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A fluoride bridged {Cr^{III}₄Dy^{III}₄} single molecule magnet

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Graphical abstract

Fluoride bridging between Dy..Dy neighbours in an octanuclear {Cr^{III}₄Dy^{III}₄} cluster of the 'square-in-square' structural type is the key reason for enhanced single molecule magnetic properties of Cr-Dy SMMs and, particularly, when compared to a reported azido bridged {Cr^{III}₄Dy^{III}₄} structural analogue.

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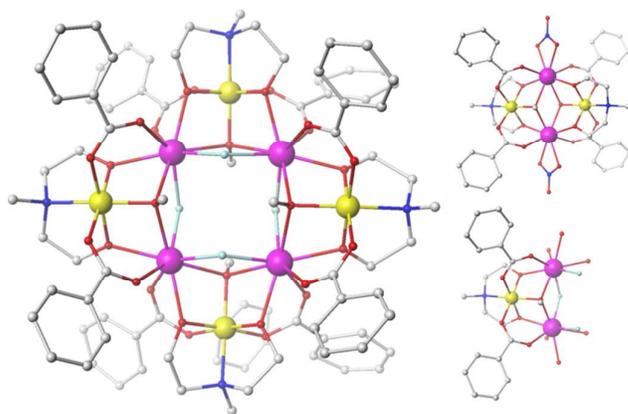
COMMUNICATION

A fluoride bridged {Cr^III_4Dy^III_4} single molecule magnet

Stuart K. Langley,[a] Craig M. Forsyth,[a] Boujemaa Moubaraki[a] and Keith S. Murray[*,a]

The synthesis of a heterometallic octanuclear {Cr^III_4Dy^III_4} complex containing fluoride bridges displays SMM behaviour, with highly coercive magnetic hysteresis loops. Intriguingly multiple relaxation processes are revealed and the relaxation times are found to be longer compared to those of an analogous complex with the same metallic core topology.

Chromium-based single-molecule magnets (SMMs) are rare due to the isotropic nature of the Cr^III ion. It has recently been shown, however, that the synthesis of polynuclear Cr^III-Ln^III type compounds, combining anisotropic Ln^III with isotropic Cr^III ions can result in SMM behaviour with large anisotropy barriers and relatively high blocking temperatures.[1] The earliest report of a Cr-4f SMM was a {Cr^III_4Dy^III_4} complex reported by Powell and co-workers.[2] Following this work two complexes of metallic core type; {Cr^III_2Dy^III_4} and {Cr^III_2Dy^III_2} were subsequently reported, these again exhibiting slow magnetic relaxation.[3,4] From our own work we have developed two separate {Cr^III_2Dy^III_2} SMM families, each of which display highly coercive magnetic hysteresis, the key feature being the strong exchange interactions between the Cr^III and Dy^III ions.[1] It was shown, via a direct comparison of these two families, that the height of the anisotropy barrier was directly related to the magnitude of the exchange between the Cr^III and Dy^III ions, an important consideration in the design of new SMMs.[1b] Further to the use of Cr^III ions, we have recently become interested in the use of electron withdrawing groups (EWGs) on ligands in the synthesis of lanthanide containing SMM complexes. These reasons stem from recent experimental evidence which reveal the modification and enhancement of the anisotropy barrier and blocking temperature in dinuclear Dy^III SMM complexes when using terminal ligands with

varying EWGs.[5] Shi and co-workers recently reported that the replacement of hydroxide bridging groups in dinuclear Dy^III motifs for the more electronegative fluoride resulted in the slow magnetic relaxation being "turned on" in the corresponding Dy-F-Dy complex.[6] Influential work by Winpenny and Bendix and coworkers has shown it possible to isolate Cr-4f complexes with fluoride bridges.[4,7] We have therefore attempted to insert fluoride bridges into one of our {Cr^III_2Dy^III_2} families, which contain μ_3 bridging ligands that can be targeted for replacement, in order to study the effect this may have on the magnetic relaxation.[1a] Herein we present our initial results, reporting the synthesis of a new heterometallic Cr^III-Dy^III SMM complex in which we successfully incorporate bridging fluoride ions into a Cr^III-Dy^III complex. The product, however, unexpectedly revealed an octanuclear {Cr^III_4Dy^III_4} core, which is structurally related to the targeted tetranuclear {Cr^III_2Dy^III_2} molecule.

