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SYNTHESIS AND THERMAL DECOMPOSITION OF THE MACROCYCLIC DINUCLEAR Ni(II) COMPLEX

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Abstract

Crystal of the complex $Ni_2L(ClO_4)_2$ was obtained by reaction of $Ni(ClO_4)_2$ and macrocyclic ligand H_2L, where L^{2-} is the dinucleating macrocycle with two 2,6-di(aminomethyl)-4-methyl phenolate entities combined by the same two lateral chains, $-(CH_2)_2-NH-(CH_2)_2-$, at the amino nitrogens. The thermal decomposition processes of the title complex were studied in a dynamic atmosphere of dry argon using TG-DTG. The kinetic analysis of the first and second thermal decomposition steps were performed via the TG-DTG curves, and the kinetic parameters were obtained from analysis of the TG-DTG curves with integral and differential methods. The most probable kinetic function was suggested by comparison of the kinetic parameters.

Keywords: dinuclear Ni(II) complex, non-isothermal kinetics, synthesis

Introduction

The macrocyclic polyamine ligands can form complexes with alkaline earth metal, transition metal and rare earth metal ions. These complexes were used to ‘mimic’ the active sites of metallobimolecules [1, 2] to evaluate appropriate system for bind and activation of small molecules [3–5] and to investigate the mutual influence of the two metal centers on the electronic, magnetic, and redox properties of such systems. As part of a study of the relation between the structure and properties, the complex $Ni_2L(ClO_4)_2$ (Fig. 1) is synthesized. The present paper reports the possible process and mechanism functions of thermal decomposition of the title complex.

Experimental

Synthesis of the complex $Ni_2L(ClO_4)_2$

H_2L

A mixture of 2,6-diformyl-4-methylphenol [6] (1.0 g, 6.1 mmol), lead(II) perchlorate trihydrate (2.8 g, 6.1 mmol) and triethylamine (0.7 g) in methanol (50 cm^3)

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was refluxed. A methanol solution (50 cm^3) of diethylenetriamine (0.66 cm^3, 6.1 mmol) was added dropwise, and the mixture was refluxed for 1 h and allowed to stand at room temperature to give $Pb_2R(ClO_4)_2\cdot CH_3OH$ as yellow microcrystals. They were separated, washed successively with methanol and ether, and dried in vacuum. The yield was 2.8 g (84.6%).

Finely ground $Pb_2R(ClO_4)_2\cdot CH_3OH$ (5.38 g, 5.08 mmol) was suspended in methanol (200 cm^3). A portion of $NaBH_4$ (2.0 g) was added to the suspension and the mixture was stirred for 15 min at room temperature, the operation of the addition of $NaBH_4$ (2.0 g) and the stirring for 15 min at room temperature was repeated twice. The resulting solution was evaporated to dryness, the residue was dissolved in water (200 cm^3) and the solution was made weakly acidic (pH=4) with dilute sulfuric acid. The resulting lead sulfate was removed by filtration, and the filtrate was made alkaline with ammonia to pH=10 and then extracted with $CHCl_3$. The $CHCl_3$ extract was dried with anhydrate Na_2SO_4 and concentrated to give light yellow precipitate. It was separated and washed with a small amount of petroleum ether, and dried in vacuum. The yield was 1.97 g (87.4%).

$Ni_2L(ClO_4)_2$

A solution of H_2L (0.24 g, 0.5 mmol) and nickel(II) perchlorate hexahydrate (0.37 g, 1 mmol) in methanol (20 cm^3) was refluxed for 1 h. The reaction mixture was allowed to stand at room temperature to give blue crystals.

TG-DTG experimental equipment and conditions

Thermogravimetric measurement were performed on Perkin Elmer model TGA7 with an argon flow rate of 20 ml min^{-1}, in the temperature range 60–700°C and with a linear heating rate of 10.00°C min^{-1}. The amount of sample used was about 4.101 mg.

