The X-Ray Structure of the Trichlorocuprate of Naphtho-15-Crown-5 Complexed Potassium

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Abstract. The structure of the trichlorocuprate of naphtho-15-crown-5 complexed potassium has been determined by X-ray analysis. The crystal contains the complex cations [K(naphtho-15-crown-5)$_2$]$^+$, the anion [Cu$_2$Cl$_6$]$^{2-}$ and water molecules. The full composition of the compound in the solid state is represented by the formula [K(naphtho-15-crown-5)$_2$]$_2$[Cu$_2$Cl$_6$] · n H$_2$O), where $n \simeq 3$. The sandwich type cations are similar to those found previously for potassium complexes with benzo-15-crown-5. The coordination number of potassium is equal to 10; the coordination polyhedron is a pentagonal antiprism. The water molecules are disordered and occupy six symmetrically independent positions with a probability of ~0.5 in the crystal. The lack of close contacts between water molecules and the remaining components enabled the treatment of the complex as a clathrate.

Key words: X-ray crystal structure, crown ether–potassium complex, trichlorocuprates, clathrates.

1. Introduction

The electron donor properties of crown ethers are responsible for the formation of complexes with metal cations. Complex formation is controlled by a mutual matching of the sizes of the cavity and of the complexed cation. The 18-membered macrocyclic units of crowns are capable of forming cavitands with potassium, whereas the 15-membered macrocycles prefer to form such complexes with sodium cations.

To differentiate the selectivity of complex formation one may change the size, the number and the kind of the electron donating atoms within the macrocycle or change the conformational flexibility of a crown ether by, for example, condensing

the macrocycle with a benzene ring. In general, benzocrown ethers behave in a similar way to the parent compounds. By contrast, benzo-15-crown-5 is also able to form 2 : 1 sandwich-like complexes of considerable stability with potassium ions [1]. The analogous naphtho-15-crown-5 is an ionophore for ion-selective membrane electrodes with a very high selectivity for potassium as compared to sodium [2]. The selectivity is much higher when compared with benzo-15-crown-5. The same is true for alkyl and some other derivatives of 15-membered benzo- and naphthocrown ethers [3]. The above-mentioned crown ethers form 1 : 1 complexes with sodium, whereas with potassium they form two types of complexes in solution: of 1 : 1 and 2 : 1 stoichiometry. Alkyl substituents do not significantly affect the stability constants but somewhat higher values are always quoted for naphtho derivatives [4]. The very high selectivity of the respective membrane electrodes, which we previously ascribed to the change in the partition of potassium ions due to the higher lipophilicity of the 2 : 1 potassium complexes as compared to the 1 : 1 sodium complexes [5], encouraged us to study the X-ray structure of the potassium complex. The chlorocuprate ion was selected as the anion because its structure is very sensitive towards the size of the counterion [6].

2. Experimental

2.1. THE SYNTHESIS OF THE TRICHLOROCUPRATE OF NAPHTHO-15-CROWN-5 COMPLEXED POTASSIUM

The synthesis of the trichlorocuprate of naphthocrown complexed potassium was carried out in a similar manner to that described earlier [7].

A mixture of 160 mg (0.5 mmole) of naphtho-15-crown-5 [8], 35 mg (0.25 mmole) of anhydrous potassium carbonate, 50 mg (0.25 mmole) of copper acetate monohydrate and 2 mL of glacial acetic acid was heated to complete dissolution. Concentrated hydrochloric acid (0.1 mL) was added to the hot clear solution and the mixture was allowed to stand at room temperature to yield almost quantitatively a crystalline brown-greenish material.

2.2. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION

The experimental data were obtained from a prismatic brown-greenish crystal (dimensions $0.15 \times 0.10 \times 0.30$ mm) on an RED-4 diffractometer (CuK$_\alpha$ radiation, graphite monochromator) by the θ–2θ scanning method.

