Covalent Linkage of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{dbm})_2]_2$ into a Dimer and a One-dimensional Polymer (dbmH = dibenzoylemethane)

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Methods have been developed for covalently linking $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{dbm})_2]$ units to give a dimer and a polymer; treatment of 2 with trans-1,2-bis(4-pyridyl)ethene (bpe) or 4,4'-bipyridine (4,4'-bpy) yields $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{dbm})_2(\text{bpe})]_2$ and $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{dbm})_2(4,4'-\text{bpy})]_2$, respectively.

An important current area of research is the development of synthetic methodologies to molecular species possessing large spin ground states, and their employment as building blocks to prepare new molecular ferromagnets.1 A number of such ferromagnets have been prepared from molecular inorganic precursors.2 In parallel, molecular inorganic complexes have been prepared with ground states possessing large values of spin $S$, particularly in Mn chemistry. The $[\text{Mn}_{116}(\text{nitroxide})_6]$ complex has a $S = 12$ ground state,3 and $[\text{Mn}_{12}\text{Ol}_2-(\text{O}_2\text{CR})_6(\text{H}_2\text{O})_4]$ complexes have a $S = 10$ ground state.4 Similarly, complexes containing the $[\text{Mn}_{111}\text{O}_2]$ and $[\text{Mn}_{111}\text{Mn}_{111}\text{O}_2\text{C}]^{1+}$ cores have $S = 3$5 and $S = 9/26$ ground states, respectively. It is clear that these and related Mn complexes represent attractive potential building-blocks to molecular ferromagnets if means could be developed to link them together. This objective is made challenging by the relative frailness of higher oxidation state Mn aggregates owing to their good oxidizing strength, the absence of metal-metal bonding and their proclivity to disproportionation making them unstable and prone to decomposition and/or other structural transformations.7 They are, however, air-stable. We are seeking suitable procedures to covalently link Mn aggregates into aggregates-of-aggregates under mild conditions, employing exogenous, bifunctional organic bridging ligands. We herein report our first crystallographically-confirmed successes along these new lines.

The complex $(\text{NBun}_4)[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{dbm})_2]$ 18 is one of a family of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CR})_7(\text{L}-\text{L})_2]^2^+ [\text{L}-\text{L} = \text{bpy},^5 \text{picolinate (pic)},^6 \text{8-hydroxyquinolinate},^9 \text{2-(hydroxymethyl)pyridine anion}]$ complexes possessing a $[\text{Mn}_{116}(\text{O}_2\text{CR})_{8}^+]$ 'butterfly' core. For $\text{L}-\text{L} = \text{pic}$, we have shown10 that the unique carboxylate bridging the central 'body' or 'hinge' Mn atoms can be selectively removed with one equiv. of Me$_3$SiCl. The same is true for 1. Thus, treatment of 1 with Me$_3$SiCl in CH$_2$Cl$_2$ leads to isolation of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{dbm})_2]$ in 73% yield; the same reaction in EtOAc leads to isolation of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{EtOAc})_2(\text{dbm})_2]$ 3 in 46% yield. The structure of 3 (Fig. 1) is centrosymmetric and shows that the Mn$_4$ unit is now planar with the two EtOAc groups on opposite sides of the central Mn$_2$0$_2$ rhomboid. The structure of 2 is similar, but lacks the EtOAc groups such that Mn(2) and Mn(2') are five-coordinate, as seen for the 'body' Mn atoms in $[\text{Mn}_{116}(\text{O}_2\text{CR})_{8}^+]$. The central Mn atoms being only five-coordinate in 2, or ligated by poorly-coordinating EtOAc groups in 3, suggested that these sites might be suitable for attachment of exogenous bridging groups; further, the anti disposition of the EtOAc groups might allow polymerization if an anti arrangement were retained in the products. Treatment of 2 with bpe (1 equiv.) in CH$_2$Cl$_2$ followed by layering with Et$_2$O (1 vol) and hexanes (1 vol) led to slow formation of deep red-brown crystals of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{bpe})]_2$CH$_2$Cl$_2$·2MeCN 4 in 83% yield. The structure of 4 (Fig. 2) shows that the Mn$_4$...
units are in a butterfly arrangement, with the two bpe ligands attached syn about the central [Mn₂O₂] rhomboid. Thus, the two bpe groups are bridging in a manner that yields a centro-symmetric, molecular, dimeric complex; although the product does contain a [Mn₆O₆]: bpe = 1:1 ratio, the desired polymer has not formed.

In a similar fashion, complex 2 was treated with 4,4'-bpy (1 equiv.) in CH₂Cl₂, and a red-brown crystalline product slowly formed in 63% yield over several days. The sparingly-soluble material was identified as [Mn₆O₆(O₂CPh)₆(dbm)₂- (4,4'-bpy)]₂, 5. Its structure† (Fig. 3) shows that the Mn₄ unit is now planar, the 4,4'-bpy groups are anti, and as a result, the product is the desired one-dimensional polymer. Three repeating [Mn₄O₂] units are shown in Fig. 3, where it can be seen that 5 is a 'zig-zag' or 'staircase' polymer; an exactly linear arrangement of [Mn₄O₂] units is precluded by the severe steric repulsions that would result between the benzoate phenyl rings.

