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A Rare μ_4-O Centred Dy_4 Tetrahedron with Coordination-Induced Local Chirality and Single-Molecule Magnet Behaviour

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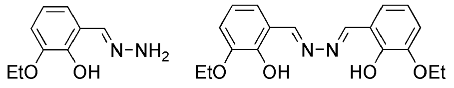
Coordination-induced chirality was achieved in a unique tetrahedral $[Dy_4(\mu_4\text{-}O)(\mu\text{-}OMe)_2(beh)_2(esh)_4]\cdot 3MeOH$ complex through a twisted diazine bridge from a Schiff base ligand. Magnetic measurements reveal weak intramolecular antiferromagnetic interactions (J = –0.3 cm^{-1}) with single-molecule magnet behaviour (U_{eff} = 23.42 K).

Introduction

Combining two or more physical properties in the same material is a difficult and exciting challenge in the field of multifunctional materials. In such systems, amalgamation of optical and magnetic properties are sought after because of their potential application in molecular electronics.[1] Recently, Train et al. were able to design and isolate a chiral oxalate based 2D ferromagnet, which exhibits large magnetochiral dichroism.[2] Similarly, the few examples of chiral coordination polymers that have been reported with magnetlike behaviour result from long-range magnetic ordering.[3] Chirality can be induced in a molecular system such as single-molecule magnets (SMMs) by using auxiliary ligands with a chiral centre.[4] However, generating coordination-induced molecular chirality through assembly of achiral components can be challenging.[5] SMMs are nanoscale magnetic particles, which exhibit slow relaxation of the magnetization, act as magnets below their blocking temperatures.[6] This superparamagnet-like behaviour generally results from the presence of a large spin ground state (S_T) and Ising-type magnetoanisotropy (D).[7] In lanthanide systems, the large intrinsic magnetic anisotropy caused by spin-orbit coupling is the main contributor to the slow relaxation of the magnetization.[8] In multinuclear SMMs, several linear,[9] cubane[10] and planar[11] tetranuclear Dy^{III} complexes have been reported, but no tetrahedral geometry was observed yet. Paramagnetic tetrahedral core complexes are appealing as they are one of the rare structural topologies that can exhibit phenomena such as spin-frustration.[12] Therefore, isolating SMMs with unique structural topologies where the interplay between the structure and magnetism is an exciting challenge. With this in mind, we have designed a lanthanide-based chiral system, where the chirality of the molecular unit is induced by the coordination of the twisted diazine bridge from our Schiff base ligands (Scheme 1). Such coordination-induced chirality is of interest in the field of chiral magnets.



Scheme 1. Left: 3-ethoxysalicylaldehyde hydrazone (Hesh); right: bis(2-hydroxy-3-ethoxybenzylidene) hydrazone (H_2beh).

Finally, in such chiral tetrahedral systems it is important to investigate the alignment of anisotropic axes not only to improve and understand the structure–property relationship such as chiral/magnetic effects but also to determine their effect on magnetic relaxation dynamics and possible frustration effects. Herein, we report the synthesis, structure and magnetic properties of the first tetrahedral Dy_4 complex, $[Dy_4(\mu_4\text{-}O)(\mu\text{-}OMe)_2(beh)_2(esh)_4]\cdot 3MeOH$, **1**·3MeOH, with coordination-induced chirality and SMM properties.

