

羧酸配体取代基对席夫碱型双核镝(III)配合物结构和磁性的影响

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摘要: 以 *N*-(2-羟基-3-甲氧基苄基)氨基脒(Hhms)与不同取代基的羧酸(RCOOH)为配体, 合成了3例席夫碱类的中心对称双核镝基配合物 $[\text{Dy}_2(\text{Hhms})_2(\text{C}(\text{CH}_3)_3\text{COO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$ (**1**)、 $[\text{Dy}_2(\text{Hhms})_2(\text{C}_{14}\text{H}_9\text{COO})_2(\text{C}_2\text{H}_5\text{OH})_2(\text{CH}_3\text{OH})_2][\text{ZnCl}_4]$ (**2**) 和 $[\text{Dy}_2(\text{Hhms})_2(\text{C}_6\text{H}_3(\text{NH}_2)_2\text{COO})_2\text{Cl}_2] \cdot 2\text{CH}_3\text{CN}$ (**3**), 并对其进行了结构和磁性表征。结构分析表明, 配合物**1**和**2**保持了相似的单帽四方反棱柱配位构型, 但**1**与**2**中羧酸与Dy(III)键合的方式不同; 配合物**2**和**3**保持了相似的酚氧和羧酸桥联结构, 但由于配位小分子的不同, 配合物**3**中Dy(III)离子的配位几何构型与**2**有所不同。磁性测试结果表明, 配合物**3**在零场下观察到显著的单分子磁体行为, 具有磁翻转有效能垒96 K。相反, 配合物**1**仅表现了快的量子隧穿弛豫行为, 甚至配合物**2**没有单分子磁体的弛豫信号。借助结构特点和各向异性轴取向等关键信息, 对3例配合物的磁构效关系进行了讨论。研究结果表明利用羧酸配体取代基能够实现分子磁各向异性以及对称性的良好调控, 从而提高镧系单分子磁体磁弛豫行为。

关键词: 双核化合物; 镝; 磁性; 羧酸配体; 单分子磁体

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Replacement of Carboxylate Ligand Substituent on Modulation of Structures and Magnetic Properties in Salen-Type Dinuclear Dy(III) Complexes

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Abstract: Three salen-type centrosymmetric dinuclear Dy(III) complexes, $[\text{Dy}_2(\text{Hhms})_2(\text{C}(\text{CH}_3)_3\text{COO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$ (**1**), $[\text{Dy}_2(\text{Hhms})_2(\text{C}_{14}\text{H}_9\text{COO})_2(\text{C}_2\text{H}_5\text{OH})_2(\text{CH}_3\text{OH})_2][\text{ZnCl}_4]$ (**2**), and $[\text{Dy}_2(\text{Hhms})_2(\text{C}_6\text{H}_3(\text{NH}_2)_2\text{COO})_2\text{Cl}_2] \cdot 2\text{CH}_3\text{CN}$ (**3**) (Hhms=(2-hydroxy-3-methoxybenzylidene)-semicarbazide), were isolated with different substituted carboxylic acid ligand, and were characterized structurally and magnetically. Structural analyses illustrate that the Dy(III) ions in complexes **1** and **2** maintain similar monocapped square-antiprism geometries, but the coordination mode of carboxylate in **1** is different from that in **2**; complexes **2** and **3** possess similar phenoxy oxygen and carboxylate bridged structure whereas the coordination geometries around the Dy(III) ions are different between **3** and **2** due to the difference of coordinated small molecules. Magnetic characterizations reveal that significant single-molecule magnet (SMM) behavior was observed under zero dc field for complex **3**, with an effective energy barrier to the reversal of magnetization of 96 K. Conversely, complex **1** only showed fast quantum tunneling relaxation even **2** was SMM-silent. Furthermore, the magneto-structural correlations in these Dy₂ complexes were discussed. The results indicate

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that utility of carboxylate ligand substituent can give rise to good modulation in the molecular anisotropy and symmetry, hence the enhanced magnetic relaxation. CCDC: 2092500, **1**; 2092502, **2**; 2092503, **3**.

Keywords: dinuclear complex; dysprosium; magnetic properties; carboxylate ligand; single-molecule magnets

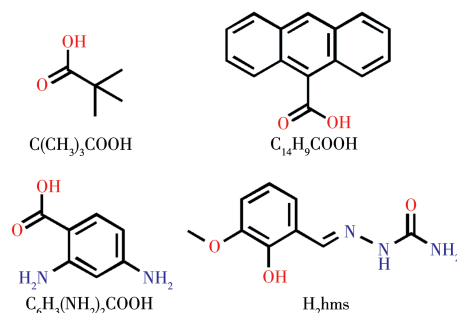
0 Introduction

Single-molecule magnets (SMMs), which exhibits slow relaxation of magnetization at the molecular level, are expected to be the smallest storage units and quantum objects, invoking intense research interest in the field of spintronic devices and quantum computing^[1-3]. Recently, optimizing the crystal field environment of a single Dy(III) center based on an electrostatic model allows blocking of magnetization reaching unprecedented liquid nitrogen temperatures^[4]. Whereas, encapsulating two or more spin centers complexes facilitate the generation of more sophisticated architectures and magnetic behavior, giving the new opportunities to design SMMs with augmented performances^[5-7]. The exploitation of new Dy(III) polymetallic complexes to drive understanding of influence factors that dictate the slow magnetic relaxation is still being established^[8-12].

