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Formation of three photoluminescent zinc(II) complexes with Zn_2O_2 cores: Examples of bi-dentate bonding modes of potentially tri- and tetra-dentate Schiff bases

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ABSTRACT

The 1:1 condensation of *N*,*N*-dimethyl-1,3-diaminoethane with 5-bromosalicylaldehyde, 3-methoxysalicylaldehyde and 3-ethoxysalicyalaldede produces three Schiff bases, HL^1 [*2-(-(3-(dimethylamino)propylimino)methyl)-4-bromophenol*], HL^2 [*2-(-(3-(dimethylamino)propylimino)methyl)-6-methoxyphenol*] and HL^3 [*2-(-(3-(dimethylamino)propylimino)methyl)-6-ethoxyphenol*], respectively. Addition of zinc(II) perchlorate to the methanol solution of HL^1 produces a phenoxo bridged dinuclear zinc(II) complex, $[Zn_2(HL^1)_4](ClO_4)_4$ (**1**), where the potential tridentate N_2O donor Schiff base, HL^1, is trapped in its zwitterionic form and behaves like a bi-dentate ligand. On the other hand, phenoxo bridged dinuclear complexes, $[(HL^2)Zn_2(L^2)(dca)_2]ClO_4$ (**2**) and $[(HL^3)Zn_2(L^3)(NCS)_2]ClO_4{\cdot}CH_3OH$ (**3**) are produced by the addition of zinc(II) perchlorate into the methanol solutions of the potential tetradentate Schiff bases, HL^2 and HL^3, respectively, followed by the addition of sodium dicyanamide or sodium thiocyanate. In both complexes, Schiff bases are trapped in their deprotonated anionic forms and non-deprotonated zwitterionic forms as well. The deprotonated ligands are coordinated in their usual chelating tetradentate manners whereas zwitterionic forms of the non-deprotonated ligands are coordinated to zinc(II) only through the imine nitrogen and phenoxo oxygen, i.e., they behave as bi-dentate ligands. The structures of the complexes have been confirmed by single crystal X-ray diffraction studies. All three complexes are dinuclear and contain Zn_2O_2 cores. All three complexes show fluorescence.

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1. Introduction

Design and synthesis of di and polynuclear complexes of transition metals attract a lot of interests now-a-days because of their potential uses in magnetism, catalysis, opto-electronic devices, molecular architectures, material science, etc. [1–6]. Schiff bases are very well-known chelating ligands to the synthetic inorganic chemists to prepare such di and polynuclear complexes [7–10]. Among all the Schiff bases, H_2salen type Schiff bases are definitely receiving the most attention, as they can form poly-nuclear complexes exploiting the bridging ability of phenoxo oxygen atoms [11–16]. N_2O donor tridentate Schiff bases could also be prepared easily and used to synthesize several di and polynuclear transition metal complexes [17–20]. The versatile ability of phenoxo oxygen atoms to bind metal ions in different coordination modes, have led to the isolation of a large number of coordination compounds with interesting molecular and crystalline architectures and different dimensionality [10,17,21–25]. A large number of phenoxo-bridged transition metal complexes have been prepared in order to examine the extent of magnetic exchange interaction in these complexes [26,27]. However, phenoxo-bridged complexes derived from d^{10} metal ions did not receive such high attention compared to the other mentioned metal ions, probably because of the lack of magnetic exchange interaction in it. In this context, it is noteworthy that the importance of the d^{10} metal complexes lies in their strong luminescence properties and potential applications in electronic and optoelectronic devices [28,29].

Focusing to zinc, it has a vital importance in metabolism, and is necessary for proper functioning of the immune system [30]. Zinc is the second most abundant transition metal in the human body and is an essential cofactor in many biological processes [31,32]. Zinc(II) may adopt varieties of geometries as a consequence of its d^{10} electronic configuration with no CFSE in any geometry. Exploiting these varieties of coordination geometries around zinc(II), various molecular architectures may be produced [33–38].

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The synthesis and characterization of new zinc(II) complexes deserve further exploration following the discovery of zinc(II) containing enzymes, e.g., carbonic anhydrase (the biological counterpart to haemoglobin), which transports CO_2 from the body. On the other hand, supramolecular systems based on coordination complexes have widely been used as photonic devices, sensors and catalysts and in host–guest chemistry [39–47]. A significant number of supramolecular zinc(II) complexes has been synthesized in the last several years [33–38]. In the present work, we have used three flexidentate Schiff bases as blocking ligands to prepare dinuclear zinc(II) complexes with Zn_2O_2 cores. In each of the complexes, zwitterionic forms of the Schiff bases are trapped. Herein, we would like to report the synthesis and characterization of two phenoxo bridged dinuclear zinc(II) complexes with pseudo-halide co-ligands. All complexes exhibit fluorescence in acetonitrile medium.

2. Experimental

All chemicals were of reagent grade and used as purchased from Sigma–Aldrich without further purification.

Caution!!! Although no problems were encountered in this work, organic ligands in the presence of perchlorates are potentially explosive. Only a small amount of the material should be prepared and it should be handled with care.

2.1. Preparations

2.1.1. Preparation of ligands

2.1.1.1. HL^1 (2-(-(3-(dimethylamino)propylimino)methyl)-4-bromophenol). The tridentate Schiff base ligand, HL^1, was prepared by refluxing *N,N*-dimethyl-1,3-diaminopropane (0.10 ml, 1 mmol) with 5-bromosalicylaldehyde (200 mg, 1 mmol) in methanol solution (20 ml) for ca. 1 h. It was not purified and used directly for the preparation of complex **1**.

2.1.1.2. HL^2 (2-(-(3-(dimethylamino)propylimino)methyl)-6-methoxyphenol). The tetradentate Schiff base ligand, HL^2, was prepared by refluxing *N,N*-dimethyl-1,3-diaminopropane (0.10 ml, 1 mmol) with 3-methoxysalicylaldehyde (152 mg, 1 mmol) in methanol solution (20 ml) for ca. 1 h. It was not purified and used directly for the preparation of complex **2**.

