Thermochimica Acta, 85 (1985) 63–66
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL PROPERTIES OF Cis-Pd COMPLEXES PdL_1X_2 (L = PLANAR DITHIO OXAMIDE ; X = Cl, Br, I)

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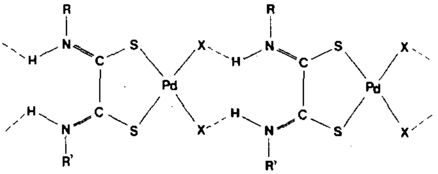
ABSTRACT

Stable cis-PdL_1X_2 coordination compounds can be obtained by adding an acetic acid solution of the ligand L in a 1:1 ratio to the Pd^{2+} solution in HX. The complex can be filtered off after 4h and is washed with acetic acid. In this study PdL_1X_2 with L = dithio oxamide (DTO), N-methyldithio oxamide (MDTO) and N,N'-dimethyldithio oxamide (DMDTO) and X = Cl, Br and I is presented.

INTRODUCTION

Peyronel et al. have determined the crystal structure of $Zn(DMDTO)_1Cl_2$ (ref.1). This structure consists of discrete molecular units, interacting through hydrogen bonds between chlorine of one unit and hydrogen of the neighbour compound. As the infrared spectra of $Pd(DMDTO)_1Cl_2$ and all other PdL_1X_2 complexes are similar to the spectrum of the Zn compound, we can assume a structure as given in Figure 1.



and other mesomeric forms

Fig.1. The structure of PdL_1X_2. R=R'=CH_3 for DMDTO, R=R'=H for DTO and R=H, R'=CH_3 for MDTO.

This complex can not be exactly planar due to the H .. H interaction on the 2 nitrogen atoms in one unit. The strength of the intermolecular hydrogen bond is influenced by the electronegative character of X and by the nature of R. This is observed in the infrared spectra of the compounds.

0040-6031/85/$03.30

EXPERIMENTAL

The thermogravimetric determinations are carried out with a Du Pont R 90 thermal analyser equipped with a 951 TGA Cahn balance in an N_2 atmosphere. The N_2 gas flow was 50 ml / min. Heating rates of 1°C, 5°C, 10°C and 20°C / min have been used. The use of these 4 available heating rates on the R 90 unit gives us more information about possible stable intermediates and about the activation energy E_a of the decomposition reactions. These calculations were carried out on a HP1000 minicomputer.

RESULTS

The thermal decomposition curves of the PdL_1X_2 compounds are given in Fig.2. All complexes are very stable and decompose between 200°C and 320°C.

The $Pd(DMDTO)_1Cl_2$ and the $Pd(MDTO)_1Cl_2$ complexes show a mass level for an intermediate. The strong intermolecular hydrogen bond between chlorine and hydrogen induces the formation of HCl according to the reaction.

$$m\ PdL_1Cl_2 \longrightarrow (PdL')_m + 2m\ HCl \uparrow$$

This is confirmed by the infrared spectra of the resulting compounds. These $(PdL')_m$ polymers are extremely stable and decompose far over 300°C.
The deprotonation in dithio oxamide was already observed for the $Pd(LH_2)_2X_2$ complexes; LH_2 = DTO, MDTO, DMDTO; X = Cl, Br, I. When $Pd(LH_2)_2X_2$ was pressed in a NaF matrix at room temperature we obtained, due to the strong electronegativity of fluorine, $Pd(LH)_2$, $NaHF_2$ and NaX. (ref.2) according to the reactions :

$$\begin{aligned}
M(LH_2)_2X_2 + 2NaF &\longrightarrow [M(LH_2)_2F_2] + 2NaX \\
[M(LH_2)_2F_2] &\longrightarrow M(LH)_2 + 2HF \\
2HF + 2NaF &\longrightarrow 2NaHF_2
\end{aligned}$$

The first step is a halide exchange in approximately hundred fold excess of NaF. The $Pd(LH_2)_2F_2$ compound was not stable due to the exceptionally strong $N^+ - H....F^-$ associations, resulting in the formation of $Pd(LH)_2$ and in the elimination of HF. The HF is then captured by NaF forming $NaHF_2$.

The other PdL_1X_2 complexes decompose without the formation of a stable intermediate as no stoichiometric compound can be assigned to the curve inflections. The final residu, obtained after heating up to 700°C, was in all cases metallic Pd. The thermal stability sequence, as indicated by the temperature of initial loss, is :

$$Pd(DMDTO)_1Cl_2 < Pd(DMDTO)_1I_2 \leq Pd(DMDTO)_1Br_2$$

$$Pd(MDTO)_1Cl_2 < Pd(MDTO)_1I_2 \leq Pd(MDTO)_1Br_2$$

$$Pd(DTO)_1Cl_2 \ < \ Pd(DTO)_1I_2 \ < \ Pd(DTO)_1Br_2$$

The slight difference between the stability of $Pd(DMDTO)_1X_2$ and $Pd(MDTO)_1X_2$ X = Br, I respectively indicates that these decompositions correspond to the destruction of the ligand and is hardly influenced by X.

