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A Dy4 Single-Molecule Magnet and Its Gd(III), Tb(III), Ho(III), Er(III) Analogues Encapsulated by 8-hydroxylquinoline Schiff Base Derivative and β -diketonate coligand

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Abstract

Five new tetranuclear complexes based on 8-hydroxyquinoline Schiff base derivative and β -diketone coligand, [Ln₄(acac)₄L₆(μ_3 -OH)₂]·CH₃CN·0.5CH₂Cl₂ (Ln = Dy Gd (1). Tb (2),(3),Ho (4) and Er (5) : HL = 5-(benzylidene)amino-8-hydroxylquinoline; acac = acetylacetonate) have been synthesized, structurally and magnetically characterized. Complexes 1-5 have similar tetranuclear structures. Each Ln^{III} ion is eight coordinated and their coordination polyhedrons can be described as being in a distorted square-antiprismatic geometry. The magnetic studies reveal that 1 features magnetocaloric effect (MCE) with the magnetic entropy change of $-\Delta S_m(T) = 25.08 \text{ J kg}^{-1} \text{ K}^{-1}$ at 2 K for $\Delta H = 7 \text{ T}$, and 3 displays slow magnetic relaxation behavior of Single Molecule Magnets (SMMs) with the anisotropic barrier of 86.20 K and pre-exponential factor $\tau_0=2.99\times10^{-8}$ s.

Introduction

Single-molecule magnets (SMMs) exhibiting slow magnetic relaxation below the blocking temperature have recently attracted increasing interest in chemistry, physics, and material science since the 1990s¹ with the prospect of high-density information storage,² quantum computing,³ magnetic refrigeration⁴ and molecule-based spintronic devices.⁵ As is now reasonably well understood, SMMs can be verified on the basis of three parameters: the magnetic blocking temperature (T_B), the strength of the coercive magnetic field (H_c), and the anisotropy barrier (U_{eff}), among which the parameter of U_{eff} is the most common one for judging the quality of SMMs.⁶ The anisotropic

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barrier arises of a SMM due to a uniaxial Ising-like magneto-anisotropy (D) acting on a nonzero spin ground state (S).⁷ A large number of studies have shown that the viability of lanthanide-based complexes in generating large barriers to spin reversal as a result of their significant magnetic anisotropy arising from the large, unquenched orbital angular momentum.⁸ Since Ishikawa and co-workers reported the first Ln-ion-based SMMs $(Bu_4N)[Tb(Pc)_2]$ $(H_2Pc = phthalocyanine)$, special attention has been paid on the lanthanide complexes in the pursuit of creating new SMMs with higher anisotropic barriers, due to their strong angular dependence of the 4f orbitals and high substantial anisotropy.⁹ Constructing Ln-based SMMs, it is noteworthy that the Dy^{III} ion contributes much more than the other lanthanide ions in exploring high energy barrier SMM properties and understanding the magnetic relaxation pathways. Dy^{III} ion, possessing 4f⁹ substantial anisotropy and a Kramers ground state of ${}^{6}H_{15/2}$, might be an appealing paramagnetic source for construction of SMMs with suitable coordination environment.¹⁰ Up to now, a large quantity of Dy^{III}-containing SMMs varying from mononuclear to dodecanuclear, and even up to hexacosanuclear, have been discovered.¹¹ Among them, some polynuclear Dy^{III} compounds display remarkable and interesting magnetic behaviors. Tetranuclear dysprosium (Dy₄) clusters have long occupied a vital position in displaying large thermal energy barrier and investigating the magnetic relaxation behavior, among which a defect-dicubane Dy₄ SMM with an anisotropic barrier of 170 K¹² and a linear tetranuclear dysprosium(III) complex displays two-step relaxation processes with a remarkably large energy barrier of 173 K.¹³ It is well-known that β -diketonates are good bidentate chelating ligands, not only ideal candidates as light-harvesting chromospheres,¹⁴ but also providing feasible ligand field to investigate the SMMs properties of simple lanthanide complexes.¹⁵ Such ligands have potential applications in theoretical and practical studies. In particular for acetylacetonate (acac), it has a significant impact in the magnetic field of complexes. 8-hydroxylquinoline derivatives have excellent structural features: (i) it can easily coordinate with Ln^{III} ions through three donor atoms; (ii) the phenoxy atom of 8-hydroxylquinoline derivatives can act as a phenoxo-O bridge between Ln^{III} ion centers, which can transmit magnetic exchange efficiently 2

between neighboring Ln^{III} ions.¹⁶ As we all know, those complexes encapsulated by 3d metal and 8-hydroxylquinoline have excellent fluorescence properties. However there are scarce magnetic properties based on 8-hydroxylquinline Schiff base derivatives, β -diketonates coligand and 4f lanthanide metal.

