

Pentagonal Bipyramidal Ln(III) Complexes Containing an Axial Phosphine Oxide Ligand: Field-induced Single-ion Magnetism Behavior of the Dy(III) Analogues

Pankaj Kalita, Naushad Ahmed,[#] Arun Kumar Bar, Sourav Dey,[#] Anukul Jana, Gopalan Rajaraman,^{*} Jean-Pascal Sutter,^{*} and Vadapalli Chandrasekhar^{*}

Cite This: *Inorg. Chem.* 2020, 59, 6603–6612

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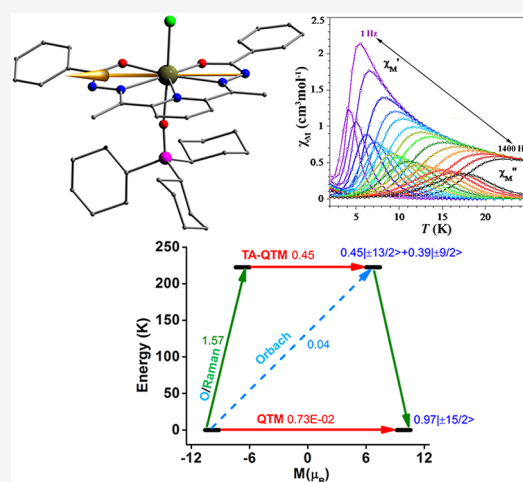
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ABSTRACT: A series of neutral homologous complexes $[(L)Ln(Cy_3PO)Cl]$ {where Ln = Gd (1), Tb (2), Dy (3), and Er (5)} and $[(L)Dy(Ph_3PO)Cl]$ (4) [$H_2L = 2,6$ -diacetylpyridine *bis*-benzoylhydrazone] were isolated. In these complexes, the central lanthanide ion possesses a pentagonal bipyramidal geometry with an overall pseudo D_{5h} symmetry. The coordination environment around the lanthanide ion comprises of three nitrogen and two oxygen donors in an equatorial plane. The axial positions are taken up by a phosphine oxide (O donor) and a chloride ion. Among these compounds, the Dy(III) (3 and 4) analogues were found to be field-induced single-ion magnets.



INTRODUCTION

There has been a significant renaissance in the chemistry of the rare-earth elements because of their photophysical properties² and their applications in catalysis¹ and in magnetic materials.³ In recent years lanthanide⁴ and some actinide complexes⁵ are finding increasing utility as molecular magnets (single-molecule and single-ion magnets (SMMs and SIMs, respectively)). These molecular systems, once magnetized, retain their magnetization for a macroscopic period of time even after the removal of the external magnetic field and are characterized by a slow relaxation of magnetization below certain temperatures (the blocking temperature T_B).⁶ This is because SMMs/SIMs are characterized by a double-well potential comprising of m_S or m_J manifolds and for such systems, perturbation of population equilibrium brought by an applied magnetic field renders net magnetization that remains magnetized until unless the activation energy (U_{eff}) is provided.⁷ Various relaxation mechanisms including quantum tunnelling are prevalent to allow the magnetization to be lost.⁸

The evidence of SMM behavior in a molecular Tb(III) complex, where the Tb(III) is sandwiched by two phthalocyanine ligands, was first reported by Ishikawa and co-workers.⁹ One of the intrinsic features of the lanthanide elements is that the 4f electrons are deeply buried inside the

[Xe] core and are considerably shielded by the 5s and 5p electrons. This results in an almost unquenched orbital angular momentum (L), which couples with the spin angular momentum (S) giving rise to the total angular momentum J .^{4d,10} Unlike transition-metal ions, the magnitude of spin-orbit coupling in the case of 4f metal ions is comparatively much larger than the crystal field, which splits the ground $2S+1L_J$ term into different J multiplets. Although the crystal field effects are small, it has a significant impact on removing the degeneracy of the $(2J + 1)$ m_J microstates corresponding to each of the J multiplets. The dynamics of magnetization relies on the relative energies of the ground J manifold; therefore, a suitable crystal field renders the requirement of large splitting between the energy levels giving rise to high energy barrier for magnetization reversal (Table 1).¹¹

Soon after this discovery, many mononuclear Ln(III) complexes were reported to be SMMs with high energy

Received: March 12, 2020

Published: April 20, 2020

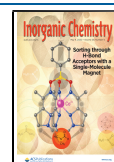


Table 1. Selected Bond and Magnetic Parameters of PBP Dy(III) Complexes

Sl No.	complex ^a	$L_{ax}-Ln-$ $L_{ax(deg)}$	average axial Ln–O/Ln– X distance (Å)	average equatorial Ln–O/Ln– N/Ln–X distance (Å)	U_{eff} (K) (H_{dc})	τ_0 (s)	ref
1	[Dy(O ^t Bu) ₂ (py) ₃][BPh ₄]	155.80	2.112	2.557	1815 (0 Oe)	1.17×10^{-12}	16e
2	[Dy(bbpen)Br]	155.79	2.163	2.586/2.851	1025 (0 Oe)	4.21×10^{-12}	16c
3	[Dy(^t BuO)Cl(THF) ₅][BPh ₄] 2THF	178.28	2.043/2.662	2.410	950 (0 Oe)	3×10^{-12}	26
4	[Dy(bbpen)Cl]	154.24	2.166	2.584/2.682	708 (0 Oe)	9.46×10^{-11}	16c
5	[L ¹ ₂ Dy(H ₂ O) ₅][I ₃ ·(L ¹) ₂ ·H ₂ O]	177.9	2.205	2.363	651 (0 Oe)	5.63×10^{-12}	16b
6	[Dy(L ²) ₂ (H ₂ O) ₅] ₂ ·Br ₆ ·2L ² ·2H ₂ O	177.82	2.221	2.354	556 (0 Oe)	9.33×10^{-12}	27
7	[Dy(Cy ₃ PO) ₂ (H ₂ O) ₅] ₂ ·Br ₃ · 2(Cy ₃ PO)·2H ₂ O·2EtOH	179.04	2.200	2.352	543 (0 Oe)	2.0×10^{-11}	28
8	[Dy(CyPh ₂ PO) ₂ (H ₂ O) ₅] ₂ ·Br ₃ · 2(CyPh ₂ PO)·EtOH·3H ₂ O	174.2	2.217	2.364	508 (0 Oe)	8.6×10^{-12}	29
9	[Dy(Cy ₃ PO) ₂ (H ₂ O) ₅] ₂ ·Cl ₃ · (Cy ₃ PO)·H ₂ O·EtOH	175.79	2.219	2.359	472 (0 Oe)	8.7×10^{-12}	28
10	[(NCN)DyCl ₂ (THF) ₂]	176.50	2.596	2.448/2.668 2.393 (Dy–C)	335 (0 Oe)	6×10^{-10}	30
11	[DyCl ₂ (THF) ₅][BPh ₄]	179.68	2.577	2.390	80.6 (0 Oe)	4.1×10^{-10}	31
12	[Dy(Bpen)Cl(OPhCl ₂ NO ₂) ₂]	165.60	2.174	2.523/2.616	86 (1 kOe)	4.65×10^{-7}	32
13	[(H ₂ L ³)Y _{0.94} Dy _{0.06} Cl ₂]	166.32	2.644	2.264/2.444	70 (0.5 kOe)	1.9×10^{-6}	17
14	[(L ⁴)Dy(Cy ₃ PO)Cl]	169.62	2.237/2.625	2.265/2.458	204 (1 kOe)	6.0×10^{-9}	this work
15	[(L ⁴)Dy(Ph ₃ PO)Cl]	174.07	2.276/2.623	2.283/2.460	241 (1.5 kOe)	2.3×10^{-10}	this work

