

## Structure of the Hydrated Potassium Hexamolybdate Complex of Hexaoxacyclooctadecane (18-Crown-6)

BY OSAMU NAGANO AND YUKIYOSHI SASAKI

Department of Chemistry, Faculty of Science, The University of Tokyo,  
The Research Centre for Spectrochemistry, Hongo, Tokyo 113, Japan

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**Abstract.**  $(C_{12}H_{24}O_6)_2 \cdot K_2Mo_6O_{19} \cdot H_2O$ , orthorhombic,  $P2_12_12_1$ ,  $a = 11.678$  (3),  $b = 11.361$  (3),  $c = 35.84$  (1) Å,  $U = 4755$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.101$  Mg m<sup>-3</sup>,  $\mu = 1.77$  mm<sup>-1</sup> (for Mo  $K\alpha$ ). A  $Mo_6O_{19}^{2-}$  anion is located between two crown-complex cations forming a sandwich structure. The sandwich structures connect with each other through a water molecule. The water molecule is strongly linked to two K<sup>+</sup> cations by an ion-dipole interaction.

**Introduction.** The merits of crown complexes in the structural study of polyanions have been described in a preceding paper (Nagano, 1979). Following the structural study of  $(C_{12}H_{24}O_6)_2 \cdot K_2MoO_4 \cdot 5H_2O$ , in which the  $MoO_4^{2-}$  anion is a precursor of polymolybdate anions, a series of 18-crown-6 complexes of  $X_2Mo_6O_{19}$  ( $X = Na, K, Rb$  and  $NH_4$ ) have been prepared and  $(C_{12}H_{24}O_6)_2 \cdot K_2Mo_6O_{19} \cdot H_2O$  has been subjected to X-ray study.

A yellow precipitate was obtained from an aqueous solution of 18-crown-6 and  $K_2MoO_4$  heated on a steam-bath for one hour (pH = 1.0; 18-crown-6 :  $K_2MoO_4$  = 1 : 3). Repeated recrystallization of the precipitate from  $CH_3CN$  gave lemon-yellow crystals. The intensities of the reflections were measured from a crystal of dimensions 0.35 × 0.40 × 0.40 mm with a Rigaku automatic four-circle diffractometer (graphite monochromator, Mo  $K\alpha$  radiation). The  $\omega$ -scan method was used because of the long  $c$  axis. Three reference reflections were measured every 50 reflections; no significant changes were observed over the period of data collection. Intensities of reflections from crystals of polymolybdate salts with a large organic ion as a counter cation are generally weak. The intensities of 3112 independent reflections [ $2\theta < 60^\circ$  and  $|F_o| > 3\sigma(|F_o|)$ ] were adopted for the structure determination.

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares technique for non-hydrogen atoms. Anisotropic temperature factors were used for all non-hydrogen atoms. The H atoms of 18-crown-6 molecules were included in

the refinement in their idealized positions ( $C-H = 1.00$  Å,  $H-C-H = 109.47^\circ$ ,  $B = 5.0$  Å<sup>2</sup>). The atomic scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 0.7$  for  $|F_o| < 10.0$ ,  $w = (50.0/|F_o|)^2$  for  $|F_o| > 50.0$  and  $w = 1.0$  otherwise. The  $R$  value ( $R = \sum w||F_o| - |F_c|| / \sum w|F_o|$ ) was 0.045. The atomic coordinates are listed in Table 1. The sandwich structure of  $(C_{12}H_{24}O_6)_2 \cdot K_2Mo_6O_{19}$  is shown in Fig. 1. A view of the crystal structure along the  $b$  axis is shown in Fig. 2.\*

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34515 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

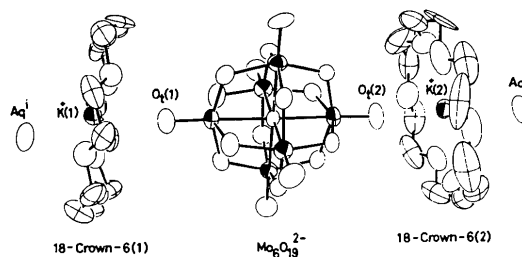


Fig. 1. The sandwich structure of  $(C_{12}H_{24}O_6)_2 \cdot K_2Mo_6O_{19}$ . The vibration ellipsoids are drawn at the 30% probability level (Johnson, 1965).  $Aq^1$  is related to  $Aq$  by the symmetry of the twofold screw axis parallel to the  $c$  axis.

