ELSEVIER

Thermochimica Acta 275 (1996) 215-224

thermochimica
acta

Determination of mechanism functions and kinetic parameters of thermodecomposition of complexes with the schiff base derived from 3-methoxysalicylaldehyde and diamine with non-isothermal TG and DTG curves

Shu-Lan Li[a,*], De-Xin Liu[a], Sheng-Qiang Zhang[a], Hong Wang[c], Zhao-He Yang[b]

[a] *Department of Chemistry, Shandong University, Jinan 250100, China*
[b] *National Laboratory of Crystal Materials, Shandong University, Jinan 250100, China*
[c] *Beijing University of Science and Technology, Beijing 100083, China*

Received 28 April 1995; accepted 26 July 1995

Abstract

The paper studies non-isothermal kinetics of monoaqua 3-methoxysalicylaldehyde-*o*-phenyldiamine copper(II) (cp1), 3-methoxysalicylaldehyde-*o*-phenyldiamine nickel(II) monohydrate (cp2), monoaqua 3-methoxysalicylaldehyde-ethyldiamine copper(II) (cp3) and 3-methoxysalicylaldehyde-ethyldiamine nickel(II) monohydrate (cp4) by use of non-isothermal TG and DTG curves. The kinetic parameters were analyzed by means of integral and differential methods, and mechanism functions of thermodecomposition reactions in their second steps were proposed. Thermodecomposition kinetic equations of the complexes are as follows:

cp1: $\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT) \times 1$

cp2 and cp3: $\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT)3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$

cp4: $\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT)2(1-\alpha)^{1/2}$

The corresponding kinetic compensation effect expressions of cp1-4 are found to be $\ln A = 0.2010E + 0.5310$, $\ln A = 0.1810E - 0.3890$, $\ln A = 0.1996E - 0.8762$ and $\ln A = 0.1800E + 0.0789$, respectively.

Keywords: Kinetics; Mechanism function; Non-isothermal; Schiff base compound; Synthesis

---

* Corresponding author.

SSDI 0040-6031(95)02687-8

1. Introduction

There has been recent interest in the study of diamine Schiff base complexes containing copper and nickel atoms as anticancer medicines [1–4], vitamin B_6-related compounds [5] and the model of oxygen-carrier [6]. It has been generally accepted that the –CH=N– group plays an important role in the properties of Schiff base complexes [7, 8]. The study of thermodecomposition has been ignored. The present paper reports the possible process and mechanism functions of thermal decomposition of the complexes of monoaqua 3-methoxysalicylaldehyde-*o*-phenlydiamine copper(II) (cp1), 3-methoxysalicylaldehyde-*o*-phenyldiamine nickel(II) monohydrate (cp2), monoaqua 3-methoxysalicylaldehyde-ethyldiamine copper(II) (cp3) and 3-methoxysalicylaldehyde-ethyldiamine nickel(II) monohydrate (cp4), together with the corrsponding kinetic compensation effect expressions obtained from the non-isothermal TG–DTG curve.

2. Experimental

2.1. Apparatus and measurements

Elemental C,H,N analyses were carried out with a Perkin–Elmer 240C elemental analyzer (USA) and the Cu^{2+} and Ni^{2+} content of the complexes were determined by EDTA titration. Melting points (m.p.) were measured on a model X_4 melting point meter (Shanghai, People's Republic of China). Thermogravimetric analysis of finely powdered sample was performed on a Perkin–Elmer model TGS-2, with a nitrogen flow rate of 40 ml min^{-1}, in the temperature range 40–980°C and with the linear heating rate of 10.00°C min^{-1}.

2.2. Synthesis of cp 1–4

In the light of Ref. [9], 3.1 g (0.020 mol) of 3-methoxysalicylaldehyde was dissolved in 30 ml of anhydrous ethanol, followed by addition of 15 ml of an alcoholic solution of 1.08 g (0.010 mol) *o*-phenyldiamine and 0.57 g (0.0100 mol) ethyldiamine. The mixture was stirred and heated on water-bath at 50–60°C for about 2h. The solution was cooled and filtered. The solid obtained was washed with water and absolute ethanol several times. The products were an orange powder with m.p. 171–172°C (yield 82.0%) and yellow powder with m.p. 164.4–165°C (yield 94.1%).

