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Novel Organically Templated Vanadyl(IV) Diarsenate and Monoarsenate with Chain Structures: Solvothermal Synthesis and Characterization of $(H_3NC_2H_4NH_3)[VO(H_2O)As_2O_7]$ and $(H_3NC_2H_4NH_3)_{0.5}[VO(H_2O)AsO_4]$

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Introduction

Recently we have synthesized a large number of ternary transition metal arsenates by a hydrothermal method. These compounds present a variety of complex crystal structures and thus interesting properties and are a challenge to complete characterization. Their structures include discrete MO_5 square pyramids or MO_6 octahedra, dimers of corner-sharing MO_5 square pyramids or edge-sharing MO_6 octahedra, tetrameric units of M−O polyhedra, and infinite chains of MO_6 octahedra sharing either trans or skew edges. They include Cu(II), Zn(II), Fe(III), Mo(VI), V(IV), and mixed-valence vanadium arsenates.[1,2] However, hydrothermal conditions are better suited for the formation of inorganic phases. In attempts to produce new materials with large internal micropore volumes within the inorganic oxide framework, we have performed the synthesis of organically templated vanadium arsenates under mild solvothermal conditions and prepared a few phases ranging from 1D chain to 2D layer to 3D framework structures. According to the results of a literaure search, only two organically templated vanadium arsenates, $H_2NC_4H_8NH_2[(VO)_2(HAsO_4)_2(H_2AsO_4)_2]$ and $H_3NC_2H_4NH_3[V(HAsO_4)_2(H_2AsO_4)]\cdot H_2O$,[3] were reported before. The former contains −V═O−V═O− chains such as those found in the 3D arsenates $NaVOAsO_4$[4] and NH_4VOAsO_4.[5] The latter contains −V−O−As−O−V− chains which are structurally similar to those found in the phosphate $SrV(PO_4)_2(H_2PO_4)$.[6] Under solvothermal conditions two novel vanadium arsenates which exhibit original backbones of isolated chains have been obtained. We report herein the first organically templated diarsenate phase $(H_3NC_2H_4NH_3)[VO(H_2O)As_2O_7]$ and the second V_2O_{10} bioctahedra-containing vanadyl(IV) monoarsenate $(H_3NC_2H_4NH_3)_{0.5}[VO(H_2O)AsO_4]$. The finite organic chains run parallel to the $-V-O-As_2-O-V-$ chains in the diarsenate whereas they are orthogonal to the $-V_2-O-As-O-V_2-$ chains in the monoarsenate. The structural relationship between the 1D structure, the 3D framework of $A_{0.5}VOAsO_4$,[1g] and the 2D layered AVO_2XO_4 (A = Sr, Ba; X = P, As)[7,8] is discussed.

Table 1. Crystallographic Data

	1	**2**
empirical formula	$As_2C_2H_{12}N_2O_9V$	$AsCH_7NO_6V$
space group	*Pnma*	$P2_1/n$
a, Å	9.7261(4)	4.6810(1)
b, Å	15.3268(6)	11.3971(3)
c, Å	7.2627(3)	11.8507(1)
β, deg		92.003(1)
V, Å^3	1082.7(4)	631.8(3)
Z	4	4
ρ_{calcd}, g cm^{-3}	2.509	2.680
μ, cm^{-1}	70.21	67.42
λ, Å	0.710 73	0.710 73
T, °C	23	23
$R(F_o)^a$	0.0299	0.0300
$R_w(F_o)^b$	0.0327	0.0321

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = \sigma^2(F_o)$.

Experimental Section

Synthesis. Chemicals of reagent grade or better were used as received. Solvothermal treatment of VO_2 (0.0995 g, 1.2 mmol), H_3AsO_4 (2 mL, 3 mol dm^{-3}), $H_2NC_2H_4NH_2$ (0.221 mL, 3.3 mmol), and *n*-butanol (8.86 mL, 1.1 mol dm^{-3}) for 2 days at 180 °C followed by cooling at 30 °C h^{-1} to room temperature yielded pale-blue bladed crystals of $H_3NC_2H_4NH_3[VO(H_2O)As_2O_7]$ (**1**), as a single-phase product (∼95% yield based on V). The measured powder X-ray pattern of the bulk product compared well with the pattern simulated from the coordinates of the single-crystal study of **1** (see below). Chemical analysis confirmed the amount of diprotonated ethylenediamine and water hydrogens (Found: C, 71.10; H, 6.72; N, 10.37. Calcd: C, 71.09; H, 6.71, N, 10.36). The reaction of VO_2 (0.0664 g, 0.8 mmol), H_3AsO_4 (1.33 mL, 4 mmol), $H_2N(CH_2)_2NH_2$ (0.067 mL, 1 mmol), $H_2N(CH_2)_3NH_2$ (0.133 mL, 1.6 mmol), *n*-butanol (2.98 mL, 1.1 mol dm^{-3}), and H_2O (2.98 mL) at 180 °C for 2 days followed by cooling at 5 °C h^{-1} to room temperature yielded a green crystalline material[9] as a major phase and a tiny amount of light-yellow columnar crystals of $(H_3NC_2H_4NH_3)_{0.5}[VO(H_2O)AsO_4]$ (**2**). Attempts to prepare **2** as a single (or major) phase have not been achieved.

