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Two unique star-like $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}]$ clusters: magnetic relaxation phenomena

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Employment of H_3L^2 (= 2-(β -naphthalideneamino)-2-hydroxyethyl-1-propanol) in manganese-lanthanide cluster chemistry has led to the isolation of two new isostructural tetrametallic $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{IV}}\text{Ln}^{\text{III}}]$ complexes (Ln = Gd, Dy), with the Dy analogue displaying temperature and frequency dependent out-of-phase signals, thus indicating possible single molecule magnetism behaviour.

The last decade has witnessed a major boost in the field of molecular magnetism. Since the discovery of the prototype single molecule magnet (SMM) $[\text{Mn}_{12}\text{OAc}]$ that could retain its magnetization once magnetized at temperatures below ~ 3 K,^[1] various significant achievements have been accomplished: i) in 2007 a hexanuclear $[\text{Mn}^{\text{III}}_6]$ cluster was reported with an energy barrier for the re-orientation of the magnetization of $U_{\text{eff}} = 86.4$ K, breaking the record of $U_{\text{eff}} = 60$ – 64 K held by the prototype SMM for ~ 15 years,^[2] ii) in 2009 a $[\text{Dy}^{\text{III}}_4]$ cluster was reported elevating the energy barrier to 170 K,^[3] iii) in 2011 Long *et al.* synthesized a radical-bridged $[\text{Dy}^{\text{III}}_2]$ complex with a blocking temperature of 8.3 K and $U_{\text{eff}} = 178$ K,^[4] while the terbium analogue displayed a blocking temperature of ~ 14 K and $U_{\text{eff}} = 326$ K,^[5] iv) in 2013 Winpenny *et al.* reported polynuclear lanthanide alkoxide complexes with U_{eff} values higher than 800 K,^[6] and v) very recently a number of pentagonal bipyramidal mononuclear Dy^{III} complexes have been reported with blocking temperatures reaching 20 K^[7] and U_{eff} values > 1000 K.^[8] From these recent benchmarks, it is apparent that the use of lanthanide ions in molecular magnetism has become a key element towards the improvement of the magnetic properties of discrete clusters and their potential technological applications as magnetic memory devices.

We previously reported the use of the naphthalene-based triol ligand 2-(β -naphthalideneamino)-2-hydroxyethyl-1-propanol, H_3L^1 ,^[9] in Co(II/III), Ni(II) and Cu(II) chemistry,^[10] and recently expanded our studies to mixed-metal Mn/Ln chemistry reporting a family of octanuclear $[\text{Mn}^{\text{III}}_6\text{Ln}^{\text{III}}_2]$ complexes,^[11] and two dodecanuclear $[\text{Mn}^{\text{III}}_6\text{Ln}^{\text{III}}_6]$ clusters (Ln = Gd, Dy).^[12] Herein, we present our efforts towards the use of H_3L^2 (=2-(β -naphthalideneamino)-2-hydroxyethyl-1-propanol) in Mn/Ln cluster chemistry, and report the synthesis, structures and magnetic properties of two tetrametallic $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}]$ clusters (Ln = Gd, Dy).

Scheme 1. The structures of H_3L^1 and H_3L^2 (top), and the coordination modes of H_3L^2 in **1** and **2** using Harris notation (bottom).

From the reaction of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Ln = Gd, Dy), H_3L^2 and NH_4SCN in 1:1:1:3 ratio in the presence of base, NEt_3 , in MeOH we were able to isolate and characterize two new heterometallic tetranuclear clusters with the general formula $[\text{Mn}_3\text{Ln}(\text{L}^2)_2(\text{HL}^2)_2(\text{naph})(\text{NCS})(\text{H}_2\text{O})(\text{MeOH})_{1.8}](0.5\text{NO}_3)(0.5\text{ClO}_4) \cdot 1.8\text{MeOH} \cdot 0.6\text{H}_2\text{O}$ (naph: naphthaldehyde; Ln: Gd, 1.1.8MeOH·0.6H₂O; Dy, 2.1.8MeOH·0.6H₂O). The structure of **1** was solved by single-crystal X-ray crystallography, while complex **2** is isostructural with **1** based on elemental analyses, IR spectra and powder XRD patterns (Figs S1 and S2). Cluster **1** crystallizes in the triclinic P-1 space group