Results and Discussion

Complex **1** crystallizes in the monoclinic space group $P2_1/n$ and can be described as a tetrahedral core-shaped molecule (Figure 1, top). It consists of four Dy^{III} ions arranged in a distorted tetrahedral fashion around the central μ_4-O atom (O19) with a Dy–O19 distance of 2.9 Å. Four of the edges are formed by two methoxide (O17, O18) and two

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diazine (N1N2, N11N12) bridges, while the remaining two edges are formed by four doubly bridged phenoxide oxygen atoms (O5, O7, O9 and O11). Within the core, the intramolecular Dy···Dy distances are in the range of 3.49–4.14 Å. The coordination environments of the octacoordinate Dy^{III} ions are filled by two nitrogen donor atoms from the diazine group of the ligand and by oxygen atoms from a combination of oxide, methoxide and phenoxide groups. Upon coordination, the fully formed beh^{2-} ligand is locked in a conformation, thus preventing the free rotation about the N–N bridge. Therefore, conformational chirality is induced. The two stereoisomers exist as a racemic mixture of enantiomers with O19 as a chiral centre (Figure 1, bottom). A close inspection of the packing arrangement reveals that two different Dy$_4$ enantiopure molecules are in different layers along the crystallographic *a* and *c* axes (Figures 2 and S1), with the shortest Dy···Dy distance of 10.07 Å between adjacent molecules. A reverse arrangement of the molecules is shown between two layers of the same enantiomers.

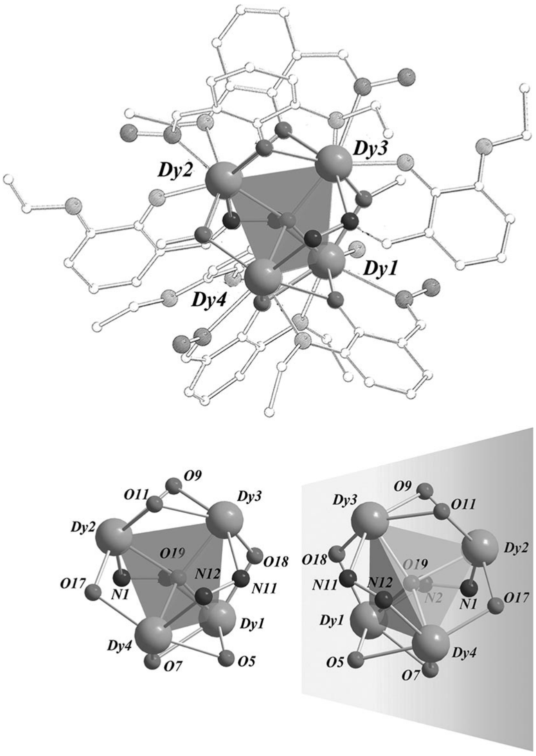

Figure 1. Top: Molecular structure of [Dy$_4$(μ$_4$-O)(μ-OMe)$_2$(beh)$_2$(esh)$_4$] (**1**). Bottom: Fully labelled tetrahedral core emphasizing different bridging modes between Dy^{III} ions of two isomers.

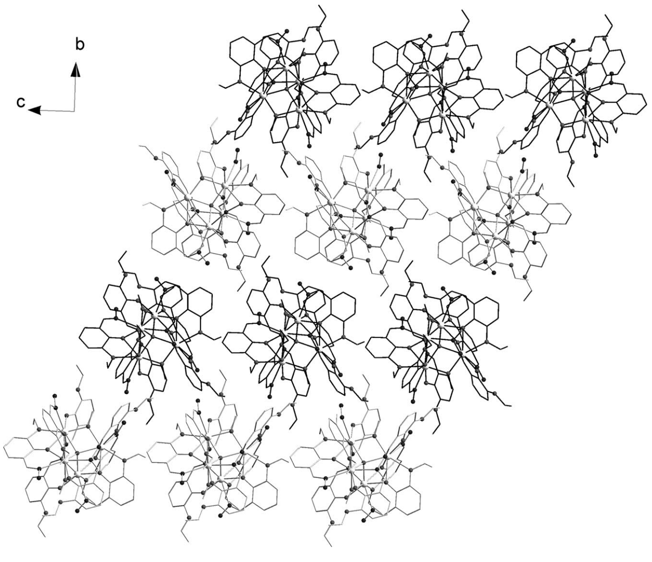

Figure 2. Crystal packing diagram of **1** along the crystallographic *a* axis showing the different stereoisomers (black and grey).