To an ethanolic solution (60 ml) of each of the above two products (0.01 mol) was added an aqueous solution (20 ml) of $Cu(Ac)_2 \cdot 4H_2O$ (0.075 ml) and $Ni(Ac)_2 \cdot 4H_2O$ (0.075 mol), with constant stirring under reflux for about 8h. The resulting solutions were evaporated at room temperature in air for about a week to give crystals of the four complexes. Elemental analyses (shown in Table 1) and single-crystal X-ray diffraction analysis [10–12] showed their molecular formulae to be

$$Cu(C_8H_7O_2)_2 \cdot (C_6H_4N_2) \cdot (H_2O) \text{ — cp1}, \quad Ni(C_8H_7O_2) \cdot (C_6H_4N_2) \cdot H_2O \text{ — cp2},$$

$$Cu(C_8H_7O_2)_2 \cdot (C_2H_4N_2) \cdot (H_2O) \text{ — cp3}, \quad Ni(C_8H_7O_2) \cdot (C_2H_4N_2) \cdot H_2O \text{ — cp4}.$$

Table 1
Elemental analyses (/%) of the four compounds cp1–4

Compounds		C	H	N	Metal atom
cp1	Calc.	60.30	4.11	6.39	14.52
	Found	60.01	4.08	5.65	14.56
cp2	Calc.	58.52	4.43	6.21	13.01
	Found	59.07	4.32	5.68	13.14
cp3	Calc.	53.00	4.94	6.87	15.62
	Found	52.85	4.91	6.88	15.56
cp4	Calc.	53.64	5.00	6.96	15.87
	Found	53.61	4.96	6.94	15.81

3. Results and discussion

3.1. Thermal decomposition process

The TG and DTG curves of cp1–4 are shown in Figs. 1–4, respectively.

According to the TG–DTG curves, each of cp 1–4 has three weight-loss stages: the first is the water loss stage, the second is the 3-methoxysalicylaldehyde loss stage and the third is the stage in which residual ligands are lost. The final products are the corresponding oxides.

The decomposition temperature and loss-in-weight rates (/%) corresponding to the stages of cp 1–4 are as follows.

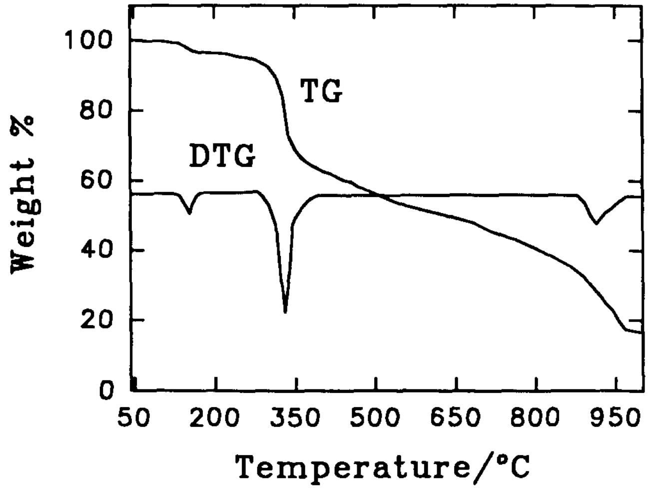

Fig. 1. TG and DTG curves of cp1.

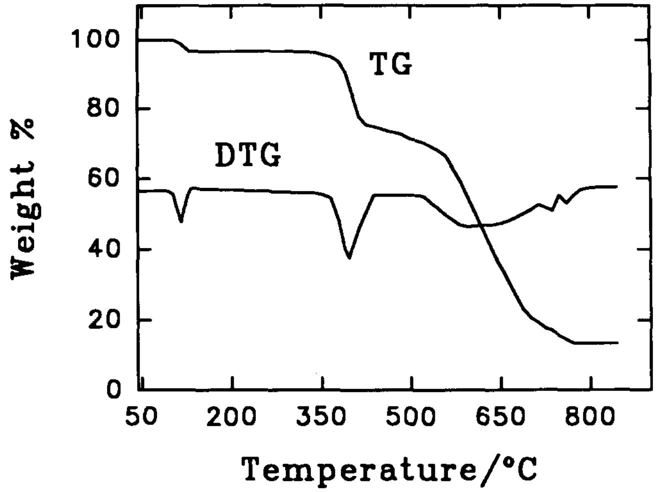

Fig. 2. TG and DTG curves of cp2.

