

A Dinuclear Dysprosium-2-quinolinecarboxylate-1, 10-Phenanthroline Compound: Crystal Structure and Magnetism Postprint

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Abstract

A dinuclear dysprosium(III) compound, $[\text{Dy}_2(\mu_2\text{-OH})_2(\text{QLC})_4(1,10\text{-phen})_2] \cdot 4\text{H}_2\text{O}$ (1) (QLC = 2-quinolinecarboxylate and 1,10-phen = 1,10-phenanthroline), was synthesized and structurally and magnetically characterized. Compound 1 crystallizes in triclinic system, space group P with $a = 10.9439(3)$, $b = 11.2823(3)$, $c = 12.2323(4)$ Å, $\alpha = 107.446(3)^\circ$, $\beta = 91.700(3)^\circ$, $\gamma = 91.511(2)^\circ$, $V = 1439.25(8)$ Å³, $Z = 1$, $\text{C}_{64}\text{H}_{50}\text{N}_8\text{O}_{14}\text{Dy}_2$, $M_r = 1480.12$, $D_c = 1.708$ g/cm³, $\rho_{\text{calc}} = 2.653$ mm⁻¹ and $F(000) = 734$. The final $R = 0.0366$ and $wR = 0.0736$ for 5816 observed reflections with $I > 2(I)$. Compound 1 contains the mononuclear $[\text{Dy}(\text{QLC})_2(1,10\text{-phen})]$ subunit formed from one 1,10-phen and two QLC ligands chelating Dy(III) ion. Two mononuclear $[\text{Dy}(\text{QLC})_2(1,10\text{-phen})]$ subunits are bridged by a pair of $\mu_2\text{-OH}$ groups to give a centrosymmetric dinuclear $[\text{Dy}_2(\mu_2\text{-OH})_2(\text{QLC})_4(1,10\text{-phen})_2]$ with each Dy(III) ion being eight-coordinated. Detailed susceptibility measurements revealed that compound 1 does not show slow magnetic relaxation under zero direct-current field but exhibits field-induced slow magnetic relaxation under 2 kOe applied field.

Full Text

Preamble

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ABSTRACT

A dinuclear dysprosium(III) compound, $[\text{Dy}(\mu\text{-OH})(\text{QLC})(1,10\text{-phen})] \cdot 4\text{H}_2\text{O}$ (**1**) (QLC = 2-quinolinecarboxylate and 1,10-phen = 1,10-phenanthroline), was synthesized and structurally and magnetically characterized. Compound **1** crystallizes in the triclinic system, space group P with $a = 10.9439(3)$, $b = 11.2823(3)$, $c = 12.2323(4)$ Å, $\alpha = 107.446(3)^\circ$, $\beta = 91.700(3)^\circ$, $\gamma = 91.511(2)^\circ$, $V = 1439.25(8)$ Å³, $Z = 1$, C₂₄H₂₀N₂O₁₀Dy, $M_r = 1480.12$, $D_c = 1.708$ g/cm³, $\rho_{\text{calc}} = 2.653$ mm⁻¹ and $F(000) = 734$. The final $R = 0.0366$ and $wR = 0.0736$ for 5816 observed reflections with $I > 2\sigma(I)$. Compound **1** contains the mononuclear $[\text{Dy}(\text{QLC})(1,10\text{-phen})]$ subunit formed from one 1,10-phen and two QLC ligands chelating the Dy(III) ion. Two mononuclear $[\text{Dy}(\text{QLC})(1,10\text{-phen})]$ subunits are bridged by a pair of $\mu\text{-OH}$ groups to give a centrosymmetric dinuclear $[\text{Dy}(\mu\text{-OH})(\text{QLC})(1,10\text{-phen})]$ structure with each Dy(III) ion being eight-coordinated.

Detailed susceptibility measurements revealed that compound **1** does not show slow magnetic relaxation under zero direct-current field but exhibits field-induced slow magnetic relaxation under a 2 kOe applied field.

