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Crystal Structure of Chloro[bis(5-chlorosalicylideniminephenyl)disulfido]-iron(III) Complex

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The complexes of transition metal ions with Schiff bases are a large and growing class of compounds of both stereochemical and magnetochemical interest. The nature of the Schiff-base complexes appears to be dependent on several factors: these include the solvent system, steric constraints imposed by ligand side groups, crystal packing considerations and hybridization states defined by the metal atom. However, it has been observed that on rare occasions some other factors, which include coordination preferences of the metal ion and specific intermolecular interactions, may also effect the result.[1,2] As part of a general study of complexes of polydentate Schiff's base ligands, we became interested in ligands that contain sulfur donors. We report here the results of the reaction of iron(III) with the polydentate Schiff-base ligand formed from 5-chloro-salicylidene and 2,2′-diaminophenyl disulfide. The investigated compound (Fig. 1) was synthesized according to a well-established method.[3]

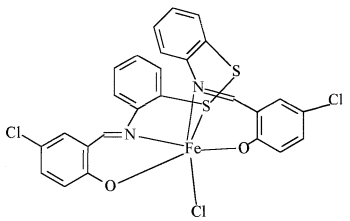

Fig. 1 Chemical structure.

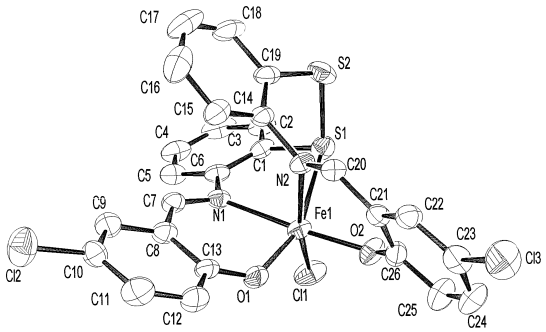

Fig. 2 The molecular structure of the title compound, showing the atom labeling scheme and 50% probability level displacement ellipsoids. All H atoms are omitted.

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 and 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 3.881(1)Å and S2 is not considered coordinated. 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 162.7(1)° only, instead of 180°. The two Fe–O bond distances are only slightly different and are similar to those found in other structures.[3,4] The two Fe–N bond distances show a similar difference in comparison with other structures.[3,4] The sulfur–sulfur distance of 2.059(1)Å is in good agreement with the values found for the other similar structure.[1,4] The magnetic moment of the compound, 5.93 BM,

Table 1 Crystal and experimental data

Formula: $C_{26}H_{16}Cl_3FeN_2O_2S_2$	
Formula weight: 614.73	
Crystal system: monoclinic	
Space group: $P2_1/c$	$Z = 4$
a = 8.926(2)Å	
b = 19.724(3)	β = 100.97(3)°
c = 15.393(7)	
V = 2660.6(1)Å^3	
D_x = 1.535 g/cm^3	
R = 0.050	wR = 0.122
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 0.286 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.370 eÅ^3	
No. of reflections used = 5197	
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 parameter

