A New Class of Bridged Diiron(III) Complex with a Schiff-base Bridge: Structure and Magnetic Properties of Di- *N,N'*-trimethylene bissalicylidenimine(bis-*N,N'*-trimethylenebissalicylideniminato)iron(III)

N. K. Chandra Babu, Balachandran Unni Nair,* T. Ramasami,* Mikio Yamasaki,† and Takashi Shibahara†
Chemical Laboratory, Central Leather Research Institute, Adyar, Madras 600020, India
†*Department of Chemistry, Okayama University of Science, 1-1, Ridai-Cho, Okayama 700*

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Schiff base, salprn has been shown to bridge two Fe(III) ions and give rise to a diiron(III) complexes with practically no magnetic coupling between the two iron(III) centres.

In the last few years, the interest in proteins having binuclear iron functional centres has greatly increased,[1-5] a trend that has been paralleled by an increase in the number of synthetic binuclear iron model compounds. [6-9] The majority of these compounds are comprised of binuclear iron(III) cores with two bridging carboxylates and a bridging oxo group mimicking the active site of Hemerythrin. Nevertheless combined magnetic and structural information is available only for a limited number of iron(III) dimeric compounds.[10,11] Schiff base complexes of transition metal ions, particularly iron(III) and manganese(III) have been extensively investigated as models for metalloenzymes.[12-15] Both mono- and di-nuclear complexes of iron(III) with N,N-ethylenebis(salicylidine)imine, salen, have been reported earlier.[16,17] The dinuclear complexes of Schiff bases reported earlier were associated with di-μ-oxo or di-μ-hydroxo bridging groups generally; although there exists one report, where two oxygen atoms derived from two independent salen ligands (each coordinated to two independent iron atoms) serve as bridging donor atoms.[16] In the case of manganese(III),a dimer of the formulation $Mn_2(salprn)_3$ has been reported.[15] Single crystal X-ray structure of the complex reveals that the two Mn(III) ions are bridged by one set of N and O donor atoms of the Schiff base. In this investigation an Fe(III) analogue to the Mn(III) dimer is reported.

For the Synthesis of di-μ-N,N'-trimethylenebis-salicylidinimin (bis-N,N'-trimethylenebis-salicylidiniminato),1. Ferrous sulphate hexahydrate (2.7 g, 0.01 mol) was refluxed in 200 mL of dry THF for 1 h. To this slurry were added salicylaldehyde (2.4 g, 0.02 mol) and 1,3-diaminopropane (0.74 g, 0.01 mol). The reaction mixture was refluxed further for a period of 1 h. The volume of the reaction mixture was reduced to 50 mL using rotary evaporator and a large excess of petroleum ether was added to precipitate the desired compound.[18] The crude product was recrystallized from acetonitrile to obtain red brown needle shaped crystal suitable for structure determination.[19]

Even though the synthetic strategy employed was to complex iron(II) with the ligand and its subsequent oxidation to the iron(III) state by molecular oxygen, no oxo bridged diiron(III) complex was formed as evident from the lack of any infra red band assignable to Fe-O-Fe frequency in the infra red spectrum of the complex. The X-ray crystal structure of the molecule shows it to be dimeric with each iron(III) ion coordinated to the donor atoms of one salprn ligand and a set of O and N atoms of another quadridentate Schiff base ligand, salprn, as shown in the ORTEP diagram (Figure1).

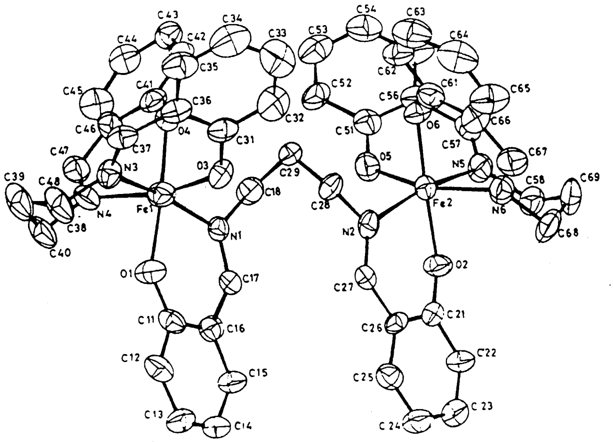

Figure 1. ORTEP diagram of $Fe_2(salprn)_3$ with selected bond lengths (Å) : Fe1-O1 1.946(4), Fe1-O3 1.912(4), Fe1-O4 1.950(4), Fe1-N1 2.177(4), Fe1-N3 2.162(4), Fe1-N4 2.142(5), Fe2-O2 1.944(4), Fe2-O5 1.937(4), Fe2-O6 1.967(4), Fe2-N2 2.185(4), Fe2-N5 2.163(4), Fe2-N6 2.181(5).

