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$A(VO)_2(AsO_4)_2$ (A = Ba or Sr): Two Vanadyl(IV) Arsenates Containing Dimers of Edge-Sharing VO_6 Octahedra

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Two new vanadyl(IV) arsenates, $Ba(VO)_2(AsO_4)_2$ and $Sr(VO)_2(AsO_4)_2$, have been synthesized hydrothermally at 230°C and characterized by single-crystal X-ray diffraction and magnetic susceptibility. Crystal data: $Ba(VO)_2(AsO_4)_2$, tetragonal, $I4_1/a$, a = 18.384(2) Å, c = 4.651(1) Å, Z = 8, and R = 0.027. $Sr(VO)_2(AsO_4)_2$: tetragonal, $I4_1/a$, a = 18.131(5) Å, c = 4.669(1) Å, Z = 8, and R = 0.034. The two compounds are isostructural. The structure consists of two types of tunnels in which Ba or Sr atoms are located. One alkaline-earth metal site is 25% occupied. The framework is composed of arsenate tetrahedra and dimers of edge-sharing $V^{IV}O_6$ octahedra.

INTRODUCTION

Recently a large number of new structures in the A–V–P–O system, where A includes alkali metal, alkaline-earth metal, and transition metal cations, have been synthesized under hydrothermal conditions (1, 2). These phosphates show a variety of new structural types with tunnel or layer structures. However, little structural work on A–V–As–O system has been reported. $A_xVOAsO_4 \cdot yH_2O$ (A = alkali metals) were prepared in polycrystalline form by redox intercalation reactions of $VOAsO_4 \cdot 2H_2O$ with metal iodides in aqueous solutions (3). Detailed structural information has been unavailable due to the lack of suitable single crystals for X-ray analysis. $NaVOAsO_4$ was prepared by solid state reaction and is isostructural with $NaVOPO_4$ (4, 5). Recently we noted that single crystals of $VO(H_2AsO_4)_2$ could be grown under hydrothermal conditions (6). Subsequent research revealed that a large number of new structures containing alkali or alkaline-earth metals can be obtained by hydrothermal methods. For example, $BaVO(AsO_4)(H_2AsO_4) \cdot H_2O$ has been synthesized hydrothermally at 230°C (7). Its structure consists of layers of corner-sharing VO_6, AsO_4, and H_2AsO_4 polyhedra with the Ba atoms and H_2O molecules between the layers. In this report, we describe an extension of our previous work to the vanadyl(IV) arsenates $A(VO)_2(AsO_4)_2$ (A = Ba or Sr). They adopt a tunnel structure and are the first compounds consisting of dimers of edge-sharing $V^{IV}O_6$ octahedra.

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EXPERIMENTAL

Synthesis

Reagent grade chemicals were used. The reaction conditions for the preparation of $Ba(VO)_2(AsO_4)_2$ and $Sr(VO)_2(AsO_4)_2$ were similar and consisted of a mixture of V_2O_3 (0.3749 g), V_2O_5 (0.4547 g), $Ba(OH)_2 \cdot 8H_2O$ (1.5775 g) (or 1.3288 g of $Sr(OH)_2 \cdot 8H_2O$), 80% H_3AsO_4 (2.5 cm^3 for Ba and 2.0 cm^3 for Sr), and H_2O (9.5 or 10 cm^3) in a 23-ml Teflon-lined autoclave. The reaction vessels were maintained at 230°C for 48 hr followed by slow cooling at 30°C hr^{-1} to room temperature. The products were filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. It was found that, in addition to the brown needle crystals of the required compounds, a small amount of green tabular crystals also crystallized from the reaction mixtures. When the cooling rate was at 5°C h^{-1}, the green crystals became the major product. The green crystals are commonly thin and plate-like. Preliminary X-ray study on the green crystals shows that they have the formulas $A(VOAsO_4)_2 \cdot xH_2O$ (A = Ba, Sr) and are structurally similar to $Sr(VOPO_4)_2 \cdot 2H_2O$ (1). However, their detailed structures have not been determined due to the poor quality of the crystals. The brown needles of the title compounds could be manually separated from the green crystals of the hydrates. Energy-dispersive X-ray fluorescence (EDX) analysis on a crystal of the Ba compound showed that the Ba : V : As mole ratio was 1 : 2.00 : 2.00. Powder X-ray diffraction using a Rigaku powder diffractometer on a sample of manually selected brown crystals of $Ba(VO)_2$

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$(AsO_4)_2$ confirmed their purity for subsequent magnetic susceptibility study.

