

## Control of the Intramolecular Magnetic Interaction by the Spin Polarization of $d_{\pi}$ -Electrons: Ferromagnetic Interaction between Iron Centres through an Organic Bridging Ligand

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The magnetic susceptibility of the dinuclear iron(III) complex  $[\text{Fe}_2(\text{bpmar})(\text{H}_2\text{O})_4](\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$  { $\text{H}_2\text{bpmar}$ —4,6-bis[*N,N*-bis(2'-pyridylmethyl)aminomethyl]-2-methylresorcinol}, in which the bridging ligand was designed by considering the topological relationship of the network of  $d_{\pi}$  spins to the bridging ligands, has indicated a ferromagnetic interaction [ $J = +0.62(3) \text{ cm}^{-1}$  and  $g = 1.956(4)$ ] between the two metal centres.

Control of magnetic interactions in multinuclear metal complexes provides the basic technology for building a molecular based ferromagnet. Some strategies for incorporation of ferromagnetic interactions in organic multi-radical compounds have been proposed,<sup>1</sup> and a spin polarization mechanism, *i.e.*, topological symmetry of the  $\pi$  electron network, was used to design high-spin organic molecules which have carbenes as the paramagnetic centres.<sup>2</sup> Is it possible to apply the concept of the spin polarization of  $d_{\pi}$ -spins to designing multinuclear metal complexes which have ferromagnetic interactions through an organic bridging ligand? In this report, the magnetic properties of dinuclear iron(III) complex  $[\text{Fe}_2(\text{bpmar})(\text{H}_2\text{O})_4](\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$ , in which the bridging ligand was designed by taking into account the spin polarization by the  $d_{\pi}$  spins of the ligand  $p_{\pi}$  electrons, are presented.

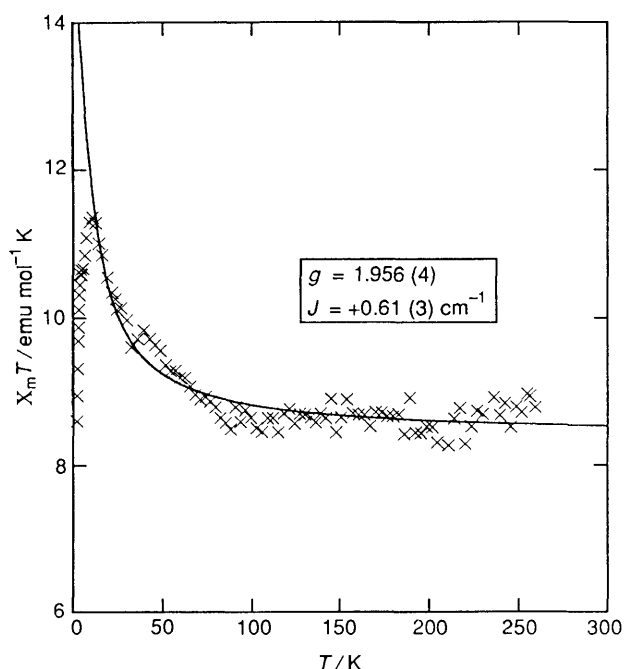
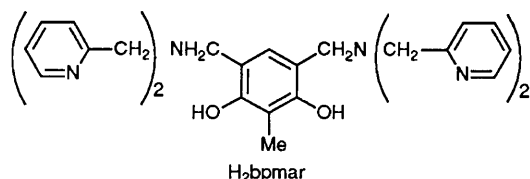


Fig. 1 Plot of  $\chi_m T$  vs.  $T$  for  $[\text{Fe}_2(\text{bpmar})(\text{H}_2\text{O})_4](\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$ . The Hamiltonian for the dinuclear system is  $\hat{H} = -2J S_1 \cdot S_2$ , where  $J$  is the coupling constant. The solid line was generated from the best fit calculation using the Van Vleck equation for the  $S = 5/2$  dimer.

$$\chi_m T = \frac{2N_g^2 \mu_B^2}{k_B} \left[ \frac{55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28}}{11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30}} \right]$$

where  $x = \exp(-J/kT)$ , and other symbols have their usual meaning.

Reaction of iron(III) nitrate ennehydrate with  $\text{H}_2\text{bpmar}$ , which was obtained by condensation of 2-methylresorcinol with *N,N*-bis(2-pyridylmethyl)amine and aqueous formaldehyde in methanol, gave a dark-blue microcrystalline solid.† Cryogenic magnetic susceptibilities were measured down to 2.0 K. A  $\chi_m T$  vs.  $T$  plot (Fig. 1) shows a gradual increase starting from 75 K as the temperature decreased, with a

