基于 2,5-噻吩二羧酸的稀土配合物的合成和表征

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摘要:以 2,5-噻吩二甲酸和稀土盐为原料,通过水热反应,合成了 3 个稀土金属配位聚合物$\{[La(OH)(SO_4)]\}_n$ (**1**), $\{[La_2(TDC)_2(SUC)]\}_n$ (**2**)和$\{[Gd_2(TDC)_2(ox)(H_2O)_4]\cdot 2H_2O\}_n$ (**3**) (H_2TDC=2,5-噻吩二甲酸,SUC=丁二酸, ox=草酸),分别用 X 射线单晶衍射、元素分析、红外光谱对配合物 **2** 和 **3** 进行了表征。实验结果表明:配合物 **2** 和 **3** 均呈现三维网络结构,其中配合物 **2** 属于正交晶系,空间群为 *Pbca*,*a*=1.372 8(4) nm,*b*=0.704 0(2) nm,*c*=2.136 2(6) nm,*Z*=8;配合物 **3** 属于单斜晶系,空间群为 *C*2/*c*,*a*=1.934 3(4) nm,*b*=0.990 5(2) nm,*c*=1.252 8(3) nm,β=107.463(4)°,*Z*=4。

关键词:2,5-噻吩二甲酸;稀土金属;晶体结构;合成
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Syntheses, Characterization and Crystal Structures of Ln(Ⅲ) Complexes Based on 2,5-Thiophenedicarboxylic Acid

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Abstract: Three lanthanide-based coordination polymers, namely $\{[La(OH)(SO_4)]\}_n$ (**1**), $\{[La_2(TDC)_2(SUC)]\}_n$ (**2**) and $\{[Gd_2(TDC)_2(ox)(H_2O)_4]\cdot 2H_2O\}_n$ (**3**) (H_2TDC=2,5-thiophenedi-carboxylic acid, SUC=succinate, ox=oxalate), were synthesized through hydrothermal reaction of H_2TDC and $Ln(NO_3)_3$ (Ln=La, Gd). Investigation on the crystal structure indicates that complex **2** and **3** feature 3D frameworks. Crystal data are orthorhombic, space group *Pbca*, *a*=1.372 8(4) nm, *b*=0.704 0(2) nm, *c*=2.136 2(6) nm, *Z*=8 for **2**; and monoclinic, space group, *C*2/*c*, *a*=1.934 3(4) nm, *b*=0.990 5(2) nm, *c*=1.252 8(3) nm, β=107.463(4)°, *Z*=4 for **3**. CCDC: 1818984, **2**; 1818985, **3**.

Keywords: thiophenedicarboxylate; lanthanide; crystal; synthesis

0 Introduction

As one of synthetic approaches, hydro (solv) thermal reaction has played an important role in the construction of inorganic-organic hybrid materials[1-3]. Based on this approach, chemists have successfully assembled a large number of topological diversity materials that are difficultly obtained from the general synthetic routine[4-7]. Owing to the coordination of organic ligand to metal ion under the hydro (solv) thermal condition resulting in the organic ligand decomposition[8-12] or formation of a new organic

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compound[13-16], it is difficult for us to design and assemble the inorganic-organic hybrid materials based on the structural information of the organic ligand under the hydro(solv)thermal condition. Hence, investigating the external physical or chemical stimuli influencing on the reformation and decomposition of organic ligand under the hydro (solv)thermal condition is of a key importance for our rational design and assembly of inorganic-organic hybrid materials.

2,5-thiophenedicarboxylic acid (here and after namely H_2TDC), when coordinated with metal ion, often exhibit diverse coordination modes, such as monodentate, bidentate, tridentate and tetradentate modes. This coordination feature makes it become a versatile building block in the construction of coordination polymers[17-34]. Like many sulfur-containing organic ligands, such as, 4,4′-dithiodipyridine[35-41] and (4-pyridylthio)acetic acid[42], however, the relatively weak CS in the H_2TDC often break down under the hydro(solv)thermal condition, resulting in a low degree of structure predictability when compared to aromatic polycarboxylate ligands, such as, 1,4-benzendicarboxylic acid[43-45] and 1,3,5-trimesic acid[46-49]. In the present paper, three polymers, namely, $\{[La(OH)(SO_4)]\}_n$ (1), $\{[La_2(TDC)_2(SUC)]\}_n$ (**2**) and $\{[Gd_2(TDC)_2(ox)(H_2O)_4]\cdot 2H_2O\}_n$ (**3**), (H_2TDC=2,5-thiophenedicarboxylic acid, SUC =succinate, ox =oxalate) have been successfully synthesized through hydrothermal reaction of H_2TDC and $Ln(NO_3)_3$ (Ln=La, Gd). The single crystal structures of **2** and **3** have been investigated.

