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Synthesis, Structure, and Properties of $BaVO_2(AsO_4)$: a New Vanadium Arsenate Containing the $V_2O_4^{2+}$ Core

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The new vanadium arsenate $BaAsVO_6$ has been synthesized hydrothermally and structurally characterized by single-crystal X-ray diffraction, IR spectroscopy, and magnetic susceptibility measurements. It crystallizes in the monoclinic system, space group $P2_1/c$ with unit cell parameters $a = 5.645(1)$ Å, $b = 10.243(1)$ Å, $c = 8.945(1)$ Å, $\beta = 90.60(1)°$, and $Z = 2$. The layered structure is built up from $V_2O_4^{2+}$ units and AsO_4^{3-} anions, the AsO_4^{3-} ligands being coordinated to two $(V_2O_4)^{2+}$ units in both, terminal and bridging μ_2-AsO_4^{3-} fashion. The $[VO_2(AsO_4)]^{2-}$ layers are separated by Ba^{2+} cations. The $V_2O_4^{2+}$ unit has no precedence in oxo-vanadium chemistry.

Introduction

Inorganic chemists have been fascinated by the solution chemistry of early transition metals such as vanadium, niobium, tantalum, or the group 6 metals molybdenum and tungsten for more than a century when it became clear that the oxoions of these metals in their highest oxidation states form a condensation series between the simple monomeric MO_4^{n-} anions and the polymeric oxides, e.g. V_2O_5 or $MoO_3 \cdot 2H_2O$.[1] A stunning variety of discrete, molecular ions ranging in complexity between species such as $[V_2O_7]^{4-}$ and $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ [2] may be isolated from solutions as a function of the pH values. Polyanions have been shown to function as ligands, and a rich coordination chemistry is evolving from the binding of “surface” oxygen atoms of polyoxometalate ions to metal cations.[3] Polyions are generally considered as model systems which might provide insight into the complex solid state systems.[4] Industrial applications of oxoions and oxides as catalysts for the oxidation of organic molecules have triggered numerous investigations in this field.[5] Recent advances in the synthetic methodology have lead to the synthesis of a plethora of new materials by hydrothermal techniques.[6−8] Whereas classical examples include natural minerals as well as synthetic zeolites and alumophosphates,[9] Haushalter et al. have used this method to prepare a new class of octahedral−tetrahedral framework structures based on anionic molybdenum and vanadium phosphates and phosphonates.[10] The dimensionalities of these structures range from molecular entities to covalent three-dimensional frameworks. As part of a program aiming at the synthesis of semiconducting chalcogenoarsenates and phosphates with porous structures,[11] we studied the reaction of arsenic acid with vanadium oxides under hydrothermal conditions. We report here the hydrothermal synthesis of the layered vanadium arsenate $BaVO_2(AsO_4)$, whose structure contains the $V_2O_4^{2+}$ core.

Experimental Section

Synthesis. Starting materials were V_2O_5 (Aldrich, 99.6% purity), $Ba(OH)_2 \cdot 8H_2O$ (Fluka, p.A. >98% purity) and H_3AsO_4 (E. Merck, 80% solution). All reactions were carried out in a 25 cm^3 tetrafluoroethylene-lined stainless steel autoclave (Berghof) under autogenous pressure. A 5 mmol (0.909 g) sample of V_2O_5, 5 mmol of $Ba(OH)_2 \cdot 8H_2O$ (0.578 g), 28 mmol (2 mL) of H_3AsO_4 and 15 mL of H_2O were reacted at 240 °C for 2 d; subsequently, the autoclave was slowly cooled to room temperature. The light yellow crystalline product was filtered, washed with distilled water and dried in a desiccator. Yield: 0.781 g (87% based on V_2O_5). The product contained a single crystalline phase as judged by a comparison of the powder pattern with the pattern computed from the atomic coordinates obtained from the structure analysis. A microanalysis of this phase by energy-dispersive X-ray fluorescence indicated the presence of the elements Ba, V, and As in a 1:1:1 ratio.

Physical Measurements. Infrared spectra were obtained on a Mattson-Instruments 2030-Galaxy FT-IR spectrometer. Magnetic susceptibility data were collected with a vibrating-sample magnetometer (Foner-magnetometer, Princeton Applied Research), which was operated between 0.2 and 1 T. The instrument was calibrated with $Hg[Co(NCS)_4]$.