The reaction of CrCl_3·6H_2O, Dy(NO_3)_3·6H_2O, benzoic acid, mdeaH_2 (*N*-methyldiethanolamine), NaF and NEt_3 in MeCN yielded red plate crystals upon crystallization from MeOH (See ESI for full experimental details). The solid state structure was determined by X-ray crystallography (Table S1) and revealed the formation of a heterometallic octanuclear complex of formula [Cr^III_4Dy^III_4F_4(OMe)_{1.12}(OH)_{2.88}(O_2CPh)_8(mdea)_4] (**1**) (Figure 1).
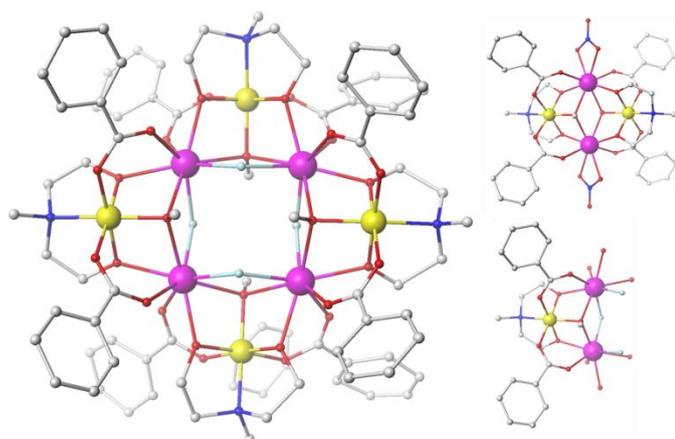
Figure 1. (left) The molecular structure of complex **1**; (right) Comparison of the triangular {Dy₂Cr} core (bottom) to related to the {Cr₂Dy₂} SMM (top). The solvent, H- and disordered-atoms are omitted for clarity. Colour scheme; Cr^{III}, yellow; Dy^{III}, purple; O, red; F, cyan; N, blue; C, light grey.

The asymmetric unit contains two halves of two molecules, with mirror symmetry generating the complete structure. The complex consists of four Cr^{III} and four Dy^{III} ions, with an inner Dy$^{III}_4$ square (av Dy…Dy distance of 3.88 Å) surrounded by a larger outer Cr$^{III}_4$ square (av Cr…Cr distance of 6.62 Å). The four Dy^{III} ions are bridged by four μ atoms and four μ₃ bridging groups, the μ₃ ligands also bridge to a single Cr^{III} ion. The μ atoms are assigned as fluoride. It is found from the X-ray data that the μ₃ atoms are disordered throughout the crystal, assigned as OMe and OH and modelled at a ratio of 0.28 (OMe): 0.72 (OH). It is conceivable that μ₃ F bridges could also be present in these positions. Evidence for fluoride is provided by elemental analysis and close inspection of the crystallographic data. The micro-analysis supports the presence of ~4.3 F$^-$ ions and thus the possibility of partially occupied μ₃ F$^-$ bridges also being found at the disordered sites. Due to the difficulty in assigning F vs O from the crystallographic data alone, the μ₃ bridges, however, are regarded as OH and OMe only. Similarly to the work by Shi and co-workers on homometallic Dy^{III} complexes,[6] this work reveals that NaF can be used to incorporate fluoride ions into Cr-4f coordination complexes.

The metallic core and surrounding ligands can be broken down into four fused {Dy₂Cr} triangular units. This motif and the bridging arrangement of benzoate, μ₃ O-atoms and mdea²⁻ ligands are identical to one half of a previously reported {Cr₂Dy₂} SMM complex (Figure 1, right), which was the targeted structural motif at the outset.[1] The metal topology found for **1** has been observed previously for the {Cr$^{III}_4$Dy$^{III}_4$} complex (**2**) mentioned earlier as the first Cr-Dy SMM.[2] A point of structural difference for **1**, compared to **2**, is the use of benzoic acid over pivalic acid and the replacement of the μ azide for μ fluoride ligands. It is clear that the presence of the fluoride ion is the key constituent towards isolating **1**, as the reaction in the absence of NaF results consistently in isolation of the {Cr$^{III}_2$Dy$^{III}_2$} butterfly complex. The four Dy^{III} ions are eight coordinate with distorted square antiprismatic geometries, with an average Dy-L$_{O,F}$ bond distance of 2.35 Å. The four Cr^{III}

