

稀土配位聚合物[M(tddc)(NO₃)(H₂O)₄]·2H₂O(M=Eu, Dy) 的合成、结构和性质

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摘要: 本文用水热法合成了 2 个稀土配位聚合物[M(tddc)(NO₃)(H₂O)₄]·2H₂O[M=Eu (**1**), M=Dy (**2**)], 并对它们进行了元素分析、红外光谱、热重等分析, 研究了它们的荧光性质, 并用 X-射线单晶衍射测定了配合物的单晶结构。两者的晶系都属于三斜晶系, *P* $\bar{1}$ 空间群。荧光实验表明配合物 **1** 在常温下具有很强的荧光。

关键词: 晶体结构; 稀土配位聚合物; 网状结构; 荧光

中图分类号: O614.33^{*}8; O614.342

文献标识码: A

文章编号: 1001-4861(2009)06-0962-06

Synthesis, Crystal Structures and Properties of Lanthanide Complexes [M(tddc)(NO₃)(H₂O)₄]·2H₂O (M=Eu, Dy)

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Abstract: Two lanthanide complexes [M(tddc)(NO₃)(H₂O)₄]·2H₂O [M=Eu (**1**), M=Dy (**2**)], where tddc²⁻=2,3-Dihydrothieno [3,4-b][1,4] dioxine-5,7-dicarboxylic acid anion, have been synthesized and characterized by elemental analysis, IR spectra, thermal analyses, powder X-ray diffraction and single-crystal X-ray analysis. Both the crystals belong to triclinic, space group *P* $\bar{1}$. For complex **1**: *a*=0.802 28(19) nm, *b*=0.985 3(2) nm, *c*=1.147 6(3) nm, α =67.107(3)°, β =89.694(4)°, γ =80.428(4)°, *V*=0.822 3(3) nm³, *Z*=2, *M_r*=550.24, *D_c*=2.222 g·cm⁻³, *F*(000)=540, the final *R*=0.039 4 and *wR*=0.094 7 for observed reflections 3 639 with *I*>2σ(*I*). For complex **2**: *a*=0.798 71(10) nm, *b*=0.983 76(13) nm, *c*=1.143 93(15) nm, α =67.108 0(10)°, β =89.823(3)°, γ =80.283(2)°, *V*=0.814 22(18) nm³, *Z*=2, *M_r*=560.24, *D_c*=2.291 g·cm⁻³, *F*(000)=536, the final *R*=0.043 6 and *wR*=0.114 0 for observed reflections 2 182 with *I*>2σ(*I*). The single crystal structures show that the two complexes are isomorphic and have one-dimensional chains structures and hydrogen bonds result in three-dimensional supramolecular structures. The complex **1** shows intense luminescence in the solid state at room temperature. CCDC: 698267, **1**; 698268, **2**.

Key words: crystal structure; lanthanide complex; network structure; luminescence

收稿日期: 2009-03-19。收修改稿日期: 2009-04-21。

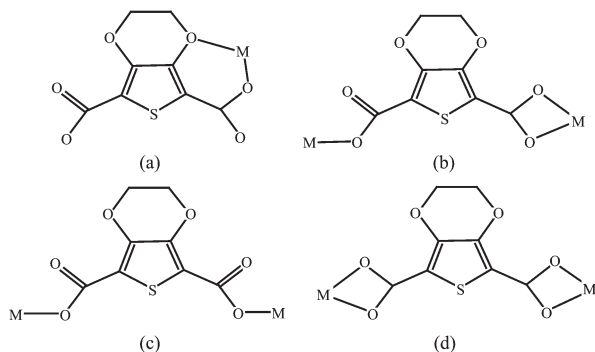
国家自然科学基金(No.20571039, 20721002)和安徽省教育厅自然科学基金项目(No.KJ2007B013)资助。

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Recently, the employment of lanthanide metal ions and bridging carboxylates ligands has become a dominant theme in the construction of some interesting arrays^[1-3]. These rare earth polymers are of great interest not only due to their intriguing topologies but also the potential applications in catalysis, optical materials, molecule-based magnets, biochemical or medical application, etc^[4-7].

