HIGH NUCLEARITY MANGANESE CARBOXYLATE CLUS-TERS: SYNTHESES, STRUCTURAL CHARACTERIZATION AND MAGNETIC PROPERTIES

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Abstract. Synthetic procedures have been developed that allow access to higher nuclearity manganese carboxylate clusters in the metal nuclearity range 7-18 and Mn oxidation state range II-IV, including mixed-valency. The structures of these discrete clusters can be considered as being composed of $[Mn_4(\mu_3-O)_2]$ butterfly units that are joined together in a number of ways; in many cases, the synthetic procedures were developed by using this observation as a guide. Certain magnetic properties of these clusters are discussed, namely the spin (S) of the ground state which has been found to be in the range S = 0-11 for the clusters described. In some cases, a qualitative rationalization of these values is possible based on spin frustration effects within the $[Mn_4O_2]$ butterfly unit.

1. Introduction

There is currently a great deal of interest in nanoscale magnetic materials, because they are expected to exhibit unusual properties.¹ The synthesis of such nanoscale magnets can be accomplished by fragmentation of bulk ferromagnets or ferrimagnets, but this approach unfortunately gives a distribution of particle sizes, and this complicates detailed studies of these systems, making difficult, for example, an accurate assessment of variation of properties as a function of particle size. An alternative strategy is to approach nanoscale dimensions from the other direction, *viz* synthesizing molecules with large numbers of unpaired electrons that are large enough to exhibit interesting magnetic properties. This strategy has the advantages that a single "particle" size can be ensured, that organic ligands on the periphery can be chosen or systematically altered to ensure crystallinity and solubility in a variety of solvents, and that X-ray crystallographic and various spectroscopic and physicochemical studies can be readily performed, in solution and/or the solid state.

One family of molecular species that have proven to be of relevance to the above topic are manganese carboxylate clusters with the metal atoms at the intermediate (II-IV) oxidation states and metal nuclearities currently up to 18. The syntheses and characterization of these clusters are the topic of this Chapter.

Originally, interest in these species was stimulated by the occurrence of dinuclear and tetranuclear oxide-bridged manganese carboxylate units at the active sites of certain proteins and enzymes,² and research objectives were the development of synthetic procedures to such molecules and their study by a variety of spectroscopic methods. It soon became apparent, however, that Mn_x/O/RCO₂⁻ chemistry was also the home of a variety of higher nuclearity. discrete clusters with a combination of aesthetically pleasing structures and unusual magnetic properties, namely the possession of electronic ground states with large spin (S) values.³ With a handful of prototypical examples identified, it became of interest to develop synthetic procedures to additional examples that would increase the available pool of clusters for study and thus provide more data points for increasing our understanding of these unusual species. This paper describes the current status of synthetic efforts in this area and summarizes the structures of the obtained materials and their ground-state spin values. Additional magnetic properties for several of the complexes to be described may be found elsewhere in this volume in the contributions by D. N. Hendrickson and D. Gatteschi.

2. Tetranuclear Complexes

2.1 TETRANUCLEAR [Mn₄O₂] BUTTERFLY COMPLEXES

Synthetic entry into $Mn_x/O/RCO_2^-$ chemistry occurred at the tetranuclear level and provided the initial example of a $[Mn_4O_2]$ butterfly-like complex.⁴ Treatment of $[Mn_3O(O_2CMe)_6(py)_3](ClO_4)$ ($3Mn^{III}$) with 2,2'-bipyridine (bpy) leads to formation of $[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$ (1; 4 Mn^{III}), isolated as the ClO₄⁻ salt. Similarly, treatment of $Mn_3O(O_2CMe)_6(py)_3$ (Mn^{II} , 2 Mn^{III}) with bpy leads to $Mn_4O_2(O_2CMe)_6(bpy)_2$ (2; 2 Mn^{II} , 2 Mn^{III}). The structures of complexes 1 and 2 are shown in Figure 1; both complexes possess a $[Mn_4(\mu_3-O)_2]$ core that may be described as two $[Mn_3(\mu_3-O)]$ triangular units sharing an edge. A more useful description, however, is as a $[Mn_4(\mu_3-O)_2]$ "butterfly"



Figure 1. The structures of (top) $[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$ (1) and (bottom) $Mn_4O_2(O_2CMe)_6(bpy)_2$ (2)



Figure 2. μ_{eff} vs temperature plots for 1 (Δ) and 2 (\bullet); the solid lines are fits to the appropriate equations.

unit, where Mn(1) and Mn(3) are the "body" Mn atoms, and Mn(2) and Mn(4) are the "wing-tip" Mn atoms. The core of 2 can be seen to be the same as that in 1 except that the absence of a seventh $MeCO_2^-$ group bridging the body Mn atoms allows the $[Mn_4O_2]$ core to adopt a planar arrangement of the four Mn atoms; the Mn^{II} ions are both at the wing-tip positions.

