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Preparation and Characterization of Compounds between 18-crown-6 and Two Potassium Mercurate(II) Salts

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Abstract

Reaction between 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) and dipotassium tetraiodomercurate(II) and dipotassium tetrathiocyanatomercurate(II) in organic solvent mixture produces $[K(18\text{-crown-6})]_2[Hg_2I_6]\cdot 2H_2O$ (**1**) and $[Hg(18\text{-crown-6})](SCN)_2$ (**2**) respectively. These two products have been isolated and characterized by elemental analysis and infrared studies. Their crystal structures have been determined. Crystal data for **1**: $a = 10.644(9)$, $b = 14.925(13)$, $c = 15.362(14)$ Å, $\beta = 103.7(1)°$, $U = 2371.0$ Å^3, space group $P2_1/c$, $Z = 2$; for **2**: $a = 8.224(7)$, $b = 8.027(7)$, $c = 15.56(1)$ Å, $\beta = 103.0(1)°$, $U = 1000.8$ Å^3, space group $P2_1/c$, $Z = 2$. Reflection data were collected on a diffractometer and the structures were solved by the heavy atom technique and refined by full-matrix least-squares. For **1** 1159 independent reflections above background were refined by full-matrix least-squares to $R = 0.070$ ($R_w = 0.075$) and for **2** 913 independent reflections above background were similarly refined to $R = 0.077$ ($R_w = 0.083$). **1** contains $[K_2(18\text{-crown-6})_2]^{2+}$ centrosymmetric dimeric cations in which two $[K(18\text{-crown-6})]^+$ cations are linked via weak K–O bonds and centrosymmetric $[Hg_2I_6]^{2-}$ anions. **2** contains centrosymmetric discrete $[Hg(18\text{-crown-6})(SCN)_2]$ molecules in which the mercury atom has an eight-coordinate hexagonal bipyramidal environment, being bonded to the sulphur atoms of two thiocyanate groups as well as to six oxygen atoms of the 18-crown-6.

Introduction

Amongst the crown ethers (or cyclic polyethers) those with six oxygen atoms such as 18-crown-6, dibenzo-18-crown-6 and dicyclohexano-18-crown-6 are known to form stable complexes with alkali metal salts, the most stable being the potassium complex [1–3]. Potassium complexes containing both simple and very complex anions have been reported but relatively few of these anions are of the type $[MX_n]$, where M is a monovalent or divalent metal and X is a halide or pseudohalide [4–6]. In an earlier paper we reported the preparation and characterization of complexes formed between dibenzo-18-crown-6 and three potassium mercurate(II) salts of the type $K_2[HgX_4]$ where X = I^-, SCN^- and CN^- [7]. Our investigation on the reaction products between 18-crown-6 and two of these salts, namely $K_2[HgI_4]$ and $K_2[Hg(SCN)_4]$, is now reported.

Experimental

Preparation procedures were as reported in an earlier paper [7] except that 18-crown-6 was used instead of the dibenzo analogue.

In the case of the reaction between 18-crown-6 and $K_2[HgI_4]$ the product obtained was yellow crystals which were recrystallized from methanol. These had an empirical formula of $[K(18C6)][HgI_3]H_2O$ from microanalysis and melting point 194–196 °C (**1**). *Anal.* Found: C, 16.7; H, 2.8; I, 42.3; K, 4.2. Calc.: C, 16.0; H, 2.9; I, 42.2; K, 4.3%. The reaction between the crown ether and dipotassium tetrathiocyanatomercurate(II) produced colourless fine crystals, the recrystallization of which in methanol gave a product that started decomposing at 228 °C (**2**). Microanalysis showed the absence of potassium and an empirical formula of $[Hg(18C6)](SCN)_2$. *Anal.* Found: C, 28.4; H, 4.1; N, 4.9; S, 11.7. Calc.: C, 28.9; H, 4.2; N, 4.8; S, 11.0%. Infrared spectra were obtained using CsI discs on a Perkin-Elmer 598 spectrometer.

Crystal data for the two products are as follows:

1: $[K(18\text{-crown-6})]_2[Hg_2I_6]\cdot 2H_2O$, $C_{24}H_{52}I_6O_{14}Hg_2K_2$, $M = 1805.2$, monoclinic, $a = 10.644(9)$, $b = 14.925(13)$, $c = 15.362(14)$ Å, $\beta = 103.7(1)°$, $U = 2371.0$ Å^3, space group $P2_1/c$, $Z = 2$, $D_m = 2.45$ g cm^{-3}, $D_c = 2.53$ g cm^{-3}, λ (Mo Kα radiation) = 0.7107 Å, $\mu = 109.2$ cm^{-1}, $F(000) = 1648$.

