Chinese Chemical Letters Vol. 15, No. 2, pp 220 – 223, 2004
http://www.imm.ac.cn/journal/ccl.html

Hydrothermal Synthesis and Structural Characterization of the Cage-based Arsenic-Vanadium Microporous Material: $[As_2V^{IV}{}_8V^{V}{}_2O_{26}]{\bullet}8H_2O$

Shou Tian ZHENG[1], Yan Qiong SUN[1], Guo Yu YANG[1,2] *

[1]Coordination and Hydrothermal Chemisrty Group, State Key Laboratory of Structural Chemistry,
Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences,
Fuzhou 350002
[2]State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093

Abstract: The complex of $[As_2V^{IV}{}_8V^{V}{}_2O_{26}]{\bullet}8H_2O$ **1** has been hydrothermally synthesized and characterized by IR, elemental analysis, EPR, TGA and single crystal X-ray diffraction analysis. The structure features of **1** are described.

Keywords: Hydrothermal synthesis, arsenic, vanadium, zeolite, cluster.

Interest in polyoxometalates is expanding rapidly due to the enormous variety of structure topologies leading to interesting and unexpected properties in such diverse field as catalysis, materials science and medicine[1-4]. Frameworks constructed from square pyramidal, octahedral, tetrahedral units are well documented in the solid-state phases of the V/O/P system[5]. For the heteropolyanions class of clusters, the V/O/As system has been extensively studied, but the linking of arsenic-vanadium clusters into molecular and supramolecular structures is much less developed[6-7]. Here we report the hydrothermal synthesis and structural characterization of a novel three-dimensional hybrid solid, $[As_2V^{IV}{}_8V^{V}{}_2O_{26}]{\bullet}8H_2O$ (**1**).

Experimental

A mixture of H_2O: V_2O_5: As_2O_5: $Ni(AC)_2{\bullet}4H_2O$: $H_2NCH_2CH_2NH_2$ in the mole ratios of 1667:11:2:5:15 was sealed in a 40 mL Teflon-lined autoclave and heated under autogenous pressure at 160°C for 3 days. The pH value was about 8.0 before and after the reaction. The black cubic crystal **1** was obtained. The data of **1** was collected on a Siemens Smart CCD diffractometer with MoK_α radiation (λ=0.71073 Å) at 293 K using an ω scan mode in the range of $5.71 < \theta < 24.96°$. The structure was determined by using SHELX-97 program. Single- crystal X-ray structural analysis shows that crystal is in a cubic system with space group *Im-3m* and cell parameters a = 16.7581(2)Å, V =

---

[*] E-mail: ygy@ms.fjirsm.ac.cn

4706.24(10)Å ^{3}, R = 0.0756, $wR2$ = 0.1820, Z = 12, Dc = 2.581 Mg/m^3, μ = 5.043 mm^{-1}, *F(000)* = 3504 , *Mt* = 1219.37. Elemental analysis (%) calcd for [$As_2V^{IV}{}_8V^{V}{}_2O_{26}$]: V:41.80, As: 12.30; found: V: 42.10, As: 12.00. IR (KBr, cm^{-1}): 1624$(\nu_{H\text{-}O\text{-}H})$, 1004.3 ($\nu_{C=O}$), 799,639 ($\nu_{\text{-O-As}}$).

Results and Disussion

Figure 1 The asymmetric unit (a) of **1** and the two building units: [$V_{10}O_{26}$] (b) and AsO_4 (c)

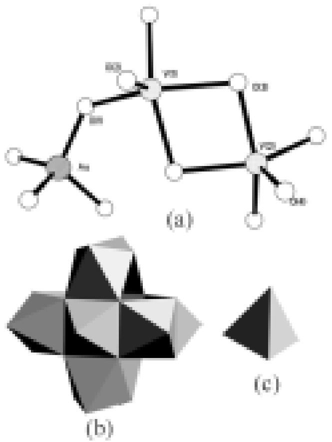
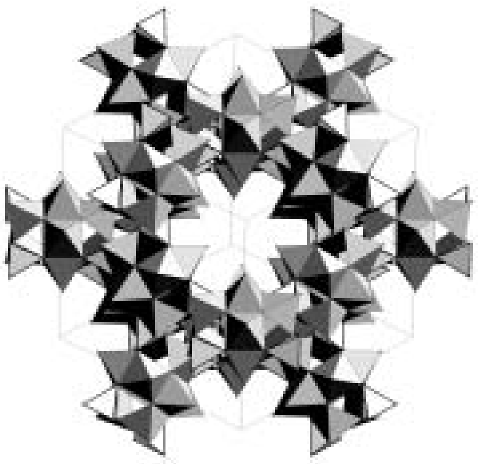


