



# Structural architectures of charge-assisted, hydrogen-bonded, 2D layered amine···tetrakisphosphonate and zinc···tetrakisphosphonate ionic materials

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This paper is dedicated to Dr. Aris Terzis, a pioneer crystallographer in Greece, on the occasion of his retirement.

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## ABSTRACT

The synthesis, characterization and structural analyses of ionic amine-phosphonate and hydrated metal ion-phosphonate compounds are reported. These are (en)(HDTMP), (NH<sub>4</sub>)(EDTMP), Zn(H<sub>2</sub>O)<sub>6</sub>(TDTMP) (en = ethylenediamine, HDTMP = hexamethylenediamine-*tetrakis*(methylenephosphonate), EDTMP = diethylenediamine-*tetrakis*(methylenephosphonate), TDTMP = tetramethylenediamine-*tetrakis*(methylenephosphonate)). All three compounds are composed of discrete anions and cations, stabilized by intricate networks of hydrogen bonds, and form 2D layered architectures.

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## 1. Introduction

Crystal engineering has become a rich research field in the last decade [1]. Researchers in the field aim for materials with desired properties that can be synthesized by design. A significant part of this field is inorganic–organic hybrid materials (a.k.a. metal organic frameworks, MOF's) [2]. These are based on coordination bonds between a polyfunctional ligand and a metal center or metal cluster. 1D, 2D and 3D architectures have appeared in the literature [3]. A less developed, but still promising area is that of organic–organic hybrids, where the metal part of the framework is absent and has been replaced with an organic cation [4]. Such compounds are not formed by cooperative bonds, but by simple ionic and/or hydrogen bond interactions [5].

Among the battery of anionic ligands available polycarboxylates are predominant [6]. Polyphosphonates have also attracted significant interest [7], because they exhibit a number of similarities, but also differences to the carboxylates: (a) Phosphonate building blocks possess three O atoms linked to the phosphorus atom in the coordinating moiety, compared to two O atoms in the case of carboxylates. This increases the possibilities for access to novel structures. (b) The phosphonic acid moiety can be doubly deprotonated in two well-defined successive steps, depending on solution

pH [8]. Carboxylic acid ligands can only be deprotonated once, see Fig. 1. Again, this allows access to a variety of potential novel phosphonate-containing structures, by simply varying the pH. (c) The phosphonate group can be (potentially) doubly esterified (in contrast to the carboxylate group that can only be monoesterified) [9]. Introduction of at least one phosphonate ester in the building block is expected to enhance solubility (in the case of very insoluble materials), or by virtue of its hydrolysis, to yield structural diversity in the end material. (d) Synthesis of metal phosphonate materials can be carried out via a number of different routes that do not necessarily give products with the same structure. There is hence a greater potential of structural diversity in the products derived. Several of these methods lend themselves to a combinatorial approach allowing high-throughput screening of candidate materials to be achieved [10].

Hydrogen bonding is a key player in self-assembly in phosphonate-containing materials due to presence of protonated phosphonate moieties (donors), deprotonated phosphonate groups (acceptors) and water (donor and/or acceptor, as most syntheses are carried out in water) [11]. The work of Clearfield et al. in this area has dealt with interaction of triphosphonates (such as nitrilo-*tris*(methylenephosphonate), 1,3,5-benzene-*tris*(phosphonic acid)) with organic amines (such as 2,2'-bipyridine, 4,4'-bipyridine, 1,7-phenanthroline, 1,10-phenanthroline, acridine, and tripropylamine) [12]. The combination of such reactants leads to self-complementary 3D hexagonal architectures that are stabilized by very strong ionic hydrogen bonds. Hydrogen bonds are also predominant in the structures of “free” phosphonic acids [13].

Our group has been active in the area of phosphonate chemistry, particularly in metal phosphonate materials [14]. In this paper

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three phosphonate ligands containing four phosphonate moieties have been studied for their ability to form ionic compounds with non-metal cations, ethylenediammonium ( $\text{en}^{2+}$ ), ammonium ( $\text{NH}_4^+$ ), and the  $\text{Zn}(\text{H}_2\text{O})_6^{2+}$  ion that forms *in situ*. Schematic structures are shown in Fig. 2. These three tetraphosphonate ligands all have the same coordinating moieties (two amino-bis(methylenephosphonate) groups), but they are linked by two (EDTMP), four (TDTMP) and six (HDTMP) methylene chains. All three phosphonates are zwitter-ionic (each phosphonate group is monodeprotonated and the N atoms are protonated). The ligand charge is “2–”, therefore it requires a “2+” charge balancing cation(s) for electroneutrality.

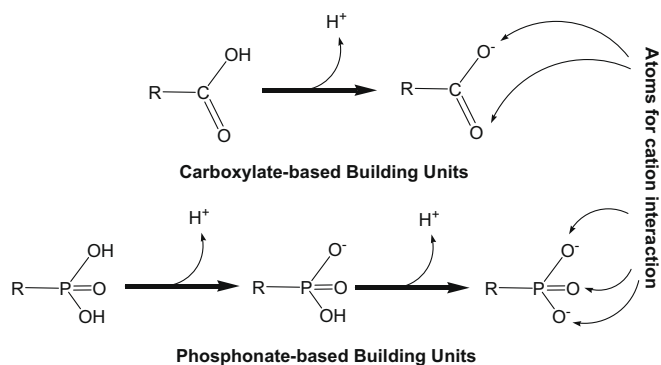


Fig. 1. Structural and functional differences between carboxylic and phosphonic acids.

