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# Syntheses, structures and luminescence behaviors of zinc(II) complexes containing a tetradentate Schiff base: Variation in nuclearity and geometry with the change of halide/pseudohalide/carboxylate and counter anion

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# HIGHLIGHTS

- ▶ Mono- and dinuclear zinc(II) halide/pseudohalide/carboxylate compounds with a Schiff base are isolated and characterized.
- ► X-ray structures show interesting variations in geometries and superstructures.
- ▶ Thermogravimetric analyses reveal their thermal stability and decomposition pattern.
- Fluorescence studies illustrate ligand based  $\pi$ - $\pi$ <sup>\*</sup> emission behaviors.

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# ABSTRACT

A series of pentacoordinated mono-/dinuclear compounds,  $[Zn(L)(Br)]PF_6$  (1),  $[Zn(L)(NCS)]ClO_4$  (2) and  $[Zn_2(L)_2(\mu-tp)](ClO_4/PF_6)_2$  (3/4) [L = N,N'-(bis(pyridin-2-yl)benzylidene)-1,3-propanediamine, tp = terephthalate dianion], have been synthesized using one-pot reactions of the building components. All the complexes are characterized using microanalytical, spectroscopic and other physicochemical results. Structures of 1–4 are solved by single crystal X-ray diffraction measurements. Structural analyses reveal that each zinc(II) center in 1 and 3 adopts a distorted trigonal bipyramidal geometry with ZnN<sub>4</sub>Br and ZnN<sub>4</sub>O chromophores, respectively, whereas zinc(II) centers in 2 and 4 have a distorted square pyramidal geometry with ZnN<sub>5</sub> and ZnN<sub>4</sub>O chromophores, respectively. Intermolecular C–H···Br, C–H···F and C–H···O hydrogen bondings along with C–H··· $\pi$  and  $\pi$ -·· $\pi$ \* fluorescence in solid states and in DMF solutions at room temperature.

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# 1. Introduction

Construction of self-assembled coordination molecules and supramolecular entities [1] of varied nuclearities formed through control and manipulation of strong metal-ligand covalent bonds [2] and multiple weak non-covalent forces [1,3–5] is the center of attraction to the coordination chemists for preparation of different varieties of functional materials [6–8]. One-pot synthesis [9] using metal ions, organic spacers and suitable terminal/bridging units in pre-assigned ratios is an efficient approach to isolate such target molecules. Schiff bases [10] are important organic ligands because of their ease of preparation, structural varieties and varied denticities. Halides [11], pseudohalides [12,13] and carboxylates [14,15] are suitable terminal and/or bridging units which in combination with organic blockers may control nuclearities and structural diversities resulting in different mono-, di- and polynuclear coordination molecules and supramolecular entities. Zinc(II) [16-18] with its d<sup>10</sup> configuration permits a wide range of symmetries and coordination numbers and it has significant use in bioinorganic chemistry [19]. Recently, we are active [20-22] to isolate different zinc(II) compounds in combination with multidentate Ndonor Schiff bases with interesting tunable molecular properties. In the present endeavor, we have chosen a tetradentate Schiff base, N,N'-(bis(pyridin-2-yl)benzylidene)-1,3-propanediamine (L, Scheme 1) to isolate zinc(II) halide, pseudohalide and carboxylate compounds. Successfully, we have isolated two mononuclear compounds [Zn(L)(Br)]PF<sub>6</sub> (1) and [Zn(L)(NCS)]ClO<sub>4</sub> (2) and two dinuclear compounds  $[Zn_2(L)_2(\mu-tp)](ClO_4/PF_6)_2$  (3/4) and X-ray crystallographically characterized. The details of syntheses,

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Scheme 1. (N<sup>p</sup>,N<sup>i</sup>,N<sup>i</sup>,N<sup>p</sup>) set in L.

structures and spectroscopic, thermal and luminescence behaviors of these compounds are described below.

# 2. Experimental

# 2.1. General remarks and physical measurements

#### 2.1.1. Materials

High purity 1,3-propanediamine (SRL, India), 2-benzoylpyridine (Lancaster, UK), terephthalic acid (Loba Chemie, India), pipyridine (Loba Chemie, India), zinc(II) bromide (SRL, India), zinc(II) acetate (E. Merck, India), ammonium thiocyanate (E. Merck, India), sodium perchlorate (Fluka, Germany) and ammonium hexafluorophosphate (Fluka, Germany) were purchased from respective concerns and used as received. Zinc(II) perchlorate hexahydrate was prepared [20] by treatment of the corresponding zinc(II) carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on a steam-bath, filtration through a fine glass-frit and preserved in a desiccator containing concentrated sulfuric acid (E. Merck, India) for subsequent uses. The Schiff base, N,N'-(bis(pyridin-2-yl)benzylidene)-1,3-propanediamine (L) was prepared by condensation of a 1:2 M ratio of 1,3-propanediamine and 2-benzoylpyridine following the reported procedure [23] and was isolated as a faint yellow gummy mass. Piperidinium terephthalate (ptp) was isolated using a method described elsewhere

Table 1

Crystallographic data and structure refinement parameters for 1-4.

[24]. All other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in open air.

#### 2.1.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr disks, 4000–400 cm<sup>-1</sup>) were recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01 M KCl solution and MeCN was used as solvent. Thermal studies were made with a Perkin-Elmer Diamond TG/DT analyzer heated from 30–700 °C (for **1** and **2**) and 30–850 °C (for **3** and **4**) under nitrogen. Ground state absorptions were measured with a Jasco model V-530 UV–Vis spectrophotometer. Fluorescence measurements in DMF solutions were done using Perkin Elmer LS55 Fluorescence Spectrometer. Solid state fluorescence measurements were done using a Hitachi Fluorescence Spectroflurimeter F-4500.

#### 2.2. General synthesis of the complexes

#### 2.2.1. $[Zn(L)(Br)]PF_6(1)$

L (0.405 g, 1 mmol) in acetonitrile (20 ml) was added dropwise to a solution containing ZnBr<sub>2</sub> (0.225 g, 1 mmol) followed by NH<sub>4</sub>-PF<sub>6</sub> (0.163 g, 1 mmol) in methanol (20 ml). The final light yellow solution was filtered and left for slow evaporation in air. After a few days colorless crystals of **1** that separated, were washed with hexane and dried *in vacuo* over silica gel indicator. The yield was 0.556 g (80%) for **1**. Anal. calcd. for C<sub>27</sub>H<sub>24</sub>N<sub>4</sub>F<sub>6</sub>PBrZn (**1**): C, 46.7; H, 3.5; N, 8.1. Found: C, 46.9; H, 3.6; N, 8.2%. IR (KBr, cm<sup>-1</sup>): v(C=N) + v(C=C) 1629, 1597;  $v(PF_6)$  839, 557. UV–Vis [DMF,  $\lambda_{max}/$  nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 274 (0.67 × 10<sup>4</sup>).  $\Lambda_M$  (MeCN, ohm<sup>-1</sup> cm<sup>2</sup> - mol<sup>-1</sup>): 120.

