Dinuclear lanthanide complexes based on amino alcoholate ligands: Structure, magnetic and fluorescent properties

Gui-Fang Sun, Cong-Ming Zhang, Jian-Ni Guo, Meng Yang, Li-Cun Li[*]

Department of Chemistry and Key Laboratory of Advanced Energy Materials Chemistry, Nankai University, Tianjin 300071, PR China

ARTICLE INFO

ABSTRACT

Two binuclear lanthanide complexes $[Ln_2(hfac)_6(HL)_2]$ (Ln^{III} = Dy(**1**), Tb(**2**); hfac = hexafluoroacetylacetonate, HL = (R)-2-amino-2-phenylethanol) have been successfully obtained by using amino alcoholate ligand. In two complexes, the Ln(III) ions are bridged by two alkoxido groups from HL ligands, resulting in binuclear complexes. The variable-temperature magnetic susceptibility studies indicate that there exists ferromagnetic interaction between two Ln(III) ions. Frequency dependent out-of-phase signals are observed for complex **1**, suggesting SMM type behavior. Complexes **1** and **2** display intensely characteristic luminescent properties.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

During the past two decades, Single molecule magnets(SMMs) have experienced three generations of development, from the initially studied 3d [1—5] metal clusters to mixed 3d—4f [6—8] clusters, and now to 4f-based [9—11] species. The drastically increased interest in 4f-based complexes is due to the inherent large magnetic moments and strong anisotropy of 4f ions. To date, many reported 4f complexes have shown magnetic relaxation behaviors, including lanthanide mono- [12—17] or poly-nuclear [18—24] complexes. For example, a heteroleptic terbium bisphthalocyanine with SMM behavior displays a large anisotropic barrier of 652 cm^{-1} [25]. Very recently, Tong and co-workers reports the symmetry strategy to suppress the quantum tunneling of the magnetization(QTM), leading to an energy barrier (U_{eff} = 1025 K) as new record [16]. A number of dysprosium(III) clusters have been shown to exhibit SMM behavior with large barriers, such as [Dy$_4$] [26—28], [Dy$_5$] [29], and [Dy$_6$] [30], showing anisotropic barriers between 170 and 800 K. Noticeably the magnetic anisotropy of lanthanide ions is strongly influenced by the ligand field (LF). A desirable LF could be produced by the careful design of the ligand around the Ln(III) ion center, achieving an easy axis of the

magnetization [31,32]. In this regard, amino alcoholate ligands have become attractive candidates for constructing SMMs due to its flexibility, diverse coordination modes [33—38], which might bring the new Ln-SMM system. In addition, the design of chiral magnetic systems is of particular interest for fundamental investigations into the magneto-chiral effect owing to their specific physical/chemical properties in optical materials [39]. Thus, in this work, we choose chiral amino alcoholate ligand (R)-2-amino-2-phenylethanol (HL, Scheme 1) to construct lanthanide complexes. Two dinuclear complexes $[Ln_2(hfac)_6(HL)_2]$ (Ln = Dy(**1**), Tb(**2**)) were achieved, the Dy derivative exhibits magnetic relaxation behavior.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were available from commercial sources and used as received without further purification. The salts of Ln(hfac)$_3$·2H$_2$O (Dy, Tb) were synthesized according to the literature [40]. C, H and N elemental analyses were carried out by a Perkin-Elmer elemental analyzer model 240. The infrared spectra were measured on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the region 4000—400 cm^{-1} with KBr pellets. Magnetic measurements were performed by a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were estimated using Pascal constants.

* Corresponding author.
  E-mail address: llicun@nankai.edu.cn (L.-C. Li).
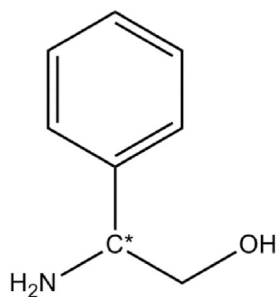
Scheme 1.

2.2. Synthesis of complexes

2.2.1. Synthesis of [Dy$_2$(hfac)$_6$(HL)$_2$] (1)

Dy(hfac)$_3$·2H$_2$O (0.0172 g, 0.02 mmol) was dissolved in 20 mL of dry n-heptane and heated to reflux for 2 h. Then the solution was cooled to 80 °C, HL (0.0048 g, 0.02 mmol) in CH$_2$Cl$_2$ (5 mL) was slowly added and the mixture was stirred at 80 °C for 20 min. The resulting solution was cooled to room temperature and then the mixture was filtered off. The clear filtrate was allowed to slowly evaporate at room temperature. After 2 days, colorless crystals were obtained. Results of elemental analysis C$_{46}$H$_{28}$Dy$_2$F$_{36}$N$_2$O$_{14}$ (%): calcd. C 30.03, N 1.52, H 1.42; found C 29.99, N 1.57, H 1.77. IR data (KBr disk, cm^{-1}): 3344 (s), 2362 (m), 1657 (s), 1536 (s), 1508 (s), 1258 (s), 1216 (s), 1146 (s), 802 (m), 662 (m), 586 (m).

2.2.2. Synthesis of [Tb$_2$(hfac)$_6$(HL)$_2$] (2)

Compound **2** was prepared by the same method but Tb(hfac)$_3$·2H$_2$O was used instead of Dy(hfac)$_3$·2H$_2$O. Results of elemental analysis C$_{46}$H$_{28}$Tb$_2$F$_{36}$N$_2$O$_{14}$ (%): calcd. C 30.15, N 1.53, H 1.43; found C 30.23, N 1.56, H 1.63. IR data (KBr disk, cm^{-1}): 3343 (s), 2361 (w), 1657 (s), 1536 (s), 1507 (s), 1259 (s), 1213 (s), 1145 (s), 802 (m), 662 (m), 586 (m), 530 (w).

