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Synthesis and Crystal Structure of Tris[(dibenzo-18-Crown-6-(Tetrahydrofuran)Potassium) Hexakis(isothiocyanato)ferrate(III) 0.3 Hydrate

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Abstract—A new complex $[K(Db18C6)(THF)]_3^+[Fe(NCS)_6]^{3-} \cdot$ 0.31 H_2O (**I**) was prepared and studied by X-ray diffraction (space group *C*2/*c*, $a = 21.954$, $b = 26.496$, $c = 15.902$ Å, $\beta = 102.24°$, $Z = 4$; direct method, least-squares refinement in the anisotropic approximation to $R = 0.098$ for 5944 independent reflections; CAD4 automated diffractometer, λMoK_α). The $[Fe(NCS)_6]^{3-}$ anion (on twofold axis) having a slightly distorted octahedral structure is connected by two K–S bonds with two complex cations connected by a twofold axis. Two independent complex cations $[K(Db18C6)(THF)]^+$ are of the host–guest type, one being statistically disordered with respect to the twofold axis with site populations of 0.5. The coordination polyhedra of K^+ are a distorted hexagonal bipyramid and pyramid.

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The present paper describes the preparation and X-ray diffraction data for the crystals of a new complex, tris[(dibenzo-18-crown-6-(tetrahydrofuran)potassium] hexakis(isothiocyanato)ferrate(III) 0.3 hydrate, $[K(Db18C6)(THF)]_3^+[Fe(NCS)_6]^{3-} \cdot 0.31\ H_2O$ (**I**). Previously, no such host–guest complexes [1] of crown ethers with metal cations containing $[Fe(NCS)_6]^{3-}$ were obtained.

EXPERIMENTAL

Synthesis. A dibenzo-18-crown-6-powder and crystalline KSCN and $Fe(NO_3)_3 \cdot xH_2O$ were mixed (in 3 : 6 : 1 molar ratio) and dissolved in a 80% tetrahydrofuran. The mixture was allowed to evaporate at room temperature. After several days, dark red (nearly black) crystals of **I** and colorless KNO_3 crystals 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 of **I** are monoclinic: $3[K(C_{20}H_{24}O_6)(C_4H_8O)]_3^+[Fe(NCS)_6]^{3-} \cdot 0.31H_2O$ ($M = 1824.79$); $a = 21.954(7)$, $b = 26.496(9)$, $c = 15.902(4)$ Å, $\beta = 102.24(3)°$, $V = 9040(5)$ Å^3, $Z = 4$, ρ(calcd)= 1.341 g/cm^3, $\mu(MoK_\alpha) = 5.13$ cm^{-1}, space group *C*2/*c*.

The intensities of 6360 reflections ($h + k = 2n$; $2\theta \le 45°$) were measured in the reciprocal space quadrant in the $\omega/2\theta$ scan mode from a 0.35 × 0.35 × 0.50 mm single crystal. The absorption corrections were applied semiempirically [2]. After exclusion of 156 systematically extinguished reflections and averaging of the intensities of 260 pairs of equivalent $hk0$ and $\bar{h}k0$ reflections ($R_{int} = 0.044$), the working array of measured $F^2(hkl)$ and $\sigma(F^2)$ comprised 5944 independent reflections.

The structure of **I** was solved by the direct method (SHELXS-97) [3] and refined by the full-matrix least-squares method relative to F^2 (SHELXL-97) [3] 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.

During the solution of structure **I** and in the early stage of the refinement, it was shown unambiguously that one of the two independent complex cations $[KDb18C6](THF)]^+$ (**B**) is statistically disordered relative to twofold axis and that each of its atoms occupies two overlapping sites with 0.5 population.

During the refinement of structure **I**, the difference electron density synthesis revealed a pronounced $\Delta\rho$ peaks on the twofold crystallographic axis, which was interpreted as O(*w*) atom of hydration water molecule. The populations of the O(*w*) site were further refined together with atom coordinates and anisotropic thermal parameters.

