COMMUNICATION

Beyond the anisotropy barrier: slow relaxation of the magnetization in both easy-axis and easy-plane Ln(trensal) complexes†

Eva Lucaccini,[a] Lorenzo Sorace,*[a] Mauro Perfetti,[a] Jean-Pierre Costes[b] and Roberta Sessoli[a]

We present a spectroscopic and magnetic (both static and dynamic) characterization of two isostructural Dy and Er complexes evidencing that, despite the different types of magnetic anisotropy, the two molecules show similar slow relaxation of the magnetization in a static magnetic field.

The number of mononuclear lanthanide complexes reported to show slow relaxation of the magnetization at low temperature has increased very rapidly after the seminal report of Ishikawa on terbium-phthalocyaninate,[1] making this one of the most studied subjects in molecular magnetism.[2] Despite the efforts and the achievements obtained to date, many open questions remain on the behaviour of these molecules, which need to be rationalized if one wishes to improve their properties in term of the blocking temperature. In particular, the relaxation processes characterizing these systems are often more complex than assumed. With the exception of few reports,[3,4] the slow relaxation of the magnetization is usually attributed to an Orbach mechanism[5] even if further experimental or theoretical confirmation is not available. However, the clarification of the different dynamics reported so far and the exploration of the different pathways for magnetic relaxation require a detailed picture of the electronic structure of these systems. Experimentally, this can only be obtained by using a combined spectroscopic and magnetic characterization of structurally simple systems.[6]

Following this approach, we present here the results obtained by a combined magnetic, Electron Paramagnetic Resonance (EPR) and Crystal Field (CF) analysis, on mononuclear lanthanide complexes having the formula Ln(trensal) (where H_3trensal = 2,2′,2″-Tris-(salicylideneimino)triethylamine) which feature crystallographically imposed trigonal symmetry (Fig. 1, inset and Fig. S1 and S2, ESI†).[7]

This series represents an ideal system for correlating the magnetization dynamics with the magnetic anisotropy because C_3 symmetry, preserved at liquid helium temperature,[7b] reduces the number of CF parameters to be determined to describe their electronic structure. These are known with great accuracy thanks to the high quality luminescence spectra which were previously analysed and reproduced for most of the derivatives in the series.[7b] In the following we will focus on Er^{III} (**1**) and Dy^{III} (**2**) derivatives, since both these ions show a ground $J = 15/2$ state but, according to phenomenological approach popularized by Long, should behave differently in terms of the low temperature dynamics.[2b]

We first analyzed the χT *vs.* T curves (Fig. 1): the room temperature values are in agreement with those expected for the $^4I_{15/2}$ and $^6H_{15/2}$ multiplets of Er^{III} and Dy^{III}, while the observed temperature dependence can be attributed to the progressive depopulation of the excited sublevels. To evaluate if this behaviour is in agreement with the CF parameters reported in ref. 7b (Table S1, ESI†) we used the home-developed software EVALUCF.[8] Here the effect of the CF over the different multiplets, arising from the spin–orbit splitting of the ground term of each rare-earth, is calculated
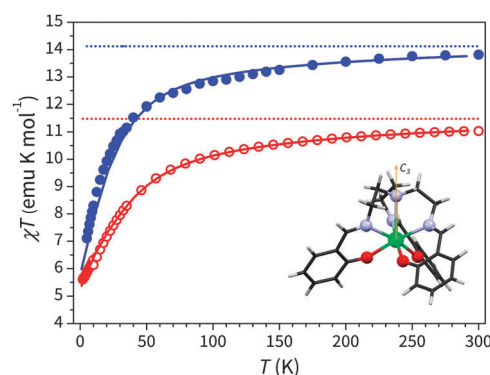

Fig. 1 Temperature dependence of the χT product for **1** (empty circles) and **2** (full circles), along with theoretical curves calculated by using the CF parameters reported in ref. 7b. Dashed lines correspond to the expected free-ion χT values. In the inset the molecular structure of Ln(trensal) is sketched, evidencing the trigonal symmetry.