Herein, we report the synthesis, structure, and magnetism of a family of tetranuclear Ln^{III} complexes, which exhibits magnetocaloric effect (MCE) for Gd^{III} complex, and large relaxation barrier for Dy^{III} complex.

Experimental section

Materials and general methods

All starting chemicals and solvents were commercially available and used without further purification. The materials $Ln(acac)_3 \cdot 2H_2O$ (Ln = Gd, Tb, Dy, Ho, Er) were prepared according to the reported literature. ¹⁷ 5-(benzylidene)amino-8-hydroxylquinoline (HL) was prepared from a reaction between 5-amino-8-hydroxylquinoline and benzylidene.¹⁸

¹H NMR and ¹³C NMR spectra were recorded on Bruker spectrometer at 400 and 100 MHz, respectively, with TMS as an internal standard. Elemental analyses (EA) for C, H and N were carried out on a PerkinElmer 240 CHN elemental analyzer. IR spectra were recorded in the range of 4000–400 cm⁻¹ with a Bruker TENOR 27 spectrophotometer using a KBr pellet. Powder X-ray diffraction (PXRD) measurements were collected on a Rigaku D/max 2500/pc/X-ray powder diffractometer with Cu-K α radiation ($\lambda = 1.540598$ Å). Thermogravimetric analysis (TGA) experiments were obtained using a NETZSCHTG 409 PC thermal analyzer in a static atmosphere from 30 to 800°C with a sample size and a heating rate of 10°C min⁻¹. UV-vis spectra were measured with a TU-1901 UV-Vis spectrometer (Shanghai, China). Magnetic measurements were measured using an MPMS XL-7 SQUID magnetometer.

Synthesis of 5-(benzylidene)amino-8-hydroxylquinoline (HL)

The 8-hydroxyquinoline Schiff base derivative ligand (HL) was synthesized in a simple aldimine condensation reaction of 5-amino-8-hydroxylquinoline (0.025 mmol) with benzaldehyde (0.025 mmol).

The synthesis of 5-amino-8-hydroxyquinoline was optimized compared to the method reported previously in the literature.¹⁹ 5-amino-8-hydroxylquinoline (0.8 g, 5 mmol) was dissolved in 30 mL of ethanol at 60°C, 0.54 g of benzaldehyde was added, and 3-4 drops of formic acid were dropped into the mixture as a catalyst. After that, the mixture was heated for 4 h at 83°C. The product was isolated from the mixture and it was purified by recrystallization from a mixed solvent of ethanol and acetone (3/1, v/v). The purified product was obtained as a brown solid (yield 0.97 g, 78.2%). ¹H NMR (400 MHz, CDCl₃) (Fig. S1 in the Supporting Information) δ 8.83 (2H, m, *J* = 6.5 Hz), 8.62 (1H, s), 8.01 (2H, d, *J* = 3.2 Hz), 7.50 (4H, dd, *J* = 12.4 Hz, 3.6 Hz), 7.20 (2H, q, *J* = 8.1 Hz). ¹³C NMR (100MHz, CDCl₃) (Fig. S2 in the Supporting Information) δ 158.89, 150.74, 148.33, 139.96, 138.09, 136.45, 133.23, 131.32, 128.81, 128.78, 124.96, 121.57, 113.70, 109.65.

Syntheses of complexes 1-5

Ln(acac)₃·2H₂O (0.02 mmol) (Ln = Gd(1), Tb(2), Dy(3), Ho(4), Er(5)) was dissolved in 20 mL of acetonitrile. Then, a 5 mL CH₂Cl₂ solution of HL (0.005 g, 0.02 mmol) was added to the stirred acetonitrile solution, and the mixture was heated for 2 h at 70 °C. Finally, the solution was cooled to room temperature and filtered. Yellow block crystals suitable for single crystal X-ray diffraction analysis were isolated by keeping the filtrate at room temperature for three days.