^aL¹ = (^tBuPO(NHⁱPr)₂; L²: hexamethylphosphoric triamide; H₂ bbpen = N,N'-bis(2-hydroxybenzyl)-N,N'-bis(2-methylpyridyl)ethylenediamine); NCN: [2,6-(2,6-C₆H₃R₂N₅CH)₂C₆H₃][−]; Bpen: N,N'-bis(2-methylenepyridinyl)ethylenediamine; H₄L³: 2,6-diacetylpyridine bis-salicylhydrazone; H₂L⁴: 2,6-diacetylpyridine bis-benzoylhydrazone

barriers (U_{eff}) and high blocking temperatures (T_B).¹² Among various types of lanthanide complexes, the mononuclear complexes are of considerable interest, as they provide a very good understanding of the influence of the ligand field on the observed magnetic properties. The recent reports on mononuclear Dy(III) complexes [Dy(Cp^{ttt})₂]⁺ (Cp^{ttt} = C₅H₂^tBu_{3-1,2,4}) and [Dy(Cp^{iPr5})(Cp*)]⁺ (Cp^{iPr5} = penta-isopropylcyclopentadienyl, Cp* = pentamethylcyclopentadienyl) revealing very high magnetization blocking temperatures of 60 and 80 K, respectively, has further spurred activity in this area of mononuclear Ln(III) complexes.¹³

Although ligand fields are much smaller compared to spin-orbit coupling among lanthanide complexes, ironically, the former happens to be the most decisive in controlling the performance of SMMs/SIMs. The spatial distribution of the electrons in the different 4f orbitals leads to inherent anisotropic shapes of the electrostatic potential surfaces associated with the m_j states in the Ln(III) ions (except Gd, Eu, La, and Lu).¹⁴ On the basis of an electrostatic argument, Rinehart and Long have proposed a qualitative model that assists in the designing of SMMs/SIMs.¹⁴ According to this model, an axial ligand field stabilizes the oblate-shaped Ln(III) ions, while a prolate-shaped Ln(III) ion requires an equatorial ligand field, because such a ligand field minimizes the electrostatic repulsion between the ligands and the metal center and maximizes the molecular magnetic anisotropy. With this clue a large number of monometallic Ln(III) complexes were prepared with interesting magnetic properties.¹⁵ Among them, the pseudo-linear pentagonal bipyramidal complexes in

the DyO₇, DyClO₆, DyXN₄O₂ (X = Cl and Br), and DyN₅O₂ coordination environment with strong axial ligand field and weak equatorial ligand field stand out as the most effective systems for the observation of high energy barriers of magnetization reversal.¹⁶

We have been utilizing various types of multidentate ligands for the synthesis of mononuclear Ln(III) complexes. In our previous work, we synthesized mononuclear pentagonal bipyramidal Ln(III) complexes by employing a pentadentate chelating ligand that provides a rigid equatorial plane.¹⁷ The axial sites in these complexes were occupied by the chloride ions, which are considerably weak-field ligands compared to N and O donors present in the ligand backbone. We thoroughly studied the magnetic properties of the Dy(III), Tb(III), and the diluted Dy(III) (in an isostructural Y(III) host) complexes, which reveal the molecular origin of slow magnetic relaxation in the Dy(III) derivative with an energy barrier of magnetization reversal of 70 K.¹⁷ To understand the role of the axial ligands in this system we have now prepared a series of neutral mononuclear pentagonal bipyramidal (PBP) complexes, [(L)-Ln^{III}(R₃PO)Cl] [(Ln = Gd (1), Tb (2), Dy (3), Er (5); R = cyclohexyl) and (Ln = Dy (4); R = phenyl)], where one phosphine oxide ligand replaces one of the two chloride ligands in the axial sites. Herein, we report the synthesis, structural characterization, and magnetic properties of 1–5. The difference in the magnetic properties was analyzed by ab initio CASSCF/RASSI-SO/SINGLE_ANISO calculation, which provides the insight to design the potential SIM.

EXPERIMENTAL SECTION

Materials and Methods. All the reagents and solvents used for the syntheses were used as received from commercial sources. The organic ligand 2,6-diacetylpyridine bis-benzoylhydrazine (H_2L) was synthesized following a reported procedure.¹⁸ Fourier transform infrared (FT-IR) spectroscopy was performed with a Bruker FT-IR spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400 series II instrument. A powder X-ray diffraction study was performed on finely ground polycrystalline material with Bruker D8 Advance powder X-ray diffractometer.

Magnetic Measurements. Magnetic measurements for all the samples were performed with a Quantum Design MPMS SS SQUID magnetometer in the temperature range of 2–300 K. The measurements were performed on polycrystalline samples. The crystalline powders of the complexes were mixed with grease (except for Gd derivative) and put in gelatin capsules. The temperature dependences of the magnetization were measured in an applied field of 1 kOe, and the isothermal field dependence of the magnetizations was collected up to 5 T. The molar susceptibility (χ_M) was corrected for sample holder and for the diamagnetic contribution of all the atoms by using Pascal's tables. AC susceptibility data were collected in zero field and with applied fields in the frequency range of 1–1500 Hz.

X-ray Crystallographic Studies. The single-crystal X-ray diffraction data of 1–5 were collected on a Rigaku Xtal LAB X-ray diffractometer system equipped with a charge-coupled device (CCD) area detector and operated at 30 W power (50 kV, 0.6 mA) to generate Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 120(2) K. Data were integrated using CrysAlis^{Pro} software with a narrow frame algorithm. Data were subsequently corrected for absorption by the program SCALE3 ABSPACK scaling algorithm.^{13a} All the structures were solved by the direct methods in SHELXTL¹⁹ and refined by the full-matrix least-squares method on F^2 (SHELXL-2014)²⁰ using the Olex-2 software.²¹ All the non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were included in idealized positions, and a riding model was used. All the mean plane analyses and crystallographic figures were generated using the DIAMOND software (version 3.2k).²² The crystal data and refinement parameters for 1–5 are summarized in Table S1 (see Supporting Information). More details on the crystallographic data are given in the X-ray crystallographic files in the CIF format.

