# Studies on Peroxomolybdates XI.
# The Crystal Structure of Potassium Decaoxooctaperoxopentamolybdate(VI)-Water(1/5), $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$

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The crystal structure of potassium decaoxooctaperoxopentamolybdate(VI)-water(1/5) has been determined and refined by the least-squares method from single-crystal X-ray diffractometer data, collected at −100 °C, to a final $R_F$-value of 0.025 for 3759 observed, independent reflexions. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.320(6)$, $b = 12.722(4)$, $c = 13.956(5)$ Å and $\beta = 92.47(3)°$ at −100 °C and $a = 15.364(4)$, $b = 12.784(3)$, $c = 13.97(4)$ Å and $\beta = 92.44(2)°$ at 25 °C. $Z = 4$.
    The yellow, rhombohedral crystals are composed of potassium ions, decaoxo-octaperoxopentamolybdate ions and water molecules. The anion may be visu-elized as being formed from two diaquatrioxotetraperoxodimolybdate ions, $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ and one molybdate ion $[MoO_4]^{2-}$ in such a way that the four coordinated water molecules have been replaced by the four oxygen atoms of the molybdate ion. The decaoxooctaperoxopentamolybdate ion thus consists of one molybdenum atom with tetrahedral coordination and four molybdenum atoms with pentagonal bipyramidal oxygen coordination. Four of the seven oxygen atoms in each pentagonal bipyramid originate from peroxo groups. Average bond distances for the seven-coordinated arrangement: Mo=O 1.69 Å, Mo–$O_{peroxo}$ 1.96 Å, Mo–$O_{equatorial\ bridging}$ 1.93 Å, M–$O_{apical\ bridging}$ 2.39 Å and $(O–O)_{peroxo}$ 1.48 Å and for the four-coordinated arrangement: Mo=O 1.77 Å.

The two systems $K^+$-$H^+$-$MoO_4^{2-}$-$H_2O_2$-$H_2O$ and $NH_3$-$H^+$-$MoO_4^{2-}$-$H_2O_2$-$H_2O$ were investigated by phase-analytical methods at this department.[1,2] There are a large number of crystalline phases in each system.[1–8] Despite the small difference in size between the potassium and the ammonium ions, unexpectedly few of the phases are isomorphous. Still more noticeable is the fact that crystals of markedly different stoichiometry are obtained from solutions of similar composition in the two systems. For example, from weakly alkaline solutions (pH 8.0–9.0) with a peroxide: mo-lybdenum ratio of approximately 1, crystals with stoichiometries corresponding to the formula $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$ and $(NH_4)_4[Mo_3O_7(O_2)_4] \cdot 2H_2O$, respectively, are formed.

A crystal structure analysis of the latter compound[7] has shown it to contain discrete heptaoxo-tetraperoxotrimolybdate ions, ammonium ions and water molecules. The structure of the former compound will be discussed in this paper.

## Experimental

*Preparation.* The crystals were prepared according to the observations made in the phase ana-

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lytical investigation.[2] 3.60 g potassium molybdate, $K_2MoO_4$, was dissolved in 10.0 ml water and the solution was cooled to 10 °C. 2.2 ml 8 M nitric acid and 2.0 ml 30 % hydrogen peroxide were added slowly during stirring and cooling. The pH of the resulting solution, which was allowed to crystallize at 20 °C, was 8.1. Yellow, rhombohedral crystals were developed within one hour.

*X-ray methods.* Intensity data were collected for $2\theta \leqslant 50°$ with a SYNTEX P2$_1$ automatic four-circle single-crystal X-ray diffractometer, using graphite-monochromated MoK$\alpha$ radiation and a crystal with the dimensions $0.08 \times 0.16 \times 0.27$ mm. The $\omega - 2\theta$ scan method was used and the $2\theta$ scan speed was allowed to vary between 2 and 8° min$^{-1}$, depending on the intensity of the reflexion. The crystal was cooled to $-100$ °C using the SYNTEX LT1 low temperature device. Cell parameters were determined (at this temperature) from a least-squares fit of refined diffractometer setting angles for 11 reflexions. Unit cell dimensions were also obtained at 25 °C from a least-squares refinement based on 47 indexed lines in a Guinier powder photograph.

