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Redetermination of *fac*-tris(benzohydroxamato)iron(III) trihydrateCeline J. Marmion,^{a*} Terry Murphy,^a Zoya Starikova^b and Kevin B. Nolan^a^aDepartment of Chemistry, The Royal College of Surgeons in Ireland, 123 St Stephen's Green, Dublin 2, Ireland, and ^bX-ray Structural Centre, General and Technical Chemistry Division, Academy of Sciences of Russia, Valivov Str. 28, Moscow B-334, 117813 Russia

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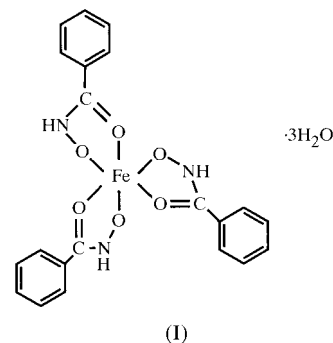
Due to its importance as a model for naturally occurring iron(III) siderophores such as desferrioxamine B, the crystal structure of the title compound, $[\text{Fe}(\text{C}_7\text{H}_6\text{NO}_2)_3]\cdot 3\text{H}_2\text{O}$, which was reported previously ($R = 0.12$, one of water molecules disordered), has been redetermined ($R = 0.041$ without disorder). The complex has pseudo-octahedral geometry around the Fe^{III} atom, with Fe—O bond lengths ranging from 1.9689 (18) to 2.0585 (17) Å and O—Fe—O bond angles in the chelate rings of 78.01 (7), 78.83 (7) and 78.95 (7)°. There is extensive hydrogen bonding involving the water molecules and the hydroxamate ligands.

Comment

Hydroxamic acids, a group of weak organic acids of general formula RCONR^1OH , are important compounds in biology and medicine, e.g. as potent and selective inhibitors of enzymes, such as peroxidases (Tam *et al.*, 1995), ureases (Arnold *et al.*, 1998) and matrix metalloproteinases (Botos *et al.*, 1996), and as hypotensive (Zamora *et al.*, 1995; Marmion *et al.*, 2000), antituberculosis, anticancer and antifungal agents (Miller, 1989, and references therein). Hydroxamic acids are also siderophores for iron(III) (Kurzak *et al.*, 1992), playing a key role in microbial iron transport, by solubilizing iron(III) from the environment and transporting it into the cell. The best known siderophore is desferrioxamine B, a hexadentate chelating agent.

The structure of tris(benzohydroxamato)iron(III) trihydrate, (I), which is a model complex for iron(III) desferrioxamine B, was first published by Lindner & Göttlicher (1969), but the R factor was 0.12 and one of the water molecules was disordered. From the reaction of $(\text{Et}_4\text{N})[\text{Fe}(\text{R}_3\text{NS}_3)\text{Cl}]$, an iron(III) complex where R_3NS_3 is the trianionic tetradentate ligand tris(2-thiolatoethyl)amine, with benzohydroxamic acid, we isolated crystals of the title complex, (I). The space group and the reduced cell parameters agreed with those of Lindner

& Göttlicher (1969). However, we obtained a much improved crystal structure which, because of its importance, we report herein.



In the course of our investigations of the reaction of $(\text{Et}_4\text{N})[\text{Fe}(\text{R}_3\text{NS}_3)\text{Cl}]$ with hydroxamic acids, compound (I) was obtained as a minor crystalline product from the filtrate of the benzohydroxamic acid reaction following removal of the precipitated material. The complex has pseudo-octahedral geometry around the Fe^{III} atom, with Fe—O bond lengths ranging from 1.9689 (18) to 2.0585 (17) Å and O—Fe—O bond angles in the chelate rings of 78.01 (7), 78.83 (7) and 78.95 (7)°. There is extensive N—H...O, O—H...O and O—H...N hydrogen bonding involving the hydroxamate ligands and the water molecules, with N—H...O in the range 2.698 (4)–2.777 (3) Å and O—H...O in the range 2.732 (3)–2.983 (3) Å.