Atom	*x*	*y*	*z*	B_{eq}/Å^2
C1	-0.2429(2)	0.7298(2)	0.5467(2)	2.43(4)
C2	-0.3981(2)	0.7334(2)	0.5097(2)	3.03(4)
C3	-0.4692(2)	0.6776(2)	0.4685(2)	3.93(5)
C4	-0.3867(2)	0.6195(2)	0.4624(2)	3.51(4)
C5	-0.2332(2)	0.6157(2)	0.4983(2)	2.94(4)
C6	-0.1598(2)	0.6714(2)	0.5415(2)	2.29(3)
C7	0.0602(2)	0.6149(2)	0.6066(2)	2.57(4)
C8	0.2201(2)	0.6041(3)	0.6408(2)	2.59(4)
C9	0.2633(2)	0.5393(2)	0.6818(2)	3.08(5)
C10	0.4138(2)	0.5268(2)	0.7169(2)	2.64(4)
C11	0.5243(2)	0.5753(2)	0.7135(3)	3.56(5)
C12	0.4850(2)	0.6378(3)	0.6726(2)	3.14(4)
C13	0.3331(2)	0.6535(3)	0.6365(2)	2.33(4)
C14	0.0673(2)	0.7182(3)	0.7781(2)	2.30(3)
C15	0.1410(2)	0.6643(2)	0.8246(2)	3.06(4)
C16	0.0606(3)	0.6206(2)	0.8689(2)	4.73(6)
C17	-0.0903(3)	0.6291(2)	0.8659(2)	4.67(6)
C18	-0.1653(2)	0.6817(2)	0.8182(3)	3.87(5)
C19	-0.0899(2)	0.7274(2)	0.7732(2)	2.72(4)
C20	0.2619(2)	0.7956(2)	0.7841(2)	2.10(3)
C21	0.3627(2)	0.8440(2)	0.7564(2)	2.13(3)
C22	0.4794(2)	0.8687(2)	0.8221(2)	2.69(4)
C23	0.5757(2)	0.9189(2)	0.8013(3)	3.05(4)
C24	0.5606(2)	0.9442(2)	0.7175(2)	3.53(5)
C25	0.4449(2)	0.9200(2)	0.6530(3)	3.60(5)
C26	0.3453(2)	0.8707(2)	0.6719(2)	2.54(4)
N1	-0.0014(2)	0.6712(2)	0.5789(2)	2.28(3)
N2	0.1505(2)	0.7649(2)	0.7345(2)	2.27(3)
O1	0.3011(2)	0.7116(2)	0.5998(2)	2.81(3)
O2	0.2311(2)	0.8510(2)	0.6072(2)	3.03(3)
S1	-0.15058(5)	0.80365(2)	0.59878(3)	2.85(1)
S2	-0.19275(5)	0.79803(2)	0.72553(3)	3.44(1)
Cl1	0.03832(6)	0.78932(3)	0.44331(3)	3.91(1)
Cl2	0.46846(7)	0.44971(3)	0.76357(4)	4.76(2)
Cl3	0.71711(6)	0.95103(3)	0.88653(4)	4.51(2)
Fe1	0.12593(3)	0.76715(2)	0.59014(2)	2.33(1)

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

is a normal value for high-spin iron(III). All H atoms bonded to C atoms were refined using a riding model and H-atom displacement parameters were restricted to be $1.2U_{eq}$ 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.

