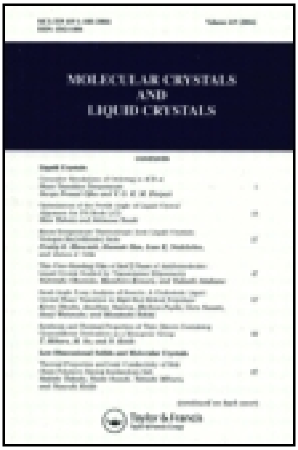

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SYNTHESIS, CHARACTERIZATION, AND STUDY OF MESOGENIC PROPERTIES OF Cu(II) AND Ni(II) COMPLEXES OF Bis- and TETRADENTATE SCHIFF'S BASES DERIVED FROM 2-HYDROXY-4-(n-ALKOXY) BENZALDEHYDES

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SYNTHESIS, CHARACTERIZATION, AND STUDY OF MESOGENIC PROPERTIES OF Cu(II) AND Ni(II) COMPLEXES OF Bis- and TETRADENTATE SCHIFF'S BASES DERIVED FROM 2-HYDROXY-4-(*n*-ALKOXY) BENZALDEHYDES

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Bis-(2-hydroxy-4-(n-alkoxy) benzaldimino) copper (II) and bis-(2-hydroxy-4 (n-alkoxy) benzaldimino) nickel (II) complexes have been synthesized by the reaction of 2-hydroxy-4-(n-alkoxy) benzaldehyde with tetraamine complexes of Cu(II) and Ni(II) under template condition. Cu(II) and Ni(II) complexes of 1,2-bis-(2-hydroxy-4-(n-alkoxy) benzaldimino) ethane and 1,3-bis-(2-hydroxy-4-(n-alkoxy) benzaldimino) propane have been synthesized from the imine complexes by amine exchange with 1,2-diaminoethane and 1,3-diaminopropane, respectively. The complexes have been characterized by spectral and magnetic studies. Some of these complexes exhibit mesogenic properties. This has been correlated to the structures of the complexes.

Keywords: square planar geometry; liquid crystal; metallomesogen; template synthesis; amine exchange reaction

INTRODUCTION

Coordination of liquid crystalline organic ligands with metal ions leads to the formation of metallomesogens, where the presence of the metal ion

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can produce different assembly structures, leading to interesting liquid crystalline properties, as reviewed in recent years [1,2]. The ability of different metal ions to arrange the coordinating ligands in a number of different orientations around the central metal ion in its complexes is the reason for the development of different assembly structures. In a metallomesogen the orientation of a nonmesogenic organic ligand surrounding the metal center may lead to different but unique assembly structure, exhibiting liquid crystalline properties [3–7]. Metal complexes of Schiff's bases have invited the attention of inorganic chemists because of the interesting properties of these complexes [8–11]. Such complexes play an important role in the development of metallomesogens [12–16]. The particular advantage of the salicylaldimine ligand system in the synthesis of metallomesogen is the considerable flexibility of the synthetic procedure. This allows the preparation of a wide variety of liquid crystalline complexes, whose properties are strongly dependent on the ligand structure and the metal ion used [17]. It is known that the reaction of 1,2-bis (2-hydroxybenzaldimino) ethane or 1,3-bis (2-hydroxybenzaldimino) propane with the metal ions such as Cu(II) and Ni(II) leads to the formation of the complexes with square planer geometry (28) and thus the donor atoms of the ligand lie on a single plane. The presence of an alkoxy group at the 5- position of the 2-hydroxybenzaldimine moiety leads to the formation of rodlike molecules, which show liquid crystalline properties [18–21]. However, the complexes, with alkoxy substitution at the 4- position of the 2-hydroxybenzaldimine moieties have not been studied so far. In the present article the syntheses, characterization, and study of liquid crystalline properties of a series of square planar Cu(II) and Ni(II) complexes of Schiff's base ligands, derived from 2-hydroxy-4-(*n*-alkoxy) benzaldehydes, have been reported.

EXPERIMENTAL

Physical Measurements

Microanalyses (C, H, N) were carried out using a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin-Elmer 783 spectrophotometer as KBr pellets. ^{1}H NMR spectra were obtained using a 300 MHz varian FT-spectrophotometer in $CDCl_3$ solution using TMS as the internal standard. Electronic spectra were recorded on a Shimadzu UV-240 UV-visible spectrophotometer. Magnetic susceptibilities were measured with the help of a PAR 155 vibrating sample magnetometer. The EPR spectra were recorded using a Varian model 109C E-Line X band spectrophotometer, fitted with a quartz Dewar for measurement at 77 K (liquid nitrogen). Spectra were calibrated using tetracyanoethylene

(TCEN) ($g = 2.3003$) in dichloromethane. The phase behavior of all the complexes were examined by Lietz laborlux 12 Pol polarizing microscope, fitted with Kofler heating stage and were confirmed by differential scanning calorimeter using a DSC-822e Mettler TOLFDO apparatus. Thermogravimetric studies of complexes were carried out using thermal analyzer DT30.