It is noteworthy that similar μ$_4$-O centred tetrahedral cores are common in transition-metal chemistry;[13] however, it is relatively rare in lanthanide chemistry. The handful of reported tetrahedral lanthanide molecules belong to the family of organometallic complexes, whereas no coordination complexes have been reported.[14] This is mainly due to the presence of small ligands in organometallic complexes, which facilitate the formation of cluster complexes without significant coordination strain. On the other hand, the encapsulation of ligands generally employed in coordination chemistry induces ligand strain, which thus leads to smaller complexes. Complex **1** represents the first example of a tetrahedral Dy$_4$ complex reported to date.

Synthetically speaking, complex **1** can only be synthesized by in situ condensation reaction of 3-ethoxysalicylaldehyde and hydrazine in a 1:2 ratio. Because of the presence of excess hydrazine, two fully formed beh^{2-} and four partially formed esh^{-} ligands participate in the formation of this tetranuclear complex. When a fully formed beh^{2-} ligand was employed prior to the complexation reaction, no crystals were isolated. The use of Et$_3$N in the reaction mixture is critical for the formation of this large complex. The Et$_3$N base helps deprotonate the H$_2$beh and Hesh chelates as well as promotes the formation of the μ$_4$-O and μ-OMe bridges from the H$_2$O/MeOH molecules introduced by the hydrated DyCl$_3$ and the employed solvent.

The dc magnetic susceptibility of **1** was carried out on a freshly prepared sample at 0.1 T between 2 and 300 K, plotted as $\chi_M T$ vs. T (Figure S2). The observed paramagnetism arises from the 4f orbitals of the Dy^{III} ion ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $J = 15/2$, $g = 4/3$, $C = 14.17$ cm^3 K mol^{-1}). The room temperature $\chi_M T$ value of 54.54 cm^3 K mol^{-1}is close to the expected value of 56.68 cm^3 K mol^{-1} for four noninteracting Dy^{III} ions. As the temperature decreases, the $\chi_M T$ product of **1** remains constant down to 70 K. A negative deviation is clearly observed below 70 K, which suggests the presence of some intramolecular antiferromagnetic interactions between the Dy^{III} ions. However, it should be noted that the thermal depopulation of Stark sublevels, crystal field effect and strong spin-orbit coupling can also be partially or totally responsible for the rapid decrease in the $\chi_M T$ product. It is therefore difficult to establish, in a definitive manner, the nature of the intracomplex magnetic interactions by using SQUID measurements only. At lower temperatures, the $\chi_M T$ product further decreases to 12.26 cm^3 K mol^{-1}at 1.8 K for **1**.

The field dependence of the magnetization below 8 K (Figures S3 and S4) does not exhibit any saturation even at 7 T for **1**. The latter behaviour is mainly due to the presence of weak intramolecular magnetic interactions between the Dy^{III} ions that make the low-lying excited states accessible, even at 1.8 K, by applying a magnetic field. The presence of magnetic anisotropy of the Dy^{III} ion is also an important contributor to this lack of magnetization saturation. Although any hysteresis effects have not been observed in the M vs. H data above 1.8 K for these complexes, ac susceptibility measurements were performed to probe possible SMM properties (Figures 3 and S5).

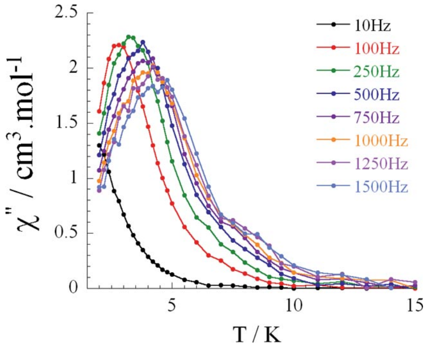

Figure 3. Frequency dependence of the out-of-phase ac susceptibility between 10 and 1500 Hz at H_{dc} = 0 T.

