Mononuclear Cu(II) complexes of novel salicylidene Schiff bases: synthesis and mesogenic properties

Carmen Cretu[a], Liliana Cseh[a*], Bai J. Tang[b], Viorel Sasca[a], Valentin Badea[c],
Georg H. Mehl[b], Sergiu Shova[d], Otilia Costisor[a]

[*] Author to whom correspondence should be addressed.
[a] *Institute of Chemistry Timisoara of Romanian Academy, Timisoara, Romania*
Tel: +40256494918 Fax: +40256494924 E-mail: lili_cseh@yahoo.com

[a] *Institute of Chemistry Timisoara of Romanian Academy, Timisoara, Romania*
[b] *Department of Chemistry, University of Hull, Hull, UK*
[c] *"Politehnica" University Timisoara, Faculty of Industrial Chemistry and Environment Engineering, 6 Vasile Pârvan Bvd, 300223, Timisoara, Romania*
[d] *Petru Poni Institute of Macromolecular Chemistry, Iasi, Romania-va rog verificati si completati*

ABSTRACT

Two new Schiff base ligands **1** and **2** (where **1** = 4-(2-hydroxybenzilidenamino)-phenyl-4-(decyloxy)-2-(pent-4-enyloxy)benzoate, **2** = 4-(4-(decyloxy)-2-hydroxybenziliden amino)-phenyl-4-(decyloxy)-2-(pent-4-enyloxy)benzoate) and their Cu(II) complexes have been synthesized and characterized. The structure of the compounds was established by elemental analysis, NMR, IR and UV-Vis. The structure of Cu(II) complex with **1** as ligand (**3**) was determined by X-ray diffraction. The mesomorphic investigation of the ligands and their complexes was studied by optical polarizing microscope (OPM) and differential scanning calorimetry (DSC). The Schiff base compounds exhibit an enantiotropic nematic phase and the copper(II) complex containing **2** as ligand (**4**) shows monotropic nematic phase behaviour, while compound **3** does not show mesomorphism.

1. Introduction

Liquid crystalline phase behavior is a fascinating state of soft matter, combining order and mobility on a molecular and supramolecular level [1]. Metal containing liquid crystals, named "metallomesogens", combine the physical characteristics exhibited by metal coordination complexes with those of organic molecules which give liquid crystals [2]. The copper(II) ion is one of the most used ion in the synthesis of metallomesogens. In the presence of Schiff bases derived from salicylaldehydes, copper(II) ions are able to close a chelate ring with planar or nearly planar arrangements around the copper and give rise to flat elongated molecules, suitable for mesophase formation [3].

The mesomorphic behavior of organic and inorganic compounds is basically dependent on their molecular architecture in which a slight change in the geometry brings about considerable change in their properties [4,5].

 [6]. comment : what do we want to say here?: suggestions: The structure-liquid crystal properties relationships   of bis(N-phenylsalicylaldiminato)copper(II) framework, shown in Fig.1 was explored extensively. [6]
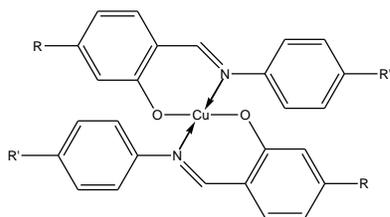
Fig. 1. The framework for Cu(II) complex with Schiff base as ligands

Ghedini *et al* [7] reported copper complexes with the bis(N-phenylsalicylaldiminato)copper(II) core , shown in Figure 1 and where the flexible chains are either alkyl or alkoxy chains of different lengths. The compounds were found

to form smectic phases, monotropic for the shorter and enantiotropic for the long tail homologues.

The complexes with Schiff bases containing three aromatic rings [8,9,**Error! Bookmark not defined.** ($R = -H$, $-OOC-C_6H_4-OC_nH_{2n+1}$ and $R' = -OOCC_6H_4OC_mH_{2m+1}$, $-OC_2H_5$) were shown to exhibit nematic and smectic phase phase behaviour. The presence of the nematic phase for these series is explained by the loss of layer ordering when the long axes of the molecules lie in the plane of the layer. When the long axes of the copper complexes lie perpendicular to the layer planes, smectic phases are formed.

The presence of a lateral substituent like halogens in a third position of salicylaldimine fragment create a larger perturbation of the planarity around the copper core with decreased of stability, giving rise to monotropic nematic phases for Cu(II) complexes containing three aromatic rings [10,11]. Also, a larger substituent causes more pronounced decrease stability.

Taking into account the results obtained previously we designed two new Schiff bases with the central motif shown in Fig. 1 with $R = -H$ or $-OC_{10}H_{21}$ and $R' = -OOC-C_6H_3-OC_{10}H_{21}(OC_5H_{10})$ (4-(decyloxy)-2-(pent-4-enyloxy)benzoate). The imines contain three phenyl rings as rigid parts of the molecules, the "molten" alkoxy end-on group assure the fluidity of the system and the 5-oxypent-1-ene, as side-on unit, promotes the nematic phase and the lowering of crystallization temperature by reduction of the symmetry of system. The olefinic group in the lateral has two functions, it is know that such groups lower the melting point when compared to their saturated hydrocarbon analogues and it has the potential to be functionalized further. The location for the attachment ing of the latral group on aromatic ring was selected to be away as far possilbe from the cooper aotm in order to minimized disturbance of planarity of the lighand system around the metal ion.

WE SHOULD have a paragraph why this work is done
Example: even though there are potentially a range of synergistic properties combination of organic and matail containing materials in the liquid crystal state, such as high birefringence, optical non-linear behaviour , magnetic properties associated with metals, these have in the main not been achieved, as the temperatures of liquid crystal pahses

metallo-mesogens tend be very high, often above 150 ˚C, leading to rapid degradation of materials and being unsuitable for the exploration of their technological potential.

