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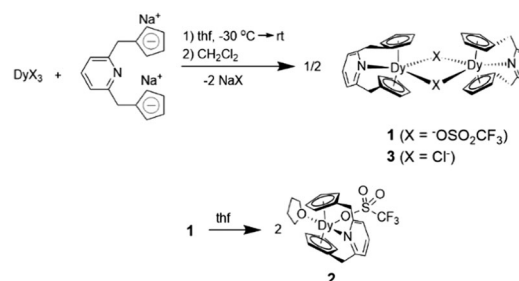
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A comparative study of magnetization dynamics in dinuclear dysprosium complexes featuring bridging chloride or trifluoromethanesulfonate ligands†

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We utilized a rigid ligand platform PyCp_2^{2-} ($\text{PyCp}_2^{2-} = [2,6-(\text{CH}_2\text{C}_5\text{H}_3)_2\text{C}_5\text{H}_3\text{N}]^{2-}$) to isolate dinuclear Dy^{3+} complexes $[(\text{PyCp}_2)\text{Dy}(\mu\text{-O}_2\text{SOCF}_3)_2]$ (**1**) and $[(\text{PyCp}_2)\text{Dy}(\mu\text{-Cl})_2]$ (**3**) as well as the mononuclear complex $(\text{PyCp}_2)\text{Dy}(\text{OSO}_2\text{CF}_3)(\text{thf})$ (**2**). Compounds **1** and **2** are the first examples of organometallic Dy^{3+} complexes featuring triflate binding. The isolation of compounds **1** and **3** allows us to comparatively evaluate the effects of the bridging anions on the magnetization dynamics of the dinuclear systems. Our investigations show that although the exchange coupling interactions differ for **1** and **3**, the dynamic magnetic properties are dominated by relaxation via the first excited state Kramers doublet of the individual Dy sites. Compounds **1** and **3** exhibit barriers to magnetization reversal ($U_{\text{eff}} = 49 \text{ cm}^{-1}$) that can be favorably compared to those of the previously reported examples of $[\text{Cp}_2\text{Dy}(\mu\text{-Cl})_2]$ ($U_{\text{eff}} = 26 \text{ cm}^{-1}$) and $[\text{Cp}_2\text{Dy}(\text{thf})(\mu\text{-Cl})_2]$ ($U_{\text{eff}} = 34 \text{ cm}^{-1}$).

Highly paramagnetic molecules featuring intrinsic magnetic anisotropy can display slow magnetic relaxation as well as magnetic hysteresis. The development of such single-molecule magnets (SMMs) could allow the manufacture of high density spin-based quantum memory¹ or spin qubit devices.² The large magnetic anisotropy of trivalent lanthanide ions has resulted in lanthanide-based SMMs with significant energy barriers to magnetization reversal (U_{eff})³ and improved blocking temperatures.⁴ Organometallic lanthanide complexes are a very important class of lanthanide-based SMMs and include fascinating examples of single ion magnets such as $\text{Er}(\text{COT})_2^{5-}$ and $\text{Cp}^*_2\text{Dy}(\text{PhBPh}_3)$.⁶ In particular cyclopentadienyl anion type ligands are used to stabilize Dy^{3+} complexes and they continue to attract attention in this regard. Examples of magnetically investigated $\text{Cp}^R\text{-Dy}$ type complexes include dinuclear Dy^{3+} complexes with bridging



Scheme 1 Synthesis of compounds **1**, **2**, and **3**.

closed-shell ligands (such as Cl^- ,⁷ $\text{CpFe}(\text{CO})_2^-$,⁸ and SSiPh_3^-)⁹ as well as radical ligand sets (bpym¹⁰ and tppz¹¹). The subtle interplay between coordination geometry and ligand donor effects and their resulting effects on the magnetization dynamics are the subject of current research and systematic experimental comparative studies are of high importance in this regard.

We were interested in utilizing the structurally rigid PyCp_2^{2-} ligand ($\text{PyCp}_2^{2-} = [2,6-(\text{CH}_2\text{C}_5\text{H}_3)_2\text{C}_5\text{H}_3\text{N}]^{2-}$) for the development of novel lanthanide platforms and the investigation of their magnetic properties. Specifically, we aimed to prepare discrete triflate complexes of Dy^{3+} which were previously not structurally or magnetically characterized. Herein we report the structural characterization and magnetic properties of two new dinuclear Dy^{3+} complexes featuring either bridging $^- \text{OSO}_2\text{CF}_3$ ($[(\text{PyCp}_2)\text{Dy}(\mu\text{-O}_2\text{SOCF}_3)_2]$ (**1**)) or Cl^- ligands ($[(\text{PyCp}_2)\text{Dy}(\mu\text{-Cl})_2]$ (**3**)) as well as the mononuclear complex $(\text{PyCp}_2)\text{Dy}(\text{OSO}_2\text{CF}_3)(\text{thf})$ (**2**) (Scheme 1).

