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Observation of unusual slow-relaxation of the magnetisation in a Gd-EDTA chelate†

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A Gadolinium EDTA chelate displays characteristic isotropic behaviour common of Gd^{III} complexes under zero applied magnetic field, and anisotropic behaviour arising from dipolar coupling and weak spin–phonon coupling under an applied magnetic field. This surprising magnetic behaviour for Gd^{III} is investigated using SQUID magnetometry and rationalized through theoretical calculations.

Gadolinium has found niches within a variety of in-demand fields, such as: neutron therapy, radiography, solid oxide fuel cells, phosphors, *etc.*[1] Most commonly, Gd^{III}-based complexes are employed in MRI contrast due to their high-spin and isotropic (lack of spin–orbit coupling) nature,[2] while also being proposed for employment in magnetic refrigeration due to their high Curie temperature and giant magnetocaloric effect,[3] as well as in quantum computing at very low temperatures.[4] Interestingly, in the mentioned work regarding quantum computing Gd polyoxometallate clusters were found to exhibit slow relaxation of the magnetization at very low temperatures ($T \leq 200$ mK). Though this behavior was only observed at microSQUID-capable temperature ranges, this finding was unexpected, and of significant interest for chemists and medical researchers alike considering the known properties of Gd^{III}. Thus, it is essential to continue to perform in-depth studies of the magnetic behavior of Gd^{III} in various systems in order to fully understand its fundamental magnetic nature.

Aside from the properties inherent to the metal center employed, exploitation of specifically chosen ligands is significant in the development of Gd complexes towards their intended application. Commonly chelating ligands are highly desirable due to their significant thermodynamic stability and unique ability to capture a wide variety of metal ions readily, thus creating a stable molecular unit with a metal center at the core.

Ethylenediaminetetraacetic acid (EDTA) has been extensively employed as a metal trapping agent in industries such as: water treatment, chemical separation, cosmetics, textiles, pulp and paper, food, dentistry and medicine.[5] This multifunctional ligand has a chelating nature with an affinity for large oxophilic lanthanide ions, therefore allowing for further coordination sites to promote binding of water and thus solubility in biological media. Chelating ligands were popularized in MRI contrast agent synthesis as they possess the likelihood of stable metal trapping, and thus leeching of the metals into biological systems is effectively reduced.[6] EDTA has also specifically been utilized in capturing and recovering ions, such as Gd^{III}, which have leeched into the body as toxins.[7]

Herein we present a Gd^{III} ethylenediaminetetraacetate chain structure, $Na[Gd(EDTA)(H_2O)_3]_n \cdot 5H_2O$, hereafter termed **Gd-EDTA** (Fig. 1). In this report we investigate the solid-state structural features through single-crystal and powder XRD, along with detailed magnetic studies performed in order to

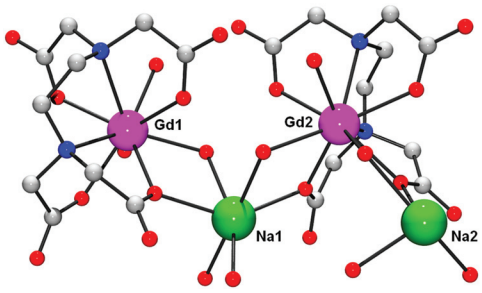

Fig. 1 Single crystal X-ray structure of $C_{10}H_{28}GdN_2NaO_{16}$ (**Gd-EDTA**), displaying the asymmetric unit present within the chain. Colour code: pink (Gd^{III}), green (Na), red (O), blue (N), grey (C). Hydrogen atoms and water molecules within the lattice omitted for clarity.

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investigate the occurring slow magnetization relaxation mechanism. Finally, in-depth *ab initio* calculations were performed to shed light on the origin of observed superparamagnet-like behaviour of slow relaxation of the magnetization. To our knowledge such behaviour has not been previously reported for Gd-based chelates.

