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The Structure of $Mo_7O_{24}^{6-}$ Ion in the Crystal of Ammonium Heptamolybdate Tetrahydrate

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The structure of a discrete polyanion, $Mo_7O_{24}^{6-}$, in the crystal of ammonium heptamolybdate tetrahydrate, previously determined by Lindqvist, has been redetermined and refined by a two-dimensional, single crystal X-ray diffraction study. The positional parameters of the oxygen atoms, which were left undetermined in the previous investigation, have been determined. Lindqvist's description of the structure still applies. However, the distortion of the polyanion has been found to be more pronounced than was previously assumed. Comparisons with molybdenum oxides and oxyacids are discussed with regard to the structure, the Mo–Mo distances and Mo–O distances.

It was revealed in the previous papers[1,2] that ammonium heptamolybdate tetrahydrate gives three endothermic peaks in the differential thermal analysis, four different crystalline states in the X-ray analysis with a Guinier focussing camera, and four steps corresponding to them in the thermo-gravimetric analysis. The first endothermic peak corresponds to dehydration, and the second and third ones to deammoniation. According to Evans, hydrates of polyacids are classified as containing zeolite type water only.[3] In the case of ammonium heptamolybdate tetrahydrate, however, the dehydration takes place without a change in the structure at first, and is eventually followed by structural collapse at the end of the dehydration. Therefore, some of the water molecules seem to play an important role in determining the crystal structure. It seems likely that the stepwise deammoniation is due to two types of NH_4^+ ions in the structure. To interpret those informations obtained in the thermal decomposition studies from the standpoint of structural chemistry, a complete structural analysis of ammonium heptamolybdate tetrahydrate is required.

The crystallographic data of ammonium heptamolybdate tetrahydrate were determined by Sturdivant,[4] the formula being $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. The structure of heptamolybdate (paramolybdate) ion, $Mo_7O_{24}^{6-}$, was investigated by Lindqvist,[5] a finite complex structure of an anion polyhedron built up of seven MoO_6 octahedra being broached. Together with the structure of octamolybdate (tetramolybdate in Lindqvist's terminology) ion, $Mo_8O_{26}^{4-}$, determined by the same investigator,[6] these represent the only examples ever known about the structure of complex isopolyacids formed with molybdenum.[7]

Lindqvist's work, however, determined molybdenum positions only, oxygen position being left undetermined. As a first step to the complete analysis of ammonium heptamolybdate tetrahydrate, the present investigation attempts to refine Lindqvist's data and determine all molybdenum and oxygen positions in the heptamolybdate ion.

Experimental

Ammonium heptamolybdate tetrahydrate crystals were obtained from aqueous solutions. They are colorless, rhomboidal plates elongated along the *a*-axis. The crystallographic data reported by Sturdivant were indeed confirmed in the present investigation. They are:

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1) E. Ma (Shimao), This Bulletin, **37**, 171 (1964).
2) E. Ma (Shimao), *ibid.*, **37**, 648 (1964).
3) R. C. Evans, "An Introduction to Crystal Chemistry," 2nd ed., Cambridge University Press, London (1964), pp. 286, 296.
4) J. H. Sturdivant, *J. Am. Chem. Soc.*, **59**, 630 (1937).
5) I. Lindqvist, *Arkiv Kemi*, **2**, 325 (1950).
6) I. Lindqvist, *ibid.*, **2**, 349 (1950).
7) I. Lindqvist, *Nova Acta Reg. Soc. Sci. Upsal.*, Ser. IV, **15**, No. 1 (1950).

$a = 8.382$ Å, $b = 36.125$ Å, $c = 10.464$ Å, $\beta = 116°0'$
Space group: $C_{2h}^{5}—P2_1/c$
Absent spectra: $(0k0)$ when k is odd
$(h0l)$ when l is odd
Four molecules per unit cell.

A crystal with the dimensions $0.18 \times 0.13 \times 0.95$ mm were used for the collection of the intensity data. Intensities for $(0kl)$ were recorded on a pack of films (multifilms) in an integrating Weissenberg camera using Cu$K\alpha$ radiation. Corrections for Lorentz and polarization factors were applied in the usual way.

