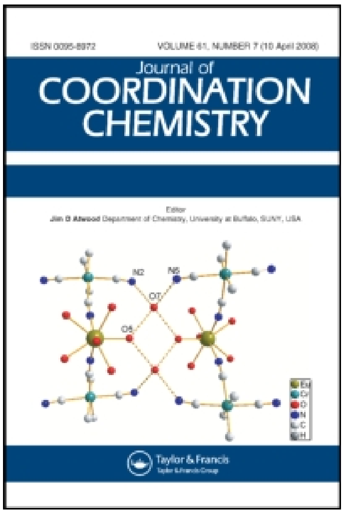

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Hydrothermal syntheses, crystal structures and thermal stabilities of three lanthanide(III) diphosphonates

Hui Chen[a]; Jing Li[a]; Zhengang Sun[a]; Yanyu Zhu[a]; Jing Zhang[a]; Yan Zhao[a]; Na Zhang[a]; Xin Lu[a]; Lei Liu[a]
[a] Faculty of Chemistry and Chemical Engineering, Institute of Chemistry for Functionalized Materials, Liaoning Normal University, Dalian 116029, P.R. China

To cite this Article Chen, Hui , Li, Jing , Sun, Zhengang , Zhu, Yanyu , Zhang, Jing , Zhao, Yan , Zhang, Na , Lu, Xin and Liu, Lei(2009) 'Hydrothermal syntheses, crystal structures and thermal stabilities of three lanthanide(III) diphosphonates', Journal of Coordination Chemistry, 62: 2, 294 — 301

To link to this Article: DOI: 10.1080/00958970802233151

URL: http://dx.doi.org/10.1080/00958970802233151

Journal of Coordination Chemistry
Vol. 62, No. 2, 20 January 2009, 294–301

Hydrothermal syntheses, crystal structures and thermal stabilities of three lanthanide(III) diphosphonates

HUI CHEN, JING LI, ZHENGANG SUN*, YANYU ZHU, JING ZHANG,
YAN ZHAO, NA ZHANG, XIN LU and LEI LIU

Faculty of Chemistry and Chemical Engineering, Institute of Chemistry for
Functionalized Materials, Liaoning Normal University, Dalian 116029, P.R. China

(*Received 14 March 2008; in final form 1 April 2008*)

Three lanthanide diphosphonates, $[NH_3(CH_2)_4NH_3]Ln[hedpH][hedpH_2]$ (Ln = Sm (**1**), Gd (**2**), Dy (**3**); hedp = 1-hydroxyethylidenediphosphonate), have been synthesized by hydrothermal reaction with 1,4-diaminobutane as the template and characterized by single-crystal X-ray diffraction, infrared spectroscopy, elemental analysis and thermogravimetric analysis. The vertex-sharing connections of the LnO_7 polyhedra and CPO_3 tetrahedra result in an infinite chain along the *b* axis. The chains are cross-linked by hydrogen bonds to form a three-dimensional network with channels containing the $[NH_3(CH_2)_4NH_3]^{2+}$ cations.

Keywords: Metal phosphonates; Crystal structure; Hydrothermal synthesis; Lanthanide(III)

1. Introduction

Metal phosphonates form interesting structures with potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and materials chemistry [1–3]. Efforts have been devoted to synthesis of inorganic-organic hybrid materials based on metal phosphonates, which exhibit a variety of structures such as one-dimensional (1-D) chains, two-dimensional (2-D) layers, and three-dimensional (3-D) networks [4–6]. Studies of metal phosphonates show that bi- and multifunctional phosphonic acids containing $–NH_2$, –OH, and –COOH functional groups provide many coordination modes resulting in new structure types and interesting properties [7, 8].

