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配合物 $[\text{Eu}(\text{4-MOBA})_3(\text{terpy})(\text{H}_2\text{O})]_2$ 的合成、表征、热分解机理及性质霍建霞^{1,2} 宋素伟⁴ 靳成伟^{1,2} 任 宁^{3,*} 耿丽娜² 张建军^{1,2,*}¹河北师范大学分析测试中心, 石家庄 050024; ²河北师范大学化学与材料科学学院, 石家庄 050024;³邯郸学院化学化工与材料学院, 河北 邯郸 056005; ⁴中石油京唐液化天然气有限公司, 河北 唐山 063210)

摘要: 合成了一个新的配合物 $[\text{Eu}(\text{4-MOBA})_3(\text{terpy})(\text{H}_2\text{O})]_2$ (4-MOBA: 4-甲氧基苯甲酸根, terpy: 2,2':6',2''-三联吡啶)。采用傅里叶变换红外(FTIR)光谱、元素分析和X射线粉末衍射(XRD)技术对标题配合物进行了表征, 用X射线单晶衍射仪测定了配合物的晶体结构, 在配合物中每个 Eu^{3+} 离子与一个三联吡啶分子、一个水分子和三个羧酸分子结合, 配位数为9, 羧酸基团的配位模式包含三种: 双齿螯合, 桥连双齿, 单齿。根据热重-差示扫描量热/傅里叶变换红外(TG-DSC/FTIR)联用技术, 研究了配合物的热分解机理。配合物的发射光谱显示出 Eu^{3+} 离子的特征荧光发射, 表明三联吡啶和4-甲氧基苯甲酸在该体系中可作为敏化集团。另外, 文中还讨论了配合物对白色念珠菌和大肠杆菌的抑菌活性。

关键词: 镧系配合物; 晶体结构; 热分解机理; 荧光; 2,2':6',2''-三联吡啶; 抑菌活性

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Synthesis, Characterization, Thermal Decomposition Mechanism and Properties of the $[\text{Eu}(\text{4-MOBA})_3(\text{terpy})(\text{H}_2\text{O})]_2$ ComplexHUO Jian-Xia^{1,2} SONG Su-Wei⁴ JIN Cheng-Wei^{1,2} REN Ning^{3,*}
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Abstract: A new complex $[\text{Eu}(\text{4-MOBA})_3(\text{terpy})(\text{H}_2\text{O})]_2$ (4-MOBA: 4-methoxybenzoate, terpy: 2,2':6',2''-terpyridine) was synthesized. The complex was characterized using Fourier transform infrared (FTIR) spectroscopy, elemental analysis, and powder X-ray diffraction (XRD). The structure of the complex was determined using single-crystal XRD. In the complex, each Eu^{3+} ion is nine coordinated to one terpy molecule, one water molecule and three carboxylate groups. The carboxylate groups are bonded to the Eu^{3+} ion in three modes: bidentate, bridging bidentate, and monodentate. Based on thermogravimetry-differential scanning calorimetry/Fourier transform infrared (TG-DSC/FTIR) measurements, we determined the thermal decomposition mechanism. The emission spectra of the complex exhibited characteristic luminescence, suggesting that terpy and 4-methoxybenzoic acid can act as sensitizing chromophores in this system. Also, bacteriostatic activities for the complex to *Candida albicans* and *Escherichia coli* are discussed.

Key Words: Lanthanide complex; Crystal structure; Thermal decomposition mechanism; Luminescence; 2,2':6',2''-Terpyridine; Antimicrobial activity

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1 Introduction

A massive interest in Ln^{3+} complexes is registered in more recent times, which stems from their possible use in biomedical and telecommunication fields and for various photonic applications^{1–9}. The absorption coefficients of the optical transitions for lanthanide ions are, however, very low which limits their practical application considerably. This drawback can be overcome through the use of organic ligand, which acts as an antenna or sensitizer, absorbing excitation light and transferring energy to the lanthanide ions, thus greatly improves the characteristic emission of rare earth ions^{10–14}. In order to obtain strong luminescent intensities, Eu^{3+} ions need a cleverly designed environment consisting of organic ligands with chromophoric groups to absorb efficiently light and subsequently populate the excited states of Eu^{3+} ions via energy transfer.

On the other hand, the lanthanide complexes with biological activities can be used at various fields, just as many studies of researchers^{15–20}. The results show that, under certain conditions, Ln^{3+} ions can not inhibit the *Candida albicans* and *Escherichia coli*, while the complexes synthesized by organic ligands and Ln^{3+} can inhibit the *Candida albicans* and *Escherichia coli* well²¹.

