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Ferromagnetically Coupled Dimanganese(III) Complex and Antiferromagnetically Coupled Diiron(III) Complex with Unsymmetrical Ligands

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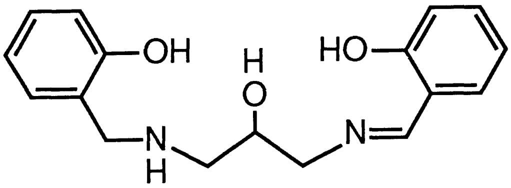
Binuclear iron(III) and manganese(III) complexes with 1-salicylideneamino-3-salicylamino-2-propanol (H_3L), $[Mn_2(L)_2]\cdot 2CH_3CN$ and $[Fe_2(L)_2]\cdot 2CH_3CN$, have been prepared and characterized by X-ray structure analysis and magnetic susceptibilities (80–300 K).

Binuclear manganese and iron complexes are of current interest because such systems are known to exist at the active site of some manganese- or iron-containing enzymes.1) We and others have recently studied on some binuclear manganese(III) complexes by using a binucleating ligand, 1,3-bis(salicylideneamino)-2-propanol.2-4) Murray et al. have also reported on binuclear iron(III) complexes with this ligand.5) During the course of our studies on this system, we have found that hydrogenation of 1,3-bis(salicylideneamino)-2-propanol in the presence of manganese or iron ion leads to formation of novel binuclear complexes with an unsymmetrical binucleating ligand, 1-salicylideneamino-3-salicylamino-2-propanol (H_3L). Isolated complexes are $[Mn_2(L)_2]\cdot 2CH_3CN$ (**1**) and $[Fe_2(L)_2]\cdot 2CH_3CN$ (**2**). Interestingly the former is a ferromagnetically coupled complex while the latter antiferromagnetically coupled. We herein report the preparation and structural characterization of these binuclear complexes.

The manganese(III) complex **1** was prepared as follows. 1,3-Bis(salicylideneamino)-2-propanol (75 mg, 0.25 mmol) was dissolved in acetonitrile and treated with 10 mg (0.25 mmol) of sodium borohydride. Then manganese(II) acetate tetrahydrate (61 mg, 0.25 mmol) was added and the mixture was refluxed for 1 h and filtered. To the filtrate was added 51 mg (0.5 mmol) of triethylamine to give black crystals of **1**. The iron(III) complex **2** was prepared by a method similar to that for **1** except for using iron(II) chloride tetrahydrate instead of manganese(II) acetate tetrahydrate.



H_3L

The molecular structure of the manganese(III) complex **1** was determined by X-ray crystallography.6) The crystal consists of centrosymmetric binuclear units, $[Mn_2(L)_2]$, and crystal solvents, CH_3CN. The ORTEP plot of $[Mn_2(L)_2]$ is shown in Fig. 1. The structure shows a dimeric unit where the two manganese atoms are bridged by the alcoholic-oxygen atoms of the two ligands, L, forming an Mn_2O_2 core. The center of symmetry lies in the center of this core. The Mn-Mn separation and Mn-O-Mn angle are 3.243(2) Å and 100.7(3)°, respectively. Each manganese atom has an N_2O_4 donor set in an elongated octahedron with the two ligands. The elongated axis is N2-Mn-O2' and the in-plane-bond distances are comparable to those found for other manganese(III) complexes.[7-10] This structural feature is attributable to the Jahn-Teller effect for a high-spin d^4 ion. The coordination mode of the ligands is unique and the core Mn-O2-Mn'-O2' plane is approximately perpendicular (92.6(2)°) to the equatorial plane formed by O1, N1, O2, and O3 (out-of-plane bridging). We can observe that the hydrogenation reaction occurs in only one side of the two imino groups of 1,3-bis(salicylideneamino)-2-propanol. The amino nitrogen atom N2 takes a tetrahedral arrangement with the normal C-N bond lengths (N2-C10 1.486(12), N2-C11 1.522(14) Å). On the other hand, the N1 atom is an imino nitrogen and takes a planar arrangement with N1-C7 bond length of 1.282(12) Å. The unsymmetrical property of the ligand may enable the square pyramidal arrangement of the N_2O_3 donors and the out-of-plane