During the data collection three standard reflexions were measured after every forty-seventh reflexion. No significant decrease in intensity of these reflexions was observed. A 96-step profile was recorded for each reflexion, and the integrated intensity value was obtained by the Lehmann-Larsen profile analysis method.[9] A total of 4306 independent reflexions were measured and 3759 of these, having $I \geqslant 2\sigma(I)$, were used in the subsequent calculations. The net intensities were corrected for Lorentz, polarization and absorption effects.

## Crystal data

$K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$   F.W. = 1220.3
Space group $P2_1/n$ (No. 14; non-standard setting)
$a = 15.320(6)$ [15.364(4)] Å, $b = 12.722(4)$ [12.784(3)] Å, $c = 13.956(5)$ [13.977(4)] Å, $\beta = 92.47(3)$ [92.44(2)]°, $V = 2717(2)$ [2743(1)] Å$^3$, $Z = 4$, $D_m = 2.93$ g cm$^{-3}$, $D_x = 2.96$ g cm$^{-3}$, $\mu(MoK\alpha) = 3.19$ mm$^{-1}$
(cell dimensions are given for $-100$ °C and, within brackets, for 25 °C).

## Structure determination

The positions of all non-hydrogen atoms were found from a three-dimensional Patterson function and subsequent electron density calculations. The refinement of an overall scale factor, atomic coordinates and isotropic thermal parameters, using the block diagonal approximation, yielded an $R$-value of 0.048 (R = $\Sigma||F_o|-|F_c||/\Sigma|F_o|$). After correction for absorption effects $R$ dropped to 0.041 and a final value of 0.025 was obtained when anisotropic thermal parameters were included for all atoms. The $F_o$ values were weighted according to $w = [\sigma^2(F_o) + 0.002 \, F_o^2]^{-1}$. The atomic scattering factors for Mo, K$^+$ and O were taken from Ref. 10. A difference synthesis calculated after the final cycle of refinement showed a maximum peak height of 1.7 e Å$^{-3}$ at (0.136, 0.296, 0.418), which is 0.9 Å from Ow3. No other peak was higher than 0.8 e Å$^{-3}$. Since
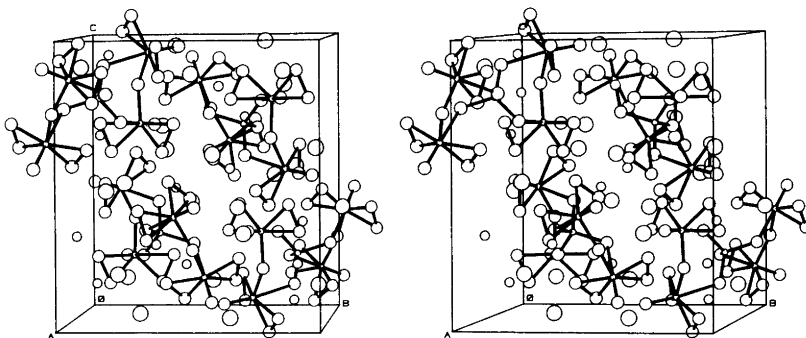


Fig. 1. Stereoscopic drawing of the unit cell of $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$. Large and small circles, not belonging to the complex ions, represent potassium ions and water molecules, respectively.

*Table 1.* Atomic fractional coordinates and equivalent isotropic thermal parameters for $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$ with their estimated standard deviations. All atoms occupy the general four-fold site $4e$ of space group $P2_1/n$. $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}a_ia_j$. Op has occupation number 0.15. Ow denotes a water oxygen atom and Op a peroxo oxygen atom.