In this report, a new Eu complex with 4-methoxybenzoic acid and 2,2':6',2''-terpyridine was synthesized. The complex was measured by series of elementary methods. Moreover, the luminescent properties and bacteriostatic activities of the complex were discussed, and thermal decomposition mechanism of the complex was also presented.

2 Materials and methods

2.1 Materials and physical measurements

All chemicals were commercially purchased and used without further purification. $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was prepared by reaction of Eu_2O_3 and hydrochloric acid in aqueous solution.

The Eu^{3+} is determined by ethylenediamine tetraacetic acid (EDTA) titration using xylenol oranges as an indicator. C, N, and H analyses were performed using a Vario-EL III elemental analyzer (Elementar, Germany). Infrared spectrum ($4000\text{--}400\text{ cm}^{-1}$) was obtained with KBr discs on a TENSOR27 spectrometer (Bruker, Germany). X-ray powder diffraction identification was carried out for the crystalline analyses by a D8 ADVANCE X-ray diffractometer in a scanning range of $5^\circ\text{--}40^\circ$ (2θ) with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418\text{ nm}$, Bruker, Germany). The data of single crystal X-ray diffraction were collected on a Smart-1000 diffractometer (Bruker, Germany). The crystal data and refinement details for the complex are presented in Table 1. The fluorescent spectrum of complex (solid) was recorded on an F-4500 Hitachi spectrophotometer at room temperature. Thermogravimetry-differential scanning calorimetry/Fourier transform infrared (TG-DSC/FTIR) was described by using the STA 449 F3 (Netzsch, Germany) coupled with TENSOR27 Fourier Transform Infrared Spectrometer (Bruker, Germany). Using the filter paper disc (diameter 6 mm) diffusion method, antibacterial activity of the $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, ligands and complex were tested.

2.2 Preparation

Table 1 Crystallographic data for the complex

Item	Value
empirical formula	$\text{C}_{78}\text{H}_{68}\text{Eu}_2\text{N}_6\text{O}_{20}$
formula weight	1713.30
T/K	298(2)
wavelength/nm	0.071073
crystal system	monoclinic
space group	$P2(1)/c$
a/nm	1.35070(13)
b/nm	2.6042(2)
c/nm	1.30890(12)
$\alpha/^\circ$	90
$\beta/^\circ$	116.992(3)
$\gamma/^\circ$	90
volume/ nm^3	4.1025(7)
Z , calculated density/ $(\text{Mg}\cdot\text{m}^{-3})$	2, 1.387
absorption coefficient/ mm^{-1}	1.585
$F(000)$	1728
crystal size/ mm^3	$0.30 \times 0.17 \times 0.11$
θ range for data collection/ $^\circ$	2.30 to 25.02
limiting indices	$-16 \leq h \leq 15$, $-26 \leq k \leq 30$, $-15 \leq l \leq 10$
reflections collected/unique	20604/7234 [$R_{\text{int}} = 0.0939$]
completeness to $\theta = 25.02^\circ$	99.9%
max. and min. transmission	0.8450 and 0.6478
data/restraints/parameters	7234/0/481
goodness-of-fit on F^2	1.056
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0785$, $wR_2 = 0.1719$
R indices (all data)	$R_1 = 0.1497$, $wR_2 = 0.1931$
largest diff. peak and hole/ $(e\cdot\text{nm}^{-3})$	1521 and -1540

Europium salt (0.2 mmol) was dissolved in measurable distilled water, and 4-methoxybenzoic acid (0.6 mmol) and terpyridine (0.2 mmol) were dissolved in measurable ethanol solvent (95%). The pH value of mixed ligands was adjusted around 5–7 with NaOH ($\text{mol}\cdot\text{L}^{-1}$) solution. Then the mixture of the two ligands solution was added dropwise into the $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ solution, stirred for about 7 h at room temperature, and then deposited for 12 h. Finally, the precipitates were obtained by filtration. Single crystal of complex was collected from the mother liquor after two weeks at room temperature. Elemental analyses for complex, calcd. (%): C 54.68, H 4.00, N 4.91, Eu 17.74; found (%): C 53.88, H 3.94, N 4.75, Eu 18.14.

