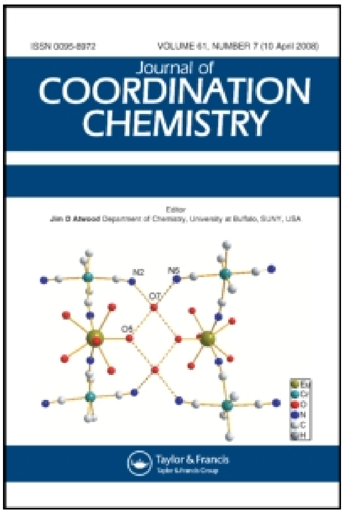

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Hydrothermal synthesis, crystal structure and thermal stability of a new 2D layered metal(II) phosphonate: $[NH_3CH_2CH_2NH_3][Fe_2(O_3PCH(OH)CO_2)_2(H_2O)_2]\cdot 2H_2O$

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In the presence of ethylenediamine template agents, a metal(II) phosphonate, $[NH_3CH_2CH_2NH_3][Fe_2(O_3PCH(OH)CO_2)_2(H_2O)_2]\cdot 2H_2O$ (**1**) has been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction as well as infrared spectroscopy, elemental analysis and thermogravimetric analysis. The compound crystallines in the monoclinic space group $P2_1/n$: Crystal data for **1**: $a=8.4523(8)$ Å, $b=9.8196(9)$ Å, $c=10.9217(10)$ Å, $\beta=105.9500(10)^\circ$, $V=871.58(14)$ Å, $Z=2$, $D_c=2.103\,\mathrm{g\,cm^{-3}}$, $R_1=0.0290$, $wR_2=0.0811$. The Fe (II) cation is octahedrally coordinated by six oxygen atoms from the three ligands and one coordinated water molecule to form a 2D layered structure with a one-dimensional channel system in the *a*-axis direction.

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

1. Introduction

Metal phosphonates are a class of inorganic–organic hybrid materials in which the phosphonate groups are covalently bonded to the metal inorganic backbone. In the recent past, there has been renewed interest in metal phosphonates, mainly due to their varied compositions, structural diversity and potential applications as sorbents, catalysts, ion-exchangers, and sensors [1–5]. Subsequent studies from several research groups have shown that the metal phosphonates usually adopt layered or pillared layered structures [6–10].

The organic part of the phosphonates plays a spacefilling role and participates in the two- and three-dimensional frameworks by strong covalent linkages. Metal phosphonates have been prepared through designing and synthesizing phosphonic acids with amine, hydroxyl, and carboxylate groups. The use of bi- and trifunctional phosphonic acids in the synthesis of metal phosphonates not only result in new

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structural types of metal phosphonates, but also bring interesting properties [11–13]. Among these studies, the phosphonic acids with hydroxyl and carboxyl groups as ligands could provide many coordination modes, resulting in various interesting structures. By using 2-hydroxylphosphonoacetic acid (H_3L) with a chiral carbon atom and three functional groups (–OH, –COOH, and $–PO_3H_2$), we recently reported a 3D metal phosphonate $Mg_{0.5}Cd[O_3PCH(OH)CO_2]$ [14], with CdO_6 and MgO_6 octahedra connected by $[O_3PCH(OH)CO_2]^{3-}$ to form a 3D framework with a one-dimensional channel system in the *a* direction. In this paper, we report the synthesis, crystal structure and thermal stability of a new 2D metal phosphonate containing 2-hydroxyphosphonoacetic acid as ligand, $[NH_3CH_2CH_2NH_3][Fe_2(O_3PCH(OH)CO_2)_2(H_2O)_2]\cdot 2H_2O$ (**1**) with a channels running along the *a*-axis.

2. Experimental

2.1. *Materials and methods*

2-hydroxyphosphonoacetic acid solution was obtained from Luoyang City Jinda 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, H and N were determined by using a PE-2400 elemental analyzer. Fe 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 analysis was 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 $[NH_3CH_2CH_2NH_3][Fe_2(O_3PCH(OH)CO_2)_2(H_2O)_2]\cdot 2H_2O$ (1)*

Compound **1** was synthesized by hydrothermal reaction; 0.28 g (1.0 mmol) $FeSO_4\cdot 7H_2O$, 1 mL (4.0 mmol) 2-hydroxyphosphonoacetic acid (48.0 wt%) and 0.04 g (1.0 mmol) NaF were dissolved in H_2O (10 mL), and then ethylenediamine was added with stirring to adjust the pH of the mixture. The mixture ($pH \approx 5$) was sealed in a 23 mL Teflon-lined stainless steel autoclave, and heated at 150°C for 3 days. After the mixture was cooled slowly to room temperature, colorless block crystals were filtered off, washed with distilled water, and dried at room temperature (Yield: 0.32 g, 58.0% based on Fe). Anal. Calcd for **1**, $C_6H_{22}Fe_2N_2O_{16}P_2$ (%): C, 13.06; H, 4.02; N, 5.08; P, 11.22; Fe, 20.24. Found: C, 13.00; H, 4.34; N, 4.99; P, 11.15; Fe, 20.11.

