

Trigonal bipyramidal 5d–4f molecules with SMM behavior†

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A family of trigonal bipyramidal (TBP) 5d–4f cyanide bridged aggregates were synthesized that exhibit slow relaxation of the magnetization below 4 K as indicated by a signal in the out-of-phase ac susceptibility data under zero field.

Single Molecule Magnets (SMMs) are a remarkable class of molecules that display magnetic bistability of molecular origin.¹ An increasing body of evidence is emerging from research on the topic that collectively supports the contention that such molecules hold excellent potential for use as memory storage units of nanometer size,² carriers of quantum bits of information³ and components of spintronic devices.⁴ The main challenge from a technological perspective is how to improve the properties of SMMs, specifically to increase the energy barriers and blocking temperatures in order to reach the limit for practical applications. Recent trends in the field include a focus on increasing magnetic anisotropy as opposed to spin in order to achieve these goals.⁵ In this vein, lanthanide and actinide ions are of special interest due to their large spin states and strong single ion anisotropies. The recognition of SMM behavior for rare earth molecules began with the observation of blocking temperatures up to 40 K for double decker lanthanide complexes by Ishikawa and coworkers.⁶ Subsequent efforts in the community have been directed at understanding and improving SMM behavior in complexes with a single lanthanide ion by controlling the crystal field environment.⁷ Leading examples were reported including organometallic lanthanide complexes^{7d,e} as well as various actinide molecules.^{5a,7i,j,8}

Apart from the importance of strong Ising-type anisotropy, recent studies have revealed that the role of exchange interactions between 4f metal centers is also an important factor.⁹ It is also worth noting that many fascinating 4f homo- and hetero-metallic

polynuclear SMMs have been reported recently including Dy₃ triangles with an unusual toroidal non-magnetic ground state that nevertheless exhibit SMM behavior through an excited state mechanism,¹⁰ as well as Dy₅ pyramids,¹¹ 3d–4f TBP,¹² 3d–4f octahedral,¹³ and 5d–4f dinuclear aggregates.¹⁴

As part of our research program in the magnetism of heavier transition metal cyanide compounds, we investigated the incorporation of Re(II) and Ln(III) ions into new cyanide-bridged 5d–4f aggregates in which the [triphosRe(CN)₃][−] building block was used to enforce 3-fold symmetry which is essential to preserve anisotropy in the final cage topology. Herein we report the a new family of trigonal bipyramidal (TBP) compounds (Et₄N)₂[(triphosRe(CN)₃)₂-(Ln(NO₃)₃)₃]-4CH₃CN (1–3) (Ln = La, Tb and Dy). The terbium and dysprosium derivatives exhibit the beginning of out-of-phase signals under zero applied field.

Reactions of (Et₄N)[triphosRe(CN)₃] with Ln(NO₃)₃·6H₂O in CH₃CN produce orange crystals of the target compounds. Single crystal X-ray data revealed that the main structural unit is a trigonal bipyramidal dianion with two Re(II) ions in the apical positions linked *via* cyanide ligands to three lanthanide complex fragments in the equatorial positions. Three nitrate anions act as bridges between the lanthanide ions in the plane whereas two additional nitrate anions coordinate to each lanthanide ion in a O,O chelating mode above and below the plane (Fig. 1). The shortest intramolecular and intermolecular Ln1–Ln2 distances are 5.160 Å and 11.098 Å respectively.

Infrared spectral studies of the compounds confirm the presence of bridging cyanide ligands with $\nu(\text{CN})$ stretches at 2072 and 2090 cm^{−1} (1), 2085 and 2101 (2), and 2086, 2103 cm^{−1} (3) which are at higher energies than the Re(II) precursor.¹⁵

Magnetic susceptibility measurements in the DC mode were performed on crushed single crystals with a Quantum Design MPMS-XL SQUID magnetometer operating from 1.8–300 K at 1000 G. AC magnetic susceptibility measurements were performed on the same sample with an oscillating field of 5 Oe. The room temperature χT value of 1.48 emu K mol^{−1} for 1 (Fig. 2) is in a good agreement with 2 isolated Re(II) ions with one unpaired electron each ($C = 0.66$ emu K mol^{−1}) and ($\chi_{\text{TBP}} = 2.49 \times 10^{-3}$).

