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Hydrothermal synthesis of a luminescent Europium(III) sulfate with three-dimensional chiral framework structure

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Abstract

The crystal structure and luminescent property of hydrothermally grown crystals of [$NaEu(H_2O)(SO_4)_2$] (**1**) are reported. The crystal structure is composed of three kinds of right-handed helical chains, {$EuOSO_4$}, {$NaOSO_4$} and {EuONa}, which are connected together to form a three-dimensional framework structure via corner-shared polyhedra. The sharp peaks in the emission spectrum of **1** are assigned and analyzed. Crystal data: Trigonal, $P3_121$, with $a = 6.904(1)$ Å, $c = 12.799(1)$ Å and $z = 3$.
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Keywords: Chiral framework; Europium; Hydrothermal synthesis; Luminescence; Sulfate

1. Introduction

There is a much current interest in the crystal engineering of noncentrosymmetric solid state solids [1]. Besides of their intriguing topological architectures, the increasing demand for chiral-related applications in heterogeneous chiral catalysis and enantioselective separation, the essential requirement for a bulk noncentrosymmetric materials to exhibit second-order nonlinear optical (NLO) effects and tribophotoluminescence are the most important driving forces [2–4]. However, the construction of such acentric or chiral assemblies presents a great challenge to conventional synthesis.

Most strategies for the designed synthesis of such kind of materials involve using potential chiral fragments. An important system is composed of inorganic double helical cores, which is generated from a combination of vanadium phosphate [5] or tetra-coordinated copper(I) atoms [6], which act as chiral subunits. Basically, the tetrahedrally coordinated sulfate ligand can be considered as precursors to provide suitable building blocks for synthesis of incorporated inorganic backbone, and might have the potential advantage to generate noncentrosymmetric or chiral networks [7]. On the other hand, there has been an upsurge in the use of lanthanide ions for constructing various fields of materials. Because of the unique nature of lanthanide ions, the assembly of lanthanide complexes offers great challenges and opportunities in terms of controlling fascinating frameworks and specific properties. For example, the narrow emission bands and the spectral character of the excited Eu(III) complexes in the visible region have potential optical-related applications as luminescence probes in clinical medicine, fluoroimmunoassay and local structure analysis [8]. This paper presents the crystal structure and luminescent property of a hydrothermally synthesized inorganic solid, [$NaEu(H_2O)(SO_4)_2$] (**1**), which is a three-dimensional framework comprising {$EuOSO_4$}, {$NaOSO_4$} and {EuONa} right-handed helical chains as subunit formed via corner and edge-shared polyhedra.

2. Experimental section

2.1. General remarks

All chemicals were of reagent grade and used as received. Infrared spectra were recorded on an FTS-40 spectrophotometer by use of pressed KBr pellets. Emission spectra

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were recorded on a Perkin–Elmer LS 55 Luminescence spectrometer.

2.2. *Synthesis of [NaEu(H_2O)(SO_4)$_2$] (**1**)*

A mixture of Eu_2O_3 (0.352 g, 1 mmol), Na_2SO_4 (0.284 g, 2 mmol) and H_2O (10 ml) was heated at 170 °C for 5 days under autogenous pressure after adjustment of pH to ca. 2.2 by addition of 10% H_2SO_4. Light yellow hexagonal-shaped crystals were isolated after the reaction solution was cooled gradually to room temperature and washed with water and ethanol (yield: about 61%). IR (solid KBr pellet/cm): 1635, 1457, 1329, 1276, 1144 m, 1005 s, 978 m, 636 s, 509 s.

Table 1
Crystal data and structural refinement for compound **1**

Compound	[NaEu(H_2O)(SO_4)$_2$]
Formula	$H_2EuNaO_9S_2$
Formula weight	385.09
Crystal color	Light yellow
Crystal system	Trigonal
Space group	$P3_121$
a (Å)	6.904(1)
c (Å)	12.799(1)
Volume (Å^3)	528.3(1)
Z	3
Calculated density (g/cm^3)	3.631
Absorption coefficient (mm^{-1})	9.582
θ for data collection (deg)	3.41–24.96
Reflections collected	1237
Data/restraints/parameters	562/0/61
Goodness-of-fit on F^2	0.965
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0324$
	$wR_2 = 0.0773$
Flack parameter	0.10(4)
Largest diff. peak and hole (e/Å^3)	0.847 and −0.909

$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = \left[\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\right]^{0.5}$.

2.3. *X-ray crystal structure determination*

The determinations of the unit cell and data collection for compound **1** were performed on a Siemens SMART CCD. The data were collected using graphite-monochromatic Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. Empirical absorption corrections were applied by using the SADABS program for the Siemens area detector [9]. The structure was solved by direct method, and refined by full-matrix least-squares methods with the SHELXTL-97 program package [10]. All non-hydrogen atoms were refined anistropically. Crystallographic data are summarized in Table 1 and the selected bond lengths and angles listed in Table 2, respectively.

