

# Syntheses, molecular and crystalline architectures, and luminescence behaviour of terephthalate bridged heptacoordinated dinuclear lead(II) complexes containing a pentadentate N-donor Schiff base

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**Abstract.** One-pot synthesis using a 2:2:1:2 molar ratio of Pb(OAc)<sub>2</sub>·3H<sub>2</sub>O, L, piperidinium terephthalate (ptp) and NaClO<sub>4</sub>/NH<sub>4</sub>PF<sub>6</sub> at room temperature affords two dinuclear compounds of the type [Pb<sub>2</sub>(L)<sub>2</sub>(μ-tp)](ClO<sub>4</sub>/PF<sub>6</sub>)<sub>2</sub> (**1/2**) [L=N,N'-(bis-(pyridin-2-yl)benzylidene)diethylenetriamine and tp = terephthalate dianion]. The compounds are characterized by microanalytical, spectroscopic, thermal and other physicochemical results. X-ray structural analyses of **1** and **2** reveal that each heptacoordinated lead(II) centre with a PbN<sub>5</sub>O<sub>2</sub> chromophore are bound by five N atoms of L and connected through O atoms of a bis(bidentate) tp bridge. The arrangements of L and tp suggest a gap around the metal centre due to occupation of a stereo-active lone pair of electrons reflecting a hemidirected coordination around the metal centre. The complexes exhibit reasonable thermal stabilities with the tolerate temperatures ca. 255°C for **1** and 263°C for **2**. The complexes display intraligand (π-π\*) fluorescence in the solid state and in DMF solutions at room temperature.

**Keywords.** Dinuclear lead(II); Schiff base; terephthalate bridge; hemidirected structures; luminescence.

## 1. Introduction

Mono-, di- and polynuclear lead(II) complexes<sup>1–18</sup> have potential applications as catalysts, porous materials, gas storages, nonlinear optical materials and luminescent devices.<sup>7,8,19–24</sup> The compounds with coordination numbers two to five show hemidirected<sup>1,2,13–16</sup> metal ligand coordination, whereas holodirected coordination<sup>1,15,16</sup> environments are found for higher coordination numbers, nine and ten. Either<sup>1,16</sup> of these two irregular coordination environments is found with coordination numbers six to eight. Schiff bases,<sup>18,25–28</sup> have been widely used as end-capping ligands affording different functional materials with interesting molecular aggregates and crystalline architectures. We have reported some lead(II) pseudohalide complexes<sup>17,18</sup> in combination with Schiff bases; interesting synthetic, structural and luminescent properties of these compounds have prompted us to explore the chemistry of lead(II) in combination with Schiff bases and aromatic dicarboxylates<sup>5,10,11,13–16</sup> such as terephthalate (tp).<sup>12–16</sup>

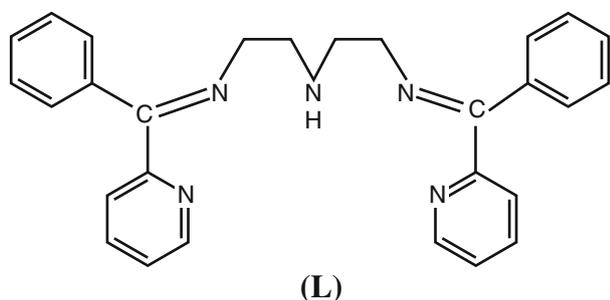
The syntheses, structures, and thermal and luminescence behaviours of two hemidirected compounds [Pb<sub>2</sub>(L)<sub>2</sub>(μ-tp)](ClO<sub>4</sub>/PF<sub>6</sub>)<sub>2</sub> (**1/2**) [L=N,N'-(bis-(pyridin-2-yl)benzylidene)diethylenetriamine; scheme 1] are described below.

## 2. Experimental

### 2.1 Materials

High purity diethylenetriamine (Spectrochem, India), 2-benzoylpyridine (Lancaster, UK), terephthalic acid (Loba Chemie, India), piperidine (Loba Chemie, India), lead(II) acetate (E Merck, India), sodium perchlorate (Lancaster, UK) and ammonium hexafluorophosphate (Fluka, Germany) were purchased and were used as received. Schiff base, N,N'-(bis-(pyridin-2-yl)benzylidene)diethylenetriamine (L) was prepared by condensation of 1:2 molar ratio of diethylenetriamine and 2-benzoylpyridine using a reported method.<sup>27</sup> Piperidinium terephthalate (ptp) was isolated by following a method described elsewhere.<sup>29</sup> All other chemicals and solvents used were AR grade.

