

# Solvothermal Synthesis, Crystal Structure and Properties of a 3D Organically Amine Templated Lanthanide Sulfate<sup>①</sup>

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**ABSTRACT** A new sulfate inorganic framework,  $\{(C_2H_8N)_9[Nd_5(SO_4)_{12}] \cdot 2H_2O\}_n$  (**1**) templated by organic amine, has been solvothermally synthesized and characterized by TGA, PXRD and single-crystal X-ray diffraction. Compound **1** crystallizes in monoclinic, space group  $C2/c$  with  $a = 20.570(5)$ ,  $b = 35.815(8)$ ,  $c = 10.106(2)$  Å,  $C_{18}H_{72}N_9Nd_5O_{50}S_{12}$ ,  $M_r = 2315.73$ ,  $V = 6765(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.274$  g·cm<sup>-3</sup>,  $\mu = 4.253$  mm<sup>-1</sup>,  $F(000) = 4520$ ,  $2.52 < \theta < 25^\circ$ ,  $\lambda(MoK\alpha) = 0.71073$  Å,  $T = 273(2)$  K, the final  $R = 0.0401$ ,  $wR = 0.1022$  and  $S = 1.042$ . X-ray diffraction analysis reveals that complex **1** possesses a 3D inorganic sulfate framework with large 20-membered ring (20 MR) and 10-membered ring (10 MR) channels constructed by two kinds of SBUs. Moreover, the UV-vis and luminescent properties of complex **1** were also investigated.

**Keywords:** crystal structure, neodymium complex, inorganic framework, fluorescence

## 1 INTRODUCTION

Over the past decades, the design and molecular self-assembly of novel solid materials are a more and more fascinating field due to their interesting topologies and potential applications in the precursors for oxides and catalysis<sup>[1-2]</sup>, ion exchange<sup>[3]</sup>, magnetic properties<sup>[4]</sup> and luminescence properties<sup>[5]</sup>. Silicates and phosphates<sup>[6]</sup> were firstly used to build inorganic frameworks, but many researches have witnessed that other tetrahedral anions such as the arsenates, sulfates, and selenates can be good candidates<sup>[7]</sup>. Recently, there has been growing interest in the study of open-framework architectures containing oxo-anions of sulfur. Since Rao *et al.* reported the first organically templated cadmium sulfate consisting of infinite linear chains and a

quasi-2D layer formed by strip-like units, more and more attention has been paid to sulfate inorganic frameworks<sup>[8]</sup> because of kinds of coordination modes of  $SO_4^{2-}$  (Scheme 1). Afterwards, Pang *et al.* have hydrothermally synthesized and X-ray structurally characterized the first example of 2D layered lanthanum sulfate containing organic templates<sup>[9]</sup>.

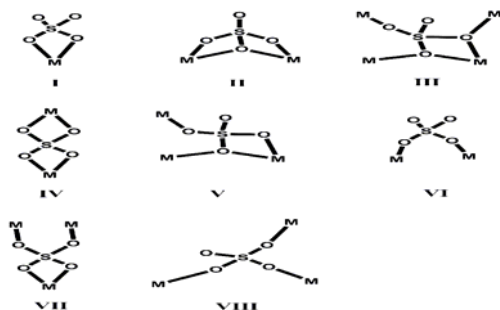
Meanwhile, many transition metal sulfates have one- or two-dimensional structures, and it has been observed that the formation of three-dimensionally extended sulfate networks is difficult<sup>[10]</sup>. So, lanthanide elements were elected to construct networks owing to their 8 to 12 coordination numbers and flexible Ln–O bond lengths which allow forming new topological, more complicated structures and their efficient fluorescent properties. Up to now, more than 50 successful examples including organic

Received 30 December 2013; accepted 24 February 2014 (CCDC 913570)

① Supported by the NSFC (No. 21001115), the Fundamental Research Funds for the Central Universities (13CX02006A, 13CX05015A), and the scientific research foundation of Shandong province Outstanding Young Scientist Award (BS2011CL041)

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amine templated lanthanide sulfate materials have been reported in literatures<sup>[11-27]</sup>. Herein, we report an inorganic sulfate framework, a 3D-channel sulfate framework, templated by 1,3-di(4-pyridyl)propane (1,3-dpp) molecules.



