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**SYNTHESIS, CHARACTERIZATION AND VERY STRONG LUMINESCENCE
OF A NEW 3-D EUROPIUM SULFATE $\text{Eu}_2(\text{H}_2\text{O})_4(\text{SO}_4)_3$**

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A new 3-D europium sulfate $\text{Eu}_2(\text{H}_2\text{O})_4(\text{SO}_4)_3$ **1** is synthesized solvothermally and characterized by single crystal X-ray diffraction, IR spectrum, TG, powder XRD, and ultraviolet excitation and emission spectrum. This compound crystallizes in the triclinic system with the space group *P*-1, $a = 6.7520(9)$ Å, $b = 9.1077(12)$ Å, $c = 10.5910(14)$ Å, $\alpha = 94.432(2)^\circ$, $\beta = 107.1170(10)^\circ$, $\gamma = 99.160(2)^\circ$, $V = 609.17(14)$ Å³, $Z = 2$. The open framework of the title compound is an eight-membered ring channel along the crystallographic *a*-axis, which is built up by EuO_8 polyhedra and SO_4 tetrahedra.

Keywords: europium sulfate, solvothermal synthesis, luminescence, 3-D.

INTRODUCTION

Over the past several decades, much effort has been made to synthesize one-, two-, and three-dimensional inorganic materials, and more attention has been paid to the synthesis of lanthanide sulfates owing to their various structures [1, 2]. Compared with other transition metals, the rare-earth elements adopt a large range of coordination numbers allowing the formation of new topological frameworks based on various polyhedra [3–10]. In particular, lanthanide ions can have amusing properties such as luminescence in both visible and near-IR regions. Although many lanthanide sulfates have been described in the literatures, e.g. the formation of $\text{La}(\text{OH})\text{SO}_4$ [11], $[(\text{C}_4\text{H}_{16}\text{N}_3)\text{La}(\text{SO}_4)_3] \cdot \text{H}_2\text{O}$ [12], $\text{La}_2(\text{SO}_4)_3(\text{H}_2\text{O})_4$, $\text{Eu}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8$ [13], $[\text{C}_2\text{N}_2\text{H}_{10}]_3[\text{Ho}_2(\text{SO}_4)_6 \cdot 2\text{H}_2\text{O}]$ [14], $[\text{C}_6\text{N}_4\text{H}_{22}]_{1.5}[\text{Ho}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}]$ [15], $[\text{C}_4\text{H}_{16}\text{N}_3][\text{La}(\text{SO}_4)_3(\text{H}_2\text{O})]$ [16], and $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5} \times [\text{Eu}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ [17], the reports on luminescence for 3-D open frameworks are comparatively limited. Since europium has an excellent luminescent property, it is vital to design and synthesize 3-D europium sulfates in order to explore their functional property. In this work, we used a mixture of alcohol and water as the solvent, and a new 3-D europium sulfate $\text{Eu}_2(\text{H}_2\text{O})_4(\text{SO}_4)_3$ **1** with strong luminescence was successfully prepared.

EXPERIMENTAL

Materials and methods. All chemicals purchased were of reagent grade and used without further purification. The IR spectrum was recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermogravimetric analyses were carried out in the N_2 atmosphere on a Diamond thermogravimetric analyzer from 50 °C to 1100 °C at a heating rate of 10 °C /min. Power XRD diffraction patterns were obtained on a Bruker D8X diffractometer with monochromatized $\text{CuK}\alpha$ (1.5418 Å) radiation at room temperature. IR and luminescent spectra were recorded from KBr pellets on a Nicolet 170SXFT/IR and Jasco FP 6500 spectrometers respectively.

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Solvothermal synthesis of 1. The title compound (average sizes: 0.15×0.13×0.12 mm) was synthesized solvothermally from a mixture of Eu₂O₃ (0.1760 g), Zn(OAc)₂·H₂O (0.0560 g), (CH₃)₂NH (0.3108 g), ethylene glycol (2.1914 g), sulfuric acid (0.2617 g, 98 %), and deionized water (3.2214 g). The final pH was 1.5. Then the mixture was kept in a 24 ml Teflon-lined autoclave and heated at 170 °C for 4 days. The autoclave was slowly cooled to room temperature, then the product was filtered and dried in air for one day to give the colorless block crystals (0.0370 g, yield 21 % based on Eu).

