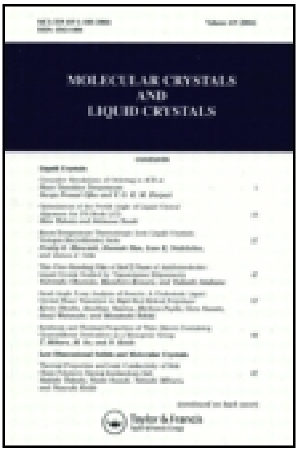

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HIGH SPIN MOLECULES: A STRUCTURAL AND MAGNETIC COMPARISON OF HIGH NUCLEARITY MANGANESE CARBOXYLATE AGGREGATES

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Abstract A structural and magnetic comparison is presented for a number of high nuclearity, higher oxidation state manganese complexes with similar ligation environments. The complexes considered are hepta-, octa-, ennea-, deca-, and dodecanuclear and contain only Mn^{III}, except for the dodecanuclear complexes, which are mixed valence ($Mn^{III}_8Mn^{IV}_4$). The ground state spins of these complexes range from very low to very high, and while the dodecanuclear complexes exhibit unusual AC magnetic susceptibility behavior, none of the other complexes show such properties. Magnetic properties, as well as structural and preparative information, are discussed.

INTRODUCTION

In the realm of high spin molecules, one particularly fruitful area of research that has produced numerous examples of molecules with many unpaired electrons has been the chemistry of high oxidation state manganese complexes containing carboxylate and oxide ligation.[1,2] Using only a limited palette of ligands and starting materials, a wide range of manganese nuclearities may be attained, including hepta-,[3] octa-,[4] ennea-,[4] deca-,[5] and dodecanuclear[6,7] complexes. Although some success has been achieved in the prediction of the metal nuclearity of products in coordination chemistry, it is still very difficult to anticipate the precise structure of the complexes obtained. Likewise, the magnetic properties of such large aggregates can be difficult to rationalize when known, and nearly impossible to predict. With various competing coupling pathways present, spin frustration is almost always a complicating factor in these manganese aggregates; however, this phenomenon is also the source of some of the large ground states found for these complexes. The small number of known complexes of this type with average metal oxidation states ≥ III show vastly different magnetic properties, with ground state spins ranging from $S=11$ [4] to $S=0$ [5]. The only discrete molecular species found to exhibit an out-of-phase component in their AC magnetic susceptibilities (χ''_M) and hysteresis loops at low temperatures, have been complexes with the general formula $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$.[7,8] These properties are still not completely understood, and it is desirable to produce additional examples of these bistable molecular materials. Because only a small number of these large aggregates exist, it becomes important to compile the known information in a rational way, in order to draw some basic conclusions about magneto-structural correlations in these complicated systems.

$(NEt_4)[Mn_7O_4(O_2CMe)_{10}(dbm)_4]$

The reaction of $[Mn_4O_2(O_2CMe)_6(py)_2(dbm)_2]$[9], (py = pyridine; dbmH = dibenzoylmethane) with $Et_4NCl{\cdot}xH_2O$ in dichloromethane yields the heptanuclear complex $(NEt_4)[Mn_7O_4(O_2CMe)_{10}(dbm)_4]$.[3] The seven distorted-octahedral Mn^{III} ions are arranged in an extended core of two fused, vertex-sharing $[Mn_4O_2]^{8+}$ units. The structure of the anion is shown in Figure 1, and the manganese oxide core of the complex is shown in Table I. The six Jahn-Teller axial elongation axes and one Jahn-Teller compression axis are not aligned in a parallel manner; in fact, the axes of two of the Mn ions are aligned perpendicularly relative to the majority of the Jahn-Teller axes.

High field (50 kG) magnetization studies at low temperatures, as well as AC susceptibility studies, seem to indicate a ground state of S=3 for this complex. However, there appears to be a low-lying S=2 excited state which complicates the interpretation of the data. This complex does not exhibit an out-of-phase component of the AC magnetic susceptibility.

