A Unique Mononuclear Iron(III) Complex with the Binucleating Ligand 2,6-Bis[*N*-(2-pyridylethyl)-iminomethyl]-4-methylphenol

MASAHIRO MIKURIYA*, KEIKO KUSHIDA

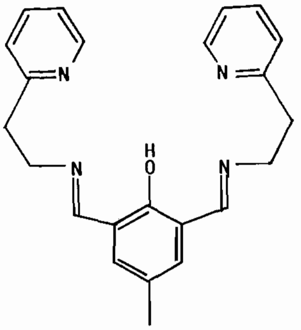
Department of Chemistry, School of Science,
Kwansei Gakuin University, Uegahara, Nishinomiya 662
(Japan)

HIROKAZU NAKAYAMA, WASUKE MORI
and MICHIHIKO KISHITA

Institute of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560 (Japan)

(Received May 10, 1989; revised July 31, 1989)

Binuclear iron complexes have attracted considerable attention since binuclear iron units were found in iron proteins such as hemerythrin, purple acid phosphatase, ribonucleotide reductase and methane monooxygenase [1]. By using a variety of ligands, synthetic model complexes have been reported. In the course of our investigation of binuclear iron complexes with the binucleating ligand 2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol (HL), we have isolated a novel mononuclear complex, [Fe(HL)Cl$_3$]. The ligand HL has been used to obtain binuclear copper [2, 3] and manganese [4] complexes. In this paper, we report the synthesis, spectral and magnetic properties, and X-ray crystal structure of the unique mononuclear iron(III) complex.



HL

The complex was prepared as follows. 2,6-Diformyl-4-methylphenol [5] (82 mg) and 2-(2-aminoethyl)pyridine (125 mg) were dissolved in 6 ml of methanol. Then iron(III) chloride hexahydrate (270 mg) and CH$_3$COONa (40 mg) were successively added. The mixture was stirred and filtered; a slow evaporation gave black crystals. *Anal.* Found: C, 51.19; H, 4.67; N, 10.25; Fe, 9.88. Calc. for Fe(C$_{23}$H$_{24}$N$_4$O)Cl$_3$: C, 51.67; H, 4.52; N, 10.49; Fe, 10.44%.

The electronic spectrum of the complex in methanol shows two absorptions in the visible region (18.1 × 10^3 cm^{-1} (ϵ = 1540 mol^{-1} dm^3 cm^{-1}), 22.3 × 10^3 cm^{-1} (ϵ = 6010 mol^{-1} dm^3 cm^{-1})). These bands can be attributed to the Cl → Fe and O(phenolate) → Fe LMCT bands, suggesting the coordination of the chloride ions and phenolate oxygen atom to the iron atom. There is no appreciable absorption in the region below 18.1 × 10^3 cm^{-1}. This is compatible with the high-spin electronic configuration of the iron(III) ion. In the high-frequency region, two strong bands arising from the Schiff base ligand are observed at 25.2 × 10^3 cm^{-1} (ϵ = 7630 mol^{-1} dm^3 cm^{-1}) and 39.1 × 10^3 cm^{-1} (ϵ = 31 500 mol^{-1} dm^3 cm^{-1}) [4].

The magnetic moment of the complex is 5.90 BM (at 294 K), which is close to the spin-only value for high-spin d^5 electronic configuration. The magnetic susceptibilities were measured over the temperature range 4.2–300 K. The magnetic data obey the Curie–Weiss law, $\chi_M = C/(T - \theta)$ with $\theta = -3$ K, indicating that the magnetic interaction is very weak (Fig. 1).

In order to elucidate the molecular structure (Fig. 2), the X-ray structure analysis of the complex was undertaken. Crystal data are: C$_{23}$H$_{24}$Cl$_3$FeN$_4$O, M = 534.7, monoclinic, space group $C2/c$, a = 18.946(3), b = 11.140(2), c = 23.261(4) Å, β = 95.90(2), V = 4883.3(15) Å^3, D_c = 1.454, D_m = 1.45 g cm^{-3}, Z = 8, μ(Mo Kα) = 9.7 cm^{-1}. A structure solution and refinement based on 2068 reflections with $|F_o| > 3\sigma(F)$ converged with a conventional

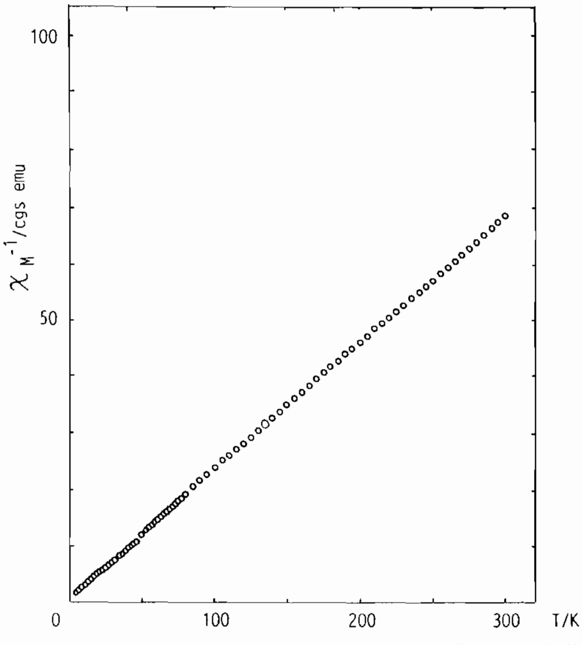


Fig. 1. Temperature dependence of the magnetic susceptibility of [Fe(HL)Cl$_3$].

