Crystal structure of bis(*N*-(2-aminoethyl)salicylaldiminato)iron(III) isothiocyanide, $[\text{Fe}(\text{C}_9\text{H}_{11}\text{N}_2\text{O})_2][\text{NCS}]$

X. Feng, X. Han and L.-Y. Wang*

Luoyang Normal University, Department of Chemistry, Luoyang, Henan 471022, P. R. China

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Abstract

$\text{C}_{19}\text{H}_{22}\text{FeN}_5\text{O}_2\text{S}$, triclinic, $P\bar{1}$ (no. 2), $a = 9.613(1) \text{ \AA}$, $b = 9.913(1) \text{ \AA}$, $c = 10.869(2) \text{ \AA}$, $\alpha = 84.958(2)^\circ$, $\beta = 89.047(2)^\circ$, $\gamma = 86.098(1)^\circ$, $V = 1029.3 \text{ \AA}^3$, $Z = 2$, $R_{\text{gt}}(F) = 0.038$, $wR_{\text{ref}}(F^2) = 0.099$, $T = 291 \text{ K}$.

Source of material

The mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.122 g, 0.5 mmol) and NH_4SCN (0.192 g, 1 mmol) were refluxed in anhydrous methanol (15 mL) at a temperature of 60°C for 50 min, then were added 20 mL methanol solution of freshly distilled salicylaldehyde and ethylenediamine simultaneously. The mixture was stirred for 5 h, then filtered. The resulting clear solution was diffused with ethyl ether vapor at room temperature under ambient for three weeks. Block-like dark-red crystals were formed and collected by filtration and dried in air (yield 0.202 g, 46 %).

Discussion

Iron complexes play an important role in biological field, catalysis application and earth chemistry research [1–4]. Schiff base complexes containing different central metal atoms such as Zn, Cu, Ni and Ru have been studied in great detail for their various crystallographic features, enzymatic reactions and magnetic properties [5–7]. To the best of our knowledge, the iron(III) salicylaldehyde Schiff base complexes have been seldom reported [8,9]. At the same time, the study of octahedron complexes involving an aromatic Schiff base as the primary ligand, isothiocyanato ion as secondary ligand can serve as a useful model for gaining a better understanding of enzyme-metal ion-substrate complexes, which plays an important role in metalloenzyme-catalyzed biochemical reactions.

Based on the studies of the iron complexes and the salicylaldehyde Schiff base, in the present ferrum enzyme imitatorial investigation, an octahedral complex of iron(III) ion with sal-en Schiff base as ligand has been template synthesized and characterized. The asymmetric unit of the crystal structure consists of a discrete $[\text{Fe}(\text{sal-en})_2]^+$ cation and a counter isothiocyanato anion (figure, top). The central iron(III) ion is six-coordinated (FeN_4O_2) and the coordination polyhedron can be described as an distorted octahedron formed by the four nitrogen atoms of the ethylenediamine molecule part, and two hydroxyl oxygen atoms from salicylaldehyde molecule part. In the complex, the salicylaldehyde-ethylenediamine Schiff base molecule acts as tridentate chelate ligand, obviously, only one of the amidocyanogen group of the ethylenediamine was involved in the reaction to salicylaldehyde to obtain the sal-en Schiff base during the template synthesis. N1, N3, O2, N2 are occupied at equatorial positions, O1, N4, are occupied at apical positions. Fe1, N1, N2, C8, N9 form a cyclopentagonal ring, and Fe1, O1, N1, N2, C1, C2 form a cyclohexagonal ring. All the atoms of two six-membered rings are almost at the

* Correspondence author (e-mail: wlyy@lynu.edu.cn)

same plane, dihedral angle between the two plane is 99.9°, while the atoms of two five-membered rings are not co-planar. The bond lengths of Fe1—O1 and Fe1—N4 are 1.91(2) Å and 2.180(2) Å, respectively. The bond lengths of Fe1—O2, Fe1—N2, Fe1—N1, Fe1—N3, are 1.910(2) Å, 2.166(3) Å, 2.108(2) Å, 2.090(2) Å, respectively. The bond length of Fe1—N4 is slightly longer than that of Fe1—N3. The bond angles of O2—Fe1—N3 and O1—Fe1—N1 are 86.99(8)° and 86.98(9)°, and the bond angles of O2—Fe1—O1 and O1—Fe1—N3 are 101.0(1)°, 97.70(9)°, respectively. The bond length of S1—C19 is 1.637(4) Å, which is a little longer than the literature reported (1.162 Å) [10]. Meanwhile, there are several intermolecular hydrogen bonds

