Opening up a dysprosium triangle by ligand oximation†

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A simple trinuclear dysprosium complex shows complex slow relaxation of the magnetisation.

The discovery of single-molecule magnet (SMM) behaviour,[1] which offers the prospect of storing and processing magnetic information at a molecular level, has led to the synthesis of an astonishing variety of coordination cluster compounds. The challenge has been to invest these molecules with the required non-zero ground spin state and uniaxial anisotropy and recently, thanks to their anisotropy and large spin, incorporating lanthanide ions into such systems has become an area of intense research activity.[2] The Dy^{III} ion seems to be especially useful in this respect, as we and others have recently demonstrated.[3] In particular, pure Dy^{III} systems can show exotic magnetic effects holding the promise of real applications in quantum computing and data storage. Complexes of Dy^{III} with up to 26 metal ions that exhibit slow relaxation of the magnetisation have been reported.[4] As a result of the inherent anisotropy of the Dy^{III} ion in a ligand field, these frequently have a ground-state which is difficult to establish, although it has been shown that the interactions between paramagnetic centres tend to be predominantly antiferromagnetic.

We have already investigated various Schiff-base ligands based on *o*-vanillin aldehyde[5] and found it especially useful in forming polynuclear dysprosium complexes. Furthermore, we have reported that when reacting the aldehyde with $DyCl_3$ a $\{Dy_3\}$ triangle is obtained[4c] which possesses novel magnetic behaviour that we have studied in detail.[4f] Given that ferromagnetic coupling is often observed in oxime-type systems,[6] although this depends on the M–N=O–M torsion angle, we decided to investigate using the Schiff-base *o*-vanillin oxime (H_2vanox) (see scheme in Fig. 1). We report here the synthesis and the magnetic properties, including an analysis based on *ab initio* calculations, of a near linear trinuclear dysprosium complex formed with H_2vanox where the metal ions are weakly ferromagnetic coupled.

The reaction between H_2vanox and $Dy(ClO_4)_3{\cdot}6H_2O$ in ethanol in the presence of triethylamine yielded colourless crystalline plates of $[Dy_3vanox_2(Hvanox)_4(EtOH)_2](ClO_4){\cdot}1\frac{1}{2}EtOH{\cdot}H_2O$ ($\mathbf{1}{\cdot}(ClO_4){\cdot}1\frac{1}{2}EtOH{\cdot}H_2O$) over two days.‡

Compound **1** crystallises in the space group $P2_1/n$, with $Z = 4$.§ Although the molecule occupies a general site it has an idealised two-fold axis through the central Dy(1) (Fig. 1). The complex contains a nearly linear Dy_3 core, with similar Dy···Dy distances (3.7191(3) and 3.737(3) Å) and a Dy···Dy···Dy angle of 166.29(1)°. The two doubly-deprotonated $(vanox)^{2-}$ ligands link all three Dy centres with the same bridging mode. The phenoxo oxygen links the central dysprosium Dy(1) to one outer metal ion and the oximato group forms an N,O-η^2-bridge to the other. Finally, the methoxy oxygens each ligate an outer dysprosium, Dy(2) or Dy(3). This coordination mode is reminiscent of that of the vanillato ligands in $\{Dy_3\}$.[4c] Two of the four $(vanoxH)^-$ ligands also bridge two dysprosiums through the phenoxo oxygens. The methoxy oxygen coordinates to the central Dy(1), while the nitrogen of the protonated oxime group coordinates to Dy(2) or Dy(3). The Dy–O–Dy angles are all similar in the range 103.89(10)°–105.27(10)°. The bridging oximato groups N(1)–O(2) and N(2)–O(5) have N–O bond lengths 1.380(4) and 1.384(4) Å, and Dy–N–O–Dy torsion angles 16.4(3)° and 14.3(3)°, respectively. The remaining two $(vanoxH)^-$ ligands each chelate an outer dysprosium through their phenoxo oxygen and oxime nitrogen. The coordination spheres of Dy(2) and Dy(3) are each completed by an ethanol ligand, making them eight-coordinate with a geometry between dodecahedral and square antiprismatic while the environment of Dy(1) is a nearly perfect dodecahedron.