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**Scheme 1.** Framework of pentadentate N-donor Schiff base (L).

## 2.2 Physical measurements

Elemental analyses were performed on a Perkin–Elmer 2400 CHNS/O elemental analyser. IR spectra (KBr discs, 4000–400  $\text{cm}^{-1}$ ) 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 dry MeCN was used as solvent. Thermal behaviours were examined with a Perkin–Elmer Diamond TG/DT analyser heated from 40 to 700°C under dinitrogen. Ground state absorptions (in dry N, N-dimethylformamide [DMF]) were made with a Shimadzu model UV-2450 UV–Vis spectrophotometer. Steady-state fluorescence measurements were done using Hitachi model F-4500 spectrofluorimeter.

## 2.3 Preparation of the complexes

Compounds **1** and **2** were obtained from methanolic solutions using a 2:2:1:2 molar ratio of lead(II) acetate, Schiff base (L), ptp and  $\text{NaClO}_4/\text{NH}_4\text{PF}_6$  as appropriate. All the reactions were performed using self-assembly at room temperature and were reproducible. The typical syntheses of the compounds are described below.

**2.3a Syntheses of  $[\text{Pb}_2(\text{L})_2(\mu\text{-tp})](\text{ClO}_4)_2$  (**1**) and  $[\text{Pb}_2(\text{L})_2(\mu\text{-tp})](\text{PF}_6)_2$  (**2**):** L (0.086 g, 0.2 mmol) in methanol (10 mL) was added dropwise to a solution of  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  (0.076 g, 0.2 mmol) dissolved in the same solvent (10 mL). To this resulting faint yellow solution, a methanolic solution (5 mL) of ptp (0.034 g, 0.1 mmol) was added slowly followed by  $\text{NaClO}_4$  (0.0281 g, 0.2 mmol) in methanol (5 mL). The final faint yellow solution was filtered through a glass-frit and left undisturbed in an open air for slow evaporation. After a week colourless microcrystals of **1** were collected and dried *in vacuo* over silica gel. Yield:

1.31 g (80%). Compound **2** was prepared similarly using the same stoichiometry and reaction conditions except that  $\text{NH}_4\text{PF}_6$  (0.0326 g, 0.2 mmol) instead of  $\text{NaClO}_4$  was used. Yield: 1.15 g (70%). **2** was also isolated by metathesis of **1** with  $\text{NH}_4\text{PF}_6$  in 1:2 ratio from a methanolic solution and constant stirring for 45 min at room temperature. The resulting yellow solution was processed as described above to afford pure **2**. The microanalytical and spectroscopic results for **2** obtained from both methods are akin which are listed here. Anal. Calc. for  $\text{C}_{64}\text{H}_{58}\text{N}_{10}\text{O}_{12}\text{Cl}_2\text{Pb}_2$  (**1**): C, 46.7; H, 3.5; N, 8.51. Found: C, 47.5; H, 3.7; N, 8.3%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{as}}(\text{COO}^-)$  1584;  $\nu_{\text{s}}(\text{COO}^-)$  1356;  $\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$  1624, 1595;  $\nu(\text{ClO}_4^-)$  1085, 623.  $\Lambda_{\text{M}}$  (MeCN,  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ): 235. UV–Vis ( $\lambda$ , nm): 269. Yield: 1.21 g (70%). Anal. Calc. for  $\text{C}_{64}\text{H}_{58}\text{N}_{10}\text{O}_4\text{F}_{12}\text{P}_2\text{Pb}_2$  (**2**): C, 44.3; H, 3.4; N, 8.1. Found: C, 44.5; H, 3.1; N, 8.3%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{as}}(\text{COO}^-)$  1585;  $\nu_{\text{s}}(\text{COO}^-)$  1358;  $\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$  1621, 1594;  $\nu(\text{PF}_6^-)$  836, 557.  $\Lambda_{\text{M}}$  (MeCN,  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ): 230. UV–Vis ( $\lambda$ , nm): 272.