Magnetochemical characterization of complexes 1 and 2 led to some interesting observations.⁴ Shown in Figure 2 are the effective magnetic moment (μ_{eff}/Mn_4) vs. temperature plots, together with the fits of the data (solid lines) to the appropriate theoretical expressions, derived assuming idealized C_{2v} core symmetry (Figure 3) and neglecting the J_{ww} interaction. All pairwise interactions were found to be negative (antiferromagnetic): using the $\hat{H} = -2J\hat{S}_i\hat{S}_i$ convention and the format 1/2, the values were $J_{bb} = -23.5/-3.1$ cm⁻¹ and $J_{wb} =$ -7.8/-2.0 cm⁻¹, with spins in the ground state of S = 3 and S = 2 for 1 and 2, respectively. The observation of these intermediate S values for totally antiferromagnetically-coupled systems was interesting and it became clear that this was due to spin frustration: this is defined in a general sense as the presence of competing exchange interactions of comparable magnitude that prevent (frustrate) the preferred pairwise alignments of the various spins within a system.⁵ In the present case of complex 1, for example, it is clearly impossible for all the spins in this antiferromagnetically-coupled system to align antiparallel, and the ground state then becomes sensitive to the exact J_{bb}/J_{wb} ratio (i.e., the relative magnitudes of the competing exchange interactions). The analysis of the data for 1 shows the spin alignments in the ground state to be as shown in Figure 3, i.e., the two body Mn spins give a resultant $S_{bb} = 1$ and the two wingtip Mn spins give a resultant $S_{ww} = 4$, with the total resultant spin being S = 4-1 = 3.

Since the preparation of 1, a number of other $[Mn_4O_2]^{8+}$ complexes have been prepared with a variety of chelates (L-L), including the anions of picolinic acid (picH), 8-hydroxyquinoline (hqnH), dibenzoylmethane (dbmH) and 2-(hydroxymethyl)pyridine (hmpH); they can all be obtained using either of the two methods summarized in equations 1 and 2; in every case investigated, the complexes have an S = 3 ground state.⁶

$$Mn_{3}O(O_{2}CR)_{6}(py)_{3} \xrightarrow[MeCN]{L-L} [Mn_{4}O_{2}(O_{2}CR)_{7}(L-L)_{2}]^{-}$$
(1)

$$4Mn^{2+} MnO_4 \xrightarrow{L-L}_{MeCN} [Mn_4O_2(O_2CR)_7(L-L)_2]^-$$
(2)
i.e.,
$$4Mn^{2+} + Mn^{7+} \rightarrow \frac{5}{4}Mn_4^{3+}$$



Figure 3. Exchange interactions in the $[Mn_4O_2]$ butterfly unit (b=body; w=wing-tip), and the Mn^{III} spin alignments in 1 (S=3).



Figure 4. The structure of $[Mn_4O_2(O_2CPh)_9(H_2O)]^-$ (3)

A recent addition to the $[Mn_4O_2]^{8^+}$ family of butterfly complexes is $[Mn_4O_2(O_2CPh)_9(H_2O)]^-$ (3; Figure 4) obtained in >90% yield as the NBu₄ⁿ⁺ salt from the reaction of $Mn(O_2CPh)_2$ and $NBu_4^nMnO_4$ in EtOH/MeCN.⁷ This complex has only PhCO₂⁻ and H₂O peripheral ligands, and is a particularly convenient and reactive source of the $[Mn_4O_2]^{8^+}$ unit (vide infra).

2.2 TETRANUCLEAR [Mn₄O₃X]⁶⁺ DISTORTED-CUBANE COMPLEXES

A second type of tetranuclear complex can be obtained from $Mn_4O_2(O_2CMe)_6(py)_2(dbm)_2$ (which is similar to $[Mn_4O_2(O_2CMe)_7(dbm)_2]^-$ but with one bridging MeCO₂⁻ replaced by two py groups): controlled potential electrolysis or disproportionation triggered by carboxylate abstraction with Me₃SiX allow access to the $3Mn^{III}$, Mn^{IV} complexes $Mn_4O_3X(O_2CMe)_3(dbm)_3$ (X = Cl⁻, 4; Br⁻, 5; N₃⁻, 6; NCO⁻, 7; MeCO₂⁻, 8);^{6,8} 4 and 5 will also form on addition of NBuⁿ₄Cl to hot MeCN solutions of $Mn_4O_2(O_2CMe)_6(py)_2(dbm)_2$. Complex 8 (X = MeCO₂⁻) is itself an excellent stepping-stone, providing alternative routes to 4-6, and also to new complexes with X = F⁻ (9) and MeO⁻ (10), on treatment with Et₂NSF₃ (DAST) or MeOH, respectively. These transformations are summarized in Figure 5 and the structure of representative complex 6 is shown in Figure 6. The $[Mn_4O_3X]^{6+}$ core is trapped-valence $3Mn^{III}$, Mn^{IV} , and the Mn^{IV} ion is the one on the virtual C₃ axis, i.e., Mn(1) in Figure 6.

