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A Linear Tetranuclear Dysprosium(III) Compound Showing Single-Molecule Magnet Behavior

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Although magnetic measurements reveal a single-relaxation time for a linear tetranuclear Dy(III) compound, the wide distribution of the relaxation time observed clearly suggests the presence of two slightly different anisotropic centres, therefore opening new avenues for investigating the relaxation dynamics of lanthanide aggregates.

10 Since the discovery of single-molecule magnets (SMMs), much effort has been directed towards the preparation of new materials incorporating a large number of metal ions, with the objective to isolate compounds possessing large spin ground state S and uniaxial Ising-like magneto-anisotropy D values.¹ Although the spin can be successfully maximized by generating ferromagnetically-coupled systems,² the maximization of D represents a major challenge.³ $4f$ -based polynuclear compounds are highly promising molecules for the development of higher-barrier SMMs, owing to their significant magnetic anisotropy arising
15 from the large unquenched orbital angular momentum.⁴ Indeed, the interest in SMMs based on $4f$ ions has grown dramatically after the observation of slow magnetic relaxation in the case of mononuclear complexes.⁵ Thus, a number of Dy^{III}-containing compounds exhibiting different topologies⁶ based on a dimeric,^{6d, 6i, 6j} a triangular,^{6b} a defect-dicubane,^{6e, 6h} or a square-pyramidal core,^{6c} or a wheel,^{6a, 6k} have been described in the literature. Among them, a tetranuclear Dy^{III}₄ coordination compound with a defect-dicubane geometry has been reported, with a record anisotropic barrier of 170 K.^{6h}

20 It has to be noticed that fewer $4f$ SMMs have been developed so far compared to $3d$ -based ones; moreover, the relaxing rates are extremely sensitive to tiny distortions of the coordination geometry in $4f$ -systems.^{5c} Therefore, there is a continuous need for the design of novel structures to enlarge the available database and thus improve our knowledge of the structure-property relationship of lanthanide-containing SMMs. In the present study, a tetradentate N,O-donor ligand, *i.e.* N-(2-carboxyphenyl)salicylideneimine (H₂L), obtained by condensation of anthranilic acid and salicylaldehyde has been used to
25 generate a linear tetranuclear Dy₄ aggregate showing SMM behavior. Strikingly, magnetization dynamics studies of this compound reveal that mainly one thermally-activated relaxation process takes place, in contrast to the apparent occurrence of a multiple relaxation process in a previously reported linear trinuclear Dy₃ compound.^{6f}

The reaction of Dy(OAc)₃·H₂O with H₂L in methanol, in the presence of triethylamine, produces yellow crystals of [Dy₄(L)₄(HL)₂(C₆H₄NH₂COO)₂(CH₃OH)₄]·5CH₃OH (**1**), whose molecular structure determined by single-crystal X-ray diffraction
30 is depicted in Figure 1. The centrosymmetric compound has a nearly linear Dy₄ core with Dy1...Dy2 and Dy1...Dy1A distances of 4.241 Å and 4.055 Å, respectively. Three different binding modes can be observed for the polydentate Schiff-base ligand in its zwitterionic and di-deprotonated forms (Scheme 1). Two central fully deprotonated, tetradentate L²⁻ ligands bind Dy atoms in a

$\eta^1:\eta^1:\eta^2:\eta^2:\mu_3$ -fashion, while two peripheral fully deprotonated L^{2-} ligands coordinate in a $\eta^1:\eta^1:\eta^2:\eta^1:\mu_2$ -fashion. Finally, two peripheral zwitterionic tridentate ligands bind in a $\eta^1:\eta^1:\eta^1:\mu_2$ -fashion, and a linear metal array is generated, which is characterized by Dy–Dy–Dy angles of 109.77° . The zwitterionic nature of the peripheral HL^- ligands prevents the coordination of the nitrogen atom to metal ions, and results in a nearly planar ligand; in contrast, the tetradentate L^{2-} ligands are remarkably distorted, most likely due to the small bite angle of the chelating units of the ligand. The coordination sphere of Dy1 is completed by a methanol molecule, producing an eight-coordinate centre with a nearly perfect square-antiprismatic geometry. The coordination environment around Dy2 is completed by a methanol molecule and an anthranilate ligand, most likely formed by decomposition of the Schiff base ligand H_2L during the coordination reaction. The resulting eight-coordinate Dy2 ion exhibits a coordination geometry in between a bi-capped trigonal prism and a square antiprism (Fig. S1 in the Supporting Information). The shortest intertetramer Dy...Dy distances is 9.27 \AA .

