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Thermal properties of chlorinated complexes of cobalt(II) and nickel(II) with 3-hydroxypyridine

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Abstract

The kinetic properties and thermal stability of $[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2] \cdot 2H_2O$ and *trans*-$[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2] \cdot 4H_2O$ were studied in a dynamic nitrogen atmosphere using TG, DTG and DSC methods. Kinetic parameters were calculated using mechanistic integral equations. For the tetrahedral cobalt(II) complex, the three-dimensional diffusion (Ginstling–Brounshtein function) D_4 mechanism governs the degradation process; for the octahedral nickel(II) complex the three-dimensional diffusion (Jander function) D_3 mechanism acts up to $\alpha \approx 0.5$ decomposition.

1. Introduction

The pharmacological importance of 3-hydroxypyridine and its substituted compounds has stimulated various trials in the use of these compounds as complexing agents with transition metal cations [1–4]. Halawani and Moustafa [5] prepared the cobalt(II) and nickel(II) complexes with 3-hydroxypyridine to give $[M(3\text{-}OHpy)_4Cl_2]$. Thermal studies of these complexes [6] determined that the three-dimensional diffusion mechanism was adopted, followed by a random nucleation mechanism at the end of the decomposition process. The subject of the present study is the evaluation of the kinetic parameters of thermal decomposition of the chlorinated complexes of cobalt(II) and nickel(II) with 3-hydroxypyridine. A comparison between the kinetic parameters and the formula structure is made.

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2. Experimental

$[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2] \cdot 2H_2O$ and *trans*-$[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2] \cdot 4H_2O$ complexes have been prepared previously [5]. An ethanolic solution of cobalt(II) chloride or nickel(II) chloride was added at room temperature to 3-hydroxypyridine dissolved in ethanol. Dry chlorine gas was bubbled through the ice-cold mixture for approx. 1 h. The precipitate was filtered off immediately, washed with small portions of cold ethanol and dry diethyl ether, and finally dried in vacuo at room temperature. Microanalyses for C, H and N were performed on a Carlo Erba elemental analyser model 1106. The Cl content was determined by a conventional method [7]. The metal contents were assayed using a Varian AA-1475 series atomic absorption spectrophotometer after digesting the complexes with water.

TG, DTG, DSC and isothermal experiments for the complexes were performed using a TA 3000 Mettler thermobalance with a heating rate of 10 K min^{-1} and 10 mg sample weight. The cell was fed with N_2 gas at a flow rate of 50 ml (NTP) min^{-1} in the temperature range of 50–1000°C. The DSC analyser unit was a DSC-30 Mettler system using the same conditions except the sample weight was 5 mg and the final temperature was 600°C. Non-isothermal TG data were processed using a computer program in BASIC which enables regression analysis and determination of kinetic and thermodynamic parameters from experimental TG/DTG non-isothermal thermogravimetric data, as developed by Beg and Qaiser [8], using an IBM PS/2 30 microcomputer.

3. Results

The complexes were characterized by their melting points and elemental analyses, which are in agreement with the proposed structures previously reported [5]. The cobalt(II) complex is dark blue in colour with a melting point of 138–140°C, while the nickel(II) complex has a yellow-brownish colour with a melting point of 197–199°C. Analytical results for the complexes are given in Table 1.

The IR, UV-VIS, NMR, mass spectral, and magnetic data revealed a tetrahedral and octahedral environment for the cobalt and nickel complexes respectively [5].

Table 1
Elemental analyses of the complexes

Complex	Found (calcd.) in %				
	C	H	N	Cl	M
$[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2] \cdot 2H_2O$	27.65 (28.26)	2.78 (2.85)	6.45 (6.59)	33.59 (33.37)	14.03 (13.88)
$[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2] \cdot 4H_2O$	33.14 (33.37)	3.26 (3.36)	7.62 (7.79)	30.80 (29.55)	8.29 (8.16)

Table 2
Thermoanalytical data for cobalt(II) and nickel(II) complexes in dynamic nitrogen atmosphere from TG and DTG analyses

Peak temp. from DTG in °C [a]			Loss of mass in wt%		Probable composition of expelled group
T_i	T_f	T_m	TG	Theory	
$[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2]\cdot 2H_2O$					
97	241	185	8.91	8.5	$2H_2O$
241	433	360	40.28		
433	499	456	5.09	61.0	2(ClOHpy)
594	731	648	16.81		
731	770	742	8.68	8.4	Cl
			79.77 [b]	77.9 [b]	
$[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2]\cdot 4H_2O$					
95	144	118	5.15	5.0	$2H_2O$
144	191	185	4.86	5.0	$2H_2O$
191	365	306	51.66	54.0	3(ClOHpy)
365	448	438	2.59		
448	615	488	16.37	18.0	(ClOHpy)
744	821	749	2.28		
			82.91 [b]	82.0 [b]	

[a] Key: i, initial; f, final; and m, maximum. [b] Total loss of mass in wt%.

