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An oxide-bridged Dy–Re^V–Dy single-molecule magnet

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ABSTRACT

The reaction of diamagnetic *trans*-$[Re^V(O)_2(py)_4]NO_3$ with $[Ln(hfac)_3(H_2O)_2]$ (Ln = Dy, Y, Tb; $hfac^-$ = 1,1,1,5,5,5-hexafluoroacetylacetonate(1−)) in chloroform yields oxide-bridged, trinuclear $[Ln(hfac)_3(H_2O)–Re(O)_2(py)_4–Ln(hfac)_3(NO_3)]$ (**DyReDy**, **YReY**, **TbReTb**). The series is isostructural to a fluoride-bridged {Dy–Cr–Dy} complex previously reported (Dreiser et al., Chem. Sci. 3 (2012) 1024) but, notably, **DyReDy** exhibits frequency-dependent out-of-phase ac susceptibility (χ'') signals at higher temperatures than the chromium analogue. Magnetic investigations of a solid solution of Dy^{3+} in **YReY** reveal the presence of a small Dy–Dy exchange interaction in **DyReDy**.

1. Introduction

The discovery that magnetically isolated molecules can exhibit a meta-stable magnetization, yielding so-called single molecule magnets (SMMs) [1], has attracted much interest in the synthesis of polynuclear metal-ion complexes [2]. The origin of SMM behavior in most 3d-based polynuclear systems is the combination of a large spin ground state and an easy axis-type anisotropy, giving rise to an energy barrier for spin-reversal. In lanthanide(III) ions the ligand-field perturbations are much weaker than the inter-electronic repulsion to the extent that the orbital angular momentum in general is left unquenched [3]. This in combination with strong spin–orbit coupling gives rise to significant anisotropy and hence renders lanthanides promising building blocks for molecular magnetic materials. Several mononuclear lanthanide SMMs with very large spin-relaxation barriers have recently been realized [4]. Interestingly, fewer polynuclear 4f complexes have shown high relaxation barriers [5] and for mixed *n*d–4f complexes, only recently the first example having a barrier exceeding 100 K was reported [6a]. One major drawback resulting from the largely shielded 4f electrons in lanthanides is the presence of only weak exchange interactions in 3d–4f and 4f polynuclear complexes. Despite the small magnitude of these interactions, the magnetic properties can be strongly affected by even very weak interactions. The vast majority of the studied *n*d–4f complexes encompass alkoxides, phenolates or carboxylates as bridging ligands with only few examples of e.g. oxide or fluoride bridges. The scarcity of oxide-bridged systems is certainly related to the extreme basicity of oxide leading to hydroxide bridges or precipitation of lanthanide hydroxides. However, oxide ligands can effectively be stabilized by high-oxidation state transition metal ions. Recently, Pointillart et al. [7] reported on an oxide-bridged $Re^V_2Dy_2$ complex exhibiting SMM behavior owing to the strong magnetic anisotropy of the Dy^{3+} ions.

We recently reported a multi-technique study of a trinuclear, fluoride-bridged Dy^{III}–Cr^{III}–Dy^{III} (**DyCrDy**) complex [8]. This compound incorporates as bridge between the dysprosium ions, the *trans*-$[Cr^{III}F_2(py)_4]^+$ (py = pyridine) unit of structural similarity to *trans*-$[Re^V(O)_2(py)_4]^+$, which however, in contrast to the former, is diamagnetic (d_{xy}^2). Herein, we show that the reaction of *trans*-$[Re^V(O)_2(py)_4]NO_3$ with $[Dy(hfac)_3(H_2O)_2]$ affords a trinuclear, oxide-bridged Dy^{III}–Re^V–Dy^{III} cluster: $[Dy(hfac)_3(NO_3)(H_2O)–Re(O)_2(py)_4–Dy(hfac)_3(H_2O)]$ (**DyReDy**). Interestingly, **DyReDy** is isomorphous and isostructural with the *trans*-difluoridochromium(III) analogue (**DyCrDy**). This facilitates a magnetic analysis of the constituent dysprosium ions without the complicating effects of exchange interactions and the (small) magnetic anisotropy of Cr(III). Notably, we find that the magnetic properties of **DyReDy** can be described consistently by the same set of parameters as derived for **DyCrDy**.

