第 28 卷第 7 期 无 机 化 学 学 报 Vol.28 No.7
2012 年 7 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 1477-1482

一种具有梯状链结构有机模板硫酸铽的合成、结构表征以及荧光性质

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摘要:本文采用溶剂热法合成了一种具有梯状链结构新的有机模板硫酸铽盐:$(C_2H_8N)[Tb(SO_4)_2\cdot H_2O]$ (**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。该晶体属于单斜晶系,$P2_1/n$ 空间群。其中 a=0.568 1(3) nm,b=1.972 7(10) nm,c=0.862 7(4) nm,β=90.658(6)°,V=0.966 7(8) nm^3,Z=4。化合物 **1** 的骨架结构由 TbO_8 多面体和 SO_4 四面体构成。S(1)和 S(2)与 Tb(1)相连接,通过 3 个 S-O-Tb 连接构成双链,而相邻的双链通过 μ_3-O(O_5)连接形成一个新的梯状链。

关键词:溶剂热法;硫酸铽盐;晶体结构;荧光
中图分类号:O614.341 **文献标识码**:A **文章编号**:1001-4861(2012)07-1477-06

Solvothermal Synthesis, Crystal Structure and Luminescence of a Organic Amine Templated Terbium Sulfate with Ladder-Like Chains

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Absract: A organic amine templated 1D terbium sulfate $(C_2H_8N)[Tb(SO_4)_2\cdot H_2O]$ (**1**) has been synthesized under solvothermal condition and structurally characterized by single-crystal X-ray diffraction, IR, TGA and ICP. The single-crystal X-ray analysis of compound **1** reveals that the crystal belongs to monoclinic, space group $P2_1/n$ with a=0.568 1(3) nm, b=1.972 7(10) nm, c=0.862 7(4) nm, β=90.658(6)°, V=0.966 7(8) nm^3, Z=4. The structure of framework **1** is constructed from TbO_8 polyhedra and SO_4 tetrahedra. S(1) and S(2) connect Tb(1) and its crystallographic partners by using three S-O-Tb linkages to generate double chains, whereas the adjacent double chains are connected by μ_3-O (O_5) to form a novel ladder-like chains. CCDC: 881421.

Key word: solvothermal synthesis; terbium sulfate; crystal structure; luminescence

Recent years, much attention has been paid to the metal solid state materials with 1D, 2D and 3D structures not only for their intriguing architectures and topologies, but also for their potential applications in catalysis[1-4], separation, ion exchange[5-8], and magnetic properties[9]. The work mainly focused on phosphates and silicates, intensive research resulted in lots of new inorganic frameworks materials with diverse structures and compositions. New solid state materials with novel topological structures and interesting properties can be formed by employed S-O-M linkages in the SO_4 tetrahedra as an effectively building unit[10-14]. Compared with other transition metals, the lanthanide centers have high coordination numbers and a variety of coordination environments allow the formation of novel topological structure. To employ a special

收稿日期:2011-12-19。收修改稿日期:2012-04-26。
教育部博士点新教师基金资助项目。
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organic amine as structure-directing agent (SDA) is one of the strategies which used in the synthesis of lanthanide sulfates. So far, several organic-templated solid state lanthanide sulfates materials have been reported[15-22]. Terbium is an important member in the rare-earth elements because of the excellent luminescence property. To the best of our knowledge, terbium sulfates templated by organic amines have less been reported[16]. In this work, we employed solvothermal method and a new 1D terbium sulfate $(C_2H_8N)[Tb(SO_4)_2 \cdot H_2O]$ (**1**) was successfully prepared in the presence of dimethylamine.

1 Experimental

1.1 Materials and methods

All chemicals purchased were of reagent grade and used without further purification. The element analysis for Tb was performed on Leeman inductivity coupled plasma (ICP) spectrometer, while the C, H and N analyses were performed on a Perkin-Elemer 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 analyse was carried out in N_2 atmosphere on a Diamond thermogravimetric analyzer from 50 to 1 000 ℃ with a heating rate of 10 ℃·min^{-1}.

