

# Studies on the Non-isothermal Kinetics of Thermal Decomposition of Copper( II) Complexes with N,N'-bis( 3-aminopropyl) Oxamide

WANG Hai-dong<sup>1</sup>, MA Pei-hua<sup>1</sup>, LI Yan-tuan<sup>2</sup>, YU Shi-ying<sup>1</sup>

(<sup>1</sup>. Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008;

<sup>2</sup>. Department of Chemistry, Qufu Normal University, Qufu Shandong 273165)

**Abstract:** The thermal decomposition of copper( II) complex with N,N'-bis( 3-aminopropyl) oxamide and non-isothermal kinetics under dynamic air atmosphere were studied by TG, DTG and DTA technique. The non-isothermal kinetics data were analyzed by means of the Achar method and the Coats-Redfern method. The possible kinetic model function was suggested by comparison of the kinetic parameters. The kinetic equation for first stage can be expressed as:  $d\alpha/dt = A e^{-E/RT} (1 - \alpha)^2$ . The second stage is:  $d\alpha/dt = A e^{-E/RT} (1 - \alpha)$ .

The mathematical expressions of  $E$  and  $\ln A$  were derived from the kinetic compensation effects.

**Key words:** Oxamide; Copper( II) complex; Thermal decomposition; Non-isothermal kinetics

**CLC number:** O627.12; O643.1    **Document code:** A    **Article ID:** 1008-858X(2001)02-0026-06

## 0 Introduction

It is known that N,N'-bis( alkylaminoalkyl) oxamidocopper( II) complexes would be suitable candidates of "complex ligands"<sup>[1]</sup>, because they can coordinate to another metal ion through the oxamide oxygens to afford polynuclear species and the remarkable efficiency of the oxamide bridge to transmit electronic effects between the metal ions, and hence this family of "complex ligands" has been played an important role in molecular magnetism<sup>[1,2,4-10]</sup>. In order to investigate the magnetism of heterometal polynuclear complexes, previously we have adopted this strategy to synthesize a series of heterometal polynuclear complexes us-

ing mononuclear complexes N,N'-bis( 3-aminopropyl) oxamidocopper( II), [Cu( oxpn)]<sup>[4,9,10]</sup>. As a part of our study on the magnetism of polynuclear complexes, we have studied the nonisothermal kinetic of thermal decomposition and thermal behavior of mononuclear Cu( II) complexes to get information on its thermal stability by TG and DTA in this paper. The kinetic parameters were obtained by integral and differential methods. The possible mechanisms of the thermal dissociation have been discussed.

## 1 Experimental

All chemicals used are of analytical grade. N,N'-bis( 3-aminopropyl) oxamidocopper( II), Cu( ox-

收稿日期: 2000-07-10

作者简介: 汪海东(1965-), 男, 副研究员。研究方向: 热分析动力学。

(pn), are prepared by previously published procedures<sup>[5]</sup>. They are recrystallized from water and dried in vacuum.

Thermal studies are performed on the TG-DTA 92 thermal analysis system (Setaram Corp.). TG and DTA runs are carried out at a heating rate of  $7.5^{\circ}\text{C} \cdot \text{min}^{-1}$  under a dynamic air atmosphere using a flow rate of  $40 \text{ ml} \cdot \text{min}^{-1}$ .

## 2 Results and discussion

### 2.1 Thermal behavior of Cu(oxpn)

The TG, DTG and DTA curves of Cu(oxpn) complex are shown in Fig. 1. The DTG curve indicates the dissociation of complex in two stages. The first transition changes from 261 to  $321^{\circ}\text{C}$ , and the mass loss observed is 28.68 against the calculated

loss of 28.83%, corresponding to the release of two nitrogens and four carbons. The second transition is from 321 to  $405^{\circ}\text{C}$ , and the mass loss observed is 41.09 against the calculated loss of 41.01%, due to the release of all other organic ligands. The thermoanalytical data of Cu(oxpn) complex are given in Table 1.

