

一种新的有机胺为模板剂的稀土硫酸钐合成, 结构表征以及荧光性质

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摘要: 本文采用正丁醇与水的混合溶剂合成一种新的以有机胺为模板剂的硫酸钐盐: $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5}[\text{Sm}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**), 并通过 X-射线衍射、红外、热重及元素分析对其进行了表征。该化合物晶体属于单斜晶系, $P2_1/c$ 空间群。其中 $a=0.655\ 15(9)\ \text{nm}$, $b=2.648\ 3(4)\ \text{nm}$, $c=0.996\ 15(13)\ \text{nm}$, $\beta=104.067\ 0(10)^\circ$, $V=1.676\ 5(4)\ \text{nm}^3$, $Z=4$ 。晶体结构分析显示化合物 **1** 中的波浪形层状结构由 SmO_9 多面体与 SO_4 多面体构成, 同时非配位水与乙二胺通过氢键连接相邻的两个层。化合物 **1** 具有较强的荧光。

关键词: 溶剂热合成法; 硫酸钐盐; 晶体结构; 荧光

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Solvothermal Synthesis, Crystal Structure and Luminescence of a New Organic Amine Templated Samarium Sulfate

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Abstract: A new organic amine templated samarium sulfate $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5}[\text{Sm}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ **1** has been synthesized under solvothermal conditions by using a mixture of *n*-butanol and water as the solvent. The colorless block crystals structurally were characterized by single-crystal X-ray diffraction $P2_1/c$ with crystal data $a=0.655\ 15(9)\ \text{nm}$, $b=2.648\ 3(4)\ \text{nm}$, $c=0.996\ 15(13)\ \text{nm}$, analysis, IR, TGA and ICP. Compound **1** crystallizes in the monoclinic space group $\beta=104.067\ 0(10)^\circ$, $V=1.676\ 5(4)\ \text{nm}^3$, $Z=4$. Crystal structure analysis shows that the waved layered framework of compound **1** is constructed from SmO_9 polyhedra and sulfate groups, while non-coordination water molecules and ethylenediamine molecules link the adjacent layers by hydrogen bonds. Compound **1** indicates a strong luminescence upon the excitation. CCDC: 843656.

Key words: solvothermal synthesis; samarium sulfate; crystal structure; luminescence

0 Introduction

In recent years, much attention has been widely paid on the organically templated open-framework inorganic microporous materials because of their wide potential applications in catalysis^[1-3], separation and

ion-exchange^[4-6]. The work mainly focused on silicates^[7], phosphites^[8-9], phosphates^[10], arsenates^[11-12], selenites^[13-14] and germinates^[15-16]. Recently, organically templated open-framework metal sulfates have been attracted much attention^[17-19]. As a building unit, the sulfate

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tetrahedron can be effectively used to construct new microporous materials with novel structures^[20]. Compared with other transition metals, the lanthanide centers have high coordination numbers and a variety of coordination environments to allow the formation of novel topological structure. Nowadays, more and more researches are devoted to the design and synthesis of lanthanide coordination compounds with some different organic ligands. One of the strategies used in synthesis of microporous materials is to employ organic amine as the structure-directing agent (SDA). More recently, some metal sulfates have been prepared by using hydrothermally synthesized. For example, lanthanum sulfates^[21-23], neodymium sulfate^[24], europium sulfate^[25], iron sulfate^[26], and uranium sulfates^[27-28], etc. Samarium is an important member in the rare-earth elements because of the excellent luminescence property. But unfortunately, open-framework samarium sulfates templated by organic amines have been not reported. Here, we report the first samarium sulfate compound $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5}[\text{Sm}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**) in the presence of ethylenediamine as (SDA)structure-directing agent.

1 Experimental

1.1 Materials and methods

All chemicals purchased were of reagent grade and used without further purification. The element analysis for Sm was performed on Leeman inductivity coupled plasma (ICP) spectrometer, while the C, H and N analyses were performed on a Perkin-Elmer 2400 elemental analyzer. IR spectrum was recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets in 4 000~400 cm^{-1} region. Thermogravimetric analyses were carried out in N_2 atmosphere on a Diamond thermogravimetric analyzer from 50 to 1 100 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$.