Synthesis. General Procedure. The following general protocol was employed for the synthesis of complexes 1–5.

The organic ligand, H_2L (1 equiv) was suspended in 30 mL of EtOH, and cyclohexyl/phenyl phosphine oxide (1 equiv) was added to it. To this white cloudy solution, the respective $LnCl_3 \cdot 6H_2O$ (1 equiv) salts were added, which results in a yellow solution. The reaction mixture was then heated under reflux conditions for 1 h and allowed to cool to room temperature. To this solution 2 equiv of NEt_3 was added, and the solution was further stirred at room temperature for 10 min. The solvent was evaporated to dryness, and the resulting yellow precipitate was washed with diethyl ether. The dried yellow precipitate was then dissolved in 10 mL of EtOH and filtered. The filtrate was kept under vapor diffusion with diethyl ether to afford needle-shaped crystals suitable for X-ray crystallography after one week. The stoichiometry of the reactants involved in each reaction, yield of the products, and their characterization data are provided below:

[(L)Gd(Cy₃PO)Cl] (1). H_2L (0.040 g, 0.100 mmol), $GdCl_3 \cdot 6H_2O$ (0.037 g, 0.100 mmol), Cy_3PO (0.030 g, 0.100 mmol), and Et_3N (28 μ L, 0.200 mmol) were used. Yield: 0.053 g, 60% (based on Gd). mp > 250 °C. IR (KBr ν/cm^{-1}): 3439(br), 3062(w), 2929(s), 2852(m), 1632(w), 1587(m), 1552(m), 1503(s), 1446(m), 1411(m), 1371(s), 1324(m), 1297(m), 1258(w), 1197(w), 1169(m), 1148(m), 1103(s), 1069(w), 1040(s), 987(w), 895(m), 854(w), 809(m), 744(m), 716(s), 679(s), 650(w), 534(m). Anal. Calcd for $C_{41}H_{52}Cl_1N_3O_3P_1Gd_1$ (886.57): C, 55.55; H, 5.91; N, 7.90. Found: C, 55.21; H, 6.36; N, 7.61%.

[(L)Tb(Cy₃PO)Cl] (2). H_2L (0.040 g, 0.100 mmol), $TbCl_3 \cdot 6H_2O$ (0.037 g, 0.100 mmol), Cy_3PO (0.030 g, 0.100 mmol), and Et_3N (28

μ L, 0.200 mmol) were used. Yield: 0.059 g, 67% (based on Tb). mp > 250 °C. IR (KBr ν/cm^{-1}): 3441(br), 3064(w), 2927(s), 2854(m), 1634(w), 1587(m), 1552(m), 1505(s), 1446(m), 1409(m), 1368(s), 1326(m), 1299(m), 1256(w), 1197(w), 1169(m), 1148(m), 1105(s), 1067(w), 1040(s), 987(w), 897(m), 856(w), 809(m), 744(m), 714(s), 679(s), 652(w), 532(m). Anal. Calcd for $C_{41}H_{52}Cl_1N_3O_3P_1Tb_1$ (888.25): C, 55.44; H, 5.90; N, 7.88. Found: C, 55.02; H, 6.56; N, 7.75%.

[(L)Dy(Cy₃PO)Cl] (3). H_2L (0.040 g, 0.100 mmol), $DyCl_3 \cdot 6H_2O$ (0.038 g, 0.100 mmol), Cy_3PO (0.030 g, 0.100 mmol), and Et_3N (28 μ L, 0.200 mmol) were used. Yield: 0.061 g, 69% (based on Dy). mp > 250 °C. IR (KBr ν/cm^{-1}): 3443(br), 3064(w), 2929(s), 2852(m), 1630(w), 1587(m), 1554(m), 1505(s), 1446(m), 1411(m), 1368(s), 1326(m), 1299(m), 1258(w), 1197(w), 1171(m), 1150(m), 1105(s), 1067(w), 1042(s), 989(w), 897(m), 854(w), 809(m), 744(m), 714(s), 679(s), 650(w), 532(m). Anal. Calcd for $C_{41}H_{52}Cl_1N_3O_3P_1Dy_1$ (891.82): C, 55.22; H, 5.88; N, 7.85. Found: C, 54.85; H, 6.39; N, 7.71%.

[(L)Y_{0.90}Dy_{0.10}(Cy₃PO)Cl] (3'). Anal. Calcd for $C_{41}H_{52}Cl_1N_3O_3P_1Y_{0.90}Dy_{0.10}$: C, 60.19; H, 6.41; N, 8.56. Found: C, 59.91; H, 6.52; N, 8.39%.

[(L)Dy(Ph₃PO)Cl] (4). H_2L (0.040 g, 0.100 mmol), $DyCl_3 \cdot 6H_2O$ (0.038 g, 0.100 mmol), Ph_3PO (0.028 g, 0.100 mmol), and Et_3N (28 μ L, 0.200 mmol) were used. Yield: 0.064 g, 72% (based on Dy). mp > 250 °C. IR (KBr ν/cm^{-1}): 3429(br), 3054(w), 2919(s), 1632(w), 1587(m), 1552(m), 1499(m), 1438(m), 1409(s), 1366(s), 1325(m), 1297(m), 1258(w), 1160(w), 1122(m), 1093(m), 1067(s), 1044(w), 989(w), 897(m), 809(m), 744(m), 714(s), 691(s), 650(s), 540(m). Anal. Calcd for $C_{41}H_{34}Cl_1N_3O_3P_1Dy_1$ (873.68): C, 56.37; H, 3.92; N, 8.02. Found: C, 55.98; H, 3.61; N, 7.89%.

[(L)Er(Cy₃PO)Cl] (5). H_2L (0.040 g, 0.100 mmol), $ErCl_3 \cdot 6H_2O$ (0.038 g, 0.100 mmol), Cy_3PO (0.030 g, 0.100 mmol), and Et_3N (28 μ L, 0.200 mmol) were used. Yield: 0.065 g, 73% (based on Er). mp > 250 °C. IR (KBr ν/cm^{-1}): 3447(br), 3068(w), 2929(s), 2852(m), 1636(w), 1587(m), 1554(m), 1505(s), 1446(m), 1413(m), 1366(s), 1326(m), 1299(m), 1260(w), 1199(w), 1169(m), 1152(m), 1107(s), 1067(w), 1044(s), 989(w), 897(m), 854(w), 809(m), 746(m), 714(s), 679(s), 650(w), 534(m). Anal. Calcd for $C_{41}H_{52}Cl_1N_3O_3P_1Er_1$ (896.58): C, 54.93; H, 5.85; N, 7.78. Found: C, 54.65; H, 6.33; N, 7.53%.