Scheme 1. Coordination mode of  $\text{SO}_4^{2-}$

## 2 EXPERIMENTAL

### 2.1 General experimental section

All chemicals and solvents employed in the synthesis were of analytical grade obtained commercially and used as received without further purification. The C, H and N microanalyses were carried out with a CE instruments EA 1110 analyzer. The FT-IR spectrum was recorded from KBr pellets in the range of  $4000 \sim 400 \text{ cm}^{-1}$  on a Bruker VERTEX-70. Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with  $\text{CuK}\alpha$  radiation equipped with an X'Celerator detector. TG curve was performed from 30 to 600 °C on a TA5200/MDSC2910 instrument at a heating rate of 10 °C/min under  $\text{N}_2$  atmosphere. Photoluminescence measurement was performed on a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate.

### 2.2 Synthesis of 1

Synthesis of  $\{(\text{C}_2\text{H}_8\text{N})_9[\text{Nd}_3(\text{SO}_4)_{12}] \cdot 2\text{H}_2\text{O}\}_n$  (**1**) A mixture of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (116 mg, 0.5 mmol), 1,3-dpp (19 mg, 0.1 mmol) and conc.  $\text{H}_2\text{SO}_4$  (205 mg, 1 mmol) was stirred in DMF solvent (10 mL, v/v, 1:1) under ultrasonic treatment in air for 15 min. Then, the mixture was sealed in a Pyrex tube and slowly heated to 100 °C from room temperature in 500 min, kept at 100 °C for 3000 min, and then

slowly cooled to 30 °C in 600 minutes. The colourless rod crystals that formed were collected and dried in air. Yield: 54% based on neodymium. Elemental analysis calcd. for  $\text{C}_{18}\text{H}_{76}\text{Nd}_5\text{N}_9\text{S}_{12}\text{O}_{50}$  (2324.75): Anal. Calcd. (%): C, 9.30; H, 3.30; N, 5.42. Found (%): C, 9.46; H, 3.70; N, 5.39. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3440(s), 3070(w), 2934(m), 2860(w), 1607(s), 1560(s), 1428(s), 1387(s), 1218(m), 1107(w), 1076 (w), 1008(m), 850(w), 807(m), 755(m), 718(w), 618(w), 513(m).

### 2.3 Structure determination

A single crystal of **1** with appropriate dimensions of  $0.100\text{mm} \times 11\text{mm} \times 0.12\text{mm}$  was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. The data were collected at 293 K on a Bruker Apex II Image Plate single-crystal diffractometer equipped with a graphite-monochromated  $\text{MoK}\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ) operating at 50 kV and 30 mA in an  $\omega$  scan mode for **1**. A total of 19116 reflections were collected in the range of  $2.88 \leq \theta \leq 25^\circ$  ( $-14 \leq h \leq 14$ ,  $-11 \leq k \leq 18$ ,  $-35 \leq l \leq 36$ ), of which 7170 were independent ( $R_{\text{int}} = 0.0409$ ). Absorption correction was applied by the correction of symmetry-equivalent reflections using the multi-scan program. The highest possible space group was chosen. The structure was solved by direct methods using SHELXS-97<sup>[28]</sup> and refined on  $F^2$  by full-matrix least-squares procedures with SHELXL-97<sup>[29]</sup>. Atoms were located from iterative examination of difference F-maps followed by the least-squares refinements of the earlier models. Hydrogen atoms on organic ligands were placed in the calculated positions and included as riding atoms with isotropic displacement parameters  $1.2 \sim 1.5$  times  $U_{\text{eq}}$  of the attached C atoms. Hydrogen atoms attached to oxygen in **1** were located by difference Fourier maps and then refined subject to the constraint  $\text{O-H} = 0.85 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . The structure was examined using the Addsym subroutine PLATON<sup>[30]</sup> to assure that no additional symmetry could be applied to the models. Crystal

structure views were obtained using Diamond v3.1f.  
The selected bond lengths and bond angles for **1** are

listed in Table 1. The hydrogen bond information for **1** is summarized in Table 2.

**Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complex 1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Nd(1)–S(4) <sup>d</sup>	3.1493(18)	Nd(1)–O(16) <sup>d</sup>	2.540(5)	Nd(2)–S(3)	3.1212(19)
Nd(1)–S(4)	3.1493(18)	Nd(1)–O(20)	2.368(5)	Nd(2)–S(4)	3.1801(19)
Nd(1)–O(14) <sup>d</sup>	2.525(5)	Nd(1)–O(20) <sup>d</sup>	2.368(5)	Nd(2)–S(5) <sup>c</sup>	3.1525(17)
Nd(1)–O(14)	2.525(5)	Nd(1)–O(22) <sup>d</sup>	2.392(5)	Nd(2)–O(11)	2.489(5)
Nd(1)–O(16)	2.540(5)	Nd(1)–O(22)	2.392(5)	Nd(2)–O(12)	2.545(5)
Nd(2)–O(15)	2.509(5)	Nd(2)–O(16)	2.630(5)	Nd(2)–O(17) <sup>c</sup>	2.624(5)
Nd(2)–O(17)	2.381(5)	Nd(2)–O(19) <sup>c</sup>	2.448(5)	Nd(2)–O(21)	2.442(5)
Nd(2)–O(23) <sup>c</sup>	2.415(5)	S(2)–O(8)	1.467(5)	S(3)–O(9)	1.469(6)
S(3)–O(10)	1.468(5)	S(3)–O(11)	1.465(5)	S(3)–O(12)	1.478(5)
S(3)–O(13)	1.446(6)	S(3)–O(14)	1.461(6)	S(3)–O(15)	1.468(5)
S(3)–O(16)	1.502(5)	S(5)–Nd(2) <sup>c</sup>	3.1525(17)	S(5)–O(17)	1.493(5)
S(5)–O(18)	1.433(5)	S(5)–O(19)	1.469(5)	S(5)–O(20)	1.464(5)
S(5)–O(21)	1.484(5)	S(5)–O(22)	1.470(5)	S(5)–O(23)	1.472(5)
S(5)–O(24)	1.449(5)	O(7)–Nd(3) <sup>b</sup>	2.446(5)	O(17)–Nd(2) <sup>c</sup>	2.624(5)
Angle	(°)	Angle	(°)	Angle	(°)
S(4)–Nd(1)–S(4) <sup>d</sup>	89.49(7)	O(22) <sup>d</sup> –Nd(1)–S(4) <sup>d</sup>	100.75(12)	O(4)–Nd(3)–O(10)	136.1(2)
O(14) <sup>d</sup> –Nd(1)–S(4) <sup>d</sup>	27.08(12)	O(11)–Nd(2)–S(4)	91.91(12)	O(5) <sup>a</sup> –Nd(3)–S(2)	101.66(13)
O(14)–Nd(1)–S(4) <sup>d</sup>	91.45(13)	O(12)–Nd(2)–S(5) <sup>c</sup>	96.37(12)	O(5) <sup>a</sup> –Nd(3)–S(3)	161.46(13)
O(14) <sup>d</sup> –Nd(1)–S(4)	91.45(13)	O(12)–Nd(2)–O(16)	75.16(16)	O(5) <sup>a</sup> –Nd(3)–O(6)	75.61(18)
O(14)–Nd(1)–S(4)	27.08(12)	O(12)–Nd(2)–O(17) <sup>c</sup>	123.21(16)	O(10)–Nd(3)–S(2)	97.67(12)
O(14) <sup>d</sup> –Nd(1)–O(14) <sup>d</sup>	105.0(3)	O(17)–Nd(2)–O(11)	147.88(16)	O(10)–Nd(3)–S(3)	27.36(12)
O(20) <sup>d</sup> –Nd(1)–O(16)	139.16(16)	O(17)–Nd(2)–O(12)	150.29(16)	O(10)–Nd(3)–O(6)	123.31(17)
O(20)–Nd(1)–O(20) <sup>d</sup>	102.4(3)	O(17)–Nd(2)–O(15)	81.88(16)	O(10)–Nd(3)–O(9)	54.57(17)
O(20)–Nd(1)–O(22) <sup>d</sup>	69.91(16)	O(21)–Nd(2)–O(15)	123.86(15)	O(1)–S(1)–O(3)	104.4(5)
O(20) <sup>d</sup> –Nd(1)–O(22)	69.91(16)	O(23) <sup>c</sup> –Nd(2)–O(21)	136.39(16)	O(1)–S(1)–O(4)	112.3(5)
O(20)–Nd(1)–O(22)	81.01(17)	O(4)–Nd(3)–O(8)	99.7(2)	O(2)–S(1)–O(1)	112.7(5)
O(20) <sup>d</sup> –Nd(1)–O(22) <sup>d</sup>	81.01(17)	O(4)–Nd(3)–O(9)	81.6(2)	O(9)–S(3)–O(12)	110.7(3)

