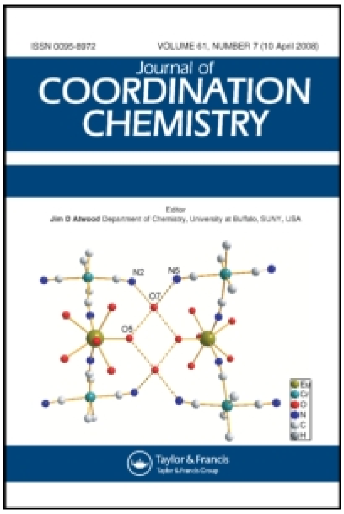

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Synthesis and structures of three triphosphonate compounds containing d^{10} transition metal ions

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Three new triphosphonate compounds, $[Zn(APTPH_4)(2,2'\text{-bipy})(H_2O)] \cdot 2H_2O$ (**1**), $[Cd(APTPH_4)(2,2'\text{-bipy})(H_2O)] \cdot 2H_2O$ (**2**), and $[Zn(APTPH_4)(phen)_2] \cdot phen \cdot 4H_2O$ (**3**) ($APTPH_6 =$ 1-aminopropane-1,1,3-triphosphonic acid, 2,2′-bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline), are synthesized by a low-temperature hydrothermal method. Compounds **1** and **2** are isomorphous, both one-dimensional (1D) coordination polymers expanded into three-dimensional (3D) supramolecular structures by hydrogen bonds and π–π stacking interactions. Compound **3** is a molecular complex and forms a 3D network through an S-shaped water hexamer. Crystal data for **1**: Triclinic, space group $P\bar{1}$, $a = 6.6814(5)$ Å, $b = 10.0929(7)$ Å, $c = 15.438(2)$ Å, $\alpha = 81.544(2)^\circ$, $\beta = 79.066(2)^\circ$, $\gamma = 82.278(2)^\circ$, $Z = 2$; for **2**: Triclinic, space group $P\bar{1}$, $a = 6.9380(8)$ Å, $b = 10.043(2)$ Å, $c = 15.681(2)$ Å, $\alpha = 81.357(2)^\circ$, $\beta = 78.510(2)^\circ$, $\gamma = 81.902(2)^\circ$, $Z = 2$; Crystal data for **3**: Triclinic, space group $P\bar{1}$, $a = 12.540(2)$ Å, $b = 12.596(2)$ Å, $c = 14.997(2)$ Å, $\alpha = 100.795(2)^\circ$, $\beta = 113.328(2)^\circ$, $\gamma = 101.358(2)^\circ$, $Z = 2$.

Keywords: 1-Aminopropane-1,1,3-triphosphonic acid; Zinc; Cadmium; Coordination polymers; Water cluster

1. Introduction

Metal phosphonate compounds have drawn attention due to their building modes and potential applications in optical, ion-exchange, catalytic and sensing properties [1–4]. Among the diverse phosphonic acid ligands, triphosphonic acids, such as aminotri(methylenephosphonic acid) ($ATMPH_6$) [5–9] and 1,4,7-triazacyclononane-1,4,7-triyl-tri(methylenephosphonic acid) ($NOTPH_6$) [10], have crystallized with many metal cations to produce various structures and proved to be good building blocks in crystal engineering. However, little attention has been paid to metal compounds of triphosphonic acids containing functional groups.

Investigation on phosphonic acids containing $–NH_2$ and their metal compounds are of current interest for potential applications in biology. Also, they are excellent

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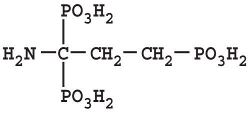

$H_2N-C(PO_3H_2)_2-CH_2-CH_2-PO_3H_2$

Scheme 1. Structure of APTPH$_6$.

precursors for the preparation of supramolecular compounds or coordination polymers. Typical examples include amino methane diphosphonic acid (AMDPH$_4$) [11, 12] and 1-amino-ethylene diphosphonic acid (AEDPH$_4$) [13–17]. In such diphosphonic acid molecules, the amidos can be incorporated into a range of multidentate ligands or used as proton acceptors, while two phosphonate groups adjacent show various coordination modes.

Thus, triphosphonate ligands with amido groups will be good precursors in crystal engineering. In order to explore such triphosphonate ligands and their metal compounds, a new triphosphonate ligand, 1-aminopropane-1,1,3-triphosphonic acid (APTPH$_6$) which contains a –C(NH$_2$)(PO$_3$H$_2$)$_2$ 'head' and a –CH$_2$CH$_2$PO$_3$H$_2$ 'tail' in its molecule (see scheme 1), has been investigated in our lab. Its copper compounds, [Cu(APTPH$_4$)(phen)(H$_2$O)]$\cdot$2.16H$_2$O (**4**) and [Cu(APTPH$_4$)(2,2′-bipy)(H$_2$O)]$\cdot$2.63H$_2$O (**5**), have been reported in our recent work [18].

