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A triacontanuclear [Zn$_{12}$Dy$_{18}$] cluster: a ring of [Dy$_4$] cubes

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The reaction between Dy(NO$_3$)$_3$·6H$_2$O, Zn(OAc)$_2$·4H$_2$O, salicylaldehyde and 2-amino-isobutyric acid, in MeOH in the presence of NEt$_3$ under solvothermal conditions, led to the isolation of the triacontanuclear mixed-metal cluster [Zn$^{II}_{12}$Dy$^{III}_{18}$(OH)$_{30}$(L)$_{12}$(sal)$_6$(OAc)$_6$(NO$_3$)$_3$(H$_2$O)$_6$](NO$_3$)$_3$·12MeOH·5H$_2$O (1·12MeOH·5H$_2$O), which displays frequency- and temperature-dependent out-of-phase magnetic susceptibility signals.

The synthesis and characterization of lanthanide-based clusters has witnessed a surge in research interest over the last few years due to the intrinsic magnetic properties that such species display. This is true for both heterometallic (3d-4f) and homometallic (4f) clusters that display enhanced magnetic properties, arising from the magnitude of the spin, as well as the spin-orbit coupling based magnetic anisotropy that the 4f species possess.[1] This makes them ideal candidates for single-molecule magnets (SMMs), *i.e.* molecules that retain their magnetization once magnetized in the absence of an external magnetic field.[2] Initially started in 2003 with the characterization of the mononuclear complexes (NBu$_2$)[Pc$_2$Ln] (Ln = Tb, Dy) that were found to display SMM behaviour with energy barriers for the re-orientation of the magnetization of 330 K and 40 K for the Tb and Dy analogues, respectively,[3] impressive energy barriers have nowadays been reported of up to 810 K[4] and 842 K.[5] While for pure 4f clusters such extremely high energy barriers have been achieved, this is clearly not the case for 3d-4f species; a literature survey reveals that the highest energy barrier reported for a 3d-4f cluster is only 103 K, for the cluster [Mn$^{III}_6$Tb$_2$(sao)$_6$(OMe)$_6$(MeOH)$_4$(H$_2$O)$_2$] (sao = the dianion of salicylaldoxime),[6] *i.e.* almost an order of magnitude smaller than the corresponding highest barrier for the 4f complexes. A recent study by *Brechin* and *Colacio*, demonstrated that this may be due to the weak interaction between the 3d and 4f metal centers, leading to small separations of the low lying split sublevels, or to the random transversal secondary magnetic field of the 4f centers created by the paramagnetic metal ion, which favours the quantum tunnelling of the magnetization.[7] Yet, 3d metal centers are important in the construction of large clusters due to their well-defined geometries, which, in most cases, can be predicted. Furthermore, the impact of diamagnetic 3d centers on increasing the U_{eff} of 4f-based SMMs has been previously reported.[8]

With the above in mind, we engaged in a project of constructing heterometallic Zn/Ln clusters upon employment of the artificial amino acid 2-amino-isobutyric acid, aibH,[9] and salicylaldehyde, salH, (Scheme 1) and herein we present the synthesis of a triacontanuclear [Zn$_{12}$Dy$_{18}$] cluster, which is the largest example of any Zn-Ln cluster reported so far, and in addition, presents slow relaxation of the magnetization.

Zn(OAc)$_2$·2H$_2$O (0.75 mmol, 0.165 g), Dy(NO$_3$)$_3$·5H$_2$O (0.75 mmol, 0.330 g), aibH (0.75 mmol, 0.077 g) and salH (0.75 mmol, 0.091 g) were added in MeOH (18 ml), in the presence of excess base, NEt$_3$ (0.32 ml, 2.3 mmol) and the resulting mixture was transferred to a Teflon-lined autoclave (23 ml) and kept at 95 ^{o}C for 12 hours. After slow cooling to room temperature at a rate of 10^{c}C/h, pale yellow rod-like crystals of [Zn$^{II}_{12}$Dy$^{III}_{18}$(OH)$_{30}$(L)$_{12}$(sal)$_6$(OAc)$_6$(NO$_3$)$_3$(H$_2$O)$_6$](NO$_3$)$_3$·12MeOH·5H$_2$O (1·12MeOH·5H$_2$O) were obtained in ~ 20% yield and collected by filtration, washed with Et$_2$O and dried in air (L = the dianion of the Schiff base between salicylaldehyde and aibH; sal: salicylate ligand). ‡

