

Studies on Peroxomolybdates XIII. The Crystal Structure of Potassium Diperoxoheptamolybdate(VI)-Water(1/10), $K_6[Mo_7O_{22}(O_2)_2] \cdot 10H_2O$

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The crystal structure of potassium diperoxoheptamolybdate(VI)-water(1/10) has been determined from single-crystal X-ray diffractometer data, collected at $-100^\circ C$, and refined by the least-squares method to a final R_F value of 0.043 for 4730 observed, independent reflections. The yellow compound crystallized in the monoclinic space group $P2_1/c$ with $a = 16.629(7)$, $b = 10.538(3)$, $c = 19.704(8)$ Å, $\beta = 103.56(3)^\circ$, $V = 3356(2)$ Å³ and $Z = 4$. The crystals were composed of potassium ions, diperoxoheptamolybdate(VI) ions and water of crystallization. The crystals investigated showed solid solubility; some of the diperoxoheptamolybdate anions had been replaced by monoperoxoheptamolybdate ions and/or by heptamolybdate ions, with the actual formula being $K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 10H_2O$, $x=0.45$. The diperoxoheptamolybdate anion had the same general appearance as the normal heptamolybdate ion with the difference that two remote, terminal oxygen atoms have been replaced by peroxy groups. The diperoxoheptamolybdate ion consisted of 5 molybdenum atoms with octahedral oxygen coordination and 2 molybdenum atoms with pentagonal-bipyramidal oxygen arrangement. Bond distances within the anion: $Mo=O_{terminal}$ 1.680(7) - 1.724(7) Å, $Mo-O_{bridging}$ 1.747(7) - 2.509(7) Å, $Mo-O_{peroxy}$ 1.929(9) - 1.954(10) Å and $(O-O)_{peroxy}$ 1.472(17) - 1.479(15) Å.

Solid products depositing from the systems $K^+/H^+/MoO_4^{2-}/H_2O_2/H_2O$ and $NH_3/H^+/MoO_4^{2-}/H_2O_2/H_2O$ have been investigated by chemical analysis, IR spectroscopy and single-crystal X-ray methods and/or powder diffractometry at this Department (a short summary is given in Ref. 1).^{2,3} A large number of crystalline compounds exist in each system. The main factors influencing the phases formed are the ratio $[O_2^{2-}]_{tot}:[Mo]_{tot}$, the acidity and the temperature of the solution.

From a potassium molybdate solution with $[O_2^{2-}]_{tot}:[Mo]_{tot} = 0.1-0.8$ and $pH = 5.8-6.8$, two crystalline diperoxoheptamolybdates can be obtained, one with orthorhombic and one with monoclinic symmetry.⁴ The former phase is ob-

tained at temperatures below $20^\circ C$ and the latter normally above $27^\circ C$. The structure of the orthorhombic potassium diperoxoheptamolybdate, $K_6[Mo_7O_{22}(O_2)_2] \cdot 8H_2O$, has been determined by Stomberg *et al.*,^{5,6} while that of the monoclinic phase is presented in this paper.

Experimental

Preparation. The crystals were prepared according to the observations made in the phase analytical investigations.^{2,3} 2.60 g Potassium molybdate, K_2MoO_4 , were dissolved in 8.0 ml water and the solution was heated to approximately $35^\circ C$. To this solution was added, with constant

stirring, a mixture of 0.76 ml 30% hydrogen peroxide and 1.1 ml 8 M nitric acid. The acidity of the final solution was adjusted to pH = 6.0 with 8 M nitric acid and the solution was left to crystallize at about 30°C. Yellow, prismatic crystals with the composition $K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 8H_2O$ appeared within a few hours. For these, x depended on the peroxide concentration of the solution. In the present case, x was 0.45. The crystals were unstable; at room temperature, they disintegrated completely within a few days.

X-ray methods. Reflection intensities were recorded at -100°C with a Syntex P2₁ automatic four-circle single-crystal X-ray diffractometer, equipped with the LT1 low temperature device (graphite-monochromated MoK α radiation, crystal size 0.14×0.18×0.36 mm, ω scan method, scan speed 1.5–11.7° min⁻¹, $2\theta_{\text{max}} = 50^\circ$). Periodical intensity measurement of a test reflection showed no significant deterioration of the crystal during the collection of the data. A 19-step profile was recorded for each reflection and the Lehmann-Larsen profile analysis method⁷ was used to calculate the intensities.⁸ Of the 5919 independent reflections which were registered, 4730 having $I \geq 3\sigma(I)$ were regarded as being observed and were used in the subsequent calculations. The 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 reflections.