X-ray Data Collection and Analysis. Crystals of $BaVO_2(AsO_4)$ have plate like habit. Preliminary investigations revealed a Laue symmetry $2/m$. The systematic extinctions ($h0l$, $l = 2n$; $0k0$, $k = 2n$) are characteristic for the space group $P2_1/c$. A crystal of approximate

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Table 1. Crystallographic Data for $BaAsVO_6$[a,b]

empirical formula	$BaVAsO_6$	V, Å^3	517.5(2)
fw	359.2	Z	2
space group	$P2_1/c$	ρ_{calc}, g·cm^{-3}	4.612
a, Å	5.645(1)	T, °C	−90
b, Å	10.243(2)	radiation (λ, Å)	Mo Kα (0.710 73)
c, Å	8.945(2)	R	0.0247
β, deg	90.61(3)	R_w	0.0276

[a] Estimated standard deviations in the least significant digit are given in parentheses. [b] Quantity minimized $= \sum w(F_0 - F_c)^2$, $w = [\sigma^2(F) + 0.009F^2]^{-1}$, $R = \sum|[F_0 - F_c]|/\sum F_0$, and $R_w = (\sum(w[F_0 - F_c]^2/\sum(wF_0)^2))^{1/2}$.

Table 2. Positional Parameters and Equivalent Isotropic Displacement Coefficients [Å^2][a] for $BaVAsO_6$

atom	x	y	z	U(eq)[a]
Ba(1)	0.34527(4)	0.19142(2)	−0.08549(2)	0.0084(1)
As(1)	0.15748(7)	0.61633(3)	0.27856(4)	0.0059(1)
V(1)	0.15631(12)	0.59032(6)	−0.08684(7)	0.0058(2)
O(1)	0.4056(6)	0.6339(3)	−0.1616(4)	0.0107(7)
O(2)	0.1962(6)	0.4375(3)	−0.0221(4)	0.0100(7)
O(3)	0.2189(6)	0.6775(3)	0.1058(4)	0.0108(7)
O(4)	−0.0131(6)	0.5296(3)	−0.2672(3)	0.0084(7)
O(5)	−0.0220(6)	0.7703(3)	−0.1434(4)	0.0090(7)
O(6)	0.4006(6)	0.5816(3)	0.3753(4)	0.0119(7)

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

dimensions 0.2 × 0.12 × 0.8 mm was mounted at the top of a glass capillary with silicon grease. X-ray diffraction data were recorded with monochromated Mo Kα radiation on an automated Siemens P4 four-circle diffractometer equipped with a LT2 low-temperature device. The unit cell dimensions and their standard deviations were determined from a least squares fit of the setting angles of 25 reflections in the range $20 \leq 2\theta \leq 30°$. Data were collected in the $\theta - 2\theta$ scan mode. The intensities of three standard reflections measured every 97 scans revealed stable crystal settings and experimental conditions. An empirical absorption correction was applied to the intensities by using the XEMP routines of the SHELXTL/PC program package, which was used for the structure calculations. Lorentz and polarization effects were taken into account as usual. Details concerning the data collection and the structure refinements are compiled in Table 1 and in ref 12.

Direct methods (TREF instruction of SHELXS) revealed the position of all metal atoms. The oxygen atoms were located from difference Fourier maps computed after least-squares refinement cycles. The final refinements resulted in conventional R values of $R = 0.025$ and $R_w = 0.028$. Details concerning the refinements are also compiled in Table 1. Final atomic parameters are given in Table 2.