ions are six coordinate with octahedral geometries, with an average Cr-L$_{O,N}$ bond distance of 1.99 Å. See Table S2 for selected bond length parameters.
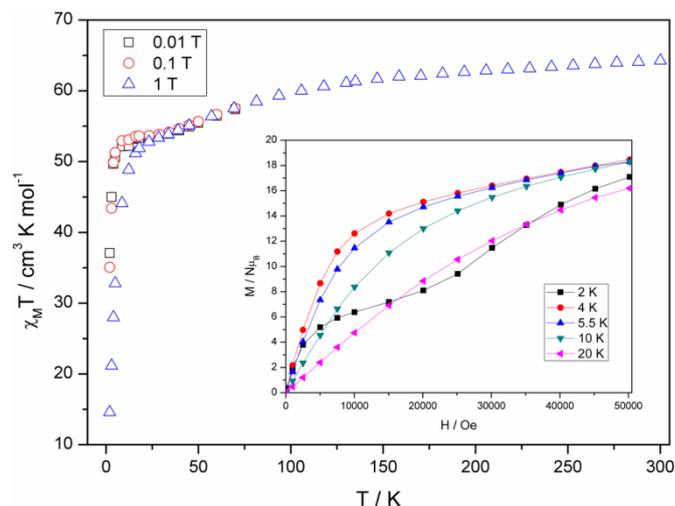

Figure 2. Plot of $\chi_M T$ versus *T* for **1** measured under 1 T (2 – 300 K), 0.1 T and 0.01 T (2 – 70 K) dc fields. Inset: Plot of isothermal magnetization versus temperature for **1**.

Direct current (dc) magnetic susceptibility measurements were performed on a polycrystalline sample of **1** in the temperature range 2 – 300 K, in applied fields of 0.01, 0.1 and 1 T. The $\chi_M T$ (χ_M = molar magnetic susceptibility) *versus T* plot for **1**, is shown in Figure 2. The room temperature $\chi_M T$ product for **1** of 64.26 cm³ K mol⁻¹ is in good agreement with the value expected for four Cr^{III} ($S = 3/2$, $g = 2$, $C = 1.875$ cm³ K mol⁻¹) and four Dy^{III} ($^6H_{15/2}$, $g = 4/3$, $C = 14.17$ cm³ K mol⁻¹) non-interacting ions, of 64.18 cm³ K mol⁻¹. As the temperature is reduced the $\chi_M T$ product decreases gradually, until 50 K where it plateaus, followed by a rapid drop below 10 K. The high temperature decrease can be attributed to the depopulation of the excited m_J states of the Dy^{III} ions, while the plateau at lower temperatures suggests non-negligible exchange interactions between the Dy^{III} and Cr^{III} ions and possibly between the Dy^{III} and Dy^{III} ions. This is not surprising considering the Cr^{III}-Dy^{III} interactions in the {Cr₂Dy₂} butterfly complex, containing the same superexchange pathways yielded values of -17 - -20 cm⁻¹, and showed a similar plateau in $\chi_M T$.[1a] The rapid decrease in $\chi_M T$ below 10 K is, as in the {Cr₂Dy₂} complex,[1a] probably indicative of magnetic blocking with field cooled (100 and 1000 Oe)/zero field cooled magnetisation studies not showing the clear bifurcation exhibited by the tetranuclear analogue.[1a]

The isothermal magnetization versus field plots (Figure 2, inset) revealed an S-shaped profile at 2 K, indicating, as in the {Cr₂Dy₂} complex,[1a] possible slow magnetic relaxation and hysteresis, while, above 4 K, the plots display a rapid increase in magnetization below 2 T, before following a more gradual linear increase, without saturating.

Due to the structural similarities a comparison of the magnetic data to the previously reported {Cr$^{III}_4$Dy$^{III}_4$}-mdea/pivalate

complex (**2**) will be made.[2] A notable difference is the absence of a plateau below 25 K for **2**, indicating stronger exchange interactions in **1**. It has been shown that strong exchange is desirable for observing SMM behaviour with a large thermal barrier to magnetization reversal and with the absence of quantum tunnelling of the magnetization (QTM).

