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New Compounds with Potential Liquid Crystal Properties. Copper(II) and Nickel(II) Complexes of N,N′-bis(4-decyloxysalicyliden-N-n-propyl)-Piperazine. Synthesis and Characterization

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The new Schiff base N,N′-bis(4-decyloxysalicyliden-N-n-propyl)-piperazine (ZOPP) was designed and synthesized. Structures were confirmed by elemental analysis and IR, ^{1}H-NMR spectroscopy. ZOPP can act as ligand through the two set of donor atoms (one set: two nitrogen atoms and one oxygen) situated on each side of the piperazine bridge. The nature of the complexes depends strongly on the metal to ligand molar ratio. Thus, starting from metal to ligand of 1 to 1 ratio, where M=Cu(II), Ni(II), binuclear complexes with a polymeric structure have been obtained, whereas at metal to ligand molar ratio of 2 to 1, discrete binuclear complexes were formed.

Keywords: copper (II) and nickel (II) complexes; Schiff base; spectral properties

INTRODUCTION

In the area of metal containing liquid crystals, interesting developments have been reported recently [1–4]. These are mainly associated with the particular properties associated with metal containing materials, such as magnetism, color, or electron transfer characteristicss (e.g., FRET) usually not found for purely organic systems. Moreover metal containing liquid crystals form a very interesting bridge between the field of LC research and supra-molecular chemistry, an area where spontaneous organization over extended domains can be

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achieved [4]. There ligands are characterized by two or more well selected donor atoms able to close chelate cycles which are responsible for shaping the metal containing core. For the design of mesomorphic behavior this core is often designed to be planar. Mesomorphic phases in such systems are induced by linking long hydrocarbon chains to the aromatic cores placed at strategic positions. These are responsible for lowering the melting points and obtaining the anisotrpic fluidic state.

For the investigation of novel metallomesogens the new Schiff base ligand N,N′-bis(4-decyloxysalicyliden-N-n-propyl)piperazine (ZOPP) was designed and synthesized. This moiety can act as a ligand through two sets of donor atoms positioned symmetrically on each side of the piperazine bridge. The conformation of the piperazine moiety establishes the nature of the complexes. Thus, when the piperazine adopts a *chair* conformation, ZOPP acts as a binucleating ligand. Mononuclear complexes can be obtained when piperazine adopts a *bath* conformation. The nature of these complexes depends on the metal to ligand molar ratio employed in the synthesis. Having in view the aim to obtain metallomesogens, the synthesis and characterization of the copper (II) and nickel (II) complexes containing ZOPP as ligand is reported.

EXPERIMENTAL

Chemical and Physical Measurements

Analytical data were obtained by a Perkin Elmer model 240 C elemental analyzer for C, N, and H. The thin layer chromatography (TLC): Merck 60 F254 plates were used. Detection was by UV fluorescence (254 nm). Column Chromatography: Flash or gravity column chromatography was carried out using Merck Kieselgel C60 230–240 mesh silica gel. IR spectra were recorded on a Jasco-400 Spectrum One FT-IR spectrophotometer, as KBr pellet, in the 400–4000 cm^{-1} range. ^{1}H-NMR analysis was carried out using a Jeol -NMR (400 MHz) spectrometer. UV/Vis spectra were recorded on a Perkin Elmer 16PC spectrophotometer. Thermomicroscopy was realised under polarised light, using an Olympus BH-2 polarising microscope with Mettler FP52 hot stage linked to an FP5 temperature control unit. The accuracy of measurements is ±1°C.

All the reagents and solvents were purchased and used without further purification.