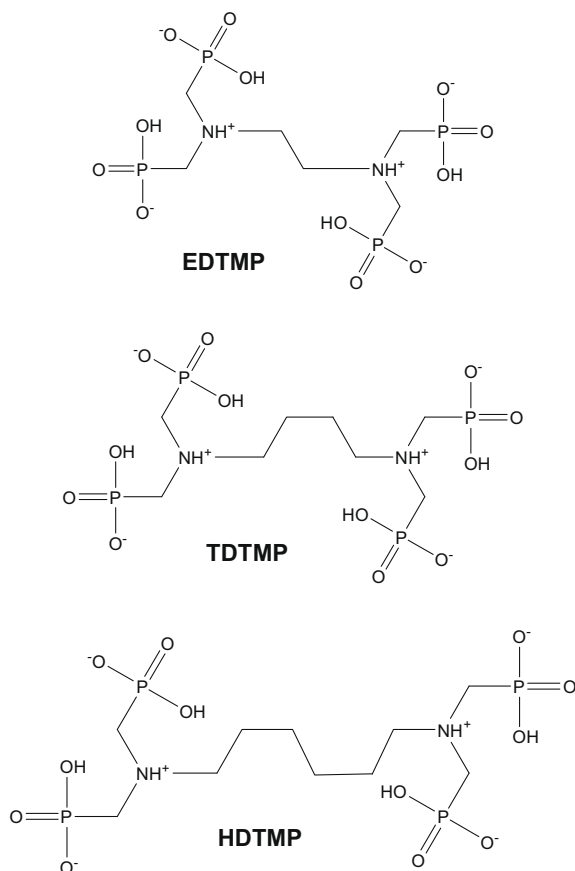


Fig. 2. The three tetraphosphonates (EDTMP, TDTMP and HDTMP) used in this paper in their zwitter-ionic form and an overall ligand charge “2–”.

## 2. Experimental

### 2.1. Materials

All water-soluble metal salts were commercial samples and were used without further purification. Ethylenediamine was from Fluka. Phosphonic acids (EDTMP, TDTMP and HDTMP) were from Solutia Inc. Stock solutions of HCl and NaOH were used for pH adjustments. In-house, deionized (DI) water was used for all syntheses.

### 2.2. Syntheses

#### 2.2.1. $(\text{en})(\text{HDTMP})\cdot 2\text{H}_2\text{O}$

The material  $(\text{en})(\text{HDTMP})\cdot 2\text{H}_2\text{O}$  was obtained from our attempts to synthesize Zn-HDTMP materials. The  $\text{Zn}^{2+}$  ion was not incorporated into the final product.  $(\text{en})(\text{HDTMP})\cdot 2\text{H}_2\text{O}$  can be synthesized according to the procedure below, without the Zn salt. A quantity of acid HDTMP (1.230 g, 2.5 mmol) is suspended in 40 mL DI water and mixed with 1.2 mL ethylenediamine (neat). The pH is adjusted to 2.0 by addition of HCl stock solution. Then a quantity of  $\text{ZnCl}_2\cdot 6\text{H}_2\text{O}$  is added (0.204 g, 1.5 mmol) under rigorous stirring. Final pH adjustment was done to 2.5. At this point a clear colorless solution forms. This solution is left under quiescent conditions at room temperature. After 2 days colorless crystals appear. They are isolated by filtration, washed with DI water and air-dried. Yield ~40%. Yields can be increased by prolonged crystallization times.

#### 2.2.2. $(\text{NH}_4)_2(\text{EDTMP})$

The material  $(\text{NH}_4)_2(\text{EDTMP})$  was obtained from our attempts to synthesize Zn-EDTMP materials. The  $\text{Zn}^{2+}$  ion was not incorporated into the final product.  $(\text{NH}_4)_2(\text{EDTMP})$  can be synthesized according to the procedure below, without the Zn salt. A quantity of acid EDTMP (0.947 g, 2.00 mmol) is suspended in 40 mL DI water. Sufficient quantity of a stock solution of  $\text{NH}_4\text{OH}$  is added until the solid dissolved. The pH is adjusted to 2.0 by addition of a stock solution of HCl. Then  $\text{ZnCl}_2\cdot 6\text{H}_2\text{O}$  is added (0.270 g, 2.00 mmol) under vigorous stirring and the final pH is adjusted to 1.8. The clear colorless solution is left undisturbed for 3 days, during which a white crystalline precipitate appears. It is filtered, washed with DI water and left to dry at room temperature. Yield ~60%.