In **1** the $(vanoxH)^-$ ligands all form intramolecular hydrogen bonds *via* the protonated oxime group (see Fig. 1). The alcohol ligands, on the other hand, all form hydrogen bonds to lattice solvent molecules or perchlorate oxygens and there are no direct intermolecular hydrogen bonds (see Fig. S1†).

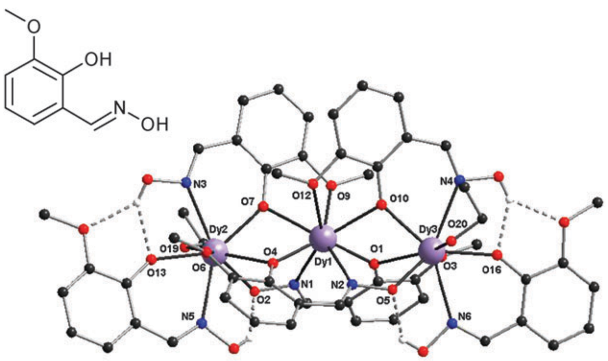

Fig. 1 Structure of $[Dy_3(vanox)_2(vanoxH)_4(EtOH)_2]^+$, **1**. Organic H atoms omitted for clarity. In the left corner a scheme of H_2vanox.

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† Electronic supplementary information (ESI) available: Molecular packing diagram, magnetic measurements and ligand synthesis. CCDC 729180. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b908194a

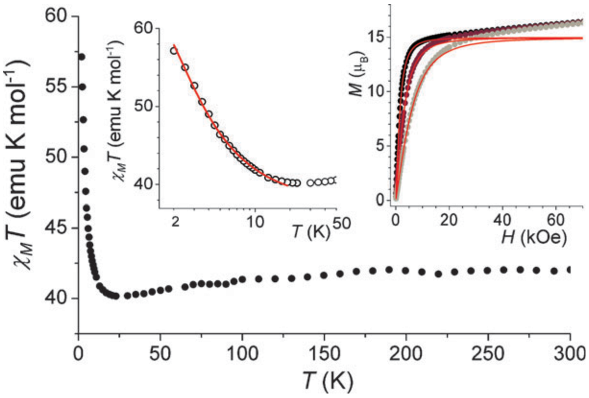

Fig. 2 Plot of χT *vs.* T for complex **1** at 1 kOe. Inset: left, semi-log plot of low temperature region; right M *vs.* H data at 1.8 K (dark grey), 3.0 K, and 5.0 K (light grey). Red solid lines are best-fit calculated values (see text).

The static magnetic susceptibility of **1** was measured on a polycrystalline sample in the temperature range 1.8–300 K in an applied field of 1 kOe. The χT value of 42.05 emu K mol^{-1} at 300 K is in close agreement with the expected value of 42.5 emu K mol^{-1} for three Dy^{III} ions (J = 15/2, g = 4/3) (Fig. 2). Upon cooling, the χT product slightly decreases to a minimum value of 40.2 emu K mol^{-1} at 20 K as a consequence of thermal depopulation of the Stark sublevels of Dy^{III} ions. Below 20 K, the χT product rises sharply to reach 58.5 emu K mol^{-1} at 1.8 K, indicative of ferromagnetic interactions. The field-dependence of the magnetisation (Fig. 2 inset right) rises abruptly at low fields before levelling to 16.4 μ_B around 15 kOe at 1.8 K, in good agreement with the expected value (3 × 5.23 μ_B) for three isolated Dy^{III} ions, and then continues to increase slowly as in other reported Dy^{III} systems as a result of the significant anisotropy.[4c,l] The maximum of the magnetisation is in relatively good agreement with the expected value (3 × 5.23 μ_B) for three isolated Dy^{III} ions, further confirming the weak ferromagnetic intracomplex interactions suggested by the χT *vs.* T data.

