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Hydrothermal synthesis and crystal and molecular structure of a three-dimensional vanado-arsonate $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$, exhibiting both $\{V{-}O{-}V\}_\infty$ chains and isolated $\{V_2O_3\}$ units

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Abstract

Brown hexagons of the mixed valence V(V)/V(IV) arsenate $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$ were isolated in low yield from the reaction of VCl_4, As_2O_5, NH_4Cl, H_2O and $(CH_3)_2NH$ in the mole ratio 1:2.5:6:169:8 at 150 °C for 144 h The structure consists of an octahedral-tetrahedral framework, exhibiting both infinite $\{V{=}O\cdots V{=}O\cdots\}_\infty$ chains and isolated binuclear units with the $\{V_2O_3\}$ core. Crystal data: orthorhombic space group *Pnma* with $a=7.204(3)$, $b=13.741(4)$, $c=14.831(3)$ Å, $V=1468(2)$ Å^3, $Z=4$, $D_{calc}=3.020$ g cm^{-3}, μ(Mo Kα)$=82.57$ cm^{-1}; structure solution and refinement converged at an R value of 0.079.

Key words: Crystal structures; Vanadium complexes, Oxo complexes; Arsenate complexes

Introduction

While the solid phases of the V/O/phosphate system have been extensively investigated [1–6], the corresponding V/O/arsenate system remains relatively unexplored. Structurally characterized examples of this latter class of solids include the layered phases $Ba[(VO)(AsO_4)(H_2AsO_4)]\cdot H_2O$ [7], $[(VO)(H_2AsO_4)_2]$ [8] and $Li_4[(VO)(AsO_4)_2]$ [8], the three-dimensional framework $Na[VO(AsO_4)]$ [9], and two recently described one-dimensional polymers $(H_2NC_4H_8NH_2)[(VO)_2(HAsO_4)_2(H_2AsO_4)_2]$ and $(H_3NCH_2CH_2NH_3)[V(HAsO_4)_2(H_2AsO_4)]\cdot H_2O$ [10]. These structural results clearly demonstrate that the chemistry of the V/O/arsenate system does not parallel that of the V/O/phosphate system in detail. The observation is related in part to the different pK_a values of H_3PO_4 and H_3AsO_4 and to the larger covalent radius of As, a feature which may endow the arsenate phases with greater structural flexibility. This characteristic may correlate, for example, with the facile Li^+ exchange reaction in β-$[VO(H_2AsO_4)_2]$ which is not observed in $[VO(H_2PO_4)_2]$ [8]. Furthermore, our recent demonstration of the existence of one-dimensional polymeric structures in the V/O/arsenate system [10] suggested an expansive and unique structural chemistry which we have sought to develop. As part of these continuing investigations, we have synthesized and structurally characterized a mixed valence V(IV)/V(V) arsenate, $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$.

Experimental

Preparation of $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$

A mixture of VCl_4, As_2O_5, NH_4Cl and H_2O in the mole ratio 1:2.5:6:139 was heated in a 23 ml Teflon-

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TABLE 1 Summary of crystallographic data for $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$

Formula	$N_3H_{13}O_{16}V_3As_3$
Formula weight	688 7
Space group	*Pnma*
a (Å)	7.204(3)
b (Å)	13.741(4)
c (Å)	14.831(3)
V (Å^3)	1468(1)
Z	4
D_{calc} (g cm^{-3})	3.020
$F(000)$	1252
Absorption coefficient (cm^{-1})	82 57
No. observed reflections ($I_o \geqslant 3\sigma(I_o)$)	1214
T_{min}/T_{max}	0 61/1.49
Absorption correction	DIFABS
Reflection/parameter ratio	9.34
R	0.079
R_w	0.082
GOF	3 76
Maximum shift/error	0 00