1 Experimental

All reagents used were commercially available and were used as received. The hydrothermal syntheses were carried out in polytetrafluoroethylene lined stainless steel containers under autogeneous pressure. The infrared spectra were recorded on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets.

1.1 Synthesis of $\{[La(OH)(SO_4)]\}_n$ (1) and $\{[La_2(TDC)_2(SUC)]\}_n$ (2)

2,5-thiophenedicarboxylic acid (0.172 g, 1.0 mmol), $La(NO_3)_3\cdot 6H_2O$ (0.433 g, 1.0 mmol) were mixed in 10.0 mL water with stirring at room temperature. After the pH value of the solution was adjusted to about 4.0 by 1.0 $mol\cdot L^{-1}$ NaOH, the solution was transferred and sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 180 ℃ and held at that temperature for 70 hours, then cooled to 30 ℃ at a rate of 5 $℃\cdot h^{-1}$. Then colorless plate crystals of **1** (which was reported by Lu et al.[50]) and colorless needle crystals of **2** were manually picked out in 20% yield respectively. Anal. Calcd. (Found) for $H_2O_{10}S_2La_2$ (**1**)(%): H, 0.40(0.52); S, 12.73(12.60). IR Spectra for **1** (KBr, cm^{-1}): 3 407(s), 2 975(s), 2 926(m), 2 891(m), 1 628(m), 1 543(m), 1 455(w), 1 384(m), 1 272(w), 1 090(s), 1 049(s), 881(m), 771(w), 645(w), 593(w), 469(w). Anal. Calcd. (Found) for $C_{16}H_8O_{12}S_2La_2$ (**2**)(%): C, 26.18 (26.49); H, 1.10 (1.02); S, 8.74 (8.65). IR Spectra for **2** (KBr, cm^{-1}): 3 489(s), 3 432(s), 2 926(w), 2 852 (w), 1 609 (s), 1 550 (s), 1 525 (s), 1 462(w), 1 385(s), 1 152(s), 1 078(s), 995(w), 777(w), 727(w), 679(w), 602(w), 532(w), 473(w).

1.2 Synthesis of $\{[Gd_2(TDC)_2(ox)(H_2O)_4]\cdot 2H_2O\}_n$ (3)

Complex **3** was prepared in the similar way as described for **1** and **2**, except that $Gd(NO_3)_3\cdot 6H_2O$ was used to replace $La(NO_3)_3\cdot 6H_2O$. Colorless block crystals of **3** were collected by filtration in 15% yield. Anal. Calcd. (Found) for $C_{14}H_{16}O_{18}S_2Gd_2$ (**3**)(%): C, 19.76 (19.63); H, 1.90(1.96); S, 7.54(7.46). IR Spectra for **3** (KBr, cm^{-1}): 3 090 (s), 2 973 (s), 2 849 (s), 2 653(s), 2 547(s), 2 035(w), 1 861(w), 1 661(s), 1 527(s), 1 478 (m), 1 417(s), 1 341(m), 1 273(s), 1 231(s), 1 161(m), 1 101(m), 1 104(m), 1 038(s), 931(s), 854(s), 756(s), 672(w), 543(m), 490(m), 463(w).

1.3 X-ray crystallography

Data were collected on a Bruker SMART Apex CCD diffractometer (Mo $K\alpha$, λ=0.071 073 nm) at 298 K for **2** and **3**, and crystal sizes of crystals for crystallography test were 0.15 mm×0.02 mm×0.01 mm (**2**) and 0.20 mm×0.14 mm×0.06 mm (**3**). Absorption corrections were applied using the multiscan program SADABS[51]. The structures were solved by direct methods, and the non-hydrogen atoms were refined anisotropically by the least-squares method on F^2

using the SHELXTL program[52]. The hydrogen atoms of organic ligand were generated geometrically (C-H 0.096 nm, N-H 0.090 nm). Crystal data, as well as details of the data collection and refinement, for the complexes are summarized in Table 1, and selected bond lengths and angles are summarized in Table S1~S3 (Supporting information).

CCDC: 1818984, **2**; 1818985, **3**.

