

A saccharinate–iron(II) complex with a free saccharin molecule present, $[\text{Fe}(\text{phen})_3]\text{sac}_2 \cdot \text{sacH} \cdot 6\text{H}_2\text{O}$

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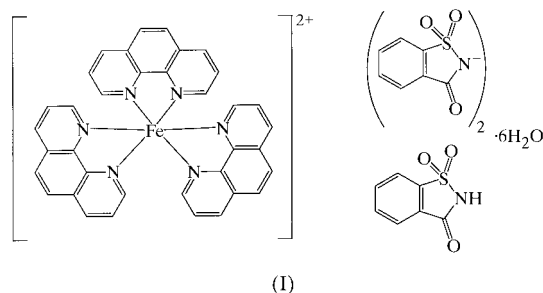
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The crystal structure of the title compound, tris(1,10-phenanthroline-*N,N'*)iron(II) bis[1,2-benzisothiazol-3(2*H*)-onate 1,1-dioxide] 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide hexahydrate, $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{C}_7\text{H}_4\text{NO}_3\text{S})_2 \cdot \text{C}_7\text{H}_5\text{NO}_3\text{S} \cdot 6\text{H}_2\text{O}$, at 120 K consists of slightly distorted octahedral $[\text{Fe}(\text{phen})_3]^{2+}$ cations (phen is 1,10-phenanthroline), two saccharinate anions and a free saccharin molecule, as well as six waters of crystallization. The compound has been confirmed as diamagnetic low-spin iron(II) by magnetic measurements. There is extensive hydrogen bonding leading to a three-dimensional network.

Comment

In our earlier papers on metal–saccharinate complexes with the bidentate ligands 2,2'-bipyridine (bipy) or phen present (Dillon *et al.*, 1999; Deng *et al.*, 2000), we summarized previous work on these systems, including examples with all the



saccharinate ligands attached to the metal (Hergold-Brundić *et al.*, 1989) and ones where saccharinate (sac) is present only as the counter-ion (Ainscough *et al.*, 1990; Li, Chen *et al.*, 1993; Li, Wei *et al.*, 1993). The only structures reported for iron(II) complexes of saccharin are those of the parent compound, $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (Haider *et al.*, 1983), and of the phen complex $[\text{Fe}(\text{phen})_3(\text{sac})_2] \cdot 4\text{H}_2\text{O}$ (Li, Wei *et al.*, 1993). In the present work, we report the structure of another tris(1,10-

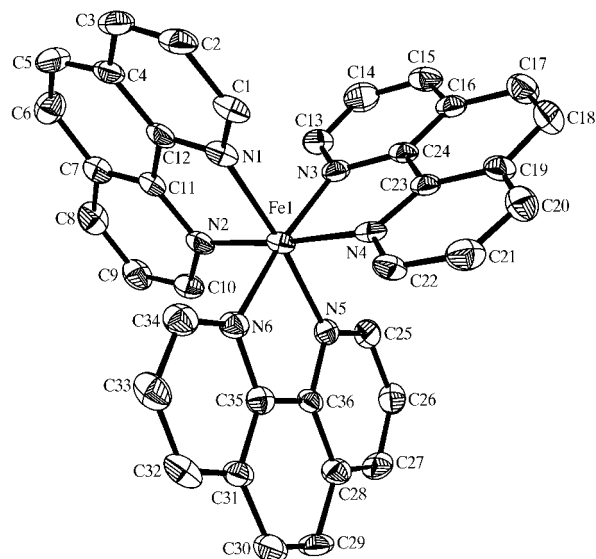


Figure 1
Drawing of the $[\text{Fe}(\text{phen})_3]^{2+}$ cation of (I) showing 70% probability displacement ellipsoids. H atoms have been omitted for clarity.

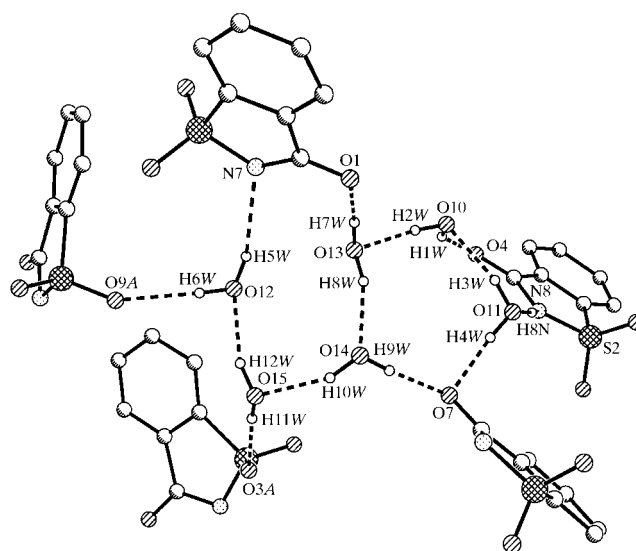


Figure 2
The hydrogen-bonding scheme of (I). Atom types are represented as follows: N regular dot pattern, O shaded bottom left to top right, S cross-hatched, C shaded and H small open circles.