Magnetochemical characterization of the $[Mn_4O_3X]^{6+}$ -containing complexes of idealized C_{3v} symmetry shows them to possess both antiferromagnetic J_{34} and ferromagnetic J_{33} exchange interactions, where $J_{34} = J(Mn^{III}...Mn^{IV})$ and $J_{33} = J(Mn^{III}...Mn^{III})$. This gives a resulting S = 9/2 ground state, as can be rationalized diagrammatically in Figure 7; antiparallel alignment of each Mn^{III} (S = 2) spin vector with the Mn^{IV} (S = 3/2) spin vector gives a total spin of S = 6 - 3/2 = 9/2.

It is of interest to note that the $[Mn_4O_3X]^{6+}$ core is more closely related to the $[Mn_4O_2]^{8+}$ butterfly core than might at first be apparent: in Figure 6, for example, removal of atoms N(1) and O(1) leaves a $[Mn_4O_2]$ butterfly unit, albeit more closed up than those in 1 or 3.

3. Higher Nuclearity Complexes

The $[Mn_4O_2]^{8+}$ (S = 3) and $[Mn_4O_3X]^{6+}$ (S = 9/2) complexes display attractive structures and relatively high values of ground state spin, and it was important











to ask whether still higher nuclearity complexes could be obtained and whether these might also demonstrate interesting structural and magnetic properties. Indeed, synthetic procedures have now been successfully developed to a variety of higher nuclearity systems; in general, the synthetic strategy has involved the use of smaller nuclearity starting materials that are "destabilized" by a number of means, the belief being that this destabilization might trigger aggregation to higher nuclearity products. While this approach does not always work, it has nevertheless been successful satisfyingly often and has provided some remarkable products.

As will become obvious from the structural descriptions to follow, many of these higher nuclearity products can be considered as two or more Mn₄ butterfly units joined together, and to facilitate subsequent discussion, we first define some terms to be employed. In Figure 8 are shown four ways in which [Mn₄O₂] butterfly units may be joined together: a) "fused" butterfly units involve the sharing of one (or more) body or wing-tip Mn atoms; in Figure 8a are shown two "body-fused" butterfly units; b) "linked" butterfly units involve the formation of additional bonds directly between atoms of two (or more) butterfly units; c) same as type b) except that additional oxide ions are incorporated; and d) "bridged" butterfly units involve exogenous bi- or poly-functional organic groups joining together two (or more) butterfly units (e.g., two such units are bridged by a pyrazine group at the wing-tip positions in Figure 8d). It should be noted that from a synthetic point of view, "bridged" butterfly units are on paper the easiest to prepare, since the identity of the potential bridging group and the reagent ratio are readily controllable, but such organic groups provide only relatively weak inter-butterfly magnetic interactions compared with "fused" or "linked" butterfly units; the latter two types are thus much more desirable from a magnetochemical viewpoint but they are, of course, much more difficult to prepare in a controlled manner.

3.1 HEPTANUCLEAR COMPLEXES

In contrast to the reaction of $Mn_4O_2(O_2CMe)_6(py)_2(dbm)_2$ with Cl⁻ in hot MeCN which leads to $Mn_4O_3Cl(O_2CMe)_3(dbm)_3$ (4),^{6a} the same reaction in CH₂Cl₂ at room temperature gives $[Mn_7O_4(O_2CMe)_{10}(dbm)_4]^-$ (11), isolated as the NEt₄⁺ salt.⁹ The structure is shown in Figure 9; the core can be considered as two wing-tip-fused butterfly units, the shared atom being Mn(4). The Cl⁻ is necessary for this transformation although it does not appear in the product; presumably it destabilizes the $[Mn_4O_2]^{8+}$ starting material by binding to a Mn atom with partial or complete displacement of a RCO₂⁻ group, triggering fragmentation and reaggregation of the tetranuclear unit.









Figure 8. Examples of four ways of joining together [Mn₄O₂] units: a) fused, b) linked, c) linked, with additional oxide bridges, and d) bridged.



Figure 9. The structure of [Mn₇O₄(O₂CMe)₁₀(dbm)₄]⁻ (11), and a side-view of its [Mn₇O₄] core.