Experimental

The title compound, (I), was prepared as follows: an aqueous benzohydroxamic acid solution (99 mg, 0.72 mmol) was added dropwise to a pink solution of $(\text{Et}_4\text{N})[\text{Fe}(\text{R}_3\text{NS}_3)\text{Cl}]$ (300 mg, 0.72 mmol) in acetonitrile (20 ml), where R_3NS_3 is the trianionic tetradentate ligand tris(2-thiolatoethyl)amine. The resulting brown solution was stirred at room temperature for 12 h, after which a fine brown precipitate was obtained and removed by filtration. The brown filtrate was cooled for two weeks during which time large red-brown needle-like crystals were obtained. These were collected by filtration, washed with diethyl ether and dried in a desiccator over phosphorus pentoxide.

Crystal data

$[\text{Fe}(\text{C}_7\text{H}_6\text{NO}_2)_3]\cdot 3\text{H}_2\text{O}$
 $M_r = 518.28$
 Monoclinic, $P2_1/n$
 $a = 12.9459$ (9) Å
 $b = 13.1082$ (9) Å
 $c = 13.9889$ (9) Å
 $\beta = 90.300$ (2)°
 $V = 2373.8$ (3) Å³
 $Z = 4$

$D_x = 1.450$ Mg m⁻³
 Mo K α radiation
 Cell parameters from 2250 reflections
 $\theta = 2.1$ – 27.0°
 $\mu = 0.69$ mm⁻¹
 $T = 200$ (2) K
 Needle, red
 0.40 × 0.10 × 0.10 mm

Data collection

SMART CCD diffractometer
 φ and ω scans
 Absorption correction: empirical
 (SADABS; Siemens, 1996)
 $T_{\text{min}} = 0.770$, $T_{\text{max}} = 0.934$
 18000 measured reflections
 5218 independent reflections

2491 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.077$
 $\theta_{\text{max}} = 27^\circ$
 $h = -16 \rightarrow 16$
 $k = -11 \rightarrow 16$
 $l = -17 \rightarrow 17$
 Intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.072$
 $S = 0.73$
 5218 reflections
 337 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0222P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

Fe1—O11	1.9753 (19)	Fe1—O12	2.0577 (18)
Fe1—O21	1.9715 (18)	Fe1—O22	2.0356 (18)
Fe1—O31	1.9689 (18)	Fe1—O32	2.0585 (17)
O11—Fe1—O12	78.01 (7)	O21—Fe1—O31	89.72 (8)
O21—Fe1—O22	78.83 (7)	O11—Fe1—O22	159.05 (8)
O31—Fe1—O32	78.95 (7)	O12—Fe1—O31	161.26 (8)
O11—Fe1—O21	97.17 (8)	O21—Fe1—O32	156.61 (7)
O11—Fe1—O31	90.86 (8)		

Table 2
 Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N11—H11 \cdots O1 ⁱ	0.89 (2)	1.84 (3)	2.725 (4)	178 (2)
N21—H21 \cdots O2	0.88 (3)	1.83 (3)	2.698 (4)	169 (3)
N31—H31 \cdots O12 ⁱⁱ	0.88 (3)	1.95 (3)	2.777 (3)	157 (2)
O1—H1A \cdots O3	0.79 (3)	2.08 (3)	2.857 (3)	168 (4)
O1—H1B \cdots O11 ⁱⁱⁱ	0.88 (3)	1.88 (3)	2.757 (3)	174 (3)
O2—H2A \cdots O3	0.80 (4)	1.94 (4)	2.732 (3)	170 (5)
O2—H2B \cdots O21 ⁱⁱⁱ	0.89 (4)	2.70 (5)	2.833 (3)	89 (3)
O3—H3A \cdots O32 ^{iv}	0.74 (3)	2.26 (3)	2.983 (3)	165 (4)
O3—H3B \cdots O31 ⁱⁱⁱ	0.88 (3)	1.97 (3)	2.797 (3)	156 (3)
O3—H3B \cdots N31 ⁱⁱⁱ	0.88 (3)	2.66 (3)	3.535 (3)	174 (3)

Symmetry codes: (i) $x-1, y, z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (iii) $-x, 1-y, -z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The H atoms attached to C atoms were allowed for as riding atoms, with a C—H distance of 0.93 \AA using *SHELXL97* (Sheldrick, 1997) defaults. The positions of the H atoms attached to N/O were refined, N—H with isotropic displacement parameters. Examination of the structure with *PLATON* (Spek, 1998) shows that there are no solvent-accessible voids in the crystal lattice.

Data collection: *SMART* (Siemens, 1996); cell refinement and data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure and prepare publication material: *SHELXL97* (Sheldrick, 1997).

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