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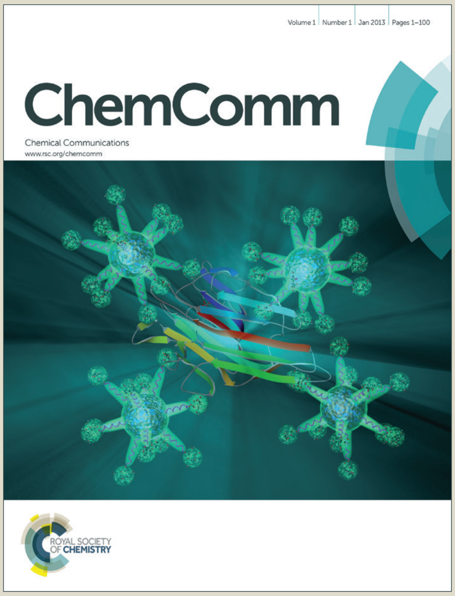

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Slow relaxation in the first penta-aza Dy(III) macrocyclic complex

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A new macrocyclic complex $DyCl_3(L_{N5})\cdot 4H_2O$ (1) has been prepared in which the Dy(III) ion is equatorially bound by an N_5-donor macrocycle (L_{N5}). Ac susceptibility data reveal slow relaxation of the magnetisation in zero field below 15 K with a distribution of relaxation rates.

The magnetism of nanoscale particles such as single molecule magnets (SMMs) has attracted considerable interest since the discovery of quantum hysteresis in a dodecanuclear $Mn_{12}Ac$ cluster at the beginning of the 1990s.[1] Other potential applications of SMMs include magneto-cooling through the magnetocaloric effect and quantum computing.[2] The requirements for such SMM behaviour are a large uniaxial anisotropy (**D**) and a large spin ground state (S). The resultant energy barrier, $|\mathbf{D}|S^2$, leads to slow relaxation of the magnetisation which can occur thermally at high temperatures, or *via* quantum tunnelling in the low temperature regime. In recent years the large magnetic anisotropy associated with the lanthanide elements has led to the observation of SMM-like behaviour in a range of mononuclear complexes, although only a small number of these exhibit true SMM behaviour in zero field.[3] The geometric requirements for slow relaxation in mononuclear complexes are specific to each lanthanide ion,[4] but the most common geometry is square-antiprismatic (pseudo-D_{4d}).[3c] Recently, Rinehart and Long postulated how the *f*-element electronic structure can be manipulated to rationalize the single ion anisotropy in 'sandwich-type' complexes with square-antiprismatic geometries.[5] The strongly ionic nature of the metal-ligand interaction in lanthanide complexes means that control of the molecular geometry is often difficult and an increasing number of examples of Ln-SMMs have been reported where the ions are in symmetry environments, far from square antiprismatic.[3a,6] The design and study of new-classes of lanthanide-based SMMs in which aspects of the coordination geometry are well-defined may aid the tailored design of Ln-SMMs and provide models to better understand the role of the symmetry of the ligand fields on the magneto-dynamics of such complexes.[7] Recent studies by Tong *et al.* revealed that Dy(III) under quasi-D_{5h} symmetry appears strongly axially symmetric and exhibits hysteresis up to 11 K.[8] However, SMMs assembled from heptacoordinate D_{5h} Ln(III) complexes are rare. To the best of our knowledge there are only three reported examples of mononuclear Ln-SMMs in which the Ln(III) ion adopts a pentagonal bipyramidal geometry.[8]

In this paper we implement the 15-membered macrocyclic ligand L_{N5} (Fig 1. left) to promote axial anisotropy in a Dy(III) complex $DyCl_3(L_{N5})\cdot 4H_2O$ **1** and show it exhibits SMM-like behaviour in zero field. Structural studies of transition metal complexes of this macrocycle were first studied by Nelson *et al.* in the 1970s.[9] More recently a pseudo-D_{5h} Mn(II) derivative has been exploited for the self-assembly of a ferromagnetically ordered 2-D network and a Mo_8Mn_{14} cluster with a large S value.[10] Yet the magnetic properties of lanthanide complexes of L_{N5} have not been studied, but offer the potential to specifically target quasi-D_{5h} coordination geometries.

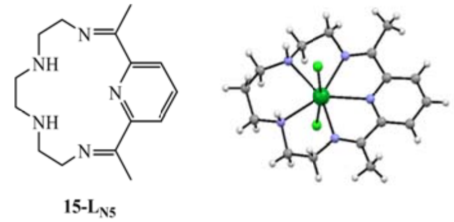

Fig. 1 Left: Molecular structure of the 15-membered ligand L_{N5} (where L_{N5} = 2,13-dimethyl-3,6,9,12,18-penta-aza-bicyclo-[12.3.1]octadeca-1(18),2,12,14,16-penta ene). Right: crystal structure of the $[Lu(16\text{-}L_{N5})Cl_2]^+$ cation of a 16-membered macrocycle, showing the pentagonal bipyramidal geometry of the Lu(III) ion.[11]