It is noteworthy that this structure has previously been reported,[8a] along with several analogous compounds with lanthanide ions.[8] Interestingly many structures were reported as monomeric units coordinated to one EDTA ligand and three water molecules.[8] Upon closer inspection of the reported X-ray structure, we can conclude that EDTA-chelated lanthanide units are in close proximity to the counter cation (Na, K, *etc.*) and can be more accurately considered as monovalent cation-bridged chains (Scheme S1† and Fig. 2).[9]

Gd-EDTA was prepared through solvothermal synthetic methods (Scheme S1†), followed by a gradual solvent evaporation procedure found to be essential for the isolation of X-ray quality single crystals (Fig. S1 and S2†). **Gd-EDTA** crystallizes to form a one-dimensional chain structure in the monoclinic space group, *Cc*, with cell constants *a*, *b*, *c* of 12.0641(4) Å, 19.3270(6) Å, and 18.6758(6) Å, respectively. The α, β, γ parameters were found to be 90°, 108° and 90°, respectively. Further crystallographic information can be found in Table S1.†

Each Gd^{III} ion is nonacoordinate; binding to one EDTA ligand, two Na ion linkers through bridging water molecules, and one additional coordinated molecule of water. The EDTA ligand is bound in a hexadentate manner through 2 N atoms (N1, N2 or N3, N4) and 4 O atoms (O12, O14, O16, O18 or O1, O3, O5, O7) of the unidentate carboxylate groups, two of which are additionally coordinated to Na. The remaining coordination sites on Gd^{III} are occupied by 2 bridging water molecule O atoms (O10, O11 or O21, O22), which, along with the O atoms (O5, O7 or O16, O18) from EDTA, provide a bridge between Gd and Na linkers. The Na linkers are also coordinated to two additional water molecules. Thus there are, in fact, three H_2O molecules coordinated to Gd^{III} within the structure, however, only one water molecule is non-bridging. The intramolecular distance between Gd···Gd ions within the chain is 6.0782(5) Å, while the closest intermolecular interchain Gd···Gd distance is 9.4729(6) Å. Thus, we can conclude that any interaction between Gd ions primarily arises from within the chain architecture, and not between separate chains in the packing arrangement (*vide infra*).

Supplementary to single crystal X-ray diffraction (XRD) measurements, X-ray powder diffraction (XRPD) experiments were performed in order to elicit the bulk purity of the crystalline material. The pattern was found to be in excellent agreement with the theoretical pattern obtained from single crystal XRD (Fig. S3†). Spectroscopic analysis was also performed on **Gd-EDTA** in order to serve as a structural fingerprint (Fig. S4†).

Direct current (dc) susceptibility measurements were performed in order to investigate the static magnetic behaviour of **Gd-EDTA**. The temperature dependence of the dc magnetic susceptibility was measured between 1.8 and 300 K with an applied dc field of 1000 Oe (Fig. 3). The room temperature χT value, 7.37 cm^3 K mol^{-1} is consistent with the theoretical value of 7.88 cm^3 K mol^{-1} for an isolated Gd^{III} ion ($^8S_{7/2}$, $S = 7/2$, $L = 0$, $g = 2$). The room temperature value of the χT product remains constant upon decrease in temperature, as is expected for isotropic Gd^{III}, however, at very low temperature we observe a slight decrease in the value to 7.12 cm^3 K mol^{-1} at 1.8 K. As aforementioned, it is reasonable to assume any interactions between Gd^{III} ions will likely arise from intra-chain interactions due to close proximity (6.0782(5) Å). The nature of the interaction pathway is much harder to determine, however it is unlikely that the Gd–O–Na–O–Gd superexchange pathway could be efficient. Thus, dipole–dipole interactions between the metal ions likely prevail as a dominant pathway (6.0782(5) Å).