Crystal data

$K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 10H_2O$, $x=0.45$.
F.W. = 1495.1. Space group $P2_1/c$ (No. 14);
 $a = 16.629(7)$ [16.656(11)] Å, $b = 10.538(3)$ [10.560(7)] Å, $c = 19.704(8)$ [19.819(7)] Å, $\beta = 103.56(3)$ [103.90(4)]°, $V = 3356(2)$ [3384(6)] Å³,
 $D_c = 2.96$ (2.89) g cm⁻³, $Z = 4$, $\mu(\text{MoK}\alpha) = 3.33$ mm⁻¹ (cell dimensions are given for -100°C and, within brackets, for 21°C for a crystal with $x=0.70$ according to chemical analysis).⁴

Structure determination

The structure was solved from Patterson and successive electron density maps. A stoichiometric model was refined. This led to too high B values

for the peroxy oxygen atoms and too short bond distances between them. The subsequent electron density difference map showed residual maxima between the peroxy oxygen atoms. This was a consequence of the nonstoichiometrical peroxide content, observed in the chemical analysis, the peroxy groups being partly replaced by oxygen atoms. This type of replacement has been observed for other peroxometallates.^{1,4,6,9,10} Least-squares refinement of an overall scale factor, atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms, followed by electron density difference calculations, were performed using various occupation numbers for the peroxy oxygen atoms and the replacing oxo oxygen atoms, keeping the sum of the occupation numbers of each oxo/peroxy group equal to one. A minimum R value of 0.053 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) was obtained with occupation number 0.75 for O3(5) and O4(5), 0.25 for O2(5), 0.80 for O3(7) and O4(7) and 0.20 for O2(7). This also led to the smoothest electron density difference map.

Absorption correction was performed using an empirical method for correcting diffractometer data for absorption effects due to Walker and Stuart.¹¹ Introduction of anisotropic thermal parameters for all non-hydrogen atoms except O2(5) and O2(7) in full matrix refinement gave $R = 0.043$ (448 parameters). Weights were calculated according to $w = [\sigma^2(F_o) + 0.004 F_o^2]^{-1}$. The atomic scattering factors for Mo, K⁺ and O were taken from Ref. 12.

An electron density difference map calculated after the final cycle of refinement showed no electron density higher than 1.5 e Å⁻³. Calculations were carried out on an IBM 3081 computer using the crystallographic programs used at this Department.^{13,14} Lists of structural factors and anisotropic thermal parameters can be obtained from the authors on request.

Results and discussion

Atomic coordinates and equivalent isotropic thermal parameters 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 anion.

The crystals of $K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 10H_2O$, $x=0.45$, are built up from potassium ions, water

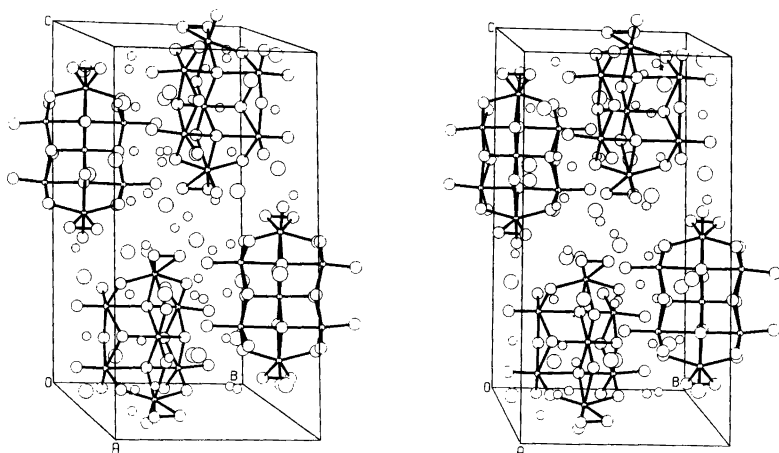


Fig. 1. Stereoscopic drawing of the unit cell of the crystalline compound $K_6[Mo_7O_{22}(O_2)_2] \cdot 10H_2O$. Large and small circles, not belonging to the complex ions, represent potassium ions and water molecules, respectively.

of crystallization and, mainly diperoxoheptamolybdate(VI) ions. Due to the nonstoichiometry of the crystals, some of the diperoxoheptamolybdate ions are statistically replaced by monoperoxoheptamolybdate ions and/or normal heptamolybdate ions. There is but a slight difference in volume between the bulky diperoxoheptamolybdate and heptamolybdate ions (see below and also Fig. 1). The nonstoichiometry will thus cause a negligible disruption in the packing of the structural units and this solid solubility is confirmed by the structure analysis.