Symmetry codes: (a)  $x, -y, 0.5+z$ ; (b)  $-1-x, y, 0.5-z$ ; (c)  $-0.5-x, 0.5-y, 1-z$ ; (d)  $-x, y, 1.5-z$

**Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for 1**

D–H···A	d(D–H) Å	d(H···A)/ Å	d(D···A)/ Å	∠DHA (°)
N(3)–H(3D)···O(13)	0.90	2.30	3.016(13)	136
N(3)–H(3D)···O(12)	0.90	2.33	2.816(11)	114
N(4)–H(4)···O(8)	0.86	2.43	3.121(11)	138
N(4)–H(4)···O(10)	0.86	2.55	3.273(7)	142
N(5)–H(5E)···O(24)	0.90	1.97	2.835(9)	162
N(3)–H(3E)···O(1) <sup>a</sup>	0.90	2.07	2.891(13)	152
N(2)–H(2A)···O(3) <sup>a</sup>	0.90	2.09	2.891(16)	148
N(1)–H(1A)···O(5) <sup>a</sup>	0.90	2.17	2.965(8)	147
N(1)–H(1A)···O(7) <sup>a</sup>	0.90	2.60	3.342(6)	140
N(5)–H(5D)···O(21) <sup>c</sup>	0.90	2.04	2.930(9)	171
N(1)–H(1A)···O(6) <sup>b</sup>	0.90	2.34	2.831(11)	114
N(1)–H(1B)···O(5) <sup>f</sup>	0.90	2.17	2.965(8)	147
N(1)–H(1B)···O(7) <sup>f</sup>	0.90	2.60	3.342(6)	140

Symmetry codes: (a)  $x, -y, 0.5+z$ ; (b)  $-x-1, y, 0.5-z$ ; (c)  $-x-0.5, -y+0.5, -z+2$ ; (f)  $-x-1, -y, -z$