 $[Gd_4(acac)_4L_6(\mu_3-OH)_2]$ ·CH₃CN·0.5CH₂Cl₂ (1). Yield: 54% (based on Gd). Anal. Calcd for C_{118.5}H₁₀₀ClGd₄N₁₃O₁₆ (2626.56): C, 54.19; H, 3.84; N, 6.93. Found: C, 54.14; H, 3.87; N, 6.95. IR(KBr, cm⁻¹): 3421(w), 3073(w), 2859(w), 1603(vs), 1508(s), 1468(s), 1390(vs), 1314(s), 1254(s), 1097(m), 1024(w), 959(w), 920(m), 881(m), 836(w), 773(w), 691(m), 649(w), 601(w), 510(w), 443(w).

 $[Tb_4(acac)_4L_6(\mu_3-OH)_2] \cdot CH_3CN \cdot 0.5CH_2Cl_2$ (2). Yield: 45% (based on Tb). Anal. Calcd for $C_{118.5}H_{100}CITb_4N_{13}O_{16}$ (2633.25): C, 54.05; H, 3.83; N, 6.92. Found: C, 54.0; H,3.42; N,6.89. IR(KBr, cm⁻¹): 3442(w), 3048(w), 2856(w), 1598(vs), 1500(s), 1459(s), 1376(vs), 1314(s), 1231(s), 1076(m), 1007(w), 973(w), 902(m), 874(m), 836(w), 760(w), 697(m), 649(w), 606(w), 510(w), 462(w).

 $[Dy_4(acac)_4L_6(\mu_3-OH)_2]$ ·CH₃CN·0.5CH₂Cl₂ (**3**). Yield: 65% (based on Dy). Anal.

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Calcd for C_{118.5}H₁₀₀ClDy₄N₁₃O₁₆ (2647.56): C, 53.76; H, 3.81; N, 6.88. Found: C, 53.79 ; H, 3.85; N, 6.84. IR(KBr, cm⁻¹): 3419(w), 3069(w), 2865(w), 1602(vs), 1510(s), 1461(s), 1394(vs), 1314(s), 1258(s), 1093(m), 1016(w), 966(w), 920(m), 877(m), 832(w), 778(w), 694(m), 652(w), 600(w), 510(w), 448(w).

[Ho₄(acac)₄L₆(μ_3 -OH)₂]·CH₃CN·0.5CH₂Cl₂ (**4**). Yield: 60% (based on Ho). Anal. Calcd for C_{118.5}H₁₀₀ClHo₄N₁₃O₁₆ (2657.29): C, 53.56; H,3.79; N, 6.85. Found: C, 53.54; H, 3.83; N, 6.86. IR(KBr, cm⁻¹): 3418(w), 3064(w), 2871(w), 1599(vs), 1512(s), 1454(s), 1389(vs), 1316(s), 1253(s), 1091(m), 1017(w), 965(w), 917(m), 873(m), 829(w), 781(w), 691(m), 650(w), 603(w), 509(w), 447(w).

 $[Er_4(acac)_4L_6(\mu_3-OH)_2]\cdot CH_3CN\cdot 0.5CH_2Cl_2$ (5). Yield: 63% (based on Er). Anal. Calcd for $C_{118.5}H_{100}ClEr_4N_{13}O_{16}$ (2666.60): C, 53.38; H, 3.78; N, 6.83. Found: C,53.41; H, 3.76; N,6.85. IR(KBr, cm⁻¹): 3415(w), 3068(w), 2861(w), 1604(vs), 1513(s), 1462(s), 1389(vs), 1319(s), 1252(s), 1091(m), 1011(w), 967(w), 925(m), 876(m), 838(w), 772(w), 691(m), 656(w), 601(w), 510(w), 443(w).