The temperature dependence of the dynamic susceptibility was studied without an applied static field in the temperature range 1.8–15 K (Fig. 3). For higher frequencies more than two maxima can be observed in the out-of-phase signal indicative of more than one relaxation process operating in this compound. Evidence of possible multiple relaxation processes has been observed in some other reported Dy^{III} complexes,[4c,l] and the comparison of wet and dried microcrystals allows us to exclude that this results from the loss of crystallisation solvent. The relaxation time of **1** was thus deduced from the frequency-dependent data between 3.5 and 8.5 K (Fig. S2†). Two bisecting lines can be obtained when modelling the behaviour with Arrhenius plots (Fig. 3, inset) corresponding to an energy gap (Δ) of 28.7 and 69.3 K and a pre-exponential factor (τ_0) of 6.3 × 10^{-5} and 5.9 × 10^{-8} s, below and above 6 K, respectively. The frequency-dependence of the ac susceptibility in an applied dc field was also measured at 7 K, which is where the dominant relaxation processes are located (Fig. S3†). With increasing field the relaxation rate $1/\tau$ remains essentially constant below 500 Oe and then slightly increases up to the highest investigated field of 2500 Oe. Therefore the strong resonant tunnelling observed in the original Dy$_3$ system is not observed here. Single crystals and higher frequency experiments are necessary to investigate further the complex dynamic behaviour of this system. The scope of this communication is however to focus on the static properties, thus we have performed a post Hartree–Fock *ab initio* estimation of the nature and orientation of the single-ion magnetic anisotropy tensor of the three Dy ions. The used CASPT2/RASSI-SO method has already proved to be suitable for such a study.[7,8] An Ising-type anisotropy was observed for the three Dy centres with the ground doublet arising mainly from $m_J = \pm 15/2$ with $g_J = 4/3$ and thus corresponding to $g_{\parallel} \approx 20$ and $g_{\perp} \approx 0$ for an effective spin $S_{\text{eff}} = 1/2$. The direction of the three easy anisotropy axes is represented in Fig. 4 where the dodecahedral environment of the Dy sites is emphasised using the approach of constructing orthogonal trapezoidal planes according to the definition of Muetterties.[9] For the central Dy^{III} ion (Dy1) the easy axis is perpendicular to the plane defined by the N1–Dy1–N2 bonds. It forms angles of 17.4° and 11.8° to the easy axes of Dy2 and Dy3, respectively, while the last two are angled only 5° to each other. In all cases the easy axis points in a direction lying between the Dy–O bonds to the harder negatively charged ligand sites and all lie along the Dy–Dy–Dy direction of the molecule as shown in Fig. 4. Thus the rupture of the triangular structure seen in the *o*-vanillin derivative has modified not only the interaction scheme but also the orientation of the easy axes which are here essentially collinear compared with the situation in the triangular {Dy$_3$} cluster where they lie at 120° to one another as a result of the *pseudo*-three-fold symmetry.[4c,f,7]

Taking into account the computed directions of the easy anisotropy axes and the g values for the $S_{\text{eff}} = 1/2$ state the χT powder data below 20 K can be reproduced assuming an average random orientation of the field and by introducing one coupling constant between the central and the two external Dy ions ($J_{\text{Dy–Dy}}$) of +3.9 (4) K (Fig. 2), where the exchange Hamiltonian is given by $H_{\text{ex}} = -J(S_1{}^zS_2{}^z + S_1{}^zS_3{}^z)$. Interestingly, with this orientation of the easy axes the dipolar contribution to intracluster interaction is ferromagnetic and rather large (J_{dip12} = 6.8 K and J_{dip13} = 6.5 K) as a consequence of the orientation of the easy axes along the vectors connecting the magnetic centres, well known to favour parallel alignment of the magnetic moments. The observed ferromagnetic interaction thus results from a partial compensation of the ferromagnetic dipolar and exchange interactions, the latter apparently antiferromagnetic in contrast to what is observed with 3d ions.[6]

In conclusion, modifying the original aldehyde ligand by condensing it with hydroxylamine has, in effect, made it possible to open out the triangle in terms of the relative positions of the metal ions whilst retaining the dodecahedral coordination geometries of the metal ions relative to those of {Dy$_3$}. In doing so we have also succeeded in aligning the individual spins such that the molecule becomes ferromagnetic (Fig. 4) as a result of a favourable dipolar interaction. This picture is fully confirmed by *ab initio* calculations. It is becoming increasingly clear in the description of 4f SMMs that such calculations are necessary to establish the effect on the crystal field of the geometry around the lanthanide and

