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Instrumental Achievements

# Crystal Structure of Chloro[bis(5-bromo-salicylideniminephenyl)disulfide]-iron(III) Complex

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The complexes of transition metal ions with Schiff bases provide a large class of compounds of both stereochemical and magnetochemical interest due to their preparative accessibility, diversity and structural variability.[1] As part of a general study of complexes of polydentate Schiff base ligands, we became interested in ligands that contained sulfur donors. We report here the results of the reaction of iron(III) with the polydentate Schiff-base ligand formed from 5-bromo-salicylaldehyde and 2,2′-diaminophenyl disulfide. The investigated compound (Fig. 1) was synthesized according to a well-established method.[2]

The structure consists of monomeric iron(III) complexes with distorted octahedral coordination (Fig. 2). The iron(III) ion is coordinated by the two phenolic oxygens, the two imine nitrogens, one sulfur and one chlorine atom. In order to achieve this coordination, the ligands form three six membered chelate rings and one five-membered chelate ring. Two of the six-membered rings involve phenolic oxygens and imine nitrogens; for one of these rings, the imine nitrogen (N1) is also included in the five-membered ring and the phenolic oxygen (O1) is *trans* to the sulfur (S1) which is involved in the five-membered ring. The third six-membered ring includes both the uncoordinated and coordinated sulfurs and the second imine nitrogen. The distance between S2 and Fe1 is 3.8907(9)Å and S2 is not considered coordinated. The Fe1 and S1 bond length is 2.6060(8)Å. In the octahedral complexes chloro[bis(salicyl-ideniminephenyl)disulfide]iron(III)[2] and {bis[2-(2-oxido-1-naphthylmethylideneamino)phenyl]disulfide}chloroiron(III),[3] the corresponding distances are 2.536(4)Å and 2.5694(7)Å, respectively. All of the O–Fe–O, O–Fe–Cl, O–Fe–N, O–Fe–S, N–Fe–S and Cl–Fe–S angles deviate more or less from 90° and the "axial" arrangement. N2–Fe–Cl1, for example is found to be

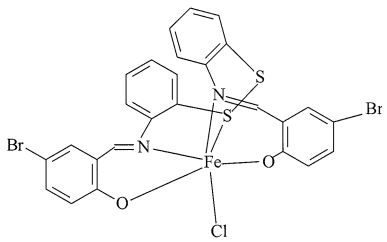


Fig. 1 Chemical structure.

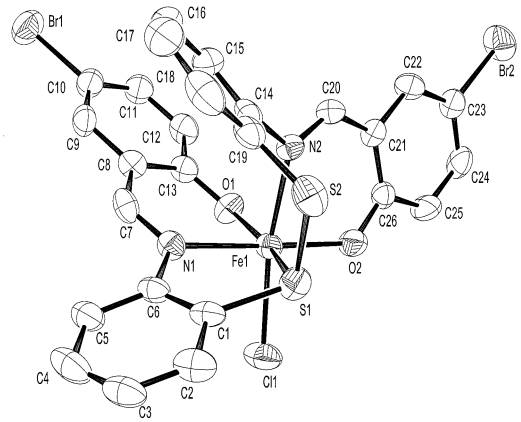


Fig. 2 The molecular structure of the title compound; showing the atom labeling scheme and 50% probability level displacement ellipsoids. All H atoms are omitted.

Table 1 Crystal and experimental data

| | |
|---|---|
| Formula: $C_{26}H_{16}Br_2ClFeN_2O_2S_2$ | |
| Formula weight: 703.65 | |
| Crystal system: monoclinic | |
| Space group: $P2_1/c$ | $Z = 4$ |
| $a = 8.925(1)$Å | |
| $b = 20.174(3)$ | $\beta = 100.73(1)^\circ$ |
| $c = 15.520(3)$ | |
| $V = 2745.6(7)$Å$^3$ | |
| $D_x = 1.702$ g/cm$^3$ | |
| $\mu$(Mo K$_\alpha$) = 3.74 cm$^{-1}$ | |
| Crystal size: 0.1 × 0.1 × 0.3 mm | |
| $\lambda$(Mo K$_\alpha$) = 0.71069 Å | |
| $2\theta$-$\omega$ scans with $2\theta_{max} = 52.0^\circ$ | |
| $R = 0.042$ | |
| $wR = 0.120$ | |
| Goodness-of-fit = 1.09 | |
| $(\Delta/\sigma)_{max} = 0.001$ | |
| $(\Delta\rho)_{max} = 0.415$ eÅ$^{-3}$ | |
| $(\Delta\rho)_{min} = -0.366$ eÅ$^{-3}$ | |
| No. of reflections used = 5376 | |
| Measurements: Enraf-Nonius CAD-4 diffractometer | |
| Program system: CAD-4 EXPRESS Software | |
| Structure determination: SHELXS86 | |
| Refinement: full-matrix least-squares (MolEN) | |

