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

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Supporting Information

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Contents

S-1: Synthesis of $DyCl_3(L_{N5})\cdot 4H_2O$ (1)

All reagents were purchased from Sigma-Aldrich and used without further purification. Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer. UV-vis data were obtained using a Beckman Coulter DU 720 General-Purpose UV-vis spectrophotometer. Mass spectrometry data were recorded on a Carlo Erba/Kratos EC/MS acquisition system and processed at a SPARC workstation. Elemental analysis measurements were performed by Atlantic Microlab Inc., Norcross, GA, USA. Far-IR spectra were collected on a Nicolet 6700 system equipped with the solid substrate beam splitter and a polyethylene detector, resolution 4 cm^{-1}. The system was purged with dry nitrogen gas before use and the data was smoothed during processing. Raman spectra were measured on a Renshaw in Via Laser Raman spectrometer with an attached Leica microscope and a red solid-state laser (785 nm).

2,6-Diacetylpyridine (0.329 g, 2.01 mmol) was added in one portion to a solution of $DyCl_3\cdot 6H_2O$ (0.759, 2.01 mmol) in MeOH (30 mL). The solution was heated to 50°C, and then triethylenetetramine (0.300 mL, 2.01 mmol) was added in one portion. The reaction mixture was heated to 85°C and refluxed for 18 h. The solvent volume was reduced by half, and the mixture was cooled to r.t. An excess of Et_2O was added, and the resulting precipitate was collected by Buchner filtration and washed well with cold Et_2O to give **1** as a beige solid (0.587 g, 47.5%). IR (cm^{-1}): 3345 (br, O-H), 3246 (w, N-H), 1629 (s, C=N), 1591 (m, py), 1492 (m, py), 1111 (w, C-N), 1010 (w, py), 813 (w, O-H). UV-vis (MeOH, nm): $\lambda_{max} = 288$. MS(ESI): *m/z* 489 $[M-Cl]^+$ (100 %). Anal. Calcd. For $C_{15}H_{31}N_5O_4Cl_3Dy$: C, 29.33; H, 5.09; N, 11.40; found C: 29.76, H: 4.91, N: 10.87%.

