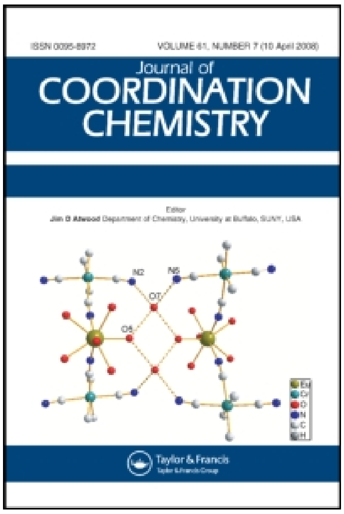

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Hydrothermal syntheses, crystal structures and thermal stability of two divalent metal phosphonates with a layered and a 3D structure

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Hydrothermal syntheses, crystal structures and thermal stability of two divalent metal phosphonates with a layered and a 3D structure

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Two new divalent metal phosphonates, $[Cu_2\{CH_3C(OH)(PO_3)_2\}(H_2O)_2]\cdot 0.5H_2O$ (**1**) and $[NH_3CH_2CH_2NH_3][Zn_3\{CH_3C(OH)(PO_3)_2\}_2(H_2O)]\cdot H_2O$ (**2**), have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction as well as with infrared spectroscopy, elemental analysis and thermogravimetric analysis. The structure of **1** comprises $[Cu_3(hedp)_2]^{2-}$ layers connected by $[CuO_4]$ units to form a 3D open-framework structure with a one-dimensional channel system along the *b* axis. In **2**, the connections of alternately arranged $[ZnO_4]$ tetrahedra, $[ZnO_6]$ octahedra and $[CPO_3]$ tetrahedra *via* vertex-sharing result in a 2D layered structure. The protonated ethylenediamine cations and water molecules are located between adjacent layers.

Keywords: Metal phosphonates; Crystal structure; Hydrothermal synthesis; Copper(II); Zinc(II)

1. Introduction

Metal phosphonate chemistry has attracted considerable attention due to their potential applications in catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry [1–4]. Compared with their phosphate analogs, the organic moieties of the phosphonate ligand RPO_3^{2-} can be modified by functional groups such as amine, hydroxyl and carboxylate. Studies of metal phosphonates have shown that bifunctional or multifunctional anionic units, such as diphosphonates, aminophosphonates or phosphonocarboxylates lead to many new materials with layered or porous structures [5–7].

A series of metal phosphonates, using phosphonic acids with amine, hydroxyl, and carboxylate groups as ligands, have been isolated in our laboratory [8].

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For construction of inorganic–organic hybrid compounds, the methylenediphosphonate ($H_2O_3PCH_2PO_3H_2$) and its derivatives [$H_2O_3PC(R)(R')PO_3H_2$] are useful ligands in the synthesis of metal phosphonates with new structural types [9–12]. In recent years, 1-hydroxyethylidenediphosphonic acid (hedpH_4) has been used as a ligand for synthesis of metal phosphonates with open-framework structures, since it can adopt various coordination modes under different reaction conditions resulting in various interesting structures [13–15]. As part of a program of investigating metal diphosphonates, we are interested in exploring new metal phosphonate compounds based on 1-hydroxyethylidenediphosphonic acid (hedpH_4). In this article, we report the synthesis, crystal structure, and thermal stability of two new divalent metal diphosphonates $[Cu_2\{CH_3C(OH)(PO_3)_2\}(H_2O)_2]\cdot 0.5H_2O$ (**1**) and $[NH_3CH_2CH_2NH_3][Zn_3\{CH_3C(OH)(PO_3)_2\}_2(H_2O)]\cdot H_2O$ (**2**) containing 1-hydroxyethylidenediphosphonic acid as ligand.

2. Experimental

2.1. *Materials and methods*

1-hydroxyethylidenediphosphonic acid solution was obtained from Taihe Chemical Factory as a water treatment agent (50.0 wt%) and used as received. Other chemicals were obtained from commercial sources and used without further purification. C, H and N were determined by using a PE-2400 elemental analyzer. Cu, Zn and P were determined by using an inductively coupled plasma (ICP) atomic absorption spectrometer. IR spectra were recorded on a Bruker AXS TENSOR-27 FT-IR spectrometer with KBr pellets in the range 4000–400 cm^{-1}. TG analyses were performed on a Perkin-Elmer Pyris Diamond thermal analysis system in static air with a heating rate of 10 $K\,min^{-1}$ from 50 to 700°C.

