

研究简报

$\text{Eu}_2(p\text{-ClC}_6\text{H}_4\text{COO})_6(\text{C}_{12}\text{H}_8\text{N}_2)_2$ 配合物 热分解机理及非等温动力学

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关键词: 铕配合物 对氯苯甲酸 1, 10-邻啡罗啉 非等温动力学 热分解
机理函数
分类号: O643.12

Thermal Decomposition Mechanism and Non-isothermal Kinetics of the Complex $\text{Eu}_2(p\text{-ClC}_6\text{H}_4\text{COO})_6(\text{C}_{12}\text{H}_8\text{N}_2)_2$

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The thermal decomposition behaviour of europium *p*-chlorobenzoate complex with 1, 10-phenanthroline and its kinetics were studied in nitrogen by non-isothermal thermogravimetry. Its thermal decomposition occurs mainly in three steps. The intermediate and residue for each step of decomposition were identified from TG curve. The kinetic parameters were obtained from analysis of the TG-DTG curves by the Achar method, the Madhusudanan-Krishnan-Ninan (MKN) method and Ozawa method respectively. The most probable mechanisms function for the first and second stage were suggested by comparing the kinetic parameters.

Keywords: europium complex *p*-chlorobenzoic acid 1, 10-phenanthroline
non-isothermal kinetics thermal decomposition mechanisms function

收稿日期: 2000-10-23。收修改稿日期: 2000-12-01。

河北师范大学科学基金资助项目 (No. L2000y08)。

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0 Introduction

The complexes formed by rare earth and aromatic carboxylic acid have many special structures and interesting luminous properties, thus arouse people's interest to study them. They can be used in many areas such as extraction and separation, germicide, catalyst, luminous materials and functional materials and so on.

The crystal structure and luminescence spectra of the europium *p*-chlorobenzoate complex with 1, 10-phenanthroline has been reported^[1], but the study for its non-isothermal kinetics and thermal decomposition mechanism is still rarely. In the present work, the thermal decomposition mechanism of europium *p*-chlorobenzoate complex with 1, 10-phenanthroline was derived and the non-isothermal kinetic data were analyzed by the Achar method^[2], the MKN method^[3] and Ozawa method^[4], respectively.

1 Experimental

The europium *p*-chlorobenzoate complex with 1, 10-phenanthroline was prepared as described previously^[1].

The TG and DTG experiments for the title compound were performed using a Perkin-Elmer's TGA7 thermogravimetric analyzer under a nitrogen atmosphere, at a flow rate of $40\text{ mL} \cdot \text{min}^{-1}$. The heating rate used were 2.5, 5, 7, $10^\circ\text{C} \cdot \text{min}^{-1}$ from ambient temperature to 925°C and the sample mass was $(1.8 \pm 0.2)\text{ mg}$.

2 Results and discussion

2.1 Thermogravimetric decomposition data

TG and DTG curves of $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$ (*p*-ClBA: *p*-chlorobenzoate; phen: 1, 10-phenanthroline) are shown in Fig. 1. The corresponding thermoanalytical data, the peak temperatures and temperature range of DTG curve and the percentages of mass loss and probable composition of the expelled groups are given in Table 1. The thermal decomposition process of $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$ can be divided into three stage as is predicted by the DTG curve (Fig 1.), and there are mass loss with maximum rate at 267 and 455°C in the DTG curve. The TG curve shows that the first stage mass loss is 26.95% between 219.1°C and 338.6°C , which coincides with the calculated value(27.0%) of losing 2mol $\text{C}_{12}\text{H}_8\text{N}_2$ and 2mol Cl from the complex. The degradation can also be demonstrated by the bond distances of the structure (Table 2). Eu-N distance is longer than other bond distance, whereas, the bond distance $\text{C}(15)\text{-Cl}$ (1) = $0.1729(12) < \text{C}(25)\text{-Cl}(2) = 0.1743(12)$ and $\text{C}(35)\text{-Cl}(3) = 0.1735(8)$. Thus Eu-N(1),

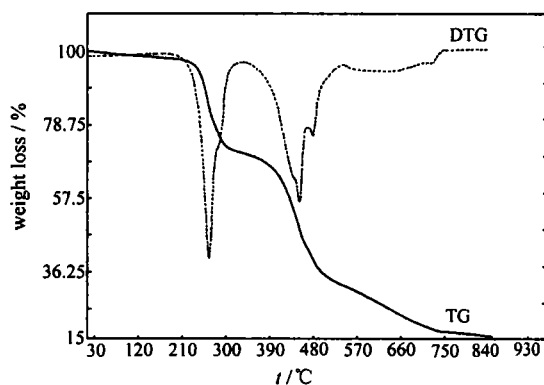


Fig. 1 TG-DTG curve of $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$ ($\beta = 2.5^\circ\text{C} \cdot \text{min}^{-1}$)

