Synthesis and Crystal Structure of Diaquabis(nitrato-O,O')ethanoliron(III) 4,7,13,16,21,24-Hexaoxa-1,10-Diaziobicyclo[8.8.8]hexacosane Trinitrate

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Received March 28, 2006

Abstract—A new complex salt diaquabis[nitrato-O,O’]ethanoliron(III) 4,7,13,16,21,24-hexaoxa-1,10-diaziobicyclo[8.8.8]hexacosane trinitrate, [Fe(NO3)2(EtOH)(H2O)2]+ [H2(Crypt-222)]2+ · (NO3)3, is synthesized. Its crystal structure has been determined by X-ray diffraction analysis: space group P 21/c, a = 14.147 Å, b = 11.443 Å, c = 23.127 Å, β = 103.66°, Z = 4. The structure is solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation to R = 0.064 for 5050 independent measured reflections (CAD-4 automated diffractometer, λMoKα radiation). In the [Fe(NO3)2(EtOH)(H2O)2]+ complex cation, the coordination polyhedron of the Fe3+ cation is a distorted pentagonal bipyramid with its base formed by four O atoms of two bidentate NO3− ligands, one O atom of the water molecule, and its axial vertices occupied by the O atoms of the EtOH molecule and the second water molecule. The alternating complex cations and NO3− anions multiplied by the 21 axis are hydrogen-bonded into infinite chains running along the y axis.

DOI: 10.1134/S0036023606120126

In this work, we describe the synthesis and results of X-ray diffraction analysis for crystals of the new complex salt diaquabis[nitrato-O,O’]ethanoliron(III) 4,7,13,16,21,24-hexaoxa-1,10-diaziobicyclo[8.8.8]hexacosane trinitrate, [Fe(NO3)2(EtOH)(H2O)2]+ [H2(Crypt-222)]2+ · (NO3)3, where [H2(Crypt-222)]2+ is the dication of 2.2.2-cryptand1 with two protonated nitrogen atoms. Similar complex iron salts have not been synthesized earlier.

EXPERIMENTAL

Synthesis of salt I. Crystalline Fe(NO3)3 · H2O and 2.2.2-cryptand in a molar ratio of 1 : 1 were dissolved in 75% aqueous ethanol. A concentrated aqueous solution of HNO3 in a noticeable molar excess was dropped to the mixture, and the resulting mixture was left open at room temperature to concentrate. After several weeks, light yellow platy crystals of complex salt I precipitated on the neck of the reaction vessel (not on its bottom or walls).

X-ray diffraction analysis. The unit cell parameters of a crystal and the three-dimensional set of reflection intensities were obtained on an Enraf-Nonius CAD-4 automated X-ray diffractometer (λMoKα radiation, graphite monochromator). The crystals of salt I are monoclinic: [Fe(NO3)2(C18H38N2O6)·(H2O)2]+ · (C18H38N2O6)2+ · (NO3)3, M = 826.50; a = 14.147(3) Å, b = 11.443(2) Å, c = 23.127(6) Å, β = 103.66(2)°, V = 3638(1) Å3, Z = 4, ρcalc = 1.509 g/cm3, µ(MoKα) = 5.13 cm−1, space group P 21/c.

The intensities of 5607 reflections were measured in a quadrant of the reciprocal space (2θ ≤ 46°) in the ω/2θ scan mode from a single crystal 0.125 × 0.50 × 0.75 mm in size. A special mode was used for measuring intensities: the final scan was carried out for all reflections including very weak ones. The reflection intensities were corrected to absorption by a semiempirical method [1]. After 320 systematically absent reflections were excluded and the intensities of 237 pairs of equivalent reflections 0kl and 0k 2l (Rint = 0.049) were averaged, the working set of measured F2(hkl) and σ(F2) values contained 5050 independent reflections.

The structure of salt I was solved by a direct method using the SHELXS97 program [2] and refined by the full-matrix least-squares method for F2 using the SHELXL97 program package [2] in the anisotropic approximation for non-hydrogen atoms (except for poorly occupied positions of disordered C atoms).