A series of metal phosphonates, using phosphonic acids with amine, hydroxyl, and carboxylate groups, have also been isolated in our laboratory [9]. For construction of inorganic-organic hybrid compounds, diphosphonic acids, $H_2O_3P–R–PO_3H_2$ (R = alkyl or aryl group), are very useful [10–12]. Recently, 1-hydroxyethylidenediphosphonic acid ($hedpH_4$) has been used as a ligand to synthesis of metal phosphonates with open-framework structures, since it can adopt various coordination modes under different reaction conditions resulting in various structures [13–15]. As part of a program of investigating metal diphosphonates, we are interested in exploring new

---

*Corresponding author. Email: szg188@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802233151

lanthanide phosphonate compounds based on 1-hydroxyethylidenediphosphonic acid ($hedpH_4$). In this article, we report the synthesis, crystal structure, and thermal stability of three new lanthanide diphosphonates $[NH_3(CH_2)_4NH_3]Ln[hedpH][hedpH_2]$ [Ln = Sm (**1**), Gd (**2**) and Dy (**3**)] containing 1-hydroxyethylidenediphosphonic acid.

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. The lanthanide(III) chlorides were prepared by dissolving corresponding lanthanide oxides (General Research Institute for Nonferrous Metals, 99.99%) in hydrochloric acid followed by recrystallization and drying. All other chemicals were used as obtained without purification. C, H and N were determined by using a PE-2400 elemental analyzer. Sm, Gd, Dy 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 800°C.

2.2. *Synthesis of $[NH_3(CH_2)_4NH_3]Sm[hedpH][hedpH_2]$ (1)*

A mixture of $SmCl_3 \cdot 6H_2O$ (0.36 g, 1 mmol), $hedpH_4$ solution (0.5 ml, 50.0 wt%), NH_4F (0.14 g, 4 mmol) and 8 ml of H_2O, adjusted by 1,4-diaminobutane to pH = 5, was sealed in a 23 ml Teflon-lined stainless steel autoclave, and then heated at 150°C for 36 h. The final pH was 6.0. After the mixture cooled slowly to room temperature, colorless block crystals were filtered off, washed with distilled water, and dried at room temperature (Yield: 0.54 g, 83.4% based on Sm). Anal. Calcd for **1**, $C_8H_{25}SmN_2O_{14}P_4$ (%): C, 14.83; H, 3.86; N, 4.32; P, 19.15; Sm, 23.22. Found: C, 14.92; H, 3.81; N, 4.27; P, 19.28; Sm, 23.35%. Selected IR bands (4000–400 cm^{-1} region): 3369, 3201, 2929, 1620, 1487, 1150, 1074, 966, 932, 817, 655, 559, 452.

2.3. *Synthesis of $[NH_3(CH_2)_4NH_3]Gd[hedpH][hedpH_2]$ (2)*

The procedure was the same as that for **1** except that $SmCl_3 \cdot 6H_2O$ was replaced by $GdCl_3 \cdot 6H_2O$ (0.36 g, 1 mmol). Yield: 0.55 g, 84.0% based on Gd. Anal. Calcd (%) for **2**, $C_8H_{25}GdN_2O_{14}P_4$: C, 14.67; H, 3.82; N, 4.28; P, 18.95; Gd, 24.03. Found: C, 14.72; H, 3.88; N, 4.35; P, 18.89; Gd, 24.12%. Selected IR bands (4000–400 cm^{-1} region): 3366, 3210, 2925, 1629, 1494, 1142, 1066, 972, 938, 823, 653, 558, 449.

2.4. *Synthesis of $[NH_3(CH_2)_4NH_3]Dy[hedpH][hedpH_2]$ (3)*

The procedure was the same as that for **1** except that $SmCl_3 \cdot 6H_2O$ was replaced by $DyCl_3 \cdot 6H_2O$ (0.36 g, 1 mmol). Yield: 0.54 g, 81.9% based on Dy. Anal. Calcd (%)

for **3**, $C_8H_{25}DyN_2O_{14}P_4$: C, 14.55; H, 3.79; N, 4.24; P, 18.79; Dy, 24.63. Found: C, 14.48; H, 3.71; N, 4.30; P, 18.72; Dy, 24.75%. Selected IR bands (4000–400 cm^{-1} region): 3360, 3205, 2939, 1644, 1486, 1149, 1073, 978, 942, 960, 815, 660, 540, 442.

