ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 6, pp. 464–467. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.N. Chekhlov, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 6, pp. 472–475.

(Dibenzo-18-Crown-6)potassium Tetrachloroferrate(III): Synthesis and Crystal Structure

A. N. Chekhlov
Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia
E-mail: anche@icp.ac.ru

Received February 21, 2008

Abstract—A new complex $[K(Db18C6)]^+[FeCl_4]^-$ (I) is synthesized and its structure is studied by X-ray diffraction analysis. The crystals are triclinic: space group $P\bar{1}$, $a = 17.998$, $b = 18.670$, $c = 19.590$ Å, $\alpha = 106.61°$, $\beta = 104.55°$, $\gamma = 113.87°$, $Z = 8$. The structure is solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation to $R = 0.057$ by 13 670 independent reflections (CAD-4 automated diffractometer, λMoK_α). All the four independent complex cations $[K(Db18C6)]^+$ are host–guest, and in each complex cation the K^+ cation is localized in the cavity of the Db18C6 crown ligand. The coordination polyhedron of K^+ (coordination number nine) is a distorted hexagonal bipyramid with the base of all six O atoms of the Db18C6 ligand, the axial vertex at the Cl atom of the $[FeCl_4]^-$ anion, and another bifurcated axial vertex at two Cl atoms of another $[FeCL_4]^-$ anion. All the four independent $[FeCL_4]^-$ anions are orientationally disordered and have somewhat distorted tetrahedral structure. In crystal **I**, the alternating complex cations $[K(Db18C6)]^+$ and $[FeCL_4]^-$ anions form infinite polymer chains by the K–Cl bonds.

DOI: 10.1134/S107032840906013X

INTRODUCTION

In this work, we describe the synthesis and X-ray diffraction results for the new crystalline complex: (dibenzo-18-crown-6)potassium tetrachloroferrate(III), $[K(Db18C6)]^+[FeCl_4]^-$ (**I**). Analogous complexes, whose crystals contain infinite polymer chains of alternating host–guest complex cations [1] and $[FeCl_4]^-$ anions, were not obtained up to now. Note that similar polymer chains are absent from the earlier studied crystal structure of the complex with the resembling composition $[Na(Db18C6)]^+[FeCl_4]^-$ [2].

EXPERIMENTAL

Synthesis The powder of dibenzo-18-crown-6 crown ether and crystalline KCl and $FeCl_3 \cdot xH_2O$ taken in a mole ratio of 1 : 1 : 1 were dissolved in 80% aqueous tetrahydrofuran. The mixture was heated and left to evaporate at room temperature. After several days, dark red (almost black) single crystals of complex **I** precipitated on the bottom of the vessel.

X-Ray diffraction analysis. The unit cell parameters of the crystal and the three-dimensional set of reflection intensities were obtained on an Enraf-Nonius CAD-4 X-ray automated diffractometer (MoK_α radiation, graphite monochromator). The crystals of compound **I** are triclinic: $[K(C_{20}H_{24}O_6)]^+[FeCl_4]^-$, $FW = 597.14$; $a = 17.998(5)$ Å, $b = 18.670(5)$ Å, $c = 19.590(5)$ Å, $\alpha = 106.61(3)°$, $\beta = 104.55(2)°$, $\gamma = 113.87(3)°$, $V = 5239(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.514$ g/cm^3, $\mu(MoK_\alpha) = 11.75$ cm^{-1}, space group $P\bar{1}$.

Intensities of 14 180 reflections were measured in a hemisphere of the reciprocal space ($2\theta \le 45°$) in the $\omega/2\theta$ scan mode from a single crystal $0.14 \times 0.40 \times 1.20$ mm in size. An absorption correction was applied to the reflection intensities by the semiempirical method [3]. After the intensities of 510 pairs of equivalent reflections $h0l$ and $\bar{h}0\bar{l}$ ($R_{int} = 0.020$) were averaged, the working set of measured $F^2(hkl)$ and $\sigma(F^2)$ values contained 13 670 independent reflections.

