

Solvothermal synthesis, crystal structure, magnetic and luminescent properties of $(\text{H}_3\text{O})_6 \cdot [\text{Co}_4(\text{H}_2\text{O})_4(\text{HPMIDA})_2(\text{PMIDA})_2] \cdot 2\text{H}_2\text{O}$

Yong Fan, Guanghua Li, Wenping Jian, Miao Yu, Li Wang, Zhenfen Tian,
Tianyou Song*, Shouhua Feng*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

Received 3 February 2005; received in revised form 15 April 2005; accepted 16 April 2005

Available online 6 June 2005

Abstract

A cobalt phosphonate $(\text{H}_3\text{O})_6 \cdot [\text{Co}_4(\text{H}_2\text{O})_4(\text{HPMIDA})_2(\text{PMIDA})_2] \cdot 2\text{H}_2\text{O}$, **1**, has been synthesized from a mild solvothermal reaction of Co(II) ion with *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA). Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with cell parameters of $a = 9.0682(18) \text{ \AA}$, $b = 10.744(2) \text{ \AA}$, $c = 12.731(3) \text{ \AA}$, $\alpha = 93.06(3)^\circ$, $\beta = 99.66(3)^\circ$, $\gamma = 90.34(3)^\circ$, $V = 1221.0(4) \text{ \AA}^3$ and $Z = 1$. Compound **1** shows a novel tetra-nuclear molecular structure. In the crystal lattice, molecules of **1** hydrogen bond to each other to form two-dimensional (2D) layers, which are further linked together by the co-crystallized H_2O molecules and H_3O^+ counter ions through hydrogen bonding to form the 3D supramolecular network. Thermogravimetric analysis, IR spectrum, magnetic susceptibility and luminescent spectra are given.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Solvothermal synthesis; Metal phosphonate; Structure; Magnetic susceptibility; Luminescent

1. Introduction

In recent years, metal phosphonates have been extensively studied partially due to their potential applications in catalysis, molecular recognition, ion exchange, non-linear optics and sensors [1–7]. Great efforts have been devoted to the syntheses of novel inorganic–organic hybrid materials based on metal phosphonates, which exhibit a variety of structures such as one-dimensional (1D) chain, 2D layer, and 3D network [8–10]. A promising field is the synthesis of metal phosphonates functionalized with carboxylic, amino [11–14], or amino-carboxylic groups [7–13]. Phosphonic acids with additional carboxylic functional groups are useful ligands for structural construction of inorganic–organic hybrid compounds, because the introduction of carboxylic groups cannot only provide additional coordination sites, but also increase the

solubility of the resulting metal phosphonates and facilitate their crystallization [10]. *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA) is a versatile ligand, which can adopt various kinds of coordination modes under different reaction conditions. The resulting metal derivatives were found to form 1D, 2D and 3D structures, some of which are supramolecular frameworks [15–24].

Solvothermal techniques have proven to be a powerful method in obtaining crystalline materials. Several metal phosphonates have been synthesized by solvothermal techniques [19,25–27], among which only one contains H_nPMIDA ($n = 0$) ligand [19]. Previously, we reported the hydrothermal synthesis of $\text{Mn}(\text{H}_2\text{O})[\text{HO}_3\text{PCH}_2\text{NH}(\text{CH}_2\text{CO}_2)_2]$, a 3D framework [29]. Zubietta and coworkers have demonstrated that the non-aqueous solvothermal conditions promote the formation of molecular species [28]. We re-investigated the synthesis of $\text{Mn}(\text{H}_2\text{O})[\text{HO}_3\text{PCH}_2\text{NH}(\text{CH}_2\text{CO}_2)_2]$ under the non-aqueous solvothermal conditions, hoping to obtain a molecular species with novel magnetic proper-

*Corresponding authors. Fax: +86 431 5168624.

E-mail address: shfeng@mail.jlu.edu.cn (S. Feng).

ties. Unfortunately, when we changed the solvent from water to ethanol, we only got some unidentified amorphous materials. When we switched from manganese to cobalt, however, we obtained crystals of a molecular compound, $(\text{H}_3\text{O})_6 \cdot [\text{Co}_4(\text{H}_2\text{O})_4(\text{HPMIDA})_2(\text{PMIDA})_2] \cdot 2\text{H}_2\text{O}$, **1**. The solvothermal synthesis, crystal structure, luminescent and magnetic properties of **1** are reported herein.