Complex	1	2	3	4
Formula	C <sub>27</sub> H <sub>24</sub> N <sub>4</sub> F <sub>6</sub> PBrZn	C <sub>28</sub> H <sub>24</sub> N <sub>5</sub> O <sub>4</sub> SClZn	$C_{62}H_{52}N_8O_{12}Cl_2Zn_2$	$C_{62}H_{52}N_8O_4F_{12}P_2Zn_2$
Formula weight	694.75	627.40	1302.76	1393.80
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Сс	P2(1)/c	C2/c	P21/c
a (Å)	20.548(6)	14.935(2)	15.027(10)	10.130(4)
b (Å)	12.349(6)	10.3925(16)	27.34(2)	14.838(6)
c (Å)	11.232(3)	18.450(3)	15.283(10)	20.044(8)
α (°)	90.00	90.00	90.00	90.00
β(°)	102.590(9)	94.378(2)	98.301(18)	90.734(12)
γ (°)	90.00	90.00	90.00	90.00
V (Å <sup>3</sup> )	2781.6(17)	2855.3(8)	6214(8)	3012(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
$ ho_{ m calcd}~({ m g~cm^{-3}})$	1.659	1.459	1.392	1.537
Ζ	4	4	4	2
T (K)	150(2)	150(2)	293(2)	293(2)
$\mu$ (mm <sup>-1</sup> )	2.442	1.070	0.925	0.942
F(000)	1392	1288	2680	1420
Crystal size (mm <sup>3</sup> )	$0.19 \times 0.15 \times 0.07$	$0.24 \times 0.22 \times 0.18$	$0.09\times16.0\times21.0$	$0.18 \times 0.16 \times 0.12$
$\theta$ ranges (°)	1.94-25.00	1.37-22.65	1.56–19.07	1.71-28.04
h/k/l	-24, 24/-14, 14/-13, 13	-16, 16/-11, 11/-19, 19	–13, 13/–24, 25/–13, 13	-13, 12/-19, 19/-25, 25
Reflections collected	12976	21548	19023	25215
Independent reflections (R <sub>int</sub> )	4860	3800	2504	6889
$T_{\rm max}$ and $T_{\rm min}$	0.84 and 0.65	0.82 and 0.77	0.92 and 0.00	0.94 and 0.92
Data/restraints/parameters	4860/2/361	3800/0/361	2504/0/399	6889/0/406
Goodness-of-fit on $F^2$	0.914	1.029	1.183	0.949
Final <i>R</i> indices $[I > 2\sigma(I)]$	R = 0.0356 and $wR = 0.0710$	R = 0.0387 and $wR = 0.0900$	R = 0.0688 and $wR = 0.1915$	R = 0.0566 and $wR = 0.1170$
R indices (all data)	R = 0.0451 and $wR = 0.0752$	R = 0.0587 and $wR = 0.1005$	R = 0.1088 and $wR = 0.2197$	R = 0.1378 and $wR = 0.1586$
Largest peak and hole $(eA^{-3})$	-0.301 and 0.300	-0.398 and 0.782	-0.248 and 1.254	-0.426 and 0.484

Weighting scheme:  $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ ,  $wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ , calcd  $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ ; x = 0.0000 (for **1**), 0.0449 (for **2**), 0.1257 (for **3**), 0.0664 (for **4**) and y = 0.0000 (for **1**), 2.3189 (for **2**), 0.0000 (for **3**), 0.0000 (for **4**); where  $P = (F_o^2 + 2F_c^2)/3$ .

#### 2.2.2. [*Zn*(*L*)(*NCS*)]*C*lO<sub>4</sub> (**2**)

Zn(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (0.372 g, 1 mmol) was dissolved in methanol (10 ml) and to this solution L (0.405 g, 1 mmol) in acetonitrile (20 ml) was added dropwise followed by NH<sub>4</sub>SCN (0.076 mg, 1 mmol) in methanol (10 ml). The resulting light yellow solution was filtered and left for slow evaporation in air to yield colorless block shaped crystals of **2**. The yield was 0.470 g (75%). Anal. calcd. for C<sub>28</sub>H<sub>24</sub>N<sub>5</sub>O<sub>4</sub>SClZn (**2**): C, 53.6; H, 3.9; N, 11.2. Found: C, 53.8; H, 3.9; N, 11.0%. IR (KBr, cm<sup>-1</sup>): v(NCS) 2092; v(C=N) + v(C=C) 1629, 1595; v(ClO<sub>4</sub>) 1093, 623. UV–Vis [DMF,  $\lambda_{max}$ /nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 281 (1.1 × 10<sup>4</sup>).  $\Lambda_{M}$  (MeCN, ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>): 110.

# 2.2.3. $[Zn_2(L)_2(\mu-tp)](ClO_4)_2$ (3) and $[Zn_2(L)_2(\mu-tp)](PF_6)_2$ (4)

To a methanolic solution (10 ml) of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.044 g, 0.2 mmol), L (0.081 g, 0.2 mmol) in methanol (10 ml) and piperidinium terephthalate (ptp) (0.034 g, 0.1 mmol) in the same solvent (5 ml) were added in succession. To this resulting solution mixture. a methanolic solution (5 ml) of NaClO<sub>4</sub> (0.028 g, 0.2 mmol) was added as counter anion. The colorless reaction mixture was kept in an open air for slow evaporation. After a few days colorless microcrystals of 3 were collected and dried in vacuo over silica gel indicator. Yield: 0.977 g (75%). Complex 4 was prepared similarly using the same reaction stoichiometry and reaction condition as in **3** except that methanolic solution (10 ml) of  $NH_4PF_6$  (0.037 g, 0.2 mmol) instead of NaClO<sub>4</sub> was added to the reaction mixture. Yield: 0.975 g (70%). 4 was also isolated by metathesis of 3 and NH<sub>4</sub>PF<sub>6</sub> in 1:2 ratio from a methanolic solution with constant stirring for 45 min at room temperature. The microanalytical and spectroscopic results for 4 obtained from both methods were very similar. Anal. Calc. for C<sub>62</sub>H<sub>52</sub>N<sub>8</sub>O<sub>12</sub>Cl<sub>2</sub>Zn<sub>2</sub> (**3**): C, 57.1; H, 4.0; N, 8.6. Found: C, 57.3; H, 3.8; N, 8.5%. IR (KBr, cm<sup>-1</sup>): v<sub>as</sub>(COO<sup>-</sup>) 1595; v<sub>s</sub>(-COO<sup>-</sup>) 1369; v(C=N) + v(C=C) 1630, 1590; v(ClO<sub>4</sub><sup>-</sup>) 1091, 624; UV-Vis [DMF,  $\lambda_{max}/nm$  ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 282 (2.85 × 10<sup>4</sup>).  $\Lambda_M$  (MeCN, ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>): 230. Anal. Calc. for  $C_{62}H_{52}N_8O_4F_{12}P_2Zn_2$  (4): C, 53.4; H, 3.8; N, 8.0. Found: C, 53.6; H, 3.7; N, 7.9%. IR (KBr, cm<sup>-1</sup>):  $v_{as}(COO^{-})$  1586;  $v_{s}(COO^{-})$  1373; v(C=N) + v(C=C) 1630, 1597;  $v(PF_6^-)$  842, 558; UV–Vis [DMF,  $\lambda_{max}/nm$  ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 280 (2.26  $\times$  10<sup>4</sup>).  $\Lambda_{\rm M}$  (MeCN, ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>): 225.

# 2.3. X-ray crystallographic analyses

Diffraction data of the single crystals of 1 and 2 were collected at 150(2) K, and for 3 and 4 at 293(2) K on a Bruker AXS SMART APEX-II CCD area-detector diffractometer using graphite monochromated Mo Ka radiation. The unit cell parameters were obtained from SAINT [25] and absorption corrections were performed with SADABS [26]. The structures were solved by direct methods and refined by full-matrix least-squares method based on  $|F|^2$  using SHELXL-97 [27]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed in calculated positions ( $d_{CH} = 0.97$  Å for methylene and 0.93 Å for phenyl) after checking their positions in the difference map. The  $U_{iso}$  values were constrained to be  $1.2U_{eq}$  of the carrier atoms for all H atoms. Several attempts to crystallize 2 and 3 gave crystals that were brittle needles and were difficult to cut. The best possible crystal that was finally selected for data collection gave diffuse diffraction spots, indicating the crystal to have a large mosaic spread. As a result of this, a few of the diffraction spots were overlapping and the integration of these spots could not be carried out properly by the processing software. A small portion of the collected reflections was therefore rejected assuming that they were incorrectly measured. Despite this, structures of 2 and 3 were refined using the available data  $(1.37^{\circ} \le \theta \le 22.65^{\circ})$  for **2** and  $1.56^{\circ} \leq \theta \leq 19.07^{\circ}$  for **3**), which was adequate to give a precise structure. Two O atoms (O5 and O7) of one perchlorate moiety in **3** are disordered with fractional occupancy of 50% for each atom. All calculations were carried out using SHELXL-97, SHELXTL [27], Mercury 2.3 [28] and ORTEP-3 [29] programs. A summary of the crystallographic data and structure determination parameters for **1–4** is given in Table 1.

