 2 moles equivalent to SAP) to give a yellow solution. A solution of metal salt ($CaBr_2$ or $SrBr_2$, 1 mole equivalent to SAP), in a small volume of methanol, was layered onto the deprotonated SAP solution. Crystalline product was obtained within 1 day. ^{1}H NMR spectroscopy was used to show that all of the products were complexes. Single crystal x-ray diffraction analysis was performed on all of the products except **CaO2**, which was found to be unsuitable.

Method 4 **(6, 7)**

Sulfurised alkylphenol (**M2** or **I2**, 1.65mmol) was dissolved in methanol (20ml). Tetrabutylammonium hydroxide (1M solution in methanol, 4.95ml, 4.95mmol) was added, followed by pivalic acid (0.17g, 1.65mmol), predissolved in methanol (10ml). $CaBr_2$ (0.66g, 2.80mmol), predissolved in methanol (15ml), was then added and the solution was stirred until solid began to precipitate out. After approx. 16h, the solid was filtered off and washed with a small volume of methanol. ^1H NMR (d_6-acetone) spectroscopy, 2D COSY NMR spectroscopy and IR spectroscopy showed that the products were pure complexes. Yield of CaM2 = 0.41g (87%). Yield of CaI2 = 0.41g (73%).

Analysis of Sulfurised Alkylphenol Complexes Prepared from Methanol Solution

For all complexes, the ^1H NMR spectra and IR spectra were found to be identical, independent of metal salt used or preparation method. Method of preparation was only found to affect the purity of the complex that was formed. Crystalline complexes were found to be less soluble in solvents for ^1H NMR spectroscopy than powder complexes, though the ^1H NMR spectra are identical. NMR spectra and elemental analyses (if available) will be given for each complex, before a general description of IR spectra.

Magnesium Cation Complex with **M2** (**MgM2**). ^1H NMR (400MHz, d_6-DMSO) δ7.47 (d, 1H, Ph), 7.43 (d, 1H, Ph), 7.34 (s, 1H, Ph), 7.21 (s, 15H, Ph), 7.17 (s, 1H, Ph), 7.14 (s, 1H, Ph), 7.06 (d, 1H, Ph), 6.91 (s, 1H Ph), 6.90 (d, 1H , Ph), 6.77 (d, 15H, Ph), 6.71 (d, 1H, Ph), 6.69 (d, 1H, Ph), 6.58 (d, 15H, Ph), 6.47 (d, 1H, Ph), 6.18 (d, 1H, Ph), 4.33 (br. s, 17H, H_2O), 3.57 (br. s, 27H, H_2O), 2.17 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.09 (s, 45H, CH_3) and 2.02 (s, 3H, CH_3).

Calcium Cation Complex with **M2** (**CaM2**). ^1H NMR (400MHz, d_6-acetone) δ7.37 (s, 1H, Ph), 7.34 (s, 1H, Ph), 7.19 (s, 1H, Ph), 7.05 (s, 1H, Ph), 7.01 (s, 1H, Ph), 6.91 (d, 1H, Ph), 6.81 (d, 1H, Ph), 6.71 (d, 1H, Ph), 6.66 (s, 1H, Ph), 6.48 (d, 1H, Ph), 6.46 (d, 1H, Ph), 6.42 (d, 1H, Ph), 6.24 (d, 1H, Ph), 6.21 (d, 1H, Ph), 5.97 (d, 1H, Ph), 5.59 (d, 1H, Ph), 5.46 (d, 1H, Ph), 4.86 (d, 1H, Ph), 3.29 (s, 19H, MeOH), 2.87 (br. s, 12H, H_2O), 2.21 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.95 (s, 3H, CH_3) and 1.52 (s, 3H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ168.23 (s, Ph), 167.59 (s, Ph), 167.41 (s, Ph), 165.15 (s, Ph), 164.62 (s, Ph), 140.24 (s, Ph), 137.77 (s, Ph), 137.01 (s, Ph), 136.34 (s, Ph), 135.88 (s, Ph), 132.97 (s, Ph), 132.57 (s, Ph), 132.25 (s, Ph), 132.18 (s, Ph), 131.73 (s, Ph), 131.58 (s, Ph), 129.51 (s, Ph), 126.28 (s, Ph), 125.10 (s, Ph), 124.96 (s, Ph), 124.90 (s, Ph), 124.49 (s, Ph), 123.68 (s, Ph), 123.38 (s, Ph), 123.30 (s, Ph), 123.14 (s, Ph), 123.03 (s, Ph), 122.79 (s, Ph), 122.16 (s, Ph), 122.09 (s, Ph), 121.80 (s, Ph), 121.68 (s, Ph), 120.93 (s, Ph), 120.60 (s, Ph), 118.72 (s, Ph), 50.12 (s, CH_3) and 20.84 (s, CH_3). Calc. for $CaC_{17}H_{24}SO_5$ (CaM2.3MeOH): C, 53.66; H, 6.36; S, 8.43%. Found: C, 53.94; H, 6.37; S, 8.35%.

Calcium Cation Complex with I2 (CaI2). ^{1}H NMR (400MHz, d_6-acetone) δ7.47 (s, 1H, Ph), 7.45 (s, 1H, Ph), 7.14 (s, 1H, Ph), 7.11 (s, 1H, Ph), 7.06 (s, 1H, Ph), 6.88 (d, 1H, Ph), 6.87 (d, 1H, Ph), 6.86 (s, 1H, Ph), 6.81 (d, 1H, Ph), 6.51 (d, 1H, Ph), 6.48 (d, 1H, Ph), 6.44 (d, 1H, Ph), 6.27 (d, 1H, Ph), 6.21 (d, 1H, Ph), 6.05 (d, 1H, Ph), 5.60 (d, 1H, Ph), 5.35 (d, 1H, Ph), 5.10 (d, 1H, Ph), 2.78 (m, 2H, CH), 2.64 (m, 1H, CH), 2.62 (m, 1H, CH), 2.45 (m, 1H, CH), 2.18 (m, 1H, CH), 1.25 (d, 6H, CH_3), 1.24 (d, 3H, CH_3), 1.21 (d, 3H, CH_3), 1.13 (d, 3H, CH_3), 1.11 (d, 3H, CH_3), 1.10 (d, 3H, CH_3), 1.09 (d, 3H, CH_3), 1.07 (d, 3H, CH_3), 0.96 (d, 3H, CH_3), 0.90 (d, 3H, CH_3) and 0.79 (d, 3H, CH_3). ^{13}C NMR (100.6MHz), d_6-acetone) δ167.97 (s, Ph), 167.60 (s, Ph), 167.42 (s, Ph), 164.90 (s, Ph), 164.78 (s, Ph), 164.01 (s, Ph), 137.03 (s, Ph), 135.88 (s, Ph), 135.73 (s, Ph), 135.36 (s, Ph), 134.71 (s, Ph), 134.56 (s, Ph), 133. 80 (s, Ph), 133.26 (s, Ph), 133.22 (s, Ph), 131.87 (s, Ph), 131.86 (s, Ph), 129.88 (s, Ph), 129.23 (s, Ph), 129.11 (s, Ph), 128.91 (s, Ph), 128.90 (s, Ph), 128.09 (s, Ph), 125.74 (s, Ph), 125.50 (s, Ph), 124.42 (s, Ph), 124.38 (s, Ph), 123.65 (s, Ph), 122.59 (s, Ph), 122.39 (s, Ph), 121.48 (s, Ph), 121.20 (s, Ph), 121.15 (s, Ph), 120.01 (s, Ph), 33.97 (s, CH), 33.94 (s, CH), 33.69 (s, CH), 33.54 (s, CH), 33.24 (s, CH), 32.43 (s, CH), 25.64 (s, CH_3), 25.46 (s, CH_3), 25.35 (s, CH_3), 25.27 (s, CH_3), 25.08 (s, CH_3), 24.97 (s, CH_3), 24.63 (s, CH_3), 24.56 (s, CH_3), 23.92 (s, CH_3), 23.77 (s, CH_3) and 23.56 (s, CH_3). Calc. for $Ca_2C_{37}H_{54}S_2O_{10}$ [$(CaI2)_2$.MeOH.5H_2O]: C, 55.34; H, 6.78; S, 7.98%. Found: C, 55.29; H, 6.68; S, 7.85%.

Calcium Cation Complex with **O2** (CaO2). ^1H NMR (400MHz, d_6-acetone) δ7.59-5.59 (3H, Ph), 3.29 (s, 4H, MeOH), 1.67-0.61 (22H, alkyl).

Strontium Cation Complex with **M2** (SrM2). ^1H NMR (400MHz, d_6-DMSO) δ7.07 (br. s, 1H, Ph), 6.64 (br. s, 1H, Ph), 6.28 (br. s, 1H, Ph), 3.17 (s, 5H, MeOH) and 2.05 (s, 3H, CH_3). Calc. for $SrC_{16}H_{22}SO_5$ (SrM2.2MeOH.H_20): C, 46.42; H, 5.36; S, 7.74%. Found: C, 46.72; H, 5.19; S, 8.02%.

Strontium Cation Complex with **I2** (SrI2). ^1H NMR (400MHz, d_6-acetone) δ7.55-5.05 (Ph) and 3.00-0.75 (alkyl). Calc. for $SrC_{18}H_{26}SO_5$ (SrI2.3H_2O): C, 48.90; H, 5.93; S, 7.25%. Found: C, 49.28; H, 5.90; S, 7.56%.

Strontium Cation Complex with **O2** (SrO2). ^1H NMR (400MHz, d_6-acetone) δ7.42 (br. s, 1H, Ph), 6.89 (br. s, 1H, Ph), 6.60 (br. s, 1H, Ph), 3.28 (s, 1H, MeOH), 1.65 (s, 2H, CH_2), 1.26 (s, 6H, CH_3) and 0.76 (s, 9H, CH_3). Calc. for $SrC_{29}H_{48}SO_5$ (SrO2.MeOH.2H_2O): C, 58.41; H, 8.11; S, 5.38%. Found: C, 58.76; H, 7.80; S, 5.16%.

Zinc Cation Complex with **M2** (**ZnM2**). ^{1}H NMR (400MHz, $CDCl_3$) δ7.37 (s, 1H, Ph), 6.85 (br. s, 1H, Ph), 6.77 (br. s, 1H, Ph) and 2.18 (s, 3H, CH_3).

Zinc Cation Complex with **I2** (**ZnI2**). ^{1}H NMR (400MHz, d_6-acetone) δ7.64-5.99 (m, 3H, Ph), 2.80-2.38 (m, 1H, CH) and 1.33-0.86 (m, 3H, CH_3).

Zinc Cation Complex with **B2** (**ZnB2**). ^{1}H NMR (400MHz, d_6-acetone) δ8.07-6.73 (m, 3H, Ph) and 1.26-0.88 (m, 9H, CH_3).

Zinc Cation Complex with **O2** (**ZnO2**). ^{1}H NMR (400MHz, $CDCl_3$) δ7.72-6.64 (m, 3H, Ph) and 1.69-0.68 (m, 17H, alkyl).

Infrared Spectroscopy Spectra

Infrared spectroscopy was used as a finger-printing method to determine if a complex had been formed. For all complexes there were characteristic differences in the IR spectrum when compared to the IR spectrum of the free sulfurised alkylphenol ligand, see table below (table 69).

