

## Notes

### Piperazinediium bis( $\mu_2$ -phthalato)zincate(II) monohydrate: A new ladder coordination polymer with a unique supramolecular architecture

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The  $\mu_2$ -bridging bidentate coordination modes of the crystallographically unique phthalate ligands in piperazinediium bis( $\mu_2$ -phthalato)zincate(II) monohydrate (**1**) result in Zn $\cdots$ Zn separations of 5.839(5) and 8.142(3) Å respectively leading to a one-dimensional Zn(II) ladder. The organic cation, ladder complex anion and lattice water in (pipH<sub>2</sub>)[Zn(pt)<sub>2</sub>] $\cdot$ H<sub>2</sub>O (**1**) (pipH<sub>2</sub>= piperazinediium, pt = phthalate) assemble into a unique supramolecular network, resulting in the following H-bonded sequence, viz., water $\cdots$ cation $\cdots$ water $\cdots$ ladder $\cdots$ water in the crystallographic *ac* plane.

**Keywords:** Coordination chemistry, Coordination polymer, Ladder complexes, Supramolecular network, Bridging ligands, Phthalates, Metal phthalates, Zinc, Zinc phthalates, Piperazinediium bis( $\mu_2$ -phthalato)zincate

The synthesis, characterization and properties of metal phthalate (pt) complexes has been a subject of several research investigations in the past decade<sup>1-47</sup>. Based on a study of the Cambridge structural database, Baca *et al.*<sup>1</sup> had reported that phthalic acid exhibits twenty six different coordination modes. Although several structurally characterized zinc phthalates are reported in the literature, an analysis of the binding modes of the phthalate ligands in these compounds reveals that phthalate functions as  $\mu_2$ -,  $\mu_3$ - and  $\mu_4$ - bridging ligands (Supplementary data, Scheme 1) resulting in the formation of one- or two- or three-dimensional polymers. Of the several neutral, cationic and anionic compounds of varying Zn:phthalate stoichiometries (Supplementary data, Table S 1), it is interesting to note that a majority of the known zinc phthalates are neutral and exhibit a zinc:phthalate ratio of 1:1. In view of the paucity of information on anionic bis (phthalate) complexes, excepting [(1,3-pnH<sub>2</sub>)[Zn(pt)<sub>2</sub>] (1,3-pnH<sub>2</sub> = 1,3-propanediammonium; pt = phthalate)<sup>17</sup>, we have

investigated the reactions of the acidic [Zn(ptH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (ptH = hydrogen phthalate)<sup>48</sup> precursor compound with organic amines (base) so that deprotonation can afford an anionic bis(phthalate) charge balanced by organic cations. Herein, the details of our research reporting on the characterization of a new ladder coordination polymer, viz., piperazinediium bis( $\mu_2$ -phthalato)zincate(II) monohydrate (pipH<sub>2</sub>)[Zn(pt)<sub>2</sub>] $\cdot$ H<sub>2</sub>O (**1**) with a unique supramolecular architecture are described.

### Experimental

All the reagents used in this study were of reagent grade and were used as received without any further purification. The precursor compound [Zn(ptH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] was prepared by a new method in increased yield. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000-400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. Raman spectra were recorded using 785 nm laser radiation for excitation on an Agiltron PeakSeeker Pro Raman instrument. UV-visible spectra were recorded using a Shimadzu UV-2450 double beam spectrophotometer in water using matched quartz cells. Diffuse reflectance spectra were recorded in the same instrument using BaSO<sub>4</sub> as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka-Munk function ( $a/S = (1-R)^2/2R$ , where  $a$  is the absorption coefficient,  $R$  the reflectance, and  $S$  the scattering coefficient. Isothermal weight loss studies were carried out in a temperature controlled electric furnace. Elemental analysis (C, H and N) was done on a Elementar vario Micro cube CHNS analyser, while TG-DTA study was performed in flowing air in Al<sub>2</sub>O<sub>3</sub> crucibles at a heating rate of 10 K min<sup>-1</sup> using a STA-409 PC simultaneous thermal analyser from Netzsch. X-ray powder patterns were recorded on a Rigaku Miniflex II powder diffractometer using Cu-K $\alpha$  radiation with Ni filter.

[Zn(ptH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1a**) was synthesised as follows: A mixture of phthalic acid (0.332 g, 2 mmol) and zinc acetate dihydrate (0.219 g, 1 mmol) was taken in distilled water (15 mL) and was heated on a water bath to reduce the volume to obtain a clear solution

(pH 4.5). Methanol (~10 mL) was added and the reaction mixture was kept undisturbed for crystallization in a refrigerator. Transparent crystals which separated after 24 h were isolated by filtration, washed with methanol and dried in air to yield 0.388 g of  $[\text{Zn}(\text{ptH})_2(\text{H}_2\text{O})_2]$  in 90% yield. This was used as a precursor for the preparation of **(1)**.

