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# *Communications*

## Hydrothermal Synthesis and Structural Characterization of the Two New Vanadium Arsenates $H_2NC_4H_8NH_2[(V^{IV}O)_2(HAsO_4)_2(H_2AsO_4)_2]$ and $H_3NCH_2CH_2NH_3[V^{III}(HAsO_4)_2(H_2AsO_4)]\cdot H_2O$

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While layered and three-dimensional (3-D) metal oxides are very common, examples of discrete 1-D transition metal oxides are quite rare. Known examples of these 1-D polymers are provided by the phosphates $Mo(OH)_3PO_4$[2] and $VO(HPO_4)\cdot 4H_2O$[3] while $Na^+$ bridged strings are found in $(PPh_4)_2[(H_3O)_2NaMo_6O_{15}(HPO_4)(H_2PO_4)_3]$.[4] The 1-D metal oxide $(Et_4N)_2[Mo_4O_8(PO_4)_{2/2}(H_{1.5}PO_4)_2]\cdot 2H_2O$,[5] which contains chains composed of metal–metal bonded $Mo_4O_8$ "cubes" bridged together by $(PO_4)_{2/2}$ groups into 1-D chains, displays a unique type of chirality. We report here the hydrothermal synthesis of the 1-D $V^{4+}$ polymer $H_2NC_4H_8NH_2[(V^{IV}O)_2(HAsO_4)_2(H_2AsO_4)_2]$ (**1**) and the $V^{3+}$ chain compound $H_3NCH_2CH_2NH_3[V^{III}(HAsO_4)_2(H_2AsO_4)]\cdot H_2O$ (**2**) which represent the first examples of 1-D vanadium arsenate polymers with organic cations.

Green plates of the 1-D material $H_2NC_4H_8NH_2[(V^{IV}O)_2(HAsO_4)_2(H_2AsO_4)_2]$ (**1**) were prepared in 86% yield by the reaction of $VCl_4$:piperazine:$As_2O_5$:$H_2O$ in the mole ratios of 1:3:5:84 at 150 °C for 72 hours. Comparison of the measured X-ray powder pattern of **1** to the pattern calculated from the coordinates of the single-crystal study show that **1** is formed as a pure single-phase material. Single-crystal X-ray diffraction studies of **1** revealed novel $[(V^{IV}O)_2(HAsO_4)_2(H_2AsO_4)_2]^{2-}$ chains and piperazine dications.[6] A projection of the unit cell contents down [001] is shown in Figure 1. The $VO_6$ octahedra are bridged by $HAsO_4$ and $H_2AsO_4$, the hydrogen atoms of which were located on the later difference Fourier maps but were kept fixed during refinement. The chains are hydrogen bonded into sheets, via–O⋯H–O–As hydrogen bonds (in the range from 2.573 to 2.777 Å), that lie in planes which are parallel to the (101) plane. The H-bonded V–As–O sheets are interleaved by the organic dications, the $NH_2$ groups of which are also H bonded to some of the O atoms of the chains. The backbone of these chains are composed of $VO_6$ octahedra sharing opposite corners generating strings running parallel to the crystallographic [001] direction as shown in Figure 2a. The –V–O–V–O– infinite chain has short V–O vanadyl contacts of 1.627(4) Å alternating with longer V–O distances of 2.248(4) Å. The short V=O bonds *trans* to longer V–O contacts (i.e., the V atoms displaced toward one of the vertices along the 4-fold axis of the octahedron) is typical of $V^{4+}$. The 4+ oxidation state is confirmed by valence sum calculations.[7] Corner sharing 1-D chains of $VO_6$ octahedra are also found in the 3-D materials $NaVOAsO_4$[8] and $NH_4VOPO_4$[9] which have

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[2] Kierkegaard, P. *Acta Chem. Scand.* **1958**, *12*, 1701.

[3] Leonowicz, M. E.; Johnson, J. W.; Brody, J. F.; Shannon, A. F.; Newsam, J. M. *J. Solid State Chem.* **1985**, *56*, 370.

