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具有经典 ACO 拓扑开放结构的三维多孔多钒氧酸盐的水热合成和晶体结构

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摘要: 本文采用水热技术合成了一种具有经典 ACO 拓扑结构的多钒氧酸盐{[$Cu_4(V^{IV}_{11}V^{V}_{7}O_{42}(PO_4))(C_3H_{10}N_2)_8$]·$4H_2O$}$_n$ (1, $C_3H_{10}N_2$=1,2-丙二胺),并且通过元素分析、红外、热重、单晶 X-射线衍射对化合物 **1** 进行了表征。晶体学分析表明,阴离子簇$[V^{IV}_{11}V^{V}_{7}O_{42}(PO_4)]^{8-}$与 8 个过渡金属配合物阳离子$[Cu(C_3H_{10}N_2)_2]^{2+}$相连而产生具有经典 ACO 拓扑结构的三维孔道结构。化合物 **1** 为四方晶系,*P*4/*nnc* 空间群,*a*=*b*=1.505 91(10) nm,*c*=1.871 3(3) nm,*V*=4.243 8(7) nm^3,*Z*=2。化合物 **1** 沿 *c* 轴方向具有 0.753 nm×0.753 nm 孔道。

关键词: 水热合成; 多钒氧酸盐; 晶体结构; ACO 拓扑结构
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Hydrothermal Synthesis and Crystal Structure of a Three-Dimensional Porous Polyoxovanadate with Typical ACO Topological Open Frameworks

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Abstract: A polyoxovanadate {[$Cu_4(V^{IV}_{11}V^{V}_{7}O_{42}(PO_4))(C_3H_{10}N_2)_8$]·$4H_2O$}$_n$ (**1**, $C_3H_{10}N_2$=1,2-diaminopropane) with typical ACO topological open framework has been synthesized by hydrothermal method. Compound **1** has been characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. Crystallographic analysis reveals that it is constructed from a anionic cluster $[V^{IV}_{11}V^{V}_{7}O_{42}(PO_4)]^{8-}$ and the transition metal complex $[Cu(C_3H_{10}N_2)_2]^{2+}$ as a bridging ligand with typical ACO topological open framework. Compound **1** crystallizes in the tetragonal system, space group *P*4/*nnc*, with *a*=*b*=1.505 91(10) nm, *c*=1.871 3(3) nm, *V*=4.243 8(7) nm^3, *Z*=2. Compound **1** possess channels with a dimension of 0.753 nm× 0.753 nm running along the *c*-axis. CCDC: 832382.

Key words: hydrothermal synthesis; polyoxovanadate; crystal structure; ACO topological open framework

0 Introduction

In the past few years, polyoxometalates (POMs) have been extensively studied owing to not only their considerable structural versatility but also comprehensive applications in catalysis, electrical conductivity, ion exchange, biological chemistry, magnetism and so on[1-4]. During the last decade, an important advance in POMs chemistry has been the rational design and assembly of extended POMs-based materials by employing polyoxo-metalate anions and secondary transition metal complex (TMC)[5-8]. So far, a number of POMs with 1D chain, 2D networks and 3D open frameworks have been reported, such as

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[{Cu (1,2-pn)$_2$}$_7$ {V$_{16}$O$_{38}$ (H$_2$O)}$_2$] ·4H$_2$O [9], [{Zn (bipy)$_2$}$_2$ V$_4$O$_{12}$][10], Cs$_{10.5}$[(V$_{16}$O$_{40}$)(Si$_{4.5}$V$_{1.5}$O$_{10}$)] ·3.5H$_2$O [11], (N$_2$H$_5$)$_2$ [Zn$_3$V$^{\text{IV}}_{12}$V$^{\text{V}}_6$O$_{42}$(SO$_4$)(H$_2$O)$_{12}$]·24H$_2$O[12], [{Cu$_3$(4,7-phen)$_3$}$_2${Mo$_{14}$O$_{45}$}][13], [H$_6$Mn$_3$V$^{\text{IV}}_{15}$V$^{\text{V}}_4$O$_{46}$(H$_2$O)$_{12}$] ·30H$_2$O [14], [Cu (en)$_2$(H$_2$O)]{[PMo$^{\text{VI}}_8$V$^{\text{IV}}_6$O$_{42}$Cu(en)$_2$][Cu$_{0.5}$(en)]$_3$} ·5.5H$_2$O[15]. In this w ork, we synthesized a polyoxovanadate {[Cu$_4$(V$^{\text{IV}}_{11}$V$^{\text{V}}_7$O$_{42}$(PO$_4$))(C$_3$H$_{10}$N$_2$)$_8$] ·4H$_2$O}$_n$ (**1**, C$_3$H$_{10}$N$_2$= 1,2-diaminopropane) with a classic ACO topological open framework[16-17].