Results and Discussion

Synthesis. Light yellow plates of $BaVO_2(AsO_4)$ were first obtained from the reaction of V_2O_3, V_2O_5, $Ba(OH)_2{\cdot}8H_2O$, and H_3AsO_4 in a mole ratio of 1:1:2:7 under hydrothermal conditions. A mixture of products was obtained; besides the title compound, $BaVO(AsO_4){\cdot}xH_2O$ and $Ba(VO)_2(AsO_4)_2$[13e] could be identified from their powder patterns. In addition, other still unidentified products were present in small amounts in the reaction product. After the composition of $BaVO_2(AsO_4)$ was known, a single phase material could be made by reacting V_2O_5 with $Ba(OH)_2$, H_3AsO_4, and H_2O in a 1:1:6:90 ratio. Careful control of the reaction temperature ($T \geq 230$ °C) is important to obtain high yields of the reaction product. The Ba^{2+} cations are situated in the van der Waals gap between the layers in linear channels formed by the O atoms of the $V_2O_4^{2+}$ and AsO_4^{3-} groups. From a structural point of view, there are no specific steric requirements for the cations. Thus, it might be possible to obtain other alkaline earth metal derivatives by modification of the reaction conditions. Still, attempts to synthesize analogous phases with the same layer structure and the Ba^{2+} cation replaced by other divalent cations were unsuccessful so far. Since the radius of Ba^{2+} is similar to the radii of other divalent cations such as Sr^{2+}, the formation of AVO_2AsO_4 (A = alkaline earth metals, divalent transition metal cations) is feasable. The successful synthesis of $BaVO_2(AsO_4)$ might depend on a pH effect, although the reaction conditions are strongly acidic in any case. A good understanding of the factors influencing the nucleation and crystal growth under hydrothermal conditions is complicated by the large number of variables in the synthesis. In addition to the mole ratios of the components, factors such as temperature, time, pH, etc. determine to some extent which solid state species is ultimately formed. Therefore, it is presently impossible to predict even the outcome of these seemingly simple reactions.

Properties. The infrared spectrum of $Ba(VO_2)(AsO_4)$ shows strong bands at 934, 905 (sh), 876, 760, 522 (sh), 501, and 451 (sh) cm^{-1}. The absorptions at 876 and 760 cm^{-1} are most likely to be assigned to the symmetric and antisymmetric stretching modes of the octahedral VO_6 units, but the AsO_4 tetrahedra are also expected to have vibration bands in that spectral region. The absorptions at 522, 501, and 451 cm^{-1} can be assigned to deformation modes of the AsO_4 tetrahedra. Susceptibility measurements of a sample of $BaVO_2(AsO_4)$ at room temperature showed diamagnetic behavior. This is consistent with the presence of V^{5+}.

Structure. The structure of $BaVO_2(AsO_4)$, which is shown in Figure 1 in a polyhedral representation, was determined by single-crystal X-ray methods. It contains two distorted VO_6 octahedra sharing a common edge. These units are linked by AsO_4 groups in a doubly bridging fashion. Furthermore, the

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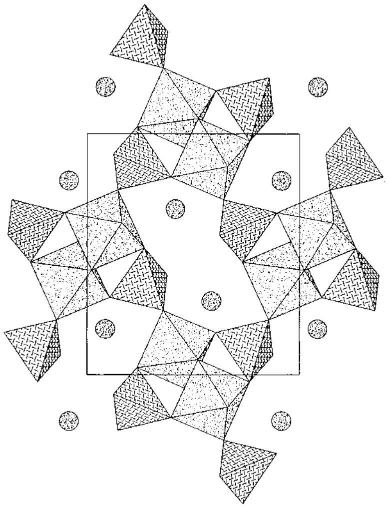

Figure 1. Polyhedral representation of the $BaVO_2(AsO_4)$ structure. View of the structure along *b*: VO_6 octahedra, dot shaded; AsO_4 tetrahedra, cross shaded; Ba, shaded balls.

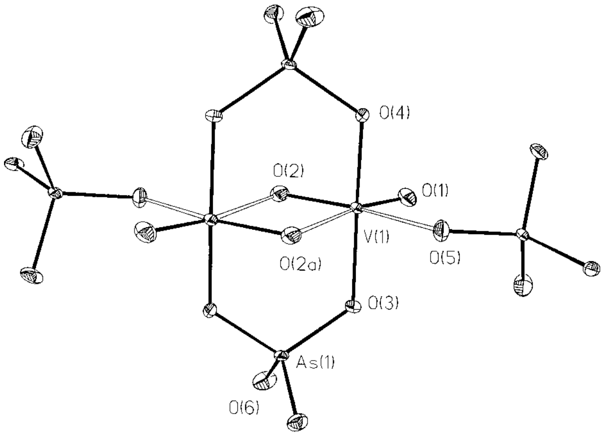

Figure 2. $[V_2O_4][AsO_4]_4$ unit and atomic labeling scheme (thermal ellipsoids 95% probability).