#### 2.2.3. $\text{Zn}(\text{H}_2\text{O})_6\cdot(\text{TDTMP})$

A mixture of TDTMP and  $\text{ZnCl}_2$  with a molar ratio of 1:1 was prepared in water at room temperature, as follows: 1 mmol (0.450 g) of solid TDTMP was dissolved in water (25 mL) with addition of NaOH until it completely dissolved. The pH was then adjusted to 2.0 by addition of HCl. Then, 1 mmol (0.136 g) of  $\text{ZnCl}_2$  was gradually added under constant stirring. The pH of the final solution was adjusted to 2.2. After several days single crystals of the final compound appeared. The crystals were collected by filtration and dried in air. Yield ~70%.

### 2.3. Single crystal determinations

X-ray diffraction data were collected on a SMART 1K CCD diffractometer at 298(2) K with Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ). Data were corrected for absorption using the empirical method employed in Sortav [15]. All structures were subsequently refined by full-matrix least squares refinement on F2 (SHELXL97) [16]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either located in the difference Fourier map or placed geometrically. Subsequent refinement of the thermal parameters was carried out isotropically in all cases. CCDC reference numbers:  $(\text{en})(\text{HDTMP})\cdot 2\text{H}_2\text{O}$  CCDC-651135;  $(\text{NH}_4)_2(\text{EDTMP})$  CCDC-625197;  $\text{Zn}(\text{H}_2\text{O})_6\cdot(\text{TDTMP})$  CCDC-287045. Copies of the data may be obtained free of charge from the CCDC, e-mail: deposit@ccdc.cam.ac.uk or www: <http://www/ccdc/cam/ac/uk>.

Crystallographic details and selected bond distances and angles are given in Tables 1–4.

#### 2.4. Sample characterization

FT-IR spectra were recorded on a FT-IR Perkin–Elmer FT 1760. ATR-IR spectra were collected on a Thermo-Electron NICOLET 6700 FTIR optical spectrometer.

### 3. Results and discussion

All three crystalline materials described herein share a common structural feature. They are layered compounds. The layered structure is composed of anionic phosphonate layers and charge-balancing cations, see Fig. 3. These layers are held together by complicated networks of hydrogen bonds. Waters of crystallization are found only in the structure of (en)(HDTMP)·2H<sub>2</sub>O.

Metric features within the tetraphosphonate backbone are trivial and close to values reported in the literature [17]. The P–O bond distances are in the range 1.444–1.591 Å, typical for organophosphonates [18]. However, upon closer examination of the P–O bond lengths it becomes evident that they are separated into two categories, the “short” and the “long” bonds. All “long” bonds are associated with the protonated –P–OH moiety, whereas the “short bonds” are from the non-protonated portion of the –PO<sub>3</sub> moiety. Distinction between the P=O and the P–O– bond lengths is not possible because these are of equivalent length, based on the crystallography results. Therefore, this leads to the conclusion that the negative charge is delocalized over the O=P–O– moiety. Similar observations have been noted for metal-coordinated (and mono-deprotonated) phosphonates [19].

#### 3.1. Crystal structure of (en)(HDTMP)·2H<sub>2</sub>O

There are discrete HDTMP<sup>2-</sup> dianions and en<sup>2+</sup> dications in the structure of (en)(HDTMP)·2H<sub>2</sub>O, see Fig. 4 (upper). The presence of waters of crystallization, HDTMP<sup>2-</sup> dianions and en<sup>2+</sup> dications leads to a complicated network of hydrogen bonds, finally yielding a 2D layered structure, see Fig. 4 (lower). They are described in de-

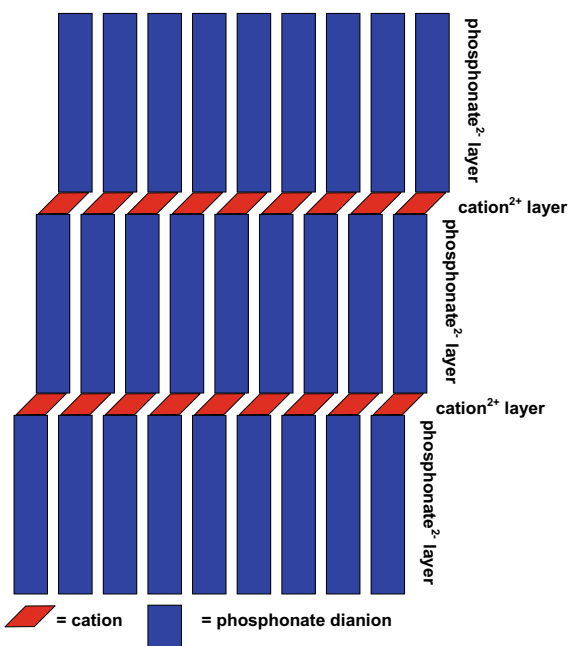


Fig. 3. The common structural feature in the three materials described herein. The cation and anion layers are assembled by hydrogen bonds.

