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Synthesis, structure, and magnetism of a ytterbium coordination polymer with 5-sulfonyl-1,2,4-benzenetricarboxylate and oxalate

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Synthesis, structure, and magnetism of a ytterbium coordination polymer with 5-sulfonyl-1,2,4-benzenetricarboxylate and oxalate

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[Yb₂(SBTC)(ox)(H₂O)₅]_n (**1**) (H₄-SBTC = 5-sulfonyl-1,2,4-benzenetricarboxylic acid and ox = oxalate) has been hydrothermally synthesized by reaction of 5-sulfonyl-1,2,4-benzenetricarboxylic acid with Yb(NO₃)₃·5H₂O. In situ formation of oxalate derived from H₄-SBTC is unprecedented and adds a new oxalate formation reaction to *in situ* ligand syntheses. Compound **1** features a 2-D bilayered coordination network, which is further extended into a 3-D supramolecular framework through interlayered hydrogen bonds. Magnetic measurements on **1** indicate that there is an antiferromagnetic interaction between Yb(III) ions.

Keywords: 5-Sulfonyl-1,2,4-benzenetricarboxylic acid; Ytterbium coordination polymer; Magnetic property

1. Introduction

Coordination polymers or metal-organic frameworks with architectural beauty and applications as molecular magnets, photoluminescence, adsorption, and catalysis are a superior class of materials [1–5]. Combination of the characteristics of organic and inorganic components offers an opportunity to incorporate useful properties within a single composite, providing access to multifunctional materials. Lanthanides attract attention for unique physical properties arising from 4f electrons [6–9]. High coordination number and flexible coordination geometry of lanthanide ions make it difficult to control preparation of lanthanide compounds. Lanthanides have high affinity for hard donors, so ligands containing oxygen are usually employed in lanthanide coordination polymers [10–15]. Lanthanide-carboxylate frameworks are extensively studied because carboxylate exhibits diverse coordination and appropriate connectivity, utilized for extension of the metal ions into high-dimensional structures [16–19]. Structural complexity has been further enhanced

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through design of multifunctional carboxylate derivatives such as sulfonate-carboxylate ligands [20–22]. The sulfonate-carboxylate with strong coordination of carboxylate and weak coordination of sulfonate has received increasing interest. 5-Sulfoisophthalic acid [23], 2-sulfoterephthalic acid [24], 3-sulfobenzoic acid [25], 4-sulfobenzoic acid [26], and 4,8-disulfonyl-2,6-naphthalenedicarboxylic acid [27] have been employed to construct coordination polymers with diverse structures and interesting properties. Nevertheless, there are still relatively few examples of coordination polymers based on sulfonate-carboxylate ligands. Herein, a sulfonate-carboxylate, 5-sulfonyl-1,2,4-benzenetricarboxylic acid (H_4 -SBTC), has been employed to construct a lanthanide coordination polymer. The H_4 -SBTC ligand, with a benzene backbone and three carboxyl and one sulfonyl functional groups, is effective in the design of a range of coordination polymers. However, the coordination chemistry of H_4 -SBTC is not investigated till the present work. In this contribution, a lanthanide coordination polymer, $[Yb_2(SBTC)(ox)(H_2O)_5]_n$ ($ox = oxalate$), has been synthesized and characterized. The formation of oxalate adds a new oxalate formation reaction to *in situ* ligand syntheses. The magnetic behavior of the compound has been studied. To the best of our knowledge, this is the first example based on H_4 -SBTC.

2. Experimental

2.1. Materials and instrumentation

All chemicals were obtained from commercial sources and used without purification. Elemental analyses were carried out on an Elementar Vario EL III analyzer and IR spectra (KBr pellets) were recorded on a PerkinElmer Spectrum One. Magnetic measurements were carried out on crystalline samples with a Quantum Design SQUID magnetometer MPMS-XL5. Magnetic data were corrected for diamagnetic contributions of the sample holder, and diamagnetic corrections were estimated from Pascal's constants for all constituents. Thermogravimetric measurements were performed with a Netzsch STA449C apparatus under nitrogen with a heating rate of 10 °C/min in Al_2O_3 containers from 30 to 800 °C.

