Assessing the exchange coupling in binuclear lanthanide(III) complexes and the slow relaxation of the magnetization in the antiferromagnetically coupled Dy$_2$ derivative†

Chun Y. Chow,$^a$ Hélène Bolvin,$^b$ Victoria E. Campbell,$^c$ Régis Guillot,$^c$ Jeff W. Kamp,$^a$ Wolfgang Wernsdorfer,$^d$ Frédéric Gendron,$^e$ Jochen Autschbach,$^n$ Vincent L. Pecoraro$^{bn}$ and Talal Mallah$^{mn}$

We report here the synthesis and the investigation of the magnetic properties of a series of binuclear lanthanide complexes belonging to the metallacrown family. The isostructural complexes have a core structure with the general formula [Ga$_2$Ln$_2$(shi$^2$)$_4$(H$_2$shi$^2$)$_2$]$_2$[C$_6$H$_5$N$_4$(CH$_3$OH)$_4$]$_2$·xC$_6$H$_5$N·xCH$_3$OH·xH$_2$O (where H$_2$shi = salicylhydroxamic acid and Ln = Gd$^{III}$, Tb$^{III}$, Dy$^{III}$, Er$^{III}$, Y$^{III}$). Apart from the Er-containing complex, all complexes exhibit an antiferromagnetic exchange coupling leading to a diamagnetic ground state. Magnetic studies, below 2 K, on a single crystal of 3 using a micro-squid array reveal an opening of the magnetic hysteresis cycle at zero field. The dynamic susceptibility studies of 3 and of the diluted DyY 6 complexes reveal the presence of two relaxation processes for 3 that are due to the excited ferromagnetic state and to the uncoupled Dy$^{III}$ ions. The antiferromagnetic coupling in 3 was shown to be mainly due to an exchange mechanism, which accounts for about 2/3 of the energy gap between the antiferro- and the ferromagnetic states. The overlap integrals between the Natural Spin Orbitals (NSOs) of the mononuclear fragments, which are related to the magnitude of the antiferromagnetic exchange, are one order of magnitude larger for the Dy$_2$ than for the Er$_2$ complex.

A major obstacle to the realization of such applications is the development of molecules with large spin-reversal barriers that will function at practical temperatures. Early efforts towards increasing this barrier involved synthesizing large transition-metal based clusters with high spin ground states. In order to increase spin, magnetic anisotropy and subsequently, the energy barrier, much of the current SMM research has shifted towards lanthanide based complexes. Due to strong unquenched orbital angular momentum and significant spin-orbit coupling, lanthanide ions possess large intrinsic anisotropy such that mononuclear lanthanide complexes can exhibit slow magnetic relaxation.

Unlike their transition-metal counterparts, lanthanide-based SMMs are at the weak-exchange limit, and have dynamic magnetic behavior which cannot be adequately described within the framework of the zero-field splitting phenomenon, which can be used to understand the origin of the energy barrier in transition-metal SMMs. Furthermore, lanthanide SMMs display dynamic magnetization behavior that can be complicated by the presence of multiple relaxation pathways. Nonetheless, when it comes to designing SMMs with large energy barriers, more metal centers may be better, as it has been shown that metal–metal exchange coupling can aid in suppressing...
Experimental section

General information

All reagents and chemicals were purchased from Sigma Aldrich or Alfa Aesar and were used without further purification. All reactions were carried out under aerobic conditions. Elemental analysis was performed by Atlantic Microlabs Inc. All reactions were carried under aerobic conditions.

Synthesis of Gd$_2$Ga$_4$ (1)

Salicylhydroxamic acid (153.1 mg, 1.000 mmol), Gd(NO$_3$)$_3$·6H$_2$O (112.8 mg, 0.2500 mmol), Ga(NO$_3$)$_3$·xH$_2$O (127.9 mg, 0.5000 mmol) were dissolved in 46 mL methanol. 13 mL pyridine was added drop wise to this solution, followed by 6.5 mL H$_2$O. The solution was stirred for 30 seconds and then filtered. Slow evaporation of half of the solution yielded crystalline compound after 2 weeks.

Synthesis of Tb$_2$Ga$_4$ (2), Dy$_2$Ga$_4$ (3), Er$_2$Ga$_4$ (4) and Y$_2$Ga$_4$ (5)

A general procedure for complexes 2, 3, 4 and 5 is as follows. Salicylhydroxamic acid (153.1 mg, 1.000 mmol), Ln(NO$_3$)$_3$·xH$_2$O (0.2500 mmol), Ga(NO$_3$)$_3$·xH$_2$O (127.9 mg, 0.5000 mmol) were dissolved in 21 mL methanol. 6 mL pyridine was added drop wise to this solution, followed by 3 mL H$_2$O. The solution was stirred for 30 seconds and then filtered. Slow evaporation of half of the solution yielded crystalline compound after 2 weeks.

