Crystal structure of [bis(2-hydroxybenzylidenethiosemicarbazone)-iron(II)] hydrate, $\text{Fe}(\text{C}_{16}\text{H}_{16}\text{N}_6\text{O}_2\text{S}_2) \cdot \text{H}_2\text{O}$

W.-S. Wu^{*I} and Y.-L. Feng^{II}

^I Huaqiao University, College of Materials, Quanzhou, Fujian, 362011 P. R. China

^{II} Zhejiang Normal University, Institute of Physical Chemistry, Jinhua, Zhejiang, 321004 P. R. China

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Abstract

$\text{C}_{16}\text{H}_{18}\text{FeN}_6\text{O}_3\text{S}_2$, monoclinic, $P12_1/n1$ (No. 14), $a = 8.9754(5) \text{ \AA}$, $b = 18.229(1) \text{ \AA}$, $c = 11.5546(7) \text{ \AA}$, $\beta = 93.006(2)^\circ$, $V = 1887.9 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.039$, $wR_{\text{ref}}(F^2) = 0.080$, $T = 293 \text{ K}$.

Source of material

To a solution of salicylaldehyde (2.0 mmol) and thiosemicarbazide (2.0 mmol) in 35 mL of ethanol was added $\text{Fe}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ (1.0 mmol). The mixture was refluxed for 2 h, resulting in a red solution. Black-red prismatic crystals suitable for structure determination were isolated by slow evaporation of the solvent at room temperature for a couple of weeks.

Discussion

The structure of the title complex consists of mononuclear Fe(II) species $\text{Fe}(\text{C}_8\text{H}_8\text{N}_3\text{OS})_2 \cdot \text{H}_2\text{O}$ ($\text{C}_8\text{H}_8\text{N}_3\text{OS}$ is 2-hydroxybenzylidenethiosemicarbazone anion) and one crystal water molecule. The central Fe(II) ion is coordinated by two nitrogen atoms, two oxygen atoms and two sulfur atoms from two tridentate ligands, forming a distorted octahedral coordination. The lengths for Fe—N bonds (2.126(2) Å, 2.149(2) Å) and Fe—O bonds (1.927(2) Å, 1.947(2) Å) are in good agreement with the corresponding bonds in the complex $[\text{Fe}(\text{C}_{14}\text{H}_9\text{N}_2\text{O}_3)(\text{CH}_3\text{OH})]_{10} \cdot$

$3\text{CH}_2\text{Cl}_2 \cdot 12.5\text{CH}_3\text{OH} \cdot 5\text{H}_2\text{O}$ [1]. The lengths for Fe—S bonds (2.4018(9) Å, 2.4626(9) Å) are longer than that ones (2.218(2) Å, 2.238(2) Å) in the complex $[\text{Fe}(\text{Am}_4\text{M})_2] \cdot \text{ClO}_4$ [2]. To form the two-dimensional structure, the molecules are connected to each other through intramolecular and intermolecular hydrogen bonds with $d(\text{N}5 \cdots \text{O}3) = 2.832 \text{ \AA}$ and $\angle \text{N}5-\text{H}5 \cdots \text{O}3 = 152.1^\circ$, $d(\text{O}3 \cdots \text{N}2^a) = 3.218 \text{ \AA}$ and $\angle \text{O}3-\text{H}31 \cdots \text{N}2^a = 163.7^\circ$, $d(\text{O}3 \cdots \text{S}1^b) = 3.448 \text{ \AA}$ and $\angle \text{O}3-\text{H}32 \cdots \text{S}1^b = 133.0^\circ$, $d(\text{N}2 \cdots \text{O}3^c) = 3.218 \text{ \AA}$ and $\angle \text{N}2-\text{H}2 \cdots \text{O}3^c = 156.0^\circ$, $d(\text{N}3 \cdots \text{O}1^d) = 2.987 \text{ \AA}$ and $\angle \text{N}3-\text{H}3A \cdots \text{O}1^d = 172.0^\circ$, $d(\text{N}6 \cdots \text{O}2^e) = 2.794 \text{ \AA}$ and $\angle \text{N}6-\text{H}6A \cdots \text{O}2^e = 159.4^\circ$ ($a: x, y, z-1$; $b: x+1/2, -y+1/2, z-1/2$; $c: x, y, z+1$; $d: x-1/2, -y+1/2, z+1/2$; $e: x-1/2, -y+1/2, z-1/2$).

