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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt20

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To cite this article: Xiao-Qing Shen , Zhong-Jun Li , Ya-Li Niu & Hai-Bin Qiao (2009) Thermal Behaviors and Decomposition Kinetics of a Ni(II) Complex with 2-Pyridinecarboxylic Acid, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 39:1, 55-59

To link to this article: http://dx.doi.org/10.1080/15533170802683230

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Thermal Behaviors and Decomposition Kinetics of a Ni(II) Complex with 2-Pyridinecarboxylic Acid

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A Ni(II) complex with 2-pyridinecarboxylic acid, [Ni ($C_6H_4NO_2$)₂(H_2O)₂]·2 H_2O , has been synthesized and its thermal decomposition in N₂ atmosphere has been investigated by TG-DTG and DSC. The results show that the thermal decomposition process of this complex can be divided into two transitions: one is assigned to water loss (involving crystal lattice water and coordinated water) and another to the main decomposition of destroying Ni–N bonds, Ni–O bonds and pyridine ring. Thermal decomposition kinetic analysis indicates that both the transitions are double-step following reactions with different singular reaction types. The kinetic parameters of thermal decomposition have been obtained by means of model-free method together with multivariate non-linear regression.

Keywords 2-pyridinecarboxylic acid, decomposition, kinetics, thermal behavior

INTRODUCTION

In recent years many reports keep an eye on the synthesis, antibiotic activities, catalytic activities and structural elucidation of various organo derivatives of pyridine due to their importance in biological system and their applications in anti-tumor agents of chemotherapy.^[1-3] In particular, as a species of super ligand, pyridines can coordinate many metal ions to form complexes through nitrogen atoms. Some of these complexes are provided with various structure characteristics and have special applications in medicine and catalysis fields.^[4] Because of their activity, substituted pyridines such as 2-pyridinecarboxylic acid, which is formed by the introduction of carboxyl, have been widely studied in the fields of synthesis, structure identification and chelating property studies.^[5,6] However, the thermal behaviors and decomposition kinetics of these compounds are rare to literature. In this paper, we report the thermal analysis of complex $[Ni(C_6H_4NO_2)_2(H_2O)_2] \cdot 2H_2O$, which is constructed by 2-pyridinecarboxylic acid. The kinetic parameters of thermal decomposition have been calculated by means of non-isothermal method and the reaction model has been derived by means of multivariate non-linear regression.

EXPERIMENTAL

Preparation of $[Ni(C_6H_4NO_2)_2(H_2O)_2] \cdot 2H_2O$ (Complex 1)

An aqueous solution of $0.024 \text{ g}(0.01 \text{ mmol}) \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added with continuous stirring to 20 ml of CH₃OH containing 0.021 g (0.2 mmol) of 2-pyridinecarboxylic acid. The resulting solution was heated under stirring to reflux for 1 h and then cooled to room temperature. After five days, bright blue crystals of title complex suitable for X-ray diffraction were obtained by being filtrated, washed with cooled water and dried under vacuum. IR (KBr): 3448, 1576, 1595, 1545, 1460, 1377, 1362, 700 cm⁻¹.

Instrumentation

Single crystal structure was determined by a Rigaku-Raxis-IVX-ray diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293(2)K.

Thermal decomposition experiments were carried out using Netzsch TG 209 and DSC 204 instruments in nitrogen atmosphere with flow rates of 20 and 70 mL min⁻¹, respectively. The heating rate for thermal decomposition employed was 10° C min⁻¹, and the rates for kinetic analysis were 5, 10, 15 and 20° C min⁻¹, respectively. IR spectra were recorded on a Nicolet IR-470 spectrometer using KBr pellets in the range of 4000–400 cm⁻¹.

RESULTS AND DISCUSSION

Crystal Structure

The crystal structure of complex **1** was found to be a monoclinic system with a = 2.5282 (5), b = 0.59083 (12), c = 1.5390 (3) Å and $\beta = 113.88^{\circ}$, the result of which was the same as that reported before.^[7] The structure drawing given in Figure 1 describes the coordination environment of Ni atom.

Received 12 January 2008; accepted 30 August 2008.

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FIG. 1. Structure drawing of complex 1.

