Chapter – 2

Study of Single Atom Bridged Binuclear Complexes of Schiff's Base Ligands with Long Alkoxy Side Chains
Besides the factors favouring the mesogenic character of the mononuclear complexes, detailed in the first chapter, introduction of a second metal ion in a metal complex of a ligand, with long side chains, also helps in manipulating the core of the resulting binuclear complex. Such binuclear complexes may attain increased polarisability and favourable orientation, so that there is adequate intermolecular interaction, for the complexes to exhibit mesogenic properties. Various homo and hetero binuclear complexes, with mesogenic properties, have been cited.

Binuclear Cu(II) & Ni(II) complexes (Fig 1), of 1,2,4,5-tetra[bis-{2'-alkyl-2'-homoalkylcarbonylvinylamino)]benzene ligands, were reported to show columnar mesogenic properties (1).

Series of binuclear complexes, of Cu(II) and VO(IV) with tetradentate ligands (Fig 2), were reported to show discotic mesogenic phases (2).

Figure 1

Figure 2

\[ X = Y = H; \quad X = OR, Y = H; \]
\[ X = Y = OR; R = (CH_2)_nCH_3 \]
\[ M = \text{Cu(II) and VO(IV)} \]
Binuclear Cu(II) complexes of β,γ-triketonates, 1-{4-alkoxy-2-hydroxyphenyl}-3-(3,4,5-trialkoxyphenyl)propane-1,3-diones and 1-{2-hydroxyphenyl}-3-(3,4,5-trialkoxyphenyl)propane-1,3-diones (Fig 3), were reported to show discotic mesophases [3].

Among the binuclear complexes, of copper, palladium, vanadyl and iron, with n-{3-hydroxypropyl}-4-alkoxysalicylaldimines and N-{3-hydroxypropyl}-4-{4-alkoxybenzoyl}salicylaldimines, Cu and Pd complexes (Fig. 4) were reported to show a smectic phase [4].

Two series of binuclear copper complexes of N,N'-(propane-2-ol)-bis(4-alkoxysalicylaldimines), were prepared (Fig. 5). In these binuclear Cu(II) complexes, the Cu(II) centres are bridged, either by acetate bridge or 3,4,5-trialkoxybenzoate bridge. The acetate bridged complexes were reported to show smectic A phases, while, the 3,4,5-trialkoxybenzoate bridged complexes were reported to show hexagonal columnar phase [5].
The first examples of heteropolynuclear metallomesogens, bearing either copper-lanthanum-copper moiety, or copper-gadolinium moiety (Fig 6), were reported, very recently. These heterotrinuclear and heterobimuclear complexes exhibit hexagonal columnar mesophase (6).
Most of the bimetallomesogens, reported in the literature, consist of disc like molecules and only a few are rod-like molecules (7-12).

However, the introduction of second metal ion may not always lead to mesogenic properties. In the mononuclear Cu(II) bis-chelate complexes of substituted salicylaldimines, the long chain alkyl substitutents are located, opposite to each other, but off-centre to the metal ion, resulting in metallomesogens (7). However, the corresponding binuclear complexes (Fig. 7), obtained by the reaction of mononuclear complex with excess of cupric chloride, are non-mesogenic in nature. These binuclear complexes are essentially having “Z” shape, with the long alkyl chain parallel to each other. This structure is not characteristic of the configurations, found in liquid crystalline molecules. Hence these binuclear complexes are non-mesogenic in nature (13).

Binuclear copper and vanadyl complexes, of enamino-β-ketonate (Fig. 8), were reported to show smectic phase, while the corresponding complexes, of iminopropyl-β-diketonates, were reported to be non-mesogenic (14).
However, binuclear complexes, bearing long terminal alkoxy chain, mesogenic or nonmesogenic in character, are expected to have fascinating physical properties, due to the possibility of facile electronic interaction, between the two metal centres. During the recent years, considerable research efforts have been devoted to the designing and syntheses of new multimetallic liquid crystals, with the aim to combine the unique properties of anisotropic fluids with the electronic and optical properties of strongly interacting multimetallic cores.

