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Hydrothermal synthesis, structure and catalytic property of a novel open-framework oxovanadium arsenate

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A three-dimensional oxovanadium arsenate has been hydrothermally synthesized and structurally determined, which is composed of novel decavanadium clusters linked by AsO_4 tetrahedra to form large cavities with 12-membered ring windows; catalytic measurements show activity for phenol hydroxylation.

Open-framework materials are of great interest from both the industrial and academic point of view due to their catalytic, adsorbent, and ion-exchange properties.[1] While the large voids, chemical stability and size discriminatory sorptive behavior of zeolite renders them very useful, open-framework solids containing transition elements could provide novel properties including catalytic, photochemical and magnetic properties inaccessible in main group systems. This has directed recent efforts to the preparation of non-silicate materials with the goal of preparing solids with larger dimensionalities or unique framework topologies or novel polyhedral connectivities. Oxide examples include aluminophosphates, zinc, ion and beryllium phosphates and arsenates.[2] The contemporary interest in oxovanadium phosphates reflects not only their practical applications as catalysts, ionic conductors, ion-exchangers and magnetic materials but also their fundamental chemistry, which is characterized by unusual structural complexity. Vanadium and oxygen in different valence states can form tetrahedral, square-pyramidal and octahedral co-ordination and aggregate by condensation of polyhedra through shared oxygen atoms. Template controlled linking of these units has led to a large number of oxovanadium phosphates with open frameworks,[3] in which two eye-catching results are the first evidence of an inorganic double helix in $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$[4] and the existence of giant voids in two three-dimensional vanadium phosphates $[HN(CH_2CH_2)_3NH]K_{1.35}[V_5O_9(PO_4)_2]\cdot xH_2O$ and $Cs_3[V_5O_9(PO_4)_2]\cdot xH_2O$.[5] Our recent interests concern oxovanadium borophosphates and two exciting compounds, VBP-J1 and VBP-J2, which are constructed of 12-membered ring crown-shaped clusters, have been synthesized.[6] To prepare oxovanadium boroarsenate, a novel microporous oxovanadium arsenate, denoted VAs-1, was synthesized. Here we report its synthesis, single crystal structure and catalytic property for phenol hydroxylation.

The oxovanadium arsenate VAs-1 was synthesized under mild hydrothermal conditions starting from a mixture of 0.4 g V_2O_5, 0.5 g KH_2AsO_4, 0.5 g H_3BO_3, 0.5 mL triethylenetetraamine, 1.2 mL HCl and 20 mL water. The starting mixture was stirred to attain homogeneity and then transferred into a 40 ml Teflon-lined autoclave and crystallized at 160 °C for two days. The initial pH value of the mixture was 8.0. The reaction led to the formation of dark-green cubic crystals in 40% yield (based on vanadium). Comparison of the experimental and simulated XRD patterns showed that the compound was obtained as a monophasic product. The presence of organoamine and borate is essential for isolation of VAs-1, although both the single crystal refinement and the chemical analysis indicate that there are no organic and boron species in VAs-1. The role of the organoamine appears to be adjustment of pH and maintenance of the reducing reaction environment. Thermogravimetric analysis shows that weight loss occurs in three steps between 30 °C and 700 °C. The total loss of 31.6% corresponds to the loss of water [13.5% from 30 °C to 220 °C (calcd. 13.1%)] and collapse of the framework. VAs-1 is thermally unstable and transforms into an amorphous phase after heating at 200 °C for two hours. Catalytic properties were measured for phenol hydroxylation using H_2O_2 as the oxidant. The reaction was carried out at 60 °C with phenol/H_2O_2 of 1.

Structure refinement indicates that VAs-1 crystallizes in the space group $I\bar{4}3m$.[7] The asymmetric unit of VAs-1 contains one As and three V atoms. The crystallographically distinct tetrahedral As atoms, having the geometry observed for monoarsenate, share four oxygen atoms with adjacent vanadium atoms with all the As–O distances of 1.662(6) Å. All vanadium atoms exist in square-pyramidal coordination (Fig. 1). The V(2) atom is coordinated by a terminal oxo group O(1) and four μ_3-oxygen atoms O(5). The geometry around each vanadium V(1) or V(3) atom is linked by four μ_3-oxo O(4) and O(5) groups and an apical terminal vanadyl V=O group. The five adjacent vanadium atoms form an unusual

