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A Non-sandwiched Macrocyclic Monolanthanide Single-Molecule Magnet: The Key Role of Axiality

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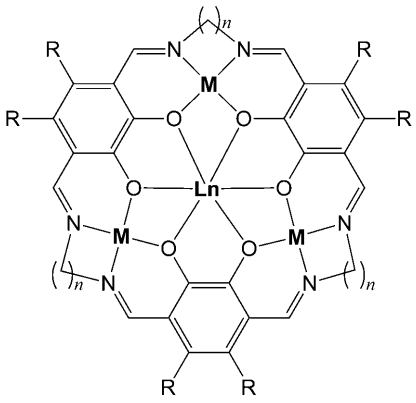
Single-molecule magnets (SMMs) have gained attention recently because of parallel/antiparallel bistability of magnetization to a given z direction of a magnetic field when that field is weakened or removed.[1] This bistability is due to an energy barrier to relaxation of the magnetization, which, at low temperatures, becomes significant with respect to ambient thermal energy and prevents loss of magnetic order. Molecules that show relaxation of the magnetization of purely molecular origin are thus described as SMMs.[2] In SMMs based on lanthanide ions the crucial magnetic anisotropy is the result of lifting the degeneracy of the ground states into new sublevels by some ligand-field potentials.

Although mononuclear lanthanide SMMs were first generated by Ishikawa and co-workers using two *macrocyclic* ligands to sandwich the lanthanide ion in a 'double-decker' fashion,[3] they can also be prepared by using a range of *acyclic* ligands such as polyoxometalates,[4] Schiff bases,[5] radicals,[6] and ketones.[7] There are several mononuclear lanthanide SMMs that also contain one or more 3d metal ions.[8] However, to the best of our knowledge, there are no examples of SMMs containing a single lanthanide ion bound *within* the cavity of just *one organic macrocycle* (rather than being sandwiched between two such macrocycles[3,9] or being part of a *metallo*macrocycle only, that is, no organic macrocycle[10]). Such a system is highly desirable as it should enhance the nuclearity/geometry control, stability, tunability and solubility of the complex, all of which are important factors for potential future applications. Here we present the first example of such a SMM.

The organic macrocycle system we selected for this purpose (Scheme 1) was inspired[11] by those reported by Nabeshima and co-workers[12] and MacLachlan and co-workers.[13]



Scheme 1. The new hexaimine [3+3] macrocycle family that we employed to generate new SMMs. The specific macrocycle, $(L^{Pr})^{6-}$, used in this work has R = H and $n = 3$, and was prepared and complexed in situ to generate the tetrametallic Zn_3Dy complex **2** (M = Zn, Ln = Dy).

Macrocyclic ligands provide discrete, metal ion binding pockets and thus offer far more predictable cluster nuclearity and structure than acyclic analogues can. Here the [3+3] macrocycle provides three N_2O_2 pockets for 3d metal ions and one central O_6 pocket for a lanthanide ion, so mixed-metal M_3Ln tetrametallic macrocyclic complexes are a predictable outcome (in comparison, unpredictable aggregates of 4–12 metal ions were obtained with acyclic ligand analogues[14]). Macrocycles usually also provide enhanced stability (macrocyclic effect), solubility (vary substituents on periphery, R, to modify solubility) and fine-tunability (vary the periphery, R and *n*, and choice of M and Ln, whilst retaining the M_3Ln core) over acyclic analogues. Schiff base links were chosen due to the reversibility of bond formation (facilitates error correction) and our experience with such systems.[15]

Initially the dialdehyde 1,4-diformyl-2,3-dihydroxybenzene (**1**) was combined with a range of aliphatic diamines in

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the presence of the desired metal ions to generate the macrocyclic complexes of interest. Here we report the first SMM obtained from this system, a Zn_3Dy complex of $(L^{Pr})^{6-}$ (Scheme 1). Whilst magnetically uninteresting, M = Zn was used in the first instance because it is less temperamental than other, redox-active metal ions; accordingly, it should simply fulfill the necessary structural role (as it often does in living systems[16]), facilitating coordination of the magnetically interesting lanthanide ion, in this case Ln = Dy, in the central binding pocket.