Single-Crystal X-ray Structure Analysis. Crystallographic data are listed in Table 1. Crystals of dimensions 0.22 × 0.28 × 0.48 mm for **1** and 0.07 × 0.08 × 0.26 mm for **2** were selected for indexing and intensity data collection on a Siemens *Smart*-CCD diffractometer using Mo Kα radiation. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). Unit cell dimensions for **1** (**2**) were determined by a least-squares fit of 4424 (2557) reflections. Of the 6777 (3591) reflections collected ($2\theta_{max}$ = 57.5°), 1231 (1093)

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(8) Unpublished results.

(9) It is a mixed-valence vanadium arsenate which crystallizes in the monoclinic cell with a = 7.331 Å, b = 19.623 Å, c = 9.719 Å, β = 91.49°. Identification of the structure has not been completed.

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Table 2. Atomic Coordinatesand Thermal Parameters (Å^2)

atom	*x*	*y*	*z*	U_{eq}[a]
		1		
V	1.18843(5)	0.75	0.22465(9)	0.0118(2)
As	0.92739(2)	0.65135(2)	0.02400(4)	0.0110(1)
O1	0.8252(2)	0.6549(1)	0.2105(3)	0.0163(5)
O2	0.8873(2)	0.5720(1)	−0.1182(3)	0.0196(5)
O3	1.0934(2)	0.6553(1)	0.0826(3)	0.0178(5)
O4	0.8943(2)	0.75	−0.0953(4)	0.0144(7)
O5	1.0990(3)	0.75	0.4096(4)	0.0217(9)
O6	1.3302(3)	0.75	−0.0287(4)	0.0253(10)
N	0.8173(2)	0.5382(2)	−0.4841(3)	0.0187(7)
C	0.9326(3)	0.4767(2)	−0.5125(5)	0.0207(9)
H1	0.73480	0.50890	−0.50030	0.05
H2	0.82290	0.55840	−0.36760	0.05
H3	0.84550	0.57790	−0.56330	0.05
H4	0.91600	0.45180	−0.61400	0.05
H5	0.92110	0.42830	−0.45200	0.05
H6A	1.41970	0.75	−0.02220	0.05
H6B	1.30960	0.75	−0.14390	0.05
		2		
V	0.47507(16)	0.35922(6)	−0.02818(6)	0.0170(2)
As	−0.01516(9)	0.45436(4)	0.14743(3)	0.0162(1)
O1	−0.1991(6)	0.5834(3)	0.1530(2)	0.0187(9)
O2	0.0972(7)	0.4253(3)	0.2792(2)	0.023(1)
O3	0.2807(7)	0.4797(3)	0.0684(2)	0.0186(9)
O4	−0.2060(7)	0.3432(3)	0.0910(2)	0.0197(10)
O5	0.3204(7)	0.2398(3)	0.0048(3)	0.026(1)
O6	0.7120(6)	0.2855(3)	−0.1534(3)	0.023(1)
N	0.5012(8)	0.5850(4)	0.3629(3)	0.026(1)
C	0.620(1)	0.5184(5)	0.4633(4)	0.028(2)
H1	0.63200	0.59080	0.30690	0.05
H2	0.37120	0.53970	0.33230	0.05
H3	0.44010	0.65800	0.39320	0.05
H4	0.71430	0.45220	0.42640	0.05
H5	0.77140	0.57400	0.50890	0.05
H6A	0.67150	0.21410	−0.17200	0.05
H6B	0.90980	0.29060	−0.15990	0.05

