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## Ligational aspects of the hydrazide-based Schiff-base, N-(4''-pyridylcarboxamido)-4-(4'-hexyloxybenzoato)salicylaldimine towards some 3d metal ions and crystal structures of the Schiff-base and Zn(II) complex

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## ABSTRACT

A novel hydrazide-based mesogenic (nematic) Schiff-base, N-(4''-pyridylcarboxamido)-4-(4'-hexyloxybenzoato)salicylaldimine, Hpychbsal (abbreviated as H<sub>2</sub>L) was prepared and its structure studied $by elemental analyses, mass, NMR and IR spectra and single crystal XRD (triclinic space group <math>P\bar{1}$  with Z = 4) techniques. The Schiff-base behaves as a uninegative bi/tridentate species in its non-mesogenic complexes of the general formula,  $[M(HL)_2]$  [M = Mn, Co, Ni, Cu and Zn] and as a dinegative tridentate species with Zn(II) in the distorted square-pyramidal complex, [ZnL · 2py], for which the crystal structure was solved (triclinic space group  $P\bar{1}$  with Z = 2). The IR and NMR spectral data imply bonding of HL<sup>-</sup> and L<sup>2-</sup> species through phenolate oxygen and/or amidic oxygen and azomethine nitrogen atoms.

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## 1. Introduction

The chemistry of hydrazine derivatives has been investigated intensively in the last decade owing to their coordinative [1-3] and pharmacological activity [1-3] as well as their use in analytical chemistry as metal-extracting agents [1-3]. As a part of our investigation [4-6] on structural and spectroscopic studies of 3d metal complexes of a series of mesogenic organic Schiff-bases, we report here, the results of our investigations on the synthesis, spectroscopic studies and crystal structure on the hydrazide-based mesogenic Schiff-base, N-(4''-pyridylcarboxamido)-4-(4'-hexyloxybenzoato)-salicylaldimine (H<sub>2</sub>L) and the corresponding 3d metal complexes.

## 2. Experimental

## 2.1. Materials

All reagents were purchased from commercial sources and used as received: 4-hydroxy benzoic acid, 1-bromohexane, 2,4-dihydroxybenzaldehyde, *N*,*N*'-dicyclohexylcarbodiimide (DCC), *N*,*N*dimethylaminopyridine (DMAP) and isonicotinic acid hydrazide are from Sigma–Aldrich, USA; all metal acetates and KOH are from Merck. The solvents received were dried using standard methods [7] when required.

## 2.2. Synthesis

The synthesis of N-(4"-pyridylcarboxamido)-4-(4'-hexyloxybenzoato)salicylaldimine, Hpychbsal (abbreviated as H<sub>2</sub>L) was achieved by proceeding through three steps, *viz.*, alkylation of 4hydroxy benzoic acid, followed by esterification and Schiff-base formation.

4-Alkoxybenzoic acid and 4-alkoxy benzoate ester of 2,4-dihydroxybenzaldehyde (Precursor Chemicals) were prepared as reported earlier [4] by proceeding through two major steps, *viz.*, alkylation of 4-hydroxy benzoic acid, followed by esterification.

 $[M(HL)_2]$  (M = Mn, Co, Ni, Cu and Zn) complexes were prepared by refluxing together hot dry ethanolic solutions of the ligand, H<sub>2</sub>L (0.92 g, 2.0 mmol in 30 mL) and the appropriate metal acetate (1.0 mmol, in 20 mL) for ~2 h at 70 °C. The reaction mixture was left over night in the flask closed with guard tube. The solid complex that separated out in each case was filtered under suction and washed repeatedly with cold ethanol and dried over fused CaCl<sub>2</sub> in a desiccator.

