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KINETICS OF THERMAL DECOMPOSITION OF MIXED LIGAND TRINUCLEAR COMPOUND OF CADMIUM(II)

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Abstract

The crystal $C_{81}H_{78}N_{12}O_6Cd_3$ was synthesized and its structure was determined by single crystal X-ray diffraction method. The complex crystallizes in the monoclinic system space group $P2_1/n$ with cell parameters, a=15.959(4) Å, b=26.222(3) Å, c=25.907(6) Å, β=101.60(2)°. The non-isothermal kinetics of the crystal was studied 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 the thermal decomposition reaction for its second step were proposed. The kinetic equation of thermal decomposition is expressed as:

$d\alpha/dt=A\exp(-E/RT)1.5(1-\alpha)^{4/3}[1/(1-\alpha)^{1/3}-1]^{-1}$. The average values of E(kJ mol^{-1}) and $\ln A/s^{-1}$ are 339.25, 43.95, respectively.

Keywords: cadmium(II) atom, kinetics, non-isothermal decomposition, Schiff-base compound

Introduction

The synthesis and complexation properties of macrocyclic Schiff-base compounds with cadmium(II) atom have attracted considerable attention in recent years [1–5], but there are few reports on the thermal stability and mechanism of thermal decomposition. Cd-MT (MT: metal sulphur protein) is the form of cadmium in the human body [6]. The structure and mechanism of Cd-MT have not been elucidated so far. So it is important to study the restoration and reaction of the large molecule in the animal body by studying the coordinating law and stability of Schiff-base compounds with cadmium(II) atoms which can be employed as models of Cd-MT. On the basis of previous work [7–13], the authors synthesized the title compound, and determined its crystal structure. Based on

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the analysis of the data of its non-isothermal kinetics, a possible mechanism of the thermal decomposition of the complex is proposed.

Experimental

Apparatus and measurements

Elemental C, H, N analyses were carried out with a Perkin-Elmer 240C elemental analyzer (USA) and the Cd^{2+} content of the complex was determined by EDTA titration. Crystal structure determination was made with an Enraf-Nonius CAD4 diffractometer. Thermogravimetric analysis of finely powdered samples was performed on a Perkin-Elmer model TGS-2 Thermogravimetric analyzer, at a nitrogen flow rate of 40 ml min^{-1}, in the temperature range 50–690°C linear heating rate of 10.00°C min^{-1}.

Single crystal of Cd(II) complex coordinated with Schiff-base and pyridine

1.05 mL salicylaldehyde was dissolved in 20 mL of 99.5% ethanol, followed by addition 0.42 mL 1,3-propylene diamine. The mixture was stirred and heated on a waterbath at 50–60°C for about 1.5 h. The solution turned yellow (H_2L). Then an aqueous solution (10 mL) of $Cd(Ac)_2{\cdot}3H_2O$ (1.42 g) was added under constant stirring at 60–70°C for about 4 h. A yellow precipitate $Cd_2C_{21}H_{22}N_2O_6$–$Cd_2(L)(CH_3COO)_2$ was obtained and washed with water and 99.5% ethanol (yield 51.3%). Elemental composition of $Cd_2C_{21}H_{22}N_2O_6$–$Cd_2(L)(CH_3COO)_2$; Calculated: C, 40.38; H, 3.52; N, 4.49; Cd, 31.54. Found: C, 39.88; H, 3.49; N, 4.48; Cd, 32.05.

The product was dissolved in pyridine at 80°C to give a saturated solution, the resulting solution was evaporated at room temperature in air for about 20 d to give a light-yellow transparent complex single crystal $C_{81}H_{78}N_{12}O_6Cd_3$.