Materials

$Cu(CH_3COO)_2.2H_2O$, $Ni(CH_3COO)_2.4H_2O$ were of Loba (India) make. 1,2-Diaminoethane and 1,3-diaminopropane of Loba (India) were used after distillation over KOH. Alkyl bromides [Sisco Chem, India] were also used after distillation.

Synthesis

Synthesis of Aldehyde

The ligands, 2-hydroxy-4-(*n*-alkoxy) benzaldehydes were synthesized following a method reported by Willamson et al. [22–23], by reacting *n*-alkyl bromide with 2,4-dihydroxybenzaldehyde in presence of $KHCO_3$ in anhydrous acetone. The products were purified by flash column chromatography using hexane-ethylacetate (96:4 v/v) as the eluent. The purity of the product obtained was checked by TLC.

Synthesis of bis-(2-hydroxy-4-(n-alkoxy) benzaldimino) copper(II) Complexes (Series I)

The complexes of series I were prepared by using the same general method. Specific details of bis-(2-hydroxy-4-(*n*-decyloxy) benzaldimino) Copper (II) representative complex are given here. To an ethanolic solution of $Cu(CH_3COO)_2.2H_2O$, (0.199 g., 0.1 mmol) an excess of ammonia was added till the hydroxide formed, and than it dissolved to form the tetra-amineCu(II) complex. To this was added an ethanolic solution of 2-hydroxy-4-(*n*-decyloxy) benzaldehyde (0.556 g., 0.2 mmol). On refluxing the reaction mixture for an hour, green-colored complex was precipitated. The complex was isolated by filtration, washed thoroughly with water and finally with ethanol, and then dried in air. The complex was further purified by crystallization from dichloromethane.

The complexes, bis-(2-hydroxy-4-(*n*-alkoxy) benzaldimino) nickel(II) (series II) were synthesized following the same method as described for series I, using an equivalent amount of $Ni(CH_3COO)_2.4H_2O$ instead of $Cu(CH_3COO)_2.2H_2O$.

Synthesis of 1,2-Bis-(2-hydroxy-4-(n-alkoxy) benzaldimino) ethane copper(II) (Series III)

The complexes of series III were prepared by using the same general method. Specific details of 1,2-bis-(2-hydroxy-4-(*n*-decyloxy) benzaldimino) ethanecopper(II) representative complex are given here. To a suspension of (0.615 g., 0.1 mmol) bis-(2-hydroxy-4-(*n*-decyloxy) benzaldimino) copper(II) complexes in 50 mL of ethanol, 1,2-diaminoethane (0.03 g., 0.05 mmol) in 5 mL ethanol was added. The reaction mixture was refluxed for 2 h. After cooling the reaction mixture the precipitated complex was filtered, washed thoroughly with ethanol, and dried in air. The complex was further purified by crystallization from dichloromethane.

The complexes, 1,2-bis-(2-hydroxy-4-(*n*-alkoxy) benzaldimino)ethane nickel(II) (series IV) were synthesized following the same method as described for series II starting with an equivalent amount of 1,2-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)nickel(II) complex.

Synthesis of 1,3-bis-(2-hydroxy-4-(n-alkoxy) benzaldimino) propane copper(II) (Series V) and 1,3-bis-(2-hydroxy-4-(n-alkoxy)benzaldimino) propanenickel(II) (Series VI)

The complexes of series V and VI were synthesized by following the same method as described for the complexes of series III and IV, respectively, using an equivalent amount of 1,3-diaminopropane instead of 1,2-diaminoethane.

The elemental analysis data and electronic spectral data of all the complexes have been collected in Table 1 and the phase transition temperatures have been collected in Table 2.