## 2.2.1. Synthesis of N-(4"-pyridylcarboxamido)-4-(4'-hexyloxybenzoato)salicylaldimine

It was prepared by refluxing absolute ethanolic solutions 4-alkoxy benzoate ester of 2,4-dihydroxybenzaldehyde (11.97 g, 35 mmol in 100 mL) and isonicotinic acid hydrazide (4.80 g, 35 mmol in 50 mL) for  $\sim$ 1 h in presence of few drops of acetic acid and leaving the solution over night. The micro-crystalline product was filtered off by suction, thoroughly washed with cold ethanol,

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recrystallized from a solution of absolute ethanol/chloroform (v/v, 1/1) and dried at room temperature; yield: 12.11 g (75%) as a white solid; m.p. 220 °C. <sup>1</sup>H NMR (300 MHz; DMSO-d<sup>6</sup>; / (Hz), Me<sub>4</sub>Si at 25 °C, ppm)  $\delta$  = 0.887 (t,  ${}^{3}I_{H-H}$  = 7.2, 3H, -CH<sub>3</sub>), 1.313-1.773 (m, 8H,  $-CH_2$ ), 4.092 (t,  ${}^{3}J_{H-H}$  = 6.6, 2H,  $-OCH_2$ ), 6.864 (1H, d,  ${}^{3}J_{H-H}$  $_{\rm H}$  = 6.9, -C<sub>5</sub>H), 6.874 (1H, s, -C<sub>3</sub>H), 7.117 (2H, d,  $^{3}J_{\rm H-H}$  = 9.0,  $-C_{3'}H$ ), 7.710 (d,  ${}^{3}J_{H-H}$  = 9.0, 1H,  $-C_{6}H$ ), 7.855 (d,  ${}^{3}J_{H-H}$  = 5.4, 2H,  $-C_{3''}H$ ), 8.064 (d,  ${}^{3}J_{H-H}$  = 8.7, 2H,  $-C_{2'}H$ ), 8.704 (s, 1H, -NCH), 8.800 (d,  ${}^{3}J_{H-H}$  = 8.1, 2H,  $-C_{2''}H$ ), 11.400 (br s, 1H, -NH), and 12.311 (br s, 1H, Ph–OH); <sup>13</sup>C{<sup>1</sup>H} NMR (75.45 MHz; DMSO-*d*<sup>6</sup>; Me<sub>4</sub>Si at 25 °C, ppm)  $\delta$  = 163.841 (-COO), 163.306 (py-CO), 161.353 (-C<sub>4'</sub>), 158.344 (-NCH), 153.136 (-C<sub>2</sub>), 150.399 (-C<sub>4</sub>), 148.001  $(-C_{2''})$ , 139.990  $(-C_{4''})$ , 132.095  $(-C_6)$ , 129.812  $(-C_{2'})$ , 121.512  $(-C_{3''})$ , 120.556  $(-C_{1'})$ , 116.798  $(-C_{1})$ , 114.713  $(-C_{5})$ , 113.436 (-C<sub>3'</sub>) and 109.974 (-C<sub>3</sub>). *m*/*z* (EI): 121 (py-CONH<sup>+</sup>, 100), 205 (C<sub>6</sub>H<sub>13</sub>-Ph-CO<sup>+</sup>, 88), IR (KBr)/cm<sup>-1</sup>: 3435br v(O-H)<sub>phenol</sub>, 3279 v<sub>s</sub>(N-H)<sub>amide</sub>, 1726vs v(>C=O), 1626w v(C=N), 1253s v<sub>as</sub>(C-O)<sub>esteric</sub>, 1153s v(C-O)<sub>phenol</sub>. Anal. Calc. for C<sub>26</sub>H<sub>27</sub>N<sub>3</sub>O<sub>5</sub> (461.51): C, 67.66; H, 5.90; N, 9.10. Found C, 67.58; H, 5.88; N, 9.07%.

