

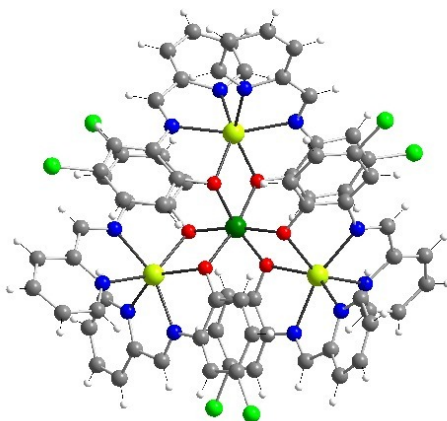


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An Investigation into the Structure Directing Properties of Organic Templates with Mn, Fe and Cu

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Chapter 1: Introduction

1.1 Single molecule magnets

Since Werner's early studies of Co(III) and Cr(III) complexes, [1] coordination compounds have been intensively studied as researchers endeavor to create new materials and to deepen their knowledge of the ways in which metal atoms can interact with each other. The interaction between more than two paramagnetic centers may give rise to materials that exhibit novel magnetic properties. It is the goal of many inorganic chemists to synthesize metal aggregates where the magnetic interactions of paramagnetic metal centers start to exhibit properties of bulk materials.

The study of nanoscale molecules is of interest because it can be expected that at this length scale classical and quantum behavior might coexist (for example, quantum tunneling in the magnetization of large spin clusters). [2] These magnets, termed single molecule magnets, have been of increasing interest since some have been shown to exhibit magnetic bistability of pure molecular origin. The slow relaxation in the magnetization is at the origin of this interesting behavior and is due to the presence of an energy barrier which has to be overcome in the reversal of the magnetic moment. This behavior has been compared to that of superparamagnetic materials.

Superparamagnetic behavior occurs when a single magnetically ordered domain has a reorientation barrier of the magnetization which is comparable to the thermal energy. [3] As a consequence, the magnetization flips freely and its time average is zero, as in a paramagnet. In an external field, it behaves like a paramagnet until the temperature is sufficiently reduced and the barrier is restored. Thus the magnetization becomes blocked, below a blocking temperature, T_B , and the superparamagnet reverts to its usual bulk behavior (i.e. ferro-, ferri-, or antiferromagnetic). To have a barrier, the system must have the magnetic states, $M = \pm S$ lying lowest, where S is the spin quantum number. For the case of axial symmetry, where the system has an integer spin in the ground state, the height of the energy barrier, Δ , can be associated with the difference between the lowest lying $M = \pm S$ states and the highest $M = 0$ state for a

negative axial zero field splitting parameter, D , as $\Delta = |D|S^2$. Therefore to produce new nanomagnetic materials based on molecular clusters it is necessary to achieve a reasonably large S ground spin state. For this purpose $S = 5/2$ ions such as high spin Mn(II) and Fe(III) appear to be well-suited. Subsequently a large ground spin state can be achieved just by using a small number of ions. Perhaps the simplest example of a single molecular magnet is a chiral Fe(III)₄ aggregate reported by Gatteschi and co-workers (fig 1.1). [4]

