



Two novel 2D lanthanide sulfate frameworks: Syntheses, structures, and luminescence properties



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ABSTRACT

Two novel lanthanide–sulfate compounds, $[\text{Ln}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8]$ ($\text{Ln} = \text{Tb}$ (**1**) and Dy (**2**)), have been synthesized under hydrothermal reactions. X-ray crystal structure analyses reveal that **1** and **2** are isomorphous and crystallize in monoclinic $C2/c$ space group, showing a layered structure. The layers bear a rare quasi-honeycomb metal arrangement, which is fastened by $\mu_3 = \eta_1:\eta_1:\eta_1$ and $\mu_2 = \eta_1:\eta_1$ sulfates. If assigning the $\mu_3 = \eta_1:\eta_1:\eta_1$ sulfate as a 3-connected node and the Ln^{3+} ion as a 4-connected node, the network can be rationalized as a binodal (3,4)-connected V_2O_5 topology with a Schläfli symbol of $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$. In addition, the infrared, thermogravimetric analysis and luminescent properties were also studied. Complexes **1** and **2** exhibit outstanding thermal stability and characteristic terbium and dysprosium luminescence.

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1. Introduction

In recent years, inorganic open-framework materials based sulfate anion have attracted great interest because of not only their fascinating structural diversities but also their various potential applications such as cathode materials, magnetic properties and luminescence properties [1–6]. As a simple tetrahedral oxo-anion, the sulfate anion displays a variety of coordination modes and bears excellent affinity to transition and rare-earth metal ions. Up to now, a number of transition metal and rare earth sulfates have been prepared and characterized [7–19]. Compared with transition metals, rare-earth elements adopt more various coordination numbers from 8 to 12 and flexible Ln–O bond lengths to give lanthanide sulfates with new topologies [7–9,14]. In addition, the lanthanide-based complexes usually exhibit interesting luminescence behavior and have important applications as fluorescent probes in many emission-related fields, especially in biochemistry [7,8]. Consequently, it is crucial to design novel lanthanide sulfates with an intriguing variety of structures to explore their optical properties and understand the formation mechanism [8,14].

To our knowledge, most of the lanthanide sulfate frameworks were synthesized under the presence of the organic amines, which

usually played a role of true templates, structural directing agents or space fillers [8,20,21]. Herein, two two-dimensional (2D) lanthanide sulfate frameworks, $[\text{Ln}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8]$ ($\text{Ln} = \text{Tb}$ (**1**) and Dy (**2**)), were prepared by $\text{Ln}(\text{NO}_3)_3$ and amino tris(methylene phosphonic acid) (ATMP) with a mole ratio of 6:1 under hydrothermal conditions. The pH value is about 1.5 adjusted by sulfuric acid aqueous solution. Interestingly, the structures of the products did not contain the ATMP ligand, while without it no products could be given, indicating that ATMP may play an important role over the synthesis procedure of **1** and **2**.

2. Experimental

2.1. Materials and methods

All chemicals were obtained from commercial sources and used without further purification. FT-IR spectra were recorded in the range of $4000\text{--}400\text{ cm}^{-1}$ on a JASCO FT/IR-430 spectrometer with KBr pellets. X-ray Powder Diffraction (XRPD) measurements were carried out on a Rigaku D/Max-2400 X-ray Diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.5418\text{ \AA}$) at room temperature. Thermogravimetric analyses were performed under a flow of nitrogen (40 mL/min) at a ramp rate of $10\text{ }^\circ\text{C}/\text{min}$, using a NETZSCH STA 449F3 instrument. Solid state luminescence properties were carried out using a F-4600 FL Spectrophotometer.

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2.2. Syntheses

2.2.1. Syntheses of **1** and **2**

The following is the general progress for the preparation of **1** and **2**. 600 μL $\text{Ln}(\text{NO}_3)_3$ (1 M, 0.6 mmol) ($\text{Ln} = \text{Tb}$ and Dy) aqueous solution and 100 μL amino tris(methylene phosphonic acid) (1 M 0.1 mmol) aqueous solution were added into a 15 mL vial with 2 mL deionized water. 1 M sulfuric acid aqueous solution was added dropwisely to adjust the pH value of the resulting solution to about 1.5 under stirring. The vial was sealed and heated at 90 $^\circ\text{C}$ in an oven for 24 h, then cooled to room temperature. Colourless block crystals of the products were obtained. $[\text{Tb}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8]$ (**1**): Yield, 36% based on Tb. $[\text{Dy}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8]$ (**2**): Yield, 32% based on Dy.

2.2.2. X-ray structure determinations

The intensity data were measured at 298(2) K on a Bruker SMART APEX II CCD area detector system with graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation. Data reduction and unit cell refinement were performed with Smart-CCD software [22]. The structures were solved by direct methods using SHELXS-97 and were refined by full-matrix least squares methods using SHELXL-97 [23]. For **1** and **2**, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the coordinated water molecules were initially found on Fourier difference maps and then restrained by using the DFIX instruction. A summary of the important crystal and structure refinement data of **1** and **2** were given in Table 1. Selected bond lengths and angles for **1** were listed in Table 2.

