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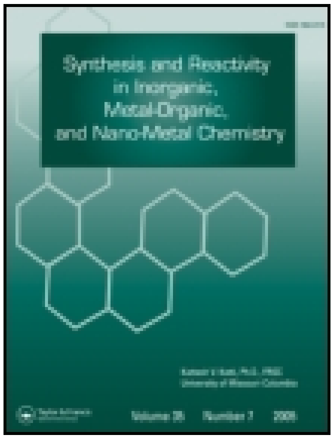

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Synthesis and Spectral Studies on 3d Metal Complexes of Mesogenic Schiff Base Ligands. Part 1. Complexes of N-(4-Butylphenyl) Salicylaldimine

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Synthesis and Spectral Studies on 3*d* Metal Complexes of Mesogenic Schiff Base Ligands. Part 1. Complexes of N-(4-Butylphenyl) Salicylaldimine

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A novel mesogenic Schiff base, N-(4-butylphenyl) salicylaldimine (Hbpsal), was prepared and its ligational behavior towards some 3*d* metal ions studied. All the metal complexes synthesized were of the general formula, $[M(bpsal)_2(H_2O)_2]$ where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The complexes were structurally characterized by elemental analyses, molar conductance, IR, NMR, and electronic spectral data. The metallo mesogenic phases of the Cu(II) complex were studied by optical microscope. The spectral data show that Hbpsal acts as a bidentate ligand towards the metal ions. Mesogenic studies indicate that the ligand shows a focalconic structure with smectic-A phase while the Cu(II) complex displays smectic-A as well as smectic-E phases.

Keywords 3*d* metal complexes, complexes of salicylaldimine derivative, liquid crystalline complexes, metallo mesogens, synthesis and spectral studies of transition metal complexes

INTRODUCTION

Molecular design and synthesis of new metallo mesogenic complexes with novel mesophases represent an active research area in metallomesogenic materials (Ghedini, et al., 1987; Hoshino, et al., 1991; Marcos, et al., 1989; Morrone and Ghehini, 1991). An extensive amount of work on coordination compounds of transition elements with various mesogens has been carried out (Duncan, 1993). It has been observed that transition metal complexes of Schiff bases are well suited for the purpose of testing their properties, due to the synthetic ease in substituting the central metal atom as well as peripheral groups (Chandrasekhar, 1992). In continuation of our studies on coordination complexes of transition metals (Narang et al., 2000; Rao and Kumar 1994; Rao and Sastry, 1994; Rao et al., 1994), we have undertaken a systematic synthesis of mesogenic ligands and their metal complexes. The present article deals with 3*d* metal complexes of the novel mesogenic Schiff base, N-(4-butylphenyl) salicylaldimine, Hbpsal (Figure 1).

EXPERIMENTAL

Materials

4-*n*-Butylaniline was purchased from Aldrich Chemical Company, U.S.A. Salicylaldehyde and metal acetates were of B.D.H. or E. Merck.

Synthesis of the Ligand

Hbpsal was prepared by refluxing absolute ethanolic solution (25 mL) of salicylaldehyde (15 mmol, 1.83 mL) and an ethanol solution (25 mL) of 4-butyl aniline (15 mmol, 2.23 mL) for ~2 h and leaving the solution at room temperature overnight. The resulting crude solid product was filtered, washed repeatedly with ethanol and recrystallized from absolute alcohol; yield, 2.65 g, 70%; m.p, 55°C. Anal. found: C, 80.05; H, 7.45; N, 5.43%; calc. for $C_{17}H_{19}NO$ (FW, 253.17): C, 80.60; H, 7.56; and N, 5.53%.

