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Synthesis and Crystal Structure of Bis(dibenzo-18-Crown-6)Cesium Tetrachloroferrate(III)

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Abstract—A new complex $[Cs(Db18C6)_2]^+[FeCl_4]^-$ was prepared and studied by X-ray diffraction (orthorhombic, space group $P2_12_12$, a = 22.934 Å, b = 24.024 Å, c = 16.665 Å, Z = 8; direct method, anisotropic full-matrix least-squares refinement, R = 0.087 for all 8800 independent reflections; CAD4 automated diffractometer, $\lambda Mo K_\alpha$). Two independent $[FeCl_4]^-$ anions have a slightly distorted tetrahedral structure. Two independent host–guest type complex cations $[Cs(Db18C6)_2]^+$ have a sandwich structure. The Cs^+ cation is located between two Db18C6 crown ligands below and above the centers of their 18-membered macrocycles and is coordinated by all 12 O atoms. The coordination polyhedron of Cs^+ (C.N. 12) is a distorted hexagonal antiprism rotated toward a hexagonal prism.

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The present paper describes the preparation and X-ray diffraction data for a new complex, bis(dibenzo-18-crown-6)cesium tetrachloroferrate(III), $[Cs(Db18C6)_2]^+[FeCl_4]^-$ (**I**). Note that host–guest cesium compounds with crown ethers [1] containing a sandwich typeCs^+ complex cation and a transition metal complex as the anion have been little studied [2].

EXPERIMENTAL

Synthesis. A dibenzo-18-crown-6-powder and crystalline CsCl and $FeCl_3 \cdot xH_2O$ were mixed in 2 : 1 : 1 molar ratio in 80% aqueous tetrahydrofuran. The mixture was heated and allowed to evaporate at room temperature. After several days, dark red needle crystals of **I** precipitated on the vessel bottom.

X-ray diffraction. The unit cell parameters and a three-dimensional set of reflection intensities were collected using a CAD4 Enraf-Nonius automated diffractometer (MoK_α radiation, graphite monochromator). The crystals are orthorhombic: $[Cs(C_{20}H_{24}O_6)_2]^+[FeCl_4]^-$ (M = 1051.34); a = 22.934(5) Å, b = 24.024(5) Å, c = 16.665(5) Å, V = 9182(4) Å^3, Z = 8, ρ(calcd) = 1.521 g/cm^3, $\mu(MoK_\alpha)$ = 13.99 cm^{-1}, space group $P2_12_12$.

The intensities of 8826 reflections were measured in the reciprocal space quadrant ($2\theta \le 50°$) in the $\omega/2\theta$ scan mode from a 0.17 × 0.36 × 1.00 mm single crystal. The absorption corrections were applied semiempirically [3]. After exclusion of 26 systematically extinguished reflections, the working array of measured $F^2(hkl)$ and $\sigma(F^2)$ comprised 8800 independent reflections.

The structure of **I** was solved by the direct method (SHELXS-97) [4] and refined by the full-matrix least-squares method relative to F^2 (SHELXL-97) [4] in the anisotropic approximation for all non-hydrogen atoms. The refinement involved almost all reflections from the working array (including very weak ones, with $I < 2\sigma(I)$), except for several reflections characterized by poor agreement between the measured and calculated F^2 values.

The positions of all H atoms of four independent Db18C6 crown ligands (a, b, c and d) were specified geometrically; their coordinates and isotropic thermal parameters were calculated by the riding model [4] during the refinement of structure **I**.

For the exposed enantiomorphic crystal, the absolute structure parameter χ = –0.02(2) was also refined [5]. In the last cycle of the refinement, the absolute shifts for all 1046 variable parameters for structure **I** were smaller than 0.001σ.

The final refinement factors were R = 0.041 and wR_2 = 0.097 over the 5535 reflections with $I \ge 2\sigma(I)$; R = 0.087 and wR_2 = 0.137 over all independent reflections; the adjustment quality factor S was 1.00 (the definitions for the wR_2 and S values were reported [4]). In the final Fourier difference synthesis, $-0.34 < \Delta\rho < 0.51$ e Å^{-3}. The f-curves used and the anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were taken from the literature [6].