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2: [Hg(18-crown-6)](SCN)$_2$, $C_{14}H_{24}N_2O_6S_2Hg$, $M = 581.1$, monoclinic, $a = 8.224(7)$, $b = 8.027(7)$, $c = 15.56(1)$ Å, $\beta = 103.0(1)°$, $U = 1000.8$ Å^3, space group $P2_1/c$, $Z = 2$, $D_m = 1.86$ g cm^{-3}, $D_c = 1.93$ g cm^{-3}, λ (Mo Kα radiation) = 0.7107 Å, $\mu = 80.8$ cm^{-1}, $F(000) = 564$.

Crystals of approximate size 0.25 × 0.3 × 0.3 mm in **1** and 0.40 × 0.25 × 0.25 mm in **2** were set up to rotate about the a axis on a Stoe Stadi2 diffractometer and data were collected via variable width ω scan. Background counts were for 20 s and a scan rate of 0.0333°/s was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 4155 (**1**) and 1817 (**2**) independent reflections were measured of which 1159 (**1**) and 913 (**2**) respectively with $I > 2\sigma(I)$ were used in subsequent refinement. An empirical absorption correction was applied to both data sets [8]. Both structures were determined by the heavy atom method. In **1** the Hg, I and K atoms were refined anisotropically with C, O and H isotropically. In **2** all non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. In both structures the hydrogen atoms were included in calculated positions. The hydrogen atoms of the water molecule in **1** could not be located.

The structures were given weighting schemes in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R values were 0.070 ($R_w = 0.075$) in **1** and 0.077 ($R_w = 0.083$) in **2**. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [9]. Calculations were carried out using SHELX76 [10] and some of our own programs on the Amdahl V7 computer at the University of Reading. Positional parameters are given in Tables 1 and 2. Molecular dimensions in the coordination spheres are listed in Tables 3 and 4. Torsion angles in the 18-crown-6 ligands are listed in Table 5. See also 'Supplementary Material'.

Results and Discussion

IR Spectra

Infrared spectra of compounds **1** and **2** have been recorded in the 4000–250 cm^{-1} region and the absorption bands are listed in Table 6. Compared with similar complexes of dibenzo-18-crown-6 these two compounds have far fewer absorption bands in the region. Apart from the relative complexity of the spectra there are two features that apparently distinguish the spectra of 18-crown-6 complexes from those of dibenzo-18-crown-6 complexes. A medium to strong intensity band at 1350 cm^{-1} in the former occurs at 1360 cm^{-1} in the latter. Similarly a very strong and broad band is observed at 1100 cm^{-1} in the former and about 1130 cm^{-1} in the latter complexes.

TABLE 1. Atomic Coordinates (×10^4) for **1**^{a}

Atom	x	y	z
Hg	−1096(2)	4051(2)	4241(2)
I(1)	2(4)	2608(3)	3701(3)
I(2)	−185(3)	4331(3)	6188(3)
I(3)	−3688(3)	4283(3)	3626(3)
K(1)	4869(11)	4211(9)	1133(10)
O(1)	3278(24)	2905(20)	1467(21)
C(2)	2022(42)	3078(32)	1520(36)
C(3)	2083(46)	3964(34)	1956(38)
O(4)	2594(30)	4614(25)	1655(26)
C(5)	2770(64)	5471(45)	2201(49)
C(6)	3402(41)	6188(30)	1706(35)
O(7)	4492(33)	5887(26)	1668(27)
C(8)	5252(59)	6634(44)	1398(51)
C(9)	6628(53)	6319(40)	1558(44)
O(10)	6559(34)	5622(26)	898(27)
C(11)	7779(65)	5311(55)	798(55)
C(12)	8165(66)	4565(49)	1269(53)
O(13)	7356(28)	3775(24)	855(24)
C(14)	7590(40)	2959(31)	1217(34)
C(15)	6723(72)	2299(58)	829(60)
O(16)	5512(33)	2503(25)	881(27)
C(17)	4582(51)	1680(41)	896(45)
C(18)	3304(49)	2144(40)	832(43)
O(100)	2864(94)	4159(65)	4140(66)

^{a}e.s.d.s given in parentheses.

