



Synthesis, crystal structures and magnetic properties of two tetranuclear lanthanide-hydroxo cubane clusters



Xi-Li Li^{a,*}, Feng-Cai Li^a, Xue-Li Zhang^a, Ying-Fan Liu^a, Ai-Ling Wang^a, Jun-Feng Tian^a, Hong-Ping Xiao^{b,**}

^a Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, PR China

^b School of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325027, PR China

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ABSTRACT

Two tetranuclear Lanthanide-hydroxo cubane clusters of composition $[\text{Ln}_4(\mu_3\text{-OH})_4(\mu\text{-O})\text{-}\eta^2\text{-acac})_4(\eta^2\text{-acac})_4]\cdot\text{C}_7\text{H}_8$ (Ln = Er **1** and Yb **2**, acac = acetylacetonate) have been prepared and characterized by elemental analyses, FTIR spectroscopy and X-ray crystallography. Single crystal X-ray analyses of **1** and **2** revealed that they are isostructural with the $\text{Ln}_4(\mu_3\text{-OH})_4^{8+}$ cluster core showing cubane-like geometry. Each cluster consists of four lanthanide atoms, four $\mu_3\text{-O}$ atoms, and eight acac ligands making up the peripheral part of the cluster. Two types of the coordination modes [$\eta^2\text{-}$ and $(\mu\text{-O})\text{-}\eta^2\text{-}$] of the acac ligands in **1** and **2** are observed. Investigations on the magnetic properties of **1** and **2** indicate that both complexes do not exhibit frequency-dependent in-phase (χ') and out-of-phase (χ'') signals in the alternating current (ac) magnetic susceptibilities of **1** and **2**. In particular, unlike most documented lanthanide β -diketonate mono- or multinuclear complexes exhibiting near-infrared (NIR) emission property, **1** and **2** do not show any detectable NIR emission at any temperature range and the reason of nonluminescence for **1** and **2** is further elucidated in this work.

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1. Introduction

The design and synthesis of polynuclear lanthanide complexes, in particular lanthanide oxo/hydroxo clusters continues to attract much attention, not merely because of their fascinating self-assembly structures but also because of the synthetic challenge and their many potential applications as functional materials in various fields, such as magnetic and optical materials as well as catalytic processes [1–9]. In quest of new molecular magnetic materials, lanthanide complexes are undoubtedly good candidates due to the fact that lanthanide ions possess large unquenched orbital angular momentum resulting in significant magnetic anisotropy, thus being appealing spin carriers for single-molecule magnets (SMMs) and single-ion magnets (SIMs) [8,10]. Particularly, the lanthanide clusters with interesting single-molecule magnet (SMM) property are highly desirable [11–12]. Among them, the prolific examples belong to Dy^{3+} -based SMMs [11–14]. To the best of our knowledge, there has no pure polynuclear Er^{3+} -containing complex with SMM property being reported so far and the

Yb^{3+} -based analogues are very scarce [15–16]. One of the main reasons is that the overall shape of free-ion electron density of Dy^{3+} ion is oblate, while the Er^{3+} and Yb^{3+} ions are prolate shape, thus the symmetry of ligand field (LF) possessing a larger effect on the magnetic anisotropy ground states of the Er^{3+} and Yb^{3+} ions than that of the Dy^{3+} ion [10].

On the other hand, in contrast to the well-established cluster chemistry of D-metal ions, to construct the nanosized analogues of lanthanides is virtually underdeveloped due to their variable and high coordination numbers (7–12) as well as minimal stereochemical preferences [17–18]. In general, the synthetic strategy known so far in literature involves two pathways. One is the direct hydrolysis of lanthanide salts, which often results in elusive products of adventitious hydrolysis [19]. For example, the lanthanide clusters $[\text{Er}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{NO}_3)_6(\text{H}_2\text{O})_{12}](\text{NO}_3)\cdot 4\text{H}_2\text{O}$ [20] and $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}](\text{ClO}_4)\cdot 8\text{H}_2\text{O}$ (Ln = Nd or Gd) [21] were obtained upon the hydrolysis of erbium nitrate or corresponding lanthanide perchlorates, respectively. The other approach is based on the ligand-controlled partial hydrolysis of the lanthanide ions [3–7]. Hydrophilic groups such as oxo and hydroxo bridge the lanthanide ions to make up a cluster core, while ligands pre-occupy the positions in the periphery in order to prevent the core from further aggregation, which is favorable to the formation of a finite-sized cluster.