The metal-templated cyclo-condensation reaction of diactetyl-pyridine with triethylenetetramine in the presence of $DyCl_3\cdot 6H_2O$ afforded the desired 15-membered N_5 macrocyle **1** in 48% yield.[9] (S-1 ESI†). For complexes of this type it is well established that no macrocycle forms in the absence of a metal cation and the five donor atoms of the macrocycle comprise the pentagonal plane with the axial sites being occupied by unidentate anionic or solvent ligands.[9] The composition of this complex was determined to be $DyCl_3(L_{N5})\cdot 4H_2O$ by micro- and thermogravimetric analysis (S-2, ESI†). The presence of a

[1+1] Schiff-base complex was confirmed by ESI MS revealing a peak at *m/z* = 489 (100%) attributable to $[M\text{-}H]^+$, (where M = $[DyL_{N5}Cl(H_2O)]^{2+}$; S-3, ESI†). Formation of the macrocycle was also evidenced by the appearance of a C=N str at ν = 1629 cm^{-1} in the IR spectrum. A very broad absorption band is also present at 3345 cm^{-1}, consistent with the presence of both lattice and co-ordinated water molecules. This is further supported by a complex band between 300 and 380 cm^{-1} in the Raman spectrum assigned to the *ν*(Dy-O) stretching mode of at least one coordinated water molecule.[12a] The presence of an axially coordinated Cl^- ion is confirmed by the observation of two *ν*(Dy-Cl) stretching modes; a medium intensity band in the far-IR spectrum at 208 cm^{-1} and a strong Raman peak at 257 cm^{-1} (S-4, ESI†)[12]. Consistent with this conclusion is the observation that the complex is a 2:1 electrolyte in methanol (S-5, ESI†). All attempts to crystallise the complex proved unsuccessful yielding only an amorphous solid (confirmed by PXRD, S-6, ESI†). In contrast, the molecular structures of the Lu(III) and Yb(III) complexes of the slightly larger 16-membered N_5 macrocycle have been elucidated by X-ray diffraction.[13] In these complexes, the cations adopt a pseudo-D_{5h} geometry with the N_5-donor macrocycle coordinating in the equatorial plane and two axial chloride ligands (Fig. 1, right). For both complexes, the N donor atoms of the macrocycle are almost coplanar. The lanthanide ions are only slightly displaced out of the N_5 plane by 0.114(2) Å for Yb(III) and 0.104(2) Å for Lu(III). These structures demonstrate the ability of the macrocycle to offer a planar N_5-donor set, favouring 7-coordinate geometries for Ln(III) ions. Given that the ionic radii of Dy(III) is slightly larger than Yb(III) and Lu(III), a search of the Cambridge Structural Database was carried out to evaluate the structures of 15-L_{N5} macrocyclic complexes that encapsulate larger cations. Interestingly, the complex containing the larger Cd(II) ion (Fig. 2)[14] also adopts pseudo-D_{5h} geometry with the N_5 donor set within 0.5 Å of the equatorial plane.

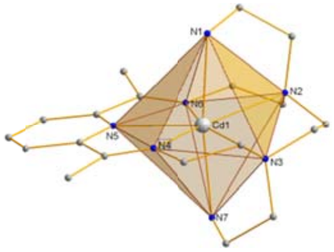

Fig. 2 Molecular structure of $[CdL_{N5}(NH_2\text{-}Et)_2]^{2+}$ showing the 7-coordinate geometry of the Cd^{2+} ion and the slightly puckered conformation of the N_5 macrocycle. The N2 and N3 donor atoms are displaced above and below the CdN_3 plane by +0.458 and -0.507 Å respectively.[14]

Given the similarities of these macrocycles to **1** in terms of number, type and position of the N_5 donor atoms and their synthesis that is templated by metal ions with atomic radii both larger and smaller than Dy(III), it is very likely that the lanthanide ion in this complex is also penta-coordinated by the LN5 ligand. Furthermore, the presence of this equatorially coordinated N5 donor set is likely to induce significant axial anisotropy.

The magnetic behaviour of **1** was probed through variable temperature magnetic susceptibility (dc and ac) measurements. The dc susceptibility of **1** in an applied field of 1000 Oe in the region 100 - 300 K revealed a $\chi_M T$ value of 14.9 $cm^3 \cdot K \cdot mol^{-1}$, consistent with the theoretical value of 14.17 $cm^3 \cdot K \cdot mol^{-1}$ for a Dy(III) ion ($^6H_{15/2}$, g = $^4/3$) (S-7, ESI†). Ac susceptibility measurements were carried out in order to probe the potential slow relaxation of the magnetisation indicative of SMM-like behaviour. The temperature dependance of the ac susceptibility of **1** measured in zero applied dc field reveals an out-of-phase component (χ'') in the susceptibility below 15 K, consistent with the onset of a slow relaxation process (Fig. 3, bottom). The absence of the maximum in χ'' has been observed for other lanthanide complexes[15] that include the Er(III) polyoxometalate-based SMM $[Er(\beta_2\text{-}SiW_{11}O_{39})_2]^{13-}$.[3b]

