

Tm(III) complexes undergoing slow relaxation of magnetization: exchange coupling and aging effects

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The present study focuses on the dynamical magnetic behaviour of exchange coupled 3d-4f complexes containing the scarcely considered non Kramers Tm³⁺ center, the 3d metal ions being either the low-spin Fe³⁺ (**1**) or the diamagnetic Co³⁺ (**2**) ion. Both complexes display field-dependent slow relaxation of magnetization. The field and temperature dependences of the relaxation rate provided indication of relevant contributions from quantum tunnelling, direct and Raman processes, with only minor effects from exchange coupling interactions. Furthermore, aged sample of **2** exhibited additional relaxation process, possibly due to solvent loss, highlighting the importance of a careful consideration of this factor when analysing the magnetization dynamics in solvated systems.

Introduction

Magnetic relaxation phenomena in complexes qualifies that the system undergo a magnetic field perturbation followed by the establishment of a new equilibrium state.^{1,2} If this is achieved by overcoming a magnetic anisotropy barrier between the two states, extended relaxation time can be obtained by increasing the height of the barrier.³ In this respect, lanthanide based complexes,^{4,5} are the leading contending complexes in showcasing slow relaxation of magnetization, with anisotropy barriers as high as 1000 K recently reported.⁶ These high energy barriers are a consequence of the large single-ion magnetic anisotropy of these systems due to the strong spin-orbit coupling of 4f systems, and of the strong axial symmetry of the obtained complexes.^{7,8} These features have flared-up the synthesis, characterization and analysis of magnetic properties of single-ion magnets, SIMs⁹⁻¹⁴ to exploit their expediency in applied science¹⁵ such as molecular spintronics¹⁶⁻¹⁹ and ultrahigh density magnetic memory devices.²⁰ Lanthanide based molecular complexes have also been proposed as potential qubits for molecular quantum computing,^{21,22} thanks to their long decoherence time at low temperature,²⁵ as well as in the understanding of basic quantum phenomenon²³ like Quantum Tunneling of magnetization (QTM),²⁴ and as building blocks of molecular based refrigerants based on magnetocaloric effect.²⁶

For the complex to behave as a pure SIM or SMM, slow relaxation of magnetization in zero field as opposed to field induced

relaxation of magnetization is of paramount importance.^{13,27,28(a,b)}

The various mechanisms involved in the relaxation of magnetization or spin-lattice relaxation are the temperature dependent *Direct* process (with rate τ_{Dir}^{-1} ²⁹) and the two-phonon *Orbach* (with rate τ_{Orb}^{-1} ³⁰) and *Raman* processes (with rate τ_{Ram}^{-1}).^{31,32} Further, temperature independent process as *Quantum Tunneling of Magnetization* (QTM, with rate τ_{QTM}^{-1} ³³) may also contribute. The characterization of relaxation rates of magnetization of Lanthanide based systems usually involves one or a combination of two or more of the aforementioned processes with the most general behaviour portrayed in equation 1:

$$\tau^{-1} = \tau_{Orb}^{-1} + \tau_{Ram}^{-1} + \tau_{Dir}^{-1} + \tau_{QTM}^{-1} \quad 1$$

where τ_{Orb}^{-1} is $\tau_0 \exp(-\Delta/k_B T)$ Δ being the effective energy barrier,³⁰ $\tau_{Ram}^{-1} = CT^n$ ^{32(a)} with $n = 9 - 11$ for lanthanide based complexes and $\tau_{Dir}^{-1} = ATH^n$ with H being the external magnetic field and $n = 2$ or 4 depending on spin parity.³³ The QTM process can be modeled by different phenomenological expression, among which the Brons-van Vleck type: $\tau_{QTM}^{-1} = \frac{(1+b^2H^2)}{(1+c^2H^2)}$ ³¹

Following the complexity of the resultant relaxation rate behaviour, numerous reports are being devoted both to improving the slow dynamics feature of lanthanide complexes and to the appropriate identification of the processes responsible for slow relaxation of magnetization.³⁴⁻³⁹

An interesting approach to achieve slow dynamics and high energy barriers is the synthesis of 3d-4f compounds,^{10,40-42} where the 3d metal can be either paramagnetic or diamagnetic.^{43,44} In particular, when the 3d metal ion is paramagnetic, the exchange-coupling interaction is often able to reduce the quantum tunnelling of the magnetization, resulting in longer relaxation times.⁴⁵⁻⁴⁸ In this

