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Thermochimica Acta 285 (1996) 191–197

thermochimica acta

Thermal and stereochemical studies of some cyclic ligand complexes of palladium(II) in the solid state

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Received 2 February 1994; accepted 26 February 1996

Abstract

1,4-Morpholine (morph), 1,4-thioxane (thiox), 1,4-dithiane (dith), *N*-methylmorpholine (Mmorph) and *N*,*N*′-dimethylpiperazine (DMP) complexes of palladium(II) were synthesized. Thermal investigations have been carried out and the stereochemical changes which occurred during thermal decomposition studied. The complexes were found to have the compositions: $[Pd(morph)_2Cl_2]$, $[Pd(thiox)_2Cl_2]$, $[Pd(dith)_2Cl_2]$, $[Pd(Mmorph)_2Cl_2]\cdot 2H_2O$, and $[Pd(DMP)_2Cl_2]$. The characterization and the configurational and conformational changes were studied using elemental and thermal analyses and IR spectral data. All the complexes were found to have square planar structures. Thermodynamic parameters such as activation energy E_a^*, and enthalpy change ΔH were evaluated for the dehydration and decomposition reactions of the complexes using standard methods. The stability of the complexes with respect to activation energy was compared and interpreted in terms of steric and inductive effects.

Keywords: Thermal studies; Stereochemical studies; Cyclic ligand complexes; Solid state

1. Introduction

Acyclic ligands with oxygen, sulphur or nitrogen donor atoms in their structures can act as good chelating agents for the transition and non-transition metal ions [1,2]. However, information on cyclic ligand complexes is still very scarce [3–6] and there has been little thermal investigation of the cyclic ligand complexes in the solid state [7–9]. The main aim of the present work is to synthesize some cyclic ligand (six-membered ring) complexes of Pd(II) and to study stereochemical changes during

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PII: S0040-6031(96)02938-3

thermal decomposition. An attempt has also been made to evaluate the activation energy for dehydration and decomposition reactions. Before heating, all the cyclic ligands function as unidentate and exist in the chair form [3,4,9] which is confirmed by IR spectral data. When the complexes are heated under non-isothermal conditions they decompose into palladium chloride. No intermediate complexes could be isolated. Thermodynamic parameters such as activation energy E_a^* and enthalpy change ΔH for the dehydration and decomposition reactions of the complexes have been evaluated. The stability of the complexes is explained in terms of the steric and inductive effects.

2. Experimental

2.1. *Materials and methods*

$PdCl_2$ was of AR grade (Johnson and Mathey, UK) and used as received. Morpholine from E. Merck (India), thioxane, dithiane, dimethylpiperazine from Aldrich Co. (USA) and methylmorpholine from Fluka (Switzerland) were used as received. Ethanol and diethyl ether were dried using standard procedures [10].

2.2. *Preparation of the complexes*

For the complex $[Pd(morph)_2Cl_2]$ $PdCl_2$ (approx. 0.5 g) was dissolved in dry ethanol (50 cm^3) in stoichiometric ratio with lithium chloride and stored for 48 h. It was then filtered. To the filtrate an ethanolic solution of the ligand (40 cm^3) was added with constant stirring. The golden yellow complex was collected by filtration, washed carefully several times with ethanol and diethyl ether, and dried over fused calcium chloride in a desiccator: yield, approx. 70%.

Complexes $[Pd(thiox)_2Cl_2]$, $[Pd(dith)_2Cl_2]$, $[Pd(Mmorph)_2Cl_2]\cdot 2H_2O$ and $[Pd(DMP)_2Cl_2]$ were synthesized similarly. Yields were 60–70% in most cases.

Palladium was estimated gravimetrically by standard procedures [11]. C, H, and N were determined using a Carlo Erba 1106 elemental analyser (Table 1). Thermal investigations (TGA and DTA) were carried out using a Shimadzu DT-30 Thermal

Table 1
Analytical data (calculated values in parentheses) of morpholine (morph), thioxane (thiox), dithiane (dith), *N*-methylmorpholine (Mmorph) and *N,N'*-dimethylpiperazine (DMP) complexes of Pd(II)

No.	Complex	Colour	Analysis %			
			Metal	Carbon	Nitrogen	Hydrogen
(1a)	$[Pd(morph)_2Cl_2]$	Light yellow	42.60(42.66)	38.45(38.49)	11.20(11.22)	6.40(6.41)
(2a)	$[Pd(thiox)_2Cl_2]$	Light yellow	27.58(27.60)	24.85(24.91)	–	4.14(4.15)
(3a)	$[Pd(dith)_2Cl_2]$	Light grey	26.70(26.77)	24.10(24.15)	–	4.09(4.22)
(4a)	$[Pd(Mmorph)_2Cl_2]\cdot 2H_2O$	Golden yellow	25.60(25.61)	28.89(28.88)	6.70(6.74)	6.20(6.25)
(5a)	$[Pd(DMP)_2]Cl_2$	Grey	26.20(26.24)	35.50(35.52)	13.80(13.81)	6.80(6.90)