The pronounced needle shape allowed the crystal to be rotated about the needle axis, a-axis, only. Therefore, intensities for $(hk0)$ were recorded photographically using the precession method ($\mu = 20°$, MoK radiation).*2 In order to cover the complete range of intensities, several photographs were taken, varying in exposure from 3 min to 17 hr. All the intensities were estimated visually using a calibration wedge. Corrections for Lorentz and polarization factors for the precession photographs were applied using the table prepared by Kraut.[8] No corrections were made for absorption.

A total of 656 independent reflections were collected.

Structure Determination

The two-dimensional structure factors, Fourier summations and least-squares refinements were computed on IBM 7074 of Matsushita Electric computing center by means of programs particularly devised for the present investigation, and subsequently on HITAC 5020E of the computing center of the University of Tokyo by 'MNSF' and 'HBLS'.*3 For the reflections obtained with Mo-$K\alpha$ radiation, the real part of the dispersion correction, $\Delta f' = -1.7$, was applied to the scattering curve of Mo.[9] Computations were performed for all reflections in the range, $\sin^2\theta < 0.98$ for $(0kl)$, and $\sin^2\theta < 0.55$ for $(hk0)$.

The coordinates of the seven Mo atoms given by Lindqvist were used as starting parameters. The structure factors were calculated with the starting parameters, the R-value (defined as $\sum\{|F_o| - |F_c|\}/\sum|F_c|$) being found to be 0.447 for $(0kl)$ and 0.365 for $(hk0)$ respectively. Although the seven heavy Mo atoms contribute much to the structure factors, the R-value could not be improved through the refinement of the Mo atoms only, for the asymmetric unit contains, besides them, twenty-eight O and six N atoms. It was extremely time-consuming to determine all of the light atoms in this case. As a first step, therefore, it was aimed in the present investigation to determine the positions of the twenty-four O atoms which are coordinated to Mo atoms, and some other atoms, if possible.

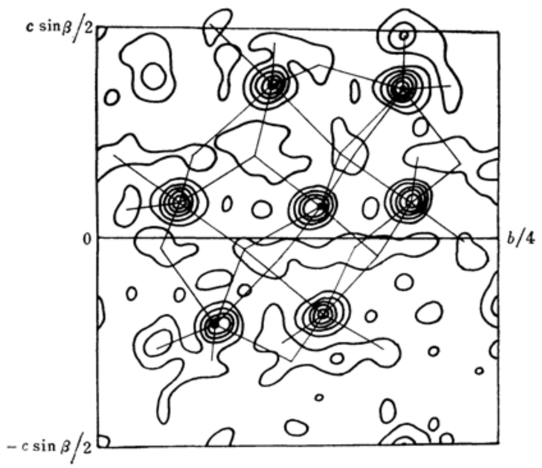

Fig. 1. (a) The final electron density projection along the a-axis.

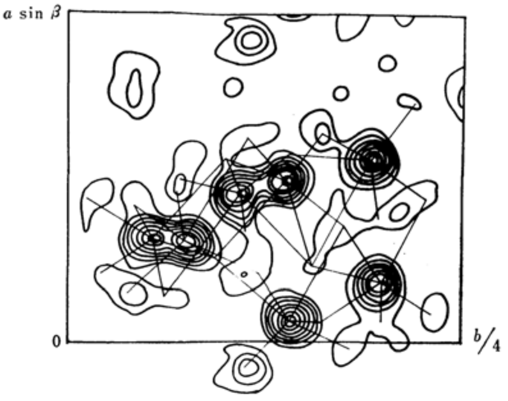

Fig. 1. (b) The final electron density projection along the c-axis.

One would not be able to obtain the oxygen positions merely from the geometrical basis of the heptamolybdate ion, because MoO_6 octahedra are considerably distorted. As Kihlborg observed,[10] for instance, an oxygen atom, which is shared by two Mo atoms at a corner, is not necessarily located on the straight line through the Mo atoms.

