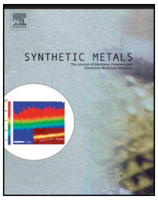
Synthetic Metals 211 (2016) 142–146

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Observation of single-molecule magnetic behavior in dinuclear Schiff base dysprosium(III) complex

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ARTICLE INFO

Article history:
Received 2 September 2015
Received in revised form 19 November 2015
Accepted 30 November 2015
Available online 7 December 2015

Keywords:
Dysprosium
Single-molecule magnet
Dinuclear
Schiff base

ABSTRACT

A dinuclear dysprosium(III) complex, namely $[Dy_2(L)_2(NO_3)_2(MeOH)_4]$ (**1**) has been synthesized by Schiff base ligand salicylidene-*o*-aminophenol (H_2L) with $Dy(NO_3)_3{\cdot}6H_2O$. Single crystal X-ray diffraction reveals that the dysprosium (III) centre in the dinuclear unit is 8-coordinated bridged by the phenoxo group of two Schiff base ligands, giving a dodecahedron geometry. Magnetic susceptibility studies reveal that complex **1** shows single molecule magnetic behavior with an energy barrier of 75.9 K.

1. Introduction

In the past two decades, the study of single-molecule magnets (SMMs) has been of increasing interest because of their potential applications in ultra-high density information storage at the molecular level and as qubits in quantum computation [1–3]. A large number of complexes displaying this property have been reported since the discovery in 1993 of the first SMM, Mn_{12} acetate [4]. After that, manganese, iron, cobalt, and nickel complexes with polynuclear topologies have been extensively studied for their unique SMM properties [5–8]. Compared to the 3d analogues, 4f-based compounds are more appealing for the development of higher-barrier SMMs, due to the large inherent anisotropy of the lanthanide ions. A number of 3d–4f SMMs have been reported [9–14], pure lanthanide SMMs are relatively scarce [15–20]. The latter molecules are rare owing to the difficulty in promoting magnetic interactions in these systems. These interactions are attained by the overlap of bridging ligand orbitals with the 4f orbitals of the lanthanide ions. Retrospectively, the synthesis and study of these pure 4f systems has literally been boosted since the discovery thata single molecular lanthanide complex displays slow relaxation of the magnetization [21].Among the lanthanide family, the dysprosium(III) ion has yielded the largest number of 4f-based SMMs, which were benefit from both the high moment and the high anisotropy of the spin–orbit coupled Dy^{III} Kramers doublet ground state ($S = 5/2$, $L = 5$, $J = 15/2$). A number of pureDy(III)-containing polynuclear SMMs with high energy barriers exhibiting various topologies with different muclearities from mononuclear to decanuclear have been reported [22–32]. Selection of suitable ligand is crucial for assembling polynuclear lanthanide cluster with slow relaxation behavior.The synthetic strategy to obtain polynuclear 4f SMMs fundamentally relies on the use of polydentate bridging ligands which can mediate magnetic interactions between the metallic centers. The choice of the bridging group is critical in the case of lanthanide systems in order to overcome the core nature of 4f orbitals and subsequently induce significant exchange interaction between the paramagnetic centers.Taking into account the coordination preference of4f ions for hard Lewis bases (HSAB theory) [33], it is possible to design polydentate ligands in order to direct the assembly of polynuclear lanthanide complexes. We have been investigating the use of Schiff base ligand salicylidene-*o*-aminophenol (H_2L) as a rigid chelate in lanthanide chemistry. Such ligand provides O,N,O,-basedtrichelating sites that are especially favorable for lanthanide ion complex formation [34].They can form dinuclear systems using thebridging phenoxide oxygen atom. Recently in our group, as the phenol

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http://dx.doi.org/10.1016/j.synthmet.2015.11.032
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group in Schiff base ligands provides an efficient super exchange pathway between lanthanide centers, it is feasible to develop Dy_2, Dy_3 and Dy_4 clusters showing single-molecule magnet behavior [35–38]. In order to continue our work, we report the synthesis, structure and magnetic properties of a unique dinuclear dysprosium(III) compound, $[Dy_2(L)_2(NO_3)_2(MeOH)_4]$ (**1**), which behaves as a SMM showing slow relaxation behavior.

2. Experimental

2.1. Materials and measurements

All operations were performed in an open atmosphere. The H_2L ligand was obtained from the reaction between *o*-aminophenol and salicylaldehyde according to the reported procedure [51]. Dy $(NO_3)_3{\cdot}6H_2O$ was prepared by the reactions of lanthanide oxide with nitric acid. Other chemicals were commercially available and generally used as supplied. Elemental (*C,H* and *N*) analyses were performed on a PerkinElmer 2400 analyzer. IR spectra were conducted on PerkinElmer 60,000 spectrophotometer. UV spectra were recorded on Shimadzu UV 2240 spectrophotometer. The magnetic susceptibilities of complex **1** were determined by a Quantum Design VSM magnetometer of superconducting quantum interference device (SQUID). The magnetization corrections are made by using Pascal's constants.

