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COMMUNICATION

Origin of SMM behaviour in asymmetric Er(III) Schiff base complex: A combined experimental and theoretical study

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Accepted 00th January 2012Chinmoy Das,[†] Apoorva Upadhyay,[†] Shefali Vaidya, Saurabh Kumar Singh,
Gopalan Rajaraman* and Maheswaran Shanmugam*

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An asymmetric erbium(III) Schiff base complex of molecular formula [Ln(HL)₂(NO₃)₃] (where Ln = Er(1) Lu (2)) was revealed by single crystal X-ray diffraction showing mononuclear SMM behaviour with U_{eff} =5.2 K. Dilution experiments with **2 exhibit U_{eff} =51.4K. *Ab initio* calculations were performed to shed light on mechanism of magnetization relaxation.**

Unprecedented effective energy barrier (U_{eff}) reported for a terbium phthalocyanin mononuclear single-molecule-magnet (SMM) in 2003 compared to any transition metal clusters reported to date is a milestone in molecular magnetism research.¹ After this intriguing discovery, numerous monomeric and multinuclear lanthanide based single-molecule magnet (SMM) flooded in the literature.² In lanthanides, majority of the SMM (more than 90%), however, reported are based on Dy(III) ion.³ Moreover, several strategy has been proposed to increase the effective energy barrier of Dy(III) containing SMMs.⁴ Even after more than a decade of research efforts, only four SMMs are known (in the absence of external bias field) to date with Er(III) and all four are however, an organometallic mononuclear SMM employing strong π electron donor ligands such as cyclooctatetraene (COT), cyclopentadienyl anion and its derivatives.⁵ Among them the [Er(COT)₂] complex holds record blocking temperature of 12 K.^{5d} Due to scarcity of Er(III) based SMM in literature and to investigate the point charged ligand like Schiff base (2-Methoxy-6-[(*E*)-phenyliminomethyl]phenol (HL)) other than π -donor ligands and its influence on the magnetization relaxation dynamics, we turned our attention in this line of interest. In this communication, we report for the first time in literature a highly unsymmetric Er(III) Schiff base complex which shows SMM behaviour in the absence of external magnetic field and its detailed electronic structure and plausible mechanism of relaxation is investigated in details through computational studies.

While one equivalent of lanthanum nitrate hydrate (Ln = Er³⁺ or Lu³⁺) reacted with two equivalent of Schiff base ligand (HL) in ethanol and crystallization in methanol yields orange coloured single crystals. The single crystal X-ray diffraction reveals the structure as [Ln(HL)₂(NO₃)₃](where Ln = Er(1) (Fig 1), Lu(2) (see FigS1 of

ESI)). Both **1** and **2** are structurally analogous to each other hence described the structure of **1** in details. Both **1** and **2** crystallized in an orthorhombic, *Aba2* space group (Table S1 of ESI). The trivalent erbium ion cationic charge is neutralized by three chelating nitrate ions which accounts for six of the coordination number out of ten. The remaining four coordination sites are occupied by the neutral HL ligand. However, the proton bound to phenolic oxygen in free ligand is migrated to the imine nitrogen atom (-C=N) becomes zwitter ionic (ZI) in nature before coordinate to the Er^{III} ion. Existence of ZI nature of this Schiff base ligand has been proved already by us^{4b, 6} and reports are known for other Schiff base containing lanthanide complexes.⁷ Thus, Er(III) ion exist in ten coordinate distorted bicapped square anti-prism geometry determined by continuous shape measurement.⁸

The average bond distances of Er-O are found to be 2.4506 Å. Selected bond lengths and bond angles are given in Table S2 of ESI. Detailed structural analysis of **1** reveals that the unit cell contains two molecules with the same molecular formula as mentioned above, however, the orientation of ligands are distinctly different from one another (similar scenario was found in unit cell of complex **2**). Between these two molecules, every ligating atom in one molecule is crystallographically distinct (**1a**, Fig 1A) where the three nitrate ions are arranged in near trigonal planar arrangement. The two ZI Schiff base ligands arranged above and below the trigonal plane. Only half of the molecule is present in the unit cell for the second molecule (**1b**, Fig 1B), the other half of the molecule is derived by inversion symmetry. In this molecule, orientation of all the ligands (three nitrates and two ZI ligands) is distinctly different from **1a**. This is further confirmed by measuring the angle \angle NEr1N and \angle NEr2N (nitrogen of nitrates and Er) of 120° and 73.63° in **1a** and **1b** respectively. The larger angle \angle NEr1N in **1a** compared to **1b** witnessing that the orientation of nitrates in both molecules are different. Existence of such isomers within the same unit cell is very rare which has been reported by us only recently for the first time in a Dy(III) analogue of complex **1**.^{4b} The nitrates coordinated to **1a** and **1b** facilitate intermolecular hydrogen bonding and the atoms involved in such bonding are detailed in Table S3 of ESI.