The diperoxoheptamolybdate ions in $K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 10H_2O$, $x=0.45$, are isostructural with those in $K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 8H_2O$, $x=0.33$,^{5,6} but are differently packed. They have the same general appearance as the normal heptamolybdate ion with the exception that two terminal oxygen atoms, one at each end of the anion, have been replaced by two peroxo groups. The symmetry of the heptamolybdate ion, which has been found to be close to m^2 (C_{2v}) in solid state structures,¹⁵ is not changed by this substitution.

A compilation of Mo–Mo distances in some normal heptamolybdate and diperoxoheptamolybdate ions is made in Table 3. Evidently the oxo-peroxo substitution has only a small influence on the structure of the heptamolybdate ion, *viz.* a small decrease in the distances from the central molybdenum atom Mo6 to the molybdenum atoms coordinating the peroxo groups (Mo5 and Mo7). This contraction seems to be

counterbalanced by a small elongation of the distances from Mo6 to the four other molybdenum atoms (Mo1–Mo4).

Distances and angles within the diperoxoheptamolybdate ion observed in the present investigation agree well with those obtained for the corresponding ion in $K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 8H_2O$, $x=0.33$,^{5,6} and, disregarding the peroxo groups, for heptamolybdates. A very small displacement of the equivalent bridging atoms O(15), O(35), O(27) and O(47) from the peroxo coordinating atoms Mo5 and Mo7 towards the molybdenum atoms Mo1–Mo4, respectively, was, however, observed. In addition, the Mo=O_{unsubstituted} bond (1.72 Å) in the normal heptamolybdate part of the structure bisects the angle between the molybdenum atom and the peroxo oxygen atoms in the diperoxoheptamolybdate part.

A detailed discussion of bonds and coordination in the heptamolybdate ion, $Mo_7O_{24}^{6-}$, is given by Hedman,^{15,16} and an elaborate examination of the pentagonal-bipyramidal oxygen arrangement about the peroxo coordinating molybdenum atoms Mo5 and Mo7 can be found in Ref. 6. The observed (O–O)_{peroxo} bond distances, 1.472(17) – 1.479(15) Å, agree well with other observations (see, e.g., Table V in Ref. 17, which covers about one hundred determinations). The coordination about the potassium ions is irregular, contact distances ranging from 2.672(7) Å and upwards (see Table 4). The structure is further stabilized by extensive hydrogen bonding (see Table 5).

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters for $K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 10H_2O$, $x=0.45$, with their estimated standard deviations. All atoms occupy the general four-fold site $4e$ of space group $P2_1/c$. The occupation numbers are 0.25 for O2(5), 0.20 for O2(7), 0.75 for O3(5) and O4(5), 0.80 for O3(7) and O4(7), and 1 for all other atoms. The B values were kept constant for O2(5) and O2(7). Ow denotes a water oxygen atom.