#### 2.2.2. Synthesis of [Ni(HL)<sub>2</sub>]

The micro-crystalline product was recrystallized from a solution of absolute ethanol/chloroform (v/v, 1/1) and dried at room temperature; yield: 0.67 g (68%) as an orange coloured solid; m.p. 310 °C (decompose). <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; J(Hz), Me<sub>4</sub>Si)  $\delta = 0.922$  (t,  ${}^{3}J_{H-H} = 6.0$ , 3H,  $-CH_{3}$ ), 1.255–1.852 (m, 8H,  $-CH_{2}$ ), 4.053 (t,  ${}^{3}J_{H-H} = 6.6$ , 2H,  $-OCH_{2}$ ), 6.787 (d,  ${}^{3}J_{H-H} = 6.9$ , 1H,  $-C_{5}$ H), 6.850 (s, 1H,  $-C_{3}$ H), 6.972 (d,  ${}^{3}J_{H-H} = 8.4$ , 2H,  $-C_{3'}$ H), 7.129 (d,  ${}^{3}J_{H-H} = 8.5$ , 1H,  $-C_{6}$ H), 8.103 (d,  ${}^{3}J_{H-H} = 7.8$ , 2H,  $-C_{3''}$ H), 8.164 (d,  ${}^{3}J_{H-H}$  = 8.0, 2H,  $-C_{2'}$ H), 8.770 (s, 1H, -NCH), 8.805 (d,  ${}^{3}J_{H-H}$  = 7.9, 2H, -C<sub>2"</sub>H), 11.399 (br s, 1H, -NH), and (Ph-OH) absent; <sup>13</sup>C{<sup>1</sup>H} NMR (75.45 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si at 25 °C, ppm)  $\delta$  = 163.933 (-COO), 163.504 (py-CO), 164.132 (-NCH), 150.713 (-C<sub>4</sub>), 132.433  $(-C_6)$ , 132.054  $(-C_{2'})$ , 120.936  $(-C_{1'})$ , 114.549  $(-C_{3'})$  and 110.791 (-C<sub>3</sub>). *m*/*z* (FAB): 121 (py-CONH<sup>+</sup>, 100), IR (KBr)/cm<sup>-1</sup>: 3280br v<sub>s</sub>(N-H)<sub>amide</sub>, 1722vs v(C=O), 1612w v(C=N), 1255s v<sub>as</sub>(C-O)<sub>esteric</sub>, 1150s v(C-O)<sub>phenol</sub>, 485s v(Ni-N), 450s v(Ni-O). Anal. Calc. for C<sub>52</sub>H<sub>52</sub>N<sub>6</sub>O<sub>10</sub>Ni (979.70): C, 63.75; N, 8.58; N<sub>2</sub>H<sub>4</sub>, 6.53; Ni, 5.99. Found: C, 63.72; N 8.51; N<sub>2</sub>H<sub>4</sub>, 6.50; Ni, 5.96%.

