

## [As<sub>4</sub>Mo<sub>6</sub>V<sub>7</sub>O<sub>39</sub>(SO<sub>4</sub>)<sup>4-</sup>: A Species with an Unusual Structure and a Model for the Different Host–Guest Properties of Poly-vanadates and -molybdates

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The synthesis and unusual structure of the novel heteropolyoxometalate (NMe<sub>4</sub>)<sub>4</sub>[As<sub>4</sub>Mo<sub>6</sub>V<sub>7</sub>O<sub>39</sub>(SO<sub>4</sub>)<sup>4-</sup>] $\cdot$ H<sub>2</sub>O **1**, which can be utilized as a model compound for the study and comparison of the different host–guest properties or carcerand functions of poly-vanadates and -molybdates, is reported.

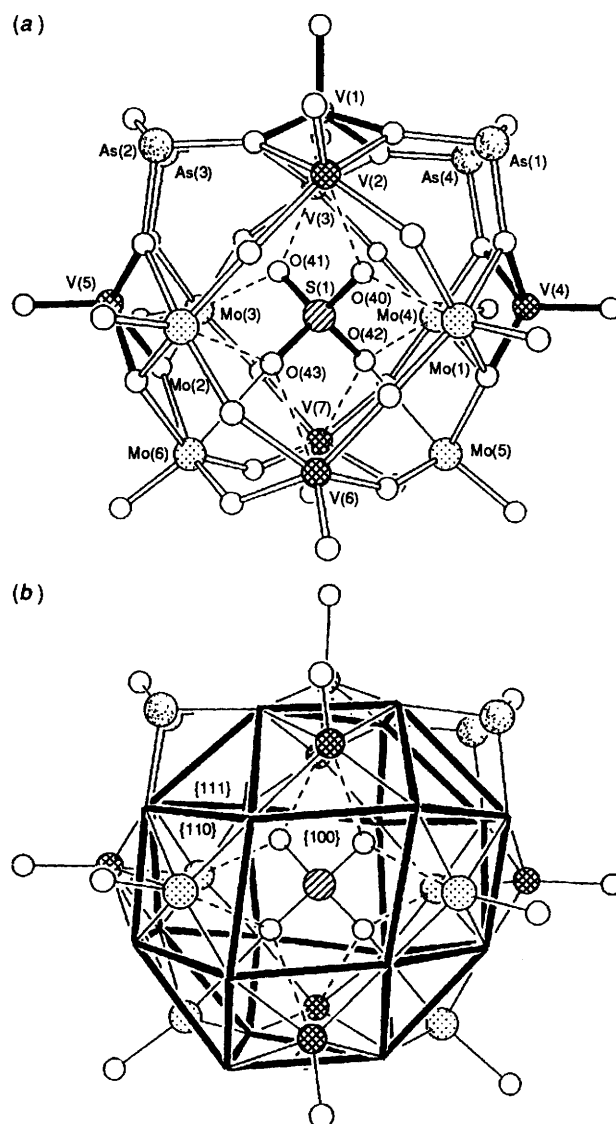
Polyoxometalates of vanadium, molybdenum and tungsten have attracted increasing attention on account of their remarkable structural and electronic properties<sup>1–3</sup> and in particular by reason of their host–guest interactions<sup>3–5</sup> or carcerand functions.<sup>3,6,7</sup> In our efforts to synthesize reduced heteropolyoxometalates with unusual host–guest properties<sup>7,8</sup> we have now succeeded in isolating the unusual cluster compound (NMe<sub>4</sub>)<sub>4</sub>[As<sub>4</sub>Mo<sub>6</sub>V<sub>7</sub>O<sub>39</sub>(SO<sub>4</sub>)<sup>4-</sup>] $\cdot$ H<sub>2</sub>O **1**, which allows a simultaneous examination of the divergent host–guest properties of vanadium(IV) and molybdenum(VI) centres with the same central anionic template in one single cluster species.