1 Experimental

1.1 Reagents and measurements

All chemical reagents were bought from commercial sources and of reagent purity. The elemental analysis (C, H, N) was performed on a Perkin-Elmer 2400 elemental analyzer. IR spectra determination was performed on a Nicolet 410 FTIR spectrometer in the range 400~4 000 cm^{-1} (KBr pellet). The thermogravimetric analysis (TGA) was carried out on a Diamond thermal analyzer under nitrogen atmosphere at a heating rate of 10 ℃ ·min^{-1}. The magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID Magnetometer in the range 2~300 K at 2 000 Oe.

1.2 Synthesis

A mixture of V_2O_5 (0.182 2 g, 1 mmol), $CuCl_2 \cdot 2H_2O$ (0.170 2 g, 1 mmol), diethylenetriamine (DETA) (0.43 mL, 4 mmol), 1,2-diaminopropane (0.17 mL, 2 mmol), and 5 mL distilled water was stirred for 1.5 h, then was neutralized to pH =9 with 50% phosphoric acid. The mixture was sealed in a 20 mL Teflon-lined stainless steel reactor and kept at 170 ℃ for 6 d. After cooled to room temperature, the product was washed with distilled water, filtered and dried in the air. Dark hexagon-shaped crystals accompanied by a little unknown yellow powder were obtained (0.153 0 g, yield 52.90% based on V). Elemental analysis: Found(%): C, 11.24; H, 3.51; N, 8.49. Calcd.(%): C, 11.07; H, 3.41; N, 8.61.

1.3 X-ray structure determination

The single crystal with dimension of 0.13 mm×0.12 mm×0.12 mm was selected by visual examination under the microscope and glued at the top of a thin glass fiber with epoxy glue in air for data collection, and the diffraction data were collected on a Bruker Smart Apex Ⅱ CCD diffractometer with a sealed tube X-ray source (Mo $K\alpha$ radiation, λ=0.071 073 nm) operating at 50 kV and 30 mA at 293 K using ω-2θ scan method. An empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL-97 software[18]. All hydrogen atoms for organic molecules were placed in the calculation position. While the H atoms of water were located from the different Fourier maps. Crystallographic data and selected bond lengths are listed in Table 1, 2 respectively.

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Table 1　Summary of crystallographic data for 1

Empirical formula	$C_{24}H_{88}Cu_4N_{16}O_{50}PV_{18}$	Absorption coefficient / mm^{-1}	2.969
Formula weight	2 603.15	F(000)	2 578
Temperature / K	296(2)	Limiting indices	$-17 \leqslant h \leqslant 17, -17 \leqslant k \leqslant 17, -22 \leqslant l \leqslant 22$
Crystal system	Tetragonal	Reflections collected / unique (R_{int})	21 027 / 1 841 (0.043 4)
Space group	*P*4/*nnc*	Max. and min. transmission	0.717 1, 0.698 9
a / nm	1.505 91(10)	Refinement method	Full-matrix least-squares on F^2
b / nm	1.505 91(10)	Data / parameters	1 841 / 166
c /nm	1.871 3(3)	Goodness-of-fit on F^2	1.022
Volume / nm^3	4.243 8(7)	Final R indices [$I>2\sigma(I)$]	R_1=0.067 0, wR_2=0.180 9
Z	2	R indices (all data)	R_1=0.096 0, wR_2=0.194 6
Calculated density / (g·cm^{-3})	2.037		

