



In-situ carboxylation and synthesis of two novel Sm(III) coordination polymers assembled from 5-hydroxyisophthalate and nitrate, chloride in hydrothermal reaction

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ABSTRACT

By reactions of 5-hydroxyisophthalic acid (H₂hisp) with Sm(NO₃)₃·6H₂O or SmCl₃·6H₂O in the presence of NaOH, two kinds of samarium coordination polymers, [Sm(H₂hbtc)(ox)_{0.5}(H₂O)₃]_n·nH₂O (**1**) (H₂hbtc²⁻ = 6-hydroxy-1,2,4-benzenetricarboxylate) and [Sm(hisp)(Hhisp)(H₂O)₂]_n·2nH₂O (**2**), have been hydrothermally synthesized and characterized. Single-crystal X-ray analyses reveal that compound **1** features a novel two-dimensional (2D) stair-like structure with oxalate ligands and the new organic ligand (H₂hbtc²⁻) but without 5-hydroxyisophthalate ligands, while compound **2** gives the expected product and displays a novel layer structure. The oxalate ligands have been formed via the in-situ reductive coupling of CO₂ molecules released from the decomposition of carboxylate ligands with the reduction of NO₃⁻ and the new organic ligands have been formed via the in-situ carboxylation under the presence of NO₃⁻. Reported herein are the syntheses of compounds **1** and **2**, crystal structures and possible mechanism information regarding the in-situ carboxylation.

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1. Introduction

In recent years, the construction of metal-organic coordination polymers has developed rapidly for their interesting molecular topologies and crystal packing motifs [1–4] along with potential applications as functional materials [5–8]. Although the high and variable coordination numbers and flexible coordination environments of lanthanide ions may cause difficulty in controlling the complexes' synthetic reactions and thereby the structures of the products, the fascinating coordination geometry and the interesting structures along with the special properties of lanthanide polymeric complexes have attracted increasing interest of chemists, and many studies have been reported in the recent literature [9–20]. In the study of lanthanide-organic coordination polymers, aromatic acids have often been used as linkers because of the rigidity of the aromatic part which favors the formation of single crystals and because of the high affinity of carboxylate function and lanthanide ion.

On the other hand, the hydro-(solvo-)thermal method has been proven to be a promising technique in the preparation of highly stable, infinite metal-ligand frameworks with much encouraging

potential for applications, including nonlinear optics, catalysis and separation, magnetism, and molecular recognition [21–24]. More recently, it has been found that in-situ reactions, such as ligand hydrolysis [25], substitution [26], oxidative coupling [27], hydroxylation [28,29], and cycloaddition [30] can often occur under hydro-(solvo-)thermal conditions, and these reactions represent promising new routes for obtaining new organic ligands and constructing novel coordination polymers under hydro-(solvo-)thermal conditions. Carboxylation of aromatic C–H bond is of considerable interest in organic synthesis [31]. Fuchita et al. [32], Grushin et al. [33], Sakakibara et al. [31], Shibahara et al. [34], etc. have reported the Pd-catalyzed or Rh-catalyzed carboxylation of aromatic C–H bonds by using CO, CO₂, O₂ and formic acid, etc. as the carbonyl sources. However, the carboxylation reactions under hydrothermal condition instead of the presence of catalysts are sparse. In this communication, we report two kinds of samarium(III) coordination polymers, [Sm(H₂hbtc)(C₂O₄)_{0.5}(H₂O)₃]_n·nH₂O (**1**) (H₂hbtc²⁻ = 6-hydroxy-1,2,4-benzenetricarboxylate) and [Sm(hisp)(Hhisp)(H₂O)₂]_n·2nH₂O (**2**), based on 5-hydroxyisophthalate with samarium nitrate and samarium chloride, respectively. To the best of our knowledge, compound **1** presents the first carboxylation reaction achieved only by nitrate samarium rather than Pd- or Rh-based catalysts under hydrothermal condition, which suggests that the hydrothermal synthesis may provide simple, clean and economic

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methods for making new organic ligands and constructing novel architecture.