Compound **1** can be prepared via the reaction of anhydrous $\text{Dy}(\text{OSO}_2\text{CF}_3)_3$ with the disodium salt PyCp_2Na_2 and subsequent work up (see the ESI†).¹² Single crystals of **1** can be obtained by crystallization from CH_2Cl_2 /hexane solvent mixtures. Dissolution of **1** in thf and crystallization from thf/hexane solvent mixtures results in a crystalline material of monomeric **2**. A dinuclear chloride-bridged complex **3** is obtained by the reaction of DyCl_3 with PyCp_2Na_2 in thf and subsequent extraction into CH_2Cl_2 and recrystallization. It is important to note that the analogous reaction

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of two equivalents of NaCp with DyCl_3 was previously reported to yield the desired dinuclear $\mu_2\text{-Cl}$ bridged product only as a mixture with a polymeric species after sublimation.⁷ Clearly, the intramolecular pyridine moiety blocks the formation of a polymeric side product and allows for a more facile access to the desired dinuclear complexes. In contrast to **1**, **3** does not dissociate in thf and a crystalline material of **3(thf)** was obtained. Thus, the triflate anions in **1** are more labile leaving groups than the chloride ions in **3**.

The molecular structures of neutral compounds **1**, **2**, and **3** were investigated by means of single crystal X-ray diffraction studies (Fig. 1, Tables S1 and S2, ESI†). The Dy^{3+} ions in all three structures have a ligand bond number of nine, with bonds to two Cp and one pyridine moiety and two additional ligands. In complexes **1**, **2**, and **3** the average Dy–C distances (2.63[1] Å, 2.628[2] Å, and 2.64[1] Å, respectively) and the Dy–N distances (2.554[9] Å, 2.538(2) Å, and 2.581(9) Å, respectively) are fairly comparable for the two triflate complexes **1** and **2** and are only slightly longer in the chloride bridged dimer **3**. The Dy–Cl distances in **3** (2.683(3) Å and 2.785(3) Å) are much longer than the Dy–O distances in **1** (2.338[9] Å and 2.346[8] Å) and **2** (Dy–O^{thf} = 2.456(1) Å and Dy–O^{OTf} = 2.335(1) Å).

For dinuclear complexes **1** and **3**, the relative orientation of the pyridine moieties on each Dy^{3+} ion to each other could result in *cis* or *trans* geometries. As has been noted previously for closely related lanthanide PyCp_2^{2-} complexes, the solid structure of **1** and **3** solely displays the *trans* isomer even though *cis* and *trans* isomers can readily interconvert as suggested by variable temperature NMR solution studies.¹²

The two bridging chloride ligands in **3** allow for an intramolecular Dy...Dy distance of 4.252(1) Å whereas the larger

bridging triflate ligands in **1** result in larger Dy...Dy distances of 6.068[1] Å. The very tight crystal packing in crystals of **2** (Fig. S1, ESI†) results in close intermolecular Dy...Dy distances of 6.541(1) Å. This close intermolecular proximity likely results in intermolecular interactions leading to weak intermolecular magnetic coupling as well as enhanced quantum tunnelling of the magnetization (*vide infra*) for **2**.

The static magnetic properties of complexes **1–3** were investigated by means of variable temperature direct current (dc) magnetometry using an applied field of 1000 Oe (Fig. 2). The room temperature $\chi_{\text{M}}T$ values of 27.90, 13.52, and 26.99 emu K mol^{−1} obtained for **1**, **2**, and **3**, respectively, are in good agreement with the expected values of 28.34 emu K mol^{−1} and 14.17 emu K mol^{−1} for di- and mononuclear Dy^{3+} complexes (⁶H_{15/2}, *S* = 5/2, *L* = 5, and *g* = 4/3). All complexes display decreases in their respective $\chi_{\text{M}}T$ values upon lowering the temperature with a more significant decrease at low temperatures for **1** and **3**. Such a decrease in $\chi_{\text{M}}T$ values is typically observed and ascribed to the depopulation of the Stark sublevels of Dy^{3+} and/or possible magnetic interactions between Dy^{3+} centres (see the computational part).¹³ Surprisingly, complex **2** features a slight increase of $\chi_{\text{M}}T$ at very low temperatures (2 K) which may be indicative of intermolecular ferromagnetic coupling but this aspect was not further investigated.