Table 2　Selected bond lengths (nm) for 1

V(1)-O(1)	0.157 9(4)	V(2)-O(4)#4	0.191 0(4)	V(3)-O(3)#2	0.195 7(4)
V(1)-O(5)#1	0.184 4(4)	V(2)-O(4)	0.191 0(4)	Cu(1)-N(2)	0.198 6(7)

Continued Table 1

V(1)-O(3)	0.186 6(4)	V(2)-O(4)#5	0.191 0(4)	Cu(1)-N(2)#6	0.198 6(7)
V(1)-O(5)	0.196 9(4)	V(3)-O(2)	0.160 5(4)	Cu(1)-N(1)#6	0.198 8(7)
V(1)-O(3)#2	0.198 5(4)	V(3)-O(4)	0.193 9(4)	Cu(1)-N(1)	0.198 8(7)
V(2)-O(6)	0.160 2(7)	V(3)-O(4)#3	0.194 0(3)	P(1)-O(7)	0.146 7(14)
V(2)-O(4)#3	0.191 0(4)	V(3)-O(5)	0.194 9(4)	P(1)-O(7)#1	0.146 7(14)

Symmetry transformations used to generate equivalent atoms: #1: x, $-y+1/2$, $-z+1/2$; #2: y, x, $-z+1/2$; #3: $-y+1/2$, x, z; #4: $-x+1/2$, $-y+1/2$, z; #5: y, $-x+1/2$, z; #6: $-x+1$, $-y+1$, $-z+1$.

2 Results and discussion

2.1 Crystal structure

Single-crystal X-ray structural analysis reveals compound **1** kepts the ACO topological open framework that constructed from $[V^{IV}_{11}V^{V}_{7}O_{42}(PO_4)]^{8-}$ cages and $[Cu(C_3H_{10}N_2)_2]^{2+}$ bridging groups (Fig.1). The polyanion of **1** is constructed of a well known $[V_{18}O_{42}]^{5-}$ shell and a disordered PO_4^{3-} anion. As a guest, PO_4^{3-} is disordered with the occupied factor of 0.25 for O(7) atoms. While the host shell $[V_{18}O_{42}]^{5-}$ consists of 18 VO_5 square pyramids by sharing the edge through 24 bridging oxygen atoms. The distances of V-O bond are between 0.157 9(4) and 0.198 5(4) nm, while the angles of O-V-O vary from 79.93(15)° to 151.40(16)°, which are similar to the previously reported ones. The Cu cation is coordinated by four N atoms from two 1,2-diaminopropanes and two O terminal atoms from two adjacent anionic cages, forming a distorted octahedral geometry structure. The Cu-O bond length is 0.253 99(44) nm, and O-Cu-O bond angle is 180.000°, which are similar

