

Studies on Peroxomolybdates XII. The Crystal Structure of Ammonium Dodecaperoxodecamolybdate(VI)-water(1/16), (NH₄)₈[Mo₁₀O₂₂(O₂)₁₂] · 16H₂O

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Persdotter, Ingeborg, Trysberg, Lennart and Stomberg, Rolf. 1986. Studies on Peroxomolybdates. XII. The Crystal Structure of Ammonium Dodecaperoxodecamolybdate(VI)-water(1/16), (NH₄)₈[Mo₁₀O₂₂(O₂)₁₂] · 16H₂O. Acta Chem. Scand. A 40: 83–90.

The crystal structure of ammonium dodecaperoxodecamolybdate(VI)-water(1/16) was determined by single-crystal X-ray methods. The compound crystallizes, as yellow truncated hexagonal prisms, in space group *P2₁/c* with *a* = 12.726(3), *b* = 18.722(4), *c* = 12.530(4) Å, β = 110.50(2)°, *V* = 2796(1) Å³ and *Z* = 2. Full-matrix least-squares refinement yielded a final *R_F*-value of 0.035 for 5293 observed [*I* > 3σ(*I*)] reflections. The crystals investigated are not fully stoichiometric, the actual formula being (NH₄)₈[Mo₁₀O_{22+x}(O₂)_{12-x}] · 16H₂O, *x* = 0.66. They are composed of ammonium ions, water of crystallization and dodecaperoxodecamolybdate(VI) ions; the latter are replaced by hendeca- and/or decaperoxodecamolybdate(VI) ions to a smaller extent.

The [Mo₁₀O₂₂(O₂)₁₂]⁸⁻ ion is centrosymmetric and the asymmetric unit can be considered to be composed of a loop of four MoO₅(O₂) polyhedra with a MoO₃(O₂)₂ polyhedron above the loop and coupled to all four MoO₅(O₂) polyhedra. The polyhedra are connected by edge- or corner-sharing. All polyhedra are pentagonal bipyramids.

Bond distances: Mo=O 1.672(4)–1.691(4) Å, Mo–O_{bridging} 1.922(4)–2.468(4) Å, Mo–O_{peroxo} 1.933(4)–2.057(4), (O–O)_{peroxo} 1.416(6)–1.487(6) Å, (Mo...Mo)_{edge-sharing} 3.196(1)–3.276(1) Å and (Mo...Mo)_{corner-sharing} 4.071(1)–4.124(1) Å.

The aqueous chemistry of oxomolybdates(VI) is very complex (see, e.g., the review article on isopolymolybdates and isopolytungstates in Ref. 1). In brief, Mo(VI) is present only as MoO₄²⁻ in strongly basic solutions. On acidification, protonation to the mono- and dibasic species HMoO₄⁻ and Mo(OH)₆ occurs. In addition polymerization to Mo₇O₂₄⁴⁻ and, in more acid solutions, to Mo₈O₂₆⁴⁻ will take place. In solution there are no detectable amounts of polynuclear species between the mononuclear ones and the heptamolybdate; this seems to be due to the high second acid constant

for the mononuclear molybdate. In contrast, solid compounds obtainable from molybdate solutions show nuclearity between one and seven.

The systems obtained on addition of hydrogen peroxide to molybdate solutions containing different counter-ions seem to be no less complex. A comprehensive investigation of which solid compounds are formed in the systems K⁺–MoO₄²⁻–H₂O₂–H⁺–H₂O and NH₄⁺–MoO₄²⁻–H₂O₂–H⁺–H₂O was performed at this department and a preliminary report of the potassium system is given in Ref. 2. By chemical analysis, IR-spectroscopy and single-crystal X-ray methods and/or powder diffraction methods a large number of crystalline phases were identified. Crystal data