2. Experimental

2.1. Synthesis and characterization

0.238 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.148 g of NH_4F were dissolved in 10 mL of ethanol, followed by the addition of 0.234 g of H_4PMIDA with vigorous stirring. To the resulting solution was added 0.6 mL of $[\text{Me}_4\text{N}]\text{OH}$ solution (15% in water) and stirred until a homogeneous reaction mixture was formed. The molar ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}:\text{NH}_4\text{F}:\text{H}_4\text{PMIDA}:[\text{Me}_4\text{N}]\text{OH}$ is 1:4:1:1. The reaction mixture was crystallized in a 23 mL PTFE-lined acid digestion bomb at 170°C for 5 days. The initial and final pH values are 4.0 and 4.5, respectively. The crystalline product **1** (red plates) was collected by vacuum filtration, washed thoroughly with ethanol and dried in air (yield 70% based on cobalt). Anal. Calcd. for $\text{H}_{50}\text{Co}_4\text{C}_{20}\text{N}_4\text{O}_{40}\text{P}_4$: C, 17.84; H, 3.74; N, 4.16. Found: C, 17.75; H, 3.90; N, 4.04. ICP results: Co 17.21 wt% (calcd 17.51 wt%) and P 9.11% (calcd 9.20 wt%). NH_4F was used in the synthesis, yet the compound does not have F^- or NH_4^+ . But it is crucial to the synthesis, so that it act as structure-directing agent and mineralizing agent [30].

The elemental analysis was conducted on a Perkin-Elmer 2400LC II elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV ICP instrument. X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The step size was 0.02° , and the count time was 4 s. The infrared (IR) spectrum was recorded within the $400\text{--}4000 \text{ cm}^{-1}$ range on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The differential thermal analysis (DTA) was performed on a Perkin-Elmer DTA 1700 differential thermal analyzer. Thermogravimetric analysis (TGA) was performed in an atmospheric environment with a heating rate of $10^\circ\text{C min}^{-1}$ on a Perkin-Elmer TGA 7 thermogravimetric analyzer. Magnetic susceptibility data were collected on 0.0166 g of sample over the temperature range of $4\text{--}300 \text{ K}$ at a magnetic field of 5 kG on a Quantum Design MPMS-7 SQUID magnetometer. Emission and excitation spectra were recorded on an Eidingberg FX900 fluorescence spectrometer with a 500 W xenon lamp. The emission spectrum was corrected for the sensitivity of the

photomultiplier tube, and the excitation spectrum was corrected for the intensity of the xenon lamp.

2.2. Crystal structure determination

A suitable single crystal of **1** with dimensions of $0.32 \times 0.12 \times 0.10 \text{ mm}^3$ was glued to a thin glass fiber and mounted on a Siemens Smart CCD diffractometer equipped with a normal-focus, 2.4-kW sealed-tube X-ray source with graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected at $298 \pm 2 \text{ K}$ and processed on a PC with the SAINT Plus software package [31]. The structure was solved in the triclinic space group $P\bar{1}$ by direct methods and was refined on F^2 by full-matrix least squares using SHELXTL97 software package [32]. The hydrogen atoms that are bonded to carbon and nitrogen atoms were located. All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data is presented in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonding distances and angles are given in Table 3.

3. Results and discussion

3.1. Synthesis and characterization

Compound **1** is readily obtained as red crystals in good yield from the reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, NH_4F ,

Table 1
Crystal data for compound **1**

Empirical formula	$\text{H}_{50}\text{Co}_4 \cdot \text{C}_{20}\text{N}_4\text{O}_{40} \cdot \text{P}_4$
Formula weight	1346.24
Temperature	293(2) K
Wavelength	0.71073 \AA
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.0682(18) \text{ \AA}$ $b = 10.744(2) \text{ \AA}$ $c = 12.731(3) \text{ \AA}$ $\alpha = 93.06(3)^\circ$ $\beta = 99.66(3)^\circ$ $\gamma = 90.34(3)^\circ$
Volume	$1221.0(4) \text{ \AA}^3$
Z	1
$F(000)$	692
Crystal size	$0.32 \times 0.12 \times 0.10 \text{ mm}^3$
Reflections collected/unique	11903/5435 [$R_{\text{int}} = 0.0463$]
Data/restraints/parameters	5435/11/368
Goodness-of-fit on F^2	0.876
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0430$, $wR_2 = 0.1038$