The crystal is triclinic, with the unit cell parameters refined by the least squares method using 15 reflections in the $\theta = 12$–$18°$ angle range. The space group is $P\bar{1}$; $a = 24.311(8)$, $b = 15.314(4)$, $c = 13.124(3)$ Å; $\alpha = 67.63(2)$, $\beta = 75.78(2)$, $\gamma = 95.44(2)°$, $V = 4282(3)$ Å^3, ρ(calcd) $= 1.354(3)$ g cm^{-3} where $Z = 2$ for the composition $C_{72}H_{94}O_{23}Cu_2K_2Cl_6$. 5970 reflections were collected in the $2° \leq \theta \leq 45°$ range, of which 4672 reflections with $I \geq 3\sigma(I)$ were used to solve
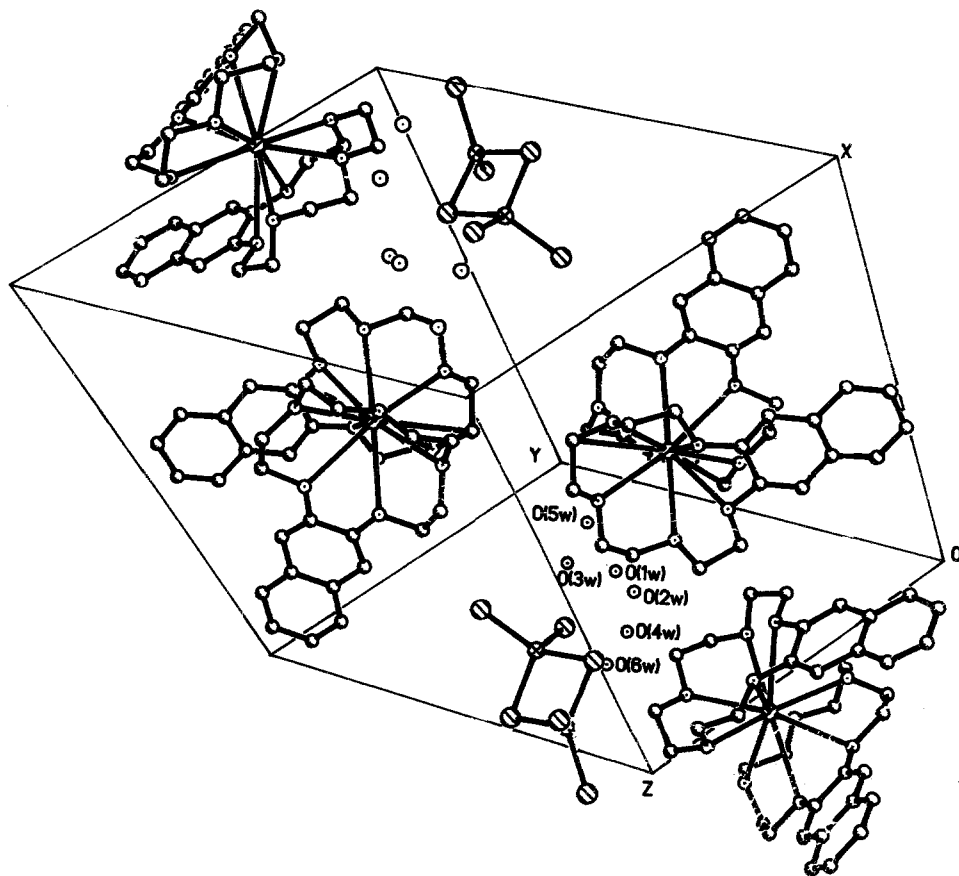
Fig. 1. The crystal packing of the title complex.

and to refine the structure. Data reduction included corrections for background and Lp effects. Absorption effects were insignificant ($\mu = 37.7$ cm^{-1}).

The structure was solved by the automatic analysis of the Paterson function using the SHELXTL [9] program. In the first stage the coordinates of the Cu, Cl and K atoms were determined. Calculation of the Fourier synthesis and its analysis enabled the localization of all non-hydrogen atoms. At this stage the difference Fourier synthesis revealed the six last peaks corresponding to water molecules. Analysis of their localization permitted an assumption that water molecules are statistically placed in the cell. For final refinement of the positions of water molecules it was assumed that they occupy the respective places with the probability coefficient equal to 0.5. The refinement was performed by the anisotropic variant for all non-hydrogen atoms and by the isotropic variant for water molecules. The positions of hydrogen atoms were calculated geometrically for CH and CH$_2$ groups and were not refined. The lack of refinement of H–atoms was limited by the number of experimental intensities. The final R factor is equal to 0.077, $R_w = 0.086$, where

TABLE I. Atomic fractional coordinates and equivalent temperature factors ($\text{Å}^2 \times 10^3$).