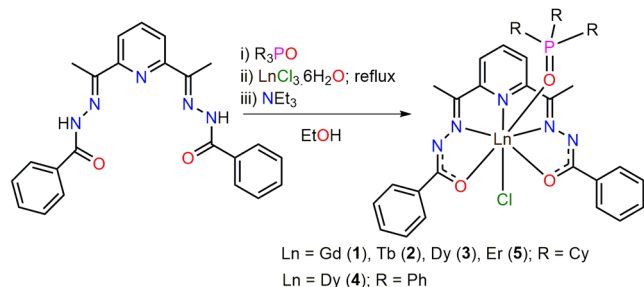
Computational Details. Post-Hartree–Fock ab initio calculations were performed on the X-ray crystal structures of all complexes using the CASSCF+RASSI-SO+SINGLE_ANISO approach as implemented in MOLCAS 8.2 program package.²³ The relativistic effects of the lanthanide ions were incorporated using the DKH Hamiltonian.²⁴ The basis set of all the atoms (Table S8 in Supporting Information) was taken from the ANO-RCC library implemented in MOLCAS 8.2 suite. First, we performed CASSCF calculations by considering 8, 9, and 11 electrons in the seven 4f orbitals of Tb(III), Dy(III), and Er(III) ions in their respective complexes. Using this active space, we computed 7 septet, 140 quintet, and 195 triplet states for Tb(III), 21 sextet states for Dy(III), and 35 quartet and 112 doublet states for the Er(III) ion. These spin-free states of each complex were mixed by RASSI-SO to calculate the spin–orbit energy levels. Finally, the g tensors and mechanism of magnetization relaxations were estimated using the SINGLE_ANISO, which interfaced with the RASSI-SO energies. In a nutshell, the CASSCF/RASSI-SO/SINGLE_ANISO method was used to compute the magnetic anisotropy, energy of the spin free and spin–orbit states, and the magnetic relaxation dynamics.

RESULTS AND DISCUSSION

Synthetic Aspects. The PBP geometry is regarded as one of the most promising coordination geometries around the Ln(III) center that can bring axiality in the ground state of Ln(III) ions, provided the axial sites are occupied by comparatively strong donor ligands. We previously reported the synthesis of mononuclear pentagonal bipyramidal Ln(III) complexes using a pentadentate chelating ligand, which

effectively provides a rigid equatorial plane. In these complexes, the two axial sites were occupied by chloride ions, which can be regarded as weak-field ligands compared to the N and O donor atoms of the pentadentate chelating ligand. Theoretical studies accompanied by experimental evidence show that oblate-shaped Ln(III) ions show high energy barriers of magnetization in the PBP geometry when the axial sites are occupied by relatively strong donor ligands compared to the equatorial sites. Keep in mind we chose trialkyl/aryl phosphine oxides to replace the chloride ions in the axial sites. Accordingly, when we treated the ligand H₂L with lanthanide chlorides in the presence of phosphine oxides followed by addition of base, we obtained neutral mononuclear [(L)Ln^{III}(R₃PO)Cl] (Ln = Dy, Tb, Gd, Er when R = cyclohexyl; Ln = Dy when R = phenyl) complexes (Scheme 1).

Scheme 1. Reaction Scheme for the Synthesis of 1–5



X-ray Crystallography. The complexes 1, 3, and 5 crystallize in the monoclinic crystal system with $P2_1/c$ (for 3) and $P2_1/n$ (for 1 and 5) space groups, whereas the complexes 2 and 4 crystallize in the triclinic crystal system with $P\bar{1}$ space group. Crystallographic data and refinement parameters of all the complexes are given in Table S1. The overall molecular structures of the complexes 1–5 are essentially identical. The molecular structure of complex 3 is shown in Figure 1, while those of 1, 2, 4, and 5 are given in the

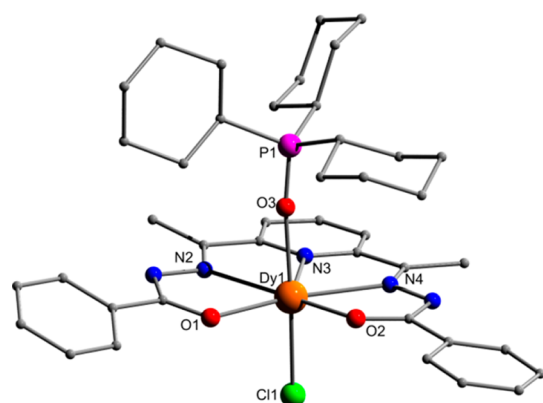


Figure 1. Molecular structure of complex 3. The H atoms are removed for clarity.

Supporting Information (Figures S1–S4). In view of the structural similarities present in the complexes we discuss below the molecular structures of complexes 3 and 4.

The complexes are formed by the coordination action of ligand *pyridyl* N atom, two *imino* N atoms, and two *carboxy* O atoms in the equatorial positions. One of the two axial sites is occupied by one chloride anion in both the two complexes.

The remaining axial site is occupied by one Cy₃PO ligand in the case of 3 and Ph₃PO ligand in the case of 4. The ligand upon chelation with the Ln(III) ions generates four five-membered rings revealing its excellent ability to stabilize the Ln(III) ions in its pentagonal coordination environment. The equatorial Dy–O/N bond distances are in the range of 2.259(2)–2.462(2) Å for 3 and 2.282(2)–2.456(2) Å for 4. The Dy–O_{axial} bond distances are 2.237(2) for 3 and 2.275(2) for 4. The Dy–Cl bond distances are 2.625(8) Å for 3 and 2.622(7) Å for 4. Interestingly, the Dy–O_{axial} bond distance in both 3 and 4 are shorter compared to the Dy–O_{equatorial} distances (Table S2 and Table S4) indicating the strong-field nature of the phosphine oxide ligand in comparison to the equatorial oxygen donors. The O_{phos}–Dy–Cl bond angles are 169.62(5)° for 3 and 174.07(5)° for 4. The immediate coordination environment of the Ln(III) ions is analyzed with Continuous-Shape Measures using the SHAPE program.²⁵ It reveals a distorted pentagonal bipyramid geometry around the Dy(III) ions with D_{5h} (*pseudo*) CF symmetry (Table S3, see Supporting Information). The pentagonal bipyramidal geometry of the Dy(III) ion in complex 3 is shown in Figure 2 (left). The shortest intermolecular Ln⋯Ln distance in 1, 3, and 4 is 8.47, 8.56, and 8.80 Å, respectively, as revealed in the solid-state packing diagram (see Figure 2 (right) for complex 3 and Figures S5 and S6 for 1 and 4). The solid-state phase purity of the complex 3' was confirmed by powder X-ray diffraction studies (Figure S7 see Supporting Information). The selected bond lengths and bond angles of complexes 1, 2, 4, and 5 are summarized in Table S4 (see Supporting Information).

