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Dinuclear lanthanide(III)/zinc(II) complexes with methyl 2-pyridyl ketone oxime†

Nikolaos C. Anastasiadis,[a,b] Christina D. Polyzou,[a,b] George E. Kostakis,[a,c] Vlasoula Bekiari,[d] Yanhua Lan,[e] Spyros P. Perlepes,[b] Konstantis F. Konidaris*[a] and Annie K. Powell*[a,e]

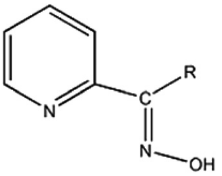
The first use of methyl 2-pyridyl ketone oxime (mpkoH) in zinc(II)/lanthanide(III) chemistry leads to the [ZnLn(mpko)$_3$(mpkoH)$_3$]-(ClO$_4$)$_2$ and [ZnLn(NO$_3$)$_2$(mpko)$_3$(mpkoH)] families of dinuclear Zn^{II}Ln^{III} complexes displaying blue-green, ligand-based photoluminescence; the Zn^{II}Dy^{III} compound shows field-induced relaxation of magnetization.

Dinuclear and polynuclear M$^{II\text{ or }III}$/Ln^{III} coordination cluster complexes, where M$^{II\text{ or }III}$ are paramagnetic 3d-metal ions and Ln^{III} is a trivalent lanthanide ion,[1] occupy a unique place among mixed-metal molecular materials as a result of the interaction between 3d and 4f electron systems giving rise, for example, to alternatives[2] to homometallic 3d-metal Single-Molecule Magnets (SMMs)[3] and magnetic refrigerants.[4] An important feature here is the fact that 4f metal ions can contribute a large spin and, for most 4f ions, also the magnetic anisotropy needed for SMM behaviour. Furthermore, the coupling between 3d and 4f metal ions can be relatively strong in terms of superexchange interaction.

However, in contrast to the plethora of studies concerning discrete 3d/4f-metal complexes, where both metal ions are paramagnetic, there is rather limited information on complexes containing Zn^{II} (a diamagnetic 3d^{10} metal ion) and paramagnetic Ln^{III} centres.[5] Such complexes are extremely useful because (i) they can help scientists to elucidate the Ln$^{III}\cdots$Ln^{III} magnetic exchange interactions in a series of isostructural M$^{II}_x$Ln$^{III}_y$ coordination clusters (M = Mn, Fe, Co, Ni, Cu; $y \geq 2$)[1c,6] and (ii) they often exhibit interesting photoluminescence properties and phenomena[7] distinctly different from those of analogous complexes containing only Ln^{III} ions.

From a synthetic inorganic chemistry viewpoint, methods must be devised to combine 3d- and 4f-metal ions within a dinuclear or polynuclear molecule. One of our preferred routes is a "one-pot" procedure involving a mixture of 3d- and 4f-metal starting materials and an organic ligand possessing distinct functionalities, or "pockets", for preferential bonding of the 3d and 4f ions. For example, the various anionic 2-pyridylmonoximes (Scheme 1) have been widely used to date in the synthesis of structurally and magnetically interesting 3d-,[8] 3d/3d′-[9] and 3d/4f-metal[10] complexes [M^{II} = paramagnetic 3d-metal ion]. However, there are no reports of their use in Zn^{II}/Ln^{III} chemistry. These ligands are, in fact, attractive for Zn^{II}/Ln^{III} chemistry because the hard, deprotonated O atom will favour binding to strongly oxophilic Ln^{III} ions, whereas the softer 2-pyridyl and oximate N atoms will favour coordination to the Zn^{II} centre.

We have been recently involved in a new research programme aiming to prepare, characterize and study discrete (*i.e.* non-polymeric), mixed Zn^{II}/Ln^{III} coordination cluster complexes with 2-pyridylmonoximate (Scheme 1) and 2,6-pyridylbisoximate bridging ligands. Our short-term goal is to



Scheme 1 General structural formula of the family of 2-pyridylmonoximes (R = H, Me, Ph, 2-pyridyl, CN, NH$_2$, *etc.*). The ligand used in this work is methyl 2-pyridyl ketone oxime (R = Me), abbreviated as mpkoH.