Synthesis of Y$_{1.8}$Dy$_{0.2}$Ga$_4$ (6)

Salicylhydroxamic acid (153.1 mg, 1.000 mmol), Dy(NO$_3$)$_3$·5H$_2$O (11.0 mg, 0.0250 mmol), Y(NO$_3$)$_3$·5H$_2$O (82.1 mg, 0.225 mmol), Ga(NO$_3$)$_3$·xH$_2$O (127.9 mg, 0.5 mmol) were dissolved in 21 mL methanol. 6 mL pyridine was added drop wise to this solution, followed by 3 mL H$_2$O. The solution was stirred for 30 seconds and then filtered. Slow evaporation of half of the solution yielded crystalline compound after 2 weeks.
<table>
<thead>
<tr>
<th>No.</th>
<th>Cryst. syst. group</th>
<th>Cryst. details</th>
<th>Mol. formula</th>
<th>$M_r$ (g mol$^{-1}$)</th>
<th>$\gamma$ (K)</th>
<th>Wavelength (Å)</th>
<th>$\alpha$, $\beta$, $\gamma$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$D_\text{calc}$ ($\text{g cm}^{-3}$)</th>
<th>$\omega$ (deg)</th>
<th>$\theta$ range for data collection (deg)</th>
<th>$F(000)$</th>
<th>$R_{1}$</th>
<th>$wR_{2}$</th>
<th>$R_{1}$</th>
<th>$wR_{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Monoclinic, $C2/c$</td>
<td>2518.21</td>
<td>Ga$_4$Y$_2$C$<em>9$H$<em>9$N$</em>{15}$O$</em>{31}$</td>
<td>2527.80</td>
<td>85(1)</td>
<td>0.71073</td>
<td>90</td>
<td>1.698</td>
<td>1.697</td>
<td>1.59–30.67</td>
<td>5069</td>
<td>4.042</td>
<td>0.0437</td>
<td>0.2382</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Monoclinic, $C2/c$</td>
<td>2532.71</td>
<td>Ga$_4$Dy$_2$C$<em>9$H$<em>9$N$</em>{15}$O$</em>{31}$</td>
<td>2518.21</td>
<td>85(1)</td>
<td>0.71073</td>
<td>90</td>
<td>1.697</td>
<td>1.697</td>
<td>1.59–30.67</td>
<td>5069</td>
<td>4.042</td>
<td>0.0437</td>
<td>0.2382</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Monoclinic, $C2/c$</td>
<td>2532.71</td>
<td>Ga$_4$Er$_2$C$<em>9$H$<em>9$N$</em>{15}$O$</em>{31}$</td>
<td>2528.21</td>
<td>85(1)</td>
<td>0.71073</td>
<td>90</td>
<td>1.697</td>
<td>1.697</td>
<td>1.59–30.67</td>
<td>5069</td>
<td>4.042</td>
<td>0.0437</td>
<td>0.2382</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Monoclinic, $C2/c$</td>
<td>2532.71</td>
<td>Ga$_4$Tb$_2$C$<em>9$H$<em>9$N$</em>{15}$O$</em>{31}$</td>
<td>2528.21</td>
<td>85(1)</td>
<td>0.71073</td>
<td>90</td>
<td>1.697</td>
<td>1.697</td>
<td>1.59–30.67</td>
<td>5069</td>
<td>4.042</td>
<td>0.0437</td>
<td>0.2382</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Monoclinic, $C2/c$</td>
<td>2532.71</td>
<td>Ga$_4$Gd$_2$C$<em>9$H$<em>9$N$</em>{15}$O$</em>{31}$</td>
<td>2528.21</td>
<td>85(1)</td>
<td>0.71073</td>
<td>90</td>
<td>1.697</td>
<td>1.697</td>
<td>1.59–30.67</td>
<td>5069</td>
<td>4.042</td>
<td>0.0437</td>
<td>0.2382</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$R_1 = \sum ||F_{\text{obs}}|| - |F_{\text{calc}}||/\sum ||F_{\text{obs}}||$, $wR_2 = \sqrt{\sum w(\Delta F)^2/(\sum wF_{\text{calc}})^2}$, where $\Delta F = F_{\text{calc}} - F_{\text{obs}}$, $w = (\sigma^2(\mu^2)+sol^2)^{-1}$, $(\sigma_{m}^{2}(F_{o}^{2})+(m+np)^{2})^{-1}$, $\sigma_m(F_{o}^{2})$ and $n$ are constants; $\sigma = \sum |u_{ij}| = p^{1/2}$.
Single-crystal X-ray diffraction

Crystal data for compound 1 were collected at 85(2) K on a Bruker SMART-APX CCD-based X-ray diffractometer equipped with a low temperature device and fine-focus Mo-target X-ray tube (λ = 0.71073 Å), operated at 1500 W power (50 kV, 30 mA). The frames were integrated with the Bruker SAI3T software package with a narrow frame algorithm. The data were processed with SADABS and corrected for absorption.

Crystal data for compound 2 were collected on a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects.

Crystal data for compounds 3, 4 and 5 were collected at 85(2) K on an AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a Micromax007HF Cu-target microfocus rotating anode (λ = 1.54187 Å), operated at 1200 W power (40 kV, 30 mA). The data were processed with CrystalClear 2.0 and corrected for absorption.25

All structures were solved and refined with the SHELXTL (version 6.12) software package.26 All non-hydrogen atoms were refined anisotropically. Hydrogen atoms are placed in their idealized positions. Additional details are provided in Table 1.

Magnetic measurements

Variable-temperature susceptibility, variable-field magnetization and ac susceptibility measurements on polycrystalline samples mullcd in eicosane were performed on a Quantum Design MPMS SQUID magnetometer. Variable-temperature dc susceptibility measurements were performed at 2000 Oe from 2–300 K. Isothermal magnetization measurements were performed at 2 K from 0–7 T. AC magnetic susceptibility measurements were done at both zero and applied fields (2000 Oe for 3 and 750 Oe for 6) with an ac drive field of 3 Oe at frequencies ranging from 1 to 1488 Hz. Dc susceptibilities were corrected for the sample holder and eicosane and for diamagnetism of constituent atoms using Pascal’s constants.

