Hydrothermal Synthesis and Structural Characterization of the Molybdenum(VI) Arsenate $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2\cdot H_2O$†

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A new molybdenum(VI) arsenate, $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2\cdot H_2O$, has been synthesised hydrothermally at 230 °C and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.708(1)$, $b = 12.262(3)$, $c = 12.281(4)$ Å, $\alpha = 115.98(2)$, $\beta = 103.36(2)$, $\gamma = 98.71(2)^\circ$, $Z = 2$ and $R = 0.0293$. The structure is composed of pyridinium cations, water molecules and $[(Mo_4O_{10})(HAsO_4)_4]^{4-}$ cluster anions. The anions, which lack Mo–Mo bonds, are linked by strong hydrogen bonds to form layers parallel to the *ac* plane with pyridinium cations between the layers. Water molecules are within the layers and are linked to both the cluster anions and pyridinium cations through hydrogen bonding.

A large number of new compounds have been synthesised by high-temperature solid-state reactions and structurally characterized in the A–Mo–P–O system where A is an alkali or alkaline-earth metal and Mo is in oxidation states below VI. A variety of novel mixed frameworks are formed by MoO_6 octahedra and PO_4 tetrahedra.[1,2] By incorporating either organic or hydrated inorganic cations in the hydrothermal synthesis, novel frameworks with large open cavities have been produced.[3]

In contrast to the rich structural chemistry of molybdenum phosphates, little is known about their arsenate analogues. To our knowledge, other than those arsenic(III)- or arsenic(V)-containing heteropolymolybdates with the Keggin-related structures, $MoAs_2O_7$[4] and $Na_4[Mo_4As_6O_{20}(OH)_2]\cdot 9H_2O$[5] are the only examples of structurally well characterized molybdenum arsenates. The former, which is an As^{III}–As^{V} mixed-valence compound, contains dimers of edge-sharing $Mo^{VI}O_6$ octahedra. The latter is an arsenic-rich Mo^{V}–As^{III} polyanion, the structure of which consists of a tetranuclear Mo_4O_{16} core with two Mo–Mo bonds. As a part of our research program to study the structural chemistry of transition-metal arsenates,[6–9] we began to synthesise new compounds in the A–Mo–As^{V}–O system using hydrothermal techniques. In this paper we present the hydrothermal synthesis, single-crystal structure, and thermal analysis of the first Mo^{VI}–As^{V} compound $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2\cdot H_2O$.

Experimental

Synthesis.—Reagent-grade chemicals were used as received. A colourless crystalline product was prepared by hydrothermal reaction of MoO_3 (0.3599 g), C_5H_5N (1.6 cm^3), H_3AsO_4 (2.5 cm^3, 80%) and water (7.5 cm^3) in a Teflon-lined autoclave (23 cm^3) at 230 °C and autogenous pressure for 4 d followed by slow cooling at 5 °C h^{-1} to room temperature. The product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. It contained colourless tabular crystals of $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2\cdot H_2O$ in 80% yield based on MoO_3 used. A powder X-ray diffraction pattern of the product compared very well with that calculated from the single-crystal data.

X-Ray Structure Analysis.—*Crystal data.* $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2\cdot H_2O$, $M = 730.0$, triclinic, space group $P\bar{1}$, $a = 7.708(1)$, $b = 12.262(3)$, $c = 12.281(4)$ Å, $\alpha = 115.98(2)$, $\beta = 103.36(2)$, $\gamma = 98.71(2)^\circ$, $U = 971.9(5)$ Å^3, $Z = 2$, $D_c = 2.494$ g cm^{-3}, $F(000) = 704$.

A crystal of dimensions 0.175 × 0.100 × 0.04 mm was selected for indexing and intensity data collection at room temperature (296 K) on a Nicolet R3m/V diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). Unit-cell parameters and the orientation matrix were determined by a least-squares fit of 17 peak maxima with 2θ ranging from 11 to 30°. Of the 3584 reflections collected ($2.5 \leqslant 2\theta \leqslant 55.0^\circ$, $+h \pm k \pm l$, scan mode 2θ–θ), 2886 unique reflections were considered observed [$I > 3.0\sigma(I)$] after Lorentz polarization and empirical absorption corrections. Correction for absorption effects was based on ψ-scans of a few suitable reflections with χ values close to 90° using the program XEMP of the SHELXTL-Plus program package;[10] T_{min} and $T_{max} = 0.715$ and 0.984.

