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Conformational control of nonplanar free base porphyrins: towards bifunctional catalysts of tunable basicity
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Turning on ROP activity in a bimetallic Co/Zn complex supported by a [2+2] Schiff-base macrocycle

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Homo-dinuclear complexes Co and Zn complexes derived from the macrocycle LH$_2$; [(2-OH)-5-(R)-C$_6$H$_4$-1,3-(CH)$_2$][(CH$_2$)$_2$CH$_2$(2-C$_6$H$_4$N)$_2$]; (R = Me, tBu), revealed near inactivity for the ring opening polymerization (ROP) of the cyclic esters \( \delta \)-valerolactone (\( \delta \)-VL) and \( \varepsilon \)-caprolactone (\( \varepsilon \)-CL). By contrast, the hetero-bimetallic complexes [LCo(NCMe)(µ-Br)ZnBr]·nMeCN (n=3 or 3.25) were found to be efficient catalysts for the ROP of \( \varepsilon \)-CL and \( \delta \)-VL.

The production of aliphatic polyesters has become a very topical area given their biodegradability and biocompatibility,[1] and given the current global issues with plastic pollution, this is likely to remain the case for the foreseeable future.[2] One viable route to such polymers is via the metal-catalyzed ring opening polymerization (ROP) of cyclic esters.[3] The choice of metal catalyst is influenced by a number factors, such as price, toxicity, activity and control. Frameworks that are capable of simultaneously binding multiple metal centres continue to be of great interest in various fields of catalysis, and this stems from the possible presence of favourable cooperative effects.[4] We have become interested in the use of Schiff-base macrocycles given that they possess multiple binding sites,[5] and our studies have been focusing on the simplest members of this family, the so-called Robson type macrocycles, derived from the [2+2] condensation of a diamine/dianiline with a dialdheyde.[6] In terms of catalysis (ROP of \( \varepsilon \)-CL), we observed beneficial cooperative effects when alkylaluminium centres are bound in a specific way to a Schiff-base macrocycle (LH$_2$, scheme 1, left) derived from the dianiline [(CH$_2$)$_2$CH$_2$(2-C$_6$H$_4$N)$_2$]], whereas the presence of aluminoxane type (Al–O–Al) bonding in such a system proved detrimental.[7] Furthermore, we noted that manganese complexes of such macrocycles were far less active with conversions for the ROP of \( \varepsilon \)-CL < 15 %.[8] It is noteworthy that the structural chemistry of this particular macrocycle is underexplored, indeed a search of the CSD revealed no hits,[9] other than our previously mentioned chemistry.[10] We have selected the metals cobalt and zinc given their relatively low cost and biocompatibility. Further, we note that the use of Zn complexes for the ROP of \( \varepsilon \)-CL is well established,[10] ROP using Co species are scant.[10]