Results and discussion

Synthesis and characterization

The flexible multidentate ligand salicylhydroxamic acid (H₂shi) has been used in the synthesis of numerous metallacrown complexes, including several single-molecule magnets. Both predictable structure types (such as 9-MC-3, 12-MC-4) as well as compounds with unpredictable molecular geometry can be synthesized with H₂shi by adjusting reaction and solvent conditions, allowing for isolation and study of a wide array of multinuclear metallacrown complexes. Pyridine (which acts as a base, a solvent and a ligand) has unique properties, which have resulted in several metallacrown complexes with both previously known and new structure types.21,39 This multipurpose

Calculated using first principle methods on a monomeric species by replacing one of the lanthanide by a diamagnetic lutetium of configuration 4f^{14}. Since the two lanthanide atoms are related by an inversion center, there is only one type of monomer. All atoms are described with all electron basis sets ANO-RCC, Ln atoms with TZP quality, N and O atoms with DZP quality and other atoms with DZ quality. The excited states of the complexes have been calculated with the SO-CASSCF method using the MOLCAS78 suite of programs (MOLCAS80 for the gadolinium complex). The active space consists of n electrons in the 7 f orbitals for an atom of configuration 4f^n. First, a CASSCF (Complete Active Space Self Consistent Field) calculation is performed; all the states with the maximal value of the spin are considered in the state average procedure. In the case of gadolinium, all the sextet states are considered in addition to the octuplet ground state. Spin–orbit coupling is evaluated as a state interaction between all CASSCF wave functions by the RASSI (Restricted Active Space State Interaction) method.23 Spin–Orbit (SO) integrals are evaluated within the AMFI approximation.31 The calculation of all the properties is implemented in a local program, g factors are calculated according to ref. 34 even in the case of non-degenerate states (see ESI† for details). The dipolar magnetic interaction is calculated as

\[
\hat{H}^{\text{dip}} = \frac{\mu_0}{4\pi R^3} \left\{ \hat{S}_A \cdot \hat{S}_B - 3\hat{M}_A \cdot \hat{M}_B \right\}
\]

where \( R \) is the intermolecular distance, \( \hat{S} \) the intermolecular direction and \( \mu_0 \) the magnetic constant. The exchange interactions are carried by the spin densities and are described by a Heisenberg–Dirac–Van Vleck (HDVV) Hamiltonian

\[
\hat{H}^{\text{Heis}} = -J \hat{S}_A \cdot \hat{S}_B ~\text{and}~ \hat{S}_A \cdot \hat{S}_B
\]

are the total and spin momentum operators for site A(B). This scheme has been first proposed by Lines in the 70s,30 it has been applied to lanthanide complexes by Sutter et al. in 2002 (ref. 36) and since 2007, is applied in the group of Chibotaru.27 A local modification of MOLCAS was used to generate natural spin orbitals (NSOs) from SO-CASSCF calculations (see ESI†).
solvent aids in crystallization by forming π-interactions and coordinates to metal sites, forming structures whose architectures are directed by π-interactions and steric effects. Here, the reaction of H$_2$shi, Ga(NO$_3$)$_3$·xH$_2$O and Ln(NO$_3$)$_3$·xH$_2$O a 4 : 2 : 1 stoichiometric ratio in a solution of methanol, pyridine and water followed by slow evaporation of solvent afforded neutral macrocyclic complexes (Scheme 1) with the general formula $[\text{Ga}, \text{Ln}_3([\text{shi}^{3−}]_2([\text{Hshi}^{2−}]_2([\text{C}_2\text{H}_5\text{N})_4([\text{CH}_3\text{OH})]\text{[H}_2\text{O}]^{-}\cdot\text{C}_5\text{H}_8\text{N}$·2CH$_3$OH·3H$_2$O). The structures of compounds 1–5 were determined by X-ray crystallography to be isostructural and crystallize in the monoclinic $C2/c$ space group (Table 1). Slight differences in the composition of bound and lattice solvents were observed across the series of complexes. Compound 6 was determined to have the same unit cell parameters and is isostructural to 3 and 5 ($Y_2$Ga$_4$). It was synthesized with 10% Dy$^{III}$ and 90% Y$^{III}$ in solution. Statistically speaking, such a reaction would form crystals composed of 81% $Y_2$Ga$_4$ (diamagnetic), 18% DyGa$_4$ and 1% DyGa$_6$ (3).

As a representative example, the structure of compound 3 (Fig. 1) can be described as a centrosymmetric μ$_2$-oxo bridged di-lanthanide core surrounded by four peripheral Ga$^{III}$ ions. In the core moiety of the asymmetric unit, one Dy$^{III}$ and two Ga$^{III}$ ions are chelated by four fully and partially deprotonated ligands and coordinated by pyridine and methanol or water solvent molecules. In Fig. 1, Dy1 is chelated by the carbonyl (O1) and hydroximate oxygens (O2) of an in-plane shi$^{3−}$ and by the carbonyl (O7) and phenoxide oxygens of an out-of-plane Hshi$^{2−}$.

The symmetry-generated hydroximate oxygen O2a also coordinates to Dy1, to form a Dy$_2$(μ$_2$-OR)$_2$ core. Hydroximate oxygen from an in-plane shi$^{3−}$ (O5) and Hshi$^{2−}$ (O11) also coordinate, bridging Dy1 to Ga2a and Ga1, respectively. Dy1 is capped by a disordered water (O510) or methanol (O500, C500) with shared occupancy, to complete the coordination sphere around Dy1 which can be described as having distorted 8-coordinate trigonal dodecahedral geometry (Table S1). The four outer Ga$^{III}$ cations, with roughly octahedral geometry, surround the two central Dy$^{III}$ ions and are ligated by fully and partially deprotonated H$_2$shi. Four fully deprotonated shi$^{3−}$ and two H$_2$shi$^{2−}$ coordinate the four Ga$^{III}$ and two Dy$^{III}$ ions to form the molecular plane (Fig. 1, left), with two doubly deprotonated Hshi$^{2−}$ pointing above and below the plane (Fig. 1, right).

