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Thermal decomposition of *N*,*N*′-ethylenebis(salicylideneiminato) diaquochromium(III) chloride

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Abstract

A complex of *N*,*N*′-ethylenebis(salicylideneiminato)diaquochromium(III) chloride, [Cr(salen) $(H_2O)_2$]Cl as a model of glucose tolerance factor (GTF) was characterized and its decomposition mechanism was studied by TG. The IR spectrum of the product of thermal decomposition was examined for the first stage. Kinetic results were obtained from the analysis of TG and DTG curves with four different methods. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Cr(III) complex; IR spectrum; Thermal decomposition; Non-isothermal kinetic

1. Introduction

Chromium(III) is an essential nutrient that has been implicated as glucose tolerance factor (GTF) in the maintenance of normal carbohydrate and lipid metabolism [1,2]. Insufficient dietary intake of Cr is linked to increased risk factors associated with Type II diabetes and cardiovascular diseases. Several GTF model complexes containing nicotinate or picolinate ligands which have much higher biological activity than chromic chloride have been synthesized and extensively studied [2–5]. Schiff base complexes of chromium(III) such as *N*,*N*′-ethylenebis(salicylideneiminato)diaquochromium(III) chloride, [Cr(salen) $(H_2O)_2$]Cl as a new kind of GTF model was also shown to reduce the symptoms of diabetes like, hyperglycemia and cholesterol in diabetic rats [6,7]. Although the structure, the substitution reaction kinetics and some reactions of [Cr(salen) $(H_2O)_2]^+$ were studied previously [8–13], no thermal decomposition data have been reported in the literatures for this complex, and the far-infrared spectra have received little attention. In this paper, we report a study of thermal decomposition and characterization of [Cr(salen) $(H_2O)_2$]Cl complex.

2. Experimental

2.1. Preparation of complex

[Cr(salen) $(H_2O)_2$]Cl was prepared essentially as described in literature [8], Salicylaldehyde (0.1 mol) and ethylenediamine (0.05 mol) were added to a solution of chromium(III) chloride hexahydrate (0.05 mol) in ethyleneglycol water–methanol (1:1:3,

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150 ml). After the mixture was refluxed for 30 min, sodium carbonate (0.03 mol) was gradually added to the solution, followed by reflux of the solution for about 3–4 h. Concentrating the solution yielded a reddish-brown precipitate, which was recrystallized from 80% methanol to give reddish orange crystals. Analysis for [Cr(salen) $(H_2O)_2$]Cl [Cr $(C_{16}H_{14}N_2O_2)$ $(H_2O)_2$Cl] C: 49.42 (49.30); H: 4.85 (4.65); N: 7.05 (7.19); Cr: 13.83 (13.42).

2.2. Techniques

TG was carried out on a Perkin Elmer TGA-7 thermogravimetric analyzer at a N_2 flow rate of 60 ml min^{-1}, and the temperature range was 313.15–773.15 K. The IR spectrum of the complex [Cr(salen) $(H_2O)_2$]Cl was examined on a Perkin Elmer 983 (KBr disc, 4000∼400 cm^{-1}, CsI disc, 400∼180 cm^{-1}) and a Shimadzu 403 infrared spectrophotometer (KBr disc, 4000∼650 cm^{-1}). The IR spectrum of the product of thermal decomposition was examined on a Shimadzu 403 infrared spectrophotometer. The molar conductance was obtained with a DDS-11A conductivity detector.

The Cr content of the complex was determined according to the reported general procedure [18]. C, H and N contents were determined using a Perkin Elmer 240 elemental analyzer.

3. Methodology

For a single TG–DTG curve, the Achar differential equation [14], the Coats–Redfern integral equation [15] and our reduced equations [16] were used to analyze the non-isothermal decomposition process. The integral, differential and our reduced equations are as follows:

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

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

$$\frac{E}{(RT_\mathrm{m}^2)} + A\left(\frac{1}{\beta}\right)f'(\alpha_\mathrm{m})\exp\left[\frac{-E}{(RT_\mathrm{m})}\right] = 0 \qquad (3)$$

$$\frac{E}{(RT_\mathrm{i}^2)} + 3A\left(\frac{1}{\beta}\right)f'(\alpha_\mathrm{i})\exp\left[\frac{-E}{(RT_\mathrm{i})}\right] - \frac{2}{T_\mathrm{i}} = 0$$

