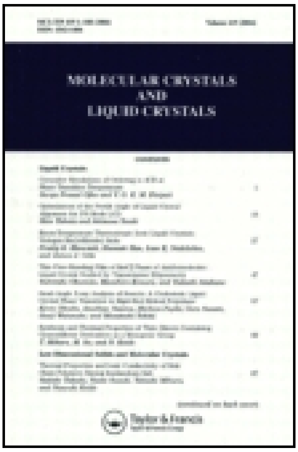

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Magnetic Studies of Polynuclear Iron (ii) Complexes and Their Application to the Synthesis of Extended Structures

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MAGNETIC STUDIES OF POLYNUCLEAR IRON (II) COMPLEXES AND THEIR APPLICATION TO THE SYNTHESIS OF EXTENDED STRUCTURES

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Abstract: The syntheses, magnetic properties, and reactions with nitrogen donors of a number of related $A_2[Fe_2Cl_6]$ salts (A = H-TMPP, PPh_4, Et_4N, $AsPh_4$, ppn) ([H-TMPP]Cl = $[H\text{-}P(C_6H_2(OMe_3)_3]Cl)$ as well as the neutral cluster $Fe_4Cl_8(THF)_6$ are discussed.

INTRODUCTION

High spin ferrous and ferric compounds are of obvious interest in magnetic studies, from both the biological and materials perspectives. Compared to ferric systems, the magnetic behavior of dinuclear and polynuclear ferrous systems have not been investigated as thoroughly. Discrete ferrous chloride structures that exhibit intriguing magnetic properties are being explored for their potential to serve as pure, soluble precursors to large clusters and low-dimensional magnetic materials.

EXPERIMENTAL

The compounds $A_2[Fe_2Cl_6]$ (A = H-TMPP, **1**; PPh_4, **2**; Et_4N, **3**; $AsPh_4$, **4**; ppn, **5**) ([H-TMPP]Cl = $[H\text{-}P(C_6H_2(OMe_3)_3]Cl)$ were prepared by the reactions of $FeCl_2$ with corresponding chloride salts AX in acetone, while $Fe_4Cl_8(THF)_6$ (**6**) was prepared by refluxing a suspension of anhydrous $FeCl_2$ in THF. Reactions of $A_2[Fe_2Cl_6]$ and $Fe_4Cl_8(THF)_6$ with nitrogen donors such as 2,2'-bipyridine, 4,4'-bipyridine and 2,2'-bipyrimidine were performed in acetone in bulk or by slow diffusion of reactant in 3 mm O.D. glass tubes. SQUID measurements were performed on Quantum Design susceptometers housed in the Physics and Astronomy Department at Michigan State University and supported by the Center For Fundamental Materials Research at Michigan State University.

RESULTS AND DISCUSSION

Two remarkably simple, discrete forms of ferrous chloride have been reported in recent years; these are the dinuclear species $[Fe_2Cl_6]^{2-}$ and the tetranuclear cluster $Fe_4Cl_8(THF)_6$.[1] Compound **1** was first synthesized in our laboratories by the unexpected reduction of ferric chloride ($FeCl_3$) by the highly basic tertiary phosphine (TMPP = tris(2,4,6-trimethoxyphenyl)-phosphine) in low yield.[1a] Compound **1** as well as a series of related ferrous chloride $A_2[Fe_2Cl_6]$ salts was later synthesized by a rational route that involves reactions of ferrous chloride $FeCl_2$ with various salts ACl (A = H-TMPP, **1**; PPh_4, **2**; Et_4N, **3**; $AsPh_4$, **4**; ppn, **5**) ([H-TMPP]Cl = [H-$P(C_6H_2(OMe_3)_3]Cl$), in excellent yields. A representative ORTEP drawing of the $[Fe_2Cl_6]^{2-}$ unit in the $[Et_4N]^+$ salt is depicted in Figure 1.