Through several Fourier syntheses and difference $|F_o - F_c(\text{Mo})|$ Fourier syntheses, the twenty-four O atoms were determined, and through several cycles of least-squares refinements the R-values were reduced to 0.309 for $(0kl)$ and 0.264 for $(hk0)$. The isotropic temperature factor for each atom obtained in the last cycle was $\exp\{-0.10(\sin^2\theta/\lambda^2)\}$. The final atomic parameters are given in Table 1 and the final Fourier maps are shown in Fig. 1. A perspective view of heptamolybdate ion is shown in Fig. 2. The list of the final values of the observed

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*2 The author is indebted to Dr. Masaki for taking he precession photographs.

[8] "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham (1959), p. 288.

*3 The author is grateful to Dr. T. Ashida for 'MNSF' and 'HBLS' programs put at his disposal.

[9] "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham (1962), p. 214.

[10] L. Kihlborg, *Arkiv Kemi*, **21**, 365 (1963).

Table 1. Final atom parameters

Atom	x	y	z
Mo(1)	0.4473	0.1073	0.3682
Mo(2)	0.3105	0.0497	0.0908
Mo(3)	0.1748	0.1963	0.0861
Mo(4)	0.0626	0.1404	−0.1812
Mo(5)	0.5630	0.1907	0.3604
Mo(6)	0.4949	0.1353	0.0753
Mo(7)	0.3105	0.0733	−0.2072
O(1)	0.5090	0.0721	0.4789
O(2)	0.2400	0.1131	0.4464
O(3)	0.1645	0.0756	0.2281
O(4)	0.5896	0.0801	0.2226
O(5)	0.3445	0.1548	0.2069
O(6)	0.6436	0.1456	0.4657
O(7)	0.4534	0.0219	0.2384
O(8)	0.1719	0.0266	−0.0300
O(9)	0.4505	0.0372	−0.0200
O(10)	0.2149	0.1042	−0.0484
O(11)	0.0131	0.2127	0.2033
O(12)	0.0913	0.2322	−0.0367
O(13)	0.4266	0.2159	0.1972
O(14)	0.0316	0.1640	−0.0334
O(15)	0.3119	0.1635	−0.0056
O(16)	−0.1125	0.1089	−0.2119
O(17)	0.0030	0.1834	−0.2831
O(18)	0.1949	0.1146	−0.2586
O(19)	0.3999	0.1908	0.4886
O(20)	0.7304	0.2077	0.4848
O(21)	0.6719	0.1590	0.2339
O(22)	0.6060	0.1037	−0.0564
O(23)	0.1337	0.0411	−0.2383
O(24)	0.4848	0.0602	−0.3058

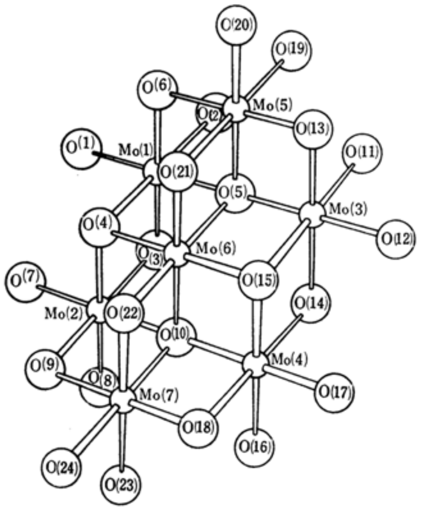

Fig. 2. A perspective view of the $Mo_7O_{24}^{6-}$ ion. Numbering of atoms are similar to those of Tables 1, 2 and 3.

Table 2. Interatomic distances

Mo–Mo		Mo–Mo	
1–2	3.179 Å	6–7	3.500 Å
2–6	3.480	3–5	3.174
1–6	3.177	4–7	3.300
3–6	3.523	1–5	3.076
4–6	3.422	2–7	3.255
5–6	3.476	3–4	3.250