The Ozawa equation [17] was also used to obtained the kinetic parameters, in which several different heating rates are needed.

$$\log\beta + \frac{0.4567E}{RT} = C \qquad (4)$$

In the above equations, α is the fractional decomposition; T, the absolute temperature (K); $\mathrm{d}\alpha/\mathrm{d}t$, the reaction rate; A, the pre-exponential Arrhenius factor (S^{-1}); β, the heating rate (K min^{-1}); E, the apparent activation energy (J mol^{-1}); R, the gas constant (J mol^{-1} K^{-1}); $f(\alpha)$ and $g(\alpha)$, the differential and integral functions; $f'(\alpha)$, the differentiation of $f(\alpha)$; C, the constant value; the subscripts m and i, the point of the maximum transformation rate and the point of the inflection of DTG curve, respectively.

4. Results and discussions

4.1. Molar conductance

The complex is soluble in common solvents, such as water, methanol, alcohol, DMF, acetone, etc. The molar conductance in water solution is 96±2 s cm^2 mol^{-1} (298.15 K, 1.0×10^{-3} mol l^{-1}). This datum gives, as expected, a 1:1 electrolytic value.

4.2. IR spectrum

The IR spectrum of the complex is shown in Fig. 1. The IR spectrum shows the absorption at 1627, 1597, 1575 and 1530 cm^{-1} attributable to C=N, C=C

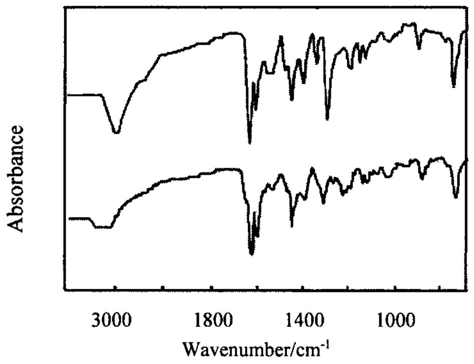

Fig. 1. IR spectra of [Cr(salen) $(H_2O)_2$]Cl (top) and the decomposition product Cr(salen)OH (bottom).

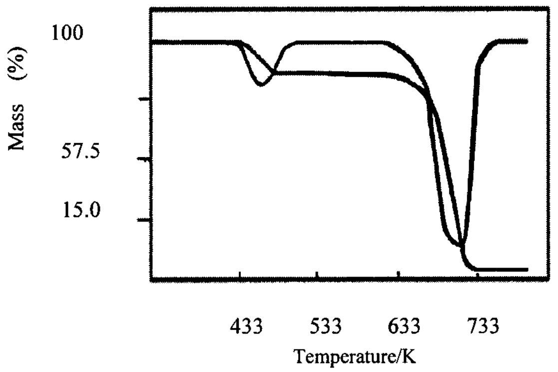

Fig. 2. TG and DTG curves of [Cr(salen) $(H_2O)_2$]Cl (β=5°C min^{-1}).

stretching frequencies of salen ligand and the absorption at 2600~3300 cm^{-1} attributable to co-ordination water molecules and $\gamma_{C\text{–}H}$ stretching frequencies. The IR bands around 385 and 375 cm^{-1} are assigned to $\gamma_{Cr\text{–}N}$, and the band at 512 cm^{-1} to $\gamma_{Cr\text{–}O}$ (phenolic), and the bands at 897, 540 and 499 cm^{-1} to ρ_r, ρ_w and $\gamma_{Cr\text{–}O}$ stretching frequencies of co-ordination water molecules [19]. These studies, as well as the molar conductance, infer that an octahedral structure of complex of chromium(III) is formed by the salen tetradentate Schiff base and two water ligands.

