

Preparation and Thermal Decomposition Kinetics of Copper(II) Complex with 1-(6-Hydroxynaphthalen-2-yl)butane-1,3-dione

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ABSTRACT: A complex of Cu(II) with 1-(6-Hydroxynaphthalen-2-yl) Butane-1,3-Dione (HNBD) was synthesized and characterized by elemental analysis, IR, UV and DTA-TG-DTG techniques. IR spectra as well as UV-visible absorption measurements indicated that Cu(II) ion was coordinated to the HNBD ligand. The TG-DTA-DTG curves showed that thermal decomposition of the anhydrous complex was a two-stage process and the residue of decomposition was CuO. The decomposition mechanism and non-isothermal kinetic parameters of the complex were obtained from the analysis of TG-DTG data using three kinds of integral methods (Coat-Redfern equation, HM equation, MKN equation) and differential method (Achar equation). The results indicate that the kinetic equations with parameters describing the thermal decomposition reaction are $\frac{d\alpha}{dt} = 3.53 \times 10^{38} [0.5(1-\alpha)^3] e^{-\frac{50250.2}{T}}$ with $E = 417.78$ kJ/mol, $A = 3.53 \times 10^{38}/s$, $\Delta S = 487.55$ J/K·mol and $n = 3$ for the first stage, $\frac{d\alpha}{dt} = 4.74 \times 10^5 (1-\alpha)^2 e^{-\frac{11723.6}{T}}$ with $E = 88.76$ kJ/mol, $A = 4.74 \times 10^5$, $\Delta S = -144.59$ J/K·mol and $n = 2$ for the second stage.

KEY WORDS: Thermal decomposition kinetics, DTA-TG-DTG, Cu(II) complex, 1-(6-hydroxynaphthalen-2-yl) butane-1,3-dione.

INTRODUCTION

The β -diketone compounds are generally bidentate ligands, which theoretically can form complexes with all the non-radioactive metals of the periodic table. Their metal complexes play an important role in the design and synthesis of molecular materials and they have been generally used as precursors for Chemical Vapor Deposition (CVD), Metal-Organic Chemical Vapor Deposition (MOCVD), laser materials, electrochemical devices, organometallic liquid crystal,

proton NMR shift reagents, the petroleum industry, and analytical chemistry [1-6]. The most important feature of β -diketonate compounds is the tautomeric equilibrium of the keto and enol forms because of the presence of β -diketonate carbonyl groups with at least one proton on the intermediate carbon atom. So many authors have also reported the synthesis, luminescence, spectroscopic characteristics, structure, and other properties of β -diketonate complexes [7-9].

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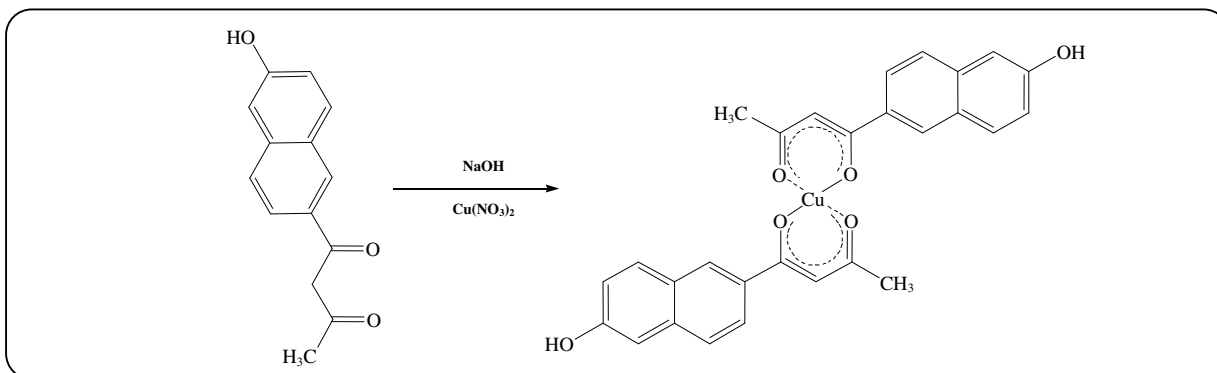


Fig. 1: Synthetic scheme of the complex.