Solid-state, variable-temperature magnetic susceptibility studies are being performed on complexes 3, 4 and 5 in the temperature range 5−300 K to characterize the magnitude of inter-[Mn₄O₂] exchange interactions mediated by the bpe and 4,4'-bpy bridges. It should be stated that these linker groups are not expected to mediate significant exchange interactions, having been chosen for their linking ability rather than from a magneto-chemical viewpoint. Preliminary data support this expectation; all three complexes show very similar VT behaviour. Complex 3 has an effective magnetic moment, \( \mu_{\text{eff}} \), per Mn₄ molecule of 7.64 \( \mu_B \) at 300 K, decreasing gradually to 5.54 \( \mu_B \) at 25 K, below which there is a steeper decrease to 3.34 \( \mu_B \) at 5.01 K; the latter is due to zero-field splitting within the lowest energy states, as described previously for a related [Mn₄O₂]⁸⁺ complex. Complexes 4 and 5 yield comparable values of \( \mu_{\text{eff}} \) per Mn₄ unit at corresponding temperatures, indicating that any exchange interactions between the Mn₄O₂ units are too small to have a significant effect except at very low temperatures. Thus, 4 and 5 may be considered as composed of only weakly-interacting [Mn₄O₂]⁸⁺ units. It is clear that the attainment of oligomers and polymers containing significantly interacting repeating units will require more suitable bridging ligands than have been used to-date in this first generation of linked species. The building blocks and methodology developed in this work, however, should prove invaluable in obtaining the second generation of species.

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Footnotes
† Crystal Data for 3: \( \text{C}_{60} \text{H}_{42} \text{O}_{22} \text{Mn}_{6} \): \( M = 1601.1 \), triclinic, \( P \bar{T} \), \( T = 113 \text{ K}, a = 13.059(3), b = 14.219(4), c = 12.054(3) \text{ Å}, \alpha = 97.26(1), \beta = 108.23(1), \gamma = 109.83(1) \text{°}, V = 1930.82 \text{ Å}^3, Z = 2, 6 \leq \theta \leq 20 \leq 45, 5041 \text{ unique}, 4187 \text{ observed reflections}, I > 3\sigma(I).

For 4: \( \text{C}_{60} \text{H}_{42} \text{N}_{2} \text{O}_{5} \text{Mn}_{2} \text{C}_{2} \text{H}_{4} \text{Cl}_{2} \cdot 2 \text{MeCN} \): \( M = 3466.2 \), monoclinic, \( P2_1/n, T = 103 \text{ K}, a = 21.019(13), b = 14.002(8), c = 29.203(20) \text{ Å}, \beta = 103.17(3) \text{°}, V = 8368.67 \text{ Å}^3, Z = 2, 6 \leq \theta \leq 20 \leq 45, 12126 \text{ unique}, 5300 \text{ observed reflections, } I > 2.3\sigma(I). \) Only the [Mn₂O₂] core atoms were refined anisotropically; no hydrogen atoms were included. The CH₂Cl₂ molecules were disordered between two sites, the ethene C atoms of the bpe groups showed some positional disorder. Final \( R(R_a) = 13.68(13.84)% \).

For 5: \( \text{C}_{60} \text{H}_{42} \text{N}_{2} \text{O}_{5} \text{Mn}_{2} \text{C}_{2} \text{H}_{4} \text{Cl}_{2} \): \( M = 1793.4 \), triclinic, \( P \bar{T} \), \( T = 127 \text{ K}, a = 12.563(6), b = 15.725(10), c = 12.505(5) \text{ Å}, \alpha = 100.60(3), \beta = 109.09(2), \gamma = 67.70(3) \text{°}, V = 2154.8 \text{ Å}^3, Z = 1, 6 \leq \theta \leq 20 \leq 45, 5640 \text{ unique}, 1646 \text{ observed reflections, } I > 2.3\sigma(I). \) All atoms were refined isotropically, and no hydrogen atoms were included. The [Mn₂O₂] repeating units lie on inversion centres. The CH₂Cl₂ molecules are disordered about inversion centres. Final \( R(R_a) = 16.26(15.56)% \).

For complexes 4 and 5, despite numerous attempts, only weakly diffracting crystals were obtained, even though a number of different crystallization conditions were explored. Thus, data collection and structure solutions were finally performed with the weakly-diffracting crystals because it was imperative to identify the extent of oligomeri-
Fig. 3 (a) The structure of the repeating unit of polymeric complex 5, the points of inter-unit connection are indicated by the dashed lines; (b) a stereoview of three repeating units of the chain.

zation and the overall structure of the compounds. This also confirmed retention of the [Mn₄O₂] structure of the repeating units. The low precision of the metric parameters represents only a minor irritation to the chemical objectives of this work.

Atomic coordinates, bond lengths and angles, and thermal parameters for structures 3–5 have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Complex 2 is a poor diffractor of X-rays; data have been collected on a small, weakly-diffracting crystal and the structure solution pursued to the point at which the described structure was confirmed.

References


8 S. Wang and G. Christou, unpublished work.
