Covalent Linkage of [$Mn_4O_2(O_2CPh)_6(dbm)_2$] into a Dimer and a One-dimensional Polymer (dbmH = dibenzoylmethane)

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Methods have been developed for covalently linking [$Mn_4O_2(O_2CPh)_6(dbm)_2$] **2** (dbmH = dibenzoylmethane) 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 [$Mn_4O_2(O_2CPh)_6(dbm)_2(bpe)]_2$ **4** and [$Mn_4O_2(O_2CPh)_6(dbm)_2(4,4'\text{-bpy})]_n$ **5**, 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 [Mn^{II}_6(nitroxide)$_6$] complex has a $S = 12$ ground state,[3] and [$Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4$] complexes have a $S = 10$ ground state.[4] Similarly, complexes containing the [$Mn_4^{III}O_2$] and [$Mn_3^{III}Mn^{IV}O_3Cl]^{6+}$ cores have $S = 3$[5] and $S = 9/2$[6] 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_x aggregates into aggregates-of-aggregates and polymers-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 (NBu^n_4)[$Mn_4O_2(O_2CPh)_7(dbm)_2$] **1**[8] is one of a family of [$Mn_4O_2(O_2CR)_7(L\text{–}L)_2]^z$ [L–L = bpy,[5] picolinate (pic),[5] 8-hydroxyquinolinate,[9] 2-(hydroxymethyl)pyridine anion[9]] complexes possessing a [$Mn_4(\mu_3\text{-}O)_2]^{8+}$ 'butterfly' core. For L—L = pic, we have shown[10] that the unique carboxylate bridging the central 'body' or 'hinge' Mn atoms can be selectively removed with one equiv. of Me_3SiCl. The same is true for **1**. Thus, treatment of **1** with Me_3SiCl in CH_2Cl_2 leads to isolation of $Mn_4O_2(O_2CPh)_6(dbm)_2$ **2** in 73% yield; the same reaction in EtOAc leads to isolation of $Mn_4O_2(O_2CPh)_6(EtOAc)_2(dbm)_2$ **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 [O(48) and O(48′)] on opposite sides of the central Mn_2O_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 $Mn_4O_2(O_2CMe)_6(bpy)_2$.[5]‡

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_2Cl_2 followed by layering with Et_2O (1 vol) and hexanes (1 vol) led to slow formation of deep red-brown crystals of [$Mn_4O_2(O_2CPh)_6(dbm)_2(bpe)]_2\cdot2CH_2Cl_2\cdot2MeCN$ **4** in 83% yield. The structure† of **4** (Fig. 2) shows that the Mn_4