TABLE 1(A) Characterization Table for the Complexes

		Elemental analysis (%) (calculated)			
Series I (n)	Molecular formula	C	H	N	Electronic spectral data[a] λmax (nm) (ε^b/dm^3 mol^{-1} cm^{-1})
5	$C_{24}H_{32}O_4N_2Cu$	60.15 (60.56)	6.89 (6.72)	5.88 (5.93)	590(190), 294(6900), 350(2810)
10	$C_{34}H_{52}O_4N_2Cu$	66.74 (66.29)	8.75 (8.45)	4.05 (4.54)	592(192), 292(7720), 350(3990)
14	$C_{42}H_{68}O_4N_2Cu$	69.67 (69.27)	9.57 (9.34)	3.54 (3.84)	592(192), 295(9700), 350(3770)
16	$C_{46}H_{76}O_4N_2Cu$	70.34 (70.45)	10.01 (9.70)	3.09 (3.57)	592(190), 295(9900), 350(3870)
18	$C_{50}H_{84}O_4N_2Cu$	71.14 (71.47)	10.09 (10.00)	3.13 (3.33)	593(194), 294(9980), 351(3892)

[a] In dichloromethane solution.

[b] Extinction coefficient.

[c] Shoulder.

TABLE 1(B) Characterization Table for the Complexes

		Elemental analysis (%) (calculated)			Electronic spectral data[a] λmax (nm) (ε[b]/dm^3 mol^{-1} cm^{-1})
Series II (n)	Molecular formula	C	H	N	
7	$C_{28}H_{40}O_4N_2Ni$	62.50 (63.87)	8.72 (8.64)	4.70 (4.48)	550(107), 285(2895), 395(1683), 320[c](3771), 335[c](3838)
10	$C_{34}H_{52}O_4N_2Ni$	66.52 (66.88)	8.75 (8.52)	4.07 (4.59)	558(85), 290(8456), 398(4470), 320[c](5300), 335[c](5632)
14	$C_{42}H_{68}O_4N_2Ni$	69.03 (69.80)	9.57 (9.42)	3.47 (3.87)	558(92), 290(4615), 398(2461), 320[c](5335), 335[c](5330)
16	$C_{46}H_{76}O_4N_2Ni$	70.68 (70.95)	10.01 (9.76)	3.40 (3.59)	560(94), 290(3746), 395(1388), 320[c](3703) 335[c](3518)
18	$C_{50}H_{84}O_4N_2Ni$	71.54 (71.94)	10.09 (10.07)	3.15 (3.35)	562(95), 292(4234), 398(2643), 320[c](5120), 335[c](3231)

[a] In dichloromethane solution.
[b] Extinction coefficient.
[c] Shoulder.

TABLE 1(C) Characterization Table for the Complexes

		Elemental analysis (%) (calculated)			Electronic spectral data[a] λmax (nm) (ε[b]/dm^3 mol^{-1} cm^{-1})
Series III (n)	Molecular formula	C	H	N	
5	$C_{26}H_{34}O_4N_2Cu.H_2O$	60.05 (61.9)	6.99 (6.92)	5.38 (5.56)	580(362), 305(4780), 360(2680), 390[c](12544)
10	$C_{36}H_{54}O_4N_2Cu.H_2O$	65.94 (65.50)	8.51 (8.49)	4.04 (4.24)	565(414), 295(5740), 350(2780), 375[c](3880)
14	$C_{44}H_{70}O_4N_2CuH_2O$	68.40 (68.43)	9.75 (9.33)	3.15 (3.62)	562(400), 295(6690), 350(2830), 373[c](3566)
16	$C_{48}H_{78}O_4N_2Cu.H_2O$	69.61 (69.60)	9.90 (9.66)	3.51 (3.38)	565(400), 295(7880), 350(3295), 375[c](3223)
18	$C_{52}H_{86}O_4N_2Cu.H_2O$	70.40 (70.63)	9.78 (9.96)	3.01 (3.17)	565(382), 295(7890), 350(3400), 307[c](3448)

[a] In dichloromethane solution.
[b] Extinction coefficient.
[c] Shoulder.

TABLE 1(D) Characterization Table for the Complexes

Series IV (n)	Molecular formula	Elemental analysis (%) (calculated) C	H	N	Electronic spectral data[a] λmax (nm) (ε^b/dm^3 mol^{-1} cm^{-1})
7	$C_{30}H_{42}O_4N_2Ni.H_2O$	63.85 (62.15)	6.98 (7.71)	5.10 (4.91)	530(181), 298(7925), 380(4000), 358^c(4592), 425^c(1700)
10	$C_{36}H_{54}O_4N_2Ni.H_2O$	66.45 (66.05)	8.51 (8.56)	4.18 (4.28)	550(195), 312(117000), 398(10300), 348^c(6747), 435^c(4300)
14	$C_{44}H_{70}O_4N_2NiH_2O$	68.43 (68.97)	9.27 (9.39)	3.67 (3.65)	545(191), 310(8645), 398(9979), 365^c(6330), 432^c(4412)
16	$C_{48}H_{78}O_4N_2Ni.H_2O$	70.05 (70.01)	9.78 (9.72)	3.35 (3.40)	540(212), 290(8537), 398(9954), 365^c(5414), 440^c(2432)
18	$C_{52}H_{86}O_4N_2Ni.H_2O$	71.37 (71.07)	10.11 (10.02)	3.22 (3.18)	542(210), 298(8934), 396(10201), 365^c(5734), 436^c(3478)

[a] In dichloromethane solution.