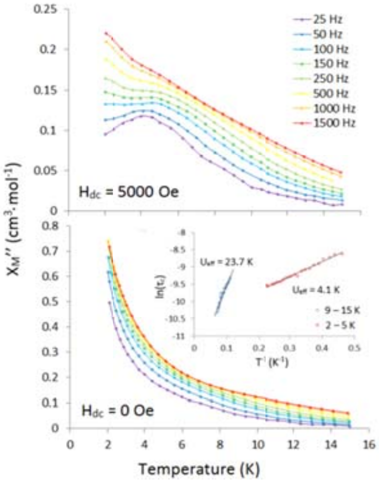

Fig. 3 Temperature dependence of the χ_M'' for **1** at different frequencies in the region 2.0 – 15 K in zero dc field (bottom) and 5000 Oe dc field (top).

In order to slow down the quantum tunnelling process, ac susceptibility measurements were carried out under a static dc field. Under a field of 5000 Oe, at low frequencies, the thermal dependence of the imaginary susceptibility reveals an enhancement of the peak feature as the quantum tunnelling is suppressed (Fig. 3, top). At higher frequencies, the maximum shifts to higher temperatures, and a shoulder to the left of the maximum emerges, consistent with the presence of more than one relaxation pathway. Similar dynamic behaviour has been reported for other families of SMMs.[3b,16] SMM-like behaviour was further confirmed by zero-field Cole-Cole plots in the region 2 – 15 K and in the frequency range 10 – 10,000 Hz, which reveal distinct maxima in the plot of χ_M' vs. χ_M'' (Fig. 4) and in the frequency dependence of χ_M''. A simultaneous fit of the frequency dependence of χ' and χ'' at fixed temperatures (S-8, ESI†) permitted the dispersivity, α and relaxation time, τ_c, to be determined. For **1**, the lack of well-defined maximum in $\chi''(T)$ and α = 0.58(7) are consistent with some dispersion in relaxation rates due to a distribution of slightly distinct anisotropic centres, as reported for other lanthanide SMMs.[15] A fit of the temperature dependence of the τ values to the Arrhenius Equation permitted the energy barrier U_{eff} and tunnelling rate (τ_o) to be determined. In the high temperature region (9 – 15 K), the energy barrier U_{eff} was found to be 23.7 K with $\tau_o = 6.4 \times 10^{-6}$ s, whereas in the region 2 - 5 K, U_{eff} = 4.13 K with $\tau_o = 2.8 \times 10^{-5}$ s (Fig. 3, bottom, inset). These energy barriers and relaxation rates are comparable with those recently reported for other Dy(III) SMMs which typically exhibit two well-defined relaxation processes,[15a,17] but smaller than the barrier reported for the D_{5h} complex reported by Liu *et al.*,[8] indicating some sensitivity to the crystal field. At high temperature the dominant relaxation method is a classical demagnetisation through thermal crossing of the energy barrier for reversal of the magnetisation. Conversely, in the low temperature regime, the proportion of molecules able to overcome this energy barrier is small and the dominant relaxation process is a quantum tunnelling phenomenon.[6a] The amorphous nature of **1** likely leads to a spread of slightly different geometric environments which directly affect both the U_{eff} and τ_o values, thereby leading to a distribution of relaxation behaviours, reminiscent of spin-glass like behaviour. Notably, the relaxation times for **1** are typical of an SMM rather than a spin-glass,[3b,15a] consistent with a molecular origin to the behaviour.

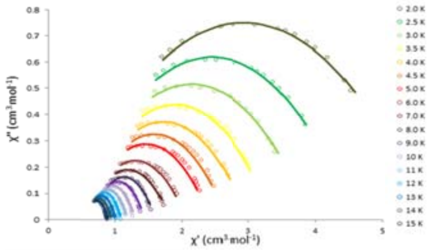

Fig. 4 Cole-Cole plot for **1** in zero dc field, between 2 and 15 K.

In conclusion, we have demonstrated for the first time that a pentagonal disposition of macrocyclic N_5 donor atoms can be used to promote anisotropy in a Dy(III) complex which exhibits SMM-like behaviour in zero field. While the amorphous nature of **1** currently precludes a full magneto-structural correlation, analytical spectroscopic, and electrical conductance measurements confirm the presence a Dy(III) ion with the L_{N5} macrocycle defining the equatorial plane and at least one bound axial water and chloride ligand. This approach is a promising strategy for the rational design of lanthanide complexes with slow relaxation of magnetization working towards the realization of high energy barrier SMMs.[3c,8] Furthermore, the use of a pentadentate macrocycle together with replaceable axial ligands presents a novel strategy for probing the dynamics of magnetization in such systems, as well as for linking together the magnetic building blocks. In this regard, detailed magnetic studies on Ln(III) complexes of L_{N5} and their derivatives are in progress. This work was financially supported by NSERC-DG, RTI, CFI, CRC, ORF, the Ministry of Ontario (ERA) and Brock University.

Notes and references

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