The thermoanalytical data for the complexes are given in Table 2. The complexes of cobalt and nickel were decomposed via intermediates to give the non-stoichiometric metal chloride as the end product. The percentage mass loss and probable composition of the expelled groups are also indicated. Characteristic decomposition curves of the cobalt(II) and nickel(II) complexes are shown in Figs. 1 and 2, respectively. Two distinct zones are shown. The experimental values are in agreement with the calculated percentages for the dehydration of the complexes. The expected endothermic DSC signal was observed over the same TG temperature range. Their corresponding enthalpies are 85.3 and 204.5 J g^{-1}. Once the complexes are dehydrated, they undergo decomposition. These steps are characterized by exothermic DSC behaviour. The ΔH values for removal of each fragment are cited in Table 3. The final residue of the pyrolytic process was characterized by IR analysis and indicated the presence of chloride salt.

The observed difference in ΔH_{total} (J g^{-1}) is due to the differences in the structures: the cobalt complex crystallizes in a tetrahedral form, the nickel complex in an octahedral structure.

Isothermal studies of the complexes were carried out in the range of temperature 400–460°C as shown in Figs. 3 and 4. The α–t curves are acceleratory with no induction period, representing an initial rapid gas evolution. Decomposition rates are cited in Table 4. Decomposition with no induction period suggests that the decomposition proceeds with rapid nucleation over the whole surface [9]. The low activation energy in the acceleratory region may result from an

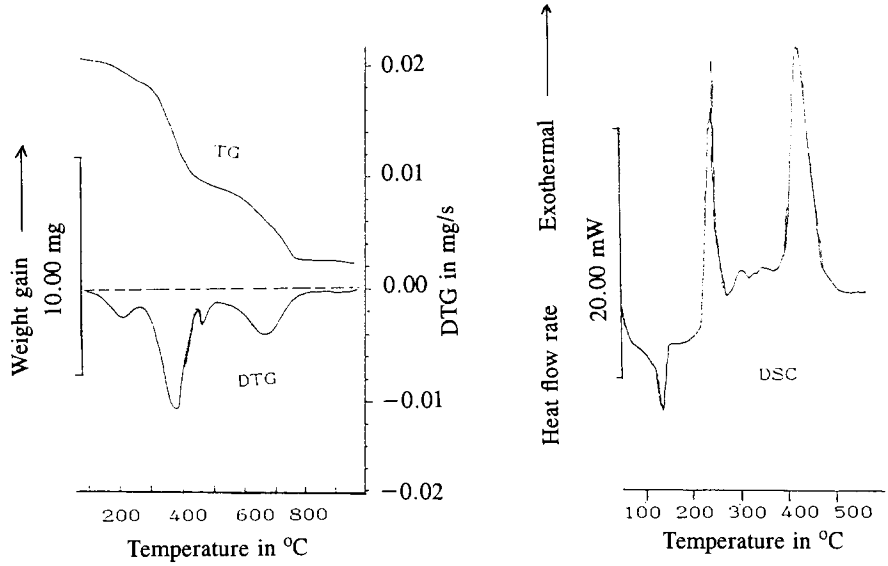

Fig. 1. TG, DTG and DSC curves for the [Co(4-Cl-3-OHpy)$_2$Cl$_2$] · 2H$_2$O complex.

energetically favourable reaction at the ligand–solid interface which, of course, disappears on complete melting [10]. The higher decomposition rate of the nickel complex is attributed to its excess water of crystallization compared with the cobalt complex.