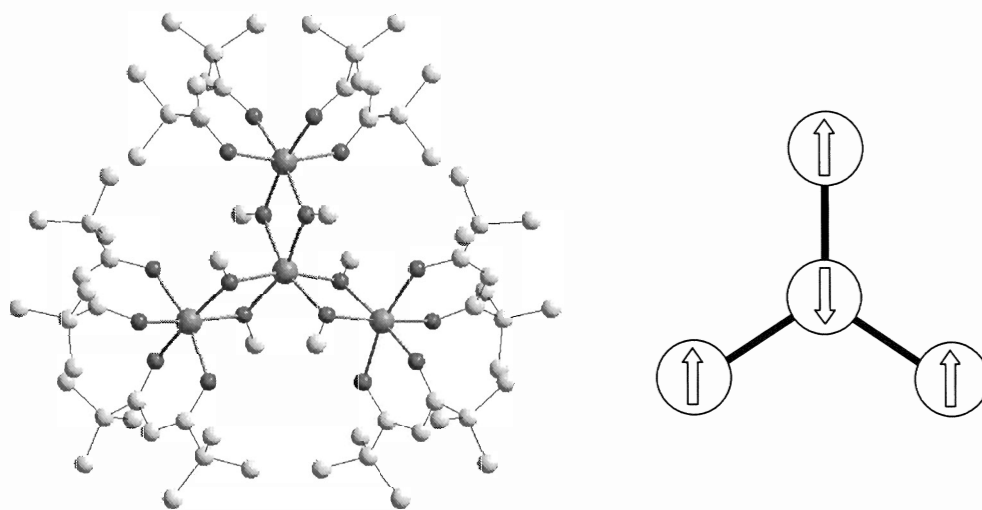


Fig 1.1 Crystal structure of $[\text{Fe}_4(\text{OCH}_3)_6(\text{dpm})_6]$ (left) (where Hdpm = dipivaloylmethane) and a representation of the spin alignment within the molecule (right). Selected bond distances and angles (\AA , $^\circ$): $\text{Fe}_c \dots \text{Fe}_p$ 3.133-3.146, $\text{Fe}_p \dots \text{Fe}_p$ 5.372-5.550, $\text{Fe}_c\text{-O}_m$ 2.010-2.017, $\text{Fe}_p\text{-O}_m$ 1.950-1.992, $\text{Fe}_p\text{-O}_d$ 1.996-2.026; $\text{Fe}_c\text{-O}_m\text{-Fe}_p$ 104.2-104.4. (where c = central, p = peripheral, m = methoxy and d=dpm).

An antiferromagnetic interaction mediated by methoxide bridges is observed between the central Fe(III) ion and the peripheral ions leading to a ground state $S = 5$. This has been interpreted as four high spin Fe(III) ions with the spin of the central Fe(III) ion aligning antiparallel to the peripheral ones (see fig 1.1). Its blocking temperature is low, due to the fact that the spin in the ground state is relatively small and the zero field splitting is also small ($D = -0.2 \text{ cm}^{-1}$). A similar motif was observed by Saalfrank and co-workers (discussed in chapter 3) however the magnetic properties have not been reported in the literature to date. [5]

Another example of a single molecule magnet is the Fe(III)_8 aggregate reported by Wieghardt and co-workers (fig 1.2). [6] Here four central Fe(III) ions are arranged in the common ‘butterfly’ configuration through two μ_3 -oxygen atoms. The remaining four Fe(III) ions each bridge to two of the central metal ions through twelve μ -hydroxide groups. The spins on the Fe(III) ions are highly frustrated and are anti-ferromagnetically coupled. The interpretation of the magnetic data is complex, given the total number of possible states is far greater than a million. Although no best-fit procedure could be attempted, the ground state has been estimated to be $S = 10$. It shows slow magnetic relaxation in the Mössbauer spectra at ca. 30 K and magnetic hysteresis below 1 K. [7] Steps in the hysteresis curve are observed due to $\Delta S = \pm 1$ transitions as the applied magnetic field is changed. Materials exhibiting hysteresis effects are bistable and potentially capable of storing information.