	x	y	z	U_{eq}
Cu(1)	0.2428(1)	0.0093(2)	0.1363(2)	54(1)
Cu(2)	0.2530(1)	0.2301(2)	−0.0621(2)	53(1)
Cl(1)	0.2157(2)	0.1515(3)	0.1380(4)	58(2)
Cl(2)	0.2738(2)	0.0837(3)	−0.0639(4)	70(3)
Cl(3)	0.1680(2)	−0.1015(4)	0.2573(4)	99(3)
Cl(4)	0.3167(2)	−0.0423(4)	0.1836(5)	93(3)
Cl(5)	0.3099(2)	0.3600(3)	−0.0885(5)	93(3)
Cl(6)	0.2125(2)	0.2827(4)	−0.1984(4)	72(3)
K(1)	0.0848(2)	−0.1382(3)	−0.2362(3)	43(2)
K(2)	0.4380(1)	0.2868(2)	−0.6463(3)	36(2)
O(1a)	0.2025(4)	−0.1531(7)	−0.2130(8)	52(5)
C(2a)	0.1998(7)	−0.2033(11)	−0.0937(13)	55(8)
C(3a)	0.1743(9)	−0.1422(13)	−0.0382(14)	66(10)
O(4a)	0.1167(5)	−0.1422(7)	−0.0397(8)	58(6)
C(5a)	0.0933(8)	−0.0682(14)	−0.110(14)	73(11)
C(6a)	0.1143(9)	0.0282(13)	−0.1051(16)	83(11)
O(7a)	0.0969(5)	0.0300(8)	−0.2011(9)	63(6)
C(8a)	0.1214(8)	0.1202(11)	−0.2998(15)	68(10)
C(9a)	0.1019(8)	0.1162(13)	−0.3980(14)	67(10)
O(10a)	0.1217(4)	0.0495(7)	−0.4365(8)	49(5)
C(11a)	0.1763(7)	0.0837(11)	−0.5183(13)	53(9)
C(12a)	0.2005(6)	−0.0010(11)	−0.5301(12)	48(8)
O(13a)	0.2065(4)	−0.0570(7)	−0.4185(8)	47(5)
C(14a)	0.2293(6)	−0.1366(11)	−0.4053(13)	45(8)
C(15a)	0.2259(6)	−0.1933(11)	−0.2858(12)	46(7)
C(16a)	0.2444(6)	−0.2768(11)	−0.2584(12)	44(8)
C(17a)	0.2649(6)	−0.3151(10)	−0.3412(13)	49(8)
C(18a)	0.2830(7)	−0.4043(12)	−0.3123(15)	61(9)
C(19a)	0.3009(8)	−0.4415(13)	−0.3897(21)	86(12)
C(20a)	0.3042(8)	−0.3892(15)	−0.5035(19)	78(12)
C(21a)	0.2875(6)	−0.2988(13)	−0.5390(13)	66(9)
C(22a)	0.2665(6)	−0.2598(11)	−0.4581(12)	48(8)
C(23a)	0.2478(6)	−0.1679(11)	−0.4878(12)	49(8)
O(1b)	0.0112(4)	−0.3244(7)	−0.0440(8)	50(5)
C(2b)	−0.0252(6)	−0.3096(11)	0.0503(12)	54(8)
C(3b)	−0.0635(7)	−0.2462(13)	−0.0012(14)	62(9)
O(4b)	−0.0274(4)	−0.1533(7)	−0.0833(8)	46(5)
C(5b)	−0.0574(7)	−0.0960(12)	−0.1519(15)	67(9)
C(6b)	−0.0661(7)	−0.1229(12)	−0.2475(14)	64(9)
O(7b)	−0.0087(4)	−0.1075(7)	−0.3229(8)	52(5)
C(8b)	−0.0130(7)	−0.1452(13)	−0.4059(14)	66(10)
C(9b)	0.0476(7)	−0.1323(12)	−0.4831(13)	64(9)

TABLE I.   (Continued.)

	x	y	z	U_{eq}
O(10b)	0.0820(4)	−0.1898(8)	−0.4209(8)	52(6)
C(11b)	0.0728(8)	−0.2864(12)	−0.4121(14)	67(9)
C(12b)	0.1005(7)	−0.3451(11)	−0.3223(13)	57(8)
O(13b)	0.0704(4)	−0.3403(7)	−0.2172(9)	60(6)
C(14b)	0.0815(6)	−0.3955(10)	−0.1192(13)	44(8)
C(15b)	0.0459(6)	−0.3865(11)	−0.0191(13)	43(8)
C(16b)	0.0507(6)	−0.4379(11)	0.0877(14)	50(8)
C(17b)	0.0922(7)	−0.5005(10)	0.1012(13)	55(8)
C(18b)	0.1003(8)	−0.5567(13)	0.2102(16)	79(10)
C(19b)	0.1406(8)	−0.6135(13)	0.2171(15)	82(10)
C(20b)	0.1740(7)	−0.6214(11)	0.1217(17)	74(10)
C(21b)	0.1687(7)	−0.5694(11)	0.0115(16)	65(9)
C(22b)	0.1283(6)	−0.5092(10)	0.0009(14)	51(8)
C(23b)	0.1193(6)	−0.4569(10)	−0.1075(12)	49(7)
O(1c)	0.5162(4)	0.1567(7)	−0.5982(9)	56(6)
C(2c)	0.5744(6)	0.2057(11)	−0.6214(13)	53(8)
C(3c)	0.5688(6)	0.2571(11)	−0.5457(13)	59(8)
O(4c)	0.5359(4)	0.3315(7)	−0.5805(8)	48(5)
C(5c)	0.5200(7)	0.3745(11)	−0.5046(14)	63(9)
C(6c)	0.4673(8)	0.3141(12)	−0.3999(13)	74(10)
O(7c)	0.4183(4)	0.3049(7)	−0.4389(8)	60(5)
C(8c)	0.3687(7)	0.2446(12)	−0.3471(13)	70(9)
C(9c)	0.3203(7)	0.2253(12)	−0.3933(13)	62(9)
O(10c)	0.3341(4)	0.1741(7)	−0.4650(7)	50(5)
C(11c)	0.3267(6)	0.0726(11)	−0.4038(12)	57(8)
C(12c)	0.3518(6)	0.0322(10)	−0.4884(12)	44(7)
O(13c)	0.4121(4)	0.0734(6)	−0.5317(8)	42(5)
C(14c)	0.4458(6)	0.0438(10)	−0.6050(12)	41(7)
C(15c)	0.5068(6)	0.0921(10)	−0.6424(12)	44(7)
C(16c)	0.5474(6)	0.0726(10)	−0.7166(13)	51(8)
C(17c)	0.5307(7)	0.0065(11)	−0.7602(12)	52(8)
C(18c)	0.5712(7)	−0.0158(13)	−0.8447(14)	71(9)
C(19c)	0.5536(10)	−0.0771(16)	−0.8878(15)	85(12)
C(20c)	0.4957(10)	−0.1212(14)	−0.8533(16)	78(12)
C(21c)	0.4554(7)	−0.1007(11)	−0.7770(15)	62(10)
C(22c)	0.4718(8)	−0.0386(11)	−0.7282(12)	55(8)
C(23c)	0.4293(6)	−0.0177(10)	−0.6470(13)	50(8)
O(1d)	0.5277(4)	0.4242(7)	−0.8532(8)	49(6)
C(2d)	0.5502(7)	0.5087(11)	−0.8421(13)	43(9)
C(3d)	0.5010(8)	0.5545(11)	−0.8153(13)	52(9)
O(4d)	0.4618(5)	0.4909(7)	−0.7061(9)	46(6)
C(5d)	0.4080(9)	0.5180(12)	−0.6807(15)	57(11)

