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Macrocyclic Polyfunctional Lewis Bases. XIII: Structure of the Trichlorocuprate of Benzo-15-crown-5 Complexed Potassium

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Abstract. The structure of the trichlorocuprate of benzo-15-crown-5 complexed potassium was determined from diffractometer data by direct and refined by least squares to $R(F) = 0.049$. The complex of the formula $[(C_{14}H_{20}O_5)_2K]_2Cu_2Cl_6$ is triclinic. It consists of two sandwich-like crown-ether-complexed potassium cations and the $Cu_2Cl_6^{2-}$ anion lying in the corner of the unit cell. The sandwich complexes do not exhibit any elements of symmetry. The anion has a flatter structure in comparison to dimers of chlorocuprates of crown-complexed sodium and large organic cations.

Key words: Potassium, benzo-15-crown-5, chlorocuprate anion, X-ray diffraction analysis

1. Introduction

In our recent work [1], the stabilization effect of crown-complexed cations on the formation of complex anions was estimated by determining the structures of trichlorocuprates of crown-complexed sodium. It had been shown that the $Cu_2Cl_6^{2-}$ dimeric anion exhibited a similar structure to the anion in trichlorocuprates of very bulky organic cations.

The structures of crown-complexed sodium cations were very similar to the structures of other reported complexes [2,3]. The coordination number of the sodium cation was equal to 7. It was coordinated to the complex anion through terminal chlorine atoms.

We were also interested in the effect of alkali cations, totally enclosed by crown ethers, on the structure of the chlorocuprate anion. In such a case, the direct coordination of the alkali cation by the anion would be impossible.

The (benzo-15-crown-5)$_2$-potassium sandwich complex [4] was chosen as a most suitable cation for the synthesis of an appropriate trichlorocuprate.

The aim of this work was the determination of the effect of a potassium cation, totally enclosed by two crown ethers, on the structure of the trichlorocuprate anion.

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2. Experimental

Suitable crystals of the trichlorocuprate of benzo-15-crown-5 complexed potassium were obtained by dissolving $Cu(CH_3COO)_2 \cdot H_2O$ (100 mg), K_2CO_3 (35 mg) and benzo-15-crown-5 (270 mg) in acetic acid (50 cm^3) and acetic anhydride (2 cm^3). After heating, conc. HCl (0.2 cm^3) was added dropwise. The solution was gradually cooled and left to stand for three days. Green crystals of the formula $(C_{14}H_{20}O_5)_2KCuCl_3$ precipitated. m.p. 139–142°C.

3. Crystallographic Data

The compound crystallized in the form of green, irregularly shaped blocks with many well-formed faces. The crystals displayed no apparent symmetry. Preliminary Weisenberg photographs confirmed that the crystals belonged to the triclinic system. A crystal with dimensions 0.17 × 0.20 × 0.30 mm was selected for data collection on an automatic four-circle Nonius CAD-4 diffractometer. The least-squares fit of angular positions for 16 reflections gave accurate cell dimensions: $a = 11.224(2)$, $b = 12.831(2)$, $c = 13.663(2)$ Å, $\alpha = 75.47(1)$, $\beta = 67.44(1)$, $\gamma = 70.46(1)°$, $V = 1695.4$ Å^3, $Z = 2$ for the unit of $(C_{14}H_{20}O_5)_2KCuCl_3$, MW = 745.64, $F(000) = 774$, $\lambda(MoK\alpha) = 0.7107$ Å, $D_x = 1.461$ g cm^{-3}, $\mu(MoK\alpha) = 10.7$ cm^{-1}.

The ω/θ scan was applied with a scan width of 1.2° and a scan speed in the range 2.4–5°/min up to $\theta_{max} = 20°$. No significant variation of standard intensities (monitored every 1 h) was observed. 5939 unique reflections were measured and 2284 of them (with $I < 2.\delta I$)) were treated as unobserved in subsequent calculations.