Determination of crystal structure

Intensity data for the colourless single-crystal blocks of $C_{81}H_{78}N_{12}O_6Cd_3$, having dimensions of 0.3×0.25×0.3 mm, was measured at 299 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized MoK_α radiation, λ=0.71073 Å; a total of 8456 independent diffraction points were collected in the range of $2.0° \leq \theta \leq 20.0°$ by the ω–2θ scan technique. No significant decomposition of the crystal occurred during its data collection, and only absorption-corrected data [14] which satisfied the $I \geq 3.0\sigma(I)$ criterion were used in the subsequent analysis. An empirical absorption correction was applied in this case [14]. Crystal data are summarized in Table 1. The structure was solved by direct methods and Cd(II) atoms were located from the E-figure, the crystal structure was figured out by use of MULTAN 82. The locations of all of the non hydrogen

Table 1 Crystal data for the compound

Name	Value
Empirical formula	$C_{81}H_{78}Cd_3N_{12}O_6$
Space group	monoclinic, $P2_1/n$
a, Å	15.959(4)
b, Å	26.222(3)
c, Å	25.907(6)
fw	1652.80
β, deg	101.60(2)
V, Å^3	10620(7)
Z	4
T(°C)	26±1
λ(Å)(MoK$_\alpha$)	0.71073
h, k, l range collected	$-15\leq h\leq 15.0$, $0\leq k\leq 25.0$, $0\leq l\leq 24$
F(000)	3360
μ, cm^{-1}	6.34
No. of data measd	10157
No. of unique data	8406(Rint=3.1%)
No. of obsd data[$I\geq 3.0\sigma(I)$]	4990
R, R_w	0.078, 0.077
Good of fit	5.70
Maximum Δ/σ	0.16
Max/min transm factors	1.035/0.834
ρ_{calcd}, g cm^{-3}	1.034

$R = \sum||Fo|^2-|Fc|^2| / \sum|Fo|^2$; $R_w = \sum(|Fo|^2-|Fd^2)\omega^{1/2} / \sum|Fo|^2\omega^{1/2}$ and $\omega = 1$.

atoms were revised by the full matrix least squares method. Generally, non-H atoms were determined with successive difference Fourier synthesis. At convergence *R*=0.078 and *R*w=0.077; final refinement details are collected in Table 1. The numbering scheme is shown in Fig. 1.

Results and discussion

Crystal structure of the complex $C_{81}H_{78}N_{12}O_6Cd_3$

The molecular structure with atoms labeled is shown in Fig. 1. The structure analysis revealed that the crystal belongs to the monoclinic system, space group

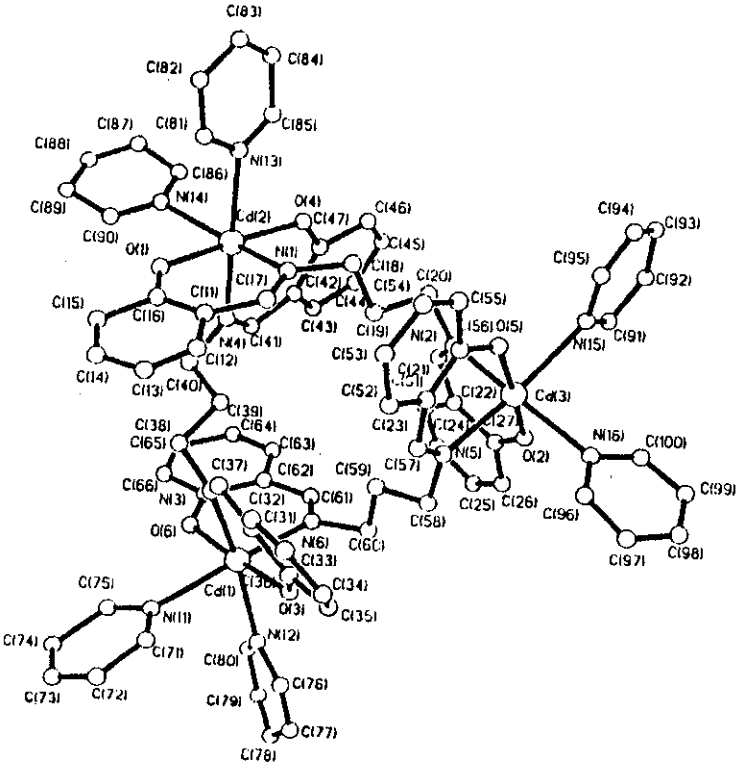

Fig. 1 Molecular structure and crystallographic numbering scheme for the single crystal

