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# Schiff base coordination flexibility toward binary cobalt and ternary zinc complex assemblies. The case of the hexadentate ligand N,N'-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine



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# ABSTRACT

A green approach to the synthesis of N,N'-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine (H<sub>2</sub>L) (1) Schiff base led to the investigation of its metal coordination reactivity under specifically set molecular stoichiometry conditions, leading to the new materials  $[Co(L)]_3(ClO_4)_34H_2O(2)$  and  $[Zn_2(L)(CH_3COO)_2]$ (3). 1–3 were characterized by elemental analysis, molar conductivity, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, UV-Vis, fluorescence, and X-ray crystallography. Crystallography reveals the conformation of the free ligand and the changes it undergoes upon coordination to Co(III) and Zn(II) ions, promoting coordination number 6 (2) and 5 (3) in the respective mononuclear and dinuclear complexes. The structural flexibility of 1 coupled with the coordination requirements of the involved metal ions, under the prevailing stoichiometric conditions, shows that the strain imposed on the ligand under the reaction conditions helps it retain its original chair conformation (3) or assume the boat conformation (2). This modulatory property of 1 is reflected upon the molecular assembly of the derived complexes and exemplifies its connection to the observed variable vet defined coordination mode and nuclearity of the arisen isolable species. It is in this regard that **3** exhibits strong fluorescence at room temperature. Collectively, **1–3** project the importance of conformational flexibility of organic ligand metal ionic binders in the pursuit of (a) structure-property correlations useful in the synthesis of functional materials, and (b) modulatory traits in metal ion-organic ligand interactions providing specificity in recognition processes. In this sense, **1** serves as a prototype, denoting the salient features that influence binary and ternary metal-L-(L') assembly formation toward new materials with unique structural and photoactive properties.

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## 1. Introduction

The rational design and synthesis of polynuclear coordination complexes involving transition-metal cores and organic spacers are of considerable current research interest [1–4]. In this regard, metal-organic frameworks with versatile architectures, erected through carefully designed organic building blocks, often exhibit structural diversity and physicochemical pluripotency. Such organic synthons bear multidentate bridging ligands capable of tuning metal coordination under variable experimental conditions, with a small energy barrier, and influencing factors such as temperature, pressure, and solvent nature [5–8].

Schiff bases constitute a group of polydentate ligands with relatively simple preparation procedures and synthetic flexibility, enabling targeted design of suitable chemical reactivity properties upon coordination to a variety of metal ions [9,10]. Salicylaldehyde and derivative Schiff bases thereof are a well-known family of organic metal ion binders, with numerous metal complexes having been constructed and used in catalysis [11–13], optoelectronic materials [14,15], ionic liquids [16,17], and biological and environmental applications [18–20]. Among them, Salen-type [N,N'-ethylene-bis(salicylideneiminato)] ligands are the most common Schiff bases studied [21–23]. Past research has revealed that the ethylene-bridge of Salen could be replaced by various molecular "fragments", thereby conferring greater rigidity [24,25]

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or flexibility [26], depending on the desired properties of the target compounds. To this end, multidentate acyclic, macrocyclic [27], as well as open-chain and cyclic compartmental [28] ligands have been obtained by using appropriately selected amines. As a result, mononuclear and polynuclear metal complexes bearing such ligands have been synthesized, either by direct metal-ligand or metal-template [29,30] reactions. Consequently, the accruing bulk of experimental and theoretical data has significantly contributed to the fundamental understanding of metal ion coordination chemistry [31] and shed light onto unknown aspects of supramolecular chemistry [32].

Associated with the great binding versatility of the metal-reacting ligands, key properties of complexes in this class of coordination compounds, including fluorescence [33], luminescence [34], electrochemical [35], liquid crystal [36], and biological [37] effects have been reported, thereby stimulating further research on these systems, with significant merit in their (bio)material applications. The structure of the arisen metal complexes in this class of materials, based on ligands bearing the piperazine core, is primarily dictated through the conformation adopted by the central piperazine ring [38–40]. Piperazine [41] can adopt, along with the two extreme chair and boat conformations, the twisted-boat and the half-boat forms. Past reports suggest that the conformation adopted by the piperazine ring is defined by metal ion-size [42] and influenced by appropriate co-ligands [43]. Based on the (a) merit of such well-defined and structurally formulated ligands capable of configuring metal ion coordination and concurrently bestowing distinct spectroscopic properties upon the arising metal ionic assembly, and (b) the scarcity of divalent metal ionic complexes bearing such ligands, we report herein the synthesis and physicochemical characterization of the N,N'-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine (H<sub>2</sub>L) ligand and its new Co(III) binary and Zn(II) ternary complexes. The observed coordination diversity linked to the distinct flexibility of the organic Schiff base (a) point to conformational modulations on its piperazine core linked to metal coordination geometry and optical electronic property correlations, and (b) denote the salient features of inorganicorganic complex recognition motifs emerging in binary and ternary systems of the aforementioned ligand with divalent and trivalent metal ions.

# 2. Experimental

#### 2.1. Materials and methods

Salicylaldehyde, 1,4-bis(3-aminopropyl)-piperazine, phosphorous pentoxide, and triethylamine were purchased from Sigma; cobalt perchlorate hexahydrate and zinc acetate dihydrate were from Merck. All reagents were of analytical grade and used without further purification. Elemental analysis was carried out on a Perkin Elmer model 240C elemental analyzer for C, N, and H and a GBC SENSAA apparatus. AAS analyses for metal ions were run on a SEN-SAA GBC SERIES AAS spectrometer. Molar electrical conductivities were measured with a WTW LF 340-A conductivity meter. Electronic spectra were recorded in solutions on a UV–Vis Perkin Elmer Lambda 12 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were run on a Jeol-NMR (400 MHz) spectrometer. IR spectra were recorded on a Jasco-400 Spectrum One FT-IR spectrometer, in the form of KBr pellets, in the 400–4000 cm<sup>-1</sup> range.

Electrochemical measurements were run on an AUTOLAB electrochemical analyser model PGSTAT 30, Metrohm Autolab, Utrecht, The Netherlands, operated via the NOVA 1.8 software at a potential scan rate of 100 mV s<sup>-1</sup>. A three-electrode cell was employed, consisting of a working electrode (Pt), Ag/AgCl (storage solution: KCl,  $c = 0.1 \text{ mol dm}^{-3}$ ) as a reference and a Pt-plate as the counter

electrode. Experiments were carried out in DMSO at room temperature under a nitrogen atmosphere. In all cases, tetrabutyl ammonium tetrafluorophosphate was used as a supporting electrolyte, with the salt concentration being  $10^{-4}$  M and that of the analyte  $5 \times 10^{-4}$  M. Fluorescence spectra were recorded on freshly prepared solutions ( $C = 10^{-5}$  M) using a Perkin Elmer LS-55 spectrophotometer; the excitation slit was set at 12.5 and that of the emission at 3.5, while the scanning speed was 100 nm/min.

#### 2.2. X-ray crystal structure determination

X-ray quality crystals of **1** were grown from alcohol, while crystals of **2** and **3** were grown from mixtures of chloroform-alcohol solutions. For the structure determination of **1–3**, single crystals of the respective compounds with dimensions  $0.43 \times 0.45 \times 0.52$ (1).  $0.18 \times 0.42 \times 0.48$  mm (2). and  $0.14 \times 0.16 \times 0.25$  (3) were mounted on a Bruker Kappa APEX II diffractometer equipped with a triumph monochromator at ambient temperature. Diffraction measurements were made using graphite monochromated Mo Ka radiation. Unit cell dimensions were determined and refined by using the angular settings of at least 50 high intensity  $(>20\sigma(I))$  reflections in the range  $10 < 2\theta < 40^{\circ}$ . Intensity data were recorded using  $\phi$  and  $\omega$  scan modes. The frames collected for each crystal were integrated with the Bruker SAINT software package [44] using a narrow-frame algorithm. Data were corrected for absorption using the numerical method (sadabs) based on crystal dimensions [45].

All structures were solved using the SUPERFLIP [46] package and refined by full-matrix least-squares method on  $F^2$  using the CRYSTALS package version 14.40b [47]. All non-disordered non-hydrogen atoms have been refined anisotropically. For the disordered non-hydrogen atoms, occupancy factors were first determined with fixed isotropic displacements. Finally, all of them were isotropically refined with fixed occupancy factors.