* Corresponding authors. Fax: +86 371 86609676.

** Corresponding authors.

E-mail addresses: lixl@zzuli.edu.cn (X.-L. Li), hp_xiao@126.com (H.-P. Xiao).

The most reported ligands in lanthanide cluster chemistry include alkoxides [22–23], phenoxides [24], aminoacides [2, 25–26], ortho-nitro phenols [27–28] and diketones [3–7]. Among them, the use of diketone ligands can lead to some interesting lanthanide clusters possessing different nuclearities. Generally speaking, the bulky diketone ligands prefer to stabilize low-nuclearity lanthanide clusters, whereas the small size ligands usually generate high-nuclearity species. For example, the use of large bulk of dibenzoylmethane ligand (ph₂acac) gave rise to the pentanuclear and tetranuclear lanthanide clusters [4,6,10,29]. The reported nonanuclear lanthanide clusters are based on the use of benzoylacetone ligand (phacac) [5], while the small size acetylacetone ligand (acac) more favors to the formations of tetradecanuclear lanthanide clusters [7,30]. This category of the ligands provides an interesting case of rationally controlling the cluster nuclearity, thus allowing the further study of fine tuning in their magnetic and optical properties. In addition, other factors, such as ionic radii of the lanthanide elements, pH values and solvent choice can also affect the cluster nuclearity [3,5,31]. Peculiarly, solvent choice has a pronounced effect on the nuclearity of obtained lanthanide clusters. For instance, we have reported two chiral tetradecanuclear hydroxo-lanthanide clusters of composition Ln₁₄(μ₄-OH)₂(μ₃-OH)₁₆(μ-η²-acac)₈(η²-acac)₁₆·6H₂O (Ln = Dy or Tb) based on acac ligand in CH₂Cl₂/petroleum ether mixed solvents [30]. Employing the same ligand, Reber and zheng reported some nonanuclear lanthanide clusters formulated as [Ln₉(μ₃-OH)₈(μ₄-O)(μ₄-OH)(acac)₁₆]·H₂O (Ln = Eu-Dy, Er and Yb) obtained in methanol solvent [3,31]. Following this idea and as a part of our continuous focus on the property studies of polynuclear lanthanide β-diketonate complexes [30,32–33], in this work, we intend to investigate the hydrolysis of heavy Er³⁺ and Yb³⁺ ions controlled by the same ligand (acac) in toluene solvent. Consequently, two novel tetranuclear clusters with the formula of [Ln₄(μ₃-OH)₄{(μ-O)-h²-acac}₄(h²-acac)₄]·C₇H₈ (Ln = Er **1** and Yb **2**), showing cubane-like geometry, were obtained. Herein, the synthesis, structures, magnetic and luminescent properties of **1** and **2** were reported.

2. Experimental

2.1. Material and physical measurements

All the reagents and chemicals were used as received from commercial sources without further purification. NH₄ acac was prepared according to a literature method [34]. Elemental analyses for C and H were performed on a PerkinElmer CHN 2400 apparatus. FTIR spectra were registered on a TENSOR27 Bruker Spectrophotometer from KBr pellets in the region of 4000–400 cm⁻¹. UV-vis absorption spectra were obtained on a UV-4802 Spectrometer. Magnetic susceptibility measurements were carried out on crystalline samples with a Quantum Design MPMS 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 Er₄(μ₃-OH)₄{(μ-O)-η²-acac}₄(η²-acac)₄]·C₇H₈ (**1**)

