第 28 卷第 1 期 无 机 化 学 学 报 Vol.28 No.1
2012 年 1 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 176-180

一种多钒氧酸有机铵盐的水热合成、晶体结构及催化性质研究

王从岭 付 洁 梅 华* 颜大伟 许 岩*
(南京工业大学化学化工学院,材料化学工程国家重点实验室,南京 210009)

摘要: 本文采用水热技术合成了一种多钒氧酸盐$[NH_3(CH_2)_4NH_3][H_2pip]_2[V_{10}O_{28}]\cdot 6H_2O$ (**1**,pip=哌嗪),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。化合物 **1** 为单斜晶系,空间群为 $P2_1/n$,晶胞参数为 a=1.229 85(10) nm,b=1.075 10(9) nm,c=1.496 71(12) nm,β=93.947 0(10)°,V=1.974 3(3) nm^3,Z=2。晶体结构分析表明,化合物 **1** 是由$[V_{10}O_{28}]^{6-}$阴离子簇、质子化的 1,4-丁二胺和哌嗪阳离子以及结晶水构成。有机阳离子和结晶水通过 O–H···O 和 N–H···O 氢键相互作用将阴离子连接形成三维结构。

关键词: 水热合成; 多钒氧酸盐; 晶体结构
中图分类号: O614.51+1 **文献标识码**: A **文章编号**: 1001-4861(2012)01-0176-05

Hydrothermal Synthesis, Crystal Structure and Catalytic Properties of a Polyoxovanadate Organicamine

WANG Cong-Ling FU Jie MEI Hua* YAN Da-Wei XU Yan*
(*College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-oriented Chemical Engineering, Nanjing University of Technology, Nanjing* 210009, *China*)

Abstract: A polyoxovanadate $[NH_3(CH_2)_4NH_3][H_2pip]_2[V_{10}O_{28}]\cdot 6H_2O$ (**1**, pip=piperazine) has been synthesized by hydrothermal method and characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, with cell parameters of a=1.229 85(10) nm, b=1.075 10(9) nm, c=1.496 71(12) nm, β=93.947 0(10)°, V=1.974 3(3) nm^3, Z=2. Crystallographic analysis reveals that it is constructed from anionic cluster $[V_{10}O_{28}]^{6-}$, protonated 1,4-butanediamine and piperazine cations, as well as waters of crystallization. Organic cations and waters of crystallization further connect the anions into a three-dimensional framework by water-anion hydrogen bonds O–H···O and cation-anion N–H···O interactions. CCDC: 848090.

Key words: hydrothermal synthesis; polyoxovanadate; crystal structure

0 Introduction

During the past few years, polyoxovanadium have been extensively studied because of their diverse structure- and property-based functionalities in catalysis, electrical conductivity, selective adsorption, biological chemistry, magnetism and so on[1-4]. During the last decade, an important advance in polyoxovanadium chemistry has been the rational design and assembly of V-O cluster anions and also V-O layers with an organic or bridging transition-metal complexed into extended three-dimensional (3D) frameworks [5]. So far, a number of polyoxovanadium with 0D clusters, 1D

收稿日期:2011-07-20。收修改稿日期:2011-09-13。
国家自然科学基金(No.20971068)资助项目。
*通讯联系人。E-mail:yanxu@njut.edu.cn

chains, 2D networks and 3D open frameworks have been reported[5-10]. Decavanadate compounds[11], as a typical polyoxovanadium, are made of $[V_{10}O_{28}]^{6-}$ units that can be more or less protonated as $[H_nV_{10}O_{28}]^{(6-n)-}$ (n= 1~4)[12-13]. The arrangement and specific orientation of the decavanadate units in their crystalline state are under active investigation in an attempt to determine the key factors for decavanadates self-assembly and design[14-20]. Organic species providing short-range bonding interactions (hydrogen bonds, C-H/π) modify the principles guiding the crystal structure[12-20]. In this work, we have successfully synthesized a polyoxovanadate $[NH_3(CH_2)_4NH_3][H_2pip]_2[V_{10}O_{28}]\cdot 6H_2O$ (**1**, pip= piperazine), constructed from anionic cluster $[V_{10}O_{28}]^{6-}$, both protonated 1,4-butanediamine and piperazine cations, as well as waters of crystallization.

1 Experimental

1.1 Reagents and measurements

All chemical reagents were purchased 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}.