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

unique reflections were considered observed ($I > 3\ \sigma(I)$) after *Lp* and absorption corrections. The absorption correction was based on symmetry-equivalent reflections using the *SADABS* program.[10] On the basis of systematic absences and statistics of intensity distribution, the space groups were determined to be *Pnma* for **1** and $P2_1/n$ for **2**. Direct methods were used to locate the V and As atoms and a few O atoms with the remaining non-hydrogen atoms being found from successive difference maps. All H atoms were located on difference Fourier maps calculated at the final stage of structure refinements. The final cycle of refinement, including the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms and fixed atomic coordinates and isotropic thermal parameters for H atoms, converged at $R = 0.0299$ and $R_w = 0.0327$ for **1** and $R = 0.030$ and $R_w = 0.0321$ for **2**. In the final difference map the deepest hole was −1.05 (−0.61) e Å^{-3} and the highest peak 0.87 (0.69) e Å^{-3}. Corrections for secondary extinction and anomalous dispersion were applied. Neutral-atom scattering factors were used. Structure solution and least-squares refinements were performed on a DEC VAX 4000/90 workstation using the *SHELXTL-Plus* programs.[11]

Additional crystallographic results are provided in Tables 2 and 3 and in the Supporting Information.

Table 3. Selected Bond Lengths (Å) and Bond Valence Sums (Σs)[a]

1		**2**	
V−O1[a]	2.029(2)	V−O1[d]	2.037(3)
V−O1[b]	2.029(2)	V−O3	2.024(3)
V−O3	2.006(2)	V−O3[e]	2.224(3)
V−O3[c]	2.006(2)	V−O4[f]	2.027(3)
V−O5	1.600(3)	V−O5	1.597(3)
V−O6	2.300(3)	V−O6	2.062(3)
Σs (V−O) = 4.02		Σs (V−O) = 3.98	
As−O1	1.681(2)	As−O1	1.707(3)
As−O2	1.643(2)	As−O2	1.664(3)
As−O3	1.671(2)	As−O3	1.723(3)
As−O4	1.772(1)	As−O4	1.676(3)
Σs (As−O) = 4.94		Σs (As−O) = 4.91	
N−C	1.480(4)	N−C	1.502(6)
N−H1	0.927(2)	N−H1	0.921(4)
N−H2	0.903(2)	N−H2	0.867(4)
N−H3	0.881(3)	N−H3	0.954(4)
C−H4	0.846(3)	C−H4	0.984(5)
C−H5	0.870(3)	C−H5	1.081(5)
O6−H6A	0.871	O6−H6A	0.862
O6−H6B	0.861	O6−H6B	0.934

[a] Symmetry codes: (a) $^1/_2 + x, y, ^1/_2 - z$; (b) $^1/_2 + x, ^3/_2 - y, ^1/_2 - z$; (c) $x, ^3/_2 - y, z$; (d) $-x, 1 - y, -z$; (e) $1 - x, 1 - y, -z$; (f) $1 + x, y, z$.

Results and Discussion

The infinite chains in **1** are composed of $VO_5(H_2O)$ octahedra and As_2O_7 bitetrahedra. As depicted in Figure 1, each V−O octahedron shares two trans edges with two As_2O_7 groups leaving the vanadyl oxygen atoms and the water ligands unshared. Adjacent chains along ⟨001⟩ are hydrogen bonded, via As−O4···H_2O−V bonds, into polyhedral sheets with the ethylenediammonium cations between the layers. The diarsenate groups possess mirror-plane symmetry such that the two AsO_4 tetrahedra are in a strictly eclipsed configuration. The As−O4−As angle of 117.1° falls outside the range, from ∼125 to 135°, typically encountered in metal diarsenates.[2] The less obtuse bridging angle and the extra long As−O4 bond (1.772 Å) may be attributed to the extensive H-bonds involved in the O4 atom. The N−C−C−N cationic chains run parallel to the anionic −V−O−As_2−O−V chains and form additional H-bonds, via four C−NH_3···O2−As bonds per cation, to the infinite chains. The shortest distances between adjacent chains with and without the interleaved organic cations are 8.48 Å (half of the length of the *bc* diagonal) and 7.26 Å (the length of *c*), respectively.

As shown in Figure 2, the infinite chains in the monoarsenate **2** are composed of the $[V_2O_8(H_2O)_2]$ bioctahedral units and AsO_4 tetrahedra. Each chain links four others on the *bc* plane via the V−H_2O···O2−As hydrogen bonding, resulting in a 3D network with the organic cations in tunnels. In turn, each of the cations links two adjacent chains via C−NH_3···O2−As bonds into sheets parallel to the (101) planes. In contrast to **1**, the cationic chains are oriented orthogonal to the −V_2−O−As−O−V_2− chains in **2**. As a consequence, adjacent chains which are linked by cations are much farther apart than those directly linked by H-bonds, i.e., 11.85 Å (the length of *c*) vs 8.22 Å (half of the length of *bc* diagonal). Structures containing discrete dimers of edge-sharing $V^{IV}O_6$ octahedra are limited in the literature. Reported examples include the 3D framework arsenates $A_{0.5}VOAsO_4$[1g] (A = Ba or Sr). In these structures, each of the V_2O_{10} units connects to six AsO_4 tetrahedra which extend into three dimensions. Here, the $[V_2O_8(H_2O)_2]$ unit connects to four AsO_4 tetrahedra which extend into opposite directions, resulting in a one-dimensional structure. Similar to the $[V_2O_8(H_2O)_2]$ bioctahedra, the dimer of V^VO_6 can only connect to four AsO_4 tetrahedra. However, the four tetrahedra point toward two nonparallel directions, resulting in the layered

