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Relaxations in heterolanthanide dinuclear single-molecule magnets†

Cite this: Chem. Commun., 2013, 49, 158

Received 28th September 2012,
Accepted 8th November 2012

DOI: 10.1039/c2cc37036k

www.rsc.org/chemcomm

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A heterospin dinuclear complex [$Dy_{0.87}Yb_{1.13}(H_2cht)_2Cl_4(H_2O)(MeCN)]\cdot MeCN$ shows shifts of the relaxation barriers with respect to the barriers observed in homospin Dy_2 and Yb_2 isostructural complexes. The origin of slow relaxation in the latter two compounds was elucidated by *ab initio* calculations.

Since their discovery twenty years ago, the fact that individual molecules known as single-molecule magnets (SMMs) can exhibit slow relaxation of magnetization and magnetic hysteresis, has attracted increasing attention in the field of molecular magnetism.[1–4] To improve the application temperature of SMMs, Dy(III) is particularly preferred in order to exploit the potential of its large magnetic anisotropy arising from the $^6H_{15/2}$ state. In this regard, many Dy-SMMs have been explored.[5–7] Of particular interest are dinuclear systems with facile manipulation of the intradimer magnetic interactions.[6] For example, strong magnetic couplings in the dinuclear complex $[Dy_2\{N(SiMe_3)_2\}_4(thf)_2(N_2)]^-$ lead to hysteresis of magnetization above 8 K;[6b] whereas a weakly coupled dimer [$Dy^{III}{}_2$(N_1,N_3-bis(3-methoxysalicylidene)diethylenetriamine)$_2$(NO_3)$_2$] shows dominant single-ion relaxations.[6e]

On the other hand, unlike the usual uniaxial anisotropy of the Dy^{III} ion, we and others have observed that the six-coordinate Yb(III) ion[8] ($^2F_{7/2}$) prefers an easy-plane anisotropy of the ground doublet state[8c] that leads to a dominant direct relaxation process. In this work, we attempted to see if we could combine and manipulate these two types of magnetic anisotropy in one molecule if, in particular, the coordination environment of each Ln centre is controllable.

In this regard, the simplest system to access is the heterodimeric system. Facile solvothermal reaction of $LnCl_3\cdot 6H_2O$ and H_3cht (1 : 1) in MeCN at 160 °C for 30 h led to isolation of a series of dimeric complexes $[Ln_2(H_2cht)_2Cl_4(H_2O)(MeCN)]\cdot MeCN$ (Ln = $Dy_{0.435}Yb_{0.565}$ (**1**), Dy (**2**), Yb (**3**); H_3cht = 1,3,5-cyclohexanetriol). It should be noted that even with a starting ratio of 1 : 1 the resulting ratio of Dy : Yb in **1** is 0.87 : 1.13, a non-stoichiometric product. Interestingly, magnetic studies of **1** show a single slow-relaxation process in the absence of an external field and two relaxation processes upon applying a magnetic field. The origins of these two relaxation processes can be well attributed to the different Ln centers by comparing the ac relaxation regions of the pure Ln compounds **2** and **3**.

All the three compounds are isostructural and crystallise in the monoclinic space group *C*2/*m* (Table S1†). The structure of **1** is described (Fig. 1a) as representative. The dinuclear complex features two seven-coordinate Ln ions sharing two deprotonated hydroxyl-*O* bridges from two H_2cht ligands. The remaining coordination sites of the Ln ions are occupied by two protonated hydroxyl-*O* atoms of the H_2cht ligands, two chlorides and a disordered terminal ligand comprising of either H_2O or MeCN molecules. Systematic analyses of the coordination geometries of the Ln ions (Fig. S1†) were performed using SHAPE 2.0[9] software, showing an intermediate geometry between capped-octahedron (C_{3v}) and capped trigonal-prism (C_{2v}) (Table S3†). Intermolecular O–H···Cl hydrogen bonds (Fig. S2†) set up the two-dimensional packing of the molecules in the *ab* plane (Fig. S3†). The shortest intermolecular Ln···Ln distance