Single-Crystal X-Ray Diffraction

Two brown crystals having dimensions of 0.04 × 0.08 × 0.51 mm for $Ba(VO)_2(AsO_4)_2$ and 0.05 × 0.05 × 0.52 mm for $Sr(VO)_2(AsO_4)_2$ were selected for indexing and intensity data collection on a Nicolet R3m/V four-circle diffractometer using monochromated Mo$K\alpha$ radiation. Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit cell parameters. No superlattice reflections were observed. The intensity data for both crystals were corrected for *Lp* and absorption effects. Correction for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90° using the program XEMP of SHELXTL PLUS program package. Based on systematic absences, statistical analysis of the intensity data and successful solution and refinement of the structures, the space groups were determined to be $I4_1/a$ (No. 88) for both compounds. Direct methods (SHELXTL PLUS) were used to locate the heavy atoms with the remaining oxygen atoms being found from successive difference maps. Atom Ba(1) is at 4*a* special positions, and all other atoms are at general positions. The Ba(2) site, which was initially considered fully occupied, showed large negative electron density on a difference Fourier map. This could be interpreted as partial occupancy of the Ba atom. Subsequent least-squares refinement including the occupancy factors for both Ba atoms indicated that the Ba(1) site was fully occupied and the occupancy factor for the Ba(2) site was only ~0.25. This result is consistent with that from EDX analysis. Therefore, the compound is formulated as $Ba(VO)_2(AsO_4)_2$. In the final cycles of refinement the occupancy factor of Ba(2) was fixed at 0.25. $Sr(VO)_2(AsO_4)_2$ is isostructural with the Ba compound with the same partial occupancy at the Sr(2) site. Neutral-atom scattering factors for all atoms were used. Anomalous dispersion corrections were applied. All calculations were performed on a DEC Micro VAX computer system using SHELXTL-Plus programs (8).

Magnetic Measurements

A 121.22-mg powder sample of $Ba(VO)_2(AsO_4)_2$ was used to collect variable-temperature magnetic susceptibility $\chi(T)$ data from 5 to 300 K in a magnetic field of 5 kG using a Quantum Design SQUID magnetometer. As suggested by Selwood (9), diamagnetic contributions for Ba^{2+}, V^{4+}, As^{5+}, and O^{2-} were estimated, which were subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibilities of the compound.

TABLE 1
Crystal Data and Intensity Collection Parameters for $Ba(VO)_2(AsO_4)_2$ and $Sr(VO)_2(AsO_4)_2$

Formula	$Ba(VO)_2(AsO_4)_2$	$Sr(VO)_2(AsO_4)_2$
M	549.1	499.3
Crystal symmetry	Tetragonal	Tetragonal
Space group	$I4_1/a$	$I4_1/a$
a/Å	18.384(2)	18.131(5)
c/Å	4.651(1)	4.669(1)
U/Å	1571.9(3)	1534.9(7)
Z	8	8
D_c/g cm^{-3}	4.640	4.322
$F(000)$	1984	1840
μ(Mo$K\alpha$)/cm^{-1}	156.0	176.2
T/°C	23	23
Scan rate/° min^{-1}	Variable; 2.93–14.65° min^{-1} in ω	Variable; 2.93–14.65° min^{-1} in ω
Scan mode	θ–2θ	θ–2θ
Scan width/°	1° plus $K\alpha$ separation	1° plus $K\alpha$ separation
2θ range/°	2.5–55	2–55
No. of reflections collected	3624	1049
Unique observed reflections [$I > 3\sigma(I)$]	799	630
Refined parameters	76	76
R^a	0.0271	0.0338
R'^b	0.0310	0.0319

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

RESULTS AND DISCUSSION

Structure

The crystallographic data for both compounds are listed in Table 1, atomic coordinates in Table 2, and selected