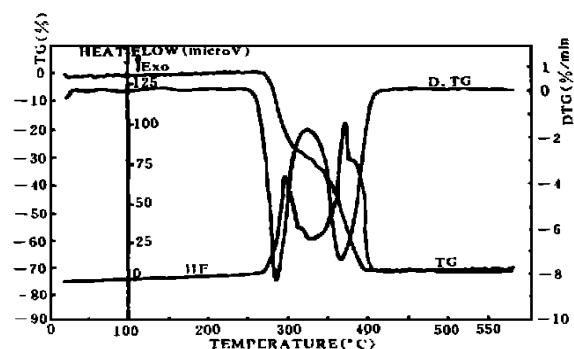


Fig. 1 TG-DTG-DTA curve of Cu(oxpn) complex

Table 1 The thermal decomposition data of Cu(oxpn) by TG-DTA

Stages of decomposition	Decomposition temperature range/ $^{\circ}\text{C}$	DTA/ $^{\circ}\text{C}$		mass loss/%	
		T <sub>p</sub> <sup>a</sup>	D.TA	TG	Theory
(1)	261-321	289.7(exo)		28.68	28.83
(2)	321-405	365.9(exo)		41.09	41.01

<sup>a</sup>T<sub>p</sub>indicates the temperature of peak in DTA curve

Two transitions are exothermic in DTA curve corresponding to the transition observed in the TG curve. The exothermic transition indicates that organic groups are oxidized under air atmosphere. Both of the exothermic peak temperatures are also given in Table 1.

The sequential thermal dissociation process of the complex is shown as follow:



### 2.2 Kinetic studies of non-isothermal decomposition

In the present paper, the Achar<sup>[11]</sup> and the Coats-Redfern<sup>[12]</sup> methods are employed to derive the kin-

etic parameter and a possible kinetic model function of thermal decomposition was suggested by comparing the kinetic parameters.

The integral and differential equations are as follows:

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

$$\ln[g(\alpha/T^2)] = \ln(A R / \beta) - E/RT \quad (2)$$

where  $\alpha$  is the fraction of decomposition,  $T$  is the absolute temperature,  $\beta$  is the heating rate,  $E$  is the activation energy in  $\text{KJ} \cdot \text{mol}^{-1}$ ,  $A$  is the pre-exponential factor,  $R$  is the gas constant in  $\text{KJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ,  $f(\alpha)$  and  $g(\alpha)$  are the most probable kinetic model functions (listed in Table 2).

