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## Field-Induced Slow Magnetic Relaxation In the First Dy(III)-centered 12-Metallacrown-4 Double-Decker

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**The reaction of Dy(O<sub>2</sub>CMe)<sub>3</sub>•xH<sub>2</sub>O and Ga(NO<sub>3</sub>)<sub>3</sub>•xH<sub>2</sub>O led to the isolation of (nBu<sub>4</sub>N)[Ga<sup>III</sup><sub>8</sub>Dy<sup>III</sup>(OH)<sub>4</sub>(shi)<sub>8</sub>] (1). The compound possesses a unique chemical structure enclosing the central magnetic Dy<sup>III</sup> ion between diamagnetic Ga<sup>III</sup>-based metallacrown 12-MC-4 ligands. The double-decker complex exhibits field-induced single-molecule magnet (SMM) behaviour with an effective energy barrier (U<sub>eff</sub>) of 39 K (27.1 cm<sup>-1</sup>). Consistent with the observed slow relaxation of magnetization, theoretical calculations suggest a ground state mainly determined by |±11/2> in the easy axis direction.**

The high demand on miniaturization of components for the development of smaller and novel devices has led to the use of nanoscale systems. Single-molecule magnets<sup>1–3</sup> are individual molecules (of a few nanometers) that have been in the spotlight of researchers for over 25 years since they have proven to be promising candidates for various applications such as high-density data storage, quantum computation, magnetic refrigeration and spintronics.<sup>4–7</sup> While in the beginning the interest was focused on polynuclear 3d-based SMMs,<sup>8</sup> right after the discovery that the mononuclear [Pc<sub>2</sub>Tb] (Pc = phthalocyaninato) complex exhibits slow relaxation of magnetization, the 4f elements became the focal point, improving immensely the SMM performance.<sup>9–11</sup> This second generation of SMMs, also known as single-ion magnets (SIMs), is based on the magnetic anisotropy of a single ion, which arises from the combination of spin-orbit coupling and the crystal field. The selection of the appropriate coordination environment, depending on both the electronic f-shell shape of the magnetic center<sup>12,13</sup> and an adequate choice of ligands,<sup>14</sup> are crucial factors for the enhancement of their properties. The latest example highlighting the

mentioned approach, is the report of a dysprosocenium complex displaying magnetic hysteresis at temperatures above 77 K where nitrogen liquefies.<sup>15</sup>

The SMM behavior of monometallic phthalocyaninato sandwich complexes of Tb<sup>III</sup> and Dy<sup>III</sup> showed that the organic ligand used is of great importance.<sup>9,16</sup> In these previous findings it has been shown that the generated D<sub>4d</sub> symmetry around the lanthanide ion reveals an effective way for the improvement of SMMs. This desired coordination environment around the lanthanide can be also achieved with the isolation of metallacrowns (MCs).<sup>17</sup> Hence, we decided to employ MCs as ligands and coordinate them with lanthanides, targeting the formation of double-decker systems. Lately, it has been observed that the use of diamagnetic metal ions in combination with anisotropic paramagnetic ones can enhance the effective energy barrier, with a few examples using Zn<sup>II</sup>, Mg<sup>II</sup>, Al<sup>III</sup> and others, already reported.<sup>18–20</sup> Furthermore, the use of diamagnetic Ga(III) ions can play the role of magnetic dilutor, isolating the central Dy(III). In such a way, the dipole-dipole interactions get weaker having as an outcome the suppression of quantum tunnelling of magnetization (QTM) leading desirably to improved magnetic properties. As such, the employment of a Ga(III)-based MC systems is a novel approach towards the synthesis of 12-MC-4 SIMs and it sets the starting line for the exploration of future structurally optimized double decker systems with improved properties.