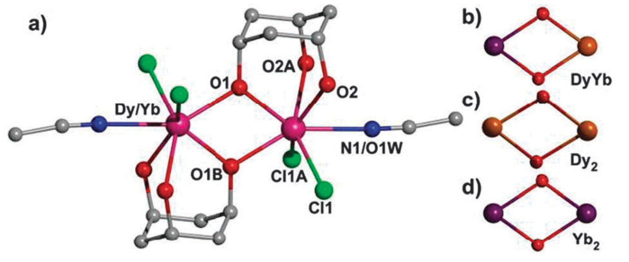

Fig. 1 Structural motifs of the hybrid DyYb complex **1**. The H_2O and MeCN ligands are disordered with equal occupancy. Color codes: orange (Dy), violet (Yb), red (O), blue (N) and grey (C). Symmetry codes, A: *x*, −*y*, *z*; B: 1 − *x*, *y*, 2 − *z*.

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† Electronic supplementary information (ESI) available: Experimental procedures, physical measurements, crystallography, computational details. CCDC 899841 (**1**), 899842 (**2**) and 899843 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc37036k

is 6.22 Å. Selected bond distances and angles for **1–3** are listed in Table S2†, showing only slight differences as Ln is varied.[6c,10] Because of the similar ionic radii of Dy^{III} and Yb^{III} ions, the metal ions cannot be distinguished by X-ray diffraction. Inductively coupled plasma (ICP) measurements were therefore conducted to study the composition of **1**. The result reveals a ratio of 1.29 : 1 for Yb^{III} : Dy^{III}. Further integration found the probabilities of different dinuclear species are, 19.1, 31.7 and 49.2% for Dy_2, Yb_2 and DyYb, respectively.[6e] This analysis reveals that the main species in **1** is the heteronuclear dimer.

Magnetic studies of **1** were performed on a microcrystalline powder sample. Dc susceptibility data at room temperature (Fig. S4†) confirm the expected value (15.1 cm^3 K mol^{-1}) for mixed Yb^{III} and Dy^{III} ions with a ratio of 1.29 : 1. As the temperature decreases the χT product remains nearly constant down to 100 K before further descending to a value of *ca.* 10 cm^3 mol^{-1} K at 2 K. This is a typical paramagnetic behavior.

Ac susceptibility measurements with and without applied dc fields were performed on **1**. Without an external field (Fig. S5†), **1** exhibits clearly frequency-dependent signals below 15 K. With an external field of 3500 Oe, two slow magnetic relaxations were observed in both the temperature- (Fig. S7†) and frequency-dependent (Fig. 2 and Fig. S8†) ac susceptibilities. In the low-temperature regime (3.8–7 K), the Cole–Cole plots of χ'' *vs.* χ' (Fig. S25†) show superposition of two semicircles and were fitted by a linear combination of two modified Debye functions (eqn (S1) and Fig. S26†).[10] The obtained parameters are summarized in Table S4†, with α parameters always less than 0.39. At temperatures above 8 K (Fig. S27†), the plots were fitted by the generalized Debye function with α in the range 0.12–0.18.

We suspected that the two relaxations were caused by the mixed species in **1**. Therefore, two pure analogues, Dy_2 (**2**) and Yb_2 (**3**), were prepared for comparison.

At room temperature, the χT values for **2** and **3** are 28.2 and 5.0 cm^3 K mol^{-1}, respectively (Fig. S4†), which are in good agreement with the expected theoretical values (28.34 and 5.14 cm^3 K mol^{-1} for **2** and **3**, respectively).[2] Upon cooling, **2** and **3** show very different behavior. For **2**, the χT value remains nearly constant until 50 K, and then decreases rapidly to a value of 15.17 cm^3 K mol^{-1} at 2 K. For **3**, the χT product decreases continuously to a minimum of 3.0 cm^3 K mol^{-1} before rising to 3.23 cm^3 K mol^{-1} at 1.8 K. The increase of χT at low temperature might indicate the presence of ferromagnetic exchange-coupling that competes with the progressive thermal depopulation of the excited Stark sublevels of the Yb^{III} ion.[8]

Ac susceptibilities show the field-dependent behavior of **2** and **3**. For **2**, frequency-dependent behavior was observed in the absence of an external dc field (Fig. S10–S12†), while this situation occurs with **3** only when an external dc field was applied (Fig. S17–S20†). Interestingly, we found the temperature-window of the relaxation zone in both **2** and **3** corresponds well to the two-relaxation region in **1** when the same field of 3500 Oe was applied.

