

clichés de Laue surexposés. Seul le composé $(\text{CeO})_4\text{Ga}_2\text{S}_5$ présente quelques raies diffuses qui respectent la symétrie quadratique et qui témoignent d'un début de mise en ordre des métaux et éventuellement des soufre S(1) sur leurs sites. En effet, comme nous l'avons déjà dit, les sites de S(1) sont à demi-occupés, en désordre statistique.

Ce déficit à la fois sur les sites cationiques et les sites anioniques est un phénomène rarement observé. Si les lacunes en cations M^{3+} s'expliquent raisonnablement par un encombrement stérique, celles des anions $\text{S}(1)^{2-}$ trouvent en conséquence une justification dans l'équilibre des charges de ces composés.

Conclusion

Une semblable occupation fractionnaire des sites de gallium et de ceux de soufre S(1) n'est concevable que par l'existence de feuillets (LnO) extrêmement stables et compacts, qui assurent la tenue de l'ensemble de la structure. De tels feuillets sont bien connus dans de nombreux composés des terres rares, mais, jusqu'à ce jour, leur individualité au sein d'une structure ne s'était pas manifestée aussi nettement.

En partant de cette structure, deux séries de composés peuvent être envisagées:

(1) La mise en ordre du gallium et du soufre S(1) devrait conduire à un réarrangement de leur réseau et à une maille plus grande et de plus basse symétrie. Une telle structure vient d'être observée dans les composés $(\text{LnO})_4\text{Ga}_2\text{S}_5$ formés par les éléments des terres rares qui suivent le cérium: praséodyme, néodyme, samarium. Dans le cas du néodyme (Dugué & Guittard, 1982), la maille orthorhombique a pour dimensions $a =$

18,293 (3), $b = 22,586$ (4), $c = 5,737$ (2) Å. Cette structure montre un réarrangement profond des atomes de soufre et des atomes de gallium qui occupent alors complètement leurs sites.

(2) Dans la structure lacunaire de $(\text{CeO})_4\text{Ga}_2\text{S}_5$, on peut imaginer d'introduire un nombre plus élevé d'atomes métalliques de charge plus petite. Dans cette voie, le composé $(\text{LaO})_4\text{Ga}_{3/2}\text{Ag}_{3/2}\text{S}_5$ a été préparé. Il possède, au-dessus de 743 K, une maille quadratique de groupe spatial $I4/mmm$ et, à plus basse température, une maille orthorhombique qui est une surstructure de la précédente et qui résulte sans doute d'une mise en ordre des atomes métalliques au moins.

Le feuillet (LnO) se caractérise dans cette structure, comme dans beaucoup d'autres, par des liaisons Ln—O relativement courtes, alors que les liaisons formées par les atomes Ln avec les non-métaux situés de part et d'autre du feuillet [ici les atomes de soufre S(2)] sont relativement longues si on les compare aux distances interatomiques des combinaisons purement sulfurées. Cela est sans doute lié au caractère fortement marqué de covalence des liaisons existant à l'intérieur du feuillet.

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The Structure of the Potassium Isopolymolybdate $\text{K}_8[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}].n\text{H}_2\text{O}$ ($n = 36 \dots 40$)

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Abstract

The crystal structure of $\text{K}_8[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}].36 \dots 40\text{H}_2\text{O}$ has been determined from three-dimensional X-ray diffraction data. The crystals are monoclinic.

space group $P2_1/c$, with cell dimensions $a = 16.550$ (4), $b = 18.810$ (3), $c = 27.730$ (5) Å, $\beta = 116.82$ (2)° for the crystal investigated, and $Z = 2$. Cascade-block least-squares refinement of positional and mostly anisotropic thermal parameters based on

12 318 independent reflexions resulted in a final R value of 0.057. The novel centrosymmetric ring-like $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{8-}$ ion with approximate $2/m$ symmetry is precipitated from moderately acidified molybdate solutions (acidity $Z = 1.8\text{--}2.0$) as the largest discrete isopolymolybdate known to date. Its unusual structure contains features typical of isopolymolybdates precipitating from less acidified solutions (*i.e.* compact groups of edge-sharing MoO_6 octahedra) as well as those of the polymeric compounds obtained from strongly acidic solutions (*i.e.* groups of corner-sharing MoO_6 octahedra forming three- and four-membered 'rings', and H_2O molecules coordinated to Mo atoms). Other features novel for isopolymolybdate structures include four of the 16 ligand H_2O molecules being coordinated to two Mo atoms simultaneously, and pentagonal bipyramidal MoO_7 polyhedra. The system of K^+ ions and H_2O molecules not coordinated to Mo is partly disordered.

Introduction

A number of different isopolymolybdates have been identified in moderately acidified aqueous solutions. The degrees of aggregation and the compositions of the solute species and of the solid compounds isolated from the solutions are essentially functions of the acidities of the aqueous systems. Since the pioneering single-crystal work of Lindqvist (1950*a,b*) who was able to determine the molecular structures of the heptamolybdate and octamolybdate ions in $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26}\cdot 5\text{H}_2\text{O}$, several other isopolymolybdates were characterized by X-ray crystal analyses.

The species isolated from solutions with acidities $Z = 1.14\text{--}1.67$ ($Z =$ molar ratio of reacted H^+ ions to initially present MoO_4^{2-} ions; see Tytko & Glemser, 1976; Tytko & Schönfeld, 1975) include $\text{Mo}_6\text{O}_{19}^{2-}$ in $[\text{HN}_3\text{P}_3\{\text{N}(\text{CH}_3)_2\}_6]_2\text{Mo}_6\text{O}_{19}$ (Allcock, Bissell & Shawl, 1973), $\text{Mo}_7\text{O}_{24}^{6-}$ in $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $\text{K}_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Lindqvist, 1950*a*; Evans, Gatehouse & Leverett, 1975), in $\text{Na}_6\text{Mo}_7\text{O}_{24}\cdot 14\text{H}_2\text{O}$ (Sjöbom & Hedman, 1973) and in $[\text{C}(\text{NH}_2)_3]_6(\text{Mo}_7\text{O}_{24})\cdot \text{H}_2\text{O}$ (Don & Weakley, 1981), $\text{Mo}_8\text{O}_{26}^{4-}$ in $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26}\cdot 5\text{H}_2\text{O}$ (Lindqvist, 1950*b*; Gatehouse, 1977) and in $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26}\cdot 4\text{H}_2\text{O}$ (Atovmyan & Krasochka, 1972; Vivier, Bernard & Djomaa, 1977), the second isomer of $\text{Mo}_8\text{O}_{26}^{4-}$ in $[\text{N}(\text{C}_4\text{H}_9)_4]_4\text{Mo}_8\text{O}_{26}$ (Fuchs & Hartl, 1976; Day, Fredrich, Klemperer & Shum, 1977), $(\text{Mo}_8\text{O}_{27})_n$ in $(\text{NH}_4)_6\text{Mo}_7\text{O}_{27}\cdot 4\text{H}_2\text{O}$ (Glemser, Wagner, Krebs & Tytko, 1970; Böschchen, Buss, Krebs & Glemser, 1973; Böschchen, Buss & Krebs, 1974), $[\text{Mo}_8\text{O}_{26}(\text{OH})_2]^{6-}$ in $(\text{C}_3\text{H}_{10}\text{N})_6[\text{Mo}_8\text{O}_{26}(\text{OH})_2]\cdot 2\text{H}_2\text{O}$ (Isobe, Marumo, Yamase & Ikawa, 1978), $\text{Mo}_{10}\text{O}_{34}^{8-}$ in $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ (Fuchs, Hartl, Hunnius & Mahjour, 1975), and $(\text{Mo}_2\text{O}_7^{2-})_n$ in $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ (Knöpnadel, Hartl, Hunnius & Fuchs, 1974).