[b] Extinction coefficient.

[c] Shoulder.

TABLE 1(E) Characterization Table for the Complexes

Series V (n)	Molecular formula	Elemental analysis (%) (calculated) C	H	N	Electronic spectral data[a] λmax (nm) (ε^b/dm^3 mol^{-1} cm^{-1})
5	$C_{27}H_{36}O_4N_2Cu.H_2O$	60.53 (60.73)	7.33 (7.12)	5.14 (5.24)	605(193), 290(11980), 350(6123)
10	$C_{37}H_{56}O_4N_2Cu.H_2O$	65.45 (65.92)	8.89 (8.61)	4.06 (4.16)	592(280), 295(12190), 358(5853), 362^c(6175)
14	$C_{45}H_{72}O_4N_2Cu.H_2O$	68.29 (68.74)	9.37 (9.42)	3.58 (3.56)	590(286), 292(12920), 350(6153), 362^c(5000)
16	$C_{49}H_{80}O_4N_2Cu.H_2O$	70.61 (69.87)	10.03 (9.74)	3.67 (3.32)	590(285), 295(13740), 350(8864), 365^c(5500)
18	$C_{53}H_{88}O_4N_2Cu.H_2O$	70.56 (70.86)	10.20 (10.02)	3.25 (3.11)	592(283), 292(13641), 354(74443), 362^c(6231)

[a] In dichloromethane solution.

[b] Extinction coefficient.

[c] Shoulder.

TABLE 1(F) Characterization Table for the Complexes

		Elemental analysis (%) (calculated)			Electronic spectral data[a]
Series VI (n)	Molecular formula	C	H	N	λmax (nm) ($\varepsilon^b/dm^3\ mol^{-1}\ cm^{-1}$)
7	$C_{31}H_{44}O_4N_2Ni.H_2O$	62.53 (63.69)	7.33 (7.87)	5.14 (4.79)	600(85), 290(8300), 400(3400), 310[c](6653), 336[c](3989)
10	$C_{37}H_{56}O_4N_2Ni.H_2O$	65.95 (66.47)	8.89 (8.68)	4.16 (4.19)	600(81), 290(8400), 400(3400), 310[c](6953), 338[c](4089)
14	$C_{45}H_{72}O_4N_2Ni.H_2O$	68.29 (69.23)	9.37 (9.23)	3.28 (3.58)	600(101), 290(10100), 400(4059), 310[c](8070), 335[c](5280)
16	$C_{49}H_{80}O_4N_2Ni.H_2O$	70.56 (70.33)	10.20 (9.86)	3.25 (3.34)	600(105), 290(6740), 310(5349), 310[c](5349), 335[c](3600)
18	$C_{53}H_{88}O_4N_2Ni.H_2O$	70.56 (71.30)	9.64 (10.08)	3.25 (3.13)	594(102), 290(5690), 400(3231), 310[c](4351), 335[c](2789)

[a] In dichloromethane solution.
[b] Extinction coefficient.
[c] Shoulder.

RESULTS AND DISCUSSION

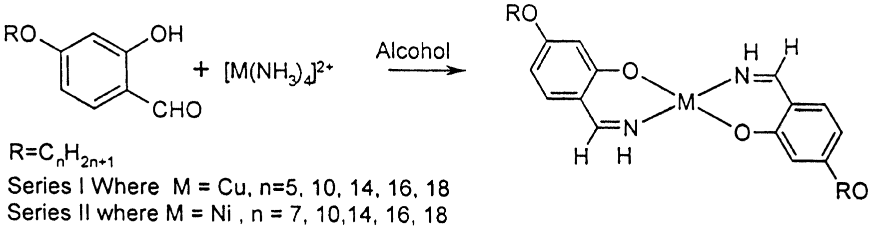
The complexes of series I and II were prepared by reacting the tetraamine complexes of bivalent metal ions with two equivalents of 2-hydroxy-4-(*n*-alkoxy) benzaldehyde. During the reaction of $[M(NH_3)_4]^{2+}$ with 2-hydroxy-4-(*n*-alkoxy) benzaldehyde in alcohol, two coordinated ammonia molecules condense with two aldehyde functional groups of two 2-hydroxy-4-(*n*-alkoxy) benzaldehyde ligands, and the remaining two coordinate ammonia molecules in $[M(NH_3)_4]^{2+}$ are replaced by two phenolate oxygen atoms, forming two six-membered chelate rings. The reaction is facilitated due to both the chelate effect and the template effect [24–26].