Intuitively, the slow relaxation at higher temperature is attributed to the Dy component of either Dy_2 or DyYb species (**Dy-of-1**), and the Yb component of either Yb_2 or DyYb species (**Yb-of-1**) should be responsible for the relaxation at lower temperature. The relaxation time (τ) is presented as a τ *vs.* $1/T$ plot in Fig. 3 and fitted using the Arrhenius law in the temperature range 8–11 K for **Dy-of-1** and 5.7–7 K for **Yb-of-1**, respectively. The obtained energy barrier U_{eff} is 100(3) K for **Dy-of-1** and 29(0) K for **Yb-of-1**.

To elucidate whether the two relaxations are from the individual behavior of the two pure compounds, in-depth dynamic analysis of both **2** and **3** were performed.

For **2**, by fitting the data above 9.5 K to the Arrhenius law $\tau = \tau_0\exp(U_{eff}/k_BT)$, an effective energy barrier to magnetization reversal of $U_{eff} = 124(2)$ K was obtained. Below 3 K, the dynamics of **2** becomes temperature independent in a pure quantum regime with a τ value of 2.4×10^{-2} s. To minimize this fast zero-field relaxation,[6d,e] a dc field of 3500 Oe was employed for further frequency-dependent measurements (Fig. S13†). The results demonstrate that relaxation time in the temperature range of 1.8–9.5 K is significantly increased under a dc field. However, no obvious influence was observed above 9.5 K, in which the thermally activated relaxation process is dominant.

For **3**, under an applied dc field of 3500 Oe, both the temperature- (Fig. S18†) and frequency-dependent (Fig. S19†) ac susceptibilities show slow-relaxation behavior of SMMs. The Cole–Cole plots were fitted by the generalized Debye function with α parameters in the range 0.09–0.29 (Fig. S20†). The obtained relaxation times (τ) above 3.8 K were fitted by the Arrhenius law, resulting in an effective energy barrier of U_{eff} = 19.5(2) K (Fig. S22†), while the linear deviation at low temperatures is ascribed the prevalent quantum tunneling.

Significant shifts of the energy barriers between **2** (124 K) and **Dy-of-1** (100 K) and between **3** (19.5 K) and **Yb-of-1** (29 K) indicate the changes of the environment of the individual Dy^{III} and Yb^{III} ions in the mixed–metal complex with respect to pure Ln complexes **2** and **3**. Indeed, since the temperatures at which the ac susceptibility measurements have been conducted exceed the exchange splitting

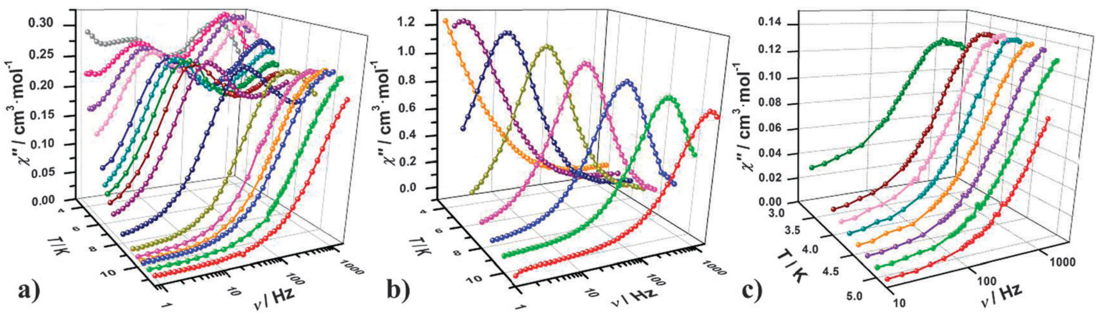

Fig. 2 Out-of-phase susceptibility χ'' *vs.* frequency ν (logarithmic scale) for **1** (a), **2** (b) and **3** (c) under a dc field of 3500 Oe.