2.2. *Synthesis of $[Cu_2\{CH_3C(OH)(PO_3)_2\}(H_2O)_2]\cdot 0.5H_2O$ (1)*

A mixture of $Cu(CH_3COO)_2\cdot H_2O$ (0.22 g, 1.1 mmol), NaF (0.17 g, 4 mmol), hedpH_4 solution (0.5 mL, 50.0 wt%), acetic acid (2 mL, 35 mmol) and 8 mL of water was sealed into a 23 mL Teflon-lined stainless steel autoclave and heated at 140°C for 2 days. After the mixture was cooled slowly to room temperature, blue plate crystals were filtered off, washed with distilled water, and dried at room temperature (Yield: 34% based on Cu). Anal. Calcd for **1**, $C_2H_9Cu_2O_{9.5}P_2$ (%): C, 6.47; H, 2.38; P, 16.63; Cu, 33.85. Found: C, 6.38; H, 2.45; P, 16.52; Cu, 33.97.

2.3. *Synthesis of $[NH_3CH_2CH_2NH_3][Zn_3\{CH_3C(OH)(PO_3)_2\}_2(H_2O)]\cdot H_2O$ (2)*

$Zn(CH_3COO)_2\cdot 2H_2O$ (0.22 g, 1 mmol), NaF (0.04 g, 1 mmol) and hedpH_4 solution (1 mL, 50.0 wt%) were dissolved in H_2O (15 mL), and then ethylenediamine was added with stirring to adjust the pH of the mixture. The mixture (pH $\approx$ 3) was sealed in a 23 mL Teflon-lined stainless steel autoclave and heated at 140°C for 2 days. After the mixture cooled slowly to room temperature, colorless plate crystals were filtered off,

Table 1. Crystal data and structure refinements for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_2H_9Cu_2O_{9.5}P_2$	$C_6H_{22}N_2O_{16}P_4Zn_3$
Formula weight	374.11	698.25
Crystal size (mm^3)	0.40 × 0.13 × 0.02	0.26 × 0.10 × 0.03
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	23.3415(11)	8.0413(5)
b (Å)	8.9555(4)	11.7508(7)
c (Å)	9.2110(4)	11.8844(7)
α (°)	90	100.9930(10)
β (°)	111.9050(10)	103.9420(10)
γ (°)	90	102.6500(10)
V (Å^3)	1786.41(14)	1027.69(11)
Z	8	2
D_c ($g \cdot cm^{-3}$)	2.782	2.256
Absorption coefficient	5.158	3.865
$F(000)$	1480	700
θ range for data collection	1.88 to 26.50	1.83 to 26.50
Limiting indices	$-28 \le h \le 29$, $-10 \le k \le 11$, $-11 \le l \le 8$	$-10 \le h \le 5$, $-13 \le k \le 14$, $-14 \le l \le 14$
Reflections collected	5081	6050
Independent reflections	1847 ($R_{int} = 0.0222$)	4136 ($R_{int} = 0.0209$)
Completeness to theta = 26.50	99.6%	97.4%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.8994 and 0.2345	0.8863 and 0.4378
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness–of–fit on F^2	1.088	1.064
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0552$, $wR_2 = 0.1440$	$R_1 = 0.0504$, $wR_2 = 0.1410$
R indices (all data)	$R_1 = 0.0603$, $wR_2 = 0.1483$	$R_1 = 0.0626$, $wR_2 = 0.1509$

$R_1 = \Sigma(|F_0| - |F_C|)/\Sigma\ |F_0|$; $wR_2 = [\Sigma w(|F_0| - |F_C|)^2/\Sigma w F_0^2]^{1/2}$.

washed with distilled water, and dried at room temperature (Yield: 26% based on Zn). Anal. Calcd for **2**, $C_6H_{22}N_2O_{16}P_4Zn_3$ (%): C, 10.31; H, 3.15; N, 4.01; P, 17.76; Zn, 27.93. Found: C, 10.22; H, 3.24; N, 4.18; P, 17.65; Zn, 27.78.

