



Preparation and thermal properties of lanthanide complexes with 2,3-dichlorobenzoic acid and 1,10-phenanthroline

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ABSTRACT

Three lanthanide complexes with a general formula $[\text{Ln}(\text{2,3-DCIBA})_3\text{phen}]_2$ ($\text{Ln}(\text{III}) = \text{Eu}(1), \text{Tb}(2), \text{Ho}(3)$; 2,3-DCIBA = 2,3-dichlorobenzoate; phen = 1,10-phenanthroline) were synthesized and characterized by elemental analysis, molar conductance, infrared and ultraviolet spectra and powder X-ray diffraction (XRD). The luminescent properties of the complexes 1 and 2 were studied. The thermal behaviors of the complexes were also discussed by thermogravimetric (TG), differential thermogravimetric (DTG) and infrared spectra (IR) techniques. The heat capacities of the complexes were measured from 259.15 to 493.02 K by means of Differential scanning calorimeter (DSC). The dependence of heat capacity on the reduce temperature x ($x = [T - (T_{\max} + T_{\min})/2]/[(T_{\max} - T_{\min})/2]$) was fitted to a polynomial equation with the least squares method for each complex. Furthermore, based on the fitted polynomial, the smoothed heat capacities and the derived thermodynamic functions ($H_T - H_{298.15\text{ K}}$), ($S_T - S_{298.15\text{ K}}$) and ($G_T - G_{298.15\text{ K}}$) in the measured temperature range were obtained with an interval of 10 K.

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1. Introduction

Many of stable ternary lanthanide complexes with aromatic acid and nitrogen-containing ligands were obtained for their certain conjugate system. They show interesting and various structures due to the different coordination models of the carboxyl groups and have been widely applied as functional materials [1–8]. In addition, the lanthanide complexes with distinct luminescent properties [9–16] may be used as luminescent probes in biomedical assays, as new fluorescence materials, as emitters in white LED devices [8]. However, their thermodynamic properties have less or not been studied. As we known, these properties are important not only for the theoretical study, but also the practical applications. Differential scanning calorimetry is a modern instrument analysis technology which can be used to determine the continuous heat capacities of materials quickly and precisely. In previous works, parts of binary lanthanide complexes with dichlorobenzoic acid have been reported by other researchers, focusing on the thermal behaviors of the complexes [17–19]. In this paper, we have synthesized and characterized a new series of complexes with a

general formula of $[\text{Ln}(\text{2,3-DCIBA})_3\text{phen}]_2$ ($\text{Ln}(\text{III}) = \text{Eu}(1), \text{Tb}(2), \text{Ho}(3)$). XRD patterns demonstrate that the three complexes are isostructural. The thermal decomposition processes of the complexes were discussed by TG technique and the final residues were verified by IR technique. Furthermore, the heat capacities $C_{p,m}$ of the three complexes were determined by means of DSC from 259.15 to 493.02 K and the thermodynamic parameters, such as the enthalpy, entropy and Gibbs free energy of the complexes relative to the standard reference temperature 298.15 K were established from the smoothed heat capacities.

2. Experimental

2.1. Materials

All chemicals were achieved from commercial sources as analytical grade and used without further purification. $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln}(\text{III}) = \text{Eu}, \text{Tb}, \text{Ho}$) were prepared by dissolving their respective oxide in hydrochloric acid, and then drying the solution by water-bath heating.

2.2. Preparation of the complexes

$\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ [$\text{Ln}(\text{III}) = \text{Eu}, \text{Tb}, \text{Ho}$] (0.5 mmol) was dissolved in distilled water. 2,3-dichlorobenzoic acid (1.5 mmol) and phen (0.5 mmol) were dissolved together in 95% ethanol solution. The pH

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Table 1

Data of elementary analyses and molar conductance of the complexes.

Complex		C%	H%	N%	Ln%	Δ_m (S cm ² mol ⁻¹)
1	Found	44.30	1.97	3.23	17.00	30.45
	Calcd	43.93	1.90	3.11	16.84	
2	Found	43.67	1.84	3.11	17.65	29.47
	Calcd	43.60	1.89	3.08	17.48	
3	Found	42.96	1.82	3.08	18.30	29.46
	Calcd	43.31	1.87	3.06	18.02	

Table 2Frequencies (cm⁻¹) of the absorption bands for the ligands and complexes.