Figure 2 A large cage in the cell unit of **1**



The asymmetric unit of **1** mainly includes two V atoms, one As atoms and four oxygen atoms. The vanadium exhibits only one type of coordination: pyramidal **(Figure 1(a))**. The pyramidal geometry around vanadium V(1) is defined by a terminal oxo group [O(2)], four μ-oxygen atom[O(1) × 2, O(3) × 2] of the shell. Another square-pyramidal geometry around V(2) is formed by four basal μ_3-oxo[O(3)] groups from the shell and an apical terminal oxo group[O(4)]. The V-O distances are found in the range 1.887(14)–1.972(5) Å, and the V=O distances are 1.57(3) and 1.62(4) Å. The As atom is in a tetrahedral environment, the average As-O(1) distance is 1.665(9) Å. Bond lengths and bond angles are listed in **Table 1**. The valence sums[8] for V(1) and V(2) atoms are +4 and +5, very consistent with the expected value for [$As_2V^{IV}{}_8V^{V}{}_2O_{26}$] which determined by charge balance of molecular formula.

The [$V^{IV}{}_8V^{V}{}_2O_{26}$] unit has idealized T_d symmetry and consists of ten VO_5 square pyramids, whereby a hollow sphere is formed **(Figure 1(b))**. Six VO_5 square pyramids share opposite edges each other to form a 6-ring. These six vanadium atoms are co-plane. Sharing two of the ten VO_5 square pyramids, two 6-ring are mutually perpendicular to form a neutral cage. The dimension of the [$V^{IV}{}_8V^{V}{}_2O_{26}$] core is 3.6×6.5×6.5 Å. In the cubic cell, 18 [$V^{IV}{}_8V^{V}{}_2O_{26}$] units, which joined together by AsO_4 bridging groups, formed a large cavity with a mean diameter of 11.896 Å along [111] direction **(Figure 2)**. It can be understood that the structure is built up from two secondary building units: the [$V^{IV}{}_8V^{V}{}_2O_{26}$] unit and the AsO_4 tetrahedron. Each [$V^{IV}{}_8V^{V}{}_2O_{26}$] unit links four others on the *bc* plane *via* the AsO_4 tetrahedron, resulting in a layer with 20-ring **(Figure 3)**. The layers are held together in a staggered fashion through AsO_4 bridging groups **(Figure 3,** the line frame represent an adjacent layer**)**. This staggered fashion of the layers generates a fascinating 12-channels' structure with dimension of 5.6×10 Å, and eight water molecules are filled in hexagonal channels **(Figure 4)**.

Table 1 Bond lengths [Å] and angles [°] for **1**

Bond	Length (Å)	Bond	Length (Å)
As-O(1)×4	1.665(9)	V(1)-O(1)×2	1.939(7)
V(1)-O(2)	1.57(3)	V(2)-O(3)×4	1.887(14)
V(2)-O(4)	1.62(4)	V(1)-O(3)×2	1.972(5)
Bond	**Angle (°)**	**Bond**	**Angle (°)**
O(1A)-As-O(1)	112.2(6)	O(3)-V(2)-O(3C)	140.7(11)
O(1)-As-O(1B)	108.1(3)	O(3)-V(2)-O(3D)	83.5(4)
O(1)-V(1)-O(1F)	86.5(4)	O(4)-V(2)-O(3)	109.6(5)
O(1)-V(1)-O(3)	147.5(6)	As-O(1)-V(1)	127.7(4)
O(1)-V(1)-O(3D)	88.3(5)	V(2)-O(3)-V(1)	98.5(4)
O(3D)-V(1)-O(3)	79.2(8)	V(1)-O(1)-V(1G)	82.2(4)
O(2)-V(1)-O(1)	106.4(6)	V(1)-O(3)-V(1E)	147.3(10)
O(2)-V(1)-O(3)	105.9(8)		

Symmetry transformations used to generate equivalent atoms: A:-x+1,y,-z B:-z+1/2, -y+1/2,x-1/2 C:-x+1,-y+1,z D: :y, x, z E: x,-y+1,z F: y, x,-z G: x, y,-z .