Figure 10. The predicted S=4 ground state of 11, assuming similarities to Figure 3. The experimentally determined ground state is S=3.

Inspection of the structure of 11 prompted the following question: knowing the magnetochemical properties of the discrete $[Mn_4O_2(O_2CR)_7(L-L)_2]^z$ complexes, might it be possible to predict the approximate ground state value of S for 11? If the relative values of the J_{bb} and J_{wb} exchange parameters do not change significantly compared with those in 1, for example, then the spinfrustrated alignments of the spins of the individual Mn^{III}ions might be similar to those in 1 (Figure 3). If so, then the resulting alignments are shown in Figure 10, which predicts a $S \approx 4$ ground state; in fact, the experimentally determined ground state was found to be S = 3. The discrepancy is undoubtedly due to the fact that the J_{bb}/J_{wb} ratio is not as it is in 1, as can be seen in Figure 9, which shows that each butterfly sub-unit is significantly distorted relative to the $[Mn_4O_2]$ core of 1, no doubt affecting the various pairwise exchange interactions mediated by the oxide bridges. In any case, the important point is not that the prediction was imperfect, but that one can achieve such a satisfying level of approximate prediction (and hence rationalization!) of the ground state spin of such a complicated system of 7Mn^{III} ions with possible total spin values of S = 0 to 14. A similar Mn₇ complex but with a central Mn^{II} ion has been prepared by Bhula and Weatherburn,¹⁰ but the ground state has not been determined.

3.2 OCTANUCLEAR COMPLEXES

Two different types of octanuclear complexes will be discussed. Treatment of complex 3 with 2,2-diethylmalonate (Et₂mal²⁻) in MeCN gives [Mn₈O₄(O₂CPh)₁₂(Et₂mal)₂(H₂O)₂]² (12; 2Mn^{II},6Mn^{III})¹¹ shown in Figure 11. Also shown is the [Mn₈O₄]¹⁴⁺ core which clearly has a 'linked-butterflies' structure formed by two connecting bonds between bridging oxides and body Mn atoms; Mn(4) and Mn(4') are the Mn^{II} centers. The complex has an S = 3ground state. The inter-butterfly bonds are on Mn^{III} Jahn-Teller elongation axes, so that intra-butterfly exchange interactions are anticipated to be stronger than the inter-butterfly interactions; indeed, except at the lowest temperatures, the experimental χ_m vs T data can be satisfactorily fit assuming no interbutterfly interactions. This analysis indicates a S = 5/2 ground state for the 'isolated' $[Mn_4O_2]^{7+}$ fragment of 12, and it is interesting to note that an S = 5/2 ground state has also been determined for [Mn₄O₂(O₂CPh)₇(bpy)₂] (13), the one-electron reduced version of 1, which contains the same $[Mn_4O_2]^{7+}$ (i.e., Mn^{II} , $3Mn^{III}$) core as seen in each half of the $[Mn_8O_4]^{14+}$ core of 12. The additional exchange interactions between two such $[Mn_4O_2]^{7+}$ units then lead to the observed S = 3 ground state of complex 12.

The reaction of complex 3 with Me₃SiCl gives another octanuclear complex $[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]^-$ (14; $8Mn^{III}$).¹² This is shown in Figure 12





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Figure 13. The $[Mn_8O_6]^{12+}$ and $[Mn_9O_7]^{13+}$ cores of 14 and 15, respectively, showing the common 'body-fused-butterflies' unit.



Figure 14. The structure of Mn₉Na₂O₇(O₂CPh)₁₅(MeCN)₂ (15)

and its core in Figure 13 which can be seen to consist of two body-fused butterfly units sharing central Mn(2). An eighth metal atom, Mn(8), is then attached to the four wing-tip Mn atoms by two oxide bridges, O(13) and O(14). This complex has a very high ground state spin of S = 11; this is undoubtedly due primarily to spin frustration effects within the fused-butterflies unit, but the structural complexity makes it difficult to rationalize this value on the basis of the properties of individual $[Mn_4O_2]^{8+}$ complexes such as 1.