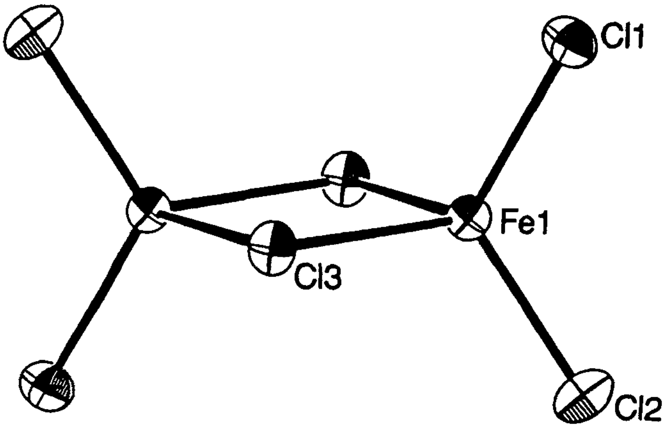

Figure 1. ORTEP drawing of the basic unit $[Fe_2Cl_6]^{2-}$ as found in the $[Et_4N]^+$ salt. Important distances (Å) and angles (deg) are: Fe1-Fe1* = 3.4232(9); Fe1-Cl1= 2.252(1); Fe1-Cl2 = 2.2440(9); Fe1-Cl3 = 2.392(1); < Fe1-Cl3-Fe1* = 91.12(3); Cl3-Fe1-Cl3* = 88.88(3).

$Fe_4Cl_8(THF)_6$ (**6**), was first structurally characterized by Bulychev *et al.* who obtained the product from the reaction of $FeCl_3$ and Cp_2ReH in THF.[1b] The compound was later reported by Cotton and coworkers who were looking for a soluble, reactive form of $FeCl_2$ to result from a redox reaction of $FeCl_3$ with metallic Fe in refluxing THF.[1c] A simplified preparation of **6** used in our laboratories involves refluxing a suspension of anhydrous $FeCl_2$ in THF, a procedure that gives highly pure $Fe_4Cl_8(THF)_6$ in nearly quantitative yield. An ORTEP drawing obtained from a structure performed in our laboratories is shown in Figure 2, and verifies the identity of the compound.

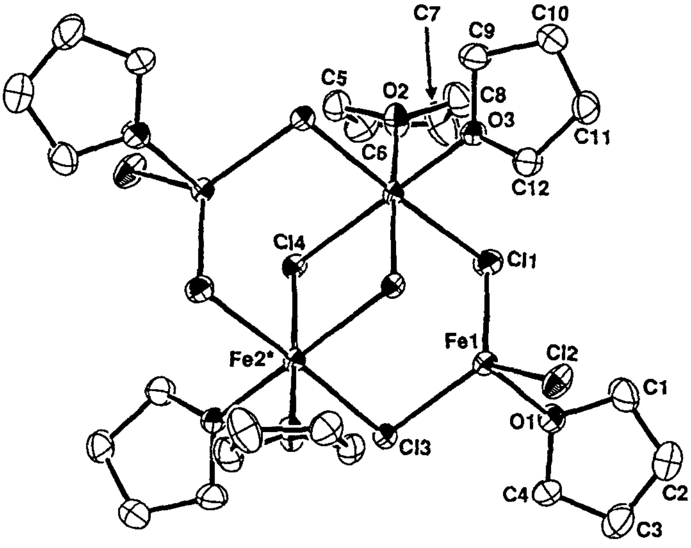

Figure 2. ORTEP drawing of the cluster $Fe_4Cl_8(THF)_6$. Important distances (Å) and angles (deg) are: Fe1-Fe1*= 6.209(2); Fe2-Fe2* = 3.739(2); Fe1-Cl1 = 2.354(1); Fe1-Cl2 = 2.261(1); Fe1-Cl3 = 2.371(1); Fe1-Cl4 = 2.682(1); Fe2-Cl1 = 2.459(1); Fe2-Cl3 = 2.461(1); Fe2-Cl4 = 2.519(2); < Fe2-Cl4-Fe2* = 96.28(4); < Fe1-Cl1-Fe2 = 97.85(5).

Magnetism of Salts Containing $[Fe_2Cl_6]^{2-}$

SQUID measurements of the $[Fe_2Cl_6]_{2-}$ salts reveal interesting behavior indicative of ferromagnetically coupled S=2 metal centers. Plots of χ_m vs temperature, μ_{eff} vs temperature, reduced magnetization vs H/T (field/temperature) and reduced magnetization vs H (field) respectively for **1** (A^+ = [H-TMPP]$^+$) are presented in Figures 3(a,b) and 4(a,b).