2.2. Synthesis of $[Yb_2(SBTC)(ox)(H_2O)_5]_n$ (**1**)

A mixture of $Yb(NO_3)_3 \cdot 5H_2O$ (0.0599 g, 0.13 mM) and 5-sulfonyl-1,2,4-benzenetricarboxylic acid (0.0385 g, 0.13 mM) in a 1:1 M ratio in 10 mL H_2O (pH 4) was introduced into a Parr Teflon-lined stainless steel vessel (25 mL). The vessel was sealed and heated to 160 °C. The temperature was held for 6 days and then the mixture was cooled naturally to obtain pale yellow crystals. Crystalline product was filtered, washed with H_2O , and dried at ambient temperature (yield: 0.009 g, 17% on the basis of $Yb(NO_3)_3 \cdot 5H_2O$). Anal. Calcd for $C_{11}H_{12}O_{18}SYb_2$ ($M_r = 810.36$): C, 16.30; H, 1.49%. Found: C, 16.22; H, 1.41%. Main IR features (cm^{-1} , KBr pellet): 3444(s), 3131(s), 2347(w), 1684(s), 1640(s), 1570(m), 1422(s), 1323(w), 1258(s), 1136(s), 1068(s), 995(m), 954(s), 863(m), 821(s), 618(m), 561(m), 538(m), 517(m).

2.3. Single-crystal structure determination

Single-crystal X-ray diffraction data of **1** were collected on a Bruker Apex II CCD diffractometer equipped with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data

reduction was performed using SAINT and corrected for Lorentz and polarization effects. Adsorption corrections were applied using SADABS [28]. The structures were solved by direct methods and successive Fourier difference syntheses and refined by full-matrix least-squares on F^2 (SHELXTL Version 5.1) [29]. All non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogens bonded to carbon were assigned to calculated positions. Hydrogens attached to oxygen were located from difference maps and refined with isotropic thermal parameters fixed at 1.5 times that of the respective oxygens. The R_1 values are defined as $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ and $wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$. Details of the crystal parameters, data collection, and refinement are summarized in table 1. Important bond lengths are listed in table 2. More details about the crystallographic data have been deposited as Supplementary material.

3. Results and discussion

3.1. Syntheses

The hydrothermal reaction of $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 5-sulfonyl-1,2,4-benzenetricarboxylic acid in a 1 : 1 ratio in an aqueous solution at 160 °C for 6 days yielded pale yellow block crystals of **1**. Single-crystal X-ray analysis revealed that there is an oxalate (ox^{2-}). Because no oxalate was directly introduced to the starting reaction mixture, we suppose that oxalate must be derived from decomposition of 5-sulfonyl-1,2,4-benzenetricarboxylic acid. The decomposition mechanism remains unclear, but it may be associated with *in situ* metal-mediated oxidation–hydrolysis of 5-sulfonyl-1,2,4-benzenetricarboxylic acid; similar situations in other systems were also reported [30, 31].

3.2. Structure description for $[\text{Yb}_2(\text{SBTC})(\text{ox})(\text{H}_2\text{O})_5]_n$ (**1**)

Compound **1** crystallizes in the monoclinic $P2_1/c$ space group and is a 2-D bilayered coordination network. The asymmetric unit of **1** contains two Yb(III) ions, one tetraanionic

Table 1. Summary of crystal data and structural refinements for **1**.

Empirical formula	$\text{C}_{11}\text{H}_{12}\text{O}_{18}\text{SYb}_2$
Formula weight	810.36
Space group	$P2_1/c$
a (Å)	8.6434(4)
b (Å)	22.8471(11)
c (Å)	9.5089(4)
α (°)	90
β (°)	109.8900(10)
γ (°)	90
$V/\text{Å}^3$	1765.77(14)
Z	4
$D_{\text{calcd}}/\text{g cm}^{-3}$	3.048
μ/mm^{-1}	10.749
GOF on F^2	1.025
$R1, wR2$ [$I > 2\sigma(I)$]	0.0216, 0.0580
$R1, wR2$ (all data)	0.0235, 0.0590