X-ray single crystal structure determination

Crystallographic data of **1-5** were measured on a BRUKER SMART-1000 CCD diffractometer with graphite monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), using a ω - φ scan at 113(2) K. The structures were solved by direct methods using the program SHELXS-97, and refined anisotropically using the full-matrix least-squares technique based on F^2 using SHELXS-97. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystal data collection and refinement details for complexes **1-5** are summarized in Table 1. Some of the figures relating to the molecular structure of **1-5** are given in the Supporting Information.(Table S1- S5) CCDC (1491596, **1**; 1491595, **2**; 1491592, **3**; 1491593, **4**; 1491594, **5**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic Data and Structure Refinements for 1-5

Complex	1	2	3	4	5

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Formula	$C_{118.5}H_{99}ClN_{13}O_{16}Gd_4$	$C_{118.5}H_{99}ClN_{13}O_{16}Tb_4$	$C_{118.5}H_{99}ClN_{13}O_{16}Dy_4$	$C_{118.5}H_{99}ClN_{13}O_{16}Ho_4$	$C_{118.5}H_{99}ClN_{13}O_{16}Er_{4}$
Formula weight	2625.55	2632.23	2646.55	2656.27	2665.59
Temperature (K)	113(2)	113(2)	113(2)	113(2)	113(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c
a (Å)	30.800(6)	30.677(6)	30.579(8)	30.518(6)	30.4688(19)
<i>b</i> (Å)	14.613(3)	14.610(3)	14.553(3)	14.610(2)	14.5825(6)
<i>c</i> (Å)	28.155(6)	28.137(6)	28.172(8)	28.148(5)	28.1141(17)
α (deg)	90	90	90	90	90
β (deg)	118.39(3)	118.34(3)	118.244(5)	118.193(3)	118.165(11)
γ (deg)	90	90	90	90	90
Volume (Å ³)	11147(4)	11099(4)	11044(5)	11061(3)	11012.3(11)
Ζ	4	4	4	4	4
Calculated density (Mg m ⁻³)	1.565	1.576	1.592	1.596	1.608
Absorption coefficient (mm ⁻¹)	2.443	2.2612	2.770	2.925	3.112
F (000)	5212	5228	5244	5260	5276
θ range for data collection (deg)	1.50 to 25.02	1.51 to 25.02	3.02 to 25.02	3.03 to 25.02	3.03to 25.02
Reflections collected	44964	40283	59037	46472	58628
Independent reflection	9843[<i>R</i> (int)=0.1199]	9786[<i>R</i> (int)=0.1312]	9721[<i>R</i> (int)=0.0473]	9714[<i>R</i> (int)=0.0350]	9695[<i>R</i> (int)=0.0431]
Data / restraints / parameters	9843 / 42 / 726	9786 / 42 / 726	9721 / 42 / 726	9714 / 42 / 726	9695 / 42 / 726
Goodness-of-fit on F^2	1.072	1.078	1.045	1.028	1.025
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0711,$	$R_1 = 0.0701$,	$R_1 = 0.0392,$	$R_1 = 0.0272,$	$R_1 = 0.0298,$
	$wR_2 = 0.1513$	$wR_2 = 0.1510$	$wR_2 = 0.1054$	$wR_2 = 0.0909$	$wR_2 = 0.0891$
<i>R</i> indices (all data)	$R_1 = 0.1249,$	$R_1 = 0.1338,$	$R_1 = 0.0515,$	$R_1 = 0.0305,$	$R_1 = 0.0392,$
	$wR_2 = 0.1888$	$wR_2 = 0.1946$	$wR_2 = 0.1120$	$wR_2 = 0.0931$	$wR_2 = 0.0970$

Result and discussion

Descriptions of Crystal Structures of 1-5. Complexes **1-5** are isomorphous and crystallize in the monoclinic C2/c space group. Therefore, only the molecular structure of **3** is discussed herein. The molecular structure of **3** is shown in Fig.1, there are four Dy^{III} ions, six L and four acac⁻ ligands, and the core structure of **3** has a tetranuclear arrangement of Dy^{III} ions with crystallographic centrosymmetric, and therefore strictly planar. All of the 8-coordinated Dy^{III} ions are linked together by a combination of the two oxygen atoms (O8, O8a) of the μ_3 -OH ligands and the phenoxo oxygen atoms (O1, O2, O3, O1a, O2a, O3a). The Dy1 ion is coordinated to seven oxygen atoms (O1, O2, O3, O4, O5, O8 and O8a) and one nitrogen atom (N1) in the pyridyl ring, while six oxygen atoms (O1a, O3, O6, O7, O8 and O8a) and two nitrogen atoms (N3 and N5) form the coordination sphere around the Dy2 ion. In the

