# Influence of Lanthanides on Spin-Relaxation and Spin-Structure in a Family of Fe7Ln4 Single Molecule Magnets

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# Influence of Lanthanides on Spin-Relaxation and Spin-Structure in a Family of $Fe_7Ln_4$ Single Molecule Magnets

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A family of isostructural undecanuclear 3*d*–4*f* coordination clusters of formula $[Fe^{III}_7Ln^{III}_4O_4(OH)_3(tea)_2(Htea)_3(Piv)_7(H_2O)_2(NO_3)_3]$, where Ln = Y (**1**), Gd (**2**), Tb (**3**), Dy (**4**); PivH ≡ pivalic acid and $H_3tea$ ≡ triethanolamine, was synthesised. The central $Fe_7$ core of the coordination cluster can be described in terms of two $\{Fe_4O_2\}$ butterfly motifs sharing a common body Fe atom. The two $Fe_4$ mean-planes subtend a dihedral angle of ca. 72°. The Tb (**3**) and Dy (**4**) compounds show Single Molecule Magnet (SMM) behaviour as confirmed by ac-susceptibility and μ-SQUID measurements. Furthermore, $^{57}Fe$ Mössbauer spectra of **1**-**4** confirm the presence of high-spin $Fe^{III}$ sites. The spectra of all complexes in the high temperature range (30-300 K) show broad overlapping doublets which were assigned to the body and wing-tip pairs of metal ions within the $Fe_7$ core. The low temperature Mössbauer spectra at low temperatures show dependence on the nature of the rare-earth metal as a result of its interaction with the iron sites. Thus, we observed a transition from fast (**2**), to intermediate (**1**) and very slow (frozen) (**3**, **4**) spin fluctuation phenomena in these compounds.

## Introduction

The continuous development and improvement of lanthanide-based materials enable access to the advanced 'green' applications and new clean energy technologies such as electric vehicles, photovoltaics, wind turbines and energy-efficient lighting.[1] Also rekindled interest is currently being paid to the synthesis and investigation of homo- and heteropolynuclear lanthanide coordination compounds possessing unusual magnetic properties.[2] The use of lanthanides to modulate the magnetic properties of transition metal single-molecule magnets has become common in recent years as a result of the discovery that the magnetic anisotropy of some lanthanides can be used to increase the barrier to reversal of magnetisation and allow for the observation of various slow relaxation phenomena including Single Molecule Magnet (SMM) behaviour.[3] In this respect, complexes containing a combination of 3*d* and 4f metal ions ([Cu-Ln],[4] [Mn-Ln],[5] [Co-Ln],[6] [Ni-Ln],[7] [Cr-Ln],[8] and [Fe-Ln][9]) have been investigated in recent years with the idea of combining the spins of transition metal ions with the large and mostly anisotropic magnetic moments of rare earth ions.

The origin of the magnetic interactions in these compounds is not as well understood as for polynuclear 3d metal complexes. With the exception of the isotropic $Gd^{III}$ (and the diamagnetic $Y^{III}$, $La^{III}$ and $Lu^{III}$) ions, the ground state of the $Ln^{III}$ ions has a first-order angular momentum, which precludes modeling the magnetism using a spin-only Hamiltonian for isotropic exchange. As has been shown previously, it is clearly advantageous to be able to compare the magnetic properties of a series of isostructural complexes differing only in the nature of the rare earth ion.

Aminoalcohols have proved to be very useful in the synthesis of high nuclearity clusters because they possess chelating and bridging capabilities.[10] Significant progress has been made in the use of diethanolamine ligands and other related tripodal ligands in the synthesis of high spin Mn[11a-c] and high nuclearity Fe[11d-g] and Ni[11d] complexes, as well as mixed-metal clusters derived from this class of ligands have been reported.[5(f,i),8a,9(b,h,k,l),12,13] In our own work, we have found aminopolyalcohol-based ligands useful for many years and particularly so for the synthesis of 3*d*/4*f* coordination clusters since the hard O donor atom favours binding to oxophilic lanthanide centres, whereas the softer N donor atom is more attracted to the 3*d* ions.[14] Furthermore, the deprotonated hydroxyethyl arms of these ligands provide excellent bridging groups, thereby favouring the formation of high nuclearity species.

To date, only a few reports on Fe-Ln coordination clusters FeDy,[9a] $Fe_3Ln$,[9(f,j)] $Fe_4Ln_2$,[9k] $Fe_7Dy_3$,[9l] $Fe_4Dy_4$,[9m] $Fe_{16}Ln_4$,[9o] $Fe_7Ln_4$,[9p] $Fe_2Ln_2$,[9(q,r)] $Fe_6Dy_3$[9u] studied by Mössbauer spectroscopy have been reported. Using this spectroscopy it is possible to obtain useful

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*Electronic Supplementary Information (ESI) available: [S1. IR spectra, Mössbauer and magnetic properties, DFT calculations]. See DOI: 10.1039/x0xx00000x* information not only about oxidation and spin state of the analyzed isotope, but also about the magnetic anisotropy of elements interacting with it.[9(r,t)] Furthermore, this method has been shown to be valid for determining spin structure of some polynuclear $Fe_xLn_y$ coordination clusters: $Fe_2Ln_2$,[9r] $Fe_3Ln$,[9j] $Fe_4Ln_2$[9k] and $Fe_6Dy_3$.[9u] Although, at low temperature the magnetic susceptibility measurements for some of these clusters[9k,u] show dominant ferromagnetic interactions within the clusters, the Mössbauer studies reveal that the interactions between the iron centres are antiferromagnetic in nature. This information helps further by providing insights into the interactions between Fe-Ln and Ln-Ln ions.[15]

## Experimental

**Preparation of Complexes:** The syntheses of compounds **1** and **4** have been previously reported.[9p] The other two compounds were synthesised in a similar manner using the corresponding lanthanide nitrate.

$[Fe^{III}{}_7Gd^{III}{}_4O_4(OH)_3(tea)_2(Htea)_3(Piv)_7(NO_3)_3(H_2O)_2]\cdot 3½MeCN$ (**2**): Yield (based on Fe): ~180 mg (~15%). Anal. calc. for $C_{65}H_{133}N_8O_{47}Fe_7Gd_4$ (loss of all lattice $CH_3CN$): C, 27.90; H, 4.79; N, 4.00; Found: C, 27.96; H, 4.82; N, 4.04.

$[Fe^{III}{}_7Tb^{III}{}_4O_4(OH)_3(tea)_2(Htea)_3(Piv)_7(NO_3)_3(H_2O)_2]\cdot 3MeCN$ (**3**): Yield (based on Fe): ~180 mg (~15%). Anal. calc. for $C_{65}H_{133}N_8O_{47}Fe_7Tb_4$ (loss of all lattice $CH_3CN$): C, 27.83; H, 4.78; N, 3.99; Found: C, 27.76; H, 4.75; N, 3.90.

Selected IR for compound **2** (KBr), /cm$^{-1}$: 3437 (b, vs), 2962 (ms), 2904 (w), 2868 (mw), 1562 (s), 1485 (s), 1459 (w), 1426 (vs), 1384 (vs), 1279 (mw), 1229 (ms), 1084 (b, s), 1030 (mw), 919 (mw), 896 (m), 785 (w), 624 (m), 596 (m), 520 (mw), 432 (mw). The IR spectra of **1, 3** and **4** have similar characteristic bands (Fig. S1).

**Physical Measurements:** Magnetic susceptibility data (1.8-300K) were collected on powdered samples using a Quantum Design model MPMS-XL SQUID magnetometer and an applied field of 0.1 T. Magnetisation data were collected between 0 and 7 T at 2, 3 and 5 K. All data were corrected for the contribution of the sample holder. *ac* susceptibility measurements were measured with an oscillating field of 3 Oe and frequencies ranging from 1 to 1500 Hz.

Mössbauer spectra were obtained both between 3 and 295 K without field and at 3 K using transverse applied magnetic fields of up to 6.5 T using a conventional spectrometer in the constant-acceleration mode equipped with a $^{57}Co$ source (3.7 GBq) in a rhodium matrix. Isomer shifts are given relative to $\alpha$-Fe at room temperature. The sample was mounted inside an Oxford Instruments Mössbauer-Spectromag 4000 Cryostat.

**Crystallography:** The new structures were determined at 100 K on a Bruker Apex II (**2**) or SMART Apex (**3**) diffractometer using Mo-K$\alpha$ radiation. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL program suite.[16] The three lattice MeCN molecules in **3** were disordered but could be refined; those in **2** were more badly disordered and were treated using SQUEEZE.[17] Electron density corresponding to 119 e in 556 Å$^3$ per $Fe_7Gd_4$ unit was found; calc. for 3½ MeCN 110 electrons.

Crystallographic data (excluding structure factors) (Table 1) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 783687 (**1**), 929496 (**2**), 929497 (**3**), 775953 (**4**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK:http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

## Results and Discussion

Here we report a reaction between $[Fe_3O(Piv)_6(H_2O)_3]Piv$, $Fe(NO_3)_3\cdot 9H_2O$, $Ln(NO_3)_3\cdot 6H_2O$ and $H_3tea$ in a molar ratio 1:3:4:23 in MeCN gave a red-brown solution from which brown crystals of $[Fe_7Ln_4O_4(OH)_3(tea)_2(Htea)_3(Piv)_7(H_2O)_2(NO_3)_3]\cdot 3MeCN$ where Ln = Y (**1**), Gd (**2**, with 3½ lattice MeCN), Tb (**3**), Dy (**4**) crystallized after several days.