is $p2_1/n$ with cell parameters a=15.959 Å, b=20.222 Å, c=25.907 Å, β=101.60(2)°, V=10620 Å^3, Z=4, D_c=1.034 g cm^{-3}, μ=6.34 cm^{-1}, $F(000)$=3360. According to the molecular structure configuration, the crystals have a more complicated trinuclear cadmium structure. The distances between the three Cd(II) atoms are almost equal (d_{12}=7.616 Å, d_{23}=7.558 Å, d_{31}=7.617 Å). Each Cd(II) atom is in the same coordination condition with two nitrogen atoms from two pyridine molecules, two oxygen atoms and one nitrogen atom from the Schiff-base ligand, and one nitrogen atom from another Schiff-base ligand to form a distorted octahedron, of which two nitrogen atoms from each Schiff-base are coordinated with two cadmium atoms, respectively. Thus the whole compound was connected by three Schiff-base ligands to form a stereo octahedron structure. Though pyridine has strong coordination activity, it is weaker than that of the Schiff-base ligand, which can be proved by comparing their bond lengths. For example, the bond length is 2.393 Å for Cd(II)–N (N from pyridine molecule), and 2.286 Å for Cd–N (N from Schiff-base ligand). This is also supported by the following discussion of thermal analysis results.

Thermal decomposition of the crystal

The TG and DTG curves of the crystal are shown in Fig. 2. The TG-DTG curves show that the crystal has three mass-loss stages: the first is the loss of pyridine, the second is the partial loss of Schiff-base ligand and the third is the stage in which the residual ligands are lost. The final product is CdO. Pyridine was decomposed completely below 150°C. The Schiff-base ligand began to be released above 270°C. The decomposition temperatures and loss-in-mass rates (%) corresponding to the stages of the compound are as follows: 60–150°C, 28.34(28.71); 270–490°C, 26.32(26.19); 490–690°C, 22.22(21.80). Values in parentheses are calculated values. The experimental values agree fairly well with the calculated values. Pyridine was decomposed completely below 150°C. The Schiff-base ligand began to leave above 270°C, which supported the conclusion inferred by the structure elucidation, namely that the coordination activity of pyridine is weaker than that of the Schiff-base. The thermal decomposition processes are shown in Fig. 3.

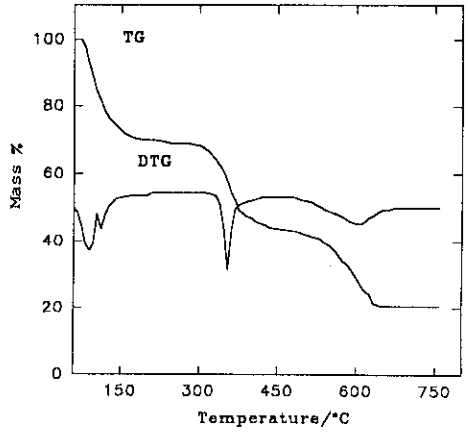

Fig. 2 TG and DTG curves of the crystal

Non-isothermal kinetics of the thermal decomposition of the crystal

The original data of non-isothermal kinetics of the thermal decomposition of the complex, obtained from the TG and DTG curves (Fig. 2), are listed in Table 2.

In this paper, we use the differential equation proposed by Achar *et al.* differential equation [15] and the Coats-Redfern integral equation [16] to analyze the non-isothermal kinetic data in the second step of thermal decomposition. Possible mechanisms of the reaction are deduced. The integral and differential equations are

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

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

In the above equations, α is the fraction of the reacted material, 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 pre-exponential factor, respectively. R is the gas constant and β is the linear heating rate. Using the possible forms of $g(\alpha)$ and $f(\alpha)$ from Table 3, the data in Table 2 are analyzed by use of Eqs (1) and (2). For Eqs (1) and (2), the kinetic analyses are completed by the linear least squares method. The results – kinetic parameters E, A and correlation coefficient r – are shown in Table 4. The results in Table 4 clearly

