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THE CRYSTAL STRUCTURE OF AMMONIUM DODECAMOLYBDOTETRAARSENATE(V) TETRAHYDRATE, $(NH_4)_4 H_4As_4Mo_{12}O_{50} \cdot 4H_2O$

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$(NH_4)_4H_4As_4Mo_{12}O_{50} \cdot 4H_2O$ is tetragonal: space group $P4_2/nnm$, Z = 2, a = 11.923 (3), c = 17.564 (2) Å. The crystal contains a discrete polyanion, $H_4As_4Mo_{12}O_{50}{}^{4-}$ of a Td point symmetry, consisting of four trigonal Mo_3O_{13} groups. They are bound each other at six oxygen atoms, four AsO_4 tetrahedra are attached from outside of the $Mo_{12}O_{46}$ cage. There is an empty cavity of the radius of 1.43 Å at the center of the polyanion.

The crystal structure of ammonium dodecamolybdotetraarsenate(V) tetrahydrate has been determined and it has been shown that the compound which was once formulated as $(NH_4)_2O \cdot As_2O_5 \cdot 6MoO_3 \cdot 4H_2O$ by H. Debray1) is dimeric, as has been shown in solutions by Contant2).

The samples were obtained as colorless octahedral crystals from a hot dilute nitric acid solution containing equivalent amounts of arsenic acid and ammonium heptamolybdate.

Crystal data: Tetragonal, a=b=11.923(1), c=17.564(2) Å; the space group is $P4_2/nnm$ with two formula units per unit cell; the linear absorption coefficient for MoKα radiation is 55.7 cm^{-1}. The intensities of the reflections were measured on a RIGAKU automatic four-circle diffractometer, using the ω-2θ scan technique. A total of 4094 reflections with $2\theta<60°$ (h>0, k>0, l>0) was collected, of which 1417 independent non-zero reflections were used. All the non-hydrogen atoms were located by the heavy atom method and least-squares refinement with anisotropic temperature factors, using a block diagonal approximation, gave an R value of 0.045.

As is shown in the polyhedra drawing in FIGURE 1, the $(H_4As_4Mo_{12}O_{50})^{4-}$ anion has the $\bar{4}3m$ (Td) symmetry. The anion is constructed by turning inside out the trigonal Mo_3O_{13} units of the Keggin molecule$^{3)}$, by joining four such units together at the corner to make up the $Mo_{12}O_{46}^{20-}$ anion, and by then adding the AsO_4 tetrahedra. Therefore, the dodecamolybdate part may be regarded as a "reversed Keggin molecule".

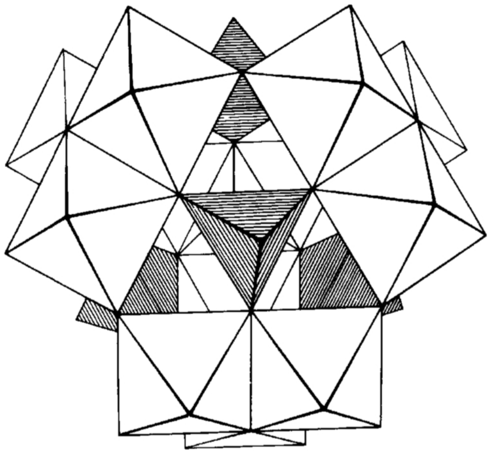
The most prominent feature of this polyanion is its large cavity at the center surrounded by twelve oxygen atoms, making the hexagonal, closed packing. The radius of the cavity was calculated to be 1.43 Å, the value of 1.40 Å being used as the ionic radius of O^{2-}. The MoO_6 octahedra are highly distorted in such a way that the molybdenum ions are strongly displaced outward. The averaged Mo-O distances, Mo-Oa, Mo-Ob, Mo-Oc, and Mo-Od, are 1.68, 1.88, 2.03, and 2.29 Å respectively, where Oa, Ob, and Oc are bound to one, two, and three molybdenum atoms respectively and where Od is shared by one arsenic and two molybdenum atoms, as is shown in Fig. 1. On the other hand, the AsO_4 tetrahedra are regular within the limits of experimental error, and the As-O distance is 1.69 Å.

Table1 Positional parameters in fractional coordinates ($\times 10^5$) with their standard deviations.

Atom	x	y	z
Mo(1)	13866(7)	6240(6)	17633(4)
Mo(2)	13976(6)	-13976(6)	3930(5)
As	11165(7)	-11165(7)	34416(6)
O(1)	25000(0)	-25000(0)	2730(76)
O(2)	25000(0)	8677(79)	25000(0)
O(3)	8290(53)	- 8290(53)	25210(50)
O(4)	2993(62)	- 2993(62)	40079(60)
O(5)	4686(49)	- 4686(49)	11309(45)
O(6)	8312(50)	-25236(55)	13707(32)
O(7)	18572(63)	14234(58)	10289(37)
O(8)	2916(70)	13826(64)	21085(42)
O(9)	19190(60)	- 3371(56)	- 1449(35)
O(H_2O)*	16157(291)	- 3117(384)	63603(178)
N(NH_4^+)	13749(135)	13749(135)	50000(0)

*) present with a probability of $\frac{1}{2}$.

Fig.1 A polyhedra model made of 12 MoO_3 octahedra and 4 AsO_4 tetrahedra.



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