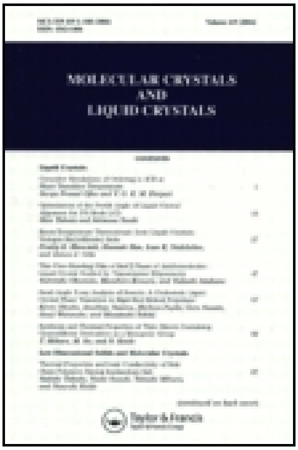

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Synthesis of New Metallomesogens Containing Ni(II) And Cu(II) Atoms*

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A few new metallomesogens contaning Ni(II) and Cu(II) atoms of the ligands 4-substituted 2′-hydroxy 4′(4″-n-hexadecyloxybenzoloxy)azobenzenes have been synthesized. The complexes have been characterized by C, H, N, microanalysis, IR, NMR and UV-Visible spectroscopies. Mesomorphic properties of all the ligands and complexes were investigated on a Leitz Laborlux 12 POL microscope provided with a heating stage.

Keywords: : Metallomesogens; IR; NMR; UV – Visible; DSC

INTRODUCTION

The increasing number of investigations of metallomesogens can be attributed to the wide variety of chemical and physical properties presented by these compounds. The presence of metals in the organic structure gives rise to important effects on the physical properties of the compounds which make them interesting substances for technical applications.

The first thermotropic metal-contaning liquid crystals were reported by Vorlander[1] in 1910. He found that the alkali-metal carboxylates, R-$(CH_2)_n$-COONa form classical lamellar phases on heating and since then many new types of mesogenic metal complexes have been synthesized. Many examples of liquid crystalline metal complexes have been reported over the years and many of these are discussed in the review articles by Giroud-Godquin and Maitlis[2] and Espinet et

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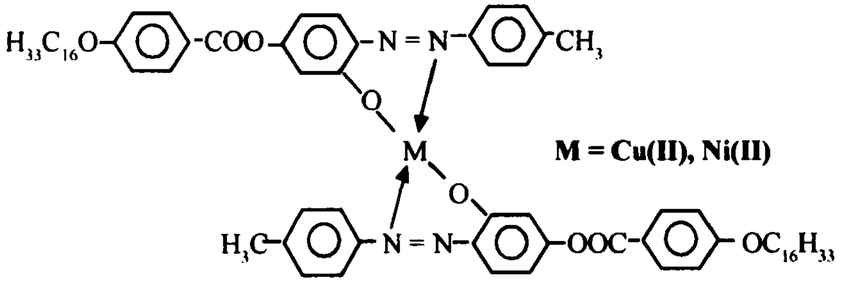
al.[3]. Giroud-Godquin and Muller-Westerhoff[4] were the first to use d-block elements to obtain metallomesogens.

Varieties of monodentate ligands, such as cyanobiphenyls[5] n-alkoxystilbazols[6], monostilbazols[7], distilbazols[8], 4-substituted pyridines[9], Ferrocenes[10] etc., bidentate ligands such as β-diketones[11,12], N-salicylideneamine[13,17] and polydentate ligands such as phthalocyanines[18] have been used to obtain metal chelates.

In an earlier study[19] we have reported two metal complexes having the following structural formula.

The initial results were highly encouraging. In the present work, further study of this type of metal complexes has been carried out by substituting-CH_3terminal with n-alkoxy groups, to examine the effect of these terminal groups on the mesomorphic properties of metal complexes.