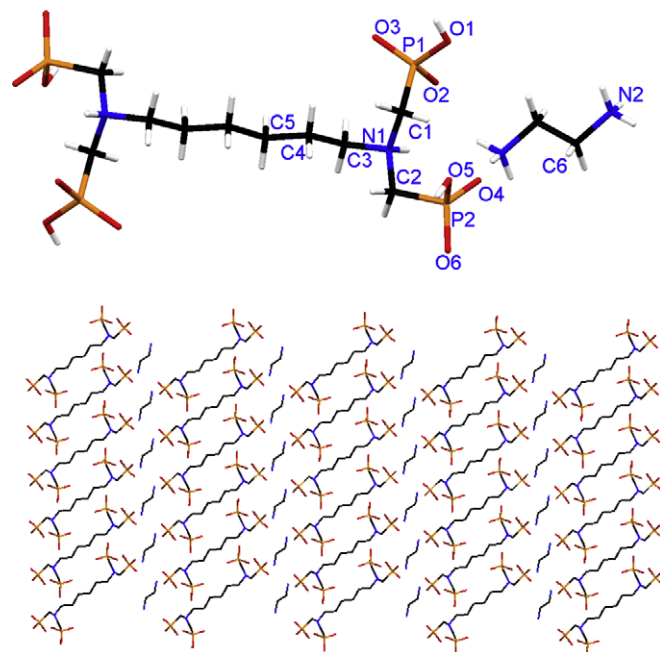


Fig. 4. Structure of HDTMP<sup>2-</sup> with the en<sup>2+</sup> dications (upper, the water molecules are omitted for clarity). Layers of HDTMP<sup>2-</sup> and en<sup>2+</sup> dications (lower) down the *b*-axis.

tail below. The –NH<sub>3</sub><sup>+</sup> portion of the en molecule is hydrogen-bonded with one of the two water molecules of crystallization O(8) (2.974 Å), and with three O–P moieties (all from different phosphonate groups) (2.708, 2.804 and 2.984 Å).

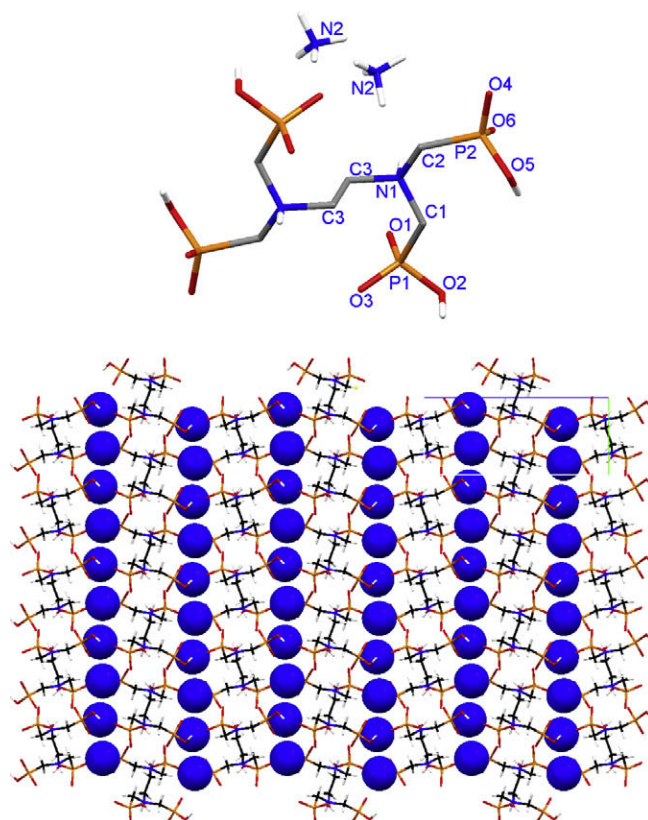


Fig. 5. Structure of EDTMP<sup>2-</sup> with the two NH<sub>4</sub><sup>+</sup> cations (upper). Layers of EDTMP<sup>2-</sup> and NH<sub>4</sub><sup>+</sup> cations, shown as blue spheres (lower) down the *a*-axis.

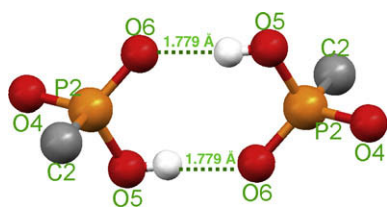


Fig. 6. Structure of the hydrogen-bonded dimer in the structure of  $(\text{NH}_4)_2(\text{EDTMP})$ .

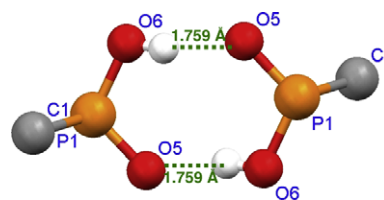


Fig. 9. Structure of the hydrogen-bonded dimer in the structure of  $\text{Zn}(\text{H}_2\text{O})_6(\text{TDTMP})$ .