$$B_{eq} = \frac{1}{3} \sum \sum_{ij} \beta_{ij} \cdot a_i \cdot a_j$$

Atom	x	y	z	$B_{eq}/\text{\AA}^2$
Mo1	0.17780(5)	0.59495(8)	0.06764(4)	0.92(2)
Mo2	0.18769(5)	0.59188(8)	0.23541(4)	0.89(2)
Mo3	0.22651(5)	0.20123(8)	0.07195(4)	0.94(2)
Mo4	0.23749(5)	0.20226(8)	0.24142(4)	0.90(2)
Mo5	0.29901(5)	0.42928(8)	-0.00174(4)	0.97(2)
Mo6	0.33891(5)	0.43767(8)	0.17368(4)	0.76(2)
Mo7	0.32345(5)	0.42659(8)	0.34122(4)	0.92(2)
K1	0.4074(1)	0.4564(2)	0.5363(1)	1.50(5)
K2	0.4264(1)	0.0300(2)	0.3424(1)	1.57(5)
K3	0.0875(1)	0.3662(2)	0.3720(1)	1.97(6)
K4	0.0272(1)	0.3181(3)	0.0779(1)	2.40(6)
K5	0.3112(1)	0.8519(2)	0.1684(1)	1.39(5)
K6	0.1290(1)	0.9517(2)	0.3025(1)	1.74(6)
O1(1)	0.0964(4)	0.5476(7)	0.0009(3)	1.7(2)
O2(1)	0.1674(4)	0.7568(7)	0.0751(3)	1.5(2)
O(12)	0.1279(4)	0.5385(6)	0.1423(3)	1.1(2)
O(15)	0.2678(4)	0.6053(6)	0.0205(3)	1.1(2)
O(126)	0.2811(4)	0.5925(6)	0.1653(3)	1.1(2)
O(1356)	0.2359(4)	0.4096(6)	0.0764(3)	1.2(2)
O1(2)	0.1130(4)	0.5537(7)	0.2790(3)	1.5(2)
O2(2)	0.1815(4)	0.7550(6)	0.2253(3)	1.2(2)
O(27)	0.2878(4)	0.6009(6)	0.3113(3)	1.0(2)
O(2467)	0.2459(4)	0.4109(6)	0.2434(3)	1.0(2)
O1(3)	0.1376(4)	0.2086(7)	0.0065(3)	1.5(2)
O2(3)	0.2542(4)	0.0431(6)	0.0786(3)	1.3(2)
O(34)	0.1691(4)	0.2121(6)	0.1472(3)	1.1(2)
O(35)	0.3129(4)	0.2533(6)	0.0268(3)	1.0(2)
O(346)	0.3208(4)	0.2586(7)	0.1710(3)	1.1(2)
O1(4)	0.1557(4)	0.2084(6)	0.2803(3)	1.1(2)
O2(4)	0.2644(4)	0.0422(7)	0.2443(3)	1.4(2)
O(47)	0.3308(4)	0.2478(6)	0.3148(3)	1.2(2)
O1(5)	0.2244(4)	0.4134(7)	-0.0755(4)	1.8(2)
O2(5)	0.394(2)	0.460(5)	-0.028(2)	1.5
O3(5)	0.3824(6)	0.531(1)	-0.0315(5)	1.5(3)
O4(5)	0.3984(6)	0.394(1)	-0.0328(5)	1.5(2)
O(56)	0.4007(4)	0.4536(7)	0.1137(3)	1.4(2)
O(67)	0.4068(4)	0.4552(6)	0.2561(3)	1.1(2)
O1(7)	0.2586(4)	0.4081(7)	0.3943(3)	1.6(2)
O2(7)	0.421(3)	0.470(6)	0.399(2)	1.5
O3(7)	0.4147(6)	0.522(1)	0.3996(5)	1.5(2)
O4(7)	0.4304(5)	0.384(1)	0.4019(4)	1.7(2)
Ow1	0.5164(4)	0.2331(7)	0.3090(4)	1.9(2)
Ow2	0.0744(5)	0.9568(8)	0.1499(4)	2.7(2)
Ow3	0.4282(4)	0.0410(7)	0.1847(4)	1.9(2)
Ow4	0.0377(4)	0.1073(8)	0.3746(4)	2.3(2)
Ow5	0.3901(5)	0.7842(7)	0.0497(4)	2.0(2)
Ow6	0.4120(4)	0.7660(7)	0.3039(4)	1.9(2)
Ow7	0.0082(4)	0.7642(7)	0.2932(4)	2.0(2)
Ow8	0.0931(7)	0.611(1)	0.4416(5)	4.1(3)
Ow9	0.2106(5)	0.7643(7)	0.3946(4)	2.4(2)
Ow10	0.4863(5)	0.7571(8)	0.4439(4)	2.5(2)

Table 2. Distances (Å) and angles (°) within the anions in $K_6[Mo_7O_{22+x}(O_2)_{2-x}] \cdot 10H_2O$, $x=0.45$.