Keywords: dinuclear Dy(III) compound; 2-quinolinecarboxylate; slow magnetic relaxation; crystal structure

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INTRODUCTION

Over the past two decades, research on the synthesis and study of single-molecule magnets (SMMs) has intensified due to their potential applications in ultra-high density information storage and molecular spintronics [1-4]. Lanthanide ions are particularly appealing candidates for constructing SMMs because they possess many electrons in f orbitals and exhibit strong spin-orbit coupling effects. Consequently, numerous lanthanide-based SMMs have been reported recently [5-8]. Among these lanthanide ions, Dy(III), a late lanthanide (4f, $n > 7$) with a large angular momentum value, displays stronger magnetic anisotropy than early lanthanides ($n < 7$) [9]. Additionally, the Dy(III) ion has an odd number of 4f electrons ($n = 9$) and is a Kramers ion with doubly-degenerate ground states [10], which has led to a wealth of interesting Dy-based SMMs, including mononuclear Dy(III) [11,12], dinuclear Dy [13-16], and multinuclear Dy(III) clusters [17].

The magnetic relaxation of lanthanide ions is strongly influenced by their coordination environment [18,19]. Carboxylate groups can form robust coordination bonds with lanthanide ions, providing high affinity for oxygen donors, which makes them suitable candidates for creating stable SMMs [20]. Furthermore, lanthanide ions have large ionic radii, high coordination numbers, and variable geometries. Carboxylate-based ligands offer diverse coordination modes due to their multiple coordination sites, which accommodate the flexible coordination geometries of lanthanide ions well [21]. In this study, the rigid ligand 2-quinolinecarboxylate (QLC) with one nitrogen and two carboxy-

late oxygen donors was selected for constructing dysprosium(III) SMMs, while 1,10-phen was employed as an ancillary capping ligand. The large skeleton of 1,10-phen serves as a chelating ligand to terminate propagation of the Dy-2-quinolinecarboxylate linkage into one-dimensional polymeric chains. The resulting centrosymmetric dinuclear compound comprises two eight-coordinated Dy(III) ions. In compound 1, each Dy(III) ion is chelated by two QLC ligands with one 1,10-phen acting as a terminal ligand, and two Dy(III) ions are bridged by a pair of μ -OH groups to form the dinuclear $[\text{Dy}(\mu\text{-OH})(\text{QLC})(1,10\text{-phen})]$ unit. To our knowledge, only the dinuclear lanthanide-QLC compound tetranuclear $[\text{Dy}(\text{QLC})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ and one-dimensional chain structures of $[\text{Pr}(\text{QLC})(\text{H}_2\text{O})]$ and $[\text{Dy}(\text{QLC})(\text{H}_2\text{O})]$ have been reported [22-25]. In these compounds, the lanthanide centers are bridged by QLC ligands, which differs from the μ -OH groups bridging Dy(III) centers in the dinuclear structure of 1. Herein, we present its synthesis, crystal structure, and magnetic properties.

EXPERIMENTAL

2.1 Materials and Instruments

All chemicals were of reagent grade and used as commercially obtained. Elemental analyses were carried out on an Elementar Vario EL III analyzer, and IR spectra (KBr pellets) were recorded on a PerkinElmer Spectrum One. Thermogravimetric measurements were performed with a Netzsch STA449C apparatus under nitrogen atmosphere in Al₂O₃ containers with a heating rate of 10 °C/min from 30 to 800 °C. Magnetic measurements were carried out on a Quantum Design MPMS-XL5 SQUID magnetometer in the temperature range of 2-300 K. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms [26].

2.2 Synthesis of the Compound $[\text{Dy}(\mu\text{-OH})(\text{QLC})(1,10\text{-phen})] \cdot 4\text{H}_2\text{O}$ (1)

A mixture of Dy₂O₃ (0.0186 g, 0.05 mmol), 2-quinolinecarboxylic acid (0.0346 g, 0.2 mmol), and 1,10-phenanthroline (0.0198 g, 0.1 mmol) in 10 mL H₂O was sealed in a 25 mL Parr Teflon-lined stainless-steel vessel. The vessel was heated to 140 °C, maintained at this temperature for 2 days, and then cooled naturally to form block colorless crystals of 1. The crystalline product was dried at ambient temperature (yield: 53.1% based on Dy). IR (KBr pellet, cm^{-1}): 3453(s), 3061(m), 1735(w), 1699(w), 1626(s), 1593(s), 1577(m), 1561(w), 1550(m), 1518(w), 1466(m), 1428(w), 1410(s), 1386(m), 1377(m), 1345(w), 1302(w), 1267(w), 1216(w), 1181(w), 1149(w), 1103(w), 1049(w), 1019(w), 976(w), 960(w), 898(w), 880(w), 864(w), 847(w), 807(w), 785(w), 774(w), 743(w), 729(w), 669(w), 629(w), 598(w), 521(w), 499(w), 483(w), 450(w).