1.2 Synthesis and characterization

A mixture of Sm_2O_3 (0.211 3 g), H_2O (1 mL), *n*-butanol (5 mL), ethylenediamine (en) (0.290 1 g) and sulfuric acid (0.425 1 g, 98%) was stirred for 2 h, while the final pH value was 3. The mixture was sealed in a 24 mL Teflon-lined autoclave and heated at 180 $^{\circ}\text{C}$ for 6 d. The product was washed with deionized water, dried at room temperature for 1 d to give the colorless block crystals. Anal Calcd.(%): Sm, 25.67; C, 6.15; N, 7.17; H, 3.61. Found: Sm, 25.71, C, 5.85; N, 7.35; H, 3.29. IR of **1** (cm^{-1}): 3 523(m), 3 417(m), 1 613(s), 1 523(s), 1 146(vs), 1 105(vs), 754(m), 608(s). In the IR spectrum of the compound **1**, the wild band at 3 523 cm^{-1} can be attributed to the presence of water. The characteristic bands for ethylenediamine are in the region 1 420~1 613 cm^{-1} . The strong bands 1 146 and 1 105 cm^{-1} are characteristic bands for S-O. Absorption at 608 cm^{-1} is due to Sm-O vibration.

1.3 Structure determination

The crystal of compound **1** was carefully singled out under a microscope and glued at the tip of a thin glass fiber with cyanoacrylate adhesive. Single-crystal structure determination was performed on a Bruker Smart Apex II CCD diffractometer at 293 K, sealed tube X-ray source (Mo $K\alpha$ radiation, $\lambda=0.071\ 073\ \text{nm}$) operating at 50 kV and 30 mA. The crystal structure was solved by the direct method and refined on F^2 by full-matrix least-squares using the SHELX97 program package^[29]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions and included in the refinement, riding on their respective parent atoms. Further details of the X-ray structural analyses for compound **1** is given in Table 1 and selected bond lengths and angles are listed in Table 2.

CCDC: 843656.

Table 1 Crystal data and structure refinement for compound 1

Empirical formula	$\text{C}_3\text{H}_{19}\text{N}_3\text{O}_{15}\text{S}_3\text{Sm}$	Absorption coefficient / mm^{-1}	3.958
Formula weight	583.74	$F(000)$	1152
Temperature / K	296(2)	Crystal size / mm	0.13×0.12×0.10
Wavelength / nm	0.071 073	θ range / ($^{\circ}$)	1.54~25.02
Crystal system	Monoclinic	$h / k / l$	-7, 7 / -31, 31 / -11, 11
Space group	$P2_1/c$	Reflections collected	11 819

Continued Table 1

a / nm	0.655 15(9)	Independent reflections (R_{int})	2 953 (0.035 9)
b / nm	2.648 3(4)	Data / restraints / parameters	2 953 / 5 / 238
c / nm	0.996 15(13)	Goodness-of-fit on F^2	1.077
$\beta / (^\circ)$	104.067 0(10)	R, wR indices [$I > 2\sigma(I)$]	0.023 2, 0.055 0
V / nm^3	1.676 5(4)	R, wR indices (all data)	0.027 4, 0.056 4
Z	4	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	771, -580
$D_c / (\text{Mg} \cdot \text{m}^{-3})$	2.313		