Compound **1** was obtained as deep blue–violet crystals by the reaction of a solution of 1.06 g (0.86 mmol) of (NH<sub>4</sub>)<sub>6</sub>[Mo<sub>7</sub>O<sub>24</sub>] $\cdot$ 4 H<sub>2</sub>O, 0.7 g (6.0 mmol) of NH<sub>4</sub>VO<sub>3</sub>, 1.50 g (7.6 mmol) of As<sub>2</sub>O<sub>3</sub>, 5.0 g (65.7 mmol) of NH<sub>4</sub>SCN and 10.0 g (91.2 mmol) of Me<sub>4</sub>NCl in 250 ml of water and 50 ml of dimethylformamide (DMF) in the presence of hydrazinium sulfate (0.82 g) and 10% H<sub>2</sub>SO<sub>4</sub> (1.4 ml) at 85 °C (pH = 2.8) for 16 hours (yield: 87.7%, based on V) and characterized by single-crystal X-ray structure analysis,<sup>†</sup> elemental analysis, X-ray powder diffractometry, manganometric titration of the number of V<sup>IV</sup> centres, thermogravimetry (for determination of water of crystallization), UV–VIS, near-IR and vibrational spectroscopy<sup>‡</sup> and atom absorption spectroscopy (As, Mo, V).

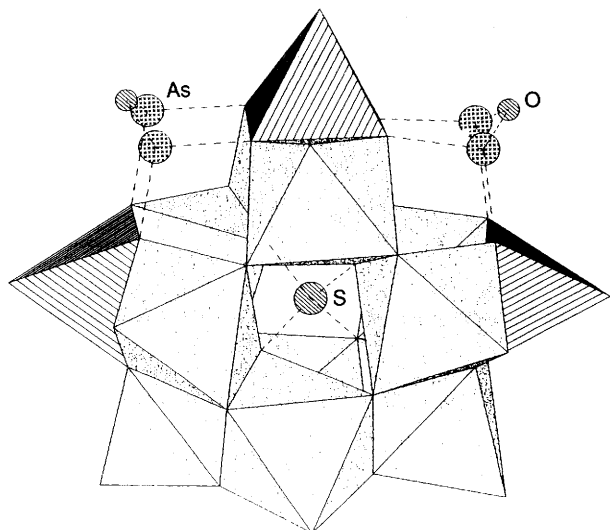
The metal cluster anion [As<sup>III</sup><sub>4</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>7</sub>O<sub>39</sub>(SO<sub>4</sub>)<sup>4-</sup> **1a** may be described as an inclusion species with a shell in which an SO<sub>4</sub><sup>2-</sup> ion is incorporated. This shell can be formally derived from the rhombicuboctahedron spanned by the 24 innershell oxygen atoms (Fig. 1; for the significance of that solid for oxometalate chemistry see ref. 1) in a simple geometrical description by capping its square planes with appropriate fragments. The structure of the anion **1a** (Fig. 1) is obtained by capping all its twelve {110} O<sub>4</sub> squares with four V=O<sup>2+</sup>, six Mo=O<sup>4+</sup> and two As<sub>2</sub>O<sup>4+</sup> units (see also refs. 8–11) and three {100} square surfaces with three V=O<sup>2+</sup> groups (according to Fig. 1). This representation leads to the following description: the cluster anion **1a** exhibits as a fundamental structural element a pseudo- $\alpha$ -Keggin-type structure, which is created by the positioning of suitable fragments on the {110} O<sub>4</sub> squares leading to the [Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>4</sub>(As<sup>III</sup><sub>2</sub>O)<sub>2</sub>O<sub>34</sub>(SO<sub>4</sub>)<sup>10-</sup> **1b** species and finally capped by three VO<sup>2+</sup> units in the above manner. It is also fascinating to see how all the different polyhedra of molybdenum, vanadium, arsenic and sulfur atom centres join together like directed building blocks<sup>12</sup> to form a distinct and well-defined arrangement, hereby formally constructing the cryptate **1a** with the novel host [As<sup>III</sup><sub>4</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>7</sub>O<sub>39</sub>]<sup>2-</sup> **1c** which is obviously able to include a sulfate ion as a guest.