4.3. The thermal decomposition process

The TG and DTG curves are shown in Fig. 2. These curves indicate that the compound [Cr(salen) $(H_2O)_2$]Cl undergoes a two-stage decomposition. The IR spectrum of the product of the first stage of the thermal decomposition was given in Fig. 1 and is similar to that of [Cr(salen) $(H_2O)_2$]Cl. The IR bands of the salen ligand C=N, C=C stretching frequencies are still observed at 1622, 1594, 1552 and 1518 cm^{-1}. A broad band in the region 3300~3600 cm^{-1} is assigned to γ_{OH} showing the involvement of hydroxide in co-ordination. This shows that the salen ligand is still present in the tested substance. TG studies at this stage showed a mass loss corresponding to one H_2O and one HCl molecule. Thus, the probable product of decomposition at this stage is Cr(salen)OH [mass loss (%): calc: 13.98, found: 13.27]. The final substance is considered to be Cr_2O_3 [mass loss (%): calc: 80.49, found: 81.38]. These results suggested that the possible decomposition processes of *N*,*N*′-ethylenebis(salicylideneiminato)diaquochromium(III) chloride are the following:

$$[\mathrm{Cr(salen)}\ (\mathrm{H_2O})_2]\mathrm{Cl} \xrightarrow{360\sim552\,\mathrm{K}} \mathrm{Cr(salen)OH} \xrightarrow{552\sim741\,\mathrm{K}} \mathrm{Cr_2O_3}$$

4.4. Non-isothermal kinetic studies

The possible forms of $f(\alpha)$, $g(\alpha)$ and $f'(\alpha)$ [16] are listed in Table 1. The original data of the decomposition processes of *N*,*N*′-ethylenebis(salicylideneiminato)diaquochromium(III) chloride at the heating rate 5 K min^{-1} are listed in Table 2, the data of T_m, α_m, T_i and α_i are 472.15 K, 0.6659, 461.15 K, 0.3217 for the first decomposition process and 708.15 K, 0.8662,

Table 1
Function forms used for present analysis [16]

Fun. No.	$f(\alpha)$	$g(\alpha)$	$f'(\alpha)$
1	$1/(2\alpha)$	α^2	$-1/(2\alpha^2)$
2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$	$-(1-\alpha)^{-1}[\ln(1-\alpha)]^{-2}$
3	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	$-(1/2)(1-\alpha)^{-4/3}[(1-\alpha)^{-1/3}-1]^{-2}$
4	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$	$-(1-\alpha)^{-1/3}[1-(1-\alpha)^{1/3}]^{-1}-1/2[1-(1-\alpha)^{1/3}]^{-2}$
5	$3/2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^2$	$(1+\alpha)^{-1/3}[(1+\alpha)^{1/3}-1]^{-1}-1/2[(1+\alpha)^{1/3}-1]^{-2}$
6	$3/2(1-\alpha)^{4/3}[\{1/(1-\alpha)^{1/3}-1\}]^{-1}$	$[\{1/(1-\alpha)\}^{1/3}-1]^2$	$-2(1-\alpha)^{1/3}[\{1/(1-\alpha)\}^{1/3}-1]^{-1}-1/2[\{1/(1-\alpha)\}^{1/3}-1]^{-2}$
7	$(1-\alpha)$	$-\ln(1-\alpha)$	-1
8–11	$(1/n)(1-\alpha)[-\ln(1-\alpha)]^{-(n-1)}$, n=(2/3, 1/2, 1/3, 1/4)	$[-\ln(1-\alpha)]^n$	$(1/n-1)[-\ln(1-\alpha)]^{-n}-1/n[-\ln(1-\alpha)]^{1-n}$
12–13	$n(1-\alpha)^{(n-1)/n}$, n=(2, 3)	$1-(1-\alpha)^{1/n}$	$-(n-1)(1-\alpha)^{-1/n}$
14–17	$(1/n)\alpha^{-(n-1)}$, n=(1, 1/2, 1/3, 1/4)	α^n	$(1/n-1)\alpha^{-n}$
18	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$	$-2(1-\alpha)$
19	$(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$	$-3(1-\alpha)^{1/2}$

Table 2
TG and DTG data on the thermal decomposition of [Cr (salen) $(H_2O)_2$] Cl (β=5°C min^{-1})

