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Solvothermal synthesis, crystal structure and properties of three new 1D and 3D organically templated lanthanide sulfates

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ABSTRACT

Three new organic amine templated lanthanide sulfates $[(CH_3)_2NH_2]_3[Y(SO_4)_3]\cdot H_2O 1$ and $[(CH_3)_2 NH_2]_9$ $[Ln_5(SO_4)_{12}]\cdot 2H_2O$ (Ln = La 2 and Ce 3) have been solvothermally synthesized under similar conditions and structurally characterized by single-crystal X-ray diffraction. Compound 1 exhibits 1D anionic chain structure compensated by protonated dimethylamine occluded in the helical $[Y-O-S]_n$ chains, while the 3D inorganic frameworks of 2 and 3 contain extra-large 20-membered ring channels. The syntheses of three compounds demonstrates that although yttrium and lanthanide belong to one family, the self-assembly of yttrium sulfate may be different from other rare-earth sulfates because Y is much lighter. The formation of 1-3 also demonstrates that the solvent plays an important role during the synthesis.

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1. Introduction

During the past two decades, inorganic solid materials have attracted much attention due to their intriguing structures and widespread applications in such as precursors for oxides and catalysis [1–3], ion exchanging [4,5] and their magnetic properties [6]. The work mainly focused on phosphates [7] and carboxylates [8], but germanates [9] and arsenates [10] have also been involved in this research. Recently, new transition metal sulfates including V, Mn, Cd and Zn have been synthesized by using organic templates. Since the first organically templated cadmium sulfate synthesized by Rao, there has been a growing interest in the study of organic amine templated sulfates framework architectures [11-19]. Compared with transition metals, rare-earth elements can adopt multivariant coordination numbers from 8 (LnO₈) to 12 (LnO₁₂) and more flexible Ln-O bond lengths to allow the formation of lanthanide sulfates with new inorganic topological frameworks. Up to now, successful examples include organic amine templated lanthanide sulfates materials have been reported in the literatures [20-37]. Although yttrium and lanthanide belong to one family, there is no organically templated yttrium sulfate been reported hitherto. In this work, we employ N,N-dimethylformamide (DMF) as solvent and dimethylamine as structural directing agent (SDA) in the synthesis. The first organic templated yttrium sulfate

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 $[(CH_3)_2NH_2]_3[Y(SO_4)_3]\cdot H_2O$ **1** and two organic templated lanthanide sulfates $[(CH_3)_2NH_2]_9[Ln_5(SO_4)_{12}]\cdot 2H_2O$ (Ln = La **2** and Ce **3**) were successfully prepared.

2. Experimental

2.1. Materials and methods

The three compounds were prepared from a mixture of lanthanide oxide (99.9%), sulfuric acid (95–98 wt.%), *N*,*N*-dimethylformamide (99.5%) and dimethylamine water solution (40%) under solvothermal conditions. All chemicals purchased were of reagent grade and used without further purification. The C, H, and N analyses were performed on a Perkin–Elemer 2400 elemental analyzer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermogravimetric analyses were carried out in N₂ atmosphere on a Diamond thermogravimetric analyzer from 50 to 1100 °C at a heating rate of 10 °C/min.

2.2. Synthesis and characterization

In a typical synthesis of compound **1**, solution was prepared by dissolving $0.1008 \text{ g } Y_2O_3$ into 7.0126 g DMF and 1.5334 g sulfuric acid under constant stirring for an hour. Then 0.1396 g dimethylamine water solution was added under constant stirring for 30 min. The final pH was 2.0. The resulting mixture was transferred into a 25 mL Teflon-lined stainless-steel autoclave and heated at 453 K for 6 days. After cooling down to the room temperature, final product was washed with ethanol and dried in air for one day to give



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the block crystals (yield 36%, with respect to Y). *Anal.* Calc.: C, 13.50%; H, 4.87%; N, 7.87%. Found: C, 14.49%; H, 4.52%; N, 7.74%. Under similar conditions, compound **2** and **3** were prepared by replacing Y_2O_3 with La₂O₃ (0.1007 g) or CeO₂ (0.1060 g). The final yields were 46% for **2** and 54% for **3** (with respect to La and Ce). For compound **2**: *Anal.* Calc.: C, 9.40%; H, 3.33%; N, 5.48%. Found: C, 9.31%; H, 3.57%; N, 5.34%. For compound **3**: *Anal.* Calc.: C, 9.29%; H, 3.62%; N, 5.41%.