Figure 3 The staggered layer structure of **1** with 20-ring along c axis

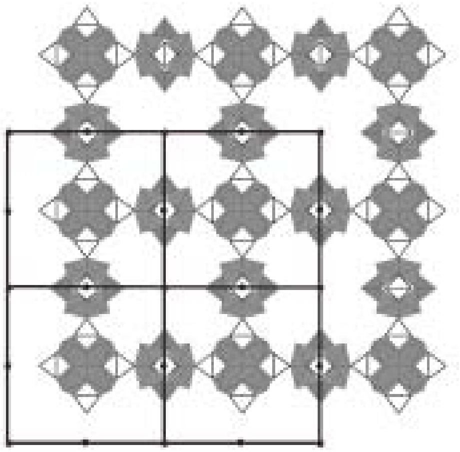
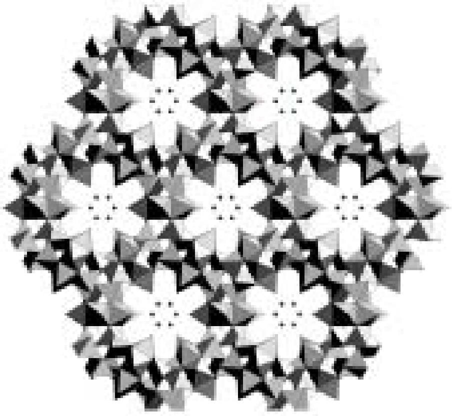


Figure 4 The 12-ring channel's structure of **1** along [111] direction



The EPR spectra of the sample were measured at room temperature. The sample shows an EPR signal (g=1.9575) that indicates the existence of V^{4+} formation, which is consistent with both black crystal and valence-bond calculation. The thermogravimetric curve, performed under Ar atmosphere, showed three distinct losses. The first one begins at 45.53°C and ends at 243.11°C, corresponding to the water molecules of **1** ($\%_{exp}$ = 11.72, $\%_{theo}$=11.81). The next two steps weight loss concerns the departure of the arsenic and collapse of the framework.

It is noteworthy that the $[As_2V^{IV}_8V^V_2O_{26}(\mu{-}H_2O)]\cdot 8H_2O$[9] was the first polyoxoanions linked by AsO_4 tetrahedron. Compound **1** can be regarded as the dehydration of $[As_2V^{IV}_8V^V_2O_{26}(\mu{-}H_2O)]$. Similar example has also ever been reported[10-11]. Compared to $[As_2V^{IV}_8V^V_2O_{26}(\mu{-}H_2O)]$ (space group *I-43m*), the structure of compound **1** appears more higher space group *Im-3m* due to the loss of the central μ-bridging water molecular. Thus leads to a drastic change in the coordination polyhedron of V and completely difference in the amount of atoms in the asymmetric unit. The coordination polyhedron of V in **1** exhibit only VO_5 square pyramid rather than VO_5 square pyramid and VO_6 octahedron in the compound $[As_2V^{IV}_8V^V_2O_{26}(\mu{-}H_2O)]$. The asymmetric unit of **1** contains one As atom, two V atoms, four O atoms and one H_2O molecule, while one As, three V, five O atoms and one H_2O molecule in the compound of $[As_2V^{IV}_8V^V_2O_{26}(\mu{-}H_2O)]$.

Acknowledgment

This work is supported by the NNSF of China (Grant No. 20271050 and 20171045), the Ministry of Finance of China, the Talents Program of Chinese Academy of Sciences.

Reference and Notes

1. A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.*, ***1998***, *98*, 239.
2. C. M. Liu, S. Gao, H. Z. Kou, *Chem. Commun*., **2001**, 1670.
3. Y. H. Wang, C. W. Hu, E. B. Wang, *Chem. J. Chin. Univ*., **2001**, *22*(3), 362.
4. B. Z. Lin, S. X. Liu, *J. Chem. Soc., Dalton Trans.*, **2002**, 865.
5. V. Soghomonian, Q. Chen, J. Zubieta, *Angew. Chem*., **1993**, *105*, 601.
6. M. H. Kahn , J. Zubieta, *Angew. Chem., Int. Ed. Engl*., **1994**, *33*, 760.
7. W. M. Bu, G. Y. Yang, L. Ye, J. Q. Xu, Y. G. Fan, *Chem. Lett.*, **2000**, *24*, 462.
8. I. D. Brownand, D. Altermatt, *Acta Cryst.*, **1985**, *B41*, 244.
9. W. M. Bu, L. Ye, G. Y. Yang, Y. G. Fun, J. Q. Xu, *Chem.Commun*., **2000**, 1279.
10. M. Cavellec, G. Ferey., *Microporous and Mesoporous Materials*, **1998**, *20*, 45.
11. M. Cavellec, D. Riou, C. Nindaous, G. Ferey, *Zeolites*, **1996**, *17*, 250.

Received 20 January, 2003