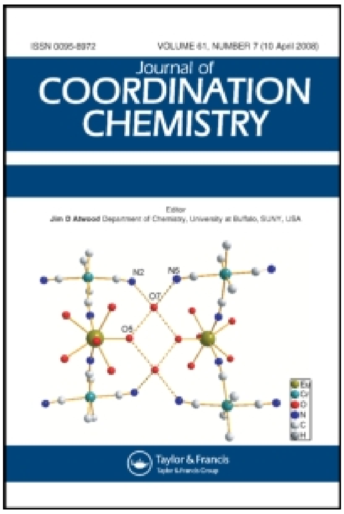

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Hydrothermal syntheses, crystal structures, and thermal stability of two new 3D open-framework metal(II) phosphonates

Lianyi Cui[a]; Zhengang Sun[a]; Hui Chen[a]; Lei Meng[a]; Dapeng Dong[a]; Cuihua Tian[a]; Zaiming Zhu[a]; Wansheng You[a]
[a] Faculty of Chemistry and Chemical Engineering, Institute of Chemistry for Functionalized Materials, Liaoning Normal University, Dalian, P.R. China

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Hydrothermal syntheses, crystal structures, and thermal stability of two new 3D open-framework metal(II) phosphonates

LIANYI CUI, ZHENGANG SUN*, HUI CHEN, LEI MENG,
DAPENG DONG, CUIHUA TIAN, ZAIMING ZHU
and WANSHENG YOU

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

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This article reports the hydrothermal synthesis and characterization of two new phosphonate compounds $NaCo[O_3PCH(OH)CO_2]$ (**1**) and $NaMn[O_3PCH(OH)CO_2]$ (**2**) based on 2-hydroxyphosphonoacetic acid (H_3L). Their structures have been characterized by single-crystal X-ray diffraction as well as with elemental analysis, infrared spectroscopy and thermogravimetric analysis. The two isomorphous compounds crystalline in the orthorhombic, space group *Pbca*: Crystal data for **1**: $a = 10.1827(8)$ Å, $b = 9.6673(8)$ Å, $c = 10.7853(9)$ Å, $V = 1061.70(15)$ Å^3, $Z = 8$, $R_1 = 0.0252$, $wR_2 = 0.0577$; Crystal data for **2**: $a = 10.4309(18)$ Å, $b = 9.7913(17)$ Å, $c = 10.9012(19)$ Å, $V = 1113.4(3)$ Å^3, $Z = 8$, $R_1 = 0.0194$, $wR_2 = 0.0536$. In the two compounds, the metal atoms are octahedrally coordinated; all oxygen atoms from the H_3L ligand are involved in coordination. The overall structures can be described as a 3D open framework with channels running along the *a* axis and the charge-compensating Na^+ cations being located at the intersections of these channels.

Keywords: Metal phosphonates; Crystal structure; Hydrothermal synthesis; Cobalt(II); Manganese(II)

1. Introduction

Metal phosphonates as a new class of inorganic–organic hybrid materials have attracted a great deal of interest as a result of their ability to form interesting structures with potential applications as sorbents, ion exchangers, catalysts, or charge-storage materials [1–3]. Efforts have been devoted to the syntheses of novel inorganic–organic hybrid materials based on metal phosphonates, which exhibt a variety of structures such as one-dimensional chain, two-dimensional layer, and three-dimensional network [4–6].

Among the various metal phosphonate compounds reported so far, those with open-framework or porous structures have received particular attention [7]. The use of bi- and trifunctional phosphonic acids in the synthesis of metal phosphonates can

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*Corresponding author. Tel.: +86-411-82156568. Fax: +86-411-82156858. Email: szg188@163.com

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result in the formation of 3D open-frameworks. Phosphonic acids with hydroxyl and carboxyl groups as ligands could provide many coordination modes, resulting in various interesting structures. In a recent article 2-hydroxyphosphonoacetic acid (H_3L) with a chiral carbon atom and three functional groups (–OH, –COOH, and –PO_3H_2) was used as a ligand to synthesize $(NH_4)Zn[O_3PCH(OH)CO_2]$, which contains a 3D open-framework consisting of interconnected 24-, 16-, and 8-atom channels [8]. We are interested in exploring 3D open-framework metal phosphonate compounds based on 2-hydroxyphosphonoacetic acid (H_3L). In this article, we report the synthesis, crystal structure, and thermal stability of two new 3D open-framework coordination compounds containing 2-hydroxyphosphonoacetic acid as ligand: $NaCo[O_3PCH(OH)CO_2]$ (**1**) and $NaMn[O_3PCH(OH)CO_2]$ (**2**) with channels running along the *a* axis and the charge-compensating Na^+ cations being located at the intersections of these channels.

