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Hydration of complexes between cobalt chloride and 15-crown-5. Crystal structure of $[Co \cdot 15\text{-crown-}5 \cdot (H_2O)_2][CoCl_4] \cdot H_2O$ and $[Co \cdot 15\text{-crown-}5 \cdot (H_2O)_2]Cl_2 \cdot H_2O$

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Abstract

Hydration of the complexes $[Co \cdot 15\text{-crown-}5 \cdot (CH_3CN)_2][CoCl_4]$ and $[Co \cdot 15\text{-crown-}5 \cdot (CH_3CN)_2][Co_2Cl_6]$ by water leads to the substitution of water for the acetonitrile ligands to afford $CoCl_2 \cdot 6H_2O$, $[Co \cdot 15\text{-crown-}5 \cdot (H_2O)_2][CoCl_4] \cdot H_2O$ and $[Co \cdot 15\text{-crown-}5 \cdot (H_2O)_2]Cl_2 \cdot H_2O$. According to X-ray structural data, cobalt is located in the cavity of 15-crown-5; the coordination polyhedron is a pentagonal bipyramid. Water molecules form a system of hydrogen bonds in both the 15-crown-5 complexes.

Introduction

Interaction of the macrocyclic polyether 15-crown-5 (15C5) with hydrated metal chlorides may afford both intra- and intercavital complexes. In the former case, a metal is incorporated by the cavity of the macrocycle to form a true crown compound. In the latter case, the crown ether is located in the second coordination sphere of the complex and bonded to the metal by hydrogen bonds through water molecules. However, if in the case of hydrated rare earth metal halides the main reason for the formation of the second-sphere complexes is obvious and associated with the impossibility of a metal entering the cavity of 15C5, it is not always clear in other cases. In particular, $ZnCl_2 \cdot 2H_2O$ forms an outer-sphere molecular complex in methanol [1], while $ZnCl_2 \cdot H_2O$ gives an intracavital complex in acetone [1]. Very hydrophilic magnesium chloride reacts with 15C5 in acetonitrile to afford the intracavital ionic compounds $[MgCl \cdot 15C5 \cdot H_2O]Cl$ and $[Mg \cdot 15C5 \cdot (H_2O)_2]Cl_2 \cdot H_2O$ [3]. Hydration of ionic intracavital complexes of copper chloride with the cations $[CuCl \cdot 15C5 \cdot CH_3CN]^+$ and $[Cu \cdot 15C5 \cdot CH_3CN]^{2+}$ provides the substitution of water molecules for acetonitrile and dissociation of copper from the cavity of the macrocycle [4]. All compounds thus formed are polymers, the crown ether being located in the second coordination sphere. The same structure is typical of $[CuBr_2 \cdot H_2O]$ complexed with 15C5 [5]. At the same time copper and cobalt nitrates crystallize as ionic intracavital compounds $[M \cdot 15C5 \cdot (H_2O)_2][NO_3]_2$ (M = Cu [6], Co [7]).

Apparently, formulation of general principles governing the behavior of metal ions on complexation with crown ethers especially in aqueous media used for extraction and in analytical chemistry requires information on complex salts of different structural types. In this connection we have studied the interaction of non-hydrated crown compounds with water and determined the crystal structure of two compounds of different structural types formed on hydration of cobalt chloride complexes with 15C5.

Results and discussion

The intracavital complexes $[Co \cdot 15C5 \cdot (CH_3CN)_2][CoCl_4]$ and $[Co \cdot 15C5 \cdot (CH_3CN)_2][Co_2Cl_6]$, the preparation and structure of which are described elsewhere [8], are very sensitive to moisture and their crystals decompose rapidly (<1 h) to give a pink syrupy material. Crystallization which takes place after the removal of the sample from the desiccator promotes the formation of at least three compounds — pink $CoCl_2 \cdot 6H_2O$, brown $[Co \cdot 15C5 \cdot (H_2O)_2][CoCl_4] \cdot H_2O$ (**I**) and yellow–brown $[Co \cdot 15C5 \cdot$

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$(H_2O)_2]Cl_2 \cdot H_2O$ (**II**). Complex **II**, when isolated from the other crystals, very rapidly turns light-green while in moisture it becomes yellow. This color change may be due to partial dissociation and addition of crystallization water.