**Static magnetic studies and theoretical calculations**

For complexes, the variable-temperature dc susceptibility measurements were performed at an applied field of 2000 Oe from 2 to 300 K (Fig. S3†); the variable-field magnetization measurements were performed at 2 K from 0 to 7 T (Fig. S3†). Globally, the general behavior of all compounds is consistent with other lanthanide complexes reported in the literature. The general temperature dependence of the $\chi T$ product for 1 (Gd$^{III}$: 8S$^7/2$, 15.9 cm$^3$ K mol$^{-1}$) is in good agreement with the expected value for two non-interacting Gd$^{III}$ ions. Upon cooling, $\chi T$ is almost constant down to $T = 10$ K and then slightly decreases to reach a value of 7.8 cm$^3$ mol$^{-1}$ K at 2 K. This decrease is probably due to an intramolecular antiferromagnetic exchange coupling between the two Gd$^{III}$ ions. The $M = f(H)$ curve increases with the applied magnetic field and reaches saturation (13.8 Bohr Magneton) at 7 T. It is possible to fit the susceptibility and the magnetization data (see Fig. 2 and 3) using a model based on the

---

**Scheme 1**

Synthesis of Ln$_2$Ga$_4$ complexes.

**Fig. 1**

X-ray crystal structure of complex 3. (left) Top view. (right) Side view. Color code: teal spheres = Dy$^{III}$; salmon spheres = Ga$^{III}$; gray = C; red = O; blue = N. Hydrogen atoms and lattice solvents are omitted for clarity.

**Fig. 2**

Temperature dependence of the $\chi T$ product for complexes 1, 2, 3 and 6. The solid lines correspond to the best fit (see text).
the spin Hamiltonian $H = -J S_{\text{Gd}1} \times S_{\text{Gd}2} + g \mu_B H S_{\text{Zn}}$. The best fit parameters are $g = 1.98$ and $J = -0.16$ cm$^{-1}$, where $g$ is the Lande factor and $J$ the interaction parameter between the local $S = 7/2$ spins of the Gd$^{3+}$ ions. This value is in agreement with those reported in the literature for a dinuclear μ-oxo Gd$^{3+}$ with a similar geometry.\textsuperscript{14} The Gd$^{3+}$ ion has no first order angular momentum and almost a negligible zero field splitting. In such a case, the dipolar interaction is expected to be very weak. Thus, the antiferromagnetic interaction found experimentally is due, mainly, to exchange and splits the low-lying spin states $S = 0$ to $7$ by an energy equal to 4.48 cm$^{-1}$ ($JS(S + 1)/2$), with $|J| = 0.16$ cm$^{-1}$ and $S = 7/2$ (see Table S2 and S3†).

**Tb$_2$Ga$_4$ 2, Dy$_2$Ga$_4$ 3 and DyYGa$_4$ 6**

The χ$T$ product and the field dependent magnetization at 2 K for 6 (Fig. 2 and 3) have the behavior expected for a mononuclear Dy$^{3+}$ complex (6H$_{15/2}$, $C = 14.17$ cm$^{-3}$ K mol$^{-1}$). Ab initio calculations allows for the determination of the energy spectrum and the associated $g_i$ values (Table S4†) ($i = 1, 2$ and $3$ are the principal directions of the $g$ tensor with $1$ corresponding to the largest value). The ground state corresponds to $M_J = \pm 15/2$, with one very large $g_1 = 19.85$ ($g_2 = 0.08$, $g_3 = 0.04$), \(\uparrow\) indicating an easy axis of the magnetization as depicted in Fig. 4 (left). The magnetization axis forms an angle of 79° with the Dy–Dy axis and is very close to the plane containing the Dy$^{3+}$ ions and the bridging oxygen atoms. The experimental magnetic data can be reproduced using the $M_J$ energy spectrum determined from ab initio calculations, which confirms the nature of the ground level ($M_J = \pm 15/2$) and the fact that the diluted compound mainly contains the paramagnetic DyYGa$_4$ species.

The χ$T$ product for 2 and 3 have the usual behavior expected for Tb$^{3+}$ and Dy$^{3+}$ ions ($F_\text{g}$ ground state $C = 11.82$ cm$^{-3}$ mol$^{-1}$ K for an isolated Tb$^{3+}$; it slowly diminishes from 300 K to around 50 K and then decreases more abruptly. This behavior is due to the thermal depopulation of excited $M_J$ sublevels and may also be caused by an antiferromagnetic interaction between the lanthanide ions. The magnetization measured at 2 K presents a sigmoidal shape at low applied magnetic fields with an inflection point around 0.5 T, which is the signature of the presence of an antiferromagnetic coupling within the two compounds. It is worth noting that the magnetization vs. field curve of 6 does not possess an inflection point and its χ$T$ product value at 2 K (10.8 cm$^{-3}$ mol$^{-1}$ K) is larger than that of 3 (2.6 cm$^{-3}$ mol$^{-1}$ K computed per 1 Dy$^{3+}$), which confirms that the inflection point in 3 is due to intra- and not to intermolecular antiferromagnetic interaction. In order to determine the value of the inflection point more accurately in the $M = f(\mu_B H)$ curve, we measured the magnetization at very low temperature on a single crystal of 3 using an array of micro-squids with the magnetic field parallel to the anisotropy axis of the crystal. The curves at $T = 1$ and 0.03 K show sharp steps and a crossing point at $\mu_B H = 0.51$ T (Fig. S1†).