2. Experimental

2.1. *Materials and methods*

2-hydroxyphosphonoacetic acid solution was obtained from Changzhou City Jianghai Chemical Factory as a water treatment agent (48.0 wt%) and used as received. Other chemicals were obtained from commercial sources and used without further purification. C and H analysis was determined by using a PE-2400 elemental analyzer. Co, Mn 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 and DTA analyses were performed on a Perkin-Elmer Pyris Diamond TG-DTA thermal analysis system in static air with a heating rate of 10 K min^{-1} from 50 to 700°C.

2.2. *Synthesis of $NaCo[O_3PCH(OH)CO_2]$ (1)*

A mixture of $Co(CH_3COO)_2 \cdot 2H_2O$ (0.25 g, 1 mmol), NH_4Cl (1.34 g, 25 mmol), NaF (0.17 g, 4 mmol), 2-hydroxyphosphonoacetic acid solution (0.5 mL, 2 mmol), acetic acid (2 mL, 35 mmol) and 8 mL of water was sealed into a 20 mL Teflon-lined stainless steel autoclave and heated at 150°C for 4 days. After the mixture cooled slowly to room temperature, purple block crystals were filtered off, washed with distilled water, and dried at room temperature (Yield: 0.17 g, 73.9% based on Co). Anal. Calcd for **1**, $C_2H_2CoNaO_6P$ (%): C, 10.23; H, 0.85; P, 13.18; Co, 25.08. Found: C, 10.31; H, 0.92; P, 13.08; Co, 24.85.

2.3. *Synthesis of $NaMn[O_3PCH(OH)CO_2]$ (2)*

Compound **2** was synthesized by a similar method to that used for compound **1.** A mixture of $Mn(CH_3COO)_2 \cdot 2H_2O$ (0.25 g, 1 mmol), NH_4Cl (1.34 g, 25 mmol), NaF (0.17 g, 4 mmol), 2-hydroxyphosphonoacetic acid solution (0.5 mL, 2 mmol), acetic acid (2 mL, 35 mmol) and 8 mL of water was sealed into a 20 mL Teflon-lined stainless steel autoclave and heated at 150°C for 4 days. After the mixture slowly cooled to room temperature, colorless prism-like crystals were collected, washed with distilled water, and dried at room temperature (Yield: 0.14 g, 60.2% based on Mn). Anal. Calcd for **2**, $C_2H_2MnNaO_6P$ (%): C, 10.40; H, 0.87; P, 13.41; Mn, 23.79. Found: C, 10.52; H, 0.95; P, 13.28; Mn, 23.58.

2.4. *Crystal structure determinations of compounds 1 and 2*

Suitable single crystals with dimensions $0.06 \times 0.06 \times 0.03\,\mathrm{mm}^3$ for **1** and $0.21 \times 0.19 \times 0.19\,\mathrm{mm}^3$ for **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 ± 2 K. A hemisphere of intensity data was collected with ω-scans, in the range of $3.47° \leq \theta \leq 26.49°$ for **1** and $3.41 \leq \theta \leq 26.49°$ for **2**. Numbers of measured and observed reflections $[I > 2\sigma(I)]$ are 5728 and 1103 ($R_{\mathrm{int}} = 0.0434$) for **1**, and 6000 and 1147 ($R_{\mathrm{int}} = 0.0177$) for **2**, respectively. An empirical absorption correction was applied using the SADABS program with $T_{\max} = 0.9001$ and $T_{\min} = 0.8057$ for **1** and $T_{\max} = 0.6274$ and $T_{\min} = 0.6004$ for **2**. The structures were solved in the space group *Pbca* by direct methods and refined by full-matrix least squares fitting on F^2 by SHELXTL-97 [9]. 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. The final Fourier map had a minimum and maximum electron density of −0.399 and $0.378\,\mathrm{e\,Å^{-3}}$ for **1** and −0.327 and $0.483\,\mathrm{e\,Å^{-3}}$ for **2**. 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.

