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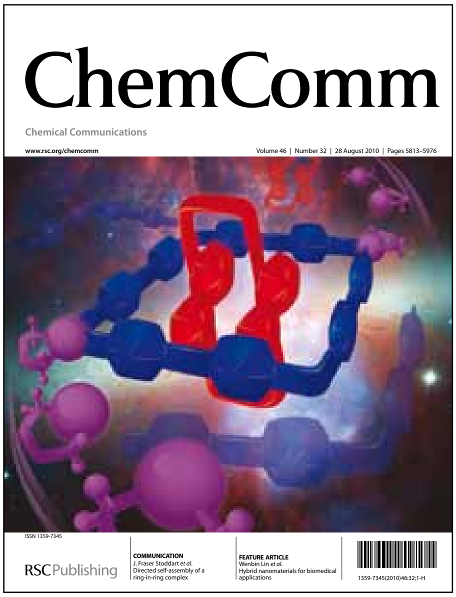

ChemComm

Chemical Communications

www.rsc.org/chemcomm Volume 46 | Number 32 | 28 August 2010 | Pages 5813–5976

ISSN 1359-7345

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ARTICLE TYPE

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

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We present a spectroscopic and magnetic (both static and dynamic) characterization of two isostructural Dy and Er complexes evidencing that, despite the different type of 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-phtalocyaninate,[1] making this one of the most studied subject in molecular magnetism.[2] Despite the efforts and the achievements obtained up 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 blocking temperature. In particular, the relaxation processes characterizing these systems are often more complex than assumed. With the exception of some reports[3,4] the slow relaxation of the magnetization is usually attributed to an Orbach mechanism[5] even if further experimental or theoretical confirmation are not available. However, the clarification of the different dynamics reported so far and the exploration of the different pathways for magnetic relaxation requires a detailed picture of the electronic structure of these systems. Experimentally, this can only be obtained by using a combined spectroscopic and magnetic characterization on 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 of formula Ln(trensal), where H_3trensal= 2,2',2"-Tris(salicylideneimino)triethylamine, featuring crystallographically imposed trigonal symmetry (Figure 1, inset and S1-S2, ESI†).[7] This series represents an ideal system to correlate the magnetization dynamics to the magnetic anisotropy because C_3 symmetry, not affected by lowering temperature, [7b] limits the number of CF parameters. These are, known with great accuracy thanks to the high quality luminescence spectra which were previously analysed and reproduced for most of the derivatives of the series.[7b] In the following we will focus on Er^{III}(**1**) and Dy^{III} (**2**) derivatives, since both these two ions show a ground J = 15/2 state but, according to phenomenological approach popularized by Long, should behave differently in terms of 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

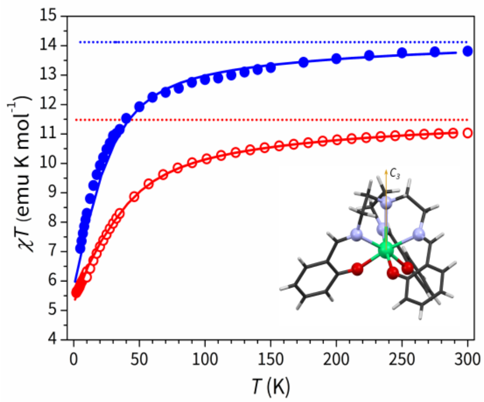

Fig. 1 Temperature dependence of the χT product for **1** (empty circles) and **2** (full circles), along with theoretical curves calculated by using the CF parameters reported in 7. Dashed lines correspond to the expected free-ion χT values. In the inset the molecular structure of Ln(trensal) is sketched,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

$^4I_{15/2}$ 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. 7 (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 using the appropriate Hamiltonian in the Wybourne formalism,[9] which for C_3 symmetry is:†

$$\hat{H}_{CF} = B_0^2\mathbf{C}_0^2 + B_0^4\mathbf{C}_0^4 + B_3^4\left(\mathbf{C}_{-3}^4 - \mathbf{C}_3^4\right) + B_0^6\mathbf{C}_0^6 + B_3^6\left(\mathbf{C}_{-3}^6 - \mathbf{C}_3^6\right) + iB'^6_3\left(\mathbf{C}_{-3}^6 + \mathbf{C}_3^6\right) + B_6^6\left(\mathbf{C}_{-6}^6 + \mathbf{C}_6^6\right) + iB'^6_6\left(\mathbf{C}_{-6}^6 - \mathbf{C}_6^6\right) \quad (1)$$

The energy difference between the different multiplets was phenomenologically adjusted to correctly reproduce the results reported in ref. 7, and the final diagonalization provided the eigenvalues and eigenvectors in terms of $|J, M_J>$ 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