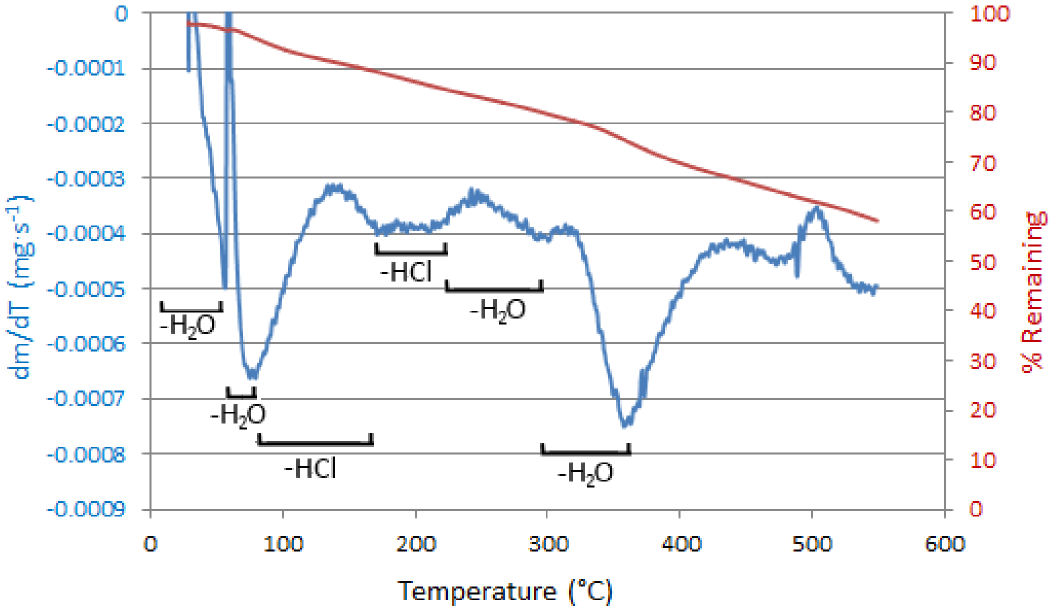
Comments on macrocycle formation

While no single crystals are available to elucidate the molecular structure of **1**, the elemental analysis, TGA and spectroscopic data confirm macrocycle formation. Firstly, there is strong literature precidence for the formation of 15-membered pentadentate N_5 macroycles via metal templated Schiff-base condensation reactions. These macrocycles can only be isolated as their metal complexes since reaction in the absence of a metal salt yield gums with properties consistent with an oligomeric product (or mixture of products) having residual unchanged carbonyl groups, consistent with literature observations.[1] The importance of the metal ion in promoting the cyclic condensation of the reactants and/or in stabilising the macrocycle once formed is well established. All of the N_5 complexes reported previously including a Mn(II) derivative adopt approximately pentagonal bipyramidal geometry with the macrocycle defining the equatorial plane.[2] We have taken great care to compare our spectroscopic data for **1** with that reported previously for N_5 complexes. Since the Dy(III) ion templates the formation of this macrocycle, we are confident that the macrocycle coordinates the Dy(III) cation via its five N_5 donors in the equatorial plane. Although we are aware that the Dy(III) cation is a little larger than the transition metal cations reported previously and that they have a weaker affinity for N donor ligands when compared with their transition metal counterparts, a search of the Cambridge Structural Database (CSD) revealed that two lanthanide ions Yb(III) and Lu(III) are able to template Schiff-base macrocycle formation and coordinate the slightly larger 16-membered macrocycle via their N_5 donors in the equatorial plane. It is well documented that formation of this class of Schiff-base macrocycle requires the size of the cation to be complementary to the size of the macrocyclic cavity. In order to investigate whether or not there was literature precedence for larger cations to template the formation of the 15-membered N_5 macrocycle we turned to the CSD and found that a Cd(II) complex is known. ESI MS, IR and Raman spectroscopic data as well as molar conductivity measurements confirm the presence of at least one axially coordinated water and chloride ligand.

S-2: TGA data for 1

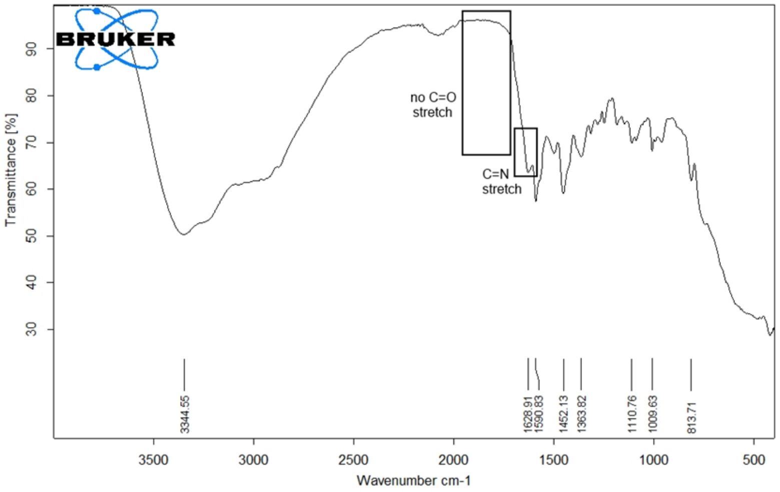
TGA measurements were performed on a Mettler Toledo TGA SDTA 851e with a 6.91 mg sample of **1** mounted in an aluminium crucible. Samples were maintained at 25°C for 20 minutes prior to heating under a helium-purged atmosphere (He flow rate: 60 mL/min) from 25°C to 600°C with a heating rate of 10°C/min.

The presence of water bound in at least two different ways is supported by the results of thermogravimetric analysis. The complex loses one water molecule at 54°C followed by a second at 70°C, consistent with weakly bound lattice solvent. By 250°C, the complex shows the loss of two HCl molecules. Elimination of HCl can occur through H^+ abstraction by Cl^- from either the secondary amine of L_{N5} or one of the two remaining water molecules. An additional two water molecules are lost at 300 and 350°C, suggesting they are either strongly H-bonded to the complex or directly involved in the inner coordination sphere of the Dy^{3+} ion. No further decomposition of the complex was observed on additional heating to 600°C leaving the last chloride ion directly bound to the Dy^{3+} ion. (Consistent with this conclusion is the observation that the complex is a 2:1 elecrolyte in methanol, see later).