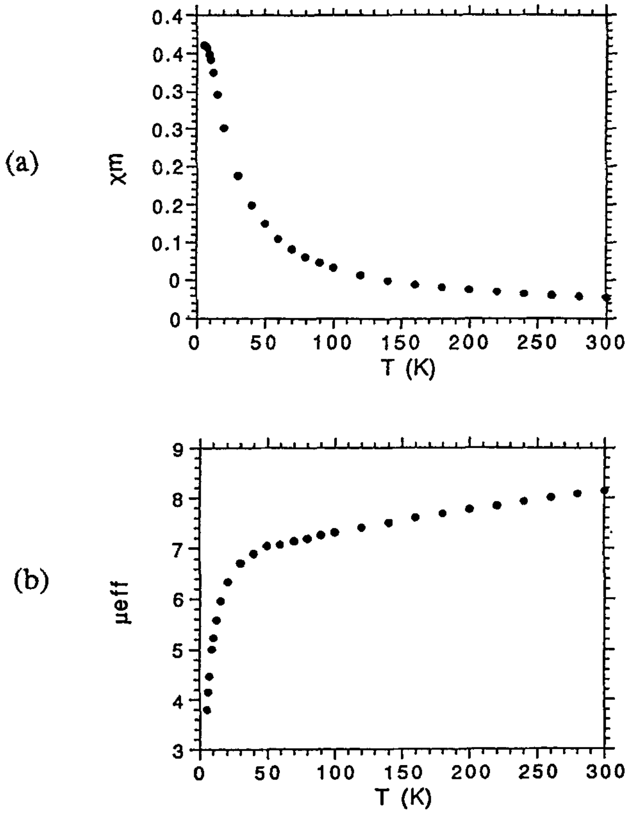

Figure 3. Plots of χ_m and effective magnetic moment vs the absolute temperature for **1** are presented in (a) and (b) respectively.

The effective magnetic moment (μ_{eff}) for **1** at 300 K (Figure 3b) is approaching 8.1 μ_B, which is much higher than what would be expected for two non-coupled high spin Fe(II) atoms (μ_{eff} = 6.9 μ_B) but is close to the theoretical value for two ferromagnetically coupled Fe(II) centers (μ_{eff} = 8.9 μ_B). The effective magnetic moment of **1** is slightly affected by the field, *i. e.*, a higher moment was observed when a stronger field was applied. No saturation was achieved even at a field strength of 5 Tesla (Figure 4a). This is supported by the reduced magnetization vs field plot in Figure 4b, where the reduced magnetization is still rising and approaching 3.9, which is much smaller than the expected value (8 for an S=4 ground state).

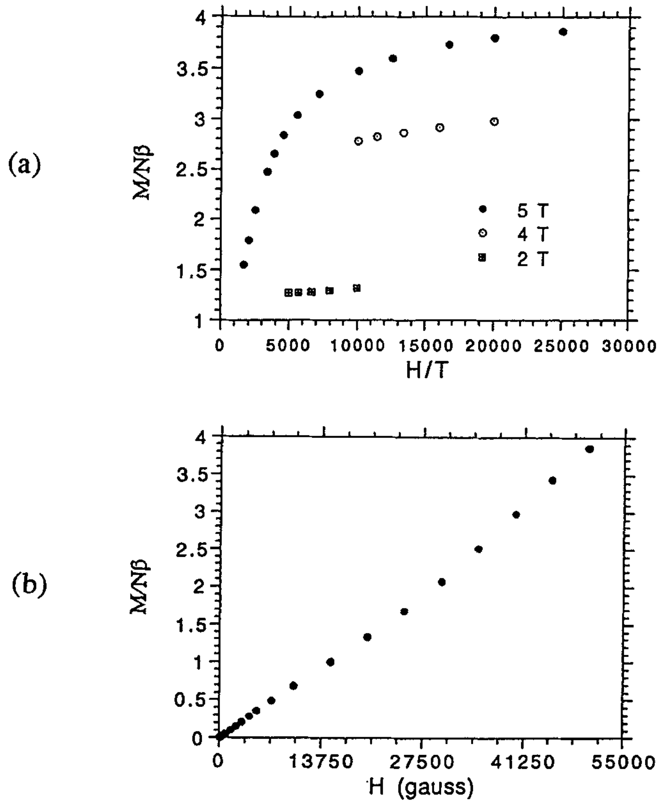

Figure 4. Plots of reduced magnetization vs the ratio of magnetic field over the absolute temperature (H/T) and the magnetic field for **1** are presented in (a) and (b) respectively.

A second example of the behavior of $[Fe_2Cl_6]^{2-}$ in a different salt **2** ($A^+ = [PPh_4]^+$) is presented in Figures 5 (a,b) and 6 (a,b).