phenanthroline)iron(II) complex, (I), with two saccharinate anions and one free saccharin molecule present, as well as six waters of crystallization. The compound has been confirmed as diamagnetic iron(II) (d^6 low spin) by magnetic measurements, which clearly eliminates the alternative possibility of an iron(III) complex with three saccharinate anions. Such a d^5 complex, if low spin, would be paramagnetic, with one unpaired electron present, while a high-spin species would have five unpaired electrons. Low spin would be expected in any case, from the position of phen in the spectrochemical series.

The structure of the title compound consists of slightly distorted octahedral $[\text{Fe}(\text{phen})_3]^{2+}$ cations, with two sacchar-

inate anions, a free saccharin molecule and six water molecules. The Fe—N distances (Table 1) are quite similar within each of the bidentate phen ligands, although the bonds are slightly longer to N3 and N4 than to the other four N atoms; the average Fe—N bond length is 1.966 Å. This compares well, for example, with the mean distance of 1.97 Å in l -[Fe(phen)₃]bis[Sb^{III}-D-tartrate]·8H₂O (Zalkin *et al.*, 1973), 1.973 Å in [Fe(phen)₃]I₂·2H₂O (Johansson *et al.*, 1978) and 1.980 Å in [Fe(phen)₃](sac)₂·4H₂O (Li, Wei *et al.*, 1993). The central Fe atom in (I) is very close to coplanarity with the four surrounding N atoms; the largest deviation is 0.014 (1) Å from the plane defined by N2, N3, N4 and N6. This compares with more significant deviations of 0.06, 0.03 and 0.008 Å in the structure of [Fe(phen)₃](sac)₂·4H₂O (Li, Wei *et al.*, 1993).

The hydrogen-bonding geometry of (I) is shown in Table 2 and displayed in Fig. 2. There is a strong, essentially linear, hydrogen bond between H8 (on N8) in the free saccharin molecule to O11 of a water molecule, with a distance of 1.70 (5) Å and a bond angle at hydrogen of 174 (4)°. The carbonyl O7 atom in one of the saccharinate anions appears to form linear hydrogen bonds with both H4W and H9W on adjacent water molecules, with distances and angles shown in Table 2. There is also a linear hydrogen bond between O3 on S1 in the second saccharinate anion and H11W (see Table 2). A shorter contact between the carbonyl O1 atom and H7W in this ion is also found at 1.853 (13) Å, but at a slightly less favourable angle of 164 (4)°. Other weaker hydrogen bonds between either the free saccharin molecule or a saccharinate anion and a water molecule are tabulated in Table 2, as well as hydrogen bonds between water molecules.

The overall hydrogen-bond scheme can be described as a three-dimensional network formed by the saccharinate anions, the free saccharin molecule and the water molecules. This network, shown in Fig. 3, leaves channels along the *b* axis where the cations reside.

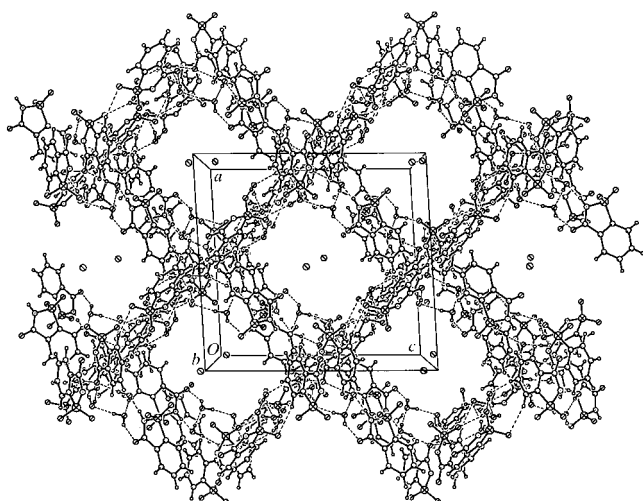


Figure 3
The packing diagram for (I) showing the three-dimensional network formed *via* hydrogen bonding by the anions, the free saccharin and the water molecules. Only the Fe centres (shaded top left to bottom right) from the cations are shown for clarity. Other atoms are represented as in Fig. 2.