TABLE 2
Positional Parameters for $Ba(VO)_2(AsO_4)_2$ and $Sr(VO)_2(AsO_4)_2$

Atom	x	y	z	U_{eq} (Å^2 × 10^3)
		$Ba(VO)_2(AsO_4)_2$		
Ba(1)	0	0.25	0.125	10(1)
Ba(2)[a]	0.2545(2)	0.5041(2)	0.113(2)	61(1)
V	0.05000(6)	0.07591(6)	0.5237(2)	8(1)
As	0.07863(3)	0.44244(3)	0.0228(1)	8(1)
O(1)	0.1542(2)	0.3946(3)	−0.065(1)	15(1)
O(2)	0.0172(2)	0.3924(2)	0.199(1)	10(1)
O(3)	0.1104(2)	0.5134(2)	0.217(1)	13(1)
O(4)	0.0967(2)	0.2944(3)	0.573(1)	15(1)
O(5)	0.0379(2)	−0.0271(2)	0.2839(9)	9(1)
		$Sr(VO)_2(AsO_4)_2$		
Sr(1)	0	0.25	0.125	16(1)
Sr(2)[a]	0.2580(3)	0.5054(3)	0.062(5)	63(1)
V	0.05017(7)	0.07688(7)	0.5250(3)	7(1)
As	0.07924(4)	0.44170(4)	0.0246(2)	7(1)
O(1)	0.1562(3)	0.3952(3)	−0.067(1)	14(2)
O(2)	0.0186(3)	0.3883(3)	0.199(1)	12(2)
O(3)	0.1118(3)	0.5129(3)	0.221(1)	13(2)
O(4)	0.0953(3)	0.2946(3)	0.569(1)	15(2)
O(5)	0.0382(3)	−0.0265(3)	0.281(1)	9(1)

[a] The occupancy factor is 0.25.

TABLE 3
Selected Bond Lengths (Å) and Bond Valence Sums (Σs) for $Ba(VO)_2(AsO_4)_2$ and $Sr(VO)_2(AsO_4)_2$

	$Ba(VO)_2(AsO_4)_2$		
Ba(1)–O(2)	2.659(4) (4×)	Ba(1)–O(4)	2.858(5) (4×)
Σs(Ba(1)–O) = 2.30			
Ba(2)–O(1)	2.852(6)	Ba(2)–O(1)	2.920(7)
Ba(2)–O(1)	2.632(6)	Ba(2)–O(1)	3.298(8)
Ba(2)–O(3)	2.698(6)	Ba(2)–O(3)	3.108(8)
Ba(2)–O(3)	3.131(7)	Ba(2)–O(3)	2.586(6)
Σs(Ba(2)–O) = 1.83			
V–O(1)	2.026(5)	V–O(2)	2.035(5)
V–O(3)	2.003(5)	V–O(4)	1.594(5)
V–O(5)	2.054(4)	V–O(5)	2.209(4)
Σs(V–O) = 4.05			
As–O(1)	1.694(5)	As–O(2)	1.673(5)
As–O(3)	1.690(5)	As–O(5)	1.705(4)
Σs(As–O) = 4.92			
	$Sr(VO)_2(AsO_4)_2$		
Sr(1)–O(2)	2.553(5) (4×)	Sr(1)–O(4)	2.819(6) (4×)
Σs(Sr(1)–O) = 2.04			
Sr(2)–O(1)	2.94(1)	Sr(2)–O(1)	2.786(9)
Sr(2)–O(1)	2.574(9)	Sr(2)–O(1)	3.14(1)
Sr(2)–O(3)	2.87(1)	Sr(2)–O(3)	2.75(1)
Sr(2)–O(3)	3.25(1)	Sr(2)–O(3)	2.448(8)
Σs(Sr(2)–O) = 1.40			
V–O(1)	2.002(5)	V–O(2)	2.068(6)
V–O(3)	2.001(6)	V–O(4)	1.590(6)
V–O(5)	2.054(5)	V–O(5)	2.203(5)
Σs(V–O) = 4.06			
As–O(1)	1.686(5)	As–O(2)	1.675(5)
As–O(3)	1.688(5)	As–O(5)	1.712(5)
Σ(As–O) = 4.93			

