Crystal Structure of the Heptamolybdate(VI) (Paramolybdate) Ion, $[Mo_7O_{24}]^{6-}$, in the Ammonium and Potassium Tetrahydrate Salts

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The crystal structures of the isomorphous salts $M^{I}_6[Mo_7O_{24}].4H_2O$ ($M = NH_4$ or K) have been refined by three-dimensional *X*-ray diffraction methods. Unit cell dimensions of these monoclinic compounds, space group $P2_1/c$ with $Z = 4$, are, ammonium salt: $a = 8{\cdot}3934 \pm 0{\cdot}0008$, $b = 36{\cdot}1703 \pm 0{\cdot}0045$, $c = 10{\cdot}4715 \pm 0{\cdot}0011$ Å, $\beta = 115{\cdot}958° \pm 0{\cdot}008°$; and potassium salt: $a = 8{\cdot}15 \pm 0{\cdot}02$, $b = 35{\cdot}68 \pm 0{\cdot}1$, $c = 10{\cdot}30 \pm 0{\cdot}02$ Å, $\beta = 115{\cdot}2° \pm 0{\cdot}2°$.

By use of multiple Weissenberg patterns, 8197 intensity data (Mo-K_α radiation) for the ammonium compound and 2178 (Cu-K_α radiation) for the potassium compound were estimated visually and used to test and refine Lindqvist's proposed structure in the space group $P2_1/c$. Lindqvist's structure was confirmed and the full matrix least-squares isotropic refinement led to R 0·076 (ammonium) 0·120 (potassium), with direct unambiguous location of the cations and water molecules in the potassium compound.

THE nature of the polymolybdate complex ion as it is formed in aqueous solution has long been controversial. The most thorough study has been carried out by precision e.m.f. methods by Sasaki and Sillén [1,2] who have shown that in acid solutions (with 3M-$NaClO_4$ supporting electrolyte) the isopoly-complex ion heptamolybdate $[Mo_7O_{24}]^{6-}$ and its protonated forms

[1] Y. Sasaki, I. Lindqvist, and L. G. Sillén, *J. Inorg. Nuclear Chem.*, 1959, **9**, 93; Y. Sasaki and L. G. Sillén, *Acta Chem. Scand.*, 1964, **18**, 1014.
[2] Y. Sasaki and L. G. Sillén, *Arkiv. Kemi*, 1968, **29**, 253.

predominate. They concluded [2] that the supposed octamolybdate ion $[Mo_8O_{26}]^{4-}$ is definitely not present in significant amounts at the temperature of their experiments (25 °C). In a critical review [2] of their own and previous work on this system they conclude that heptamolybdate is a major acid–alkali solution species * of Mo^{VI} and that it is represented in the solid state in isomorphous crystals of ammonium heptamolybdate tetrahydrate, $[NH_4]_6[Mo_7O_{24}],4H_2O$, also in the corresponding potassium, and possibly the rubidium [4] salts.

The first-named compound, known commercially as ammonium paramolybdate,[5] is readily crystallized from solutions of molybdenum trioxide in ammonium hydroxide. Many formulations were suggested for it,[5-8] but, as often happens in situations where radically different formulations vary only slightly in their critical composition ratios of the heavy and light elements, the conclusive evidence was provided by X-ray crystallography. The monoclinic unit cell was thus shown to contain 4 units of $[NH_4]_6[Mo_7O_{24}],4H_2O$.[9]

The structure of the heptamolybdate ion was solved by crystal-structure analysis, by Lindqvist,[10] who established the peculiar butterfly-shaped configuration adopted by the molecular ion. This result did not confirm the only previously proposed structure,[11] although this flat trigonal configuration was later found in certain heteropoly-complexes. Owing mainly to the limited computing facilities available at that time, Lindqvist did not carry his determination beyond the resolution of any but the molybdenum atoms, and the positions of the molecular oxygen atoms were inferred from assumed octahedral co-ordination with molybdenum and appropriate edge sharing. Thus, detailed dimensional information such as bond lengths was still not available.

Subsequently, there have been three crystal structure studies of the heptamolybdate anion in an effort to resolve the oxygen atoms and refine their positions by least-squares analysis. Shimao [12] reported a preliminary two-dimensional study of the ammonium salt. However, full three-dimensional analysis of the same compound by Evans,[13] and of the isomorphous potassium salt by Gatehouse and Leverett [14] were carried out independently and contemporaneously but have only been briefly described. It was realized that these three-dimensional studies complemented one another in that the former allowed accurate determination of the heptamolybdate anion configuration, whilst the latter enabled direct unambiguous location of the cations within the structure. We now report those two X-ray structure analyses.

* It has recently been reported [3] that in the presence of other cations, specificially Mg^{2+}, wholly different polyanions and equilibria are found.

[3] W. G. Baldwin and G. Weise, *Arkiv. Kemi*, 1969, **31**, 419.
[4] B. M. Gatehouse and P. Leverett, unpublished results.
[5] L. Svanberg and H. Struve, *J. prakt. Chem.*, 1848, **44**, 282.
[6] W. Delffs, *Pogg. Ann.*, 1852, **85**, 453.
[7] M. Delafontaine, *Arch. phys. nat.*, 1865, [2], **23**, 17.
[8] A. Rosenheim, *Z. anorg. Chem.*, 1916, **96**, 141.

EXPERIMENTAL

(*a*) $[NH_4]_6[Mo_7O_{24}],4H_2O$ (by H. T. E.)

Preparation.—Single crystals, suitable for Weissenberg photography, were grown from an aqueous solution of commercial reagent-grade ammonium paramolybdate. Such crystals were ground to a powder to obtain powder diffraction data.

Data Measurement.—The recently developed Hagg–Guinier focussing powder diffraction camera [15] was used with Cr-$K_{\alpha 1}$ radiation ($\lambda = 2{\cdot}29862$ Å) to obtain a powder pattern of maximum resolution. A set of 69 2θ values indexed with the aid of the single-crystal reflections were analyzed by a least-squares program to refine Sturdivant's [9] unit-cell parameters. The single-crystal diffraction intensities were recorded by multiple-film Weissenberg photography with Mo-K_α radiation. A total of 8197 independent reflections [representing the complete contents of a reflecting sphere of radius $(\sin\theta)/\lambda$ 0·7000] were estimated visually. Data were grouped according to 12 Weissenberg levels made by rotation about the a axis (h = 0—11), and a separate scale factor assigned to each group. Lorentz and polarization corrections were made in the usual way, but no dispersion or extinction corrections were attempted. Absorption corrections were also omitted, since it was felt that the level of refinement based on film data sought in this analysis would not be seriously affected. This view is based on the relatively low linear absorption coefficient ($\mu = 28{\cdot}0$ cm^{-1}) and the small size of the crystal (*ca.* 0·2 × 0·1 × 0·1 mm), which is somewhat elongated along the a axis and therefore approximates to a rotating cylinder in the recording geometry.

Structure Analysis.—Lindqvist's [10] molybdenum co-ordinates were used to phase the first three-dimensional electron-density synthesis, which revealed all light-atom positions except those of hydrogen. Co-ordinates taken from this map were used to initiate full-matrix least-squares analysis [16] of the structure parameters. The refinement converged smoothly through 10 cycles, with 176 parameters, including individual isotropic thermal parameters, allowed to vary in the later stages. The data were weighted in three groups (where F_o represents a scaled absolute value): for $F_o > 4F_o$ (min), $\sqrt{w} = 4F_o$ (min)/F_o; for $4F_o$ (min) $> F_o > F_o$ (min), $\sqrt{w} = 1$; for $F_o < F_o$ (min), $\sqrt{w} = 0$ (2664 reflections). This process led to R 0·082.

At this point a difference synthesis showed only low but clear saddles at each molybdenum site, oriented in such a way that the presence of a small amount of libration of the heptamolybdate group around a central point was suggested. Two cycles of refinement were therefore calculated including anisotropic thermal parameters for each of the seven molybdenum atoms, but holding the 12 scale factors constant. This step reduced R to a final value of 0·076. The resulting ellipsoids had only small eccentricity [root-mean-square amplitudes of vibration were 0·12 (min) and 0·16 Å (max) for each molybdenum atom except

[9] J. H. Sturdivant, *J. Amer. Chem. Soc.*, 1937, **59**, 630.
[10] I. Lindqvist, *Arkiv. Kemi*, 1950, **2**, 325.
[11] J. S. Anderson, *Nature*, 1937, **140**, 850.
[12] E. Shimao, *Bull. Chem. Soc. Japan*, 1967, **40**, 1609.
[13] H. T. Evans, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 3275.
[14] B. M. Gatehouse and P. Leverett, *Chem. Comm.*, 1968, 901.
[15] G. Hägg and N.-O. Ersson, *Acta Cryst.*, 1969, **A25**, *S*64.
[16] All computations were carried out with the 'X-Ray '67' program system, ed. J. M. Stewart, Computer Science Center, Univ. of Maryland, Technical Report, 67 58.

