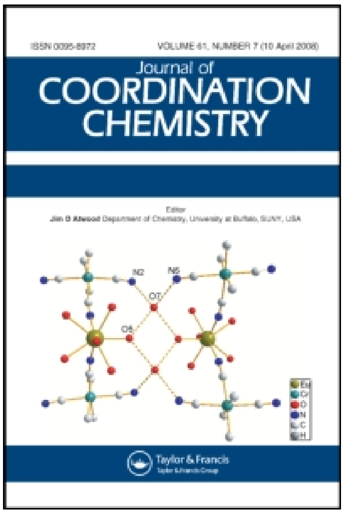

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Hydrothermal synthesis, crystal structure and magnetic properties of a samarium coordination polymer $\{[Sm_2(sb)_2(ox)(H_2O)_6] \cdot 2H_2O\}$ <b> <i>n</i>

Xing Li[a]; Jian-Guo Pan[a]
[a] The State Key Laboratory Base of Novel Functional Materials and Preparation Science, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang 315211, P.R. China

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Hydrothermal synthesis, crystal structure and magnetic properties of a samarium coordination polymer $\{[Sm_2(sb)_2(ox)(H_2O)_6]\cdot 2H_2O\}_n$

XING LI* and JIAN-GUO PAN

The State Key Laboratory Base of Novel Functional Materials and
Preparation Science, Faculty of Materials Science and Chemical Engineering,
Ningbo University, Ningbo, Zhejiang 315211, P.R. China

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Hydrothermal reaction of 4-sulfobenzoic acid monopotassium salt, $H_2C_2O_4\cdot 2H_2O$ and $Sm(NO_3)_3\cdot 6H_2O$, gave a new polymeric complex $\{[Sm_2(sb)_2(ox)(H_2O)_6]\cdot 2H_2O\}_n$ (**1**), (H_2sb = 4-sulfobenzoic acid, ox = oxalate). X-ray diffraction analysis reveals that the complex, belonging to the triclinic system, space group $P\bar{1}$, $a = 5.9384(1)$, $b = 7.9136(2)$, $c = 14.7920(5)$ Å, $V = 646.92(3)$ Å^3, $Z = 2$, possesses a two-dimensional framework constructed by eight-coordinate Sm(III) centers. Magnetic susceptibility data of **1** are consistent with the existence of weak anti-ferromagnetic interactions. Thermogravimetric analysis shows that the structural framework of the compound is stable; the luminescence for **1** is also discussed.

Keywords: Hydrothermal synthesis; Crystal structure; Coordination complex; Magnetic susceptibility

1. Introduction

The coordination chemistry of rare earth elements has attracted much attention because of the potential of these materials in applications such as nonlinear optical devices, catalysts, molecular magnets and sensors [1–5]. The key for architecture of polymeric lanthanide compounds is to select suitable organic ligands. Due to the high affinity of lanthanide ions for oxygen and the coordination versatility of carboxylates, rigid multi-carboxylate ligands are selected to construct such architectures, especially terephthalate acid, which forms a variety of structures through short bridges from one carboxylate or long bridges via the benzene ring; a number of coordination complexes of lanthanides with multi-carboxylate ligands have been reported [6–10]. 4-Sulfobenzoic acid (H_2sb) and terephalatic acid (H_2ta) possess similar structures; however, few complexes of H_2sb have been reported [11–14], perhaps from the sulfonic group having weak coordination ability in contrast to carboxylate.

The versatility of H_2sb arises from its variable coordinative modes through sulfonic and carboxylate groups: monodentate, chelating-bidentate, bridging-bidentate,

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*Corresponding author. Tel.: +86 574 87600874. Fax: +86 574 87600734. Email: lixing@nbu.edu.cn

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and bridging-multidentate. Auxiliary bridging ligands such as pyrazine, 4,4′-bipyridine or oxalate (ox), may result in new framework structures. We have begun construction of lanthanide complexes using sb and ox as building blocks. Herein we report the hydrothermal synthesis and crystal structure of a new polymeric compound, $\{[Sm_2(sb)_2(ox)(H_2O)_6]\cdot 2H_2O\}_n$ (**1**). Magnetic properties are also discussed.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals of reagent grade were commercially available and used without further purification. The infrared spectrum was taken on a Magna 750 FTIR spectrophotometer as KBr pellets from 4000–400 cm^{-1}. Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. Variable-temperature magnetic susceptibility data for polycrystalline samples of **1** were obtained in an external field of 10,000 G on a SQUID magnetometer from 4.97 to 299.97 K. Fluorescent properties were measured on an Edinburgh Instruments analyzer model FL920. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449C instrument.