	Energies (cm^{-1})							
1	0	54	102	109	321	568	619	651
2	0	50	98	172	414	577	645	787
	Amplitude of $\left\|M_J\right\rangle$ 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	$8.7\%\left\|\pm\frac{13}{2}\right\rangle,24.3\%\left\|\pm\frac{7}{2}\right\rangle,33.1\%\left\|\pm\frac{1}{2}\right\rangle,20.2\%\left\|\mp\frac{5}{2}\right\rangle,5.3\%\left\|\mp\frac{11}{2}\right\rangle$							

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

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 $|M_J>$ (Table 1 and Fig. S3 ESI†). So we could calculate the effective *g* values for the ground doublets of the two derivatives as $g_\perp^{eff} = 13$, $g_{//}^{eff} = 1.2$ for **1** and $g_\perp^{eff} = 9.6$, $g_{//}^{eff} = 2.6$ for **2**. Experimental confirmation of this estimate could be gained by EPR spectroscopy on microcrystalline powder samples, both at X- and W- band (Fig. 2 and S4 ESI†), which confirmed the expected trend, with **1** being easy axis ($g_{//} = 11.8 \pm 0.4 > g_\perp = 3.6 \pm 0.1$) while **2** is easy plane ($g_\perp = 9.4 \pm 0.5 > g_{//} = 1.8 \pm 0.1$). 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.

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 *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 $|J, M_J>$ 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-S8, ESI†),[12] evidences quite 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 with the energy difference between the ground and the first excited doublet obtained by the luminescent 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.

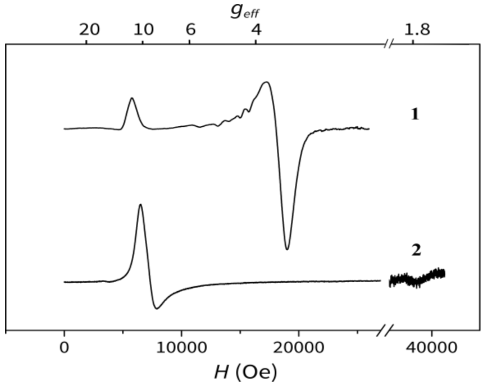

Fig. 2 W-band (94.3 GHz) spectra of a microcrystalline powder sample of **1** and **2**, recorded at 5 K.

To analyse this issue in more detail we performed experiments on 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 on 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-S10, ESI†). The analysis of the relaxation rate as a function of the field at low temperature (*T* =1.8 K) is reported in Figure 3(a), and points to a competition between 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 is to be attributed to the increased relevance of direct process. On these grounds, we tentatively analyzed the observed behaviour using eq. (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 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 Figure 3(b): the weak temperature dependence of τ observed at low temperature suggests a

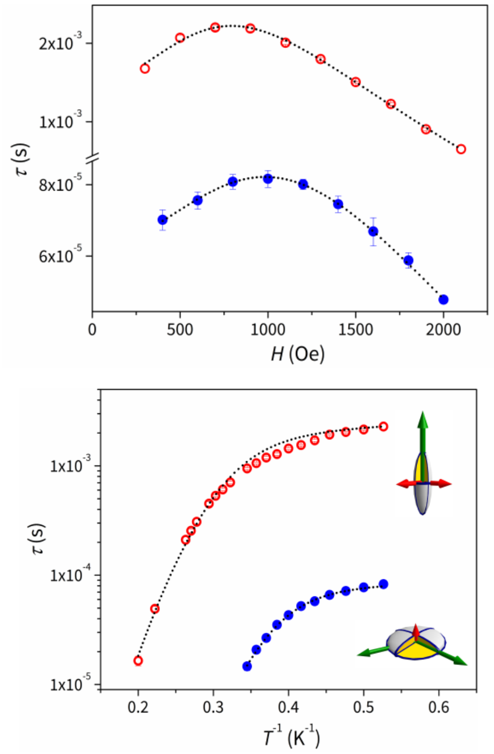

Fig. 3 Field (upper) and temperature (lower) dependence of the relaxation times of Y:Er(trensal) (empty circles) and Y:Dy(trensal) (full circles) and best fit curves obtained by using eqs. 2 and 3. The ellipsoids in lower panel graphically represent the anisotropy of the susceptibility tensors of the ground doublet of the two derivatives.

contribution by 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 by the field dependent measurements. On these grounds we analysed the temperature dependence of the relaxation rates for diluted samples by using eq. (3):

$$\tau^{-1} = \frac{B_1}{1+B_2H^2} + A_1H^4T + A_2H^2T + CT^n + \tau_0^{-1}\exp\left(-\Delta/kT\right) \qquad (3)$$

where the first three terms are the same as in eq. (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 none 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 the magnetization is associated in lanthanide complexes to the magnetic anisotropy, and stresses the absolute importance of complementing the magnetic characterization of these systems with spectroscopic techniques. It is clear that only a multitechnique approach allows 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.

