

Synthesis, structural and magnetic characterisation of a new Mn–Gd pivalate: preparation from a pre-formed hexanuclear cluster †

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The synthesis and crystal structures of two isostructural Mn(III)Ln(III) pivalates (Ln = Gd, Dy) are reported; magnetic data are presented for $[\text{Mn}_2\text{Gd}_2\text{O}_2(\text{O}_2\text{CCMe}_3)_8(\text{HO}_2\text{CCMe}_3)_2(\text{MeOH})_2]$, the susceptibility behaviour being dominated by strong antiferromagnetic coupling between the di- μ -oxo-bridged Mn(III) centres; this complex represents the first reported example of ferromagnetic coupling between Mn and Gd in a discrete polynuclear complex.

Since the discovery of ferromagnetic coupling between copper(II) and gadolinium(III)¹ a number of groups have begun to explore routes to 3d–4f complexes.^{2–6} However, there are few reports on the magnetic interactions between other 3d–4f mixtures^{2,4} and further model complexes are required to better understand the nature of this magnetic coupling. Gadolinium is the simplest paramagnetic lanthanoid to study as orbital contributions to the magnetic moment of this ion are negligible.

We have previously utilised pre-formed copper^{–7} or nickel-pyridonate⁴ complexes to prepare 3d–4f clusters. Recently we reported the Mn(II)Mn(III) complex $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CCMe}_3)_{10}(\text{C}_4\text{H}_8\text{O})_4]$ **1** as a useful starting reagent in preparation of high nuclearity manganese clusters.⁸ The presence of the negatively charged and coordinatively flexible pivalate ligand suggested the complex may prove useful in reaction with large, electro-positive Ln(III) ions permitting further exploration of the behaviour of transition metal-bound ligands towards Ln(III) ions.^{4,7}

Complex **1** (0.316 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and a solution of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1.26 mmol) in MeOH (5 cm^3) was slowly added to give a clear yellow-brown solution. The reaction mixture was stirred for 24 h, the volume reduced *in vacuo* to ca. 15 ml and the solution filtered through Celite. After standing for 5 d at ambient temperature $[\text{Mn}_2\text{Gd}_2\text{O}_2(\text{O}_2\text{CCMe}_3)_8(\text{HO}_2\text{CCMe}_3)_2(\text{MeOH})_2] \cdot \text{CH}_2\text{Cl}_2$ (**2**· CH_2Cl_2) was deposited as orange blocks in 27% yield.‡ Replacement of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ by $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in the reaction yields the isostructural complex $[\text{Mn}_2\text{Dy}_2\text{O}_2(\text{O}_2\text{CCMe}_3)_8(\text{HO}_2\text{CCMe}_3)_2(\text{MeOH})_2] \cdot \text{CH}_2\text{Cl}_2$ (**3**· CH_2Cl_2) in a similar yield.‡

X-Ray structural studies§ reveal a $\{\text{Gd}(\mu_3\text{-O})\text{Mn}_2(\mu_3\text{-O})\text{Gd}\}$ core based on a Mn(III) di- μ -oxo-bridged dimer, each oxide further bridging to a Gd(III) centre creating a chair or distorted butterfly configuration (Fig. 1). The complex possesses crystallographically imposed twofold symmetry. Each Gd ion is nine coordinate with distorted capped square-antiprismatic geometry (the upper square face is formed by O(2C), O(1C), O(1D) and O(2D)—the lower face formed by O(1), O(2E), O(1M) and O(2B) by O(1A)) bonded to nine oxygen atoms from five pivalate ligands which show a variety of bonding modes, a μ_3 -oxide and a molecule of MeOH.

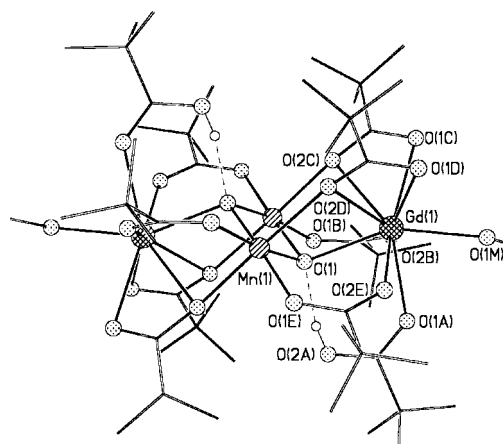


Fig. 1 Structure of complex **2**. Selected bond length (Å): Mn(1)–O(1) 1.900, Mn(1)–O(1′) 1.875, Mn(1)–O(1B′) 1.937, Mn(1)–O(1E) 1.943, Mn(1)–O(2C′) 2.223, Mn(1)–O(2D) 2.297; Gd(1)–O(1) 2.372, Gd(1)–O(2E) 2.375, Gd(1)–O(2B) 2.384, Gd(1)–O(1M) 2.390, Gd(1)–O(1A) 2.490, Gd(1)–O(2D) 2.493, Gd(1)–O(1C) 2.517, Gd(1)–O(2C) 2.537, Gd(1)–O(1D) 2.537 Å (average e.s.d. 0.011 Å).