2.3. Crystal structure determination and refinement

Complexes **1** and **2** crystal structures were determined on a Rigaku Saturn diffractometer equipped with a CCD area detector and graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å) at 113 K. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically and refined as riding atoms with a common fixed isotropic thermal parameter. The direct methods were used to solve the structure by using SHELXS-97 and SHELXL-97 program [41,42]. Relevant experimental conditions and crystallographic data are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. The structure description of complexes 1 and 2

Single-crystal X-ray diffraction analysis demonstrates that complexes **1** and **2** are isomorphic compounds with dinuclear structure and crystallize in the monoclinic C_2 space group. As shown in Fig. 1 and Fig. S1, the Ln(III) ion is eight coordinated by six oxygen atoms of three hfac molecules and two oxygen atoms from two HL ligands. The two metal ions are bridged by the two μ_2-O from two alcoholate groups (O7 and O8) to form a binuclear structure. The lengths of the Ln–O bonds (O7 and O8) are in the range of 2.305(2)–2.333(3) Å for complex **1** and 2.281(3)–2.302(3) Å for complex **2**. The Ln$_2$O$_2$ core displays a propinquity

parallelogram shaped structure and the Dy–O–Dy angles are 108.1(1)° for Dy–O7–Dy and 108.5(1)° for Dy–O8–Dy. The Tb–O–Tb angles are 107.7(1)° and 107.5(1)° for Tb–O7–Tb and Tb–O8–Tb, respectively. In the binuclear unit, the Ln…Ln distances are 3.756 Å for **1** and 3.699 Å for **2**. Continuous shape measures have been performed with SHAPE to evaluate the actual shape of the coordination spheres of the Ln center [43,44]. The lower CShM values of the shape measures are found relative to square antiprism (D_{4d}) and biaugmented trigonal prism (C_{2v}) (1.116 and 1.155 for Tb1; 1.045 and 1.070 for Tb2) for Tb centers. Therefore, the coordination spheres of the lanthanide ions in complex **2** could be considered as the intermediate between square antiprism and biaugmented trigonal prism (Table 3). The coordination sphere of Dy1 could be described as triangular dodecahedron (D_{2d}), while the coordination polyhedral of Dy2 is considered as biaugmented trigonal prism (C_{2v}). Such differences in the geometries around the Ln(III) ions could have important effects on the magnetic relaxation behaviors of two complexes. The packing diagram of complexes **1** and **2** are shown in Fig. 2 and Fig. S2, respectively. The shortest Ln…Ln contacts between binuclear units are 10.744(2) Å for complex **1** and 10.533(3) Å for complex **2**.

3.2. Magnetic properties

Variable-temperature magnetic susceptibilities of complexes **1** and **2** are measured under 1000 Oe applied magnetic field in 300–2 K. For compound **1**, the variation of $\chi_M T$ versus T is plotted in Fig. 3 (left). At room temperature, the $\chi_M T$ value is 28.61 cm^3 K mol^{-1}, which is close to the expected value of 28.34 cm^3 K mol^{-1} for two non-interacting Dy(III) ions (^{6}H$_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$, $C = 14.17$ cm^3 K mol^{-1}). Upon cooling, $\chi_M T$ value almost keeps a constant in the temperature range of 300–100 K, then increases to a maximum value of 30.60 cm^3 K mol^{-1} at 20 K. Further cooling, $\chi_M T$ value drops sharply to reach a minimum of 23.98 cm^3 K mol^{-1} at 2 K. These indicate that there exists ferromagnetic interaction between Dy(III) ions, which is strong enough to overwhelm the contribution of the thermal depopulation of the Stark levels of the Dy(III) ions.

For complex **2**, the $\chi_M T$ value is 24.03 cm^3 K mol^{-1} at room temperature, which is in good agreement with the expected values 23.64 cm^3 K mol^{-1} of two independent Tb(III) (^{7}F$_6$, $S = 3$, $L = 3$, $g = 3/2$, $C = 11.82$ cm^3 K mol^{-1}). As shown in Fig. 3 (right), the $\chi_M T$ value with decreasing temperature almost remains a constant from 300 to 55 K, then it decreases dramatically to reach a value of 11.64 cm^3 K mol^{-1} at 2 K. The magnetic behavior for complex **2** is ascribed to the combination of the crystal-field effects of the Tb(III) ions and the possible magnetic interaction between the Tb ions.

In order to study the magnetic dynamics, alternating current (ac) susceptibility measurements are performed for **1** and **2**. The frequency-dependent signals of both in-phase (χ') and out-of-phase component (χ'') are observed under a zero dc field for **1** (Fig. 4), indicating the onset of slow magnetic relaxation behavior. The relaxation time τ data of complex **1** derives from the χ'' peaks follow the Arrhenius formula $\tau = \tau_0 \exp(\Delta_{eff}/k_B T)$ (Fig. 5). The pre-exponential factor $\tau_0 = 7.0 \times 10^{-6}$ s and the effective energy barrier $\Delta/k_B = 12.54$ K are obtained and the value of τ_0 is consistent with those reported for Dy-based SMMs (10^{-6} to 10^{-11} s) [45,46]. For complex **2**, no frequency dependent phenomenon is found from the out-of-phase of the ac susceptibility above 2 K (Fig. 6). As known, the magnetic relaxation of lanthanide ion is very sensitive to the geometry of metal ion. The difference magnetic relaxation behaviors for two complexes may arise from the different coordination geometries around the lanthanide ions in two compounds. On the hand, Tb(III) ion is a non-Kramer ion which can not guarantee a bistability ground state [47,48].