[4] Haushalter, R. C.; Lai, F. W. *Inorg. Chem.* **1989**, *28*, 2904.

[5] Mundi, L. A.; Haushalter, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 6340.

[6] Crystal data for **1**: orthorhombic, space group *Pbca* with $a$ = 14.567(1), $b$ = 17.495(1), and $c$ = 7.277(1) Å, $V$ = 1854.5(4) Å$^3$, $Z$ = 8 and $D_{calc}$ = 2.807 g cm$^{-3}$. $R(R_w)$ = 0.029(0.036) for 136 variables and 2084 observed data with $I > 3\sigma I$.

[7] Brown, I. D.; Wu, K. K. *Acta Crystallogr.* **1976**, *B32*, 1957.

[8] Haddad, A.; Jouini, T.; Piffard, Y. *Eur. J. Solid State Chem.* **1992**, *29*, 57.

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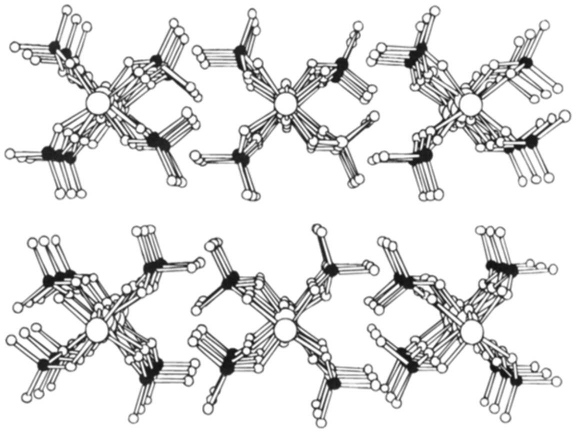

**Figure 1.** Projection of the structure of **1** down the [001] direction with the interlamellar organic cations omitted for clarity. The individual 1-D chains are H-bonded into sheets via the $H_xAsO_4$ groups.

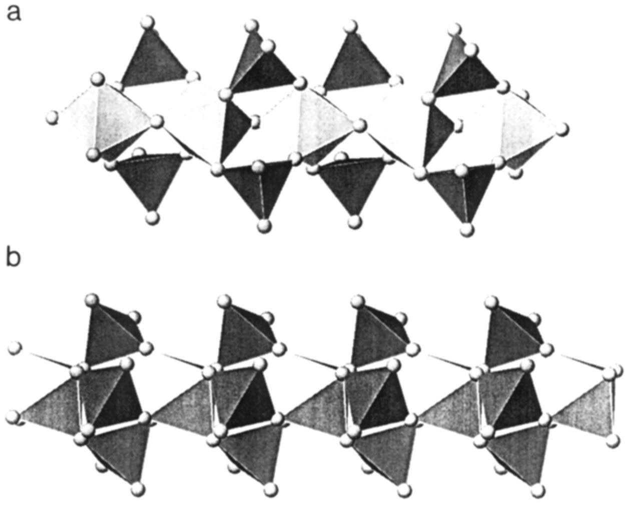

**Figure 2.** (a) Polyhedral representation of the chain of edge sharing $V^{4+}$ octahedra and $\{AsO_4\}$ tetrahedra in **1**. (b) Similar view of the $V^{3+}$ octahedra and $\{AsO_4\}$ groups in **2**.

chains sharing trans vertices and alternating cis−trans vertices, respectively. In contrast to the very darkly colored $NaVOPO_4$ and $NH_4VOPO_4$, arsenate **1** is transparent and green.