All hydrogen atoms were found at the expected positions and refined using soft constraints. By the end of the refinement, they were positioned using riding constraints. Crystal data and structure refinement parameters of 1-3 are presented in Table 1. Illustrations were drawn by Diamond 3.1 package [48]. Details on the crystallographic studies as well as atomic displacement parameters are given as Supporting Information in the form of cif files. Further experimental crystallographic details for **1**:  $\theta_{max}$  = 34.99°; number of reflections collected/unique/used,  $25144/4910 [R_{int} = 0.0156]/$ 3158;  $(\Delta \rho)_{\text{max}}/(\Delta \rho)_{\text{min}} = 0.18/-0.20 \text{ e/Å}^3$ ;  $R/R_w$  (for all data), 0.0737/0.0619. For **2**:  $\theta_{max} = 27.37^{\circ}$ ; number of reflections collected/unique/used, 53952/9545 [ $R_{int} = 0.0245$ ]/5735; ( $\Delta \rho$ )<sub>max</sub>/  $(\Delta \rho)_{\rm min} = 1.25/-0.74 \, {\rm e}/{\rm \AA}^3$ ;  $R/R_w$  (for all data), 0.0802/0.1382. For **3**:  $\theta_{\text{max}} = 30.65^{\circ}$ ; number of reflections collected/unique/used, 23734/8577 [ $R_{int} = 0.0460$ ]/3818; ( $\Delta \rho$ )<sub>max</sub>/( $\Delta \rho$ )<sub>min</sub> = 1.24/-0.73 e/Å<sup>3</sup>; *R*/*R<sub>w</sub>* (for all data), 0.1200/0.1264.

#### 2.3. Syntheses

# 2.3.1. N,N'-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine, (H<sub>2</sub>L) (1)

Salicylaldehyde (3.7 g, 30 mmol), 1,4-bis(3-aminopropyl)piperazine (3.0 g, 15 mmol) and  $P_2O_5/SiO_2$  (0.050/0.13 g) were grounded thoroughly for 30 min in a mortar to provide a yellow soft powder. The powder was placed in a flask with 75 ml of ethanol and stirred for 3 h. The arising solid precipitate was removed by filtration. Slow evaporation of the filtrate gave yellow crystals suitable for crystallographic characterization. Yield: 4.5 g (83%). *Anal.* Calc. for C<sub>24</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub> (408.54): C, 70.6; H, 7.9; N, 13.7. Found: C, 70.8, H, 7.8, N, 13.5%. <sup>1</sup>H NMR (400 MHz), CDCl<sub>3</sub>/ $\delta$  [ppm]: 1.88 (m, 2H, CH<sub>2</sub>, *J* = 6.89, 6.89, 6.85 Hz); 2.41–2.47 (m, 6H, <sub>exo</sub>CH<sub>2</sub>N (CH<sub>2</sub>CH<sub>2</sub>)<sub>pip</sub>, *J* = 7.58, 7.20 Hz); 3.61–3.64 (t, 2H, CH<sub>2</sub>, *J* = 6.74,

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# Crystal data and structure refinement parameters for $H_2L(1)$ , $[Co(L)]_3(CIO_4)_34H_2O(2)$ and $[Zn_2(L)(CH_3COO)_2](3)$ .

	1	2	3
Empirical formula	$C_{24}H_{32}N_4O_2$	C <sub>72</sub> H <sub>98</sub> Cl <sub>3</sub> Co <sub>3</sub> N <sub>12</sub> O <sub>22</sub>	$C_{28}H_{36}N_4O_6Zn_2$
Formula weight	408.54	1766.79	655.38
Crystal system	monoclinic	monoclinic	monoclinic
Т (К)	295	295	295
Space group	$P2_1/c$ (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	$P2_1/c$ (no. 14)
a (Å)	21.9135(13)	30.535(12)	12.434(5)
b (Å)	5.8162(3)	17.535(6)	17.968(6)
<i>c</i> (Å)	8.9060(5)	19.449(15)	12.739(4)
β(°)	92.031(4)	123.747(7)	95.112(9)
V (Å <sup>3</sup> )	1134.4(1)	8659(8)	2834.8(17)
Ζ	2	4	4
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.20	1.36	1.74
Absorption coefficient $\mu$ (mm <sup>-1</sup> )	0.077	0.735	1.741
Range of h, k, l	$-32 \rightarrow 35, 0 \rightarrow 9, -14 \rightarrow 34$	$-39 \rightarrow 38, 0 \rightarrow 22, -24 \rightarrow 24$	$-17 \rightarrow 17, -25 \rightarrow 25, -13 \rightarrow 18$
Goodness-of-fit (GOF) on $F^2$	0.979	0.986	1.036
No. of reflections used <sup>a</sup> /parameters refined	3158/136	5735/497	3818/361
R	0.042 <sup>b</sup>	0.051 <sup>b</sup>	0.046 <sup>b</sup>
R <sub>w</sub>	0.055 <sup>b</sup>	0.116 <sup>b</sup>	0.119 <sup>b</sup>

 $w = w' \times [1 - (\Delta F_{obs})/6 \times \Delta F_{est})^2]^2$  where  $w' = [P_0T_0'(x) + P_1T_1'(x) + \dots P_{n-1}T_{n-1}'(x)]^{-1}$  and  $P_i$  are the coefficients of a Chebychev series in  $t_i(x)$ , and  $x = F_{calc}^2/F_{calc}^2 \max w = (1/4F_{obs}^2) \times 1$ .

<sup>a</sup> Reflections with  $l > 2\sigma(l)$ .

<sup>b</sup> R values are based on *F* values,  $R_w$  values are based on  $F^2$ .

6.74 Hz); 6.86 (t, 1H, Ar*H*, *J* = 7.89, 7.89 Hz); 6.95 (d, 1H, Ar*H*, *J* = 8.30 Hz); 7.30 (dd, 1H, Ar*H*, *J* = 9.07, 8.12 Hz); 7.23 (d, 1H, Ar*H*, *J* = 9.09 Hz,); 8.34 (s, 1H, *H*C=N); 13.55 (s, 1H, OH). <sup>13</sup>C NMR (400 MHz), CDCl<sub>3</sub>/δ [ppm]: 27.93 (C9), 53.20 (C10), 55.87 (C11,12), 57.47 (C8), 117.01 (C2), 118.42 (C4), 118.77 (C6), 131.10 (C5), 132.66 (C3), 161.30 (C7), 164.96 (C1). FT-IR [KBr, cm<sup>-1</sup>]: 3481 (br, w), 3061 (w), 3003 (w), 2946 (w), 2880 (m), 2810 (m), 2776 (m), 1631 (s), 1578 (m), 1494 (m), 1456 (m), 1412 (m), 1345 (m), 1314 (m), 1278 (m), 1203 (m), 1150 (m), 1022 (m), 978 (w), 960 (w), 846 (m), 751 (m), 652 (w), 465 (w). UV-Vis (CHCl<sub>3</sub> 7·10<sup>-4</sup>M) λ<sub>max</sub> [nm] (ε/L mol<sup>-1</sup> cm<sup>-1</sup>): 274(1000), 316(3500), 409(171). Fluorescence (CHCl<sub>3</sub>, 20 °C, 10<sup>-5</sup> M): λ<sub>ex</sub> 350 nm; λ<sub>em</sub> 450 nm.