Similar to the copper chloride crown complexes [4], hydration of the cobalt chloride ones leads to the substitution of water for acetonitrile. In this case, however, the complexes formed are still ionic with the metal in the cavity, the water molecules occuping the axial positions of a pentagonal bipyramid (Figs. 1 and 2). Moreover, despite a large excess of water, one can see the tetrahedral anion $[CoCl_4]^{2-}$ in the structure of complex **I**, and only a small portion of the starting material transforms into the purely inorganic material $CoCl_2 \cdot 6H_2O$ (its fraction increases in the case of the complex with the counterion $[Co_2Cl_6]^{2-}$).

The geometrical parameters of the Co1 coordination polyhedron in the cation of complex **I** are indicative of its minor distortion (Table 1). The bond angles formed by Co–O(CE) bonds are close to ideal and the average value is 72±1°. The mean value of the angles OW–Co1–O(CE) is equal to 90±4°, while for the angles OW–Co1–OW′ it is equal to 174.3°. The bond distances Co1–O(CE) (mean 2.19±0.02 Å) are close to those found in non-hydrated complexes of $CoCl_2$ with 15C5 [8] and in the cation $[Co \cdot 15C5 \cdot (H_2O)_2][NO_3]_2$ (2.18±0.02 Å) [7]. The interatomic distance Co–OW is also quite common and coincides with that found in ref. 7 (2.08±0.01 Å).

The fragment $-O-CH_2-CH_2-O-$ of the crown ether of complex **I** has an ideal *trans*, ±*gauche*,*trans* configuration (Table 2), while a polygon made of oxygen atoms has a twist conformation. Bond lengths and bond angles in the crown ether are not unusual and equal to 1.42±0.01 Å (C–O), 1.46±0.02 Å (C–C), 116±2° (<COC) and 108±1° (<CCO).

The substitution of water for acetonitrile ligands, on the one hand, simplifies the structure but introduces some specific features arising from the formation of a complex system of hydrogen bonds, on the other. As can be seen from Fig. 1, this bonding uniting all fragments of the complex involves both coordinated and crystallized water molecules. The corresponding main parameters are given in Table 3.

The crown ether in complex **II** is located in a disordered way at the crossing of the three two-fold axes and, as a result, the unprecedently large dispersion of the values of bond lengths and angles in the macrocycle, as well as a noticeable distortion of the coordination polygon, is observed. This strongly complicates a comparison of geometric parameters of the crown fragments in the two similar ions in terms of composition and structure cations in complexes **I** and **II**. An analysis of independent values of geometrical characteristics of the Co polyhedron in complex **II** (Table 4) leads to the following mean bond lengths and bond angles: Co–O(CE) = 2.22 ± 0.05 Å, OW1–Co–O(CE) = 90.0 ± 3.5°, O(CE)–Co–O′(CE) = 72±3°. The polygon formed by oxygen atoms of the polyether molecules has a twist conformation. A deviation of atoms O7a and O7b from the mean plane of the other three oxygens is equal to ±0.24 Å; the torsion angle O4O7bO7O4c is equal to −17.8°. The hydrogen bonds in **II** are