As the magnetization data strongly suggest that compound **1** displays slow magnetic relaxation, variable temperature and frequency alternating current (ac) experiments were performed to probe the dynamics of the relaxation. Compound **1** was subjected to an ac magnetic field of 3.5 Oe oscillating at
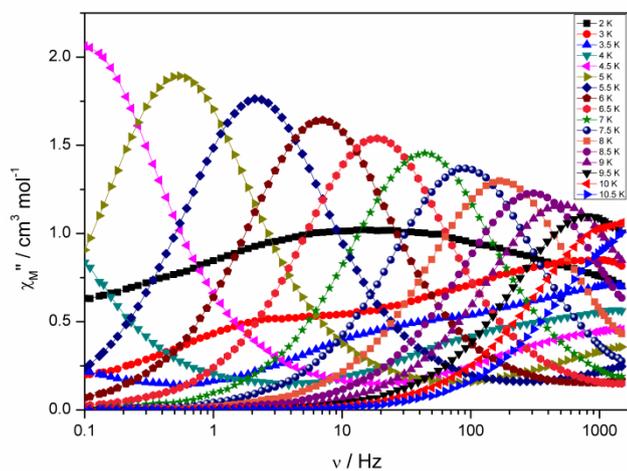

Figure 3. Frequency dependence of χ_M'' for **1** in a zero applied dc field, with an ac field of 3.5 Oe.

frequencies ranging from 0.1 – 1500 Hz at temperatures between 1.8 – 10.5 K. The presence of frequency dependent signals of both the in-phase (χ_M') (Figure S1) and out-of-phase (χ_M'') (Figure 3) susceptibility components confirm the presence of SMM behaviour. The relaxation times (τ) can be determined from the $\chi_M''_{max}$ values from the isothermal χ_M'' versus frequency plots ($\tau = (2\pi\nu)^{-1}$). Interestingly, we see that multiple relaxation processes are observed. The first and most prominent process reveals $\chi_M''_{max}$ values which are temperature dependent between 4.5 and 10 K over the entire frequency range. This indicates that the relaxation does not cross-over to a pure quantum tunnelling regime at temperatures above 4.5 K. At all temperatures it is found that the relaxation is thermally activated and plots of $\ln(\tau)$ versus $1/T$ are linear (Figure S2). Fitting the data to the Arrhenius law [$\tau = \tau_o exp(U_{eff}/k_B T)$] yields a significant effective barrier to magnetization reversal of $U_{eff} = 55$ cm^{-1} with $\tau_o = 6.1 \times 10^{-8}$ s (R = 0.99). A second increase in χ_M'' can be observed up to 5.5 K at higher frequencies indicative of a second faster relaxation process (Figure S3). Following this profile at temperatures lower than 5.5 K the relaxation time for this second process slows down as expected, shifting the signals to lower frequency, and also revealing behaviour indicative of a third relaxation process. This is clearly observed at 3 K via a plateau and a maximum in χ_M''. Not enough data are available to be able to derive thermal energy barriers and relaxation times of these two faster processes. The Cole-Cole plots of χ_M' *versus* χ_M'' corroborate this analysis. At temperatures between 4.5 and

10 K (Figure S4) the data clearly reveal semicircular profiles indicating a single relaxation process, however at high frequencies a second process becomes observable at temperatures up to 5.5 K. Plotting the Cole-Cole data at temperatures between 2 – 5.5 K (Figure S5) the second and third processes are observable, best seen at 3.5 K.

The appearance of multiple processes in 3d-4f systems has been observed for example in a {Co$^{II}_2$Dy$^{III}_2$} complex which reveals that both a regime associated with relaxation through excited Kramers doublets of individual metal ions, and an exchange-blocked relaxation regime derived from the cooperative coupling of the 3d and 4f ions.[8] This conclusion was derived from *ab initio* calculations; it has already been shown via *ab initio* calculations of the {Cr$_2$Dy$_2$} complex that the {Dy$_2$Cr} unit in **1** is likely to display strong magnetic exchange, evidence of which is provided from the dc magnetic data, which can allow for an exchange coupled relaxation regime. The large disorder found for the μ_3 bridging groups throughout the crystal may account for the variable relaxation processes. i.e. different bridging ligands can relate differing exchange strengths and thus anisotropy barriers.[1c] In-depth *ab initio* calculations (if possible) would need to be performed in an attempt to understand the different relaxation processes in **1**.