It is reported that 2,3-dihydro-thieno [3,4-b][1,4]dioxine-5,7-dicarboxylic acid (H₂tddc) ligand as a building block can bridge the metal centers using the carboxylate oxygen atoms, or both the carboxylate and oxygen atoms in the 1,4-dioxane, and diversified coordination modes come forth when the tddc ligand assumes as mono-dentate, bi-dentate, tri-dentate or tetra-dentate coordination mode^[8] (see Scheme 1). In order to explore this field, we synthesis two new complexes: [Eu(tddc)(NO₃)(H₂O)₄]·2H₂O (**1**) and [Dy(tddc)(NO₃)(H₂O)₄]·2H₂O (**2**) with the tddc ligand acting as a tri-dentate ligand by using hydrothermal synthesis, which were characterized by elemental analysis, thermal analyses, powder X-ray diffraction, single-crystal X-ray analysis and spectroscopic analysis (IR and the fluorescence).



Scheme 1 Diversified coordination modes of the tddc²⁻ ligand

1 Experimental

1.1 General information and materials

All starting chemicals and solvents used in this synthesis were of reagent quality and purchased from commercial sources without further purification. IR spectra were recorded on a Fourier Nicolet FT-10SX spectrophotometer with pressed KBr pellets. Carbon and hydrogen analyses were performed on a PE-240C

Elemental Analyzer. The emission spectra were recorded on an America SLM 48000DSCF spectrometer. The TG analyses were performed on Perkin Elmer Pyris 1 TGA Thermogravimetric Analyzer heat from 25 ~750 °C at 20.00 °C·min⁻¹. The X-ray powder diffraction (XRD) patterns of the compounds were collected on a Phillips X-pert X-ray powder diffractometer at room temperature.

1.2 Synthesis

H₂tddc (0.230 g, 0.1 mmol) was dissolved in distilled water (*ca.* 7.5 mL) at ambient temperature, followed by the addition, with stirring, of NaOH solution (1 mol·L⁻¹) until pH=7. Then 1 mL C₂H₅OH and Eu(NO₃)₃·6H₂O (0.892 g, 0.2 mmol) or Dy(NO₃)₃·6H₂O (0.912 g, 0.2 mmol) were added to the solution in order. The final mixture was transferred to a Parr Teflonlined reaction vessel (*ca.* 25 mL) and placed inside a preheated oven at 373 K for 3 days, respectively. After the reaction, the vessel was allowed to cool slowly to room temperature, light-yellow needlelike crystals for **1** and colorless needlelike crystals for **2** were yielded. Yield is 35 mg (63%) and 33 mg (59%) respectively. Anal. Calcd. for C₈H₁₆EuNO₁₅S (**1**)(%): C, 17.46; H, 2.93; N, 2.55. Found(%): C, 17.50; H, 2.89; N, 2.50. IR (KBr disc/cm⁻¹): 3 443s, 1 594m, 1 523m, 1 465w, 1 440 m, 1 385s, 1 357vs, 1 250w, 1 202w, 1 093s, 982w, 853 m, 796m, 738w, 459w. Anal. Calcd. for C₈H₁₆DyNO₁₅S (**2**)(%): C, 17.51; H, 2.94; N, 2.55. Found(%): C, 17.59; H, 2.86; N, 2.51. IR (KBr disc/cm⁻¹): 3 444m, 1 596m, 1 525m, 1 466w, 1 442m, 1 385m, 1 357s, 1 250m, 1 092 s, 983w, 854m, 796m, 731w, 460w.

