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3-((4,6-二甲基-2-嘧啶基)硫代)-丙酸和菲咯啉三元稀土配合物的晶体结构和发光性能

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摘要: 制备了以3-((4,6-二甲基-2-嘧啶基)硫代)-丙酸(HL)和菲咯啉(Phen)为配体的2个三元稀土配合物$[Eu(L)_3(Phen)]_2\cdot 2H_2O$ (**1**)和$[Tb(L)_3(Phen)]_2\cdot 2H_2O$ (**2**),并对其结构进行了表征。单晶X射线衍射分析表明它们是同构的。2个稀土离子(Ln)由4个羧酸配体桥接,形成二聚体排列。其余2个羧酸配体和Phen以双齿螯合方式与Ln配位。Ln的配位数为9,具有扭曲的单端方形反棱柱配位多面体构型。固态光致发光测试表明,这2种配合物都显示了金属中心的特征发射带。

关键词: 菲咯啉;3-((4,6-二甲基-2-嘧啶基)硫代)-丙酸;稀土配合物;单晶结构;光致发光
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Ternary lanthanide complexes of 3-((4,6-dimethyl-2-pyrimidinyl)thio)-propanoic acid and 1,10-phenanthroline: Crystal structure and photoluminescent property

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Abstract: Two ternary lanthanide complexes, $[Eu(L)_3(Phen)]_2\cdot 2H_2O$ (**1**) and $[Tb(L)_3(Phen)]_2\cdot 2H_2O$ (**2**), based on 3-((4,6-dimethyl-2-pyrimidinyl)thio)-propanoic acid (HL) and 1,10-phenanthroline (Phen) were prepared and structurally characterized. Single-crystal X-ray diffraction analyses reveal that they are isostructural. Two lanthanide ions (Ln) are bridged by four carboxylate ligands. The rest two carboxylate ligands and Phen coordinate with Ln with bidentate chelating mode, forming the dimeric arrangement. The coordination number of Ln is nine with a distorted mono-capped square antiprismatic coordination polyhedron. The solid-state photoluminescent measurements suggest that both complexes showcase the characteristic emission bands of the metal center. CCDC: 2129656, **1**; 2129657, **2**.

Keywords: 1,10-phenanthroline; 3-((4,6-dimethyl-2-pyrimidinyl)thio)-propanoic acid; lanthanide complex; crystal structure; photoluminescent

Due to the forbidden nature of the 4*f* transitions and the lower molar absorption coefficients, lanthanide ions show very weak luminescence. Thus, the "antenna" ligand is mandatory. The triplet energy level of the antenna should meet the energy level of the lanthanide ion[1-2]. Among the wide range of antenna ligands, carboxylate and 1,10-phenanthroline (Phen) are proven to be the widely accepted antenna. Some ternary rare

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earth complexes based on carboxylate and Phen have been established. Here gives some carboxylate ligands: *N*-((benzoylamino)thioxomethyl)glycine, *N*-(*p*-acetamidobenzenesulfonyl)glycine, malic acid, mandelic acid, *N*-((4-methylphenyl)sulfonyl)glycine, *L*-proline, 2,4-dinitro-benzoic acid, and α-naphthyl acetic acid[3-14]. Furthermore, the biological activity of some rare earth complexes based on 2-((4,6-dimethyl-2-pyrimidinyl) thio)-acetic acid has been reported[15-16].

In this work, considering the potential antenna property of carboxylate and Phen, the 3-((4,6-dimethyl-2-pyrimidinyl)thio)-propanoic acid (HL), as well as Phen, were introduced to react with lanthanide (Eu, Tb) ions giving the corresponding ternary lanthanide complexes. Meanwhile, we proved the prepared products are two isostructural lanthanide complexes. Importantly, some unique solid-state photoluminescent properties were found in this system.