In structure **I**, the positions of all H atoms of two Db18C6 crown ligands (a and b) and two THF mole-

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

Bond	d, Å	Bond	d, Å	Bond	d, Å
Fe–N(1)	2.044(4)	K(a)–O(1a)	2.764(3)	K(b)–O(1b)	2.80(1)
Fe–N(2)	2.038(4)	K(a)–O(4a)	2.734(3)	K(b)–O(4b)	2.70(1)
Fe–N(3)	2.043(4)	K(a)–O(7a)	2.735(3)	K(b)–O(7b)	2.74(1)
S(1)=C(1)	1.622(5)	K(a)–O(10a)	2.781(3)	K(b)–O(10b)	2.74(1)
N(1)=C(1)	1.159(4)	K(a)–O(13a)	2.714(3)	K(b)–O(13b)	2.69(1)
S(2)=C(2)	1.612(5)	K(a)–O(16a)	2.744(3)	K(b)–O(16b)	2.82(1)
N(2)=C(2)	1.158(4)	K(a)–O(1c)	2.723(4)	K(b)–O(1d)	2.77(1)
S(3)=C(3)	1.631(5)	K(a)–S(1)	3.332(2)		
N(3)=C(3)	1.151(4)				
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(1)FeN(2)	91.0(1)	N(2)FeN(2)'	90.1(2)	FeN(3)C(3)	173.2(3)
N(1)FeN(3)	88.5(1)	N(2)FeN(3)'	179.0(1)	K(a)S(1)C(1)	117.0(2)
N(1)FeN(1)'	177.9(2)	N(3)FeN(3)'	90.4(2)	S(1)C(1)N(1)	178.6(4)
N(1)FeN(2)'	90.4(1)	FeN(1)C(1)	177.0(4)	S(2)C(2)N(2)	178.9(4)
N(1)FeN(3)'	90.0(1)	FeN(2)C(2)	172.7(4)	S(3)C(3)N(3)	179.2(4)
N(2)FeN(3)	89.7(1)				

* Symmetric transformations: (') $-x$, y, $1/2 - z$.

cules (c and d) were specified geometrically; their coordinates and isotropic thermal parameters were calculated by the riding model [3] during the refinement. In the last cycle of the refinement, the absolute shifts for all 669 variable parameters were smaller than 0.001σ.

The final refinement factors were $R = 0.044$ and $wR_2 = 0.080$ over the 3400 reflections with $I \geq 2\sigma(I)$; $R = 0.098$ and $wR_2 = 0.135$ over all independent reflections; the adjustment quality factor S was 0.90 (the definitions for the wR_2 and S values were reported [3]). In the final Fourier difference synthesis, $-0.27 < \Delta\rho < 0.26\ e\text{Å}^{-3}$. The f-curves used and the anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were taken from the literature [4].

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 as cif files (no. 677868).

RESULTS AND DISCUSSION

The asymmetrical part of the unit cell of crystal **I** contains a half $[Fe(NCS)_6]^{3-}$, anion, one and a half complex cations $[K(Db18C6)(THF)]^+$ (A and 1/2B), and ~0.15 hydration water molecules. The structures of these complex ions are shown in the figure, selected bond lengths and bond angles are given in the table.

