

Magnetic Properties of Iron(III) Complexes with Pendant-Armed Alcohols of 1, 4, 7, 10-Tetraazacyclododecane (Cyclen) Ligands.

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Abstract

The magnetic properties of the compounds $[\text{Fe}\{\text{H}_2\text{THED}\}(\text{FeCl}_3)]\text{Cl}$ (**1**), $[\text{Fe}_3(\text{TRED})_2(\text{N}_3)_2]\text{Cl}\cdot 5\text{H}_2\text{O}$ (**2**) and $[\text{Fe}_4\text{O}_2(1,4\text{-DHED})_2(\text{N}_3)_4]\cdot 6\text{MeOH}$ (**3**) are reported (H_4THED) is (1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane), (H_3TRED) is 1,4,7-tris (2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane) and (H_2DHED) is (1,4-bis (2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane). Variable temperature magnetic susceptibility measurements of **1**, **3** complexes possess $S = 0$ spin ground states, while **2** has an $S = 2$ spin ground state.

Key words: Iron (III) Complexes, Antiferromagnetic Coupling, Magnetic Susceptibility, Cyclen derivatives.

I. Introduction

The structural correlation of binuclear and polynuclear clusters of iron have received a considerable attention over the past years due to their wide range of biological activities and molecular magnetism. Iron-oxo centers are found in several enzymes like non-heme metalloproteins, Hemerythrin, ribonucleotide reductase, and methane monooxygenase.¹⁻⁶

The magnetic properties for these compounds depend mainly on the nature of the bridging ligands, such as chloro, azido, oxo, hydroxo and alkoxide oxygen bridging of iron atoms.⁷⁻²¹

Molecular oxide-bridged iron(III) clusters are almost always antiferromagnetically coupled, some iron clusters exhibit spin frustration effects or

display particular topologies that result in a reasonably large ground-state spin (S) values.²²⁻³⁰

Herein, the magnetic behavior of iron(III) compounds containing of H_4THED , H_3TRED and H_2DHED ligands are studied by temperature variable magnetic susceptibility measurements.

The x-ray crystal structures of these complexes (Figure 1) are described in detail elsewhere.³¹

The structural analyses revealed dinuclear iron(III) molecular structure in case of H_4THED ligand, $[\text{Fe}\{\text{H}_2\text{THED}\}(\text{FeCl}_3)]\text{Cl}$ (**1**), while trinuclear and tetranuclear iron(III) compounds $[\text{Fe}_3(\text{TRED})_2(\text{N}_3)_2]\text{Cl}\cdot 5\text{H}_2\text{O}$ (**2**) and $[\text{Fe}_4\text{O}_2(1,4\text{-DHED})_2(\text{N}_3)_4]\cdot 6\text{MeOH}$ (**3**) were formed by using H_3TRED and H_4DHED , respectively.