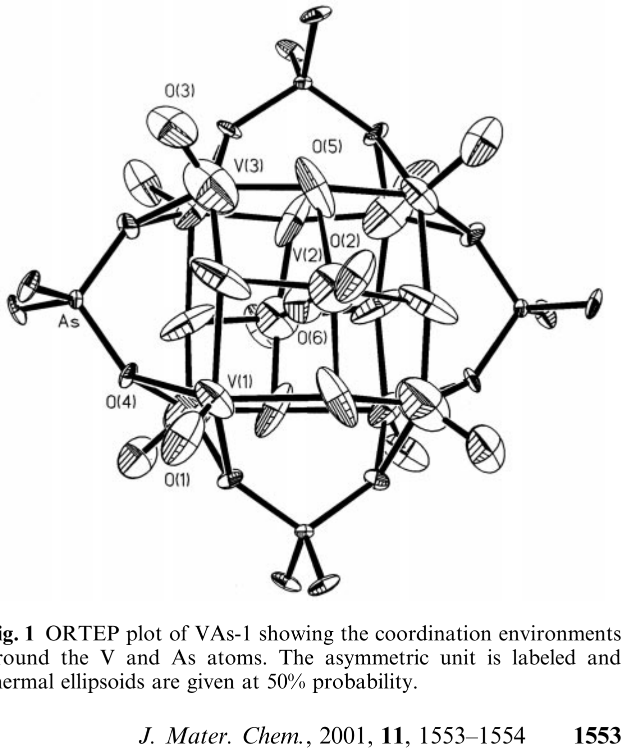

Fig. 1 ORTEP plot of VAs-1 showing the coordination environments around the V and As atoms. The asymmetric unit is labeled and thermal ellipsoids are given at 50% probability.

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cross-shaped V_5 pentamer with the central V(2) atom sharing each of its four basal edges with four additional square-pyramidal vanadium atoms. The V5 pentamer has been observed in the block unit of $[HN(CH_2CH_2)_3NH]K_{1.35}[V_5O_9(PO_4)_2]\cdot xH_2O$ and $Cs_3[V_5O_9(PO_4)_2]\cdot xH_2O$, which is composed of five square-pyramidal VO_5 groups also with a cross shape. Two pentamers are fused to form a decavanadium cage with a water molecule encapsulated in its center (Fig. 2b). According to bond valence sum calculations and charge balance,[8] VAs-1 is formulated as $[As_2V^{IV}_8V^{V}_2O_{26}(H_2O)]\cdot 8H_2O$. The assignment of oxidation states for the vanadium atoms is confirmed by the valence sum calculation results for V1, V2, V3 of 4.05, 5.06 and 4.16. The valence calculations identify O(6) [BVS = 0.27] as a water molecule. It is well-known that polyoxovanadates have a marked tendency to form isopolyanions of various types exhibiting a wide variety of ratios of V(IV) to V(V) with from two to eighteen V(IV) centers being observed. Among known decavanadium clusters, the decavanadium moiety of VAs-1 is new. A $V_{10}O_{26}$ cluster cage has been observed in $[(C_2H_5)_4N]_4[V_{10}O_{26}]\cdot H_2O$,[9] which is isomeric to VAs-1. The difference between them arises in the fusing mode (Fig. 2). The decanuclear cage $[V^{IV}_2V^{V}_8O_{27}]$ of VAs-1 shows four $[V_4O_{16}]$ windows with four AsO_4 tetrahedra capped to form a closed cage. The AsO_4 tetrahedra are linked to two perpendicular decavanadium clusters by four μ_3-oxygen atoms. Hence a three-dimensional network forms.

A prominent feature of VAs-1 is the large voids in the V–As–O framework centered at (000), which have rigorous $\bar{4}3m$ symmetry, with diameter 18.42 Å (Fig. 3). These cavities are highly symmetric and filled with eight water molecules. The interconnection of the large cavities generates a fascinating channel topology. Each cavity possesses six 12-membered ring windows with diameter of 11.99 Å, through which it communicates with six neighboring symmetrical equivalent cavities. These channels intersect at the cavities forming a three-dimensional channel system.

Phenol hydroxylation measurements show that VAs-1 has catalytic activity for phenol hydroxylation. Catechol, hydroquinone and benzoquinone are the only products with 15.84% conversion of phenol. The product distribution indicates that hydroquinone prevails with a yield of 59.60%.

In conclusion, a new open-framework oxovanadium arsenate has been synthesized under hydrothermal conditions. It is constructed by novel decavanadium cluster moieties which are linked by AsO_4 tetrahedra forming large cavities that possess 12-membered ring channels. Catalytic measurements show activity for phenol hydroxylation with high selectivity to hydroquinone. Ongoing work concerns systematically studying the magnetic and catalytic properties of VAs-1. The present work also provides the possibility to prepare compounds with larger dimensionalities in the V–As–O system.

