

THERMAL BEHAVIOUR OF COMPLEX CATION–COMPLEX ANION TYPE COORDINATION COMPOUNDS.

Part V *

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ABSTRACT

The irreversible thermochromism of two coordination compounds of the type $[\text{Ni}(\text{AA})_3][\text{PdCl}_4] \cdot n\text{H}_2\text{O}$, where AA = 1,10-phenanthroline (phen) or 4,7-diphenyl-1,10-phenanthroline (bathophen), is reported. The colour change is caused by an unusual thermal behaviour of the complex cation–complex anion type coordination compounds, namely the migration of ligands, in the solid state, between the coordination spheres of metal ions. This paper deals also with the thermal stability and non-isothermal decomposition kinetics of the two cited compounds.

INTRODUCTION

Following previous work concerning thermal stability and ligand migration between the two coordination spheres of complex cation–complex anion type coordination compounds [1–4] this paper deals with the compounds $[\text{Ni}(\text{phen})_3][\text{PdCl}_4] \cdot 5.5\text{H}_2\text{O}$ and $[\text{Ni}(\text{bathophen})_3][\text{PdCl}_4] \cdot 6\text{H}_2\text{O}$ [phen = 1,10-phenanthroline; bathophen = 4,7-diphenyl-1,10-phenanthroline].

EXPERIMENTAL

The syntheses of the two compounds are similar. The $\text{Ni}(\text{AA})_3^{2+}$ ions were obtained by adding the stoichiometric amount of organic ligand to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in ethanol. The $[\text{PdCl}_4]^{2-}$ complex anion was

* For Part IV in this series see Ref. 1.

prepared in aqueous solution by treating anhydrous PdCl_2 with an aqueous solution of HCl. After mixing the solutions containing the two complex ions, the compounds $[\text{Ni}(\text{AA})_3][\text{PdCl}_4] \cdot n\text{H}_2\text{O}$ were precipitated: $[\text{Ni}(\text{phen})_3][\text{PdCl}_4] \cdot 5.5\text{H}_2\text{O}$ as a pink-brown amorphous powder and $[\text{Ni}(\text{batho-phen})_3][\text{PdCl}_4] \cdot 6\text{H}_2\text{O}$ as a pink crystalline powder. The compounds were subsequently vacuum filtered, washed with ethanol and dried in vacuum over P_2O_{10} . An alternative method of synthesis for crystalline $[\text{Ni}(\text{phen})_3][\text{PdCl}_4] \cdot 5.5\text{H}_2\text{O}$ consists in using an aqueous solution of KCl instead of HCl in order to obtain the $[\text{PdCl}_4]^{2-}$ ion.

The thermal curves of the compounds were recorded by means of a Q 1500D Derivatograph (MOM, Budapest) of Paulik-Paulik-Erdey type in a static air atmosphere at various heating rates in the range $1.25\text{--}10 \text{ K min}^{-1}$. The crystalline state of the compounds was investigated by using a Philips PW 1140 X-ray diffractometer, using chromium K_α radiation. In order to record the diffuse reflectance electronic spectra, a Carl Zeiss VSU-2 spectrophotometer was used with MgO as a standard.

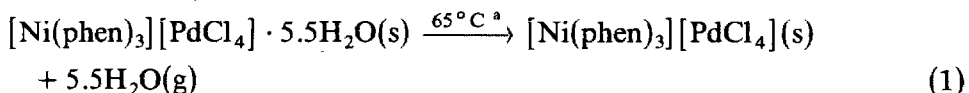
In order to obtain the values of the non-isothermal kinetic parameters in the framework of the model of the "reaction order", four methods, those according to Coats and Redfern [5], Flynn and Wall, for constant heating rate [6], Doyle and Gorbachev [7] and modified Coats-Redfern [8] were applied. The experimental data were processed by a program written in BASIC language [9] and run on a TIM-S computer. The same program allowed generation of the TG curve using the experimental values of the kinetic parameters on the coordinates $(\alpha, t^\circ\text{C})$ and fitting it to the experimental points.