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[a] *Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-mail: konstantis.konidaris@gmail.com*
[b] *Department of Chemistry, University of Patras, GR-265 04 Patras, Greece*
[c] *Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, UK*
[d] *Department of Aquaculture, Technological Educational Institute of Western Greece, GR-30200 Messolonghi, Greece*
[e] *Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstrasse 15, 76131 Karlsruhe, Germany. E-mail: annie.powell@kit.edu*

† Electronic supplementary information (ESI) available: Full experimental details of the synthesis of complexes **1**·2H$_2$O and **4**, analytical data for all complexes, short experimental for single-crystal X-ray crystallography, metric parameters for the H bonds in **1**·2H$_2$O, and structural (Fig. S1–S4), optical (Fig. S5 and S6) and magnetic (Fig. S7 and S8) plots. CCDC 1021513 (**1**·2H$_2$O) and 1021514 (**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03663a

establish routes for such complexes and to isolate the maximum number of products from a given ligand. Our longer-term goal is to force the carefully designed Zn^{II}-ligand moiety of the heterometallic complex to act as an efficient sensitizer, and one that is more efficient than the organic-only chromophore in exciting Ln^{III} ions (mainly Eu^{III}, Tb^{III} and Dy^{III}) for emission in the visible region of the spectrum.[11] It is also well known[12] that highly luminescent Ln^{III} complexes are of interest for a wide variety of photonic applications such as planar waveguide amplifiers, light-emitting diodes and bio-inspired luminescent probes. Most of the electronic transitions of the Ln^{III} ions involve a redistribution of electrons within the 4f sub-shell. Electric dipole selection rules forbid such transitions but these rules are relaxed by several mechanisms, such as coupling with vibrational states, *J*-mixing and mixing with opposite-parity wave functions (5d orbitals, ligand orbitals or charge transfer states). The coupling between these vibrational and electronic states and the 4f wavefunctions depends on the strength of the interaction between the 4f orbitals and the surrounding ligands; in view of the shielding of the 4f orbitals, the degree of mixing remains small, and so are the oscillator strengths of the f–f transitions.[12b] As a consequence, even if many Ln^{III} compounds display a good quantum yield, direct excitation of the Ln^{III} ions rarely yields highly luminescent materials. This disadvantage may be overcome by employing suitable organic[12,13] or d-block[14] (making use of fully-allowed, low-energy charge transfer transitions from p-character systems to d-character systems, *e.g.* luminescent complexes of d^6 and d^8 metal ions) chromophores as antenna groups to generate sensitised emission from Ln^{III} ions. In this communication we describe our preliminary efforts towards the realisation of the short-term goal mentioned above, *i.e.* to establish the chemistry of the Zn^{II}/Ln^{III}/2-pyridyl-monoxime system.

Reactions of $Zn(ClO_4)_2{\cdot}6H_2O$, mpkoH, Et_3N and $Ln(NO_3)_3{\cdot}6H_2O$ in a 1 : 6 : 3 : 2 molar ratio in MeOH at room temperature gave pale yellow (Ln = Eu, Gd, Tb) or pale orange (Ln = Dy, Ho) solutions, which upon storage at 15 °C gave pale yellow $[ZnLn(mpko)_3(mpkoH)_3](ClO_4)_2{\cdot}2H_2O$ (Ln = Eu, **1**·2H$_2$O; Ln = Gd, **2**·2H$_2$O; Ln = Tb, **3**·2H$_2$O) and almost colourless $[ZnLn(NO_3)_2(mpko)_3(mpkoH)]$ (Ln = Dy, **4**; Ln = Ho, **5**) complexes; typical yields were in the 50–60% range. The structures of **1**·2H$_2$O and **4** were solved by single-crystal X-ray crystallography,‡ while the identity of **2**·2H$_2$O, **3**·2H$_2$O and **5** was confirmed by unit cell determination, IR spectroscopy and elemental (C, H, N) analyses.