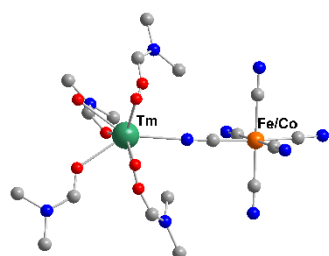
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respect we thought useful to evidence the effect of the exchange coupling by comparing the dynamic magnetic behaviour of isostructural systems where the 3d metal ion is either paramagnetic or diamagnetic. In particular, we focused on a family of complexes for which this strategy has already been successfully applied by two of us to the analysis of static magnetic behaviour.^{49,50} Since only scattered reports of magnetic properties of Tm based compounds are available^{51,52} and until very recently no evidence of slow relaxation of magnetization existed in literature for such complexes,⁵³ we decided to analyse the dynamic magnetic behaviour of Tm(dmf)₄(H₂O)₃(μ-CN)-X(CN)₅·1.25H₂O compounds. Here, X = Fe³⁺ (**1**), Co³⁺ (**2**) both 3d ions being in their low spin state due to the hexacyanide coordination.⁴⁹ The basic structural unit of this molecule is shown in Scheme 1: the coordination polyhedron around the Tm³⁺ ion showcases a bicapped trigonal prism geometry and the X³⁺ ion sits in a distorted octahedron.⁵⁰ The unit cell comprised of four discrete heterodinuclear molecules is shown in Fig. S1



Scheme 1 View of the molecular structure of **1** and **2**. Blue balls: nitrogen atoms; Red balls: oxygen atoms; Grey balls: carbon atoms.

Previous studies showed the existence of non-negligible exchange interactions between Fe³⁺ and Tm³⁺ in **1**, and provided some evidence of easy axis anisotropy for Tm³⁺ in **2**,⁵⁴ suggesting this might behave as a SIM.

Inspired by these preliminary results, herein we present extensive exploration of the magnetic dynamics in the aforementioned complexes over a wide range of frequency, dc magnetic field, temperature and aging time. The study revealed that both the complexes show slow relaxation of magnetization, but only in the presence of an external magnetic field. The field and temperature dependences of the relaxation rate provided indication of relevant contributions from quantum tunnelling, direct and Raman processes, with only minor effects from exchange coupling interactions. Furthermore, aged sample of **2** exhibited additional relaxation process, possibly due to solvent loss, a factor only seldom considered in the analysis of the magnetization dynamics of solvated systems.^{55,56}

Experimental section

Samples were synthesized as previously reported in literature.⁴⁹ The ac magnetic investigations were performed on polycrystalline

samples pressed in a 5 mm pellet, over a range of fields and temperature. The measurements were executed on Quantum Design PPMS in ac mode, with a superimposed 5 Oe oscillating magnetic field. The slower dynamics however was probed using a more sensitive Quantum Design MPMS SQUID magnetometer (0.1 to 1 kHz). The resulting information were presented in paramagnetic molar susceptibilities. The same SQUID was employed to explore the magnetic direct-current (dc) susceptibility measurements in a 1 kOe dc magnetic field and the isothermal magnetization at different temperatures (1.9, 2.5, 4.5 K). To authenticate that the measured magnetic properties were exactly from the molecules and to avoid the chances of possible complications as a result of the complex suffering with significant decomposition and/or distortion of the structure, the polycrystalline samples were evaluated for purity using the X-ray powder diffraction technique. For **2** the spectrum obtained from the Bruker D8 advance powder diffractometer equipped with a Cu source (K_{α} , $\lambda = 1.54 \text{ \AA}$) overlapped the theoretical spectrum obtained from the X-ray molecular structure, as shown in Fig. S2.

Results and discussion

Preliminary dc characterization was performed to ensure that the magnetic behaviour of the two complexes was consistent with that reported in literature. This was indeed the case, as reported in Fig. S3.^{43,51}

Ac magnetic dynamical analysis

Alternating current susceptibility measurements were carried out to explore the slow magnetic relaxation dynamics of **1** and **2**. No imaginary component of the susceptibility was observed for both samples between 10 Hz to 10 kHz even at the lowest investigated temperature (2 K), with no applied field. However, a field induced, frequency dependent maximum was observed in χ'' for both complexes at 2 K, indicating that the complexes demonstrate field-induced slow relaxation of magnetization (Figures 1 and 2). The low temperature (2 K) relaxation dynamics of **1** as a function of external magnetic field is shown in Fig. 1a-inset (additional data are reported in Figure S4). It is quite clear that a small field $H > 250 \text{ Oe}$ is required to trigger the slowdown of magnetization dynamics in **1**. The observed behaviour has been reproduced using the generalized Debye model³⁰ (solid lines in Fig. 1a-inset), which allowed to extract the corresponding relaxation time as a function of magnetic field (Fig. 1a, main panel). The relaxation time passes through a maximum around 1 kOe, and then rapidly decrease at higher field, suggesting a competition between Quantum tunneling and direct relaxation processes. Accordingly, these data were analytically reproduced using equation 1.⁵⁷ The best fit parameters, providing the solid line in Fig. 1a,main panel, are reported in Table 1. They clearly evidence the persistence of non-negligible QTM even at relatively high field, a somehow unexpected occurrence since in lanthanide based complexes, this is often expected to be quenched in presence of a dc magnetic field.^{43,58} Furthermore, the direct process shows a H^2 dependence as expected for a non Kramers ion.