Two of the five pivalate ligands chelate Gd (*e.g.* via O(1C) and O(2C)) and further bridge to a Mn(III) ion (*via* O(2C)), this is in contrast to the more usual tridentate 1,1,3-bridging mode found in **1** where three metal centres are bridged. This unusual mode of coordination is also found in the 2D polymer $[\text{Gd}_2\text{Co}_3(\text{edta})_3(\text{H}_2\text{O})_{11}]$.⁹ Two further pivalate ligands are found in the usual 1,3-bridging mode linking Gd to each Mn centre. The remaining pivalate ligand is protonated and therefore unidentate: the proton forming a hydrogen bond to the μ_3 -oxide.

Each Mn(III) centre is in a distorted octahedral environment typical for a d_4 metal (bond length ranges: Mn– O_{eq} 1.88–1.94 Å, Mn– O_{ax} 2.22–2.30 Å; bond angle ranges: *cis* at Mn 81.1–96.1, *trans* at Mn 172.5–178.0°). Equatorial sites are occupied by the two bridging oxides and oxygen atoms from 1,3 bridging pivalate ligands while axial sites are filled by oxygen atoms from the Gd-chelating pivalate ligands. Intermolecular H-bonding (Fig. 2) is present between the oxygen atom of a chelating pivalate and the hydrogen atom of a terminal MeOH molecule on a neighbouring cluster and *vice versa*.

It was not possible to determine unambiguously whether the μ_3 -bridging oxygen atom is protonated from X-ray crystallography. The bond lengths between Mn and the μ_3 -bridging oxygen atom and the Mn...Mn separation are consistent with values found for the central $\{\text{Mn}_2\text{O}_2\}^{2+}$ fragment found in $\{\text{Mn}_4\text{O}_2\}^{n+}$ butterfly complexes.¹⁰ Further evidence comes from bond valence sum analysis^{11,12} which confirms the valency of the Mn(III) centres and strongly suggests O(1) to be an oxide (O(1) calculated valence = 1.8) with a strong H-bond to a protonated pivalate ligand rather than the alternative description of an hydroxide H-bonding to a deprotonated O_2CCMe_3

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/4125/>

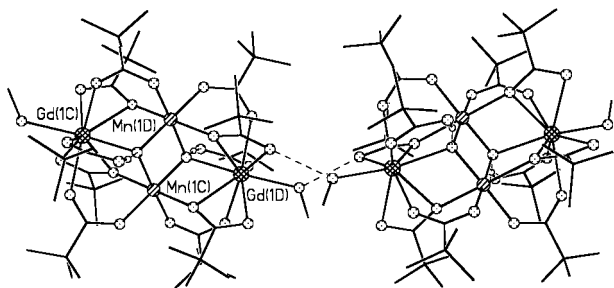


Fig. 2 Intermolecular H-bonding in 2.

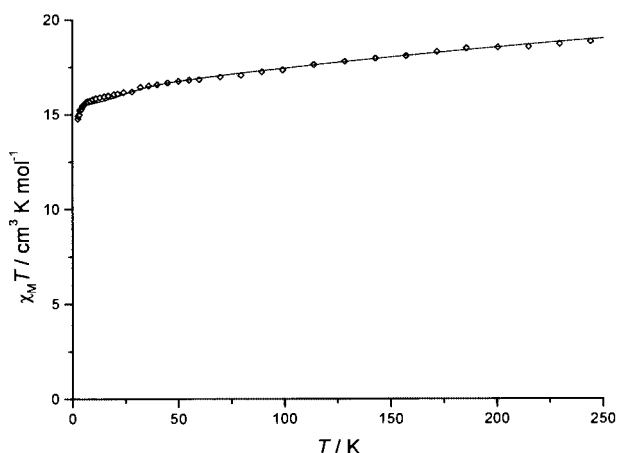


Fig. 3 Plot of $\chi_M T$ vs. T for 2. Observed data shown as open diamonds; calculated data as solid line.

ligand. Comparing the structures of 1 and 2 the central $\{\text{Mn}_2\text{O}_2\}^{2+}$ core of 1 has been preserved in the formation of 2 suggesting that the use of a preformed complex can exert a degree of control over the reaction.