Note: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for compound 1

Sm(1)-O(8)	0.234 5(2)	Sm(1)-O(3)	0.252 2(3)	N(2)-C(2)	0.148 0(5)
Sm(1)-O(4a)	0.240 4(3)	Sm(1)-O(12)	0.252 4(2)	N(3)-C(3)	0.147 7(5)
Sm(1)-O(3W)	0.244 1(3)	Sm(1)-O(10b)	0.254 6(2)	C(1)-C(2)	0.150 1(6)
Sm(1)-O(2)	0.250 3(2)	Sm(1)-O(11)	0.254 9(3)		
Sm(1)-O(9b)	0.251 0(2)	N(1)-C(1)	0.148 1(5)		
O(8)-Sm(1)-O(3W)	77.02(9)	O(8)-Sm(1)-O(11)	141.84(9)	O(12)-S(1)-O(9)	110.91(15)
O(8)-Sm(1)-O(2)	129.69(9)	O(3W)-Sm(1)-O(11)	68.65(9)	O(1)-S(2)-O(4)	110.85(16)
O(3W)-Sm(1)-O(2)	95.44(9)	O(2)-Sm(1)-O(11)	71.40(8)	O(1)-S(2)-O(2)	110.74(17)
O(8)-Sm(1)-O(3)	74.69(9)	O(3)-Sm(1)-O(11)	109.27(8)	O(4)-S(2)-O(2)	109.88(16)
O(3W)-Sm(1)-O(3)	72.92(9)	O(12)-Sm(1)-O(11)	55.28(8)	O(1)-S(2)-O(3)	110.89(17)
O(2)-Sm(1)-O(3)	55.90(8)	O(10)-S(1)-O(11)	112.26(15)	O(4)-S(2)-O(3)	109.41(16)
O(8)-Sm(1)-O(12)	146.96(8)	O(10)-S(1)-O(12)	111.65(15)	O(2)-S(2)-O(3)	104.90(15)
O(3W)-Sm(1)-O(12)	122.75(9)	O(11)-S(1)-O(12)	105.85(15)	N(1)-C(1)-C(2)	109.5(3)
O(2)-Sm(1)-O(12)	78.22(8)	O(10)-S(1)-O(9)	105.24(14)	N(2)-C(2)-C(1)	110.3(3)
O(3)-Sm(1)-O(12)	133.58(8)	O(11)-S(1)-O(9)	111.04(15)		

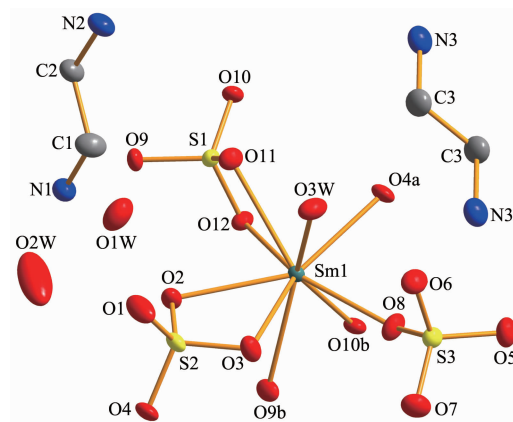
Symmetry transformations used to generate equivalent atoms: a: $x-1, y, z$; b: $x, -y+1/2, z-1/2$.

2 Results and discussion

2.1 Structure analysis

Single crystal X-ray diffraction study indicates that compound **1** in monoclinic space group $P2_1/c$. The structural analysis reveals that compound **1** is an protonated ethylenediamine templated samarium sulfate and consists of inorganic anionic 2D $[\text{Sm}(\text{SO}_4)_3(\text{H}_2\text{O})]_n^{3n-}$ layer, charge compensated by the protonated ethylenediamine cations. As shown in Fig.1, the asymmetric unit of compound **1** contains one samarium atom, 3 sulfate groups, 1.5 protonated ethylenediamine, one coordinated and two free water molecules. The Sm atom is nine-coordinated by eight oxygen atoms from five SO_4 groups and one O atom from water molecule. The Sm-O distances range from 0.234 6(3) to 0.254 8(3) nm, while the average value of Sm-O bond length is 0.248 3(3)

nm. The angles of O-Sm-O are between $55.27(8)^\circ$ and $146.90(9)^\circ$. All the S atoms are tetrahedrally coordinated



Thermal ellipsoids are drawn at 50% probability, Symmetry codes: a: $x-1, y, z$; b: $x, -y+1/2, z-1/2$

Fig.1 ORTEP view of the $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5}[\text{Sm}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ structure showing the atom labeling scheme

by four O atoms with the S-O distances of 0.145 3(3)~0.148 9(3) nm, which are similar to the lanthanide sulfates reported previously. There are three crystallographic independent S atoms: S(1) form only one S-O-Sm linkage through one μ_2 -O, S(2) form four S-O-Sm linkages through four μ_2 -O and S(3) makes three S-O-Sm linkages through three μ_2 -O.