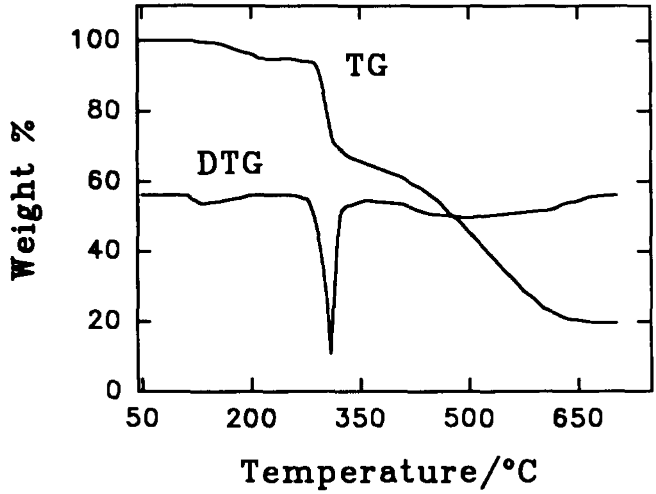

Fig. 3. TG and DTG curves of cp3.

(1) cpl: 139–175°C, 3.85(3.95); 213–396°C, 32.97(33.12); 396–980°C, 46.16(45.53).

(2) cp2: 70–138°C, 3.75(3.99); 317–511°C, 29.67 (29.93); 511–780°C, 51.06(49.67).

(3) cp3: 108–241°C, 4.57(4.40); 245–380°C, 32.00(32.44); 380–668°C, 43.83(43.56).

(4) cp4: 81–238°C, 5.10(4.47); 326–425°C, 32.46(32.45); 425–795.5°C, 44.59(44.55).

Values in parentheses are calculated values. The experimental values are in accordance with the calculated values.

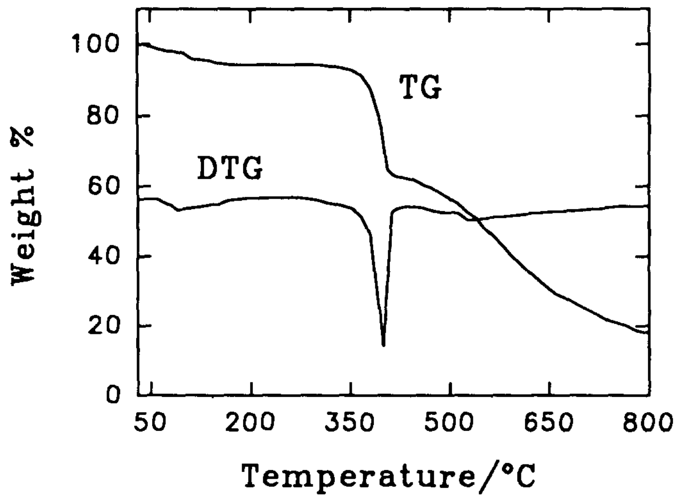

Fig. 4. TG and DTG curves of cp4.

3.2. Non-isothermal kinetics of thermodecomposition of the complexes

The possible forms of g(α) and f(α) are listed in Table 2. The original data of non-isothermal kinetics of thermodecomposition of the four complexes, obtained from the TG and DTG curves (Figs. 1–4), are listed in Tables 3–6, respectively.

