

## Preparation and Study of Thermal Decomposition Mechanism of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O

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The complex of Zn(AcO)<sub>2</sub>•2H<sub>2</sub>O and threonine was prepared in the mixture solvent of water-acetone, the composition of which was identified as Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O by chemical and elemental analyses. The complex was investigated by XRD, IR, TG-DTG and DSC methods. The result of TG-DTG shows that the thermal decomposition processes of the complex can be divided into three stages, which were dehydration (I), partial decomposition (II) and complete decomposition into ZnO (III). Dehydration enthalpy was 126.89 kJ•mol<sup>-1</sup>, decomposition enthalpy of the stage (II) was 79.50 kJ•mol<sup>-1</sup>. The study of non-isothermal kinetics shows that the mechanism of the dehydration stage was Maple Power of  $n=3/2$ , the apparent activation energy  $E$  was 145.32 kJ•mol<sup>-1</sup> and the pre-exponential factor  $A$  was  $1.4125 \times 10^{17} \text{ s}^{-1}$ , and that of ligand-losing process was nucleation and growth mechanism (Avrami-Erofeev equation  $n=1/2$ ), its  $E$  was 189.33 kJ•mol<sup>-1</sup>, and  $A$  was  $3.4674 \times 10^{18} \text{ s}^{-1}$ . The empirical kinetics model equations of the investigated processes were proposed.

**Keywords** Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O, preparation, characterization, thermal analysis

### Introduction

$\alpha$ -Amino acids as additive have a wide application in medicines, foodstuff and cosmetics.<sup>1-3</sup> The synthetic methods of amino acid have been reviewed.<sup>4,5</sup> The solubility property of Zn(AcO)<sub>2</sub>-Thr-H<sub>2</sub>O (Thr=Threonine) system at 298.15 K has been investigated by the semimicro-phase equilibrium method, in which the phase region of the complex did not exist.<sup>6</sup> The preparation of Zn(Thr)SO<sub>4</sub>•H<sub>2</sub>O was reported in Ref. 7: 3 times volume of acetone relative to that of water was added into the reaction solution with the molar ratio of ZnSO<sub>4</sub>:L- $\alpha$ -Thr of 1:1, and the solid complex was obtained. The solubility of the product was too big to crystallize in the ZnSO<sub>4</sub>-Thr-H<sub>2</sub>O system, however by adding the amount of acetone into the system, the solubility of the product in the mixed solution decreased and the product was precipitated out. In the phase diagram, the phase region of the acid was reduced and separated from the phase region of salt, and then the phase region of complex was formed.

In this paper, the solid complex of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O was prepared in the mixture solvent of water-acetone (the optimum volume ratio of 1:9). This compound was characterized by chemical and elemental analyses, IR, XRD, TG-DTG, DSC and the non-isothermal kinetic parameters and the mechanism of the former two processes were obtained.

### Experimental

#### Materials

Zn(AcO)<sub>2</sub>•2H<sub>2</sub>O, A.R. (made in Xi'an Chemical Reagent Company); L- $\alpha$ -Thr, B.R. (Shanghai Kangda Reagent Company), purity >99.9%; acetone (C<sub>3</sub>H<sub>6</sub>O), A.R. (made in Xi'an Chemical Reagent Company) with its density 0.79 g•cm<sup>-3</sup> at 298.15 K; the conductivity of the deionized water is  $5.48 \times 10^{-8} \text{ s} \cdot \text{cm}^{-1}$  with its density 0.99705 g•cm<sup>-3</sup> at 298.15 K; and the others are of A.R. grade.

#### Analytical methods

The Zn<sup>2+</sup> was determined complexometrically with EDTA. Thr was analyzed by the formalin method, and the Zn<sup>2+</sup> was removed by precipitating it with K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> before it was titrated. The blank titration was performed for comparison. Carbon, hydrogen, and nitrogen analyses were carried out on a 2400-type (P. E. Ltd.) elemental analyzer.