For polymetallic Dy(III) - SMMs, the ligand field effect, the geometry, the local symmetry around the Dy(III) ions, and the existence of magnetic interactions between the Dy(III) sites will result in the significant divergence of magnetic relaxation behavior^[13-16]. Optimizing the electronic structure of molecules and unraveling internal magneto-structural correlations are essential driving forces behind the rapid development of novel nanomagnets. To achieve the objective, the design of polydentate ligands assembling various types of Dy(III) complexes and ligand field has become the primary consideration. Carboxylates exhibit excellent performance in the construction of complexes because of their demonstrated coordination motif versatility^[17-19]. And the diversity and variability of substitution groups of carboxylic ligands are conducive to the generation of appropriate steric hindrance fitting well with the coordination geometries of Dy(III) ions^[20-21]. Moreover, the origin of the concept of the hard-soft acid-base (HSAB) theory, lanthanide ion prefers to bond with oxygen atoms, and resulting adduct tend to have a more ionic

character in its bonding^[22-23]. The carboxylic ligands match the nature of Dy(III) ions and induce the orientation of electron density to produce magnetic anisotropy. Also, the incorporation of electron - donating groups (*e.g.*, amino, aryl, alkyl, alkoxy) on carboxylic ligands can pose positive effects on the electron density of the donor oxygen atoms and intensify coordination field strength-enhancing the magnetic properties of this family. However, carboxylate - based polymetallic Dy(III) - SMMs with intriguing magnetic behaviors are still scarce, which is probably attributed to the complexity of carboxylates coordination, resulting in unclear magnetic anisotropy orientation and a significant contribution of the quantum tunneling of magnetization (QTM) to the relaxation dynamics^[24-26].

Based on the above considerations, to further efficiently control the carboxylic coordination, we selected various carboxylic acid ligands with different steric hindrance and electron donor ability substituent and combined them with polydentate Schiff - base ligand with relatively fixed coordination cavities to construct polymetallic complexes (Scheme 1). Herein, three novel Dy(III)-based complexes, [Dy₂(Hhms)₂(C(CH₃)₃COO)₂(H₂O)₄](NO₃)₂ (**1**), [Dy₂(Hhms)₂(C₁₄H₉COO)₂(C₂H₅OH)₂(CH₃OH)₂][ZnCl₄] (**2**), and [Dy₂(Hhms)₂(C₆H₃(NH₂)₂COO)₂Cl₂] · 2CH₃CN (**3**) (H₂hms=2 - hydroxy - 3 - methoxybenzylidene)-semicarbazide) were isolated in a centrosymmetric binuclear architecture. The structural



Scheme 1 Structures of carboxylic acid ligands and Schiff-base ligand

characterization and magnetic properties of complexes **1-3** were investigated. Through magneto-structural correlations analysis, the present work highlights the importance of ligand substitution and molecule symmetry in controlling magnetic relaxation and provides a feasible way to develop high-performance carboxylate-based polymetallic SMMs.

1 Experimental

1.1 Materials and measurements

All chemical reagents and solvents were obtained commercially and used in the reactions without further treatment, except for the ligand of H₂hms, which was synthesized by an analogous method described in the literature^[21]. Powder X-ray diffraction measurements were carried out on a Bruker D8 ADVANCE X-ray powder diffractometer at 40 kV and 40 mA, using Cu K α radiation ($\lambda=0.154\ 18\ \text{nm}$) ranging from 5° to 50° (2 θ) to verify the phase purity of the polycrystalline samples. The FT-IR spectra were recorded with pressed KBr pellets in a range of 4 000-400 cm⁻¹ on a Tensor 27 spectrometer (Bruker Optics, Ettlingen, Germany). Elemental analyses (C, H, N) were collected on an Elementar Vario EL III analyzer. Magnetic susceptibility measurements were conducted on a Quantum Design MPMS-XL7 SQUID magnetometer in a temperature range of 2-300 K with 1 000 Oe applied field. Alternating-current (ac) measurements were performed on the same magnetometer at ac frequencies ranging from 1 to 1 000 Hz using a 2.0 Oe oscillating ac field. The measured susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

1.2 Synthesis of [Dy₂(Hhms)₂(C(CH₃)₃COO)₂(H₂O)₄](NO₃)₂ (**1**)

A mixture of Dy(NO₃)₃·6H₂O (0.045 6 g, 0.1 mmol), C(CH₃)₃COOH (0.010 2 g, 0.1 mmol) and H₂hms (0.021 0 g, 0.1 mmol) in methanol (4 mL) and dichloromethane (4 mL) was added sodium azide (0.006 5 g, 0.1 mmol). After stirring for 3 h, the resultant solution was filtered and allowed to stand undisturbed at room temperature. The yellowish block crystals suitable for single-crystal X-ray diffraction were

obtained by slow evaporation of the filtrate after 5 d. Yield: *ca.* 56% (32 mg) based on Dy(III). Elemental Anal. Calcd. for C₂₈H₄₆Dy₂N₈O₂₀(%): H, 4.07; C, 29.51; N, 9.83. Found(%): H, 4.43; C, 29.67; N, 9.52. IR (KBr, cm⁻¹): 3 340 (s), 3 043 (s), 2 584 (w), 2 420 (w), 1 667 (s), 1 568 (s), 1 451 (s), 1 415 (s), 1 385 (m), 1 366 (m), 1 357 (s), 1 225 (m), 1 089 (m), 1 018 (s), 956 (m), 787 (m), 741 (m), 669 (m), 614 (m), 493 (w).