1 Experimental

1.1 Material and methods

HL was prepared following the published literature[16]. All other chemicals were analytically pure from commercial sources and used without further purification. Elemental analyses on C, H, S, and N were performed on a German Elementary Vario EL Ⅲ instrument. The IR spectra were recorded on KBr disks using a Nicolet-Avatar 370 spectrometer between 400 and 4 000 cm^{-1}. Thermogravimetric (TG) analyses were carried out on a NETZSCH STA 449 C unit at a heating rate of 10 ℃·min^{-1}. Photoluminescence studies were performed on an Edinburgh FLS920 fluorescent spectrometer in a solid state.

1.2 Syntheses of complexes 1 and 2

A mixture of HL (0.641 g, 3.0 mmol) and Phen (0.198 g, 1.0 mmol) was dissolved in 50 mL ethanol. Then, the lanthanide nitrate hexahydrate (1.0 mmol) was added to the mixture. $NH_3 \cdot H_2O$ was added dropwise until the pH value was 6.5. The mixture was kept stirring overnight at room temperature. A large amount of white precipitate was formed. After filtration and washing with water and ethanol, the white solid was obtained. Single crystals suitable for single-crystal X-ray diffraction were obtained from the filtrate after *ca*. 8 d.

Complex $[Eu(L)_3(Phen)]_2 \cdot 2H_2O$ (**1**): white solid, Yield: 0.104 g, 54%. IR (ATR, cm^{-1}): 3 442(m), 2 924(w), 1 608(vs), 1 582(vs), 1 557(s), 1 478(w), 1 423(s), 1 393(s), 1 340(w), 1 269(s), 1 225(m), 1 176(w), 1 013(w), 883(w), 764(m), 710(w), 545(w). Anal. Calcd. for $C_{39}H_{43}EuN_8O_7S_3$(%): C, 47.61; H, 4.41; N, 11.39; S, 9.77. Found(%): C, 48.09; H, 4.48; N, 11.98; S, 10.39.

Complex $[Tb(L)_3(Phen)]_2 \cdot 2H_2O$ (**2**): white solid, 0.114 g, 59%. IR (ATR, cm^{-1}): 3 422(w), 3 050(w), 2 923(w), 1 604(vs), 1 580(vs), 1 551(s), 1 425(vs), 1 339(m), 1 304(m), 1 264(vs), 1 208(m), 1 139(m), 1 102(m), 1 004(w), 948(w), 845(m), 730(m), 690(m), 545(w). Anal. Calcd. for $C_{39}H_{43}N_8O_7S_3Tb$(%): C, 47.27; H, 4.37; N, 11.31; S, 9.71. Found(%): C, 47.39; H, 4.61; N, 11.96; S, 10.00.

1.3 X-ray crystallography

A suitable crystal was covered in mineral oil and mounted on a glass fiber and directly transferred to a Brucker D8 advance diffractometer equipped with a sealed Mo tube and a graphite monochromator using Mo *Kα* radiation (λ =0.071 073 nm). All structures were solved by the direct methods using SHELXS[17-18] and refined on F^2 with SHELXL and Olex2[19]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were determined with theoretical calculations. Multi-scan absorption correction was applied to the intensity data using the SADABS program[20]. SQUEEZE routine in PLATON was employed to remove the corresponding Q peaks, which may be identified as two water molecules[16,21].

The crystal data and structure refinement parameters for the complexes are summarized in Table 1. Images of the crystal structures were generated by Diamond, version 3.2 (software copyright, Crystal Impact GbR).

CCDC: 2129656, **1**; 2129657, **2**.

