Two lanthanide-hydroxo clusters with different nuclearity: Synthesis, structures, luminescent and magnetic properties

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ABSTRACT

Under the identical reaction conditions, two new Tb^{III} and Sm^{III}-hydroxo clusters with different nuclearity have been prepared and characterized by X-ray crystallography, spectroscopic methods and magnetic measurements. Solid-state structure analyses reveal that the Tb^{III} cluster shows a pentanuclear square pyramidal shape of the composition $[Tb_5(\mu_3\text{-OH})_4(\mu_4\text{-OH})(dbm)_{10}] \cdot 2H_2O$ (**1**, dbm$^-$ = dibenzoylmethanate) with the dbm ligands presenting two types of coordination modes [η^2-and (μ-O)-η^2-]. The Sm^{III} species presents a tetranuclear parallelogram structure formulated as $[Sm_4(\mu_3\text{-OH})_2(dbm)_{10}] \cdot 12H_2O$ (**2**), and three types of coordination modes [η^2-, (μ-O)-η^2- and (μ-O)$_2$-η^2-] for dbm ligands are observed. The measurements of magnetic properties indicate that the direct-current (dc) magnetic behaviors of two clusters mainly result from the thermal depopulation of the Stark sublevels of the Tb^{III} and Sm^{III} ions, respectively. Meanwhile, alternating current (ac) magnetic susceptibility of **1** is also assessed. Investigations on luminescence properties show that **2** displays characteristic emission of the Sm^{III} ion in visible range, while **1** does not exhibit any detectable emission. The interpretations of different emission behaviors for **1** and **2** are also presented in detail.

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1. Introduction

Recently, much attention has been paid to the exploitation of polynuclear lanthanide (Ln) clusters not only due to their novel structural diversity but also to the synthetic challenge as well as their fascinating photophysical and magnetic properties originating from unique 4f electronic configurations of Ln^{III} ions [1—3]. Regarding the luminescence property, Ln^{III} ions, especially Eu^{III}, Tb^{III} and Sm^{III} ions possess remarkable features such as large stokes shift, narrow emission band and long emission lifetime [4,5]. Apart from their impressive emissions, Ln^{III} ions such as Dy^{III} and Tb^{III} ions having large unquenched orbital angular momentum resulting in significant magnetic anisotropy, are appealing spin carriers for the design of single-molecule magnets (SMMs) [6]. As a result, a plethora of polynuclear Ln^{III} clusters have been synthesized, and most of them show excellent luminescent properties and interesting SMMs behavior [7—16].

In contrast with the well-established cluster chemistry of d-block transition-metal ions, the preparation of polynuclear Ln^{III} clusters, in particular Ln^{III} oxo/hydroxo species is virtually underdeveloped mainly owing to variable and high coordination numbers (usually 7—12) as well as minimal stereochemical preferences of Ln^{III} ions [17,18]. Usually, the synthetic strategy involves two pathways. One is the direct hydrolysis of lanthanide salts, often resulting in elusive products of adventitious hydrolysis [19]. The other approach is based on the ligand-controlled partial hydrolysis of Ln^{III} ions [7—12]. Hydrophilic groups such as oxo and hydroxo bridge the Ln^{III} ions to make up a cluster core, while ligands preoccupy the positions in the periphery in order to prevent the core from further aggregation, favorable for the formation of a finite-sized cluster. The most utilized ligands in Ln^{III} cluster chemistry include alkoxides [20,21], phenoxides [22], aminoacides [23,24], ortho-nitro phenols [25,26] and β-diketones [7—10]. Among them, β-diketone ligands are attractive because of the following attributes: (1) β-diketone is able to sensitize efficiently the emitting of Ln^{III} ions via "antenna effect" [27,28]; (2) β-diketone can adopt preferential bidentate chelating mode to bind Ln^{III} ions and provide suitable ligand field (LF) to satisfy the requirement of strong magnetic anisotropy for the occurrence of a SMM behavior [10,29—31].