[a] *Dipartimento di Chimica "U. Schiff" and UdR INSTM, Università di Firenze, Via della Lastruccia 3-13, Sesto Fiorentino(FI), Italy. E-mail: lorenzo.sorace@unifi.it; Fax: +39 0554573372; Tel: +39 0554573336*

[b] *Laboratoire de Chimie de Coordination 205, route de Narbonne 31077 Toulouse, Cedex 4, France*

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using the appropriate Hamiltonian in the Wybourne formalism,[9] which for C_3 symmetry is:†

$$
\begin{aligned}
\hat{H}_{CF} &= B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_{-3}^4 - C_3^4) + B_0^6 C_0^6 \\
&\quad + B_3^6 (C_{-3}^6 - C_3^6) + iB_3'^6 (C_{-3}^6 + C_3^6) + B_6^6 (C_{-6}^6 + C_6^6) \\
&\quad + iB_6'^6 (C_{-6}^6 - C_6^6)
\end{aligned}
\tag{1}
$$

The energy difference between the different multiplets was phenomenologically adjusted to correctly reproduce the results reported in ref. 7b, and the final diagonalization provided the eigenvalues and eigenvectors in terms of the $|J, M_J\rangle$ components. The effect of a magnetic field was then evaluated over a 55 point grid to obtain the powder average susceptibility at different temperatures.[8] This approach, without any free parameters, reproduced very well the experimental curves for both derivatives, lending further support to the correctness of the parameter set.

The resulting energy patterns for the two ground multiplets are reported in Table 1: a gap of 54 and 50 cm^{-1} is calculated between the ground and first excited doublets for **1** and **2**, respectively. The corresponding ground state wavefunctions are characterized in both cases by large mixing of different $|M_J\rangle$ (Table 1 and Fig. S3, ESI†). By calculating the effect of the magnetic field over the energy levels of the two complexes we could calculate the effective g values for the ground doublets of the two derivatives as $g_\perp^{eff} = 1.2$, $g_\parallel^{eff} = 13$ for **1** and $g_\perp^{eff} = 9.6$, $g_\parallel^{eff} = 2.6$ for **2**. Experimental confirmation of this estimate could be obtained by EPR spectroscopy on microcrystalline powder samples, both at X- and W- band (Fig. 2 and Fig. S4, ESI†), which confirmed the expected trend, with **1** being the easy axis ($g_\parallel = 11.8 \pm 0.4 > g_\perp = 3.6 \pm 0.1$) and **2** the easy plane ($g_\perp = 9.4 \pm 0.5 > g_\parallel = 1.8 \pm 0.1$). The observed g values for **1** are also in agreement with the saturation value of the M vs. H curve, slightly higher than the calculated one (Fig. S5, ESI†). At any rate, the combined luminescence, EPR and dc magnetic analysis provided a sound quantitative description of the electronic structure of these systems, evidencing the different character of the magnetic anisotropy of the two derivatives, as expected on the basis of the prolate and oblate charge distribution of the two ions.[2b,10] Since **1** is an easy axis system with a non-negligible gap between the ground and the first excited doublet, it may be expected to show slow relaxation of the magnetization at low temperature with an Arrhenius like dependence of the relaxation rate, while **2** should not.

Table 1 Energies of the 8 doublets of the $J = 15/2$ multiplets calculated with the CF parameters reported in ref. 7b, and corresponding composition of ground doublets. Contributions lower than 5% are not reported. See ESI for more details

Energies (cm^{-1})							
1	0	54	102	109	321	568	619	651
2	0	50	98	172	414	577	645	787

Amplitude of $|M_J\rangle$ contributing to ground doublets

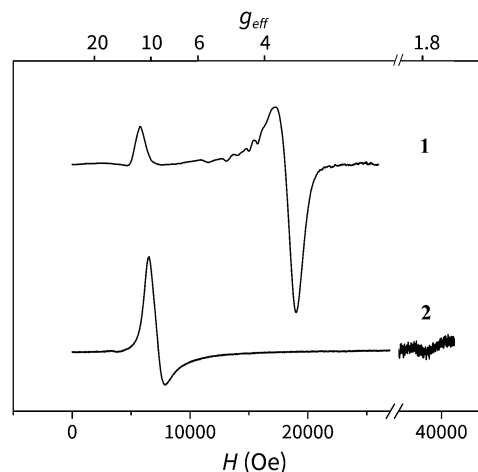|	
1	$68.4\% \left\|\pm\frac{13}{2}\right\rangle, 5\% \left\|\pm\frac{7}{2}\right\rangle, 10.4\% \left\|\pm\frac{1}{2}\right\rangle, 11.6\% \left\|\mp\frac{13}{2}\right\rangle$
2	$8.7\% \left\|\pm\frac{13}{2}\right\rangle, 24.3\% \left\|\pm\frac{7}{2}\right\rangle, 33.1\% \left\|\pm\frac{1}{2}\right\rangle, 20.2\% \left\|\mp\frac{5}{2}\right\rangle, 5.3\% \left\|\mp\frac{11}{2}\right\rangle$