Synthesis of 4(n-decyloxysalicylaldehyde) (1) *(Fig. 1)*

1 g (7.24 mmol) 4-hydroxysalicylaldehyde, 1.5 ml (7.24 mmol) 1-bromodecane in DMF (10 ml) and 0.73 g (7.24 mmol) $KHCO_3$ as base

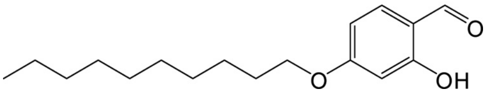


FIGURE 1 Structure of compound (**1**).

were refluxed under vigorous stirring in a nitrogen atmosphere for 4 hours. After cooling to room temperature, the solid was removed by filtration. The filtrate was diluted with distilled water (20 ml) and acidulated with aqueous HCl solution until pH = 2. The organic layer was separated and the aqueous layer was extracted with chloroform (3 × 10 ml). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed by concentration under reduced pressure. The crude aldehyde was purified by column chromatography (SiO_2) using toluene as eluent (Rf = 0.58).

IR (film) $\nu_{max}[cm^{-1}]$: 2916, 2880, 2852, 1691, 1644, 1636, 1630, 1580, 1510, 1466, 1376, 1354, 1334, 1292, 1218, 1204, 1192, 1180, 1168, 1136, 1116, 1018, 804, 760, 718, 636, 572, 540.

Synthesis of N,N′-bis(4-decyloxysalicyliden-N-n-propyl) piperazine (ZOPP) (**2**) *(Fig. 2)*

0.7 g (2.51 mmol) 4-hydroxysalicylaldehyde (**1**) dissolved in 10 ml dry ethanol was treated with 0.2 ml (1.25 mmol) 1,4-bis(3-amino-propyl)-piperazine. The mixture was refluxed for 2 h and then cooled slowly to room temperature. The formed yellow solid was filtered and washed with methanol. Yield: 0.58 g (64%); m.p. = 65–66°C;

Anal: calcd for $C_{44}H_{72}N_4O_4$ (721.08): C 73.29%, H 10.06%, N 7.77%; found C 72.98%, H 10.34%, N 7.88%;

^{1}**H-NMR** (400 MHz),$CDCl_3/\delta$ [ppm]: 13.92 (s, 1H, H^6); 8.13 (s, 1H, H^5); 7.06 (d, 1H, H^7); 6.35 (m, 2H, $H^{8,9}$); 3.95 (t, 2H, H^{10}); 3.58 (t, 2H, H^4); 2.57 (m, 6H, $H^{1,1',2}$); 1.89 (m, 2H, H^{11}); 1.77 (m, 2H, H^3); 1.26–1.43 (m, 14H, H^{12-18}); 0.88 (t, 3H, H^{19});

IR (KBr pellet) ν_{max} $[cm^{-1}]$: 2941, 2918, 2850, 2812, 2794, 2769, 2360, 1625, 1575, 1521, 1473, 1437, 1415, 1356, 1302, 1274, 1228, 1173, 1147, 1055, 1017, 970, 856, 796, 756, 720, 660, 631, 582, 466.

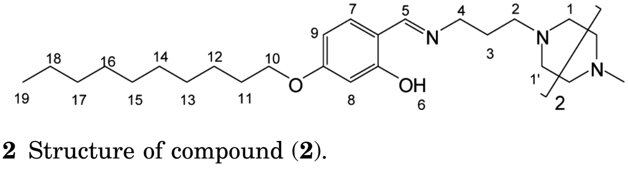


FIGURE 2 Structure of compound (**2**).

Synthesis of $Cu_2(ZOPP\text{-}2H)(CH_3COO^-)_2 2C_2H_5OH$ (3)

0.3 g (0.4 mmol) (**2**) dissolved in 20 ml ethanol was treated with a solution of 0.16 g (0.8 mmol) $Cu(CH_3COO)_2{\cdot}H_2O$ dissolved in 10 ml ethanol. The mixture was stirred at 55–60°C for 3 h and then cooled slowly to room temperature. The solid, which had precipitated was filtered, washed several times with H_2O and purified by recrystallization from dichloromethane and diethyl ether. A brown-green solid was obtained. Yield: 0.27 g (64.28%) m.p. = 156–160°C.

Anal: calcd for $C_{52}H_{88}N_4O_{10}Cu_2$ (1054.51): C 59.17; H 8.41; N 5.31; found: C 59.21; H 9.18; N 5.26.