X-Ray crystallographic analysis of compounds **2** and **3** showed that these $Fe_7Ln_4$ compounds crystallise in the monoclinic space group *C*2/*c* with Z = 8, isotypically to the previously reported compounds **1** and **4**,[9p] and are all isostructural. The structure of all compounds consists of an $Fe_7Ln_4$ cage-like coordination cluster (Fig. 1) with an irregular structural conformation. The $[Fe_7Ln_4(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_3)(\mu_3\text{-}O_{Htea})]^{20+}$ core comprises two cubanes corresponding to $[Fe_2Ln_2(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2]$ and $[Fe_2Ln_2(\mu_4\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O_{Htea})]$ which are fused together via the shared Fe1 vertex. There are two $\mu_4$-$O^{2-}$ ions in each cubane (O1, O2, O3 and O4) and these bridges between one lanthanide and three iron ions including the common Fe1 vertex (Fig. 1). Within each cubane subunit the iron centres are also part of a $\{Fe_4O_2\}$-butterfly-unit, again with the $Fe1_{(body)}$ atom being shared to give a “Siamese-twin” butterfly motif with approximately perpendicular “side-face”-"*body-to-body*" with a dihedral angle of ca. 72° between their mean planes. The crystal structure is stabilized by a variety of intermolecular O···H-O hydrogen bonds involving the H atoms of two water molecules, monoprotonated $Htea^{2-}$ and two $^-OH$-groups, and O atoms of different pivalate and diprotonated $tea^{3-}$ ligands, and a nitrate group. The three $Htea^{2-}$ and two $tea^{3-}$ groups are bound to up to four Fe and Ln atoms, acting as three (2+1) monoprotonated $\eta^2:\eta^1:\eta^2:\mu_3$, $\eta^2:\eta^1:\eta^3:\eta^1:\mu_4$ and two fully deprotonated $\eta^1:\eta^1:\eta^2:\eta^2:\mu_3$, $\eta^2:\eta^1:\eta^2:\eta^2:\mu_4$ triethanolamine ligands. Peripheral ligation about the core is provided by five $\eta^1:\eta^1:\mu$, one chelating (with a Ln4) and a terminal (with Ln4 and hydrogen bond by H(432) of one neighbouring water molecule) pivalate ligands plus two apical water molecules (on Ln2 and Fe5) and three $NO_3^-$ groups (two chelating to Ln1 and Ln3, and one which exhibits a double hydrogen-bonding interaction between atom O71 of a nitrate anion and atoms H(22) and H(442) of $Htea^{2-}$ (O22) and water (O44) molecules. The $Fe^{III}$ centres all have distorted octahedral geometries except for Fe(3) which is trigonal-bipyramidal ($\tau \approx 0.71$, see SI). The three Ln centres, are eight-coordinate with triangular dodecahedron (for Ln(1) and Ln(3)) and biaugmented trigonal prism (for Ln(4)) geometries. The Ln(2) is

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nine-coordinate with spherical capped square antiprism geometry.

**Table 1.** Crystal data and refinement details for compounds **1-4.**

| | 1[9p] | 2 | 3 | 4[9p] |
|---|---|---|---|---|
| Formula | $C_{71}H_{142}Fe_7N_{11}O_{47}Y_4$ | $C_{72}H_{143.5}Fe_7Gd_4N_{11.5}O$ | $C_{71}H_{142}Fe_7N_{11}O_{47}Tb_4$ | $C_{71}H_{142}Dy_4Fe_7N_{11}O_{47}$ |
| $M_r$ | 2648.55 | 2942.43 | 2928.59 | 2942.91 |
| Crystal System | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | *C*2/*c* | *C*2/*c* | *C*2/*c* | *C*2/*c* |
| T (K) | 100(2) | 100(2) | 100(2) | 150(2) |
| *a* (Å) | 43.5252(18) | 43.357(5) | 43.521(2) | 43.6168(15) |
| *b* (Å) | 19.6880(8) | 19.735(2) | 19.6914(9) | 19.7236(7) |
| *c* (Å) | 30.3545(12) | 30.376(6) | 30.4499(15) | 30.5768(11) |
| *β* (°) | 125.5050(10) | 125.406(4) | 125.444(1) | 125.495(2) |
| *V* (Å$^3$) | 21175.0(15) | 21185(6) | 21259.2(18) | 21416.3(13) |
| Z | 8 | 8 | 8 | 8 |
| $D_{calc}$ (g cm$^{-3}$) | 1.662 | 1.845 | 1.830 | 1.825 |
| *F*(000) | 10872 | 11760 | 11704 | 11736 |
| μ (Mo-Kα) (mm$^{-1}$) | 3.184 | 3.486 | 3.638 | 3.761 |
| Reflections collected | 78121 | 107863 | 66060 | 72035 |
| Unique reflections | 24001 | 29758 | 23938 | 23603 |
| $R_{int}$ | 0.0519 | 0.0474 | 0.0281 | 0.0405 |
| Parameters | 1276 | 1244 | 1267 | 1219 |
| $R_1$ (I > 2σ(I)) | 0.0403 | 0.0325 | 0.0392 | 0.0438 |
| $wR_2$ (all data) | 0.1016 | 0.0692 | 0.1315 | 0.1137 |
| *S* (all data) | 1.018 | 1.060 | 1.049 | 0.988 |
| *CCDC number* | 783687 | 929496 | 929497 | 775953 |

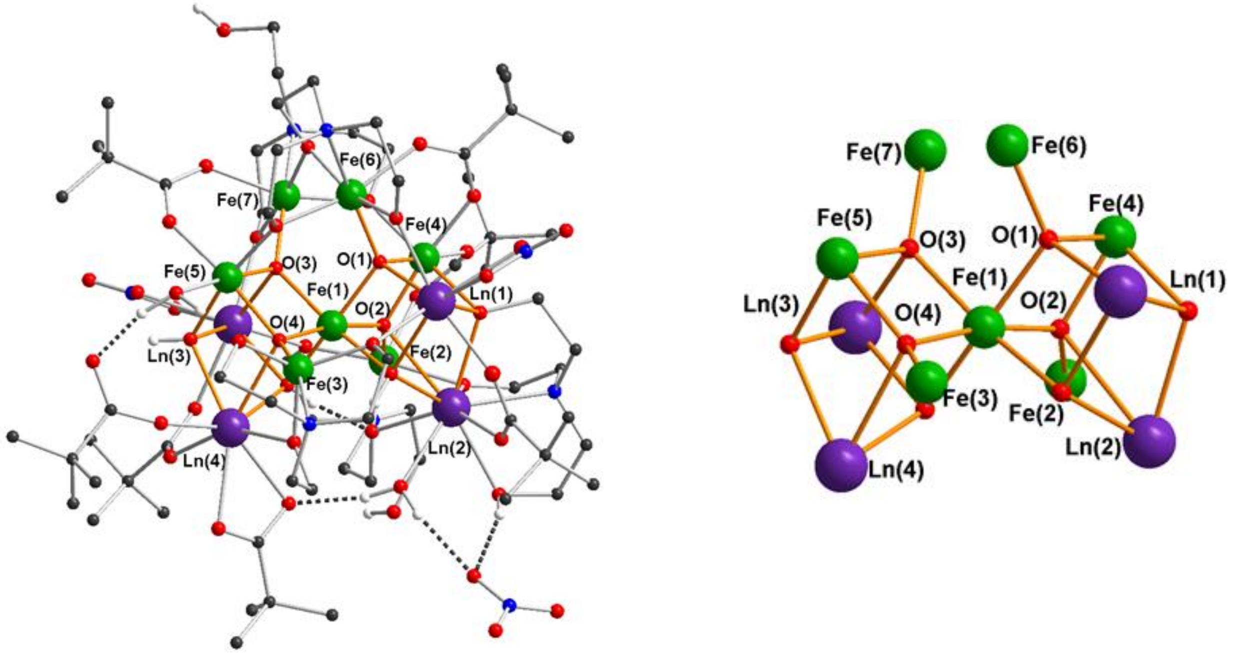

**Fig. 1**. Molecular structure (left) and {$Fe_7Ln_4O_4(\mu_3\text{-}O_{Htea})(OH)_3$}core (right) of complexes **1-4**.

## Magnetic Properties

*DC* magnetic susceptibility measurements for compounds **1** - **4** were performed with an applied magnetic field of 0.1 T in the temperature range 1.8–300 K. The plots of $\chi T$ *vs* T are shown in Fig. 2. For compound **1** ($Fe_7Y_4$) containing diamagnetic $Y^{III}$ ions, the room temperature $\chi T$ has a value of 9.1 $cm^3mol^{-1}K$, much smaller than that expected for seven uncoupled $Fe^{III}$ ions ($S$ = 5/2), indicating significant antiferromagnetic interactions between the $Fe^{III}$ ions. On lowering the temperature, $\chi T$ decreases in accord with the presence of strong antiferromagnetic interactions. In the temperature range 30 – 10 K, the $\chi T$ approaches a plateau at 4.5 $cm^3mol^{-1}K$, consistent with a ground state of $S$ = 5/2 (4.375 $cm^3mol^{-1}K$ for $g$ = 2). The decrease in the $\chi T$ value below 10 K can be attributed to intermolecular antiferromagnetic interactions, as commonly seen in antiferromagnetically $Fe^{III}$ coordination clusters.[18]

For compound **2** ($Fe_7Gd_4$), the room temperature $\chi T$ value is 40.7 $cm^3mol^{-1}K$, and decreases steadily to 34.2 $cm^3mol^{-1}K$ at 20 K and then drops more rapidly to 12.5 $cm^3mol^{-1}K$ at 1.8 K. Complex **3** behaves in a similar fashion to **2**: the $\chi T$ value of 56.4 $cm^3mol^{-1}K$ at 300 K decreases with decreasing temperature to 48.3 $cm^3mol^{-1}$ K at 20 K, and then drops to 36.4 $cm^3mol^{-1}K$ at 1.8 K. For compound **4** ($Fe_7Dy_4$), the room temperature $\chi T$ value is 69.5 $cm^3mol^{-1}K$ and first decreases to 59.4 $cm^3mol^{-1}K$ at 20 K, then rapidly increases to reach a maximum of 81.2 $cm^3mol^{-1}$ K at 2.8 K before dropping to 79.8 $cm^3mol^{-1}K$ at 1.8 K.