Mo_7, which is 0·12 Å isotropic], but a true evaluation of these parameters would require a data set which is not grouped by h values as is this one. Nevertheless, the process used has reduced the systematic error due to anisotropic thermal motion of the heavy atoms and thus slightly improved the determination of the atomic positional parameters, which is our primary object. A final difference synthesis showed a background which varied almost entirely between ± 2 eÅ^{-3}, with no fluctuations $> \pm 3$ eÅ^{-3}, and displaying no recognizably significant features. In the latter calculations scattering factors for neutral atoms were taken from ref. 17. Final observed and calculated structure factors for both compounds are listed in Supplementary Publication No. SUP 21181 (8 pp., 1 microfiche).* Since there were only 15 reflections in levels with $h = 10$ and 11, these were not included in later stages of refinement and are not listed. Final parameters and their associated errors are listed in Table 1.

TABLE 1

Structure and thermal parameters for $[NH_4]_6[Mo_7O_{24}],4H_2O$

(*a*) Structure and isotropic thermal parameters

Groups	Atom	x	y	z	B/Å^2
$[Mo_7O_{24}]^{6-}$	Mo(1)	0·44524(16)	0·10746(3)	0·36519(13)	1·43(2)
	Mo(2)	0·32336(16)	0·05126(3)	0·09506(13)	1·49(2)
	Mo(3)	0·18159(16)	0·19594(4)	0·08413(14)	1·69(2)
	Mo(4)	0·06692(15)	0·13990(4)	−0·18375(13)	1·52(2)
	Mo(5)	0·56135(15)	0·19144(3)	0·35645(13)	1·49(2)
	Mo(6)	0·30859(16)	0·07382(4)	−0·20489(13)	1·61(2)
	Mo(7)	0·48971(15)	0·13579(3)	0·07435(12)	1·23(2)
	O(1)	0·5760(13)	0·0724(3)	0·4698(11)	1·75(18)
	O(2)	0·4618(14)	0·0190(3)	0·2129(11)	1·98(19)
	O(3)	0·1010(15)	0·2310(3)	−0·0370(13)	2·91(23)
	O(4)	−0·0127(15)	0·1783(3)	−0·2876(12)	2·65(21)
	O(5)	0·3269(12)	0·1232(3)	0·4515(11)	1·47(17)
	O(6)	0·1238(15)	0·0284(3)	0·0041(13)	2·72(22)
	O(7)	0·0876(14)	0·2010(3)	0·1995(12)	2·41(20)
	O(8)	−0·1124(15)	0·1086(3)	−0·2504(12)	2·71(21)
	O(9)	0·4875(14)	0·2070(3)	0·4753(12)	2·32(12)
	O(10)	0·1274(14)	0·0459(3)	−0·3000(12)	2·61(21)
	O(11)	0·7624(14)	0·2149(3)	0·4050(11)	2·20(20)
	O(12)	0·4548(13)	0·0687(3)	−0·2804(11)	2·05(19)
	O(13)	0·6457(12)	0·1444(3)	0·4371(10)	1·59(17)
	O(14)	0·4302(11)	0·0447(3)	−0·0359(10)	1·18(15)
	O(15)	0·4094(13)	0·2201(3)	0·1951(11)	1·63(17)
	O(16)	0·2049(12)	0·1217(3)	−0·2802(10)	1·32(16)
	O(17)	0·6569(12)	0·1658(3)	0·1785(10)	1·32(16)
	O(18)	0·5578(11)	0·1174(3)	−0·0489(10)	1·05(15)
	O(19)	0·2552(10)	0·0786(2)	0·2207(9)	0·71(14)
	O(20)	0·0283(12)	0·1565(3)	−0·0203(10)	1·21(16)
	O(21)	0·5312(12)	0·0950(3)	0·1995(10)	1·17(16)
	O(22)	0·3162(12)	0·1702(3)	−0·0386(10)	1·09(15)
	O(23)	0·3639(12)	0·1532(3)	0·2147(10)	1·15(15)
	O(24)	0·2521(12)	0·0995(3)	−0·0430(10)	1·34(17)
H_2O	O(25)	0·7896(16)	0·0403(4)	0·0915(14)	3·65(26)
	O(26)	0·9405(15)	0·1130(4)	0·4369(13)	2·98(23)
	O(27)	0·2152(16)	0·0280(4)	0·4336(14)	3·67(27)
	O(28)	0·4079(17)	0·2078(4)	0·7692(15)	4·24(29)
NH_4^+	N(1)	0·8312(19)	0·0361(4)	0·3757(16)	3·22(30)
	N(2)	0·9394(17)	0·1127(4)	0·1647(14)	1·97(22)
	N(3)	0·8060(18)	0·2494(4)	0·1760(16)	2·54(26)
	N(4)	0·1300(15)	0·1890(4)	0·4912(13)	1·88(22)
	N(5)	0·7818(18)	0·0345(4)	0·7498(15)	2·51(26)
	N(6)	0·5911(17)	0·1496(4)	0·7193(14)	2·20(24)

(*b*) Anisotropic thermal parameters for Mo ($\beta \times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	709(20)	27(1)	372(13)	11(4)	240(13)	10(3)
Mo(2)	703(20)	22(1)	507(14)	0(3)	286(14)	4(3)
Mo(3)	795(21)	28(1)	480(15)	44(4)	248(14)	−1(3)
Mo(4)	605(20)	27(1)	425(14)	16(4)	134(14)	−1(3)
Mo(5)	704(19)	28(1)	383(13)	−21(4)	204(13)	−12(3)
Mo(6)	761(20)	31(1)	436(14)	14(4)	273(13)	−17(3)
Mo(7)	544(18)	24(1)	350(13)	5(3)	201(13)	6(3)

* In the form: $t = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

(*b*) $K_6[Mo_7O_{24}],4H_2O$ (by B. M. G. and P. L.)

Preparation.—Crystalline $K_6[Mo_7O_{24}],4H_2O$ was prepared by dissolving molybdenum trioxide (May and Baker, analytical-reagent grade) in aqueous potassium hydroxide solution, the pH of which was adjusted to 6, and slowly evaporated until the product crystallized. The product was analysed for potassium and molybdenum by atomic

* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1973, Index issue.

[17] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 395.

absorption spectroscopy (Found: Mo, 49·0; K, 17·0. Calc. for $K_6Mo_7O_{24}$: Mo, 49·3; K, 17·2%).

Data Measurement.—Unit cell parameters and symmetry were obtained from single-crystal oscillation, Weissenberg, and precession photographs. Hagg–Guinier powder diffraction data (120 2θ values indexed with the aid of the single-crystal reflections) were analysed to refine the unit-cell constants as for the ammonium compound. Intensity data were collected from a small prismatic crystal of dimensions 0·3 (*a*) × 0·06 (*b*) × 0·04 mm, oriented for rotation about the *a* axis. Intensities for the levels 0—4*kl* were recorded with Cu-K_α radiation by the multiple-film Weissenberg technique, and a total of 2178 independent reflections was estimated visually. It was felt that this rather limited amount of data would be sufficient to determine the structure completely, although it was expected that the *x* co-ordinates of the atoms would be obtained with slightly less accuracy than would the other positional parameters. Data were grouped according to the five Weissenberg levels and a separate scale factor used for each level in the final stages of refinement. Lorentz and polarization corrections were made in the usual way; no corrections were made for absorption, or extinction. The scattering curves used were those of ref. 18 for Mo^0, ref. 19 for K^+, and ref. 20 for O^{2-}; the first two were corrected for the effects of anomalous dispersion according to ref. 21.