2.3 Single-Crystal Structure Determination

A single crystal of **1** with dimensions of 0.09 mm × 0.06 mm × 0.05 mm was selected and mounted on a glass fiber. Single-crystal X-ray diffraction data were collected on a Rigaku Oxford SuperNova Single Source diffractometer with an Eos detector and Mo-K radiation ($\lambda = 0.71073 \text{ \AA}$). The CrysAlisPro software (Agilent Technologies) was used for collecting data frames, indexing reflections, determining lattice constants, and performing absorption correction and data reduction [27]. The structure was solved by direct methods and successive Fourier difference synthesis (SHELXT-2014) [28] and refined by full-matrix least-squares method on F^2 (SHELXTL-2014) [29]. The lattice water molecule (O2W) is disordered over two positions with occupancies of 0.649 and 0.351. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon atoms were assigned to calculated positions. Hydrogen atoms bound to oxygen atoms were located in difference Fourier maps and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{O})$ and O-H bond distance of 0.85 Å. Hydrogen atoms of the disordered O2W could not be located. The R values are defined as $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ and $wR = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$. The final $R = 0.0366$ and $wR = 0.0736$ ($w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.6918P]$, where $P = (F_o^2)/3$) for 5816 observed reflections. $(\Delta)_{\text{max}} = 0.002$, $(\Delta)_{\text{min}} = 1.628$ and $(\Delta)_{\text{min}} = -0.790 \text{ e/\AA}^3$. The largest residual peak is within 0.9 Å of the Dy(III) ion, resulting from the smear effect of the lanthanide ion. Selected important bond parameters are listed in Table 1.

RESULTS AND DISCUSSION

3.1 Crystal Structure Description

Compound **1** features a centrosymmetric dinuclear structure with one Dy(III) ion, one hydroxyl group, two QLC ligands, one 1,10-phen ligand, and two solvent water molecules in the asymmetric unit. As shown in Fig. 1 [Figure 1: see original paper], the Dy(1) ion is eight-coordinated by three carboxylate oxygen atoms (O(2), O(4), and O(5)) and one nitrogen atom N(1) from two QLC ligands, two nitrogen atoms from one 1,10-phen ligand, and two hydroxyl oxygen atoms (O(1) and O(1A)) (Fig. 2 [Figure 2: see original paper]). The Dy-O and Dy-N bond distances range from 2.227(3) to 2.472(3) Å and 2.563(4) to 2.634(3) Å, respectively (Table 1). The two crystallographically independent QLC ligands display two types of coordination modes: one binds a Dy(III) ion in a chelating mode via its carboxylate group, while the other chelates a Dy(III) ion through its nitrogen and one carboxylate oxygen atom (Fig. 1). As depicted in Fig. 1, one 1,10-phen and two QLC ligands simultaneously chelate a Dy(III) ion to form a mononuclear [Dy(QLC)(1,10-phen)] unit. Two [Dy(QLC)(1,10-phen)] subunits are bridged by a pair of -OH groups to generate a centrosymmetric dinuclear [Dy(-OH)(QLC)(1,10-phen)] unit with a Dy(1) ⋯ Dy(1) distance of 3.664(2) Å and a Dy(1)-O(1)-Dy(1) angle of 109.92°. Intramolecular ⋯ interactions between aromatic rings of the QLC ligands and 1,10-phen ligands are observed (Fig. 1) with centroid-to-centroid

distances of 3.7007(1), 3.7340(1), 3.7258(1), and 3.8942(1) Å and dihedral angles of 3° and 6°, respectively. In the crystal packing, the closest intermolecular Dy ⋯ Dy separation is 9.988 Å (Fig. 3 [Figure 3: see original paper]).

Additionally, intermolecular ⋯ interactions between aromatic rings of the QLC ligands are observed with centroid-to-centroid distances of 3.5000(1), 3.8092(1), and 3.6151(1) Å and dihedral angles of 3°, 2°, and 0°, respectively. The O(1)W lattice water molecule bonds to the dinuclear molecule through hydrogen bonding between the water molecule and hydroxyl oxygen (Table 2). Finally, hydrogen bonds between the lattice water molecules are observed in compound 1 (Table 2).