Distance		Angle	
Mo1—O1(1)	1.726(7)	O1(1)—Mo1—O2(1)	106.0(3)
Mo1—O2(1)	1.724(7)	O1(1)—Mo1—O(12)	95.2(3)
Mo1—O(12)	1.943(6)	O1(1)—Mo1—O(15)	101.9(3)
Mo1—O(15)	1.941(6)	O1(1)—Mo1—O(1356)	93.2(3)
Mo1—O(126)	2.259(7)	O1(1)—Mo1—O(126)	161.8(3)
Mo1—O(1356)	2.168(7)	O(126)—Mo1—O2(1)	90.6(3)
O1(1)—O2(1)	2.755(10)	O(126)—Mo1—O(12)	74.1(2)
O1(1)—O(12)	2.713(9)	O(126)—Mo1—O(15)	83.7(2)
O1(1)—O(15)	2.851(9)	O(126)—Mo1—O(1356)	71.7(2)
O1(1)—O(1356)	2.844(9)	O2(1)—Mo1—O(12)	99.7(3)
O(126)—O2(1)	2.856(9)	O2(1)—Mo1—O(15)	95.1(3)
O(126)—O(12)	2.545(9)	O2(1)—Mo1—O(1356)	159.4(3)
O(126)—O(15)	2.813(9)	O(1356)—Mo1—O(12)	85.7(3)
O(126)—O(1356)	2.595(9)	O(1356)—Mo1—O(15)	73.1(3)
O2(1)—O(12)	2.807(9)	O(12)—Mo1—O(15)	153.3(3)
O2(1)—O(15)	2.709(9)		
O(1356)—(12)	2.802(9)		
O(1356)—(15)	2.454(9)		
Mo2—O1(2)	1.716(7)	O1(2)—Mo2—O2(2)	105.1(3)
Mo2—O2(2)	1.731(7)	O1(2)—Mo2—O(12)	97.7(3)
Mo2—O(12)	1.954(6)	O1(2)—Mo2—O(27)	102.4(3)
Mo2—O(27)	1.962(6)	O1(2)—Mo2—O(2467)	97.1(3)
Mo2—O(126)	2.309(6)	O1(2)—Mo2—O(126)	165.5(3)
Mo2—O(2467)	2.128(7)	O(126)—Mo2—O2(2)	87.6(3)
O1(2)—O2(2)	2.736(9)	O(126)—Mo2—O(12)	72.8(2)
O1(2)—O(12)	2.768(9)	O(126)—Mo2—O(27)	83.4(2)
O1(2)—O(27)	2.870(9)	O(126)—Mo2—O(2467)	71.9(2)
O1(2)—O(2467)	2.893(9)	O2(2)—Mo2—O(12)	100.0(3)
O(126)—O2(2)	2.827(9)	O2(2)—Mo2—O(27)	93.3(3)
O(126)—O(12)	2.545(9)	O2(2)—Mo2—O(2467)	155.9(3)
O(126)—O(27)	2.853(9)	O(2467)—Mo2—O(12)	86.2(3)
O(126)—O(2467)	2.608(9)	O(2467)—Mo2—(27)	72.3(2)
O2(2)—O(12)	2.827(9)	O(12)—Mo2—O(27)	152.1(3)
O2(2)—O(27)	2.689(9)		
O(2467)—O(12)	2.792(9)		
O(2467)—O(27)	2.417(9)		
Mo3—O1(3)	1.722(7)	O1(3)—Mo3—O2(3)	105.5(3)
Mo3—O2(3)	1.725(7)	O1(3)—Mo3—O(34)	94.6(3)
Mo3—O(34)	1.946(6)	O1(3)—Mo3—O(35)	104.0(3)
Mo3—O(35)	1.939(6)	O1(3)—Mo3—O(1356)	91.4(3)
Mo3—O(346)	2.280(6)	O1(3)—Mo3—O(346)	158.0(3)
Mo3—O(1356)	2.202(7)	O(346)—Mo3—O2(3)	94.2(3)
O1(3)—O2(3)	2.744(10)	O(346)—Mo3—O(34)	72.2(2)
O1(3)—O(34)	2.699(9)	O(346)—Mo3—O(35)	83.3(2)
O1(3)—O(35)	2.888(9)	O(346)—Mo3—O(1356)	71.0(2)
O1(3)—O(1356)	2.828(9)	O2(3)—Mo3—O(34)	99.7(3)
O(346)—O2(3)	2.958(9)	O2(3)—Mo3—O(35)	95.4(3)
O(346)—O(34)	2.504(9)	O2(3)—Mo3—O(1356)	160.9(3)
O(346)—O(35)	2.816(9)	O(1356)—Mo3—O(34)	87.4(3)
O(346)—O(1356)	2.602(9)	O(1356)—Mo3—O(35)	71.5(2)
O2(3)—O(34)	2.810(9)	O(34)—Mo3—O(35)	151.9(3)
O2(3)—O(35)	2.715(9)		
O(1356)—O(34)	2.871(9)		
O(1356)—O(35)	2.429(9)		