Compound	$\nu_{\text{C-N}}$	$\nu_{\text{C=O}}$	$\nu_{\text{as(COO}^-)}$	$\nu_{\text{s(COO}^-)}$	$\Delta\nu(\nu_{\text{as}} - \nu_{\text{s}})$	$\delta_{\text{C-H}}$	$\nu_{\text{Ln-O}}$
Phen	1561	–	–	–	–	854,738	–
2,3-DCIHBA	–	1692	–	–	–	–	–
1	1520	–	1620	1409	211	846,728	418
2	1520	–	1624	1410	214	843,729	419
3	1519	–	1626	1411	215	843,729	419

of the solution was controlled in 6–7 using 1 mol L⁻¹ NaOH solution. The ethanol solution of the two ligands then was added dropwise into the LnCl₃·6H₂O aqueous solution under stirring. The reaction mixture was continually stirred about 10 h at room temperature, and then deposited overnight. Subsequently, the precipitates were filtered out, washed with 95% ethanol and dried in a far infrared dryer. The powders finally were stored in a silica-gel desiccator for the later characterization.

2.3. Apparatus and conditions of experiment

The carbon, hydrogen, and nitrogen contents in the complexes were determined on a Vario-EL III elemental analyzer and the metal content was assayed using an EDTA titration method. Infrared spectra were recorded at room temperature with KBr discs on a BRUKER TENSOR27 spectrometer from 4000 to 400 cm⁻¹. Ultra-violet spectra were depicted in a SHIMADZU 2501 spectrometer. The fluorescent spectra were measured on an F-4500 Hitachi spectrophotometer in the solid state at room temperature. Molar conductivity was measured by DDS-307 conductometer (Shanghai Precision & Scientific Instrument CO.LED). X-ray diffraction identification was carried out for the crystalline analyses by a Bruker D8 ADVANCE X-ray diffractometer in a scanning range of 5–50° (2 θ) with CuK α radiation (λ = 1.5418 Å). The thermal stability of the complexes was conducted with a Perkin Elmer TGA7 thermogravimetric analyzer and TG-DTG curves were recorded. The samples (about 3 mg) were heated in a platinum crucible from 298 to 1173 K under a dynamic N₂ atmosphere at a heating rate of 5 K min⁻¹.

Heat capacities of the prepared complexes were performed on a NETZSCH DSC 200 F3 in the temperature range of 259.15–493.02 K at a heating rate of 10 K min⁻¹ using indirect measurement method. The atmosphere was nitrogen gas and the flow rate is 40 mL min⁻¹. The heat capacity of the reference standard material sapphire was measured to verify the reliability of the heat capacity measurement method by DSC and the relative deviations of our experimental results were within $\pm 0.50\%$, compared with the recommended values by NIST [20] in the entire measured temperature range. The heat capacity of the material can be determined by creating a blank baseline profile, a reference standard substance (sapphire) profile and then a sample profile. All experiments were carried out in almost the same conditions. The mass of the reference standard substance sapphire (12.75 mg) or a sample loaded in an aluminum crucible sealed with a pierced lid was accurately weighted on heating. Here, the weights of aluminum crucibles are as equal as possible. The apparatus has an automatic data processing program, from which we can obtain the heat capacity values of the sample at different temperature by the indirect measurement method. The samples

mass was about 11 mg based on their molar mass of 1804.36, 1818.27 and 1830.28 g mol⁻¹, respectively.

3. Results and discussion

3.1. Elemental analysis

The results of elementary analyses are listed in Table 1. From Table 1, it can be seen that the experimental data are consistent well with the theoretical values, indicating that the complexes have a composition of [Ln(2,3-DCIBA)₃phen]₂ [(where Ln(III) = Eu(1), Tb(2), Ho(3)) as anticipated.

3.2. Molar conductance

The prepared complexes were dissolved in DMSO (dimethyl sulfoxide) solution and their molar conductivity was determined with DMSO as a reference. The values of molar conductance given in Table 1 are all less than 40 S cm² mol⁻¹, indicating that the three complexes are non-electrolyte in DMSO [21].