Further, the introduction of additional metal centres, in particular paramagnetic metal centres, to a paramagnetic monometallic metallomesogen, is also expected to lead to different magnetic properties (15 - 22), due to spin interaction between the two paramagnetic centres.

Such binuclear complexes with long chains are also of significance in biochemical processes, wherein multi metallic protein complexes, with long non-coordinating side chains, play important roles. Several of metalloenzymes, particularly those, which catalyse the redox reactions, bear binuclear metal core, bridged through an endo hetero atom of the peptide chain or exo oxo or hydroxo group. The facile electronic interaction, between metal centres in metalloenzymes, is considered to be the key feature for the electron transfer or oxygenase or oxidase activity of the binuclear metalloenzymes, in the biological systems. Some of the redox Cu(II) enzymes, like tyrosinase and laccase, have binucleating active sites, with strong antiferromagnetic interaction.

The magnetic interaction between two paramagnetic centres is commonly explained by considering an indirect spin exchange, of the unpaired electrons on the two paramagnetic centres, mediated through the intermediate bridge anion. In binuclear copper (II) complexes, magnetic interaction is considered to take place through an indirect exchange interaction between the $d$-orbitals, containing unpaired electrons over the two Cu(II) paramagnetic centres, mediated through the orbital, present over the intermediate bridging atom. The orbital, of the intervening bridging atom involved in the super exchange is a filled $p$ orbital.

In case of exo-hydroxo or endo-alkoxo or endo-phenoxo bridging in binuclear copper(II) complexes, there is overlap of the $d_{x^2-y^2}$ orbital of two copper(II) centres with the filled $p_x$ orbital of the bridging oxide. This gives rise to a diamagnetic ground state and an excited paramagnetic triplet state, with a separation in energy of $2J$, where $J$ denotes the value of spin exchange interaction (fig 9).
If $2J > kT$, all molecules are in singlet ground state and the molecule is diamagnetic, while for $2J = kT$, the magnetic susceptibility depends on Boltzmann population distribution, of singlet and triplet states and leads to paramagnetism.

The extent of intermetallic interaction in a binuclear complex depends on

1. the energies of the interacting orbitals and
2. the variation in geometrical parameters such as
   a. metal–ligand bond length
   b. M–L–M bridge angle ($\theta$)
   c. dihedral angle between the metal coordination planes, $\theta$ and
   d. degree of planarity of the bridging unit

Extensive studies, on di-µ-hydroxo bridged copper dimer (23, 24), established the existence of a linear relationship between $2J$ and Cu-O-Cu bond angle ($\theta$).

The crystal structure study by Mckee and Smith (25), of binuclear copper(II) complexes, bridged by single alkoxy oxygen, were shown to have a maximum Cu-O-Cu angle of 135°. The magnetic moment of the complex was found to be 0.6 BM per Cu(II) centre at room temperature, indicating the presence of a strong antiferromagnetic interaction. The antiferromagnetic interaction decreases with the decrease in $\theta$.

In addition to the optimum value of the M-L-M angle ($\theta$), the planarity of the binuclear core structure is also an important requirement, for the electronic interaction to take place. Kahn et al. (26) showed the dependence of the value of $J$ on the dihedral angle ($\theta$), between the two copper coordination planes in O-bridged non-planar dimmers. There is maximum antiferromagnetic interaction between the magnetic orbitals, when the coordination planes are planar, $\theta$ being zero. Any distortion of the binuclear core structure from the planarity, resulting in increase in dihedral angle, reduces the overlap of copper(II) $d_{2g}$ orbitals with the...
bridging oxide ion orbitals, and as a consequence the exchange interaction is weakened.

