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Solvothermal synthesis, crystal structure and luminescence property of a new 1D organic amine templated europium sulfate with helical chains

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ABSTRACT

A new organic amine templated 1D europium sulfate $[H_3O]_2[(CH_3)_2NH_2][Eu(SO_4)_3]$ **1** has been solvothermally synthesized and structurally characterized by single-crystal X-ray, IR and TGA. Structure analysis indicates that the structure of **1** exhibits a 1D chain structure compensated by protonated dimethylamine and water cations. The strong red fluorescence for **1** has been observed in the solid state.

During the past two decades, great efforts have been made to obtain new inorganic solid state materials with different compositions and structures owing to their wide applications such as precursors for oxides and catalysis, ion exchanging and magnetic properties [1–3]. The work mainly focused on phosphates, germanates and arsenates [4–6]. Recently, new sulfates have been elaborated using organic templates [7]. 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 [7–24]. Indeed, the ability of rare earth elements to adopt a large range of coordination numbers and flexible Ln–O bond lengths [25] allows obtaining new topologies based on various polyhedra. Up to now, some successful examples of 1D organic amine templated rare earth sulfate materials have been reported. For examples, zigzag chain structural $[(C_4H_{16}N_3)La(SO_4)_3]\cdot H_2O$ [7,15,19] employed diethylenetriamine (DETA) as organic template; $(C_2H_8N)[Ho(SO_4)_2\cdot H_2O]$ [23] is an interesting 1D ladder-like structure constructed from four-ring building units; $[C_6N_4H_{22}]_{1.5}[Ho_2(SO_4)_6H_2O]$ [20] is an intriguing 1D triple ladder. Because of excellent luminescence property, europium is an important member in the rare earth elements. Unfortunately, organic amine templated europium sulfates are much less developed. It is therefore vital to synthesize new organic templated europium sulfate compounds in order to explore their luminescence property. 2D and 3D organic amine templated europium sulfates $[C_2N_2H_{10}]_{1.5}[Eu(SO_4)_3(H_2O)]\cdot 2H_2O$ [12] and $(C_2H_8N)_9[Eu_5(SO_4)_{12}]\cdot 2H_2O$ [13] have been reported, but no 1D europium sulfate was prepared till now. In this work, we used a large amine (1,3,5-triazine-2,4,6-triamine) as a second structure directing agent (SDA) to prevent the formation of 2D or 3D Eu–O–S frameworks and a new 1D europium sulfate $[H_3O]_2[(CH_3)_2NH_2][Eu(SO_4)_3]$ **1** was successfully obtained.

Compound **1** was synthesized in solvothermal conditions from a mixture of Eu_2O_3, N,N-dimethylformamide (DMF), 1,3,5-triazine-2,4,6-triamine and concentrated sulfate [26]. The molecule structural

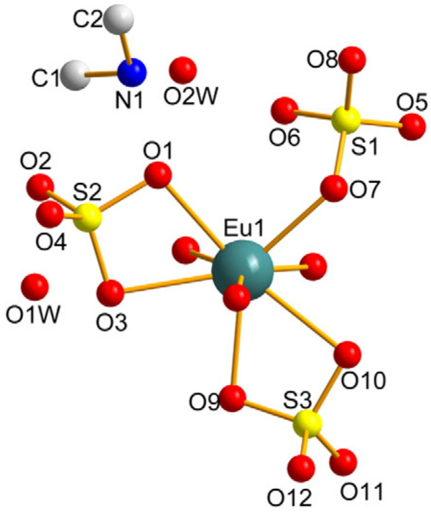

Fig. 1. ORTEP view of the $[H_3O]_2[(CH_3)_2NH_2][Eu(SO_4)_3]$ structure showing the atom labeling scheme.

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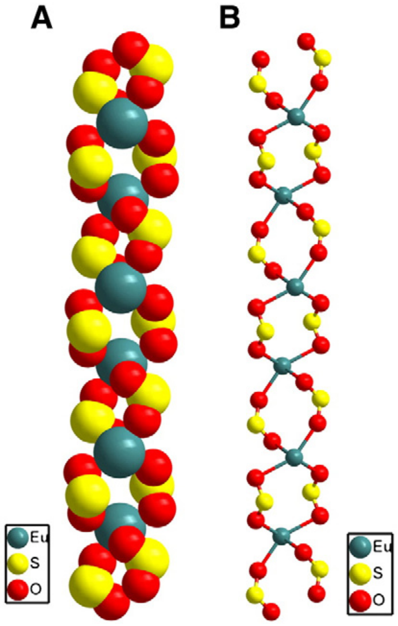

Fig. 2. (A) A space-filling diagram of two intertwined helices that enclose the 4-membered ring. (B) Ball-stick diagram of two intertwined helices.