Free sulfurised alkylphenol IR spectrum	Complex IR spectrum
Strong broad band at approx. 3300cm^{-1}, assigned as O-H str.	Band reduced in strength to weak and split into several overlapped broad bands, assigned as loss of SAP phenolic protons, with remaining bands due to O-H str. for methanol.
Strong sharp band at approx. 2900cm^{-1} for all SAP except M2, assigned as C-C alkyl str.	Unchanged
Medium sharp band at approx. 1500cm^{-1}, always overlapped with band at approx. 1485cm^{-1}	No longer present
Strong sharp band at approx. 1485cm^{-1}, overlapped with less strong bands	Strong sharp band with no overlapped bands
Strong/medium band at approx. 1230cm^{-1}	Shifted or reduced in strength, depending on SAP
Strong/medium band at approx. 820cm^{-1}	No longer present

Table 69. Summary of IR analysis on free SAP versus complex.

In general the complex IR spectra have fewer peaks and most peaks that are common to both free SAP and complex are shifted in the complex IR spectrum.

2.4. Sulfurised Alkylphenol Complexes Prepared From Acetone And Water Solution

General Preparation

Metal salt ($Mg(NO_3)_2$, $MgBr_2$, $Ca(NO_3)_2$, $CaBr_2$, $Sr(NO_3)_2$, $SrBr_2$, $Ba(NO_3)_2$, $BaBr_2$, LiBr, $NaNO_3$, KI or $ZnCl_2$, 1 mole equivalent to SAP) was added to water (6ml), followed by water (2ml) and then acetone/water solution (25:75 acetone/water, 2ml). A solution of sulfurised alkylphenol (SAP, 0.10g) plus KOH (2 moles equivalent to SAP) in acetone/water solution (50:50 acetone/water, 2ml) was layered onto the acetone/water solution. Single crystal x-ray diffraction was used to show that the crystalline products were complexes. The reactions to form SrM2, BaM2, LiM2, NaM2, KM2, ZnM2,

CaO2, **BaO2** and **MgO2** produced powders and so were not analysed. The reactions to form **CaM2**, **CaB2**, **SrI2**, **MgI2**, **CaB2** and **SrO2** formed crystals that were unsuitable for single crystal x-ray diffraction.

MgM2 (**12**) prepared using $Mg(NO_3)_2$. Single crystal x-ray diffraction showed that a complex had been prepared. ^{1}H NMR (d_6-DMSO, 400MHz) δ7.21 (br. s, 1H, Ph), 6.78 (br. d, 1H, Ph), 6.58 (br. d, 1H, Ph) and 2.08 (s, 3H, CH_3). Not enough crystals could be prepared for any other form of analysis.

CaI2 prepared using $CaBr_2$.

SrB2 (**13**) prepared using $SrBr_2$. Single crystal x-ray diffraction showed that a complex had been prepared. ^{1}H NMR (d_6-DMSO, 400MHz) δ7.35 (s, 1H, Ph), 6.85 (br. d, 1H, Ph), 6.37 (br. s, 1H, Ph) and 1.18 (s, 9H, CH_3). Calc. for $SrC_{20}H_{38}SO_9$ [$Sr(H_2O)_7$.**B2**]: C, 44.31; H, 7.06; S, 5.91%. Found: C, 44.35; H, 6.60; S, 5.59%.

BaI2 (**14**) prepared using $BaBr_2$. Single crystal x-ray diffraction showed that a complex had been prepared. ^{1}H NMR (400MHz, d_6-acetone) δ7.22 (s, 1H, Ph), 6.94 (br. d, 1H, Ph), 6.77 (br. d, 1H, Ph), 3.14 (br. s, 6H, H_2O), 2.71 (m, 1H, CH) and 1.12 (d, 6H, CH_3).

BaB2 (**15**) prepared using $BaBr_2$. Single crystal x-ray diffraction showed that a complex had been prepared. ^{1}H NMR (d_6-acetone) spectroscopy showed that the crystalline product contained clusters. ^{1}H NMR (400MHz, d_6-acetone) δ7.72-7.32 (br. s plus smaller peaks, 2H, Ph), 6.94-6.80 (br. s plus smaller peaks, 2H, Ph), 6.75-6.06 (br. s plus smaller peaks, 2H, Ph), 3.09 (br. s, 3H, H_20) and 1.28-1.03 (br. s plus smaller peaks, 18H, CH_3). Calc. for $BaC_{20}H_{36}SO_8$ [$Ba(H_2O)_6$.B2]: C, 41.86; H, 6.32; S, 5.59%. Found: C, 42.00; H, 6.11; S, 5.59%.

2.5. Sulfurised Alkylphenol Complexes Prepared from Acetonitrile and Water Solution

General Preparation

Sulfurised alkylphenol (**M2** or **I2**, 0.05g) was dissolved in acetonitrile (approx. 10ml) plus a small volume of water (<2ml) and tetrabutylammonium hydroxide (1M solution in methanol, 2 mole equivalents to SAP) to give a yellow solution. Metal salt ($MgBr_2$, $SrBr_2$ or $BaBr_2$, 1 mole equivalent to SAP) was dissolved in acetonitrile with the addition of a minimum volume of water and this solution was layered onto the deprotonated SAP solution. Within 1 week, powder and crystalline product had precipitated out from the solutions. All of the crystalline products were found to be unsuitable for single crystal x-ray diffraction and no other analysis was performed.

2.6. Alternative Sulfurised Alkylphenol Ligands

2,2'-Thiobis-(4-*tert*-butylcatechol) (**DHB2**) (**16**)

Sulfur dichloride (3.10g, 0.03mol) as added dropwise to a stirred, 0°C solution of 4-*tert*-butylcatechol (10.00g, 0.06mol) in DCM (100ml) to give a green solution. After 6h, the solvent was removed to give an oil. The solid product was precipitated out using *n*-

pentane. The crude product (solid and oil) was recrystallised from warm petroleum ether (40-60°)/acetone by rapid cooling to give crystals which were found by single crystal x-ray diffraction to be a 1:1 complex of **DHB2** with acetone. Yield crude product = 3.83g (35%). Yield from recrystallisation of 1g crude product (solid and oil) = 0.61g (61%). The product from recrystallisation was shown to be pure by ^{1}H NMR (d_6-acetone) spectroscopy. ^{1}H NMR (400MHz, d_6-acetone) δ7.90 (br. s, 1H, OH), 6.86 (s, 1H, Ph), 6.82 (s, 1H, Ph), 2.08 (s, 3H, acetone) and 1.18 (s, 9H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ145.96 (s, Ph), 144.47 (s, Ph), 143.75 (s, Ph), 122.45 (s, Ph), 121.23 (s, Ph), 114.32 (s, Ph), 35.12 (s, $C(CH_3)_3$), 32.13 (s, CH_3) and 31.05 (s, acetone). Calc. for $C_{23}H_{32}SO_5$ (**DHB2**.acetone): C, 65.69; H, 7.67; S, 7.62%. Found: C, 65.92; H, 7.66; S, 7.43%. *m/z* 362 (**DHB2** M^+), 291 ($M-C_4H_8O$), 198 ($M-C_{10}H_{12}O_2$) and 166 ($M-C_{10}H_{12}SO_2$).

2,2'-Sulfinylbis-(4-methylphenol) (MOM2) (17)

$CaBr_2$ (0.10g, 0.42mmol) was added to water (6ml) followed by water (2ml) and then THF/water solution (25:75 THF/water, 2ml). A solution of **M2** (0.10g, 0.41mmol) and KOH (0.05g, 0.89mmol) in THF/water solution (50:50 THF/water, 2ml) was layered onto the THF/water solution. After 1 month, a small number of crystals had formed from the solution, which were shown by single crystal x-ray diffraction to be **MOM2**. Not enough crystals were obtained for any other form of analysis.

2,2'-Sulfonylbis-(4-methylphenol) (DOM2) (18)

M2 (1.97g, 8.00mmol) was added to a solution of glacial acetic acid (15ml) and hydrogen peroxide (9ml, 35% w/w). The mixture was heated to reflux for 1h and then extra hydrogen peroxide (4ml, 35% w/w) was added. The solution was heated to reflux for a further 1h, before water (150ml) was added and the solution allowed to cool. After approx. 16h, crystalline product had formed from the solution, which was filtered off and washed with water. Yield = 0.61g (27%). The crude product was recrystallised from acetone/water to give crystals, which were shown by single crystal x-ray diffraction to be **DOM2**. ^{1}H NMR (400MHz, d_6-acetone) δ9.46 (s, 1H, OH), 7.58 (s, 2H, Ph), 7.32 (d, 2H, Ph), 6.87 (d, 2H, Ph) and 2.27 (s, 6H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ155.60 (s, Ph), 137.73 (s, Ph), 130.49 (s, Ph), 130.18 (s, Ph), 126.53 (s, Ph), 118.95 (s, Ph) and 20.69 (s, CH_3). *m/z* 278 (M^+), 108 ($M-C_7H_6SO_3$).

2.6.3. Preparation of Complexes with the Alternative Sulfurised Alkylphenol Ligands

2.6.3.1. Complexes with 2,2'-Thiobis-(4-*tert*-butylcatechol) (DHB2)

Method 1

DHB2 (0.05g, 0.14mmol) was dissolved in methanol (approx. 15ml). Tetrabutylammonium hydroxide (1M solution in methanol, 0.55ml, 0.55mmol) was added and the solution went yellow then dark brown/orange. Metal salt ($CaBr_2$, $SrBr_2$ or $BaBr_2$, 0.28mmol), predissolved in methanol (approx. 2ml), was added and the solution instantly became intense dark blue.

For the reaction with $CaBr_2$, solid precipitated out from the solution within 1 week, to give a dark orange solution and pale green solid. The solid was filtered off to give an intense dark blue solution and blue solid. Yield = 0.01g. After 2 months, the solution became orange.

For the reaction with $SrBr_2$, solid precipitated out from the solution within 1 day. After 1 week, the solution was dark orange with grey solid. The solid was filtered off and the solid and solution quickly went intense dark blue. Yield = <0.01g. After 2 months, the solution became dark orange with brown/red solid in it.

For the reaction with $BaBr_2$, solid began to precipitate out from the solution within 1 minute. After 1 week, the solution was dark orange with pale pink solid. The solid was filtered off and the solid and solution quickly went intense dark blue. Yield = 0.03g. After 2 months, the solution was colourless with orange/brown solid in it.

All of the solids that were isolated were found to be insoluble in all useful ^1H NMR spectroscopy solvents and so no analysis was carried out.

Method 2

DHB2 (0.10g, 0.28mmol) and KOH (0.06g, 10.7mmol) were stirred in water (25ml) until **DHB2** dissolved, to give a weak dark pink/brown solution. Metal salts were added to 1ml portions of this solution.

Metal Salt	Observations after addition of metal salt (no mixing)	Observations after mixing
LiBr	No change	Solution became slightly darker
NaCl	No change	Solution became slightly darker
NaI	No change	Solution became slightly darker
Na(Ac)	No change	Solution became slightly darker
KI	No change	Solution became slightly darker
$Mg(NO_3)_2$	Pink ppt in pink solution	Pink ppt in pink solution
$Ca(OH)_2$	Pink ppt/pink solution, blue meniscus	Intense dark blue solution
$CaCl_2$	Intense dark blue solution	Intense dark blue solution
$CaBr_2$	Intense dark blue solution	Intense dark blue solution
$Ca(NO_3)_2$	Blue ppt in pink solution	Intense dark blue solution
$SrBr_2$	Intense dark blue solution	Intense dark blue solution
$Ba(NO_3)_2$	Pink ppt/pink solution, blue meniscus	Intense dark blue solution
V_2O_5	Brown ppt in brown solution	Black ppt in black solution
$CrCl_3$	Pale pink ppt in pink solution	Dark green solution
$Fe(NO_3)_3$	Dark red ppt in brown solution	Black ppt in black solution
$CoBr_2$	Brown solution	Dark purple ppt/brown solution
$NiCl_2$	Pink ppt in pink solution	Grey ppt in brown solution
$Cu(Ac)_2$	Pink solution	Dark brown ppt/brown solution
$ZnCl_2$	Pink ppt in pink solution	Pink ppt in pink solution
$PbCl_2$	No change	Brown ppt in brown solution

Table 70. Summary of observations on adding metal salts to deprotonated DHB2 solution.