Structure Analysis.—Lindqvist's [10] co-ordinates for molybdenum were used to phase the first three-dimensional electron-density synthesis which immediately revealed the positions of the six independent potassium ions. Three cycles of least-squares refinement of the molybdenum and potassium atom parameters and an overall scale factor reduced *R* to 0·20. The subsequent difference synthesis enabled location of the twenty-four anion oxygen atoms and the four oxygen atoms of the water molecules. The refinement converged smoothly through twelve cycles in which positional and isotropic thermal parameters were allowed to vary, and in the final cycles individual level scale factors were also varied. The weighting scheme of ref. 22 was adopted, of the form: $w = 1/(A + B|F_0| + C|F_0|^2)$, where $A = 17·22$, $B = -3·73$, and $C = 0·21$; it

TABLE 2

Structure and thermal parameters for $K_6[Mo_7O_{24}],4H_2O$

Groups	Atom	x	y	z	B/Å^2
$[Mo_7O_{24}]^{6-}$	Mo(1)	0·4461(7)	0·1060(1)	0·3708(3)	0·53(7)
	Mo(2)	0·3230(7)	0·0503(1)	0·0972(3)	0·60(7)
	Mo(3)	0·1757(7)	0·1970(1)	0·0930(3)	0·66(7)
	Mo(4)	0·0612(7)	0·1407(1)	−0·1805(3)	0·50(7)
	Mo(5)	0·5652(7)	0·1912(1)	0·3672(3)	0·51(7)
	Mo(6)	0·3077(7)	0·0732(1)	−0·2028(3)	0·52(7)
	Mo(7)	0·4936(7)	0·1363(1)	0·0781(3)	0·42(7)
	O(1)	0·591(6)	0·069(1)	0·478(4)	
	O(2)	0·461(6)	0·071(1)	0·224(4)	
	O(3)	0·081(6)	0·233(1)	−0·029(4)	
	O(4)	−0·027(6)	0·180(1)	−0·291(4)	
	O(5)	0·327(7)	0·123(1)	0·459(4)	
	O(6)	0·114(6)	0·027(1)	0·001(4)	
	O(7)	0·067(6)	0·201(1)	0·200(4)	
	O(8)	−0·128(6)	0·108(1)	−0·242(4)	
	O(9)	0·493(7)	0·206(1)	0·489(4)	
	O(10)	0·129(6)	0·045(1)	−0·299(4)	
	O(11)	0·776(7)	0·215(1)	0·414(4)	
	O(12)	0·448(6)	0·069(1)	−0·283(4)	
	O(13)	0·658(7)	0·142(1)	0·446(4)	2·8(3)
	O(14)	0·420(7)	0·044(1)	−0·031(4)	
	O(15)	0·415(7)	0·222(1)	0·200(4)	
	O(16)	0·193(7)	0·121(1)	−0·280(4)	
	O(17)	0·665(7)	0·166(1)	0·192(4)	
	O(18)	0·559(7)	0·120(1)	−0·037(4)	
	O(19)	0·253(7)	0·077(1)	0·229(4)	
	O(20)	0·020(7)	0·156(1)	−0·021(4)	
	O(21)	0·534(7)	0·094(1)	0·208(4)	
	O(22)	0·314(6)	0·171(1)	−0·037(4)	
	O(23)	0·358(7)	0·153(1)	0·218(4)	
	O(24)	0·250(7)	0·099(1)	−0·043(4)	
H_2O	O(25)	0·810(7)	0·044(1)	0·098(4)	
	O(26)	0·953(6)	0·111(1)	0·426(4)	2·8(3)
	O(27)	0·197(6)	0·025(1)	0·432(4)	
	O(28)	0·430(7)	0·206(1)	0·774(4)	
K^+	K(1)	0·8246(24)	0·0354(3)	0·3805(13)	2·50(25)
	K(2)	0·9461(21)	0·1155(3)	0·1661(12)	1·61(21)
	K(3)	0·7938(24)	0·2484(3)	0·1769(14)	2·43(25)
	K(4)	0·1339(21)	0·1889(3)	0·4968(12)	1·60(21)
	K(5)	0·7789(22)	0·0375(3)	0·7505(12)	1·83(22)
	K(6)	0·5798(20)	0·1470(3)	0·7177(12)	1·44(20)

[18] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

[19] J. Berghuis, J. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1958, **8**, 478.

[20] T. Suzuki, *Acta Cryst.*, 1960, **13**, 279.

[21] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[22] D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. Truter, 'Computing Methods and the Phase Problem in Crystallography,' Pergamon Press, Oxford, 1961.

was found to be satisfactory except for a few of the strongest reflections ($F_0 > 10{\cdot}0$) which were assigned individual weights. The final R was 0·120 with all parameter changes much less than the estimated errors. A final difference electron-density synthesis showed only minor maxima and minima which were between $\pm 0{\cdot}2$ of the mean electron-density value of oxygen atoms in the structure. No attempt was made to locate hydrogen atoms. Final parameters and their associated errors in Table 2.

The most severe error in this analysis is doubtless caused by absorption ($\mu = 340\ cm^{-1}$), but no corrections for this have been made. It was felt that the structure analysis of the ammonium salt was much better suited for the refinement of the dimensions of the heptamolybdate polyion, and the analysis of the potassium salt would serve mainly as confirmatory evidence of the overall structure, particularly with regard to the cation locations. Therefore no attempt has been made to extend further and correct the data set for the potassium salt.

RESULTS AND DISCUSSION

The colourless monoclinic crystals of the ammonium salt have a stubby prismatic habit as reported previously by Groth,[23] who gave the formula as $(MoO_4)_3$-$(NH_4)_3H_3{\cdot}(MoO_4)_3(NH_4)_2H_4$. They commonly show three prominent zones of faces parallel to the axes [100], [001], and [101], truncated by a large pinacoid b {010}. There is a perfect cleavage parallel to this last face. Sturdivant[9] measured the unit cell from carefully calibrated oscillation photographs, and from systematic extinctions he deduced the space group to be $P2_1/c$. This unit cell has been used in all subsequent crystallographic studies. Hagg–Guinier powder diffraction data have been used to refine cell constants of both compounds (Table 3).

For the ammonium compound Groth[23] gives β 115·98° and $a:b:c$ 0·2334 : 1 : 0·2936. The crystal forms given by Groth must be transformed by the matrix $\frac{1}{3}$,0,$-\frac{1}{3}$/010/001 to conform to the X-ray setting. Sturdivant found the D_m for the ammonium compound at 25 °C to be $2{\cdot}871 \pm 0{\cdot}003$ g cm^{-3}, in close agreement with the calculated value of 2·872 g cm^{-3}. D_m for the potassium salt is $3{\cdot}23 \pm 0{\cdot}01$ g cm^{-3}, and D_c 3·41 g cm^{-3}.

TABLE 3

Unit-cell parameters, distances in Å, angles in °.

	NH_4 salt [a]	NH_4 salt [b]	K salt [a]
a	$8{\cdot}3934 \pm 0{\cdot}0008$	$8{\cdot}399 \pm 0{\cdot}011$	$8{\cdot}1318 \pm 0{\cdot}0004$
b	$36{\cdot}170 \pm 0{\cdot}005$	$36{\cdot}197 \pm 0{\cdot}008$	$35{\cdot}6097 \pm 0{\cdot}0016$
c	$10{\cdot}4715 \pm 0{\cdot}0011$	$10{\cdot}485 \pm 0{\cdot}006$	$10{\cdot}3376 \pm 0{\cdot}0006$
β	$115{\cdot}958 \pm 0{\cdot}008$	$116{\cdot}00 \pm 0{\cdot}07$	$115{\cdot}397 \pm 0{\cdot}005$
$a:b:c$	0·23197 : 1 : 0·28940	0·23204 : 1 : 0·28966	0·22836 : 1 : 0·29030

[a] Powder refinement. [b] Ref. 9.

Structure of the Polyion.—The unusual configuration of the heptamolybdate group $[Mo_7O_{24}]^{6-}$ suggested by Lindqvist[10] has been wholly confirmed by these studies; the following discussion of the detailed geometry of the polyion is made on the basis of the more accurately determined ammonium salt structure. The geometry of the polyion derived from the two structures reported here is found to be the same. It consists of seven MoO_6 octahedra condensed by edge sharing into a structure that has point symmetry $2mm(C_{2v})$. Figure 1(a) shows the arrangement in terms of polyhedra, in which three octahedra are approximately in line in the central horizontal level, two are attached forward at a level above, and two more forward at a level below. The molecular ion has no centre of symmetry and lies in a general position in the unit cell.