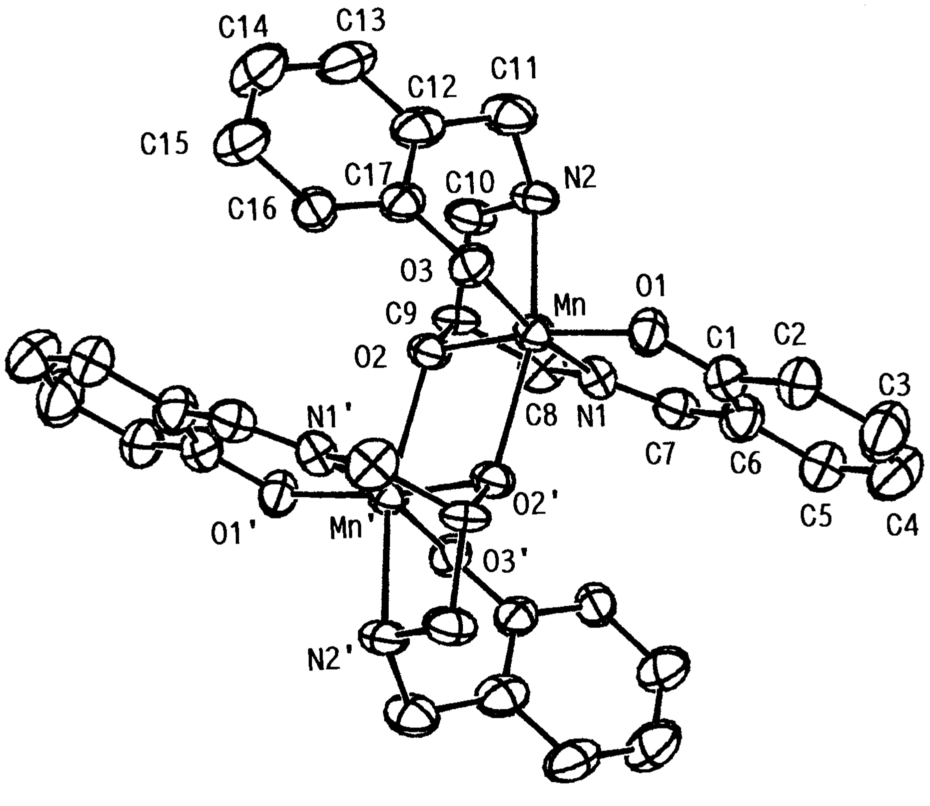


Fig. 1. Perspective view of $[Mn_2(L)_2]\cdot 2CH_3CN$ (**1**). Selected bond distances (*l*/Å) and angles (φ/°) are: Mn-Mn' 3.243(2), Mn-O1 1.900(6), Mn-O2 1.939(6), Mn-O2' 2.265(7), Mn-O3 1.922(7), Mn-N1 2.000(9), Mn-N2 2.330(9); Mn-O2-Mn' 100.7(3). Molecular structure of $[Fe_2(L)_2]\cdot 2CH_3CN$ (**2**) is similar to this structure (Fe-Fe' 3.187(2), Fe-O1 1.918(7), Fe-O2 2.085(7), Fe-O2' 2.018(9), Fe-O3 1.943(9), Fe-N1 2.153(11), Fe-N2 2.210(11); Fe-O2-Fe' 101.9(4)).

bridging of the alcoholic-oxygen atoms. This is a novel example of binuclear complexes with a new type of unsymmetrical ligands.

The molecular structure of the iron(III) complex **2** is similar to that of **1**. Each iron atom has an N_2O_4 donor set in a distorted octahedron, however, the elongation on one axis is no longer observed due to the spherical $t_{2g}{}^3e_g{}^2$ configuration of Fe^{3+}. The Fe-O2' bond is 2.018(9) Å and in the same range as those found for other alkoxo-bridged binuclear iron(III) complexes.[5] The Fe-N2 distance (2.210(11) Å) is somewhat long, however, this elongation may be a result of constraints imposed by the unique arrangement of the ligand.

Variable temperature magnetic susceptibility data were collected on powdered samples of **1** and **2** in the temperature range 80–300 K. The data were analyzed with the van Vleck equation based on the Heisenberg model ($\mathcal{H}=-2JS_1\cdot S_2$). For complex **1**, the effective magnetic moment per Mn, μ_{eff}, rises gradually from 5.08 B.M. at 280 K to 5.56 B.M. at 81 K (Fig. 2). The behavior is characteristic of intramolecular ferromagnetic coupling, and the fitting parameters are $J=+4.5$ cm^{-1}, $g=2.00$. This manganese(III) complex is unique in being ferromagnetic, since the large majority of the structurally characterized binuclear manganese(III) complexes are antiferromagnetic[2-4,7,9,10] and only two examples, $[Mn_2L'_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2](ClO_4)_2$ ($L'=C_6H_{15}N_3$, $C_9H_{21}N_3$) are known to be ferromagnetic.[11] On the other hand, the magnetic susceptibility data of the iron(III) complex **2** could be interpreted in terms of the intramolecular antiferromagnetic coupling (μ_{eff}/Fe=5.61 B.M. (297 K), 5.01 B.M. (81 K), $J=-2.8$ cm^{-1}, $g=2.00$). The different magnetic behavior may stem from the following reason. The $d_{x^2-y^2}$ metal orbitals directed along the M-O bonds are occupied in the high-spin d^5 complex **2** and the observed magnetism may be due to the antiferromagnetic coupling through the pathway $d_{x^2-y^2}-p-d_{x^2-y^2}$. On the other hand, the $d_{x^2-y^2}$ orbitals along the in-plane M-O bonds are unoccupied in the high-spin d^4 complex **1**, although the unpaired electron lies in the d_{z^2} orbitals along the out-of-plane M-O bonds. This may lead to the observed ferromagnetism.