In this paper, we report the preparation of two new bidentate Schiff bases derived from salicylaldehyde and their Cu(II) complexes, as well the investigation of liquid crystal properties of synthesized compounds. The focus is on the formation of nematic phase behaviour, as this is the least ordered, experimentally and theoretically most investigated and technologically most important liquid crystal phase.

2. Experimental

2.1 Materials and methods

All solvents were of reagent grade and used without further purification. The chemicals were purchased from Merck or Aldrich Chemical Company and used as received.

Elemental analyses of products were carried out using a Perkin Elmer 240C-CHN analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Lambda 400 or Bruker 500 spectrometer (400 and 100 MHz or 500 and 125 MHz respectively, for ^{1}H and ^{13}C) spectrometer using tetramethysilane as internal standard. All reactions were monitored by thin-layer chromatography carried out on 0.2 nm Merck silica gel plates (60-F254). Column chromatography was performed on silica gel (Merck Kieselgel C60, 230-400 mesh).

IR spectra were recorded on a Jasco-400 Spectrum One FT-IR spectrophotometer, as KBr pellet, in the 400-4000 cm^{-1} range. UV-visible spectra were recorded on an UV-Vis Perkin Elmer Lambda 12 spectrometer on solutions. The molar conductance measurements were carried on WTW LF 340-A conductivity meter.

The identification of previously reported compounds was made by ^{1}H-NMR and melting points comparison with literature data.

The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (DSC 882e, Mettler-Toledo Inc.) which was operated at a scanning rate 10ºC/min in nitrogen against an indium standard, both on heating and cooling. Optical textures of the phases between crossed-polarizers were observed using an Olympus BX-50 optical microscope equipped with a Mettler-Toledo FP82HT hot

stage, and pictures were taken using a CoolSnap (Roper Scientific) digital ccd camera connected to a PC.

Crystallographic measurements were carried out on Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated MoKα radiation. The single crystals were positioned at 40 mm from the detector and 319 frames were measured each for 350 s over 1° scan width. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [12]. The structures were solved by direct methods using Olex2 [13] software with the SHELXS structure solution program and refined by full-matrix least-squares on F^2 with SHELXL-97 [14]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms were placed in calculated positions, riding on their carrier atoms. The both decyloxy and enyloxy groups of the ligand were found to be disordered in two resolvable positions and their positional parameters were refined in combination with PART, SADI and EADP restraints using anisotropic/isotropic model for non-H atoms. A weak diffraction for several selected single-crystals has been observed and the resolution of the collected X-ray data was estimated to be at 0.9 Å. Nevertheless the structure could be easily solved and electron density of the molecule was well defined allowing determining the atomic connectivity. The main crystallographic data together with refinement details are summarized in Table 1. CCDC-//// contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2 Preparation of compounds

The intermediate compounds methyl 4-(decyloxy)-2-hydroxybenzoate, methyl 4-(decyloxy)-2-(pent-4-enyloxy)benzoate and 4-(decyloxy)-2-(pent-4-enyloxy)benzoic acid were obtained according to literature methods [15] and were previously reported by our group [16].

4-Nitrophenyl 4-(decyloxy)-2-(pent-4-enyloxy) benzoate. N,N'-Dicyclohexyl carbodiimide (DCC) (0.68 g, 3.3 mmol) and 4-dimethylaminopyridine (DMAP) (5.9 mg, 0.048 mmol) were added to a stirred solution of 4-(decyloxy)-2-(pent-4-enyloxy) benzoic acid (1 g, 2.75 mmol) and p-nitrophenol (0.573 g, 4.125 mmol) in dry CH_2Cl_2 (10 ml).

The mixture was stirred at room temperature for 6 h. The precipitate was filtered off and the solvent was removed under reduced pressure. The crude product was crystallized from ethanol to give a colorless solid. R_f (CH_2Cl_2) = 0.63; Yield: 1 g (75 %); Anal. calcd. for $C_{28}H_{37}NO_6$ (483.60): C 69.54, H 7.71, N 2.90. Found: C 69.48, H 7.94, N 2.78 %. ^{1}H-NMR (400 MHz) CDCl$_3$/δ [ppm]: 0.86-0.90 (t, 3H, H[1]), 1.22-1.53 (m, 14H, H[2-8]), 1.77-1.97 (2cv, 4H, H[9,15]), 2.24-2.29 (q, 2H, H[16]), 4.03 (m, 4H, H[10,14]), 4.98 (m, 2H, H[18]), 5.81 (m, 1H, H[17]), 6.51 (t, 2H, H[11,13]), 7.37 (m, 2H, H[19,19']), 8.02 (d, 1H, H[12]), 8.29 (m, 2H, H[20,20']).
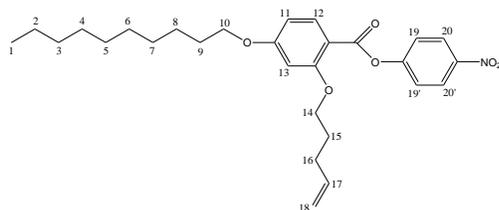
4-(2-Hydroxybenzilidenamino)-phenyl-4-(decyloxy)-2-(pent-4-enyloxy)benzoate (1). A solution of SnCl$_2$·2H$_2$O (1.35 g, 6 mmol) in EtOH (25 ml) was added under reflux to a solution of 4-nitrophenyl 4-(decyloxy)-2-(pent-4-enyloxy) benzoate (0.48 g, 1 mmol) in EtOH (8 ml) under nitrogen and maintained at reflux for 24 h. After cooling, the mixture was poured into ice and the *pH* value was adjusted to 7 using NaOH. The mixture was extracted with ethyl acetate. The ethyl acetate solution was washed three times with brine and was dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduce pressure. The mixture product contained amine was used forward without purification. At a solution of this mixture in EtOH (10 ml) was added drop wise salicylaldehyde (0.11 ml, 1.102 mmol). The reaction mixture was heated under reflux until the reaction was complete (2.5 h). The yellow solid product was obtained by cooling, filtered off and washed with EtOH. R_f(n-Hexane/AcOEt) = 0.7; Yield: 0.26 g (50%). ^{1}H-NMR (500 MHz) CDCl$_3$/δ [ppm]: 0.87-0.91 (t, 3H, H[35]), 1.28-1.49 (m, 14H, H[28-34]), 1.76-1.99 (m, 4H, H[27,22]), 2.25-2.33 (q, 2H, H[23]), 4.03 (m, 4H, H[21,26]), 4.96-5.05 (m, 2H, H[25]), 5.78-5.84 (m, 1H, H[24]), 6.50-6.56 (m, 2H, H[3,5]), 6.92-7.04 (m, 2H, H[17,19]), 7.24-7.41 (m, 6H, H[9-12,18,20]), 8.04 (d, 1H, H[6]), 8.62 (s, 1H, H[14]), 13.22 (s, 1H, OH); ^{13}C-NMR (125 MHz)