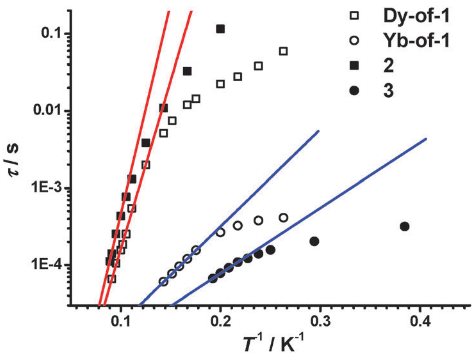

Fig. 3 Magnetization relaxation time (τ) *vs.* T^{-1} under a dc field of 3500 Oe for **1–3**. The solid lines correspond to Arrhenius law fittings.

in all three complexes, the extracted barriers correspond to the slow relaxation of individual Dy^{III} and Yb^{III} ions in these compounds.[6a,7d]

To get more insight into the origin of observed relaxation processes, we have performed high level *ab initio* calculations on individual Ln centers with the MOLCAS 7.6 program package[11a] (see ESI† for computational details,[11b,c] and results). The obtained local energies on Ln sites, local *g*-tensor directions of the local main anisotropy axes, exchange coupling constants, exchange spectrum, and comparison of the experimental and calculated magnetic properties for **2** and **3** are shown in Fig. S30–S35 and Tables S5–S17†.

It was found that the doublet ground-state of the Dy ions in **2** is strongly axial (g_x and g_y are relatively small, see Table S7†), which means that the quantum tunneling of magnetization (QTM) in the ground state is suppressed. This causes the relaxation to occur *via* the first excited states on Dy^{III} ions. Accordingly, the blocking barrier extracted from the Arrhenius fitting of the temperature dependence of the relaxation time (Fig. S14†) is in agreement with the calculated energy of first excited Kramers doublet on individual Dy^{III} ions (85 cm^{-1} = 122 K, see Table S6†). Contrary to this, the calculated g_x and g_y for the doublet ground state of Yb^{III} in **3** are *ca.* 1 and 2, respectively (Table S13†). This means that QTM on individual Yb^{III} sites is a dominant relaxation process at all temperatures. This conclusion is in line with the observation that no blocking of magnetization is observed in **3** without an additional dc magnetic field. The energy of the first excited doublet on Yb sites is 177 cm^{-1} (Table S12†), which means that the relaxation of **3** in an applied dc field is not of activated type.[8c] Detailed dynamic analysis with multiple relaxation processes fit also suggests the absence of an Orbach process (part 5, ESI†). This was also indicated by plots of the relaxation time τ *vs.* T on a log–log scale for both **Yb-of-1** (Fig. S21†) and **3** (Fig. S28†), however, we tentatively reserve the Arrhenius fits to demonstrate the difference of relaxations between them. A similar picture is realized in the mixed DyYb complex of **1**. Without an applied dc field only the Dy site in the DyYb complex will show magnetization blocking, while the Yb site will be subject to strong QTM. By applying a dc field, the latter will show slow relaxation of magnetization and a separate maximum in $\chi''(\nu)$ (Fig. 3a), again as is the case of individual Yb sites in **3**.

In summary, we have synthesized and characterized a heterospin dinuclear SMM with two slow magnetic relaxations arising from the individual Dy^{III} and Yb^{III} ions; *ab initio* calculations suggest that the relaxation on Dy sites is an activated Orbach process involving the first excited Kramers doublet, while the relaxation on Yb sites occurs *via* a direct process. The difference of activation energies in pure and mixed–metal complexes is due to small geometrical changes of the environment of the Ln ions. To address the effects of entanglement between the local states on Ln ions in these complexes, we will need to explore still lower temperatures, not exceeding the exchange splitting in these complexes.[6a] These studies will be addressed in future work.

This work was supported by the NSFC (Grant nos 91122032, 90922009 and 21121061) and the "973 Project" (2012CB821704). L.U. is a postdoc of the FWO-Vlaanderen (Flemish Science Foundation).

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