AsO_4 units act as terminal ligands to neighboring VO_6 octahedra. Each AsO_4 unit is linked to three VO_6 octahedra, its fourth vertex being free and pointing into the interlayer region. Thus, the characteristic motif of the structure are $[(VO_2)_2(AsO_4)_2]^{4-}$ blocks linked by sharing four common vertices in the projection plane. A view of the $V_2O_4^{2+}$ unit with the four surrounding AsO_4^{3-} ligands is shown in Figure 2. The vanadium atoms are located inside an octahedron of oxygen atoms, the average V−O distance within the octahedron being 1.942 ± 0.315 Å. The V atoms are displaced off center toward one of the O edges. The C_{2v} displacement is caused by the presence of two short *cis* V═O bonds of the octahedron (π-bonding effects); each of these short bonds has a corresponding long V···O bond trans to it. Typically, in vanadium oxides and phosphates such as $VOPO_4$[14] the VO_6 octahedron is distorted in a square pyramidal fashion, one very short V═O bond being trans to one elongated V···O bond. This type of distortion often occurs with compounds containing the VO_2^+ vanadyl ion, which has a strong V═O bond with σ and π character. The increasing π-bond character drives the distortion. The prototype material, showing this type of distortion is MoO_3;[15] another example, $(NH_4)(V^vO_2)_3(SeO_2)_2$, has been reported recently.[16] The degree of distortion can be estimated quantitatively by using the equation $\Delta = {}^{1}/_{6}\sum((R_\mathrm{i} - \bar{R})/\bar{R}^2)$, where R_i and $\bar{R}$ are the individual and average bond lengths.[17] The calculation shows that the distortion is comparable to that in MoO_3.[15]

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Ba(VO_2)(AsO_4)$

Bond Lengths[a]

Ba(1)−O(1A)	3.162(3)	Ba(1)−O(5B)	3.126(3)	As(1)−O(6)	1.655(3)
Ba(1)−O(1B)	2.741(3)	Ba(1)−O(6B)	2.838(3)	V(1)−O(1)	1.627(3)
Ba(1)−O(2)	2.720(3)	Ba(1)−O(6A)	2.607(3)	V(1)−O(2)	1.685(3)
Ba(1)−O(3A)	2.811(3)	As(1)−O(3)	1.706(3)	V(1)−O(2A)	2.243(3)
Ba(1)−O(4B)	2.820(3)	As(1)−O(4A)	1.706(3)	V(1)−O(3)	1.970(3)
Ba(1)−O(5A)	2.784(3)	As(1)−O(5C)	1.696(3)	V(1)−O(4)	1.969(3)
				V(1)−O(5)	2.159(3)

Bond Angles[b]

O(1)−V(1)−O(2)	106.5(1)	O(3)−As(1)−O(4A)	111.7(1)
O(1)−V(1)−O(2A)	171.3(1)	O(3)−V(1)−O(5)	84.0(1)
O(1)−V(1)−O(3)	95.0(1)	O(3)−As(1)−O(5C)	104.4(1)
O(1)−V(1)−O(4)	99.5(1)	O(3)−As(1)−O(6)	112.2(2)
O(1)−V(1)−O(5)	94.2(1)	O(4)−V(1)−O(5)	81.8(1)
O(2)−V(1)−O(3)	95.7(1)	O(4A)−As(1)−O(5C)	109.8(1)
O(2)−V(1)−O(2A)	81.3(1)	O(4A)−As(1)−O(6)	103.6(1)
O(2A)−V(1)−O(3)	80.2(1)	O(5C)−As(1)−O(6)	115.3(1)
O(2)−V(1)−O(4)	92.9(1)	V(1)−O(2)−V(1A)	98.7(1)
O(2A)−V(1)−O(4)	83.7(1)	V(1)−O(3)−As(1)	126.1(2)
O(2)−V(1)−O(5)	159.3(1)	V(1)−O(4)−As(1A)	123.6(1)
O(2A)−V(1)−O(5)	78.3(1)	V(1)−O(5)−As(1D)	113.8(1)
O(3)−V(1)−O(4)	160.4(1)		

