Novel Mixed-Valence Vanadium Arsenate Frameworks with Large Cavities: Hydrothermal Synthesis and Crystal Structures of $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2$ and $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2 \cdot H_2O$

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Introduction

In an effort to produce new materials with novel frameworks and interesting properties, we recently employed hydrothermal methods to the synthesis of transition-metal arsenates. This has resulted in new groups of compounds[1] which exhibit various polyhedral connections and interesting thermal properties. In an attempt to extend our work to mixed-valence vanadium arsenates, we have obtained two new porous structures containing both $V^{IV}O_5$ ($V^{IV,V}O_5$) pyramids and $V^{IV,V}O_6$ ($V^{IV}O_6$) octahedra in the arsenate lattices. Unlike organically templated phosphates of molybdenum[2] or vanadium,[3] these new open frameworks contain large cavities and tunnels in which only alkali-metal cations reside. Furthermore, it is found that in the two structures, which differ by one lattice water in composition, not only connectivities among various polyhedra are altered[4] but also redistribution of charge on the central metal ions of polyhedra is observed. Recent examples, which exhibit structure frameworks affected by lattice water contents, include several compounds in the $A(VOPO_4)_2 \cdot xH_2O$ system;[5] e.g., the trihydrate $Pb(VOPO_4)_2 \cdot 3H_2O$[5] adopts a tunnel structure whereas the tetrahydrate $Pb(VOPO_4)_2 \cdot 4H_2O$[6] is layered, which, however, can be deduced from the structure of trihydrate. The two nickel phosphates $Ni(VOPO_4)_2 \cdot 3H_2O$[7] and $Ni(VOPO_4)_2 \cdot 4H_2O$[8] do not have any obvious structural relationship between them. Nonetheless, no charge variations occur due to inclusion of water molecules in these crystal lattices. We report herein the first examples of hydrothermal synthesis products from the alkali-metal–vanadium–arsenate system, two new mixed-valence compounds, $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2$ and $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2 \cdot H_2O$.

Experimental Section

Synthesis. Mixtures of dark-brown crystals (major phase) of $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2$ (**1**) and deep-green crystals (minor phase) of $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2 \cdot H_2O$ (**2**) were obtained by the reaction of CsOH (1.7989 g, 50%), VO_2 (0.4976 g), V_2O_5 (0.1819 g), H_3AsO_4 (1.5 mL, 80%), C_5H_5N (3.0 mL), and water (7.0 mL) in a Teflon-lined autoclave (23 mL) at 230 °C for 4 d. It was found that the green phase often grew together with the dark-brown crystals such that manual separation of the two phases was always incomplete. The optimized synthetic conditions for obtaining a single phase of either **1** or **2** have not been achieved. Single crystals of **1** could be selected directly from the product. The size and quality of a crystal of **2** were often too small and poor. On one occasion, a suitable crystal of **2** was obtained by cutting off the green part of a dark-brown crystal. Both crystals were subsequently used for X-ray diffraction.

Table 1. Crystallographic Data

	1	**2**
empirical formula	$H_2As_4Cs_3V_4O_{21}$	$H_4As_4Cs_3V_4O_{22}$
space group	*C*2/*c* (No. 15)	*Pbcn* (No. 60)
a, Å	16.369(3)	17.544(4)
b, Å	9.702(2)	7.260(2)
c, Å	12.901(3)	18.279(5)
β, deg	101.26(2)	
V, Å^3	2009.5(8)	2328(1)
Z	4	4
ρ_{calcd}, g cm^{-3}	4.099	3.590
μ, cm^{-1}	137.95	119.13
λ, Å	0.710 73	0.710 73
T, °C	24	23
$R(F_o)$[a]	0.0275	0.0458
$R_w(F_o)$[b]	0.0297	0.0486