| Atom | x | y | z | $B_{eq}/Å^2$ |
|------|------|------|------|------|
| Mo1 | 0.27784(3) | 0.20369(3) | 0.20931(3) | 1.07(1) |
| Mo2 | 0.35952(3) | 0.16515(3) | 0.45863(3) | 1.08(1) |
| Mo3 | 0.48640(3) | 0.33321(3) | 0.30525(3) | 0.86(1) |
| Mo4 | 0.59028(3) | 0.51813(3) | 0.15465(3) | 1.07(1) |
| Mo5 | 0.70642(3) | 0.41177(3) | 0.37609(3) | 0.96(1) |
| K1 | 0.43534(9) | 0.24460(9) | 0.01084(8) | 2.14(3) |
| K2 | 0.00628(8) | 0.13791(9) | 0.10354(7) | 1.59(3) |
| K3 | 0.35061(8) | 0.52578(10) | 0.12553(8) | 2.16(3) |
| K4 | 0.27256(9) | 0.43357(9) | 0.40300(8) | 2.06(3) |
| K5 | 0.68215(9) | 0.19263(9) | 0.17280(8) | 2.31(3) |
| K6 | 0.64841(8) | 0.14398(8) | 0.46297(7) | 1.64(3) |
| O1(1) | 0.2592(3) | 0.3594(3) | 0.2089(2) | 1.81(9) |
| O2(1) | 0.2740(2) | 0.3151(3) | 0.1125(2) | 1.61(9) |
| O3(1) | 0.3257(2) | 0.1138(3) | 0.1116(2) | 1.72(9) |
| O4(1) | 0.3391(2) | 0.0680(3) | 0.2097(2) | 1.78(9) |
| O5(1) | 0.1727(3) | 0.1612(3) | 0.2017(3) | 2.03(10) |
| O(12) | 0.2897(2) | 0.2099(3) | 0.3461(2) | 1.31(8) |
| O1(2) | 0.4528(3) | 0.1119(3) | 0.3773(3) | 2.16(10) |
| O2(2) | 0.4782(3) | 0.1145(3) | 0.4807(3) | 2.11(10) |
| O3(2) | 0.3695(3) | 0.2254(3) | 0.5862(2) | 2.04(9) |
| O4(2) | 0.2935(3) | 0.2693(3) | 0.5301(2) | 1.88(9) |
| O5(2) | 0.3044(3) | 0.0521(3) | 0.4776(3) | 1.93(9) |
| O1(4) | 0.5687(3) | 0.6504(3) | 0.2202(2) | 1.77(9) |
| O2(4) | 0.5059(2) | 0.6319(3) | 0.1385(2) | 1.66(9) |
| O3(4) | 0.5125(3) | 0.4316(3) | 0.0720(2) | 1.97(9) |
| O4(4) | 0.5742(3) | 0.3664(3) | 0.1316(3) | 2.01(9) |
| O5(4) | 0.6619(2) | 0.5539(3) | 0.0721(2) | 1.72(9) |
| O(45) | 0.6708(2) | 0.4822(3) | 0.2581(2) | 1.56(9) |
| O1(5) | 0.6017(3) | 0.4655(3) | 0.4364(2) | 1.83(9) |
| O2(5) | 0.6491(2) | 0.3873(3) | 0.4966(2) | 1.71(9) |
| O3(5) | 0.7708(3) | 0.2819(3) | 0.4019(3) | 1.86(9) |
| O4(5) | 0.7765(3) | 0.3164(3) | 0.3003(3) | 1.84(9) |
| O5(5) | 0.7821(2) | 0.5005(3) | 0.4150(2) | 1.51(9) |
| O(13) | 0.4245(2) | 0.2583(3) | 0.2202(2) | 1.44(8) |
| O(23) | 0.4320(2) | 0.3237(3) | 0.4143(2) | 1.43(9) |
| O(43) | 0.4818(2) | 0.4667(2) | 0.2676(2) | 1.36(8) |
| O(53) | 0.5963(2) | 0.2905(2) | 0.3227(2) | 1.25(8) |
| Ow1 | 0.9600(3) | 0.3772(3) | 0.3007(3) | 3.2(1) |
| Ow2 | 0.0780(3) | 0.3869(3) | 0.1581(3) | 2.5(1) |
| Ow3 | 0.1047(4) | 0.3505(5) | 0.4422(4) | 5.4(2) |
| Ow4 | 0.5240(3) | 0.0888(3) | 0.1282(3) | 2.9(1) |
| Ow5 | 0.6574(3) | 0.0292(3) | 0.3054(3) | 2.3(1) |
| Op | 0.135(2) | 0.293(3) | 0.419(3) | 5(1) |

there is sufficient space near Ow3 this may indicate that a small amount of the water molecule Ow3 has been replaced by hydrogen peroxide. Similar observations were made for $(C_{10}H_9N_2)$

$[H\{VO(O_2)_2(C_{10}H_8N_2)\}_2] \cdot xH_2O_2 \cdot (6-x)H_2O$, $x \approx 0.5$ and for $(C_{10}H_9N_2)[VO(O_2)_2(C_{10}H_8N_2)] - \cdot (3+x)H_2O_2 \cdot (2-x)H_2O$, $x = 0.4$.[11,12] No other water molecule seems to have been replaced in this way.