Results and discussion

Compositions of H_2L and complex $Ni_2L(ClO_4)_2$

Analytical data for the ligand H_2L and complex were as follows:

H_2L: Found (%): C, 67.18; H, 9.10; N, 17.89. Calc. for $C_{26}H_{42}N_6O_2$: C, 67.83; H, 8.94; N, 18.26. ^1H NMR ($CDCl_3$): δ 2.19 (6H, 2×$ArCH_3$), 2.70 (16H, 4×CH_2CH_2), 3.80 (8H, 4×$ArCH_2$), 4.12 (6H, 6×NH), 6.72 (4H, 4×ArH), 7.50 (2H, 2×ArOH).

$Ni_2L(ClO_4)_2$: Found (%): C, 37.53, H, 5.12, N, 9.49. Calc. for $Ni_2C_{26}H_{40}Cl_2N_6O_{10}$: C, 38.05; H, 5.36; N, 10.24.

Structure analysis result shows that the complex molecular formation conforms to Fig. 1.

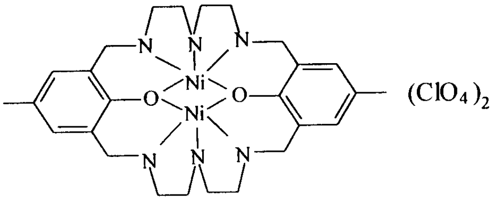

Fig. 1 $Ni_2L\ (ClO_4)_2$

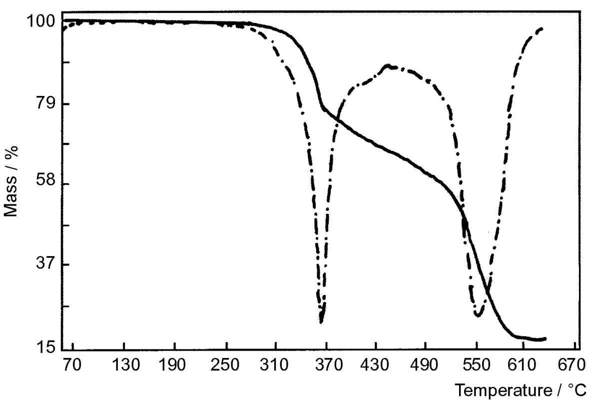

Fig. 2 TG-DTG curves of $Ni_2L(ClO_4)_2$

Thermal decomposition process

The TG-DTG curves of the complex in the temperature range 60–700°C are shown in Fig. 2. They show that the thermal decomposition processes of the complex $Ni_2L(ClO_4)_2$ involves two steps. The probable thermal decomposition steps of the complex are

$$Ni_2L(ClO_4)_2 \xrightarrow{253\text{–}453^{\circ}C} Ni_2(C_8H_{22}N_6)_2(ClO_4)_2 \xrightarrow{453\text{–}612^{\circ}C} 2NiO$$

The kinetics of the thermal decomposition reactions for the complex $Ni_2L(ClO_4)_2$

In this paper, the Achar *et al.* differential equation [7] and the Coats-Redfern integral equation [8] are used to analyze the kinetic problems for the thermal decomposition processes of the complex. The equations are

Coats-Redfern integral equation

$$\ln\frac{g(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \qquad (1)$$

Achar differential equation

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)}\right]=\ln\frac{A}{\beta}-\frac{E}{RT} \tag{2}$$

In the above equations, α is the fraction of the reacted materials, T is the absolute temperature; $f(\alpha)$ and $g(\alpha)$ are differential and integral mechanism functions, respectively. E and A are the derived apparent activation energy and preexponental factor, respectively. R is the gas constant and β is the linear heating rate. In order to obtain the kinetic information of the complex $Ni_2L(ClO_4)_2$, nineteen possible forms of $f(\alpha)$ and $g(\alpha)$ were selected and used to fit the above two equations. The selected $f(\alpha)$ and $g(\alpha)$ forms are listed in Table 1.