In this article, by hydrothermal reactions of APTPH$_6$, ZnO or CdO and the second ligand 2,2′-bipy or phen, three new phosphonate compounds, [Zn(APTPH$_4$)(2,2′-bipy)(H$_2$O)]$\cdot$2H$_2$O (**1**), [Cd(APTPH$_4$)(2,2′-bipy)(H$_2$O)]$\cdot$2H$_2$O (**2**) and [Zn(APTPH$_4$)(phen)$_2$]$\cdot$phen$\cdot$4H$_2$O (**3**), are obtained and characterized by elemental analysis (EA), infrared spectra (IR), thermogravimetric analysis (TG) and X-ray single crystal diffraction. The photoluminescence of the three compounds are also studied. Differences between the three compounds and other metal–APTP compounds are also discussed.

2. Experimental

2.1. *Materials and methods*

The 1-aminopropane-1,1,3-triphosphonic acid (APTPH$_6$) was prepared following US Patent 4100167 [19]. The other starting materials were purchased from commercial sources and used without further purification. The IR spectra were recorded from KBr pellets from 400–4000 cm^{-1} on a Thermo Nicolet Avatar 360 FT-IR spectrometer with spectral resolution of 4.00 cm^{-1}. Thermogravimetric studies were carried out with a NETZSCH-TA4 at a heating rate 10°C min^{-1} under air. The elemental analysis data were obtained from a Perkin-Elmer 240B elemental analyzer.

2.2. *Low-temperature hydrothermal synthesis*

Synthesis of 1. A mixture of APTPH$_6$ 0.0748 g (0.25 mmol), ZnO 0.0101 g (0.125 mmol), 2,2′-bipy 0.0391 g (0.25 mmol) and distilled water 1 mL was mixed and sealed in a Teflon reactor and then heated at 80°C for 12 days. Colorless crystals for single crystal diffraction analysis were obtained. Yield: 80%. EA: Anal. C 27.28, H 4.21, N 7.34, Calcd for $C_{13}H_{24}N_3O_{12}P_3Zn$: C 27.27, H 4.22, N 7.34. IR (solid KBr pellet, $\nu\,cm^{-1}$): 3535 (s), 3390 (bs), 3100 (s), 1608 (m), 1600 (m), 1525 (m), 1494 (w), 1479 (m), 1446 (m), 1385 (w), 1321 (w), 1213 (s), 1187 (s), 1147 (s), 1101 (s), 1025 (s), 1102 (s), 914 (s), 837 (m), 759 (m), 735 (m), 651 (m), 532 (m), 465 (m).

Synthesis of 2. A mixture of $APTPH_6$ 0.0748 g (0.25 mmol), CdO 0.0160 g (0.125 mmol), 2,2′-bipy 0.0391 g (0.25 mmol) and distilled water 2 mL was mixed and sealed in a Teflon reactor and then heated at 80°C for 10 days. Colorless crystals for single crystal diffraction analysis were obtained. Yield: 10%. EA: Anal. C 25.15, H 3.90, N 6.76, Calcd for $C_{13}H_{24}N_3O_{12}P_3Cd$: C 25.20, H 3.90, N 6.78. IR (solid KBr pellet, $\nu\,cm^{-1}$): 3389 (bs), 2922 (s), 1600 (m), 1512 (m), 1478 (m), 1442 (m), 1384 (w), 1321 (w), 1184 (s), 1088 (s), 1053 (s), 1020 (s), 1016 (s), 912 (s), 910 (m), 760 (m), 735 (m), 651 (m), 535 (m), 473 (m), 450 (m).

Synthesis of 3. A mixture of $APTPH_6$ 0.0748 g (0.25 mmol), ZnO 0.0101 g (0.125 mmol), phen 0.0743 g (0.375 mmol) and distilled water 1 mL was mixed and sealed in a Teflon reactor and then heated at 80°C for 20 days. Colorless crystals for single crystal diffraction analysis were obtained. Yield: 33%. EA: Anal. C 48.10, H 4.32, N 10.09, Calcd for $C_{39}H_{42}N_7O_{13}P_3Zn$: C 48.04, H 4.34, N 10.05. IR (solid KBr pellet, $\nu\,cm^{-1}$): 3400 (s), 3054 (m), 1625 (m), 1590 (m), 1515 (m), 1497 (w), 1425 (s), 1381 (w), 1344 (w), 1223 (m), 1144 (s), 1103 (m), 1089 (m), 1067 (m), 959 (m), 930 (m), 866 (m), 846 (m), 789 (w), 771 (w), 725 (s), 674 (w), 637 (w), 553 (m), 509 (m), 461 (m).