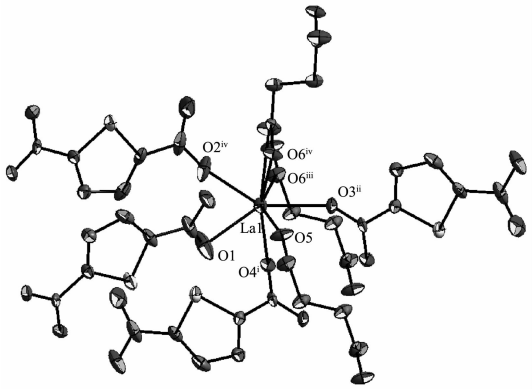
Table 1　Crystal data and details of data collection and refinement for the complexes 2 and 3

Complex	**2**	**3**
Formula	$C_8H_4O_6SLa$	$C_{14}H_{16}O_{18}S_2Gd_2$
Formula weight	367.08	850.89
Crystal System	Orthorhombic	Monoclinic
Space group	*Pbca*	*C*2/*c*
a / nm	1.372 8(4)	1.934 3(4)
b / nm	0.704 0(2)	0.990 5(2)
c / nm	2.136 2(6)	1.252 8(3)
β / (°)		107.463(4)
V / nm^3	2.064 7(11)	2.289 6(9)
Z	8	4
D_c / (g·cm^{-3})	2.357	2.499
μ / mm^{-1}	4.340	6.747
Data, parameter	2 034, 145	2 238, 156
θ range / (°)	1.91~24.99	2.33~25.99
Observed reflection	2 034	2 078
R_1 [$I>2\sigma(I)$]	0.025 4	0.030 9
wR_2 (all data)	0.050 9	0.063 6

2　Results and discussion

Complex **2** consists of two La(Ⅲ) cations, two TDC^{2-} and one SUC^{2-} ligands. Crystal structure analysis reveals that the central La(Ⅲ) cation is nine-coordinated by four carboxylates of four TDC^{2-} ligands with one in bidentate mode and three in monodentate mode, and three carboxylates from three SUC^{2-} ligands with one in bidentate mode and two in monodentate mode in capped square antiprism geometry as shown in Fig.1. The bond lengths of LaO are in the range from 0.238 8(3) to 0.296 5(4) nm, slightly longer than those of $[Ln(INO)(H_2O)(SO_4)]_n$ (INO=isonicotinate-*N*-oxide)[53]. The 2D structure of $\{[La_2(SUC)]\}_n^{4n+}$ in **2** can be viewed as each SUC^{2-} ligand with its each oxygen atom bridged with two adjacent La(Ⅲ) cations (La⋯La=0.420 1 nm) as shown in Fig.2a, while the 3D structure of **2** can be viewed as adjacent two 2D structures connected through oxygen atoms of the TDC^{2-} ligand with its one carboxylate coordinated to two La(Ⅲ) cations from one 2D layer in *syn-syn* mode and another coordinated to two La(Ⅲ) from adjacent layer in *syn-syn* and chelate mode as shown in Fig.2b. It was noted that such a unique coordination mode has not observed in TDC-based complex on the survey of Cambridge Data Base[54].

Single-crystal structural analysis reveals that



Symmetry codes: [i] $-x+2, y+1/2, -z+1/2$; [ii] $x, -y-1/2, z+1/2$; [iii] $x, y+1, z$; [iv] $-x+3/2, y+1/2, z$

Fig.1　Coordination environment of La(Ⅲ) centers in **2** with 50% probability ellipsoids

complex **3** consists of two Gd(Ⅲ) cations, two TDC^{2-} ligands, one ox^{2-} and six water molecules. There are two independent Gd(Ⅲ) centers in the asymmetry unit in **3** (Fig.3). One (Gd1) is eight-coordinated respectively by four TDC^{2-} ligands in monodentate mode and two ox^{2-} in bidentate mode in a di-capped trigonal prism coordination geometry. The other (Gd2) is eight-coordinated by four TDC^{2-} ligands in monodentate mode and four water molecules in a di-capped trigonal prism coordination geometry. The bond lengths of GdO are in the range from 0.230 8(4) to 0.249 2(4) nm, very close to those of $[Gd_6Cu_{24}(\mu_3\text{-}OH)_{30}(mAla)_{16}(ClO_4)(H_2O)_{22}](ClO_4)_{17}(OH)_2\cdot 20H_2O$ (mAla=2-methylalanine)[55]. The 2D structure of $\{[Gd(TDC)]\}_n^{n+}$ in **3** can be viewed as each TDC^{2-} ligand coordinated to four Gd(Ⅲ) cations with its each carboxylate bridged with two Gd(Ⅲ) cation in *anti-syn* mode and each Gd(Ⅲ) cation coordinated with four oxygen atoms respectively from four TDC^{2-} ligands (Fig.4a), while the 3D structure of **3** can be viewed as the adjacent 2D structures pillared by ox^{2-} ligand as shown in Fig.4b.