The reaction of bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)copper(II) and bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)nickel(II) complexes with 1,2-diaminoethane or 1,3-diaminopropane in alcohol leads to amine exchange and results in the formation of the tetradentate Schiff's base complexes. The amine exchange is facilitated due to the coordination of the azomethine nitrogen to the metal ion as well as due to the enhanced stability of the resulting complexes, imparted by the formation of another five-or six-membered chelate ring.

TABLE 2 Transition Temperatures °C of the Series I, II, III, IV, V, and VI

	Transition temperatures °C	
R = *n*-alkyl group	Smectic C	Isotropic
Series I: *Bis(2-hydroxy-4-n-alkoxybenzaldimino)Cu(II)*		
Pentyl		173
Decyl		158
Tetradecyl		150
Hexadecyl		150
Octadecyl	(115)	149
Series II: *Bis(2-hydroxy-4-n-alkoxybenzaldimino)Ni(II)*		
Heptyl		247
Decyl		211
Tetradecyl		195
Hexadecyl		185
Octadecyl	(180)	185
Series III: *1,2-Bis(2-hydroxy-4-n-alkoxybenzaldimino)ethane Cu(II)*		
Pentyl		185
Decyl		178
Tetradecyl	120	163
Hexadecyl	132	160
Octadecyl	115	154
Series IV: *1,2-Bis(2-hydroxy-4-n-alkoxybenzaldimino)ethane Ni(II)*		
Heptyl		199
Decyl	(152)	170
Tetradecyl	(152)	157
Hexadecyl	96	136
Octadecyl	90	151
Series V: *1,3-Bis(2-hydroxy-4-n-alkoxybenzaldimino)propane Cu(II)*		
Pentyl		230
Decyl		192
Tetradecyl		196
Hexadecyl		180
Octadecyl		175
Series VI: *1,3-Bis(2-hydroxy-4-n-alkoxybenzaldimino)propane Ni(II)*		
Heptyl		146
Decyl		160
Tetradecyl		155
Hexadecyl		140
Octadecyl	(114)	130

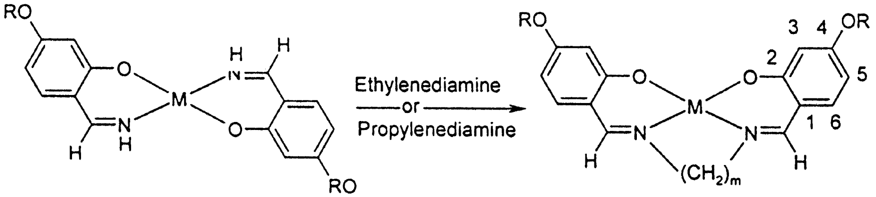
Values in parentheses indicate monotropic transitions.



SCHEME 1

The elemental analysis data agree well with the expected composition of the complexes. In some of the complexes water molecule is found to be present as a molecule of crystallization, and this has been confirmed by thermogravimetric analyses (TGA). The TGA data show that the water molecule is lost below 110°C, indicating that it is water of crystallization. Comparison of the IR spectra of the free ligands with that of the complexes of series I and II indicates the appearance of two new bands ca. 3336 cm^{-1} and ca. 1618 cm^{-1}. These bands have been assigned to NH and $C=N$ stretching vibrations of the coordinated ligands. Further, the OH stretching band of the phenolic hydroxyl groups of the free ligand disappears in the IR spectra of complexes, supporting the deprotonation of the phenolic hydroxyl groups of the ligand during complexation. In the IR spectra of the complexes of the series III, IV, V, and VI, the band due to the NH stretching disappears and the band due to $C=N$ stretching occurs at 10 cm^{-1} lower frequency than the corresponding complexes of series I and II. This is because of the exchange of ammonia by 1,2-diaminoethane or 1,3-diaminopropane, which removes the aldimine NH proton of the complexes of series I and II. There is a greater π-delocalization in the complexes of series III to VI, leading to the lowering of $\nu_{C=N}$.