3 Results and discussion

3.1 Infrared spectra

The absorption bands of 4-methoxybenzoic acid, 2,2':6',2''-terpyridine and complex $[\text{Eu}(\text{4-MOBA})_3(\text{terpy})(\text{H}_2\text{O})_2]$ are listed in Table 2. For the complex, the $\nu_{\text{as}(\text{COO}-)}$ vibration is identified as the strong band at 1535 cm^{-1} . The band assigned to the vibration of $\nu_{\text{s}(\text{COO}-)}$ is observed at 1414 cm^{-1} . The characteristic absorption peak at 1687 cm^{-1} of $\nu_{\text{C=O}}$ for 4-MOHA disappeared in the complex, and the band assigned to the vibration of $\nu_{(\text{Eu}-\text{O})}$ is ob-

Table 2 IR bands for free ligands and complex

Ligand/Complex	$\nu_{\text{C=N}}/\text{cm}^{-1}$	$\delta_{\text{C-H}}/\text{cm}^{-1}$	$\nu_{\text{C=O}}/\text{cm}^{-1}$	$\nu_{\text{as(COO)}}/\text{cm}^{-1}$	$\nu_{\text{s(COO)}}/\text{cm}^{-1}$	$\nu_{\text{Eu-O}}/\text{cm}^{-1}$
4-MOHBA			1687			
terpy	1581	833, 764				
complex	1606	858, 783		1535	1414	408

served at 408 cm^{-1} in the complex. These facts may indicate that the carboxylate groups are bonded to Eu^{3+} ions. The band in the free terpy at 1581 and $833\text{--}764\text{ cm}^{-1}$ assigned to $\nu_{\text{C=N}}$ and $\delta_{\text{C-H}}$, respectively. The band $\nu_{\text{C=N}}$ and $\delta_{\text{C-H}}$ in the IR spectra of complex is slightly shifted to higher frequency. The result suggests that the nitrogen atoms of terpy ligand also coordinate to the Eu^{3+} ion.

3.2 X-ray powder diffraction

The X-ray power diffraction of free ligands and complex are shown in Fig.1. Compared with two ligands, the relative intensity and diffraction angles of the main diffraction peaks for the complex are significantly different. There are some new diffraction peaks in the complex, while the diffraction peaks of the two ligands were disappeared in the complex. Therefore, the complex is a kind of new substance, instead of the mixture of two ligands and europium salt²².

Fig.1 X-ray power diffraction patterns of complex and free ligands
(a) complex, (b) terpy, (c) 4-MOHBA

3.3 Structural description of $[\text{Eu}(\text{4-MOBA})_3(\text{terpy}) \cdot (\text{H}_2\text{O})_2]$

The structure and coordination geometry of the complex are shown in Fig.2. Selected bond lengths for the complex are listed in Table 3. The complex crystallizes in monoclinic crystal system and $P2(1)/c$ space group. The crystal structure data of the complex reveal that the dinuclear unit consists of two Eu^{3+} ions, six 4-methoxybenzoic acid ligands, two terpy ligands and two coordinated water molecules. The asymmetry unit contains only half of the dinuclear unit, that is, the two Eu^{3+} ions are equivalent. Each Eu^{3+} ion is coordinated to a tridentate terpy, a bound water and three 4-methoxybenzoic acid ligands, which adopt different coordination modes: bidentate, monodentate, and bridging bidentate. As a result, the nine-coordinated Eu^{3+} ion center adopts a distorted monocapped square antiprismatic molecular geometry. Eu1-O bond distances for the bidentate 4-methoxybenzoic acid (O7 and O8) are $0.2515(7)$ and $0.2469(7)$ nm, respectively. The two Eu^{3+} ions are connected to form a binuclear molecular dimer *via* a bridging bidentate 4-methoxybenzoic acid (O4 and O5) with Eu1-O bond distances of $0.2308(8)$ nm to O4 and $0.2342(8)$ nm to O5. A monodentate 4-methoxybenzoic acid (O1) is also coordinated to the Eu^{3+} ion center and the Eu1-O1 bond distance

Table 3 Selected bond lengths for the complex

Bond	Length/nm	Bond	Length/nm
Eu1—O4	0.2308(8)	Eu1—O5#1	0.2342(8)
Eu1—O1	0.2393(8)	Eu1—O8	0.2469(7)
Eu1—O7	0.2515(7)	Eu1—O10	0.2517(7)
Eu1—N3	0.2598(10)	Eu1—N1	0.2606(11)
Eu1—N2	0.2638(8)

Fig.2 Crystal structure of complex (a), coordination geometry of Eu^{3+} ion (b)