occurring between nitrogen atom from ethylenediamine and sulfur atom, which is from isothiocyanato ion of a neighboring molecule, N2—H2A...S1^{#1}, 3.544(3) Å, 150.4°, the bond length of N2—H2A...S1^{#1} is slightly longer than that reported in the literature (3.322 Å) [11], N2—H2B...N5, 3.099(4) Å, 60.2°, N4—H4A...S1^{#2}, 3.573(3) Å, 147.3°, N4—H4B...N5, 3.055(5) Å, 154.1°. The bond length of H2A...S1^{#1} is 2.73 Å, which does not fall in the region of 2.2 Å to 2.5 Å, and this leads to be presence of the weak hydrogen bonds [11]. Thus the structure of the complex can be viewed as a one-dimensional chain linked via the weak intermolecular hydrogen bonds (figure, bottom).

Table 1. Data collection and handling.

Crystal:	dark-red block, size 0.28 × 0.33 × 0.44 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	8.58 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\max}$:	50.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	5373, 3483
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2977
$N(\text{param})_{\text{refined}}$:	253
Program:	SHELXTL [12]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(2A)	2i	0.0071	0.3296	0.3527	0.071
H(2B)	2i	0.1108	0.4230	0.3808	0.071
H(4A)	2i	0.4616	0.3160	0.3228	0.069

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(4B)	2i	0.3540	0.4053	0.3752	0.069
H(3)	2i	0.3814	0.5163	-0.2111	0.076
H(4)	2i	0.5355	0.3824	-0.3155	0.098
H(5)	2i	0.6300	0.1822	-0.2204	0.099
H(6)	2i	0.5646	0.1101	-0.0223	0.086
H(7)	2i	0.2530	0.5679	-0.0350	0.058
H(8A)	2i	0.0753	0.6216	0.0917	0.078
H(8B)	2i	0.1656	0.6170	0.2117	0.078
H(9A)	2i	-0.0530	0.5548	0.2783	0.081
H(9B)	2i	-0.0570	0.4501	0.1780	0.081
H(12)	2i	-0.0303	-0.1793	0.3626	0.078
H(13)	2i	-0.2167	-0.2051	0.2416	0.091
H(14)	2i	-0.2659	-0.0510	0.0737	0.089
H(15)	2i	-0.1337	0.1304	0.0291	0.076
H(16)	2i	0.1656	-0.0678	0.4131	0.063
H(17A)	2i	0.4391	0.0529	0.3874	0.088
H(17B)	2i	0.3360	0.0234	0.4990	0.088
H(18A)	2i	0.2912	0.2518	0.5186	0.089
H(18B)	2i	0.4544	0.2264	0.5135	0.089

