Fig. 1. Stereoscopic view of the silver fulminate crystal. The thermal ellipsoids are the 50% probability surfaces.

Our observations of anisotropic thermal motion of the Ag atoms along the c axis (Table 2) differ substantially from those reported earlier (Britton & Dunitz, 1965); the present study shows a r.m.s. amplitude of 0·168 (1) Å along the axis, whereas an anisotropic thermal motion of 0·34 Å had been reported before. The anisotropic motion of 0·168 (1) Å found in the present study supports the 'three-center

bond' Ag—C—Ag (Fig. 1) suggested by Britton & Dunitz (1965) to a much greater extent than their own value of 0·34 Å.

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Structure of the Potassium Molybdate Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)

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Abstract. $(C_{12}H_{24}O_6)_2 \cdot K_2MoO_4 \cdot 5H_2O$, triclinic, $P1$, $a = 12.089$ (2), $b = 10.547$ (2), $c = 8.472$ (2) Å, $\alpha = 113.14$ (2), $\beta = 77.88$ (2), $\gamma = 100.39$ (2)°, $U = 965.34$ (8) Å^3, $Z = 1$, $D_m = 1.50$, $D_x = 1.47$ Mg m^{-3}, $\mu = 0.625$ mm^{-1} (for Mo $K\alpha$). One potassium ion is coordinated to an 18-crown-6 molecule and two water molecules. The other potassium ion is coordinated to another 18-crown-6 molecule, one water molecule and the molybdate anion. Both potassium ions are displaced from the mean oxygen planes of the corresponding 18-crown-6 molecules by 0·92 and 0·78 Å respectively.

Introduction. Crystals of polymolybdate and polytungstate salts often contain many waters of crystallization. The crystals, especially those with zeolitic

water molecules, are not stable during X-ray work because of the release of water molecules. By the use of a crown complex ion as a counter cation, it can be anticipated that (1) crown complexes of polymolybdate salts will be able to be crystallized in organic solvents, (2) a variety of crown compounds will make a series of counter cations of different sizes, (3) different cations in a certain crown compound will make a variety of counter cations of different charges. Therefore, the preparation of polymolybdate salts with crown compounds may provide crystals of better quality for X-ray work and may also enlarge the field of polymolybdate chemistry. In this study, we have prepared the 18-crown-6 complex of K_2MoO_4, which is considered to be one of the precursors of polymolybdate salts (Tytko & Glemser, 1976).

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

	x	y	z		x	y	z
Mo	5000 (1)	5000 (1)	5000 (2)	C(1)	1489 (8)	2632 (8)	2419 (12)
K(1)	2524 (2)	−554 (2)	2029 (3)	C(2)	1516 (8)	3058 (9)	4316 (12)
K(2)	7399 (2)	7966 (2)	7768 (3)	C(3)	2251 (7)	2532 (8)	6324 (10)
O(1)	919 (5)	1266 (6)	1780 (7)	C(4)	3027 (8)	1635 (9)	6395 (11)
O(2)	2098 (5)	2126 (6)	4549 (7)	C(5)	3267 (9)	−649 (10)	5891 (13)
O(3)	2517 (5)	242 (6)	5857 (8)	C(6)	2745 (10)	−2119 (10)	5217 (12)
O(4)	2668 (6)	−2493 (6)	3421 (8)	C(7)	2258 (8)	−3924 (9)	2679 (12)
O(5)	1434 (5)	−3466 (6)	668 (7)	C(8)	2205 (8)	−4273 (9)	781 (11)
O(6)	975 (5)	−1525 (6)	−524 (8)	C(9)	1262 (8)	−3833 (9)	−1087 (11)
O(7)	8414 (5)	10918 (6)	8732 (7)	C(10)	464 (7)	−2920 (9)	−1101 (11)
O(8)	7001 (6)	10011 (6)	11273 (7)	C(11)	285 (8)	−621 (9)	−628 (11)
O(9)	7012 (6)	7214 (6)	10784 (8)	C(12)	866 (8)	813 (10)	−55 (11)
O(10)	7660 (5)	5337 (6)	7500 (8)	C(13)	7663 (8)	11781 (8)	10157 (11)
O(11)	8978 (5)	6190 (6)	4888 (7)	C(14)	7580 (8)	11369 (8)	11665 (11)
O(12)	8850 (5)	8992 (6)	5325 (7)	C(15)	6882 (11)	9531 (10)	12680 (12)
Aq(1)	4665 (6)	1037 (7)	2133 (9)	C(16)	6249 (11)	8099 (11)	12151 (12)
Aq(2)	4505 (9)	2616 (12)	85 (12)	C(17)	6523 (9)	5810 (10)	10266 (13)
Aq(3)	4140 (7)	8147 (7)	9257 (9)	C(18)	7412 (9)	4922 (9)	8951 (12)
Aq(4)	5827 (6)	9253 (7)	7039 (9)	C(19)	8375 (8)	4427 (8)	6094 (12)
Aq(5)	5824 (6)	1963 (7)	6722 (9)	C(20)	8455 (7)	4819 (8)	4546 (11)
O'(1)	5547 (6)	3458 (6)	4677 (9)	C(21)	8958 (7)	6626 (9)	3500 (11)
O'(2)	4312 (7)	4725 (9)	3221 (12)	C(22)	9544 (7)	8076 (9)	3915 (11)
O'(3)	3976 (7)	5493 (8)	6861 (12)	C(23)	9373 (7)	10380 (9)	5819 (12)
O'(4)	6071 (5)	6406 (6)	5174 (8)	C(24)	8582 (7)	11320 (8)	7261 (11)

