

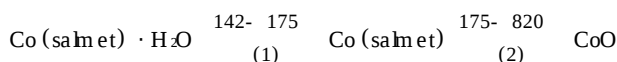
研究简报

水杨醛-L-甲硫氨酸希夫碱钴(II)配合物的热分解动力学

孟凡芹^a 李淑兰^{*a} 刘德信^a 杨兆荷^b

(^a 山东大学化学系, ^b 山东大学晶体材料国家重点实验室, 济南 250100)

本文合成了一种新的希夫碱配合物, 水杨醛-L-甲硫氨酸—水合钴(II), $\text{Co(salmet)} \cdot \text{H}_2\text{O}$, 并用非等温热重法研究了它的热分解反应动力学。TG 及DTG 曲线表明配合物按两步分解:



用 Arrhenius 微分法和 Coats-Redfern 积分法联合求出两步骤的动力学。步骤(1)、(2)的动力学方程分别表示如下:

$$d\alpha/dt = A \cdot e^{-E/RT} (1-\alpha) [-\ln(1-\alpha)]$$

$$d\alpha/dt = A \cdot e^{-E/RT} (1-\alpha)^2 [(1-\alpha)^{-1} - 1]$$

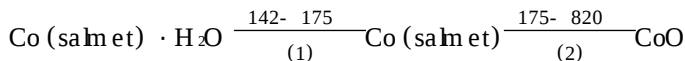
关键词: 希夫碱配合物 热分解 非等温动力学

THERMOCOMPOSITION KINETICS OF COBALT(II) COMPLEX WITH SCHIFF BASE DERIVED FROM SALICYLALDEHYDE AND L-METHIONINE

Meng Fanqin^a Li Shulan^{*a} Liu Dexin^a Yang Zhaohe^b

(^aDepartment of Chemistry, ^bState Key Laboratory of Crystal Materials, Shandong University, Jinan 250100)

A new Schiff base complex, salicylaldehyde-L-methionineimine monohydrate cobalt(II), $\text{Co(salmet)} \cdot \text{H}_2\text{O}$, was synthesized and its thermodecomposition kinetics was investigated under non-isothermal condition. TG and DTG curves indicate that the complex decomposed in two steps:



Kinetics of the two steps was calculated by the combination of Arrhenius differential and Coats-Redfern integral methods. Kinetic equations of step (1) and (2) can be expressed respectively as follows:

$$d\alpha/dt = A \cdot e^{-E/RT} (1-\alpha) [-\ln(1-\alpha)]$$

$$d\alpha/dt = A \cdot e^{-E/RT} (1-\alpha)^2 [(1-\alpha)^{-1} - 1]$$

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* 通讯联系人。

第一作者: 孟凡芹, 女, 26岁, 山东大学95届硕士研究生。

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1 Introduction

Cobalt (II) complexes of Schiff bases have been extensively investigated for their significance as models of natural dioxygen carriers, and for their potential application in oxygen separation and storage, catalytic oxidation, and anticancer medicine. Recently, attempts have been specially made to exploit analogous complexes derived from amino acids^[1-3], owing to their being promising for the understanding of metal-protein binding in biological systems. As thermal aspects are essential to complexes, the thermodecomposition process of $\text{Co}(\text{salmet}) \cdot \text{H}_2\text{O}$ was studied in this paper by TG-DTG technique, and the corresponding non-isothermal kinetics was discussed.

2 Experimental

2.1 Synthesis and Characterization of $\text{Co}(\text{salmet}) \cdot \text{H}_2\text{O}$

0.75 g of L-methionine was dissolved in 30 ml of 1:1 (V/V) EtOH-H₂O solution. To this was added 0.52 ml of salicylaldehyde dissolved in 10 ml of EtOH. Let the reaction proceed for 2 hrs on a 50 °C water-bath while stirring. Then a solution of 1.25 g of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ in 20 ml of boiling water was added dropwise to the above Schiff base solution under 1 GPa of N₂. The brown-yellow precipitate was filtered while kept warm an hour later, washed with EtOH and H₂O, and dried in a vacuum desiccator. Yield, 85.5%.

Analysis of the solid product, Found (wt %): C 43.58, H 4.66, N 4.20, Co 17.86; Calcd (wt %): C 43.90, H 4.57, N 4.27, Co 17.88.