3.3. Infrared spectra

Table 2 presents the important infrared frequencies of the organic ligands and the complexes. The band of $\nu_{\text{C=O}}$ at 1692 cm⁻¹ due to the COOH group in the free acid ligand disappears completely in the spectra of the complexes, whereas there appear two bands around 1620–1626 and 1409–1411 cm⁻¹ that arise from asymmetric and symmetric vibrations of the COO⁻ group, which indicates that the oxygen atoms of carboxylic groups have formed coordinative bonds with Ln(III) ion [22]. Meanwhile, the appearance of absorption band at 418–419 cm⁻¹ attributed to the $\nu_{\text{Ln-O}}$ may also suggest that the oxygen atoms from the carboxylic groups are coordinated to the Ln(III) ion [23]. The bands of $\nu_{\text{C-N}}$ (1561 cm⁻¹) and $\delta_{\text{C-H}}$ (854 and 738 cm⁻¹) in the spectrum of 1,10-phenanthroline ligand are observed to shift to lower wavenumbers in the spectra of the complexes, suggesting the coordination of the two nitrogen atoms of the neutral ligand to Ln(III) ion [24].

3.4. Ultraviolet spectra

The ligands and complexes were recorded in DMSO solution by UV spectra with DMSO as a reference, respectively. The spectra data are listed in Table 3. The maximum absorption wavelength of the free acid ligand 2,3-DCIHBA is 256.0 nm with an absorbency of 0.02. The main absorption peaks of the complexes are 264.2–265.1 nm, which draws a conclusion that the free acid ligands were coor-

Table 3
UV absorption of the ligands and complexes (λ (nm), $A_{\max}$).

Compound	$\lambda_{\max}$ (nm)	$A_{\max}$
Phen	265.0	0.31
2,3-DCIIBA	256.0	0.02
[Eu(2,3-DCIIBA) ₃ phen] ₂	265.1	0.88
[Tb(2,3-DCIIBA) ₃ phen] ₂	264.2	1.20
[Ho(2,3-DCIIBA) ₃ phen] ₂	265.1	0.80

dinated to the metal ion forming a π -conjugated system [25]. Moreover, compared with the complexes, the maximum absorption peak of phen at 265.0 nm is similar to that of in the complexes, indicating that the formation of the coordination bonds of Ln–N should have no significant influence on the UV absorption of the phen [12]. However, the absorptivity is enhanced from 0.31 to 0.88, 1.2 or 0.80 for three complexes, respectively, suggesting a bigger chelating ring is formed.

3.5. Fluorescence spectra

The excitation and emission spectra of the complexes 1 and 2 were recorded in solid state at room temperature. The excitation wavelengths of the complexes were performed in the range of 200–400 nm. The fluorescent spectra were recorded in the range of 400–700 nm at a selective excitation wavelength 320 nm, and they exhibit strong characteristic luminescence of europium and terbium ions, as shown in Figs. 1 and 2. In addition, the complexes 1 and 2 exhibit red and green luminescence, respectively, under the radiation of UV light. For the complex 1, three main emission peaks of the Eu(III) ion are observed at 579.6, 591.6 and 617.4 nm, corresponding to the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively. The $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition occurs at 591.6 nm and the three peaks 614.8, 617.4 and 619.6 nm belong to the $^5D_0 \rightarrow ^7F_2$ electric dipole transition which appears the dividing, which is similar to the complex in the literature [26]. The $^5D_0 \rightarrow ^7F_2$ transition is stronger than the $^5D_0 \rightarrow ^7F_1$ and its rate is about 2.5, indicating that the symmetry of the Eu(III) ion in the coordination compound is lower and have no symmetry centre [27,28]. For the complex 2, four main emission peaks in the luminescence spectrum at about 490, 545, 585 and 620 nm are the corresponding characteristic peaks of Tb(III) ion, which are assigned to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$, respectively. The most intense emission band arises from the $^5D_4 \rightarrow ^7F_5$ transition, which is the preferred transition in terbium-containing complexes [29]. As we known the luminescence intensity of solid Ln(III) (Ln = Eu, Tb)