#### 2.2.3. Synthesis of $[Zn(HL)_2]$

Yield: 0.71 g (72%) as a yellow solid; m.p. 230 °C (decompose); <sup>1</sup>H NMR (300 MHz; C<sub>5</sub>D<sub>5</sub>N; *J* (Hz), Me<sub>4</sub>Si)  $\delta$  = 0.847 (t, <sup>3</sup>*J*<sub>H-H</sub> = 6.2, 3H,  $-CH_3$ ), 1.235–1.718 (m, 8H,  $-CH_2$ ), 3.981 (t,  ${}^{3}J_{H-H} = 6.5$ , 2H,  $-OCH_2$ ), 6.774 (d,  ${}^{3}J_{H-H} = 6.0$ , 1H,  $-C_5H$ ), 6.850 (s, 1H,  $-C_3H$ ), 7.196 (d,  ${}^{3}J_{H-H}$  = 8.0, 2H,  $-C_{3'}$ H), 7.438 (d,  ${}^{3}J_{H-H}$  = 8.1, 1H,  $-C_{6}$ H), 7.387 (d,  ${}^{3}J_{H-H}$  = 8.0, 2H,  $-C_{3''}$ H), 7.583 (d,  ${}^{3}J_{H}$ -H = 8.0, 2H,  $-C_{2'}H$ ), 8.750 (s, 1H, -NCH), 8.791 (d,  ${}^{3}J_{H-H} = 7.9$ , 2H,  $-C_{2''}H$ ), 11.394 (br s, 1H, -NH), and (Ph-OH) absent; <sup>13</sup>C{<sup>1</sup>H} NMR (75.45 MHz; C<sub>5</sub>D<sub>5</sub>N; Me<sub>4</sub>Si at 25 °C, ppm)  $\delta$  = 163.930 (-COO), 172.415 (py-CO), 168.517 (-NCH), 150.369 (-C<sub>4</sub>), 132.624 (-C<sub>6</sub>), 114.979 ( $-C_{3'}$ ) and 108.213 ( $-C_{3}$ ). m/z (FAB): 121 (py-CONH<sup>+</sup>, 100), IR (KBr)/cm<sup>-1</sup>: 3280  $\nu_s$ (N–H)<sub>amide</sub>, 1724vs  $\nu$ (>C=O), 1608w v(C=N), 1253s vas(C-O)esteric, 1148s v(C-O)phenol, 482s v(Zn-N), 448s v(Zn-O); the IR data for  $[M(HL)_2]$  (M = Mn, Co and Cu) are similar. Anal. Calc. for  $C_{52}H_{52}N_6O_{10}Zn(984.30)$ : C, 63.32; N, 8.52; N<sub>2</sub>H<sub>4</sub>, 6.50; Zn, 6.63. Found: C, 63.29; N 8.50; N<sub>2</sub>H<sub>4</sub>, 6.47; Zn, 6.60%.

#### 2.2.4. Synthesis of $[ZnL \cdot 2py]$

Light-yellow coloured crystalline solid; <sup>1</sup>H NMR (300 MHz; C<sub>5</sub>D<sub>5</sub>N; *J* (Hz), Me<sub>4</sub>Si)  $\delta$  = 0.845 (t, <sup>3</sup>*J*<sub>H-H</sub> = 6.1, 3H, -CH<sub>3</sub>), 1.230–1.711 (m, 8H, -CH<sub>2</sub>), 3.979 (t, <sup>3</sup>*J*<sub>H-H</sub> = 6.3, 2H, -OCH<sub>2</sub>), 6.769 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.1, 1H, -C<sub>5</sub>H), 6.852 (s, 1H, -C<sub>3</sub>H), 7.211 (d, <sup>3</sup>*J*<sub>H-H</sub> = 8.3, 2H, -C<sub>3</sub>''H), 7.430 (d, <sup>3</sup>*J*<sub>H-H</sub> = 8.0, 1H, -C<sub>6</sub>H), 7.390 (d, <sup>3</sup>*J*<sub>H-H</sub> = 8.3, 2H, -C<sub>3</sub>''H), 7.580 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.9, 2H, -C<sub>2</sub>'H), 8.755 (s, 1H, -NCH), 8.788 (d, <sup>3</sup>*J*<sub>H-H</sub> = 8.2, 2H, -C<sub>2</sub>''H); <sup>13</sup>C{<sup>1</sup>H} NMR (75.45 MHz;

C<sub>5</sub>D<sub>5</sub>N; Me<sub>4</sub>Si at 25 °C, ppm)  $\delta$  = 164.330 (−COO), 170.517 (−NCH), 151.468 (−C<sub>4</sub>), 131.689 (−C<sub>6</sub>), 114.980 (−C<sub>3'</sub>) and 108.218 (−C<sub>3</sub>), IR (KBr)/cm<sup>-1</sup>: 1725vs v(>C=O), 1605s v(C=N), 1256s  $v_{as}(C=O)_{esteric}$ , 1140s  $v(C=O)_{phenol}$ , 478s v(Zn=N), 455s v(Zn=O). Anal. Calc. for C<sub>36</sub>H<sub>35</sub>N<sub>5</sub>O<sub>5</sub>Zn (683.08): C, 63.30; N, 10.25; N<sub>2</sub>H<sub>4</sub>, 4.68; Zn, 9.57. Found: C, 63.29; N 10.21; N<sub>2</sub>H<sub>4</sub>, 4.65; Zn, 9.55%.