1.3 X-ray crystal structure determination

Data collection was performed on a Bruker Smart Apex CCD diffractometer by using graphite-monochromatized Mo K α radiation ($\lambda=0.071\ 073$ nm) at room temperature. Data reduction was performed by using the SAINT version 6.02 software^[9]. The data were corrected for absorption by using the program SADBAS within the SAINTPLUS package. The structures were solved by direct methods and refined with the SHELXTL program^[10]. Refinement of the structures was done by full-matrix least-squares methods based on F^2 . The hydrogen atom positions were fixed geometrically

and allowed to ride on the parent atoms. The selected bond lengths and angles are listed in Table 2. relevant crystallographic data are listed in Table 1, the CCDC: 698267, 1; 698268, 2.

Table 1 Crystal data collection and structure refinement details for the complexes 1 and 2

Empirical formula	C ₈ H ₁₆ NO ₁₅ SEu (1)	C ₈ H ₁₆ NO ₁₅ SDy (2)
Formula weight	550.24	560.24
<i>T</i> / K	293(2)	293(2)
λ (Mo <i>K</i> α) / nm	0.071 073	0.071 073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / nm	0.802 28(19)	0.798 71(10)
<i>b</i> / nm	0.985 3(2)	0.983 76(13)
<i>c</i> / nm	1.147 6(3)	1.143 93(15)
α / (°)	67.107(3)	67.108(2)
β / (°)	89.694(4)	89.823(2)
γ / (°)	80.428(4)	80.283(2)
<i>V</i> / nm ³	0.822 3(3)	0.814 22(18)
<i>Z</i>	2	2
<i>D_c</i> / (g·cm ⁻³)	2.222	2.291
μ / mm ⁻¹	4.023	4.801
<i>F</i> (000)	540	536
Reflns. collected	4 953	4 330
Unique reflns. (<i>R</i> _{int})	3 639 (0.027 1)	3 109 (0.025 1)
Observed reflections [<i>I</i> >2 σ (<i>I</i>)]	2 671	2 685
Parameters refined	235	235
Goodness-of-fit on <i>F</i> ²	1.015	1.088
Final <i>R</i> indices <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.039 4, 0.094 7	0.040 9, 0.105 1

Table 2 Selected bond lengths (nm) and angles (°) in complexes 1 and 2

Complex 1					
Eu(1)-O(5)	0.227 2(5)	Eu(1)-O(12)	0.241 0(6)	O(7)-C(8)	0.124 2(10)
Eu(1)-O(7)	0.242 7(6)	Eu(1)-O(13)	0.244 7(6)	O(8)-C(8)	0.127 0(9)
Eu(1)-O(8)	0.247 2(6)	Eu(1)-O(14)	0.239 2(6)	O(9)-N(1)	0.127 5(9)
Eu(1)-O(9)	0.265 0(6)	Eu(1)-O(15)	0.240 4(6)	O(10)-N(1)	0.126 0(9)
Eu(1)-O(10)	0.245 6(6)	O(5)-C(7)	0.127 8(9)	O(4)-C(8)	0.126 0(9)
O(5)-Eu(1)-O(7)	86.28(19)	O(9)-Eu(1)-O(15)	77.3(2)	O(13)-Eu(1)-O(14)	139.5(2)
O(5)-Eu(1)-O(8)	131.96(18)	O(5)-Eu(1)-O(9)	69.77(18)	O(13)-Eu(1)-O(15)	143.1(2)
O(10)-Eu(1)-O(12)	76.4(2)	O(5)-Eu(1)-O(10)	86.37(19)	O(7)-Eu(1)-O(14)	128.1(2)
O(10)-Eu(1)-O(13)	71.65(19)	O(5)-Eu(1)-O(12)	145.5(2)	O(7)-Eu(1)-O(15)	82.6(2)
O(10)-Eu(1)-O(14)	79.6(2)	O(10)-Eu(1)-O(15)	127.0(2)	O(7)-Eu(1)-O(12)	91.6(2)
O(5)-Eu(1)-O(13)	74.6(2)	O(5)-Eu(1)-O(15)	75.4(2)	O(7)-Eu(1)-O(13)	74.5(2)
O(5)-Eu(1)-O(14)	132.0(2)	O(12)-Eu(1)-O(14)	74.4(2)	O(14)-Eu(1)-O(15)	77.3(2)
O(12)-Eu(1)-O(13)	71.6(2)	O(12)-Eu(1)-O(15)	138.5(2)	O(9)-N(1)-O(10)	116.3(7)
O(7)-Eu(1)-O(8)	53.06(19)	O(7)-Eu(1)-O(10)	146.12(18)	O(7)-C(8)-O(8)	121.2(8)
O(8)-Eu(1)-O(10)	141.56(18)	O(8)-Eu(1)-O(14)	75.5(2)	O(9)-Eu(1)-O(12)	116.45(19)
O(8)-Eu(1)-O(12)	69.0(2)	O(8)-Eu(1)-O(15)	75.0(2)	O(9)-Eu(1)-O(13)	111.2(2)