We acknowledge the financial support of MIUR through project Futuro in Ricerca 2012 (RBFR12RPD1) and of EC through the ERC-AdG MolNanoMas (267746).

Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedure; Experimental setup; Powder X-ray diffractograms; EPR spectra; isothermal magnetization curves, original *ac* susceptibility data. See DOI: 10.1039/b000000x/

1 N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.*, 2003, **125**, 8694
2 (a) D. N. Woodruff, R. E. P. Winpenny, and R A. Layfield, *Chem. Rev.*, 2013, **113**, 5110 (b) J. D. Rinehart and J. C. Long *Chem. Sci.* 2011, **2**, 2078 (c) L. Sorace, C. Benelli, D. Gatteschi, *Chem. Soc. Rev.*, 2011, **40**, 3092 (d) M. A. AlDamen, S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, C. Martì-Gastaldo, A. Gaita-Arino, F. Luis and O. Montero, *Inorg. Chem.*, 2009, **48**, 3467
3 (a) G. Cucinotta, M. Perfetti, J. Luzon, M. Etienne, P. E. Car, A. Caneschi, G. Calvez, K. Bernot, R. Sessoli, *Angew. Chem.-Int. Ed.* 2012, **51** 1606 (b) M.-E. Boulon, G. Cucinotta, J. Luzon, C. Degl'Innocenti, M. Perfetti, K. Bernot, G. Calvez, A. Caneschi, R. Sessoli, *Angew. Chem.-Int. Ed.* 2013, **52,** 350
4 (a) R. J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E. J. L. McInnes, L. F. Chibotaru, R. E. P. Winpenny, *Nature Chem.* 2013 **5** 673; (b) K. Bernot, J. Luzon, L. Bogani, M. Etienne, C. Sangregorio, M. Shanmugam, A. Caneschi, R. Sessoli and D. Gatteschi, *J. Am. Chem. Soc.*, 2009, **131**, 5573; (c) H. L. C. Feltham, Y. Lan, F. Klöwer, L. Ungur, L. F. Chibotaru, S. Brooker and A. K. Powell *Chem. Eur. J.* 2011, **17**, 4362
5 R. Orbach, *Proc. R. Soc. London, Ser. A*, 1961, **264**, 458
6 (a) J. D. Rinehart and J. R: Long, *Dalton Trans.* 2012,**41**, 13572; (b) N. Magnani, R. Caciuffo, E. Colineau, F. Wastin, A. Baraldi, E. Buffagni, R. Capelletti, S. Carretta, M. Mazzera, D. T. Adroja, M. Watanabe and A. Nakamura, *Phys. Rev. B*, 2009, **79**, 104407
7 (a) P. V. Bernhardt, B. M. Flanagan and M. J. Riley, *Aust. J. Chem.*, 2000, **53**, 229; (b) B. M. Flanagan, P. V. Bernhardt, E. R. Krausz, S. R. Lüthi and M. J. Riley, *Inorg. Chem.*, 2002, **41**, 5024
8 E. Lucaccini, Master thesis, Univ. of Florence, 2013
9 C. Görller-Walrand and K. Binnemans, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. K. A. Gschneidner, Jr. and L. Eyring, 1996, vol. 23, p. 121
10 J. Sievers, *Z. Phys. B: Condens. Matter Quanta*, 1982, **45**, 289
11 D. Gatteschi, R. Sessoli, J. Villain, *Molecular nanomagnets,* Oxford University Press, Oxford, 2006
12 H. B. J. Casimir and F. K. Du Prè, *Physica*, 1938, **5**, 507
13 K. Meihaus, J. Rinehart, J. R. Long, *Inorg. Chem.* **2011**, 50, 8484
14 A. Fort, A. Rettori, J. Villain, D. Gatteschi and R. Sessoli, *Phys. Rev. Lett.*, 1998, **80**, 612
15 A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Dover, New York, 1986
16 (a) J. M. Zadrozny, M. Atanasov, A. M. Bryan, C.-Y. Lin, B. D. Rekken, P P. Power, F. Neese and J. R. Long, *Chem. Sci***.**, 2013,**4**, 125; (b) J.-L. Liu, K. Yuan, J.-D. Leng, L. Ungur, W. Wernsdorfer, F.-S. Guo, L. F. Chibotaru, and M.-L. Tong *Inorg. Chem.* 2012, **51**, 8538