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COMMUNICATION

Single molecule magnet behaviour in a rare trinuclear $\{\text{Cr}^{\text{III}}\text{Dy}_2^{\text{III}}\}$ methoxo-bridged complex

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The reaction of the chromium (III) chloride tetrahydrofuran complex with the dipivaloylmethane ligand, the lanthanide alcoholic salt $\text{DyCl}_3 \cdot \text{CH}_3\text{OH}$ and the (1,1,1-tris(hydroxymethyl)-ethane ligand yielded to the formation of a new trinuclear chromium-dysprosium complex. Magnetic investigations revealed that the new 3d-4f complex exhibits single molecule magnet behaviour.

The interest in Single Molecule Magnets (SMMs)¹ raised considerably when researchers realized that in principle, SMMs could be used for high-density information storage,² and more recently as magnetic refrigerants³ or in molecular spintronics.⁴ Single molecule magnets exhibit slow relaxation of the magnetization from a purely molecular origin and are characterized by two essential features which are a large ground spin state (*S*) and a large magnetic anisotropy.

During the last decades, a peculiar attention has been placed on the synthesis of homo- and heterometallic 3d complexes with SMM behaviour.⁵ But recently, in the search for more efficient SMMs, it has been demonstrated that the incorporation of a highly anisotropic 4f ions into 3d matrices can enhance the SMM properties.⁶ The use of anisotropic 4f ions for the design of efficient SMMs led to the emergence of two promising families which are the mononuclear 4f⁷ and the polynuclear 4f⁸ SMMs. Interestingly, in the race for the design of efficient single molecule magnets, a strong effort has been devoted on the use of only few transition metal ions such as Mn^{III/IV}, Co^{II} and Ni^{II} ions.⁹ However, it has been demonstrated recently¹⁰ that the combination of a highly anisotropic 4f ion with a highly isotropic 3d ion such as Cr^{III} ion can lead to the formation of 3d-4f clusters with higher blocking temperature. Up to now two different approaches for the synthesis of Cr^{III}-Ln^{III} SMMs have been explored. The first one is based on fluoride bridges¹¹ $\{\text{Ln}^{\text{III}}\text{-F-Cr}^{\text{III}}\}$ and has led to rarely

observed polynuclear complexes with magneto-caloric effect¹² or SMM behaviour.¹³ The second one is based on $\{\text{Cr}^{\text{III}}\text{-O-Ln}^{\text{III}}\}$ bridges and contains only few examples, with up to now less than ten reports.^{10,14} Few reports¹⁵ also have shown that the slow relaxation of the magnetization process is not always observed for Cr^{III}-Ln^{III} complexes, highlighting the necessity of advanced design and careful magnetic investigations.

Herein, we report the synthesis, structure and magnetic properties of a new neutral hetero-trinuclear coordination complex $[\text{CrDy}_2(\text{OCH}_3)_4(\text{dpm})_5(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}$ (**1**) with rarely observed Cr-Ln methoxo and methanol-bridges. **1** (see Fig. 1) was obtained from a multi-step reaction of $\text{DyCl}_3 \cdot \text{CH}_3\text{OH}$, $\text{CrCl}_3 \cdot (\text{THF})_3$, hdpm (dipivaloylmethane), $\text{H}_3\text{L} = 1,1,1\text{-tris(hydroxymethyl)-ethane}$ in $\text{Et}_2\text{O}/\text{CH}_3\text{OH}$ solvent mixture. The reaction originally designed to afford a "star-shaped" $\{\text{CrDy}_3\}$ complex, with a central chromium atom coordinated to three dysprosium atoms through two L³⁻ tripodal ligands, unexpectedly led to the formation of an incomplete star shaped complex comprising only betadiketonates and bridging methanol-methoxide units. The one-step reaction synthesis was attempted as an alternative to the unsuccessful essays through the two-steps approach employed for the preparation of MFe_3 (*M* = Cr, V) stars.¹⁶ In order to get more insights on the role of the H_3L tripodal ligand during the reaction, many attempts were conducted with and without the ligand, as described in the supporting information, leading to the conclusion that the presence of the ligand is required.