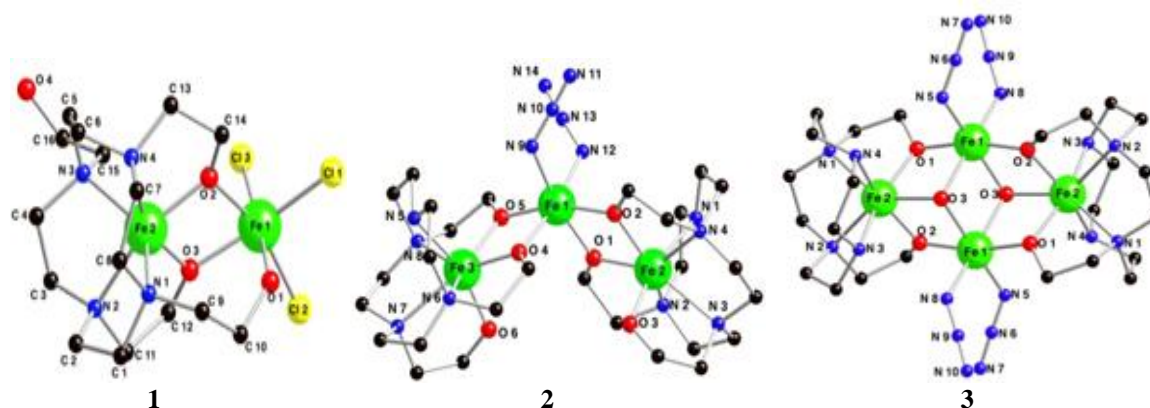


Figure 1: crystal structures of compounds 1, 2, and 3.³¹

II. Magnetic measurements

All magnetic experiments were performed by The Lewis Magnetism Laboratory (The University of Manchester), Variable temperature (2-300 K) magnetic susceptibility measurements were carried out on polycrystalline samples, using a Quantum

Design MPMS-XL SQUID magnetometer operating at 1 and 10 kG magnetic field. Magnetization experiments were performed at 2 and 4 K, with a magnetic field varying from 0 to 7 T. Diamagnetic corrections for the compounds were estimated from Pascal's constants³² and magnetic data were

corrected for diamagnetic contributions of the sample holder.

III. Results and Discussion

The magnetic moment (μ) is defined from magnetic susceptibility (χ) by Equation 1 using an array of constants (k_B = Boltzmann's, N = Avagadro's, β = Bohr magneton)

$$\mu = \sqrt{\frac{3k_B}{N\beta^2}} \cdot \sqrt{\chi T} \quad \dots\dots\dots(1)$$

Magnetic susceptibility is the sum of two contributions: diamagnetic and paramagnetic susceptibility. The molar paramagnetic susceptibility (or molar susceptibility) is a much stronger effect than diamagnetism. Its value is independent of the magnetic field, but temperature(T)dependent. In magnetically dilute systems $\chi \propto 1/T$ such that a system may be described by the Curie constant (C).

$$C = \chi T = \frac{N\beta^2}{3k_B} g^2 [S(S+1)] \approx \frac{g^2}{8} S(S+1) \quad \dots\dots\dots(2)$$

For systems with n equivalent non-interacting paramagnetic centres Equation 2 can be developed to Equation 3.

$$\chi T \approx \frac{g^2}{8} \cdot n \cdot S(S+1) \quad \dots\dots\dots(3)$$

The Curie law is often only applicable at high temperature and low field. In magnetically non-dilute systems there are often deviations from the Curie Law, and experimental data can often be fitted in cases of extended systems with the Curie-Weiss Law, Equation 4.

$$\chi = \frac{C}{T - \Theta} \quad \dots\dots\dots(4)$$

Θ is the Weiss constant given by the intercept of $1/\chi$ vs T plot, and it is positive when the magnetic interaction is ferromagnetic and negative when it is antiferromagnetic.. Magnetic exchange interaction or coupling constants J are a measure of energy (cm^{-1}) and are positive for ferromagnetic interactions and negative for antiferromagnetic interactions if the interaction is described by, Equation 5.

$$H^{\wedge} = -J S_i^{\wedge} \cdot S_j^{\wedge} \quad \dots\dots\dots(5)$$

where S^{\wedge} represent spin operators of centres i and j, H is called the spin-Hamiltonian.

IV. Magnetic properties of [Fe {HTHED}(FeCl₃)]Cl

Magnetic susceptibility data of of [Fe{HTHED}(FeCl₃)]Cl were measured on a microcrystalline sample in the temperature range 2-300 K with an applied field of 10000 G. The $\chi_m T$

product of (Figure 2) declines gradually from the value of ca. 7.70 $\text{cm}^3 \text{K mol}^{-1}$ at room temperature to ca. 7.0 $\text{cm}^3 \text{K mol}^{-1}$ at 50 K, where it drops more rapidly to 2.15 $\text{cm}^3 \text{K mol}^{-1}$ at 2 K. The $\chi_m T$ value at room temperature is slightly lower than the theoretical value for two uncoupled of Fe³⁺ with ($S = 5/2$, $g = 2.00$) of 8.75 $\text{cm}^3 \text{K mol}^{-1}$, which is typical of an antiferromagnetically coupled pair of iron(III) centres, and the drop from 50 to 2 K can be ascribed to antiferromagnetic exchange coupling within the dimeric unit. The temperature dependent magnetic susceptibility data suggest that the Fe atoms possess a diamagnetic ground state, but the paramagnetic states remain populated at 2 K. this is supported by the magnetisation measurement with a plateau of ca. 8 μ_B at high field at 2 K, corresponding to population of $M_s = \pm 4$ for $g = 2$. The isothermal variation of the magnetisation M versus H in the field range 0-7000 G at temperatures 2 and 4 K are shown in (Figure 3). The slow of steady increase in magnetic moment suggest that excited state levels are very close in energy to the diamagnetic ground state (Figure 4). Thus, the excited levels are stabilized upon increasing the field. The ground state for this molecule is $S = 0$, but with low energy excited spin states.