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

Table 2. Atomic Coordinates and Temperature Factors (Å^2)

	x	*y*	*z*	U_{eq}[a]
		Arsenate **1**		
Cs(1)	0.26325(2)	0.22869(4)	0.17466(3)	0.0175(1)
Cs(2)	0.50000	0.04949(8)	0.75000	0.0309(2)
As(1)	0.46355(3)	0.22334(5)	0.01117(4)	0.0065(2)
As(2)	0.83723(3)	0.12737(5)	0.02556(4)	0.0066(2)
V(1)	0.54742(5)	0.49560(9)	0.13449(7)	0.0080(2)
V(2)	0.64987(5)	0.05198(9)	0.04626(7)	0.0069(2)
O(1)	0.3842(2)	0.1208(4)	0.0312(3)	0.011(1)
O(2)	0.4911(2)	0.3159(4)	0.1224(3)	0.012(1)
O(3)	0.5409(2)	0.1248(4)	–0.0157(3)	0.012(1)
O(4)	0.7607(2)	0.0084(4)	0.0133(3)	0.011(1)
O(5)	0.9278(2)	0.0505(4)	0.0133(3)	0.010(1)
O(6)	0.5000	0.5483(6)	0.2500	0.015(2)
O(7)	0.4279(2)	0.3117(4)	–0.1010(3)	0.011(1)
O(8)	0.6546(3)	0.0084(4)	0.1673(3)	0.017(1)
O(9)	0.6393(2)	0.4608(4)	0.1969(3)	0.015(1)
O(10)	0.8111(2)	0.2556(4)	–0.0608(3)	0.009(1)
O(11)	0.8588(2)	0.1967(4)	0.1512(3)	0.014(1)
H(11)	0.8989(2)	0.1428(4)	0.1887(3)	0.08
		Arsenate **2**		
Cs(1)	0.67567(5)	0.10525(13)	0.26483(5)	0.0238(3)
Cs(2)[b]	0.47303(13)	0.13985(39)	0.46644(14)	0.0405(7)
As(1)	0.12953(7)	0.06975(18)	0.33202(6)	0.0083(4)
As(2)	0.16855(7)	0.07040(17)	0.55358(6)	0.0080(4)
V(1)	0.2382(1)	0.3512(3)	0.4294(1)	0.0071(6)
V(2)	–0.0525(1)	0.1398(3)	0.3279(1)	0.0085(6)
O(1)	0.1793(5)	0.2655(14)	0.3431(5)	0.016(3)
O(2)	0.0427(5)	0.0706(13)	0.3708(5)	0.013(3)
O(3)	0.1750(5)	–0.1179(13)	0.3629(5)	0.017(3)
O(4)	0.1243(5)	0.0360(14)	0.2402(5)	0.015(3)
O(5)	0.1596(5)	0.2361(14)	0.4921(5)	0.014(3)
O(6)	0.904(5)	0.0577(14)	0.6054(5)	0.016(3)
O(7)	0.1897(5)	–0.1343(14)	0.5165(5)	0.013(2)
O(8)	0.2441(6)	0.1292(14)	0.6107(5)	0.019(3)
O(9)	0.2113(5)	0.5648(12)	0.4321(5)	0.011(2)
O(10)	0	0.2384(22)	0.25	0.019(4)
O(11)	–0.0874(5)	0.3212(16)	0.3659(5)	0.019(3)
O(12)[c]	–0.0078(17)	0.3712(34)	0.7212(14)	0.039(8)

[a] U_{eq} is defined as one-third of the trace of the orthorgonalized $\mathbf{U}_{ij}$ tensor. [b] Site occupancy 0.5. [c] Water oxygen; site occupancy 0.5.