2.2. *Preparation*

2.2.1. Preparation of $\{[Sm_2(sb)_2(ox)(H_2O)_6]\cdot 2H_2O\}_n$. A mixture of 4-sulfobenzoic acid monopotassium salt (0.072 g, 0.3 mmol), $H_2C_2O_4\cdot 2H_2O$ (0.025 g, 0.2 mmol), $Sm(NO_3)_3\cdot 6H_2O$ (0.146 g, 0.4 mmol) and water (15 mL) was sealed in a 25 mL stainless reactor with a Teflon liner and heated to 140°C for 72 h. After cooling to room temperature, light yellow block-like crystals were obtained. Yield: 55%. Elemental analysis for $C_{16}H_{24}O_{22}S_2Sm_2$ (933.18) Calcd (%): C, 20.59; H, 2.59; S, 6.87. Found: C, 20.31; H, 2.50; S, 6.92. IR (KBr, cm^{-1}): 3446(s), 1643(m), 1597(s), 1541(vs), 1495(w), 1417(vs), 1294(w), 1188(vs), 1128(vs), 1055(s), 1041(s), 1011(s), 870(w), 850(w), 735(s), 700(m), 621(m), 557(m), 471(m).

2.3. *X-ray crystallography*

A light-yellow crystal having dimensions 0.60 mm × 0.10 mm × 0.08 mm was mounted on a glass fiber. Data collection for **1** was performed on a Siemens SMART-CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. A total of 3310 reflections were collected in the range $1.43° < \theta < 25.09°$ using the $\omega - 2\theta$ scan mode, with 2233 observed with $I > 2\sigma(I)$. Absorption corrections were applied using the SADABS program [15]. The structure was solved by direct methods; metal atoms were located from E-maps and other non-hydrogen atoms were derived from the successive difference Fourier syntheses. Hydrogen atoms were located from the difference map and refined isotropically. The structure was refined on F^2 by full-matrix least-square techniques using the SHELXTL-97 program package [16]. The final cycle of refinement gave rise to

Table 1. Summary of crystal data and structure refinement for **1**.

Empirical formula	$C_{16}H_{24}O_{22}S_2Sm_2$
Formula weight	933.18
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	
a	5.93840(10)
b	7.9136(2)
c	14.7920(5)
α	74.505(2)
β	84.261(2)
γ	75.078(2)
Volume (Å^3)	646.92(3)
Z, Calculated density (Mg m^{-3})	2, 2.395
Absorption coefficient (mm^{-1})	4.758
F(000)	452
Crystal size (mm^3)	0.60 × 0.10 × 0.08
θ range for data collection (°)	1.43–25.09
Limiting indices	$-7 \le h \le 7$, $-8 \le k \le 9$, $-15 \le l \le 17$
Reflections collected/unique	3310/2233 [$R_{\text{int}} = 0.0289$]
Completeness to $\theta = 25.09$	97.0%
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.6087
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2233/0/198
Goodness-of-fit on F^2	1.118
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0430$, $wR_2 = 0.1081$
R indices (all data)	$R_1 = 0.0497$, $wR_2 = 0.1154$

$R = 0.0430$, $wR = 0.1081$, $w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 7.0951P]$, where $P = 1/3$ $[F_o^2 + 2F_c^2]$, $S = 1.118$. A summary of crystallographic data of **1** and details of the structure refinement are listed in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of* $\{[Sm_2(sb)_2(ox)(H_2O)_6]\cdot 2H_2O\}_n$