2.3. *X-ray crystallographic analysis*

Crystallographic measurements were obtained on a Bruker SMART CCD area-detector diffractometer at room temperature (293 K) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All data were corrected for absorption using the program SADABS. The structures were solved by direct methods using the program SHELXS-97 [20]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL-97. Hydrogen atoms were directly obtained from difference Fourier maps and several DFIX commands were applied on hydrogen atoms of water molecules in compounds **2** and **3**. Drawings were produced with Diamond 3.0 and Mercury 1.4.1. Crystallographic data and structure refinement parameters are listed in table 1. Selected bond lengths (Å) and angles (°) for the three compounds are listed in table 2. Hydrogen bond details for **1** and **3** (Å and °) are listed in table 3. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication No. CCDC 630842 (**1**), 630844 (**2**) and 630843 (**3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) (1223) 336033; Email for inquiry: deposit@ccdc.cam.ac.uk)

Table 1. Crystallographic data and structure refinement for **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{13}H_{24}N_3O_{12}P_3Zn$	$C_{13}H_{24}N_3O_{12}P_3Cd$	$C_{39}H_{42}N_7O_{13}P_3Zn$
Formula weight	572.63	619.66	975.08
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.6814(5)	6.9380(8)	12.5340(2)
b (Å)	10.0929(7)	10.043(2)	12.596(2)
c (Å)	15.438(2)	15.681(2)	14.997(2)
α (°)	81.544(2)	81.357(2)	100.795(2)
β (°)	79.066(2)	78.510(2)	113.328(2)
γ (°)	82.278(2)	81.902(2)	101.358(2)
V (Å^3)	1005.0(2)	1051.6(2)	2037.8(3)
Z	2	2	2
F(000)	588	624	936
Crystal size (mm^3)	0.37 × 0.34 × 0.25	0.67 × 0.14 × 0.09	0.30 × 0.27 × 0.18
Goodness-of-fit on F^2	1.043	1.076	1.027
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0269$, $wR_2 = 0.0674$	$R_1 = 0.0259$, $wR_2 = 0.0664$	$R_1 = 0.0443$, $wR_2 = 0.1142$
R indices (all data)	$R_1 = 0.0291$, $wR_2 = 0.0686$	$R_1 = 0.0277$, $wR_2 = 0.0674$	$R_1 = 0.0627$, $wR_2 = 0.1251$
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ (e Å^{-3})	0.502, −0.376	1.333, −0.500	0.548, −0.727

(a) $R_1 = [\Sigma(|F_o| - |F_o|)/\Sigma|F_o|$; (b) $wR_2 = [\Sigma[w(|F_o|2 - |F_o|2)2]/\Sigma[w(|F_o|2)2]]1/2$, $w = 1/[\sigma_2|F_o|2 + (xp)_2 + yp]$, where $p = [|F_o|2 + 2|F_o|2]/3$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**.

1		**2**		**3**	
Zn(1)–O(3)	2.074(2)	Cd(1)–O(1)	2.223(2)	Zn(1)–O(4)	2.036(2)
Zn(1)–O(4)	2.089(2)	Cd(1)–O(2)	2.271(2)	Zn(1)–O(1)	2.051(2)
Zn(1)–N(2)	2.132(2)	Cd(1)–O(4)	2.273(2)	Zn(1)–N(5)	2.152(3)
Zn(1)–N(3)	2.133(2)	Cd(1)–N(2)	2.323(2)	Zn(1)–N(3)	2.158(2)
Zn(1)–O(1)	2.135(2)	Cd(1)–N(1)	2.323(2)	Zn(1)–N(4)	2.238(2)
Zn(1)–O(1W)	2.147(2)	Cd(1)–O(3W)	2.328(2)	Zn(1)–N(2)	2.257(2)
O(3)–Zn(1)–O(4)	94.44(6)	O(1)–Cd(1)–O(2)	171.44(7)	O(4)–Zn(1)–O(1)	92.34(8)
O(3)–Zn(1)–N(2)	88.56(6)	O(1)–Cd(1)–O(4)	96.15(8)	O(4)–Zn(1)–N(5)	95.5(2)
O(4)–Zn(1)–N(2)	171.94(6)	O(2)–Cd(1)–O(4)	87.30(7)	O(1)–Zn(1)–N(5)	105.43(9)
O(3)–Zn(1)–N(3)	93.34(6)	O(1)–Cd(1)–N(2)	94.92(8)	O(4)–Zn(1)–N(3)	98.59(9)
O(4)–Zn(1)–N(3)	95.73(6)	O(2)–Cd(1)–N(2)	92.42(7)	O(1)–Zn(1)–N(3)	91.05(9)
N(2)–Zn(1)–N(3)	76.60(6)	O(4)–Cd(1)–N(2)	96.96(7)	N(5)–Zn(1)–N(3)	157.82(9)
O(3)–Zn(1)–O(1)	173.51(6)	O(1)–Cd(1)–N(1)	90.21(8)	O(4)–Zn(1)–N(4)	171.2(2)
O(4)–Zn(1)–O(1)	89.68(5)	O(2)–Cd(1)–N(1)	88.01(7)	O(1)–Zn(1)–N(4)	90.42(9)
N(2)–Zn(1)–O(1)	88.02(6)	O(4)–Cd(1)–N(1)	166.93(7)	N(5)–Zn(1)–N(4)	75.7(2)
N(3)–Zn(1)–O(1)	91.23(6)	N(2)–Cd(1)–N(1)	71.05(7)	N(3)–Zn(1)–N(4)	89.7(2)
O(3)–Zn(1)–O(1W)	89.91(6)	O(1)–Cd(1)–O(3W)	88.10(8)	O(4)–Zn(1)–N(2)	91.92(8)
O(4)–Zn(1)–O(1W)	89.27(6)	O(2)–Cd(1)–O(3W)	84.28(7)	O(1)–Zn(1)–N(2)	166.23(9)
N(2)–Zn(1)–O(1W)	98.23(6)	O(4)–Cd(1)–O(3W)	86.64(8)	N(5)–Zn(1)–N(2)	87.2(2)
N(3)–Zn(1)–O(1W)	173.80(7)	N(2)–Cd(1)–O(3W)	175.01(8)	N(3)–Zn(1)–N(2)	75.36(9)
O(1)–Zn(1)–O(1W)	85.12(6)	N(1)–Cd(1)–O(3W)	105.02(8)	N(4)–Zn(1)–N(2)	87.33(9)