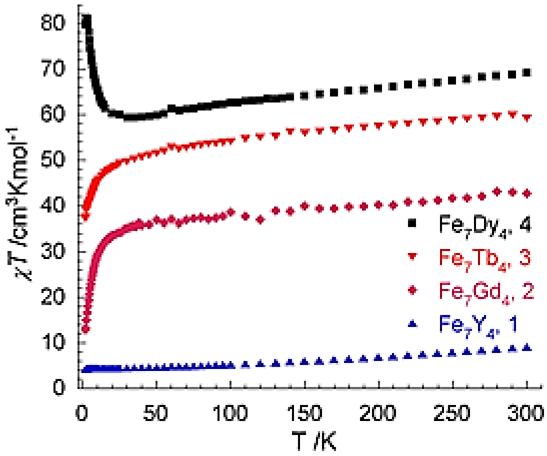

**Fig. 2.** $\chi T$ *vs* T plots at 1000 Oe for compounds **1-4.**

To assess the nature of magnetic interactions between the $Ln^{III}$ – $Ln^{III}$ ions, the magnetic contribution of the $Fe_7$ moiety was subtracted from the susceptibility products of compounds **2-4** using the data from the $Fe_7Y_4$ compound **1**. As shown in Fig. S2, the decrease at low temperatures in the $\chi T$ *vs* T curves for **2** ($Fe_7Gd_4$) and **3** ($Fe_7Tb_4$) suggests the presence of antiferromagnetic $Ln^{III}$-$Ln^{III}$ coupling, while the increase of the adjusted $\chi T$ below 20 K observed in **4** ($Fe_7Dy_4$) indicates a ferromagnetic arrangement of the $Dy^{III}$ ions. It is worth to mention that the extracted ferro- or antiferromagnetic interaction in case of these compounds could also result from the weak $Ln^{III}$-$Fe^{III}$ coupling. Hence, work now is in progress to substitute Fe ions with diamagnetic Ga or Al ions in order to extract the real contribution of the $Ln_2$ units to the magnetism of studied compounds. In the past such attempts were done in our group and proved to be successful.[15, 19]

The field dependence of the magnetization for **1** - **4** agrees with the results obtained from the $\chi T$ data. The M *vs* H measurements of the magnetisation up to 7 T were performed at 2, 3 and 5 K for all compounds, and are shown in Fig. S3. The field dependence of the magnetisation for **1** ($Fe_7Y_4$) at low temperatures (2, 3 and 5 K) reveals that the magnetisation increases smoothly with the applied *dc* field without saturation even at 7 T ($M$ ~ 5 $\mu_B$). The absence of saturation indicates the presence of small magnetic anisotropy and/or the lack of a well-defined ground state. For compounds **2**, **3** and **4**, the values of the magnetization at 7 T are 34.0, 25.1 and 27.0 $\mu_B$, respectively. All of them are far lower than the value expected if all the spins are ferromagnetically aligned. The values achieved at the highest field are rather low, but not unusual: the values of ~5-6 $\mu_B$ are expected for $Dy^{III}$ or $Tb^{III}$ and ~7 $\mu_B$ for $Gd^{III}$ single ions in polycrystalline samples. For compound **2** ($Fe_7Gd_4$), the value of the magnetisation at 7 T of ~ 34.0 $\mu_B$ is in relatively good agreement with the value expected for seven antiferromagnetically coupled $Fe^{III}$: 5 $\mu_B$ and four weakly coupled $Gd^{III}$ ions: 4 x ~7 = ~ 28 $\mu_B$. The lack of saturation on the M *vs* H data also supports the presence of antiferromagnetic interactions and the intrinsic magnetic anisotropy of the $Tb^{III}$ and $Dy^{III}$ ions in compounds **3** and **4**: like for compound **1** and **2**, the magnetization values are in good agreement with susceptibility data, and show expected values for seven antiferromagnetically coupled $Fe^{III}$ and four weakly coupled $Dy^{III}$ or $Tb^{III}$ ions: 1 x 5 + 4 x ~5-6 = ~ 25-29 $\mu_B$.

The M *vs* H data for compound **3** shows how the magnetization increases in two steps at 2 K (Figure S3). First, the magnetization increases abruptly, reaching a step at about 11-12 $\mu_B$ at a field of ~10 KOe. The further increase in the applied field, makes the magnetization to increase rapidly again and approaches a value of ~25.0 $\mu_B$ at 70 KOe. This type of inflection is usually observed when the applied magnetic field overwhelms weak antiferromagnetic interactions between the spins and stepwise is aligning these spins. However, the presence of very anisotropic Tb ions in this compound makes it difficult to determine the magnitude of the magnetic exchange interaction and which magnetic spins are involved in this process.

Generally speaking, the evolution of the magnetisation curves between 4 and 70 KOe and non-saturation at high fields indicate the presence of an appreciable magnetic anisotropy in the ground state contributed from the high spin and anisotropic four Ln ions. Due to the magnetic anisotropy present in all compounds, *ac* susceptibility measurements were performed under zero dc fields. There is no out-of-phase signal shown above 2 K for compounds **1** ($Fe_7Y_4$) and **2** ($Fe_7Gd_4$). However, in case of compounds **3** ($Fe_7Tb_4$) and **4** ($Fe_7Dy_4$) below 6 K, both frequency-dependence in-phase, $\chi'$, and out-of-phase, $\chi''$, signals are detected, indicating a slow relaxation of their magnetisation. The shape and frequency dependence of the in-phase ($\chi'$) and out-of-phase signals ($\chi''$) strongly suggest that these compounds are single molecule magnets with maxima (at 1500 Hz) in $\chi''$ at 2.75 K and 2.95 K for **3** and **4**, respectively (Fig. 3).

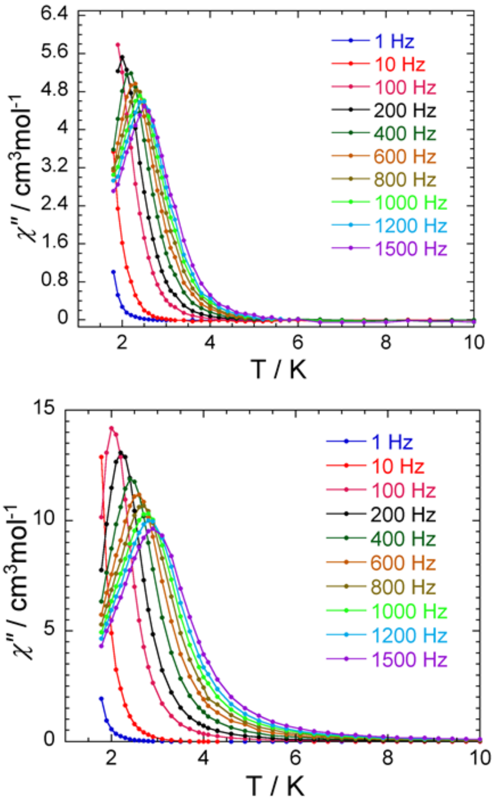

**Fig. 3.** Plots of the out-of-phase *ac* susceptibility signals *versus* temperature for **3** (top) and **4** (bottom).

The relaxation time can consequently be deduced from the frequency sweeping *ac* data (Fig. 4).

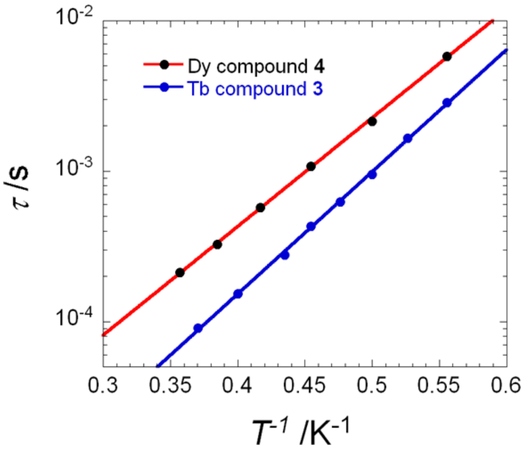

**Fig. 4.** The relaxation time of compound **3** and **4** under zero *dc* field. The solid lines represent the respective Arrhenius law with the parameters discussed in the text.

In both cases, the data between 1.8 and 2.8 K follow an Arrhenius activated behaviour with an energy gap (Δ) of 18.7 K and a pre-exponential factor ($\tau_0$) of $8.6\times10^{-8}$ s for Tb compound **3**, and of 16.9 K and $4.6\times10^{-7}$ s for Dy compound **4** (Fig.4). In general, the *ac* behaviour of both compounds is very similar. The Cole-Cole plot of $\chi''$ vs $\chi'$ at low temperature exhibits a roughly semicircular shape. However, it is not well fitted by using a generalized Debye model. As shown in Figure S4, the fit of Cole-Cole diagram at 2.2 K gives $\alpha$ = 0.1245 (6), $\chi_0$ = 40.07(1) cm$^3$mol$^{-1}$, $\chi_{inf}$ = 7.04(1) cm$^3$mol$^{-1}$. The small $\alpha$ parameter suggests that there might be one dominant relaxation process. In order to study the relaxation behavior further and check for quantum tunneling effects above 1.8 K, the *ac* measurements under an applied *dc* field were done on both compounds. The application of a *dc* field did not have any obvious influence on the relaxation process for the Tb compound **3**, but had a slight effect for the dysprosium containing compound (**4**). Therefore, further *ac* measurements as a function of the external *dc* field were done on the $Fe_7Dy_4$ (**4**). With the increase of *dc* field the relaxation process slows down and the optimum field is observed at 750 Oe (Fig. S4).