Metallacrowns, firstly reported in 1989 by Pecoraro and Lah,<sup>21</sup> are inorganic analogues of organic crown ethers and they possess a repeating [-M-N-O]<sub>n</sub> unit which assists in the formation of the characteristic MC cyclic motif. These complexes have the ability to encapsulate a central metal ion in their cavity, similar to crown ethers, and their ring size varies from 9-MC-3 to 60-MC-20.<sup>22</sup> Recently, the incorporation of 4f metal ions in the central cavity of those compounds, has brought them into the forefronts of the field since these molecules can be excellent choices for molecular recognition,<sup>23</sup> molecular magnetism<sup>24</sup> and luminescent technologies.<sup>25,26</sup>

Lately, the enhancement of the inherent luminescent properties of lanthanides using diamagnetic Ga(III) ions as periphery ring metal ions, have been reported.<sup>21,24,27</sup> Pecoraro and coworkers synthesized a Ga(III)/Ln(III) 12-MC-4 complex using salicylhydroxamic acid, in which they have extensively investigated the structural and

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luminescent properties.<sup>24</sup> However, magnetic studies have not yet been performed. Herein, we report the synthesis, structural and magnetic characterization of the first double-decker Ga(III)/Dy(III) 12-MC-4 complex using salicylhydroxamic acid as an organic bridging/chelating ligand. Theoretical calculations were employed in order to assist with the deeper understanding of the magnetic behaviour of our compound. To the best of our knowledge, no double-decker or sandwich-type Ln(III)-Metallacrown complex has been published up to now.

The general reaction of Ga(NO<sub>3</sub>)<sub>3</sub>•xH<sub>2</sub>O, Dy(O<sub>2</sub>CMe)<sub>3</sub>•xH<sub>2</sub>O, shaH<sub>2</sub> (Scheme 1, SI), Bu<sub>4</sub>NClO<sub>4</sub> and piperidine in a 8:1:8:3:8 molar ratio, in MeOH gave a white suspension that under extended stirring remained undissolved. Upon filtration, the colorless solution was left to slowly evaporate which led to the formation of small colorless plate crystals of (Bu<sub>4</sub>N)[Ga<sup>III</sup><sub>8</sub>Dy<sup>III</sup>(OH)<sub>4</sub>(shi)<sub>8</sub>] (1) in ~35 % yield. The chemical and structural identity of complex 1 was proven by single-crystal X-ray crystallography, elemental analyses (C, H, N) and IR spectroscopy (Supporting Information).

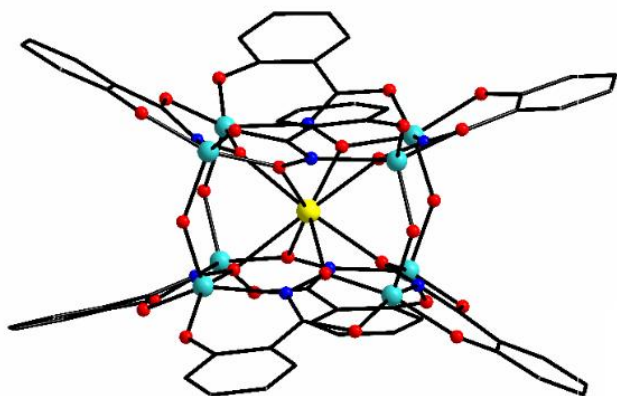


Fig. 1 Schematic representation of complex 1. Color scheme: Ga<sup>III</sup>, aqua; Dy<sup>III</sup>, yellow; N, blue; O, red; C, black. H atoms are omitted for clarity.

