Neodymium 1D systems: targeting new sources for field-induced slow magnetization relaxation

Amanpreet Kaur Jassal,[a] Núria Aliaga-Alcalde,[b*] Montserrat Corbella,[c*] Daniel Aravena,[d] Eliseo Ruiz[e*], and Geeta Hundal[a*]

Two non-isostructural homometallic 1D Neodymium species that display field-induced slow magnetization relaxations are presented together with theoretical studies that endorse the experimental data and provide more insight on their magnetic performance. From the latest, we establish that intramolecular exchange interactions among Nd^{III} ions for the two compounds are negligible and dipolar exchanges prevail, leading to the conclusion that, magnetically, both systems are better described as organized 1D single molecule magnets (SMMs). Our studies also suggest that Nd^{III} ions provide great versatility toward the achievement of homometallic chains with slow relaxation of the magnetization.

Single molecule magnets (SMMs) and single chain magnets (SCMs) stand for 0D and 1D coordination compounds that present slow relaxation of the magnetization and magnetic hysteresis at low temperatures.[1] SMM behavior arises from the combination of large ground-state spin S and zero-field splitting parameter D in isolated anisotropic compounds (mono- or poly-nuclear systems); the slow magnetic relaxation[2] in SCMs however, appears from the magnetic interactions between anisotropic repeating units along well-isolated single chains.[3] Particular ratios between anisotropy and exchange interactions among the metallic centers in the chains, allow the existence of SCM behavior.[4] The interesting link between SMMs and SCMs still deserves further theoretical investigation because the 1D organization of SCMs can induce a significant increase in the energy barrier for the reversal of the magnetization;[5] this being the original motivation for the construction of SCMs.[6]

So far, many of the SCMs reported in the literature are derived from 3*d* ions,[7] mixed 3*d*-4*f* ions[8] or pre-formed bridged 3*d* SMMs.[9] Much recently, homometallic 4*f* SCMs[10] have been presented with special interest, toward the creation of new magnetic materials,[11] due to the large anisotropic values of lanthanide carriers (mainly because of their strong spin–orbit contributions) and their moderate magnetic exchange couplings.[12] Everything considered, homometallic 4*f* SCMs deserve further experimental and theoretical studies. Hitherto, Dy^{III}, Tb^{III}, Er^{III} and Ho^{III} ions have been primarily employed[13] but further understanding of the field requires a look on other Ln^{III} ions as well, for e.g. Nd^{III} presented here. Nd^{III} coordination compounds (0D or 1D) have been mostly studied because of their luminescent properties at the near-IR region[14] although it has been shown that few mononuclear Nd^{III} systems behave as SMMs.[15]

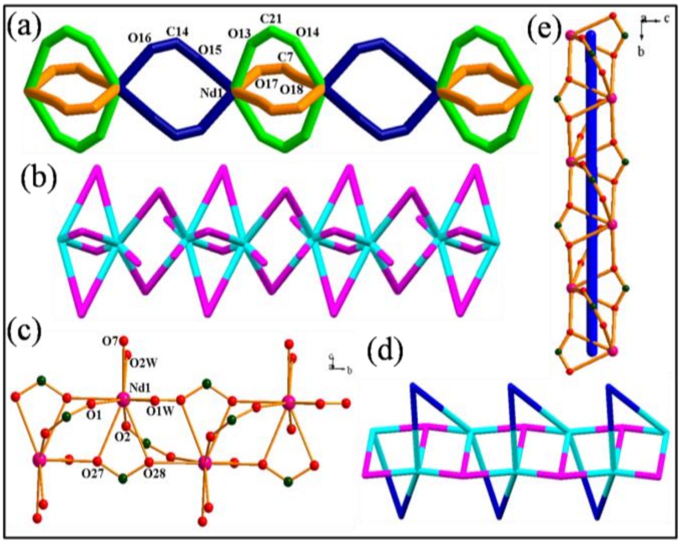

Fig. 1 (a) **L1** bridged paddlewheel dimeric units (green and orange color) further bridged by L1 (blue color), forming linear tapes along *a* axis, in **1**. (b) [1 0 0] chains of **1** with 2-connected uninodal net. (c) ball-n-stick representation showing coordination environment around Nd^{III} in **2**. (d) Acetate bridged ladder along [0 1 0] with **L2** bridged zig-zag railing in **2**. (e) Helical chain of **2** along the *b* axis. Terminally bonded ligands are not shown in d and e.