The *ac* susceptibilities as a function of frequency were carried out again under 750 Oe. Fitting the data by an Arrhenius law, the effective energy gap (Δ) now is 16.2 K and the pre-exponential factor ($\tau_0$) at $7.7\times10^{-7}$ s. Within the experimental uncertainty this energy gap is almost same as the one under zero field, indicating that the quantum tunneling effect in this compound is not very pronounced.

To confirm the SMM behavior of compound **4** ($Fe_7Dy_4$), detailed magnetization (M) *vs. dc* field studies were carried out to look for hysteresis, the analytic property of a magnet (Fig. 5).

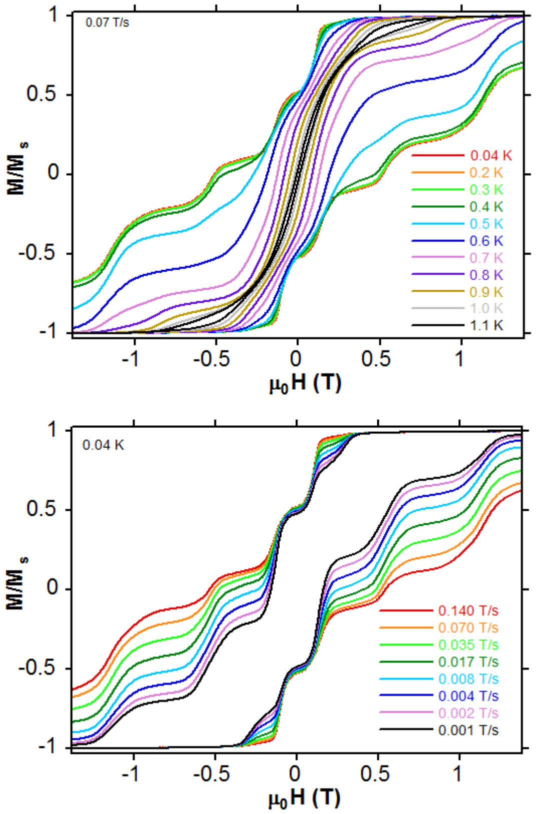

**Fig. 5.** Field dependence of the magnetization of **4**: the temperature dependence at a fixed scan rate of 0.07 Ts$^{-1}$ (top) and the scan-rate dependence at a fixed temperature of 0.04 K (bottom). The magnetization is normalized to its saturation value ($M_s$).

The data were collected on single-crystals of **4** using a micro-SQUID apparatus.**[20]** Hysteresis loops were indeed observed below 1.1 K, whose coercivities increase with decreasing temperature and increasing field sweep rate, as expected for the superparamagnetic-like properties of an SMM below its blocking temperature, reaching about 0.5 T at 0.3 K and lower. It can be seen that no evident QTM steps are recorded around zero field, also confirmed by ac measurements. The loops at various sweeping rates show a pretty wide crossing field range, indicating the distribution of molecular environments in this single crystal, which is consistent with molecular structure.

## Mössbauer Spectroscopy

The local probe of Mössbauer spectroscopy is proving very useful for helping to investigate the effects of the presence highly anistropic ions on the local electronic structure of iron centres as well as proving useful to probe the nature of magnetic interactions within such coordination compounds and help to assign spin orientations. The Mössbauer spectra of **1-4** were measured using a range of temperatures between 300 and 3 K as well as under applied fields up to 6.5 T at 3K (Fig. 6). At 77 K (Figs. S5 and S6) and above, broadened doublets corresponding to the superposition of five doublets which can be assigned to seven $Fe^{III}$ sites are observed. Since in all compounds the crystallographic environments of Fe(4) and Fe(5) are analogous to that of Fe(1) and similarly the environments of Fe(6) and Fe(7) are comparable to that of to Fe(2), the isomer shifts of these ions were constrained to the same value. This avoids over-parameterisation and makes it possible to use fitting parameters corresponding to three isomer shifts, five quadrupole splittings and one line width.

The approximation we have used is reasonable because the $Fe^{III}$ ions in **1-4** all have very similar average Fe – ligand bond lengths and Fe – ligand - M (M = Fe or Ln) angles, and as a result should exhibit pretty similar isomer shifts and quadrupole splitting values. The smallest isomer shift, $\delta$, and largest quadrupole splitting, $\Delta E_Q$, were assigned to the Fe(3) site which is five-coordinate. The doublets with a relative area of two have been assigned to the Fe(4) and Fe(5) pair and the Fe(6) and Fe(7) pair of ions, respectively. The remaining doublets were assigned to Fe(1) and Fe(2).

Broad transitions from 90 K to 3 K for **1** ($Fe_7Y_4$) and from 40 K to 3 K for both **3** ($Fe_7Tb_4$) and **4** ($Fe_7Dy_4$) compounds from doublet to magnetic sextets are observed in the zero-field Mössbauer spectra. At temperatures lower than 70 K (for **1**) or 40 K (for **3** and **4**), the Mössbauer spectra are dominated by intermediate relaxation phenomena with magnetic hyperfine lines developing below 20 K superimposed on a sharp absorption envelope at the centre of the spectrum. With decreasing temperature, the intensity of the magnetic sub-spectra increase at the expense of the central doublet. Only for compounds **3** ($Fe_7Tb_4$) and **4** ($Fe_7Dy_4$) well-defined magnetic spectra (a superposition of five sextets) are obtained at 3 K, indicating that the spin relaxation has crossed from a fast to a slow regime with respect to the Mössbauer timescale. Thus, at 3 K the Mössbauer spectrum of **1** ($Fe_7Y_4$) is still a superposition of broadened sextets and paramagnetic doublets.

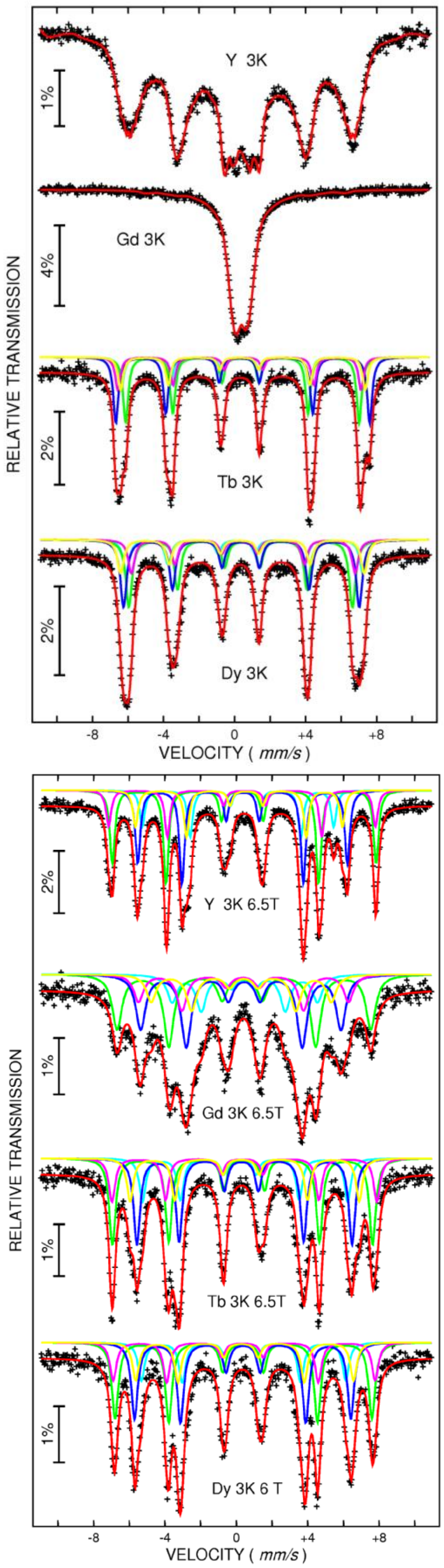

**Fig. 6.** Mössbauer spectra for **1-4** at 3 K in zero-field (top) and 3 K in applied magnetic fields of 6 or 6.5 T (bottom).

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This can be attributed to the dynamic behaviour of magnetic exchange correlations within the $Fe_7$ fragments. Mössbauer spectra are dependent on the lifetime of these correlations and if this lifetime is longer than the Larmor period of the nuclear moment, the Mössbauer spectrum shows broad sextets corresponding to intermediate relaxation times of between $10^{-7}$ and $10^{-9}$ s. The observed superposition of sextets and doublets indicates a fairly wide distribution of relaxation times between the iron nuclei in **1** ($Fe_7Y_4$), which is also in line with the large differences in local coordination geometries which affect the hyperfine and thus internal magnetic fields. Since the Y ions are diamagnetic, we conclude that the well-defined magnetic patterns for the compounds **3** ($Fe_7Tb_4$) and **4** ($Fe_7Dy_4$) result from slow intracluster relaxations in conjunction with internal molecular dipolar fields.

These internal fields result from the non-reversal of the magnetisation mediated via ground and/or excited states $M_J$ of the $Dy^{III}$ or $Tb^{III}$ ions at the low temperature being sensed by the iron nuclei spin moments.

In contrast to **1** ($Fe_7Y_4$), **3** ($Fe_7Tb_4$) and **4** ($Fe_7Dy_4$), the Mössbauer spectrum for **2** ($Fe_7Gd_4$) at 3 K presents a broad doublet. It appears that in **2** ($Fe_7Gd_4$), due to the presence of paramagnetic Gd ions close to $Fe_7$ central fragment, a weak spin–spin interaction appears between them, the paramagnetic spin relaxation is faster and the magnetic structure disappears. The observation that for both **1** ($Fe_7Y_4$) and **2** ($Fe_7Gd_4$) well defined magnetic spectra (six absorption-lines) are obtained only at 3 K and with external magnetic fields of 1 T and higher, indicates that the spin-relaxation has crossed from fast to slow with respect to the Mössbauer time scale.