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were obtained for twelve phases in the potassium system and thirteen in the ammonium system.³⁻¹⁰ A summary is given in Ref. 10. The crystal structures of the following of these were determined, viz. $K_2[Mo_2O_3(O_2)_4(H_2O)_2] \cdot 2H_2O$,³ $(NH_4)_4[Mo_3O_7(O_2)_4] \cdot 2H_2O$,⁷ $K_4[Mo_4O_{12}(O_2)_2]$,⁵ $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$,⁸ $K_6[Mo_7O_{22}(O_2)_2] \cdot 8H_2O$,^{4,6} $K_5[Mo_7O_{21}(O_2)_2(OH)] \cdot 6H_2O$,⁷ $K_6[Mo_7O_{22}(O_2)_2] \cdot 10H_2O$,⁹ $(NH_4)_4[Mo_8O_{24}(O_2)_2(H_2O)_2] \cdot 4H_2O$, and $(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}] \cdot 16H_2O$ (the present paper; a preliminary report is given in Ref. 1). In the case of $M_2[Mo(O_2)_4]$ the ammonium compound does not seem to be formed, while the potassium salt was shown to be very unstable, decomposing within 1 h at room temperature, and to have a large unit cell. The structure analysis was therefore performed on the somewhat more stable tetraamminezinc(II) salt, $[Zn(NH_3)_4][Mo(O_2)_4]$.¹² These structure determinations have proved the existence of both peroxo mono-, di-, tri-, tetra-, penta-, hepta-, octa- and decamolybdates. Furthermore it was noticed that, despite similar ionic radii, the potassium and ammonium compounds crystallizing from solutions of comparable composition differ markedly. Hitherto only four of the investigated ammonium compounds have been shown to have isomorphous potassium counterparts.

Judging from these chemical, phase-analytical and structural work on the potassium and ammonium peroxomolybdate(VI) systems the following conclusions can be drawn.

1. Addition of small amounts of hydrogen peroxide to molybdate solutions ($[H_2O_2]:[Mo] < 0.5$) results in a low degree of oxo-peroxo replacement in a wide pH range. The oxomolybdate chemistry is not changed to any appreciable extent by this limited substitution, representative anions being $[Mo_7O_{22+x}(O_2)_{2-x}]^{6-}$,^{4,6,9} $[Mo_7O_{21}(O_2)_2(OH)]^{5-}$,⁷ and $[Mo_8O_{24}(O_2)_2(H_2O)_2]^{5-}$.⁷ In these cases a terminal oxygen atom at each end of the anion is replaced by a peroxo group. This replacement may be incomplete.

2. From molybdate solutions to which has been added hydrogen peroxide in large amounts ($2 \leq [O_2^{2-}]:[Mo] \leq 4$) peroxide-rich crystals containing only mono- or dinuclear species are obtained, e.g. $K_2[Mo(O_2)_4]$ and $K_2[O\{MoO(O_2)_2(H_2O)\}_2] \cdot 2H_2O$.³

3. If moderate amounts of hydrogen peroxide are added to molybdate solutions (0.5

$\leq [O_2^{2-}]:[Mo] \leq 1.6$) several crystalline compounds are obtained, examples being $(NH_4)_4[Mo_3O_7(O_2)_4] \cdot 2H_2O$,⁷ $K_4[Mo_4O_{12}(O_2)_2]$,⁵ $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$,⁸ and $(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}] \cdot 16H_2O$ (the present paper). Unexpectedly, these compounds seem to be more polynuclear than those obtained from the corresponding peroxide-free solutions. Thus, four phases with $[O_2^{2-}]:[Mo] \approx 1.2$ may crystallize from slightly acidic ammonium molybdate solutions. The crystal structure of one of them will be presented in this paper. This phase may correspond to one which Hansson *et al.* formulate $2(NH_4)_2O \cdot 5MoO_3 \cdot (5-x)O \cdot 9H_2O$ ($x < 1.5$).¹³

Experimental

Preparation. According to the phase-analytical investigations crystals could be suitably obtained by dissolving 3.72 g ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in 2.80 ml 30% hydrogen peroxide and 1.50 ml water and adjusting pH to 2.8-3.0 with 8 M nitric acid. Yellow crystals in the form of truncated hexagonal prisms, developed within 24 h at 20°C.