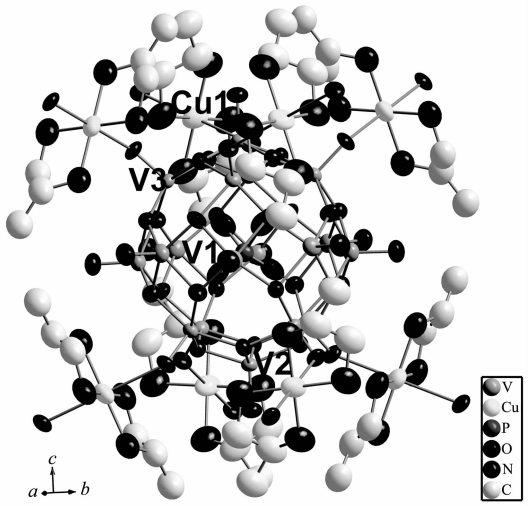

Fig.1 View of the structure of the building unit of open framework **1**

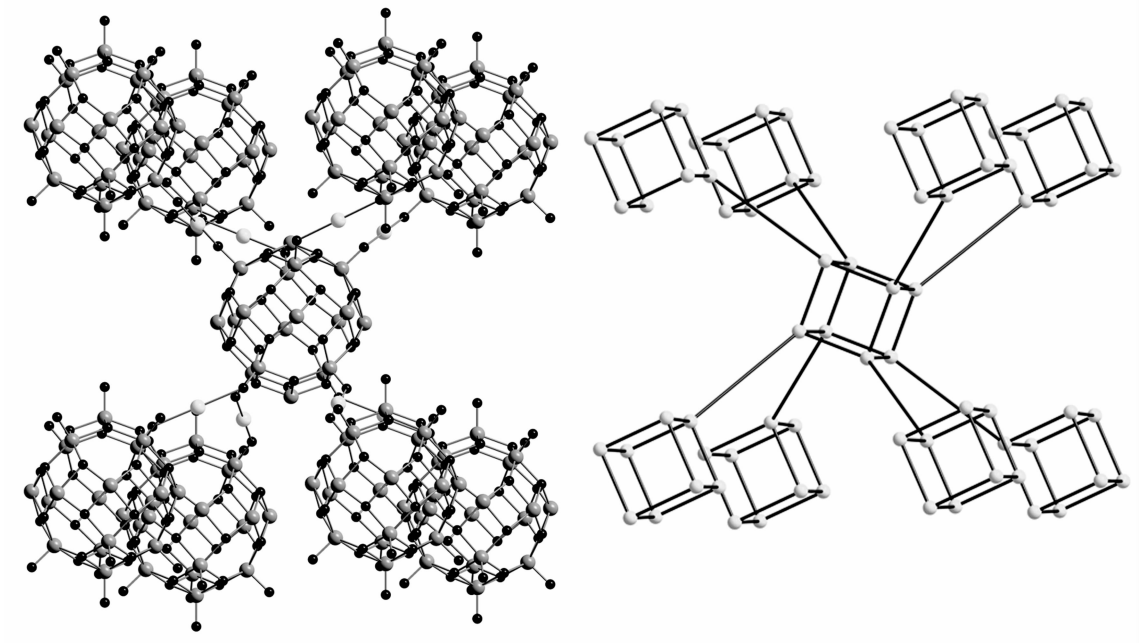

Fig.2 Second building unit of open framework of **1**

to the previously reported analogues $[Cu(C_3H_{10}N_2)_2]_4[V_{18}O_{42}(NO_3)]\cdot 10H_2O$ [17], and $[Cu(C_3H_{10}N_2)_2]_4[H_5V_{18}O_{42}(Cl)]\cdot 8H_2O$[19], while the bond angle of V-O-Cu is 127.344(204)°, in accordance with the Co-O-P bond angle of $CoPO_4$. In the ACO topological framework of $CoPO_4$, each μ_2-oxygen atom connects two D4R units, while each D4R unit links eight neighboring D4R units through μ_2-oxygen atoms. Similary, in the open framework of **1**, each μ_2-briging group $[Cu(C_3H_{10}N_2)_2]^{2+}$ connects two polyanions $[V^{IV}_{11}V^{V}_{7}O_{42}(PO_4)]^{8-}$, while each $[V^{IV}_{11}V^{V}_{7}O_{42}(PO_4)]^{8-}$ anion connects eight adjacent $[V^{IV}_{11}V^{V}_{7}O_{42}(PO_4)]^{8-}$ through eight μ_2-briging group $[Cu(C_3H_{10}N_2)_2]^{2+}$ (Fig.2). Compared with $CoPO_4$, the building unit $[V^{IV}_{11}V^{V}_{7}O_{42}(PO_4)]^{8-}$ and μ_2-briging group $[Cu(C_3H_{10}N_2)_2]^{2+}$ are much bigger than the unit D4R ($P_4Co_4O_{12}$) and μ_2-O; correspondingly, 14-membered ring channels are generated in the open framework of **1** (8-membered ring channels for $CoPO_4$). The narrowest diameter of the 14-membered channels is about 0.753 nm×0.753 nm (Fig.3). Bond valence sum calculations[20] suggest that there are 11 V^{IV} atoms in **1**. The calculation results give a value of 4.441 for V(1), 4.456 for V(2), 4.110 for V(3), the average value is 4.296, which is very closed to the expected value of 4.389 for $[V^{IV}_{11}V^{V}_{7}]$.