EXPERIMENTAL

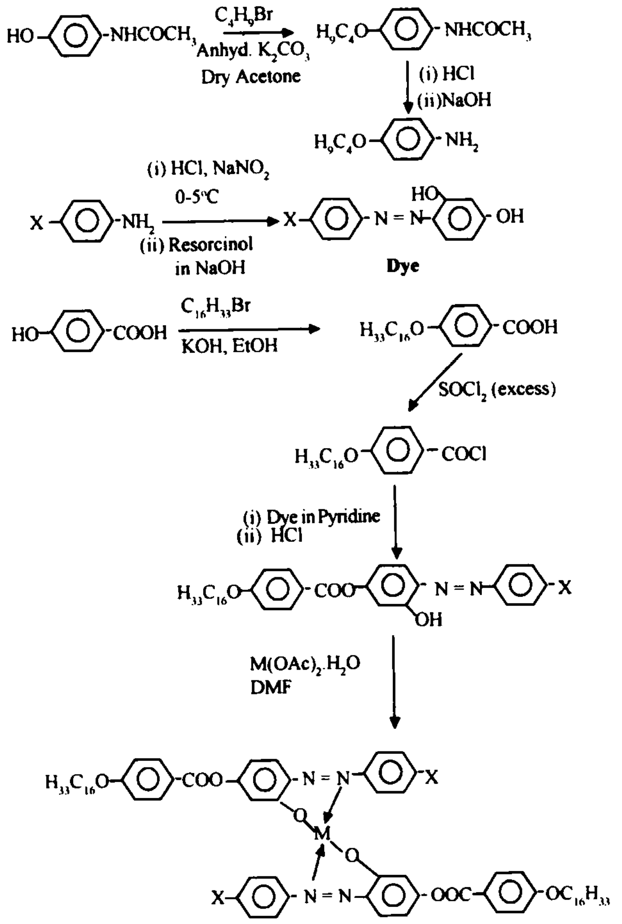
Charaterization

The chemical structures of ligands and metal complexes were confirmed by using a combination of elemental analysis and spectroscopic method. Elemental analysis of the compounds were performed on a Coleman carbon-hydrogen analyser, IR spectra were determined via KBr pellets, using Schimadzu IR-408 spectrophotometer. ^1H NMR spectra were obtained with a Perkin-Elmer model R-32 spectrometer. The UV-Visible spectra were recorded on Hitachi U-2000 spectrophotometer. Thermal analysis were performed with a mettler TA 4000 DSC apparatus with a heating rate of 5°C min^{-1}. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with a heating stage.

Synthesis

4-Methoxyaniline, sodium nitrite, resorcinol, paracetamol, thionylchloride, pyridine (Sisco Chem.), 4-hydroxybenzoic acid, n-alkyl halides (BDH) were used as received. All the solvents were dried and distilled prior to use.

The synthesis of ligands and their Cu(II) and Ni(II) complexes was carried out by following scheme 1.



X	Dye	Ligand	M	Complex
$-OCH_3$	DA1	1L	Cu	Cu(1L)$_2$
$-OCH_3$	DA1	1L	Ni	Ni(1L)$_2$
$-OC_4H_9$	DA2	4L	Cu	Cu(4L)$_2$
$-OC_4H_9$	DA2	4L	Ni	Ni(4L)$_2$

SCHEME 1

4-n-Butoxy aniline was synthesized by the reaction of n-butyl bromide with paracetamol in presence of anhydrous K_2CO_3 using dry acetone followed by hydrolysis[20]. 4-Methoxy 2′,4′-dihydroxyazobenzene (DA1) and 4-n-butyloxy2′,4′-dihydroxy azobenzene (DA2) were synthesized by using conventional method of diazotization and coupling[21]. 4-n-Hexadecyloxybenzoic acid and 4-n-hexadecyloxybenzoylchloride were synthesized by the modified method of Dave and Vora[22].

General procedure for synthesis of Ligands

The following two ligands were synthesized.

(i) 4-Methoxy 2′-hydroxy 4′(4″-n-hexadecyloxybenzoyloxy)azobenzene(**1L**)

(ii) 4-n-Butyloxy 2′-hydroxy 4′(4″-n-hexadecyloxybenzoyloxy)azobenzene(**4L**)

DA1 (for 1L) / DA2 (for 4L) (0.01 mole) was dissolved in dry pyridine (10 ml) and a cold solution of a 4-n-hexadecyloxybenzoylchloride (0.01 mole) in dry pyridine(10 ml) was added slowly to it with constant stirring in an ice bath. The mixture was allowed to stand overnight at room temperature. It was acidified with 1:1 dilute hydrochloric acid. The solid separated was filtered off and crystallized from acetic acid till constant transition temperatures were obtained.