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

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

Yb(1)–O(6)#1	2.259(3)	Yb(2)–O(4)#3	2.272(3)
Yb(1)–O(15)	2.276(3)	Yb(2)–O(1)	2.279(3)
Yb(1)–O(2)	2.315(3)	Yb(2)–O(18)	2.315(3)
Yb(1)–O(12)#2	2.328(3)	Yb(2)–O(11)	2.315(3)
Yb(1)–O(10)#2	2.337(3)	Yb(2)–O(5)#1	2.331(3)
Yb(1)–O(7)#2	2.342(3)	Yb(2)–O(13)	2.348(3)
Yb(1)–O(16)	2.354(3)	Yb(2)–O(17)	2.375(3)
Yb(1)–O(14)	2.352(3)	Yb(2)–O(3)#4	2.396(3)

Symmetry codes: #1 $x-1, y, z-1$; #2 $x, y, z-1$; #3 $x1, y, z$; #4 $-x+1, -y, -z$.

5-sulfonyl-1,2,4-benzenetricarboxylate (SBTC⁴⁻), one oxalate (ox²⁻), and five coordinated waters. As depicted in figure 1, both Yb(III) ions are eight-coordinate with O₈ donor sets. Yb1 is coordinated to four carboxylate oxygens (O2, O6A, O10B, and O12B; symmetry codes: A $x-1, y, z-1$; B $x, y, z-1$) from two SBTC⁴⁻ and one oxalate, one sulfonate oxygen (O7B), and three waters (O14, O15, and O16). The coordination sphere of Yb2 consists of six carboxylate oxygens (O1, O4C, O3D, O5A, O11, and O13; symmetry codes: C $x-1, y, z$; D $-x+1, -y, -z$) from four SBTC⁴⁻ and one oxalate and two waters (O17 and O18). The coordination geometry of Yb(III) can be best described as distorted square antiprisms (figure 2). The Yb–O distances vary from 2.259(3) to 2.396(3) Å (table 2). SBTC⁴⁻ serves as a heptadentate ligand bridging seven ytterbium ions through six monodentate carboxylate oxygens and one sulfonate oxygen (scheme 1), leaving the other two sulfonate oxygens

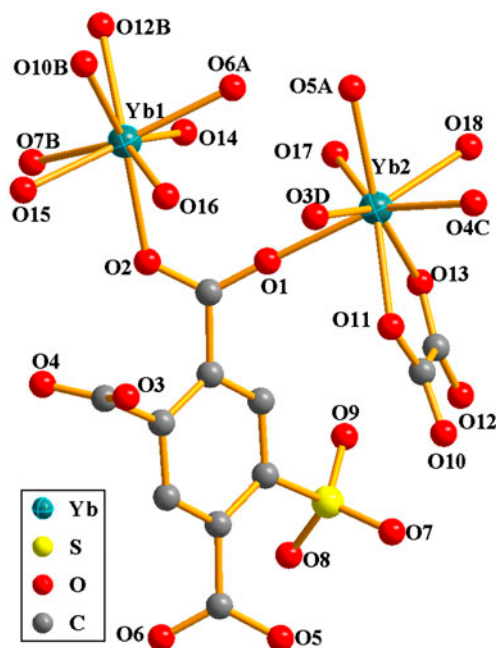


Figure 1. Molecular structure of **1**. Symmetry codes for the generated atoms: A $x-1, y, z-1$; B $x, y, z-1$; C $x-1, y, z$; D $-x+1, -y, -z$.