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(Figure 1); its metallic core describes a central Gd^{III} ion bridged to three peripheral manganese centers *via* six μ -OR groups from the four deprotonated/partially-deprotonated naphthalene-triol ligands present in the structure. Two of the ligands are fully deprotonated, L³⁻, adopting a 3.2211 coordination mode (Harris notation),^[13] while the remaining two are partially deprotonated, HL²⁻, with a 2.2101 binding mode. The lanthanide center completes its eight-coordinate sphere with a chelating naphthaldehyde group, arising upon the *in situ* breaking of the Schiff-base triol ligand. All three manganese centers are six-coordinate, completing their coordination environment with the presence of solvate molecules (for Mn2) and one terminal thiocyanate ligand (for Mn3). Mn2 and Mn3 are in the 3+ oxidation state as confirmed by bond-valence sum calculations^[14] (BVS values: 3.14 and 3.06, for Mn2 and Mn3, respectively), with both of them adopting a JT-distorted octahedral geometry, while Mn1 is found in the 4+ oxidation level (BVS value: 3.94). The coordination sphere of the lanthanide center was found following SHAPE^[15] analysis to be square antiprismatic (Table S1). The metallic cores of **1** and **2** have a star-like topology, which is extremely rare in Mn/Ln chemistry, with only two previous examples reported,^[16] while this is the first case in which the 3d centers are found in a mixed-valent state.

Figure 1. The molecular structure of the cation of **1**, highlighting the orientation of the two *Jahn-Teller* axis (bold line). Solvent molecules and H atoms are omitted for clarity. Color code: Mn^{IV} = purple, Mn^{III} = red, Gd^{III} = dark-yellow, O = green, S = yellow, N = blue, C = grey.

Variable temperature *dc* magnetic susceptibility data were collected for both complexes in the temperature range 5–300 K under an applied field of 0.1 T, and are plotted as $\chi_M T$ versus T plots in Figure 2. For **1**, the room temperature $\chi_M T$ value of 15.30 cm³ K mol⁻¹ is very close to the expected value of 15.75 cm³ K mol⁻¹ for two non-interacting Mn^{III} (with $g = 2.0$), one Mn^{IV} ($g = 2.0$) and one Gd^{III} ions ($g = 2.00$). Upon cooling the value of $\chi_M T$ remains almost unchanged until ~100 K, below which it decreases to a minimum value of 5.09 cm³ K mol⁻¹ at 5 K. For **2**, the room temperature $\chi_M T$ value of 21.75 cm³ K mol⁻¹ is very close to the expected value of 21.97 cm³ K mol⁻¹ for two non-interacting Mn^{III} (with $g = 2.0$), one Mn^{IV} ($g = 2.0$) and one Dy^{III} ions ($S = 5/2$, $L = 5$, $J = 15/2$, $g_J = 4/3$). Upon cooling the value of $\chi_M T$ remains fairly constant until ~120 K, below which it decreases to a final value of 12.01 cm³ K mol⁻¹ at 5 K.

Figure 2. $\chi_M T$ vs. T plot for complexes **1** ([Mn₃Gd]) and **2** ([Mn₃Dy]) under an applied *dc* field of 0.1 T. The solid line represents a simulation of the magnetic susceptibility data for **1** (see text for details).

Figure 3. M vs. H plot for complex **1** ([Mn₃Gd]) in the 1–7 T and 2.0–6.0 K field and temperature range. The solid lines represent a simulation of the magnetization isotherms in the 2–6 K temperature range (see text for details).