Mo4-O1(4)	1.712(6)	O1(4)-Mo4-O2(4)	104.3(3)
Mo4-O2(4)	1.742(7)	O1(4)-Mo4-O(34)	94.4(3)
Mo4-O(34)	1.940(6)	O1(4)-Mo4-O(47)	103.9(3)
Mo4-O(47)	1.918(6)	O1(4)-Mo4-O(2467)	90.5(3)
Mo4-O(346)	2.257(6)	O1(4)-Mo4-O(346)	158.7(3)
Mo4-O(2467)	2.203(7)	O(346)-Mo4-O2(4)	94.9(3)
O1(4)-O2(4)	2.728(9)	O(346)-Mo4-O(34)	72.8(2)
O1(4)-O(34)	2.684(9)	O(346)-Mo4-O(47)	83.8(2)
O1(4)-O(47)	2.862(9)	O(346)-Mo4-O(2467)	72.7(2)
O1(4)-O(2467)	2.801(9)	O2(4)-Mo4-O(34)	99.9(3)
O(346)-O2(4)	2.966(10)	O2(4)-Mo4-O(47)	93.5(3)
O(346)-O(34)	2.504(9)	O2(4)-Mo4-O(2467)	162.0(3)
O(346)-O(47)	2.801(9)	O(2467)-Mo4-O(34)	89.1(3)
O(346)-O(2467)	2.645(9)	O(2467)-Mo4-O(47)	72.5(3)
O2(4)-O(34)	2.821(9)	O(34)-Mo4-O(47)	153.9(3)
O2(4)-O(47)	2.669(10)		
O(2467)-O(34)	2.912(9)		
O(2467)-O(47)	2.448(9)		
Mo5-O1(5)	1.684(7)	O1(5)-Mo5-O3(5)	103.2(4)
Mo5-O3(5)	1.950(10)	O1(5)-Mo5-O4(5)	102.7(4)
Mo5-O4(5)	1.929(9)	O1(5)-Mo5-O(15)	96.0(3)
Mo5-O(15)	2.002(7)	O1(5)-Mo5-O(35)	99.7(3)
Mo5-O(35)	1.936(7)	O1(5)-Mo5-O(1356)	103.4(3)
Mo5-O(56)	2.509(7)	O1(5)-Mo5-O(56)	175.2(3)
Mo5-O(1356)	2.067(6)	O(56)-Mo5-O3(5)	80.8(3)
O1(5)-O3(5)	2.852(12)	O(56)-Mo5-O4(5)	82.1(3)
O1(5)-O4(5)	2.826(12)	O56-Mo5-O(15)	82.0(2)
O1(5)-O(15)	2.748(10)	O(56)-Mo5-O(35)	80.0(2)
O1(5)-O(35)	2.772(10)	O(56)-Mo5-O(1356)	71.8(2)
O1(5)-O(1356)	2.954(9)	O3(5)-Mo5-O4(5)	44.6(5)
O(56)-O3(5)	2.922(12)	O3(5)-Mo5-O(15)	78.2(4)
O(56)-O4(5)	2.947(12)	O3(5)-Mo5-O(35)	124.7(4)
O(56)-O(15)	2.985(9)	O3(5)-Mo5-O(1356)	143.2(4)
O(56)-O(35)	2.890(9)	O4(5)-Mo5-O(15)	122.3(4)
O(56)-O(1356)	2.707(9)	O4(5)-Mo5-O(35)	81.6(4)
O3(5)-O4(5)	1.472(17)	O4(5)-Mo5-O(1356)	147.1(4)
O3(5)-O(15)	2.491(12)	O(15)-Mo5-O(35)	147.5(3)
O4(5)-O(35)	2.526(12)	O(15)-Mo5-O(1356)	74.2(3)
O(1356)-O(15)	2.454(9)	O(1356)-Mo5-O(35)	74.6(3)
O(1356)-O(35)	2.429(9)		
Mo5-O2(5)	1.80(4)	O2(5)-Mo5-O1(5)	107(1)
O2(5)-O1(5)	2.81(4)	O2(5)-Mo5-O(56)	78(1)
O2(5)-O(56)	2.76(4)	O2(5)-Mo5-O(15)	101(2)
O2(5)-O(15)	2.93(4)	O2(5)-Mo5-O(35)	102(1)
O2(5)-O(35)	2.90(4)	O2(5)-Mo5-O(1356)	149(1)
Mo6-O(56)	1.747(7)	O(56)-Mo6-O(67)	105.2(3)
Mo6-O(67)	1.757(7)	O(56)-Mo6-O(126)	103.1(3)
Mo6-O(126)	1.881(7)	O(56)-Mo6-O(346)	101.0(3)
Mo6-O(346)	1.910(7)	O(56)-Mo6-O(1356)	83.6(3)
Mo6-O(1356)	2.272(6)	O(56)-Mo6-O(2467)	174.0(3)
Mo6-O(2467)	2.315(6)	O(2467)-Mo6-O(67)	80.7(3)
O(56)-O(67)	2.784(9)	O(2467)-Mo6-O(126)	76.1(2)
O(56)-O(126)	2.843(9)	O(2467)-Mo6-O(346)	76.8(2)
O(56)-O(346)	2.823(9)	O(2467)-Mo6-O(1356)	90.5(2)
O(56)-O(1356)	2.707(9)	O(67)-Mo6-O(126)	101.2(3)
O(2467)-O(67)	2.671(9)	O(67)-Mo6-O(346)	101.1(3)
O(2467)-O(126)	2.608(9)	O(67)-Mo6-O(1356)	171.2(3)
O(2467)-O(346)	2.645(9)	O(1356)-Mo6-O(126)	76.7(3)