Fig.3 Dinuclear units of complex formed 1D chain by offset face-to-face $\pi\cdots\pi$ weak stacking interactions

is 0.2393(8) nm, whereas the coordinated water molecule has a Eu1—O10 bond distance of 0.2517(7) nm. Completing the coordination sphere of the Eu^{3+} ion is a tridentate terpy molecule, which is bound through its three nitrogen atoms (N1, N2, N3) with an average Eu1—N bond distance of 0.2614 nm. The average distance of Eu1—O (O1, O4, O5, O6, O7) bond is 0.2405 nm, which is shorter than the distance of Eu1—N bond. It indicates that the terpy ligands loss much easier than 4-methoxybenzoic acid ligands.

What's more, the dinuclear units of the complex are assembled into 1D chain by two offset face-to-face $\pi\cdots\pi$ weak stacking interactions between terpyridine rings containing N2 and N1 on neighboring as shown in Fig.3. The distance of the terpyridine rings is 0.4194 nm.

3.4 Thermal decomposition processes of the complexes

The TG/DTG-DSC methods were used to describe thermal decomposition of synthesized complex in air as shown in the Fig.4. The thermal decomposition results are presented in Table 4. The gaseous products from TG experiments were also detected online and identified by using three-dimensional infrared spectra as shown in Fig.5. According to the TG-DTG curves of the complex, we can know that the complex has five decomposition steps. For the complex, the first decomposition step occurs in the temperature range of 353.15–387.15 K with a weight loss of 2.53% against calculated weight loss of 2.10% for two water molecules, which can be ascribed to the loss of two coordinated water molecules. On the DSC curve, endothermic peak is observed at about 372.45 K, which can prove the decomposition of two

Fig.4 TG-DTG and DSC curves of complex

water molecules. The second and third decomposition steps occur in the temperature range of 387.15–491.15 K and 491.15–645.15 K with a weight loss of 9.21% and 27.06%, respectively, against calculated weight loss of 27.47% for all terpy, corresponding to the loss of terpy and part of 4-methoxybenzoic acid ligands. The fourth and fifth decomposition steps take place in the temperature range of 645.15–715.15 K and 715.15–853.15 K with a weight loss of 20.71% and 20.90%, respectively. There is a weak exothermic peak (689.25 K) and a strong exothermic peak (733.05 K) on the DSC curve, corresponding to the degradation and oxidation of the remains of 4-methoxybenzoic acid ligands. As a result, the total weight loss is 80.41% against calculated weight value of 79.46%, indicating that the residue is Eu_2O_3 . From the three-dimensional infrared spectra of the complex as shown in Fig.5, there are two characteristics absorption process. The first step for the weak absorption peak (3852–3570, 1843–1795 cm^{-1}) mainly

Table 4 Thermal decomposition data for the complex

Complex	Temperature range/K	$T_p(\text{DTG})/\text{K}$	Mass loss rate/%		$T_p(\text{DSC})/\text{K}$	Probable expelled groups
			Found	Calcd		
[Eu(4-MOBA) ₃ (terpy)(H ₂ O)] ₂	353.15–387.15	371.05	2.53	2.1 ^a	372.45	2H ₂ O
	387.15–491.15	468.55	9.21	27.23 ^b	—	2terpy + part of 4-MOBA
	491.15–645.15	535.65	27.06	—	—	—
	645.15–715.15	703.65	20.71	50.13 ^c	689.25	remaining 4-MOBA-3O
	715.15–853.15	730.25	20.90	—	733.05	—

^atotal loss rate of 2H₂O; ^btotal loss rate of 2terpy; ^ctotal loss rate of (4-MOBA-3O); T_p : peak temperature.

Found means the data of experiment value, Calcd means the data of calculated value.

Fig.5 Stacked plot of the FTIR spectra of the evolved gases for the complex as observed in the online (TG/FTIR) system at the heating rate of $10\text{ K}\cdot\text{min}^{-1}$

Fig.6 FTIR spectra of the evolved gases for the complex at 385.15 and 726.15 K

attributed to the coordination water decomposition as shown in Fig.6 at 385.15 K. From the FTIR spectra at 726.15 K, the strong absorption bands of CO_2 ($2360\text{--}2344$, 667 cm^{-1}) are observed. In addition, there are some small molecular absorption, such as H_2O ($3899\text{--}3575$, $1850\text{--}1710\text{ cm}^{-1}$), $\nu_{\text{C=O}}$ ($1846\text{--}1650\text{ cm}^{-1}$) alkanes ($1508\text{--}1343\text{ cm}^{-1}$) and alkenes ($1690\text{--}1640\text{ cm}^{-1}$), indicating that the aromatic rings of the 4-methoxybenzoic acid ligands may be broken, which is consistent with the analysis of TG.