Complex **1**·2H$_2$O crystallizes in the triclinic space group $P\bar{1}$. Its structure consists of dinuclear cations $[ZnEu(mpko)_3(mpkoH)_3]^{2+}$ (Fig. 1), ClO_4^- anions and solvate H$_2$O molecules. The metal ions are bridged by the three oximate groups of the η^1:η^1:η^1:μ mpko$^-$ ligands. The Zn^{II} ion is coordinated by six nitrogen atoms belonging to the “chelate” part of these ligands. This metal ion has a facial distorted octahedral geometry, the *trans* coordination angles being in the range 155.2(3)–158.4(3)°. The Eu^{III} centre is bound to an O$_3$N$_6$ set of donor atoms. The oxygen atoms (O4, O5, O6) belong to the deprotonated oximate groups of the $\{Zn(mpko)_3\}^-$ unit, while the six nitrogen atoms belong to the three bidentate chelating (η^1:η^1) mpkoH ligands. Using the Continuous Shape Measure (CShM) approach,[15] the coordination geometry of Eu^{III} can be best described as spherical capped square antiprismatic (Fig. S1†), the capping atom being N5; since the CShM value for this geometry (1.80735) is very close to that for the spherical tricapped trigonal prismatic geometry (1.80967), the Eu^{III} ion can also be considered as having the latter. Most 9-coordinate metal ions possessing three 5-membered chelating rings and three monodentate ligands (the three monodentate “ligands” for Eu are the terminally coordinated oximate oxygen atoms O4, O5 and O6) form polyhedra that appear very close to the interconversion path between the capped square antiprism and tricapped trigonal prism.[15]

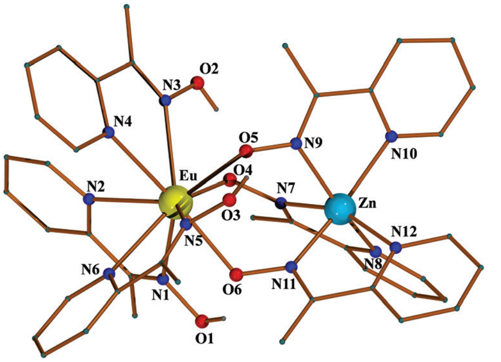

Fig. 1 Partially labelled plot of the cation that is present in the structure of **1**·2H$_2$O. Most H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Eu⋯Zn 4.028(5), Eu–N 2.603(8)–2.728(7), Eu–O 2.313(6)–2.354(6), Zn–N 2.104(8)–2.196(7); N1–Eu–N2 59.1(2), N9–Zn–N10 74.6(3).

There are three strong intramolecular (intracationic) hydrogen bonds with uncoordinated oxime oxygens (O1, O2, O3) as donors and the coordinated oximate oxygens (O6, O4 and O5, respectively) as acceptors. There are also H-bonded parallelograms of the type $HOH{\cdots}O(ClO_2)O{\cdots}HOH{\cdots}O(ClO_2)O$ (Fig. S2†) and single $HOH{\cdots}O(ClO_3)$ H bonds in the crystal structure of the complex, which is further stabilized by weak intermolecular π–π stacking interactions and C–H⋯π interactions to form 2D honeycomb layers parallel to the plane formed by *c* and the bisection line of the *a*0*b*.

Complex **4** crystallizes in the monoclinic space group *Cc*. Its structure consists of dinuclear molecules $[ZnDy(NO_3)_2(mpko)_3(mpkoH)]$. The molecular structure of **4** is similar to that of the cation $[ZnEu(mpko)_3(mpkoH)_3]^{2+}$, the main difference being the replacement of two *N*,*N*′-bidentate chelating mpkoH ligands of the latter with two bidentate chelating nitrato groups in the former (Fig. 2). This replacement gives neutral molecules (and not cations) in **4** and the Dy^{III} centre is thus bound to an O$_7$N$_2$ donor set. The coordination polyhedron of Dy^{III} can be described as a spherical capped square antiprism (Fig. S3†) with the oxime nitrogen N8 as the capping atom, although descriptions as a spherical tricapped trigonal prism and muffin are equally acceptable. Again there is evidence for a strong intramolecular O4–H(O4)⋯O3 H bond; two

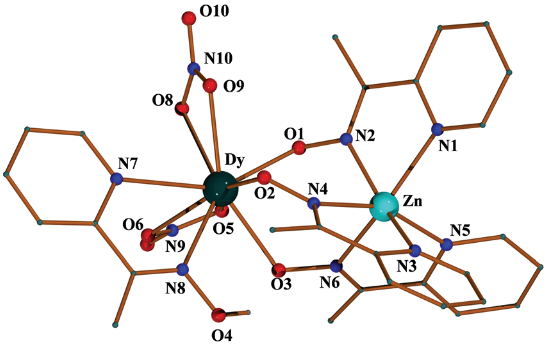

Fig. 2 Partially labeled plot of the molecule that is present in the structure of **4**. Only the H atom of the neutral oxime group of the unique mpkoH ligand is shown. Selected interatomic distances (Å) and angles (°): Dy···Zn 3.954(2), Dy–O(nitrato) 2.445(3)–2.566(2), Dy–O(oximato) 2.245(2)–2.343(2), Dy–N7 2.673(3), Dy–N8 2.535(3), Zn–N 2.103(2)–2.247(2); O8–Dy–O9 51.2(1), N7–Dy–N8 60.8(1), N1–Zn–N2 74.5(1).

weak C–H···π interactions (Fig. S4†) extend the structure into two dimensions forming layers parallel to the *ab* plane and giving a **sql** topology.