2 Results and discussion

2.1 Crystal structure

Complexes **1** and **2** are isostructural with monoclinic space group *C*2/*c* (Table 1). Selected bond

Table 1　Crystallographic data of complexes 1 and 2

Parameter	1	2
Empirical formula	$C_{78}H_{86}Eu_2N_{16}O_{14}S_6$	$C_{78}H_{86}N_{16}O_{14}S_6Tb_2$
Formula weight	1 967.93	1 981.85
Temperature / K	273.15	273.15
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a / nm	2.901 7(5)	2.900 61(11)
b / nm	1.269 8(3)	1.261 20(5)
c / nm	2.937 5(8)	2.935 21(16)
β / (°)	117.590(5)	117.507 0(10)
Volume / nm^3	9.592(4)	9.523 9(7)
Z	4	4
μ / mm^{-1}	1.486	1.665
F(000)	3 920.0	3 936.0
Crystal size / mm	0.497×0.129×0.07	0.499×0.078×0.053
2θ range for data collection / (°)	2.810-28.588	2.872-28.621
Index ranges	$-37 \leqslant h \leqslant 37, -16 \leqslant k \leqslant 16, -38 \leqslant l \leqslant 38$	$-37 \leqslant h \leqslant 37, -16 \leqslant k \leqslant 16, -38 \leqslant l \leqslant 38$
Reflection collected	74 688	73 978
Independent reflection	11 070 (R_{int}=0.133 8)	11 012 (R_{int}=0.117 9)
Data, restraint, parameter	11 071, 0, 520	11 012, 0, 520
Goodness-of-fit on F^2	1.038	1.018
Final *R* indexes [$I \geqslant 2\sigma(I)$]	R_1=0.065 1, wR_2=0.121 5	R_1=0.060 5, wR_2=0.110 9
Final *R* indexes (all data)	R_1=0.138 7, wR_2=0.141 7	R_1=0.124 1, wR_2=0.127 6
Largest diff. peak and hole / ($e \cdot nm^{-3}$)	1 460, −785	1 153, −677

lengths and bond angles are listed in Table 2 and Table 3, respectively. Both complexes feature the dimeric arrangement (Fig. 1). Two metal centers are bridged by four carboxylate ligands with Eu…Eu separation of 0.391 57(8) nm and Tb…Tb separation of 0.387 68(4) nm. The metal center is nine-coordinated with one Phen molecule (chelating η^2 mode) and three L^- ions, in which three coordination modes can be confirmed: μ_3:η^2-η^1, μ_2:η^1-η^1, and η^2. Thus, the coordination polyhedron of Ln is a distorted mono-capped square antiprism, which can be widely observed in the published lanthanide complexes. The Eu—O bond lengths ranging from 0.236 0(3) to 0.254 5(3) nm and Tb—O bond lengths ranging from 0.232 4(3) to 0.251 9(3) nm agree with the reported single bond values in the carboxylate lanthanide complexes[22-24]. As

Table 2　Selected bond lengths of complexes 1 and 2

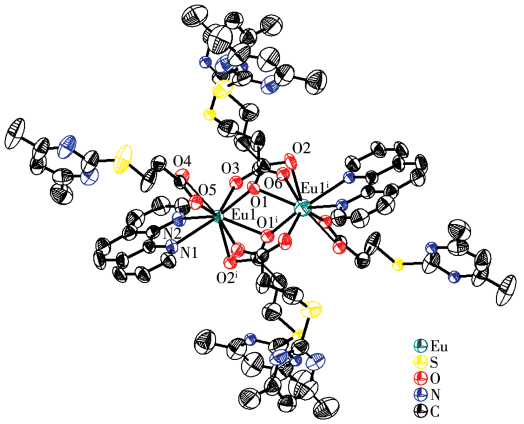
1					
Eu1…Eu1^{i}	0.394 61(8)	Eu1—O4	0.252 5(4)	Eu1—O2	0.235 4(4)
Eu1—O3	0.248 1(4)	Eu1—O1^{i}	0.260 3(4)	Eu1—O5^{i}	0.259 5(4)
Eu1—N1	0.258 7(5)	Eu1—N2	0.257 2(5)	Eu1—O1	0.235 0(4)
Eu1—O6^{i}	0.234 9(4)				
2					
Tb1…Tb1^{i}	0.390 88(5)	Tb1—O4	0.246 5(3)	Tb1—O2	0.230 7(3)
Tb1—O3^{i}	0.231 9(3)	Tb1—O1	0.231 4(3)	Tb1—O5^{i}	0.257 3(4)
Tb1—N1	0.255 2(5)	Tb1—N2	0.255 9(4)	Tb1—O1^{i}	0.258 0(3)
Tb1—O6	0.249 2(4)				