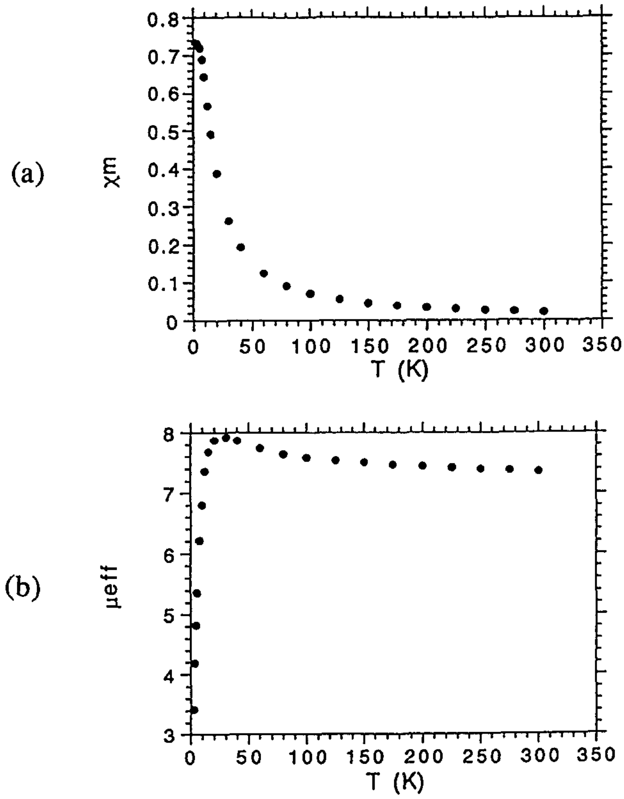

Figure 5. Plots of χ_m and effective magnetic moment vs the absolute temperature for **2** are presented in (a) and (b) respectively.

For the $[PPh_4]^+$ salt, the effective magnetic moment at room temperature is lower than that of $[HTMPP]^+$, but increases with decreasing temperature; furthermore the reduced magnetization is much higher (at 5 Tesla and 2K the value is 6.6 as shown in Figure 6a). The plot of μ_{eff} vs T increases and reaches a maximum of ~8.0 μ_B at 20 K before zero-field splitting and intermolecular antiferromagnetic coupling effects become dominant (Figure 5b). These results support the conclusion that the cation (through packing influences) plays an important role in mediating the magnetic properties of $[Fe_2Cl_6]^{2-}$; the results of different packing motifs are evident by examining the bridging Fe-Cl-Fe bond angle (which is directly related to superexchange) and the shortest Cl····Cl contacts between nearest neighbor $[Fe_2Cl_6]^{2-}$ units.

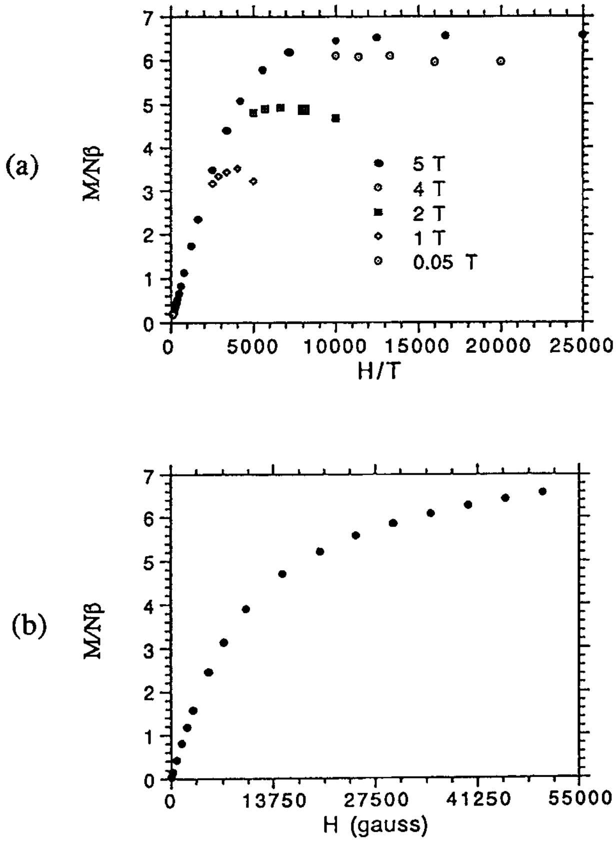

Figure 6. Plots of reduced magnetization vs the ratio of magnetic field over the absolute temperature (H/T) and the magnetic field for **2** are presented in (a) and (b) respectively.