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

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

Co(1)–O(1)	2.080(3)	Co(2)–O(16)	1.986(3)
Co(1)–O(4)	2.078(3)	Co(2)–N(2)	2.167(3)
Co(1)–O(6)	2.115(3)	P(1)–O(1)	1.536(3)
Co(1)–O(11)	2.060(3)	P(1)–O(2)	1.499(3)
Co(1)–O(14)#1	2.116(3)	P(1)–O(3)	1.522(3)
Co(1)–N(1)	2.192(3)	P(1)–C(1)	1.829(4)
Co(2)–O(8)	2.097(3)	P(2)–C(6)	1.828(4)
Co(2)–O(12)	2.100(3)	P(2)–O(8)	1.525(3)
Co(2)–O(13)	2.126(3)	P(2)–O(9)	1.510(3)
Co(2)–O(15)	2.132(4)	P(2)–O(10)	1.563(3)
O(1)–Co(1)–O(6)	162.34(11)	O(16)–Co(2)–O(8)	105.99(11)
O(1)–Co(1)–O(14) ^a	87.37(11)	O(16)–Co(2)–O(12)	89.24(11)
O(4)–Co(1)–O(1)	93.25(12)	O(16)–Co(2)–O(13)	92.04(11)
O(4)–Co(1)–O(6)	89.45(12)	O(16)–Co(2)–O(15)	92.24(14)
O(4)–Co(1)–O(14) ^a	171.93(12)	O(8)–Co(2)–N(2)	86.51(12)
O(6)–Co(1)–O(14) ^a	87.58(11)	O(12)–Co(2)–N(2)	80.60(11)
O(11)–Co(1)–O(1)	105.47(11)	O(13)–Co(2)–N(2)	77.25(11)
O(11)–Co(1)–O(4)	90.60(12)	O(15)–Co(2)–N(2)	98.69(15)
O(11)–Co(1)–O(6)	91.94(11)	O(16)–Co(2)–N(2)	164.03(12)
O(11)–Co(1)–O(14) ^a	97.00(11)	O(2)–P(1)–O(1)	111.83(17)
O(1)–Co(1)–N(1)	85.12(11)	O(2)–P(1)–O(3)	112.87(18)
O(4)–Co(1)–N(1)	82.62(12)	O(3)–P(1)–O(1)	113.35(18)
O(6)–Co(1)–N(1)	77.91(12)	O(1)–P(1)–C(1)	102.18(16)
O(11)–Co(1)–N(1)	167.79(12)	O(2)–P(1)–C(1)	107.78(19)
O(14) ^a –Co(1)–N(1)	89.42(12)	O(3)–P(1)–C(1)	108.04(18)
O(8)–Co(2)–O(12)	90.48(11)	O(8)–P(2)–O(10)	109.12(18)
O(8)–Co(2)–O(13)	160.35(11)	O(9)–P(2)–O(8)	115.58(17)
O(8)–Co(2)–O(15)	85.64(13)	O(9)–P(2)–O(10)	111.09(16)
O(12)–Co(2)–O(13)	97.59(11)	O(8)–P(2)–C(6)	104.51(17)
O(12)–Co(2)–O(15)	176.10(13)	O(9)–P(2)–C(6)	110.90(17)
O(13)–Co(2)–O(15)	85.96(13)	O(10)–P(2)–C(6)	104.94(19)

^a $-x + 1, -y + 1, -z$.

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

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(10)–H(10)...O(2W) ^b	0.82	2.29	3.030(5)	151.2
O(15)–H(15A)...O(2) ^b	0.812(19)	1.98(3)	2.732(5)	154(5)
O(15)–H(15B)...O(7) ^a	0.86(5)	2.02(5)	2.826(5)	156(5)
O(16)–H(16A)...O(4W)	0.86(2)	2.23(5)	2.750(4)	120(5)
O(16)–H(16B)...O(1W)	0.87(2)	1.96(4)	2.719(5)	145(6)
O(16)–H(16B)...O(13)	0.87(2)	2.52(5)	2.961(4)	113(4)
O(1W)–H(1WA)...O(6) ^a	0.95(2)	2.07(7)	2.959(5)	155(13)
O(1W)–H(1WB)...O(11) ^c	0.95(2)	2.11(4)	2.936(5)	144(5)
O(1W)–H(1WB)...O(4) ^c	0.95(2)	2.64(4)	3.418(6)	140(5)
O(2W)–H(2WA)...O(7) ^d	0.99(2)	1.95(4)	2.828(5)	147(5)
O(2W)–H(2WB)...O(3) ^e	0.982(19)	1.89(3)	2.832(5)	161(5)
O(3W)–H(3WA)...O(9) ^c	0.97(2)	2.00(3)	2.926(4)	158(5)
O(3W)–H(3WB)...O(16)	0.99(2)	1.77(3)	2.712(5)	159(5)
O(4W)–H(4WA)...O(16)	0.96(2)	1.83(3)	2.750(4)	158(5)

Symmetry transformations used to generate equivalent atoms: ^a $-x + 1, -y + 1, -z$; ^b $-x + 1, -y, -z$; ^c $x + 1, y, z$; ^d $-x + 1, -y + 1, -z + 1$; ^e $-x + 1, -y, -z + 1$.

H₄PMIDA and [Me₄N]OH in a 1:4:1:1 ratio under the solvothermal conditions (170 °C, 5 days) in ethanol.