Synthesis of the Complexes

To a methanolic solution (50 mL) of Hbpsal (4 mmol, 1.0 g) was slowly added a methanolic solution (20 mL) of the respective metal acetate (2 mmol, ~0.49 g) with stirring over a period of 10 min. The reaction mixture was magnetically stirred for 2 h at room temp. During this period, the solid complex started separating. The solution was then reduced to half of

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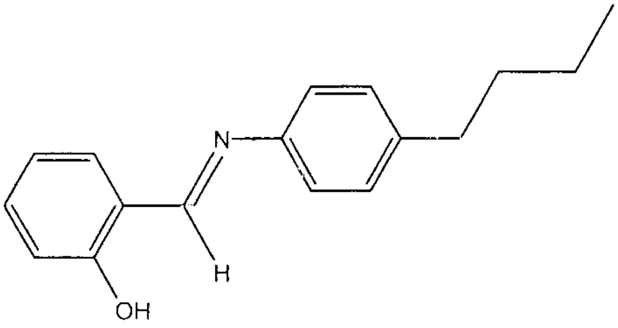

FIG. 1. Structure of Hbpsal.

its volume under reduced pressure and left overnight at room temp. The solid complex that separated out was filtered by suction and recrystallized in ethanol and dried over fused $CaCl_2$ in a desiccator.

Analysis of the Complexes and Physical Measurements

In order to determine the metal content, a weighed quantity (~80 mg) of the complex was heated successively with aqua regia (0.5 mL) and conc. H_2SO_4 (2 drops to destroy the organic matter. The resultant aqueous extract (weakly acidic with respect to HCl) was titrated against a standard solution (0.025 M) of the disodium salt of EDTA using a literature procedure (Jeffery et al., 1989).

The molar conductances of the complexes in 0.001 M DMSO solutions were measured at room temperature on a WTW conductivity meter. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday electrobalance using $Hg[Co(NCS)_4]$ as the calibrant. Infrared spectra (4000–400 cm^{-1}) were recorded on an FT IR (Jasco 5300) spectrophotometer in KBr pellets while the electronic spectra were recorded on a Cary 2390 spectrophotometer in Nujol mulls. The ^1H and ^{13}C NMR spectra of all the organic ligands and the Zn(II) complex were recorded in DMSO-d_6 solutions on a Jeol FX-90Q multinuclear spectrometer. The water content of the complexes was determined by thermal analyses over the temperature range 80–160°C. Nitrogen was determined by micro-analysis. The mesogenic phases were detected with the help of a polarizing optical microscope (Leitz) equipped with a Mettler FP 82 hot stage.

RESULTS AND DISCUSSION

The formation of the complexes may be represented by the following equation:

$$M(OAc)_2 \cdot nH_2O + 2Hbpsal \xrightarrow[MeOH]{Reflux2\,h}$$
$$M(bpsal)_2 \cdot 2H_2O + 2AcOH + (n\text{-}2)H_2O$$
$$(M = Mn, Co, Ni, Cu \text{ and } Zn) \qquad (1)$$

All of the complexes are microcrystalline in their appearance and are yellow/brown/green/light cream in color (Table 1); they are fairly stable at room temperature and are soluble in common organic solvents such as methanol, ethanol, acetone, benzene, acetonitrile, carbon tetrachloride DMF and DMSO, but are insoluble in water. The

TABLE 1
Analytical and physico-chemical data of M(II) complexes of Hbpsal

Ligand/complex (emp. formula, formula wt.) (m.p., °C)	Color (% yield)	Found (calcd.) % C	H	N	M	Wt. loss found (calcd.) at 150°C	Molar conductance[a]
$[Mn(bpsal)_2(H_2O)_2]$ ($C_{34}H_{40}N_2O_4Mn$, 595.62) (230[b])	Brown (80)	66.94 (68.56)	6.60 (6.71)	4.58 (4.70)	9.11 (9.22)	6.05 (6.04)	11.2
$[Co(bpsal)_2(H_2O)_2]$ ($C_{34}H_{40}N_2O_4Co$, 599.61) (170)	Yellow (77)	67.23 (68.10)	6.67 (6.69)	4.50 (4.67)	9.67 (9.83)	5.91 (6.00)	12.0
$[Ni(bpsal)_2(H_2O)_2]$ ($C_{34}H_{40}N_2O_4Ni$, 599.37) (210[b])	Green (83)	67.08 (68.12)	6.54 (6.67)	4.59 (4.67)	9.59 (9.79)	5.94 (6.00)	15.6
$[Cu(bpsal)_2(H_2O)_2]$ ($C_{34}H_{40}N_2O_4Cu$, 604.22) (110)	Brown (84)	66.39 (67.58)	6.50 (6.62)	4.53 (4.63)	10.42 (10.52)	5.79 (5.96)	10.8
$[Zn(bpsal)_2(H_2O)_2]$ ($C_{34}H_{40}N_2O_4Zn$, 606.07) (180)	Cream (70)	66.14 (67.38)	6.52 (6.60)	4.50 (4.63)	10.69 (10.79)	5.83 (5.94)	08.4