# 2.3.2. [Co(L)]<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub>4H<sub>2</sub>O (2)

H<sub>2</sub>L (0.50 g, 1.2 mmol) in CHCl<sub>3</sub>-MeOH (1:1 v/v, 20 ml) was treated with Et<sub>3</sub>N (0.51 ml, 3.7 mmol) and Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.89 g, 2.4 mmol) dissolved in MeOH (10 ml). The mixture was stirred for 1 h at room temperature and the derived green-brown solid was isolated, washed with methanol, and dried in air, affording a crystalline product. Yield 0.68 g (98%). Brown single crystals suitable for X-ray analysis were obtained by slow evaporation of the mother liquor CHCl<sub>3</sub>-MeOH 1:1 (v/v). Anal. Calc. for C<sub>72</sub>H<sub>98</sub>Cl<sub>3-</sub> Co<sub>3</sub>N<sub>12</sub>O<sub>22</sub> (1766.79): C, 48.95; H, 5.59; N, 9.51; Cl, 6.02; Co, 10.01. Found: C, 48.83; H, 5.61; N, 9.47; Cl, 6.09; Co, 10.11%. FT-IR [KBr, cm<sup>-1</sup>]: 3445 (br, w), 3042 (w), 3015 (w), 2938 (w), 2902 (w), 2878 (w), 1623 (vs), 1595 (s), 1541 (m), 1471 (m), 1455 (s), 1404 (w), 1365 (w), 1337 (m), 1311 (s), 1254 (w), 1236 (w), 1213 (w), 1169 (w), 1153 (w), 1093 (vs), 970 (m), 903 (w), 847 (w), 767 (m), 738 (w), 622 (m), 595 (w), 567 (w), 497 (w), 468 (w), 441 (w), 417 (w). Molar conductivity  $\Lambda_M$ ,  $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$  (DMF,  $4 \times 10^{-4}$  M): 67. UV–Vis (DMF,  $4 \times 10^{-4}$  M)  $\lambda_{max}$  [nm] ( $\epsilon/L$  mol<sup>-1</sup> cm<sup>-1</sup>): 383(3100), 497(525), 580(220), 654(140). Fluorescence (DMF, 20 °C, 5  $\times$  10<sup>-5</sup> M):  $\lambda_{ex}$  293 nm;  $\lambda_{em}$  331 nm.

#### 2.3.3. [Zn<sub>2</sub>(L)(CH<sub>3</sub>COO)<sub>2</sub>] (3)

 $H_2L$  (0.50 g, 1.2 mmol) in EtOH (15 ml) was slowly treated with  $Zn(CH_3COO)_2 \cdot 2H_2O$  (0.53 g, 2.4 mmol) dissolved in EtOH (30 ml). The yellow solid formed was collected by filtration and washed with hot ethanol. Yield 0.65 g (82%). Pale yellow crystals were obtained by crystallization from ethanol-chloroform solutions. *Anal.* Calc. for  $C_{28}H_{36}N_4O_6Zn_2$  (655.38): C, 51.32; H, 5.54; N, 8.55; Zn, 19.95. Found: C, 51.23; H, 5.81; N, 8.47; Zn, 19.78.<sup>8</sup>. <sup>1</sup>H NMR

(400 MHz), CDCl<sub>3</sub>, DMSO-d<sub>6</sub>/δ [ppm]: 2.02 (m, 5H, CH<sub>2</sub>, CH<sub>3acetate</sub>); 2.78 (m, 2H, exoCH<sub>2</sub>N); 3.14 (m, 4H, N(CH<sub>2</sub>CH<sub>2</sub>)<sub>pip</sub>); 3.88 (t, 2H, CH<sub>2</sub>); 6.54–6.56 (d, 1H, ArH, J = 7.17); 6.82–6.86 (d, 1H, ArH, J = 8.50 Hz); 7.05–7.07 (d, 1H, ArH, J=7.74 Hz); 7.21–7.24 (d, 1H, ArH, I = 7.68 Hz; 8.11 (s, 1H, HC=N). <sup>13</sup>C NMR (400 MHz), CDCl<sub>3</sub>, DMSO-d<sub>6</sub>/δ [ppm]: 21.54 (C26); 26.60 (C9), 52.54 (C10), 59.76 (C8,11,13), 117.93 (C2,4,6), 134.60 (C5), 135.26 (C3), 168.98 (C7), 169.97 (C1), 179.26 (C25). FT-IR [KBr, cm<sup>-1</sup>]: 3017 (w), 2907 (m), 2860 (m), 1641 (vs), 1601 (s), 1572 (s), 1539 (s), 1447 (vs), 1450 (vs), 1398 (s), 1336 (s), 1315 (s), 1282 (m), 1210 (w), 1188 (m), 1140 (m), 1129 (m), 1087 (m), 1054 (m), 1032 (m), 974 (w), 958 (m), 926 (w), 910 (w), 883 (w), 850 (w), 804 (w), 781 (w), 755 (m), 736 (w), 683 (m), 642 (w), 601 (m), 562 (w), 458 (m), 412 (w). Molar conductivity  $\Lambda_M$ ,  $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$  (CHCl<sub>3</sub>,  $10^{-3} \text{ M}$ ): 0. UV–Vis (CHCl<sub>3</sub>,  $10^{-3}$  M)  $\lambda_{max}$  [nm]: 280(1860), 367(2830), 387(1270). Fluorescence (CHCl<sub>3</sub>, 20 °C,  $10^{-5}$  M):  $\lambda_{ex}$  368 nm;  $\lambda_{em}$ 446 nm

# 3. Results

#### 3.1. Synthesis

The synthesis of both the organic ligand and the associated binary-ternary metal compounds was pursued through efficient reactions. Specifically, the ligand N,N'-bis[(2-hydroxybenzilidenea-mino)-propyl]-piperazine (H<sub>2</sub>L) was synthesized through a Schiff base condensation reaction of salicylaldehyde and 1,4-bis(3-aminopropyl)-piperazine in the presence of P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> in ethanol (vide infra). The stoichiometric reaction is shown in Scheme 1:

The organic metal ion binder was subsequently employed in a reaction with Co(II). The specific reactivity was pursued in a mixture of CHCl<sub>3</sub>-MeOH, using Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O as a starting material in MeOH. Et<sub>3</sub>N was used as a base to deprotonate the acidic phenol moieties of the H<sub>2</sub>L ligand, thereby promoting binding to oxidized Co(III), according to the stoichiometric equation shown in Scheme 2:

In a third reactivity pattern,  $Zn(CH_3COO)_2 \cdot 2H_2O$  reacted with  $H_2L$  in ethanol, affording a material shown in the stoichiometric reaction (Scheme 3):

The materials are stable in the air. They are insoluble in water. **1** is soluble in most organic solvents, with **2** being soluble in DMSO and DMF, and **3** being soluble in chloroform.



Scheme 1. Synthetic route to H<sub>2</sub>L (1).

#### 3.2. X-ray crystal structure description

## 3.2.1. $(C_4H_8N_2)(C_3H_6N=CH-C_6H_4-OH)_2(H_2L)(1)$

The organic metal ionic binder ligand crystallizes in the monoclinic system, space group  $P2_1/c$ , with two molecules in the unit cell. The crystal structure of **1** contains discrete molecules (Fig. 1), each sitting on a center of inversion. Bond lengths and angles for **1** are given in Table 2. The **H**<sub>2</sub>L molecule consists of two salicylaldehyde moieties symmetrically disposed around the piperazine bridge and pointing away in opposite directions. In the piperazine bridge, the bond lengths in N(2)C(11), N(2)C(12) and C(11)C(12) of 1.452(3), 1.449(1) and 1.509(2) Å, respectively, are within the expected range for CN and CC single bonds of 1.469 and 1.524 Å, respectively [49]. The values of the two piperazine nitrogen angles CNC of 108.25(8) and 111.67(12) support the  $sp^3$  hybridization with a pyramidal VSEPR molecular geometry around the nitrogen atoms.

In order to determine the piperazine conformation, the position of the following three planes was considered: plane A described by one of the N(2)C(11)C(12) atom set, plane **B** described by the two pairs of C(11)C(12) atoms in the piperazine ring, and plane C defined by the second N(2)C(11)C(12) atom set. As the dihedral angle between planes **A** and **B** (51.87°) is equal to that between planes **B** and **C**, and that between **A** and **C** is 0, it can be concluded that the piperazine ring is in the stable *chair* conformation [50]. This assertion is also supported by the torsion angle N(2)C(11)C(12)N(2) of 59.3(1)°. The dihedral angle  $CCNC_{exo}$ C(11)C(12)N(2)C(10), of 179.36(8)° indicates that the methylene group of C(10) is in the equatorial position. The view of  $H_2L$  along the *b* axis in Fig. 2 shows a very regular layered arrangement of the molecules in the plane (010). The two phenyl rings belonging to a single molecule are parallel to each other, with the distance between their planes being 4.44 Å. The distance  $O(1) \cdots N(1)$  of 2.567(1) Å, considered a strong interaction (i.e.  $d(N \cdots O) = 2.53 -$ 2.55 Å), and the OH(11)N angle value of 152.94(6) denote the presence of intramolecular hydrogen bonds between the OH group and the imino nitrogen, a common feature in Schiff bases (Fig. 1). Fur-



Scheme 2. Synthetic route to  $[Co(L)]_3(ClO_4)_34H_2O(2)$ .



Scheme 3. Synthetic route to [Zn<sub>2</sub>(L)(CH<sub>3</sub>COO)<sub>2</sub>] (3).