#### 3. Results and discussion

#### 3.1. Synthesis and formulation

The pentacoordinated mononuclear compound  $[Zn(L)(Br)]PF_6$ (1) was isolated as colorless crystals through one-pot synthesis of a 1:1:1 M ratio of ZnBr<sub>2</sub>, L and NH<sub>4</sub>PF<sub>6</sub> from methanol–acetonitrile (1:1) solution mixture at room temperature. Use of 1:1:1 M ratio of Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, L and NH<sub>4</sub>SCN in the same solvent mixture resulted in **2**. Compounds **3** and **4** were obtained using a 2:2:1:2 M ratio of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, L, ptp and NaClO<sub>4</sub>/NH<sub>4</sub>PF<sub>6</sub>. **4** was also isolated by metathesis of **3** and NH<sub>4</sub>PF<sub>6</sub> in 1:2 ratio from a methanolic solution. Compounds **1** and **2** were also isolated from Zn(OAc)<sub>2</sub>· ·2H<sub>2</sub>O and L by adding respective halide/pseudohalide i.e. NaBr in **1** and NH<sub>4</sub>SCN in **2** followed by the addition of NH<sub>4</sub>PF<sub>6</sub> in **1** and



**Fig. 1.** The asymmetric units for the complexes: (a) **1** and (b) **2**. Displacement ellipsoids are drawn at 30% probability for all non-hydrogen atoms.

NaClO<sub>4</sub> in **2**. To get X-ray quality single crystals we used ZnBr<sub>2</sub> in **1**,  $Zn(ClO_4)_2 \cdot 6H_2O$  in **2** and  $Zn(OAc)_2 \cdot 2H_2O$  in **3** and **4**. The reactions are summarized in the following equations:

$$ZnBr_2 + L + NH_4PF_6 \xrightarrow[(1)]{MeOH-MeCN} [Zn(L)(Br)]PF_6$$
(1)

$$Zn(ClO_4)_2 \cdot 6H_2O + L + NH_4SCN \xrightarrow{MeOH-MeCN} [Zn(L)(NCS)]ClO_4 \qquad (2)$$

$$Zn(OAc)_{2} . 2H_{2}O + L + ptp \xrightarrow{MeOH} [Zn_{2}(L)_{2}(\mu-tp)](CIO_{4})_{2} \\ (3) \\ MH_{4}PF_{6} \\ [Zn_{2}(L)_{2}(\mu-tp)](PF_{6})_{2} \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (3) \\ (4) \\ (4) \\ (3) \\ (4) \\ (4) \\ (4) \\ (3) \\ (4$$

The new complexes were characterized by microanalytical (C, H and N), spectroscopic, thermal and other physicochemical results. The microanalytical results are in good conformity with the formulations of **1–4**. The moisture-insensitive complexes are stable over long periods of time in powdery and crystalline states. Compounds **1** and **2** are soluble in methanol, ethanol, acetonitrile, dimethylformamide and dimethylsulfoxide whereas **3** and **4** are moderately soluble in these solvents at room temperature but upon warming they are completely soluble. In MeCN solutions, **1** and **2** behave as 1:1 electrolytes with a uni-positive molecular cation and a uni-negative anion present outside the coordination sphere; on the other hand **3** and **4** show 2:1 electrolytic behavior [30] with a bi-positive molecular cation and two uni-negative anions present outside the coordination sphere, as reflected in their respective conductivity values (vide Experimental). Thus the formulations of the compounds can be made from their conductance values. In IR spectra, v(C=N) plus v(C=C) stretching vibrations of the metalbound Schiff base are observed within 1630–1590 cm<sup>-1</sup> range. Compound 2 shows characteristic asymmetric thiocyanate stretching vibration at 2092 cm<sup>-1</sup>. The position of the band strongly suggests N-coordination rather than S-bonding [31]. The stretching vibrations of terephthalate (tp) in **3** and **4** are seen as strong  $v_{as}(COO^{-})$  and  $v_{s}(COO^{-})$  in the range 1585–1595 cm<sup>-1</sup> and 1365–1375 cm<sup>-1</sup>, respectively indicating bis(monodentate) behavior of terephthalate dianion [32]. Additionally, presence of hexafluorophosphate stretches in **1**, and **4** at  $\sim$ 840 and 555 cm<sup>-1</sup> and perchlorate bands at  $\sim$ 1090 and 625 cm<sup>-1</sup> in **2** and **3** (vide Experimental) are indicative of non-coordination [31] to the metal center. X-ray study corroborates this hypothesis. In DMF solutions, L shows absorption maxima at 274 nm and the corresponding zinc(II) compounds 1-4 exhibit bands at  $\sim$ 280 nm (Fig. S7) assignable to ligand-based charge transfer [33].

# 3.2. Description of crystal structures

ORTEP diagrams with atom numbering schemes and perspective views of the crystalline architectures in **1–4** are shown in



**Fig. 2.** (a) A perspective view of 2D sheet structure in **1** formed through cooperative C—H···B hydrogen bonds and C—H··· $\pi$  interactions in *ac*-plane. (b) 2D sheet structure in **2** formed through C—H··· $\pi$  interactions and multiple C—H···O hydrogen bonds in an interwoven fashion parallel to crystallographic *ab*-plane.

Figs. 1–4 and Figs. S1 and S2. Selected bond distances and bond angles relevant to the metal coordination spheres and the non-covalent bonding parameters are set in Tables 2–4. Single crystal X-ray structure analyses show that compounds **1–4** consist of mono-/dinuclear units which are further engaged in different kinds of cooperative hydrogen bondings like C–H···Br, C–H···F and C–H···O along with C–H··· $\pi$  and  $\pi$ ··· $\pi$  interactions as the case among themselves resulting in different crystalline architectures.