3.3 ENNEA-, DECA- AND UNDECANUCLEAR COMPLEXES

An enneanuclear complex related to 14 is obtained when complex 3 is treated in CH_2Cl_2 with dibenzoyl peroxide $(PhCO_2)_2$; the product is $Mn_9Na_2O_7(O_2CPh)_{15}(MeCN)_2$ (15; $9Mn^{111})^{12}$ shown in Figure 14. The comparison of its core with that of 14 (Figure 13) shows that it also has a bodyfused-butterflies structure, but now with two additional Mn^{111} ions connected to the wing-tip Mn atoms and, additionally, to the central body Mn atom, which is five-coordinate. These structural differences have a dramatic effect on the ground state spin of 15 which is S = 4 compared with S = 11 for 14. A similar complex but without the Na⁺ ions has been made by Armstrong and coworkers.¹³

Two decanuclear complexes are available of which we shall mention only one.14 Solutions of Mn₄O₂(O₂CPh)₆(MeCN)₂(pic)₂ in dimethylacetamide slowly yield crystalline Mn₁₀O₈(O₂CPh)₆(pic)₈ (16; 10Mn^{III}), the transformation no doubt being triggered by the strong donor properties of this solvent. The structure of 16 (Figure 15) shows a linked-butterflies unit, Mn(1,2,3,4) and Mn(1',2',3',4'), with two additional Mn atoms, Mn(5) and Mn(5'), and two additional oxide bridges. This topology results in an S = 0 ground state for 16. Three other Mn₁₀ complexes are currently known, none of which contains carboxylate groups but instead amine- or phenoxide-based ligands. [Mn₁₀O₁₄(tren)₆](CF₃SO₃)₈ (4Mn^{III}, 6Mn^{IV})^{15a} contains a planar Mn₆ central unit with four other Mn atoms above and below this plane; the ground state is not known. (NEt₄)₂[Mn₁₀O₂Cl₈((OCH₂)₃CMe)₆]^{15b} contains 2Mn^{II},8Mn^{III}and a $[Mn_8(\mu_6-O)_2]^{24+}$ core that can be described as two edge-fused Mn₆ octahedra, each containing a μ_6 -O²⁻ ion; the ground state of this anion is unknown. $(NMe_4)_4[Mn_{10}O_4Br_{12}(biphen)_4]^{16}$ contains $6Mn^{II}_4Mn^{III}$ and a $[Mn_{10}O_4]^{16+}$ core that is again unrelated to the [Mn₄O₂] butterfly unit common in Mn carboxylate chemistry; the complex has a S = 12 ground state, and as such shares with $[Mn_6(hfac)_{12}(NITPh)_6]$ (NITPh = a nitronyl nitroxide radical)¹⁷ the distinction of possessing the highest ground state spin value in Mn cluster chemistry.

Complex 3 can also be used to access undecanuclear complexes. Treatment of complex 3 with Me₃SiX (X = N_3 , NCO) gives



Figure 15. The structure of $Mn_{10}O_8(O_2CPh)_6(pic)_8$ (16) and its $[Mn_{10}O_8]^{14+}$ core



Figure 16. The structure of $[Mn_{11}O_{10}Cl_2(O_2CMe)_{11}(bpy)_2(MeCN)_2(H_2O)_2]^{2+}$ (18)

 $[Mn_{11}O_{10}X_6(O_2CPh)_{11}(solv)_4]^2$ (17; solv = H₂O or MeCN).¹⁸ A related complex is available from the reaction of complex 1 with Me₃SiCl, which gives $[Mn_{11}O_{10}Cl_2(O_2CMe)_{11}(bpy)_2(solv)_4]^{2+}$ (18).¹⁹ These complexes are all $9Mn^{III}, 2Mn^{IV}$, and the structure of 18 is shown in Figure 16. The $[Mn_{11}O_{10}X_2]^{13+}$ core is rather interesting, being a mix of the $[Mn_4O_2]^{8+}$ butterfly and [Mn₄O₃X]⁶⁺ distorted-cubane types; it can be described as consisting of two body-fused butterfly units (as in 14 and 15) which are wing-tip-fused with two distorted cubane units as found in 4-10. The resulting complex has an S = 5 ground state. The latter can be rationalized as shown in Figure 17: each $[Mn_4O_3C1]^{6+}$ unit is S = 9/2 (as in 4) but spin frustration effects (as in 1) within the 'bridging' body-fused-butterflies unit can lead to a resultant S = 4 for the central Mn₃ unit, and antiparallel alignment of these three spins leads to the observed S = 5 ground state. Note that this represents a ferrimagnetic-like situation for the spin alignments in the three subsections of the cluster, akin to the ferrimagnetic-like situation in mixed-metal linear trinuclear metal complexes, such as the Mn^{II}Cu^{II}Mn^{II} species that has a S = 5/2-1/2+5/2 = 9/2ground state.20



Figure 17. Rationalization of the S=5 ground state of 17 and 18.