CDCl$_3$/δ [ppm]: 14.17 (C35), 22.72 (C34), 26.02 (C28), 28.29 (C22), 29.59-29.16 (C27, C29-C32), 30.05 (C23), 31.93 (C33), 68.02 (C4), 68.39 (C21, C26), 100.23 (C3), 105.39 (C1), 110.98 (C5), 115.31 (C17, C25), 117.27 (C15), 119.13 (C19), 122.07 (C11, C12), 122.96 (C9, C10), 132.34 (C20), 133.18 (C6), 134.54 (C18), 137.75 (C24), 145.84 (C8), 150.05 (C13), 161.11 (C2), 161.64 (C14), 162.57 (C16), 164.04 (C4), 164.59 (C7);
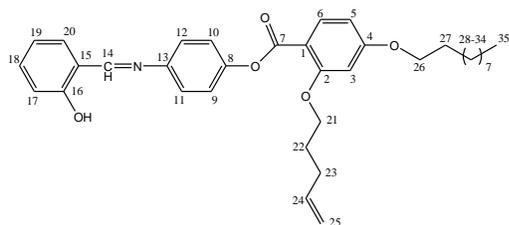
IR (KBr pellet) ν$_{max}$ [cm^{-1}]: 3449(br, w), 3081(w), 3061(w), 2951(m), 2920(s), 2867(m), 2850(s), 1735(vs), 1606(vs), 1572(s), 1506(s), 1466(m), 1455(m), 1424(m), 1388(m), 1328(m), 1280(m), 1267(m), 1234(s), 1199(vs), 1182(vs), 1148(m), 1127(s), 1105(m), 1049(m), 1034(s), 1021(s), 981(m), 908(m), 877(m), 832(m), 815(m), 756(m), 723(w), 690(w), 629(m), 596(w), 557(w), 527(w), 459(w), 443(w), 412(w); UV-Vis (CHCl$_3$, 10^{-4}M) (ε/Lmol^{-1}cm^{-1}) λ$_{max}$ [nm]: 268(26500), 302(22000), 341(17600).

4-(4-(Decyloxy)-2-hydroxybenzilidenamino)-phenyl-4-(decyloxy)-2-(pent-4-enyloxy) benzoate (2). A solution of SnCl$_2$·2H$_2$O (2.79 g, 12.402 mmol) in EtOH (10 ml) was added under reflux to a solution of 4-nitrophenyl 4-(decyloxy)-2-(pent-4-enyloxy)benzoate (1 g, 2.067 mmol) in EtOH (50 ml) under nitrogen and maintained at reflux for 24 h. After cooling, the mixture was poured into ice and the *p*H value was adjusted to 7 using NaOH. The mixture was extracted with ethyl acetate. The ethyl acetate solution was washed three times with brine and was dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduce pressure. The mixture product contained amine was used forward without purification. At a solution of this mixture in EtOH (10 ml) was added drop wise a solution of 4-decyloxy-salicylaldehyde (0.517 g, 1.860 mmol) in EtOH (20 ml). The reaction mixture was heated under reflux until the reaction was complete (2.5 h). The yellow solid product was obtained by cooling, filtered off and