X-Ray method. Intensity data were recorded at $-100^\circ C$ for $2\theta \leq 56^\circ$ using a SYNTEX P2₁ X-ray diffractometer, equipped with the LT1 low temperature device (graphite-monochromated $MoK\alpha$ radiation, crystal size $0.13 \times 0.18 \times 0.32$ mm, ω - 2θ scan method, 2θ scan speed $2.5-29.3^\circ \text{min}^{-1}$). Integrated intensity values were obtained with the Lehmann-Larsen profile analysis method.¹⁴ Two test reflexions, measured after each fourteenth reflexion, showed no significant difference in intensity during the collection of the data. A total of 6735 independent reflexions were recorded and 5293 of these, having $I \geq 3\sigma(I)$, were used in the subsequent calculations. The net intensities were corrected for Lorentz, polarization and absorption effects. The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

Crystal data

$(NH_4)_8[Mo_{10}O_{22} + x(O_2)_{12} - x] \cdot 16H_2O$, $x = 0.66$.
F.W. = 2117.36 Space group $P2_1/c$ No. 14).

$a = 12.726(3) \text{ \AA}$, $b = 18.722(4) \text{ \AA}$, $c = 12.530(4) \text{ \AA}$, $\beta = 110.50(2)^\circ$, $V = 2796(1) \text{ \AA}^3$, $Z = 2$. $D_x = 2.521 \text{ g cm}^{-3}$, $\mu(MoK\alpha) = 2.27 \text{ mm}^{-1}$.

Structure determination

The five molybdenum atoms in the asymmetric unit were located from the Patterson function while the positions of the remaining non-hydrogen atoms were derived from successive electron density maps. Block-diagonal refinement of an overall scale factor, atomic coordinates and isotropic thermal parameters for all non-hydrogen atoms yielded an R -value of 0.049 ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) after absorption correction, using an empirical method for correcting diffractometer data for absorption effects which is due to Walker and Stuart.¹⁵ Introduction of anisotropic thermal parameters for molybdenum reduced the R -value to 0.042.

One unacceptably short peroxy oxygen bond distance as well as an increased electron density between the oxygen atoms of this peroxy group showed that the non-stoichiometrical peroxide content, observed in the chemical analysis, could be associated with this peroxy group, being partly replaced by an oxygen atom. This type of replacement has been observed not only for other peroxopolymolybdates,^{4,6} but also for other peroxometallates.^{16,17} An oxygen atom, partially replacing this peroxy group, was, therefore, introduced and positional and isotropic thermal parameters for these three atoms were refined, while all other positional and thermal parameters were kept constant. A minimum R -value was ob-

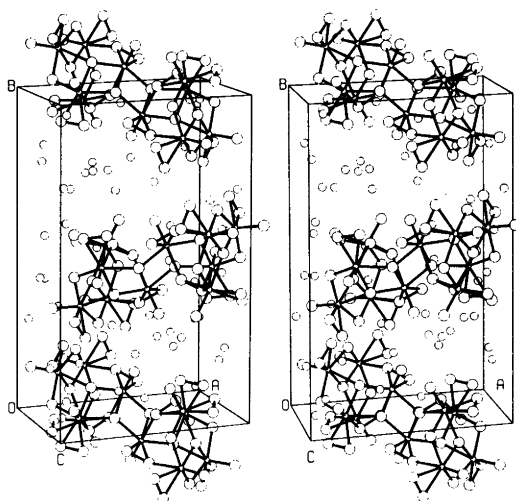


Fig. 1. Stereoscopic drawing of the unit cell of $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{22}(\text{O}_2)_{12}] \cdot 16\text{H}_2\text{O}$. Circles not belonging to the complex ions represent ammonium ions and water molecules.

tained for an occupation number of 0.33 for the oxo oxygen atom. The water oxygen atoms and the ammonium nitrogen atoms could not be unequivocally distinguished and the hydrogen atoms could not be located. Finally, an overall scale factor and positional and anisotropic thermal parameters were refined by the full-matrix

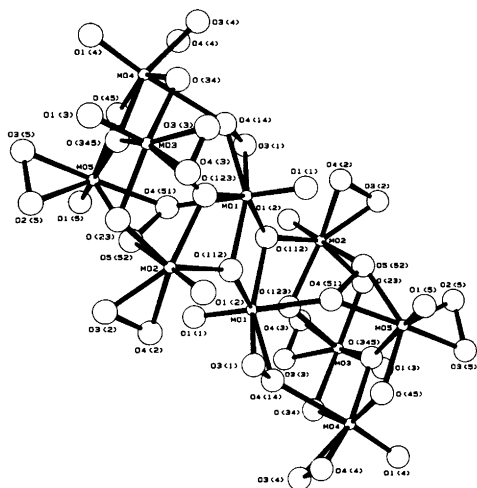


Fig. 2a. The complex ion $[\text{Mo}_{10}\text{O}_{22}(\text{O}_2)_{12}]^{8-}$.