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centrosymmetric unit, the Dy1 and Dy2 ions are eight coordinated, and their coordination polyhedrons can be described as being in a distorted square-antiprismatic geometry (Fig.2). The coordination geometry of Dy^{III} ions were analysised by utilizing SHAPE 2.0. (Table S6 in Supporting Information) The two square bases of the square antiprism for Dy1 consist of O1, O8a, O8, and N1, and O2, O3, O4 and O5, whereas for Dy2, the two square bases are defined by the atoms O1a, O6, O7 and O8, and N3, N5, O2 and O3. The two square antiprisms share three oxygen atoms O2, O3 and O8, which form a triangle, and the distances of three lengths of O2-O3, O2-O8, O3-O8 are 2.6636(65), 2.7440(64), 2.7818(52) Å. A square antiprism can be defined by an angle (α) describing its elongation or flatness. This parameter, that is, α , is the angle between the S8 axis of the square antiprism and the central atom ligand bond. This angle is also defined as $\alpha = \gamma/2$, γ being the angle between opposite bonds within one hemisphere. For a soft-sphere model with a repulsion energy law $\approx 1/\gamma^6$, the ideal α value amounts to 57.16°.²⁰ As depicted in Fig.3 in the Supporting Information, for the Dy1 ion in 3, the hemisphere including the atoms O1, O8, O8a, and N1 is strongly distorted since the angles α are 57.59(5)° and 50.99(5)°(Table S7 in the Supporting Information), which are respectively 0.435° and 6.165° outside the perfect value. This distortion is most likely due to the small bite angle of the μ_3 -OH ligand $(O8-Dy1-O8a = 70.20(16)^\circ)$. The second hemisphere, where $\alpha = 59.91(5)^\circ$ and 62.84(5)° (Table S7 in the Supporting Information) indicating large deviations from the ideal values. For the Dy2 ion the α angles are 53.75(5)°, 55.55(0)°, 53.89(5)°, 64.28(0)° (Table S7 in the Supporting Information), indicating large deviations from the ideal values. This is most likely due to the constrains imposed on the Dy^{III} ion by the Schiff base ligands. There are four bidentate anionic acac groups above and below the planar core coordinating to four Dy^{III} ions, respectively. The four Dy^{III} ions are precisely coplanar (Fig.3), and two triply bridging hydroxide (O8, O8a) atoms lie approximately 0.8822Å above and below the Dy4 plane. The μ_3 -OH groups form near symmetrical bridges to the metal centers, with Dy1–O8, Dy2–O8, and Dy1a–O8 distances of 2.362(4), 2.313(4), and 2.335(4) Å, respectively, as well as Dy1-O8-Dy2, Dy1-O8-Dy1a and Dy1a-O8-Dy2 angles of 98.40(15)°, 109.81(16)°, and 111.30(16)°,

respectively. Finally, the four Dy^{III} ions are located at the corners of a parallelogram. The shortest intramolecular $Dy^{...}Dy$ distance, which is 3.5391(9) Å, is at the edge of the parallelogram between Dy1 and Dy2. The Dy-O distances in **3** are in the range of 2.279(4)-2.413(4) Å, the Dy–N bond lengths are in the range of 2.516(5)-2.552(5) Å and the O-Dy-O angles are in the range of 67.25(14)°-146.55(14)°.



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solvent molecules have been omitted for clarity.



Fig. 2 Coordination polyhedrons for the adjacent Dy^{III} ions in complex 3.



Fig. 3 Parallelogram view of complex 3 with HL partially omitted for clarity.