It can be seen that two 2-pyridinecarboxylic acid molecules chelate Ni atom using their O and N atoms to form the plane of a distorted octahedron, and two H_2O molecules occupy the axis direction. Two other H_2O molecules connect the structure unit through hydrogen bonds (O2-H.— O4). A hydrogen bond is weaker than coordination bond, but it also plays an important role in the construction of crystal units and would provide extra stability to the whole structure.

Thermal Decomposition of Complex 1

The typical TG–DTG and DSC curves of complex **1** are shown in Figures 2 and 3, respectively. Two transitions appeared in the decomposition process. The first transition, which starts from 50°C and ends at 180°C, is a consecutive weight loss process containing two endothermic peaks at 102 and 167°C and two DTG peaks at 98 and 165°C. This thermal event, giving a total ΔH value of 630.6 Jg⁻¹, is due to the removal of water from complex **1**. The calculated mass loss of 19.18% for this thermal event agrees well with that revealed by the TG curve (19.02%). The second transition, which ranges from 313 to 430°C, is related to the thermal decomposition of [Ni(C₆H₄NO₂)₂]. The two consecutive endothermic peaks at 321 and 401°C involving a



FIG. 2. TG-DTG curve of complex 1.



FIG. 3. DSC curve of complex 1.

total ΔH value of 393.6 Jg⁻¹, with a consecutive weight loss in TG curve and two associated DTG peaks at 331 and 399°C can be attributed to the breaking of coordination bonds (Ni–N, Ni–O) and the destruction of pyridine ring. Total mass loss of 70.44% up to 500° is less than the calculated value of 80.08% by taking NiO as the final product, which is because of the carbon deposition resulted from decomposed products in N₂ atmosphere.^[8]

It is of interest to further investigate the enthalpy changes of this complex in first transition. Two slightly overlapped endothermic peaks appeared in DSC curve with the peak temperatures at 102 and 167°C, giving total ΔH value of 630.6 Jg⁻¹(see Figure 3), correspond to the removal of two crystal lattice water and two coordinated water, respectively. We use the peak-separation technology to calculate the ΔH value of each peak. The calculated curves are presented in Figure 4, and the calculated results shown in Table 1. The ΔH values given for these two endothermic peaks are 286.5 and 324.6 Jg⁻¹, respectively. It can be seen that two types of bonding mode result in these water being lost at different temperatures and the heat absorbed for eliminating crystal lattice water is less than that absorbed for eliminating coordinated water.



FIG. 4. Peak-separation for first transition of DSC curve.

Peak-separation results for the first transition of decomposition Position/°C Onset/°C Endset/°C Area /Jg1 Shape 1 95.4571 56.409 119.425 286.4991 2 165.3691 135.347 177.593 324.6029

TABLE 1

Non-Isothermal Kinetics of Thermal Decomposition

Model-Free Estimation of Activation Energy

A series of dynamic scans with different heating rates results in a set of data, that exhibits the same degree of conversion (α) at different temperatures. Based on this, two methods are developed by Friedman as well as Ozawa-Flynn-Wall (OFW) to determine the kinetic parameters without having to presuppose a certain model. Figure 5 shows the TG curves of complex 1 decomposition from 35 to 460°C with the heating rate of 5, 10, 15 and 20°C min⁻¹, respectively. The basic data (β , α , T) taken from the TG curves are used in the equations below:

Ozawa-Flynn-Wall equation^[9]

$$\ln \beta = \ln \left(\frac{AE}{R}\right) - \ln g(\alpha) - 5.3305 - 1.052 \cdot \frac{E}{RT} \quad [1]$$

where β is heating rate, α degree of conversion, $g(\alpha)$ mechanism function, E activation energy, A pre-exponential factor and Rgas constant.

Friedman equation,^[10]

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha=\alpha j} = \ln[A \cdot f(a)_j] - \frac{E}{RT}$$
[2]

where $d\alpha/dt$ is the rate of conversion, and $f(\alpha)$ mechanism function.

From Equations (1) and (2), it is seen that the graphs $\ln\beta$ versus 1/T and $\ln (d\alpha/dt)$ versus 1/T both show straight lines

TG /% 90 80 5°C/min 70 10°C/min 60 15°C/min 50 20°C/mir 40 30 250 300 400 50 100 150 200 350 450 Temperature /° С

FIG. 5. TG curves with different heating rates.