[a] Molar conductance (ohm^{-1} cm^2/mole) in 10^{-3} M methanol solution.
[b] Decomposition temperature.

melting/decomposition temperature of the complexes were determined on a manually controlled melting point apparatus with the rate of heating fixed at 2°C/min in the transition region. Thermal analyses of the complexes correspond to the loss of lattice water in the temperature range, 80–100°C.

The electrical conductivity values measured in 10^{-3} M methanol solutions of all the complexes lie in the range 8.40–15.60 $\mathrm{ohm^{-1}\,cm^2/mol}$, indicating their non-ionic nature (Geary, 1971). The solutions kept at this concentration for several days did not show any change in their appearance and in the conductance values. This indicates that no ionic species are formed even after keeping the solutions over several days. Further, the absence of acetate groups in the complexes implies that the di-positive charge of the metal ion is balanced by the deprotonated form of the ligand.

Mesomorphism

The ligand upon heating shows a hazy phase over the 38–49°C range with isotropic melting point at 55°C, and the fluid displays a focalconic texture resembling discotic liquid crystals over the range 42–49°C. The Cu(II) complex, upon heating/cooling from the isotropic point (110°C), displays a smectic-A phase at 98°C (Figure 2) and smectic-E phase at 105°C. The details are shown in Table 2.

The data in Table 2 is consistent with the fact that incorporation of a metal center into the mesogenic ligand leads to a more ordered mesophase of the metal complex (Ghedini, et al., 1987; Hoshino, et al., 1991; Lai, and Lin, 1997; Marcos, et al., 1989; Morrone and Ghehini, 1991). The change in molecular geometry apparently is due to the fact that the Cu(II) complex being more symmetrical than the ligand due to the presence of alkyl chains on both ends. Further, the polarity of the coordination bond in the Cu(II) complex is believed to enhance transverse inter-molecular association and thus promote a smectic phase (Hoshino, et al., 1990).

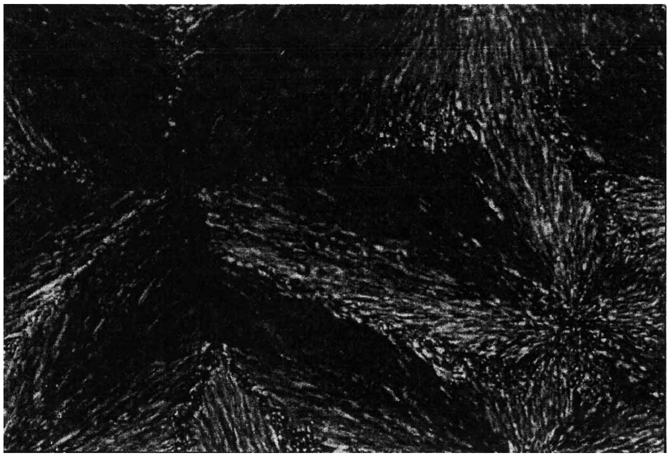

FIG. 2. Black/white photomicrograph of $[\mathrm{Cu(bpsal)_2(H_2O)_2}]$ in smetic-A phase at 98°C obtained on cooling the isotropic liquid.