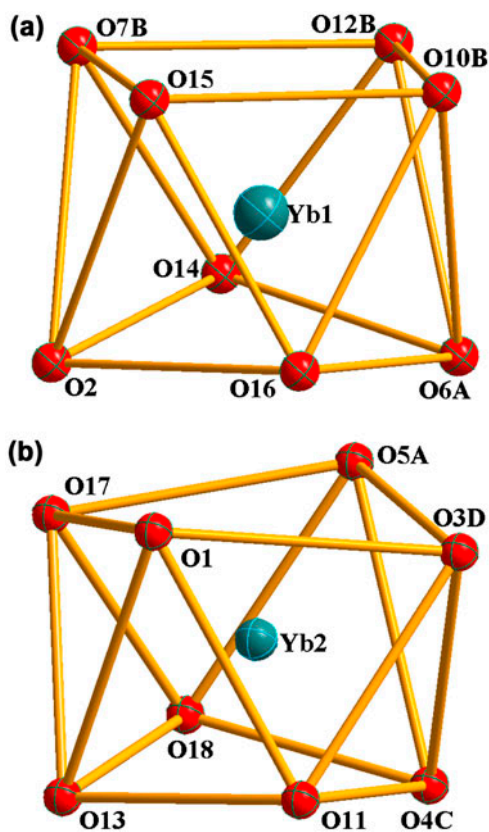
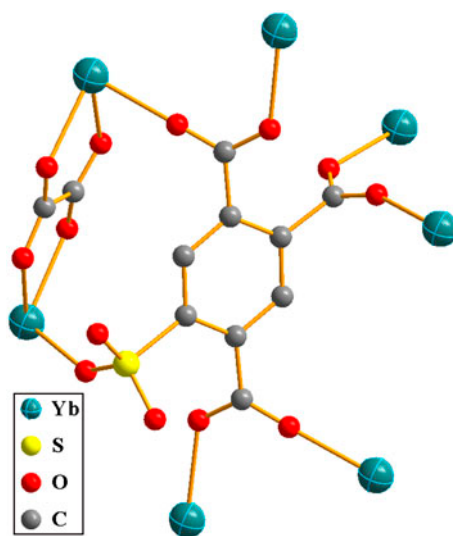


Figure 2. Coordination polyhedra around the Yb in 1.



Scheme 1. Coordination modes of SBTC⁴⁻ and ox²⁻.

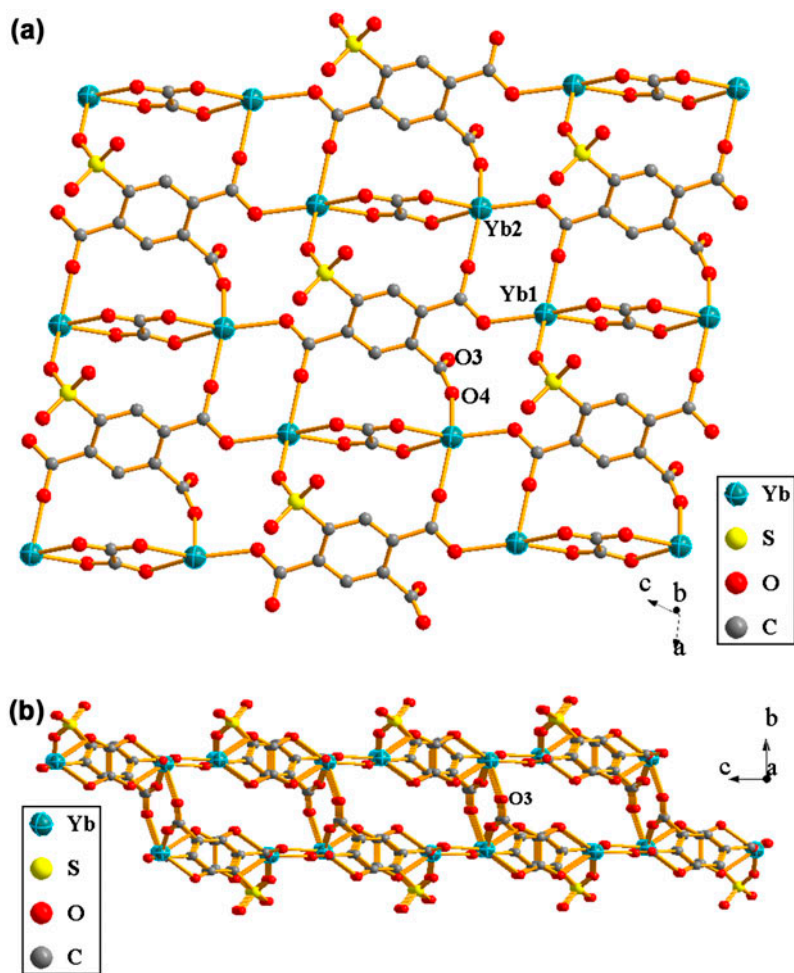


Figure 3. The 2-D (a) single layer and (b) bilayer of **1**.