The structure of compound **I** was solved by a direct method using the SHELXS-97 program package [4] and refined by the full-matrix least-squares method for F^2 (SHELXL-97) [4] in the anisotropic approximation for nearly all non-hydrogen atoms. Almost all reflections from the working set, including very weak reflections with $I < 2\sigma(I)$, except for several reflections with poorly consistent measured and calculated F^2 values, were used in the refinement.

The noticeable peaks $\Delta\rho$ were revealed by the anisotropic refinement of structure **I** in the difference Fourier synthesis. They unambiguously indicate that all the Cl atoms of the four independent $[FeCl_4]^-$ anions are disordered over two positions each: over the main position (with a site occupancy of ~0.9) and the poorly occupied position (~0.1). Then the total site occupancies of these disordered positions along with other

Selected bond lengths and bond angles in structure **I***

Bond	*d*(a), Å	*d*(b,) Å	*d*(c), Å	*d*(d), Å	Bond	*d*, Å	Angle	φ, deg
Fe–Cl(1)	2.171(2)	2.169(1)	2.176(2)	2.172(2)	K(a)–Cl(1a)	3.379(3)	Fe(a)Cl(1a)K(a)	152.5(2)
Fe–Cl(2)	2.164(2)	2.156(1)	2.191(2)	2.173(2)	K(a)–Cl(1b)	3.358(2)	Fe(a)Cl(2a)K(b)^{ii}	148.1(1)
Fe–Cl(3)	2.148(2)	2.192(2)	2.168(2)	2.184(2)	K(a)–Cl(2b)	3.599(3)	Fe(b)Cl(1b)K(a)	96.84(5)
Fe–Cl(4)	2.178(2)	2.175(1)	2.176(2)	2.191(2)	K(b)–Cl(2a)^{i}	3.312(2)	Fe(b)Cl(2b)K(a)	90.41(7)
K–O(1)	2.750(3)	2.765(3)	2.776(3)	2.750(3)	K(b)–Cl(3b)	3.355(2)	Fe(b)Cl(3b)K(b)	90.52(6)
K–O(4)	2.761(3)	2.753(2)	2.777(2)	2.775(2)	K(b)–Cl(4b)	3.370(2)	Fe(b)Cl(4b)K(b)	90.42(6)
K–O(7)	2.783(2)	2.722(3)	2.739(2)	2.752(3)	K(c)–Cl(1c)	3.597(5)	Fe(c)Cl(1c)K(c)	82.6(1)
K–O(10)	2.785(2)	2.780(3)	2.743(3)	2.762(3)	K(c)–Cl(2c)	3.605(3)	Fe(c)Cl(2c)K(c)	82.19(8)
K–O(13)	2.721(3)	2.773(3)	2.747(3)	2.743(2)	K(c)–Cl(1d)	3.488(2)	Fe(c)Cl(3c)K(d)^{ii}	143.6(1)
K–O(16)	2.762(2)	2.722(3)	2.773(2)	2.735(2)	K(d)–Cl(3c)^{i}	3.466(2)	Fe(d)Cl(1d)K(c)	149.94(9)
					K(d)–Cl(2d)	3.389(3)	Fe(d)Cl(2d)K(d)	89.84(8)
					K(d)–Cl(3d)	3.547(4)	Fe(d)Cl(3d)K(d)	85.62(9)

* In the upper half of the table, letters a, b, c, and d at the chemical symbols and numbers of atoms are omitted for brevity and placed in titles of the columns. Superscripts *i* and *ii* mark the symmetrically transformed basis atoms: ^{i} *x* + 1, *y*, *z*; ^{ii} *x* – 1, y, *z*.

parameters were refined by the least-squares method, introducing four additional varied parameters [4]. The parameters of the poorly occupied Cl positions were refined in the isotropic approximation.

In structure **I**, the positions of all hydrogen atoms of the four independent Db18C6 crown ligands were specified geometrically: their coordinates and isotropic thermal parameters were calculated using the riding model [4] in the refinement procedure. In the last cycle of the refinement, the absolute shifts of all 1222 variable parameters of structure **I** were less than 0.002σ.

The final refinement parameters are $R = 0.036$ and $wR^2 = 0.090$ for 9900 reflections with $I \geq 2\sigma(I)$; $R = 0.057$ and $wR^2 = 0.108$ for all independent reflections; the goodness-of-fit *S* is 1.05 (the definition for wR^2 and *S* is given in [4]). In the final difference Fourier synthesis, $-0.40 < \Delta\rho < 0.39$ *e* Å^{-3}.

