Hydrothermal Synthesis and Structural Characterization of a New Vanadyl(IV) Arsenate: $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$†

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A new vanadyl(IV) arsenate, $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$, has been synthesised hydrothermally at 230 °C and characterized by single-crystal X-ray diffraction, thermogravimetric analysis, and magnetic susceptibility. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.222(2)$, $b = 6.570(2)$, $c = 11.540(3)$ Å, $\beta = 102.87(2)°$, $Z = 4$ and $R = 0.0297$. The structure consists of layers of corner-sharing VO_6, AsO_4 and H_2AsO_4 polyhedra, extending parallel to the (101) crystallographic plane with the Ba atoms and H_2O molecules between the layers. The connectivity formula for a layer is ${}^{2}_{\infty}[(VOO_{2/2}O_{3/2})(AsOO_{3/2})\{As(OH)_2O_{2/2}\}]^{2-}$. The adjacent layers are linked by O–Ba–O bonds and hydrogen bonding.

Recently a large number of new structures in the A–V–P–O system, where A includes alkali-metal and alkaline-earth-metal cations, have been synthesised and structurally characterized.[1,2] The synthetic approaches were two-fold, namely solid-state reactions and hydrothermal methods. These phosphates show a variety of new structural types with cage, tunnel, or layer structures. However, little structural work on vanadium arsenates has been reported. Enjalbert *et al.*[3] reported the solid-state synthesis and crystal structure of $V_4As_2O_{13}$, which consists of a cubic close-packed oxygen atom array with the tetravalent vanadium atoms in octahedra sharing edges and corners, and with AsO_4 tetrahedra sharing corners with VO_6 octahedra. The compounds $VOAsO_4$ and its hydrate $VOAsO_4\cdot 2H_2O$ are isostructural with their phosphate analogues.[4] Also $A_xVOAsO_4\cdot yH_2O$ were prepared in polycrystalline form by redox intercalation reactions of $VOAsO_4\cdot 2H_2O$ with metal iodides in aqueous solution.[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 synthesis. The present work deals with the synthesis and structural characterization of the first member in this family, $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$.

Experimental

Synthesis.—Reagent-grade chemicals were used. For the crystal growth of $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$, $Ba(OH)_2\cdot 8H_2O$ (1.655 g), VO_2 (0.415 g), 80% H_3AsO_4 (5 cm^3) and water (7 cm^3) were placed in a Teflon-lined autoclave (23 cm^3). The reaction vessel was maintained at 230 °C and autogenous pressure for 4 d and then cooled at 5 °C h^{-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 green prismatic crystals of the required compound, a small amount of blue tabular crystals of $VO(H_2AsO_4)_2$ also crystallized from the reaction mixture. Separation was performed easily because of the differences in colour, crystal habit, and size. The X-ray powder pattern of the green product compared well with that calculated from the single-crystal data.

X-Ray Crystallography.—*Crystal data.* $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$, $M = 502.2$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.222(2)$, $b = 6.570(2)$, $c = 11.540(3)$ Å, $\beta = 102.87(2)°$, $U = 829.5(4)$ Å^3, $Z = 4$, $D_c = 4.021$ g cm^{-3}, $F(000) = 916$.

A green prismatic crystal of dimensions 0.06 × 0.11 × 0.20 mm was selected for indexing and intensity data collection at room temperature (296 K) on a Nicolet R3m/V diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Unit-cell parameters and the orientation matrix were determined by a least-squares fit of 13 peak maxima with 2θ ranging from 9 to 27°. Of the 1820 reflections collected ($2.0 \leqslant 2\theta \leqslant 50°$, $\pm hkl$, scan mode 2θ–θ), 1212 unique reflections were considered observed [$I > 3.0\sigma(I)$] after Lorentz polarization and empirical absorption corrections (maximum, minimum transmission factors = 0.947, 0.207).[7] On the basis of systematic absences and successful solution and refinement of the structure, the space group was determined to be $P2_1/n$.