On the basis of intensity statistics, successful structure solution and refinement, the space group was determined to be $P\bar{1}$. Direct methods were used to locate Mo and As atoms with the remaining non-hydrogen atoms being found from successive difference maps. On the basis of bond-length bond-strength calculations,[11] the Mo and As atoms are hexa- and penta-valent, respectively. Three of the oxygen atoms, O(4), O(6) and O(14), were found to be considerably undersaturated; O(4) and O(6) are arsenate oxygens, O(14) appears as a water oxygen. Further support of the calculation results is gained from the colour of the crystals, a phenomenon indicative of an oxidation state of VI for molybdenum in the crystal. In order to balance the charge, six more hydrogen atoms besides those in the pyridine molecules should be included in the formula. Therefore, each formula unit should contain two $HAsO_4^{2-}$ groups, one water molecule and two pyridinium cations ($C_5H_5NH^+$). All of the hydrogen atoms except that on C(8) were located on difference maps at the final stage of refinements. Atom H(8C) was calculated based on a riding model. 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 (0.8 e Å^{-3}) on the final Fourier difference map is at a distance of 0.76 Å from As(2). The weighting scheme of the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

form $w = 1/[\sigma^2(F_o) + 0.001\,02F_o^2]$, with $\sigma(F^2)$ from counting statistics gave satisfactory agreement analyses. Final $R(F_o)$ and $R'(F_o)$ values were 0.0293 and 0.0318 $[R' = (\Sigma w^{\frac{1}{2}}||F_o| - |F_c||)/\Sigma w^{\frac{1}{2}}|F_o|]$. Calculations were performed on a DEC VAX 4000/90 computer system using SHELXTL-Plus programs. Neutral-atom scattering factors and corrections for anomalous dispersion were from ref. 12.

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 (TGA), using a Seiko SSC-5000 thermogravimetric analyser, was performed on a powder sample of $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$ in flowing N_2 with a heating rate of 5 °C min^{-1}. The TGA curve showed three steps of weight loss at ≈187, ≈415 and ≈774 °C. In order to characterize the decomposition product a sample of $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$ was heated at 650 °C under $N_2(g)$ for 1 d. The X-ray powder pattern of the product indicated that it was MoO_3.

Results and Discussion

Structure.—Final positional parameters are listed in Table 1. Selected bond distances and bond-valence sums are given in Table 2. The bond-valence sums for Mo and As are in good accord with their formal oxidation states. All atoms are at general positions. The molybdenum and arsenic atoms are six- and four-co-ordinated, respectively.

A perspective view of the structure in a direction parallel to the *a* axis is given in Fig. 1. The structure consists of $[(Mo_4O_{10})(HAsO_4)_4]^{4-}$ anions, pyridinium cations, and water molecules. The anion $[(Mo_4O_{10})(HAsO_4)_4]^{4-}$, depicted in Fig. 2, resides on an inversion centre and is a cluster of two edge-sharing octahedral dimers of Mo_2O_{10} connected by four $HAsO_4^{2-}$ groups. The four Mo and two As(2) atoms are nearly coplanar (maximum deviation 0.01 Å) and are bridged by six O atoms into a ring which forms a least-squares plane (mean deviation 0.35 Å, maximum deviation 0.72 Å) approximately parallel to (100). The Mo–Mo distance within an edge-sharing dimer is 3.321 Å. Each of the MoO_6 octahedra in the Mo_2O_{10} unit has two very short molybdenum to oxygen bonds which define the molybdenyl groups Mo=O and commonly occur in molybdenum(VI) compounds. The average Mo=O bond length in $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$ is 1.698(5) Å, which is slightly longer than that observed in $MoAs_2O_7$ (1.678 Å). As shown by the O ••• O distances 2.53–3.00 Å for $Mo(1)O_6$ and 2.53–2.90 Å for $Mo(2)O_6$, and the O–Mo–O bond angles 72.0–103.8° for $Mo(1)O_6$ and 73.8–104.2° for $Mo(2)O_6$, both