The sharp steps are the result of the crossover from an antiparallel (antiferromagnetic: AF) to a parallel (ferromagnetic: F) alignment of the anisotropic moments of the two Dy$^{3+}$ ions. The field value of the crossing point allows for computation of the energy difference $\Delta E (\Delta E = g_1 \beta \times \mu_B H = 19.47 \times 0.496 \times 0.51)$ between the AF and the F states and was found equal to 4.9 cm$^{-1}$. The magnetic dipolar interaction between the two Dy$^{3+}$ ions (Table S5†), determined by ab initio calculations of the isolated ion shows that the minimum energy is obtained when the magnetization moments are antiparallel, which is expected because the easy magnetization axis is almost perpendicular to the Dy–Dy axis. These calculations lead to an AF–F energy gap of 1.26 cm$^{-1}$ well below the experimental one extracted from the magnetization data (4.9 cm$^{-1}$). In order to account for the experimental energy gap, we introduced an additional interaction due to an exchange coupling between the two Dy$^{3+}$ ions (see Experimental section). A good fit of the data of 3 is obtained using a $J_{\text{ex}}$ value of $-0.29$ cm$^{-1}$ (Fig. 3, S1 and Table S5†). The difference between the calculated and the experimental data at low temperature (Fig. S1†) is the signature of intermolecular dipolar interaction within the crystal that can be observed at such low temperatures.

For the Tb complex 2, the situation is similar to that of the Dy analogue; an easy axis of magnetization is present, where $g_1 = 17.85$ and $g_2 = 0$ for the $M_J = \pm 6$ ground levels (Table S6, see ESIF†). It forms an angle of 79° with the Tb–Tb intermetallic
axis (Fig. S2†). The computed dipolar interaction leads to a splitting between the AF (ground level) and the F states of 0.5 cm⁻¹, which is not sufficient to reproduce the experimental data (Table S7†). Introducing an additional antiferromagnetic exchange interaction, 2|J|M₂² (J = -0.12 cm⁻¹), increases this energy by 2.7 cm⁻¹ and affords a reasonable fit of the data (Fig. 3 and Table S7†).

**Er₂Ga₄**

The χT value at room temperature (22.7 cm³ mol⁻¹ K) corresponds to two isolated Er³⁺ ions (Er³⁺, ⁴I₁₅/₂, C = 11.5 cm⁻¹ K mol⁻¹) (Fig. S3†). Upon cooling, χT slightly decreases and reaches a value of 12.9 cm³ K mol⁻¹ at 2 K, as expected for anisotropic ions. The $M = \mu_B H$ curve increases sharply between 0 and 1 T and then continuously up to 7 T without reaching saturation (Fig. S3†).

No inflection point is present at low magnetic field, which excludes the presence of an antiferromagnetic coupling as for the other compounds. For the ground state, the *ab initio* calculations give three different $g$ values: $g_1 = 9.94$, $g_2 = 5.25$ and $g_3 = 0.25$ (Table S8†). The magnetization is planar, with two non-equivalent directions. The largest magnetization direction (along $g_1$) is found in a direction forming an angle of 32° with the intermetallic axis and lies almost in the Er₂O₂ plane (Fig. 4, right).

The magnetization curve, computed from *ab initio* calculations, does not fit the experimental one. A scaling factor of 1.8 increases the energy of the first excited state and reduces the effect of second order Zeeman interaction (see ESI† for the details of the calculations) and improves the agreement of theoretical and experimental curves, in particular above 1 T. Since the planes of magnetization form a small angle with the intermetallic axis, the dipolar interaction is ferromagnetic. The behavior in the weak field region is reproduced by considering the presence of a supplementary ferromagnetic coupling between the two ions due to exchange ($J_{exch} = 2.4$ cm⁻¹) (Table S9 and Fig. S3†). It is worth noting that when the ground state has a small $M_s$ value and the excited states are close to the ground state as in the present case, a very small error in the energies and in the $g_i$ values may have a dramatic effect on the shape of the magnetization curve. This is why here, a scaling factor that changes the ground-excited state gap was necessary to better reproduce the magnetic data. In addition, if the ratio between $g_i$ and $g_3$ is different, the shape of the magnetization curve in the low field region is changed. For instance, if $g_1$ is close to $g_2$ (i.e. close to 10, which defines an anisotropic easy plane of magnetization), the experimental curve can be reproduced without considering an additional ferromagnetic exchange interaction between the two Er³⁺ ions.

In summary, the magnetic studies together with theoretical calculations show that there is an easy axis of magnetization for the Dy and the Tb complexes with an intra-molecular dipolar antiferromagnetic interaction, while for Er there is an easy plane of magnetization that leads to a ferromagnetic dipolar interaction between the two ions. Furthermore, an additional interaction due to exchange between the metal ions is necessary to reproduce the experimental data that was found to be antiferromagnetic for the Dy and the Tb complexes and ferromagnetic (or absent) for the Er one. The analysis of the $g$ values of the ground doublets allows us to extract the spin and the orbital contributions to the overall magnetization (Table S10†).