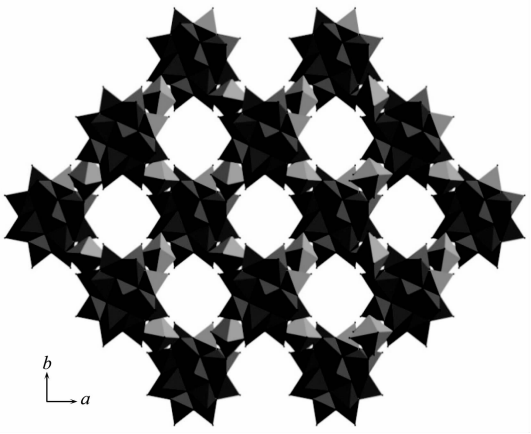

Fig.3　Polyhedral view of **1** along *c* axis

2.2　Infrared spectra

Two strong bands in the IR spectrum of **1** at 978 and 692 cm^{-1} are due to ν (V=O) and ν(O-V-O), respectively. The typical sharp peaks for 1,2-diaminopropane are in the region of 1 383~1 600 cm^{-1}. Weak band at 1 050 cm^{-1} is ascr ibed to ν(P-O). In addition, the broad bands in the 3 135~3 444 cm^{-1} are due to ν(O-H) and ν(N-H) (Fig.4).

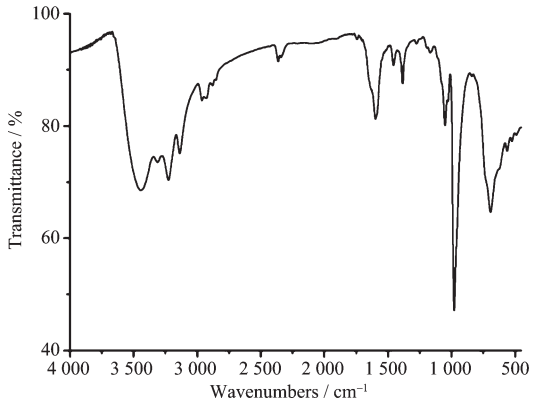

Fig.4　IR spectrum of **1**

2.3　TG analysis

As shown in Fig.5, the total weight loss is 26.20% in the range of 38~670 ℃, which is very in agreement with the calculation value (25.55%). The weight loss 2.89% from 38 to 88 ℃ are assigned to the removal of the crystal water molecules (calcd. 2.77%). The weight loss of 23.31% from 88 to 670 ℃ is attributable to the decomposition of 1,2-diaminopropane (Calcd. value: 22.78%).

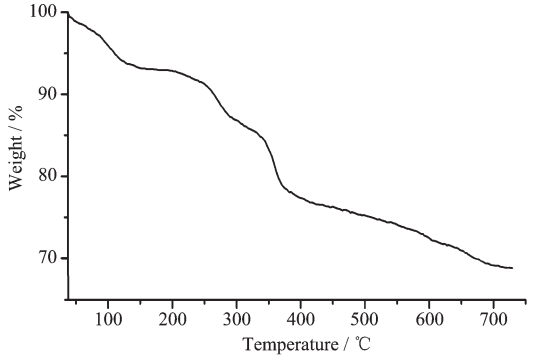

Fig.5　TG curve of **1**

2.4　Magnetic analysis

Preliminary magnetic study has been performed on the crystal sample of **1** in the range of 2~300 K (Fig.6). The effective magnetic moment (μ_{eff}) of **1** at 300 K is 4.87μ_B which is smaller than the expected total value (6.80μ_B) of eleven uncoupled S=1/2 spins of V^{4+} atoms and four uncoupled S=1/2 spins of Cu^{2+} atoms. Upon cooling, the μ_{eff} continuously decreases to a minimum value of 2.81μ_B at 2 K. The magnetic data of **1** were fitted to the Curie-Weiss law in the range of 120.1~300 K, and the best fit was C=3.743 emu·mol·K^{-1} and θ=−85.66 K, characteristic of the antiferromagnetic

interactions of **1**.