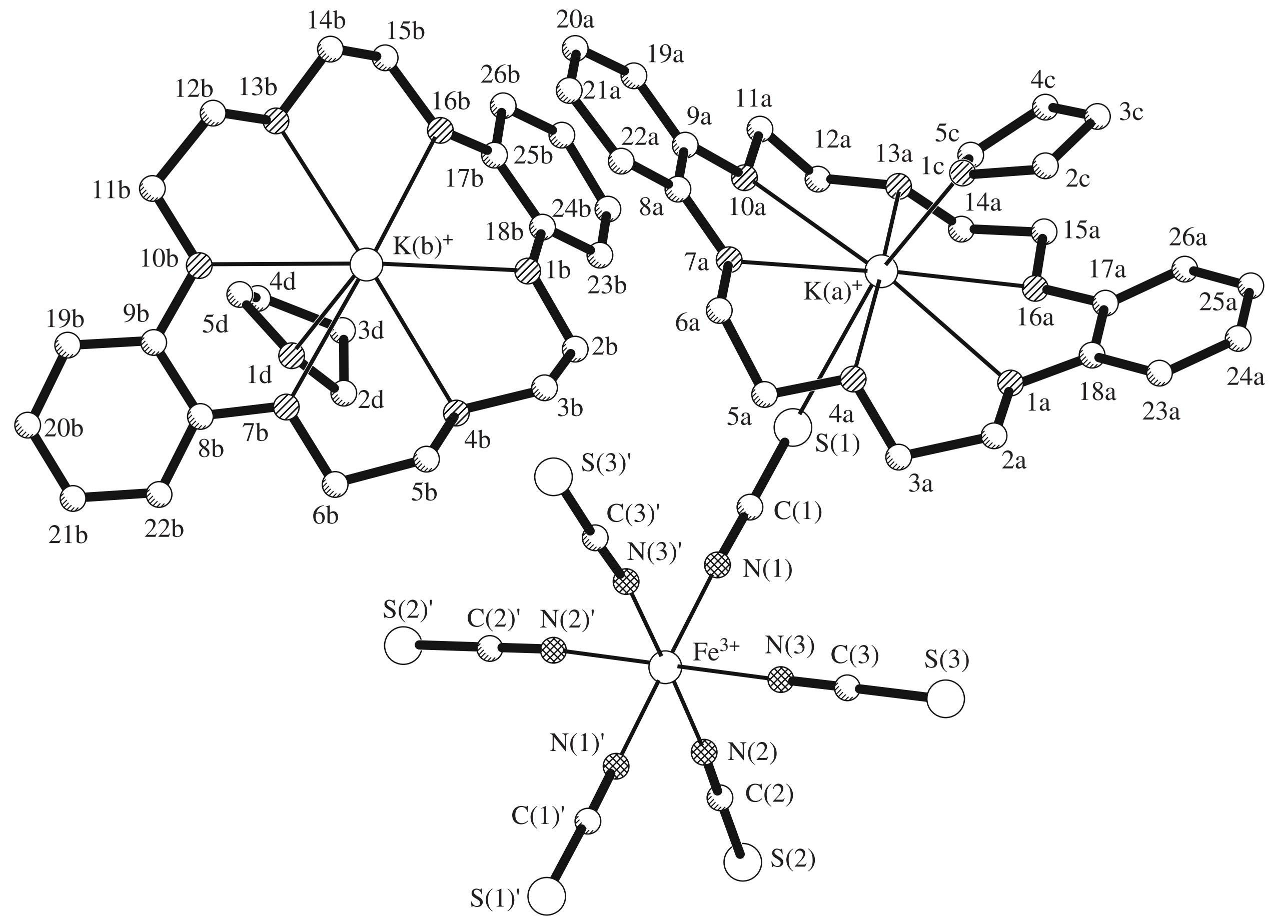
Two separate structural units can be conventionally distinguished in crystal **I**, namely, a compound complex anion $[Fe(NCS)_6(A)_2]^-$ and a statistically disordered complex cation $[K(Db18C6)(THF)]^+$ (B). The symmetrical complex anion $[Fe(NCS)_6(A)_2]^-$ consists of the $[Fe(NCS)_6]^{3-}$ anion and two complex cations, $[K(Db18C6)(THF)]^+$ (A and A') connected by a crystallographic twofold axis and connected to the $[Fe(NCS)_6]^{3-}$ anion by two K(a)–S(1) and K(a)'–S(1)' bonds (the prime marks a symmetric transformation of the basis unit, see notes to the table).

In **I**, the $[Fe(NCS)_6]^{3-}$ anion (on a twofold axis) has a slightly distorted octahedral structure. All six SCN^- ligands are coordinated by Fe^{3+} according to the isothiocyanate type through N atoms. The average length of the Fe–N coordination bonds in the $[Fe(NCS)_6]^{3-}$ anion of **I** (2.042(3) Å) is 0.10–0.15 Å smaller than the sum of the effective ionic radius of the Fe^{3+} cation (0.645 Å for C.N. 6 [5]) and the van der Waals radius of nitrogen (1.50–1.55 Å [6,7]).

All three independent Fe–N=C bond angles in the $[Fe(NCS)_6]^{3-}$ anion of **I** are smaller than 180° by 3°–7°. All three independent SCN^- ligands are nearly linear. The S=C and N=C bond lengths in **I** are close to statistical mean values for isothiocyanates.

