

铕与 2,4-二氯苯甲酸一维链状配位聚合物的合成, 晶体结构和发光性质

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摘要: 溶液法合成了一个新的铕配位聚合物 $[\text{Eu}(\text{2,4-DCIBA})_3(\text{CH}_3\text{CH}_2\text{OH})_2]_n$ (2,4-DCIBA=2,4-二氯苯甲酸根), 并用 X-射线单晶衍射分析确定了其晶体结构。配合物晶体属于三斜晶系, $P\bar{1}$ 空间群。标题配合物是无限一维链状聚合物, 中心 Eu^{3+} 离子通过桥联双齿 2,4-二氯苯甲酸根氧原子连接。 Eu^{3+} 离子的配位数为 8, 分别与 4 个桥联双齿 2,4-二氯苯甲酸根的 4 个氧原子、1 个螯合双齿 2,4-二氯苯甲酸根的 2 个氧原子和 2 个乙醇分子的 2 个氧原子配位。紫外灯照射下配合物发出强的红光, 配合物的荧光光谱中, 5 个峰位于 580、593、619、652 和 699 nm, 分别对应于 Eu^{3+} 离子的 $^5D_0 \rightarrow ^7F_J (J=0\sim4)$ 跃迁。

关键词: 铕; 2,4-二氯苯甲酸; 一维链; 荧光

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Synthesis, Crystal Structure and Fluorescence Property of a 1D Chain Europium Coordination Polymer with 2,4-dichlorobenzoic Acid

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Abstract: A europium coordination polymer $[\text{Eu}(\text{2,4-DCIBA})_3(\text{CH}_3\text{CH}_2\text{OH})_2]_n$ (2,4-DCIBA=2,4-dichlorobenzoate) was prepared by solvent method and its structure was determined by X-ray diffraction single-crystal structure analysis. The complex crystallizes in triclinic crystal system, $P\bar{1}$ space group. The title complex is a infinite 1D chain polymeric structure through oxygen atoms of bidentate-bridging 2,4-DCIBA anions linking up the neighboring central Eu^{3+} ions. Each Eu^{3+} ion is eight-coordinated with four oxygen atoms of four bidentate-bridging 2,4-DCIBA anions, two oxygen atoms of one bidentate-chelating 2,4-DCIBA anion and two oxygen atoms of two ethanol molecules. This complex exhibits strong red fluorescence radiated by ultraviolet light and the fluorescence spectrum has five peaks at 580, 593, 619, 652 and 699 nm corresponding to $^5D_0 \rightarrow ^7F_J (J=0\sim4)$ transitions of the Eu^{3+} ion. CCDC: 667995.

Key words: europium; 2,4-dichlorobenzoic acid; 1D chain; fluorescence

The construction and crystal engineering of luminescent lanthanide complexes have been studied^[1~7], due to their interesting photophysical properties which have potential application in luminescent label, magnetic molecular materials and electroluminescent material. Consequently, a variety of ligands such as cryptands, podands, calixarenes, macrocyclic ligands, β -diketone,

carboxylic acid derivatives, terphenyl ligands and proteins^[8~13] are adopted to prepare for such complexes. Especially, much attention has been focused on the design and assembly of lanthanide complexes with carboxylic acid^[14~16] because of the large variety of architectures that result from coordination versatility of the carboxylate ligands and variable coordination numbers

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of the metal centers. Among these compounds, aromatic carboxylic acids are of more attractive ligands due to not only their intrinsic rigid traits and various coordination modes of the carboxylate but also further forming π - π stacking or hydrogen bonds making the complex more stable. In recent years, our group has done some work to synthesize a series of complexes of halobenzoic acids with interesting structures^[17-19]. As a part of our systematic studies, this paper reports a infinite 1D chain coordination polymer $[\text{Eu}(\text{2,4-DCIBA})_3(\text{CH}_3\text{CH}_2\text{OH})_2]_n$ assembled from the reaction of europium nitrate with a 2,4-dichlorobenzoic acid. The properties of this europium complex have been studied by ultraviolet absorption spectrum, fluorescence excitation and emission spectra and thermogravimetric analysis.

1 Experimental

1.1 Materials and physical measurement

All analytical grade chemicals and solvents were purchased commercially and used without further purification. $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was made by the reaction of europium oxide (99.99%) and nitric acid.

The thermogravimetric analysis was performed with a WCT-1A Thermal Analyzer. The UV spectrum was measured on a TU-1810 Ultraviolet-Visible spectrophotometer. The excitation spectrum and emission spectrum of the solid sample were recorded on an F-4500 Fluorescence Spectrophotometer.

