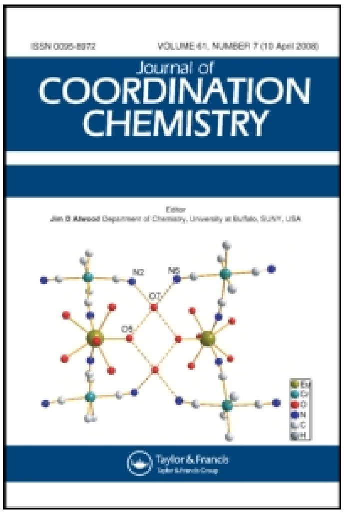

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Mono- and dinuclear Zn(II) complexes of Schiff-base ligands: syntheses, characterization and studies of photoluminescence

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To cite this Article Chattopadhyay, Tanmay , Mukherjee, Madhuparna , Banu, Kazi Sabnam , Banerjee, Arpita , Suresh, Eringathodi , Zangrando, Ennio and Das, Debasis(2009) 'Mono- and dinuclear Zn(II) complexes of Schiff-base ligands: syntheses, characterization and studies of photoluminescence', Journal of Coordination Chemistry, 62: 6, 967 — 979

To link to this Article: DOI: 10.1080/00958970802385837

URL: http://dx.doi.org/10.1080/00958970802385837

Journal of Coordination Chemistry
Vol. 62, No. 6, 20 March 2009, 967–979

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Mono- and dinuclear Zn(II) complexes of Schiff-base ligands: syntheses, characterization and studies of photoluminescence

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(*Received 2 April 2008; in final form 9 June 2008*)

Six Schiff-bases HL^1-HL^4, L^5 and L^6 [HL^1 = 2,6-*bis*[1-(2-aminoethyl)pyrolidine-iminomethyl]-4-methyl-phenol, HL^2 = 2,6-*bis*[1-(2-aminoethyl)piperidine-iminomethyl]-4-methyl-phenol, HL^3 = *N*-{1-(2-aminoethyl)pyrolidine}salicylideneimine, HL^4 = *N*-{1-(2-aminoethyl)piperidine}salicylideneimine, L^5 = 2-benzoyl pyridine-*N*-{1-(2-aminoethyl)pyrolidine}, L^6 = 2-benzoyl-pyridine-*N*-{1-(2-aminoethyl)piperidine}] have been synthesized and characterized. Zn(II) complexes of those ligands have been prepared by conventional sequential route as well as by template synthesis. The same complexes are obtained from the two routes as evident from routine physicochemical characterizations. All the Schiff-bases exhibit photoluminescence originating from intraligand (π–π^*) transitions. Metal mediated fluorescence enhancement is observed on complexation of HL^1-HL^4 with Zn(II), whereas metal mediated fluorescence quenching occurs in Zn(II) complexes of L^5 and L^6.

Keywords: Schiff-bases; Zinc complexes; Photoluminescence property

1. Introduction

Zinc is essential to all forms of life [1] and the second most abundant trace metal after iron in biological systems. Its role in many cases is functional and in other cases structural [2]. Natural selection of zinc to carry on various functions is from intrinsic versatility of coordination and geometry, kinetic lability of its complexes and on its ability to act as a Lewis acid catalyst. ^{1}H NMR and fluorescence spectroscopy are used to study Zn-enzymes as well as their model compounds [3]. Search for reagents which can be fluorescence sensors for zinc(II) has been an active area [4–15]. Schiff-bases do fluoresce, but systematic studies of photo-luminescence of Schiff-base complexes of Zn(II), especially the utilization of Schiff-bases as sensor

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802385837

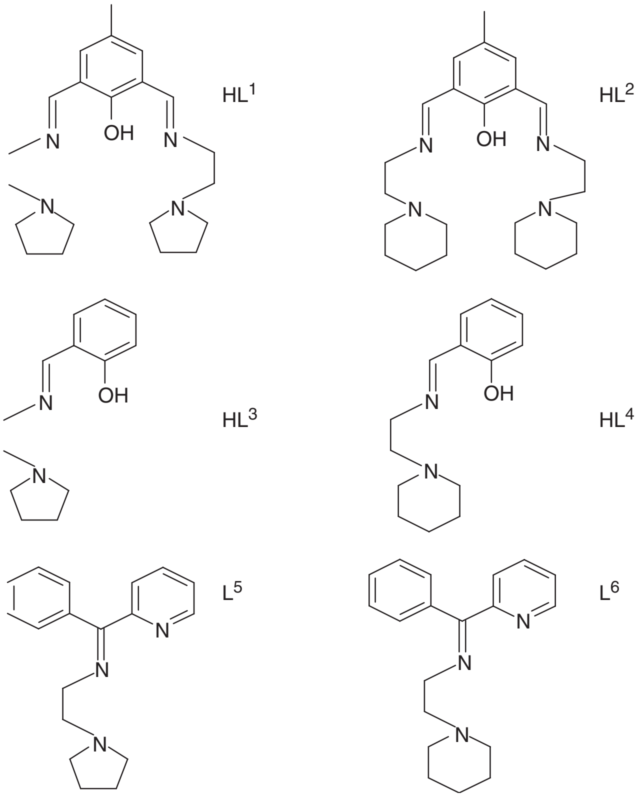

Chart 1.

for Zn(II), are not well explored [16–20]. To get a better understanding of how the structural features of Schiff-bases control the intrinsic luminescence, as well as that of their Zn(II) complexes, we have designed six Schiff-bases (chart 1) and herein report the syntheses, characterization and spectroscopic studies of these and the corresponding Zn(II) complexes.