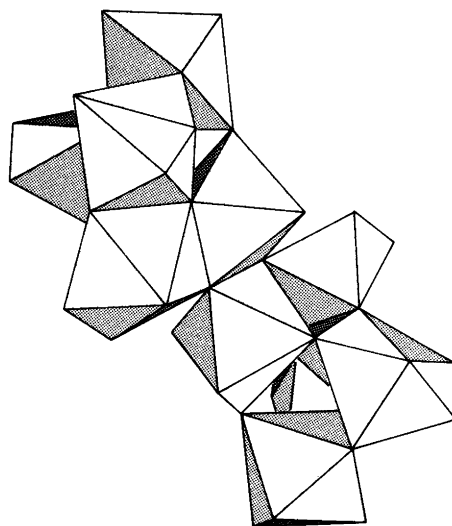


Fig. 2b. Alternative representation of the complex ion.

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters for $(\text{NH}_4)_x[\text{Mo}_{10}\text{O}_{22+x}(\text{O}_2)_{12-x}] \cdot 16\text{H}_2\text{O}$, $x = 0.66$, with their estimated standard deviations. All atoms occupy the general four-fold site $4e$ of space group $P2_1/c$. O2(3) has occupation number 0.33 and O3(3) and O4(3) have occupation number 0.67. A denotes an ammonium nitrogen atom or a water oxygen atom. A12 and A13 have occupation number 0.5.

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
Mo1	0.47066(4)	0.07051(2)	0.41889(4)	1.14(1)
Mo2	0.23550(4)	-0.00187(2)	0.40038(4)	1.30(1)
Mo3	0.16837(4)	0.12556(2)	0.20910(4)	1.37(1)
Mo4	0.34362(4)	0.12442(2)	0.07836(4)	1.46(1)
Mo5	0.32366(4)	-0.04337(2)	0.12400(4)	1.36(1)
O1(1)	0.5063(3)	0.1377(2)	0.5150(3)	1.9(1)
O3(1)	0.5704(3)	0.0861(2)	0.3350(3)	1.53(9)
O4(14)	0.4641(3)	0.1234(2)	0.2814(3)	1.46(9)
O(123)	0.3109(3)	0.0845(2)	0.3598(3)	1.39(9)
O(112)	0.4053(3)	-0.0018(2)	0.4977(3)	1.36(9)
O1(2)	0.1884(4)	0.0326(2)	0.4983(4)	2.2(1)
O3(2)	0.1506(4)	-0.0893(2)	0.3531(4)	2.5(1)
O4(2)	0.2492(4)	-0.1005(2)	0.4491(4)	2.2(1)
O(23)	0.1251(3)	0.0324(2)	0.2614(3)	1.8(1)
O1(3)	0.0501(4)	0.1363(2)	0.0942(4)	2.3(1)
O2(3)	0.154(1)	0.1871(9)	0.310(1)	2.3(5)
O3(3)	0.1770(7)	0.2144(4)	0.2928(7)	2.2(2)
O4(3)	0.1131(6)	0.1596(4)	0.3282(6)	2.2(2)
O(345)	0.2514(3)	0.0600(2)	0.1335(3)	1.46(9)
O(34)	0.2752(3)	0.1855(2)	0.1639(3)	1.8(1)
O1(4)	0.2575(4)	0.1352(2)	-0.0579(4)	2.3(1)
O3(4)	0.4377(4)	0.2109(2)	0.0928(4)	2.2(1)
O4(4)	0.4897(4)	0.1463(2)	0.0688(4)	2.4(1)
O(45)	0.4024(3)	0.0265(2)	0.0671(3)	1.8(1)
O1(5)	0.3961(4)	-0.1173(2)	0.1140(4)	2.2(1)
O2(5)	0.1699(4)	-0.0778(2)	0.0653(3)	2.2(1)
O3(5)	0.2040(3)	-0.0493(2)	-0.0284(3)	2.2(1)
O4(51)	0.4272(3)	-0.0228(2)	0.2885(3)	1.52(9)
O5(52)	0.3207(3)	-0.0589(2)	0.2804(3)	1.53(9)
A1	0.4259(5)	0.2713(3)	0.3491(4)	3.4(2)
A2	0.6602(4)	0.2290(3)	0.3984(5)	3.5(2)
A3	-0.0350(4)	-0.0614(3)	0.1213(5)	3.9(2)
A4	0.6523(5)	0.0129(3)	0.1691(5)	4.2(2)
A5	0.6719(6)	0.2245(4)	0.6918(6)	5.7(2)
A6	0.2021(5)	0.3150(3)	0.0606(5)	3.6(2)
A7	0.6248(4)	-0.1044(2)	0.2973(4)	2.5(1)
A8	-0.101(1)	0.050(1)	0.310(1)	16.4(8)
A9	0.1853(8)	-0.2056(6)	-0.0909(9)	9.7(4)
A10	0.102(1)	-0.2250(8)	0.123(1)	17.8(8)
A11	0.0037(9)	0.3024(6)	0.248(1)	11.3(5)
A12	0.030(2)	-0.149(2)	0.485(2)	14.(5)
A13	0.107(2)	0.084(2)	0.672(3)	16.(5)

