

Letter

Studies on Peroxomolybdates.

X. The Crystal Structures of

$(\text{NH}_4)_4[\text{Mo}_3\text{O}_7(\text{O}_2)_4] \cdot 2\text{H}_2\text{O}$,
 $\text{K}_5[\text{Mo}_7\text{O}_{21}(\text{O}_2)_2(\text{OH})] \cdot 6\text{H}_2\text{O}$ and
 $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{24}(\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$.
 A Preliminary Report

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Phase analytical studies of the system $\text{M}^+ - \text{Mo(VI)} - \text{H}^+ - \text{H}_2\text{O}_2$ ($\text{M}^+ = \text{NH}_4^+$ or K^+) in aqueous media have shown that a large number of crystalline peroxomolybdates, mainly polynuclear peroxomolybdates, exist. Our investigations indicate the existence of both peroxy mono-, di-, tri-, tetra-, hepta-, octa-, nona- and decamolybdates in the solid state. Some are remarkably stable, while others disintegrate within minutes at room temperature. The crystal structures of some peroxomono-, peroxodi-, peroxotetra- and peroxoheptamolybdates have been determined, viz. $[\text{Zn}(\text{NH}_3)_4]_2[\text{Mo}(\text{O}_2)_4]$,¹ $\text{K}_2[\text{O}\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})_2\}_2] \cdot 2\text{H}_2\text{O}$,² $\text{K}_4[\text{Mo}_4\text{O}_{12}(\text{O}_2)_2]$,^{3,4} and $\text{K}_6[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2] \cdot 8\text{H}_2\text{O}$.⁴⁻⁶ In a preliminary report some results concerning the preparation of crystalline products formed by the isothermal evaporation of aqueous solutions containing molybdates and hydrogen peroxide in the pH range 4–8 are described.⁷ In the present paper a short account of the investigation of a peroxotri-, a peroxohepta- and a peroxo-octamolybdate is given.

I. $(\text{NH}_4)_4[\text{Mo}_3\text{O}_7(\text{O}_2)_4] \cdot 2\text{H}_2\text{O}$. Crystals of $(\text{NH}_4)_4[\text{Mo}_3\text{O}_7(\text{O}_2)_4] \cdot 2\text{H}_2\text{O}$ (I) can be obtained from an alkaline (pH 8.3–9.2) ammonium molybdate solution ($[\text{Mo}] \approx 3.5 \text{ M}$) in which the $[\text{H}_2\text{O}_2] : [\text{Mo}]$ ratio is 0.7–1.2. The crystals are triclinic, space group $P\bar{1}$, with $a = 8.56$, $b = 13.22$, $c = 8.52 \text{ \AA}$, $\alpha = 105.2$, $\beta = 105.2$ and $\gamma = 104.9^\circ$. $Z = 2$.

The structure of I has been determined from reflexion intensities collected with an X-ray dif-

fractometer (PAILRED) with $\text{MoK}\alpha$ radiation. Reflexions with $\sin \theta/\lambda < 0.67$ from nine zones with rotation about the a -axis were registered. Least-squares refinement of the derived atomic positions using anisotropic temperature parameters yielded $R = 0.045$ for 2845 reflexions, corrected for absorption effects.

The crystals consist of ammonium ions, tetraperoxotrimolybdate ions and water of crystallization. The anion is shown in Fig. 1. The three molybdenum atoms are situated at the corners of an isosceles triangle whose base is 3.37 \AA . This Mo–Mo distance is comparable to Mo–Mo distances found in the hepta- and octamolybdate ions. One of the molybdenum atoms is tetrahedrally surrounded by four oxygen atoms, one of which forms a bridge to the two other molybdenum atoms. This results in a weakening of the bond between this oxygen atom and the tetrahedrally coordinated molybdenum atom as is apparent from the longer bond distance, 1.85 \AA , as compared to the distance, 1.75 \AA , between the tetrahedrally coordinated molybdenum atom and each of the three remaining oxygen atoms. The two other molybdenum atoms are both coordinated to seven oxygen atoms in the pentagonal bipyramidal arrangement found in many

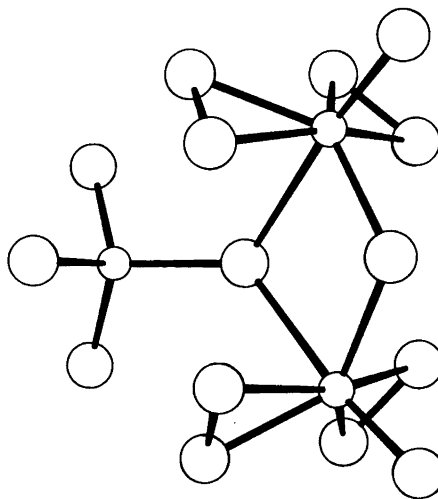


Fig. 1. The tetraperoxotrimolybdate ion, $[\text{Mo}_3\text{O}_7(\text{O}_2)_4]^{4-}$.