Continued Table 2

O(8)-Eu(1)-O(13)	111.1(2)	O(9)-Eu(1)-O(10)	49.71(18)	O(9)-Eu(1)-O(14)	66.2(2)
O(7)-Eu(1)-O(9)	151.86(18)	O(7)-Eu(1)-O(15)	82.6(2)	O(8)-Eu(1)-O(9)	136.58(18)
Complex 2					
Dy(1)-O(5)	0.226 7(5)	Dy(1)-O(12)	0.240 3(6)	O(9)-N(1)	0.125 5(9)
Dy(1)-O(7)	0.240 7(6)	Dy(1)-O(13)	0.243 2(6)	O(10)-N(1)	0.126 2(9)
Dy(1)-O(8)	0.247 4(6)	Dy(1)-O(14)	0.238 1(6)	O(7)-C(8)	0.124 3(10)
Dy(1)-O(9)	0.264 6(5)	Dy(1)-O(15)	0.239 4(6)	O(8)-C(8)	0.125 7(9)
Dy(1)-O(10)	0.245 4(5)	O(5)-C(7)	0.127 7(9)		
O(5)-Dy(1)-O(7)	86.46(19)	O(12)-Dy(1)-O(13)	71.8(2)	O(8)-Dy(1)-O(9)	136.78(17)
O(9)-Dy(1)-O(15)	77.98(17)	O(12)-Dy(1)-O(14)	74.3(2)	O(8)-Dy(1)-O(10)	141.64(18)
O(5)-Dy(1)-O(8)	131.75(18)	O(7)-Dy(1)-O(8)	52.71(19)	O(8)-Dy(1)-O(12)	69.4(2)
O(5)-Dy(1)-O(9)	69.75(18)	O(12)-Dy(1)-O(15)	138.6(2)	O(8)-Dy(1)-O(13)	111.41(19)
O(10)-Dy(1)-O(12)	76.1(2)	O(7)-Dy(1)-O(9)	152.06(18)	O(8)-Dy(1)-O(14)	75.32(19)
O(5)-Dy(1)-O(10)	86.50(18)	O(7)-Dy(1)-O(10)	146.39(18)	O(8)-Dy(1)-O(15)	74.60(19)
O(10)-Dy(1)-O(13)	71.44(18)	O(13)-Dy(1)-O(14)	139.6(2)	O(9)-Dy(1)-O(10)	49.47(16)
O(5)-Dy(1)-O(12)	145.5(2)	O(7)-Dy(1)-O(12)	91.8(2)	O(9)-Dy(1)-O(12)	116.14(19)
O(10)-Dy(1)-O(14)	79.74(19)	O(13)-Dy(1)-O(15)	142.9(2)	O(9)-Dy(1)-O(13)	110.67(17)
O(5)-Dy(1)-O(13)	74.5(2)	O(7)-Dy(1)-O(13)	75.0(2)	O(9)-Dy(1)-O(14)	66.50(19)
O(10)-Dy(1)-O(15)	127.42(18)	O(7)-Dy(1)-O(14)	127.5(2)	O(9)-N(1)-O(10)	116.5(6)
O(5)-Dy(1)-O(14)	132.1(2)	O(14)-Dy(1)-O(15)	77.5(2)	O(7)-C(8)-O(8)	120.2(8)
O(5)-Dy(1)-O(15)	75.3(2)	O(7)-Dy(1)-O(15)	82.1(2)		