Major IR bands of the complex: $\nu_{\text{C}=\text{N}}$ 1636.9, $\nu_{\text{C}-\text{O}}$ 1195.3, $\nu_{\text{Co}-\text{O}}$ 473.6, $\nu_{\text{Co}-\text{N}}$ = 335.1 cm^{-1} .

2.2 Thermogravimetric Analysis

TG and DTG curves of the complex were obtained on a Perkin-Elmer TGS-2 thermogravimeter. The heating rate was programmed to be 10 °C/min with the protecting stream of N₂ flowing at 40 ml/min.

3 Results and Discussion

3.1 Thermal Decomposition Process

The TG and DTG curves of the complex are shown in Fig. 1, which indicate that the complex decomposed in two steps. The first weight-loss stage has a decomposition temperature range of 142~175 °C, with a weight loss of 5.67%, which corresponds to the loss of a molecule of water (calcd 5.49%). The

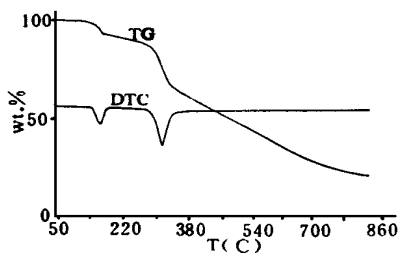
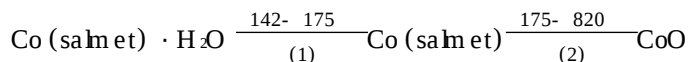
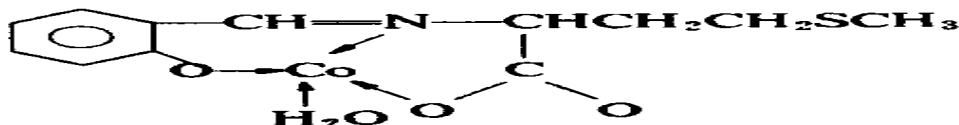


Fig. 1 TG and DTG curves of $\text{Co}(\text{salmet}) \cdot \text{H}_2\text{O}$

second stage shows the continuous weight loss between 175 and 820 °C, and only 20.88% of the original sample was left. With its calculated weight percentage of 22.80%, CoO is supposed to be the final product. The above decomposition process is thus suggested as:



The fact that the water molecule lost at quite a high temperature suggests that the H_2O coordinated with the metal ion. This conclusion is favored by the four-coordinate feature of cobalt (II)^[4], and helps to deduce the structure of the complex as: with N, O, O of the Schiff base ligand^[5] and O of the water as its four coordinate atoms, respectively.



3.2 Non-Isothermal Kinetics

On the basis of 19 kinetic functions in both differential and integral forms commonly used in recent reviews^[6], non-isothermal kinetics of the two steps was investigated using Achar differential method^[7] and Coats-Redfern integral method^[8].

Table 1 Data for Step (1) of Thermodecomposition of $\text{Co (salmet)} \cdot \text{H}_2\text{O}$ Obtained from TG and DTG Curves

No.	α_i	$T_i(\text{K})$	$(d\alpha/dt)_i(\text{s}^{-1})$
1	0.1716	428	0.1062
2	0.2525	431	0.1592
3	0.3416	433	0.1796
4	0.4241	435	0.2062
5	0.5214	437	0.2450
6	0.6188	439	0.2246
7	0.7310	441	0.1837
8	0.7921	443	0.1543
9	0.9472	446	0.1013

Table 2 Data for Step (2) of Thermodecomposition of $\text{Co (salmet)} \cdot \text{H}_2\text{O}$ Obtained from TG and DTG Curves

No.	α_i	$T_i(\text{K})$	$(d\alpha/dt)_i(\text{s}^{-1})$
1	0.3160	583	0.0454
2	0.3661	585	0.0517
3	0.4190	587	0.0581
4	0.4751	589	0.0599
5	0.5276	591	0.0594
6	0.5798	593	0.0574
7	0.6382	595	0.0524
8	0.6762	597	0.0434
9	0.7178	599	0.0361
10	0.7566	601	0.0318

The original kinetic data for step (1) and (2) obtained from the TG and DTG curves are listed in Table 1 and 2, respectively, in which T_i is the temperature at any point i on the TG and DTG curves, α_i is the corresponding decomposition rate