**(1a)**: Anal. (%): Found (calcd) for  $\text{ZnC}_{16}\text{O}_{10}\text{H}_{14}$  (431.69): C 44.22 (44.51); H 3.18 (3.28); ptH<sub>2</sub> 76.92 (76.97); ZnO 18.74 (18.85); IR (cm<sup>-1</sup>): 3557-2527 (b), 1688 (s), 1585 (s), 1393 (s), 1283 (w), 1146 (w), 897 (w), 758 (w), 669 (w); Raman (cm<sup>-1</sup>): 3083, 1638 (s), 1587 (s), 1416 (w), 1382 (w), 1260 (s), 1159 (w), 1041 (s), 769 (s), 642 (w), 546 (w), 436 (w). UV-vis (in nm): 232, 282.

Compound **(1a)** prepared from the above reaction (0.431 g, 1 mmol) and piperazine (0.086 g, 1 mmol) were taken in distilled water (~15 mL). The volume of the reaction mixture was reduced to ~10 mL by heating it on a water bath and the clear solution thus obtained (pH 7) was kept undisturbed for crystallization at room temperature. The needle shaped transparent crystals obtained in four days were washed with ice cold water followed by methanol and dried in air to yield compound **(1)**, yield: 0.409 g (82%).

**(1)**: Anal. (%): Found (calcd) for  $\text{ZnC}_{20}\text{O}_9\text{N}_2\text{H}_{22}$  (499.83): C 48.12 (48.06); H 4.41 (4.45); N 5.59 (5.61); ptH<sub>2</sub> 66.4 (66.47); ZnO 16.38 (16.28); IR (cm<sup>-1</sup>): 3660 (s), 3427 (s), 3030-2220 (b), 1552 (s), 1400 (s), 1371(s), 1083 (s), 962 (w), 833 (w), 761(s), 706 (w), 650 (w), 613 (w), 586 (w), 459 (w). Raman (cm<sup>-1</sup>): 1591 (s), 1564 (w), 1406, 1373 (w), 1149 (s), 1041 (s), 839 (s), 653 (w), 482 (w); UV-DRS (in nm): 246, 274. DTA (in °C): 155 (endo), 347 (exo), 472 (exo).

For the XRD studies, intensity data for **(1)** were collected at room temperature on a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ). The data integration and reduction were carried out using SAINT-PLUS software<sup>49</sup>. The structure was solved with direct methods using SHELXS-97 and refinement was done against F<sup>2</sup> using SHELXL-97<sup>50</sup>. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms attached to the aromatic ring were introduced in the calculated positions and included in the refinement riding on their respective parent C atoms. One of the H atoms (H2W) attached to the lattice water molecule (OW) could not be located and was fixed in its idealized position with the aid of DFIX

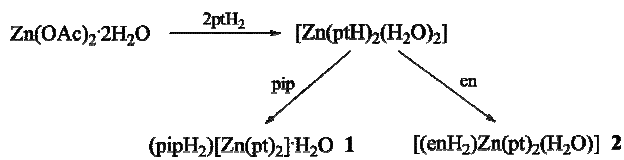
command. The data acquisition and selected crystal refinement data for **(1)** are summarised in Table 1.

## Results and discussion

The structure of  $[\text{Zn}(\text{ptH})_2(\text{H}_2\text{O})_2]$  (ptH=hydrogen phthalate), prepared by an aqueous reaction of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  with K(ptH) has been reported in the literature<sup>48</sup>. In this work we have employed a rational synthetic protocol, namely, a carboxylate exchange reaction for the synthesis of  $[\text{Zn}(\text{ptH})_2(\text{H}_2\text{O})_2]$  **(1a)**. Thus the reaction of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  with phthalic acid (ptH<sub>2</sub>) in 1:2 mole ratio afforded **(1a)** in high yield, to be used as a precursor for the synthesis of **(1)**. The reaction of **(1a)** with the cyclic diamine piperazine (pip) in 1:1 mole ratio resulted in the deprotonation of hydrogen phthalate leading to a high yield formation of a bis(phthalate)zincate(II) charge balanced by piperazinedium dication in **(1)** (Scheme 1). The generality of this methodology can be evidenced by the formation of  $[(\text{enH}_2)[\text{Zn}(\text{pt})_2](\text{H}_2\text{O})]$  **(2)** by use of ethylenediamine (en) in the above reaction instead of piperazine (See Supplementary data).

