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Thermal decomposition kinetics of M (mnt) (5-NO_2-phen) (M=Co^{II}, Cu^{II}, Zn^{II}) complexes

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Abstract

Studies of the non-isothermal decomposition of M (mnt) (5-NO_2-phen) (M=Co^{II}, Cu^{II}, Zn^{II}) were carried out by thermogravimetry. The thermal decomposition mechanisms and associated kinetics have been investigated. The kinetic parameters were obtained from an analysis of the TG–DTG curves by integral and differential methods. The most probable kinetic model functions were suggested by comparison of the kinetic parameters. Mathematical expressions for the kinetic compensation effect were derived. © 1998 Elsevier Science B.V.

Keywords: Metal complex; Mixed ligand; Non-isothermal kinetics; TG; Thermal decomposition

1. Introduction

Recently, we have reported the synthesis and properties of cobalt (II), cupper (II) and zinc (II) complexes of mixed ligand (L=mnt, L′=bpy) [1–3]. Subsequently, we have synthesized a series of complexes of the type M (mnt) (5-NO_2-phen) (M=Co^{II}, Cu^{II}, Zn^{II}) [4]. These complexes have potential electronic application as a result of their gas-sensitivity, photosensitivity and photoconductivity properties. It is known that these complexes have potential applications as gas sensors, photovoltaic cell, non-linear optical devices and molecular devices [5]. The aim of this investigation was to show the influence of the nature of the metal on the thermal stability of these complexes of the mixed ligand (L=mnt, L′=5-NO_2-phen) type and to provide valuable data for their applications, we studied the thermal decomposition processes of these complexes by TG and DTG techniques and the kinetic parameters were obtained by integral and differential methods. The possible decomposition mechanisms are also discussed.

2. Experimental

2.1. Synthesis procedures

Complexes Co (mnt) (5-NO_2-phen)·0.5H_2O (I), Cu (mnt) (5-NO_2-phen) (II) and Zn (mnt) (5-NO_2-phen)·0.5H_2O (III) have been synthesized by reaction of disodum 1,2-dicyanoethlene-1,2-dithiolate [Na_2 (mnt)] with the relative metal complex M (5-NO_2-phen) Cl_2, respectively. The structure and properties of the M (mnt) (5-NO_2-phen) were determined by

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elemental analysis, molar conductivity, molar susceptibility, IR, UV-VIS, EPR and fluorescence spectra [4].

2.2. Instrumental

Thermogravimetric analysis was performed on a Perkin–Elmer TGS-2 thermobalance, employing the following conditions: sample mass: 3.00 mg; heating rate: 5°C min^{-1}; atmosphere: static air; temperature range: 30–830°C.

All the thermogravimetric data were analysed on an AT-486 computer.

3. Result and discussion

3.1. Thermal analysis

The TG–DTG curves of the complexes in the temperature range 30–830°C are shown in Figs. 1–3. They show that the thermal decomposition processes of complexes I and II involve three stages and complex III four stages. The TG–DTG data are given in Table 1.

The stoichiometry of the thermal decompositions of complexes I–III can be expressed by the following schemes:

(a) Co $(C_{12}H_7N_3O_2)$ $(C_4S_2N_2)\cdot 0.5H_2O$ (I)→ $Co(C_{12}H_7N_3O_2)$ $(C_4S_2N_2)$ (I′)→$Co(C_{12}H_7N_3O_2)_{1/2}$ $(C_4S_2N_2)$→$CoSO_4$

(b) Cu $(C_{12}H_7N_3O_2)$ $(C_4S_2N_2)$ (II)→Cu $(C_{12}H_7N_3O_2)_{2/3}$ $(C_4S_2N_2)$→CuS_2→Cu_2S

(c) Zn $(C_{12}H_7N_3O_2)$ $(C_4S_2N_2)\cdot 0.5H_2O$ (III)→Zn $(C_{12}H_7N_3O_2)$ $(C_4S_2N_2)$(III′)→Zn $(C_{12}H_7N_3O_2)_{1/3}$ $(C_4S_2N_2)$→$Zn(C_3S_2N)$→ZnO