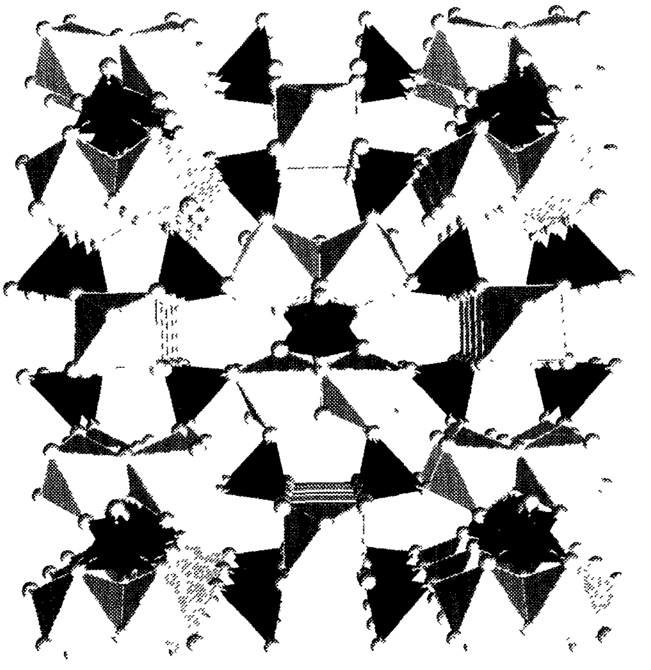

Fig. 1 A polyhedral representation of the structure of $(NH_4)_3[(VO)(V_2O_3)(AsO_4)(HAsO_4)]$, viewed along the axis of the one-dimensional chains.

lined Parr acid digestion bomb at 150 °C for 72 h. To the resultant blue solution was added $(CH_3)_2NH$ (8 mmol), and the mixture was heated at 150 °C for an additional 72 h. Brown polygons of the title compound were isolated in *c.* 5% yield with $(NH_4)VO(AsO_4)$ as the major product in 95% yield. IR (KBr pellet, cm^{-1}): 2959(sh), 2924(s), 2854(m), 1638(w), 1384(m), 1265(m), 1096(sh), 1026(m), 800(s), 653(w), 618(w), 526(w), 463(m).

X-ray structure determination

X-ray data was collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a 12 kW rotating anode generator. The crystal dimensions (0.10×0.05×0.20 mm) and weak diffraction profiles necessitated the use of the rotating anode system. Table 1 summarizes the crystal parameters and details of the structure solution and refinement. The arsenate group associated with As(2) is

TABLE 2. Atomic coordinates and isotropic temperature factors for $(NH_4)[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$

Atom	x	y	z	B_{eq}
As(1)	0 5353(2)	0 4002(1)	0.38266(9)	1.29(2)
As(2)	0.2189(8)	0.2500	0.7622(3)	1.7(1)
As(3)	0.1431(9)	0 2500	0 7403(3)	1 8(1)
V(1)	0.2529(5)	0 2500	0.2583(2)	1.34(7)
V(2)	0.3490(4)	0 3730(2)	0.5812(2)	1.76(5)
O(1)	0 540(2)	0.2500	0 2076(8)	1.2(3)
O(2)	0.342(1)	0.3509(7)	0 3411(6)	1 6(2)
O(3)	0.726(1)	0.3537(8)	0.3362(6)	1.9(2)
O(4)	0.520(2)	0.5189(6)	0.3549(6)	1.8(2)
O(5)	0.551(1)	0 3820(7)	0.4945(6)	1.7(2)
O(6)	0 188(1)	0 4345(8)	0 5320(7)	2.2(2)
O(7)	0.280(2)	0 2500	0 5475(9)	1.8(3)
O(8)	0.235(2)	0 3519(7)	0.7025(7)	2.4(2)
O(9)	0 082(2)	0.2500	0 8480(9)	2.1(3)
O(10)	−0.071(5)	0 2500	0 680(2)	2.9(7)
N(1)	0.390(3)	0.2500	0.006(1)	2.9(5)
N(2)	0 580(2)	−0.001(1)	0.1633(9)	3 8(4)

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$

TABLE 3 Selected bond lengths (Å) and angles (°) for $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$