2.3. Determination of crystal structure

Single crystals of compounds **1–3** were carefully selected under a microscope and glued at the tip of a thin glass fiber with cyanoacrylate adhesive. Single-crystal structure determination by XRD was performed on a Bruker Apex2 CCD equipped with a normal focus at 273 K, sealed tube X-ray source (Mo K α radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. Crystal structures were solved by direct method and refined on F^2 by full-matrix least squares methods using the SHELX97 program package [38]. All non-hydrogen atoms were refined anisotropically. All H atoms for the organic template were placed in the calculation position, while the H atoms of the water molecule in 2 and **3** were located from different map. Further details of the X-ray structural analysis for **1–3** are given in Table 1. The selected bond lengths and angles are listed in Table S1.

3. Results and discussion

3.1. Structure description

3.1.1. Crystal structure of 1

Compound **1** crystallizes in triclinic space group $P\bar{1}$. structural analysis reveals that **1** is dimethylamine templated 1D yttrium sulfate. The structure of **1** consists of inorganic anionic $[Y(SO_4)_3]_n^{3n-1}$

Table 1

Crystal data and structure refinement for 1-3.

chains, charge compensated by protonated dimethylamine cations. The asymmetric unit of **1** contains one yttrium atom, three sulfate groups and three protonated dimethylamine, as shown in Fig. 1. In compound **1**, Y is eight-coordinated by O atoms from sulfates, forming distorted bicapped trigonal prism geometry. The bond distances of Y–O vary from 2.237(8) to 2.436(8) Å, whereas the angles of O–Y–O are between 59.1(3) and 150.7(3)°. Since Y is much lighter than lanthanide, Y–O bond distances are a little shorter than Ln–O distances as found in the reported lanthanide sulfates [11–19]. Of the three different S atoms, S(1) and S(2) make three S–O–Y linkages and link two Y atoms through three μ_2 –O; while S(3) forms two S–O–Y linkages as a ligand of one Y atom through two μ_2 -O.

To the best of our knowledge, this is the first organic amine templated vttrium sulfate. Compared with other reported rare earth sulfates. SO₄ and LnO₂ polyhedra are mostly connected by μ_2 -O and μ_{2} -O atoms, which open up the possibility to form 1D inorganic framework [10a, 13, 22b, 22i]. In compound 1, all the SO₄ and YO₈ polyhedra are connected by μ_2 -O, forming a chain consisting of 4-membered rings. (Fig. 2a). The structure of inorganic framework of 1 can be described as double helical chains with terminal SO₄ tetrahedra attached. Y atoms are connected by the bridging sulfates (S(1), S(2)) and their crystallographic partners) to form a single helical $[-Y-O-S-O-]_n$ chain, while adjacent helical chains are further linked by O-Y-O linkages to generate an intertwined -Y-O-S-Odouble helices of the same handedness (Fig. 2b and c). As shown in Fig. 3, the non-coordination water molecules are involved in hydrogen bonding with oxygen atoms from adjacent $[Y(SO_4)_3]_n^{3n-}$ chains to generate a 2D layered super molecule assembly along [001] direction. Hydrogen bonds for compound 1 are given in Table S2. The fully protonated organic amine molecules are inserted between the layers, and also involved in hydrogen bonding interactions with oxygen atoms of inorganic framework (Fig. 4).