Method 3

DHB2 (0.05g, 0.14mmol) and metal salt ($CaBr_2$, $SrBr_2$, $BaBr_2$, $CuCl_2$ or $NiCl_2$, 0.28mmol) were dissolved in methanol (approx. 15ml) and ammonia gas was allowed to slowly diffuse into the solution.

For the reaction with $CaBr_2$, the solution went green, then turquoise, then an intense dark blue as the ammonia diffused through the solution, taking approx. 10min for the whole of the solution to become dark blue. After 1 day, orange/brown solid had precipitated out from the solution and the solution was orange.

For the reaction with $SrBr_2$, the solution became completely intense dark blue within 5min. After 1 week, orange solid had precipitated out from the solution, which was also orange.

For the reaction with $BaBr_2$, the solution became completely intense dark blue within 2min. After 1 week, pale blue solid had precipitated out from the solution.

For the reaction with $CuCl_2$, the solution went completely intense dark brown/black within 2min.

For the reaction with $NiCl_2$, the meniscus became brown with the solution below taking 5min to become bright yellow. A small quantity of yellow solid precipitated out from the solution. After 1 day, the solution was black with violet crystals precipitated out from it. The crystalline product was found to be unsuitable for single crystal x-ray diffraction.

The reaction was also carried out without any metal salt added and for this reaction the solution went yellow after 5min, then dark green, then black.

Method 4

Ca granules (0.02g, 0.55mmol) were added to methanol (7ml), followed by methanol (1ml). A solution of **DHB2** (0.10g, 0.28mmol) in methanol (4ml) was layered onto the methanol solution. No change was observed after 1 day and so the Ca granules were activated by warming, which caused gases to be liberated. Within 1 day of the Ca granules being activated, the solution became black. After 1 month, the solution was orange with orange solid precipitated out from the solution.

Method 5

$Ca(OH)_2$ (0.02g, 0.28mmol) was dissolved in water (10ml) and then filtered. Under nitrogen gas flow, a solution of methanol/water (50:50 methanol/water, 10ml) was layered onto the $Ca(OH)_2$ solution followed by a solution of **DHB2** (0.05g, 0.14mmol) in methanol (10ml). After 3 months, a small quantity of blue solid had precipitated out from the solution, which was pale orange.

Method 6

$CaBr_2$ (0.07g, 0.28mmol) was added to water (7ml) followed by water (2ml). A solution of THF/water (25:75 THF/water, 2ml) was layered onto the $CaBr_2$ solution, followed by a solution of **DHB2** (0.05g, 0.14mmol) and KOH (0.03g, 0.53mmol) in THF/water (50:50 THF/water, 2ml). Within 1 day, the solution became intense dark blue. After 1 month, pale brown solid had precipitated out from the solution, which was orange.

Method 7

Metal hydroxide (LiOH, KOH, 1.38mmol) was added to a degassed solution of DMI (25ml) under nitrogen. The solution was warmed to dissolve the metal hydroxide. **DHB2** (0.10g, 0.28mmol) was added to the solution and the solution slowly went yellow. After 1 month, the solution containing LiOH had gone dark orange/brown in colour.

$CaBr_2$ (0.13g, 0.55mmol) was added to the solution containing KOH and the solution became brown/orange in colour.

Method 8

A solution of **DHB2** in d_6-acetone was prepared and the ^1H NMR spectrum collected. The ^1H NMR spectrum was as expected. A KOH pellet was mixed in the solution with a small volume of d^1-methanol to give an intense dark red solution. This solution was filtered and the ^1H NMR (d_6-acetone) spectrum collected. The ^1H NMR spectrum was very different to the spectrum for **DHB2.**

2.6.3.2. Complexes with 2,2'-Sulfonylbis-(4-methylphenol) (DOM2)

Method 1

Methanol (6ml) was layered onto a solution of metal salt ($CaBr_2$ or $SrBr_2$, 0.18mmol) in methanol (1ml). A dark yellow solution of **DOM2** (0.05g, 0.18mmol) plus KOH (0.02g, 0.36mmol) in methanol (approx. 3ml) was layered onto the methanol. As yet, nothing has precipitated out of the solution.

Method 2

Metal salt ($CaBr_2$ or $SrBr_2$, 0.18mmol) was added to water (6ml), followed by water (2ml). A solution of acetone/water (25:75 acetone/water, 4ml) was layered onto the water before a dark yellow solution of **DOM2** (0.05g, 0.18mmol) plus KOH (0.02g, 0.36mmol) in acetone/water (50:50 acetone/water, 2ml). As yet, nothing has precipitated out from the solution.

Method 3

DOM2 (0.05g, 0.18mmol) and $CaBr_2$ (0.06g, 0.25mmol) were dissolved in methanol (approx. 15ml) and ammonia gas was allowed to diffuse into the solution. After 2 weeks, powder and crystals had precipitated out from the solution.

3. Calix[8]arene Complexes

3.2. Calix[8]arene Ligands

para-Isopropylcalix[8]arene (IC8) (19)

para-Isopropylphenol (45.63g, 0.34mol), paraformaldehyde (17.50g, 0.50mol) and xylene (300ml) were stirred under nitrogen. Sodium hydroxide solution was added (1ml, 10M in water, 0.01mol) and the mixture was brought to reflux with stirring and under nitrogen flow. Solid began to precipitate out from the solution after 30min. After 6h, the solution was left to cool. The solid that precipitated out from the solution was filtered off and washed with water and then acetone. Impurities were removed by heating the crude product in methanol. Yield = 25.89g (52%). ^{1}H NMR ($CDCl_3$ or CD_2Cl_2) spectroscopy, IR spectroscopy and single crystal x-ray diffraction were used to show that the product was pure **IC8**. ^{1}H NMR (400MHz, $CDCl_3$) δ9.52 (s, 1H, OH), 7.01 (s, 2H, Ph), 4.34 (br. s, 1H, CH_2), 3.47 (br. s, 1H, CH_2), 2.79 (m, 1H, CH) and 1.17 (d, 6H, CH_3). ^{13}C NMR (100.6MHz, CD_2Cl_2) δ147.10 (s, Ph), 143.24 (s, Ph), 129.51 (s, Ph), 126.72 (s, Ph), 33.68 (s, CH_2), 32.25 (s, CH) and 24.31 (s, CH_3). Calc. for $C_{80}H_{96}O_8$: C, 81.04; H, 8.16%. Found: C, 81.14; H, 8.42%. *m/z* 1184 (M^+).

3.4. Calix[8]arene Salts

3.4.2. Inorganic Calix[8]arene Salts

Method 1

para-*tert*-Butylcalix[8]arene (**BC8**, 0.05g, 0.39mmol) was stirred in DMF under nitrogen. Metal hydroxide (LiOH, NaOH or KOH, 2.3mmol) was added and the solution was warmed and stirred. When solid had precipitated from solution, the DMF was decanted off and replaced with diethyl ether. The solid was filtered off and washed with ether.

Product from LiOH. Yield = 0.22g. The product was found to be insoluble in all useful ^{1}H NMR spectroscopy solvents. IR spectroscopy indicated that the product included partially deprotonated calixarene.

Product from NaOH. Yield = 0.57g. IR spectroscopy and ^1H NMR (d_6-DMSO) spectroscopy indicated a simple complex. ^1H NMR (400MHz, d_6-DMSO) δ17.21 (br. s, 1H, OH), 14.27 (br. s, 2H, OH), 7.94 (s, 5H, DMF), 6.84 (s, 16H, Ph), 3.70 (br. s, 8H, CH_2), 2.88 (s, 16H, DMF), 2.72 (s, 16H, DMF) and 1.15 (s, 72H, CH_3).

Product from KOH. Yield = 0.12g. IR spectroscopy and ^1H NMR (CD_2Cl_2) spectroscopy indicated a simple complex. ^1H NMR (400MHz, CD_2Cl_2) δ8.48 (br. s, 1H, OH), 7.95 (s, 2H, DMF), 7.20 (s, 16H, Ph), 4.37 (br. s, 7H, CH_2), 3.54 (br. s, 7H, CH_2), 2.91 (s, 6H, DMF), 2.82 (s, 6H, DMF), 2.05 (br. s, 62H, H_2O) and 1.26 (s, 72H, CH_3).

Method 2

BC8 (0.20g, 0.15mmol) was stirred under nitrogen in methanol. Tetrabutylammonium hydroxide (1M solution in methanol, 0.30ml, 0.30mmol) was added followed by DMI (2.0ml). Once the solution was clear, a solution of the metal salt ($ZnCl_2$ or $MgBr_2$, 1.54mmol) in methanol was carefully added. A small quantity of solid precipitated from the solution immediately. Within 1 week, crystals had formed from the solution.

For the reaction with $ZnCl_2$, the mixture was agitated in a sonic bath for 5min and then the solid was filtered off. Yield = 0.16g. ^1H NMR (d_6-DMSO) spectroscopy on the white powder showed a simple, salt structure. ^1H NMR (400MHz, d_6-DMSO) δ11.00 (br. s, 5H, OH), 7.01 (s, 16H, Ph), 3.78 (br. s, 16H, CH_2) and 1.15 (s, 72H, CH_3).

For the reaction with $MgBr_2$, ^1H NMR (d_6-DMSO) spectroscopy on the crystals showed a salt structure. No yield was determined. ^1H NMR (400MHz, d_6-DMSO) δ13.36 (br. s, 4H, OH), 7.01 (s, 16H, Ph), 3.75 (br. s, 16H, CH_2) and 1.18 (s, 72H, CH_3).

3.4.3. Organic Calix[8]arene Salts

Method 1

BC8 (0.25g, 0.19mmol) and tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol) were stirred under nitrogen in diethyl ether until the calixarene dissolved. The solvent was removed under vacuum. Dry diethyl ether was added to the off-white solid and within 1 day crystals had formed. ^{1}H NMR ($CDCl_3$) spectroscopy on the crystals showed the presence of the tetrabutylammonium cation and partially deprotonated calixarene. No yield was determined. ^{1}H NMR (400MHz, $CDCl_3$) δ7.07 (s, 16H, Ph), 3.90 (br. s, 12H, CH_2), 3.07 (t, 28H, CH_2), 1.51 (t, 28H, CH_2), 1.30 (q, 28H, CH_2), 1.25 (s, 72H, CH_3) and 0.87 (t, 43H, CH_3).

Method 2

BC8 (0.25g, 0.19mmol) was stirred in diethyl ether under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol) was added and the calixarene dissolved. Metal salt ($MgCl_2$, LiBr or $CaBr_2$, 0.96mmol) was added. The solution was then either stirred or cooled to yield powder or crystals and powder respectively. ^{1}H NMR (CD_2Cl_2) spectroscopy analysis on the products showed the tetrabutylammonium cation and the partially deprotonated calixarene.

Method 3

BC8 (0.25g, 0.19mmol) was stirred in diethyl ether under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol), followed by DMF (0.09ml, 1.16mmol) was added. Metal salt ($Ca(NO_3)_2$, NaI, LiBr or $SrBr_2$, 1.16mmol) was added and the solution stirred until the metal salt was no longer visible. The solid that precipitated out from the solution was filtered off.