least-squares method; this led to an R -value of 0.035. The atomic scattering factors for Mo and O were taken from Ref. 18 (that for O was used for both O and N; *vide supra*). Weights were calculated according to $w = [\sigma^2(F_o) + 0.003|F_o|^2]^{-1}$.

A difference map calculated after the final refinement cycle showed no peak higher than 1.0 $\text{e}\text{\AA}^{-3}$ and there were no notable minima.

Calculations were carried out on an IBM 3033 computer, using the crystallographic programs

Table 2. Distances (Å) and angles (°) within the $[\text{Mo}_{10}\text{O}_{22}(\text{O}_2)_{12}]^{8-}$ anion.

Distance		Angle	
Mo1–O1(1)	1.689(4)	O1(1)–Mo1–O3(1)	102.2(2)
Mo1–O3(1)	1.933(4)	O1(1)–Mo1–O4(14)	99.7(2)
Mo1–O4(14)	1.964(4)	O1(1)–Mo1–O(123)	99.0(2)
Mo1–O(123)	1.922(4)	O1(1)Mo1–O(112)	101.8(2)
Mo1–O(112)	2.019(4)	O1(1)–Mo1–O(112)'	98.0(2)
Mo1–O(112)'	2.020(4)	O1(1)Mo1–O4(51)	178.3(2)
Mo1–O4(51)	2.322(4)	O4(51)–Mo1–O3(1)	76.8(1)
O1(1)–O3(1)	2.824(5)	O4(51)–Mo1–O4(14)	80.6(1)
O1(1)–O4(14)	2.798(5)	O4(51)–Mo1–O(123)	82.6(1)
O1(1)–O(123)	2.751(5)	O4(51)–Mo1–O(112)	78.6(1)
O1(1)–O(112)	2.885(5)	O4(51)–Mo1–O(112)'	80.5(1)
O1(1)–O(112)'	2.808(5)	O3(1)–Mo1–O4(14)	44.0(2)
O4(51)–O3(1)	2.660(5)	O3(1)–Mo1–O(123)	125.3(2)
O4(51)–O4(14)	2.785(5)	O3(1)–Mo1–O(112)	146.0(2)
O4(51)–O(123)	2.819(5)	O3(1)–Mo1–O(112)'	80.5(2)
O4(51)–O(112)	2.759(5)	O4(14)–Mo1–O(123)	83.1(2)
O4(51)–O(112)'	2.816(5)	O4(14)–Mo1–O(112)	150.4(2)
O3(1)–O4(14)	1.461(5)	O4(14)–Mo1–O(112)'	124.1(2)
O3(1)–O(112)'	2.555(5)	O(123)–Mo1–O(112)	73.6(2)