1.2 Synthesis

A mixture of V_2O_5 (0.403 2 g, 2.22 mmol), piperazine (0.097 5 g, 1.13 mmol), 1,4-butanediamine (0.102 9 g, 1.17 mmol), phosphoric acid (0.2 mL, 2.93 mmol), and 10 mL distilled water was stirred for 0.5 h, then was neutralized to pH=7 with 6 mol·L^{-1} NaOH. The mixture was sealed in a 20 mL Teflon-lined stainless steel reactor and heated to 160 ℃ for 7 d. After cooled to room temperature, the product was washed with distilled water, filtered and dried in the air. Orange schistic-like crystals with a little unknown yellow powder were obtained (0.186 3 g, yield 31.5% based on V). Elemental analysis: found(%): C, 11.92; H, 3.80; N, 6.39; Calcd.(%): C, 10.81; H, 3.75; N, 6.31.

1.3 X-ray structure determination

The single crystals of compounds **1** was singled out under the microscope and glued at the tip of a thin glass fiber with epoxy glue in open air for data collection, and the crystallographic data were collected on a Bruker Apex Ⅱ CCD with Mo $K\alpha$ radiation (λ=0.071 073 nm) at 296 K using ω-2θ scan method. The crystal structure was solved by direct method and refined on $|F|^2$ by full-matrix least-squares methods using the SHELX97 program package[21]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organoamine for complexes 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 and 2, respectively.

CCDC: 848090.

Table 1　Summary of crystallographic data for 1

Empirical formula	$C_{12}H_{50}N_6O_{34}V_{10}$	Absorption coefficient / mm^{-1}	2.370
Formula weight	1 331.98	F(000)	1 332
Temperature / K	296(2)	Crystal size / mm	0.13×0.12×0.12
Crystal system	Monoclinic	Limiting indices	$-13 \leqslant h \leqslant 14, -12 \leqslant k \leqslant 12, -18 \leqslant l \leqslant 17$
Space group	$P2_1/n$	Reflections collected / unique (R_{int})	14 088 / 3 650 (0.054 9)
a / nm	1.229 85(10)	Max. and min. transmission	0.764 1, 0.748 1
b / nm	1.075 10(9)	Refinement method	Full-matrix least-squares on $\|F\|^2$
c / nm	1.496 71(12)	Data / parameters	3 650 / 298
β / (°)	93.947 0(10)	Goodness-of-fit on F^2	1.004
Volume / nm^3	1.974 3(3)	Final R indices [$I>2\sigma(I)$]	R_1=0.035 9, wR_2=0.078 0
Z	2	R indices (all data)	R_1=0.062 0, wR_2=0.085 8
Calculated density / (g·cm^{-3})	2.241		

Table 2 Selected bond lengths (nm) for 1

V(1)-O(5)	0.168 0(3)	V(3)-O(3)	0.203 9(3)	O(1)-V(3)#1	0.234 6(2)
V(1)-O(3)	0.169 9(3)	V(3)-O(1)#1	0.234 6(2)	O(4)-V(4)#1	0.200 8(2)
V(1)-O(4)	0.192 5(2)	V(4)-O(10)	0.160 7(3)	O(4)-V(2)#1	0.202 6(3)
V(1)-O(2)	0.192 6(2)	V(4)-O(8)	0.182 1(3)	O(6)-V(5)#1	0.183 8(3)
V(1)-O(1)	0.209 6(2)	V(4)-O(7)#1	0.184 2(3)	O(7)-V(4)#1	0.184 2(3)
V(1)-O(1)#1	0.211 9(2)	V(4)-O(2)	0.200 5(3)	O(9)-V(5)#1	0.183 3(3)
V(2)-O(11)	0.161 6(3)	V(4)-O(4)#1	0.200 8(2)	C(1)-N(1)	0.150 3(6)
V(2)-O(12)	0.180 5(3)	V(4)-O(1)	0.223 6(2)	C(1)-C(2)	0.151 1(6)
V(2)-O(6)	0.184 6(3)	V(5)-O(13)	0.161 4(3)	C(2)-N(2)	0.148 8(5)
V(2)-O(2)	0.198 6(3)	V(5)-O(9)#1	0.183 3(3)	C(3)-N(1)	0.149 0(6)
V(2)-O(4)#1	0.202 6(3)	V(5)-O(6)#1	0.183 8(3)	C(3)-C(4)	0.150 6(6)
V(2)-O(1)#1	0.224 6(2)	V(5)-O(8)	0.191 0(3)	C(4)-N(2)	0.148 4(5)
V(3)-O(14)	0.160 1(3)	V(5)-O(5)	0.205 2(3)	C(5)-C(6)	0.150 5(6)
V(3)-O(9)	0.185 0(3)	V(5)-O(1)	0.230 6(2)	C(5)-C(5)#2	0.153 5(8)
V(3)-O(7)	0.187 0(3)	O(1)-V(1)#1	0.211 9(2)	C(6)-N(3)	0.149 7(5)
V(3)-O(12)	0.187 7(3)	O(1)-V(2)#1	0.224 6(2)		

