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Synthesis and Crystal Structure of (Dibenzo-18-crown-6)(iodo)(trichlorometane)potassium

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Abstract—A new complex compound (dibenzo-18-crown-6)(iodo)(trichlorometane)potassium was obtained. Its crystal structure was studied by X-ray structural analysis. The complex molecule is built by the "guest–host" type: its K^+ cation is in the crown ligand hollow and is coordinated via its all six O atoms, and also via the iodine ligand I and one Cl atom of the ligand $CHCl_3$ molecule. The coordination polyhedron of this K^+ cation is a slightly distorted hexagonal bipyramid. In the crystal structure the complex molecules are connected in infinite chains by intercomplex hydrogen bonds $Cl_3C–H\cdots I^i$ between the ligand molecule $CHCl_3$ and the iodine ligand of a neighboring complex molecule.

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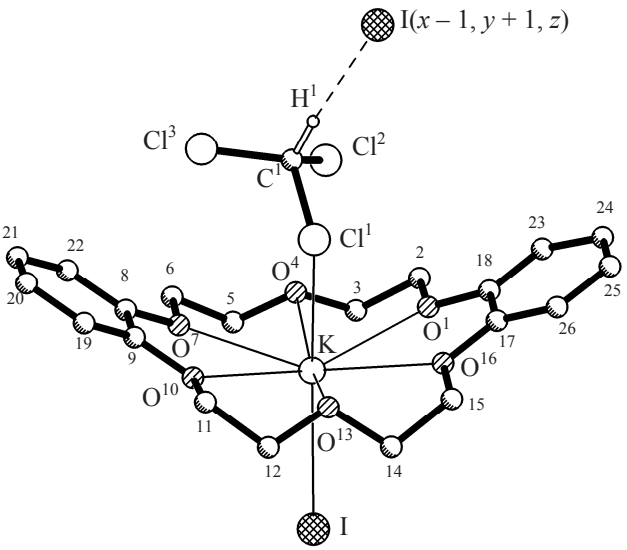
In the present paper the preparation of crystals of the new complex compound (dibenzo-18-crown-6)(iodo)(trichlorometane)potassium (**I**) and the results of its X-ray crystal analysis are described. Similar "guest–host" complexes [1] of the crown ether dibenzo-18-crown-6 with alkali metals halides, which have a chloroform (trichloromethane) molecule as an additional ligand, were not obtained up to the present, and their structure was not studied.

The crystal structure of compound **I** contains one symmetrically independent individual complex molecule. Its structure is shown in the figure, and main bond lengths and valence and torsion angles are given in Tables 1–3.

The ligand molecule $CHCl_3$ in the complex molecule of compound **I** is reorientation disordered, i.e. it has four various orientations, the main orientation and three improbable orientations, which result from the rotations of the molecule $CHCl_3$ at various angles approximately around its $C^1–H^1$ bond. Therefore all atoms of the molecule $CHCl_3$ occupy four different positions in a crystal with the following populations: 0.75 (1), 0.113 (9), 0.069 (4), and 0.068 (6).

When considering the geometric structure of complex molecule **I** we shall take into account only the main orientation of the ligand $CHCl_3$ molecule having a 75% probability and the main positions of its atoms. The main orientation of the disordered $CHCl_3$ molecule in complex **I** can be characterized by the following torsion angles: $KCl^1C^1H^1$ 153(1) and $O^4KCl^1C^1$ 8.4(4).



Molecular structure of complex **I** (dibenzo-18-crown-6)-(iodo)(trichlorometane)potassium in a crystal. For clarity sake lthe ow-populated positions of atoms of the disordered ligand molecule $CHCl_3$ and of atoms H of the crown ligand are not shown. The intercomplex hydrogen bond $C^1–H^1\cdots I$ (x – 1, y + 1, z) with a symmetrically multiplied iodide ligand is shown by a dashed line.