2. Experimental section

2.1. Synthesis of the two complexes

2.1.1. The hydrothermal reaction of 5-hydroxyisophthalic acid, NaOH and $\text{Sm}(\text{NO}_3)_3$ for compound **1**

A mixture of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.088 g), 5-hydroxyisophthalic acid (0.3 mmol, 0.055 g), NaOH (0.3 mmol, 0.012 g) and water (5 mL) was heated to 110 °C for 3 d. Orange block crystals of compound **1** were obtained when cooling to room temperature. The crystals (21% yield) were recovered by filtration, washed with distilled water and dried in air. Elem. anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_{13}\text{Sm}$: C, 24.50; H, 2.40. Found: C, 24.48; H, 2.45. IR (KBr, cm^{-1}): 3434 (vs), 1634 (vs), 1613 (vs), 1582 (s), 1426 (m), 1386 (s), 1317 (m), 1013 (w), 852 (w), 800 (s), 730 (m).

2.1.2. The hydrothermal reaction of 5-hydroxyisophthalic acid, NaOH and SmCl_3 for compound **2**

A mixture of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ (0.073 g, 0.2 mmol), 5-hydroxyisophthalic acid (0.055 g, 0.3 mmol), NaOH (0.012 g, 0.3 mmol) and water (5 mL) was heated to 110 °C for 3 d. Yellow block crystals of compound **2** (56% yield) were obtained when cooling to room temperature. The crystals were recovered by filtration, washed with distilled water and dried in air. Elem. anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{SmO}_{14}$: C, 32.95; H, 2.88. Found: C, 32.93; H, 2.91. IR (KBr, cm^{-1}): 3408 vs, 1713 m, 1626 m, 1600 s, 1543 s, 1526 s, 1486 s, 1460 s, 1408 vs, 1273 m, 1221 m, 1121 w, 1043 w, 1004 w, 973 w, 913 w, 895 w, 808 m, 786 m, 730 m.

2.2. Physical measurements

The compositions of the two complexes were confirmed by elemental analysis, IR and single-crystal X-ray analysis. It is quite surprising that single-crystal X-ray analysis of compound **1** illustrated the presence of oxalate (ox^{2-}) ligand and a new organic ligand of 6-hydroxy-1,2,4-benzenetricarboxylate ($\text{H}_2\text{hbtc}^{2-}$), and the absence of 5-hydroxyisophthalic acid, whereas compound **2** showed a unexpected product. Because no ox^{2-} and $\text{H}_2\text{hbtc}^{2-}$ ligands were directly introduced to the starting mixture of compound **1**, it is proposed that the ox^{2-} and $\text{H}_2\text{hbtc}^{2-}$ ligands might be derived from the 5-hydroxyisophthalic acid.

2.3. X-ray structural studies

Diffraction data of complexes **1–4** were collected on a Bruker SMART 1000 CCD area detector diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in φ and ω scan modes. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97 [35]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths for complexes **1–4** are listed in Table 2.

Crystallographic data for the four complexes in this paper have been deposited at the Cambridge Crystallographic data center, CCDC nos. 630262 and 630261 are for complexes **1** and **2**, respectively. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving-.html> (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge