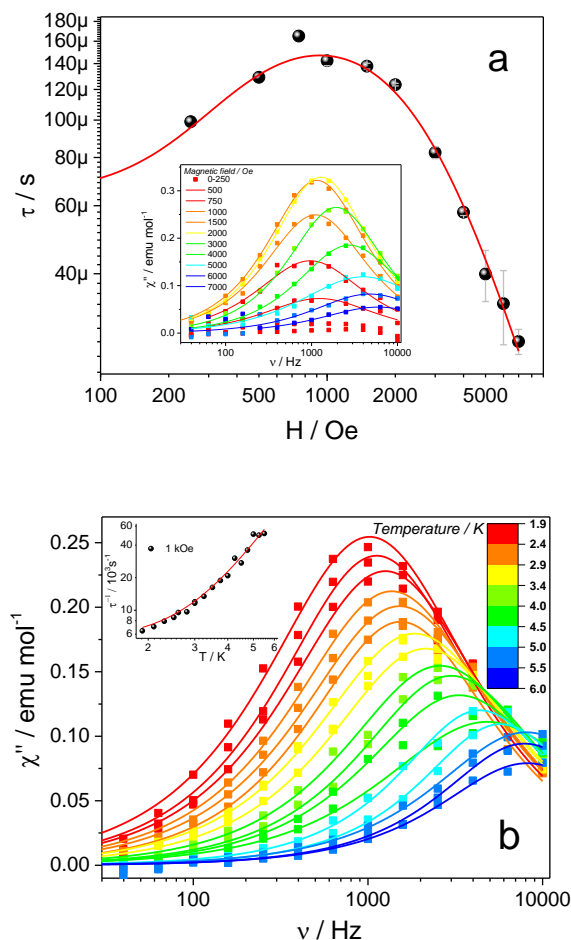


Fig. 1 (a) Plot of relaxation time of **1** at 2 K as a function of applied magnetic field, (inset) Field response of the out-of-phase χ'' susceptibility signal of **1** measured at 2 K, the lines are fits using the Debye expression. (b) Temperature behaviour of χ'' of **1** measured at 1 kOe (solid lines are the Debye fits), (inset) Extracted relaxation times as a function of temperature at 1 kOe.

As the maximum in relaxation time is observed between 1 kOe to 2 kOe for **1**, these two extreme fields were chosen to conduct the study of the dynamics as function of temperature. The maximum in the out-of-phase susceptibility is observable, within the range of available frequencies, up to 9 K (Fig. 1b-main panel and Fig. S5). At the lower temperature ends, there is still a quite evident temperature dependence at both fields, indicating that the QTM is not dominating the relaxation. The corresponding relaxation times extracted at the respective magnetic fields are shown in Fig. S6. When reported in an Arrhenius plot, a deviation of relaxation time from a linear curve is clearly observed (Fig. 1b-inset), indicating a pure Orbach type mechanism is not expected to hold.⁵⁹ This is indeed confirmed by fitting the curve using equation 1 (Fig. 1b and Fig. S6), keeping the parameters derived by the field dependent data set fixed: the obtained best fit parameters are reported in Table 1, suggesting that no Orbach process is actually active. The comparison of the temperature dependence of the relaxation rate evidences a strict similarity for the two fields, since both values are close to the maximum of the field dependent curve. The only difference is observed at $T < 3$ K, the 2kOe data evidencing a faster

relaxation, a signature of the relevance of the direct process, whose weight increase with field.

Table 1 Observed magnetic relaxation dynamics fits parameters observed as function of magnetic field and temperature in **1**.

	$A / \text{Ks}^{-1}\text{Oe}^{-2}$	a / s^{-1}	b / Oe^{-2}	c / Oe^{-2}	$C / \text{s}^{-1}\text{K}^n$	n
2 K - H scan	$(3.67 \pm 0.36) \times 10^4$	15580 ± 880	$(2.47 \pm 0.42) \times 10^4$	$(4.13 \pm 0.42) \times 10^4$	-	-
1 kOe - T scan	$(3.67 \pm 0.36) \times 10^4$	12715	$(2.47 \pm 0.42) \times 10^4$	$(4.13 \pm 0.42) \times 10^4$	139.7 ± 52	3.43 ± 0.23
2 kOe - T scan	$(3.67 \pm 0.36) \times 10^4$	13697	$(2.47 \pm 0.42) \times 10^4$	$(4.13 \pm 0.42) \times 10^4$	31 ± 2.1	4.18 ± 0.04

* For simplicity only change in a is shown where the b and c coefficients were kept constant.