The first stage			The second stage		
T (K)	α	dα/dt	T (K)	α	dα/dt
448.15	0.1396	0.4358	658.15	0.0821	0.2267
451.15	0.1732	0.5283	663.15	0.1195	0.2902
454.15	0.2139	0.6353	668.15	0.1554	0.3698
457.15	0.2627	0.7567	673.15	0.2144	0.4623
460.15	0.3203	0.8910	678.15	0.2739	0.5738
463.15	0.3879	1.0342	683.15	0.3451	0.7010
466.15	0.4656	1.1790	688.15	0.4353	0.8343
469.15	0.5531	1.3121	693.15	0.5428	0.9588
472.15	0.6491	1.4114	698.15	0.6511	1.0659
475.15	0.7499	1.4428	703.15	0.7673	1.1040
478.15	0.8491	1.3739	708.15	0.8662	1.0582
			713.15	0.9528	0.7919

695.65 K, 0.6123 for the second decomposition process, respectively.

Using the possible forms of $f(\alpha)$, $g(\alpha)$ and $f'(\alpha)$ in Table 1, the data in Table 2 and the data of T_m, α_m, T_i and α_i are analyzed by use of Eqs. (1)–(3). For Eqs. (1)–(3), the kinetic analysis is completed by a computer. The results are shown in Tables 3 and 4.

A method of selection of the most probable function of thermal decomposition mechanism from a single TG curve was suggested by Zhanghuai et al. [20] on the basis of comparison of kinetic parameters values of E and A from Eqs. (1) and (2). This method was also used to conclude the function of decomposition mechanism of some compounds in previous papers. The results in Table 3 show that the values of E and A from the two equations are approximately the same and the linear correlation coefficient is better when the mechanism function is function No. 12 in Table 1. But others, such as No. 3 also nearly have values of E and A and better coefficients from the two equations. It seems that the probable unique function of thermal decomposition mechanism for the first decomposition process is difficult to conclude by using Eqs. (1) and (2) only. However, as compared with the results obtained by using the reduced Eq. (3), it is clearly shown that only No. 12 in Table 3 has approximately the same values of E and A among the three equations. Thus, the most probable function of mechanism of the first decomposition process can be concluded as the function No. 12 (abstract surface mechanism [21]) in Table 1.

The results calculated in Table 4 also clearly show that the values of E and A yielded by three

Table 3
Results of the kinetic analysis of the first decomposition process of [Cr(salen) $(H_2O)_2Cl$]

Fun. No.	$f(\alpha)$ method			$g(\alpha)$ method			$f'(\alpha)$ method	
	ln A	E (kJ)	r	ln A	E (kJ)	r	ln A	E (kJ)
1	46.91	182.00	0.9909	51.89	209.44	0.9983	97.06	397.71
2	56.79	221.50	0.9990	57.31	231.83	0.9997	92.79	384.15
3	59.57	237.56	0.9999	58.26	240.88	0.9999	91.68	385.68
4	67.77	268.22	0.9994	63.25	259.26	0.9998	95.14	398.74
5	36.51	151.80	0.9832	43.85	188.28	0.9969	95.36	399.58
6	78.00	306.53	0.9966	79.85	320.57	0.9955	114.07	470.26
7	43.57	165.38	0.9930	34.85	140.36	0.9982	39.04	172.51
8	30.57	116.02	0.9896	21.82	91.01	0.9981	−4.43	12.35
9	23.99	91.34	0.9859	15.21	66.33	0.9978	−7.69	4.09
10	17.28	66.67	0.9784	8.45	41.66	0.9981	−8.93	2.14
11	13.84	54.33	0.9709	4.94	29.31	0.9975	−9.45	1.59
12	30.59	119.40	0.9999	28.29	119.03	0.9999	24.76	119.97
13	34.28	134.73	0.9987	29.74	125.76	0.9997	28.77	137.22
14	19.00	73.42	0.9693	23.95	100.88	0.9982	–	–
15	4.70	19.14	0.7751	9.57	46.58	0.9978	–	228.06
16	−0.23	1.04	0.0715	4.54	28.48	0.9976	–	209.45
17	−2.79	−8.00	0.4937	1.89	19.43	0.9962	–	200.16
18	68.15	257.34	0.9755	49.17	192.84	0.9864	67.61	281.29
19	55.17	211.36	0.9835	8.05	38.28	0.8950	52.52	226.57

Table 4
Results of the kinetic analysis of the second decomposition process of [Cr(salen) $(H_2O)_2$]Cl