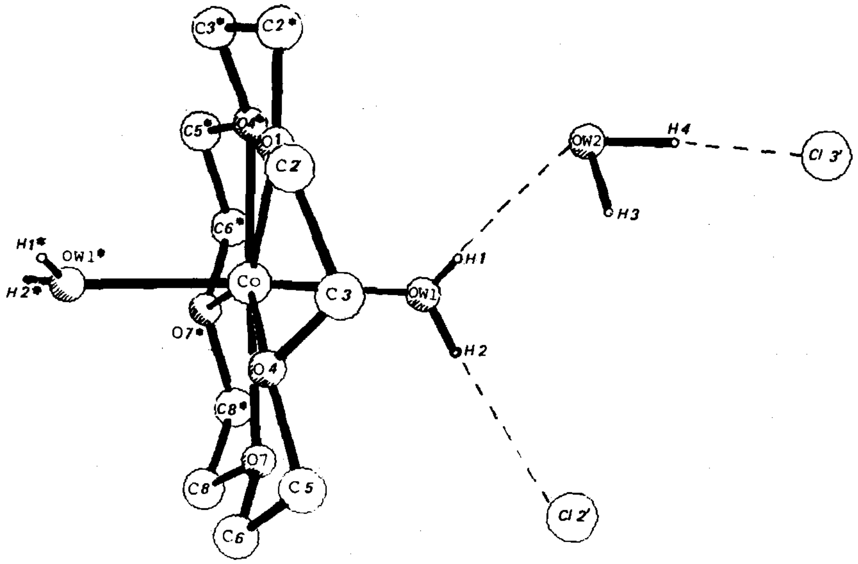

Fig. 1. The structure of the cation $[Co \cdot 15C5(H_2O)_2]^{2+}$ in **I**.

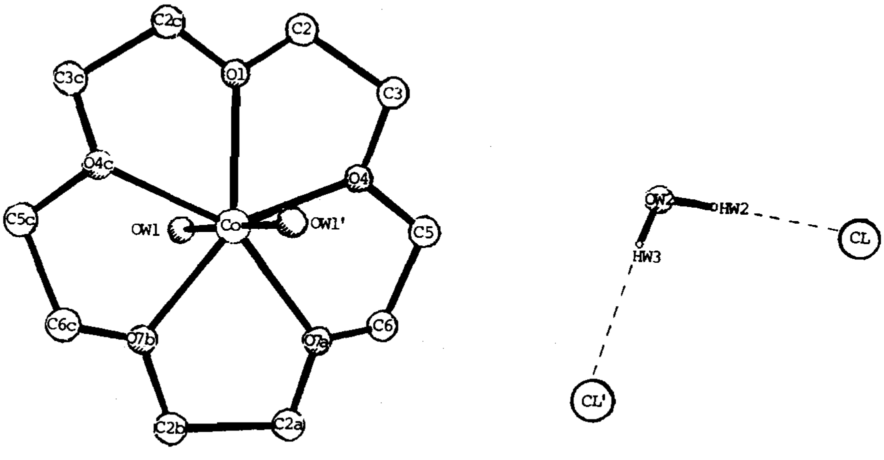

Fig. 2. The structure of [Co·15C5·$(H_2O)_2]Cl_2·H_2O$.

TABLE 1. Main bond lengths and bond angles in the complex [Co·15-C-5·$(H_2O)_2][CoCl_4]·H_2O$

Bond	Distance (Å)	Bond	Angle (°)	Bond	Angle (°)
Co1–OW1	2.076(4)	OW1–Co1–O1	92.9(6)	O4–Co1–O4′	141.8(6)
Co1–O1	2.166(2)	OW1–Co1–O4	94.0(6)	O4–Co1–O7′	144.8(6)
Co1–O4	2.213(2)	OW1–Co1–O7	82.4(6)	O7–Co1–O7′	73.8(6)
Co1–O7	2.172(2)	OW1–Co1–OW1′	174.3(7)	O4–Co1–O7′	72.9(6)
Co2–Cl1	2.263(2)	OW1–Co1–O4′	87.9(6)	Cl1–Co2–Cl3	109.1(1)
Co2–Cl2	2.296(2)	OW1–Co1–O7′	93.0(6)	Cl1–Co2–Cl1′	110.0(1)
Co2–Cl3	2.273(2)	O1–Co1–O4	70.9(6)	Cl1–Co2–Cl2	108.4(1)
Co2–Cl1′	2.263(2)	O1–Co1–O7	143.1(6)	Cl2–Co2–Cl1′	108.4(1)
		O4–Co1–O7	73.0(6)	Cl3–Co2–Cl1′	109.1(1)

TABLE 2. The conformation of 15-crown-5 in complex I

Atoms 1–2–3–3	Torsion angle, 2–3 (°)	Atoms 1–2–3–4	Torsion angle, 2–3 (°)
O1–C2–C3–O4	−45.5	O4–C5–C6–O7	52.9
C2*–O1–C2–C3	−154.6	C5–C6–O7–C8	−177.5
C2–C3–O4–C5	−179.9	C6–O7–C8–C8*	178.7
C3–O4–C5–C6	−172.4	O7–C8–C8*–O7*	−54.8