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

Compound	1	2
Formula	$\text{C}_{10}\text{H}_{12}\text{O}_{13}\text{Sm}$	$\text{C}_{16}\text{H}_{17}\text{O}_{14}\text{Sm}$
M_r	490.55	583.65
Temperature (K)	273(2)	273(2)
Crystal system	Triclinic	Triclinic
Space group	P_{-1}	P_{-1}
a (Å)	7.9649(7)	9.0534(8)
b (Å)	8.7254(7)	9.8512(8)
c (Å)	11.1083(9)	12.5830(11)
α (°)	106.9130(10)	102.5440(10)
β (°)	97.6280(10) ^a	103.1040(10)
γ (°)	102.8990(10) ^a	109.4140(10)
V (Å ³)	703.60(10)	977.19(15)
Z	2	2
D_{calcd} (mg/m ³)	2.315	1.984
μ (mm ⁻¹)	4.248	3.080
$F(000)$	476	574
Crystal size (mm)	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20
θ (°)	2.54–25.05	2.31–25.10
Reflections/collected/unique	3652/2448	5155/3415
	[$R(\text{int}) = 0.0109$]	[$R(\text{int}) = 0.0160$]
Completeness (%)	97.9	98.2
Max. and min. transmission	0.4837 and 0.3622	0.5778 and 0.4584
Data/restraints/parameters	2448/12/250	3415/3/301
Goodness-of-fit on F^2	1.145	1.032
R_1, wR_2 ($I > 2\sigma(I)$)	0.0194, 0.0468	0.0250, 0.0611
Largest diff. peak/hole ($e/\text{Å}^3$)	0.469/−0.678	0.893/−1.044e

Table 2
Selected bond distances (Å) and bond angles (°) for compounds **1** and **2**^a

Compound 1			
Sm(1)–O(1)	2.513(3)	Sm(1)–O(2)	2.495(3)
Sm(1)–O(6B)	2.402(2)	Sm(1)–O(7B)	2.369(3)
Sm(1)–O(8)	2.484(2)	Sm(1)–O(9)	2.476(3)
Sm(1)–O(10)	2.388(4)	Sm(1)–O(11)	2.557(3)
O(2)–Sm(1)–O(1)	52.26(9)	O(7A)–Sm(1)–O(6B)	91.56(9)
O(9)–Sm(1)–O(8)	65.03(8)		
Compound 2			
Sm(1)–O(1)	2.570(3)	Sm(1)–O(2)	2.505(3)
Sm(1)–O(6)	2.297(3)	Sm(1)–O(7A)	2.330(3)
Sm(1)–O(8B)	2.464(3)	Sm(1)–O(8C)	2.652(3)
Sm(1)–O(9C)	2.464(3)	Sm(1)–O(11)	2.583(3)
Sm(1)–O(12)	2.455(3)		
O(2)–Sm(1)–O(1)	51.31(9)	O(9C)–Sm(1)–O(8C)	50.57(8)
O(8B)–Sm(1)–O(8C)	66.10(10)	O(6)–Sm(1)–O(7A)	102.58(10)

^a Symmetry transformations for equivalent atoms: Compound **1**: A: $-x+1, -y+1, -z+1$; B: $x, y, z-1$; C: $-x+1, -y, -z$; D: $x, y, z+1$. Compound **2**: A: $x, -y+2, -z$; B: $-x, -y+1, -z$; C: $x+1, y+1, z$; D: $x-1, y-1, z$.

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3. Results and discussion

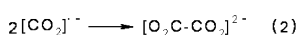
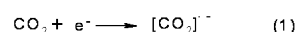
3.1. Reduction and substitution mechanism for compound **1**

The mechanism by which compound **1** was synthesized is of particular interest, considering neither oxalate ligand nor $\text{H}_2\text{hbtc}^{2-}$ ligand was present as reactants. By reactions of lanthanide nitrate with 5-hydroxyisophthalic acid under the molar ratio of $\text{H}_2\text{his}:\text{NaOH} = 1:1.3$ or $1:1.6$, Xu and Li [36] had hydrothermal synthesized a series of lanthanide 5-hydroxyisophthalate coordination polymers, $[\text{Ln}(\text{C}_8\text{H}_4\text{O}_5)(\text{H}_2\text{O})_5] \cdot (\text{H}_2\text{O}) \cdot (\text{C}_8\text{H}_4\text{O}_5)_{1/2}$ ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{and Er}$), with two-dimensional (2D) anion-cation layered structures constructed by helical cation chains using organic