2. Experimental

2.1. Synthesis

Trans-$[Re(O)_2(py)_4]I$ was prepared by boiling $ReO_2I(PPh_3)_2$ [9] in pyridine and $[Ln(hfac)_3(H_2O)_2]$ (Ln = Y, Tb, Dy) was synthesized

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according to a published method [10]. Chloroform was reagent grade (Lab-Scan, stabilized with EtOH, 1%). All other reagents were purchased from commercial sources and used without further purification. *Trans*-$[Re(O)_2(py)_4]NO_3$ was prepared from *trans*-$[Re(O)_2(py)_4]I$ by metathesis with $Pb(NO_3)_2$ in acetonitrile, filtration, and evaporation of the solvent at room temperature. $[Dy(hfac)_3(H_2O)_2]$ (100 mg, 0.12 mmol) was dissolved in $CHCl_3$ (2 mL) and added to a solution of *trans*-$[Re(O)_2(py)_4]NO_3$ (12 mg, 0.020 mmol) in $CHCl_3$ (2 mL) without stirring. The pale orange solution was left for 24 h to give bronze-orange colored needles of **DyReDy**, which were isolated by suction filtration and washed with chloroform. Yield: (15 mg) 38% based on Re. Identical procedures with similar yields were used to prepare **YReY** and **TbReTb** and dilutions of Dy^{3+} in **YReY**. These were all shown to be isostructural with **DyReDy** by powder X-ray diffraction experiments. *Anal.* Calc. (found) for $H_{28}C_{50}N_5O_{18}F_{36}Dy_2Re$ (**DyReDy**): C: 27.52% (27.53%), H: 1.29% (1.04%), N: 3.20% (3.15%). *Anal.* Calc. (found) for $H_{28}C_{50}N_5O_{18}F_{36}Y_2Re$ (**YReY**): C: 29.51% (29.47%), H: 1.39% (1.27%), N: 3.44% (3.43%). *Anal.* Calc. (found) for $H_{28}C_{50}N_5O_{18}F_{36}Tb_2Re$ (**TbReTb**): C: 27.61% (27.90%), H: 1.30% (1.13%), N: 3.22% (3.26%).

2.2. Crystallography

Single-crystal X-ray diffraction data were collected at 122 K on a Nonius KappaCCD area-detector diffractometer employing Mo Kα radiation (λ = 0.71073 Å) equipped with an Oxford Cryostreams low-temperature device. The structures were solved using direct methods (SHELXS97) and refined using SHELXL97 software package [11]. All non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were fixed as riding their parent atom in a fixed geometry. CCDC-867847 contains the supplementary crystallographic data for this paper. Table 1 summarizes the crystallographic data and refinement parameters. Powder X-ray crystallographic data were collected on a STOE Stadi-P powder diffractometer equipped with PSD-detector using Cu (1.54060 Å) radiation monochromated with curved germanium. Theoretical powder diffractograms were generated from the single crystal structure data by use of the software "Mercury CSD 3.0" from The Cambridge Crystallographic Data Center [12].

Table 1
Crystallographic data for **DyReDy**.

	DyReDy
Formula	$C_{50}H_{28}Dy_2F_{36}N_5O_{18}Re$
M_r (g mol^{-1})	2181.97
Color, shape	Orange, prisms
Crystal size/mm	0.315 × 0.056 × 0.054
Crystal system	monoclinic
Space group	*C*2/*c*
T/K	122
a (Å)	26.1531(18)
b (Å)	15.914(2)
c (Å)	18.7766(19)
V (Å^3)	7067.2(13)
β (°)	115.267(9)
Z	4
ρ_{calc} (g cm^{-3})	2.051
F (000)	4152
μ(Mo $K\alpha$) (mm^{-1})	3.96
θ range (°)	2.2–28.1
Reflections collected	147 297
Unique reflections	8546
Params/restraints	534/3
Reflections ($I > 2\sigma(I)$)	6142
Goodness-of-fit (GOF)	1.07
R_1[a] ($I > 2.00\sigma(I)$)	0.038
R_1[a] (all data)	0.067
wR_2[b] (all data)	0.097
Max/min $\Delta\rho$ (e Å^{-3})	2.30/−1.66