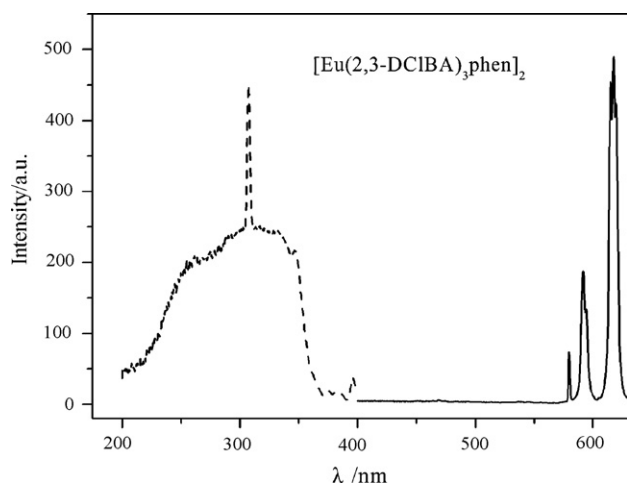


Fig. 1. Excitation spectra ($\lambda = 615$ nm) and luminescence spectra ($\lambda = 320$ nm) of the complex 1.

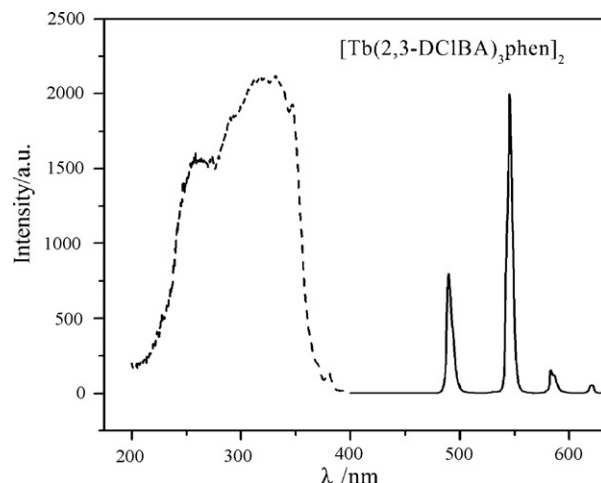


Fig. 2. Excitation spectra ($\lambda = 545$ nm) and luminescence spectra ($\lambda = 320$ nm) of the complex 2.

chlorides is quite weak, but from Figs. 1 and 2 we can see that the luminescence intensity of Ln(III) (Ln = Eu, Tb) complexes are remarkable strong.

3.6. XRD

The powder diffraction patterns of the complexes have been recorded and depicted in Fig. 3. From the patterns, it is evident that the three complexes are isostructural.

3.7. Thermal decomposition processes of the complexes

The thermal analytical data of the complexes 1–3 are summarized in Table 4. The TG–DTG curves of the complexes at a heating rate of 5 K min^{−1} under a dynamic N₂ atmosphere are shown in Figs. 4–6, respectively.

As seen from the DTG curves, the thermal decomposition processes of the three complexes present three main stages, respectively. For the complex 1 [Eu(2,3-DCIIBA)₃phen]₂ the first stage mass loss is 19.75% between 514.14 and 627.84 K, which coincides with the loss of two phen molecules with a calculated mass loss of 19.97%. The second and third stages take place at 627.84 K and continue to 1045.83 K with a loss of 61.24% (theoretical mass loss is 60.54%), corresponding to the loss of the rest groups. The characteristic absorptions of the final residue are similar to IR spectrum of

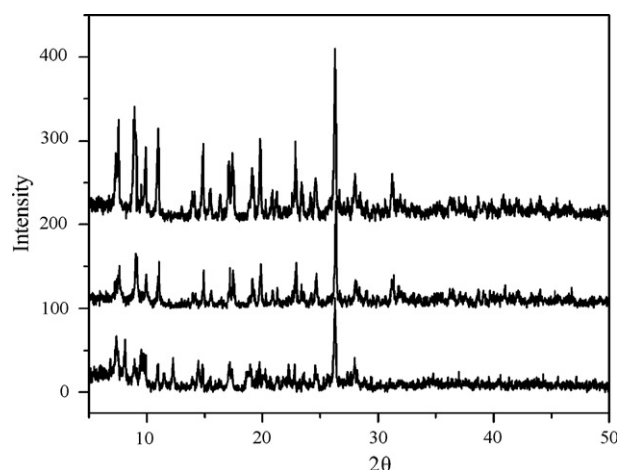


Fig. 3. XRD patterns of the complexes.

