

Synthesis and the Thermal Decomposition Reaction of Copper(II) Oxamide Complexes

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Abstract: Three mononuclear complexes were synthesized and characterized by elemental analyses, molar conductivity and IR spectral studies. A kinetic study of the thermal decomposition reactions of copper(II) complexes with N, N'-bis(alkylaminoalkyl)oxamide was carried out using TG and DTA technique under dynamic air atmosphere. The non-isothermal kinetics data were analyzed by means of the Achar method and the Coats-Redfern method. The most probable kinetic model was suggested by comparison of the kinetic parameters. The activation energies, entropies, and the pre-exponential factor of the thermal decomposition reactions were calculated with thermogravimetric curves. The initial temperature of decomposition was compared with those obtained for the complexes N, N'-bis(2-aminopropyl)oxamidocopper(II), N, N'-bis(2-aminopropyl)oxamidocopper(II), and N, N'-bis(3-aminopropyl)oxamidocopper(II). The sequence of thermal stability is: Cu(oxpn) > Cu(oxap) > Cu(oxen).

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

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1 Introduction

One of the best strategies to design and synthesize heterometal polynuclear complexes is the use of mononuclear complexes as ligands, i.e., "complex ligands" that contains a metal and can function as ligands to a second metal ion^[1-3]. It is known that N, N'-bis(alkylaminoalkyl)oxamidocopper(II) complexes would be suitable candidates of "complex ligands"^[4], because they can coordinate to another metal ion through the oxamide oxygens to afford polynuclear species and the remarkable efficiency of

the oxamidate 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^[1,2,4-10]. In order to investigate the magnetism of heterometal polynuclear complexes, we have previously adopted this strategy to synthesize a series of heterometal polynuclear complexes using mononuclear complex N, N'-bis(2-aminoethyl)oxamidocopper(II), N, N'-bis(2-aminopropyl)oxamidocopper(II), and N, N'-bis(3-aminopropyl)oxamidocopper(II) (abbreviated Cu(oxen), Cu(oxap), and Cu(oxpn)) as ligand^[3,7,9,10]. In spite of the considerable importance of this "complex

ligands" to synthesize the heterometal polynuclear complexes, very little work has been done on the thermal properties.

Methods of thermal analysis have made tremendous progress during the last few decades and have found wide applications range of. Nowadays these techniques are important tool in research and routine analysis. TG and DTA are valuable techniques for the study of the thermal properties of various compounds.

The aim of the present work is to pursue a more detailed study of the transformation of these mononuclear complexes when they undergo upon heating, and to understand the mechanism and the conditions and products of their thermal decomposition. Furthermore, we have studied the non-isothermal kinetics of thermal decomposition of these complexes. The kinetic parameters were obtained by integral and differential methods. The possible mechanisms of the thermal decomposition have been discussed.

2 Experimental

2.1 Preparation of complexes

All chemicals used in the work were analytical grade. The mononuclear complexes Cu(oxen), Cu(oxap) and Cu(oxpn) were prepared by previously published procedures^[5]. They were recrystallized from water and dried in vacuum.

2.2 Apparatus

Analysis of carbon, hydrogen and nitrogen was performed with a Perkin-Elmer elemental analyzer Model 240. Metal contents were determined by EDTA titration. IR spectra were recorded with a Nicolet FT-IR spectrophotometer using KBr pellets. Molar conductances were measured with a DDS-11A conductometer.

Thermal studies were performed on a TGDTA⁹² simultaneous analyzer (Setaram Corp.). TG and DTA runs were carried out at a heating rate of 7.5°C·min⁻¹ under a dynamic air atmosphere using a flow rate of 40 ml·min⁻¹. α -Al₂O₃ was used as reference

material. Alumina crucibles were used to hold 3~5 mg samples for analyses.

3. Results and discussion

3.1 Elemental Analysis

Results from the elemental analysis are listed in Table 1.