Fig. 1. Molecular structure and atom labeling scheme of 1 (H<sub>2</sub>L). Hydrogen atoms are omitted for clarity, with the exception of the phenolic protons forming hydrogen bonds with imino nitrogens.

Table 2	
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Selected bond lengths [4	Å] and angles	[°] in <b>1-3</b> .
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1		2		2	
1		2		3	
Bond lengths [Å]					
C(1)-O(1)	1.344(2)	Co(1)-O(1)	1.891(4)	Zn(1)-O(1)	1.928(4)
C(7)-N(1)	1.271(2)	Co(1)-O(2)	1.920(4)	Zn(1)-N(1)	1.990(9)
C(1)-C(6)	1.403(1)	Co(1)-N(1)	1.933(10)	Zn(1)-N(2)	2.117(10)
C(10)-N(2)	1.459(2)	Co(1)-N(2)	1.944(4)	Zn(1)-O(3)	2.091(5)
C(11)–N(2)	1.452(3)	Co(1)-N(3)	2.012(5)	Zn(1)-O(4)	2.287(4)
C(12)-N(2)	1.449(1)	Co(1)-N(4)	1.986(8)	Zn(2)-O(2)	1.923(4)
C(11)-C(12)	1.509(2)	Co(2)-O(3)	1.919(11)	Zn(2)-N(4)	2.004(8)
		Co(2)-N(5)	1.934(6)	Zn(2)-N(3)	2.120(1)
		Co(2)-N(6)	1.995(5)	Zn(2)-O(6)	2.087(5)
				Zn(2)-O(5)	2.260(4)
Bond angles (°)					
C(11)-N(2)-C(12)	108.25(8)	O(2)-Co(1)-O(1)	178.07(14)	O(1)-Zn(1)-N(1)	94.80(16)
		O(2)-Co(1)-N(1)	89.07(16)	O(3) - Zn(1) - O(4)	58.79(14)
		O(2)-Co(1)-N(2)	90.48(14)	N(1)-Zn(1)-N(2)	91.97(17)
		O(2)-Co(1)-N(3)	87.16(16)	N(2)-Zn(1)-O(1)	118.70(15)
		O(2)-Co(1)-N(4)	93.59(16)	N(2)-Zn(1)-O(3)	105.92(15)
		O(1)-Co(1)-N(1)	89.45(16)	N(2)-Zn(1)-O(4)	96.70(13)
		O(1)-Co(1)-N(2)	88.49(14)	N(1)-Zn(1)-O(3)	150.42(16)
		O(1)-Co(1)-N(3)	94.19(15)	N(1)-Zn(1)-O(4)	96.48(14)
		O(1)-Co(1)-N(4)	88.12(16)	O(1)-Zn(1)-O(4)	142.33(14)
		N(1)-Co(1)-N(4)	167.48(18)	O(1)-Zn(1)-O(3)	96.81(15)
		N(2)-Co(1)-N(3)	167.65(16)	O(2)-Zn(2)-N(4)	95.64(16)
		N(1)-Co(1)-N(2)	98.38(16)	O(5)-Zn(2)-O(6)	57.75(14)
		N(1)-Co(1)-N(3)	93.70(19)	N(4)-Zn(2)-N(3)	91.48(15)
		O(3)-Co(2)-O(3)	176.34(16)	N(3)-Zn(2)-O(2)	119.41(15)
		O(3)-Co(2)-N(5)	88.37(19)	N(3)-Zn(2)-O(6)	104.03(15)
		O(3)-Co(2)-N(5)	89.23(19)	N(3)-Zn(2)-O(5)	99.23(14)
		O(3)-Co(2)-N(6)	89.44(15)	N(4)-Zn(2)-O(6)	150.92(15)
		O(3)-Co(2)-N(6)	93.47(15)	N(4)-Zn(2)-O(5)	95.96(14)
		N(5)-Co(2)-N(6)	168.09(20)	O(2)-Zn(2)-O(5)	139.20(14)
		N(5)-Co(2)-N(5)	98.53(22)	O(2)-Zn(2)-O(6)	97.78(15)
		N(6)-Co(2)-N(5)	93.26(20)		

thermore, the value of 1.756(1) (Å) for the H(11)···N(1) distance and the shorter C(1)O(1) bond distance of 1.344(2) Å compared to the theoretical value of 1.362 Å support the strengthened Hbond through  $\pi$ -delocalization [51].

Within a layer, contiguous molecules disposed parallel to each other are separated by a molecule slanted with an angle of 53.3°. The distance between the main planes of the benzene rings belonging to neighboring molecules in parallel layers is of 2.607 Å. The smallest centroid-centroid distance between them within a stack is 5.054 Å (smaller than 6.0 Å) and the angle between the centroid--centroid vector and the normal to the ring plane is 31.05°. These data suggest the presence of a  $\pi$ - $\pi$  offset, weakly slipped, interlayer interaction [52].

## 3.2.2. $[Co(L)]_3(ClO_4)_3 \cdot 4H_2O(2)$

Compound **2** crystallizes in the monoclinic system, space group C2/c (no. 15), with four molecules in the unit cell (Fig. 3A, B). The arranged molecules within the unit cell can be seen in Fig. 4. All

relevant bond lengths and angles with their estimated standard deviations are given in Table 2 (see also Supporting Information Table S1). The asymmetric unit consists of one and a half complex units  $[Co(L)]^+$ , one and a half perchlorate anions and two water molecules. Based on this fact, for the purpose of better understanding and projecting a physical meaning to the structure of 2, it was preferably deemed appropriate to describe the compound as one consisting of three well-defined mononuclear complex units [Co(L)]<sup>+</sup>, which share among them three perchlorate ions and four water molecules. Consequently, the number of units per unit cell Z is 4. Two of the three mononuclear  $[Co(1)L]^+$  units are identical and differ slightly from the third mononuclear [Co(2)L]<sup>+</sup> unit. Each Co(III) ion is octahedrally coordinated to a doubly deprotonated L<sup>2–</sup> organic binder, with the coordination environment formulated by the N<sub>4</sub> set of ligand terminals arising from two imino nitrogen and two piperazine nitrogen atoms in the basal plane. The sites of deprotonation of the ligand H<sub>2</sub>L are the acidic phenol groups on both ends of the ligand. In all three cases of mononuclear units,



Fig. 2. Crystal structure of 1 (H<sub>2</sub>L) in the *ac* plane.



Fig. 3. Molecular structure and atomic labeling scheme of a Co(L) mononuclear assembly in 2, in two different views (A and B) portraying the conformational state of the piperazine ring and its influence on the Co(III) assembly. Hydrogen atoms are omitted for clarity.

the Co(III) ion and the N<sub>4</sub> donor set are almost coplanar. The average CoN distance of 1.967 Å is slightly shorter compared to the theoretical radii sum for an octahedrally coordinated Co(III) center and an sp<sup>3</sup> nitrogen of 2.005 Å. The CoN<sub>imino</sub> bond lengths are shorter than the Co–N<sub>piperazine</sub> distances, but still in the range reported for similar compounds. The two ligand phenolic oxygen atoms occupy the apical positions of the octahedron, with the Co–O<sub>phenolic</sub> distances between 1.891(4) and 1.920(4) Å, rather unequal, but still in the range reported for similar compounds. Very small differences may also be noticed in the Co–N and Co–O bond lengths between the Co(1) and Co(2) assemblies. The *trans* angles O(1)Co(1)O(2) of 178.1(1)° and O(3)Co(2)O(3) of 176.3 (2)° are close to linearity, emphasizing the fact that both oxygen atoms

are placed at the vertices of an almost undistorted octahedron, but with small differences between the two types of Co(III) centers. The average imino C–N bond distance of 1.292(7) Å is longer and the average C–O<sub>phen</sub> distance of 1.322(7) Å is shorter than the corresponding distances in the free ligand, thereby showing a more pronounced  $\pi$ -delocalization.