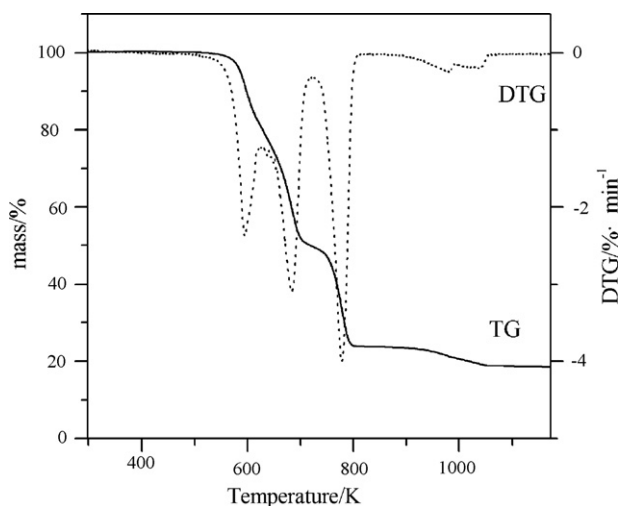
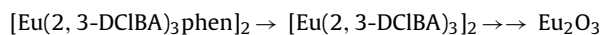
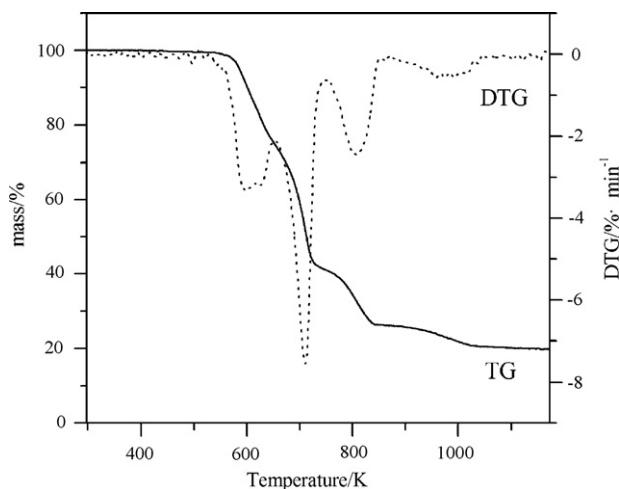
Table 4

Thermal decomposition data for the complexes 1–3 from TG-DTG analysis.