The structure was solved in the $P1$ space group with the MULTAN-80 program [5]. The E-map showed the Cu_2Cl_6 group, two potassium ions and fragments of crown rings. Visible fragments of the structure were arranged centrosymmetrically around the centre of the Cu_2Cl_6 group. Subsequent refinement was carried out in the $P\bar{1}$ space group after appropriate translation of the model taken from the E-map. The model was completed from the first difference Fourier map and refined by the least-squares procedure, at first isotropically and then anisotropically using the SHELX-76 program system [6]. After the refinement of heavy atoms had converged, the difference Fourier map was calculated and revealed most of the hydrogen atoms. However, they did not behave satisfactorily during free refinement and were subsequently refined as 'riding' on their parent carbon atoms with constrained distances of 1.08 Å and one common isotropic temperature factor. The following weighting scheme was applied during refinement:

$$w = 1.46/(\delta^2(F) + 0.001F^2).$$

Atomic scattering factors were taken from *International Tables*, Vol. IV [8]. The final

$$R = \sum[\,||F_o| - |F_c||\,]/(\sum|F_o|)$$

was equal to 0.049. The highest density in the final difference Fourier synthesis was equal to 0.51 in the vicinity of the Cu_2Cl_6 group and 0.21 e Å^{-3} elsewhere.

The final atomic coordinates are given in Table I with equivalent isotropic temperature factors (Figure 1). Other data concerning the structure may be obtained from the authors on request.

Table I. Atomic coordinates and equivalent isotropic temperature factors ($\times 10^4$) with e.s.d.'s in parentheses

Atom	x/a	y/b	z/c	U_{eq}
Cu(1)	255(1)	914(1)	8853(1)	421
Cl(2)	103(2)	828(1)	10590(1)	884
Cl(3)	1383(2)	2192(1)	8207(1)	738
Cl(4)	-505(2)	1246(1)	7512(1)	742
K(5)	6496(1)	7523(1)	7495(1)	464
O(1)	6096(3)	7384(3)	5472(3)	570
C(2)	6962(5)	6426(4)	4988(4)	562
C(3)	8358(5)	6539(5)	4693(4)	617
O(4)	8589(3)	6527(3)	5641(2)	555
C(5)	9713(5)	6932(5)	5452(4)	652
C(6)	9374(6)	8182(5)	5310(4)	670
O(7)	8500(4)	8563(5)	6301(3)	651
C(8)	8153(7)	9765(5)	6230(5)	798
C(9)	7085(7)	10100(5)	7243(5)	802
O(10)	5880(4)	9855(3)	7386(3)	670
C(11)	5109(8)	10606(5)	6771(5)	855
C(12)	4026(7)	10107(5)	6838(5)	789
O(13)	4733(4)	9120(3)	6330(3)	672
C(14)	3972(5)	8522(5)	6246(4)	591
C(15)	4731(5)	7548(4)	5767(4)	526
C(16)	4115(6)	6868(5)	5620(4)	678
C(17)	2736(7)	7144(7)	5972(6)	904
C(18)	1998(7)	8073(8)	6448(6)	1002
C(19)	2609(6)	8781(6)	6584(4)	778
O(21)	7123(4)	5085(3)	8209(3)	701
C(22)	8530(6)	4601(6)	7913(6)	948
C(23)	9017(7)	5118(7)	8502(7)	1115
O(24)	8789(4)	6275(4)	8141(4)	932
C(25)	8893(9)	6926(8)	8814(8)	1232
C(26)	7649(10)	7185(9)	9756(6)	1246
O(27)	6592(6)	7862(4)	9389(3)	891
C(28)	5388(10)	8109(7)	10254(5)	1012
C(29)	4278(10)	8798(6)	9830(5)	1067
O(30)	4037(4)	8213(3)	9182(3)	769
C(31)	3293(6)	7436(5)	9775(5)	827
C(32)	3339(6)	6738(5)	9053(5)	758
O(33)	4691(4)	6146(3)	8667(3)	682
C(34)	5041(7)	5280(5)	8109(4)	653
C(35)	6392(8)	4711(4)	7845(4)	679
C(36)	6888(10)	3813(5)	7267(5)	1037
C(37)	5998(17)	3522(9)	6980(9)	1527
C(38)	4699(16)	4069(9)	7236(9)	1450
C(39)	4186(9)	4956(6)	7819(5)	930

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma)$ [7].