As shown in Fig. 1, the powder X-ray diffraction pattern is consistent with the simulated one based on the

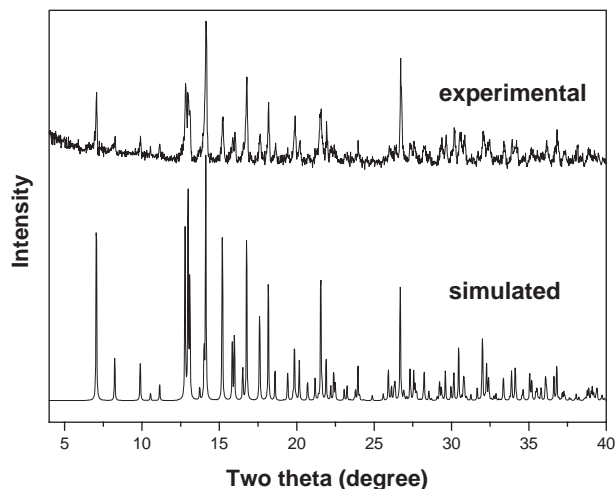


Fig. 1. Experimental and simulated power X-ray diffraction patterns for **1**.

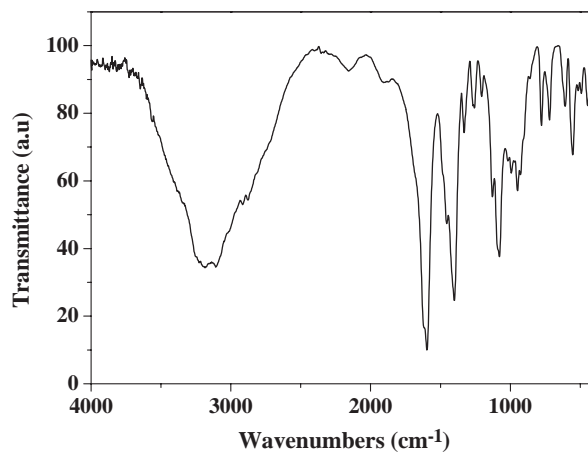


Fig. 2. Infrared spectrum of **1**.

single crystal X-ray diffraction analysis, indicating the phase purity of the synthesized sample. The difference in reflection intensities between the simulated and experimental patterns was due to the variation in crystal orientation for the powder sample.

The IR spectrum is shown in Fig. 2. The broad band from 3630 to 2474 cm⁻¹ is attributed to O–H asymmetric stretch of the lattice water, H₃O⁺ and PO–H. The broadness of the band is due to the strong hydrogen bond. The band at 1610 cm⁻¹ is normally due to the water bending vibration. The multiple bands in the region of 1140–900 cm⁻¹ are phosphonate P–O vibrations. The remaining bands are those typical of the *N*-(phosphonomethyl)iminodiacetic salts [33].

Combined TGA–DTA curves for **1** are shown in Fig. 3. The strong endothermic peak centered at 270 °C is due to the loss of hydration water molecules and condensation of the hydroxyl groups. The calculated

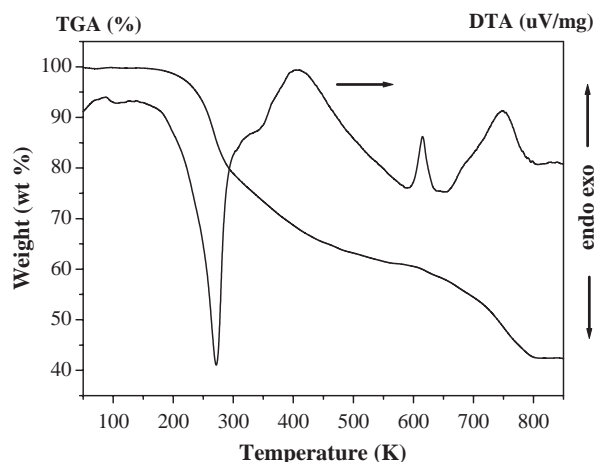


Fig. 3. TGA–DTA curves for 1.

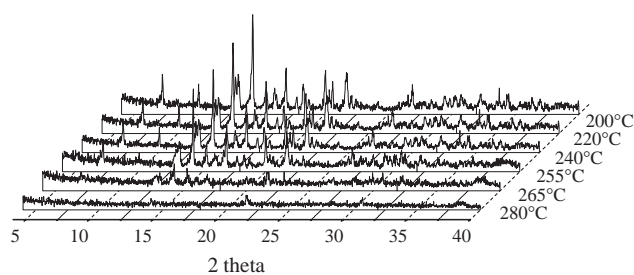


Fig. 4. X-ray thermodiffractometric pattern for 1.

weight loss for this process is 17.7% and the observed weight loss is 18.2%. In the range of 280–620 °C the mass loss is 39.6% (calculated value 42.2%), due to the combustion of the carboxylic groups with a very broad and strong exothermic peak centered at ~407 °C. The combustion of the organic starts at 620 °C with an