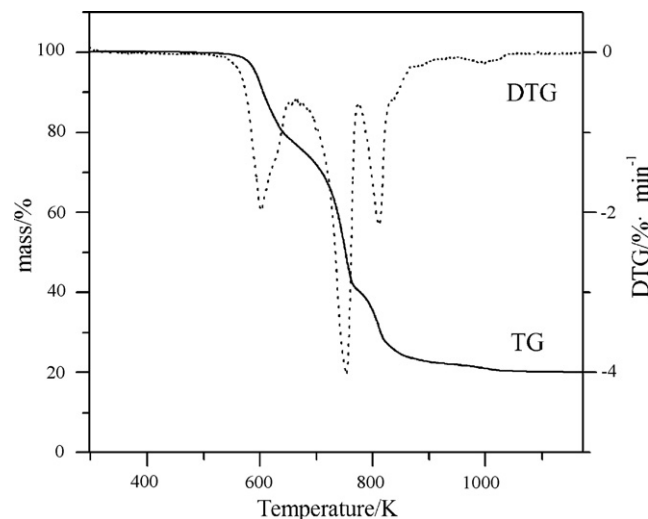
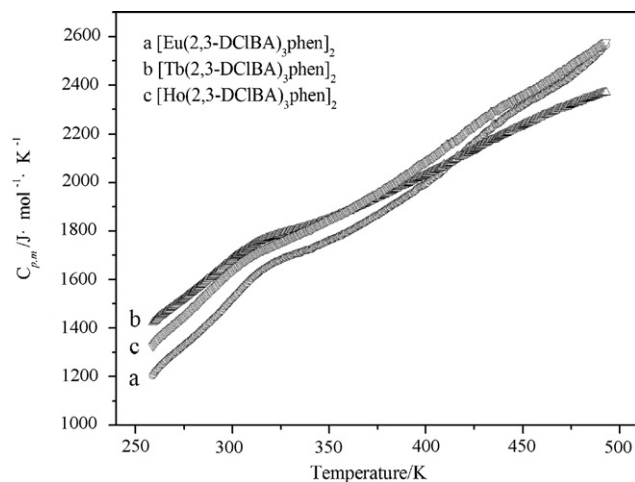
Complex	Step	Temperature range (K)	DTG T_p (K)	Mass loss rate (%)		Probable Expelled groups	Residue(%)	
				Found	Calcd.		Obs.	Calcd.
1	I	514.14–627.84	595.81	19.75	19.97	2phen	–	–
	II	627.84–725.53	684.70	30.71	–	$x(2,3\text{-DCIBA})$	–	–
	III	725.53–1045.83	779.18	30.53	–	$(6-x)(2,3\text{-DCIBA})\text{-}3\text{O}$	Eu_2O_3	–
2	I	514.72–655.53	603.09	25.17	–	2phen+ $x(2,3\text{-DCIBA})$	–	–
	II	655.53–749.80	711.86	33.31	–	–	–	–
	III	749.80–1044.96	807.03	20.61	–	$(6-x)(2,3\text{-DCIBA})\text{-}3.5\text{O}$	$1/2\text{Tb}_4\text{O}_7$	–
3	I	517.60–667.88	603.32	23.21	–	2phen+ $x(2,3\text{-DCIBA})$	–	–
	II	667.88–776.97	753.59	36.44	–	–	–	–
	III	776.97–1038.56	812.59	19.89	–	$(6-x)(2,3\text{-DCIBA})\text{-}3\text{O}$	Ho_2O_3	–
				79.54 ^a	79.36 ^a	–	20.31	20.64

 T_p is the peak temperature of DTG.^a The total loss rate.

the standard sample Eu_2O_3 . Therefore, Up to 1045.83 K, the complex 1 was completely degraded into Eu_2O_3 with a total loss of 80.99% (theoretical loss is 80.51%). Based on the above analysis, the thermal decomposition of the complex 1 can be described as the following process:

**Fig. 4.** TG-DTG curves of the complex 1 at a heating rate of 5 K min^{-1} .**Fig. 5.** TG-DTG curves of the complex 2 at a heating rate of 5 K min^{-1} .

For the complexes 2 and 3, they have similar thermal decomposition stages. Here, the complex 2 is selected as a representative for the thermal analysis. The first mass loss stage takes place between 514.72 and 655.53 K with a mass loss of 25.17%, which corresponds to the loss of two phen molecules and partial 2,3-DCIBA ligands.

**Fig. 6.** TG-DTG curves of the complex 3 at a heating rate of 5 K min^{-1} .**Fig. 7.** Molar heat capacity $C_{p,m}$ of the complexes as functions of temperature T in the temperature range.

Complex 1 [Eu(2,3-DCIBA)₃phen]₂

$$C_{p,m}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 1866.53481 + 538.5433x + 509.79171x^2 + 210.38569x^3 - 1161.58492x^4 - 78.04671x^5 + 686.47247x^6 \quad R^2 = 0.9997 \quad \text{SD} = 6.0565$$

Complex 2 [Tb(2,3-DCIBA)₃phen]₂

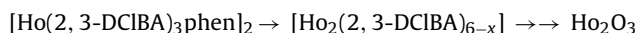
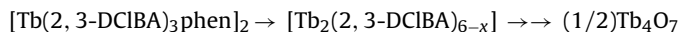
$$C_{p,m}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 1938.12532 + 399.58347x + 253.92084x^2 + 84.57623x^3 - 575.23617x^4 - 4.46018x^5 + 285.04963x^6 \quad R^2 = 0.9996 \quad \text{SD} = 5.5512$$

Complex 3 [Ho(2,3-DCIBA)₃phen]₂

$$C_{p,m}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 1956.74226 + 552.28398x + 352.6551x^2 + 10.53234x^3 - 754.95227x^4 + 68.28757x^5 + 406.56437x^6 \quad R^2 = 0.9998 \quad \text{SD} = 4.40656$$

Scheme 1.