Yield from $Ca(NO_3)_2$ = 0.47g, from NaI = 0.63g, from LiBr = 0.65g and from $SrBr_2$ = 0.33g. ^1H NMR ($CDCl_3$ or CD_2Cl_2) spectroscopy analysis on the products indicated that they were are all salts of **BC8** with the tetrabutylammonium cation.

Method 4

BC8 (0.25g, 0.19mmol) was stirred in diethyl ether under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol) followed by DMSO (0.08ml, 1.16mmol) was added. $CaBr_2$ (0.27g, 1.15mmol) was added to the clear solution and the mixture stirred until solid was precipitated from the solution. The solid was filtered off. By ^1H NMR (d_6-DMSO) spectroscopy it was found that the product was a tetrabutylammonium cation salt with **BC8**.

Method 5

BC8 (0.25g, 0.19mmol) was stirred in methanol under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol) followed by DMI (2.0ml) was added. A solution of NaI (0.23g, 1.54mmol) in methanol was added to the calixarene solution. Water was added dropwise until solid precipitated out from the solution (total 9ml water used). The solid was filtered off to yield 0.34g of white powder, which was found by ^1H NMR (CD_2Cl_2) spectroscopy to be a salt of **BC8** with the tetrabutylammonium cation.

Method 6 (21)

IC8 (0.20g, 0.17mmol) was stirred in methanol under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 1.01ml, 1.01mmol) was added and the solution stirred until the **IC8** had dissolved. Metal salt (NaI or LiBr, 1.35mmol) was added and within 1 day crystals had formed from the solution. ^{1}H NMR ($CDCl_3$ or CD_2Cl_2) spectroscopy showed that the crystals were salts of **IC8** with the tetrabutylammonium cation. Single crystal x-ray diffraction analysis was performed on the crystalline material from the reaction with NaI.

For the reaction with NaI, ^{1}H NMR (400MHz, $CDCl_3$) 13.52 (br. s, 3H, OH), 6.90 (s, 16H, Ph), 3.87 (br. s, 14H, CH_2), 2.99 (t, 16H, CH_2), 2.74 (q, 8H, CH), 1.47 (m, 15H, CH_2), 1.29 (m, 14H, CH_2), 1.16 (d, 48H, CH_3) and 0.86 (t, 23H, CH_3). Calc. for $C_{112}H_{166}N_2O_8$ [$(Bu_4N^+)_2(IC8^{2-})$]: C, 80.62; H, 10.03; N, 1.68%. Found: C, 80.32; H, 10.30; N, 1.66%.

3.5. Calcium Cation Calix[8]arene Complexes

From Solutions Containing *N,N*-Dimethylformamide

Method 1 (22)

IC8 (0.25g, 0.21mmol) was stirred in DMF under nitrogen. $Ca(OH)_2$ (0.13g, 1.69mmol) was added and the mixture agitated in a sonic bath for 30min. Within 1 week, crystals had formed from the solution. The crystals were analysed by single crystal x-ray diffraction, which showed that the crystals were a calcium complex with **IC8** with C_{2h} symmetry. The crystals were found by ^{1}H NMR (CD_2Cl_2) spectroscopy to possess C_{2v} symmetry in solution. ^{1}H NMR (400MHz, CD_2Cl_2) δ16.84 (s, 1H, OH), 13.38 (s, 2H, OH), 7.89 (s, 5H, DMF), 7.14 (d, 2H, Ph), 6.84 (d, 2H, Ph), 6.81 (d, 2H, Ph), 6.73 (d, 2H, Ph), 4.66 (d, 1H, CH_2), 4.18 (d, 2H, CH_2), 4.16 (d, 1H, CH_2), 3.27 (d, 1H, CH_2), 3.21 (d, 1H, CH_2), 3.06 (d, 2H, CH_2), 2.90 (s, 15H, DMF), 2.84 (s, 15H, DMF), 2.69 (m, 4H, CH) and 1.19-1.07 (overlapped doublets, 24H, CH_3). ^{13}C NMR (100.6MHz, CD_2Cl_2) δ162.59 (s, DMF), 147.11 (s, Ph), 143.27 (s, Ph), 129.52 (s, Ph), 126.73 (s, Ph), 36.55 (s, DMF), 33.68 (s, CH_2), 32.27 (s, CH), 30.05 (s, DMF) and 24.32 (s, CH_3).

Method 2

IC8 (0.23g, 0.19mmol) was stirred under nitrogen in diethyl ether. DMF (0.09ml, 1.16mmol) and tetrabutylammonium hydroxide (1M solution in methanol, 1.00ml, 1.00mmol) were added and the solution went clear. $CaBr_2$ (0.27g, 1.14mmol) was added and the solution was stirred and warmed. White solid precipitated out from the solution, which was filtered off. Yield = 0.15g (51%). By ^{1}H NMR (CD_2Cl_2) spectroscopy it was found that the product was slightly impure, but that the main product had C_{2v} symmetry. ^{1}H NMR (400MHz, CD_2Cl_2) δ16.69 (s, 0.5H, OH), 13.42 (s, 1H, OH), 9.59 (s, 4H, free **IC8** OH), 7.85 (s, 2H, DMF), 7.15 (s, 4H, Ph), 6.93 (s, 22H, free **IC8** Ph), 6.85 (s, 4H, Ph), 6.81 (s, 4H, Ph), 6.74 (s, 4H, Ph), 4.80 (d, 2H, CH_2), 4.16 (d, 4H, CH_2), 4.15 (d, 2H, CH_2), 3.31 (d, 2H, CH_2), 3.22 (d, 2H, CH_2), 3.18 (s, 6H, DMF), 3.14 (s, 6H, DMF), 3.08 (d, 4H, CH_2), 2.77-2.68 (m, 8H, CH), 1.17 (d, 64H, free **IC8** CH_3), 1.16 (d, 6H, CH_3), 1.15 (d, 6H, CH_3), 1.13 (d, 6H, CH_3), 1.11 (d, 6H, CH_3) and 1.08 (d, 6H, CH_3).

Method 3

IC8 (0.25g, 0.21mmol) was stirred in methanol under nitrogen. DMF (0.10ml, 1.27mmol) was added, followed by tetrabutylammonium hydroxide (1M solution in methanol, 0.84ml, 0.84mmol). As soon as the solution became clear, $CaCl_2$ (0.19g, 1.27mmol) was added. The mixture was stirred until all of the solid had dissolved and then agitated in a sonic bath for 10min. The solution was cooled to precipitate out white solid, which was then filtered off. Yield = 0.07g (22%). ^1H NMR (CD_2Cl_2) spectroscopy on the product indicated that it had C_{2v} symmetry in solution. ^1H NMR (400MHz, CD_2Cl_2), δ7.16 (d, 4H, Ph), 6.85 (d, 4H, Ph), 6.82 (d, 4H, Ph), 6.74 (d, 4H, Ph), 4.81 (d, 2H, CH_2), 4.15 (d, 6H, CH_2), 3.32 (d, 2H, CH_2), 3.21 (d, 2H, CH_2), 3.09 (d, 4H, CH_2), 2.77-2.68 (m, 8H, CH) and 1.19-1.08 (m, 48H, CH_3).

Method 4

DMF (0.5ml) was added to $CaBr_2$ (0.07g, 0.31mmol), before methanol (3ml). A filtered solution of **BC8** (0.10g, 0.08mmol) and KOH (0.03g, 0.46mmol) in diethyl ether (6ml) plus a minimum of methanol was layered onto the methanol solution. Within 1 day, crystalline solid had formed from the solution. The crystalline product was found to be unsuitable for single crystal x-ray diffraction.

From Ethanol and Water

A solution of ethanol/water (50:50 ethanol/water, 2ml) was layered onto a solution of $CaBr_2$ (0.08g, 0.34mmol) in water (1ml). Ethanol (6ml) was layered onto the ethanol/water solution before a solution of **IC8** (0.10g, 0.08mmol) plus KOH (0.03g, 0.53mmol) in ethanol (2ml). After 3 months, crystalline product had formed from the solution.

From Acetone and Water

Method 1

Water (1ml) was layered onto a solution of $CaBr_2$ (0.08g, 0.34mmol) in water (1ml). A solution of acetone/water (50:50 acetone/water, 2ml) was layered onto the water layer, then acetone/water (75:25 acetone/water, 2ml), before a solution of **IC8** (0.10g, 0.08mmol) and KOH (0.05g, 0.84mmol) in acetone (6ml) plus a minimum of water. After 2 months, crystalline product had formed from the solution.

Method 2

$CaBr_2$ (0.04g, 0.17mmol) was dissolved in water (1ml). A solution of acetone/water (50:50 acetone/water, 1ml), then a solution of acetone/water (75:25 acetone/water, 1ml) was layered onto the $CaBr_2$ solution, before a solution of **IC8** (0.05g, 0.04mmol), KOH (0.01g, 0.18mmol) and DMF (0.02g, 0.27mmol) in acetone (9ml). Within 2 months, crystalline product had formed from the solution.

Method 3

Water (2ml) was added to $Ca(OH)_2$ (0.05g, 0.67mmol) and Li_2CO_3 (0.01g, 0.14mmol). A solution of acetone/water (75:25 acetone/water, 2ml) was layered onto the water solution. **IC8** (0.10g, 0.08mmol) and **DMPD** (0.02g, 0.14mmol) were mixed in acetone

(8ml) with warming and a concentrated solution of KOH in water was added dropwise until the solution began to go clear. The solution was stirred until it became completely clear and then was allowed to cool to ambient temperature. The **IC8** solution was layered onto the acetone/water solution. Within 1 month, crystalline product had formed from the solution.

3.6. Strontium Cation Calix[8]arene Complexes

From *N,N*-Dimethylformamide

BC8 (0.50g, 0.39mmol) was stirred in DMF (25ml) under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 1.93ml, 1.93mmol) was added and the solution became clear. $SrBr_2$ (0.69g, 1.94mmol) was added without stirring. Crystals and powder began to precipitate out from the solution within 10min. The DMF was decanted off and replaced by diethyl ether 3 times before the product was filtered off and washed with a small volume of diethyl ether. Yield = 0.46g. ^1H NMR ($CDCl_3$) spectroscopy and IR spectroscopy were used to show that a complex had been prepared. The ^1H NMR spectrum was very broad and the peaks were overlapped. ^1H NMR (400MHz, $CDCl_3$) δ7.22-6.90 (br. m, 16H, Ph) and 1.27-0.88 (br. m, 72H, CH_3).

From Methanol (24)

IC8 (0.20g, 0.17mmol) was stirred in methanol (15ml) under nitrogen. Pivalic acid (0.03g, 0.29mmol), predissolved in methanol (2ml), was added followed by tetrabutylammonium hydroxide (1M solution in methanol, 1.3ml, 1.3mmol). $SrBr_2$

(0.30g, 0.84mmol) in methanol (5ml) was added, without stirring, once the ligand solution had become clear. After approximately 2h, crystals had begun to form from the solution. The ^{1}H NMR (CD_2Cl_2) spectrum was very broad indicating a strontium complex. The crystalline product was found to be unsuitable for single crystal x-ray diffraction. The solution was stirred and the solid that precipitated out from the solution was filtered off. Yield = 0.12g.

From Acetone and Water

Method 1

Water (1ml) was layered onto a solution of $SrBr_2$ (0.12g, 0.34mmol) in water (1ml). A solution of acetone/water (75:25 acetone/water, 2ml) was layered onto the water layer, before a solution containing **IC8** (0.10g, 0.08mmol), KOH (0.04g, 0.71mmol) and carboxylic acid (2-acetamidobenzoic acid or thiophene-2-carboxylic acid, 0.09mmol) in acetone (12ml), which had been filtered first. Crystalline solid had formed from the solution containing thiophene-2-carboxylic acid after 1 month and from the solution containing 2-acetamidobenzoic acid after 3 months.