3.2 General Properties of the Mononuclear Complexes

These mononuclear complexes are very soluble in water to give stable solutions at room temperature, and practically insoluble in ethanol, methanol, carbon tetrachloride, chloroform and benzene. In the solid state all of the Cu(II) mononuclear complexes are fairly stable in air, thus allowing physical measurements. For the three Cu(II) mononuclear complexes, the observed molar conductance values in water solution at 25°C (in the 10~20 Ω⁻¹ cm² mol⁻¹ range) are given in Table 1. These values indicate that the three complexes have nonelectrolyte properties.

3.3 Infrared Spectra

Since the IR spectra of all the three mononuclear complexes are similar, the discussion is confined to the most important vibrations of the 200~4 000 cm⁻¹ region in relation to the structure. The IR absorption bands of the complexes are given in Table 1. We will only discuss the selected infrared bands, with most relevant IR absorption bands from the IR spectra of the mononuclear N,N'-bis(alkylamino-alkyl) oxamidocopper(II). The IR spectra at 1 585~1 620 cm⁻¹ for the mononuclear fragment attributable to carbonyl stretching vibration [ν(C=O)]. On the other hand, the IR spectra at 710~730 cm⁻¹ are due to carbonyl bending vibration [δ(C=O)] of the complexes. In addition, the appearances of the band at 3 250~3 320 cm⁻¹ are assigned to ν(NH₂) stretching of the amido group.

3.4 Thermal decomposition reactions of Cu(oxpn) (1)

The TG, DTG and DTA curves of Cu(oxpn)

complex are shown in Fig. 1. The DTG curve indicates the decomposition of the complex in two stages. The first transition occurs from 261 to 321°C, and

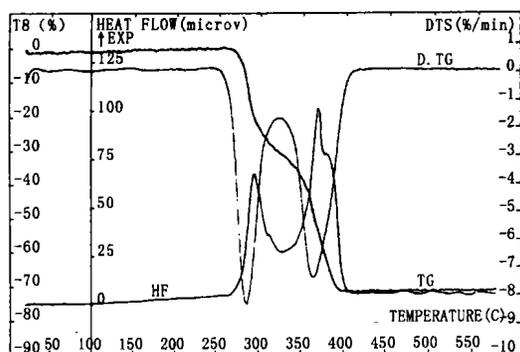


Fig. 1 TG-DTG-DTA curves of Cu(oxap) complex

the mass loss is 28.68% versus the calculated loss of 28.86%, corresponding to the release of $C_3H_{12}N_2$. The second transition is from 321 to 422°C, and the mass loss observed is 41.09% vs. the calculated loss of 40.98%, due to the release of all other organic ligands. The thermoanalytical data for Cu(oxpn) complex are given in Table 2.

The DTA curve shows two exothermic effects, at 289.7 and at 365.9°C. The exothermic effect indicates that organic groups are oxidized under air atmosphere. The former corresponds to the decomposition of the complex to $CuC_5H_4N_2O_2$. The second exothermic peak corresponds to the formation of CuO.

Table 1 Analytical data of the complexes

Complexes	Color	Found (Calcd.) (%)				Δ_M ($S \cdot cm^2 \cdot mol^{-1}$)	IR (cm^{-1})		
		C	H	N	Cu		$\nu(C=O)$	$\delta(C=O)$	$\nu(NH_2)$
Cu(oxpn) violet-red		36.28	5.98	21.09	23.87	10	1620	725	3285
		(36.43)	(6.11)	(21.24)	(24.09)				
Cu(oxap) pale-red		36.30	6.02	21.12	24.21	20	1588	716	3320
		(36.43)	(6.11)	(21.24)	(24.09)				
Cu(oxen) violet-red		30.31	5.02	23.51	26.72	18	1585	720	3250
		(30.57)	(5.13)	(23.77)	(26.95)				