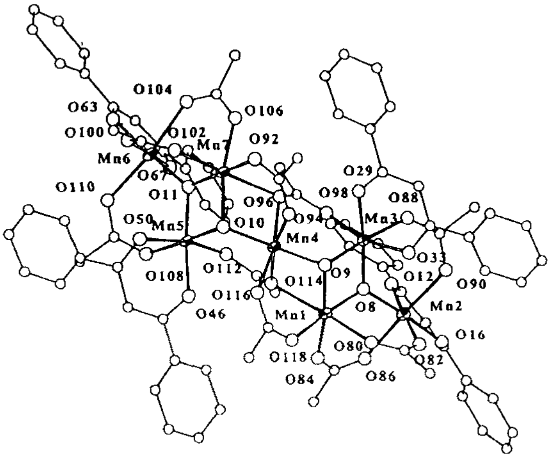


FIGURE 1. $[Mn_7O_4(O_2CMe)_{10}(dbm)_4]^-$

$(NBu^n_4)[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]$

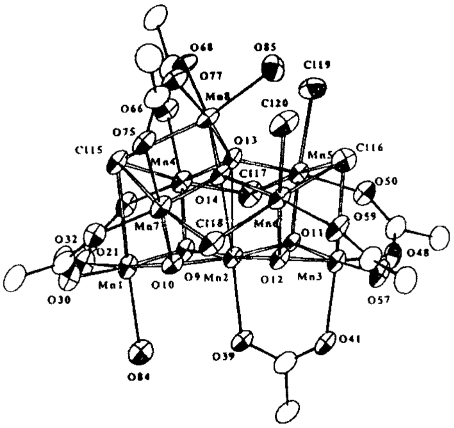


FIGURE 2. $[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]^-$

Treatment of the complex $(NBu^n_4)[Mn_4O_2(O_2CPh)_9(H_2O)]$,[4] which contains a $[Mn_4O_2]^{8+}$ "butterfly" core, with four equivalents of Me_3SiCl in dichloromethane, gives the complex $(NBu^n_4)[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]$ in approximately 50% yield.[4] The anion is shown in Figure 2. The core of this complex, as shown in Table I, consists of two Mn_4O_2 units fused through a "body" Mn ion with the eighth Mn atom connected to the resultant $[Mn_4O_7]$ unit by two μ_4-oxide ions. In addition, there are six chloride ions in terminal, μ-, μ_3-, and μ_4- ligation modes. The Jahn-Teller axes of the Mn^{III} ions are oriented in many directions, but are located predominantly along the manganese-chloride bonds.

The reduced magnetization data of this octanuclear complex vs. temperature show nearly superimposable isofield lines, and can be fit to a ground state of S=11, with g=1.92 and D=0.04 cm^{-1}. AC magnetic susceptibility measurements confirm the S=11 ground state. Despite the very high ground state spin value, no out-of-phase component of the AC susceptibility is observed.

$[Mn_9Na_2O_7(O_2CPh)_{15}(MeCN)_2]$

The reaction of $(NBu^n_4)[Mn_4O_2(O_2CPh)_9(H_2O)]$ with benzoyl peroxide in MeCN, followed by addition of $NaClO_4$, gives the enneanuclear complex $[Mn_9Na_2O_7(O_2CPh)_{15}(MeCN)_2]$.[4] An ORTEP representation of the structure is shown in Figure 3. The core, which is shown in Table I, can be viewed as a heterometallic undecanuclear aggregate, with the Na^+ ions forming an integral part of the cluster. The $[Mn_9O_7]^{13+}$ core is similar to that of $[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]$. However, two Mn ions are connected to the fused butterfly unit via three μ_3-oxides, and the unique central Mn of the basal unit is five-coordinate rather than seven-coordinate.

Reduced magnetization studies indicate that this complex has an S=4 ground state. Fitting of the reduced magnetization data gives g=1.94 and D= -0.25 cm^{-1}. AC magnetic susceptibility measurements confirm the assignment of the ground state as S=4 and show that there is no out-of-phase component (χ''_M) present.