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	1.965 (3)	Fe1—N4	1.973 (3)
Fe1—N2	1.963 (3)	Fe1—N5	1.963 (3)
Fe1—N3	1.974 (3)	Fe1—N6	1.957 (3)
N1—Fe1—N2	82.55 (11)	N2—Fe1—N6	93.44 (11)
N1—Fe1—N3	91.50 (11)	N3—Fe1—N4	82.77 (11)
N1—Fe1—N4	94.89 (11)	N3—Fe1—N5	93.00 (11)
N1—Fe1—N5	173.96 (11)	N3—Fe1—N6	173.03 (11)
N1—Fe1—N6	93.15 (11)	N4—Fe1—N5	89.67 (10)
N2—Fe1—N3	92.31 (11)	N4—Fe1—N6	91.66 (11)
N2—Fe1—N4	174.42 (11)	N5—Fe1—N6	82.75 (11)
N2—Fe1—N5	93.23 (11)		

Experimental

Compound (I) was prepared by adding a warm solution of 1,10-phenanthroline (0.4488 g, 2.46 mmol) in water (50 ml), with stirring, to a warm clear solution of [Fe(sac)₂(H₂O)₄]·2H₂O (0.4386 g, 0.83 mmol) in water (30 ml). A deep-red solution formed, was stirred for some time, and then left to stand. Fine red crystals formed after four weeks. These were separated, washed with 10 ml of cold distilled water and dried in air at room temperature. Elemental analyses, performed by the microanalytical services of the Department of Chemistry, University of Durham, both before and after the crystal structure determination, indicated an average composition of [Fe(phen)₃](sac)₂·sacH·3H₂O; found: C 57.18, H 3.72, N 10.66%; calculated for C₅₇H₄₃FeN₉O₁₂S₃: C 57.15, H 3.62, N 10.52%. It is therefore probable that other material was present containing less water of crystallization than found in the crystals whose X-ray structure was determined in this work. Magnetic measurements were performed on a Johnson–Matthey–Evans magnetic susceptibility balance; the complex was shown to be diamagnetic.

Crystal data

[Fe(C ₁₂ H ₈ N ₂) ₃](C ₇ H ₄ NO ₃ S) ₂ · C ₇ H ₅ NO ₃ S·6H ₂ O	$D_x = 1.572 \text{ Mg m}^{-3}$
$M_r = 1252.08$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 869 reflections
$a = 16.113 (4) \text{ \AA}$	$\theta = 10.20\text{--}21.52^\circ$
$b = 19.079 (5) \text{ \AA}$	$\mu = 0.487 \text{ mm}^{-1}$
$c = 17.227 (4) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 92.873 (5)^\circ$	Rectangular plate, red
$V = 5289 (2) \text{ \AA}^3$	$0.48 \times 0.19 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD diffractometer	14 753 independent reflections
ω scans	7374 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (SHELXTL-NT; Bruker, 1998)	$R_{\text{int}} = 0.115$
$T_{\text{min}} = 0.830$, $T_{\text{max}} = 0.954$	$\theta_{\text{max}} = 30.45^\circ$
47 439 measured reflections	$h = -22 \rightarrow 20$
	$k = -26 \rightarrow 26$
	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 0.6223P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.145$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.990$	$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
14 753 reflections	$\Delta\rho_{\text{min}} = -0.70 \text{ e \AA}^{-3}$
812 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N8—H8N...O11	0.92 (5)	1.70 (5)	2.614 (4)	174 (4)
O10—H1W...O4	0.89 (4)	2.19 (2)	2.989 (4)	148 (4)
O10—H2W...O13 ⁱ	0.90 (3)	1.87 (3)	2.756 (4)	171 (5)
O11—H3W...O10	0.90 (3)	1.87 (4)	2.740 (4)	161 (5)
O11—H4W...O7	0.90 (3)	1.85 (3)	2.741 (3)	174 (4)
O12—H5W...N7 ⁱⁱ	0.90 (3)	2.70 (2)	3.547 (5)	157 (5)
O12—H6W...O9 ⁱⁱⁱ	0.90 (3)	2.13 (4)	2.917 (4)	146 (5)
O13—H7W...O1	0.90 (3)	1.85 (2)	2.732 (4)	164 (4)
O13—H8W...O14 ^{iv}	0.90 (3)	1.95 (2)	2.820 (5)	163 (5)
O14—H9W...O7 ^v	0.90 (3)	1.84 (3)	2.740 (4)	176 (4)
O14—H10W...O15	0.90 (3)	1.97 (2)	2.817 (4)	157 (5)
O15—H11W...O3	0.90 (3)	2.02 (2)	2.922 (4)	176 (3)
O15—H12W...O12 ^{vi}	0.90 (3)	1.92 (2)	2.787 (4)	161 (4)

Symmetry codes: (i) $1-x, -y, 2-z$; (ii) $1-x, -y, 1-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$.

All water H atoms and the amino H atom of the free saccharin molecule were refined. All water O—H distances were restrained to be 0.9 Å, with s.u.'s of 0.005 Å. Other H atoms were treated as riding (C—H = 0.93 Å).

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1421). Services for accessing these data are described at the back of the journal.

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