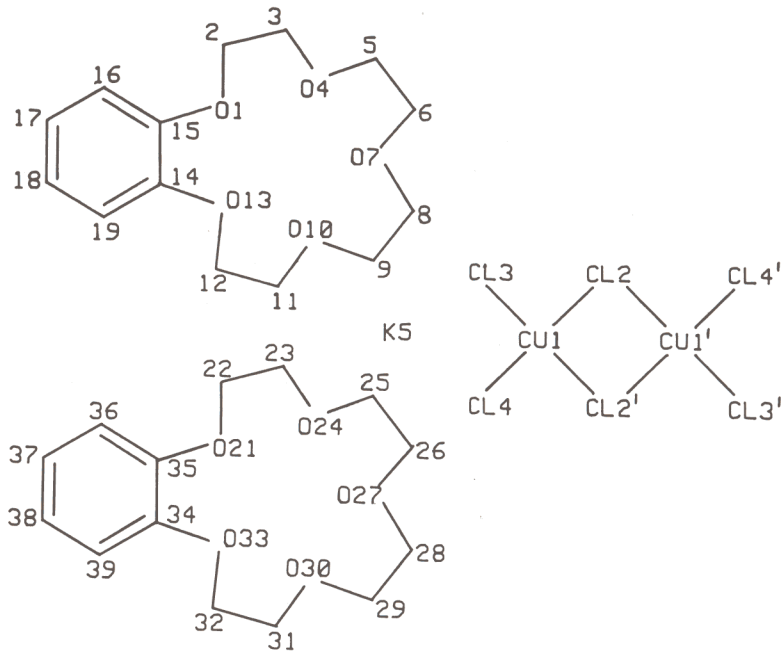

Fig. 1. The numbering scheme of the (benzo-15-crown-5)$_2$KCuCl$_3$ complex.

4. Results and Description of the Structure

The bond lengths and angles for the complex are collected in Table II. The structure consists of two sandwich complexes of crown-complexed potassium and a discrete dimeric $Cu_2Cl_6^{2-}$ anion lying at the centre of symmetry of the unit cell (Figure 2).

The centrosymmetric $Cu_2Cl_6^{2-}$ unit consists of a Cu_2Cl_2 square, built by two copper atoms and two bridging chlorines and of two pairs of terminal chlorines at slightly shorter distances from copper, placed on opposite sides of the plane of the square (Table III).

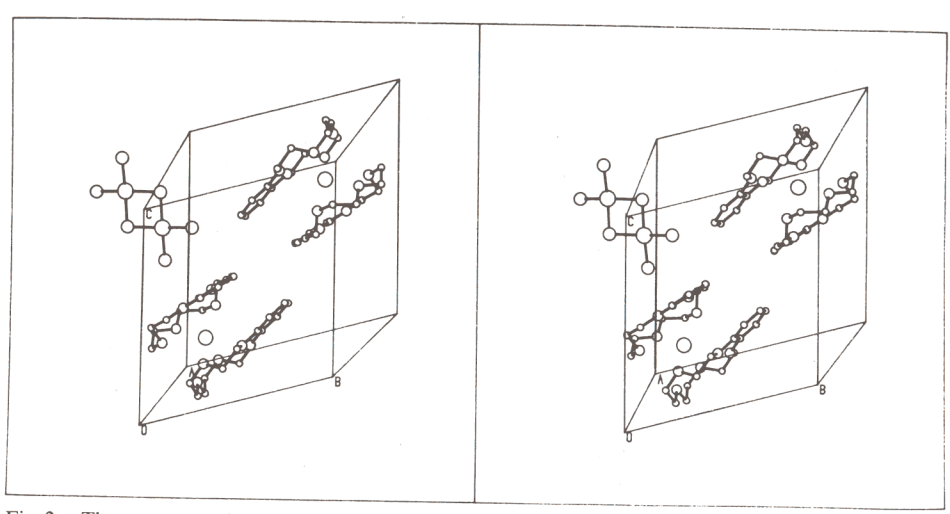

Fig. 2. The structure of the complex.