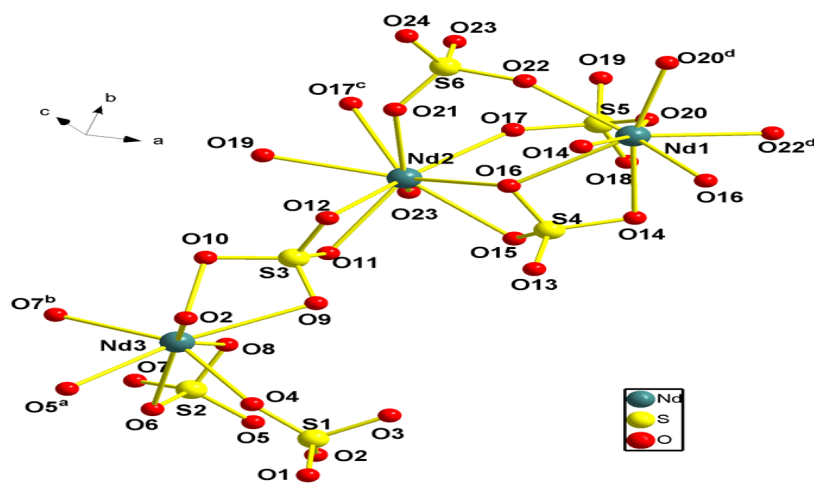
### 3 RESULTS AND DISCUSSION

#### 3.1 Structural description

Complex **1** was synthesized by the reaction of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 1,3-dpp and concn.  $\text{H}_2\text{SO}_4$  in DMF

through the conventional hydrothermal method in a Pyrex tube. Complex **1** is isostructural with Eu<sup>[24]</sup>, Tb<sup>[26]</sup>, La and Ce<sup>[31]</sup> and Sm<sup>[32]</sup>, but it is the first porous neodymium sulfate with large 20-membered ring (20 MR) and 10-membered ring (10MR) channels, and the synthesis method is different and more moderate than the reported ones, so it is important to analyze the structure of compound **1**. Although 1,3-dpp was added, it does not coordinate in the final structure. X-ray single-crystal diffraction reveals that complex **1** has a 3D inorganic sulfate framework with a large 20-membered ring (20MR) and 10-membered ring (10 MR) channels. Complex **1** crystallizes in monoclinic *C2/c* space group and the asymmetric unit of **1** contains 50 non-hydrogen atoms, 33 of which belong to the molecular cage including three Nd atoms, six sulfate groups, one water molecule and protonated dimethylamine cations. As shown in Fig. 1, Nd(1) and Nd(3) are eight-coordinated by oxygen atoms from six sulfate

groups to form a distorted bicapped trigonal-prismatic geometry, while Nd(2) is nine-coordinated by oxygen atoms from six sulfate groups to form a distorted bicapped trigonal-prismatic geometry. The bond distances of Nd–O vary from 2.381(5) to 2.630(5) Å, while the angles O–Nd–O are in between 54.57(17) and 150.29(16)°, which are comparable with those for other reported Nd compounds<sup>[10]</sup>. Six crystallographically independent S atoms adopt six coordination modes in complex **1** and can be divided into 4 groups (Scheme 1): S(1) is linked by two  $\mu_2$ -O and two O<sub>u</sub> (uncoordinated O atoms) to make two S–O–Nd linkages (Mode VI); S(2) and S(3) are bonded by four  $\mu_2$ -O atoms to make four S–O–Nd linkages (Modes VII and IV); S(4) and S(5) are bonded by one  $\mu_3$ -O, two  $\mu_2$ -O and one O<sub>u</sub> to make four S–O–Nd linkages (Modes II and V); S(6) is coordinated by three  $\mu_2$ -O and one O<sub>u</sub> to make three S–O–Nd linkages (Mode VIII).



**Fig. 1.** Coordination environment around the Nd<sup>III</sup> ions in **1**. All hydrogen atoms, protonated dimethylamine and H<sub>2</sub>O are omitted for clarity (Symmetry codes: (a)  $x, -y, 0.5+z$ ; (b)  $-1-x, y, 0.5-z$ ; (c)  $-0.5-x, 0.5-y, 1-z$ ; (d)  $-x, y, 1.5-z$ )

It is noteworthy that there exist N–H···O hydrogen bonds acting as a structure-directing role among the protonated dimethylamine cations and sulfate groups, strengthening the cohesion of the title compound. One protonated dimethylamine cation has two hydrogen atoms, which can be a good H-donor. At the same time, there are four oxygen atoms in one sulfate group acting as a good H-acceptor. The details of hydrogen bonds are listed in

Table 2.