#### Equipments

The TG-DTG and DSC analyses for the title compound were conducted on a P. E. 2100 Company thermal analyzer in a 60 mL•min<sup>-1</sup> N<sub>2</sub> atmosphere, the heating rate of TG-DTG was 10 °C•min<sup>-1</sup> and that of DSC was 5.0, 10.0, 20.0 and 40.0 °C•min<sup>-1</sup>. The

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weight of the sample was about 1 mg. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as reference material in the DSC measurements. The IR analysis was conducted on a BEQ, UZNDX-550 spectrometer (KBr discs). An X-ray powder diffractometer typed in D/max-III with Cu K $\alpha$  radiation was used.

### Preparation of the complex

Zn(AcO)<sub>2</sub>•2H<sub>2</sub>O and *L*- $\alpha$ -Thr (in a mole ratio of 1 : 1) were dissolved in the deionized water. This solution was allowed to stand for 8 h at 60–70 °C and cooled to room temperature. Zn(Thr)<sup>2+</sup> (aq.) was produced from the reaction of Zn(AcO)<sub>2</sub> with Thr in water (*lg K* is 4.43<sup>8</sup>). The white solid compound was obtained when adding nine times volume of acetone relative to that of water to the reaction system. After suction filtration, followed by washing with small amounts of acetone and drying to constant weight in vacuum, the white powder was obtained. The experimental results of water and acetone with the different volume ratios are given in Table 1. XRD indicates that the distance between faces of the strong diffraction rays was respectively *d* = 0.6835 (72), 0.6641 (100), 0.3893 (75), 0.3423 (54), 0.3129 (49), 0.3033 (56), 0.2563 (91), and *d* = 5.0692 (100), 4.7872 (28), 4.7263 (32), 4.3806 (40), 4.3000 (48), 4.0922 (58), 3.8504 (38) and 3.7112 (74) nm, and the diffraction peak graph of the complex was different from either that of Thr or that of Zn(AcO)<sub>2</sub>•2H<sub>2</sub>O, showing that the new phase was formed.

## Results and discussion

### Composition

The results of the chemical and elemental analyses of the complex are listed as Zn 19.09%, Thr 35.08%, C 28.24%, H 5.56%, N 4.36% compared with the calculation value: Zn 19.31%, Thr 35.18%, C 28.38%, H 5.66%, N 4.14%, which shows that the composition of the compound is Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O.

### IR spectrum

IR absorption data for the main groups of the complex and the ligand are summarized in Table 2. The non-existence of the characteristic absorption bands of

group —COOH at 1700–1750 cm<sup>-1</sup> for the complex reveals that Thr still keeps its zwitterion structure.<sup>7</sup> and the wide shifts of  $\nu_{as}(-NH_3^+)$  and  $\nu_{as}(COO^-)$  for the complex in contrast with ligand show that Zn<sup>2+</sup> binds to the oxygen atom on carboxylic group and the nitrogen atom in amino group of Thr.  $\nu(OH)$  of alcoholic hydroxyl in the complex appears unchanged compared to that of ligand, indicating that the oxygen atom in the —C—OH group does not coordinate to Zn<sup>2+</sup>.<sup>9</sup> The wide characteristic absorption band of  $\nu_{as}(OH^-)$  at 3440.7 cm<sup>-1</sup> reveals that the complex contains H<sub>2</sub>O molecules. The characteristic absorption of  $\nu(ZnO)$  at 364 cm<sup>-1</sup> is not present,<sup>10</sup> which indicates that the role of water is crystal water.

### Thermal behavior and decomposition mechanism

The curves of TG-DTG and DSC of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O are shown in Figures 1 and 2.

Concerning the TG-DTG curve, it displays four peaks during the thermal decomposition.