General procedure for synthesis of metal complexes

A solution of (0.01 mole) metal acetate in hot dry DMF (30 ml) was added slowly with continuous shaking to the hot solution of the ligand (0.02 mole) in dry DMF (30 ml). The whole mixture was then refluxed for 3 hours to obtain the desired complexes $M(1L)_2$ and $M(4L)_2$ where M = Cu(II) and Ni(II). All the metal complexes were crystallised from DMF till constant transition temperatures were obtained.

RESULTS AND DISCUSSION

The elemental analysis of all the ligands and metal complexes are in accord with the structure. Table-I summarizes the IR and UV- Visible spectroscopy data for the complexes. The ν(-OH) band is absent in the infrared spectra of all the metal complexes. This indicated that the phenolic proton is exchanged upon complexation. The ν(-N=N-) band of the free ligands is shifted by 30–35 cm^{-1} to a higher wave number suggesting that the metal ion is co-ordinated to the phenolic oxygen and the nitrogen of azo central linkage. In addition to these, all the metal complexes showed a characteristic band of metal-oxygen in the range of 505–515 cm^{-1}. Diaz et al.[17] have reported an absorption band between 359 and 387 nm for Cu(II), Pd(II) and VO(IV) complexes possessing two aromatic rings in the ligand. In the present work, the absorption band is obtained between 553 and 679 nm. The high absorption values obtained in the present work are attributed to the higher magnitude of the conjugation in the molecules of the metal complexes possessing three aromatic rings in the ligand. Marcos et al.[23] have also reported high absorption values in the range of 645 and 670 nm for complexes possessing three aromatic rings in the ligand. These results confirm co-ordination of the ligand to metal(II) ion. Table-II sumarizes the NMR data for the ligands and their Ni(II) complexes which further confirm the proposed structures for all the metal complexes.

TABLE I IR and UV-Visible spectroscopic data for ligands and their Cu(II) and Ni(II) complexes

Compound	*ν/cm^{-1}*				*λ/nm*
	OH	*C=O*	*N=N*	*M-O*	
1L	3600–3200	1740	1635	–	237.5, 322.5
4L	3500–3200	1735	1635	–	237.5, 343
$Cu(1L)_2$		1730	1670	505	553, 560.5
$Ni(1L)_2$		1735	1665	515	579, 600, 676
$Cu(4L)_2$		1730	1670	510	558, 569.5, 585
$Ni(4L)_2$		1730	1670	515	621, 651, 679

TABLE II 1HNMR data for the ligands and their Ni(II) complexes

Compound	*^1HNMR ($CDCl_3/TMS$), δ/PPM, J/Hz*
1L	0.95(t, 3H, -CH_3), 1.3–1.9(m, 28H, 14 X-CH_2), 4.05 (S, 3H, -OCH_3), 4.15(t, 2H, -OCH_2-), 6.75(d, J=9, 2H at C-3′ and C-5′), 7.05(d, J=9, 2H at C-3 and C-5), 7.3–7.5(m, 5H at C-2, C-6, C-6′, C-3″ and C-5″), 7.9(d, J=9, 2H at C-2″ and C-6″), 13.5(S, 1H, -OH).
4L	0.9–1.0(m, 6H, 2 X-CH_3). 1.4–1.9(m, 32H, 16 X-CH_2), 4.0(t, 4H, 2 X -OCH_2-), 6.8(d, J=9, 2h at C-3′ and C-5′), 7.0(d, J=9, 2H at C-3 and C-5), 7.4–7.6(m, 5H at C-2, C-6, C-6′, C-3″ and C-5″), 8.1(d, J=9, 2H at C-2″ and C-6″), 13.4(S, 1H, -OH)
$Ni(1L)_2$	0.95(t, 6H, 2 × -CH_3), 1.1–1.9(m, 56H, 28 X-CH_2-), 4.05–4.15(m, 10H, 2 X-OCH_2- and 2 X-OCH_3), 6.7(d, J=9, 4H, arom), 7.0–7.1(m, 4H, arom), 7.25-7.4(m, 10H, arom), 8.1(d, J=9, 4H, arom)
$Ni(4L)_2$	0.9(t, 6H, 2 X-CH_3), 1.1–1.8(m, 64H, 32 X-CH_2-), 3.95–4.05(m, 8H, 4 X-OCH_2-), 6.85(d, J=9, 4H, arom), 7.1–7.3(m, 4H, arom), 7.6–7.75(m, 10H, arom), 8.0–8.15(m, 4H, arom)