Variable temperature magnetization vs. field measurements were carried out for **1** (Fig. S2, ESI†), **2** (Fig. S4, ESI†), and **3** (Fig. S6, ESI†). For all three complexes, magnetic saturation is approximately reached at 7 T. The magnetization values are significantly smaller than the expected free ion values (10 μ_{B} per Dy^{3+} ion). This observation is indicative of breaking the degeneracy of the ⁶H_{15/2} ground states by crystal/ligand field effects. Additionally, the *M* vs. *H/T* curves for complexes **1** (Fig. S3, ESI†), **2** (Fig. S5, ESI†), and **3** (Fig. S7, ESI†) are non-superimposable as a result of the magnetically highly anisotropic Dy^{3+} ion(s).

The magnetization dynamics of compounds **1–3** were probed by alternating current (ac) magnetometry. All three complexes display signals in the out-of-phase component (χ_{M}'') of the ac magnetic susceptibility in the absence of an externally applied dc field. The maximum of χ_{M}'' of complex **1** (Fig. 3; see Fig. S8 for χ_{M}') remains temperature independent at temperatures between 1.8 and 6 K. At a temperature of above 6 K the maxima of the χ_{M}'' signal become temperature dependent

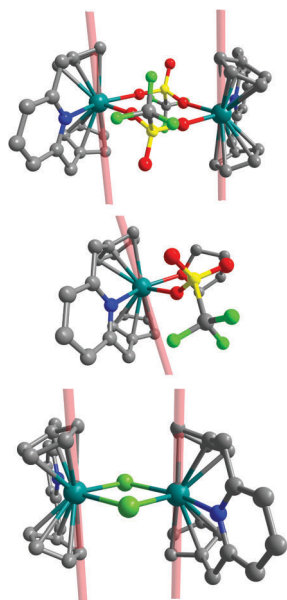


Fig. 1 Molecular structures of neutral dinuclear $[(\text{PyCp}_2)\text{Dy}(\mu_2\text{-O}_2\text{SO}_2\text{CF}_3)_2]$ (top), $[(\text{PyCp}_2)\text{Dy}(\mu_2\text{-Cl})_2]$ (bottom), and mononuclear $(\text{PyCp}_2)\text{Dy}(\text{OSO}_2\text{CF}_3)(\text{thf})$ (center) in crystals of **1**, **3**, and **2**, respectively. Teal = Dy, yellow = S, red = oxygen, blue = N, light green = F, green = Cl, and grey = C. Hydrogen atoms and co-crystallized solvent molecules have been omitted for clarity. The pink transparent lines indicate g_{zz} directions of the magnetic ground states.

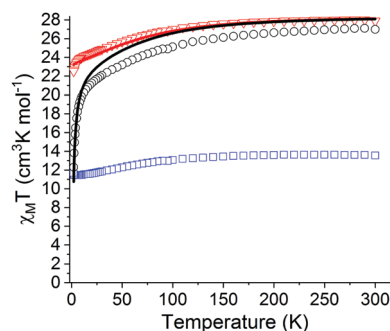


Fig. 2 Temperature dependence of $\chi_{\text{M}}T$ for **1** (red triangles), **2** (blue squares), and **3** (black circles) (1000 Oe; 2–300 K). The solid lines are fits of the data (see text).

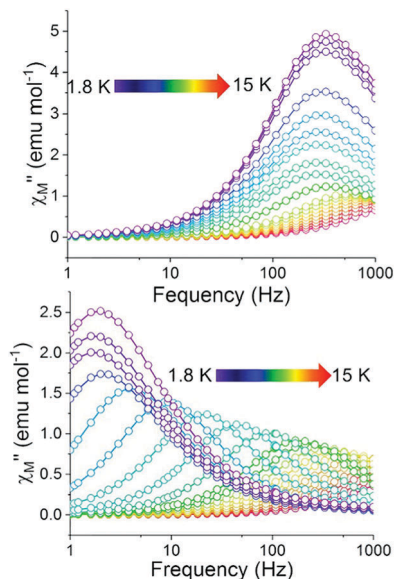


Fig. 3 Frequency dependence of the out-of-phase component (χ_M'') of the ac susceptibility of **1** (top) and **3** (bottom) at an applied dc field of 0 Oe in the temperature range of 1.8–15 K (2 Oe switching field).