## 2.4 X-ray data collection and structure refinement

Diffraction data of the single crystals of **1** and **2** were collected at 293 K on a Bruker AXS SMART APEX–II CCD area–detector diffractometer using graphite monochromated Mo– $\text{K}\alpha$  radiation. The unit cell parameters were obtained from SAINT<sup>30</sup> and absorption corrections were performed with SADABS.<sup>31</sup> The structures were solved by direct methods using SHELXS-97<sup>32</sup> and refined by full-matrix least-squares method based on  $F^2$  using SHELXL-97.<sup>32</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were fixed geometrically and refined using a riding model. All calculations were carried out using SHELXTL,<sup>32</sup> PLATON<sup>33</sup> and Mercury 2.3<sup>34</sup> programs. A summary of the crystallographic data and structure determination parameters is given in table 1.

## 3. Results and discussion

### 3.1 Synthesis and formulation

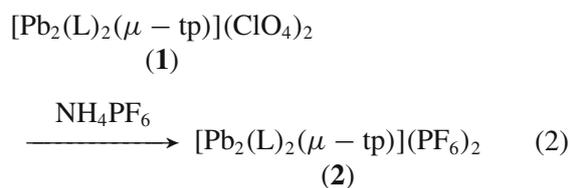
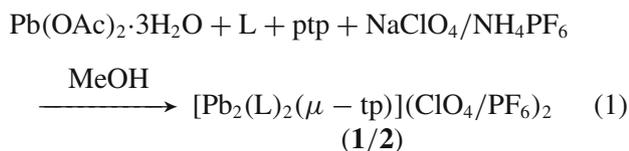
A 2:2:1:2 molar ratio of the building components at room temperature in methanol yielded heptacoordinated dinuclear compounds of type  $[\text{Pb}_2(\text{L})_2(\mu\text{-tp})](\text{ClO}_4/\text{PF}_6)_2$  (**1/2**). Compound **2** was also isolated by metathesis of **1** in methanol using  $\text{NH}_4\text{PF}_6$ . The reactions were reproducible as was evident from repetitive microanalytical results, spectral behaviours and other

**Table 1.** Crystallographic data and structure refinement parameters in **1** and **2**.

Compounds	<b>1</b>	<b>2</b>
Chemical formula	C <sub>64</sub> H <sub>58</sub> N <sub>10</sub> O <sub>12</sub> Cl <sub>2</sub> Pb <sub>2</sub>	C <sub>64</sub> H <sub>58</sub> N <sub>10</sub> O <sub>4</sub> F <sub>12</sub> P <sub>2</sub> Pb <sub>2</sub>
Formula mass	1644.48	1735.52
Crystal system	Monoclinic	Monoclinic
Space group	P21/n	P21/n
<i>a</i> /Å	11.889(4)	11.925(3)
<i>b</i> /Å	11.543(4)	11.546(3)
<i>c</i> /Å	23.804(8)	24.445(6)
$\alpha$ /°	90	90
$\beta$ /°	92.236(5)	93.742(7)
$\gamma$ /°	90	90
<i>V</i> /Å <sup>3</sup>	3264.5(18)	3358.7(14)
<i>T</i> /K	293(2)	293(2)
$\lambda$ /Å	0.71073	0.71073
<i>Z</i>	2	2
$\mu$ /mm <sup>-1</sup>	5.300	5.141
<i>D</i> <sub>calc</sub> /g m <sup>-3</sup>	1.673	1.716
<i>F</i> (0 0 0)	1612	1692
Crystal size/mm <sup>3</sup>	0.18 × 0.16 × 0.14	0.28 × 0.22 × 0.17
$\theta$ ranges/°	1.71 to 23.66	1.67 to 22.13
<i>h</i> / <i>k</i> / <i>l</i>	−13, 13/−12, 13, −26, 26	−12, 12/−12, 12, −25, 25
Reflections collected	27545	23750
Independent reflections	4909	4180
Data/restraints/parameters	4909/0/406	4180/0/424
<i>R</i> <sub>int</sub>	0.099	0.120
Final <i>R</i> <sub>1</sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0447	0.0502
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0910	0.1161
Final <i>R</i> <sub>1</sub> values (all data)	0.0960	0.0896
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.1123	0.1396
Goodness of fit on <i>F</i> <sup>2</sup>	1.017	1.008
Largest peak and hole (e Å <sup>-3</sup> )	0.770 and −0.656	0.836 and −0.706