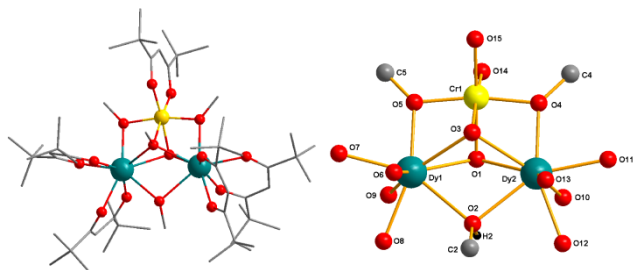


Fig. 1 Left: Ball and stick representation of crystal structure of **1**. Right: Simplified ball and stick representation of the core of **1** with labelled atoms. Molecules of solvent and hydrogen atoms were omitted for clarity. Colour code: Dy: teal, Cr: yellow, O: red, C: grey.

Suitable single crystals of **1**,¹⁷ which crystallizes in the triclinic space group $P-1$, were obtained by slow vapour diffusion of methanol in the ether solution of **1**. Full crystallographic data and structural refinements for **1** are shown in Table S1 (see SI). Selected bond lengths, angles and bond valence sum (BVS) values for **1** are listed in Table S2 and S3 (see SI). The trinuclear central core formed by atoms Cr1, Dy1 and Dy2, shows two μ_3 -methoxo bridges (atoms: O1, O3) one above and one below the plane of the metal ions. Three additional μ_2 -bridges define the edges of the triangle with two methoxide ligands (atoms: O4, O5) linking the Cr ion to the Dy ones, and a neutral methanol molecule bridging the two Dy ions. In **1**, the chromium atom is octahedrally coordinated (see Fig. S1, SI) by six oxygen atoms from one dpm⁻ ligand and four methoxide ligands, with Cr...O bond lengths ranging from 1.925(5) to 2.019(5) Å. The calculated BVS value of 3.14 for the Cr atom confirmed its expected oxidation state of +3. The interatomic bond distances of 3.1546(17), 3.1417(14) and 3.8865(9) Å for Cr1...Dy1, Cr1...Dy2 and Dy1...Dy2, respectively, revealed the presence of a *quasi*-isosceles triangle formed by the metal center core. Each dysprosium atom (Dy1 and Dy2) is surrounded by eight oxygen atoms leading to an 8-fold coordination and represented by a distorted square anti-prismatic geometry (see Fig. S2, and Table S4, SI). The Φ_{average} and α_{average} values¹⁸ of 46.3° and 57.7°, and of 46.4° and 58.4° respectively for Dy1 and Dy2, confirm the distortion of the coordination geometry of the two dysprosium(III) ions. The values for each Dy(III) ions are different than the expected values of 45° (Φ) and 54.74° (α) for an ideal D_{4d} symmetry and indicate compression of the square antiprism polyhedra. The eight oxygen atoms belong to two dpm⁻ ligands, three methoxide ligands, and one methanol, with Dy...O bond lengths ranging from 2.160(5) to 2.557(5) Å for Dy1 and from 2.270(5) to 2.544(5) Å for Dy2, the largest values observed for Dy-O2 distances as expected for a neutral methanol ligand. In fact, a careful study of the crystal structure and charge balance calculation for **1** revealed that an additional H atom is present on the O2 atom bridging the two Dy atoms. Indeed, it can be observed that the carbon atom C2 is outside the plane formed by {Cr1Dy1Dy2O2} atoms (see Fig. S3a, SI), compared to the two others similar carbon atoms C4 and C5 which are aligned with the two similar planes formed by {Cr1Dy1Dy2O4} atoms and by {Cr1Dy1Dy2O5} atoms respectively for C4 and C5 atoms (See Fig. S3b, SI).

The presence of a similar H atom placed on the oxygen atom of a methoxide group, to form a coordinating methanol molecule, was observed by Powell & *al.*¹⁹ Moreover, as for the coordinating methanol molecules reported by Powell & *al.*, a longer C...O bond distance for C2...O2 is observed in **1**, compared to the other two (C4...O4 and C5...O5), thus supporting the presence of a coordinating methanol molecules. Indeed, the longer C2...O2 bond length of 1.441(10) Å is in good agreement with the ones reported for the three methanol molecules, respectively of 1.425(6), 1.428(6) and 1.435(6) Å. In **1**, the C2...O2 bond length is longer than the 1.391(10) and 1.405(9) Å respectively for C4...O4 and C5...O5 bond lengths (see Fig. 2). The crystal structure refinement of **1** also showed (see SI Fig. S2) that a terminal (-CH₃)₃ group (C54, C55, C56) of the dpm⁻ ligand connected to the Cr1 atom is disordered over two sets of positions rotated by 60° with site-occupancy factors of 0.632(10) (C54A, C55A, C56A) and 0.368(10) (C54B, C55B, C56B). The complex is surrounded by methanol molecules as solvent in the lattice.