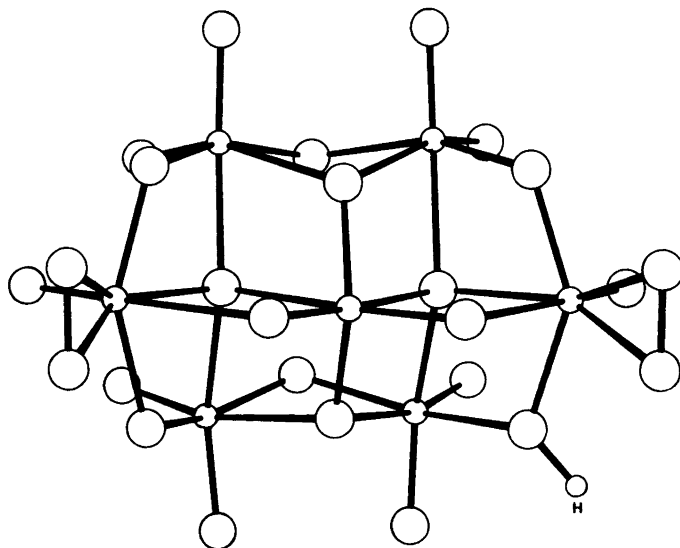


Fig. 2. The hydroxodiperoxoheptamolybdate ion, $[\text{Mo}_7\text{O}_{21}(\text{O}_2)_2(\text{OH})]^{5-}$.

peroxo complexes (see *e.g.* Ref. 2). From a structural point of view, the tetraperoxotrimolybdate ion can be thought of as being built up of a molybdate ion and a tetraperoxodimolybdate ion in the following way. The two pentagonal bipyramids of the tetraperoxodimolybdate ion (see Fig. 1 in Ref. 2) are turned about their common corner (the bridging oxygen atom) until the two coordinated water molecules coalesce; these water molecules are then replaced by one oxygen atom of the molybdate ion.

The bond distances in the two pentagonal bipyramids in I are: $\text{Mo}=\text{O}$ 1.67–1.69 Å, $\text{Mo}-\text{O}_{\text{apical}}$ 2.33 Å, $\text{Mo}-\text{O}_{\text{equatorial}}$ 1.94–2.01 Å and $(\text{O}-\text{O})_{\text{peroxo}}$ 1.47–1.49 Å.

II. $\text{K}_5[\text{Mo}_7\text{O}_{21}(\text{O}_2)_2(\text{OH})] \cdot 6\text{H}_2\text{O}$. Crystals of potassium hydroxodiperoxoheptamolybdate(VI)-6-water (II) can be obtained from moderately acidic (pH 3.0–5.3) potassium molybdate solutions to which hydrogen peroxide has been added to such an extent that the resulting $[\text{H}_2\text{O}_2]:[\text{Mo}]$ ratio is 0.3–1.0. They are monoclinic, space group $P2_1/n$, with $a=17.03$, $b=17.42$, $c=10.25$ Å, $\beta=98.66^\circ$, $V=3006$ Å³ and $Z=4$. $D_m=3.07$ g cm⁻³ and $D_c=3.076$ g cm⁻³.

Intensities were obtained with the automatic single crystal diffractometer PAILRED using $\text{MoK}\alpha$ radiation. 2743 intensities from 18 zones were used in the least-squares refinement of the derived atomic positions. With anisotropic temperature parameters the R -value based on all the reflexions, corrected for absorption effects, is 0.065.