It is also clear from the dramatic decrease in susceptibility and the lower than expected μ_B values that the large zero-field splittings (D) of Fe(II) are complicating the overall spin ladder, thereby rendering a simplified isotropic Heisenberg fitting unjustified. In fact, it may even be the case that J and D are of a similar magnitude. A summary of structural parameters and maximum magnetic moments for the series $A_2[Fe_2Cl_6]$ (A = H-TMPP, **1**; PPh_4, **2**; Et_4N, **3**; $AsPh_4$, **4**; ppn, **5**) is presented in Table I.

Ferrous salt	<Fe-Cl_{bridge}-Fe	d(Cl····Cl) (inter)	max μ_{eff} at (0.1 T)
$[HTMPP]_2[Fe_2Cl_6]$	88.64(8)°		8.1 (300 K)
$[Et_4N]_2[Fe_2Cl_6]$	91.12(3)°	6.462(2) Å	7.25 (300 K)
$[Ph_4As]_2[Fe_2Cl_6]$	91.12(4) °	5.584(3) Å	7.4 (300 K)
$[Ph_4P]_2[Fe_2Cl_6]$	91.79(3)°	5.619(2) Å	7.25 (20 K)
$[ppn]_2[Fe_2Cl_6]$	91.8(2);° 88.9(2)°	5.694(8) Å	5.9 (30 K)

Table I. Summary of key data for salts of $[Fe_2Cl_6]^{2-}$.

Magnetism of $Fe_4Cl_8(THF)_6$

Magnetic measurements of $Fe_4Cl_8(THF)_6$ in the temperature range of 79-294 K by the Faraday method have previously been reported by Bulychev *et al.* and the results suggested an overall ferromagnetically coupled Fe(II) tetramer.[1b] We undertook a more thorough investigation of the magnetism of the is fascinating cluster, with particular attention to the low temperature range and to field dependence studies, our goal being to establish the true magnetic ground state if possible DC SQUID susceptibility measurements of **6** are depicted in the plots of μ_{eff} vs temperature, reduced magnetization vs H/T (field/temperature) and reduced magnetization vs H (field) as shown in Figures 7 (a-c). As can be seen from these data, the effective magnetic moment approaches the theoretical value for four ferromagnetically coupled Fe(II) atoms (18.9 BM). The transition observed in the plot of M/Nβ vs H is characteristic of "metamagnetic" behavior, with antiferromagnetic-like coupling is observed below 15000 gauss while ferromagnetic-like coupling is observed above 15000 gauss. This has been observed for both inorganic [2a-b] and organic compounds.[2c-d]