**Table 2** Mathematical expressions for different mechanisms

No.	mechanism	symbol	$g(\alpha) = \frac{\int d\alpha}{f(\alpha)} = kt$	$f(\alpha) = \frac{1}{k} (\frac{d\alpha}{dt})$
1	Powlaw	P <sub>1</sub>	$\dot{\alpha}^{1/4}$	$4\dot{\alpha}^{1/4}$
2			$\dot{\alpha}^3$	$3\dot{\alpha}^3$
3			$\dot{\alpha}^2$	$2\dot{\alpha}^2$
4			$\alpha$	1
5			$\dot{\alpha}^3$	$\frac{2}{3}\dot{\alpha}^{-1/2}$
6	Avrami-Erofeev	A <sub>1.5</sub>	$[-\ln(1-\alpha)]^{2/3}$	$\frac{2}{3}(1-\alpha)[-ln(1-\alpha)]^{1/3}$
7	Avrami-Erofeev	A <sub>2</sub>	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-ln(1-\alpha)]^{1/2}$
8	Avrami-Erofeev	A <sub>3</sub>	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-ln(1-\alpha)]^{2/3}$
9	Avrami-Erofeev	A <sub>4</sub>	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-ln(1-\alpha)]^{3/4}$
10	Prout-Tompkins	B <sub>1</sub>	$[-\ln(1-\alpha)]^2$	$\frac{1}{2}(1-\alpha)[-ln(1-\alpha)]^{-1}$
11			$[-\ln(1-\alpha)]^3$	$\frac{1}{3}(1-\alpha)[-ln(1-\alpha)]^{-2}$
12			$[-\ln(1-\alpha)]^4$	$\frac{1}{4}(1-\alpha)[-ln(1-\alpha)]^{-3}$
13	Abstract surface	R <sub>2</sub>	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
14	Abstract surface	R <sub>3</sub>	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
15	1-D diffusion	D <sub>1</sub>	$\dot{\alpha}$	$1/(2\alpha)$
16	2-D diffusion	D <sub>2</sub>	$\alpha + (1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$
17	3-D diffusion	D <sub>3</sub>	$(1-(1-\alpha)^3)^2$	$\frac{3}{2}(1-\alpha^{2/3})(1-(1-\alpha^{1/3}))^{-1}$
18	Ginstling-Brouns	D <sub>4</sub>	$(1-2\alpha^3)-(1-\alpha^{2/3})$	$\frac{3}{2}[(1-\alpha^{-1/3}-1)^{-1}]$
19	Avrami-Erofeev	A <sub>1</sub>	$-\ln(1-\alpha)$	$1-\alpha$
20	Second order	F <sub>2</sub>	$(1-\alpha^{-1}-1)$	$(1-\alpha^2)$
21	Third order	F <sub>3</sub>	$(1-\alpha^{-2})$	$\frac{1}{2}(1-\alpha)^3$
22			$1-(1-\alpha)^{1/4}$	$4(1-\alpha^{3/4})$
23			$(1-\alpha^{-1/2})$	$\frac{1}{2}(1-\alpha^{-2/3})$
24			$[(1-\alpha^{-1/3}-1)^2]$	$\frac{3}{2}(1-\alpha^{4/3})[(1-\alpha^{-1/3}-1)^{-1}]$
25			$[1-(1-\alpha^{1/3})^{1/2}]$	$6(1-\alpha^{2/3})[1-(1-\alpha^{1/3})^{1/2}]$
26			$[1-(1-\alpha^{1/2})]^{1/2}$	$4[(1-\alpha)[1-(1-\alpha)^{1/2}]^{1/2}]$
27			$1-(1-\alpha^2)$	$\frac{1}{2}(1-\alpha^{-1})$
28			$1-(1-\alpha^3)$	$\frac{1}{3}(1-\alpha^{-2})^{-2}$
29			$1-(1-\alpha^4)$	$\frac{1}{4}(1-\alpha^{-3})$

**Table 3** Basic data for Cu(oxpn) determined by TG-DTG

No.	Stage 1			Stage 2			
	T/K	$\alpha$	$d\alpha/dt$	No.	T/K	$\alpha$	$d\alpha/dt$
1	539.56	0.0208	1.1522	1	618.66	0.1429	2.9860
2	542.66	0.0312	1.8686	2	621.76	0.1805	3.5911
3	545.76	0.0625	2.9443	3	625.16	0.2180	4.7294
4	548.96	0.1042	4.7318	4	628.36	0.2556	6.0555
5	552.16	0.1562	6.8786	5	631.76	0.3083	7.2565
6	555.56	0.2500	8.7379	6	636.06	0.4211	7.9752
7	559.86	0.4271	9.6351	7	640.06	0.5113	7.7503
8	563.96	0.6146	8.7356	8	643.06	0.5639	7.1892
9	567.36	0.6979	6.9272	9	645.76	0.6241	6.5865
10	570.36	0.7500	5.0332	10	648.66	0.6842	6.1831
11	573.26	0.7917	3.5795	11	651.86	0.7444	5.9303
12	576.16	0.8438	2.9374	12	654.66	0.8045	5.5293
13	579.06	0.8750	2.5664	13	657.66	0.8571	4.9149
14	581.86	0.8958	2.2998	14	660.16	0.8947	4.1383
15	584.86	0.9375	2.0773	15	662.66	0.9398	3.2782
16	587.76	0.9583	1.8732	16	665.26	0.9624	2.3809
17	590.56	0.9792	1.7480	17	667.66	0.9774	1.5950