The lanthanide(III)–N(mpkoH) and –O(oximato) bond lengths around Eu^{III} and Dy^{III} in **1**·2H$_2$O and **4** show the expected tendency towards shorter values in the latter in line with the lanthanide(III) contraction. Compounds **1**·2H$_2$O and **4** are the first structurally characterized heterometallic Zn^{II}/Ln^{III} complexes with 2-pyridyloxime/oximate ligation.

Upon maximum excitation at 400 nm, solid **4** displays photoluminescence at 448, 483 and 540 nm at room temperature (Fig. 3). The most probable origin of emission is ligand-based as the excitation and emission spectra of both mpkoH and **4** are observed in the same region. Thus, somewhat to our disappointment, no significant Dy^{III} emission was detected. Almost identical excitation and emission spectra are observed for solid samples of **1**·2H$_2$O and **3**·2H$_2$O (Fig. S5 and S6†), supporting our view that no Ln^{III} emission appears. Although not desirable, this is not an unusual situation for lanthanide(III) complexes with certain types of organic ligands.[16] In our case, this means that the energy transfer from the organic ligands to Ln^{III} is not efficient, probably because the energy levels of the excited states of these ions lie higher than that of the excited state of the {Zn-mpko$^-$}moiety; this requires a change of the ligand in the Zn^{II} moiety of the complex.

The room temperature $\chi_M T$ product for **4** (14.30 cm^3 K mol^{-1}) under an applied dc field of 1000 Oe is consistent with the expected value of 14.17 cm^3 K mol^{-1} for one isolated Dy^{III} ion ($^6H_{15/2}$ free ion, S = 5/2, L = 5, g_J = 4/3). The product decreases slowly to a value of 12.58 cm^3 K mol^{-1} at 2.2 K, before a small upturn at 2.0 K (Fig. 4, left). The decrease in $\chi_M T$ is due to the progressive depopulation of the Dy^{III} excited-state Stark sublevels.[16] The small upturn below 2 K could be due to a weak ferromagnetic interaction between the complexes.[17] The field dependence of magnetization shows that the magnetization reaches 5.4 μ_B at 70 kOe after a rapid increase at low fields (Fig. 4, right). The observed non-saturated magnetization at the highest field is much lower than the expected 10 μ_B for the Dy^{III} ion indicating some anisotropy in the system.[17,18]

The dynamic magnetic properties of **4** were probed using ac susceptometry. Practically no signals for the out-of-phase component of the ac susceptibility were observed in the absence of a dc field at 1.8 K (Fig. S7†). However, an intense signal is observed with the application of an external dc field of 1000 Oe. Thus, on application of this field the positions of the maxima of the out-of-phase signals become strongly frequency-dependent (Fig. 5) as expected for a Single-Ion Magnet (SIM). The application of this field suppresses fast zero-field tunnelling of the magnetization, which is a well-documented behaviour for Ln^{III}-based SIMs and SMMs.[17] To calculate the characteristic time and the barrier to relaxation of **4**, the relaxation times were fitted with the frequencies occurring at the χ''_{max} of the frequency-dependent ac susceptibility data (Fig. 5, left) by using the Orbach thermally activated relaxation law $\tau = \tau_0 \exp(U_{eff}/k_B T)$. Linear data following this law were only obtained between 4 K and 5.5 K (solid line, Fig. 5, right), with an effective energy barrier of U_{eff} = 33.3 K and $\tau_0 = 2.0 \times 10^{-7}$ s. This suggests that the relaxation might follow a quantum regime below 4 K or that there is more than one thermally activated relaxation process in the complex. Thus, complex **4** can

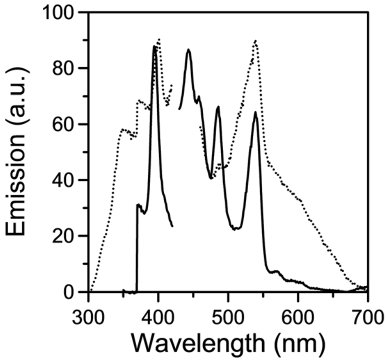

Fig. 3 Solid-state room-temperature excitation (emission at 540 nm, left) and emission (excitation at 400 nm, right) of mpkoH (dotted curves) and complex **4** (solid curves).