#### 3.2.1. [Zn(L)(Br)]PF<sub>6</sub> (1) and [Zn(L)(NCS)]ClO<sub>4</sub> (2)

The structures of 1 (Fig. 1a) and 2 (Fig. 1b) consist of  $[Zn(L)(Br)]^+$ and  $[Zn(L)(NCS)]^+$  cation, respectively and  $PF_6^-$  in **1** and  $ClO_4^-$  in **2** as counter anion. The zinc(II) center in **1** has a distorted trigonal bipyramidal (tbp) [34] [ $\tau$  = 0.53] geometry with ZnN<sub>4</sub>Br chromophore ligated by four N atoms (N7, N8, N3 and N9 of L1) and one terminal bromide. A distorted square pyramidal (sp) ( $\pi = 0.43$ ) [34] environment around zinc(II) center in **2** is observed with a ZnN<sub>5</sub> chromophore ligated by four N atoms (N1, N2, N3 and N4) of the chelated Schiff base (L) and one N atom (N5) of terminal thiocyanate. In contrast, a reported pentacoordinated mononuclear zinc(II) thiocyanate complex [16] with a tetradentate macrocyclic N-donor ligand results in trigonal bipyramidal environment around the metal center. Earlier, we have reported a zinc(II) thiocyanate complex [22] using a tetradentate Schiff base with butylenic arm that adopts a distorted trigonal bipyramidal geometry, whereas complex **2** with tetradentate Schiff base having propylenic arm affords a distorted square pyramidal geometry. Thus different molecular geometries may arise due to the difference in length of the chains in the Schiff bases. One  $N^{p}$  (N9) and one  $N^{i}$  (N8) atom [ $N^{p} = N(pyr$ idine) and  $N^{i} = N(imine)$ ] of L along with the terminal halide define the equatorial plane in **1** and the remaining  $N^p$  (N7) and  $N^i$  (N3) atoms of the Schiff base occupy the axial sites. The basal plane of 2 consists of two N<sup>p</sup> (N1 and N4) and two N<sup>i</sup> (N2 and N3) atoms of L while the apical position is occupied by N5 atom of the terminal pseudohalide. The larger ionic radius of bromide in **1** results in longer Zn—Br distance [2.3890(8) Å] over Zn—N bond lengths (Table 2). Compound 2 has Zn-N(Schiff base) bond distances within a range of 2.084(3)-2.150(3) Å (Table 2) which are somewhat shorter than the reported [16] one. The smaller Zn—N(thiocyanate) bond distance over the other Zn-N(Schiff base) distances indicates stronger coordination of the anionic thiocvanate over the other neutral N-donor centers. The Zn–N(thiocvanate) bond distance is almost comparable to the reported complex [16]. The quasi-linear N-donor thiocyanate is ligated to zinc(II) center in an almost linear fashion (Table 2). L forms two five-membered and one six-membered chelate loop around zinc(II) center in both 1 and 2. The propylenic arm of the Schiff base in 1 and 2 is to some extent puckered. The zinc(II) center in **1** and **2** departs 0.084 Å and 0.598 Å, respectively from the corresponding mean plane (N8, N9, Br1 for 1 and N1, N2, N3, N4 for 2) towards the axial N3 atom in 1 and N5 atom in 2.

In the crystalline state, mononuclear units of **1** are associated by weak  $C-H\cdots$ Br hydrogen bonds (Table 3) affording a 1D zigzag



**Fig. 3.** (a) Molecular structure of [Zn<sub>2</sub>(L)<sub>2</sub>(μ-tp)]<sup>2+</sup> in **3** with atom numbering scheme and 10% thermal ellipsoid probability for all non-hydrogen atoms. (b) A view of 1D chain in **3** formed through π···π interactions along crystallographic *b*-axis.



**Fig. 4.** (a) ORTEP representation of  $[Zn_2(L)_2(\mu-tp)]^{2+}$  in **4** with atom numbering scheme and 30% thermal ellipsoid probability for all non-hydrogen atoms. (b) Extended 3D network structure in **4** formed through C—H···O and C—H···F hydrogen bonds.

chain (Fig. S1a) along crystallographic *c*-axis. The chains further pack through weak intermolecular  $C-H\cdots\pi$  interactions (Table 3) along crystallographic *ac* plane leading to a 2D sheet structure (Fig. 2a). Each mononuclear unit is coordinated with a hexafluorophosphate moiety by  $C-H\cdots$ F hydrogen bondings (Table 3). Intermolecular edge-to-face  $C-H\cdots\pi$  interactions (Table 3) join two adjacent molecules of **2** to construct a supramolecular 1D chain (Fig. S1b) along crystallographic *a*-axis. The 1D chains pack along-side each other to give a 2D sheet structure in *ab* plane (Fig. 2b) through multiple interwoven  $C-H\cdots$ O hydrogen bondings with the perchlorate ions embedded among the chains.

# 3.2.2. $[Zn_2(L)_2(\mu-tp)](ClO_4)_2$ (**3**) and $[Zn_2(L)_2(\mu-tp)](PF_6)_2$ (**4**)

The centrosymmetric dinuclear units of **3** and **4** (Figs. 3a and 4a) have an inversion center located at the middle of the benzene ring of the tp bridge. Each pentacoordinated zinc(II) center in **3** has a trigonal bipyramidal geometry ( $\tau = 0.52$ ) whereas zinc (II) centers of compound **4** adopt a distorted square pyramidal geometry ( $\tau = 0.367$ ) [34]. The coordination polyhedron around each zinc(II)

center in 3 and 4 is best described with a ZnN<sub>4</sub>O chromophore ligated with four N atoms of the Schiff base and one O atom of bridging tp unit. One N<sup>p</sup> (N2) and one N<sup>i</sup> (N3) atom of L along with the O4 atom of tp unit define the equatorial plane in 3, whereas remaining N<sup>p</sup> (N1) and N<sup>i</sup> (N4) atoms of the Schiff base occupy the axial sites. The basal plane of **4** consists of two N<sup>i</sup> (N2, N3), one N<sup>p</sup> (N1) of the chelated Schiff base (L) and O1 atom of the tp bridge, while the apical position is occupied by rest N<sup>p</sup> (N4) atom of L. The smaller Zn–O(tp) bond distances [Zn1–O4 1.990(7) Å in **3** and Zn1–O1 2.021(3)Å in **4**] over the other Zn–N(Schiff base) distances [2.087(8)–2.129(8) Å in **3** and 2.105(4)–2.148(4) Å in **4**] [14] is indicative of the stronger coordination of the anionic O atom of tp over the neutral N-donors of the Schiff base. Each zinc (II) center in **3** and **4** deviates 0.146 Å and 0.267 Å, respectively from mean basal plane (N2, N3 and O4 in 3 and N1, N2, N3 and O1 in 4) towards apical N1 atom in 3 and apical N4 atom in 4. The three equatorial bond angles in 3, N2-Zn1-O4 [125.0(3)°], N3-Zn1-O4 [107.5(3)°] and N2–Zn1–N3 [126.1(3)°] show slight deviation from 120° (avg. 119.53°), whereas the axial N1–Zn1–N4

Table 2		,			
Selected bond	distances	(Å) and	bond	angles (°)	for 1-4.