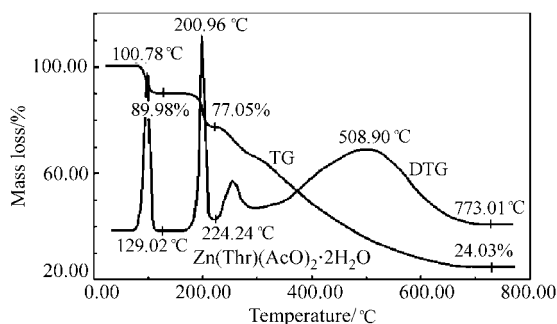
Obviously, the former two processes are discriminable and identified as dehydration and decomposition processes but for the latter two processes, it can be regarded as one integral process because its indiscernibility. So the decomposition processes of the compound Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O can be divided into three stages: dehydration (I), partial decomposition (II) and complete decomposition into ZnO (III). The decomposition-interruption tests for identifying the intermediates were carried out by IR method. In the first stage from 75 to 129 °C, a mass loss of 10.02% was observed, corresponding to the loss of two molecules of water 10.99%. The IR spectra of the products show that the wide characteristic absorption peaks for water molecules have disappeared. In the second stage, the complex is decomposed from 129 to 224 °C. The characteristic absorption peaks for the complex and Zn(AcO)<sub>2</sub> appear in the spectra of the decomposition products, indicating that certain amounts of Zn(Thr)(AcO)<sub>2</sub> have been transformed into Zn(AcO)<sub>2</sub>. The mass loss corresponding to the formation of Zn(Thr)(AcO)<sub>2</sub>•Zn(AcO)<sub>2</sub> from Zn(Thr)(AcO)<sub>2</sub> is 11.38%. The experimental mass

**Table 1** Experimental results of water and acetone with the different volume ratios

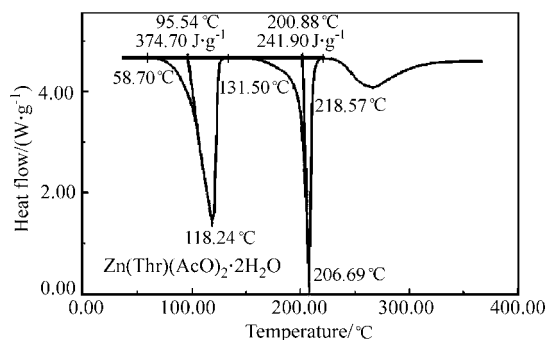
Volume ratio	1 : 3	1 : 5	1 : 8	1 : 9	1 : 13	1 : 17
Phenomenon	turbid	turbid	precipitate	precipitate	precipitate decreasing gradually	
Yield/%	—	—	18	34	21	19

**Table 2** Data of IR absorption for main groups of ligand and complex (cm<sup>-1</sup>)

Sample	$\nu_{NH_3^+}^{as}$	$\nu_{NH_3^+}^s$	$\delta_{NH_3^+}^{as}$	$\delta_{NH_3^+}^s$	$\nu_{COO^-}^{as}$	$\nu_{COO^-}^s$	$\nu_{OH}$	$\nu_{C-OH}$
Ligand	3133.1	2050.9	1627.1	1479.2	1550.0	1416.9	—	1107.4
Complex	3219.7	2109.3	1644.5	1405.0	1614.5	1375.5	3440.7	1108.6



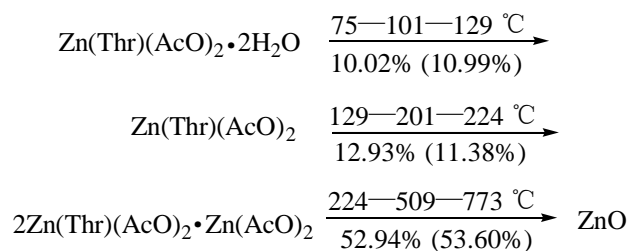
**Figure 1** TG-DTG curve of  $\text{Zn(Thr)(AcO)}_2 \cdot 2\text{H}_2\text{O}$  ( $\beta = 10.0 \text{ } ^\circ\text{C} \cdot \text{min}^{-1}$ ).