Now, we report two new non-isostructural Nd^{III} chains, compounds **1** and **2**, containing 3,5- and 2,4-dinitrobenzoic acids, **L1** and **L2**, respectively. Despite two different arrangements (different coordination numbers, geometry and distances among Nd^{III} ions, Fig. 1) both systems, **1** and **2**, display field induced slow magnetization relaxations, pointing out the rich versatility yet unexplored of 1D Nd^{III} systems in the field of molecular magnetism. Recently, Arauzo *et al.*[16] accomplished the first reported Nd^{III} homometallic chain that presents field dependence relaxation of the magnetization by the use of cyanoacetate ligands (system differs crystallographically from the two presented in this work). Here, we extend such family by the addition of **1** and **2** and provide theoretical proof disclosing the relevance of dipolar interactions in front of Nd$^{III}\cdots$Nd^{III} exchange interactions and therefore, implying that at least **1** and **2** should be better described as organized 1D SMMs.

Compound **1**, {[Nd(μ_2-**L1**)$_3$(H$_2$O)$_2$].C$_2$H$_3$N}$_n$, was achieved by mixing $Nd(NO_3)_2\cdot 6H_2O$ with (**L1**) at room temperature meanwhile compound **2**, [Nd(μ_2-**L2**)(**L2**) (CH$_3$COO)(H$_2$O)$_2$]$_n$, was attained after the hydrothermal reaction at 120 °C of $Nd(CH_3COO)_3\cdot H_2O$ with (**L2**). Compound **1** is centrosymmetric where geometry around the Nd^{III} ion is bicapped trigonal prismatic with six sites occupied by carboxylate oxygens of **L1** and the remaining two sites by H_2O molecules. Four carboxylate groups from four centrosymmetric **L1** ligands coordinate two Nd^{III} ions, in a μ_2-κ^2, η^1:η^1 mode (mode I), with *syn-syn* and *syn-anti* conformation to form paddle wheel type centrosymmetric dimers (Fig. 1a). The successive dimeric units are further bridged by two more centrosymmetric **L1** ligands, again in mode I, with *syn-syn* conformation. The dihedral angles between two Nd-OCO planes in the dimer with Nd-OCO plane in this bridging link are 45.28(5) ° and 46.38(3) °, forming twisted ribbons (Fig. 1a) parallel to *a* axis. The two intrachain Nd⋯Nd distances are 4.267 (8) Å and 5.348(7) Å, respectively. Among chains, the shortest Nd⋯Nd distance is above 12.6 Å. From a topological perspective, this structure consists of chains [1 0 0] with a 2-connected uninodal net (Fig. 1b).

Compound **2** belongs to chiral space group P2$_1$ and shows two similar but crystallographically independent molecules in the unit cell (Only one of them has been discussed here and shown in the Fig. 1). In each one of them Nd^{III} is nine coordinated (Fig. 1c), in a trigonal prismatic tricapped geometry. Three sites are occupied by the acetate ions binding in a (μ_2-κ^3, η^1:η^2) mode (mode II), with a *syn-syn* conformation forming a ladder type architecture. Two H_2O molecules and one **L2** ligand are coordinating terminally whereas the second **L2**, in mode I, and *syn-syn* conformation, further links this ladder forming a spiral railing around this ladder (dihedral angle between metal-acetate plane and Nd-OCO-L2 plane is 89.74(9) °) (Fig. 1d). The resultant 1D polymer is a left handed helical chain about the *b* axis (Fig. 1e). Finally, intermolecular interactions between Nd⋯Nd go over 7.7 Å. The average Nd-O bond lengths, 2.4291(17) Å and 2.498 (3) Å for compounds **1** and **2** respectively, are comparable to those reported earlier for other Nd^{III}-O complexes.[14] (See Fig. S1-S6,Table S1-S5, ESI for details on X-ray structures).