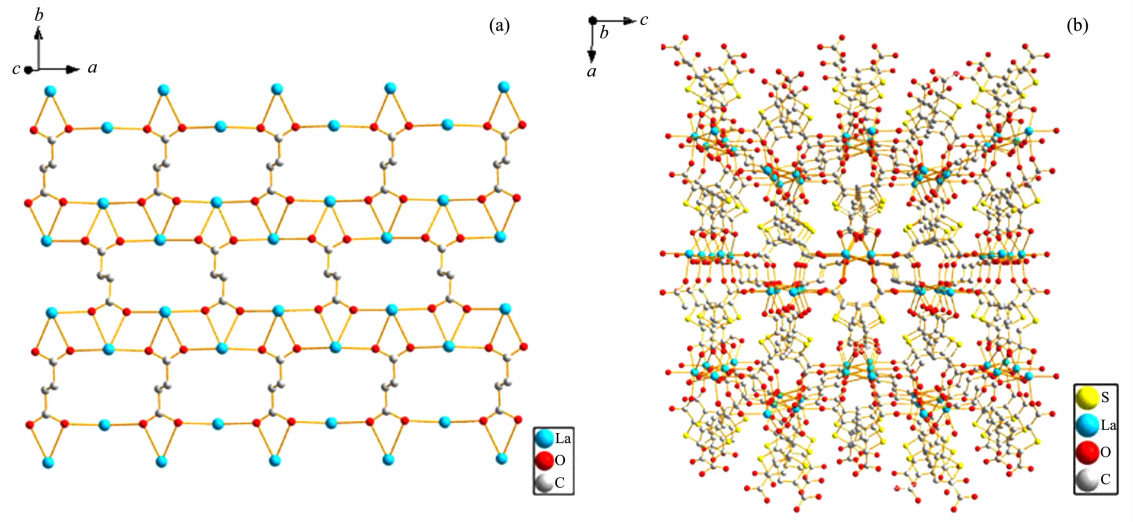
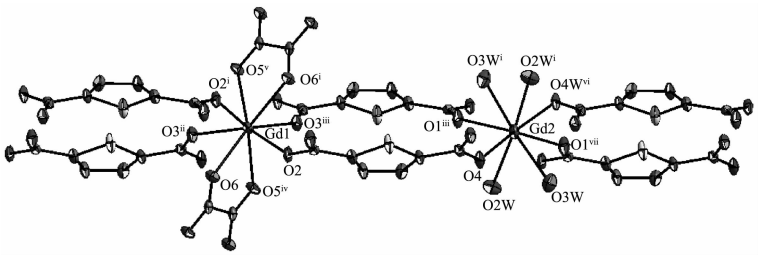


Fig.2 (a) 2D structure of $\{[La_2(SUC)]\}_n^{4n+}$ in **2**; (b) 3D structure of **2**



Symmetry codes: [i] $-x, y, -z+1/2$; [ii] $x+1/2, y-1/2, z$; [iii] $x-1/2, y-1/2, z+1/2$; [iv] $-x, -y, -z$; [v] $x, -y, z+1/2$; [vi] $-x-1, y, z+1/2$; [vii] $x-1/2, y-1/2, z$

Fig.3 Coordination environment of two independent Gd(Ⅲ) centers in **3** with 50% probability ellipsoids

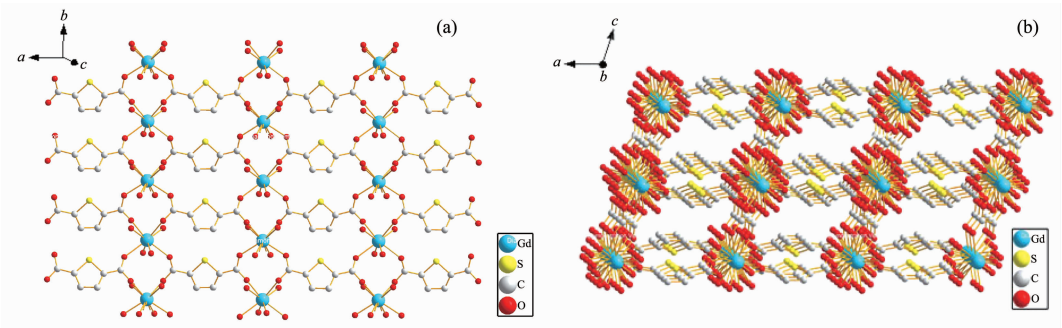


Fig.4 (a) Layer structure of $\{[Gd(TDC)]\}_n^{n+}$ in **3**; (b) 3D structure of **3**

3 Conclusions

In summary, three we have reported syntheses of three lanthanide-based 3D coordination polymers through hydrothermal reaction of $Ln(NO_3)_3$ (Ln=La, Gd) and H_2TDC, and the crystal structure of complexes **2** and **3**. H_2TDC decomposed into oxalic acid, succinic acid and sulphuric acid in these reactions, respectively.

Supporting information is available at http://www.wjhxxb.cn

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