2.4. *Crystal structure determinations of 1 and 2*

Suitable single crystals for **1** and **2** were glued to a thin glass fiber and mounted on a Bruker Smart APEX II X-diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 ± 2K. A hemisphere of intensity data was collected with ω-scans in the range $1.88° \le \theta \le 26.50°$ for **1** and $1.83° \le \theta \le 26.50°$ for **2**. An empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares fitting on F^2 using SHELXTL-97 [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically, fixed isotropic thermal parameters, and included in the structure factor calculations. A summary of crystal data and structure refinements for the two compounds are listed in table 1. Selected bond lengths and angles are given in table 2.

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

Compound **1**			
Cu(1)–O(1#)	1.9886(16)	Cu(3)–O(2)#4	1.9288
Cu(1)–O(4)#1	1.9374	Cu(3)–O(1)#1	2.0301(15)
Cu(2)–O(5)#2	1.9415	Cu(3)–O(8)	2.042(5)
Cu(2)–O(9)	1.973(5)	Cu(3)–O(4)	2.3621(19)
Cu(3)–O(6)#3	1.9195		
O(4)#1–Cu(1)–O(4)	180	O(9)#2–Cu(2)–O(9)	180.000(1)
O(4)#1–Cu(1)–O(1)	84.2	O(6)#3–Cu(3)–O(2)#4	168.8
O(4)–Cu(1)–O(1)	95.8	O(6)#3–Cu(3)–O(1)#1	92.46(5)
O(4)#1–Cu(1)–O(1)#1	95.8	O(2)#4–Cu(3)–O(1)#1	93.04(6)
O(4)–Cu(1)–O(1)#1	84.2	O(6)#3–Cu(3)–O(8)	89.60(14)
O(1)–Cu(1)–O(1)#1	180	O(2)#4–Cu(3)–O(8)	87.59(14)
O(5)#2–Cu(2)–O(5)	180	O(1)#1–Cu(3)–O(8)	165.06(15)
O(5)#2–Cu(2)–O(9)#2	91.39(15)	O(6)#3–Cu(3)–O(4)	88.82(6)
O(5)–Cu(2)–O(9)#2	88.61(15)	O(2)#4–Cu(3)–O(4)	102.06(6)
O(5)#2–Cu(2)–O(9)	88.61(15)	O(1)#1–Cu(3)–O(4)	73.2
O(5)–Cu(2)–O(9)	91.39(15)	O(8)–Cu(3)–O(4)	92.06(14)
Compound **2**			
Zn(1)–O(1#)	1.933(5)	Zn(2)–O(10)#3	1.977(4)
Zn(1)–O(3)#1	1.932(5)	Zn(3)–O(2)	1.996(5)
Zn(1)–O(13)#2	1.945(4)	Zn(3)–O(5)	2.010(5)
Zn(1)–O(9)	1.971(4)	Zn(3)–O(11)	2.018(5)
Zn(2)–O(4)	1.907(4)	Zn(3)–O(15)	2.115(5)
Zn(2)–O(12)#3	1.928(4)	Zn(3)–O(8)	2.313(4)
Zn(2)–O(8)	1.951(4)	Zn(3)–O(14)	2.336(6)
O(1)–Zn(1)–O(3)#1	112.0(2)	O(5)–Zn(3)–O(11)	97.36(19)
O(1)–Zn(1)–O(13)#2	112.63(19)	O(2)–Zn(3)–O(11)	164.63(19)
O(3)#1–Zn(1)–O(13)#2	103.6(2)	O(5)–Zn(3)–O(15)	103.4(2)
O(1)–Zn(1)–O(9)	127.0(2)	O(11)–Zn(3)–O(15)	88.4(2)
O(3)#1–Zn(1)–O(9)	99.8(2)	O(2)–Zn(3)–O(8)	92.04(18)
O(13)#2–Zn(1)–O(9)	98.80(19)	O(2)–Zn(3)–O(5)	97.59(19)
O(4)–Zn(2)–O(12)#3	108.0(2)	O(11)–Zn(3)–O(8)	84.55(18)
O(4)–Zn(2)–O(8)	105.30(19)	O(15)–Zn(3)–O(8)	166.07(19)
O(12)#3–Zn(2)–O(8)	119.9(2)	O(2)–Zn(3)–O(14)	84.33(19)
O(4)–Zn(2)–O(10)#3	113.2(2)	O(5)–Zn(3)–O(14)	166.69(19)
O(12)#3–Zn(2)–O(10)#3	101.20(19)	O(11)–Zn(3)–O(14)	80.30(18)
O(8)–Zn(2)–O(10)#3	109.38(19)	O(8)–Zn(3)–O(14)	77.34(16)