Symmetry codes: ^{i} 1/2−*x*, 1/2−*y*, 1−*z* for **1**; ^{i} 1/2−*x*, 1/2−*y*, 1−*z* for **2**.

Table 3 Selected bond angles of complexes 1 and 2

1					
O1—Eu1—Eu1^{i}	39.47(9)	O5^{i}—Eu1—N1	72.31(13)	O3—Eu1—Eu1^{i}	123.37(9)
O1^{i}—Eu1—Eu1^{i}	35.02(8)	O5^{i}—Eu1—N2	79.59(12)	O3—Eu1—O1^{i}	155.69(15)
O1—Eu1—O1^{i}	74.49(13)	O6^{i}—Eu1—Eu1^{i}	68.32(8)	O3—Eu1—O4	52.80(11)
O1—Eu1—O3	88.35(13)	O6^{i}—Eu1—O1^{i}	72.28(11)	O3—Eu1—O5^{i}	145.18(12)
O1—Eu1—O4	74.37(11)	O6^{i}—Eu1—O3	83.13(12)	O3—Eu1—N1	73.42(13)
O1^{i}—Eu1—O5^{i}	50.96(11)	O6^{i}—Eu1—O4	124.92(11)	O3—Eu1—N2	79.42(12)
O1—Eu1—O5^{i}	124.15(11)	O6^{i}—Eu1—O5^{i}	95.11(12)	O4—Eu1—Eu1^{i}	109.34(9)
O1—Eu1—O6^{i}	73.41(12)	O6^{i}—Eu1—N1	77.12(13)	O4—Eu1—O1^{i}	137.35(12)
O1—Eu1—N1	146.76(15)	O6^{i}—Eu1—N2	139.16(13)	O4—Eu1—O5^{i}	139.97(12)
O1^{i}—Eu1—N1	110.46(12)	N1—Eu1—Eu1^{i}	138.00(11)	O4—Eu1—N1	110.10(14)
O1—Eu1—N2	142.93(12)	N2—Eu1—Eu1^{i}	149.55(11)	O4—Eu1—N2	70.05(14)
O1^{i}—Eu1—N2	126.72(12)	N2—Eu1—N1	61.08(16)	O5^{i}—Eu1—Eu1^{i}	85.99(8)
O2—Eu1—Eu1^{i}	69.87(9)	O2—Eu1—O4	74.36(11)	O2—Eu1—N2	80.65(13)
O2—Eu1—O1^{i}	67.72(13)	O2—Eu1—O5^{i}	75.85(12)	O2—Eu1—N1	133.75(15)
O2—Eu1—O1	79.39(14)	O2—Eu1—O6^{i}	136.43(13)	O2—Eu1—O3	128.86(13)
2					
O1—Tb1—Tb1^{i}	39.41(9)	O5^{i}—Tb1—Tb1^{i}	84.29(8)	O2—Tb1—O5^{i}	72.57(14)
O1^{i}—Tb1—Tb1^{i}	34.70 (1)	O5^{i}—Tb1—N1	79.65(14)	O2—Tb1—O6	129.40(13)
O1—Tb1—O1^{i}	74.11(13)	O5^{i}—Tb1—N2	72.58 (14)	O2—Tb1—N1	81.13(13)
O1—Tb1—O2	78.15(13)	O6—Tb1—Tb1^{i}	124.55(8)	O2—Tb1—N2	133.64(15)
O1—Tb1—O3^{i}	74.91(13)	O6—Tb1—O1^{i}	152.44(11)	O3^{i}—Tb1—Tb1^{i}	68.35(9)
O1—Tb1—O4	74.15(14)	O6—Tb1—O4	53.22(11)	O3^{i}—Tb1—O1^{i}	73.69(12)
O1—Tb1—O5^{i}	123.31(12)	O6—Tb1—O5^{i}	144.61(11)	O3^{i}—Tb1—O4	122.23(13)
O1^{i}—Tb1—O5^{i}	51.32(13)	O6—Tb1—N1	79.56(13)	O3^{i}—Tb1—O5^{i}	97.21(14)
O1—Tb1—O6	88.71(13)	O6—Tb1—N2	72.98(14)	O3^{i}—Tb1—O6	81.89(13)
O1—Tb1—N1	142.76(13)	N1—Tb1—Tb1^{i}	149.39(9)	O3^{i}—Tb1—N1	139.36(14)
O1i—Tb1—N1	146.82(13)	N1—Tb1—N2	61.67(15)	O3^{i}—Tb1—N2	78.34(15)
O1—Tb1—N2	147.27(12)	N2—Tb1—Tb1^{i}	137.48(11)	O4—Tb1—Tb1^{i}	109.37(9)
O1^{i}—Tb1—N2	111.48(13)	O2—Tb1—O4	73.52(11)	O4—Tb1—O1^{i}	137.39(12)
O2—Tb1—Tb1^{i}	69.11(9)	O4—Tb1—N2	110.52(14)	O4—Tb1—O5^{i}	140.56(13)
O2—Tb1—O1^{i}	67.97(12)	O2—Tb1—O3^{i}	137.39(12)	O4—Tb1—N1	70.20(13)

