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Structural Characterization of a Tris-salicylate Coordination for Iron(III) with the Tripodal Ligand O-TRENSOX

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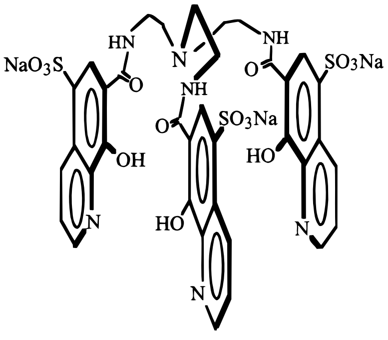
We recently reported the thermodynamic characterization in aqueous solution of Fe (III) complexation with O-TRENSOX.[1] This tris-bidentate tripodal ligand consists of three 8-hydroxyquinoline-5-sulfonate subunits (named sulfoxinate) connected to a tris(2-aminoethyl)amine (tren) framework via amide linkages at the ortho (7-) positions of their hydroxy groups. O-TRENSOX was found to form a protonated complex with Fe(III) in acidic medium (pH < 1). We report in this communication the structural characterization of the protonated ferric complex with O-TRENSOX formed in acidic medium at $[H^+] \approx 1$ M. The structure revealed a tris-salicylate mode of bonding for Fe(III) involving the amide oxygens and the *ortho*-hydroxy oxygens of the quinoline. A salicylate mode of bonding has been proposed by Raymond and co-workers for protonated ferric complexes of triscatechoyl-amide ligand having a tripodal backbone containing three catecholate binders connected to a spacer through amide linkages.[2] The salicylate coordination was deduced in particular from paramagnetic ^{2}H NMR measurements of the deuteriomethyl MECAM ligand coordinated to Fe(III).[3] During submission of this communication, a paper from the group of K. Raymond describing the crystallographic structure of ferric complexes with the tris-salicylate tripodal ligands tris[(2-hydroxybenzoyl)-2-aminoethyl]amine (TRENSAM) and tris[(2-hydroxy-3-methoxybenzoyl)-2-aminoethyl]amine (TREN(3M)SAM) was published.[4] The structure of these ligands allows only the salicylate mode of bonding since the catecholate “box” has been suppressed by methylation (for TREN(3M)SAM). The structure described in this report constitutes a crystallographic evidence of a tris-salicylate coordination for Fe(III) with a tripodal ligand having bidentate chelating subunits that allows the two modes of coordination.



O-TRENSOX

Experimental Section

Materials. O-TRENSOX was synthesized according to the method earlier described.[5] An aqueous solution of complex was prepared by dissolving 10^{-3} M of the ligand O-TRENSOX and 2×10^{-2} M of ferric perchlorate hydrate (Aldrich) in 1 M $HClO_4$. Allowing a solution of the complex to stand several days gave small orange crystals suitable for X-ray diffraction measurements.

X-ray Measurements. X-ray Data Collection and Crystal Structure Determination of $[Fe(C_{36}H_{31}N_7O_{15}S_3)]ClO_4 \cdot 6.5H_2O$. Data were collected at 293K for 3 days on a small orange platelet crystal of dimensions $0.1 \times 0.1 \times 0.05$ mm using the SIEMENS SMART CCD area detector diffractometer system equipped with a normal focus molybdenum-target tube operated at 2 kW (50 kV, 40 mA). The data were processed through the SAINT data reduction and SADABS softwares.[6]

The complex $[Fe(C_{36}H_{31}N_7O_{15}S_3)]ClO_4 \cdot 6.5H_2O$ ($M_w = 1170.26$) crystallizes in the monoclinic system, in $P2_1/n$ space group with the cell parameters ($a = 12.084(1)$ Å, $b = 21.171(2)$ Å, $c = 18.211(2)$ Å, $\beta = 100.92(1)°$, $V = 4574.3(7)$ Å^3, $Z = 4$, $\mu = 0.627$ mm^{-1}). 16 315 reflections were collected, 6449 independent reflections were used in the structural analysis. The structure was solved using an automatic Patterson procedure with the SHELXS-86 program[7] and refined against all F^2 (SHELXL-93).[8] All non-hydrogen atoms were refined with anisotropic thermal parameters. The perchlorate anion is hydrogen bonded to the amide nitrogen N21 and some water molecules, and 6.5 water molecules have been localized and are hydrogen bonded to the complex to sulfonate groups and amide nitrogen atoms.