1.3 Synthesis of [Dy₂(Hhms)₂(C₁₄H₉COO)₂(C₂H₅OH)₂(CH₃OH)₂][ZnCl₄] (**2**)

A mixture of DyCl₃·6H₂O (0.037 7 g, 0.1 mmol), ZnCl₂ (0.027 3 g, 0.2 mmol), C₁₄H₉COOH (0.133 2 g, 0.6 mmol) and, H₂hms (0.021 0 g, 0.1 mmol) in methanol (4 mL) and ethanol (4 mL) was added sodium azide (0.013 0 g, 0.2 mmol). After stirring for 3 h, the resultant solution was filtered and allowed to stand undisturbed at room temperature. The yellowish block crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of the filtrate after one week. Yield: *ca.* 45% (35 mg) based on Dy(III). Elemental Anal. Calcd. for C₅₄H₅₈Cl₄Dy₂N₆O₁₄Zn(%): H, 3.78; C, 41.97; N, 5.44. Found(%): H, 3.52; C, 41.69; N, 5.41. IR (KBr, cm⁻¹): 3 345 (s), 3 294 (s), 3 248 (s), 3 092 (m), 2 932 (m), 2 856 (m), 1 689 (s), 1 602 (m), 1 586 (s), 1 482 (s), 1 454 (s), 1 383 (s), 1 110 (s), 1 093 (m), 854 (w), 823 (w), 784 (w), 744 (m), 669 (m), 615 (m), 494 (w).

1.4 Synthesis of [Dy₂(Hhms)₂(C₆H₃(NH₂)₂COO)₂Cl₂]·2CH₃CN (**3**)

A mixture of H₂hms (0.021 0 g, 0.1 mmol), C₆H₃(NH₂)₂COOH (0.015 2 g, 0.1 mmol), and DyCl₃·6H₂O (0.037 7 g, 0.1 mmol) in acetonitrile (4 mL) was placed in a 20 mL Teflon-line autoclave kept for three days at 90 °C, and then cooled down to room temperature at a rate of 5 °C·h⁻¹ to form yellowish block crystals suitable for X-ray analysis. Yield: *ca.* 58% (35 mg) based on Dy(III). Elemental Anal. Calcd. for C₃₆H₄₀Cl₂Dy₂N₁₂O₁₀(%): H, 3.37; C, 36.13; N, 14.05. Found(%): H, 3.55; C, 36.49; N, 14.02. IR (KBr, cm⁻¹): 3 433 (s), 3 369 (s), 3 293 (s), 3 076 (m), 2 954 (s), 2 867 (w), 2 244 (w), 1 687 (s), 1 607 (s), 1 562 (s), 1 446 (s), 1 416 (s), 1 385 (s), 1 272 (m), 1 113 (s), 1 091 (s), 976 (m), 857 (w), 824 (w), 767 (w), 732 (m), 667 (m), 614 (m), 494 (w).

1.5 X-ray single-crystal diffraction analysis

Single-crystal X-ray data for complexes **1-3** were collected at room temperature on a Bruker Apex II CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). Cell determination and data reduction were processed with the SAINT processing program. The absorption correction based on multiscan was applied in SADABS. By using Olex2^[27], the structures were solved by direct methods with SHELXT and refined by full-matrix least-squares techniques against F^2 using SHELXL - 2014 programs^[28]. All non-hydrogen atoms were refined anisotropically. The acidic hydrogen atoms were found from the electron density map and were refined freely. All other hydrogen atoms were placed in calculated geometrical positions and refined using the riding model. The crystallographic data and structure refinement summary are summarized in Table S1 (Supporting information). Selected bond distances and angles are listed in Table S2.

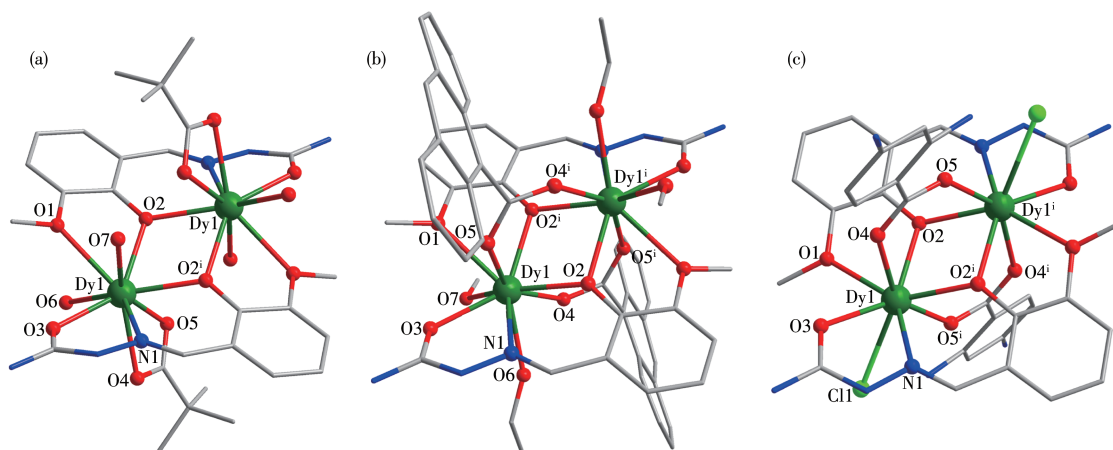
CCDC: 2092500, **1**; 2092502, **2**; 2092503, **3**.