2. Experimental

2.1. *Materials*

High purity salicylaldehyde, 2-benzoylpyridine, and 1-(2-aminoethyl)pyrolidine were purchased from Fluka and 1-(2-aminoethyl)piperidine from Lancaster Chemical Company Inc. Zinc(II) chloride was purchased from Merck Chemical Company Inc. and used as received. 2,6-diformyl-4-methylphenol was prepared according to the literature method [21]. All other chemicals were of AR grade.

2.2. *Physical measurements*

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on KBr disks

(400–4000 cm^{-1}) with a Perkin-Elmer RXI FTIR spectrophotometer. Uv–Vis spectra were measured on a Hitachi U-3501 spectrophotometer. Fluorescence spectra of the ligands and complexes were recorded in acetonitrile solution with a Perkin-Elmer model LS 50B Luminescence spectrometer. Quantum yields of the ligands as well as the complexes were determined at room temperature by a relative method using anthracene as the standard [22]. Molar conductance measurements were performed in a Systronics 304 conductivity meter. The cell constant was calibrated with 0.02 M KCl solution. Thermal analyses (TG–DTA) were carried out on a Shimadzu DT-30 thermal analyzer in flowing dinitrogen (flow rate: 30 cm^3 min^{-1}).

2.3. *Synthesis of ligands*

HL^1: An ethanolic solution (5 mL) of 1-(2-aminoethyl)pyrolidine (0.228 g, 2 mmol) was added dropwise to a heated ethanolic solution (10 mL) of 2,6-diformyl-4-methylphenol (0.164 g, 1 mmol) and the resulting deep yellow solution was stirred for 24 h. Then the solvent was removed under reduced pressure, giving a yellow liquid from which pure HL^1 was isolated through column chromatography. Yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$; δ): 1.68–1.78 (m, 8H), 2.22 (s, 3H, Ar–CH_3), 2.43–2.56 (m, 8H), 2.77 (t, $J = 7.4$, 4H), 3.71 (t, $J = 7.8$, 4H), 7.67 (s, 2H, Ar–H), 8.28 (s, HC=N) and 10.12 (s, Ph–OH); ^{13}C NMR (300 MHz, δ, $CDCl_3$): 164.8, 163.78, 161.7, 138.0, 131.7, 57.7, 56.2, 54.3, 23.4 and 19.9.

HL^2: This ligand was prepared similarly to HL^1 by using 1-(2-aminoethyl)piperidine (0.256 g, 2 mmol) instead of 1-(2-aminoethyl)pyrolidine. It was also a yellow liquid at room temperature. Yield: 83%. ^{1}H NMR (300 MHz, $CDCl_3$; δ): 1.17–1.25 (m, 4H), 1.51–1.52 (m, 8H), 2.13 (s, 3H), 2.20–2.41 (m, 8H), 2.59 (t, $J = 7.5$, 4H), 3.66 (t, $J = 7.7$, 4H), 7.35 (s, 2H, Ar–H), 8.48 (s, HC=N), 10.42 (s, Ph–OH); ^{13}C NMR (300 MHz, δ, $CDCl_3$): 164.8, 159.4, 132.1, 131.8, 127.1, 59.4, 55.7, 54.6, 25.7, 24.0 and 20.0.

HL^3: An ethanolic solution (5 mL) of 1-(2-aminoethyl)pyrolidine (0.114 g, 1 mmol) was added dropwise to a heated ethanolic solution (10 mL) of salicylaldehyde (0.122 g, 1 mmol) and the resulting mixture was stirred for 2 h. Then, under reduced pressure, solvent was removed leaving an oily mixture. Column chromatographic separation yielded pure ligand as yellow liquid. Yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$; δ): 1.64–1.68 (m, 4H), 2.44–2.48 (m, 4H), 2.68 (t, $J = 7.2$, 2H), 3.62 (t, $J = 6.9$, 2H), 6.76 (t, $J = 15.0$, 1H, Ar–H), 6.84 (d, $J = 9.0$, 1H, Ar–H), 7.10–7.19 (m, 2H, Ar–H), 8.23 (s, 1H, HC=N), 13.37 (s, br, Ph–OH); ^{13}C NMR (300 MHz, δ, $CDCl_3$): 165.2, 161.0, 131.9, 131.0, 118.6, 118.2, 116.7, 58.7, 56.5, 54.3 and 23.3.