2.1.1.3. HL^3 (2-(-(3-(dimethylamino)propylimino)methyl)-6-ethoxyphenol). It was prepared in a method similar to that for the ligand, HL^2, except that 3-ethoxysalicylaldehyde (166 mg, 1 mmol) was used instead of 3-methoxysalicylaldehyde. It was not purified and used directly for the preparation of complex **3**.

2.1.2. Preparation of complexes

*2.1.2.1. $[Zn_2(HL^1)_4](ClO_4)_4$ (**1**).* A methanol solution (10 ml) of zinc(II) perchlorate hexahydrate (185 mg, 0.5 mmol) was added to the methanol solution of the ligand HL^1 and the resulting solution was refluxed for ca. 1 h. A light yellow crystalline solid was separated out after 2 days and collected by filtration. X-ray quality single crystals of complex **1** were obtained after few days on slow evaporation of the methanol solution of the complex in open atmosphere.

Yield: 1235 mg, 74% (based on zinc). *Anal.* Calc. for $C_{48}H_{68}Br_4Cl_4N_8O_{20}Zn_2$ ($M = 1669.28$ g mol^{-1}): C, 34.54; H, 4.11; N, 6.71. Found: C, 34.1; H, 4.0; N, 6.9%. FT-IR (KBr, cm^{-1}): 1085 (Cl–O); 1630 (C=N). λ_{max} (nm) [ε_{max}(L mol^{-1} cm^{-1})] (acetonitrile): 228 (1.97×10^4); 267 (8.31×10^3); 371 (2.67×10^3). M.P.: >200 °C.

*2.1.2.2. $[(HL^2)Zn_2(L^2)(dca)_2]ClO_4$ (**2**).* A methanol solution (10 ml) of zinc(II) perchlorate hexahydrate (370 mg, 1 mmol) was added to the methanol solution of the ligand HL^2 and the resulting solution was refluxed for ca. 30 min. A methanol–water (2:1) solution (10 ml) of sodium dicyanamide (89 mg, 1 mmol) was then added and the refluxing was continued for an additional 1 h. A light yellow crystalline precipitate of complex **2** was separated out after 2 days and collected by filtration. Single crystals, suitable for X-ray diffraction, were obtained after few days on slow evaporation of the of the methanol solution of the complex in open atmosphere.

Yield: 609 mg, 73%. *Anal.* Calc. for $C_{30}H_{39}ClN_{10}O_8Zn_2$ ($M = 833.9$ g mol^{-1}): C, 43.21; H, 4.71; N, 16.80. Found: C, 43.1; H, 4.5; N, 16.9%. FT-IR (KBr, cm^{-1}): 1085 (Cl–O); 1629 (C=N); 2173, 2226, 2292 (dca). λ_{max} (nm) [ε_{max}(L mol^{-1} cm^{-1})] (acetonitrile): 230 (1.85×10^4); 271 (9.64×10^3); 363 (3.01×10^3). M.P.: >200 °C.

*2.1.2.3. $[(HL^3)Zn_2(L^3)(NCS)_2]ClO_4{\cdot}CH_3OH$ (**3**).* A methanol solution (10 ml) of zinc(II) perchlorate hexahydrate (370 mg, 1 mmol) was added to the methanol solution of the ligand HL^3 and the resulting solution was refluxed for ca. 30 min. A methanol–water (2:1) solution (10 ml) of sodium thiocyanate (81 mg, 1 mmol) was then added and the refluxing was continued for an additional 1 h. It was cooled and kept for few days to get pale yellow crystals of complex **3**, which were collected by filtration. Single crystals, suitable for X-ray diffraction, were obtained after few days on slow evaporation of the methanol solution in open atmosphere.

Yield: 676 mg, 77%. *Anal.* Calc. for $C_{31}H_{47}ClN_6O_9S_2Zn_2$ ($M = 878.05$ g mol^{-1}): C, 42.40; H, 5.39; N, 9.57. Found: C, 42.2; H, 5.1; N, 9.7%. FT-IR (KBr, cm^{-1}): 1085 (Cl–O); 1615 (C=N); 2091 (NCS). λ_{max} (nm) [ε_{max}(L mol^{-1} cm^{-1})] (acetonitrile): 233 (2.01×10^4); 275 (9.29×10^3); 365 (3.71×10^3). M.P.: >200 °C.

2.2. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded with a Perkin–Elmer Spectrum Two spectrophotometer. Electronic spectra in acetonitrile were recorded on a Perkin–Elmer Lambda 35 UV–Vis spectrophotometer. Fluorescence spectra in acetonitrile were obtained in Shimadzu RF-5301PC spectrofluorometer at room temperature. Lifetime measurements were recorded using Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBHDAS6 software. Intensity decay profiles were fitted to the sum-of exponentials series

$$I(t) - \sum_i A_i exp(-t/\tau_i)$$

where A_i is a factor representing the fractional contribution to the time-resolved decay of the component with a lifetime of τ_i. The intensity-averaged life times (τ_{av}) are determined using the following equation:

$$< \tau >= \sum_i A_i \tau_i^2 / \sum_i A_i \tau_i$$

Powder X-ray diffractions were performed on a Bruker D8 instrument with Cu Kα radiation.

2.3. X-ray crystallography

Suitable crystals of the complexes were used for data collection using a 'Bruker D8 QUEST area detector' diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The molecular structures were solved by direct method and refined by full-matrix least squares on F^2 using the SHELX-97 and SHELX-2013 package [48,49]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [50]. In the crystal structure of complex **3**, the thiocyanate group has been refined using two positions with occupation factor 0.84 and 0.16, respectively. Also the methanol molecule has been refined with the oxygen atom at two positions with occupation factors 0.8 and 0.2, respectively. The details of crystallographic data and refinements are given in Table 1. Selected bond lengths and bond angles are gathered in Tables 2 and S1 (Supplementary information), respectively.