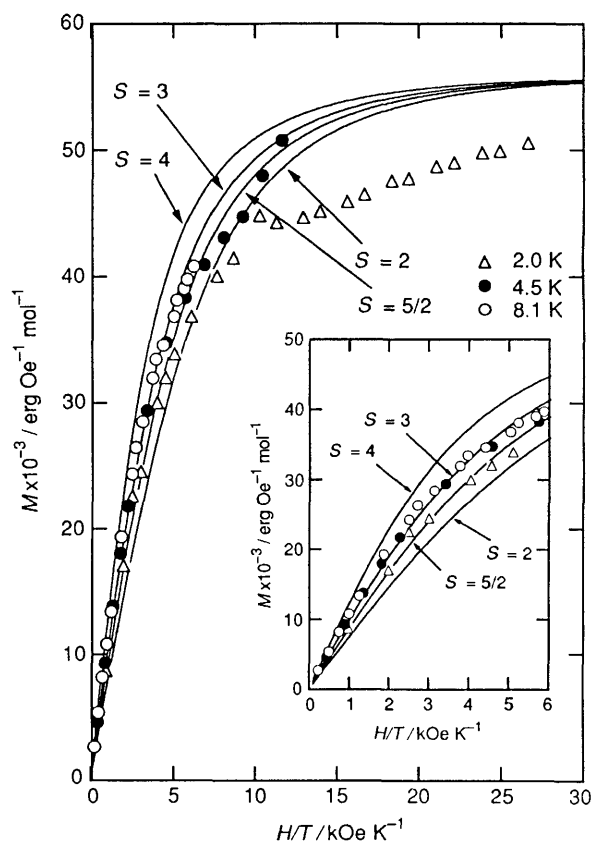


Fig. 2 Plots of magnetization ( $M$ ) of  $[\text{Fe}_2(\text{bpmar})(\text{H}_2\text{O})_4](\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$  at 2.0, 4.5 and 8.1 K vs. temperature-normalized field strength ( $H/T$ ). Theoretical magnetization curves (solid lines) are given by the Brillouin function  $[B_J(x)]$  with  $J = S = 2, 5/2, 3; 4 \times 10^3 \text{ erg Oe}^{-1} \text{ mol}^{-1} = 1 \text{ A m}^2 \text{ mol}^{-1}; 4\pi \times 10^{-6} \text{ kOe K}^{-1} = \text{A m}^{-1} \text{ K}^{-1}$ .

$$M = M_s B_J(x) \text{ with } x = Jg\mu_B H/k_B T$$

where  $M_s$  is the saturation magnetization. In this calculation,  $g$  was fixed at 1.956, as obtained from the magnetic susceptibility measurement.

† The compounds have been fully characterized by elemental analysis and spectroscopy:  $^1\text{H}$  NMR for  $\text{H}_2\text{bpmar}$  (400 MHz,  $\text{CD}_3\text{Cl}$ )  $\delta$  2.55 (s, 3H, *Me*-resorcinol), 3.69 (s, 4H,  $\text{CH}_2$ -resorcinol), 3.84 (s, 8H,  $\text{CH}_2$ -pyridine), 6.59 (s, 1H, *H*-resorcinol), 7.12 (td, 4H,  $J$  6.11 and 1.22 Hz, pyridine ring), 7.32 (d, 4H,  $J$  7.93 Hz, pyridine ring), 7.60 (td, 4H,  $J$  7.63 and 1.83 Hz, pyridine ring) and 8.55 (d, 4H,  $J$  3.97 Hz, pyridine ring).

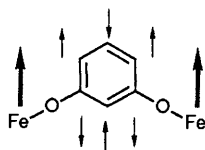


Fig. 3 Spin polarization scheme

maximum  $\chi_m T$  value ( $11.356 \text{ emu mol}^{-1} \text{ K}$ ;  $10^6/4\pi \text{ emu} = 1 \text{ m}^3$ ) being reached at 10.8 K. This magnetic behaviour indicates the existence of a ferromagnetic interaction between the two metal centres. An abrupt decrease of the  $\chi_m T$  value below 10 K is due to an intermolecular antiferromagnetic interaction. The magnetic susceptibility data above 10 K were used to evaluate the coupling parameter  $J$ . A least-squares calculation on the Van Vleck equation for the  $S = 5/2$  dinuclear system gave best fit parameters of  $J = +0.62(3) \text{ cm}^{-1}$  and  $g = 1.956(4)$ . Magnetizations as a function of applied field up to 5 T at 2.0, 4.5 and 8.1 K (Fig. 2) were measured. The experimental magnetization values at 8.1 K are greater than the values predicted by the Brillouin function for  $S = 5/2$ . The spin multiplicity, as a result of the ferromagnetic interaction, is greater than  $S = 3$  at 8.1 K from the data for the low magnetic field region. The spin multiplicity would be lower than the high-spin iron(III) value of  $5/2$  if the ferromagnetic interaction did not exist. The data at 2 and 4.5 K indicate a lower spin multiplicity than at 8.1 K because of the intermolecular antiferromagnetic interaction.

The iron(III) atoms are in the high-spin state, so the irons have both  $d_{\sigma}$ - and  $d_{\pi}$  spins. There are two contributions to magnetic interactions. The two iron atoms are isolated by two

oxygen and three (or four) carbon atoms. This makes a direct overlap of the magnetic orbitals (the  $d_{\sigma}$  spins on the iron atoms) negligible, which leads to the absence of an antiferromagnetic exchange interaction through a  $\sigma$  pathway. The second contribution is the propagation of the ferromagnetic interaction due to the spin polarization by the  $d_{\pi}$  spins of the  $p_{\pi}$  electrons on the organic ligand. If we assume an  $\alpha$ -spin on the iron, a  $\beta$  spin on the carbon atom is induced by a superexchange interaction through the  $p_{\pi}$  electrons of the coordinating oxygen atom. This  $\beta$  spin is polarized as an  $\alpha$  spin on the adjacent carbon atoms, and so on. Finally an  $\alpha$  spin on the other iron atom is induced; *i.e.* the ferromagnetic interaction between the two iron centres is propagated (Fig. 3). In conclusion, ferromagnetic interactions in multinuclear metal complexes can be obtained if the bridging ligand is designed by considering the topological symmetry of the  $d_{\pi}$  electrons with respect to the ligand  $p_{\pi}$  electrons network.

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