Symmetry codes: ^{i} 1/2−x, 1/2−y, 1−z for **1**; ^{i} 1/2−x, 1/2−y, 1−z for **2**.



Hydrogen atoms and solvents are omitted for clarity; Symmetry code: ^{i} 1/2−x, 1/2−y, 1−z

Fig.1 Drawing of the molecular structure of dinuclear Eu complex **1** with an ellipsoid probability of 50%

is apparent, the O—C—O bond angle of μ_2:η^1-η^1 mode (126.3(5)°) is larger than those of μ_3: η^2 - η^1 mode (120.6(5)°) and η^2 mode (121.8(5)°). It should be noted that the molecular structures of complexes **1** and **2** are highly consistent with the published complexes $[RE(L)_3(Phen)]_2 \cdot nH_2O$ (RE=Nd, Sm, and Y; for Sm and Nd: n=2; for Y: n=0)[16].

2.2 TG analysis

The TG properties of complexes **1** and **2** were measured from 25 to 1 000 ℃ (Fig.2). They showcase almost identical TG curves. Thus, only complex **1** will be discussed in detail here. A slight weight loss can be observed before 225 ℃, which may indicate the removal of two water molecules (Obsd. 1.3%; Calcd. 1.8%) in the sample. These results agree with the single crystal X-ray diffraction analyses and the published isostructural complexes $[RE(L)_3(Phen)]_2 \cdot 2H_2O$ (RE=Nd, Sm)[16]. Further weight loss can be observed at around 1 000 ℃.