Analyser under dynamic nitrogen atmosphere, with a heating rate of 10 K min^{-1} and α-alumina as standard reference substance. E_a^* was evaluated from the TG curves using the equation of Horowitz and Metzger [12]. ΔH was evaluated from the DTA curve using the relation, $\Delta H = KA$ [13], where K is the heat transfer coefficient (cell constant or calibration constant). The cell was a platinum crucible and its constant K was evaluated using indium metal, $CaC_2O_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$ [14,15], as calibrant. A is the total area under a particular DTA curve measured with a compensating planimeter with optical tracer (Fuji Corona 027). Values for the cell constant were evaluated using different calibrants and were more or less identical. Solid residues obtained after pyrolysis were identified by qualitative analysis. IR spectra were recorded with Perkin-Elmer models 363, 597, 783 and 843 in KBr/CsI discs.

3. Results and discussion

3.1. $[Pd(morph)_2Cl_2]$ (1a)

This complex (1a) has been reported earlier [5, 17] but differs in chemical composition and method of preparation from the present work. On pyrolysis, under non-isothermal conditions, the complex (1a) is stable upto 130°C and decomposes into $PdCl_2$ with the loss of two molecules of ligand in the range 131–275°C, as found in the TGA curve. It has two endothermic DTA peaks at 208 and 243°C (Fig. 1). Values of the

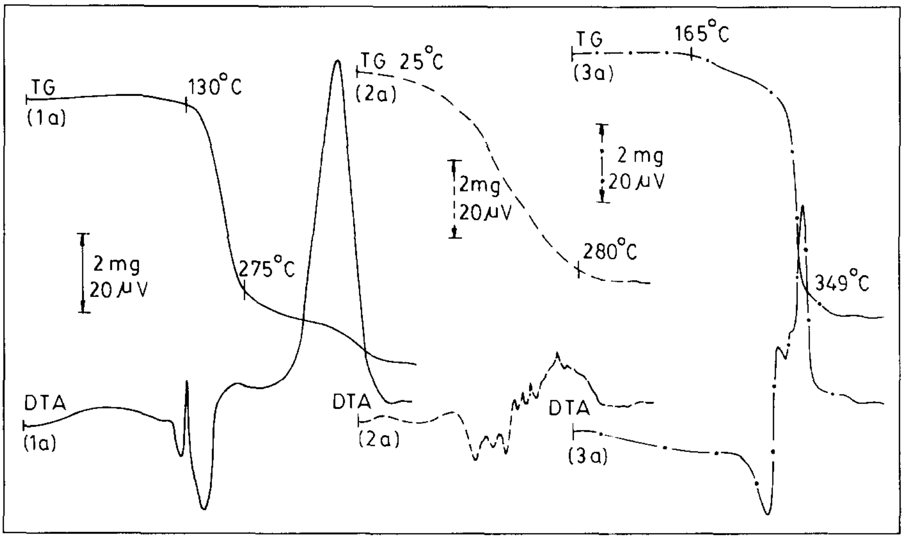

Fig. 1. Thermal curves of $[Pd(morph)_2Cl_2]$ (1a) (——), sample mass 9.4 mg; $[Pd(thiox)_2Cl_2]$ (2a) (- - -), sample mass 9.3 mg; and $[Pd(dith)_2Cl_2]$ (3a) (–·–·–), sample mass 10.0 mg.

Table 2
Thermal parameters of cyclic ligand[a] complexes of Pd(II)

No.	Decomposition	TG temp. range/°C	DTA peak temp./°C Exo.	DTA peak temp./°C Endo.	E_a^*/kJ mol^{-1} TG	Enthalpy change ΔH/ (kJ mol^{-1})
1(a)	$[Pd(morph)_2Cl_2] \rightarrow PdCl_2$	131–275	–	208 243	119	65
2(a)	$[Pd(thiox)_2Cl_2] \rightarrow PdCl_2$	25–280	-	100 134 152	31	13
3(a)	$[Pd(dith)_2Cl_2] \rightarrow PdCl_2$	165–349	342	324	114	103
4(a)	$[Pd(Mmorph)_2Cl_2]\cdot 2H_2O \rightarrow [Pd(Mmorph)_2Cl_2]$	50–100	–	88	41	44
4(b)	$[Pd(Mmorph)_2Cl_2] \rightarrow PdCl_2$	190–266	–	188 256	80	34
5(a)	$[Pd(DMP)_2Cl_2] \rightarrow PdCl_2$	25–290	171	236 274	36	54

[a] Morpholine (morph), thioxane (thiox), dithiane (dith), *N*-methylmorpholine (Mmorph) and *N,N'*-dimethylpiperazine (DMP).

thermal parameters E_a^* and ΔH for the decomposition reaction have been evaluated and are given in Table 2.