In order to further probe the static behaviour isotherm magnetisation data was collected between 1.8 and 7 K (Fig. 3 and S5†). The *M vs. H* data below 7 K demonstrates a rapid increase in magnetisation at low magnetic fields up to 1 T, followed by a gradual increase to plateau at 6.77μ_B at 1.8 K. The *M vs. H*/*T* data displays similar behaviour, inherent to Gd^{III}, where the curves experience magnetic saturation and are all

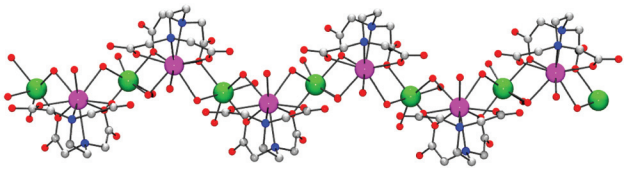

Fig. 2 Single crystal X-ray structure of **Gd-EDTA**, displaying the chain architecture. Colour code: pink (Gd^{III}), green (Na), red (O), blue (N), grey (C). Hydrogen atoms and water molecules within the lattice omitted for clarity.

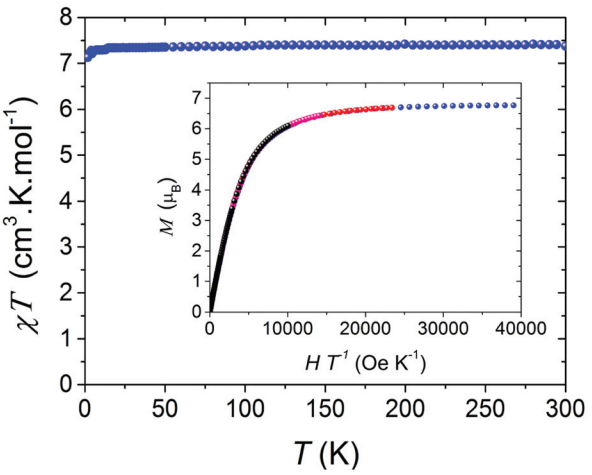

Fig. 3 Temperature dependence of the χT product at 1000 Oe for **Gd-EDTA**. Inset: *M vs.* HT^{-1} plot for **Gd-EDTA** at 1.8 K (blue), 3 K (red), 5 K (pink) and 7 K (black).

overlaid on a single master curve. This behaviour indicates that the anisotropy of Gd(III) ions is small (see below).

We subsequently probed the behaviour of this complex in aqueous solution (2 mmol), and found that the dc data, once again, exhibited behaviour characteristic of isotropic Gd^{III}, however, there was no low temperature drop in χT product (Fig. S6†). This indicates that there may no longer be close contact between Gd^{III} ions within the chain network, as the network is diluted. The reduced magnetisation data in solution (Fig. S7†) was very similar to that of the solid state, however, isotherm magnetic data in the *M vs. H*/*T* plot showed that a saturation point was not reached, and the curves did not overlay on a single master curve (Fig. S8†). This phenomenon is most often attributed to anisotropic behaviour, implying that the ionic anisotropy of Gd^{III} is in this case significantly stronger than in the crystalline sample.

Given the chain-like structure of this **Gd-EDTA** complex, we chose to explore the potential dynamic behaviour through ac magnetic susceptibility studies. Under zero applied dc field there was no temperature dependent signal observed, as expected for a Gd^{III} complex. However, when a dc field was applied a significant signal was observed, and thus the dynamic behaviour of **Gd-EDTA** was investigated between 18 and 1.8 K under an optimal applied dc field of 4500 Oe. Frequency dependent in-phase (χ') and out-of-phase (χ'') magnetic susceptibility plots can be seen in Fig. 4, S9–S10.† Two distinct relaxation processes can be observed, and were thus modelled accordingly. The effective energy barriers and relaxation times were obtained through fitting data using the Arrhenius equation ($\tau = \tau_0 \exp(U_{eff}/kT)$, which elicited a value of U_{eff} = 6.1 K ($\tau_0 = 4 \times 10^{-2}$ s) for the slow relaxation process (Fig. S11†), and U_{eff} = 84 K ($\tau_0 = 8 \times 10^{-7}$ s) for the fast relaxation process, as can be seen in Fig. S12.†

