

High Spin Molecules: $(\text{NBu}^n)_2[\text{Mn}_8\text{O}_4(\text{O}_2\text{CPh})_{12}(\text{Et}_2\text{mal})_2(\text{H}_2\text{O})_2]$, a Mixed-valence Manganese(II/III) Aggregate with Dicarboxylate Ligation, an Unusual Linked-butterfly Structure, and an $S = 3$ Ground State

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Treatment of $(\text{NBu}^n)_4[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]$ with $\text{Na}_2(\text{Et}_2\text{mal})$ in MeCN leads to a nuclearity and oxidation level change to give $(\text{NBu}^n)_2[\text{Mn}_8\text{O}_4(\text{O}_2\text{CPh})_{12}(\text{Et}_2\text{mal})_2(\text{H}_2\text{O})_2]$ **1**; the crystal structure and magnetochemical studies show the core of the anion to have a unique topology consisting of two linked $[\text{Mn}_4\text{O}_2]$ butterfly units and to possess an $S = 3$ ground state, respectively.

Over the last several years, it has become clear that Mn chemistry at the intermediate oxidation levels (II–IV) represents a rich and fertile area for the discovery of a variety of high nuclearity molecular aggregates. Metal nuclearities up to 12 have so far been reported.^{1,2} These species have been of interest from both a purely structural perspective and because they have demonstrated a propensity to possess ground states with large values of spin, S .^{3–5} The latter is a consequence of (i) the presence of ferromagnetic exchange interactions between at least some of the paramagnetic Mn ions^{4,5} and/or (ii) a topological arrangement of the Mn ions such that spin frustration effects are operative.^{4–6} It is essential to obtain as large a data base of complexes as possible if a detailed understanding of the above important effects is to be achieved. For this reason, we have vigorously pursued the development of different synthetic methodologies to high

nuclearity Mn aggregates. Recently, we turned our attention to the use of dicarboxylates. This family of ligands has not been employed to date to prepare molecular Mn_x aggregates;† in the case of malonic acids, for example, they have been used previously only for the synthesis of Mn monomers⁷ or polymers.⁸ We herein report the first use of a malonic acid derivative to form a high nuclearity Mn_x product; the use of 2,2-diethyl malonate (3,3-pentanedicarboxylate, $\text{Et}_2\text{mal}^{2-}$) is shown to lead to a molecular Mn₈ aggregate, and we describe its unique ‘linked-butterfly’ structure and its unusual magnetochemical properties.

Treatment of $(\text{NBu}^n)_4[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]$,⁹ a 4 Mn^{III} complex with a $[\text{Mn}_4(\mu_3\text{-O})_2]^{8+}$ core possessing a butterfly structure, with $\text{Na}_2(\text{Et}_2\text{mal})$ (2 equiv.) in MeCN leads, after a week of stirring, to a brown solution and an off-white solid. The latter $[\text{NaO}_2\text{CPh}$ and unconverted $\text{Na}_2(\text{Et}_2\text{mal})]$ was removed by filtration, and the MeCN evaporated *in vacuo* to give a brown solid. This was recrystallized twice from CH_2Cl_2 –hexanes to give $(\text{NBu}^n)_2[\text{Mn}_8\text{O}_4(\text{O}_2\text{CPh})_{12}(\text{Et}_2\text{mal})_2(\text{H}_2\text{O})_2]$ ·4 CH_2Cl_2 (1·4 CH_2Cl_2) in 44% yield and analytical purity;‡ three of the four CH_2Cl_2 molecules are lost on drying the solid *in vacuo*. The structure§ of the anion of **1** is shown in Fig. 1. The anion lies on an inversion centre and has a $[\text{Mn}_8(\mu_4\text{-O})_2(\mu_3\text{-O})_2]$ core with peripheral ligation provided by the carboxylate groups and two H_2O molecules, the latter on Mn(1) and Mn(1′). As far as we can ascertain, this topological arrangement of eight metal ions is unique for any metal,¶ and it can conveniently be described as two $[\text{Mn}_4\text{O}_2]$ butterfly units [atoms Mn(1–4) and their symmetry-related partners] linked *via* one $\mu_3\text{-O}^{2-}$ ion in each unit converting to a μ_4 mode and thus providing the two ‘inter-butterfly’ bonds, Mn(1)–O(6′) and Mn(1′)–O(6); these are also the longest Mn–O²⁻ bonds in the molecule. The dihedral angle between the two Mn₃ planes within each butterfly is 162.15°; thus, the butterfly units have been rather ‘flattened’ by this linkage relative to $(\text{NBu}^n)_4[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]$ (dihedral angle 131.0°).