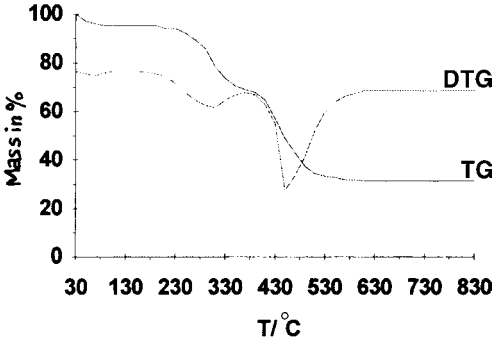

Fig. 1. TG–DTG curves of Co (mnt) (5-NO_2-phen)·0.5H_2O.

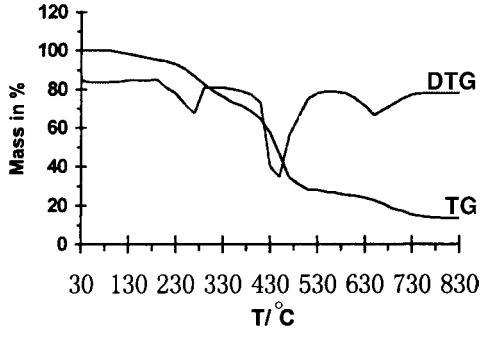

Fig. 2. TG–DTG curves of Cu (mnt) (5-NO_2-phen).

3.2. Thermal decomposition kinetics

We used the Narahari Achar [6] and the Coats–Redfern [7] method to derive the kinetics parameters and a possible kinetic model function of thermal decomposition was suggested by comparing the kinetic parameters.

The Narahari Achar equation is:

$$\ln[(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)] = \ln(A/\beta) - E/RT \qquad (1)$$

The Coats–Redfern equation is:

$$\ln[g(\alpha)/T^2] = \ln(AR/\beta E) - E/RT \qquad (2)$$

where α is the reaction fraction of decomposition, β the heating rate, E the activation energy in J/mol, A the frequency factor, R the gas constant in J/mol K, and $g(\alpha)$ and $f(\alpha)$ are the most probable kinetic model functions. We took the complex III for stage (1) as an example to demonstrate the process.

From the TG–DTG curves of the complex III, the base data (T, α, $\mathrm{d}\alpha/\mathrm{d}T$) for stage (1) can be obtained as shown in Table 2.

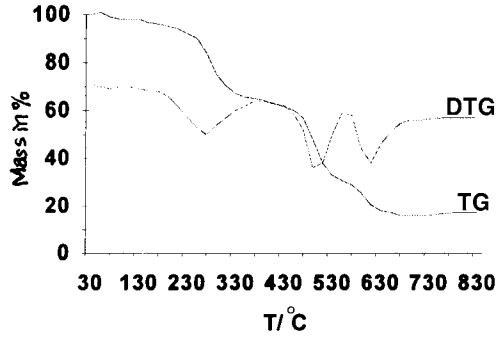

Fig. 3. TG–DTG curves of Zn (mnt) (5-NO_2-phen)·0.5H_2O.

Table 1
The thermal decomposition data of three complexes by TG–DTG

Stages of decomposition	TG plateaux/°C		DTG peak/°C	% mass loss found (calculated)	Residue/%		Residue found	Colour theory
					Found	Calc.		
Co (mnt) (5-NO_2-phen)·0.5H_2O								
(1)	31	83	58	2.58 (2.08)				
(2)	171	406	290	24.53 (25.98)				
(3)	406	533	444	38.72 (36.14)	35.60	35.80	black	black
Cu (mnt) (5-NO_2-phen)								
(1)	162	297	275	16.59 (17.48)				
(2)	297	486	450	53.81 (52.68)				
(3)	507	741	651	11.19 (11.18)	18.64	18.65	black	black
Zn (mnt) (5-NO_2-phen)·0.5H_2O								
(1)	31	90	67	2.47 (2.05)				
(2)	139	456	262	33.25 (34.17)				
(3)	456	506	482	24.19 (23.01)				
(4)	506	643	581	22.50 (22.30)	19.59	18.45	white	white