2.5. *Crystal structure determinations of 1–3*

Suitable single crystals for **1**–**3** 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. The cell constants were indexed from reflections obtained from 60 frames with an exposure time of 10 s/frame. A hemisphere of intensity data was collected with ω–scans in the range $2.07^\circ \leq \theta \leq 26.50^\circ$ for **1**, $2.06^\circ \leq \theta \leq 26.50^\circ$ for **2** and $2.06^\circ \leq \theta \leq 26.49^\circ$ for **3**. 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 by SHELXTL-97 [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically with fixed isotropic thermal parameters, and included in the structure factor calculations. A summary of crystal data and structure refinements for the three compounds is listed in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

Compounds **1**–**3** are isostructural, hence only the structure of **2** will be discussed in detail as representative. Compound **2** crystallizes in triclinic space group $P\bar{1}$, consisting of one unique Gd(III) ion, two independent $hedp^{4-}$ ligands and one $[NH_3(CH_2)_4NH_3]^{2+}$ cation in the asymmetric unit (figure 1). A fragment of the chain structure is illustrated in figure 2. Each Gd is seven-coordinate with seven phosphonate oxygen atoms from four separate $hedp^{4-}$ ligands. The Gd–O distances range from 2.271(5) to 2.481(5) Å (see table 2), which are comparable to those reported for other Gd(III) phosphonate compounds [17, 18]. The average Ln–O distances are 2.378(6) Å for **1**, 2.359(5) Å for **2** and 2.331(11) Å for **3**, only small change in bond distance with decreasing radius of the lanthanide.

Two $hedp^{4-}$ groups in **2** have different coordination environments, one is tetradentate chelating two Gd ions through four phosphonate oxygen atoms (O1, O2, O4 and O5) and the other $hedp^{4-}$ is tridentate connecting two Gd ions through three phosphonate oxygen atoms (O8, O10 and O12). In two $hedp^{4-}$ groups, three phosphonate oxygens (O6, O9 and O13) are protonated and two phosphonate oxygens (O3 and O11) are pendant; two hydroxyl oxygen atoms (O7 and O14) from two other $hedp^{4-}$ ligands are not coordinated and are protonated.

Compound **2** can be described as a 3-D open-framework structure with channels along the *b* axis. The structure is dissimilar to $[Ln(hedpH_3)(hedpH_2)] \cdot 5H_2O$ [19], which contains hydrogen bonds between water molecules in the interstitial region of the crystal. In the network structure of **2**, the connections of GdO_7 polyhedra and CPO_3 tetrahedra *via* vertex-sharing result in an infinite chain (figure 3). The chains are

Table 1. Crystal data and structure refinement for **1**–**3**.

Compounds	**1**	**2**	**3**
Empirical formula	$C_8H_{25}SmN_2O_{14}P_4$	$C_8H_{25}GdN_2O_{14}P_4$	$C_8H_{25}DyN_2O_{14}P_4$
Formula weight	647.53	654.43	659.68
Crystal size (mm^3)	0.09 × 0.05 × 0.04	0.07 × 0.06 × 0.05	0.27 × 0.15 × 0.13
Temperature (K)	295(2)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	10.1366(19)	10.1305(13)	10.099(3)
b	10.594(2)	10.5444(14)	10.494(2)
c	10.894(2)	10.9416(14)	10.967(3)
α	66.282(3)	66.076(2)	65.839(3)
β	89.375(3)	89.166(2)	88.949(4)
γ	68.535(3)	68.490(2)	68.473(3)
V (Å^3)	983.9(3)	981.5(2)	974.5(4)
Z	2	2	2
D_{Calcd} (g cm^{-3})	2.186	2.214	2.248
Absorption coefficient (mm^{-1})	3.383	3.778	4.236
$F(000)$	642	646	650
θ range for data collection (°)	2.07–26.50	2.06–26.50	2.06–26.49
Limiting indices	$-11 \le h \le 12$, $-12 \le k \le 13$, $-13 \le l \le 1$	$-12 \le h \le 12$, $-13 \le k \le 11$, $-13 \le l \le 13$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-11 \le l \le 13$
Reflections collected	5700	5846	5705
Independent reflections	3967 ($R_{\mathrm{int}} = 0.0365$)	3967 ($R_{\mathrm{int}} = 0.0336$)	3932 ($R_{\mathrm{int}} = 0.0257$)
Completeness to $\theta = 26.50$	97.1%	97.3%	97.3%
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.8738 and 0.7551	0.8278 and 0.7779	0.6048 and 0.3976
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.018	1.014	1.127
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0546$, $wR_2 = 0.1103$	$R_1 = 0.0464$, $wR_2 = 0.0896$	$R_1 = 0.0786$, $wR_2 = 0.2185$
R indices (all data)	$R_1 = 0.0779$, $wR_2 = 0.1217$	$R_1 = 0.0640$, $wR_2 = 0.0998$	$R_1 = 0.0804$, $wR_2 = 0.2194$