TABLE I. (Continued.)

	x	y	z	U_{eq}
C(6d)	0.3688(8)	0.4940(14)	−0.7421(15)	57(11)
O(7d)	0.3537(5)	0.3923(8)	−0.7034(9)	51(6)
C(8d)	0.3208(8)	0.3635(15)	−0.7668(16)	66(11)
C(9d)	0.3115(8)	0.2560(15)	−0.7254(15)	63(11)
O(10d)	0.3649(5)	0.2212(7)	−0.7505(9)	51(6)
C(11d)	0.3817(8)	0.2259(12)	−0.8634(16)	55(10)
C(12d)	0.4427(7)	0.2147(11)	−0.8947(13)	45(9)
O(13d)	0.4785(5)	0.2883(7)	−0.8797(9)	49(6)
C(14d)	0.5393(7)	0.3040(11)	−0.9221(13)	38(8)
C(15d)	0.5666(6)	0.3816(10)	−0.9059(12)	33(7)
C(16d)	0.6240(6)	0.4099(10)	−0.9419(11)	44(7)
C(17d)	0.6584(6)	0.3641(10)	−1.0034(11)	40(7)
C(18d)	0.7189(8)	0.3934(11)	−1.0532(13)	52(9)
C(19d)	0.7497(7)	0.3532(15)	−1.1153(15)	65(10)
C(20d)	0.7233(9)	0.2802(15)	−1.1321(16)	65(11)
C(21d)	0.6661(9)	0.2455(11)	−1.0836(14)	56(10)
C(22d)	0.6308(6)	0.2877(11)	−1.0213(11)	39(7)
C(23d)	0.5690(6)	0.2586(10)	−0.9739(11)	44(7)
O(1w)	0.0012(9)	0.5776(16)	0.3553(19)	52(7)
O(2w)	0.1135(8)	0.3622(14)	0.5210(17)	62(6)
O(3w)	0.0035(9)	0.6895(15)	0.3771(17)	77(6)
O(4w)	−0.1171(7)	0.5221(13)	0.4467(15)	90(5)
O(5w)	0.0860(7)	0.6681(13)	0.2931(15)	101(5)
O(6w)	−0.1998(7)	0.5598(13)	0.5110(15)	115(5)

$w = [\sigma(F) + 0.005414F^2]^{-1}$.

The coordinates of the basic atoms are shown in Table I.

3. Results and Discussion

3.1. THE CRYSTAL STRUCTURE

Figure 1 presents the contents of the centrosymmetric triclinic cell. The crystal is built up of two crystallographically independent complex cations [K(naphtho-15-crown-5)$_2$]$^+$, and [Cu$_2$Cl$_6$]$^{2-}$ anions and solvating water molecules. The structure is ionic in character (Figure 1). It may be described as a distorted antifluorite structure, in which the bulky complex potassium cations determine the packing whereas the dimeric Cu$_2$Cl$_6$ anions fill the empty space between them.

The coordination number of the potassium complex in relation to the dimeric anion is equal to 4; the coordination number of the dimer in relation to the potassium complexes is equal to 8.
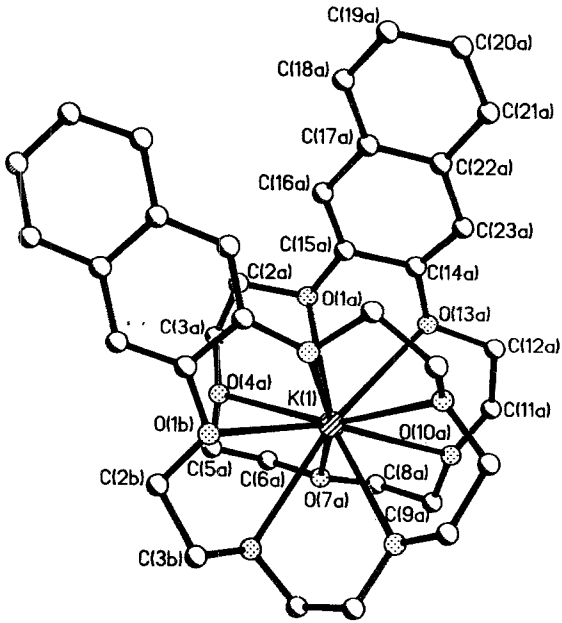
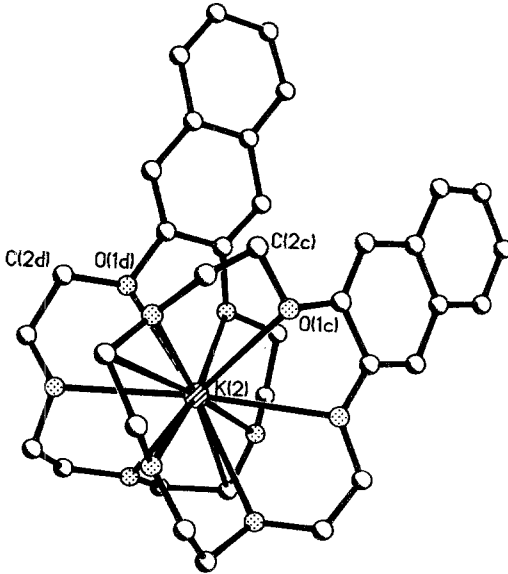Fig. 2.   (a) The structures of the naphtho-15-crown-5–potassium complexes.