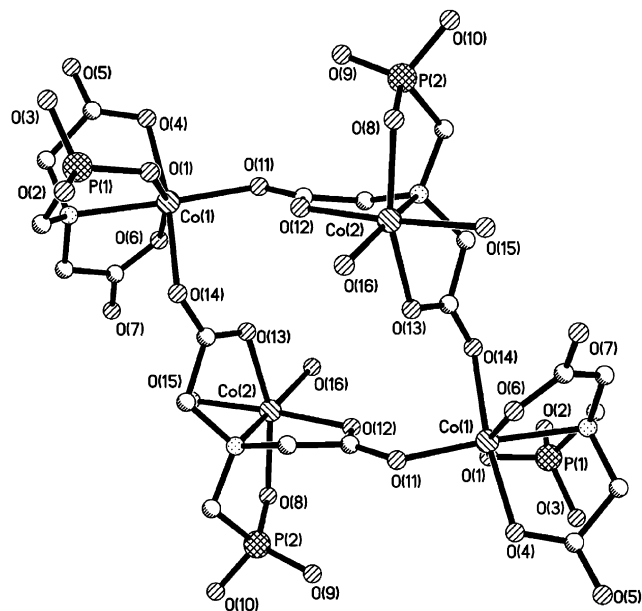


Fig. 6. Molecular structure of 1.

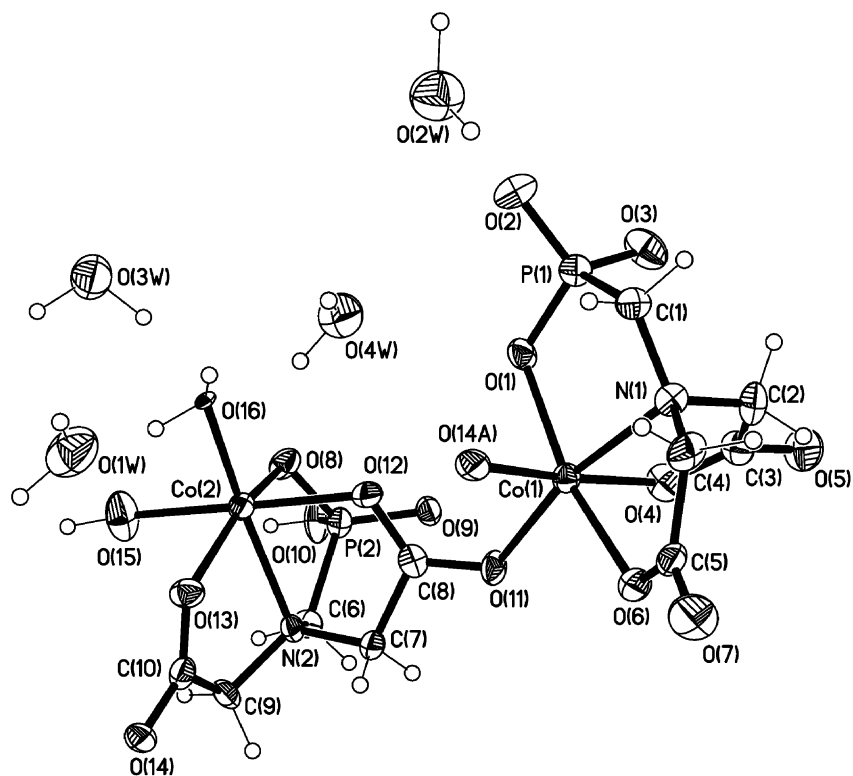


Fig. 5. ORTEP view of the structure of 1 showing the atom-labeling scheme (50% thermal ellipsoids).

exothermic peak centered at 747 °C. TGA curve shows a continuous weight loss about 37.8% (calculated value 38.1%) in this temperature range. The final thermal decomposition products at 805 °C were amorphous.

A thermodiffractometric study of **1** (Fig. 4) was undertaken to characterize the water loss. The 3D lattice of **1** is only stable up to 240 °C, and above this temperature the structure began to collapse.

3.2. Description of the structure

As shown in Figs. 5 and 6, **1** is a tetra-nuclear compound with crystallographically imposed inversion center symmetry in the middle. Each Co(1) center adopts a slightly distorted octahedral coordination

geometry, with three oxygen and one nitrogen donor atoms from a tetradentate chelating PMIDA ligand occupying four vertices. The rest two vertices are occupied by two oxygen donor atoms from two bridging carboxylic groups of two neighboring HPMIDA ligands. The Co(1)–O bond lengths are in the range from 2.060(3) to 2.115(3) Å, and the Co(1)–N bond length is 2.192(3) Å. The O–Co–O and O–Co–N bond angles deviate from the values for an ideal octahedron. Each Co(2) center adopts a distorted octahedral coordination geometry, with three oxygen and one nitrogen donor atoms from a tetradentate chelating HPMIDA ligand occupying four vertices and two water molecules occupying the remaining two vertices. The two carboxylic moieties of the HPMIDA ligand bridge