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

cross-linked by hydrogen bonds to form a three-dimensional network (figure 4). The O⋯O distances are 2.606(8) and 2.491(7) Å for O(6)⋯O(11)$^{\mathrm{i}}$ and O(9)⋯O(3)$^{\mathrm{ii}}$ (symmetry code: i: $x, y, z+1$; ii: $x+1, y-1, z$), respectively. The $[NH_3(CH_2)_4NH_3]^{2+}$ cations reside in the channels with extensive hydrogen-bonding interactions. The three shortest N⋯O distances are 2.714(8), 2.750(9) and 2.845(8) Å for N(1)⋯O(11)$^{\mathrm{iii}}$, N(2)⋯O(3), and N(1)⋯O(7) (symmetry code for iii: $-x+1$, $-y-1$, $-z-1$), respectively (see table 3). The bond lengths and angles for $[NH_3(CH_2)_4NH_3]^{2+}$ are normal.

3.2. *IR spectra*

IR spectra for the three compounds are almost identical and only the spectrum of **2** will be discussed. The IR spectrum of **2** exhibits a few broad bands in the 2500–3500 cm^{-1} range, corresponding to O–H stretching of hydroxyl groups and N–H stretching of $[NH_3(CH_2)_4NH_3]^{2+}$ cations. The O–H bending vibration of the hydroxyl groups is

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

Compounds	**1**	**2**	**3**
Ln(1)–O(8)	2.287(6)	2.271(5)	2.230(12)
Ln(1)–O(2)#1	2.344(6)	2.326(5)	2.301(11)
Ln(1)–O(4)	2.339(6)	2.328(5)	2.302(12)
Ln(1)–O(5)#1	2.359(6)	2.339(5)	2.307(11)
Ln(1)–O(1)	2.385(5)	2.363(5)	2.332(10)
Ln(1)–O(10)#2	2.424(5)	2.402(5)	2.404(11)
Ln(1)–O(12)#2	2.508(6)	2.481(5)	2.444(10)
O(8)–Ln(1)–O(2)#1	83.5(2)	82.97(19)	82.3(4)
O(8)–Ln(1)–O(4)	98.8(2)	100.55(19)	101.2(5)
O(2)#1–Ln(1)–O(4)	78.4(2)	78.11(18)	77.1(4)
O(8)–Ln(1)–O(5)#1	125.3(2)	123.1(2)	121.8(5)
O(2)#1–Ln(1)–O(5)#1	75.3(2)	75.58(18)	76.2(4)
O(4)–Ln(1)–O(5)#1	124.3(2)	124.56(19)	124.8(4)
O(8)–Ln(1)–O(1)	150.2(2)	150.93(19)	151.7(4)
O(2)#1–Ln(1)–O(1)	124.5(2)	124.79(18)	125.1(4)
O(4)–Ln(1)–O(1)	79.40(19)	79.60(17)	80.7(4)
O(5)#1–Ln(1)–O(1)	76.7(2)	76.99(17)	76.6(4)
O(8)–Ln(1)–O(10)#2	87.0(2)	85.76(18)	83.4(4)
O(2)#1–Ln(1)–O(10)#2	137.2(2)	136.68(18)	132.9(4)
O(4)–Ln(1)–O(10)#2	144.4(2)	145.19(17)	149.9(4)
O(5)#1–Ln(1)–O(10)#2	76.8(2)	76.14(17)	73.9(4)
O(1)–Ln(1)–O(10)#2	78.56(19)	78.88(17)	81.7(4)
O(8)–Ln(1)–O(12)#2	76.4(2)	77.35(19)	77.5(4)
O(2)#1–Ln(1)–O(12)#2	140.1(2)	139.76(17)	139.0(4)
O(4)–Ln(1)–O(12)#2	71.2(2)	71.59(17)	72.3(4)
O(5)#1–Ln(1)–O(12)#2	143.88(19)	144.10(16)	144.4(4)
O(1)–Ln(1)–O(12)#2	74.8(2)	75.17(17)	76.2(4)
O(10)#2–Ln(1)–O(12)#2	76.17(19)	76.63(16)	79.8(4)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y$, $-z-1$; #2: $-x+1$, $-y-1$, $-z-1$.