For recent years, there are lots of 2D layered successful examples including organic amine templated lanthanide sulfates have been reported, such as $\text{La}_2(\text{H}_2\text{O})_2(\text{C}_2\text{H}_{10}\text{N}_2)_3(\text{SO}_4)_6 \cdot 4\text{H}_2\text{O}$ [30], $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5}[\text{Eu}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ [25], $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5}[\text{Nd}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ [24]. But there is no organic amine templated samarium sulfates reported. The structure of inorganic framework of **1** can be described as interesting corrugated layers with terminal SO_4 tetrahedra attached to them. [S(2) O_4] tetrahedra connected two adjacent [Sm O_9] polyhedras to form a zigzag chain (Fig.2a), while [S(3) O_4] tetrahedra connected two adjacent zigzag chains to form an interesting corrugated layer (Fig.2b). Two lattice water molecules O2w and O3w are linked together via the hydrogen bonding interactions to form a $(\text{H}_2\text{O})_2$ unit, with the O2w...O3w distance of 0.285 8(6) nm, and the O-H...O angle of 155.242(5)°. The $(\text{H}_2\text{O})_2$ units are involved in the hydrogen bonding with the O atoms from [SO $_4$] groups in the inorganic framework to generate a soft 3D supermolecular open framework (Fig.3). The protonated ethylenediamine cations are located in the channels and involved hydrogen bonding interactions

with the soft framework and make it more stable. The hydrogen-bondings have also been found between amine cations and the lattice water molecule. The selected H-bonding information is presented in Table 3.

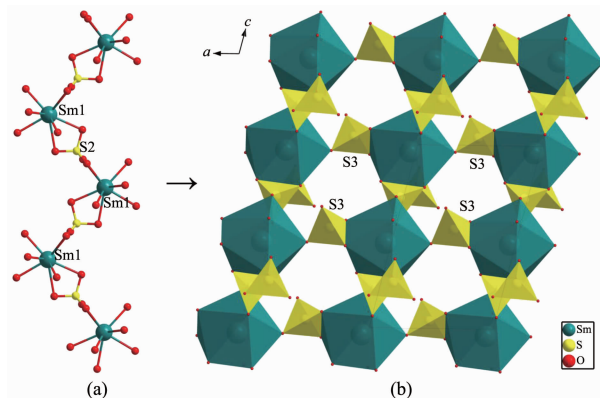


Fig.2 (a) Ball-stick view of inorganic zigzag chain in compound **1**; (b) Two adjacent zigzag chains to generate 2D layer structure along the *b*-axis

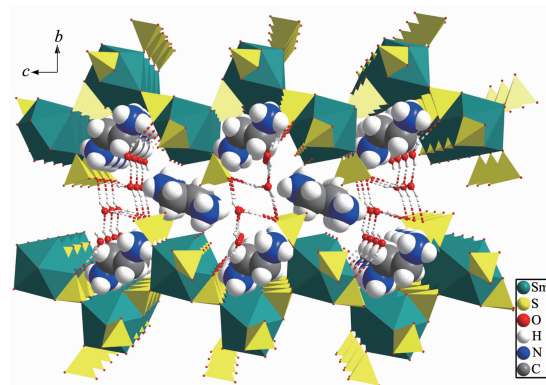


Fig.3 3D open framework in compound **1**, in which the adjacent layers are connected by the $(\text{H}_2\text{O})_2$ groups by hydrogen bonding interaction

Table 3 Selected hydrogen bonds for compound **1**

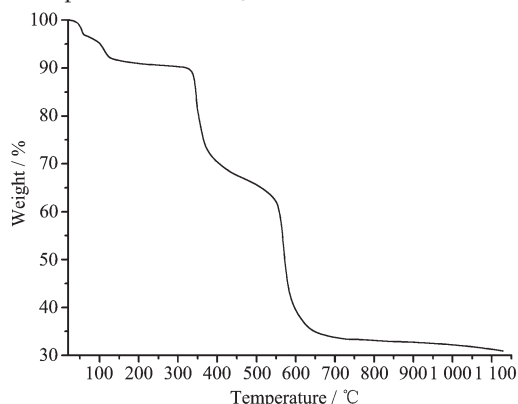
D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠(DHA) / (°)
O2W-H2WA...O1W	0.084(5)	0.208(5)	0.285 8(6)	155(7)
N1-H1C...O1	0.089	0.250	0.324 5(5)	142.0
N1-H1C...O2	0.089	0.236	0.300 8(5)	129.0
N1-H1C...O10	0.089	0.245	0.288 4(4)	110.0
N1-H1D...O9	0.089	0.208	0.296 7(4)	171.0
N1-H1E...O12	0.089	0.211	0.296 4(5)	160.0
O2W-H2WB...O11	0.84(4)	0.212(5)	0.289 9(6)	153(6)
N2-H2C...O3	0.089	0.222	0.303 7(5)	152.0
N2-H2D...O2W	0.089	0.203	0.287 4(6)	157.0
N2-H2D...O7	0.089	0.238	0.284 6(5)	113.0
N2-H2E...O5	0.089	0.194	0.281 6(4)	168.0
O1W-H1WA...O7	0.085(3)	0.196(4)	0.275 3(5)	154(4)