Method 2

A solution of acetone/water (50:50 acetone/water, approx. 5ml) was layered onto a solution of $SrBr_2$ (0.12g, 0.34mmol) in water (1ml). A solution of **IC8** (0.10g, 0.08mmol), **DMPD** (0.05g, 0.35mmol) plus KOH (0.03g, 0.53mmol) in acetone/water (75:25 acetone/water, 2ml) was layered onto the acetone/water solution. Within 2 weeks, crystalline product had formed from the solution.

Preparation of the Mixed Metal Ion Complex with **IC8**

Method 1

A solution of ethylene glycol/water (50:50 ethylene glycol/water, 1ml) was layered onto $SrBr_2$ (0.18g, 0.51mmol) in ethylene glycol/water solution (50:50 ethylene glycol/water, 2ml). **IC8** (0.15g, 0.13mmol) was dissolved in acetone (10ml) by the addition of KOH (0.04g, 0.71mmol) and minimum water. This solution was layered onto the ethylene glycol/water solution. Within 1 month, crystals had formed from the solution. Single crystal x-ray diffraction showed that the crystals were a SrK**IC8** complex.

Method 2 (**23**)

Water (1ml) was layered onto a solution of $SrBr_2$ (0.12g, 0.34mmol) in water (1ml). A solution of acetone/water (75:25 acetone/water, 2ml) was layered onto the water layer before a solution containing **IC8** (0.10g, 0.08mmol), KOH (0.04g, 0.71mmol) and **TMCM** (0.02g, 0.09mmol) in acetone (10ml). Within 1 month crystals had formed from the solution, which were found by single crystal x-ray diffraction to be the same SrK**IC8** complex as formed by method 1. ^{1}H NMR (400MHz, $CDCl_3$) δ9.52 (s, 1H, OH), 7.01 (s, 2H, Ph), 6.85 (br. s, 14H, Ph), 4.33 (br. s, overlapped CH_2), 3.49 (br. s, overlapped, CH_2), 2.80 (m, overlapped, CH) and 1.13 (br. s, 48H, CH_3). Calc. for $SrKC_{86}H_{119}O_{17}$ [SrK(**IC8**$^{3-}$).2acetone.7H_2O]: C, 66.57; H, 7.73%. Found: C, 66.27; H, 7.63%.

Method 3

A solution of ethylene glycol/acetone (50:50 ethylene glycol/acetone, 2ml), then a solution of ethylene glycol/acetone (25:72 ethylene glycol/acetone, 4ml) was layered onto a solution of $SrBr_2$ (0.12g, 0.34mmol) in ethylene glycol (1ml). A solution of IC8 (0.10g, 0.08mmol) and KOH (0.03g, 0.53mmol) in acetone (6ml) plus a small volume of ethylene glycol (<1ml) was layered onto the ethylene glycol solution. Within 2 months, crystalline product had formed from the solution.

4. Co-Ligands

4.2. Ethylene Glycol Mimics

4.2.2. Preparation of Ethylene Glycol Mimic Molecules

1,4-Dimethylpiperazine-2,3-dione (DMPD) (25)

Diethyloxalate (8.29g, 56.7mmol) was added to a stirred solution of *N,N'*-dimethylethylenediamine (5.00g, 56.7mmol) in dry diethyl ether (120ml). Within 5min, solid had begun to precipitate out of the solution. The solution was stirred for approx. 7h then left for approx. 16h before the solid was filtered off. Yield of white microcrystalline solid = 7.49g (93%). The ^1H NMR (d_6-acetone) spectrum showed that the product was pure. ^1H NMR (400MHz, d_6-acetone), δ3.60 (s, 4H, CH_2) and 2.96 (s, 6H, CH_3). Calc. for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71%. Found: C, 50.40; H, 7.28; N, 19.61%. *m/z* 142 (M^+), 114 ($M-C_2H_4$ or $M-O_2$).

1,4-Di-*tert*-butylpiperazine-2,3-dione (DBPD) (26)

Oxalyl chloride (1.47g, 0.012mol) was added slowly to a stirred solution of *N,N'*-di-*tert*-butylethylenediamine (2.00g, 0.012mol) and triethylamine (2.35g, 0.023mol) in DCM (180ml). By-products in the yellow solution were extracted into water. The DCM solution was dried over $MgSO_4$ and then the solvent was removed. Diethyl ether (150ml) was added and the mixture was agitated in a sonic bath for 10min. Cream powder precipitated out from the solution, which was filtered off. Yield = 0.88g (33%). ^1H NMR ($CDCl_3$) spectroscopy was used to show that the product was pure. ^1H NMR (400MHz, $CDCl_3$) δ3.48 (s, 2H, CH_2) and 1.46 (s, 9H, CH_3). Calc. for $C_{12}H_{22}N_2O_2$: C, 63.69; H, 9.80; N, 12.38%. Found: C, 63.54; H, 9.97; N, 12.27%. *m/z* 226 (M^+), 183 ($M-C_3H_7$), 169 ($M-C_4H_9$), 127 ($M-C_7H_{15}$), 115 ($M-C_6H_7O_2$).

1,4-Bis-(2-hydroxyethyl)-piperazine-2,3-dione (BHPD) (27)

Diethyloxalate (0.99g, 6.75mmol) was added to a stirred solution of *N,N'*-bis-(2-hydroxyethyl)-ethylenediamine (1.00g, 6.75mmol) in DMF (150ml) under nitrogen. Once all of the amine had dissolved, the solution was heated to reflux for 2h then allowed to cool. The solvent was removed to yield a slightly yellow oil, from which, after 1 day, solid began to precipitate out. DMF was added, followed by a small volume of acetone (<20ml) until a cloudy solution was obtained. Crystalline solid precipitated out from the solution, which was filtered off to yield 0.56g (41%). The ^1H NMR (CD_3OD) spectrum showed that the product was pure. ^1H NMR (400MHz, CD_3OD) δ3.73 (t, 4H, CH_2), 3.70 (s, 4H, CH_2) and 3.57 (t, 4H, CH_2). Calc. for $C_8H_{14}N_2O_4$: C, 47.52; H, 6.98; N, 13.85%. Found: C, 47.81; H, 7.28; N, 14.14%. *m/z* 202 (M^+), 159 ($M-C_2H_3O$), 143 ($M-C_2H_3O_2$), 114 ($M-C_4H_8O_2$).

Copper Cation Complex with DMPD (CuDMPD) (28)

A methanol interface (1ml) was layered onto a solution of **DMPD** (0.15g, 1.06mmol) in methanol (approx. 5ml). A pale blue solution of $CuCl_2$ (0.18g, 1.06mmol) in methanol (approx. 5ml) was layered onto the methanol interface. The solvent was allowed to slowly evaporate off down to approximately half the original volume, which yielded green crystals. IR spectroscopy was used to show that the crystals were not recrystallised **DMPD**. Calc. for $CuC_6H_{10}N_2O_2Cl_2$ [Cu(**DMPD**)(Cl)$_2$]: C, 26.05; H, 3.64; N, 10.13%. Found: C, 26.35; H, 3.75; N, 10.37%. *m/z* 142 (**DMPD** M^+), 114 (**DMPD**-C_2H_4).

Copper Cation Complex with DBPD (CuDBPD) (29)

A green solution of $CuCl_2$ (0.08g, 0.47mmol) in ethanol (approx. 5ml) was layered onto a solution of **DBPD** (0.05g, 0.22mmol) in ethanol (approx. 5ml). Within 4h, dark green crystals had formed from the solution. Single crystal x-ray diffraction showed that the crystals were a complex of copper with **DBPD**. Calc. for $CuCl_2C_{12}H_{22}N_2O_2$ [Cu(**DBPD**)(Cl)$_2$] : C, 39.95; H, 6.15; N, 7.76%. Found: C, 40.19; H, 6.27; N, 7.77%.

Calcium Cation Complex with BHPD (CaBHPD)

Method 1

BHPD (0.05g, 0.25mmol) was dissolved in methanol (approx. 10ml) and then tetrabutylammonium hydroxide (1M solution in methanol, 0.33ml, 0.33mmol) was added. A solution of $CaBr_2$ (0.04g, 0.17mmol) in methanol (approx. 5ml) was layered onto the **BHPD** solution. Solid began to precipitate out of the solution after 1 day. The solution was warmed and stirred for maximum yield. The solid was filtered off. The solid was found to be insoluble in all useful ^1H NMR spectroscopy solvents and so no analysis was obtained.

Method 2

$CaBr_2$ (0.09g, 0.38mmol) was added to water (approx. 6ml), followed by water (1ml). Water/acetone solution (75:25 water/acetone, 2ml) was layered onto the water solution, before a solution of **BHPD** (0.05g, 0.25mmol) plus KOH (0.03g, 0.53mmol) in water/acetone (50:50 water/acetone, 2ml). Within 1 week, a small quantity of powder had precipitated out from the solution. Within 1 month, a small number of crystals had formed from the solution.

4.3. Carboxylic Acids

4.3.3. Preparation of Carboxylic acid Ligands

2,6-Bis-(2,2-dimethylpropionylamino)-benzoic acid (DTMC) (30)

2,6-Diaminotoluene (2.00g, 16.4mmol) and triethylamine (3.32g, 32.8mmol) were stirred in diethyl ether for 1h. Trimethylacetyl chloride (3.96g, 32.8mmol) was added dropwise to the stirred solution and solid began to precipitate out immediately. Water was added and the mixture was stirred for 1h. The solid was filtered off and washed with water and diethyl ether. Yield = 4.07g (86%). The ^1H NMR (d_6-acetone) spectrum and mass spectrum of the intermediate product *N*-[3-(2,2-dimethylpropionylamino)-2-methylphenyl]-2,2-dimethylpropionamide showed it was pure. ^{1}H NMR (400MHz, d$_6$-acetone) δ8.24 (br. s, 2H, NH), 7.20 (d, 2H, Ph), 7.08 (t, 1H, Ph) and 1.30 (s, 21H, CH$_3$). *m/z* 290 (M$^+$), 233 (M-C$_4$H$_9$), 206 (M-C$_5$H$_8$O) and 122 (M-C$_{10}$H$_{16}$O$_2$ or M-C$_{10}$H$_{18}$NO).

N-[3-(2,2-Dimethylpropionylamino)-2-methylphenyl]-2,2-dimethylpropionamide (2.00g, 6.89mmol) was stirred and warmed in water (50ml). Potassium permanganate solution (4.35g, 27.55mmol in 150ml water) was added slowly to the warm solution. Once all of the potassium permanganate solution had been added, the dark purple solution was heated to reflux for 3h and then the resulting dark brown solution was left to cool. The mixture was filtered to remove brown manganese dioxide. Unreacted starting material was removed from the filtrate by extraction with diethyl ether. The aqueous layer was cooled to below 5°C and conc. HCl was added dropwise. White solid precipitated out of the solution, which was filtered off and washed with cold water. Yield = 0.91g (41%). ^{1}H NMR (d$_6$-acetone) spectroscopy and IR spectroscopy showed that the product was pure. ^{1}H NMR (400MHz, d$_6$-acetone) δ10.14 (br. s, 1H, NH), 8.21 (d, 2H, Ph), 7.46 (t, 1H, Ph) and 1.27 (s, 18H, CH$_3$). Calc. for C$_{17}$H$_{24}$N$_2$O$_4$: C, 63.73; H, 7.55; N, 8.74%. Found: C, 64.01; H, 7.64; N, 8.64%. *m/z* 320 (M$^+$), 245 (M-C$_5$H$_{15}$), 218 (M-C$_5$H$_{10}$O$_2$), 189 (M-C$_5$H$_9$O$_3$N) and 161 (M-C$_9$H$_{19}$O$_2$).