A similar study was performed on **2**. Fig. 2a-main figure and Fig. S7 show the magnetization dynamics of **2** for magnetic field varying from 0 to 5 kOe, and the inset of Fig. 2a showcase the extracted relaxation times. The solid line in inset of Fig. 2a is the best fit achieved with the parameters revealed in Table 2. An interestingly highlight of the fitting parameters is the field dependence of the direct term, which was found to be H^4 , instead of the norm H^2 expected for non-Kramers' systems. Although this is an unorthodox development, however the focal point is the fact that in either cases Direct term is seen to have a major impact on the relaxation dynamics of both the derivatives. Moreover, we note that the accuracy of the fit is reduced for points below 800 Oe: one can attribute this deviation to the fact that the raw susceptibility data at those fields was unexpectedly noisy, thus hampering calculation of a more precise magnitude of the relaxation time. At any rate, the field dependence clearly evidences that, as observed for complex **1**, QTM and direct processes play a crucial role in the reversal of magnetization of **2**.

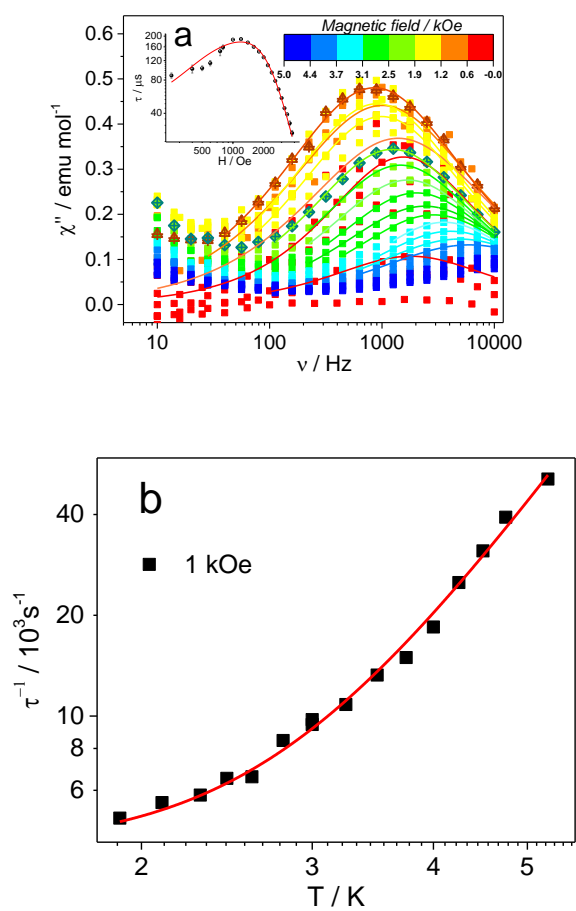


Fig. 2 (a) Magnetic field behaviour of the out-of-phase χ'' susceptibility signal of **2** measured at 2 K (The lines are fits using the Debye expression), 1 kOe and 2 kOe data are highlighted with different symbols, (inset) The extracted relaxation times plotted against the magnetic field. (b) Magnetic relaxation time at 1 kOe of (freshly pressed pellet), indicating a significant contribution of QTM and a small effective barrier.

Since a maximum in relaxation time is observed at 1 kOe this field was chosen for temperature dependent dynamic experiments. This choice was further induced by the analysis of the width of the distribution parameter on field variation, achieving a maximum at 1 kOe (Fig. S7-right) and a minimum at 2 kOe, thus making the latter another interesting field value to explore the dynamics.

The temperature dependent study at 1 and 2 kOe dc magnetic field depicts maxima in χ'' at about 1 kHz in **2**, moving out and fading away from the experimental range at higher temperature as reported in Fig. S8,9. The peaks observed in the imaginary component were reproduced with the Debye model to extract the corresponding relaxation time at 1 kOe is shown in Fig. 2b as function of temperature. The absence of a linear behaviour over the whole temperature range in the Arrhenius plot indicate the temperature-dependent relaxation is not governed by an Orbach process. Accordingly, quantitative analysis of the data required inclusion of contributions from multiple relaxation mechanisms like quantum tunnelling or/and Raman. Tentative breakdown reveals a significant contribution of quantum tunnelling, in accordance with dynamical outcome observed for **1**, and the resulting magnitude is

within error range of the contribution observed from the fit of field data as shown in Table 2. The relaxation times obtained from the 2 kOe susceptibility curves along with the 1 kOe relaxation times for comparison purposes is shown in Fig. S10.

Table 2 Observed magnetic relaxation dynamics fits parameters observed as function of magnetic field and temperature in freshly pressed pellet of **2**.