3

*Table 2.* Distances (Å) and angles (°) within the $[Mo_5O_{10}(O_2)_a]^{6-}$ anion.

| | | | |
|---|---|---|---|
| Mo1−O1(1) | 2.001(3) | | |
| Mo1−O2(1) | 1.957(3) | | |
| Mo1−O3(1) | 1.947(3) | | |
| Mo1−O4(1) | 1.965(4) | O1(1)−Mo1−O2(1) | 44.0(2) |
| Mo1−O(12) | 1.911(3) | O1(1)−Mo1−O5(1) | 100.4(2) |
| Mo1−O5(1) | 1.697(4) | O1(1)−Mo1−O(13) | 81.0(2) |
| Mo1−O(13) | 2.350(4) | O2(1)−Mo1−O3(1) | 86.8(2) |
| O1(1)−O2(1) | 1.485(5) | O2(1)−Mo1−O5(1) | 100.8(2) |
| O1(1)−O5(1) | 2.848(5) | O2(1)−Mo1−O(13) | 80.3(2) |
| O1(1)−O(13) | 2.838(5) | O3(1)−Mo1−O4(1) | 44.9(2) |
| O2(1)−O3(1) | 2.681(5) | O3(1)−Mo1−O5(1) | 98.8(2) |
| O2(1)−O5(1) | 2.821(5) | O3(1)−Mo1−O(13) | 80.3(2) |
| O2(1)−O(13) | 2.793(5) | O4(1)−Mo1−O(12) | 90.5(2) |
| O3(1)−O4(1) | 1.494(5) | O4(1)−Mo1−O5(1) | 99.9(2) |
| O3(1)−O5(1) | 2.773(5) | O4(1)−Mo1−O(13) | 78.7(2) |
| O3(1)−O(13) | 2.788(5) | O2(4)−Mo1−O1(1) | 88.2(2) |
| O4(1)−O(12) | 2.753(5) | O1(12)−Mo1−O5(1) | 97.2(2) |
| O4(1)−O5(1) | 2.809(5) | O1(12)−Mo1−O(13) | 82.7(2) |
| O4(1)−O(13) | 2.752(5) | | |
| O(12)−O1(1) | 2.724(5) | | |
| O(12)−O5(1) | 2.710(5) | | |
| O(12)−O(13) | 2.835(5) | | |
| | | | |
| Mo2−O1(2) | 1.983(4) | | |
| Mo2−O2(2) | 1.924(4) | | |
| Mo2−O3(2) | 1.938(4) | | |
| Mo2−O4(2) | 1.965(4) | O1(2)−Mo2−O2(2) | 44.5(2) |
| Mo2−O(12) | 1.947(3) | O1(2)−Mo2−O5(2) | 100.1(2) |
| Mo2−O5(2) | 1.694(4) | O1(2)−Mo2−O(23) | 77.7(2) |
| Mo2−O(23) | 2.397(3) | O2(2)−Mo2−O3(2) | 86.5(2) |
| O1(2)−O2(2) | 1.480(5) | O2(2)−Mo2−O5(2) | 100.7(2) |
| O1(2)−O5(2) | 2.825(6) | O2(2)−Mo2−O(23) | 81.8(2) |
| O1(2)−O(23) | 2.766(5) | O3(2)−Mo2−O4(2) | 44.7(2) |
| O2(2)−O3(2) | 2.646(5) | O3(2)−Mo2−O5(2) | 102.3(2) |
| O2(2)−O5(2) | 2.791(6) | O3(2)−Mo2−O(23) | 83.4(2) |
| O2(2)−O(23) | 2.850(5) | O4(2)−Mo2−O(12) | 86.3(2) |
| O3(2)−O4(2) | 1.483(5) | O4(2)−Mo2−O5(2) | 102.9(2) |
| O3(2)−O5(2) | 2.832(5) | O4(2)−Mo2−O(23) | 79.5(2) |
| O3(2)−O(23) | 2.904(5) | O(12)−Mo2−O1(2) | 91.3(2) |
| O4(2)−O(12) | 2.676(5) | O(12)−Mo2−O5(2) | 96.6(2) |
| O4(2)−O5(2) | 2.866(5) | O(12)−Mo2−O(23) | 77.9(2) |
| O4(2)−O(23) | 2.808(5) | | |
| O(12)−O1(2) | 2.810(5) | | |
| O(12)−O5(2) | 2.723(5) | | |
| O(12)−O(23) | 2.752(5) | | |
| | | | |
| Mo4−O1(4) | 1.950(3) | | |
| Mo4−O2(4) | 1.948(4) | | |
| Mo4−O3(4) | 1.960(4) | | |
| Mo4−O4(4) | 1.971(4) | O1(4)−Mo4−O2(4) | 44.6(2) |
| Mo4−O(45) | 1.913(4) | O1(4)−Mo4−O5(4) | 102.4(2) |
| Mo4−O5(4) | 1.687(4) | O1(4)−Mo4−O(43) | 78.1(2) |
| Mo4−O(43) | 2.429(3) | O2(4)−Mo4−O3(4) | 88.0(2) |
| O1(4)−O2(4) | 1.479(5) | O2(4)−Mo4−O5(4) | 99.7(2) |
| O1(4)−O5(4) | 2.841(5) | O2(4)−Mo4−O(43) | 78.8(2) |