3.5 Photoluminescence investigation

The luminescent properties of complex $[\text{Eu}(\text{4-MOBA})_3(\text{terpy})\cdot$

Fig.7 Emission spectra of the complex

$(\text{H}_2\text{O})_2$ have been investigated at room temperature. The emission spectra of the complex is shown in Fig.7, and the excitation wavelength is 394 nm. The emission spectrum shows peaks at 580, 595, 618, 651, and 695 nm, which originated from $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions of Eu^{3+} , respectively. The $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} corresponding to hypersensitive transition has a high intensity, indicates that the Eu^{3+} is located at a low-symmetry local site without an inversion center^{23,24}. The complex exhibits strong emission bands of Eu^{3+} ion. It indicates that the energy-transfer from the ligands to the Eu^{3+} by intersystem crossing is efficient, which is probably attributed to the matching of energy levels between excited states of ligands and excited states of Eu^{3+} ²⁵. Moreover, it proves that 4-MOBA and terpy are good chromophore to absorb energy and transfer to Eu^{3+} ions, emitting the characteristic fluorescence of Eu^{3+} ion.

3.6 Bacteriostatic activities

The bacteriostatic activities of complex and ligands to *Candida albicans* (fungus) and *Escherichia coli* (bacteria) were determined with three different concentrations at 303.15 K. The bacteriostatic activities data were presented by the diameter of bacteriostatic ring as shown in Table 5. The results show that the complex has good bacteriostatic action to *Candida albicans* and *Escherichia coli*. What's more, the bacteriostatic activities of the complex enhanced with the increase of the concentration in the range of tested concentrations. The bacteriostatic mechanism is presumably that the complex has a good lipophilic nature arising from chelation²⁶.

Table 5 Bacteriostatic activities of ligands and complex with three different concentrations at 303.15 K

Ligand/Complex		Diameter of bacteriostatic ring for three times in parallel/mm								
		8 mmol·L ⁻¹			16 mmol·L ⁻¹			32 mmol·L ⁻¹		
		I	II	III	I	II	III	I	II	III
<i>Candida albicans</i>	4-MOBA	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	terpy	6.0	6.0	6.0	10.3	12.6	9.5	20.1	19.0	18.6
	$\text{EuCl}_3\cdot 6\text{H}_2\text{O}$	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	complex	13.3	15.1	14.4	17.6	21.1	22.4	26.6	29.4	28.1
<i>Escherichia coli</i>	4-MOBA	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	terpy	6.0	6.0	6.0	7.5	8.0	8.0	14.6	14.5	14.6
	$\text{EuCl}_3\cdot 6\text{H}_2\text{O}$	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	complex	6.2	6.8	7.3	11.6	12.1	12.9	15.9	15.4	16.7

The filter diameter was 6.0 mm.

4 Conclusions

In summary, we synthesized a new europium complex with ligands 4-methoxybenzoic acid and 2,2':6',2''-terpyridine, which was confirmed by elemental analysis, FTIR and XRD. The complex crystallizes in monoclinic crystal system and $P2(1)/c$ space group. Each Eu^{3+} ion is coordinated to a tridentate terpy, a bound water molecule and three 4-methoxybenzoic acid ligands adopting three coordination modes: bidentate, monodentate, and bridging bidentate. As a result, the nine-coordinated Eu^{3+} ion center adopts a distorted monocapped square antiprismatic molecular geometry. Thermal decomposition process of the complex was discussed by TG-DSC/FTIR technology and IR spectra of the evolved gases show complex broken down into H_2O , CO_2 and other gaseous molecules as well as the gaseous organic fragments. What's more, the europium complex had good fluorescence properties due to the antenna effect of ligands and had good bacteriostatic action to *Candida albicans* and *Escherichia coli*. Therefore, the complex $[\text{Eu}(\text{4-MOBA})_3(\text{terpy})(\text{H}_2\text{O})_2]$ can be used at optical material and biological fields.

Supplementary data: Crystallographic data for the structure reported in this paper are deposited in the Cambridge Crystallographic Data Center with CCDD reference number 1409015 for the complex.

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