3.4 DODECANUCLEAR COMPLEXES

 $Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4$ (19; R = Me) was first prepared in 1980²¹ by Lis from the reaction of $Mn(O_2CMe)_2 \bullet 4H_2O$ and $KMnO_4$ in aqueous acetic acid. We have extended this to analogues with a variety of R groups by ligand substitution of 19 with excess RCO_2H (R \neq Me).²² These complexes are $8Mn^{III}, 4Mn^{IV}$, and the structure of 19; R = Et is shown in Figure 18. The $[Mn_{12}O_{12}]^{16+}$ core consists of a central $[Mn_4^{IV}O_4]$ cubane held within a nonplanar ring of $8Mn^{III}$ ions by eight O²⁻ bridges. This beautiful structure, however, is again nothing more than Mn_4O_2 butterfly units joined together. This is emphasized by Figure 18 (bottom) which shows the core minus the four O²⁻ ions of the central cube; the core of 19 is thus four wing-tip-fused butterfly units, with the inner body Mn atoms being Mn^{IV} and bridged by O²⁻ ions to give a central cube i.e. the core is four wing-tip-fused, body-linked butterflies.

In addition to their structural aesthetics, these complexes also possess unusual magnetochemical properties.^{22,23,24,25,26} They possess S = 10 ground states (some have S = 9), and it is interesting to note that this is readily rationalizable: it is known that Mn^{III}/Mn^{IV} exchange interactions are antiferro-



magnetic and relatively strong compared with much weaker Mn^{III}/Mn^{III} interactions;²⁷ thus, if we concentrate only on one [Mn₄O₂] sub-unit, the Mn^{IV} (S = 3/2) spin and the three Mn^{III} (S = 2) spins should align antiparallel, as shown. The tendencies for antiferromagnetically-coupled Mn^{III} spins to align antiparallel are thus frustrated. Further, since (i) the wing-tip Mn^{III} ions are each shared between two butterfly units and (ii) the Mn^{IV}-O-Mn^{IV} angles are rather acute (94-101°) suggesting ferromagnetic interactions within the cubane core, the wing-tip fusion of four such butterfly units will place the eight Mn^{III} spins all parallel to each other and antiparallel to those of the Mn^{IV} ions, giving a predicted ground state of S = 16 - 6 = 10 (observed S = 9 or 10).

The related complex $Fe_4Mn_8O_{12}(O_2CMe)_{16}(H_2O)_4$ (20; $4Fe^{III}$, $4Mn^{III}$, $4Mn^{IV})^{28}$ has also been prepared and found to have an S = 2 ground state. This decrease from S = 9 or 10 for the homometallic species is intuitively in the right direction: Fe^{III}/Mn^{III} interactions are more strongly antiferromagnetic than analogous Mn^{III}/Mn^{III} interactions,²⁹ and spin frustration effects between competing Mn^{IV}/Mn^{III} and Fe^{III}/Mn^{III} interactions might be expected to result in

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the M^{III} spins not all being parallel; thus, the ground state would be expected to decrease significantly, as observed.

Another derivative of the $[Mn_{12}O_{12}]^{16+}$ core has been obtained²⁴ by oneelectron reduction with I. [Mn₁₂O₁₂(O₂CEt)₁₆(H₂O)₄]⁻ (21) has been structurally characterized as the PPh₄⁺ salt to identify the locus of the added electron; interestingly, the latter has added to an outer (formerly Mn^{III}) atom rather than a central Mn^{IV} atom, probably to avoid the strain in the central cubane unit that would result from introduction of a Mn^{III} Jahn-Teller distortion. Anion 21 is thus Mn^{II} , $7Mn^{III}$, $4Mn^{IV}$, and it has an S = 19/2 ground state. The only other Mn_{12} complex known is $Mn_{12}(OH)_4(O_2CMe)_2L_6$ (L = a polydentate Schiff-base ligand)³⁰ which contains 12Mn^{II} and its structure cannot consequently be described in terms of [Mn₄O₂]⁸⁺ units. The Mn^{II} ions are weakly coupled antiferromagnetically but the ground state of the complex is currently unclear. There is also a hexadecanuclear complex known, namely Mn₁₆Ba₈Na₂Cl(OH)₈(CO₃)₄L₈ (L is a polydentate ligand),³¹ which contains 9Mn^{II}, 7Mn^{III}, but very little is currently known about this species.

3.5 OCTADECANUCLEAR COMPLEXES

The reaction of complex 3 with KHphth (H₂phth = phthalic acid) leads to the complex $[K_4Mn_{18}O_{16}(O_2CPh)_{22}(phth)_2(H_2O)_4]$ (22; 18Mn^{III}),³² the highest nuclearity Mn cluster currently known. The structure of 22 is shown in Figure 19, and the $[Mn_{18}O_{16}]^{22+}$ core is again composed of $[Mn_4O_2]^{8+}$ butterfly units: the central portion of the core comprises three body-fused butterfly units, as shown below, with two additional $[Mn_4O_2]$ units then linked *via* the wing-tip positions to the top and bottom of this central sub-core by six additional oxide bridges.