The magnetic behavior of compounds **1** and **2** was studied by means of magnetic susceptibility experiments in the range of temperatures of 1.8-300 K applying 0.5 and 0.3 T dc fields, respectively. As shown in Fig. 2, the room temperature $\chi_M T$ values of **1** and **2** are 1.73 and 1.69 cm^3 K mol^{-1}, in that order, which are only slightly higher than the expected value for an isolated Nd^{III} ion of 1.64 cm^3 K mol^{-1} (ground level $^4I_{9/2}$)[17] pointing out that the magnetic exchange interactions among the Nd^{III} centers, for both chains, should be rather weak or negligible. Upon cooling, the $\chi_M T$ values of both compounds, **1** and **2** decrease gradually, reaching the values of 0.52 and 0.79 cm^3 K mol^{-1} at the lowest temperatures, in that order. The magnetization curves of **1** and **2** measured at 2.0 K are pretty similar (insets Fig. 2), showing a gradual increase from the lowest to the highest fields with the absence of plateau in both cases. Maximum values of 1.2 and 1.5 μ_B were found for **1** and **2**, respectively, where the unsaturated magnetization suggests the presence of magnetic anisotropy and/or the presence of low-lying excited states that might be populated when a field is applied.[18]

In both systems, such magnetic response could be explained by the facts that: a) the M_J sublevels could be split by the crystal field in the Nd^{III} centers where, on cooling the excited M_J sublevels, should be progressively depopulated.[19] and/or b) the magnetic exchange interaction/s among neighbor metal ions in the chain. Compounds **1** and **2** present both exclusively Nd^{III} ions attached by carboxylate bridges with *syn-syn* and/or *syn-anti* conformations that could provide antiferro- or weak antiferro/ferro-magnetic exchanges, a part from the contributions of the alkoxo groups in the case of **2**.[20,21] From an experimental point of view, it is not trivial to determine the relative nature and strength of the exchange contribution/s, as equally difficult is the analysis of the crystal field role of the ions in the net magnetic behavior.[22] The correct interpretation of these parameters and their effects requires theoretical studies, as key analyses for the proper description of the magnetic behavior. Hence, to further investigate the interplay of local crystal field and coupling effects for compounds **1** and **2**, CASSCF+RASSI calculations were performed, as implemented in the MOLCAS 7.8 software package.[23]

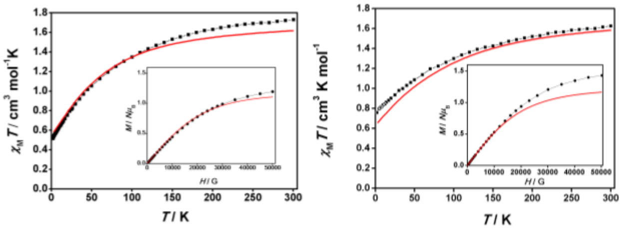

Fig. 2 (left) Plot of $\chi_M T$ *vs* T for **1** (black dots correspond to the experimental measures while red line is the simulated curve using the CASSCF results for a truncated model chain using the POLY_ANISO code, see Computational Studies section). Inset: $M/N\mu_B$ *v sH* at 2 K. (right) Plot of $\chi_M T$ *vs* T for **2**. Inset: $M/N\mu_B$ *vs H* at 2 K.

The CASSCF+RASSI (or CASSCF+QDPT) approach is especially appropriate to handle the magnetic anisotropy in lanthanide systems,[24,25] as it considers the multi reference nature of the low-lying electronic energy spectrum of lanthanide-based compounds and includes the state mixing due to spin-orbit coupling, which is crucial for SMM/SCM properties. Starting from the X-ray diffraction structures, the molecular chains where truncated to monomeric models, where the immediate coordination environment of the Nd^{III} ions was preserved. Neighbor Nd^{III} ions were modeled as La^{III} *ab initio* model potentials (truncated geometries are presented in ESI, Fig. S7). 35 quartet and 112 doublet roots were considered for the CASSCF step, while the employed ANO basis set had the following contraction patterns: Nd [9s8p6d4f3g2h]; O [4s3p1d]; N [4s3p21d]; C [3s2p]; H [2s]. Spin Hamiltonian parameters (such as *g*-factors) were calculated through the SINGLE_ANISO program.[26]

The calculated values collected in Table 1 show a large anisotropy for the two systems, **1** and **2**, with a relatively low energy for the first excited state (77.8 cm^{-1} and 87.3 cm^{-1} for **1** and **2**, respectively). In Fig. 2, calculated magnetization and susceptibility curves are represented together with the experimental ones, with reasonable agreement in both cases, assuming that the exchange interaction is negligible[24] and only the dipolar term is taken into account (performed with the POLY_ANISO code).[27] Verification of the shape of the curve remaining constant was performed by increasing the number of Nd^{III} centers (from 2 to 10 centres) in the truncated chain structure employed in the simulation. This assumption was also previously shown valid in Ho^{III} compounds.[28] The largest $\chi_M T$ value at low temperature for **2** in comparison with **1** is due to the larger magnetic moment of the ground state for the system **2** as reflected in the g_z values shown in Table 1.