The atomic arrangement in the molecule ion is essentially that found in a rock-salt type of structure. Its relationship in this sense to other isopoly-ion structures has been previously pointed out by Evans.[24] The heptamolybdate structure can be derived from that

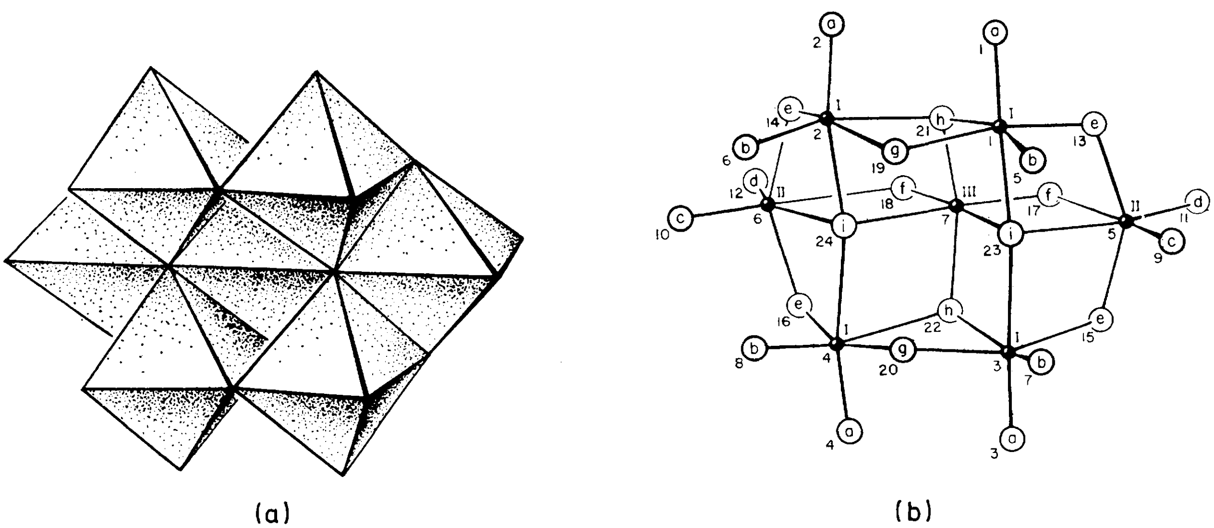

FIGURE 1 The heptamolybdate in molecule $[Mo_7O_{24}]^{6-}$ showing (a) MoO_6 groups as condensed polyhedra, and (b) bonding between atoms and the atom numbering system used for the molybdenum and oxygen atoms. Letter and Roman numeral designations indicate atoms equivalent by molecular symmetry $2mm$ (see Table 4)

[23] P. Groth, 'Chemische Kristallographie,' vol. 2, Wilhelm Engelman, Leipzig, 1908, p. 603.

[24] H. T. Evans, jun., *Inorg. Chem.*, 1966, **5**, 967.

of decavandate $[V_{10}O_{28}]^{6-}$ by removing three MO_6 octahedra. In the idealized heptamolybdate ion, there

TABLE 4

Interatomic distances (Å) in the $K_6[Mo_7O_{24}],4H_2O$ and $[NH_4]_6[Mo_7O_{24}],4H_2O$

Atoms	K salt	NH_4 salt	Mean sym. equiv. $[NH_4]$
(*a*) Mo–Mo			
Mo(1)–Mo(2)	3·239(7)	3·263(2)	Mo^{I}–Mo^{I} 3·25
Mo(3)–Mo(4)	3·252(7)	3·247(2)	
Mo(5)–Mo(7)	3·401(7)	3·404(2)	Mo^{II}–Mo^{III} 3·43
Mo(6)–Mo(7)	3·448(7)	3·458(2)	
Mo(1)–Mo(5)	3·196(10)	3·204(2)	Mo^{I}–Mo^{III} 3·19
Mo(2)–Mo(6)	3·154(8)	3·187(2)	
Mo(3)–Mo(5)	3·234(9)	3·219(2)	
Mo(4)–Mo(6)	3·193(9)	3·202(2)	
Mo(1)–Mo(7)	3·377(8)	3·385(2)	Mo^{I}–Mo^{III} 3·40
Mo(2)–Mo(7)	3·407(10)	3·407(2)	
Mo(3)–Mo(7)	3·430(10)	3·415(2)	
Mo(4)–Mo(7)	3·398(10)	3·395(2)	
Mo(1)–Mo(3)	4·268(9)	4·244(2)	Mo^{I}–Mo^{I} 4·24
Mo(2)–Mo(4)	4·241(9)	4·225(2)	
Mo(5)–Mo(6)	6·775(7)	6·788(2)	Mo^{II}–Mo^{III} 6·79
(*b*) Mo–O, type (1)			
Mo(1)–O(1)	1·80(4)	1·721(11)	Mo^{I}–O^{a} 1·72
Mo(2)–O(2)	1·77(4)	1·725(11)	
Mo(3)–O(3)	1·73(4)	1·709(13)	
Mo(4)–O(4)	1·75(4)	1·710(12)	
Mo(1)–O(5)	1·70(6)	1·708(9)	Mo^{I}–O^{b} 1·73
Mo(2)–O(6)	1·77(4)	1·732(12)	
Mo(3)–O(7)	1·69(5)	1·718(11)	
Mo(4)–O(8)	1·82(4)	1·764(13)	
Mo(5)–O(9)	1·68(5)	1·709(11)	Mo^{III}–O^{c} 1·72
Mo(6)–O(10)	1·71(4)	1·733(12)	
Mo(5)–O(11)	1·79(5)	1·754(11)	Mo^{III}–O^{d} 1·75
Mo(6)–O(12)	1·68(6)	1·743(10)	
(*c*) Mo–O, type (2)			
Mo(1)–O(13)	2·02(5)	2·019(10)	Mo^{I}–O^{e} 1·97
Mo(2)–O(14)	1·82(6)	1·954(9)	
Mo(3)–O(15)	2·00(5)	1·956(10)	
Mo(4)–O(16)	1·91(6)	1·954(9)	
Mo(5)–O(13)	1·95(4)	1·893(10)	Mo^{II}–O^{e} 1·92
Mo(5)–O(15)	1·97(4)	1·915(10)	
Mo(6)–O(14)	1·93(4)	1·919(9)	
Mo(6)–O(16)	1·92(4)	1·945(9)	
Mo(1)–O(19)	1·93(4)	1·951(9)	Mo^{I}–O^{g} 1·94
Mo(2)–O(14)	1·93(5)	1·923(8)	
Mo(3)–O(20)	1·96(4)	1·912(10)	
Mo(4)–O(20)	1·89(5)	1·970(9)	
Mo(5)–O(17)	2·44(6)	2·506(9)	Mo^{II}–O^{f} 2·53
Mo(6)–O(18)	2·62(4)	2·554(9)	
Mo(7)–O(17)	1·75(4)	1·732(10)	Mo^{III}–O^{f} 2·74
Mo(7)–O(18)	1·60(6)	1·756(9)	
(*d*) Mo–O, type (3)			
Mo(1)–O(21)	2·13(6)	2·198(9)	Mo^{I}–O^{h} 2·29
Mo(2)–O(21)	2·24(4)	2·252(9)	
Mo(3)–O(22)	2·28(5)	2·250(9)	
Mo(4)–O(22)	2·23(4)	2·260(9)	
Mo(7)–O(21)	1·95(4)	1·902(10)	Mo^{III}–O^{h} 1·90
Mo(7)–O(22)	1·90(4)	1·888(9)	
(*e*) Mo–O, type (4)			
Mo(1)–O(23)	2·20(4)	2·177(10)	Mo^{I}–O^{i} 2·18
Mo(2)–O(24)	2·17(4)	2·176(10)	
Mo(3)–O(23)	2·17(4)	2·185(10)	
Mo(4)–O(24)	2·18(4)	2·172(10)	
Mo(5)–O(23)	2·21(4)	2·171(10)	Mo^{II}–O^{i} 2·16
Mo(6)–O(24)	2·10(5)	2·152(9)	
Mo(7)–O(23)	2·24(5)	2·242(10)	Mo^{III}–O^{i} 2·25
Mo(7)–O(24)	2·27(4)	2·251(10)	
(*f*) O–O, type (1)–type (1)			
O(1)–O(5)	2·83(7)	2·728(14)	O^{a}–O^{b} 2·74
O(2)–O(6)	2·81(5)	2·741(15)	
O(3)–O(7)	2·76(6)	2·750(16)	
O(4)–O(8)	2·81(6)	2·737(17)	
O(9)–O(11)	2·75(9)	2·727(14)	O^{c}–O^{d} 2·76
O(10)–O(12)	2·68(7)	2·789(14)	

TABLE 4 (*Continued*)