Single-Crystal X-ray Structure Analysis. Crystallographic data are listed in Table 1. Crystals of dimensions 0.08 × 0.20 × 0.22 mm^3 for **1** and 0.04 × 0.15 × 0.18 mm^3 for **2** were used for indexing and intensity data collection on a Nicolet R3m/V diffractometer using Mo Kα radiation. Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit-cell parameters. Octants collected: $\pm h,k,l$ (hkl) for **1** (**2**). Of the 2898 (2499) reflections collected 2033

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(1) $BaVO(AsO_4)(H_2AsO_4) \cdot H_2O$: Cheng, C.-Y.; Wang, S.-L. *J. Chem. Soc., Dalton Trans.* **1992**, 2395. $A(VO)_2(AsO_4)_2$ (A = Ba, Sr): Wang, S.-L.; Cheng, C.-Y. *J. Solid State Chem.* **1994**, *109*, 277. $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2 \cdot H_2O$: Wang, S.-L.; Hsu, K.-F.; Nieh, Y.-P. *J. Chem. Soc., Dalton Trans.* **1994**, 1681. $SrCoAs_2O_7$: Horng, J.-C.; Wang, S.-L. *Acta Crystallogr.* **1994**, *C50*, 488. $LiFeAs_2O_7$: Wang, S.-L.; Wu, C.-H.; Liu, S.-N. *J. Solid State Chem.*, in press. $M_2As_2O_7(H_2O)_2$ (M = Co, Ni): Wang, S.-L.; Horng, J.-C.; Lee, Y.-H. *J. Chem. Soc., Dalton Trans.*, in press.

(2) Haushaler, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31.

(3) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 610.

(4) Hawthorne, F. C. *Z. Kristallogr.* **1992**, *201*, 183.

(5) (a) Lii, K.-H. *J. Chin. Chem. Soc.* **1992**, *39*, 569. (b) Wang, S.-L.; Kang, H.-Y.; Cheng, C.-Y.; Lii, K.-H. *Inorg. Chem.* **1991**, *30*, 3496.

(6) Kang, H.-Y.; Lee, W.-C.; Wang, S.-L.; Lii, K.-H. *Inorg. Chem.* **1992**, *31*, 4743.

(7) Lii, K.-H.; Mao, L.-F. *J. Solid State Chem.* **1992**, *96*, 436.

(8) Lii, K.-H.; Wu, L.-S.; Gau, H.-M. *Inorg. Chem.* **1993**, *32*, 4153.