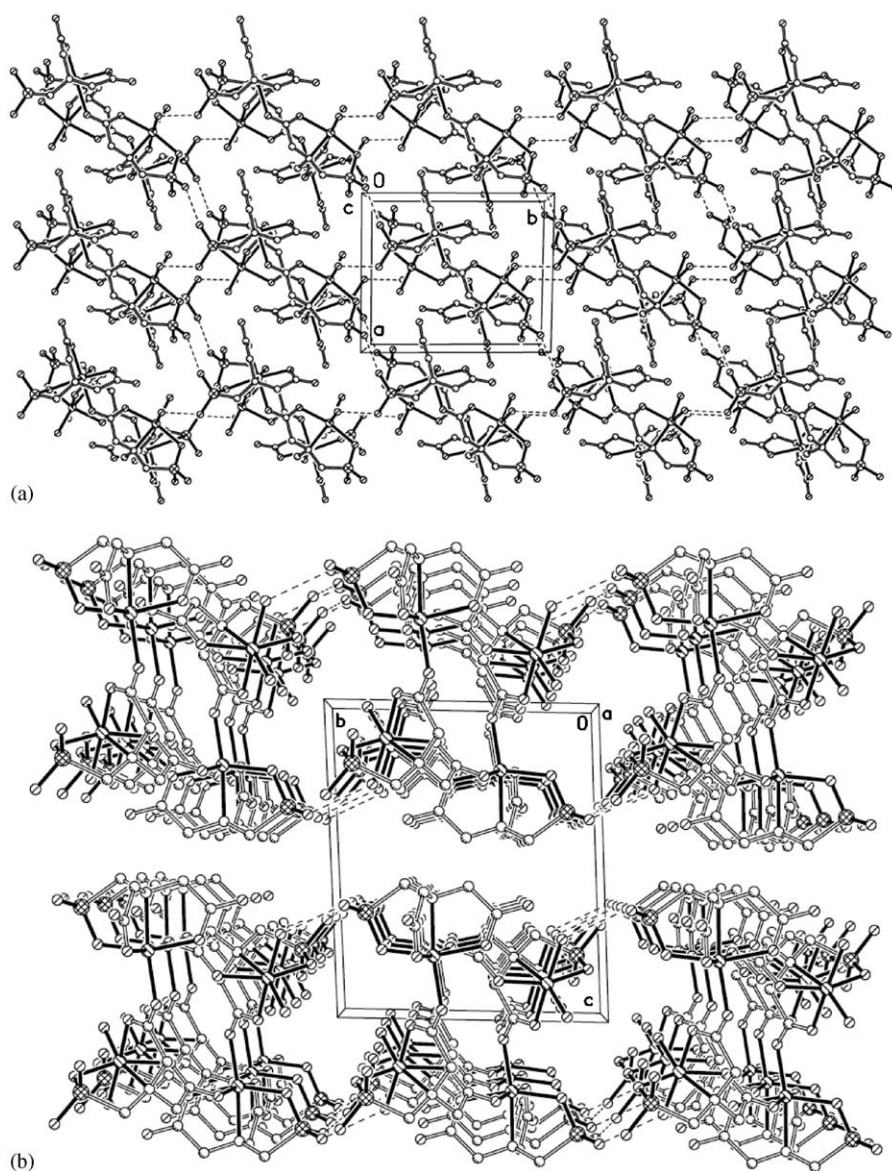


Fig. 7. (a) The layers formed by **1** through hydrogen bonds along *ab* plane (shown down the *c* direction). Co-crystallized H₂O and H₃O⁺ are omitted for clarity. (b) The layers formed by **1** through hydrogen bonds along *ab* plane (shown down the *a* direction) Co-crystallized H₂O and H₃O⁺ are omitted for clarity.

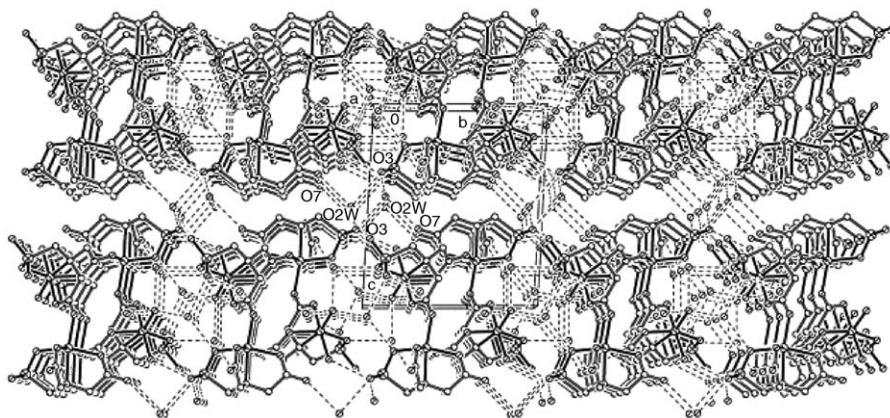


Fig. 8. A diagram showing the 3D supramolecular network of **1**.

over two adjacent Co(1) centers, resulting in a tetranuclear rhombic structure. The Co(2)–O bond lengths fall between 1.986(3) and 2.132(4) Å, and the O–Co–O bond angles are in the range from 85.7(2) to 97.5(7). These bond lengths and angles are similar to other cobalt(II) phosphonates [23]. According to the consideration of the charge balance and the acidic environment of synthesis system, six of the crystal water molecules are ionized, which is a common feature in many reported literatures [34].