1.2 Synthesis and characterization

A mixture of Tb_2O_3 (0.188 1 g), isopropyl alcohol (5.030 6 g), dimethylamine water solution (2.107 6 g) and sulfuric acid (1.503 2 g, 98%), in a molar ratio of 1∶143.8∶32.2∶25.9, was stirred for 1 h. The final pH was 2. Then the mixture was kept in a 24 mL Teflon-lined autoclave and heated at 160 ℃ for 4 d. The autoclave was slowly cooled to the room temperature, and then the product was filtered, dried in air for one day to obtain the colorless block crystals. Anal. Calcd. (%): Tb, 38.27; C, 5.78; N, 3.37; H, 2.41. Found (%): Tb, 38.23, C, 5.80; N, 3.36; H, 2.44.

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 using ω-2θ scan method, sealed tube X-ray source (Mo $K\alpha$ radiation, λ=0.071 073 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[23]. 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: 881421.

Table 1 Crystal data and structure refinement for compound 1

Empirical formula	$C_2H_{10}NO_9S_2Tb$	Absorption coefficient / mm^{-1}	7.781
Formula weight	415.15	F(000)	792
Temperature / K	296(2)	Crystal size / mm	0.13×0.12×0.10
Wavelength / nm	0.071073	θ range / (°)	2.06~25.00
Crystal system	Monoclinic	h / k / l	−5, 6 / −23, 23 / −10, 10
Space group	$P2_1/n$	Reflections collected	4 913
a / nm	0.568 1(3)	Independent reflections (R_{int})	1 663 (0.045 0)
b / nm	1.972 7(10)	Data / restraints / parameters	1 663 / 21 / 142
c / nm	0.862 7(4)	Goodness-of-fit on F^2	1.004
β / (°)	90.658(6)	R, wR indices ($I>2\sigma(I)$)	0.068 6, 0.161 1
V / nm^3	0.966 7(8)	R, wR indices (all data)	0.089 1, 0.167 4
Z	4	Largest diff. Peak and hole / (e·nm^{-3})	2 118, −2 526
D_c / (g·cm^{-3})	2.852		

Table 2　Selected bond lengths (nm) and angles (°) for compound 1

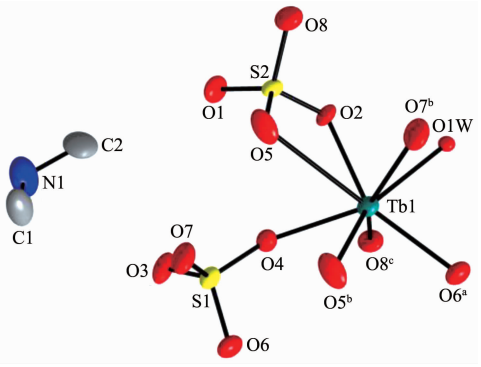
Tb(1)-O(6)[a]	0.228 1(8)	Tb(1)-O(1W)	0.238 8(6)	S(2)-O(1)	0.145 6(8)
Tb(1)-O(5)[b]	0.231 2(7)	Tb(1)-O(5)	0.285 5(9)	S(2)-O(2)	0.148 3(8)
Tb(1)-O(2)	0.233 9(8)	S(1)-O(3)	0.144 2(7)	S(2)-O(5)	0.149 7(8)
Tb(1)-O(4)	0.234 0(7)	S(1)-O(7)	0.147 6(9)	S(2)-O(8)	0.151 2(9)
Tb(1)-O(7)[b]	0.234 8(8)	S(1)-O(4)	0.148 7(8)	C(1)-N(1)	0.144 1(16)
Tb(1)-O(8)[c]	0.238 0(8)	S(1)-O(6)	0.150 2(9)	C(2)-N(1)	0.144 3(17)
O(6)[a]-Tb(1)-O(5)[b]	82.5(3)	O(2)-Tb(1)-O(5)	53.7(2)	O(3)-S(1)-O(4)	110.2(5)
O(6)[a]-Tb(1)-O(2)	146.9(3)	O(6)[a]-Tb(1)-O(1W)	78.6(2)	O(3)-S(1)-O(6)	112.0(5)
O(5)[b]-Tb(1)-O(2)	128.6(3)	O(2)-Tb(1)-O(1W)	68.7(2)	O(7)-S(1)-O(6)	107.7(5)
O(6)[a]-Tb(1)-O(4)	123.9(3)	O(4)-Tb(1)-O(1W)	137.6(2)	O(1)-S(2)-O(2)	113.7(5)
O(2)-Tb(1)-O(4)	80.5(3)	O(7)[b]-Tb(1)-O(1W)	71.9(3)	O(2)-S(2)-O(5)	106.8(5)
O(4)-Tb(1)-O(7[b]	134.5(3)	O(8)[c]-Tb(1)-O(1W)	77.1(3)	O(2)-S(2)-O(8)	108.4(5)
O(6)[a]-Tb(1)-O(5)	151.2(2)	O(3)-S(1)-O(7)	109.4(5)	C(1)-N(1)-C(2)	116.9(10)