RESULTS AND DISCUSSION

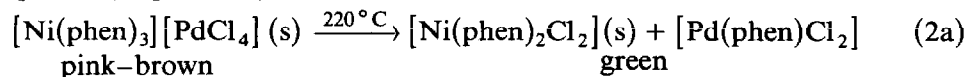
From the X-ray diffractograms, by using Scherrer's formula [10], the following values of the mean crystallite size, l , have been obtained: for the crystalline variant of $[\text{Ni}(\text{phen})_3][\text{PdCl}_4] \cdot 5.5\text{H}_2\text{O}$, $l = 175 \text{ \AA}$; for $[\text{Ni}(\text{batho-phen})_3][\text{PdCl}_4] \cdot 6\text{H}_2\text{O}$, $l = 290 \text{ \AA}$.

Decomposition of $[\text{Ni}(\text{phen})_3][\text{PdCl}_4] \cdot 5.5\text{H}_2\text{O}$

According to the derivatographic data, the first step of decomposition consists of dehydration:



followed by a first migration of the ligands between the two coordination spheres (migration I):



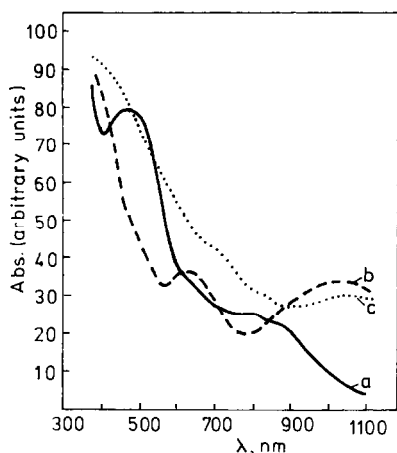
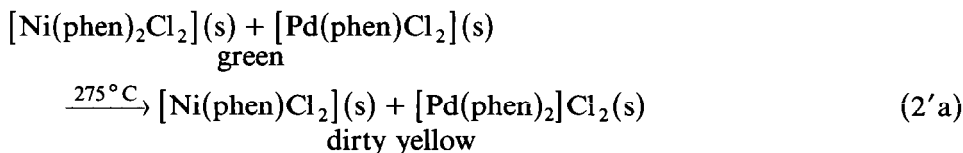


Fig. 1. Diffuse reflectance spectra of (a) $[\text{Ni}(\text{phen})_3][\text{PdCl}_4] \cdot 5.5\text{H}_2\text{O}$ (—); (b) $[\text{Ni}(\text{phen})_2\text{Cl}_2] + \text{Pd}(\text{phen})\text{Cl}_2$ (- - - - -); (c) $[\text{Ni}(\text{phen})\text{Cl}_2] + [\text{Pd}(\text{phen})_2]\text{Cl}_2$ (· · · · ·).

which occurs without change of weight. Migration I is accompanied by an exothermic peak, which is clearly shown on the DTA curve. The nature of the products obtained in reaction (2a) was confirmed by electronic spectroscopy (Fig. 1). The electronic spectrum of $[\text{Ni}(\text{phen})_3][\text{PdCl}_4] \cdot 5.5\text{H}_2\text{O}$ emphasizes the characteristic bands of both $[\text{Ni}(\text{phen})_3]^{2+}$ [4,11,12] and $[\text{PdCl}_4]^{2-}$ ions [13]. On the other hand, the electronic spectrum of the green material exhibits the absorption bands due to the presence of $[\text{Ni}(\text{phen})_2\text{Cl}_2]$ complex [12]: $16\,340\text{ cm}^{-1}$ (${}^3T_{1g}(\text{F}) \leftarrow {}^3A_{2g}$) and 9520 cm^{-1} (${}^3T_{2g} \leftarrow {}^3A_{2g}$). By treating the green mixture $[\text{Ni}(\text{phen})_2\text{Cl}_2] + [\text{Pd}(\text{phen})\text{Cl}_2]$ with ethanol, we separated the two compounds: the nickel(II) complex is soluble, whereas the palladium complex is only sparingly soluble in ethanol. From the alcoholic solution, $[\text{Ni}(\text{phen})_2\text{Cl}_2]$ was crystallized by removing the ethanol. The diffuse reflectance spectrum for this nickel complex compound was also recorded; this spectrum is identical with the spectrum reported in ref. 12.