TGA and PXRD. The thermal stabilities of 1-5 were studied on crystalline samples in an air atmosphere with a heating rate of 10°C min⁻¹ in the temperature range 30-800°C (Fig.S4 in the Supporting Information). For 1-5, the TGA curves are very similar since they are isomorphic. Herein, complex 3 will be used as a representative illustration. The crystalline sample was kept for a period of time under ambient conditions resulting in the spontaneous loss of solvent molecules, so that no solvent loss occurred in the 30–155 °C range. The weight loss from $155-210^{\circ}$ c is 1.35%, which corresponds to the loss of free CH₂Cl₂ solvent molecules. From 210 °C to 270 °C, there is no weight loss. The weight loss from 270-310°C is 1.49%, which corresponds to the loss of free CH₃CN solvent molecule, being identical with the calculated value 1.54 %. All molecules integral tendencies for all of the TG curves are very similar, which display a main weight loss taking place between 310 and 600 °C, which is related to the release of the organic ligands. Complexes 1-5 are stable in air, supported by their stimulated and experimental powder X-ray diffraction (PXRD) patterns (Fig.S5 in the Supporting Information). The main peaks displayed in the measured patterns matched well with the simulated patterns generated from single-crystal X-ray diffraction data. Several missing or extra minor peaks could be attributed to the loss of the solvent molecules in the unit cell during the sample preparation, which is unavoidable.

UV-vis spectra

The UV-vis spectra of ligand HL, $Dy(acac)_3 \cdot 2H_2O$, and complexes 1-5 are

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measured at room temperature in CH₂Cl₂ solution and we displayed in Fig.S6 in the Supporting Information. For the HL ligand, two main absorption bands were clearly observed at ca. 251 and 368 nm. 251 nm may be attributed to $\pi \rightarrow \pi^*$ transition of the aromatic rings, and 368 nm may be attributed to $n \rightarrow \pi^*$ transition of - C=N - unsaturated double bands. Complexes **1-5** display similar absorption profiles centered at ca. 261 and 410 nm. Relative to the free Schiff base ligand, the two main bands are distinctly red-shifted, which might be assigned to the coordination effect between the Schiff base ligand and the Ln^{III} cations.

Magnetic properties

The solid-state magnetic susceptibility measurements of 1-5 were studied in the 2-300K range under an applied magnetic field of 1000 Oe (Fig.4) For 1, the observed room-temperature $\chi_{\rm M}T$ value is 33.09 cm³ K mol⁻¹, which is slightly higher than the theoretical value of 31.52 cm³ K mol⁻¹ for four uncoupled Gd^{III} ions (${}^{8}S_{7/2}$, g = 2).²¹ As shown in Fig.4, during the cooling process, the $\chi_M T$ remains almost invariable in the temperature range of 300-60 K, and then decreases sharply, reaching a minimum value of 15.21 cm³ K mol⁻¹ at 2 K. The downward slope for the $\chi_M T$ tending toward zero at base temperatures can only be attributed, in the absence of any zerofield splitting or close contact with other molecules, to a weak intramolecular antiferromagnetic exchange between the Gd^{III} centers. Between 2 and 300 K, the linear fit of χ_{M}^{-1} vs. T obeys the Curie-Weiss law, with $C = 33.19 \text{ cm}^{3} \text{ K mol}^{-1}$ and $\theta =$ -1.86 K. (Fig. S7 in the Supporting Information) The negative value further supports the occurrence of antiferromagnetic coupling between the Gd^{III} ion.²² According to the formula of literature,²³ we fit the $\chi_M T$ versus T data. Experimental $\chi_M T$ vs. T plot of Gd₄ clusters was fitted using the Hamiltonian (1) based on the model given in the inset of Fig.5. The data fitted nicely with g = 2.1 and J = -0.03 cm⁻¹ for 1 (R =0.997917). The low J values also suggest weak antiferromagnetic exchange between the adjacent Gd^{III} ions.

$$H_{\rm Gd4} = -J(\rm Gd1\rm Gd2 + \rm Gd1a\rm Gd2a + \rm Gd1\rm Gd1a + \rm Gd2\rm Gd1a + \rm Gd1\rm Gd2a) - g\mu_{\rm B}H \cdot \sum_{i=1}^{4} Gdi \quad (1)$$

For complex **2**, the $\chi_{\rm M}T$ value at room temperature is 48.53 cm³ K mol⁻¹, which

is close to the expected value of 47.28 cm³ K mol⁻¹ for four uncoupled Tb^{III} ions (⁷F₆, g = 3/2).²⁴ A slight increase in $\chi_M T$ is observerd at the temperature range of 300 to 75 K. Upon future decreasing the temperature, the value of $\chi_M T$ gradually reduces to 40.98 cm³ K mol⁻¹ at 2 K. This phenomenon may arise from the ferromagnetic interaction compensating the decrease of the $\chi_M T$ value which originated from the depopulation of the Stark sublevels.²⁵