2.3. *Crystal structure determinations of 1*

A suitable single crystal with dimensions $0.33\times 0.28\times 0.13\ mm^3$ for **1** was 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 295 K. A hemisphere of intensity data was collected with ω-scans, in the range of $2.72^\circ < \theta < 26.99^\circ$. The total number of measured reflections and observed unique reflections were

Table 1. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_6H_{22}Fe_2N_2O_{16}P_2$
Formula weight	551.90
Crystal size (mm^3)	$0.33 \times 0.28 \times 0.13$
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	8.4523(8)
b (Å)	9.8196(9)
c (Å)	10.9217(10)
β (°)	105.9500(10)
V (Å^3)	871.58(14)
Z	2
D_c (g cm^{-3})	2.103
Absorption coefficient	1.937
F (000)	564
Theta range for data collection	2.72 to 26.99
Limiting indices	$-10 \le h \le 9$, $-10 \le k \le 12$, $-13 \le l \le 9$
Reflections collected	4943
Independent reflections	1901 ($R_{\text{int}} = 0.0199$)
Completeness to $\theta = 26.50$	99.8%
Absorption correction	Empirical
Max. and min. transmission	0.7910 and 0.5673
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.088
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0290$, $wR_2 = 0.0811$
R indices (all data)	$R_1 = 0.0305$, $wR_2 = 0.0820$

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

4943 and 1901, respectively. An empirical absorption correction was applied using the SADABS program with $T_{\max} = 0.7910$ and $T_{\min} = 0.5673$. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXTL-97 [15]. 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. The final Fourier map had a minimum and maximum electron density of -0.730 and $0.758\,\text{e}\,\text{Å}^{-3}$. A summary of crystal data and structure refinements for **1** are listed in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Syntheses*

Under hydrothermal conditions, a new iron phosphonate compound **1**, has been prepared. Fluoride was added to improve crystallization of the final products. The same compound was obtained in the absence of NaF. The ethylenediamine was employed as a structure directing agent, and to adjust the pH of the reaction mixture. When the pH is low (2.5–4.5), a recently reported compound $[Fe(CH(OH)(CO_2)(PO_3H)(H_2O)_2]$ was obtained [10], however, increasing the pH to 4.5–5.5 in the same reaction mixture promotes formation of **1**. Other amines have been used to adjust the pH of the reaction mixture, but we failed to collect suitable single crystals for X-ray diffraction.

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

Fe(1)–O(3)#1	2.0528(16)	P(1)–O(1)	1.5206(17)
Fe(1)–O(2)	2.1165(16)	P(1)–O(2)	1.5208(16)
Fe(1)–O(1W)	2.1226(18)	P(1)–O(3)	1.5248(16)
Fe(1)–O(5)#2	2.1626(16)	O(4)–C(1)	1.432(3)
Fe(1)–O(6)#1	2.1669(17)	O(5)–C(2)	1.262(3)
Fe(1)–O(4)#2	2.2065(16)	O(6)–C(2)	1.259(3)
O(3)#1–Fe(1)–O(2)	95.32(7)	O(2)–Fe(1)–O(5)#2	84.51(6)
O(3)#1–Fe(1)–O(1W)	169.00(7)	O(1W)–Fe(1)–O(5)#2	90.25(7)
O(2)–Fe(1)–O(1W)	92.12(7)	O(3)#1–Fe(1)–O(6)#1	86.46(7)
O(3)#1–Fe(1)–O(5)#2	98.51(7)	O(2)–Fe(1)–O(6)#1	105.29(7)
O(1W)–Fe(1)–O(6)#1	83.77(7)	O(5)#2–Fe(1)–O(6)#1	168.64(7)
O(3)#1–Fe(1)–O(4)#2	91.82(6)	O(2)–Fe(1)–O(4)#2	156.39(6)
O(1W)–Fe(1)–O(4)#2	84.50(7)	O(5)#2–Fe(1)–O(4)#2	72.17(6)
O(6)#1–Fe(1)–O(4)#2	97.57(6)	C(1)–O(4)–Fe(1)#3	115.04(12)
P(1)–O(2)–Fe(1)	133.03(10)	C(2)–O(6)–Fe(1)#1	128.13(14)
P(1)–O(3)–Fe(1)#1	129.99(10)	C(2)–O(5)–Fe(1)#3	117.96(14)