The final coordinates and the thermal parameters of the atoms of structure **I**, the tables of bond lengths and bond and torsion angles are deposited with the Cambridge Crystallographic Data Centre (no. 677867).

RESULTS AND DISCUSSION

The crystal structure of **I** contains two symmetrically independent $[Cs(Db18C6)_2]^+$ complex cations and two symmetrically independent $[FeCl_4]^-$ anions. The figure

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

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Fe(1)–Cl(11)	2.161(3)	Cs(1)–O(1a)	3.512(5)	Cs(2)–O(1c)	3.452(5)
Fe(1)–Cl(12)	2.140(3)	Cs(1)–O(4a)	3.080(6)	Cs(2)–O(4c)	3.075(6)
Fe(1)–Cl(13)	2.165(3)	Cs(1)–O(7a)	3.368(5)	Cs(2)–O(7c)	3.424(5)
Fe(1)–Cl(14)	2.193(3)	Cs(1)–O(10a)	3.309(5)	Cs(2)–O(10c)	3.304(5)
		Cs(1)–O(13a)	3.321(7)	Cs(2)–O(13c)	3.280(6)
Fe(2)–Cl(21)	2.154(3)	Cs(1)–O(16a)	3.399(5)	Cs(2)–O(16c)	3.410(5)
Fe(2)–Cl(22)	2.165(3)	Cs(1)–O(1b)	3.248(6)	Cs(2)–O(1d)	3.278(6)
Fe(2)–Cl(23)	2.149(3)	Cs(1)–O(4b)	3.270(5)	Cs(2)–O(4d)	3.220(6)
Fe(2)–Cl(24)	2.191(3)	Cs(1)–O(7b)	3.350(6)	Cs(2)–O(7d)	3.229(6)
		Cs(1)–O(10b)	3.457(5)	Cs(2)–O(10d)	3.310(6)
		Cs(1)–O(13b)	3.402(5)	Cs(2)–O(13d)	3.412(5)
		Cs(1)–O(16b)	3.285(6)	Cs(2)–O(16d)	3.456(5)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
Cl(11)Fe(1)Cl(12)	109.3(2)	Cl(12)Fe(1)Cl(14)	109.2(1)	Cl(21)Fe(2)Cl(24)	110.9(1)
Cl(11)Fe(1)Cl(13)	109.0(2)	Cl(13)Fe(1)Cl(14)	109.4(1)	Cl(22)Fe(2)Cl(23)	108.7(2)
Cl(11)Fe(1)Cl(14)	110.8(1)	Cl(21)Fe(2)Cl(22)	108.6(2)	Cl(22)Fe(2)Cl(24)	109.6(1)
Cl(12)Fe(1)Cl(13)	109.2(2)	Cl(21)Fe(2)Cl(23)	109.9(2)	Cl(23)Fe(2)Cl(24)	109.2(1)

shows one of each species. Selected bond lengths and bond angles are given in the table.

The crystal structure of **I** has approximately *c*/2 translational pseudosymmetry: the coordinates of corresponding atoms are connected by rough relations: $x' \approx x$, $y' \approx y$, and $z' \approx z + 1/2$. These relations hold more accurately for heavy atoms, Cs(1) and Cs(2), and Fe(1) and Fe(2).

In **I**, two independent $[FeCl_4]^-$ anions have a slightly distorted tetrahedral structure. From the U_{eq} values for Cl atoms and Fe–Cl bond lengths, one can conclude that both anions execute enhanced torsion thermal vibrations around longer bonds, Fe(1)–Cl(14) and Fe(2)–Cl(24). The other Fe–Cl bonds in **I** are somewhat shortened due to the enhanced thermal vibrations of most terminal Cl atoms.