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	2i	0.22733(4)	0.26981(4)	0.21864(4)	0.0419(2)	0.0470(2)	0.0439(2)	-0.0121(2)	-0.0044(2)	0.0059(2)
S(1)	2i	0.25682(9)	0.75772(8)	0.63989(9)	0.0652(5)	0.0578(5)	0.0821(6)	-0.0068(4)	0.0099(5)	-0.0078(4)
O(1)	2i	0.3828(2)	0.2202(2)	0.1163(2)	0.056(1)	0.053(1)	0.067(1)	0.0058(9)	0.004(1)	0.010(1)
O(2)	2i	0.0797(2)	0.1929(2)	0.1390(2)	0.062(1)	0.058(1)	0.052(1)	-0.0194(9)	-0.018(1)	0.0067(9)
N(1)	2i	0.2127(2)	0.4576(2)	0.1110(2)	0.042(1)	0.041(1)	0.057(2)	-0.0060(9)	-0.003(1)	-0.001(1)
N(2)	2i	0.0708(2)	0.3848(3)	0.3193(2)	0.045(1)	0.075(2)	0.059(2)	-0.014(1)	0.007(1)	-0.008(1)
N(3)	2i	0.2367(2)	0.0950(2)	0.3415(2)	0.045(1)	0.061(1)	0.052(1)	-0.015(1)	-0.013(1)	0.012(1)
N(4)	2i	0.3748(2)	0.3200(3)	0.3552(2)	0.047(1)	0.068(2)	0.060(2)	-0.021(1)	-0.004(1)	-0.003(1)
N(5)	2i	0.2374(4)	0.5619(5)	0.4775(4)	0.121(3)	0.145(4)	0.082(2)	-0.050(3)	0.018(2)	-0.054(3)
C(1)	2i	0.4239(3)	0.2674(3)	0.0056(3)	0.041(1)	0.050(2)	0.058(2)	-0.013(1)	0.001(1)	-0.006(1)
C(2)	2i	0.3711(3)	0.3930(3)	-0.0528(3)	0.044(1)	0.051(2)	0.046(2)	-0.017(1)	-0.006(1)	-0.002(1)
C(3)	2i	0.4162(4)	0.4335(4)	-0.1730(3)	0.071(2)	0.071(2)	0.050(2)	-0.028(2)	0.004(2)	-0.002(2)
C(4)	2i	0.5093(4)	0.3549(4)	-0.2349(4)	0.095(3)	0.097(3)	0.063(2)	-0.051(2)	0.023(2)	-0.022(2)
C(5)	2i	0.5646(4)	0.2350(4)	-0.1784(4)	0.070(2)	0.088(3)	0.097(3)	-0.033(2)	0.038(2)	-0.042(2)
C(6)	2i	0.5245(3)	0.1912(3)	-0.0597(4)	0.055(2)	0.055(2)	0.105(3)	-0.009(2)	0.011(2)	-0.014(2)
C(7)	2i	0.2739(3)	0.4829(3)	0.0063(3)	0.049(2)	0.041(1)	0.054(2)	-0.010(1)	-0.010(1)	0.008(1)
C(8)	2i	0.1163(3)	0.5624(3)	0.1592(3)	0.062(2)	0.048(2)	0.085(2)	-0.003(1)	0.009(2)	-0.006(2)
C(9)	2i	0.0033(3)	0.4905(3)	0.2331(4)	0.047(2)	0.064(2)	0.092(3)	0.001(1)	0.010(2)	-0.009(2)
C(10)	2i	0.0039(3)	0.0887(3)	0.1692(3)	0.046(2)	0.046(1)	0.052(2)	-0.006(1)	-0.005(1)	-0.011(1)
C(11)	2i	0.0346(3)	-0.0065(3)	0.2707(3)	0.041(1)	0.048(2)	0.055(2)	-0.007(1)	-0.001(1)	-0.007(1)
C(12)	2i	-0.0506(3)	-0.1165(3)	0.2955(3)	0.062(2)	0.054(2)	0.081(2)	-0.018(1)	-0.007(2)	0.004(2)
C(13)	2i	-0.1612(4)	-0.1325(3)	0.2237(4)	0.064(2)	0.062(2)	0.106(3)	-0.027(2)	-0.009(2)	-0.009(2)
C(14)	2i	-0.1907(4)	-0.0396(3)	0.1236(4)	0.061(2)	0.067(2)	0.099(3)	-0.016(2)	-0.026(2)	-0.020(2)
C(15)	2i	-0.1111(3)	0.0690(3)	0.0965(3)	0.063(2)	0.058(2)	0.071(2)	-0.005(2)	-0.026(2)	-0.009(2)
C(16)	2i	0.1511(3)	0.0012(3)	0.3501(3)	0.051(2)	0.049(2)	0.056(2)	-0.008(1)	-0.005(1)	0.010(1)
C(17)	2i	0.3542(3)	0.0857(4)	0.4276(3)	0.059(2)	0.087(2)	0.071(2)	-0.024(2)	-0.030(2)	0.027(2)
C(18)	2i	0.3696(4)	0.2253(4)	0.4666(3)	0.064(2)	0.108(3)	0.051(2)	-0.033(2)	-0.019(2)	0.008(2)
C(19)	2i	0.2493(3)	0.6408(4)	0.5433(3)	0.048(2)	0.077(2)	0.063(2)	-0.006(2)	0.011(2)	-0.002(2)

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