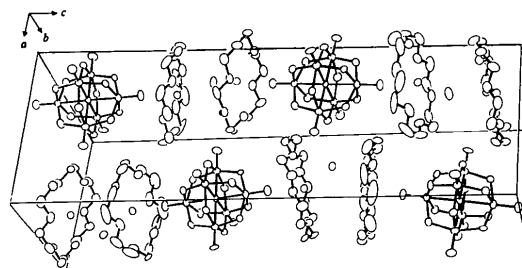


Fig. 2. The crystal structure.

Table 1. Fractional coordinates ( $\times 10^4$ ) and estimated standard deviations of the non-hydrogen atoms

	x	y	z
(a) $Mo_6O_{19}^{2-}$ anion			
Mo(1)	2945 (1)	-70 (2)	606 (1)
Mo(2)	2544 (1)	186 (1)	1893 (1)
Mo(3)	4714 (1)	10 (2)	1314 (1)
Mo(4)	763 (1)	91 (2)	1182 (1)
Mo(5)	2792 (2)	2089 (1)	1211 (1)
Mo(6)	2683 (1)	-1983 (1)	1289 (1)
$O_c$	2725 (8)	45 (10)	1249 (3)
$O_t(1)$	3084 (11)	-191 (14)	144 (3)
$O_t(2)$	2377 (12)	273 (13)	2355 (3)
$O_t(3)$	6146 (9)	-60 (15)	1364 (3)
$O_t(4)$	-665 (8)	123 (13)	1137 (3)
$O_t(5)$	2858 (11)	3556 (10)	1191 (4)
$O_t(6)$	2625 (12)	-3452 (10)	1323 (4)
$O_b(13)$	4499 (8)	-110 (13)	780 (3)
$O_b(14)$	1300 (8)	1 (14)	677 (3)
$O_b(15)$	2939 (10)	1573 (11)	692 (3)
$O_b(16)$	2879 (11)	-1689 (10)	761 (3)
$O_b(23)$	4174 (9)	162 (11)	1824 (3)
$O_b(24)$	979 (9)	189 (11)	1715 (3)
$O_b(25)$	2624 (10)	1804 (9)	1739 (3)
$O_b(26)$	2514 (10)	-1486 (10)	1798 (3)
$O_b(35)$	4343 (10)	1668 (9)	1280 (3)
$O_b(36)$	4297 (11)	-1607 (11)	1339 (3)
$O_b(45)$	1198 (10)	1724 (10)	1149 (3)
$O_b(46)$	1097 (10)	-1553 (10)	1235 (3)
(b) Potassium cations and water			
K(1)	1729 (3)	52 (4)	4393 (1)
K(2)	2247 (3)	595 (3)	3106 (1)
Aq	902 (13)	1338 (12)	3753 (3)
(c) 18-Crown-6(1)			
O(1)	2892 (12)	-2090 (10)	4483 (3)
O(2)	505 (13)	-2030 (12)	4507 (4)
O(3)	-550 (10)	192 (14)	4663 (3)
O(4)	644 (12)	2304 (12)	4499 (3)
O(5)	3046 (12)	2116 (11)	4427 (4)
O(6)	4042 (9)	-45 (14)	4225 (3)
C(1)	2149 (22)	-3088 (19)	4429 (6)
C(2)	1117 (23)	-2987 (18)	4639 (7)
C(3)	-534 (18)	-1883 (20)	4696 (6)
C(4)	-1121 (18)	-885 (27)	4561 (6)
C(5)	-1114 (23)	1243 (22)	4561 (7)
C(6)	-406 (21)	2253 (23)	4696 (5)
C(7)	1423 (21)	3190 (17)	4632 (7)
C(8)	2488 (19)	3176 (15)	4394 (6)
C(9)	4011 (21)	2101 (20)	4206 (7)
C(10)	4657 (17)	1013 (23)	4296 (6)
C(11)	4623 (17)	-1038 (20)	4358 (5)
C(12)	3904 (20)	-2096 (19)	4269 (5)