The final coordinates and thermal parameters of atoms in structure **I** and the tables of bond lengths, bond angles, and torsion angles were deposited with the Cambridge Structural Database as the cif file (no. 677 681).

RESULTS AND DISCUSSION

Crystal structure **I** contains four symmetrically independent and structurally similar complex cations $[K(Db18C6)]^+$ (with the K(a), K(b), K(c), and K(d) atoms) and four $[FeCl_4]^-$ anions (Fe(a), Fe(b), Fe(c), and Fe(d) atoms). The structure and ion packing in crystal structure **I** are shown in the figure. Selected bond lengths and bond angles are listed in the table.

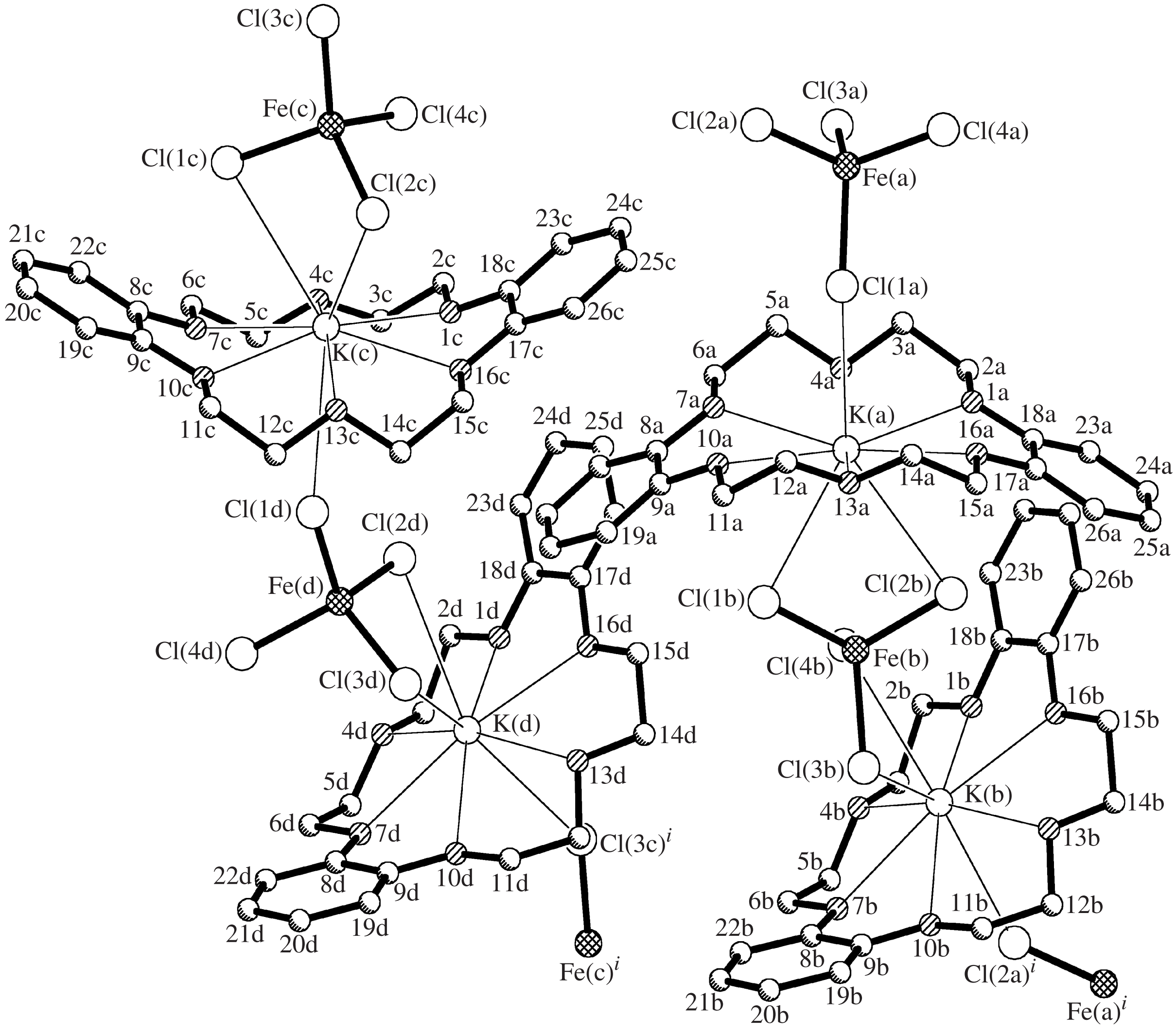
In structure **I**, all the four independent $[FeCl_4]^-$ anions (a, b, c, and d) are disordered. Each of them has two orientations with the corresponding two sets of positions of the chlorine atoms (the main and poorly occupied positions): Cl(1a)–Cl(4a) with a site occupancy of 0.884(5) and Cl(1a)'–Cl(4a)' with 0.116(5), Cl(1b)–Cl(4b) with an occupancy of 0.906(3) and Cl(1b)'–Cl(4b') with 0.094(3), Cl(1c)–Cl(4c) with 0.879(8) and Cl(1c')–Cl(4c') with 0.121(8), and Cl(1d)–Cl(4d) with 0.918(9) and Cl(1d)'–Cl(4d)' with an occupancy of 0.082(9).