TABLE 2
Mesophase recognition by optical microscope

Compound	Transition temp (°C) and mesophase (s)
Hbpsal	$\mathrm{K} \xrightarrow{42^\circ\mathrm{C}} \mathrm{SA} \xrightarrow{49\text{–}55^\circ\mathrm{C}} 1$
$[\mathrm{Cu(bpsal)_2(H_2O)_2}]$	$\mathrm{K} \xrightarrow{98^\circ\mathrm{C}} \mathrm{SA} \xrightarrow{105^\circ\mathrm{C}} \mathrm{SE} \xrightarrow{110^\circ\mathrm{C}} 1$

K = Crystalline, S = smectic, I = isotropic liquid.

Magnetic Moments and Electronic Spectra

The room temperature magnetic moments and electronic spectral data of the complexes are included in Table 3.

The μ_{eff} values of the Co(II) and Ni(II) complexes imply an octahedral geometry around the metal ion, while that of the Mn(II) and Cu(II) complexes fall within the normal ranges and provide no information about the stereochemistry. All of the three expected transitions for the octahedral geometry of the Co(II) and Ni(II) complexes are observed in their electronic spectra; further, the ν_2/ν_1 ratio in their spectra supports the assigned stereochemistry (Figgis, 1976). The transition assignments and the ligand-field parameters, viz., 10 Dq, B′, β and LFSE values calculated from the absorptions of the Co(II) and Ni(II) complexes are also included in Table 3; the β values imply that the nature of M-L bond in the present complexes is partially covalent (Lever, 1968).

Infrared Spectra

The IR spectrum of N-(butyl)phenylsalicylaldimine, Hbpsal, is dominated by (1) C-H stretching and bending vibrations of the methyl/methylene groups of the butyl chain, (2) O-H stretching and bending and C-O stretching vibrations of the phenolic group, (3) >C=N stretching of the azomethine moiety, and (4) C-H stretching, out-of-plane C-H bending and overtone and combination bands of disubstituted aromatic rings. Of all the above bands, only those diagnostic of coordination to the metal ion, are listed in Table 4 along with the $\nu_{\mathrm{as}}(\mathrm{CH_3})$ and $\nu_{\mathrm{s}}(\mathrm{CH_2})$ bands. The prominent IR spectral data of the metal complexes of Hbpsal may be discussed as follows: (1) The $\nu(\mathrm{OH})_{\mathrm{phenolic}}$ band [arising at 3490 $\mathrm{cm^{-1}}$ in the spectrum of the ligand] disappears in the spectra of the complexes and the $\nu(\mathrm{C\text{-}O})_{\mathrm{phenolic}}$ undergoes a bathochromic shift upon metal complexation by ~20 $\mathrm{cm^{-1}}$. These features imply deprotonation of the phenolic group and coordination through the phenolate anion; (Silverstein, and Webster, 2002) (2) The $\nu(\mathrm{C{=}N})$ band is shifted from 1620 to ~1610 $\mathrm{cm^{-1}}$ in the spectra of the complexes; coordination through this group to a metal ion is usually implied by a bathochromic shift of the band; but the exact magnitude of the bathochromic shift may be visualized only when the position is compared to that of the free ligand devoid of any

TABLE 3
Electronic spectral data (cm^{-1}) and ligand field parameters of M(II) complexes of Hbpsal

Complex [μ_{eff} (B.M)]	λmax (cm^{-1}) (ν_1, ν_2, ν_3)	Spectroscopic terms of the complex		Dq (cm^{-1})	B′ (cm^{-1})	β	β^0 (%)	LFSE[a]
		SLJ	S′L′J′					
[Mn(bpsal)$_2$(H$_2$O)] [5.89]	15,625	$^6A_{1g}$	$^4T_{1g}(G)$	—	—	—		—
[Co(bpsal)$_2$(H$_2$O)][b] [4.95]	9,090	$^4T_{1g}(F)$	$^4T_{2g}(F)$	1030	869	0.89	11	98.1
	18,348	$^4T_{1g}(F)$	$^4A_{2g}(F)$					
	20,920	$^4T_{1g}(F)$	$^4T_{1g}(P)$					
[Ni(bpsal)$_2$(H$_2$O)][c] [3.05]	10,526	$^3A_{2g}(F)$	$^3T_{2g}(F)$	1052	788	0.75	25	150.0
	17,094	$^3A_{2g}(F)$	$^3T_{1g}(F)$					
	26,315	$^3A_{2g}(F)$	$^3T_{1g}(P)$					
[Cu(bpsal)$_2$(H$_2$O)] [1.90]	14,084	^2E_g	$^2T_{2g}$	1408	—	—		100.6