**Figure 2** DSC curve of the complex ( $\beta = 10.0 \text{ } ^\circ\text{C} \cdot \text{min}^{-1}$ ).

loss is 12.93%. In the third stage, the IR spectrum of the final decomposition products coincides with the standard IR spectrum of ZnO, indicating that the intermediates are further decomposed to ZnO from 224 to 773 °C. The formation of ZnO from the original complex should be accomplished with the experimental mass loss of 52.94%. This value is approximately in agreement with the experimental value of 53.60%. On the basis of above-mentioned results, the thermal decomposition mechanism of  $\text{Zn(Thr)(AcO)}_2 \cdot 2\text{H}_2\text{O}$  was postulated to be as Scheme 1. In order to understand the former two decomposition processes of the title compound, DSC experiments were conducted. The DSC curves consisted also of the former two processes. Compared with TG-

### Scheme 1



DTG curve, the two steps can be regarded as water-losing and ligand-losing processes and the enthalpy change is 126.89, 79.50  $\text{kJ} \cdot \text{mol}^{-1}$ , respectively.

### Non-isothermal decomposition kinetics

In order to obtain the most probable mechanism function and the corresponding kinetic parameters for the former two decomposition processes of the complex from the DSC curves, the following six integral methods and two differential methods were employed.

In Table 3,  $\alpha$  is the fractional decomposition,  $T$  the temperature ( $^\circ\text{C}$ ) at time  $t$ ,  $T_0$  the initial temperature at which DSC curve deviates from the baseline,  $R$  the gas constant,  $A$  the pre-exponential factor,  $E$  the apparent activation energy,  $\beta$  the heating rate,  $f(\alpha)$  and  $G(\alpha)$  are the differential and integral mechanism functions, respectively,  $T_p$  is the peak temperature of DSC curve. The data needed for the equations of the integral and differential methods  $\beta$ ,  $T_0$ ,  $T_i$ ,  $\alpha_i$ ,  $(dH/dt)_i$ ,  $i=1, 2, 3 \dots n$ , were obtained from the DSC curves and summarized in Tables 4 and 5. After substituting all the mechanism function forms<sup>20</sup> of  $f(\alpha)$  and  $G(\alpha)$  and the original data in Tables 4 and 5 into Eqs. (1)–(8), the values of  $A$  and  $E$  can be calculated at various heating rates of 5.0, 10.0, 20.0, and 40.0  $^\circ\text{C} \cdot \text{min}^{-1}$ , and the variance  $Q$  was got by the linear least-squares method on the computer. All the calculated results from the eight methods for the water-losing and ligand-losing processes at 5.0, 10.0, 20.0, and 40.0  $^\circ\text{C} \cdot \text{min}^{-1}$  are shown in Tables 6 and 7.

**Table 3** The kinetic analysis methods

Method	Equation	
Ordinary-integral <sup>11</sup>	$\ln[G(\alpha)/T^2] = \ln[(AE/\beta R)(1 - 2RT/E)] - E/RT$	(1)
Universal-integral <sup>12,13</sup>	$\ln[G(\alpha)/(T - T_0)] = \ln A/\beta - E/RT$	(2)
Mac Callum-Tanner <sup>14</sup>	$\lg[G(\alpha)] = \lg(AE/\beta R) - 0.4828E^{0.4357} - (0.449 + 0.217E)/0.001T$	(3)
Šatava-Šesták <sup>15</sup>	$\lg G(\alpha) = \lg(AE/\beta R) - 2.315 - 0.4567E/RT$	(4)
Agrawal <sup>16</sup>	$\ln[G(\alpha)/T^2] = \ln\{(AR/\beta R)[1 - 2RT/E]/[1 - 5(RT/E)^2]\} - E/RT$	(5)
Starink <sup>17</sup>	$\ln[\beta/T^{1.8}] = C_s - E/RT$	(6)
Ozawa-Doyle <sup>18</sup>	$\lg\beta_i = \lg[AE/RG(\alpha)] - 2.315 - 0.4567(E/RT_i)$	(7)
Kissinger <sup>19</sup>	$\ln[\beta_i/T_{pi}^2] = \ln[AR/E] - E/RT_{pi}$	(8)