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(10) Sheldrick, G. M. *SADABS*; Siemens Analytical X-ray Instrument: Madison, WI, 1995.

(11) Sheldrick, G. M. *SHELXTL-Plus Crystallographic System*, Release 4.21; Siemens Analytical X-ray Instrument: Madison, WI, 1991.

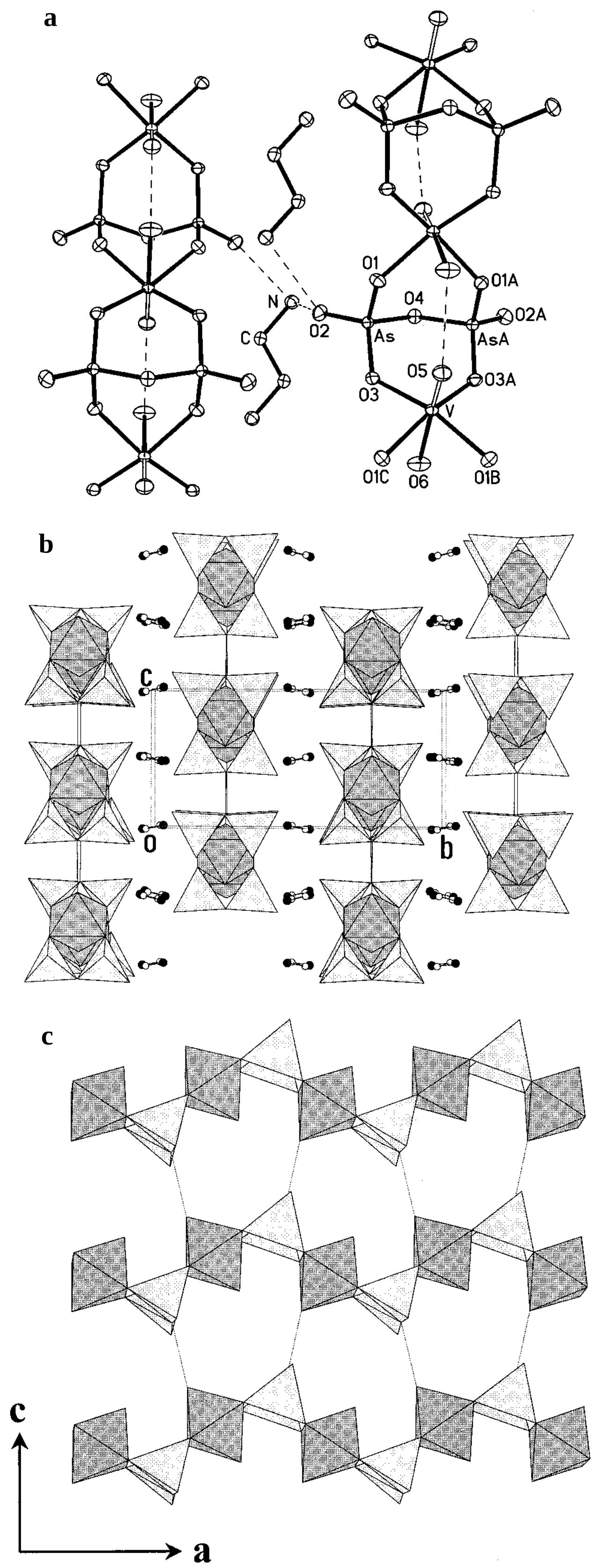

Figure 1. Structure of $(H_3NC_2H_4NH_3)[VO(H_2O)As_2O_7]$. (a) Section of the $-V-O-As_2-O-V-$ chains with the hydrogen bonds (dashed lines) to the cations. Symmetry codes: (A) $x, 1.5 - y, z$; (B) $0.5 + x, 1.5 - y, 0.5 - z$; (C) $0.5 + x, y, 0.5 - z$. Thermal ellipsoids are shown at 50% probability. (b) Projection of the structure down to the *a*-axis. (c) Section of the hydrogen-bonded polyhedral sheet running parallel to the (101) planes. Hydrogen bonds between polyhedra are shown as single lines. All H atoms are omitted for clarity.