The ^{1}H NMR spectrum of a representative diamagnetic nickel(II) complex 1,2-bis-(2-hydroxy-4-(*n*-octadecyloxy)benzaldimino)ethanenickel(II) (from series IV, Scheme 2) has been recorded in $CDCl_3$. In the spectrum the signals due to the aromatic protons H^5 and H^6 appear at δ 7.9 and 8.15 as two doublets, while the signal due to H^3 appears at δ 7.26 as a singlet. The signal due to the alkyl protons appears within the range δ 0.9–2.6 as a multiplet and integrates to 74 protons, which is in agreement with the number of protons present in the alkyl chains of the ligand molecule. The triplet, which integrates to four protons, at δ 4.0 has been assigned to the four equivalent protons of the 1,2-diaminoethane moiety of the ligand. The signal due to the aldehyde protons appears at δ 8.50 as a singlet and integrates to two protons.



$R=C_nH_{2n+1}$
Series III & V where M = Cu, n = 5, 10, 14, 16, 18
Series IV & VI where M = Ni, n = 7, 10, 14, 16, 18

m = 2 for series III & IV
3 for series V & VI

SCHEME 2

Electronic Spectral Studies

All the complexes are insoluble in nonpolar solvents like benzene, toluene, and petroleum ether as well as polar solvents like ethyl alcohol, methyl alcohol, acetonitrile, acetone, etc., but they are soluble in dichloromethane and chloroform. The electronic spectra of the complexes were recorded in dichloromethane solution having concentration ca. 10^{-4} M, and the spectral data have been recorded in Table 1. The Cu(II) complexes of series I, III, and V show a broad band in the visible region of the electronic spectra. This is the characteristic *d-d* transition band in tetragonal Cu(II) complexes. In the Ni(II) complexes of series II, IV, and VI a broad band appears in the visible region along with a shoulder at ca. 335 nm and there is no absorption beyond 600 nm. This is the characteristic of the square planer Ni(II) complexes [27–28]. In the electronic spectra of the complexes of series I and II, the band due to the *d-d* transition appears at ca. 592 nm and ca. 558 nm, respectively. In the complexes of the series III & IV the same band due to *d-d* transition undergoes a blue shift and appears at ca. 565 nm and ca. 540 nm, respectively. The blue shift indicates that the tetradentate Schiff's base ligands bearing 1,2-diaminoethane moieties in the complexes of series III and IV create a stronger ligand field around the metal ion, leading to greater splitting of the *d* orbitals. Hence, higher energy is required for *d-d* transition and the band shift to higher frequency (lower λ region). A stronger field is created because in the tetradentate Schiff's base complexes of series III and IV the ligand atoms are more planar around the metal ion. The negative charges of the lone pair of the ligands are more directed to the $d_{x^2-y^2}$ and d_{z^2} orbitals of the metal ion. In the complexes of series V and VI the band due to the *d-d* transition appears at ca. 592 nm and ca. 600 nm, respectively. Thus in the complexes of series V and VI, though the ligands are tetradentate Schiff's bases, the ligand field is approximately same or less than the ligand field in the complexes of series I and II, which bear two bidentate 2-hydroxy-4-(*n*-alkoxy)benzaldimine ligands. The lowering in the ligand field strength around the metal center in the complexes of the tetradentate Schiff's base ligands 1,3-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)propane compared to the ligand field strength in the complexes of the tetradentate Schiff's base ligands 1,2-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)ethane may be attributed to the distortion in planarity of the donor atoms, imparted by the presence of the propylene moiety in the former complexes. A five-membered middle ring in the series III and IV complexes makes the ligand more planar than the six-membered middle ring in the series V and VI complexes. In the electronic spectra of the complexes of the series I, III, and V a band appears at ca. 350 nm due to metal to ligand charge transfer (MLCT) transition, as indicated by the high extinction coefficient values of this band. In the complexes of series II, IV, and VI a similar MLCT band appears at ca. 370 nm.

All the complexes show another band at ca. 292 nm in the electronic spectra. This band in UV region has been attributed to the intraligand transition, as the same band appears in the electronic spectra of the free ligands. In the electronic spectra of the complexes, the position of the intraligand transition band undergoes a shift, compared to the same for the free ligands. This change in the energy may be due to the complexation of the ligand with the metal ion. The extinction coefficient of the d-d transition bands in the electronic spectra of bis-chelated complexes of 2-hydroxy-4-(*n*-alkoxy)benzaldimine in series I and II is lower than the same of the complexes of series III and IV (Table 1). This is because in the former there is a center of symmetry, whereas in the latter two nitrogen and two oxygen atoms are on the same side, resulting in a noncentrosymmetric arrangement of the donor atoms.

