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Synthesis, crystal structure and fluorescence property of 1-D europium complex with 2,3-difluorobenzoate

SONG Jinhao (宋金浩), WU Xiaoshuo (吴小说), LI Xia (李　夏)

(Department of Chemistry, Capital Normal University, Beijing 100048, China)

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Abstract: A new chain europium complex $[Eu(2,3\text{-}DFBA)_3\cdot(H_2O)_2]_n$ (2,3-DFBA=2,3-difluorobenzoate) was synthesized by solvent method. X-ray single-crystal diffraction analysis revealed that Eu^{3+} ions were linked through 2,3-DFBA groups via alternate bidentate-bridging and tridentate chelating-bridging coordination modes to form a one-dimensional (1-D) polymeric chain. Each Eu^{3+} ion is eight-coordinated by six O atoms of five 2,3-DFBA ligands and two water molecules. The abundant hydrogen bonds between chains resulted in a two-dimensional (2-D) network structure. The titled complex crystallizes in monoclinic system, space group $P2_1/c$, with a=0.79977(2) nm, b=2.99156(7) nm, c=0.93260(2) nm, and β=100.691(1)°. The complex exhibited strong red fluorescence under ultraviolet light, and the $^5D_0\rightarrow{}^7F_j$ (j=0~4) transitions of Eu^{3+} ion were observed in its emission spectrum.

Keywords: europium complex; 2,3-difluorobenzoic acid; crystal structure; fluorescence; rare earths

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In recent years, luminescent lanthanide complexes have attracted much attention due to their excellent photophysical properties and potential applications in different interesting areas[1–4]. The research has been focused on lanthanide complexes with carboxylic acid because they show various interesting molecular structures and luminescence for practical applications[5–16]. Benzoic acid and its derivatives have been widely used in the coordination complexes of rare earth because they are rigid ligands with various coordination modes and can form π-π stacking or hydrogen bonds to stabilize the complexes. By reducing the fluorescence quenching effect of the vibrational C–H bond[17,18], fluorinated organic ligands can significantly strengthen the luminescence intensity of complexes. We chose 2,3-difluorobenzoic acid to prepare a new chain europium complex, namely $[Eu(2,3\text{-}DFBA)_3\cdot(H_2O)_2]_n$ (2,3-DFBA=2,3-difluorobenzoate). The crystal structure, thermal stability and fluorescence emission spectrum were reported in this paper.

1 Experimental

1.1 Reagents and instruments　All analytical grade reagents and solvents were purchased commercially and used without further purification. $EuCl_3\cdot6H_2O$ was prepared by the reaction of Eu_2O_3 (99.90%) and hydrochloric acid.

Solid-state excitation and emission spectra were recorded on an F-4500 fluorescence spectrophotometer at room temperature. The TG- DTA analysis experiment was carried out on a WCT-1A Thermal Analyzer.

1.2 Synthesis of the title complex　A stoichiometric amount of 2,3-difluorobenzoic acid and $EuCl_3\cdot6H_2O$ were dissolved in 95% ethanol, respectively. The pH of the 2,3-difluorobenzoic acid was adjusted to the range of 5–6 with 2 mol/L NaOH solution. Then the ethanol solution of $EuCl_3\cdot6H_2O$ was added dropwise to the mixed solution. The mixture was heated under reflux with stirring for 2 h. Single crystals suitable for X-ray investigation were obtained from the mother liquor after a week (Yield: 42.25%).

1.3 Single-crystal structure determination　A single crystal of the titled complex with dimensions of 0.15 mm×0.20 mm×0.20 mm was carefully selected and mounted on a glass fiber. Data were collected at 296(2) K on a Bruker Smart 1000 CCD diffractometer equipped with a graphite monochromatized Mo Kα radiation (λ=0.071073 nm). Semi-empirical absorption corrections were applied using the SADABS program. The structure was solved by direct method. The coordinates of all non-hydrogen atoms and the anisotropical parameters were refined by full-matrix least-squares method. The hydrogen atoms were placed in calculated positions. All calculations were carried out on a

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Corresponding author: LI Xia (**E-mail:** xiali@mail.cnu.edu.cn; **Tel.:** +86-10-68903033)

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computer by using SHELXS-97 and SHELXL-97 programs. The crystallographic data and structure refinement of the titled complex are summarized in Table 1. The selected bond lengths and bond angles of the titled complex are listed in Table 2.