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

2　Results and discussion

2.1　Structure analysis

Single crystal X-ray diffraction study indicates that compound **1** is in monoclinic space group $P2_1/n$. The structural analysis reveals that compound **1** is a dimethylamine templated 1D terbium sulfate with a novel structure. As shown in Fig.1, the asymmetric unit of compound **1** contains 15 non-hydrogen atoms, including one terbium atom, two sulfate groups and one coordinated water and one free dimethylamine. The Tb atom is eight-coordinated by seven O atoms from six SO_4^{2-} groups and one O atom from the water molecule. The Tb-O distances range from 0.228 1(8) to 0.285 5(9) nm, while the average value of Tb-O bond length is 0.240 5(7) nm. The angles of O-Tb-O are between 53.7(2)° and 151.2(2)°, similar to other lanthanide compounds reported earlier[13-22]. The S-O distances range from 0.144 2(7) to 0.151 2(9) nm, which is similar to those reported rare-earth sulfates[13-20].



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

Fig.1　Coordination environments of Tb^{3+} in $(C_2H_8N)[Tb(SO_4)_2\cdot H_2O]$

Compared to other rare-earth sulfates, in the structures of terbium sulfates, SO_4 and TbO_x polyhedra are mostly connected by μ_2-O, which open up the possibility to shape 1D or 2D inorganic framework. As shown in Fig.2a, S(1) makes three [Tb-O-S] linkages, and connected two adjacent Tb by using three μ_2-O to generate a $[\text{-Tb-O-S-O-}]_n$ chain. And S(2) through one μ_2-O and two μ_3-O to make the single $[\text{-Tb-O-S-O-}]_n$ chain stable, while μ_3-O connected adjacent $[\text{-Tb-O-S-O-}]_n$ chains to form a novel ladder-like chain (Fig.2b). 1D chains and 2D layered lanthanide sulfates including

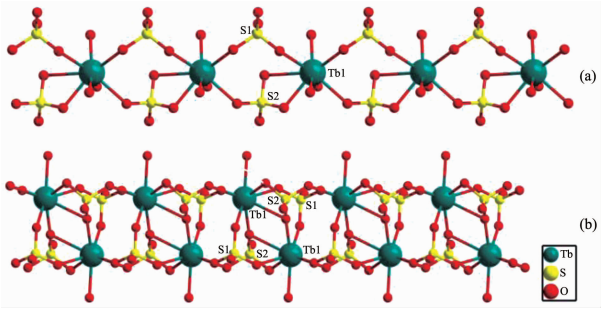


Fig.2　(a) Ball-stick view of $[\text{-Tb-O-S-O-}]_n$ chain in compound **1**; (b) Adjacent double chains connected by μ_3-O atoms to form novel ladder-like chains in compound **1**