Final cycle refinement including 708 parameters and 36 restraints converged to $R(F) = 0.079$ (for 4120 $F > 4\sigma(F)$), $wR(F^2) = 0.198$ and restrained goodness of fit $S = 1.016$ for all 6449 F^2 [$(\Delta/\sigma)_{max} = 0.05$, $\Delta\rho_{max} = 0.78$ e Å^{-3}, $\Delta\rho_{min} = -0.35$ e Å^{-3}]. The highest peak on the difference Fourier map was localized near oxygen O5 of the perchlorate anion.

Results and Discussion

The solid complex was isolated from aqueous solution containing the ligand O-TRENSOX (denoted LH_7^+ in its protonated form) and Fe(III) in acidic medium (1 M $HClO_4$). Crystals suitable for X-ray analysis formed when the solution was left standing for several days. A slow evaporation of H_2O upon slight warming favored the formation of the crystalline product.

X-ray analysis showed a cationic complex according to the chemical formula $[FeLH_4]ClO_4$. The structure determination revealed a tris-salicylate coordination for Fe(III) slightly distorted

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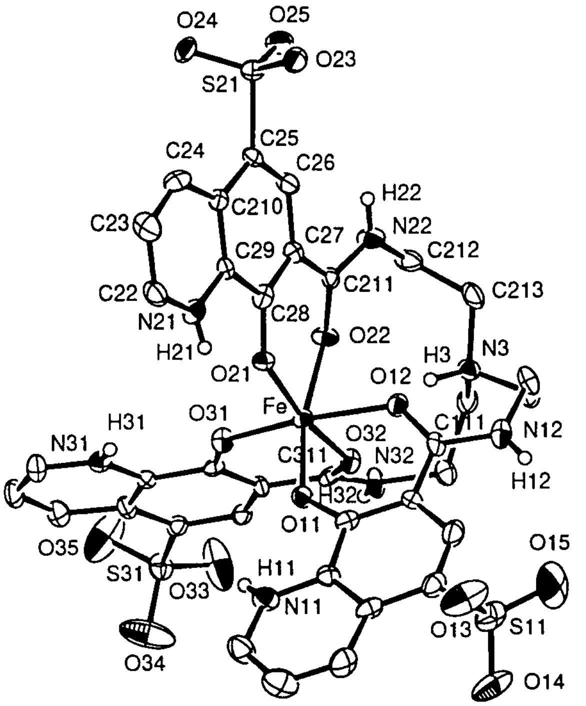

Figure 1. Thermal ellipsoid plot (30% probability ellipsoids) of the Fe−O-TRENSOX complex ($[FeLH_4]^+$ species) showing the numbering scheme. Hydrogen atoms on carbons have been omitted for clarity. Selected distances (Å): Fe−O1 1.939(5), Fe−O21 1.939(5), Fe−O31 1.942(5), Fe−O12 2.044(5), Fe−O22 2.032(5), Fe−O32 2.023(5).

from octahedral geometry and corresponding to the facial isomer. An ORTEP view of the complex is depicted in Figure 1. The average six-membered chelate ring O*n*1−Fe−O*n*2 (n = 1, 2, or 3 for each arm of the ligand) angles are 86.5° (compared to 90° for an ideal octahedron). Six O−Fe−O angles are in the range 95.2−96.9° and three in the range 80.7−81.4°. The apical O−Fe−O angles are 167.1°, 167.7°, and 167.8° (compared to 180° for an octahedron). The trigonal twist angle (60° for an ideal octahedron) has been calculated to be 51.4°.[9] The dihedral angles between the coordination planes O11−Fe−O12 and O21−Fe−O22, O11−Fe−O12 and O31−Fe−O32, and O21−Fe−O22 and O31−Fe−O32 are 81.75°, 78.71°, and 76.93°, respectively.