Compound **1** is stable in air and insoluble in common solvents. IR spectroscopic studies indicate major peaks from functional groups of organic ligands in the compound, which are confirmed by the crystal structure. The presence of water is clearly identified by the well-defined, strong band at 3446(s) cm^{-1} for ν(O–H). The sulfonate group R–SO_3^- shows strong bands due to ν(S–O) vibrations generally found in the region 1300–1055 cm^{-1} (see Experimental section). The ν(C–S) peaks were in the region 1011–1055 cm^{-1}. The peak at 1597(s) cm^{-1} is assigned to the ν_s(C=O) vibration; 1643(m) cm^{-1}, ν(COO); 1541(vs) cm^{-1}, (C–C)$_{\text{skeletal}}$; 1495(m) cm^{-1}, (C–C)$_{\text{aromatic}}$; 1417(s) cm^{-1}, δs(C=O). Single X-ray analysis reveals **1** possesses a two-dimensional framework constructed by Sm(III), sb^{2-} and ox^{2-}. The local coordination environment around Sm(III) (figure 1) shows that each Sm(III) center is coordinated by eight oxygen atoms, three from water, two from oxalates, one from sulfonate oxygen and the others from carboxylate oxygens. The carboxylic and sulfonic groups of 4-sulfobenzoic acid are deprotonated during formation of **1** and each sb^{2-} ligand is tridentate, linking three metal ions via one sulfonate oxygen with Sm–$O_{sulfonic}$ distance of 2.408(6) Å and

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

O(1)–Sm#2	2.332(6)
O(2)–Sm#3	2.378(5)
O(3)–Sm	2.407(6)
O(6)–Sm	2.438(6)
O(7)–Sm#1	2.437(6)
O(8)–Sm	2.442(6)
O(9)–Sm	2.456(6)
O(10)–Sm	2.436(7)
O(1)#2–Sm–O(2)#3	110.8(2)
O(1)#2–Sm–O(3)	81.0(2)
O(2)#3–Sm–O(3)	73.8(2)
O(1)#2–Sm–O(10)	76.5(2)
O(2)#3–Sm–O(10)	68.4(2)
O(3)–Sm–O(10)	124.6(2)
O(1)#2–Sm–O(7)#1	144.8(2)
O(2)#3–Sm–O(7)#1	87.0(2)
O(3)–Sm–O(7)#1	75.2(2)
O(10)–Sm–O(7)#1	138.6(2)
O(1)#2–Sm–O(6)	143.2(2)
O(2)#3–Sm–O(6)	83.0(2)
O(3)–Sm–O(6)	135.7(2)
O(10)–Sm–O(6)	77.7(2)
O(7)#1–Sm–O(6)	66.22(19)
O(1)#2–Sm–O(8)	74.4(2)
O(2)#3–Sm–O(8)	139.4(2)
O(3)–Sm–O(8)	144.2(2)
O(10)–Sm–O(8)	74.3(3)
O(7)#1–Sm–O(8)	112.0(2)
O(6)–Sm–O(8)	73.7(2)
O(1)#2–Sm–O(9)	75.1(2)
O(2)#3–Sm–O(9)	146.8(2)
O(3)–Sm–O(9)	75.1(2)
O(10)–Sm–O(9)	141.8(2)
O(7)#1–Sm–O(9)	74.0(2)
O(6)–Sm–O(9)	112.4(2)
O(8)–Sm–O(9)	73.8(3)

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y$, $-z+2$; #2: $-x+1$, $-y+1$, $-z+1$; #3: $-x$, $-y+1$, $-z+1$.

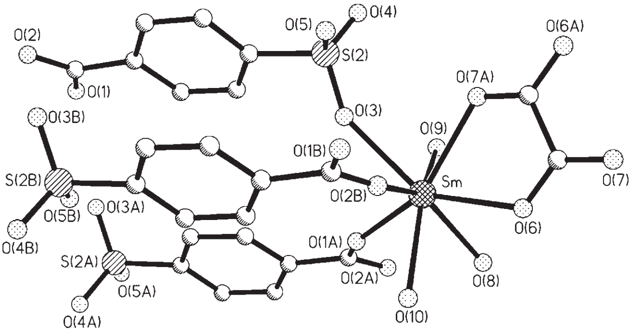


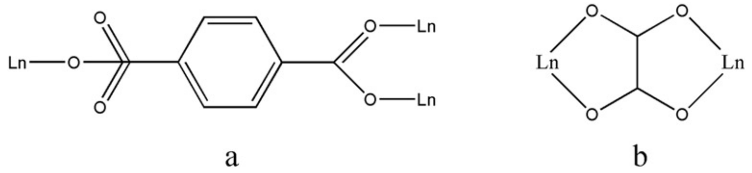
Figure 1. Local coordination environment of Sm^{3+} for **1**, isolated water molecules are omitted for clarity.

two carboxylate oxygens of one carboxylate with Sm–$O_{carboxylic}$ distances of 2.332(7) and 2.377(6) Å, respectively (scheme 1a); each oxalate is quadridentate chelating-bridging two metal ions (scheme 1b).