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

2.3. Magnetic measurements

Magnetization measurements were performed on a Quantum-Design MPMS-XL SQUID magnetometer equipped with a 50 kOe dc magnet. Dc measurements were conducted in an applied field of 1000 Oe. Ac susceptibility was measured with frequencies in the range of 1–1500 Hz, in an ac field amplitude of 3.8 Oe and with or without small static (dc) fields ($H_{dc} \leqslant 5000$ Oe). All measurements were performed on polycrystalline samples immobilized in frozen *n*-eicosane matrices to prevent orientation of the crystallites in the field. The data were corrected for diamagnetic contributions form the sample (by Pascal constants), *n*-eicosane and sample holder (polycarbonate). Cluster magnetization curves were simulated by full diagonalization of the Hamiltonian in Eq. (1). The powder average was calculated by use of a 16-point Lebedev-Laikov grid [13]. The calculations were performed using a home-written Matlab® code.

3. Results and discussion

Addition of an excess of $[Dy(hfac)_3(H_2O)_2]$ (hfac$^-$ = 1,1,1,5,5,5-hexafluoroacetylacetonate(1−)) in chloroform to a solution of *trans*-$[Re^V(O)_2(py)_4]NO_3$ in chloroform affords orange needles of **DyReDy**. No polynuclear ensembles incorporating *trans*-$[Re^V(O)_2(py)_4]^+$ or derivatives are found in the literature. The coordination of *trans*-$[Re^V(O)_2(py)_4]^+$ to Dy^{III} may seem surprising taking into account the positive charge and, especially, the Re^V that effectively reduces the basicity of the oxido ligand by π-donation from the oxide to Re^V. However, on mixing of the two precursors a distinct color shift is observed suggesting association also in solution. Analysis of X-ray diffraction data obtained on a single-crystal reveals that **DyReDy** crystallizes in the monoclinic space group *C*2/*c*. The Re–O distance of 1.767(3) Å is in between the two different Re–O distances (1.74 and 1.79 Å) determined for *trans*-$[Re^V(O)_2(py)_4]Cl\cdot 2H_2O$ [14]. The Dy–O–Re bridging angle is 176.79(19)° thus showing that the preference for linear bridging in isoelectronic fluoride is also present for oxide [15]. The coordination sphere of Dy1 consists of three hfac$^-$ ligands and one bidentate nitrate ion which is engaged in hydrogen bonding to a water molecule coordinated at Dy2 in a neighboring molecule. This gives rise to an infinite chain of trinuclear units connected by N–O···H–O hydrogen bonds exactly as observed in **DyCrDy**. As evidenced by powder X-ray diffraction (see Supporting information), isostructural compounds are obtained by using $[Y(hfac)_3(H_2O)_2]$ (yielding **YReY**) or $[Tb(hfac)_3(H_2O)_2]$ (yielding **TbReTb**) as starting materials. (See Fig. 1).

The field-dependent magnetization of **DyReDy** at 1.8 K is shown in Fig. 2, left. At the maximum field of 5 T, the moment reaches 10.5 μ_B which is significantly less than the expected $2g_JJ = 2 \times 4/3 \times 15/2 = 20\ \mu_B$ from the $^6H_{15/2}$ term predicted by Hund's rules, indicative of strong magnetic anisotropy. The static magnetic susceptibility ($\chi = M/H$ with H_{dc} = 1 kOe) is shown in the right part of Fig. 2. The high-temperature value of the χT product is 27.5 cm^3-K mol^{-1} which is in good agreement with the value expected for two uncorrelated Dy^{3+} ions ($J = 15/2$, $g_J = 4/3$, $C = 14.17$ cm^3-K mol^{-1}). When the temperature is lowered the progressive thermal depopulation of excited ligand field states gives rise to the decrease of the χT product. At 10 K, the χT goes through a plateau, and below it drops more steeply at the lowest temperatures. For comparison with the related **DyCrDy** cluster, the Dy-only part of the χT product of **DyCrDy** is plotted as obtained by subtracting