HL^4 was prepared similarly to HL^3 by using 1-(2-aminoethyl)piperidine (0.128 g, 1 mmol) instead of 1-(2-aminoethyl)pyrolidine, and the ligand was also oily in nature at room temperature. Yield: 77%. ^{1}H NMR (300 MHz, $CDCl_3$; δ): 1.34–1.37 (m, 2H), 1.46–1.53 (m, 4H), 2.35–2.57 (m, 4H), 2.53–2.57 (t, $J = 6.9$, 2H), 3.60–3.65 (t, $J = 6.5$, 2H), 6.73–6.76 (t, $J = 14.0$, 1H, Ar–H), 6.86 (d, $J = 8.5$, 1H, Ar–H), 7.11–7.16 (m, 2H, Ar–H), 8.23 (s, 1H, HC=N), 13.41 (s, br, Ph–OH); ^{13}C NMR (300 MHz, δ, $CDCl_3$): 165.3, 161.1, 131.9, 131.0, 118.6, 118.2, 116.8, 59.3, 56.8, 54.6, 25.7 and 24.0.

L^5: An ethanolic solution (5 mL) of 1-(2-aminoethyl)pyrolidine (0.114 g, 1 mmol) was slowly added to a heated ethanolic solution (10 mL) of 2-benzoylpyridine (0.183 g, 1 mmol) and the resulting mixture was refluxed for 24 h. Then under reduced pressure solvent was removed and an oily mixture was obtained. Column chromatographic separation yielded pure ligand as a yellow liquid. Yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$; δ): 1.67–1.71 (m, 4H), 2.46–2.52 (m, 4H), 2.75–2.83 (m, 2H), 3.45–3.57 (m, 2H), 7.13–8.63 (m, 9H, Ar–H).

L^6 was prepared similarly to HL^5 by using 1-(2-aminoethyl)piperidine (0.128 g, 1 mmol) instead of 1-(2-aminoethyl)pyrolidine. Yield: 81%. Yield: 0.24 gm (81%). ^{1}H NMR (300 MHz, $CDCl_3$; δ): 1.34–1.39 (m, 2H), 1.48–1.59 (m, 4H), 2.34–2.47 (m, 4H), 2.49 (t, $J = 5.8$, 2H), 3.49 (t, $J = 6.1$, 2H), 7.14–8.64 (m, 9H, Ar–H).

2.4. *Synthesis of the complexes*

The complexes were prepared by two routes: (a) conventional sequential route and (b) template synthetic route.

(a) **Synthesis of the complexes by conventional sequential route**:

$[Zn_2L^1Cl_3]$ (1): A methanolic solution (5 mL) of $ZnCl_2$ (0.272 g, 2 mmol) was added dropwise to a heated methanolic solution (10 mL) of HL^1 (0.356 g, 1 mmol) and the resulting mixture was stirred for 24 h. Yield: 80%. Anal. Calcd for $[Zn_2L^1Cl_3]$ (**1**): C, 42.63; H, 5.24; N, 9.47. Found: C, 42.62; H, 5.23; N, 9.64. Ω ($ohm^{-1}\,cm^2\,mol^{-1}$): 12.8. Selected IR data on KBr (ν/cm^{-1}): 1646, 1548, 1452.

$[Zn_2L^2Cl_3]$ (2) was prepared by following the procedure adopted for **1** with HL^2 (0.384 g, 1 mmol) instead of HL^1. Yield: 78%. Anal. Calcd for $[Zn_2L^2Cl_3]$ (**2**): C, 44.58; H, 5.65; N, 9.04. Found: C, 44.57; H, 5.66; N, 9.03. Ω ($ohm^{-1}\,cm^2\,mol^{-1}$): 12.6. Selected IR data on KBr (ν/cm^{-1}): 1644, 1546, 1455.

$[Zn(H)L^3Cl_2] \cdot H_2O$ (3): A methanolic solution (5 mL) of $ZnCl_2$ (0.136 g, 1 mmol) was added dropwise to a heated methanolic solution (10 mL) of HL^3 (0.218 g, 1 mmol) and the resulting mixture was stirred for 12 h. Yield: 76%. Anal. Calcd for $[Zn(H)L^3Cl_2] \cdot H_2O$ (**3**): C, 44.19; H, 4.81; N, 7.93. Found: C, 44.20; H, 4.82; N, 7.94. Ω ($ohm^{-1}\,cm^2\,mol^{-1}$): 10.2. Selected IR data on KBr (ν/cm^{-1}): 1632, 1540, 1448.

$[Zn(H)L^4Cl_2] \cdot H_2O$ (4) was prepared following the same method as for **3** with HL^4 (0.232 g, 1 mmol) instead of HL^3. Yield: 78%. Anal. Calcd for $[Zn(H)L^4Cl_2] \cdot H_2O$ (**4**): C, 77.41; H, 7.52; N, 15.05. Found: C, 77.42; H, 7.51; N, 15.06. Ω ($ohm^{-1}\,cm^2\,mol^{-1}$): 9.4. Selected IR data on KBr (ν/cm^{-1}): 1630, 1539, 1460.

$[ZnL^5Cl_2]$ (5): A methanolic solution (5 mL) of $ZnCl_2$ (0.136 g, 1 mmol) was added dropwise to a heated methanolic solution (10 mL) of HL^5 (0.279 g, 1 mmol) and the resulting mixture was refluxed for 24 h. Yield: (81%). Anal. Calcd for $[ZnL^5Cl_2]$ (**5**): C, 52.17; H, 5.07; N, 10.14. Found: C, 52.17; H, 5.07; N, 10.14. Ω ($ohm^{-1}\,cm^2\,mol^{-1}$): 8.9. Selected IR data on KBr (ν/cm^{-1}): 1633, 1586, 1441.