Single crystal structure determination. The single crystal of compound **1** was adhered at the tip of a thin glass fiber by epoxy glue in air for data collection, and the diffraction data were collected on a Bruker Apex 2 CCD with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K using ω -2 θ scan mode. An empirical absorption correction was applied. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic molecule for the title compound were refined in calculated positions, assigned isotropic thermal parameters, and allowed to ride their parent atoms, while the water H atoms were located from the difference map. All calculations were performed using the SHELX-97 program package [18]. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 421108, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif. (Further details of the X-ray structural analysis for Eu₂(H₂O)₄(SO₄)₃ are given in Table 1 and the selected bond lengths and angles for the compound are listed in Table 2).

Table 1

Crystal Data and Structure Refinement for Eu₂(H₂O)₄(SO₄)₃

Empirical formula	H ₈ Eu ₂ O ₁₆ S ₃
Formula weight	664.16
Temperature, K	293(2)
Wavelength, \AA	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions, \AA , deg.	$a = 6.7520(9)$, $b = 9.1077(12)$, $c = 10.5910(14)$ $\alpha = 94.432(2)$, $\beta = 107.1170(10)$, $\gamma = 99.160(2)$
Volume, \AA^3 , <i>Z</i>	609.17(14), 2
Calculated density, mg/m ³	3.621
Absorption coefficient, mm ⁻¹	10.809
<i>F</i> (000)	620
Crystal size, mm	0.15×0.13×0.12
θ range for data collection, deg.	2.03—25.50
Limiting indices	$-6 \leq h \leq 8$, $-9 \leq k \leq 10$, $-12 \leq l \leq 10$
Reflections collected / unique	3209 / 2227 [$R(\text{int}) = 0.0225$]
Completeness to $\theta = 25.50\%$	98.1
Absorption correction	Semi-empirical from equivalents
Max. / min. transmission	0.3571 / 0.2940
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2227 / 12 / 215
GOOF on F^2	1.051
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0274$, $wR_2 = 0.0664$
<i>R</i> indices (all data)	$R_1 = 0.0300$, $wR_2 = 0.0683$

Table 2

Selected Bond Lengths (Å) for $\text{Eu}_2(\text{H}_2\text{O})_4(\text{SO}_4)_3$ **1**

Eu(1)—O(3)	2.378(3)	Eu(1)—O(10)#2	2.448(3)	Eu(2)—O(4)	2.385(3)
Eu(1)—O(3W)	2.380(3)	Eu(1)—O(9)#3	2.474(3)	Eu(2)—O(2)	2.445(3)
Eu(1)—O(7)#1	2.380(3)	Eu(2)—O(1)#4	2.301(3)	Eu(2)—O(1W)	2.391(3)
Eu(1)—O(8)	2.398(3)	Eu(2)—O(12)#1	2.340(3)	Eu(2)—O(9)	2.963(3)
Eu(1)—O(2W)	2.410(3)	Eu(2)—O(5)#5	2.350(3)	S(1)—O(3)	1.455(3)
Eu(1)—O(4W)	2.412(3)	Eu(2)—O(11)#6	2.375(3)	S(3)—O(4)	1.495(3)
O(3)—Eu(1)—O(8)	145.31(11)	O(1)#4—Eu(2)—O(2)	153.68(11)	O(3)—S(1)—O(2)	109.10(19)
O(3)—Eu(1)—O(2W)	70.03(11)	O(2)—Eu(2)—O(9)	51.30(9)	O(10)—S(1)—O(2)	109.98(18)
O(3W)—Eu(1)—O(8)	110.20(10)	O(5)#5—Eu(2)—O(9)	104.66(10)	O(6)—S(2)—O(8)	109.28(19)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z+1$; #2 $x+1, y, z$; #3 $-x+1, -y+1, -z+1$; #4 $-x, -y, -z$; #5 $x-1, y, z$; #6 $x-1, y, z-1$.