washed with EtOH. R_f(n-Hexane/AcOEt) = 0.68; Yield: 0.45 g (34%). ^{1}H-NMR (500 MHz) CDCl$_3$/δ [ppm]: 0.86-0.91 (t, 6H, H[35,35']), 1.28-1.47 (m, 28H, H[28-34, 28'-34']), 1.77-1.99 (m, 6H, H[27,27',22]), 2.26-2.33 (q, 2H, H[23]), 3.97-4.08 (m, 6H, H[21,26,26']), 4.95-5.05 (m, 2H, H[25]), 5.76-5.89 (m, 1H, H[24]), 6.47-6.55 (m, 4H, H[3,5,17]), 7.21-7.30 (m, 5H, H[9-12,20]), 8.02-8.05 (d, 1H, H[6]), 8.52 (s, 1H, H[14]), 13.68 (s, 1H, OH); ^{13}C-NMR (125 MHz) CDCl$_3$/δ [ppm]: 14.11 (C35, C35'), 22.57 (C25), 25.98 (C34, C34'), 28.25-30.00 (C22, C23, C27-32, C27'-C32'), 31.89 (C33, C33'), 67.98 (C21), 68.24-68.34 (C26, C26'), 100.20 (C3), 101.54 (C17), 105.34 (C5), 107.59 (C1), 111.05 (C19), 115.25 (C15), 121.80 (C9-C12), 122.82 (C25), 133.49 (C24), 134.45 (C20), 137.71 (C6), 145.86 (C8), 149.54 (C13), 161.45 (C2), 161.56 (C14), 163.56 (C16), 164.05 (C4), 164.50 (C7);
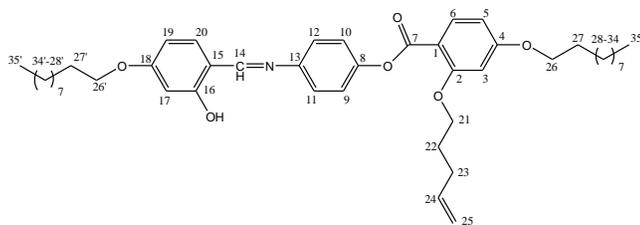
IR (KBr pellet) ν_{max} [cm^{-1}]: 3446(br,w), 3074(w), 2952(m), 2937(m), 2919(s), 2874(m), 2849(s), 1746(s), 1617(s), 1602(s), 1573(m), 1512(m), 1466(m), 1428(w), 1402(w), 1392(w), 1330(m), 1286(m), 1229(m), 1193(vs), 1184(vs), 1160(m), 1134(m), 1117(m), 1023(s), 970(w), 913(w), 873(w), 835(m), 819(w), 799(w), 766(w), 741(w), 723(w), 693(w), 651(w), 615(w), 593(w), 528(w), 466(w), 457(w), 433(w), 418(w); UV-Vis (CHCl$_3$, 10^{-4}M) λ_{max} [nm] (ε/Lmol^{-1}cm^{-1}): 254(20900), 301(19900), 341(24300).

Bis-[4-(2-hydroxybenzilidenamino)-phenyl-4-(decyloxy)-2-(pent-4-enyloxy) benzoato]copper (II) (3). Cu(CH$_3$COO)$_2$·H$_2$O (0.030 g, 0.152 mmol) in 15 ml EtOH was added with stirring to a hot solution of **1** (0.170 g, 0.304 mmol) in 22 ml EtOH. The mixture was heated at reflux for 1h. After cooling to r.t., the green solid was filtered and washed with EtOH. Yield: 0.135 g (75 %). ^{1}H-NMR (500 MHz) CDCl$_3$/δ [ppm]: 0.87-0.90 (t, 3H, H[35]), 1.27-1.49 (m, 14H, H[28-34]), 1.79-1.89 (br, 4H, H[27,22]), 2.23 (br, 2H, H[23]), 4.01 (br, 4H, H[21,26]), 4.91-5.00 (br, 2H, H[25]), 5.77 (br, 1H, H[24]), 6.47-6.50 (brm, 2H,

H^{3,5}), 7.99 (br, 1H, H^6); IR (KBr pellet) ν_{max} [cm^{-1}]: 3078(w), 2925(m), 2852(m), 1709(s), 1608(vs), 1574(m), 1534(m), 1500(m), 1464(s), 1449(s), 1433(m), 1395(w), 1377(m), 1357(w), 1330(s), 1294(m), 1265(s), 1242(s), 1221(m), 1205(s), 1177(s), 1160(m), 1147(s), 1116(s), 1065(m), 1047(m), 1016(m), 987(w), 925(w), 901(w), 875(m), 826(m), 799(w), 755(m), 742(w), 694(w), 669(w), 644(w), 620(w), 572(w), 550(w), 527(w), 466(w), 446(w), 430(w), 418(w), 404(w); UV-Vis (CHCl$_3$, 5·10^{-5}M) λ_{max} [nm] (ε/Lmol^{-1}cm^{-1}): 261(52800), 301(54600), 401(17000), 673(200). Molar conductance (DMF, 10^{-3}M) Λ_M, Ω^{-1}mol^{-1}cm^2: 1.67.

Bis-[4-(4-(Decyloxy)-2-hydroxybenzilidenamino)-phenyl-4-(decyloxy)-2-(pent-4-enyloxy)benzoato]copper (II) (4). Cu(CH$_3$COO)$_2$·H$_2$O (0.042 g, 0.210 mmol) in EtOH (20 ml) was added to a hot solution of **2** (0.300 g, 0.420 mmol) in EtOH-CHCl$_3$ (6:1 v/v, 35 ml). The mixture was heated at reflux for 1h. After cooling to r.t., a green solid was filtered and washed with EtOH and MeOH. Yield: 0.287 g (91%). ^{1}H-NMR (500 MHz) CDCl$_3$/δ [ppm]: 0.87-0.90 (t, 6H, H$^{35,35'}$), 1.25-1.45 (m, 28H, H$^{28-34, 28'-34'}$), 1.79-1.89 (br, 6H, H$^{27,27',22}$), 2.23 (br, 2H, H^{23}), 4.01 (br, 6H, H$^{21,26,26'}$), 4.93-5.00 (m, 2H, H^{25}), 5.77 (br, 1H, H^{24}), 6.47-6.49 (br, 4H, H^{3,5,17}), 7.98 (br, 1H, H^6); IR (KBr pellet) ν_{max} [cm^{-1}]: 2921(w), 2851(w), 1704(w), 1606(m), 1520(w), 1503(w), 1468(w), 1433(w), 1372(w), 1313(w), 1269(w), 1249(w), 1181(m), 1128(w), 1074(w), 1031(w), 1015(w), 914(w), 880(w), 846(w), 811(w), 760(w), 722(w), 655(w), 607(w), 579(w), 546(w), 427(w), 403(w); UV-Vis (CHCl$_3$, 5·10^{-5}M) λ_{max} [nm] (ε/Lmol^{-1}cm^{-1}): 261(55800), 303(58200), 381(31600), 673(200); Molar conductance, (DMF, 10^{-3}M) Λ_M, Ω^{-1}mol^{-1}cm^2: 1.58.