Thirty-one types of kinetic model functions [8] were into Eqs. (1) and (2), respectively. The values of E, ln A and the linear correlation coefficients (r) of different model functions were calculated from a weighted least–squares plot of $\ln[(d\alpha/dT)/f(\alpha)]$ vs. $1/T$ and of $\ln[g(\alpha)/T^2]$ vs. $1/T$. The results are listed in Table 3. Comparing the kinetic parameters from methods, we selected the probable kinetic model function No. 6 whose values of E and ln A were very close to each other with the better value of r. We conclude that the kinetic equation of thermal decomposition of complex III for stage (1) is $d\alpha/dt = A/\beta \cdot e^{-E/RT} \times 3/2(1-\alpha)^{4/3}/[(1-\alpha)^{-1/3}-1]$.

It shows that the first stage of decomposition for complex III is controlled by D_3 diffusion mechanism. The calculated values of the kinetic parameters of three complexes for each stage and their probable kinetic model functions are summarized in Table 4.

Table 2
Data for stage (1) of Zn (mnt) (5-NO_2-phen)·0.5H_2O determined by TG–DTG

Data point	T/K	α	$d\alpha/dT$
1	310.52	0.1183	1.9591×10^{-2}
2	311.77	0.1428	1.9259×10^{-2}
3	313.02	0.1673	2.0919×10^{-2}
4	315.52	0.2244	2.2085×10^{-2}
5	323.02	0.3510	1.6881×10^{-2}
6	325.52	0.3959	1.8368×10^{-2}
7	328.12	0.4408	1.7399×10^{-2}
8	330.52	0.4816	1.4889×10^{-2}
9	333.02	0.5142	1.1204×10^{-2}
10	335.51	0.5428	1.3892×10^{-2}
11	338.01	0.5877	2.1507×10^{-2}
12	340.51	0.6489	2.7425×10^{-2}
13	343.01	0.7183	2.5524×10^{-2}
14	345.51	0.7306	2.3377×10^{-2}
15	348.01	0.8244	2.6535×10^{-2}
16	349.26	0.8612	3.1241×10^{-2}

3.3. The kinetic compensation effect

According to the mathematical expression for the kinetic compensation effect $\ln A = aE + b$ [9], we fitted the kinetic parameters (E and ln A) obtained from the differential methods by the linear least-squares method. The obtained values of a and b are listed in Table 4.

4. Conclusions

Thermal analysis results obtained for the complexes I to III indicate that the complexes under study, when thermally decomposed, release water (I and III), at first, the dehydration temperature being ca. 90°C; the release of ligand is a three-stage (II, III′), two-stage (I′)

Table 3
Results of kinetic analysis for stage (1) of Zn (mnt) (5-NO_2-phen))·0.5H_2O