In order to promote the applications of β -diketonate complexes, the knowledge of the thermal behavior and thermodynamic data are useful and essential. In previous literature, the thermo-chemistry and the kinetics of the β -diketone complexes have been reported [10,11]. However, no attempt appears to have been made to anchor 1-(6-HydroxyNaphthalen-2-yl)Butane-1,3-Dione (HNBD) ligand and study the thermal behavior and kinetics of HNBD complexes. In present work, the preparation and characterization of new complex of HNBD with copper(II) is reported. Also, the thermal behavior of the complex is discussed in details and different thermodynamic activation parameters are calculated.

EXPERIMENTAL SECTION

Chemicals

1-(6-HydroxyNaphthalen-2-yl) Butane -1,3- Dione (HNBD, 99.5%) was provided by Huangshi Shengkang Pharmaceutical Co. Ltd. Other chemicals and reagents used were of analytical grade.

Analysis and Physical Measurements

The Copper (II) of the complex was determined by EDTA volumetric analysis. The contents of carbon, and hydrogen were carried out on a PE 2400 elemental analyzer. UV-visible spectra were recorded in DMF on Shimadzu UV-2501PC spectrophotometer. The infrared spectra were measured on a Nicolet IMP410 FTIR spectrometer with KBr pellets. The amount of water of the complex was determined from TG curve.

The TG, DTG and DTA curves were performed on a Perkin Elmer Pyris Diamond TG/DTA simultaneous thermal analyzer. The experiments were carried out

in dynamic nitrogen atmosphere (100 mL / min) with a heating rate of 10 K/min in the temperature range of 298-1123 K. A platinum crucible (diameter 5 mm) was used with alumina as the reference material.

Preparation of copper complex with HNBD

The method of preparation of copper complex was described in Ref. [8]. The synthetic scheme is shown in Fig. 1. 5.0mmol HNBD and 2.0mmol $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 50mL 95% ethanol under heating, then 5% aqueous solution of sodium hydroxide was added dropwise with stirring and adjusted to $\text{pH} = 6-7$. The green-yellowish precipitate was formed immediately, and the mixture was stirred for 2h under temperature range of 60–70 °C. After filtration, the precipitate was repeatedly washed with ethanol and distilled water. The green-yellow powder was dried under silica gel for 3 days. The copper complex $[\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_3)_2 \cdot \text{H}_2\text{O}]$ was obtained. (Anal. Calcd. for $\text{C}_{28}\text{H}_{24}\text{O}_7\text{Cu}$ (%): C 62.74, H 4.51, Cu 11.86; Found: C 62.52, H 4.50, Cu 11.95).

RESULTS AND DISCUSSION

IR Spectra

The IR spectra of copper complex and ligand were shown in Fig.2. Some data were quite different between the ligand and the complex, which showed the structure change of the ligand after coordination. The IR spectra of the HNBD and the complex were very similar from 4000 to 1650 cm^{-1} , which assigned to the stretching vibrations of hydroxy groups of naphthol and water, unsaturated C–H and saturated C–H. But they are substantially different in the range of 1650–400 cm^{-1} . The strong carbonyl stretching peak at 1631 cm^{-1} in HNBD

shifted to 1625 cm^{-1} , which indicated the interaction of the carbonyl and copper(II) ion within the complex. However, there was another new strong peak at 1519 cm^{-1} in the complex attributable to the characteristic $\text{C}=\text{C}$ stretching peak of the HNBD ligand coordinating with the central $\text{Cu}(\text{II})$ ion in the form of an alkenol anion [7,12]. Coordination of the oxygen atom was confirmed with the presence of new bands at $475\text{--}450\text{ cm}^{-1}$ region assignable to $\nu(\text{Cu-O})$ for the complex [13]. The $\nu(\text{C-O}$ or $\text{C-CO-C})$ frequency shifted in the complex towards or higher values as a result of coordination of the oxygen to the metal ion [14].

UV-Visible spectra

The UV-visible spectra of the HNBD and the complex in DMF were shown in Fig. 3. The UV-visible spectra of the HNBD in DMF solution exhibited two broad absorption bands at 265.5 and 330.0 nm, which corresponded to the $\pi\rightarrow\pi^*$ electronic transfer on the naphthyl ring and the $n\rightarrow\pi^*$ electronic transfer on the carbonyl group [7,12]. The UV-visible spectra of the complex in DMF solution also showed two broad absorption bands. The former band has no change, but the latter one red-shifted about 9 nm, which indicated that the HNBD ligand forms a bigger conjugate system after coordination with the copper ion.