Magnetic Properties. The temperature dependence of the molar magnetic susceptibility (χ_M) for 1–3 and 5 are plotted in Figure 3, and the field dependence of the magnetization for these compounds can be found in Figure S9. The corresponding behavior for 4 is summarized in Figure S8. The values of the product of the molar magnetic susceptibility with temperature, $\chi_M T$ (in cm³ mol⁻¹ K), found at 300 K are 7.85 (Gd), 11.79 (Tb), 14.14 and 14.10 (Dy), and 11.18 (Er), in good accordance with the values expected for the isolated ions (i.e., 7.88, 11.81, 14.17, and 11.48 cm³ mol⁻¹ K, respectively). For the Tb, Dy, and Er derivatives the $\chi_M T$ slowly decreases as T is lowered in agreement with the anticipated crystal field effect. The absence of any contribution from intermolecular exchange interactions is confirmed by the perfect Curie behavior down to 2 K for Gd. For the Tb and Dy derivatives, the field-dependent magnetization at 2–5 K shows a fast rise at lower field regions and remain almost unchanged above 15 kOe (at 2 K) to reach 4.8 (2), 5.14 (3), and 5.09 (4) μ_B at high field (5 T). To probe the dynamics of the magnetization relaxation, AC susceptibility behavior was investigated without and with applied static fields. No out-of-phase component (χ''_M) was found for the Tb and Er derivatives down to 2 K (see Figure S10 in Supporting Information). However, the Dy complexes 3 and 4 exhibited a χ''_M signal, but no maximum was observed above 2 K (see Figure S10 in Supporting Information).

Such a behavior was suggesting relaxation driven by quantum tunneling of magnetization (QTM), which was reduced by applying a static field. For 3, the optimum applied field was estimated at $H_{DC} = 1$ kOe (see Figure S11). The AC susceptibility study performed in this field within the frequency domain 1–1500 Hz yielded well-defined maxima for χ''_M between 4 and 18 K (Figure 4). Relaxation times (τ) were assessed by fitting $\chi''_M = f(\text{Frq})$ for different temperatures with

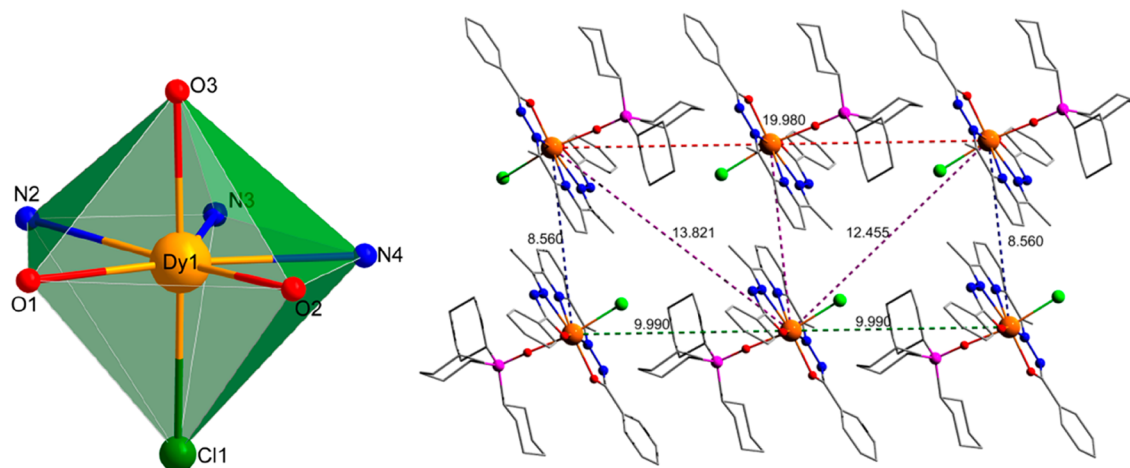


Figure 2. (left) Coordination polyhedron of Dy(III) and (right) solid-state packing diagram of complex 3.

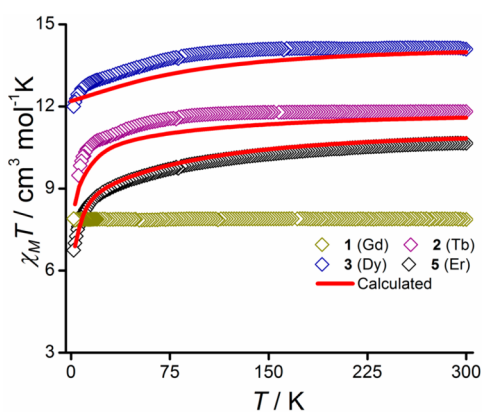


Figure 3. Temperature dependence of the product of the molar magnetic susceptibility with temperature, $\chi_M T$, under 1 kOe applied magnetic field for complexes 1–3 and 5. Solid red lines represent the ab initio calculated data. The computed data for 5 were reduced by 2% to meet the experimentally observed.

an extended Debye model; best-fit parameters are gathered in Table S5. The very small a parameter is indicative for a narrow distribution width for the relaxation time over the whole temperature domain, suggesting that mainly one relaxation process is operative. The temperature dependence of the relaxation time, plotted in log scale in Figure 4, develops to a more linear variation above 10 K, which is the behavior anticipated for a thermally activated process (Orbach). Deviation from linearity of $\ln(\tau) = f(T^{-1})$ for lower T indicates that other processes also come into play. Analysis of the behavior over the whole T range was obtained by summing the contributions of the Orbach, Raman, and direct processes ($\tau = \tau_0 \exp(U_{\text{eff}}/k_B T) + 1/(CT^n) + 1/(AT)$). The latter were required to reproduce the lower T behavior. Best fit gave a thermal energy barrier for magnetization reversal, $U_{\text{eff}}/k_B = 204 \pm 3$ K with $\tau_0 = (6 \pm 1) \times 10^{-9}$ s, $C = 0.015$ K $^{-1}$ s $^{-1}$, $n = 4.5$, and $A = -1.30$ s $^{-1}$.

The dilution of 3 in a matrix of isomorphous Y complex, 3' hereafter, gave very similar results (see Figure S12 in Supporting Information). For this sample, however, a maximum was observed in the $\chi''_M = f(T)$ behavior in zero field, but a QTM contribution was discernible at low temperature. This was suppressed upon applying a small DC field of 750 Oe. The temperature dependence of the relation

times between 2 and 17.5 K (Figure 4 and Table S6) parallels that obtained for the pure Dy derivative 3, and contributions of the Orbach, Raman, and direct processes were taken into account to reach a good modeling. Best fit to the experimental data for 3' yielded $U_{\text{eff}}/k_B = 208 \pm 5$ K, $\tau_0 = (6 \pm 2) \times 10^{-9}$ s, $C = 4.3 \times 10^{-3}$ K $^{-1}$ s $^{-1}$, $n = 5.0$, and $A = -0.30$ s $^{-1}$. The comparison of the behavior for 3 and its diluted form 3' shows that the observed behavior is clearly of molecular origin.