The second and third stages belong to the loss of the remaining 2,3-DCIBA ligands which undergo the decomposition with a mass loss of 53.92% from 655.53 to 1044.96 K. Up to 1044.96 K, there is no mass change with the increase of temperature, suggesting that a final residue of Tb₄O₇ has been formed, which is verified by the residue IR spectrum that has similar characteristic absorptions as the standard sample spectra of Tb₄O₇. So, on the basis of the above analytical results, the thermal decomposition of the complexes 2 and 3 are presented as the following:



We can draw a conclusion from the above analyses that the three complexes all have good thermostability due to the higher decomposed temperature until 514 K and the final residues are their respective oxide. In addition, Ln–N bonds of the complexes break firstly in the TG experiments, which may be explained by the longer bond of Ln–N than that of Ln–O because of the stronger coordination ability of oxygen atom than nitrogen atom.

3.8. Heat capacities of the prepared complexes

From the thermal analytical data, all of the three complexes have no mass loss until 514 K at a liner heating rate of 5 K min^{−1}, indicating they are thermostable. So we measured the molar heat capacities of the three complexes by DSC from 259.15 to 493.02 K. Four times parallel experiments were carried out and the average molar heat capacity values (see Table 1 in supplementary data) of each complex were obtained from the measured values. The curves of molar heat capacity values $C_{p,m}$ vs temperature for the three complexes are plotted in Fig. 7. It can be seen from Fig. 7 the $C_{p,m}$ of the complexes with temperature increasing have a similar changing trend, which also demonstrates the three complexes are isostructural. Over the measured temperature range there is no obvious endothermic or exothermic peak existing in the $C_{p,m}$ curves. However, there is a phenomenon that the curves are not smooth at temperature from 300 K to 350 K and the causes are under further study. The average values of the parallel experimental heat capacities for each complex were fitted to a polynomial, respectively, in the reduced temperature (x) ($x = [T - (T_{\max} + T_{\min})/2] / [(T_{\max} - T_{\min})/2]$) by means of the least-squares method [30,31] and the corresponding equations, correlation coefficients R^2 and standard deviations of the fitting results are given in Scheme 1, in which $x = (T - 376.085)/116.935$, T is the experimental temperature, $T_{\max}$ and $T_{\min}$ are the respec-

tive upper limit (493.02 K) and lower limit (259.15 K) in the above measured temperature region.

3.9. Thermodynamic functions of the complexes

Thermodynamic functions of the complexes were calculated on the basis of the fitted polynomial of the heat capacities as a function of the reduced temperature (x) according to the following thermodynamic equations:

$$H_T - H_{298.15\text{ K}} = \int_{298.15\text{ K}}^T C_{p,m} dT \quad (1)$$

$$S_T - S_{298.15\text{ K}} = \int_{298.15\text{ K}}^T C_{p,m} T^{-1} dT \quad (2)$$

$$G_T - G_{298.15\text{ K}} = \int_{298.15\text{ K}}^T C_{p,m} dT - T \int_{298.15\text{ K}}^T C_{p,m} T^{-1} dT \quad (3)$$

Smoothed values of $C_{p,m}$ and the derived values of fundamental thermodynamic functions of the complexes relative to the standard reference temperature 298.15 K are listed in Tables 2–4 (see Supplementary data), respectively, with an interval of 10 K.

4. Conclusions

In summary, the title complexes have been successfully synthesized. The complexes 1 and 2 show strong emission. The thermal decomposition processes of the three complexes present three stages and they are all thermally stable. Heat capacities of the complexes were measured by a differential scanning calorimeter over the temperature range from 259.15 to 493.02 K and the average values of experimental heat capacities of the three complexes were fitted to a polynomial equation, respectively. Additionally, the thermodynamic functions of the complexes were derived from the fitted polynomial equations of heat capacities $C_{p,m}$ relative to the standard reference temperature 298.15 K.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tca.2010.09.011](https://doi.org/10.1016/j.tca.2010.09.011).

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