The mesomorphic behaviour of all the compounds prepared was studied by optical polarizing microscopy and the associated enthalpy changes of 1L and Cu(II)(1L)$_2$ were determined by differential scanning calorimetry (DSC). Table-III summarizes the transition temperatures for the ligands and their Cu(II) and Ni(II) complexes and Table-IV summarize the DSC data of 1L and Cu(II)(1L)$_2$. Figure 1 shows DSC curves of 1L and Cu(II)(1L)$_2$.

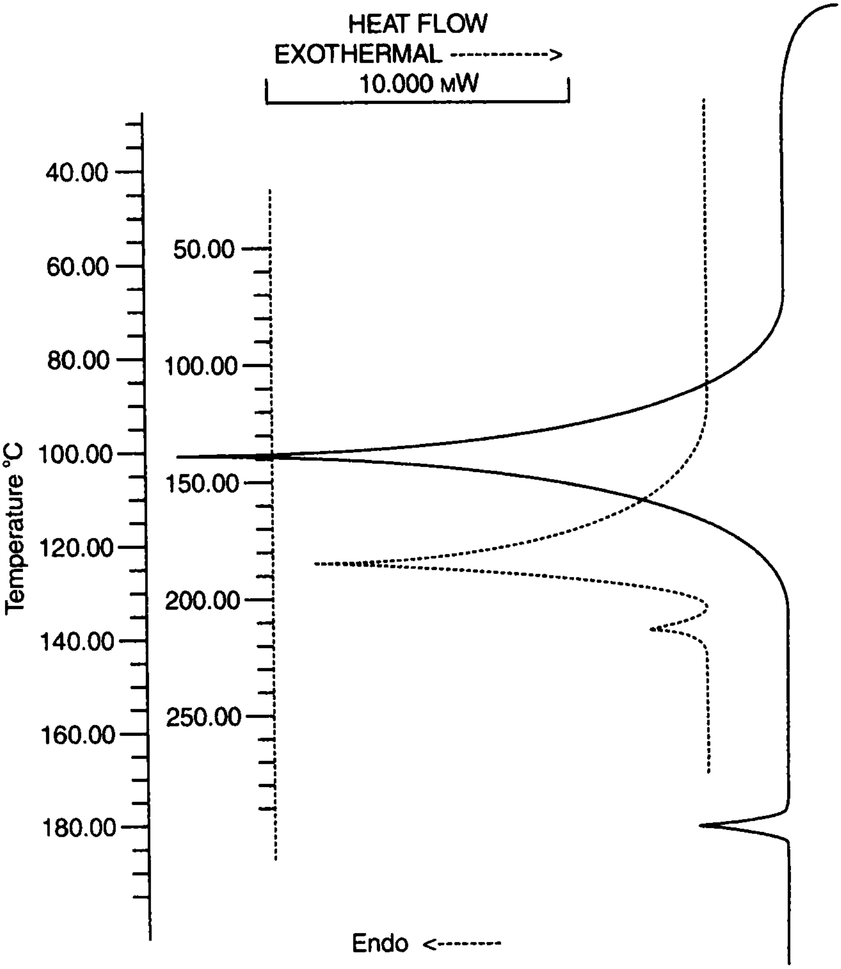


FIGURE 1 DSC curves of 1L (solid line) and Cu(II) (1L)$_2$ (dotted line)

Both the ligands are thermally stable and their phase transitions were reproducible on subsequent heating whereas their metal complexes decompose partially in the isotropic state.

Comparing with the data reported in Table-III, a general trend can be noted. The transition temperatures for the organometallic complexes are significantly higher than those of parent ligand. Cu(II) and Ni(II) complexes of ligand 4L containing $-OC_4H_9$ terminal chain at one end exhibit a little higher nematic thermal stability than the respective metal complexes of ligand 1L containing-OCH_3 terminal group. It seems that increment of methylene groups at one end of the molecules from methoxy to n-butyloxy, endows it with higher polarizability which is reflected in the slightly higher nematic thermal stabilities, while all other factors being common in the metal complexes. Ni(II) complexes have little higher nematic thermal stability than their Cu(II) analogues, probably due to the short Ni-Ni distance between contiguous molecules. Sirigu et al.[24,25] and Diaz et al.[17] have also observed higher mesophase thermal stabilities for Pd(II) complexes than their Cu(II) analogues.