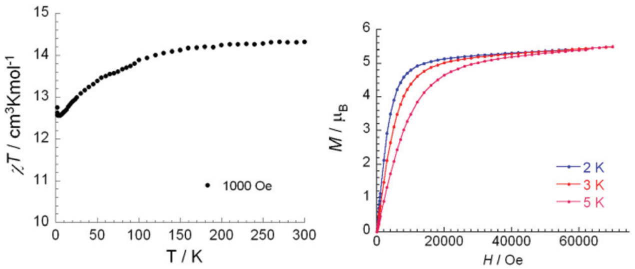

Fig. 4 Temperature dependence of $\chi_M T$ for **4** (left) and molar magnetization *vs.* field at indicated temperatures (right, the solid lines are guides for the eyes).

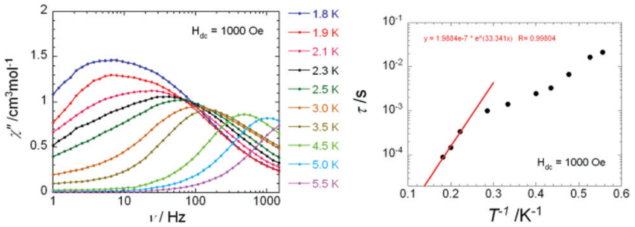

Fig. 5 Frequency dependence of the out-of-phase component of the ac susceptibility under an external dc field of 1000 Oe at the indicated temperatures (left) and the relaxation time of **4** as a function of temperature (dots) plotted against a thermally activated Arrhenius law (solid line) (right).

be termed as an "emissive field-induced SMM/SIM".[1c,19] The observation of more than one well-resolved pathway for magnetic relaxation remains a rarity among mononuclear SMMs.[20]

Conclusions

In conclusion, the members of the first two families of Zn^{II}/Ln^{III}/2-pyridylmonoximate complexes have been prepared. The complexes exhibit ligand-based blue-green photoluminescence, while Zn^{II}/Dy^{III} is considered to be a field-induced single-ion magnet. We are currently trying to investigate the possible presence of members of a third family of products in the Ln(NO$_3$)$_3$·xH$_2$O/Zn(ClO$_4$)$_2$·xH$_2$O/mpkoH general reaction system (we have strong evidence for this). Work is also in progress to enhance the aromatic content of the dinuclear Zn^{II}Ln^{III} complexes by employing anionic phenyl 2-pyridine ketone oxime (R = Ph in Scheme 1) as a bridging ligand and PhCO$_2^-$ (instead of NO$_3^-$ or mpkoH) as terminal groups, with the hope of achieving efficient energy transfer from the Zn^{II}-ligand moiety to the lanthanide and "switch on" Ln^{III}-based emission. Achieving Dy^{III}-based emission in a Zn^{II}Dy^{III} SIM would enable us to correlate luminescence and magnetism[20a,21] since, in theory, the highest energy f–f transitions in the emission spectra of mononuclear Dy^{III} SIMs can be modelled to provide a direct picture of the splitting of the ground J multiplet.