1.2 Synthesis of $[\text{Eu}(\text{2,4-DCIBA})_3(\text{CH}_3\text{CH}_2\text{OH})_2]_n$

1.2 mmol 2,4-dichlorobenzoic acid was dissolved in 25 mL ethanol, the mixture was heated with stirring and the pH value was adjusted to about 4.1 by 2 mol·L⁻¹ sodium hydroxide aqueous solution. And then $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.4 mmol) was added into the mixture. The resulting solution was filtered and the filtrate was kept at room temperature. The colorless needle-like single crystals suitable for X-ray structural analysis were obtained after a week.

1.3 Crystal structure determination

A single crystal with dimensions of 0.24 mm × 0.20 mm × 0.18 mm was carefully selected for structure analysis. The data collection was carried out on a Bruker SMART 1000 CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$). Total of 24 710 reflections collected in the range of $1.83^\circ \leq \theta \leq 27.00^\circ$, of which 6 506 were independent with $R_{\text{int}} = 0.040\ 6$. Semi-empirical absorption corrections were applied using the SADABS program. The structure was solved by direct method. The coordinates and the anisotropical parameters of all nonhydrogen atoms were refined by full-matrix least-squares method on F^2 . Hydrogen atoms were determined with theoretical calculations. A summary of the crystallographic data and details of the structure refinements are listed in Table 1. The selected bond lengths and bond angles of the title complexes are given in Table 2.

Table 1 Crystal data and structure refinement for the complex

Empirical formula	$\text{C}_{25}\text{H}_{21}\text{Cl}_2\text{EuO}_8$	Calculated density / ($\text{Mg} \cdot \text{m}^{-3}$)	1.799
Formula weight	814.08	Absorption coefficient / mm^{-1}	2.665
Temperature / K	296(2)	$F(000)$	800
Wavelength / nm	0.071 073	Crystal size / mm	0.24 × 0.20 × 0.18
Crystal system	Triclinic	θ range for data collection / ($^\circ$)	1.83~27.00
Space group	$P\bar{1}$	Limiting indices	$-12 \leq h \leq 12, -16 \leq k \leq 16, -17 \leq l \leq 17$
a / nm	0.963 85(2)	Completeness to $\theta=27.00^\circ$ / %	99.1
b / nm	1.288 04(3)	Reflections collected	24 710
c / nm	1.400 20(3)	Independent reflections (R_{int})	6 506 (0.040 6)
α / ($^\circ$)	113.085 0(10)	Observed reflections [$I > 2\sigma(I)$]	5 786
β / ($^\circ$)	90.227 0(10)	Goodness-of-fit on F^2	1.029
γ / ($^\circ$)	108.228 0(10)	Final R indices [$I > 2\sigma(I)$]	$R_1=0.029\ 3, wR_2=0.058\ 7$
Volume / nm^3	1.502 84(6)	R indices (all data)	$R_1=0.035\ 5, wR_2=0.061\ 2$
Z	2		

Table 2 Bond lengths (nm) and bond angles (°) of the complex

Eu1-O6A	0.230 9(2)	Eu1-O5	0.236 5(2)	Eu1-O4B	0.231 9(2)
Eu1-O3	0.239 3(2)	Eu1-O7	0.245 0(2)	Eu1-O8	0.247 2(2)
Eu1-O2	0.248 2(2)	Eu1-O1	0.254 9(2)		
O6A-Eu1-O4B	153.04(8)	O6A-Eu1-O5	103.98(8)	O4B-Eu1-O5	83.36(7)
O5-Eu1-O3	143.70(8)	O6A-Eu1-O3	78.71(7)	O4B-Eu1-O3	110.82(7)
O6A-Eu1-O7	84.21(8)	O4B-Eu1-O7	74.44(8)	O3-Eu1-O7	75.75(8)
O6A-Eu1-O8	73.63(8)	O5-Eu1-O7	140.34(8)	O4B-Eu1-O8	84.66(8)
O5-Eu1-O8	71.38(8)	O3-Eu1-O8	140.67(8)	O6A-Eu1-O2	126.71(8)
O4B-Eu1-O2	80.12(8)	O7-Eu1-O8	74.14(8)	O5-Eu1-O2	76.36(8)
O3-Eu1-O2	73.71(8)	O7-Eu1-O2	129.50(7)	O6A-Eu1-O1	77.57(8)
O4B-Eu1-O1	128.82(8)	O8-Eu1-O2	145.63(8)	O5-Eu1-O1	70.68(8)
O3-Eu1-O1	74.78(7)	O7-Eu1-O1	147.79(8)	O2-Eu1-O1	51.70(7)
O8-Eu1-O1	124.14(7)				

Symmetry transformations used to generate equivalent atoms: A: $-x+2, -y, -z+2$; B: $-x+1, -y, -z+2$.