3. Results and discussion

3.1. *X-ray structure*

Compounds **1** and **2** are isomorphous with the space group *Pbca*. Compound **1** is taken as an example to describe their structures in detail. Analysis of the single crystal data reveals one Co(II) ion, one L^{3-} ($L = O_3PCH(OH)CO_2$) ligand, and one Na^+ ion in the asymmetric unit of compound **1** (figure 1). Each cobalt(II) ion is octahedrally coordinated by three phosphonate oxygen atoms from three separate L^{3-} ligands (the Co–O distances range from 2.016(2) to 2.159(2) Å), two carboxylate oxygen atoms from two separate L^{3-} ligands (the Co–O bond lengths are 2.112(2) and 2.148(2) Å, respectively) and one hydroxyl oxygen atom (the Co–O bond length is 2.205(2) Å). These values are close to those reported for other analogous six-coordinate cobalt(II) phosphonates [10–12].

As a result, all the oxygen atoms from the L^{3-} ligand are involved in coordination, monodentate connecting cobalt ions. Each $[CPO_3]$ tetrahedron connects three $[CoO_6]$ octahedra *via* three phosphonate oxygen atoms, and each $[CoO_6]$ octahedron connects three $[CPO_3]$ tetrahedra through three phosphonate oxygen atoms. The three $[CPO_3]$ tetrahedra pointed to *a*, *b*, and *c* directions, the O(1)–Co(1)–O(2)#1, the O(2)#1–Co(1)–O(3)#3 and O(3)#3–Co(1)–O(1) angles are 105.76(9), 96.94(8)

Table 1. Crystal data and structure refinement for compounds **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_2H_2CoNaO_6P$	$C_2H_2MnNaO_6P$
Formula weight	234.93	230.94
Crystal size (mm^3)	$0.06 \times 0.06 \times 0.03$	$0.21 \times 0.19 \times 0.19$
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a (Å)	10.1827(8)	10.4309(18)
b (Å)	9.6673(8)	9.7913(17)
c (Å)	10.7853(9)	10.9012(19)
V (Å^3)	1061.70(15)	1113.4(3)
Z	8	8
D_c (g cm^{-3})	2.939	2.755
Absorption coefficient	3.583	2.705
$F(000)$	920	904
θ range for data collection	3.47 to 26.49	3.41 to 26.49
Limiting indices	$-10 \le h \le 12$, $-12 \le k \le 11$, $-13 \le l \le 12$	$-12 \le h \le 13$, $-12 \le k \le 12$, $-10 \le l \le 13$
Reflections collected	5728	6000
Independent reflections	1103 ($R_{\text{int}} = 0.0434$)	1147 ($R_{\text{int}} = 0.0177$)
Completeness to $\theta = 26.50$	100.0%	99.9%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.9001 and 0.8057	0.6274 and 0.6004
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.035	1.077
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0252$, $wR_2 = 0.0577$	$R_1 = 0.0194$, $wR_2 = 0.0536$
R indices (all data)	$R_1 = 0.0340$, $wR_2 = 0.0618$	$R_1 = 0.0206$, $wR_2 = 0.0544$

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

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

Compound **1**			
Co(1)–O(1)	2.029(2)	Co(1)–O(4)#2	2.205(2)
Co(1)–O(2)#1	2.016(2)	Co(1)–O(5)#2	2.112(2)
Co(1)–O(3)#3	2.159(2)	Co(1)–O(6)#1	2.148(2)
O(2)#1–Co(1)–O(1)	105.76(9)	O(1)–Co(1)–O(4)#2	155.12(8)
O(2)#1–Co(1)–O(5)#2	169.81(8)	O(5)#2–Co(1)–O(4)#2	71.27(8)
O(1)–Co(1)–O(5)#2	84.42(9)	O(3)#3–Co(1)–O(4)#2	91.79(8)
O(2)#1–Co(1)–O(6)#1	90.56(8)	O(5)#2–Co(1)–O(3)#3	83.30(9)
O(1)–Co(1)–O(6)#1	90.12(8)	O(6)#1–Co(1)–O(3)#3	171.99(8)
O(5)#2–Co(1)–O(6)#1	88.82(9)	O(2)#1–Co(1)–O(4)#2	98.54(8)
O(2)#1–Co(1)–O(3)#3	96.94(8)	O(6)#1–Co(1)–O(4)#2	84.28(8)
O(1)–Co(1)–O(3)#3	90.55(8)		
Compound **2**			
Mn(1)–O(1)	2.0986(14)	Mn(1)–O(4)#3	2.3361(14)
Mn(1)–O(2)#2	2.1882(14)	Mn(1)–O(5)#3	2.2332(14)
Mn(1)–O(3)#1	2.0995(14)	Mn(1)–O(6)#1	2.2180(14)
O(1)–Mn(1)–O(3)#1	110.72(6)	O(5)#3–Mn(1)–O(4)#3	67.05(5)
O(1)–Mn(1)–O(6)#1	92.63(5)	O(2)#2–Mn(1)–O(4)#3	91.59(5)
O(3)#1–Mn(1)–O(6)#1	88.30(5)	O(6)#1–Mn(1)–(4)#3	82.41(5)
O(2)#2–Mn(1)–O(6)#1	170.88(5)	O(3)#1–Mn(1)–O(5)#3	164.64(5)
O(1)–Mn(1)–O(2)#2	89.31(5)	O(2)#2–Mn(1)–O(5)#3	83.62(5)
O(3)#1–Mn(1)–O(2)#2	99.35(5)	O(6)#1–Mn(1)–O(5)#3	87.71(5)
O(1)–Mn(1)–O(4)#3	151.01(5)	O(1)–Mn(1)–O(5)#3	84.28(5)
O(3)#1–Mn(1)–O(4)#3	97.72(5)		