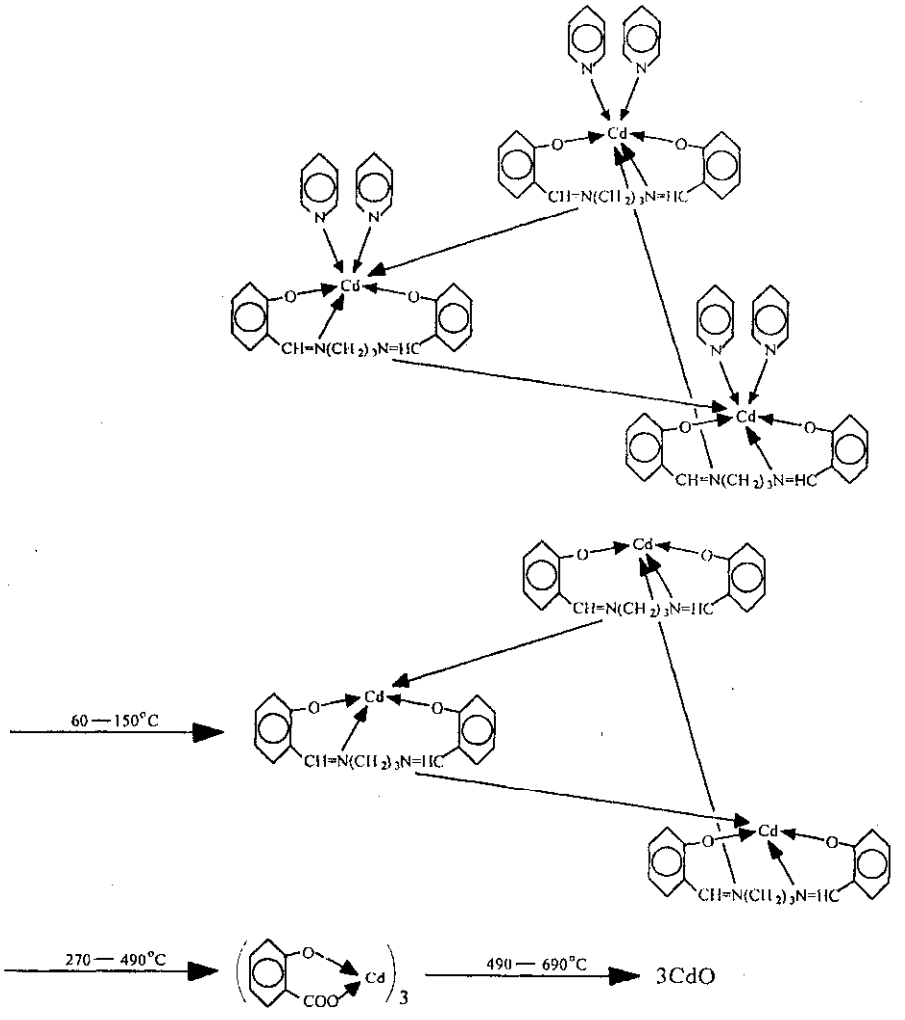

Fig. 3 Thermal decomposition process scheme for the crystal

Table 2 Non-isothermal kinetic data of the second step of the thermal decomposition of the crystal

No.	α_i	T_i(K)	$(d\alpha/dt)_i(S^{-1})$	No.	α_i	T_i(K)	$(d\alpha/dt)_i(s^{-1})$
1	0.06947	783	0.1161	2	0.09733	793	0.1503
3	0.1342	803	0.1844	4	0.1884	813	0.2322
5	0.2390	823	0.2732	6	0.3053	833	0.3142
7	0.3783	843	0.3552	8	0.4576	853	0.3962
9	0.5428	863	0.4235	10	0.6283	873	0.4372
11	0.7194	883	0.3893	12	0.7912	893	0.3142
13	0.8473	903	0.2527	14	0.8928	913	0.1981
15	0.9348	923	0.1510	16	0.9651	933	0.1161