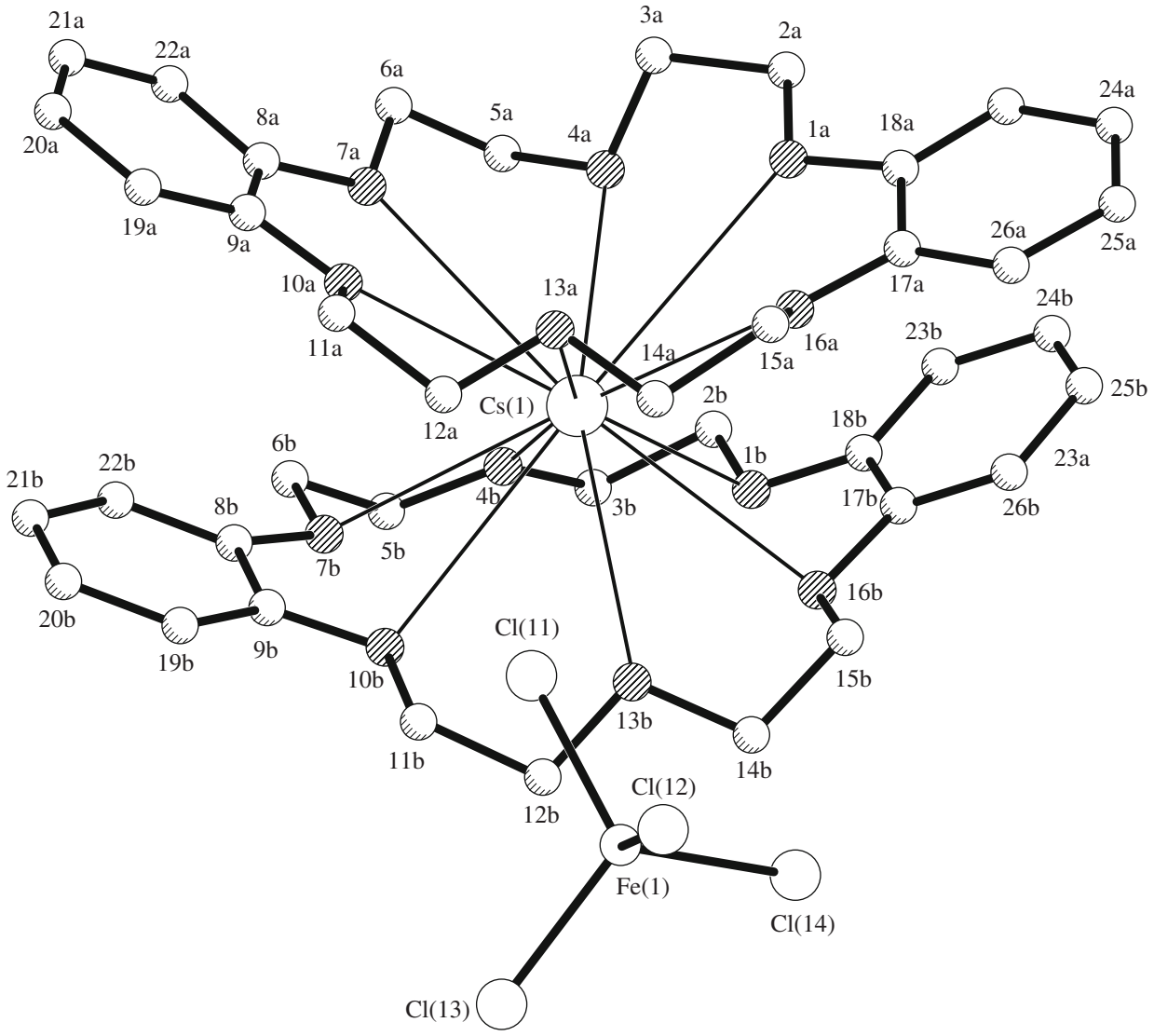
The average Fe–Cl bond length in **I** (2.165 ± 0.014 Å) is markedly smaller than the sum of the effective ionic radii of the Fe^{3+} cation (0.49 Å for C.N. 4) and the Cl^- anion (1.81 Å) [7] and also smaller than the sum of the covalent radii of the Fe and Cl atoms [8].