The two CH<sub>2</sub>CH<sub>2</sub> piperazine straps form a double five-membered chelate ring with the cobalt central ion. As a consequence, the "bite" angles N(3)Co(1)N(4) of  $74.2(2)^{\circ}$  and N(6)Co(2)N(6) of  $75.0(2)^{\circ}$  are smaller, and the metal-piperazine nitrogen distances are longer than usual. The C(13)N(3)C(11) angles of  $104.7(4)^{\circ}$  belonging to the piperazine ring are compressed compared to the same angles in the free ligand of  $108.25(8)^{\circ}$ . The two NC pair dis-



**Fig. 4.** Perspective view of the crystal structure of **2** along the *b* axis. Perchlorate anions (green-red) are also shown in their crystal lattice locations with respect to the Co(III) octahedral centers (light blue) and water molecules (isolated red spheres). (Colour online.)

tances within the piperazine ring in the complex are different (1.486(8) and 1.517(8) Å) and longer than the corresponding bonds in the free ligand (1.452(3)–1.449(1) Å). Moreover, the range of torsion angles  $C(13)-C(14)-N(4)-C(15)_{propyl}$  of 166.1(5)–173.6(4)° is quite noticeable. The relevant torsion angles N–C–C–N of 6.1(6) and 6.4(5) for  $Co(1)^{\circ}$  (3.1(6) for Co(2)) in **2** are drastically reduced compared to the corresponding torsion angle in the free ligand (59.3(1)°), thereby confirming the switch of the piperazine conformation from *chair* to *boat* through metal ion complexation [53] and accounting for the "reinforced" effect induced by the presence of the two straps tagging the two piperazine nitrogen donors [54,55].

The molecular packing along the b axis in the unit cell (Fig. 4) shows a parallel arrangement of the molecules in layers, with rows and columns, with water molecules and perchlorate anions filling in the empty voids. The architecture is held together through van der Waals forces and hydrogen bonds. Weak C–H…O and weaker  $C-H \cdots C$  interactions do exist in **2** yet their contribution to the packing and crystal-linked molecular conformation of the material at hand is not as significant as that of the existing O-H···O hydrogen bonds [56–58] (see Supporting Information Table S2). Strong hydrogen bonding interactions form infinite zig-zag chains, alternating water molecules and perchlorate anions (from Cl1 and Cl2). The chains are parallel to the [101] lattice direction and form a one dimensional crystal arrangement. The third perchlorate anion together with the O18 water molecule, when duplicated by symmetry, gives groups which lie in an orthogonal arrangement to the former infinite chains. This way, the emerging crystal lattice arrangement seems like that it creates cellular voids in which the Co(III) complex cations are placed, having no interactions between them. Fig. 5A and B show the aforementioned crystal lattice architecture in the presence and absence of the cobalt complexes, respectively.

# 3.2.3. $[Zn_2(C_{24}H_{30}N_4O_2)(CH_3COO)_2]$ (3)

Compound **3** crystallizes in the monoclinic system, space group  $P2_1/c$ , with four molecules in the unit cell. The crystal structure of **3** reflects the presence of discrete ternary complex Zn(II) units. A view of the complex is shown in Fig. 6 and the crystal packing in the crystallographic unit cell along the *a* axis is given in Supplementary Information Fig. S1. All relevant bond lengths and angles are given in Table 2 (see also Supporting Information Table S1). The fundamental unit of **3** is a dinuclear complex of Zn(II) bearing both the ligand L and acetato groups. The bound ligand is doubly deprotonated with the sites of deprotonation being the phenolic

moieties of the salicylidene groups. The Schiff base ligand L accommodates two Zn(II) ions - almost identical, each located on the respective side of the piperazine bridge and bonded to one imino and one piperazine nitrogen atoms, one phenolic oxygen and two acetato oxygen atoms. The so configured coordination around Zn(II) leads to well-defined N<sub>2</sub>O<sub>3</sub> coordination polyhedra. The coordination geometry around Zn(II) can be described as a slightly distorted square pyramid ( $\tau$  0.13 for Zn(1) and 0.20 for Zn(2)) [59,60], with the basal plane defined by the NO<sub>3</sub> donor set arising from the imino nitrogen, one phenolic oxygen and two oxygen atoms belonging to the bidentate acetate. The Zn(II)-donor atom bond distances are in the expected values [61]. The presence of the acetato ligand, with the O(3)Zn(1)O(4) bond angles of  $58.8(1)^{\circ}$  $(57.8(1)^{\circ} \text{ for Zn}(2))$ , commonly encountered in chelate carboxylato binding motifs [62], are mainly responsible for the observed distortion. Thus, along with the above mentioned angles, the cis angles in the range  $94.8(2)-96.8(2)^{\circ}$  for Zn(1) ( $95.6(2)-97.8(2)^{\circ}$  for Zn(2)) and the trans O(1)Zn(1)O(4) and N(1)Zn(1)O(3) angles of 142.3(1) and 150.4(2)°, respectively, (139.2(1) and 150.9(2)° for Zn(2)) fall in the range reported for such distorted geometries [60]. The dinuclear assembly is stabilized through forcing Zn(II) ions above the basal plane by 0.491 Å. Further, the angles between the apical piperazine nitrogen, Zn(II) and the donor atoms in the basal plane - which should be equal to 90°, are spread in a quite broad range, between 91° and 119°.

The torsion angle NCCN in **3** has almost the same value of  $61.2(5)^{\circ}$  and  $58.5(5)^{\circ}$ , respectively, as in the free ligand  $(59.3(1)^{\circ})$ , thereby indicating a chair conformation of the piperazine core for both of them, different from the boat conformation in **2**  $(6.1(6)^{\circ}$  and  $6.4(5)^{\circ}$  for Co(1) and  $3.1(6)^{\circ}$  for Co(2)). Compared to the free ligand, small changes can be noticed in the piperazine bridge, which support the preservation of its stable *chair* conformation. Consequently, the two CNC angles of  $108.25(8)^{\circ}$  in the free ligand become  $105.9(3)^{\circ}$  and  $109.3(4)^{\circ}$  in the dinuclear Zn(II) complex; the same angles are compressed in the mononuclear Co(III) complex ( $104.7(4)^{\circ}$  and  $105.4(3)^{\circ}$  for Co(1) and  $103.3(4)^{\circ}$  for Co(2)) as a result of the conformational changes of the piperazine bridge.

In the salicylidene moieties, the average OC distance of 1.290(2) Å and the average imino CN distance of 1.284(2) Å are shorter and longer, respectively, than the corresponding distances in the free ligand (1.344(2) and 1.271(2) Å, respectively), thereby indicating charge density delocalization upon metal coordination.

The perspective view of the unit cell shows that the complex is stacked in a zig-zag layer fashion. The molecular packing along the



**Fig. 5.** Crystal structure in **2** along the *b* axis in the presence (**A**), and absence (**B**) of  $[Co(L)]^*$  assemblies. Hydrogen bonding in the crystal lattice is shown in blue, with the perchlorate anions (green-red) and water molecules (red-gray) participating in H-bond formation. (Colour online.)



Fig. 6. Molecular structure and atom labeling scheme of 3. H atoms are omitted for clarity.

*a* axis in the unit cell (see Supplementary Information Fig. S1) shows that the molecules are arranged in parallel layers. An intermolecular distance of 3.32(1) Å between O(3)<sub>acetate</sub> and C(11)<sub>piperazine</sub> belonging to neighboring molecules show hydrogen bond interactions responsible for this supramolecular association.

# 3.3. Spectral studies

## 3.3.1. NMR spectroscopy

The <sup>1</sup>H NMR spectrum of **1** (see Supporting Information Fig. S2) shows signals of protons belonging to -OH and -CH=N at 13.55 and 8.34 ppm, respectively. The value of 13.55 ppm for a phenolic proton associated with short  $N \cdots O$  and  $N \cdots H$  distance suggests strengthening of the N<sub>imine</sub>-O<sub>phen</sub> intramolecular hydrogen bonding interaction through  $\pi$  delocalization [63], termed resonanceassisted hydrogen bond [51]. The <sup>13</sup>C NMR spectrum displays a pattern of signals consistent with the structure of the free ligand (see Supporting Information Fig. S3). In the <sup>1</sup>H NMR spectrum of 3, the first signal is not present and the second one is shifted to lower values compared to its position in the free ligand, consistent with the coordination of the deprotonated ligand  $(\mathbf{L}^{2-})$  to the metal centers. The bound acetato ligand emerges in the <sup>1</sup>H NMR spectrum through the signal of the corresponding protons at 2.02 ppm (see Supporting Information Fig. S4) and in the <sup>13</sup>C NMR spectrum at 21.54 and 179.26 ppm (see Supporting Information Fig. S5).