However, further information can be gained from the spectra measured at 3 K under applied fields. Whereas for all four compounds it is difficult to assign the sextets between 3 K at 1 T and 3K at 4 T, it is clear that the spectra are well defined. However, they arise from the superposition of five sextets with very similar hyperfine parameters. The deviation in $B_{eff}$ vs $B_{appl}$ essentially contains information about the orientation of the spin relative to the applied field and spin relaxation mechanisms. Such behaviour can give us insights into the local electronic structure.

The observed changes for **1-4** in the effective ($B_{eff}$) magnetic field values are consistent with the presence of local spin polarisation along the applied magnetic field direction as seen for antiparallel (antiferromagnetically) spin-coupled $Fe^{III}$ complexes. However, we can expect that the varying coupling strengths between the different iron centres will lead to some pairs becoming coupled parallel (ferromagnetically).

Analysing the Fe-O-Fe angles and comparing them with the values reported in the literature,[21] we find that the closest possible Fe centres which can be ferromagnetically coupled to the central and shared Fe(1) are the Fe(4) and Fe(5) ions (angles 97.7 and 93.9°, and 94.5 and 94.9°, respectively). The remaining four iron ions, Fe(2), Fe(3), Fe(6) and Fe(7) have angles to the central Fe(1), Fe(4) and Fe(5) chain varying from 119.9 to 134.6° which suggest an antiferromagnetic interaction. From the magnetic susceptibility measurements result antiferromagnetic behavior for $Fe_7Y_4$, as well as $Fe_7Gd_4$ and $Fe_7Tb_4$, is seen. Therefore, we have expected a similar behaviour for the $Fe_7Dy_4$ compound, i.e. all interaction to be antiferromagnetic. Indeed, Mössbauer studies prove the antiferromagnetic behaviour of the central $Fe_7$ core in $Fe_7Dy_4$. To support this conclusion, we have determined the *J* values using a magnetostructural correlation originally developed for dimers that utilizes both the Fe-O distances and Fe-O-Fe angles[21] and later on improved and extended to polynuclear topologies.[22] The *J* values (Fig. 7) are without a doubt all AF but are of two types: relatively strong (- 19 to - 32 $cm^{-1}$) and weak (- 4 to - 9 $cm^{-1}$).

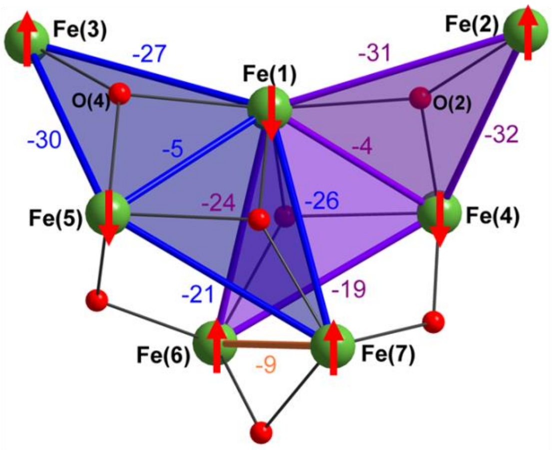

**Fig. 7.** $Fe_7$ core of $Fe_7Ln_4$ compounds showing the calculated *J* values ($cm^{-1}$) for each $Fe^{III}_2$ pair in **4** ($Fe_7Dy_4$) based on bond lengths and angles extracted from the cif-files. Red arrows show the possible spin structure of the $Fe_7$ core.

Using obtained values, the ground state can thus be rationalized by an antiparallel alignment of spins due to strong interactions and a parallel alignment of spins due to weak ones (Fig. 7). This possible magnetic structure fits very well with that found from the evolution of Mössbauer spectra with the applied field and suggests that in compound **4** the interactions between Fe-Dy or Dy-Dy ions are ferromagnetic, but which one is dominating must be proved by more sophisticated techniques. The $Fe_7Ln_4$-family represents the largest Fe-Ln polynuclear system to be analysed in this way. Our results demonstrate that with help of Mössbauer spectroscopy we can evaluate, and with the applied field, control the magnetic structure in molecular clusters. It makes this technique well-suited for heterometallic molecular clusters where other methods may prove uncertain. The analysis of Mössbauer spectra shows that the presence of high spin and high anisotropic near-neighbors does influence spin-relaxation, but not spin structure of the studied Fe-Ln aggregates.

## DFT calculations

We performed DFT calculations on the gadolinium-based molecule ($Fe_7Gd_4$), where Gd has just half-filled 4*f*-states. DFT calculations were carried out with the Vienna ab-initio simulation package (VASP),[23,24] at the level of the spin-polarized generalized-gradient approximation (GGA).[25] We use Hubbard U correction (GGA+U) which accounts for the strong on-site Coulomb interactions among

Fe (3*d*; U = 5 eV) and Gd (4*f;* U = 4 eV) electrons.[26] We used the projector augmented wave (PAW) method for the description of the ionic cores.[27, 28] To avoid any interaction from the periodic image, we keep vacuum of ~12 Å between two subsequent edges of the molecule. A large supercell of $a \times b \times c$ ($a = b = c$ = 30 Å) dimension was used, with the molecule in the center of the cell. The energy cutoff for the plane wave expansion was 400 eV. A gamma-point sampling (1×*1*×*1 grid*) of the Brillouin zone is performed. In selective dynamics, we keep Gd and Fe-positions fixed. All other atoms are allowed to move within the cell till the force and total energy difference reach to 0.05 eV/Å and $10^{-5}$ eV, respectively. The relaxation procedure followed the conjugated gradient method for the energy minimization. We used the relaxed cell to perform self-consistent electronic structure calculations.

Experimentally Gd atoms found in +3 oxidation state, and our fully relaxed **2** ($Fe_7Gd_4$) shows the same depiction. We find a total magnetic moment for $Gd^{III}$ ≈ 6.9 $\mu_B$, which is very close to experimentally observed 7 $\mu_B$. In **2** ($Fe_7Gd_4$), four gadolinium atoms show weak ferromagnetic coupling. We performed calculations with two spin-arrangements on iron sites: (a) ferromagnetic, and (b) anti-ferromagnetically coupled Fe atoms. The anti-ferromagnetically coupled iron sites are energetically more favorable by ~20 meV. In the mixed Fe-Gd polynuclear cluster in **2**, we find Fe atoms exist in +3 oxidation state. Iron(III) atoms are known to have a coordination number of six, and in **2** Fe atoms clearly coupled with 6 octahedrally bonded oxygen atoms (Fig. 8).

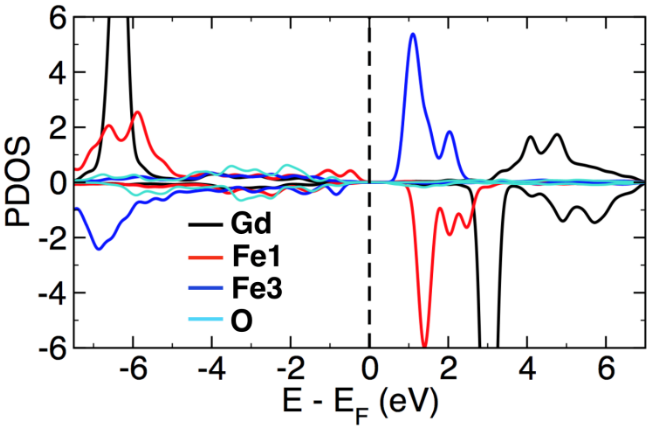

**Fig. 8.** Partial density of states (PDOS; states-$(eV)^{-1}$-$atom^{-1}$-$spin^{-1}$) of Gd, $Fe_1$, $Fe_3$ and O-atoms in ($Fe_7Gd_4$) polynuclear cluster (**2**). Black (dashed) vertical lines mark the Fermi levels ($E_F$).

Bond length of Fe-O and angles Fe-O-Fe are compared in SI (Table S2) for molecule and molecular unit in experiments.

Because the configuration of $Fe^{III}$ has 5*d*-electrons, we would expect to see five unpaired spins in complexes with Fe. Since Fe exists in the high-spin magnetic state, the electrons are distributed as 3 in Fe($t_{2g}$) and 2 in Fe($e_g$) levels. However, the calculated $Fe^{III}$ moment is ~4.2 $\mu_B$, which is slightly lower than observed. The reduced moments on Fe-sites can easily be attributed to the increased bonding strength of $Fe^{III}$ with oxygen atoms, where oxygen gains some induced moment (sometimes as high as 0.1 $\mu_B$) and subsequently reducing the $Fe^{III}$ moment. We compare Fe-O bond-length and Fe-O-Fe bond-angles from molecular crystal (experimental) and calculated molecule **2** ($Fe_7Gd_4$). The calculated average Fe-O bond-length of 2.01 Å is lower by ~2.5% compared to the observed average Fe-O bong-length of 2.06 Å. However, there is no noticeable change compared to the experimentally assessed range of Fe-O-Fe bond-angle. The calculated angle of Fe(1)-$O_1$-Fe(4) and Fe(1)-$O_2$-Fe(4); as well as Fe(1)-$O_3$-Fe(5) and Fe(1)-$O_4$-Fe(5) sets are (97.88°; 96.56°) and (95.14°; 94.52°), respectively, and very close to observed (97.7°; 93.9°) and (94.5°; 94.9°). The calculated Fe(2), Fe(3), Fe(6) and Fe(7) have angles to the central Fe(1), Fe(4) and Fe(5) chain varying from 121.30° to 134.80° in agreement with experiments, i.e., 119.9° to 134.6°. We find a total magnetic moment of ~31.8 $\mu_B$ on Fe-Gd polynuclear cluster slightly less than the observed total moment of ~33 $\mu_B$ [i.e., 5 (Fe) + 4*7 (Gd)]. The calculated projected density of states (PDOS) obtained by projecting the wave functions on atomic states (Fig. 8), clearly shows a hybridization of oxygen atoms with antiferromagnetically connected $Fe_7$ core of $Fe_7Gd_4$ compounds. The PDOS of oxygen is chosen from $Fe^{III}$ octahedral environment. This hybridization slightly suppresses the localized spin moment of $Fe^{III}$ but preserves the large magnetic moment of the $Gd^{III}$ ion (6.9 $\mu_B$) in $Fe_7Gd_4$ compounds.