Table 1 Calculated CASSCF+RASSI energies ($\mathrm{cm^{-1}}$) and *g*-factors for the five lowest Kramers' doublets for the truncated models of compounds **1** and **2**.

	1				**2**			
	Energy	g_z	g_y	g_x	*Energy*	g_z	g_y	g_x
1	0.0	3.514	2.012	1.021	0.0	4.122	1.730	0.622
2	77.8	0.100	1.842	3.075	87.3	3.035	1.504	0.971
3	171.8	4.037	1.130	0.106	188.0	4.415	0.862	0.297
4	225.6	0.967	2.319	3.255	285.0	0.197	1.902	2.837
5	259.3	3.615	1.973	1.294	325.8	0.619	2.881	3.474

In addition, to investigate the magnetization dynamics, the temperature dependent alternating current (ac) susceptibility data for **1** and **2** were collected with and without applied dc fields. In the absence of a dc field, neither peaks nor frequency dependence were observed for the in-phase (χ_M') and out-of-phase (χ_M'') signals for any of the compounds under study. However, when a small dc field was applied, frequency dependence was observed for both systems due to the full or partial suppression of the quantum tunneling relaxation of the magnetization. To find the optimal dc field, parallel experiments for **1** and **2** were performed at 2.0 K when applying dc fields in the range of 0-0.3 T (Fig. S8) and 0-0.4 T (Fig. S9), respectively. As a result, 0.20 T and 0.35 T dc fields (those that induce the slowest relaxation) were chosen as the optimum fields for **1** and **2**, in that order. Afterward, we performed dynamic ac magnetic susceptibility measurements for **1** and **2** (applying the corresponding dc magnetic field) as a function of temperature. The ac signals become frequency-dependent below approx. 7.0 K for **1** and **2** and maxima peaks were observed around 5.0 K in both cases as well (Fig. 3). Therefore, both systems display typical SMM behaviors, in agreement with the theoretical calculations, where the relatively large transversal components of the magnetic moment (g_x and g_y in Table 1) are consistent with the lack of slow relaxation at zero-field.

The ac susceptibility data plotted as Cole-Cole plots between 1.8 and 7.0 K (used T (K): 1.8, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0) for the two compounds show relatively symmetrical shapes (Fig. 4 top). In both cases, the fitting of the corresponding Cole-Cole data were performed with the CC-FIT program.[29] From here it was found that the α parameters were always below 0.18 for **1** and 0.15 for **2**, in that order, indicating all together the existence in both systems of a single magnetization relaxation process with a narrow distribution of relaxation times.[30]

The fitting also provided the relaxation times, τ's, for **1** and **2** at each temperature. By means of the Arrhenius law, the energy barrier defined as U_{eff}/K and the pre-exponential factor for the Arrhenius law (τ_0) were obtained (Fig. 4 bottom). This way, compound **1** show values of U_{eff}/K = 27 K (19 $\mathrm{cm^{-1}}$) and $\tau_0 = 4.1 \cdot 10^{-7}$ s and compound **2** of U_{eff}/K = 29 K (20 $\mathrm{cm^{-1}}$) and a $\tau_0 = 3.1 \cdot 10^{-7}$ s, in that order. Overall, these two non-isostructural, homometallic 1D systems display similar magnetic behavior which lies between the expected range for a SCM, comparable also to other 4*f*- and 3*d*-4*f*-SCMs and SMMs in the literature.[31]

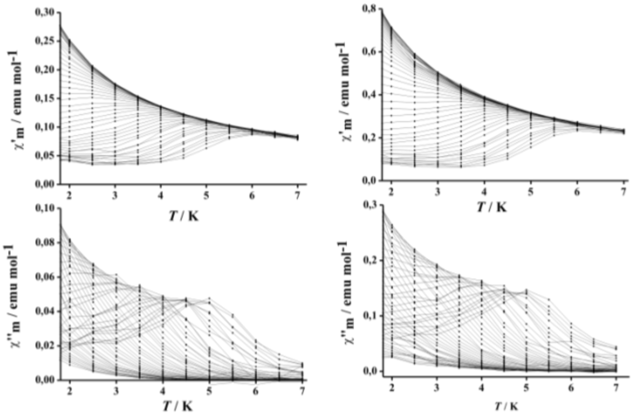

Fig. 3 In-phase (top) and out-of-phase susceptibilities (bottom) of compounds **1** (left) and **2** (right) applying an external dc magnetic field.