IR spectra show that the morpholine is coordinated through the nitrogen in the chair form. The ν(N–H) stretching frequency which is usually found at about 3300 cm^{-1} [16,17] in the free ligand was shifted to lower frequencies at 3250, 3209, 3180, 3070 cm^{-1} due to electron withdrawal from the nitrogen to the metal. This suggests that the ligand is coordinating through the nitrogen and exists only in the chair form. The ν(M–N) bands were found at around 460, 431, 320 cm^{-1}, see Table 3. No intermediate complex could be isolated.

3.2. $[Pd(thiox)_2Cl_2]$ (2a)

This complex has been reported earlier [3] but thermal investigations have not yet been carried out on it. On pyrolysis under non-isothermal condition, complex (2a) decomposes to $PdCl_2$ in a single step losing two molecules of the cyclic ligand in the temperatures range 25–280°C as shown in the TGA curve (Fig. 1). The corresponding DTA peaks are endothermic and appear at 100, 134, 152°C (Table 2). Values of E_a^* and ΔH are given in Table 2.

IR absorption bands for ν(C–S–C) which are usually found at around 666 cm^{-1} [3,4] in the free ligand were shifted to lower frequencies and appeared at about 655 and 641 cm^{-1}, suggesting that the coordination of the ligand to metal occurs through sulphur only. The ν(Pd–S) appeared at about 340, 333, 220 cm^{-1}, see Table 3. No intermediate complex could be isolated.

Table 3
IR spectral data (cm^{-1})[a] for Pd(II) cyclic ligand[b] complexes

No	Complex	$\nu(NH)$ + $\nu(OH)$	$\nu(CH_2)$	$\delta(NH)$ + $\delta(HOH)$	$\delta(CH_2)$	$\tau(NH)$ + $\rho_w(NH)$ + $\tau(CH_2)$	$\nu(CN)$ + $\nu(C-C)$ + $\nu_a(COC)$	$\rho r(CH_2)$ + $\nu_s(COC)$	$\nu(CSC)$	$\nu(M-L)$
(1a)	$[Pd(morph)_2Cl_2]$	3250(sbr) 3209(vs) 3180(sh) 3070(s)	2980(ms) 2960(ms) 2865(vs) 2400(w)	1651(ms) 1640(s) 1615(w)	1480(sh) 1450(vs) 1418(s)	1395(s) 1360(ms)	1100(ms) 1090(ms) 1080(w) 1039(s)	890(vs) 824(ms)		460(s) 431(s) 320(w)
(2a)	$[Pd(thiox)_2Cl_2]$		2850(br) 2745(ms)		1440(s) 1412(sh)	1325(s) 1305(w) 1280(vw) 1260(w) 1215(ms)	1180(s) 1155(ms) 1097(s) 1052(w) 1020(vw)	940(w) 930(sh) 917(ms) 845(ms) 830(w) 820(w)	655(ms) 641(sh) 615(w)	340(ms) 333(w) 220(w)
(3a)	$[Pd(dith)_2Cl_2]$	2971(sbr) 2842(s)		1407(ms) 1394(ms)	1284(s) 1270(sh) 1264(s)	1150(s) 1140(w) 1000(s)	903(vs) 894(ms)	654(s) 640(ms) 630(sh) 615(vw) 600(ms)	430(s) 370(ms) 315(w) 280(w)	
(4a)	$[Pd(Mmorph)_2Cl_2]\cdot 2H_2O$	3450(br) 3400(vs) 3320(s) 3205(ms)	2800(br) 2770(w)	1650(w) 1615(ms)	1490(ms) 1390(ms)	1360(w) 1340(ms) 1320(s) 1220(s)	1120(w) 1129(w) 1050(ms)	820(s) 815(w) 740(ms)		400(ms) 320(w) 300(w)
(5a)	$[Pd(DMP)_2Cl_2]$	3235(sbr) 3135(br) 3100(s)	2937(s) 2895(w) 2830(vw)	1670(w) 1625(s)	1487(w) 1468(w) 1456(vs) 1446(sh)	1359(sh) 1334(vw) 1280(w) 1230(ms)	1180(s) 1155(sh) 1140(s)	982(s) 850(w)		415(w) 380(w) 300(s) 285(ms)

[a] vs, very strong; s, strong; ms, medium strong; sbr, strong broad; br, broad; sh, shoulder; w, weak; vw, very weak.