The dinuclear complex contains two Salprn ligands in the *cis*-ß geometry with a third acting as a binucleating agent which occupies the two remaining cis positions on each iron center. It is of interest to note that no single donor atom is shared between the two iron(III) centers in this dimeric complex. This appears to be the first report where two iron(III) ions are bridged by a Schiff base ligand like salprn. This structure differs from previous example in which salen is a bridging ligand, in the mode and nature of bridging.[16] Another feature of the structure reported in this work is that there is a considerable distortion in the octahedral environment around both iron(III) ions. Large deviations of valence angles from strain free values are observed in the arrangements of both donor atoms around Fe(III) centers and the methylene units in the backbone of the ligands. The valence angles in the coordination environment around Fe(III) ions range from 83.2 to 101.2° as against the strain free value of 90° for an octahedron. Similarly the valence angle in the central methylene unit of the bridging Schiff base C18-C29-C28 is 118.2° which deviates significantly from the strain free angle around a tetrahedral carbon. Typically, the bond angles O1-Fe1-O4, O3-Fe1-N4 and N1-Fe1-N3 are 172.8, 164.8 and 169.5° respectively. A similar arrangement around Fe2 center is also evident from the observed bond angles O2-Fe2-O6, O5-Fe2-N6 and N2-Fe2-N5 being 169.7, 162.7 and 168.5° respectively. In other words, there is considerable deviation from 180° expected for a regular octahedral environment around each iron center. In the case of manganese(III) salprn dimer each salicylidineiminato moiety was

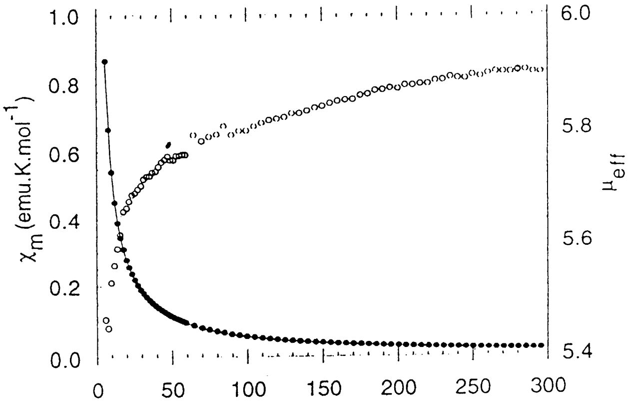

Figure 2. Temperature dependence of magnetic susceptibility. Solid line, theoretical fit for J = -0.067 + 0.0027 cm^{-1}.

bent about a line through its oxygen and nitrogen donor atoms.[20] The folding of the salicylidiniminato residue in the manner observed for manganese(III) derivative was reported to be a necessary condition for the coplanar bonding to be maintained about the manganese atom. In the iron(III) dimer reported in this study, the folding of trimethylene groups in the salprn ligand is of interest. The two iron(III) ions in the dimer are bridged by two independent nitrogen donor sites, N1 and N2 connected by the trimethylene bridge. The folding of this trimethylene bridge would be expected to determine the metal-metal distance and orientation in the new complex reported in this study. Such type of Schiff base bridging between two Fe(III) centres is being reported for the first time.

Studies on the long range electron transfer reactions have proved the existence of long range coupling of metal centres. Hence, it becomes important to know whether a Schiff base type bridging ligand will be capable of such a long range coupling between two metal centres. Magnetic susceptibility data were collected using a SQUID susceptometer working at 0.5 T field strength in the 6-300 K temperature range. The SQUID output were corrected for the contribution of the sample holder and for the diamagnetism of the constituent atoms by use of the Pascal constant. The magnetic moment of the diiron(III) complex decreases from 6.92 BM at 300 K to 6.48 BM at 6 K indicating that the coupling is indeed very weak. The temperature dependent magnetic behaviour was modeled using the theory of Heisenberg, Dirac and Van Vleck for magnetic coupling in a binuclear system. Neither spin-orbit coupling nor zero field splitting have been modeled. The expression for the temperature dependent susceptibility has been derived from the general isotropic exchange Hamiltonian

$H = -2J\,S_1S_2$ where $S_1 = S_2 = 5/2$ as;

$$\chi_m = \frac{Ng^2ß^2}{kt} \bullet \frac{2e^{2x}+10e^{6x}+28e^{12x}+60e^{20x}+110e^{30x}}{1+3e^{2x}+5e^{6x}+7e^{12x}+9e^{20x}+11e^{30x}}$$

where x = J/kT. A reasonable fit of the experimental data has been obtained with J = -0.067 + 0.0027 cm^{-1} and g = 1.92 (Figure2).

The magnitude of J demonstrates that the antiferromagnetic coupling between the two iron(III) centers is nearly negligible.

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18 Analytical Data: Found: C, 64.25; H, 5.23; N, 9.71; Fe, 11.12%. Calc. For $Fe_2(salprn)_3.CH_3CN$: C, 64.07; H, 5.13 N, 9.87; Fe, 11.24%.

19 Crystal data. $Fe_2O_6N_7C_{53}H_{51}$, 0.17 x 0.16 x 0.15 mm, M = 993.73, monoclinic, space group $P2_1/a$, a = 21.650 (3), b = 15.845 (3), c = 15.316(2)Å, β = 108.76(1)°, *U* = 4975.7(12) Å^3, Z = 4, D_c = 1.327 g cm^{-3}, μ(Mo-K_α) = 5.89 cm^{-1}, T = 22°C, $R = \Sigma|\,|F_o| - |F_c|\,|/\Sigma|F_0|$ = 7.41, $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$ = 9.29, $w = 1/[(\sigma|F_o|)^2 + g|F_o|^2]$, for 4843 observed reflections $[\,|F_o| \geq 6\sigma|F_o|\,]$. Data were collected on Mac Science MXC18 diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.7107Å) and employing the ω(2θ< 30°), ω- 2θ (2θ> 30°) scan method in the range of 22°< 2θ< 29°.

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