[a] Symmetry transformations used to generate equivalent atoms follow. $1 - x, 1 - y, -z$: O(1A), O(3A). $1 - x, y - {}^1/_2, -{}^1/_2 - z$: O(1B). $-x, 1 - y, -z$: O(2A), O(4A), O(5A). $-x, y - {}^1/_2, -{}^1/_2 - z$: O(4B), O(5B). $x, {}^3/_2 - y, {}^1/_2 + z$: O(5C). $1 - x, y - {}^1/_2, {}^1/_2 - z$: O(6A). $x, {}^1/_2 - y, z - {}^1/_2$: O(6B). [b] Symmetry transformations used to generate equivalent atoms follow. $-x, 1 - y, -z$: As(1A), V(1A), O(2A), O(4A). $x, {}^3/_2 - y, {}^1/_2 + z$: O(5C). $x, {}^3/_2 - y, z - {}^1/_2$: As(1D).

Figure 2 shows the $[(VO_2)_2(AsO_4)_2]^{4-}$ segment of the structure with the atom labelling scheme. Important interatomic distances and angles are given in Table 3. Two AsO_4^{3-} ligands bridge the $V_2O_4^{2+}$ core in a chelating fashion which is reminiscent of the bonding in A-frame compounds.[18] The short (V−O(1) and V−O(2)) and long (V(1)−O(1(a) and V−O(3)) V−O bonds are in the plane defined by the naked oxygen atoms. Two terminal AsO_4^{3-} groups complete the octahedral coordination of the metal atoms. The V−V distance is at 3.002(1) Å approximately 0.1 Å shorter than that in related V^{5+} polyanions such as $[V_{10}O_{28}]^{6-}$ ($\bar{d}_{V-V} \approx 3.1$ Å)[19] or in the AsO_4^{3-}-bridged V^{IV} compound $Ba(VO)_2(AsO_4)$ (d_{V-V}: 3.349 Å).[13e] This is surprising, because according to Pauling's rules[20] highly charged central atoms should repel each other electrostatically. Dinuclear metal−metal-bonded V_2L_{10} units with short V−V distances are well-known for V^{3+} or V^{4+}.[21] Evidence for the presence of V^{5+} is given by the susceptibility data and bond order sums. Using the Brown−Altermatt formalism[21] for the bond length/bond valence relationship for V^{5+}−O and As^{5+}−O, bond-order sums for the cations and anions can be calculated. Motifs of the mutual adjunction[22] and bond-order sums for both cations and anions were calculated using $s = \exp[-(d - d_0)/B]$ with $B = 37$ pm; d_0(V−O) = 1.803 Å, d_0(As−O) = 1.767

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Table 4. Motifs of Mutual Adjunction and Bond Orders for $Ba(VO_2)(AsO_4)$

atom	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	CN	s_i
Ba	$^2/_3$	$^1/_3$	$^1/_3$	$^2/_4$	$^1/_3$	$^2/_3$	9	2.176
As			$^1/_3$	$^1/_4$	$^1/_3$	$^1/_3$	4	4.917
V	$^1/_3$	$^2/_3$	$^1/_3$	$^1/_4$	$^1/_3$		6	4.950

Å, and d_0(Ba−O) = 2.285 Å[22] are given in Table 4. The calculated bond-order sums for both cations and anions are in good agreement with the formal oxidation state assignments Ba^{2+}, As^{5+}, and V^{5+}. The average As−O bond length of 1.691 Å agrees very well with the sum of the corresponding ionic radii of 1.685 Å.[23] The As−O(6) bond is shortened ($d_{As-O(6)}$ = 1.655(3) Å), because O(6) is not involved in the vanadium coordination.

The $V_2O_4^{2+}$ unit has no precedence in oxo−vanadium chemistry. In contrast, mixed valent polynuclear vanadium oxoanions have been described. In aqueous solution, the VO_2^+ and VO^{2+} cations, or some of their complexes if present in solution, are known to associate to form a $V_2O_3^{3+}$ ion. Whereas in acid solution a direct equilibrium exists between the V^{5+} species $V_2O_5 \cdot xH_2O$ and the vanadyl cation VO_2^+ at ambient temperature and normal pressure, the $V_2O_4^{2+}$ species, which is formed by a dimerization of monomeric VO_2^+ units, can be captured from hydrothermal reactions. Therefore, one might speculate that other still unknown oxometalate species may be accessible under appropriately modified reaction conditions.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles and anisotropic parameters (6 pages). Ordering information is given on any current masthead page.

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