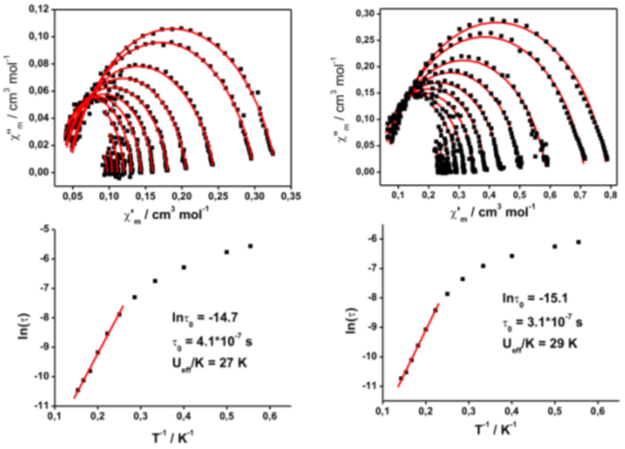

Fig. 4 (Top) Cole-Cole plots for **1** (left) and **2** (right) obtained using the ac susceptibility data applying an external dc magnetic field. (Bottom) The lnτ vs. T^{-1} plots of **1** (left) and **2** (right). The solid lines are best fits in all the plots.

In summary, we have described two different 1D Nd^{III} systems, compounds **1** and **2**,that present slow relaxation of the magnetization by applying an external dc field, with U_{eff}/K values comparable to other lanthanides SMM and SCM in the literature. These two compounds are crystallographically non-isostructural, fact that emphasizes the unexplored possibilities of Nd^{III} systems in the field of molecular magnetism and at the same time, our theoretical studies show that the Nd···Nd exchange interactions in the two systems are negligible, been the dipolar contribution the main factor to explain the magnetic performance, behaving both as organized 1D SMMs.

A.K. Jassal thanks Department of Science and Technology for INSPIRE fellowship. G.H. thanks University Grants Commission (India) for research grant under UPE (University with potential for excellence) scheme for GNDU, for financial assistance. The research reported here was supported by the Spanish Ministerio de Economía y Competitividad (grants CTQ2011-23862-C02-0, CTQ2012-32247and CTQ2012-30662). E.R. thanks Generalitat de Catalunya for an ICREA Academia fellowship. D.A. thanks CONICYT+PAI "Concurso nacional de apoyo al retorno de investigadores/as desde el extranjero, convocatoria 2014 82140014". The authors thankfully acknowledge the computer resources, technical expertise and assistance provided by the CESCA

Notes and references

[a]Department of Chemistry, Centre of Advance Studies-II, Guru Nanak Dev University, Amritsar, Punjab, India.

[b]ICREA (Institució Catalana de Recerca i Estudis Avançats) – ICMAB-CSIC (Institut de Ciència de Materials de Barcelona), Campus UAB, 08193 Bellaterra, Spain.

[c]Departament de Química Inorgànica and Institut de Nanociència i Nanotecnologia, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain.

[d]Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Casilla 40, Correo 33, Chile

[e]Departament de Química Inorgànica and Institut de Recerca de Química Teòrica i Computacional, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.

† This article is dedicated to Late Professor Maninder Singh Hundal.

‡ Electronic Supplementary Information (ESI) available: [X-Ray experimental details, tables of selected bond lengths (Å) and angles ($_o$), Important Hydrogen bond distances (Å) and angles ($_o$), detail of Thermo gravimetric analysis and IR spectroscopy, graphs of Magnetic properties, CCDC no. **1051022** and **1051023**].

1 (a) R. Gheorghe, A. M. Madalan, J.-P. Costes, W. Wernsdorfer, M. Andruh, *Dalton Trans*., 2010, **39**, 4734-4736. (b) Y. Wang, X.-L. Li, T.-W. Wang, Y. Song, X.-Z. You, *Inorg. Chem*., 2010, **49**, 969-976. (c) L. Bogani, C. Sangregorio, R. Sessoli, D. Gatteschi, *Angew. Chem., Int. Ed*., 2005, **44**, 5817-5821. (d) K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi, R. Sessoli, *J. Am. Chem. Soc*., 2006, **128**, 7947-7956. (e) X. Wang, X. Bao, P. Xu and L. Li, *Eur. J. Inorg. Chem*., 2011, 3586-3591.