Weighting scheme:  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $\text{calcd } w = 1 / [\sigma^2(F_o^2) + (xP)^2 + yP]$ ;  $x = 0.0464P$  (for **1**),  $0.0739$  (for **2**) and  $y = 1.5647$  (for **1**),  $0.0000$  (for **2**)

physicochemical properties. The details of the reactions are summarized in Eqs. 1 and 2:

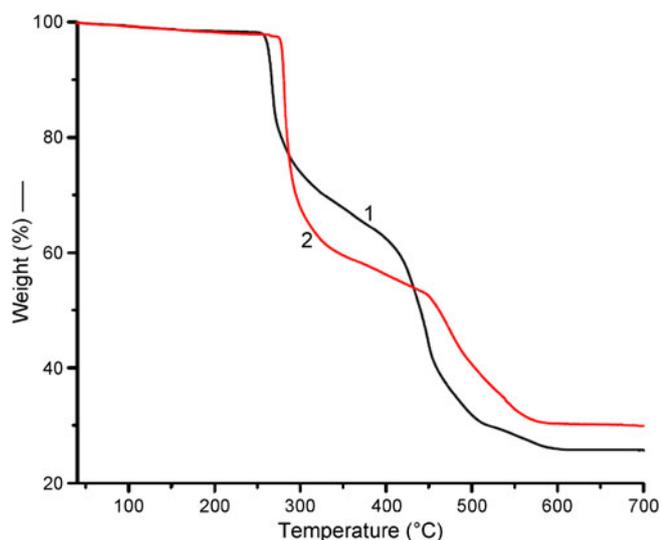


The compounds were characterized using microanalytical, spectroscopic thermal and other physicochemical results. The microanalytical results are in conformity with formulations **1** and **2**. The moisture- insensi-

tive compounds are soluble in common organic solvents such as acetonitrile, dimethylformamide, dimethylsulphoxide, but are insoluble in water. MeCN solutions of **1** and **2** show conductivity values [ $\Lambda_M$  (MeCN, ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>): 235 (**1**) and 230 (**2**)] corresponding to 2:1 electrolytic behaviour.<sup>35</sup>

### 3.2 Spectroscopic features

In IR spectra, the stretching vibrations of tp in **1** and **2** are seen as strong  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  absorptions at ca. 1585 cm<sup>-1</sup> and ca. 1360 cm<sup>-1</sup>, respectively. The metal bound Schiff base (L) in complexes **1** and **2** show  $\nu(\text{C}=\text{N})$  plus  $\nu(\text{C}=\text{C})$  stretching frequencies<sup>36</sup> at ca. 1625 and ca. 1595 cm<sup>-1</sup>. Several weak bands in the range 2970–2920 cm<sup>-1</sup> assignable to aliphatic  $\nu(\text{C}-\text{H})$  stretching vibration are routinely observed. The presence of perchlorate bands at 1085 and 623 cm<sup>-1</sup> in **1** and hexafluorophosphate stretches at 836 and 557 cm<sup>-1</sup> in



**Figure 1.** Thermal behaviours of **1** and **2**.

**2** are noticed, reflecting counter anionic view<sup>36</sup> with no metal coordination. In DMF solutions, L and ptp show absorption bands at 266 nm and 281 nm, respectively whereas the corresponding lead(II) complexes exhibit bands at 269 nm (for **1**) and 272 nm (for **2**) assignable to ligand based  $n\text{-}\pi^*/\pi\text{-}\pi^*$  charge transfer transition.<sup>37</sup>