The geometry of the iron coordination sphere may be compared to the tris-salicylate complexes Fe(TRENSAM) and Fe(TREN-(3M)SAM) recently published.[4] The average Fe−O (carbonyl oxygen) bond length of 2.033 Å in the Fe(O-TRENSOX) complex is shorter than those of 2.07 and 2.08 Å in Fe(TRENSAM) and Fe(TREN(3M)SAM) while the average Fe−O (hydroxyl oxygen) bond lengths are very close: 1.940 Å for the former and 1.92 Å for the two latter. It should be noted that these values are significantly shorter than values determined for tris-catecholate complexes[10,11] (2.015−2.030) Å. Recently, the structure of the tris(8-hydroxyquinolinato) iron(III) complex has been described[12] providing the Fe−O (hydroxyl oxygen) bond distances over the range 1.936−1.996 Å. The short Fe−O (═C) distance in our complex indicates some negative charge is located at the carbonyl oxygen atoms in relation to resonance form −C═N−. This results in (i) an average C═O bond of 1.265 Å, the length of which is longer than an average C═O double bond (e.g. 1.23 Å as in peptides) and slightly shorter than a C−O single bond, and (ii) the planarity of the bonds around the amide nitrogen atoms. In addition, each quinoline ring containing the C−C(═O) bond is planar and the oxygen and nitrogen atoms of the amide group are displaced by about 0.2−0.4 Å from the both sides of each quinoline plane.

An interesting structural feature of the complex is the conformation of the tertiary amine. The N3−H3 bond of the protonated nitrogen atom is turned toward the iron coordination sphere and approximately along the 3-fold axis of the complex. The H3···O*n*2 distances are 2.17(8), 2.31(8), and 2.32(8) Å and the N3−H3−O*n*2 angles are 144.9°, 137.2°, and 129.4° for n = 1, 2, and 3, respectively, indicating intramolecular hydrogen bonds between the ammonium hydrogen and the three carbonyl oxygen atoms coordinated to iron. The structure also reveals intra-ring hydrogen bonds between the pyridinium hydrogen and the quinoline oxygen (coordinated to iron). The H*n*1···O*n*1 (n = 1, 2, and 3) distances have been measured to 2.31, 2.23, and 2.32 Å, respectively, with N−H−O angles of 106.0°, 109.8°, and 97.3°. The N···O distances are 3.046, 3.124, and 3.054 Å.

In summary, the crystal structure shows the metal ion in a slightly distorted octahedral environment. An important feature of the structure is that the six oxygen atoms coordinated to Fe(III) are hydrogen bonded either to the quinolinium or to the tertiary nitrogen atoms. This is assumed to organize the tripodal ligand around the metal in order to create a cavity which tightly fits the metal and, consequently, to stabilize the structure of the complex. This complex has been found to be stable in highly acidic medium (up to 2 M $HClO_4$) suggesting that the positive charges on the pyridine nitrogens are assumed to repel incoming H^+ necessary for dissociation.

Our result demonstrates that a hexadentate tripodal ligand in which the chelating subunits are attached to a central framework via amide linkage at the ortho positions of their phenolic hydroxy groups can coordinate Fe(III) in a salicylate mode when protonated species of complex are formed in acidic medium. Our previous solution studies supported the formation of a bis-salicylate complex $[FeLH_5(H_2O)_2]^{2+}$ for which one arm of the ligand is not involved in the coordination with iron. The amount of the crystalline product was increased upon a slow evaporation of water. This suggests that an equilibrium between the weakly soluble $[FeLH_4]^+$ species and the soluble $[FeLH_5(H_2O)_2]^{2+}$ species is established in acidic aqueous solution where $[FeLH_5(H_2O)_2]^{2+}$ is the major species according to

$$[FeLH_4]^+_{(solid)} + H_3O^+ + H_2O \rightleftharpoons [FeLH_5(H_2O)_2]^{2+}$$

This result suggests that a bis-salicylate coordination is favored in aqueous solution in relation to a possible strain in the ligand with the tris-salicylate coordination.

Finally it is emphasized that the two modes of coordination are available for O-TRENSOX depending on the protonation state of the ferric complex: the salicylate mode, clearly characterized for the protonated complex in the solid state, and the oxinate mode for the unprotonated complex.

Supporting Information Available: Complete tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, intramolecular hydrogen bonds distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The trigonal twist angle is defined by viewing the O12−O22−O32 and O11−O21−O31 planes in projection perpendicular to the 3-fold axis of the complex. It is calculated as the average dihedral angle between O11−D1−D2−O12 (51.8°), O21−D1−D2−O22 (51.5°), and O31−D1−D2−O32 (51.1°) (D1 and D2 are the centers of the O11−O21−O31 and O12−O22−O32 triangles).

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