Two unique star-like [MnIVMnIII2LnIII] clusters: magnetic relaxation phenomena

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Employment of H3L2 (= 2-(β-naphthalideneamino)-2-hydroxyethyl-1-propanol) in manganese-lanthane cluster chemistry has led to the isolation of two new isostructural tetrametallic [MnIV2MnIII2LnIII] 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) [Mn12OAc] that could retain its magnetization once magnetized at temperatures below ~3 K,[1] various significant achievements have been accomplished: i) in 2007 a hexanuclear [MnIII6] 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 [DyIII4] cluster was reported elevating the energy barrier to 170 K,[3] iii) in 2011 Long et al. synthesized a radical-bridged [DyIII2] 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 \( U_{\text{eff}} \) values higher than 800 K,[6] and v) very recently a number of pentagonal bipyramidal mononuclear DyIII complexes have been reported with blocking temperatures reaching 20 K[7] and \( U_{\text{eff}} \) 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, \( \text{H}_3\text{L}_1 \),[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 [MnIII6LnIII2] complexes,[11] and two dodecanuclear [MnIII6LnIII2] clusters (Ln = Gd, Dy).[12] Herein, we present our efforts towards the use of H3L2 (=2-(β-naphthalideneamino)-2-hydroxyethyl-1-propanol) in Mn/Ln cluster chemistry, and report the synthesis, structures and magnetic properties of two tetrametallic [MnIV2MnIII2LnIII] clusters (Ln = Gd, Dy).

Scheme 1. The structures of H3L1 and H3L2 (top), and the coordination modes of H3L2 in 1 and 2 using Harris notation (bottom).

From the reaction of Mn(ClO4)2·6H2O, Ln(NO3)3·6H2O (Ln = Gd, Dy), H3L2 and NH4SCN in 1:1:1:3 ratio in the presence of base, NEt3, in MeOH we were able to isolate and characterize two new heterometallic tetranuclear clusters with the general formula [MnIII2LnIII(L)L2(HL)L(NCS)](H2O)(MeOH)1.8(0.5NO3)(0.5ClO4)1.8 MeOH·0.6H2O (naph: naphthaldehyde; Ln: Gd, Dy). The structure of 1 was solved by single-crystal X-ray crystallography, while complex 2 is isosstructural 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.
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 cm$^3$ K mol$^{-1}$ is very close to the expected value of 15.75 cm$^3$ 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 cm$^3$ K mol$^{-1}$ at 5 K. For 2, the room temperature $\chi_M T$ value of 21.75 cm$^3$ K mol$^{-1}$ is very close to the expected value of 21.97 cm$^3$ K mol$^{-1}$ for two non-interacting Mn$^{III}$ (with $g = 2.0$), one Mn$^{IV}$ ($g = 2.0$) and one Dy$^{III}$ ions ($S = 5/2, L = 5, J = 15/2, g = 4/3$). 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 cm$^3$ K mol$^{-1}$ at 5 K.
Two new heterometalllic tetracnuclear [MnIVMnIII2Ln] (Ln = Gd, Dy) star-like clusters have been synthesized with the use of the H3L2 (= 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: (C77.80H80.4GdMn3N5O16.8S)∙0.5(ClO4)∙0.5(NO3)∙1.8(CH3OH)∙0.6(H2O), 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, R1 (I > 2σ) = 0.064 and wR2 (all data) = 0.201 for 32407 reflections collected, 14826 observed reflections (I > 2σ(I)) of 21792 (Rint = 0.032) unique reflections and 1171 parameters, GOF = 1.07. CCDC reference number: 1470482.

Conclusions

Figure 4. Plot of the in-phase χ"ac"(top) and out-of-phase χ"dc" signals (bottom) for 2 in ac susceptibility studies vs. T in a 3.5 G oscillating field at the indicated frequencies.