The direct current (dc) magnetic susceptibility measurements on **1** were carried out by using a Quantum Design MPMS SQUID magnetometer on a 9.3 mg microcrystalline sample pressed in a pellet to avoid field induced orientation of the crystallites. The dc magnetic susceptibility data, i.e. M/H ratios (see Fig. 2 inset), were recorded in an applied field of 1 kOe between 1.8-45 K and 10 kOe between 45-300 K. The $\chi_M T$ product (see Fig. 2) values of 29.90 cm³ K mol⁻¹ at 300 K is in good agreement with the calculated value of 30.18 cm³ K mol⁻¹ for one spin-only Cr^{III} ion ($S = 3/2$, $g = 2$, $C = 1.875$ emu K mol⁻¹) and two Dy^{III} ions ($S = 5/2$, $L = 5$, ${}^6\text{H}_{15/2}$, $g = 4/3$, $C = 14.17$ emu K mol⁻¹). As the temperature is decreased, the $\chi_M T$ product sharply decreases until 7.5 K to reach a value of 21.37 emu K mol⁻¹, which may be ascribed to the presence of intramolecular interactions or to the progressive depopulation of the excited stated m_J of the Dy^{III} ions. Below 7 K, the $\chi_M T$ product increases again to reach the value of 23.22 emu K mol⁻¹ at 1.8 K. Such an increase suggests that the Dy magnetic moments tend to align parallel to each other. Both exchange and dipolar interactions are expected to contribute, given the short Dy-Dy distance. However, the sign of dipolar interaction depends on the orientation of the local magnetic moments in respect of the Dy-Dy vector, as a strong easy axis anisotropy is expected for Dy^{III} ion in low symmetry environment. In order to get insights on the ground state magnetic anisotropy directions of the Dy ions of compound **1**, preliminary investigations by electrostatic calculations using the Magellan software²⁰ were performed (see SI). As shown on Figure S17 the easy magnetization axis for the two Dy ions are roughly aligned along the Dy1-O9 bond and the Dy2-O10 bond with dpm ligands forming an angle of 29.6° between them. With the Dy1-Dy2 vector they form angles of 71.7° and 77.9° for Dy1 and Dy2, respectively. These results indicate that the dipolar interaction should align the Dy magnetic moments antiparallel to each other, suggesting that exchange interactions must be active though its nature cannot easily be assessed. In fact, also an antiferromagnetic interaction with the Cr spin would result in parallel alignment of the Dy magnetic moment.

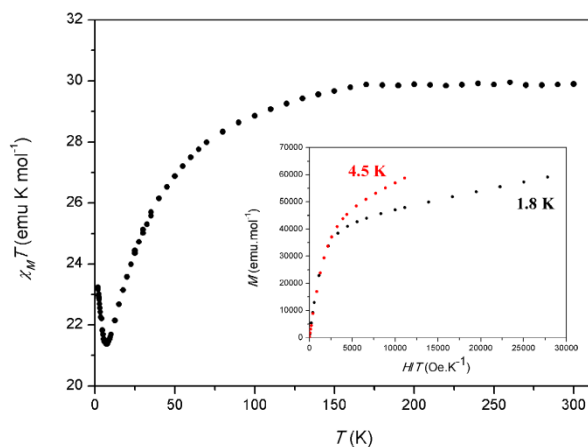


Fig. 2 Plot of $\chi_M T$ versus T for **1** measured under 1 kOe (1.8-45 K) and 10 kOe (45-300 K) dc fields. Inset: Magnetization vs reduced variable H/T , at 1.9 K (black points) and at 4.5 K (red points).