3. Results and discussion

3.1. *Structure description*

Crystal structures of 1 and 2. Single crystal analysis shows that **1** and **2** are isomorphous, so only **1** is discussed in detail. In **1**–**3**, each APTPH$_6$ lose two proton

Table 3. Hydrogen bonds for **1** and **3** (Å and °).

D–H···A	d(D–H)	d(H···A)	D(D···A)	∠(DHA)
Compound **1**[a]				
O(3W)–H(2W3)···O(5)	0.88(8)	2.44(8)	3.231(4)	149(7)
O(3W)–H(1W3)···O(9)#2	0.77(5)	2.14(5)	2.897(3)	170(5)
O(2W)–H(2W2)···O(1W)#3	0.83(5)	2.46(5)	3.094(3)	134(4)
O(2W)–H(2W2)···O(2)#3	0.83(5)	2.41(5)	3.084(3)	139(4)
O(2W)–H(1W2)···O(9)#2	0.92(3)	1.85(4)	2.693(3)	151(3)
O(1W)–H(1W1)···O(6)	0.69(3)	2.20(3)	2.843(2)	154(4)
O(1W)–H(2W1)···O(7)#4	0.82	1.98	2.744(2)	154.7
N(1)–H(1C)···O(4)#1	0.89	2.32	3.212(2)	178.4
N(1)–H(1B)···O(6)#5	0.89	1.96	2.790(2)	153.5
N(1)–H(1A)···O(3W)#6	0.89	2.1	2.933(3)	155.1
O(8)–H(3)···O(2W)	0.89(3)	1.70(3)	2.582(3)	169(3)
O(5)–H(2)···O(7)#6	0.73(3)	1.83(3)	2.560(2)	171(4)
O(2)–H(1)···O(7)#7	0.70(3)	1.94(3)	2.629(2)	169(4)
Compound **3**[b]				
O(3W)–H(2W3)···O(3W)#1	0.85(2)	2.29(4)	3.14(4)	178(13)
O(2W)–H(1W2)···O(1W)	0.86(2)	2.13(9)	2.803(7)	134(11)
O(1W)–H(1W1)···O(5)	0.86(2)	1.95(4)	2.780(4)	161(10)
O(4W)–H(2W4)···O(5)#2	0.85(2)	2.22(5)	2.781(4)	124(5)
O(4W)–H(1W4)···O(4)#3	0.85(2)	2.16(3)	2.868(5)	140(4)
O(1W)–H(2W1)···O(3)#4	0.87(2)	1.97(2)	2.832(4)	176(6)
O(2)–H(2)···N(6)#5	0.82(4)	1.85(4)	2.660(4)	171(4)
O(9)–H(3)···O(3)#4	0.82	1.71	2.496(3)	158.3
O(5)–H(1)···O(4W)#6	0.82	1.99	2.781(4)	162
N(1)–H(1C)···N(7)#5	0.89	2.12	2.866(3)	140.4
N(1)–H(1B)···N(5)	0.89	2.46	3.236(3)	145.2
O(2W)–H(2W2)···O(3W)	0.877	2.06	2.799(1)	141.7
N(1)–H(1B)···O(4)	0.89	2.45	3.002(3)	120.5

Symmetry transformations used to generate equivalent atoms:

[a] #1: $x+1, y, z$; #2: $x-1, y, z$; #3: $x, y-1, z$; #4: $x-1, y+1, z$; #5: $-x+1, -y+2, -z+1$; #6: $-x+1, -y+1, -z+1$; #7: $x, y+1, z$.

[b] #1: $-x+1, -y+1, -z$; #2: $x-1, y, z$; #3: $-x+1, -y+1, -z+1$; #4: $-x+2, -y+2, -z+1$; #5: $x+1, y, z+1$; #6: $x+1, y, z$.

and transfers a proton to the amino-nitrogen atom, forming an anion of APTPH$_4^{2-}$. Figure 1(a) shows the coordination environment of Zn atoms in **1**. Each zinc displays a slightly distorted octahedral geometry with three oxygen atoms from two different APTPH$_4^{2-}$ ions, two nitrogen atoms from a chelated 2,2′-bipy ligand, and one oxygen atom from a coordinated water. The Zn–O distances range from 2.074(2) to 2.147(2) Å, whereas Zn–N distance varies from 2.132(2) to 2.133(2) Å. The corresponding values of **2** are in the range 2.223(2)–2.328(2) Å (Cd–O) and 2.323(2) Å (Cd–N), respectively.