Table II. Bond distances (Å) and angles (°)

Chlorocuprate anion			
Cu(1)–Cl(2)	2.290(2)	Cl(2)–Cu(1)–Cl(2′)	84.6(1)
Cu(1)–Cl(3)	2.208(2)	Cl(2)–Cu(1)–Cl(3)	94.7(1)
Cu(1)–Cl(4)	2.198(2)	Cl(2)–Cu(1)–Cl(4)	155.9(1)
Cu(1)–Cl(2′)	2.292(2)	Cl(3)–Cu(1)–Cl(2′)	
Cu(1)–Cu(1′)	3.389(1)	Cl(3)–Cu(1)–Cl(4)	95.9(1)
		Cl(4)–Cu(1)–Cl(2′)	
		Cu(1)–Cl(2)–Cu(1′)	95.4(1)
Coordination of K^+ cation			
K(5)–O(1)	3.021(4)	K(5)–O(21)	2.959(4)
K(5)–O(4)	2.935(3)	K(5)–O(24)	2.871(5)
K(5)–O(7)	2.757(4)	K(5)–O(27)	2.777(6)
K(5)–O(10)	2.816(4)	K(5)–O(30)	2.868(3)
K(5)–O(13)	2.953(4)	K(5)–O(33)	2.877(4)
Crown part			
O(1)–C(2)	1.417(6)	C(2)–O(1)–Cl(5)	118.6(5)
O(1)–Cl(5)	1.381(6)	O(1)–C(2)–C(3)	105.3(5)
C(2)–C(3)	1.509(8)	C(2)–C(3)–O(4)	108.5(4)
C(3)–O(4)	1.411(7)	C(3)–O(4)–C(5)	113.1(4)
O(4)–C(5)	1.431(8)	O(4)–C(5)–C(6)	112.7(4)
C(5)–C(6)	1.498(9)	C(5)–C(6)–O(7)	109.3(4)
C(6)–O(7)	1.424(6)	C(6)–O(7)–C(8)	112.3(4)
O(7)–C(8)	1.446(7)	O(7)–C(8)–C(9)	108.5(5)
C(8)–C(9)	1.489(8)	C(8)–C(9)–O(10)	112.7(7)
C(9)–O(10)	1.420(10)	C(9)–O(10)–C(11)	115.0(5)
O(10)–C(11)	1.407(8)	O(10)–C(11)–C(12)	108.3(5)
C(11)–C(12)	1.516(13)	C(11)–C(12)–O(13)	105.0(5)
C(12)–O(13)	1.436(7)	C(12)–O(13)–C(14)	117.0(5)
O(13)–C(14)	1.373(9)	O(13)–C(14)–C(15)	113.9(4)
C(14)–C(15)	1.409(7)	O(13)–C(14)–C(19)	126.5(6)
C(14)–C(19)	1.364(8)	C(15)–C(14)–C(19)	119.6(7)
C(15)–C(16)	1.370(10)	O(1)–C(15)–C(14)	113.5(5)
C(16)–C(17)	1.379(9)	O(1)–C(15)–C(16)	125.7(4)
C(17)–C(18)	1.357(12)	C(14)–C(15)–C(16)	120.8(5)
C(18)–C(19)	1.389(14)	C(15)–C(16)–C(17)	118.5(6)
		C(16)–C(17)–C(18)	121.0(9)
		C(17)–C(18)–C(19)	121.0(7)
		C(14)–C(19)–C(18)	119.0(6)
O(21)–C(22)	1.422(7)	C(22)–O(21)–C(35)	118.7(5)
O(21)–C(35)	1.358(10)	O(21)–C(22)–C(23)	105.7(6)
C(22)–C(23)	1.494(15)	C(22)–C(23)–O(24)	109.3(7)
C(23)–O(24)	1.411(10)	C(23)–O(24)–C(25)	115.2(7)
O(24)–C(25)	1.445(14)	O(24)–C(25)–C(26)	112.7(9)
C(25)–C(26)	1.498(11)	C(25)–C(26)–O(27)	109.0(7)
C(26)–O(27)	1.401(12)	C(26)–O(27)–C(28)	110.9(5)
O(27)–C(28)	1.414(8)	O(27)–C(28)–C(29)	109.3(6)
C(28)–C(29)	1.493(14)	C(28)–C(29)–O(30)	112.3(6)
C(29)–O(30)	1.440(12)	C(29)–O(30)–C(31)	114.0(5)
O(30)–C(31)	1.407(8)	O(30)–C(31)–C(32)	109.2(5)
C(31)–C(32)	1.466(11)	C(31)–C(32)–O(33)	105.0(6)
C(32)–O(33)	1.404(6)	C(32)–O(33)–C(34)	119.5(6)
O(33)–C(34)	1.369(8)	O(33)–C(34)–C(35)	113.7(7)