Charge considerations indicate a 2 Mn^{II}, 6 Mn^{III} oxidation level description, and the Mn^{II} ions are assigned as Mn(4) and Mn(4′) on the basis of the longer average Mn–O bond lengths at these ions (avg. 2.185 Å and no individual value shorter than 2.1 Å) compared with those for the other ions (avg. 2.000–2.041 Å), and the clear presence of a Jahn–Teller axial elongation at Mn atoms Mn(1), Mn(2) and Mn(3), as expected for a near-octahedral, high-spin Mn^{III} (d^4) ion.

Two other structural points are worthy of comment: firstly, two carboxylates are monodentate and their unligated O atoms, O(66) and O(66′), are hydrogen bonded to the terminally bound H_2O molecules, O(7) and O(7′) [O(66)···O(7) = 2.639(18) Å]; secondly, the Et_2mal groups are bound in an asymmetric tridentate manner providing a four-membered chelate ring at Mn(4′) and a six-membered chelate ring at Mn(2). Bridging atoms O(13) and O(13′) thus provide additional linkages between the two butterfly units, no doubt contributing to the formation and stabilization of an octanuclear product.

Complex **1** joins only a very small family of Mn or Fe oxo aggregates of nuclearity eight, which currently comprise

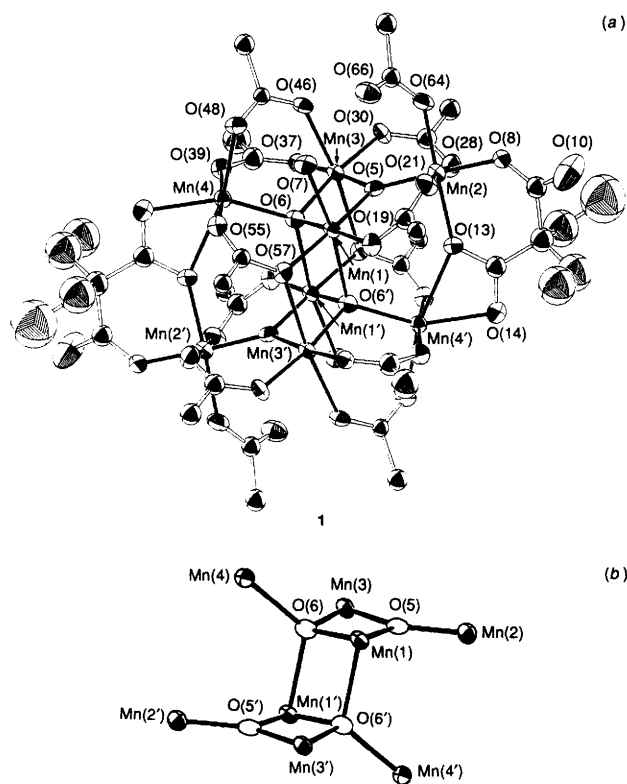


Fig. 1 The structure of the anion of **1** (a), together with a view of the $[\text{Mn}_8\text{O}_4]$ core (b). Primed and unprimed atoms are related by the inversion centre. Selected interatomic distances (Å) are: Mn(1)···Mn(2), 3.396(4); Mn(1)···Mn(3), 2.851(4); Mn(1)···Mn(4), 3.463(3); Mn(2)···Mn(3), 3.420(3); Mn(3)···Mn(4), 3.427(4); Mn(1)···Mn(1′), 3.128(3); Mn(1)···Mn(3′), 3.290(4); Mn(1)···Mn(4′), 3.733(3); Mn(2)···Mn(4′), 4.105(4); Mn(1)–O(5), 1.888(10); Mn(1)–O(6), 1.891(10); Mn(1)–O(6′), 2.258(10); Mn(2)–O(5), 1.874(10); Mn(3)–O(5), 1.867(9); Mn(3)–O(6), 1.902(10); Mn(4)–O(6), 2.113(10).

$\text{Mn}_8\text{O}_4(\text{O}_2\text{CMe})_{12}(\text{pic})_4$ (picH = picolinic acid)^{2,10} $(\text{NBu}^n)_4[\text{Mn}_8\text{O}_6\text{Cl}_6(\text{O}_2\text{CPh})_7(\text{H}_2\text{O})_2]^9$ and $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{taccn})_6]\text{Br}_8$ (taccn = 1,4,7-triazacyclononane),¹¹ all of which have core structures very different to **1**.