Along these lines and as a part of our continuous focus on the

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properties of mono- and polynuclear Ln^{III} β-diketonate complexes [32–35], in this work, we intend to investigate the hydrolysis of the Tb^{III} and Sm^{III} ions controlled by the same β-diketone ligand, dibenzoylmethane (Hdbm), in CH_2Cl_2/n-C_6H_{14} mixed solvents. As a consequence, two new Ln^{III} clusters with different nuclearity were obtained under the identical reaction conditions. The Tb^{III} cluster shows a pentanuclear square pyramidal shape of the composition $[Tb_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(dbm)_{10}]\cdot 2H_2O$ (**1**, dbm$^-$ = dibenzoylmethanate), while the Sm^{III} species presents a tetranuclear parallelogram structure with the formula $[Sm_4(\mu_3\text{-}OH)_2(dbm)_{10}]\cdot 12H_2O$ (**2**). Different nuclearity is attributed to the effect of lanthanide contraction [36]. Herein we report the synthesis, structures, emission characteristics and magnetic properties of **1** and **2**.

2. Experimental

2.1. Material and physical measurements

All chemicals and reagents were commercially available and used as received. Elemental analysis for C and H were conducted on a Vario EL III Elemental analyzer. The IR spectra were registered on a TENSOR27 Bruker Spectrophotometer from KBr pellets in the range of 4000–400 cm^{-1}. UV−vis absorption spectra were recorded on UV-4802 Spectrometer. Photoluminescence studies were performed on an Edinburgh Instruments FLS980 fluorescence spectrometer at room temperature. Magnetic susceptibility measurements were carried out on crystalline samples with a Quantum Design MPMP-XL 7 superconducting quantum interference device (SQUID) magnetometer in the temperature range of 1.8–300 K. Diamagnetic corrections were carried out considering both the sample holder as the background and the diamagnetism of the constituent atoms estimated from Pascal's constant.

2.2. Synthesis

2.2.1. Synthesis of $[Tb_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(dbm)_{10}]\cdot 2H_2O$ (**1**)

A solution of $TbCl_3\cdot 6H_2O$ (0.2 mmol, 74 mg) in 10 mL cold water was added slowly with stirring to a solution of Hdbm (0.6 mmol, 135 mg) in 45 mL 95% ethanol. $NH_3\cdot H_2O$ (1.0 M) was added to keep pH value of 7.0–7.5, resulting in yellow precipitates. Stirring was continued for about 30 min and the yellow precipitates were filtered, washed with sufficient water and air-dried. Yield: 78% (based on $TbCl_3\cdot 6H_2O$). The block pale yellow crystals of **1** were obtained by recrystallization in CH_2Cl_2/n-C_6H_{14} mixed solvents (1:1, 10 mL). Elemental *Anal.* calc. for $C_{150}H_{115}O_{27}Tb_5$: C, 57.30; H, 3.69; Found: C, 57.17; H, 3.47%. Main IR peaks (KBr, cm^{-1}): 1607 (s) (C=O stretching), 3624 (w) (O−H stetching), 1517 (s) (enol, C=C stretching in dbm$^-$).

2.2.2. Synthesis of $[Sm_4(\mu_3\text{-}OH)_2(dbm)_{10}]\cdot 12H_2O$ (**2**)

2 was prepared using the same procedures as described above for the synthesis of **1**, but using $SmCl_3\cdot 6H_2O$ (0.2 mmol, 73 mg) in place of $TbCl_3\cdot 6H_2O$. The product was obtained as yellow solids in 72% yield (based on $SmCl_3\cdot 6H_2O$). The block yellow crystals of **2** were obtained using the same method as that of **1**. Elemental *Anal.* calc. for $C_{150}H_{136}O_{34}Sm_4$: C, 58.42; H, 4.44; Found: C, 58.29; H, 4.32%. Main IR peaks (KBr, cm^{-1}): 1598 (s) (C=O stretching), 3623 (w) (O−H stretching), 1520 (s) (enol C=C stretching in dbm$^-$).