2 Results and discussion

2.1 Description of crystal structures

Both complexes **1** and **2** are isostructural and crystallize in the triclinic $P\bar{1}$ space group. Only structure **1** is described in detail. A perspective view of **1** with the labelling scheme is given in Fig.1. In compound **1**, the central Eu³⁺ atoms are coordinated by nine O atoms, in which three are from two tddc ligands which coordinate in a mode of Scheme 1(b), two from one nitril and four from the coordinated water

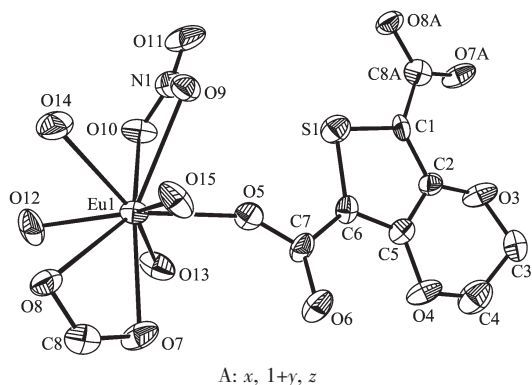


Fig.1 A perspective view of complex **1** with atom numberings, 50% probability thermal ellipsoids

molecules. The occurrence of this coordination mode leads to a 1D polymeric chain structure along the *b* axis as shown in Fig.2a and the distance between neighboring Eu³⁺ ions is 0.985 3 nm. The chains stack

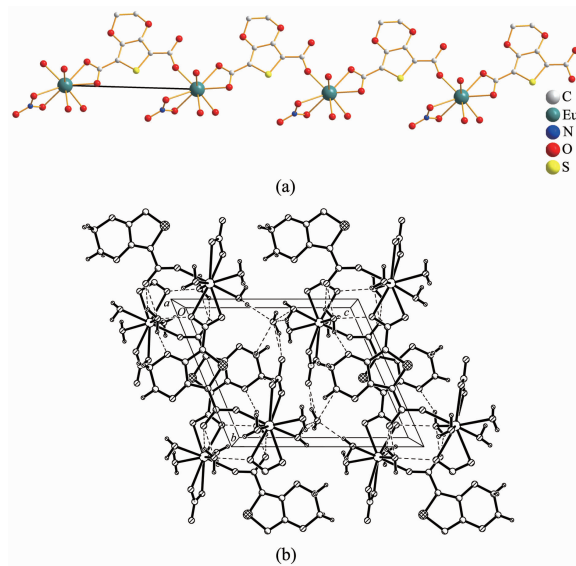


Fig.2 (a) 1D chain structure for complex **1** along *b* axis; (b) 3D supermolecular structure of the complex **1**, showing intermolecular hydrogen bonds between adjacent chains along *b* axis

along a axis in ABAB fashion which may reduce the repulsion for a higher stabilization and the 1D chains are linked to a 3D network through a mass of O—H···O

hydrogen bonds between adjacent chains (see Fig.2b). All intra- and intermolecular hydrogen bonds are given in Table 3.