#### 2.3. Physical measurements

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL AL-300 MHz FTNMR multinuclear spectrometer; C, H, and N contents were micro analyzed on Elemental Vario EL III Carlo Erba 1108 analyzer. Infrared spectra were recorded on JASCO FT/IR (model-5300) spectrophotometer in the 4000–400 cm<sup>-1</sup> region. The mass spectra were recorded on JEOL SX-102 (EI/FAB) mass spectrometers. The UV–Vis spectra were recorded on Shimadzu spectrophotometer, model, Pharmaspec, UV 1700. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday balance.

# 2.4. X-ray crystallographic data collection and refinement of the structure

X-ray data for compounds  $H_2L$  [*ab83m*] and [*ZnL* · 2*py*] [ab64m] were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Ka radiation ( $\lambda$  = 0.71073 Å) with  $\omega$ -scan method. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined from the setting angles of 9745/8981 reflections in the range of  $2.69^{\circ} < \theta < 27.85^{\circ}$  $2.25^{\circ} < \theta < 27.37^{\circ}$ . Integration and scaling of intensity data was accomplished using SAINT program [8]. The structure was solved by direct methods using SHELXS97 [9] and refinement was carried out by full-matrix least-squares technique using SHELXL97 [9]. Anisotropic displacement parameters were included for all nonhydrogen atoms. In [ZnL · 2py], the atoms C22, C23 and C24 are disordered over two positions and their site-occupation factors were refined to 0.737(6) and 0.263(6). The distance of the disordered side chain atoms were restraint with DFIX command. In H<sub>2</sub>L, all N-bound H atoms, O-bound H atoms and H atoms of the water molecules were located in a difference Fourier map and their positions and isotropic parameters were refined. All other hydrogen atoms were positioned geometrically and treated as riding atoms, with C–H distances in the range of 0.93–0.97 Å and with  $U_{iso}(H)$  values of  $1.5U_{eq}(C)$  for methyl hydrogen and  $1.2U_{eq}(C)$  for other hydrogen atoms.

Magnetic and electronic spectral data <sup>a</sup> of complexes of H <sub>2</sub> L	

Complex	Colour	μ <sub>eff</sub> (BM)	d-d transitions (cm <sup>-1</sup> )	Transition		Assignment
				Ground state(s)	Excited state(s)	
[Mn(HL) <sub>2</sub> ]	yellow	5.14	30120, 24038	$^6A_{1g}$	${}^{4}E_{g}(D);$ ${}^{4}A_{1g}$	octahedral
[Co(HL) <sub>2</sub> ]	reddish brown	diamag.	13333, 23310	<sup>2</sup> B <sub>2</sub> ; <sup>2</sup> E	<sup>2</sup> A <sub>1</sub> ; <sup>2</sup> A <sub>1</sub>	square pyramidal <sup>b</sup> (l.s.) (M–M bonding)
[Ni(HL) <sub>2</sub> ]	yellow	diamag.	23474, 25773	$^{1}A_{1g}$	<sup>1</sup> A <sub>2g</sub> ; <sup>1</sup> B <sub>1g</sub>	square planar
[Cu(HL) <sub>2</sub> ]	yellowish green	3.67	15798	xy	$x^2 - y^2$	octahedral

<sup>a</sup> Spectra recorded in solutions of DMSO/chloroform (1:1 v/v).

<sup>b</sup> The ground state configuration with increasing energy:  $(xy, (b_2)^2)$ ;  $(xz, yz, (e))^4$ ;  $(z^2, (a_1))$ .