Table 3. The geometry (\AA , $^\circ$) of hydrogen bonds in **1**.

	D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
Intralayer	O14–H14A \cdots O13#5	0.85	2.26	3.074(4)	160.0
	O15–H15A \cdots O5#6	0.85	1.95	2.749(4)	155.6
	O15–H15B \cdots O10#7	0.85	2.01	2.816(4)	157.4
	O16–H16A \cdots O11#7	0.85	2.18	2.999(4)	161.1
	O16–H16B \cdots O3#7	0.85	1.95	2.783(4)	167.5
	O17–H17A \cdots O8#8	0.85	1.95	2.778(4)	164.4
	O18–H18A \cdots O2#5	0.85	2.01	2.807(4)	156.3
	O14–H14B \cdots O9#5	0.85	1.82	2.661(4)	167.5
	O17–H17B \cdots O12#5	0.85	2.39	3.169(4)	151.6
Interlayer	O18–H18B \cdots O8#9	0.85	2.05	2.858(4)	158.3

Symmetry codes: #5 $x, -y+1/2, z-1/2$; #6 $x, y, z-1$; #7 $-x+1, -y, -z$; #8 $x-1, y, z-1$; #5 $x-1, y, z$; #9 $x-1, -y+1/2, z-1/2$.

uncoordinated. The ox^{2-} bridges two ytterbium ions with chelating to form five-membered rings (scheme 1). Yb(III) ions are interconnected by ox^{2-} and SBTC^{4-} through Yb–O bonds, except for the Yb–O3 bond, to generate a 2-D laminar layer, as shown in figure 3 (a). The seventh donor (O3) from SBTC^{4-} functions as a linker between the two layers to form a 2-D bilayer along the *ac* plane, as depicted in figure 3(b). Within the bilayer, there are hydrogen bonds between the coordinated waters and carboxylate and sulfonate (table 3) with the O···O distance varying from 2.749(4) to 3.074(4) Å. The bilayer is further extended into a 3-D supramolecular framework through interlayered hydrogen bonds with the O···O distance ranging from 2.661(4) to 3.169(4) Å (figure 4 and table 3).

3.3. Magnetic properties

The temperature dependence of magnetic susceptibility for **1** has been examined in an applied magnetic field of 1 kOe from 300 to 2.5 K. Plots of χ_M versus *T* together with $\chi_M T$ versus *T*, where χ_M is the molar magnetic susceptibility per Yb(III), are shown in figure 5. The $\chi_M T$ value at 300 K is $2.27 \text{ cm}^3 \text{ K mol}^{-1}$, slightly lower than $2.57 \text{ cm}^3 \text{ K mol}^{-1}$ for an uncoupled Yb(III) ($S=1/2$, $L=3$, ${}^2F_{7/2}$, $g=8/7$). As the temperature decreases, $\chi_M T$ decreases to $1.34 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.5 K, indicating the result of a combination of the progressive depopulation of excited Stark sublevels and exchange interaction between Yb(III) ions. The magnetic susceptibility data between 300 and 45 K obey the Curie–Weiss law, $\chi_M = C/(T-\theta)$, where the Curie constant *C* and Weiss constant θ are $C = 2.37 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -21.3 \text{ K}$ ($R = \sum[(\chi_M T)_{\text{calc}} - (\chi_M T)_{\text{obs}}]^2 / \sum(\chi_M T)_{\text{obs}}^2 = 7.3 \times 10^{-4}$), respectively. The Curie constant is in agreement with the expected value of $2.57 \text{ cm}^3 \text{ K mol}^{-1}$ for a free Yb(III) ion. The negative Weiss constant