3. Results and discussion

3.1. *Crystal structure description*

Light yellow crystals of **1** were obtained from the hydrothermal reaction of Eu_2O_3 and Na_2SO_4 in acidified aqueous solution heated at 170 °C for 5 days. Single crystal X-ray diffraction study revealed that compound **1** crystallizes in the chiral space group $P3_121$. It is a three-dimensional framework built up from {$EuOSO_4$}, {NaO SO_4} and {EuONa} right-handed helical chains. The symmetry expanded local structure and the coordination environments around Eu, Na and S atoms in **1** are shown in Fig. 1. Each Eu^{III} cation is nine-coordinated in slightly disordered tricapped trigonal prismatic geometry. It is coordinated by eight oxygen atoms of six sulfate ligands (Eu–O = 2.400(7)–2.520(7) Å) and one aqua ligand (Eu–O = 2.399(14) Å) with O–Eu–O angles involving the neighbor oxygen atoms in the 95.3(2)–56.4(2)° range. The coordination environment around each sulfide(VI) is almost of a regular tetrahedron with the S–O distances ranging from 1.482(8) to 1.492(7) Å and O–S–O angles from 105.6(4)° to 111.2(4)°, respectively. The eight oxygen atoms of six

Table 2
Selected bond lengths (Å) and angles (deg) for compound **1**

Bond length	(Å)	Bond angle	(deg)	Bond angle	(deg)
Eu–O(3)	2.397(13)	O(1)^{i}–Eu–O(1)	76.7(3)	O(2)–Na–O(5)^{iii}	80.4(2)
Eu–O(1)	2.401(7)	O(1)–Eu–O(5)^{i}	73.9(2)	O(4)^{iii}–Na–O(5)^{iii}	70.0(3)
Eu–O(5)	2.407(8)	O(3)–Eu–O(5)	69.8(2)	O(4)#5–Na–O(5)^{iii}	87.2(3)
Eu–O(4)	2.492(6)	O(3)–Eu–O(4)	71.4(2)	O(2)–Na–O(1)^{i}	62.9(2)
Eu–O(2)	2.517(6)	O(5)–Eu–O(4)	71.7(2)	O(4)^{iii}–Na–O(1)^{i}	90.2(2)
Na–O(2)	2.386(9)	O(1)–Eu–O(4)^{i}	85.9(2)	O(5)^{iv}–Na–O(1)^{i}	52.3(2)
Na–O(4)^{iii}	2.455(7)	O(1)–Eu–O(2)^{i}	68.7(2)	O(2)^{i}–S–O(5)^{ii}	110.8(4)
Na–O(5)^{iii}	2.545(6)	O(5)^{i}–Eu–O(2)^{I}	76.4(2)	O(2)^{i}–S–O(1)^{v}	111.3(4)
Na–O(1)^{i}	2.880(7)	O(4)–Eu–O(2)^{I}	56.3(2)	O(5)^{ii}–S–O(1)^{v}	108.3(4)
S–O(2)^{i}	1.483(7)	O(1)–Eu–O(2)	75.4(2)	O(2)^{i}–S–O(4)	105.4(4)
S–O(5)^{ii}	1.485(8)	O(5)–Eu–O(2)	76.4(2)	O(5)^{ii}–S–O(4)	111.7(4)
S–O(1)^{v}	1.487(7)	O(2)–Na–O(4)^{iii}	78.4(2)	O(1)^{v}–S–O(4)	109.4(4)
S–O(4)	1.490(7)	O(4)^{iii}–Na–O(4)^{iv}	77.6(4)		

Symmetry transformations used to generate equivalent atoms: (i) $-x, -x+y, -z+1/3$; (ii) $-y+1, x-y+1, z+1/3$; (iii) $-x+y, -x+1, z-1/3$; (iv) $-x+1, -x+y, -z+1/3$; (v) $-y, x-y+1, z+1/3$.

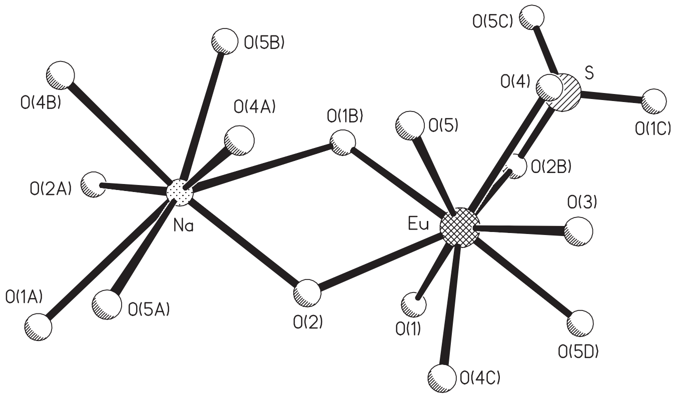

Fig. 1. The symmetry expanded local structure in **1**, showing the atom connectivities and coordination environments of Eu^{III}, S^{VI} and Na^{I} atoms, respectively.