**Table 4** Data for the decomposition process of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O in stage I at different heating rates

5 (°C•min <sup>-1</sup> )			10 (°C•min <sup>-1</sup> )			20 (°C•min <sup>-1</sup> )			40 (°C•min <sup>-1</sup> )		
<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub>i</sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub>i</sub>	<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub>i</sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub>i</sub>	<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub>i</sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub>i</sub>	<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub>i</sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub>i</sub>
90	1.2896	0.1030	102	2.1502	0.2167	115	9.2814	0.3677	119	12.4432	0.2870
91	1.2594	0.1192	103	2.0875	0.2370	116	9.0148	0.3925	120	11.9350	0.3101
92	1.2310	0.1363	104	2.0224	0.2591	117	8.6800	0.4202	121	11.1573	0.3376
93	1.2058	0.1558	105	1.9580	0.2826	118	8.2584	0.4510	122	10.0485	0.3709
94	1.1806	0.1762	106	1.8848	0.3079	119	7.6880	0.4864	123	8.5778	0.4130
95	1.1548	0.1974	107	1.8104	0.3353	120	6.8944	0.5281	124	6.4719	0.4668
96	1.1233	0.2201	108	1.7341	0.3648	121	5.3934	0.5817	125	3.6637	0.5395
97	1.0868	0.2450	109	1.6517	0.3959	122	1.9573	0.6663	126	2.3909	0.6200
98	1.0452	0.2718	110	1.5692	0.4293	123	1.5698	0.7590	127	3.0608	0.6933
99	0.9979	0.3008	111	1.4775	0.4657	124	3.5786	0.8301	128	4.7163	0.7554
100	0.9469	0.3315	112	1.3882	0.5043	125	5.8776	0.8830	129	6.6305	0.8075
101	0.8952	0.3637	113	1.2970	0.5447	126	7.5640	0.9223	130	8.4084	0.8504
102	0.8442	0.3991	114	1.2096	0.5867	127	8.9218	0.9511	131	10.0023	0.8856
103	0.7925	0.4369	115	1.1129	0.6316	128	10.0874	0.9708	132	11.4037	0.9133
104	0.7396	0.4764	116	1.0236	0.6808	129	10.9244	0.9831	133	12.5741	0.9350
105	0.6892	0.5196	117	0.9536	0.7311				134	13.5058	0.9516
106	0.6451	0.5652	118	0.9108	0.7823				135	14.2142	0.9640
107	0.6066	0.6188	119	0.9325	0.8336						
108	0.5746	0.6678	120	1.0658	0.8824						
109	0.5519	0.7191	121	1.3435	0.9260						
110	0.5485	0.7702	122	1.7819	0.9599						
111	0.5653	0.8213	123	2.2928	0.9811						
112	0.6101	0.8690	124	2.6424	0.9917						
113	0.7088	0.9145	125	2.8012	0.9964						
114	0.8908	0.9534									
115	1.1768	0.9801									
116	1.4446	0.9936									
117	1.5750	0.9982									
	<i>T</i> <sub>0</sub> =51.08 °C		<i>T</i> <sub>0</sub> =58.70 °C			<i>T</i> <sub>0</sub> =60.88 °C			<i>T</i> <sub>0</sub> =70.12 °C		
	<i>T</i> <sub>p</sub> =109.96 °C		<i>T</i> <sub>p</sub> =117.62 °C			<i>T</i> <sub>p</sub> =122.52 °C			<i>T</i> <sub>p</sub> =126.22 °C		
	<i>H</i> <sub>0</sub> =250.299 mJ		<i>H</i> <sub>0</sub> =232.314 mJ			<i>H</i> <sub>0</sub> =354.082 mJ			<i>H</i> <sub>0</sub> =263.571 mJ		

**Table 5** Data for the decomposition process of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O in stage II at different heating rates