All the four independent $[FeCl_4]^-$ anions in structure **I** have somewhat distorted tetrahedral structure in each of two orientations. The terminal Cl atoms accomplish appreciably higher thermal vibrations than the central Fe atoms. When further discussing the geometry of structure **I**, we will consider only the main positions of the disordered Cl atoms in the four independent $[FeCl_4]^-$ anions.

In structure **I**, the average Fe–Cl bond length (2.174 ± 0.009 Å) is noticeably less than the sum of the effective ion radii of the Fe^{3+} cation (0.49 Å for coordination number four) and Cl^- anion (1.81 Å) [5] and less than the sum of the covalent radii of the Fe and Cl atoms [6].

For each of the four independent complex cations $[K(Db18C6)]^+$ (a, b, c, and d) in structure **I**, the K^+ cation is localized in the cavity of the corresponding Db18C6 ligand and is coordinated by all six O atoms and by three Cl atoms of two $[FeCl_4]^-$ anions. The coordination polyhedra of each K(a)–K(d) atom (coordination number nine) are distorted hexagonal bipyramids with the base of all the six O atoms of the corresponding Db18C6 ligand, the axial vertex of the Cl atom of the $[FeCl_4]^-$ anion, and the second (bifurcate) axial vertex at two Cl atoms of another adjacent $[FeCl_4]^-$ anion.

The average K–O bond length in structure I (2.756 ± 0.016 Å) is noticeably less than the sum of the effective ion radii of the K+ cation (1.55 Å for coordination number nine) [5] and the van der Waals radius of the oxygen atom (1.40–1.52 Å [7, 8]).



Fragment of the crystal structure of complex **I**. The hydrogen atoms at the Db18C6 ligands and poorly occupied positions of the disordered Cl atoms are omitted for clarity.

In structure **I**, the average length of the interionic K–Cl bonds (3.455 ± 0.095 Å) is by ~0.1 Å more than the sum of the above indicated effective ion radii of the K$^+$ cation and Cl$^-$ anion (3.36 Å). The K–Cl bonds in structure **I** exhibit a large scatter over length (3.312(2)–3.605(3) Å) for steric reasons.

Twelve Cl atoms (of sixteen Cl atoms) in the four independent [FeCl$_4$]$^-$ anions are bridging and participate in the K–Cl bonds. The FeClK bond angles (table) for four Cl atoms are close to 150°, for four other atoms they are slightly larger than 90°C, and for the last four atoms they are slightly smaller than 90°C.

For structure **I** in four [K(Db18C6)]$^+$ complex cations, the K(a)–K(d) atoms exhibit the following deviations from the root-mean-square plane of six O atoms of the corresponding Db18C6 ligand: 0.384(1) (a), 0.361(1) (b), 0.454(1) (c), and 0.391(1) (d) Å. All the K$^+$ cations deviate toward the bend of two benzene rings of the corresponding Db18C6 ligand.