Direct current (dc) magnetic susceptibility measurements were performed on polycrystalline sample of **1** in temperature range 2.0 -

300 K with an applied magnetic field of 0.1 Tesla (Fig 2). The room temperature (RT) $\chi_M T$ value of $11.48 \text{ cm}^3 \text{ K mol}^{-1}$ is observed for **1** which is an expected value ($11.47 \text{ cm}^3 \text{ K mol}^{-1}$) with $g = 6/5$; $^4I_{15/2}$. The $\chi_M T$ value decreases gradually from RT to 80 K which could be likely due to depopulation of m_j levels. Below this temperature, $\chi_M T$ value plummeted and reaches $2.98 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.0 K. Multiple factors could likely to contribute for the drastic decrease in $\chi_M T$ value at low temperature such as magnetization blockage, intermolecular antiferromagnetic interaction and dipolar interaction.

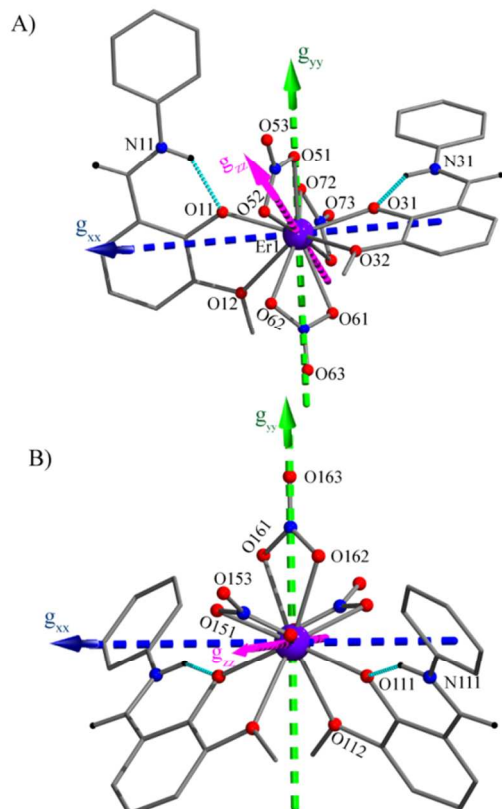


Fig 1. Ball and stick representation of crystal structure of **1**. A) Crystal structure of one of the molecule in the unit cell of **1**, where three nitrates ion arranged in near trigonal planar arrangement, (B) A geometric isomer (second molecule) with distinctly different orientation of nitrates and Schiff base ligands are shown. The sky blue dotted bonds represent the intramolecular hydrogen bonding. The dotted arrows on both molecules represent the g -anisotropy orientation. Colour code: purple = Er(III), blue = N, red = O, grey = C.

Isothermal field dependent magnetization measurements performed on polycrystalline sample of **1** show a sharp increase in magnetization at low field limit, with the linear response to the magnetic moment upon increasing the magnetic field without any saturation (Inset, Fig 2). The quite low magnetization value observed at high field limit (at 2.0 K) indicative of magnetic anisotropy associated with complex **1**, such scenario has been witnessed in many anisotropic metal complexes.^{2a, 9} The presence of magnetic anisotropy is further confirmed by the non-superimposable nature of reduced magnetization curves (Fig S2 of ESI).