5 (°C•min <sup>-1</sup> )			10 (°C•min <sup>-1</sup> )			20 (°C•min <sup>-1</sup> )			40 (°C•min <sup>-1</sup> )		
<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub>i</sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub>i</sub>	<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub>i</sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub>i</sub>	<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub>i</sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub>i</sub>	<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub>i</sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub>i</sub>
193	1.3780	0.2099	197	2.8100	0.2046	204	9.0150	0.2074	213	12.004	0.2125
194	1.3230	0.2318	198	2.7310	0.2257	205	8.7920	0.2243	214	11.565	0.2375
195	1.2490	0.2584	199	2.6240	0.2504	206	8.5060	0.2443	215	1.0500	0.2666
196	1.1560	0.2934	200	2.4890	0.2794	207	8.1590	0.2679	216	10.387	0.3012
197	1.0210	0.334	201	2.3000	0.3149	208	7.7130	0.2963	217	9.5400	0.3423

Continued

5 (°C•min <sup>-1</sup> )			10 (°C•min <sup>-1</sup> )			20 (°C•min <sup>-1</sup> )			40 (°C•min <sup>-1</sup> )		
<i>T</i> <sub>i</sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub><i>i</i></sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub><i>i</i></sub>	<i>T</i> <sub><i>i</i></sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub><i>i</i></sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub><i>i</i></sub>	<i>T</i> <sub><i>i</i></sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub><i>i</i></sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub><i>i</i></sub>	<i>T</i> <sub><i>i</i></sub> / °C	(d <i>H</i> /d <i>t</i> ) <sub><i>i</i></sub> / (mJ•s <sup>-1</sup> )	<i>α</i> <sub><i>i</i></sub>
198	0.8610	0.3835	202	2.0680	0.3588	209	7.1360	0.3310	218	8.4780	0.3917
199	0.6570	0.4469	203	1.7700	0.4129	210	6.3800	0.3744	219	7.2040	0.4523
200	0.4370	0.5228	204	1.4050	0.4811	211	5.4260	0.4285	220	5.9140	0.5240
201	0.2470	0.6135	205	1.0180	0.5638	212	4.2900	0.4960	221	4.5770	0.6070
202	0.0960	0.7153	206	0.6610	0.6597	213	3.2230	0.5783	222	3.9950	0.6969
203	0.0304	0.8142	207	0.4260	0.7720	214	1.6870	0.6760	223	4.7810	0.7804
204	0.7920	0.8865	208	1.1490	0.8676	215	1.3810	0.7839	224	6.6370	0.8480
205	1.1900	0.9299	209	2.0890	0.9293	216	3.1330	0.8721	225	8.7550	0.8993
206	1.4100	0.9537	210	2.6900	0.9626	217	5.9700	0.9317	226	10.626	0.9367
207	1.5130	0.9637	211	2.9980	0.9796	218	7.8240	0.9674	227	12.051	0.9620
208	1.5650	0.9762	212	3.1450	0.9884	219	9.1570	0.9864	228	13.059	0.9787
<i>T</i> <sub>0</sub> =154 °C			<i>T</i> <sub>0</sub> =160 °C			<i>T</i> <sub>0</sub> =162 °C			<i>T</i> <sub>0</sub> =175 °C		
<i>T</i> <sub>p</sub> =202.1 °C			<i>T</i> <sub>p</sub> =206.69 °C			<i>T</i> <sub>p</sub> =214.54 °C			<i>T</i> <sub>p</sub> =221.9 °C		
<i>H</i> <sub>0</sub> =148.176 mJ			<i>H</i> <sub>0</sub> =155.434 mJ			<i>H</i> <sub>0</sub> =255.02 mJ			<i>H</i> <sub>0</sub> =181.04 mJ		

**Table 6** Kinetic parameters obtained for the dehydration process of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O in stage I at different heating rates