They contain, as the most characteristic structural feature, compact groups of predominantly edge-sharing MoO_6 octahedra.

From strongly acidic solutions in which the poly-anion structures are broken down, a different group of polymeric compounds can be crystallized. They are exemplified by $\text{KMo}_5\text{O}_{15}(\text{OH})(\text{H}_2\text{O})_2$ (Krebs & Paulat-Böschchen, 1976), $\text{NaMo}_5\text{O}_{15}(\text{OH})(\text{H}_2\text{O})_2$ (Hedman & Strandberg, 1978), $\alpha\text{-MoO}_3\cdot \text{H}_2\text{O}$ (Böschchen & Krebs, 1974; Oswald, Günter & Dubler, 1975), and $\text{MoO}_3\cdot 2\text{H}_2\text{O}$ (Krebs, 1969, 1970, 1972; Åsbrink & Brandt, 1971) and contain, as structural features, polymeric nets of corner-sharing MoO_6 octahedra forming three- and four-membered 'rings', and H_2O molecules coordinated to Mo atoms.

If the solutions are slightly less acidic than necessary for obtaining the polymeric products ($Z = 1.8$), previous investigations suggested the existence of a large discrete isopolymolybdate for which formulae such as $\text{H}_7\text{Mo}_{24}\text{O}_{78}^{5-}$ (Jander, Jahr & Heukeshoven, 1930), $\text{Mo}_{19}\text{O}_{59}^{4-}$ and $\text{Mo}_{18}\text{O}_{56}^{4-}$ (Sasaki & Sillén, 1968) were put forward. In the course of Glemser's extensive studies on the reactions in acidified molybdate and tungstate solutions (*e.g.* Glemser, Holznagel, Höljtje & Schwarzmann 1965; Glemser, Holznagel & Ali, 1965; Glemser & Tytko, 1969; Tytko & Glemser, 1970), Tytko, Schönfeld, Buss & Glemser (1973) showed from a careful analysis of ultracentrifuge molecular weight measurements, of Raman spectra, of potentiometric equilibrium curves and of X-ray lattice parameters, the macro-isopolyanion to be a 36-molybdate and proposed the formula $\text{Na}_8\text{Mo}_{36}\text{O}_{112}\cdot 80\text{H}_2\text{O}$ for the sodium salt. To prove the existence and to define the structure of this 36-molybdate, which is supposed to be the largest isopolyanion known, we prepared the potassium salt (Böschchen, 1974) and determined its crystal structure from single-crystal diffractometer data. Preliminary reports on the novel structure have been given by us earlier (Paulat-Böschchen, 1979; Krebs & Paulat-Böschchen, 1979).

Experimental

The compound was prepared by the reaction of equal volumes of 0.2 M aqueous K_2MoO_4 solution and 0.4 M aqueous HNO_3 at room temperature. Colourless, transparent columnar crystals of $\text{K}_8[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]\cdot 36 \dots 40\text{H}_2\text{O}$ separated from the solution after 3–6 days. Chemical analysis: found: K 5.0% (by flame photometry), Mo 53.1% (by atomic absorption), H_2O 14.8% (by thermogravimetry; constant weight reached at 593 K); calculated for $\text{K}_8[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]\cdot 37\text{H}_2\text{O}$ ($M_r = 6513.40$): K 4.80, Mo 53.03, H_2O 14.66%. If the crystals are isolated from the solution, they rapidly lose part of the hydrate water.

Therefore, it was not possible to determine precisely their water content by chemical analysis. For all X-ray investigations, the crystals were sealed in Mark capillaries together with a drop of mother liquor. Even with these precautions the unit-cell dimensions vary significantly from crystal to crystal due to slightly different contents of non-coordinated H_2O molecules, and the location of some of the very poorly ordered ones was difficult (see below).

$K_8[Mo_{36}O_{112}(H_2O)_{16}] \cdot 36 \dots 40H_2O$ crystallizes in the monoclinic system. For the crystal investigated here, the unit-cell dimensions (see *Abstract*) were obtained from least-squares refinement of four-circle diffractometer coordinates of 20 reflexions at 293 K. All results given in this paper refer to these values. Typical cell dimensions for a different crystal [the one which we used for the preliminary investigations (Paulat-Böschchen, 1979)] are: $a = 16.436$ (4), $b = 18.739$ (3), $c = 27.651$ (5) Å, $\beta = 117.00$ (2)°, $V = 7588$ Å³. This indicates an additional loss of about six of the labile H_2O molecules per cell compared to the first crystal. From systematic absences observed on Weissenberg and precession photographs ($h0l$ with $l \neq 2n$ and $0k0$ with $k \neq 2n$), the space group was determined to be $P2_1/c$. An experimental density of $D_m = 2.81$ (1) g cm⁻³ was measured pycnometrically which compares to an X-ray density of $D_c = 2.81$ g cm³ for a cell content of two formula units of $K_8[Mo_{36}O_{112}(H_2O)_{16}] \cdot 37H_2O$.

For the structure determination a complete set of non-equivalent X-ray diffraction data in the range up to $(\sin \theta)/\lambda = 0.64$ Å⁻¹ was collected on a Syntex $P2_1$ diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å, 2θ - θ scan, scan width 2.0° in $2\theta + \alpha_1 - \alpha_2$ separation, intensity-dependent scan speed between 3 and 30° min⁻¹ in 2θ , parallel graphite monochromator), using a clear crystal of size 0.30 × 0.24 × 0.22 mm. No deterioration of the crystal occurred during data collection as shown by three reference reflexions measured every 150 reflexions. The data were reduced by Lorentz-polarization-factor corrections. An absorption correction was not necessary ($\mu = 31.0$ cm⁻¹). From the total of 17 980 reflexions measured, 12 318 were statistically above background on the basis that $I > 1.96 \sigma(I)$ and were used for the structure determination and the refinements.

Structure determination and refinement

The structure could be solved by multiresolution direct methods, using the *MULTAN* program system (Germain, Main & Woolfson, 1971) (*XTL* version) with a restricted preliminary set of 6156 reflexions up to $(\sin \theta)/\lambda = 0.46$ Å⁻¹. From the E map calculated with the 468 phases of the best set, 14 out of the 18 Mo

atoms could be located; all other atomic positions were obtained from subsequent difference Fourier maps.

The structure was refined by least-squares methods, at the full-matrix isotropic refinement stage, using the Syntex *EXTL* (1976) program system. The final refinement with anisotropic temperature factors for most of the atoms except K(5), K(6) and O(w16) to O(w36) was with the block-diagonal least-squares program incorporated in the *SHELXTL* system (Sheldrick, 1979). In the final cycles, 946 variables were refined in blocks of 55. The expression minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on the statistical variances of the counting rates. The atomic scattering factors for Mo, K and O were taken from *International Tables for X-ray Crystallography* (1974). Account was taken of the real part of the anomalous dispersion. The final difference Fourier map did not show significant features above 0.6 e Å⁻³. There were clear indications for some of the H atoms in the difference map. However, as no complete set could be obtained, no H atoms were included in the structural model. The final R factors were $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o| = 0.057$, $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.055$. All calculations were made on a Data General Eclipse Computer, using programs of the Syntex *EXTL* and the Sheldrick *SHELXTL* systems.