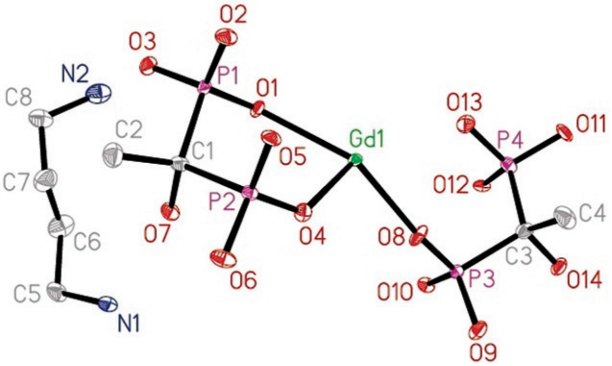

Figure 1. Asymmetric unit of **2** showing the atom labeling. Thermal ellipsoids are shown at the 30% probability level. All H atoms and water molecules are omitted for clarity.

located at 1640 cm^{-1}. The weak absorption band around 1486 cm^{-1} is due to bending of C–H. The set of bands between 1200 and 900 cm^{-1} are assigned to stretching vibrations of tetrahedral CPO_3 groups [20, 21]. Additional medium and sharp bands at low energy (between 850 and 400 cm^{-1}) are probably due to bending vibrations of CPO_3.

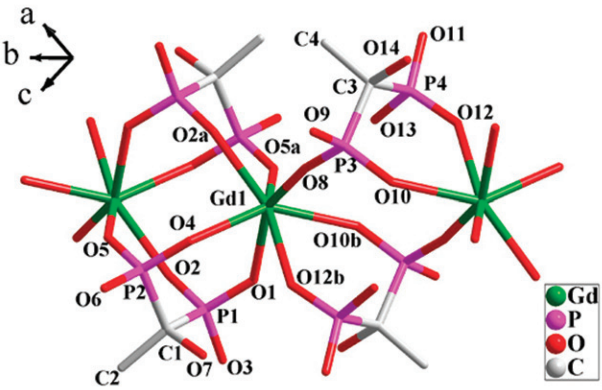

Figure 2. A fragment of the chain in **2** along *b* axis. Symmetry codes: (a) $-x+1, -y, -z-1$; (b) $-x+1, -y-1, -z-1$.