2-(2,2-Dimethylpropionylamino)-6-methylbenzoic acid (TMCM) (31)

Trimethylacetyl chloride (1.60g, 0.013mol) was added in 6 portions to a stirred solution of 2-amino-6-methylbenzoic acid (2.00g, 0.013mol) and triethylamine (1.34g, 0.013mol) in diethyl ether (100ml). By-products were extracted into water before the diethyl ether was dried over $MgSO_4$ and then the solvent was removed to yield an oil. Solid product was obtained by agitating the oil in *n*-pentane in a sonic bath for 15min. The solid was filtered off. Yield = 1.04g (33%). ^1H NMR (d_6-acetone) spectroscopy was used to show that the product was pure. ^1H NMR (400MHz, d_6-acetone) δ11.90 (v. br. s, 0.22H, CO_2H), 10.16 (br. s, 0.43H, NH), 8.30 (d, 1H, Ph), 7.35 (t, 1H, Ph), 7.00 (d, 1H, Ph), 2.52 (s, 3H, CH_3) and 1.25 (s, 9H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ177.49 (s, CO_2H), 171.19 (s, CO), 140.97 (s, Ph), 140.45 (s, Ph), 132.83 (s, Ph), 127.35 (s, Ph), 123.10 (s, Ph), 121.08 (s, Ph), 120.21 (s, Ph), 41.04 (s, CH_3), 28.18 (s, CH_3) and 23.25 (s, $C(CH_3)_3$). *m/z* 235 (M^+), 160 ($M-C_3H_7O_2$) and 133 ($M-C_5H_{10}O_2$).

2-[(Adamantane-1-carbonyl)-amino]-6-methylbenzoic acid (ACM) (32)

Adamantane-1-carbonyl chloride (2.63g, 0.013mol) was added in 6 portions to a stirred solution containing 2-amino-6-methylbenzoic acid (2.00g, 0.013mol) and triethylamine (1.34g, 0.013mol) in diethyl ether (100ml). Water (100ml) was added and then the solid was filtered off and washed with diethyl ether. Yield = 1.22g. The ^1H NMR (CD_2Cl_2) spectrum and crystal structure of this product showed that it was not **ACM**. A second crop of solid was isolated from the filtrate and this was shown by ^1H NMR (CD_2Cl_2) spectroscopy to be **ACM**. Yield = 0.08g (2%). ^1H NMR (400MHz, CD_2Cl_2) δ9.88 (br. s, 0.33H, NH), 7.62 (t, 1H, Ph), 7.37 (d, 1H, Ph), 7.27 (d, 1H, Ph), 2.76 (s, 3H, CH_3), 2.09 (br. s, 1H, CH), 2.05 (s, 9H, CH_2) and 1.78 (br. s, 6H, CH). *m/z* 313 (M^+), 122 ($M-C_{12}H_{17}NO$) and 105 ($M-C_{12}H_{16}O_3$).

2-(2,2-Dimethylpropionylamino)-5-methylbenzoic acid (TMCHM) (33)

Trimethylacetyl chloride (0.80g, 6.63mmol) was added in 3 portions to a stirred solution containing 2-amino-5-methylbenzoic acid (1.00g, 6.62mmol) and triethylamine (0.67g, 6.62mmol) in diethyl ether (75ml). By-products were removed by filtration. The diethyl ether was removed to give an oil from which solid product was obtained by addition of *n*-pentane and agitation in a sonic bath for 10min. The solid was filtered off. Yield = 1.22g (78%). ^{1}H NMR (d_6-acetone) spectroscopy was used to show that the product was pure. ^{1}H NMR (400MHz, d_6-acetone) δ11.37 (br. s, 1H, NH), 8.67 (d, 1H, Ph), 7.91 (s, 1H, Ph), 7.41 (d, 1H, Ph), 2.33 (s, 3H, CH_3) and 1.27 (s, 9H, CH_3). ^{13}C NMR (100.6MHz, d_6-acetone) δ177.95 (s, CO_2H), 170.97 (s, CO), 141.52 (s, Ph), 136.47 (s, Ph), 132.76 (s, Ph), 132.64 (s, Ph), 121.10 (s, Ph), 116.02 (s, Ph), 41.25 (s, $C(CH_3)_3$), 28.25 (s, CH_3) and 21.04 (s, CH_3). Calc. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95%. Found: C, 66.14; H, 7.38; N, 5.99%. *m/z* 235 (M^+), 160 ($M-C_3H_7O_2$), 151 ($M-C_5H_8O$) and 133 ($M-C_5H_{10}O_2$).

2-[(Adamantane-1-carbonyl)-amino]-5-methylbenzoic acid (ACHM) (34)

Adamantane-1-carbonyl chloride (1.31g, 6.59mmol) was added in 3 portions to a stirred solution containing 2-amino-5-methylbenzoic acid (1.00g, 6.62mmol) and triethylamine (0.67g, 6.62mmol) in diethyl ether (75ml). By-products were removed by filtration. The diethyl ether was removed to give an oil from which solid product was obtained by addition of *n*-pentane and agitation in a sonic bath for 40min. The solid was filtered off. Yield = 1.63g (79%). ^{1}H NMR (d_6-acetone) spectroscopy was used to show that the product was pure. The product was recrystallised from methanol to give crystalline ACHM. ^{1}H NMR (400MHz, d_6-acetone) δ11.32 (br. s, 0.77H, NH), 8.68 (d, 1H, Ph), 7.89 (s, 1H, Ph), 7.38 (d, 1H, Ph), 2.31 (s, 3H, CH_3), 2.50 (br. s, overlapped, CH), 1.96 (br. s, 7H, CH_2) and 1.76 (br. s, 7H, CH). ^{13}C NMR (100.6MHz, d_6-acetone) δ177.44 (s, CO_2H), 171.02 (s, CO), 141.61 (s, Ph), 141.46 (s, Ph), 136.36 (s, Ph), 132.64 (s, Ph), 121.25 (s, Ph), 116.17 (s, Ph), 43.29 (s, CH_3), 40.39 (s, CH_2), 37.67 (s, CH_2), 29.61 (s, CH) and 21.03 (s, $C(CH_2)_3$). Calc. for $C_{19}H_{25}NO_4$ (ACHM.H_2O): C, 68.86; H, 7.60; N, 4.23%. Found: C, 68.95; H, 7.83; N, 4.32%. *m/z* 313 (M^+), 135 (M-$C_{11}H_{16}NO$).

4.3.4. Preparation of Carboxylic Acid Complexes

Ammonium Cation Salt with DTMC (35)

2,6-bis-(2,2-Dimethylpropionylamino)-benzoic acid (**DTMC**, 0.05g, 0.16mmol) and metal salt ($CoBr_2$, $CuCl_2$, $Cu(NO_3)_2$, $ZnCl_2$, $Ni(NO_3)_2$ and LiBr, 0.16mmol) were dissolved in methanol and ammonia gas was allowed to diffuse into the solution over time.

The crystalline product from $CuCl_2$, $ZnCl_2$, LiBr, and from when no metal salt was included, was found to be an ammonium salt with **DTMC** by IR spectroscopy and single crystal x-ray diffraction. ^1H NMR (400MHz, d_6-DMSO) δ14.08 (s, 2H, NH), 8.20 (d, 2H, Ph), 7.19 (br. s, 4H, NH_4), 7.14 (t, 1H, Ph) and 1.20 (s, 18H, CH_3). Calc. for $C_{17}H_{27}N_3O_4$ [(NH_4^+)(**DTMC**$^-$)]: C, 60.51; H, 8.07; N, 12.45%. Found: C, 60.35; H, 8.32; N, 12.32%. *m/z* 337 (M^+), 320 (M-NH_3) and 149 (M-$C_8H_{16}N_2O_3$ or M-$C_9H_{18}NO_3$).

The crystalline product from $CoBr_2$ was found to consist of 3 types of crystal including colourless crystals of the ammonium salt, red crystals and yellow crystals. The red crystals and the yellow crystals were found to be unsuitable for single crystal x-ray diffraction.

The blue crystalline product from $Cu(NO_3)_2$ and the violet crystalline product from $Ni(NO_3)_2$ were found to be unsuitable for single crystal x-ray diffraction.

Calcium Cation Complex with DTMC (CaDTMC) (36)

DTMC (0.05g, 0.16mmol) and $CaBr_2$ (0.04g, 0.16mmol) were dissolved in methanol and ammonia gas was allowed to diffuse into the solution over time. Crystalline product was obtained within 3 weeks. The crystalline product was found to be a mixture of a calcium complex with **DTMC** and an ammonium salt with **DTMC** by IR spectroscopy, ^1H NMR (CD_3OD) spectroscopy, single crystal x-ray diffraction and elemental analysis. ^1H NMR (400MHz, CD_3OD) δ8.18 (d, 2H, Ph), 7.27 (t, 1H, Ph) and 1.27 (s, 18H, CH_3).

Strontium Cation Complex with DTMC (SrDTMC)

DTMC (0.05g, 0.16mmol) and $SrBr_2$ (0.06g, 0.16mmol) were mixed in water (approx. 10ml) until the $SrBr_2$ dissolved. **DTMC** was found to be insoluble in water. Ammonia was allowed to diffuse into the mixture over time and within 3 months crystalline product had formed from the solution.

Calcium Cation Complex with TMCM (CaTMCM)

$Ca(OH)_2$ (0.03g, 0.42mmol) was dissolved in water (3ml) and then the solution was filtered. Water (1ml), acetone/water solution (50:50 acetone/water, 2ml) and then acetone/water solution (75:25 acetone/water, 2ml) were layered on before a solution of **TMCM** (0.05g, 0.21mmol) in acetone (3ml). Within 2 weeks, crystalline product had formed from the solution.

Calcium Cation Complex with TMCHM (CaTMCHM)

Method 1

$CaBr_2$ (0.05g, 0.21mmol) was added to water (6ml), followed by water (2ml). A solution of methanol/water (50:50 methanol/water, 2ml) was layered onto the water, before a solution of **TMCHM** (0.05g, 0.21mmol) plus *tert*-butylamine (0.02g, 0.21mmol) in methanol/water (75:25 methanol/water, 2ml). After 1 month, crystalline product had formed from the solution.

Method 2

$Ca(OH)_2$ (0.03g, 0.42mmol) was dissolved in water (3ml) and then the solution was filtered. Water (1ml), acetone/water solution (50:50 acetone/water, 2ml) and then acetone/water solution (75:25 acetone/water, 2ml) were layered on, before a solution of **TMCHM** (0.05g, 0.21mmol) in acetone (3ml). Within 2 weeks, crystalline product had formed from the solution.

2-Acetamidobenzoic Acid Complexes

Method 1

2-Acetamidobenzoic acid (0.30g, 1.69mmol) was stirred in ethanol under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 1.69ml, 1.69mmol) was added and once the solution became clear, $CaBr_2$ (0.20g, 0.85mmol) or $SrBr_2$ (0.30g, 0.84mmol), predissolved in ethanol, was added. White solid began to precipitate out from the solutions immediately after the addition.

Yield from $CaBr_2$ = 0.23g (70%). ^1H NMR (d_6-DMSO) spectroscopy was used to show that a calcium complex with 2-acetamidobenzoic acid had been prepared. ^1H NMR (400MHz, d_6-DMSO) δ13.55 (br. s, 0.59H, NH), 8.45 (d, 1H, Ph), 8.01 (d, 1H, Ph), 7.29 (t, 1H, Ph), 6.94 (t, 1H, Ph), 2.04 (s, 3H, CH_3).