bond distances and bond valence sums (10) in Table 3. Bond valence sums for the V and As atoms in both structures are in good accordance with their formal oxidation states. The coordination numbers (CN) of Ba^{2+} and Sr^{2+} are determined on the basis of the maximum gap in the cation–oxygen distances ranked in increasing order. In the mean time the agreement with the valence sum rule and the maximum cation–anion distance, L_{max}, suggested by Donnay and Allmann (11) are also checked. Atom Ba(1) is coordinated by eight oxygen atoms and the ninth oxygen atom is at 3.228 Å. The value of Ba(1) is significantly greater than 2. The average Ba(1)–O bond distance (2.759 Å) is a little shorter than the calculated Ba–O distance (2.80 Å) based on Ba^{2+} (1.42 Å, CN = 8) and O^{2-} (1.38 Å, CN = 3) and accordingly Ba(1) is tightly bonded to oxygen atoms and does not exhibit large thermal parameters. Based on the bond valence sums for $Sr(VO)_2(AsO_4)_2$, Sr(1) appears perfectly bonded and Sr(2) is loosely bound. In the following only the structure of $Ba(VO)(AsO_4)_2$ will be discussed because the two compounds are isostructural.

Figure 1 is a view of the $Ba(VO)_2(AsO_4)_2$ structure along

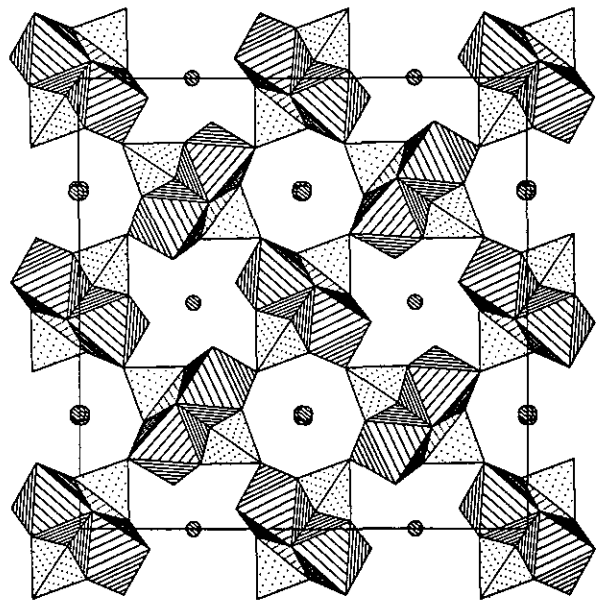

FIG. 1. View of the $Ba(VO)_2(AsO_4)_2$ structure along [001]. In this representation the corners of octahedra and tetrahedra are O atoms and the V and As atoms are at the center of each octahedron and tetrahedron, respectively.

the c axis. It consists of two different tunnels in which the Ba atoms are located. Atom Ba(2) is located in the tunnel with octagonal window which is formed by the edges of four octahedra and four tetrahedra. Each Ba(2) site is only 25% occupied. The other type of tunnel is occupied by Ba(1). The framework is composed of arsenate tetrahedra and dimers of edge-sharing VO_6 octahedra. Each dimer sits on an inversion center. The coordination of V is characteristic of vanadyl(IV) compounds, i.e., one very short V=O bond length is 1.59 Å which is about 0.4 Å shorter than the four equatorial V–O bonds, and a sixth ligand is weakly bonded *trans* to the V=O bond. The vanadyl oxygens are directed into the tunnels filled with Ba(1). As shown by the O...O distances 2.631–3.031 Å, the VO_6 octahedron is strongly distorted. The common edge of two VO_6 octahedra is shorter than those which are unshared such that the separation of the vanadium ions is somewhat increased. The shortening of shared edge is an evidence that the structure is essentially ionic. Eight of the ten vertexes of a dimer are shared with six different AsO_4 tetrahedra with the remaining two vanadyl oxygens being unshared (Fig. 2). Two of the six AsO_4 tetrahedra are bidentate ligands and form bridges between the two V atoms in a dimer, and the other four tetrahedra are coordinated to the dimer as monodentate ligands. Each AsO_4 tetrahedron shares its four apexes with three different dimers. To our knowledge, $Ba(VO)_2(AsO_4)_2$ is the first compound containing dimer of edge-sharing $V^{IV}O_6$ octahedra. The phosphate analogue Ba