Table 1 Thermal Decomposition Data for $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$ from TG and DTG Analysis

stage	temp range/°C	DTG peak temp/°C	loss of mass/%		probable composition of expelled groups	intermediate
			TG	theory		
I	219.1 ~ 338.6	267	26.95	27.0	- 2phen, - 2Cl	$\text{Eu}_2(p\text{-ClBA})_4(\text{BA})_2$
II	338.6 ~ 539.7	455	38.46	38.95	- 4 <i>p</i> -ClBA	$\text{Eu}_2(\text{BA})_2$
III	539.7 ~ 745.1	—	12.91	12.03	- $\text{C}_{14}\text{H}_8\text{O}$	Eu_2O_3
			78.32 ^a	77.98 ^a		

a: Total loss of mass (%).

Table 2 Main Bond Distance⁽¹⁾ (nm)

Eu-O(1)	0.2355(8)	Eu-O(2)	0.2390(6)	Eu-O(3)	0.2526(5)
Eu-O(4)	0.2397(7)	Eu*-O(5)	0.2323(6)	Eu-O(6)	0.2360(5)
Eu-N(1)	0.2593(7)	Eu-N(2)	0.2669(8)	C(15)-Cl(1)	0.1729(12)
C(25)-Cl(2)	0.1743(12)	C(35)-Cl(3)	0.1735(8)		

Eu-N(2) [Eu*-N(1*), Eu*-N(2*)] and C(15)-Cl(1) [C(15*)-Cl(1*)] bonds were considered to be broken down at the same time, as indicated by the broken line in Fig. 2.

In the second-stage, $\text{Eu}_2(p\text{-ClBA})_4(\text{BA})_2$ is decomposed at 338.6 ~ 539.7°C with the mass loss of 38.46%. The theoretical mass loss is 38.95% corresponding to the loss of 4mol *p*-ClBA and the formation of $\text{Eu}_2(\text{BA})_2$. Actually, this stage decomposition includes two steps. The TG curve shows the third stage began at 539.7°C and completed at 745.1°C accompanied with 12.91% mass loss. It is in agreement with the theoretical value of the mass loss of 12.03%, corresponding to the loss of $\text{C}_{14}\text{H}_8\text{O}$ and the formation of Eu_2O_3 . On the basis of experimental and calculated results, the thermal decomposition mechanism of $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$ is postulated to be as follows:



2.2 Non-isothermal decomposition kinetics

In the present work, the Achar method, the Madhusudanan-Krishnan-Ninan(MKN) method and the Ozawa method have been applied to study the kinetics of the first decomposition processes of the europium *p*-chlorobenzoate complex with 1, 10-phenanthroline. The differential, integral and Ozawa equations are as follows:

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/(RT) \quad (d\alpha/dt = \beta d\alpha/dT) \quad (1)$$

$$\ln[g(\alpha)/T_{1.9215}] = \ln(AE/\beta R) + 3.7721 - 1.9215\ln E - 0.12039 E/T \quad (2)$$

$$\lg \beta + 0.4567 E/(RT) = C \quad (3)$$

where α is the fraction of conversion, $d\alpha/dt$ is the rate of conversion, T is the absolute tempera-

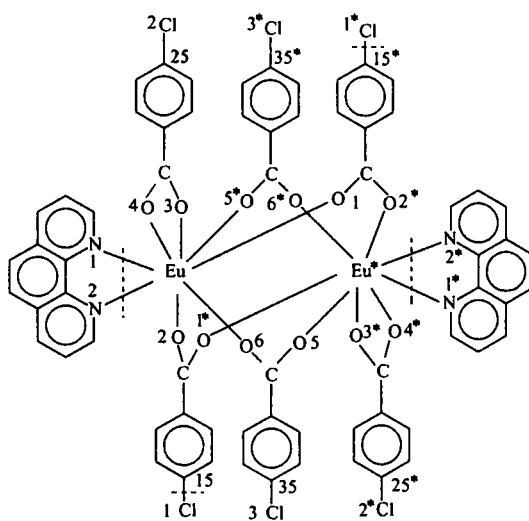
Fig. 2 Molecular structure of $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$