[b] Morpholine (morph), thioxane (thiox), dithiane (dith), *N*-methylmorpholine (Mmorph), *N,N'*-dimethylpiperazine (DMP).

3.3. *[Pd(dith)$_2$Cl$_2$] (3a)*

On heating under non-isothermal conditions, complex (3a) decomposes in a single step and loses two molecules of cyclic ligand in the range 165–349°C as reflected in the TGA curve, see Fig. 1. The corresponding DTA peaks appear at 324 (endothermic) and 342°C (exothermic). Thermodynamic parameters E_a^* and ΔH have been evaluated and are given in Table 2. IR spectral data show that the cyclic ligand functions as monodentate and exists in the chair form [4].

3.4. *[Pd(Mmorph)$_2$Cl$_2$]·2H$_2$O (4a)*

This complex has not been reported previously. The presence of lattice water is confirmed by the IR absorption bands at 3450 and 3400 cm^{-1} for ν (O–H) and 1650 and 1615 cm^{-1} for δ(H–O–H). On pyrolysis under non-isothermal condition, complex (4a) undergoes dehydration by losing two molecules of lattice water in the range 50–100°C. It is then converted into $PdCl_2$ by losing two molecules of cyclic ligand in the range 190–266°C, as reflected in the TGA curve (Fig. 2), and the corresponding endothermic DTA peaks were found at 188 and 256°C. Values of E_a^* and ΔH for the dehydration and decomposition reactions are given in Table 2.

As indicated by the IR absorption bands, the bonding is through oxygen rather than through the sterically hindered nitrogen atom, since the asymmetric and symmetric stretching frequencies which were found at around 1105 and 830 cm^{-1} (in the free ligand) are shifted to lower wavenumbers at 1050 and 820, 815 cm^{-1} [18]. This is in marked contrast to the morpholine complex (1a) [16, 17]. No intermediate complex could be isolated.

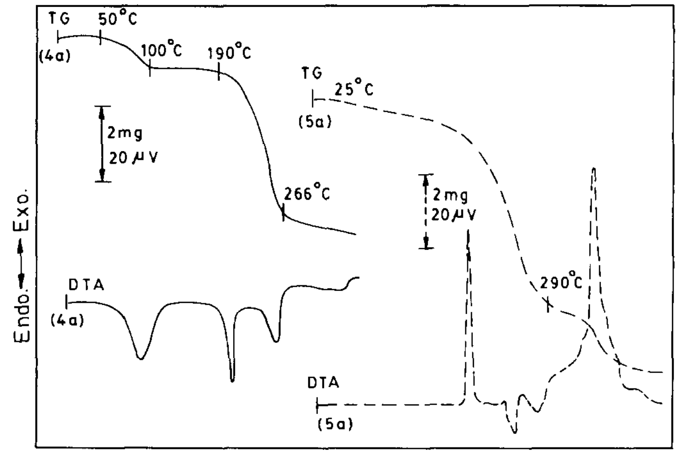

Fig. 2. Thermal curves of [Pd(Mmorph)$_2$Cl$_2$] · 2H$_2$O (4a) (——), sample mass 6.8 mg; and [Pd(DMP)$_2$Cl$_2$] (5a) (- - - -), sample mass 10.0 mg.

3.5. $[Pd(DMP)_2Cl_2]$(5a)

This complex has been reported earlier [4], but differs from the present composition. Thermal investigation has not been reported previously. On pyrolysis under non-isothermal conditions, the complex undergoes decomposition to $PdCl_2$ in a single step by losing two molecules of the cyclic ligand in the range 25–290°C as reflected in the TGA curve, and the corresponding DTA peaks appear at 236, 274 (endothermic) and 171°C (exothermic) (Fig. 2). Values of E_a^* and ΔH are given in Table 2. As indicated by the IR absorption bands, the cyclic ligand functions as unidentate and exists in the chair form [4].

The stability order of the Pd(II) complexes follows the trend DMP = thiox < Mmorph < dith < morph. The stability order may be explained on the basis of steric and inductive effects [19]. In the case of nitrogen co-ordinating ligands, the order is DMP < Mmorph < morph which is due to the steric effect of methyl group (s) on the nitrogen atom(s). In the case of thioxane and dithane complexes, the thioxane complex is less stable than the dithane as a result of the inductive effect.

Acknowledgements

The authors are grateful to the Regional Sophisticated Instrumentation Centres (C.D.R.I.), Lucknow, Madras and Shillong for IR spectra and elemental analyses.

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