Table 3 Selected hydrogen bonds for compound 1

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
O1W–H1WA···O7	0.085(2)	0.226(3)	0.295 9(11)	139(3)
N1–H1D···O1	0.09	0.233	0.319 7(18)	162.0
N1–H1E···O1	0.09	0.224	0.308 1(18)	156.0
N1–H1E···O4	0.09	0.255	0.304 5(14)	116.0
O1W–H1WB···O8	0.085(2)	0.247(3)	0.320 3(10)	144(3)
C2–H2B···O3	0.096	0.242	0.330 3(18)	153.0
C2–H2C···O3	0.096	0.250	0.336 0(18)	149.0

ladder-type structure have been reported[13,24-25]. The vast majority of reported 1D lanthanide sulfates contain the zigzag [Tb-O-S] chain. The inorganic framework of compound **1** can also be described as four-membered ring building units, each of them framed from two SO_4 tetrahedra and two TbO_8 polyhedra. By sharing the edges, two adjacent four-membered rings are connected to each other to form a 1D ladder-like chain of **1**. Two adjacent ladder-like chains form a 2D layer by hydrogen bonding interactions (Fig.3). The protonated organic amine cations are inserted between the ladders, and involving hydrogen bonding with the O atoms from [SO_4] groups in the inorganic framework to generate a soft 3D supermolecular framework (Fig.4).

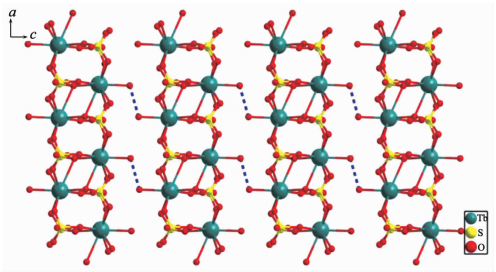


Fig.3 Two adjacent ladder chains formed 2D layer structure by hydrogen bonding

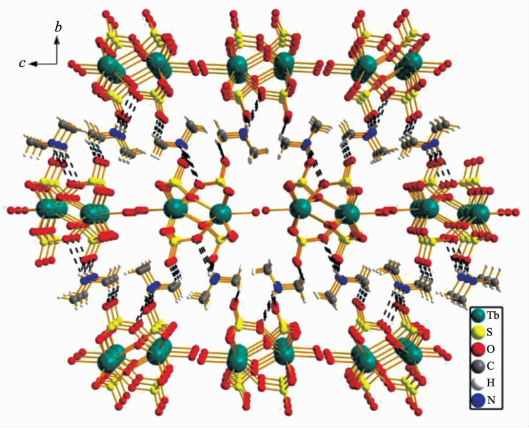


Fig.4 3D open framework in compound **1**

Hydrogen bonds for compound **1** are presented in Table 3.

2.2 IR spectrum of 1

IR of **1** (cm^{-1}): 3 438(s), 2 976(vs), 2 780(vs), 1 588 (m), 1 470(s), 1 118(vs), 648(s), 616(s) (Fig.5). In the IR spectrum of compound **1**, the wild band at 3 438 cm^{-1} can be attributed to the presence of water. The bands at 2 976 and 2 780 cm^{-1} are due to O-H and N-H vibrations. The typical sharp peaks for dimethylamine are in the region 1 380~1 600 cm^{-1}, and characteristic bands due to the SO_4^{2-} are in the 1 118 and 616 cm^{-1} region. The absorption at 648 cm^{-1} can be attributed to Tb-O vibration.