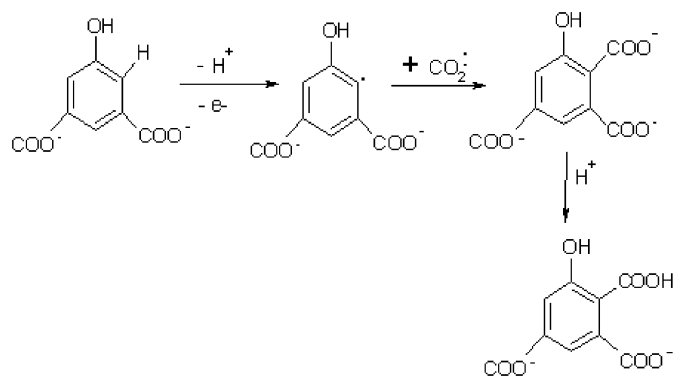
ligands as templates. Whereas, compound **1** was obtained under a weak acidic condition with the molar ratio of $\text{H}_2\text{hispc} : \text{NaOH} = 1:1$, indicating that pH value may play important role on the formation of ox^{2-} and $\text{H}_2\text{hbtc}^{2-}$ ligands. Moreover, when using SmCl_3 instead of SmNO_3 as the lanthanide salt under the similar reaction condition, compound **2**, $[\text{Sm}(\text{hispc})(\text{Hhispc})(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$, was isolated. In compound **2**, however, expected product without ox^{2-} and $\text{H}_2\text{hbtc}^{2-}$ ligands was shown, indicating that nitrate might play a mechanistic role in the formation of ox^{2-} and $\text{H}_2\text{hbtc}^{2-}$ ligands although nitrate was not incorporated into the product [37] since many phenomena of in-situ ligand synthesis, such as reductive coupling [38], oxidation-hydrolysis [39], decarboxylation [40], nitration substitution [41] and so on, occurred when nitrate groups were present. Barrett Adams et al. [42] also found that the nitrate groups were critical to the formation of oxalate linkages via the reductive coupling of atmospheric CO_2 and that in the absence of these species, no products containing oxalate were formed. Typically, the oxalate anion formation under hydrothermal conditions may be attributed to the in-situ reductive coupling of CO_2 molecules released from carboxylate ligands through C–C bond cleavage [38], and the decomposition of carboxylate ligands might proceed with the reduction of NO_3^- [43]. The CO_2 to $\text{C}_2\text{O}_4^{2-}$ reduction is usually described in Scheme 1, it consists of the anionic radical formation and the subsequent radical coupling [38]. At the time, the aromatic C–H bonds in ortho-position of hydroxyl groups might be activated with the presence of NO_3^- , as 4,6-nitro-5-oxido-1,3-benzenedicarboxylate ligands have been in-situ synthesized from 5-hydroxyl-1,3-benzenedicarboxylic acid under the hydrothermal reaction of 5-hydroxyl-1,3-benzenedicarboxylic acid with $\text{Pb}(\text{NO}_3)_2$ [41]. Then, owing to the presence of CO_2 anionic radicals and the mild-acid condition, the activated aromatic C radical in ortho-position of hydroxyl groups might react with CO_2 anionic radicals to afford the ultimate $\text{H}_2\text{hbtc}^{2-}$ ligands via the in-situ carboxylation as shown in Scheme 2 [44]. This unique chemical rearrangement reaction is repeatable with similar yields at the given conditions.

3.2. Crystal structure of $[\{\text{Sm}(\text{H}_2\text{hbtc})(\text{C}_2\text{O}_4)_{0.5}(\text{H}_2\text{O})_3\} \cdot \text{H}_2\text{O}]_n$ (**1**)