2.3. X-ray crystallography

X-ray single crystal data of **1** and **2** were collected on a Bruker SMART APEX II CCD area detector equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature using both Φ- and ω-scan modes. The structures were obtained by direct methods and refined on F^2 by full matrix least-squares using SHELXTL97 crystallographic software package with anisotropic displacement parameters for all non-hydrogen atoms. All H atoms were introduced in calculations using the riding model. The crystallographic data and structures refinement parameters of **1** and **2** were summarized in Table 1, and selected bond lengths and angles were listed in Table S1 (in ESI).

3. Results and discussion

3.1. Structural description

3.1.1. The structure of $[Tb_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(dbm)_{10}]\cdot 2H_2O$ (**1**)

Single-crystal structure analysis revealed that **1** crystallizes in the tetragonal space group $P4/n$. The asymmetric unit of **1** consists of two unique Tb^{III} ions, one bridging μ_3-OH, one bridging μ_4-OH moiety along with two and half a dbm ligands (Fig. 1). The carbon atoms (C37, C38 and C39) from half a dbm ligand are disorder over two sites with 50% occupancy for each site. Five Tb^{III} ions are linked together through five hydrophilic hydoxo bridges (O6, O6A, O6B, O6C and O7) to give the $[Tb_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)]^{10+}$ cluster core, presenting a highly regular square-based pyramidal geometry (Fig. 2). Each triangular face of the square pyramid is capped by one μ_3-OH moiety, while four Tb^{III} ions in the square-based plane are connected by one μ_4-OH group. In addition, a total of ten peripheral dbm ligands surround the [Tb$_5$] cluster core and exhibit two different coordination modes. Four of them are terminally chelating with η^2-coordination mode and the remainders are bridging chelating with $(\mu\text{-}O)$-η^2-coordination mode, bonding two Tb^{III} ions located at the base of the square pyramid. Besides, each Tb^{III} ion is eight-coordinate and bound by eight oxygen atoms to form TbO$_8$ local geometry. The square-based Tb1 atoms are bound by eight oxygen atoms from one chelating (two oxygen atoms) and two bridging (three oxygen atoms) dbm ligands as well as one bridging μ_4-OH and two μ_3-OH moieties to form TbO$_8$ bicapped trigonal prism (BTP) arrangement. The O1 and O7 atoms cap the two quadrilateral faces O3–O4−O2−O3A and O3−O3A−O6−O6A of the trigonal prism (Fig. S1a in ESI), respectively. The Tb1−O7 (from μ_4-OH) distance is 2.594(3) Å, which is longer than those of Tb1−O6A (from μ_3-OH, 2.375(5) Å) and Tb1−O (from dbm, average 2.275 Å).

Table 1
Crystallographic data and structure refinement parameters for **1** and **2**.

	1	2
Chemical formula	$C_{150}H_{115}O_{27}Tb_5$	$C_{150}H_{136}O_{34}Sm_4$
Formula weight	3144.02	3083.99
Crystal system	Tetragonal	Triclinic
Space group	$P4/n$	$P\bar{1}$
a (Å)	19.4876(2)	15.3293(5)
b (Å)	19.4876(2)	16.1015(6)
c (Å)	18.5408(5)	16.7810(6)
$\alpha(°)$	90.00	116.848(4)
β (°)	90.00	109.572(3)
$\gamma(°)$	90.00	91.848(3)
V (Å^3)	7041.2(2)	3398.0(2)
Z	2	1
D_{calcd} (g/cm^3)	1.483	1.507
μ/mm^{-1}	2.547	1.781
data/restraints/parameters	6273/968/418	12179/30/847
θ range (°)	3.03–25.09	2.96–25.20
R_{int} (on F^2)	0.1003	0.0750
GOF on F^2	1.090	1.049
R_1[a] [$I > 2\sigma(I)$]	0.0569	0.0530
wR_2[b] (all data)	0.1653	0.1568

[a] $R_1 = \sum||Fo|\text{-}|Fc||/\sum|Fo|$.
[b] $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.