A frequency dependent ac signal was observed below 15 K, which indicates slow relaxation of the magnetization of **1**, as expected for an SMM. Although a full frequency dependent peak was not observed, the maxima can be observed for a wide range of frequencies between 7 and 1.8 K. This range of data is sufficient to extract an energy barrier for **1**. The relaxation time deduced from this data is consistent with an activated behaviour (Figure S6), with an energy gap of 23.42 K and a pre-exponential factor, τ_0, of 8.2×10^{-8} s. The latter value is consistent with the expected range ($\tau_0 = 10^{-6}$ to 10^{-11} s) for an SMM.

In order to investigate the low-temperature behaviour, single-crystal dc magnetization measurements of **1** were carried out on a micro-SQUID[15] magnetometer between 0.04 and 5 K (Figures 4, S7, S8). Temperature-dependant hysteresis loops with steps were observed with a large coercive field opening at very low temperatures (H_c = 0.6 T at 0.04 K). The step at 0.5 T indicates the presence of resonant quantum tunnelling of the magnetization (QTM) and/or reversal of the magnetization of individual Dy^{III} ions. The absence of a step at H = 0 simply indicates that the QTM is less efficient at zero field. This shift of step position is most likely affected by the weak exchange coupling present within the Dy^{III} ions. This type of behaviour is typical for lanthanide-based SMMs.[1b]

In pure lanthanide systems, the slow relaxation of the magnetization originates mainly from the local anisotropy of the 4f ions. Therefore, it is crucial to determine the direction of the local anisotropy axis on each Dy^{III} site. The ab initio[16,17] calculated directions of the anisotropy axes for the four Dy sites are shown in Figure 5. The four anisotropic axes in **1** point in all different directions, which correlate with four crystallographically nonequivalent Dy^{III} ions. The calculated g tensors on the Dy^{III} sites are strongly anisotropic (Table 1), although less axial than in the previously investigated dysprosium complexes.[6i,11d] Furthermore, by means of simulations a good agreement was obtained for the experimental dc susceptibility data (Figure S9). The exchange coupling between magnetic ions was considered within the Lines approximation.[18] For the simplicity of the model, we used a single exchange parameter to simulate all exchange interactions in the Dy_4 system. The Lines parameter J of the exchange interaction between the Dy^{III} ions was found to be $J_{ex} = -0.30$ cm^{-1}.[19] The latter simulation confirms the overall antiferromagnetic exchange coupling present between the Dy^{III} ions, which can be correlated with the observed step in the hysteresis loop that occurs at 0.6 T. The spread of the calculated exchange spectrum between the lowest Kramer's doublets on the Dy sites (Table S1) is of the order of the obtained activation energy.

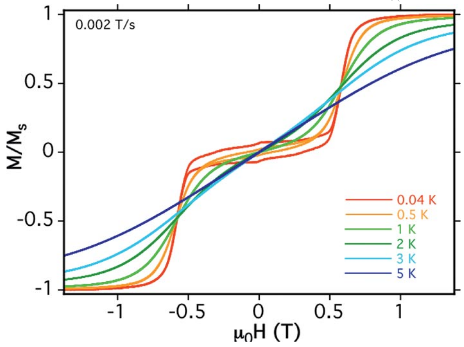

Figure 4. Magnetization (M) vs. applied dc field sweeps at the indicated sweep rate and temperatures for **1**.