Thermal behavior

The DTA-TG-DTG curves for the thermal decomposition of $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_3)_2\cdot\text{H}_2\text{O}$ were shown in Fig.4 ($\beta=10\text{ K/min}$). It could be seen that, the dried sample contains one molecule of physically adsorbed water, which is gradually evolved in the temperature range of $30\text{--}134^\circ\text{C}$ without any substantial change in the DTA curve. Thermal decomposition of the anhydrous complex showed two stages. The first stage of decomposition process occurred between 134 and 367°C with 53.5% mass loss (calculated loss 53.4%). There was a small endothermic effect at 293°C on the DTA curve due to the loss of two naphthol molecules. The second stage took place between 367 and 828°C with 28.4% mass loss (calculated loss 28.4%). The DTA curve displayed a strong and broad exothermic peak at 537.5°C attributable to the oxidative decomposition of other organic fragments of ligand. The final decomposition product was CuO (found: 14.8% and calculated: 14.8%). The most probable thermal decomposition scheme can be expressed in Fig.5.

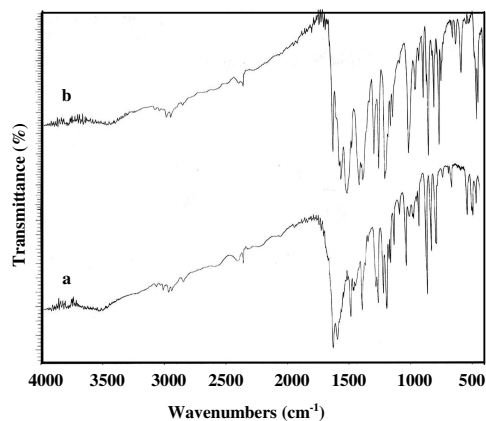


Fig. 2: IR spectra of the HNBD (a) and the complex (b).

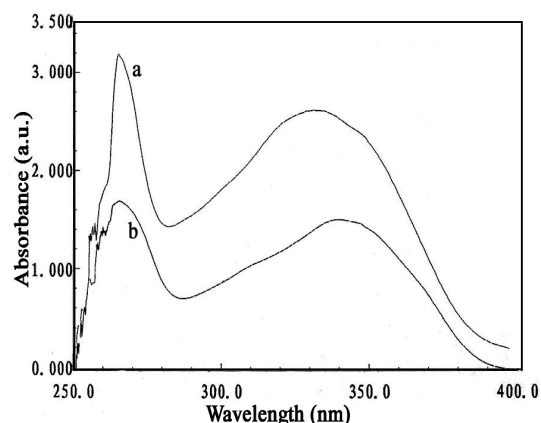


Fig. 3: UV-visible spectra of the HNBD (a) and the complex (b).

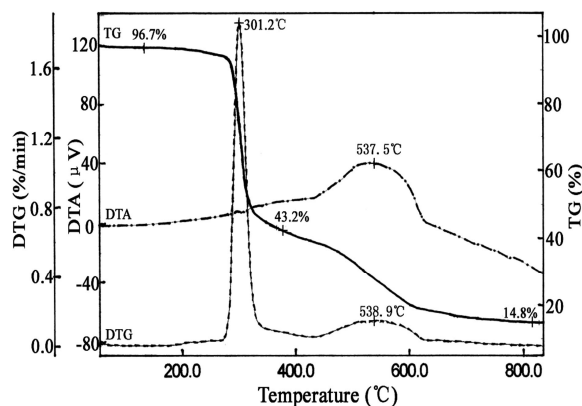


Fig. 4: DTA-TG- DTG curves of $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_3)_2\cdot\text{H}_2\text{O}$.