As(1)–O(2)	1.666(9)	V(1)–O(1)	1 61(1)
As(1)–O(3)	1.666(9)	V(1)–O(2)	1 96(1)
As(1)–O(4)	1.686(9)	V(1)–O(3)	2.01(1)
As(1)–O(5)	1.681(9)	V(1)–O(2a)	1 96(1)
As(2)–O(8)	1 66(1)	V(1)–O(3a)	2.01(1)
As(2)–O(9)	1 61(1)	V(1)–O(1a)	2.20(1)
As(2)–O(10)	1.74(4)	V(2)–O(4)	2.00(1)
As(2)–O(8a)	1.66(1)	V(2)–O(5)	1.94(1)
		V(2)–O(6)	1.61(1)
		V(2)–O(7)	1.832(6)
		V(2)–O(8)	2 00(1)
		V(2)–O(9)	2.60(1)
O(1)–V(1)–O(1a)	178.3(4)	O(4)–V(2)–O(5)	85.0(4)
O(2)–V(1)–O(3)	166 0(5)	O(4)–V(2)–O(6)	99.6(5)
O(2a)–V(1)–O(3a)	166.0(5)	O(4)–V(2)–O(7)	160.6(5)
O(1)–V(1)–O(2)	84.6(4)	O(4)–V(2)–O(8)	82.9(4)
O(1)–V(1)–O(3)	81.5(4)	O(5)–V(2)–O(6)	101.9(5)
O(1)–V(1)–O(2a)	96 6(4)	O(5)–V(2)–O(7)	94 7(5)
O(1)–V(1)–O(3a)	97.3(4)	O(5)–V(2)–O(8)	155 8(4)
O(2)–V(1)–O(2a)	90 0(6)	O(6)–V(2)–O(7)	99.4(6)
O(2)–V(1)–O(3a)	88 1(4)	O(6)–V(2)–O(8)	100.7(5)
O(3)–V(1)–O(3a)	90 4(6)	O(7)–V(2)–O(8)	90 0(5)
V(1)–O(1)–V(1a)	141 8(7)		