TABLE 2. Atomic Coordinates (×10^4) for **2**^{a}

Atom	x	y	z
Hg	0	0	0
S(100)	1206(10)	2654(11)	324(5)
C(100)	1410(33)	3287(37)	−667(26)
N(100)	1580(44)	3735(40)	−1304(19)
O(1)	171(26)	507(23)	1807(14)
C(2)	−1407(42)	565(38)	2038(22)
C(3)	−2333(39)	1804(51)	1465(24)
O(4)	−2768(20)	1179(26)	559(12)
C(5)	−3652(46)	2410(51)	−39(27)
C(6)	−4105(36)	1568(42)	−935(19)
O(7)	−2637(24)	1475(27)	−1263(13)
C(8)	−2931(43)	722(55)	−2100(25)
C(9)	−1418(56)	530(49)	−2418(23)

^{a}e.s.d.s given in parentheses.

Compound **2** has a medium-to-strong intensity band at 2140 cm^{-1} due to the C=N stretch of the thiocyanate group. Apart from the above the spectra of compounds **1** and **2** are remarkably similar, despite differences in the metal ion coordinated to the crown ether ligand. The very intense, very broad and prob-

TABLE 3. Dimensions in the Coordination Sphere in **1**[a]

$[Hg_2I_6]^{2-}$ anion	
Hg–I(1)	2.674(5)
Hg–I(2)	2.947(4)
Hg–I(3)	2.718(4)
Hg–I(2*)	2.924(5)
I(1)–Hg–I(2)	111.5(15)
I(1)–Hg–I(3)	118.5(16)
I(1)–Hg–I(2*)	109.5(16)
I(2)–Hg–I(3)	113.4(16)
I(2)–Hg–I(2*)	93.0(14)
I(3)–Hg–I(2*)	107.8(15)
Hg–I(2)–Hg(1)	87.0(15)
Geometry of the potassium ion in $[K_2(\text{18-crown-6})_2]^{2+}$	
K(1)–O(1)	2.71(3)
K(1)–O(4)	2.79(3)
K(1)–O(7)	2.69(4)
K(1)–O(10)	2.85(4)
K(1)–O(13)	2.85(3)
K(1)–O(16)	2.69(4)
K(1)–O(10**)	3.14(4)
O(1)–K(1)–O(4)	58.4(10)
O(1)–K(1)–O(7)	117.7(12)
O(1)–K(1)–O(10)	89.4(8)
O(1)–K(1)–O(13)	120.5(11)
O(1)–K(1)–O(16)	62.4(11)
O(1)–K(1)–O(10**)	93.9(10)
O(4)–K(1)–O(7)	60.7(11)
O(4)–K(1)–O(10)	119.6(12)
O(4)–K(1)–O(13)	172.1(12)
O(4)–K(1)–O(16)	120.9(12)
O(4)–K(1)–O(10**)	91.1(11)
O(7)–K(1)–O(10)	59.7(12)
O(7)–K(1)–O(13)	117.9(11)
O(7)–K(1)–O(16)	170.2(12)
O(7)–K(1)–O(10**)	99.1(11)
O(10)–K(1)–O(13)	60.9(11)
O(10)–K(1)–O(16)	119.5(12)
O(10)–K(1)–O(10**)	89.2(11)
O(13)–K(1)–O(16)	59.1(11)
O(13)–K(1)–O(10**)	96.7(11)
O(16)–K(1)–O(10**)	90.7(11)

[a]Starred items: *symmetry element $-x$, $1-y$, $1-z$; **symmetry element $1-x$, $1-y$, $-z$.

TABLE 4. Dimensions in the Coordination Sphere in **2**

Hg–S(100)	2.356(9)
Hg–O(1)	2.813(22)
Hg–O(4)	2.779(19)
Hg–O(7)	2.837(18)
S(100)–Hg–O(1)	74.4(4)
S(100)–Hg–O(4)	87.7(5)
S(100)–Hg–O(7)	89.4(5)
O(1)–Hg–O(4)	59.9(5)
O(1)–Hg–O(7)	60.6(6)
O(4)–Hg–O(7)	61.5(6)