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

and 90.55(8), respectively. The C2 atoms connect two [CoO_6] octahedra *via* two carboxylate oxygen atoms and one [CPO_3] tetrahedron *via* C1 atoms (figure 2).

The above polyhedra are interconnected, resulting in the formation of a complex 3D open framework type with channels running along the *a* axis, with the charge-compensating Na^+ cations being located at the intersections of these channels (figure 3). Different from the channels of other compounds reported [11, 13], the channels are not closed circles, but overlapped by one sequence –O1–Co1–O5–C2–O6–Co1–O1– and two

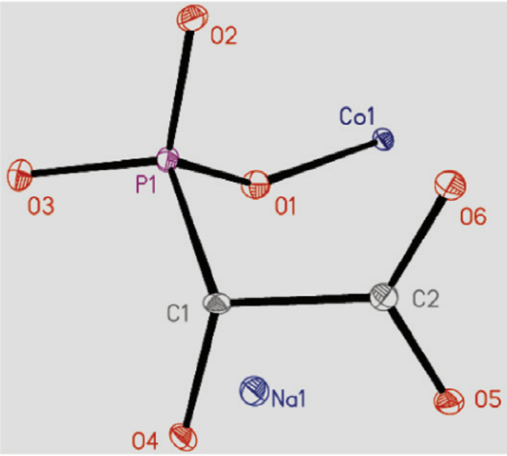

Figure 1. Asymmetric unit of $NaCo[O_3PCH(OH)CO_2]$ showing the atom labeling. Thermal ellipsoids are shown at the 50% probability level.

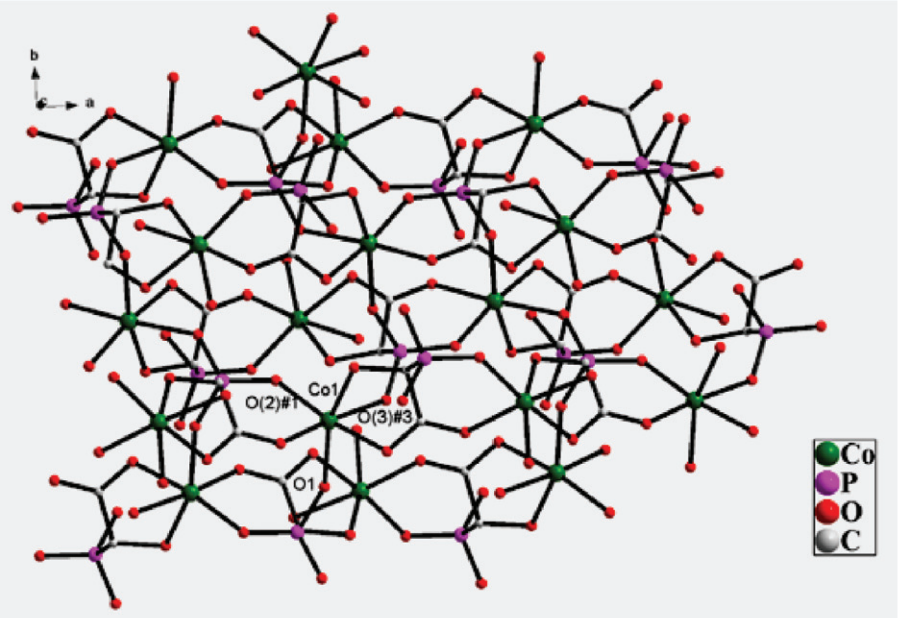

Figure 2. Three-dimensional structure of $NaCo[O_3PCH(OH)CO_2]$. All H and Na atoms have been omitted for clarity. Symmetry codes for the generated atoms: #1; $-x+1$, $-y+2$, $-z+1$, #3; $-x+1/2$, $y+1/2$, z.