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

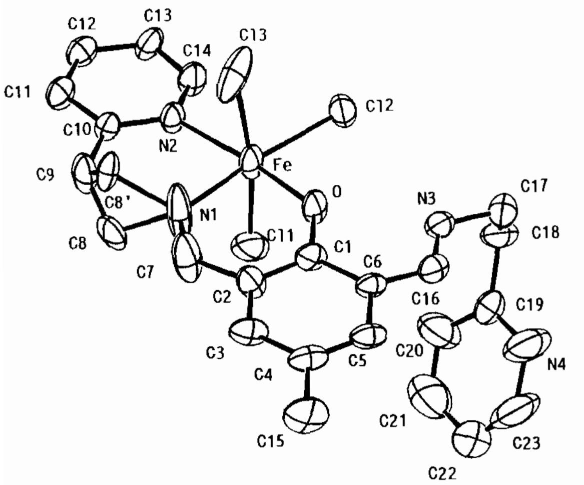


Fig. 2. Molecular structure of [Fe(HL)Cl_3]. Selected bond lengths (Å) and angles (°): Fe–O, 1.957(7); Fe–N(1), 2.137(9); Fe–N(2), 2.207(7); Fe–Cl(1), 2.329(3); Fe–Cl(2), 2.341(3); Fe–Cl(3), 2.351(3); O–Fe–N(1), 84.8(4); O–Fe–Cl(2), 86.4(2); N(1)–Fe–N(2), 89.4(4); N(2)–Fe–Cl(2), 99.5(2); Cl(1)–Fe–Cl(3), 171.0(1).

discrepancy factor of 0.079. In the course of the refinement it became apparent that the carbon atom C(8) is subjected to disorder. The carbon atom was divided into two positions with an occupancy factor of 0.5. In harmony with the spectral and magnetic properties, the molecule is a mononuclear complex [Fe(HL)Cl_3] where the octahedral coordination around the iron atom is formed by three chloride ions and three donor atoms (a phenolate oxygen, an imino nitrogen, and a pyridyl nitrogen) of the binucleating ligand. The phenolic proton seems to be close to the imino nitrogen rather than the pyridyl nitrogen, since no direct evidence of a protonated form of the pyridyl group is available from the infrared spectra. Positional parameters and temperature factors are shown in Table 1.

It is worth noting that the mononuclear complex has been isolated, because the first step in the synthesis of heterometal binuclear complexes consists of preparing the mononuclear species. The present result suggests a synthetic route for preparing heterometal complexes with the binucleating ligand having equivalent coordination sites. Such a study is now under way.

TABLE 1. Positional parameters (×10^4) and equivalent isotropic temperature factors (Å^2)

Atom	x	y	z	B_{eq}
Fe	1932(1)	1746(1)	1620(1)	6.3
Cl(1)	2934(2)	1815(3)	2288(1)	10.1
Cl(2)	2235(1)	−105(2)	1237(1)	6.4
Cl(3)	821(2)	1774(4)	1066(1)	11.1
O	2433(3)	2480(5)	1014(3)	6.9
N(1)	1706(7)	3554(7)	1847(5)	14.1
N(2)	1369(4)	1109(6)	2346(3)	4.8
N(3)	3344(3)	1602(6)	374(3)	5.1
N(4)	5147(5)	1444(11)	590(5)	12.9
C(1)	2650(5)	3573(8)	916(3)	5.2
C(2)	2413(5)	4611(8)	1191(4)	5.9
C(3)	2629(5)	5761(8)	1055(4)	5.9
C(4)	3096(5)	5906(8)	630(4)	6.3
C(5)	3354(5)	4888(8)	357(4)	5.7
C(6)	3142(4)	3711(8)	497(3)	4.6
C(7)	1939(8)	4523(9)	1655(5)	11.3
C(8)	1688(11)	3690(16)	2594(9)	7.6
C(8′)	922(9)	3725(15)	2119(7)	5.0
C(9)	1066(6)	3153(8)	2641(5)	7.9
C(10)	1024(4)	1817(7)	2698(3)	4.6
C(11)	647(5)	1313(8)	3130(4)	5.3
C(12)	634(4)	85(8)	3197(4)	5.2
C(13)	1005(5)	−664(8)	2847(4)	5.8
C(14)	1374(5)	−90(8)	2433(4)	6.6
C(15)	3350(6)	7188(9)	483(5)	9.3
C(16)	3474(4)	2715(8)	246(3)	5.3
C(17)	3730(5)	572(9)	155(4)	6.2
C(18)	4202(5)	6(9)	661(4)	6.8
C(19)	4757(5)	875(8)	923(4)	5.8
C(20)	4807(7)	1085(12)	1496(5)	10.6
C(21)	5312(8)	1926(14)	1720(6)	14.2
C(22)	5778(7)	2460(12)	1396(6)	11.3
C(23)	5636(7)	2278(15)	836(6)	14.3

References

1 S. J. Lippard, *Angew. Chem., Int. Ed. Engl., 27* (1988) 344.
2 J. J. Grzybowski, P. H. Merrell and F. L. Urbach, *Inorg. Chem., 17* (1978) 3078.
3 R. R. Gagne, R. P. Kreh and J. A. Dodge, *J. Am. Chem. Soc., 101* (1979) 6917.
4 M. Mikuriya, Y. Kawasaki, T. Tokii, S. Yanai and A. Kawamori, *Inorg. Chim. Acta, 156* (1989) 21.
5 H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn., 45* (1972) 1759.