Continued Table 3

N3-H3C...O1W	0.089	0.193	0.275 2(5)	152.0
N3-H3D...O6	0.089	0.197	0.284 5(5)	167.0
N3-H3E...O1	0.089	0.236	0.297 8(5)	127.0
N3-H3E...O3	0.089	0.245	0.328 8(5)	157.0
N3-H3E...O3W	0.089	0.253	0.306 0(5)	119.0
O1W-H1WB...O5	0.086(2)	0.195(3)	0.279 0(4)	169(5)
C1-H1A...O2W	0.097	0.26	0.334 2(7)	134.0
C2-H2A...O12	0.097	0.246	0.337 6(5)	158.0
C2-H2B...O10	0.097	0.232	0.327 0(5)	164.0

2.2 Thermal analysis

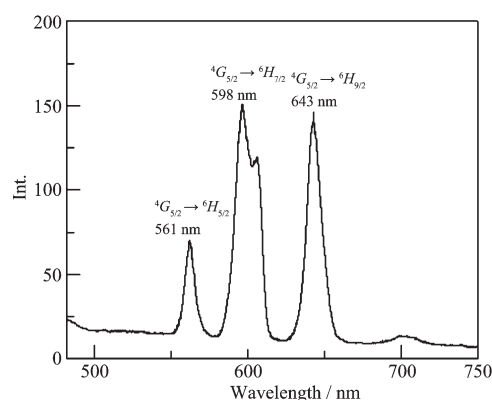
Thermal analysis shows that the total weight loss of **1** is 69.1% (calcd. 70.23%). As shown in Fig.4, the weight loss of 9.7% in the range of 20 ~300 °C corresponds to the removal of the lattice and coordinated water molecules (calcd. 9.23%). The second step loss of 16.2% in the range of 300~350 °C can be attributed to removal of ethylenediamine (calcd. 15.91%), the weight loss of 41.2% in the range of 350~1 100 °C can be attributed to loss SO₃ (calcd. 41.0%). The final product is Sm₂O₃.

Fig.4 TG curve of compound **1**

2.3 Photoluminescence

Optical property investigation shows compound **1** exhibits excellent luminescent property. As shown in Fig.5, the photoluminescence spectrum of compound **1** possesses the emission characteristic peaks of Sm³⁺ ion. It is attributed to $^4G_{5/2} \rightarrow ^6H_J$ ($J=5/2, 7/2, 9/2, 11/2$) transitions: 561 nm, $^4G_{5/2} \rightarrow ^6H_{5/2}$; 598 nm and 606 nm, $^4G_{5/2} \rightarrow ^6H_{7/2}$; 643 nm, $^4G_{5/2} \rightarrow ^6H_{9/2}$; 698.5 nm, $^4G_{5/2} \rightarrow ^6H_{11/2}$. Above luminescence property is in agreement with the reported Sm compounds^[31]. It can predict that the four excitation bands are all the effective energy excitation

for the luminescence of Sm³⁺ ions.

Fig.5 Solid-state emission spectra of **1** at room temperature

3 Conclusions

In summary, we have successfully synthesized samarium sulfate [C₂N₂H₁₀]_{1.5}[Sm(SO₄)₃(H₂O)] · 2H₂O by using H₂O/*n*-butyl alcohol as solvent. The compound exhibits of a novel 2D zigzag layer structure, and the layers are further connected by (H₂O)₂ groups via hydrogen bonds interactions to form a soft 3D supermolecular open framework. While the protonated ethylenediamine are inserted in the channels of the 3D structure and make the structure more stable through the hydrogen bonding interactions. The luminescent spectra of the compounds reveal that the rare-earth organic template sulfates not only possess luminescence nature but also become promising photoluminescence materials.

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