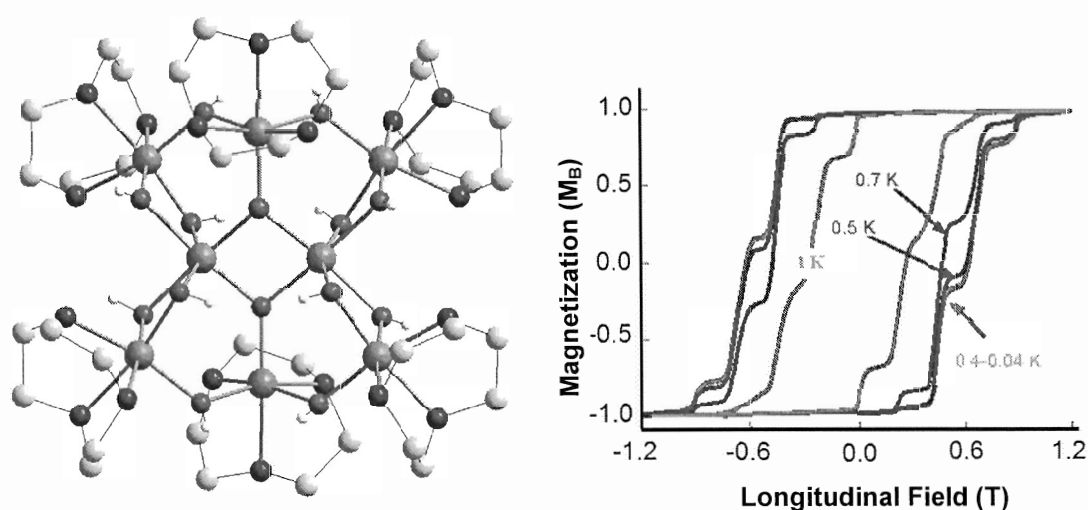


Fig 1.2 Structure of the $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ cation in the crystal (left) (where tacn = 1,4,7-triazacyclononane) and the hysteresis observed in the magnetization profile (right).

It warrants mentioning that the solvent may play a crucial role in the formation of aggregates. In each of the previous examples solvent derived molecules have formed bridges between metal centers in the form of hydroxide, methoxide and acetate groups.

Kahn and co-workers have shown how Fe(II) 1,2,4-triazole complexes (Htrz) can be fine tuned by doping the sample with 4-amino-1,2,4-triazole (4-NH₂trz) giving bistability at room temperature (fig 1.4). [13] These compounds have since been explored for use in various applications including display systems and memory devices. [14]

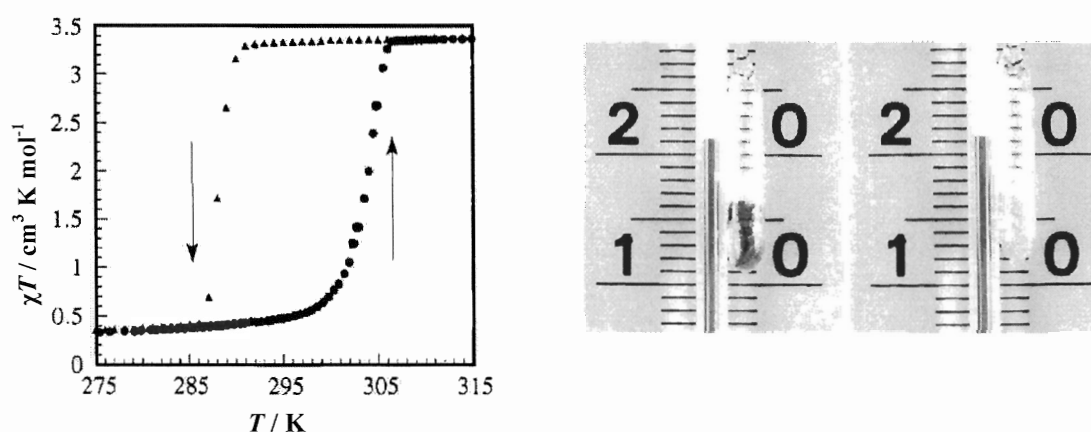


Fig 1.4 The plot of the product of the molar magnetic susceptibility, χ , and temperature, T , against temperature for $[\text{Fe}(\text{Htrz})_{3-3x}(\text{4-NH}_2\text{trz})_{3x}](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ (left) with $x = 0.05$ in both warming (\bullet) and the cooling modes (\blacktriangle) and photographs of $[\text{Fe}(\text{Htrz})_{3-3x}(\text{4-NH}_2\text{trz})_{3x}](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ with $x = 0.05$ in the $S = 0$ (left) and $S = 2$ (right) states at 294 K (right).

While there are many examples of electronic bistability for Fe(II) complexes, prior to the complexes reported by Oshio and co-workers, [15] there were few examples of ST hysteresis effects in ferric compounds. They reported two systems for producing high temperature Fe(III) ST complexes. This was achieved this using complexes with the Schiff base ligands of pyridine-2-carboxaldehyde with 2-aminophenol (Hpap) and of 8-aminoquinoline with salicylaldehyde (Hqsal) of the general types shown in fig 1.5.