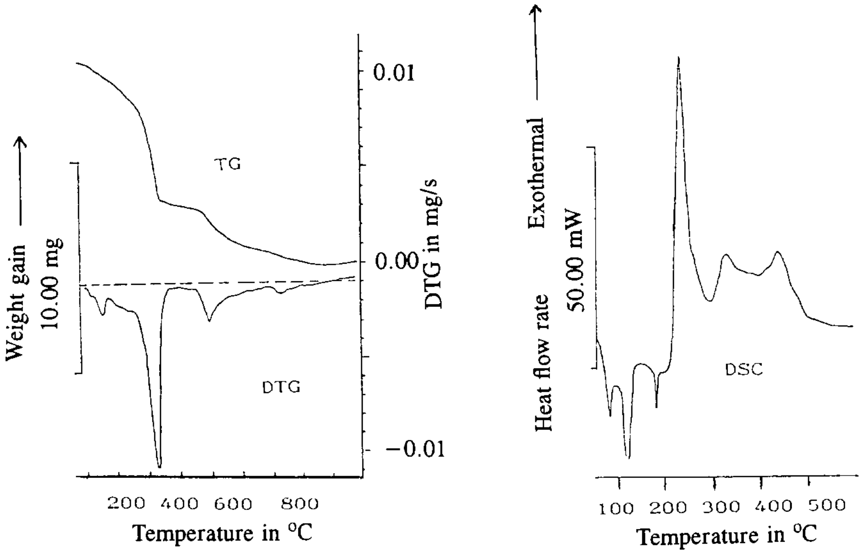

Fig. 2. TG, DTG and DSC curves for the [Ni(4-Cl-3-OHpy)$_4$Cl$_2$] · 4H$_2$O complex.

Table 3
DSC temperature and ΔH for the thermal decomposition of the complexes in dynamic N_2 atmosphere

Stage	DSC temp. in °C	ΔH in J g^{-1}	ΔH_{total} in J g^{-1}
$[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2]\cdot 2H_2O$			
I	138.4 (endo)	85.1	
II	252.5 (exo)	371.5	1419.9
III	534.3 (exo)	963.3	
$[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2]\cdot 4H_2O$			
I	83.0 (endo)		
II	121.5 (endo)	335.3	
III	187.0 (endo)		
IV	213.0 (exo)	616.6	1658.1
V	336.0 (exo)	64.7	
VI	451.0 (exo)		

These excess water molecules can facilitate the diffusion process which enhances decomposition at low temperatures.

The non-isothermal TG curves for both complexes exhibit two major stages of decomposition. Evaluation of the reaction mechanism has been discussed by Šesták and Berggren [11] and Satava [12]. A series of $f(\alpha)$ forms was proposed by Satava

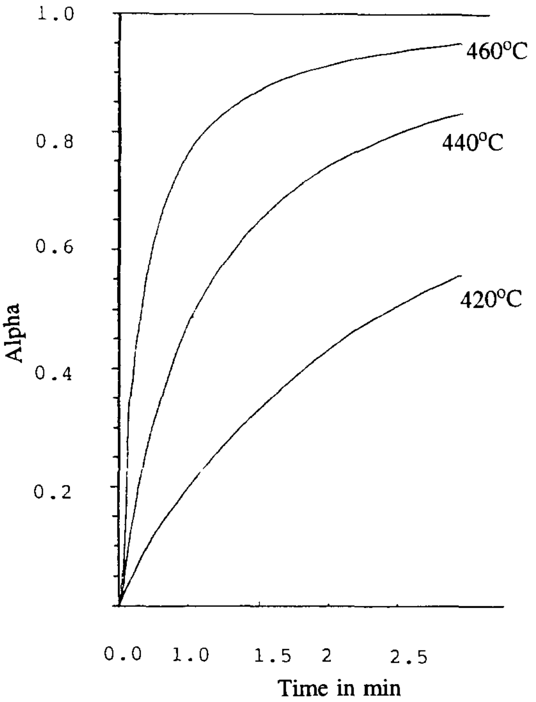

Fig. 3. Isothermal studies for the $[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2]\cdot 2H_2O$ complex.

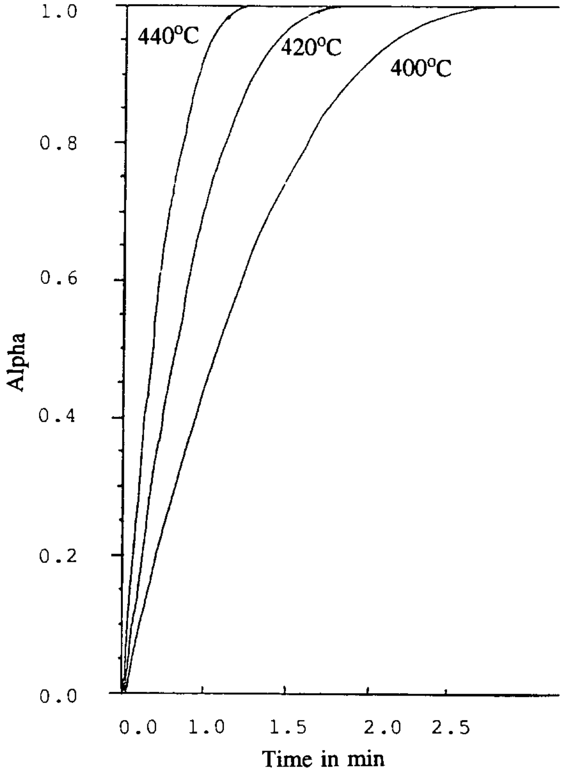

Fig. 4. Isothermal studies for the $[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2]\cdot 4H_2O$ complex.

