and a secondary hydration sphere. Eighteen of the twenty-one water molecules are connected through a network of hydrogen bonds. $W(1)$, $W(6)$ and $W(10)$, which bridge peptide molecules, are not involved in any water–water interactions. Water molecules $W(15)$, $W(18)$, $W(19)$ and $W(20)$, on the other hand, do not form any hydrogen bond with the peptide molecules, and constitute the secondary hydration shell. Each of the water molecules, $W(2)$, $W(3)$, $W(8)$, $W(9)$, $W(11)$, $W(16)$ and $W(21)$ form two hydrogen bonds with the peptide molecules, while the rest of the water form only one hydrogen bond with the peptide molecules. Thirteen of the water molecules have a tetrahedral environment and the rest have trigonal arrangements of hydrogen bonds about them. The minimal solvent content of structure (II) allows for considerable direct intermolecular hydrogen bonding. There are five peptide–peptide and three peptide–water interactions. Only one of these involves an amide group, $O(3)C\cdots N(6)C$ $(-x, 0{\cdot}5+y, 1-z) = 2{\cdot}940$ (13) Å. The lone water molecule serves to bridge three siderophore molecules *via* hydrogen bonds, $W(1)\cdots O(6)$, $W(1)\cdots O(3\varepsilon)$ and $W(1)\cdots O(1\kappa)$. The acetonitrile does not hydrogen bond, but is involved in a number of close contacts. Despite the fact that the molecules *A, B* and *C* of ferrirubin have different modes of solvent interactions, the conformational differences in the three molecules are not very significant. It appears that, at least for ferrirubin, solvent interactions have very little effect on the conformation of the peptide backbone.

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Structure of Diaquaoxodiperoxomolybdenum(VI)–1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) Monohydrate, [MoO(O₂)₂(H₂O)₂].C₁₂H₂₄O₆.H₂O

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Abstract. $M_r = 494{\cdot}30$, orthorhombic, $A2_1ma$, $a = 12{\cdot}882$ (2), $b = 13{\cdot}683$ (2), $c = 12{\cdot}020$ (2) Å, $V = 2118{\cdot}7$ (6) Å³, $Z = 4$, $D_m = 1{\cdot}570$ (2), $D_x = 1{\cdot}550$ g cm⁻³, λ(Mo $K\alpha$) = $0{\cdot}71069$ Å, $\mu = 6{\cdot}77$ cm⁻¹, $F(000) = 1024$, $T = 293$ (2) K. Final $R = 0{\cdot}028$ for 1252 observed reflections. The Mo atom has a distorted pentagonal bipyramidal seven-coordination with the two peroxo groups and one water in the equatorial plane, and the double-bonded O and another water at the apices. Two O atoms of the 18-crown-6 are on the mirror plane, but the symmetry of the crown is actually close to D_{3d} with the configurations at C—C *gauche*, at C—O *trans*. Five of the O atoms of the crown are hydrogen-bonded to water molecules; the sixth O does not participate in hydrogen bonding. The presence of the peroxo groups was unexpected, since no strong oxidizing agent was added in the preparation of the compound.

$[MoO(O_2)_2(H_2O)_2].C_{12}H_{24}O_6.H_2O$

Introduction. The present work is part of a larger study of the co-condensation products of MoO_3 with various organic ligands. MoO_3 and tetrahydrofuran (THF) were co-condensed in a 'metal vapor' reactor at 77 K. The resulting gray–green solid was stirred at room temperature with excess THF under exposure to air and light, which produced a yellow solution. Addition of a small amount of water, then 18-crown-6, followed by slow evaporation yielded yellow crystals from which a specimen was selected for X-ray diffraction. The structure analysis unexpectedly showed the presence of two peroxo ligands bonded to the molybdenum. The peroxomolybdenum compounds described in the literature (Spivack & Dori, 1975), are formed by the addition of hydrogen peroxide to soluble molybdenum compounds. The peroxo compound described in this study was formed by oxygen uptake from the air involving Mo^{VI}, THF and water (DeKock & McAfee, 1985). The presence of the peroxo groups was confirmed by permanganate titration. Recently Ledon, Varescon, Malinski & Kadish (1984) observed similar uptake of oxygen with an Mo^{VI} porphyrin compound, 2-propanol and water.