As shown in figure 1(b), the –C(NH$_2$)(PO$_3$H$_2$)$_2$ 'head' in APTPH$_4^{2-}$ provides a O1–P1–O3 bridge to connect two adjacent Zn atoms, forming a one-dimensional (1D) linear chain in the form of [Zn(APTPH$_4$)(2,2′-bipy)(H$_2$O)]$_n$ along the *a* axis. Meanwhile, the 1D chain is stabilized by the chelating effect of a Zn1–O1–P1–C1–P2–O4 hexacyclic ring.

On the other hand, the 'tail' phosphonate group plays an important role in constructing strong hydrogen bonds. O7 in the 'tail' phosphonate group forms a hydrogen bond motif of $R_2^2(16)$ with neighboring H(O5), connecting two [Zn(APTPH$_4$)(2,2′-bipy)(H$_2$O)]$_n$ linear chains to a dimer. Then the dimers extend along the *b* axis by another H-bond between O7 and neighboring H(O2), forming a 2D

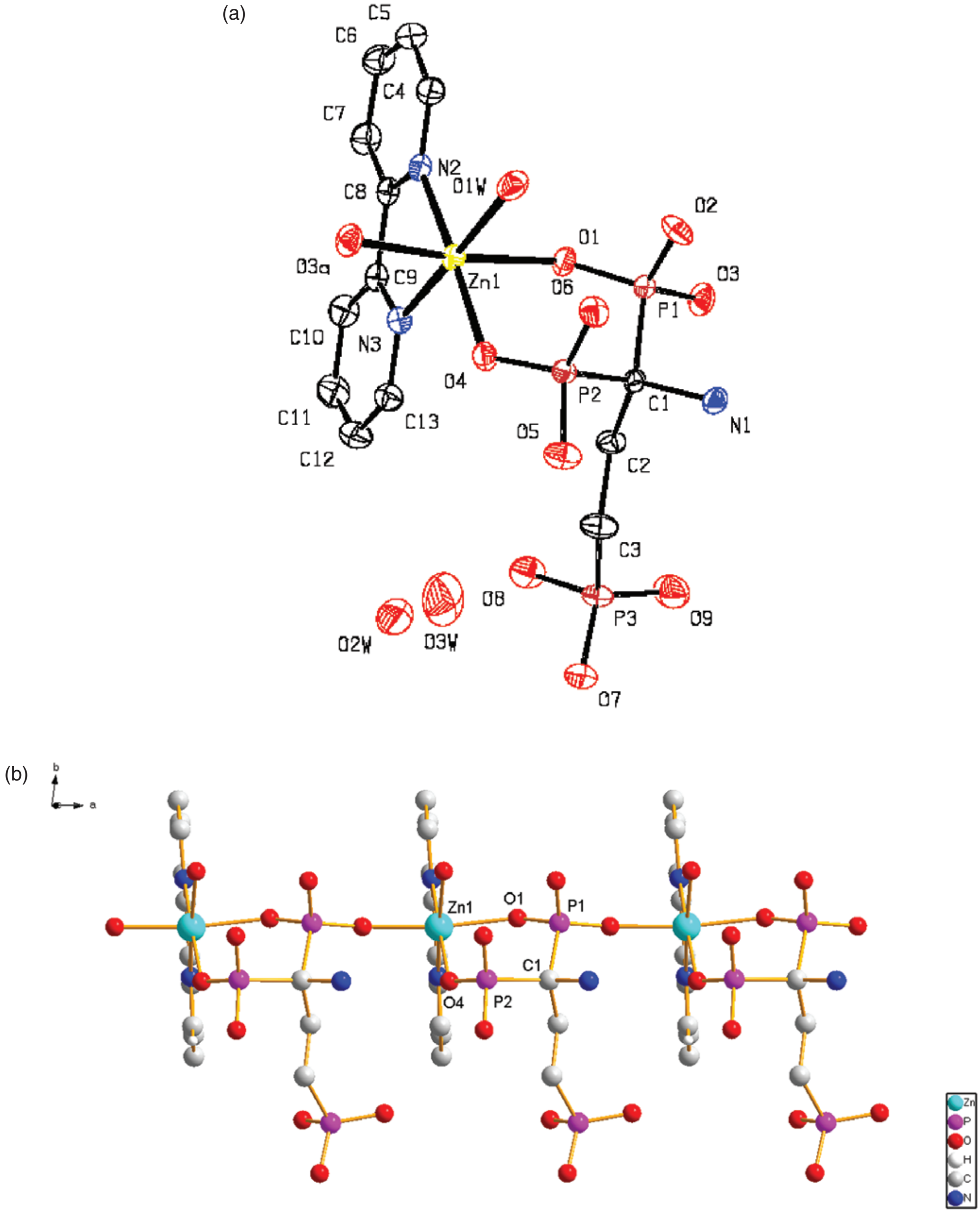

Figure 1. (a) The ORTEP of **1** with thermal ellipsoids at the 50% probability. All hydrogen atoms are omitted for clarity. (b) One chain of **1** viewed at the *c** axis. All hydrogen atoms are omitted for clarity.

pillared layer structure along the *ab* plane. The two kinds of P–OH · · · O–P bonds give very short distances of 2.560(2) and 2.629(2) Å, similar to a previous report [21]. The protonated amino group gives three intermolecular hydrogen bonds which help to stabilize the 2D layer structure. The 2,2′-bipy rings of adjacent 1D linear chains, which are alternately attached to each other, exhibit very strong π–π stacking interactions with the face-to-face distance of 3.326–3.350 Å and connect the 2D layers into a 3D supramolecular structure (see S-1 in supporting information).