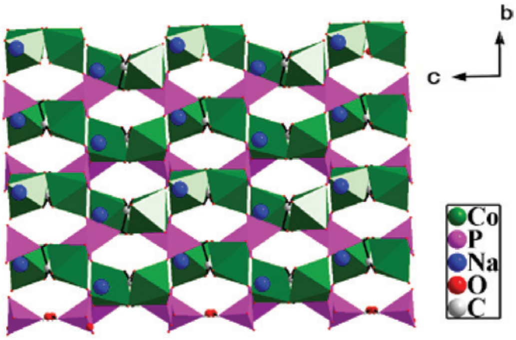

Figure 3. Polyhedral views of three-dimensional structure of NaCo[O_3PCH(OH)CO_2] showing channels along the *a* axis. The green octahedral are [CoO_6], the purple tetrahedral are [O_3PC].

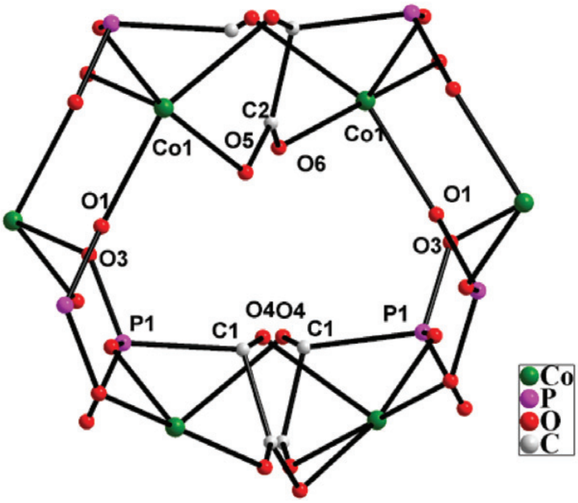

Figure 4. NaCo[O_3PCH(OH)CO_2] viewed along the *a* axis showing the holes in the structure.

sequences –O3–P1–C1–O4–, with O1, O3 and O4 from different organic ligands (figure 4). The dimensions of the channels are ca 2.6 Å (O5–O4) × 4.5 Å (O3–O3).

3.2. *IR spectra*

The IR spectra of the two compounds are almost identical, thus only the spectrum of compound **1** will be discussed. A very strong absorption band around 3448 cm^{-1} corresponds to the O–H stretching vibrations of hydroxyl group of **1**, indicating the hydroxyl oxygen atom is still protonated. This is in agreement with the results of the single-crystal X-ray diffraction studies. A strong band at 1630 cm^{-1} is observed, which is shifted at least 70 cm^{-1} from the expected value of uncoordinated carboxylic acid (ν(C–O) typically around 1725–1700 cm^{-1}) [14]. This large shift is due to the carboxylate function coordinated to the metal. The set of bands between 1274 cm^{-1} and 811 cm^{-1} (1177, 1148, 1081, 987 cm^{-1}) are assigned to stretching vibrations of the tetrahedral CPO_3 groups. The P=O and P–O stretching and bending bands appear

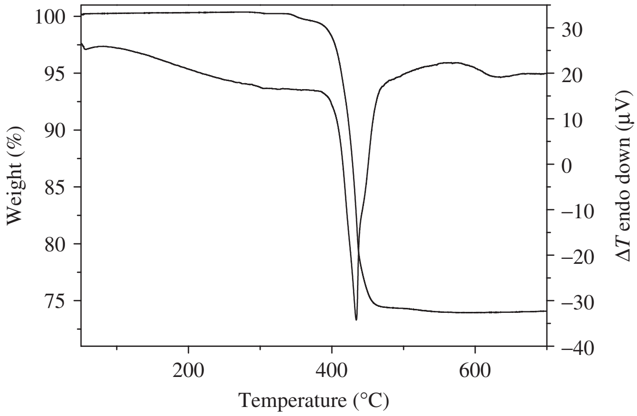

Figure 5. TG–DTA curves for NaCo[$O_3PCH(OH)CO_2$] (**1**).