Acknowledgements

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Notes and references

‡ Crystallographic data for complex **1**·2H$_2$O: C$_{42}$H$_{49}$EuZnN$_{12}$O$_{16}$Cl$_2$, M_r = 1266.16, triclinic, $P\bar{1}$, a = 13.8641(15) Å, b = 14.5627(19) Å, c = 15.190(2) Å, α = 96.519(11)°, β = 113.081(10)°, γ = 109.850(9)°, V = 2543.6(6) Å^3, Z = 2, D_c = 1.653 g cm^{-3}, μ (Mo Kα, λ = 0.71073 Å) = 1.878 mm^{-1}, T = 180(2) K, 17 067 reflections collected, 10 653 unique (R_{int} = 0.0919), R_1 on F (wR_2 on F^2) = 0.0606 (0.1164) for 4678 observed ($I > 2\sigma(I)$) reflections. Crystallographic data for **4**: C$_{28}$H$_{29}$DyZnN$_{10}$O$_{10}$, M_r = 893.48, monoclinic, Cc, a = 15.9387(11) Å, b = 9.3158(4) Å, c = 22.5168(17) Å, β = 94.590(6)°, V = 3332.6(4) Å^3, Z = 4, D_c = 1.781 g cm^{-3}, μ (Mo Kα, λ = 0.71073 Å) = 3.015 mm^{-1}, T = 180(2) K, 11 098 reflections collected, 6259 unique (R_{int} = 0.0265), R_1 on F (wR_2 on F^2) = 0.0191 (0.0480) for 6209 observed ($I > 2\sigma(I)$) reflections. Unit cell information: complex **2**·2H$_2$O: triclinic, $P\bar{1}$, a = 13.8894 Å, b = 14.6063 Å, c = 15.2384 Å, α = 96.985°, β = 112.719°, γ = 109.824°, V = 2566.45 Å^3. Complex **3**·2H$_2$O: triclinic, $P\bar{1}$, a = 13.8574 Å, b = 14.5554 Å, c = 15.1713 Å, α = 96.684°, β = 112.834°, γ = 109.960°, V = 2539.08 Å^3. Complex **5**: monoclinic, Cc, a = 15.9450 Å, b = 9.3192 Å, c = 22.499 Å, β = 95.061°, V = 3330.2 Å^3. CCDC numbers 1021513 (**1**·2H$_2$O) and 1021514 (**4**).

1 For review-type articles, see: (*a*) C. D. Polyzou, C. G. Efthymiou, A. Escuer, L. Cunha-Silva, C. Papatriantafyllopoulou and S. P. Perlepes, *Pure Appl. Chem.*, 2013, **85**, 315; (*b*) J. W. Sharples and D. Collison, *Coord. Chem. Rev.*, 2014, **260**, 1; (*c*) H. L. C. Feltham and S. Brooker, *Coord. Chem. Rev.*, 2014, **276**, 1.

2 For example, see: (*a*) C. G. Efthymiou, Th. C. Stamatatos, C. Papatriantafyllopoulou, A. J. Tasiopoulos, W. Wernsdorfer, S. P. Perlepes and G. Christou, *Inorg. Chem.*, 2010, **49**, 9737; (*b*) S. Schmidt, D. Prodius, V. Mereacre, G. E. Kostakis and A. K. Powell, *Chem. Commun.*, 2013, **49**, 1696; (*c*) K. Chandra Mondal, A. Sundt, Y. Lan, G. E. Kostakis, O. Waldmann, L. Ungur, L. F. Chibotaru, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2012, **51**, 7550; (*d*) G. J. Sopasis, A. B. Canaj, A. Philippidis, M. Siczek, T. Lis, J. R. O'Brien, M. M. Antonakis, S. Pergantis and C. J. Milios, *Inorg. Chem.*, 2012, **51**, 5911; (*e*) D. Dermitzaki, G. Lorusso, C. P. Raptopoulou, V. Psycharis, A. Escuer, M. Evangelisti, S. P. Perlepes and Th. C. Stamatatos, *Inorg. Chem.*, 2013, **52**, 10235.

3 C. J. Milios and R. E. P. Winpenny, *Struct. Bonding*, 2015, **164**, 1.

4 M. Evangelisti and E. K. Brechin, *Dalton Trans.*, 2010, **39**, 4672.

5 For example, see: (*a*) W.-K. Wong, X. Yang, R. A. Jones, J. H. Rivers, V. Lynch, W.-K. Lo, D. Xiao, M. M. Oye and A. L. Holmes, *Inorg. Chem.*, 2006, **45**, 4340; (*b*) S. Akine, F. Utsuno, T. Taniguchi and T. Nabeshima, *Eur. J. Inorg. Chem.*, 2010, 3143.

6 W.-R. Yu, G.-H. Lee and E.-C. Yang, *Dalton Trans.*, 2013, **42**, 3941.

7 (*a*) C. E. Burrow, T. J. Burchell, P.-H. Lin, F. Habib, W. Wernsdorfer, R. Clerac and M. Murugesu, *Inorg. Chem.*, 2009, **48**, 8051; (*b*) T. D. Pasatoiu, A. M. Madalan, M. Zamfirescu, C. Tiseanu and M. Andruh, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11448.