Crystal structure of 3. The structure of **3** is quite different from **1** and **2**. **3** is a molecular unit of [Zn(APTPH$_4$)(phen)$_2$], in which each zinc center displays a slightly distorted octahedral N_4O_2 geometry, while that in **1** and **2** was N_2O_4. The six-coordinate Zn is chelated by one APTPH$_4^{2-}$ ion and two phen ligands, and the bond lengths are in the range 2.035(2)–2.050(2) Å (Zn–O) and 2.150(3)–2.257(2) Å (Zn–N). A third phen ligand is uncoordinated, and its orientation is approximately parallel to a coordinated one, at a distance of 14.064 Å.

Two [Zn(APTPH$_4$)(phen)$_2$] units are joined together by two H-bond modes: connection between H(O9) and neighboring O3 and bridging of water molecules O4W and O1W. H-bonds formed by amidos and phosphonate groups also connect the uncoordinated phen ligand and [Zn(APTPH$_4$)(phen)$_2$]. In addition, strong π–π interactions are observed among the phen rings, including the coordinated and uncoordinated ones, of which the shortest face-to-face distance is 3.464 Å. Combination of π–π interactions and hydrogen bonds gives a 3D supramolecular structure (see S-2 in supporting information).

A D6 water cluster exists in the 3D supramolecular structure. The water cluster is S-shaped, and water hexamer structures reported previously mostly display ring motifs [22–25]. Figure 2(b) shows the S-shaped D6 cluster: three water molecules (O1W, O2W, O3W) are connected by hydrogen bonds with $O \cdots O$ distances in the range 2.799–2.802 Å, shorter than that of liquid water (2.85 Å) [26]. Water molecule O3W forms a relatively weak H-bond with O3W′ at a distance of 3.140 Å. Thus, the six lattice water molecules self-assemble to form a water hexamer of S-shape (<O1W O2W O3W = 136.41°, <O2W O3W O3W′ = 103.85°). The water hexamer is stabilized by strong hydrogen bonds between the host [Zn(phen)$_2$(APTPH$_4$)] units and the water molecule O1W.

3.2. *FT-IR spectra*

The IR spectra of **1**, **2** and **3** are similar, as shown in figure 3. The broad peaks centered at 3389–3400 cm^{-1} suggest water in these three compounds. A series of characteristic peaks in the range 1425–1625 cm^{-1} are attributed to 2,2-bipy in **1** and **2** and phen in **3** [27]. The P–O stretching vibrations in the region 1187–910 cm^{-1} and the O–P–O bending vibrations in the region 553–450 cm^{-1} are common features [28].

3.3. *Thermal studies*

As shown in figure 4, the TG curve for **1** shows stability to 117°C in air, then decomposes till 215°C with a weight loss of 9.57% (Calcd 9.44%), attributed to the release of two lattice water molecules and one coordinated water molecule. The weight loss occurring between 215 and 800°C corresponds to decomposition of the APTPH$_4^{2-}$ and 2,2-bipy. The residue at 1000°C is assumed to be ZnP_3O_7, with the observed total weight loss of 52.55% (Calcd 52.80%). The decomposition of **2** is similar to that of **1**. The temperature from 118 to 180°C indicates loss of three