0020-1669/94/1333-3845$04.50/0

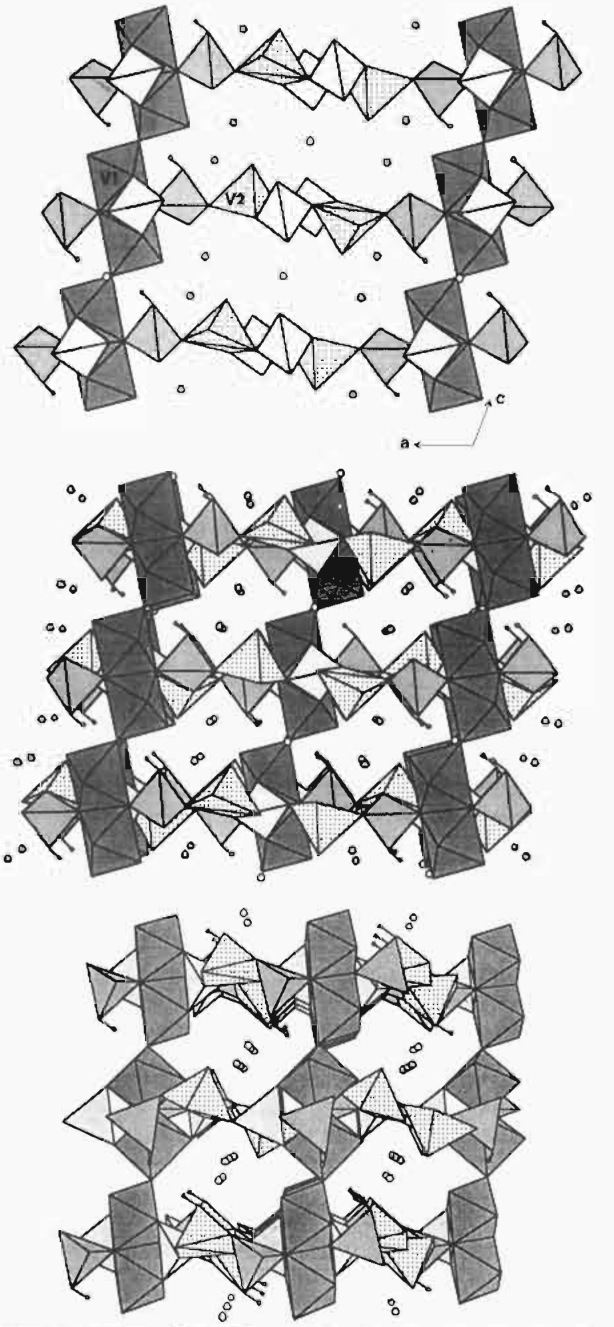

Figure 1. (a) Top: Section of an infinite two-dimensional net in $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2$. (b) Middle: Perspective view of the structure along the [010] direction. (c) Bottom: View down the [110] direction. In these representations, the corners of polyhedra are O atoms and the V and As atoms are at the center of each octahedron (or square pyramid) and tetrahedron, respectively. Stippled circles are Cs(1) cations. Large open circles are Cs(2) cations. Small open circles are H atoms of the $HAsO_4$ groups.

(1388) unique reflections were considered observed ($I \geq 3.0\sigma(I)$) after Lorentz–polarization and empirical absorption corrections for compound **1** (**2**). Correction for absorption effects was based on ψ scans of a few suitable reflections with χ values close to 90°. On the basis of the systematic absences, the space groups were determined to be *C*2/*c* for **1** and *Pbcn* for **2**. Direct methods were used to locate the metal, arsenic, and a few oxygen atoms, with the remaining non-hydrogen atoms being found from successive difference maps. The hydrogen atom in **1** was located from a difference Fourier map calculated at the final stage of structure analysis. No meaningful electron densities of hydrogen atoms for **2** could be found. The final cycles of refinement, including those for the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms for both **1** and **2** and fixed atomic coordinates and the isotropic thermal parameter for the H atom for **1**, converged at R = 0.0275 and R_w = 0.0297 for **1** and R = 0.0458 and R_w = 0.0486 for **2**.

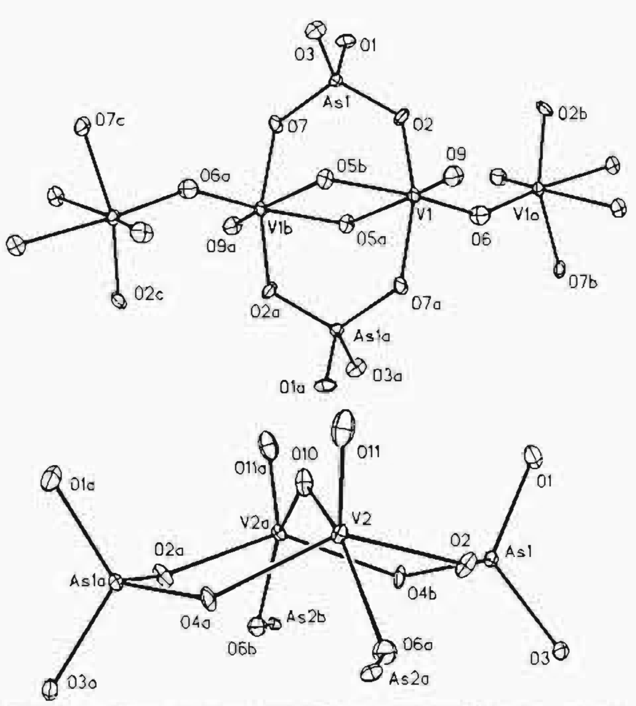

Figure 2. (a) Top: Section of an infinite chain showing the edge-sharing dimers of mixed-valence VO_6 octahedra in $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2$. (b) Bottom: A corner-sharing dimer of mixed-valence VO_5 square pyramids in $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2 \cdot H_2O$. The dimer has a 2-fold symmetry with the V–O–V bond angle equal to 135.2°. The V atom is off the basal plane by 0.54 Å. Thermal ellipsoids are shown at the 60% probability level.