X-ray crystallography reveals that compound **1**, crystallized as $[\text{Sm}(\text{H}_2\text{hbtc})(\text{ox})_{0.5}(\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$, features a novel 2D stair-like network (Fig. 1). As shown in Fig. 2, each Sm center is coordinated by nine oxygen atoms: two oxygen atoms from one oxalate ligand, four oxygen atoms from three $\text{H}_2\text{hbtc}^{2-}$ ligands, and three oxygen atoms from three water molecules, resulting in a distorted monocapped square-antiprism geometry. The Sm–O bond distances range from 2.369(3) to 2.557(3) Å and the O–Sm–O angles range from 65.03(8)° to 147.03(10)°. Each $\text{H}_2\text{hbtc}^{2-}$ ligand adopts chelate-bidentate coordination mode (as shown in Chart 1a) to link three Sm(III) ions, in which 4-carboxylic group of $\text{H}_2\text{hbtc}^{2-}$ ligand bridges two Sm(III) ions forming a dinuclear unit with the Sm...Sm distance of 5.282 Å. Each two of such units are connected together through sharing $\text{H}_2\text{hbtc}^{2-}$ ligands to form a one-dimensional (1D) double chain structure along the *c* direction (Fig. 3(a)). In addition, the oxalate ligand acts as a tetradentate ligand to bond two Sm(III) ions from adjacent chains, forming a 1D ladder-like structure (Fig. 3(b)), which features 24-membered parallelogram grids with dimensions of 6.410 × 11.108 Å. Importantly, the plane of 1D ladder-like structure is acclivitous with that of 1D double chain structure with the dihedral angle of 68.36(2)°,



Scheme 1. The $\text{C}_2\text{O}_4^{2-}$ formation via reduction of CO_2 .



Scheme 2. Proposed mechanism for 5-hydroxyisophthalate ligands carboxylation to yield 6-hydroxy-1,2,4-benzenetricarboxylate.

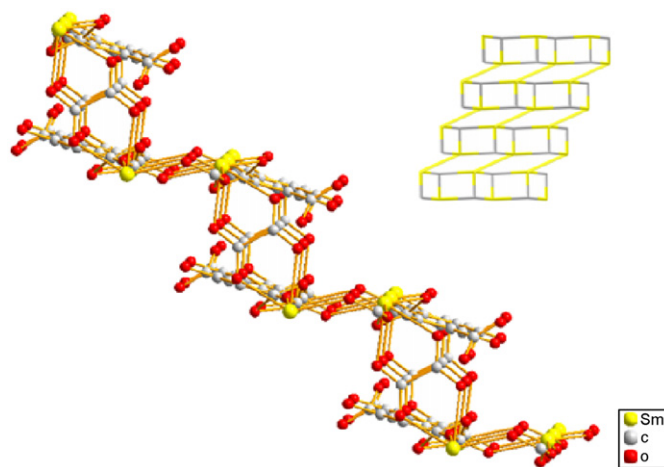


Fig. 1. Outer plot: The 2D stair-like structure of compound **1**; Inner plot: The simplified 2D stair-like network perspective view of compound **1**. Hydrogen atoms have been omitted for clarity.

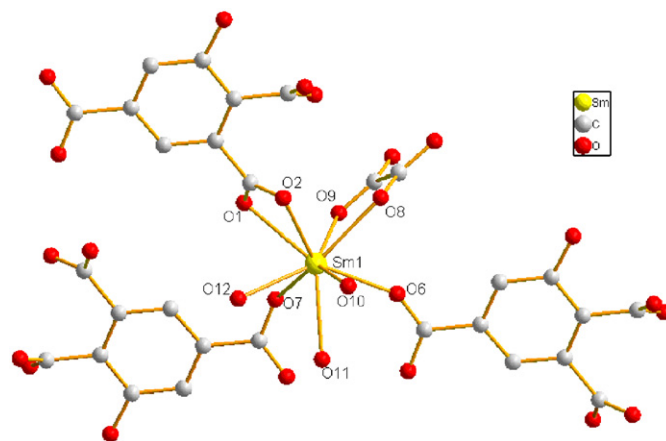
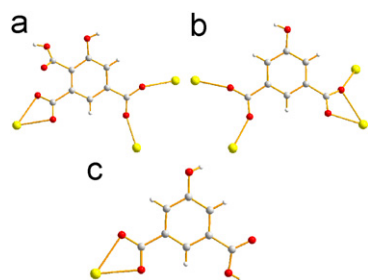


Fig. 2. Diagram showing the coordination environment of the Sm(III) in compound **1**.