In the structure the $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ion, including the coordinated water molecules and part of the cation-water system, is very well defined, and all the positional and thermal parameters could be obtained with considerable precision. In contrast, part of the cation-water system (H_2O molecules not coordinated to Mo) is much less well defined, and the structural model could only be completed by including partial occupancy factors for some of the disordered K⁺ ions and water molecules. This situation is in accordance with the easy loss of crystal water observed macroscopically, and it is reminiscent of many other macromolecules with very low or no charge density on the molecular surface, resulting in a 'quasi-liquid' structure of the very weakly bonded hydrate water molecules. In the cation-water system it was difficult to distinguish initially between partly occupied K⁺ sites and fully occupied O sites because of the very similar K-O and O-O distances. However, from electron density maps during the later stages of refinement, electron density integration over a sphere of radius 1.4 Å clearly indicated the K⁺ sites. The formal occupancy factors for the K⁺ ions (neutral-K form factors) were refined together with the other variables and were found to be about 0.66 (2) for K(2), K(3) and K(4), 0.57 (3) for K(5a), K(5b) and K(5c), and 0.44 (3) for K(6a), K(6b) and K(6c) each; no destructive correlation to the temperature parameters was observed. Assuming that the space left in the partly vacant K⁺ sites is occupied by H_2O molecules, the rounded occupational factors given in Table 1 for the

Table 1. $K_8[Mo_3O_{12}(H_2O)_{16}] \cdot nH_2O$ ($n = 36 \dots 40$):
coordinates of the atoms and equivalent isotropic
thermal parameters B_{eq} (\AA^2)

The B_{eq} values are calculated as one third of the orthogonalized B_{ij}
tensor: $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	B_{eq}
Mo(1)	0.74779 (7)	0.48025 (5)	0.03680 (4)	2.3
Mo(2)	0.59091 (7)	0.43876 (5)	0.08974 (4)	2.3
Mo(3)	0.95486 (7)	0.36806 (5)	0.09683 (4)	2.3
Mo(4)	0.73034 (6)	0.28596 (5)	0.08337 (4)	1.7
Mo(5)	0.58175 (6)	0.24554 (5)	-0.03878 (4)	1.7
Mo(6)	0.64218 (8)	0.28614 (5)	0.15569 (4)	2.6
Mo(7)	0.14471 (7)	0.23249 (5)	0.16659 (4)	2.2
Mo(8)	0.92824 (6)	0.20640 (5)	0.14026 (4)	1.7
Mo(9)	0.79172 (6)	0.16569 (5)	0.01120 (4)	1.5
Mo(10)	0.62442 (6)	0.12445 (5)	0.11004 (4)	1.6
Mo(11)	0.69650 (7)	0.11021 (5)	0.20505 (4)	2.0
Mo(12)	0.28693 (6)	0.07822 (5)	0.24078 (4)	1.7
Mo(13)	0.03092 (6)	0.05154 (5)	0.15275 (4)	1.8
Mo(14)	0.77932 (6)	0.07751 (5)	0.11702 (4)	1.7
Mo(15)	0.63062 (6)	0.03806 (5)	0.00519 (4)	1.6
Mo(16)	0.71969 (6)	-0.03277 (5)	0.10297 (4)	1.7
Mo(17)	0.89253 (7)	0.11028 (5)	0.13423 (4)	2.1
Mo(18)	0.73721 (7)	0.15086 (5)	0.00846 (4)	2.1
O(1)	0.7800 (6)	0.5478 (4)	0.0076 (4)	3.6
O(2)	0.6327 (6)	0.5066 (4)	0.1113 (3)	3.5
O(3)	0.7274 (6)	0.5179 (4)	0.0856 (3)	3.4
O(4)	0.6227 (5)	0.4721 (4)	0.0171 (3)	2.5
O(5)	0.4776 (5)	0.4549 (4)	-0.1166 (3)	2.9
O(6)	0.7107 (5)	0.3733 (4)	0.0621 (3)	2.3
O(7)	0.8641 (5)	0.4361 (4)	0.0761 (3)	3.0
O(8)	0.5715 (5)	0.3367 (4)	-0.0516 (3)	2.2
O(9)	0.5948 (6)	0.3662 (4)	0.1377 (3)	2.9
O(10)	0.0514 (6)	0.4151 (4)	0.1155 (4)	3.7
O(11)	0.9349 (6)	0.3357 (5)	0.0354 (4)	3.5
O(12)	0.7544 (6)	0.2966 (5)	-0.1130 (5)	4.9
O(13)	0.6325 (8)	0.3062 (5)	-0.2174 (4)	5.0
O(14)	0.0182 (5)	0.2760 (4)	0.1378 (3)	2.4
O(15)	0.8614 (5)	0.2973 (4)	0.1077 (3)	2.0
O(16)	0.6094 (5)	0.2289 (4)	0.1010 (3)	1.9
O(17)	0.6472 (5)	0.1777 (4)	-0.1648 (3)	2.5
O(18)	0.7237 (5)	0.2849 (4)	0.1425 (3)	2.6
O(19)	0.6167 (5)	0.2432 (4)	0.0371 (3)	2.0
O(20)	0.4751 (5)	0.2152 (4)	0.0618 (3)	2.8
O(21)	0.7378 (4)	0.2547 (4)	0.0055 (3)	1.6
O(22)	0.9318 (5)	0.2211 (4)	0.2005 (3)	2.4
O(23)	0.7908 (4)	0.1833 (3)	0.0959 (3)	1.7
O(24)	0.6353 (4)	0.1413 (4)	0.0341 (3)	1.6
O(25)	0.5138 (5)	0.1083 (4)	-0.1432 (3)	2.1
O(26)	0.1992 (6)	0.3115 (4)	0.1806 (4)	3.9
O(27)	0.1385 (6)	0.2102 (5)	0.1063 (3)	3.7
O(28)	0.9062 (5)	0.1839 (4)	0.0523 (3)	2.2
O(29)	0.7781 (5)	0.1508 (4)	-0.0532 (3)	1.9
O(30)	0.8078 (5)	0.1189 (5)	-0.1636 (4)	3.8
O(31)	0.6788 (6)	0.1708 (4)	-0.2548 (3)	3.3
O(32)	0.7646 (5)	0.1028 (5)	0.1713 (3)	2.8
O(33)	0.6524 (5)	0.0751 (4)	0.0637 (3)	2.0
O(34)	0.5167 (5)	0.0383 (4)	0.0371 (3)	2.4
O(35)	0.2303 (5)	0.1689 (4)	0.2122 (3)	2.2
O(36)	0.0450 (5)	0.1573 (4)	0.1638 (3)	1.9
O(37)	0.9081 (5)	0.1017 (4)	0.1401 (3)	2.0
O(38)	0.7778 (5)	0.0747 (3)	0.0354 (3)	1.6
O(39)	0.6591 (5)	0.0334 (3)	-0.0675 (3)	1.7
O(40)	0.6678 (5)	0.0565 (4)	0.1472 (3)	1.8
O(41)	0.3094 (5)	0.0232 (4)	0.2376 (3)	2.1
O(42)	0.1466 (5)	0.0388 (4)	0.1874 (3)	2.3
O(43)	0.3969 (5)	0.1066 (4)	0.2659 (3)	3.1
O(44)	0.2664 (6)	0.0734 (4)	0.2957 (3)	3.2
O(45)	0.2780 (5)	0.0738 (4)	0.1579 (3)	2.5
O(46)	0.0104 (6)	0.0500 (4)	0.0869 (3)	3.0
O(47)	0.8257 (5)	0.0012 (4)	0.0667 (3)	2.7
O(48)	0.9798 (5)	0.0337 (4)	0.1572 (3)	2.5
O(49)	0.8063 (5)	0.0124 (4)	0.1270 (3)	2.0
O(50)	0.6634 (5)	0.0496 (4)	0.0115 (3)	2.0
O(51)	0.7174 (5)	-0.1049 (4)	-0.0576 (3)	2.2
O(52)	0.8918 (6)	-0.1322 (4)	0.1939 (3)	3.7
O(53)	0.7769 (5)	-0.1460 (4)	0.0843 (3)	2.6
O(54)	0.6415 (6)	0.1990 (4)	0.0103 (3)	3.4
O(55)	0.9573 (6)	-0.1731 (4)	0.1247 (4)	3.6
O(56)	0.8123 (6)	-0.2111 (4)	0.0089 (3)	3.5
O(w1)	0.7430 (6)	0.4028 (5)	-0.0328 (3)	3.2
O(w2)	0.9741 (6)	0.3945 (5)	0.1831 (3)	3.6
O(w3)	0.4872 (7)	0.2550 (5)	-0.2084 (4)	4.8
O(w4)	0.1394 (6)	0.2578 (5)	0.2491 (3)	3.6
O(w5)	0.5352 (6)	0.0961 (6)	0.2540 (4)	4.3