In order to investigate the magnetization relaxation dynamics, we performed ac susceptibility measurement with the ac amplitude of 1.0 Oe on polycrystalline sample of **1** in the range of 0.5 K to 8.0 K with and without an applied external magnetic field (Fig 3A, Fig S3 of ESI). The ac data below 1.8 K were measured with the aid of IHelium3 setup. Complex **1**, clearly shows frequency dependent out-of-phase susceptibility (χ_M'') signal in the absence of external dc

magnetic field (Fig 3A), which is characteristic signature of a single-molecule magnet (SMM). Observation of zero field SMM property for an asymmetric complex like **1** is quite rare and it is the first example to the best of our knowledge to show zero field SMM behaviour with point charged ligands such as nitrates and HL ligand (see Table S4 in ESI).¹⁰

In order to confirm the molecular origin of magnetization relaxation, ac susceptibility measurements were performed on 5% (data not shown) and 50% diluted sample of **1** (Fig S4 of ESI). The diluted samples were synthesized as per the synthetic method given in ESI by taking respective equivalence of $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (where Ln = Er or Lu) according to the percentage dilution. From Fig 3A, it is apparent that there are more than one relaxation processes are operative. The relaxation observed above 2.0K is without a clear maxima, however, below 2.0 K the maxima in χ_M'' is markedly visible in complex **1**. Arrhenius plot was constructed from the ac measurement of 100% and 50% diluted sample of **1** and the estimated anisotropic energy barrier (U_{eff}) for the magnetization relaxation is found to be 5.2 K (Fig S5 of ESI) and 51.4 K (Inset of Fig 3A) respectively. The increased U_{eff} on 50% diluted sample of **1** unambiguously confirms that the relaxation dynamics is of molecular origin. Temperature dependant heat capacity measurement performed on **1** undoubtedly shows that there is no sign of magnetic phase transition at low temperature (Fig S6 of ESI). This further supports that the observed χ_M'' signals are purely molecular in origin. The present study illustrates the importance of performing experiments at ultra-low temperatures as this offers quantitatively the barrier height for magnetization reversal. The observed energy barrier for **1**, however, is significantly lower than the organometallic Er(III) mononuclear SMM reported in literature.^{5a, 5c, d} Below 0.8 K (100%) and 1.3 K (50%), Arrhenius plot deviates from linearity which could be likely due to the other faster relaxation process such as QTM and/or direct processes and/or dipolar interactions in **1**. Such faster relaxation processes have been witnessed in other mononuclear SMMs reported in the literature.^{2d, 3, 5a, 11}

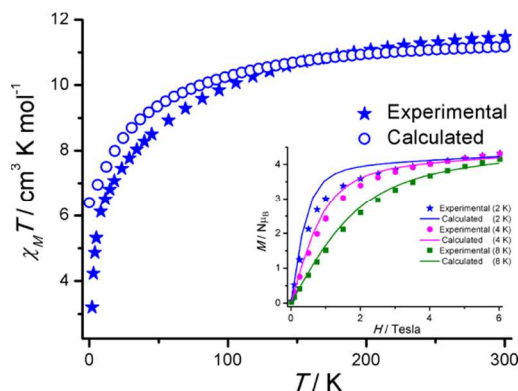


Fig 2. Dc magnetic susceptibility measurement performed on polycrystalline sample of **1** measured at 0.1 Tesla. The filled star represents the experimental data, the open circle represents the CASSCF+RASSI computed magnetic susceptibility from the crystal structure of **1**. Inset: Field dependant magnetization measurement performed on polycrystalline sample of **1** (symbols) at the indicated temperature. The solid lines represent the CASSCF+RASSI computed magnetization value of **1**.

In order to suppress/quench the faster QTM relaxation process in **1**, we performed ac measurement in the presence of an optimum dc bias field (0.5 Tesla) for **1**. Frequency dependent χ_M'' signals were witnessed in higher temperature (above 3.0 K) region however, the signals are very broad without any maxima (see Fig S3 of ESI) which hamper extraction of the magnetization reversal barrier. The Cole-Cole plot unambiguously confirms that more than one relaxation processes are operational even in the presence of external

magnetic field (Fig 3B). The major relaxation process was fitted to a generalised Debye model, with α parameters varies from 0.16 to 0.29 suggest that moderate distribution of relaxation times, which could be due to weak dipolar interactions (Table S5 in the ESI).

To analyse the g -tensors, relative energies of Kramers doublets (KDs), crystal field parameters and to construct the *ab initio* blockade barrier, CASSCF+RASSI calculations have been performed on complex **1** using MOLCAS 7.8 code.¹² Calculations were performed on both the geometrical isomers **1a** and **1b** with seven 4f orbitals and eleven 4f electrons in the active space (see ESI Table S6-S10 in computational details).