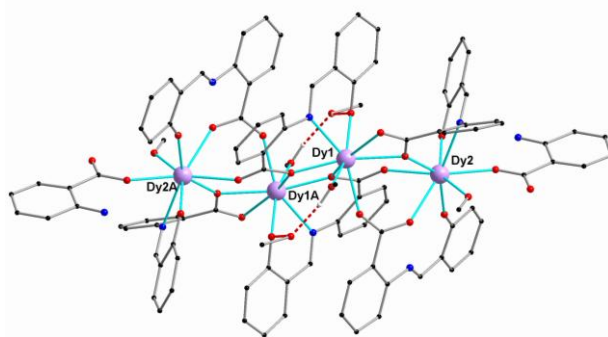
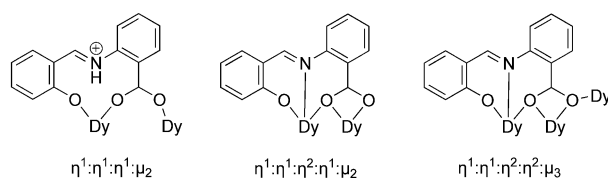


Fig. 1 The molecular structure of compound **1**. Hydrogen atoms and lattice solvent molecules are omitted for clarity. Color scheme: pink Dy, red O, blue

N.



Scheme 1 Binding modes of the ligands HL^- ($\eta^1:\eta^1:\eta^1:\mu_2$) and L^{2-} ($\eta^1:\eta^1:\eta^2:\eta^1:\mu_2$ and $\eta^1:\eta^1:\eta^2:\eta^2:\mu_3$) observed in compound **1**.

Direct-current (dc) magnetic susceptibility studies of **1** have been carried out in an applied magnetic field of 1 kOe in the temperature range 300 - 2 K. The plot of $\chi_M T$ vs. T , where χ_M is the molar magnetic susceptibility, is shown in Fig. 2. The observed $\chi_M T$ value of $56.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K is very close to the expected value of $56.7 \text{ cm}^3 \text{ K mol}^{-1}$ for four uncoupled Dy^{III} ions (${}^6H_{15/2}$, $S = 5/2$, $L = 5$, $J = 15/2$, $g = 4/3$). From 300 to 20 K $\chi_M T$ gradually decreases, and subsequently drops to reach a minimum of $31.7 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K, as a consequence of the progressive depopulation of excited Stark sublevels of the Dy^{III} ions.⁷

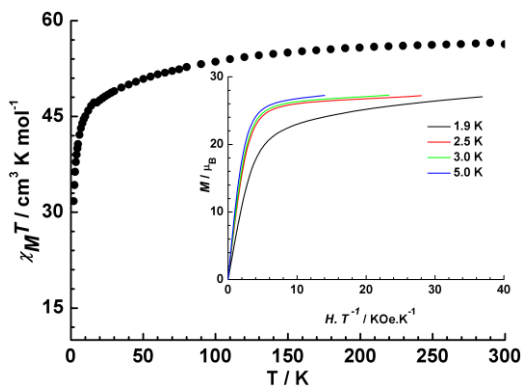


Fig. 2 Temperature dependence of the $\chi_M T$ product at 1 kOe; Inset: M vs. H/T plot at different temperatures below 5 K.

Magnetization (M) data were collected in the 0 - 70 kOe field range at different temperatures. The nonsuperimposition of the M vs. H/T data on a single master-curve (inset of Fig. 2) suggests the presence of a significant magnetic anisotropy and/or low-lying excited states. The magnetization increases rapidly at low field and eventually reaches the value of $27.0 \mu_B$ at 1.9 K and 70 kOe without clear saturation. This value is much lower than the expected saturation value of $40 \mu_B$ for four non-interacting Dy^{III} ions, most likely due to the crystal-field effect at the Dy^{III} ion that eliminates the 16-fold degeneracy of the ${}^6H_{15/2}$ ground state.⁸

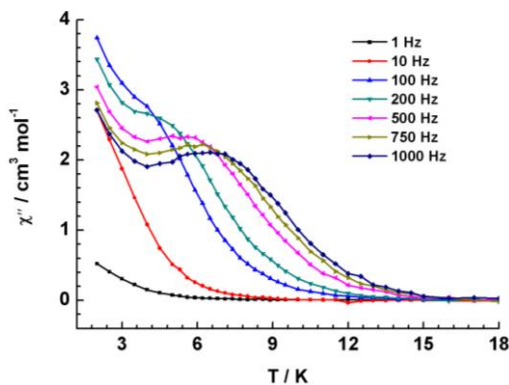


Fig. 3 Temperature dependence of the out-of-phase ac susceptibility of **1** under zero-dc field.