The results of the X-ray structure analysis show that the distances of the oxygen atoms of this central SO<sub>4</sub><sup>2-</sup> group to the nearest vanadium [V(2), V(3), V(6) and V(7)] and four molybdenum centres [Mo(1)–(4)] are in the range 2.56–2.67 Å. The distances of two oxygen atoms of the sulfate group [O(42) and O(43)] to the nearest molybdenum atoms [Mo(5) and Mo(6)] are 2.38 and 2.44 Å (Fig. 1). The structural data are consistent with all the molybdenum and the vanadium atoms just mentioned being octahedrally coordinated (Fig. 2). The other three V<sup>IV</sup> [V(1), V(4) and V(5)] polyhedra are unequivocally square pyramids with V $\cdots$ O(SO<sub>3</sub>) distances

between 3.25 and 3.34 Å (Fig. 2). This shows the remarkable ability of V<sup>IV</sup> centres to create octahedral or square-pyramidal coordination geometries at the same time, a kind of hybrid behaviour Mo<sup>VI</sup> atoms are apparently not capable of. Cluster



**Fig. 1** (a) Structure of the cluster anion **1a**. (b) Rhombicuboctahedron, of which the O<sub>4</sub> squares are capped by 7 V=O<sup>2+</sup>, 6 Mo=O<sup>4+</sup> and 2 As<sub>2</sub>O<sup>4+</sup> groups as described in the text [V atoms crosshatched, Mo atoms regularly and As atoms randomly dotted, the S atom marked with diagonal lines; the two shortest metal–O(SO<sub>3</sub>) distances are shown with unbroken lines]. Selected (and partly averaged) distances (Å): As–μ<sub>3</sub>–O 1.79, As–μ<sub>2</sub>–O 1.78, Mo(5) $\cdots$ Mo(1), Mo(4) 3.75, Mo(5) $\cdots$ V(6), V(7) 3.53, V(4) $\cdots$ Mo(1), Mo(4), Mo(5) 3.16, V(4) $\cdots$ As(1), As(4) 3.48, V(1) $\cdots$ V(2), V(3) 3.09, S(1)–O(40), O(41) 1.45, S(1)–O(42), O(43) 1.48, O(40)–Mo(1) 2.56, O(40)–V(2) 2.67, O(41)–Mo(3) 2.58, O(41)–V(3) 2.66, O(42)–Mo(4) 2.67, O(42)–Mo(5) 2.38, O(42)–V(7) 2.61, O(43)–Mo(2) 2.58, O(43)–Mo(6) 2.44, O(43)–V(6) 2.58, O(40) $\cdots$ V(1), V(4) 3.29, O(41) $\cdots$ V(1), V(5) 3.30, O(42) $\cdots$ V(4) 3.29, O(43) $\cdots$ V(5) 3.33.



**Fig. 2** Polyhedral representation of the cluster anion **1a** indicating its model character for the different host-guest or carcerand properties of poly-vanadates and -molybdates and demonstrating the hybrid behaviour of the  $V^{IV}$  centres (see text). The six  $OMoO_5$  and four  $OVO_5$  octahedra are shown by a randomly dotted and the three  $OVO_4$  square pyramids by a hatched pattern.

anion **1a** unifies these two coordination types in one single cluster species for the first time (Fig. 2).