## Conclusions

We reported a combined magnetic and Mössbauer study on a new family of mixed $Fe^{III}$-$Ln^{III}$ polynuclear clusters comprising a $[Fe_7Ln_4]^{33+}$ core. The magnetic and Mössbauer data were considered in terms of the two tetranuclear butterfly type $Fe_4$ cores interacting with four lanthanide ions. The isostructural compounds reported herein involve three different rare-earth $Ln^{III}$ cations: diamagnetic $Y^{III}$, paramagnetic but isotropic $Gd^{III}$ and the two magnetically anisotropic ions. The $Fe_4Ln_2$ subcores of the complexes are characterized by strong antiferromagnetic $Fe_{wing}$-$Fe_{body}$ and very weak antiferromagnetic $Fe_{body}$-$Fe_{body}$ interactions. The low temperature *ac* susceptibility measurements show the existence of slow relaxation characteristic for SMM behavior of the cluster moment for **3** ($Fe_7Tb_4$) and **4** ($Fe_7Dy_4$) with energy barriers for reversal of magnetization $U_{eff}$ of 18.7 and 16.9 K, respectively. The high-spin $S = 5/2$ state of the $Fe^{III}$ ions atoms was confirmed via the isomer shift observed in the Mössbauer spectra. The Mössbauer data were also analyzed to help assign the specific interactions between the two different $Fe_{wing}$ and $Fe_{body}$ sites in the core. The Mössbauer in-field data proved clearly the antiparallel spin orientation of the $Fe_{body}$ and $Fe_{wing}$ sites. Besides, at ~30 K spin blocking was found to occur in **3** ($Fe_7Tb_4$) and **4** ($Fe_7Dy_4$) in the Mössbauer time window (~$10^{-8}$ s), in agreement with the SMM behavior demonstrated by the ac susceptibility measurements (~$10^{-1}$ - $10^{-4}$ s). The low-temperature (3 - 10 K) spectra for **3** ($Fe_7Tb_4$) and **4** ($Fe_7Dy_4$) are revealing complete spin blocking in the absence of applied field for all Fe sites (five ordered sextets). At these temperatures, the spectra for **2** ($Fe_7Gd_4$) only show a small inset of relaxation at an intermediate rate, whereas for **1** ($Fe_7Y_4$) the spectral evolution is nontrivial and will be reported in more detail in a specialized journal.

We have demonstrated that the magnetic interactions in heteropolynuclear Fe-Ln clusters, especially those incorporating highly anisotropic lanthanides, can be better understood using a combination of magnetic susceptibility measurements, $^{57}$Fe Mössbauer spectroscopy and DFT calculations.

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## Dedication

This article is dedicated to the memory of Prof. Constantin Turta, a great mentor and the leading pioneer in the field of Fe-Ln coordination chemistry, Mössbauer spectroscopy and magnetism.

## Notes and references

1 (a) X. Qin, X. Liu, W. Huang, M. Bettinelli and X. Liu, *Chem. Rev.*, 2017, **117** (5), 4488; (b) X. Wang, R. R. Valiev, T. Y. Ohulchanskyy, H. Agren, C. Yang and G. Chen, *Chem. Soc. Rev.*, 2017, **46**, 4150; (c) D. Prodius, V. Smetana, S. Steinberg, M. Wilk-Kozubek, Y. Mudryk, V. K. Pecharsky and A.-V. Mudring, *Mater. Horiz.*, 2017, **4**, 217; (d) H. Dong, L.-D. Sun and C.-H. Yan, *Chem. Soc. Rev.*, 2015, **44**, 1608; (e) K. Liu, X. J. Zhang, X. X. Meng, W. Shi, P. Cheng and A. K. Powell, *Chem. Soc. Rev.*, 2016, **45**, 2423; (f) J. Y. Jin, T. Y. Ma, Y. J. Zhang, G. H. Bai and M. Yan, *Sci. Rep.*, 2016, **6**, 32200.

2 (a) T. C. Monson, T. E. Stevens, J. L. Leger, J. L. Manson, K. S. Lovejoy, A. L. Newsham and R. E. Del Sesto, *Chem. Commun.*, 2017, **53**, 11682; (b) D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.*, 2013, **113** (7), 5110; (c) D. Prodius, F. Macaev, Y. Lan, G. Novitchi, S. Pogrebnoi, E. Stingaci, V. Mereacre, C. E. Anson and A. K. Powell, *Chem. Commun.*, 2013, **49**, 9215; (d) L. Rosado Piquer and E. C. Sanudo, *Dalton Trans.*, 2015, **44**, 8771; (e) E. M. Pineda, Y. Lan, O. Fuhr, W. Wernsdorfer and M. Ruben, *Chem. Sci.*, 2017, **8**, 1178; (f) E. Bartolomé, A. Arauzo, J. Luzón, J. Bartolomé and F. Bartolomé, in *Handbook of Magnetic Materials, Vol. 26* (Ed.: E. Brück), Elsevier, 2017, pp. 1-289; (g) E. Moreno-Pineda, M. Damjanović, O. Fuhr, W. Wernsdorfer and M. Ruben, *Angew. Chem.*, 2017, **129**, 10047; (h) K. L. M. Harriman, J. L. Brosmer, L. Ungur, P. L. Diaconescu and M. Murugesu, *J. Am. Chem. Soc.*, 2017, **139**, 1420; (i) Y.-C. Chen, J.-L. Liu, W. Wernsdorfer, D. Liu, L. F. Chibotaru, X.-M. Chen and M.-L. Tong, *Angew. Chem., Int. Ed.*, 2017, **56**, 4996.

3 (a) G. Cucinotta, M. Perfetti, J. Luzon, M. Etienne, P.-E. Car, A. Caneschi, G. Calvez, K. Bernot and R. Sessoli, *Angew. Chem., Int. Ed.*, 2012, **51**, 1606; (b) S.-D. Jiang, B.-W. Wang, G. Su, Z.-M. Wang and S. Gao, *Angew. Chem., Int. Ed.*, 2010, **49**, 7448; (c) R. J. Blagg, C. A. Muryn, E. J. L. McInnes, F. Tuna and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2011, **50**, 6530; (d) J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *Nat. Chem.*, 2011, **3**, 538; (e) J. W. Sharples and D. Collison, *Coord. Chem. Rev.*, 2014, **260**, 1; (f) K. Liu, W. Shi and P. Cheng, *Coord. Chem. Rev.*, 2015, **289**, 74.

4 (a) J.-P. Costes, J.-M. Clemente-Juan, F. Dahan and J. Milon, *Inorg. Chem.*, 2004, **43**, 8200; (b) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba and J. Mrozinski, *J. Am. Chem. Soc.*, 2004, **126**, 420; (c) M.-B. Zhang, J. Zhang, S.-T. Zheng and G.-Y. Yang, *Angew. Chem.*, 2005, **117**, 1409; (d) J.-J. Zhang, S.-M. Hu, S.-C. Xiang, T. Sheng, X.-T. Wu and Y.-M. Li, *Inorg. Chem.*, 2006, **45**, 7173; (e) F. Mori, T. Nyui, T. Ishida, T. Nogami, K-Y. Choi and H. Nojiri, *J. Am. Chem. Soc.*, 2006, **128**, 1440; (f) C. Aronica, G. Pilet, G. Chastanet, W. Wernsdorfer, J.-F. Jacquot and D. Luneau, *Angew. Chem., Int. Ed.*, 2006, **45**, 4659; (g) G. Novitchi, J.-P. Costes, J.-P. Tuchagues, L. Vendier and W. Wernsdorfer, *New J. Chem.*, 2008, **32**, 197; (h) G. Novitchi, W. Wernsdorfer, L. Chibotaru, J.-P. Costes, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2009, **48**, 1614; (i) G. Novitchi, G. Pilet, L. Ungur, V. V. Moshchalkov, W. Wernsdorfer, L. F. Chibotaru, D. Luneau and A. K. Powell, *Chem. Sci.*, 2012, **3**, 1169; (j) Z.-M. Zhang, L.-Y. Pan, W.-Q. Lin, J.-D. Leng, F.-S.Guo, Y.-C. Chen, J.-L. Liu and M.-L. Tong, *Chem. Commun.*, 2013, **49**, 8081; (k) I. A. Kuhne, N. Magnani, V. Mereacre, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Chem. Commun.*, 2014, **50**, 1882; (l) R. Modak, Y. Sikdar, G. Cosquer, S. Chatterjee, M. Yamashita and S. Goswami, *Inorg. Chem.*, 2016, **55**, 691; (m) I. A. Kühne, G. E. Kostakis, C. E. Anson and A. K. Powell, *Inorg. Chem.*, 2016, **55**, 4072.