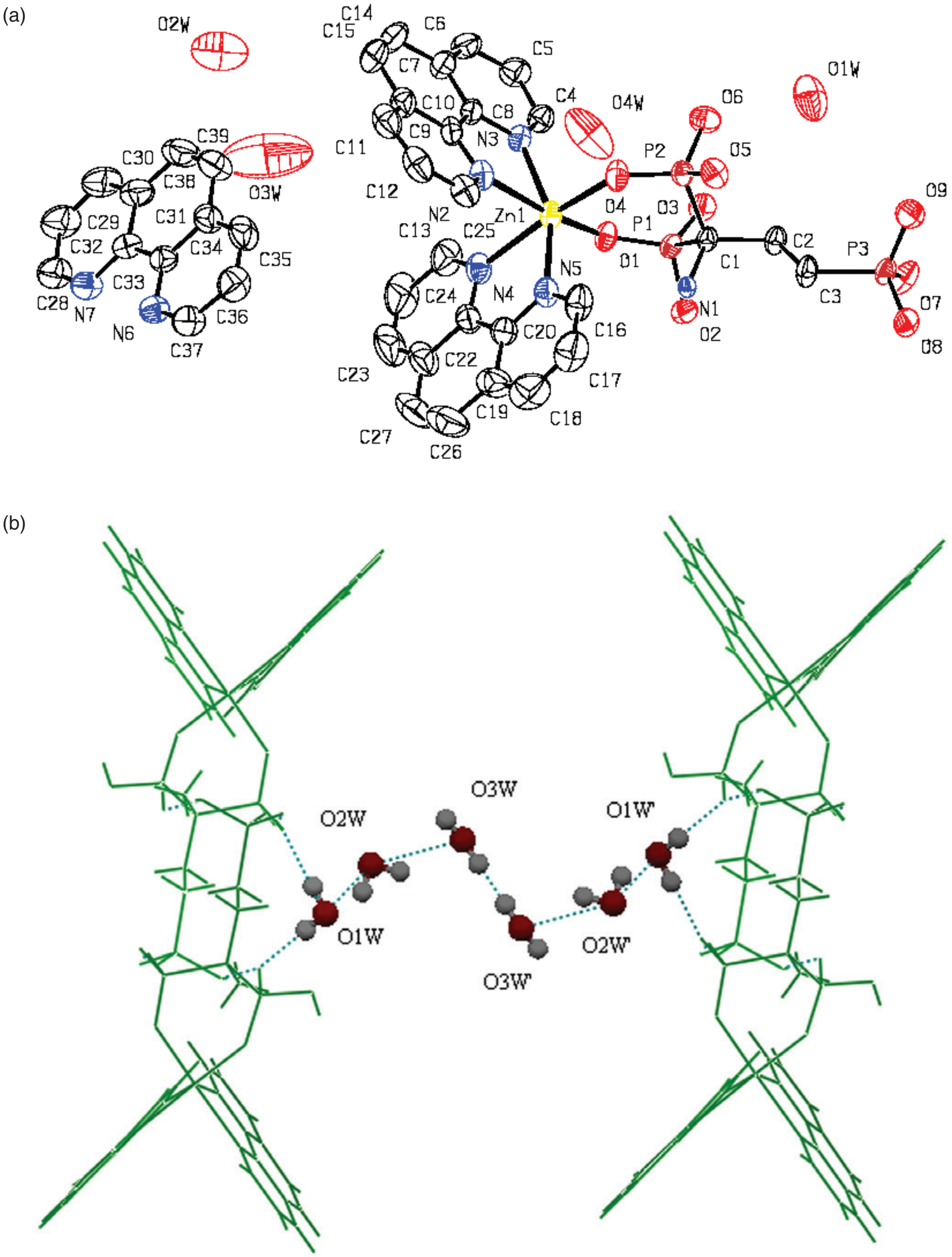

Figure 2. (a) The ORTEP of **2** with thermal ellipsoids at the 50% probability. All hydrogen atoms are omitted for clarity. (b) Hydrogen-bonding motif of the S-shaped water hexamer.

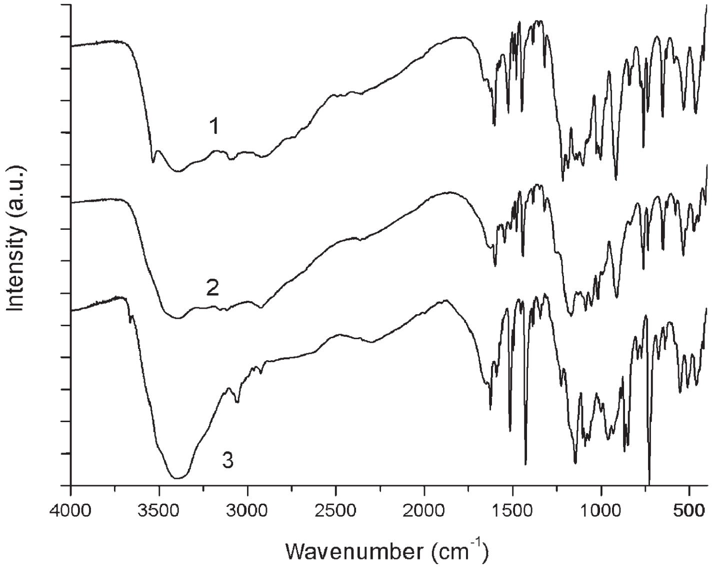

Figure 3. IR spectra of **1**, **2** and **3**.

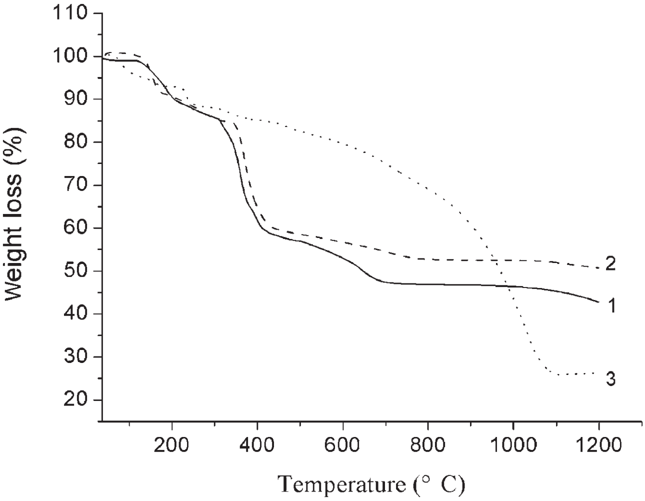

Figure 4. TG diagrams of **1**, **2** and **3**.