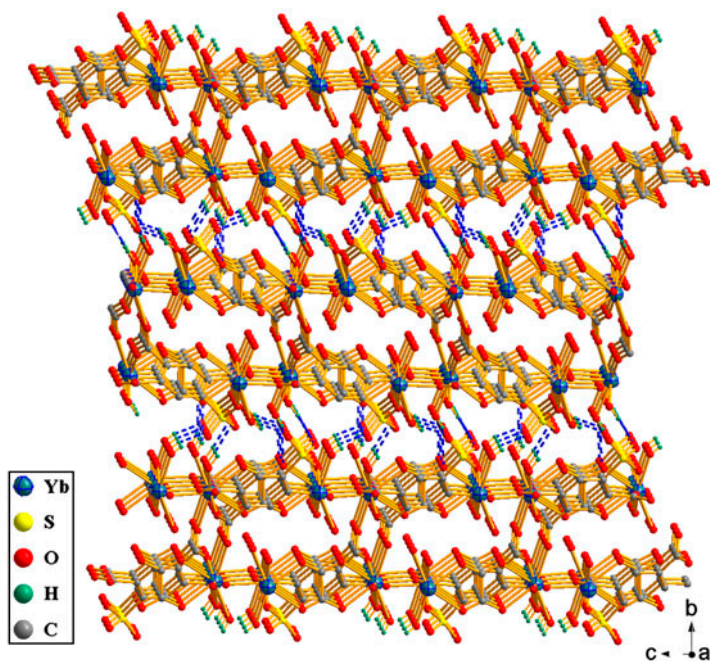


Figure 4. 2-D bilayers linked by hydrogen bonds to form a 3-D structure in **1**. Only interlayered hydrogen bonds (dashed lines) are shown.

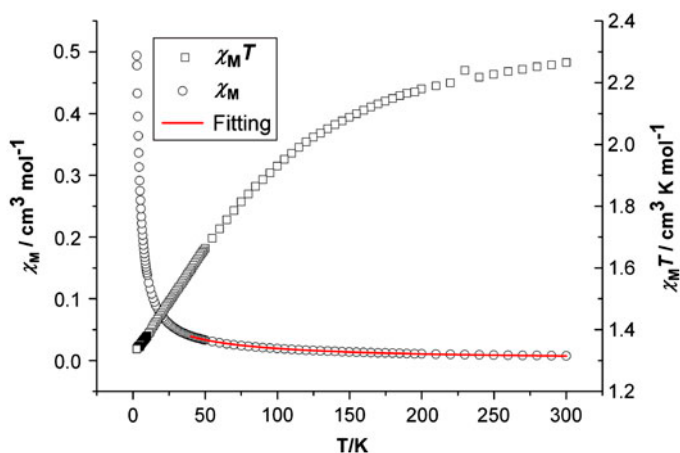


Figure 5. Plots of χ_M and $\chi_M T$ vs. T for **1**. The solid line represents the best theoretical fit.

suggests the presence of dominant antiferromagnetic interactions between spin carriers. Effects of thermal depopulation of Yb(III) excited states that result from spin–orbit coupling and a low symmetry crystal field [32] might also be partially responsible for the decrease of $\chi_M T$ when the temperature is lowered.

3.4. IR and thermogravimetric analyses studies

The IR spectrum of **1** shows strong bands at 1442–1684 cm^{-1} , characteristic of carboxylate. Absorptions at 950–1250 cm^{-1} are typical of sulfonate. The sharp absorptions at 618 cm^{-1} can be assigned to C–S stretches (figure S1 in Supplementary material). To examine the thermal stability of **1** and its structural variation as a function of temperature, thermogravimetric analyses were performed on crystalline samples. Compound **1** displays continual weight loss within the test temperature range, which indicates that the decomposition of the organic ligand follows loss of water (figure S2 in Supplementary material).

4. Conclusion

A sulfonate-carboxylate 5-sulfonyl-1,2,4-benzenetricarboxylic acid with Yb(III) has been employed to synthesize a coordination polymer $[\text{Yb}_2(\text{SBTC})(\text{ox})(\text{H}_2\text{O})_5]_n$ (**1**) under hydrothermal conditions. *In situ*, formation of oxalate may be associated with *in situ* metal-mediated oxidation–hydrolysis of 5-sulfonyl-1,2,4-benzenetricarboxylic acid. Compound **1** is a 2-D bilayered coordination network, which forms a 3-D supramolecular framework through interlayered hydrogen bonds. The magnetic properties of the compound were investigated.

Supplementary material

CCDC-926,230 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via

<http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: t44 1,223,336,033; Email: deposit@ccdc.cam.ac.uk).

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