The plot of $(\chi_m)^{-1}$ versus the temperature is shown in Figure 5. The compound shows weak antiferromagnetic coupling present between the iron(III) centres and the calculated parameters for magnetic interaction from the Curie-Weiss law are $C = 8.0 \text{ cm}^3 \text{K mol}^{-1}$ and $\Theta = -13.0$ above 300 K.

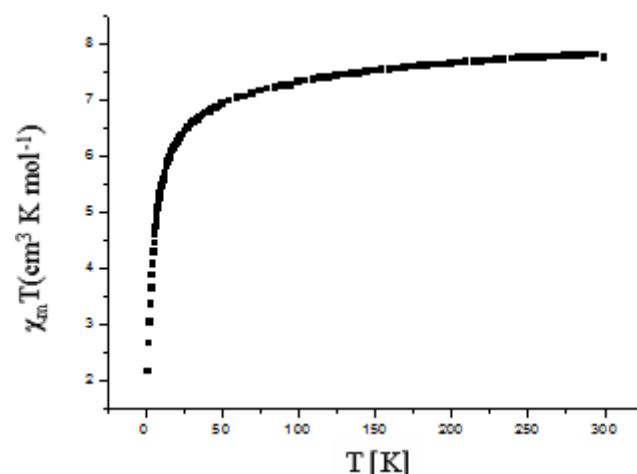


Figure 2: Plot of $\chi_m T$ versus T for of [Fe{HTHED}(FeCl₃)]Cl

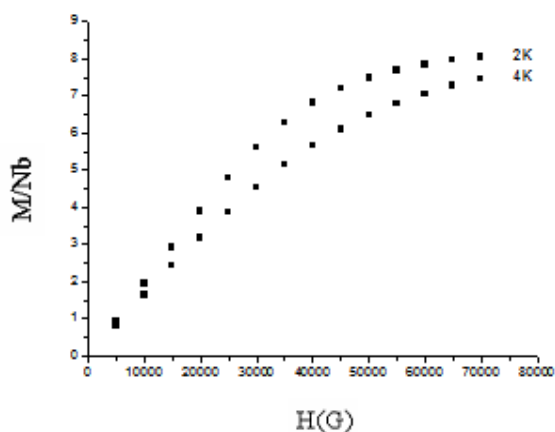


Figure 3: Isothermal magnetisation of [Fe{HTHED}(FeCl₃)]

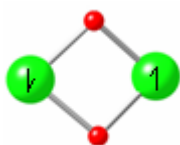


Figure 4: Coupling scheme in of [Fe{HTHED}(FeCl₃)]Cl

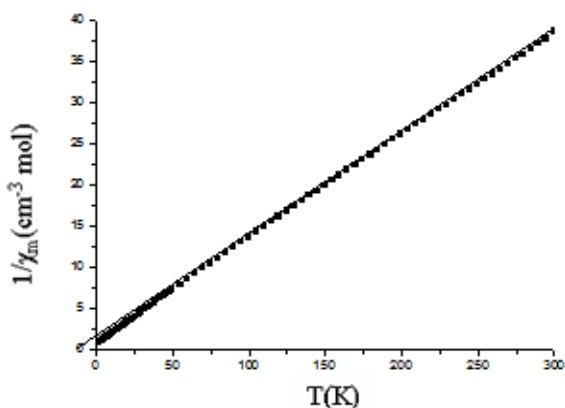


Figure 5: Plot 1/χ_m v T for [Fe{HTHED}(FeCl₃)]Cl, (line = linear fit Curie-Weiss Law).