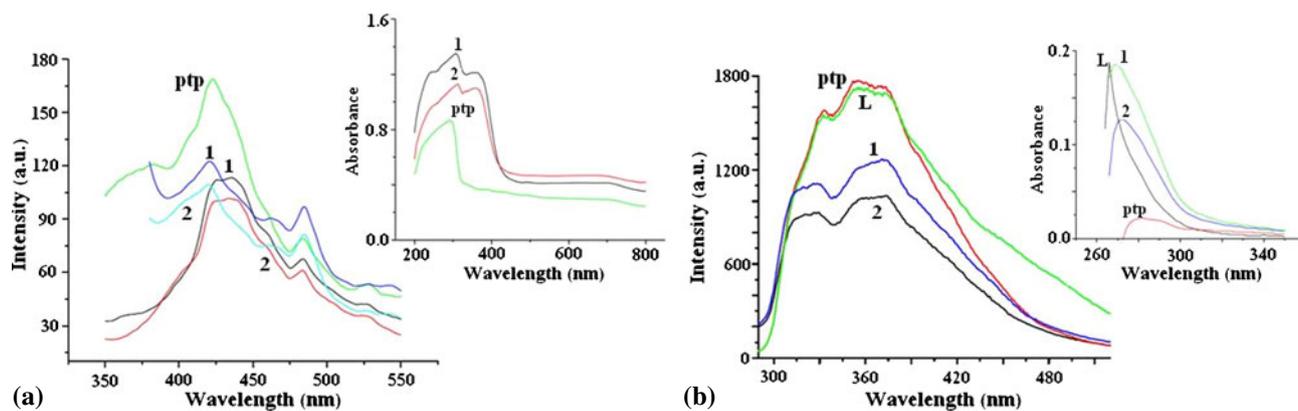
### 3.3 Thermal analysis

Thermogravimetric and differential thermal analyses (TG-DTA) of compounds **1** and **2** were carried out to examine their thermal stabilities. The crushed single-crystals of **1** and **2** were heated between 40 and 700°C temperature in the static atmosphere of dinitrogen at a heating rate of 10°C min<sup>-1</sup>. The TG curves (figure 1)

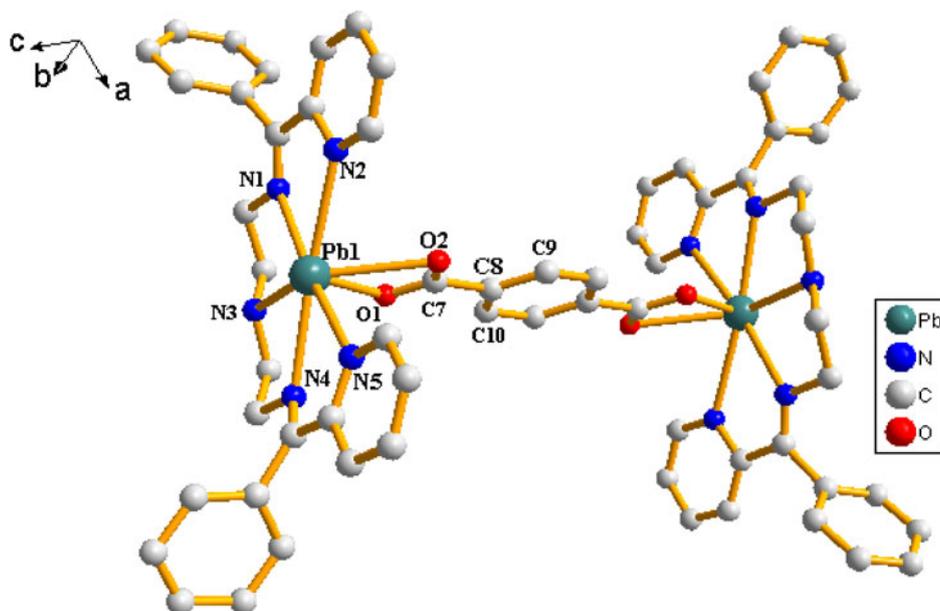
show that both the compounds simultaneously loose two Schiff bases (for **1**; obs.: 57.31%, calc.: 57.16%, for **2**; obs.: 55.4%, calc.: 53.92%) in the first step of the pyrolysis process between the temperature range 255–456°C in **1** and 263–483°C in **2**. The second step weight loss is associated with the removal of tp dianion (for **1**; obs.: 14.46%, calc.: 10.81%, for **2**; obs.: 11.27%, calc.: 10.20%) in both the compounds. The weight (for **1**; obs.: 26.27%, calc.: 27.20%, for **2**; obs.: 30.75%, calc.: 25.77%) of the final residue corresponds to two PbO units.