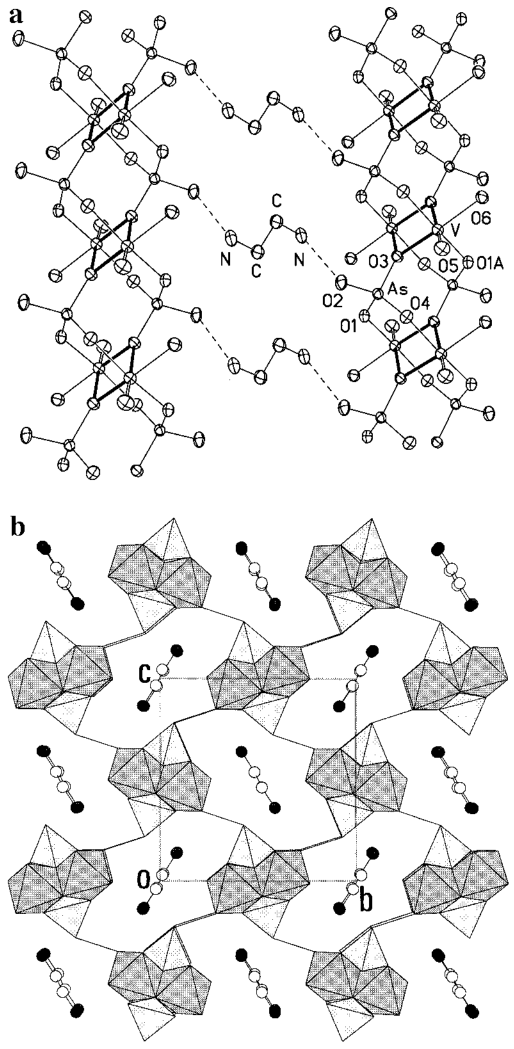

Figure 2. Structure of $(H_3NC_2H_4NH_3)_{0.5}[VO(H_2O)AsO_4]$. (a) Section of the $-V_2-O-As-O-V_2-$ chains with the hydrogen bonds to the cations. Symmetry code: (A) $-x, 1 - y, -z$. Thermal ellipsoids are shown at 50% probability. (b) Projection of the structure down to the *a*-axis. The infinite chains cross-link by hydrogen bonds (single lines between the polyhedra) into a 3D network.

feature of the vanadium(V) compounds AVO_2XO_4 (A = Sr, Ba; X = P, As).[7,8]

In addition to the bond-valence-sum calculations,[12] a magnetic susceptibility study of **1** also confirms the d^1 character of the V centers. The isolated $VO_5(H_2O)$ octahedra in the diarsenate **1** are more distorted than those in the $[V_2O_8(H_2O)_2]$ units in **2** ($\Delta \times 10^4 = 105$ vs 92).[13] This could be attributed to the intrachain H-bonds from the (H_2O) ligands to the vanadyl O atoms on neighboring octahedra. The water molecules are trans to the vanadyl O atoms in **1** but cis in **2**. In the TG analysis of **1**, evolution of the loosely bound water molecules occurred over 150−250 °C. The observed weight loss of 4.41% compared well with the calculated value of 4.40%. In the TG curve, a further weight loss can be described in two steps. The step in the temperature range from ~260 to 430 °C corresponded to the decomposition of ethylenediammonium cations (calcd 15.16%) and the release of O_2 (1.5 mol/formula unit, calcd 11.73%) from the As_2O_7 group. The final step, from ~430 to ~800 °C, was attributed to the sublimation of As_2O_3 (calcd 48.38%). The observed total weight loss (74.99%) for these

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(12) Brown, I. D.; Altrmatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(13) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

two steps can be compared well with the calculated value (75.27%) based on the above interpretation. The final decomposition product has a nominal composition of VO_2 (calcd 20.28%).

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Supporting Information Available: X-ray crystallography data including tables of complete crystal data, atomic coordinates, bond distances and angles, and anisotropic thermal parameters for $(H_3NC_2H_4NH_3)[VO(H_2O)As_2O_7]$ and $(H_3NC_2H_4NH_3)_{0.5}[VO(H_2O)AsO_4]$ and plots of TG/DT analyses and molar susceptibility study for $(H_3NC_2H_4NH_3)[VO(H_2O)As_2O_7]$ (8 pages). Ordering information is given on any current masthead page.

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