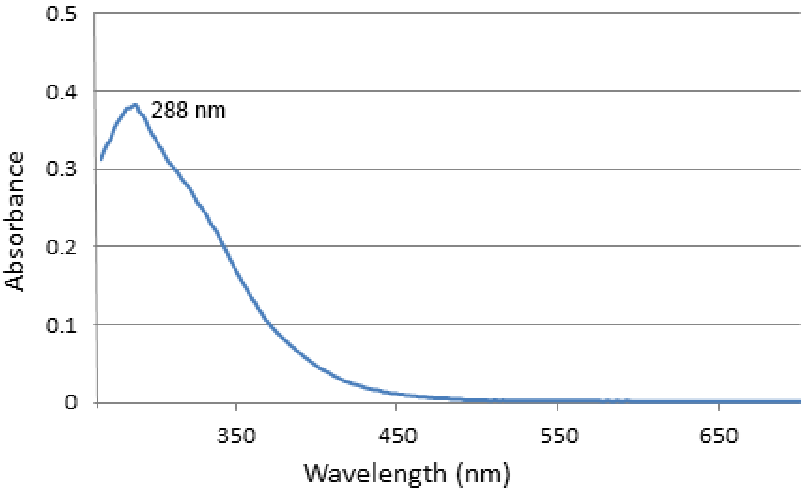


S-3: Spectroscopic and ESI mass spectrometry data for 1

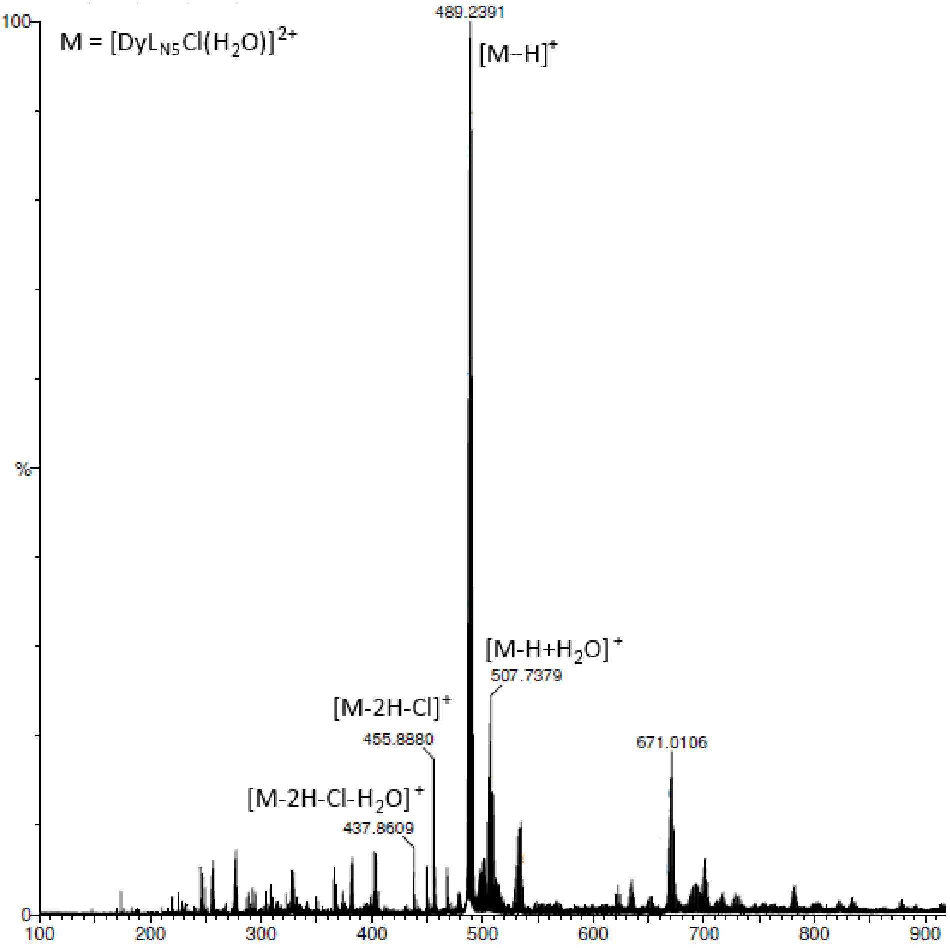
The IR spectrum of **1** shows a peak at 1629 cm^{-1} corresponding to imine (C=N) stretch, and the absence of a peak corresponding to C=O stretch, confirming that macrocyclization has occurred. The spectrum also exhibits medium-to-strong bands at *ca.* 1591 and 1452 cm^{-1}, consistent with the two highest-energy pyridine-ring vibrations of the coordinated pyridine ring. It is worth noting that the lack of a ν(C=O) at 1690 cm^{-1} eliminates the possibility that the complex comprises of an open chain potentially ocatadentate ligand, that was observed for cyclo-condenstation reactions in the presence of Sr^{2+} and Ba^{2+} ions. A very broad absorption band is also present at 3345 cm^{-1} consistent with the presence of both lattice and co-ordinated water molecules. In addition, the strong absorption at 530 cm^{-1} is assigned to the rocking mode of water most likely H-bonded to uncoordinated ether or NH groups.[3] Two ν(N-H) bands at 3200 - 3400 cm^{-1} are also consistent with the presence of a mononuclear Schiff-base complex of this macrocycle.[3]