2 A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem., Int. Ed*., 2001, **40**, 1760-1763.

3 (a) G. Aromí and E. K. Brechin, *Struct. Bonding*, 2006, **122**, 1-67. (b) D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, *Oxford University Press*, *Oxford*, 2006.

4 J. Lajzerowicz, J. J. Niez *J. Phys. Lett.,* 1979, **40**, L165-L169.

5 (a) H.-L. Suna, Z.-M. Wang, S. Gao, *Coord. Chem. Rev*., 2010, **254**, 1081-1100. (b) R. Sessoli, A. K. Powell, *Coord. Chem. Rev*., 2009, **253**, 2328-2341. (c) L. Bogani, A. Vindigni, R. Sessolia, D. Gatteschi, *J. Mater. Chem*., 2008, **18**, 4750-4758. (d) R. Inglis, L. F. Jones, C. J. Milios, S. Datta, A. Collins, S. Parsons, W. Wernsdorfer, S. Hill, S. Perlepes, S. Piligkos, E. K. Brechin, *Dalton Trans.*, 2009, 3403-3412. (e) C. Milios, S. Piligkos, E. K. Brechin, *Dalton Trans.*, 2008, 1809-1817. (f) A. M. Ako, V. Mereacre, R. Clerac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson, A. K. Powell, *Chem. Commun.*, 2009, 544-546.

6 (a) R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon *J. Am. Chem. Soc.*, 2002, **124**, 12837-12844. (b) W.-X. Zhang, R. Ishikawa, B. Breedlove, M. Yamashita, *RSC Adv*., 2013, **3**, 3772-3798.

7 (a) X. Y. Duan, X. Cheng, J. G. Lin, S. Q. Zang, Y. Z. Li, C. J. Zhu, Q. J. Meng, *Cryst. Eng. Comm.*, 2008, **10**, 706-714. (b) S. Su, C. Qin, S. Song, Z. Guo, R. Deng, W. Chen, X. Song, S. Wang, G. Li, H. Zhang, *Cryst. Eng. Comm*., 2011, **13**, 6057-6064.

8 (a) D. Visinescu, A. M. Madalan, M. Andruh, C. Duhayon, J.-P. Sutter, L. Ungur, W. Van den Heuvel, L. F. Chibotaru, *Chem.–Eur. J.*, 2009, **15**, 11808-11814. (b) R. Gheorghe, A. M. Madalan, J.-P. Costes, W. Wernsdorfer, M. Andruh, *Dalton Trans*., 2010, **39**, 4734-4736.

9 H.B. Xu, B.W. Wang, F. Pan, Z.M. Wang, S. Gao, *Angew. Chem., Int. Ed.,* 2007, **46**, 7388-7392.

10 F. Luo, Z.-w. Liao, Y.-m. Song, H.-x. Huang, X.-Z. Tian, G.-M. Sun, Y. Zhu, Z.-Z. Yuan, M.-B. Luo, S.-J. Liu, W.-Y. Xu, X.-F. Feng, *Dalton Trans*., 2011, **40**, 12651-12655.

11 Y.-G. Huang, X.-T. Wang, F.-L. Jiang, S. Gao, M.-Y. Wy, Q. Gao, W. Wei, M.-C. Hong, *Chem. Eur. J.* **2008**, 14, 10340-10347.

12 (a) H. Ke, G.-F. Xu, Y.-N. Guo, P. Gamez, C. M. Beavers, S. J. Teatd, J. Tang, *Chem. Commun*., 2010, **46**, 6057-6059. (b) R. Sessoli, A. K. Powell, *Coord. Chem. Rev*., 2009, **253**, 2328-2341. (c) S. K. Langley, B. Moubaraki, C. M. Forsyth, I. A. Gass, K. S. Murray, *Dalton Trans.*, 2010, **39**, 1705-1708 (d) X. Wang, X. Bao, P. Xu, L. Li *Eur. J. Inorg. Chem.* 2011, 3586-3591.