Using $V_2O_3$ as the V source and ethylenediamine as the organic template has allowed the isolation of $H_3NCH_2CH_2NH_3[V(HAsO_4)_2(H_2AsO_4)]{\cdot}H_2O$ (**2**), a 1-D vanadium arsenate polymer with $V(III)O_6$ octahedra. The reaction of $V_2O_3$:HCl:ethylenediamine:$As_2O_5$:$H_2O$ in the mole ratios of 1:16:18:13:222 at 150 °C for 72 h gives a 45% yield of green needles of **2**. Single-crystal X-ray diffraction shows[10] that compound **2**, like arsenate **1**, also has $VO_6$ octahedra bridged into 1-D chains via $\{HAsO_4\}$ and $\{H_2AsO_4\}$ groups. The main difference between the two polymers is that arsenate **2** contains chains of isolated $VO_6$ octahedra (Figure 2b) with two $\{HAsO_4\}$ and one $\{H_2AsO_4\}$ per vanadium octahedron, but with no covalent intrachain −V−O−V− interactions. The two extra free vertices in the octahedra of **2** as compared to **1** are compensated by two vertices from an additional $\{AsO_4\}$ tetrahedron. Unlike the distorted octahedra of $V^{4+}$ found in **1**, the octahedra in **2** are quite regular and the V−O bonds all lie in the range of 2.000(4)−2.017(4) Å indicative of $V^{3+}$. This oxidation state is confirmed by valence sum calculations. The high quality of the diffraction data allowed the resolution of the H atoms on the $\{AsO_4\}$ tetrahedra, two of which were found on O1 and O2 terminally bound to As1 while one each were found on O11 on As2 and O10 on As3 respectively. Whereas arsenate **1** has its chains hydrogen bonded into sheets with the organic cations between the layers, the chains in arsenate **2** are in an arrangement more reminiscent of the close packing of cylinders (Figure 3). Also shown in Figure 3 is the water molecule that is hydrogen bonded to the arsenate tetrahedra from three different chains. The chains are also H-bonded to the $-NH_3^+$ groups of the ethylenediammonium cations. Chains structurally similar to those found in **2** were recently reported in the vanadium phosphate $Sr_2[V(PO_4)_2(H_2PO_4)]$.[11]

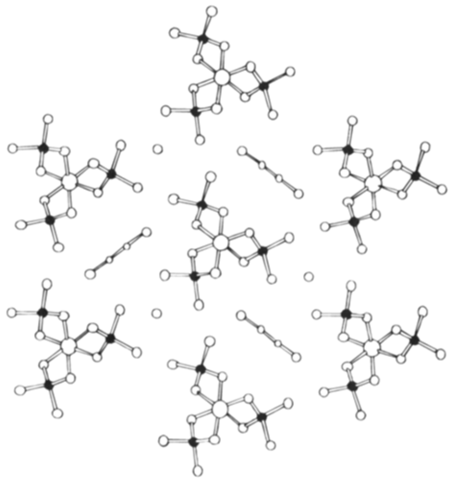

**Figure 3.** Projection of the structure of **2** down the [100] direction showing the pendant arsenate groups H-bonded to the other chains, the $H_2O$ and to the ethylenediammonium cations.

In summary, the results reported here show that it is possible to prepare by means of hydrothermal synthesis a new type of 1-D inorganic oxide based on $VO_6$ octahedra and $AsO_4$ tetrahedra. The solid-state structures of both materials are strongly influenced by the hydrogen bonding of the pendant $H_xAsO_4$ groups to one another and to the polar organic cationic templates.

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**Supplementary Material Available:** Additional experimental crystallographic details (12 pages); observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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[9] Haushalter, R. C.; Chen, Q.; Soghomonian, V.; Zubieta, J.; O'Connor, C. J. *J. Solid State Chem.*, in press.

[10] Crystal data for **2**: monoclinic, space group $P2_1$ with $a = 4.774(2)$, $b = 16.072(1)$, and $c = 8.687(1)$ Å, $\beta = 90.56(2)°$, $V = 666.5(2)$ Å$^3$, $Z = 2$. $R(R_w) = 0.021(0.029)$ for 189 variables and 1917 observed data with $I > 3\sigma I$.

[11] $Sr_2[V(PO_4)_2(H_2PO_4)]$: Lii, K.-H.; Lee, T.-C.; Liu, S.-N., Wang, S.-L. *J. Chem. Soc., Dalton Trans.* **1993**, 1051.