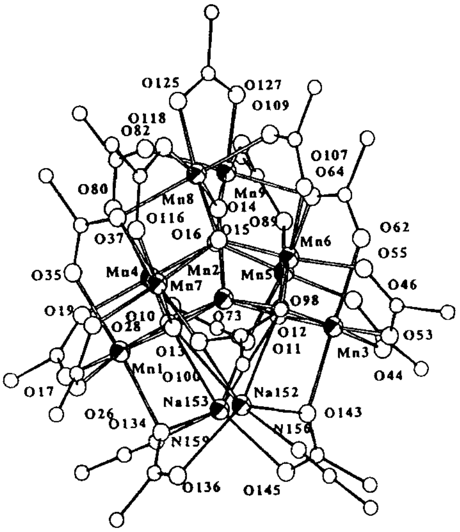


FIGURE 3. $[Mn_9Na_2O_7(O_2CPh)_{15}(MeCN)_2]$

$[Mn_{10}O_8(O_2CPh)_6(pic)_8]$

A rearrangement and aggregation of the $[Mn_4O_2]^{8+}$ "butterfly" $[Mn_4O_2(O_2CPh)_6(pic)_2]$[10] (Hpic = picolinic acid), occurs in the extremely polar solvent N, N-dimethylacetamide, with formation of a low but reproducible yield of $[Mn_{10}O_8(O_2CPh)_6(pic)_8]$ over a period of about a week upon dilution with dichloromethane.[5] The structure is shown in Figure 4 and the $[Mn_{10}O_8]^{14+}$ core is depicted in Table I. The core possesses an abundance of both μ_3- and μ_4-bridging oxides, creating a very compact, highly interconnected structure. The core can be viewed as either two edge-sharing Mn_4O_2 units connected to two additional Mn atoms by μ-oxides, or alternatively as two edge-sharing open faced cubane units capped by two $[Mn_3O]^{7+}$ units.

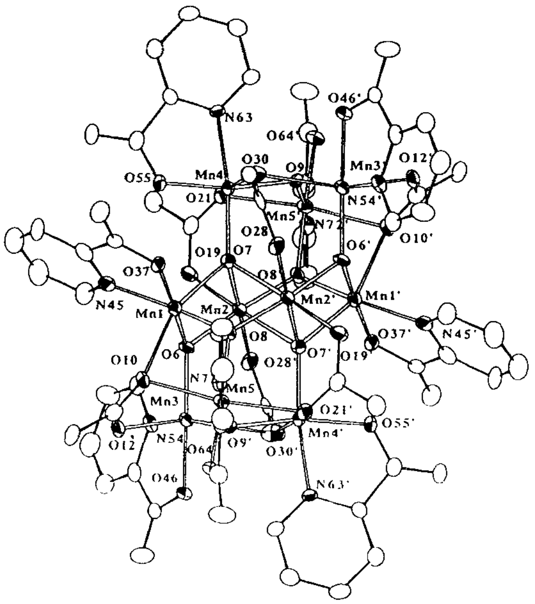


FIGURE 4. $[Mn_{10}O_8(O_2CPh)_6(pic)_8]$

Preliminary attempts to fit DC variable field magnetization data for this compound have proven difficult, because isofield lines do not saturate even at 50 kG, indicating the probable population of a low lying excited state and/or the presence of zero-field splitting. Both AC and DC susceptibility data show rapidly decreasing $\chi_M'T$ at low temperatures, indicating a low ground state. However, the AC $\chi_M'T$ data do not drop as rapidly with decreasing temperature as the DC $\chi_M T$, indicating that zero field splitting of a low lying excited state may be causing the DC data to drop more sharply at higher temperatures. The ground state appears to be S= 0 with possible low-lying excited states. More experiments are planned to confirm this tentative assignment.

$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^n$ (n=0, -1)

A group of large aggregates possessing a number of very unusual magnetic properties is the family of dodecanuclear complexes of formula $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$. The R=Me version can be easily synthesized by the comproportionation reaction of $KMnO_4$ with $Mn(OAc)_2 \cdot 4H_2O$ in 60% aqueous acetic acid.[6] Complexes containing other R groups such as R=Ph and R=Et may be synthesized by ligand substitution of the R=Me complex. These mixed-valence $Mn^{III}{}_8Mn^{IV}{}_4$ complexes may also be reduced by one electron using an organic iodide salt to give the $Mn^{II}Mn^{III}Mn^{IV}$ analog.[11,12] A representative of this type of complex is illustrated in Figure 5. The $Mn_{12}O_{12}$ core is shown in Table I.

Determination of the ground state by both very low and high field magnetization studies gives S=9 or S=10, depending on the carboxylate used and the number of lattice solvent molecules, for the neutral species,[7,8] and S=19/2 for the one-electron reduced species.[11,12] In addition to these large ground states, each complex also exhibits a frequency-dependent out-of-phase component of the AC magnetic susceptibility (χ_M''), unlike all of the previously discussed complexes. The reduced analog also exhibits such behavior, even in the presence of large separating cations. It is the first ionic species to do