Method	<i>β</i> /(°C•min <sup>-1</sup> )	<i>E</i> /(kJ•mol <sup>-1</sup> )	lg <i>A</i> /( <i>A</i> in s <sup>-1</sup> )	<i>r</i>	<i>Q</i>	<i>d</i> •10 <sup>3</sup>	Function
Ordinary-integral	5	146.16	17.7336	0.9895	0.6016	6.338	26
	10	124.99	14.7291	0.9919	0.1914	1.554	26
	20	148.09	17.8887	0.9848	0.1130	1.712	26
	40	160.16	19.5013	0.9719	0.3465	9.737	26
Universal-integral	5	148.79	16.4748	0.9898	0.6000	6.085	26
	10	127.63	13.5443	0.9922	0.1908	1.482	26
	20	150.78	16.6428	0.9854	0.1129	16.50	26
	40	162.78	18.2260	0.9728	0.3462	94.23	26
Mac	5	144.84	17.5103	0.9904	0.1129	10.89	26
	10	123.70	14.5109	0.9927	0.0381	4.200	26
Collum-Tanner	20	147.11	17.7095	0.9861	0.0213	2.958	26
	40	159.34	19.3463	0.9740	0.0652	16.93	26
Šatava-Šesták	5	144.94	17.5633	0.9904	0.1129	10.88	26
	10	124.97	14.7100	0.9927	0.0359	2.624	26
	20	147.08	17.7475	0.9861	0.0213	2.958	26
	40	158.62	19.3056	0.9740	0.0653	16.93	26
Agrawal	5	146.16	17.7326	0.9895	0.6017	63.38	26
	10	124.99	14.7276	0.9919	0.1914	15.54	26
	20	148.09	17.8876	0.9848	0.1130	17.12	26
	40	160.16	19.5004	0.9719	0.3465	97.37	26
Starink		152.35		0.9830	0.0751		
mean		145.32	17.15				
Kissinger		152.8	18.8	0.9829			
Ozawa		151.4		0.9842			

**Table 7** Kinetic parameters obtained for the decomposition process of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O in stage II at different heating rates

Method	$\beta/(\text{C}\cdot\text{min}^{-1})$	$E/(\text{kJ}\cdot\text{mol}^{-1})$	$\lg A/(A \text{ in } \text{s}^{-1})$	$r$	$Q$	$d\cdot 10^4$	Function
Ordinary-integral	5	182.95	18.09	0.9930	0.0464	3.253	13
	10	194.90	19.54	0.9890	0.0802	8.811	13
	20	188.19	18.75	0.9807	0.1255	24.20	13
	40	190.11	18.91	0.9963	0.0223	0.829	13
Universal-integral	5	184.97	16.80	0.9931	0.0464	3.253	13
	10	196.87	18.22	0.9892	0.0831	8.682	13
	20	190.20	17.46	0.9811	0.1256	23.77	13
	40	191.96	17.61	0.9964	0.0022	0.816	13
Mac	5	183.53	18.11	0.9935	0.0088	0.566	13
	10	195.63	19.58	0.9898	0.0151	1.542	13
Collum-Tanner	20	188.99	18.80	0.9822	0.0237	4.242	13
	40	191.08	18.98	0.9966	0.0042	0.145	13
Šatava-Šesták	5	181.46	17.92	0.9935	0.0088	0.566	13
	10	192.89	19.33	0.9898	0.0152	1.542	13
	20	186.62	18.58	0.9822	0.0237	4.224	13
	40	188.59	18.74	0.9966	0.0042	0.145	13
Agrawal	5	182.95	18.09	0.9930	0.0464	3.253	13
	10	194.90	19.54	0.9890	0.0802	8.811	13
	20	188.19	18.75	0.9807	0.1255	24.21	13
	40	190.11	18.91	0.9963	0.0230	0.089	13
Starink		190.93		0.9947	0.0240		
Mean		189.33	18.54				
Kissinger		191.40	19.01				
Ozawa		189.70					

$E$ ,  $A$ ,  $r$ , and  $Q$  obtained by the above methods are the reference foundation to choose the most probable mechanism function. Based on the following four conditions:<sup>20,21</sup> (1) the values of  $E$  and  $\lg A$  selected are in the ordinary range of the thermal decomposition kinetic parameters for solid materials ( $E=80\text{--}250 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\lg A=7\text{--}30 \text{ s}^{-1}$ ), (2) the liner correlation coefficient  $r$  is greater than 0.98, (3) the values of  $E$  and  $A$  obtained with the integral and differential methods are approximately the same, (4) the mechanism function selected must be in agreement with the tested sample state. The results of satisfying the above-mentioned conditions at the same time are the final ones as listed in Tables 6 and 7, and the relevant function is the reaction mechanism one of the water-losing and ligand-losing processes of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O.