Table 1 Atomic coordinates for $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$

Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	0.032 31(6)	0.247 40(4)	0.482 93(4)
Mo(2)	0.019 01(6)	0.233 64(4)	0.745 09(4)
As(1)	0.246 16(6)	0.020 72(4)	0.554 50(4)
As(2)	−0.010 75(7)	−0.014 47(5)	0.809 03(5)
O(1)	0.120 5(4)	0.125 8(3)	0.579 6(3)
O(2)	0.231 0(5)	−0.060 3(3)	0.399 7(3)
O(3)	0.203 5(5)	−0.076 2(3)	0.614 3(3)
O(4)	0.468 1(5)	0.119 2(4)	0.644 9(4)
O(5)	−0.121 6(5)	−0.138 3(3)	0.658 4(3)
O(6)	−0.186 1(6)	0.017 1(4)	0.870 6(4)
O(7)	0.145 0(6)	−0.047 5(4)	0.897 8(4)
O(8)	0.092 2(5)	0.116 3(3)	0.806 7(3)
O(9)	−0.115 2(6)	0.290 2(4)	0.835 7(4)
O(10)	0.234 9(5)	0.340 4(4)	0.833 8(4)
O(11)	−0.085 1(6)	0.316 0(4)	0.410 4(4)
O(12)	0.251 2(5)	0.350 4(4)	0.561 9(4)
O(13)	−0.056 1(5)	0.289 7(3)	0.623 8(3)
O(14)	0.515 8(6)	0.220 2(4)	0.407 1(4)
N(1)	0.662 3(7)	0.428 0(5)	0.644 9(5)
N(2)	0.707 1(10)	0.389 8(7)	0.164 2(8)
C(1)	0.634 6(9)	0.431 5(6)	0.749 1(7)
C(2)	0.719 6(12)	0.539 1(7)	0.865 5(7)
C(3)	0.833 3(11)	0.641 0(6)	0.872 9(6)
C(4)	0.860 4(10)	0.634 3(6)	0.764 7(7)
C(5)	0.771 5(10)	0.525 1(7)	0.648 6(7)
C(6)	0.684 9(14)	0.344 3(9)	0.041 0(10)
C(7)	0.571 5(16)	0.225 8(10)	−0.046 5(8)
C(8)	0.481 0(12)	0.159 7(8)	0.000 4(13)
C(9)	0.508 6(13)	0.201 4(14)	0.119 3(17)
C(10)	0.619 3(11)	0.319 6(11)	0.205 5(9)