The activation energy E_a of the $(PdL')_m$ polymer formation reaction is determined with the variable heating rate method proposed by Flynn and Wall (ref.3). In this approach, the decomposition profile of $Pd(DMDTO)_1Cl_2$ and $Pd(MDTO)_1Cl_2$ is recorded at the 4 available heating rates. The temperature at the chosen decomposition levels for each heating rate is given in Table 1.

TABLE 1

Temperatures at chosen decomposition levels of $Pd(DMDTO)_1Cl_2$ and $Pd(MDTO)_1Cl_2$ for each heating rate and the corresponding E_a calculated by the method of Flynn and Wall.

	Weight loss (%)	Temperature (°C)				E_a (kJ/mole)
		Heating rate (°C/min)				
		1	5	10	20	
$Pd(DMDTO)_1Cl_2$	2.0	192.0	216.0	227.0	237.0	122.4
	6.0	206.0	232.5	243.5	255.0	120.0
	10.0	216.0	243.5	254.5	266.0	122.4
	14.0	224.0	253.0	264.0	276.0	121.6
$Pd(MDTO)_1Cl_2$	2.0	194.0	213.3	223.5	231.5	146.8
	6.0	207.8	227.2	238.0	247.2	149.0
	10.0	214.9	234.8	246.2	256.4	146.1
	14.0	220.3	241.0	252.5	264.0	142.8

Fig. 3 shows the decompositions and the Arrhenius plot for $Pd(DMDTO)_1Cl_2$. The measured values of temperature and heating rate are used to calculate E_a for each decomposition level (Table 1). For $Pd(DMDTO)_1Cl_2$ E_a = 122 kJ/mole and for $Pd(MDTO)_1Cl_2$ E_a = 146 kJ/mole (average values).

ACKNOWLEDGEMENTS

The authors thank J.Janssens for writing the computer programs.

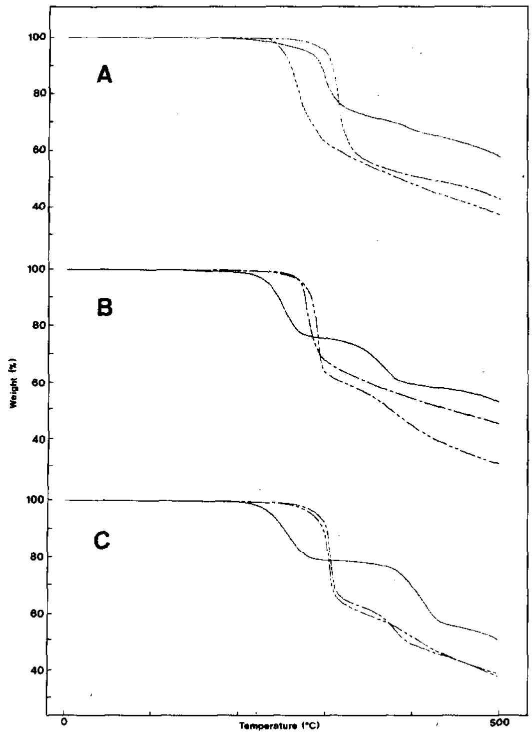


Fig.2. Decomposition curves of A : $Pd(DTO)_1X_2$; B : $Pd(MDTO)_1X_2$; C : $Pd(DMDTO)_1X_2$ X = Cl (——), Br (— - —), I (—---) (heating rate 10°C/min).

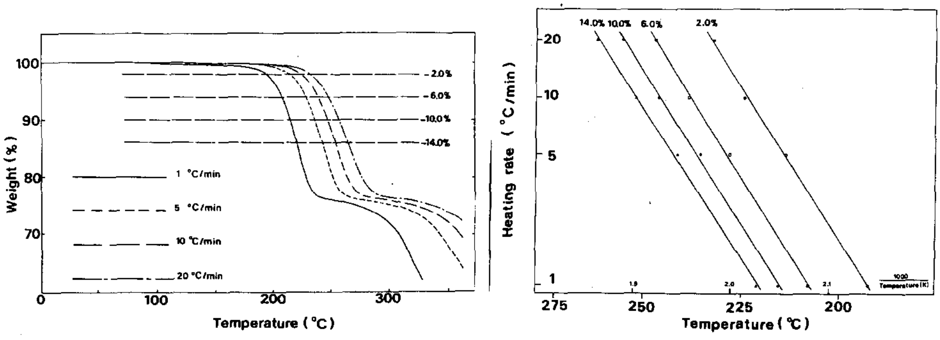


Fig.3. Decomposition curves and Arrhenius-plot of $Pd(MDTO)_1Cl_2$.

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