STRUCTURE OF $K_6[Mo_7O_{22}(O_2)_2] \cdot 10H_2O$

O(2467)—O(1356)	3.257(9)	O(1356)—Mo6—O(346)	76.4(2)
O(67)—O(126)	2.813(9)	O(126)—Mo6—O(346)	141.3(3)
O(67)—O(346)	2.833(9)		
O(1356)—O(126)	2.595(9)		
O(1356)—O(346)	2.602(9)		
Mo7—O1(7)	1.680(7)	O1(7)—Mo7—O3(7)	102.5(4)
Mo7—O3(7)	1.954(10)	O1(7)—Mo7—O4(7)	102.6(4)
Mo7—O4(7)	1.949(9)	O1(7)—Mo7—O(27)	95.9(3)
Mo7—O(27)	1.977(6)	O1(7)—Mo7—O(47)	98.2(3)
Mo7—O(47)	1.966(7)	O1(7)—Mo7—O(2467)	102.7(3)
Mo7—O(67)	2.432(6)	O1(7)—Mo7—O(67)	175.0(3)
Mo7—O(2467)	2.059(6)	O(67)—Mo7—O3(7)	81.5(3)
O1(7)—O3(7)	2.839(12)	O(67)—Mo7—O4(7)	82.3(3)
O1(7)—O(47)	2.837(11)	O(67)—Mo7—O(27)	81.9(2)
O1(7)—O(27)	2.722(9)	O(67)—Mo7—O(47)	81.7(2)
O1(7)—O47)	2.762(10)	O(67)—Mo7—O(2467)	72.4(2)
O1(7)—O(2467)	2.930(9)	O3(7)—Mo7—O4(7)	44.5(4)
O(67)—O3(7)	2.887(12)	O3(7)—Mo7—O(27)	80.5(3)
O(67)—O4(7)	2.906(11)	O3(7)—Mo7—O(47)	124.1(3)
O(67)—O(27)	2.909(9)	O3(7)—Mo7—O(2467)	145.3(3)
O(67)—O(47)	2.897(9)	O4(7)—Mo7—O(27)	124.4(4)
O(67)—O(2467)	2.671(9)	O4(7)—Mo7—O(47)	80.6(4)
O3(7)—O4(7)	1.479(15)	O4(7)—Mo7—O(2467)	146.8(3)
O3(7)—O(27)	2.539(11)	O(27)—Mo7—O(47)	147.6(3)
O4(7)—O(47)	2.531(11)	O(27)—Mo7—O(2467)	73.6(2)
O(2467)—O(27)	2.417(9)	O(2467)—Mo7—O(47)	74.9(3)
O(2467)—O(47)	2.448(9)		
Mo7—O2(7)	1.81(5)	O2(7)—Mo7—O1(7)	104(2)
O2(7)—O1(7)	2.76(5)	O2(7)—Mo7—O(67)	80(1)
O2(7)—O(67)	2.78(5)	O2(7)—Mo7—O(27)	97(2)
O2(7)—O(27)	2.83(5)	O2(7)—Mo7—O(47)	108(2)
O2(7)—O(47)	3.06(6)	O2(7)—Mo7—O(2467)	152(2)