3.2 IR Spectra and TG Analysis

The IR spectrum of compound 1 exhibits a broad absorption centered at 3453 cm⁻¹, corresponding to O-H stretching vibrations of hydroxyl groups and water molecules. Strong bands at 1626 and 1593 cm⁻¹ belong to asymmetric stretching vibrations of the carboxylate group, while symmetric stretching vibrations appear at 1410 and 1386 cm⁻¹. The thermogravimetric analysis (TGA) curve of 1 is shown in Fig. 4 [Figure 4: see original paper]. The TGA curve shows the first weight loss between 30 and 150 °C, attributed to removal of solvent water molecules (observed 5.11%, calculated 4.86%). Combustion of the organic ligands begins at 230 °C.

3.4 Magnetic Properties

Direct-current (dc) magnetic susceptibilities of 1 were collected under an applied magnetic field of 1 kOe in the temperature range of 300–2 K. The magnetic properties of 1 in the form of χT versus T , where χ is the molar magnetic susceptibility per dinuclear molecular unit, are shown in Fig. 5 [Figure 5: see original paper]. The χT value is 28.29 cm³ K mol⁻¹ at 300 K, consistent with the expected value for two uncoupled Dy(III) ions in the $^6H_{5/2}$ ground state ($S = 5/2$, $L = 5$, $g = 4/3$, and $C = 14.17$ cm³ K mol⁻¹). As the temperature is lowered, the χT product increases gradually to a maximum value of 31.02 cm³ K mol⁻¹ at 44 K. Upon further cooling, the χT product decreases sharply to a minimum value of 22.58 cm³ K mol⁻¹ at 2 K (Fig. 5). A protuberance around 44 K in the χT versus T curve indicates intramolecular ferromagnetic interaction between the Dy(III) ions within the dimeric unit. This interaction is strong enough to compensate for the decrease in χT resulting from depopulation of Stark states. However, such intramolecular ferromagnetic interaction at higher temperature is rarely observed for lanthanide compounds, as it is generally masked by thermal population of low-lying excited states and strong magnetic anisotropy of lanthanide ions [30,31]. The decrease in χT products at low temperature suggests that intermolecular antiferromagnetic coupling begins to dominate the magnetic behavior for the ground states of 1.

Field dependence of the magnetization at 2 K shows a rapid increase at low

field followed by a slow linear increase at high field (Fig. 5 insert). The M value at 50 kOe is 16.8 N at 2 K, which is much lower than the theoretical saturation value of 20 N, indicating large magnetic anisotropy for Dy(III) ions. The reduced M value can be ascribed to the small total quantum number for Dy(III) ions produced by depopulation of Stark levels of the H / g ground state under ligand-field perturbation [32].

To probe slow magnetic relaxation behavior, alternating-current (ac) magnetic susceptibility measurements were performed on 1. Under zero-dc field with an ac field of 2.5 Oe, no peaks were observed in the in-phase (χ') and out-of-phase (χ'') susceptibilities versus T curves at the high frequency of 997 Hz for 1 (Fig. 5b). Thus, compound 1 shows no slow magnetic relaxation, which may result from zero-field quantum tunneling of magnetization frequently associated with lanthanide ions [33]. To suppress quantum tunneling of magnetization, a dc field of 2 kOe was applied. As shown in Fig. 5b, well-shaped peaks are observed in the χ' and χ'' susceptibilities versus T curves at 997 Hz (Fig. 5b), indicating that quantum tunneling of magnetization of Dy(III) ions in compound 1 is suppressed. The temperature dependences of χ' and χ'' susceptibilities under 2 kOe dc field for 1 (Fig. 5b) demonstrate that compound 1 exhibits field-induced slow magnetic relaxation.

CONCLUSION

In conclusion, $[\text{Dy}(\mu\text{-OH})(\text{QLC})(1,10\text{-phen})] \cdot 4\text{H}_2\text{O}$ (1) constructed from QLC and 1,10-phen mixed ligands has been synthesized and characterized. Compound 1 consists of mononuclear $[\text{Dy}(\text{QLC})(1,10\text{-phen})]$ subunits bridged by $\mu\text{-OH}$ groups to form a dinuclear structure. While compound 1 shows no slow magnetic relaxation under zero-dc field, likely due to fast magnetic relaxation, it exhibits clear field-induced slow magnetic relaxation under an applied magnetic field.

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