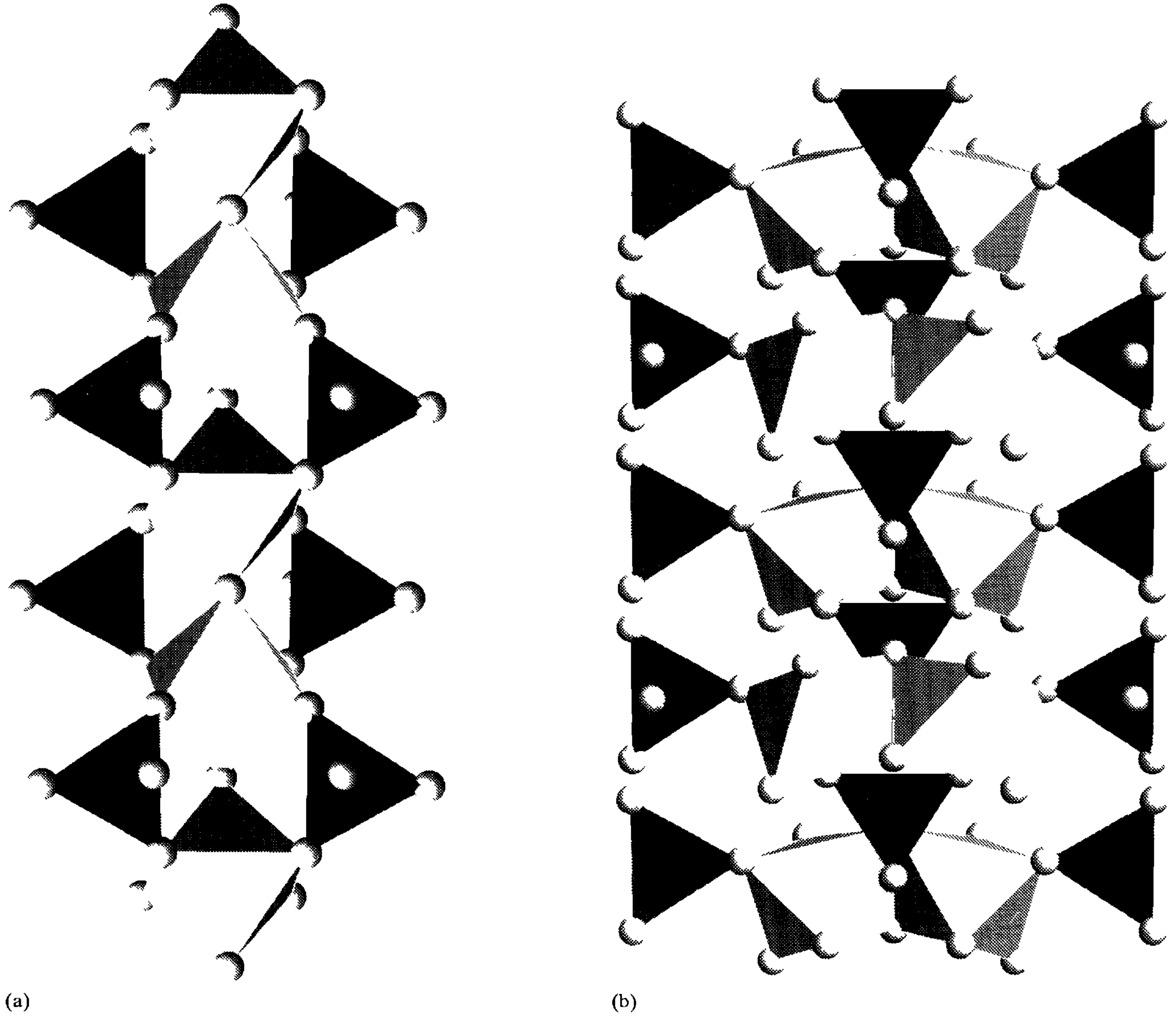

Fig 2. (a) A view of the one-dimensional chain of corner-sharing $\{VO_6\}$ octahedra; (b) a view of a column of isolated edge-sharing $\{V_2O_{10}\}$ binuclear units.

disordered as a consequence of adopting equal populations of the two possible orientations of the $\{HAsO_4\}^{2-}$ tetrahedra with respect to the $\{V_2O_{10}\}$ stacks associated with V(2). In Figs. 1 and 2, one orientation of the tetrahedra has been chosen for the sake of clarity, although a statistical disordering over the two possible sites occurs in the structure. The disorder was modelled by assigning half occupancies to each of the two possible locations for As(2). The model was deemed adequate in view of the chemical reasonableness, the absence of significant excursions of electron density in this region in the final Fourier map, and the well-behaved temperature factors associated with the $\{As(2)O_4\}$ unit. Non-hydrogen atoms were refined using anisotropic temperature factors. Atomic positional parameters and bond lengths and angles are presented in Tables 2 and 3, respectively.

Results and discussion

The structure of $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$ consists of a three-dimensional framework constructed from vanadium octahedra and arsenate tetrahedra, as shown in Fig. 1. The structure is most unusual in possessing both infinite $\{V{=}O\cdots V{=}O\cdots\}_\infty$ chains and isolated binuclear units with the $\{V_2O_3\}$ core. The structural motif based on the oxovanadium chain, illustrated in Fig. 2(a), consists of $\{VO_6\}$ octahedra corner-sharing through oxo groups in a long–short al-

TABLE 4. Non-bonded contacts to 3.3 Å for $(NH_4)_3[(VO)(V_2O_3)(AsO_4)(HAsO_4)]$

N(1)...O(1)	3.18(2) [1][a]	N(2)...O(4)	3.19(2) [4]
N(1)...O(3)	2.99(2) [2]	N(2)...O(2)	2.80(2) [4]
N(1)...O(5)	3.05(2) [2]	N(2)...O(3)	3.26(2) [2]
N(1)...O(9)	3.22(3) [3]	N(2)...O(4)	2.88(2) [5]
N(1)...O(10)	2.77(3) [4]	N(2)...O(6)	2.88(2) [6]
		N(2)...O(6)	3.38(2) [4]
		N(2)...O(8)	3.09(2) [6]
		N(2)...O(8)	3.13(2) [7]

[a] The number in brackets refers to the symmetry operation relating atoms: [1]: x, y, z, [2] $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; [3]: $x, y, z-1.0$; [4]: $x-\frac{1}{2}, \frac{1}{2}y, \frac{1}{2}-z$; [5]: $x, \frac{1}{2}y, z$; [6]: $\frac{1}{2}+x, \frac{1}{2}y, \frac{1}{2}-z$; [7]: $1.0-x, \frac{1}{2}+y, 1.0-z$.

ternation to provide the zig-zag $\{V{=}O\cdots V{=}O\cdots\}_\infty$ backbone. The coordination at each vanadium site is completed by oxygen donors from each of four symmetrically bridging $(AsO_4)^{3-}$ groups. In this fashion, each $\{VO_6\}$ octahedron is bridged to each of two adjacent octahedra by two bridging $\{AsO_4\}$ tetrahedra to produce the structural unit of corner-sharing vanadium octahedra and arsenic tetrahedra shown in Fig. 2(a). The remaining two oxygen atoms of each $\{AsO_4\}$ group serve to bridge this chain to two neighboring $\{V_2O_3\}$ binuclear units. Each As(1) tetrahedron thus assumes corner-sharing interactions with four different vanadium sites.