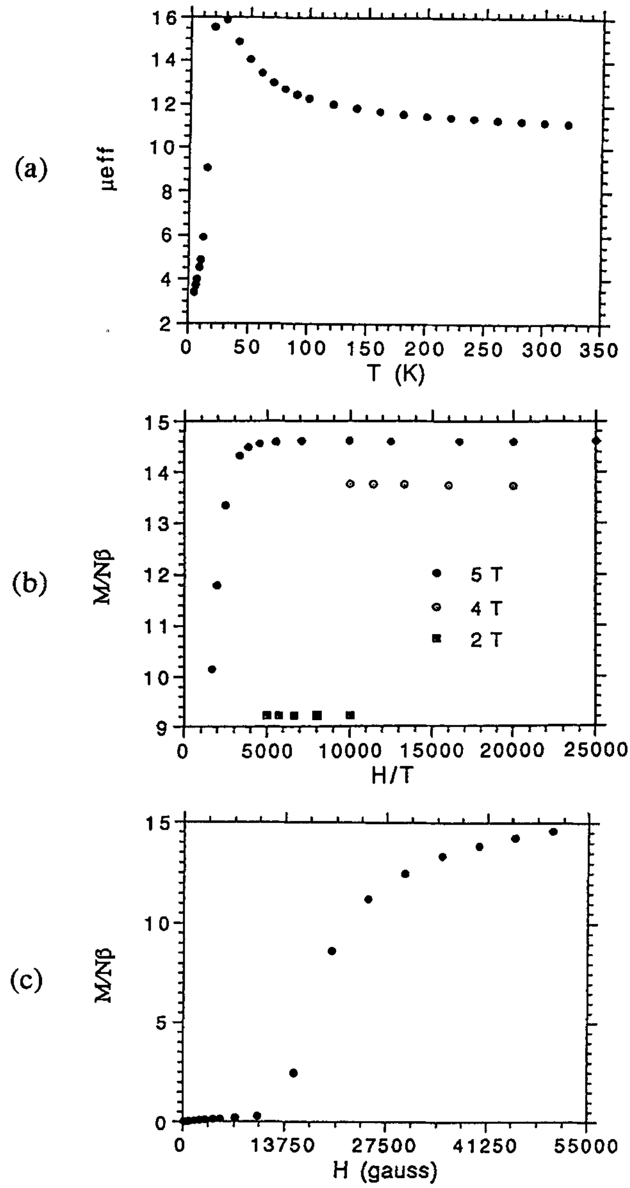

Figure 7. Plots of μ_{eff} vs T, reduced magnetization vs the ratio of magnetic field over the absolute temperature(H/T) and reduced magnetization versus magnetic field for **6** are presented in (a), (b) and (c) respectively.

Reactions of Polynuclear Ferrous Compounds with Nitrogen Donors

The nitrogen donors 2,2'-bipyridine (2,2'-bpy), 4,4'-bipyridine (4,4'-bpy), and 2,2'-bypyrimidine (bpym) were reacted with $A_2[Fe_2Cl_6]$ (A = PPh_4 and Et_4N) and $Fe_4Cl_8(THF)_6$ to explore the possibility of preparing polymeric structures with cooperative interactions. The $[Fe_2Cl_6]^{2-}$ core appears to cleave in many of these reactions as evidenced by the isolation and structural characterization.of $Fe_2Cl_4(\mu\text{-}2,2'\text{-bpym})(2,2'\text{-bpym})_2$ with antiferromagnetically coupled Fe(II) centers. Two related compounds ($Fe_2(NSC)_4(2,2'\text{-bpym})_3$ [3a] and $Co_2(NSC)_4(2,2'\text{-bpym})_3$ [3b]) have been recently reported and also exhibit antiferromagnetic coupling behavior

Reactions of the cluster $Fe_4Cl_8(THF)_6$ with nitrogen donors proceed with retention of the cluster framework. In addition to the organic nitrogen donors, a new inorganic building block $[Mn(2,2'\text{-bpym})_2][BF_4]_2$ with unligated nitrogen donors available for bridging to another metal has been synthesized and fully characterized (Figure 8);[4] the cation $[Mn(2,2'\text{-bpym})_2]^{2+}$ was used in a reaction with $Fe_4Cl_8(THF)_6$ to form an extended material that displays ferrimagnetic behavior. Efforts to crystallize this and the products from the bipyrimidine and 4,4'-bipyridine reactions are in progress.

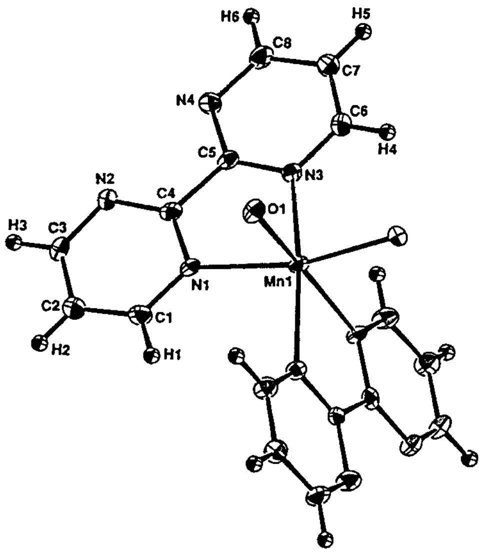

Figure 8. ORTEP of $[Mn(bpym)_2(H_2O)_2]^{2+}$. Important distances (Å) and angles (deg) are: Mn1-O1 = 2.168(4); Mn1-N1 = 2.258(5); Mn1-N3 = 2.263(5); < O1-Mn1-O1* = 83.7(2); < N1-Mn1-N3 = 73.2(2).

Conclusions and Future Directions

Discrete forms of ferrous chloride exhibit large magnetic moments indicative of ferromagnetic coupling behavior; quantitative fittings await determination of the zero-field splitting parameters from epr data. Mössbauer data will also complement these studies and allow for a complete picture of the magnetic interpretation. These systems constitute promising precursors to larger ordered arrays with cooperative properties. In- depth analyses of the structural and magnetic properties of such di- and tetranuclear molecules will help build a foundation of understanding to bridge the gap between small molecular units and extended structures built from them. Given the unusual properties of the Fe(II) compound, the ferromagnetically coupled cluster $Co_4Cl_8(THF)_6$ and the Mn analogue are also being pursued for the synthesis of polymeric frameworks.

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