3. Results and discussions

3.1 Synthesis and characterization

The synthesis of the Schiff base ligands was performed following a multi-step synthesis as is shown in the Scheme 1. The first and second step are etherification reactions of methyl 2,4-dihydroxybenzoate in the *para* (yield 85 %) subsequently *ortho* position (yield 97 %). The third step is a deprotection of carboxylic group. The subsequent esterification of [2-(pent-4-enyloxy) benzoic acid? proper name] with 4-nitrophenol lead in the corresponding nitro derivative (yield 75 %). The intermediate amine 4-

aminophenyl 4-(decyloxy)-2-(pent-4-enyloxy) benzoate was synthesized by a reduction with tin(II) chloride and used in a condensation reaction with corresponding aldehyde without preliminary purification. The new Schiff bases **1** and **2** obtained (yields: 50 and 34 %, respectively) were characterized by by a range of spectroscopic methods such ^{1}H-NMR, ^{13}C-NMR, IR and UV-Vis spectrocopy. **1** and **2** are stable in air and soluble in most organic solvents.

The mononuclear copper(II) complexes **3** and **4** were prepared by reacting the appropriate ligand with copper(II) acetate dihydrate in EtOH (for **3**) or in mixture of EtOH-CHCl$_3$ (for **4**). The complexes were isolated in good yields and are soluble in chloroform, dimethylformamide, tetrahydrofurane and ethyl acetate. The copper(II) complexes were characterized by molar conductivity, ^{1}H-NMR, UV-Vis and IR spectroscopy. The proposed structures are in full agreement with the spectroscopic data.
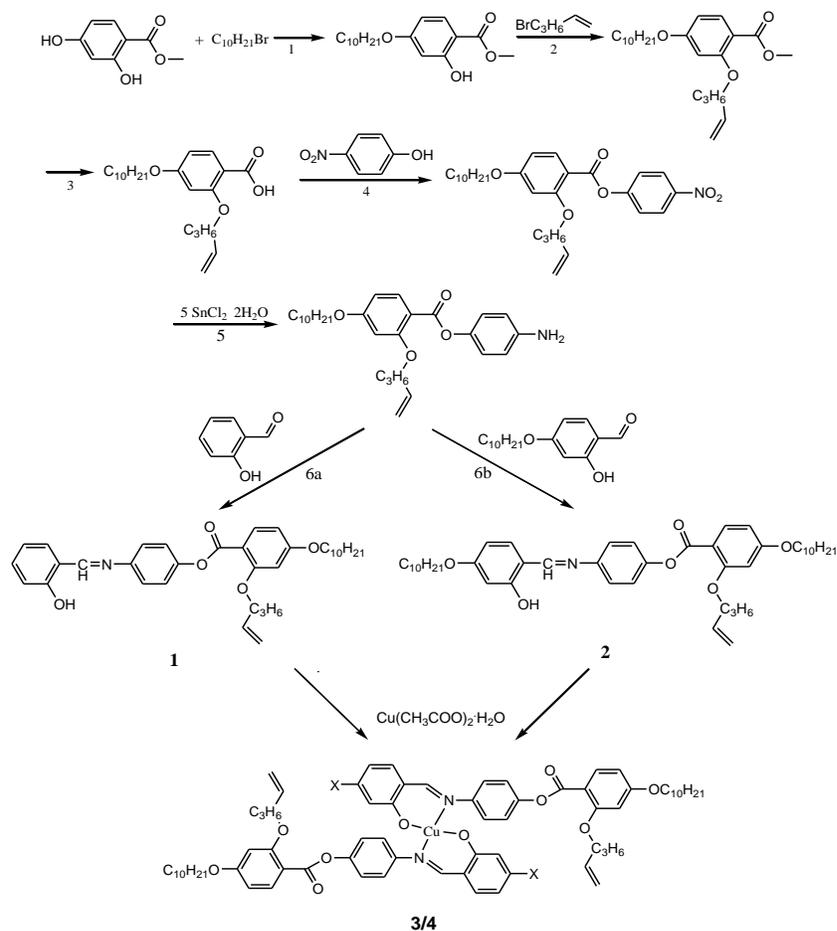
Scheme 1. Synthetic route to Schiff base ligands and its Cu(II) complexes: (1) K_2CO_3 anh., 4Å molecular sieves, butanone, Δt, 85%; (2) K_2CO_3 anh., KI, 4Å molecular sieves, butanone, Δt, 97%; (3) a) NaOH, H_2O, MeOH, THF, r.t., Δt, b) HCl, H_2O, 79%; (4) DCC, DMAP, DCM, r.t., 6 h, 75%; (5) a) EtOH, N_2 atm. Δt, 25 h, b) NaOH, H_2O; (6a) EtOH, Δt, 2.5 h, 50%; (6b) EtOH, Δt, 2.5 h, 34%.

The ^{1}H-NMR data of the Schiff base compounds give definite evidence for the molecular structure. The signals with a value (ppm) at 8.62 for **1** (see SI Fig. S1) and 8.52 ppm for **2** (see SI Fig. S3), respectively, belong to δ(HC=N) and are well within the range

expected for imine compounds [17]. The signals at 13.22ppm (for **1**) and 13.68 ppm (for **2**) are attributed to phenolic protons. In the ^{13}C-NMR spectrum, the signal due to the azomethine carbon atom was observed at 161.64 ppm (for **1**) (see SI Fig. S2) and 161.56 ppm (for **2**) (see SI Fig. S4) respectively. The proton signals for the copper(II) complexes are wide, shifted and some are not detectable namely the protons signals from the respective phenolic and imine group and the proton signals from the two aromatic rings (CH = CH) located in the vicinity of the coordination sphere of the metal ion complexes. This behavior could de due to the interference between the frequencies of resonance of the unpaired electron of paramagnetic copper(II) ion to the resonance frequency of the nuclei in its vicinity [18,19].