For complex **3**, the $\chi_{\rm M}T$ value at room temperature is 58.33 cm³ K mol⁻¹, which is higher than the expected value of 56.68 cm³ K mol⁻¹ for four uncoupled Dy^{III} ions (⁶H_{15/2}, g = 4/3). As the temperature is decreased, the $\chi_{\rm M}T$ value of **3** is increases gradually to 61.29 cm³ K mol⁻¹ at 98 K, which may indicate the presence of weak ferromagnetic coupling between Dy^{III} ions. With further cooling, the $\chi_{\rm M}T$ value decreases to 44.60 cm³ K mol⁻¹ at 2 K.²⁶

For complexes 4 and 5, the the $\chi_M T$ value at room temperature are 56.49 and 48.17 cm³ K mol⁻¹, respectively, which are close to the expected theoretical values (4: 56.28; 5: 45.92 cm³ K mol⁻¹) for four non-interacting lanthanide ions. The $\chi_M T$ value gradually decreased to a minimum of 24.84 and 21.32 cm³ K mol⁻¹ at 2 K upon cooling from 300 K. This continuous decrease may be ascribed to the antiferromagnetic interactions between the Ln^{III} (Ho^{III} and Er^{III}) ions within tetranuclear unit and/or the thermal depopulation of Ln^{III} Stark sublevels.



Fig. 4 Temperature dependence of the $\chi_{\rm M}T$ products for complexes 1-5 at 2–300 K with a dc applied field of 1000 Oe.



Fig.5 The experimental $\chi_M T$ vs. T for complexes 1. Red solid line is the best fit obtained.

For complex 1, Magnetization measurements were investigated in the range of 0–8 T at 2–10 K (Fig.6). The plot of *M* versus *H* displays a steady increase with the increasing magnetic field. *M* reaches a value of 28.24 $N\beta$ at 2 K and 8 T, which is close to the theoretical saturation value for four Gd^{III} ions where g = 2. Magnetic entropy change $\Delta S_{\rm m}$, a key parameter in evaluating the MCE, can be derived by applying the Maxwell equation to the experimentally obtained magnetization data.(Fig.7)

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$$-\Delta S_m(T) = \int_0^H [\partial M(T,H) / \partial T]_H dH$$

In general, the $-\Delta S_{\rm m}$ values increase gradually as the temperature is reduced, but rise progressively with increasing applied fields, reaching a maximum of 25.08 J kg⁻¹ K⁻¹ at T = 2 K and $\Delta H = 7$ T, which is lower than the theoretical limiting value of 26.3 J kg⁻¹ K⁻¹ calculated from $nR\ln(2S+1)/M_{\rm w}$, where S = 7/2, and $M_{\rm w} = 2626.56$ g mol⁻¹. This difference between experimental and theoretical values may be attributed to antiferromagnetic interactions.²⁷





Fig. 6 Magnetization versus the dc field in the temperature range of 2-10 K for complex 1

Fig.7 The temperature-dependencies of $-\Delta Sm$ at selected ΔH values obtained from magnetization.

To investigate the dynamics of the magnetization, the temperature dependence of ac magnetic susceptibilities for complex 3 were characterized at the indicated frequencies (111–2311 Hz) under an oscillating ac field of 3 Oe. As shown in Fig.8 and Fig.9, both the temperature and frequency dependencies of the ac susceptibilities measured under zero-dc field for 3 reveal the presence of slow relaxation of the magnetization, typical of SMM behavior. Below approximately 20 K, both in-phase (χ') and out-of-phase (χ'') of **3** become frequency dependent, and two distinct peaks for the out-of-phase ac signals (χ'') is evident during the frequency range 311 Hz to 2311 Hz, indicating the possible occurrence of a multiple relaxation process. Such a behavior has been described in recent several reports and has been attributed to the occurrence of different Ln^{III} sites in the crystal lattice.²⁷ The data plotted as Cole–Cole plots show a relatively symmetrical shape (Fig.10), and the best fits of the out-of-phase vs. in-phase susceptibility in the range of 2–14 K were obtained with $\alpha =$ 0.11-0.53. This suggests a relatively wide distribution of the relaxation time and the presence of more than one relaxation mode.²⁹ The relaxation parameters in the format of $\ln(\tau)$ versus 1/T plots were analyzed using the Arrhenius law, $\tau = \tau_0 \exp(U_{\text{eff}}/k_{\text{B}}T)$, giving an effective energy barriers ($U_{\text{eff}}/k_{\text{B}}$) of 86.20K with a preexponential factor (τ_0) of 2.99×10^{-8} s for 3 (Fig.11). The obtained τ_0 value falls into the expected range of 10^{-5} - 10^{-12} s³⁰ for the Dy-based SMMs reported previously. Besides, Ac magnetic