Table 3. Selected Bond Lengths (Å) and Bond-Valence Sums (Σs)

arsenate **1**		arsenate **2**	
V(1)–O(2)	1.964(4)	V(1)–O(1)	1.986(10)
V(1)–O(6)	1.881(2)	V(1)–O(5)	1.979(9)
V(1)–O(9)	1.597(4)	V(1)–O(9)	1.621(9)
V(1)–O(5)^{a,a}	2.317(3)	V(1)–O(3)^e	1.962(10)
V(1)–O(5)^b	2.074(4)	V(1)–O(7)^e	2.037(9)
V(1)–O(7)^c	1.979(4)	V(1)–O(9)^f	2.261(9)
Σs(V(1)–O)	4.55^b	Σs(V(1)–O)	4.12^c
V(2)–O(3)	1.964(4)	V(2)–O(2)	1.912(9)
V(2)–O(4)	1.988(4)	V(2)–O(4)^g	1.924(9)
V(2)–O(1)^d	1.975(4)	V(2)–O(6)^h	1.996(10)
V(2)–O(1)^b	1.970(4)	V(2)–O(10)	1.841(6)
V(2)–O(9)	1.597(4)	V(2)–O(11)	1.609(11)
Σs(V(2)–O)	4.06^c	Σs(V(2)–O)	4.65^b
As(1)–O(1)	1.695(4)	As(1)–O(1)	1.680(10)
As(1)–O(2)	1.678(4)	As(1)–O(2)	1.680(9)
As(1)–O(3)	1.676(4)	As(1)–O(3)	1.676(10)
As(1)–O(7)	1.685(4)	As(1)–O(4)	1.670(9)
Σs(As(1)–O)	5.01	Σs(As(1)–O)	5.01
As(2)–O(4)	1.689(4)	As(2)–O(5)	1.653(10)
As(2)–O(5)	1.694(4)	As(2)–O(6)	1.669(9)
As(2)–O(10)	1.669(4)	As(2)–O(7)	1.675(10)
As(2)–O(11)	1.726(4)	As(2)–O(8)	1.741(10)
Σs(As(2)–O)	4.87	Σs(As(1)–O)	5.02

^{a} Symmetry codes: (a) $x - {}^1/_2, y + {}^1/_2, z$; (b) ${}^3/_2 - x, {}^1/_2 - y, -z$; (c) $1 - x, 1 - y, -z$; (d) $1 - x, -y, -z$; (e) ${}^1/_2 - x, {}^1/_2 + y, z$; (f) ${}^1/_2 - x, y - {}^1/_2, z$; (g) $-x, y, {}^1/_2 - z$; (h) $-x, -y, 1 - z$. ^{b} R_0[10] of V^V–O is used. ^{c} R_0 of V^{IV}–O is used.

In the final difference map, the deepest hole was −1.24 (−1.52) e Å^{-3} and the highest peak 2.42 (2.58) e Å^{-3} for **1** (**2**). 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.[9]

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(9) Sheldrick, G. M. *SHELXTL-Plus Crystallographic System*, release 4.21; Siemens Analytical X-ray Instruments: Madison, WI, 1991.