Single-crystal diffraction studies unveiled that complex 1 crystallizes in the monoclinic P2/c space group (Table S1). The oxidation states and the assignment of the ligands' protonation/deprotonation level in 1 were based on metric parameters and charge balance considerations. The compound consists of a [Ga<sup>III</sup><sub>8</sub>Dy<sup>III</sup>(OH)<sub>4</sub>(shi)<sub>8</sub>]<sup>-</sup> anion which is counterbalanced by a Bu<sub>4</sub>N<sup>+</sup> cation, while there are also MeOH and H<sub>2</sub>O molecules in the lattice. The anion comprises eight Ga<sup>III</sup> atoms and one Dy<sup>III</sup> atom arranged in a sandwich-like topology. The Ga<sup>III</sup> atoms are located above and below the planes of the central lanthanide ion. The basal Ga<sup>III</sup> atoms are bridged via the oximate groups of eight triply deprotonated shi<sup>3-</sup> ligands in a η<sup>1</sup>:η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup>:μ<sub>3</sub> fashion, while the two deckers are connected to each other via the four μ-OH bridges. The oximate O atoms provided by the ligand are coordinated to the central Dy<sup>III</sup> atom, serving as linkers of the two deckers. As a result, the Dy<sup>III</sup> is enclosed by eight O atoms and possesses a distorted square antiprismatic coordination geometry (distorted D<sub>4d</sub>) around the dysprosium ion (CShM = 1.18, Figure S1, Table S4). All Ga atoms are five-coordinate with slightly distorted to almost perfect square pyramidal geometries (τ = 0.26 - 0.06) as it was defined by the trigonality index parameters.<sup>28</sup> The overall {Ga<sup>III</sup><sub>8</sub>Dy<sup>III</sup>(μ-OH)<sub>4</sub>(μ-NO)<sub>8</sub>}<sup>15+</sup> core of 1 (Figure S2) reveals that the basal Ga•••Ga and the

Ga•••Dy distances are in the ranges of 4.691(1)-4.714(1) and 3.716(1)-3.747(1) Å, respectively, while the Ga•••Ga distances between the two deckers are between 3.387(1) and 3.418(2) Å. The Ga-O-N-Ga torsion angles lie within the 165.3-176.4° range. As it is observed the torsion angles are quite close to 180° and that explains the almost perfect planarity of the two 12-MC-4 planes. Finally, the Dy•••Dy intermolecular distances are in the range of 13.406(1) - 13.691(1) Å meaning that the Dy atoms are isolated in such an arrangement (Figure S3). Certain critical geometrical parameters were acquired for complex 1 in order to get a deeper understanding of the inner coordination sphere of the dysprosium ion (Figure 2).

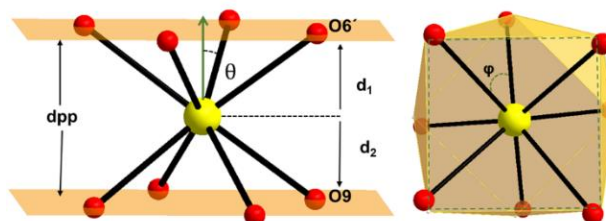


Figure 2. Structural parameters discussed in the text for complex 1. Yellow ball: Dysprosium, red ball: oxygen.

The θ angle, which corresponds to compression or elongation along the tetragonal axis depending on its value, is the angle between the four-fold axis and the Ln-O bond direction. The magic value for perfect eight-coordinate square antiprismatic systems is θ = 54.74°, whilst larger angles are consistent with compression and smaller ones correspond to elongation.<sup>12,29</sup> Complex 1 possess an average θ value of 54.29° revealing a subtle axial elongation for the surrounding of the central lanthanide ion. Another important parameter that was calculated is the skew angle φ, which defines the angle between the diagonals of the two O<sub>4</sub>-planes. When φ is 0 a perfect square prismatic geometry is expected, while when φ is 45° a perfect square antiprismatic geometry is expected. Complex 1 possesses an average φ value of 36.40° which further supports the finding of distorted square antiprismatic geometry of the central Dy<sup>III</sup> ion. The interplanar distance (dpp), was found to be 2.710(1) Å, while the distances d<sub>1</sub> and d<sub>2</sub> were both found to be 1.355(0) Å. Finally, compound 1 is the first and only example of a sandwich-type or double-decker lanthanide 12-MC-4 complex and the first possessing diamagnetic Ga<sup>III</sup> metal ions as the periphery metal ions, encapsulating a paramagnetic Dy<sup>III</sup> ion in the middle.