### 3.4 Fluorescence properties

The photoluminescence behaviours of the dicarboxylate (ptp) and the corresponding lead(II) compounds **1** and **2** are examined in DMF solutions and in solid state at room temperature (298 K). The free Schiff base (L) is a gummy mass, so its fluorescence behaviour cannot be measured in solid state; however such study with its DMF solution is made. The spectral patterns are shown in figure 2a, b. Upon photoexcitation at the corresponding absorption bands (281 nm for ptp and 266 nm for L) the DMF solutions of ptp and L exhibit a main fluorescent emission centred at 355 nm with a weak emission at 333 nm, whereas **1** and **2** show two intense emission bands at ca. 330 and 360 nm upon excitation at 269 and 272 nm, respectively. The luminescence behaviour in all cases may be attributed to an intraligand ( $\pi \rightarrow \pi^*$ ) emission. In the solid state ptp absorbs at 292 nm whereas the corresponding lead(II) compounds absorb at 245, 305 and 355 nm (**1**) and at 310 and 355 nm (**2**). Ptp shows emissions at 423 and 486 nm ( $\lambda_{\text{ex}} = 292$  nm) which may be due to the intraligand ( $\pi \rightarrow \pi^*$ ) transition. Compound **1** exhibits main emissions at 421 nm



**Figure 2.** (a) Solid state fluorescence behaviours of ptp, **1** and **2**, and inset: solid state absorption spectra of ptp, **1** and **2**. (b) Fluorescence behaviours of L, ptp, **1** and **2** in DMF solutions, and inset: absorption spectra of L, ptp, **1** and **2** in DMF solutions.



**Figure 3.** Molecular structure of  $[\text{Pb}_2(\text{L})_2(\mu\text{-tp})]^{2+}$  in **1** showing hemidirected coordination environments of lead(II).

( $\lambda_{\text{ex}} = 305$  nm) and 436 nm ( $\lambda_{\text{ex}} = 355$  nm) with a weak emission band at 486 nm, whereas **2** has main emissions at 420 nm ( $\lambda_{\text{ex}} = 310$  nm) and 437 nm ( $\lambda_{\text{ex}} = 355$  nm) with a weak emission at 487 nm. The bands at ca. 420 nm in both **1** and **2** may be assigned to the ptp based intraligand ( $\pi \rightarrow \pi^*$ ) transition, whereas the band at ca. 435 nm may arise due to the ligand (L) based transition.<sup>38,39</sup> The weak emission band at ca. 485 nm in both the complexes arises presumably due to either L or ptp based transition. Each band in solid state is red-shifted as compared to that in solution which may be due to intermolecular interactions arising from close proximity of the compounds in solid state leading to more stable excimer formation.

### 3.5 Description of the crystal structures of $[\text{Pb}_2(\text{L})_2(\mu\text{-tp})](\text{ClO}_4)_2$ (**1**) and $[\text{Pb}_2(\text{L})_2(\mu\text{-tp})](\text{PF}_6)_2$ (**2**)

Structural analyses show that compounds **1** and **2** are made up of dinuclear cation  $[\text{Pb}_2(\text{L})_2(\text{tp})]^{2+}$  with one tp bridge in a bis(bidentate) fashion and two pentadentate Schiff base chelators; two non-coordinated perchlorates (in **1**) and hexafluorophosphates (in **2**) are present as counter ions. Molecular structures of the dinuclear entities of these compounds are shown in figures 3 and S1. Selected bond distances and angles are given in table 2. The dinuclear units in **1** and **2** lie about a crystallographic inversion centre located at the middle of the

benzene ring of the tp bridge. The symmetry related metal centres have Pb...Pb separations 11.465 Å and 11.447 Å, respectively in **1** and **2**.