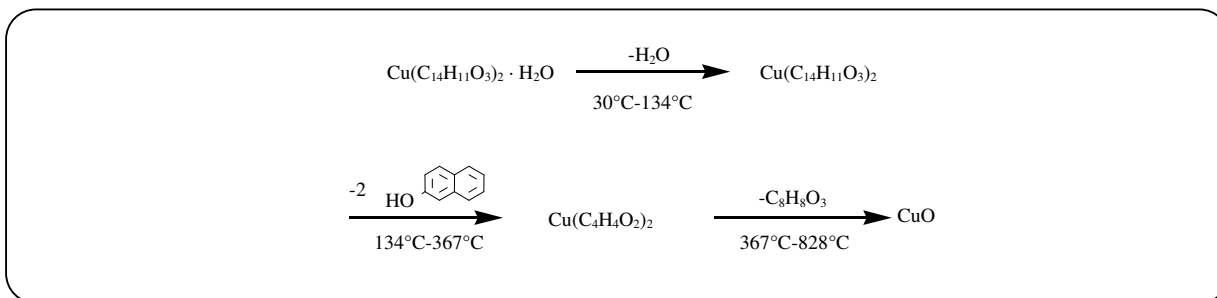


Fig. 5: Thermal decomposition scheme for the complex.

The Non-isothermal decomposition kinetic studies

Determination of kinetic mechanism

In general, the equation in the non-isothermal decomposition kinetics of solid-state reactions is presented as [15]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha), \quad (\beta = dT/dt) \quad (1)$$

From Eq. (1), the Achar equation and the Coats-Redfern equation are deduced:

Achar equation [16]:

$$\ln\left[\frac{d\alpha/dt}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \quad (2)$$

Coats-Redfern equation [17]:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (3)$$

Where α is the reaction fraction of decomposition, $d\alpha/dt$ is the rate of conversion, β is the linear heating rate, A is the pre-exponential factor, E is the apparent activation energy, R is gas constant, T is the absolute temperature, $f(\alpha)$ and $g(\alpha)$ are the differential and integral mechanism functions respectively.

The basic parameters of T , α and $d\alpha/dt$ obtained from the TG-DTG curves were listed in Table 1. In our work, the determination of the mechanism was calculated using an IBM computer with a BASIC program. The first stage of the complex was taken as an example to demonstrate the process. On substitution of the basic parameters in Table 3 and the fourteen types mechanism function $f(\alpha)$ and $g(\alpha)$ [18] into Eqs.(2) and (3), the values of E , $\ln A$ and the linear correlation coefficients r of different mechanism function were calculated from weighted least-

squares plot of $\ln[d\alpha/dt/f(\alpha)]$ vs. $\frac{1}{T}$ and of $\ln[g(\alpha)/T^2]$ vs. $[1/T]$. The results were listed in Table 2. When the values of E and $\ln A$ obtained by the two methods were approximately equal and the linear correlation coefficient was better, it could be concluded that the relevant function was the probable thermal decomposition mechanism of the complex.

Comparing the kinetic parameters for the first stage of decomposition of the complex, it could be suggested that the function of the possible mechanism should be No.14 and corresponding the values of E , $\ln A$ and r were 436.29 kJ/mol^{-1} , 94.21 and 0.9796 for Achar method, 416.65 kJ/mol^{-1} , 88.51 and 0.9914 for Coats-Redfern method. These values of E and $\ln A$ by Achar method and Coats-Redfern method accorded with the calculated values in Table 3 obtained by MKN method and HM method. Therefore, it can be concluded that the decomposition in the first stage was controlled by chemical reaction (third order) and the kinetic equation of this process was $d\alpha/dt = Ae^{-E/RT} \cdot 0.5(1-\alpha)^3$.

According to the same method, the calculated kinetic parameters E , $\ln A$ and linear correlation coefficients r for the second stage of the thermal decomposition were listed in Table 3. The values of E , and $\ln A$ obtained by Achar method ($E=99.90 \text{ kJ}\cdot\text{mol}^{-1}$, $\ln A=14.28$, $r=0.9940$) and Coats-Redfern method ($E=96.63 \text{ kJ}\cdot\text{mol}^{-1}$, $\ln A=12.71$, $r=0.9989$) were approximately the same and the linear correlation coefficients r were better when the function is No.13 in Ref. [15], and in accordance with those by MKN method and HM method. Consequently, the decomposition of the second stage may be chemical reaction (second order) model, and the kinetic equation was $d\alpha/dt = Ae^{-E/RT} \cdot (1-\alpha)^2$.

Table 1: Base data for thermal decomposition of the complex.