2 Results and discussion

2.1 Description of crystal structures

Complexes **1-3** were structurally characterized by X-ray crystallography (Table S1). **1** and **2** crystallize in the monoclinic space group $C2/c$, while **3** crystallizes in space group $P2_1/n$. **1-3** are all centrosymmetric binuclear structures and the asymmetric unit of the com-

plex contains one-half of the entire molecule. The Dy(III) ions in **1** and **2** have similar monocapped square-antiprism geometries with an $\{O_8N\}$ coordination sphere (Fig.S1 and Table S3). Two antiparallel Hhms⁻ ligands bind to the Dy(III) ion by two phenoxy oxygen atoms (O2, O2ⁱ), one methoxy group (O1), one aldehyde group (O3), and one Schiff-base nitrogen atom (N1), and the remaining coordination sites are filled by two carboxylic oxygen atoms (O4, O5) and two H₂O molecules for **1** or a superposition of CH₃OH and C₂H₅OH for **2** (O6, O7) (Fig. 1). In **1**, the C(CH₃)₃COO⁻ groups act as chelating ligands, with it coordinating to a single Dy(III) ion, while in **2**, the C₁₄H₉COO⁻ groups bridge the two Dy(III) centers in a $\mu_2:\eta^1:\eta^1$ fashion. It is important to note that the different coordination patterns of carboxylate in **1** and **2** do not affect the configurational differences between them. For complex **3**, the Dy(III) centers are coordinated by Hhms⁻ ligands and carboxylic oxygen atoms in a manner essentially the same as that in **2** except for two alcohol oxygen atoms substituted by one Cl⁻ ion. Therefore, the Dy(III) ion in **3** has a $\{DyO_6NCl\}$ coordination sphere, forming a square-antiprism geometry. The two Dy(III) centers are bridged by two phenoxy oxygen atoms (O2 and O2ⁱ) of two Hhms⁻ ligands, besides, the RCOO⁻ groups with distinct terminal substituent bridge two Dy(III) atoms in a $\mu_2:\eta^1:\eta^1$ fashion in **2** and **3**, with the Dy...Dy intramolecular distance of 0.378 1(1), 0.365 6(8) and 0.364 8(7) nm respectively, as well as Dy—O—Dy



Hydrogen atoms and solvent molecules are omitted for clarity; Symmetry codes: ⁱ2-x, 1-y, 1-z for **1**; ⁱ1-x, 1-y, 1-z for **2**; ⁱ1-x, 1-y, 1-z for **3**

Fig.1 Molecular structures of complexes **1** (a), **2** (b), and **3** (c)

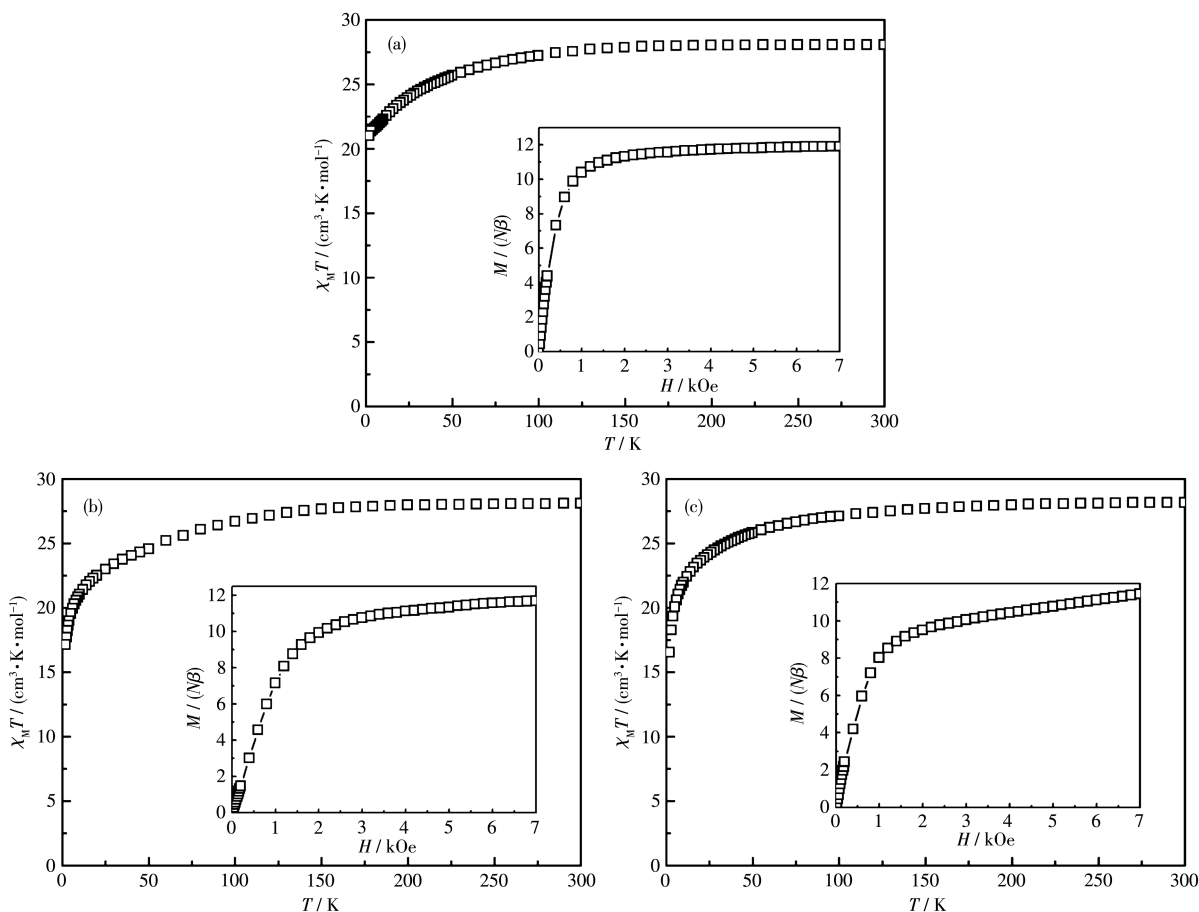
angle of 107.19° , 101.81° , and 101.23° respectively. The Dy—O bond lengths are in a range of 0.230 5(3)-0.263 7(2) nm, being the longest related to the methoxy oxygen atom distances. The shortest Dy—O bond lengths in **1-3** involve aldehyde oxygen (for **1**) or one of bridged phenoxide oxygen (for **2** and **3**) with 0.230 5(3), 0.232 7(2), and 0.231 5(5) nm respectively. The Dy—O distances within O, N, O-tridentate pocket of Hhms⁻ ligand are shorter than that within O,O-bidentate pocket of Hhms⁻ ligand. The Dy—C_{carboxylate} bond lengths of the bidentate bridging coordination mode in **2** (AVG: 0.237 1 nm) and **3** (AVG: 0.233 2 nm) show shorter distance than that of the chelating coordination mode in **1** (AVG: 0.244 2 nm), which may be associated with the different terminal substituents of carboxylic acid ligands. The Dy—N (0.247 8(6)-0.256 7(3) nm) and Dy—Cl (0.278 3(1) nm) bonds present quite long distances. Furthermore, the shortest inter-dimer Dy...