The UV-vis spectrum of **1** shows **λ_{max} at 288 nm (ε = 3820), corresponding to the π-to-π* electronic transition of the macrocyclic ligand.**



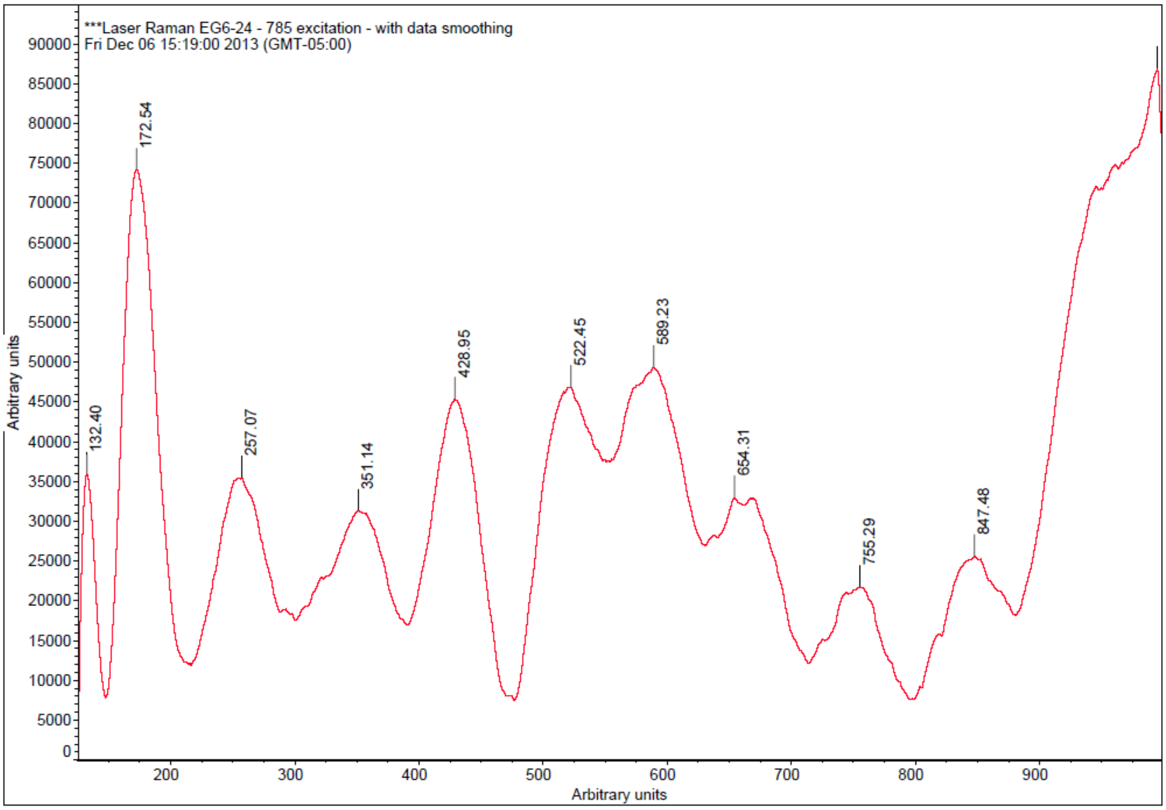
The ESI mass spectrum of **1** shows **a** peak at *m/z* = 489 (100%) corresponding to the complex $[DyL_{N5}Cl(H_2O)]^{2+}$ minus a proton: $[M-H]^+$. That is, **1** has lost its chloride counterions and 3 lattice water molecules. There are also peaks at *m/z* = 456 and 438 corresponding to the loss of coordinated chlorine ($[M-2H-Cl]^+$) and coordinated water ($[M-2H-Cl- H_2O]^+$) respectively. It should be noted that there is no evidence in the mass spectrum to support the formation of a larger [2:2]complex.[4]