2.2. Synthesis of $[Dy_2(L)_2(NO_3)_2(MeOH)_4]$

A 10 mL acetonitrile solution of H_2L (0.213 g, 1 mmol) was slowly added 30 mL methanol solution of $Dy(NO_3)_3{\cdot}6H_2O$ (0.457 g, 1 mmol), then triethylamine (0.1 g, 1 mmol) was put in under stirring. The solution was refluxed for 3 h and the filtrate was kept in room temperature. Orange crystals of 1, suitable for single crystal X-ray diffraction analysis were obtained in one week. Yield: 0.528 g (52.84%). Anal. (wt%) Calcd for $C_{30}H_{34}Dy_2N_4O_{14}$: C, 40.15; H, 3.92; N, 6.33. Found: C, 38.11; H, 3.66; N, 2.93. IR (KBr, cm^{-1}): 3400 (s), 3211(w), 3049 (w), 2849 (w), 2777 (w), 1610 (vs), 1583 (s), 1550 (s), 1471 (vs), 1388 (s), 1293 (vs), 1243 (vs), 1224 (w), 1176 (m), 1152 (m), 1123 (m), 1111(w), 1038 (s), 1019 (vs), 976 (s), 866 (s), 831 (s), 765 (w), 749 (s), 603 (m), 506 (m), 466 (m), 445 (w). UV–vis spectrum in CH_3OH [λ_{max}(nm)]: 413, 289, 228.

Table 1
Crystallographic data for complex **1**.

Crystal data	1
CCDC number	941535
Empirical formula	$C_{30}H_{34}Dy_2N_4O_{14}$
Formula weight	999.61
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbcn
a (Å)	18.4559(10)
b (Å)	10.0557(11)
c (Å)	18.8833(8)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3504.5(5)
Z	4
Calculated density (Mg/m^3)	1.895
Absorption coefficient (mm^{-1})	4.303
F (0 0 0)	1944
θ range	3.09–25.00
Limiting indices	$-21 \leq h \leq 17$ $-4 \leq k \leq 11$ $-22 \leq l \leq 12$
Reflections collected	8981
Completeness to theta = 27.48°	98.9%
Data/restraints/parameters	3058/3/234
Goodness-of-fit on F^2	1.080
Final *R* indices [I > 2σ(I)]	$R_1 = 0.0922$ $wR_2 = 0.2195$
R indices (all data)	$R_1 = 0.1114$ $wR_2 = 0.2450$

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**.

Bond lengths for **1**			
Dy(1)–O(1)	2.226(8)	Dy(1)–O(2)	2.331(9)
Dy(1)–O(2a)	2.348(9)	Dy(1)–O(4)	2.362(10)
Dy(1)–O(3)	2.376(11)	Dy(1)–O(6)	2.428(11)
Dy(1)–N(1)	2.477(9)	Dy(1)–O(5)	2.591(13)
Dy(1)–N(2)	2.937(15)		
Bond angles for **1**			
O(2)–Dy(1a)–O(2a)	69.9(3)	Dy(1a)–O(2a)–Dy(1)	110.1(3)
O(2)–Dy(1)–O(2a)	69.9(3)	Dy(1)–O(2)–Dy(1a)	110.1(3)

2.3. X-ray crystallographic analysis

The crystal structures of **1** was collected on a Rigaku R-AXIS RAPID imaging-plate X-ray single crystal diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) at 293 K. The structures were solved by the direct method and refined by the full-matrix least squares on F^2 using the SHELXTL-97 software package [52] All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were introduced in calculations using the riding model. Their crystallographic data and structures refinement parameters are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Structural description of $[Dy_2(L)_2(NO_3)_2(MeOH)_4]$

The reaction between H_2L and $Dy(NO_3)_3{\cdot}6H_2O$ (1:1 ratio) in CH_3CN/CH_3OH (1:3 ratio), in the presence of triethylamine (1 equivalents) yielded orange crystals of $[Dy_2(L)_2(NO_3)_2(MeOH)_4]$ (**1**). Suitable for single crystal X-ray diffraction analysis were obtained by slow evaporation of the solvent for one week. X-ray crystallographic analysis reveals that complex **1** crystallizes in the Orthorhombic, Pbcn space group. The perspective view of the molecular structures of **1** is represented in Fig. 1a. In the dinuclear *trans*-dysprosium(III) cores, the metal centers are bridged by the phenoxo groups of two antiparallel, or "head-to-tail" H_2L ligands with Dy1–O2–Dy1a angle of 110.1(3)°, Dy-Dy distance equal to 3.8361(10) Å. The central core Dy_2O_2 appears to be nearly rhombic, the two Dy–O distances being 2.331(9) and 2.348(9) Å. One terminal phenoxo group coordinates the dysprosium ion with a short distance Dy–O1 of 2.226(8) Å. In **1**, the *trans* symmetric unit consists of one Dy(III) ion, one H_2L ligand, one nitrate anion and two methanol molecules. The dysprosium(III) centre in the dinuclear unit is 8-coordinated with one N atoms and two O atoms from one Schiff base ligand, two nitrate O atoms, two methanol O atoms, one O atoms from another Schiff base ligand, giving a dodecahedron geometry (Fig. 1b).

3.2. Magnetic properties

The temperature-dependent magnetic susceptibility data of **1** was measured for crystalline samples at an applied magnetic field of 1000 Oe in the temperature range of 2–300 K (Fig. 2). The experimentally obtained $\chi_M T$ values are 27.56 $cm^3\,K\,mol^{-1}$ at