$[ZnL^6Cl_2]$ (6) was prepared by the same procedure as for **5** with HL^6 (0.293 g, 1 mmol). Yield: 74%. Anal. Calcd for $[ZnL^6Cl_2]$ (**6**): C, 53.20; H, 5.36; N, 6.53. Found: C, 53.21; H, 5.35; N, 6.52. Ω ($ohm^{-1}\,cm^2\,mol^{-1}$): 8.9. Selected IR data on KBr (ν/cm^{-1}): 1638, 1588, and 1442.

(b) **Synthesis of the complexes by template synthetic route:**

The following general procedure was adopted to prepare the complexes with this technique. A methanolic solution (5 mL) of the amine was added to a methanolic

Table 1. Crystallographic data and details of refinements for **3**, **4** and **5**.

	3 · H_2O	**4** · H_2O	**5**
Empirical formula	$C_{13}H_{20}Cl_2N_2O_2Zn$	$C_{14}H_{22}Cl_2N_2O_2Zn$	$C_{19}H_{23}Cl_2N_3Zn$
Formula weight	372.58	386.61	429.67
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\ 2_1/c$	$P\ 2_1/c$
Unit cell dimensions (Å, °)			
a	8.966(3)	9.207(3)	14.0126(10)
b	9.936(3)	19.942(5)	12.4930(9)
c	10.782(3)	9.960(3)	11.0340(8)
α	93.026(10)	90	90
β	109.807(10)	110.21(1)	92.505(1)
γ	115.652(10)	90	90
V (Å^3)	791.8(4)	1716.1(9)	1929.8(2)
Z	2	4	4
D_{Calcd} (mg m^{-3})	1.563	1.496	1.479
$F(000)$	384	800	888
μ (Mo-Kα) (mm^{-1})	1.890	1.747	1.556
Collected reflections	6011	9881	11404
Indep. reflections	3352	3885	4487
R_{int}	0.0587	0.0867	0.0220
Observed reflections	2712	2236	4143
θ range (°)	2.07–27.96	2.04–28.38	1.45–28.22
R_1 $[I > 2\sigma(I)]$	0.0922	0.0729	0.0274
wR_2 $[I > 2\sigma(I)]$	0.2245	0.1547	0.0651
Goodness-of-fit on F^2	1.064	0.976	1.040
Residuals (e Å^{-3})	2.199, −1.143	0.714, −1.268	0.414, −0.310

solution (15 mL) of the aldehyde dropwise. The resulting yellow solution was refluxed for 2 h. Then a methanolic solution of $ZnCl_2$ (5 mL) was added and reflux was continued for another 1 h. After cooling, the resultant solution was kept in a $CaCl_2$ desiccator. Crystalline compound was obtained after a few days.

2.5. *X-ray data collection and structure determination*

Intensity data for all the structures were collected at 100 K on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation source. The program SMART [23] was used for data collection, indexing reflection and determination of lattice parameters, SAINT [23] for integration of the reflection intensity and scaling, and SADABS [24] for absorption correction. The structures were solved by direct methods and subsequent Fourier analysis [25] and refined by full-matrix least squares on F^2 with all observed reflections [26]. Crystallographic data and refinement details are displayed in table 1. Selected bond lengths and angles are given in table 2 for **3** and **4** and in table 3 for **5**.

3. Results and discussion

3.1. *Syntheses and characterization*

The Schiff-base ligands HL^3, HL^4, L^5 and L^6 were synthesized by conventional condensation of aldehydes and amine maintaining a 1 : 1 ratio, whereas for HL^1 and HL^2 the aldehyde-amine ratio was kept at 1 : 2. All the ligands were characterized by conventional spectroscopic techniques. The ^{1}H and ^{13}C NMR spectral data of the ligands with their corresponding assignments are reported in the experimental section and the data are consistent with the proposed structures of the ligands as depicted in chart 1. Zinc complexes are prepared by conventional sequential reaction and template reaction. The compositions and the structures of the complexes are determined by routine physico-chemical techniques as well as by single crystal X-ray analysis (in those cases when suitable single crystals were obtained). Analytical data suggest the formation of the same species from the two synthetic routes. Elemental analyses reveal the formation of mononuclear species with HL^3, HL^4, L^5 and L^6 having metal-ligand ratio 1 : 1, and binuclear species with HL^1 and HL^2 (metal-ligand ratio of 2 : 1). Molar conductivity measurements of the complexes in DMSO suggest that all the complexes are non-electrolytes (Experimental section) [27], indicating that chloro ligands in the complexes are in the metal coordination sphere. Complexes **3** and **4** contain one mole of lattice water per mole of the complex and thermogravimetric analyses show a percentage weight loss of 4.5 for **3** in the temperature range 65–95°C and a percentage weight loss of 4.7 for **4** in the range 68–98°C. IR stretching frequencies, attributed to the azomethine group, were observed in the range 1630–1638 cm^{-1} for **3**–**6**, and at 1646 and 1644 cm^{-1} in case of **1** and **2**, respectively. No band corresponding to formyl is observed in the IR spectra for the latter species, indicating condensation of both the formyl groups of 4-methyl-2,6-

Table 2. Selected bond lengths (Å) and angles (°) for **3** and **4**.