The total 3D framework of compound **1** can be described from two kinds of secondary building units (SBUs): SBU-1 and SBU-2. SBU-1 is a 20-membered ring formed by four NdO<sub>9</sub>, six NdO<sub>8</sub> and ten SO<sub>4</sub> polyhedra; and SBU-2 is a 10-membered ring constructed by three NdO<sub>8</sub>, two NdO<sub>9</sub> and five SO<sub>4</sub> groups. Neighboring 10 and 20-membered rings are connected by bridging SO<sub>4</sub>

groups to form an open framework with a 3D channel. There are two kinds of channels with 10- and 20-members extending along the *c* axis (Fig. 2). Each 20MR channel is surrounded by six 10 MR, and these are alternately surrounded by three 20 MR and three 10 MR channels. The approximate window sizes for 20 MR and 10 MR are  $7\text{\AA} \times 11\text{\AA}$  and  $5.3\text{\AA} \times 5.3\text{\AA}$ , respectively. The percent void

volume in the 3D network of **1** is 57.1% calculated by PLATON software<sup>[30]</sup>. It is interesting that 1,3-dpp was added in the reaction mixture, but it does not participate in coordinating the structure. Therefore, the 1,3-dpp and dimethylamine molecules are believed to be a template in constructing the inorganic frameworks.

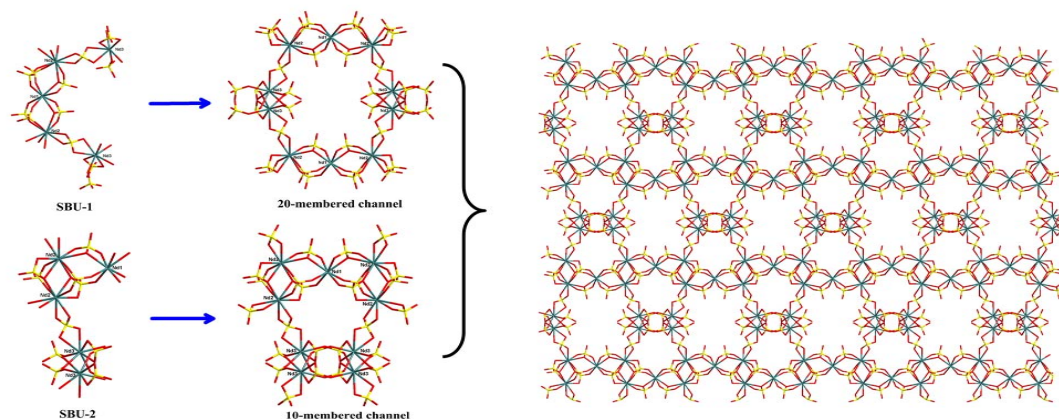


Fig. 2. Structure of the open framework including 10 MR and 20 MR channels of **1** along the *c* axis

### 3.2 IR spectrum

The solid FT-IR spectrum of **1** shows a broad peak centered at  $3500\text{ cm}^{-1}$ , which indicates the presence of water molecules (Fig. S1). The characteristic bands for dimethylamine are in the region of  $1400\sim 1600\text{ cm}^{-1}$ . The spectra show bands centred around  $1050\text{ cm}^{-1}$  and a band in the  $600\text{ cm}^{-1}$  region can be attributed to the sulfate ion.

### 3.3 Thermal stability and PXRD result

The thermal stability of **1** was examined by

thermogravimetric analysis (TGA) in dry nitrogen atmosphere from 30 to  $600\text{ }^{\circ}\text{C}$  (Fig. 3a). For compound **1**, it is interesting that a stepwise lose gravity progress is detected, corresponding to the removal of free water and dimethylamine molecules. The powder X-ray diffraction (PXRD) pattern of **1** is in agreement with that simulated from the single-crystal structure of **1**, indicating phase purity of **1** (Fig. 3b).