The orientation of the $[Fe(NCS)_6]^{3-}$ anion relative to the $[K(Db18C6)(THF)]^+$ complex cation (A) bound to it is characterized by the following torsion angles: O(1a)–K(a)–S(1)–C(1), 69.8(2)°; O(4a)–K(a)–S(1)–C(1), 8.2(2)°; and O(7a)–K(a)–S(1)–C(1), –54.2(2)°.

In the $[K(Db18C6)(THF)]^+$ (A and B) complexes in structure **I**, the K^+(a) or K^+(b) cation resides in the Db18C6 crown cavity and is coordinated by the six O atoms of the crown ligand and by O(1c) or O(1d) atoms of THF. In addition, the K^+(a) cation is coordinated by



Structure of complex **I** in the crystal. The second positions of atoms of the statistically disordered complex cation (B) and H atoms of the Db18C6 and THF ligands are omitted for clarity. The symmetrically transformed basis atoms are primed.

the S(1) atom of $[Fe(NCS)_6]^{3-}$. Thus, the coordination polyhedron of K^+(a) in **I** is a distorted hexagonal bipyramid with two axial vertices occupied by S(1) and O(1c). The coordination polyherdron of K^+(b) is a distorted hexagonal pyramid with the O(1d) atom in the axial position. The bases of the coordination polyhedra of both potassium atoms are formed by six O atoms of the corresponding Db18C6 ligand (a or b).

In the $[K(Db18C6)(THF)]^+$ (A) cation, the average K(a)–O bond length is 2.742 ± 0.018 Å, that in the statistically disordered complex cation (B) is somewhat longer (K(b)–O, 2.751 ± 0.038 Å). These average lengths are somewhat shorter than the sum of the K^+ effective ionic radius (1.51 Å for C.N. 8 and 1.46 Å for C.N. 7) [5] and the van der Waals radius of oxygen (1.40–1.52 Å) [6, 7]. The average K(a)–O and K(b)–O bond lengths and the C.N.s of K^+(a) and K^+(b) obey an opposite correlation. In the complex cation (A), the K(a)–S(1) bond length (3.332(2) Å) is nearly equal to the sum of the above-mentioned K^+ ionic radius for C.N. 8 and the van der Waals radius of sulfur (1.80–1.85 Å) [6, 7].

The K^+(a) cation in complex A deviates from the root-mean-square plane through six O atoms of Db18C6 by 0.157(1) Å toward the O(1c) atom of the THF molecule. In the disordered complex B, the K^+(b) cation deviates from the root-mean-square plane through six O atoms of Db18C6 by 0.232(4) Å in the direction opposite to the THF O(1d) atom.

The bond lengths and bond angles of the two Db18C6 ligands in **I** are standard. Both crown ligands (a and b) have a butterfly conformation with approximate C_{2v} symmetry where all O–CH_2–CH_2–O intracyclic torsion angles (τ) are about ±65° (*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). All other τ angles outside the benzene rings are in the range of 180° ± 14° (*trans* type). The conformation of two Db18C6 ligands found in **I** is most frequent, being observed in 90% of known crystal structures containing these ligands.

The benzene rings in the two Db18C6 ligands of **I** are planar to within ±0.005(4)–0.013(9) Å. The dihedral angles between the root-mean-square planes of two benzene rings of each of the two Db18C6 ligands (a and

b) are 122.9(1)° and 116.2(7)°, respectively. The average $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ bond length in the rings of **I** is close to statistical mean value (for C,H-substituted benzene rings).

Structure **I** comprises two independent THF molecules (c and d). One (c) is somewhat disordered, all its C atoms have large thermal amplitudes. The molecule (d) is statistically disordered, all its atoms having site populations of 0.5. Due to the disorder of THF molecules in **I**, many of their bond lengths and bond and torsion angles are markedly distorted.

The conformation of the THF (c) molecule is a distorted O(1),C(2) half-chair, that of THF (d) molecule is a distorted envelope with C(3d) atom deviating from the plane. Each $[\mathrm{K(Db18C6)(THF)}]^+$ cation (A and B) in **I** has a THF molecule (c or d) on that side of the 18-membered macrocycle cavity to which two its benzene rings are turned.

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