A trigonal planar geometry, (sp² hybridization) of the bridging atom, leads to good overlap between the copper(II) dx²- y² orbitals and the bridging oxide ion orbitals, with consequent strong antiferromagnetic coupling. As the geometry of the bridging atom approaches pyramidal/tetrahedral geometry, (sp³ hybridization) with concomitant development of dihedral angle between adjacent Cu-ligand planes, the J value approaches to zero, or becomes overall positive, and gives rise to ferromagnetism.

The substitutions over the ligands have a significant effect on the electron density on the two paramagnetic metal centres and hence on the extent of the super exchange interaction. An electron withdrawing group on the ligand reduces the electron density on the metal ion, whereas, an electron releasing group increases the electron density, with consequent increase and decrease, respectively, of the spin exchange interaction between the two metal centres.

The substitution on the ligand may also affect the planarity of the molecule and hence the overlap of the metal orbitals with the orbitals of the bridging atoms.

Various binuclear complexes with different exogenous bridges, like halo- (27) alkoxo- (28) sulphide- (29) carboxylato- (30) hydroxo- (31) azido- (32) pyrazolato- (33) etc. have been studied extensively.

Binuclear complexes with endogenous bridges have been found to be of following two types.

a. In the binuclear complexes of tridentate Schiff's bases, derived by the condensation of salicylaldehyde with amino alcohol, amino phenols or amino acids, bridging occurs via phenolate, alkoxo or carboxylate (Fig.10)(34).

![Figure 10](image-url)
b. Binuclear complexes derived from open or closed compartmental ligands.

(Fig.11)(35).

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} & \quad \text{O} & \quad \text{R} \\
\text{N} & \quad \text{O} & \quad \text{O} & \quad \text{R} \\
\text{H}_3\text{C} & \quad \text{O} & \quad \text{O} & \quad \text{R} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} = \text{CH}_3, \text{C}_6\text{H}_5 \\
\end{align*}
\]

\[
\begin{align*}
\text{MeO} & \quad \text{O} & \quad \text{Me} & \quad \text{O} & \quad \text{O} \\
\text{R} & \quad \text{N} & \quad \text{N} & \quad \text{R} \\
\text{R} & \quad \text{H}, \text{CH}_3 \\
\end{align*}
\]

Figure 11

In the above "a" type of binuclear complexes, with endogenous bridges, the spin exchange has been shown to take place through the two O^- bridges and the binuclear Cu(II) complexes are found to be highly antiferromagnetic in character. In view of the interesting properties of the binuclear complexes with long side chains, it was thought of interest to study the binuclear complexes of above "a" type of ligands, derived by the condensation of salicylaldehyde containing long alkoxy chains with amino alcohols.

In a recent communication Chunge. K. Lai et al. reported similar binuclear Cu(II) complexes of Schiff's base ligands, derived by the reaction of 3-aminopropanol with 4-(n-alkoxy)-2-hydroxybenzaldehyde (4). However, they studied only the mesogenic properties of the complexes and have not investigated their magnetic properties. They also, did not investigate the effect of other structural changes on the Schiff's base ligand, on the mesogenic properties of the binuclear complexes.

In this Chapter the synthesis, characterisation, study of magnetic and the liquid crystalline properties of a series of Cu(II) and Ni(II) binuclear complexes of Schiff's base ligands, derived by condensation of 4-(n-alkoxy)-2-hydroxybenzaldehyde with 2-aminoethanol (L^1 - series) and 3-aminopropanol (L^2 - series) (Scheme 1), have been described. The study, in this Chapter, includes a total of twelve binuclear Schiff's base ligand complexes of both Cu(II) and Ni(II), where n-alkoxy moiety contains C_5,C_10,C_14,C_16 chains.
Experimental

Physical Measurements & Materials

The physical measurements & materials are, as described in the previous chapter. In addition, 2-aminoethanol and 3-aminopropanol, of Sisco, India make were used, as received.