The replacement of OPCy $_3$ for OPPh $_3$ in the apical position of Dy appeared to have no significant incidence on the magnetic behaviors; the AC susceptibility features for 4 (Figure S13 and Table S7 in Supporting Information) are very similar to that obtained for 3. To reproduce the temperature dependence of the relaxation time for 4 required to consider contributions from Orbach, Raman, and direct processes; the best fit to the experimental behavior gave $U_{\text{eff}}/k_B = 241 \pm 7$ K, $\tau_0 = (2.3 \pm 0.9) \times 10^{-10}$ s, $C = (5.97 \pm 0.03) \times 10^{-3}$ K $^{-1}$ s $^{-1}$, $n = 5.1$, and $A = 0.2 \pm 0.7$ s $^{-1}$.

It is satisfying to see that the energy barrier for magnetization reversal, U_{eff}/k_B , for the Dy(III) complexes reported herein is significantly increased with respect to the homologue complex with Cl $^-$ ligands in the apical positions. This could be attributed to the stronger axial field due to the phosphine oxide ligand. A detailed comparison of the bond and magnetic properties of the present complexes with the reported pentagonal bipyramidal Dy(III) complexes having other equatorial ligands (including monodentate ones) and axial groups of various crystal field strengths are given in Table 1.

Computational Study. To rationalize the experimentally observed magnetization relaxation, we performed ab initio CASSCF/RASSI+SO/SINGLE_ANISO calculations 23 on the X-ray structures of complexes 2–5 and the previously reported complex 6, 17 in which both the axial positions were occupied by the Cl $^-$ ligands. The X-ray analysis revealed that complexes 2 and 5 consist of two molecules in the asymmetric unit, and we performed our calculations on the one molecule for each of the complexes.

The computed energy of the eight low-lying Kramers doublets (KDs) generated from the $^6\text{H}_{15/2}$ state spans from zero to 903 K in complexes 3 and 4 and to 942 K in complex 6 (Table 2). The g tensors $g_x \approx g_y \approx 0$ and $g_z \approx 20$ for complexes 3, 4, and 6 demonstrate the Ising behavior of Dy(III) ion in these complexes. The g_{zz} axis of ground KD is found to lying on the equatorial plane due to the strong crystal field generated

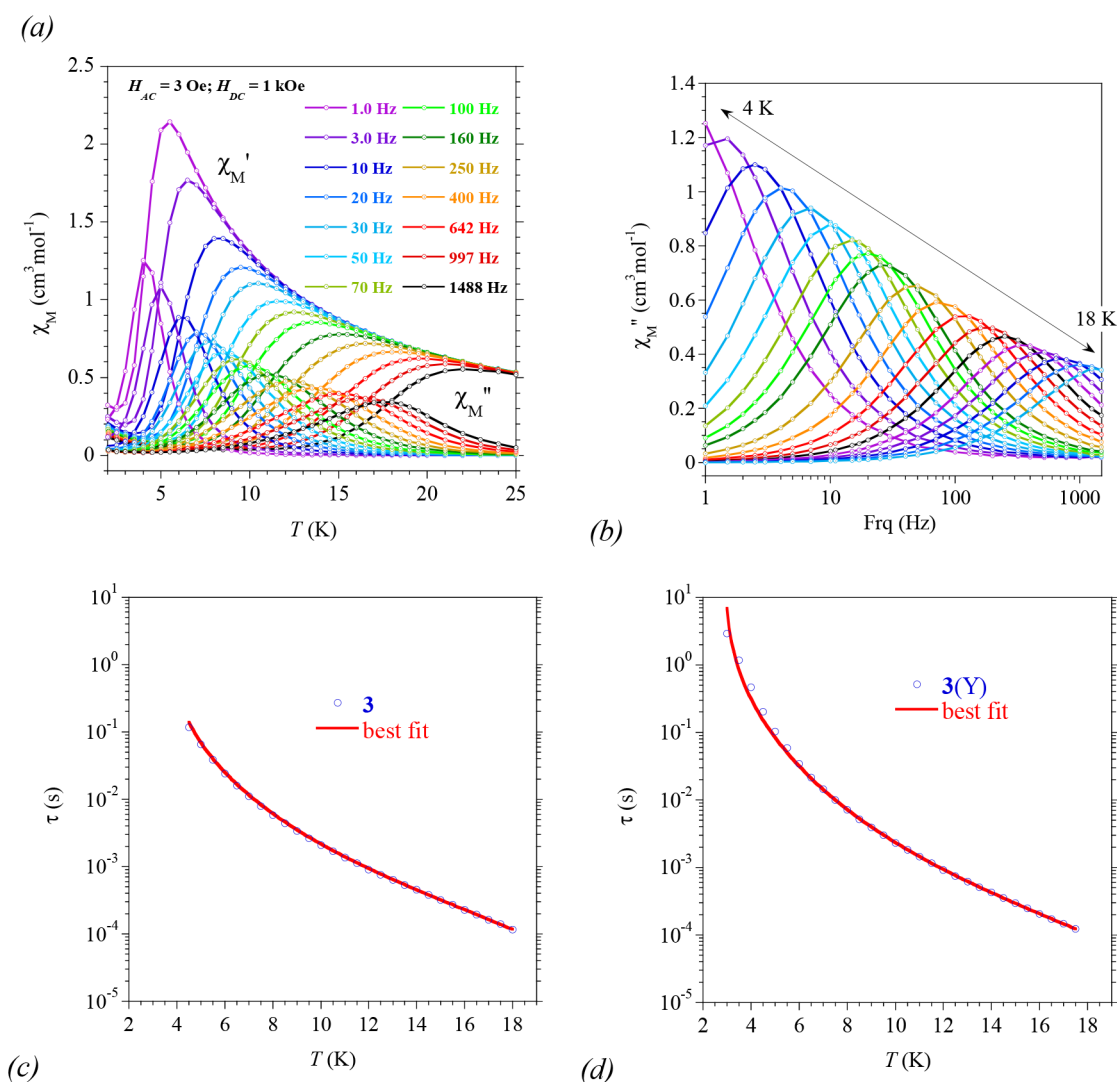


Figure 4. (a, b) AC susceptibility behaviors for **3**; (c) temperature dependence of the relaxation times for **3**, and (d) for diluted compound **3'**; the solid red lines are the best fits (see text).

from the equatorial ligand (Figures 5 and S14). We plotted the beta electron density of Dy in complexes **3**, **4**, and **6** using the procedure introduced by Ruiz and co-workers.³³ Since the beta electron density is found to orient along the axial Cl–Dy–O bond (Cl–Dy–Cl bond in **6**), the g_{zz} anisotropy axis is oriented along the perpendicular direction of it to minimize the electrostatic repulsion (Figure 6). The large thermally assisted quantum tunneling (TA-QTM) value of 0.41, 0.64, and 0.24 μ_B in the first excited KDs suggest the relaxation will occur ideally through the first excited state KD (Figures 5 and S14). This suggests U_{cal} values of 222.6, 222.9, and 211.0 K for complexes **3**, **4**, and **6**, respectively. These values are consistent with the estimate obtained from the experiments except for **6**, where U_{cal} values are overestimated (for **3** 208 K, **4** 241 K, and **6** 70 K). We also analyzed the composition of the computed wave function to get more insight about the extent of mixing of the m_j levels. The ground KD is found to be consist of $m_j = \pm 15/2$ ($\sim 97\%$) with the negligible ($\sim 0.02\%$) mixing with $m_j = \pm 11/2$ states. The strong mixing in the first excited KD leads to very large TA-QTM, which forces the complex to relax via this state.