brit-2n2         2380(8)         Zn1-N5         1961(4)         Zn1-Q4         1990(7)           Zn2-N8         2082(3)         Zn1-N4         2103(3)         Zn1-N1         2129(8)           Zn2-N7         2149(4)         Zn1-N4         2103(3)         Zn1-N3         2087(8)           Zn2-N7         2128(4)         Zn1-N2         2130(3)         Zn1-N3         2087(8)           Zn2-N3         2128(4)         Zn1-N2         2130(3)         Zn1-N3         2087(8)           Zn2-N7         2149(4)         Zn1-N2         2130(3)         Zn1-N3         2087(8)           Zn2-N3         2128(1)         N5-C28         1.161(5)         04-C9         1.260(13)           Zn1-N1         2.148(4)         Sz-C28         1.629(5)         01-C9         1.241(14)           Zn1-N3         2.17(4)         Sz/C38         1.82.17(4)         04-C31-N3         1.52.17(4)           Q1-C28         1.250(5)         Sz         Sz         Sz         1.352.17(4)         04-C1-N4         95.2(3)           Q2-C28         1.250(5)         Sz	Bond distances for <b>1</b>		Bond distances for <b>2</b>		Bond distances for <b>3</b>	
Zn2-NS         208(3)         Zn1-N1         2.103(3)         Zn1-N1         2.123(3)           Zn2-N7         2.149(4)         Zn1-N3         2.050(3)         Zn1-N2         2.125(8)           Zn2-N3         2.123(4)         Zn1-N3         2.064(3)         Zn1-N3         2.067(8)           Zn2-N3         2.07(3)         Zn1-N2         2.130(3)         Zn1-N3         2.067(8)           Zn1-N1         2.021(3)         S3-C28         1.629(5)         01-C9         1.241(14)           Dond distances for 4         Zn1-N1         2.105(4)         Zn1-N1         Zn1-N2         Zn105(4)         Zn1-N3         Zn17(4)         Zn1-N3         Zn17(4)         Zn1-N3         Zn12(14)         04-C3         N5-C28         Zn1-N3         S25(2)         Zn1-N3         Zn12(14)         04-C3         N5-C28         Zn1-N3         Zn12(14)         N5-Zn1-N3         Zn12(14)         N5-Zn1-N3         Zn12(14)         N5-Zn1-N3         S25(2)         Zn1-N3         Zn12(14)         N5-Zn1-N3         Zn12(14)         N5-Zn1-N3         Zn12(14)         N5-Zn1-N4         S2(2)(3)         N5-Zn1-N4         S2(2)(3)         N5-Zn1-N4         S2(2)(3)         N5-Zn1-N4         S2(2)(3)         N5-Zn1-N4         S2(2)(3)         N5-Zn1-N4         S2(2)(3) <t< td=""><td>Br1—Zn2</td><td>2.3890(8)</td><td>Zn1—N5</td><td>1.961(4)</td><td>Zn1-04</td><td>1.990(7)</td></t<>	Br1—Zn2	2.3890(8)	Zn1—N5	1.961(4)	Zn1-04	1.990(7)
2n2-N7 $2,149(4)$ $2n1-N4$ $2,103(3)$ $2n1-N2$ $2,128(4)$ $2n1-N3$ $2,058(3)$ $2n1-N3$ $2,057(8)$ $2n2-N9$ $2,071(3)$ $2n1-N2$ $2,103(3)$ $2n1-N4$ $2,107(8)$ $2n2-N9$ $2,071(3)$ $2n1-N2$ $2,103(3)$ $2n1-N4$ $2,107(8)$ $Bord$ $Bird$ $Bird$ $1.629(5)$ $01-C9$ $1.241(14)$ $Bord$ $Bird$ $2,021(3)$ $2n1-N2$ $2.201(3)$ $2n1-N2$ $2.021(3)$ $2n1-N2$ $2,105(4)$ $2n1-N3$ $2.117(4)$ $2.117(4)$ $2.125(5)$ $Dir       Dir Dol cangles for 1       Bond angles for 2       Bond angles for 3       Dir S(3) N>-2n2-N8 12.60(214) N5-2n1-N3 118.21(14) 04-2n1-N4 95.2(3) NN=2n2-N3 78.38(14) N3-2n1-N4 118.21(14) 04-2n1-N4 95.2(3) NN=2n2-N4 12.60(214) N5-2n1-N1 118.21(14) 04-2n1-N4 95.2(3) NN=2n2-N4 12.60(21) N5-2n1-N2 88.2(213) N3-2n1-N4 95.2(3)$	Zn2—N8	2.082(3)	Zn1-N1	2.103(3)	Zn1-N1	2.129(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Zn2—N7	2.149(4)	Zn1-N4	2.150(3)	Zn1-N2	2.125(8)
Zn2-N9         2.071(3)         Zn1-N2         2.13(3)         Zn1-N4         2.107(3)           N5-C28         1.161(5)         04-C9         1.250(13)           S3-C28         1.629(5)         01-C9         1.241(14)           Bond distances for 4         2.021(3)	Zn2—N3	2.128(4)	Zn1–N3	2.084(3)	Zn1–N3	2.087(8)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Zn2—N9	2.071(3)	Zn1–N2	2.130(3)	Zn1-N4	2.107(8)
Bond distances for 4         53-C28         1.629(5)         01-C9         1.241(14)           Bond distances for 4         2.021(3)         -         1.241(14)         -			N5-C28	1.161(5)	04–C9	1.250(13)
Bond distances for 4           Zn1-O1         2021(3)           Zn1-N1         2.148(4)           Zn1-N2         2.105(4)           Zn1-N2         2.105(4)           Zn1-N2         2.117(4)           Zn1-N4         2.121(4)           O1-C28         1.282(5)           D2-C28         1.250(5)           Bond angles for 1         Bond angles for 2           N9-Zn2-N8         156.02(14)           N8-Zn2-N7         7.09(14)           N9-Zn2-N8         156.02(14)           N9-Zn2-N8         16.02(14)           N9-Zn2-N8         17.09(14)           N9-Zn2-N7         7.09(14)           N9-Zn2-N8         17.09(14)           N9-Zn2-N7         7.09(14)           N9-Zn2-N7         7.09(14)           N9-Zn2-N7         10.12(10)           N9-Zn2-N7         7.09(14)           N9-Zn2-N7         10.12(13)           N9-Zn2-N7         7.09(14)           N9-Zn2-N7         10.12(13)           N9-Zn2-N7         10.12(14)           N5-Zn1-N1         10.32(12)           N9-Zn2-N7         10.12(14)           N9-Zn2-N7         10.12(10)           N3-Zn2-N7			S3-C28	1.629(5)	01	1.241(14)
Zn1-O1         2021(3)           Zn1-N1         2.148(4)           Zn1-N2         2.105(4)           Zn1-N3         2.117(4)           Ol-C28         1.282(5)           O2-C28         1.282(7)           NS=Zn2-N8         126.02(14)           NS=Zn2-N3         87.88(14)           NS=Zn2-N7         77.09(14)           NS=Zn2-N7         97.01(10)           N1-Zn1-N4         97.67(13)           O4-Zn1-N2         125.0(3)           NS-Zn2-N7         101.26(13)           NS-Zn2-N7         101.26(13)           NS-Zn2-N7         101.26(13)           NS-Zn2-N7         101.26(13)           NS-Zn2-N7         101.26(13)           NS-Zn2-N7         101.26(14)           NS-Zn2-N7         101.26(14)           NS-Zn2-N7         101.26(14)           NS-Zn2-N7         101.26(14)           NS-Zn2-N7         101.26(14)           NS-Zn2-N7	Bond distances for <b>4</b>					
Zn1-N1         2.148(4)           Zn1-N2         2.105(4)           Zn1-N3         2.117(4)           Zn1-N4         2.121(4)           Ol-C28         1.282(5)           O2-C28         1.250(5)           Bond angles for 1         Bond angles for 2           Bond angles for 1         Bond angles for 3           N9-Zn2-N8         1260(214)           N5-Zn1-N3         118.21(14)         04-Zn1-N3           N8-Zn2-N8         126.02(14)           N3-Zn1-N1         132.87(12)         04-Zn1-N4           N8-Zn2-N7         77.09(14)         N3-Zn1-N1           N9-Zn2-Br1         104.19(10)         N1-Zn1-N4         97.67(13)           N9-Zn2-Br1         97.01(10)         N1-Zn1-N4         97.67(13)         04-Zn1-N2         125.03)           N9-Zn2-N7         101.26(13)         N5-Zn1-N1         103.2(12)         N3-Zn1-N2         126.13)           N9-Zn2-N7         101.26(13)         N5-Zn1-N1         107.7(4)         N4-Zn1-N2         76.6(3)           N9-Zn2-N7         101.26(13)         N5-Zn1-N1         108.76(14)         04-Zn1-N1         155.3(3)           N7-Zn2-Br1         102.86(13)         N3-Zn1-N1         175.2(4)         N4-Zn1-N1	Zn1-01	2.021(3)				
Zn1-N2         2.105(4)           Zn1-N3         2.117(4)           Zn1-N4         2.121(4)           01-C28         1.282(5)           02-C28         1.250(5)           Bond angles for 1         Bond angles for 2           NS-Zn2-N8         125.02(14)           NS-Zn2-N7         77.09(14)           NS-Zn2-N7         77.09(14)           NS-Zn2-N7         97.09(14)           NS-Zn2-N8         125.02(10)           NS-Zn2-N7         77.09(14)           NS-Zn2-N7         97.07(10)           NS-Zn2-N8         132.87(12)           NS-Zn2-N7         101.26(13)           NS-Zn2-N7         101.4(10)           NZ-Zn2-N7         101.4(10)           NZ-Zn2-N7         101.4(10)           NZ-Zn2-N7         101.4(10)           NZ-Zn1-N1         176.1(2)	Zn1–N1	2.148(4)				