Table 1 (cont.)

	x	y	z	B_{eq} (\AA^2) [†]	
O(w6)	0.0447 (6)	0.0551 (4)	0.2413 (3)	3.0	
O(w7)	0.5668 (5)	0.0680 (4)	0.1480 (3)	3.1	
O(w8)	0.8606 (5)	-0.0647 (4)	0.0450 (3)	2.6	
K(1)	1.0 [‡]	0.6603 (3)	0.4364 (2)	0.1497 (2)	4.7
K(2)	0.5	0.3549 (3)	0.3963 (3)	0.3806 (2)	4.3
K(3)	0.5	0.3568 (5)	0.1496 (4)	0.3952 (3)	6.8
K(4)	0.5	0.0267 (5)	0.2372 (4)	0.0020 (3)	7.2
K(5a)		0.5929 (12)	0.2204 (7)	0.1738 (5)	6.2 (5)
K(5b)	1.0	0.6457 (11)	0.2000 (7)	0.1908 (5)	4.7 (4)
K(5c)		0.7377 (10)	0.2003 (8)	0.2314 (6)	5.3 (5)
K(6a)		0.2352 (9)	0.4445 (9)	0.1519 (9)	4.3 (5)
K(6b)	0.5	0.2327 (11)	0.4289 (11)	0.1305 (14)	3.2 (5)
K(6c)		0.2191 (16)	0.4184 (13)	0.1052 (16)	4.7 (6)
O(w9)	1.0	0.8447 (8)	0.4198 (7)	0.2180 (5)	6.7
O(w10)	1.0	0.3439 (8)	0.2652 (7)	0.3211 (5)	7.4
O(w11)	1.0	0.0006 (7)	0.4136 (6)	0.4808 (4)	5.4
O(w12)	1.0	0.5204 (7)	0.1238 (6)	0.0913 (4)	4.9
O(w13)	1.0	0.5355 (6)	0.0370 (6)	0.2548 (4)	4.6
O(w14)	1.0	0.9160 (7)	0.0097 (6)	0.2685 (5)	5.7
O(w15)	1.0	0.8506 (9)	0.0512 (7)	0.4254 (6)	7.6
O(w16)	0.5	0.1213 (10)	0.1610 (8)	0.3160 (7)	8.5 (7)
O(w17)	0.5	0.5109 (11)	0.4209 (10)	0.0286 (7)	6.5 (6)
O(w18)	0.5	0.5134 (13)	0.3544 (11)	0.1389 (8)	4.7 (5)
O(w19)	0.5	0.2568 (12)	0.4435 (9)	0.2711 (8)	5.1 (5)
O(w20)	0.5	0.6227 (17)	0.0200 (13)	0.1752 (10)	6.2 (5)
O(w21)	0.5	0.6839 (19)	0.0074 (15)	0.2203 (12)	8.1 (7)
O(w22)	0.5	0.1118 (20)	0.3588 (16)	0.0236 (12)	8.8 (7)
O(w23)	0.5	0.8887 (26)	0.1179 (22)	0.3363 (16)	13.5 (13)
O(w24)	0.5	0.3820 (25)	0.3423 (19)	0.0130 (14)	12.0 (10)
O(w25)	0.5	0.9182 (12)	0.2867 (10)	0.4202 (7)	3.3 (4)
O(w26)	0.5	0.9196 (17)	0.2568 (14)	0.3980 (10)	6.6 (6)
O(w27)	0.5	0.4288 (20)	0.2153 (15)	0.1785 (11)	6.6 (6)
O(w28)	0.5	0.3770 (27)	0.2313 (21)	0.1681 (16)	11.4 (12)
O(w29)	0.5	0.7036 (16)	0.0510 (13)	0.2639 (10)	6.0 (6)
O(w30)	0.5	0.7150 (25)	0.0286 (20)	0.3001 (15)	11.1 (10)
O(w31)	0.5	0.2893 (21)	0.3181 (17)	0.0883 (12)	9.6 (9)
O(w32)	0.5	0.3747 (29)	0.3539 (23)	0.2260 (17)	14.7 (14)
O(w33)	0.5	0.0308 (27)	0.0482 (22)	0.4827 (16)	13.7 (13)
O(w34)	0.33	0.8054 (35)	0.1937 (29)	0.2651 (20)	10.5 (15)
O(w35)	0.33	0.8559 (30)	0.2502 (26)	0.2767 (17)	7.9 (11)
O(w36)	0.33	0.8828 (18)	0.2964 (15)	0.2741 (10)	3.2 (5)

[†] The atoms K(5a)–K(6c) and O(w16)–O(w36) were refined with isotropic temperature factors.

[‡] For the atoms K(1)–K(6c) and O(w9)–O(w36) the site occupancy factors are given.

K^+ ions are very probably close to reality. The partial occupancy factors for the water molecules were not refined. They were obtained from electron density observations in the Fourier and difference Fourier maps and/or from space requirements. The coordinates given for the cation–water system result in a consistent set of interatomic distances. For the crystal investigated the number of H_2O molecules not coordinated to Mo adds up to 37 per formula unit [including 3/2 water molecules at or near the partly vacant K(2), K(3) and K(4) sites which are not included in Table 1]. It should represent reasonably well the true water content, as indicated by the final difference Fourier map.