O4(14)–O(123)	2.577(5)	O(123)–Mo1–O(112)'	144.6(2)
O(112)–O(123)	2.363(5)	O(112)–Mo1–O(112)'	72.6(2)
O(112)–O(112)'	2.391(7)		
Mo2–O1(2)	1.672(4)	O1(2)–Mo2–O3(2)	104.2(2)
Mo2–O3(2)	1.935(4)	O1(2)–Mo2–O4(2)	98.8(2)
Mo2–O4(2)	1.933(4)	O1(2)–Mo2–O(112)	97.8(2)
Mo2–O(112)	2.076(4)	O1(2)–Mo2–O(123)	101.5(2)
Mo2–O(123)	2.033(4)	O1(2)–Mo2–O(23)	101.5(2)
Mo2–O(23)	1.925(4)	O1(2)–Mo2–O5(52)	172.6(2)
Mo2–O5(52)	2.391(4)	O5(52)–Mo2–O3(2)	76.0(2)
O1(2)–O3(2)	2.851(6)	O5(52)–Mo2–O4(2)	76.2(2)
O1(2)–O4(2)	2.742(6)	O5(52)–Mo2–O(112)	76.2(1)
O1(2)–O(112)	2.837(6)	O5(52)–Mo2–O(123)	80.8(1)
O1(2)–O(123)	2.878(6)	O5(52)–Mo2–O(23)	85.9(2)
O1(2)–O(23)	2.791(6)	O3(2)–Mo2–O4(2)	43.0(2)
O5(52)–O3(2)	2.686(6)	O3(2)–Mo2–O(112)	122.3(2)
O5(52)–O4(2)	2.692(6)	O3(2)–Mo2–O(123)	149.0(2)
O5(52)–O(112)	2.769(5)	O3(2)–Mo2–O(23)	81.5(2)
O5(52)–O(123)	2.881(5)	O4(2)–Mo2–O(112)	81.7(2)
O5(52)–O(23)	2.960(5)	O4(2)–Mo2–O(123)	147.1(2)
O3(2)–O4(2)	1.416(6)	O4(2)–Mo2–O(23)	124.1(2)
O3(2)–O(23)	2.520(6)	O(112)–Mo2–O(123)	70.2(1)
O4(2)–O(112)	2.624(6)	O(112)–Mo2–O(23)	144.2(2)
O(123)–O(112)	2.363(5)	O(123)–Mo2–O(23)	76.6(2)
O(123)–O(23)	2.454(5)		
Mo3–O1(3)	1.691(4)	O1(3)–Mo3–O3(3)	102.8(3)
Mo3–O3(3)	1.949(8)	O1(3)–Mo3–O4(3)	99.2(3)
Mo3–O4(3)	1.966(7)	O1(3)–Mo3–O(23)	96.7(2)
Mo3–O(23)	2.008(4)	O1(3)–Mo3–O(345)	97.3(2)
Mo3–O(345)	2.054(4)	O1(3)–Mo3–O(34)	100.6(2)
Mo3–O(34)	1.992(4)	O(123)–Mo3–O3(3)	87.9(3)
Mo3–O(123)	2.247(4)	O(123)–Mo3–O4(3)	82.6(2)
O1(3)–O3(3)	2.850(9)	O(123)–Mo3–O(23)	70.2(1)
O1(3)–O4(3)	2.790(8)	O(123)–Mo3–O(345)	77.8(1)

Table 2 cont.