The structure was solved by direct methods and successive Fourier syntheses. Bond-strength calculations were carried out to help locate the four hydrogen atoms on a Fourier difference map. The structure was refined by full-matrix least squares based on F values. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The atomic positions and isotropic thermal parameters for the hydrogen atoms were fixed ($U_{iso} = 0.08$ Å^2). The largest residual electron density (2.06 e Å^{-3}) on the final Fourier difference map is at a distance of 0.9 Å from Ba. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.0010F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final $R(F_o)$ and $R'(F_o)$ values are 0.0297 and 0.0312 ($R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}F_o$). Calculations were performed on a DEC MicroVAX II computer system using SHELXTL-Plus programs.[8] Neutral-atom scattering factors and corrections for anomalous dispersion were from ref. 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Thermal Analysis.—Thermogravimetric analysis (TG), using a Du Pont 951 thermogravimetric analyser, was performed on a powder sample of $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$ in flowing N_2 with a heating rate of 5 °C min^{-1}. In order to characterize the decomposition products an experiment was performed in which the compound was heated in flowing N_2 at 600 °C for 8 h.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Atomic coordinates for $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$

Atom	*X/a*	*Y/b*	*Z/c*
Ba	0.846 44(4)	0.155 40(7)	0.548 33(4)
V	0.635 7(1)	0.484 3(2)	0.318 3(1)
As(1)	0.352 61(7)	0.376 2(1)	0.378 92(6)
As(2)	0.602 33(7)	−0.003 9(1)	0.258 87(6)
O(1)	0.820 3(4)	0.485 7(8)	0.351 9(4)
O(2)	0.652 8(5)	0.187 8(7)	0.353 6(4)
O(3)	0.456 6(5)	0.468 1(8)	0.313 0(5)
O(4)	0.613 8(5)	0.489 8(8)	0.176 3(4)
O(5)	0.684 3(5)	0.477 7(7)	0.518 4(5)
O(6)	0.386 8(6)	0.137 0(8)	0.437 2(5)
O(7)	0.233 0(5)	0.333 0(8)	0.259 2(5)
O(8)	0.628 0(5)	−0.210 9(7)	0.347 0(4)
O(9)	0.455 1(4)	0.023 0(8)	0.191 8(4)
O(10)	0.075 6(5)	0.235 2(8)	0.478 3(5)

Table 2 Selected bond distances (Å) and bond valence sums (Σs) for $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$

Ba–O(1)	3.104(5)	Ba–O(2)	2.764(5)
Ba–O(3)	3.136(6)	Ba–O(4)	2.936(6)
Ba–O(4)	3.181(5)	Ba–O(5)	2.763(5)
Ba–O(6)	3.281(7)	Ba–O(7)	2.988(6)
Ba–O(9)	2.792(5)	Ba–O(10)	2.910(6)
Ba–O(10)	2.751(5)		
Σs(Ba–O) = 1.96			
V–O(1)	2.021(5)	V–O(2)	1.991(5)
V–O(3)	1.999(6)	V–O(4)	1.602(5)
V–O(5)	2.252(5)	V–O(8)	2.035(5)
Σs(V–O) = 4.08			
As(1)–O(3)	1.644(6)	As(1)–O(6)	1.719(5)
As(1)–O(5)	1.648(6)	As(1)–O(7)	1.722(5)
Σs[As(1)–O] = 5.04			
As(2)–O(1)	1.699(6)	As(2)–O(2)	1.681(5)
As(2)–O(8)	1.684(5)	As(2)–O(9)	1.671(5)
Σs[As(2)–O] = 5.01			
O(6)–H(6)	0.74	O(7)–H(7)	0.91
O(10)–H(10a)	1.07	O(10)–H(10b)	0.63
H(6) ··· O(8)	1.87	H(7) ··· O(9)	1.73
H(10a) ··· O(1)	1.69	H(10b) ··· O(9)	2.07

Visual microscopic examination of the product of heat treatment showed that it was a mixture of colourless and dark green solids. The powder X-ray diffraction pattern of the mixture cannot be indexed.

Magnetic Measurements.—A polycrystalline sample (306.18 mg) was used to collect variable-temperature magnetic susceptibility $\chi(T)$ data from 4 to 300 K in a magnetic field of 3 kG (0.3 T) using a Quantum Design SQUID magnetometer. As suggested by Selwood,[10] diamagnetic contributions for Ba^{2+}, V^{4+}, As^{5+} and O^{2-} were estimated and subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibility (χ_M) of the compound.