Zn1-N3       2.117(4)         Zn1-N4       2.121(4)         01-C28       1.250(5)         Bond angles for 1       Bond angles for 2         N9-Zn2-N8       1260(214)         N3-Zn1-N3       118.21(14)       04-Zn1-N3         N9-Zn2-N8       1260(214)         N3-Zn2-N7       77.09(14)       N3-Zn1-N2         N9-Zn2-N8       101(10)         N9-Zn2-N7       77.09(14)         N3-Zn1-N4       97.67(13)         O4-Zn1-N4       97.67(13)         N9-Zn2-N7       77.09(14)         N9-Zn2-N8       82.2(13)         N3-Zn1-N4       97.67(13)         N3-Zn2-Br1       104.19(10)         N5-Zn1-N4       101.32(12)         N3-Zn2-N7       101.26(13)         N9-Zn2-N3       78.13(13)         C28-N5-Zn1       177.2(4)         N4-Zn1-N1       105.1(3)         N3-Zn2-N7       101.01(14)         N5-Zn1-N1       108.76(14)         N2-Zn2-N7       101.48(10)         N3-Zn1-N2       102.64(13)         N3-Zn1-N1       105.13(3)         N3-Zn1-N4       7.612)         N2-Zn1-N4       158.84(12)         O4-C9-O1       12	Zn1-N2	2.105(4)				
Zn1-N4         2.121(4)           01-C28         1.282(5)           02-C28         1.250(5)           Bond angles for 1         Bond angles for 2         Bond angles for 3           N9-Zn2-N8         126.02(14)         N5-Zn1-N3         118.21(14)         04-Zn1-N4         195.2(3)           N8-Zn2-N8         87.88(14)         N3-Zn1-N1         132.87(12)         04-Zn1-N4         95.2(3)           N8-Zn2-N7         77.09(14)         N3-Zn1-N1         92.87(13)         04-Zn1-N4         87.9(3)           N3-Zn2-Br1         104.19(10)         N1-Zn1-N4         97.67(13)         04-Zn1-N2         125.0(3)           N9-Zn2-N7         78.13(13)         C28-N5-Zn1         177.2(4)         N4-Zn1-N2         126.1(3)           N9-Zn2-N7         101.02(13)         N5-Zn1-N1         108.76(14)         04-Zn1-N1         105.1(3)           N9-Zn2-N7         161.01(14)         N5-Zn1-N2         102.64(13)         N3-Zn1-N1         105.1(3)           N7-Zn2-Br1         129.34(10)         N1-Zn1-N4         76.19(12)         N4-Zn1-N1         157.3(3)           N7-Zn2-Br1         101.48(10)         N3-Zn1-N4         76.9(12)         N4-Zn1-N1         157.3(3)           N7-Zn2-Br1         101.48(10)         N3-Zn1	Zn1-N3	2.117(4)				
01-C28         1.282(5)           02-C28         1.250(5)           Bond angles for 1         Bond angles for 2         Bond angles for 3           N9-Cn2-N8         126.02(14)         N5-Zn1-N3         118.21(14)         04-Zn1-N3         107.5(3)           N8-Zn2-N3         87.88(14)         N3-Zn1-N1         132.87(12)         04-Zn1-N4         95.2(3)           N8-Zn2-N7         77.09(14)         N3-Zn1-N2         88.22(13)         03-Zn1-N4         87.9(3)           N9-Zn2-Br1         104.19(10)         N5-Zn1-N4         97.67(13)         04-Zn1-N2         126.1(3)           N9-Zn2-Br1         107.4(19)         N1-Zn1-N4         101.32(12)         N3-Zn1-N2         126.1(3)           N9-Zn2-N7         101.26(13)         N5-Zn1-N1         108.76(14)         04-Zn1-N1         105.1(3)           N9-Zn2-N7         101.26(13)         N5-Zn1-N1         108.76(14)         04-Zn1-N1         75.7(3)           N8-Zn2-Br1         129.3(10)         N1-Zn1-N2         77.76(12)         N4-Zn1-N1         75.7(3)           N8-Zn2-Br1         101.48(10)         N3-Zn1-N4         76.9(12)         N4-Zn1-N1         157.3(3)           N2-Zn1-N1         101.48(10)         N3-Zn1-N2         75.6(2)         N2-Zn1-N1 <t< td=""><td>Zn1-N4</td><td>2.121(4)</td><td></td><td></td><td></td><td></td></t<>	Zn1-N4	2.121(4)				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	01–C28	1.282(5)				
Bond angles for 1         Bond angles for 2         Bond angles for 3           N9-2n2-N8         126.02(14)         N5-2n1-N3         118.21(14)         04-2n1-N3         107.5(3)           N8-2n2-N3         87.88(14)         N3-2n1-N1         132.87(12)         04-2n1-N4         95.2(3)           N8-2n2-N7         77.09(14)         N3-2n1-N2         88.22(13)         N3-2n1-N4         97.9(3)           N9-2n2-Br1         104.19(10)         N5-2n1-N4         97.67(13)         04-2n1-N2         125.0(3)           N9-2n2-N3         78.13(13)         C28-N5-2n1         177.2(4)         N4-2n1-N2         126.1(3)           N9-2n2-N7         101.01(14)         N5-2n1-N1         108.76(14)         04-2n1-N1         105.1(3)           N3-2n2-N7         101.01(14)         N5-2n1-N1         102.64(13)         N3-2n1-N1         105.1(3)           N8-2n2-Br1         129.34(10)         N1-2n1-N2         102.64(13)         N3-2n1-N1         105.1(3)           N7-2n2-Br1         101.48(10)         N3-2n1-N4         76.9(12)         N4-2n1-N1         19.3(2)           N2-2n1-N1         90.49(13)         N3-2n1-N4         158.84(12)         04-C9-01         123.3(12)           N1-2n1-N2         139.16(13)         N3-2n1-N4         158.8(	02–C28	1.250(5)				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Bond angles for <b>1</b>		Bond angles for <b>2</b>		Bond angles for <b>3</b>	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N9-Zn2-N8	126.02(14)	N5-Zn1-N3	118.21(14)	04—Zn1—N3	107.5(3)
$\begin{array}{c cccccc} N8-Zn2-N7 & 77.09(14) & N3-Zn1-N2 & 88.22(13) & N3-Zn1-N4 & 87.9(3) \\ N9-Zn2-Br1 & 104.19(10) & N5-Zn1-N4 & 97.67(13) & 04-Zn1-N2 & 125.0(3) \\ N3-Zn2-Br1 & 97.01(10) & N1-Zn1-N4 & 101.32(12) & N3-Zn1-N2 & 126.1(3) \\ N9-Zn2-N3 & 78.13(13) & C28-N5-Zn1 & 177.2(4) & N4-Zn1-N2 & 76.6(3) \\ N9-Zn2-N7 & 101.26(13) & N5-Zn1-N1 & 108.76(14) & 04-Zn1-N1 & 105.1(3) \\ N3-Zn2-N7 & 161.01(14) & N5-Zn1-N2 & 102.64(13) & N3-Zn1-N1 & 105.7(3) \\ N8-Zn2-Br1 & 129.34(10) & N1-Zn1-N2 & 77.76(12) & N4-Zn1-N1 & 157.3(3) \\ N7-Zn2-Br1 & 101.48(10) & N3-Zn1-N4 & 76.91(12) & N2-Zn1-N1 & 99.1(3) \\ N2-Zn1-N4 & 158.84(12) & 04-C9-01 & 123.3(12) \\ N5-C28-S3 & 178.1(4) & & & & & & & & & & & & & & & & & & &$	N8-Zn2-N3	87.88(14)	N3—Zn1—N1	132.87(12)	04—Zn1—N4	95.2(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N8-Zn2-N7	77.09(14)	N3-Zn1-N2	88.22(13)	N3-Zn1-N4	87.9(3)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N9–Zn2–Br1	104.19(10)	N5-Zn1-N4	97.67(13)	04-Zn1-N2	125.0(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N3—Zn2—Br1	97.01(10)	N1-Zn1-N4	101.32(12)	N3-Zn1-N2	126.1(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N9-Zn2-N3	78.13(13)	C28-N5-Zn1	177.2(4)	N4-Zn1-N2	76.6(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N9-Zn2-N7	101.26(13)	N5-Zn1-N1	108.76(14)	04-Zn1-N1	105.1(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N3-Zn2-N7	161.01(14)	N5-Zn1-N2	102.64(13)	N3-Zn1-N1	76.7(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N8-Zn2-Br1	129.34(10)	N1-Zn1-N2	77.76(12)	N4-Zn1-N1	157.3(3)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N7–Zn2–Br1	101.48(10)	N3-Zn1-N4	76.91(12)	N2-Zn1-N1	99.1(3)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $			N2-Zn1-N4	158.84(12)	04	123.3(12)
Bond angles for 4 $01-Zn1-N1$ $90.49(13)$ $01-Zn1-N2$ $139.16(13)$ $01-Zn1-N3$ $108.26(13)$ $01-Zn1-N4$ $93.88(13)$ $N1-Zn1-N2$ $76.38(14)$ $N1-Zn1-N3$ $161.22(14)$ $N1-Zn1-N4$ $100.03(13)$ $N2-Zn1-N4$ $89.46(14)$ $N2-Zn1-N4$ $126.19(13)$ $N3-Zn1-N4$ $78.25(14)$ $01-C28-02$ $122.0(4)$			N5-C28-S3	178.1(4)		
01-Zn1-N1 $90.49(13)$ $01-Zn1-N2$ $139.16(13)$ $01-Zn1-N3$ $108.26(13)$ $01-Zn1-N4$ $93.88(13)$ $N1-Zn1-N2$ $76.38(14)$ $N1-Zn1-N3$ $161.22(14)$ $N1-Zn1-N4$ $100.03(13)$ $N2-Zn1-N3$ $89.46(14)$ $N2-Zn1-N4$ $126.19(13)$ $N3-Zn1-N4$ $78.25(14)$ $01-C28-02$ $122.0(4)$	Bond angles for <b>4</b>					
$\begin{array}{llllllllllllllllllllllllllllllllllll$	01-Zn1-N1	90.49(13)				
$\begin{array}{llllllllllllllllllllllllllllllllllll$	01-Zn1-N2	139.16(13)				
$\begin{array}{llllllllllllllllllllllllllllllllllll$	01-Zn1-N3	108.26(13)				
N1-Zn1-N276.38(14)N1-Zn1-N3161.22(14)N1-Zn1-N4100.03(13)N2-Zn1-N389.46(14)N2-Zn1-N4126.19(13)N3-Zn1-N478.25(14)O1-C28-O2122.0(4)	01-Zn1-N4	93.88(13)				
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N1-Zn1-N2	76.38(14)				
N1-Zn1-N4100.03(13)N2-Zn1-N389.46(14)N2-Zn1-N4126.19(13)N3-Zn1-N478.25(14)O1-C28-O2122.0(4)	N1-Zn1-N3	161.22(14)				
N2-Zn1-N389.46(14)N2-Zn1-N4126.19(13)N3-Zn1-N478.25(14)O1-C28-O2122.0(4)	N1-Zn1-N4	100.03(13)				
N2-Zn1-N4 126.19(13) N3-Zn1-N4 78.25(14) O1-C28-O2 122.0(4)	N2-Zn1-N3	89.46(14)				
N3-Zn1-N4 78.25(14) 01-C28-O2 122.0(4)	N2-Zn1-N4	126.19(13)				
01–C28–O2 122.0(4)	N3-Zn1-N4	78.25(14)				
	01–C28–O2	122.0(4)				