Dy distance is equal to 0.721 9, 1.018 9, and 0.835 6 nm respectively.

2.2 Magnetic properties

The magnetic properties of **1-3** were measured using a SQUID magnetometer. The sample purity was first checked by powder X-ray diffraction experiment comparing experimental diagram to theoretical one obtained from the crystal structure (Fig.S2).

The variable-temperature magnetic susceptibility for **1-3** was collected between 2 and 300 K under an applied magnetic field of H_{dc} being 1 kOe. At 300 K, $\chi_M T$ products were 28.07, 28.02, 28.16 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **1-3**, respectively (Fig.2), which are slightly lower than the value expected for two ensembles of Dy(III) ions in the free-ion approximation. On cooling, the $\chi_M T$ products underwent a slow decline and then decreased rapidly at low temperatures to reach a value of 21.00, 20.17, and 16.53 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ respectively at 2 K. The



Inset: variable-field magnetization data for **1-3** at 2 K where lines are guides to the eyes

Fig.2 Temperature dependence of $\chi_M T$ for complexes **1-3** under 1 000 Oe field

reduction of $\chi_M T$ for all three complexes is accounted for by the gradual depopulation of the Stark sublevels and/or intramolecular antiferromagnetic interactions. The magnetization data of **1-3** at 2 K are depicted in the inset of Fig.2. The plots of M vs H showed a rapid increase below 1 kOe, and the slight increase reaching the maximum magnetizations of $11.9N\beta$, $11.0N\beta$, $11.4N\beta$ at 7 kOe, which were much lower than the theoretical saturation value of $20N\beta$ for the Dy_2 dimer. The unsaturated magnetization indicates strong magnetic anisotropy of $Dy(III)$ ions^[29-30].

The magnetization relaxation dynamics were investigated by studying the temperature (T) and frequency (ν) dependence of ac magnetic susceptibilities. Complex **2** displayed no out-of-phase signal in ac susceptibility measurements in zero-field (Fig.S3). As a result of a strong QTM of $Dy(III)$ ions, the temperature-dependent out-of-phase signals of **1** only showed a small tail below 4 K (without peak maximum) under zero dc field (Fig.3).

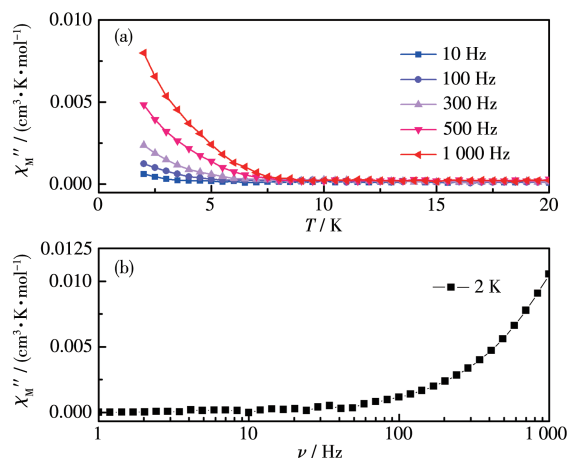


Fig.3 Temperature-dependent out-of-phase χ'' ac susceptibility signals (a) and frequency-dependent out-of-phase χ'' ac susceptibility signals (b) for **1** under zero dc field