Table 1. Main bond lengths (d, Å) in structure **I**[a]

Bond	d	Bond	d
K–I	3.530(1)	C^3–O^4	1.417(3)
K–Cl^1	3.493(4)	O^4–C^5	1.422(3)
K–O^1	2.776(2)	C^5–C^6	1.483(4)
K–O^4	2.761(3)	C^6–O^7	1.435(3)
K–O^7	2.771(2)	O^7–C^8	1.372(3)
K–O^{10}	2.820(2)	C^8–C^9	1.398(4)
K–O^{13}	2.776(3)	C^9–O^{10}	1.369(3)
K–O^{16}	2.761(2)	O^{10}–C^{11}	1.433(3)
Cl^1–C^1	1.765(7)	C^{11}–C^{12}	1.481(4)
Cl^2–C^1	1.731(7)	C^{12}–O^{13}	1.414(3)
Cl^3–C^1	1.731(8)	O^{13}–C^{14}	1.422(3)
–	–	C^{14}–C^{15}	1.484(4)
O^1–C^{18}	1.375(3)	C^{15}–O^{16}	1.430(3)
O^1–C^2	1.431(3)	O^{16}–C^{17}	1.371(3)
C^2–C^3	1.486(4)	C^{17}–C^{18}	1.393(4)

[a] Main positions of Cl^1, Cl^2, Cl^3, and C^1 of the disordered ligand $CHCl_3$ molecule given in Table 1 have a population 0.75(1).

The cation K^+ of the complex molecule of compound **I** is in a cavity of the crown ligand, being coordinated by its all six O atoms, by iodide ligand I, and also by the Cl^1 atom of the ligand molecule $CHCl_3$. A coordination polyhedron of this cation K^+ (CN 8) is a slightly distorted hexagonal bipyramid with a foundation containing six O atoms of the crown ligand and two opposite apexes at the iodide ligand I and at the Cl^1 atom.

The average length of six coordination K–O bonds is 2.777±0.014 Å, which is noticeably less than the sum of effective ionic radius of the K^+ cation (1.51 Å for CN 8) [2] and van der Waals radius of the oxygen atom 1.40–1.52 Å [3,4]. The length of the coordination K–I bond is also noticeably less than the sum of the above-mentioned K^+ ionic radius and the effective ionic radius of the I^- anion 2.20 Å [2], whereas the length of the K–Cl^1 coordination bond is greater by 0.18–0.23 Å than the sum of the above-mentioned K^+ ionic radius and van der Waals radius of the chlorine atom 1.75–1.80 Å [3, 4]. Thus, the coordination K–Cl^1 bond with the ligand $CHCl_3$ is rather weak.

The K^+ cation in the molecule of compound **I** deviates by 0.530(1) Å from the mean-square plane of six O atoms to the side of the iodide ligand I (to the side opposite to folding of two benzene rings of the crown ligand).

Table 2. Main valence angles (ω, deg) in structure **I**

Angle	ω	Angle	ω
$IKCl^1$	166.94(6)	KCl^1C^1	106.9(2)
IKO^1	98.78(6)	$Cl^1C^1Cl^2$	109.5(4)
IKO^4	91.84(6)	$Cl^1C^1Cl^3$	110.2(5)
IKO^7	98.30(6)	$Cl^2C^1Cl^3$	111.6(4)
IKO^{10}	105.75(6)	$C^{18}O^1C^2$	117.0(2)
IKO^{13}	106.21(6)	$O^1C^2C^3$	107.6(3)
IKO^{16}	104.90(6)	$C^2C^3O^4$	109.7(3)
Cl^1KO^1	88.1(1)	$C^3O^4C^5$	112.8(3)
Cl^1KO^4	101.21(8)	$O^4C^5C^6$	109.4(3)
Cl^1KO^7	87.8(1)	$C^5C^6O^7$	107.8(3)
Cl^1KO^{10}	68.4(1)	$C^6O^7C^8$	117.0(2)
Cl^1KO^{13}	60.74(8)	$O^7C^8C^9$	115.6(2)
Cl^1KO^{16}	69.8(1)	$C^8C^9O^{10}$	115.9(2)
O^1KO^{10}	155.34(8)	$C^9O^{10}C^{11}$	116.9(2)
O^4KO^{13}	161.95(8)	$O^{10}C^{11}C^{12}$	108.2(3)
O^7KO^{16}	156.73(8)	$C^{11}C^{12}O^{13}$	109.6(3)
O^1KO^{16}	55.74(6)	$C^{12}O^{13}C^{14}$	113.5(3)
O^1KO^4	60.33(6)	$O^{13}C^{14}C^{15}$	109.1(3)
O^4KO^7	61.21(7)	$C^{14}C^{15}O^{16}$	107.9(3)
O^7KO^{10}	55.14(7)	$C^{15}O^{16}C^{17}$	117.2(3)
$O^{10}KO^{13}$	60.50(6)	$O^{16}C^{17}C^{18}$	116.0(2)
$O^{13}KO^{16}$	60.09(6)	$O^1C^{18}C^{17}$	115.6(2)