Recent work by Williams et al. has shown how the use of hetero-dinuclear complexes can result in enhanced catalytic performance.[11] In particular, it was reported that an in-situ generated catalyst comprising the hetero-dinuclear Zn-Mg complex bearing a diphenolate tetramine macrocycle (scheme 1, right) used in conjunction with its homo-dinuclear Zn-Zn and Mg-Mg counterparts performed better for the copolymerization of CO$_2$ with epoxides than did the homo-dinuclear complexes alone. Given the very similar solubility properties of the three species, it was not possible to crystallize selectively the Mg-Zn hetero-dinuclear complex. However, subsequent studies by the same group have shown that it is possible to access such species via mono-metalation, followed by the addition of the second metal,[11a] and the molecular structures of a number of mixed-metal species were reported.[11b,c] Interestingly, Williams et al. also observed that for ROP of \( \varepsilon \)-CL and \( \delta \)-LA, a mixed Ti/Zn system displayed moderate/high activity whilst the mono-Ti system was inactive.[11d] We also note that cooperative effects have also been observed for a homo-dinuclear zinc complex in lactide polymerization.[12] Given this, we have re-focused our efforts on the [2+2] Schiff-base systems and have extended our studies in an attempt to access mixed-metal systems. Herein, we report that homodinuclear cobalt and zinc complexes bearing the macrocycle L (1 - 3, scheme 2) are readily accessible. Furthermore, on reacting 1 with Br$_2$Zn a complex 4 related to 1 was formed differing only
Figure 1. Molecular structure of 1Bu.0.5MeCN. Solvent omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Co(1) – Br(1) 2.4847(6), Co(1) – O(1) 2.004(2), Co(1) – O(2) 2.043(2), Co(1) – N(1) 2.088(3), Co(1) – N(3) 2.105(3); O(1) – Co(1) – O(2) 178.52(9), N(1) – Co(1) – N(3) 108.77(11), O(1) – Co(1) – Br(1) 92.98(7), N(3) – Co(1) – Br(1) 128.17(8), N(1) – Co(1) – Br(1) 2.058(2), Co(1) – N(4) 2.126(2), Co(1) – N(5) 2.108(3), Zn(1) – Br(1) 2.387(4), Zn(1) – Br(2) 2.3412(5), Zn(1) – O(1) 1.9792(19), Zn(1) – N(1) 2.015(3); Co(1) – O(1) – Zn(1) 103.93(8), N(3) – Co(1) – N(4) 107.92(9), O(2) – Co(1) – N(3) 90.50(9), O(2) – Co(1) – N(5) 167.52(9), O(1) – Zn(1) – N(1) 93.30(9), Br(1) – Zn(1) – Br(2) 113.655(18).

Reaction of the [2+2] Schiff-base macrocycle ([2-(OH)-5-(R)-C6H5-1,3-(CH3)2]CH2CH2(2-C6H4N2)]; (R = Me, tBu) with 2.1 equivalents of CoBr2 afforded, following work-up, green prisms on recrystallization from a saturated solution of acetonitrile at 0 °C in about 70% yield. The molecular structure of 1Bu.0.5MeCN is shown in figure 1, with selected bond lengths and angles given in the caption; for 1Me.4MeCN see ESI figure S1. The complex is a salt of formula [CoBr6(N2)][CoBr6(NCMe)]·0.5MeCN (1Bu.0.5MeCN). In the cation, the cobalt centre is five-coordinate with a trigonal bipyramidal pattern; the apical sites are occupied by O atoms of phenolates, with the bromide and two N atoms in the equatorial sites. Concentration of the mother-liquor afforded more of 