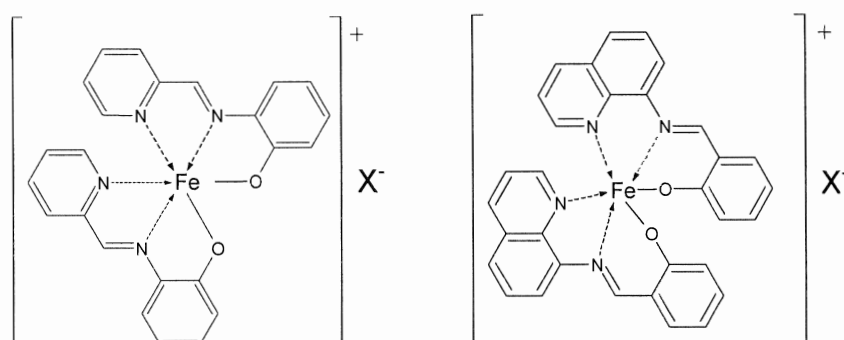


Fig 1.5 Diagram of $[\text{Fe}(\text{pap})_2]\text{X}$ (left) and $[\text{Fe}(\text{qsal})_2]\text{X}$ (right) type complexes.

Structurally these complexes are very simple with each Fe(III) ion having a N_4O_2 coordination sphere. Both complexes exhibit a ST and electronic bistability around room temperature. In the case of $[\text{Fe}(\text{pap})_2](\text{ClO}_4)$ the hysteresis loop is about 20 K centered at 252 K. $[\text{Fe}(\text{qsal})_2](\text{NCS})$ has a significantly larger apparent hysteresis loop of around 70 K between 210 and 280 K. Oshio proposed that the observed ST hysteresis effects are due to π - π mediated cooperativity in the tightly packed framework of the crystal structure.

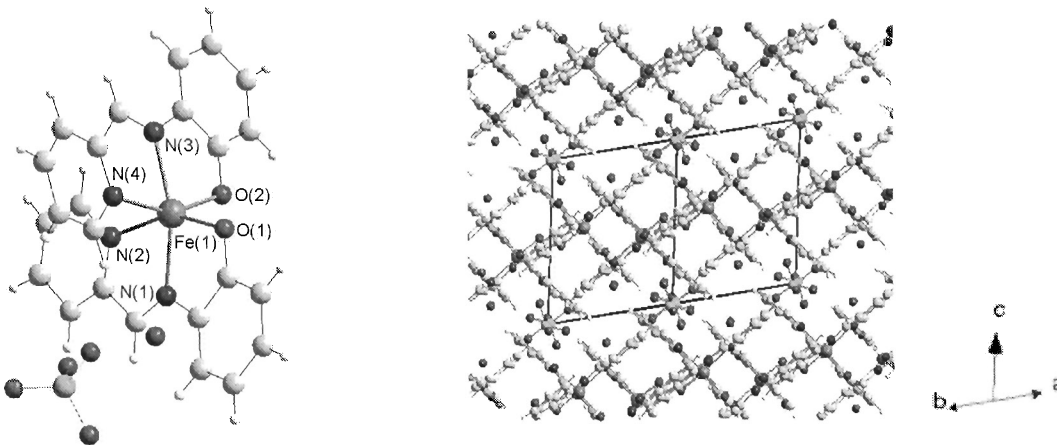


Fig 1.6 View of the mononuclear $[\text{Fe}(\text{pap})_2](\text{ClO}_4)\cdot\text{H}_2\text{O}$ complex with atomic labeling (left) and the molecular packing showing the strong π - π stacking between complexes (right).

Using the water adduct of $[\text{Fe}(\text{pap})_2](\text{ClO}_4)\cdot\text{H}_2\text{O}$, Sato and co-workers observed the first example of light-induced excited spin state trapping (LIESST effect) for an Fe(III) complex (fig 1.6 and 1.7). [16] This was originally thought to be impossible for an Fe(III) complex due to the small structural change associated with the spin transition. [17] When the sample was irradiated with light (400 - 600 nm) at 5 K, an increase in the magnetization was observed which persisted for periods of at least 10 h.