Table 2
Selected bond lengths (Å) of **1**, **2** and **3**.

	1	2	3
Zn(1)–O(2)	2.067(5)	2.089(2)	2.077(3)
Zn(1)–O(2)*	2.088(5)	–	–
Zn(1)–O(8)	1.979(5)	2.021(2)	2.036(3)
Zn(1)–N(5)	2.038(6)	2.094(2)	2.076(3)
Zn(1)–N(21)	–	2.025(2)	2.031(4)
Zn(1)–N(21)*	2.078(6)	–	–
Zn(1)–N(1)	–	2.102(2)	2.112(4)
Zn(2)–O(2)	–	2.033(2)	2.021(3)
Zn(2)–O(8)	–	1.999(2)	1.993(3)
Zn(2)–O(15)	–	2.355(2)	2.387(3)
Zn(2)–N(33)	–	1.966(2)	1.925(4)
Zn(2)–N(38)	–	1.954(2)	1.967(5)

Symmetry transformation: * = 1 − *x*, −*y*,1 − *z*.

3. Results and discussion

3.1. Synthesis

The tridentate Schiff-base ligands, HL^1, HL^2 and HL^3, were synthesized by the condensation of *N,N*-dimethyl-1,3-diaminopropane, respectively, with 5- bromosalicylaldehyde, 3-methoxysalicylaldehyde and 3-ethoxysalicyalaldede in 1:1 M ratio, following the literature method [7–10]. Addition of zinc(II) perchlorate hexahydrate to the methanol solution of HL^1 produced a deep yellow solution. Single crystals of phenoxo-bridged dinuclear complex **1**, suitable for X-ray diffraction, were grown from it. On the other hand, complexes **2** and **3** were produced by the addition of zinc(II) perchlotate hexahydrate into the methanol solution of HL^2 and HL^3, respectively, followed by the addition of sodium dicyanamide or sodium thiocyanate. Both are phenoxo bridged dinuclear complexes. It is to be noted here that the use of zinc(II) bromide or zinc(II) chloride and HL^1 produced mononuclear zinc(II) complexes, $[Zn(HL^1)Br_2]$ and $[Zn(HL^1)Cl_2]$ respectively, the structures of which were reported by different groups [51,52]. HL^2 was also used to prepare similar mononuclear zinc(II) complex, $[Zn(HL^2)(SCN)_2]\cdot CHCl_3$, [53]. Use of zinc(II) iodide with a very similar ligand produced similar mononuclear complex, $[Zn(HL)I_2]\cdot CH_3OH$ {*HL* = 2-(-(3-(diethylamino)propylimino)methyl)-4-bromophenol} [54]. It is to be noted here, in all complexes, the Schiff bases are present in their zwitterionic forms. The increased acidity of the medium due to the presence of perchlorate or halide is responsible for the non-deprotonation of the Schiff base. The lower coordinating ability of perchlorate compared to halides may be the driving force for the formation of phenoxo-bridged dinuclear complex, **1**. On the other hand, in both **2** and **3**, one of the Schiff bases is present in its zwitterionic form. The increase in pH due to the addition of dicyanamide or thiocyanate may be responsible for the deprotonation of one of the Schiff bases. The formation of all three complexes is shown in Scheme 1.

It is to be noted here, HL^1 is a potential tridentate ligand and uses its two donor sites to bind zinc(II) in complex **1**. On the other hand, HL^2 and HL^3 are potential tetradentate ligands. Their bi-dentate and tetradentate bonding modes are observed in complexes **2** and **3**. Thus all three Schiff bases are behaving as pendant ligands. The term 'pendant' is applied to a potential polydentate ligand having additional donor groups attached to its periphery. A large number of pendant ligands are used by different groups in a variety of different chemical applications [55–59]. The importance of these pendant ligands lies in their ability to perturb metal ions at additional coordination sites, in competition with external substrates, as well as to provide connection points for other molecules.