Table 1 — Crystal data and structure refinement for  $(\text{pipH}_2)[\text{Zn}(\text{pt})_2] \cdot \text{H}_2\text{O}$  **(1)**

Empirical formula	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>9</sub> Zn
Formula wt (g mol <sup>-1</sup> )	499.77
Temp. (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	8.142(3)
<i>b</i> (Å)	21.537(8)
<i>c</i> (Å)	11.782(5)
$\beta$ (°)	99.441(7)
Vol. (Å <sup>3</sup> )	2038.1(14)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (mg/m <sup>3</sup> )	1.629
Abs. coeff. (mm <sup>-1</sup> )	1.263
F(000)	1032
Crystal size (mm <sup>3</sup> )	0.16 x 0.14 x 0.12
$\theta$ range for data collection (°)	1.89 to 26.50
Index ranges	-10 ≤ <i>h</i> ≤ 10, -26 ≤ <i>k</i> ≤ 26, -14 ≤ <i>l</i> ≤ 14
Reflections collected/unique	20445/4201 (R(int) = 0.0698)
Completeness to $\theta = 26.50^\circ$	99.5 %
Abs. corr.	Multi scan
Max. and min. Transmission	0.859 and 0.817
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/ restraints/ parameters	4201/3/286
Goodness-of-fit on F <sup>2</sup>	0.981
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0412, wR2 = 0.1038
R indices (all data)	R1 = 0.0627, wR2 = 0.1107
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.616 and -0.481



Scheme 1

The high formation tendency of **(1)** (or **(2)**) can be evidenced by their facile isolation in a single pot reaction of  $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$  with  $\text{ptH}_2$  in the presence of pip (or en) in 1:2:1 mole ratio in aqueous medium (Supplementary data). It is interesting to note that irrespective of the order of mixing of these reagents, the product formed is always **(1)** (or **(2)**). Compound **(1)** can also be prepared by an aqueous reaction of  $(\text{pipH}_2)(\text{ptH})_2 \cdot 2\text{H}_2\text{O}^{51}$  with  $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$  at room temperature. The composition of the precursor compound  $[\text{Zn}(\text{ptH})_2(\text{H}_2\text{O})_2]$ , **(1)** and **(2)** was arrived at based on elemental analysis, ZnO formed on pyrolysis and weight loss studies.

The infrared spectra of  $[\text{Zn}(\text{ptH})_2(\text{H}_2\text{O})_2]$ , **(1)** and **(2)** exhibit several sharp signals in the mid-IR region indicating the presence of organic moieties (Supplementary data, Figs S1–S4). A strong signal at  $1688 \text{ cm}^{-1}$  in the free ligand ( $\text{ptH}_2$ ) is also observed in  $[\text{Zn}(\text{ptH})_2(\text{H}_2\text{O})_2]$ , indicating the presence of (free  $-\text{COOH}$  moiety) in the bis(hydrogen phthalate) compound. The absence of a signal in the region  $1680\text{--}1710 \text{ cm}^{-1}$  clearly indicates the formation of the fully deprotonated phthalate dianion in **(1)** or **(2)**. The intense band at  $1552 \text{ cm}^{-1}$  in the IR spectrum of **(1)** can be assigned for the asymmetric stretching vibration of the carboxylate group ( $\nu_{\text{asym}}$ ). Two bands are observed at  $1400$  and  $1371 \text{ cm}^{-1}$  respectively in the IR spectrum of **(1)**. Interestingly compound **(1)** exhibits two signals at  $1406$  and  $1373 \text{ cm}^{-1}$  in its Raman spectrum (Supplementary data, Fig. S3) with the former being more intense and assignable for symmetric stretching vibration ( $\nu_{\text{sym}}$ ) of the carboxylate group.

The UV-visible spectrum of the precursor compound  $[\text{Zn}(\text{ptH})_2(\text{H}_2\text{O})_2]$  in water was similar to that of free  $\text{ptH}_2$  spectrum, and can be attributed to the intra-ligand charge transfer of aromatic phthalate (Supplementary data, Fig. S5). The UV-DRS spectrum of **(1)** show bands at  $246$  and  $274 \text{ nm}$  while that of **(2)** at  $230$  and  $283 \text{ nm}$ , that can be attributed to intra-ligand charge transfer of aromatic phthalate (Supplementary data, Fig. S6). Compounds **(1a)**, **(1)** and **(2)** can be decomposed to ZnO by heating in a furnace at  $500 \text{ }^\circ\text{C}$ , which was confirmed from the featureless IR spectrum of the residues obtained on

pyrolysis (Supplementary data, Fig. S7). The phase purity of **(1)** was confirmed by a comparison of its experimental X-ray powder pattern with the theoretical pattern calculated from its single crystal data (Supplementary data, Fig. S8). Based on a combination of spectral data, weight loss study and elemental analytical data, compound **(2)** can be formulated as  $[(\text{enH}_2)\text{Zn}(\text{pt})_2(\text{H}_2\text{O})]$ .