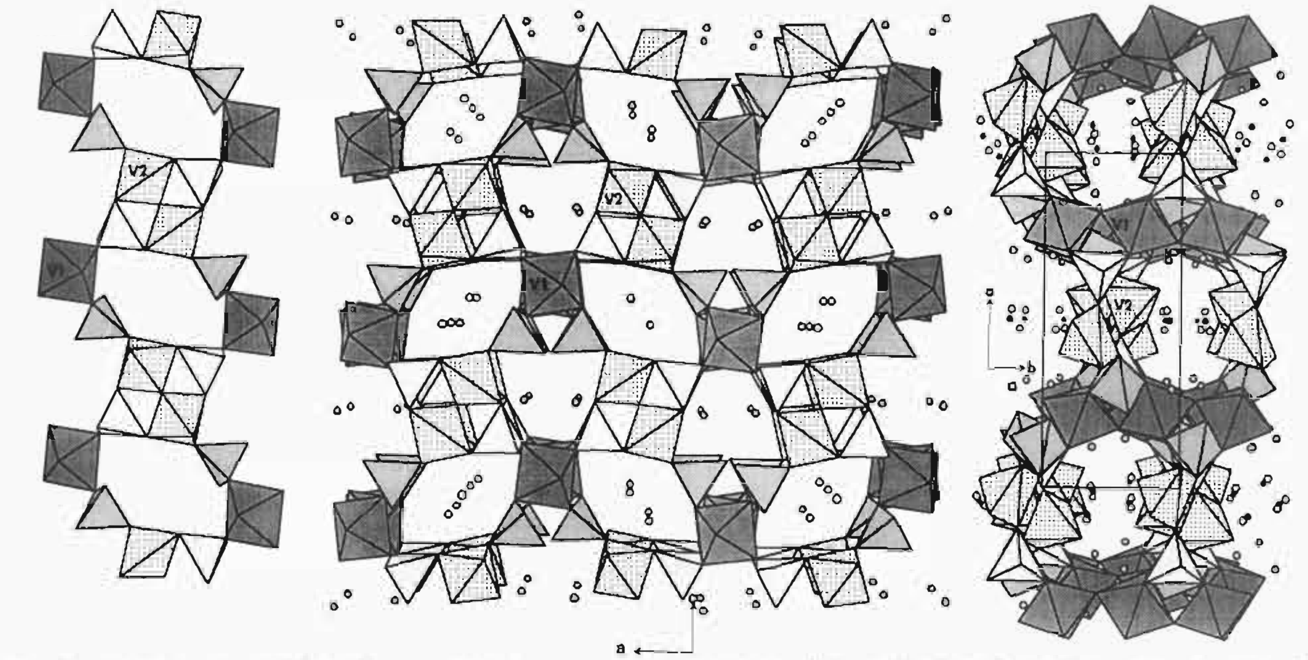

Figure 3. (a) Left: Section of infinite ribbons parallel in the structure of $Cs_3(VO)_2(V_2O_3)(AsO_4)_2(HAsO_4)_2{\cdot}H_2O$. (b) Center: View along the *b* axis showing how ribbons are connected. (c) Right: View down to the *c* axis showing infinite chains of corner-sharing $V^{IV}O6$ octahedra and large tunnels where Cs cations and water molecules reside. Black circles are water oxygens.

Additional crystallographic results are provided in Tables 2 and 3 and in the supplementary material.

Results and Discussion

Both frameworks of arsenate **1** and arsenate **2** are constructed from polyhedral units of VO_5, VO_6, $HAsO_4$, and AsO_4 groups. Arsenate **1** may be described by stacking two-dimensional polyhedral nets (Figure 1a) along the vector $(\mathbf{a} + \mathbf{b})/2$. The infinite nets are composed of infinite chains of alternating edge-sharing and corner-sharing $V(1)O_6$ octahedra and finite chains of discrete pyramids of $V(2)O_5$ sharing corners with tetrahedra of arsenate and hydrogen arsenate groups. These two types of chains interlink together such that large cavities each consisting of a 14-membered ring (longest atom-to-atom distance equal to the *a* length, ~16.4 Å) are formed in the structure. Large tunnels with an opening of 10-membered rings (Figure 1b,c) in the directions [100], [010], and [110] are also observed. Cations Cs(1) and Cs(2) reside in these tunnels, and both sites are fully occupied. Linkages between adjacent nets are provided by arsenate groups. Each AsO_4 tetrahedron chelates to two edge-sharing VO_6 octahedral dimers in the two infinite chains belonging to adjacent nets.