Fun. No.	$f(\alpha)$ method			$g(\alpha)$ method			$f'(\alpha)$ method	
	ln A	E (kJ)	r	ln A	E (kJ)	r	ln A	E (kJ)
1	48.65	281.93	0.9718	56.36	337.92	0.9911	94.84	582.2
2	60.56	351.64	0.9944	62.44	374.74	0.9961	79.82	500.64
3	64.63	382.51	0.9985	63.86	390.68	0.9978	79.96	510.00
4	75.06	440.31	0.9994	69.88	423.53	0.9994	91.14	573.55
5	38.12	236.51	0.9562	48.22	306.08	0.9875	93.38	586.34
6	88.10	512.55	0.9950	90.98	539.11	0.9946	141.06	857.3
7	49.65	280.65	0.9863	38.99	232.97	0.9987	56.04	359.03
8	35.18	199.20	0.9770	24.50	151.54	0.9988	28.45	202.65
9	27.85	158.47	0.9669	17.15	110.79	0.9987	11.71	109.43
10	20.41	117.75	0.9464	9.66	70.08	0.9988	−1.96	37.65
11	16.61	97.38	0.9270	5.80	49.72	0.9989	−5.10	23.57
12	33.31	193.97	0.9999	31.08	194.03	0.9982	26.41	194.13
13	38.12	222.86	0.9974	32.91	206.08	0.9994	35.40	247.77
14	18.36	107.27	0.9169	26.03	163.27	0.9904	–	–
15	2.86	19.95	0.4821	10.47	75.94	0.9889	–	414.40
16	−2.46	−9.15	0.2681	5.05	46.85	0.9868	–	395.89
17	−5.22	−23.71	0.6041	2.21	32.27	0.9845	–	386.67
18	80.94	454.04	0.9555	58.05	336.67	0.9776	116.34	702.32
19	64.60	367.35	0.9691	11.30	75.30	0.8507	85.35	529.82

equations are approximately the same when the probable function of the mechanism is taken as function No. 12 in Table 1 for the second decomposition processes.

The apparent activation energy of the thermal decomposition processes were also calculated by the use of the Ozawa equation Eq. (4), in which four different heating rates were used. The original data of TG curves are listed in Table 5. The calculated results are shown in Table 6. As can be seen from Table 6 that the values of E of the two thermal decomposition processes are all in agreement with those calculated by Eqs. (1)–(3) when the probable function of the mechanism is function No. 12 in Table 1.

Table 5
TG data on the thermal decomposition of [Cr (salen) $(H_2O)_2$]Cl at different heating rates over the range of temperature 458.05–736.31 K

β (K min^{-1})	m (mg)[a]	α			
		0.3	0.5	0.8	0.85
The first stage					
5	3.244	458.05	467.16	476.77	479.91
10	2.799	468.96	476.60	487.57	490.78
15	2.055	473.84	483.83	491.88	494.64
20	2.581	478.03	487.10	497.47	499.86
The second stage					
5	3.244	679.98	691.16	704.22	707.53
10	2.799	695.76	705.66	715.62	724.79
15	2.055	700.16	712.02	727.54	729.54
20	2.581	708.10	719.70	734.61	736.31

[a] The amount of sample.

Thus, the kinetic equations in both the first and the second decomposition processes are as follows:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)2(1-\alpha)^{1/2}$$

Table 6
The values of E calculated by using the Ozawa equation

	α			
	0.3	0.5	0.8	0.85
The First stage				
E (kJ)	120.28	122.03	128.00	128.48
r	0.9980	0.9982	0.9967	0.9946
The Second stage				
E (kJ)	191.30	194.63	182.20	199.16
r	0.9917	0.9976	0.9921	0.9908

5. Conclusions

1. The probable product of thermal decomposition of complex [Cr (salen) $(H_2O)_2$]Cl at the first stage is Cr(salen)OH, which is confirmed by using IR spectrum and TG studies.
2. The most probable kinetic function is $f(\alpha)=2(1-\alpha)^{1/2}$ in both the first and the second decomposition processes of complex [Cr (salen) $(H_2O)_2$]Cl, which means that the two thermal decomposition processes are all the abstract surface process.

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