Atoms	K salt	NH_4 salt	Mean sym. equiv. $[NH_4]$
(*g*) O–O, type (1)–type (2)			
O(1)–O(13)	2·71(5)	2·725(15)	O^{a}–O^{e} 2·70
O(2)–O(14)	2·68(6)	2·667(14)	
O(3)–O(15)	2·77(5)	2·694(16)	
O(4)–O(16)	2·74(6)	2·723(15)	
O(1)–O(19)	2·87(5)	2·821(13)	O^{a}–O^{g} 2·79
O(2)–O(19)	2·75(6)	2·791(14)	
O(3)–O(20)	2·80(5)	2·784(15)	
O(4)–O(20)	2·78(6)	2·781(15)	
O(5)–O(13)	2·84(8)	2·851(13)	O^{b}–O^{e} 2·84
O(6)–O(14)	2·72(8)	2·852(14)	
O(7)–O(15)	2·93(8)	2·808(14)	
O(8)–O(16)	2·84(8)	2·853(14)	
O(5)–O(19)	2·73(6)	2·745(13)	O^{b}–O^{g} 2·73
O(6)–O(19)	2·78(5)	2·734(15)	
O(7)–O(20)	2·68(6)	2·671(15)	
O(8)–O(20)	2·69(5)	2·776(15)	
O(9)–O(13)	2·78(7)	2·739(15)	O^{c}–O^{e} 2·78
O(9)–O(15)	2·83(6)	2·753(15)	
O(10)–O(14)	2·77(5)	2·821(15)	
O(10)–O(16)	2·75(5)	2·804(16)	
O(11)–O(13)	2·84(6)	2·804(15)	O^{d}–O^{e} 2·82
O(11)–O(15)	2·84(6)	2·818(14)	
O(12)–O(14)	2·84(7)	2·796(14)	
O(12)–O(16)	2·80(7)	2·842(14)	
O(11)–O(17)	2·71(5)	2·779(14)	O^{d}–O^{f} 2·80
O(12)–O(18)	2·93(5)	2·808(14)	
(*h*) O–O, type (1)–type (3)			
O(1)–O(21)	2·77(6)	2·808(14)	O^{a}–O^{h} 2·84
O(2)–O(21)	2·83(5)	2·824(14)	
O(3)–O(22)	2·94(6)	2·849(15)	
O(4)–O(22)	2·91(5)	2·864(15)	
(*i*) O–O, type (1)–type (4)			
O(5)–O(23)	2·81(7)	2·845(14)	O^{b}–O^{i} 2·87
O(6)–O(24)	2·91(6)	2·911(15)	
O(7)–O(23)	2·87(6)	2·842(14)	
O(8)–O(24)	2·90(6)	2·892(14)	
O(9)–O(23)	3·16(5)	3·136(16)	O^{c}–O^{i} 3·12
O(10)–O(24)	3·07(5)	3·103(16)	
(*j*) O–O, type (2)–type (2)			
O(13)–O(17)	2·78(7)	2·856(13)	O^{e}–O^{f} 2·88
O(14)–O(18)	2·95(6)	2·865(13)	
O(15)–O(17)	2·88(7)	2·917(14)	
O(16)–O(18)	2·97(6)	2·897(13)	
O(17)–O(18)	2·70(5)	2·776(13)	O^{f}–O^{f} 2·78
(*k*) O–O, type (2)–type (3)			
O(13)–O(21)	2·80(5)	2·866(14)	O^{e}–O^{h} 2·87
O(14)–O(21)	2·86(5)	2·877(13)	
O(15)–O(22)	2·87(5)	2·860(14)	
O(16)–O(22)	2·88(5)	2·879(13)	
O(17)–O(21)	2·81(6)	2·816(13)	O^{f}–O^{h} 2·81
O(18)–O(21)	2·78(7)	2·825(13)	
O(17)–O(22)	2·83(6)	2·771(13)	
O(18)–O(22)	2·70(7)	2·824(12)	
O(19)–O(21)	2·47(6)	2·495(12)	O^{g}–O^{h} 2·53
O(20)–O(22)	2·53(8)	2·556(12)	
(*l*) O–O, type (2)–type (4)			
O(13)–O(23)	2·60(5)	2·509(13)	O^{e}–O^{i} 2·48
O(14)–O(24)	2·38(6)	2·465(13)	
O(15)–O(23)	2·53(5)	2·473(14)	
O(16)–O(24)	2·41(6)	2·472(13)	
O(17)–O(23)	2·67(8)	2·686(13)	O^{f}–O^{i} 2·68
O(18)–O(24)	2·60(8)	2·673(12)	
O(19)–O(23)	2·86(6)	2·855(13)	O^{g}–O^{i} 2·85
O(19)–O(24)	2·90(7)	2·852(12)	
O(20)–O(23)	2·81(5)	2·817(13)	
O(20)–O(24)	2·84(7)	2·869(13)	
(*m*) O–O, type (3)–type (4)			
O(21)–O(23)	2·57(6)	2·572(13)	O^{h}–O^{i} 2·59
O(21)–O(24)	2·64(5)	2·599(13)	
O(22)–O(23)	2·57(6)	2·578(13)	
O(22)–O(24)	2·63(5)	2·611(13)	
(*n*) O–O, type (4)–type (4)			
O(23)–O(24)	3·11(5)	3·117(15)	O^{g}–O^{g} 3·12

are three different kinds of molybdenum atoms, all in distorted octahedral co-ordination: four Mo^{I}, two Mo^{II}, and one Mo^{III} [see Figure 1(b)]. Of the oxygen atoms there are twelve bonded to a single Mo atom [type (1)], eight bonded to two Mo each [type (2)], two bonded to three Mo [type (3)], and two bonded to four Mo [type (4)].