Average lengths of covalent bonds of the crown ligand in the structure of compound **I** are as follows: 1.372(3) Å for the bonds O^1–C^{18}, O^7–C^8, C^9–O^{10}, and O^{16}–C^{17}; 1.432(3) Å for the bonds O^1–C^2, C^6–O^7, O^{10}–C^{11}, and C^{15}–O^{16}; 1.419(3) Å for the bonds C^3–O^4, O^4–C^5, C^{12}–O^{13}, and O^{13}–C^{14}; 1.484(4) Å for the bonds C^2–C^3, C^5–C^6, C^{11}–C^{12}, and C^{14}–C^{15}; 1.383(8) Å for the C–C bonds in its benzene ring. These average bond lengths are close to the average for bonds of this type

Table 3. Main torsion angles (τ, deg) in structure **I**

Angle	τ	Angle	τ
$C^{18}O^1C^2C^3$	172.0(3)	$C^9O^{10}C^{11}C^{12}$	176.7(3)
$O^1C^2C^3O^4$	63.2(4)	$O^{10}C^{11}C^{12}O^{13}$	66.5(4)
$C^2C^3O^4C^5$	–179.7(3)	$C^{11}C^{12}O^{13}C^{14}$	–178.8(3)
$C^3O^4C^5C^6$	–176.2(3)	$C^{12}O^{13}C^{14}C^{15}$	–173.2(3)
$O^4C^5C^6O^7$	–66.4(4)	$O^{13}C^{14}C^{15}O^{16}$	–62.8(4)
$C^5C^6O^7C^8$	–177.6(3)	$C^{14}C^{15}O^{16}C^{17}$	–174.1(3)
$C^6O^7C^8C^9$	–178.9(3)	$C^{15}O^{16}C^{17}C^{18}$	175.5(3)
$O^7C^8C^9O^{10}$	–2.4(4)	$O^{16}C^{17}C^{18}O^1$	0.5(4)
$C^8C^9O^{10}C^{11}$	175.8(3)	$C^{17}C^{18}O^1C^2$	–178.9(3)

in dibenzo-18-crown-6 ligands. For the crown ligand in the structure of compound **I** valence angles COC at the atoms O^1, O^7, O^{10}, and O^{16} [average 117.0(2)] are close to 120°, and those at the atoms O^4 and O^{13} [average 113.1(3)] are close to the tetrahedral angle 109.5°.

The crown ligand in the structure of compound **I** has the usual butterfly conformation with of the C_{2v} approximate symmetry, where all its intracyclic torsion angles OCH_2CH_2O are close to ±65° (*gauche*-form), two torsion angle $O^7C^8C^9O^{10}$ and $O^{16}C^{17}C^{18}O^1$ are close to 0° (*cis*-form), and all other intracyclical torsion angles outside benzene ring are within the range of 180±8° (*trans*-form).

Its two benzene rings are planar within the limits of the deviations of ±0.007(3) and ±0.010(3) Å for six C atoms of the first and second rings (in the order of decreasing numeration of their atoms). The angle between mean square planes of these two benzene ring is 124.1(1)°. Mean square planes of these two benzene ring form, respectively, the angles of 31.5(1)° and 24.5(1)° with the mean square plane of six O atoms of this ligand.

In the crystal structure of compound **I** there are unusual intercomplex hydrogen bonds $Cl_3C–H\cdots I^i$ (between the disordered ligand molecule $CHCl_3$ and the iodide ligand I), symmetrical conversion being (*i*) $x - 1, y + 1, z$. For such one independent H-bond with a probability of 75%, which is an H-bond according to the known criteria [5], the corresponding interatomic distances and angles are as follows: $C^1–H^1$ 0.98, $H^1\cdots I^i$ 2.92, $C^1\cdots I^i$ 3.889(6) Å; $\angle(C^1H^1\cdots I^i)$ 168°. In crystal **I** complex molecules **I** are connected by these intercomplex H-bonds into infinite chains along the line passing through two points with the crystallographic coordinates (0, 0, 0) and (–1, 1, 0).

Apart from the above-mentioned intercomplex H-bonds, all other short intermolecular contacts in the crystal structure of compound **I** are close to or slightly less than the sums of corresponding van der Waals radii of atoms.

EXPERIMENTAL

Complex I. A powder of dibenzo-18-crown-6 and crystalline potassium iodide KI in a molar ratio 1:1 were dissolved in aqueous tetrahydrofuran. The solution was evaporated up the formation of a precipitate, which was dissolved in chloroform, and the solution was left at room temperature for evaporating the solvent. Several days later colorless transparent crystals of complex **I** precipitated at the vessel bottom.