TABLE 3. Parameters of hydrogen bonds in complexes I and II

Complex	D–H...A	Transformation of atom A	D–H (Å)	H...A (Å)	D...A (Å)	DHA (°)
I	OW1–H2...Cl2	x, $0.5-y$, $-z$	0.80	2.47	3.26	173
	OW1–H1...OW2	x, y, z		2.07	2.68	174
	OW2–H4...Cl3	$1-x$, $1-y$, $1-z$	1.16	2.05	3.20	174
II	OW2–HW2...Cl	x, y, z	0.82	2.43	3.24	169
	OW2–HW3...Cl	$0.5-x$, $1-y$, $0.5-z$	0.77	2.47	3.23	172

TABLE 4. Main bond lengths and bond angles in the complex $[Co\cdot 15\text{-}C\text{-}5\cdot(H_2O)_2]Cl_2\cdot H_2O$

Bond	Distance (Å)	Bond	Angle (°)	Bond	Angle (°)
		OW–Co–OW′	174.3(2)		
Co–OW1	2.079(4)	OW1–Co–O7	86.6(2)	O7a–Co–O7b	75.4(3)
Co–O7	2.122(6)	OW1–Co–O4	85.1(2)	O7b–Co–O4c	74.1(3)
Co–O4	2.235(6)	OW1–Co–O1	90.0(2)	O1–Co–O4	68.8(3)
Co–O1	2.243(6)	OW1–Co–O7a	93.4(2)	O4–Co–O7a	74.1(3)
		OW1–Co–O4a	94.9(2)	O4c–Co–O1	68.8(3)

TABLE 5. Atom coordinates ($\times 10^4$) and temperature factors ($A^2 \times 10^3$) in complex **I**

Atom	*x*	*y*	*z*	*U*[a]
Co(1)	1440(1)	2500	5000	78(3)
Co(2)	7316(1)	1823(1)	7500	56(1)
Cl(1)	6406(2)	1137(1)	6397(1)	71(1)
Cl(2)	9588(2)	1509(2)	7500	56(1)
Cl(3)	6872(3)	3465(2)	7500	80(1)
OW(1)	1335(4)	3594(3)	4139(2)	55(1)
OW(2)	3428(7)	4717(7)	3696(7)	120(4)
O(1)	3620(5)	2500	5000	78(3)
C(2)	4335(7)	1839(5)	4519(5)	74(3)
C(3)	3483(8)	1576(5)	3856(5)	83(3)
O(4)	2169(4)	1365(3)	4159(3)	59(1)
C(5)	1212(10)	1093(5)	3589(5)	87(3)
C(6)	−102(8)	1033(5)	3970(5)	85(3)
O(7)	−309(4)	1943(3)	4368(3)	60(2)
C(8)	−1541(7)	2002(7)	4808(7)	94(4)

[a]Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*(*i*, *j*) tensor.

TABLE 6. Atom coordinates ($\times 10^4$) and temperature factors ($A^2 \times 10^3$) in complex **II**

Atom	*x*	*y*	*z*	*U*[a]
Co	1250	1250	1250	31(1)
Cl	1250	6250	2614(1)	54(1)
OW(1)	1250	1250	383(2)	52(1)
OW(2)	733(4)	4469(3)	2289(2)	52(1)
C(2)	−1744(6)	1802(4)	1314(3)	92(3)
O(7)	−456(6)	1990(3)	1198(3)	44(2)
O(4)	428(7)	2440(4)	1171(3)	45(2)
C(5)	1250	3017(4)	1250	80(3)
C(6)	2732(19)	2737(10)	1085(8)	62(6)
C(3)	−835(15)	2550(13)	1457(9)	57(6)
O(1)	−1209(9)	1250	1250	59(3)

[a]Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*(*i*, *j*) tensor.

formed only between the molecules of water of crystallization and Cl^- anions (Table 3).

In conclusion, a coexistence in the reaction mixture of two types of compounds with single (**II**) and complex (**I**) anions is an additional support for the proposal put forward earlier on the mechanism of formation of inclusion salts [9], the main steps of which are ionization and dissociation of a salt, insertion into the macrocycle cavity and autocomplex formation.