Function no.	Integral method			Differential method		
	ln A/s^{-1}	E/(kJ mol^{-1})	r	ln A/s^{-1}	E/(kJ mol^{-1})	r
1	22.58	80.29	0.9757	11.42	49.43	0.9572
2	25.39	89.03	0.9287	16.73	64.90	0.9654
3	28.17	99.78	0.9886	22.31	83.26	0.9655
4	25.30	92.58	0.9850	17.66	71.22	0.9657
5	17.02	72.08	0.9704	4.57	37.72	0.9325
6	37.68	123.87	0.9932	36.26	119.39	0.9818
7	13.42	52.88	0.9911	9.94	42.68	0.8347
8	10.63	35.25	0.9911	2.62	23.23	0.6298
9	9.51	26.44	0.9911	−1.11	13.50	0.4226
10	7.55	17.62	0.9911	−4.98	3.78	0.1279
11	6.67	13.22	0.9911	−6.99	−1.08	0.0366
12	10.26	48.53	0.9884	5.06	33.56	0.7998
13	9.99	47.16	0.9872	4.19	30.64	0.7834
14	9.31	44.51	0.9843	2.27	24.62	0.7387
15	7.08	37.41	0.9720	−4.00	6.55	0.3518
16	14.90	58.85	0.9746	3.76	27.99	0.8733
17	−1.14	15.97	0.9616	−12.07	−14.88	0.5945
18	−4.19	8.83	0.9446	−14.93	−22.02	0.7212
19	−5.94	5.25	0.9149	−16.45	−25.60	0.7629
20	13.42	52.88	0.9911	9.94	42.68	0.8347
21	16.63	62.57	0.9926	16.22	60.74	0.8714
22	21.70	73.54	0.9901	23.89	78.80	0.8898
23	32.38	98.76	0.9794	38.54	114.93	0.9076
24	3.16	26.51	0.9329	−17.26	−29.56	0.9156
25	0.23	18.93	0.8807	−30.81	−65.69	0.9581
26	−1.96	13.55	0.8194	−44.84	−101.82	0.9569
27	34.90	111.24	0.9920	31.37	101.03	0.9640
28	56.06	169.59	0.9922	52.52	159.38	0.9835
29	77.10	227.94	0.9924	73.54	217.74	0.9892
30	0.08	19.52	0.9795	−6.82	−0.36	0.0150
31	0.46	20.84	0.9835	−5.21	4.32	0.1641

Table 4
All metal complexes stage's kinetic model functions and correspond compensation effect

Metal complex	Stage	Function No.	Integral method			Differential method			Compensation effect		
			E/(kJ mol^{-1})	ln A/s^{-1}	r	E/(kJ mol^{-1})	lnA/s^{-1}	r	a	b	r
Co^{II}	(1)	23	136.23	47.46	0.9860	136.85	47.82	0.8282	0.3765	−6.41	0.9995
	(2)	29	222.29	38.50	0.9932	235.54	40.98	0.9764	0.2124	−8.54	0.9972
	(3)	23	352.92	55.11	0.9820	320.16	49.47	0.9573	0.1688	−7.47	0.9995
Cu^{II}	(2)	1	135.92	15.56	0.9800	135.75	15.55	0.9722	0.1757	−8.03	0.9987
	(3)	6	292.79	30.29	0.9744	275.65	27.77	0.9117	0.1353	−8.38	0.9987
Zn^{II}	(1)	6	123.87	37.68	0.9932	119.39	36.26	0.9818	0.3699	−6.71	0.9991
	(2)	29	154.31	22.58	0.9946	168.70	25.56	0.9839	0.2046	−8.56	0.9937
	(3)	21	497.84	74.09	0.9985	488.42	72.66	0.9861	0.1612	−6.61	0.9999
	(4)	5	307.32	34.40	0.9988	327.46	37.13	0.9417	0.1451	−7.66	0.9996

process; the initial and final temperature of decomposition of the complexes (I′, II and III′) for first stage are in the range 171–406°C, 162–297°C and 139–456°C, respectively. It is concluded that it is possible to establish the following relative thermal stability order: Co (mnt) (5-NO_2-phen)>Cu (mnt) (5-NO_2-phen)>Zn (mnt) (5-NO_2-phen).

From Table 4, there is no regular variation in the values of the kinetic parameters of decomposition of the complexes. The activation energy of the dehydration reactions for complexes I and III is in the range 113.39–136.85 kJ/mol. The activation energy of the decomposition reaction for complexes I′, II and III′ is in the range 135.92–497.84 kJ/mol which indicates that the metal–ligand bond is strong.

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