Table 2 Thermal decomposition data for Cu(II) complexes from TG-DTG-DTA

Complexes	Stages	Decomposition temperature range/°C	DTA/°C		mass loss/%		probably expelled composition
			T_p^a	TG	Theoretical		
Cu(oxpn)	(1)	261-321	290(exo)	28.68	28.86	$N_2C_3H_{12}$	
	(2)	321-422	366(exo)	41.09	40.98	$C_5H_4N_2O$	
Cu(oxap)	(1)	213-259	245(exo)	14.72	14.44	$2NH_3 + 4H$	
	(2)	259-308	285(exo)	13.33	13.66	3C	
	(3)	308-456	373(exo)	40.83	41.74	$C_5H_6N_2O$	
Cu(oxen)·H ₂ O	(1)	37-161	76(endo)	7.13	7.10	H ₂ O	
	(2)	161-266	223(exo)	10.43	10.65	NCH	
	(3)	266-361	294(exo)	9.26	9.47	$NH_3 + 6H$	
	(4)	361-468	421(exo)	41.57	41.81	$C_5H_2N_2O$	

aT_p , temperature of peak; endo; endothermic; exo; exothermic

3.5 Thermal decomposition reactions of Cu(oxap)(2)

The TG, DTG, and DTA curves of the Cu(oxap) complex are shown in Fig. 2. It can be seen that the thermal dissociation of the Cu(oxap) complex is different from that of the Cu(oxpn) complex. Three

stages of the dissociation of complex are observed in DTG curve. The decomposition starts from 213°C and ends at 259°C, showing that two moles of ammonia and two moles of hydrogen are escaped. The mass loss observed is 14.72% against calculated 14.44%. The second stage is in continuation with

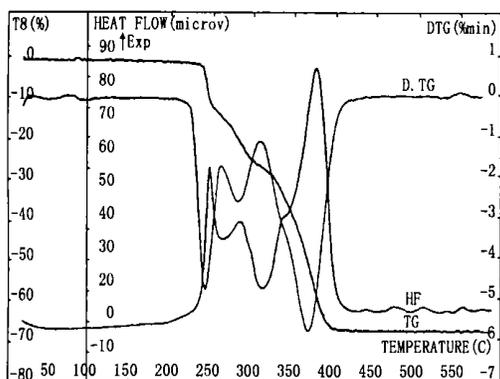


Fig. 2 TG-DTG-DTA curves of Cu(oxap) complex

the first stage from 259°C to 308°C. The mass loss observed is 13.33% against calculated loss of 13.66%, corresponding to the dissociation of three carbons. The third stage is from 308°C to 456°C. The mass loss observed is 40.83% against calculated loss of 41.73%, due to the release of all other organic ligands. The thermoanalytical data for the complex are also listed in Table 2.

There are three exothermic peaks in DTA curve corresponding to the transitions observed in the TG curve. The exothermic peak temperatures are 245.5°C, 284.5°C and 372.8°C. The first decomposition exothermic effect corresponds to $\text{CuC}_8\text{H}_6\text{N}_2\text{O}_2$. The second to its decomposition to $\text{CuC}_5\text{H}_6\text{N}_2\text{O}_2$ and the latter exothermic peak corresponds to CuO .

3.6 Thermal decomposition reactions of Cu(oxen)·H₂O (3)

The TG, DTG and DTA curves of the Cu(oxen)·H₂O complex are shown in Fig. 3. Four stages of the dissociation of complex are observed in DTG curve. The decomposition starts from 37°C and ends at 161°C, the mass loss observed is 7.13% against calculated 7.10%, corresponding to the release of one mole of water. The second stage is from 161°C to 266°C. The mass loss observed is 10.43 versus calculated 10.65%, showing that one mole of NCH group is expelled. The third stage is in continuation with the first stage from 266°C to 361°C. The mass loss observed is 9.26% against calculated loss of

9.47%, corresponding to the dissociation of one mole of ammonia and three moles of hydrogen. The last stage is from 361°C to 468°C. The mass loss observed is 41.57% against calculated loss of 41.81%, due to the release of all other organic ligands. The thermoanalytical data for Cu(oxen)·H₂O complex are listed in Table 2.