The IR spectra of the complexes have been analyzed in comparison with that of the free ligands in the region of 4000–400 cm^{-1}. In the spectra of the ligands a strong absorption band around 1606 cm^{-1} for **1** and 1617 cm^{-1} for **2** is observed and can be assigned to the C=N group. In the spectra of **3** and **4**, this band is sharper and shifted to lower frequencies by about 10 cm^{-1}. The phenolic ν(C–O) stretching vibration in the free Schiff bases is observed at 1280 for **1** and 1286 cm^{-1} for **2**. This band is shifted in the complexes to 1294 and 1313 cm^{-1}, respectively, thus indicating coordination of the phenolic oxygen. In the spectra of the two complexes, new weak bands are observed in the range of 600-400 cm^{-1}, assigned to M – O and M – N bonds, respectively.

The UV-VIS spectra recorded in chloroform solutions of the ligands showed few absorption bands in the range 254–302 nm assigned to π-π* transitions of the aromatic rings. The band observed at 341 nm correspond to the n-π* transition of the C=N group. The electronic spectra of the mononuclear complexes (CHCl$_3$ solution) exhibit a new broad band at 673 nm (see SI Fig. S5 and Fig S6), which could be attributed to the $^2A_{1g} \rightarrow {}^2B_{1g}$ transitions corresponding to Cu(II) ion in a square-planar geometry [20,21,22]. Both complexes give an unresolved broad band around 480 nm corresponding charge transfer band.

The molar conductivity data, measured at 24°C using solutions of the complexes in CHCl$_3$, showed the presence of non-electrolyte behavior for both complexes.

3.2 X-ray structure of 3

The single-crystal X-ray study has shown that the crystal **3** has a molecular crystal structure built from the neutral entities. A view along with the atomic labelling scheme is depicted in Fig. 2. The bond lengths and angles are summarized in Table 1.
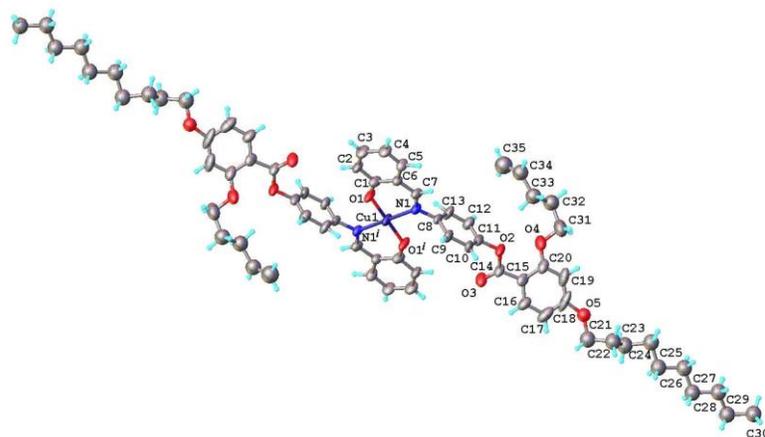
Fig. 2. X-ray molecular structure of **3** with thermal ellipsoids at 50% probability level. Only one of two disordered components is shown.

This **3** molecule is characterised by own (? I do not understand ?) symmetry, imposed by the special position of the central Cu atom, which sits on crystallographic inversion centre. Therefore, the central Cu atom exhibits a strictly square-planar N_2O_2 coordination provided by two symmetry equivalent bidentate ligands with Cu1-O1 and Cu1-N1 distances of 1.871(4) and 2.003(5) Å, respectively. These values are in good agreement with those found for the reported tetra-coordinated copper(II) complexes containing similar Schiff base ligands [23,24,25].

Table 1. Bond lengths (Å) and angles (°) for **3**.

Bond lengths [Å]			
Cu1-N1	2.003(5)	C15-C20	1.42(1)
Cu1-O1	1.871(4)	C16-C17	1.39(1)
C1-C2	1.408(9)	C17-C18	1.36(1)
C1-C6	1.396(9)	C18-C19	1.38(1)
C1-01	1.337(7)	C18-O5	1.39(1)
C2-C3	1.390(8)	C19-C20	1.37(1)
C3-C4	1.40(1)	C20-O4	1.351(9)

C4-C5	1.357(9)	C31-O4	1.42(1)
C5-C6	1.413(8)	C31-C32	1.55(1)
C6-C7	1.441(9)	C21-C22	1.535(9)
C7-N1	1.298(7)	C21-O5	1.42(1)
C8-C9	1.386(9)	C22-C23	1.510(8)
C8-C13	1.38(1)	C23-C24	1.536(8)
C8-N1	1.425(8)	C24-C25	1.520(9)
C9-C10	1.389(9)	C25-C26	1.517(9)
C10-C11	1.37(1)	C26-C27	1.520(9)
C11-C12	1.379(9)	C27-C28	1.524(9)
C11-O2	1.422(8)	C28-C29	1.513(9)
C12-C13	1.361(9)	C29-C30	1.522(9)
C14-C15	1.49(1)	C32-C33	1.54(1)
C14-O2	1.358(7)	C33-C34	1.54(1)
C14-O3	1.199(9)	C34-C35	1.335(8)
C15-C16	1.37(1)		