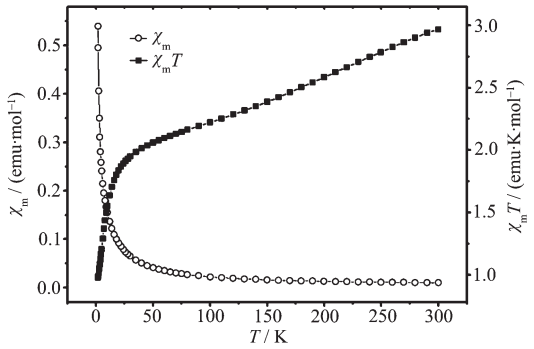

Fig.6 Temperature dependence of $\chi_m T$ and χ_m for **1**

3 Conclusions

In conclusion, a 3D porous Polyoxovanadate $\{[Cu_4(V^{IV}_{11}V^{V}_{7}O_{42}(PO_4))(C_3H_{10}N_2)_8]\cdot 4H_2O\}_n$ with typical ACO topological open framework was synthesized by hydrothermal method. The synthesis of compound **1** demonstrates that it is an effective path to design POMs-based materials through the careful selection of polyoxometalate anions and secondary transition metal complex. An exploration of functional properties of the compound is currently under way.

References:

[1] Klemperer W G, Wall C G. *Chem. Rev.*, **1998**,**98**:297-306

[2] Katsoulis D E. *Chem. Rev.*, **1998**,**98**:359-387

[3] Maspoch D, Molina D R, Veciana J. *Chem. Soc. Rev.*, **2007**, **36**:770-818

[4] Gouzerh P, Proust A. *Chem. Rev.*, **1998**,**98**:77-111

[5] Muller A, Peters F. *Chem. Rev.*, **1998**,**98**:239-271

[6] Pope M T, Muller A. *Angew. Chem. Int. Ed.*, **1991**,**30**:34-48

[7] Livage J. *Coord. Chem. Rev.*, **1998**,**178/180**:999-1018

[8] Chirayil T, Zavalij P Y, Whittingham M S. *Chem. Mater.*, **1998**,**10**:2629-2640

[9] Lin B Z, Liu S X. *Chem. Commun.*, **2002**,**18**:2126-2127

[10]Zhang Y P, Zapf P J, Meyer L M, et al. *Inorg. Chem.*, **1997**, **36**:2159-2165

[11]Wang X Q, Liu L M, Zhang G, et al. *Chem. Commun.*, **2001**, **23**:2472-2473

[12]Khan M I, Yohannes E, Powell D. *Chem. Commun.*, **1999**,**1**: 23-24

[13]Hagrman D, Zapf P J, Zubieta J. *Chem. Commun.*, **1998**,**12**: 1283-1284

[14]Khan M I, Yohannes E, Powell D. *Inorg. Chem.*, **1999**,**38**: 212-213

[15]Pan C L, Xu J Q, Chu D Q, et al. *Inorg. Chem. Commun.*, **2003**,**6**:939-941

[16]Feng P Y, Bu X H, Stucky G D. *Nature*, **1997**,**388**:735-741

[17]Xu Y, Nie L B, Zhu D R, et al. *Cryst. Growth Des.*, **2007**,**7**: 925-929

[18]Sheldrick G M. *SHELXTL Version* 5.10. *Bruker AXS Inc*, USA: Madsion, Wisconsion, **1997**.

[19]CUI Xiao-Bing(崔小兵), ZHENG Shou-Tian(郑寿添), DING Lan(丁兰), et al. *Chinese J. Struct. Chem.*(*Jiegou Huaxue Xuebao*), **2003**,**22**:491-494

[20]Brown I D, Keeffe M O′, Navrotsky A. *Structure and Bonding in Crystals*. New York: Academic Press, **1981**:2