The ab initio computed energy barrier for the magnetization reversal does not affect significantly when one Cl^- ion in the axial position (complex **6**) is replaced by the neutral Cy_3PO or Ph_3PO ligand (complexes **3** and **4**, respectively). The energy spectrum depends on the ligand field generated from the equatorial ligands, which is found to be the same in all the complexes. We analyzed the LoProp charges to get more insight into the axiality of the three complexes. The LoProp charge of the axial oxygen atoms is found to be larger than that of the equatorial nitrogen and oxygen atoms in **3** and **4** (Table S9 and Figure S15). More importantly, the ratio of the average axial/equatorial LoProp charges is found to be almost the same in the complexes **3** and **4**, which is consistent with similar U_{cal} values estimated in these complexes. The LoProp charges of the axial chlorine atoms and equatorial oxygen atoms are found to be very close in **6**, which implies the less axial nature of this complex compared to **3** and **4**. However, the average axial/equatorial LoProp charge greater than 1.7 implies significant axiality in this complex.

The crystal field parameter of the three complexes was estimated using the Steven formalism ($\hat{H}_{CF} = \sum_k \sum_{q=-k}^{+k} B_k^q \tilde{O}_k^q$, where B_k^q and \tilde{O}_k^q is computed crystal field parameter and

Table 2. Computed Energy and the Associated g -Tensors of the Low-lying KDs Generated from the ${}^6H_{15/2}$ State of Complexes 3, 4, and 6

energy (K)	g_x	g_y	g_z	angle of g_{zz} axis between the ground and higher excited KDs (deg)
complex 3				
0.0	0.013	0.030	19.741	
222.6	0.910	1.684	13.977	16.2
277.1	0.661	3.360	11.281	19.3
334.9	0.044	1.050	13.447	87.8
516.4	1.005	3.829	12.313	3.6
599.6	2.148	5.995	13.311	92.5
700.0	0.467	1.645	12.249	90.7
903.6	0.145	0.743	17.531	90.4
complex 4				
0.0	0.020	0.041	19.734	
222.9	0.954	2.781	13.614	3.7
284.1	0.627	1.875	11.962	6.0
398.2	1.326	1.612	16.936	88.6
518.3	0.969	4.094	12.524	16.4
624.5	11.040	6.990	1.617	89.9
724.2	1.384	3.050	11.564	91.1
903.2	0.108	0.870	17.209	90.1
complex 6				
0.0	0.009	0.016	19.741	
211.0	0.454	1.287	14.174	0.0
281.1	0.683	0.816	12.236	0.0
509.2	1.955	3.683	11.188	90.0
635.5	0.010	2.340	16.111	90.0
704.3	1.061	3.553	10.520	90.0
829.9	3.445	5.293	8.380	90.0
942.3	1.253	1.728	15.285	90.0

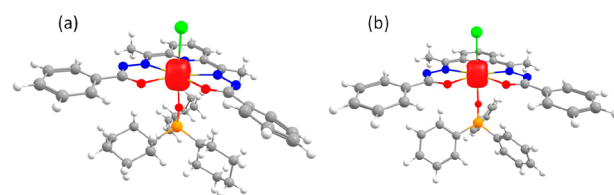


Figure 6. (a) The beta electron density of complex 3. (b) The beta electron density of complex 4. Color code: Dy-yellow, Cl-green, P-violet, O-red, N-blue, C-gray, H-white.

Stevens operator, respectively) as implemented in SINGLE - ANISO suite to get more insight on the relaxation mechanism. That the axial crystal field parameter B_2^0 is found to be larger in 4 compared to 3 implies stronger axiality in 4, which agrees well with the U_{eff} value (Table S10). However, that the B_2^2 value in complex 6 is found to be similar implies lower axiality here comparing to 3 and 4.

Furthermore, we modeled the complexes 3a, 4a, and 6a (where the equatorial ligand was removed) from complexes 3, 4, and 6, respectively, to achieve the axial limit in each of these complexes. The anisotropy axis is found to be oriented along the Cl–Dy–O bond due to the absence of equatorial ligand field (Figure S16). The beta electron density is found to be oblate in nature, and the g_{zz} axis is oriented along the axial Cl–Dy–O bond (Cl–Dy–Cl bond in 6) to minimize the electrostatic repulsion (Figure 7). The ab initio calculations on these models reveal that the energy splitting of the eight KDs generated from the ${}^6H_{15/2}$ state rises to 2864, 2787, and 2616 K for 3a, 4a, and 6a, respectively (Table S11). The absence of equatorial ligand field leads to higher LoProp charge in the Dy center and metal-coordinated oxygen atoms, revealing the axial limit that can be achieved in this set of complexes (Table S12). It is also reflected in the computed crystal field parameter in which larger B_2^0 value is found