W=2.921 mg, β=10°C min^{-1}

Table 3 The common forms of $f(\alpha)$ and $g(\alpha)$

No.	Mechanism	$g(\alpha)$	$f(\alpha)$
1	One-dimensional diffusion, 1D	α^2	$1/(2\alpha)$
2	Valensi equation, two-dimensional diffusion, 2D	$\alpha+(1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$
3	Ginstling-Brounshtein equation, three-dimensional diffusion, 3D	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
4	Jander equation, three-dimensional diffusion, 3D	$[1-(1-\alpha)^{1/3}]^2$	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
5	Zhuralev-Lesokin-Tempelmen equation, three-dimensional diffusion, 3D	$\{[1/(1-\alpha)]^{1/3}-1\}^2$	$1.5(1-\alpha)4/3[1/(1-\alpha)^{1/3}-1]^{-1}$
6	Avrami-Erofeev n=1, First-order decay	$-\ln(1-\alpha)$	$1-\alpha$
7	Avrami-Erofeev n=1.5	$[-\ln(1-\alpha)]^{2/3}$	$1.5[(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
8	Avrami-Erofeev n=2	$[-\ln(1-\alpha)]^{1/2}$	$2[(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
9	Avrami-Erofeev n=3	$[-\ln(1-\alpha)]^{1/3}$	$3[(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
10	Avrami-Erofeev n=4	$[-\ln(1-\alpha)]^{1/4}$	$4[(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
11	Contracting area	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)]^{1/2}$
12	Contracting volume	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)]^{2/3}$
13	Mampel power law	$\alpha^{1/4}$	$4\alpha^{3/4}$
14	Second-order decay	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$
15	1.5 order decay	$(1-\alpha)^{1/2}$	$2(1-\alpha)^{3/2}$

Table 4 Kinetic parameters of the second step of the thermal decomposition of the crystal obtained by integral and differential methods

Function No.	Integral method			Function No.	Differential method		
	E/kJ mol^{-1}	ln$A$/s^{-1}	$\|r\|$		E/kJ mol^{-1}	ln$A$/s^{-1}	$\|r\|$
1	198.78	24.94	0.9702	1	113.54	12.01	0.8128
2	223.01	28.02	0.9813	2	160.72	18.40	0.9259
3	223.78	28.18	0.9855	3	182.23	20.11	0.9555
4	256.13	31.62	0.9921	4	222.25	26.09	0.9841
5	336.18	43.86	0.9997	5	342.32	44.04	0.9987
6	139.47	17.64	0.9977	6	127.11	15.23	0.9962
7	88.25	10.14	0.9974	7	75.88	7.79	0.9925
8	62.63	6.28	0.9970	8	50.27	3.98	0.9852
9	37.02	2.24	0.9959	9	24.66	0.06	0.9475
10	24.22	0.05	0.9943	10	11.85	−1.99	0.8219
11	112.81	12.74	0.9859	11	67.08	5.57	0.9003
12	120.97	13.63	0.9910	12	87.09	8.15	0.9626
13	12.42	−2.38	0.8861	13	−72.83	−14.62	0.8816
14	212.35	28.92	0.9921	14	247.17	33.18	0.9833
15	45.83	4.39	0.8787	15	187.14	23.51	0.9934

show that the values of E and A obtained from the two equations are approximately the same, the linear correlation coefficients are better when the probable mechanism functions of the complex are $f(\alpha)=1.5(1-\alpha)^{4/3}[1/(1-\alpha)^{1/3}-1]^{-1}$, $g(\alpha)=[\{1/(1-\alpha)\}^{1/3}-1]^2$. We concluded that the probable mechanisms of the second step of thermal decomposition of the complex is as given by the Zhuralev-Lesokin-Tempelman equation. The corresponding kinetic equation is $d\alpha/dt=A\exp(-E/RT)1.5(1-\alpha)^{4/3}[1/(1-\alpha)^{1/3}-1]^{-1}$. The average values of E/kJ mol^{-1} and ln$A$/s^{-1} are 339.25, 43.95, respectively.

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