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

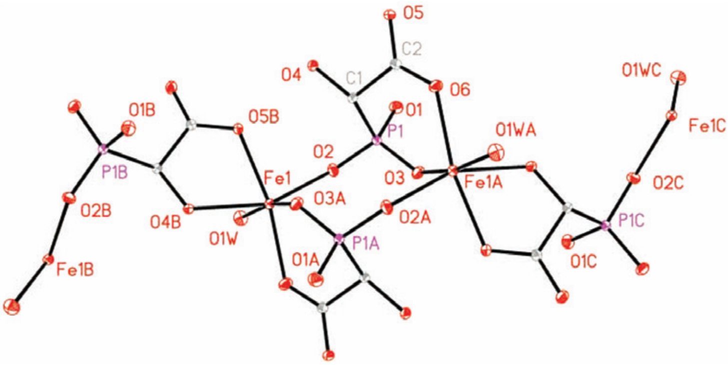

Figure 1. Asymmetric unit of **1** showing the atom labeling. Thermal ellipsoids are shown at the 30% probability level. Symmetry codes: A: $-x$, $-y+1$, $-z+1$; B: $-x+1/2$, $y-1/2$, $-z+3/2$; C: $-x+1$, $-y+2$, $-z+1$.

3.2. *Crystal structure*

A single crystal X-ray structure analysis of **1** revealed that it crystallizes in the monoclinic space group $P2_1/n$. The structure is illustrated in figure 1. The structure of **1** is composed of $[Fe_2(O_3PCH(OH)CO_2)_2(H_2O)_2]^{2-}$ building units and $[NH_3CH_2CH_2NH_3]^{2+}$ cations. Each Fe atom adopts distorted octahedral coordination geometry with six oxygen atoms from the three equivalent L^{3-} ($L = O_3PCH(OH)CO_2$) anions and one coordinated water molecule. The Fe–O bond lengths are in the range of 2.0528(16)–2.2065(16) Å. These values are close to those reported for other six-coordinate iron (II) phosphonates [16–18].

The L^{3-} ligand serves as a pentadentate ligand. Other than phosphonate oxygen O1, all oxygens in L^{3-} are involved in coordination to the Fe atoms; these oxygen atoms chelate and bridge one Fe atom, respectively. The overall structure can be described as the stacking of 2D layers along the *a*-axis (figure 2). In each layer, two $[FeO_5(H_2O)]$ octahedra and two $[CPO_3]$ tetrahedra share coordinated phosphonate oxygens

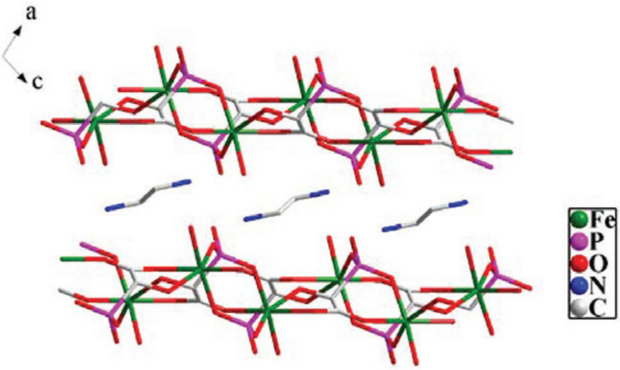

Figure 2. Packing diagram of **1** projected along the *a*-axis.

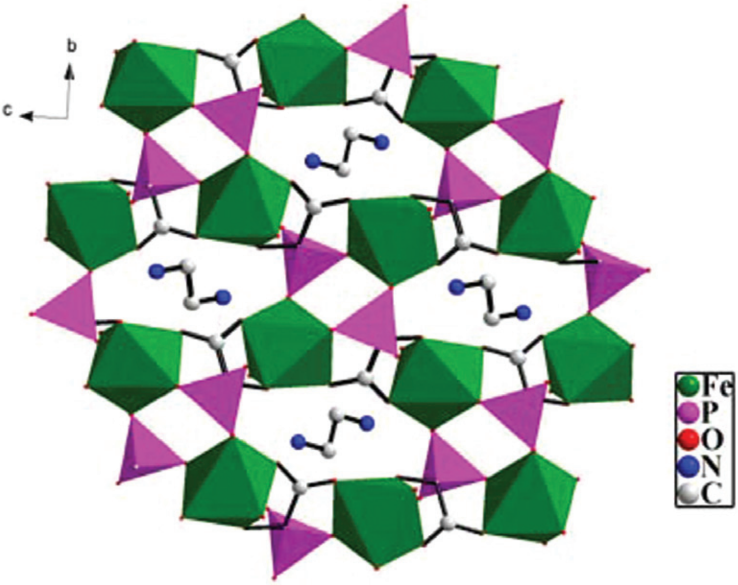

Figure 3. Polyhedral views of two-dimensional framework structures of **1** in the *bc* plane. All H atoms and water molecules are omitted for clarity.