The different host-guest or carcerand properties of polyvanadates and -molybdates are a result of the different interactions between the central species, possibly an oxoanion, and the adjacent  $V^{IV}$  and  $Mo^{VI}$  centres. With vanadium atoms appearing in the same cluster along with molybdenum centres and a rather highly charged anion like  $AsO_4^{3-}$  being the central unit of such a heteropolyoxometalate,  $V^{IV}O_6$  octahedra are exclusively formed as well as  $Mo^{VI}O_6$  ones {e.g. the  $\alpha$ -Keggin derivative  $[As_2Mo_8V_4(AsO_4)]^{5-}$  **2a** with  $d[V-O(AsO_3)] = d[Mo-O(AsO_3)] = 2.30-2.38 \text{ \AA}$ }.<sup>13</sup> If the central anion is exchanged for  $SO_4^{2-}$  the weaker attractive interaction forces between the electrophilic  $V^{IV}$  centres and the nucleophilic oxygen atoms of the central template (compared to **2a**) favour the formation of **1a**, because the attractive interactions ( $V^{IV} \cdots \text{anion}$ ) weaken with the decreasing negative charge of the enclosed oxoanion. In comparison with  $V^{IV}$ , the  $Mo^{VI}$  centres are still more electrophilic as a result of the availability of empty d orbitals and, therefore, they show a stronger interaction with the oxygen atoms of the central sulfate ion of **1a**. It is for this reason that the  $Mo^{VI}$  centres reduce the electron density at the oxygen atoms of the interior sulfate ion which are not attached to them so that these oxygen atoms [O(40) and O(41)] exhibit a noticeable tendency to form weaker interactions with the  $V^{IV}$  centres than in case of  $Mo^{VI}$  with O(42) and O(43). This is the main structural feature of **1a**: for the first time (as far as we know) vanadium and molybdenum atoms enter into competition with one another in the presence of a sulfate ion as central unit. As a result of this 'contest' the Mo centres are obviously able to interact stronger with the oxygens of the sulfate ion than the V ones. This accords with the observation that the central sulfate ion of **1a** seems to be shifted to the 'lower' sphere of the cavity as is apparent from the fact that Mo [Mo(5) and Mo(6)] and none of the V atoms take part in the formation of the two shortest metal-O( $SO_3$ ) distances (see above and Fig. 1.).

These facts explain why the cluster anion **1a** has an unusually low symmetry ( $C_2$ ) for a rather simple polyoxometalate. The  $T_d$  symmetry of the free sulfate ion is lowered to local  $C_{2v}$  symmetry in conformity with the different host-guest properties of the Mo and V centres. This can also be seen from the IR spectrum which shows a splitting of the bands due to the  $\nu_3$  ( $F_2$ ) and  $\nu_4$  ( $F_2$ ) fundamentals in the free ion.

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### Footnotes

† Crystal data for **1**:  $C_{16}H_{50}As_4Mo_6N_4O_{44}SV_7$ ,  $M = 2266.5$ , monoclinic, space group  $P2_1/n$ ,  $a = 13.693(4)$ ,  $b = 28.306(8)$ ,  $c = 15.747(3)$  Å,  $\beta = 92.51(2)^\circ$ ,  $U = 6098(3)$  Å<sup>3</sup>,  $\mu = 4.429 \text{ mm}^{-1}$ ,  $Z = 4$ ,  $T = 294 \text{ K}$ ,  $R = 0.079$  {6293 unique reflections [ $F_o > 4.0\sigma(F_o)$ ];  $5^\circ < 2\theta < 50^\circ$ }. Data (Mo-K $\alpha$  radiation, graphite monochromator) were collected using a Siemens R3m/V diffractometer. The structure was solved by direct methods. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Characteristic IR data for **1**,  $\nu/\text{cm}^{-1}$  (KBr, 1200–500  $\text{cm}^{-1}$ ):  $\nu_3(SO_4)$  1199m, 1143m, 1083m; 1006sh;  $\nu(V=O)$  982s;  $\nu(Mo=O)$  949m;  $\nu_{as}(M-O-M')$ ;  $M, M' = Mo, V, As$  829m, 801m, 761m, 727w, 689w;  $\nu_4(SO_4)$  662m, 597m, 554w. *VIS-near IR data* (KBr,  $10^{-3} \text{ v/cm}^{-1}$ ) for **1**: 11.5, 12.8 (intervalence charge transfer). Results of the bond valence sum calculations<sup>14</sup> (average values) for **1**:  $Mo^{VI}$  5.9,  $V^{IV}$  4.3,  $As^{III}$  3.0,  $S^{VI}$  6.1. These values are consistent with the assumption that **1a** is composed of six  $Mo^{VI}$  and seven  $V^{IV}$  centres. The small deviations are probably mainly caused by electron delocalization between the vanadium and molybdenum centres. This might be related to the energy of a presumably intervalence charge transfer ( $V^{IV} \rightarrow Mo^{VI}$ ) at the wavenumbers listed above.

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