Syntheses of 4-n-alkoxy-2-hydroxybenzaldehyde

Synthesis of 4-n-alkoxy-2-hydroxybenzaldehydes was carried out using a reported procedure as described in chapter 1.

Syntheses of bis[N-(2'-hydroxyethyl)-4-(n-alkoxy)-2-hydroxybenzaldiminate]-nickel(II) (series – I):

All the complexes were synthesized by using the following general procedure:

The Schiff’s bases N-(2’-hydroxyethyl)-4-(n-alkoxy)-2-hydroxybenzaldimine, were prepared in situ, by refluxing 4-(n-alkoxy)-2-hydroxybenzaldehyde (1 mmol) with 2-aminoethanol (1 mmol), for 2 h, in 10 mL dry ethanol. To this Schiff’s base solution, 25 mL ethanolic solution of nickel(II) acetate, 0.2489 g. (1 mmol) was added. This mixture was heated gently, under reflux, with stirring for 4 h. The solid complex, thus separated, was isolated by filtration through suction, washed thoroughly with dry ethanol and was dried in air.

Syntheses of Bis[N-(2’-hydroxyethyl)-4-(n-alkoxy)-2-hydroxybenzaldiminate]-copper(II) (series – II) complexes were synthesized by following the same general method, as described for series – I, using an equivalent amount of copper acetate, instead of nickel acetate.

Syntheses of Bis[N-(3’-hydroxypropyl)-4-(n-alkoxy)-2-hydroxybenzaldiminate]-nickel(III) (series – III) complexes were achieved, by following the same general method, as described for series – I, using 3-aminopropanol, instead of 2-aminoethanol, for the in situ generation of the Schiff’s bases, N-(3’-hydroxypropyl)-4-(n-alkoxy)-2-hydroxybenzaldimine.
Syntheses of, Bis[N-(3'-hydroxypropyl)-4-(n-alkoxy)-2-hydroxybenzaldiminato]-copper(II) (series - IV) complexes were synthesised by following the same general method, as described for series - I, using 3-aminopropanol, instead of 2-aminoethanol, for the in situ generation of the Schiff's base, N-(3'-hydroxypropyl)-4-(n-alkoxy)-2-hydroxybenzaldimine, and it was reacted with an equivalent amount of copper acetate, instead of nickel acetate.

The complexes of the series - IV had been synthesised by Chunge K. Lai et al. (4) earlier, using another method. They have been re-synthesised, by the above different method, mainly to study the magnetic properties and to compare the properties of the complexes of this series with that of the complexes of series - II.

Result and Discussion

The reactions of one equivalent of copper acetate or nickel acetate with Schiff's bases, formed in situ, by the reaction between 4-n-alkoxy-2-hydroxybenzaldehyde and 2-aminoethanol or 3-aminopropanol, in dry ethanol, lead to the formation of the binuclear complexes, in moderate to good yield (Scheme 1). Microanalytical data (C, H, N) correspond well to the expected composition of these complexes (Table 1).

\[
\begin{align*}
R=\text{C}_n\text{H}_{2n+1}, & \quad n=5, 10, 14, 16 \\
m=2 \text{ for series L1 and } m=3 \text{ for series L2.}
\end{align*}
\]

Scheme 1

with series L¹, M = Ni(II) for series I & M = Cu(II) for series II and with series L², M = Ni(II) for series III & M = Cu(II) for series IV.
The structure of similar binuclear copper complexes, both with and without alkoxy chain, on the ligands, was reported, respectively, by Chunge et al. (4) and E. Sinn et. al. (34), on the basis of X-ray crystallographic studies. In the present study, the complexes could not be obtained in the suitable crystalline form, for X-ray study. Hence, by drawing analogy to the reported crystal structure, the probable structures are shown in the Scheme 1.