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

| Atom | *x* | *y* | *z* | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| C1 | -0.2416(3) | -0.2327(1) | 0.0445(2) | 2.79(6) |
| C2 | -0.3965(3) | -0.2362(2) | 0.0078(2) | 3.65(7) |
| C3 | -0.4674(3) | -0.1824(2) | -0.0338(2) | 3.73(7) |
| C4 | -0.3872(4) | -0.1255(2) | -0.0401(2) | 4.35(8) |
| C5 | -0.2326(3) | -0.1219(2) | -0.0046(2) | 3.32(6) |
| C6 | -0.1588(3) | -0.1748(1) | 0.0400(2) | 2.73(5) |
| C7 | 0.0607(3) | -0.1190(1) | 0.1036(2) | 2.89(6) |
| C8 | 0.2212(3) | -0.1074(1) | 0.1384(2) | 2.78(6) |
| C9 | 0.2645(3) | -0.0457(1) | 0.1769(2) | 3.25(7) |
| C10 | 0.4136(3) | -0.0327(1) | 0.2126(2) | 3.28(7) |
| C11 | 0.5240(3) | -0.0793(1) | 0.2083(2) | 3.52(6) |
| C12 | 0.4868(3) | -0.1396(2) | 0.1706(2) | 3.50(7) |
| C13 | 0.3344(3) | -0.1562(1) | 0.1334(2) | 2.73(5) |
| C14 | 0.0678(3) | -0.2181(1) | 0.2739(1) | 2.70(5) |
| C15 | 0.1387(3) | -0.1653(1) | 0.3193(2) | 3.35(6) |
| C16 | 0.0595(4) | -0.1220(2) | 0.3643(2) | 4.50(8) |
| C17 | -0.0914(5) | -0.1316(2) | 0.3615(2) | 5.04(10) |
| C18 | -0.1671(4) | -0.1829(2) | 0.3148(2) | 4.63(9) |
| C19 | -0.0892(3) | -0.2276(1) | 0.2697(2) | 3.17(6) |
| C20 | 0.2621(3) | -0.2938(1) | 0.2808(2) | 2.64(5) |
| C21 | 0.3635(2) | -0.3418(1) | 0.2545(2) | 2.43(5) |
| C22 | 0.4787(3) | -0.3669(1) | 0.3212(2) | 2.96(6) |
| C23 | 0.5715(3) | -0.4180(1) | 0.3026(2) | 2.86(6) |
| C24 | 0.5557(3) | -0.4432(1) | 0.2198(2) | 3.69(7) |
| C25 | 0.4436(4) | -0.4187(1) | 0.1537(2) | 3.77(7) |
| C26 | 0.3453(3) | -0.3689(1) | 0.1703(2) | 2.58(5) |
| N1 | -0.0006(2) | -0.1749(1) | 0.0763(1) | 2.64(5) |
| N2 | 0.1507(2) | -0.26417(9) | 0.2313(1) | 2.32(4) |
| O1 | 0.3036(2) | -0.21363(9) | 0.0973(1) | 3.09(4) |
| O2 | 0.2339(2) | -0.35020(9) | 0.1065(1) | 3.24(4) |
| Cl1 | 0.04107(8) | -0.28971(4) | -0.05728(4) | 4.08(2) |
| Fe1 | 0.12807(4) | -0.26752(2) | 0.08852(2) | 2.44(1) |
| Br1 | 0.47141(4) | 0.05053(2) | 0.26348(3) | 4.84(1) |
| Br2 | 0.71739(3) | -0.45328(2) | 0.39564(2) | 4.58(1) |
| S1 | -0.14845(7) | -0.30407(3) | 0.09799(5) | 3.20(2) |
| S2 | -0.19108(8) | -0.29741(4) | 0.22412(5) | 3.82(2) |

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Bond distances (Å) and angles (˚)

| | | | |
|---|---|---|---|
| C(1) – S(1) | 1.788(3) | C(6) – N(1) | 1.420(3) |
| C(7) – N(1) | 1.290 (3) | C(10) – Br(1) | 1.885(3) |
| C(13) – O(1) | 1.295(3) | C(14) – N(2) | 1.425(3) |
| C(19) – S(2) | 1.752(3) | C(20) – N(2) | 1.285(3) |
| C(23) – Br(2) | 1.894(2) | C(26) – O(2) | 1.321(3) |
| N(1) – Fe(1) | 2.182(2) | N(2) – Fe(1) | 2.188(2) |
| O(1) – Fe(1) | 1.891(2) | O(2) – Fe(1) | 1.911(2) |
| Cl(1) – Fe(1) | 2.2955(8) | Fe(1) – S(1) | 2.6060(8) |
| S(1) – S(2) | 2.067(1) | | |

| | | | |
|---|---|---|---|
| O(1) – Fe(1) – O(2) | 96.37(8) | O(1) – Fe(1) – N(1) | 85.97(8) |
| O(2) – Fe(1) – N(1) | 175.74(8) | O(1) – Fe(1) – N(2) | 89.42(8) |
| O(2) – Fe(1) – N(2) | 85.94(7) | N(1) – Fe(1) – N(2) | 90.53(7) |
| O(1) – Fe(1) – Cl(1) | 107.89(6) | O(2) – Fe(1) – Cl(1) | 92.34(6) |
| N(1) – Fe(1) – Cl(1) | 90.32(6) | N(2) – Fe(1) – Cl(1) | 162.69(6) |
| O(1) – Fe(1) – S(1) | 159.93(6) | O(2) – Fe(1) – S(1) | 101.08(6) |
| N(1) – Fe(1) – S(1) | 76.03(6) | N(2) – Fe(1) – S(1) | 82.05(5) |
| Cl(1) – Fe(1) – S(1) | 81.39(3) | S(2) – S(1) – Fe(1) | 112.23(4) |

162.69(6)˚ only, instead of 180˚. The two Fe–O bond distances are only slightly different and are similar to those found in other structures.[2,3] The two Fe–N bond distances are almost identical. The sulfur–sulfur distance of 2.0669(12)Å is in good agreement with the values found for the other similar structure.[2,3] The magnetic moment of the compound, 5.91 BM, is a normal value for high-spin iron(III). The crystal structure was solved by direct methods.[4] All the non-hydrogen atoms were refined anisotropically. The positions of the H atoms bonded to C atoms were calculated, and refined using a riding model, and H atom displacement parameters were restricted to be 1.2$U_{eq}$ of the parent atom. Table 1 shows the crystal and experimental data, while final atomic parameters are given in Table 2. The bond distances and angles are shown in Table 3.

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