TABLE 5

Angles (°) in $K_6[Mo_7O_{24}],4H_2O$ and $[NH_4]_6[Mo_7O_{24}],4H_2O$

Atoms	K salt	NH_4 salt	Mean sym. equiv. $[NH_4]$
(a) O–Mo–O, type (1)–type (1)			
O(1)–Mo(1)–O(5)	108(2)	105·5(5)	O^{a}–Mo^{I}–O^{b} 105·3
O(2)–Mo(2)–O(6)	105(2)	104·9(5)	
O(3)–Mo(3)–O(7)	102(2)	106·8(6)	
O(4)–Mo(4)–O(8)	104(2)	104·0(5)	
O(9)–Mo(5)–O(11)	105(2)	103·8(5)	O^{c}–Mo^{II}–O^{d} 105·3
O(10)–Mo(6)–O(12)	104(2)	106·7(5)	
(b) O–Mo–O, type (1)–type (2)			
O(1)–Mo(1)–O(13)	90(2)	93·2(4)	O^{a}–Mo^{I}–O^{e} 94·0
O(2)–Mo(2)–O(14)	97(2)	92·7(4)	
O(3)–Mo(3)–O(15)	96(2)	94·4(5)	
O(4)–Mo(4)–O(16)	97(2)	95·8(5)	
O(1)–Mo(1)–O(19)	100(2)	100·2(4)	O^{a}–Mo^{I}–O^{g} 99·6
O(2)–Mo(2)–O(19)	96(2)	99·7(5)	
O(3)–Mo(3)–O(20)	98(2)	100·4(5)	
O(4)–Mo(4)–O(20)	99(2)	97·9(5)	
O(5)–Mo(1)–O(13)	99(2)	99·5(4)	O^{b}–Mo^{I}–O^{e} 100·0
O(6)–Mo(2)–O(14)	98(2)	100·7(5)	
O(7)–Mo(3)–O(15)	105(2)	99·5(5)	
O(8)–Mo(4)–O(16)	99(2)	100·1(5)	
O(5)–Mo(1)–O(19)	97(2)	97·0(4)	O^{b}–Mo^{I}–O^{g} 96·1
O(6)–Mo(2)–O(19)	97(2)	96·7(5)	
O(7)–Mo(3)–O(20)	94(2)	94·6(5)	
O(8)–Mo(4)–O(20)	93(2)	95·9(5)	
O(9)–Mo(5)–O(13)	100(2)	98·9(5)	O^{a}–Mo^{II}–O^{e} 99·5
O(9)–Mo(5)–O(15)	101(2)	98·7(5)	
O(10)–Mo(6)–O(14)	99(2)	101·0(5)	
O(10)–Mo(6)–O(16)	98(2)	99·2(5)	
O(11)–Mo(5)–O(13)	99(2)	100·5(5)	O^{d}–Mo^{II}–O^{e} 100·2
O(11)–Mo(5)–O(15)	98(2)	100·3(5)	
O(12)–Mo(6)–O(14)	104(2)	99·4(4)	
O(12)–Mo(6)–O(16)	102(2)	100·7(4)	
O(11)–Mo(5)–O(17)	78(2)	79·3(4)	O^{d}–Mo^{II}–O^{f} 79·2
O(12)–Mo(6)–O(18)	83(2)	79·2(4)	
(c) O–Mo–O, type (1)–type (3)			
O(1)–Mo(1)–O(21)	89(2)	90·7(4)	O^{a}–Mo^{I}–O^{h} 90·6
O(2)–Mo(2)–O(21)	89(2)	89·5(4)	
O(3)–Mo(3)–O(22)	93(2)	91·0(5)	
O(4)–Mo(4)–O(22)	93(2)	91·3(5)	
(d) O–Mo–O, type (1)–type (4)			
O(5)–Mo(1)–O(23)	91(2)	98·4(4)	O^{b}–Mo^{I}–O^{i} 94·0
O(6)–Mo(2)–O(24)	94(2)	95·7(5)	
O(7)–Mo(3)–O(23)	95(2)	92·7(5)	
O(8)–Mo(4)–O(24)	92(2)	95·0(6)	
O(9)–Mo(5)–O(23)	108(2)	107·2(5)	O^{c}–Mo^{II}–O^{i} 106·4
O(10)–Mo(6)–O(24)	107(2)	105·5(4)	
(e) O–Mo–O, type (2)–type (2)			
O(13)–Mo(5)–O(17)	78(2)	79·7(4)	O^{e}–Mo^{II}–O^{f} 79·6
O(15)–Mo(5)–O(17)	81(2)	81·4(4)	
O(14)–Mo(6)–O(18)	79(2)	78·2(3)	
O(16)–Mo(6)–O(18)	80(2)	78·9(4)	
O(17)–Mo(7)–O(18)	107(2)	105·5(4)	O^{f}–Mo^{III}–O^{f} 105·5
(f) O–Mo–O, type (2)–type (3)			
O(13)–Mo(1)–O(21)	85(2)	85·5(4)	O^{e}–Mo^{I}–O^{h} 85·7
O(14)–Mo(2)–O(21)	89(2)	86·0(4)	
O(15)–Mo(3)–O(22)	84(2)	85·4(4)	
O(16)–Mo(4)–O(22)	88(2)	85·8(4)	
O(17)–Mo(7)–O(21)	99(2)	101·5(4)	O^{f}–Mo^{III}–O^{h} 101·0
O(17)–Mo(7)–O(22)	102(2)	99·8(4)	
O(18)–Mo(7)–O(21)	102(2)	101·0(4)	
O(18)–Mo(7)–O(22)	101(2)	101·5(4)	
O(19)–Mo(1)–O(21)	75(2)	73·6(3)	O^{g}–Mo^{I}–O^{h} 74·0
O(19)–Mo(2)–O(21)	72(2)	72·9(3)	
O(20)–Mo(3)–O(22)	73(2)	75·3(4)	
O(20)–Mo(4)–O(22)	75(2)	74·0(4)	
(g) O–Mo–O, type (2)–type (4)			
O(13)–Mo(1)–O(23)	77(2)	73·3(4)	O^{e}–Mo^{I}–O^{i} 73·2
O(14)–Mo(2)–O(24)	72(2)	73·1(4)	
O(15)–Mo(3)–O(23)	74(2)	73·1(4)	
O(16)–Mo(4)–O(24)	72(2)	73·4(4)	
O(19)–Mo(1)–O(23)	87(2)	87·3(4)	O^{g}–Mo^{I}–O^{i} 87·3
O(19)–Mo(2)–O(24)	90(2)	87·9(4)	
O(20)–Mo(3)–O(23)	85(2)	86·6(4)	
O(20)–Mo(4)–O(24)	88(2)	87·5(4)	
O(13)–Mo(5)–O(23)	77(2)	75·9(4)	O^{e}–Mo^{II}–O^{i} 74·8
O(15)–Mo(5)–O(23)	74(2)	74·2(4)	
O(14)–Mo(6)–O(24)	72(2)	74·3(4)	
O(16)–Mo(6)–O(24)	74(2)	74·0(4)	
O(17)–Mo(5)–O(23)	70(2)	69·7(3)	O^{f}–Mo^{II}–O^{i} 69·1
O(18)–Mo(6)–O(24)	66(2)	68·6(3)	
O(17)–Mo(7)–O(23)	83(2)	84·0(4)	O^{f}–Mo^{III}–O^{i} 83·1
O(18)–Mo(7)–O(24)	82(2)	82·7(4)	
(h) O–Mo–O, type (3)–type (4)			
O(21)–Mo(1)–O(23)	73(2)	72·3(4)	O^{h}–Mo^{I}–O^{i} 71·8
O(21)–Mo(2)–O(24)	73(2)	71·9(4)	
O(22)–Mo(3)–O(23)	71(2)	71·1(4)	
O(22)–Mo(4)–O(24)	73(2)	73·2(4)	
O(21)–Mo(7)–O(23)	76(2)	76·3(4)	O^{h}–Mo^{III}–O^{i} 76·9
O(21)–Mo(7)–O(24)	77(2)	77·0(4)	
O(22)–Mo(7)–O(23)	77(2)	76·7(4)	
O(22)–Mo(7)–O(24)	77(2)	77·7(4)	
(i) O–Mo–O, type (4)–type (4)			
O(23)–Mo(7)–O(24)	87(2)	87·9(3)	O^{i}–Mo^{III}–O^{i} 87·9
(j) Pole-to-pole			
O(1)–Mo(1)–O(23)	158(2)	158·6(4)	O^{a}–Mo^{I}–O^{i} 158·7
O(2)–Mo(2)–O(24)	159(2)	156·9(4)	
O(3)–Mo(3)–O(23)	162(2)	158·6(5)	
O(4)–Mo(4)–O(24)	162(2)	160·5(4)	
O(11)–Mo(5)–O(23)	148(2)	149·0(4)	O^{d}–Mo^{II}–O^{h} 148·4
O(12)–Mo(6)–O(24)	149(2)	147·8(4)	
O(5)–Mo(1)–O(21)	162(2)	162·7(4)	O^{b}–Mo^{I}–O^{h} 162·2
O(6)–Mo(2)–O(21)	163(2)	163·6(5)	
O(7)–Mo(3)–O(22)	161(2)	161·1(5)	
O(8)–Mo(4)–O(22)	161(2)	162·9(5)	
O(9)–Mo(5)–O(17)	177(2)	176·8(4)	O^{c}–Mo^{II}–O^{f} 175·4
O(10)–Mo(6)–O(18)	173(2)	174·1(4)	
O(13)–Mo(1)–O(19)	157(2)	155·3(4)	O^{e}–Mo^{I}–O^{g} 155·7
O(14)–Mo(2)–O(19)	157(2)	155·3(4)	
O(15)–Mo(3)–O(20)	153(2)	155·7(4)	
O(16)–Mo(4)–O(20)	157(2)	155·8(4)	
O(13)–Mo(5)–O(15)	149(2)	148·7(4)	O^{e}–Mo^{II}–O^{e} 147·3
O(14)–Mo(6)–O(16)	145(2)	145·9(4)	
O(17)–Mo(7)–O(24)	170(2)	171·8(4)	O^{f}–Mo^{III}–O^{i} 171·2
O(18)–Mo(7)–O(23)	170(2)	170·5(4)	
O(21)–Mo(7)–O(22)	143(2)	143·3(4)	O^{h}–Mo^{III}–O^{h} 143·3

Detailed bond lengths and angles in the crystal structures and their associated errors are given in Tables 4 and 5, together with those for the molecule ion idealized to $2mm$ symmetry for the ammonium salt. The deviations from the mean are not large, and are consistent with what may be expected under the influence of neighbouring cations in the crystal and hydrogen bonding to surrounding water molecules and ammonium ions. It seems reasonable to assume that the heptamolybdate ion has the ideal symmetry in the free state in solution. The similarity between the arrangement of seven edge-shared MoO_6 octahedra in the heptamolybdate polyanion and the basic repeating units which form the infinite chain of layer structures in polymolybdates obtained from melts has been discussed elsewhere.[25]

The Mo–O bond lengths span a considerable range in the idealized structure (1·71—2·42 Å). Generally one may consider that the Mo–O bond length will be shorter, the fewer the molybdenum atoms which are shared by the oxygen atom. Thus, mean Mo–O distances are: for oxygen of type (4) sharing four molybdenums is 2·21; for type (3) sharing three molybdenums 2·04, for type (2) sharing two molybdenums 2·00, and for type (1), unshared, 1·72 Å. The last are found to occur in pairs for the exterior molybdenum atoms, forming V-shaped MoO_2 groups, where the mean angle is 105·2°.