Table II. (*continued*)

C(34)–C(35)	1.391(10)	O(33)–C(34)–C(39)	125.8(6)
C(34)–C(39)	1.375(14)	C(35)–C(34)–C(39)	120.6(6)
C(35)–C(36)	1.397(9)	O(21)–C(35)–C(34)	115.0(5)
C(36)–C(37)	1.384(23)	O(21)–C(35)–C(36)	125.3(7)
C(37)–C(38)	1.337(22)	C(34)–C(35)–C(36)	119.7(9)
C(38)–C(39)	1.338(15)	C(35)–C(36)–C(37)	118.0(9)
		C(36)–C(37)–C(38)	122.3(12)
		C(37)–C(38)–C(39)	120.6(16)
		C(34)–C(39)–C(38)	118.9(10)

Table III. Selected torsion angles (°)

Cl(2)–Cu(1′)–Cu(1)–Cl(3)	30.5
Cl(2)–Cu(1′)–Cu(1)–Cl(4)	– 147.4
C(15)–O(1)–C(2)–C(3)	175.9
C(2)–O(1)–C(15)–C(14)	180.0
O(1)–C(2)–C(3)–O(4)	62.5
C(2)–C(3)–O(4)–C(5)	– 163.8
C(3)–O(4)–C(5)–C(6)	82.3
O(4)–C(5)–C(6)–O(7)	68.2
C(5)–C(6)–O(7)–C(8)	178.7
C(6)–O(7)–C(8)–C(9)	171.5
O(7)–C(8)–C(9)–O(10)	– 64.7
C(8)–C(9)–O(10)–C(11)	– 77.4
C(9)–O(10)–C(11)–C(12)	168.6
O(10)–C(11)–C(12)–O(13)	– 64.8
C(11)–C(12)–O(13)–C(14)	– 177.6
C(12)–O(13)–C(14)–C(15)	– 178.3
O(13)–C(14)–C(15)–O(1)	0.0

The benzo-15-crown-5 ligands exhibit some approximate symmetry, with the mirror perpendicular to the crown planes (Table IV) and bisecting the aromatic rings and the O(7) and O(27) atom in each crown, respectively. The five oxygen atoms in each crown lie in one plane within 0.28 and 0.33 Å. Crown 1 is more flat, especially in the region up to 3 atoms from the aromatic ring.

The crown-complexed potassium cation does not exhibit any elements of symmetry. The two aromatic rings lie on the same side of the complex, almost facing each other. The potassium cation is coordinated by 10 oxygen atoms of the ligands with bond lengths varying from 2.757 to 3.021 Å. There is no coordination between potassium and the hexachlorocuprate anion.