Table 3 Base Data for $\text{Eu}_2(p\text{-CIBA})_6(\text{phen})_2$ Determined by TG-DTG ($\beta = 2.5^\circ\text{C} \cdot \text{min}^{-1}$)

No.	stage 1			stage 2		
	T/K	α	$d\alpha/dT$	T/K	α	$d\alpha/dT$
1	506.29	0.0223	0.17	653.95	0.0612	0.21
2	509.1	0.0320	0.19	656.77	0.0677	0.22
3	511.91	0.0394	0.22	659.58	0.0752	0.23
4	514.72	0.0509	0.29	662.39	0.0823	0.24
5	517.54	0.0635	0.37	665.2	0.0903	0.28
6	520.35	0.0839	0.47	668.02	0.0992	0.31
7	523.16	0.1028	0.55	673.64	0.1171	0.34
8	525.97	0.1255	0.67	676.45	0.1275	0.37
9	528.79	0.1570	0.81	679.27	0.1395	0.43
10	531.6	0.2012	1.05	682.08	0.1522	0.45
11	534.41	0.2465	1.29	684.89	0.1652	0.49
12	537.23	0.3006	1.57	687.71	0.1800	0.55
13	540.04	0.3856	1.75	690.52	0.1990	0.62
14	542.85	0.4561	1.70	693.33	0.2175	0.68
15	545.66	0.5189	1.49	696.14	0.2370	0.73
16	548.48	0.5727	1.28	698.96	0.2630	0.82
17	551.29	0.6276	1.07	701.77	0.2869	0.87
18	554.1	0.6677	0.97	704.58	0.3132	0.94
19	556.91	0.7052	0.88	707.39	0.3392	0.98
20	559.73	0.7404	0.83	710.21	0.3735	1.04
21	562.54	0.7779	0.82	713.02	0.4021	1.07
22	565.35	0.8117	0.79	715.83	0.4325	1.09
23	568.16	0.8402	0.74	721.46	0.4988	1.12
24	570.98	0.8751	0.62	724.27	0.5313	1.23
25	573.79	0.893	0.47	728.49	0.5898	1.29
26	576.6	0.9133	0.36	734.11	0.6488	0.92
27	579.42	0.9248	0.30	736.93	0.6774	0.76
28	582.23	0.9386	0.24	739.74	0.6985	0.69
29	585.04	0.9467	0.19	742.55	0.7170	0.67
30	587.85	0.9538	0.17	762.24	0.8584	0.56
31	590.67	0.9616	0.16	765.05	0.8730	0.47
32	593.48	0.9675	0.13	767.87	0.8883	0.40
33				770.68	0.8977	0.35
34				773.49	0.9078	0.32
35				776.3	0.9182	0.31

ture, A is the pre-exponential factor, R is the gas constant, E is the apparent activation energy, β is the linear heating rate, $f(\alpha)$ and $g(\alpha)$ are the differential and integral mechanism functions, respectively, C is a constant.

The entropy of activation (ΔS) and the free energy of activation (ΔG) can be calculated using the following equations^[5,6]:

$$A = kT_s / h \exp(\Delta S / R) \quad (4)$$

$$k(T) = A \exp(-E / RT) \quad (5)$$

$$k(T) = \nu \exp(-\Delta G / RT) \quad (6)$$

Comparing (5) with (6), leads to

$$A \exp(-E/RT) = \nu \exp(-\Delta G/RT) \quad (7)$$

where k is the Boltzmann constant, T_s is peak temperature, h is the Planck constant, ν is the Einstein Vibration frequency. All the computational work was done on an IBM computer using a BASIC program.

The basic parameters of α , T and $d\alpha/dT$ obtained by the TG-DTG curve (Fig. 1) are listed in Table 3. By substituting the basic parameters in Table 3 and the 30 different mechanism functions $f(\alpha)$ and $g(\alpha)$ in reviews^[7] into eqs. (1) and (2), the kinetic parameters E , $\ln A$ and linear correlation coefficients r in Table 4 and Table 5 were obtained with the linear least squares method. If all the following conditions, such as: (1) the values of E and $\ln A$ obtained by the differential and integral methods are approximately equal and (2) the linear correlation coefficient is better, are satisfied at the same time, the relevant function with the above-mentioned satisfying conditions is the probable mechanism function of thermal decomposition of the complex.