Mass spectral studies

The FAB mass spectrum of representative complexes, one each from series – II (ethanolamine Schiff’s base with C10 alkoxy chain) III & IV (propanolamine Schiff’s base C10 alkoxy chain) were recorded to support the composition of the complexes, as shown in scheme 1. The spectra are shown in Fig 12.

In the mass spectrum of bis[N-(2′-hydroxyethyl)-4-(n-decaoxy)-2-hydroxybenzaldiminato]copper(II) (series – II), the peak with the maximum intensity, at m/z = 767, corresponds to the molecular ion (Cu2L12)+. The calculated molecular weight of the complex is 765.92. The peak at m/z = 446 corresponds to (Cu2L1), the peak observed at m/z = 384 corresponds to (CuL1), the peak at m/z = 242 corresponds to (Cu[L1 – C10H21]), i.e., loss of one alkyl side chain.

In the mass spectrum of Bis[N-(3′-hydroxypropyl)-4-(n-decaoxy)-2-hydroxybenzaldiminato]nickel(II) (series – III), the peak with the maximum intensity, at m/z = 783, corresponds to the molecular ion (Ni2L22)+. The calculated molecular weight of the complex is 784.20. The peak at m/z = 392 corresponds to (NiL2), the peak at m/z = 252 corresponds to (Ni[L2 – C10H21]), i.e., loss of one alkyl side chain.

In the mass spectrum of Bis[N-(3′-hydroxypropyl)-4-(n-decaoxy)-2-hydroxybenzaldiminato]copper(II) (series – IV), the peak with the maximum intensity, at m/z = 793, corresponds to the molecular ion (Cu2L22)+. The calculated molecular weight of the complex is 793.90. The peak at m/z = 460 corresponds to (Cu2L2), the peak observed at m/z = 397 corresponds to (CuL2), the peak at m/z = 257 corresponds to (Cu[L2 – C10H21]), i.e., loss of one alkyl side chain.

The pattern of formation of the fractions in the complexes of series – IV is same as in the case of the Cu(II) complexes of series – II. The sequences of the formation of the fractions, in all three cases, support the structure of the complexes, as shown in scheme 1.
IR spectral studies

The comparison of the band positions in the IR spectra of the complexes (Fig 13), with those of the corresponding free ligands, reveals information, regarding the coordination of the ligand atoms to the metal centres. In the IR spectrum of the free Schiff’s base ligands, the band due to the C=N stretching vibration is known to appear at 1640 – 1625 cm\(^{-1}\). In the IR spectrum of the complex, the same band is found to appear at ca. 1620 cm\(^{-1}\) (4). The lowering of the C=N stretching frequency, in the complexes, indicates the coordination of the aldimine nitrogen atom to the metal centre (36). Further, the band due to the phenolic C-O stretching, in the phenoxo bridged M\(_2\)O\(_2\) moiety, is known to appear at 1560 – 1540 cm\(^{-1}\) (37). In the IR spectra of the complexes, reported here, the appearance of an intense band at ca. 1545 cm\(^{-1}\) confirms the presence of the M\(_2\)O\(_2\) core in the binuclear complexes.

Electronic spectral studies:

All the complexes are insoluble in polar solvents, like, methanol, ethanol, acetonitrile, ethylacetate, as well as in the non-polar solvent petroleum ether. However, the complexes are freely soluble in benzene, toluene, chloroform and dichlormethane. The electronic spectral studies of the complexes have been carried out in dichloromethane solution, having concentration in the range of 10\(^{-3}\) – 10\(^{-5}\) (M). The spectral data are collected in Table 1 and shown in Fig. 14.