To probe the dynamics of this system, the temperature and frequency dependences of the ac susceptibilities have been measured under zero-dc field (Figs. 3 and S3-4) for **1**. Both measurements reveal a slow relaxation of the magnetization that is typical for a SMM behavior. Cole-Cole plots (Fig. S5) with a nearly semi-circle shape have been obtained. The analysis of the plots gives an α parameter close to zero (single-relaxation process) for the temperature range 5.5 – 9 K, whereas α increases below 5.5 K indicating a wide distribution of the relaxation time.^{6i, 9} The relaxation time was extracted from the frequency-dependent data between 1.9 and 9 K (Fig. 4). Below 3 K, a temperature-independent relaxation regime is observed with a characteristic time of 0.00068 s. This behavior is expected for a SMM when the quantum tunneling of the magnetization becomes dominant (*i.e.* faster than the thermal-activated relaxation).^{6d, 10} As the time scale of this quantum regime is relatively fast it explains the absence of M vs. H hysteresis effects at 1.9 K considering the slow field sweeping-rate of our magnetometer. Above 3 K, the dynamics is clearly temperature dependent, and thus influenced by both quantum and thermal pathways for the relaxation

(Fig. 4). An estimation of the energy barrier, *i.e.* 20 K, can be obtained by fitting τ values above 5.5 K using an Arrhenius law. All these magnetic parameters clearly evidence the SMM nature of this remarkable Dy^{III} compound.

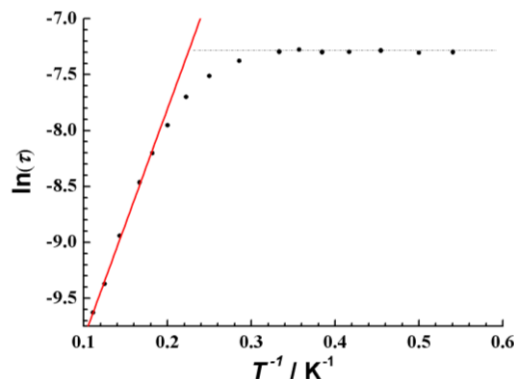


Fig. 4 Relaxation time, $\ln \tau$, versus T^{-1} plot for **1** under zero-dc field. The solid line is fitted with the Arrhenius law (see text).

In summary, a new linear Dy₄ compound has been obtained from a polydentate Schiff-base ligand H₂L, whose zwitterionic and di-deprotonated forms reveal three different binding modes. This linear Dy₄ compound behaves as a SMM with an energy barrier of 20 K, and a quantum regime of relaxation below 3 K. It should be noted that the relaxing rate reflects the local molecular symmetry and is extremely sensitive to tiny distortions of the coordination geometry of 4f ions;^{5c} hence, the wide distribution of the relaxation time in compound **1** is probably associated with the existence of two slightly different anisotropic centres.^{6f, 6h} Detailed ab initio calculations are required to better understand the dynamics of the magnetization in polynuclear lanthanide-based systems.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: Detailed experimental procedures, additional crystallographic diagrams and magnetic diagram. The structure has some disorder, full details are supplied in the cif file. CCDC number xxxxxx. See DOI: 10.1039/b000000x/

[‡] Crystal data for the complex: C₁₀₇H₁₀₄Dy₄N₈O₃₁, $M_r = 2648.01$, triclinic, space group $P\bar{1}$, $a = 11.6562(8)$, $b = 15.2677(11)$, $c = 15.6126(11)$ Å, $\alpha = 108.1370(10)$, $\beta = 93.2150(10)$, $\gamma = 103.1300(10)^\circ$, $V = 2547.1(3)$ Å³, $Z = 1$, $T = 150(2)$ K, $D_c = 1.726$ g cm⁻³, $R_{\text{int}} = 0.0332$, 38509 reflections collected, $R_1(wR_2) = 0.0363(0.0849)$ and $S = 1.002$ for 11938 observed reflections out of 15831 unique reflections with $I > 2\sigma(I)$. Data collection, structure solution and refinement used SHELXL.¹¹

[§] Magnetic measurements were performed in the temperature range 1.9 ~ 300 K, using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

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