8 K. F. Konidaris, V. Bekiari, E. Katsoulakou, C. P. Raptopoulou, V. Psycharis, E. Manessi-Zoupa, G. E. Kostakis and S. P. Perlepes, *Dalton Trans.*, 2012, **41**, 3797.

9 S. Ross, T. Weyhermuller, E. Bill, K. Wieghardt and P. Chaudhuri, *Inorg. Chem.*, 2001, **40**, 6656.

10 C. D. Polyzou, H. Nikolaou, C. Papatriantafyllopoulou, V. Psycharis, A. Terzis, C. P. Raptopoulou, A. Escuer and S. P. Perlepes, *Dalton Trans.*, 2012, **41**, 13755.

11 (*a*) T. D. Pasatoiu, A. M. Madalan, M. U. Kumke, C. Tiseanu and M. Andruh, *Inorg. Chem.*, 2010, **49**, 2310; (*b*) T. D. Pasatoiu, C. Tiseanu, A. M. Madalan, B. Jurca, C. Duhayon, J. P. Sutter and M. Andruh, *Inorg. Chem.*, 2011, **50**, 5879; (*c*) M. A. Palacios, S. Titos-Padilla, J. Ruiz, J. M. Herrera, S. T. A. Pope, E. K. Brechin and E. Colacio, *Inorg. Chem.*, 2014, **53**, 1465.

12 (*a*) J.-C. Bunzli, *Acc. Chem. Res.*, 2006, **39**, 53; (*b*) J.-C. G. Bűnzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048.

13 S. Swavey and R. Swavey, *Coord. Chem. Rev.*, 2009, **253**, 2627.

14 D. Sykes and M. D. Ward, *Chem. Commun.*, 2011, **47**, 2279.

15 A. Ruiz-Martinez, D. Casanova and S. Alvarez, *Chem. – Eur. J.*, 2008, **14**, 1291.

16 N. C. Anastasiadis, C. M. Granadeiro, N. Klouras, L. Cunha-Silva, C. P. Raptopoulou, V. Psycharis, V. Bekiari, S. S. Balula, A. Escuer and S. P. Perlepes, *Inorg. Chem.*, 2013, **52**, 4145.

17 H. L. C. Feltham, Y. Lan, F. Klower, L. Ungur, L. F. Chibotaru, A. K. Powell and S. Brooker, *Chem. – Eur. J.*, 2011, **17**, 4362.

18 M. Ren, D. Pinkowicz, M. Yoon, K. Kim, L.-M. Zheng, B. K. Breedlove and M. Yamashita, *Inorg. Chem.*, 2013, **52**, 8342.

19 As has been suggested,[1c] the term "field-induced SMM" appears to be misleading as such compounds are not magnets as they show no slow relaxation (and no hysteresis) in the absence of a field.

20 (*a*) J. Long, J. Rouquette, J.-M. Thibaud, R. A. S. Ferreira, L. D. Carlos, B. Donnadieu, V. Vieru, L. F. Chibotaru, L. Konczewicz, J. Haines, Y. Guari and J. Larionova, *Angew. Chem., Int. Ed.*, 2015, **54**, 2236; (*b*) A. Watanabe, A. Yamashita, M. Nakano, T. Yammura and T. Kajiwara, *Chem. – Eur. J.*, 2011, **17**, 7428; (*c*) M. Jeletic, P.-H. Lin, J. J. Le Roy, I. Korobkov, S. I. Gorelsky and M. Murugesu, *J. Am. Chem. Soc.*, 2011, **133**, 19286; (*d*) J. Ruiz, A. J. Mota, A. Rodriguez-Diéguez, S. Titos, J. M. Herrera, E. Ruiz, E. Cremades, J. P. Costes and E. Colacio, *Chem. Commun.*, 2012, **48**, 7916.

21 (*a*) J. Long, R. Vallat, R. A. S. Ferreira, L. D. Carlos, F. A. Almeida Paz, Y. Guari and J. Larionova, *Chem. Commun.*, 2012, **48**, 9974; (*b*) G. Cucinotta, M. Perfetti, J. Luzon, M. Etiene, P.-E. Car, A. Caneschi, G. Calvez, K. Bernot and R. Sessoli, *Angew. Chem., Int. Ed.*, 2012, **51**, 1606.