One feature of arsenate **1** is the existence of edge-sharing $V(1)O_6$ octahedra dimers in infinite chains. The two octahedra in the dimer (Figure 2a) are related by an inversion center and are highly distorted.[10] According to valence-bond calculations,[11] atom V(1) has an average valence of 4.5+ (Table 3). This may be interpreated as $V^{IV}O_6$ octahedra and $V^{V}O_6$ octahedra alternating in the infinite chains. On the other hand, the bond-valence sum indicates that the oxidation state for V(2) is 4+. Thus, in arsenate **1**, discrete $V^{IV}O_5$ square pyramids reside in the finite chains and mixed-valence $V^{IV,V}O_6$ octahedra are in the infinite chains.

Arsenate **2** consists of infinite ribbons (Figure 3) lying the *ac* plane. The building block of each ribbon is constructed from 8-membered rings of polyhedra, namely, two $V(1)O_6$ octahedra, two $V(2)O_5$ square pyramids, two AsO_4, and two $HAsO_4$ tetrahedra. The rings are connected such that dimers of corner-sharing VO_5 pyramids, $V_2(2)O_9$ units (Figure 2b), are formed in the ribbon. The three-dimensional structure of arsenate **2** is formed by stacking ribbons along the *b* axis. In this direction, neighboring ribbons are related by an inversion center and are connected by $V(1)O_6$ octahedra only. Infinite chains of corner-sharing VO_6 octahedra are therefore formed parallel to the *b* axis (Figure 3c). The $-V{=}O{-}V-$ bonds are alternately short and long in the chains.

Note that on the *ac* plane there is no linkage among the ribbons and they are apart by a distance equal to *a*. As the consequence of stacking, tunnels, each surrounded by four infinite ribbons (two on the plane, one above and one below the plane), are formed along the *c*-axis direction. Both cations, Cs(1) and Cs(2), and water molecules reside in these tunnels. Although the tunnel opening is only a 10-membered ring, the interior of each of these tunnels is quite large. Both Cs(2) cations and water molecules are disordered in these spacious tunnels. Cations Cs(1) are confined to 8-membered rings (Figure 3b) in the *ac* plane and are thus ordered. Interestingly, in contrast to the case of arsenate **1**, bond-valence calculations show that the oxidation state of the six-coordinated atom V(1) is 4+ and that of five-coordinated atom V(2) is 4.5+. Thus, corner-sharing $V^{IV}O_6$ octahedra reside in the infinite chains and mixed-valence $V^{IV,V}O_5$ square pyramids are confined to discrete dimers in the structure of arsenate **2**.

In summary, two novel mixed-valence vanadium arsenates have been synthesized hydrothermally and structurally characterized by single-crystal X-ray diffraction. Both crystals consist of large cavities and tunnels. There appears no structural relationship between them. Although the two compounds differ in composition only by a lattice water, their crystal structures and charge distributions on the vanadium atom sites are dramatically different.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, anisotropic thermal parameters, and bond distances (5 pages). Ordering information is given on any current masthead page.

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(10) Bond angles (deg; atom labels correspond to those in Figure 2a): O(2)–V(1)–O(5a), 80.1; O(2)–V(1)–O(5b), 84.8; O(2)–V(1)–O(6), 92.6; O(2)–V(1)–O(7a), 159.1; O(2)–V(1)–O(9), 103.5; O(7a)–V(1)–O(9), 95.6; O(7a)–V(1)–O(6), 92.9; O(7a)–V(1)–O(5a), 79.5; O(7a)–V(1)–O(5b), 85.3; O(6)–V(1)–O(9), 98.7; O(6)–V(1)–O(5a), 92.7; O(6)–V(1)–O(5b), 166.5; O(5a)–V(1)–O(5b), 73.8; O(5a)–V(1)–O(9), 167.8; O(5b)–V(1)–O(9), 94.8; V(1)–O(6)–V(1a), 148.4; V(1)–O(5a)–V(1b), 106.2.

(11) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.