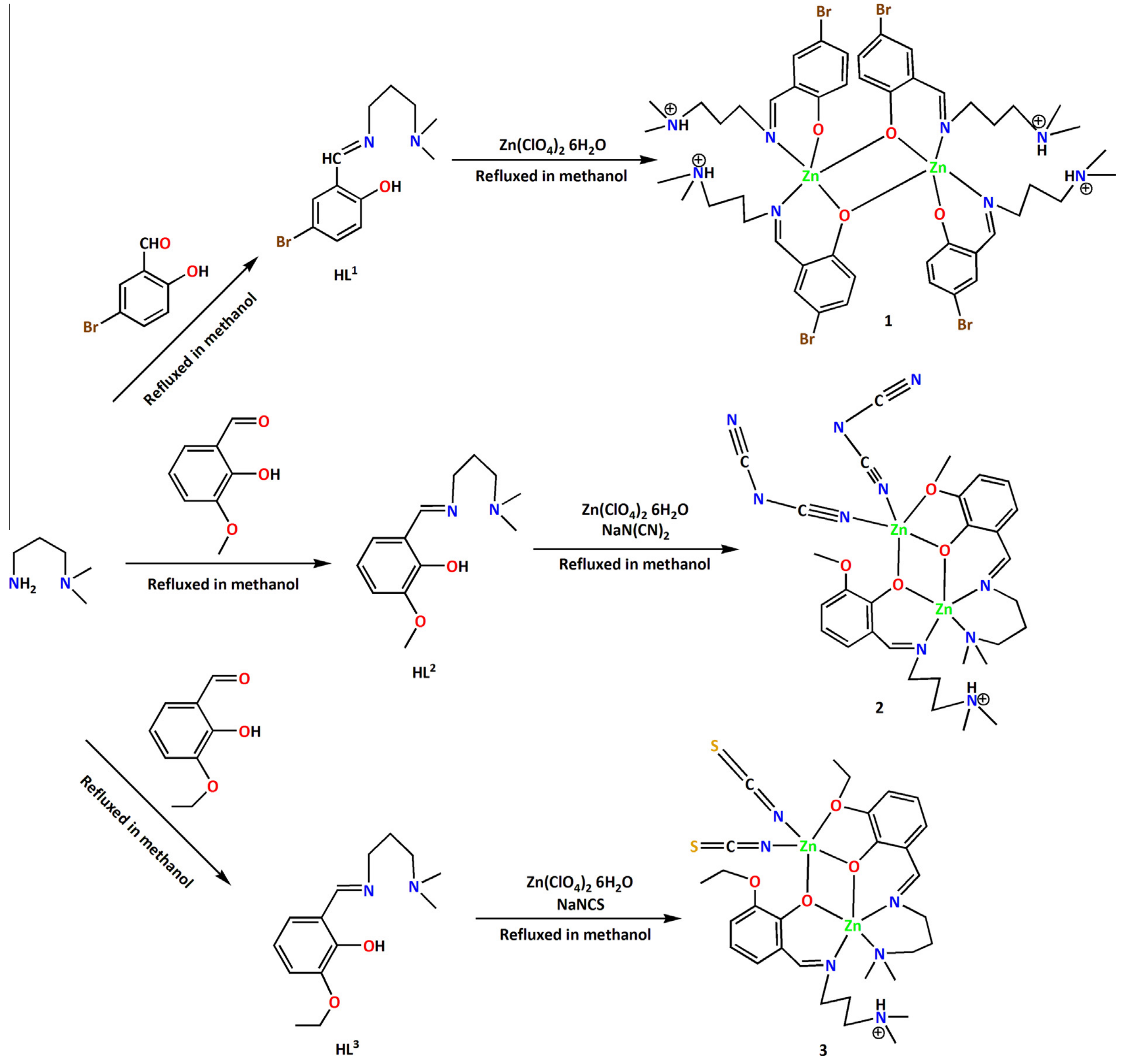
3.2. Structure description

3.2.1. Complex $[Zn_2(HL^1)_4](ClO_4)_4$ (1)

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. A perspective view of complex **1** with selective atom numbering scheme is shown in Fig. 1. In the asymmetric unit, each of the zinc(II) centres is coordinated by two phenoxo oxygen atoms, O(1) and O(2) and two imine nitrogen atoms, N(1) and N(3) from two zwitterionic Schiff bases (HL^1). The fifth coordination site of each zinc(II)

Table 1
Crystal data and refinement details of complexes **1**, **2** and **3**.

Complex	1	2	3
Formula	$C_{48}H_{68}Br_4Cl_4N_8O_{20}Zn_2$	$C_{30}H_{39}ClN_{10}O_8Zn_2$	$C_{31}H_{47}ClN_6O_9S_2Zn_2$
T (K)	100	100	100
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	10.222(5)	9.620(1)	9.305(1)
b (Å)	13.091(5)	11.749(1)	23.758(2)
c (Å)	14.074(5)	16.827(1)	17.394(1)
α (°)	74.665(5)	84.948(2)	–
β (°)	73.008(5)	81.592(2)	98.345(2)
γ (°)	67.572(5)	73.888(2)	–
Z	1	2	4
D_{calc} (g cm^{-3})	1.690	1.534	1.533
μ (mm^{-1})	3.405	1.465	1.499
F(000)	840	860	1824
Total reflections	24840	32676	79287
Unique reflections	6224	8307	7005
Observed data [$I > 2\sigma(I)$]	3961	6439	5560
No. of parameters	364	470	505
R_{int}	0.050	0.056	0.083
*R*1, *wR*2 (all data)	0.1020, 0.1968	0.0573, 0.0767	0.0675, 0.1190
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0612, 0.1724	0.0352, 0.0701	0.0476, 0.1094



Scheme 1. Preparation of the complexes.

centre is occupied by a symmetry related phenoxo oxygen atom, O(2)* (symmetry transformation: * = 1 − *x*, −*y*,1 − *z*). The zinc(II)···zinc(II) distance within the dinuclear unit is 3.277(2) Å. The geometry of the penta-coordinated metal center may conveniently be measured by the Addison parameter (τ) [$\tau = (\alpha - \beta)/60$, where α and β are the two largest Ligand–Metal–Ligand angles of the coordination sphere ($\tau = 0$ infers an ideal square pyramid and $\tau = 1$ infers a perfect trigonal bipyramid)] [60]. The Addison parameter is 0.76 indicating the actual geometry of the zinc(II) centre is close to trigonal bipyramid.

The complex forms two intermolecular hydrogen bonds. The hydrogen atom H(1) attached with the free amine nitrogen atom N(1) of the zwitter-ionic Schiff base is hydrogen bonded with an oxygen atom O(5) of a perchlorate anion. Similarly, the hydrogen atom H(17) attached with N(17) of another zwitter-ionic Schiff base forms a hydrogen bond with the oxygen atom O(10) as shown in Fig. 2. The details of the hydrogen bonding interactions are given in Table 3.