RESULTS AND DISCUSSION

The asymmetric unit of **1** (Fig. 1) contains 21 crystallographically independent non-hydrogen atoms, all belonging to the inorganic framework, including two europium atoms, four water molecules, and three sulfate groups. Two europium atoms are both coordinated by 8 oxygen atoms: the Eu(1) atom is coordinated by five oxygen atoms from two sulfate groups and three water molecules, while the Eu(2) atom is coordinated by eight oxygen atoms including seven from sulfate groups and one from water. Both of the two europium atoms have the typical geometrical parameters. The Eu(1)—O bond distances vary from 2.378(3) to 2.474(3) Å. The O—Eu(1)—O bond angles are ranging from 70.03(11)° to 145.31(11)°. The Eu(2)—O bond distances vary from 2.301(3) to 2.963(3) Å, while the O—Eu(2)—O angles are between 51.30(9) and 153.68(11)°. The values are comparable with those reported previously [19, 20]. Three independent S atoms are tetrahedrally coordinated to four oxygen atoms with S—O distances ranging from 1.455(3) to 1.495(3) Å. S(1) is coordinated by one μ_3 -O and three μ_2 -O atoms, and it makes five S—O—Eu linkages; S(2) is coordinated by one terminal O and three μ_2 -O atoms and makes three S—O—Eu linkages; while S(3) is coordinated by four μ_2 -O atoms and makes S—O—Eu linkages. The S—O—S bond angles are between 109.10(19)° and 109.98(18)°, which is in agreement with 109.28°. Water molecules including O1w, O2w, O3w, and O4w are attached to Eu atoms. The structure of the framework of compound **1** can be described as a building unit

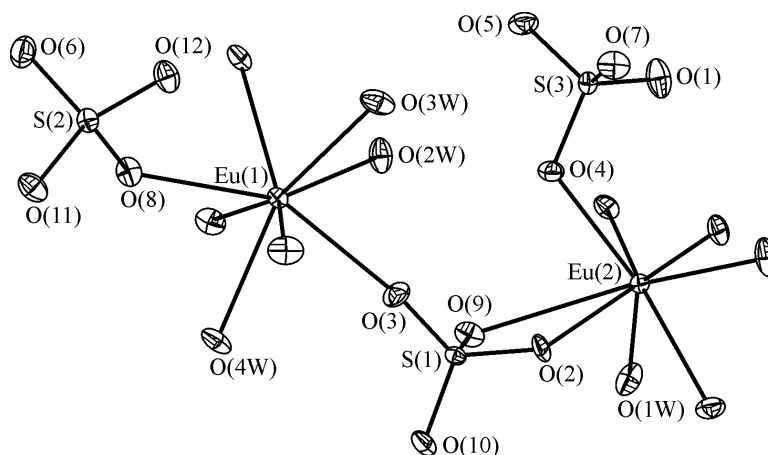


Fig. 1. Asymmetric unit of $\text{Eu}_2(\text{H}_2\text{O})_4(\text{SO}_4)_3$

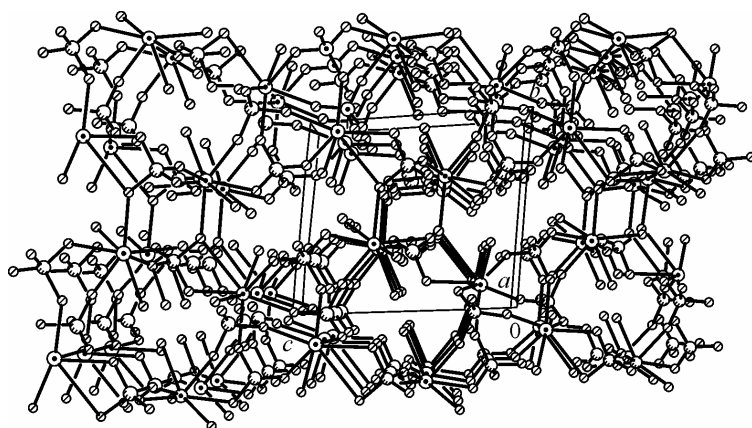


Fig. 2. Structure of the open framework of compound **1** along the *a*-axis

of an 8-membered ring (Eu_4S_4), which is assembled from four EuO_8 polyhedra and four SO_4 tetrahedra. The adjacent EuO_8 and SO_4 polyhedra are sharing the corner or edge to generate the eight-membered ring. Furthermore, the building units (Eu_4S_4) are linked to each other by 4-membered rings to make a double crankshaft zigzag chain. Neighboring double chains are connected by 4-membered rings to generate a Eu—O—S layer along the crystallographic *a*-axis, which is further linked by bridging SO_4 groups to form the 3-D framework of compound **1** (Fig. 2).

The IR spectrum of the title compound shows strong bands in the $3500\text{—}3200\text{ cm}^{-1}$ range assignable to O—H bands with the participation of water molecules. Strong bands in the $1142\text{—}1074\text{ cm}^{-1}$ are associated with the stretching vibrations of S—O groups. The absorption at $651\text{—}581\text{ cm}^{-1}$ can be attributed to the Eu—O vibration.