In Table 1 the final positional parameters of all atoms are listed together with the equivalent isotropic temperature factors calculated from the refined anisotropic thermal parameters. For K(5), K(6) and O(w16) through O(w36) the refined isotropic values are given.*

* Lists of structure factors, of anisotropic thermal parameters and of the O–Mo–O and Mo–O–Mo bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36730 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the list the oxygen atoms O(1) to O(56) and the Mo-coordinated water molecules O(w1) to O(w8) are part of the anion, the water molecules O(w9) to O(w36) are part of the poorly ordered cation hydrate system without direct contact to Mo.

Description and discussion of the structure

The crystal structure consists of an arrangement of discrete $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ macro-isopolyanions separated by a system of hydrated K^+ ions and additional H_2O molecules. The novel and unexpected structure of the 36-molybdate ion in $K_8[Mo_{36}O_{112}(H_2O)_{16}] \cdot 36 \dots 40H_2O$ differs considerably from previous proposals. It consists of two 18-molybdate subunits related to each other by a centre of inversion, the subunits being connected *via* four common O atoms O(35), O(41), O(42) and O(45) to form an elongated 'ring' around the *b* axis. In Fig. 1 the complete $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ion is shown; Fig. 2 gives one half of the anion with the numbering of the atoms. The arrangement of the anions in the unit cell is drawn in Fig. 3. In Table 2 the Mo—O and Mo...Mo interatomic distances of the 36-molybdate anion are listed. As the symmetry of the $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ion (which is exactly $\bar{1}$) is very close to $2/m$, all bond data related by this pseudo mirror plane are written in one line in pairs in Table 2. The atoms Mo(9), O(4), O(19), O(21), O(33), O(38), O(53), O(w1) and O(w8) are situated on this pseudo mirror plane. If the linking polyhedra around Mo(12) and Mo(12') are ignored, additional approximate partial mirror planes perpendicular to the first are present in each of the remaining

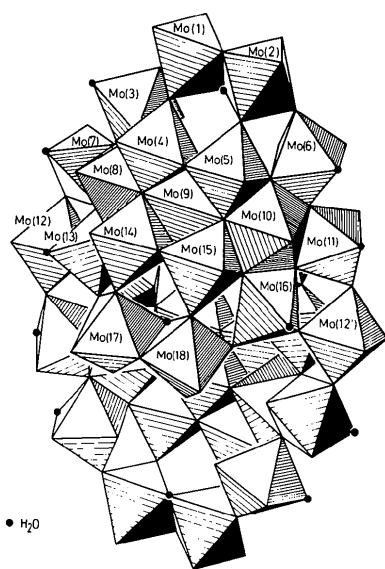


Fig. 1. $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ anion.

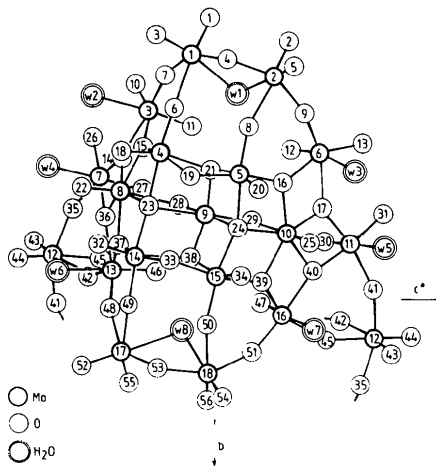


Fig. 2. Asymmetric unit (one half) of the $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ anion in the same orientation as in Fig. 1 with atomic numbering. To indicate the connexion principle of the two halves of the centrosymmetric 36-isopolyanion, the linking polyhedron around Mo(12) is drawn twice.

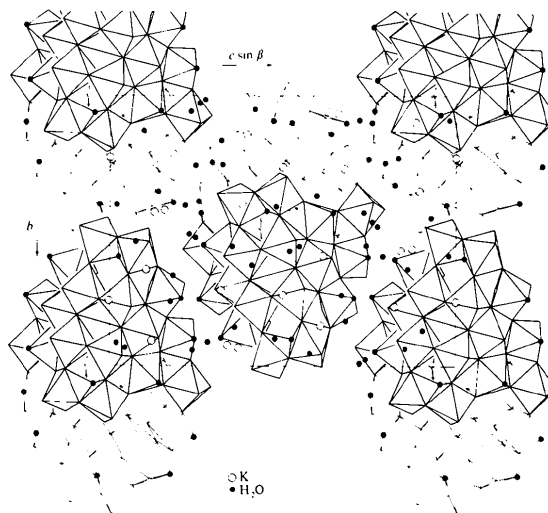
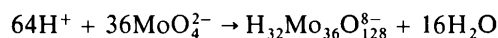


Fig. 3. Unit cell of the $K_8[Mo_{36}O_{112}(H_2O)_{16}] \cdot 36 \dots 40H_2O$ structure projected parallel to $[100]$. For the sake of clarity, not all of the non-coordinating hydrate H_2O molecules are included. $K(5a.b.c)$ and $K(6a.b.c)$ are drawn each as one symbol only.

17-molybdate fragments. They pass through Mo(7), Mo(8), Mo(9), Mo(10), Mo(11), O(22), O(23), O(24), O(25), O(27), O(28), O(29), O(30), O(w4) and O(w5).

The formal stoichiometric equation describing the formation of the 36-molybdate in solution is



so that the Z^+ value defined as the ratio of the stoichiometric coefficients p and q to the left side of the equation is $Z^+ = p/q = 1.78$. The structure of the 36-molybdate anion clearly reflects the intermediate conditions of acidification used in preparing the

Table 2. Mo—O bond lengths and Mo···Mo interatomic distances (Å), with standard deviations

Mo—O bond lengths (*E*: terminal oxygen; *D*, *T*, *Q*: oxygen bonded to two, three, and four Mo, respectively)