Experimental. Yellow, prismatic crystal of approximate dimensions $0.55 \times 0.25 \times 0.17$ mm. Syntex $P\bar{1}$ diffractometer, graphite monochromator, Mo $K\alpha$ radiation, θ–2θ scan, scan speed $1°$ min^{-1}, 2θ range $2.0°$ plus α_1, α_2 angular separation. 15 reflections used for measuring lattice parameters. Ratio of background time to scan time 1:2, one octant of reciprocal space measured, $2\theta_{max} = 55°$. Three standard reflections, intensity variation $\pm 4.4\%$. 1328 unique reflections measured, h 0–16, k 0–17, l 0–15, 1252 with $F^2 > 2\sigma$ used in refinement. No absorption correction. D_m by flotation in $CHCl_3/CCl_4$. Reflections observed: hkl, $k + l = 2n$; $hk0$, $h = 2n$, possible space groups: $A2_1ma$ (No. 36), $Am2a$ (No. 40) and $Amma$ (No. 63), first space group adopted, because of distribution of peaks in Patterson map, and confirmed by refinement. Mo atom and assumed octahedron surrounding it located on Patterson map. Subsequent refinement and difference Fourier maps revealed the non-H atoms of the crown ether and one additional water molecule. One of the O atoms (on the mirror plane) in the coordination sphere of the Mo atom had to be moved off this plane, thus giving the Mo atom seven coordinating atoms instead of the assumed six. This resulted in two pairs of O atoms at short distances, which were then interpreted as peroxo groups. Some but not all H atoms showed up in the difference Fourier map. In last cycles of full-matrix least-squares refinement, positional and anisotropic thermal parameters varied for all non-H atoms (132 parameters), H atoms included at calculated positions with isotropic B and not refined. Final $R = 0.028$ (1252 reflections), $R_w = 0.031$, $S = 1.71$. $(\Delta/\sigma)_{max} = 0.04$, $(\Delta/\sigma)_{mean} = 0.005$. Final $\Delta\rho$ excursions -0.15 to

$+0.32$ e $Å^{-3}$ (near Mo atom). Computer programs: local versions of those of Zalkin (undated). Quantity minimized $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = C + Bt^2 + |0.02(C - Bt)|^2$ [C is integrated count, B total background count and t $(= 2)$ ratio of scan time to background time]. Scattering factors from *International Tables for X-ray Crystallography* (1974), for Mo scattering factor for Mo^{3+} was used.

Discussion. The final parameters are listed in Table 1.* The molybdenum coordination polyhedron (Fig. 1a) has mirror symmetry. The Mo atom, the double-bonded

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, interatomic distances and angles, and distances to the least-squares plane through the six crown O atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39857 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters (for* Mo $\times 10^5$, *for* O *and* C $\times 10^4$) *and* B_{eq} *for the non*-H *atoms*

B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoids.

|	x	y	z	$B_{eq}(Å^2)$
Mo	0	0	21926 (4)	2.84 (1)
O(1)	3852 (4)	0	1685 (5)	6.4 (2)
C(2)	3652 (6)	837 (7)	1059 (6)	8.5 (3)
C(3)	3781 (5)	1702 (7)	1814 (7)	8.6 (3)
O(4)	2954 (3)	1714 (3)	2590 (4)	6.2 (1)
C(5)	3008 (6)	2503 (4)	3353 (8)	8.0 (2)
C(6)	2070 (7)	2498 (4)	4071 (8)	8.2 (2)
O(7)	2122 (4)	1722 (3)	4832 (4)	6.7 (1)
C(8)	1254 (7)	1715 (6)	5565 (8)	9.3 (3)
C(9)	1343 (7)	862 (7)	6289 (6)	9.7 (3)
O(10)	1222 (5)	0	5656 (5)	6.5 (2)
O(20)	−1274 (4)	0	2072 (4)	4.6 (1)
O(21)	454 (3)	955 (4)	1153 (4)	7.3 (1)
O(22)	333 (3)	1367 (2)	2252 (5)	6.9 (1)
O(23w)	−104 (6)	0	3923 (4)	8.2 (2)
O(24w)	1706 (3)	0	2826 (4)	3.2 (1)
O(25w)	3419 (4)	0	4742 (5)	4.8 (2)
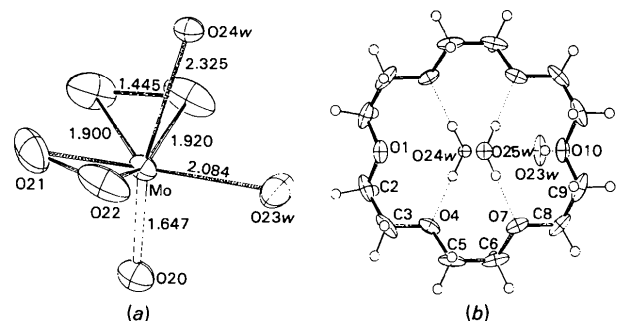
Fig. 1. (a) *ORTEP*II (Johnson, 1976) view of the Mo^{VI} moiety in $|MoO(O_2)_2(H_2O)_2|.18$-crown-6.H_2O. The thermal ellipsoids are given at 25% probability. Distances in Å; e.s.d.'s for bonds to Mo are 0.003–0.005 Å, for the O(21)–O(22) bond 0.006 Å. (b) Projection of the 18-crown-6 ether with surrounding water molecules, approximately perpendicular to the least-squares plane of the O atoms. Thermal ellipsoids at 25% probability. H atoms are shown by circles of arbitrary size. Dotted lines are hydrogen bonds.