Table 2
Several kinetic functions used for the present analysis

Function no.	Function form	
	Differential form f(α)	Integral form g(α)
1	$1/2\alpha$	α^2
2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
3	$3[(1-\alpha)^{-1/3}-1]^{-1}/2$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
4	$3(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}/2$	$[1-(1-\alpha)^{1/3}]^2$
5	$3(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}/2$	$[(1+\alpha)^{1/3}-1]^2$
6	$3(1-\alpha)^{4/3}[\{1/(1-\alpha)^{1/3}-1\}]^{-1}/2$	$[1/(1-\alpha)^{1/3}-1]^2$
7	$1-\alpha$	$-\ln(1-\alpha)$
8	$3(1-\alpha)[-\ln(1-\alpha)]^{1/3}/2$	$[-\ln(1-\alpha)]^{2/3}$
9	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
11	$4(1-\alpha)[-\ln(1-\alpha)^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
12	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
14	1	α
15	$2\alpha^{1/2}$	$\alpha^{1/2}$
16	$3\alpha^{2/3}$	$\alpha^{1/3}$
17	$4\alpha^{3/4}$	$\alpha^{1/4}$
18	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
19	$2(1-\alpha)^{3/2}$	$(1-\alpha)^{1/2}$

Table 3
Data determined by TG and DTG of cp1 (peak II)

Data no.	α_i	T_i/K	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{s}^{-1}$	Data no.	α_i	T_i/K	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{s}^{-1}$
1	0.1594	583	0.2933	2	0.1913	588	1.2465
3	0.2477	593	2.3883	4	0.3237	598	3.9596
5	0.4411	603	6.0860	6	0.5000	605	7.0392
7	0.6268	608	6.6097	8	0.6907	610	5.1537
9	0.7555	613	3.5406	10	0.7858	615	2.315
11	0.8165	618	1.4351	12	0.8638	623	0.7333

$w = 1.3799$ mg, $\beta = 10^\circ\mathrm{C}\ \mathrm{min}^{-1}$

Table 4
Data determined by TG and DTG of cp2 (peak II)

Data no.	α_i	T_i/K	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{s}^{-1}$	Data no.	α_i	T_i/K	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{s}^{-1}$
1	0.1052	645	1.6554	2	0.1553	651	5.9641
3	0.1973	653.9	7.7329	4	0.2474	657	9.9098
5	0.324	660.5	11.4519	6	0.3968	663	12.9259
7	0.5133	667	14.5133	8	0.5737	669	13.5608
9	0.627	671	12.6991	10	0.7353	675	10.5902
11	0.8105	678	8.1864	12	0.8464	681	6.4856

$w = 2.6519$ mg, $\beta = 10^\circ\mathrm{C}\ \mathrm{min}^{-1}$

Table 5
Data determined by TG and DTG of cp3 (peak II)

Data no.	α_i	T_i/K	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{s}^{-1}$	Data no.	α_i	T_i/K	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{s}^{-1}$
1	0.1134	581	2.553	2	0.162	585	3.938
3	0.24	589	6.707	4	0.371	593	13.37
5	0.5316	596	16.49	6	0.6045	597	15.32
7	0.7716	601	6.92	8	0.8402	605	2.94
9	0.0846	577	1.341				

$w = 2.377$ mg, $\beta = 10^\circ\mathrm{C}\ \mathrm{min}^{-1}$

Table 6
Data determined by TG and DTG of cp4 (peak II)

Data no.	α_i	T_i/K	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{s}^{-1}$	Data no.	α_i	T_i/K	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{s}^{-1}$
1	0.1022	643	1.0619	2	0.1869	653	2.3362
3	0.2505	658	3.0796	4	0.3365	663	4.4270
5	0.4649	668	6.9730	6	0.1398	648	1.7698
7	0.6565	673	10.09	8	0.8650	678	6.4423
9	0.9519	683	1.9114				

$w = 3.97$ mg, $\beta = 10^\circ\mathrm{C}\ \mathrm{min}^{-1}$

In this paper, we use the Achar et al. differential equation [13] and the Coats–Redfern's integral equation [14] to analyze the non-isothermal kinetic data in the second steps of the thermodecomposition reactions. Possible mechanisms of the reactions are deduced. The integral and differential equations are

$$\ln[g(\alpha)/(T^2)] = \ln[AR/(\beta E)(1-2RT/E)] - E/(RT) \tag{1}$$

$$\ln[d\alpha/dt/f(\alpha)] = \ln A/\beta - E/(RT) \tag{2}$$

In the above equations, α is the fraction of reacted material, T is the absolute temperature, and $f(\alpha)$ and $g(\alpha)$ are differential and integral mechanism functions, respectively. E and A are the derived apparent activation energy and pre-exponential factor, respectively. R is the gas constant and β is the linear heating rate.