which results in a novel 2D stair-like network (Fig. 1). This particular structure is rather rare among known molecular frameworks [45,46], and it is different from the structures reported by Xu et al., which present 2D anion–cation-layered structures constructed by helical cation chains using organic ligands as templates. In the crystal, the 2D networks are connected by hydrogen bonds to form a 3D supramolecular architecture containing 1D channels along the *a*-axis. Free water



Scheme 3. Coordination mode of the carboxylate ligands.

molecules (O13), which are hydrogen bonded to the hydroxyl groups (O5) of H_2hbtc^{2-} ligands, are accommodated within the channel. Selected bond distances and bond angles for compound are listed in Table 2.

3.3. Crystal structure of $\{[Sm(hisp)(Hhisp)(H_2O)_2] \cdot 2H_2O\}_n$ (**2**)

Compound **2**, however, presents a novel 2D layer structure composed of 1D $Ln-O-C-O-Ln$ chains cross-linked by the phenylene moieties of the 5-hydroxyisophthalic acid (Fig. 4). As shown in Fig. 5, each Sm(III) ion is nine-coordinated and

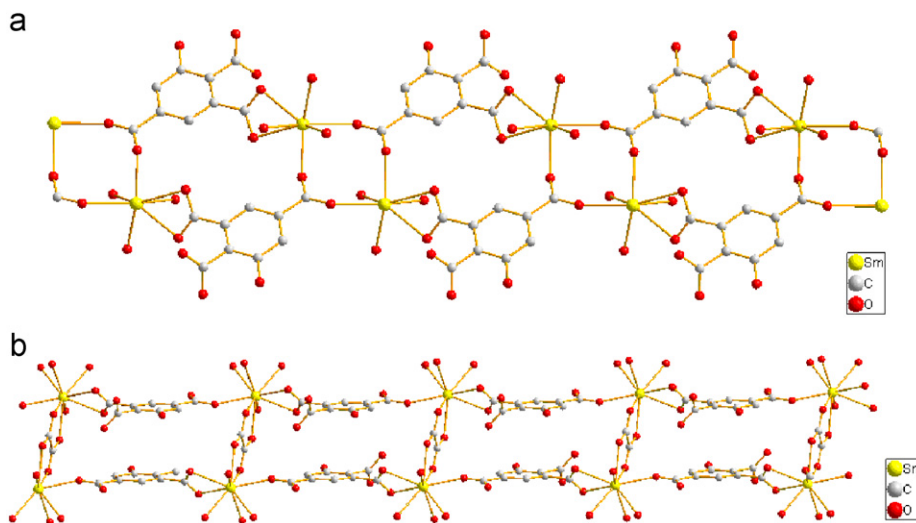


Fig. 3. (a) The 1D double chain of **1** viewed along b -axis. Hydrogen atoms and oxalate ligands coordinated to the Sm(III) have been omitted for clarity. (b) The 1D ladder-like structure of **1**. Hydrogen atoms and partial H_2hbtc^{2-} ligands have been omitted for clarity.