Table 2. *Distances* (Å) *involving the potassium ion and water molecules*

K(1)—O(1)	3·054 (6)	K(2)—O(7)	2·985 (6)
K(1)—O(2)	2·852 (6)	K(2)—O(8)	2·905 (7)
K(1)—O(3)	3·012 (6)	K(2)—O(9)	2·887 (7)
K(1)—O(4)	2·778 (7)	K(2)—O(10)	2·763 (6)
K(1)—O(5)	2·983 (6)	K(2)—O(11)	2·975 (6)
K(1)—O(6)	2·916 (6)	K(2)—O(12)	2·843 (6)
K(1)—Aq(1)	2·817 (8)	K(2)—Aq(4)	2·814 (7)
K(1)—Aq(3^i)	2·778 (8)	K(2)—O'(4)	2·793 (7)
Aq(1)—O'(1)	2·821 (10)	Aq(3)—Aq(4)	2·882 (11)
Aq(1)—Aq(2)	2·890 (14)	Aq(4)—O'(4)	2·828 (10)
Aq(2)—O'(2)	2·738 (16)	Aq(4)—Aq(5^{iii})	2·974 (12)
Aq(2)—Aq(5^{ii})	2·842 (12)	Aq(5)—O'(1)	2·860 (10)
Aq(3)—O'(3)	2·710 (12)		

Roman numerals refer to the following equivalent positions: (i) x, $-1 + y$, $-1 + z$, (ii) x, y, $-1 + z$, (iii) x, $1 + y$, z.

Colourless crystals were obtained from an aqueous solution of 18-crown-6 and K_2MoO_4 (pH 7·0–7·5; 18-crown-6:K_2MoO_4 = 2:1). This crystal is soluble in some polar solvents (*e.g.* CH_3OH and CH_3CN). The intensities of the reflections were measured with a Rigaku automatic four-circle diffractometer (graphite monochromator, Mo $K\alpha$ radiation, ω–2θ scan method). The intensities of 4830 independent reflections, $F. > 3\sigma(|F|)$, were adopted for the structure determination. The crystal for X-ray analysis (0·36 × 0·36 × 0·40 mm) was sealed in a capillary to prevent sublimation.

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 the 18-crown-6 molecules were included in the refinement in their idealized positions (C—H = 1·00 Å, H—C—H = 109·47°). 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 $w = 0.2$ for $|F_o| < 15$, and $w = 1.0$ otherwise. The final R value ($R = \sum w \| F_o| - |F_c\| / \sum w|F_o|$) was 0·053. The atomic coordinates, interatomic distances and bond angles are listed in Tables 1, 2 and 3.* The complex cations are shown in

* Lists of structure factors, anisotropic thermal parameters, H atom coordinates and bond lengths and angles in the 18-crown-6 molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34022 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and bond angles* (°) *in the molybdate anion*