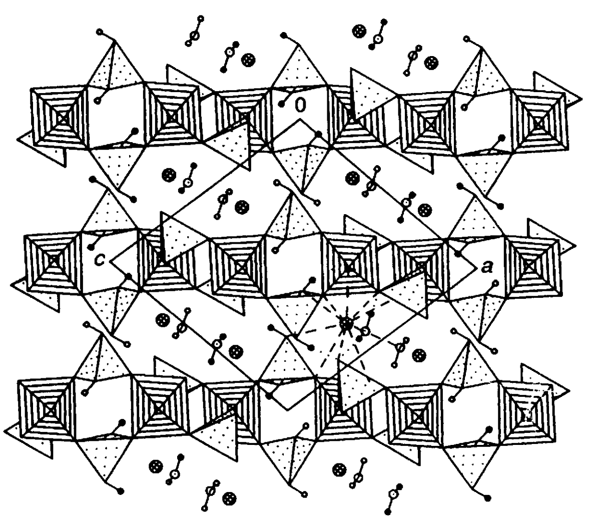

Fig. 1 View of the $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$ structure along [010]. In this representation the corners of octahedra and tetrahedra are O^{2-} ions; the vanadium and arsenic ions are at the centre of each octahedron and tetrahedron, respectively. Cross-hatched circles are Ba^{2+} ions, dotted circles are water oxygens and small open circles are H atoms. The Ba–O bonds and hydrogen bonding are represented by dashed and dotted lines, respectively

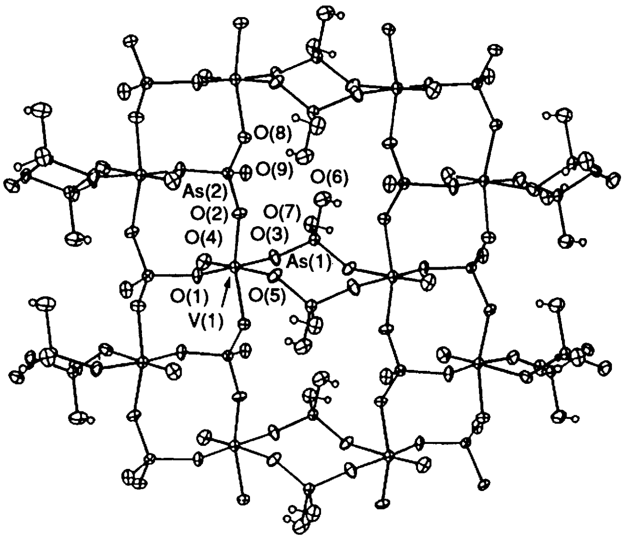

Fig. 2 Section of a layer in the $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$ structure. Thermal ellipsoids for non-hydrogen atoms are shown at the 60% probability level; small open circles are H atoms

Results and Discussion

Structure.—Final positional parameters are listed in Table 1. Selected bond distances and bond-valence sums[11] are given in Table 2. The bond-valence sums are in good accord with the formal oxidation states. All atoms have point symmetry 1.

A view of the crystal structure in a projection parallel to the *b* axis is given in Fig. 1. The structure consists of layers of VO_6 octahedra, AsO_4 tetrahedra, and H_2AsO_4 groups lying in the (101) plane with the Ba atoms and water molecules between the layers. Connection between adjacent layers is provided by O–Ba–O and hydrogen bonding through water molecules and $H_2AsO_4^-$ groups. The hydrogen atoms of a water molecule are hydrogen bonded to two AsO_4^{3-} tetrahedra in adjacent layers. The later molecules are also co-ordinated to the Ba atoms. Thus, in the TG analysis the release of the lattice water molecule, which occurs at rather high temperature, is not resolved from the step corresponding to the dehydration of $H_2AsO_4^-$ (see below). Atom O(8) of a AsO_4^{3-} tetrahedron acts as a hydrogen-bond acceptor to H(6) of a $H_2AsO_4^-$ group in the same layer. The fourth hydrogen bond is between O(9) of AsO_4^{3-} and H(7) of $H_2AsO_4^-$ in adjacent layers. The oxygen-to-oxygen distances in the hydrogen bonds are in the range 2.58–2.75 Å. Within a layer each VO_6 octahedron shares corners with three AsO_4^{3-} tetrahedra and two $H_2AsO_4^-$ groups with the vanadyl oxygen, O(4), being unshared (Fig. 2). Each AsO_4^{3-} tetrahedron has one oxygen atom, O(9), which is not co-ordinated to the V atom and therefore does not form part of the layer connectivity. Each $H_2AsO_4^-$ group shares two corners with two vanadium octahedra, and the two hydroxyl groups are involved in the hydrogen bonding scheme only and do not link to any V atom. The connectivity formula for a layer can be represented as ${}^{2}_{\infty}[(VOO_{2/2}O_{3/2})(AsOO_{3/2})\{As(OH)_2O_{2/2}\}]^{2-}$.