Complex 22 is structurally interesting but magnetochemically it is rather disappointing, having an S = 0 ground state. Paradoxically, however, its S = 0 ground state makes 22 unusual, for S = 0 ground states are the exception rather than the rule in Mn carboxylate chemistry.



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Figure 19. The structure of $K_4Mn_{18}O_{16}(O_2CPh)_{22}(phth)_2(H_2O)_4$ (22) Figure 20. Stereoview of three repeating $[Mn_4O_2]$ units in the polymer $[Mn_4O_2(O_2CPh)_6(4,4'-bpy)(dbm)_2]_n$

3.6 "BRIDGED" BUTTERFLY COMPLEXES

A number of products have been obtained that can be described as [Mn₄O₂]⁸⁺ butterfly units joined together by polyfunctional organic ligands; we shall describe here only a representative sample. The butterfly complex Mn₄O₂(O₂CPh)₆(EtOAc)₂(dbm)₂ contains two labile EtOAc groups and represents a convenient starting point for oligomerization studies. Treatment with trans-1,2-bis(pyridyl)ethane (bpe) gives $[Mn_4O_2(O_2CPh)_6(bpe)(dbm)_2]_2$ (23).³³ with 4,4'-bipyridine (4,4'-bpy)An analogous reaction gives $[Mn_4O_2(O_2CPh)_6(4,4'-bpy)(dbm)_2]_n$ (24) which is a one-dimensional polymer (Figure 20).³³ The bridging groups bpe and 4,4'-bpy do not mediate strong inter-butterfly exchange interactions, and complexes 23 and 24 thus behave magnetochemically as essentially isolated [Mn₄O₂] units.



Most recently, work has been initiated to introduce into Mn carboxylate cluster chemistry the types of ligands finding elegant employment with mononuclear metal species for formation of helicate products.³⁴ To date, efforts have concentrated on *bis*-bipyridyl ligands, and two interesting products have been obtained. Treatment of $[Mn_3O(O_2CMe)_6(py)_3]^+$ with L1 gives $[Mn_4O_2(O_2CMe)_4(L1)_2]^{2+}$ (25, $2Mn^{II}, 2Mn^{III}$) shown in Figure 21.³⁵ It contains two dinuclear fragments held together only by two Mn-O bonds. In contrast, treatment of $[Mn_3O(O_2CEt)_6(py)_3]^+$ with L2 gives $[Mn_8O_4(O_2CEt)_{14}(L2)_2]^{2+}$ (26; $8Mn^{III})^{35}$ shown in Figure 22; in this case, two $[Mn_4O_2]^{8+}$ butterfly units are bridged only by the two L2 ligands. Complex 25 has a S = 0 ground state, and complex 26 behaves magnetochemically as essentially isolated $[Mn_4O_2]^{8+}$ units.



Figure 21. The structure of $[Mn_4O_2(O_2CMe)_4(L1)_2]^{2+}$ (25)



Figure 22. The structure of $[Mn_8O_4(O_2CEt)_{14}(L2)_2]^{2+}$ (26)

4. Summary and Conclusions

Manganese carboxylate chemistry has clearly proven to be a rich source of molecular (and occasionally polymeric) species at a variety of oxidation levels and with aesthetically pleasing structural properties. Further, this area has also yielded complexes of interest *vis-à-vis* their magnetochemical properties and non-zero values of ground state spin. As has been discussed, the structures of the higher nuclearity complexes may be usefully described as the result of joining together [Mn₄O₂] butterfly units, and the spin frustration effects that result in the S = 2-3 ground states of the latter no doubt are a major contributor to the (usually) intermediate-to-high values of ground state spin S in the higher nuclearity species.

In Table 1 are collected the pertinent details of the complexes discussed, excluding those in Section 3.6. There is no correlation between the magnitude of S and the nuclearity of a given complex, and bigger is clearly not better in this regard. One point, however, does seem to warrant comment: the presence of Mn^{IV} appears to favor higher values of S. Except for 20, whose S is decreased by the presence of Fe^{III}, the presence of Mn^{IV} in complexes 4-10, 17, 19 and 21 gives $S \ge 9/2$, probably due to the relatively strong exchange interactions within their [Mn^{III}(μ -O)₂Mn^{IV}] units which dominate Mn^{III}/Mn^{III} interactions and therefore enforce parallel alignment of the spins of Mn^{III} ions near the Mn^{IV} ions. There is no real correlation between S and the method of nuclearity build-up, i.e., fusion or linkage of butterfly units. Both methods mediate strong exchange interactions between the component Mn atoms, in contrast to the bridged complexes 23, 24 and 26 which contain magnetochemically essentially "isolated" [Mn4O₂]²⁺ units.