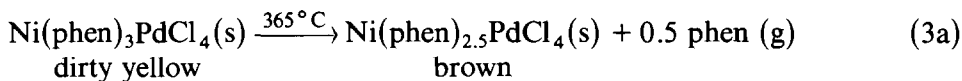
At higher temperatures a second migration (migration II) occurs



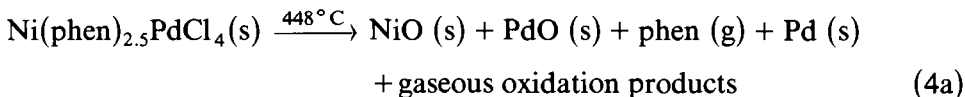
The electronic spectrum of this dirty yellow mixture (Fig. 1c) suggests the presence of two yellow compounds: $[\text{Ni}(\text{phen})\text{Cl}_2]$ and $[\text{Pd}(\text{phen})_2]\text{Cl}_2$; the shoulders at $\approx 700\text{ nm}$ and $\approx 830\text{ nm}$ as well as the weak band at 1050 nm are characteristic for $[\text{Ni}(\text{AA})\text{Cl}_2]$ polynuclear coordination compounds (AA = 1,10-phenanthroline or 2,2'-dipyridyl) [14].

^a The temperatures above the arrows correspond to the maximum reaction rate, i.e. to the peak on the DTG or DTA curve.

The mixture obtained in reaction (2'a) then undergoes loss of phenanthroline according to the equation



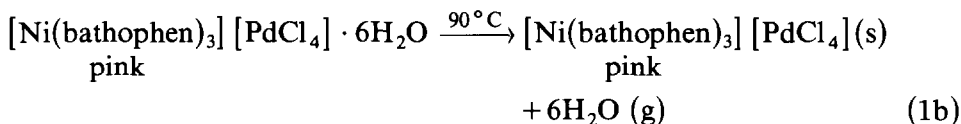
followed at higher temperatures by a complex oxidative degradation



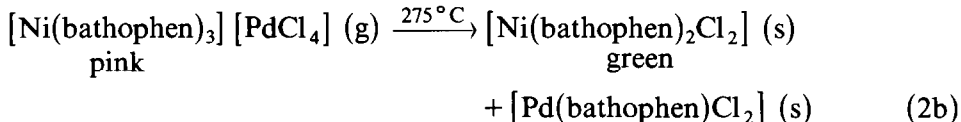
The overall reaction appears as a single stage at higher heating rates and is relatively poorly resolved or lower ones. The solid products have been identified from the X-ray diffractogram.

Decomposition of [Ni(bathophen)₃][PdCl₄] · 6H₂O

As a first reaction exhibited by the derivatogram of this compound, dehydration occurs according to the equation

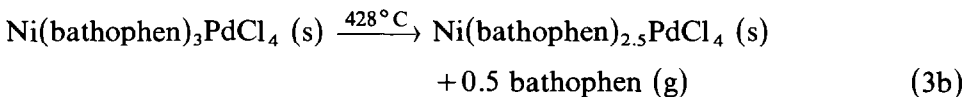


The product of reaction (1b) then undergoes migration

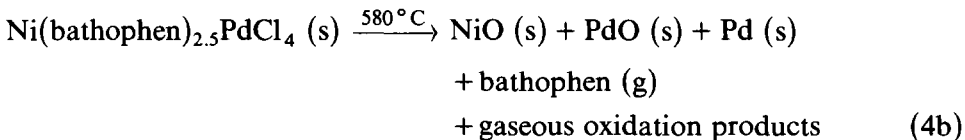


A secondary migration as in the previous case has not been detected. The electronic spectrum of the light green mixture [Ni(bathophen)₂Cl₂] + [Pd(bathophen)Cl₂], together with that of the parent compound, [Ni(bathophen)₃][PdCl₄] · 6H₂O, are presented in Fig. 2. These spectra are similar to those shown in Fig. 1.

At higher temperature, the product of reaction (2b) undergoes partial decomposition, according to the equation



followed by a complex oxidative degradation



Reaction (4b) appears on the derivatogram at all the heating rates used as a single stage.