[12] and the mechanism is obtained from the plot which gives the best representation of the experimental data. For evaluating the kinetic parameters from the mechanistic equations, the Coats–Redfern [13] equation is recommended in several reports [14,15]. The general equation used is

$$\ln g(\alpha)/T^2 = \ln(AR/QE) - (E/RT) \tag{1}$$

In order to determine the reaction order, Eqs. (2) and (3) were used. The reaction order can be estimated by comparing the corresponding r values calculated together with reaction orders n of 0.33, 0.5, 0.66, 1 and 2

Table 4
Isothermal decomposition reaction rate of the complexes in dynamic N_2 atmosphere

$[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2]\cdot 2H_2O$			
Temp. in °C	420	440	460
Reaction rate in (mg s^{-1}) × 10^{-3}	6.67	16.3	62.0
$[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2]\cdot 4H_2O$			
Temp. in °C	400	420	440
Reaction rate in (mg s^{-1}) × 10^{-3}	16.0	26.67	50.07

Table 5
Reaction order determination for the decomposition of the complexes utilizing Eqs. (2) and (3)

$[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2]\cdot 2H_2O$						
r values	0.9906	0.9856	0.9877	0.9888	0.9893	0.9928
Reaction order	1	0	1/3	1/2	2/3	2
$[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2]\cdot 4H_2O$						
r values	0.9893	0.9920	0.9927	0.9914	0.9909	0.9826
Reaction order	1	0	1/3	1/2	2/3	2

Table 6
Kinetic parameters for the decomposition of the complexes using mechanistic equations together with the Coats–Redfern method

Stage	E in kJ mol^{-1}	log A in s^{-1}	ΔS^* in J K^{-1} mol^{-1}	r	Kinetic model
$[Co(4\text{-}Cl\text{-}3\text{-}OHpy)_2Cl_2]\cdot 2H_2O$					
I	75.66	2.72	−91.76	0.9923	D_4
II	40.45	0.73	−132.6	0.9913	D_3
$[Ni(4\text{-}Cl\text{-}3\text{-}OHpy)_4Cl_2]\cdot 4H_2O$					
I	73.38	3.31	−81.20	0.9938	D_3
II	43.37	0.15	−108.5	0.9931	$F_n = 2$

$$\log[1-(1-\alpha)]^{1-n}/(1-n)T^2 \text{ vs. } 1/T \quad \text{for } n \neq 1 \tag{2}$$

$$\log[-\log(1-\alpha)]/T^2 \text{ vs. } 1/T \quad \text{for } n = 1 \tag{3}$$

The above treatment shows that the reaction order n for the decomposition up to $\alpha = 0.5$ varies with the complex type: it is 2 and 1/3 for the cobalt and nickel complexes, respectively, as shown in Table 5.

Calculated values of E, log A and ΔS^* using the mechanistic equations, with the correlation coefficients for the two major stages of decomposition, are cited in Table 6; $\Delta S^* = R \ln Ah/kT_i$, and k and h are Boltzmann's and Planck's constants, respectively; T_i is the initial decomposition temperature.

Kinetic parameters calculated by analysis of α values corresponding to the decomposition of the complexes according to the previously discussed method [8] are cited in Table 6. The table shows that the first stage of decomposition for both complexes is controlled by the D_4 (cobalt) and D_3 (nickel) diffusion mechanisms, followed by the D_3 mechanism for the cobalt complex and by a random nucleation mechanism ($F_n = 2$) for the nickel complex for the second stage, respectively. It is also concluded from the calculated parameters that the pyrolysis of both complexes is a low-energy process, which is confirmed by the low activation energy. Also, addition of chlorine to the hydroxypyridine ring enhances the decomposition of the complexes as compared with those of non-chlorinated hydroxypyridine [6]. The negative ΔS^* values reflect that the activated complexes have more ordered structures [16] after the dehydration process.

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