In the electronic spectra of the binuclear copper complexes of series – II, the band due to the d-d transition appears at ca. 620 nm. whereas, the same d-d transition band for the binuclear copper complexes of series – IV appears at ca. 560 nm. These bands have been assigned to the d-d transition, on the basis of the low values of the molar extinction coefficients. In the latter class of the binuclear copper complexes, the blue shift, in the position of the d-d transition band, indicates that the field created around the copper(II) centres, by the ligands of the L\(_2\) series, is stronger compared to the same created by the ligands of the L\(_1\) series, in the former class of complexes. The variation in the field strength may be attributed to the size of the chelate rings, formed by the iminoalkoxy moiety, in the two classes of complexes. The chelate ring formed by the 4-n-alkoxy-2-hydroxybenzaldimino moiety with the
copper(II) centres, is six-membered and is common in all the complexes, while the
chelate ring formed by the iminoethyloxy moiety, with copper(II) centres, is five-
membered in the former class of complexes and the chelate ring, formed by the
iminoisopropoxy moiety, with the copper(II) centres, is six membered in the latter
class of complexes. The six membered chelate rings, being more flexible than the
five-membered chelate ring, create a stronger field around the copper metal
centres in the later class of complexes.

In the electronic spectra of the binuclear complexes, of the series – III, a band
due to the d-d transition appears at ca 620 nm, supporting the square planar
structure of the Ni(II) complexes. The d – d band could not be observed in case of
the binuclear nickel (II) complexes of the series – I, because of their poor solubility.

In all the Cu(II) and Ni(II) complexes, bands of high intensity are observed at ca
330 and ca 280 nm. These are intraligand bands, as similar bands are obtained in
the electronic spectra of the free Schiff’s bases. The positions of these bands are
found to be sensitive to the length of the n-alkoxy chain, as well as the iminoalkoxy
moiety.

**Magnetic Properties of the Binuclear Cu(II) complexes:**

Magnetic susceptibility measurements show that the binuclear nickel complexes
are diamagnetic as expected for the square planar Ni(II) centres. The binuclear
copper complexes are paramagnetic. However, the room temperature magnetic moment
values for the binuclear copper complexes are very low. The lowering of the room temperature
magnetic moments of the binuclear Cu(II) complexes, compared to that expected for
one unpaired electron on two Cu(II) centres, indicates the presence of antiferromagnetic
coupling between the adjacent

![Figure 15: $\chi_m$ vs $T$ plot of (L$^2$Cs)$_2$Cu$_2$. Solid line is obtained theoretically applying the Bleaney–Bowers equation and the dots represent the experimental values.](image)
Cu(II) ions in the Cu₂O₂ core

To study the extent of spin exchange interaction between the two metal centres in the binuclear complexes, the magnetic susceptibilities were determined in the temperature range 80 – 300 K. The results of the magnetic susceptibility measurement for the complex bis[N-(2'-hydroxypropyl)-4-(n-pentoxy)-2-hydroxybenzaldiminato]copper(II) is given as a function of temperature in the Fig 15. The magnetic susceptibility values at different temperature were also calculated, using the Bleaney – Bowers equation (38).

The best fit of the experimental data with the calculated values was obtained for $2J = -161.6 \text{ cm}^{-1}$ using $g = 1.77$. The generalised R factor, the convenient statistical factor defining the quality of the fit of the experimental value with the calculated value using following equation, was found to be $8.03 \times 10^{-3}$.

$$R = \frac{\sqrt{\sum (X_m(\text{obs}) - X_m(\text{cal}))^2}}{\sum X_m(\text{obs})^2}^{1/2}$$

The antiferromagnetic interaction parameter, $2J = -161.6 \text{ cm}^{-1}$ in the complex of the series – IV indicates moderately strong antiferromagnetic interaction. The extent of antiferromagnetic interaction was found to be less than analogous complexes, without long side chain ($J > 400$) (34). This may be attributed to the presence of medium length alkoxy chain at the 4- position of the two 2-hydroxybenzaldimino moieties of the ligands, in the present complexes. The steric effect and the probable intermolecular hydrophobic interaction between the side chains, affect the plane of the bridged complexes and hence the extent of overlap of the paramagnetic orbitals with the bridged O⁻ orbital is reduced, resulting in lower J values. In the propanol amine Schiff’s base complexes (series – IV) the antiferromagnetic interaction is much less. This may be, because of the six membered chelate rings formed, which affects Cu—O—Cu angle $\Phi$ and thus reduces the interaction between the two paramagnetic centres.