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

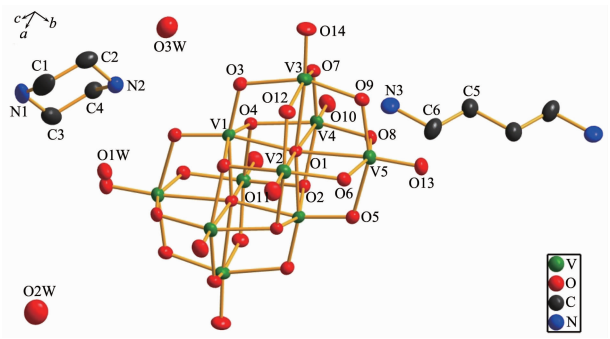
1.4 Catalysis experiment

According to our previous work[23-25], the oxidation of styrene was performed in 50 mL double necked round-bottomed flask fitted under the condition of water cooled condenser and magnetic stirrer. Styrene (0.75 mL, 6.4 mmol) and compound **1** (50 mg) were respectively mixed in the flasks with 7.5 mL CH_3CN solvent, and kept heating at 333 K. The hydrogen peroxide (30%) (2.2 mL, 21.1 mmol) was added to the blended solution. The mixture was analyzed by a gas chromatograph (GC-6890, FID; 30 m ×0.32 mm capillary column) after 2 hours′s reaction.

2 Results and discussion

2.1 Crystal structure

Single-crystal X-ray analysis shows that compound **1** consists of $[V_{10}O_{28}]^{6-}$ anionic cluster, protonated 1,4-butanediamine and piperazine cations, and waters of crystallization (Fig.1). The ployoxoanion cluster is built up from five independent vanadium atoms, by means of an inversion center, an octahedrally packed cluster of 10 edge-shared VO_6 octahedra. The decavanadate anions exhibit a well-known cage-like structure, in which six vanadium atoms (V(1), V(3), V(5) and their crystallographic partners) are in the same plane, and four vanadium atoms (V(2), V(4) and their crystallographic partners) above and below the plane, with bond lengths in the range of 0.160 1(3)~0.169 9(3) nm for terminal oxygen and 0.180 5(3)~0.234 6(2) nm for bridging oxygen atoms. The O-V-O angles are in the range of 74.08(9)°~106.39(12)° and 154.33(1)°~174.83(12)° for *cis*- and *trans*-related bonds, respectively, consistent with $[V_{10}O_{28}]^{6-}$ clusters observed in other compounds[12-19]. In compound **1**, protonated 1,4-butanediamine and piperazine cations maintain the charge balance.



Thermal ellipsoids are drawn at 50% probability; Hydrogens are omitted for clarity

Fig.1 ORTEP view of the compound **1** structure showing the atom labeling scheme

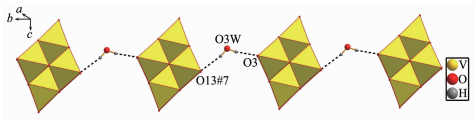
It is worth of mentioning that there are a variety of O–H···O and N–H···O hydrogen bonds (Table 3). The out-projecting oxygen atoms of decavanadate clusters

Table 3 Distances and angles of the hydrogen bond interactions in 1

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠D–H···A / (°)
N1–H1C···O8#4	0.090	0.235	0.311 3(5)	142
N1–H1D···O10#6	0.090	0.246	0.307 6(4)	126
N1–H1D···O11#6	0.090	0.257	0.327 0(4)	135
N1–H1D···O4#7	0.090	0.212	0.292 0(5)	147
N2–H2C···O3W	0.090	0.189	0.276 9(5)	164
N2–H2D···O1W	0.090	0.192	0.280 5(4)	168
N3–H3C···O2W#3	0.089	0.192	0.279 2(4)	166
N3–H3D···O9	0.089	0.203	0.290 5(4)	168
N3–H3E···O1W#5	0.089	0.227	0.286 0(4)	123
N3–H3E···O14#5	0.089	0.226	0.303 3(4)	144
O1W–H1WB···O7#8	0.083(3)	0.187(3)	0.269 4(4)	173(4)
O1W–H1WA···O8	0.081(3)	0.189(3)	0.269 9(4)	177(2)
O2W–H2WB···O2#8	0.080(4)	0.224(5)	0.298 7(5)	155(4)
O3W–H3WA···O3	0.082(3)	0.199(2)	0.279 7(4)	170(4)
O3W–H3WB···O13#7	0.081(4)	0.207(4)	0.286 7(4)	167(5)