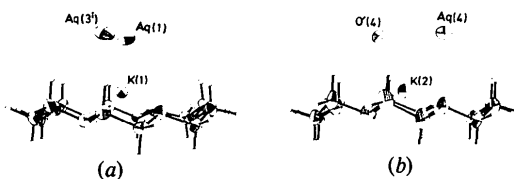| 1	2	3	1–2	1–2–3
O'(1)—Mo—O'(2)			1·766 (7)	109·3 (4)
O'(2)—Mo—O'(3)			1·773 (10)	106·5 (5)
O'(3)—Mo—O'(4)			1·748 (10)	107·9 (4)
O'(4)—Mo—O'(1)			1·764 (7)	112·5 (3)
O'(1)—Mo—O'(3)				111·2 (4)
O'(2)—Mo—O'(4)				108·2 (4)

Fig. 1. (a) $C_{12}H_{24}O_6 \cdot K(1)^+$ and (b) $C_{12}H_{24}O_6 \cdot K(2)^+$ complex cations viewed along a direction in the mean plane. The vibration ellipsoids are drawn at the 30% probability level (Johnson, 1965) [(i) $x, -1 + y, -1 + z$].
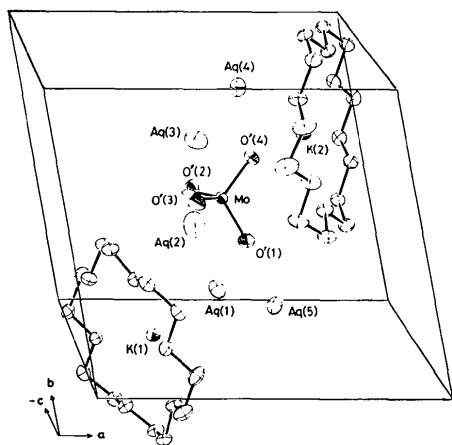

Fig. 2. The crystal structure viewed along the c axis.

Fig. 1 and a view of the crystal structure along c is in Fig. 2.

Discussion. The two 18-crown-6 molecules have approximate D_{3d} symmetry, analogous to that found in most complexes of this crown compound (Nagano, Kobayashi & Sasaki, 1978). The average C—C and C—O bond lengths are 1·479 Å (1·471–1·521 Å) and 1·426 Å (1·410–1·447 Å) respectively. The average C—C—O and C—O—C bond angles are 108·46° (105·88–110·31°) and 111·16° (110·24–112·06°) respectively. The torsion angles about C—C bonds are within ±9° of staggered conformations (±60°). Those about C—O bonds are within ±10° of antiplanar conformations (180°). Both potassium ions, K(1) and K(2), are coordinated to the six O atoms of different 18-crown-6 molecules. K(1) is coordinated to one water molecule and directly to one O atom of the molybdate anion. K(2) is coordinated to two water molecules and interacts with the molybdate anion through a water molecule because of the steric

hindrance between two large complex cations. There is no significant difference between the K—O (of MoO_4^{2-}) and K—O (of H_2O) bond lengths. The potassium ion (ionic diameter 2·66 Å) is more suitable for complexation with 18-crown-6 (diameter of cavity 2·6–3·2 Å) than those of other alkaline ions. The potassium ion in the complex of 18-crown-6.KNCS is located on the mean oxygen plane of the 18-crown-6 (Dunitz, Dobler, Seiler & Phizackerley, 1974). It is characteristic that both potassium ions in the present complex, K(1) and K(2), are displaced from the mean oxygen planes of the corresponding 18-crown-6 molecules by 0·92 and 0·78 Å respectively. The molybdate anion is approximately tetrahedral. Each of the four O atoms of the molybdate anion is linked by a hydrogen bond to at least one water molecule. The waters of crystallization are not zeolitic as frequently found in crystals of poly-molybdate and polytungstate salts. They interact with one another as well as with potassium ions and the molybdate anion. The 18-crown-6.K$^+$ cations are too large (compared with the MoO_4^{2-} anion) to form anhydrous crystals. Crystals having few or no water molecules are expected for the 18-crown-6 complexes of polymolybdate salts larger than K_2MoO_4. The structural analysis of $(C_{12}H_{24}O_6)_2 \cdot K_2Mo_6O_{19} \cdot H_2O$ is in progress.

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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