1Bu.0.5MeCN plus small amounts of an orange/red product, identified as [CoBr6(N2)][CoBr6(NCMe)][Br]4.5MeCN (2Bu.4.5MeCN), the structure of which is similar to that observed for 1Bu.0.5MeCN, differing mainly in the composition of the anions, namely Br- and CoBr4(NCMe); the molecular structure is shown in figure S2 (ESI). Similar interaction of LH2 with 2.1 equivalents of ZnBr2 afforded, following work-up, yellow prisms of [Zn1Br6]2[BnOH][(ZnBr4(NCMe))]·MeCN (3Bu·MeCN) in good yield. Use of excess ZnBr2 (> 4 equivalents) also afforded 3Bu·MeCN as the only crystalline product. Again, the structure (ESI, figure S4) is very reminiscent of 1Bu.0.5MeCN, with the zinc adopting a trigonal bipyramidal geometry in the cation; for the structure of 3Me·MeCN, see figure S5. Having isolated and characterized these homo-dinuclear products, we then targeted the formation of a mixed-metal system. Complex 1Bu was reacted with ZnBr2 to afford a yellow product, however, the structure, namely [CoBr6(N2)][CoBr6(Zn0.32Br0.68(NCMe))]·0.25MeCN (4Bu.0.25MeCN), turned out to be very similar to 1 differing only in the composition of the anion, the latter having cobalt:zinc occupancy 68.4:32.6(17) (ESI, figure S5). We note that the structures of both 3Me·Bu and 4Bu·Bu are analogous to the equivalent manganese complex (see CUVYID in CCDC).[13] Given this disappointing result, both 1Me and 1Bu were treated with Et2Zn (one equivalent) and on work-up (acetonitrile), brown/red products were isolated in good yield. Single crystals were grown from acetonitrile on prolonged standing (3 days) at ambient temperature. The molecular structure of 5Bu.3.25MeCN is shown in figure 2, with bond lengths/angles given in the caption; for 5Me·3MeCN see figure S6, ESI. In 5Bu·3.25MeCN, the macrocycle binds two metals (Co and Zn) in an ordered way. The Co5+ is bound in a distorted octahedral geometry by two cis phenolates and two cis imines of the macrocycle, a rather distant bromide (Co(1)-Br(1) 2.9383(5) Å), and a single molecule of acetonitrile. The Zn ion is in close proximity to the Co ion; the bromide and one of the phenolates each coordinate to the Zn. The tetrahedral coordination about the Zn is completed by an imine and a mono-dentate bromide. One might describe the octahedron of Co(1) and the tetrahedron around Zn(1) as sharing a common edge (O(1) and Br(1)). The two metals are separated at a distance 3.2399(5) Å. The magnetic moments of 5 (5.1 – 5.3) are consistent with high spin Co(II) complexes,[13] whilst the 1H NMR spectra are broad and spread over a large window (+140 to -40 ppm). The cobalt and zinc complexes 1, 3 and 5 (R = Me, tBu) have been screened for their ability to ring open polymerize δ-VL and ε-CL; runs were conducted in the presence of benzyl alcohol [BnOH]. For complexes 1 and 3, a variety of conditions were used in the attempted ROP of δ-VL including temperatures in the range 40 to 130 °C, differing ratios of [δ-VL][Ca]·[BnOH] and over different times, however on each occasion there was no sign of polymer upon
Table 1. ROP of δ-VL using complexes 1-5