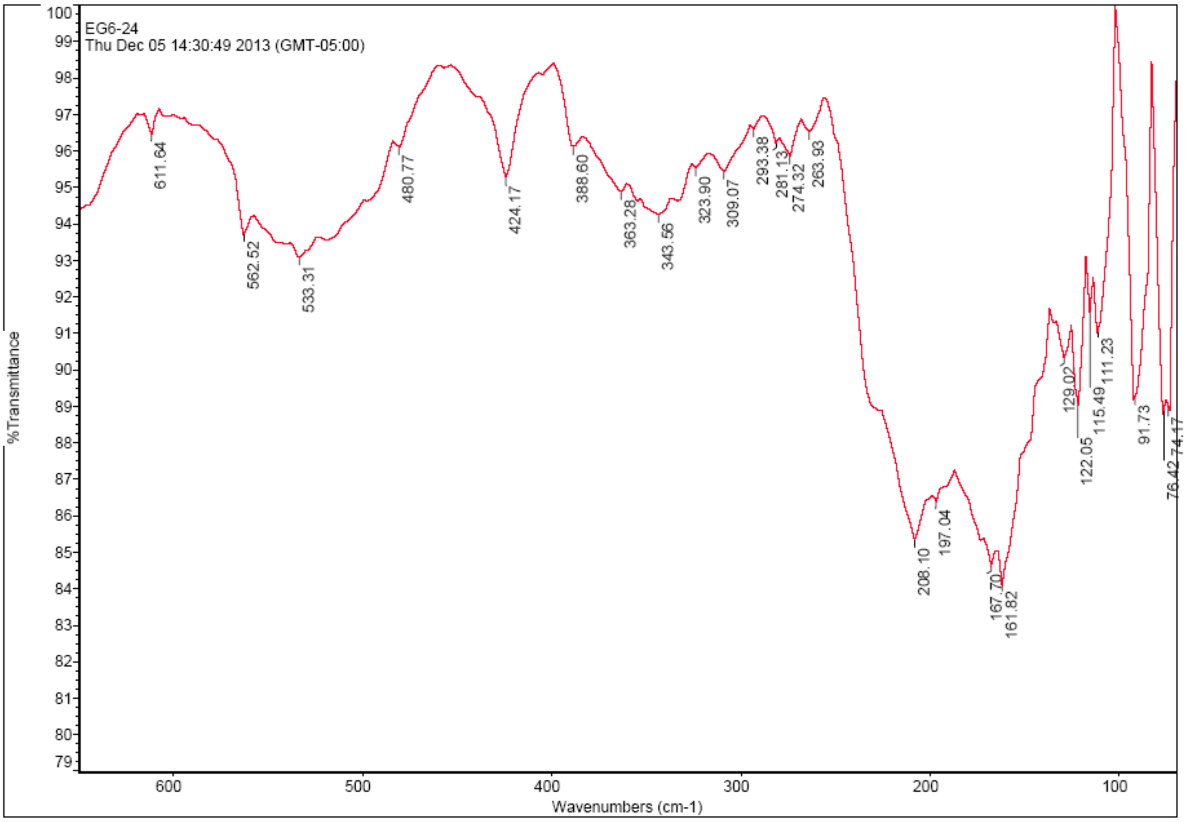
S-4: Far-IR and Raman spectroscopic studies