IR (KBr pellet) $\nu_{max}[cm^{-1}]$: 3460, 2923, 2851, 1608, 1589, 1530, 1470, 1431, 1400, 1365, 1346, 1306, 1218, 1121, 1034, 835, 795, 686, 619, 417.

UV/Vis (CH_2Cl_2) λ[nm]: 727.50, 471.14(s).

Synthesis of $Cu(ZOPP\text{-}2H)$ (4)

0.3 g (0.4 mmol) (**2**) dissolved in 20 ml ethanol was treated with a solution of 0.08 g (0.4 mmol) $Cu(CH_3COO)_2{\cdot}H_2O$ in 10 ml ethanol. The mixture was stirred at 55–60°C for 4 h and then cooled to room temperature. The solid was filtered and green solid was obtained. Yield: 0.2 g (66.6%) m.p. = 155–164°C.

Anal: calcd. for $C_{44}H_{70}N_4O_4Cu$ (781.46): C 67.57; H 9.03; N 7.17; found: C 67.57; H 9.21; N 7.06.

IR (KBr pellet) $\nu_{max}[cm^{-1}]$: 2925, 2853, 2808, 2767, 2360, 1620, 1605, 1529, 1466, 1435, 1400, 1322, 1241, 1175, 1148, 1015, 840, 773, 610, 453, 417, 406.

UV/Vis (CH_2Cl_2) λ[nm]: 605.87.

Synthesis of $Ni_2(ZOPP\text{-}2H)(CH_3COO^-)_2\ 4H_2O$ (5)

0.3 g (0.4 mmol) (**2**) dissolved in 20 ml ethanol was treated with a solution of 0.2 g (0.8 mmol) $Ni(CH_3COO)_2{\cdot}4H_2O$ in 10 ml ethanol. The resulting mixture was stirred at 50°C for 3 h and then the solvent removed under reduced pressure. The solid was purified by recrystallization from chloroform/ diethyl ether. A green solid was obtained. Yield: 0.22 g (51.4%) m.p. = 144–149°C.

Anal: calcd for $C_{48}H_{84}N_4O_{12}Ni_2$ (1024.48): C 56.22; H 8.26; N 5.47; found: C 56.16; H 8.89; N 5.86.

IR (KBr pellet) $\nu_{max}[cm^{-1}]$: 2924, 2853, 1605, 1538, 1487, 1467, 1433, 1401, 1352, 1305, 1209, 1119, 1000, 847, 789, 658, 615, 462, 407.

UV/Vis ($CHCl_3$) λ[nm]: 670.18, 507.65(s).

Synthesis of $Ni(ZOPP\text{-}2H)$ (6)

0.3 g (0.4 mmol) (**2**) dissolved in 20 ml ethanol was treated with a solution of 0.103 g (0.4 mmol) $Ni(CH_3COO)_2{\cdot}4H_2O$ in 7 ml ethanol.

The resulted mixture was refluxed for 3 h. The solid was filtered and washed with hot methanol. A green solid was obtained. Yield: 0.2 g (62.5%) m.p. = 87–98°C.

Anal: calcd for $C_{44}H_{70}N_4O_4Ni$ (776.47): C 68.00; H 9.09; N 7.21; found: C 68.29; H 9.24; N 6.90.

IR (KBr pellet) $\nu_{max}[cm^{-1}]$: 2923, 2852, 2806, 2767, 1605, 1531, 1467, 1437, 1398, 1373, 1315, 1231, 1200, 1142, 1120, 1001, 827, 787, 620, 459, 435.

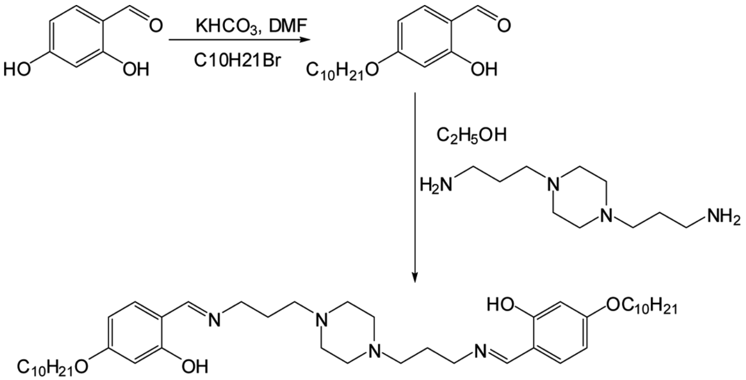
UV/Vis ($CHCl_3$) λ[nm]: 614.60.