Metal ions are linked through carboxylate and sulfonate oxygen atoms of sb^{2-} to give a double chain structure with the nearest Sm–Sm distance 5.938 Å, indicating no direct interaction between Sm–Sm. The chains are further joined by oxalate ligands to form the two-dimensional layer structure (figure 2). Through hydrogen-bonding interactions the two-dimensional structure becomes a three-dimensional framework (figure 3). Different kinds of hydrogen bonding are observed in the structure: (a) hydrogen bonding between coordinated water and non-coordinated water (O ··· O distances, 2.759–2.760 Å); (b) coordinated water and sulfonate oxygen (O ··· O distances, 2.734–2.808 Å); (c) non-coordinated water and oxalate oxygen (O ··· O distances, 2.814–2.954 Å) [17].

3.2. *Magnetic properties*

The temperature dependent susceptibility of $\{[Sm_2(sb)_2(ox)(H_2O)_6]\cdot 2H_2O\}_n$ was measured in the range 4.97–299.97 K on a SQUID magnetometer in 10,000 G; the χ_m



Scheme 1. Ligands coordination models.

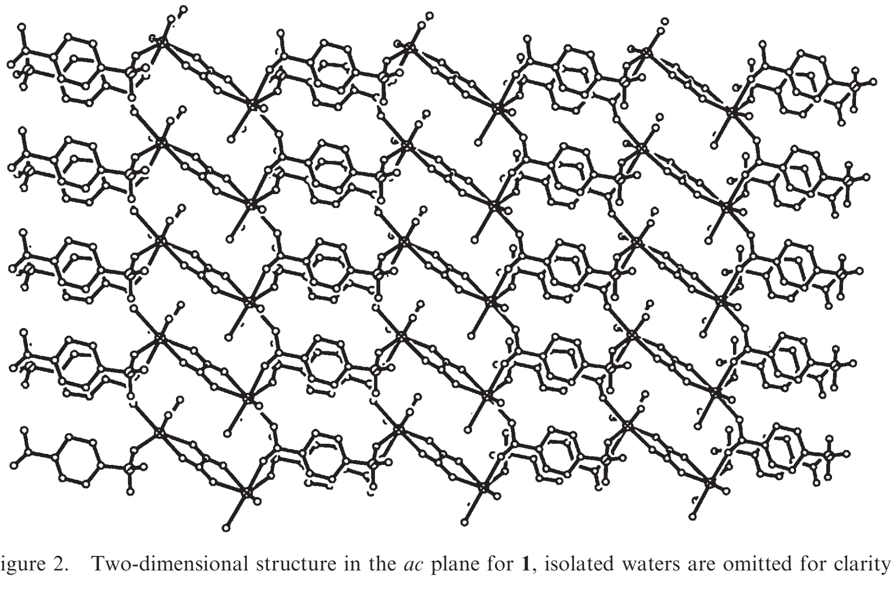


Figure 2. Two-dimensional structure in the *ac* plane for **1**, isolated waters are omitted for clarity.

and $1/\chi_m$ *versus* T plots are shown in figure 4. The χ_m value increases as the temperature decreases; the value of the effective moment (μ_{eff}) is $1.26\,cm^3\,K\,mol^{-1}$ at room temperature and decreases continuously upon cooling, indicating the presence of an anti-ferromagnetic interaction between metal centers. According to the structural data, the complex may have two types of magnetic exchange interaction of Sm–Sm ions: one through a short bridge via the carboxylate of sb and the other through oxalate. The weak magnetic exchange via phenyl of sb^{2-} can be neglected [18].