The desired mixed-metal zinc(II)–dysprosium(III) macrocyclic complex of $(L^{Pr})^{6-}$ was prepared by reaction of a 3:3:1:3 ratio of **1**, zinc(II) acetate dihydrate, dysprosium(III) nitrate hexahydrate, and 1,3-diaminopropane at room temperature in methanol. Vapor diffusion of diethyl ether into the orange reaction solution led to the desired macrocyclic complex, $[Zn_3Dy(L^{Pr})(NO_3)_3(MeOH)_3]\cdot 4H_2O$ (**2**·3 H_2O), precipitating as an analytically pure orange powder. Consistent with the successful formation of the desired macrocyclic complex, IR spectroscopy revealed a new band at 1627 cm^{-1} corresponding to the stretch of the imine bonds. No bands corresponding to unreacted aldehyde (1660 cm^{-1}) or amine (3360, 3282, and 1601 cm^{-1}) were present.

Yellow single crystals of $[Zn_3Dy(L^{Pr})(NO_3)_3(MeOH)_3]\cdot 1.5\,MeOH\cdot H_2O$ (**2**·1.5 MeOH·H_2O) were obtained by slow vapor diffusion of diethyl ether into a solution of **2**·4 H_2O in methanol. The X-ray crystal structure determination (refinement details are given in the Supporting Information) confirmed the anticipated binding mode of the macrocycle to three zinc(II) ions and one lanthanide ion (Figure 1). As expected, the large nine-coordinate dysprosium(III) ion is bound in the central O_6 cavity, while the smaller five-coordinate zinc(II) ions are bound in the outer N_2O_2 sites. The O_9 coordination of the dysprosium(III) ion is completed by a nitrate ion, bound through both oxygen atoms, on one face of the macrocycle, and a solvent methanol molecule on the other face of the macrocycle. Two of the zinc(II) ions have square-pyramidal coordination geometry slightly distorted towards trigonal bipyramidal (τ[17] = 0.110 and 0.008), and each has one nitrate ion coordinated through one oxygen atom. The remaining zinc(II) ion has an octahedral geometry, with two axially coordinated methanol molecules. Overall, the macrocycle is not perfectly flat, rather it adopts a slightly curved conformation. The dysprosium(III) ions in neighboring complexes are about 10 Å apart. One of the axially coordinated nitrate ions and an axially coordinated methanol molecule hydrogen bond to water molecules of solvation.

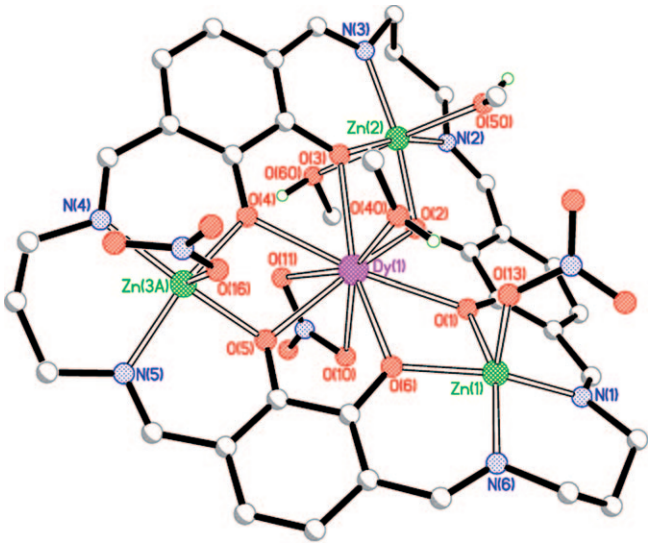

Figure 1. Crystal structure of $[Zn_3Dy(L^{Pr})(NO_3)_3(MeOH)_3]\cdot 1.5\,MeOH\cdot H_2O$ (**2**·1.5 MeOH·H_2O). For clarity, lattice solvent molecules, a minor component of disordered atoms (major component is shown), and non-acidic hydrogen atoms have been omitted.

At room temperature the χT product for **2**·4 H_2O (13.88 $cm^3\,Kmol^{-1}$) under an applied DC field of 1000 Oe is consistent with the expected value for one isolated dysprosium(III) ion ($S = 5/2$, $L = 5$, $g = 4/3$, $C = 14.17\ cm^3\,Kmol^{-1}$). The χT product decreases to a value of 10.3 $cm^3\,Kmol^{-1}$ at 2 K, before a small upturn at 1.8 K (Figure 2). The decrease in the χT value with temperature