**Discussion.** The two 18-crown-6 molecules form a 'garland' structure with approximate  $D_{3d}$  symmetry, analogous to that found in most complexes of this crown compound. The average values of bond distances and bond angles in the two 18-crown-6.  $K^+$  cations are listed in Table 2. The apparent thermal vibrations of atoms within an 18-crown-6(2) molecule are larger than those within an 18-crown-6(1) molecule. In particular, distortions of the structure of the 18-

Table 1 (cont.)

	x	y	z
(d) 18-Crown-6(2)			
O(7)	2722 (15)	-1749 (11)	3254 (3)
O(8)	445 (14)	-1075 (17)	3089 (4)
O(9)	-100 (13)	1323 (19)	3032 (4)
O(10)	1733 (19)	2841 (15)	2830 (4)
O(11)	3925 (16)	2205 (16)	2981 (4)
O(12)	4465 (10)	-188 (18)	3014 (3)
C(13)	1794 (33)	-2532 (21)	3173 (6)
C(14)	691 (36)	-2002 (35)	3308 (7)
C(15)	-641 (19)	-637 (29)	3156 (8)
C(16)	-862 (20)	355 (53)	2946 (8)
C(17)	-218 (26)	2380 (35)	2805 (6)
C(18)	680 (43)	3215 (28)	2936 (7)
C(19)	2787 (45)	3655 (17)	2920 (6)
C(20)	3737 (48)	3125 (33)	2770 (9)
C(21)	5016 (27)	1716 (38)	2866 (8)
C(22)	5288 (20)	687 (33)	3078 (7)
C(23)	4721 (25)	-1258 (29)	3206 (7)
C(24)	3788 (30)	-2162 (24)	3112 (7)

crown-6(2) molecule appear in the part C(16)...C(20). The reason for the apparently large vibrations and the distortions seems to be disorder of the 18-crown-6(2) molecule. However, the disorder could not be analyzed because of the appearance of broad unresolved peaks of electron density on the Fourier maps. The  $K(2)^+$  cation is more loosely bound to a  $Mo_6O_{19}^{2-}$  anion and a water molecule than is  $K(1)^+$ .  $K^+ \dots O_t$  and  $K^+ \dots H_2O$  distances are listed in Table 3.

Each Mo atom of an  $Mo_6O_{19}^{2-}$  anion is surrounded by a distorted octahedron consisting of one central  $O_c$ , one terminal  $O_t$ , and four bridging  $O_b$  atoms. This anion has approximate  $O_h$  symmetry. The distortions of  $O_b$  atoms from the ideal structure of  $O_h$  symmetry, which were estimated by the least-squares method, are larger than those of  $O_t$  atoms in  $[HN_3P_3(NMe_2)_6]_2 \cdot Mo_6O_{19}$  (Allcock, Bissell & Shawl, 1973). No great difference in the distortions of  $O_b$  and  $O_t$  atoms was detected in the present complex. The average bond distances and bond angles in the  $Mo_6O_{19}^{2-}$  anion are listed in Table 2. The anion is between two complex cations to form a sandwich structure (Fig. 1). The sandwich structures connect with each other through one water molecule (Fig. 2). A characteristic packing feature is that the four  $Mo_6O_{19}^{2-}$  anions are related by a pseudo fourfold screw axis parallel to  $c$ , giving rise to the extra extinction rule:  $00l$  can be observed only if  $l = 4n$ .

Each  $K^+$  cation is surrounded by a nearly planar hexagon of O atoms of a corresponding 18-crown-6 molecule. Hexagonal-bipyramidal coordination is further formed by a terminal  $O_t$  atom of the anion and a water molecule.  $K(1)^+$  and  $K(2)^+$  are displaced from the mean oxygen planes of the different 18-crown-6 molecules by 0.27 and 0.26 Å respectively.