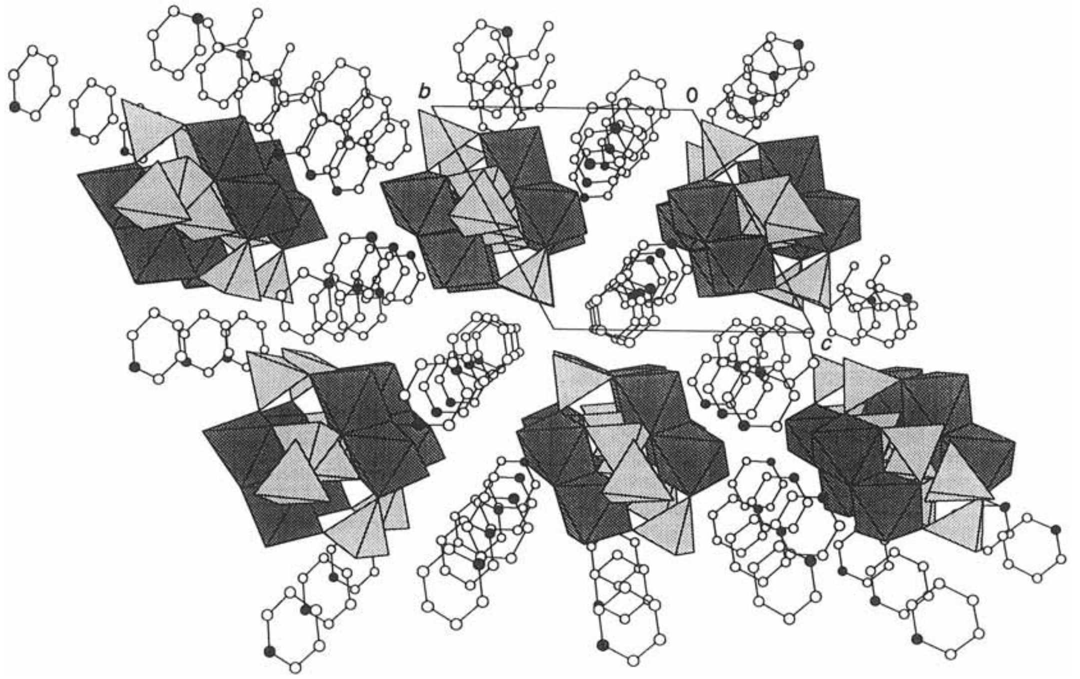

Fig. 1 View of the $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$ structure along the [100] direction. In this representation the corners of octahedra and tetrahedra are O^{2-} ions; the molybdenum and arsenic ions are at the centre of each octahedron and tetrahedron, respectively. Filled and open circles are N and C atoms, respectively. Water molecules, which are located between cluster anions along the viewed direction, are not shown and H atoms are omitted for clarity

octahedra are strongly distorted. The shortest O ··· O distance involves the two O atoms forming the common edge between the MoO_6 octahedra in the Mo_2O_{10} unit. The octahedral distortion can be estimated by using the equation $\Delta = (1/6)\Sigma[(R_i - \bar{R})/\bar{R}]^2$, where R_i = individual bond length and $\bar{R}$ = average bond length.[14] The calculation results show that $Mo(1)O_6$ is more distorted than $Mo(2)O_6$ ($10^4\Delta = 36.2$ *vs.* 26.8) in $[(Mo_4O_{10})(HAsO_4)_4]^{4-}$. Both are considerably more distorted than that in $MoAs_2O_7$ ($10^4\Delta = 18.0$). The greater distortion may be due to a variety of polyhedral connections.

Table 2 Selected bond distances (Å) and bond valence sums (Σ*s*) for $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$*

Mo(1)–O(1)	2.363(4)	Mo(1)–O(3a)	2.186(3)
Mo(1)–O(11)	1.684(6)	Mo(1)–O(5a)	2.018(4)
Mo(1)–O(12)	1.706(3)	Mo(1)–O(13)	1.895(4)
Σ*s*[Mo(1)–O] = 6.08			
Mo(2)–O(1)	2.277(4)	Mo(2)–O(2a)	2.293(3)
Mo(2)–O(8)	1.991(5)	Mo(2)–O(9)	1.692(5)
Mo(2)–O(10)	1.709(3)	Mo(2)–O(13)	1.910(5)
Σ*s*[Mo(2)–O] = 6.01			
As(1)–O(1)	1.691(4)	As(1)–O(2)	1.680(4)
As(1)–O(3)	1.679(5)	As(1)–O(4)	1.714(3)
Σ*s*[As(1)–O] = 4.92			
As(2)–O(5)	1.695(3)	As(2)–O(6)	1.709(5)
As(2)–O(7)	1.650(5)	As(2)–O(8)	1.693(5)
Σ*s*[As(2)–O] = 4.98			
O(4)–H(4)	0.821(4)	O(14)–H(14A)	0.821(5)
O(6)–H(6)	1.172(6)	O(14)–H(14B)	0.865(4)
N(1)–H(1N)	0.846(4)	N(2)–H(2N)	1.174(6)
H(4) ··· O(2b)	1.820	H(14A) ··· O(3b)	2.212
H(6) ··· O(7c)	1.507	H(14B) ··· O(5a)	2.035
H(1N) ··· O(14)	1.897		

* Symmetry codes: (a) −*x*, −*y*, 1 − *z*; (b) 1 − *x*, −*y*, 1 − *z*; (c) −*x*, −*y*, 2 − *z*.