Table 1. Data collection and handling.

Crystal:	red-black prism, size $0.11 \times 0.15 \times 0.18 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71069 \text{ \AA}$)
μ :	10.52 cm^{-1}
Diffractometer, scan mode:	Rigaku R-Axis RAPID, ω/ϕ
$2\theta_{\text{max}}$:	54.96°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	4311, 4311
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2416
$N(\text{param})_{\text{refined}}$:	253
Programs:	SHELXS-97 [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(31)	4e	0.2555	0.2489	-0.5801	0.075
H(32)	4e	0.3953	0.2466	-0.5057	0.075
H(2)	4e	0.2059	0.2600	0.2898	0.051
H(3A)	4e	0.0337	0.3475	0.3001	0.065
H(3B)	4e	-0.0138	0.3918	0.1963	0.065
H(5)	4e	0.2078	0.2343	-0.3531	0.043
H(6A)	4e	0.0561	0.1398	-0.3728	0.058
H(6B)	4e	0.0049	0.0983	-0.2712	0.058
H(3)	4e	0.6715	0.0845	-0.0655	0.067
H(4)	4e	0.7569	-0.0067	0.0563	0.075
H(5)	4e	0.6786	-0.0147	0.2422	0.071
H(6)	4e	0.5080	0.0687	0.3050	0.061
H(7)	4e	0.3505	0.1680	0.2776	0.046
H(11)	4e	0.6597	0.4415	0.0010	0.063
H(12)	4e	0.7494	0.5201	-0.1328	0.071
H(13)	4e	0.6769	0.5096	-0.3265	0.069
H(14)	4e	0.5100	0.4207	-0.3843	0.059
H(15)	4e	0.3542	0.3242	-0.3513	0.044