The Cu(II) complexes exhibit paramagnetism corresponding to one unpaired electron as expected for square planar d^9 Cu(II) complexes. The Ni(II) complexes are diamagnetic as expected for a d^8 ion in a square planar geometry. The EPR spectra of the Cu(II) complexes were recorded in dichloromethane solution at 77 K. The diamagnetic Ni(II) complexes are EPR silent.

Mesogenic Behavior

The phase transition temperatures of all the complexes are recorded in Table 2. The phase transition temperatures indicate that among the complexes of series I, the complex with ligand having C_{18} alkoxy chain exhibit mesogenic behavior. It is monotropic in nature and exhibits Smectic C phase. The similar trend is also observed in case of the complexes of series II, where only the complexes with C_{18} side chain are mesomorphic, exhibiting a Smectic C phase. Table 2 shows that the complexes 1,2-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)ethanecopper(II) of series III, with

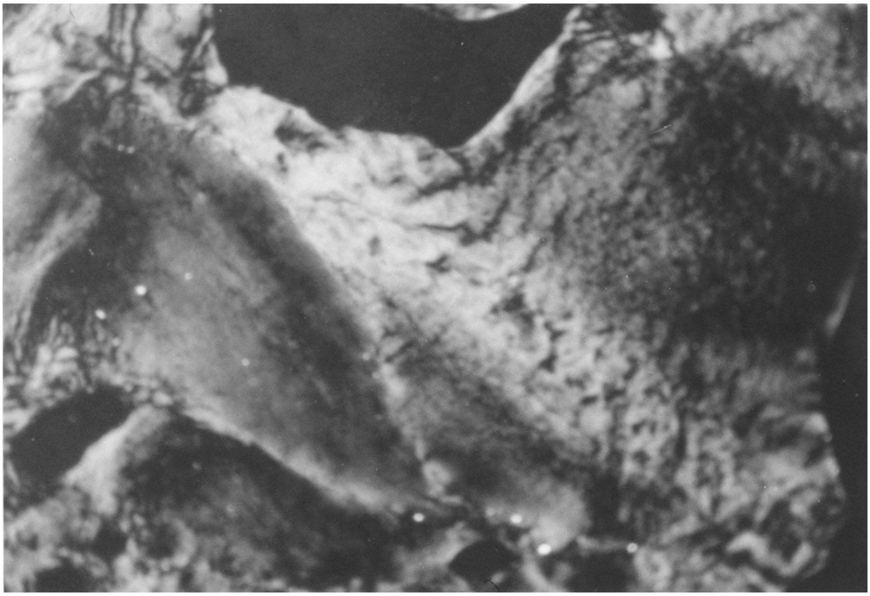


FIGURE 1 Optical polarization micrographs of Cu-14 (series III), Smectic C texture at 120°C. (See COLOR PLATE II)

C_5 and C_{10} alkoxy chain, do not show mesomorphic behavior, while the C_{14}, C_{16}, and C_{18} homologues are mesomorphic in nature. These complexes show enantiotropic Smectic C phase (Fig. 1). In the case of 1,2-Bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)ehtanenickel(II) complexes of series IV, the complex with C_7 alkoxy chain is nonmesomorphic in nature, while the C_{10} and C_{14} homologues show monotropic Smectic C phase and the C_{16} and C_{18} homologues show enantiotropic Smectic C phase. All the complexes of series V are nonmesomorphic in nature, while in case of the complexes of series VI only the complex with C_{18} alkoxy chain shows monotropic Smectic A phase (Fig. 2). In the differential scanning calorimetric (DSC) studies the phase transition temperatures were found to be in agreement with those observed using the polarizing microscope.