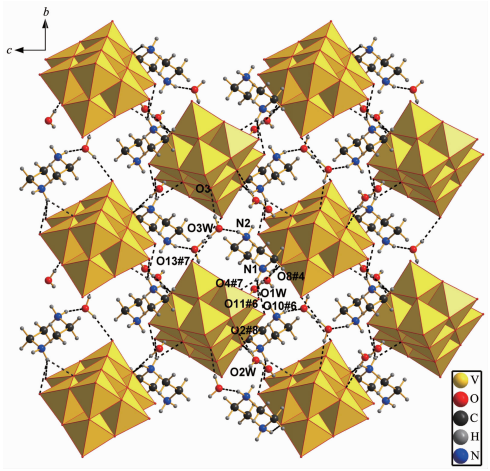
Symmetry transformations used to generate equivalent atoms: #3: $-x$, $2-y$, $-z$; #4: $1/2-x$, $-1/2+y$, $-1/2-z$; #5: $-1/2-x$, $1/2+y$, $-1/2-z$; #6: x, $-1+y$, z; #7: $-x$, $1-y$, $-1-z$; #8: $1/2+x$, $3/2-y$, $1/2+z$.

are strongly hydrogen-bonded to waters of crystallization and organic cations, with the O···O and O···N distances in the range of 0.269 4(4)~0.327 0(4) nm. Interestingly, decavanadate units are assembled into 1D chains by means of O(3w)–H···O(3) and O(3w)–H···O(13) hydrogen bonding interactions (Fig.2). In addition, adjacent 1D chains are linked by N(1) and N(2) of the piperazine cations using hydrogen bonds to generate a 2D soft layer, as shown in Fig.3. Then, the hydrogen bonds connect 1,4-butanediamine cations between the adjacent soft layers to make a soft 3D supermolecular open framework, as depicted in Fig.4. To best of our



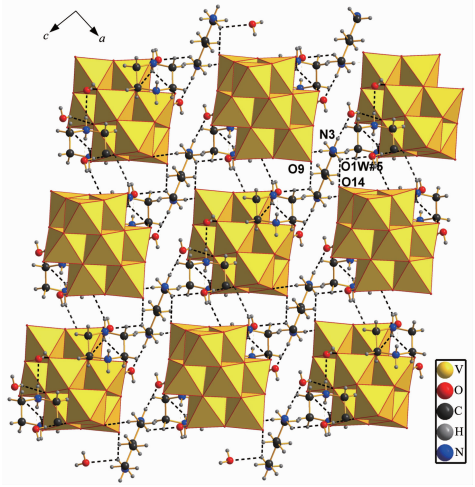
Symmetry codes: #7: $-x$, $1-y$, $-1-z$

Fig.2　Adjacent decavanadate are connected by hydrogen bonding from waters of crystallization to make 1D chains



Symmetry codes: #4: $1/2-x$, $-1/2+y$, $-1/2-z$; #6: x, $-1+y$, z; #7: $-x$, $1-y$, $-1-z$; #8: $1/2+x$, $3/2-y$, $1/2+z$

Fig.3　Adjacent 1D chains are connected by hydrogen bonding from piperazine cations to make a soft layer



Symmetry codes: #5: $-1/2-x$, $1/2+y$, $-1/2-z$

Fig.4　1,4-butanediamine cations filled by hydrogen bonds between the adjacent polyanion layers to make a 3D framework

knowledge, decavanadates including two types of protonated organic amine cations are very rare. The assignment of oxidation states for V of **1** are based on bond valence sum calculations[22], which give average oxidation of +5 for V. The calculated value is in agreement with the formula of **1**. The synthesis of compound **1** demonstrates that the presence of two types organic species providing hydrogen bonding interactions can modify new vanadates.

2.2 Infrared spectra

The IR spectrum of **1** shows two strong bands, the one in 951 cm^{-1} is due to ν(V=O), while the other at 561~830 cm^{-1} are attributed to ν(O-V-O) and ν(V-O_b). Typically sharp peaks for 1,4-diaminobutane and piperazine are at the region of 1 383~1 616 cm^{-1}. In addition, the broad bands at 3 018~3 444 cm^{-1} are due to ν(O-H) and ν(N-H).