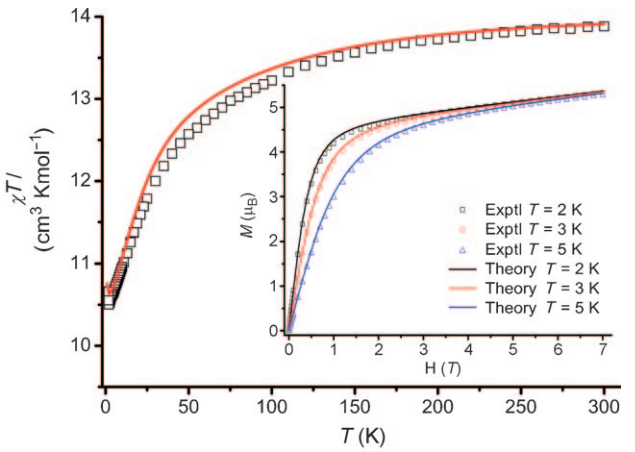

Figure 2. Temperature dependence of χT for **2**·4 H_2O. Inset: Molar magnetization versus field at indicated temperatures. The solid lines are the ab initio calculated curves (see the text).

may be the result of thermal depopulation of the $^6H_{15/2}$ ground state of the Dy^{III} ion. The simulations based on ab initio calculations (see below) indicate that the small upturn below 2 K is due to a weak ferromagnetic interaction between the complexes. The field dependence of the magnetization at 2 K shows that the magnetization reaches 5.3 μB, but a residual slope is observed at high field (> 60 kOe) indicating failure of the magnetization to saturate and some anisotropy in the system (Figure 2, inset).[18]

Ab initio calculations for the complex **2**·4 H_2O were performed by using a CASSCF/CASPT2 approach that includes the spin-orbit coupling,[19] and their magnetic properties simulated by the approach recently developed by some of us[20,21] (see the Supporting Information). Only a single phenomenological parameter, $zJ' = 0.005\ cm^{-1}$, was used in the

main plot of Figure 2 to simulate the small upturn of χT at low temperature. The ligand field splitting of the ground $^5H_{15/2}$ atomic multiplet of Dy^{III}, with the total angular momentum $J = L + S = 15/2$ ($L = 5$, $S = 5/2$), giving rise to eight Kramers doublets is relatively weak (391 cm^{-1}), which is a result of relatively long Dy–O bond lengths (average Dy–O bond length is 2.438 Å). The main anisotropy axis of the Dy^{III} ion (see Figure S4 in the Supporting Information) is oriented almost parallel (5.05°) to the plane formed by the three Zn ions.

The dynamic magnetic properties of the complex were further probed by using AC measurements. The out-of-phase component of the AC susceptibility is very weak (with a χ''/χ' ratio of 1:53) in a zero DC field, but becomes significantly more intense with the application of an external DC field of 1500 Oe (see Figure S1). The position of the maxima of the susceptibilities also becomes strongly frequency-dependent, as expected for SMMs. This behavior is probably due to fast zero-field tunneling of the magnetization between sublevels, which is suppressed with the application of the DC field. Such activity is known for SMMs,[22] including Schiff base systems similar to $(L^{Pr})^{6-}$.[23]

A 1500 Oe field was chosen for further AC susceptibility measurements because the relaxation process was shown to be slowest (38 Hz) at this field (see Figure S2). Strong frequency dependence of AC susceptibility with varying temperature was observed under this field (Figure 3, top).

To extract the characteristic time and the barrier to relaxation of **2**·4H_2O, the relaxation times were fitted by using the Orbach thermally activated relaxation law $\tau = \tau_0 \exp(U_{eff}/k_B T)$.[1,2] Linear data corresponding to the law were only obtained between 4 K and 5.5 K (solid line, Figure 3, bottom), with an effective energy barrier of $U_{eff} = 25.8$ K and a relaxation time of $\tau_0 = 1.2 \times 10^{-6}$ s in this region. Below 4 K, the relaxation becomes weakly temperature dependent but does not follow linear behavior. This suggests that the relaxation might follow a quantum regime below 4 K or that there is more than one thermally activated relaxation process present in this system.

To determine if the relaxation of **2**·4H_2O is governed by a single thermal process, a Cole–Cole plot of the in-phase versus out-of-phase susceptibilities at low temperatures was constructed. If one relaxation process dominates, the plot will have a semicircular shape with a small value of α. Fitting the data using a generalized Debye model[24] gives a high α value of 0.27–0.48 (Figure 4), further suggesting that there is likely to be more than one relaxation process operating at low temperatures.