3.2.2. Complex $[(HL^2)Zn_2(L^2)(dca)_2]ClO_4$ (**2**)

Complex **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of dinuclear $[(HL^2)Zn_2(L^2)(dca)_2]^+$ cation and perchlorate anion. A perspective view of complex **2** is shown in Fig. 3. Within the dinuclear unit, two penta-coordinated zinc(II) centres are bridged by phenoxo oxygen atoms, O(2) and O(8) of two molecules of the Schiff base. The other coordination sites of Zn(1) centre are occupied by an amine nitrogen atom, N(1) and an imine nitrogen atom, N(5), from a deprotonated Schiff base $(L^2)^-$ and an imine nitrogen atom, N(21) from a zwitterionic Schiff base (HL^2) and that of Zn(2) are occupied by a methoxy oxygen atom, O(15) of the deprotonated Schiff base $(L^2)^-$ and two nitrogen atoms, N(33) and N(38), from two terminal dicyanamides. The zinc(II)···zinc(II) distance within the dinuclear unit is 3.1828(5) Å. The saturated six membered chelate ring, Zn(1)–N(1)–C(2)–C(3)–C(4)–N(5), exhibits an intermediate conformation between chair and half-chair with puckering parameters $q = 0.616(2)$ Å, $\theta = 2.64(19)°$, $\phi = 252(4)°$ [61–63]. The Addison parameters are 0.67 for Zn(1) and 0.41 for Zn(2), indicating the actual geometries of zinc(II) are intermediate between trigonal bipyramid and square pyramid.

The hydrogen atom H(1) attached with the free amine nitrogen atom N(17) of the zwitter-ionic Schiff base is hydrogen bonded with a symmetry related nitrogen atom N(42)[b] (Symmetry

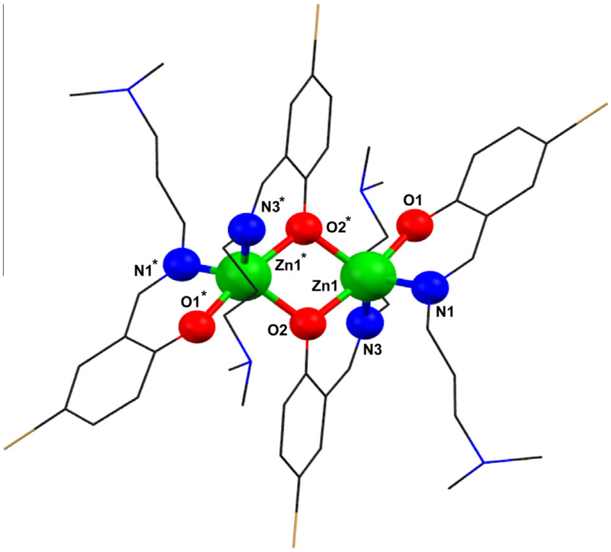


Fig. 1. Perspective view of the complex **1** with selective atom numbering scheme of the metal and coordinating atoms. Hydrogen atoms are omitted for clarity.

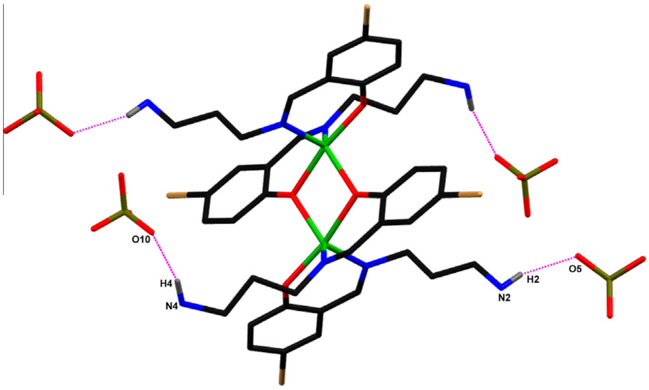


Fig. 2. Inter-molecular hydrogen bonding interactions among the complex moiety and the counter anions in complex **1**. Only the interacting hydrogen atoms are shown in figure. Methyl groups of amine nitrogen atoms are omitted for clarity.

Table 3
Hydrogen bonding distances (Å) and angles (°) for complex **1** and **2**.

Complex	D–H···A	D–H (Å)	D···A (Å)	H···A (Å)	∠D–H···A (°)
1	N(1)–H(1)···O(5)	0.91	2.790(14)	1.89	171
	N(17)–H(17)···O(10)	0.91	2.857(12)	1.98	162
2	N(17)–H(1)···N(42)^a	0.89	2.909(3)	2.09	153

Symmetry transformations: a = 1 – *x*,1 – *y*,1 – *z*. D = donor; H = hydrogen; A = acceptor.

transformation: *b* = 1 – *x*,1 – *y*,1 – *z*) of a dicyanamide anion from a neighbouring molecule to form a dimeric structure (Fig. 4). The details of the hydrogen bonding interactions are given in Table 3.

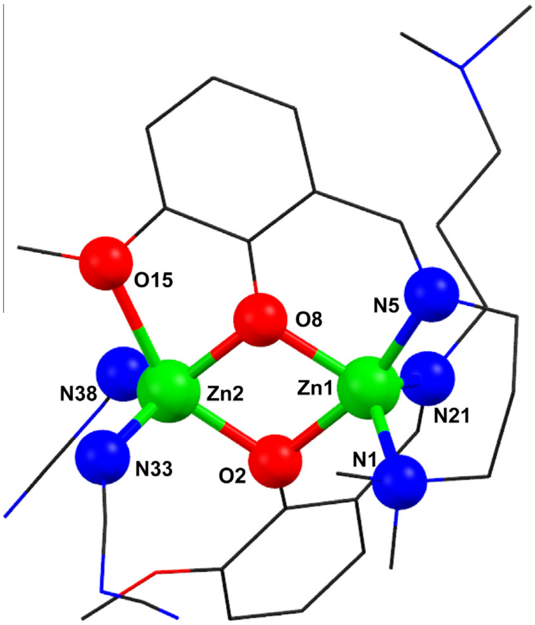


Fig. 3. Perspective view of the complex **2** with selective atom numbering scheme of the metal and coordinating atoms. Hydrogen atoms are omitted for clarity.