2.3 TG analysis

As shown in Fig.5, total weight loss is 28.90% in the range of 38~550 ℃, which is in agreement with the calculated value (31.73%). Weight loss of 7.90% from 72 to 205 ℃ is assigned to the removal of the crystal water molecules (calculated value: 8.11%). Weight loss of 11.70% from 205 to 370 ℃ is attributable to the decomposition of piperazine (calculated value: 13.24%). Weight loss 9.20% from 370 to 550 ℃ is due to the decomposition of 1,4-diaminobutane (calculated value: 6.77%).

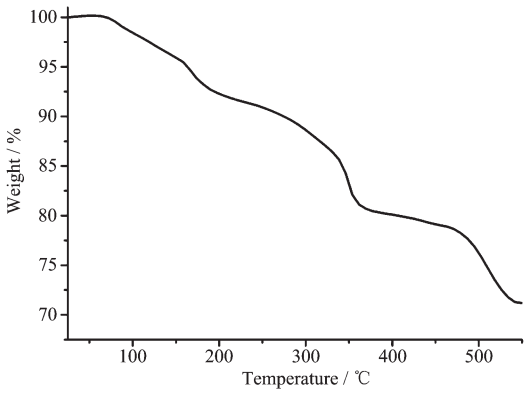


Fig.5 Thermogravimetric analysis of **1**

2.4 Catalytic property

Although the 5% conversion of styrene is poor, selectivity of benzaldehyde, benzoic acid and epoxide were 100%, 0% and 0%, respectively. The catalytic property results show that compound **1** has low conversion and high selectivity for benzaldehyde.

References:

[1] Müller A, Peters F, Pope M T, et al. *Chem. Rev.*, **1998**,**98**:239-272

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

[3] Dolbecq A, Dumas E, Mayer C R, et al. *Chem. Rev.*, **2010**, **110**:6009-6048

[4] Long D L, Tsunashima R, Cronin L. *Angew. Chem., Int. Ed.*, **2010**,**49**:1736-1758

[5] Xu Y, Zhou G P, Zhu D R. *Inorg. Chem.*, **2008**,**47**:567-571

[6] Zhou G P, Xu Y, Guo C Y, et al. *J. Cluster Sci.*, **2007**,**18**:388-395

[7] Khan M I, Yohannes E, Doedens R J. *Angew. Chem., Int. Ed.*, **1999**,**38**:1292-1294

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

[9] Rarig R S J, Zubieta J. *Dalton Trans.*, **2003**,**9**:1861-1868

[10]Zhang Z B, Xu Y, Zheng L, et al. *Z. Anorg. Allg. Chem.*, **2010**,**636**:1576-1579

[11]Evans H. *Inorg. Chem.*, **1966**,**5**:967-977

[12]Jouffret L, Rivenet M, Abraham F. *Inorg. Chem. Commun.*, **2010**,**13**:5-9

[13]Kojima T, Antonio M R, Ozeki T. *J. Am. Chem. Soc.*, **2011**, **133**:7248-7251

[14]Klitincová L, Rakovsk E, Schwendt P, et al. *Inorg. Chem. Commun.*, **2010**,**13**:1275-1277

[15]Klitincová L, Rakovsk E, Schwendt P. *Inorg. Chem. Commun.*, **2008**,**11**:1140-1142

[16]Gil-García R, Zichner R, Díez-Gómez V. *Eur. J. Inorg. Chem.*, **2010**:4513-4525

[17]Zhang X M, Chen X M. *Inorg. Chem. Commun.*, **2003**,**6**:206-209

[18]Zheng L, Wang Y S, Wang X Q, et al. *Inorg. Chem.*, **2001**,**40**: 1380-1385

[19]Duraisamy T, Ojha N, Ramanan A, et al. *Chem. Mater.*, **1999**, **11**:2339-2349

[20]Khan M I, Chen Q, Goshorn D P. *J. Am. Chem. Soc.*, **1992**, **114**:3341-3346

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

[22]Brown I D. *Chem. Rev.*, **2009**,**109**: 6858-6919

[23]Chen Q, Cui Y, Sun Q, et al. *Z. Anorg. Allg. Chem.*, **2009**, **635**:2302-2308

[24]Mei H, Yan D W, Chen Q. *Inorg. Chim. Acta*, **2010**,**363**:2265-2268

[25]SUN Yue-Xia(孙月霞), ZHANG Zhi-Bin(张志斌), SUN Qi(孙琪), et al. *Chem. J. Chin. Univ.* (*Gaodeng Xuexiao Huaxue Xuebao*), **2011**,**27**:556-560