and move to higher frequencies. The latter observation indicates the dominant quantum tunnelling of the magnetization (QTM) at low temperatures (<6 K) and a transition to a thermally activated process at higher temperatures. This transitional behaviour of the magnetization dynamics is qualitatively also observed for complexes **2** and **3**. For the mononuclear complex **2**, the signals in χ_M'' are observed at 0 Oe dc field, albeit at higher frequencies (Fig. S9 and S10, ESI†). Above 9 K, the χ_M'' maxima shift to frequencies beyond the 1 kHz instrument limit which prevents the extraction of an effective energy barrier to magnetization reversal (U_{eff}) (*vide infra*). Application of dc fields resulted in significant shifts of the χ_M'' maxima to lower frequencies (as compared to zero field measurements) which were clearly temperature dependent above 2.5 K. However, for all fields studied, we obtained ill-defined shoulders in the ac data which are indicative of the presence of multiple, overlapping relaxation pathways (see Fig. S11 and S12, ESI†). The variable temperature ac susceptibility of **3** (Fig. 3 and Fig. S13, ESI†) is well defined in the absence of dc fields. The maxima of χ_M'' remain temperature independent up to a temperature of 4 K (QTM) and become temperature dependent at higher temperatures.

Cole–Cole plots (χ_M'' vs. χ_M') corresponding to the above discussed ac magnetization data for complexes **1** and **3** are shown in Fig. S14 and S15 (ESI†), respectively. Quantitative relaxation times were extracted by fitting the data for each temperature using the generalized Debye model (solid lines in Fig. S14 and S15, ESI†) and used to construct the Arrhenius plots ($\ln \tau$ vs. $1/T$) as shown in Fig. 4. The barrier height U_{eff} was determined by fitting the linear temperature dependent part of the Arrhenius plots (the predominant Orbach relaxation mechanism). Interestingly, we obtained identical U_{eff} values for complexes **1** and **3** of 70 K (49 cm^{-1}) and pre-exponential factors τ_0 of $4.8 \times 10^{-7} \text{ s}$ and $7.2 \times 10^{-7} \text{ s}$, respectively. The non-linear dependence of

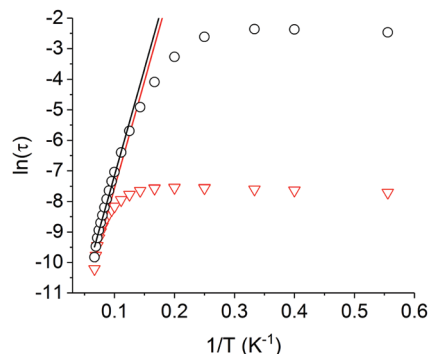


Fig. 4 Arrhenius plots of magnetization relaxation time data for **1** (red triangles) and **3** (black circles) in the zero dc field. The lines correspond to fits to the Arrhenius equation yielding $U_{\text{eff}} = 70 \text{ K}$ (49 cm^{-1}) and 70 K (49 cm^{-1}), and $\tau_0 = 4.8 \times 10^{-7} \text{ s}$ and $7.2 \times 10^{-7} \text{ s}$ for **1** and **3**, respectively.

τ at low temperatures of the Arrhenius plot is indicative of the presence of other relaxation pathways such as Raman and quantum tunnelling processes.¹⁴ The similarity in the magnetization dynamics of **1** and **3** is also confirmed by ac measurements performed for magnetically dilute (Dy:Y = 1: ~12) analogues which display almost identical temperature dependences of χ_M' and χ_M'' (Fig. S16–S19, ESI†).