Mo(1)—O(1)	1.715 (10)	<i>E</i>
Mo(1)—O(3)	1.691 (11)	<i>E</i>
Mo(1)—O(4)	1.937 (7)	<i>D</i>
Mo(1)—O(7)	1.921 (7)	<i>D</i>
Mo(1)—O(6)	2.303 (8)	<i>D</i>
Mo(1)—O(<i>w</i> 1)	2.391 (9)	<i>D</i>
Mo(3)—O(10)	1.690 (9)	<i>E</i>
Mo(3)—O(11)	1.696 (10)	<i>E</i>
Mo(3)—O(7)	1.856 (8)	<i>D</i>
Mo(3)—O(14)	2.077 (7)	<i>T</i>
Mo(3)—O(15)	2.163 (8)	<i>T</i>
Mo(3)—O(<i>w</i> 2)	2.320 (10)	<i>E</i>
Mo(4)—O(18)	1.693 (9)	<i>E</i>
Mo(4)—O(6)	1.726 (7)	<i>D</i>
Mo(4)—O(19)	1.911 (7)	<i>D</i>
Mo(4)—O(15)	1.971 (8)	<i>T</i>
Mo(4)—O(23)	2.130 (7)	<i>Q</i>
Mo(4)—O(21)	2.295 (8)	<i>T</i>
Mo(7)—O(26)	1.689 (8)	<i>E</i>
Mo(7)—O(27)	1.682 (10)	<i>E</i>
Mo(7)—O(35)	1.849 (6)	<i>D</i>
Mo(7)—O(14)	2.045 (8)	<i>T</i>
Mo(7)—O(36)	2.148 (8)	<i>T</i>
Mo(7)—O(<i>w</i> 4)	2.377 (11)	<i>E</i>
Mo(8)—O(22)	1.668 (9)	<i>E</i>
Mo(8)—O(14)	2.007 (8)	<i>T</i>
Mo(8)—O(15)	2.015 (7)	<i>T</i>
Mo(8)—O(36)	1.969 (7)	<i>T</i>
Mo(8)—O(37)	1.998 (7)	<i>T</i>
Mo(8)—O(23)	2.085 (6)	<i>Q</i>
Mo(8)—O(28)	2.335 (9)	<i>D</i>
Mo(9)—O(28)	1.749 (6)	<i>D</i>
Mo(9)—O(21)	1.869 (7)	<i>T</i>
Mo(9)—O(38)	1.890 (7)	<i>T</i>
Mo(9)—O(23)	2.377 (8)	<i>Q</i>
Mo(13)—O(46)	1.700 (9)	<i>E</i>
Mo(13)—O(42)	1.728 (7)	<i>D</i>
Mo(13)—O(48)	1.843 (8)	<i>D</i>
Mo(13)—O(36)	2.010 (7)	<i>T</i>
Mo(13)—O(37)	2.121 (8)	<i>T</i>
Mo(13)—O(<i>w</i> 6)	2.363 (9)	<i>E</i>
Mo(14)—O(32)	1.699 (10)	<i>E</i>
Mo(14)—O(49)	1.740 (7)	<i>D</i>
Mo(14)—O(33)	1.949 (6)	<i>D</i>
Mo(14)—O(37)	1.982 (8)	<i>T</i>
Mo(14)—O(23)	2.108 (7)	<i>Q</i>
Mo(14)—O(38)	2.252 (8)	<i>T</i>
Mo(17)—O(52)	1.710 (10)	<i>E</i>
Mo(17)—O(55)	1.694 (10)	<i>E</i>
Mo(17)—O(48)	1.933 (7)	<i>D</i>
Mo(17)—O(53)	1.908 (7)	<i>D</i>
Mo(17)—O(49)	2.282 (7)	<i>D</i>
Mo(17)—O(<i>w</i> 8)	2.440 (8)	<i>D</i>
Mo(12)—O(43)	1.714 (8)	<i>E</i>
Mo(12)—O(44)	1.705 (11)	<i>E</i>
Mo(12)—O(35)	1.936 (7)	<i>D</i>
Mo(12)—O(41)	1.954 (7)	<i>D</i>
Mo(12)—O(42)	2.243 (6)	<i>D</i>
Mo(12)—O(45)	2.237 (9)	<i>D</i>

Mo···Mo distances (standard deviations 0.002 Å)

Mo(1)···Mo(2)	3.383
Mo(1)···Mo(3)	3.718
Mo(1)···Mo(4)	3.930
Mo(3)···Mo(4)	3.883
Mo(3)···Mo(7)	3.825
Mo(3)···Mo(8)	3.372
Mo(4)···Mo(5)	3.245
Mo(4)···Mo(8)	3.285
Mo(4)···Mo(9)	3.463
Mo(4)···Mo(14)	4.027
Mo(7)···Mo(8)	3.354
Mo(7)···Mo(12)	3.718
Mo(7)···Mo(13)	3.824
Mo(8)···Mo(9)	3.347
Mo(8)···Mo(13)	3.311
Mo(2)···Mo(6)	3.702
Mo(2)···Mo(5)	3.931
Mo(6)···Mo(5)	3.886
Mo(6)···Mo(11)	3.840
Mo(6)···Mo(10)	3.358
Mo(5)···Mo(10)	3.302
Mo(5)···Mo(9)	3.451
Mo(5)···Mo(15)	4.008
Mo(11)···Mo(10)	3.357
Mo(11)···Mo(12)	3.724
Mo(11)···Mo(16)	3.796
Mo(10)···Mo(9)	3.342
Mo(10)···Mo(16)	3.315

Table 2 (*cont.*)

Mo(8)···Mo(14)	3.307	Mo(10)···Mo(15)	3.292
Mo(9)···Mo(14)	3.456	Mo(9)···Mo(15)	3.462
Mo(12)···Mo(13)	3.851	Mo(12)···Mo(16)	3.869
Mo(13)···Mo(14)	3.852	Mo(16)···Mo(15)	3.861
Mo(13)···Mo(17)	3.703	Mo(16)···Mo(18)	3.709
Mo(14)···Mo(15)	3.250		
Mo(14)···Mo(17)	3.925	Mo(15)···Mo(18)	3.909
Mo(17)···Mo(18)	3.356		

compound, between those for typical isopoly-molybdates (low acidification) and those for the polymeric compounds obtained in more strongly acidic solutions. Structural features of both types of compounds are present in the 36-molybdate. Thus, the two halves of the anion each contain one compact group of five predominantly edge-sharing MoO₆ octahedra [octahedra centred at Mo(4), Mo(5), Mo(9), Mo(14) and Mo(15)], characteristic of polymolybdate structures such as the hepta- and octamolybdates. On the other hand, groups of corner-sharing octahedra forming rings of three or four of them, and H₂O molecules coordinated directly to molybdenum, are observed in the present ion, and are characteristic of the polymeric compounds. The 36-molybdate contains in each half six three-membered rings of corner-sharing octahedra [groups of octahedra centred at Mo(1)—Mo(3)—Mo(4), Mo(2)—Mo(5)—Mo(6), Mo(7)—Mo(12)—Mo(13), Mo(11)—Mo(12')—Mo(16), Mo(13)—Mo(14)—Mo(17) and Mo(15)—Mo(16)—Mo(18)]. Such groups are also found, for example, as part of the polymeric anion structure of the so-called 'decamolybdates' KMo₅O₁₅·(OH)(H₂O)₂ (Krebs & Paulat-Böschen, 1976) and NaMo₅O₁₅(OH)(H₂O)₂ (Hedman & Strandberg, 1978) which crystallize either on addition of slightly more acid to the solution or by raising the temperature to 313 K. In addition, two 'rings' of four corner-sharing MoO₆ octahedra are contained in each 18-molybdate subunit of the 36-molybdate [octahedra around Mo(1)—Mo(2)—Mo(4)—Mo(5) and Mo(14)—Mo(15)—Mo(17)—Mo(18)], which resemble those present in the structure of MoO₃·2H₂O (Krebs, 1972; Åsbrink & Brandt, 1971).

The direct coordination of H₂O molecules to the metal as in the present 36-molybdate is also a characteristic feature of all polymeric compounds precipitating from highly acidic molybdate solutions. Examples are the decamolybdates, α-MoO₃·H₂O (Böschen & Krebs, 1974; Oswald, Günter & Dubler, 1975), and MoO₃·2H₂O.

The most remarkable features of the structure, however, which as yet are unknown in the chemistry of isopolymolybdates and of compounds in the system MoO₃·water, are the presence of MoO₇ polyhedra and of bridging H₂O molecules coordinated simultaneously to two Mo atoms. The MoO₇ polyhedra [two in each half of the 36-molybdate, central atoms Mo(8) and Mo(10)] can be viewed as pentagonal bipyramids.

They are linked through the five equatorial edges to neighbouring octahedra, and both through a sixth edge to Mo(9). It is interesting to note that the groups of nine polyhedra forming each quarter of the 36-molybdate are very similar to the basic structural motifs in the oxides $Mo_{17}O_{47}$ (Kihlborg, 1960) and Mo_3O_{14} (Kihlborg, 1963), in spite of the completely different conditions of formation.