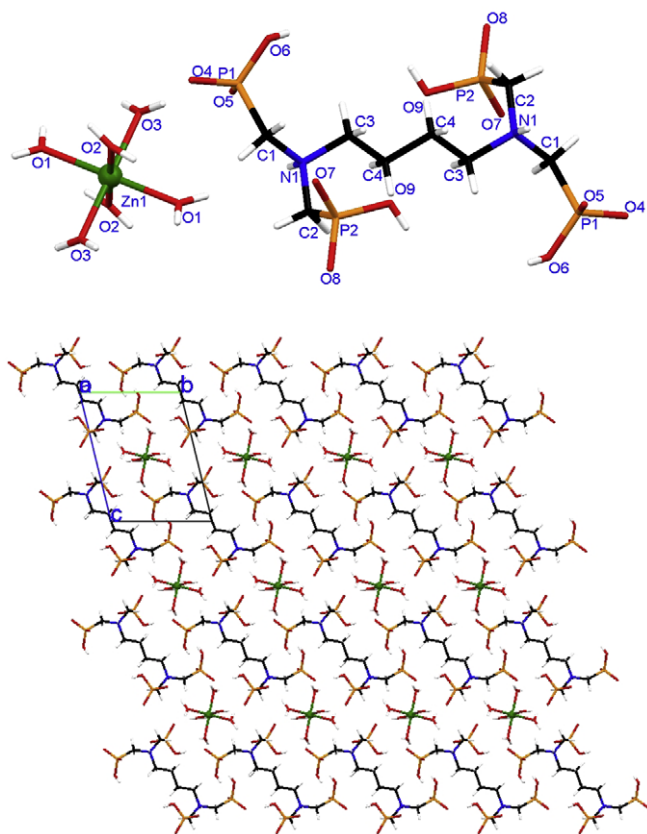


Fig. 7. Structure of  $\text{TDTMP}^{2-}$  dianion with the  $\text{Zn}(\text{H}_2\text{O})_6^{2+}$  dication (upper). Layers of  $\text{TDTMP}^{2-}$  and  $\text{Zn}(\text{H}_2\text{O})_6^{2+}$  dications down the  $a$ -axis (lower).

The two waters of crystallization are located in the vicinity of the  $\text{en}^{2+}$  dication. One water molecule (O(8)) forms hydrogen bonds with the  $\text{N}(1)\text{--H}^+$  moiety (2.963 Å), with the  $^+\text{H}_3\text{N}(2)$  group of the  $\text{en}^{2+}$  cation (2.974 Å), and with the O(4) from a deprotonated phosphonate ligand,  $\text{--O--P}$  (2.999 Å). The second water molecule (O(7)) participates in three hydrogen bonds, one with a  $\text{--P--O}(1)\text{H}$  group (2.553 Å), and two hydrogen bonds with two deprotonated  $\text{P--O}(3)^-$  moieties (2.729 and 2.743 Å) from neighboring phosphonate ligands.

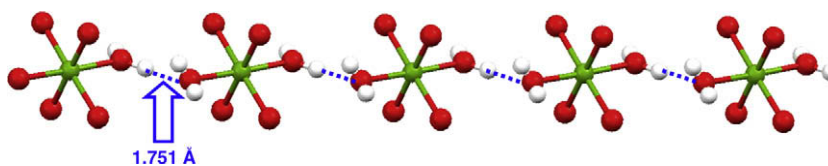


Fig. 8.  $\text{Zn}(\text{H}_2\text{O})_6^{2+}$  dications (part of the "inorganic layer") linked by hydrogen bonds.

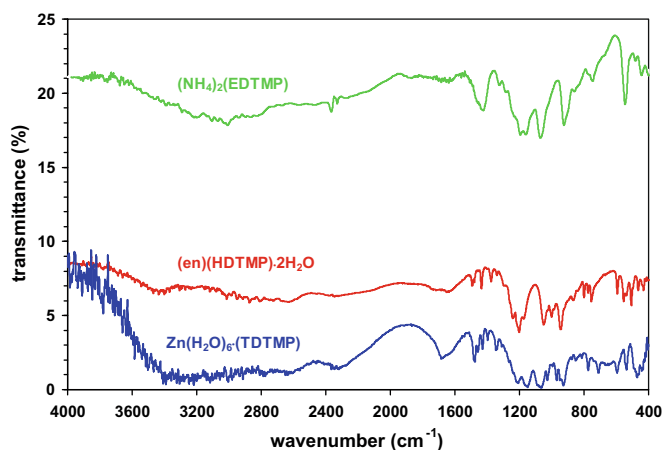


Fig. 10. FT-IR spectra of compounds  $(\text{en})(\text{HDTMP})\cdot 2\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2(\text{EDTMP})$ , and  $\text{Zn}(\text{H}_2\text{O})_6(\text{TDTMP})$ .

The  $\text{P}(1)\text{O}_3\text{H}^-$  phosphonate participates in four hydrogen bonds.  $\text{P--O}(1)$  connects to a water molecule O(7) (2.553 Å).  $\text{P--O}(3)$  forms two hydrogen bonds with two symmetry-related water molecules O(7) (2.743 and 2.729 Å). Finally,  $\text{P--O}(2)$  is only hydrogen bonded to protonated  $\text{H--O}(5)\text{P}(2)$  (2.533 Å).

The  $\text{P}(2)\text{O}_3\text{H}^-$  phosphonate group takes part in five hydrogen bonds. Protonated  $\text{P--O}(5)$  connects to a  $\text{P--O}(6)$  group from a neighboring phosphonate (2.533 Å).  $\text{P--O}(4)$  H-bonds to a water molecule O(8) (2.999 Å) and to a protonated N(2) from en (2.804 Å). Finally,  $\text{P--O}(6)$  interacts with two protonated N(2) groups from two different en molecules (2.708 and 2.984 Å).