Fig. 2.   (b) The structures of the naphtho-15-crown-5–potassium complexes.

TABLE II.   Potassium to oxygen dis-
tances [Å] in the complex cation.

| | Molecule | |
	A	B
K(1)–O(1)	2.972(8)	3.006(8)
K(1)–O(4)	2.851(7)	2.891(7)
K(1)–O(7)	2.786(8)	2.784(8)
K(1)–O(10)	2.929(9)	2.834(8)
K(1)–O(13)	3.096(9)	2.988(8)
	C	D
K(2)–O(1)	2.887(8)	2.903(8)
K(2)–O(4)	2.834(7)	2.879(9)
K(2)–O(7)	2.770(8)	2.779(10)
K(2)–O(10)	2.849(9)	2.818(9)
K(2)–O(13)	2.957(9)	2.969(9)

The water molecules fill the empty spaces and are not bound to the complex anions or complex cations by O-H...Cl or O-H...O hydrogen bonds. The O(1w) and O(4w) molecules are bound to each other by hydrogen bonds with the O...O distance equal to 2.74 Å. Analogously the O...O distance between O(2w) and O(3w) is equal to 2.72 Å. It is worth adding that two such associates cannot be located simultaneously in one vacancy. The O(5w) and O(6w) water molecules can be located together and they can also be in contact with water molecules: O(5w) with O(2w) and O(4w); O(6w) with O(1w) and O(3w).

The statistical distribution of the water molecules in the crystal permitted an assumption that there are approximately three water molecules per one dimeric anion. The lack of close contacts between water molecules and the remaining components enabled the treatment of the complex as a clathrate [10].

3.2. STRUCTURE OF COMPLEX CATIONS

A sandwich-like arrangement of the complex was observed, as was predicted *a priori* from the topological analogy of the 15-membered crown ether and the effective diameter of the potassium cation. In this case the K^+ is located between two 15-membered rings and is bound to all ten oxygen atoms. There are no contacts between the potassium cation and the chlorine atoms of the dimeric trichlorocuprate anion, as found in analogous trichlorocuprates of benzo-15-crown-5 and dibenzo-18-crown-6 complexed sodium [11]. Table II shows the K...O distances for two complex $[K(naphtho-15-crown-5)_2]^+$ cations, which are in the range of 2.770–3.096 Å. Hence the coordination number of potassium is equal to 10 and the

TABLE III.   Distances of selected atoms [Å] from the mean planes of planar fragments of naphtho-15-crown-5 moieties.

(a) Complex cation 1.

I	O(1d)	O(4d)	O(7d)	O(10d)	O(13d)					
	0.083	−0.254	0.327	−0.273	0.116					
II	O(1c)	O(4c)	O(7c)	O(10c)	O(13c)					
	−0.059	0.222	−0.299	0.258	−0.122					
III	C(14d)	C(15d)	C(16d)	C(17d)	C(18d)	C(19d)	C(20d)	C(21d)	C(22d)	C(23d)
	0.045	0.050	−0.029	−0.044	−0.015	0.038	0.053	−0.027	−0.026	−0.019
IV	C(14c)	C(15c)	C(16c)	C(17c)	C(18c)	C(19c)	C(20c)	C(21c)	C(22c)	C(23c)
	−0.002	0.029	0.000	−0.031	0.013	0.010	0.003	0.019	−0.017	−0.010

Dihedral angles

[1] I–III   1.6°
[2] II–IV   18.7°
[3] I–II   7.8°
[4] III–IV   11.0°

[1] the dihedral angle between the oxygen mean plane and the plane of the naphtho residue of molecule d.

[2] the dihedral angle between the oxygen mean plane and the plane of the naphtho residue of molecule c.

[3] the dihedral angle between the oxygen mean planes of molecules d and c.

[4] the dihedral angle between the naphtho residue mean planes of molecules d and c.

coordination polyhedron is a pentagonal antiprism (Figure 2).

These distances are similar to those found for other sandwich-like potassium complexes. For example they are equal to 2.78–2.96 Å [12] for the potassium complex with benzo-15-crown-5 or 2.777 to 3.021 Å for the trichlorocuprate of benzo-15-crown-5 complexed potassium.