ESR spectral studies

In the ESR spectrum (Fig 16) of the complex bis[N-(2'-hydroxypropyl)-4-(n-pentoxy)-2-hydroxybenzaldiminato]copper(II) a single signal is obtained in the spectrum having $g = 1.77$. This shows that there is an average octahedral field.
around the metal ion. This may be because of the intermolecular interaction between the complex molecules. The square planar Cu(II) centre interacts with the O\(^-\) of the two neighbouring complexes along the axial direction, leading to a distorted octahedral field around the metal ion.

The diamagnetic Ni(II) complexes are EPR silent. Thus the microanalytical, spectral and magnetic studies support the structure of the binuclear complexes, as suggested in the scheme.

**Mesogenic properties**

The liquid crystalline behaviours of all the binuclear complexes have been studied, using polarizing microscope. The phase transition temperatures of all the complexes are recorded in Table 2. Among the complexes of series – IV, the complex with C\(_5\) alkoxy chain was observed to be non-mesomorphic in nature, while the complexes bearing C\(_{10}\), C\(_{14}\) and C\(_{16}\) alkoxy chain exhibit Smectic C phase on cooling as observed in earlier studies (4). However, all the complexes of the series – I, II & III were found to be non-mesomorphic in nature. The difference in the mesogenic properties may be attributed to the size and the planarity of the chelate rings in the complexes. The ligands in all the complexes form a six membered ring by the bidentate coordination of the 4-n-alkoxy-2-hydroxybenzaldimino moiety with the metal centre. However, the ligands in the complexes of the series – I & II form a five membered chelate ring, by the bidentate coordination of the iminoethyloxy moiety with the metal centre, while the ligands in the complexes of the series – III & IV form a six membered chelate ring with the iminopropoxy moiety in a similar fashion. Further, the five membered chelate rings in the complexes of the series – I & II, with two CH\(_2\) groups are less hydrophobic, while the complexes of the series – III & IV, with three CH\(_2\) groups are expected to be relatively more hydrophobic. Because of the above two factors, the complexes of the series – I & II do not exhibit mesogenic properties.

Cu(II) complexes of series – IV are mesogenic, while, corresponding Ni(II) complexes are nonmesogenic. This is probably, because, the structures and polarizabilities of Ni(II) complexes are not suitable for mesogenic character.
Table 1: Characterization data