For complex **3**, the out-of-phase (χ'') component of the temperature-dependent ac susceptibility exhibited one maximum in the 3.5 K (100 Hz)-8 K (1 000 Hz) range, which indicates the slow relaxation of magnetization of **3** (Fig.4). But a tail of the peak was observed below 3 K, and this observation suggests a temperature-independent QTM regime at lower temperatures, as is

often observed for $Ln(III)$ -containing systems. Consistently, the frequency dependence of the maximum in association with single relaxation mode appeared on the plot of the χ'' vs the frequency between 1 and 1 000 Hz. The Cole-Cole plot of χ'' vs χ' clearly identified single relaxation process and were fitted using a generalized Debye model^[31] with CCFIT package^[32] to extract the relaxation times (τ) (Fig.S4). The fitting gave a relatively narrow distribution of τ with a small coefficient α from 0.19 to 0.34. Insight into the dynamic magnetization under zero dc field of **3** was obtained through plots of $\ln \tau$ vs T^{-1} (Fig.5). An Arrhenius fitting of the high-temperature region gave unphysical parameters of $U_{eff}=68$ K and $\tau_0=6.30\times 10^{-8}$ s. In the whole temperature range, a combination of multiple relaxation pathways including Orbach, Raman, and QTM processes can be considered here. The data for **3** were fitted using Eq.1: $\tau^{-1} = \tau_{QTM}^{-1} + CT^n + \tau_0^{-1} \exp[-U_{eff}/(k_B T)]$, where U_{eff} is the Orbach parameters, C and n are the Raman parameters, and τ_{QTM}^{-1} is the QTM rate. The best fit parameters were found to be $U_{eff}=96$ K, $\tau_0=3.1 \times 10^{-10}$ s, $C=0.122$ s⁻¹·K^{-4.77}, $n=4.77$ and $\tau_{QTM}=5.7$ ms. To get a better understanding of the magnetic relaxation, we also tried to fit the relaxation time of zero-field data with only QTM and Raman processes, however, no better results were obtained by leaving out the Orbach term (Fig.S5).

The ac magnetic susceptibility was further investigated under an applied static field. Applying a dc field of 1 000 Oe induces slower relaxation with shifting peak maxima toward lower frequency (Fig.S6), indicating a significant suppression of QTM. Cole-Cole plots in a range of 4-9 K were obtained (Fig.S7) and fitted using the generalized Debye model^[31] to give the relaxation time τ (Fig.5) and distribution coefficient α (0.15-0.27). The thermal energy barrier was estimated from the high-temperature data of $\ln \tau$ vs T^{-1} plot to be 83 K with $\tau_0=2.1\times 10^{-8}$ s (Fig. 5). An additional term of Raman processes was required to fit the relaxation time behavior in the whole temperature range. The obtained satisfied parameters were $U_{eff}=98$ K, $\tau_0=7.4\times 10^{-9}$ s, $C=0.133$ s⁻¹·K^{-4.32}, $n=4.32$. Furthermore, if we only considered the Raman process for τ without the Orbach process, the fitting line did not fit well the $\ln \tau$ vs T^{-1} plots