Table 3. A compilation of Mo—Mo distances (Å) in the $[Mo_7O_{22}(O_2)_2]^{6-}$ anions in $K_6[Mo_7O_{22}(O_2)_2] \cdot 10H_2O$ (A) (this paper) and $K_6[Mo_7O_{22}(O_2)_2] \cdot 8H_2O$ (B)^{5,6} and in the $[Mo_7O_{24}]^{6-}$ anions in $(NH_3CH_2CH_2CH_3)_6[Mo_4] \cdot 3H_2O$ (C),¹⁷ $(NH_3CH(CH_3)_2)_6[Mo_7O_{24}] \cdot 3H_2O$ (D)¹⁷ and $Na_6[Mo_7O_{24}] \cdot 14H_2O$ (E)¹³.

Distance	A	B	C	D	E
Mo1—Mo2	3.271(2)	3.308(4)	3.276(1)	3.287(1)	3.274(2)
Mo3—Mo4	3.301(2)	3.300(4)	3.254(1)	3.293(1)	3.276(2)
Mo1—Mo5	3.205(1)	3.215(4)	3.219(1)	3.230(1)	3.211(2)
Mo2—Mo7	3.205(2)	3.215(4)	3.224(1)	3.202(1)	3.214(2)
Mo3—Mo5	3.187(1)	3.210(5)	3.223(1)	3.221(2)	3.193(4)
Mo4—Mo7	3.191(1)	3.210(5)	3.214(1)	3.205(1)	3.204(6)
Mo1—Mo3	4.224(2)	4.217(3)	4.214(1)	4.227(2)	4.161(5)
Mo2—Mo4	4.185(2)	4.217(3)	4.214(1)	4.163(2)	4.175(5)
Mo6—Mo1	3.415(2)	3.469(3)	3.407(1)	3.377(1)	3.413(2)
Mo6—Mo2	3.446(1)	3.469(3)	3.410(1)	3.427(1)	3.426(2)
Mo6—Mo3	3.459(1)	3.465(4)	3.423(1)	3.388(1)	3.431(5)
Mo6—Mo4	3.440(1)	3.465(4)	3.401(1)	3.431(2)	3.409(6)
Mo6—Mo5	3.365(2)	3.394(2)	3.432(1)	3.373(1)	3.445(2)
Mo6—Mo7	3.373(2)	3.394(2)	3.456(1)	3.399(1)	3.422(2)

Table 5. Hydrogen bond distances in $K_6[Mo_7O_{22}(O_2)_2] \cdot 10H_2O$. Distances less than 3.0 \AA are included. Ow denotes a water oxygen atom. Estimated standard deviations are 0.01 \AA .

Distance/Å		Distance/Å		Distance/Å	
Ow1...O(67) ⁱ	3.00	Ow5...O(15) ⁱ	2.73	Ow9...O(27) ⁱ	2.88
Ow2...O2(2) ^j	2.94	Ow6...O(27) ^j	2.73	Ow10...O4(5) ^{vi}	2.69
Ow3...O(67) ⁱⁱ	2.86	Ow7...O1(4) ^v	2.83	Ow10...O3(7) ⁱ	2.80
Ow3...O(346) ^j	2.88	Ow7...O1(2) ^j	2.87	Ow10...O3(5) ^{vi}	2.93
Ow4...O(12) ⁱⁱⁱ	2.79	Ow8...O2(1) ^{vi}	2.98		
Ow4...O1(1) ^{iv}	2.94	Ow9...O(15) ^{vi}	2.80		

Symmetry codes:

i	(x, y, z)	iv	($x, \frac{1}{2} - y, \frac{1}{2} + z$)	vii	($1 - x, \frac{1}{2} + y, \frac{1}{2} - z$)
ii	($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$)	v	($\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$)		
iii	($\bar{x}, -\frac{1}{2} + y, \frac{1}{2} - z$)	vi	($x, \frac{3}{2} - y, \frac{1}{2} + z$)		

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