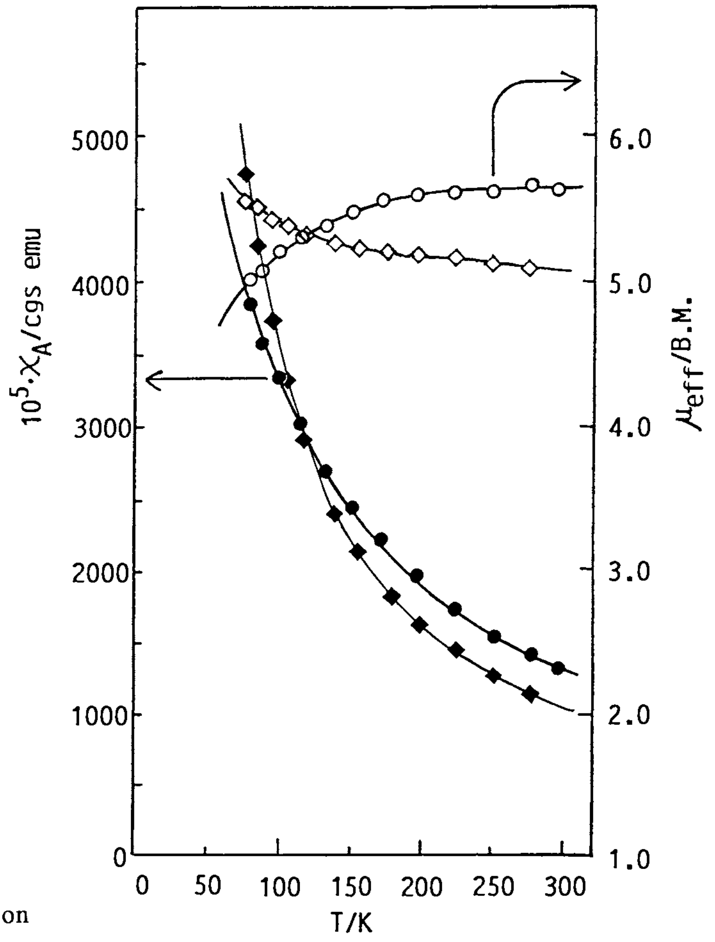
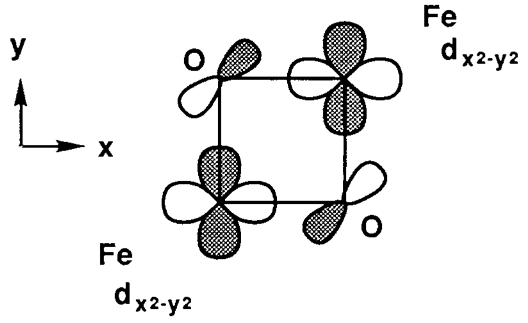
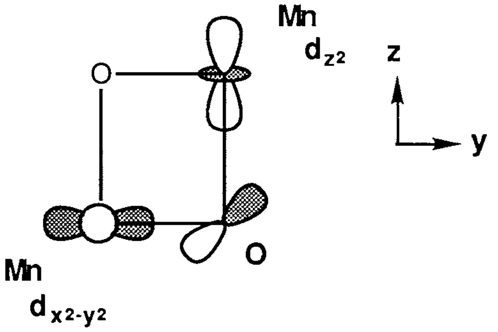


Fig. 2. Temperature dependences of magnetic susceptibilities and effective magnetic moments of **1** (◆ , ◇) and **2** (● , ○).



$Fe^{III}{}_2(L)_2$

antiferromagnetic



$Mn^{III}{}_2(L)_2$

ferromagnetic

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6) Crystal data for **1**: $Mn_2O_6N_6C_{38}H_{40}$, F.W.=786.6, monoclinic, space group $P2_1/c$, a=13.815(6), b=9.227(5), c=14.621(8) Å, β=103.31(4)°, V=1813.6(17) Å^3, Z=2, D_m=1.39, D_c=1.44 g cm^{-3}, μ(Mo-Kα)=7.19 cm^{-1}, R=0.070, R_w=0.081. 3200 reflections were measured in the range $2 \le 2\theta \le 48°$; 1758 with $I \ge 3\sigma(I)$ were assumed observed. For **2**: $Fe_2O_6N_6C_{38}H_{40}$, F.W.=788.5, monoclinic, space group $P2_1/c$, a=14.026(4), b=9.265(2), c=14.465(2) Å, β=104.81(2)°, V=1817.2(7) Å^3, Z=2, D_m=1.43, D_c=1.44 g cm^{-3}, μ(Mo-Kα)=8.49 cm^{-1}, R=0.072, R_w=0.082. 3680 reflections were measured in the range $2 \le 2\theta \le 48°$; 1620 with $I \ge 3\sigma(I)$ were assumed observed. For the determination of both structures, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by the direct methods and refined by the full-matrix least-squares methods using the SDP program package.
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