[a] LFSE values are given in kJmole^{-1}.
[b] $\nu_2/\nu_1 = 2.01$.
[c] $\nu_2/\nu_1 = 1.62$.

TABLE 4
IR spectral data[a] (cm^{-1}) of Hbpsal and the metal complexes

Ligand/complexes	ν(C=N)	ν_{as}(CH$_3$)	ν_s(CH$_2$)	ν(C-O) (phenolic)	ν(O-H) (water)
Hbpsal[b]	1620 s	2955 s	2852 s	1363	—
[Mn(bpsal)$_2$(H$_2$O)$_2$]	1608 s	2955 s	2856 s	1348	3434 b
[Co(bpsal)$_2$(H$_2$O)$_2$]	1610 s	2950 s	2858 s	1340	3454 b
[Ni(bpsal)$_2$(H$_2$O)$_2$]	1610 s	2952 s	2852 s	1348	3445 b
[Cu(bpsal)$_2$(H$_2$O)$_2$]	1610 s	2955 s	2856 s	1348	3445 b
[Zn(bpsal)$_2$(H$_2$O)$_2$]	1608 s	2952 s	2854 s	1340	3454 b

[a] b = broad, s = strong, m = medium and w = weak.
[b] $\nu(OH)_{phenolic}$ occurs at 3490 b.

hydrogen bonding; and (3) An additional prominent and broad band, in contrast to the shallow nature of the $\nu(OH)_{phenolic}$ band in the free ligand, arises in the spectra of all the complexes due to the ν(OH) of coordinated water molecules.

NMR Spectra

The ^{1}H NMR and the ^{13}C{^{1}H} NMR spectral data of Hbpsal and the Zn(II) complex along with the assignments are given in Tables 5 and 6, respectively. The numbering scheme of the carbon atoms of Hbpsal is as shown in Figure 3. The proton NMR spectrum of the ligand (Hbpsal) is expected to show a broad peak (due to phenolic-OH), a singlet (due to $-$N=CH), four doublets (due to C$_2'$H, C$_3''$ H, C$_3$H, and C$_6$H), three triplets (due to C$_4''$H C$_4$H and C$_5$H) and a multiplet due

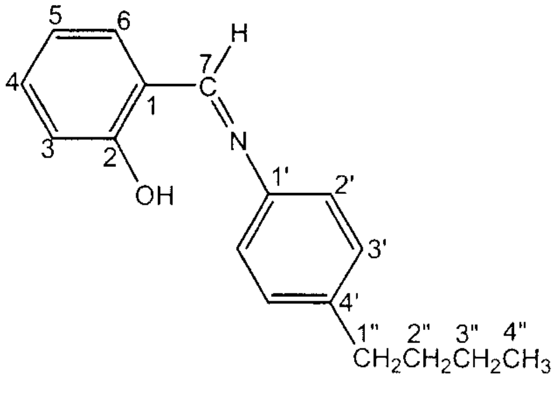

FIG. 3. Numbering scheme of Hbpsal.