Table 3 Hydrogen bonding geometry for complexes **1** and **2**

Doner—H···Acceptor	D—H / nm	H···A / nm	D···A / nm	D—H···A / (°)
Complex 1				
O(1)—H(1B)···O(2)#1	0.085	0.194	0.273 3(9)	154.00
O(1)—H(1C)···O(11)#2	0.085	0.214	0.290 2(10)	149.00
O(2)—H(2D)···O(6)#3	0.085	0.209	0.287 4(8)	153.00
O(12)—H(12)···O(1)	0.096	0.191	0.266 8(9)	134.00
O(12)—H(12B)···O(1)#4	0.085	0.210	0.291 8(9)	160.00
O(13)—H(13A)···O(3)#3	0.096	0.216	0.304 0(9)	152.00
O(13)—H(13B)···O(6)#5	0.096	0.198	0.279 9(9)	141.00
O(14)—H(14B)···O(11)#6	0.085	0.200	0.281 2(9)	157.00
O(14)—H(14C)···O(2)#7	0.085	0.240	0.324 6(9)	170.00
O(15)—H(15A)···O(3)#8	0.096	0.222	0.309 0(9)	149.00
O(15)—H(15B)···O(7)#9	0.085	0.250	0.311 8(8)	130.00
C(3)—H(3A)···O(9)#8	0.097	0.211	0.307 8(11)	174.00
C(4)—H(4A)···O(1)#10	0.097	0.250	0.309 9(12)	120.00
Complex 2				
O(1)—H(1B)···O(2)#1	0.085	0.195	0.273 1(9)	154.00
O(1)—H(1C)···O(11)#2	0.085	0.213	0.288 9(10)	149.00
O(2)—H(2D)···O(6)#3	0.085	0.209	0.286 6(8)	153.00
O(12)—H(12A)···O(1)	0.096	0.190	0.266 1(9)	134.00
O(12)—H(12B)···O(1)#4	0.085	0.211	0.292 0(9)	160.00
O(13)—H(13A)···O(3)#3	0.096	0.216	0.304 1(8)	152.00
O(13)—H(13B)···O(6)#5	0.096	0.197	0.279 0(8)	142.00
O(14)—H(14B)···O(11)#6	0.085	0.200	0.280 4(9)	158.00
O(14)—H(14C)···O(2)#7	0.085	0.239	0.323 4(9)	170.00
O(15)—H(15A)···O(3)#8	0.096	0.222	0.308 6(8)	149.00
O(15)—H(15B)···O(7)#9	0.085	0.250	0.311 4(8)	130.00
C(3)—H(3A)···O(9)#8	0.097	0.211	0.307 3(11)	176.00
C(4)—H(4A)···O(1)#10	0.097	0.245	0.303 1(13)	118.00

Symmetry codes **1**: #1: $x, -1+y, z$; #2: $1-x, 1-y, 1-z$; #3: $1-x, 1-y, 2-z$; #4: $1-x, -y, 1-z$; #5: $1-x, -y, 2-z$; #6: $-x, 1-y, 1-z$; #7: $-1+x, -1+y, z$; #8: $-x, 1-y, 2-z$; #9: $-x, -y, 2-z$; #10: $x, y, 1+z$; **2**: #1: $x, -1+y, z$; #2: $1-x, 1-y, 1-z$; #3: $1-x, 1-y, 2-z$; #4: $1-x, -y, 1-z$; #5: $1-x, -y, 2-z$; #6: $-x, 1-y, 1-z$; #7: $-1+x, -1+y, z$; #8: $-x, 1-y, 2-z$; #9: $-x, -y, 2-z$; #10: $x, y, 1+z$.

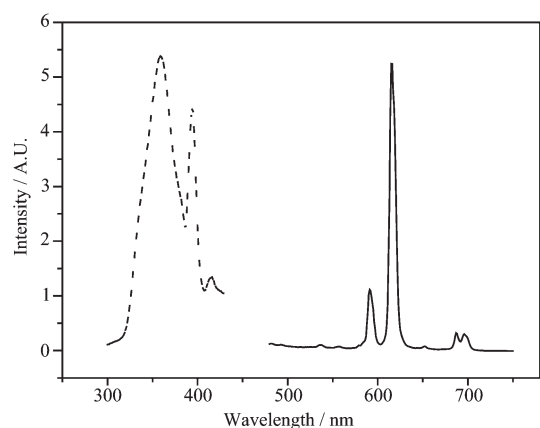
2.2 Fluorescence properties

In order to study the photophysical properties of these complexes, the photoluminescent properties of the ligand and the two compounds have been measured in the solid state at room temperature. From the spectra, it can be found that free ligand and complex **2** have no luminescences, while its complex **1** exhibits intense photoluminescence. As shown in Fig.3, under excitation of 359 nm and 394 nm, complex **1** has four metal cen-