5 (a) C. Benelli, M. Murrie, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1999, 4125; (b) C. Zaleski, E. Depperman, J. Kampf, M. Kirk and V. Pecoraro, *Angew. Chem., Int. Ed.*, 2004, **43**, 3912; (c) A. Mishra, W. Wernsdorfer, K. Abboud and G. Christou, *J. Am. Chem. Soc.*, 2004, **126**, 15648; (d) A. Mishra, W. Wernsdorfer, S. Parsons, G. Christou and E. K. Brechin, *Chem. Commun.*, 2005, 2086; (e) V. Mereacre, A. M. Ako, R. Clérac, W. Wernsdorfer, G. Filoti, J. Bartolomé, C. E. Anson and A. K. Powell, *J. Am. Chem. Soc.*, 2007, **129**, 9248; (f) V. Mereacre, A. M. Ako, R. Clérac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson and A. K. Powell, *Chem.-Eur. J.*, 2008, **14**, 3577; (g) V. Mereacre, D. Prodius, A. M. Ako, N. Kaur, J. Lipkowski, C. Simmons, N. Dalal, I. Geru, C. E. Anson, A. K. Powell and C. Turta, *Polyhedron*, **27**, 2459; (h) T. C. Stamatatos, S. J. Teat, W. Wernsdorfer and G. Christou, *Angew. Chem., Int. Ed.*, 2009, **48**, 521; (i) A. M. Ako, V. Mereacre, R. Clérac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson and A. K. Powell, *Chem. Commun.*, 2009, 544; (j) M. Li, Y. Lan, A. M. Ako, W. Wernsdorfer, C. E. Anson, G. Buth, A. K. Powell, Z. M. Wang and S. Gao, *Inorg. Chem.*, 2010, **49**, 11587; (k) C. Papatriantafyllopoulou, W. Wernsdorfer, K. A. Abboud and G. Christou, *Inorg. Chem.*, 2011, **50**, 421; (l) J. Feuersenger, D. Prodius, V. Mereacre, R. Clérac, C. E. Anson and A. K. Powell, *Inorg. Chem. Commun.*, 2011, **14**, 1851; (m) M. Ledezma-Gairaud, L. Grangel, G. Aromí, T. Fujisawa, A. Yamaguchi, A. Sumiyama and E. C. Sañudo, *Inorg. Chem.*, 2014, **53**, 5878; (n) M. Savva, K. Skordi, A. D. Fournet, A. E. Thuijs, G. Christou, S. P. Perlepes, C. Papatriantafyllopoulou and A. J. Tasiopoulos, *Inorg. Chem.*, 2017, **56**, 5657; (o) L. B. L. Escobar, G. P. Guedes, S. Soriano, R. A. A. Cassaro, J. Marbey, S. Hill, M. A. Novak, M. Andruh and M. G. F. Vaz, *Inorg. Chem.*, 2018, **57**, 326. (p) A. A. Alaimo, A. Worrell, S. D. Gupta, K. A. Abboud, C. Lampropoulos, G. Christou and T. C. Stamatatos, *Chem.-Eur. J.*, 2018, **24**, 1-6; doi:10.1002/chem.201706098.

6 (a) V. Chandrasekhar, B. M. Pandian, R. Azhakar, J. J. Vittal and R. Clérac, *Inorg. Chem.,* 2007, **46**, 5140; (b) Y. G. Huang, X. T. Wang, F. L. Jiang, S. Gao, M. Y. Wu, Q. Gao, W. Wei and M. C. Hong, *Chem.-Eur. J.*, 2008, **14**, 10340; (c) T. Yamaguchi, J.-P. Costes, Y. Kishima, M. Kojima, Y. Sunatsuki, N. Bréfuel, J.-P. Tuchagues, L. Vendier and W. Wernsdorfer, *Inorg. Chem*., 2010, **49**, 9125; (d) K. C. 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; (e) L. Zhao, J. Wu, S. Xue and J. Tang, *Chem. Asian J*., 2012, **7**, 2419; (f) Z.-M. Zhang, L.-Y. Pan, W.-Q. Lin, J.-D. Leng, F.-S.Guo,Y.-C. Chen, J.-L. Liu and M.-L. Tong, *Chem. Commun*., 2013, **49**, 8081; (g) Y. Peng, V. Mereacre, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2017, **46**, 5337; (h) S. Chen, V. Mereacre, Z. Zhao, W. Zhang and Z. He, *New J. Chem.*, 2018, DOI: 10.1039/C7NJ04022A.

7 (a) E. K. Brechin, S. Harris, S. Parsons and R. E. P. Winpenny*, J. Chem. Soc., Dalton Trans.,* 1997**,** 1665; (b) J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Inorg. Chem.,* 1997, **36**, 4284; (c) T. Shiga, N. Ito, A. Hidaka, H. Okawa, S. Kitagawa and M. Ohba, *Inorg. Chem.,* 2007, **46***,* 3492; (d) A. M. Madalan, N. Avarvari, M. Fourmiguè, R. Clérac, L. F. Chibotaru, S. Clima and M. Andruh, *Inorg. Chem.,* 2007, **47**, 940; (e) C. G. Efthymiou, T. C. Stamatatos, C. Papatriantafyllopoulou, A. J. Tasiopoulos, W. Wernsdorfer, S. P. Perlepes and G. Christou, *Inorg. Chem.*, 2010, **49**, 9737; (f) K. C. Mondal, G. E. Kostakis, Y. Lan, C. E. Anson and A. K. Powell, *Inorg. Chem.,* 2011, **50**, 11604; (g) Y. Li, Q. Shang, Y.-Q. Zhang, E.-C. Yang and X.-J. Zhao, *Chem.-Eur. J.*, 2016, **22**, 18840; (h) L. Jiang, Y. Liu, X. Liu, J. Tian and S. Yan, *Dalton Trans.*, 2017, **46**, 12558.

8 (a) J. Rinck, G. Novitchi, W. van den Heuvel, L. Ungur, Y. Lan, W. Wernsdorfer, C. E. Anson, L. F. Chibotaru and A. K. Powell, *Angew. Chem., Int. Ed.,* 2010, **49**, 7583; (b) T. Birk, K. S. Pedersen, C. Aa. Thuesen, T. Weyhermüller, M. Schau-Magnussen, S. Piligkos, H. Weihe, S. Mossin, M. Evangelisti and J. Bendix, *Inorg. Chem*., 2012*,* **51**, 5435; (c) J. Rinck, Y. Lan, C. E. Anson and A. K. Powell, *Inorg. Chem.*, 2015, **54**, 3107; (d) A. McRobbie, A. R. Sarwar, S. Yeninas, H. Nowell, M. L. Baker, D. Allan, M. Luban, C. A. Muryn, R. G. Pritchard, R. Prozorov, G. A. Timco, F. Tuna, G. F. S. Whitehead and R. E. P. Winpenny, *Chem. Commun.*, 2011, **47**, 6251. (e) L. Qin, J. Singleton, W.-P. Chen, H. Nojiri, L. Engelhardt, R. E. P. Winpenny and Y.-Z. Zheng, *Angew. Chem., Int. Ed.,* 2017, **56**, 16571; (f) K. R. Vignesh, S. K. Langley, A. Swain, B. Moubaraki, M. Damjanović, W. Wernsdorfer, G. Rajaraman and K. S. Murray, *Angew. Chem., Int. Ed.,* 2017, DOI: 10.1002/anie.201711844.

9 (a) M. Ferbinteanu, T. Kajiwara, K-Y. Choi, H. Nojiri, A. Nakamoto, N. Kojima, F. Cimpoesu, Y. Fujimura, S. Takaishi and M. Yamashita, *J. Am. Chem. Soc.,* 2006, **128**, 9008; (b) M. Murugesu, A. Mishra, W. Wernsdorfer, K. Abboud and G. Christou, *Polyhedron,* 2006, **26**, 613; (c) F. Pointillart, K. Bernot, R. Sessoli and D. Gatteschi, *Chem.-Eur. J.,* 2007, **13***,* 1602; (d) J.-P. Costes, A. Dupuis and J.-P. Laurent, *Eur. J. Inorg. Chem*., 1998**,** 1543; (e) J.-P. Costes, F. Dahan, F. Dumestre, J. M. Clemente-Juan, J. Garcia-Tojal and J.-P. Tuchagues, *Dalton Trans*., 2003**,** 464; (f) C. I. Turta, D. N. Prodius, V. M. Mereacre, S. G. Shova, M. Gdaniec, Yu. A. Simonov, V. Kuncser, G. Filoti, A. Caneschi and L. Sorace, *Inorg. Chem. Comm.,* 2004**, 7**, 576; (g) A. Figuerola, J. Ribas, M. Llunell, D. Casanova, M. Maestro, S. Alvarez and C. Diaz, *Inorg. Chem.,* 2005, **44**, 6939; (h) A. M. Ako, V. Mereacre, R. Clérac, I. J. Hewitt, Y. Lan, C. E. Anson and A. K. Powell, *Dalton Trans.,* 2007, 5245; (i) S. Mukherjee, Y. Lan, G. Novitchi, G. E. Kostakis, C. E. Anson and A. K. Powell, *Polyhedron*, 2009, **28**, 1782; (j) J. Bartolomé, G. Filoti, V. Kuncser, G. Schinteie, V. Mereacre, C. E. Anson, A. K. Powell, D. Prodius and C. Turta, *Phys. Rev. B*, 2009, **80**, 014430; (k) M. N. Akhtar, V. Mereacre, G. Novitchi, J.-P. Tucheagues, C. E. Anson and A. K. Powell, *Chem.-Eur. J.,* 2009, **15**, 7278; (l) G. Abbas, Y. Lan, V. Mereacre, W. Wernsdorfer, R. Clérac, G. Buth, M. T. Sougrati, F. Grandjean, G. J. Long, C. E. Anson and A. K. Powell, *Inorg. Chem.,* 2009, **48**, 9345; (m) D. Schray, G. Abbas, Y. Lan, V. Mereacre, A. Sundt, J. Dreiser, O. Waldmann, G. E. Kostakis, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.,* 2010, **49**, 5185; (n) Y.-F. Zeng, G.-C. Xu, X. Hu, Z. Chen, X.-H. Bu, S. Gao and E. C. Sañudo, *Inorg. Chem.,* 2010, **49**, 9734; (o) A. Baniodeh, I. J. Hewitt, V. Mereacre, Y. Lan, G. Novitchi, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2011, **40**, 4080; (p) V. Mereacre, D. Prodius, Y. Lan, C. Turta, C. E. Anson and A. K. Powell, *Chem.-Eur. J.*, 2011, **17**, 123; (q) H. Xiang, V. Mereacre, Y. Lan, T.-B. Lu, C. E. Anson and A.K. Powell, *Chem. Commun*., 2013,**49**, 7385; (r) V. Mereacre, A. Baniodeh, C. E. Anson and A. K. Powell, *J. Am. Chem. Soc*., 2011*,* **133**, 15335; (s) I. Nemec, M. Machata, R. Herchel, R. Boča and Z. Trávníček, *Dalton Trans*., 2012, **41**, 14603; (t) V. Mereacre, *Angew. Chem., Int. Ed.,* 2012, **51**, 9922; (u) S. Schmidt, D. Prodius, G. Novitchi, V. Mereacre, G. E. Kostakis and A. K. Powell, *Chem. Commun.*, 2012, **48**, 9825; (v) S. Schmidt, D. Prodius, V. Mereacre, G. E. Kostakis and A. K. Powell, *Chem. Commun*., 2013, **49**, 1696.