$(d\alpha/dt)_i = \beta(dw/dT)_i / (w_0 - w_\infty)$ in which $(dw/dT)_i$ is the height of the peak in the DTG curve, β is the heating rate and, w_0 and w_∞ are the initial and final weight of that stage, respectively. Calculated kinetic parameters (E , A) and correlation coefficients (r) of

step (1) and (2) are listed in Table 3 and 4

Table 3 Results of Analysis of the Data for Step (1) in Table 1 by Achar

Differential method and Coats-Redfern Integral method

function No.	integral method			differential method		
	E (kJ/mol)	$\ln A$ (s^{-1})	$ r $	E (kJ/mol)	$\ln A$ (s^{-1})	$ r $
1	294.98	78.01	0.9846	150.09	39.46	0.8094
2	338.05	89.56	0.9922	233.83	62.25	0.9447
3	357.21	93.48	0.9948	271.86	71.39	0.9712
4	396.89	104.71	0.9978	342.67	91.22	0.9902
5	261.29	66.12	0.9805	102.36	23.71	0.6856
6	538.50	144.66	0.9941	555.09	150.69	0.9858
7	227.59	60.39	0.9979	211.40	57.39	0.9806
8	149.31	38.52	0.9979	133.11	35.55	0.9614
9	110.16	27.50	0.9979	93.97	24.54	0.9334
10	71.02	16.34	0.9977	54.83	13.42	0.8486
11	51.45	10.65	0.9976	35.26	7.77	0.7276
12	180.34	46.22	0.9957	105.19	26.97	0.9222
13	194.81	49.95	0.9977	140.59	36.48	0.9675
14	143.86	36.44	0.9838	- 1.02	- 2.07	0.0123
15	68.29	15.28	0.9820	- 76.59	- 23.19	0.7341
16	43.11	8.01	0.9799	- 101.77	- 30.39	0.8364
17	30.52	4.26	0.9775	- 114.37	- 34.09	0.8706
18	356.28	96.83	0.9775	423.82	116.87	0.9582
19	98.95	24.96	0.8954	317.61	86.44	0.9694

Table 4 Results of Analysis of the Data for Step (2) in Table 2 by Achar

Differential method and Coats-Redfern Integral method

function No.	integral method			differential method		
	E (kJ/mol)	$\ln A$ (s^{-1})	$ r $	E (kJ/mol)	$\ln A$ (s^{-1})	$ r $
1	272.04	51.62	0.9868	74.44	12.15	0.5784
2	312.78	59.59	0.9906	146.71	26.53	0.8266
3	329.41	61.59	0.9919	176.18	31.16	0.8763
4	363.09	68.72	0.9942	232.39	42.87	0.9305
5	237.35	41.94	0.9846	25.38	- 0.45	0.2432
6	475.53	92.04	0.9981	401.06	77.99	0.9827
7	203.38	38.41	0.9963	102.15	18.58	0.8371
8	132.31	23.62	0.9961	31.08	3.81	0.4535
9	96.77	16.13	0.9959	- 4.46	- 3.65	0.0763
10	61.23	8.50	0.9955	- 40.01	- 11.24	0.5852
11	43.46	4.56	0.9949	- 57.76	- 15.11	0.7304
12	164.26	29.35	0.9922	17.82	0.33	0.232
13	176.63	31.60	0.9938	45.93	5.77	0.5375
14	131.09	22.89	0.9858	- 66.51	- 16.54	0.6261
15	60.63	8.13	0.9834	- 136.98	- 31.23	0.8857
16	37.14	2.97	0.9803	- 160.47	- 36.3	0.9205
17	25.39	0.26	0.9764	- 172.21	- 38.92	0.9333
18	299.76	58.84	0.9997	270.81	53.69	0.9826
19	74.49	11.89	0.9937	186.48	35.44	0.9536

The results obtained from the two different methods are approximately the same when based on function No. 7 for step (1) and function No. 18 for step (2), which correspond to the mechanisms of nucleation and growth ($n=1$) and second order chemical reaction, respectively. The kinetic equations are expressed as follows:

$$\text{step (1): } d\alpha/dt = A \cdot e^{-E/RT} (1-\alpha) [-\ln(1-\alpha)]$$

$$\text{step (2): } d\alpha/dt = A \cdot e^{-E/RT} (1-\alpha)^2 [(1-\alpha)^{-1} - 1]$$

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