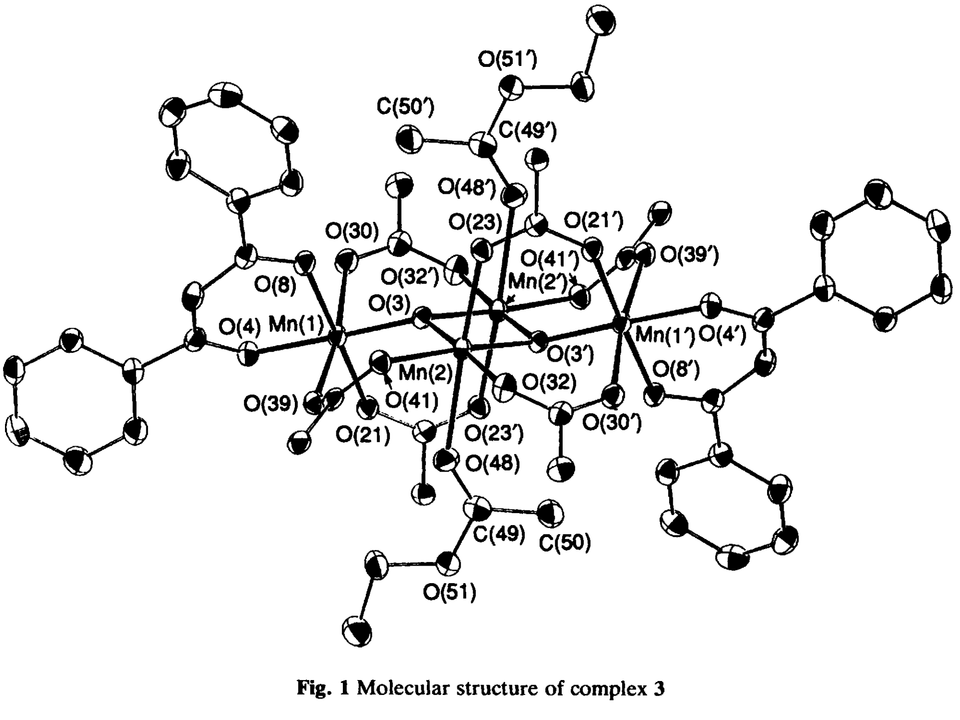

Fig. 1 Molecular structure of complex **3**

units are in a butterfly arrangement, with the two bpe ligands attached *syn* about the central [Mn_2O_2] rhomboid. Thus, the two bpe groups are bridging in a manner that yields a centrosymmetric, molecular, dimeric complex; although the product does contain a [Mn_4O_2] : 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 CH_2Cl_2, and a red-brown crystalline product slowly formed in 63% yield over several days. The sparingly-soluble material was identified as [$Mn_4O_2(O_2CPh)_6(dbm)_2$-(4,4′-bpy)]$_n$ **5**. Its structure† (Fig. 3) shows that the Mn_4 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 [Mn_4O_2] 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 [Mn_4O_2] 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-[Mn_4O_2] 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, μ_{eff} per Mn_4 molecule of 7.64 μ_B at 300 K, decreasing gradually to 5.54 μ_B at 25 K, below which there is a steeper decrease to 3.34 μ_B at 5.01 K; the latter is due to zero-field splitting within the lowest energy states, as described previously for a related [Mn_4O_2]$^{8+}$ complex.[5] Complexes **4** and **5** yield comparable values of μ_{eff} per Mn_4 unit at corresponding temperatures, indicating that any exchange interactions between the Mn_4O_2 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 [Mn_4O_2]$^{8+}$ 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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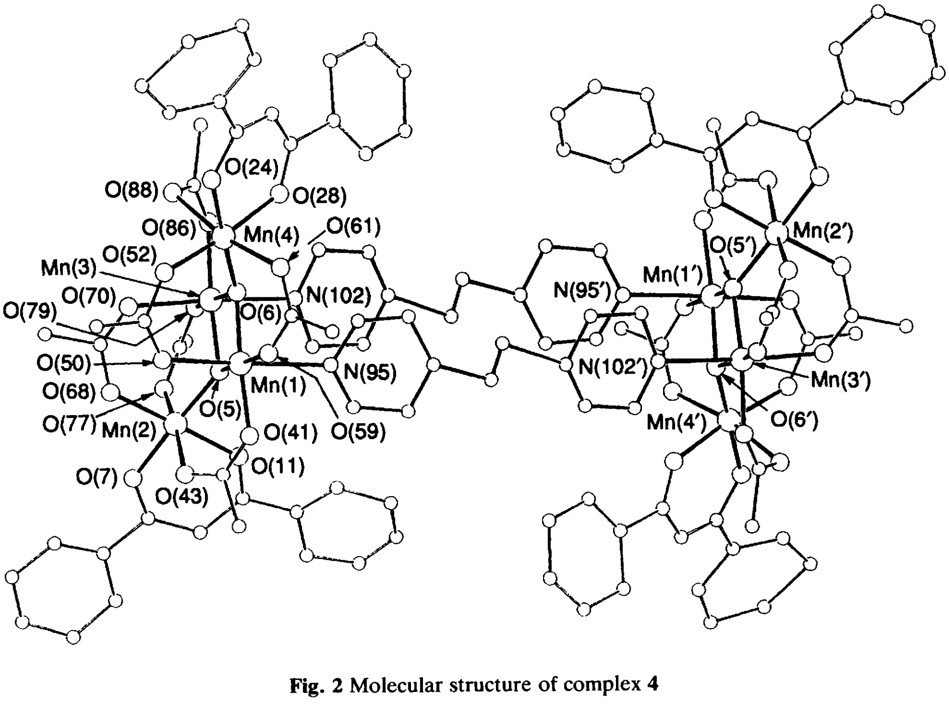

Fig. 2 Molecular structure of complex **4**

Footnotes

† *Crystal Data* for **3**: $C_{80}H_{68}O_{22}Mn_4$: M = 1601.1, triclinic, $P\bar{1}$, T = 113 K, a = 13.059(3), b = 14.219(4), c = 12.054(3) Å, α = 97.26(1), β = 108.23(1), γ = 109.83(1)°, V = 1930.82 Å^3, Z = 2, $6° \leq 2\theta \leq 45°$, 5041 unique, 4187 observed reflections, $I > 3\sigma(I)$. All non-hydrogen atoms were refined anisotropically, except four C atoms in a seriously disordered solvent molecule near an inversion centre. Hydrogen atoms were refined with isotropic thermal parameters. Final $R(R_w)$ = 5.10 (5.43)%.