	$A / \text{Ks}^{-1}\text{Oe}^{-2}$	a / s^{-1}	b / Oe^{-2}	c / Oe^{-2}	$C / \text{s}^{-1}\text{K}^n$	n
2 K - H scan	$(8.6 \pm 0.35) \times 10^{11}$	21505 ± 11493	$(1.8 \pm 0.43) \times 10^3$	$(3.99 \pm 1.8) \times 10^3$	-	-
1 kOe - T scan	$(8.6 \pm 0.35) \times 10^{11}$	15970	$(1.8 \pm 0.43) \times 10^3$	$(3.99 \pm 1.8) \times 10^3$	69.9 ± 23	4 ± 0.2
2 kOe - T scan	$(8.6 \pm 0.35) \times 10^{11}$	33493	$(1.8 \pm 0.43) \times 10^3$	$(3.99 \pm 1.8) \times 10^3$	3.51 ± 1.34	5.4 ± 0.23
5 K - H scan	$(2.06 \pm 0.19) \times 10^{11}$	47163 ± 1959	$(3.9 \pm 0.96) \times 10^4$	$(6.47 \pm 1.1) \times 10^4$	-	-

It is worth noting that the exponent n of the Raman process observed for both complexes is quite smaller (3.5 - 5.5) than the expected value (9 - 12). However, a smaller n value is now almost routinely reported for molecular based complexes and attributed to both acoustic (lattice) and optical (molecular) vibrations taking part in the relaxation process.³² Finally the absence of Orbach like process leads to the conclusion of the relaxation observed in the Thulium based complexes not being related to the presence of an anisotropy barrier.^{28(a),60}

Magnetic dynamics comparison of Fe and Co derivative

Up to now, only a single example of Tm^{3+} based complexes behaving as SIM in zero field has been reported in literature, despite the fact that the prolate shape of the $m_j = \pm 6$ should be favoured by equatorial type ligands.⁵³ This is usually attributed to the non-Kramers nature of the ion coupled to the difficulty in obtaining a purely uniaxial symmetry, which lead to efficient mixing of m_j states and faster relaxation promoted by QTM.⁶¹ Even field induced slow magnetic relaxation has been scarcely reported in the past for Tm^{3+} complexes.^{51,52(a),62} In addition to increase this small number of slow relaxing Tm^{3+} complexes our study was aimed at investigating the effects on the dynamics properties when the transition metal coordinated ion is either paramagnetic and exchange-coupled ($\text{Tm}^{3+}\text{-Fe}^{3+}$), or diamagnetic ($\text{Tm}^{3+}\text{-Co}^{3+}$). The comparison between the observed spin dynamics of complexes **1** and **2** in fixed temperature, variable field and vice versa conditions, is shown in Fig 3 (a,b).

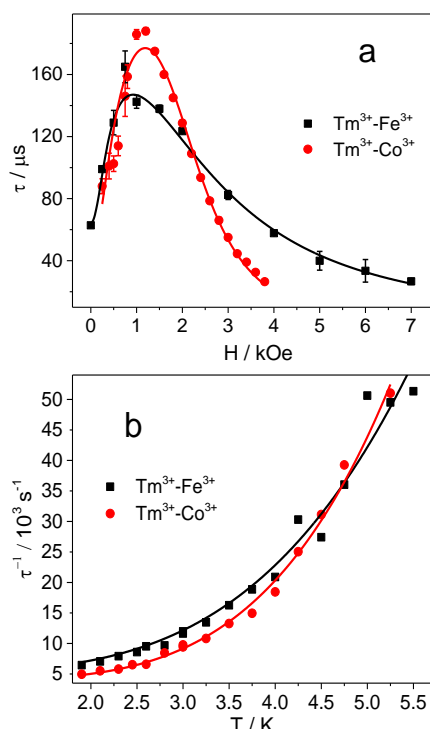


Fig. 3 (a) Field dependence of the magnetization relaxation time for **1** and **2** measured at 2 K (b) Temperature dependence of the relaxation rate for **1** and **2** measured in an applied static field of 1 kOe.

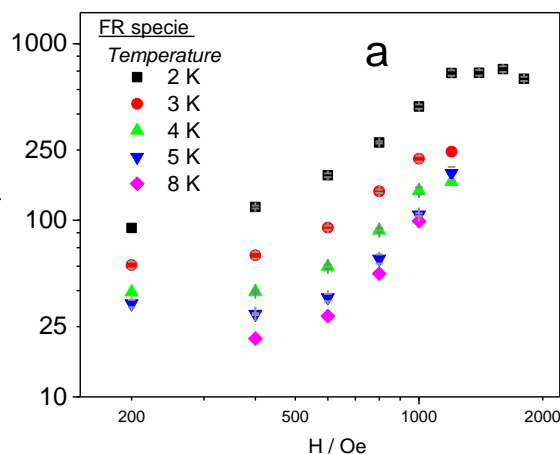
As discussed above spin dynamics in both the complexes followed a non-linear temperature dependent behaviour, which implied slow relaxation of magnetization is triggered by multiple mechanisms, but exclude two-phonon Orbach ones (Table 1, 2). While the effect of temperature on τ^{-1} is almost identical in both cases, a more pronounced difference in relaxation rate is evident in the field dependence at 2 K. Indeed, the longest relaxation time, observed for the two complexes in the 1-2 kOe range, is almost 30% slower for Co^{3+} derivative than for Fe^{3+} one. Despite not being a huge effect, we may relate this to the effect of the exchange-coupled center. This induces a bias field on the adjacent spin, resulting in a less effective QTM process. However, we suggest that on applying the field, the residual QTM is less effectively quenched than in the Co^{3+} derivative, resulting in a slower rate at the optimum field of the latter derivative. As a whole, however, Fig. 3 demonstrate quite similar responses to magnetic field and temperature for both complexes, confirming that the exchange interaction between the Tm^{3+} and the Fe^{3+} ion is weak, and it is not crucial in driving the relaxation.