Temperature dependent in-phase (χ') and out-of-phase (χ'') magnetic susceptibility studies were subsequently performed in order to further confirm the results obtained through frequency dependent ac measurements. Peak shifting phenomena were observed with significantly broader peaks than those observed from frequency dependent data due to the occurrence of multiple relaxation processes. These plots can be seen in Fig. S13 and S14.† Furthermore, the ac behaviour was also investigated in aqueous solution, where a signal was no longer observed. This drastic change in magnetic behaviour is certainly derived from modified interaction between Gd ions and spin–phonon coupling.

In order to gain insight into the origin of the unusual dynamic magnetic behaviour of **Gd-EDTA**, *ab initio* calculations of CASSCF/RASSI/SINGLE_ANISO type were performed using the MOLCAS program package[10] on reasonable fragments involving individual Gd sites (see ESI for details, Fig. S15–S19, Tabel S2 and S3†). The calculations reveal a relatively weak zero-field splitting of the ground spin S = 7/2, of ~0.6 cm^{-1} for both types of metal sites (Fig. 5). These values are in agreement with the anisotropy parameters obtained from density functional theory (DFT) calculations employing the B3LYP functional in the ORCA program package.[11] Furthermore, the splitting of isotropic S = 7/2 under an applied field of 0.45 T, used in the present work, is 2.94 cm^{-1}, while the total splitting including the calculated ZFS on Gd^{III} does not exceed 3.5 cm^{-1}. This shows that the activation barriers extracted above cannot correspond to any excited states on gadolinium sites and are therefore fictitious ones.

Broken-symmetry DFT calculations performed on binuclear fragment models revealed negligible exchange interaction between Gd sites within the chain. Therefore, intra- and inter-chain magnetic interactions between Gd sites are mostly of dipolar origin. Calculations show that the dipolar coupling between two isotropic spins S = 7/2 of the nearest neighbour Gd^{III} ions induce a splitting of only ~0.38 cm^{-1}. Given the lowest measuring temperature of 1.8 K, this interaction cannot be responsible for the observed slowing down of magnetic relaxation.[12] Actually, the situation is quite the opposite: the dipolar interaction will contribute to speeding up the magnetic

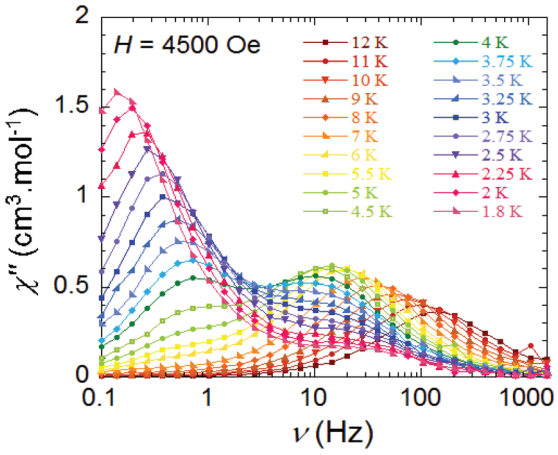

Fig. 4 Frequency dependence of the out-of-phase (χ'') susceptibility for **Gd-EDTA** between 1.8 and 12 K under a 4500 Oe applied dc field.