V. Magnetic properties of [Fe₃(TRED)₂(N₃)₂]Cl

The magnetic behaviour of this compound in the form of a plot χ_mT of versus T, within a field of 10000 G is shown in (Figure 6). At room temperature, χ_mT was equal to 6.3 cm³ K mol⁻¹, this is lower than the anticipated room temperature value of 13.125 cm³ K mol⁻¹ for three non-coupled Fe³⁺ centres, S = 5/2 with g = 2.00.

As the temperature decreases to 2.0 K, the value of χ_mT goes down to 2.96 cm³ K mol⁻¹. χ_mT decreases constantly with decreasing temperature until reaching a plateau at 40 K of around 3.75 cm³ K mol⁻¹. This suggests that antiferromagnetic interaction dominates at low temperature between paramagnetic centres. The calculated values of χT, using Equation (2) with

g = 2, are 4.375, 3.0 and 1.875 cm³ K mol⁻¹ for S = 5/2, 2 and 3/2, respectively, and the experimental results are consistent with a ground state of S = 2. This is supported by variable field magnetisation measurements. The isothermal curve of reduced magnetisation saturated between 3.9-4.15 μ_B, is shown in(Figure 7)

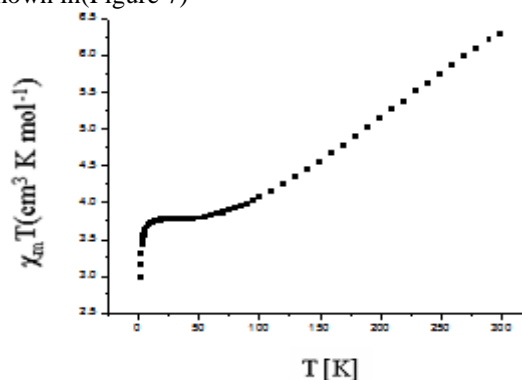


Figure 6: Plot of χ_mT versus T for [Fe₃(TRED)₂(N₃)₂]Cl

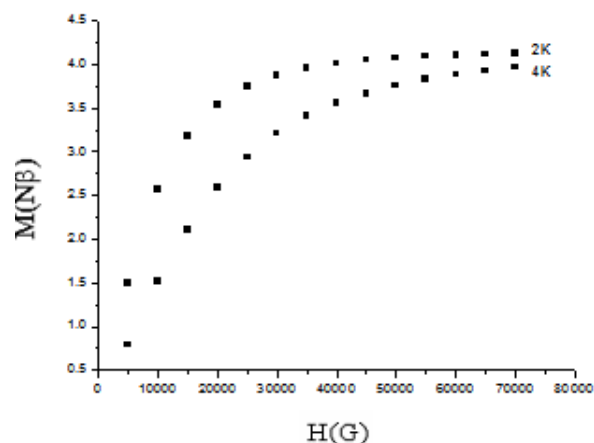


Figure 7: Isothermal of magnetisation of [Fe₃(TRED)₂(N₃)₂]

The magnetic interaction calculated from the Curie-Weiss Law with C = 13.63 cm³ K mol⁻¹ and Θ = -375 above 250 K. The large negative Θ value indicates indeed that a strong antiferromagnetic coupling is present between the iron (III) ions.

V. Magnetic properties [Fe₄O₂(1,4-DHET)₂(N₃)₄]

The temperature dependent magnetic susceptibility of [Fe₄O₂(1,4-DHET)₂(N₃)₄] was measured at 10000 G in the range of 2-300 K. χ_mT at room temperature for the compound is 8.10 cm³ K mol⁻¹ (Figure 8). For four non-interacting Fe^{III} centers S = 5/2 with g = 2.00, the room temperature χ_mT value would be 17.50 cm³ K mol⁻¹. χ_mT at room temperature is therefore less than expected, indicating that there is a moderate antiferromagnetic interaction

between the Fe centres. There is a constant drop in the value of $\chi_m T$ to $0.15 \text{ cm}^3 \text{ K mol}^{-1}$, as the temperature decreases to 2.0 K.