The synthetic procedures described, particularly the use of complex 3, have proven excellent routes into a variety of higher nuclearity products, and there is no reason to believe that this particular well has run dry; new results are appearing all the time.³⁶ On the contrary, we look forward to future developments in this exciting hybrid area of coordination chemistry, structural chemistry, and magnetochemistry.

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Complex	Oxidation State ^a	Structure ^b	S
$[Mn_4O_2(O_2CR)_7(L-L)_2]^2$ (1-3)	4Mn ^{III}	-	3
$[Mn_4O_3X(O_2CR)_3(dbm)_3]$ (4-10)	$3Mn^{III},Mn^{IV}$	-	9/2
$[Mn_7O_4(O_2CMe)_{10}(dbm)_4]^{-}(11)$	7Mn ^{III}	F	3
$[Mn_8O_4(O_2CPh)_{12}(Et_2mal)_2(H_2O)_2]^{2-}$ (12)	$2Mn^{II}$, $6Mn^{III}$	L	3
$[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]^-$ (14)	8Mn ^{III}	F	11
$[Mn_{9}Na_{2}O_{7}(O_{2}CR)_{15}]^{2}$ (15)	9Mn ^{III}	F	4
$[Mn_{10}O_8(O_2CPh)_6(pic)_8]$ (16)	10Mn ^{III}	L	0
$[Mn_{11}O_{10}X_6(O_2CR)_{11}(solv)]^2$ (17)	9Mn ^{III} ,2Mn ^{IV}	F	5
$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (19)	8Mn ^{III} ,4Mn ^{IV}	F+L	9 or 10
$[Fe_4Mn_8(O_2CMe)_{16}(H_2O)_4]$ (20)	4Fe ^{III} ,4Mn ^{III} ,4Mn ^{IV}	F+L	2
$[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]^{-}(21)$	Mn ^{II} ,7Mn ^{III} ,4Mn ^{IV}	F+L	19/2
$[Mn_{18}O_{16}(O_2CPh)_{22}(phth)_2(H_2O)_4]^4$ (22)	18Mn ^{III}	F+L	0

TABLE 1. Summary of Ground State Spin S Value for Complexes 1-22

a) All complexes are trapped-valence.

b) F = fused butterflies; L = linked butterflies

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 $[Mn_{11}O_{10}X_6(O_2CPh)_{11}(solv)_4]^{2-}$ (17; solv = H₂O or MeCN).¹⁸ A related complex is available from the reaction of complex 1 with Me₃SiCl, which gives $[Mn_{11}O_{10}Cl_2(O_2CMe)_{11}(bpy)_2(solv)_4]^{2+}$ (18).¹⁹ These complexes are all $9Mn^{II}_{,2}Mn^{IV}_{,2}$ and the structure of **18** is shown in Figure 16. The $[Mn_{11}O_{10}X_2]^{13+}$ core is rather interesting, being a mix of the $[Mn_4O_2]^{8+}$ butterfly and [Mn₄O₃X]⁶⁺ distorted-cubane types; it can be described as consisting of two body-fused butterfly units (as in 14 and 15) which are wing-tip-fused with two distorted cubane units as found in 4-10. The resulting complex has an S = 5 ground state. The latter can be rationalized as shown in Figure 17: each $[Mn_4O_3Cl]^{6+}$ unit is S = 9/2 (as in 4) but spin frustration effects (as in 1) within the 'bridging' body-fused-butterflies unit can lead to a resultant S = 4 for the central Mn₃ unit, and antiparallel alignment of these three spins leads to the observed S = 5 ground state. Note that this represents a ferrimagnetic-like situation for the spin alignments in the three subsections of the cluster, akin to the ferrimagnetic-like situation in mixed-metal linear trinuclear metal complexes, such as the Mn^{II}Cu^{II}Mn^{II} species that has a S = 5/2-1/2+5/2 = 9/2ground state.20



Figure 17. Rationalization of the S=5 ground state of 17 and 18.



Figure 1. The structures of (top) $[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$ (1) and (bottom) $Mn_4O_2(O_2CMe)_6(bpy)_2$ (2)



Figure 2. μ_{eff} vs temperature plots for 1 (Δ) and 2 (O); the solid lines are fits to the appropriate equations.



Figure 3. Exchange interactions in the $[Mn_4O_2]$ butterfly unit (b=body; w=wing-tip), and the Mn^{III} spin alignments in 1 (S=3).



Figure 4. The structure of $[Mn_4O_2(O_2CPh)_9(H_2O)]^-$ (3)



Figure 6. The structure of $Mn_4O_3(N_3)(O_2CMe)_3(dbm)_3$ (6)



Figure 7. Exchange interactions in the $[Mn_4O_3X]^{6+}$ unit, and spin alignments giving the S=9/2 ground state.