Each $HAs(1)O_4{}^{2-}$ tetrahedron is connected to four MoO_6 octahedra through three O atoms. Atoms O(2) and O(3) of a $HAs(1)O_4{}^{2-}$ group bridge over two Mo atoms within a Mo_2O_{10} unit. The third corner of the $HAs(1)O_4{}^{2-}$ group, O(1), is bonded to two Mo atoms of the other Mo_2O_{10} unit.

As shown in Fig. 3, connection among cluster anions is provided primarily by hydrogen bonding through $HAsO_4{}^{2-}$ groups. Atom O(2) of $HAs(1)O_4$ and O(7) of $HAs(2)O_4$ act respectively as hydrogen-bond acceptors of $HAs(1)O_4{}^{2-}$ and $HAs(2)O_4{}^{2-}$ groups belonging to adjacent cluster anions. The short O(2) ··· O(4) and O(6) ··· O(7) distances (2.636, 2.635 Å) represent strong hydrogen bonding. Atom O(7) is a stronger hydrogen-bond acceptor as indicated by less saturation in its valence [Σ*s* = 1.37 for O(7) *vs.* 1.62 for O(2)] and shorter O ··· H distance (1.507 *vs.* 1.820 Å). Therefore, each cluster anion is connected to four others to form layers parallel to the *ac* plane. Water molecules are within the layers and are hydrogen-bonded to both the cluster anions and pyridinium cations. The

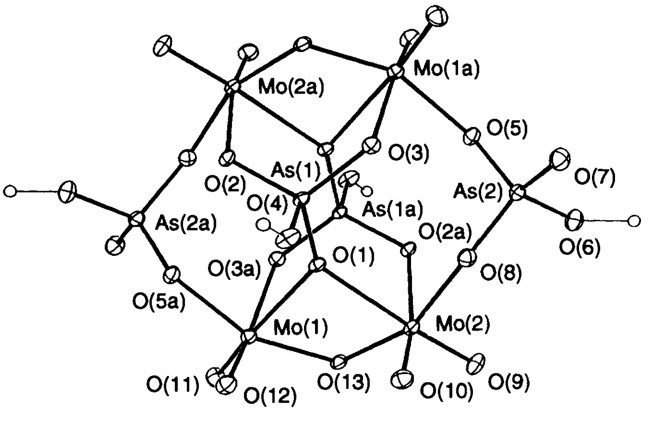

Fig. 2 An ORTEP[13] drawing of the cluster anion $[(Mo_4O_{10})(HAsO_4)_4]^{4-}$ in a direction approximately parallel to [100]. Small open circles are H atoms