TABLE 5. Torsion Angles in **1** and **2**

Angle				**1**	**2**
O(1)	C(2)	C(3)	O(4)	52.0	70.6
C(2)	C(3)	O(4)	C(5)	–172.7	–178.1
C(3)	O(4)	C(5)	C(6)	–179.4	–176.9
O(4)	C(5)	C(6)	O(7)	–62.1	–75.3
C(5)	C(6)	O(7)	C(8)	–166.8	–179.5
C(6)	O(7)	C(8)	C(9)	167.5	–176.5
O(7)	C(8)	C(9)	O(10)	67.9	59.3
C(8)	C(9)	O(10)	C(11)	169.5	–172.9
C(9)	O(10)	C(11)	C(12)	97.0	–171.5
O(10)	C(11)	C(12)	O(13)	71.2	–[a]
C(11)	C(12)	O(13)	C(14)	179.3	–
C(12)	O(13)	C(14)	C(15)	174.8	–
O(13)	C(14)	C(15)	O(16)	–59.7	–
C(14)	C(15)	O(16)	C(17)	–152.5	–
C(15)	O(16)	C(17)	C(18)	–172.8	–
O(16)	C(17)	C(18)	O(1)	–49.7	–
C(17)	C(18)	O(1)	C(2)	–161.9	–
C(18)	O(1)	C(2)	C(3)	–165.4	–

[a]In **2** atoms O(10), C(11), .. etc. are not unique, being related by the crystallographic centre of symmetry to O(1), C(2), etc.

TABLE 6. Infrared Absorption Bands (cm^{-1}) for **1** and **2** in the Region of 4000–250 cm^{-1}

1	2950(w, sh), 2920(s, br), 2835(w), 1970(w, br), 1474(m), 1454(m), 1436(w), 1352(s, sp), 1310(w), 1288(m), 1254(m), 1134(m, sh), 1100(s, br), 1040(w, sh), 960(vs), 868(vw), 838(m), 530(vw), 516(vw).
2	2920(m, br), 2860(w, sh), 2830(w), 2140(m, s), 1476(w, br), 1458(vw), 1350(m), 1286(w), 1248(w), 1240(vw, sh), 1136(m, sh), 1100(vs, br), 1056(w), 968(m), 960(m), 838(m), 620(w, br).

s, strong; m, medium; w, weak; br, broad; sh, shoulder; sp, sharp; v, very.

ably multi-component CH$_2$ stretching vibration band of the free ligand has a peak at 2860 cm^{-1}; on complexation the intensity is much reduced and the band becomes asymmetrical with the peak at 2920 cm^{-1}. On the other hand the strong band due to bending CH$_2$ modes at 1355 cm^{-1} of the free ligand is slightly downshifted to 1350 for the complexes. Likewise the bands at 1115 and 846 cm^{-1} shifted down to 1100 and 838 cm^{-1} respectively on complexation, while the medium band of the ligand at 985 cm^{-1} are absent in the complexes. The metal–oxygen, Hg–S and Hg–I bands are most likely to be found in the far infrared region.

Description of Structures

The structure of **1** consists of $[K_2(18\text{-crown-}6)_2]^{2+}$ cations and $[Hg_2I_6]^{2-}$ anions together with water molecules. The anions are centrosymmetric and each mercury atom is coordinated to a tetrahedron of four iodine atoms, two of which are bridging. This is reflected in the bond lengths; bridging Hg–I bonds at 2.947(4) and 2.924(5) Å being longer than terminal Hg–I bonds at 2.674(5) and 2.718(4) Å. These Hg–I distances are very close to those reported in other $[Hg_2I_6]^{2-}$ anions [11, 12]. Figure 1 shows the molecule.

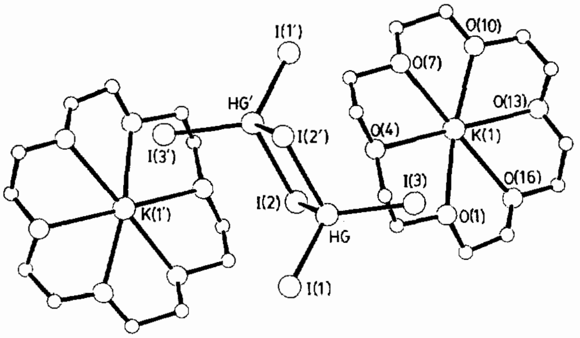

Fig. 1. Structure of $[K_2(18\text{-crown-}6)_2][Hg_2I_6]\cdot 2H_2O$. The water molecules have been omitted for clarity.