RESULTS AND DISCUSSIONS

The Schiff base N,N′-bis(4-decyloxysalicyliden-N-n-propyl)-piperazine (ZOPP) (**2**) was designed with the aim to obtain binuclear metal complexes with potential mesogenic properties. It contains two coordination sites linked by the piperazine bridge, forming a symmetrical molecule. The nature of the complexes depends strongly on the initial metal to ligand molar ratio.

The ligand ZOPP was synthesized following the routed shown in the Scheme 1.

N,N′-bis(4-decyloxysalicyliden-N-n-propyl)piperazine (**2**) was synthesized in two steps. The first step consists in the synthesis of 4(n-decyloxysalicylaldehyde) from 4-hydroxysalicylaldehyde and 1-bromodecane and in the second step 4(n-decyloxysalicyl-aldehyde) forms in a direct condensation reaction with 1,4-bis(3-aminopropyl)-piperazine. The formation of 4(n-decyloxysalicylaldehyde) was controlled by TLC. Confirmation of the structure of the compounds was



SCHEME 1 Synthetic route to ZOPP.

obtained from elemental analyses, IR and ^{1}H-NMR data. The new band which appears at 1625 cm^{-1} in the IR spectrum of (**2**) compared to the spectrum of (**1**), is attributed to the new formed C=N bond [5]. Also, the IR spectrum of compound (**2**) does not contain the characteristic bands of the reactants, namely that at 3360 and 3280 cm^{-1} in the spectrum of 1,4-bis-(3-aminopropyl) piperazine and that of the corresponding aldehyde at 1691 cm^{-1}(C=O). The bands in the 2740–2825 cm^{-1} region are assigned to the ν(C-H) of N-CH$_2$ (alkylic) modes of the piperazinic fragment [6,7]. The identity of the Schiff base was confirmed by ^{1}H-NMR spectroscopy. The signal at 8.13 ppm in the ^{1}H-NMR spectrum of (**4**) is due to the formation of an azomethinic bond. In addition, new signals at 3.58, 2.57 and 1.77 ppm appear, which are attributed to protons belonging to the bis-(n-propyl) piperazine fragment.

Copper (II) and nickel (II) complexes (**3**), (**4**), (**5**) and (**6**) were obtained following a direct metal-ligand synthesis. It was estabilished that the structure of the complexes depends strongly on the metal to ligand molar ratio.

Thus, starting from a 2:1 metal to ligand ratio, the copper (**3**) and nickel (**5**) complexes were obtained.

In the infrared spectrum of the complexes, the characteristic bands of the ligand can be observed and some of them are shifted or are not present as a result of coordination. The spectra of (**3**) and (**5**) show the peaks assigned to the $\nu_{C=N}$ mode at 1608 and 1605 cm^{-1}, respectively. Also, the band assigned to the $\nu_{C–O}$ mode is shifted to 1218 and 1209 cm^{-1} for the two complexes, respectively. The coordination of the piperazine nitrogens is evidenced by the changes in the region of 2750 cm^{-1} in the spectra of the complexes. The bands attributable to ν(C–H) of N–CH$_2$ modes of the piperazinic moiety disappear, suggesting the involvement of piperazine nitrogen in coordination. The copper and nickel-nitrogen vibrations appear in the region between 450–600 cm^{-1} and vibrational modes associated with metal(II) – oxygen(acetate) have been identified at 686 cm^{-1} and 658 at cm^{-1} for (**3**) and (**5**) complexes, respectively.