Solid state, direct-current (dc) magnetic susceptibility studies were performed in the temperature range of 2 – 300 K on a freshly prepared and analytical pure (see Supporting Information) microcrystalline sample of 1•5H<sub>2</sub>O under an applied field of 0.1 T. The χ<sub>M</sub>T product at 300 K is slightly above the value of 14.17 cm<sup>3</sup>K mol<sup>-1</sup> expected for one non-interacting Dy<sup>III</sup> ion (<sup>6</sup>H<sub>15/2</sub>, S = 5/2, L = 5, J = 15/2, g = 4/3) (Figure S4). The χ<sub>M</sub>T product shows a slow and steady decrease upon cooling from 300 K till 50 K, while after that a sharper decrease is observed till 2 K, where it reaches the value of 9.18 cm<sup>3</sup> K mol<sup>-1</sup>. The decrease at low temperature is characteristic for the depopulation of the Zeeman split crystal field levels. The field dependence of magnetization was also measured for complex 1 in the temperature range of 2 - 10 K under a variety of magnetic fields

of the 0 - 7 T range (Figure S5). As displayed in Figure S6, the values of magnetization increase sharply at low fields while after that a more continuous increase is observed for compound **1**. The value of magnetization of complex **1** at 2 K under the applied field of 7 T is  $5.95 \mu_B$ , not reaching saturation. The lack of saturation in magnetization is suggestive of the presence of magnetic anisotropy and/or population of the Dy<sup>III</sup> low-lying states.

To further understand the observed magnetic behaviour of complex **1**, theoretical calculations were carried out using the SIMPRE computational package.<sup>30</sup> The static magnetic susceptibility (Figure S4) was successfully simulated with a relative error of  $E = 1.2 \cdot 10^{-4}$  using the Radial Effective Charge (REC) model ( $D_r = 1.26 \text{ \AA}$  and  $Z_r = 0.045$ ) (see details in SI).<sup>31</sup> The calculated magnetization curves are also in a good agreement with the experimental data (Figure S5).

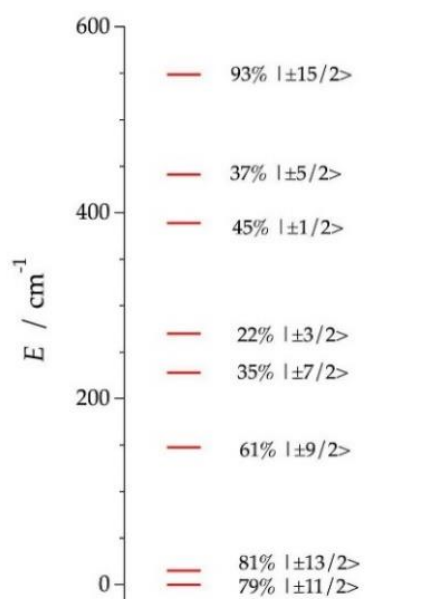


Fig. 3 Energy diagram of Dy(III) electronic sublevels according to performed calculations.

According to our calculations, the ground state wave function is mainly composed by 79% of the  $|\pm 11/2\rangle$  microstates in the easy axis direction, which is congruent with the observed slow relaxation of the magnetization. The first excited doublet is located at about  $15 \text{ cm}^{-1}$ , showing a large contribution (81%) of another high spin microstate ( $\pm 13/2$ ) and widely separated from the rest of energy levels (Figure 3). This distribution of the energy levels is similar to other Dy-based compounds with  $D_{4d}$  symmetry such as  $\text{Pc}_2\text{Dy}^{32}$ ,  $[\text{Dy}(\text{W}_5\text{O}_{18})_2]^{9-33}$  or  $[\text{PPh}_4][\text{Dy}\{\text{Pt}(\text{SAC})_4\}_2]^{34}$ , where the ground and first excited doublets are dominated either by  $\pm 11/2$  or  $\pm 13/2$ , while  $\pm 15/2$  governs the highest in energy Kramers doublet. This contrasts with very axial systems like dysprosocenium<sup>10,11</sup> where a large negative  $B_2^0$  stabilizes an isolated  $\pm 15/2$  ground state. Furthermore, the distortion of the local symmetry, quantified by the skew angle ( $\phi = 36.40^\circ$ ), results in remarkable contributions of extra-diagonal CFPs that induce mixing between the  $M_J$  microstates as one can observe in Tables S5 and S6. Indeed, a fit of the magnetic properties by only considering the diagonal CFPs could not reach satisfactory results,

emphasizing the important role of the non-negligible extradiagonal terms to model the properties of **1**. Regarding the total splitting of the ground- $J$  multiple, we found that it is about  $550 \text{ cm}^{-1}$ , which suggests that the MC framework provides a moderately large ligand field, although comparable with other oxygen-coordinated Dy<sup>III</sup> compounds reported in the literature.<sup>35,36</sup> More details about the employed electrostatic model are available in the Supporting Information.