#### Table 3

Hydrogen bond distances (Å) and angles (°) for **1–4** and C—H $\cdots \pi$  interactions (Å, °) for **1** and **2**.

Compounds	D—H···A	D—H	$H{\cdots}A$	$D{\cdots}A$	$D \!\!-\!\! H \!\!\cdot \!\cdot \!\cdot \!A$
1	C2−H2···F8 <sup>a</sup>	0.93	2.50	3.119(5)	124
	C17—H17A· · · Br1 <sup>b</sup>	0.97	2.91	3.548(5)	124
2	C8—H8· · · O3 <sup>c</sup>	0.93	2.56	3.274(5)	134
	C15—H15A · · · O1	0.97	2.51	3.474(5)	170
	$C22-H22\cdots O4^d$	0.93	2.41	3.264(5)	152
	C27−H27···O4 <sup>e</sup>	0.93	2.49	3.170(5)	130
3	C12—H12·…O1	0.93	2.54	2.843(16)	100
	C15-H15O6 <sup>f</sup>	0.93	2.51	3.14(2)	125
	C16—H16·O5 <sup>f</sup>	0.93	2.59	3.40(3)	145
	C22−H22B····O3 <sup>g</sup>	0.97	2.42	3.203(13)	137
	C23—H23A····O3	0.97	2.54	3.466(14)	160
	C28—H28····O2	0.93	2.51	3.413(15)	164
4	C19—H8· · · O2 <sup>e</sup>	0.93	2.30	3.213(7)	169
	C27−H13···F6 <sup>h</sup>	0.93	2.37	3.175(6)	144
	C14—H18·…O2	0.97	2.57	3.371(5)	147
	$C1-H24\cdots F4^{i}$	0.97	2.36	3.213(6)	152
1	$C(18)$ - $H(18)$ ··· $Cg(6)^{j}$	0.93	2.93	3.708(5)	142
2	$C(13)$ - $H(13A)$ ··· $Cg(6)^k$	0.97	2.79	3.678(5)	153

[157.93(3)°] angle deviates slightly larger than 180°, reflecting that the coordination geometry around each zinc(II) in the compound is a slightly distorted trigonal bipyramid. The degree of distortion from ideal square pyramidal geometry is seen in *cisoid* 

 $[76.38(14)-126.19(13)^{\circ}]$  and *transoid*  $[139.16(13)-161.22(14)^{\circ}]$  bond angles in **4**. Zinc(II) centers in **3** and **4** are linked through a bis(monodentate) tp bridge with Zn···Zn separations of 10.994 Å and 10.809 Å, respectively.

The tetradentate Schiff base (L) is twisted around the metal(II) center such that the two planes containing the unsaturated chelate rings [(Zn1, N1, C29, C13, N3) and (Zn1, N2, C1, C2, N4) in **3** and (Zn1, N1, C5, C6, N2) and (Zn1, N3, C16, C17, N4) in **4** are inclined to each other at 56.42° and 52.01°, respectively. The propylenic arm of L is to some extent puckered in both the compounds. The values of dihedral angles 23.65° in **3** and 19.84° in **4** between the carboxylate group (C9, O1, O4 for **3** and C28, O1, O2 for **4**) and benzene ring (C10, C11, C12 for **3**, C29, C30, C31 for **4**) are in line with the twisting of the tp bridge upon coordination to metal atoms. The carboxylate group shows the expected trigonal geometry. For monodentate carboxylate coordination, significant differences are observed in the values of the carbon–oxygen bond distances: the values are 1.241(14)/1.250(13) Å for **3** and 1.250(5)/1.282(5) Å for **4**.