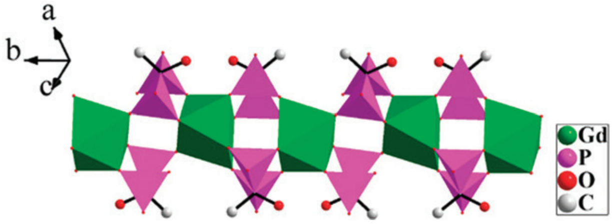

Figure 3. Polyhedral representation of the chain in **2** along *b* axis. GdO_7 polyhedra are shaded in green and CPO_3 tetrahedra are shaded in purple (color online only). All H atoms have been omitted for clarity.

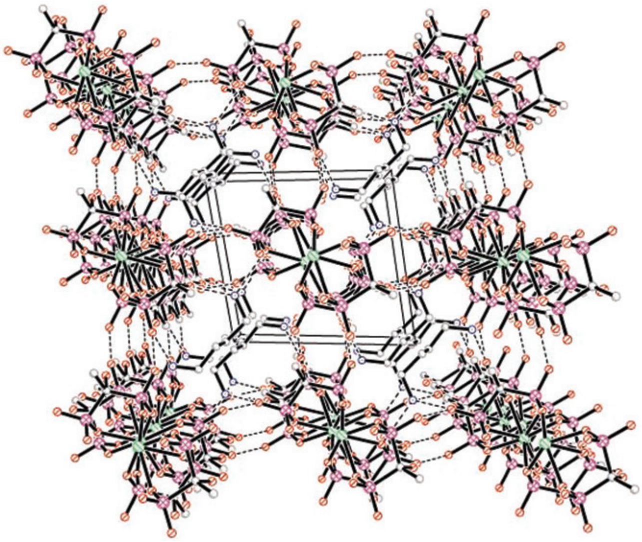

Figure 4. Crystal packing of **2** viewed along *b* axis.

Table 3. Distances between hydrogen bonded atoms (Å) for **1**–**3**.

D–H···A	**1**	**2**	**3**
O(6)–H(6A)···O(11)^{i}	2.601(9)	2.606(8)	2.583(16)
O(9)–H(9A)···O(3)^{ii}	2.491(8)	2.491(7)	2.472(16)
N(1)–H(1A)···O(12)^{i}	2.868(9)	2.872(8)	2.861(18)
N(1)–H(1A)···O(4)^{iv}	3.054(9)	3.079(8)	3.063(19)
N(1)–H(1B)···O(7)	2.855(10)	2.845(8)	2.848(18)
N(1)–H(1C)···O(11)^{iii}	2.725(10)	2.714(8)	2.72(2)
N(2)–H(2D)···O(1)^{v}	2.991(10)	3.010(9)	3.00(2)
N(2)–H(2D)···O(5)^{vi}	3.068(10)	3.051(9)	3.03(2)
N(2)–H(2D)···O(10)^{vii}	3.305(10)	3.271(9)	3.25(2)
N(2)–H(2E)···O(14)^{iii}	2.982(10)	3.001(9)	3.00(2)
N(2)–H(2F)···O(3)	2.730(10)	2.750(9)	2.73(2)

Symmetry transformations used to generate equivalent atoms: i: $x, y, z+1$; ii: $x+1, y-1, z$; iii: $-x+1, -y-1, -z-1$; iv: $-x+1, -y-1, -z$; v: $-x, -y, -z-1$; vi: $x-1, y, z$; vii: $x-1, y+1, z$.

3.3. *Thermogravimetric analysis*

Thermogravimetric analysis curves for compounds **1**–**3** are similar and **2** was used as an example. Thermogravimetric analysis of **2** indicates complicated overlapping steps of weight losses. The first step starts at 305°C, completed at 385°C, corresponding to release of 1,4-diaminobutane. The observed weight loss of 13.93% is close to the calculated value (13.75%). The weight loss above 385°C is due to decomposition of the organic faction.

Supplementary material

Crystallographic data for the structure of **1**–**3** reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC Number 641422 for **1**, 641421 for **2** and 641420 for **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

This research was supported by grants from the Natural Science Foundation of Liaoning Province of China (20062140).