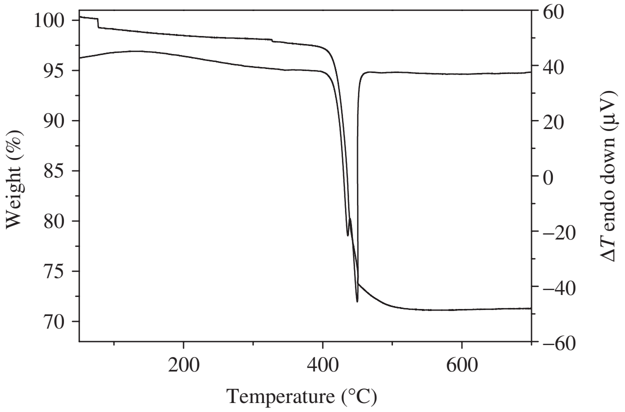

Figure 6. TG–DTA curves for NaMn[$O_3PCH(OH)CO_2$] (**2**).

in the region of 1100–900 cm^{-1}. Additional intensive and sharp bands at low energy (658, 587, and 489 cm^{-1}) are found. These bands are probably due to bending vibrations of the tetrahedral O_3PC groups and Co–O stretching vibrations.

3.3. *Thermogravimetric analysis*

Combined TG–DTA curves for **1** and **2** are shown in figures 5 and 6, respectively. The TG curve indicates that **1** undergoes a rapid weight loss at about 380°C and completed at about 474°C. The total mass loss is 25.0% upon heating to 474°C in static air (calculated 24.7%); compound **2** is thermally stable up to about 405°C and weight loss completed at 501°C, the total mass loss is 25.7% (calculated 25.1%), in good agreement with theoretical values calculated for the following thermal decomposition reactions:

$$\begin{aligned} 6\mathrm{NaM[O_3PCH(OH)CO_2]}\ (s) + 9\mathrm{O_2}\ (g) &\rightarrow 2\mathrm{M_3(PO_4)_2}\ (s) + 2\mathrm{Na_3PO_4}\ (s) \\ &\quad + 6\mathrm{H_2O}\ (g) + 12\mathrm{CO_2}\ (g)\,(\mathrm{M} = \mathrm{Co}, \mathrm{Mn}). \end{aligned}$$

Stronger endothermal peaks appear at approximately 435 and 450°C in the DTA curves of **1** and **2**, respectively, corresponding to the decomposition of the organic groups.

Supplementary material

Crystallographic data for **1** and **2** reported in this article have been deposited with the Cambridge Crystallographic Data center, CCDC Number 602595 for **1** and 602597 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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References

[1] A.K. Cheetham, G. Férey, T. Loiseau. *Angew. Chem., Int. Ed.*, **38**, 3268 (1999).
[2] J. Zhu, X. Bu, P. Feng, G.D. Stucky. *J. Am. Chem. Soc.*, **122**, 11563 (2000).
[3] A. Clearfield. *Curr. Opin. Solid State. Mater. Sci.*, **6**, 495 (2002).
[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] K. Maeda. *Micropor. Mesopor. Mater.*, **73**, 47 (2004).
[8] R.B. Fu, H.S. Zhang, L.S. Wang, S.M. Hu, Y.M. Li, X.H. Huang, X.T. Wu. *Eur. J. Inorg. Chem.*, 3211 (2005).
[9] (a) G.M. Sheldrick. *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997); (b) G.M. Sheldrick. *SHELXS 97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[10] P. Yin, S. Gao, Z.M. Wang, C.H. Yan, L.M. Zheng, X.Q. Xin. *Inorg. Chem.*, **44**, 2761 (2005).
[11] A. Turner, P.A. Jaffrès, E.J. MacLean, D. Villemin, V. McKee, G.B. Hix. *J. Chem. Soc., Dalton Trans.*, 1314 (2003).
[12] A. Distler, S.C. Sevor. *Chem. Commun.*, ,959 (1998).
[13] W.R. Gemmill, M.D. Smith, B.A. Reisner. *J. Solid State Chem.*, **178**, 69 (2002).
[14] N. Stock, T. Bein. *J. Mater. Chem.*, **15**, 1384 (2005).