TABLE 5
^1H NMR spectral data[a] of Hbpsal and the Zn(II) complex

Proton	Hbpsal	$[Zn(bpsal)_2(H_2O)_2]$
Ar-OH	14.40	absent
$-N{=}CH$	8.70 s	9.00 s
$-CH_3$	0.87 t	0.88 t
$-CH_2$	1.30 m	1.35 m
Ar-H	6.2–8.0 m	6.5–8.3 m

[a] ^1H NMR Spectral data are given in δ with respect to tetramethylsilane; s = singlet; d = doublet; t = triplet; m = multiplet.

to the methylene groups of the alkyl chain. The prominent features in the spectrum of the corresponding Zn(II) complex, as underlined in Table 6, are: (1) the disappearance of the phenolic-OH signal, and (2) a slight downfield shift of the $-N{=}CH$ signal while retaining its singlet nature. These features imply coordination through the phenolate oxygen and the azomethine nitrogen. Further, a new and broad signal, observed in the spectrum of the complex at 3.4 ppm, could be attributed to the coordinated water molecule of the complex.

The $^{13}C\{^1H\}$ NMR spectra of the ligand (Hbpsal) as well as the Zn(II) complex show all the signals expected for the 15 non-equivalent carbon atoms of the ligand. The signal assignments shown in Table 6 were based on the expected positions, which were calculated by applying the principle of substituent additivity.

TABLE 6
$^{13}C\{^1H\}$ NMR spectral data[a] of Hbpsal and the Zn(II) complex

Carbon	Hbpsal	$[Zn(bpsal)_2(H_2O)_2]$
$-N{=}CH$	162.58	163.56
C_1	119.03	119.00
C_2	159.00	160.02
C_3	116.54	116.19
C_4	133.80	133.78
C_5	121.80	121.61
C_6	129.20	129.11
$C_{1'}$	119.23	119.22
$C_{2'}$	145.58	145.51
$C_{3'}$	141.34	141.32
$C_{4'}$	132.21	132.20
$C_{1''}$	32.70	32.54
$C_{2''}$	25.00	25.00
$C_{3''}$	21.70	21.58
$C_{4''}$	13.71	13.64

[a] ^{13}C NMR data measured in ppm (with respect to $CDCl_3$ signal at 77.00 ppm);
s = singlet; d = doublet; t = triplet; m = multiplet.

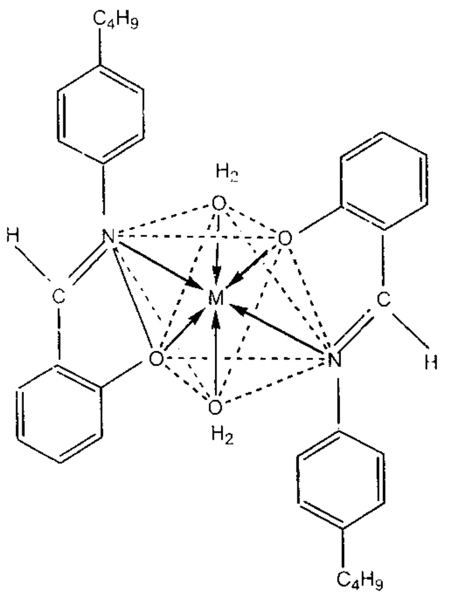

FIG. 4. Proposed structure of $[M(bpsal)_2(H_2O)_2]$.

The $-N{=}CH$ signal appearing at 162.58 in the spectrum of the ligand undergoes downfield shift by 0.98 ppm in the spectrum of the complex, which can be inferred on account of coordination to the metal ion through the azomethine nitrogen (Domiano et al., 1984). The slight downfield shift of the C_2 resonance signal is indicative of bonding through the phenolate oxygen. However, the methyl and methylene carbon signals remain almost at the same positions as in Hbpsal. The slight upfield shift in some of the resonance signals may be attributed to electron delocalization (Paolucci et al., 1980).

CONCLUSION

In the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) the ligand, Hbpsal, acts as a uninegative bidentate ligand coordinating through the azomethine nitrogen and phenolate oxygen where the M:L ratio was found to be 1:2. The metal ion is believed to have an octahedral environment and the additional two sites in the polyhedron are provided by water molecules. The proposed structures are shown in Figure 4.

The Cu(II) complex shows mesogenic activity displaying a smectic-A phase at 98°C (Figure 2) and smectic-E phase at 105°C.

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