Using the possible forms of $g(\alpha)$ and $f(\alpha)$ in Table 2, the data in Tables 3–6 were analyzed by use of Eqs. (1) and (2); the kinetic analyses were then completed by the linear least squares method. The results – kinetic parameters E, A and correlation coefficient r – are shown in Tables 7–10.

The results in Tables 7–10 clearly show that the values of E and A obtained from the two equations are approximately the same; the linear correlation coefficients are satisfactory and the values of E and $\ln A$ are in the range of $E/(\mathrm{kJ\ mol^{-1}})$ 80–250 and $\ln(A/\mathrm{s^{-1}})$ 16.91–69.09; these thermal parameters of the thermodecomposition reaction of the solid compounds [15] suggest that the probable mechanism functions of cp 1–4 are logically functions 13, 8, 8 and 12 (Table 2), respectively. We concluded that the

Table 7

Result of analysis of the thermal decomposition data of cp1 (peak II) by integral and differential methods

Function no.	Integral method			Differential method		
	$E/(\mathrm{kJ\ mol^{-1}})$	$\ln(A/\mathrm{s^{-1}})$	$\lvert r\rvert$	$E/(\mathrm{kJ\ mol^{-1}})$	$\ln(A/\mathrm{s^{-1}})$	$\lvert r\rvert$
1	278.97	53.88	0.9833	210.16	42.63	0.6451
2	313.39	60.4	0.9866	272.26	54.7	0.7578
3	327.66	61.87	0.9878	298.11	58.51	0.7955
4	356.69	67.92	0.9894	347.21	68.58	0.8513
5	248.71	45.26	0.9816	167.15	31.45	0.5566
6	454.87	88.32	0.9906	494.48	98.81	0.9415
7	196.57	38.32	0.9901	212.94	44.19	0.8465
8	127.71	24.31	0.9896	144.08	30.2	0.6067
9	93.28	17.2	0.989	109.65	23.12	0.503
10	58.85	9.95	0.9878	75.22	15.92	0.3712
11	41.63	6.21	0.9863	58.01	12.24	0.2947
12	162.69	30.48	0.9876	139.31	28.38	0.5521
13	173.34	32.32	0.9888	163.85	33.01	0.8272
14	134.48	25.17	0.982	65.67	13.96	0.273
15	62.23	10.41	0.979	−6.57	−0.73	0.0294
16	38.15	5.26	0.9752	−30.66	−5.8	0.1376
17	26.11	2.55	0.9703	−42.7	−8.41	0.191
18	281.75	56.14	0.9875	360.22	74.42	0.922
19	63.62	11.56	0.9391	286.58	58.61	0.86

Table 8
Result of analysis of the thermal decomposition data of cp2 (peak II) by integral and differential methods

Function no.	Integral method			Differential method		
	E/(kJ mol^{-1})	ln(A/s^{-1})	|r|	E/(kJ mol^{-1})	ln(A/s^{-1})	|r|
1	435.06	77.04	0.9886	326.5	61.01	0.8621
2	479.66	84.73	0.9929	405.5	74.97	0.9243
3	497.77	86.62	0.9943	437.77	79.44	0.941
4	534.56	93.51	0.9965	499.29	90.83	0.9644
5	393.17	66.9	0.9857	266.75	47.62	0.8058
6	657.67	116.51	0.9987	683.85	125.02	0.9937
7	291.02	51.86	0.9982	288.02	55.07	0.9406
8	190.34	33.41	0.9981	187.33	36.64	0.8754
9	140	24.08	0.9981	136.99	27.34	0.7984
10	89.65	14.62	0.9979	86.65	17.92	0.6428
11	64.48	9.79	0.9977	61.48	13.12	0.5116
12	248.25	43.08	0.9948	195.74	37.29	0.8258
13	261.76	45.23	0.9963	226.5	42.58	0.8777
14	212.02	36.89	0.988	103.45	20.89	0.5334
15	100.49	16.42	0.9866	−8.07	0.48	0.0534
16	63.32	9.39	0.985	−45.24	−6.5	0.2946
17	44.73	5.76	0.983	−63.83	−10.08	0.4037
18	396.58	71.7	0.9958	472.58	89.26	0.9941
19	81.25	13.59	0.9326	380.3	71.47	0.9807