1 The nomenclature name of 2.2.2-cryptand is 4,7,13,16,21,24-hexaoxa-1,10-diaziobicyclo[8.8.8]hexacosane. Hereafter, the 2.2.2-cryptand dication will be named the 2.2.2-cation for brevity.
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.

First, a model for the structure of salt I with the ordered 2.2.2-cation was obtained by a direct method. At the final stage of refinement, an analysis of peaks from the difference electron density synthesis revealed that each of the six atoms (C(2), C(9), C(11), C(18), C(19), and C(26)) of the 2.2.2-cation (three atoms are bonded to each of the two N atoms) is disordered over two positions, one main position and the other poorly occupied. We had to split each position of the N(1) and N(10) atoms into two very close positions (the main and poorly occupied, namely, N(1) and N(1'), N(10) and N(10')) in order for the poorly occupied positions of these C atoms to have appropriate lengths of the bonds with the N(1) and N(10) atoms. The total occupancies of all disordered positions were refined by the least-squares method, and the coordinates of the poorly occupied positions of the C atoms were refined in the isotropic approximation. Probably, in the 2.2.2-cation the average length of five equatorial \( \text{Fe}^{3+} \)–O bonds (except \( \text{Fe}^{3+}(0.71 \pm 0.06 \text{ Å}) \)) is slightly shorter than the sum of the effective ionic radius of the \( \text{Fe}^{3+} \) cation (0.71 Å for the coordination number 7) \(^2\) and the van der Waals radius of the oxygen atom (1.40–1.52 Å) \(^5, 6\).

The average length of seven \( \text{Fe}–\text{O} \) coordination links in the complex cation in salt I is 2.07 ± 0.08 Å. The average length of two axial \( \text{Fe}–\text{O}(1\text{e}) \) and \( \text{Fe}–\text{O}(w2) \) bonds (1.97 ± 0.01 Å) is 0.14 Å shorter than the average length of five equatorial \( \text{Fe}–\text{O} \) bonds (2.11 ± 0.06 Å). These average \( \text{Fe}–\text{O} \) bond lengths in salt I are slightly shorter than the sum of the effective ionic radius of the \( \text{Fe}^{3+} \) cation (0.71 Å for the coordination number 7) \(^4\) and the van der Waals radius of the oxygen atom (1.40–1.52 Å) \(^5, 6\).

For the complex cation in salt I, the following deviations from the root-mean-square plane of the O(1a), O(2a), O(1b), O(2b), and O(w1) atoms that form the base of the \( \text{Fe}^{3+} \) polyhedron are observed: O(1a) –0.028(2), O(2a) 0.039(2), O(1b) 0.018(2), O(2b) –0.034(2), O(w1) 0.005(2), \( \text{Fe}^{3+} \) 0.033(1), O(1e) 1.995(3), and O(w2) –1.945(3) Å. The \( \text{Fe}^{3+} \) cation somewhat deviates from this plane toward the O(1e) atom. The root-mean-square planes of the two \( \text{NO}_3^- \) ligands (a and b) form small angles of 2.2(2)° and 3.4(2)°, respectively, with the root-mean-square plane of the five O atoms of the base of the \( \text{Fe}^{3+} \) polyhedron.

The two \( \text{NO}_3^- \) ligands (a and b) and three \( \text{NO}_3^- \) anions (c, d, and f) are nearly planar. The average length of the N–O bonds (1.230 ± 0.026 Å) is slightly shorter than the average value for \( \text{NO}_3^- \) anions (1.239 ± 0.020 Å) \(^7\). The individual N–O bond lengths and ONO bond angles for these ligands and the \( \text{NO}_3^- \) anions are noticeably differentiated. The N–O bonds with the O atoms that coordinate the \( \text{Fe}^{3+} \) cation or participate in strong interionic hydrogen bonds are much longer than the N–O bonds with the other O atoms, which have elevated thermal vibration amplitudes. The C(2e)–C(3e) bond in the

\(^2\) The effective ionic radius of the \( \text{Fe}^{3+} \) cation for seven-coordination is not given in \(^4\), but its average value for six- and eight-coordination is presented.