#### 3.3.2. FT-IR spectroscopy

The FT-IR spectra of 2 and 3 are very complex. Bands, however, belonging to the ligand and differences in the spectra of the two compounds can be observed. Thus, the strong  $v_{C} = N$  peak of the free ligand at 1631  $\text{cm}^{-1}$  is shifted to 1623 in **2** and 1641  $\text{cm}^{-1}$  in **3**. In the spectra of the free ligand 1 and that of 3, bands of medium intensity at 1278 and 1282 cm<sup>-1</sup>, respectively, emerge. According to Okishi et al. [64], these bands belong to piperazine in the *chair* conformation. In this frequency range, a weak peak at 1254 cm<sup>-1</sup> can be observed in **2**. Moreover, a band assigned to the piperazine skeleton appears at 847 and 850  $\text{cm}^{-1}$  in **2** and **3**. respectively. compared to 846  $\text{cm}^{-1}$  in the free ligand. The spectrum of **2** shows a strong peak at 1093 cm<sup>-1</sup> and a medium intensity absorption at 622 cm<sup>-1</sup> assigned to ionic perchlorate stretching vibrations. Strong antisymmetric and symmetric vibrations at 1539 and 1447 cm<sup>-1</sup>, respectively, in the spectrum of **3** are attributed to the bidentate acetato ligand, with the difference between them  $(\Delta v)$  corresponding to its chelate binding mode [65]. Furthermore, the new band at 683 cm<sup>-1</sup> may be assigned to the  $\delta$ (OCO) vibration of the bound acetato group [66]. In the spectra of the two complexes, new weak bands observed at 595  $cm^{-1}$  (2) and 601  $cm^{-1}$ (3) are attributed to M–O stretching vibrations. At lower frequencies, in the range 412–497 cm<sup>-1</sup>, weak resonances can be assigned to the M–N bonds.

# 3.3.3. UV–Vis spectroscopy

The electronic spectrum of the free ligand (1) (chloroform solution) exhibits two intense bands at 274 and 316 nm, assignable to  $\pi$ - $\pi$ \* transitions, and a broad band at 409 nm, which may be attributed to n- $\pi$ \* transitions. In the spectrum of **2**, *d*-*d* transitions characteristic of octahedral Co(III) can be observed. Thus, the bands at 497, 580 and 654 nm attributable to  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$  transitions, respectively, are present. The pronounced splitting of  ${}^{1}T_{1g}$ , is indicative of a *trans*-octahedral geometry [67,68], which was confirmed by the X-ray crystal structure. In the spectrum of **3**, recorded in fresh chloroform solutions, the strong band at 367 nm can be assigned to a charge transfer transition. The bands at 280 and 387 nm may be assigned to intraligand  $\pi$ - $\pi$ \* transitions [69].

#### 3.3.4. Fluorescence spectroscopy

The fluorescence spectrum of the free ligand **1** shows a very weak emission peak ( $\lambda_{em}$  = 450 nm), which is attributed to electron delocalization involving the C=N double bond and a large intramolecular charge transfer effect [70]. The spectrum of **2** also shows a weak emission peak centered at 331 nm, hypsochromically shifted compared to the fluorescence behavior of ligand **1** and compound 3. This shift may be associated with changes in the metal ion coordination environment due to the adopted boat configuration of the piperazine moiety, in contrast to the *chair* conformation in **1** and **3**. The spectrum of 3 shows a typically intense fluorescence band usually observed in similar Schiff-base Zn(II) complexes [26], with the emission maximum centered at 446 nm and originating in a  $\pi$ - $\pi^*$ singlet ligand-centered excited state (Fig. 7). Fluorescence enhancement through complexation could be attributed to the increase in rigidity of the ligand forming a chelate ring, which can minimize the loss of energy through vibrational motions and increase the emission efficiency [71]. This behavior is of significant interest to us as it opens up the opportunity for photochemical applications of this material [72].

#### 3.4. Cyclic voltammetry

Cyclic voltammetric measurements of **1** and **3** were carried out in DMSO solutions ( $5 \times 10^{-4}$  M). The voltammogram in **1** shows a reduction wave at  $E_{\rm pc} = -0.96$  V and a corresponding oxidation wave at  $E_{\rm pa} = -0.70$  V. Further out, ill-defined oxidation processes at positive potentials are also observed. In the case of **3**, given the redox inactivity of Zn(II), reduction waves, likely ligand-based, at  $E_{\rm pc}$  values of -0.50 and -0.80 V were observed, with the corresponding oxidation feature appearing at -0.70 V. Collectively, the data suggest an irreversible redox activity associated with the organic ligand in its metal-free and metal-bound forms, albeit illdefined in both cases (Pt working electrode, scan rate: 100 mV s<sup>-1</sup>) and in line with those previously reported [73].

### 4. Discussion

# 4.1. The coordination flexibility of a chelator in the assembly of metal ionic complexes

The synthetic assembly of well-defined metal ion complexes with organic (O,N) chelator ligands rides on the (a) nature of the organic core and anchoring branch terminals, (b) denticity, oxidation state and size of the metal ion involved in coordination, (c) the



**Fig. 7.** Fluorescence spectra of Schiff base ligand 1 ( $H_2L$ ) and compound 3 in CHCl<sub>3</sub> and compound 2 in DMF (10<sup>-5</sup> M) at room temperature.

coordination mode capability of the terminal ligand anchors, and (d) coordination flexibility of the ligand and its ability to fold in upon itself or sequester upon folding, one or more metal ions of varying oxidation states and size. Undoubtedly, a well-configured organic ligand may possess more than one attributes in its quest for coordination to a metal ion. In the present case, the employed H<sub>2</sub>L ligand is multidentate, bulky, and appears to possess binding terminals that ensure metal ion coordination in a plethora of modes and fashions. It belongs to a series salicylaldehyde Schiff bases synthesized and structurally characterized in our laboratory, starting with N,N'-bis[(2-hydroxybenzilideneamino)-ethyl]piperazine [74]. In comparison to a previously reported synthesis, the present one was based principally in green chemistry [75], taking advantage of condensation under solvent-free conditions, short reaction time, simplicity of the Schiff base condensation reaction and work-up, an efficient and inexpensive catalyst  $(P_2O_5/SiO_2)$ and a highly pure product isolated in good yield. The open chain ligand 1, bears two (N,N,O) donor sets located symmetrically on both sides of the piperazine ring in the most stable chair conformation. N,N'-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine (H<sub>2</sub>L) and its mononuclear Mn(III), Fe(III), Co(III), Ni(II) have been previously reported [76], while recently, El-Sherif et al. [77] has also reported the biological activity of the specific ligand and its mononuclear Co(II), Ni(II) and Cu(II) complexes against some bacteria and fungi. In all cases, however, the nature of the ligand and that of the complexes involved were established only by NMR and IR spectra. To this end, the herein reported ligand H<sub>2</sub>L is the first representative of its family that's been crystallographically characterized in its free and metal chelated forms.

# 4.2. The piperazine conformation and the nuclearity of metal ionic assembly

The investigation of the chemical reactivity of the H<sub>2</sub>L ligand toward divalent metal ions led to the isolation of a binary (Co(III)) and a ternary (Zn(II)) complex under the same molecular stoichiometry conditions in alcoholic media. In the first case, coordination of the ligand was accompanied by oxidation of Co(II) to Co(III) [78]. Under stoichiometric conditions, the doubly deprotonated ligand literally engulfs the metal ion, thereby creating a well-configured cleft hosting it, while concurrently orients the terminal aromatic salicylidene rings so as to provide an opening for metal ion access to its geometrically dictated position (Fig. 3). Mass balance and charge neutralization required that perchlorate ions counterbalance the positively charged species. The arisen mononuclear octahedral complex of Co(III) contained the core piperazine ring in a boat conformation, in contrast to the chair conformation of its metal-free state. The overall formulated assembly denotes the influence of factors on metal ion complex assembly, fingerprinting its identity in the specifically arisen coordination environment.