	3	**4**
Zn–O(1)	1.944(6)	1.926(4)
Zn–N(1)	2.021(7)	2.031(5)
Zn–Cl(1)	2.258(2)	2.259(2)
Zn–Cl(2)	2.210(3)	2.213(3)
O(1)–C(1)	1.336(9)	1.329(7)
N(1)–C(7)	1.267(11)	1.293(7)
N(1)–C(8)	1.466(11)	1.463(7)
O(1)–Zn–N(1)	93.8(3)	95.5(2)
O(1)–Zn–Cl(1)	107.78(19)	109.63(15)
O(1)–Zn–Cl(2)	114.57(18)	113.69(13)
N(1)–Zn–Cl(1)	110.0(2)	109.52(13)
N(1)–Zn–Cl(2)	113.5(2)	111.05(15)
Cl(2)–Zn–Cl(1)	115.13(10)	115.60(8)

Table 3. Selected bond lengths (Å) and angles (°) for **5**.

Zn–N(1)	2.226(1)	Zn–Cl(1)	2.2664(4)
Zn–N(2)	2.107(1)	Zn–Cl(2)	2.2714(4)
Zn–N(3)	2.228(1)	N(2)–C(6)	1.274(2)
		N(2)–C(13)	1.466(2)
N(1)–Zn–N(2)	73.77(5)	N(2)–Zn–Cl(1)	111.54(4)
N(1)–Zn–N(3)	152.31(5)	N(2)–Zn–Cl(2)	132.08(4)
N(1)–Zn–Cl(1)	93.15(4)	N(3)–Zn–Cl(1)	100.09(4)
N(1)–Zn–Cl(2)	96.91(4)	N(3)–Zn–Cl(2)	98.94(4)
N(2)–Zn–N(3)	78.75(5)	Cl(1)–Zn–Cl(2)	115.896(17)

diformylphenol with amine 1-(2-aminoethyl)pyrolidine or 1-(2-aminoethyl)piperidine, to yield ligands HL^1 and HL^2, respectively (chart 1).

3.2. *Structure description of 3, 4 and 5*

The ORTEP views of **3** and **4**, shown in figures 1 and 2, respectively, have similar structural features. The coordination environment around Zn atom in both the complexes is slightly distorted tetrahedron, where the four vertices are occupied by two chlorides, the imine nitrogen and the phenolato oxygen of the Schiff-base. The Zn–Cl, Zn–N and Zn–O bond distances have comparable values within their e.s.d.'s, and, as expected, the chelating O(1)–Zn–N(1) bond angle has the higher deviation from ideal tetrahedron [93.8(3) and 95.5(2)° in the two complexes]. The C=N bond distance in the salicylidene ligand of *ca* 1.28 Å does not manifest any anomaly.

The N atom of pyrolidine and piperidine rings is protonated and does not take part in coordination. Although complexes **3** and **4** are similar, they show interesting difference in the $ZnCl_2$ [figures 3(a) and 3(b)]. Cl(1) and Cl(2) are displaced by 2.91 and 0.28 Å from the phenolato mean plane in **3**, while the corresponding figures in **4** are 2.56 and 1.04 Å. This feature is dictated by the crystal packing and involvement of Cl(1) in H bond interaction. Both complexes possess one water of crystallization per complex

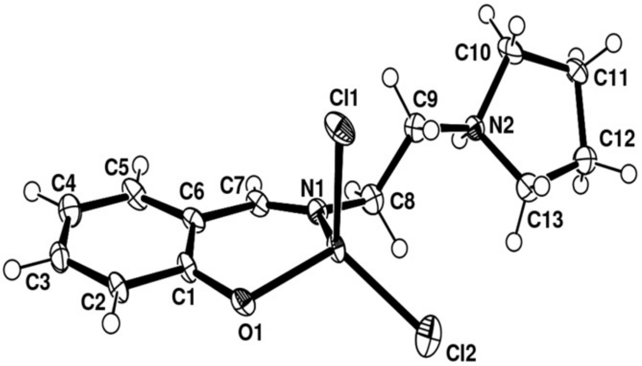

Figure 1. ORTEP view of **3** with atom numbering scheme.

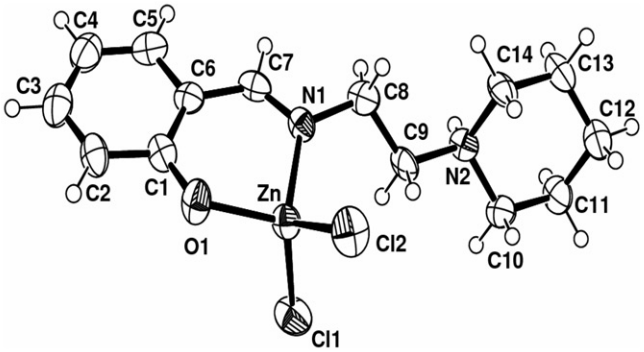

Figure 2. ORTEP view of **4** with atom numbering scheme.

unit which takes part in extensive H-bonding interaction to produce polynuclear species (figures 4 and 5).