Table 9
Result of analysis of the thermal decomposition data of cp3 (peak II) by integral and differential methods

Function no.	Integral method			Differential method		
	E/(kJ mol^{-1})	ln(A/s^{-1})	|r|	E/(kJ mol^{-1})	ln(A/s^{-1})	|r|
1	514.9	102.96	0.9911	414.84	85.64	0.8519
2	559.19	111.54	0.9927	492.48	101.04	0.9053
3	576.96	113.76	0.9932	523.83	106.03	0.9221
4	613.02	121.29	0.9937	583.77	118.44	0.9459
5	471.09	91.54	0.99	352.14	70.35	0.8051
6	732.88	146.3	0.9922	763.57	155.69	0.9806
7	330.17	66.42	0.9933	332.28	70	0.8982
8	216.84	43.24	0.9931	218.95	46.83	0.8065
9	160.18	31.55	0.9929	162.29	35.16	0.7125
10	103.51	19.73	0.9925	105.62	23.37	0.5524
11	75.18	13.72	0.992	77.29	17.39	0.4366
12	288.34	56.92	0.9932	242.38	50.68	0.7803
13	301.8	59.31	0.9935	272.35	56.48	0.8295
14	252.54	50.06	0.9907	152.48	32.75	0.5558
15	121.36	23.23	0.9899	21.37	5.96	0.0984
16	77.63	14.08	0.9891	−22.42	−3.15	0.1055
17	55.77	9.4	0.9881	−44.29	−7.78	0.207
18	432.34	87.84	0.9866	512.09	107.24	0.9764
19	80.08	15.34	0.9008	422.18	87.93	0.9527

Table 10
Result of analysis of the thermal decomposition data of cp4 (peak II) by integral and differential methods

Function no.	Integral method			Differential method		
	E/(kJ mol^{-1})	ln(A/s^{-1})	|r|	E/(kJ mol^{-1})	ln(A/s^{-1})	|r|
1	415.84	73.42	0.9975	336.90	61.95	0.8952
2	463.69	81.74	0.9980	429.21	78.39	0.9572
3	484.77	84.19	0.9976	470.86	84.60	0.9737
4	523.43	92.37	0.9957	548.57	98.99	0.9886
5	375.67	63.64	0.9969	279.70	49.03	0.8502
6	683.80	121.41	0.9821	781.62	142.16	0.9874
7	294.72	52.56	0.9900	356.53	66.79	0.9859
8	192.81	33.88	0.9897	254.62	48.13	0.9745
9	141.85	24.44	0.9893	203.66	38.71	0.9607
10	90.89	14.87	0.9885	152.70	29.17	0.9308
11	65.42	9.97	0.9875	127.23	24.32	0.9023
12	242.77	42.02	0.9971	240.00	44.51	0.9273
13	258.71	44.65	0.9955	278.84	51.30	0.9608
14	202.41	35.06	0.9974	123.47	23.61	0.6217
15	95.70	15.48	0.9971	16.76	4.10	0.1113
16	60.12	8.75	0.9967	−18.81	−2.58	0.1264
17	42.34	5.26	0.9962	−36.60	−6.01	0.2420
18	435.47	79.00	0.9598	589.58	109.96	0.9731
19	105.51	18.35	0.8431	473.06	87.63	0.9846

probable mechanisms of thermodecomposition in the second steps of cp 1-4 are: cp1, Mampel equation; cp2 and cp3, Avrami–Erofeev equation Coring and Growth ($n = 1.5$); cp4, Contraction Geometry Shape (Cylinder Symmetry). The non-isothermal kinetic equations of these processes are

(1) cp1: $d\alpha/dt = A\exp(-E/RT) \times 1$

(2) cp2 and cp3: $d\alpha/dt = A\exp(-E/RT)3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$

(3) cp4: $d\alpha/dt = A\exp(-E/RT)2(1-\alpha)^{1/2}$

3.3. The kinetic compensation effect

According to the mathematical expression for the kinetic compensation effect, $\ln A = aE + b$[16], we fitted the obtained kinetic parameters obtained (E and $\ln A$) (see Tables 7–10) using Eqs. (1) and (2) by the linear least-squares method, and obtained the kinetic compensation parameters a and b. The results indicate that the kinetic parameters E and A may be connected through a and b. The values of a and b are given in Table 11.