Yield from $SrBr_2$ = 0.35g (95%). ^1H NMR (d_6-DMSO) spectroscopy was used to show that a strontium complex with 2-acetamidobenzoic acid had been prepared. ^1H NMR (400MHz, d_6-DMSO) δ13.56 (br. s, 0.59H, NH), 8.44 (d, 1H, Ph), 8.00 (d, 1H, Ph), 7.28 (t, 1H, Ph), 6.94 (t, 1H, Ph), 2.00 (s, 3H, CH_3).

Method 2

2-Acetamidobenzoic acid (0.25g, 1.40mmol) was dissolved in methanol under nitrogen. $MgBr_2$ (0.20g, 0.68mmol), predissolved in methanol, was added to the solution. Tetrabutylammonium hydroxide (1M solution in methanol, 1.40ml, 1.40mmol) was added to the clear solution. White solid began to precipitate out from the solution within 1min. The solid was filtered off, yield = 0.18g (64%). ^{1}H NMR (d_6-DMSO) spectroscopy was used to show that the product was a complex. ^{1}H NMR (400MHz, d_6-DMSO) δ13.25 (br. s, 0.59H, NH), 8.45 (d, 1H, Ph), 8.05 (d, 1H, Ph), 7.32 (t, 1H, Ph), 6.96 (t, 1H, Ph), 2.06 (s, 3H, CH_3).

5. Overbased Systems

5.2. Calcium Cation Complex with p-*tert*-Butylcalix[8]arene (One)

5.2.2. Preparation of the Calcium Cation Complex with BC8

Method 1 (37)

BC8 (1.00g, 0.77mmol) was stirred under nitrogen in diethyl ether. DMF (0.36ml, 4.62mmol) was added to the cloudy solution, followed by tetrabutylammonium hydroxide (1M solution in methanol, 4.60ml, 4.60mmol) to yield a clear solution. $CaBr_2$ (1.09g, 4.32mmol) was added and the mixture was agitated in a sonic bath for 30min. The mixture was cooled to yield a white powder, which was filtered off. Yield = 0.92g (73% yield). By IR spectroscopy the product was found to be a complex. ^{1}H NMR (400MHz, CD_2Cl_2) δ16.60 (br. s, 1H, core OH), 13.46 (br. s, 2H, OH), 7.30 (d, 4H, Ph), 7.05 (d, 4H, Ph), 6.98 (d, 4H, Ph), 6.88 (d, 4H, Ph), 6.56 (br. s, 2H, OH), 4.79 (d, 2H, CH_2), 4.19 (d, 2H, CH_2), 4.17 (d, 4H, CH_2), 3.33 (d, 2H, CH_2), 3.26 (d, 2H, CH_2), 3.10 (d, 4H, CH_2), 1.25 (s, 36H, CH_3) and 1.18 (s, 36H, CH_3). ^{13}C NMR (100.6MHz, CD_2Cl_2) δ152.81 (s, Ph), 148.91 (s, Ph), 146.84 (s, Ph), 145.52 (s, Ph), 143.67 (s, Ph), 141.04 (s, Ph), 132.12 (s, Ph), 131.13 (s, Ph), 129.83 (s, Ph), 129.63 (s, Ph), 129.26 (s, Ph), 125.76 (s, Ph), 125.15 (s, Ph), 124.60 (s, Ph), 123.92 (s, Ph), 36.13 (s, CH_2), 35.33 (s, CH_2), 34.31 (s, CH_2), 34.12 (s, CH_2), 33.96 (s, CH_2), 32.59 (s, CH_2), 31.72 (s, CH_3), 31.67 (s, CH_3) and 31.54 (s, $C(CH_3)_3$).

Impurities were removed by dissolving a sample of the complex in chloroform, filtering off the insoluble particulates and then allowing the solvent to evaporate off. Calc. for $Ca_3C_{267}H_{363}NO_{38}$ [$Ca_3(BC8^{2-})_3$.DMF.13H_20]: C, 72.31; H, 8.25; N, 0.32%. Found: C, 72.29; H, 8.11; N, 0.30%.

The product was recrystallised from DCM/diethyl ether. Single crystal x-ray diffraction showed that the crystalline product was a complex of calcium with **BC8**. ^1H NMR (400MHz, CD_2Cl_2) δ16.29 (br. s, 1.5H, core OH), 13.53 (br. s, 3H, OH), 7.23 (s, 4H, Ph), 7.02 (s, 4H, Ph), 6.94 (s, 4H, Ph), 6.86 (s, 4H, Ph), 6.54 (br. s, 2H, OH), 4.92 (d, 2H, CH_2), 4.21 (d, 2H, CH_2), 4.16 (d, 4H, CH_2), 3.30 (d, 2H, CH_2), 3.21 (d, 2H, CH_2), 3.09 (d, 4H, CH_2), 1.24 (s, 36H, CH_3) and 1.16 (s, 36H, CH_3).

Method 2

BC8 (0.20g, 0.15mmol) was stirred in methanol under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 0.80ml, 0.80mmol) was added followed by DMF (0.5ml). The solution remained cloudy. $CaBr_2$ (0.29g, 1.23mmol) dissolved in methanol was added and the mixture was agitated in a sonic bath for 10min. The mixture was cooled and then the white solid was filtered off to yield 0.16g (64% yield). The product, by ^1H NMR (CD_2Cl_2) spectroscopy, was found to have C_{2v} symmetry.

5.2.4. Solution State Structure of the Calcium Cation Complex with BC8

Method 1

BC8 (0.25g, 0.19mmol) was stirred in dry diethyl ether under nitrogen. Deuterated DMF (d_7-DMF, 0.09ml, 1.16mmol) was added to the mixture, followed by tetrabutylammonium hydroxide (1M solution in methanol, 0.77ml, 0.77mmol). $CaBr_2$ (0.27g, 1.14mmol), predissolved in a minimum volume of methanol, was added as soon as the solution became clear. The solution was stirred for approx. 5min, then agitated in a sonic bath for 50min. The solid that had precipitated out from the solution was filtered off. Yield = 0.15g. The ^1H NMR (CD_2Cl_2) spectrum showed that the product was the calcium cation complex with BC8. The peaks for free DMF were not visible on the spectrum.

Method 2

A C_{2v} symmetry complex of calcium ions with BC8 (0.10g, 0.031mmol) was stirred in d^1-methanol (CH_3OD, approx. 3.7ml) under nitrogen. Minimum DCM was added to the mixture to dissolve all of the solid. The solution was then left overnight before the solvent was removed and the ^1H NMR spectrum of the white powder was obtained. The process was repeated once. The ^1H NMR spectra showed a change in intensity of the peaks at 16.62, 13.42 and 6.54ppm, relative to the calixarene alkyl proton peak at 4.18ppm.

Method 3

A small sample of the calcium cation complex with **BC8** was dissolved in a minimum of DCM. The DCM was removed and the solid analysed by ^1H NMR (CD_2Cl_2) spectroscopy, which showed that some of the complex had decomposed.

5.2.5.1. Effect of *N,N*-Dimethylformamide on the Symmetry of the Calcium Cation Complex with BC8 in Solution

Method 1

A calcium complex with **BC8** with C_{2v} symmetry was dissolved in deuterated chloroform under nitrogen. After filtration, the ^1H NMR spectrum of the complex was obtained which showed C_{2v} symmetry as expected. A few drops of deuterated DMF were added under nitrogen and the ^1H NMR spectrum was obtained on the solution, which showed that the solution contained a mixture of **BC8**, C_{2v} symmetry complex and at least one other symmetry complex.

Method 2

A C_{2v} symmetry complex of calcium ions with **BC8** (0.0160g) was dissolved in deuterated chloroform (1.2ml). The ^1H NMR spectrum was obtained for the complex. A solvent solution was prepared using 1 drop of deuterated DMF (0.0112g) in deuterated chloroform (1ml) and aliquots of 3 drops of this solvent solution were added to the C_{2v} symmetry complex solution with the ^1H NMR spectrum of the solution obtained after each addition. After each addition of solvent solution, slight changes in the spectrum were observed.

5.2.5.2. Effect of Ethylene Glycol and Methanol on the Symmetry of the Calcium Cation Complex with BC8 in Solution

The above method was used for additions of other solvents to a C_{2v} symmetry complex, where the average mass of C_{2v} symmetry complex was 0.0179g. The solvents that were used were ethylene glycol and d_1-methanol, where 1 drop of ethylene glycol weighed 0.0274g and 1 drop of CH_3OD weighed 0.0112g. As for additions of DMF, slight changes in the ^1H NMR spectrum were observed after each addition of solvent solution.

5.2.5.3. Effect of DMPD on the Symmetry of the Calcium Cation Complex with BC8 in Solution

A calcium complex with **BC8** with C_{2v} symmetry was dissolved in deuterated chloroform under nitrogen. A small quantity of **DMPD** was added to the solution, the solution was then filtered, before the ^1H NMR spectrum was collected. The ^1H NMR spectrum showed a broadened C_{2v} symmetry spectrum. The **DMPD** peaks on the ^1H NMR spectrum were too small for a ratio of **DMPD** to **BC8** to be calculated. More **DMPD** was added to the solution and the ^1H NMR spectrum was collected, which was broad and overlapped. No C_{2v} symmetry peaks could be identified in the spectrum. The ^1H NMR spectrum gave a ratio of **DMPD** to **BC8** of **4DMPD:1BC8**. Another quantity of **DMPD** was added to the solution and the ^1H NMR spectrum was collected.

The ^{1}H NMR spectrum of the solution was broad and resembled a spectrum for a calixarene salt. From the integrations on the ^{1}H NMR spectrum the solution contained approx. 66**DMPD**:3DMF:1**BC8**. ^{1}H NMR (400MHz, $CDCl_3$) δ8.01 (s, 3H, DMF), 6.96 (br. s, 16H, Ph), 3.53 (s, 263H, **DMPD** CH_2), 3.06 (s, 394H, **DMPD** CH_3), 2.96 (s, 15H, DMF), 2.88 (s, 15H, DMF) and 1.19 (br. s, 72H, CH_3).

5.2.5.4. Effect of *N,N*-Dimethylformamide of the Symmetry of the Calcium Cation Complex with IC8 in Solution

A calcium complex with **IC8**, which possessed C_{2v} symmetry in solution, was dissolved in $CDCl_3$ under nitrogen. 5 drops of d_7-DMF were added to the solution, the solution was then filtered and analysed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum showed a broadened C_{2v} symmetry spectrum with some decomposition to **IC8** salt. The ratio of DMF to total **IC8** from the ^{1}H NMR spectrum was 3DMF:1**IC8** and the ratio of DMF to C_{2v} symmetry complex was 12DMF:1**IC8**. Another 10 drops of d^7-DMF were added, the solution was filtered and the ^{1}H NMR spectrum on the solution was collected. The spectrum showed that the complex had become a simple salt with a ratio of DMF to **IC8** of 2DMF:1**IC8**. ^{1}H NMR (400MHz, $CDCl_3$) δ8.01 (s, 2H, DMF), 6.94 (s, 16H, Ph), 2.98 (s, 6H, DMF), 2.87 (s, 6H, DMF), 2.76 (m, 8H, CH) and 1.16 (d, 48H, CH_3).

5.2.6. Effect of Carbon Dioxide on the Calcium Cation Complex with BC8

5.2.6.1. Carbon Dioxide Gas

A solution of the C_{2v} symmetry calcium ion complex with **BC8** in CD_2Cl_2 was left overnight in an atmosphere of carbon dioxide gas. White solid precipitated out from the solution, which was found by IR spectroscopy to be calcium carbonate. The remaining solution was found by IR spectroscopy to contain **BC8**.