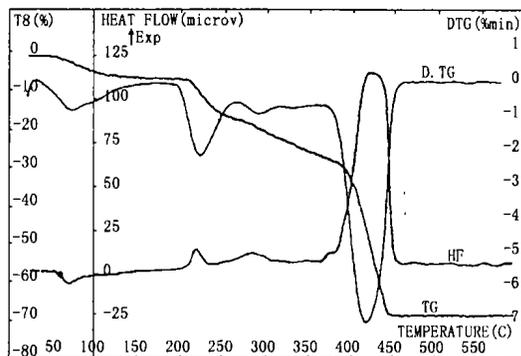
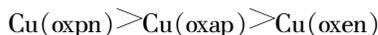


Fig. 3 TG-DTG-DTA curves of Cu(oxen)H₂O complex

The DTA curve shows one endothermic effect at 76°C and three exothermic effects at 223°C, 294°C and 421°C. The former corresponds to the release of one mole of water to $\text{CuC}_6\text{H}_{12}\text{N}_4\text{O}_2$, the second to its decomposition to $\text{CuC}_5\text{H}_{11}\text{N}_3\text{O}_2$, while the third corresponds to the decomposition of the complex to $\text{CuC}_5\text{H}_2\text{N}_2\text{O}_2$, and the latter to its decomposition to CuO .

Therefore, according to the results of the above mentioned thermal analysis. The thermal analysis data were compared with those obtained for three complexes. The initial temperatures of decomposition indicate that the sequence of thermal stability is:



This results shown that the N, N' - bis (alkyl-aminoalkyl)oxamidocopper(II) complexes with 6-5-6 member fused chelates are more stable than the complexes with 5-5-5 member rings, and 5-5-5 member fused chelates are stable than 4-5-4 members rings.

3.7 Kinetic studies of non-isothermal decomposition

In the present paper, the Achar^[11] and the

Coats—Redfern^[12] methods were used to derive the kinetic 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:

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

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

where α is the fraction of decomposition, da/dt is the fraction decomposed per second, T is the temperature in degree Kelvin, β is the heating rate, E is the activation energy in kJ mol^{-1} , A is the pre-exponential factor, R is the gas constant in $\text{kJ mol}^{-1} \text{K}^{-1}$, $f(\alpha)$ and $g(\alpha)$ are the most probable kinetic model functions^[13].

The basic parameters of T , α , and da/dt were obtained from the TG and DTG curves of $\text{Cu}(\text{oxpn})$, $\text{Cu}(\text{oxap})$, and $\text{Cu}(\text{oxen})$ complexes, respectively. The kinetic analysis was completed with the linear least-squares method. Comparing the kinetic parameters from different methods, we selected the

probable kinetic model function by which the calculated values of E and $\ln A$ were close to each other with the better linear correlation coefficient. Then, it can be concluded that kinetic equation of thermal decomposition of three complexes for the every stage.

The calculated values of the kinetic parameters of three complexes for each transition and their probable kinetic model functions were given in Table 3 and Table 4.

The entropy of activation (Δ_s^*) was calculated from the equation:

$$A = k \frac{T}{h} e^{\Delta_s^*/R} \quad (3)$$

where k : Boltzmann's constant; h : Planck's constant; T : DTG peak temperature. The obtained values of Δ_s^* were also given in Table 4. The values of activation entropy for three complexes are negative indicating a more ordered structure in the activated state than reactants and that the reactions are slower than the normal^[14,15].