Compound **(1)** exhibits an endothermic event with a peak in DTA at  $155 \text{ }^\circ\text{C}$  in its TG-DTA graph (Supplementary data, Fig. S9). The TG curve is parallel to the  $x$ -axis uptill  $150 \text{ }^\circ\text{C}$  and from  $150\text{--}200 \text{ }^\circ\text{C}$  a gradual decrease in mass by 3% equivalent to loss of one water molecule is observed. Above  $200 \text{ }^\circ\text{C}$ , the DTA curve shows only exothermic peaks at  $347 \text{ }^\circ\text{C}$  and  $470 \text{ }^\circ\text{C}$ , accompanied by a rapid drop in mass that can be attributed to decomposition of **(1)**. Although no detailed description of the thermal decomposition processes can be made, in view of the absence of mass spectral data of the emitted fragments, it is noted that the residual mass of 16.82% is in very good agreement for the formation of ZnO. The featureless IR spectrum of the residue and its matching powder pattern with ZnO provide evidence for the oxide phase. (Supplementary data, Fig. S10). The results of weight loss study at  $500 \text{ }^\circ\text{C}$  add credence to the TG-DTA data.

Compound **1** crystallises in the centrosymmetric monoclinic  $P2_1/c$  space group. Its crystal structure consists of an unique Zn(II) ion, two crystallographically independent phthalate ligands and a lattice water molecule, all of which are located in general positions, and two unique piperazinium ( $\text{pipH}_2$ )<sup>2+</sup> dications located on inversion centres (Fig. 1). In **(1)** both the unique

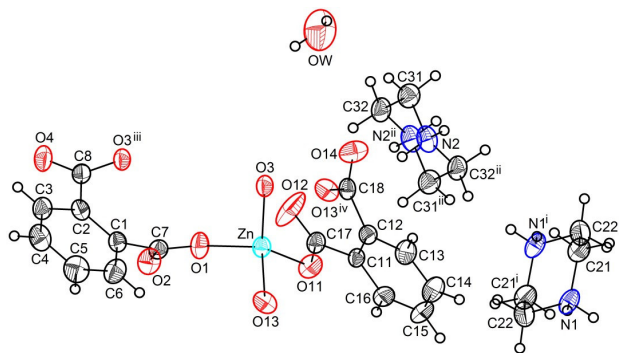


Fig. 1 – Crystal structure of  $(\text{pipH}_2)[\text{Zn}(\text{pt})_2] \cdot \text{H}_2\text{O}$  (**1**) showing the atom labelling scheme and the coordination sphere of Zn(II) in **(1)**. [Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as circles of arbitrary radius. Symmetry code:(i)  $2-x, 1-y, -z$ ; (ii)  $-x, 1-y, 1-z$ ; (iii)  $1-x, 1-y, 2-z$ ; (iv)  $-1+x, y, z$ ].

piperazines are diprotonated and adopt a chair conformation and their geometric parameters are in the normal range comparable with reported data<sup>52-61</sup> of piperazinedium cations (Supplementary data, Table S2).

The central metal is tetrahedrally coordinated to four oxygen atoms from four symmetry related phthalate anions. The Zn-O bond distances range from 1.953(2) to 1.992(6) Å while the O-Zn-O angles vary between 99.07(10) and 122.22(9)°, indicating a distorted {ZnO<sub>4</sub>} tetrahedron (Table 2). Both the unique phthalate ligands in the crystal

structure exhibit a  $\mu_2$ -bridging bidentate binding coordination mode with each of the -COO group in a ligand bonded to Zn(II) in a monodentate fashion (Supplementary data, Fig. S11). The first unique phthalate ligand (O11, O13) in each formula unit links two symmetry related Zn(II) ions via O11 and O13 atoms, resulting in the formation of an infinite chain extending along *a*-axis with a Zn···Zn separation of 8.142(3) Å. A pair of the second unique phthalate ligands (O1, O3) serve as a crosslink between two such infinite chains by bridging two symmetry related Zn(II) ions on either chain via the O1 and O3 atoms with a shorter Zn···Zn separation of 5.839(5) Å. The net result of the  $\mu_2$ -bridging bidentate binding modes of the unique pt ligands in (1) is the formation of a one-dimensional Zn(II) ladder (Fig. 2).

An analysis of the crystal structure of (1) reveals that the unique organic cations, the ladder complex anion and the lattice water are involved in three types of H-bonding interactions, viz., N-H···O, O-H···O and C-H···O (Table 3). All the uncoordinated

Table 2 — Selected bond lengths and angles for (pipH<sub>2</sub>)[Zn(pt)<sub>2</sub>]·H<sub>2</sub>O (1)

Bond lengths (Å)			
Zn-O(11)	1.953(2)	Zn-O(3)	1.968(2)
Zn-O(1)	1.965(2)	Zn-O(13)	1.992(2)
Bond angles (°)			
O(11)-Zn-O(1)	108.70(10)	O(11)-Zn-O(13)	99.07(10)
O(11)-Zn-O(3)	122.22(9)	O(1)-Zn-O(13)	110.13(9)
O(1)-Zn-O(3)	104.17(9)	O(3)-Zn-O(13)	112.38(9)

