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

Citation for published version:

Digital Object Identifier (DOI):
10.1039/C6RA09066D

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
RSC Advances

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
Two unique star-like [MnIVMnIII2LnIII] clusters: magnetic relaxation phenomena

Thomais G. Tziotzi,a Milosz Siczek,b Tadeusz Lis,b Ross Inglis*cd and Constantinos J. Milios*a

Employment of H3L2 (= 2-(β-naphthalideneamino)-2-hydroxyethyl-1-propanol) in manganese-lanthanide cluster chemistry has led to the isolation of two new isostructural tetrametallic [MnIII2MnIVLnIII] 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 $U_{eff} = 86.4$ K, breaking the record of $U_{eff} = 60-64$ 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 $U_{eff} = 178$ K,[4] while the terbium analogue displayed a blocking temperature of ~14 K and $U_{eff} = 326$ 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 DyIII 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, $H_3L^1$, in Co(II/III), Ni(II) and Cu(II) chemistry,[9] and recently expanded our studies to mixed-metal Mn/Ln chemistry reporting a family of octanuclear [MnIII6LnIII2] complexes,[10] and two dodecanuclear [MnIII6LnIII6] clusters (Ln = Gd, Dy).[11] 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 [MnIVMnIII2LnIII] clusters (Ln = Gd, Dy).

From the reaction of Mn(ClO4)2.6H2O, Ln(NO3)3.6H2O (Ln = Gd, Dy), $H_3L^2$ 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 [MnIIILnII]{[HL2](naph)(NCS)(MeOH)(H2O)}0.5NO3)0.5ClO4)1.8 MeOH0.6H2O (naph: naphthaldehyde; Ln: Gd, Dy, 2.18MeOH0.6H2O). 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.

a. Department Of Chemistry, University of Crete, Voutes 71003, Herakleion, Greece. Fax: +30-2810-545001; Tel: +30-2810-545099; E-mail: komil@uoc.gr
b. Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, Wroclaw 50-383, Poland.
c. EaStCHEM School of Chemistry, The University of Edinburgh, David Brewster Road, EH9 3FJ, Edinburgh, UK. Email: r.inglis@ed.ac.uk
d. Footnotes relating to the title and/or authors should appear here.
electronic Supplementary Information (ESI) available: Full details of the experimental microanalyses and crystallographic data. See DOI 10.1039/x0xx000000x
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 ($S = 5/2$, $L = 5$, $J = 15/2$, $g_i = 4/3$). 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.

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 PHF$^{[17]}$ and employing the Hamiltonian in eqn (1)

$$\hat{H} = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) - 2J_2(\hat{S}_2 \cdot \hat{S}_3) - 2J_3(\hat{S}_3 \cdot \hat{S}_4 + \hat{S}_4 \cdot \hat{S}_5)$$

afforded the parameters $J_1 = -0.52$ cm$^{-1}$, $J_2 = 0.12$ cm$^{-1}$, $J_3 = -0.36$ cm$^{-1}$, $g_{\text{Mn}(IV)} g_{\text{Mn}(III)} g_{\text{Gd}(III)} = 2.00$. 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$^{III}$Gd] complex ($J_{\text{Mn}(III)}$-$\text{Gd}$).
Conclusions

Two new heterometallic tetranuclear $[\text{Mn}^{III}\text{Mn}^{II}\text{Ln}]$ (Ln = Gd, Dy) star-like clusters have been synthesized with the use of the $\text{H}_2\text{L}^2$ (= 2-(β-naphthalideneamino)-2-hydroxyethyl-1-propanol) ligand in mixed-metal Mnn/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.

Acknowledgements

CJM would like to thank the Greek Ministry of Education under "THALES" project (MIS 377064).

Notes and references