These surprising findings were further investigated by means of *ab initio* calculations of the CASSCF/RASSI/SINGLE_ANISO type, using the MOLCAS 8.0 program.¹⁵ Both Dy sites of dinuclear complexes **1** and **3** were calculated separately by replacing one Dy^{3+} ion with a diamagnetic Lu^{3+} ion and displayed very similar properties (Table S3, ESI†). The ground state Kramers doublets (KDs) of the Dy^{3+} ions in all three complexes are predominantly $m_J = \pm 15/2$ in character with small contributions from $m_J = \pm 11/2$ (Fig. 5) with corresponding g_z values of 19.3, 18.8, and 19.1 for **1**, **2**, and **3**, respectively. The first excited state KDs of dinuclear complexes **1** and **3** are mostly $m_J = \pm 11/2$ in character whereas for mononuclear **2** a highly mixed doublet was calculated with contributions from $\pm 5/2$, $\pm 3/2$, and $\pm 1/2$ and others. The energies of the first excited state KDs for **1** and **3** are very similar (138 cm^{-1} and 134 cm^{-1}) and significantly higher than those of compound **2** (84 cm^{-1}). Based on the calculated probabilities for tunnelling, Raman, and Orbach processes (arrows in Fig. 5), we propose that the magnetic relaxation for all three complexes occurs *via* a thermally assisted quantum tunnelling of the magnetization (TA-QTM) process involving the first excited state. The calculated values of **1** and **3** are in very good agreement with the identical U_{eff} values determined experimentally and suggest that the magnetization dynamics in **1** and **3** are dominated by the single ion magnetic anisotropy. This point is further supported by the small magnetic coupling constants ($J_{\text{exch}} = +0.018 \text{ cm}^{-1}$ and -0.138 cm^{-1} ; $J_{\text{dipolar}} = +0.032 \text{ cm}^{-1}$ and 0.0892 cm^{-1}) which were calculated within the Lines model using the POLY-ANISO routine (fits in Fig. 2 and Tables S4, S5, ESI†).¹⁶ Interestingly, substitution of $-\text{OSO}_2\text{CF}_3$ by Cl^- (in going from **1** to **3**) results in a change from ferro- to antiferro-magnetic coupling ($J_{\text{total}} = 0.05 \text{ cm}^{-1}$ and -0.05 cm^{-1}) but the small magnitude is expected to significantly

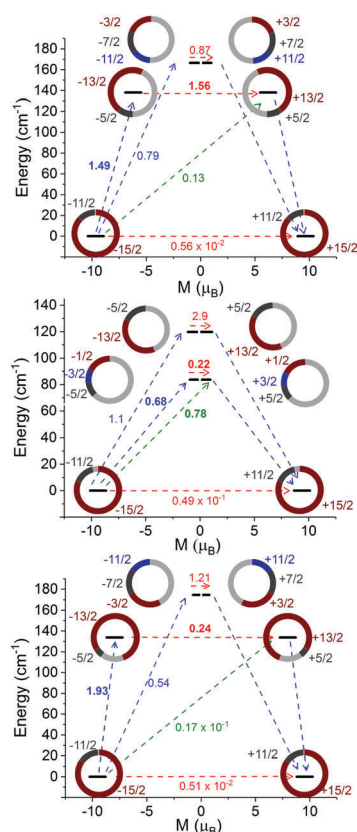


Fig. 5 Magnetization blocking barrier for single Dy sites in **1** (top), **2** (center), and **3** (bottom) computed *ab initio*. The black lines indicate KDs as a function of computed magnetic moments; green/blue and red arrows indicate pathways through Orbach/Raman relaxation and QTM/TA-QTM. The numbers on each arrow are the mean absolute values for the corresponding matrix element of the transition magnetic moment. The donut diagrams indicate the nature of the contributing m_J states to KDs (light grey = combined contributions of several other m_J states).

affect the magnetization dynamics only at much lower temperatures than the experimentally employed ones.

The sterically rigid, capping ligand PyCp_2^{2-} allowed for the isolation of the first structurally characterized $\mu\text{-O}_2\text{SOCF}_3$ bridged dinuclear Dy complex **1** which can readily dissociate into monomeric **2**. The “blocking” intramolecular pyridine moiety in PyCp_2^{2-} allows for the facile synthesis of the dinuclear $\mu\text{-Cl}$ bridged complex **3**. The easy access to **3** stands in contrast to the competing formation of polymeric $\mu\text{-Cl}$ bridged systems that were reported for bis-cyclopentadienyl Dy^{3+} complexes, and emphasizes the synthetic value of PyCp_2^{2-} for the formation of novel organometallic lanthanide complexes. All three complexes display a slow relaxation of their magnetization and compounds

1 and **3** exhibit the same effective barrier to magnetization reversal of 49 cm^{-1} . The surprising similarity is explained by computational results that suggest that the magnetic relaxation dynamics involves TA-QTM *via* the first excited state of the single Dy sites. We are currently investigating the reactivity of complexes **1** and **2** as the increased leaving group ability of triflate would be expected to allow for facile ligand substitution chemistry.

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