The basic parameters of  $T$ ,  $\alpha$  and  $d\alpha/dt$  obtained from the TG and FTG curves are listed in Table 3. Twenty-nine types of kinetic model functions are into E(qs·(1) and(2), respectively. The kinetic analysis was completed with the linear least-squares method and the results are shown in Table 4 and 5. When the values of  $E$  and  $\ln A$  obtained with the two methods are approximately the same and the linear correlation coefficient is better, it can be concluded that the function is the function of the probable thermal decomposition mechanism of the complex.

For the first stage, the kinetic equation of thermal decomposition of Cu(oxpn) complex is:

$$d\alpha/dt = A e^{E/RT} (1 - \alpha)^2$$

It shows that the first stage of dissociation

for Cu(oxpn) is controlled by F<sub>2</sub>(chemical reaction) mechanism.

The kinetic equation of decomposition for the second stage of the complex is:

$$d\alpha/dt = A e^{E/RT} (1 - \alpha)$$

It shows that the second stage of decomposition for Cu(oxpn) is controlled by F<sub>1</sub>(nucleation and growth) mechanism.

### 2.3 The kinetic compensation effect

According to the frequently used mathematical expression for the kinetic compensation effect  $\ln A = \alpha E + b$ <sup>13</sup>, we fitted the kinetic parameters ( $E$  and  $\ln A$ ) obtained from the integral methods by the linear least-squares method. The kinetic compensation parameters  $a$  and  $b$  are listed in Table 6.

**Table 4** Kinetic parameter for the thermal decomposition data of Cu(oxpn): stage 1

Function No.	Integral method			Differential 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	38.76	5.76	0.8901	-163.59	-34.11	0.9527
2	54.83	9.43	0.9010	-147.54	-30.50	0.9321
3	86.92	16.54	0.9103	-115.45	-23.44	0.8603
4	183.24	37.24	0.9184	-19.18	-2.81	0.1084
5	119.03	23.51	0.9145	77.09	17.53	0.4758
6	166.49	34.30	0.9679	79.01	19.16	0.8218
7	122.53	24.73	0.9667	35.05	9.62	0.5702
8	78.56	15.02	0.9640	-8.90	-0.05	0.1813
9	56.56	10.06	0.9609	-30.88	-4.96	0.5405
10	518.34	109.55	0.9703	430.65	94.33	0.9618
11	782.16	165.54	0.9706	694.37	151.39	0.9666
12	1046.02	221.42	0.9708	958.10	208.96	0.9683
13	213.68	43.41	0.9443	73.87	16.94	0.6642
14	226.02	45.78	0.9530	104.89	23.36	0.8055
15	375.87	77.85	0.9221	173.36	37.76	0.6916
16	411.39	85.10	0.9364	244.55	52.74	0.8260
17	461.46	94.73	0.9549	340.19	72.25	0.9225
18	427.61	87.20	0.9430	216.13	44.99	0.7793
19	254.47	53.26	0.9992	166.92	38.09	0.9263
20	369.42	78.86	0.9963	353.01	78.99	0.9800
21	362.98	79.87	0.9519	539.11	120.58	0.9791
22	232.64	46.98	0.9572	120.39	26.48	0.8505
23	83.70	17.02	0.9444	-143.25	-29.39	0.7209
24	585.58	122.25	0.9828	526.29	113.15	0.9806
25	108.31	20.93	0.9489	-12.77	-1.44	0.2396
26	102.16	19.72	0.9394	-37.62	-6.70	0.5707
27	143.12	28.80	0.8750	-205.28	-43.02	0.7974
28	118.21	13.46	0.8421	-391.38	-83.52	0.8809
29	101.01	19.74	0.8156	-577.47	-124.13	0.9079