TABLE 6

Selected structures containing bent MO_2 groups; distances (Å), angles (°)

Compound or ion	No. of groups	L *	α
$[Mo_7O_{24}]^{6-}$	7	1·72	105·2 [a]
$[TeMo_6O_{24}]^{6-}$	6	1·71	106·6 [b]
$[H_6Cr^{III}Mo_6O_{24}]^{6-}$	6	1·71	105·7 [c]
$[H_4Co_2^{III}Mo_{10}O_{38}]^{6-}$	10	1·71	105·4 [d]
$[Ce^{IV}Mo_{12}O_{42}]^{12-}$	12	1·70	103·6 [e]
$Ag[(PO_4)MoO_2]$	2	1·77	104·0 [f]
MoO_3	1	1·70	103·6 [g]
$Co[MoO_4]$	2	1·72	103·9 [h]
$[H_2W_{12}O_{42}]^{10-}$	6	1·73	103·2 [i]
$[V_{10}O_{28}]^{6-}$	2	1·69	106·5 [j]
$K[VO_3],H_2O$	1	1·66	106·0 [k]

[a] Present work. [b] H. T. Evans, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 3275. [c] A. Perloff, *Inorg. Chem.*, 1970, **9**, 2228. [d] H. T. Evans, jun., and J. S. Showell, *J. Amer. Chem. Soc.*, 1969, **91**, 6881. [e] D. D. Dexter and J. V. Silverton, *J. Amer. Chem. Soc.*, 1968, **90**, 3589. [f] P. Kierkegaard and S. Holmén, *Arkiv. Kemi*, 1964, **23**, 213. [g] L. Kihlborg, *Arkiv. Kemi*, 1963, **21**, 357. [h] G. W. Smith and J. A. Ibers, *Acta Cryst.*, 1965, **19**, 269. [i] R. Allmann, *Acta Cryst.*, 1971, **B27**, 1393. [j] H. T. Evans, jun., *Inorg. Chem.*, 1966, **5**, 967. [k] H. T. Evans, jun., *Z. Krist.*, 1960, **114**, 17.

* L denotes the short M–O bond length (see text).

Such discernible groups have been commonly found in isopoly- and heteropoly-complexes of groups (5) and (6) elements. Table 6 lists a selection of these, where L denotes the short M–O bond length and α the bond angle in the MO_2 group. The consistency of this characteristic configuration suggests a rather rigid π-bond system in which the bond number is *ca.* 1·5, as has been previously suggested for the vanadate complexes.[23] Such a configuration may tend to increase the stability of the poly-complexes.

Evidently the oxygen atoms of the MoO_2 group may be involved in further, more distant, bonding with other cations. The central Mo^{III} atom of the heptamolybdate ion also conforms to the V-shaped configuration with two short bonds with lengths (mean 1·75 Å, and α 104·8°). The oxygen atoms O^f are further shared with Mo^{II} at a distance of 2·42 Å (Table 4). The need for the central Mo atom to adopt this distorted co-ordination may help to explain why this poly-ion has the unusual bent configuration rather than the much more symmetrical Anderson structure.[11] In the heteropoly-complexes $[TeMo_6O_{24}]^{6-}$, $[H_6CrMo_6O_{24}]^{3-}$, etc., where the Anderson structure does obtain, the central ion is quite stable in a regular octahedral co-ordination.

Attention was drawn recently [26,27] to the fact that the same compact unit of seven octahedra exists in $Ti_7O_{24}Et_{19}$, the first hydrolysis product of titanium tetraethoxide.[28] Other aspects of the structural chemistry of the heptamolybdate molecule ion and its relation to other similar complexes have been discussed.[27] We are carrying out a refinement of the structure of the

[25] B. M. Gatehouse and P. Leverett, *J. Chem. Soc.* (*A*), 1971, 2107.
[26] A. F. Ried, personal communication.
[27] H. T. Evans, jun., *Perspectives in Structural Chem.*, 1971, 1.
[28] K. Watenpaugh and C. M. Caughlin, *Chem. Comm.*, 1967, 76.

TABLE 7

Cation ··· oxygen distances (Å), <3·5 Å

Atoms	K salt	NH_4 salt	Mean K, NH_4
(*a*) Cation–O, H_2O (<3·5 Å)			
M(1) ··· O(1)	2·78(5)	3·020(17)	2·94, 3·05 *
M(1) ··· O(2)	2·79(5)	2·876(18)	
M(1) ··· O(10)	3·06(4)	3·130(20)	
M(1) ··· O(10)′	3·19(4)	3·233(20)	
M(1) ··· O(21)	3·09(4)	3·195(18)	
M(1) ··· O(25)	2·88(5)	2·844(21)	
M(1) ··· O(26)	2·87(4)	2·911(19)	
M(1) ··· O(27)	2·87(5)	3·022(19)	
M(1) ··· O(27)′	2·94(4)	3·195(20)	
M(2) ··· O(5)	3·29(4)	3·345(17)	2·97, 3·09 *
M(2) ··· O(7)	3·17(4)	3·388(18)	
M(2) ··· O(17)	3·02(6)	3·104(16)	
M(2) ··· O(18)	2·96(5)	3·003(16)	
M(2) ··· O(19)	2·68(5)	2·744(15)	
M(2) ··· O(20)	2·68(5)	2·842(16)	
M(2) ··· O(23)	3·44(5)	3·670(16)	
M(2) ··· O(25)	2·76(4)	2·863(18)	
M(2) ··· O(26)	2·65(5)	2·846(17)	
M(3) ··· O(3)	3·02(4)	3·026(18)	2·99, 3·07 †
M(3) ··· O(4)	2·88(4)	2·966(18)	
M(3) ··· O(7)	2·73(5)	2·863(18)	
M(3) ··· O(9)	2·90(4)	3·024(18)	
M(3) ··· O(11)	2·78(5)	2·864(18)	
M(3) ··· O(11)′	2·96(5)	2·991(18)	
M(3) ··· O(15)	3·33(6)	3·581(16)	
M(3) ··· O(17)	3·15(4)	3·275(18)	
M(4) ··· O(3)	2·82(4)	2·909(18)	2·97, 3·04 *
M(4) ··· O(4)	3·00(6)	3·062(16)	
M(4) ··· O(5)	2·94(5)	3·027(16)	
M(4) ··· O(7)	2·90(5)	2·948(17)	
M(4) ··· O(9)	3·02(6)	3·145(16)	
M(4) ··· O(11)	2·82(6)	2·962(16)	
M(4) ··· O(16)	3·24(4)	3·277(17)	
M(4) ··· O(26)	3·07(4)	3·100(18)	
M(4) ··· O(28)	2·91(4)	2·904(18)	
M(5) ··· O(1)	2·80(4)	3·004(18)	2·98, 3·07 *
M(5) ··· O(2)	2·84(5)	2·964(18)	
M(5) ··· O(6)′	2·87(4)	2·948(17)	
M(5) ··· O(6)	3·28(4)	3·266(19)	
M(5) ··· O(8)	2·63(4)	2·824(19)	
M(5) ··· O(19)	3·12(6)	3·191(17)	
M(5) ··· O(12)	2·81(5)	2·899(17)	
M(5) ··· O(25)	3·49(5)	3·556(19)	
M(5) ··· O(27)	2·98(4)	2·975(20)	
M(6) ··· O(4)	3·45(5)	3·514(17)	3·01, 3·11 ‡
M(6) ··· O(5)	2·72(4)	2·872(16)	
M(6) ··· O(8)	2·63(5)	2·794(17)	
M(6) ··· O(9)	3·00(4)	3·104(19)	
M(6) ··· O(12)	2·99(4)	3·144(18)	
M(6) ··· O(13)	3·13(6)	3·189(16)	
M(6) ··· O(16)	3·30(6)	3·398(16)	
M(6) ··· O(18)	2·78(5)	2·815(16)	
M(6) ··· O(20)	3·46(5)	3·493(17)	
M(6) ··· O(28)	2·62(5)	2·786(18)	

TABLE 7 (*Continued*)