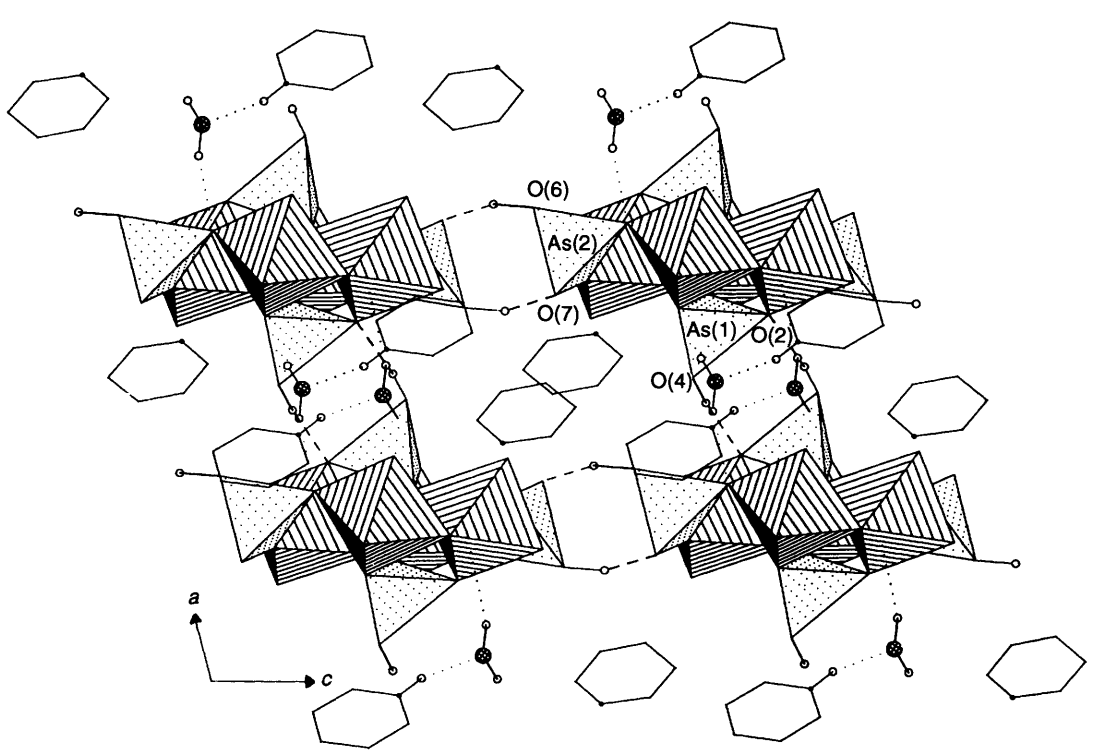

Fig. 3 View of the $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$ structure along [010]. Cross-hatched circles and open circles are water oxygen and H atoms, respectively. The hydrogen bonds between cluster anions are shown as dashed lines, other hydrogen bonds as dotted lines. Hydrogen atoms which are not involved in hydrogen bonding are omitted for clarity

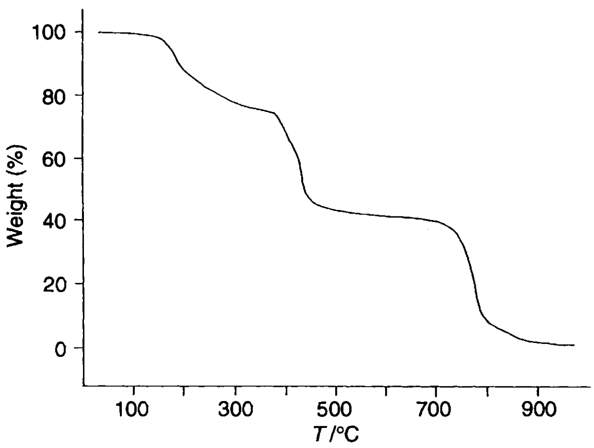

Fig. 4 Thermogravimetric analysis of $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$

hydrogen bonds between water and the cations are stronger than that between water and cluster anions (1.90 *vs.* 2.12 and 2.04 Å). The cations are located between the layers. Two pyridinium cations are involved in the hydrogen bonding with water and the other two are located in the tunnel which is surrounded by four hydrogen-bonded cluster anions.

Thermal Analysis.—The TGA curve of $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2{\cdot}H_2O$ (Fig. 4) is divided into three stages. The first, which occurs from ≈150 to ≈380 °C, is attributed to the loss of two pyridine molecules and a water of hydration. The observed weight loss (23.9%) is in good agreement with the calculated value (24.1%). The second stage is between ≈380 and ≈520 °C and could be due to the release of O_2, As_2O_3, and two water molecules according to the reaction $H_2(Mo_2O_5)(HAsO_4)_2 \longrightarrow As_2O_3(\uparrow) + O_2(\uparrow) + 2H_2O(\uparrow) + 2MoO_3$. The observed total weight loss in this stage (36.1%) compares well with the calculated value of 36.4%. The third stage occurs above 720 °C and is due to the sublimation of MoO_3.

In summary, a new Mo^{VI}–As^{V} compound has been synthesised hydrothermally using a Teflon-lined autoclave, and characterized by single-crystal X-ray diffraction and TG analysis. Recently, many new compounds in the A–V–As–O and A–Fe–As–O systems have been synthesised under similar hydrothermal conditions. Most have different structures from their phosphate analogues. Combining this fact and the rich structural chemistry observed in the phosphate systems, the synthesis of many more transition-metal arsenates with novel structures will be forthcoming.

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