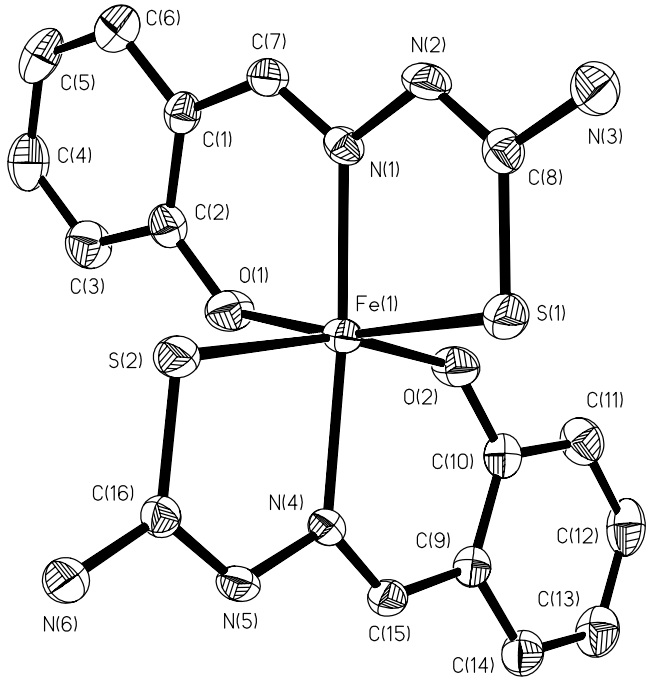
Crystal structure of [bis(2-hydroxybenzylidenethiosemicarbazone)-iron(II)] hydrate, $Fe(C_{16}H_{16}N_6O_2S_2) \cdot H_2O$

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

Received August 8, 2003, accepted and available on-line November 16, 2003; CCDC-No. 1267/1136



Abstract

$C_{16}H_{18}FeN_6O_3S_2$, monoclinic, $P12_1/n1$ (No. 14), $a = 8.9754(5)$ Å, $b = 18.229(1)$ Å, $c = 11.5546(7)$ Å, $\beta = 93.006(2)°$, $V = 1887.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.039$, $wR_{ref}(F^2) = 0.080$, $T = 293$ K.

Source of material

To a solution of salicylaldehyde (2.0 mmol) and thiosemicarbazide (2.0 mmol) in 35 mL of ethanol was added $Fe(SO_4)_2 \cdot 7H_2O$ (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 $Fe(C_8H_8N_3OS)_2 \cdot H_2O$ ($C_8H_8N_3OS$ is 2-hydroxybenzylidenethiosemicarbazono 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 $[Fe(C_{14}H_9N_2O_3)(CH_3OH)]_{10} \cdot 3CH_2Cl_2 \cdot 12.5CH_3OH \cdot 5H_2O$ [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 $[Fe(Am_4M)_2] \cdot ClO_4$ [2]. To form the two-dimensional structure, the molecules are connected to each other through intramolecular and intermolecular hydrogen bonds with d(N5···O3) = 2.832 Å and ∠N5–H5···O3 = 152.1°, d(O3···N2^a) = 3.218 Å and ∠O3–H31···N2^a = 163.7°, d(O3···S1^b) = 3.448 Å and ∠O3–H32···S1^b = 133.0°, d(N2···O3^c) = 3.218 Å and ∠N2–H2···O3^c = 156.0°, d(N3···O1^d) = 2.987 Å and ∠N3–H3A···O1^d = 172.0°, d(N6···O2^e) = 2.794 Å and ∠N6–H6A···O2^e = 159.4° (*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 × 0.15 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	10.52 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω/φ
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4311, 4311
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2416
$N(param)_{refined}$:	253
Programs:	SHELXS-97 [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

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

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

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)

Acknowledgment. We are grateful for financial support from the National Science Foundation of Fujian Province, China (No. E0210026).

References

1. Liu, S.-X.; Lin, S.; Lin, B.-Z.; Lin, C.-C.; Huang, J.-Q.: [30]Metallacrown-10 Compounds: $[Mn(C14H_9N_2O_3)(CH_3OH)]_{10} \cdot 5CH_2Cl_2 \cdot 16CH_3OH \cdot H_2O$ and $[Fe(C_{14}H_9N_2O_3)(CH_3OH)]_{10} \cdot 3CH_2Cl_2 \cdot 12.5CH_3OH \cdot 5H_2O$. Angew. Chem. Int. Ed. **40** (2001) 1084-1087.
2. West, D. X.; Swearingen, J. K.; Valdes-Martinez J.; Hernandez-Ovtega, S.; El-Sawaf A. K.; van Meurs F.; Castineiras, A.; Garcia, I.; Bermejo, E.: Sepectral and structural studies of iron(III), cobalt(II, III) and nickel(II) complexes of 2-pyridineformamide N(4)-methylthiosemicarbazone. Polyhedron **18** (1999) 2919-2929.
3. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-47.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.