Magnetic dynamics evolution with ageing of $[\text{Tm}^{3+}\text{-Co}^{3+}]$ pressed pellet

While studying the magnetization dynamics of complex **2** we noticed the progressive emergence of a new, additional maximum in the out-of-phase susceptibility signal on ageing of the sample. This was missing in the freshly pressed pellet, while a three-month old pellet showed a weak peak at low frequencies (Fig. S11). This prompted us to monitor the dynamics of **2** on an aged sample (six months), since we thought this aspect could be of interest for the

general community of molecular magnetism. The signature of a second well pronounced slow relaxation (hereafter SR) process was found to overlap with a process closely resembling the one of the freshly pressed sample (see above), which was faster (hereafter termed as fast relaxation process, FR). An extensive set of ac measurements as a function of temperature and field revealed that at low temperatures only FR process is visible, followed by coexistence of both the processes at 4 K, eventually leading to an almost complete suppression of the FR one and the dominance of the SR process, approximately above 10 K. (Fig. S12-16). The extrapolated field dependent relaxation times of both the processes at variable temperature are reported in Fig. 4a, b.

For the FR specie (Fig. 4a), at 2 K the relaxation rate is observed to increase at small fields, followed by a plateau above 1 kOe. The observed increase in relaxation rate is consistent with the results reported above for the freshly prepared sample. Higher temperatures led to gradual decrease in τ , until, above 1 kOe and 3 K, the relaxation rate is almost temperature independent. The SR process could be analysed at higher fields 1 - 10 kOe in the same temperature range (Fig. 4b). The corresponding peak in χ'' is only clearly observed from 4 K onwards. The field dependence at 8 K evidences a smooth increase in rate up to 4 kOe followed by a linear decrease at higher fields. This clearly indicates that also for SR species the direct and QTM processes are active and dominating in different field regions. Since the transition to the higher field domain is not initiated abruptly, it is justified to state that at intermediate fields (2.5 - 3.8 kOe) the two processes govern the relaxation equally. The fact that slow relaxation of magnetization is governed by multiple mechanisms is quite expected, not only in lanthanide based complexes but in other magnetic materials as well. ^{43,53,58,63}



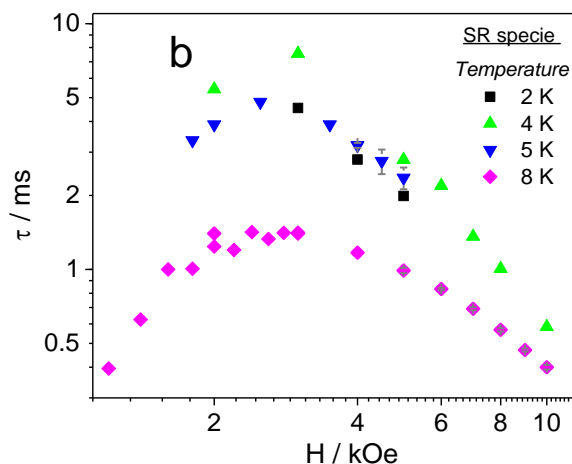


Fig. 4 Relaxation time as a function of static magnetic field for complex **2** (6-month old pellet) for fast (a) and slow (b) relaxing species. Data points are missing at certain fields and temperature due to the merging of the peaks pertaining to the two different processes.

The analysis of relaxation time under different conditions summarized in Fig. 4, also corroborated that SR process is essentially evident at high temperature and high field. This was exploited and confirmed by conducting temperature dependent ac susceptibility scan at 1, 2, 5 and 10 kOe on the aged sample (Fig. S17-20). It is quite clear that only FR process is active at 1 kOe, while SR process dominates at higher fields, with a coexistence region around 2 kOe, where peaks of the two processes overlap. The relaxation times obtained by Debye fitting of these data are shown in Fig S21 for FR process and in Fig. 5 for SR one. The latter data were fitted to equation 1, providing the best fit parameters reported in Table S1 (corresponding curves are shown as solid lines in Fig. 5). It is quite clear that Raman process is almost field independent as should be the case, with the n value in close proximity to that observed for the fresh pellet. The anomaly observed is that QTM, already evident by a qualitative analysis of the experimental data, tend to increase with increasing dc magnetic field, as highlighted in the Arrhenius plot (inset of Fig. 5). A possible explanation of such anomalous behaviour stems from the energy landscape boasting a ground singlet and an excited doublet. In the presence of magnetic field, and with an increase in magnitude, the doublet split and the energy difference decreases between the lower doublet and the ground singlet. This in effect lead to faster relaxation times via quantum tunnelling of magnetization. This is however a best case consequence as structural and energy pattern details of the aged samples are not available to further corroborate this point.