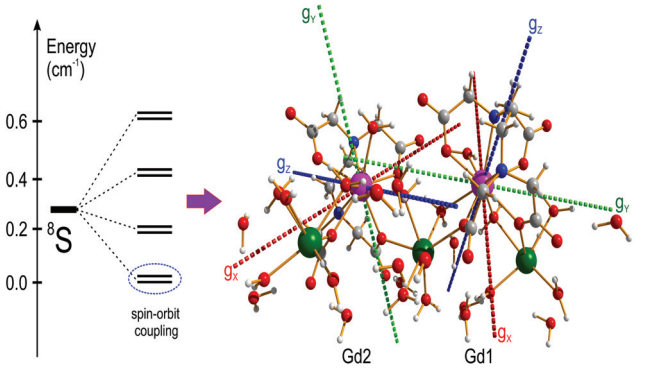

Fig. 5 Magnetic anisotropy of the ground Kramers doublets on Gd sites with respect to the molecular frame, arising due to spin–orbit coupling on metal sites (Table S3†). Note at temperatures higher than the splitting of the ground ^8S term, the Gd^{III} ion is magnetically isotropic.

relaxation on Gd sites. This is in agreement with the absence of magnetic relaxation in zero dc field, a behaviour generally expected for (almost) isotropic magnetic sites, in which fast quantum tunnelling of magnetization (QTM) is expected due to large transversal magnetic moments ($\sim\mu_B$). For an applied dc field of 0.45 T the QTM is almost completely suppressed, since the $\ln(\tau)$ *vs.* $1/T$ does not show any tendency towards saturation even at the lowest temperature (Fig. S11†). This means that the observed slow magnetic relaxation processes in **Gd-EDTA** are due to interlevel spin–phonon transitions of direct and Raman type on each Gd site. Given the splitting of several wave numbers under dc field, one might be surprised that the relaxation time at 1.8 K exceeds 1 s. One should have in mind, however, that the gadolinium possesses a much weaker spin–phonon coupling compared to other lanthanide (and actinide) ions, which should scale as $\sim 10^{-3}$ following the ratio of their crystal-field splittings.

This means that the spin–phonon relaxation rates in Gd complexes will be many orders of magnitude smaller than in strongly anisotropic compounds, explaining why the former can exhibit magnetization blocking at T up to 18 K (Fig. S10†) on the time scale of measured ac susceptibility, corresponding to direct spin–phonon transition between the levels, *i.e.*, in the total absence of a blocking barrier. Contrary to other lanthanides, the relaxation of magnetization does not reduce to a dynamic within the two lowest levels even at low temperatures, but instead involves transitions between many levels. This becomes evident within simulations of the temperature dependence of τ in the low-T domain, which is found to differ greatly from a conventional case (Fig. S20†).[13]

Conclusions

We have discovered unique magnetic properties of a **Gd-EDTA** chelate. The zero-field behaviour is typical of a theoretical Gd^{III} paramagnet, however, under an applied static magnetic field we observe peak shifting phenomena characteristic of anisotropic field-induced molecular magnets. This behaviour has been attributed to spin–phonon transitions between Gd levels which are not separated by any blocking barrier. This new mechanism of slow relaxation of magnetization becomes possible due to small spin–phonon rates on Gd^{III} ions. The observed slow magnetic relaxation is not a universal feature of Gd compounds since it is absent for the same complex in aqueous solution. Further insight in the mechanism of relaxation in such compounds will require additional measurements of relaxation time at different applied fields and for different degrees of diamagnetic dilution, while also going to much lower temperatures.[14] Overall the present findings should be a caution for chemists and medical researchers alike to extensively explore the magnetic properties of Gd contrast agents prior to their employment, as well as to magnetochemists not to overlook Gd due to its isotropic nature.

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12 Note that intermolecular magnetic interaction in crystals can contribute to blocking of magnetization only at temperatures significantly lower than the interaction between neighbour sites (corresponding exchange/dipolar splitting), and only for quasi one-dimensional structures, single-chain magnets.[13] If the interaction between the chains is not sufficiently weak, or in the case of magnetic structures of higher dimensionality, the magnetic ordering induced by intermolecular interaction will occur before this interaction can contribute to magnetization blocking on individual sites.

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