Preliminary magnetic measurements on 2 (Fig. 3) reveal a net antiferromagnetic interaction between the metal centres. The susceptibility data[¶] can be fitted using a simple model based on a square with a metal ion at each corner, and interactions along the edges (J_1) and diagonals (J_2 and J_3). The spin Hamiltonian $H = -J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1) - J_2S_2S_4 - J_3S_1S_3$ (where S_1 and S_3 are the spins on Gd(III) centres and S_2 and S_4 are spins on the Mn(III) centres) yields the exchange parameters $J_2 = -62.91 \text{ cm}^{-1}$ for coupling between Mn(III) centres; $J_1 = +2.44 \text{ cm}^{-1}$ for coupling between Mn(III) and Gd(III); $J_3 = -0.012 \text{ cm}^{-1}$ for coupling between Gd(III) centres.

The fit is satisfactory at higher temperatures but shows differences between calculated and observed values at low temperatures. The two Mn–Gd superexchange pathways are very similar (Mn(1)–O(1) 1.900(11), Mn(1A)–O(1) 1.875(11) Å; Mn(1)–O(1)–Gd(1) 108.2(5), Mn(1A)–O(1)–Gd(1) 108.8(5)°). The large antiferromagnetic coupling between the Mn(III) centres means that each $\{\text{Mn}_2\text{Gd}\}$ triangle is spin-frustrated making the intensity of the coupling difficult to define. This frustration may account for the poor fit at low temperature. Other possible explanations include zero-field splitting of the

Mn(III) ion and inter-molecular exchange *via* the H-bond illustrated in Fig. 2. The magnitude of the magnetic coupling between the Mn(III) ions is consistent with, if a little higher than, that found between μ -oxo-bridged octahedral Mn(III) ions in $\{\text{Mn}_4\text{O}_2\}^{n+}$ butterfly complexes.¹⁰ This synthetic approach has provided the first example of ferromagnetic exchange between Mn and Gd in a discrete polynuclear complex and may prove useful in preparation of further 3d–4f carboxylates.

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Notes and references

‡ Complex 2. Found: C, 39.4; H, 6.29. Calc. for $\text{C}_{53}\text{H}_{100}\text{Cl}_2\text{Gd}_2\text{Mn}_2\text{O}_{24}$: C, 39.3; H, 6.35%. Complex 3. Found: C, 38.9; H, 6.13. Calc. for $\text{C}_{53}\text{H}_{100}\text{Cl}_2\text{Dy}_2\text{Mn}_2\text{O}_{24}$: C, 39.1; H, 6.31%.

§ Crystal data: for $\text{C}_{52}\text{H}_{100}\text{Gd}_2\text{Mn}_2\text{O}_{24} \cdot \text{CH}_2\text{Cl}_2$ 2: monoclinic, $I2a$, $a = 22.761(13)$, $b = 13.423(7)$, $c = 24.023(10)$ Å, $\beta = 108.22(2)^\circ$, $U = 6972(6)$ Å³, $M = 1618.6$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.899 \text{ mm}^{-1}$, $T = 220.0(2)$ K; refinement used 375 parameters and gave $R1 = 0.0767$ for 2425 data with $F_o > 4\sigma(F)$, $wR2 = 0.2033$ for 4559 unique data ($2\theta \leq 45^\circ$) and 664 restraints. For $\text{C}_{52}\text{H}_{100}\text{Dy}_2\text{Mn}_2\text{O}_{24} \cdot \text{CH}_2\text{Cl}_2$ 3: monoclinic, $I2a$, $a = 22.641(9)$, $b = 13.418(4)$, $c = 24.024(8)$ Å, $\beta = 108.15(3)^\circ$, $U = 6935(4)$ Å³, $M = 1629.13$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.899 \text{ mm}^{-1}$, $T = 200.0(2)$ K; refinement used 375 parameters and gave $R1 = 0.0327$ for 5010 data with $F_o > 4\sigma(F)$, $wR2 = 0.0687$ for 6135 unique data ($2\theta \leq 50^\circ$) and zero restraints. CCDC reference number 186/1713. See <http://www.rsc.org/suppdata/dt/1999/4125/> for crystallographic files in .cif format.

¶ Variable-temperature magnetic measurements on 2 in the region 2.5–250 K in an applied field of 0.1 T were made using a Metronique Ingenierie MS03 SQUID magnetometer with samples sealed in gelatine capsules. Diamagnetic corrections for the sample and sample holder were applied to the data.

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