Symmetry transformations used to generate equivalent atoms:
For **1**: #1 $-x+1/2, -y-1/2, -z+2$; #2 $-x, -y, -z+2$; #3 $x, -y, z-1/2$; #4 $-x+1/2, y+1/2, -z+5/2$.
For **2**: #1$-x+1, -y+2, -z+1$; #2 $x+1, y, z$; #3 $-x, -y+1, -z+1$.

3. Results and discussion

3.1. *Crystal structure*

Compound **1** crystallizes in space group $C2/c$. The asymmetric unit is shown in figure 1. Within the asymmetric unit, three crystallographically independent Cu ions are found. The occupancy at both Cu1 and Cu2 is 0.5. The Cu1 ion is four-coordinate with four phosphonate oxygen atoms (O1, O4, O1A, O4A) from two separate hedp^{4-} ligands. The Cu2 is also four-coordinate by two phosphonate oxygen atoms (O5 and O5B) from two different hedp^{4-} ligands and two oxygen atoms (O9 and O9B) from two water molecules. The Cu3 ion, however, is five-coordinate with four phosphonate oxygen atoms (O1A, O2C, O4, O6D) from four separate hedp^{4-} ligands and one oxygen atom (O8) from water. The Cu–O bond lengths range from 1.9195 to 2.3621(19) Å, comparable to those in other Cu phosphonate compounds [17–19].

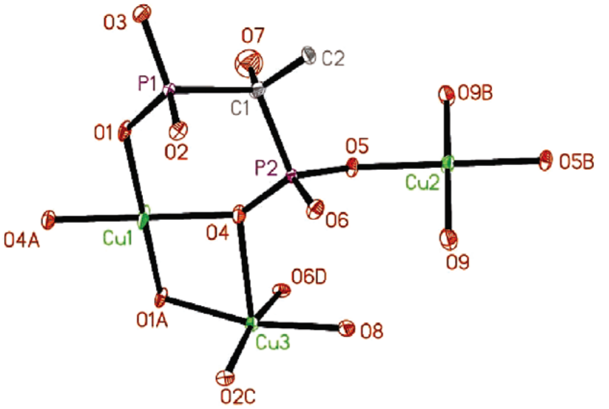

Figure 1. Asymmetric unit of **1** showing the atom labeling. Thermal ellipsoids are shown at the 30% probability level. All H atoms and water molecules are omitted for clarity. Symmetry codes: A: $-x+1/2$, $-y-1/2$, $-z+2$; B: $-x$, $-y$, $-z+2$; C: x, $-y$, $z-1/2$; D: $-x+1/2$, $y+1/2$, $-z+5/2$.

There is one 1-hydroxyethylidenediphosphonic acid in the asymmetric unit. The hedp^{4-} is a hepta-dentate ligand, connecting six Cu ions through five phosphonate oxygen atoms; one phosphonate oxygen atom (O3) and one hydroxyl oxygen atom (O7) from the hedp^{4-} ligand are not coordinated to Cu. Based on charge balance, the 1-hydroxyethylidenediphosphonic acid should carry four negative charges, in other words, the four phosphonate oxygen atoms of each hedp^{4-} ligand should be deprotonated to balance the charges of two Cu(II) ions.

Compound **1** can be described as a 3D open-framework structure with a one-dimensional channel system along the *b* axis. The structure is dissimilar to the copper diphosphonate $Cu_4\{CH_3C(OH)(PO_3)_2\}_2(C_4H_4N_2)(H_2O)_4$ [20], which comprises $\{Cu_4(hedp)_2(H_2O)_2\}_n$ layers connected by pyrazine bridges to form a 3D framework structure. In **1**, two [Cu(3)O_5] distorted trigonal bipyramids and one [Cu(1)O_4] unit are interconnected into a trimer *via* edge-sharing, and these trimers are further linked by bridging [CPO_3] tetrahedra leading to a $[Cu_3(hedp)_2]^{2-}$ anion layer (figure 2). The layers are linked by [Cu(2)O_4] units to form a 3D open-framework structure with a one-dimensional channel system along the *b* axis (figure 3). The channel is assembled by 16-atom rings (9.1 Å × 4.6 Å, estimated by measuring the distances between the centers of opposite atoms), which consist of four Cu, four P, and eight O atoms with the sequences Cu–O–P–O–Cu–O–P–O–Cu–O–P–O–Cu–O–P–O.