Crystal data and structure refinement parameters of ligand H\_2L [ab83m] and  $[ZnL\cdot 2py]~[\textit{ab64m}]$ 

Empirical formula	C26H29N3O6	C36H35N5O5Zn
Formula weight	479.52	683.06
Cell axes (Å)		
а	11.1888(6)	10.2286(8)
b	13.1068(7)	11.6022(9)
С	18.2186(10)	17.0491(13)
Cell angles (°)		
α	80.904(1)	108.619(1)
β	74.771(1)	90.103(1)
γ	73.494(1)	115.916(1)
Cell volume V (Å) <sup>3</sup>	2461.6(2)	1700.7(2)
Crystal system	triclinic	triclinic
Crystal size (mm)	$0.19 \times 0.14 \times 0.09$	$16\times10\times0.06$
Temperature (K)	273(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Space group	PĪ	PĪ
F(000)	1016	712
Density (Mg/m <sup>3</sup> )	1.294	1.334
No form. Unit Z	4	2
Absorption coefficient (mm <sup>-1</sup> )	0.093	0.771
Reflections collected/unique [R(int)]	23929/8669 [0.0229]	16496/5968 [0.0204]
Completeness to $\theta$ = 25.00 (%)	99.7	99.7
Absorption correction	none	none
Refinement method	full-matrix least-	full-matrix least-
	squares on F <sup>2</sup>	squares on $F^2$
Data/restraints/parameters	8669/0/665	5968/79/452
H min, max	-13, 13	-12, 12
K min, max	-15, 15	–13, 13
L min, max	-21, 21	-20, 20
$\theta$ min, max	1.16, 25.0	2.02, 25.0
Goodness-of-fit on F <sup>2</sup>	1.029	1.044
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0403,$	$R_1 = 0.0353$ ,
	$wR_2 = 0.1020$	$wR_2 = 0.0948$
R indices (all data)	$R_1 = 0.0502,$	$R_1 = 0.0387$ ,
	$wR_2 = 0.1107$	$wR_2 = 0.0975$
Largest difference peak and hole ( $e \text{ Å}^{-3}$ )	0.202 and -0.195	0.289 and -0.194

#### 3. Results and discussion

#### 3.1. Physical properties and spectral investigation

The white-coloured Schiff-base ligand ( $H_2L$ ) is soluble in hot chloroform, DMSO, DMF and pyridine but insoluble in water, methanol, ethanol, and acetonitrile; the orange-coloured Ni(II) complex, [Ni(HL)<sub>2</sub>], is soluble in chloroform, and hot DMSO and DMF; [Zn(HL)<sub>2</sub>]/[ZnL · 2py] is only soluble in hot/cold pyridine; all other complexes are soluble in DMSO, DMF and pyridine. The Schiff-base showed a nematic meso-phase at 168 °C under a polar-

izing microscope while none of the corresponding metal complexes were found to show any mesogenic behaviour. The structures and purity of the parent ligand and of the complexes were checked and confirmed by elemental analyses and IR, <sup>1</sup>H NMR and EI/FAB mass spectra.

The room temperature magnetic moments and electronic spectral data of the present complexes are included in Table 1. The overall geometry around the metal ion has been assigned (Table 1) not only on the basis of  $\mu_{\text{eff}}$  values and the nature of the electronic spectra, but also on the basis of denticity of the ligand (vide IR and NMR) and the number of the ligands coordinated to the metal ion (vide elemental analyses). The  $\mu_{eff}$  values imply anti-ferromagnetic/ferromagnetic type interactions in the Mn(II) and Cu(II) complexes respectively. The Mn<sup>II</sup> complex provides with extremely weak bands in the electronic spectrum in an octahedral environment of the metal ion [10]. The diamagnetic reddish brown complex. [Co(HL)<sub>2</sub>], may be understood to have a low-spin squarepyramidal geometry with M-M bonding [11]. The yellow-coloured complex, [Ni(HL)<sub>2</sub>], implies square-planar [12] type geometry; it is fairly common practice to assign the first band to the  ${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$ transition and the second major band to the  ${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$  transition assuming a square-planar geometry [13].