In compound **1**, two coordination modes have been observed for H_n PMIDA ($n = 0$ or 1) ligand. A different coordination mode has been reported, by Wood and coworkers [19], in a hexa-nuclear Co complex of PMIDA, in which the phosphonate oxygen atoms bridge over the neighboring Co centers.

As shown in Fig. 7, each molecule of **1** hydrogen bonds to four adjacent molecules to form 2D layers through O(15)H, O(2), O(10)H and O(3), with distances between the hydrogen bonded oxygen pairs of 2.732(5) and 2.468 Å for O(15)–H \cdots O(2) and O(10)–H \cdots O(3), respectively. As shown in Fig. 8, the co-crystallized H₂O molecules and H₃O⁺ counter-ions in between the layers further extend the structure into a 3D network through hydrogen bonding. The distances between the hydrogen bonded oxygen pairs are of 2.830 and 2.827 Å for O(2W) \cdots O(3) and O(2W) \cdots O(7), respectively.

3.3. Magnetic susceptibility and luminescence properties

The temperature dependence of magnetic susceptibility ranging from 4 to 300 K for **1** was measured (see Fig. 9). The experimental data were fitted using the Curie–Weiss equation $X_m = C_m/(T - \theta)$, with $C_m = 6.44 \text{ emu K}^{-1} \text{ mol}^{-1}$ and $\theta = -6.35 \text{ K}$. This result indicates there exists a weak antiferromagnetic interaction in **1** caused by the superexchange coupling between the molecules. At 300 K, the calculated effective magnetic moment for per cobalt atom, $\mu_{\text{eff}} = 4.99 \mu_B$. This value

falls in the range of the expected values of 4.70–5.20 μ_B for the octahedral Co²⁺ ion [35].

High spin metal centers are known to quench luminescence through electron transfer process. To our surprise, compound **1** is luminescent at room temperature. As shown in Fig. 10, the photoluminescence (PL) spectrum of **1** in the solid state has been measured with the excitation wavelength of 250 nm at room temperature. Two emission maxima have been observed at 398 and 600 nm, respectively. Luminescent metal phosphonates are scarcely known [36,37]. To our best knowledge, compound **1** is the first luminescent cobalt phosphonate compound.

4. Conclusions

A novel cobalt(II) inorganic–organic hybrid compound $(H_3O)_6 \cdot [Co_4(H_2O)_4(HPMIDA)_2(PMIDA)_2] \cdot 2H_2O$ has been solvothermally synthesized from the Co (II) ion and H₄PMIDA and structurally characterized by single crystal X-ray diffraction analysis. The product is produced in a single phase, which is confirmed by powder X-ray diffraction. The extended structure of the title compound features a 3D supramolecular network. The temperature dependence of magnetic susceptibility shows a weak antiferromagnetic interaction. Compound **1** is luminescent in the solid state at room temperature with emission maxima at 398 and 600 nm, respectively.

Acknowledgment

We thank the National Natural Science Foundation of China (Grant Nos. 20071013 and 20301007), the State Basic Research Project of China (Grant G2000077507). We thank Dr. Datong Song for revising the manuscript.

Appendix A. supplementary data

The online version of this article contains additional supplementary data. Please visit [doi:10.1016/j.jssc.2005.04.024](https://doi.org/10.1016/j.jssc.2005.04.024).

