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On the Structure of Hexamolybdodiarsenate Complexes in Aqueous Solution

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Results of large-angle X-ray scattering measurements on a molybdoarsenate solution, containing a polymolybdate species with 6 Mo and 2 As atoms according to emf measurements, have been compared with theoretical curves calculated for assumed models for such complexes, based on crystal structure determinations. Satisfactory agreement is found for a complex with the formula $Mo_6As_2O_{27}$, which is thus a conceivable structure for the hexamolybdoarsenate complex(es) in the solution.

Heteropoly complexes formed in the aqueous system $H^+ - MoO_4^{2-} - HAsO_4^{2-}$ can be written as $(H^+)_p(MoO_4^{2-})_q(HAsO_4^{2-})_r$. Potentiometric and spectrophotometric data have been interpreted in terms of two series of dominant complexes having (p,q,r) values equal to $(p,9,1)$ and $(p,6,2)$, respectively.[1,2] As reported in a previous paper[3] X-ray diffraction measurements on solutions containing the $(p,9,1)$ complexes show them to have the same structure as that of discrete complexes, Mo_9AsO_{34}, which occur in crystals of $Na_3Mo_9AsO_{31}(OH_2)_3 \cdot 12H_2O$.[4] Since crystals containing discrete $(p,6,2)$ complexes were not known at the time of that investigation, results from similar measurements on solutions of these complexes could be compared only with an assumed structure having the formula $Mo_6As_2O_{26}$ and based on the structure of $TeMo_6O_{24}^{6-}$ determined by Evans.[5] The solution diffraction data were not, however, consistent with this structure. In particular, the radial distribution curve for the solution did not contain peaks, which could be related to the long Mo–Mo distances in the structure. The reason could be that the assumed $(p,6,2)$ complexes in solution are less regular than that of the suggested structure, that the solutions investigated contain a mixture of complexes having different structures, or that the complexes contain less than six Mo atoms. The latter possibility was discussed in the previous paper[3] and a comparison was made with structures containing only three Mo atoms in which long Mo–Mo distances do not occur.

Some recent papers[6–9] have now, however, reported results on structure determinations of crystals which contain discrete units with six Mo atoms and one or two As atoms. In the present paper comparisons are made between shape functions calculated for these complexes and the shape function derived from the diffraction measurements on a (12,6,2) solution.

Discrete complexes $HMo_6As_2O_{26}^{5-}$, corresponding to an (11,6,2) complex, with a structure which is the same as that of the idealized model previously suggested for the $(p,6,2)$ complexes (Fig. 1), have been found in crystals of $[N(CH_3)_4]_2Na_3HMo_6As_2O_{26} \cdot 7H_2O$.[8]

In crystals of guanidinium hexamolybdobis(phenylarsonate) tetrahydrate, discrete units $(C_6H_5As)_2Mo_6O_{25}H_2^{4-}$ have been found.[6] If the phenyl groups are replaced by oxygen atoms the resulting $As_2Mo_6O_{27}$ unit (Fig. 1) will have a structure which is conceivable for the $(p,6,2)$ complexes.

In crystals of guanidinium hexamolybdomethylarsonate hexahydrate discrete units $CH_3AsMo_6O_{21}(H_2O)_6$ occur.[9] With the methyl group replaced by oxygen the formula is $AsMo_6O_{22}(H_2O)_6^{3-}$ and the structure is as shown in Fig. 1. Although the group contains only one As atom it has been included here for comparison.

The comparisons have been done with the use of functions derived as described in previous papers.[3,10]

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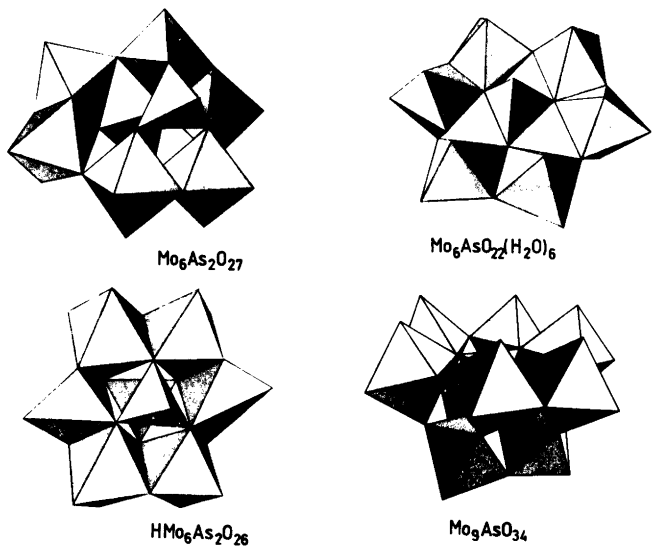

Fig. 1. Possible structures for molybdoarsenate complexes.

The radial distribution function for the (12,6,2) solution [3] was used for the derivation of a shape function for the unknown complexes by eliminating from it, as far as possible, contributions from intermolecular interactions and from known intramolecular interactions (ClO_4^-, H_2O). This was done by means of a reference solution, which contained all molybdenum bonded in $Mo_5P_2O_{23}$ complexes.[3] The resulting function (Fig. 2a) is compared with calculated shape functions for the known complexes, obtained by adding the contributions from all intramolecular interactions and from intermolecular interactions approximated by assuming the complexes to occupy spherical holes in an evenly distributed electron density. The calculations are referred to a stoichiometric unit of volume containing one Mo atom. For the reference solution the unit of volume was chosen so as to contain the same number of water molecules. The concentrations are given in Table 1.