Distance		Angle	
O1(3)–O(23)	2.772(6)	O(123)–Mo3–O(34)	90.1(2)
O1(3)–O(345)	2.822(6)	O3(3)–Mo3–O4(3)	44.2(3)
O1(3)–O(34)	2.840(6)	O3(3)–Mo3–O(23)	122.5(3)
O(123)–O3(3)	2.920(9)	O3(3)–Mo3–O(345)	144.8(3)
O(123)–O4(3)	2.789(8)	O3(3)–Mo3–O(34)	75.9(3)
O(123)–O(23)	2.454(5)	O4(3)–Mo3–O(23)	79.8(2)
O(123)–O(345)	2.705(5)	O4(3)–Mo3–O(345)	157.3(2)
O(123)–O(34)	3.005(5)	O4(3)–Mo3–O(34)	119.6(2)
O3(3)–O4(3)	1.47(1)	O(23)–Mo3–O(345)	82.8(2)
O3(3)–O(34)	2.423(9)	O(23)–Mo3–O(34)	151.1(2)
O4(3)–O(23)	2.548(8)	O(345)–Mo3–O(34)	72.2(2)
O(23)–O(345)	2.687(5)	O1(3)–Mo3–O(123)	166.4(2)
O(345)–O(34)	2.384(5)		
Mo3–O2(3)	1.77(2)	O2(3)–Mo3–O1(3)	104.2(6)
O2(3)–O1(3)	2.73(2)	O2(3)–Mo3–O(123)	83.0(6)
O2(3)–O(123)	2.68(2)	O2(3)–Mo3–O(23)	102.9(6)
O2(3)–O(23)	2.96(2)	O2(3)–Mo3–O(345)	156.8(6)
O2(3)–O(34)	2.78(2)	O2(3)–Mo3–O(34)	95.2(6)
Mo4–O1(4)	1.687(4)	O1(4)–Mo4–O3(4)	98.8(2)
Mo4–O3(4)	1.984(4)	O1(4)–Mo4–O4(4)	102.0(2)
Mo4–O4(4)	1.948(5)	O1(4)–Mo4–O(45)	99.4(2)
Mo4–O(45)	2.004(4)	O1(4)–Mo4–O(345)	99.9(2)
Mo4–O(345)	1.970(4)	O1(4)–Mo4–O(34)	103.1(2)
Mo4–O(34)	1.967(4)	O1(4)–Mo4–O4(14)	173.2(2)
Mo4–O4(14)	2.468(4)	O4(14)–Mo4–O3(4)	77.0(2)
O1(4)–O3(4)	2.793(6)	O4(14)–Mo4–O4(4)	78.6(2)
O1(4)–O4(4)	2.831(6)	O4(14)–Mo4–O(45)	87.3(1)
O1(4)–O(45)	2.823(6)	O4(14)–Mo4–O(345)	82.3(1)
O1(4)–O(345)	2.806(6)	O4(14)–Mo4–O(34)	71.1(1)
O1(4)–O(34)	2.868(6)	O3(4)–Mo4–O4(4)	43.6(2)
O4(14)–O3(4)	2.796(6)	O3(4)–Mo4–O(45)	121.6(2)
O4(14)–O4(4)	2.827(6)	O3(4)–Mo4–O(345)	152.0(2)
O4(14)–O(45)	3.105(5)	O3(4)–Mo4–O(34)	81.0(2)
O4(14)–O(345)	2.943(5)	O4(4)–Mo4–O(45)	78.5(2)
O4(14)–O(34)	2.612(5)	O4(4)–Mo4–O(345)	148.2(2)
O3(4)–O4(4)	1.459(6)	O4(4)–Mo4–O(34)	121.7(2)
O3(4)–O(34)	2.567(6)	O(45)–Mo4–O(345)	75.4(2)
O4(4)–O(45)	2.500(6)	O(45)–Mo4–O(34)	144.9(2)
O(45)–O(345)	2.430(5)	O(345)–Mo4–O(34)	74.5(2)
O(345)–O(34)	2.384(5)		
Mo5–O1(5)	1.691(4)	O1(5)–Mo5–O2(5)	101.7(2)
Mo5–O2(5)	1.944(4)	O1(5)–Mo5–O3(5)	97.9(2)
Mo5–O3(5)	1.986(4)	O1(5)–Mo5–O(45)	99.2(2)
Mo5–O(45)	1.930(4)	O1(5)–Mo5–O4(51)	93.0(2)
Mo5–O4(51)	2.057(4)	O1(5)–Mo5–O5(52)	98.7(2)
Mo5–O5(52)	1.995(4)	O1(5)–Mo5–O(345)	171.5(2)
Mo5–O(345)	2.163(4)	O(345)–Mo5–O2(5)	85.8(2)
O1(5)–O2(5)	2.824(6)	O(345)–Mo5–O3(5)	84.6(2)
O1(5)–O3(5)	2.779(6)	O(345)–Mo5–O(45)	72.6(2)
O1(5)–O(45)	2.762(6)	O(345)–Mo5–O4(51)	85.0(1)
O1(5)–O4(51)	2.731(5)	O(345)–Mo5–O5(52)	85.5(1)
O1(5)–O5(52)	2.803(6)	O2(5)–Mo5–O3(5)	44.4(2)
O(345)–O2(5)	2.800(6)	O2(5)–Mo5–O(45)	132.0(2)

Table 2 cont.