tered (MC) emission bands: 591 nm ($^5D_0 \rightarrow ^7F_1$), 616 nm ($^5D_0 \rightarrow ^7F_2$), 687 nm ($^5D_0 \rightarrow ^7F_3$) and 696 nm ($^5D_0 \rightarrow ^7F_4$)^[11].

2.3 Thermogravimetric analyses and XRD patterns

The TGA curves of the two compounds are shown in Fig.4. The weight-loss of **1** and **2** are very similar and can be divided into two steps. The TGA measurement for **1** exhibits a weight loss of 20.8% from 30 °C to 220 °C, which corresponds to the loss of two lattice water



Real line is emission spectrum and dashed is excitation spectrum

Fig.3 Luminescence spectrum of complex **1**

molecules and four coordinated water molecules (calc. 19.6%). Compound **1** was stable to 300 °C, and then began to decompose upon further heating. The thermogravimetric analysis of **2** indicates that the loss of two free water molecules and four coordinated water molecules (19.2%) takes place between 30 °C and 254 °C (calculated: 19.2%) and the decomposition occurs at 270 °C.

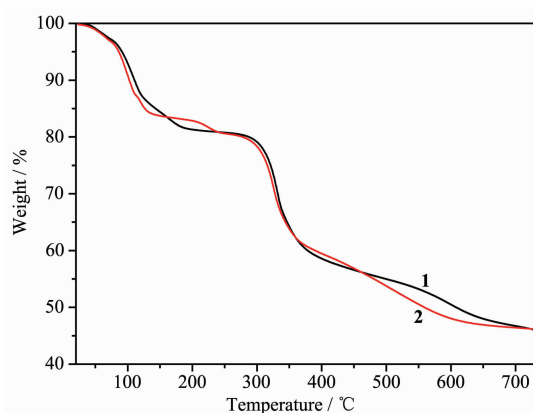


Fig.4 TGA curves of complexes **1** and **2**

The structures of **1** and **2** were further confirmed by matching their X-ray powder patterns with those generated from the corresponding single crystals (see Fig.5). Acceptable matches were observed between the simulated single-crystal X-ray data patterns and the experimental powder X-ray diffraction patterns for bulk crystalline samples as obtained from the synthesis of compounds **1** and **2**.

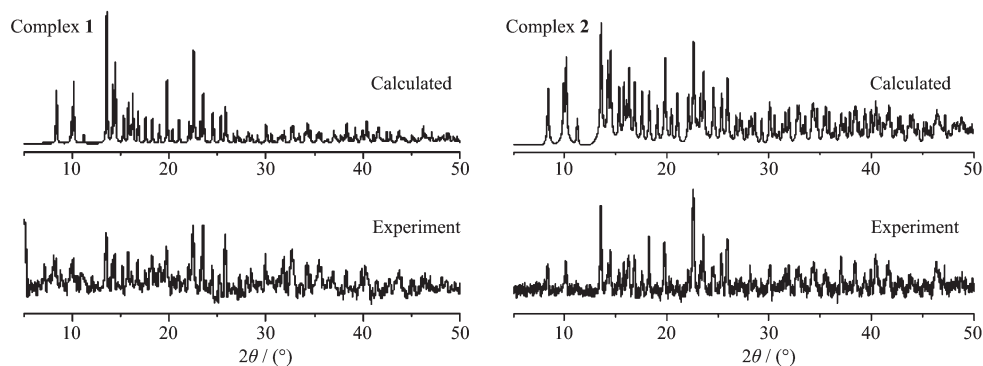


Fig.5 Simulated (up) and experimental (down) XRD patterns for complexes **1** (left) and **2** (right) at room temperature

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