4

*(Table 2 (cont.)*

| | | | |
|---|---|---|---|
| O1(4)−O(43) | 2.784(5) | O3(4)−Mo4−O4(4) | 44.4(2) |
| O2(4)−O3(4) | 2.715(5) | O3(4)−Mo4−O5(4) | 98.4(2) |
| O2(4)−O5(4) | 2.783(5) | O3(4)−Mo4−O(43) | 79.3(2) |
| O2(4)−O(43) | 2.803(5) | O4(4)−Mo4−O(45) | 87.8(2) |
| O3(4)−O4(4) | 1.485(5) | O4(4)−Mo4−O5(4) | 103.5(2) |
| O3(4)−O5(4) | 2.768(5) | O4(4)−Mo4−O(43) | 76.0(2) |
| O3(4)−O(43) | 2.824(5) | O(45)−Mo4−O1(4) | 88.2(2) |
| 04(4)−O(45) | 2.693(5) | O(45)−Mo4−O5(4) | 99.3(2) |
| O4(4)−O5(4) | 2.878(5) | O(45)−Mo4−O(43) | 83.3(2) |
| O4(4)−O(43) | 2.732(5) | | |
| O(45)−O1(4) | 2.689(5) | | |
| O(45)−O5(4) | 2.748(5) | | |
| O(45)−O(43) | 2.911(5) | | |
| | | | |
| Mo5−O1(5) | 1.966(4) | | |
| Mo5−O2(5) | 1.955(3) | | |
| Mo5−O3(5) | 1.950(4) | | |
| Mo5−O4(5) | 1.960(4) | O1(5)−Mo5−O2(5) | 44.1(2) |
| Mo5−O(45) | 1.933(3) | O1(5)−Mo5−O5(5) | 101.0(2) |
| Mo5−O5(5) | 1.691(3) | O1(5)−Mo5−O(53) | 77.2(2) |
| Mo5−O(53) | 2.382(3) | O2(5)−Mo5−O3(5) | 87.0(2) |
| O1(5)−O2(5) | 1.473(5) | O2(5)−Mo5−O5(5) | 99.1(2) |
| O1(5)−O5(5) | 2.828(5) | O2(5)−Mo5−O(53) | 80.1(2) |
| O1(5)−O(53) | 2.733(5) | O3(5)−Mo5−O4(5) | 44.8(2) |
| O2(5)−O3(5) | 2.689(5) | O3(5)−Mo5−O5(5) | 99.9(2) |
| O2(5)−O5(5) | 2.779(5) | O3(5)−Mo5−O(53) | 81.6(2) |
| O2(5)−O(53) | 2.810(5) | O4(5)−Mo5−O(45) | 88.2(2) |
| O3(5)−O4(5) | 1.490(5) | O4(5)−Mo5−O5(5) | 101.6(2) |
| O3(5)−O5(5) | 2.792(5) | O4(5)−Mo5−O(53) | 80.1(2) |
| O3(5)−O(53) | 2.851(5) | O(45)−Mo5−O1(5) | 89.9(2) |
| 04(5)−O(45) | 2.709(5) | O(45)−Mo5−O5(5) | 97.4(2) |
| O4(5)−O5(5) | 2.835(5) | O(45)−Mo5−O(53) | 82.2(2) |
| O4(5)−O(53) | 2.811(5) | | |
| O(45)−O1(5) | 2.755(5) | | |
| O(45)−O5(5) | 2.727(5) | | |
| O(45)−O(53) | 2.855(5) | | |
| | | | |
| Mo3−O(13) | 1.766(3) | | |
| Mo3−O(23) | 1.771(3) | | |
| Mo3−O(43) | 1.778(3) | O(13)−Mo3−O(23) | 106.4(2) |
| Mo3−O(53) | 1.776(3) | O(13)−Mo3−O(43) | 107.7(2) |
| O(13)−O(23) | 2.831(5) | O(13)−Mo3−O(53) | 113.9(2) |
| O(13)−O(43) | 2.861(5) | O(23)−Mo3−O(43) | 107.8(2) |
| O(13)−O(53) | 2.969(5) | O(23)−Mo3−O(53) | 109.9(2) |
| O(23)−O(43) | 2.867(5) | O(43)−Mo3−O(53) | 111.0(2) |
| O(23)−O(53) | 2.904(5) | | |
| O(43)−O(53) | 2.928(5) | | |

Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Refs. 13 and 14. A list of observed and calculated structure factors is available from the authors on request.

## Results and discussion

Positional parameters and $B_{eq}$ are given in Table 1 and distances and angles within the anion in Table 2. Fig. 1 shows a stereoscopic view of the cell content and Fig. 2 the anion.
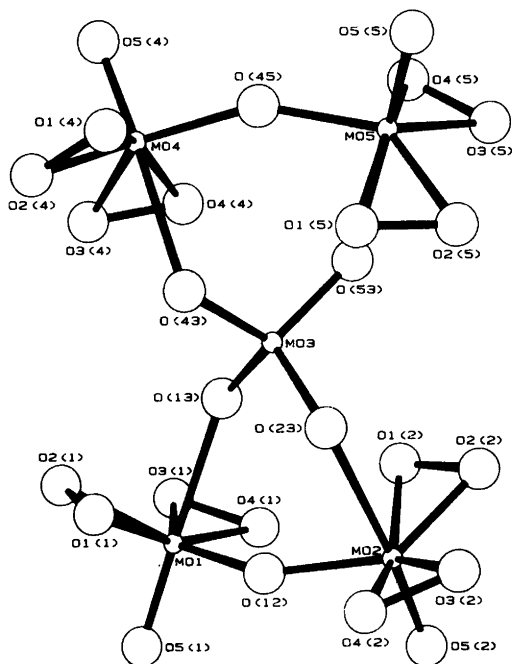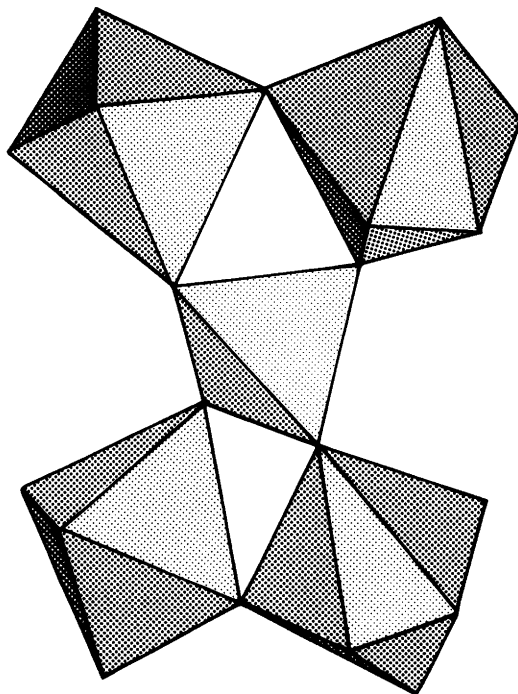
*Fig. 2a.* The complex ion $[Mo_5O_{10}(O_2)_8]^{6-}$.