The $Mo_6As_2O_{27}$ function (Fig. 2b) agrees well with the experimental curve (Fig. 2a). This complex is rather irregular with its long Mo–Mo distances spread out over the regions 5.6 to 6.2 Å and 6.9 to 7.0 Å. Corresponding peaks of approximately the same size occur in the experimental curve. Also, the 3.5 Å peaks are practically identical in the two functions (Fig. 2a and 2b) indicating a closely similar distribution of distances.

The $HMo_6As_2O_{26}$ function (Fig. 2c) differs only slightly from the one previously reported,[3] which was based on an assumed idealized model. The 3.5 Å peak differs in shape and in size from the experimental function (Fig. 2a), and peaks at larger distances are not consistent in the two curves.

The $Mo_6AsO_{22}(H_2O)_6$ function also shows large deviations from the derived function.

The comparisons between the calculated and the derived shape functions thus show that the $Mo_6As_2O_{27}$ structure is a conceivable structure for

Table 1. Compositions of the investigated molybdoarsenate solution (12,6,2) (stoich. volume $V=1186$ Å^3) and the molybdophosphate solution (8,5,2) used as the reference (stoich. volume $V=1164$ Å^3).

Atom	Concentrations in mol/l		Number of atoms in the unit of volume	
	(12,6,2)	(8,5,2)	(12,6,2)	(8,5,2)
Mo	1.40	1.77	1.00	1.24
As	0.467	–	0.333	–
P	–	0.71	–	0.50
Na	3.73	4.25	2.67	2.98
Cl	2.80	2.12	2.00	1.49
O	62.1	62.5	44.3	43.8
H	90.0	91.7	64.3	64.3

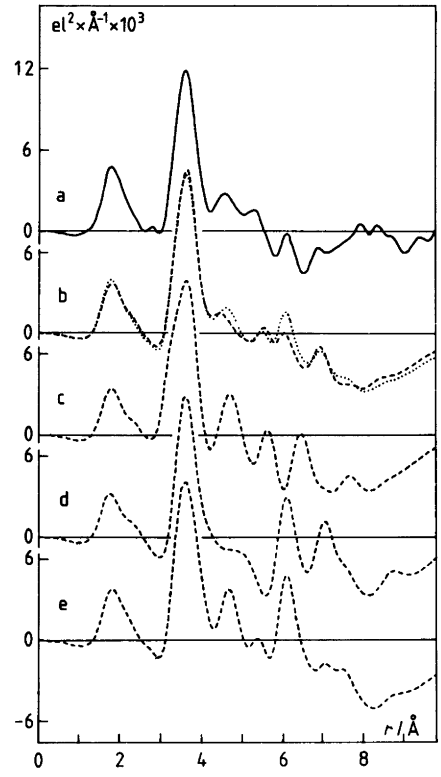

Fig. 2. Shape functions for molybdoarsenate complexes in solution. a. The function derived from the RDF of the investigated (12,6,2) solution. b. Calculated functions for $Mo_6As_2O_{27}$ units (dashed line) and for a mixture of $Mo_6As_2O_{27}$ and Mo_9AsO_{34} units in the ratio 2:1 (dotted line). c–e. Calculated shape functions for $Mo_6As_2O_{26}$, $Mo_6AsO_{22}(H_2O)_6$ and Mo_9AsO_{34} units.

the complex(es) in a (12,6,2) solution, while the $Mo_6As_2O_{26}$ structure is not in agreement with the solution scattering data. In solutions of the (10,6,2) and (11,6,2) complexes, as established from the potentiometric and spectrophotometric data,[1,2] the structures may be different. Crystals containing the discrete $Mo_6As_2O_{26}$ units (Fig. 1) are obtained from an (11,6,2) solution. Moreover, Filowitz and Klemperer [11] have interpreted ^{17}O NMR spectra of a (10,6,2) anion in solution to be consistent with the $Mo_6As_2O_{26}$ structure. The series of (*p*,6,2) complexes, $p=10$, 11 and 12, may thus consist of complexes having different structures.

Since the complex nature of the structures of the heteropolymolybdates limits the comparisons to known structures, other structural arrangements cannot be excluded, however. Also, the conclusions depend on the assumptions made, that the solutions contain one dominant complex rather than a mixture of complexes, and that the intermolecular interactions in the reference solution can be used as an approximation for the corresponding interactions in the unknown solution. The first assumption is based on the results of the potentiometric measurements. The second assumption has been previously shown [3] to be valid.

At the high total molybdenum concentration prevailing in the (12,6,2) solution investigated, $Mo_{tot}=1.4$ M, the presence of a small amount of Mo_9AsO_{34} complexes cannot be excluded. The shape function for this complex (Fig. 2e) is rather similar to that of $Mo_6As_2O_{27}$. The 3.5 Å peaks do not differ and other peaks occur at nearly equal distances. The major difference is the size of the 6.1 Å peak, which is much larger for Mo_9AsO_{34} than for $Mo_6As_2O_{27}$. The shape function obtained for a mixture of these two complexes in the ratio 1:2 (Fig. 2b) slightly improves the agreement with the experimental curve.

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