3. Result and discussion

3.1. Crystal structures

Single-crystal X-ray diffraction analyses reveal that **1** and **2** are isostructural and crystallize in the monoclinic $C2/c$ space group. Therefore, we take **1** as a representative to describe their structures in detail. Compound **1** features a (3,4)-connected 2D network which is formed by 3-connected SO_4^{2-} anion and 4-connected Tb^{3+} ion (Fig. 1). The asymmetric unit contains 12.5 non-hydrogen atoms, which all are owned by the inorganic framework, including one terbium atom, four oxygen atoms from four terminal water molecules and one point five sulfate groups. As shown in Fig. 1a, each Tb^{3+} ion is eight-coordinated and have a distorted square antiprismatic $\{\text{O}_8\}$ donor set, completed by four terminal

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

	1	2
Formula	$\text{Tb}_2\text{H}_{16}\text{O}_{20}\text{S}_3$	$\text{Dy}_2\text{H}_{16}\text{O}_{20}\text{S}_3$
Mr.	750.15	757.31
Cryst. system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
$a/\text{Å}$	13.5255(11)	13.4951(15)
$b/\text{Å}$	6.7222(6)	6.7070(8)
$c/\text{Å}$	18.2758(15)	18.240(2)
$\alpha/^\circ$	90	90
$\beta/^\circ$	102.129(2)	102.050(3)
$\gamma/^\circ$	90	90
$V(\text{Å}^3)/Z$	1624.6(2)/4	1614.5(3)/4
$d_{\text{calcd.}}, \text{g}/\text{cm}^3$	3.067	3.116
$F(000)$	1416.0	1424.0
$R_1, (I > 2\sigma(I))$	0.0229(1355)	0.0125(1384)
$wR_2(\text{all data})$	0.0626(1402)	0.0342(1404)
Max/mean shift in final cycle	0.002/0.000	0.001/0.000

$$^a R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right\}^{0.5}$$

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for **1**.

Tb1–O1	2.307(4)	Tb1–O5	2.321(3)
Tb1–O7	2.331(4)	Tb1–O9	2.366(4)
Tb1–O4	2.368(3)	Tb1–O2	2.430(3)
Tb1–O8	2.444(4)	Tb1–O10	2.484(3)
O1–Tb1–O5	79.92(14)	O1–Tb1–O7	88.23(15)
O5–Tb1–O7	70.70(13)	O1–Tb1–O9	146.85(13)
O5–Tb1–O9	79.71(15)	O7–Tb1–O9	109.14(16)
O1–Tb1–O4	144.11(12)	O5–Tb1–O4	125.67(13)
O7–Tb1–O4	79.43(13)	O9–Tb1–O4	68.55(12)
O1–Tb1–O2	99.79(13)	O5–Tb1–O2	141.25(12)
O7–Tb1–O2	147.83(13)	O9–Tb1–O2	80.61(15)
O4–Tb1–O2	75.92(12)	O1–Tb1–O8	70.19(12)
O5–Tb1–O8	134.15(13)	O7–Tb1–O8	74.34(15)
O9–Tb1–O8	140.74(13)	O4–Tb1–O8	74.03(12)
O2–Tb1–O8	79.20(13)	O1–Tb1–O10	73.26(12)
O5–Tb1–O10	74.59(12)	O7–Tb1–O10	142.97(13)
O9–Tb1–O10	76.27(13)	O4–Tb1–O10	133.13(12)
O2–Tb1–O10	68.47(12)	O8–Tb1–O10	125.26(12)

water molecules and four oxygen atoms from four sulfate anions. The Tb–O and S–O bond lengths are in the range of 2.307(4)–2.484(3) and 1.458(4)–1.472(4) Å, respectively, which are similar to those reported for other lanthanide compounds based on sulfate anion [7,8,19].

The sulfates in **1** adopt two coordination modes: $\mu_3 = \eta_1:\eta_1:\eta_1$ and $\mu_2 = \eta_1:\eta_1$ (Scheme 1). The $\mu_3 = \eta_1:\eta_1:\eta_1$ one bridges three Tb^{3+} ions to give a Tb_3 triangle with the average $\text{Tb} \cdots \text{Tb}$ distance of 5.78 (2) Å. Each of the Tb_3 triangles is fastened only by one $\mu_3 = \eta_1:\eta_1:\eta_1$ sulfate in the center and the neighboring Tb_3 ones share one edge to result in a ladderlike chain (Fig. 1b). Every $\mu_2 = \eta_1:\eta_1$ sulfate links two Tb^{3+} ions from two neighboring ladderlike chains. The $\text{Tb} \cdots \text{Tb}$ distance is 6.12 (1) Å. The adjacent ladderlike chains are further linked together by the $\mu_2 = \eta_1:\eta_1$ sulfates to form a 2D layer structure (Fig. 1c).

To get better insight of this 2D framework, topology analysis has been programmed by using TOPOS software [24]. As shown in Fig. 2, the framework can be rationalized as a binodal (3,4)-connected V_2O_5 topology by assigning the $\mu_3 = \eta_1:\eta_1:\eta_1$ sulfate as a 3-connected node and the Tb^{3+} ion as a 4-connected node with a Schläfli symbol of $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$.

When the lanthanide connectivity alone is considered in the structure, a quasi-honeycomb arrangement is observed (Fig. 3). To our knowledge, the formation of such network in lanthanide containing compounds is rarely reported.

3.2. Infrared spectroscopy

Complexes **1** and **2** have similar FT-IR spectra showing only slight shifts in some band positions (Fig. S1). The strong and broad absorption bands in the range of 3000–3500 cm^{-1} in **1** and **2** are attributed to the characteristic peaks of OH vibration. The band at around 1640 cm^{-1} is due to the bending modes of water molecules coordinated to metal ions. The strong band at about 1145 cm^{-1} and middle band at 610 cm^{-1} correspond to the vibration modes of the S–O groups ions. These assignments are consistent with those reported previously [6,8,25].

3.3. Thermal properties

The thermal stabilities of **1** and **2** were examined by thermogravimetric (TG) analysis in a nitrogen atmosphere from 25 to 1000 $^\circ\text{C}$. As shown in Fig. 4, the TG curves of **1** and **2** are similar and three mass steps are observed. In the first step, the weight loss of **1** and **2** in the range of 25–230 $^\circ\text{C}$ are 19.24% and 19.08%, respectively,

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