In the case of zinc, the employed binary system bearing a Zn(II):H<sub>2</sub>L stoichiometry of 2:1 led to the isolation of a ternary dinuclear assembly of Zn(II). The metal ion binder appears to spread its coordination capacity terminals over two Zn(II) ions, thereby providing room for vacant positions in their respective coordination spheres. To this end, the acetato groups of the initially employed Zn(II) salt, occupy two sites in the coordination sphere of each Zn(II) center, acting as bidentate binders. The arising complex units get stabilized with a coordination number five at variance with the previously observed higher coordination number observed for Co(III) (absence of acetate groups). Mass and charge considerations require that the dinuclear Zn<sub>2</sub>L assembly be neutral in the presence of the two acetato moieties. The undisputed observation, however, that the deprotonated ligand continues to retain its chair conformation similar to the one in its original metal-free state indicates the propensity of that organic substrate to fulfill its coordination requirements without major re-arrangements. Physicochemical characterization of all three species through, among others, FT-IR, UV–Vis, fluorescence, and NMR were crucial in the identification of all three materials. Furthermore, molar conductivity measurements on freshly prepared DMF solutions showed the 1:1 electrolyte-type behavior for **2** and the non-electrolyte nature of **3** in CHCl<sub>3</sub> [79]. Ultimate proof was provided through X-ray crystallography.

It appears, therefore, that the chair piperazine conformation can be preserved by complexation leading to dinuclear metal complexes, whereas the boat conformation is found in mononuclear ones. Ostensibly, the adoption of the chair conformation is in line with a more relaxed, less strained, positioning of the deprotonated organic ligand toward metal ions, such as Zn(II), thereby promoting dinuclear assembly formation in the presence of the bidentate acetato group. In stark contrast to that, wrapping around the metal ion, such as Co(III), forces the piperazine core to modulate its spatial structure so as to accommodate the coordination requirement of an octahedral sphere. That, in turn places considerable strain on the piperazine core, thereby forcing it to switch conformation from "chair" to "boat". Collectively, therefore, fulfillment of metal ion coordination sphere requirements and the flexibility of the ligand core with its bidentate terminals appear to be linked to the nuclearity of the arising complex and reflect the modular nature of the organic metal ion binder. It is in this respect that efforts should be made to target binary mononuclear Zn(II)-L or ternary M-L-L' assemblies, forcing the piperazine-core ligand to adopt the "boat" conformation, in line with the observations made on the Co(III) complex.

#### 4.3. Schiff folding linked to optical activity

The Schiff base itself exhibits negligible fluorescence activity in its metal-free state. Upon metal ion coordination, 1 folds itself around the metal ion in ways that promote a complex assembly, thereby providing weak fluorescence for 2 and enhanced fluorescence for 3. In the case of 3, retention of the chair conformation upon metal ion complexation in a dinuclear Zn(II) assembly is associated with enhanced fluorescence activity (vide supra). The mononuclear assembly, on the other hand, characterized by wrapping of the ligand around the metal ion (Co(III)), is associated with weak yet shifted fluorescence signals compared to those of the free ligand. Ostensibly, the (a) chair versus boat conformation of the piperazine core ring, (b) nuclearity of the metal-L assembly, and (c) coordination geometry of the arising complex in 2 and 3, collectively influence fluorescence in the requisite complexes. It's also worth noting that  $\lambda_{em}$  in each case of complexes is distinct and may be associated with the coordination geometry, nuclearity or piperazine conformation of the arising species or all of those factors; these collective factors could influence the mechanisms associated with the optical activities observed. In this regard, the observed fluorescence properties would be interesting to investigate and compare under the distinctly variably assumed conformations of the ligand in mononuclear and dinuclear (or higher nuclearity) complex assemblies of these metal ions. This work is currently under investigation in our lab. Collectively, the research data from this work suggest that carefully configured metal ions binders can be employed in chemical reactivity patterns targeting well-defined binary and ternary M-L-(L') assemblies of distinct nuclearity, charge, structural and electronic optical properties.

# 5. Conclusions

The nature and structural properties of organic chelators play an essential role in metal binding processes, giving rise to specifically designed metal assemblies of variable nuclearity, coordination number and physicochemical properties. The herein synthesized Schiff base  $H_2L$  adopts a stable configuration, with a *chair* conformation of the piperazine ring in its metal-free state. Its structure and anchoring terminals promote binary M-L and ternary M-L-(L') assembly formation of variable nuclearity and physicochemical identity. Its structural flexibility and choice of chair (3) versus boat (2) conformation upon metal ion binding reflect the modular coordination capability exemplified through complexation, nuclearity, binary vs. ternary nature of the investigated system, metal coordination geometry and electronic and chemical properties in the solid state and in solution. To the extent that ligand 1 possesses features influencing metal ionic assembly linked to defined physicochemical properties (2 and 3), solid state crystaloptical property correlation and metal ion-ligand assembly recognition specificity, further work into the synthesis of flexible, appropriately configured organic metal ion binders, merits in-depth investigations leading to novel materials. Such work is currently ongoing in our labs.

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#### Appendix A. Supplementary data

CCDC 978594, 978592 and 978593 contains the supplementary crystallographic data for  $H_2L$  (1),  $[Co(L)]_3(ClO_4)_3 \cdot 4H_2O$  (2) and  $[Zn_2(L)(CH_3COO)_2]$  (3) respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retriev-ing.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.poly.2014.08.035.

### References

- [1] M. Du, C.P. Li, C.S. Liu, S.M. Fang, Coord. Chem. Rev. 257 (2013) 1282.
- [2] M. Kurmoo, Chem. Soc. Rev. 38 (2009) 1353.
- [3] R.Q. Zou, H. Sakurai, Q. Xu, Angew. Chem., Int. Ed. 45 (2006) 2542.
- [4] T. Tao, Y.H. Lei, Y.X. Peng, Y. Wang, W. Huang, Z.X. Chen, X.Z. You, Cryst. Growth Des. 12 (2012) 4580.
- [5] D.W. Bruce, D. O'Hare, R.I. Walton (Eds.), Molecular Materials, Wiley-VCH, Weinheim, 2010.
- [6] H.C. Zhou, J.R. Long, O.M. Yaghi, Chem. Rev. 112 (2012) 673.
  [7] P. Horcajada, C. Serre, D. Grosso, C. Boissiere, S. Perruchas, C. Sanchez, G. Ferey,
- Adv. Mater. 21 (2009) 1931. [8] W. Zhang, R.G. Xiong, Chem. Rev. 112 (2012) 1163.
- [9] S. Patai, The Chemistry of the Carbon-Nitrogen Double Bond, J. Wiley & Sons,
- London, 1970. 101 E. Lungrais, S. Thabet, Application, Applications of Schiff house, Mar. 11 D. 11
- [10] E. Jungreis, S. Thabet, Analytical Applications of Schiff bases, Marcell Dekker, New York, 1969.
- [11] A. Corma, H. García, F.X. Llabrés, I. Xamena, Chem. Rev. 110 (2010) 4606.
- [12] R.D. Jones, D.A. Summerville, F. Basolo, Chem. Rev. 79 (1979) 139.
- [13] P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 248 (2004) 1717
- [14] P. Wang, Z. Hong, Z. Xie, S. Tong, O. Wong, C. Lee, N. Wong, L. Hung, S. Lee, Chem. Commun. (2003) 1664.
- [15] C.M. Che, C.C. Kwok, S.W. Lai, A.F. Rausch, W.J. Finkenzeller, N.Y. Zhu, H. Yersin, Chem. Eur. J. 16 (2010) 233.
- [16] A.E. Visser, R.P. Swatloski, W.M. Reichert, J.H. Davis Jr., R.D. Rogers, R. Mayton, S. Sheff, A. Wierzbicki, Chem. Commun. (2001) 135.
- [17] A. Ouadi, B. Gadenne, P. Hesemann, J.J. Moreau, I. Billard, C. Gaillard, S. Mekki, G. Moutiers, Chem. Eur. J. 12 (2006) 3074.
- [18] H.Y. Shrivastava, B.U. Nair, Anal. Bioanal. Chem. 375 (2003) 169.
- [19] D. Chen, A.E. Martell, Y. Sun, Inorg. Chem. 28 (1989) 2647.
- [20] O.L. Harle, M. Calvin, J. Am. Chem. Soc. 68 (1946) 2612.
- [21] Y. Abe, K. Nakabayashi, N. Matsukawa, H. Takashima, M. Iida, T. Tanase, M. Sugibayashi, H. Mukai, K. Ohta, Inorg. Chim. Acta 359 (2006) 3934.
- [22] A.K. Singh, S. Kumari, T.N. Guru Row, J. Prakash, K. Ravi Kumar, B. Sridhar, T.R. Rao, Polyhedron 27 (2008) 3710.
- [23] R. Paschke, D. Balkow, E. Sinn, Inorg. Chem. 41 (2002) 1949.
- [24] T. Yu, K. Zhang, Y. Zhao, C. Yang, H. Zhang, L. Qian, D. Fan, W. Dong, L. Chen, Y. Qiu, Inorg. Chim. Acta 361 (2008) 233.