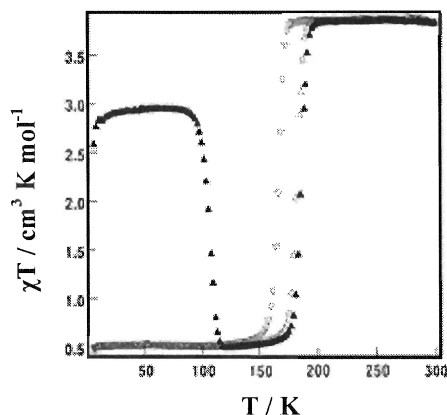


Fig 1.7 χT versus T plots for $[\text{Fe}(\text{pap})_2](\text{ClO}_4)\cdot\text{H}_2\text{O}$. The sample was cooled from 300 to 5 K (∇) and then warmed from 5 to 300 K (Δ) at a rate of 2 K min^{-1} . The sample was cooled to 5 K and irradiated with light before being warmed at a rate of 2 K min^{-1} (\blacktriangle).

This suggests that the transition from low spin to high spin had been induced. This was supported by Mössbauer experiments, which at 13 K reveal a wide quadrupole-split doublet ($\Delta Q = 3.08 \text{ mm s}^{-1}$, $\delta = 0.11 \text{ mm s}^{-1}$ where Q is the nuclear quadrupole moment and δ is the chemical isomer shift), before illumination, representing the low spin state. The spectrum measured after a 15 min illumination period shows a narrow quadrupole-split ($\Delta Q = 1.14 \text{ mm s}^{-1}$, $\delta = 0.44 \text{ mm s}^{-1}$) representing the high spin state. Oshio and co-workers also studied various other solvent adducts of $[\text{Fe}(\text{pap})_2](\text{ClO}_4)$. [18] Subtle changes in the molecular packing were shown to significantly affect the ST profile.

1.3 Rigid acyclic ligands and macrocycles

Rigid acyclic ligands can be used to generate a degree of control over the observed chemistry. An example of this has already been highlighted in the previous section where the Hpap and Hqsal ligands have been used to create cooperativity mediated through π - π stacking.

Rigidity has proven useful in performing enantioselective catalysis. One example is shown in fig 1.8. This chiral Mn(III) Schiff base complex has been developed as an enantioselective catalyst for the epoxidation of a wide variety of alkenes. [19] The Schiff base ligand is formed by the 2:1 condensation of salicylaldehyde, or a derivative, with an optically pure *trans*-1,2-diaminocyclohexane. The chirality of the diamine present in the ligand is used to control the chirality of the product formed in the catalytic reaction with a selectivity greater than 90%. The chloride analogue of the Mn(III) Schiff base complex of *trans*-(1R,2R)-1,2-diaminocyclohexane condensed with 2,4-di-*tert*-butylsalicylaldehyde is shown in fig 1.8. [20]

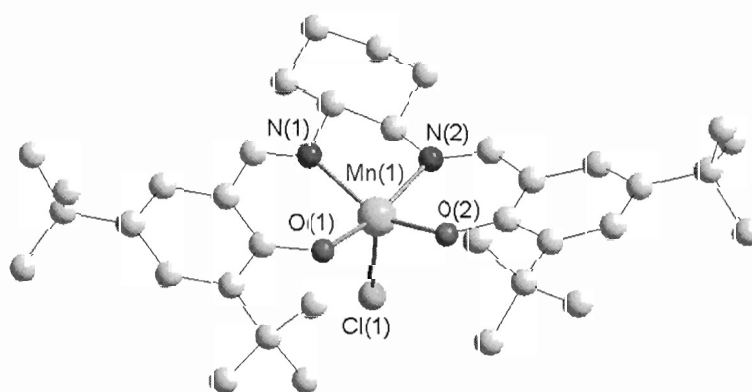


Fig 1.8 The structure of a Mn(III) Schiff base compound formed from the complexation of *trans*-(1R,2R)-1,2-diaminocyclohexane condensed with two equivalents of 2,4-di-*tert*-butylsalicylaldehyde.