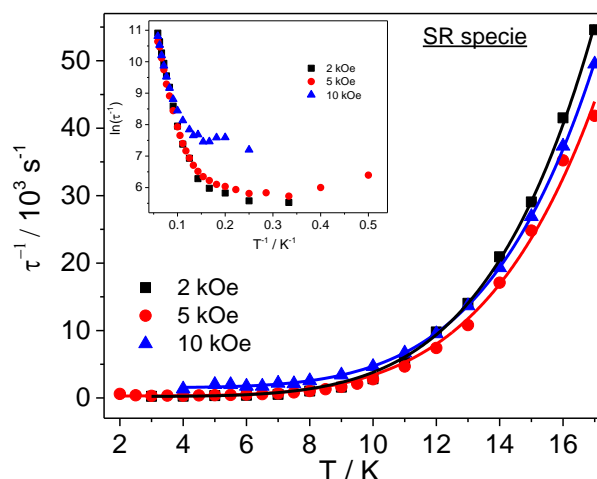


Fig. 5 Temperature dependence of the relaxation rate of complex **2** (6-month old pellet) for the SR species at different magnetic fields and best fit curves obtained using parameters reported in Table S1. The inset shows the corresponding Arrhenius plots.

Additional information acquired from the behaviour of aged sample under variable field and temperature conditions led to two important conclusions. First, the number of molecules undergoing each process is varying with field and temperature. The dominance of species relaxing through one process over the other is quite clear (Fig. S12-20), the FR being the dominant process at low field and low temperature (2 K, 1 kOe), while the SR dominates at higher fields and frequencies (5 K, 3 kOe and higher) with a smooth transition between the two regimes. Concurrent to this, one note the shift of the peak of the FR process in the aged sample to slightly lower frequencies compared to the fresh sample. This insinuates that even if this process can be in principle attributed to the same species responsible for that observed in the fresh sample, it is however slower for aged samples. (Fig. S22).

The set of results described in this section were challenged and put to test by a comparative study performed on a new freshly pressed pellet. The dynamics as function of temperature and magnetic field showed a complete overlap with the previous data, with no additional peaks in χ'' (Fig. S23). In conjunction, the time evolved emergence of the unique moieties in complex **1** was also investigated at several temperature and fields *via* ac susceptibility measurements after a period of six months. Interestingly, no indication of a second relaxation process was observed (Fig. S24).

Discussion on ageing

It is well known that both local molecular symmetry and intermolecular interactions play a crucial role in determining the low temperature magnetization dynamics in molecular complexes.⁶⁴ In the previous section it has been experimentally proven that two unique relaxation channels (FR, SR) coexist in the cobalt derivative as a result of the aging of the pellet under study. This might be attributed to the formation of two different species, in a way similar to that first suggested for Mn_{12} polynuclear SMMs.⁶⁵⁻⁶⁷ In that case the observed behaviour was attributed to the fact that a certain percentage of the molecules possessed different molecular structures from the majority ones, which lead

to different anisotropies. A similar behaviour has been later reported also in lanthanide based complexes.^{55,56,68,69} In the present case, the heterodinuclear structural unit of **2** form a 3D network with water molecules from crystallization:⁴⁹ it can then be suggested that when the sample was pressed in a pellet this resulted in a partial loss of solvent. This is of peculiar importance, since the water molecules in the lattice generate an extended network of hydrogen bonds, which might be able to transmit weak exchange coupling interactions. The induced structural modification was however not large enough to generate multiple species in the complex, i.e. majority of the molecules behaved as one unit, hence a single peak in χ'' was observed (Fig. 2). However, since the loss of solvent increased with lapse of time, an increasing percentage of molecules were forced to distinguish their behaviour and two unique species emerged.

On the other hand, the iron derivative turned out to be immune to aging effects and hosts only one species. This behaviour can be tentatively attributed to the existence of two types of interactions in the complex, the short range $\text{Tm}^{3+}\text{---Fe}^{3+}$ and the long range $\text{Tm}^{3+}\text{---Tm}^{3+}$ via hydrogen bond promoted by solvent. Upon ageing and pressing of sample, the solvent is expected to evaporate, thus affecting the long range interaction while the short-range $\text{Tm}^{3+}\text{---Fe}^{3+}$ interaction remains unaffected. Since the latter is however stronger than the former and can be considered more relevant in determining the dynamic behaviour, no major variation is observed on aging. On the contrary, for **2** there is no 3d-4f interaction, and the loss of solvent can lead to a decrease in $\text{Tm}^{3+}\text{---Tm}^{3+}$ distance which is capable of affecting the observed dynamic behaviour. We stress again here that in the absence of further indications and evidences, theoretical and experimental, this is a purely speculative explanation.