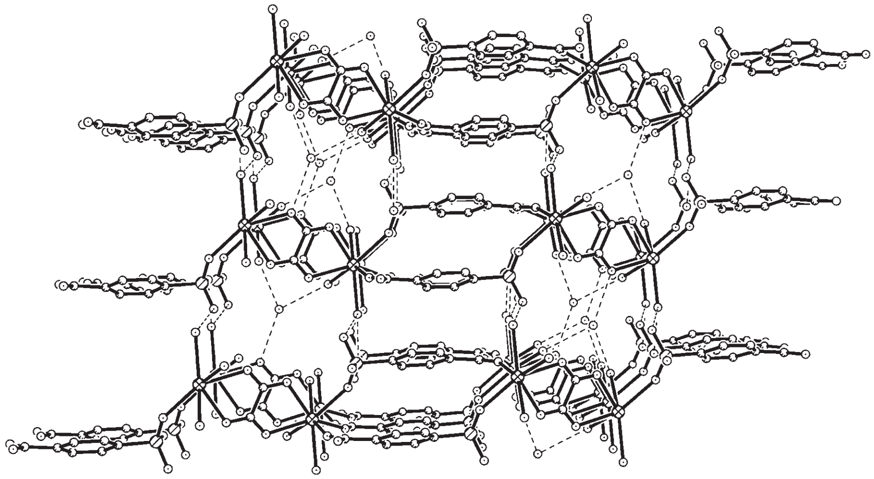


Figure 3. Packing structure along *a* of **1**.

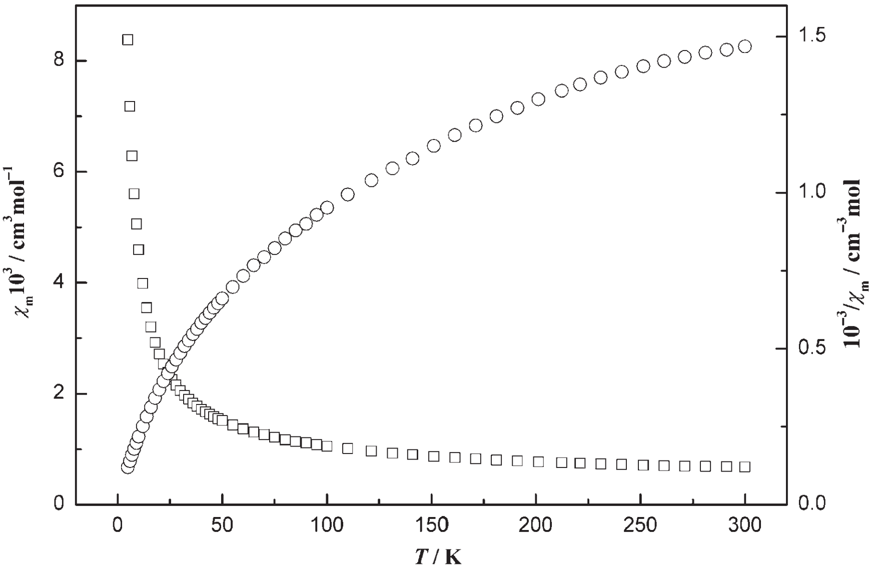


Figure 4. Temperature dependent plots of χ_m and $1/\chi_m$ *vs*. T for **1**, (O) $1/\chi_m$, (□) χ_m.

3.3. *Fluorescent measurements and thermogravimetric analysis*

In the solid state, upon photo-excitation at 402 nm, the complex displays two weak fluorescent emissions at 558 and 565 nm, one strong emission at 595 nm and two middle-intensity emissions at 602 and 642 nm (shown in figure 5). Since free 4-sulfobenzoic acid and oxalate do not exhibit photoluminescence at this condition, the photoluminescence emission may be assigned to radiative decay of samarium ions: 558 and 565 nm attributed to $^5D_0 \rightarrow {}^7F_0$, 595 nm attributed to $^5D_0 \rightarrow {}^7F_1$, and 642 nm