<div align="center">Bond angles (°)</div>

C6-C1-C2	118.8(5)	C17-C18-O5	110.6(12)
O1-C1-C2	118.6(6)	C19-C18-O5	128.3(13)
O1-C1-C6	122.6(6)	C20-C19-C18	120.2(9)
C3-C2-C1	120.7(7)	C19-C20-C15	120.1(8)
C2-C3-C4	119.8(7)	O4-C20-C15	116.2(7)
C5-C4-C3	119.9(6)	O4-C20-C19	123.6(9)
C4-C5-C6	121.3(7)	O4-C31-C32	107.4(10)
C1-C6-C5	119.5(6)	N11-Cu1-N1	180
C1-C6-C7	122.8(5)	O1-Cu1-N1	91.47(19)
C5-C6-C7	117.5(6)	O11-Cu1-N1	88.53(19)
N1-C7-C6	127.0(6)	O1-Cu1-O11	180
C9-C8-N1	121.4(6)	C7-N1-C8	116.2(5)
C13-C8-C9	118.1(7)	C7-N1-Cu1	123.7(5)
C13-C8-N1	120.3(5)	C8-N1-Cu1	120.0(3)
C8-C9-C10	120.8(7)	C1-O1-Cu1	130.5(4)
C11-C10-C9	118.7(6)	C14-O2-C11	117.4(5)
C10-C11-C12	121.7(7)	C20-O4-C31	120.1(7)
C10-C11-O2	119.1(6)	O5-C21-C22	101.6(13)
C12-C11-O2	119.2(7)	C23-C22-C21	99.2(10)
C13-C12-C11	118.7(7)	C22-C23-C24	108.6(10)
C12-C13-C8	122.0(6)	C25-C24-C23	98.2(10)
O2-C14-C15	112.8(6)	C26-C25-C24	109.8(11)
O3-C14-C15	125.3(6)	C25-C26-C27	112.6(14)
O3-C14-O2	121.9(6)	C26-C27-C28	108.8(15)
C16-C15-C14	116.3(8)	C29-C28-C27	110.8(14)
C16-C15-C20	117.7(7)	C28-C29-C30	108.1(16)
C20-C15-C14	126.0(6)	C33-C32-C31	112.7(12)
C15-C16-C17	122.4(9)	C34-C33-C32	126.9(15)
C18-C17-C16	118.4(8)	C35-C34-C33	125.3(19)
C17-C18-C19	121.1(8)	C18-O5-C21	135.0(14)

The crystal structure of **3** essentially results from the parallel packing of supramolecular ribbons along *a* crystallographic axis, as shown in Fig. 3. The formation of supramolecular ribbons are realised due to the short intermolecular C-H···O contacts, which can be interpreted as the weak hydrogen bonds. A perspective view of this supramolecular architecture is shown in Fig. 4.
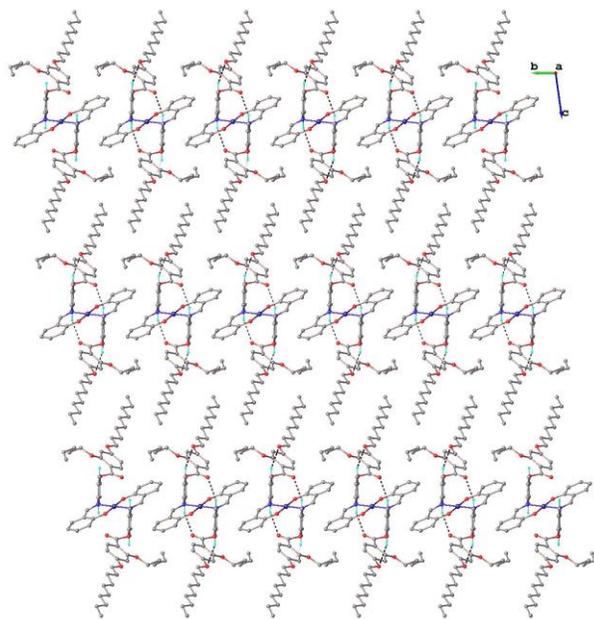
Fig. 3. View of the crystal structure **3** along *a* crystallographic axis
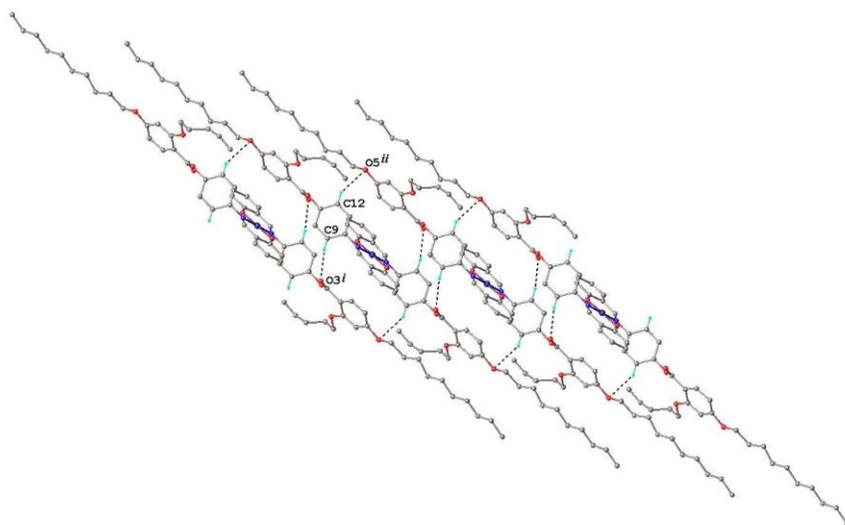
Fig. 4. View of one-dimensional supramolecular aggregation in the crystal structure of **3**. H-bonds are shown in dashed lines.

H-bonds parameters: C12−H⋯O5 [C12−H 0.93 Å, H⋯O5 (-1 + *x, y, z*) 2.78 Å, C12⋯O5 3.54(1) Å, C12−H⋯O5 139.7°]; C9−H⋯O3 [C9−H 0.93 Å, H⋯O3 (1 - *x, -y, -z*) 2.49 Å, C9⋯O3 3.37(1) Å, C9−H⋯O3 157.6°].