Compound **2** crystallizes in space group $P\bar{1}$. The structure is illustrated in figure 4. Within **2**, two different types of Zn ions are found. The Zn1 and Zn2 ions are tetrahedrally coordinated by four oxygen atoms from hedp^{4-} ligands. The Zn3 ion is a distorted octahedron. Five of the six coordination positions are filled with four phosphonate oxygen atoms (O2, O5, O8, O11) and one hydroxyl oxygen atom (O14) from two hedp^{4-} ligands. The remaining site is occupied by oxygen atom (O15) from one water molecule. The Zn–O bond lengths range from 1.907(4) to 2.336(6) Å. These values are in agreement with those reported for other Zn phosphonate compounds [5–7].

Compound **2** shows a 2D layered structure, and the protonated ethylenediamine cations and water molecules are located between two adjacent layers (figure 5).

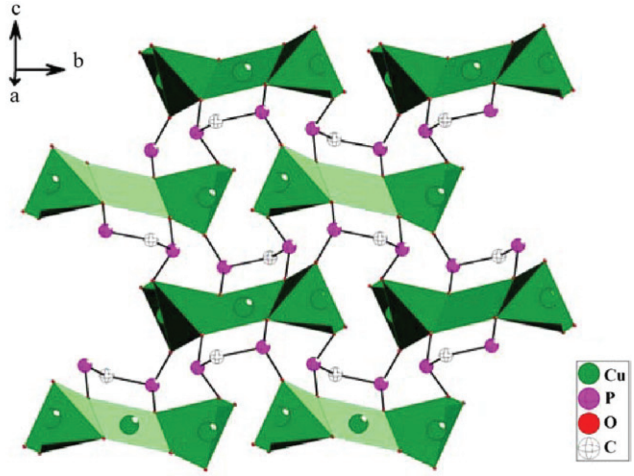

Figure 2. A ball-and-stick and polyhedral representation of the framework structure of **1**.

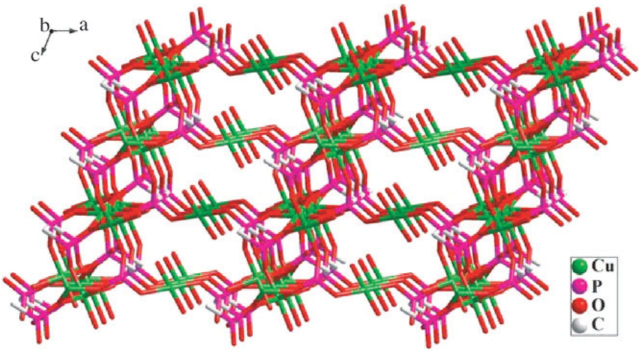

Figure 3. View of the 3D framework structure of **1** along the *b* axis.

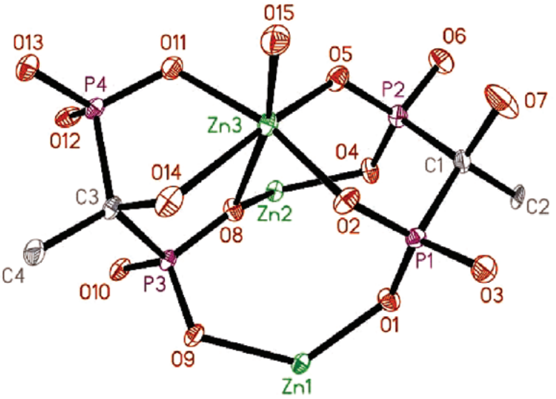

Figure 4. Asymmetric unit of **2** showing the atom labeling. Thermal ellipsoids are shown at the 30% probability level. All H atoms, ethylenediamine cations and water molecules are omitted for clarity.