* Correspondence author (e-mail: wuwenshi@sohu.com)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Fe(1)	4e	0.33212(4)	0.25732(2)	−0.02881(3)	0.0360(2)	0.0367(2)	0.0262(2)	−0.0004(2)	0.0027(2)	0.0006(2)
S(1)	4e	0.14234(9)	0.34330(4)	0.01946(7)	0.0520(5)	0.0419(5)	0.0430(5)	0.0083(4)	0.0068(4)	0.0032(4)
S(2)	4e	0.1433(1)	0.16398(5)	−0.08439(7)	0.0628(5)	0.0433(5)	0.0344(4)	−0.0168(4)	−0.0006(4)	0.0022(4)
O(3)	4e	0.2952(2)	0.2375(1)	−0.5128(2)	0.042(1)	0.106(2)	0.040(1)	0.002(1)	−0.0017(9)	−0.006(1)
N(1)	4e	0.3105(2)	0.2313(1)	0.1489(2)	0.029(1)	0.038(1)	0.031(1)	−0.004(1)	0.006(1)	−0.005(1)
N(2)	4e	0.2135(3)	0.2694(1)	0.2174(2)	0.049(2)	0.052(2)	0.028(1)	0.002(1)	0.012(1)	0.000(1)
N(3)	4e	0.0404(3)	0.3576(1)	0.2279(2)	0.061(2)	0.048(2)	0.057(2)	0.014(1)	0.024(1)	0.001(1)
N(4)	4e	0.3100(2)	0.2744(1)	−0.2130(2)	0.032(1)	0.033(1)	0.028(1)	−0.001(1)	−0.001(1)	−0.003(1)
N(5)	4e	0.2160(2)	0.2286(1)	−0.2792(2)	0.042(1)	0.041(1)	0.025(1)	−0.004(1)	−0.004(1)	0.000(1)
N(6)	4e	0.0570(3)	0.1331(1)	−0.2991(2)	0.061(2)	0.042(2)	0.041(2)	−0.012(1)	−0.011(1)	0.002(1)
O(1)	4e	0.4890(2)	0.1851(1)	−0.0279(2)	0.051(1)	0.056(1)	0.042(1)	0.017(1)	0.012(1)	0.005(1)
O(2)	4e	0.4797(2)	0.3356(1)	−0.0312(2)	0.046(1)	0.054(1)	0.039(1)	−0.016(1)	−0.003(1)	0.001(1)
C(1)	4e	0.4815(3)	0.1272(2)	0.1566(3)	0.034(2)	0.032(2)	0.043(2)	−0.001(1)	−0.004(1)	0.000(1)
C(2)	4e	0.5327(3)	0.1331(2)	0.0437(3)	0.036(2)	0.039(2)	0.044(2)	0.003(1)	−0.002(1)	−0.006(2)
C(3)	4e	0.6369(4)	0.0816(2)	0.0088(3)	0.055(2)	0.056(2)	0.058(2)	0.016(2)	0.006(2)	−0.005(2)
C(4)	4e	0.6888(4)	0.0272(2)	0.0823(4)	0.052(2)	0.045(2)	0.090(3)	0.011(2)	0.002(2)	−0.007(2)
C(5)	4e	0.6417(4)	0.0221(2)	0.1929(4)	0.046(2)	0.041(2)	0.089(3)	0.000(2)	−0.007(2)	0.018(2)
C(6)	4e	0.5393(4)	0.0719(2)	0.2297(3)	0.047(2)	0.048(2)	0.059(2)	−0.002(2)	−0.001(2)	0.007(2)
C(7)	4e	0.3757(3)	0.1763(2)	0.2017(2)	0.043(2)	0.039(2)	0.032(2)	−0.005(2)	0.003(1)	−0.000(1)
C(8)	4e	0.1360(3)	0.3198(2)	0.1642(2)	0.034(2)	0.035(2)	0.040(2)	−0.006(1)	0.005(1)	−0.004(1)
C(9)	4e	0.4810(3)	0.3757(2)	−0.2271(2)	0.032(2)	0.035(2)	0.039(2)	−0.001(1)	0.009(1)	−0.000(1)
C(10)	4e	0.5265(3)	0.3811(2)	−0.1098(3)	0.030(2)	0.036(2)	0.049(2)	−0.001(1)	0.006(1)	−0.003(2)
C(11)	4e	0.6285(4)	0.4366(2)	−0.0767(3)	0.050(2)	0.051(2)	0.057(2)	−0.011(2)	0.003(2)	−0.008(2)
C(12)	4e	0.6824(4)	0.4837(2)	−0.1570(4)	0.050(2)	0.038(2)	0.090(3)	−0.013(2)	0.017(2)	−0.007(2)
C(13)	4e	0.6389(4)	0.4778(2)	−0.2725(3)	0.057(2)	0.047(2)	0.069(3)	−0.008(2)	0.021(2)	0.004(2)
C(14)	4e	0.5399(4)	0.4248(2)	−0.3063(3)	0.055(2)	0.043(2)	0.052(2)	−0.001(2)	0.016(2)	0.002(2)
C(15)	4e	0.3768(3)	0.3231(2)	−0.2719(2)	0.045(2)	0.037(2)	0.030(2)	0.004(2)	0.008(1)	0.002(1)
C(16)	4e	0.1384(3)	0.1762(2)	−0.2294(2)	0.035(2)	0.032(2)	0.034(2)	0.002(1)	−0.003(1)	−0.003(1)

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