Figure 6 represents the ORTEP view of **5** with atom numbering scheme. The coordination sphere around Zn atom can be described as a highly distorted trigonal bipyramid where the equatorial trigonal plane is constructed by chlorides and the imine N atom, while N donors of the pyridine and piperidine occupy axial positions. The Zn–N bond distances involving the latter N donors are significantly longer [2.226(1) and 2.228(1) Å] than the value measured for the imine N (2.107(1) Å). The amine nitrogen is coplanar with the azomethine pyridine fragment (max atom displacement of 0.03 Å), and the phenyl ring forms a dihedral angle of 67.46(4)° with the cited mean

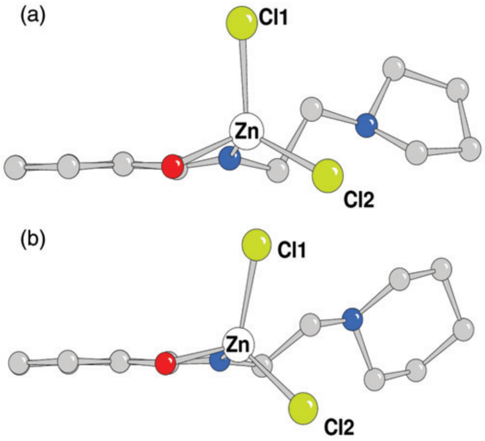

Figure 3. (a) Perspective view of **3** down C1-C6 showing the arrangement of the $ZnCl_2$ moiety with respect to the phenolato ring. (b) Perspective view of **4** down C1-C6 showing the arrangement of the $ZnCl_2$ moiety with respect to the phenolato ring.

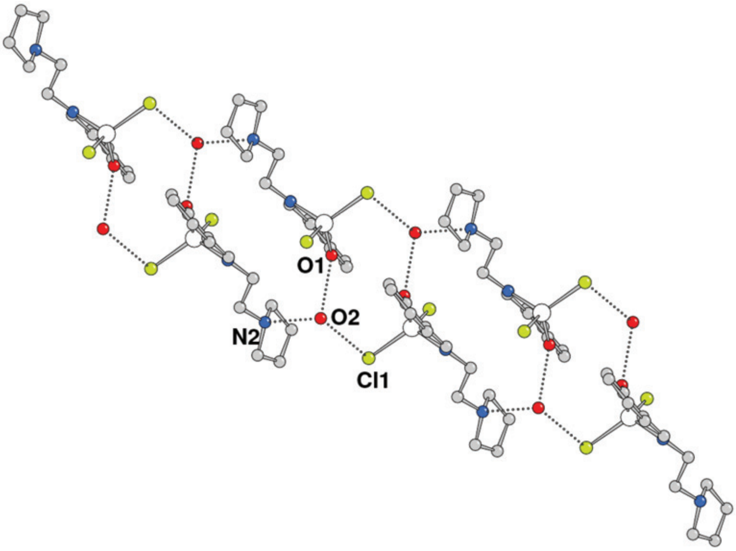

Figure 4. Polymeric structure formed by H-bond interactions in **3**.

plane. The bond angles reported in table 3 give an indication of the distortion in the coordination sphere, and it is worth noting the value assumed by the N(1)–Zn–N(3) angle of 152.31(5)° which allows formation of two strained five-membered rings. The azomethine bond length N(2)–C(6), of 1.274(2) Å, is comparable with values detected in **3** and **4**.

3.3. *Absorption and fluorescence properties*

The absorption band maxima exhibited by HL^3, HL^4, L^5 and L^6 in the range 230–256 nm is assigned to a $\pi \rightarrow \pi^*$ transition and remains almost unchanged in the

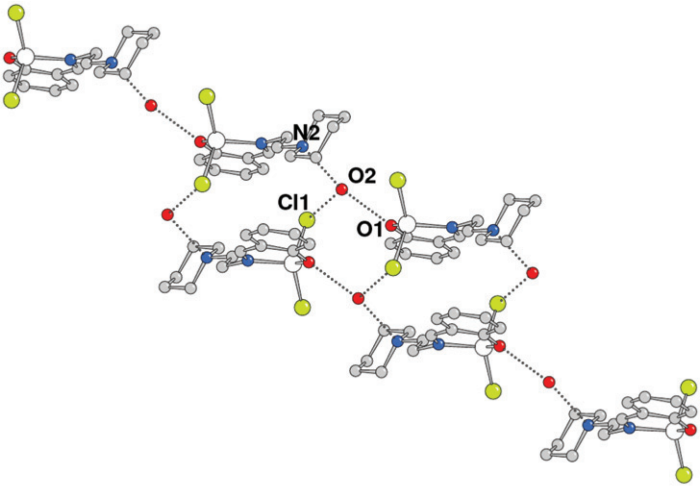

Figure 5. Polymeric structure formed by H-bond interactions in **4**.