In order to get a qualitative insight into the nature (F or AF) of the exchange interaction between the metal ions and particularly the difference between the Gd, Tb and Dy complexes on one hand and the Er complex on the other hand, we determined the Natural Spin Orbitals (NSOs) for the magnetic axes on one lanthanide site (Fig. 5, S4 and S5, see ESI†). These orbitals permit the determination of the spin magnetization (‘spin density’) for a given direction of the magnetic field. The comparison of the overlap integrals between NSOs on different centers within the binuclear complexes for the Dy and the Er cases show that they are about ten times larger for Dy₂Ga₄ then for Er₂Ga₄ (Tables S11, S12 and S13†). Since the overlap integrals between NSOs are directly related to the magnitude of the antiferromagnetic contribution to the exchange interaction, one can conclude that such interaction is expected to be much larger for the Dy₂Ga₄ than for Er₂Ga₄ as found experimentally. The origin of the difference in behavior between the two complexes may be related to the weaker magnetization density on the bridging oxime ligands for

---

Fig. 5 NSOs for the Dy³⁺ complex determined along direction 1 corresponding to the orientation of the magnetization axis. One Dy³⁺ has been replaced by a Lu³⁺ ion. The isosurfaces are weighted by the corresponding occupation that is indicated below each plot.
Er\textsuperscript{III} than for Dy\textsuperscript{III} (Fig. 5, S4 and S5\textsuperscript{†}). It is difficult to draw more quantitative conclusions from this qualitative analysis on the ferromagnetic exchange contribution.

Low temperature micro-squid studies

For compound 3, at $\mu_0 H = 1$ T and $T = 0.03$ K, the magnetic moment is saturated. Upon decreasing the field with a sweep rate of 0.035 T s\textsuperscript{−1}, the magnetization undergoes a sharp decrease to around 5% of saturation (Fig. 6, top). The $M = f(\mu_0 H)$ curves at different temperatures cross at 0.51 T. An opening of the hysteresis was observed at zero field with a coercive field $\mu_0 H_C = 540$ Oe. Upon decreasing the magnetic field sweep rate from 0.28 to 0.008 T s\textsuperscript{−1}, the coercive field decreases from 678 to 421 Oe indicating the occurrence of quantum tunneling of the magnetization because the width of the hysteresis loop depends on the field sweep rate (Fig. S6\textsuperscript{†}). The sharp step at 0.51 T is the result of crossover from the F to the AF states as explained in the previous section.

An opening of the hysteresis loop, at such low temperature where only ground state is populated, has never been observed, to the best of our knowledge, in an antiferromagnetically coupled binuclear Dy\textsubscript{2} complex. Since no hysteresis loop can occur when all the molecules are in the antiferromagnetic state (diamagnetic state) and since the excited ferromagnetic one cannot be populated at $T = 0.03$ K, the presence of the residual 5% magnetization below the step at 0.51 T can be due to the

![Fig. 6](top) $M/M_S = c(\mu_0 H)$ at 0.03, 0.5 and 1 K for dc field sweep rate of 0.035 T s\textsuperscript{−1} for complex 3. (bottom) Field-dependent energy diagram showing the different relaxation processes for the binuclear complex 3.

![Fig. 7](Temperature-dependence of the out-of-phase ($\chi''$) ac magnetic susceptibility for 3 under zero applied dc field (top) and 2000 Oe (middle); and (bottom) ln(c) vs. $1/T_B$ where $T_B$ Arrhenius plot with data extracted from the frequency-dependent data at zero applied dc field for the low (▲) and the high (▼) temperature processes. The solid lines are the best linear fit.)

This journal is © The Royal Society of Chemistry 2015

Chem. Sci., 2015, 6, 4148–4159 | 4155

Open Access Article. Published on 07 May 2015. Downloaded on 5/11/2020 10:14:16 AM. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.
presence of residual molecules in the ferromagnetic state. Actually, at large positive magnetic field, the moments are in the $| - \rightarrow - >$ configuration of the ferromagnetic state. Upon decreasing the field at a given sweep rate, the majority of the molecules undergo a crossover from the ferro- $| - \rightarrow - >$ to the antiferromagnetic $| - \rightarrow + >$ state, but a small amount remains in the ferro- $| - \rightarrow - >$ configuration (see Fig. 6, bottom). In order to support the above-proposed mechanism, we first cooled down the sample at zero applied magnetic field. This leads to a state where all Dy-dimers are in the antiferromagnetic ground state. Then, we performed minor hysteresis loops below the critical field for the ferromagnetic state (0.5 T). A typical example is presented in Fig. S6† performed in the ±3000 Oe region. A paramagnetic signal with a small hysteresis is observed, which is probably due to a mononuclear Dy(III) species (2%) that are present in the crystals. Only when the field is larger than the critical field for the ferromagnetic state, a large hysteresis is observed, which is due to molecules that are trapped in the ferromagnetic state.

This results in a residual magnetization below 0.51 T. When the field is driven to zero, a tiny drop in the magnetization is observed (Fig. S7†) that can be assigned to the reversal of the magnetization from the $| - \rightarrow - >$ to the $| + \rightarrow (| - \rightarrow + >)$ configurations by a direct tunneling process (Fig. 6, bottom). The tunneling probability at zero field from $| - \rightarrow - >$ to $| + \rightarrow (| - \rightarrow + >$ is rather weak but a clear step that is sweep rate dependent can be noticed. Upon decreasing the field to negative values, the reversal of the magnetization occurs probably via a direct transition from the $| - \rightarrow - >$ to the $| + \rightarrow (| - \rightarrow + >$ configuration. And finally at $\mu B H = -0.51$ T the majority of the molecules that were in the antiferromagnetic $| + \rightarrow (| - \rightarrow + >$ state undergo the crossover to the $| + \rightarrow + >$ ferromagnetic one.

**Dynamic susceptibility studies**

Ac susceptibility measurements may bring complementary information on the dynamics of the magnetization reversal at higher temperatures. A frequency dependence of the out-of-phase component of the susceptibility was observed only for the Dy$_2$ derivative 3 and the Dy diluted one 6, with all other compounds showing no out-of-phase behavior. For compound 3, ac susceptibility measurements were first performed under zero dc applied external field, in the temperature range between 2 and 22 K and frequency range from 1 to 1488 Hz with an ac drive field of 3 Oe (Fig. 7 (top), S8 and S9†).