In the structure of **I** two independent sandwich complex cations, $[Cs(Db18C6)_2]^+$, the Cs(1) and Cs(2) atoms located between two Db18C6 ligands (a and b for Cs(1) and c and d for Cs(2)) below and above the centers of their 18-membered macrocycles are coordinated by all 12 O atoms of the Db18C6 ligands. The coordination polyhedra of the Cs(1) and Cs(2) cations (C.N. 12) is a distorted hexagonal antiprism somewhat "rotated" toward a hexagonal prism. The bases of each antiprism (at Cs(1) and Cs(2)) are formed by all six O atoms of the corresponding Db18C6 ligand. At the Cs^+(1) cation, one antiprism base is rotated with respect to the other one (with appropriate atom numbering) by ~22.5°, that at Cs^+(2), by ~25.5° (in the case of an ideal hexagonal antiprism, this angle is 30°).

The average Cs–O bond lengths (3.327 ± 0.087 Å) are close to the sum of the Cs^+ effective ionic radius (1.88 Å for C.N. 12) [7] and the van der Waals radius of oxygen (1.40–1.52 Å) [9, 10].

The Cs^+(1) cation deviates from the root-mean-square planes through six O atoms of its two Db18C6 ligands (a and b) by 1.940(3) Å and 1.910(3) Å, respectively. The Cs^+(2) cation deviates from the root-mean-square planes through six O atoms of its two Db18C6 ligands (c and d) by 1.929(2) Å and 1.895(3) Å, respectively. In the two complex cations of **I**, the angles between the root-mean-square planes through six O atoms of two Db18C6 ligands (a and b; c and d) are small (5.7(1)° and 5.4(1)°, respectively). In both complex cations, two benzene rings of each of the four Db18C6 crown ligands are turned in the same direction.

The average bond lengths of the four independent crown ligands (a, b, c, and d) in structure **I** are as follows: 1.370(5) Å for O(1)–C(18), O(7)–C(8), C(9)–O(10), and O(16)–C(17); 1.430(5) Å for O(1)–C(2), C(6)–O(7), O(10)–C(11), and C(15)–O(16); 1.418(5) Å for C(3)–O(4), O(4)–C(5), C(12)–O(13), and O(13)–C(14); 1.491(7) Å for C(2)–C(3), C(5)–C(6), C(11)–C(12), and C(14)–C(15); and 1.383(7) Å for the benzene C⋯C bonds. These



Fragment of the structure of complex **I** in the crystal. One sandwich type $[Cs(Db18C6)_2]^+$ cation and one $[FeCl_4]^-$ anion are shown. The H atoms of the Db18C6 ligands are omitted for clarity.

average distances are close to the statistical mean values for bonds of this type [11].

Two crown ligands (b and d) in **I** have similar butterfly type conformations with approximate C_{2v} symmetry. The other two crown ligands (a and c) have similar asymmetric conformations, one being the mirror image of the other with shifted atom numbering.

The conformations of the four Db18C6 ligands in **I** are such that all their O–CH_2–CH_2–O torsion angles are about ±60° (*gauche* type) and two torsion angles, O(7)–C(8)–C(9)–O(10) and O(16)–C(17)–C(18)–O(1), are about 0° (*cis* type). Most of the other intracyclic torsion angles outside the benzene rings are in the range of 180° ± 20° (*trans* type). Among the latter type, there are exceptions: two angles, C(3a)–O(4a)–C(5a)–C(6a) and C(2c)–C(3c)–O(4c)–C(5c), are of the *gauche* type and two angles, C(15a)–O(16a)–C(17a)–C(18a) and C(8c)–C(9c)–O(10c)–C(11c), are of partially eclipsed type.

The benzene rings of the crown ligands of **I** are planar (±0.005(6) to ±0.013(7) Å). The dihedral angle between the root-mean-square planes of two benzene rings of each of Db18C6 ligand (a, b, c, and d) are 138.0(3)°, 136.3(3)°, 136.6(3)°, and 135.4(3)°, respectively. Two benzene rings of each crown ligand form the following angles with the root-mean-square plane through the six O atoms of the given crown ligand: 31.0(2)° and 18.5(3)° (a), 15.5(2)° and 28.4(2)° (b), 19.2(3)° and 30.4(2)° (c), and 25.7(3)° and 19.4(2)° (d).

In the crystal structure of **I**, all short intermolecular (interionic) contacts are close to or somewhat smaller than the sums of the corresponding van der Waals radii of the atoms.

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