### 3.2. Crystal structure of $(\text{NH}_4)_2(\text{EDTMP})$

There are discrete  $\text{EDTMP}^{2-}$  dianions and  $\text{NH}_4^+$  cations in the structure of  $(\text{NH}_4)_2(\text{EDTMP})$ , see Fig. 5 (upper). The presence of  $\text{EDTMP}^{2-}$  dianions and  $\text{NH}_4^+$  cations leads to a complicated network of hydrogen bonds, finally yielding a 2D layered structure, see Fig. 5 (lower). They are described in detail below.

Each of the ammonium cations participates in five hydrogen bonds, all with non-protonated  $\text{P--O}$  groups from different phosphonate ligands: with O(3) $\text{--P}(1)$  (2.895 Å), with O(2) $\text{--P}(1)$  (2.929 Å), with O(4) $\text{--P}(2)$  (2.949 Å), with O(3) $\text{--P}(1)$  (2.799 Å) and with O(6) $\text{--P}(1)$  (2.820 Å).

The P(1)O<sub>3</sub>H<sup>-</sup> phosphonate group participates in five hydrogen bonds. Protonated P–O(2)H participates in a hydrogen bond with the ammonium N(2) group of the NH<sub>4</sub><sup>+</sup> cation (2.929 Å) and the non-protonated group O(4)–P(2) from a neighboring phosphonate (2.559 Å). The group P–O(1) forms only one H-bond with the protonated N(1)H<sup>+</sup> group belonging to another EDTMP molecule (2.648 Å). Finally, P–O(3) forms two H-bonds with two symmetry-related N(2) groups from two different en molecules (2.799 and 2.895 Å).

The P(2)O<sub>3</sub>H<sup>-</sup> phosphonate group also participates in five hydrogen bonds. Protonated P–O(5)H participates in a hydrogen bond with the non-protonated P(2)–O(6) group from a neighboring phosphonate. At the same time non-protonated P(2)–O(6) hydrogen bonds with the protonated P(2)–O(5)–H moiety with the same phosphonate group. This creates a hydrogen-bonded dimer, the structure of which is shown in Fig. 6. A similar phosphonate hydrogen-bonded dimer has been observed in the structure of 2-phosphonobutane-1,2,4-tricarboxylic acid monohydrate (PBTC·H<sub>2</sub>O) [20].

**Table 1**  
Crystallographic data for (en)(HDTMP)·2H<sub>2</sub>O, (NH<sub>4</sub>)<sub>2</sub>(EDTMP) and Zn(H<sub>2</sub>O)<sub>6</sub>(TDTMP).

Material	(en)(HDTMP)·2H <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> (EDTMP)	Zn(H <sub>2</sub> O) <sub>6</sub> (TDTMP)
Empirical formula	C <sub>6</sub> H <sub>22</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub>	C <sub>6</sub> H <sub>26</sub> N <sub>4</sub> O <sub>12</sub> P <sub>4</sub>	C <sub>8</sub> H <sub>34</sub> N <sub>2</sub> O <sub>18</sub> P <sub>4</sub> Zn
Formula weight	312.20	470.19	621.65
Space group	P $\bar{1}$	P2 <sub>1</sub> /c	P $\bar{1}$
<i>a</i> (Å)	6.195(1)	8.012(2)	5.8905(8)
<i>b</i> (Å)	7.489(1)	6.8313(9)	8.990(1)
<i>c</i> (Å)	15.955(3)	16.526(2)	11.817(2)
$\alpha$ (°)	84.472(3)	90	73.506(2)
$\beta$ (°)	85.319(3)	98.76(1)	76.200(2)
$\gamma$ (°)	67.881(3)	90	75.428(2)
<i>V</i> (Å <sup>3</sup> )	681.7(2)	893.9(2)	571.2(1)
<i>Z</i>	2	2	1
<i>T</i> (K)	293(2)	293(2)	293(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.521	1.747	1.807
$\mu$ (mm <sup>-1</sup> )	0.352	0.491	1.442
Meas./Unique/Obs. Refl.	3616/2746/2176	5524/1982/1794	2771/1641/1462
Parameters	161	138	154
<i>R</i> <sub>int</sub>	0.0185	0.0224	0.0108
<i>R</i> <sub>1</sub> [ <i>R</i> <sub>1</sub> ( <i>F</i> <sub>o</sub> ) <sub>all</sub> ]	0.0547 [0.0683]	0.0341 [0.0385]	0.0292 [0.0338]
<i>wR</i> <sub>2</sub> [ <i>wR</i> <sub>2</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sub>all</sub> ]	0.1560 [0.1633]	0.0935 [0.0961]	0.0753 [0.0777]
GoF	1.076	1.146	1.061