CCDC: 667995.

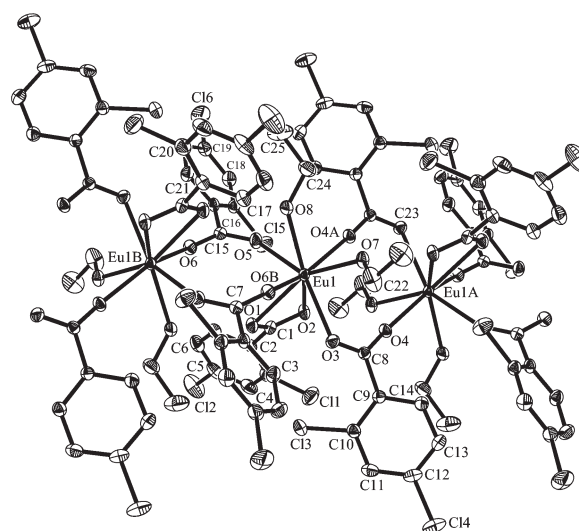
2 Results and discussion

2.1 Crystal structure description of

$[\text{Eu}(\text{2,4-DClBA})_3(\text{CH}_3\text{CH}_2\text{OH})_2]_n$

The crystal structure of the title complex is shown in Fig.1. The neighboring Eu^{3+} ions are linked by two 2,4-DClBA groups in bidentate-bridging coordination mode to form an infinite 1D chain. In the chain distances of neighboring Eu^{3+} ions, $\text{Eu1A} \cdots \text{Eu1}$ and $\text{Eu1} \cdots \text{Eu1B}$ are 0.468 5(5) and 0.503 5(5) nm, respectively, and the bond angle of $\text{Eu1A} \cdots \text{Eu1} \cdots \text{Eu1B}$ is 165.2° . The title complex is different from complexes $[\text{Eu}(\text{2-IBA})_3 \cdot \text{H}_2\text{O}]_n$ [17] (2-IBA=2-iodobenzoate) and $\text{Tb}(\text{o-ClC}_6\text{H}_4\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$ [20] ($\text{o-ClC}_6\text{H}_4\text{CO}_2 = m\text{-chlorobenzoate}$). The later two complexes have also an infinite 1D chain structure, in which Eu^{3+} or Tb^{3+} ions are linked through carboxylate groups via bridging-chelating-bridging tetradentate coordination mode. $\text{Eu}(\text{2,4-DClBA})_3(\text{CH}_3\text{CH}_2\text{OH})_2$ composes independent structure unit with one Eu^{3+} ion, three 2,4-DClBA anions and two ethanol molecules. Each Eu^{3+} ion is eight-coordinated and surrounded by eight oxygen atoms, of which four oxygen atoms are from four bidentate-bridging 2,4-DClBA anions, two oxygen atoms from one bidentate-chelating 2,4-DClBA anion, and other two oxygen atoms provided by two ethanol molecules. Thereby, $\text{Eu}(\text{2,4-DClBA})_3(\text{CH}_3\text{CH}_2\text{OH})_2$ as building block was assembled through

2,4-DClBA anions to form infinitely extended -Eu-O-C-O-Eu- chain.

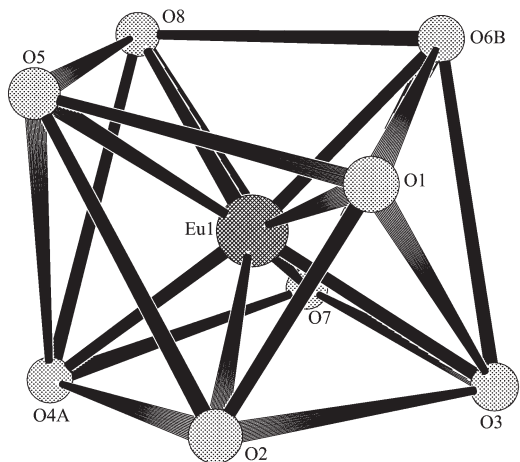


Symmetry code: A: $-x+2, -y, -z+2$; B: $-x+1, -y, -z+2$

Fig.1 Molecular structure of the complex

The local environment around the Eu^{3+} ion can be best described as a approximate square antiprism geometry (Fig.2). The upper and lower planes of the square antiprism are structured by O1, O5, O8, O6B and O2, O3, O7, O4A, respectively, with a dihedral angle of 9.8° between them. And the mean deviation from the upper and lower planes is 0.013 5 and 0.0143 6 nm, respectively. The bond lengths of Eu-O range from 0.230 9(2) to 0.254 9(2) nm, and the average bond length is 0.241 7 nm. The bond angles of O-