Table 4 Results of Kinetic Analysis of $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$ for Stage 1 ($\beta = 2.5^\circ\text{C} \cdot \text{min}^{-1}$)

function No.	Achar method			MKN method		
	$E/(\text{kJ} \cdot \text{mol}^{-1})$	$\ln(A/\text{s}^{-1})$	r	$E/(\text{kJ} \cdot \text{mol}^{-1})$	$\ln(A/\text{s}^{-1})$	r
1	93.0	20.9	0.6374	201.8	41.1	0.9340
2	132.6	29.4	0.7894	221.9	45.1	0.9480
3	151.0	32.1	0.8408	230.9	45.8	0.9542
4	185.0	40.0	0.9051	249.8	50.2	0.9651
5	69.6	13.2	0.5334	185.4	34.9	0.9257
6	287.1	63.6	0.9813	317.8	66.1	0.9889
7	89.8	21.8	0.8994	136.2	27.9	0.9771
8	41.5	11.0	0.7696	87.86	17.1	0.9753
9	17.4	5.5	0.5010	63.7	11.6	0.9735
10	-6.8	-0.08	0.2562	39.6	5.98	0.9694
11	-18.9	-3.0	0.6245	27.5	3.05	0.9644
12	38.8	9.3	0.5497	113.6	21.8	0.9542
13	55.8	12.8	0.7198	120.5	23.1	0.9624
14	-12.3	-1.8	0.1629	96.5	18.4	0.9282
15	-64.9	-13.5	0.7598	43.9	6.68	0.9144
16	-82.5	-17.6	0.8581	26.3	2.54	0.8967
17	-91.3	-19.7	0.8918	17.6	0.33	0.8732
18	191.9	45.4	0.9964	198.6	42.7	0.9988
19	140.9	32.9	0.9795	42.3	7.44	0.9382
20	40.4	9.6	0.3968	61.4	10.7	0.9217
21	234.7	53.7	0.9557	281.1	59.8	0.9785
22	379.7	85.3	0.9661	426.0	91.3	0.9790
23	524.6	116.7	0.9703	571.0	122.8	0.9792
24	294.0	69.7	0.9964	195.4	44.24	0.9519
25	64.3	14.5	0.7820	124.2	23.7	0.9663
26	-114.4	-24.7	0.7348	73.8	13.5	0.8800
27	-216.5	-47.9	0.8451	59.6	10.4	0.8407
28	-318.6	-71.2	0.8841	49.8	8.2	0.8077
29	-8.8	-1.1	0.2284	55.9	9.1	0.9562
30	12.4	3.1	0.2436	52.4	8.5	0.9463

For the first stage of decomposition of the title compound, it can be seen that from the data in

Table 5 Results of Kinetic Analysis of $\text{Eu}_2(p\text{-CIBA})_6(\text{phen})_2$ for Stage 2 ($\beta = 2.5^\circ\text{C} \cdot \text{min}^{-1}$)

function No.	Achar method			MKN method		
	$E/(\text{kJ} \cdot \text{mol}^{-1})$	$\ln(A/\text{s}^{-1})$	r	$E/(\text{kJ} \cdot \text{mol}^{-1})$	$\ln(A/\text{s}^{-1})$	r
1	120.7	20.9	0.8433	185.1	27.4	0.9800
2	154.8	26.3	0.9208	203.6	30.2	0.9870
3	169.4	27.4	0.9431	211.5	30.1	0.9896
4	196.9	32.4	0.9701	227.5	33.0	0.9936
5	96.8	14.3	0.7784	168.4	22.1	0.9752
6	279.5	47.1	0.9971	282.5	43.1	0.9989
7	105.1	19.5	0.9671	121.0	17.7	0.9971
8	60.9	11.9	0.9224	76.9	10.1	0.9967
9	38.9	8.0	0.8457	54.8	6.2	0.9964
10	16.8	4.0	0.5805	32.7	2.1	0.9954
11	5.79	1.9	0.2425	21.7	0.076	0.9933
12	63.8	11.4	0.8296	102.2	13.5	0.9897
13	77.5	13.5	0.8993	108.0	14.2	0.9928
14	22.5	4.7	0.3568	86.9	11.3	0.9770
15	-26.7	-3.7	0.4709	37.7	2.8	0.9691
16	-43.0	-6.7	0.6752	21.4	-0.3	0.9568
17	-51.2	-8.2	0.7473	13.2	-2.1	0.9356
18	187.7	34.3	0.9966	169.4	26.7	0.9956
19	146.4	26.2	0.9947	29.9	2.2	0.8795
20	71.6	12.9	0.7259	54.1	5.7	0.9735
21	237.4	41.8	0.9894	253.4	40.0	0.9974
22	369.8	63.8	0.9934	385.7	62.0	0.9975
23	502.2	85.7	0.9949	518.1	83.8	0.9976
24	270.2	49.8	0.9874	153.8	25.9	0.9199
25	84.4	14.4	0.9232	111.1	14.5	0.9942
26	-60.1	-9.3	0.5503	64.5	7.7	0.9422
27	-142.7	-23.7	0.7551	49.6	5.1	0.9027
28	-225.3	-38.2	0.8210	38.9	3.2	0.8615
29	17.8	3.7	0.4837	48.3	4.4	0.9906
30	39.2	6.9	0.7135	45.4	4.0	0.9865