The water molecule is strongly linked to  $K(1)^+$  and  $K(2)^+$  cations by ion-dipole interaction. TG measure-

Table 2. The average values of bond distances (Å) and bond angles (°) in the two 18-crown-6. K<sup>+</sup> cations and an Mo<sub>6</sub>O<sub>19</sub><sup>2-</sup> anion

18-Crown-6(1). K(1) <sup>+</sup> cation			18-Crown-6(2). K(2) <sup>+</sup> cation		
C—C	1.47 (4)	[1.41–1.51]	C—C	1.45 (7)	[1.37–1.54]
C—O	1.41 (3)	[1.37–1.44]	C—O	1.42 (6)	[1.31–1.57]
K—O	2.82 (2)	[2.77–2.88]	K—O	2.79 (2)	[2.72–2.88]
C—C—O	110 (2)	[107–114]	C—C—O	109 (4)	[105–113]
C—O—C	113 (2)	[110–116]	C—O—C	113 (3)	[107–118]
Mo <sub>6</sub> O <sub>19</sub> <sup>2-</sup> anion					
Mo—Mo	3.281 (2)	[3.273–3.290]	Mo—O <sub>b</sub> —Mo	116.9 (5)	[116.2–118.0]
Mo—O <sub>c</sub>	2.320 (10)	[2.305–2.335]	Mo—O <sub>c</sub> —Mo	90.0 (4)	[89.4–90.6]
Mo—O <sub>t</sub>	1.674 (11)	[1.670–1.683]	O <sub>c</sub> —Mo—O <sub>t</sub>	179.8 (5)	[178.2–181.6]
Mo—O <sub>b</sub>	1.926 (11)	[1.890–1.959]	O <sub>c</sub> —Mo—O <sub>b</sub>	76.6 (5)	[75.8–77.6]
			O <sub>t</sub> —Mo—O <sub>b</sub>	103.4 (5)	[101.8–106.0]

Table 3. Distances (Å) and angles (°) involving the potassium ions

K(1)—O <sub>t</sub> (1) <sup>†</sup>	2.703 (11)	K(2)—O <sub>t</sub> (2)	2.720 (11)
K(1)—Aq	2.888 (13)	K(2)—Aq	2.926 (14)
K(1)—Aq—K(2)	107.7 (5)		
Aq—K(1)—O <sub>t</sub> (1) <sup>†</sup>	142.1 (3)		
Aq—K(2)—O <sub>t</sub> (2)	148.5 (3)		

\* (i) refers to the following equivalent position:  $\frac{1}{2} + x, -y, \frac{1}{2} + z$ .

ment of the present crystal showed that the water molecule was released from the crystal lattice at a temperature as high as 363 K. This obviously indicates that the water molecule is not zeolitic.

The calculations were performed on a HITAC 8700/8800 computer at the Computer Centre of the

University of Tokyo using a local version of UNICS (Sakurai, 1967).

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## Structure of (+)<sub>589</sub>-mer-Bis(diethylenetriamine)cobalt(III) Bromide 1·6-Hydrate

BY K. OKIYAMA, S. SATO AND Y. SAITO

*The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan*

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**Abstract.**  $C_8H_{26}CoN_6^{3+} \cdot 3Br^- \cdot 1.6H_2O$ , [Co( $C_4H_{13}N_3$ )<sub>2</sub>]<sup>3+</sup>·3Br<sup>-</sup>·1.6H<sub>2</sub>O, monoclinic, *P*2<sub>1</sub>, *a* = 22.168 (3), *b* = 14.154 (1), *c* = 8.644 (2) Å, β = 96.44 (2)°, *Z* = 6, *D*<sub>x</sub> = 1.973 Mg m<sup>-3</sup>, μ(Mo Kα) = 5.36 mm<sup>-1</sup>. The structure has been refined to *R* = 0.038 on 3537 observed reflections. The two terdentate molecules coordinate to Co in *mer* positions. The complex cation has approximate twofold symmetry. The four five-membered chelate rings take an envelope form. The absolute configuration of the complex ion may be described as *trans*-λ-NH.

**Introduction.** Of the three possible isomers of [Co(dien)<sub>2</sub>]<sup>3+</sup>, the structures of *s*-facial and *u*-facial isomers have already been reported (Kobayashi, Marumo & Saito, 1972; Konno, Marumo & Saito, 1973). A crystal of the third isomer, (+)<sub>589</sub>-mer-[Co(dien)<sub>2</sub>]Br<sub>3</sub>·1.6H<sub>2</sub>O, has been subjected to X-ray crystal analysis in order to establish the absolute configuration and conformational details. The well known empirical rule relating the absolute configuration to the net chirality of the complex cannot be applied to this complex, since the net chirality is zero. The crystals