TABLE 2 Parameters E and $\lg A$ for the thermal decomposition of title complex by using OFW analysis

Partial mass loss (α)	First transition		Second transition		
	$\overline{E/(kJ \cdot mol^{-1})}$	$lg(A/s^{-1})$	$E/(kJ \cdot mol^{-1})$	$lg(A/s^{-1})$	
0.02	62.76 ± 5.73	6.30	186.48 ± 23.79	12.56	
0.05	55.06 ± 3.18	5.19	137.41 ± 4.41	8.15	
0.10	50.52 ± 2.19	4.56	177.16 ± 2.57	11.49	
0.20	47.07 ± 1.40	4.09	201.66 ± 1.67	13.55	
0.30	45.49 ± 1.41	3.87	209.38 ± 1.66	14.21	
0.40	45.11 ± 1.65	3.90	213.89 ± 4.01	14.60	
0.50	49.50 ± 3.71	4.36	218.24 ± 6.57	14.98	
0.60	71.17 ± 5.75	6.85	221.97 ± 8.93	15.29	
0.70	69.39 ± 3.15	6.48	224.92 ± 12.11	15.56	
0.80	67.64 ± 2.76	6.23	224.87 ± 15.22	15.60	
0.90	65.61 ± 3.65	6.01	230.69 ± 25.08	16.11	
0.98	64.50 ± 6.24	1.96	258.37 ± 26.42	18.25	

with slopes $m_{(1)} = -1.052 E/R$ and $m_{(2)} = -E/R$, respectively. The slopes of these straight lines are directly proportional to the reaction activation energy (E). The calculated results obtained by using both Equations are shown in Table 2 and 3, respectively.

The comparable values of E and $\lg A$ of each transition by using different methods indicates that the kinetic parameters thus obtained are reasonable, and furthermore, the dependence of activation energy on the degree of conversion (E_{α} -dependence), given in Tables 2 and 3, shows that the activation energy is not a constant. Two maximums appear with the extent of decomposition, which betokens that the two transitions of thermal decomposition of title complex both are double-step reactions.^[11]

TABLE 3

Parameters E and lgA for the thermal decomposition of title complex by using Friedman analysis

Partial	First trans	ition	Second transition		
$loss(\alpha)$	$E/(kJ \cdot mol^{-1})$	$lg(A/s^{-1})$	$E/(kJ \cdot mol^{-1})$	$lg(A/s^{-1})$	
0.02	46.89 ± 1.64	3.99	91.51 ± 32.72	4.44	
0.05	44.92 ± 1.72	3.78	183.11 ± 1.85	11.89	
0.10	43.03 ± 1.76	3.56	221.17 ± 2.72	15.08	
0.20	41.71 ± 2.023	3.38	225.21 ± 5.32	15.50	
0.30	45.17 ± 2.39	3.85	222.14 ± 9.91	15.31	
0.40	48.49 ± 3.29	4.23	228.44 ± 14.64	15.85	
0.50	69.42 ± 10.10	6.57	234.20 ± 14.95	16.31	
0.60	69.91 ± 0.44	6.20	234.79 ± 17.14	16.38	
0.70	67.80 ± 0.48	6.11	235.74 ± 23.56	16.49	
0.80	64.02 ± 3.59	5.83	235.67 ± 30.09	16.55	
0.90	61.13 ± 8.56	5.68	256.55 ± 49.75	18.23	
0.98	73.97 ± 23.59	7.35	311.67 ± 28.44	22.32	



	Renote paramotors and name quanty after nonmour regression					
Transition	Corr. Coeff.	Reg. Par.	Step	E (kJmol ⁻¹)	$\lg\left(A/\mathrm{s}^{-1}\right)$	Foll. React.
1st	0.998804	0.00100	IR3	54.89332	5.14834	0.47698
2nd	0.999876	0.00100	IF1 IF1	124.28316	9.72111 7.98461	
			II F1	268.73316	19.07224	0.11801

TABLE 4 Kinetic parameters and fitting quality after nonlinear regression

Kinetic parameters of a reaction can be estimated from the maximums of Friedman method or OFW method, also from the average values of the two methods. According to OFW method, the activation energies and pre-exponential factors of thermal decomposition of title complex are E1 = 62 kJmol^{-1} , $\lg (A1/s^{-1}) = 6.3$, and $E2 = 69 \text{ kJmol}^{-1}$, $\lg (A2/s^{-1}) = 6.5$ for first transition, while $E1 = 186 \text{ kJmol}^{-1}$, $\lg (A1/s^{-1}) = 12.6$, and $E2 = 258 \text{ kJmol}^{-1}$, $\lg (A2/s^{-1}) = 18.3$ for the second, respectively. The values of these parameters would offer initial values for getting reaction model by means of non-linear regression (NLR)^[12] and would be optimized finally.