Four independent Db18C6 crown ligands (a, b, c, and d) in structure **I** have the following covalent bond lengths: 1.372(3) Å for O(1)–C(18), O(7)–C(8), C(9)–O(10), and O(16)–C(17); 1.428(3) Å for O(1)–C(2), C(6)–O(7), O(10)–C(11), and C(15)–O(16); 1.420(3) Å for C(3)–O(4), O(4)–C(5), C(12)–O(13), and O(13)–C(14); 1.489(4) Å for C(2)–C(3), C(5)–C(6), C(11)–C(12), and C(14)–C(15); 1.381(4) Å for $\mathrm{C}\overset{...}{-}\mathrm{C}$ at the benzene rings. These average values are close to the average statistical one for bonds of this type [9].

All the four independent Db18C6 crown ligands in structure I have a distorted butterfly conformation with the roughly approximate symmetry C_{2v}. In each of the four crown ligands, two benzene rings are bent to one side of the averaged plane of the central eighteen-membered macroheterocycle. The four Db18C6 ligands have such a conformation that all O–CH_2–CH_2–O torsion angles are close to ±65° (*gauche* type) and two O(7)–C(8)–C(9)–O(10) and O(16)–C(17)–C(18)–O(1) torsion angles are close to 0° (*cis* type). All other intracyclic torsion angles outside the benzene rings lie in a range of 180° ± 9° (*trans* type).

The dihedral angle between the root-mean-square planes of two benzene rings of each of the four Db18C6 ligands (a, b, c, and d) is 123.5(1)°, 119.7(1)°, 124.4(1)°, and 121.4(1)°, respectively. Two benzene rings compose the following dihedral angles with the root-mean-square plane of six O atoms of this crown ligand: 29.7(1)° and 26.9(1)° (a), 31.7(1)° and 28.5(1)° (b), 26.9(1)° and 28.8(1)° (c), and 28.9(1)° and 29.8(1)° (d).

In crystal structure I, the alternating $[K(Db18C6)]^+$ complex cations and $[FeCl_4]^-$ anions are linked by the K–Cl bonds to form polymer chains infinite along the *x* axis. Structure **I** contains two such symmetrically independent chains of translationally multiplied complex cations (a and b) and anions (a and b) and also from the complex cations (c and d) and anions (c and d). The fragments of these two chains are seen in the figure. In the chain of complex ions a and b, two benzene rings of one Db18C6 ligand (a) and two benzene rings of another Db18C6 ligand (b) are bent to different sides (one to another). In the chain consisting of complex ions c and d, two benzene rings of one Db18C6 ligand (c) and two benzene rings of another Db18C6 ligand (d) are bent to the same side (one from another). In these chains, the angles between the root-mean-square planes of six O atoms of two pairs of the Db18C6 ligands (a, b) and (c, d) are 37.09(4)° and 35.17(4)°, respectively.

In crystal structure **I**, all short distances between the nearest atoms of the adjacent polymer chains are close to or slightly shorter than the sums of the van der Waals radii of the corresponding atoms.

REFERENCES

1. *Host–Guest Complex Chemistry. Macrocycles. Synthesis, Structures, Applications*, Vogtle, F. and Weber, E., Eds., Berlin: Springer, 1985.
2. Rogers, R.D. and Song, Y., *Chem. Crystallogr.*, 1995, vol. 25, no. 9, p. 579.
3. North, A.C.T., Philips, D.C., and Mathews, F.S., *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1968, vol. 24, no. 3, p. 351.
4. Sheldrick, G.M., *The SHEL-97. Manual*, Göttingen (Germany): Univ. of Göttingen, 1997.
5. Shannon, R.D., *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, vol. 32, no. 5, p. 751.
6. Batsanov, S.S., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 12, p. 3015.
7. Pauling, L., *The Nature of the Chemical Bond*, New York: Cornell Univ., 1960.
8. Bondi, A., *J. Phys. Chem.*, 1964, vol. 68, no. 3, p. 441.
9. Alleb, F.H., Kennard, O., and Watson, D.G., et al., *J. Chem. Soc., Perkin Trans.*, 1987, no. 12, p. 2.