Experimental

Crystals of non-hydrated complexes $[Co\cdot 15C5\cdot(CH_3CN)_2][CoCl_4]$ and $[Co\cdot 15C5\cdot(CH_3CN)_2]$-$[Co_2Cl_6]$ spread on a watch glass were placed in a desiccator containing water at the bottom. After the formation of a pink homogeneous liquid (10–12 h) the watch glass was removed and placed on a microscope table, where the crystallization was visually followed with subsequent classification and selection of crystals.

An X-ray structural study of crystals **I** ($C_{10}H_{26}O_8Cl_4Co_2$, MW = 534) and **II** ($C_{10}H_{26}O_8Cl_2Co$, MW = 404), sealed in glass capillaries was performed on an automatic Nicolet P3/R3 diffractometer (λ Mo Kα radiation, Nb-filter, $\theta/2\theta$-scanning up to $2\theta = 50°$).

Crystals of complex **I** ($0.2\times0.2\times0.2$ mm) are orthorhombic with unit cell parameters $a = 9.993(2)$, $b = 13.579(2)$, $c = 16.813(3)$ Å, $V = 2267.7(6)$ Å^3, space group *Pbcm*, $Z = 4(m;2;1)$, $\rho_{calc} = 1.56$ g cm^{-3}.

Crystals of complex **II** ($0.2\times0.2\times0.15$ mm) are also orthorhombic: $a = 9.844(2)$, $b = 17.445(4)$, $c = 23.989(5)$ Å, $V = 4119(1)$ Å^3, space group *Fddd*, $Z = 8(222;2;1)$, $\rho_{calc} = 1.37$ g cm^{-3}.

1098 and 558 independent reflections with $I > 3\sigma(I)$ were used in the case of complexes **I** and **II**, respectively. The structures were solved by the heavy atom method using the SHELXTL program. Calculations were made on a Nova-3 computer. No corrections on absorption were made ($\mu_I = 20.1$ and $\mu_{II} = 11.6$ cm^{-1}). The models were refined by a full matrix least-squares routine in the anisotropic (for all non-hydrogen atoms) approximation. Hydrogen atoms were evaluated from the difference synthesis of electronic density and refined isotropically. The atomic coordinates of hydrogen atoms of the macrocycle in complex **I** were calculated using the geometrical considerations. Site occupancies for disordered crown-ether atoms in structure **II** were refined. The final values of the R and R_w factors are equal to 0.036 and 0.041 for I and 0.031 and 0.035 for **II**, respectively. The coordinates of non-hydrogen atoms and H atoms of the water molecules, as well as isotropic equivalent temperature factors are given in Tables 5 and 6.

References

1 F. Dejehet, R. Debust and J.-P. Declercq, *J. Chim. Phys. Phys.-Chim. Biol., 83* (1986) 85.

2 V. K. Belsky, N. R. Streltsova, B. M. Bulychev, P. A. Storozhenko, L. V. Ivakina and A. I. Gorbunov, *Inorg. Chim. Acta, 164* (1989) 211.

3 N. R. Streltsova, B. M. Bulychev, V. K. Belsky and O. K. Kireeva, *Zh. Obsch. Khim., 61* (1991) 795.

4 N. R. Streltsova, V. K. Belsky, B. M. Bulychev and O. K. Kireeva, *Zh. Neorg. Khim.*, in press.

5 J. Feneau-Dupont, E. Arte, J. P. Declercq, G. Germain and M. Van Meerssche, *Acta Crystallogr., Sect. B, 35* (1979) 1217.

6 F. Dejehet, R. Debuyst, Y. Y. Wei, J.-P. Declercq and B. Tinant, *J. Chim.-Phys. Phys.-Chim. Biol., 84* (1987) 975.

7 E. M. Hold, N. W. Alcock, R. R. Hendrixon, G. D. Malpass, R. G. Ghirardelly and R. A. Palmer, *Acta Crystallogr., Sect. B, 37* (1981) 1080.

8 N. R. Streltsova, V. K. Belsky, B. M. Bulychev and O. K. Kireeva, *III Int. Symp. Inclusion Phenomena, Novosibirsk, USSR, 1989,* p. 55.

9 N. R. Streltsova, V. K. Belsky, L. V. Ivakina, P. A. Storozhenko and B. M. Bulychev, *Koord. Khim., 13* (1987) 1101.