No.	The first stage			The second stage		
	T (K)	α	$d\alpha/dt$	T (K)	α	$d\alpha/dt$
1	550.8	0.049	0.086	699.2	0.086	0.054
2	554.4	0.054	0.167	708.6	0.105	0.055
3	558.0	0.067	0.337	719.3	0.131	0.064
4	560.8	0.091	0.686	730.2	0.157	0.073
5	563.6	0.125	0.997	738.4	0.184	0.085
6	565.6	0.163	1.151	746.2	0.210	0.096
7	567.6	0.212	1.373	754.1	0.240	0.105
8	569.3	0.263	1.564	762.4	0.273	0.112
9	570.7	0.306	1.694	769.3	0.303	0.122
10	572.7	0.353	1.791	776.2	0.333	0.132
11	573.4	0.395	1.844	784.3	0.378	0.138
12	574.8	0.446	1.865	792.2	0.416	0.135
13	576.2	0.495	1.845	802.9	0.472	0.136
14	577.6	0.545	1.792	810.7	0.513	0.136
15	579.1	0.598	1.700	818.7	0.551	0.136
16	580.6	0.643	1.584	826.7	0.592	0.135
17	582.0	0.685	1.443	835.7	0.637	0.133
18	583.8	0.728	1.262	844.8	0.682	0.127
19	585.5	0.764	1.075	854.9	0.730	0.118
20	587.5	0.797	0.874	864.9	0.772	0.106
21	589.8	0.826	0.669	874.7	0.809	0.089
22	592.4	0.851	0.482	885.6	0.839	0.059
23	595.5	0.871	0.332	899.2	0.861	0.036
24	598.7	0.886	0.235	909.5	0.873	0.035
25	602.5	0.899	0.168	921.1	0.888	0.033
26				932.6	0.903	0.032
27				945.7	0.918	0.029
28				957.5	0.929	0.027
29				971.8	0.944	0.023
30				985.7	0.955	0.020

Table 2: Results of kinetic analysis for the first stage of the complex.

Function No.	Achar method			Coats-Redfern method		
	E (kJ·mol ⁻¹)	lnA (s ⁻¹)	r	E (kJ·mol ⁻¹)	lnA (s ⁻¹)	r
1	-127.73	-27.48	0.6649	35.30	5.05	0.9105
2	70.32	15.16	0.4706	149.85	30.24	0.9694
3	30.46	6.67	0.2369	109.97	21.71	0.9679
4	-9.39	-1.95	0.0791	70.14	13.05	0.9653
5	-29.32	-6.35	0.2466	50.18	8.61	0.9613
6	78.46	15.92	0.4305	196.83	39.20	0.9551
7	102.32	20.64	0.5425	207.06	41.05	0.9607
8	186.40	38.36	0.6126	349.45	71.11	0.9400
9	246.03	50.50	0.7324	382.11	77.55	0.9506
10	318.96	64.67	0.8343	423.69	85.09	0.9624
11	271.24	54.41	0.7736	395.78	79.02	0.9549
12	150.03	31.99	0.7154	229.55	47.08	0.9706
13	293.16	62.75	0.9322	313.04	65.32	0.9885
14	436.29	94.21	0.9796	416.65	88.51	0.9914

Table 3: Kinetic parameters determined by various methods.

Stage	Methods	n	E (kJ·mol ⁻¹)	ln(A / s ⁻¹)	ΔS (J·K ⁻¹ ·mol ⁻¹)	r
First	Achar		436.29	94.21	532.90	0.9796
	Coats-Redfern		416.65	88.51	485.51	0.9914
	MKN	2.9	405.60	85.45	460.07	0.9916
	HM	2.9	412.57	86.85	471.71	0.9920
	Average		417.78	88.76	487.55	
Second	Achar		99.90	14.28	-134.50	0.9940
	Coats-Redfern		96.63	12.71	-147.56	0.9989
	MKN	1.9	92.74	12.13	-152.38	0.9989
	HM	1.9	100.60	13.15	-143.90	0.9950
	Average		97.47	13.07	-144.59	

Determination of kinetic parameters

When determined kinetic function model was a simple order function model, MKN (Madhusudanan-Krishnan-Ninan) method and HM (Horowitz-Metzger) method [Eqs. (4) and (5)] were also applied to process the TG-DTG data to calculate the kinetic parameters and the accurate reaction order and the kinetic

parameters obtained by MKN method and HM method were used to check the agreement with those by Achar method and Coats-Redfern method.