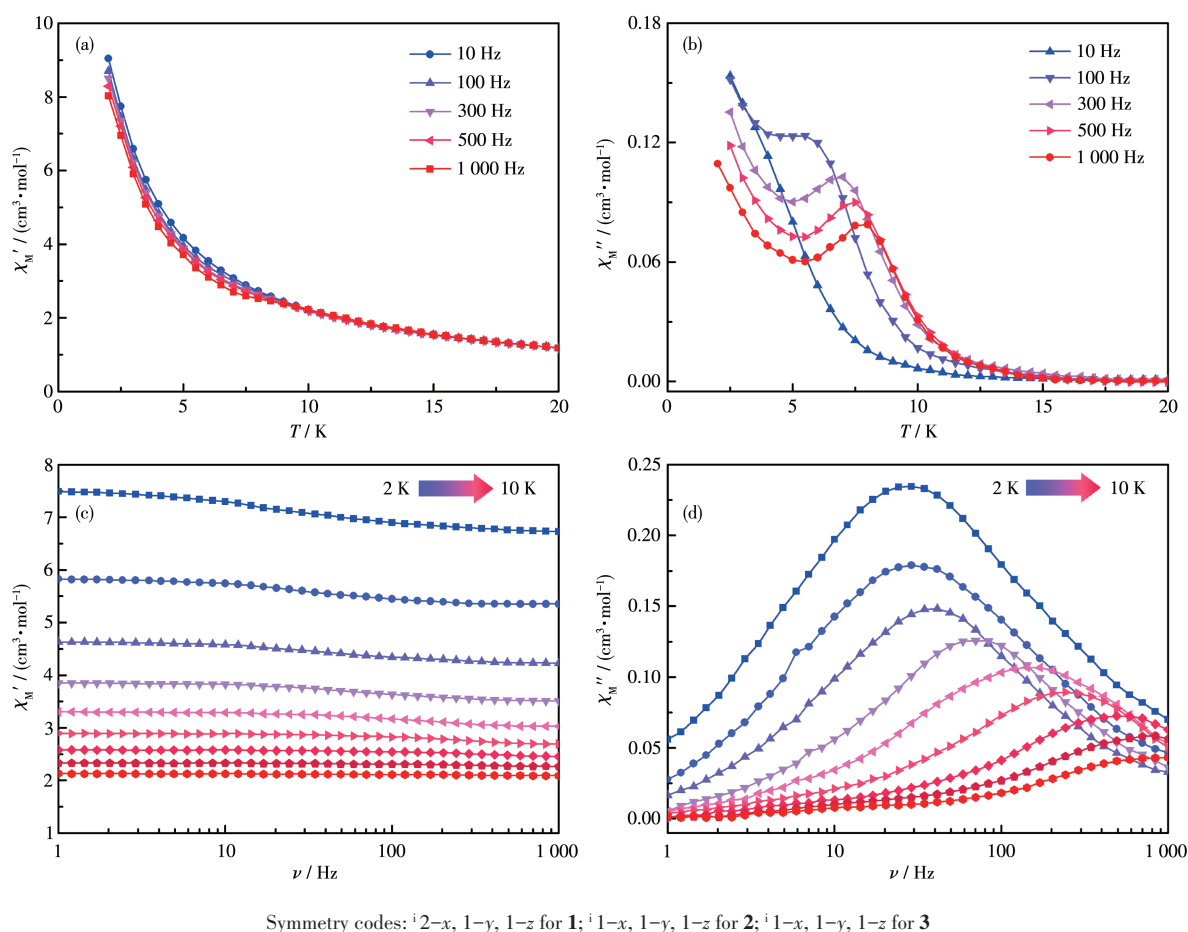


Fig.4 Temperature-dependent in-phase χ' (a) and out-of-phase χ'' (b) ac susceptibility signals for **3** under 0 Oe dc field;
Frequency-dependent in-phase χ' (c) and out-of-phase χ'' (d) ac susceptibility signals for **3** under 0 Oe dc field

(Fig.S5), also suggesting the existence of a thermally activated relaxation in **3**.

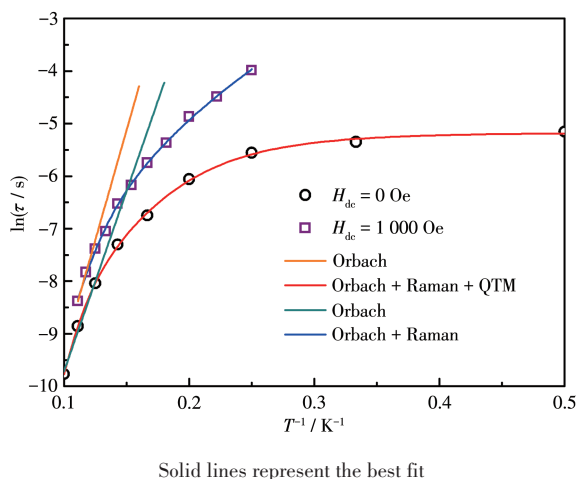


Fig.5 Relaxation data plotted as $\ln \tau$ vs T^{-1} for **3**

From the ac susceptibilities, we can see that complex **3** has the highest energy barrier. The structures of **2** and **3** are analogous, with the major difference being

in R substituent of carboxylate ligand and the coordinated small molecules with four superposed $\text{CH}_3\text{OH}/\text{C}_2\text{H}_5\text{OH}$ in **2** and two Cl^- in **3**. It should be noted that there is no change in the coordination modes of Hhms^- and RCOO^- between them. In addition, complexes **1** and **2** have a similar coordination configuration, with the main distinction only in the bonding mode of carboxylate which leads to the relative differences in the spatial arrangement of ligands. However, their magnetic properties are quite different: **1** exhibits a frequency-dependent behavior under zero dc field though without a clear peak, while **2** does not show magnetic relaxation behavior.

To further better understand the SMM properties of **1-3**, Fig.6 depicts the simulated principal magnetic axes of Dy(III) ions in each molecule defined by the Magellan program^[33]. The directions of the calculated anisotropy axis of Dy(III) in **1** are found to be tilted