10 (a) E. M. Rumberger, S. J. Shah, C. C. Beedle, L. N. Zakharov, A. L. Rheingold and D. N. Hendrickson, *Inorg. Chem.,* 2005, **44**, 2742; (b) M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud and G. Christou, *J. Am. Chem. Soc.,* 2004, **126**, 4766; (c) C. Boskovic, W. Wernsdorfer, K. Folting, J. C. Huffmann, D. N. Hendrickson and G. Christou, *Inorg. Chem*., 2002, **41**, 5107; (d) T. Glaser, I. Liratzis, T. Lügger and R. Fröhlich, *Eur. J. Inorg. Chem*., 2004, 2683; (e) C. I. Yang, G. H. Lee, C. S. Wur, J. G. Lin and H. L. Tsai, *Polyhedron*, 2005, **24**, 2215.

11 (a) R. W. Saalfrank, A. Scheurer, R. Prakash, F. W. Heinemann, T. Nakajima, F. Hampel, R. Leppin, B. Pilawa, H. Rupp and P. Müller, *Inorg. Chem.,* 2007, **46**, 1586; (b) M. Manoli, A. Prescimone, R. Bagai, A. Mishra, M. Murugesu, S. Parsons, W. Wernsdorfer, G. Christou and E. K. Brechin, *Inorg. Chem.,* 2007, **46**, 6968; (c) G. Rajaraman, M. Murugesu, E. C. Sañudo, M. Soler, W. Wernsdorfer, M. Helliwell, C. Muryn, J. Raftery, S. J. Teat, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.,* 2004, **126**, 15445; (d) D. Foguet-Albiol, K. Abboud and G. Christou, *Chem. Commun.,* 2005, 4282; (e) R. W. Saalfrank, C. Deutscher, S. Sperner, T. Nakajima, A. M. Ako, E. Uller, F. Hampel and F. W. Heinemann, *Inorg. Chem.,* 2004, **43**, 4372; (f) R. W. Saalfrank, H. Maid and A. Scheurer, *Angew. Chem., Int. Ed.,* 2008, **47**, 8794; (g) L. F. Jones, P. Jensen, B. Moubaraki, K. J. Berry, J. F. Boas, J. R. Pilbrow and K. S. Murray, *J. Mater. Chem.,* 2006, **16**, 2690.

12 W.-G. Wang, A. Zhou, W.-X. Zhang, M.-L. Tong, X.-M. Chen, M. Nakano, C. C. Beedle and D. N. Hendrickson, *J. Am. Chem. Soc.*, 2007, **129**, 1014 (and references therein).

13 R. W. Saalfrank, R. Prakash, H. Maid, F. Hampel, F. W. Heinemann, A. X. Trautwein and L. H. Böttger, *Chem.-Eur. J*., 2006, **12**, 2428.

14 G. Kostakis, I. J. Hewitt, A.M. Ako, V. Mereacre and A. K. Powell, *Phil. Trans*. 2010, **368**, 1509.

15 Y. Peng¸ V. Mereacre, C. E. Anson, and A.K. Powell**,** *Phys. Chem. Chem. Phys.,* 2016, **18**, 21469-21480

16 G. M. Sheldrick, SHELXTL 6.12, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719-1173, USA (2003).

17 A. L. Spek, *J .Appl. Cryst.,* 2003, **36**, 7.

18 A. M. Ako, O. Waldmann, V. Mereacre, F. Klöwer, I. J. Hewitt, C. E. Anson, H.U. Güdel and A.K. Powell, *Inorg. Chem*. 2007, **46**, 756.

19 (a) S. Chen, V. Mereacre, G. E. Kostakis, C. E. Anson and A. K. Powell, *Inorg. Chem. Front.*, 2017, **4**, 927; (b) S. Chen, V. Mereacre, C. E. Anson and A. K. Powell, *Dalton Trans*., 2016, **45**, 9336.

20 W. Wernsdorfer, *Supercond. Sci. Technol.*, 2009, **22** , 064013.

21 (a) B. S. Snyder, G. S. Patterson, A. J. Abrahamson and R. H. Holm, *J. Am. Chem. Soc.* 1989, **111**, 5214; (b) M. Mikuriya*,* Y. Kakuta*,* R. Nukada*,* T. Kotera and T. Tokii*, Bull. Chem. Soc. Jpn.* 2001*,* **74***,* 1425; (c) T. Weyhermüller, R. Wagner and P. Chaudhuri, *Eur. J. Inorg. Chem*., 2011, 2547.

22 H. Weihe and H. U. Güdel, *J. Am. Chem. Soc.* 1997, **119**, 6539.

23 G. Kresse and J. Furthmüller, *Comput. Mater. Sci*., 1996, **6**, 15.

24 G. Kresse and J. Furthmüller, *Phys. Rev. B, 1996,* **54**, 11169.

25 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett., 1996,* **77**, 3865.

26 S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys and A. P. Sutton, *Phys. Rev. B, 1998,* **57**, 1505.

27 P. E. Blöchl, *Phys. Rev. B, 1994,* **50**, 17953.

28 G. Kresse and D. Joubert, *Phys. Rev. B, 1999,* **59**, 1758.

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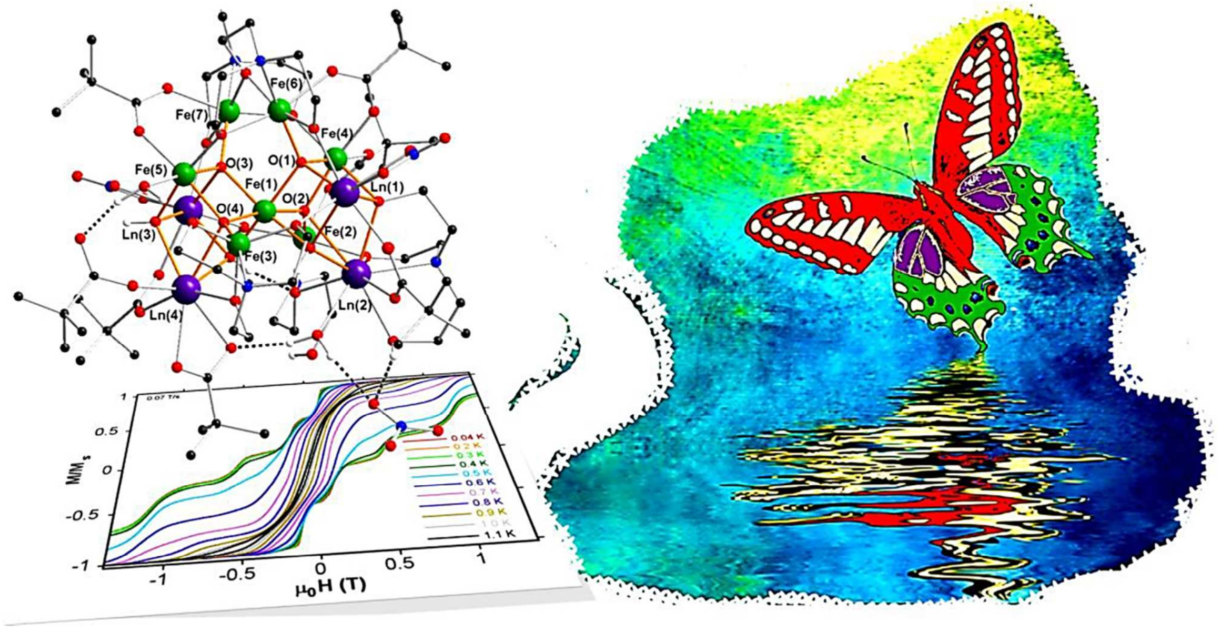
## Graphical Abstract to the article:

# Influence of Lanthanides on Spin-Relaxation and Spin-Structure in a Family of $Fe_7Ln_4$ Single Molecule Magnets

Denis Prodius, Valeriu Mereacre,* Prashant Singh, Yanhua Lan, Samir Mameri, Duane D. Johnson, Wolfgang Wernsdorfer, Christopher E. Anson and Annie K. Powell



A family of undecanuclear Fe-Ln clusters, comprise butterfly motifs, was explored and two are found to behave as single molecule magnets