MKN equation [19]:

$$\ln\left[\frac{g(\alpha)}{T^{1.9215}}\right] = \ln\left(\frac{AE}{\beta R}\right) + 3.7721 - 1.9215 \ln E - \frac{0.12039E}{T} \quad (4)$$

HM equation [20]:

$$\ln[g(\alpha)] = \ln\left(\frac{ART_s^2}{\beta E}\right) - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \quad (5)$$

Where $g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}$ [$n=1$, $g(\alpha)=-\ln(1-\alpha)$], n is

the reaction order, T_s is a temperature where $\alpha = 1 - \frac{1}{e}$,

$\theta = T - T_s$. Plotting $\ln\left[\frac{g(\alpha)}{T^{1.9215}}\right]$ vs. $1/T$ at different

amounts of n , we obtained the values of E , $\ln A$ and r , respectively. When r is the biggest, the corresponded n is the reaction order we desired, and its kinetics parameters were obtained, too. Then substituting the best values of the reaction order (n) and the original data in Table 1 into Eq. (5) and plotting $\ln[g(\alpha)]$ vs. θ , the values of E and $\ln A$ can also be calculated by HM method.

The entropy of activation, ΔS , can be calculated using the Following equation [21]:

$$A = \frac{kT_p}{h} e^{\Delta S/R} \quad (6)$$

where, k is the Boltzmann's constant, h the Planck's constant and T_p the peak temperature.

The apparent activation energy E , the pre-exponential factor $\ln A$, the entropy of activation ΔS , the reaction order n and the linear correlation coefficients r obtained by MKN method and HM method were listed in Table 3. These kinetic parameters by MKN method and HM method were in good agreement with those by Achar method and Coats-Redfern method [Eqs.(2) and (3)], and the decomposition reaction order of the first and second stage was 3 and 2, which were also in accordance with the kinetic mechanism by Achar method and Coats-Redfern method.

Substituting $f(\alpha)$ with $0.5(1-\alpha)^3$ and $(1-\alpha)^2$, E with 417.78 and 88.76 $\text{kJ}\cdot\text{mol}^{-1}$ (average values), A with $e^{88.76} = 3.53 \times 10^{38}$ and $e^{13.07} = 4.74 \times 10^5 \text{ s}^{-1}$ (average values) in Eq. (1) respectively, the kinetic Eqs.(7) and (8) for the decomposition of the complex could be obtained:

$$\frac{d\alpha}{dt} = 3.53 \times 10^{38} [0.5(1-\alpha)^3] e^{-\frac{50250.2}{T}} \text{ for the first stage, } (7)$$

$$\frac{d\alpha}{dt} = 4.74 \times 10^5 (1-\alpha)^2 e^{-\frac{11723.6}{T}} \text{ for the second stage. } (8)$$

CONCLUSIONS

The IR spectra as well as UV-visible absorption measurements provided evidence that Cu(II) ion were coordinated to the HNBD ligand. The thermal decomposition mechanism and the non-isothermal kinetics of $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_3)_2 \cdot \text{H}_2\text{O}$ were investigated by means of DTA-TG-DTG technique. The results showed that thermal decomposition of $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_3)_2 \cdot \text{H}_2\text{O}$ was the removal of one molecule of physically adsorbed water below 134 °C at first, and then the decomposition of anhydrous complex exhibited two stages. The first stage was the elimination of two naphthol molecules between 134 and 367 °C, which was controlled by chemical reaction (third order) with the corresponding activation energy (E) of 417.78 $\text{kJ}\cdot\text{mol}^{-1}$, the pre-exponential factor (A) of $3.53 \times 10^{38} \text{ s}^{-1}$, the entropy of activation (ΔS) of 487.55 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and the reaction order (n) of 3. The second stage was the oxidative decomposition of other organic fragments of ligand between 367 and 828 °C, which might be chemical reaction (second order) mechanism with the corresponding activation energy (E) of 88.76 $\text{kJ}\cdot\text{mol}^{-1}$, the pre-exponential factor (A) of $4.74 \times 10^5 \text{ s}^{-1}$, the entropy of activation (ΔS) of $-144.59 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and the reaction order (n) of 2.

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