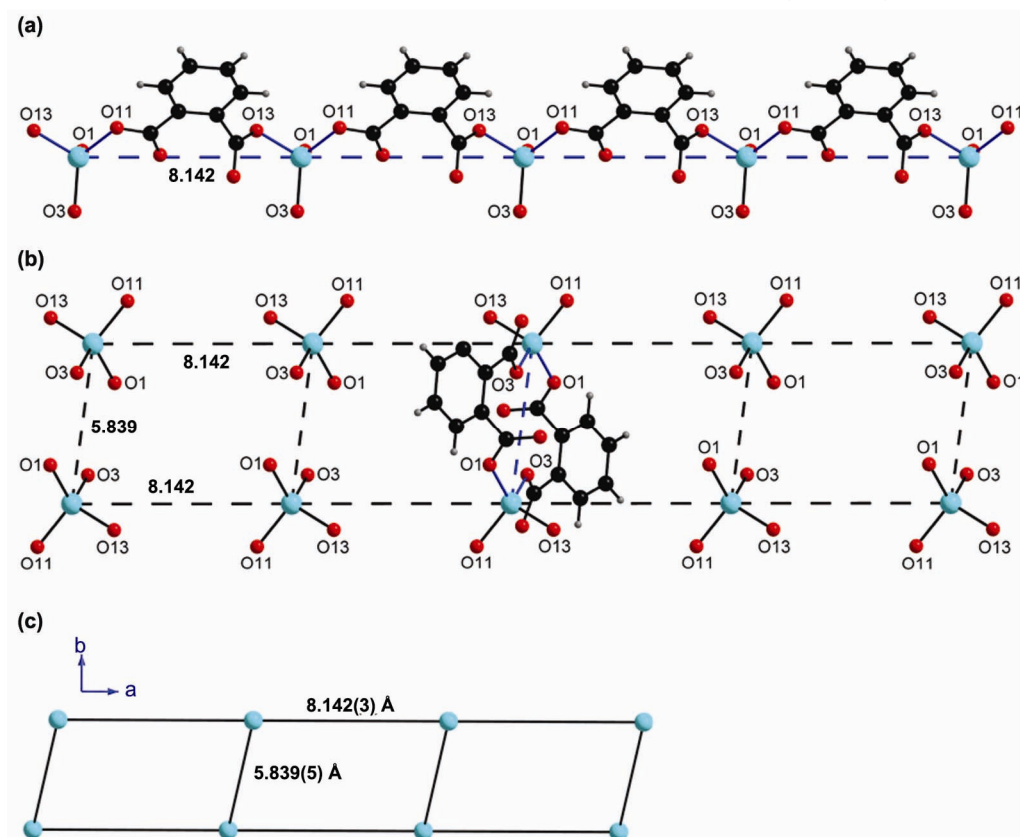


Fig. 2 – (a) A portion of the infinite chain extending along *a*-axis with Zn···Zn separation of 8.142 Å due to the bridging bidentate coordination mode of the first unique phthalate (O11, O13) ligand. (b) A pair of the second unique (O1, O3) ligands cross link two infinite chains with Zn···Zn separation of 5.839 Å. For clarity the crosslink is shown only for the middle Zn(II) ion in each chain. (c) A portion of the infinite Zn(II) ladder in (1) extending along *a*-axis. For clarity only the Zn(II) points in the ladder are shown.

O atoms of the unique phthalate ligands, viz., O2, O4, O12 and O14 function as H-acceptors and are linked to the unique cations via N-H...O interactions. Although both the unique organic cations exhibit only N-H...O and C-H...O interactions, (Supplementary data, Fig. S12) it is interesting to note that one unique cation (N2) is linked to the lattice water (OW) via a C31-H18B...OW (symmetry code  $x, y, z$ ) interaction, unlike the other cation (N1) which is linked to a phthalate oxygen by a C21-H9B...O3 (symmetry code  $x, y, z-1$ ) bond. As a result, the unique cations are differently disposed in the crystal structure, with the N1 cations located in the ladder cavity, and the N2 cations positioned on either side of a water decorated ladder in the crystallographic  $ac$  plane (Supplementary data, Fig. S13). The lattice water makes this structure more remarkable as each of the unique cations are lined by water molecules on either side. The OW-H2W...O2 (symmetry code  $-x+1, -y+1, -z+2$ ) interaction between the lattice water and the phthalate oxygen O2 organises the water molecules on either side of the ladder. The net effect of the C31-H18B...OW and OW-H2W...O2 interactions involving the N2 cation, lattice water and the phthalate oxygen is an assembly of a unique supramolecular architecture such that each layer of N2 cations or the ladder anion is on either side of the water layers, resulting in the following H-bonded sequence, i. e., water...cation...water...ladder...water and so on in the crystallographic  $ac$  plane (Fig. 3).