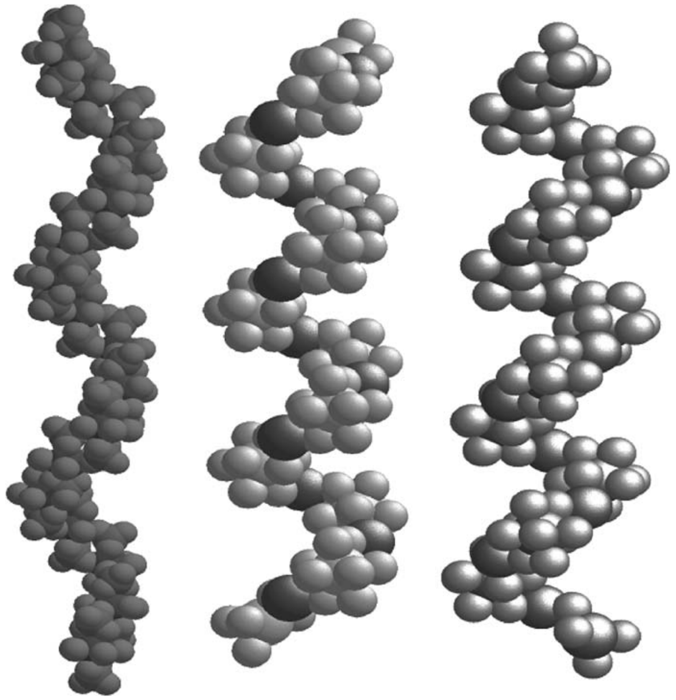

Fig. 2. Space-filling presentations of the three different right-handed single-helices formed by coupled linking up the tricapped trigonal prismatic $\{EuO_9\}$, tetrahedral $\{SO_4\}$ and square-antiprismatic $\{NaO_8\}$ units in **1**.

sulfates around each sodium(I) atom form distorted square-antiprismatic geometry with Na–O distances of 2.386(10)–2.883(8) Å. It is quite interesting to note that every two of the tricapped trigonal prism $\{EuO_9\}$, tetrahedron $\{SO_4\}$ and square-antiprism $\{NaO_8\}$ units link each other to form three kinds of helices along the screw 3_1 axis (Fig. 2). Consequently, all of these helical chains are entangled each other through edge and corner shared polyhedra to generate an interesting three-dimensional framework structure (Fig. 3). Due to the Na^+ cation effects, the network of **1** is quite different to previous published Li^+, NH_4^+ and Rb^+ complexes [11].

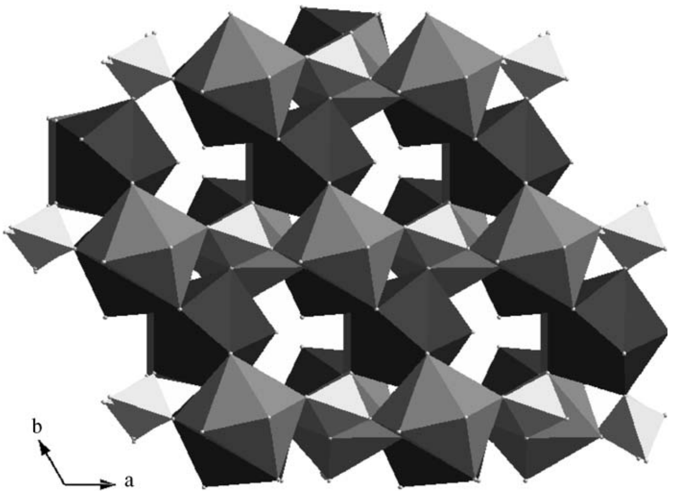

Fig. 3. Polyhedral representation of the three-dimensional framework of **1** viewed down the 3_1 axis ($\{EuO_9\}$: dark gray tricapped trigonal prism, $\{SO_4\}$: light gray tetrahedron and $\{NaO_8\}$: medium gray square-antiprism).