- [25] M.M. Abd-Elzaher, Synth. React. Inorg. Met.-Org. Chem. 30 (9) (2000) 1805.
- [26] D. Pucci, I. Aiello, A. Bellusci, A. Crispini, M. Ghedini, M. La Deda, Eur. J. Inorg. Chem. (2009) 4274.
- [27] T. Katsuki, Chem. Soc. Rev. 33 (7) (2004) 437.
- [28] P.A. Vigato, S. Tamburini, L. Bertolo, Coord. Chem. Rev. 251 (2007) 1311.
- [29] O. Costisor, L. Saity, W. Linert, Rev. Inorg. Chem. 25 (4) (2005) 285.
- [30] O. Costisor, W. Linert, Rev. Inorg. Chem. 24 (2) (2004) 62.
- [31] (a) K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420;
   (b) P. Roy, K. Dhara, M. Manassero, P. Banerjee, Inorg. Chim. Acta 362 (2009) 2927.
- [32] (a) P. Guerriero, S. Tamburini, P.A. Vigato, Coord. Chem. Rev. 139 (1995) 17;
   (b) A.W. Kleij, Eur. J. Inorg. Chem. (2009) 193.
- [33] G.B. Roy, Inorg. Chim. Acta 362 (2009) 1709.
- [34] C.R. Bhattacharjee, G. Das, P. Mondal, N.V.S. Rao, Polyhedron 29 (2010) 3089.
   [35] A. Vijayaraj, R. Prabu, R. Suresh, G. Jayanthi, J. Muthumary, V. Narayanan,
- Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 41 (2011) 963. [36] B. Donnio, D. Guillon, R. Deschenaux, D.W. Bruce, in: J.A. McCleverty, T.J. Mayer (Eds.) Comprehensive Coordination Chemistry, H. Elsavier, Oxford
- Meyer (Eds.), Comprehensive Coordination Chemistry II, Elsevier, Oxford, 2003, pp. 357–627.
   [37] A.S. Gaballa, M.S. Asker, A.S. Barakat, S.M. Teleb, Spectrochim. Acta, Part A 67
- (2007) 114.
- [38] C. Cretu, L. Cseh, G.H. Mehl, O. Costisor, Mol. Cryst. Liq. Cryst. 481 (2008) 26.
   [39] O. Costişor, I. Pantenburg, R. Tudose, G. Meyer, Z. Anorg, Allg. Chem 630 (2004)
- 1645. [40] R. Tudose, I. Pantenburg, G. Meyer, O. Costișor, M. Brezeanu, Rev. Roum. Chim. 49 (8) (2004) 663.
- [41] M. Boiocchi, M. Bonizzoni, L. Fabbrizzi, F. Foti, M. Licchelli, A. Taglietti, M. Zema, Dalton Trans. (2004) 653.
- [42] (a) K. Kubono, N. Hyrayama, H. Kokusen, K. Yokoi, Anal. Sci. 19 (2003) 645; (b) A. Vijayaraj, R. Prabu, R. Suresh, R.S. Kumari, V. Kaviyarasan, V. Narayanan, Bull. Korean Chem. Soc. 33 (11) (2012) 3581.
- [43] A.R. Paital, D. Mandal, X. Huang, J. Li, G. Aromì, D. Ray, Dalton Trans. (2009) 1352.
   [44] Bruker Analytical X-ray Systems, Inc., Apex2, Version 2 User Manual, M86–
- E01078, Madison, WI, 2006. [45] Siemens Industrial Automation, Inc. sadabs: Area-Detector Absorption Correction, Madison, WI, 1996.
- [46] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, J. Appl. Cryst. 36 (2003) 1487.
- [47] L. Palatinus, G. Chapuis, J. Appl. Cryst. 40 (2007) 786.
- [48] Crystal and Molecular Structure Visualization, Ver. 3.1, Crystal Impact, Rathausgasse 30, 53111, Bonn, Germany.
- [49] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. II (1987) S1.
- [50] R.-B. Xu, N. Zhang, H.-Y. Zhou, S.-P. Yang, Y.-Y. Li, D.-H. Shi, W.-X. Ma, X.-Y. Xu, J. Chem. Crystallogr. 42 (2012) 928.
- [51] (a) P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, J. Am. Chem. Soc. 122 (2000) 10405;
- (b) V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, J. Am. Chem. Soc. 113 (1991) 4917.[52] C. Zhang, G. Rheinwald, V. Lozan, B. Wu, P.-G. Lassahn, H. Lang, C. Janiak, Z.
- Anorg, Allg. Chem. 628 (2002) 1259.
- [53] J.B. Ray, P. Mohamad, P.J. Jerry, Acta Cryst. E63 (2007) m1913.
- [54] P. Weinberger, O. Costisor, R. Tudose, O. Baumgartner, W. Linert, J. Mol. Struct. 519 (2000) 21.
- [55] O. Costișor, R. Tudose, I. Pantenburg, G. Meyer, Z. Naturforsch. 57B (2002) 1454.
- [56] G.F. Fabiola, S. Krishnaswamy, V. Nagarajan, V. Pattabhi, Acta Cryst. D53 (1997) 316.
- [57] T. Steiner, Angew. Chem., Int. Ed. 41 (2002) 48.
- [58] T. Steiner, W. Saenger, J. Am. Chem. Soc. 114 (1992) 10146.
- [59] M.-A. Munoz-Hernandez, T.S. Keizer, P. Wei, S. Parkin, D.A. Atwood, Inorg. Chem. 40 (2001) 6782.
- [60] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
- [61] (a) E. Prince, International Tables for Crystallography, Mathematical, Physical and Chemical Tables, Springer, 2004. p. 850;
  (b) R. Ghosh, S.H. Rahaman, C.-N. Lin, T.-H. Lu, B.K. Ghosh, Polyhedron 25
- (2006) 3104.
- [62] T. Ishioka, A. Murata, Y. Kitagawa, K.T. Nakamura, Acta Cryst. C (1997) 1029.
- [63] J. Chin, F. Mancin, N. Thavarajah, D. Lee, A. Lough, D.S. Chung, J. Am. Chem. Soc. 125 (2003) 15276.
- [64] Y. Okishi, Y. Imai, K. Aida, J. Inorg. Nucl. Chem. 35 (1973) 101.
- [65] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., John Wiley & Sons, Inc. Publication, New York, 1986.
- [66] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, Inc. Publication, New York, 1963.
- [67] P.V. Bernhardt, G.A. Lawrance, J. Chem. Soc., Dalton Trans. (1989) 1059.
- [68] F. Rafat, M.Y. Siddiqi, K.S. Siddiqi, J. Serb. Chem. Soc. 69 (8-9) (2004) 641.
- [69] W.-Y. Bi, X.-Q. Lü, W.-L. Chai, W.-J. Jin, J.-R. Song, W.-K. Wong, Inorg. Chem. Commun. 11 (2008) 1316.
- [70] L. Wang, W. Qin, W. Liu, Inorg. Chem. Commun. 13 (2010) 1122.
- [71] D.-D. Qin, Z.-Y. Yang, G.-F. Qi, Spectrochim. Acta, Part A 74 (2009) 415.
- [72] A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra, Polyhedron 25 (2006) 1753.
- [73] I. Kaya, S. Uysal, J. Appl. Polym. Sci. 120 (2011) 3325.
- [74] (a) M. Safta, C. Wikete, M.-L. Boillot, O. Costişor, Ann. West Univ. Timişoara Ser. Chem. 10 (3) (2001) 1017;

(b) C. Wikete, F. Popa, M.-L. Boillot, O. Costişor, Ann. West Univ. Timişoara Ser. Chem. 10 (3) (2001) 1041.
[75] A. Bhattacharya, V.C. Purohit, Org. Proc. Res. Dev. 7 (2003) 254.
[76] H. Kuma, S. Yamada, Bull. Chem. Soc. Jpn. 531 (1980) 3218.

- [77] A.A. El-Sherif, M.R. Shehata, M.M. Shoukry, M.H. Barakat, Spectrochim. Acta, Part A 96 (2012) 889.
  [78] S. Banerjee, J.-T. Chen, C.-Z. Lu, Polyhedron 26 (2007) 686.
  [79] W. Geary, J. Coord. Chem. Rev. 7 (1971) 81.