The computed energy window of the all the eight low-lying KDs for both the complexes **1a** and **1b** are spanned over 494 and 499 cm^{-1} respectively (see Table S6-S7). The g -tensors in the ground state KD in **1a** ($g_x=1.03$, $g_y=2.77$, $g_z=13.99$) and **1b** ($g_x=0.04$, $g_y=0.07$, $g_z=15.78$) are showing axiality but lacks the pure Ising type nature ($g_{xx}=g_{yy}=0$, $g_{zz}=20$) as both possess significant transverse component. The computed orientation of principal magnetization axes (g_{zz}) are found to be oriented towards one of the $-O$ atom ($O(52)$ -Er- g_{zz} is titled by 11.8 degrees, see Fig 1) of the attached $-NO_3$ ligand for both the complexes **1a** and **1b** (see Fig S7 and Table S8-S9).

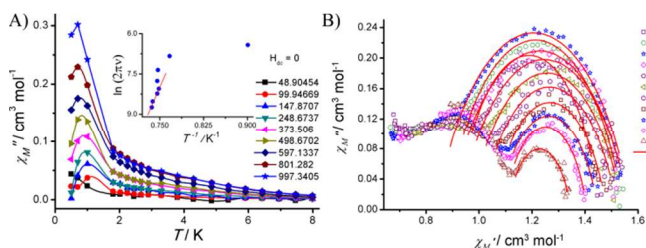


Fig 3. A) Alternating current magnetic susceptibility measurement performed on polycrystalline sample of **1**(100%) showing the frequency dependent out-of-phase susceptibility signals (χ_M'') in the absence of external magnetic field. Inset: Arrhenius plot constructed from ac relaxation dynamics of 50% diluted sample. B) Cole-Cole plot derived from ac measurement of complex **1** (100%) in the presence of an optimum magnetic field of 0.5 Tesla.

The wave function analysis shows a strong mixing of ground state with excited state m_J levels. Moreover, our calculations suggest that for both the molecules **1a** and **1b**, major contribution for the ground state comes from $|\pm 13/2\rangle$ with significant mixing from other higher excited states as expected for a low-symmetric complex (Fig 4). The principal magnetization axes of first excited states are tilted by 86.8 and 90° from their ground states for **1a** and **1b** respectively and this estimates the calculated barrier height to be 70.4 K and 150.9 K respectively (see Table S8-S9, Fig S7 and Fig.4). Although the computed spin Hamiltonian (SH) parameters reproduce the experimental magnetic data ($\chi_M T(T)$ and $M(H)$) some deviations at low temperatures (Fig 2 and its inset) is observed. This and the deviation observed between the computed magnetization barrier to the experimental effective energy barrier could be correlated to strong QTM predicted between the ground state KDs, hyperfine interactions and strong intermolecular interactions which are likely to be present in complex **1** (closest metal-metal distance is 9.264 (5) Å).¹³ Existence of multiple relaxation processes even in the presence of bias dc field (Fig. 3B) which strongly supports this observation. Dilution experiments ascertain this fact as the barrier height upon 50% dilution raises from 5 K to 50 K suggesting that dipolar contributions are significant and even 50% dilution can enhance the barrier height by an order of magnitude.

Despite significant transverse anisotropy found for complex **1**, it exhibits zero field SMM behaviour while structurally analogous Dy(III) complex reported by us earlier exhibits field induced SMM behaviour.^{4b} This suggest that the present ligand environment better suits for a prolate ion such as Er(III). Based on the electrostatic

model popularized by Long and co-workers recently, the largest m_J value will be stabilized in prolate Er(III) ion by engineering the ligand fields in equatorial position around this ion.¹⁴ This qualitative prediction is proven experimentally using COT and/or cp^* ligands or in a three coordinate Er(III) complex reported by Tang and co-workers recently.^{5d, 15} Undoubtedly in complex **1**, in addition to the equatorial position, point charged ligands are found in the axial position as well. Presence of four oxygen donor atoms (derived from two HL ligand) in axial position in **1a**, stabilizes $|\pm 13/2\rangle$ as the ground state. Besides the low symmetry environment around Er(III) ion in **1a** lead to significant transverse anisotropy (Table S10 of ESI). Even though molecule **1b** also stabilized with an $|\pm 13/2\rangle$ ground state, the computed anisotropic energy barrier is larger than **1a**, this is because in **1b** contains only two oxygen donors (two phenoxo atom of HL) in the axial position of the Er(III) ion. As the number of donor atoms decreases in axial position, the ground state-excited state gap increases. Further, between the two geometrical isomers **1b** is predicted to be more symmetric (lesser deviation (1.32) compared to ideal bicapped square anti-prism geometry as calculated by SHAPE program⁸) than **1a** (deviation 1.83). This leads to more reduction in the transverse component in **1b** and diminishes the ground state QTM effect.