Mo–O	
Mo(1)–O(1)	1.800 Å
–O(2)	2.400
–O(3)	2.425
–O(4)	2.300
–O(5)	2.175
–O(6)	2.050
Mo(2)–O(3)	2.430
–O(4)	2.375
–O(7)	1.800
–O(8)	1.675
–O(9)	2.000
–O(10)	2.370
Mo(3)–O(5)	2.075
–O(11)	2.475
–O(12)	1.750
–O(13)	2.050
–O(14)	1.750
–O(15)	2.125
Mo(4)–O(10)	1.925
–O(14)	1.900
–O(15)	2.250
–O(16)	1.800
–O(17)	1.813
–O(18)	1.900
Mo(5)–O(5)	2.350
–O(6)	1.925
–O(13)	1.825
–O(19)	2.150
–O(20)	1.650
–O(21)	2.350
Mo(6)–O(4)	2.400
–O(10)	2.375
–O(5)	2.325
–O(15)	1.725
–O(21)	1.900
–O(22)	2.290
Mo(7)–O(9)	2.200
–O(10)	2.424
–O(18)	1.800
–O(22)	2.150
–O(23)	1.825
–O(24)	2.150

and the calculated structure factors has been deposited in the editorial office of this Bulletin.*4

Discussion

The skeleton of heptamolybdate polyanion, which had been determined by Lindqvist, was confirmed in the present investigation, *viz.*, seven MoO_6 octahedra join by sharing edges to form a compact structure unlike the coplanar structure found for $TeMo_6O_{24}^{6-}$. The idealized structure built up of the seven MoO_6 octahedra is considerably distorted in the actual heptamolybdate structure. Displacement of Mo(6) is most remarkable, as compared with its six adjacent Mo atoms. A displacement of Mo(6) by 0.122 Å in the direction of Mo(4) would locate Mo(6) at almost equal distances from six adjacent Mo atoms.

The bond lengths and the interbond angles are given in Tables 2 and 3. The Mo–Mo distances between octahedra sharing edges lie in the range 3.076—3.523 Å, which is wider than the values, 3.21—3.48 Å reported by Lindqvist. The distortion of the polyanion structure was found to be even more pronounced than had been previously assumed by Lindqvist. Lindqvist pointed out that the mean value of the Mo–Mo distances including Mo(6) is longer than that of pairs excluding Mo(6). This holds true in the present investigation, too; 3.430 Å for the mean value of pairs of Mo–Mo distances including Mo(6) and 3.206 Å for pairs excluding Mo(6) respectively.

There are two Mo–Mo distances sharing corners, *viz.*, Mo(1)–Mo(3) and Mo(2)–Mo(4). They are 4.176 Å and 4.225 Å respectively, being a little shorter than those reported by Lindqvist, 4.30 and 4.27 Å. And yet they are longer than any value reported on molybdenum oxides by Magnéli[11] and Kihlborg.[10,12-14] However, the sharing of edges is the primary factor determining the structure of heptamolybdate ion, while the sharing of corners is merely a result of association of octahedra sharing edges.

TABLE 3. INTERBOND ANGLES

Mo-Mo-Mo		Ideal value
1-6-2	60°23′	(60°)
1-6-3	78°0′	(90°)
1-6-4	103°35′	(120°)
1-6-5	56°30′	(60°)
1-6-7	110°29′	(120°)
2-6-4	77°40′	(90°)
2-6-5	113°50′	(120°)
2-6-7	58°10′	(60°)
3-6-4	55°48′	(60°)
3-6-5	54°3′	(60°)
3-6-7	110°30′	(120°)
4-6-5	109°49′	(120°)
5-6-7	160°36′	(180°)

The lower limit of the Mo–Mo distances sharing edges, 3.076 Å, is shorter than any value of Mo–Mo distances sharing edges in MoO_3,[13,15] Mo_8O_{23},[14,16] Mo_9O_{26},[16] Mo_4O_{11},[10,17] $Mo_{17}O_{47}$[12] and molybdenum bronzes.[18,19] And yet the value is longer than the geometrically ideal value of 2.65 Å given by Magnéli.[11] Since heptamolybdate is a compact polyanion formed primarily by sharing edges, the repulsive effect between the molybdenum atoms seems to be weaker than that in the above mentioned structures, in which the sharing of corners is the primary factor. An unusually short distance of 2.5 Å was reported on MoO_2,[20] which is considered to be due to a direct interaction between the molybdenum atoms.

The Mo–O distances fall between 1.650 Å and 2.510 Å. The lower limit agrees with those values reported by Kihlborg on MoO_3 and on $Mo_{17}O_{47}$, by Stephenson and Wadsley on $K_{0.26}MoO_3$,[18] by Smith and Ibers on $CoMoO_4$,[19] and by Cotton *et al.* on a molybdenum oxalate complex.[21] The upper limit agrees only with that which was reported on $K_{0.26}MoO_3$, and is longer than those reported on other compounds.