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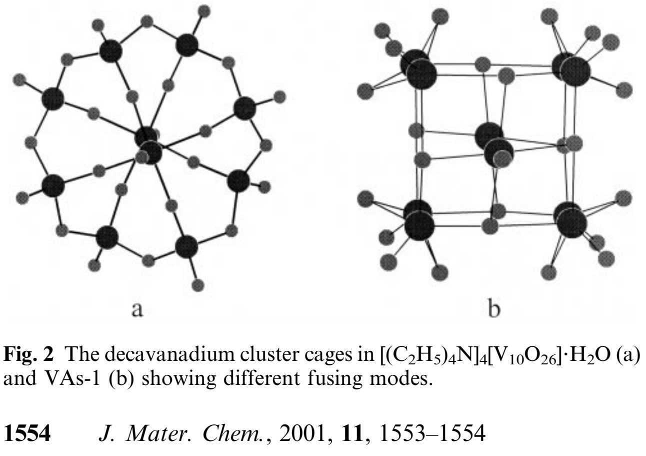

Fig. 2 The decavanadium cluster cages in $[(C_2H_5)_4N]_4[V_{10}O_{26}]\cdot H_2O$ (a) and VAs-1 (b) showing different fusing modes.

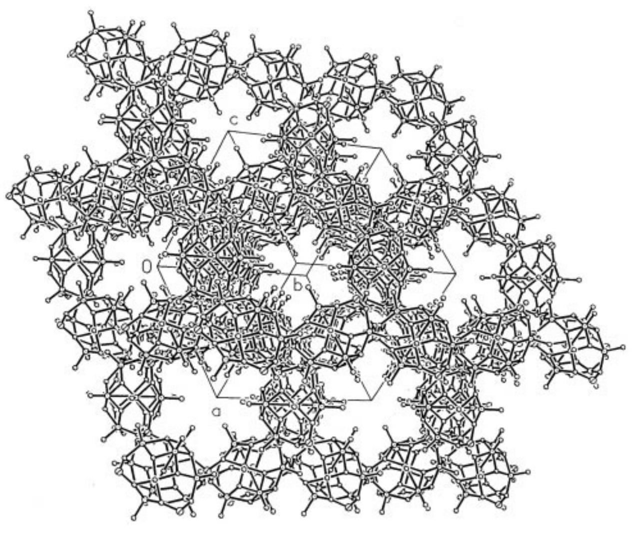

Fig. 3 The 12-membered ring channels of VAs-1 viewed along the [111] direction.

Notes and references

1 A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268; M. E. Davis and R. F. Lobo, *Chem. Mater.*, 1992, **10**, 756; P. B. Venuto, *Microporous Mater.*, 1994, **2**, 297; J. V. Smith, *Chem. Rev.*, 1988, **88**, 149.

2 T. E. Gier and G. D. Stucky, *Nature*, 1991, **349**, 508; G. Centi, F. Trifire, J. R. Ebner and V. M. Franchett, *Chem. Rev.*, 1988, **88**, 55; G. Albert, *Acc. Chem. Res.*, 1978, **11**, 163; A. Clearfield, *Chem. Rev.*, 1988, **88**, 125.

3 M. Roca, M. D. Marcos, P. Amoros, A. Beltran-Porter, A. J. Edwards and D. Beltran-Porter, *Inorg. Chem.*, 1996, **35**, 5613; Y. Lu, R. C. Haushalter and J. Zubieta, *Inorg. Chim. Acta*, 1998, **268**, 257; Z. Bircsak and W. T. A. Harrison, *Inorg. Chem*, 1998, **37**, 3204, and references therein.

4 V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, *Science*, 1993, **259**, 1569.

5 M. I. Khan, L. M. Meyer, R. C. Haushalter, A. L. Schweitzer, J. Zubieta and J. L. Dye, *Chem. Mater.*, 1996, **8**, 43.

6 Y. Zhao, G. Zhu, W. Liu, Y. Zou and W. Pang, *Chem. Commun.*, 1999, 2219; Y. Zhao, Z. Shi, S. Ding, N. Bai, W. Liu, Y. Zou, G. Zhu, P. Zhang, Z. Mai and W. Pang, *Chem. Mater.*, 2000, **12**, 2550.

7 Crystal data for VAs-1: $[As_2V^{IV}_8V^{V}_2O_{26}(H_2O)]\cdot 8H_2O$, $M = 1237.38$, cubic, space group $I\bar{4}3m$, $a = 16.708(2)$ Å, $\alpha = 90°$, $V = 4664.4(9)$ Å^3, $Z = 4$, $D_c = 1.762$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å. The single crystal structure determination was performed on a Siemens P4 four circle diffractometer. Data were collected at 293(2) K in the θ range 1.72–25.06°. Of the total 2915 reflections measured, 633 were independent with 440 observed. The structure was refined by direct methods using the SHELXTL (Ver. 5.01) program to residual $R_1 = 0.1099$, $wR_2 = 0.1392$ for all refections, and $R_1 = 0.0569$, $wR_2 = 0.0775$ for the observed reflections. CCDC reference number 160407. See http://www.rsc.org/suppdata/jm/b1/b102336p/ for crystallographic data in .cif or other electronic format.

8 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.

9 A. Bino, S. Cohen and C. Heitner-Wirguin, *Inorg. Chem.*, 1982, **21**, 429.