(O2 and O3) to form rectangular, corner-shared [$Fe_2P_2O_4$] building units (figure 3). These so-built units are then cross–linked *via* carboxylate oxygen and hydroxyl oxygen atoms to form layers in *bc* plane. Connecting in this manner results in 1D channels defined by 18-membered rings (4Fe1, 2P1, 2C1, 2C2, 2O2, 2O4, 2O5, 2O6) in the *a*-axis direction (figure 4). The $[NH_3CH_2CH_2NH_3]^{2+}$ serve as charge–compensating cations which are located between two adjacent iron phosphonate layers (figure 2).

3.3. *IR spectra*

The IR spectrum of **1** exhibits a few broad bands between 2500–3500 cm^{-1}, corresponding to O–H stretches of hydroxyl groups (including water molecules and the 2-hydroxyphosphonoacetic acid) and N–H stretches of $[NH_3CH_2CH_2NH_3]^{2+}$ cations.

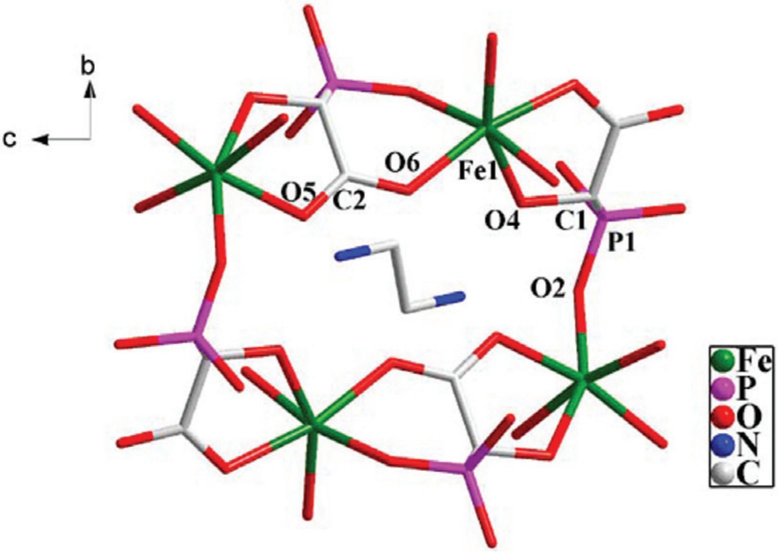

Figure 4. View of the framework for **1** along the *a*-axis showing holes in the structure.

A medium absorption band around 3420 cm^{-1} corresponds to O–H stretching vibrations of hydroxyl group of **1**, indicating the hydroxyl oxygen atom is still protonated, in agreement with the single-crystal X-ray diffraction studies. No band is seen at ca 1715 cm^{-1} corresponding to ν(C=O) for the free acid (–COOH). However, there are two pairs of strong bands centered at 1574, 1450 and 1388, 1289 cm^{-1}, which are assigned to the asymmetrical and symmetrical stretching vibrations of C–O groups present as COO^{-} moieties [19]. The set of bands between 1100 and 900 cm^{-1} are due to stretching vibrations of the tetrahedral O_3PC groups [20, 21].

3.4. *Thermogravimetric analysis*

The thermogravimetric analysis diagram of **1** in the 50–800°C temperature range in static air indicates complicated overlapping steps of weight loss. The first step starts at 50°C, completed at 248°C, corresponding to the release of two lattice water molecules and ethylenediamine. The observed weight loss (17.5%) is very close to the calculated value (17.8%). The weight loss (6.7%) in the temperature range 248–290°C, corresponding to the release of two coordinated water molecules, is in good agreement with the calculated value (6.5%). The weight loss (23.3%) above 290°C is due to decomposition of the organic faction (calculated 23.9%) and the collapse of the lattice structure. Thermogravimetric analysis of **1** revealed that the framework is thermally stable to about 290°C.

4. Conclusion

A divalent metal phosphonate has been prepared under hydrothermal reaction conditions by combination of Fe cations with 2-hydroxyphosphonoacetic acid in the presence of ethylenediamine template agents. The structure of **1** can be described as a 2D layered structure with a one-dimensional channel system along the *a*-axis; the ethylenediamines are located between two adjacent iron phosphonate layers. By using 2-hydroxylphosphonoacetic acid (H_3L) with a chiral carbon atom as ligand, we attempted to synthesize a chiral porous material. However, the single-crystal X-ray structural analysis indicates that **1** crystallizes in an achiral space group.

Supplementary material

Crystallographic data for the structure of **1** reported in this article has been deposited with the Cambridge Crystallographic Data center, CCDC Number 623380 for **1**. 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; E-mail: deposit@ccdc.cam.ac.uk).

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