The crystals of II are composed of potassium ions, protonated diperoxoheptamolybdate ions and water

of crystallization. The anion is in principle built in the same way as the isoheptamolybdate ion,^{8–10} the difference being the replacement of two oxygen atoms at each end of the ion by two peroxo groups (see Fig. 2) in the same way as was found in $\text{K}_6[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2] \cdot 8\text{H}_2\text{O}$.⁶

The hydrogen atom belonging to the diperoxoheptamolybdate anion is bonded to a bridge-forming oxygen atom. As a consequence the bond distances from this oxygen atom to the two molybdenum atoms are larger than the corresponding distances in the unprotonated diperoxoheptamolybdate ion. The proton interacts by hydrogen bonding with a bridge-forming oxygen atom of a neighbouring diperoxoheptamolybdate ion. This oxygen atom has a position equivalent to that to which the proton is bonded. The diperoxoheptamolybdate anions are thus coupled together by hydrogen bonding to form parallel chains running through the whole crystal.

Observed bond distances in II are: $\text{Mo}=\text{O}$ 1.65–1.74 Å, $\text{Mo}-\text{O}_{\text{peroxo}}$ 1.92–1.95 Å, $\text{Mo}-\text{O}$ 1.77–2.48 Å, and $(\text{O}-\text{O})_{\text{peroxo}}$ 1.40–1.43 Å.

III. $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{24}(\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$. Ammonium diaquadiperoxoheptamolybdate(VI)-4-water (III) crystallizes from acidic (pH 1.5–2.8) ammonium molybdate solutions to which small amounts of hydrogen peroxide have been added ($[\text{H}_2\text{O}_2]:[\text{Mo}] < 0.6$). The crystals of III are monoclinic, space group $P2_1/a$, with $a=19.799(3)$, $b=7.913(1)$, $c=10.435(2)$ Å, $\beta=114.69(2)^\circ$, $V=1485.4(5)$ Å³. $Z=2$.

The structure determination is based on intensities

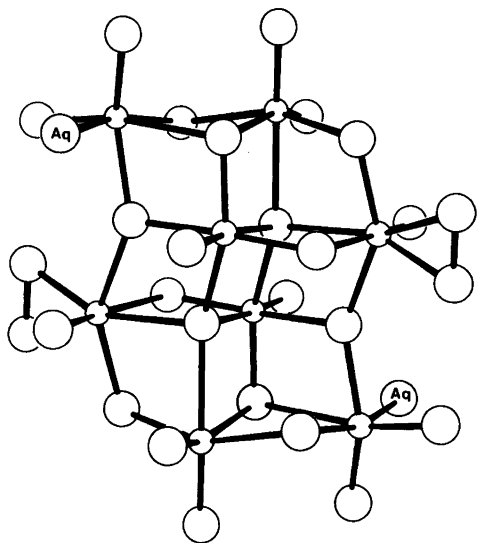


Fig. 3. The diaquadiperioxooctamolybdate ion, $[\text{Mo}_8\text{O}_{24}(\text{O}_2)_2(\text{H}_2\text{O})_2]^{4-}$.

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obtained with the automatic single crystal diffractometer PAILRED using $\text{MoK}\alpha$ radiation. Least-squares refinement using anisotropic temperature parameters resulted in an R -value of 0.040 for 2452 observed reflexions.

The crystals of III contain ammonium ions, diaquadiperioxooctamolybdate ions and water of crystallization. Six of the eight molybdenum atoms of the anion are octahedrally coordinated to oxygen atoms while two, each of which being coordinated to a peroxo group, are seven-coordinated in the pentagonal bipyramidal arrangement often observed in peroxo complexes. The anion of III is shown in Fig. 3.

The replacement of two oxygen atoms by two peroxo groups causes no changes in the molybdenum configuration in the heptamolybdate ion.^{5, this paper} In the diaquadiperioxooctamolybdate ion the linkage of the molybdenum-oxygen polyhedra differs, however, from both the α -¹¹ and β -form¹²⁻¹⁴ of the isoctamolybdate ion.

The obtained bond distances in III are: $\text{Mo}=\text{O}$ 1.68–1.72 Å, $\text{Mo}-\text{O}_{\text{bridge}}$ 1.76–2.43 Å, $\text{Mo}-\text{O}_{\text{water}}$ 2.17 Å, $\text{Mo}-\text{O}_{\text{peroxo}}$ 1.95 Å, and $(\text{O}-\text{O})_{\text{peroxo}}$ 1.43 Å. These values are close to corresponding values in other peroxopolymolybdates.

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