The magnetic susceptibility characteristics of complex **1** have been examined in a 10.0 kG ($1 \text{ G} = 10^{-4} \text{ T}$) field in the 5.0–320.00 K range [Fig. 2(a)] and as a function of field (0.5–10.0 kG) in the 2.00–4.00 K range [Fig. 2(b)]. At 320.0 K, complex **1** has an effective magnetic moment of $7.45 \mu_{\text{B}}$ per molecule, which is considerably less than the $14.6 \mu_{\text{B}}$ spin-only value expected for a $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_6$ complex. As is evident in Fig. 2, μ_{eff} decreases gradually to $5.95 \mu_{\text{B}}$ at 40 K, whereupon there is a more rapid decrease to $4.26 \mu_{\text{B}}$ at 5.01 K in a 10.0 kG field.

Since the Mn–O bond lengths that interconnect the two $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_3$ butterflies within complex **1** are long, the 10.0 kG data for complex **1** were analysed as if it were composed of two non-interacting butterfly units. Furthermore, in each butterfly unit it was assumed that the two different wing-tip/body exchange interactions ($\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{III}}/\text{Mn}^{\text{III}}$) are the same. As shown in Fig. 2(a), the 10.0 kG data could be fit assuming two non-interacting butterfly units with two J values for each butterfly [wing-tip/body (J_1) and body/body (J_2)]; the best fit gave $J_1 = -13.8 \text{ cm}^{-1}$, $J_2 = -30.1 \text{ cm}^{-1}$ and $g = 1.92$. This best fit of the 10.0 kG data indicated that each butterfly unit has an $S = 5/2$ ground state.

The 2.00–4.00 K variable field reduced magnetization ($M/N\mu_{\text{B}}$) data [Fig. 2(b)] were analysed by assuming only the

ground state is thermally populated at these very low temperatures. A fit of these data employing a full-matrix diagonalization of the spin-Hamiltonian matrix including Zeeman and zero-field interactions indicated that complex **1** has an $S = 3$ ground state. In Fig. 2(b), it can be seen that this fit of the low-temperature magnetization data to an $S = 3$ state is very good; the fitting parameters were $g = 1.93$ and $D = 4.92 \text{ cm}^{-1}$.

If complex **1** may be viewed as two weakly interacting $S = 5/2$ butterfly complexes, then its $S = 3$ ground state results from spin frustration within the $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_6$ assembly. Previously, we have communicated that fusing together two $\text{Mn}^{\text{III}}_4\text{O}_2$ butterfly units at the wing-tips gives a $\text{Mn}^{\text{III}}_7\text{O}_4$ complex which has an $S = 3$ ground state.¹²

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Footnotes

† While our work was nearing completion, the first molecular Mn aggregate with a dicarboxylate was reported employing phthalic acid: see ref. 13.

‡ Analytical data (C, H, N) for the vacuum-dried, monosolvated solid were satisfactory.