Alternating-current (ac) susceptibility measurements were performed for complex **1** in a zero-applied dc field, with a 3 Oe ac field oscillating at frequencies from 1-1400 Hz in the temperature range of 1.9-5.5 K. Complex **1** displays frequency-dependant tails of signals below 5.5 K at zero field, indicative of the presence of fast relaxation of magnetization (Figure S6-S9). This means that the slow relaxation of magnetization and QTM coexist. The lack of the appearance of the  $\chi''$  peak maxima at zero field led to further investigations, using the assistance of an applied field of 1000 Oe (at frequencies from 1-1400 Hz and at a temperature range of 1.9-5.5 K) aiming to shift the peaks and suppress the QTM (Figure S10). After the application of the external field, the field-induced SMM behaviour of compound **1** is clearly pronounced since the  $\chi'$  and  $\chi''$  values are significantly increased and the peaks maxima are clearly visible (Figure 4). In zero dc field the Kramer Dy(III) ions, which possess an easy-axis anisotropy, can be affected by the dipole-dipole and hyperfine interactions, allowing the mixing of the ground state  $M_J$  microstates thus advancing the QTM over thermal relaxation processes.<sup>13,37</sup> In order to reduce or even remove the QTM, an external magnetic field was employed. The Cole-Cole plots for **1** in the temperature range of 1.9 K-5.5 K display semicircular shapes and a generalized Debye model (Cole-Cole model) was used for fitting of the data.<sup>38,39</sup> The obtained  $\alpha$  values are in the range of 0.47- 0.36, implying a distribution of relaxation times and possibly indicating the presence of multiple relaxation pathways due to a combination of thermally assisted processes and QTM, proven additionally from the fitting discussed.

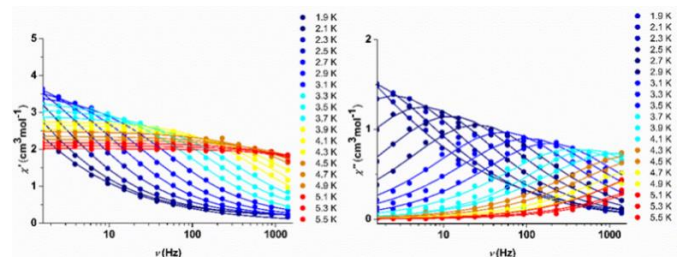
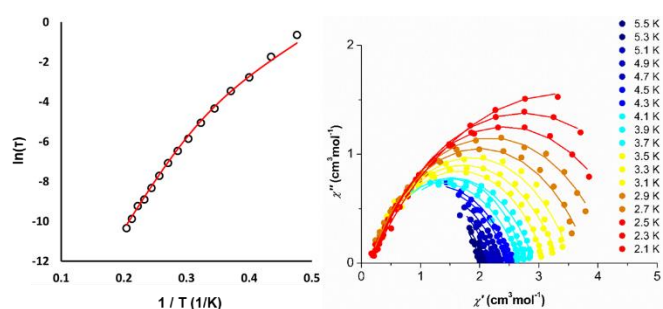


Fig. 4 Frequency-dependent ac susceptibilities in an applied field of 1000 Oe for complex **1**. The solid lines represent fitting of the data.