For the two independent complex cations the dihedral angle between the mean planes formed by oxygen atoms of the macrocycles is equal to 7.8° (for K_1) and 11.6° (for K_2), i.e. they are close to parallel. The deviations of the oxygen atoms from the mean planes calculated by the least squares method are in the range of −0.322 to 0.348 Å (Table III).

The substantial difference between this structure and the structure of the potassium iodide complex with benzo-15-crown-5 lies in the different location of the aromatic systems. The benzo-15-crown-5 complex has C_i symmetry [13] which determines the structure of the coordination polyhedron – the pentagonal antiprism.

TABLE III.   (Continued.)

(b) Complex cation 2.

I	O(1a)	O(4a)	O(7a)	O(10a)	O(13a)					
	0.103	−0.273	0.348	−0.272	0.094					

II	O(1b)	O(4b)	O(7b)	O(10b)	O(13c)					
	−0.128	0.274	−0.322	0.239	−0.063					

III	C(14a)	C(15a)	C(16a)	C(17a)	C(18a)	C(19a)	C(20a)	C(21a)	C(22a)	C(23a)
	0.004	−0.023	0.013	0.012	0.013	−0.022	−0.005	0.011	0.000	−0.003

IV	C(14b)	C(15b)	C(16b)	C(17b)	C(18b)	C(19b)	C(20b)	C(21b)	C(22b)	C(23b)
	0.014	0.014	−0.006	−0.002	−0.014	0.006	0.005	0.008	0.008	−0.033

Dihedral angles

[1]	I–III	22.9°
[2]	I–II	11.6°
[3]	II–IV	16.1°
[4]	III–IV	25.0°

[1] the dihedral angle between the oxygen mean plane and the plane of the naphtho residue of molecule a.

[2] the dihedral angle between the oxygen mean plane and the plane of the naphtho residue of molecule b.

[3] the dihedral angle between the oxygen mean planes of molecules a and b.

[4] the dihedral angle between the naphtho residue mean planes of molecules a and b.

TABLE III.   (Continued.)

(c) The complex anion.

Cu(1)	Cu(2)	Cl(1)	Cl(2)
−0.040	−0.040	0.040	0.040

Distances of terminal chlorine atoms from the Cu_2Cl_2 mean plane

Cl(3)	−1.440
Cl(4)	−1.791
Cl(5)	−1.686
Cl(6)	1.417

TABLE IV.   Selected torsional angles [°].

	A	B	C	D
C(15)–O(1)–C(2)–C(3)	178.6	−173.7	−171.2	164.3
O(1)–C(2)–C(3)–O(4)	66.2	−65.9	−65.6	64.6
C(2)–C(3)–O(4)–C(5)	−167.0	168.2	170.3	−168.6
C(3)–O(4)–C(5)–C(6)	76.4	−76.4	−79.4	77.3
O(4)–C(5)–C(6)–O(7)	62.0	−63.3	−64.0	64.3
C(5)–C(6)–O(7)–C(8)	−174.1	171.4	176.2	−174.0
C(6)–O(7)–C(8)–C(9)	179.1	178.1	−172.1	175.5
O(7)–C(8)–C(9)–O(10)	−64.6	65.9	63.0	−65.2
C(8)–C(9)–O(10)–C(11)	−85.8	84.8	80.9	−83.8
C(9)–O(10)–C(11)–C(12)	164.8	−167.4	−170.8	165.3
O(10)–C(11)–C(12)–O(13)	−63.3	60.9	64.2	−55.5
C(11)–C(12)–O(13)–C(14)	−178.0	172.5	175.9	−169.2
C(12)–O(13)–C(14)–C(15)	−172.4	−177.3	−179.9	176.6
O(13)–C(14)–C(15)–O(1)	−2.2	−1.9	−1.3	−0.5
C(14)–C(15)–O(1)–C(2)	−177.6	−179.0	176.2	−174.3

In the case of the trichlorocuprate of naphtho-15-crown-5 complexed potassium (Figure 2), one of the aromatic systems is rotated in the parallel mean plane of the macrocycle to form an angle of about 30° between the aromatic rings. The trichlorocuprate anion probably determines the location of aromatic residues in the case of the naphtho-15-crown-5 complex in a similar way to that of the trichlorocuprate of benzo-15-crown-5 complexed potassium [7].

3.3. THE STRUCTURE OF THE NAPHTHO-15-CROWN-5 LIGAND

The naphtho-15-crown-5 molecules forming complexes with potassium cations have an identical conformation. It may be described as one *cis* configuration around the C-C bonds and four ±*gauche*, ±*gauche*, ∓*gauche*, ∓*gauche* conformations, respectively (Table IV). There are 8 *trans* and 2 *gauche* conformations around the C-O bonds. In this case the ±*gauche* and ±*gauche* fragment is present at the C(5) and C(9) carbon atoms forming a conformation which, according to Dale [14], could be described as biangular. This biangular conformation is characteristic for free benzo-15-crown-5 as well as for its complexes. It was found for example in benzo-15-crown-5 [15], in the chlorocuprate of benzo-15-crown-5 complexed potassium [7] and in the calcium complex of benzo-15-crown-5 [16]. It was also observed in 4,5-benzo-15-crown-5-dicarboxylic acid [17] and in the complex of amidosulfonic acid with benzo-15-crown-5 [18]. The position of the angular fragments is determined by the character of interactions between the crown ether and the respective cations or the neutral guest molecules.