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Scheme 1. The ligands discussed in the text

Cluster **1** crystallizes in the monoclinic C2/c space group (Figure 1); its metallic core (Figure 2) consists of three pairs of corner-sharing
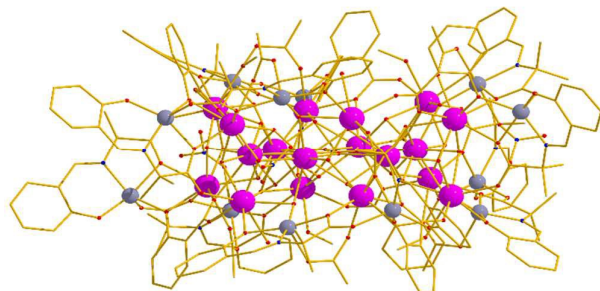
Figure 1. The molecular structure of the cation of **1** in side-view . Colour code: Zn[II] = blue-grey, Dy[III] = pink, O = red, N = blue, C = white.
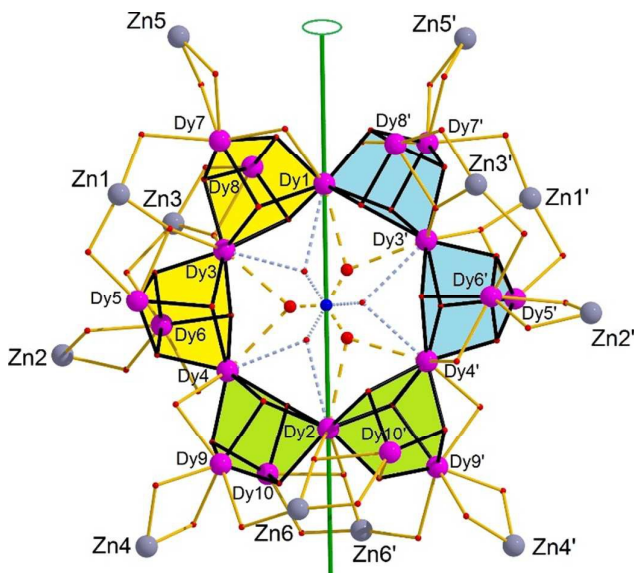

Figure 2. The magnetic core of **1**, highlighting the arrangement of the pairs of [Dy4] cubes. Symmetry code: ' = 1-x, y, 1.5-z. Central disordered nitrate ligand is marked with dashed lines. The nitrate anion located at the center of the complex is disordered over two positions, of which one is marked with blue and the other with orange dashed bonds. The green line indicates a two-fold axis crossing N1, Dy1 and Dy2.

[Dy$_4$(OH)$_4$] cubes, arranged in circular fashion. All cubes are distorted with their edge dimensions ranging from 2.228 to 2.435 Å, Dy-O(H)-Dy angles in the 95.47 – 113.04° range, and Dy···Dy distances in the 3.450 – 4.187 Å range. Each dimer of [Dy$_4$(OH)$_4$] cubes is connected to four Zn[II] centers *via* a combination of alkoxide, hydroxide and acetate bridges (Figure S2), forming a {Dy$_7$Zn$_4$(OH)$_{10}$(L)$_4$(sal)$_2$(OAc)$_2$} bowl-shaped building block encapsulating a nitrate anion in its cavity (Figure 3). Of the twelve ligands formed *in situ* that are present in the molecule, six are found in a 4.2211 coordination mode (Harris notation)[10] and six in a 3.2111 mode, while all six salicylate ligands adopt a 4.221 mode (Figure S3). All six acetates ligands are found in the usual η^1:η^1:μ mode, bridging Dy[III] and Zn[II] centers, while thirty μ_3-OH$^-$ and a disordered nitrate anion located at the centre of the molecule complete the bridging ligands within the molecule. All Zn centers are five-coordinate, adopting square-pyramidal geometry, besides Zn3 which is six-coordinate with an octahedral arrangement. Furthermore, for Zn6 there is a long interaction with O$_{NO3}$ at ~2.76 Å, therefore