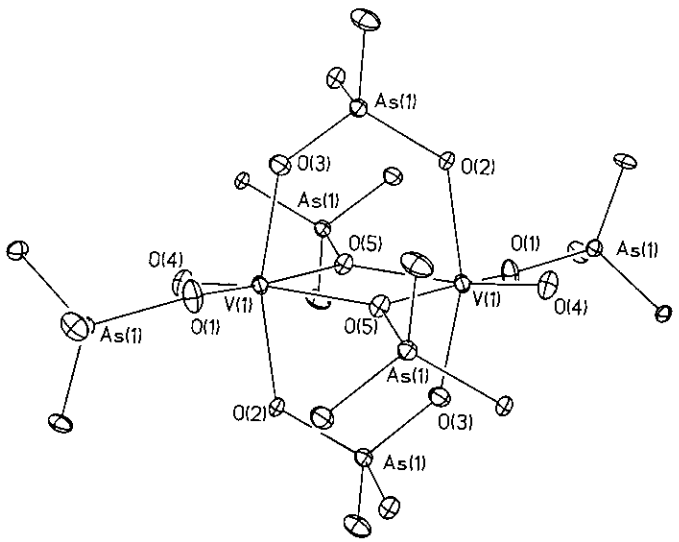

FIG. 2. The coordination of arsenate ligands around a dimer of edge-sharing VO_6 octahedra in $Ba(VO)_2(AsO_4)_2$.

$(VO)_2(PO_4)_2$ (12), which adopts a rather different crystal structure, consists of V_2O_{10} units built up from one VO_6 octahedron and one VO_5 pyramid sharing a corner. Dimer of edge-sharing $V^{III}O_6$ octahedra has been observed in $NaV_3P_3O_{12}$ (13).

Magnetic Susceptibility

Figure 3 shows the molar susceptibility and inverse molar susceptibility of $Ba(VO)_2(AsO_4)_2$ plotted as a function of temperature. The data were fitted in the temperature range 12–300 K using the Curie–Weiss formula $\chi_M = C/(T - \theta)$ with $C = 0.733$ cm^3 · K · mole^{-1} and $\theta = -11.8$ K. From the relation $C = N\mu_{eff}^2/3k_B$ one obtains the effective magnetic moment $\mu_{eff} = 1.71$ per vanadium which is in good agreement with the spin-only value for a d^1 ion of 1.73 μ_B. The deviation of $1/\chi_M$ to larger values with decreasing temperature below ~10 K may arise from antiferromagnetic interaction between adjacent vanadium ions.

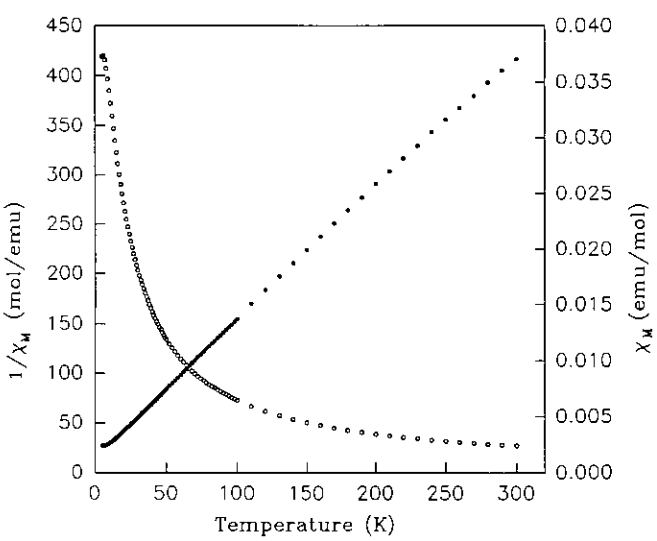

FIG. 3. Plot of molar susceptibility (χ_M, open circles) and inverse molar susceptibility ($1/\chi_M$, solid circles) as a function of temperature for $Ba(VO)_2(AsO_4)_2$.

Vanadium arsenates have shown a rich crystal chemistry. The simple hydrothermal technique that we have used is useful for crystal growth of these arsenates. Further research on the hydrothermal synthesis of new transition metal arsenates is in progress.

Supplementary Material Available

Tables of anisotropic thermal parameters and bond angles and tables of observed and calculated structure factors may be obtained by writing the corresponding author.

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