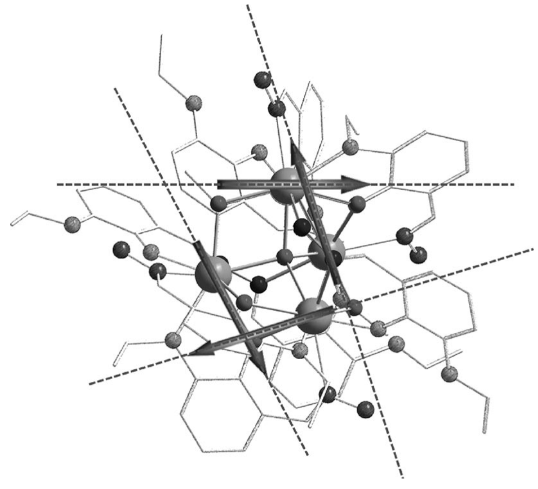

Figure 5. Calculated magnetic axes corresponding to the lowest Kramer's doublet (dotted lines) and the orientation of the local magnetic moment in the ground state (arrow) in **1**.

Table 1. Main values of the g tensor for the lowest two Kramer's doublets.

Kramer's doublet		Main value of g tensors Dy1	Dy2	Dy3	Dy4
1	g_x	0.1514	0.3235	0.1090	0.0766
	g_y	0.4139	1.0767	0.2927	0.1558
	g_z	18.4125	18.1889	18.5495	19.4623

Conclusions

In summary, we designed and successfully synthesized the first coordination-induced chiral lanthanide SMM. The latter complex adopts a rare tetrahedral geometry, where a μ_4-O atom lies in the centre of the tetrahedral hole created by the four Dy^{III} ions. The slow relaxation of the magnetization found in complex **1** confirms the SMM nature of the isolated system. To facilitate such studies, we are currently exploring the possibilities of isolating enantiopure complexes. Finally, the presented results demonstrate the viability of our synthetic methodology in isolating coordination-induced chirality with SMM behaviour by using specifically designed ligands and appropriate metal centres.

Experimental Section

To a solution of 3-ethoxysalicylaldehyde (0.25 mmol, 41.4 mg) in MeOH (30 mL) was added $DyCl_3{\cdot}6H_2O$ (0.125 mmol, 47.1 mg), Et_3N (0.5 mmol, 76 μL) and then $N_2H_4{\cdot}H_2O$ (0.5 mmol, 26 μL) while stirring. The resulting clear yellow solution was stirred for 30 s and then filtered. After 2–3 weeks, yellow needle-shaped crystals of $[Dy_4(\mu_4\text{-}O)(\mu\text{-}OMe)_2(beh)_2(esh)_4]{\cdot}3MeOH$ (**1**·3MeOH) were isolated. Yield ≈ 19.1%. IR (KBr): 3431 (br.), 3234 (w), 1610 (s), 1543 (m), 1460 (s), 1383 (w), 1321 (m), 1217 (s), 1109 (m), 1067 (m), 1015 (w), 886 (w), 850 (w), 778 (w), 731 (s) cm^{-1}.

Crystallographic Information for 1·3MeOH: $C_{77}H_{98}Dy_4N_{12}O_{22}$, $M = 2193.67$, monoclinic, space group $P2_1/n$, $a = 13.1654(14)$, $b = 46.467(5)$, $c = 14.0254(15)$ Å, $\beta = 109.157(2)°$, $V = 8105.5(15)$ Å^3, $T = 200$ K, $Z = 4$, 36464 reflections measured, 7332 unique ($R_{int} = 0.1208$), which were used in all calculations, $R_1 = 0.0761$, $wR_2 = 0.2218$. CCDC-800957 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): X-ray crystallography, magnetic properties and computational details are included.

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[19] The corresponding parameters of the Ising exchange interaction between the effective spins $\tilde{S} = 1/2$ of the lowest Kramer's doublets of the Dy^{III} sites i and j are calculated as $\tilde{J}_{i,j} = 25\cos\phi_{i,j}J$, where $\phi_{i,j}$ is the angle between their anisotropy axes (Figure 5) (see ref.[6i]). Note, however, that the exchange interaction is not of pure Ising-type in the present case because of the non-perfect axiality of the lowest Kramer's doublets on the Dy^{III} sites, which contain non-negligible transverse components of the g tensors (Table 1).

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