To probe this effect of ligand field on **1** further calculation were performed on model complexes (see ESI Table S11-S13 and Fig S8-S9). Two models have been constructed on **1a** with the molecular formula of $[Er(HL)(NO_3)_3]$ (**1a-A**) and $[Er(NO_3)_3]$ (**1a-B**) by systematically removing the ZI Schiff base ligands which are occupying the axial positions. The model complex **1a-A** with only one axial ligand field, possess the barrier height of 111.4 K with less transverse anisotropy as compared to complex **1a**. The model **1a-B** with no axial ligands stabilizes the $m_J|\pm 15/2\rangle$ as a ground state with U_{eff} value of 189.1 K. The studies performed on model complexes evidently suggests that presence of these axial ligands in complex **1** not only reduces the barrier height but also introduces significant transverse anisotropy leading to increase in QTM between the ground state KDs. This is also reflected in the computed crystal field parameters as well as the transversal magnetic moments (Fig 4) which is consistent with a faster QTM between the ground state KDs for **1a** than **1b**.¹⁶

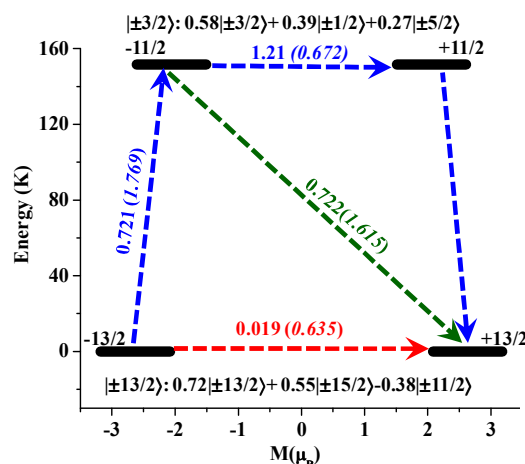


Fig 4. Low-lying two Kramers doublets for **1b** along with possible relaxation pathways and composition of wave function of these KDs. The numbers provided are the computed transversal magnetic moment. Dashed blue and red lines shows TA-QTM via first excited state and ground state QTM respectively. Dashed green lines show the Orbach process. Numbers in parentheses are for molecule **1a**.

Apart from this relaxation process, thermally activated QTM (TA-QTM) and Orbach process are also operational via the first excited state. Our calculations, for the first time not only explain the

observed differences between **1a** over **1b** but also suggest that increase in axial ligands enhance the QTM in low-symmetry complexes like **1**.

In conclusion, the reported complex **1** serves as a surrogate marker to understand factor influencing faster relaxation of magnetization and the role of ligand field in determining the electronic structure of Er(III) mononuclear SMM. Dilution experiment performed increased the barrier height by an order of magnitude. Ab initio calculations suggest that presence of axial ligands not only diminishes the U_{eff} value but also introduce the transverse anisotropy at the ground state. We believe such kind of study has been carried out for the first time in an asymmetric Er(III) complex and these considerations are important for the design of novel Er(III) based single molecule magnets.

Notes and references

Department of Chemistry, Indian Institute of Technology Bombay,

Powai, Mumbai, Maharashtra, India-400076. Email:

eswar@chem.iitb.ac.in (MS), rajaraman@chem.iitb.ac.in (GR); Phone:

+91-22-2576-7187; Fax: +91-22-2576-7192.

† Shares equal contribution.

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Electronic Supplementary Information (ESI) available: Detailed synthesis and crystallographic information files are given along with necessary supporting dc and ac magnetic measurements. Computational details, computed energies of Kramers doublets and crystal field parameters of **1** and its model complexes along with the orientation of g-anisotropy for the respective species are given. CCDC number: 1036694 and 1047967 See DOI: 10.1039/c000000x/

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