Table 6 Calculated Values of Kinetics Parameters of $\text{Eu}_2(p\text{-CIBA})_6(\text{phen})_2$ for Stage 1

	$E/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta G/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S/(\text{J} \cdot \text{mL}^{-1})$	$\ln(A/\text{s}^{-1})$	r
Achar method	191.9	123.0	127.6	45.4	0.9964
MKN method	198.6	142.0	104.8	42.7	0.9988
average value	195.3	132.5	116.2	44.1	0.9976

Table 7 Calculated Values of Kinetics Parameters of $\text{Eu}_2(p\text{-CIBA})_6(\text{phen})_2$ for Stage 2

	$E/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta G/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S/(\text{J} \cdot \text{mL}^{-1})$	$\ln(A/\text{s}^{-1})$	r
Achar method	279.5	178.1	139.6	47.1	0.9971
MKN method	282.5	205.5	106.0	43.1	0.9989
average value	281.0	191.8	122.8	45.1	0.9980

Table 4, the possible mechanism function is function No. 18 ($f(\alpha) = (1 - \alpha)^2$, $g(\alpha) = (1 - \alpha)^{-1} - 1$). The kinetic equation of this process is $d\alpha/dt = A \exp(-E/RT)(1 - \alpha)^2$. For the second stage of decomposition of the title compound, it can be seen that from the data in Table 5, the possible mechanism function is function No. 6 ($f(\alpha) = 3/2(1 - \alpha)^{4/3} [1/(1 - \alpha)^{1/3} - 1]^{-1}$, $g(\alpha) =$

$[\{1/(1-\alpha)\}^{1/3}-1]^2$). The kinetic equation of this process is $d\alpha/dt = A\exp(-E/RT)^{3/2}(1-\alpha)^{4/3}[\{1/(1-\alpha)\}^{1/3}-1]^{-1}$. By substituting $\ln A$, E in the first and second stages of decomposition obtained through the differential and integral methods into equations (4) and (7), the values of ΔS and ΔG in Table 6 and Table 7 were obtained. Furthermore, in order to judge the precise values of the most probable mechanism obtained, in the present study the Ozawa method (equation (3)) is used to calculate the activation energy value of the first and second decomposition process of $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$ ($E_1 = 200.5 \text{ kJ} \cdot \text{mol}^{-1}$, $r = 0.9843$ and $E_2 = 279.7 \text{ kJ} \cdot \text{mol}^{-1}$, $r = 0.9956$). We found that the E and r values are much close to the average value given by the differential and integral methods.

3 Conclusions

The thermal decomposition of the $\text{Eu}_2(p\text{-ClBA})_6(\text{phen})_2$ occurs mainly in three steps. The kinetic equation for the first stage of decomposition reaction is $d\alpha/dt = A\exp(-E/RT)(1-\alpha)^2$. The second stage of decomposition mechanism is three-dimensional (Zhuralev, Lesokin and Tempelman equation) Model D3, the kinetic equation is $d\alpha/dt = A\exp(-E/RT)^{3/2}(1-\alpha)^{4/3}[\{1/(1-\alpha)\}^{1/3}-1]^{-1}$. In the first stage, the activation energy is $195.3 \text{ kJ} \cdot \text{mol}^{-1}$, the free energy of activation is $132.5 \text{ kJ} \cdot \text{mol}^{-1}$, the entropy of activation (ΔS) is $116.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. In the second stage, the activation energy is $281.0 \text{ kJ} \cdot \text{mol}^{-1}$, the free energy of activation is $191.8 \text{ kJ} \cdot \text{mol}^{-1}$, the entropy of activation (ΔS) is $122.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

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