The field dependence of the magnetization M vs H plots performed at 1.8 and 4.5 k (see Fig. S6), show a fast increase of the M values up to 10 kOe to reach values of $7.64 \mu_B$ and $6.03 \mu_B$, respectively for $T = 1.8$ K and $T = 4.5$ K, followed by quasi linear increase up to 50 kOe, to reach values of $10.59 \mu_B$ (at 1.8 K) and $10.52 \mu_B$ (at 4.5 K). Furthermore, the non-superposition of the two M vs H/T curves as well as the lack of saturation even at high field confirm the presence of a significant magnetic anisotropy and suggest that single molecule magnet behaviour can be observed for complex **1**. This is reinforced by the presence of a 8-fold coordination in a distorted square anti-prism for the two Dy^{III} ions (see Fig. S2, SI) which is one of the favourable coordinate geometries adopted by a lanthanide ion in SMM complexes.²¹ In order to gain more insights into the dynamics of the magnetization, low temperature alternating current (ac) magnetic measurements were performed on **1** employing a home-made inductive probe adapted to an Oxford instruments Maglab2000 platform.²² Initially, the frequency and temperature dependences of the ac susceptibilities were measured under zero-dc field for the frequency range of 0.1-60 kHz (see Fig. 3 and S7-S8, SI). The shape and frequency dependence of the ac susceptibility signal indicate the SMM nature of **1**. At low temperatures, below 6 K, the presence of out-of-phase (χ_M'') ac signal indicating the occurrence of slow relaxation of the magnetization.

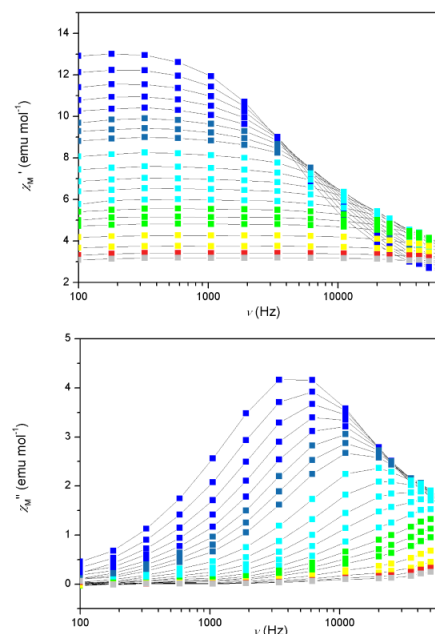


Fig. 3 Frequency dependence of the in-phase χ_M' (top) and the out-of-phase χ_M'' (bottom) signals, components of the molar ac susceptibility of **1** measured under zero dc field in the 0.1-60 kHz frequency range from 1.6 (blue) to 6 K (grey).

In order to obtain quantitative information concerning the mechanism of magnetic relaxation, the frequency dependence of χ_M' and χ_M'' at fixed temperatures was examined. The data were reproduced with an extended Debye model²³ to take into account also a possible dispersion of the relaxation time. The Argand plots were used to investigate the width of the relaxation time distribution and the extracted relaxation times are reported in Fig. 4. The best fit of the in-phase versus out of phase susceptibility in the range of 1.6-3.1 K was obtained with a values from 0.14-0.19 under zero dc-field (see Fig. S13 and S14, and Table S5, SI) indicating a relatively narrow relaxation time distribution.^{6d} Complex **1** displays a thermally activated regime but the temperature dependence strongly deviates from the linear behaviour expected by the Arrhenius law²⁴ $\tau = \tau_0 \exp(\Delta E/k_B T)$, where ΔE is energy gap between the ground and the excited state(s) involved in the Orbach relaxation mechanism and τ_0 the pre-exponential factor. While the highest temperature data can be reproduced with $\Delta E = 19.7 \pm 0.5$ K, and $\tau_0 = 8.4 \times 10^{-9}$ s ($R = 0.99892$), a satisfactory simulation of all data can be obtained by employing a simple formula where a temperature independent relaxation channel has been added to the Arrhenius relaxation rate:

$$\tau^{-1} = \Gamma_{QT} + \tau_0^{-1} + \exp\left(-\frac{\Delta E}{k_B T}\right)$$

The best fit parameters are $\Delta E = 13.7 \pm 0.7$ K, and $\tau_0 = 4.5 \pm 1 \times 10^{-8}$ s and $\Gamma_{QT} = 2.9 \pm 0.3 \times 10^4$ s⁻¹. The analysis was repeated in the presence of a static field of 800 Oe (see Figs. S9 to S12, S15 and Table S6 SI). Also in this case a narrow distribution of relaxation time with a values in the range 0.17-0.27, was observed (see Table S5, SI). The fitting of the extracted times (solid dots in Figure 4) using the two channels model provided $\Delta E = 13.4 \pm 0.5$ K, and $\tau_0 = 5.0 \pm 1 \times 10^{-8}$ s and $\Gamma_{QT} = 9.9 \pm 1 \times 10^3$ s⁻¹.