The complex shows significant intra and inter-molecular C–H···π interactions. The hydrogen atom, H(19B) attached with C(19) is involved in an intra-molecular C–H···π interaction with the chelate ring **R^4** [Zn(1)–O(8)–C(8)–C(7)–C(6)–N(5)]. On the other hand, the hydrogen atom, H(28) attached with C(28) is involved in inter-molecular C–H···π interaction with the phenyl ring **R^6** [C(7)–C(8)–C(9)–C(10)–C(11)–C(12)] of a symmetry related (1 + *x*,*y*,*z*) molecule. Similarly, the hydrogen atom, H(30B), attached with the methyl carbon atom C(30) shows another inter-molecular C–H···π interaction with a symmetry related (*x*,–1 + *y*,*z*) phenyl ring **R^7** [C(23)–C(24)–C(25)–C(26)–C(27)–C(28)]. The combination of these two inter-molecular C–H···π interactions produced a 2D sheet structure as shown in Fig. 5. The details of the geometric features of the C–H···π interactions are given in Table 4.

3.2.3. Complex [(HL^3)Zn$_2$(L^3)(NCS)$_2$]ClO$_4$·CH$_3$OH (**3**)

The structure of complex **3** is very similar to that of complex **2**. It crystallizes in the monoclinic space group *P*2$_1$/*c*. The asymmetric unit consists of a dinuclear *[(HL^3)Zn(L^3)Zn(NCS)$_2$]$^+$* cation, one perchlorate anion and a methanol of crystallization. A perspective view of complex **3** is shown in Fig. 6. The Zn(1) centre is surrounded by an amine nitrogen atom, N(1), one imine nitrogen atom, N(5), and a phenoxo oxygen atom, O(8), from a deprotonated Schiff base ligand, (L^3)$^-$, and a phenoxo oxygen atom, O(2), and an amine nitrogen atom, N(21), from a zwitterionic Schiff base (*HL^3*). On the other hand, Zn(2) centre is coordinated by a phenoxo oxygen atom, O(8) and an ethoxy oxygen atom, O(15), of the deprotonated Schiff base, one phenoxo oxygen atom, O(2), of the zwitterionic Schiff base and two nitrogen atoms, N(33) and N(38), from two terminal thiocyanates. Thus two penta-coordinated zinc(II) centres are bridged by phenoxo oxygen atoms, O(2) and O(8). The zinc(II)···zinc(II) distance within the dinuclear unit is 3.1427(7) Å. The saturated six membered chelate ring, Zn(1)–N(1)–C(2)–C(3)–C(4)–N(5), exhibits an intermediate conformation between chair and half-chair with puckering parameters *q* = 0.606(4) Å, θ = 173.8(4)°, θ = 73(3)° [61–63]. The Addison parameters are 0.67 for Zn(1) and 0.35 for Zn(2), indicating the actual geometries of zinc(II) are intermediate between trigonal bipyramid and square pyramid.

The complex shows both intra and inter-molecular C–H···π interactions. The hydrogen atom, H(31B) attached with C(31) is involved in an intra-molecular C–H···π interaction with the phenyl ring **R^6** [C(7)–C(8)–C(9)–C(10)–C(11)–C(12)] On the other hand, the hydrogen atom, H(206) attached with C(200) is involved in an inter-molecular C–H···π interaction with the phenyl ring **R^7** [C(24)–C(25)–C(26)–C(27)–C(28)–C(29)] of a symmetry related (*x*,1/2-*y*,1/2 + *z*) methanol molecule as shown in Fig. 7. The details

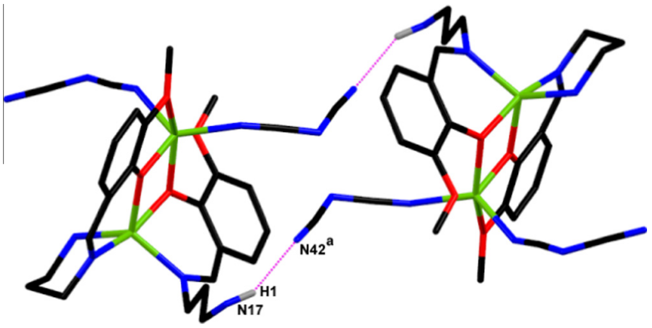


Fig. 4. Hydrogen bonding interactions in complex **2** forming a dimeric structure. The methyl groups of amine nitrogens and hydrogen atoms except the interacting ones are omitted for clarity.

of the geometric features of the C–H···π interactions are given in Table 4.

3.3. IR, electronic and luminescence spectra

In IR spectra of all three complexes distinct bands due to the azomethine (C=N) groups within the range of 1615–1630 cm^{-1} are routinely noticed [64,65]. The strong band at 1085 cm^{-1} give evidence for the presence of ionic perchlorate in each of the complex [66]. The dicyanamide anion in complex **2** shows three characteristic IR absorptions located in the region 2170–2300 cm^{-1} [67]. A strong band at 2091 cm^{-1} in the IR spectrum of **3** indicates the presence of thiocyanate, which is evident from the crystal structure determination [68]. IR spectra of all three complexes are given in Figs. S1–S3. The IR spectra of the complexes have also been compared with those of the free ligands in order to determine the coordination sites that may get involved in chelation. The imine (C=N) stretching vibration is found in free ligands, HL^1, HL^2 and HL^3, at 1647, 1643 and 1633 cm^{-1}, respectively. The bands are shifted to lower frequency in the complexes. These shifts are due to the reduction of double bond characters of the C=N bonds, caused by the coordination of nitrogen atoms to the zinc(II) centers and are in agreement with results obtained from other similar complexes described previously [69]. The intensity of strong bands around 3300 cm^{-1} due to O–H stretching vibrations in the IR spectra of free ligands has been drastically reduced due to the participation of phenoxo oxygen atoms in coordination resulting with concomitant deprotonation of the ligands. Positions of bands corresponding to C–O stretching vibrations in free ligands also shift towards lower frequency region in complexes due to participation of the oxygen atoms in coordination. At the same time, new bands in the region of 500 cm^{-1} arise in the complexes indicating zinc(II)–O vibrations.