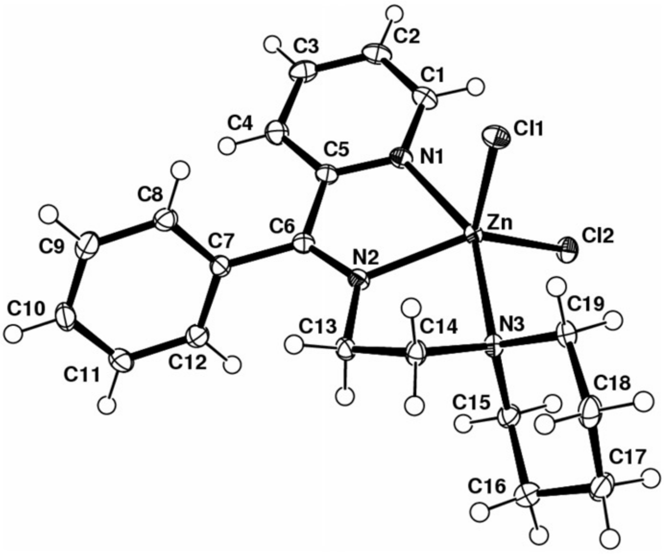

Figure 6. ORTEP view of **5** with atom numbering scheme.

spectra of their corresponding Zn complexes. The other band maximum exhibited by the same ligands in the range 281–312 nm is also probably due to the $\pi \rightarrow \pi^*$ transition associated with azomethine linkage [28]; this band shows a bathochromic shift in the complexes indicating azomethine coordination to zinc. HL^3 and HL^4 also show a weak band at ~410 nm as a consequence of the $n \rightarrow \pi^*$ transition [28] which blue shifts in the complexes. The complexes do not show appreciable absorption in the region above 430 nm in acetonitrile, in accord with the d^{10} electronic configuration of the Zn(II) ion, with the exception of LMCT maxima for phenolato in HL^3 and HL^4 complexes [28], showing line broadening with a tail running into the visible part of the spectrum. For complexes with ligands L^5 and L^6 no LMCT band is observed above 320 nm and they are colorless.

Both HL^1 and HL^2 show band maxima at ~350 and ~235 nm corresponding to $\pi \rightarrow \pi^*$ transitions and at ~450 nm corresponding to $n \rightarrow \pi^*$ transition of azomethine and phenol. In complex of HL^2 the band maximum due to $\pi \rightarrow \pi^*$ is red shifted, as expected, contrary to the slight blue shift exhibited by HL^1 complex. In **1** and **2** the LMCT bands also show line broadening, with a tail running into the visible region as observed in **3** and **4**, where no other absorptions above 430 nm are observed.

All the ligands are fluorescent although florescence intensities of mono-nucleating ligands are low (φ ranges from 0.003–0.005) in comparison with the bi-nucleating ligands (φ ranges from 0.015–0.017). Dramatic enhancement in fluorescence intensity is observed (table 4) on complexation with Zn(II), except for complexes with L^5 and L^6 where fluorescence quenching occurs (figure 7). Complexes **3** and **4** show red shift of emission bands with nearly a threefold increment in emission intensity in comparison with their corresponding ligands (figure 8; table 4). On the other hand, complexes **1** and **2** exhibit blue shift of emission band with about fourfold increment in emission intensity when compared to their corresponding ligands (figure 9; table 4).

Generally, Schiff-base systems exhibit fluorescence due to intraligand $\pi \rightarrow \pi^*$ transitions. The ligand shows enhanced fluorescence intensity on complexation with zinc. The emission is neither MLCT (metal-to-ligand charge transfer) nor LMCT in nature. Since a similar emission is also observed for the free ligand, but with reduced intensity, we tentatively assign it to the intraligand (π–π^*) fluorescence. After complexation, the free rotation of the flexible bonds of the ligand is reduced and

Table 4. Absorption and emission spectral data for complexes and free ligands in acetonitrile.

	Absorption	Emission	
Compound	λ_{max}, nm (ε, $M^{-1} cm^{-1}$)	λ_{em}, nm	φ
1	382(15420), 320(20810), 234(31261)	450	0.053
2	384(17231), 353(22313), 240(32145)	452	0.031
3	380(14530), 319(21345), 258(28765)	481	0.011
4	379(15662), 323(21897), 254(27885)	455	0.014
5	290(13665), 280(23451), 231(31432)	–	–
6	292(13883), 281(25481), 238(32121)	–	–
HL^1	452(10200), 354(17500), 236(27500)	472	0.015
HL^2	448(11323), 356(18321), 228(29456)	486	0.017
HL^3	412(9912), 311(11209), 230(23213)	437	0.004
HL^4	410(11512), 312(10921), 253(21345)	436	0.003
L^5	356(15234), 285(19023), 256(23341)	448	0.004
L^6	350(16124), 281(18242), 235(22321)	474	0.005

energy dissipation through non-radiative channels is reduced. With respect to HL^3 and HL^4, π-conjugation in HL^1 and HL^2 becomes nearly double and at the same time complexes of the di-nucleating ligands attain greater rigidity to reduce energy dissipation through non-radiative channels, and hence dinuclear Zn(II) complexes show much higher fluorescence intensity compared with the complexes of analogue mononuclear ligand systems. The red-shift of emission bands observed in **3** and **4**, compared with the corresponding free ligand, is expected. However, the blue-shift of emission bands for **1** and **2** with respect to the corresponding free ligands is not usual, though our observation is in agreement with earlier reports having similar ligand system [14]. It is well documented that 4-methyl-2,6-diformylphenol, the precursor of ligands HL^1 and HL^2, exhibits a blue shift of its own emission band after treatment with a base like piperidine, caused by the co-existence of the undissociated phenol and phenoxide anion in the mixture. The ligands L^5 and L^6 are observed to be slightly more fluorescent