The distances from each molybdenum atom to its six oxygen neighbours are shown in Fig. 3. The

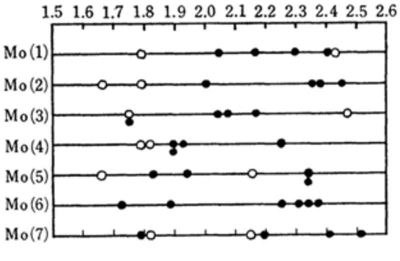

Fig. 3. The Mo–O distances for each Mo atom. The open circles represent the terminal bond.

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*4 The complete data of the F_o-F_c table are kept as Document No. 6705 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥500 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

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11) A. Magnéli, *Nova Acta Reg. Soc. Sci. Upsal.*, Ser. IV, **14**, No. 8 (1950).

12) L. Kihlborg, *Acta Chem. Scand.*, **14**, 1612 (1960).

13) L. Kihlborg, *Arkiv Kemi*, **21**, 357 (1963).

14) L. Kihlborg, *ibid.*, **21**, 365 (1963).

15) G. Andersson and A. Magnéli, *Acta Chem. Scand.*, **4**, 793 (1950).

16) A. Magnéli, *ibid.*, **2**, 501 (1948).

17) A. Magnéli, *ibid.*, **2**, 861 (1948).

18) N. C. Stephenson and A. D. Wadsley, *Acta Cryst.*, **19**, 241 (1965).

19) G. W. Smith and J. A. Ibers, *ibid.*, **19**, 269 (1965).

20) A. Magnéli, *Arkiv Kemi, Mineral., Geol.*, **24**, A, No. 2 (1946).

21) F. A. Cotton, S. M. Morehouse and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).

arrangements of each MoO_6 octahedra represent a considerable distortion from a regular coordination. In the structure of heptamolybdate ion, the systematic variations in the interatomic distances were not observed, in contrast to those which were reported in the following cases; two short, two intermediate and two long Mo–O distances in MoO_3, three short and three long bonds in Mo_4O_{11}, and one short, four intermediate and one long bonds in Mo_8O_{23}.

In the structure of Mo_8O_{23} a progressive increase in distortion of MoO_6 octahedra was observed from the middle toward the slab boundaries. The same kind of progressive distortion was reported about the slabs of Mo_4O_{11}. In the structure of heptamolybdate ion, however, the distortion of octahedra is perfectly irregular, showing no such progression of bond lengths with location of octahedra. This may be due to the fact that Mo_4O_{11} and Mo_8O_{23} possess sub-structures of ReO_3 type, which extend infinitely in two dimensions and are of finite widths in the third dimension, while heptamolybdate is a discrete polyanion.

Kihlborg observed that when two molybdenum atoms are bonded with one oxygen, there is a tendency of increase in the sum of the distances with increasing distortion.[22] He exemplified it in MoO_3, Mo_8O_{23} and Mo_4O_{11}. However this tendency was not found to exist in the case of heptamolybdate ion.

The terminal Mo–O distances are generally shorter than the rest as are indicated with open circles in Fig. 3. The mean value of the terminal Mo–O distances is 1.943 Å, while that of the rest is 2.149 Å.

There are twelve shared edges in the polyanion of heptamolybdate, the mean value of the O–O distances along the shared edges being 2.80 Å. Some values of the shared edges fall in the range, 2.15—2.25 Å. Such a shortening of the shared edges was discussed by Pauling as a criterion of ionic character of the bonds.[23]

To determine the positions of NH_4^+ ions and of water molecules, a three-dimensional, complete analysis is in progress.

The author wishes to express his sincere gratitude to Professor Kenji Osaki for kind direction and continued interest in this investigation. He is grateful to Professor Kumasaburo Kodera and Professor Sukeji Kachi for encouraging discussions and valuable suggestions. Thanks are due to Dr. Minoru Ozasa of Matsushita Electronics Corporation for arrangement for computing with IBM 7074.

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[22] L. Kihlborg, *Arkiv Kemi*, **21**, 471 (1963).

[23] L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca (1960), p. 562.