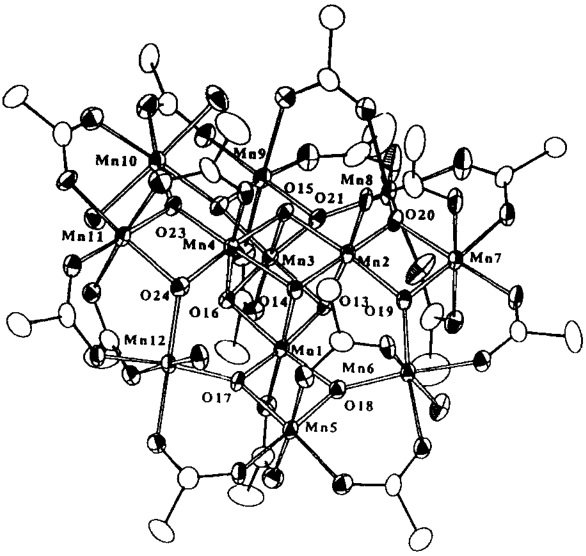
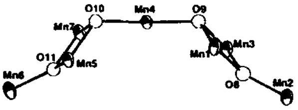
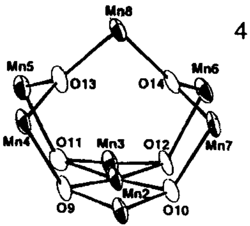
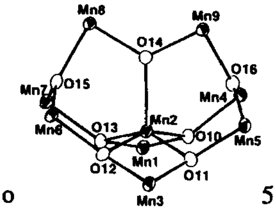
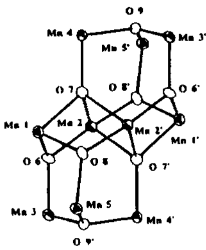
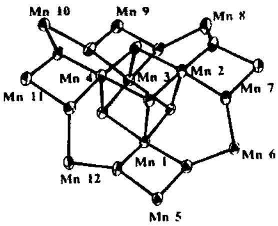


FIGURE 5. $[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]^-$

TABLE I. Comparison Of Magnetic Properties Of High Nuclearity Manganese Aggregates

COMPLEX	G.S.	χ''_M	CORE	REF.
$(NEt_4)[Mn_7O_4(O_2CMe)_{10}(dbm)_4]$ $7Mn^{III}$	**3**	no		3
$(NBu^n_4)[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2$ $8Mn^{III}$	**11**	no		4
$[Mn_9Na_2O_7(O_2CPh)_{15}(MeCN)_2]$ $9Mn^{III}$	**4**	no		4
$[Mn_{10}O_8(O_2CPh)_6(pic)_8]$ $10Mn^{III}$	**0?**	no		5
$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ $8Mn^{III}$, $4Mn^{IV}$	**9,10**	yes		7, 8, 12
$(PPh_4)[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ Mn^{II},$7Mn^{III}$,$4Mn^{IV}$	**19/2**	yes		11, 12

so, indicating that this property is due to intramolecular rather than intermolecular interactions. Non-superimposability of isofield lines of increasing field strength in the magnetization experiments and direct measurements through high field EPR indicate that this complex has significant zero-field splitting (D is approximately 0.5 cm^{-1}). These complexes also exhibit hysteresis loops at low temperature.

SUMMARY

The results presented above on some selected high nuclearity manganese complexes are summarized in Table I. The first conclusion that can be easily drawn from the data is that there is indeed a wide range of ground states possible for these higher nuclearity manganese complexes. The numerical values for the ground states of some of the complexes have been rationalized elsewhere,[4b,13,14] based on effects of metal geometry and oxidation state on the strengths of various magnetic exchange interactions in the complexes.

Perhaps the most interesting result is the fact that although the dodecanuclear and octanuclear complexes have very similar ground states (S=9-10 and S=11, respectively), their AC magnetic susceptibility properties are quite different. The zero-field splitting parameter, D, is much larger for the Mn_{12} complex (D~0.5 cm^{-1}) than for the Mn_8 complex (D=0.04 cm^{-1}). The zero-field splitting of the ground state in a polynuclear Mn^{III}_x complex is predominantly due to the single-ion zero-field interactions for each of the Mn^{III} ions in the complex. The z-axis of each Mn^{III} ion can be defined as the Jahn-Teller elongation axis. This same axis is usually the principle axis for defining the paramagnetic structure of the ion as well, including the zero-field splitting parameter, D. The D parameter of a polynuclear metal aggregate in which the Mn^{III} ions are coupled in such a way as to produce a ground state S can thus be expressed as a vectorial sum of the zero-field interactions at each ion in the complex. Using this rationale, the Mn_{12} complex possesses a large zero-field splitting and a large degree of magnetic anisotropy because it has a near-parallel alignment of its Jahn-Teller axes; in contrast, the elongation axes of the Mn_8 are not aligned, and hence a relatively small magnetic anisotropy results, despite the large spin ground state. The origin of the out-of-phase signal and the hysteresis effects are believed to lie in the magnetic anisotropy of the complex.[15] It would, of course, be beneficial to obtain additional complexes with a variety of ground state spins and varying degrees of magnetic anisotropy so that these emerging theories can be tested. Thus, the role of the synthetic inorganic chemist remains essential here, at the interface of molecular and bulk magnetic properties.

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