Table 2. *Dimensions of the* 18-*crown*-6 *ether*

1 2 3 4	Distance (Å) 2–3	Angle (°) 1–2–3	Torsion angle (°) 1–2–3–4 (e.s.d.'s 1·1°)	Deviation of O from least-squares plane (Å) (e.s.d.'s 0·006 Å)
C(2)'–O(1)–C(2)–C(3)	1·393 (8)	110·5 (9)	174·5	+0·210
O(1)–C(2)–C(3)–O(4)	1·501 (12)	107·6 (5)	−70·2	
C(2)–C(3)–O(4)–C(5)	1·415 (9)	108·9 (5)	179·4	−0·223
C(3)–O(4)–C(5)–C(6)	1·418 (9)	113·4 (6)	175·5	
O(4)–C(5)–C(6)–O(7)	1·485 (11)	109·4 (5)	72·6	
C(5)–C(6)–O(7)–C(8)	1·403 (9)	110·1 (6)	177·7	+0·241
C(6)–O(7)–C(8)–C(9)	1·424 (9)	111·8 (6)	177·3	
O(7)–C(8)–C(9)–O(10)	1·460 (12)	108·2 (6)	−67·2	
C(8)–C(9)–O(10)–C(9)'	1·413 (8)	109·7 (6)	177·4	−0·246
C(9)–O(10)–C(9)'–C(8)'		113·2 (9)		

O(20) and the two water molecules, O(23w) and O(24w), are in the mirror plane. The peroxo group, O(21)–O(22), with its mirror equivalent and O(23w) form the equatorial plane of a distorted pentagonal bipyramid of which O(20) and O(24w) are the apices. The Mo—peroxo distances [average 1·910 (12) Å], the Mo=O distance [1·647 (5) Å] and the O—O distance in the peroxo group [1·445 (6) Å] are within the range of distances observed earlier for monomeric and dimeric peroxomolybdates as reviewed by Spivack & Dori (1975) (respectively 1·91–2·00, 1·64–1·68, 1·36–1·55 Å). The distances of O(21), O(22) and O(23w) to the least-squares plane through these atoms, the equatorial plane of the distorted pentagonal bipyramid, are respectively −0·046, +0·076 and −0·059 Å. The distance of the Mo atom to this plane is −0·359 Å. The apical water molecule is leaning away from the peroxo groups with an O(20)—Mo—O(24w) angle of 165·9 (2)°. This presumably puts O(24w) into a more favorable position for hydrogen bonding to the crown ether (see below). This distortion is more severe than observed before by Le Carpentier, Schlupp & Weiss (1972) and Le Carpentier, Mitschler & Weiss (1972) (respectively 173·9 and 177·0°). The distance from the Mo to the apical water O(24w) [2·325 (4) Å] is longer than the distance to the equatorial water O(23w) [2·084 (5) Å]. In the aquaoxodiperoxo Mo^{VI} complexes reported in the reviews quoted above, the distances to the apical waters range from 2·35–2·45 Å. The short Mo—O(23w) distance will be discussed below.

The 18-crown-6 ether (Fig. 1b, Table 2) also has mirror symmetry, with O(1) and O(10) in the mirror plane. The average C—C distance is 1·482 (18) Å, the average C—O distance 1·411 (11) Å. The average O—C—C angle is 109·0 (9)°, which is close to ideally tetrahedral; the average C—O—C angle is slightly larger at 112·4 (1·2)°. The distances of the O atoms to the least-squares plane through these atoms are within ±0·25 Å. The actual symmetry of the crown is close to the D_{3d} symmetry usually observed for 18-crown-6 complexes, as described by Dunitz, Dobler, Seiler & Phizackerley (1974) for complexes with KNCS, RbNCS and CsNCS, and by Elbasyouny, Brügge, von
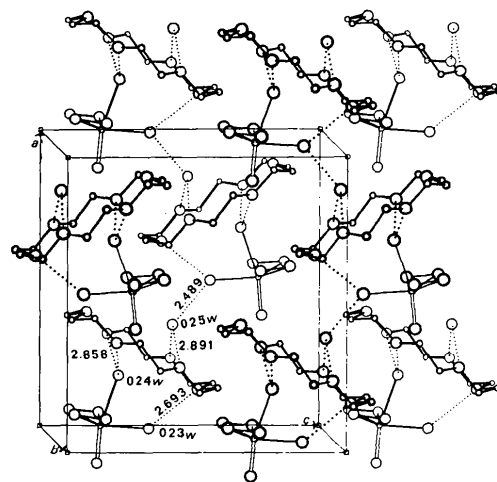

Fig. 2. Packing diagram for |MoO(O₂)₂(H₂O)₂|.18-crown-6.H₂O. Small circles are Mo and C atoms, larger circles O atoms and water molecules. Hydrogen bonds are shown by dotted lines. The e.s.d.'s in the distances (in Å) indicated are 0·009 Å to O(23w) and 0·005 Å to the other atoms.