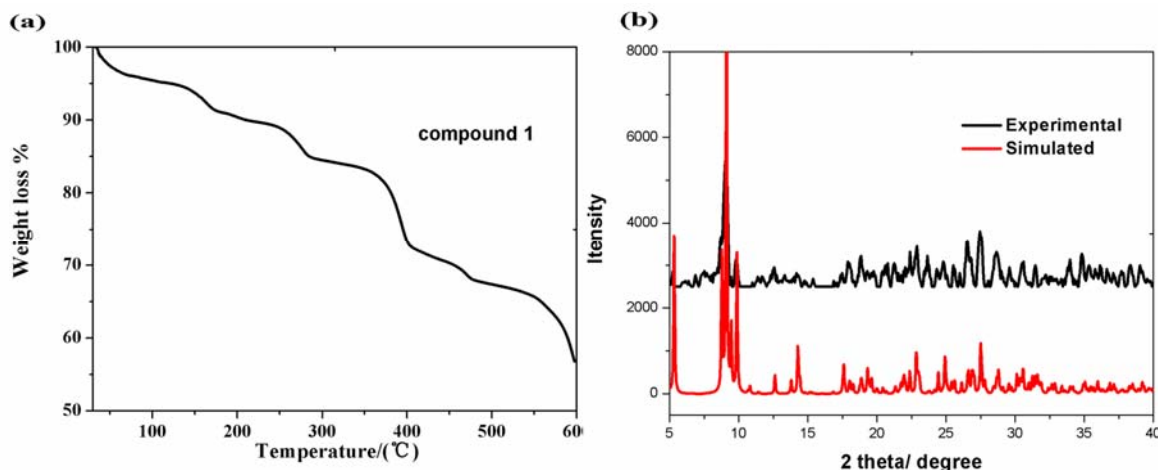


Fig. 3. (a) TG curve of complex **1**, (b) Experimental and simulated XRD spectra of complex **1**

### 3.4 Luminescent property

The room temperature UV-vis spectrum of compound **1** was measured in the solid state at ambient temperature, indicating that the absorption increases rapidly with decreasing the wavelength due to the intra-ligand absorption (Fig. 4a). From the UV studies, we concluded that the absorption bands of the Nd<sup>3+</sup> ions appeared to exhibit primary ground state Stark splitting of the eigenstates due to

the possible crystal field effects. Considering the possibility application of porous framework in photoactive materials, the photoluminescence spectrum of **1** was also measured in the solid state at ambient temperature (Fig. 4b). Upon 582 nm excitation, **1** exhibits an intense emission band centered at ~870 nm contributed to the excitation of Nd<sup>3+</sup> ions and there is no upconversion process observed in compound **1**<sup>[33]</sup>.

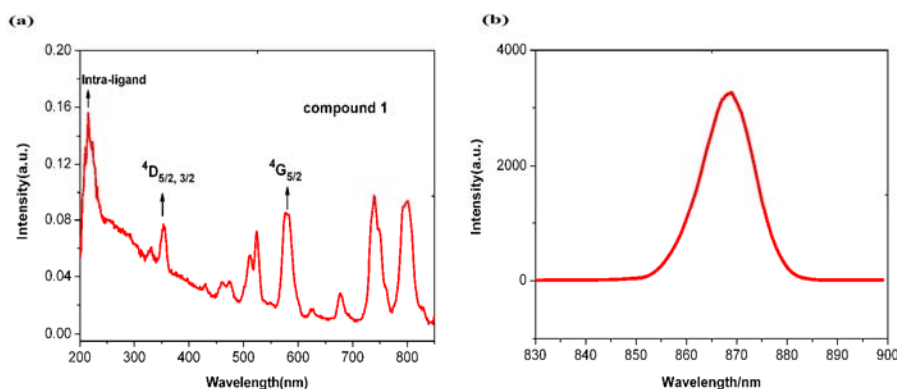


Fig. 4. (a) Solid-state UV-vis spectra and (b) Emission spectra of complex **1** at room temperature

## 4 CONCLUSION

In summary, the synthesis and structure of a lanthanide (Nd) sulfate complex is described. As far as we know, complex **1** is the first neodymium

sulfate open-framework with large 20-membered ring (20 MR) and 10-membered ring (10 MR) channels. Additionally, complex **1** shows strong solid-state UV-vis spectra and photoluminescent emission at room temperature.

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