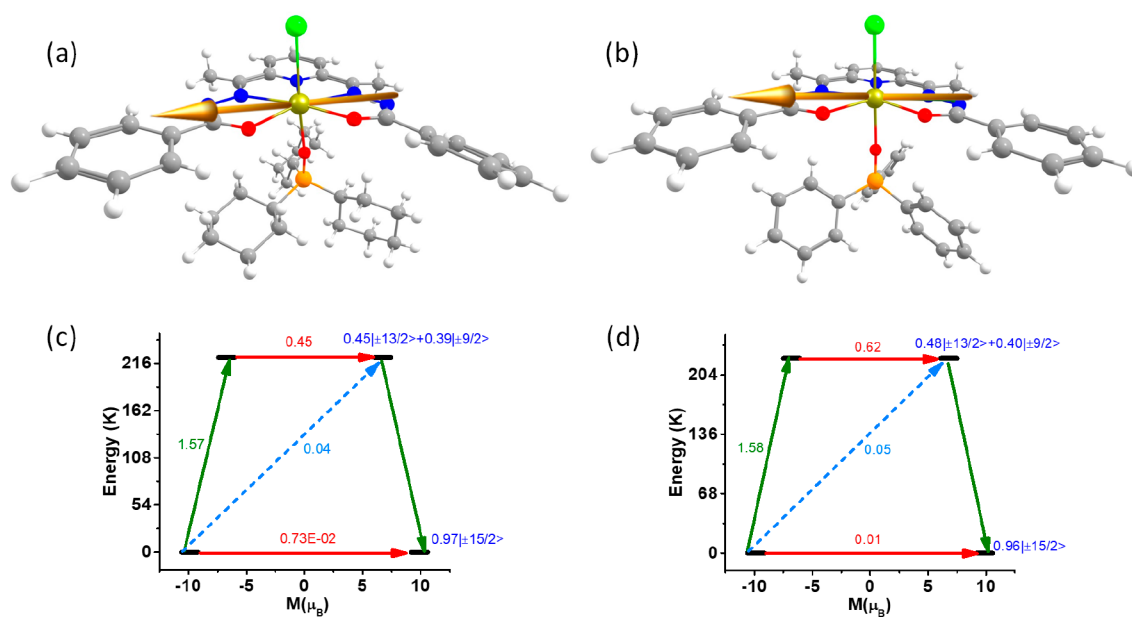


Figure 5. Orientation of the anisotropy axis of Dy(III) ion in complexes 3 (a) and 4 (b). (c, d) The plausible relaxation mechanisms for 3 and 4, respectively. The red arrows show the QTM and TA-QTM via ground and higher excited KD, respectively. The sky dotted arrows show the Orbach process for the relaxation. The green arrows show the possible mechanism of magnetic relaxation. The blue characters imply the m_j composition of the KDs. Color code: Dy-yellow, Cl-green, P-oreng, O-red, N-blue, C-gray, H-white.

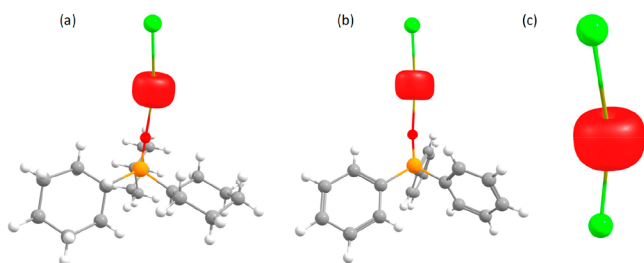


Figure 7. (a) The beta electron (spin-down) density of model 3a. (b) The beta electron density of model 4a. (c) The beta electron density of model 6a. Color code: Dy-yellow, Cl-green, P-orange, O-red, N-blue, C-gray, H-white.

compared to original complexes (Table S13). The magnetization relaxation is found to occur via the fourth excited KD due to the strong transverse anisotropy, which leads to U_{cal} values of 2540, 2471, and 2248 K in 3a, 4a, and 6a, respectively (Figure S17).

In the case of complex 2, a large tunnel splitting (Δ_{tun}) of 2.26 cm^{-1} is found between the two pseudo ground KDs, which triggers the magnetization relaxation via the ground state (Table S14). The ground-state anisotropy axis is found to be lying on the equatorial plane due to the strong equatorial ligand field (Figure S18). In case of complex 5 the computed large QTM value of $0.22 \mu_{\text{B}}$ between the ground-state KD also suggests the relaxation via ground state, which is supported by no out-of-phase signals in ac susceptibility (Figure S18 and Table S15).

SUMMARY

Mononuclear 4f complexes (Gd^{III} , Dy^{III} , Er^{III} , and Tb^{III}) have been assembled using a multifunctional chelating ligand. The ligand enforces a pentagonal equatorial architecture around the metal ion. The two axial sites are taken up by a chloride and a phosphine oxide ligand. Thus, the overall coordination geometry around the lanthanide metal ion is distorted pentagonal bipyramidal. Magnetic studies on these complexes reveal that the Dy^{III} analogues show a slow relaxation of magnetization under the presence of small DC fields. A large tunneling gap between the ground as well as consequent excited non-Kramers doublets of Tb^{III} and a very high quantum tunneling between the ground-state Kramers doublets in the Er^{III} complex prevents these complexes from revealing a single-ion magnet behavior. The strategy adopted in the present instance of using a rigid ligand that enforces a pentagonal equatorial plane around the lanthanide ion is clearly effective in enabling the designed assembly of single-ion magnets. An improvement in this strategy would be to effect modifications in the ligand design to decrease the effective crystal field in the equatorial plane and increase it in the axial sites. We are currently examining these possibilities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00751>.

X-ray crystallographic table of complexes 1–5; molecular structures of complexes 1 (CCDC 1989266), 2 (CCDC 1989267), 4 (CCDC 1989270), and 5 (1989271), crystal packing diagrams of 1 and 4, table of bond distances and angles; table of continuous shape

measures calculations; powder X-ray diffraction pattern of 3'. details of magnetic properties of 1–5; details of computational calculations of complexes 1–5 (PDF)

Accession Codes

CCDC 1989266–1989268 and 1989270–1989271 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Vadapalli Chandrasekhar – Tata Institute of Fundamental Research Hyderabad, Gopanally 500107, Hyderabad, India; Department of Chemistry, IIT Kanpur, Kanpur 208016, India; orcid.org/0000-0003-1968-2980; Email: vc@tifrh.res.in, vc@iitk.ac.in

Jean-Pascal Sutter – Laboratoire de Chimie de Coordination du CNRS, Université de Toulouse, CNRS, Toulouse, France; orcid.org/0000-0003-4960-0579; Email: sutter@lcc-toulouse.fr

Gopalan Rajaraman – Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India; orcid.org/0000-0001-6133-3026; Email: rajaraman@chem.iitb.ac.in

Authors

Pankaj Kalita – School of Chemical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India; Tata Institute of Fundamental Research Hyderabad, Gopanally 500107, Hyderabad, India; orcid.org/0000-0002-1240-5633

Naushad Ahmed – Tata Institute of Fundamental Research Hyderabad, Gopanally 500107, Hyderabad, India

Arun Kumar Bar – School of Chemical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India

Sourav Dey – Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India

Anukul Jana – Tata Institute of Fundamental Research Hyderabad, Gopanally 500107, Hyderabad, India; orcid.org/0000-0002-1657-1321

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.inorgchem.0c00751>

Author Contributions

#Authors contributed equally in this manuscript

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

V.C. is thankful to the Dept. of Science and Technology, New Delhi, India, for a National J. C. Bose Fellowship. P.K. is thankful to National Institute of Science Education and Research, Bhubaneswar, and Tata Institute of Fundamental Research, Hyderabad, for doctoral and postdoctoral fellowships, respectively. N.A. is thankful to Tata Institute of Fundamental Research, Hyderabad, for a postdoctoral fellowship. S.D. thanks UGC for SRF fellowship. G.R. acknowledges

DST/SERB for funding (CRG/2018/000430; DST/SJF/CSA-03/2018-10; SB/SJF/2019-20/12).

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