In the IR spectrum of H<sub>2</sub>L the broad absorptions centered at 3435 and 3279 cm<sup>-1</sup> may be assigned to the  $v(O-H)_{phenol}$  and  $v_s(N-H)_{amide}$  vibration [14]; further, the strong bands occurring at 1726 and 1253 cm<sup>-1</sup> may be assigned [14] to  $v(\supset C=O)$  and v(C-O) modes of aromatic ester; the band occurring at 1626 cm<sup>-1</sup> may be assigned to v(C=N) absorption of the azomethine moiety; these bands are shifted to lower frequencies in the complexes, indicating that the nitrogen atom of the azomethine group is coordinated to the metal ion [15]. Coordination through a nitrogen atom of the ligand is also implied by the appearance of a new band in the complexes in the region, 468–485 cm<sup>-1</sup>, assignable to v(M-N) [16,17]. Coordination through phenolate oxygen to the metal ion is implied by the shifts of the v(C-O) band in the complexes [18] and by the appearance of new bands, assignable to v(M-O), in the 443–455 cm<sup>-1</sup> region in the spectra of the complexes.

A comparison of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectral data of the ligand with those of the Ni(II) and Zn(II) complexes shows the absence of the phenolic-OH signal (12.311 ppm) and a significant shift in the peak position of the -N=CH signal [from 8.704 ppm of the ligand to 8.770, 8.750, and 8.755 ppm in [Ni(HL)<sub>2</sub>], [Zn(HL)<sub>2</sub>] and [ZnL · 2py], respectively] and the absence of the -N-H signal at 11.400 ppm exclusively in [ZnL · 2py], a complex of the di-deprotonated ligand, imply bonding through the phenolate oxygen and azomethine nitrogen atoms. Similar shifts observed in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra were of considerable magnitude in the case of the carbon atoms directly attached to the bonding atoms and



Fig. 1. Molecular structure and atomic labeling scheme of the H<sub>2</sub>L [ab83m] of 30% ellipsoid probability.



Fig. 2. Packing of molecules in the unit cell of H<sub>2</sub>L [ab83m] showing intermolecular and intramolecular H-bonding.



Fig. 3. Molecular structure and atomic labeling scheme of [ZnL · 2py] [ab64m] of 30% ellipsoid probability.



**Fig. 4.** Packing diagram of molecules  $[ZnL \cdot 2py]$  [*ab64m*] along *a*-axis in the unit cell.

amidic carbon. Thus, the NMR spectral data imply bi-dentate bonding (>C=N, and phenolate oxygen) of HL<sup>-</sup> in [Ni(HL)<sub>2</sub>] and tri-dentate bonding (>C=N, phenolate oxygen and amidic oxygen) of HL<sup>-</sup> and L<sup>2-</sup>, respectively in [Zn(HL)2] and [ZnL · 2py].

## 3.2. Crystal structure and molecular association

Both ligands  $[H_2L]$  [*ab83m*] and  $[ZnL \cdot 2py]$  [*ab64m*] are crystallized in triclinic space group, *viz.*,  $P\overline{1}$  with Z = 4 and Z = 2, respectively. The crystal data and structure refinement details for  $[H_2L]$  [*ab83m*] and [ZnL  $\cdot$  2py] [*ab64m*] are given in Table 2. The asymmetric unit of H<sub>2</sub>L contains two crystallographically independent molecules and two water molecules, while [ZnL  $\cdot$  2py] comprises one ligand molecule and two pyridine solvent molecules in the asymmetric unit. The molecular structure and atomic labeling scheme of the ligand and the Zn(II) complex are as shown in Figs. 1 and 3 and the packing diagrams of the ligand and the complex are as shown in Figs. 2 and 4.