§ Crystal data for $1\cdot 4\text{CH}_2\text{Cl}_2$: $\text{C}_{134}\text{H}_{164}\text{N}_2\text{O}_{38}\text{Cl}_8\text{Mn}_8$, $M = 3133.89$, monoclinic, $P2_1/c$, $a = 16.247(5)$, $b = 27.190(8)$, $c = 17.715(5) \text{ \AA}$, $\beta = 113.95(1)^\circ$, $U = 7152.0 \text{ \AA}^3$, $Z = 2$, $D_c = 1.455 \text{ g cm}^{-3}$, $\lambda = 0.71069 \text{ \AA}$, $T = -165^\circ\text{C}$, $6^\circ < 2\theta < 45^\circ$, $R(R_w) = 8.36(8.61)\%$ for 4133 unique reflections with $I > 3\sigma(I)$. The structure was solved by MULTAN and Fourier techniques, and refined by full-matrix least-squares analysis. All non-hydrogen atoms were readily located and were well behaved, except for the Me carbon atoms of the cation and the Et carbon atoms of the dicarboxylate group, which had large thermal parameters. The anion lies on a centre of symmetry; the asymmetric unit contains half the anion, one cation and two CH_2Cl_2 molecules. One of the latter had 100% occupancy while the other refined to approximately 75% occupancy. In the final refinement cycles, Mn, O and Cl atoms were refined anisotropically, C atoms were refined isotropically, and H atoms were included in calculated positions [those on O(7) were omitted] and with fixed thermal parameters. The final difference Fourier map was essentially featureless, the largest peak being 1.3 e \AA^{-3} in the vicinity of the partially occupied solvent molecule. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ The structure of $1\cdot 4\text{CH}_2\text{Cl}_2$ does have some similarities to complexes which can best be described as containing sheets of fused partial M_3O_4 cubes.^{14,15}

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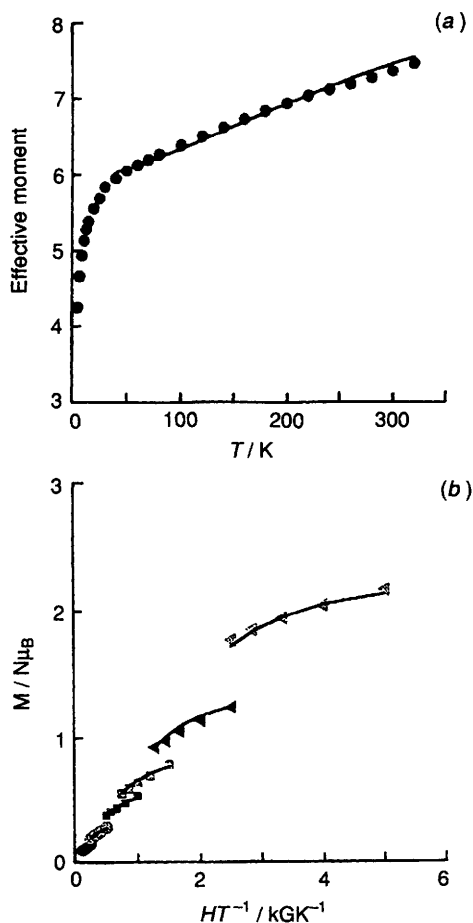


Fig. 2 (a) Effective magnetic moment, μ_{eff} (μ_{B}), per molecule vs. temperature and (b) reduced magnetization, $M/N\mu_{\text{B}}$, vs. HT , for complex $1\cdot\text{CH}_2\text{Cl}_2$. (●, 0.5; ⊙, 1.0; ■, 2.0; ⊞, 3.0; ▼, 5.0; ▽, 10.0 kG). The solid lines are fits to the experimental data. The temperature-independent paramagnetism (TIP) terms for (a) and (b) were held constant at 800×10^{-6} and 1600×10^{-6} cgsu, respectively; see text for other fitting parameters.

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