If the two heptacoordinate Mo(8) and Mo(10) polyhedra are added to the central compact edge-sharing pentameric Mo(4)—Mo(5)—Mo(9)—Mo(14)—Mo(15) unit, the resulting fragment is very similar to the heptamolybdate structure; this may give an indication about the possible mechanism of formation of the 36-molybdate, which may involve an intact compact unit like $Mo_7O_{24}^{6-}$ as a starting nucleus [for

possible formation mechanisms of polymolybdates see Tytko & Glemser (1976)].

There are two unusual bridging H_2O molecules in each half of the 36-molybdate anion, O(w1) coordinating to Mo(1) and Mo(2), O(w8) being bonded to Mo(17) and Mo(18). The arguments for interpreting these bridging atoms as doubly protonated oxygens are the chemical analysis (eight K^+ per anion) and the very long bond distances of 2.387 (8)—2.441 (8) Å which exclude other possibilities (Schröder, 1975) and favourable intramolecular hydrogen bonding [$O(w1) \dots O(21)$ 2.998 (8), $O(w8) \dots O(38)$ 2.914 (8) Å]. An interesting similar case of bridging H_2O has recently been reported for the $[(C_6H_5As)_2Mo_6O_{24}(H_2O)]^{4-}$ ion (Kwak, Rajković, Pope, Quicksall, Matsumoto & Sasaki, 1977; Matsumoto, 1978) where the labile bonding of this H_2O molecule [$Mo-O$ 2.393 (14) and 2.478 (15) Å] gives rise to a rapid structural change of the heteropolyanion in solution.

Table 3. $K \dots O$ interatomic distances with standard deviations (Å)

K(1)—O(3)	2.919 (12)	K(3)—O(3)	3.005 (12)
K(1)—O(5)	2.889 (9)	K(3)—O(5)	2.925 (12)
K(1)—O(6)	3.136 (10)	K(3)—O(8)	3.184 (11)
K(1)—O(18)	3.073 (9)	K(3)—O(20)	3.102 (10)
K(1)—O(31)	3.232 (10)	K(3)—O(44)	2.861 (10)
K(1)—O(41)	3.031 (9)	K(3)—O(w10)	2.934 (15)
K(1)—O(44)	2.959 (9)	K(3)—O(w22)	2.943 (32)
K(1)—O(w9)	2.789 (11)	K(3)—O(w24)	3.104 (43)
K(1)—O(w17)	3.160 (15)		
K(1)—O(w18)	2.778 (23)	K(4)—O(11)	2.805 (13)
		K(4)—O(27)	2.685 (10)
K(2)—O(20)	2.834 (9)	K(4)—O(28)	3.073 (13)
K(2)—O(25)	2.988 (11)	K(4)—O(56)	2.856 (14)
K(2)—O(34)	2.894 (8)	K(4)—O(w11)	2.889 (14)
K(2)—O(49)	3.099 (10)	K(4)—O(w22)	2.610 (31)
K(2)—O(53)	2.872 (12)	K(4)—O(w26)	2.618 (25)
K(2)—O(w10)	2.927 (15)		
K(2)—O(w19)	2.864 (15)		
K(2)—O(w20)	2.909 (28)		
	(5a)	(5b)	(5c)
K(5)—O(13)	2.827 (19)	2.654 (21)	2.701 (25)
K(5)—O(18)	2.934 (23)	2.751 (19)	2.854 (19)
K(5)—O(31)	2.755 (15)	2.783 (15)	2.705 (18)
K(5)—O(32)		2.908 (19)	2.646 (20)
K(5)—O(w12)	2.738 (17)	2.966 (15)	
K(5)—O(w18)	2.806 (25)		
K(5)—O(w23)			3.249 (37)
K(5)—O(w27)	2.779 (42)		
K(5)—O(w30)			3.078 (31)
K(5)—O(w36)			2.805 (30)
	(6a)	(6b)	(6c)
K(6)—O(1)			3.199 (48)
K(6)—O(2)	3.019 (26)	2.791 (31)	2.768 (32)
K(6)—O(10)	2.794 (17)	2.849 (25)	2.916 (38)
K(6)—O(26)	2.771 (21)	2.795 (31)	3.025 (41)
K(6)—O(w15)	2.809 (23)	2.769 (25)	2.721 (27)
K(6)—O(w19)	3.159 (32)		
K(6)—O(w22)		3.030 (39)	
K(6)—O(w29)	2.891 (33)		3.131 (52)
K(6)—O(w31)		2.752 (47)	
K(6)—O(w32)	2.859 (42)	2.985 (45)	

A survey of the bond data given in Tables 2 and 3 shows: The shortest Mo—O bond distances are observed for the axial terminal bonds in the pentagonal MoO_7 bipyramids with 1.664 (7) Å for Mo(10)—O(25) and 1.668 (9) Å for Mo(8)—O(22). They are *trans* to the unusually long axial bridge bonds Mo(10)—O(29), 2.362 (6) Å, and Mo(8)—O(28), 2.335 (9) Å. As a compensation for these weak bonds, the bonds from O(28) and O(29) to their second bond partner, namely Mo(9), are unusually short with 1.749 (6) and 1.719 (8) Å, respectively. The nonbonded O...O distances from O(28) and O(29) towards their equatorial neighbours in the pentagonal bipyramids which by no means indicate steric crowding [shortest distances O(29)...O(24) 2.651 (11), O(28)...O(23) 2.680 (11) Å] show that this bonding situation is caused by electronic rather than steric reasons. There is steric crowding, however, within the pentagonal bases of the bipyramids: The nonbonded O...O distances here are between 2.306 (12) Å for O(36)...O(37) and 2.392 (11) Å for O(15)...O(23), making them by far shorter than all other O...O distances within the 36-molybdate anion. Other distances between O atoms of the same MoO_6 or MoO_7 polyhedron range from 2.528 (10) Å for O(33)...O(38) to 2.998 (12) Å for O(21)...O(w1). There is a distinct tendency towards smaller values for common edges of the polyhedra. If coordinated H_2O is involved, the distances are rather shorter than longer.

The Mo...Mo distances are distinctly different according to the type of connexion with average values of 3.351 Å for linking edges and 3.841 Å for linking corners.