Table 1 Function forms used for the analysis

Function no.	Integral function form, $g(\alpha)$	Differential function form, $f(\alpha)$
1	α^2	$1/(2\alpha)$
2	$\alpha+(1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$
3	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
4	$[1-(1-\alpha)^{1/3}]^2$	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
5	$[(1+\alpha)^{1/3}-1]^2$	$1.5(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$
6	$[1/(1-\alpha)^{1/3}-1]^2$	$1.5(1-\alpha)^{4/3}[1/(1-\alpha)^{1/3}-1]^{-1}$
7	$-\ln(1-\alpha)$	$(1-\alpha)$
8	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
9	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[1-\ln(1-\alpha)]^{1/2}$
10	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
11	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
12	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
13	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
14	α	1
15	$\alpha^{1/2}$	$2\alpha^{1/2}$
16	$\alpha^{1/3}$	$3\alpha^{2/3}$
17	$\alpha^{1/4}$	$4\alpha^{3/4}$
18	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$
19	$(1-\alpha)^{-1/2}$	$2(1-\alpha)^{3/2}$

Using the possible forms of $g(\alpha)$ and $f(\alpha)$, the data in Tables 2, 3 are analyzed using the two equations (1 and 2). The kinetic analysis were completed on an IBM computer. The T term in $\ln[AR(1-2RT/E)/(\beta E)]$ of Eq. (1) was assigned to the value

Table 2 Data of the first step of the thermal decomposition for $Ni_2L(ClO_4)_2$

No.	α	T/K	$d\alpha/dt$
1	0.4747	578	0.3484
2	0.5469	582	0.4556
3	0.627	586	0.536
4	0.7359	590	0.67
5	0.8579	594	0.8308
6	0.9976	598	0.9916
7	0.1163	602	1.1256
8	0.1353	606	1.3399
9	0.1576	610	1.5543
10	0.184	614	1.8223
11	0.2147	618	2.0635
12	0.2512	622	2.3047
13	0.2966	626	3.1623
14	0.6402	642	5.7886
15	0.6681	646	4.4486

of the mean temperature of the original data. The data for kinetic analysis of the two decomposition steps are shown in Tables 2, 3, and the results of the kinetic analysis are listed in Tables 4, 5.

The results in Tables 4, 5 show that the values from the two methods are approximately the same and the linear correlation coefficients are better when the probable mechanism functions are function no. 5 for the first step and no. 13 for the second step. Their kinetic parameters are listed in the correct range [9] (E=80–250 kJ mol^{-1}, ln$A$=16.9–69.09). We conclude that the kinetic equations of the thermal decomposition for the complex are

The first step:

$$\frac{d\alpha}{dt}=\frac{A}{\beta}e^{-E/RT}1.5(1+\alpha)^{2/3}[(+\alpha)^{1/3}-1]^{-1}$$

The second step:

$$\frac{d\alpha}{dt}=\frac{A}{\beta}e^{-E/RT}3(1+\alpha)^{2/3}$$

The physical meaning of the kinetic analysis is that in the first step of the thermal decomposition, the reaction was a diffusion-controlled reaction. There was a phase

Table 3 Data of the second step of the thermal decomposition for $Ni_2L(ClO_4)_2$

No.	α	T/K	dα/dt
1	0.03938	741	1.22
2	0.05159	746	1.2781
3	0.06447	751	1.3362
4	0.7821	756	1.3943
5	0.9229	761	1.4523
6	0.1073	766	1.5104
7	0.1234	771	1.5685
8	0.1412	776	1.6847
9	0.1596	781	1.8009
10	0.1798	786	1.9171
11	0.2021	791	2.1495
12	0.2285	796	2.4339
13	0.265	801	3.1371
14	0.3191	806	4.2409
15	0.3885	811	5.577
16	0.466	816	6.5065
17	0.5472	821	7.2036
18	0.626	826	7.05522
19	0.6978	831	7.3779
20	0.7617	836	6.8551
21	0.8172	841	6.0999
22	0.9081	846	5.2865
23	0.9092	851	3.9504

boundary that affected the reaction rate, and the reaction was the three-dimensional diffusion one that took place in a sphere with a certain radius. In the second step there was a contraction geometry shape reaction which took place in a sphere with a certain radius.

