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An asymmetric erbium(III) Schiff base complex of molecular formula \([\text{Ln}](\text{HL})_2(\text{NO}_3)_3\) (where \(\text{Ln} = \text{Er}(1)\) 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 \(U_{eff}=51.4\) K. 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, 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.\(^5\) 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 \((\text{Ln} = \text{Er}^{3+}\) or \(\text{Lu}^{3+}\)) 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 \([\text{Ln}(\text{HL})_2(\text{NO}_3)_3]\)(where \(\text{Ln} = \text{Er}(1)\) (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 crystalized 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\(^{3+}\) ion. Existence of ZI nature of this Schiff base ligand has been proved already by us\(^6\) 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 involved in such bonding are detailed in Table S3 of ESI. Both \(1\) and \(2\) are structurally analogous to each other hence described the structure of \(1\) in details. Both \(1\) and \(2\) crystalized 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\(^{3+}\) ion. Existence of ZI nature of this Schiff base ligand has been proved already by us\(^6\) 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.\(^8\)
300 K with an applied magnetic field of 0.1 Tesla (Fig 2). The room temperature (RT) $\chi_M T$ value of 11.48 cm$^3$ K mol$^{-1}$ is observed for 1 which is an expected value (11.47 cm$^3$ K mol$^{-1}$) with g = 6/5; $^{4}\text{i}_{15/2}$. The $\chi_M T$ value decreases gradually from RT to 80 K which could be likely due to depopulation of $m_i$ levels. Below this temperature, $\chi_M T$ value plummeted and reaches 2.98 cm$^3$ 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.

In order to investigate the magnetization relaxation dynamics, we performed ac measurement in the presence of an optimum dc bias field (0.5 Tesla) for 1. The ac data below 1.8 K were measured with the aid of 1.0 Oe on polycrystalline sample of 1. Below 0.8 K, the $\chi''_M$ signals were purely molecular in origin. Temperature dependant heat capacity measurement performed on 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. The presence of magnetic anisotropy is further confirmed by the non-superimposable nature of reduced magnetization curves (Fig S2 of ESI).

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. 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 Helium3 setup. Complex 1, clearly shows frequency dependent out-of-phase susceptibility ($\chi''_M$) 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).

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 Ln(NO$_3$)$_3$·xH$_2$O (where Ln = Er or Lu) according to the percentage dilution. From Fig3A, 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 $\chi''_M$ 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 ($U_{\text{eff}}$) 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 $U_{\text{eff}}$ 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 $\chi''_M$ 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.

Below 0.8 K $\chi''_M$ 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). 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 $\chi''_M$ 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 (KD), 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. 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 (gₓ=1.03, gᵧ=2.77, gₚ=13.99) and 1b (gₓ=0.04, gᵧ=0.07, gₚ=15.78) are showing axiality but lacks the pure Ising type nature (gₓ=gᵧ,gₚ=0, gₓ=gᵧ=20) as both possess significant transverse component. The computed orientation of principal magnetization axes (gₓ,y,z) are found to be tilted towards one of the –O atom (O(52)-Er-gₓ,ᵧ,.z is tilted by 11.8 degrees, see Fig 1) of the attached –NOₓ ligand for both the complexes 1a and 1b (see Fig S7 and Table S8-S9).

The wave function analysis shows a strong mixing of ground state with excited state mₗ levels. Moreover, our calculations suggest that for both the molecules 1a and 1b, major contribution for the ground state comes from |±13/2⟩ 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 degrees from the principal axes of the first excited states for complex 1a, and by 11.8 degrees from the principal axes of the first excited states for complex 1b. 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.⁵⁴, ⁵⁵

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 |±13/2⟩ 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 |±13/2⟩ 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 (less deviation (1.32) compared to ideal bicapped square anti-prism geometry as calculated by SHAPE program) 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 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)(NOₓ)] (1a-A) and [Er(NOₓ)] (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 m₁=±15/2 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

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 I 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

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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

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