The Mo—O bond distances for the different kinds of O atoms vary in quite wide limits (Table 2): from 1.664 (7) to 1.715 (10) Å (average 1.693 Å) for Mo—O(terminal) bonds, from 1.719 (8) to 2.362 (6) Å (av. 1.952 Å) for Mo—O bonds with oxygen con-

Table 4. $K_8[Mo_{36}O_{112}(H_2O)_{16}] \cdot 36 \dots 40H_2O$: interatomic $O \dots O$ distances $\leq 3.3 \text{ \AA}$ between H_2O molecules not coordinated to Mo and from the cation-water system to the $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ anion

O(w9)...O(w2)	2.76 (1)	O(w19)...O(w32)	3.23 (3)
O(w9)...O(w6)	3.04 (1)	O(w20)...O(25)	3.15 (2)
O(w9)...O(w36)	2.71 (3)	O(w20)...O(32)	2.86 (2)
O(w10)...O(20)	3.01 (1)	O(w20)...O(w7)	3.02 (3)
O(w10)...O(35)	3.29 (1)	O(w20)...O(w30)	3.10 (3)
O(w10)...O(w3)	2.86 (1)	O(w21)...O(32)	2.91 (2)
O(w11)...O(46)	3.14 (1)	O(w22)...O(1)	2.91 (2)
O(w11)...O(46')	2.95 (1)	O(w22)...O(11)	3.12 (2)
O(w11)...O(47)	3.06 (1)	O(w22)...O(w23)	3.27 (3)
O(w11)...O(47')	3.21 (1)	O(w22)...O(w31)	2.77 (3)
O(w11)...O(w8)	2.73 (2)	O(w23)...O(w23')	3.10 (4)
O(w11)...O(w25)	2.88 (2)	O(w23)...O(w26)	3.04 (4)
O(w12)...O(33)	2.78 (1)	O(w23)...O(w29)	3.08 (4)
O(w12)...O(54)	2.97 (1)	O(w23)...O(w30)	3.08 (4)
O(w12)...O(w7)	2.78 (2)	O(w23)...O(w35)	2.90 (4)
O(w12)...O(w20)	2.92 (3)	O(w24)...O(54)	2.84 (3)
O(w13)...O(9)	3.25 (1)	O(w25)...O(12)	2.90 (2)
O(w13)...O(13)	3.28 (1)	O(w25)...O(29)	2.97 (2)
O(w13)...O(43)	2.78 (1)	O(w25)...O(30)	2.84 (2)
O(w13)...O(w5)	2.76 (1)	O(w25)...O(55)	2.95 (2)
O(w13)...O(w7)	2.73 (1)	O(w26)...O(12)	2.80 (3)
O(w13)...O(w20)	3.15 (3)	O(w26)...O(30)	2.99 (3)
O(w13)...O(w21)	3.06 (3)	O(w26)...O(55)	2.73 (3)
O(w13)...O(w29)	2.69 (3)	O(w26)...O(w35)	3.04 (4)
O(w13)...O(w30)	2.66 (3)	O(w26)...O(w36)	3.29 (4)
O(w14)...O(32)	3.24 (1)	O(w27)...O(w3)	2.89 (3)
O(w14)...O(52)	3.29 (1)	O(w27)...O(w7)	2.91 (3)
O(w14)...O(w2)	2.76 (1)	O(w27)...O(w31)	3.18 (4)
O(w14)...O(w6)	2.70 (1)	O(w27)...O(w32)	3.22 (4)
O(w14)...O(w19)	2.85 (2)	O(w28)...O(w3)	3.08 (3)
O(w14)...O(w23)	2.94 (3)	O(w28)...O(w31)	2.60 (4)
O(w15)...O(12)	3.22 (1)	O(w28)...O(w32)	2.82 (4)
O(w15)...O(w1)	2.67 (1)	O(w29)...O(13)	3.07 (3)
O(w15)...O(w23)	3.08 (3)	O(w29)...O(w34)	3.16 (4)
O(w15)...O(w30)	3.20 (3)	O(w31)...O(56)	3.17 (3)
O(w15)...O(w33)	3.05 (3)	O(w32)...O(26)	2.71 (3)
O(w15)...O(w33')	2.67 (3)	O(w32)...O(w3)	2.81 (4)
O(w16)...O(44)	3.17 (2)	O(w32)...O(w5)	2.63 (4)
O(w16)...O(w4)	2.71 (2)	O(w33)...O(1)	3.02 (3)
O(w16)...O(w6)	2.74 (2)	O(w34)...O(13)	3.11 (4)
O(w16)...O(w23)	2.67 (3)	O(w34)...O(31)	3.19 (4)
O(w17)...O(4)	2.84 (2)	O(w34)...O(32)	2.92 (4)
O(w17)...O(4')	2.90 (2)	O(w35)...O(22)	2.95 (4)
O(w17)...O(6)	3.14 (2)	O(w35)...O(30)	3.26 (4)
O(w17)...O(8)	3.24 (2)	O(w35)...O(31)	3.04 (4)
O(w17)...O(w18)	3.29 (3)	O(w36)...O(22)	2.89 (4)
O(w18)...O(31)	3.02 (2)	O(w36)...O(30)	3.00 (4)
O(w18)...O(w5)	2.98 (2)	O(w36)...O(31)	3.16 (4)
O(w19)...O(w30)	2.74 (3)	O(w36)...O(55)	2.92 (4)

nected to two Mo, 1.869 (7) to 2.311 (7) Å (av. 2.063 Å) for Mo—O(triply bridging), 2.057 (8) to 2.377 (8) Å (av. 2.170 Å) for Mo—O(quadruply bridging) bonds, 2.320 (10) to 2.402 (9) Å (av. 2.367 Å) for Mo—OH₂(terminal) and 2.387 (8) to 2.441 (8) Å (av. 2.415 Å) for Mo—OH₂(bridging) bonds. In spite of the large variation of the individual values, the average distances show very well the increase to be expected with decreasing formal valence bond strengths [see, for example, Schröder (1975)]. Bond-order sums estimated according to different models (Pauling, 1947; Donnay & Allmann, 1970; Schröder, 1975) lead to a consistent set of values 6.0 ± 0.2 for Mo and 2.0 ± 0.2 for O.

The large 36-molybdate anions are separated in the crystal structure by the system of eight K⁺ ions and 40 H₂O molecules per formula unit. In Tables 3 and 4 interatomic distances for the K⁺ coordinations and for the hydrate water molecules are given. Parts of this system are poorly ordered, and partial occupancy factors had to be introduced for several atoms. In individual cells, different sets of these sites can be chosen to give consistent packing systems with the distances in Table 4. The coordinations of the K⁺ are normal; the geometry of the H₂O...H₂O and H₂O...O system (Table 4) indicates some degree of hydrogen bonding between the anions and the cation-hydrate arrangement. However, as a whole, the packing of the hydrate water system appears quite loose and the bonding forces very weak, in accordance with the easy loss of water.

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The Structure of Magnetite: Defect Structure II

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Abstract

$Mg_{0.04}Fe_{2.96}O_4$ is cubic, $Fd\bar{3}m$, with $a = 8.3930$ (6) Å. The structure of magnetite from a skarn-type iron-ore deposit has been refined to a weighted R of 0.024 using 145 unique averaged reflections collected at room temperature on a single-crystal diffractometer with $Mo\ K\alpha$ ($\lambda = 0.7107$ Å) radiation. The oxygen positional parameter (u) is 0.2547 (1). Residual electron density peaks at equipoint positions 48(f) and 96(h) have been assigned, respectively, to interstitial Fe^{3+} in a second tetrahedrally coordinated position and to interstitial Fe^{2+} , Fe^{3+} in a second octahedrally coordinated position. Corresponding vacancies are present in the tetrahedral and octahedral cation positions of the ideal

inverse-spinel structure: Fe, Mg occupancies for these positions are 0.93 and 0.95, respectively. Weak $\langle 110 \rangle^*$ diffraction streaks are attributed to lattice strain associated with the high concentration of point defects. This defect structure is basically different from that reported earlier for essentially 'pure' Fe_3O_4 from a different mineral paragenesis (chlorite schist).

Introduction

Magnetite has the inverse-spinel structure, with space group $Fd\bar{3}m$ (No. 227) and ideal structural formula TM_2O_4 , where T is Fe^{3+} in tetrahedral coordination with oxygen and M is Fe^{3+} and Fe^{2+} in octahedral