13 a) N. Ishikawa, M. Sugita, W. Wernsdorfer, *J. Am. Chem. Soc.*, 2005, **127**, 3650-3651; b) N. Ishikawa, M. Sugita, W. Wernsdorfer, *Angew. Chem. Int. Ed.*, 2005, **44**, 2931-2935; c) S.Takamatsu, T. Ishikawa, S.-y. Koshihara, N. Ishikawa, Inorg. Chem., 2007, **46**, 7250-7252.

14 (a) S. Chen, R.-Q. Fan, C.-F. Sun, P. Wang, Y.-L. Yang, Q. Su, Y. Mu, *Cryst. Growth Des*. 2012, **12**, 1337-1346 (b) F. Dai, P. Cui, F. Ye, D. Sun *Cryst. Growth Des*., 2010, **10**, 1474-1477.

15 (a) Y.-L. Wang, Y.-L. Jiang, Z.-J. Xiahou, J.-H. Fu, Q.-Y. Liu, *Dalton Trans*., 2012, **41**, 11428-11437. (b) J. Gu, Z. Gao, Y. Tang, *Cryst. Growth Des*. 2012, **12**, 3312-3323.

16 A. Arauzo, A. Lazarescu, S. Shova, E. Bartolomé, R. Cases, J. Luzón, J. Bartolomé, C. Turta, *Dalton Trans.*, 2014, **43**, 12342-12356.

17 J. Rossat-Mignod, *Systematics and the Properties of the Lanthanides NATO ASI Series*, 1983, **109**, 255-310.

18 D. Zeng, M. Ren, S.-S. Bao, L. Li, L.-M. Zheng, *Chem. Commun*., 2014, **50**, 8356-8359.

19 D. T. Thielemann, M. Klinger, T. J. A. Wolf, Y. Lan, W. Wernsdorfer, M. Busse, P. W. Roesky, A.-N. Unterreiner, A. K. Powell, P. C. Junk, G. B. Deacon, *Inorg. Chem*., 2011, **50**, 11990-12000.

20 H. Arora, R. Mukherjee, *New J. Chem.*, 2010, **34**, 2357-2365.

21 F. J. Kettles, V. A. Milway, F. Tuna, R. Valiente, L. H. Thomas, W. Wernsdorfer, S. T. Ochsenbein, M. Murrie, *Inorg. Chem*., 2014, **53**, 8970-8978.

22 T. Hamamatsu, K. Yabe, M. Towatari, S. Osa, N. Matsumoto, N. Re, A. Pochaba, h. Mrozinski, J.-L. Gallani, A. Barla, P. Imperia, C. Paulsen, J.-P. Kappler, *Inorg. Chem.*, 2007, **46**, 4458-4468.

23 F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-A. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, M., B. O. Roos, B. O., L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh, , *J. Comput. Chem.*, 2010, **31**, 224-247.

24 D. Aravena, E. Ruiz, *Inorg. Chem*., 2013, **52**, 13770-13778.

25 S. Gómez-Coca, D. Aravena, R. Morales, E. Ruiz, *Coord. Chem. Rev.*, 2015, **289–290**, 379-392.

26 L. F. Chibotaru, ,L. Ungur *J. Chem. Phys.* 2012, **137**, 064112-064122.

27 L. F. Chibotaru, L.,Ungur, A. Soncini *Angew. Chem. Int. Ed.* 2008, **47**, 4126-4129.

28 J. D. Leng, J. L. Liu, W. Q. Lin, S. Gomez-Coca, D. Aravena, E. Ruiz and M. L. Tong, *Chem Commun*, 2013, **49**, 9341-9343.

29 CC-FIT, Copyright © 2014 Nicholas F. Chilton.

30 Y.-N. Guo, G.-F. Xu, Y. Guo and J. Tang, *Dalton Trans.*, 2011, **40**, 9953- 9963.

31 (a) M. Menelaou, F. Ouharrou, L. Rodríguez, O. Roubeau, S. J. Teat, N. Aliaga-Alcalde, *Chem. Eur. J.*, 2012, **18**, 11545-11549. (b) M.-X. Yao, Q. Zheng, K. Qian, Y. Song, S. Gao, J.-L. Zuo, *Chem. Eur. J.*, 2013, **19**, 294-303. (c) M. A. Palacios, S. Titos-Padilla, J. Ruiz, J. M. Herrera, S. J. A. Pope, E. K. Brechin, E. Colacio, *Inorg. Chem.*, 2014, **53**, 1465-1474.