The aldimine complexes of series I and II, with alkoxy chain up to C_{16} are nonmesogenic in nature. Only the complex with C_{18} shows mesomorphism. Marcos et al. [11] also observed that the Cu(II) complexes of the ligand 2-hydroxy-5-(*n*-alkoxy)benzaldehyde up to C_{14} alkoxy chain do not exhibit mesomorphism. This may be because in these complexes the ligand atoms have less planar disposition around the metal ion, as revealed by electronic spectral studies, and hence there is less intermolecular interaction. Only in case of the complexes of the ligand with C_{18} alkoxy chain, mesogenic

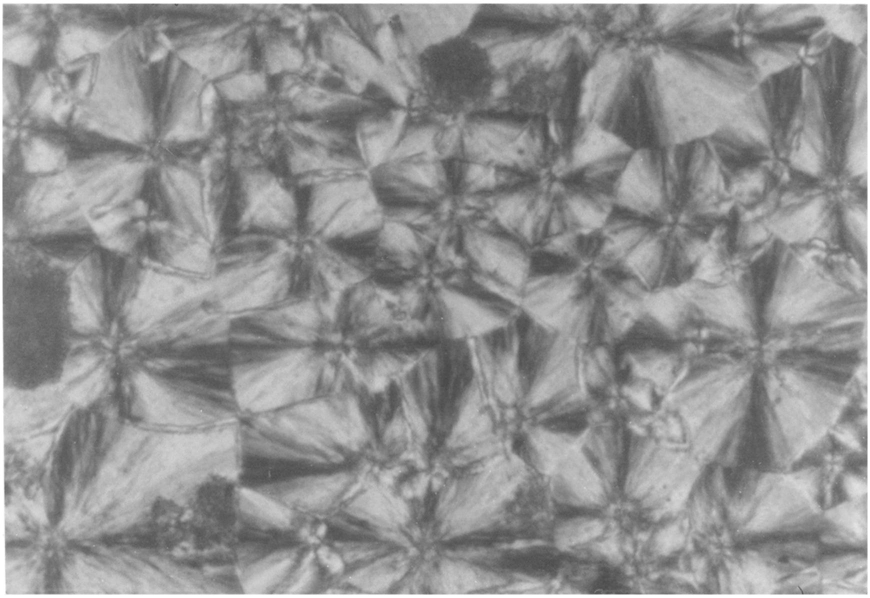


FIGURE 2 Optical polarization micrographs of Ni-18 (series VI), Smectic A texture at 114°C. (See COLOR PLATE III)

property is observed. This may be due to increase in the polarizability of the molecule due to the presence of longer C_{18} alkoxy group.

It is observed that though the tetradentate Schiff's base ligands 1,2-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)ethane and of 1,3-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)propane do not exhibit liquid crystalline property, some of their complexes are mesogenic in nature. In case of the complexes described in the present study the mesophase ranges are wider than the corresponding ligands, though there is increase in the volume and lowering in the length-to-width ratio in the complexes. In the complexes of tetradentate Schiff's bases 1,2-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)ethane the donor atoms are strongly bound to the metal ion due to the chelate effect. The complexes are more planar in structure with greater intermolecular interaction, and hence mesomorphic property is observed in the complexes of the ligands with alkoxy chain C_{10} onwards. There is also an increase in polarizability of the complex molecules. The complexes with 1,2-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)ethane form a rigid molecular structure appropriate for the mesogenic property but the alkoxy chains are oriented in bent manner, unlike the straight chain orientation in the 5-alkoxy analogs [18]. Hence the mesogenic property is exhibited only by the complexes with longer side chain, with higher polarizability. The

Ni(II) complexes (series IV) exhibit mesogenic properties for the complexes with C_{10} and higher alkoxy chain, while in case of Cu(II) complexes (series III) the mesogenic property is exhibited in complexes with C_{14} alkoxy chain and onwards.

In the complexes of 1,3-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)-propane Schiff's bases the chelate ring formed with the metal ion is six membered. This results in greater distortion in the planarity and hence the complexes of the ligands, with shorter alkoxy chains, do not exhibit mesomorphic property [29]. Only the complex of the ligand, with C_{18} alkoxy chain, shows mesogenic property.

The Ni(II) complexes with shorter alkoxy chains exhibit mesogenic property, whereas corresponding Cu(II) complexes are nonmesogenic. This may be attributed to the greater ligand field stabilization energy and hence greater stability of the square planar Ni(II) complexes, compared to the corresponding Cu(II) complexes. The radius of Ni(II) ion is more suitably adjusted within the core of the salen type of ligands, resulting in a square planar complex [10]. The square planar geometry of Ni(II) complexes makes them prone to show mesogenic property.

On heating a fresh sample the melting and clearing point transitions are observed; however after the first heating, only clearing transition is observed; similar behavior has been observed by Shaffer *et al.* [10] as well. In all the cases, decomposition begins to occur shortly above the clearing point. It is observed that though the Schiff's base ligands do not show any liquid crystal behavior, on complexation with Cu(II) or Ni(II) the resulting complexes show mesomorphism. Thus in these systems the liquid crystal behavior is observed due to the incorporation of the metal ion and formation of the chelate rings.

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