TABLE III Transition temperatures (°C) for ligands and their Cu(II) and Ni(II) metal complexes

Compound	*Transition*	*temperatures/°C*
	N	*I*
1L	102	183
4L	90	187
$Cu(1L)_2$	185	212 (d)
$Ni(1L)_2$	188	217 (d)
$Cu(4L)_2$	191	218 (d)
$Ni(4L)_2$	199	230 (d)

(d) Partial decomposition.

TABLE IV DSC data

Compound	*Heating rate /°Cmin^{-1}*	*Transition*	*Peak*	*ΔH/Jg^{-1}*	*ΔS/Jg^{-1}k^{-1}*
			Temperature (°C)		
1L	05	Cr-N	101.0	26.043	0.06940
		N-I	183.8	0.327	0.00071
$Cu(II)(1L)_2$	05	Cr-N	185.5	35.017	0.07630
		N-I	212.4	0.554	0.00141

Earlier we have reported[19] Ni(II) and Cu(II) complexes with terminal methyl group. Ni(II) complexe is nematogenic (Cr 182 N 203 I) and Cu(II) complexe is non-mesogenic (Cr 185 I). In the present study, terminal methyl group is changed to n-alkoxy group. All the present metal complexes exhibit nematic mesophase with higher thermal stability. n-Alkoxy group induce much higher polarizability in the aromatic system compared to methyl group. This will result in higher thermal stability of the present metal complexes.

It is interesting to note that all the metal complexes exhibit only nematic mesophase. The nematic phase was clearly identified by its very fluid threaded texture (see microphotograph of Ni(II)$(4L)_2$ at 170°C.) and by the typical nematic droplets observed on cooling from the isotropic liquid[26].

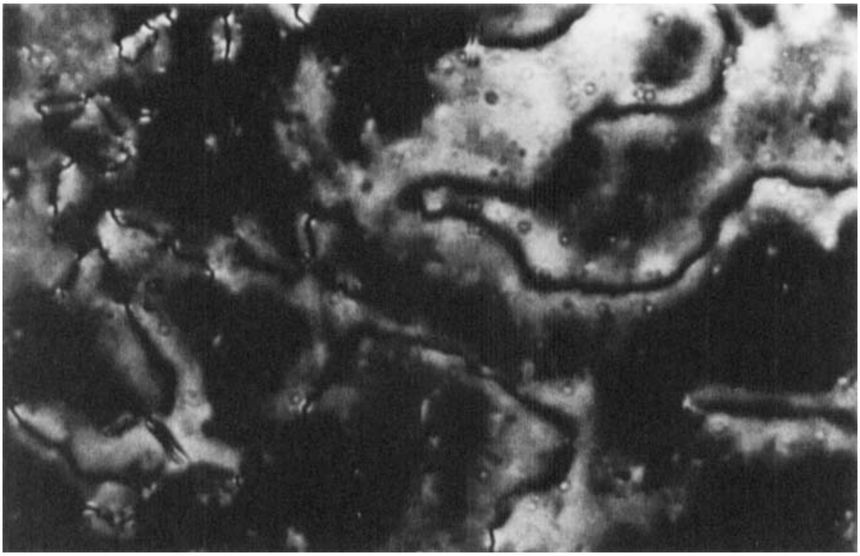


FIGURE 2 Microphotograph of Ni(II)$(4L)_2$ at 170°C (See Color Plate II at the back of this issue)

CONCLUSION

Two ligands and their Cu(II) and Ni(II) metal complexes have been synthesized. All the compounds synthesized exhibit nematic mesomorphism. The nematic thermal stability of the metal complexes is significantly higher than those of the parent ligands.

The thermal stability of the n-alkoxy complexes is higher than the less polar methyl complexes. Thus complexes also follow the similar trend of mesophase thermal stability like the trend normally observed in individual non-metallomesogens.

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