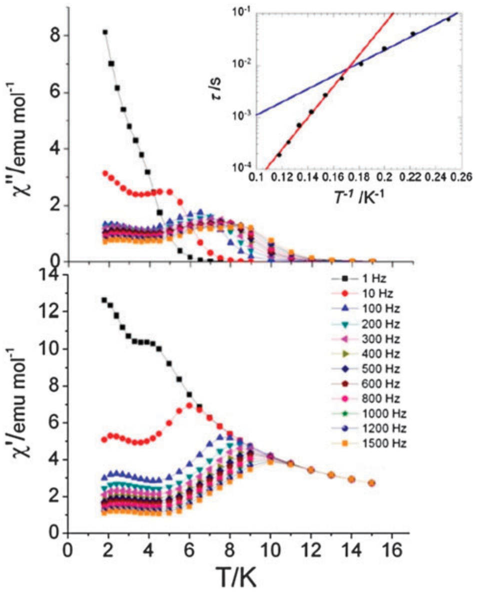

Fig. 3 Temperature dependence of the in-phase signal, χ' (top), out-of-phase signal, χ'' (bottom), and the resulting Arrhenius plot (inset) from the ac susceptibility measurements of **1** without an applied static field.

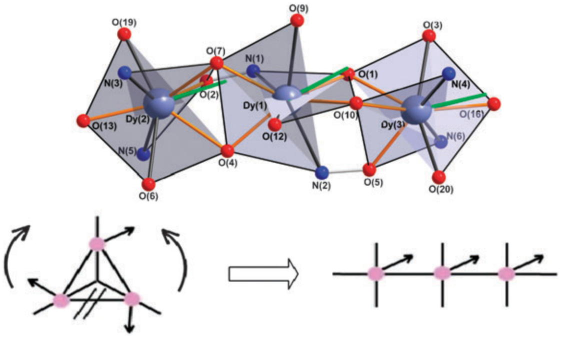

Fig. 4 Top: polyhedral representation of the metal ion centres in **1** showing orthogonal trapezoidal planes with the coordination bonds to hard donors highlighted orange superimposed to the calculated easy axes of magnetic anisotropy tensors and the observed easy-axis (green). Bottom: schematic view of the effect of the opening of the triangle.

the factors which determine the orientation of the anisotropy. Thus it seems for the increasing number of lanthanide-based SMMs being discovered, it will be important to combine theoretical investigations and experimental studies to identify the anisotropy direction and gauge its influence on parameters such as the sign of the magnetic interaction and the energy barrier height. These insights should help in ligand design for further enhancement of SMM properties.

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Notes and references

‡ **1**·$ClO_4\cdot 1\frac{1}{2}EtOH\cdot H_2O$. $Dy(ClO_4)_3\cdot 6H_2O$ (114 mg, 0.2 mmol) was added to a 3 ml ethanolic solution containing H_2vanox (64 mg, 0.4 mmol) and triethylamine (60 μl, 0.6 mmol). The solution was heated with stirring for 30 min. After standing for 2 d at room temperature colourless crystalline plates (42 mg, 36%) formed which readily lose solvent. Calc. (%) for $C_{52}H_{69}ClDy_3N_6O_{28}$ (corresponds to $\{Dy_3\}\cdot 5H_2O$): C 35.31; H 3.88; N 4.75. Found (%): C 35.41; H 3.74; N 4.51. IR (KBr disk, cm^{-1}): 3434, 3941, 1629, 1603, 1559, 1462, 1331, 1274, 1239, 1219, 11094, 1074, 959, 851, 755, 734, 629.

§ Crystal data for **1**: $C_{55}H_{69}ClDy_3N_6O_{26.5}$, $M = 1761.11$, monoclinic, $P2_1/n$, $a = 22.3234(13)$, $b = 12.1453(7)$, $c = 24.1194(14)$ Å, $\beta = 94.405(1)°$, $U = 6520.0(7)$ Å^3, $T = 100$ K, $Z = 4$, $D_c = 1.794$ Mg m^{-3}, μ(Mo-Kα) = 3.530 mm^{-1}, $F(000) = 3472$, colourless plate 0.22 × 0.19 × 0.08 mm. 34 986 reflections measured, 14 520 unique ($R_{int} = 0.0267$). 848 parameters, w$R_2 = 0.0929$, $S = 1.054$ (all data); $R_1 = 0.0338$ (13 671 data with $I > 2\sigma(I)$); largest final difference peak/hole +3.14 (amongst disordered perchlorate)/−1.45 e Å^{-3}.

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