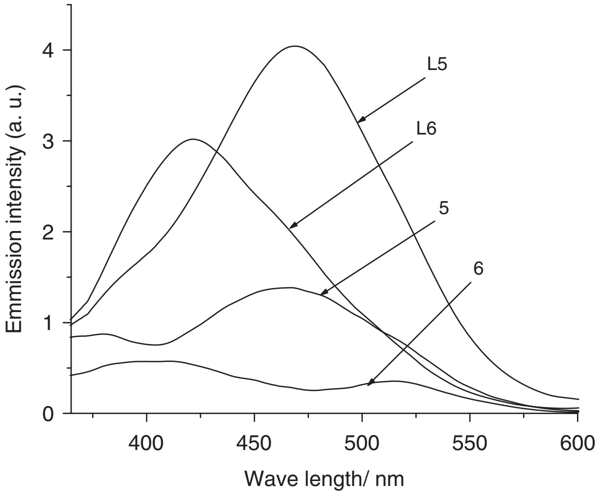

Figure 7. Emission spectra of **5** and **6** and of the corresponding ligands.

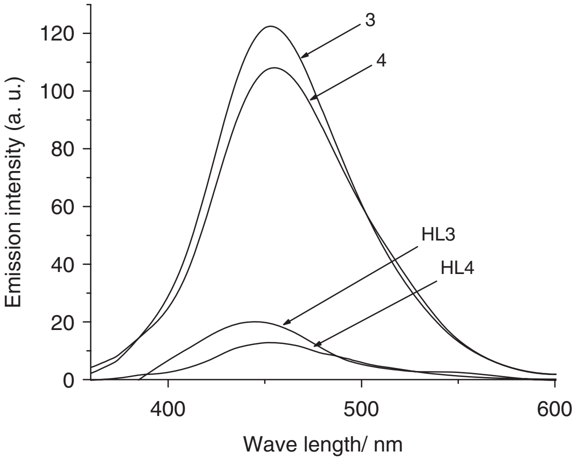

Figure 8. Emission spectra of **3** and **4** and of the corresponding ligands.

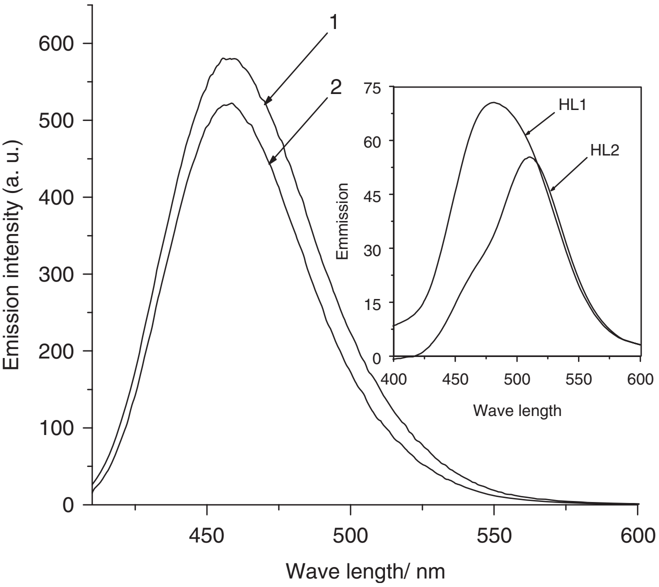

Figure 9. Emission spectra of **1** and **2** and of the corresponding ligands (inset).

than HL[3] and HL[4], most likely as a result of greater conjugation and lesser flexibility in the former case.

In this article, we report the synthesis and characterization of six new Schiff-bases HL[1]–HL[4], L[5] and L[6], derived from 2,6-diformyl-4-methylphenol/salicylaldehyde/2-benzylpyridine with 1-(2-aminoethyl)piperidine or 1-(2-aminoethyl)pyrolidine and of their complexes with Zn(II). HL[1] and HL[2] contain two azomethine side arms, while the others possess just one azomethine arm and a bit more extended conjugated system. HL[1] and HL[2] show higher luminescence efficiency in comparison with HL[3] and HL[4], a result connected with the more extended conjugation as well as with the higher rigidity in the former cases. Metal mediated fluorescence enhancement is observed on complexation of HL[1]–HL[4] with Zn(II). L[5] and L[6] also exhibit photoluminescence originated from intraligand (π–π*) transition as for HL[1]–HL[4], but, the ligands in **5** and **6** exhibit metal mediated fluorescence quenching, originating from energy dissipation through non-radiative channels in metal complexes. The single crystal X-ray structure analyses of **3**, **4** and **5** are reported. In **5** both azomethine and amine N atoms take part in coordination with the metal to form two five-membered chelate rings; in **2** and **3** the amine nitrogen is protonated and does not take part in coordination.

Supplementary material

CCDC numbers for **3**, **4** and **5** are 6,68,348, 6,71,715 and 6,68,350, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 lEZ, UK [Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgement

The authors wish to thank the Council of Scientific and Industrial Research, New Delhi, for financial support.

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