In order to determine the spin ground state of this compound, magnetization data were collected in the range of 0-7000 G at 2 and 4 K (Figure 9). The magnetization plots at these temperatures are consistent with a diamagnetic ground state with low-lying excited states of larger multiplicity that are populated with increasing field. The magnetization data cannot be fitted to a simple function as the compound does not have an isolated spin ground state. The low spin ground state of $[\text{Fe}_4\text{O}_2(1,4\text{-DHET})_2(\text{N}_3)_4]$ can be explained by considering the competing intramolecular interactions between the Fe centres, (Figure 10) for a possible simplified coupling scheme. The magnetic parameters calculated from the Curie- Weiss Law are $C = 12.92 \text{ cm}^3 \text{ K mol}^{-1}$ and $\Theta = -195$ above 250 K. The large negative Θ value and broad maximum in $\chi_m(T)$, indicate indeed that a strong antiferromagnetic coupling is present between the iron(III) centres.

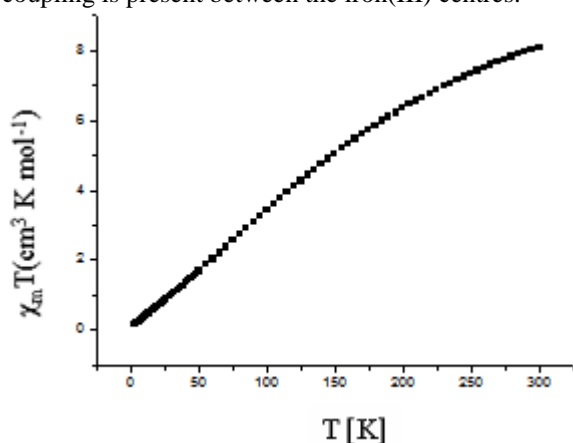


Figure 8: Plot of χ_m vs T for $[\text{Fe}_4\text{O}_2(1,4\text{-DHET})_2(\text{N}_3)_4]$

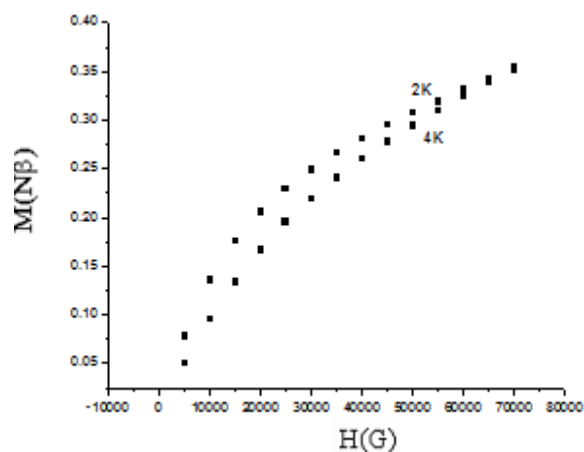


Figure 9: Isotherms of magnetisation of $[\text{Fe}_4\text{O}_2(1,4\text{-DHET})_2(\text{N}_3)_4]$

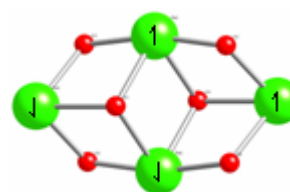


Figure 10: Possible magnetic coupling scheme in $[\text{Fe}_4\text{O}_2(1,4\text{-DHET})_2(\text{N}_3)_4]$

VI. Conclusion

The magnetostructural of three complexes have been characterized by variable-temperature magnetic susceptibility studies, which indicate the magnetic interactions between the Fe atoms centres in the bimetallic unit, trimetallic unit and tetrametallic unit are dominated by antiferromagnetic coupling for these complexes. The magnetic studies of complexes **1** and **3** have revealed that have an $S = 0$ ground state, as expected for oxide/alkoxide bridged FeIII systems with an even number of metal atoms, while **2** has an $S = 2$ spin ground state. However, on increasing the nuclearity either ferromagnetic or competing antiferromagnetic exchange interactions could lead to clusters with interesting magnetic properties.

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