In Figure 3, the magnetization data is presented for complex **1** as a M vs. H plot. We were able to successfully simulate both the magnetic susceptibility and magnetization data, assuming a 3- J model with: i) J_1 between Mn1-Mn2 and Mn1-Mn3, ii) J_2 between the trivalent Mn centers (Mn2-Mn3), and iii) J_3 between the Gd center and its peripheral manganese centers. Using the program PHIL^[17] and employing the Hamiltonian in eqn (1)

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3) - 2J_2(\hat{S}_2\hat{S}_3) - 2J_3(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_4 + \hat{S}_3\hat{S}_4) \quad (1)$$

afforded the parameters $J_1 = -0.52$ cm⁻¹, $J_2 = 0.12$ cm⁻¹, $J_3 = -0.36$ cm⁻¹, $g_{\text{Mn(IV), Mn(III), Gd(III)}} = 2.00$. These parameters lead to a spin-frustrated system with a band of near degenerate S states of value $S = 0$, $S = 1$ and $S = 2$, all within ~1.5 cm⁻¹, as expected due to the very weak interactions present within the cluster. The magnitude and nature of parameters J_2 and J_3 are in agreement with the previously reported star-like [Mn^{III}₃Gd] complex ($J_{\text{Mn(III)-Gd}}$).

$\mu_{\text{Mn(III)}} = 0.56 \text{ cm}^{-1}$ vs. 0.12 cm^{-1} in **1**, $J_{\text{Mn-Gd}} = -0.23 \text{ cm}^{-1}$ vs. -0.36 cm^{-1} in **1**,^[16a] and the Mn-Gd interaction, J_3 , also falls within the range for previously reported values.^[18] It is worth noting that to avoid over-parameterization problems, we treated the system with only one Mn-Gd interaction, J_3 . Given the expected small magnitude of both $\text{Mn}^{\text{III}}\text{-Gd}$ and $\text{Mn}^{\text{IV}}\text{-Gd}$ interactions due to the core-like nature of the $4f$ electrons, we chose not to distinguish between the two distinct interactions present in **1**. Given the relatively large magnetic moment of cluster **2**, *ac* magnetic susceptibility measurements were performed on a polycrystalline of **2** in the 1.8–8 K range in zero applied *dc* field and a 3.5 G *ac* field oscillating at 200–1000 Hz frequency. The in-phase signal decreases upon decreasing temperature, indicating the presence of low-lying excited states with larger “*S*” values than the ground-state (Figure 4, top), while in addition frequency-dependent out-of-phase (χ'') “tails” are observed below $\sim 3.7 \text{ K}$ (Figure 4, bottom, and Fig. S3), suggesting possible single molecule magnetism behaviour. On the contrary, complex **1** displays no out-of-phase signals, clearly showing that the magnetic relaxation of cluster **2** is mainly due to the presence of the Dy^{III} center and not the Mn^{III} centers.

Figure 4. Plot of the in-phase $\chi_m'T$ (top) and out-of-phase χ_m'' signals (bottom) for **2** in *ac* susceptibility studies vs. *T* in a 3.5 G oscillating field at the indicated frequencies.

Conclusions

Two new heterometallic tetranuclear $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_2\text{Ln}]$ (Ln = Gd, Dy) star-like clusters have been synthesized with the use of the H_3L^2 (= 2-(β -naphthalideneamino)-2-hydroxyethyl-1-propanol) ligand in mixed-metal Mn/Ln chemistry. They represent the first examples of a mixed-valent Mn/Ln complex with a star-like topology, and the magnetic properties of the Dy analogue, **2**, suggest possible single molecule magnetism behaviour.

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Notes and references

§ Crystal data for **1**: $(\text{C}_{77.80}\text{H}_{80.4}\text{GdMn}_3\text{N}_5\text{O}_{16.8}\text{S}) \cdot 0.5(\text{ClO}_4) \cdot 0.5(\text{N O}_3) \cdot 1.8(\text{CH}_3\text{OH}) \cdot 0.6(\text{H}_2\text{O})$, *M* = 1857.61, triclinic, space group P-1, *a* = 16.077(7) Å, *b* = 16.201(7) Å, *c* = 18.740(8) Å, α = 70.68(4)°, β = 84.13(4)°, γ = 68.67(3)°, *V* = 4290(3) Å³, *Z* = 2, *T* = 100 K, *R*₁ (*I* > 2 σ) = 0.064 and *wR*₂ (all data) = 0.201 for 32407 reflections collected, 14826 observed reflections (*I* > 2 σ (*I*)) of 21792 (*R*_{int} = 0.032) unique reflections and 1171 parameters, *GOF* = 1.07. CCDC reference number: 1470482.

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