3.3 Investigation of mesomorphic properties

The mesomorphic properties of the ligands and Cu(II) complexes were investigated by differential scanning calorimetry (DSC) and optical polarized microscopy (OPM). The phase transition temperatures and the associated thermal data are summarized in Table 2.

Table 2. Phase transition temperature (°C) and associated enthalpy changes ($\Delta H/Jg^{-1}$; in the brackets).

	Transition	T(°)	$\Delta H/Jg^{-1}$
1	Cr′→N→I	77.5; 83.0	65.07; 1.2
	I→N→Cr″	63.x; 58.x	−; 68.15
2	Cr′→N→I	54.7; 87.3	34.88; 1.88
	I→N→Cr″	84.7; −	1.89; −
3	Cr→I	132.0	−
4	Cr′→I	116.8	49.43
	I→N→Cr″	92.5; 73.9	1.13; 38.83

Cr – crystalline, N – nematic phase, I – isotropic phase

The materials show a number of very interesting features. The transition temperatures from the crystalline to neamitc state are low, For the non–chelated ligands **1** and **2** they are at 77.5 °C and 54.7 °C, in line with other materials which show this fundamental architetural motif. [15] The transiton enthalpies for the nematic to isotropic transitions of 1.2 Jg^{-1} for **1** and 1.88 Jg^{-1} for **2** are in the range with those typically observed for isotropisation transitions from the nematic phase of rod shaped thermotropic liquid crystals. The structure of the phase was confirmed by optical polarizing microscopy. In the mesophase temperature interval schlieren textures with two and four brush defects were observed, typical for the formation of a neamtic phase, as example of such as photomicrograph is shown in Figure 5a. The comparison of the mesomorphic properties for Schiff bases **1** and **2** with a compounds with a similar structural motif, but without lateral chains confirms this line of argument. There melting points above 100 °C and highly ordered smectic phases were observed. [6]

The lateral chains which have been introduced in **1** and **2** prevent efficient packing of the aromatic groups in a smectic register and promote thus the formation of a nematic phase at relatively low temperatures. [33]. Quite surprising is the small temperature difference in in the isotropisation tmeratures of compounds **1** and **2**, being only 4 ˚C, even though a dodecyl chain has been added in **2,** when compared to **1**. This could be rationalized by the the formation of antiparallel correlated species in the nematic phase for **1**, stabilizing thus the formation of the LC state,

This overall trend is retained for the compounds **3** and **4**. The melting points are very low when compared to the no substituted analogues, whe transitions are approximately 70 ˚C higher. If one assumes that the additional lateral chains in 3 and 4 would have a simple plastifying effect and compares with the appropriate analogues [6] , the non-substitued materials exhibit still liquid melting points being still about 50˚C higher than observed for **3** and **4**. Does not show liquid crystalline phase behaviour. However 4 shows on cooling a nemaitc phase, evidenced by an enthalpy signal of 1.13 Jg^{-1} on cooling and the the spontaneous formation of a marbled texture , an example is shown in Figure 5b., which is stable to 73.9 ˚C. When **4** is compared to **2**, an increase in the melting point by 19.5 ˚C is observed and a destabilization of the nematic phase to an thermodynamically unstable monotropic neamtic phase is detected. However the nematic phase is stable at a highe temperature than in **2**. These liquid crystal transitions are by about 80 to 100˚C lower, depending which analogue one selects for comparison, than in the lateally non-substituted systems and address hence one of the majore problems in the invesitgaiton of metallo-mesogens. That is the formation of liquid crystal phases at high temperatures were degradation of the organo-metal species in the LC state occurs over time, making investigation in the LC state very difficult and essentially any potential application of such materials. The square planar complex 4 shows here shows a low ordered nematic phase stable of up to below 80 ˚C.

. 12. The
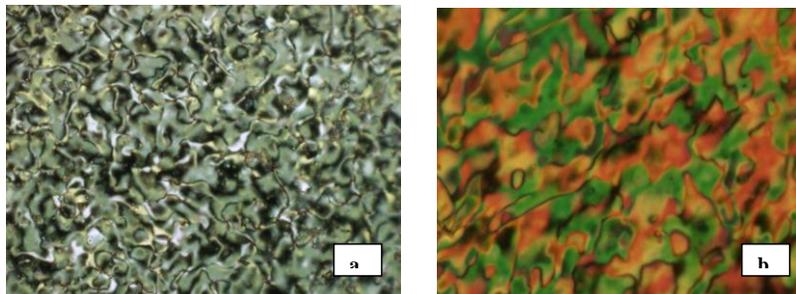
Fig. 5. Optical polarizing microscopy pictures, crossed polrizers, magnification x100; a) Schlieren texture of enantiotropic nematic phase for **2** at 80ºC on cooling

b) marbled texture of **the** monotropic nematic phase for **4** at 85 ºC on cooling

4. Conclusions

Two new mesomorphic Schiff bases and their mononuclear cooper(II) complexes were synthesized and characterized. Investigation of mesomorphic properties shows enantiotropic nematic phase for ligands and monotropic nematic phase formation for complex **4**. The introduction of side-end alkoxy chain, decrease the transition temperature from 77.5 (for **1**) to 54.65 °C (for **2**) and increase nematic range from 5.5 to 21.5 °C.

The X-ray study of complex **3** showed a square planar geometry around the copper atom. The side-on group attached to the farthest benzene ring from the copper atom has the desired effects: (i) the decreasing of the transition points and (ii) keeping the planarity around the metal ion. The structural motifs explored here open up the path to systematic design route to close to room temperature liquid crystal organometallic copper complexes.

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