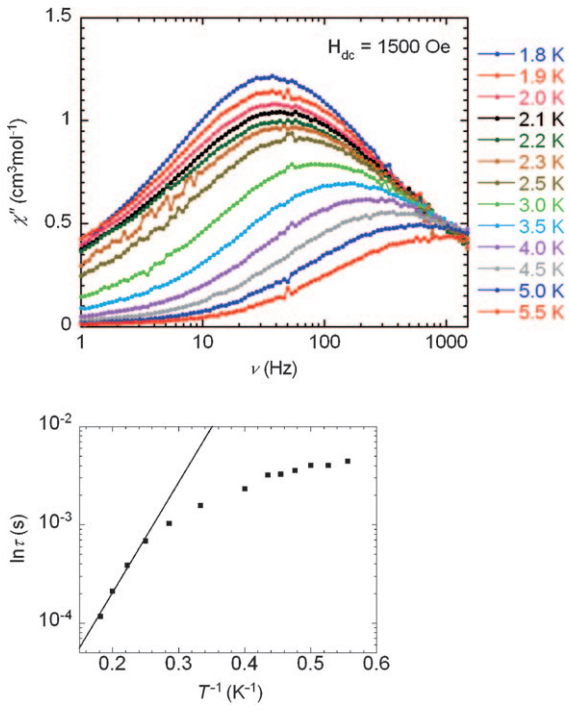

Figure 3. Top: Frequency dependence of the out-of-phase component of the AC susceptibility under an external DC field of 1500 Oe. Bottom: The relaxation time of **2**·4H_2O as a function of temperature (dots) plotted against a thermally activated Arrhenius law (solid line).

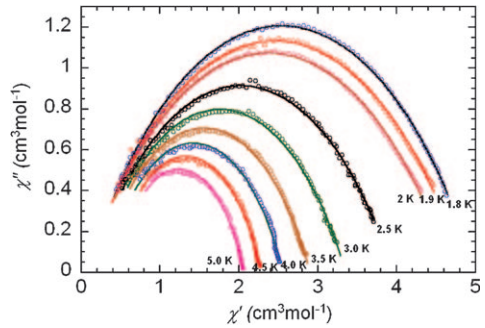

Figure 4. Cole–Cole plots at indicated temperatures. The solid lines are the fittings with a generalized Debye model. The parameters are discussed in the text.

The existence of fast tunneling of magnetization in **2**·4H_2O is also supported by the calculated g tensor of the ground Kramers doublet, which is not axial ($g_x = 0.10$, $g_y = 0.25$, $g_z = 18.15$). As discussed before in the case of the Co_7 wheel,[20] the non-negligible transverse components g_x and g_y induce the tunneling dynamics of magnetization due to the magnetic field present in the crystal. On the contrary, the highly efficient single-lanthanide SMMs of Ishikawa et al.[3,9] are perfectly axial due to the presence of an eightfold symmetry axis in their double-decker structure. Thus the present results show that the *magnetic axiality* of the ground Kramers doublet plays a key role for the SMM performance of single-lanthanide complexes. This finding is general for lanthanide complexes. For instance, recently a series of Dy^{III}-based compounds[25] have shown similar behavior of AC susceptibility, that is, no maxima of χ" unless a DC field was applied. On this basis, future strategies for the synthesis of efficient lanthanide-based SMMs (initially to get blocking of the magnetization, a maximum in χ", without applying a DC field, then optimizing the barrier) should be directed towards the use of *highly axial single-lanthanide building*

blocks. How to make these mononuclear units is largely an open question at present. While a perfect axiality clearly exists in high-symmetry complexes, it was also found that small deviations from it, amounting to only a few degrees, destroys the SMM properties.[4] Interestingly, mononuclear lanthanide centers with high magnetic axiality have also been found in low-symmetry complexes.[26] Accordingly, it is possible that such lanthanide blocks can be used for the design of efficient polynuclear SMMs, in which the site symmetry of lanthanide ions cannot be preserved. Improving our understanding of conditions for high magnetic axiality in low-symmetry complexes and the synthesis of such units deserves thorough investigation.

In conclusion, we have prepared a tetranuclear Zn_3Dy single-molecule magnet that shows weak frequency dependence of the out-of-phase component of AC susceptibility. In the presence of an external DC field (1500 Oe) the out-of-phase and in-phase components are similar in magnitude because the DC field inhibits quantum tunneling of the magnetization. To the best of our knowledge, this is the first SMM with a single lanthanide ion bound inside the cavity of a single organic macrocycle. We have also gained a critical insight, from ab initio calculations on this complex, in that magnetic axiality is the key to blocking of the magnetization in monolanthanide SMM complexes.

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