	1	2	3
Empirical formula	$C_6H_2YN_3O_{13}S_3$	C ₁₈ H ₇₆ La ₅ N ₉ O ₅₀ S ₁₂	$C_{18}H_{76}Ce_5N_9O_{50}S_{12}$
Formula weight	533.39	2298.15	2304.20
Temperature (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	ΡĪ	C2/c	C2/c
Unit cell dimensions			
a (Å)	9.905(8)	20.728(2)	20.681(4)
b (Å)	9.974(8)	36.776(4)	36.326(7)
c (Å)	10.948(9)	10.1472(11)	10.152(2)
α (°)	72.44(3)	114.3520(10)	114.531(2)
β (°)	75.35(5)		
γ (°)	86.27(3)		
Volume (Å ³)	997.6(14)	7046.9(13)	6938(2)
Ζ	2	4	4
Calculated density (Mgm ⁻³)	1.776	2.166	2.206
Absorption coefficient (mm ⁻¹)	3.300	3.431	3.686
F(000)	548	4496	4516
Crystal size (mm)	$0.15 \times 0.13 \times 0.12$	$0.14 \times 0.13 \times 0.12$	$0.14 \times 0.13 \times 0.12$
θ range for data collection (°)	2.01-25.02	1.98-25.02	1.12–27.19
Limiting indices	$-11\leqslant h\leqslant 10$, $-11\leqslant k\leqslant 11$,	$-24\leqslant h\leqslant 21,-43\leqslant k\leqslant 43,$	$-25\leqslant h\leqslant 26,-46\leqslant k\leqslant 46,$
	$-13 \leqslant l \leqslant 13$	$-11 \leqslant l \leqslant 12$	$-12 \leqslant l \leqslant 12$
Reflections collected/unique (R _{int})	7107/3484 (0.030)	24007/6213 (0.0261)	25301/7055 (0.0573)
Completeness to θ = 25.49 (%)	98.9	99.8	91.2
Maximum and minimum transmission	0.6928 and 0.6373	0.6836 and 0.6452	0.6660 and 0.6264
Data/restraints/parameters	3484/9/250	6213/469/460	7055/30/431
Goodness-of-fit on F^2	1.052	1.150	1.065
Final R indices $[I>2\sigma(I)]$	$R_1 = 0.0402$	$R_1 = 0.0350$	$R_1 = 0.0527$
	$wR_2 = 0.1045$	$wR_2 = 0.0949$	$wR_2 = 0.1416$
R indices (all data)	$R_1 = 0.0539$	$R_1 = 0.0375$	$R_1 = 0.0591$
	$wR_2 = 0.1180$	$wR_2 = 0.0963$	$wR_2 = 0.1523$
Largest diff. peak and hole ($e^{\text{Å}^{-3}}$)	0.801 and -0.639	2.974 and -1.239	3.898 and -2.350



Fig. 1. ORTEP view of the $[(CH_3)_2NH_2]_3[Y(SO_4)_3]\cdot H_2O$ structure showing the atom labeling scheme.



Fig. 2. (a) Polyhedra structure of the $[Y(SO_4)_3]_n^{3n-}$ chain in **1**; (b) single helical $[-Y-O-S-O-]_n$ chain; (c) an intertwined [-Y-O-S-O-] double helices of the same handedness.

3.1.2. Crystal structure of 2 and 3

Compounds 2 and 3 are isostructural and crystallize in monoclinic space group C2/c. We take compound 2 as an example to describe the structure. Although these two compounds are similar with our previous work [34,37], it is vital to study their structures. The asymmetric unit of 2 contains three lanthanum atoms, six sulfate groups and five protonated dimethylamine cations (Fig. S1). The metal atoms La(1) and La(2) are eight-coordinated by O atoms, while La(3) is nine-coordinated by O atoms. The average bond distance of La-O is 2.431 Å, whereas the angles of O-La-O are between 46.1(2) and 166.99(9)°. Six crystallographic independent S atoms can be divided into four groups: S(3) is bonded by three μ_2 -O atoms and one Ot (terminal O atom) to generate three S–O– La linkages; S(2) and S(5) are coordinated by four μ_2 -O atoms to form four S–O–La linkages; S(1) and S(4) are bonded by one μ_3 -O, two μ_2 -O atoms and one Ot to form four S–O–La linkages; while S(6) is coordinated by seven O atoms, one of them (O21) is fully

occupied and the other six (O22, O23, O24, O22a, O23a, and O24a) have the same occupied factors of 0.5. The average S–O bond distance is 1.474 Å, which is comparable to those of similar bonds reported earlier [11–19].

The structure of **2** can be described as two types of secondary building units (SBUs). Two $[La_3(SO_4)_6]^{3-}$ fragments connect with each other by sharing La(1) to form the SBU-1 $[La_5(SO_4)_{12}]^{9-}$. Two adjacent SBU-1s are linked by bridging [SO₄] tetrahedra to generate an interesting 20MR structure (Fig. 5). SBU-2 is 10MR. Adjacent 10 and 20MRs are connected by bridging SO₄²⁻ groups to form an open framework with a 3D channel system (Fig. S2a). Both 10 and 20MR channels are arranged in an ordered close packing structure. Each 20MR channel is surrounding by six 10MRs, and they are alternately surrounded by three 20MRs and three 10MRs. The approximate window sizes for 20MR and 10MR are 5.3 \times 9.5 and 3.8 \times 3.8 Å², respectively. Interestingly, there are other rectangular 20MR-r channels along the crystallographic [101] direction (Fig. S2b). The pore size of rectangular 20MR is about $2.9 \times 12.8 \text{ Å}^2$. We used the PLATON software to calculate the percent void volume in the 3D network of **2**, and the result is 48.5%. The appearance of disordered SO_4 in both types of 20MRs leads to different inorganic frameworks and pore sizes. As shown in Fig. 6, protonated dimethylamine cations and free water molecules are located in the 10MR and both types of 20MR channels of the inorganic framework by strong hydrogen bonding interactions between H atoms of organic amine molecules and O atoms of the open-framework of 2. The protonated dimethylamine cations cannot be removed without collapse of framework of 2 and 3. One hundred and twenty six free water molecules in 20MR channels are connected each other by strong hydrogen bonding to form an interesting zigzag chain along *c* axis. The distances between two adjacent water molecules are 2.86(2) and 2.94(2) Å respectively (Fig. 6d). Hydrogen bonds for compound 2 are given in Table S3.