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Micro analytical data (%)</th>
<th>Electronic spectral data $^b$</th>
<th>λ nm (e, mol$^{-1}$ dm$^3$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>Series-I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L$^1$C$_5$)$_2$Ni$_2$</td>
<td>54.43</td>
<td>6.02</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td>(54.60)</td>
<td>(6.17)</td>
<td>(4.53)</td>
</tr>
<tr>
<td>(L$^1$C$_{10}$)$_2$Ni$_2$</td>
<td>50.36</td>
<td>7.67</td>
<td>3.70</td>
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<tr>
<td></td>
<td>(63.80)</td>
<td>(8.25)</td>
<td>3.53</td>
</tr>
<tr>
<td>(L$^1$C$_{14}$)$_2$Ni$_2$</td>
<td>64.67</td>
<td>8.68</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>(64.97)</td>
<td>(8.88)</td>
<td>(3.03)</td>
</tr>
<tr>
<td>Series-II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L$^1$C$_5$)$_2$Cu$_2$</td>
<td>53.81</td>
<td>6.15</td>
<td>4.50</td>
</tr>
<tr>
<td></td>
<td>(53.76)</td>
<td>(6.08)</td>
<td>(4.48)</td>
</tr>
<tr>
<td>(L$^1$C$_{10}$)$_2$Cu$_2$</td>
<td>60.00</td>
<td>7.67</td>
<td>3.77</td>
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<tr>
<td></td>
<td>(59.60)</td>
<td>(7.58)</td>
<td>(3.66)</td>
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<td>63.00</td>
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<tr>
<td></td>
<td>(62.94)</td>
<td>(8.43)</td>
<td>(3.19)</td>
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<tr>
<td>Series-III</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(L$^2$C$_5$)$_2$Ni$_2$</td>
<td>55.69</td>
<td>6.16</td>
<td>4.27</td>
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<tr>
<td></td>
<td>(55.95)</td>
<td>(6.52)</td>
<td>(4.35)</td>
</tr>
<tr>
<td>(L$^2$C$_{10}$)$_2$Ni$_2$</td>
<td>61.00</td>
<td>7.71</td>
<td>3.50</td>
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<tr>
<td></td>
<td>(61.27)</td>
<td>(7.91)</td>
<td>(3.57)</td>
</tr>
<tr>
<td>(L$^2$C$_{14}$)$_2$Ni$_2$</td>
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<td>8.59</td>
<td>3.09</td>
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<tr>
<td></td>
<td>(64.33)</td>
<td>(8.71)</td>
<td>(3.12)</td>
</tr>
<tr>
<td>(L$^2$C$_{16}$)$_2$Ni$_2$</td>
<td>65.30</td>
<td>8.95</td>
<td>2.84</td>
</tr>
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<td></td>
<td>(65.58)</td>
<td>(9.03)</td>
<td>(2.94)</td>
</tr>
<tr>
<td>Series-IV</td>
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<td>(L$^2$C$_5$)$_2$Cu$_2$</td>
<td>55.16</td>
<td>6.24</td>
<td>4.54</td>
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<td></td>
<td>(55.13)</td>
<td>(6.43)</td>
<td>(4.28)</td>
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<td>(L$^2$C$_{10}$)$_2$Cu$_2$</td>
<td>60.58</td>
<td>7.78</td>
<td>3.45</td>
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<tr>
<td></td>
<td>(60.53)</td>
<td>(7.82)</td>
<td>(3.53)</td>
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<tr>
<td>(L$^2$C$_{14}$)$_2$Cu$_2$</td>
<td>63.82</td>
<td>8.73</td>
<td>3.39</td>
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<td></td>
<td>(63.64)</td>
<td>(8.61)</td>
<td>(3.09)</td>
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<tr>
<td>(L$^2$C$_{16}$)$_2$Cu$_2$</td>
<td>64.90</td>
<td>8.99</td>
<td>2.80</td>
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<td></td>
<td>(64.93)</td>
<td>(8.94)</td>
<td>(2.91)</td>
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$^a$ Calculated values are given parentheses. $^b$ in dichloromethane solution.
<table>
<thead>
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<th>R = n-alkyl group</th>
<th>Transition temperatures °C</th>
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<td>Smectic C</td>
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<td>Series - IV: Bis[N-(3'-hydroxypropyl)-4-(n-alkoxy)-2-hydroxybenzaldiminato]copper(II)</td>
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<td>[L²C₈]₂Cu₂</td>
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<tr>
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<tr>
<td>[L²C₁₄]₂Cu₂</td>
<td>140</td>
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<tr>
<td>[L²C₁₆]₂Cu₂</td>
<td>133</td>
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</table>
Figure 12: FAB mass spectrum of the complex of the series II with C₁₀ alkoxy chain.
Figure 13 IR spectrum of the complex of the series III with C14 alkoxy chain as KBr.

Palette in the range 4000 to 500 cm⁻¹.
Figure 14: A representative electronic spectrum of the complex of the series IV with C<sub>18</sub> alkoxy chain in dichloromethane.
Figure 16: ESR spectrum of the complex of the series IV with C₃ alkoxy chain in dichloromethane/toluene (1:1 v/v) solution at 77 K
Reference


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