The temperature dependent out-of-phase susceptibility plot (Fig. 7, top) show that upon increasing the frequency of the oscillating field, the temperature of the maxima ($T_{\text{max}}$) shifts toward high temperatures as expected, while the value of the maxima of the $\chi''$ signals does not behave as usual. When the frequency increases, it first reaches a maximum intensity at 450 Hz ($T_{\text{B450}} = 4.00$ K) and then decreases. This behavior is

---

**Fig. 8** (top) Temperature-dependence of the out-of-phase ($\chi''$) ac magnetic susceptibility for 6 under zero applied dc field (top) and 750 Oe applied dc field (bottom). Insets: ln($\tau$) vs. $1/T_B$ where $T_B$ is the temperature of the maxima of the $\chi''$ curves.

**Fig. 9** Temperature-dependence of the out-of-phase ($\chi''$) ac susceptibility for 3 in zero dc field (---), in 2000 Oe dc field (---) and for 6 in 750 Oe dc field (---) at 1284 Hz.
consistent with the fact that the slow relaxation probed corresponds to an excited state that is more and more populated when the temperature of the maximum is shifted upward and is evidence that the relaxation process observed is due to the excited ferromagnetic state that lies at 4.9 cm\(^{-1}\) above the ground non-magnetic one. Assuming an activated relaxation process \((\tau = \tau_0 \exp(U_{\text{eff}}/k_B T))\) in the 2–5 K region, it is possible to fit \(\ln \tau\) vs. \(1/T\) from the out-of phase data, where \(\tau = 1/(2\pi f)\) and \(T_\text{B} \equiv \text{the temperature of the } \chi'' = f(T) \text{ curves, and find } \tau_0 = 3.6 \times 10^{-6} \text{ s and } U_{\text{eff}} = 18 \text{ K} \) (Fig. 7, bottom). The \(\chi'' = f(T)\) curves display shoulders at higher temperatures in the 10–14 K region that appear only for frequencies above 500 Hz. In the 10–14 K region, the temperature is larger than the energy due to antiferromagnetic coupling, the coupling can then be neglected and the ions behave as if they were isolated. This second relaxation process can then be assigned to the isolated Dy\textsuperscript{III} ions. The analysis of the data leads to a thermal activated behavior relaxation process with \(\tau_0 = 6.8 \times 10^{-6} \text{ s and } U_{\text{eff}} = 26 \text{ K} \) (Fig. 7, bottom).

The \(\chi'' = f(T)\) curves for different temperatures (Fig. S8\( ^\dagger \)) show only one maximum that shifts to high frequency upon heating. The intensity of the curves follow the behavior observed in Fig. 7 i.e. the magnitude of \(\chi''\) increases from 2 to 4.25 K and then decreases, attesting that the relaxation process is due to the excited ferromagnetic state.

The Cole–Cole plots for compound 3 at zero applied dc field were obtained for temperatures between 2 and 11 K (Fig. S10\( ^\dagger \)). The plots have close to an ideal semicircular shape indicating that only a few relaxation processes are present. The semicircles were fitted using a generalized Debye model.\(^{44} \) The fits provided values for the \(\alpha\) parameter, which decreased with increasing temperature, from 0.18 at 2 K to 0.032 at 11 K (Fig. S10\( ^\dagger \)). The low \(\alpha\) value at high temperatures indicates that only one relaxation process is present. As the temperature is decreased, the \(\alpha\) parameter increases because at low temperatures, the tunneling process starts to compete with the activated direct process.

The ac data for compound 3 were also recorded in the presence of an applied 2000 Oe dc field. The same general behavior with two relaxation processes, as for the zero dc field case, is observed, but with some differences in the relative intensities. (Fig. 7 (middle) and S11\( ^\dagger \)). Upon increasing the frequency, the intensity of \(\chi''\) increases and reaches a maximum at 36 Hz \((T_{\text{B},\text{ns}} = 3.0 \text{ K)}\), instead of 450 Hz under zero dc field. The high temperature process starts to be observable at 88 Hz instead of 450 Hz when a dc field of 2000 Oe is applied, which is compatible with a process due to the uncoupled Dy\textsuperscript{III} ions.

The temperature-dependent out-of-phase ac susceptibility for 6 under zero dc applied field (Fig. 8 top and S12\( ^\dagger \)) revealed a frequency dependent maxima in the 5–15 K temperature range with a tail at low temperature due to quantum tunneling of the magnetization, as is generally observed for Dy\textsuperscript{III} ions.\(^{44} \) This last process can also be observed in the low temperature regime in the frequency-dependent data (Fig. S13\( ^\dagger \)), where the maxima positions are relatively temperature independent. The barrier extracted from the frequency-dependent data for 6 at zero applied dc field is \(U_{\text{eff}} = 31 \text{ K, with } \tau_0 = 7.0 \times 10^{-6} \text{ s} \) (Fig. 8 top), very close to the high temperature process of the binuclear compound 3 \((U_{\text{eff}} = 26 \text{ K and } \tau_0 = 76.8 \times 10^{-6} \text{ s})\), which confirms that the high temperature process in 3 is indeed due to the uncoupled moments. At lower temperature, the relaxation tends to be temperature independent (Fig. 8, top), as expected when the quantum tunneling process dominates.