TABLE V.   Interatomic distances [Å] and valence angles [°] in the crown ether moieties.

Distance	A	B	C	D	Average
O(1)–C(2)	1.44(2)	1.44(2)	1.44(2)	1.43(2)	1.44
C(2)–C(3)	1.48(3)	1.50(2)	1.48(3)	1.48(3)	1.49
C(3)–O(4)	1.41(2)	1.44(2)	1.45(2)	1.41(2)	1.43
O(4)–C(5)	1.45(3)	1.40(2)	1.39(2)	1.41(2)	1.41
C(5)–C(6)	1.46(2)	1.51(3)	1.53(2)	1.49(3)	1.50
C(6)–O(7)	1.41(3)	1.44(2)	1.42(2)	1.42(2)	1.42
O(7)–C(8)	1.43(2)	1.43(3)	1.41(2)	1.44(3)	1.43
C(8)–C(9)	1.50(3)	1.51(2)	1.50(3)	1.50(3)	1.50
C(9)–O(10)	1.38(2)	1.44(2)	1.44(2)	1.46(2)	1.43
O(10)–C(11)	1.39(2)	1.43(2)	1.42(2)	1.41(2)	1.41
C(11)–C(12)	1.52(3)	1.53(3)	1.50(3)	1.48(3)	1.51
C(12)–O(13)	1.44(2)	1.43(2)	1.42(2)	1.46(2)	1.44
O(13)–C(14)	1.36(2)	1.35(2)	1.35(2)	1.41(2)	1.37
C(14)–C(15)	1.45(2)	1.45(2)	1.47(2)	1.42(3)	1.45
C(15)–O(1)	1.36(2)	1.33(2)	1.35(2)	1.39(2)	1.36
C(15)–C(16)	1.34(2)	1.36(2)	1.35(2)	1.33(2)	1.35
C(16)–C(17)	1.43(3)	1.45(2)	1.41(3)	1.43(2)	1.43
C(17)–C(18)	1.42(2)	1.43(3)	1.46(3)	1.40(2)	1.43
C(17)–C(22)	1.43(2)	1.45(2)	1.41(2)	1.42(2)	1.43
C(18)–C(19)	1.35(4)	1.37(3)	1.35(3)	1.33(3)	1.35
C(19)–C(20)	1.38(3)	1.37(3)	1.38(3)	1.35(3)	1.37
C(20)–C(21)	1.42(3)	1.40(3)	1.37(3)	1.34(3)	1.38
C(21)–C(22)	1.42(3)	1.41(2)	1.41(3)	1.41(3)	1.41
C(22)–C(23)	1.46(2)	1.42(2)	1.44(2)	1.43(2)	1.44
C(23)–C(14)	1.34(2)	1.37(2)	1.33(3)	1.30(2)	1.34

The interatomic distances and valence angles are shown in Table V and they do not differ from those found in other 15-membered crown ethers. The naphtho groups are planar and the mean distances of the carbon atoms are equal to 1.40 Å and the average endocyclic angles are in the range of 120°. They form dihedral angles of 1.6 to 22.9° (Table III) with the mean plane of the five oxygen atoms of the macrocycle, determined by the packing conditions in the crystal.

3.4. STRUCTURE OF THE $[Cu_2Cl_6]^{-2}$ ANION

The binuclear anion is shown in Figure 3. Two of the chlorine atoms act as bridges for two copper atoms and the Cu-Cl distances range from 2.314 to 2.352 Å. The remaining four chlorine atoms are terminal and the Cu-Cl distances range from 2.157 to 2.177 Å. The copper atoms are located at a distance equal to 3.331 Å (Table VI). The coordination polyhedron is a distorted tetrahedron with the Cl-Cu-

TABLE V. (Continued.)