5. Discussion

The crystal structure of the compound consists of benzo-15-crown-5 complexed potassium cations and a discrete hexachlorodicuprate anion. The geometry is triclinic.

The structure of the (Benzo-15-crown-5)$_2$K$^+$ complex (Figure 3) differs from that described in the structure of the (Benzo-15-crown-5)$_2$KI compound [4]. The most significant difference is the lack of symmetry and the position of the aromatic rings, lying very near each other. The

Table IV. Least-squares planes with deviations of atom positions (in Å). Atoms defining the planes are asterisked

Anion	0		
Cu(1)*	0		
Cu(1′)*	0		
Cl(2)*	0		
Cl(2′)*	0.819		
Cl(3)	−0.895		
Cl(4)			
Oxygen atoms			
O(1)*	0.077	O(21)*	0.140
O(4)*	−0.255	O(24)*	−0.285
O(7)*	0.337	O(27)*	0.333
O(10)*	−0.280	O(30)*	−0.239
O(13)*	0.121	O(33)*	0.051
Aromatic rings			
C(14)*	−0.003	C(34)*	0.006
C(15)*	0.008	C(35)*	−0.001
C(16)*	−0.006	C(36)*	−0.002
C(17)*	−0.002	C(37)*	0.002
C(18)*	0.007	C(38)*	0.005
C(19)*	−0.004	C(39)*	−0.007

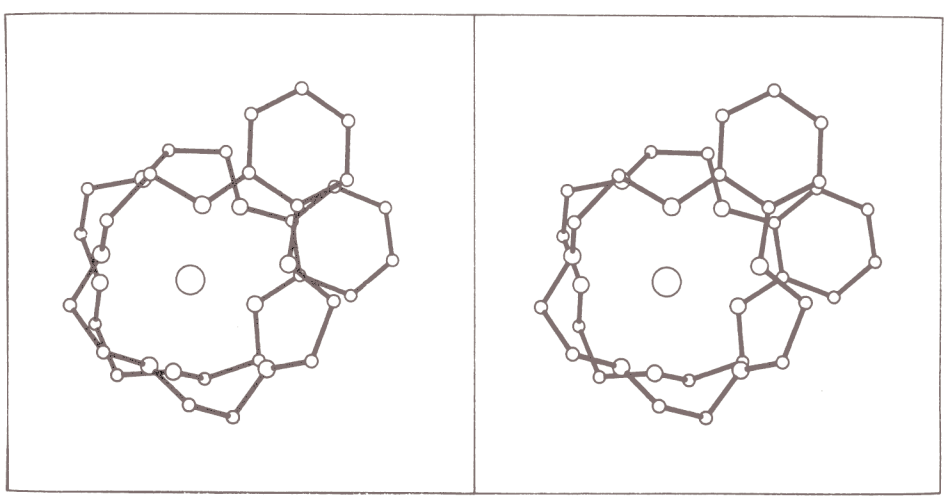

Fig. 3. The structure of the (benzo-15-crown-5)$_2$K$^+$ cation.

planes of the aromatic rings and the oxygen atoms form angles equal to 162.04° and 166.92°, respectively. The aromatic ring planes converge and form an angle of 163.69°. The K–O distances are very similar to the distances in the (Benzo-15-crown-5)$_2$KI compound.

The structure of the $Cu_2Cl_6^{2-}$ anion strongly depends on the size of the counter-cation. The bigger the cation the larger the tendency of a tetrahedral conformation around the copper atoms. In our case, in spite of the fact that the cation is evidently larger than the (Benzo-15-crown-5)Na$^+$ complex, the anion accepts a more planar structure. The angle between the

Cu_2Cl_2 square and the plane formed by Cu(1), Cl(3) and Cl(4) atoms is equal to 31.62° compared to 45° for the anion in the $[(Benzo\text{-}15\text{-}crown\text{-}5)\text{-}Na]_2Cu_2Cl_6$ complex.

The above differences may be explained by the attaining of a conformation by the compound enabling the most effective packing in the crystal.

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