References

[1] A. Clearfield. Metal Phosphonate Chemistry. In *Progress in Inorganic Chemistry*, K.D. Karlin (Ed.), Vol. 47, p. 371 (1998), and references therein.
[2] A. Clearfield. *Curr. Opin. Solid State. Mater. Sci.*, **6**, 495 (2002).
[3] S.Y. Song, J.F. Ma, J. Yang, M.H. Cao, K.C. Li. *Inorg. Chem.*, **44**, 2140 (2005).
[4] Y. Fan, G.H. Li, Z. Shi, D. Zhang, J.N. Xu, T.Y. Song, S.H. Feng. *J. Solid State Chem.*, **177**, 4346 (2004).

[5] S.S. Bao, T.W. Wang, Y.Z. Li, L.M. Zheng. *J. Solid State Chem.*, **179**, 413 (2006).

[6] S. Bauer, H. Muller, T. Bein, N. Stock. *Inorg. Chem.*, **44**, 9464 (2005).

[7] J.G. Mao, Z.K. Wang, A. Clearfield. *Inorg. Chem.*, **41**, 3713 (2002).

[8] P. Yin, L.M. Zheng, S. Gao, X.Q. Xin. *Chem. Commun.*, 2346 (2001).

[9] (a) L.Y. Cui, Z.G. Sun, Z.M. Liu, W.S. You, Z.M. Zhu, L. Meng, H. Chen, D.P. Dong. *Inorg. Chem. Commun.*, **9**, 1232 (2006); (b) D.P. Dong, J. Li, Z.G. Sun, X.F. Zheng, H. Chen, L. Meng, Y.Y. Zhu, Y. Zhao, J. Zhang. *Inorg. Chem. Commun.*, **10**, 1109 (2007); (c) Z.G. Sun, L.Y. Cui, Z.M. Liu, D.P. Dong, L. Meng, H. Chen, L.C. Zhang, Z.M. Zhu, W.S. You. *Inorg. Chem. Commun.*, **9**, 1121 (2006); (d) L. Meng, J. Li, Z.G. Sun, X.F. Zheng, D.P. Dong, H. Chen, Y.Y. Zhu, Y. Zhao, J. Zhang. *Z. Anorg. Allg. Chem.*, **643**, 571 (2008).

[10] K. Barthelet, C. Merlier, C. Serre, M.R. Cavellec, D. Riou, G. Férey. *J. Mater. Chem.*, **12**, 1132 (2002).

[11] R.C. Finn, R.S. Rarig, Jr, J. Zubieta. *Inorg. Chem.*, **41**, 2109 (2002).

[12] P. Yin, X.C. Wang, S. Gao, L.M. Zheng. *J. Solid State Chem.*, **178**, 1049 (2005).

[13] X.Y. Yi, L.M. Zheng. *J. Solid State Chem.*, **168**, 263 (2002).

[14] P. Yin, S. Gao, Z.M. Wang, C.H. Yan, L.M. Zheng, X.Q. Xin. *Inorg. Chem.*, **44**, 2761 (2005).

[15] B. Liu, Y.Z. Li, L.M. Zheng. *Inorg. Chem.*, **44**, 6921 (2005).

[16] (a) G.M. Sheldrick. *SHELXTL-97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997); (b) G.M. Sheldrick. *SHELXTL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[17] J.L. Song, C. Lei, J.G. Mao. *Inorg. Chem.*, **43**, 5630 (2004).

[18] D.K. Cao, Y.Z. Li, Y. Song, L.M. Zheng. *Inorg. Chem.*, **44**, 3599 (2005).

[19] K.L. Nash, R.D. Rogers, J. Ferraro, J. Zhang. *Inorg. Chim. Acta*, **269**, 211 (1998).

[20] Z.M. Sun, J.G. Mao, B.P. Yang, S.M. Ying. *Solid State Sci.*, **6**, 295 (2004).

[21] A. Cabeza, X. Ouyang, C.V.K. Sharma, M.A.G. Aranda, S. Bruque, A. Clearfield. *Inorg. Chem.*, **41**, 2325 (2002).