Table 3 — Hydrogen bonding geometry for (pipH<sub>2</sub>)[Zn(pt)<sub>2</sub>].H<sub>2</sub>O (1)

D-H...A	$d(D-H)$ (Å)	$d(H...A)$ (Å)	$d(D...A)$ (Å)	$\angle DHA$ (°)	Sym. code
N1-H12A...O2	0.900	1.828	2.645	149.83	$x, y, z-1$
N1-H11B...O12	0.900	1.843	2.676	152.97	$x+1, y, z-1$
N1-H11B...O14	0.900	2.554	3.162	125.44	$x, y, z-1$
N2-H15A...O14	0.900	1.744	2.627	166.44	$-x+1, -y+1, -z+1$
N2-H16B...O4	0.900	1.854	2.727	162.90	$x, y, z$
C21-H9B...O3	0.970	2.345	3.142	149.91	$x, y, z-1$
C31-H18B...OW	0.970	2.386	3.117	131.61	$x, y, z$

Table 4 — Zn...Zn distances in two related (bis( $\mu_2$ -phthalato)zincate(II) complexes

Comp.	Ligand binding mode	Space group	Dimensionality	Zn...Zn distance (Å)	Ref.
[Zn(ptH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Monodentate	$P2_1/c$	0-D	---	48
(1,3-pnH <sub>2</sub> )[Zn(pt) <sub>2</sub> ] <sup>a</sup>	$\mu_2$ -bidentate <sup>c</sup>	$Pbca$	1-D chain	5.453	17
(pipH <sub>2</sub> )[Zn(pt) <sub>2</sub> ].H <sub>2</sub> O <sup>b</sup>	$\mu_2$ -bidentate <sup>c</sup>	$P2_1/c$	1-D ladder	5.839(5) 8.142(3)	This work

<sup>a</sup>One unique cation; <sup>b</sup>Two crystallographically independent cations; <sup>c</sup>Two unique pt ligands.

The availability of structural details of several zinc-phthalates and also piperazinedium compounds (Supplementary data, Tables S3 and S4) permits a comparative study, the details of which are described herein. It is interesting to note that many structurally characterized zinc phthalates crystallize in the  $P2_1/c$  space group. A similar trend is also observed in the compounds containing the (pipH<sub>2</sub>) dication<sup>52-61</sup> (Supplementary data, Table S4), which is in line with the space group statistics reported in the Cambridge Database<sup>62</sup>. Although the coordination number of Zn in these compounds varies from 4 to 6, it is noted that tetracoordination is the most preferred geometry, which is also found in the title compound (1). An analysis of the binding modes of the phthalate reveals that the  $\mu_2$ -bridging bidentate coordination mode observed in (1) is the most preferred binding mode. In this context, it is interesting to note that in the closely related bis(phthalate) compound (1,3-pnH<sub>2</sub>)[Zn(pt)<sub>2</sub>] (1,3-pnH<sub>2</sub> = 1,3-propanediammonium)<sup>17</sup> (Table 4) containing the tetracoordinated Zn(II) ions are linked into an infinite chain with Zn...Zn separation of 5.453 Å (Supplementary data, Fig. S14). This contradictory behaviour can be attributed to the difference in structure directing ability of the organic cations, viz., the cyclic piperazinedium cation in (1) and the acyclic 1,3-pnH<sub>2</sub> dication in (1,3-pnH<sub>2</sub>)[Zn(pt)<sub>2</sub>]. Unlike (1) which contains two

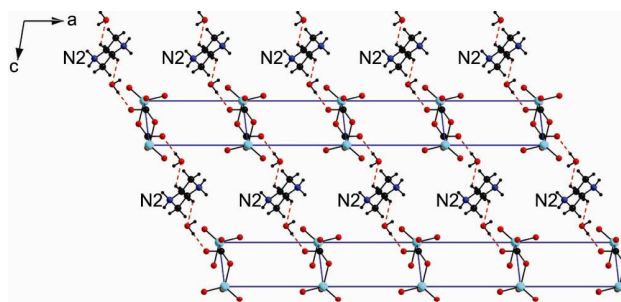


Fig. 3 — The supramolecular architecture of (pipH<sub>2</sub>)[Zn(pt)<sub>2</sub>].H<sub>2</sub>O (1) showing the sequence, i.e., water...cation...water...ladder...water and so on in the crystallographic  $ac$  plane. H-bonds are shown in red broken lines. [For clarity only the N2 cations are shown].

independent  $\text{pipH}_2$  dications and a lattice water in addition to the two unique pt ligands in the asymmetric unit, the crystal structure of  $(1,3\text{-pnH}_2)[\text{Zn}(\text{pt})_2]$  has an unique  $1,3\text{-pnH}_2$  dication but no lattice water due to which it is devoid of  $\text{O-H}\cdots\text{O}$  interactions. Compound (1) exhibits three varieties of H-bonds in its crystal structure, viz.,  $\text{N-H}\cdots\text{O}$ ,  $\text{C-H}\cdots\text{O}$  and  $\text{O-H}\cdots\text{O}$ . The presence of lattice water leads to more varieties of weak interactions (Supplementary data, Table S4) involving the H-donors and the O-acceptor of water, resulting in an aesthetic organization of the contents of the asymmetric unit as is observed in the title compound.