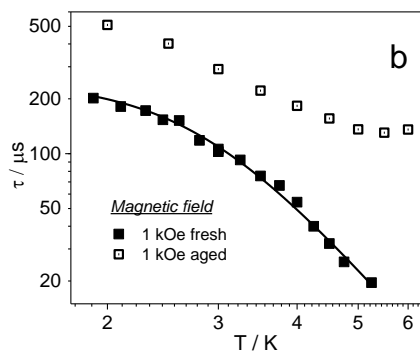
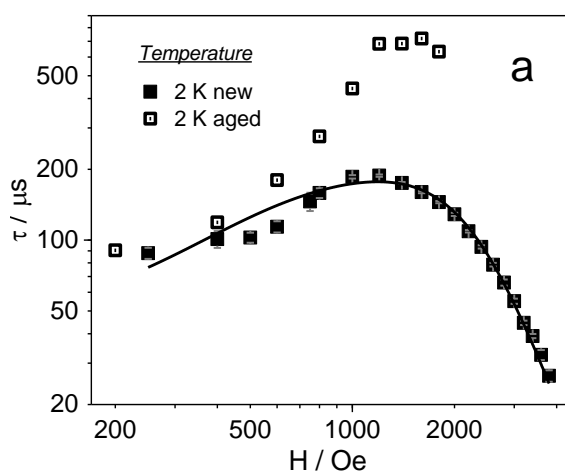


Fig. 6 Comparative behaviour of τ of FR specie as function of temperature (a) and field (b) for a fresh and aged pellet in complex **2**.

So far it is pointed out that ageing of the sample lead to emergence of a new specie; however, as anticipated in the earlier section, the spin dynamics of the FR specie also evolved with time (Fig. S22). This is illustrated in detail in Fig. 6 (a,b), where a comparison of the FR dynamics for the new and six month old sample is reported. Under identical magnetic field and temperature conditions, aged sample showed a slower relaxation of magnetization. Furthermore, the increase in relaxation is not smooth and does not follow a clear pattern. τ is observed to be almost field- independent for the two samples till 400 Oe, then deviating to follow a systematic increase to their respective maxima, as shown in Table S2. Extraction of data points for the aged sample to the full range of field was not achieved, as at high enough fields SR specie gained strength leading to a not so clear peak of FR specie in the susceptibility data. On the other hand, variable temperature data at fixed field of 1 kOe, show the two samples following a similar slope to feature decrease of relaxation time with temperature till 3 K. This is followed by deviation that tend to grow with temperature, till an almost saturation of τ for the aged sample is observed, while the fresh sample continue to follow a negative slope to increase in temperature (Table S2).

Unfortunately, a similar study could not be performed for SR specie, as it is proven in the earlier sections that SR specie is a time evolving feature and appear only in the aged sample. However, since SR specie was also found to be a high temperature and field feature, it was deemed thorough to probe the field dependence of the ac susceptibility at high temperature. The resulting in- and out-of-phase components as function of frequency performed at 5 K on the new sample, along with the behaviour of the alpha parameter are shown in Fig. S25. A clearly defined single peak is observed at exactly the frequency expected from the earlier data. The corresponding field dependence of τ at 2 K and 5 K is shown in Fig. S26. This reaffirms the fact that only FR specie exists in the new sample and SR specie is due to aging and is a high field, high temperature process.

Conclusions

In the present report we have demonstrated that two thulium based complexes, either single-ion or exchange-coupled, undergo field-induced relaxation of magnetization. For both derivatives the observed dependence of relaxation time τ on field and temperature

evidenced that multiple processes are at work, including small contributions from the Raman and direct processes and a crucial role of quantum tunnelling of magnetization. Furthermore, no evidence of relaxation via an Orbach process could be detected. This points out once more that the observation of field induced slow relaxation of the magnetization is not, by itself, an indication of Single Molecule Magnet behaviour.

The analysis of the dynamic magnetic behaviour further pointed out that the structural distortions induced as a result of solvent loss resulted in interesting dynamics in the Cobalt derivative, whereas the Iron derivative was found immune to such changes owing to the weak exchange interactions present in the complex. The likely formation of two different species resulted in two different relaxation processes observable as a function of field, temperature and age of the sample. In this respect, the present paper suggests that the spin dynamics of the lanthanide based complexes must be extensively scrutinized to isolate/identify the ageing effects in order to deepen the understanding of the origin of reversal of magnetization in a vast range of experimental conditions.

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