For **4**: $C_{168}H_{124}N_4O_{36}Mn_8 \cdot 2CH_2Cl_2 \cdot 2MeCN$: M = 3466.2, monoclinic, $P2_1/c$, T = 103 K, a = 21.019(13), b = 14.002(8), c = 29.203(20) Å, β = 103.17(3)°, V = 8368.67 Å^3, Z = 2, $6° \leq 2\theta \leq 45°$, 12126 unique, 5300 observed reflections, $I > 2.33\sigma(I)$. Only the [Mn_4O_2] core atoms were refined anisotropically; no hydrogen atoms were included. The CH_2Cl_2 molecules were disordered between two sites. The ethene C atoms of the bpe groups showed some positional disorder. Final $R(R_w)$ = 13.68 (13.84)%.

For **5**: $C_{82}H_{60}N_2O_{18}Mn_4 \cdot 2.5CH_2Cl_2$: M = 1793.4, triclinic, $P\bar{1}$, T = 127 K, a = 12.563(6), b = 15.725(10), c = 12.505(5) Å, α = 100.60(3), β = 109.09(2), γ = 67.70(3)°, V = 2154.8 Å^3, Z = 1, $6° \leq 2\theta \leq 45°$, 5640 unique, 1646 observed reflections, $I > 2.33\sigma(I)$. All atoms were refined isotropically, and no hydrogen atoms were included. The [Mn_4O_2] repeating units lie on inversion centres. The CH_2Cl_2 molecules are disordered about inversion centres. Final $R(R_w)$ = 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 pursued with the weakly-diffracting crystals because it was imperative to identify the extent of oligomeri-

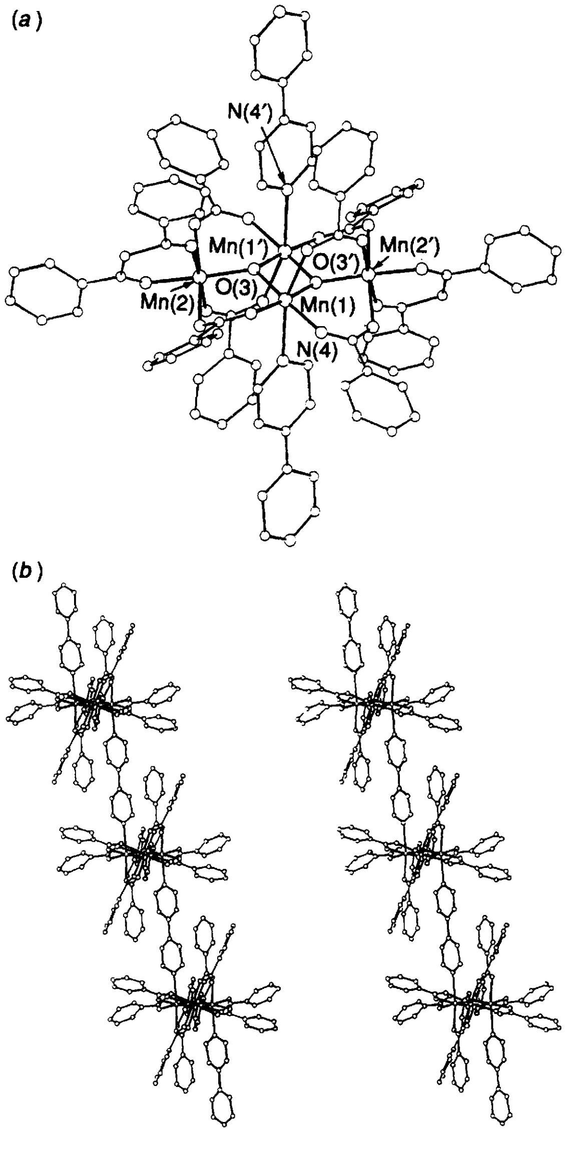

Fig. 3 (*a*) The structure of the repeating unit of polymeric complex **5**, the points of inter-unit connection are indicated by the dashed lines; (*b*) a stereoview of three repeating units of the chain

zation and the overall structure of the compounds. This also confirmed retention of the $[Mn_4O_2]$ 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.

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