In summary it is shown that the bis(hydrogen phthalate) compound  $[\text{Zn}(\text{ptH})_2(\text{H}_2\text{O})_2]$  is a useful precursor for the preparation of new coordination polymers as demonstrated by the synthesis and structure characterization of the title compound.

### Supplementary data

Crystallographic data (excluding structure factors) for the structure of  $(\text{pipH}_2)[\text{Zn}(\text{pt})_2]\cdot\text{H}_2\text{O}$  (1) reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1418344. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk). Other supplementary data associated with this article, viz., Tables S1-S4 and Figs S1-S14 and details of synthesis of (1) and (2), are available in electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA\\_54A\(11\)1402-1408\\_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_54A(11)1402-1408_SupplData.pdf).

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### References

- Baca S G, Filippova I G, Gherco O A, Gdaniec M, Simonov Yu A, Gerbeleu N V, Franz P, Basler R & Decurtins S, *Inorg Chim Acta*, 357 (2004) 3419.
- Baca S G, Filippova I G, Gerbeleu N V, Simonov Yu A, Gdaniec M, Timco G A, Gherco O A & Malaestean Yu L, *Inorg Chim Acta*, 344 (2003) 109.
- Burke N J, Burrows A D, Donovan A S, Harrington R W, Mahon M F & Price C E, *Dalton Trans*, (2003) 3840.
- Baca S G, Simonov Y A, Gerbeleu N V, Gdaniec M, Bourosh P N & Timco G A, *Polyhedron*, 20 (2001) 831.
- Chen Y, Zhang J, Cheng J-K, Kang Y, Li Z-J & Yao Y-G, *Inorg Chem Commun*, 7 (2004) 1139.
- Hu T-L, Zou R-Q, Li J-R & Bu X-H, *Dalton Trans*, (2008) 1302.
- Huang F-P, Tian J-L, Chen G-J, Li D-D, Gu W, Liu X, Yan S-P, Liao D -Z & Cheng P, *Cryst Eng Comm*, 12 (2010) 1269.
- Li C-B, Li Y-W, Fang W, Liu B & Li D -O, *Acta Crystallogr E*, 62 (2006) m3541.
- Li R-X, Li S-X, Wu Q-Y, Liu G-Y & Liu F -Q, *Acta Crystallogr E*, 63 (2007) m2874.
- Thirumurugan A & Rao C N R, *J Mater Chem*, 25 (2005) 3852.
- Yao J, Huang W, Li B, Gou S & Xu Y, *Inorg Chem Commun*, 5 (2002) 711.
- Liang X, Weishaupl M, Parkinson J A, Parsons S, McGregor P A & Sadler P J, *Chem Eur J*, 9 (2003) 4709.
- Lu X, Chen Y-Y, Li P-Z, Bi Y-G, Yu C, Shi X-D & Chi Z -X, *J Coord Chem*, 63 (2010) 3923.
- Zhang S-C & Sun J, *Acta Crystallogr E*, 62 (2006) m3107.
- Zheng Y-Q, Zhang J & Liu J-Y, *Cryst Eng Comm*, 12 (2010) 2740.
- Cai H, Xiao Y-L, Guo Y & Li J-G, *Acta Crystallogr C*, 70 (2014) 722.
- Padmanabhan M, Joseph K C, Puranik V G, Huang & Li J, *Solid State Sci*, 9 (2007) 491.
- Burrows A D, Harrington R W, Mahon M F & Price C E, *J Chem Soc Dalton Trans*, (2000) 3845.
- Gong Y, Wang R, Yuan D, Su W, Huang Y, Yue C, Jiang F & Hong M, *Polyhedron*, 26 (2007) 5309.
- Liu Y-Y, Ma J-F, Yang J, Ma J-C & Ping G -J, *Cryst Eng Comm*, 10 (2008) 565.
- Wang X-L, Bi Y-F, Liu G-C, Lin H-Y, Hu T-L & Bu X -H, *Cryst Eng Comm*, 10 (2008) 349.
- Zhang W-L, Liu Y-Y, Ma J-F, Jiang H & Yang J, *Polyhedron*, 27 (2008) 3351.
- Zhou L, *Asian J Chem*, 24 (2012) 1415.
- Simonov Yu A, Baca S G, Filippova I G, Gdaniec M, Gherco O A & Gerbeleu N V, *Russian J Coord Chem*, 30 (2004) 727.
- Xiong W -L, Liu Q -Y, Zhang N & Wang L, *Acta crystallogr C*, 68 (2012) m235.
- Xu C, Guo Q, Wang X, Hou H & Fan Y, *Cryst Growth Des*, 11 (2011) 1869.
- Su Z, Xu J, Fan J, Liu D-J, Chu Q, Chen M-S, Chen S-S, Liu G-X, Wang X-F & Sun W-Y, *Cryst Growth Des*, 9 (2009) 2801.
- Li B, Li B, Zhu X, Lu X & Zhang Y, *J Coord Chem*, 57 (2004) 1361.
- Chen S-S, Fan J, Okamura T, Chen M-S, Su Z, Sun W-Y & Ueyama N, *Cryst Growth Des*, 10 (2010) 812.
- Xu J, Sun X, Yang L, Yan X, Bi C & Sun M, *Z Anorg Allg Chem*, 640 (2014) 236.
- Li J, Zhou J-H, Li Y-Z & Chen X-T, *Wuji Huaxue Xuebao*, 20 (2004) 841.
- Kan W-Q, Yang J, Liu Y-Y & Ma J-F, *Cryst Eng Comm*, 14 (2012) 6934.