In the crystalline state both **3** and **4** pack through intermolecular face-to-face  $\pi \cdots \pi$  interactions through two closest pyridine rings (Table 4) and join two adjacent molecules to afford a supramolecular 1D chain along crystallographic *b*-axis and *a*-axis, respectively (Fig. 3b and S2b). Different intermolecular C—H···O hydrogen bonds (Table 3) form a 2D sheet structure (Fig. S2a) parallel to *ac*-plane in **3**. On the other hand, C—H···F and C—H···O

Table	4						
$\pi \cdot \cdot \cdot \pi$	interactions	(Å.	°)	for	3	and	4

Compounds	Cg–Cg	Cg–Cg distance	Dihedral angle ( <i>i</i> , <i>j</i> )	Perpendicular distances between baricentres $(i, j)$
3	Cg5–Cg5 <sup>l</sup>	3.713(6)	0.00	3.655(4)
4	Cg5–Cg5 <sup>m</sup>	3.789(3)	0.00	3.506(17)

Symmetry codes: a = 1/2 + x, -1/2 + y, z; b = x, -y, -1/2 + z; c = 2 - x, -1/2 + y, 1/2 - z; d = 1 - x, -1/2 + y, 1/2 - z; e = x, 1/2 - y, 1/2 + z; f = -1 + x, y, z; g = 1 - x, 1 - y, 1 - z; h = -1 + x, y, z; i = 1 - x, -1/2 + y, 1/2 - z; i = 1/2 - x, 3/2 - y, 1 - z; h = -1 + x, y, z; i = 1 - x, -1/2 + y, 1/2 - z; j = -1/2 + x, 1/2 - y, -1/2 + z; k = 1/2 - x, 3/2 - y, 1 - z; l = 1/2 - x, 3/2 - y, 1 - z; m = -x, -y, -z. [For **1**, Cg(6): C(1)  $\rightarrow$  C(2)  $\rightarrow$  C(9)  $\rightarrow$  C(15)  $\rightarrow$  C(16)  $\rightarrow$  C(10); for **2**, Cg(6): C(7)  $\rightarrow$  C(8)  $\rightarrow$  C(9)  $\rightarrow$  C(10)  $\rightarrow$  C(11)  $\rightarrow$  C(12) for **3**, Cg(5): N(1)  $\rightarrow$  C(15)  $\rightarrow$  C(16)  $\rightarrow$  C(31)  $\rightarrow$  C(20); for **4**, Cg(5): (N(1)  $\rightarrow$  C(1)  $\rightarrow$  C(2)  $\rightarrow$  C(3)  $\rightarrow$  C(4)  $\rightarrow$  C(5)].

(Table 3) hydrogen bondings among the dinuclear units in **4** result in an extended 3D network structure (Fig. 4b).

#### 3.3. Thermogravimetric studies

TG–DTA curve shows that pyrolysis of **1** starts around 280 °C (Fig. S3). The weight loss (obs.: 66.4%, calcd.: 69.7%) within the temperature range 280–650 °C is associated with the simultaneous decomposition of the Schiff base and the terminal halide in a continuous fashion with an endothermic effect at 322 °C. TG–DTA curve (Fig. S4) shows that compound **2** is stable up to 166 °C. The weight loss (obs.: 05.1%, calcd.: 09.3%) in the first step between

166–175 °C is in line with the release of the terminal thiocyanate. The next step in the range of 260–680 °C with an exothermic effect at 312 °C corresponds to a large weight loss (obs.: 54.9%, calcd.: 64.5%) due to the removal of the L moiety. Compound **3** is stable up to 311 °C (Fig. S5). It loses two L in two different steps (obs.: 28.3%, calcd.: 31.0% and obs.: 35.1%, calcd.: 31.0%) within the temperature ranges 311–349 °C and 439–790 °C, respectively. Compound **3** shows an exothermic effect at 111 °C and an endothermic effect at 280 °C during its decomposition. Terephthalate dianion dissociates (obs.: 14.0%, calcd.: 12.7%) in a single step between the temperature range 349–439 °C. TG–DTA curve of **4** (Fig. S6) shows a simultaneous weight loss due to the removal of



Fig. 5. (a) (i) Solid state fluorescence behaviors of compounds 1 and 2, and (ii) fluorescence behaviors of L, 1 and 2 in DMF solutions. (b) (i) Solid state fluorescence behaviors of ptp, 3 and 4 and (ii) fluorescence behaviors of L, ptp, 3 and 4 in DMF solutions.

two L and terephthalate dianion (obs.: 61.6.8%, calcd.: 69.9%) in a single step between the temperature range 280–846 °C with an endothermic effect at 323 °C. Moreover, the thermogravimetric analyses reveal that **1** is more stable than **2** and again **3** is more stable than **4**.

#### 3.4. Luminescence behaviors

The photoluminescence behaviors of the dicarboxylate (ptp) and the compounds (1-4) were examined in DMF solutions and in the solid state at room temperature (298 K). As the Schiff base (L) was isolated in the form of a gummy mass, its fluorescence behavior could not be measured in solid state. The spectral patterns are shown in Fig. 5. In DMF solution free L exhibits a broad fluorescent emission centered at 365 nm along with a weak emission at 330 nm upon photoexcitation at the corresponding absorption band (274 nm; Fig. S7). The corresponding compounds 1 and 2 show emission bands at the same wavelength with higher intensity when excited at 274 and 281 nm (Fig. S7), respectively. Ptp, upon excitation at 281 nm (Fig. S7) gives a broad emission band ca. 362 nm along with a weak band ca. 333 nm. Compounds 3 and 4 also exhibit more intense emission bands at the same wavelength as shown by L and ptp upon excitation to their corresponding absorption bands (282 nm for 3 and 280 nm for 4; Fig. S7). Therefore the emission bands in 1-4 may be assigned to the ligand (L and/or ptp) based  $\pi - \pi^*$  transitions. In the solid state, upon excitation at 292 nm (Fig. S8), ptp exhibits the main emission centered at 423 nm with two weak bands at 370 nm and 486 nm. Compounds 1 and 2 show photoluminescence characteristics with main emission centered at 423 and 421 nm, respectively upon excitation at their corresponding absorption bands (300 nm for 1 and 272 nm for 2; Fig. S8) which may presumably be due to ligand based  $\pi$ - $\pi$ <sup>\*</sup> transition. **3** and **4** show emissions centered at 370, 430 and 485 nm when excited to their corresponding absorption bands (326 nm for 3 and 315 nm for 4; Fig. S8). The intensity of the emission bands in 3 and 4 are also increased with respect to ligands as seen in DMF solutions. These emissions are assignable to the ligand (L and/or ptp) based  $\pi - \pi^*$  transitions [35–38]. The greater intensity of luminescence in the complexes over the ligands may be attributed to the metal-perturbed intraligand  $\pi - \pi^*$  transition becoming more permissible upon coordination. The emission band for each compound is red-shifted in the solid state as compared to that in solution, which may be due to intermolecular interactions arising from the close proximity of the molecules in the crystalline state, leading to stable excimer formation.

#### 4. Conclusion

Four luminous zinc(II) halide/pseudohalide/carboxylate complexes in combination with a tetradentate N-donor Schiff base have been synthesized and X-ray crystallographically characterized. Using different terminal/bridging units, variation in crystalline architectures is observed. Trans-bis(monodentate) bridging behavior of tp in **3** and **4** is seen. A subtle change in coordination geometry (tbp to sp) in **1** and **2** is observed with changing the terminal units from Br<sup>-</sup> to NCS<sup>-</sup> whereas variation of counter anion changes geometry (tbp to sp) in **3** and **4**. Structures of **1–4** represent reliability of the combination of strong covalent bonds and weak non-covalent interactions in crystal engineering for the rational design of functional materials at molecular level.

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#### Appendix A. Supplementary material

Crystalline architectures (Figs. S1 and S2) of **1–4** formed through different non-covalent interactions, thermal decomposition patterns (Figs. S3–S6) of **1-4**, UV–Vis spectra in DMF solutions (Fig. S7) and in solid-states (Fig. S8) of L, ptp and **1–4** are available in the supporting information. Full cif depositions, excluding structure factor amplitudes, reside with the Cambridge Crystallography Data center, CCDC-826782 for **1**, CCDC-826784 for **2**, CCDC-893270 for **3** and CCDC-893271 for **4**. Copies of the data can be obtained, free of charge, on application from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 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.molstruc.2012.12.018.

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