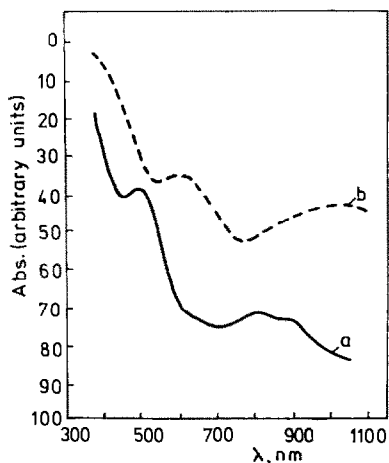


Fig. 2. Diffuse reflectance spectra of (a) $[\text{Ni}(\text{bathophen})_3][\text{PdCl}_4] \cdot 6\text{H}_2\text{O}$ (—); (b) $[\text{Ni}(\text{bathophen})_2\text{Cl}_2] + [\text{Pd}(\text{bathophen})\text{Cl}_2]$ (- - - - -).

Significant portions of the diffractograms, corresponding to the mixture of solid products from reactions (4a) and (4b), are given in Fig. 3. As can be seen from Fig. 3b, the same mixture of solid products from (4b) exhibits a mere consolidated lattice of metallic palladium, probably because of the higher temperature at which reaction (4b) occurs.

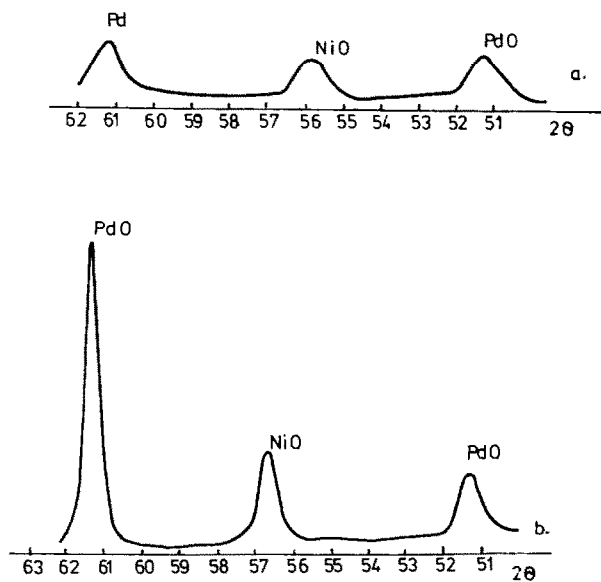


Fig. 3. Diffraction lines corresponding to the mixture of solid products from reactions (4a) and (4b).

TABLE 1

Non-isothermal kinetic parameters values for reactions (3a) and (3b)

Method	Coats-Redfern	Flynn-Wall $\beta = ct$	Doyle-Gorbachev	Modified Coats-Redfern
(3a) $\beta = 5.41 \text{ K min}^{-1}$				
E (kcal mol ⁻¹)	37.32	37.84	37.32	37.64
A (s ⁻¹)	1.42×10^{10}	2.37×10^{10}	1.43×10^{10}	1.97×10^{10}
n	1.1	1.1	1.1	1.1
r^a	-0.9916	-0.9920	-0.9916	-0.9920
(3b) $\beta = 5.79 \text{ K min}^{-1}$				
E (kcal mol ⁻¹)	48.43	48.58	48.43	49.07
A (s ⁻¹)	9.18×10^{12}	1.07×10^{13}	9.22×10^{12}	1.58×10^{13}
n	1	1	1	1
r	-0.99887	-0.99899	-0.99887	-0.99890

^a Correlation coefficient of the linear regression.*Non-isothermal kinetic analysis*

The only kinetically workable reactions are those described by the chemical equations (3a) and (3b) as well as (4a) and (4b). The corresponding values of the non-isothermal kinetic parameters, activation energy, E , preexponential factor, A , and reaction order, n , are given in Tables 1 and 2. The inspection of these results shows quite satisfactory agreement between the non-isothermal kinetic parameter values obtained by various methods. The values obtained for reaction order close to 1 for reaction (3a) and unity for reaction (3b), together with values of the preexponential factors close to those predicted by the transition state theory [15], seem to correspond to a true unimolecular decomposition. As far as the reactions (4) are concerned,

TABLE 2

Non-isothermal kinetic parameter values for reactions (4a) and (4b)