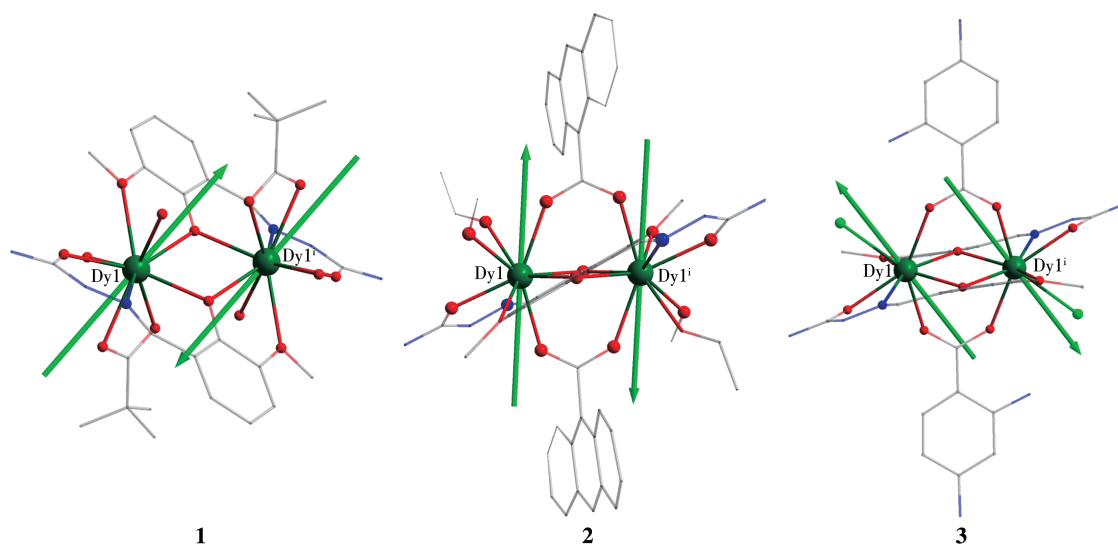


Fig.6 Magnetic anisotropy axes (green lines) predicted by Magellan program for Dy(III) centers in complexes **1-3**

towards the O4 atom belonging to the bidentate $\text{—C(CH}_3)_3\text{COO}^-$ anion and bridged phenoxo oxygen atoms (O2). Both of them make a small angle of 17.4° and 34° respectively. While the anisotropy axes of complex **2** show parallel arrangement through the middle of each $\text{C}_{14}\text{H}_9\text{COO}^-$ ligands, almost perpendicular to the bridged phenoxo oxygen atoms (O2 and O2ⁱ). For dinuclear complex **3**, the anisotropy of the Dy(III) ion is nearly oriented along with the Dy—O_{carboxylate} (O4) and Dy—Cl bonds, which deviation angles are in a range of 17.5° – 18.9° . These illustrate the fact that the bonding mode of carboxylate and the coordination of chloride anions affect the magnetic anisotropy of the Dy(III) ion and the SMM properties.

From the analysis of the anisotropic axis above, the most magnetic axes in the ground states are closer along with the carboxylic oxygen moieties. It is well-known that the magnetic anisotropy of an Ln(III) ion is extremely sensitive to its coordination environment^[34-39]. Even changes in the second coordination sphere ligated atoms could also lead to a significant variation on the single-ion anisotropy of the Ln(III) ions, as demonstrated by Sessoli and co-workers^[40-42]. In **3**, the two strongly electron-donating groups —NH_2 through inductive effects increase the charge of axially shortest carboxylic oxygen donor thus strengthening the axial component of crystal field relative to **1** and **2**. Careful inspection of the bond distance of complexes **1-3**

reveals that the different electron-donating effects induced by the R substituent are necessarily felt by the carboxylic oxygen ligands, and consequently has an effect on the strength of the chemical bond to the Dy(III) ions. This is indeed suggested by the shortest Dy—O_{carboxylate} bond for **3** (Dy—O4 0.232 6(4) nm, Dy—O5 0.233 7(5) nm). Whilst simultaneously, coordination of a chloride ion, in place of two solvent molecules (H_2O or CH_3OH /EtOH), reduces the coordination number, resulting in the Dy(III) ions in square antiprismatic environments with D_{4d} symmetry, which are much different from the monocapped square-antiprism in **1** and **2**. Moreover, among complexes **1-3**, the shortest intramolecular Dy $\cdots$ Dy distances (0.364 8(7) nm) and the smallest Dy—O—Dy angles (101.23°) are found for **3**, which may have a positive influence on the magnetic exchange coupling between two Dy(III) ions. In contrast to **3**, complex **2** did not show magnetic relaxation behavior. It might be associated with the relatively high charge distribution of the O_{phenoxo} atoms (O2 and O2ⁱ) lying on the transverse plane (perpendicular to the magnetic anisotropy easy axis) which contributes to transverse ligand field, and thus is disadvantageous to obtain the high magnetic anisotropy of oblate Dy(III) ion. In total, the different magnetic properties of **3** and **1-2** mainly result from the differences of ligand substitution by the non-coordinating electron-donating group, coordination geometry, and magnetic interaction between two Dy(III)

ions. The results emphasize that the utility of the ligand substitution can give rise to good modulation in molecule symmetry, as well as the magnetic anisotropy of Ln(III) ion, thus improving SMM performance.

3 Conclusions

In summary, a series of dinuclear Dy(III) complexes based on different substituted carboxylate ligand and Schiff-base H₂hms ligands have been reported. In complexes **1** and **2**, donor atom sets around the Dy(III) ions are the nearly same as a {DyO₈N} coordination sphere, whereas, in **3**, the Dy(III) ions exhibit a {DyO₆NCl} coordination environment. Complex **3** exhibited zero-field SMM behavior with a high thermal energy barrier for the reversal of the magnetization (96 K), revealing a significant improvement in performance across the series. The large U_{eff} value observed for **3** is a consequence of the enhanced magnetic anisotropy and local symmetry promoted by the presence of the significant electron-donating groups —NH₂ on the carboxylic oxygen atoms and the coordinated chloride ligands reducing the coordination number of the Dy(III) ions, resulting in a higher symmetry environment (D_{4d} symmetry) of the Ln(III) ions. The results demonstrate that the non-coordinating ligand substitution and coordination small molecule play essential roles in charge distributions of the ligand-field environments and molecular symmetry thus an SMM performance, which should be considered seriously and utilized efficiently during the rational design of new SMMs.

Supporting information is available at <http://www.wjhxxb.cn>

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