As shown in Fig. 2(b), the second structural motif consists of isolated binuclear $\{V_2O_{10}\}$ units constructed from edge-sharing $\{VO_6\}$ octahedra. The central core consists of a trioxodivanadium unit $\{(VO)_2(\mu\text{-}O)\}$ with the *syn* orientation of the terminal oxo groups. The coordination requirements of each vanadium site are completed by bonding to two oxygen donors from each of two adjacent As(1) units, an oxygen donor of an As(2) group, and an unusual bridging oxygen from a second As(2) site. The presence of a bridging oxo group and of the bridging arsenate oxygen results in edge-sharing of octahedra to produce the $\{V_2O_{10}\}$ unit. The vanadium–oxygen bond length to the bridging arsenate oxygen, V(2)–O(9), is significantly elongated, as a result both of the requirement to bridge two vanadium centers and of the *trans* influence of the terminal oxo groups of the V(2) centers.

The arsenate tetrahedra of the As(2) type are associated exclusively with the binuclear vanadium sites. Each tetrahedron adopts a symmetrical bridging mode to a $\{V_2O_{10}\}$ unit through two oxygen donors while a third oxygen adopts a monodentate bridging mode to an adjacent $\{V_2O_{10}\}$ unit. The fourth oxygen of this $\{HAsO_3\}^{2-}$ unit is protonated and pendant, as suggested by the As(2)–O(10) distance of 1.74(4) Å.

As shown in Fig. 1, the binuclear units stack in such a fashion as to sandwich a column of As(2) tetrahedra. While the As(2) site serves in this fashion to bridge adjacent stacks of isolated $\{V_2O_{10}\}$ octahedra, the As(1) tetrahedra bridge $\{V_2O_{10}\}$ units of one stack to those of an adjacent stack and to a neighboring linear chain. In this way, each $\{V{=}O\cdots V\}_\infty$ chain is attached to four adjacent As(2)-bridged $\{V_2O_{10}\}$ double columns through bridging As(1) tetrahedra.

As shown in Table 4, the material exhibits extensive hydrogen bonding, involving both the ammonium cations with arsenate oxygens and oxo groups and the pendant, protonated arsenate oxygen O10 with the ammonium cations.

The dark color of the crystals of $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$ suggests a mixed valence species, a feature confirmed by the structural study. Charge requirements indicate the oxidation state assignment of 2 × V(IV) sites and 1 × V(V) site. Valence sum calculations [11] are consistent with delocalization of the electrons over both V(1) and V(2) sites, which exhibit bond numbers of 4.40 and 4.45, respectively.

The structure of $(NH_4)_3[(VO)(V_2O_3)(AsO_4)_2(HAsO_4)]$ supports the argument that the detailed chemistry of the V/O/arsenate system is quite distinct from that of the V/O/phosphate system. Under similar reaction conditions, the V/O/phosphate system yields $(NH_4)[VO(PO_4)]$, a structure consisting of one-dimensional chains of $\{VO_6\}$ octahedra linked by $(PO_4)^{3-}$ tetrahedra [12]. While vanadium phosphate phases containing $\{V\text{–}O\text{–}V\}_\infty$ chains as structural motifs are quite common and while several examples of phases containing isolated $\{V_xO_y\}$ oligomers have been described [4], structures containing both one-dimensional polymers and isolated vanadate clusters are unknown in the V/O/phosphate system. The structure of $(NH_4)_3[(VO)(V_2O_3)(AsO_4)(HAsO_4)]$ demonstrates that substitution of $\{AsO_4\}$ groups for $\{PO_4\}$ tetrahedra enhances the structural possibilities and provides novel three-dimensional frameworks, in this instance characterized by the presence of both one-dimensional chain and binuclear oxovanadium structural motifs.

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