The medium-intensity far-IR band at 208 cm^{-1} and the strong Raman peak at 257 cm^{-1} for complex **1** are assigned[5] to the stretching vibration of the terminal Dy^{III}-Cl bond, $\nu(Dy\text{-}Cl)_t$. Few reliable studies on low-frequency IR and Raman spectra of complexes containing lanthanide(III)-chloride bonds have been made.[5,6] The frequencies of the observed bands/peaks are indicative of 7- or 8-coordinate complexes.[5] For example, the far-IR spectrum of the 8-coordinate complex $[DyCl_2(H_2O)_6]Cl$ exhibits the $\nu_{as}(Dy\text{-}Cl)_t$ and $\nu_s(Dy\text{-}Cl)_t$ bands at 219 and 162 cm^{-1}, respectively; the corresponding Raman peaks appear at 243 and 169 cm^{-1}.[5] The far-IR spectrum of complex $[DyCl_3(LH_2)]$ (where LH_2 is the tetradentate Schiff base diethyl(ethylenebis-β-aminocrotonate), for which a 7-coordinate geometry has been proposed for the Dy^{III} center, shows the $\nu(Dy\text{-}Cl)_t$ bands in the 230-240 cm^{-1} region. Ln-O bonds are more difficult to assign from far-IR and Raman studies, but the Raman peaks corresponding to the ν(Ln–O) stretching modes for $[DyCl_2(H_2O)_6]Cl$ are observed in the form of a complex contour at about 290–360 cm^{-1},[5a] which is observed between 300 and 380 cm^{-1} for complex **1**.

Raman spectrum of **1**



Far IR spectrum of **1**



S-5 Molar conductivity data

Conductivity measurements were carried out using an Oakton CON 6+ Handheld Conductivity Meter with cell constant K = 1. The probe was calibrated using standard solutions of KCl at 20°C. A methanolic 0.5 mM solution of the complex (30.7 mg (0.005 mol) of sample in 100 mL of MeOH) were prepared, and measurements were obtained in triplicate with precision < 1%.

$G_{ave} = 80.2\ \mu S$

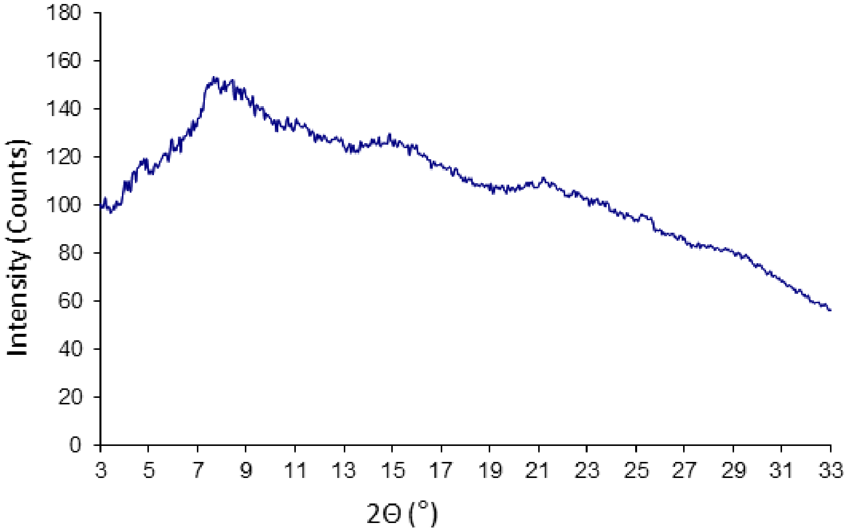
$\kappa = G \cdot K = 80.2\ \mu S \cdot 1\ cm^{-1} = 80.2\ \mu S \cdot cm^{-1}$

$\Lambda_M = \kappa/c = 80.2\ \mu S \cdot cm^{-1} \cdot 1\ L/0.0005\ mol \cdot 1000\ cm^3/1\ L = 160.4\ S \cdot cm^2 \cdot mol^{-1}$

Following the methodology of Geary[7] which has been extensively applied to determine the electrolyte nature of this class of macrocyclic complexes in solution, the value of 160.4 $S \cdot cm^2 \cdot mol^{-1}$ in methanol is consistent with a 2:1 electrolyte solution.