Each lead(II) centre in **1** and **2** lies in an unsymmetrical seven-coordinated environment with a  $\text{PbN}_5\text{O}_2$  chromophore, and is bound by five N atoms of L and two O atoms of tp dianion. The arrangement of Schiff base (L) and the tp dianion suggest a gap in the coordination geometry around the metal ion, occupied by a stereo-active lone pair of electrons on lead(II). The observation in shortening of the Pb–N and Pb–O bonds on the side of the lead(II) ion opposite to the position of the putative lone pair (table 2) corroborates the presence of the stereo-active lone pair.<sup>1,2</sup> Based on the structural discussion by Shimoni-Livny *et al.*,<sup>1</sup> the coordination around the lead(II) centre in **1** and **2**, may be regarded as hemidirected<sup>1,2,13,16</sup> with a significant gap *trans* to the chelating L and tp ligands (figures 3 and S1) similar to a reported compound  $[\text{Pb}(\text{DOTAM})](\text{ClO}_4)_2 \cdot 4.5\text{H}_2\text{O}$  (DOTAM = 1,4,7,10-tetrakis(carbamoylmethyl)-1,4,7,10-tetraazacyclododecane).<sup>2</sup>

The value ( $2.75^\circ$  and  $2.66^\circ$ ) of dihedral angles between carboxylate groups (C7, O1, O2 for **1** and C21, O1, O2 for **2**) and benzene rings (C8, C9, C10 for **1** and C18, C19, C20 for **2**) in **1** and **2** is in line with the quasi-planarity of the tp bridge upon coordination. Four five-membered and one four-membered rings are formed around each metal ion in **1** and **2** by L and tp unit, respectively. Significant differences [ $1.230(13)/1.266(13)$  Å (for **1**) and  $1.199(14)/1.291(14)$  Å (for **2**)] are observed in values

**Table 2.** Selected bond distances (Å) and bond angles (°) for **1** and **2**.

Bond distances for <b>1</b>		Bond distances for <b>2</b>	
Pb1–N1	2.682(8)	Pb1–N1	2.789(11)
Pb1–N2	2.803(11)	Pb1–N2	2.608(10)
Pb1–N3	2.567(8)	Pb1–N3	2.682(10)
Pb1–N4	2.676(8)	Pb1–N4	2.769(10)
Pb1–N5	2.820(11)	Pb1–N5	2.706(10)
Pb1–O1	2.311(8)	Pb1–O1	2.308(8)
Pb1–O2	2.720(8)	Pb1–O2	2.698(9)
O1–C7	1.266(13)	O1–C21	1.291(14)
O2–C7	1.230(13)	O2–C21	1.199(14)
Bond angles for <b>1</b>		Bond angles for <b>2</b>	
O1–Pb1–N1	84.5(3)	O1–Pb1–N1	99.8(3)
O1–Pb1–N2	100.3(3)	O1–Pb1–N2	74.3(3)
O1–Pb1–N3	74.2(3)	O1–Pb1–N3	83.5(3)
O1–Pb1–N4	82.4(3)	O1–Pb1–N4	97.7(3)
O1–Pb1–N5	99.5(3)	O1–Pb1–N5	84.1(3)
N1–Pb1–N2	57.5(3)	N1–Pb1–N2	123.9(3)
N1–Pb1–N3	65.4(3)	N1–Pb1–N3	171.1(3)
N1–Pb1–N4	131.3(3)	N1–Pb1–N4	112.7(3)
N1–Pb1–N5	170.4(3)	N1–Pb1–N5	57.7(3)
N2–Pb1–N3	122.9(3)	N2–Pb1–N3	64.9(3)
N2–Pb1–N4	171.2(3)	N2–Pb1–N4	123.3(3)
N2–Pb1–N5	113.0(3)	N2–Pb1–N5	66.2(3)
N3–Pb1–N4	65.9(3)	N3–Pb1–N4	58.4(3)
N3–Pb1–N5	124.1(3)	N3–Pb1–N5	131.1(3)
N4–Pb1–N5	58.2(3)	N4–Pb1–N5	170.4(3)
O1–C7–O2	122.5(12)	O1–C21–O2	122.6(13)
O2–Pb1–N1	103.0(3)	O2–Pb1–N1	71.7(3)
O2–Pb1–N2	71.9(3)	O2–Pb1–N2	125.3(3)
O2–Pb1–N3	124.9(3)	O2–Pb1–N3	104.7(3)
O2–Pb1–N4	104.1(3)	O2–Pb1–N4	71.2(3)
O2–Pb1–N5	73.9(3)	O2–Pb1–N5	103.4(3)
O1–Pb1–O2	50.8(2)	O1–Pb1–O2	51.0(3)