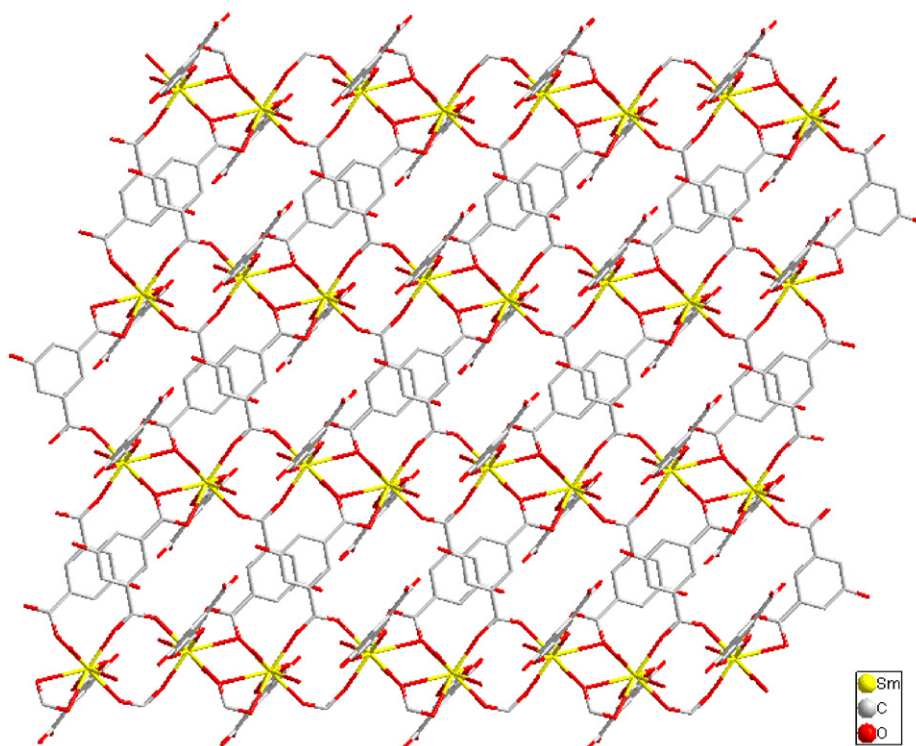


Fig. 4. Diagram showing the 2D layer structure of compound **2** viewed along c axis. Hydrogen atoms have been omitted for clarity.

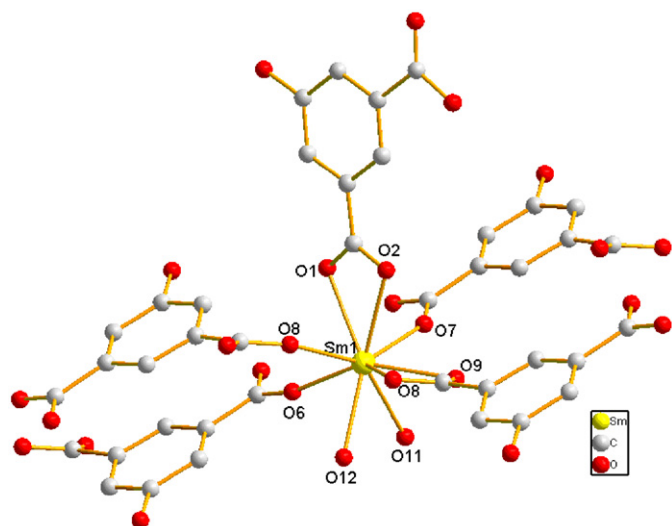


Fig. 5. Diagram showing the coordination environment of the Sm(III) in compound 2.

surrounded by five oxygen atoms from four hisp^{2-} anions, two oxygen atoms from one Hhisp^- anion, and two oxygen atoms from two terminal water molecules to form a distorted monocapped square antiprism. The Sm–O bond distances range from 2.297(3) to 2.652(3) Å, and the O–Sm–O angles range from 50.57(8)° to 149.86(10)°. In one unit of compound 2, there exist two kinds of anions for H_2hisp and their coordination modes are shown in Chart 1b and c. Each pair of Sm(III) ions with a separation of 4.289 Å are assembled by virtue of bridging μ_2 -oxygen atoms of carboxylates from hisp^{2-} anions. Further the dimers are linked by bridging bidentate carboxyl groups from hisp^{2-} anions into 1D Sm–O–C–O–Sm chains along the a -axis. So the hisp^{2-} anions perform chelate-bridging tridentate coordination mode at one side of carboxylate groups and bridging bidentate coordination mode at the other side of carboxylate groups. As a result, the chains are cross-linked by the phenylene moieties of the 5-hydroxyisophthalic acid to yield the final layers (Fig. 4), which are decorated with Hhisp^- anions. Along the a -axis, the Hhisp^- ligands are arranged up and down the 2D layer alternately. Compared with the lanthanide 5-hydroxyisophthalate coordination polymers reported by Xu et al., our samarium 5-hydroxyisophthalate coordination polymer has been obtained under lower pH value with the molar ratio of $\text{H}_2\text{hisp} : \text{NaOH} = 1:1$, which result in the incomplete deprotonation of carboxylate ligands. Some ligands are completely deprotonated and others must be monoprotonated to maintain electroneutrality, which lead to the different 2D layers from that of Xu et al. [36]. Meanwhile, different carboxylate ligands also result in the different structure of compound 2 from that of compound 1 although the same metal centers with the same coordination number exist in compounds 1 and 2. Selected bond distances and bond angles for compound are listed in Table 2.