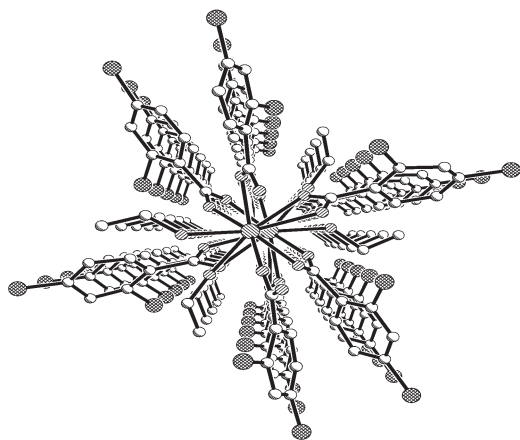
Eu1-O (carboxyl) vary in the range of $51.70(7)^\circ \sim 153.04(8)^\circ$.



Symmetry code: A: $-x+2, -y, -z+2$; B: $-x+1, -y, -z+2$

Fig.2 Coordination geometry of Eu^{3+} ion in the complex

Viewed down the a -axis (Fig.3), bidentate-bridging 2,4-DClBA anions, bidentate-chelating 2,4-DClBA anions and ethanol molecules symmetrically array around coordination chain, respectively. Corresponding phenyl rings are strictly parallel, and the distance of neighboring phenyl rings is 0.32 nm. In the whole molecule, the inner chain is taking on strong π - π interaction owing to interactional phenyl rings of 2,4-DClBA anions, which further stabilizes complex structure.



Symmetry code: A: $-x+2, -y, -z+2$; B: $-x+1, -y, -z+2$

Fig.3 Packing diagram of the complex along the a -axis

2.2 Thermogravimetric analysis

The analysis was performed in air atmosphere with a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ in the temperature range from 20 to 1 000 $^\circ\text{C}$.

In the DTA curve, there appear two small endothermic peaks at 124.0 and 228.0 $^\circ\text{C}$, respectively. And there are two exothermic peaks at 567.0 and 476.0 $^\circ\text{C}$. A weight loss of 11.25% equivalents to the removal of two ethanol molecules (calculated: 11.31%), then the complex decomposes step by step. The residue Eu_2O_3 was obtained, corresponding to the total loss of 78.8% (calculated: 78.98%).

2.3 Photophysical property

The UV spectrum of complex ($10^{-4} \text{ mol} \cdot \text{L}^{-1}$, DMF solution) suggests the band of 272.0 nm ($\epsilon = 7.04 \times 10^4$) can be attributed to π - π^* transition of the ligands, which indicates that ligand can transfer the absorption energy to the Eu^{3+} ion.

The solid sample of the complex emits intense red fluorescence under ultraviolet light. Its excitation spectrum was recorded in the range of 200~400 nm, setting 612 nm as the emission wavelength. The emission spectrum of the complex was observed in the range of 550~700 nm under the excitation wavelength of 394 nm, in which there are five main peaks: 580, 593, 619, 652 and 699 nm, corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions of the Eu^{3+} ion, respectively (Fig.4). And the main emission bands at 619 nm with a shoulder peak of 613 nm.

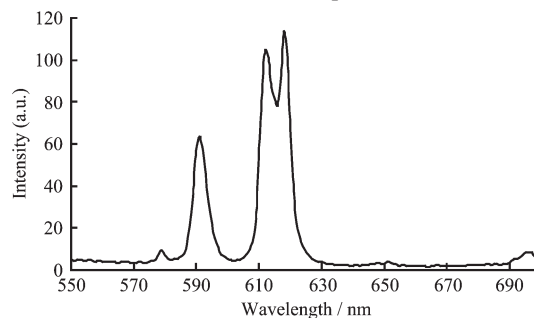


Fig.4 Fluorescence spectrum of the complex ($\lambda_{\text{ex}}=394 \text{ nm}$)

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