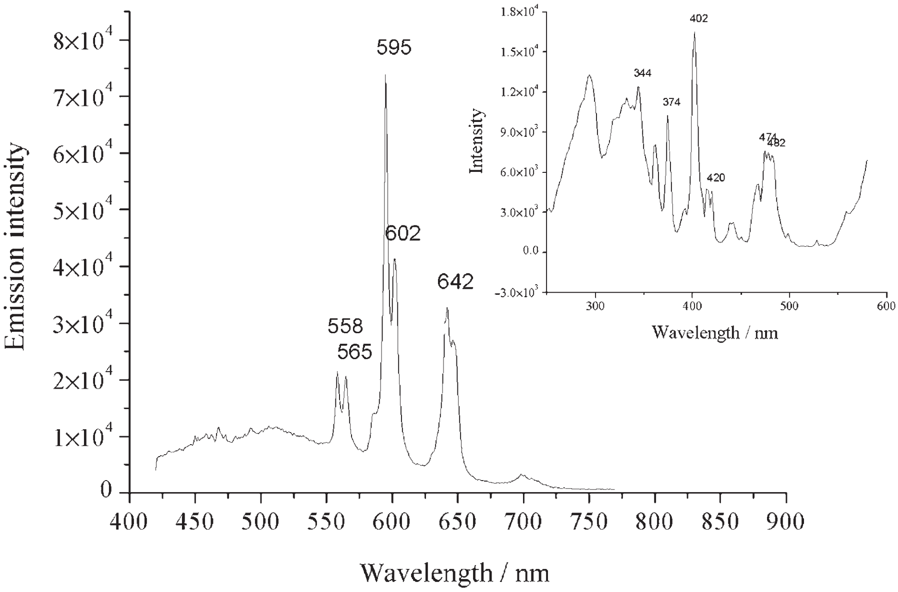


Figure 5. The solid state photoluminescence spectrum for **1** at room temperature.

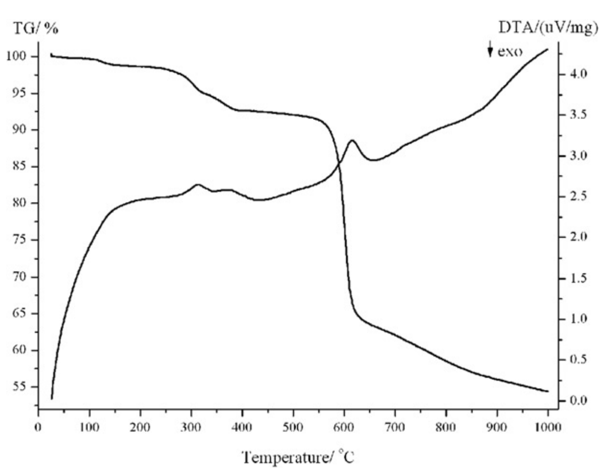


Figure 6. The thermogravimetric analysis (TGA) and differential thermal analysis.

attributed to ${}^5D_0 \rightarrow {}^7F_2$ transitions [19]; photoluminescence from the organic ligand can be ignored.

Thermogravrimetic analysis of the complex was performed under a flow of nitrogen from room temperature to 1000°C at a heating rate of $10^\circ C\,min^{-1}$. The first weight loss of 2.11% (Calcd: 1.93%) from 100 to 271°C corresponds to one guest water molecule per formula unit $\{[Sm_2(sb)_2(ox)(H_2O)_6] \cdot 2H_2O\}_n$; the second weight loss of 2.07% from 271 to 320°C corresponds to another guest water molecule per formula unit. Up to 390°C, the weight loss of 7.41% (Calcd: 7.72%) corresponds to four water molecules per formula unit; further heating gives slow weight loss with increasing temperature. Differential thermal analysis (DTA) studies show a strong heat absorption at a phase change from 560 to 650°C, indicating collapse of the structural framework of the compound. Compound **1** (figure 6) may be a candidate as a stable and solvent-resistant fluorescent material.

In conclusion, we have isolated a samarium polymer, $\{[Sm_2(sb)_2(ox)(H_2O)_6] \cdot 2H_2O\}_n$, through hydrothermal reaction of 4-sulfobenzoic acid and oxalate, showing a different bridge ligand to synthesize new functional materials.

Supplementary data

Crystallographic data (excluding structure factors) for the complex in this article have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publications, CCDC 205858. Copies of the data can be obtained free of charge from the CCDC, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk; www: www.ccdc.cam.ac.uk.

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