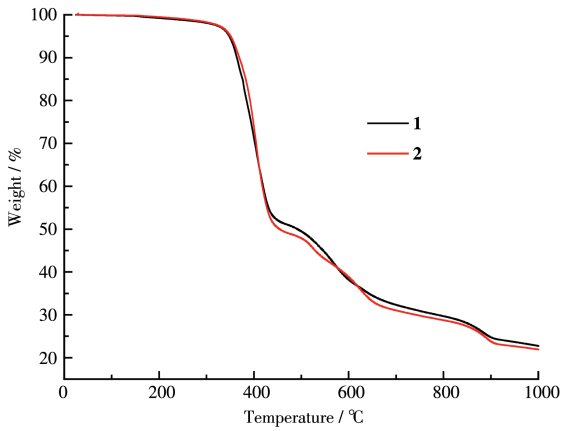


Fig.2　TG curves of complexes **1** and **2**

2.3 Photoluminescent property

The solid-state photoluminescent property of complexes **1** and **2** was measured and the emission spectra are shown in Fig.3. After excited at 347 nm, three emission bands could be confirmed in the emission spectra of complex **1**: 593 and 595 nm ($^5D_0 \rightarrow {}^7F_1$ transition); 616, 619, and 621 nm ($^5D_0 \rightarrow {}^7F_2$ transition); 689, 694, and 699 nm ($^5D_0 \rightarrow {}^7F_4$ transition). The most intense bands at 616, 619, and 621 nm corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition. The intensity ratio between $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition indicates that the Eu is not located on the centrosymmetric site in the solid state, which agrees with the single crystal diffraction analysis. The luminescent lifetime for complex **1** was 1.5 ms. The quantum yield was 87.3%. Due to the isostructural feature, the emission pattern of complex **2** was excited at 347 nm as well. Four characteristic emission bands were observed. Three weak bands at 490 nm ($^5D_4 \rightarrow {}^7F_6$ transition), 584 nm ($^5D_4 \rightarrow {}^7F_4$ transition), and 622 nm ($^5D_4 \rightarrow {}^7F_3$ transition) could be observed. The most intense band at 545 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition. The luminescent lifetime of complex **2** (1.3 ms) was almost identical to complex **1**. However, the quantum yield (60.4%) was lower than complex **1**.

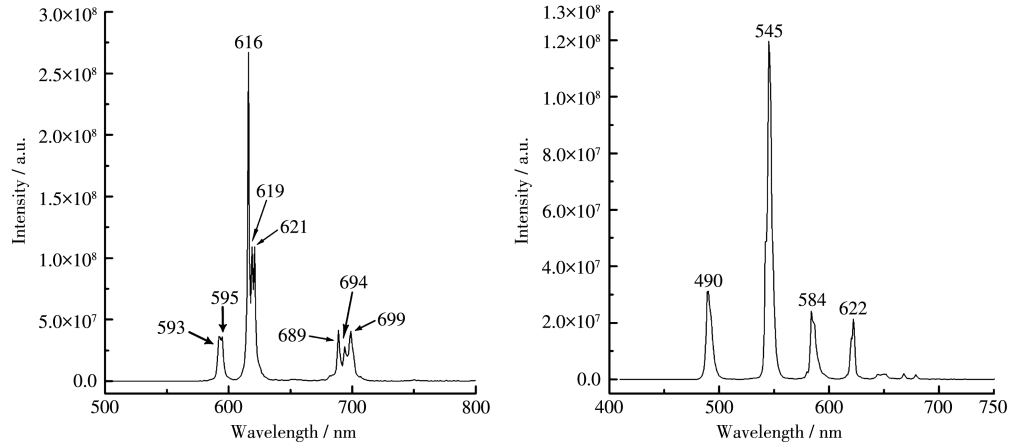


Fig.3　Solid-state emission spectra of complexes **1** (left) and **2** (right) at room temperature

3 Conclusions

Two ternary lanthanide complexes of 3-((4,6-dimethyl-2-pyrimidinyl)thio)-propanoic acid (HL) and Phen, $[Ln(L)_3(Phen)]_2 \cdot 2H_2O$ (Ln=Eu (**1**), Tb (**2**)), were prepared and the molecular structures were established

by single crystal X-ray diffraction analysis. Both complexes feature a dimeric arrangement, in which two lanthanide metal ions are bridged by four carboxylate ligands. Solid-state photoluminescent measurement reveals that complexes **1** and **2** manifest the characteristic emission bands of the metal center. Complex **1** possessed a high quantum yield of 87.3%.

Conflicts of interest: There are no conflicts to declare.

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