3.2. IR spectroscopy

The IR spectrum of compound **1** (Fig. S3) shows that the band at about 3420 cm^{-1} can be assigned to water. The typical sharp signals for dimethylamine are in the region $1380-1650 \text{ cm}^{-1}$, and the characteristic bands of SO_4^{2-} are in the 1129 and 662 cm⁻¹ region. The bands at 3213 and 2984 cm⁻¹ are assigned to O-H bonding and N-H bonding vibrations, respectively. The band at 609 cm⁻¹ can be attributed to the Y-O vibration. The IR spectrum of compounds **2** and **3** are similar with compound **1** and the spectrum are in Figs. S4 and S5.

3.3. Thermogravimetric analysis

The thermogravimetric analyses (TGA) of complexes 1-3 were performed in a N₂ atmosphere when heated to 1000 °C at a rate of 10 °C min⁻¹. For compound **1**, total weight loss is 74.1%, which is in agreement with the calculated value 74.2% (Fig. S6). The weight loss of 28.3% in the range of 40-330 °C corresponds to the removal of free water and three dimethylamine molecules (the calculated value is 29.1%). The weight loss of 45.8% in the range of 330-1080 °C can be attributed to the loss of SO₃ (the calculated value is 45.0%). The final product is Y_2O_3 . For compound **2**, the total weight loss is 60.3%, which is in agreement with the calculated value 61.4% (Fig. S7). The weight loss of 1.9% in the range of 30-100 °C corresponds to the removal of two free water molecules. The second step loss of 34.7% in the range of 100-550 °C can be attributed to all the dimethylamine and some of SO₃. The weight loss of 23.7% in the range of 550-800 °C can be attributed to loss of SO₃. The final product is La₂O₃. The weight loss curve of compound **3** is similar to compound **2** (Fig. S7). The final product is CeO₂.



Fig. 3. The 2D layered super molecule assembly along [001] direction generated by the non-coordination water molecule which are involved hydrogen bonding with oxygen atoms from adjacent [Y(SO₄)₃]_n³ⁿ⁻ chain.



Fig. 4. Packing view of 1 along the *b*-axis (the fully protonated organic amine molecules are inserted between the layers. The protonated amines are also involved in hydrogen bonding with oxygen atoms from inorganic framework).

4. Conclusions

In summary, we have successfully synthesized three lanthanide sulfate $[(CH_3)_2NH_2]_3[Y(SO_4)_3]\cdot H_2O$ **1** and $[(CH_3)_2 NH_2]_9 [Ln_5 (SO_4)_{12}]\cdot 2H_2O$ (Ln = La **2** and Ce **3**) by using DMF as solvent. Compare with early reported compounds, compound **1** keeps quite different structure. In the structure of **1**, YO₉ polyhedra are linked by sulfate groups to generate a new inorganic chain with helical $[Y-O-S]_n$ chains. 3D

inorganic frameworks of compounds **2** and **3** contain extra-large 20-membered ring channels. The formation of **1–3** demonstrates that although yttrium and lanthanide belong to one family, the self-assembly of yttrium sulfate may be different from other rareearth sulfates, because yttrium is much light. $[(CH_3)_2NH_2]_3[Y(-SO_4)_3]\cdotH_2O$ **1** possesses 1D helical chains, while **2** and **3** possess 3D porous structures. Synthesis process also highlights the importance of solvent.



Fig. 5. (a) The SBU-1 of $[La_5(SO_4)_{12}]^{9-}$ in **2**; (b) the structure of the 20MR in **2**.



Fig. 6. The protonated dimethylamine molecules are located in the 20MR-1(a) and 2(b).

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Appendix A. Supplementary material

CCDC 822490, 825934 and 825935 contains the supplementary crystallographic data for the compounds **1–3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.10.066.

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