A thermal analysis shows that the total weight loss of **1** is 51.51 %, which is in agreement with the calculated value (54.22 %) (as shown in Fig. 3). The weight loss of 10.18 % in the range of $50\text{—}230^\circ\text{C}$ corresponds to the removal of coordination water (the calculated value is 10.84 %). The weight loss of 42.33 % in the range of $230\text{—}1066^\circ\text{C}$ can be attributed to the loss of SO_3 (the calculated value is 43.38 %). The final product is Eu_2O_3 .

Due to the excellent luminescent properties of Eu(III) ions, the luminescence of $\text{Eu}_2(\text{H}_2\text{O})_4(\text{SO}_4)_3$ containing Eu(III) ions was investigated. The emission spectrum of the title compound at room temperature upon excitation at 306 nm exhibits the characteristic transition of $^5D_0 \rightarrow ^7F_J$ ($J = 1\text{—}4$) of Eu(III) ions. The strongest emission band is at 616 nm, a medium emission band is at 592 nm, and two weak emission bands are at 652.5 nm and 698.5 nm, which are attributed to $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions of Eu(III) ions respectively (Fig. 4). The luminescence intensity of

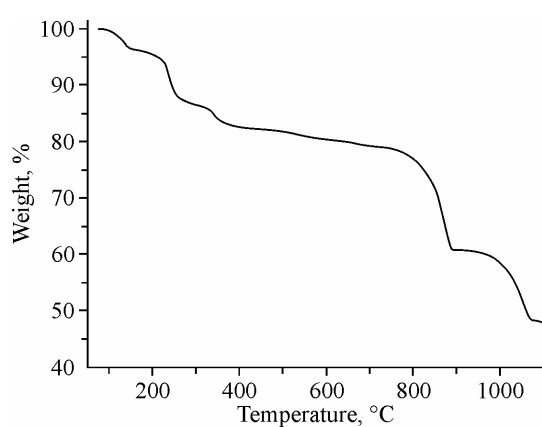


Fig. 3. TG curve of compound **1** (Temperature varies from 50°C to 1100°C at a heating rate of $10^\circ\text{C}/\text{min}$ in the N_2 atmosphere)

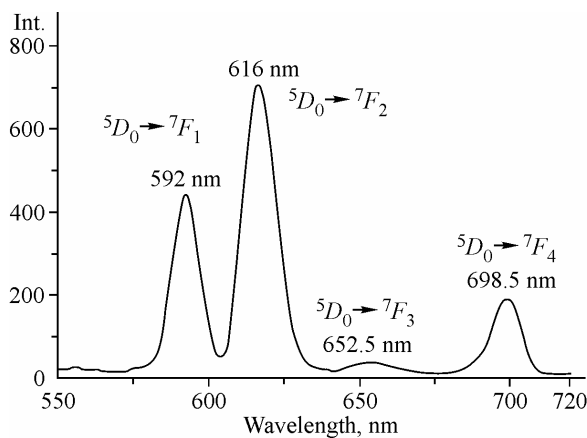


Fig. 4. Solid state excitation and emission spectrum of **1** at room temperature

compound **1** is much stronger than that of previously reported 2-D layered $\text{Eu}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8$ [14] and $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5}[\text{Eu}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ [17]. Although we used the same conditions to measure the luminescence of compound **1**, the luminescence intensity of compound **1** is 5 times than that of $\text{Eu}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8$ and 2 times than that of $[\text{C}_2\text{N}_2\text{H}_{10}]_{1.5}[\text{Eu}(\text{SO}_4)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$. The enhanced fluorescence efficiency of compound **1** is attributed to the fact that bridging SO_4 groups link the Eu—O—S layers into a 3-D framework which effectively increases the rigidity of Eu atoms and reduces the energy loss by thermal vibrations. The strong luminescence efficiency in the red light region indicates that compound **1** is an excellent candidate for red fluorescent materials.

CONCLUSIONS

In the present work, we have successfully synthesized a new 3-D europium sulfate $\text{Eu}_2(\text{H}_2\text{O})_4(\text{SO}_4)_3$ with a strong luminescent property, and it has been characterized by single-crystal X-ray diffraction, thermal analysis, IR absorption spectroscopy, ultraviolet excitation, and emission spectrum. The 3-D framework with interesting eight-membered ring channels is built up by EuO_8 polyhedra and SO_4 tetrahedra connected to form the eight-membered ring channels along the crystallographic *a*-axis. Luminescent investigation indicates that compound **1** is an excellent candidate for fluorescent materials.

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