Table 4
Geometric features (distances in Å and angles in °) of the C–H···π interactions obtained for complex **2** and **3**.

Complex	C–H···Cg(Ring)	H···Cg (Å)	C–H···Cg (°)	C···Cg (Å)
2	C(19)–H(19B)–Cg(4)	2.64	146	3.506(3)
	C(28)–H(28)–Cg(6)^b	2.84	126	3.481(3)
	C(30)–H(30B)–Cg(7)^c	2.60	159	3.537(3)
3	C(31)–H(31B)–Cg(6)	2.93	132	3.657(9)
	C(200)–H(206)–Cg(7)^d	2.67	142	3.500(7)

Symmetry transformations: b = 1 + *x*,*y*,*z*; c = *x*, −1 + *y*,*z*; d = *x*,1/2 − *y*,1/2 + *z*.

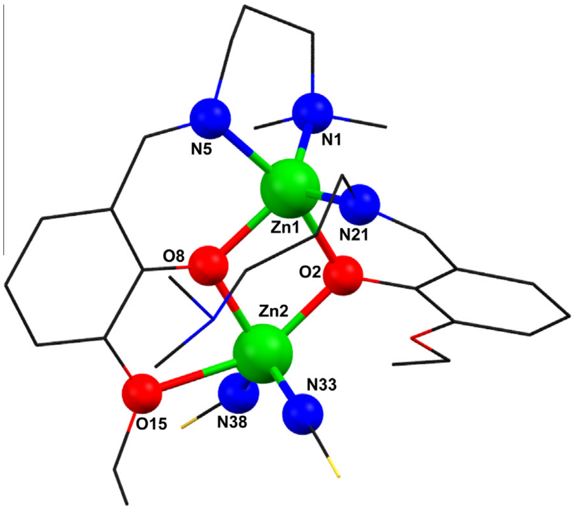


Fig. 6. Perspective view of the complex **3** with selective atom numbering scheme of the metal and coordinating atoms. Hydrogen atoms are omitted for clarity.

The electronic spectra of complexes and ligands are recorded in acetonitrile medium in the range 200–1000 nm. Absorption spectra of ligands (HL^1, HL^2 and HL^3) exhibit three bands, of which bands around 230 nm may be attributed to π–π* transitions and the bands observed around 310 and 370 nm may be assigned to n–π* transitions [70]. Although the same trends have been maintained in the complexes, slight shifts in the positions of these bands are observed as a result of complexation. There is no bands corresponding to *d–d* electronic transitions as expected for zinc(II) complexes with d^{10} electronic configurations [69]. The UV–Vis absorption spectra of all the complexes are shown in Figs. S4–S6, Supplementary information.

All the complexes and ligands exhibit luminescence in acetonitrile medium. These are assigned to intra-ligand (π–π*) fluorescence [21]. The ligands, HL^1, HL^2 and HL^3, display emission

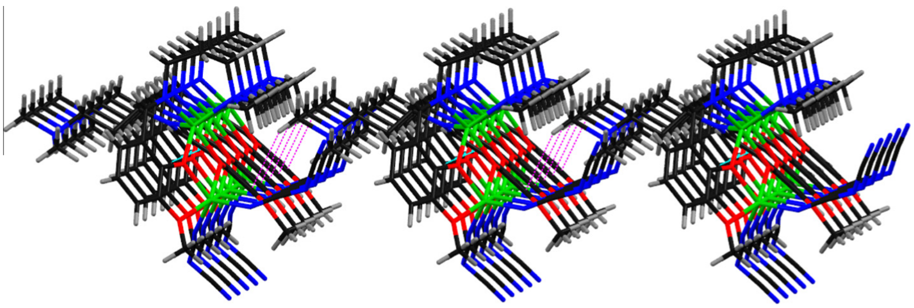


Fig. 5. The two-dimensional sheet structure formed in complex **2** via inter-molecular C–H···π interactions.

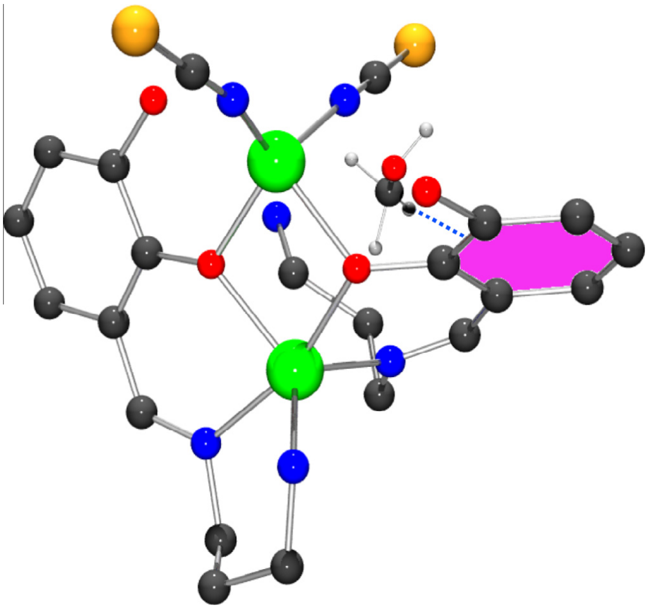


Fig. 7. Inter-molecular C–H···π interaction in complex **3**.