Comparing the ac data of compound **1** with the analogous complex **2**, we also find a striking difference in behaviour. Maxima in χ_M'' versus frequency plots are observed for **2**, only between 1.8 - 2.2 K, with an energy barrier of 10 cm^{-1}. A potential reason for the disparity points to the presence of the bridging fluoride ions, which is the key difference between the two complexes. It has been shown recently that electronegative groups associated with terminal or bridging ligands can have a profound effect on the anisotropy barrier and hence the relaxation time.[5,6] Compound **1** therefore provides further evidence of the importance of bridging F$^-$ atoms in SMM synthesis and properties.
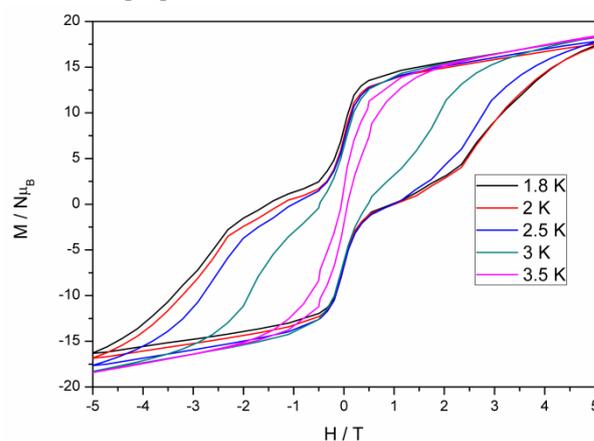

Figure 4. Plot of magnetization (*M*) *versus* field (*H*) for **1**, sweeping the field with an average sweep rate of 0.003 T/s, at the temperatures indicated.

Even with the presence of multiple relaxation mechanisms, the large thermal barrier and lack of observable QTM implies long

relaxation times for the slow process. We therefore performed variable-field magnetization measurements to probe the relaxation time on a longer time-scale, and the presence of magnetic hysteresis. It was found that using sweep rates accessible with a conventional magnetometer, which on average was 0.003 T/s, we were able to observe open magnetic hysteresis loops at temperatures up to 3.5 K (Figure 5). The coercive field is maximum at 1.8 K, of value $H_c \approx 1.5$ T, steadily decreasing as the temperature is raised. There is a prominent loss of the magnetization at $H = 0$, indicating that QTM, which was not apparent on the much faster time scale of the dynamic ac experiment, is indeed active.

Significantly, compound **1** unambiguously joins the small number of Cr^{III}-Ln^{III} based SMMs displaying magnetic hysteresis with large coercive fields, emphasising the great potential towards the use of Cr^{III} ions in SMM synthesis. Extrapolation to lower temperature of the Arrhenius plot (see above) deduced from experimental data showed that compound **1** displays a true blocking temperature (relaxation of 100 s) of 3.8 K which is greater than that of complex **2** (~1 K). Furthermore, **1** displays properties on par with the best performing 3d-4f SMMs.[1a,8,9]

In conclusion, we have synthesised a novel octanuclear heterometallic {Cr_4Dy_4} complex containing fluoride bridges. The complex reveals a metallic core that describes a 'square-in-square' motif, similar to a previously reported {$Cr^{III}_4Dy^{III}_4$} (**2**) complex.[2] We have presented preliminary magnetic data and have shown that complex **1** is a rare lanthanide-based SMM which displays magnetic hysteresis with a wide coercive field. This is therefore one of the best examples of any 3d-4f SMM reported. These results emphasize that the Cr^{III} ion is a much underused ion in SMM synthesis, providing further evidence the ion should be explored to greater extent particularly because of the strong magnetic exchange it engenders in clusters. The intriguing evidence of multiple relaxation processes in **1**, which, as indicated above, could result from disorder in the OH/OMe bridges, combined with the F bridges, and the reasons for the large difference in relaxation time(s) compared to **2** is currently being investigated and the results will be reported in due course.

Notes and references

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