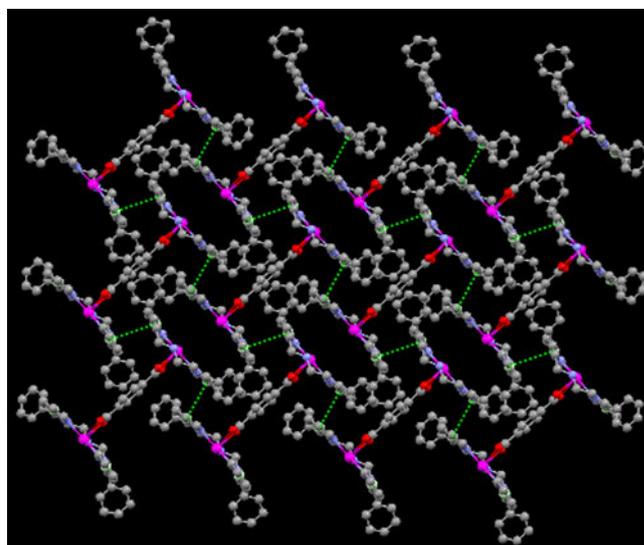
of the C–O bond distances for the bidentate chelating carboxylate bridges.

In the crystalline states, individual units of **1** and **2** are assembled through weak face-to-face  $\pi \cdots \pi$  interactions among the adjacent pyridine rings [Cg(1)–Cg(1) and Cg(2)–Cg(2); table 3] of L resulting in 2D sheet structure (figure 4) parallel to crystallographic *ab* plane.

**Table 3.**  $\pi \cdots \pi$  interactions (Å, °) in **1** and **2**.

Compounds	Cg–Cg	Cg–Cg distance	Dihedral angle ( <i>i, j</i> )	Perpendicular distances between baricentres ( <i>i, j</i> )	Slippage
<b>1</b>	Cg1–Cg1 <sup>a</sup>	3.953(8)	0	3.814(5)	1.037
	Cg2–Cg2 <sup>b</sup>	4.925(8)	0	4.924(9)	2.505
<b>2</b>	Cg1–Cg1 <sup>c</sup>	4.654(9)	0	4.191(6)	2.025
	Cg2–Cg2 <sup>d</sup>	3.898(9)	0	3.838(6)	0.683

Symmetry Codes: a = 2 – x, 1 – y, 2 – z; b = 1 – x, –y, 2 – z; c = 1 – x, 1 – y, 2 – z; d = 2 – x, –y, 2 – z  
 [For **1**: Cg(1) = N(2)–>C(18)–>C(29)–>C(30)–>C(31)–>C(32), Cg(2) = N(5)–>C(1)–>C(2)–>C(3)–>C(4)–>C(5); for **2**: Cg(1) = N(1)–>C(1)–>C(2)–>C(11)–>C(3)–>C(4), Cg(2) = N(4)–>C(9)–>C(25)–>C(24)–>C(23)–>C(22)]

**Figure 4.** A view of 2D sheet structure in **1/2** formed through  $\pi \cdots \pi$  stacking parallel to *ab* plane.

#### 4. Conclusion

Two tp bridged centrosymmetric dicationic dinuclear compounds of lead(II) in combination with a pentadentate Schiff base ligand are synthesized and X-ray crystallographically characterized. The metal centres in both the compounds are linked through the dicarboxylate bridge in a bis(bidentate) fashion. The lead(II) centres in **1** and **2** have hemidirected heptacoordinated geometry with a stereo-active lone pair located at the opposite site of the Schiff base and tp. The compounds are examples of good luminous materials. We are now active in extending such work using paramagnetic 3d ions like manganese(II), cobalt(II), nickel(II) and copper(II) in combination with different tailored polycarboxylates and organic blockers with varied denticities.

#### Supplementary information

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic

Data Centre Nos. 899543 (1) and 899544 (2). Copies of this information can be obtained, free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

The electronic supplementary information (figure S1) can be seen in [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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