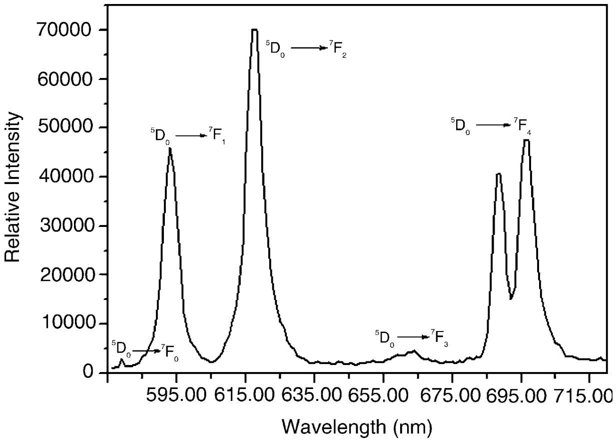

Fig. 4. Luminescent spectrum of **1** in the crystalline state excited at 393 nm.

3.2. Photoluminescent property

In principle, the number of the observed components and their relative intensities and energy spacing are related to their structural information about site symmetry and the number of different coordination sites of the Eu(III) ion [12]. When the Eu^{3+} compound **1** was excited at 393 nm, the fluorescence spectrum in the powder state at 273 K exhibits intense red luminescence bands recorded in the range of 575–715 nm, which arises from the $^5D_0 \rightarrow {}^7F_J$ $(J = 0, 1, 2, 3, 4)$ transitions for Eu^{3+} ion (Fig. 4). The single symmetric forbidden emission peak at 579 nm for $^5D_0 \rightarrow {}^7F_0$ transition indicates the presence of one Eu^{3+} local environment without an inversion center. The 593 nm emission peak respected to the $^5D_0 \rightarrow {}^7F_1$ transition has magnetic dipole character, which is independent of the coordination environment and only weakly dependent on crystal field effects. The $^5D_0 \rightarrow {}^7F_{2,4}$ transitions in the

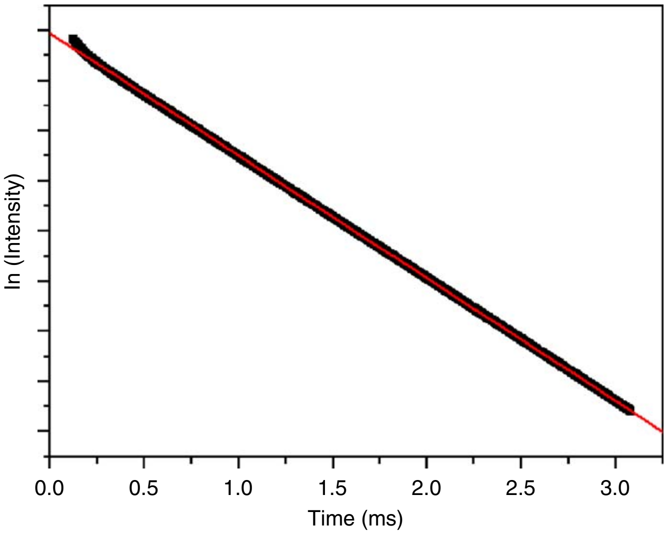

Fig. 5. $^5D_0$ decay curves detected within the $^5D_0 \rightarrow {}^7F_2$ region at 223 K and excited at 393 nm. The straight lines represent the best fit ($r^2 = 0.9996$) to the data considering a single decay behavior.

605–635 and 680–710 nm regions are essentially purely electric dipole in character, and its intensity is strongly dependent on the odd-parity components of the crystal field symmetry [13–14]. The integrated intensity ratio of $^5D_0 \rightarrow {}^7F_1/{}^5D_0 \rightarrow {}^7F_2$ transitions is about 2, which further confirms that the local symmetry of the Eu^{3+} site does not have an inversion center. The luminescent behavior of **1** is slightly different to that of Eu^{3+} doped compounds [15], since these luminescent centers often have more than one local environments and lower Eu^{3+} concentration. The decay curve (in natural log scale) of $^5D_0 \rightarrow {}^7F_2$ transition excited at 393 nm are well fitted by a single-exponential function, yielding lifetime values of 407.9 μs, which further confirmed the presence of one local Eu^{3+} environment in **1** (Fig. 5). The photoluminescent property study has confirmed that Eu^{3+} ions present one local environment and absent of inversion symmetry, which is in good agreement with single-crystal X-ray analysis result.

4. Conclusions

In conclusion, the synthesis, crystal structure and luminescent property of a europium(III) sulfate have been revealed. It adopts three kinds of helical chains in the sulfate framework. The luminescent properties of **1** have also been reported. The sharp lines in the emission spectrum are assigned. The conclusions drawn from the relative intensities of $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions and emission decay study are consistent with the crystallographic results. Further research to synthesize new chiral luminescent chiral europium(III) complexes is in progress.

5. Supplementary material

Tables of atomic coordinates and equivalent isotropic parameters, bond distances and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for **1** are available from the authors on request. Further details of the crystal-structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-416235.

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