The electronic spectra of the complexes were recorded with the aim to obtain information regarding the geometry of the metal ions. The UV/Vis spectra of freshly prepared dichloromethane and chloroform solutions were recorded. The spectra of the complexes (**3**) and (**5**) recorded at room temperature show a broad band centered at 728 nm for (**3**) and 670 nm for (**5**) and also a shoulder at 471 nm and 507 nm for (**3**) and (**5**) respectively. The geometry around copper(II) and nickel(II) is five-coordinate: one piperazinic nitrogen atom and one azomethinic nitrogen atom, one phenolic and two carbonylic oxygen atoms from

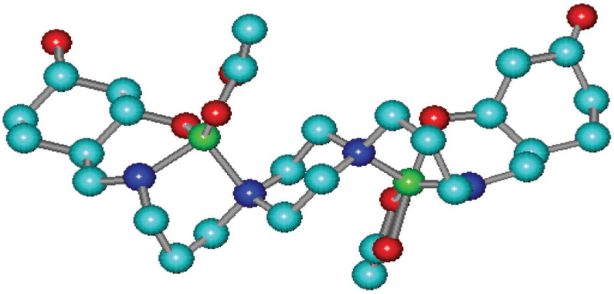


FIGURE 3 The proposed structure of the complexes (**3**) and (**5**).

acetate group (Fig. 3) accommodate these coordination requirements. The bands are assigned to the $A_1 \leftarrow E$ transition for the complex (**3**) and $^1E' \leftarrow ^1A'_1$, $^1E'' \leftarrow ^1A'_1$ for the complex (**5**), altogether this indicates a trigonal bipyramide structure [10] for these complexes.

The copper (**4**) and nickel (**6**) complexes were obtained using a ratio of 1:1 of metal to ligand. The elemental analyses indicate however that for one ion metal corrsponding one ligand. The way of coordination of metals was established on the IR, UV-Vis spectrum and melting point.

In the infrared spectrum of the complexes (**4**) and (**6**), fairly strong $\nu_{C=N}$ bands are found at 1605 cm^{-1}. A shift of this band towards lower frequencies in the spectrum of the complex compared with that of the free ligand indicates the involvement of the nitrogen lone electron pair of the azomethine group of the Schiff base in the bonding to the central metal atom and the formation of a coordinating linkage. The phenolic ν_{C-O} band found at 1228 cm^{-1} in the spectrum of the Schiff base shows a slight shift towards lower frequency and appears at 1241 cm^{-1} in the spectrum of the complex (**4**) and at 1231 cm^{-1} the spectrum of the complex (**6**). This may be due to the change in environment of the C–O bond due to the formation of the C–O–Cu linkage. An examination of the region around 2750 cm^{-1} shows that the bands due to ν(C–H) of $N-CH_2$ (alkyls) appear at almost the same positions as in the free base, which indicates that the nitrogen atoms of the piperazinic fragment remains uncoordinated.

The geometry around the copper(II) and nickel(II) for the complexes (**4**) and (**6**) is essentially four-coordinate. This is achieved by the donor atoms, namely two azomethinic nitrogen atoms and two phenolic oxygen atoms (Figure 4). The bands are tentatively assigned to the transition $^2A_{1g} \leftarrow ^2B_{1g}$, which indicates a square-planar structure [8] for these complexes.

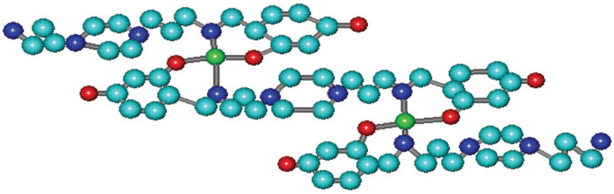


FIGURE 4 The proposed structure of complexes (**4**) and (**6**).

The polymeric nature [9,10] of these two complexes is also supported by their thermal behavior observed on heating (they do not show a sharp melting points).

CONCLUSIONS

A new Schiff base and four new complexes were obtained and characterized.

The compounds do not show mesomorphism. However, we consider that a slight modification of the ligand structure, such as extending the aromatic group of the ligand by one further phenyl ring should result in stable liquid crystalline phase behaviour in such complexes.

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