Table 3 Mathematical expressions for different mechanisms

Complex	Stage	mechanism	symbol	$f(\alpha) = 1/k(d\alpha/dt)$
Cu(oxpn)	(1)	Chemical reaction (second order)	C ₂	$(1-\alpha)^2$
	(2)	N and G	A ₁	$1-\alpha$
Cu(oxap)	(1)	Chemical reaction (second order)	C ₂	$(1-\alpha)^2$
	(2)	diffusion 3D	D ₆	$3/2(1-\alpha)^{4/3} \{ [1/(1-\alpha)^{1/3}] - 1 \}^{-1}$
	(3)	N and G	A ₁	$1-\alpha$
Cu(oxen)·H ₂ O	(1)	Chemical reaction(second order)	C ₂	$(1-\alpha)^2$
	(2)	N and G	A ₁	$1-\alpha$
	(3)	diffusion 3D	D ₆	$3/2(1-\alpha)^{4/3} \{ [1/(1-\alpha)^{1/3}] - 1 \}^{-1}$
	(4)	diffusion 3D	D ₆	$3/2(1-\alpha)^{4/3} \{ [1/(1-\alpha)^{1/3}] - 1 \}^{-1}$

Table 4 Kinetic parameter of the Copper(II) complex

Complex	Stage	Integral method				Differential method			
		$E/\text{kJ} \cdot \text{mol}^{-1}$	$\ln A/\text{s}^{-1}$	$\Delta_s^*/\text{JK}^{-1} \cdot \text{mol}^{-1}$	r	$E/\text{kJ} \cdot \text{mol}^{-1}$	$\ln A/\text{s}^{-1}$	$\Delta_s^*/\text{JK}^{-1} \cdot \text{mol}^{-1}$	r
Cu(oxpn)	(1)	369.42	78.86	-213.82	0.9953	353.01	78.99	-213.81	0.9800
	(2)	210.54	38.39	-220.86	0.9993	193.84	39.07	-220.72	0.9900
Cu(oxap)	(1)	603.17	140.98	-208.31	0.9842	610.10	145.28	-208.06	0.9783
	(2)	477.86	101.04	-211.68	0.9979	460.32	99.81	-211.79	0.9979
	(3)	159.08	28.75	-223.36	0.9981	162.01	33.09	-222.19	0.9984
Cu(oxen)·H ₂ O	(1)	68.95	22.74	-220.18	0.9890	67.21	23.87	-219.77	0.9884
	(2)	115.43	26.23	-221.92	0.9373	111.86	28.03	-221.37	0.9742
	(3)	274.35	54.43	-217.14	0.9758	226.41	54.09	-217.03	0.9752
	(4)	254.85	43.13	-220.58	0.9949	232.27	43.08	-220.59	0.9856

4 Conclusion

Thermal analysis results indicated that copper(II) complexes with N, N' -bis(alkylaminoalkyl) oxamide were an excellent mononuclear complex ligands for the highly thermal stability. Comparing with the temperature of decomposition of the three complexes, their relative thermal stability can be obtained as follow: $Cu(oxpn) > Cu(oxap) > Cu(oxen)$. The results indicate that the N, N' -bis(alkylaminoalkyl) oxamidocopper(II) complexes with 6-5-6 member fused chelates are more stable than the complexes with 5-5-5 member rings, and 5-5-5 member fused chelates are stable than 4-5-4 member rings, which is the same as that in an aqueous solution of complex^[16,17]

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草酰胺合铜(II)配合物的合成和热分解反应

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摘要:合成了3种单核配合物,通过元素分析、摩尔电导和红外光谱进行了表征。在动态空气下,采用热重和差热技术研究了 N, N' -双氨烷基草酰胺合铜(II)配合物热分解动力学。用Achar法和Coats—Redfern法分析了非等温动力学数据,并对比动力学参数提出了最合适的热分解动力学模型。由热重曲线计算出了热分解反应的活化能、热焓和指前因子。对比配合物 N, N' -双-2-氨基乙基草酰胺合铜(II)、 N, N' -双-2-氨基丙基草酰胺合铜(II)和 N, N' -双-3-氨基丙基草酰胺合铜(II)初始分解温度,配合物的热稳定性排序为: $Cu(oxpn) > Cu(oxap) > Cu(oxen)$ 。

关键词:草酰胺合铜(II)配合物;热分解;非等温动力学