Applying a dc magnetic field may slow down the tunneling and make other processes more visible. In the presence of an optimal 750 Oe dc field (see ESI, Fig. S14\( ^\dagger \)), the maxima in the \(\chi'' = f(T)\) plot for 6 can be observed (Fig. 8, bottom). Quantum tunneling of the magnetization has been mostly quenched as evidenced by the absence of overlapping peaks in the frequency-dependent data (Fig. S15\( ^\dagger \)) and the disappearance of the low temperature tail in the temperature dependent data (Fig. 8).

A linear fit of the high temperature data gives an energy barrier \(U_{\text{eff}} = 107 \text{ K, with } \tau_0 = 1.79 \times 10^{-6} \text{ s} \) (Fig. 8, bottom). As expected, the barrier is much higher than for the zero-field case of 31 K. It is about half the value of the computed energy difference between the ground and the first excited states \((153 \text{ cm}^{-1} \text{ (220 K)} \) (Table S4\( ^\dagger \)), which is consistent with the persistence of a relaxation by quantum tunneling via the ground state and via the first excited one. The persistence of quantum tunneling is due to the lack of a perfect axial tensor \((g_1 = 19.47, g_2 = 0.08 \text{ and } g_3 = 0.04)\) and thus to a small mixing between the ground and the excited \(M_1\) states.

The comparison of the \(\chi''\) curves at 1284 Hz measured at zero and 2000 Oe for 3 and at 750 Oe for 6 (Fig. 9) shows that the maximum of \(\chi'' = f(T)\) for 3 and 6 are at the same temperature, which confirms that the high temperature process in 3 is actually due to the isolated Dy\textsuperscript{III} ions.

In order to check that the relaxation processes are well related to the mononuclear Dy\textsuperscript{III} species and not to the presence of large amounts of the Dy\textsubscript{2} ones within the crystal, we carried magnetization studies on a single crystal of compound 6 using the micro-squid arrays. The \(M = f(\mu_0 H)\) curves in the \(\pm 1 \text{ T}\) range at different temperatures and sweep rates (Fig. S16 and S17\( ^\dagger \)) of the field are all consistent with a mononuclear Dy\textsuperscript{II} ion with a tunneling of the magnetization near zero field and a slower relaxation when a magnetic field is applied, completely consistent with the ac data. A small step is observed close to 0.5 T due to the Dy\textsubscript{2} species present in compound 6. The corresponding magnetization is around 6%, which is less than the value expected from statistical distribution (11%), which render the magnetic behavior of compound 6 mainly due to the mononuclear species.

Concluding remarks

Utilizing the metallacrown synthetic approach, we investigated the properties of a family of isosstructural Ln\textsubscript{2}Ga\textsubscript{4} complexes, where the Ln\textsuperscript{III} ions are bridged by oxygen atoms forming the diamond-like Ln\textsubscript{2}O\textsubscript{2} core. The experimentally observed antiferromagnetic coupling for the Gd, Tb and Dy containing complexes was shown, using \textit{ab initio} calculations, to be due to exchange and not to dipolar interaction. For the Er-based complex, no experimental evidence of antiferromagnetic coupling was observed. The analysis of the overlap and the exchange integrals between the NSOs shows that the exchange...
coupling is about ten times larger for Dy than for Er. The magnetization changes from an easy axis to an easy plane between the Dy and the Er complexes but there is no evidence that this is related to the nature of the exchange interaction.

The presence of an easy axis of magnetization for the DyIII within the binuclear species leads to a slow relaxation of the magnetization for Dy2, despite the presence of the antiferromagnetic coupling. Two relaxation processes are observed and assigned to the ferromagnetic excited state and to the uncoupled ions. The uncoupled ions have a slightly larger barrier assigned to the ferromagnetic excited state and to the uncoupled ions. The successive deprotonation of salicylhydroxamic acid is as follows: H3shi (deprotonation of the hydroximate and phenol oxygens) and shi2/C0 (deprotonation of the hydroximate oxygen), Hshi/C0 (deprotonation of the hydroximate and phenol oxygens) and shi/H2shi (fully deprotonated).

Theoretical calculations estimate that single ion anisotropy lies in the 7/2 manifold by 2 cm⁻¹ (Table S2†). The evaluation of the dipolar interaction from ab initio calculations leads to an energy separation between the 7/2 manifold by 2 cm⁻¹, which is about 10% of the overall separation.

The principal values of the g tensor for all compounds are labeled by 1, 2 and 3 with 1 being the largest and 3 the smallest value; the molecular axes x, y and z; the z axis corresponds to the Ln–Ln intermolecular axis and the x axis lies within the LnOOLn plane, where O are the bridging oxygen atoms.

Acknowledgements

This research was supported in part by the National Science Foundation under grant CHE-1361779 and by ANR-13-B810-0001-03 MolQuSpin. VLP and TM acknowledge the Blaise Pascal International Chair for financial support. F.G. and J.A. acknowledge support Department of Energy, Office of Basic Energy Sciences, Heavy Element Chemistry (DE-FG02-09ER16066). The SQUID facility at the University of Michigan is funded by the National Science Foundation, NSF-MRI grant CHE-1040008.

Notes and references

† The successive deprotonation of salicylhydroxamic acid is as follows: H3shi (fully protonated), H2shi- (deprotonation of the hydroximate oxygen), Hshi- (deprotonation of the hydroximate and phenol oxygens) and shi- (fully deprotonated).

‡ Theoretical calculations estimate that single ion anisotropy lifts the degeneracy of the local S = 7/2 manifold by 2 cm⁻¹ (Table S2†). The evaluation of the dipolar interaction from ab initio calculations leads to an energy separation between the ground and the highest excited state of about 0.4 cm⁻¹, which is about 10% of the overall separation.


25 R. Corporation, Tokyo, Japan.