Conclusions

It can be concluded from the above results that the thermal decomposition processes are in two steps. In the first step the complex lost the two 2,6-di(aminomethyl)-4-methyl phenolate entities and the most probable mechanism for the

Table 4 Result of the kinetic analysis of the first step of the thermal decomposition for $Ni_2L(ClO_4)_2$

Function	Integral method			Differential method		
no.	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
1	235	42.47	0.9971	245.66	47.75	0.9979
2	246.85	44.25	0.9952	265.13	51.04	0.997
3	251.27	43.67	0.9944	272.42	51.03	0.9963
4	260.17	45.53	0.9926	286.6	53.93	0.9943
5	220.59	37.23	0.9985	224.8	41.24	0.9972
6	288.53	51.43	0.9859	329.14	62.63	0.9865
7	131.9	23.51	0.9888	165.63	33.38	0.9902
8	84.55	14.27	0.9879	118.28	24.19	0.9889
9	60.88	9.55	0.987	94.6	19.51	0.9871
10	37.2	4.67	0.9849	70.93	14.71	0.983
11	25.36	2.09	0.9821	59.09	12.23	0.9786
12	121.72	20.65	0.9935	144.36	28.34	0.9949
13	125.01	20.94	0.9921	151.45	29.39	0.9938
14	112.43	19.36	0.9969	123.08	24.68	0.9928
15	51.14	7.38	0.9964	61.8	12.8	0.9668
16	30.71	3.15	0.9957	41.37	8.67	0.9244
17	20.5	0.88	0.9948	31.15	6.52	0.8722
18	154.97	28.38	0.9761	208.17	42.09	0.9751
19	11.12	–0.98	0.6522	186.9	37.04	0.9829

Table 5 Result of the kinetic analysis of the second step of the thermal decomposition for $Ni_2L(ClO_4)_2$

Function	Integral method			Differential method		
no.	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
1	288.76	40.24	0.9969	247.63	37.81	0.9801
2	311.35	43.2	0.9975	288.11	43.52	0.9871
3	320.61	43.19	0.9973	304.94	44.67	0.9878
4	339.49	46.23	0.9964	336.89	49.72	0.9864
5	266.61	34.41	0.9959	215.87	30.52	0.9739
6	403.39	56.49	0.9884	432.75	64.85	0.9733
7	178.27	24.74	0.9929	192.5	30.83	0.9583
8	114.45	15.02	0.9925	128.68	21.15	0.9283
9	82.54	10.06	0.9919	96.77	16.23	0.8931
10	50.62	4.93	0.9907	64.85	11.19	0.8153
11	34.67	2.24	0.989	48.9	8.58	0.7375
12	156.21	20.43	0.9969	144.57	22.57	0.9623
13	163.15	21.16	0.9961	160.55	24.69	0.9631
14	137.78	18.08	0.9966	96.65	15.7	0.9151
15	62.69	6.58	0.9957	21.15	4.3	0.4724
16	37.13	2.49	0.9946	–4.01	0.33	0.1034
17	24.55	0.29	0.9929	–16.59	–1.75	0.3989
18	233.64	33.74	0.9727	288.36	45.96	0.9357
19	34.73	2.85	0.7624	240.43	37.7	0.9468

first thermal decomposition is no. 3 ($f(\alpha)=1.5(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$, $g(\alpha)=[(1+\alpha)^{1/3}-1]^2$). In the second step it lost the two diethylenetriamine entities and the most probable mechanism for the second thermal decomposition is no. 13 ($f(\alpha)=3(1-\alpha)^{2/3}$, $g(\alpha)=1-(1-\alpha)^{1/3}$). The final residues were nickel oxides (NiO). The thermal decomposition processes reflected the structure characteristic of the complex and the coordination of the nitrogens of the macrocycle may be a stable factor of the complex.

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