**Table 5** Kinetic parameter for the thermal decomposition data of Cu(oxpn) : stage 2

Function No.	Integral method			Differential 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	23.23	1.18	0.9546	-135.68	-24.64	0.8817
2	34.52	3.63	0.9627	-124.37	-22.30	0.8569
3	57.14	8.24	0.9697	-101.76	-17.79	0.7888
4	124.94	21.34	0.9745	-33.93	-4.77	0.3431
5	79.73	12.68	0.9722	33.89	7.95	0.3028
6	136.80	24.24	0.9994	120.07	24.94	0.9761
7	99.92	17.06	0.9992	83.18	17.79	0.9533
8	63.06	9.74	0.9993	46.30	10.52	0.8716
9	44.62	5.96	0.9992	27.86	6.80	0.7324
10	431.74	80.27	0.9993	415.12	80.94	0.9972
11	652.95	121.84	0.9993	636.40	123.62	0.9984
12	874.18	163.30	0.9993	857.70	166.75	0.9988
13	161.05	27.89	0.9924	79.95	16.46	0.8555
14	175.938	30.44	0.9962	117.91	23.36	0.9565
15	260.51	46.70	0.9764	101.72	20.56	0.6447
16	302.20	54.24	0.9869	187.36	36.40	0.8948
17	362.56	64.57	0.9965	304.59	57.46	0.9877
18	321.66	56.55	0.9909	152.75	28.23	0.8202
19	210.54	38.39	0.9993	193.84	39.07	0.9900
20	352.60	66.20	0.9805	421.59	82.91	0.9685
21	444.68	85.64	0.9165	649.36	127.45	0.9541
22	183.98	31.75	0.9976	136.89	26.72	0.9752
23	103.16	18.43	0.9052	-185.78	-33.31	0.7658
24	514.37	94.14	0.9967	532.36	101.30	0.9922
25	82.65	12.99	0.9958	24.57	5.96	0.6238
26	75.18	11.66	0.9912	-5.96	0.29	0.1467
27	79.31	12.69	0.9242	-261.70	-47.93	0.8122
28	53.00	7.50	0.8704	-489.46	-91.36	0.8647
29	36.30	4.08	0.8134	-717.23	-134.92	0.8831

**Table 6** The stage's kinetic model function and compensation effect of Cu(oxpn) complexes

Stage	Function No.	Integral method			Differential method			Compensation effect		
		$E/\text{kJ} \cdot \text{mol}^{-1}$	$\ln A/\text{s}^{-1}$	r	$E/\text{kJ} \cdot \text{mol}^{-1}$	$\ln A/\text{s}^{-1}$	r	a	b	r
(1)	20	369.42	78.86	0.9953	353.01	78.99	0.9800	0.2128	-1.17	0.9999
(2)	19	210.54	38.39	0.9993	193.84	39.07	0.9900	0.2903	-2.23	0.9999

**Acknowledgments:**

This work has been supported by the National Natural Science Foundation of China.

**References:**

- [1] H. Ojima and K. Nonoyama. Copper(II) Complexes With N,N'-bis(alkylaminoalkyl) oxamides and Related Ligands [J]. *Coord. Chem. Rev.*, 1988, 92:85.

[2] P. Yu, O. Kahn, K. Nakatani, E. Codjovi, et al. Design of a Molecular-Based Ferromagnet through Polymerization Reaction in the Solid State of Mn<sup>II</sup>Cu<sup>II</sup> Molecular Units. Crystal Structure of MnCu( obze)(H<sub>2</sub>O)<sub>4</sub> · H<sub>2</sub>O (obze=Oxamido-N<sup>+</sup>benzoato-N<sup>-</sup>ethanoato) [J]. *J. Am. Chem. Soc.*, 1991, 113:6558.