analysis [27] reveals that compound **1** is dimethylamine templated 1D europium sulfate and the linear inorganic chain $[Eu(SO_4)_3]_n^{3n-}$ in **1** is constructed from EuO_8 and SO_4 polyhedra. The asymmetric unit of compound **1** contains one europium atom, three sulfate groups, one protonated dimethylamine and two H_3O^+ cations, as shown in Fig. 1. In the inorganic chain of **1**, Eu(1) is eight-coordinated by O atoms from five sulfates to form a distorted bicapped trigonal-prismatic geometry. The bond distances of Eu–O vary from 2.341(3) to 2.487(3) Å, whereas the angles of O–Eu–O are between 56.60(10) and 153.01 (10)°. In the reported $[C_2N_2H_{10}]_{1.5}[Eu(SO_4)_3(H_2O)]\cdot 2H_2O$ [12], SO_4 tetrahedra and EuO_x polyhedra are connected by μ_2–O atoms to form a 2D inorganic framework; but in the structures of $(C_2H_8N)_9[Eu_5(SO_4)_{12}]\cdot 2H_2O$ [13], SO_4 polyhedra and EuO_x polyhedra are connected by μ_2–O and μ_3–O atoms to generate a 3D inorganic framework. In the framework of **1**, the europium atoms are connected by μ_2–O atoms (no any μ_3–O in the compound **1**) to make a 1D [—Eu–O–S—]$_n$ chain. There are three independent S atoms in **1** (Fig. S1), S(1) and S(2) make three S–O–Eu linkages and link two Eu atoms through three 2-coordinated oxygen atoms; S(3) makes two S–O–Eu linkages as a ligand of one Eu atom through two 2-coordinated oxygen atoms. All the S atoms are tetrahedrally coordinated by four O atoms with the S–O distances 1.435(4) to 1.506(3) Å, which is similar with the reported lanthanide sulfates [7–24]. The O–S–O angles are within the expected range of tetrahedral geometry.

The reported 1D lanthanum sulfate $[(C_4H_{16}N_3)La(SO_4)_3]\cdot H_2O$ [7,15,19] contains infinite zigzag {—La–μ–O–La–μ–O–La—} chains, $[C_6N_4H_{22}]_{1.5}[Ho_2(SO_4)_6H_2O]$ [20] is an interesting 1D triple ladder, while $(C_2H_8N)[Ho(SO_4)_2\cdot H_2O]$ [23] is an interesting 1D ladder-like structure. The structure of inorganic chain of **1** is much different, which can be described as double helical chains with terminal SO_4 tetrahedra attached to them. Eu atoms were connected by the bridging sulfates (S(1) and S(2)) to form a single helical [—Eu–O–S–O—]$_n$ chain and other helical chains were further linked by O–Eu–O linkages to generate an intertwined —Eu–O–S–O— double helices of the same handedness, as shown in Fig. 2. These kinds of double helices are particularly rare in inorganic materials [28–30]. There are two crystallographically independent protonated water (H_3O^+) cations in **1**. The protonated water (H_3O^+) cation was not observed in the previously reported organic templated europium sulfates. Interestingly, O2w makes four O–H…O hydrogen bonds with O atoms from double helices to generate a flat layer along a axis, as shown in Fig. 3A. The remaining protonated water cations (O1w) connect adjacent layers by three hydrogen bonds to generate a 3D soft open framework along b axis, as shown in Fig. 3B. The protonated dimethylamine molecules are located in the channels and hydrogen bonding interactions are involved in the soft framework to make it more stable (Fig. 4).

It must be noted that dimethylamine, along with formic acid, would be the product of decomposition of DMF [31]. Though important during the synthesis process, the organic amine 1,3,5-triazine-2,4,6-triamine was not included in the compound. We have tried to synthesize without 1,3,5-triazine-2,4,6-triamine, but the final product turns to be 3D $(C_2H_8N)_9[Eu_5(SO_4)_{12}]\cdot 2H_2O$ [13] instead of a 1D compound **1**. Therefore the 1,3,5-triazine-2,4,6-triamine is absolutely necessary in the formation of **1**. The formation of **1** demonstrates that a large organic amine could prevent the further connections between adjacent 1D chains.

Because of the excellent luminescent properties of Eu^{3+}, compound **1** was investigated and showed red luminescence. Fig. 5 showed the solid state emission spectrum of $[H_3O]_2[(CH_3)_2NH_2][Eu(SO_4)_3]$ **1** at room temperature under excitation at 394 nm. The emission spectrum exhibits the characteristic transition of Eu^{3+} ion. The emission bands occurring at 591, 616, 655 and 698 nm can be assigned to $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4). The emission band $^5D_0 \rightarrow {}^7F_1$ at 591 nm is a magnetic dipole transition and its intensity should vary with the crystal field strength acting on the Eu^{3+} ion. The $^5D_0 \rightarrow {}^7F_2$ transition, on the other hand, is an electric dipole transition and the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition increases as the site symmetry of the Eu^{3+} ions decreases. The red emission of the $^5D_0 \rightarrow {}^7F_2$ transition

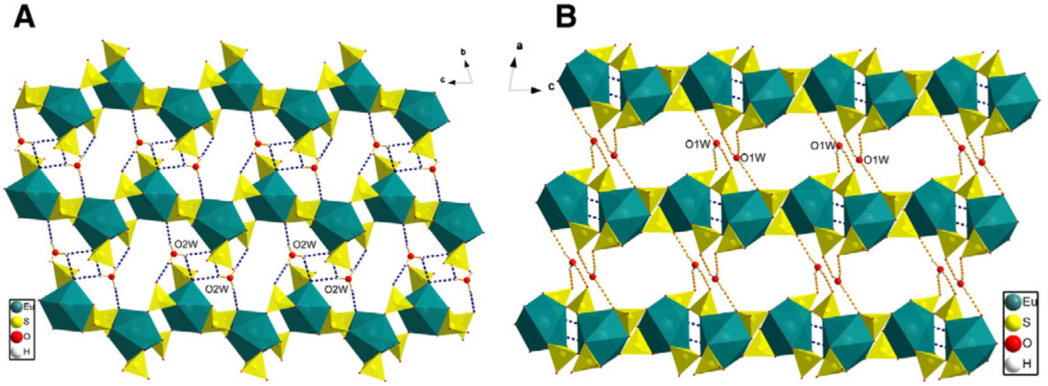

Fig. 3. (A) O2w makes a flat layer by four hydrogen bonds along a axis. (B) O1w cation connects adjacent layers by three hydrogen bonds to make 3D soft open framework along b axis.