it may be described as adopting *pseudo*-octahedral geometry. Regarding the 4f- centers, their ideal geometries were found upon performing a SHAPE analysis[11]: Dy1, Dy4 are nine-coordinate adopting tricapped trigonal prismatic geometry, Dy2 and Dy3 are nine-coordinate with a spherical tricapped trigonal prismatic arrangement, Dy5/Dy7/Dy9 are eight-coordinate adopting square antiprismatic geometry, while finally Dy6/Dy8 and Dy10 are eight-coordinate adopting triangular dodecahedral geometry (Figure S4).
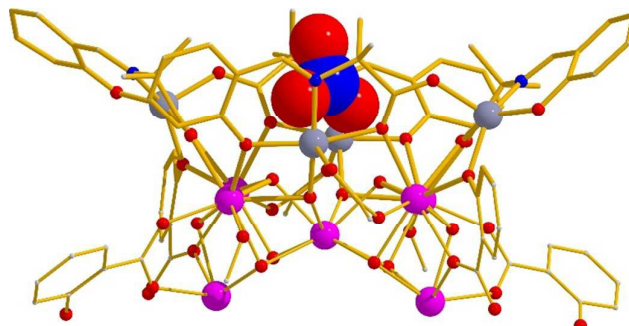

Figure 3. The {Dy$_7$Zn$_4$(OH)$_{10}$(L)$_4$(sal-COO)$_2$(OAc)$_3$} bowl-shaped building block of **1** encapsulating a NO$_3^-$ group (in space-fill mode). Colour code: same as in Fig. 1.

In the crystal, each cluster is connected with four neighboring clusters via eight C-H···π interactions [two unique: ∠C5G-H5G···Cg1 (C1D, C2D, C3D, C4D, C5D, C6D) 153°, H5G···Cg1 2.75 Å, C5G···Cg1 3.6246(18) and ∠C5H-H5H···Cg2 (C1B, C2B, C3B, C4B, C5B, C6B) 154°, H5H···Cg2 2.59 Å, C5H···Cg2 3.4702(18)]. In this arrangement, a square grid forms parallel to the (1, 0 -1) plane. The planes are offset and separated by 14.117 Å (Figure S5).

Variable temperature dc magnetic susceptibility measurements were collected for **1**·12MeOH·5H$_2$O in the temperature range 5-300 K under an applied field of 0.1 T, and are plotted as $\chi_M T$ versus T in Figure 4. The room temperature $\chi_M T$ value of 246.77 cm^3 K mol^{-1} is very close to the expected value of 253.72 cm^3 K mol^{-1} for eighteen non-interacting Dy[III] (S = 5/2, L = 5, J = 15/2, g_j = 4/3). Upon cooling the value of $\chi_M T$ remains almost constant until ~150 K, below which it decreases to its minimum value of 173.38 cm^3 K mol^{-1} at 5 K. While the decrease of the $\chi_M T$ values upon cooling normally suggests the presence of dominant antiferromagnetic interactions, this conclusion cannot be safely drawn here, since the curvature is expected to be affected by additional factors such as the depopulation of the Stark sublevels of the Dy[III] centers. Yet, for purely qualitative reasons we performed a Curie-Weiss analysis of the magnetic susceptibility data in the 50 – 300 K temperature range, yielding a negative θ value of -4.92 K. Given the large magnetic moment present even at 5 K, we performed ac magnetic susceptibility studies in order to investigate possible magnetic relaxation phenomena; the in-phase signal, plotted as $\chi_M' T$ versus T (Figure S9) decreases upon decreasing temperature, indicating the presence of low-lying excited states with larger "S" values than the ground-state, while in addition frequency-dependent out-of-phase