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

C1 - C6	1.380(2)	C1 - C2	1.395(3)
C1 - S1	1.787(2)	C2 - C3	1.365(3)
C3 - C4	1.375(3)	C4 - C5	1.379(3)
C5 - C6	1.384(3)	C6 - N1	1.421(2)
C7 - N1	1.275(2)	C7 - C8	1.440(2)
C8 - C13	1.413(2)	C8 - C9	1.446(3)
C9 - C10	1.371(3)	C10 - C11	1.381(3)
C10 - Cl2	1.713(2)	C11 - C12	1.398(3)
C12 - C13	1.399(2)	C13 - O1	1.286(2)
C14 - C15	1.378(3)	C14 - C19	1.403(3)
C14 - N2	1.428(2)	C15 - C16	1.381(3)
C16 - C17	1.350(4)	C17 - C18	1.370(3)
C18 - C19	1.386(3)	C19 - S2	1.751(2)
C20 - N2	1.284(2)	C20 - C21	1.431(2)
C21 - C26	1.384(2)	C21 - C22	1.395(2)
C22 - C23	1.389(3)	C23 - C24	1.365(3)
C23 - Cl3	1.756(2)	C24 - C25	1.374(3)
C25 - C26	1.385(2)	C26 - O2	1.340(2)
N1 - Fe1	2.197(2)	N2 - Fe1	2.192(2)
O1 - Fe1	1.891(2)	O2 - Fe1	1.895(2)
S1 - S2	2.059(1)	S1 - Fe1	2.599(1)
Cl1 - Fe1	2.289(1)		
C6 - C1 - C2	121.5(2)	C6 - C1 - S1	119.9(2)
C2 - C1 - S1	118.6(2)	C3 - C2 - C1	119.1(2)
C2 - C3 - C4	119.7(2)	C3 - C4 - C5	121.5(2)
C4 - C5 - C6	119.5(2)	C1 - C6 - C5	118.7(2)
C1 - C6 - N1	118.9(2)	C5 - C6 - N1	122.4(2)
N1 - C7 - C8	125.8(2)	C13 - C8 - C7	123.2(2)
C13 - C8 - C9	119.8(2)	C7 - C8 - C9	117.0(2)
C10 - C9 - C8	119.4(2)	C9 - C10 - C11	120.9(2)
C9 - C10 - Cl2	120.2(2)	C11 - C10 - Cl2	118.8(2)
C10 - C11 - C12	120.3(2)	C11 - C12 - C13	121.1(2)
O1 - C13 - C12	119.4(2)	O1 - C13 - C8	122.3(2)
C12 - C13 - C8	118.3(2)	C15 - C14 - C19	120.1(2)
C15 - C14 - N2	120.2(2)	C19 - C14 - N2	119.7(2)
C14 - C15 - C16	119.8(2)	C17 - C16 - C15	120.9(2)
C16 - C17 - C18	119.7(2)	C17 - C18 - C19	121.8(2)
C18 - C19 - C14	117.7(2)	C18 - C19 - S2	117.5(2)
C14 - C19 - S2	124.4(2)	N2 - C20 - C21	126.7(2)
C26 - C21 - C22	118.9(2)	C26 - C21 - C20	124.7(2)
C22 - C21 - C20	116.2(2)	C23 - C22 - C21	119.5(2)
C24 - C23 - C22	121.5(2)	C24 - C23 - Cl3	120.2(2)
C22 - C23 - Cl3	118.3(2)	C23 - C24 - C25	118.9(2)
C24 -C25 - C26	121.0(2)	O2 - C26 - C21	121.4(2)
O2 - C26 - C25	118.4(2)	C21 - C26 - C25	120.2(2)
C7 - N1 - C6	118.0(2)	C7 - N1 - Fe1	122.7(1)
C6 - N1 - Fe1	119.3(1)	C20 - N2 - C14	116.0(2)
C20 - N2 - Fe1	120.6(1)	C14 - N2 - Fe1	121.9(1)
C13 - O1 - Fe1	131.4(1)	C26 - O2 - Fe1	130.0(1)
C1 - S1 - S2	103.3(1)	C1 - S1 - Fe1	96.5(1)
S2 - S1 - Fe1	112.4(1)	C19 - S2 - S1	105.3(1)
O1 - Fe1 - O2	96.6(1)	O1 - Fe1 - N2	89.3(1)
O2 - Fe1 - N2	85.8(1)	O1 - Fe1 - N1	85.1(1)
O2 - Fe1 - N1	176.1(1)	N2 - Fe1 - N1	90.8(1)
O1 - Fe1 - Cl1	108.1(1)	O2 - Fe1 - Cl1	92.1(1)
N2 - Fe1 - Cl1	162.7(1)	N1 - Fe1 - Cl1	90.7(1)
O1 - Fe1 - S1	159.3(1)	O2 - Fe1 - S1	101.6(1)
N2 - Fe1 - S1	82.3(1)	N1 - Fe1 - S1	76.2(1)
Cl1 - Fe1 - S1	81.3(1)		

References

1. A. Elmali, Y. Elerman, I. Svoboda, H. Fuess, K. Griesar, and W. Haase, *Z. Naturforsch*., **1994**, *49b*, 365.
2. A. Elmali, Y. Elerman, I. Svoboda, and H. Fuess, *Acta Crystallogr*., **1993**, *C49*, 1365.
3. J. A. Bertrand and J. L. Breece, *Inorg. Chim. Acta*, **1974**, *8*, 267.
4. M. Gerloch and F. E. Mabbs, *J. Chem. (A)*, **1967**, 1598.