5.2.6.2. Bis-(4-nitrophenyl)carbonate

A solution of the calcium complex with **BC8** that possessed C_{2v} symmetry was dissolved under nitrogen in $CDCl_3$. ^1H NMR spectroscopy confirmed that the solution of the complex had C_{2v} symmetry. An aliquot of bis-(4-nitrophenyl)carbonate (1 mole equivalent to the complex, in $CDCl_3$) was added and the solution became bright yellow. Solid began to precipitate out from the solution. The solid was redissolved by the addition of d_7-DMF (less than 0.1ml). ^1H NMR spectroscopy on the solution, before and after the addition of DMF, showed that the solution contained deprotonated **BC8** with high symmetry.

5.3. Calcium Cation Complex with p-*tert*-Butylcalix[8]arene (Two)

5.3.2. Preparation of Mixtures Containing a Low Symmetry Calix[8]arene Complex

From Methanol

Tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol) was added to a stirred solution of **BC8** (0.25g, 0.19mmol) in methanol under nitrogen. The solution remained cloudy. $CaBr_2$ (0.23g, 0.93mmol) was stirred in and the solution was warmed. After 3 months, solid precipitated from solution. This was filtered off and washed with methanol. Yield = 0.09g. The ^1H NMR spectrum (CD_2Cl_2) indicated that the product contained mainly a tetrabutylammonium cation salt with **BC8**, plus some low symmetry product.

From 1,3-Dimethylimidazolidinone (20)

BC8 (0.25g, 0.19mmol) was stirred in DMI under nitrogen. Tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol) was added and the solution went clear. $CaBr_2$ (0.27g, 1.16mmol) was stirred in. Within 1 month, product precipitated out from the solution. The white solid was filtered off. Yield = 0.24g. The ^1H NMR spectrum (CD_2Cl_2) of the product showed that the product was a mixture of mainly tetrabutylammonium cation salt with **BC8**, with a small quantity of a low symmetry complex.

Recrystallisation of the product from methanol and DCM gave a crystalline product, which by ^1H NMR (CD_2Cl_2) spectroscopy, was found to be mainly **BC8** with a small quantity of the low symmetry complex.

Recrystallisation of the product from DMI and DCM gave crystals within 3 months, which were found by ^1H NMR (CD_2Cl_2) spectroscopy to be a simple calcium ion salt with **BC8**. ^1H NMR (400MHz, CD_2Cl_2) δ9.70 (s, 1H, OH), 7.10 (s, 8H, Ph), 3.22 (s, 57H, DMI), 2.69 (s, 86H, DMI) and 1.24 (s, 36H, CH_3).

From Methanol Plus 1,3-Dimethylimidazolidinone

Method 1

Tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol) was added to a stirred solution of **BC8** (0.25g, 0.19mmol) in methanol under nitrogen. DMI (2.0ml) was added and the solution went clear within 2 minutes. $Ca(NO_3)_2$ (0.23g, 0.96mmol) was dissolved in methanol and then pipetted onto the calixarene solution. With cooling, crystals were formed from the solution within 1 month. By ^1H NMR (CD_2Cl_2) spectroscopy the crystals were found to be mainly **BC8** with a small quantity of a low symmetry complex. The solution was warmed and stirred and the solid that precipitated out from the solution was filtered off. Yield = 0.05g. The ^1H NMR (CD_2Cl_2) spectrum of the white powder was the same as the spectrum for the crystals.

Method 2

BC8 (0.20g, 0.15mmol) was stirred in methanol under nitrogen. DMI (2.0ml) was added followed by tetrabutylammonium hydroxide (1M solution in methanol, 0.84ml, 0.84mmol) and the solution was stirred until it became clear. Calcium acetate (0.15g, 0.84mmol) was added and the mixture agitated in a sonic bath for 6min. A small quantity of powder precipitated from the solution, which, upon standing, changed into crystals. ^{1}H NMR (CD_2Cl_2) spectroscopy showed that the crystals were a mixture of deprotonated **BC8** and a low symmetry complex. The solution was agitated in a sonic bath for 10min and the powder that precipitated out from the solution was filtered off. Yield = 0.09g. The ^{1}H NMR (CD_2Cl_2) spectrum of the powder indicated that the powder was mainly **BC8** with some low symmetry complex.

Method 3

IC8 (0.25g, 0.21mmol) was stirred in methanol under nitrogen. DMI (2.0ml) and glacial acetic acid (0.05g, 0.84mmol) were added, followed by $Ca(OH)_2$ (0.08g, 1.06mmol). The solution remained cloudy and so was agitated in a sonic bath for 120min. The white solid that precipitated out from the solution was filtered off to yield 0.30g. ^{1}H NMR (CD_2Cl_2) spectroscopy showed the powder was mainly **IC8** with a small quantity of low symmetry complex.

From Diethyl Ether Plus *N,N*-Diethylformamide

BC8 (0.25g, 0.19mmol) was stirred under nitrogen in diethyl ether. DEF (0.13ml, 1.16mmol) and then tetrabutylammonium hydroxide (1M solution in methanol, 0.96ml, 0.96mmol) were added and the **BC8** dissolved to give a clear solution. $CaBr_2$ (0.27g, 1.44mmol) was added and the mixture was agitated for 20min in a sonic bath. The solid that precipitated out from the solution was filtered off. Yield = 0.19g. The product was found by ^1H NMR ($CDCl_3$) spectroscopy to be mainly **BC8** with some low symmetry complex.

From Methanol Plus *N,N*-Diethylformamide

BC8 (0.20g, 0.15mmol) was stirred in methanol under nitrogen. DEF (2.0ml) and then tetrabutylammonium hydroxide (1M solution in methanol, 0.77ml, 0.77mmol) were added and the solution gradually became clear. A solution of $Ca(NO_3)_2$ (0.22g, 0.93mmol) in methanol was added and over 1 week, solid began to precipitate out from the solution. The reaction mixture was agitated for 5min in a sonic bath. The white powder was filtered off to yield 0.13g, which was found by ^1H NMR (CD_2Cl_2) spectroscopy to be mainly **BC8** with some low symmetry complex.

5.3.3. Preparation of a Pure Low Symmetry Complex

Method 1

BC8 (0.20g, 0.15mmol) was stirred in DMF under nitrogen. $CaBr_2$ (0.36g, 1.54mmol) was dissolved in DMF and then added to the mixture. The solution remained cloudy. Tetrabutylammonium hydroxide (1M solution in methanol) was added dropwise to the solution with stirring. The solution went clear after addition of approximately 0.05ml tetrabutylammonium hydroxide (0.05mmol). After the addition of a total of 1.15ml tetrabutylammonium hydroxide (1.15mmol) the solution became very slightly cloudy. No more tetrabutylammonium hydroxide was added. Within 3 days, crystals had begun to form from the solution. The ^{1}H NMR (CD_2Cl_2) spectrum of the crystals showed that they were a mixture of low symmetry complexes.

Method 2 (38)

Method 1 was repeated with a total of 1.1ml tetrabutylammonium hydroxide (1M solution in methanol) added to give a clear solution. Within 1 day, crystalline solid and powder had precipitated out from the solution. After 1 week, only crystalline solid was present (no powder). Single crystal x-ray diffraction on the crystalline product showed that a calcium complex with **BC8** had been formed. ^{1}H NMR (400MHz, d_6-DMSO) δ7.95 (s, 5H, DMF), 7.02 (s, 1H, PH), 2.89 (s, 15H, DMF), 2.73 (s, 15H, DMF) and 1.19 (s, 9H, CH_3). ^{1}H NMR (400MHz, CD_2Cl_2) δ7.62 (br. s, 8H, DMF), 7.28-6.76 (multiple peaks, 8H, Ph), 5.02-2.96 (multiple peaks, 8H, CH_2), 2.62 (br. s, 48H, DMF) and 1.29-1.02 (multiple peaks, 72H, CH_3).

5.4. Calcium Cation Complex with a Calcium Carbonate Core

5.4.2. Preparation of the Calcium Cation Complex with a Calcium Carbonate Core

Method 1

A complex of calcium ions with **M2** (**CaM2**, 0.10g, approx. 0.12mmol) was dissolved in acetone (30ml) to give a yellow solution. **DMPD** (0.10g, 0.70mmol) was added to the solution and the solution stirred until the **DMPD** dissolved. Solid began to precipitate out of the solution as soon as the **DMPD** dissolved. The solid was filtered off. A yield was not calculated. The ^{1}H NMR (d_6-DMSO) spectrum indicated that the product contained **M2** and **DMPD**, but was very broad.

Method 2

Acetone (2ml) was layered onto a solution of **DMPD** (0.08g, 0.56mmol) in acetone (approx. 5ml). A solution of **CaM2** (0.05g, approx. 0.07mmol) in acetone (approx. 5ml) was layered onto the acetone solution. Solid began to precipitate out of the solution as soon as the **CaM2** solution was added.

Method 3 (39)

Methanol (1ml) was layered onto a solution of **DMPD** (0.08g, 0.56mmol) in acetone (2ml). Acetone (approx. 6ml) was layered onto the methanol before a solution of CaM2 (0.05g, approx. 0.07mmol) in acetone (2ml). Within 1 day, crystals had formed from the solution. Single crystal x-ray diffraction showed that the crystals were a complex with the formula $Ca_{10}(M2^{2-})_8(CO_3^{2-})_2(DMPD)_4(MeOH)_4.8acetone$. ^{1}H NMR (400MHz, d_6-DMSO) δ7.12 (br. s, 2H, **M2** Ph), 6.66 (br. s, 2H, **M2** Ph), 6.38 (br. s, 2H, **M2** Ph), 3.51 (s, 4H, **DMPD** CH_2), 2.91 (s, 6H, **DMPD**, CH_3), 2.09 (s, 6H, **M2** CH_3) and 2.07 (br. s, 4H, acetone). Calc. for $Ca_{10}C_{142}H_{171}S_8O_{43.5}N_8$ [$Ca_{10}(M2^{2-})_8(DMPD)_4(CO_3^{2-})_2(MeOH)_4.9.5H_2O$]: C, 51.02; H, 5.16; N, 3.35; S, 7.67%. Found: C, 51.12; H, 4.96; N, 3.35; S, 7.39%.

Method 4

Ethanol (1ml) was layered onto a solution of **DMPD** (0.08g, 0.56mmol) in acetone (2ml). Acetone (approx. 6ml) was layered onto the methanol before a solution of **CaM2** (0.05g, approx. 0.07mmol) in acetone (2ml). As yet, nothing has precipitated out of the solution.

Method 5

A solution of **DMPD** (0.08g, 0.56mmol) in acetone (2ml) was layered onto ethylene glycol (1ml). Acetone (1ml), methanol (1ml) and then acetone (6ml) were layered onto the **DMPD** solution before **CaM2** (0.05g, approx. 0.07mmol) in acetone (2ml). As yet, nothing has precipitated out of the solution

Method 6

Methanol (1ml) was layered onto a solution of **DMPD** (0.08g, 0.56mmol) in acetone (2ml). Acetone (approx. 6ml) was layered onto the methanol before a solution of SAP complex (**CaI2** or **SrM2**, 0.05g) in acetone (2ml).

For the reaction with **CaI2**, solid began to precipitate out of the solution within 1min.

For the reaction with **SrM2**, nothing has as yet precipitated out of the solution.

Method 7

Methanol (1ml) was layered onto a solution of **DBPD** (0.11g, 0.49mmol) in acetone (2ml). Acetone (approx. 6ml) was layered onto the methanol before a solution of **CaM2** (0.05g, approx. 0.07mmol) in acetone (2ml). As yet, nothing has precipitated out of the solution.

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Appendices (CD ROM)

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