Distance		Angle	
O(345)–O3(5)	2.795(6)	O2(5)–Mo5–O4(51)	130.4(2)
O(345)–O(45)	2.430(5)	O2(5)–Mo5–O5(52)	87.7(2)
O(345)–O4(51)	2.852(5)	O3(5)–Mo5–O(45)	90.3(2)
O(345)–O5(52)	2.826(5)	O3(5)–Mo5–O4(51)	168.7(2)
O2(5)–O3(5)	1.487(6)	O3(5)–Mo5–O5(52)	131.7(2)
O2(5)–O5(52)	2.729(6)	O(45)–Mo5–O4(51)	90.6(2)
O3(5)–O(45)	2.776(6)	O(45)–Mo5–O5(52)	130.8(2)
O(45)–O4(51)	2.835(5)	O4(51)–Mo5–O5(52)	43.0(2)
O4(51)–O5(52)	1.486(5)		

described in Refs. 19 and 20. Lists of structure factors and anisotropic thermal parameters are available from the authors on request.

Results and discussion

Positional parameters and B_{eq} are listed in Table 1 and distances and angles within the anion in Table 2. Fig. 1 shows the positions of the non-hydrogen atoms in the unit cell and Fig. 2 the complex anion.

The crystals of $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{22} + x(\text{O}_2)_{12} - x] \cdot 16\text{H}_2\text{O}$, $x = 0.66$, consist of ammonium ions, water of crystallization and dodecaperoxododecamolybdate(VI) ions. Some of these anions have been proved to be replaced by hendeca- and/or decaperoxododecamolybdate(VI) ions, thus confirming the non-stoichiometry observed by the chemical analysis.

This is the first peroxopolymolybdate with both monoperoxo- and diperoxomolybdate units known to the authors. Stomberg, however, recently synthesized and determined the structure of a new peroxotungstate, $\text{K}_6[\text{W}_4\text{O}_8(\text{O}_2)_6(\text{CO}_3)] \cdot 6\text{H}_2\text{O}$, which was shown to contain both monoperoxo- and diperoxotungstate units.²¹ Due to the non-stoichiometry of the title compound there are also MoO_6 -octahedra in some of the anions.

The $[\text{Mo}_{10}\text{O}_{22}(\text{O}_2)_{12}]^{8-}$ anion is centrosymmetric. Each molybdenum atom is pentagonal-bipyramidally surrounded by seven oxygen atoms and displaced 0.28–0.37 Å from the respective equatorial plane in the way observed in many peroxometallates (see, e.g., the compilation of observed displacements of the metal atom from the equatorial plane in peroxometallates given in Ta-

ble V in Ref. 22). The anion can be considered to be built up of eight $\text{MoO}_3(\text{O}_2)$ and two $\text{MoO}_3(\text{O}_2)_2$ polyhedra sharing corners and edges (Fig. 2), the former forming a puckered eight. All four $\text{MoO}_3(\text{O}_2)$ units of each loop are connected to a $\text{MoO}_3(\text{O}_2)_2$ polyhedron situated outside the loop. As is evident from Table 2 the four $\text{MoO}_3(\text{O}_2)$ polyhedra are very similar, but differ, of course, geometrically from the $\text{MoO}_3(\text{O}_2)_2$ polyhedron, the latter having two peroxo groups. In all the pentagonal-bipyramidal polyhedra the peroxo groups form part of the respective equatorial plane. All the peroxo groups are bonded side-on to the molybdenum atoms.

As is usually observed in pentagonal-bipyramidal oxoperoxometallates the two $\text{M}-\text{O}_{\text{apical}}$ bond lengths differ considerably, one being considered to be a double bond (1.672(4)–1.691(4) Å in this case), while the other is very weak (2.163(4)–2.468(4) Å). The $\text{M}-\text{O}_{\text{equatorial}}$ bonds, being 1.992(4)–2.076(4) Å, have a bond order close to unity. When a peroxo oxygen atom forms a bridge to a second molybdenum atom (these are long $\text{M}-\text{O}_{\text{apical}}$ bonds) the bond to the first molybdenum atom is slightly weakened. The ability of the peroxo groups to share one or both of its oxygen atoms seems to be one of the main reasons for the complexity of peroxometallates.

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Received August 29, 1985.