Multivariate Non-Linear Regression (NLR)

Mode-free method has solved the problem of kinetic parameters and these data can be used to estimate potential model on which the reaction occurred. NLR allows a direct fit of the model to the experimental data without a transformation and there are no limitations with respect to the complexity of the model. For this reason, NLR method can be used and iterative procedures can be employed for estimating of the reaction model of a thermal decomposition process.

Selecting mechanism function $f(\alpha)$ of different singular reaction types;^[13] testing all two-step reaction types to which individual steps are linked as consecutive (d:f), parallel (d:p) and independent (d:i);^[13] setting the initial values of the parameters of *E* and lg*A* according to mode–free method, the calculation of the regress values is carried out. To minimize the deviance, least squares (LSQ) method is used and a smooth convergence is ensured.

The calculated curves were obtained by means of NLR. These curves were fitted to the experimental ones and corrected with least-squares procedure. During this procedure in order to get high fitting quality kinetic parameters of initial values are optimized. Considering fitting quality (characterized by correlation coefficient and relative precision), the mechanism of d:f, $A \xrightarrow{R3} B \xrightarrow{F1} C$, is the most suitable for the reaction of the first transition, and d:f, $A \xrightarrow{F1} B \xrightarrow{F1} C$, is the most suitable for that of the second one. The kinetic parameters and statistical characterization after the NLR are listed in Table 4 and graphic presentations of the curve fitting are shown in Figure 6(a) and (b). From Figure 6 it can be seen that the experimental data and the nonlinear regression model fit very well.

In short, the results of the kinetic analysis above show that the thermal decomposition of $[Ni(C_6H_4NO_2)_2(H_2O)_2]\cdot 2H_2O$ preferably performs as two double-step following reactions. In the first transition: $E1 = 55 \text{ kJmol}^{-1}$, $\lg (A1/s^{-1}) = 5.2$; $E1 = 98 \text{ kJmol}^{-1}$, $\lg (A1/s^{-1}) = 9.8$. In the second transition: $E1 = 124 \text{ kJmol}^{-1}$, $\lg (A1/s^{-1}) = 7.8$; $E2 = 269 \text{ kJmol}^{-1}$, $\lg (A1/s^{-1}) = 19.1$.



FIG. 6(a). Curve fitting of first transition, simulated with reaction types R3 and F1. ∇,◊, △,□ experimental plots, — integral plots.
(b) Curve fitting of second transition, simulated with reaction types F1 and F1.

(b) Curve number of second transition, simulated with reaction types F1 and F ∇ , \Diamond , \triangle , \Box experimental plots, — integral plots.

CONCLUSIONS

- 1. Thermal analysis indicates that the process of $[Ni(C_6H_4NO_2)_2(H_2O)_2]\cdot 2H_2O$ decomposition includes two transitions. The first transition is assigned to the loss of water; the second corresponds to the decomposition of $[Ni(C_6H_4NO_2)_2]$. Two types of bonding mode result in the crystal lattice water and the coordinated water being lost at different temperatures.
- 2. Kinetic analysis shows that the thermal decomposition of $[Ni(C_6H_4NO_2)_2(H_2O)_2]\cdot 2H_2O$ preferably performs as two double-step following reactions. The first one for water loss is in a mode of d:f, $A \xrightarrow{R3} B \xrightarrow{F1} C$: a 3-dimensional phase boundary reaction (R3) with E1 = 55 kJmol⁻¹, lg $(A1/s^{-1}) = 5.2$, is followed by a 1st order reaction (F1) with E2 = 98 kJmol⁻¹, lg $(A2/s^{-1}) = 9.7$; The second one for main decomposition is d:f, $A \xrightarrow{F1} B \xrightarrow{F1} C$: an 1st order reaction (F1) with E1 = 124 kJmol⁻¹, lg $(A1/s^{-1}) = 8.0$, is followed by a 1st order reaction (F1) with E1 = 124 kJmol⁻¹, lg $(A1/s^{-1}) = 8.0$, is followed by a 1st order reaction (F1) with E2 = 269 kJmol⁻¹, lg $(A2/s^{-1}) = 19.1$.

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