The VO_6 octahedron is distorted as a result of the displacement of the V atom towards one of the apical oxygen

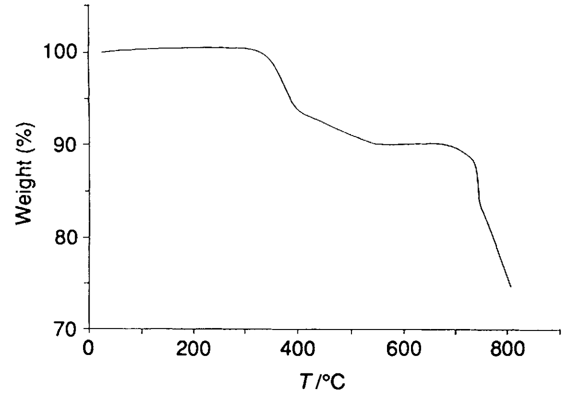

Fig. 3 Thermogravimetric analysis of $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$ in flowing N_2 at 5 °C min^{-1}

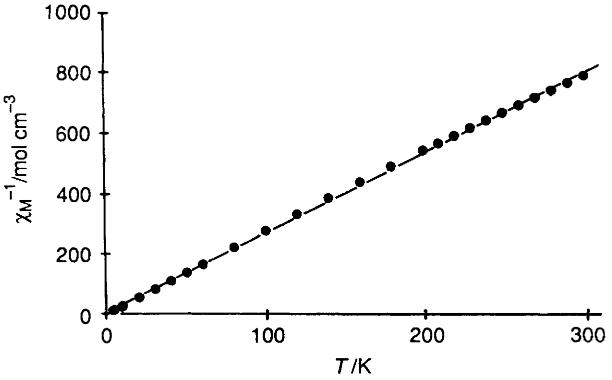

Fig. 4 Plot of $1/\chi_M$ (●) as a function of temperature. The solid line represents a least-squares fit to the data from 4 to 300 K according to $\chi = C/(T - \theta)$

atoms. This kind of deformation is characteristic of most vanadyl(IV) compounds. The As(1) atom is tetrahedrally co-ordinated to four O atoms, two of which belong to the hydroxyl groups. As usual in protonated anion groups, the As–OH bond lengths (≈ 1.72 Å) are considerably longer than the two others (≈ 1.65 Å). The $As(2)O_4^{3-}$ tetrahedron is more regular and the As(2)–O bond lengths are within the range 1.671–1.699 Å. The shortest As(2)–O bond involves the oxygen atom, O(9), which is not co-ordinated to the V atom. The co-ordination number of Ba is assigned on the basis of two criteria: the maximum gap in the Ba–O distances and the bond valence sums for Ba. Therefore, the Ba atom is co-ordinated by 11 oxygen atoms with an average Ba–O distance of 2.964 Å.

Thermal Analysis.—The TG curve for $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$ (Fig. 3) is divided into three stages. The first stage, which occurs from 300 to ≈ 410 °C, is attributed to the loss of lattice water and dehydration of $H_2AsO_4^-$ to meta-arsenate AsO_3^-. The second stage occurs between temperatures of ≈ 410 and 550 °C which may be due to the release of $\frac{1}{2}$ O_2 to give As^{III}. The observed total weight loss (10.0%) of the first two stages can be compared with the calculated value of 10.35% based on the above interpretation. Furthermore, there is a third sharp fall in weight beyond 680 °C which suggests vaporization of As_2O_3 from the decomposition products.

Magnetic Susceptibility.—A plot of the reciprocal molar susceptibility for polycrystalline $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$ *vs.* temperature is linear down to 4 K as shown in Fig. 4. The data were fitted in the temperature range 4–300 K using the Curie–Weiss formula $\chi_M = C/(T - \theta)$ with $C = 0.377$ cm^3 K mol^{-1} and $\theta = -2.3$ K. From the relation $C = N\mu_{eff}^2/3k_B$, one obtains the effective magnetic moment $\mu_{eff} = 1.74$ per vanadium, which is in agreement with the spin-only value for a d^1 ion of 1.73 μ_B.

In conclusion, a new vanadyl(IV) arsenate $BaVO(AsO_4)(H_2AsO_4)\cdot H_2O$ was synthesised hydrothermally under mild conditions using a Teflon-lined autoclave, and structurally characterized by single-crystal X-ray diffraction. Both TG analysis and magnetic susceptibility data confirm the formula. The compound crystallizes in a new structure type. Preliminary experiments indicate that reactions similar to that discussed here with metal cations in place of Ba^{2+} yield many novel structures.

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