water molecules (8.82%), close to the calculated value (8.72%), then decomposition of the $APTPH_4^{2-}$ and 2,2-bipy occurs up to 800°C. The final product is CdP_3O_7 with observed total weight loss of 47.63% (Calcd 48.79%). Compared with **1** and **2**, **3** is unstable over 50°C, losing four lattice water molecules till 218°C with a weight loss of 7.65% (Calcd 7.39%). The decomposition of the $APTPH_4^{2-}$ and phen starts at the same time and is complete at 1100°C. The observed total weight loss of 74.51% is slightly larger than the calculated value (73.92%) if the final product is ZnP_3O_6.

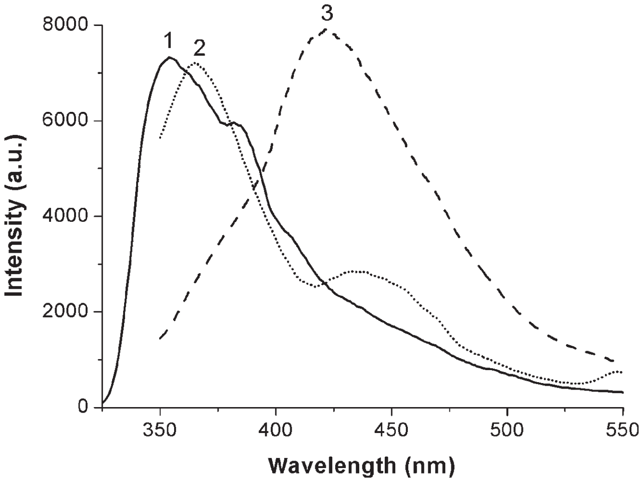

Figure 5. The photoluminescence spectra of **1**, **2** and **3**.

3.4. *Photoluminescence property studies*

The photoluminescence spectra of **1**–**3** were detected in solid state at room temperature, depicted in figure 5. Compound **1** exhibits blue photoluminescence with an emission maximum at 354 nm when excited at 280 nm, while there is an emission maximum at 364 nm for **2** and 424 nm for **3**, both excited at 330 nm. The emission bands may be attributed to the emission of ligand-to-metal charge transfer (LMCT).

3.5. *Discussion*

A series of transition metal compounds with the triphosphonate ligand, 1-aminopropane-1,1,3-triphosphonic acid ($APTPH_6$), have been synthesized and characterized, $[Zn(APTPH_4)(2,2'\text{-bipy})(H_2O)] \cdot 2H_2O$ (**1**), $[Cd(APTPH_4)(2,2'\text{-bipy})(H_2O)] \cdot 2H_2O$ (**2**), $[Zn(APTPH_4)(phen)_2] \cdot phen \cdot 4H_2O$ (**3**), $[Cu(APTPH_4)(phen)(H_2O)] \cdot 2.16H_2O$ (**4**) and $[Cu(APTPH_4)(2,2'\text{-bipy})(H_2O)] \cdot 2.63H_2O$ (**5**). All these compounds are synthesized by the same low-temperature hydrothermal method but display different structural motifs. Compounds **1**, **2** and **5** all contain $APTPH_4^{2-}$, 2,2′-bipy and coordinated water. According to the Jahn-Teller effect, Cu^{2+} prefers to be five coordinated. So in **5**, Cu displays a square-pyramidal geometry which is chelated by $APTPH_4^{2-}$ and a 2,2′-bipy ligand; one coordinated water lies at the vertex of the square pyramid. Thus, **5** can only be a molecular complex. In contrast, in **1** and **2**, Zn^{2+} and Cd^{2+} adopt six-coordinated octahedral geometry, which need another $APTPH_4^{2-}$ to coordinate, so **1** and **2** are one-dimensional coordination polymers.

The Jahn–Teller effect can also explain the differences between **3** and **4**. Compound **4** adopts a similar coordination mode to **5**, while in **3** Zn^{2+} is six coordinate. So there is only one coordinated phen in **4** while in **3** two phen ligands chelate and one is uncoordinated. In conclusion, the different structures in these five compounds are caused by the different coordination modes of corresponding metal ions.

4. Conclusion

This article describes the synthesis, structures and photoluminescence of three d^{10} transition metal compounds based on the triphosphonate ligand $APTPH_6$. Compounds **1** and **2** are isomorphous and exhibit one-dimensional coordination polymers, while **3** is a molecular complex with an S-shaped water hexamer. Previously reported compounds, $Cu(APTPH_4)(phen)(H_2O)\cdot 2.16H_2O$ (**4**) and $Cu(APTPH_4)(2,2'\text{-bipy})(H_2O)\cdot 2.63H_2O$ (**5**), are discussed for contrast. The five compounds are synthesized in similar conditions but illustrate different structural motifs due to different metal centers.

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