Angle	A	B	C	D	Average
C(15)–O(1)–C(2)	116(1)	118(1)	120(1)	118(1)	118
O(1)–C(2)–C(3)	104(1)	105(1)	105(1)	107(1)	105
C(2)–C(3)–O(4)	110(2)	108(1)	110(1)	109(1)	109
C(3)–O(4)–C(5)	113(2)	112(1)	115(1)	114(1)	114
O(4)–C(5)–C(6)	114(1)	115(2)	114(1)	113(2)	114
C(5)–C(6)–O(7)	110(2)	105(1)	109(1)	110(1)	109
C(6)–O(7)–C(8)	112(1)	108(1)	112(1)	113(1)	111
O(7)–C(8)–C(9)	109(2)	109(2)	110(1)	109(2)	109
O(8)–C(9)–C(10)	115(2)	112(1)	113(1)	114(1)	114
C(9)–O(10)–C(11)	114(1)	113(1)	115(1)	112(1)	114
O(10)–C(11)–C(12)	109(1)	107(2)	109(1)	110(2)	109
C(11)–C(12)–O(13)	105(2)	105(1)	106(1)	108(2)	106
C(12)–O(13)–C(14)	118(1)	118(1)	117(1)	119(1)	118
O(13)–C(14)–C(15)	112(1)	112(1)	112(1)	111(2)	112
C(14)–C(15)–O(1)	113(1)	114(1)	114(1)	114(1)	114
C(23)–C(14)–C(15)	122(2)	121(1)	120(1)	122(1)	121
C(14)–C(15)–C(16)	119(2)	120(2)	121(2)	121(2)	120
C(15)–C(16)–C(17)	123(2)	120(2)	120(1)	119(2)	121
C(16)–C(17)–C(22)	118(1)	120(1)	121(2)	120(1)	120
C(22)–C(17)–C(18)	119(2)	116(2)	116(2)	117(1)	117
C(16)–C(17)–C(18)	123(1)	124(2)	124(2)	124(2)	124
C(17)–C(18)–C(19)	123(2)	121(2)	122(2)	123(2)	122
C(18)–C(19)–C(20)	119(2)	122(2)	121(2)	121(2)	121
C(19)–C(20)–C(21)	121(2)	121(2)	120(2)	120(2)	121
C(20)–C(21)–C(22)	121(2)	119(2)	121(2)	122(2)	121
C(21)–C(22)–C(23)	124(1)	122(2)	121(2)	125(2)	123
C(21)–C(22)–C(17)	117(1)	121(2)	120(2)	118(1)	119
C(17)–C(22)–C(23)	119(1)	117(1)	118(2)	117(2)	118
C(22)–C(23)–C(14)	120(1)	122(2)	120(1)	121(2)	121

Cl angles ranging from 88.5 to 132.8°. The geometry is similar to that found by other authors [19].
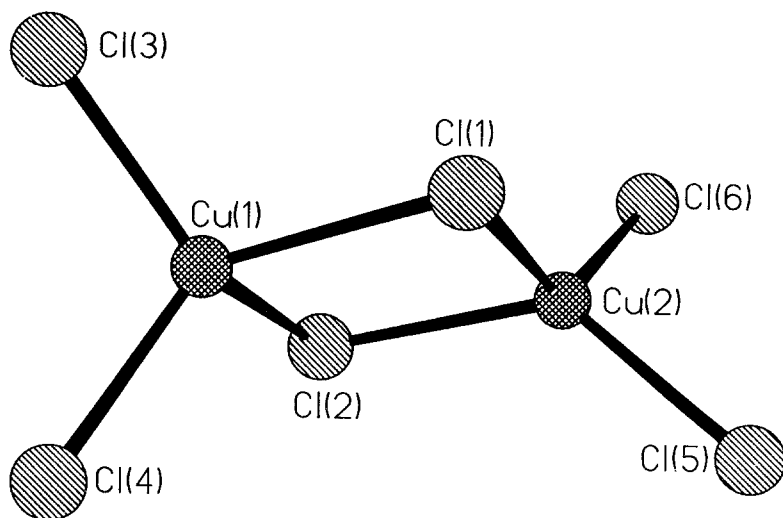
4. General Discussion

The benzo- and naphthocrown ethers form very similar complexes of the sandwich type with potassium cations. In all cases sandwich-like structures were observed in which the coordination number of potassium is high and equal to 10.

The dimeric trichlorocuprate anion, in contrast to polymeric trichlorocuprate anions, is formed when the countercation has a large volume. This phenomenon occurs in the case of tetraphenyl-phosphonium or tetraphenyl-arsonium chloro-

TABLE V.   (Continued.)

	Å		Å
Cu(1)–Cu(2)	3.331(3)		
Cu(1)–Cl(1)	2.342(6)	Cu(2)–Cl(1)	2.320(5)
Cu(1)–Cl(2)	2.314(5)	Cu(2)–Cl(2)	2.352(6)
Cu(1)–Cl(3)	2.157(6)	Cu(2)–Cl(5)	2.170(6)
Cu(1)–Cl(4)	2.163(6)	Cu(2)–Cl(6)	2.177(6)
	[°]		[°]
Cl(1)–Cu(1)–Cl(2)	88.9(2)	Cl(1)–Cu(2)–Cl(2)	88.5(2)
Cl(1)–Cu(1)–Cl(3)	103.2(2)	Cl(2)–Cu(2)–Cl(6)	103.6(2)
Cl(2)–Cu(1)–Cl(3)	131.5(3)	Cl(2)–Cu(2)–Cl(5)	130.7(2)
Cl(1)–Cu(1)–Cl(4)	124.9(3)	Cl(1)–Cu(2)–Cl(6)	132.8(2)
Cl(2)–Cu(1)–Cl(4)	105.1(2)	Cl(1)–Cu(2)–Cl(5)	102.8(2)
Cl(3)–Cu(1)–Cl(4)	105.5(2)	Cl(5)–Cu(2)–Cl(6)	102.8(2)

Fig. 3.   The structure of the $Cu_2Cl_6^{2-}$ anion.

cuprates. Complex cations, formed by complexation of alkali cations with crown ethers, also belong to this group. The dimeric anion structure enables us to conclude that the naphthocrown ether complexed potassium ion, as a very bulky cation or in other words as a superalkali metal cation, leads to anions similar in structure to other chlorocuprate anions of large countercations [6].

Acknowledgements

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