Atoms	K salt	NH_4 salt
(*b*) H_2O–O (<3·5 Å)		
O(25) ··· O(6)	3·10(8)	3·338(18)
O(25) ··· O(6)′	2·90(6)	2·887(18)
O(25) ··· O(14)	2·88(7)	2·717(15)
O(25) ··· O(18)	3·32(5)	3·349(16)
O(25) ··· O(21)	3·42(8)	3·471(16)
O(26) ··· O(5)	2·95(8)	3·200(14)
O(26) ··· O(8)	3·75(7)	3·496(16)
O(26) ··· O(10)	3·49(5)	3·487(18)
O(26) ··· O(13)	2·72(8)	2·723(15)
O(26) ··· O(16)	2·84(5)	2·836(15)
O(26) ··· O(17)	3·22(5)	3·316(15)
O(26) ··· O(21)	3·25(6)	3·306(15)
O(27) ··· O(1)	3·42(7)	3·300(16)
O(27) ··· O(10)	3·13(7)	3·246(17)
O(27) ··· O(12)	3·19(5)	3·147(17)
O(27) ··· O(19)	2·97(7)	3·015(16)
O(28) ··· O(4)	3·61(7)	3·480(17)
O(28) ··· O(9)	3·19(7)	3·424(17)
O(28) ··· O(15)	2·67(5)	3·725(17)
O(28) ··· O(16)	3·51(6)	3·477(17)
O(28) ··· O(22)	2·80(7)	2·800(16)

* Co-ordination no. 9. † Co-ordination no. 8. ‡ Co-ordination no. 10.

octamolybdate ion $[Mo_8O_{26}]^{4-}$ suggested by Lindqvist;[29] a brief description of an independent study has appeared.[30]

Cations and Water Molecules.—(*a*) *Ammonium salt.* In structure determinations of this type, where a small number of heavy scatterers are embedded in a large number of light atoms, it is often not possible to distinguish ammonium ions from water molecules on the basis of *X*-ray scattering alone. The thermal motions of these groups are usually much greater than the larger elements of the structure, thus further obscuring their basic form factors which are already very similar. Some sort of crystal chemical criterion must then be used to distinguish them. The simplest to apply is that which requires that no two ammonium ions may approach each other closer than 3·7 Å. This is the shortest such distance in $(NH_4)_2O$,[31] and a search of ammonium-containing structures shows no distance <3·8 Å. Before the last stage of structure refinement all intermolecular sites for H_2O and $[NH_4]^+$ as recognized on the electron-density synthesis were represented by oxygen atoms in the least-squares analysis. In this case it is easily shown that only one assignment of $[NH_4]^+$ ions to these sites will satisfy the shortest-distance criterion. This assignment was used in the last stages of the least-squares analysis to find the best thermal parameters. Corresponding results are given in Table 1. The mean N–O distance varies from 3·04—3·11 Å for the six cations, overall mean 3·06 Å (see Table 7).

(*b*) *Potassium salt.* The ammonium ion positions are completely consistent with those found by the unambiguous location of the heavier potassium ions and the water molecules in the isomorphous potassium compound. The potassium ions occupy positions between the anions in irregular eight- and nine-co-ordination with oxygen. The mean K–O distances for the potassium–oxygen polyhedra are in the rather narrow range of 2·94—3·01 Å (Table 7) and compare favourably with the distances in potassium molybdate,[32] and in potassium di-,[33] tri-,[34] and tetra-molybdates.[25] The oxygen co-ordination around K(2), K(3), K(5), and K(6) is irregular eight-fold, while that of K(1) and K(4) is irregular nine-fold if a maximum K–O distance of 3·4 Å is assumed. With a distance of 3·5 Å as a maximum, the co-ordination of K(6) is ten-fold and that of K(2) and K(5) is nine-fold.

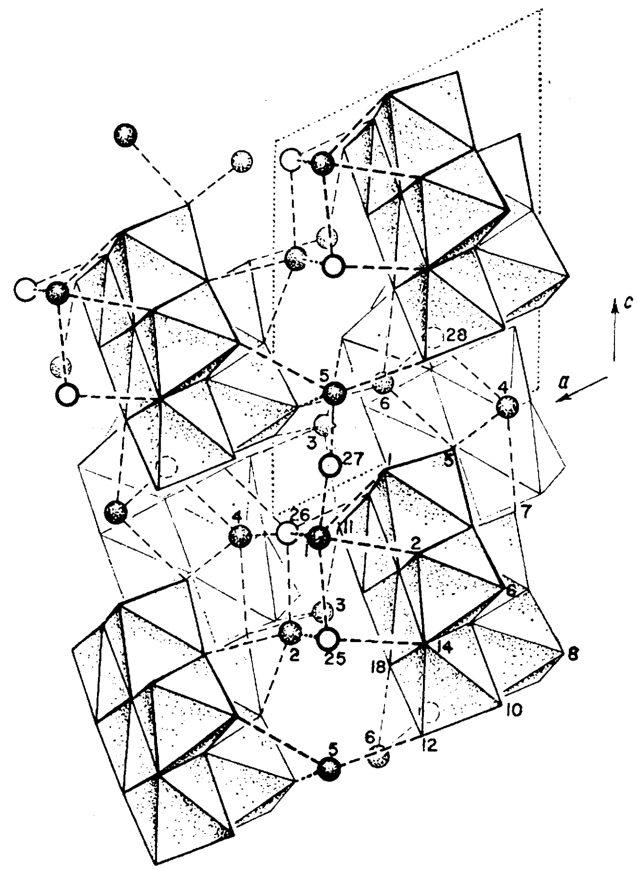

FIGURE 2 View of the crystal structure along the y axis from $y = \frac{1}{2}$ to $y = 0$. Open circles represent water molecules, shaded circles ammonium cations. The atom numbering system used for the oxygen and nitrogen atoms is shown

(*c*) *Role of cations and water molecules in the crystal structure.* The heptamolybdate molecules are assembled in layers extended normal to the y axis. In these layers the cations and water molecules serve to bind the molecules together by a complex system of ionic and hydrogen bonds. A view of one of these layers along the y axis is shown in Figure 2. In the

[29] I. Lindqvist, *Arkiv. Kemi*, 1950, **2**, 349.

[30] L. O. Atovmyan and O. N. Krasochka, *Zhur. strukt. Khim.*, 1972, **13**, 342.

[31] W. J. Seimons and D. H. Templeton, *Acta Cryst.*, 1954, **7**, 194.

[32] B. M. Gatehouse and P. Leverett, *J. Chem. Soc.* (*A*), 1969, 849.

[33] S. A. Magarill and R. F. Klevtsova, *Kristallografiya*, 1971, **16**, 4, 742.

[34] B. M. Gatehouse and P. Leverett, *J. Chem. Soc.* (*A*), 1968, 1398.

ammonium salt there is naturally much more opportunity for hydrogen-bond formation than in the potassium salt, and much of the difference in detail in the inter-cationic dimensions in the two structures must be due to the lack of the extra hydrogen atoms in the potassium salt. Several of the nitrogen atoms, such as N(2), N(3), N(5), and N(6), each have four markedly shortened distances to neighbouring oxygen atoms (2·74—3·00 Å) suggesting rather strong hydrogen bonds deployed in approximately tetrahedral arrays. We notice, however, that these same contacts are notably shorter than the average in the potassium salt also.

Thermogravimetric analysis of the potassium salt [35] indicated that two molecules of water were lost at *ca.* 115 and two at *ca.* 150 °C, which agrees with the observation that two water molecules [O(25) and O(26)] are found to ' bridge ' a pair of potassium ions lying between adjacent heptamolybdate ions while two are situated elsewhere, each bonded to a pair of cations, and are apparently not so strongly held in the structure (see Figure 2).

The molecular layers are *ca.* 9 Å thick, four lying within the *b* axis repeat unit, related to each other alternately by a glide plane and symmetry centres. There are several strong links across the glide plane, with N(3) or K(3) lying almost on the plane, forming strong bonds on both sides. On the other hand, only one such bond is formed by N(1) or K(1) in the interlayer region containing the symmetry centres. It seems likely, therefore, that the observed perfect cleavage of the crystals parallel to (010) occurs in this inter-layer region. The structure may then be considered to be made up of rigid double layers of heptamolybdate molecule ions, strongly cemented together by the cations and water molecules with a glide plane at the centre, and very weakly bound to adjacent double layers in the region of the symmetry centres.

[4/1515 *Received*, 22*nd July*, 1974]

[35] P. Leverett, Ph.D. Thesis, Monash University, 1970.