References

- [1] C. Maillet, P. Janvier, M. Pipelier, T. Praveen, Y. Andres, B. Bujoli, *Chem. Mater.* 13 (2001) 2879.
- [2] I.O. Benitez, B. Bujoli, L.J. Camus, C.M. Lee, F. Odobel, D.R. Talham, *J. Am. Chem. Soc.* 124 (2002) 4363.
- [3] V.V. Krishnan, A.G. Dokoutchaev, M.E. Thompson, *J. Catal.* 196 (2000) 366.
- [4] G. Cao, H. Hong, T.E. Mallouk, *Acc. Chem. Res.* 25 (1992) 420.
- [5] B. Zhang, A. Clearfield, *J. Am. Chem. Soc.* 119 (1997) 2751.
- [6] H.E. Katz, G. Scheller, T.M. Putvinski, M.L. Schilling, W.L. Wilson, C.E.D. Chidsey, *Science* 254 (1991) 1485.
- [7] G. Alberti, in: J.M. Lehn (Ed.), *Comprehensive Supramolecular Chemistry*, Pergamon, Elsevier Science, Ltd., Oxford, UK, 1996, p. 7.
- [8] E. Stein, A. Clearfield, M.A. Subramanian, *Solid State Ion.* 83 (1996) 113.
- [9] A. Clearfield, *Curr. Opin. Solid State Mater. Sci.* 1 (1996) 268.
- [10] A. Clearfield, *Metal phosphonate chemistry*, in: K.D. Karlin (Ed.), *Progress in Inorganic Chemistry*, vol. 47, Wiley, New York, 1998, pp. 371–510 (and references therein).
- [11] F. Fredoueil, M. Evain, D. Massiot, M. Bujoli-Doeu, B. Bujoli, *J. Mater. Chem.* 11 (2001) 1106.
- [12] M. Riou-Cavellec, M. Sanselme, M. Nogues, J.M. Greneche, G. Ferey, *Solid State Sci.* 4 (2002) 619.
- [13] A. Clearfield, D.M. Poojary, B. Zhang, B. Zhao, A. Derecskei-Kovacs, *Chem. Mater.* 12 (2000) 2745.
- [14] P. Ayyappan, O.R. Evans, B.M. Foxman, K.A. Wheeler, T.H. Warren, W.B. Lin, *Inorg. Chem.* 40 (2001) 5954.
- [15] B. Zhang, D.M. Poojary, A. Clearfield, *Inorg. Chem.* 37 (1998) 249.
- [16] D.M. Poojary, B. Zhang, A. Clearfield, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2324.
- [17] B. Zhang, D.M. Poojary, A. Clearfield, G.-Z. Peng, *Chem. Mater.* 8 (1996) 1333.
- [18] D.M. Poojary, A. Clearfield, *J. Organomet. Chem.* 512 (1996) 237.
- [19] S.O.H. Gutschke, D.J. Price, A.K. Powell, P.T. Wood, *Angew. Chem. Int. Ed.* 38 (1999) 1088.
- [20] J.G. Mao, A. Clearfield, *Inorg. Chem.* 41 (2002) 2319.
- [21] J.G. Mao, Z. Wang, A. Clearfield, *Inorg. Chem.* 41 (2002) 6106.
- [22] J.L. Song, J.G. Mao, Y.Q. Sun, H.Y. Zeng, R.K. Kremer, A. Clearfield, *J. Solid State Chem.* 177 (2004) 633.
- [23] J.L. Song, A.V. Prosvirin, H.H. Zhao, J.G. Mao, *Eur. J. Inorg. Chem.* (2004) 3706.
- [24] F.A.A. Paz, F.N. Shi, J. Klinowski, J. Rocha, T. Trindade, *Eur. J. Inorg. Chem.* (2004) 2759.
- [25] J. Salta, Y.-D. Chang, J. Zubieta, *J. Chem. Soc. Chem. Commun.* (1994) 1039.
- [26] C.J. Warren, D.J. Rose, R.C. Haushalter, J. Zubieta, *Inorg. Chem.* 37 (1998) 1140.
- [27] P.T. Wood, W.T. Pennington, J.W. Kolis, B. Wu, C.J.O. Connor, *Inorg. Chem.* 32 (1993) 129.
- [28] J. Salta, Y.-D. Chang, J. Zubieta, *J. Chem. Soc. Chem. Commun.* (1994) 1039.
- [29] Y. Fan, G.H. Li, Z. Shi, D. Zhang, J.N. Xu, T.Y. Song, S.H. Feng, *J. Solid State Chem.* 177 (2004) 4346.
- [30] R.R. Xu, W.Q. Pang, Q.S. Huo, J.H. Yu, J.S. Chen, *Zeolite and Porous Materials*, Science Publishing Company, China, 2004, pp. 237–240, and reference therein.
- [31] *Software Packages SMART and SAINT*, Siemens Analytical X-ray Instruments Inc, Madison, WI, 1996.
- [32] *SHELXTL*, version 5.1, Siemens Industrial Automation, Inc, Madison, WI, 1997.
- [33] A. Cabeza, X.O. Yang, C.V.K. Sharma, M.A.G. Aranda, S. Bruque, A. Clearfield, *Inorg. Chem.* 41 (2002) 2325.
- [34] S.T. Zheng, J. Zhang, G.Y. Yang, *Solid State Sci.* 7 (2005) 149 and reference therein.
- [35] R.L. Carlin, *Magnetochemistry*, Springer, Berlin/Heidelberg, 1986, pp. 53–65.
- [36] J.L. Song, H.H. Zhao, Jiang-Gao Mao, K.R. Dunbar, *Chem. Mater.* 16 (2004) 1884.
- [37] F. Serpaggi, G. Ferrey, E. Antic-Fidancev, *J. Solid State Chem.* 148 (1999) 347.