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## Studies on Peroxomolybdates

### VIII. The Structure of the Diperoxotetramolybdate (VI) Ion, $[\text{Mo}_4\text{O}_{12}(\text{O}_2)_2]^{4-}$ , and of the Diperoxoheptamolybdate (VI) Ion, $[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2]^{6-}$

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A proof of the existence of mono- and dinuclear peroxomolybdates has been furnished by the determination of the crystal structures of  $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_2]$  and  $\text{K}_2[\text{O}(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2](\text{H}_2\text{O})_2$ .<sup>1,2</sup> It would seem that peroxopolymolybdates also ought to exist since investigations of the crystalline products formed during the isothermal evaporation of solutions containing potassium molybdates and hydrogen peroxide in the pH range 4–8 have shown that at low  $\text{H}_2\text{O}_2:\text{Mo}$  ratios (0.1–0.8) crystals with rather large cell dimensions tend to form.<sup>3</sup> Judging from cell dimensions, densities, and empirical formulae, at least three different diperoxoheptamolybdates ought to exist within the pH range 4–7. The structure of one of these diperoxoheptamolybdates,  $\text{K}_6[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2](\text{H}_2\text{O})_8$ , has been determined and the anion is described below (I), while the structure of  $\text{K}_5\text{HMo}_7\text{O}_{22}(\text{O}_2)_2(\text{H}_2\text{O})_8$  is under consideration. For the latter compound a total of 3500 independent reflexion intensities have been

collected by a PAILRED diffractometer. The crystals of  $\text{K}_5\text{HMo}_7\text{O}_{22}(\text{O}_2)_2(\text{H}_2\text{O})_8$  are monoclinic, belonging to space group  $P2_1/c$ , with  $a=10.25$  Å,  $b=17.39$  Å,  $c=18.50$  Å, and  $\beta=114.70^\circ$ .

In the pH range 7–8 a tetragonal peroxomolybdate with the simple empirical formula  $\text{KMoO}_4$  is obtained. The structure analysis has shown that it is, in fact, a diperoxotetramolybdate with an unusual structure (see II below).

The analyses of the peroxopolymolybdates have shown that the peroxide content deviates more or less from the "ideal" value within the existence range of the phase in question. It is, however, possible to obtain a compound with the approximate stoichiometric composition, by choosing the conditions carefully. The intensity data for the diperoxoheptamolybdate were collected and processed before the comprehensive investigation of the crystalline solids separating out from solutions containing potassium molybdate and hydrogen peroxide was started, and it turned out that the structure investigation had been performed on a crystal with the composition  $\text{K}_x[\text{Mo}_7\text{O}_{22-x}(\text{O}_2)_x](\text{H}_2\text{O})_8$  where  $x=1.70$ . This was corrected for during the structure analysis.

The intensities of 1592 and 902 independent reflexions for I and II, respectively, were collected by the photographic Weissenberg method using  $\text{CuK}\alpha$  radiation.

The structures have been determined by the usual methods to the  $R$  values 0.109 and 0.098 for I and II, respectively.

**Results.** I. The crystals of  $\text{K}_6[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2](\text{H}_2\text{O})_8$  are orthorhombic,<sup>4</sup> belonging to space group  $C2cm$ , with  $a=8.487$  Å,  $b=19.047$  Å,  $c=19.974$  Å,  $V=3228.8$  Å<sup>3</sup>, and  $Z=4$ .

The  $[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2]^{6-}$  complex ion is shown in Fig. 1. It is evident that this diperoxoheptamolybdate has the same general appearance as the normal heptamolybdate,<sup>5</sup> the difference being that two peroxo groups replace two oxygen atoms, one at each end of the heptamolybdate. The two molybdenum atoms coordinated to the peroxo groups are thus surrounded by the pentagonal bipyramidal arrangement of ligand atoms frequently encountered in transition metal peroxo compounds. The remaining five molybdenum atoms are distortedly octahedrally coordinated by oxygen atoms as in the normal heptamolybdate.

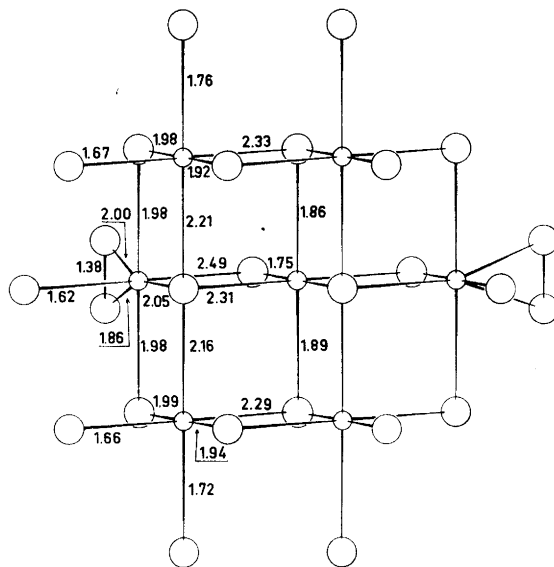


Fig. 1. The anion  $[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2]^{6-}$ . Large circles represent oxygen atoms and small ones molybdenum atoms. (The drawing is somewhat idealized.)

II. Crystals of  $\text{K}_4[\text{Mo}_4\text{O}_{12}(\text{O}_2)_2]$  are tetragonal, belonging to space group  $P4_12_12$ , with  $a=8.304 \text{ \AA}$ ,  $c=22.413 \text{ \AA}$ ,  $V=1545.5 \text{ \AA}^3$ , and  $Z=4$ .<sup>6</sup>

atoms are six-coordinated in a distorted octahedral manner and each peroxy group is coordinated to all four molybdenum atoms of the anion.

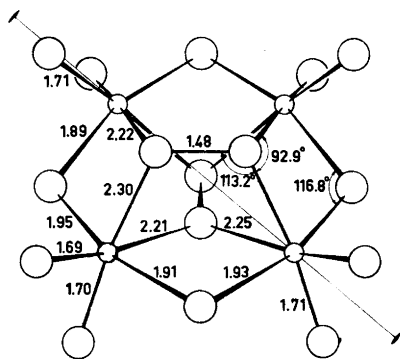


Fig. 2. Bond distances and angles in the  $[\text{Mo}_4\text{O}_{12}(\text{O}_2)_2]^{4-}$  ion.

The anion has the appearance shown in Fig. 2. Obviously, this is a new type of peroxy complex. All the molybdenum

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