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($\chi_M{}^{''}$) signals are observed below ~4.5 K (Figure 5), suggesting possible single-molecule magnetism behaviour for the cluster.
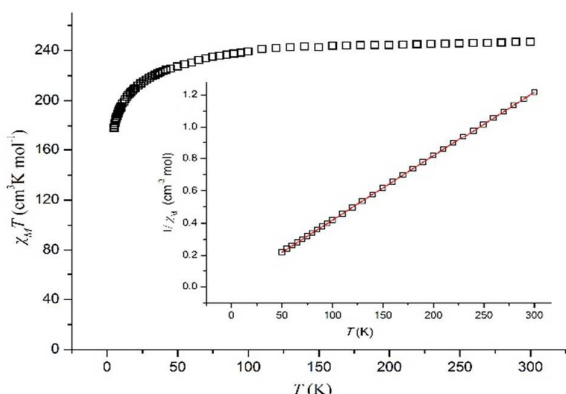

Figure 4. $\chi_M T$ vs. T plot for complex **1**·12MeOH·5H$_2$O under an applied *dc* field of 0.1 T. Inset: Curie-Weiss analysis in the 50 – 300 K temperature range.
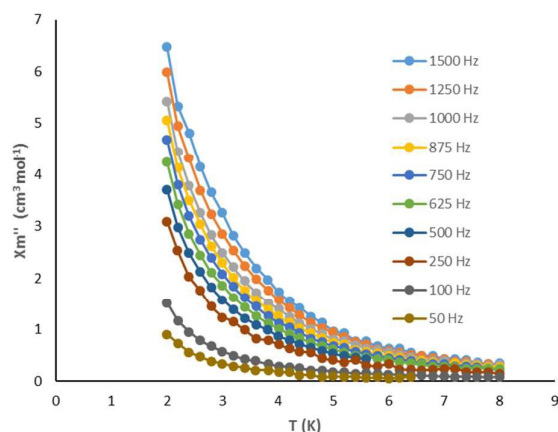

Figure 5. Plot of the out-of-phase $\chi_M{}''$ signals for **1**·12MeOH·5H$_2$O in ac susceptibility studies vs. T in a 3.5 G oscillating field at the indicated frequencies, under zero static dc field.

In conclusion, we have reported the synthesis, structure and magnetic studies of a triacontanuclear [Zn$_{12}$Dy$_{18}$] cluster, upon employment of 2-amino-isobutyric acid and salicylaldehyde. To the best of our knowledge this is the largest example of any Zn-Ln cluster reported so far, as well as one of the largest 3d-4f complexes, in general.[12] Further studies are underway as a means of obtaining more lanthanide analogues of this beautiful cluster, as well as isolating analogous paramagnetic [M$_{12}{}^{II}$Dy$_{18}$] complexes (M = Ni, Co, Cu).

Acknowledgements

Notes and references

‡ Crystal data for **1**: C$_{200}$H$_{274}$Dy$_{18}$N$_{18}$O$_{135}$Zn$_{12}$, M = 8799.79, monoclinic, space group C2/c, a = 35.409 (18) Å, b = 30.501 (12) Å, c = 31.789 (13) Å, β = 115.52 (5)°, V = 30983 (26)Å^3 , Z = 4, T = 85 K, R1 (I > 2σ) = 0.070 and wR2 (all data) = 0.203 for 59325 reflections collected, 16041 observed reflections (I > 2σ(I)) of 26275 (R$_{int}$ = 0.054) unique reflections and 1692 parameters, GOF = 1.22. CCDC reference number: 1420263.

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