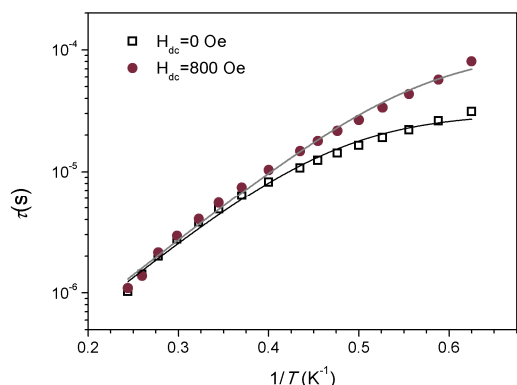


Fig. 4 Arrhenius plot for **1** under zero dc field (open squares) and under an applied field (solid circles) with the best fit curves (black and grey lines, respectively) obtained adding to the Orbach process a temperature independent contribution to the relaxation.

The energy barrier extracted from the data under an applied field is relatively similar to the one in zero dc field, though the efficiency of the underbarrier process leading to the observed decrease of slope at low temperature is slightly reduced. Such a moderate effect of an external magnetic field can be rationalized with the presence of a weak exchange interaction between the Dy ions as suggested by the low temperature increase of χT . Exchange magnetic interactions have already been suggested to significantly reduce the efficiency of tunnelling in zero field of 4f ions,^{14a, 25} though this is not valid when the anisotropy axes of the 4f ions are strongly non-collinear to each other.²⁶

In conclusion, we obtained a new trinuclear $\{\text{Cr}^{\text{III}}\text{Dy}^{\text{III}}\}_2$ methoxy-bridged complex. The crystal structure study reveals that the two dysprosium ions display a distorted square-anti-prismatic geometry, which has been demonstrated as favourable coordination geometry for lanthanide ions to exhibit single molecule magnet behaviour in zero static field. Full magnetic studies revealed and confirmed that complex **1** exhibits single molecule magnet behaviour which was not always observed for all of the reported chromium-lanthanide complexes. The current compound joins the very small family of existing chromium-lanthanide molecule-based magnets and makes this report really promising. Despite the highlight of a new member of the relatively confidential Cr-Ln complex family with oxo-bridging ligands and with SMM behaviour, further investigations concerning the evaporability and the synthesis are necessary and will be carried out in order to understand and control the different steps of the reaction. Additional efforts will be devoted to the synthesis of the complete "star shaped" $\{\text{CrLn}_3\}$ complex as the present results indicate that the combination of Cr^{III} and Dy^{III} ions can lead to SMM behaviour in zero static field.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, selected bond lengths, angles and further magnetic data.

‡ **Crystal data.** $\text{C}_{61}\text{H}_{115}\text{O}_{16}\text{Cr}_1\text{Dy}_2$, $M = 1480.52 \text{ g.mol}^{-1}$, triclinic, $a = 10.849(5)$, $b = 14.788(5)$, $c = 24.988(5) \text{ \AA}$, $\alpha = 102.980(5)$, $\beta = 94.757(5)$, $\gamma = 109.062(5)^\circ$, $V = 3639(2) \text{ \AA}^3$, $T = 293 \text{ K}$, space group $P-1$, $Z = 2$, $\rho_{\text{calcd}} = 1.351 \text{ g.cm}^{-3}$. $F(000) = 1528$; 28156 data measured, 11696 unique ($R_{\text{int}} = 0.0808$); $R_1 = 0.0518$ and $wR_2 = 0.1094$ ($[I > 2\sigma(I)]$); $R_1 = 0.1032$ and $wR_2 = 0.1196$ (all data, 783 parameters, 255 restraints). CCDC-1408766.

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