An aqueous solution of NH₄acac (75 mL, 2 mol/L) was added slowly with stirring to a solution of 0.1 mmol ErCl₃·6H₂O (0.381 g) in 10 mL cold water. NH₃·H₂O (1.0 M) was added to keep pH value being 7.0–7.5, resulting in white precipitates. Stirring was continued for about 2 h and the white precipitates were filtered, washed with sufficient water and air-dried in approximately 72%

yield (based on ErCl₃·6H₂O). The block colorless crystals of **1** were obtained by recrystallization in toluene solvent (5 mL). Elemental analysis (%) calcd. for **1** (C₄₇H₆₈O₂₀Er₄): C 34.80, H 4.23; Found: C 35.06, H 4.35. IR data (KBr, cm⁻¹): 1596 (s) (C=O stretching), 3647 (w) (O—H stretching), 1513 (s) (enol C=C stretching in acac).

2.2.2. Synthesis of Yb₄(μ₃-OH)₄{(μ-O)-η²-acac}₄(η²-acac)₄]·C₇H₈ (**2**)

This complex was prepared using the same procedure as described above for the synthesis of **1**, but using YbCl₃·6H₂O (0.1 mmol, 0.387 g) in place of ErCl₃·6H₂O. The product was obtained as white solids in approximately 69% yield (based on YbCl₃·6H₂O). The block colorless crystals of **2** were obtained using the same method as that of **1**. Elemental analysis (%) calcd. for **1** (C₄₇H₆₈O₂₀Yb₄): C 34.31, H 4.17; Found: C 34.76, H 4.06. IR data (KBr, cm⁻¹): 1598 (s) (C=O stretching), 3645 (w) (O—H stretching), 1512 (s) (enol C=C stretching in acac).

2.3. X-ray data collection and structure determination

The crystal structures of **1** and **2** were determined 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 F₂ by full matrix least-squares using SHELXTL-97 crystallographic software package with anisotropic displacement parameters for all non-hydrogen atoms. All H atoms were introduced in calculations using the riding model. Their crystallographic data and structures refinement parameters were summarized in Table 1. Selected bond lengths and angles were listed in Table 2.

3. Results and discussion

3.1. Structural description

X-ray single crystal analyses revealed that complexes **1** and **2** are isostructural and crystallize in the tetragonal space group I41/a displaying the cubane-like geometry. So only the structure of **1** is described in detail. The asymmetric unit of **1** consists of one unique Er³⁺ ion along with two chelating acac ligands, one bridging μ₃-OH moiety and half a toluene solvent molecule (Fig. 1). Four Er³⁺ ions are linked together through four hydrophilic hydroxo bridges (O5, O5A, O5B and O5C) to give the [Er₄(μ₃-OH)₄]⁸⁺ cluster core, in

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

	1	2
Chemical formula	C ₄₇ H ₆₈ O ₂₀ Er ₄	C ₄₇ H ₆₈ O ₂₀ Yb ₄
Formula weight	1622.05	1645.17
Crystal system	Tetragonal	Tetragonal
Space group	I41/a	I41/a
α (Å)	13.9128(2)	13.9257(5)
b (Å)	13.9128(2)	13.9257(5)
c (Å)	32.5639(12)	32.633(4)
α = γ = β (°)	90.00	90.00
V (Å ³)	6303.3(3)	6328.4(8)
Z	4	4
D _{calcd} (g/cm ³)	1.709	1.727
μ/mm ⁻¹	5.333	5.918
data/restraints/params	2810/31/185	2822/30/181
θ Range (°)	3.18 - 25.10	3.18 - 25.09
Rint (on F ₂)	0.0414	0.0314
GOF on F ₂	1.082	1.210
R ₁ [I > 2σ(I)] ^a	0.0612	0.0364
wR ₂ (all data) ^b	0.1169	0.0904

^a R₁ = ∑|F_o - F_c| / ∑F_o.

^b wR₂ = [∑w(F_o - F_c)² / ∑w(F_o)²]^{1/2}.

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