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susceptibility data in zero dc field reveal that complexes 2, 4 and 5 do not show any out-of phase (χ'') ac signals typical of SMM under zero application of a dc field (Fig. S8 – S10).



Fig. 8 Temperature dependence of the in-phase(left) and out-of-phase(right) components of the ac



magnetic susceptibility for **3** in zero dc fields with an oscillation of 3.0 Oe.

Fig.9 Frequency dependence of the in-phase (left) and out-of-phase (right) ac susceptibility of 3

below14 K, under zero-dc field.



Fig. 10 Cole–Cole plots measured at 2–14 K for 3 ($H_{dc} = 0$ Oe), the solid lines are the best fits to the experimental data, obtained with the generalized Debye model with $\alpha = 0.11-0.53$.

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Fig. 11 Plot of $\ln(\tau)$ versus T^1 for **3**, the red solid line is fitted with the Arrhenius law

Conclusion

In conclusion, a new phenoxo-O bridged tetranuclear Dy^{III} complex and its Gd^{III}, Tb^{III}, Ho^{III}, Er^{III} analogues have been synthesized by using a chelating 8-hydroxyquinoline Schiff base and β -dikettonate coligand, in which four lanthanide ions are coplanar in a rhombic frame. The magnetocaloric effect (25.08 J kg⁻¹ K⁻¹) was detected for Gd complex. Moreover, magnetic studies of dynamics of the magnetizations for Dy complex, show that it exhibits slow magnetic relaxation behavior, typical of SMM behavior, resulting in a high energy barrier of 86.20 K $(\tau_0=2.99\times10^{-8}s)$, which is different from a previously studied {Dy₄} SMM^{27b} of multiple magnetic relaxation processes. Compared with the previous {Dy₄} SMM encapsulated by 5-(4-fluorobenzylidene)-8-hydroxylquinolin and acetylacetonate, we replaced the ligand with 5-(benzylidene)amino-8-hydroxylquinolin in this article. Two series of $\{Dy_4\}$ clusters exhibit similar tetranuclear structure, but they display remarkably difference in crystal space group and magnetic behaviors. For the previous Dy4 complex, it crystallize in the orthorhombic *pbcn* space group, and several peaks appears on the Ac magnetic susceptibility curves, and magnetic studies show that the exhibits two magnetic relaxation processes, giving two effective energy barriers, U_{eff} =48 K and U_{eff} = 121 K for the slow relaxation phase and fast relaxation phase, respectively. Whereas, for the Dy4 complex in this article, it crystallize in the monoclinic C2/c space group, and Ac magnetic susceptibility curves show two peaks.

One distinct peak is observed in 12 K, another peaks around 2 K is not complete. According to the Arrhenius law, effective energy barrier of 86.20 K (τ_0 =2.99×10⁻⁸s) were obtained. Compared two Dy4 complexes, the magnetic properties significant difference is mostly due to the minor change of terminal substituent of 8-hydroxylquinoline Schiff base ligand, which caused the different electron density and steric hindrance around the Dy^{III} ions. So we infer that SMMs behavior of lanthanide complexes can be finely adjusted by changing the terminal substituent of the 8-hydroxyquinoline Schiff base ligand, which can be a relatively simple way of attaining higher barrier SMMs as opposed to the more synthetically challenging methods, such as inducing coupling of the metal centers using radical bridges or organometallic complexes.^{6a} This methodology can provide a tool for future design of SMMs leading to potential applications in high-tech devices.

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Table of contents



Herein, we report the synthesis, structure, and magnetism of five tetranuclear Ln^{III} complexes encapsulated by 5-(benzylidene)amino-8-hydroxylquinoline and β -dikettonate coligand.