3.4. Thermogravimetric analyses

The thermal stability of the two compounds was measured by TGA on polycrystalline samples in N_2 atmosphere (Fig. 6). TGA curves of compound 1 exhibit three main steps of weight losses. The first step (55–250 °C) corresponds to the release of aqua ligands and lattice water molecules. The observed weight loss of 14.09% is close to the calculated value (14.68%). The second step (about 250–374 °C) corresponds to the complete decomposition of oxalic acid ligand. The third step (about 374–799 °C) corresponds

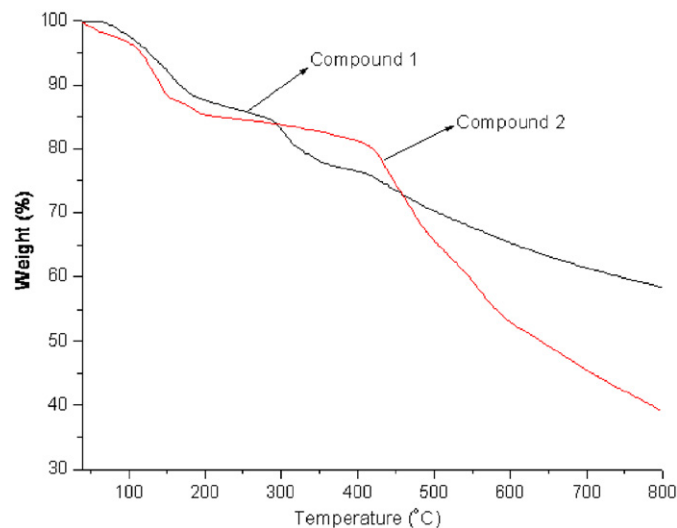


Fig. 6. TGA curves of compounds 1 and 2.

to the partial decomposition of the H_2hbtc ligands with the observed weight loss of 18.65%. TGA curves of compound 2 exhibit two main steps of weight losses. The first step started at 83 °C and completed at 220 °C, which corresponds to the release of aqua ligands and lattice water molecules. The observed weight loss of 12.52% is close to the calculated value (12.36%). The second step (about 380–799 °C) corresponds to the partial decomposition of the H_2hisp ligands with the observed weight loss of 42.62%. From the slopes of the TGA curves, we expect that the decomposing processes of compounds 1 and 2 are not complete at 800 °C.

4. Conclusions

In summary, by using two kinds of samarium salts (nitrate and chloride) as reactants, we have hydrothermally synthesized two different kinds of 2D Sm(III) coordination polymers. Single-crystal X-ray analyses reveal that compound 1 features a novel 2D stair-like structure with oxalate ligands and a new organic ligand, 6-hydroxy-1,2,4-benzenetricarboxylate, while compound 2 gives the expected product and displays a novel 2D layer structure. We propose that the formation of oxalate be attributed to the in-situ reductive coupling of CO_2 molecules released from the decomposition of carboxylate ligands with the reduction of NO_3^- and that the new organic ligands be formed via the in-situ carboxylation under the presence of NO_3^- . This study illustrates that organic ligands can undergo self-reaction under hydrothermal conditions and further suggests that more novel structures can be obtained by hydrothermal or solvothermal methods even with common ligands.

Acknowledgment

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Appendix A. Supplementary material

CCDC nos. 630262 and 630261 contain the supplementary crystallographic data for compounds 1 and 2, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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