Fig. 2 W-band (94.3 GHz) spectra of microcrystalline powder samples of **1** and **2**, recorded at 5 K.

To investigate this point, variable frequency ac magnetic susceptibility experiments were performed for complexes **1** and **2** as a function of temperature, with and without applied dc field. In the absence of the dc field, none of the two complexes showed out-of phase magnetic susceptibility, χ''. This is not surprising, since quantum tunneling (QT) of magnetization[11] is expected to play a relevant role due to the mixture of different $|J, M_J\rangle$ characterizing the ground doublets of the two derivatives. However, when applying dc fields in the range of 200–2400 Oe at 1.9 K, a clear slow relaxation process is unexpectedly observed for both complexes, the maximum of the relaxation time being observed at an applied field of about 800 Oe and 900 Oe for **1** and **2**, respectively (Fig. S6, ESI†).

The Arrhenius plot of the temperature dependence of the relaxation times, obtained by fitting the χ'' vs. ν curves to a Debye model (Fig. S7 and S8, ESI†),[12] evidences quite a similar trend for the two derivatives, with large deviation from linear behaviour at lower temperatures. A tentative fit of the high temperature region results in the following parameters: $\tau_0 = (2.7 \pm 0.5) \times 10^{-8}$ s, $\Delta = 22 \pm 1$ cm^{-1} for **1**, and $\tau_0 = (5 \pm 2) \times 10^{-7}$ s, $\Delta = 7 \pm 1$ cm^{-1} for **2**. The two estimated barriers are clearly in contrast to the energy difference between the ground and the first excited doublet obtained by the luminescence data, indicating that the outcome of the phenomenological fit to the Arrhenius law has no physical meaning in this case, thus excluding that the observed barrier is connected to an Orbach process. Since both the easy axis **1** and the easy-plane **2** complexes show slow relaxation of the magnetization, it is quite clear that other mechanisms should account for the observed slow relaxation.

To analyse this issue in more detail we performed experiments on a isomorphous Y(trensal) complex doped with 5.8% and 3.1% of Er^{III} and Dy^{III}, respectively (see ESI†) to rule out the possibility of effects due to intermolecular interactions. These are indeed known to play a relevant role in the magnetic relaxation of single-molecule magnets, especially in mononuclear and f-element systems.[13]

Both systems showed field and temperature dependences of the dynamic susceptibility which are largely similar to those of the pure samples (Fig. S9 and S10, ESI†). The analysis of the relaxation rate as a function of the field at low temperature ($T = 1.8$ K) is reported in the upper panel of Fig. 3 and points to a competition between
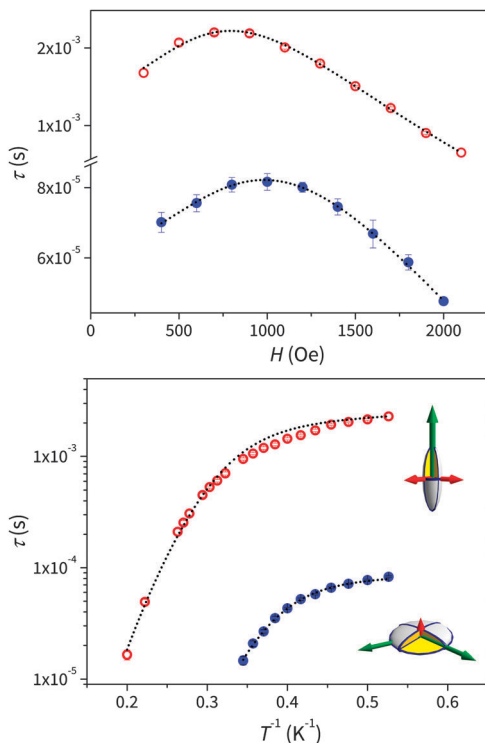
Fig. 3 Field (upper) and temperature (lower) dependence of the relaxation times of Y:Er(trensal) (empty circles) and Y:Dy(trensal) (full circles) and best fit curves obtained by using eqn (2) and (3). The ellipsoids in lower panel graphically represent the anisotropy of the susceptibility tensors of the ground doublet of the two derivatives.