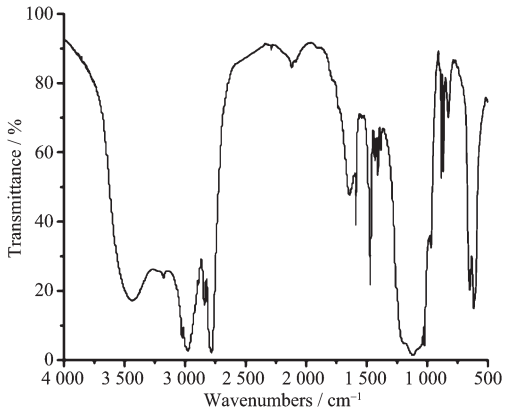


Fig.5 IR spectrum of compound **1**

2.3 Thermal analysis

Thermal analysis shows that the total weight loss of **1** is 56.04% , which is agreement with the calculated value (55.94%). As shown in Fig.6, the weight loss of 10.30% in the range of 50~290 ℃ can be attributed to the removal of organic amine (calcd. 10.84%). The weight loss of 45.74% in the range of 250~1 000 ℃ corresponds to the loss of the coordination water and SO_3 (calcd. 45.10%). The final residue is Tb_2O_3.

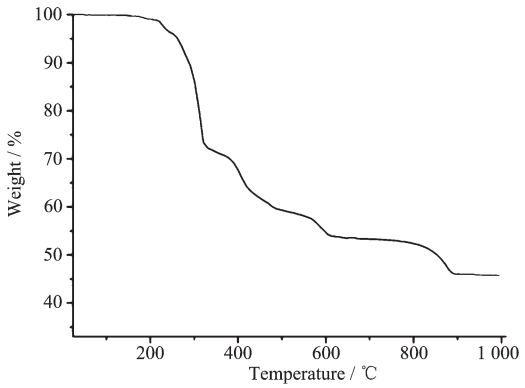


Fig.6　TG curve of compound **1**

2.4 Photoluminescence

Optical property investigation shows that compound **1** exhibits excellent luminescent property. As presented in Fig.7, the photoluminescence spectra of compound **1** possesses the emission characteristic peaks of Tb^{3+} ion. It is attributed to $^5D_4 \rightarrow {}^7H_J$ (J=6, 5, 4, 3) transitions: 490 nm, $^5D_4 \rightarrow {}^7H_6$; 544 nm, $^5D_4 \rightarrow {}^7H_5$; 585 nm, $^5D_4 \rightarrow {}^7H_4$; 622 nm, $^5D_4 \rightarrow {}^7H_3$. Above lumine-scence property is in agreement with the reported Tb^{3+} compounds. It can predict that the four excitation bands are all the effective energy excitation for the luminescence of Tb^{3+} ions. The luminescence intensity of compound **1** is much stronger than other reported Tb compound[16]. The enhanced efficiency of **1** is attributed to the coordination environment and strong hydrogen bonds between inorganic [Tb-O-S] chains and protonated organic amine cations increase the rigidity of Tb^{3+} ions effectively, and reduce the loss of energy.

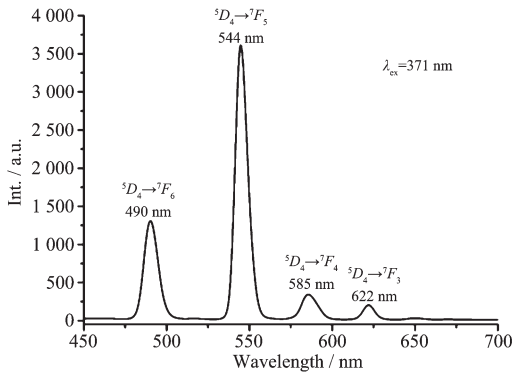


Fig.7　Solid-state emission spectra of **1** at room temperature

3 Conclusions

In summary, we have successfully synthesized a new terbium sulfate $(C_2H_8N)[Tb(SO_4)_2 \cdot H_2O]$ by using isopropyl alcohol as solvent. The compound exhibits an interesting 1D ladder-like structure, which is constructed from four-ring building units. Compound **1** demonstrates the possibility of synthesizing new organic-templated sulfate-based inorganic materials through solvothermal methods. The luminescent spectra of the compounds reveal that the rare-earth organic templated sulfates can become promising photoluminescence materials.

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