**Table 2**  
Bond lengths [Å] and angles [°] for (en)(HDTMP)·2H<sub>2</sub>O.<sup>a</sup>

Bonds	Angles				
C(1)–N(1)	1.488(4)	N(1)–C(1)–P(1)	112.84(19)	O(2)–P(1)–O(1)	109.71(15)
C(1)–P(1)	1.825(3)	N(1)–C(2)–P(2)	114.5(2)	O(3)–P(1)–C(1)	111.02(15)
C(2)–N(1)	1.504(4)	C(4)–C(3)–N(1)	114.9(2)	O(2)–P(1)–C(1)	103.54(14)
C(2)–P(2)	1.830(3)	C(3)–C(4)–C(5)	109.8(2)	O(1)–P(1)–C(1)	101.68(13)
C(3)–C(4)	1.510(4)	C(5)#1–C(5)–C(4)	112.7(3)	O(4)–P(2)–O(6)	120.82(16)
C(3)–N(1)	1.521(4)	N(2)–C(6)–C(6)#2	109.4(3)	O(4)–P(2)–O(5)	106.58(14)
C(4)–C(5)	1.526(4)	C(1)–N(1)–C(2)	113.2(2)	O(6)–P(2)–O(5)	110.12(13)
C(5)–C(5)#1	1.519(6)	C(1)–N(1)–C(3)	113.1(2)	O(4)–P(2)–C(2)	108.03(14)
C(6)–N(2)	1.486(4)	C(2)–N(1)–C(3)	111.5(2)	O(6)–P(2)–C(2)	104.70(14)
C(6)–C(6)#2	1.505(6)	O(3)–P(1)–O(2)	118.24(15)	O(5)–P(2)–C(2)	105.65(15)
N(1)–H(5)	0.91(4)	O(3)–P(1)–O(1)	111.15(14)		
O(1)–P(1)	1.565(2)				
O(2)–P(1)	1.498(2)				
O(3)–P(1)	1.489(3)				
O(4)–P(2)	1.492(3)				
O(5)–P(2)	1.572(2)				
O(6)–P(2)	1.497(2)				

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1  $-x+3, -y, -z$  #2  $-x+1, -y+1, -z+1$ .

### 3.3. Crystal structure of Zn(H<sub>2</sub>O)<sub>6</sub>(TDTMP)

There are discrete TDTMP<sup>2-</sup> dianions and Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> dications in the structure of Zn(H<sub>2</sub>O)<sub>6</sub>(TDTMP), see Fig. 7 (upper). This result is somewhat surprising because reaction of Zn<sup>2+</sup> with HDTMP in similar conditions yields a Zn-HDTMP inorganic organic hybrid [17a]. At present we have no satisfactory explanation for this. One can link this absence of TDTMP coordination to Zn<sup>2+</sup> to a reduced basicity of the phosphonate oxygens. The metric features of the Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> octahedron are expected and comparable to those of [Zn(H<sub>2</sub>O)<sub>6</sub>](triflate)<sub>2</sub> [21] and a Zn<sub>6</sub> cluster with the ligand N-(phosphonomethyl)-N-methylglycine containing non-coordinated Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> dications in the lattice [22]. Also, an Mg ionic material containing non-coordinating aminoethylphosphonate has been reported that contains Mg(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> dications in the lattice [23]. The presence of TDTMP<sup>2-</sup> dianions and Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> dications (there are no waters of crystallization in the structure) leads to an intricate network of hydrogen bonds, finally yielding a 2D layered structure, see Fig. 7 (lower). They are described in detail below.

The Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> dication participates in a total of fourteen hydrogen bonds. Two of them (O···O 2.733 Å) are with neighboring Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> dication, thus creating a one-dimensional ‘wire’, as part

**Table 3**  
Bond lengths [Å] and angles [°] for (NH<sub>4</sub>)<sub>2</sub>(EDTMP).<sup>a</sup>

Bonds	Angles		
C(1)–N(1)	1.500(2)	N(1)–C(1)–P(1)	114.65(12)
C(1)–P(1)	1.8279(19)	N(1)–C(2)–P(2)	116.25(12)
C(2)–N(1)	1.501(2)	N(1)–C(3)–C(3)#1	112.59(17)
C(2)–P(2)	1.8287(19)	C(1)–N(1)–C(2)	111.81(14)
C(3)–N(1)	1.505(2)	C(1)–N(1)–C(3)	114.52(14)
C(3)–C(3)#1	1.525(3)	C(2)–N(1)–C(3)	112.12(14)
O(1)–P(1)	1.4821(14)	O(1)–P(1)–O(3)	117.90(9)
O(2)–P(1)	1.5639(15)	O(1)–P(1)–O(2)	108.21(9)
O(3)–P(1)	1.5030(14)	O(3)–P(1)–O(2)	111.54(8)
O(4)–P(2)	1.4943(15)	O(1)–P(1)–C(1)	107.25(9)
O(5)–P(2)	1.5745(14)	O(3)–P(1)–C(1)	108.80(9)
O(6)–P(2)	1.5032(15)	O(2)–P(1)–C(1)	101.86(9)
		O(4)–P(2)–O(6)	118.85(9)
		O(4)–P(2)–O(5)	108.31(9)
		O(6)–P(2)–O(5)	109.33(8)
		O(4)–P(2)–C(2)	103.73(9)
		O(6)–P(2)–C(2)	108.63(8)
		O(5)–P(2)–C(2)	107.36(9)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1  $-x+1, -y+1, -z+2$ .