Deuten, Dickel, Knöchel, Koch, Kopf, Melzer & Rudolph (1983) for complexes with neutral molecules.

The crown ether in this study is hydrogen-bonded to three water molecules in the mirror plane: the O(4) atoms are bonded to the apical water molecule, O(24w), of an Mo moiety below the crown, the O(7) atoms to the 'free' water, O(25w), above the crown, and the O(10) atom is bonded to the equatorial water, O(23w), of the Mo moiety. O(1) is the only O atom of the crown that does not participate in hydrogen bonding. The bonding of the 18-crown-6 to the water molecules, rather than directly to the transition metal, is also observed in other aqua–transition-metal complexes as for example in a complex containing the hexaaqua-manganese group, reported by Vance, Holt, Varie & Holt (1980).

The packing diagram is given in Fig. 2. The Mo moieties, the crown-ether molecules and the 'free' water molecules are hydrogen-bonded together to form infinite columns with mirror symmetry, extending in the

direction of the a axis. There are no hydrogen bonds between the columns. The distances between O atoms involved in hydrogen bonding (2·489–2·891 Å) are within the distances accepted for normal hydrogen bonding in crystalline hydrates as reported by Chiari & Ferraris (1982), except the shortest one, which is between $O(23w)$ and $O(25w)$. As can be seen in Fig. 1, $O(23w)$ has a large anisotropic thermal component perpendicular to the mirror plane. This may indicate that there is disorder, by which this molecule is displaced from the mirror plane, so that the actual $O(25w)–O(23w)$ distance is somewhat longer than the observed average distance. This would also lengthen the short $Mo–O(23w)$ distance mentioned above.

The 18-crown-6 in the complex described here lacks the usual crystallographic center of symmetry observed in other complexes and has instead a crystallographic mirror plane. This makes possible coordination to different groups above and below the ring. As mentioned by Elbasyouny et al. (1983) no stable binary complex of only water and 18-crown-6 has been found. In other transition metal.H_2O.18-crown-6 complexes (e.g. Vance et al., 1980), the coordinating water molecules are part of a positively charged hydrated transition-metal moiety and other negatively charged species are present in the crystal. In the complex described here no charged species are present. Apparently the Mo^{VI} atom makes the H atoms of the

coordinating water molecules sufficiently acidic to facilitate hydrogen bonding to the crown. The short distance between $O(23w)$ and $O(25w)$ may have the same effect on the H atoms of the 'free' water molecule.

Computing costs were provided by the OSU Computer Center.

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trans-Bis(tert-butylamine)dichloroplatinum(II), C8H22Cl2N2Pt

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Abstract. $M_r = 412·27$, monoclinic, $P2_1/c$, $a = 6·248$ (3), $b = 20·569$ (21), $c = 10·676$ (9) Å, $\beta = 92·27$ (6)°, $V = 1371$ (2) Å^3, $Z = 4$, $D_m = 2·01$ (2), $D_x = 1·997$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0·71069$ Å, $\mu = 11·120$ mm^{-1}, $F(000) = 784$, $T = 295$ K, $R = 0·043$, $R_w = 0·040$ for 2519 unique observed reflections. The coordination around the Pt atom is square planar. The compound, which was synthesized in our laboratory, is the trans isomer. The Pt–N bond lengths are 2·041 (6) and 2·053 (6) Å, while the Pt–Cl bond lengths are 2·299 (2) and 2·296 (2) Å. The structure is stabilized by intermolecular hydrogen bonds between the amino groups and the chlorine atoms.

Introduction. Continuing our studies on platinum amine compounds, we have synthesized trans-[Pt-(t-butylamine)$_2$Cl$_2$] and determined its molecular and crystal structure. It was synthesized from the hot aqueous reaction of K$_2$PtCl$_4$ with the amine. Because of the bulkiness of the ligand, the trans isomer is obtained.

Experimental. Synthesis: 1 ml of tert-butylamine was added to 0·5 g of K$_2$PtCl$_4$ dissolved in 5 ml of hot water. The mixture was heated (~350 K) with stirring until a precipitate appeared and the solution became yellow. The mixture was then evaporated to dryness under vacuum. The residue was washed with water and