As expected, the potassium atom in the cation sits in the plane of the six oxygen atoms with potassium–oxygen distances ranging from 2.69(4) to 2.85(4) Å, which is within the range observed in $[K(18\text{-crown-}6)]^+$ cations [13, 14]. However, the conformation of the 18-crown-6 ligand (illustrated by the torsion angles in Table 5) is not the usual D_{3d} geometry with O–C–C–O angles alternately *ca.* ±60° and C–O–C–C *ca.* 180°. Variations from this geometry are primarily concentrated on the position of O(10), e.g. C(9)–O(10)–C(11)–C(12) 97.0°, with concomitant smaller adjacent variations which allow the ligand to surround the metal in an approximately planar manner. Indeed the maximum deviation of an oxygen atom from the O_6 plane is 0.24 Å, with the potassium atom 0.17 Å from this plane. The most unusual feature about the cation is that the potassium atom is only 3.14(4) Å from an oxygen atom O(10) of another ligand and this interaction is presumably responsible for the unusual ring conformation. This $K-O(10^{**})$ distance is only slightly outside the usual range for such bonds in crown ether complexes, so that the complex can be considered as a dimer (Fig. 2). The potassium atom is only 3.77(1) Å from I(3). This iodine position is *trans* to $O(10^{**})$ {$I(3)-K-O(10^{**})$ 176.3(12)°} and so the potassium ion can be considered to have a distorted hexagonal bipyramidal geometry. The K–I distance is slightly longer than those observed in related structures, e.g. 3.500 Å in $[K(DB\text{-}18\text{-}C\text{-}6)]_2[HgI_4]$ [7], 3.525 Å in $[K(DB\text{-}18\text{-}C\text{-}6)]I\cdot H_2O$ [13] and 3.598 Å in $[K(18\text{-crown-}6)][CuI_2]$ [6].

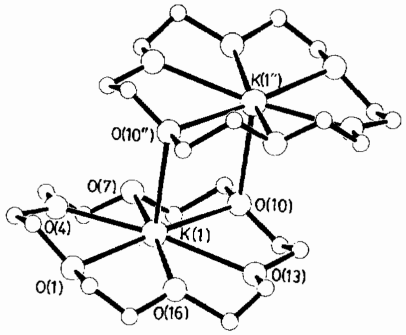

Fig. 2. The dimeric nature of the $[K_2(18\text{-crown-}6)_2]^{2+}$ cation.

The isolation of $[Hg(18\text{-crown-}6)](SCN)_2$ is unexpected and parallels the experience of Pears *et al.* [15] who accidentally obtained the iodide analogue $[Hg(18\text{-crown-}6)]I_2$, although the chloride $[Hg(18\text{-crown-}6)]Cl_2$ is previously known [16]. Just like the case of the two halides the mercury atom in compound **2** sits directly on the plane of the six oxygen atoms and is eight-coordinated. Symmetry also dictates that the two Hg–S distances be identical. The Hg(1)–S(100) distance at 2.356(9) Å is slightly shorter than the value of 2.543 observed in $[K(DB\text{-}18\text{-}C\text{-}6)]_2[Hg(SCN)_4]$ [17] and the range reported in $Mg[Hg(SCN)_4]\cdot 2H_2O$ (2.523 to 2.579 Å [18]). The average Hg–O distance of 2.810(22) Å is comparable to the corresponding values of 2.825 and 2.862 Å in the chloride and iodide analogues respectively. The conformation of the ligand is the expected D_{3d} in the $[Hg(18\text{-crown-}6)](SCN)_2$ molecule with O–C–C–O torsion angles close to ±60° and C–C–O–C to 180°. The molecule is shown in Fig. 3.

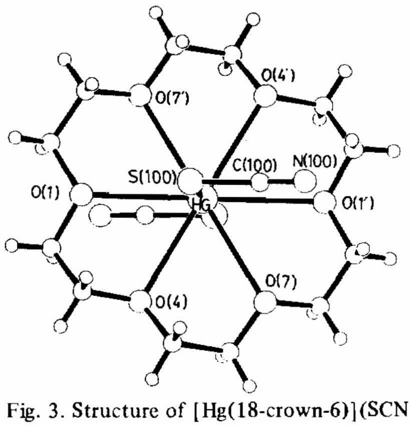

Fig. 3. Structure of $[Hg(18\text{-crown-}6)](SCN)_2$.

Carbon–carbon and carbon–oxygen distances in the crown ether are normal in both compounds.

Conclusions

Reaction between dipotassium mercurate(II) salts and 18-crown-6 gave products which were of different types from those obtained when these salts reacted with dibenzo-18-crown-6, even when the conditions were essentially identical. This probably is due to the existence of complex equilibria involving mercury and halides or pseudo-halides in organic media in the presence of crown ethers.

Supplementary Material

Thermal parameters, hydrogen atom positions and remaining dimensions are available from the authors on request.

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