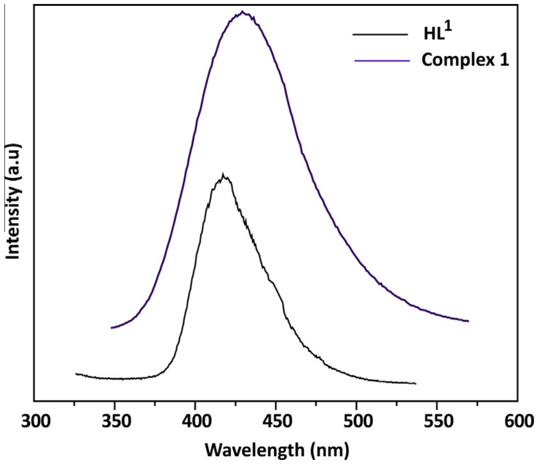


Fig. 8. Steady-state photoluminescence decay profile of *HL^1* and complex **1**.

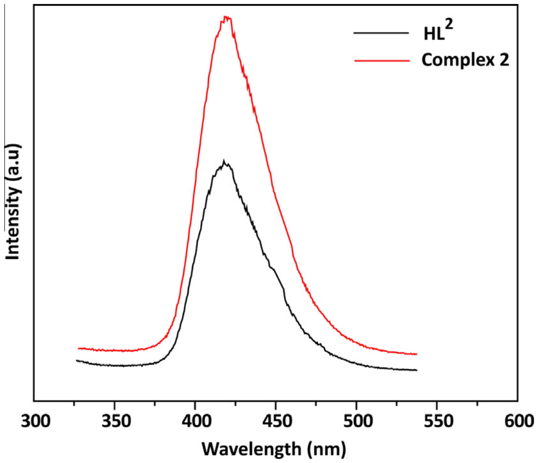


Fig. 9. Steady-state photoluminescence decay profile of *HL^2* and complex **2**.

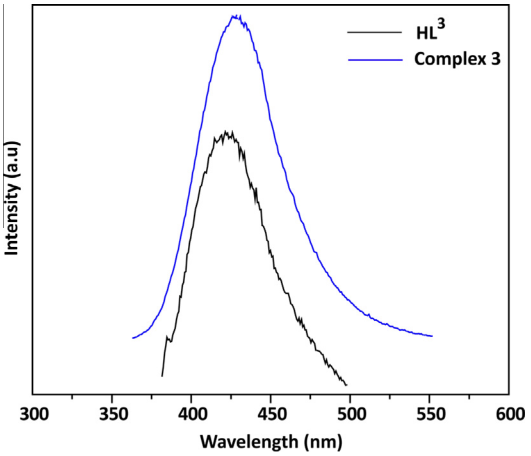


Fig. 10. Steady-state photoluminescence decay profile of *HL^3* and complex **3**.

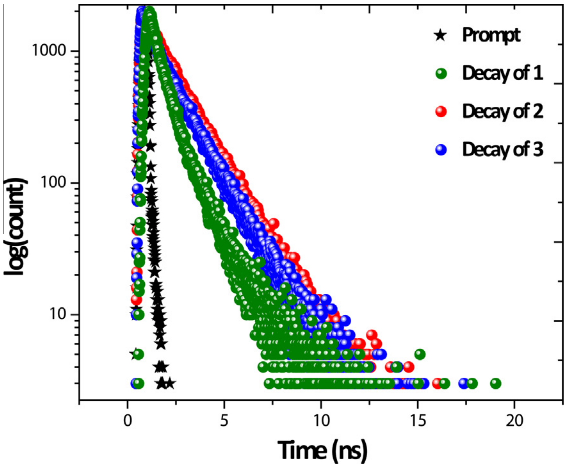


Fig. 11. Time dependent photoluminescence decay profile of all three complexes.

Table 5
The details data of the photoluminescence and time-resolved photoluminescence decays of complexes **1**, **2** and **3**.

Samples	λ_{ex} (nm)	λ_{em} (nm)	τ (ns)	χ^2
1	371	420	2.39	1.087132
2	363	414	9.14	1.073078
3	365	417	8.78	1.023388

maxima at 415, 407 and 413 nm when excited at 364, 357 and 361 nm, respectively. The emission spectra of the zinc(II) complexes closely resemble the emission spectra of the ligands (Figs. 8–10). The emission intensities of zinc(II) complexes are stronger than that of free ligands, as were also observed in similar complexes [69]. These results suggest that these ligands may be used as suitable agents to detect zinc(II) and may have potential uses as zinc(II) sensors [71]. The strong fluorescence of zinc(II) complexes compared to ligands may be facilitated by the difficulty to oxidise or reduce zinc(II) with its stable *d^{10}* configuration [72]. Enhancement of fluorescence through complexation opens up the opportunity for potential photochemical applications of these complexes [73].

The fluorescence lifetimes of the complexes are investigated in acetonitrile solution at room temperature. The lifetimes of **1**, **2** and **3** are about 2.39, 9.14 and 8.78 ns respectively (Fig. 11). Details of the luminescence data of the complexes are listed in Table 5.

3.4. Powder XRD data

The experimental powder XRD patterns of the bulk product of all the complexes are in good agreement with the simulated XRD patterns from single crystal X-ray diffraction, confirming purity of the bulk samples (Figs. S7–S9). The simulated patterns were calculated from the single crystal structural data (cif file) using the CCDC Mercury software.

4. Concluding remarks

The whole work can be concluded in three statements. Firstly, the synthesis and characterization of three new zinc(II) Schiff base complexes containing Zn_2O_2 cores unambiguously show that the potential tri and tetradentate Schiff bases are acting as bi-dentate ligands, keeping the remaining donor sites pendant. Secondly, in all three complexes, zwitterionic forms of the Schiff bases are trapped. Lastly, the increase in emission intensities of zinc(II) complexes compared to that of ligands suggests the potential uses of the ligands as zinc(II) sensors. Keeping in mind the novel role of zinc(II) complexes in the field of electronic and opto-electronic research, the present findings provide insight and serve as a prototype for preparing other such complexes.

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Appendix A. Supplementary data

CCDC 1008388, 1008117 and 1008116 contains the supplementary crystallographic data for complexes **1**–**3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.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.2014.12.018.

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