We plotted  $\ln(\tau)$  versus  $1/T$  (Figure 5) and a linear behaviour is observed for the high temperature regime, revealing the presence of a thermally activated Orbach pathway. A fit was obtained taking into account the Raman process as well which dominates at the low temperature regime according to the equation  $\tau^{-1} = CT^n + \tau_0^{-1}\exp(-U_{\text{eff}}/K_B T)$ , where  $CT^n$  corresponds to the Raman relaxation and the last terms relate to the Orbach relaxation pathway.<sup>40</sup> The best fit parameters are  $n = 9.0(4)$ ,  $C = 0.0019(5) \text{ s}^{-1}\text{K}^{-9}$ ,  $U_{\text{eff}} = 39.00 \pm 0.04 \text{ K}$

27.1 cm<sup>-1</sup>,  $\tau_0 = 2.27(5) \times 10^{-8}$  s (Figure 5). The larger value of  $U_{eff}$  when compared to the energy of the first Kramers Doublet suggests a complex relaxation process that may imply the second excited state as has been shown in other Dy complexes<sup>41,42</sup> and/or indicate the presence of off-resonance phonons that are thermally activated above the energy of the first excited state, inducing fast relaxation<sup>10,43</sup>. Finally, due to the rather modest observed anisotropy barrier and the strong presence of the Raman component, we also performed a fit using uniquely the Raman process (Figure S12), which evidenced that the Orbach contributions dominates at the high temperature regime. More details can be found as a Supporting Information.



**Fig. 5** (left) Arrhenius plot showing the magnetization relaxation of **1** under an applied field of 1000 Oe. (right) Cole-Cole plots for compound **1** using the ac susceptibility data under a field of 1000 Oe from 2.1 K to 5.5 K. The solid lines represent the best fit obtained using the generalized Debye model.

Preliminary photoluminescence studies have been performed and shown in Figure S13. Complex **1** shows a strong blue emission upon maximum excitation at 341 nm. The excitation spectrum clearly shows that there is a direct excitation of the Dy(III) ion through f-f transitions (Figure S14). While the broad band at ~375 nm is most likely due to strong charge transfer effects, the bands at 474, 581, 670 and 757 nm can be attributed to the characteristic  $^4F_{9/2} \rightarrow ^6H_{15/2}$ ,  $^4F_{9/2} \rightarrow ^6H_{13/2}$ ,  $^4F_{9/2} \rightarrow ^6H_{11/2}$  and  $^4F_{9/2} \rightarrow ^6H_{9/2}$  emission transitions of Dy<sup>III</sup> ions, respectively.<sup>44</sup> Up to now, neither fluorescence nor absorption spectra associated with lanthanide centres have been reported in Ln-based phthalocyanine (Pc) double-decker complexes.<sup>45</sup>

In conclusion, we have shown that the reaction of Ga(NO<sub>3</sub>)<sub>3</sub>•H<sub>2</sub>O, and Dy(O<sub>2</sub>CMe)<sub>3</sub>•xH<sub>2</sub>O in the presence of salicylhydroxamic acid leads to the isolation of a novel Ln(III) double-decker 12-MC-4 or sandwich type complex, which shows slow relaxation of magnetization both at zero and with an applied magnetic field. Experimental measurements further confirmed the SMM nature of our {Ga<sub>2</sub>Dy} complex upon application of an external field of 1000 Oe, giving an effective energy barrier of  $U_{eff} = 39.00 \pm 0.04$  K (27.1 cm<sup>-1</sup>) and a relaxation time  $\tau_0 = 2.3(5) \times 10^{-8}$  s, while photoluminescence studies recorded the dysprosium-based emission of the compound. This work paves the way to the use of metallacrowns as a versatile scaffold for the rational design of SIMs. Based on this proof-of-concept, more exciting compounds with improved properties can be envisioned, following a judicious chemical design of the coordination environment. Work in progress

involves the isolation and characterization of more members of the lanthanide series, such as Tb<sup>III</sup>, Ho<sup>III</sup>, Er<sup>III</sup>, as well as the deeper investigation of the role the Ga(III) ions play regarding the observed slow relaxation of magnetization of the resulting novel {Ga<sub>2</sub>Dy} compound.

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## Conflicts of interest

"There are no conflicts to declare".

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