Method	Coats-Redfern	Flynn-Wall $\beta = ct$	Doyle-Gorbachev	Modified Coats-Redfern
(4a) $\beta = 10.61 \text{ K min}^{-1}$				
E (kcal mol ⁻¹)	34.12	34.70	34.13	-
A (s ⁻¹)	7.85×10^5	1.55×10^6	8×10^5	-
n	1.9	1.8	1.9	-
r	-0.9860	-0.9889	-0.9860	-
(4b) $\beta = 10.06 \text{ K min}^{-1}$				
E (kcal mol ⁻¹)	38.73	40.02	38.73	38.52
A (s ⁻¹)	2.57×10^7	7.01×10^7	2.53×10^7	2.42×10^7
n	1.6	1.6	1.6	1.5
r	-0.9998	-0.9999	-0.9998	-0.9999

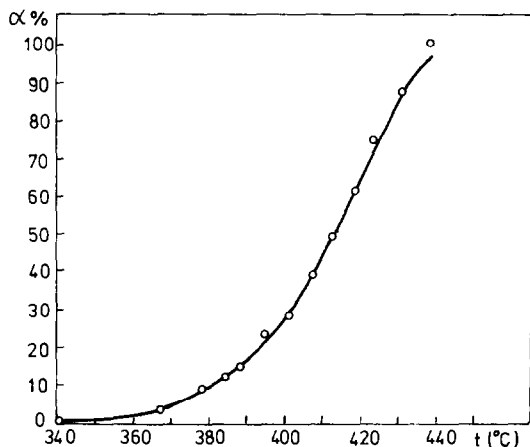


Fig. 4. Regenerated TG curve in coordinates $(\alpha, t^{\circ}\text{C})$ for reaction 3b at $\beta = 5 \text{ K min}^{-1}$: (—) calculated curve; (○) experimental points.

values of the reaction order higher than unity suggest the existence of structural units consisting of more than one molecule in various ratios, which undergo decomposition. In Fig. 4 the regenerated TG curve for reaction (3b) using the Coats–Redfern non-isothermal kinetic parameters, is given in coordinates $(\alpha, t^{\circ}\text{C})$. The experimental points lie on the curve, thus confirming the validity of the applied method.

Using the DTA signal corresponding to migration I of the ligands (2a and 2b) and applying the Coats–Redfern method, we made an attempt to evaluate the values of the non-isothermal kinetic parameters. By this means the following results were obtained

For $[\text{Ni}(\text{phen})_3][\text{PdCl}_4]$

$$E = 70.60 \text{ kcal mol}^{-1}$$

$$A = 3.31 \times 10^{29} \text{ s}^{-1}$$

$$n = 2$$

$$r = -0.9999$$

$$k_{220^{\circ}\text{C}} = 2.56 \times 10^{-2} \text{ s}^{-1}$$

For $[\text{Ni}(\text{bathophen})_3][\text{PdCl}_4]$

$$E = 155.11 \text{ kcal mol}^{-1}$$

$$A = 2.26 \times 10^{60} \text{ s}^{-1}$$

$$n = 1.6$$

$$r = 0.9992$$

$$k_{275^{\circ}\text{C}} = 9 \times 10^{-2} \text{ s}^{-1}$$

Although the method used to evaluate the kinetic parameters for the migration is not very reliable, and the obtained values of the activation energy and preexponential factor are somewhat unusual, the rate constant values for the migration reactions (2a) and (2b) are quite understandable. Thus, this attempt to determine the non-isothermal kinetic parameters for the ligand migration between the two coordination spheres could be considered for the moment as being valid. The value of 2 for the reaction order suggests an elementary reaction between two particles, such as the complex anion and the complex cation. It is interesting to note that the activation

energy of reaction (2b) is greater than that determined for reaction (2a). This difference may be explained by the greater size of bathophenanthroline in comparison with the unsubstituted phenanthroline. Consequently, the migration in the solid state of the first-mentioned ligand must be more difficult than that of the second.

CONCLUSIONS

(1) Experimental data concerning the thermal stability of $[\text{Ni}(\text{phen})_3][\text{PdCl}_4] \cdot 5.5\text{H}_2\text{O}$ and $[\text{Ni}(\text{bathophen})_3][\text{PdCl}_4] \cdot 6\text{H}_2\text{O}$ have been obtained.

(2) For the kinetically workable decomposition reactions the non-isothermal kinetic parameters have been evaluated.

(3) The non-isothermal kinetic parameters for the migration of the ligands between the two coordination spheres of the metal ions have been evaluated.

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