- 33 Cheng P-C, Kuo P-T, Liao Y-H & Xie M-Y, Hsu W & Chen J-D, *Cryst Growth Des*, 13 (2013) 623.
- 34 Singh N & Anantharaman G, *Cryst Eng Comm*, 16 (2014) 7914.
- 35 Liu B, *J Inorg Organomet Polym Mater*, 24 (2014) 536.
- 36 Li Y-W, Ma H, Chen Y-Q, He K-H, Li Z-X & Bu X-H, *Cryst Growth Des*, 12 (2012) 189.
- 37 Zhang M-D, Qin L, Yang H-T, Li Y-Z, Guo Z-J & Zheng H-G, *Cryst Growth Des*, 13 (2013) 1961.
- 38 Zhao N, Deng Y-E, Liu P, An C-X, Wang T-X & Lian Z-X, *Polyhedron*, 85 (2015) 607.
- 39 Wang X-L, Chen B-K, Lin H-Y, Bi Y-F & Liu G-C, *J Chem Crystallogr*, 38 (2008) 339.
- 40 Zhu H-L, Lin J-L, Xu W, Zhang J & Zheng Y-Q, *J Coord Chem*, 64 (2011) 2088.
- 41 Chen Q-L, Chen H-B & Zhou Z-H, *J Mol Struct*, 1035 (2013) 198.
- 42 Song Y-S, Yan B & Chen Z-X, *Appl Organomet Chem*, 20 (2006) 44.
- 43 Mu Y-J, Ma X-L, Han B, Qin G-F, Niu Y-Y & Lü H-X, *Polyhedron*, 67 (2014) 44.
- 44 Liu Y-Y, Liu H-Y, Ma J-F, Yang Y & Yang J, *Cryst Eng Comm*, 15 (2013) 1897.
- 45 Bai H-Y, Ma J-F, Yang J, Zhang L-P, Ma J-C & Liu Y-Y, *Crystal Growth Des*, 10 (2010) 1946.
- 46 Li R-X, Wu Q-Y & Liu F-Q, *Acta Crystallogr E*, 66 (2010) m258.
- 47 Tao Z-L, Cui J-H, Qin L & Zheng H-G, *Wuji Huaxue Xuebao*, 28 (2012) 2633.
- 48 Wen W, Jimin X, Xuan Y & Yuan N, *Anal Sci*, 23 (2007) x241.
- 49 SMART V5.630, SAINT-PLUS V6.45 and SADABS, (Bruker-Nonius Analytical X-ray Systems Inc., Madison, Wisconsin, USA) 2003.
- 50 Sheldrick G M, *Acta Crystallogr A*, 64 (2008) 112.
- 51 Jin Z M, Pan Y J, He Ling, Li Z G & Yu K B, *Anal Sci*, 19 (2003) 333.
- 52 Srinivasan B R, Dhuri S N, Poisot M, Näther C & Bensch W, *Z Naturforsch*, 59b (2005) 1083.
- 53 Srinivasan B R, Dhuri S N, Poisot M, Näther C & Bensch W, *Z Anorg Allg Chem*, 631 (2005) 1087.
- 54 Srinivasan B R, Näther C & Bensch W, *Acta Crystallogr E*, 59 (2003) m639.
- 55 Srinivasan B R, Naik A R, Näther C & Bensch W, *Acta Crystallogr E*, 60 (2004) m1384.
- 56 Qui D T & Palacios E, *Acta Crystallogr C*, 46 (1990) 1212.
- 57 Havlíček D, Plocek J, Němec I, Gyepes R & Mička Z, *J Solid State Chem*, 150 (2000) 305.
- 58 Jayaraman K, Choudhory A & Rao C N R, *Solid State Sci*, 4 (2002) 413.
- 59 Srinivasan B R, Naik A R, Dhuri S N, Näther C & Bensch W, *J Chem Sci*, 123 (2011) 55.
- 60 Ishira H, Horiuchi K, Svoboda I, Fuess H, Gesing T M, Buhl J C & Terao H, *Z Naturforsch*, 61b (2006) 69.
- 61 Ishira H, Horiuchi K, Gesing T M, Dou S, Buhl J C & Erk P, *Z Naturforsch*, 57b (2002) 503.
- 62 For space group statistics see <http://www.ccdc.cam.ac.uk/products/csd/statistics/>.