<table>
<thead>
<tr>
<th>Run</th>
<th>Cat.</th>
<th>[δ-VL]: [Cat]:BnOH</th>
<th>T(°C)</th>
<th>t(h)</th>
<th>Conv. (%)</th>
<th>Mn (×10^2)</th>
<th>Mw/Mn</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5Bu</td>
<td>50:1:1</td>
<td>130</td>
<td>24</td>
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<td>100:1:1</td>
<td>130</td>
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<td>92.8</td>
<td>2.14</td>
<td>0.93</td>
<td>1.15</td>
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<td>6.89</td>
<td>4.97</td>
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<td>0.45</td>
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<td>97.0</td>
<td>2.68</td>
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<td>0.45</td>
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<td>500:1:1</td>
<td>130</td>
<td>24</td>
<td>4.4</td>
<td></td>
<td>0.22</td>
<td></td>
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</tbody>
</table>

* By ^1^H NMR spectroscopic analysis. * Mw values were determined by GPC in THF vs PS standards and were corrected with a Mark-Houwink factors (0.58 for poly(δ-VL) * (F.W.[M]/[BnOH]) [conversion]. * Polydispersity index (Mw/Mn) were determined by GPC.

work-up. However, for the mixed-metal systems 5, activity was observed when the temperature reached 130 °C, in the presence of one equivalent of BnOH (at this temperature, no activity was observed for 1 and 3 – see figure 3 for the relative rates of the 5Bu derivatives). Data for runs is given in table 1 (see also figures 19-24 ESI) and reveals that 5Bu out-performs 5Me, which is thought to be due to the increased solubility of the former in the reaction solvent. In these mixed-metal systems, the Co to Zn distance may favour coordination of a monomer to both metal centres, and then as in the ROP of propylene oxide,[16] one metal acts as a Lewis acid with the other using its M-OR function to attack the carbonyl group. Highest conversions were achieved with ratios between 100:1:1 and 500:1:1 at 130 °C, with all the runs showing good control with PDIs in range 1.15-1.30; above and below this temperature only trace polymer was observed. Use of either 12h (run 6) or no solvent (i.e. a melt, run 7) was less controlled. Analysis of the polymer indicated the presence of benzyloxy and hydroxyl end groups (figure S22, ESI). There was evidence of transesterification and all observed Mw values were significantly lower than the calculated values (see figure S21, ESI). In the case of ɛ-CL, the situation was more pronounced with no conversion evident by ^1^H NMR spectroscopy for catalyst systems 1 and 3. By contrast, systems using 5Me and 5Bu were efficient catalysts at 130 °C over 24 h, with similar conversion results observed using the ratios between 50:1:1 and 500:1:1; above and below this temperature only trace polymer was observed. As for the δ-VL runs, good control was observed, except for when using either 12h or a melt. From a kinetic study, it was observed that the polymerization rate exhibited near first order dependence of the CL concentration at 130 °C. The rate of polymerization for ɛ-CL (Kobs=2.12×10^-2 (h^-1)) for 5Bu was less than half that for δ-VL (Kobs=6.10×10^-3 (h^-1)) for 5Bu, which is consistent with other reports.[17] The observed molecular weights were lower than the calculated values, suggesting the presence of a chain transfer agent (H2O or BnOH). This was also evident in the MALDI-TOF mass spectra, a number of families of peaks were observed separated by 114 mass units (figures S26, S27, ESI); the highest were typically about 7000. For example, in the case of 5Bu (run 4, table 2), peaks in the spectrum can be assigned to

4926, 5039, and 5154 using the formula C36H36O6(O(CH2)n)CO2H-OH for n = 42, 43 and 44 respectively. The ^1^H NMR spectra of the PCL (e.g. figure S28) revealed the presence of benzyloxy and OH end groups. It also proved possible to ROP r-LA using the mixed-metal systems, albeit in much poorer yields. Moreover, co-polymerization of δ-VL and ɛ-CL was possible as was ɛ-CL with r-LA (see table S1 and figures S33-43, ESI for preliminary results).

In conclusion, we have isolated and structurally characterized homo- and mixed-metal (Co/Zn) complexes of a [2+2] macrocyclic Schiff-base. Screening of these complexes for the ROP of the cyclic esters δ-vlalorolactone (δ-VL) and ε-caprolactone (ε-CL) revealed that whilst the homo-dinuclear complexes are either virtually inactive (δ-VL) or inactive (ε-CL), the mixed-metal systems are efficient catalysts at 130 °C, suggestive that the metals are able to ‘turn each other on’.

Conflicts of interests

There are no conflicts to declare.
Table 2. ROP of e-CL using complexes 1-5.

<table>
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<th>Run</th>
<th>Cat.</th>
<th>[e-CL]:[Cat]</th>
<th>T(°C)</th>
<th>thh</th>
<th>Conv. (%a)</th>
<th>Mw x 10^2</th>
<th>Mw/Mn x 10^2</th>
<th>PDI</th>
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<td>7.87</td>
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<td>1.66</td>
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</table>

(a) By 1H NMR spectroscopic analysis. (b) Mw values were determined by GPC in THF vs PS standards and were corrected with a Mark-Houwink factors (0.56 for poly(e-CL) (F.W.[M]/[BnOH])(conversion) (c) Polydispersity index (Mw/Mn) were determined by GPC.

Acknowledgements

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Note and References

Monomer
\[ n=1; \delta-\text{VL} \]
\[ n=2; \omega-\text{CL} \]

Homo-dinuclear
\[ [[\text{MBr}]] [[\text{MBr(NCMe)}]] \]
\[ M = \text{Co, Zn} \]

Hetero-dinuclear
\[ \{\text{LCo(NCMe)}\}[[\mu-\text{Br}]\text{ZnBr}] \]

Polymers/copolymers

415x187mm (300 x 300 DPI)