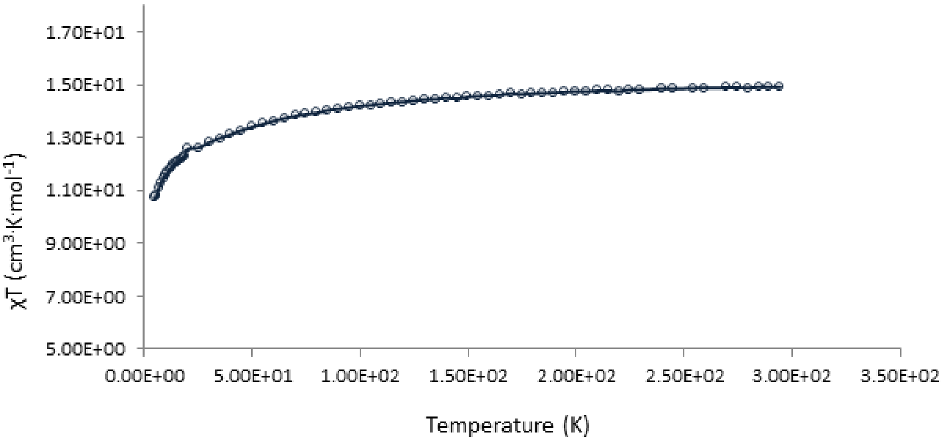
S-6: PXRD data for 1

Powder X-ray diffraction experiments on **1** were undertaken on a Bruker D8 Discover powder diffractometer equipped with a Hi-Star detector and GADDS software package. Data were collected at room temperature in the range $2.5 < 2\theta < 33.5^{o}$, and were recorded in 0.05^{o} steps using Cu-Kα_1 radiation ($\lambda = 1.54187$ Å) with the tube operating at 40 kV and 40 mA with an initial beam diameter of 0.5 mm. No well-resolved features were detected out to 33.5^{o} confirming the amorphous nature of **1**.



S-7: Dc magnetic susceptibility data for 1

Dc magnetic susceptibility measurements were performed using a Quantum Design SQUID magnetometer MPMS, at an applied field of 0.1 T, from 5 – 300 K. A high-temperature $\chi_M T$ value of 14.9 $cm^3 \cdot mol^{-1}$ was observed, consistent with the theoretical value of 14.17 $cm^3 \cdot mol^{-1}$ for a Dy^{3+} ion ($^6H_{15/2}$).

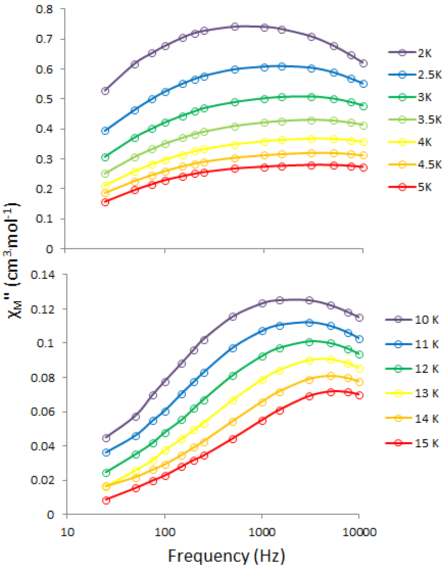


S-8: Additional ac susceptibility data for 1

Ac measurements were carried out using a Quantum Design PPMS, with an oscillating field of 3.5 Oe over 17 frequencies between 10 and 10,000 Hz, from 2 – 15 K.