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

The crystals of $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$ consist of potassium ions, decaoxoperoxopentamolyb-date ions and water molecules. The polyanion has almost $D_2$ (222) symmetry. It is composed of a central molybdenum atom with tetrahedral oxygen coordination and four Mo atoms which are seven-coordinated by oxygen atoms in a pen-tagonal-bipyramidal arrangement. Each oxygen atom in the tetrahedral arrangement forms a bridge to an outer Mo atom. The four outer Mo atoms are further connected in pairs by an oxy-gen bridge. The geometry of the anion can thus be described as a central tetrahedron sharing cor-ners with four pentagonal bipyramids which in turn share corners in pairs. The two dimeric moieties have an appearance which closely re-sembles that of the diaquatrioxotetraperoxodi-molybdate ion, $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$.[3,15] From this point of view the octaperoxopentamolybdate ion may be visualized as a composite of two diaq-uatetraperoxodimolybdate ions $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ and one molybdate ion $[MoO_4]^{2-}$, the four water ligands in the two dimolybdate ions having been replaced by the four oxygen atoms

of the molybdate ion, *i.e* $2[Mo_2O_3(O_2)_4(H_2O)_2]^{2-} + [MoO_4]^{2-} \rightarrow [Mo_5O_{10}(O_2)_8]^{6-} + 4H_2O$.

In contrast to the solutions depositing $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$, ammonium peroxomo-lybdate solutions of similar composition give a compound of quite different stoichiometry, *viz.* $(NH_4)_4[Mo_3O_7(O_2)_4] \cdot 2H_2O$. These crystals con-tain ammonium ions, heptaoxotetraperoxotrimo-lybdate ions and water molecules.[7] Comparison between the octaperoxopentamolybdate ion and the tetraperoxotrimolybdate ion shows that they both contain $Mo_2O_3(O_2)_4(H_2O)_2^{2-}$ and $MoO_4^{2-}$ ions as building units. In the tetraperoxotrimolybdate ion one oxygen atom from a $MoO_4^{2-}$ ion replaces two water molecules in the $Mo_2O_3(O_2)_4(H_2O)_2^{2-}$ unit, whereas there is a 1 : 1 substitution in the octaperoxopentamolybdate ion.

The pentagonal bipyramids of oxygen atoms surrounding the four molybdenum atoms are al-most identical, which is evident from Table 2. The equatorial plane is formed from two laterally coordinated peroxo groups and one oxygen bridge. These five atoms are about equally re-mote from the central atom ($Mo-O_{peroxo}$ 1.92–

2.00 Å, $Mo-O_{bridge}$ 1.91–1.95 Å). The apical positions are occupied by one terminal oxygen atom ($Mo=O$ 1.69–1.70 Å) and another oxygen atom which weakly bridges to the four-coordinated molybdenum atom. The molybdenum atoms are displaced 0.316–0.364 Å from the equatorial planes towards the terminal oxygen atoms. The peroxo groups have an average $O-O$ distance of 1.484 Å, which is in excellent agreement with values obtained in other peroxomolybdates containing building units of the same ligand arrangement.[3,4]

The configuration of oxygen atoms about the four-coordinated molybdenum atom is close to tetrahedral. These $Mo-O$ bond lengths, 1.766(3)–1.778(3) Å, do not differ significantly from those observed in isolated molybdate ions, 1.76–1.77 Å,[16,17] or from the average $Mo-O_{terminal}$ distance calculated for tetrahedral coordination, 1.77 Å.[18,19] The bonding influence from the seven-coordinated molybdenum atom must, therefore, be very weak, which is also reflected by the long $Mo-O$ distance of 2.35–2.43 Å. In the tetraperoxotrimolybdate ion the bridging influence is, however, evident.[7] The $MoO_4^{2-}$ moiety in this ion has only one bridging oxygen atom and shows a distorted tetrahedral geometry. The three $Mo-O_{terminal}$ bonds have a mean length of 1.743 Å while the fourth oxygen atom is situated at a distance of 1.844 Å and 2.319 Å from the four-coordinated and the seven-coordinated molybdenum atoms, respectively.

Potassium ions are surrounded by an irregular arrangement of 6–10 oxygen atoms at distances less than 3.0 Å. The structure is further stabilized by hydrogen bonding.

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