The data in Table 6 indicates that the values of  $E$  and  $A$  from mechanism function No. 26<sup>20</sup> by Eqs. (1)–(6) are in good agreement with the calculated values obtained by Kissinger's method and Ozawa's Method, *i.e.*, the corresponding Mampel Power Law ( $n=3/2$ ) will control the water-losing process. Substituting  $f(\alpha)$  with  $2/3\alpha^{-1/2}$ ,  $E$  with  $145.32 \text{ kJ}\cdot\text{mol}^{-1}$  (average value),  $\lg A$

( $A \text{ in } \text{s}^{-1}$ ) with 17.15 in the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot f(\alpha) \cdot \exp\left(-\frac{E}{RT}\right)$$

the kinetics equation of the water-losing process of Zn(Thr)(AcO)<sub>2</sub>•2H<sub>2</sub>O was obtained:

$$\frac{d\alpha}{dT} = \frac{9.417 \times 10^{16}}{\beta} \cdot \alpha^{-\frac{1}{2}} \cdot \exp\left(-\frac{17479.0}{T}\right)$$

Similarly, from Table 7 it can be concluded that for the ligand-losing process the most probable mechanism function is No. 13:<sup>20</sup> nucleation and growth mechanism (Avrami-Erofeev equation),  $E$  is  $189.33 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\lg A$  ( $A \text{ in } \text{s}^{-1}$ ) is 18.54,  $f(\alpha)$  is  $2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$ , and the kinetics equation is

$$\frac{d\alpha}{dT} = \frac{6.935 \times 10^{18}}{\beta} \cdot (1-\alpha)[(-\ln(1-\alpha))]^{\frac{1}{2}} \cdot \exp\left(-\frac{22772.4}{T}\right)$$

## Conclusions

Solid complex  $\text{Zn}(\text{Thr})(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$  was prepared in a water-acetone system. The non-isothermal kinetics and the decomposition mechanism of  $\text{Zn}(\text{Thr})(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$  were studied by means of TG-DTG, DSC and IR spectrometry. The thermal decomposition processes of the complex can be divided into three stages. In the first stage, the complex dehydrates from 75 to 129 °C and  $\text{Zn}(\text{Thr})(\text{AcO})_2$  is formed. In the second stage, anhydrous  $\text{Zn}(\text{Thr})(\text{AcO})_2$  is decomposed into  $\text{Zn}(\text{Thr})(\text{AcO})_2 \cdot \text{Zn}(\text{AcO})_2$  and finally  $\text{Zn}(\text{Thr})(\text{AcO})_2 \cdot \text{Zn}(\text{AcO})_2$  is decomposed completely into ZnO at 773 °C. The non-isothermal decomposition mechanism and the kinetic parameters of the water-losing and ligand-losing processes were obtained from the analysis of DSC curves at various heating rate of 5.0, 10.0, 20.0, and 40.0 °C·min<sup>-1</sup> by six integral and two differential methods. The results show that for the first stage the Mampel Power Law ( $n=3/2$ ) controls the water-losing process and the corresponding activation energy is 145.32 kJ·mol<sup>-1</sup>, the pre-exponential factor  $\lg A$  ( $A$  in s<sup>-1</sup>) is 17.15, and for the ligand-losing process nucleation and growth mechanism (Avrami-Erofeev equation  $n=1/2$ ) is the most probable mechanism function, the corresponding activation energy is 189.33 kJ·mol<sup>-1</sup> and the pre-exponential factor  $\lg A$  ( $A$  in s<sup>-1</sup>) is 18.54.

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