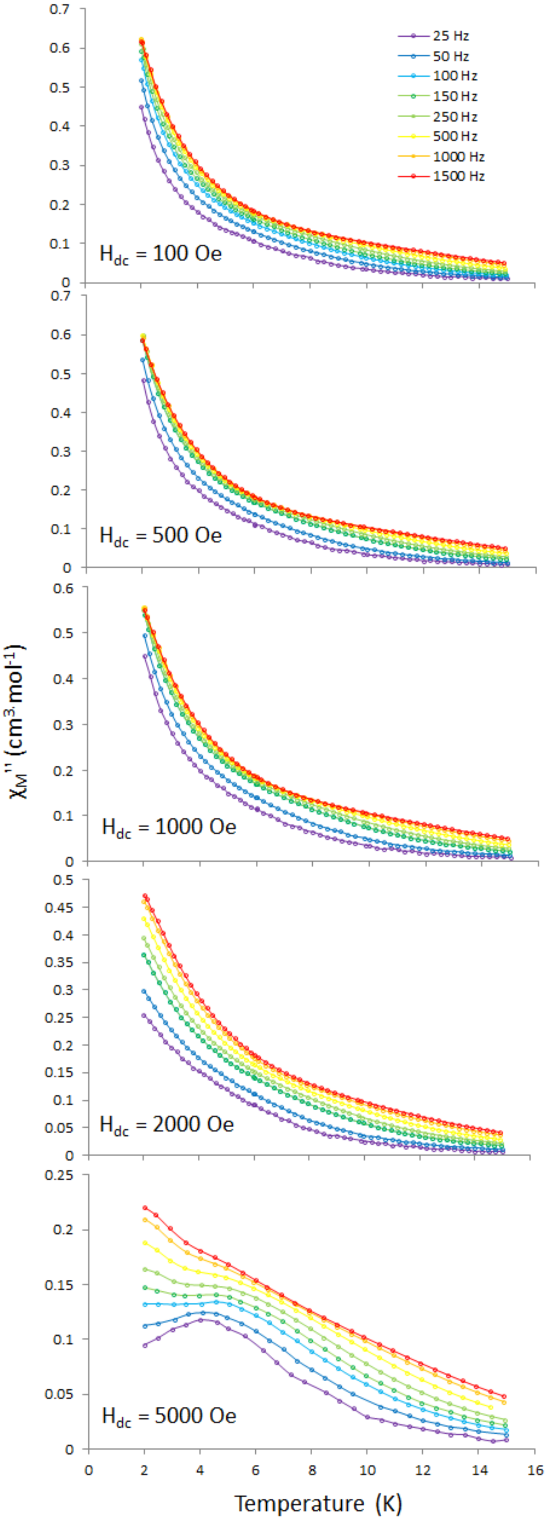
χ_M'' vs. ν plots for 1

χ_M'' vs. frequency plots in zero applied field from 2-5 K (top) and 10-15 K (bottom) show the frequency-dependent susceptibility of **1**, characteristic of an SMM.



χ_M'' vs. T plots in various applied dc fields

χ_M'' vs. temperature plots in various static fields, showing that a fairly large applied dc field of 0.5 T is required to suppress quantum tunnelling and shift the χ_M'' maxima to higher temperatures, allowing the calculation of U_{eff} and τ_0.



Equations

The Cole-Cole model describes ac susceptibility as

$$\chi(\omega) = \chi_S + \frac{\chi_0 - \chi_S}{1 + (i\omega\tau_c)^{1-\alpha}}$$

Eqn. 1

where ω = 2πf, χ_0 is the isothermal (low frequency) susceptibility, χ_c is the adiabatic (high frequency) susceptibility, τ_c is the temperature-dependent relaxation time, and α is a measure of the dispersivity of relaxation times, with α = 0 reflecting a single Debye-like relaxation time and α = 1 reflecting an infinitely wide dispersion of τ_c values. Dividing Eqn. 1 into its real and imaginary parts gives:

$$\chi^{'} = \chi_S + \frac{(\chi_0 - \chi_S)}{2}\left\{1 - \frac{sinh[(1-\alpha)ln(\omega\tau_c)]}{cosh[(1-\alpha)\ln(\omega\tau_c)] + cos\left[{}^{1}/_{2}(1-\alpha)\pi\right]}\right\}$$

Eqn. 2

$$\chi^{''} = \frac{(\chi_0 - \chi_S)}{2}\left\{1 - \frac{sin\left[{}^{1}/_{2}(1-\alpha)\pi\right]}{cosh[(1-\alpha)\ln(\omega\tau_c)] + cos\left[{}^{1}/_{2}(1-\alpha)\pi\right]}\right\}$$

Eqn. 3

The Arrhenius equation, relating relaxation time τ_c to temperature T, is given by:

$$\tau_c = \tau_0 e^{U_{eff}/k_B T}$$

Eqn. 4

where τ_0 is the tunnelling rate and U_{eff} is the effective energy barrier.

S-9: References

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