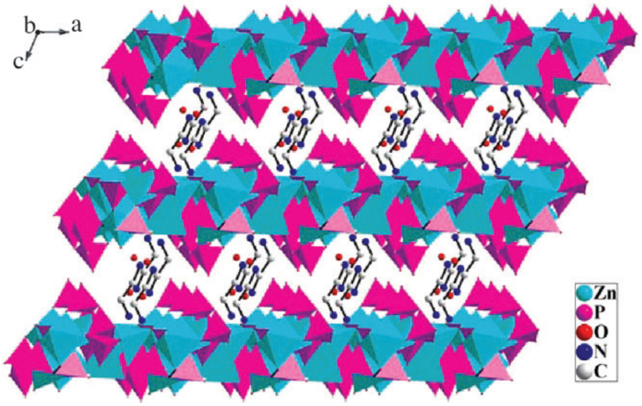

Figure 5. The 2D layered structure of **2** viewed along the *b*-axis.

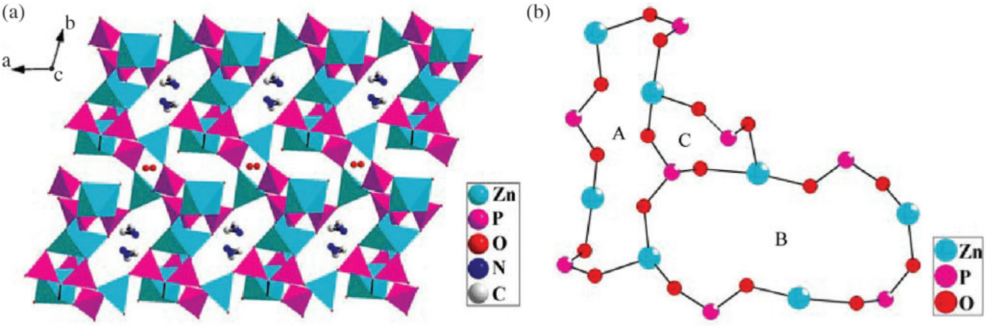

Figure 6. (a) Polyhedral representation of a Zn(II) phosphonate layer for **2** in the *ab* plane; (b) Ball and stick representation of **2** viewed in the *ab* plane, showing the three channel systems.

Within the layer, the connections of alternately arranged [ZnO_4] tetrahedra, [ZnO_6] octahedra and [CPO_3] tetrahedra *via* vertex-sharing result in a layered structure in the *ab* plane (figure 6a). The result of connections in this manner is the formation of three channel systems (figure 6b). Channels (A) and (B) are 16-member rings assembled with the same sequences Zn–O–P–O–Zn–O–P–O–Zn–O–P–O–Zn–O–P–O and the charge-compensating protonated ethylenediamine cations reside in channel (A). Channel (C) is an 8-member ring and the water molecules reside in this channel.

3.2. *IR spectra*

The IR spectra were recorded between 4000 and 400 cm^{-1} and the two compounds are similar. The absorption band at 3454 cm^{-1} for **1** can be assigned to the O–H stretching vibrations of hydroxyl groups (including water molecules and the 1-hydroxyethylidenediphosphonic acid). A sharp band at 1637 cm^{-1} is attributed to the H–O–H bending vibration of water molecules [22]. The weak absorption band at 1429 cm^{-1} is due to the bending vibration of C–H. The set of bands between 1200 and 900 cm^{-1} is assigned to the stretching vibrations of the tetrahedra CPO_3 groups [23,24]. The IR spectrum of **2** also shows a weak band at 2942 cm^{-1} which can be attributed to the N–H stretching vibrations of the protonated [$NH_2CH_2CH_2NH_2$] molecules [21].

3.3. *Thermogravimetric analysis*

Thermogravimetric analyses of **1** and **2** have been performed in the temperature range 50–700°C. The first step of **1** starts at 70°C and is completed at 302°C, corresponding to the release of water. The observed weight loss of 12.15% is very close to the calculated value (12.03%). The weight loss above 365°C is due to decomposition of the organic faction. Thermogravimetric analysis diagram of **2** indicates complicated overlapping steps of weight loss. The weight loss (20.25%) in the temperature range 50–605°C is higher than those calculated (18.79%) for removal of water, the release of ethylenediamine molecules and the decomposition of the phosphonate group.

Supplementary material

Crystallographic data for the structure of **1** and **2** reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC Number 634150 for **1** and 641417 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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