3.4. Factors influencing the stability of the complexes

First, there are same ligands and different central ions between cp1 and cp2 and between cp3 and cp4. However, cp1 has lower temperature than cp2, and cp3 has lower

Table 11
Calculated values of kinetic compensation parameters for the four complexes

Complex	*a*	*b*	*r*
cp1	0.2010	0.5310	0.9991
cp2	0.1810	−0.3890	0.9987
cp3	0.1996	−0.8762	0.9977
cp4	0.1800	0.0789	0.9987

temperature than cp4 when losing the Schiff base ligand. The reason is that with the radii of the central metal ions becoming greater, the steric effect of the ligands becomes greater and the stability gets weaker.

On the other hand, when the central ions are same but the Schiff base ligands are different (between cp1 and cp3 and between cp2 and cp4), the amino-group of the ligands of cp1, cp2 is $-N-C_6H_4-N-$, and the amino-group of cp3, cp4 is $-N-CH_2CH_2-N-$, the coordination strength of Schiff base to central metal ions and the stability of the complexes are influenced by two aspects: one is the steric effect, i.e., the steric effect of $-C_6H_4-$ is greater than that of $-CH_2CH_2-$, and this weakens the coordination strength of the ligands to central metal ions; the other is the conjugating effect, i.e., the conjugating large π-bonds of the ligands of cp1, cp2 contribute to the stability of the complexes. The steric effect is, however, much greater than the conjugating effect. Therefore, the ligand-loss temperature of cp1 is lower than that of cp3 and the temperature of the second step of thermodecomposition of cp4 is higher than that of cp2.

References

[1] P. Lumme, Inorg. Chim. Acta, 92 (1984) 241.
[2] M.A. Ali and S.E. Livingstone, Coord. Chem. Rev., 13 (1974) 101.
[3] M. Das and S.E. Livingstone, Inorg. Chim. Acta, 19 (1976) 5.
[4] S.E. Livingstone, Coord. Chem., 20 (1980) 141.
[5] J.T. Worbleski and G.J. Long, Inorg. Chem., 16 (1977) 2752.
[6] E.C. Niederhoffer, J.H. Timmons and A.E. Martell, Chem. Rev., 84 (1984) 137.
[7] E.M. Hodnett et al., J. Med. Chem., 15 (1972) 339.
[8] S.E. Livingstone, Coord. Chem., 20 (1980) 141.
[9] C.W. Na, G.L. Zhao, G.F. Liu and B. Li, J. Jilin Univ. (Natural Science Edition), 2 (1988) 103.
[10] De-Xin Liu, Xue-Gui Cui, Shu-Lan Li, Xiai-Yan Li and Hong-Jian Sun, Chem. Res. in Chin. Univ., 9(2) (1993) 194.
[11] De-Xin Liu, Shu-Lan Li, Xue-Gui Cui and Xiao-Yan Li, Chem. J. Chin. Univ., 14(7) (1993) 897.
[12] Hong Wang, Shu-Lan Li, De-Xin Liu, Xue-Gui Cui, Xiao-Yan Li, Acta Chim. Sinica, 52 (1994) 676.
[13] B.N. Narahari Achar, G.W. Bridley and J.H. Sharp, Proc. Int. Clay Conf., Jerusalem, 1966, vol. 1, p. 67.
[14] A.W. Coats and J.P. Redfern, Nature (London), 68 (1964) 201.
[15] R.Z. Hu, Z.Q. Yang and Y.J. Liang, Thermochim. Acta, 123 (1988) 135.
[16] J. Zsako, J. Therm. Anal., 9 (1976) 101.