2 Results and discussion

2.1 Crystal structure The crystal structure and atomic numbering of the titled complex are shown in Fig. 1. The complex is regarded as a polymeric chain composed of [Eu(2,3-DFBA)$_3$·(H$_2$O)$_2$] units. In the asymmetric unit, each Eu^{3+} ion is coordinated to eight atoms, of which one oxygen atom is from the monodentate carboxylate group, two oxygen atoms from bidentatebridging carboxylate groups, three oxygen atoms from tridentate chelating-bridging carboxylate groups, and two oxygen atoms from two water molecules. The coordination geometry of Eu^{3+} ion can be described as a distorted square-antiprism. The upper and lower planes of the square-antiprism are structured by O1, O2, O7, O8 and O2A, O3, O5, O6, respectively, with a dihedral angle of 4.6° between them. And the mean deviation from the upper and lower planes is 0.02678 and 0.03874 nm, respectively. The Eu–O (carboxylate) distances are in a range of 0.2267(7) to 0.2583(6) nm with the average bond length of 0.2402 nm. The Eu1–O (water) distances are 0.2460(8) and 0.2430(8) nm, respectively, with the average bond distance of 0.2445 nm. The O–Eu1–O bond angles range from 51.8(2) to 156.3(3)°. In the titled complex, Eu^{3+} ions are bridged by 2,3-DFBA groups in two modes: Eu1…Eu1A are bridged

Table 1 Crystal data and structure refinement for the title complex

Empirical formula	$C_{21}H_{13}EuF_6O_8$
Formula weight	659.27
Crystal size/mm	0.15×0.20×0.20
Temperature/K	296(2)
Wavelength/nm	0.071073
Crystal system	Monoclinic
Space group	$P2_1/c$
a/nm	0.79977(2)
b/nm	2.99156(7)
c/nm	0.93260(2)
α/(°)	90.00
β/(°)	100.691(1)
γ/(°)	90.00
V/nm^3	2.19257(9)
Z	4
Dc/(mg/m^3)	1.997
μ/mm^{-1}	2.959
F(000)	1280
θ/(°)	2.7~25.5
Limiting indices	$-9\leqq h\leqq 9$, $-36\leqq k\leqq 29$, $-11\leqq l\leqq 9$
Reflections collected/unique	11536/4036 [R(int)=0.035]
Data / restraints/parameters	4036/4/341
Goodness-of-fit on F^2	1.564
Final R indices [I>2sigma (I)]	R_1=0.659, wR$_2$=0.1468
R indices (all data)	R_1=0. 0699, wR_2=0.1481

Table 2 Selected bond lengths (nm) and angles (°) for the titled complex*

Eu1–O1	0.2440(7)	Eu1–O2	0.2583(6)
Eu1–O2A	0.2430(7)	Eu1–O3	0.2371(7)
Eu1–O5	0.2319(7)	Eu1–O6	0.2267(7)
Eu1–O7	0.2460(8)	Eu1–O8	0.2430(8)
O1–Eu1–O7	76.9(3)	O1–Eu1–O2	51.8(2)
O2A–Eu1–O1	118.2(2)	O2A–Eu1–O7	140.2(3)
O2A–Eu1–O2	66.5(2)	O3–Eu1–O8	144.7(2)
O3A–Eu1–O2	74.4(2)	O3–Eu1–O1	96.8(3)
O3–Eu1–O7	143.7(3)	O3–Eu1–O2	79.6(2)
O5–Eu1–O3	71.9(2)	O5–Eu1–O8	141.8(3)
O5A–Eu1–O2	142.8(2)	O5–Eu1–O1	81.3(3)
O5–Eu1–O7	71.8(3)	O5–Eu1–O2	121.0(2)
O6–Eu1–O5	91.1(3)	O6–Eu1–O3	101.9(3)
O6–Eu1–O8	89.9(3)	O6A–Eu1–O2	80.8(2)
O6–Eu1–O1	156.6(3)	O6–Eu1–O7	79.6(3)
O6–Eu1–O2	145.8(2)	O7–Eu1–O2	119.3(2)
O8A–Eu1–O2	74.8(2)	O8–Eu1–O1	82.8(3)
O8–Eu1–O7	70.8(3)	O8–Eu1–O2	72.5(2)

* Symmetry transformations used to generate equivalent atoms: A: -1+x, y, z

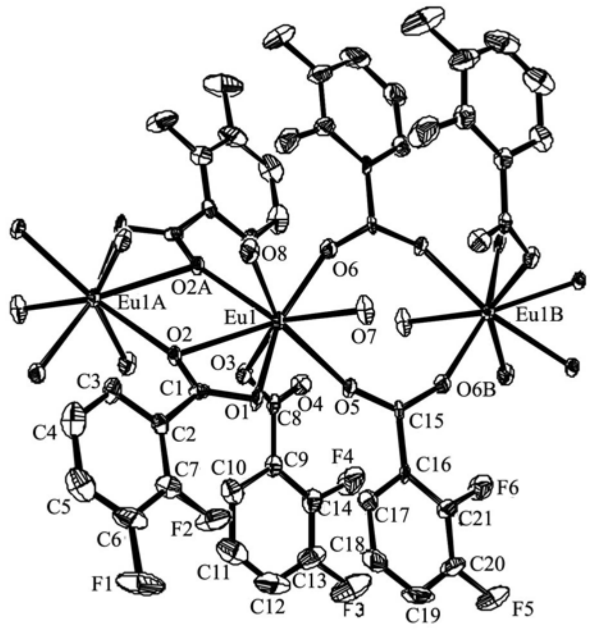

Fig. 1 Asymmetric unit of the titled complex