The bond distances and angles for the  $[ZnL \cdot 2py]$  complex are shown in Table 3. As per the crystal structure of the complex, the ligand coordinates to the Zn(II) ion through phenolate oxygen (O(2)), amidic oxygen (O(1))and azomethine nitrogens (N(1)); further, two pyridine molecules act as solvent molecules, thus, rendering the overall geometry around Zn(II) to distorted square pyramid. The details of the hydrogen-bonded geometry of H<sub>2</sub>L are tabulated in Table 4. The crystal structure of H<sub>2</sub>L is stabilized by both intra- and intermolecular N–H…O, O–H…N and O– H…O hydrogen bond interactions. The two water molecules bridge

Table 3
Bond lengths (Å) and angles (°) involved in the square pyramidal unit of the complex
[ZnL · 2py] [ <b>ab64m</b> ]

N(1)-	2.0370(16)	N(1)-Zn(1)-	115.83(6)	O(1)-Zn(1)-	93.71(6)
Zn(1)		N(5)		N(4)	
N(4)-	2.0793(17)	N(1)-Zn(1)-	140.04(7)	O(2)-Zn(1)-	88.80(6)
Zn(1)		N(4)		N(1)	
N(5)-	2.0737(17)	N(5)-Zn(1)-	103.60(7)	O(2)-Zn(1)-	91.50(7)
Zn(1)		N(4)		N(4)	
0(1)-	2.0764(14)	N(1)-Zn(1)-	76.96(6)	O(2)-Zn(1)-	98.83(7)
Zn(1)		O(1)		N(5)	
0(2)-	1.9840(14)	N(5)-Zn(1)-	95.51(6)	O(2) - Zn(1) -	163.15(7)
Zn(1)		0(1)		0(1)	

Table 4 Hydrogen bonds geometry  $(\hat{A}, \circ)$  for the ligand H<sub>2</sub>L [*ab83m*]

D–HA	d(D- H)	<i>d</i> (HA)	<i>d</i> (DA)	<i>d</i> (DA)	Symmetry
N(2)- H(2N)O(1W)#1	0.92(2)	1.87(2)	2.793(2)	178(2)	x + 1, y, z
N(5)- H(5N)O(2W)#1	0.90(2)	1.91(2)	2.804(2)	173(2)	x + 1, y, z
O(2)-H(2O)N(3)	0.91(2)	1.80(2)	2.613(2)	146(2)	x, y, z
O(7)-H(7O)N(6)	0.86(2)	1.82(2)	2.587(2)	148(2)	x, y, z
O(1W)- H(1W)N(4)#2	0.89(2)	1.94(2)	2.828(2)	174(2)	-x + 2, -y + 2, -z
O(1W)- H(2W)O(6)#3	0.86(2)	1.99(2)	2.846(2)	174(2)	<i>x</i> , <i>y</i> – 1, <i>z</i>
O(2W)– H(3W)O(1)#4	0.82(2)	2.17(2)	2.986(2)	171(2)	<i>x</i> – 1, <i>y</i> , <i>z</i>
O(2W)– H(4W)N(1)#2	0.88(2)	1.97(3)	2.846(2)	173(2)	-x + 2, -y + 2, -z

the two ligand molecules through O-H...N and O-H...O hydrogen bonds, thereby forming an infinite hydrogen bonded network chain along the crystallographic *a* axes. Only the non-conventional interactions, *viz.*, C-H...O and C-H...N, are observed in the crystal structure of the [ZnL · 2py] complex.

## 4. Conclusion

The mesogenic (nematic) Schiff-base, N-(4"-pyridylcarboxamido)-4-(4'-hexyloxy-benzoato)salicylaldimine (H<sub>2</sub>L) coordinates to M(II) (M = Mn, Co, Ni, Cu, Zn) as a uninegative tri-dentate species to yield non-mesogenic complexes of the type, [M(HL)<sub>2</sub>], which are believed to involve M–M bonding. The complex [Zn(HL)<sub>2</sub>] gives rise, from a solution of pyridine, to single crystals of the non-mesogenic square-pyramidal complex, [ZnL · 2py]; as per the crystal structure, the complex involves di-negative tridentate species of the ligand, L<sup>2–</sup>, which coordinates to the metal ion through phenolate oxygen, amidic oxygen and azomethine nitrogen atoms.

### 5. Supplementary data

CCDC 672486 and 672487 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or

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