two different field dependent relaxation processes. The increase in relaxation time observed in lower fields indicates that, on applying the field, QT processes are reduced, while the decrease observed at higher fields should be attributed to the increased relevance of the direct process. On these grounds, we tentatively analyzed the observed behaviour using eqn (2):

$$\tau^{-1} = \frac{B_1}{1 + B_2 H^2} + A_1 H^4 T + A_2 H^2 T \qquad (2)$$

where the first term represents the field dependence of QT process,[14] the second one the direct process for a Kramers ion without hyperfine interactions, and the third one is the direct process for a Kramers ion in the presence of hyperfine interaction.[15] Indeed, both samples contain magnetic and non-magnetic nuclei. The best fit curves provided in both cases very small values for the direct process not involving hyperfine interaction (parameters: $A_1 = (2.0 \pm 1.8) \times 10^{-12}$ s^{-1} K^{-1} Oe^{-4}, $A_2 = (1.4 \pm 0.1) \times 10^{-4}$ s^{-1} K^{-1} Oe^{-2}, $B_1 = (71 \pm 4) \times 10$ s^{-1}, $B_2 = (2.7 \pm 0.4) \times 10^{-6}$ Oe^{-2} for **1**; $A_1 = (3 \pm 2) \times 10^{-11}$ s^{-1} K^{-1} Oe^{-4}, $A_2 = (2.0 \pm 0.1) \times 10^{-3}$, s^{-1} K^{-1} Oe^{-2} $B_1 = (158 \pm 2) \times 10^2$ s^{-1}, $B_2 = (9.2 \pm 0.7) \times 10^{-7}$ Oe^{-2} for **2**). The temperature dependence of the relaxation time for the diluted systems are reported in the lower panel of Fig. 3: the weak temperature dependence of τ observed at low temperature suggests a contribution by the QT process, whereas the temperature dependence observed at higher T indicates that relaxation proceeds by exchange of energy with lattice vibrations. The observed curvature of the Arrhenius plot indicates a non-negligible

influence of direct and/or Raman processes in determining the relaxation rate,[15,16] the former having been confirmed using the field dependent measurements. On these grounds we analysed the temperature dependence of the relaxation rates for diluted samples by using eqn (3):

$$\tau^{-1} = \frac{B_1}{1 + B_2 H^2} + A_1 H^4 T + A_2 H^2 T + C T^n + \tau_0^{-1} \exp(-\Delta/kT)$$

$$(3)$$

where the first three terms are the same as in eqn (2), the fourth is the Raman one, and the fifth is the Orbach one. Due to the large number of parameters involved we fixed the first three to the values obtained by the analysis of the field dependent relaxation rate. For none of the two derivatives reasonable fits could be obtained by including Orbach processes in addition to the direct and QT ones, while a Raman process, with variable exponent n, provided reasonable reproduction of the data (best fit values $n = 9$ for **1** and $n = 11$ for **2**). Therefore it is evident that the relaxation is not occurring *via* the first excited doublet in any of the two derivatives.

In summary we conclude that, despite Er(trensal) being an easy axis type complex and Dy(trensal) an easy plane one, the two molecules show slow relaxation of the magnetization, both as a function of temperature and of the field. This observation invalidates the general assumption that the slow dynamics of magnetization is associated with the magnetic anisotropy in lanthanide complexes, and stresses the absolute importance of complementing the magnetic characterization of these systems with spectroscopic techniques.[17] It is clear that only a multitechnique approach allows us to understand the factors affecting the magnetization dynamics and relaxation mechanisms in these systems and can provide a valuable feedback to develop new synthetic strategies.

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17 During the submission of this manuscript we were informed that another group is currently working on the magnetic characterization of Er(trensal): J. Dreiser, private communication.