Unit-cell parameters of the crystal and the three-dimensional set of reflection intensities for the X-ray structural analysis were obtained on an Enraf–Nonius CAD-4 X-ray autodiffractometer (MoK_α radiation, a graphitic monochromator). The crystals of compound **I** are triclinic: $[KI(C_{20}H_{24}O_6)(CHCl_3)]$, M 645.76; a 9.285(2), b 9.430(2), c 16.392(3) Å, α 73.88(2), β 86.97(2), γ 74.44(2), V 1327.9(5) Å^3, Z 2, d_{calc} 1.615 g cm^{-3}, μ(MoK_α) 16.97 cm^{-1}, space group $P\overline{1}$.

Intensities of 4985 reflections were measured in the inverse space hemisphere ($2\theta \le 50^o$) by the method of ω/2θ scanning from a single crystal of the 0.21× 0.40 × 0.61 mm size. The intensities of reflections were corrected for the absorption by the semiempirical method [6]. After averaging the intensities of 312 pairs of equivalent reflections $h0l$ and $\overline{h}0\overline{l}$ (R_{int} 0.026) the working array of measured $F^2(hkl)$ and $\sigma(F^2)$ consisted of 4673 independent reflections.

The structure of complex **I** was deciphered by a direct method using the program SHELXS-97 [7] and was refined by the full-matrix least squares method F^2 using the program SHELXL-97 [7] in the approximation of anisotropic thermal vibrations for non-hydrogen atoms, except for low-populated positions of disordered non-hydrogen atoms of the ligand molecule $CHCl_3$ with parameters refined in the isotropic approximation. In the refining we used almost all reflections of the working array [including very weak reflections with $I < 2\sigma(I)$], except for several reflections with measured and calculated F^2 values, which poorly agree with each other.

When refining the structure of complex **I** we have found that the ligand molecule $CHCl_3$ in it is reorientation disordered over four various orientations, and all its atoms occupy four various positions in a unit cell: the main position and three low-populated positions (see above). The total populations of the corresponding disordered positions (alongside with their coordinates and heat parameters) were then refined by the least squares method, entering four additional variable parameters [7].

Positions of all H atoms in complex **I** were objectively localized in a Fourier synthesis of electron density differences in the intermediate stage of the anisotropic refining. Further all H atoms of the crown

ligand and disordered $CHCl_3$ molecule were set geometrically, and their coordinates and isotropic heat parameters were calculated by the horseman model [7] within the procedure of refining structure of compound **I** by the least squares method.

This method was used also to refine isotropic extinction coefficient for the exposed crystal of compound **I**: *g* 0.0032(7) [7]. In the last cycle of the full-matrix refining the absolute shifts of all 339 varied parameters of structure **I** were less than 0.001σ.

Final R-factors are as follows: $R1$ = 0.034 and $wR2$ = 0.086 by 3950 observable reflections with $I \geq 2\sigma(I)$; $R1$ = 0.045 and $wR2$ = 0.125 by all 4673 measured independent reflections; the quality factor of "fitting" S 1.06 (definition of the wR_2 and S values is given in the manual [7]). In the final Fourier synthesis of the difference electron density: $-0.50 < \Delta\rho < 0.45$ e Å^{-3}.

The final coordinates and heat parameters of atoms in complex **I** and also complete tables of bond lengths, valence and torsion angles, etc. in the form of a cif-file are filed in the Cambridge bank of structural data [8] (deposit number 696171).

REFERENCES

1. *Host–Guest Complex Chemistry of Macrocycles. Synthesis, Structure, Applications*, Vogtle, F. and Weber, E., Eds., Berlin: Springer, 1982.
2. Shannon, R.D., *Acta Cryst. (A.),* 1976, vol. 32, no. 5, p. 751.
3. Pauling, L., *Nature of the Chemical Bond*, New York: Cornell Univ. Press, 1960.
4. Bondi, A., *J. Phys. Chem*., 1964, vol. 68, no. 3, p. 441.
5. Taylor, R. and Kennard, O., *J. Am. Chem. Soc*., 1982, vol. 104, no. 19, p. 5063.
6. North, A.C.T., Phillips, D.C., and Mathews, F.S., *Acta Cryst. (A.),* 1968, vol. 24, no. 3, p. 351.
7. Sheldrick, G.M., *The SHELX-97 Manual*, Göttingen (Germany): Univ. of Göttingen, 1997.
8. Allen, F.H., *Acta Cryst. (B.),* 2002, vol. 58, no. 3/1, p. 380.