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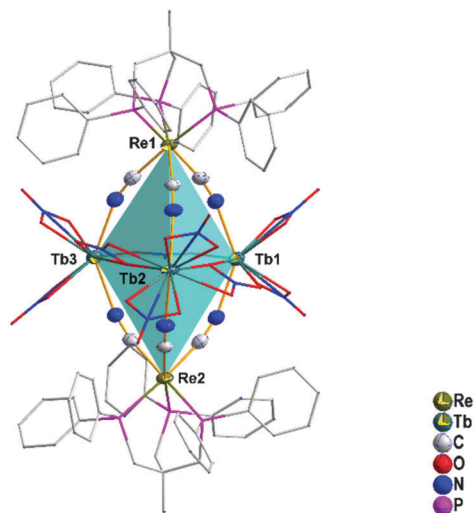


Fig. 1 Molecular structure of $[(\text{triphosRe}(\text{CN})_3)_2(\text{Tb}(\text{NO}_3)_3)_3]^{2-}$ in **(2)**. Hydrogen atoms were omitted for clarity.

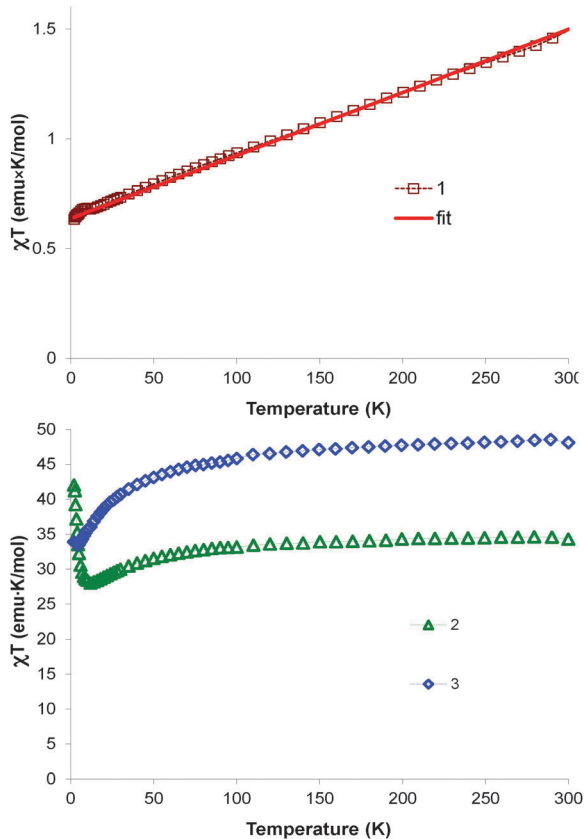


Fig. 2 Temperature dependence of the χT product for **1** (\square), **2** (Δ) and **3** (\diamond). Red solid line corresponds to the fit using PHI for **1**.

Magnetic susceptibility data for **1** were fitted using PHI¹⁶ and found to be dominated by a large temperature independent paramagnetism (TIP) of the Re(II) ions ($g = 1.88$, $\chi_{\text{TIP}} = 2.49 \times 10^{-3}$) which had been previously documented for the Re(II) precursor.¹⁵ The room temperature χT value of $34.4 \text{ emu K mol}^{-1}$ for **2** is in accord with two Re(II) ions ($S = 1/2$, $g = 1.9$) and three Tb(III) ions

($g = 1.45$, $J = 6$) and ($\chi_{\text{TIP}} = 4.0 \times 10^{-3}$) ($C = 33.8 \text{ emu K mol}^{-1}$). The χT slowly decreases as the temperature is lowered and then increases to a maximum of $42 \text{ emu K mol}^{-1}$ at 2 K. The Weiss constant is -5 K . The room temperature χT value of $47.6 \text{ emu K mol}^{-1}$ for **3** is in good agreement with two Re(II) ions ($S = 1/2$, $g = 1.9$) and three Dy(III) ions ($g = 1.4$, $J = 15/2$) and ($\chi_{\text{TIP}} = 4.5 \times 10^{-3}$) ($C = 47 \text{ emu K mol}^{-1}$). As in the case of **2**, the χT values for **3** gradually decrease at lower temperature and then slightly increase to a maximum of $33.4 \text{ emu K mol}^{-1}$ at 2 K; the Weiss constant is -5.5 K . This decrease in χT values at lower temperatures may be a consequence of the depopulation of excited m_j sublevels of the Tb(III) and Dy(III) ions as well as weak antiferromagnetic exchange interactions between the Ln(III) and Re(II) metal spins. The magnetization *versus* field data of **1** (Fig. S1, ESI[†]) are consistent with the presence of two independent $S = 1/2$ Re(II) ions as expected. The lack of saturation even at 7 T ($1.7 \mu_B$) is not surprising given the anisotropic nature of these ions. The magnetization *versus* field data of **2** (Fig. S3, ESI[†]) exhibit a fast increase in slope below 0.6 T followed by a slow increase up to $15.1 \mu_B$ at 7 T which is consistent with three independent Tb(III) ($3 \times 4.5 \mu_B$) and two independent Re(II) magnetic spin centers ($1.7 \mu_B$). The field dependence of the magnetization data at temperatures between 2 and 4.5 K show a non-superposition of the iso-field lines indicating the presence of significant anisotropy (Fig. S3, ESI[†]). Similar behavior was observed for **3** (Fig. 3 inset) with a maximum of $19.2 \mu_B$ at 7 T. This value is