**Table 4**  
Selected bond lengths [Å] and angles [°] for Zn(H<sub>2</sub>O)<sub>6</sub>(TDTMP).

Bonds		Angles			
Zn(1)–O(1)	2.099(2)	O(2)–Zn(1)–O(2)	179.999(2)	O(2)–Zn(1)–O(3)	91.17(10)
Zn(1)–O(2)	2.049(2)	O(2)–Zn(1)–O(1)	91.88(9)	O(1)–Zn(1)–O(3)	91.19(9)
Zn(1)–O(3)	2.106(2)	O(2)–Zn(1)–O(1)	88.12(9)	O(1)–Zn(1)–O(3)	88.81(9)
P(2)–O(7)	1.492(2)	O(1)–Zn(1)–O(1)	180.0(13)	O(3)–Zn(1)–O(3)	180.00(13)
P(2)–O(8)	1.501(2)	O(2)–Zn(1)–O(3)	91.17(10)	O(7)–P(2)–O(8)	117.49(13)
P(2)–O(9)	1.569(2)	O(2)–Zn(1)–O(3)	88.83(10)	O(7)–P(2)–O(9)	107.13(12)
P(1)–O(5)	1.499(2)	O(1)–Zn(1)–O(3)	88.81(9)	O(8)–P(2)–O(9)	112.02(12)
P(1)–O(4)	1.501(2)	O(1)–Zn(1)–O(3)	91.19(9)	O(5)–P(1)–O(4)	116.09(13)
P(1)–O(6)	1.557(2)	O(2)–Zn(1)–O(3)	88.83(10)	O(5)–P(1)–O(6)	111.60(12)
				O(4)–P(1)–O(6)	108.12(14)

of the [Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>]<sub>n</sub> layer, see Fig. 8. The remaining twelve H-bonds are exclusively with phosphonate oxygens from layers below and above. Bond distances are in the range 2.618–2.972 Å.

The P(1)O<sub>3</sub>H<sup>−</sup> phosphonate group takes part in six hydrogen bonds. Three of them are with Zn-bound water molecules (2.797, 2.972 and 2.809 Å). It is interesting to note that the protonated P(1)–O(6)–H moiety along with a non-protonated group P(1)–O(5) create a hydrogen bonded dimer with the corresponding P–O groups of a neighboring P(1) phosphonate. The structure of this dimer (analogous to that formed in the structure of (NH<sub>4</sub>)<sub>2</sub>(EDTMP) is shown in Fig. 9.

The P(2)O<sub>3</sub>H<sup>−</sup> phosphonate group takes part in five hydrogen bonds. Three of them are with Zn-bound waters (2.718, 2.737 and 2.621 Å). The protonated P(2)–O(9)–H group hydrogen bonds to a non-protonated P(1)–O(4) moiety (2.569 Å). Finally, there is a hydrogen bond between non-protonated P(2)–O(7) and the –NH<sup>+</sup> amine moiety of a neighboring phosphonate (2.854 Å).

The P(1)O<sub>3</sub>H<sup>−</sup> phosphonate group takes part in five hydrogen bonds. Two of them participate in the hydrogen-bonded dimer mentioned above. Two of them are with Zn-bound waters (2.752 and 2.949 Å). Finally, there is a hydrogen bond between non-protonated P(1)–O(4) and a protonated P(2)–O(9)–H moiety of a neighboring phosphonate (2.569 Å).

### 3.4. Vibrational spectroscopy

Vibrational spectroscopy was employed as well to further characterize these compounds. FT-IR spectra are shown in Fig. 10. Mid IR spectra (400–4000 cm<sup>−1</sup> region) of the tetraphosphonate products display a multitude of bands in the region 1100–1270 cm<sup>−1</sup> assigned to the P=O stretch. A doublet in the region 920–970 cm<sup>−1</sup> is assigned to the –P–OH antisymmetric and symmetric stretching vibrations. The strong band in the region 1045–1055 cm<sup>−1</sup> is tentatively assigned to an antisymmetric vibration mode of the –CPO<sub>3</sub> group. Bands in the spectra for all compounds are also observed in the 400–550 cm<sup>−1</sup> region. These are assigned to the –PO<sub>3</sub> symmetric and –PO<sub>3</sub> antisymmetric bending modes. Broad bands in the region 1640–1670 cm<sup>−1</sup> in the spectra of (en)(HDTMP)·2H<sub>2</sub>O and Zn(H<sub>2</sub>O)<sub>6</sub>(TDTMP) are due to lattice water and Zn-bound water, respectively. Such bands are absent in the spectrum of (NH<sub>4</sub>)<sub>2</sub>(EDTMP), which is anhydrous.

## 4. Conclusions

The three ionic materials reported herein share a 2D structural motif. They are layered compounds with anionic tetraphosphonate layers separated with cationic layers. These structures are held together by an intricate network of hydrogen bonds, which act as the driving for the self assembly process. The field of metal phosphonate chemistry is growing rapidly. The area of frameworks composed of organic ionic components is also expected to grow in

parallel and act in a supporting fashion. A viable goal is the designed synthesis of supramolecular arrays in a predictable fashion by use of appropriate reactants.

### Supplementary data

CCDC 651135, 625197 and 287045 contain the supplementary crystallographic data for compounds (en)(HDTMP)·2H<sub>2</sub>O, (NH<sub>4</sub>)<sub>2</sub>(EDTMP), and Zn(H<sub>2</sub>O)<sub>6</sub>(TDTMP). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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