[3] F. Lioret, M. Julve, R. Ruiz, et al. Crystal Structure and Magnetic Properties of MnCu( obbz)(H<sub>2</sub>O)<sub>3</sub> · DMF (obbz=N, N<sup>-</sup>Oxamidobis( benzoato) and DMF=Dimethylformamide), a Precursor of the Molecular-Based Magnet MnCu( obbz) · H<sub>2</sub>O with  $T_c=14\text{K}$  [J]. *Inorg. Chem.*, 1993, 32:27.

- [4] Y·T·Li, C·W·Yan, S·H·Miao and D·Z·Liao. Ferromagnetically Coupled Heterodinuclear Copper(II)-Chromium(III) Complexes with N,N'-bis(2-aminopropyl) oxamidocopper(II) [J]. Polyhedron., 1998, 15: 2491.
- [5] Y·Journaux, J·Sletten and O·Kahn. Tunable Interaction in  $\mu$ -Oxamido Copper(II) Binuclear Complexes [J]. Inorg. chem., 1985, 24: 4063.
- [6] Y·T·Li, Z·H·jiang, S·L·Ma, et al. [J]. Polyhedron., 1993, 23: 2781.
- [7] Y·T·Li, D·Z·Liao, Z·H·Jiang and G·L·Wang. Synthesis and Magnetic studies of Copper(II)-Lanthanide(III) Complexes with N,N'-bis(2-aminopropyl) oxamidocopper(II) [J]. Polyhedron., 1995, 14(15/16): 2209.
- [8] Y·T·Li, Z·H·Jiang, S·L·Ma, et al. Synthesis and Magnetic Properties of Copper(II)-Lanthanide(III)-Copper(II) Trinuclear Complex with N,N'-bis(2-aminopropyl) oxamido Ligand [J]. Trans. Met. Chem., 1994, 19(3): 332.
- [9] Y·T·Li, C·W·Yan, Y·F·Lu, and X·Z·Liao. Synthesis and Magnetic Properties of  $\mu$ -Oxamido Heterobinuclear Iron(II)-Copper(II) Complexes [J]. Synth. React. Inorg. Met.-Org. Chem., 1998, 28(7): 1091.
- [10] Y·T·Li, C·W·Yan, S·L·Bao and D·Z·Liao. Synthesis and Magnetic Studies of Heterobinuclear Copper(II)-Iron(II) Complexes with N,N'-bis(3-aminopropyl) oxamide as Ligand [J]. Synth. React. Inorg. Met.-Org. Chem., 1999, 29(5): 737.
- [11] B·N·Achar, G·W·Brindley and J·H·Sharp. Vol. 1. [C]. Proc. Intern. Clay Conf., Jerusalem, 1966.
- [12] A·W·Coats and J·P·Redfern. Kinetic Parameters from Thermogravimetric Data [J]. Nature, 1964, 201: 68.
- [13] J·Zsako. The Kinetic Compensation Effect [J]. J. Therm. Anal., 1976, 9: 101.

## N,N'-双(3-氨基丙基)草酰胺合铜非等温热分解动力学研究

汪海东<sup>1</sup>, 马培华<sup>1</sup>, 李延团<sup>2</sup>, 余世英<sup>1</sup>

(1. 中国科学院青海盐湖研究所, 青海 西宁 810008;  
2. 山东曲阜师范大学化学系, 山东 曲阜 273165)

**摘要:** 采用 TG-DTG-DTA 热分析技术研究了 N,N'-双(3-氨基丙基)草酰胺合铜(II)配合物在动态空气气氛中的热行为;用微分法(Achar 法)和积分法(Coats-Redfern 法)协同处理非等温 TG 数据,通过对比热分解动力学参数 E 和 lnA,提出了配合物第一阶段热分解动力学方程:  $d\alpha/dt = Ae^{-E/RT} (1 - \alpha)^2$  及第二阶段热分解动力学方程:  $d\alpha/dt = Ae^{-E/RT} (1 - \alpha)$ ;并由动力学补偿效应获得了 E 和 lnA 的数学表达式。

**关键词:** 草酰胺; Cu(II) 配合物; 热分解; 非等温动力学