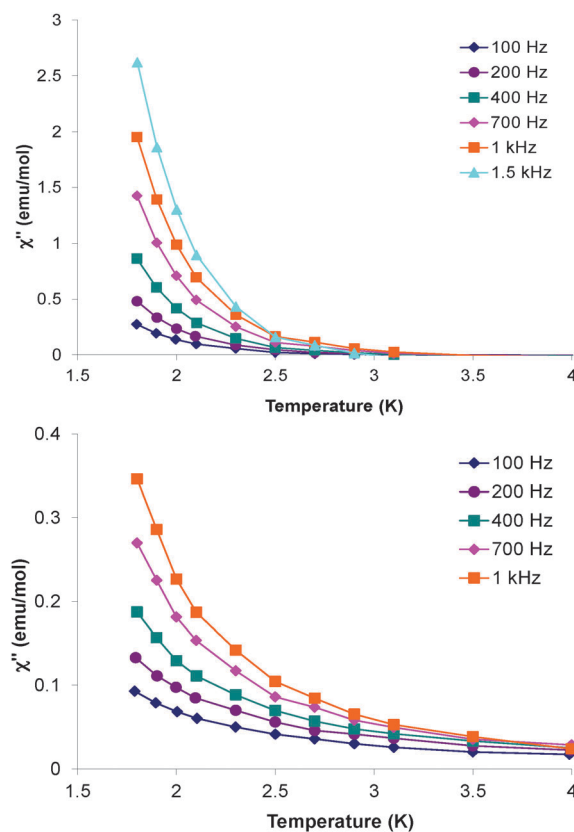


Fig. 3 Temperature dependence of the out-of-phase AC susceptibility data for **2** (top) and **3** (bottom) under zero-dc field.

consistent with three uncorrelated Dy(III) ($3 \times 5.23 \mu_B$) and two uncorrelated Re(II) magnetic centers.

Given the anisotropic nature of the compounds **2** and **3**, the AC susceptibility studies were performed which revealed the beginning of an out-of-phase signal χ'' for both compounds below 4 K in the absence of an applied field (Fig. 3). These data support the existence of slow relaxation of the magnetization characteristic of SMM behavior although no obvious maxima appear above 1.8 K. This is nonetheless a notable result because it is quite unusual to obtain AC signals in the absence of a DC applied field for lanthanide SMMs. The energy barriers and relaxation times were approximated using a method recently employed by Bartolome *et al.*¹⁷ based on the following equation:

$$\ln\left(\frac{\chi''}{\chi'}\right) = \ln(\omega\tau_0) + E_a/k_B T$$

The calculated energy barrier of **2** was found to be 8.5 cm^{-1} whereas the relaxation time is $1.51 \times 10^{-8} \text{ s}$. Efforts to obtain more relaxation data and to observe maxima by applying a field led only slight enhancement of the out-of-phase signal with an energy barrier of $\sim 6 \text{ cm}^{-1}$ under a 1000 Oe applied field. For **3** the energy barrier at zero field was found to be 2.9 cm^{-1} and τ_0 is $6 \times 10^{-7} \text{ s}$. Similarly, applying a 1000 Oe DC field did not lead to appreciable changes in the out-of-phase signal (4.24 cm^{-1} , $\tau_0 = 7.36 \times 10^{-7} \text{ s}$), but the appearance of a second relaxation event was noted.

In summary, a new type of 5d–4f cyanide bridged aggregate is reported with two members of the new family exhibiting slow relaxation of the magnetization below 4 K. Efforts to extend the series to other lanthanides and to tune the co-ligands in this family of compounds are underway.

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