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THERMAL STUDIES ON PURINE COMPLEXES. IX. PALLADIUM(II) COMPLEXES WITH 8-ALKYL SUBSTITUTED THEOPHYLLINES

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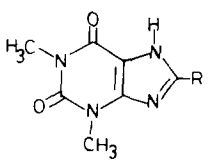
ABSTRACT

Palladium complexes of the PdL_2Cl_2 type (L = 8-ethyl, 8-propyl 8-isopropyl and 8-pentyl theophylline), were synthesized in acid medium. The thermal behaviour of these complexes has been studied by TG, DTG and DSC techniques. A scheme of thermal decomposition has been proposed.

INTRODUCTION

Recently, interest has been shown in the Pd(II) and Pt(II) complexes of *N*-methyl substituted xanthines [1–8], since these compounds can serve as models of biologically important analogues [9], and because of the potential antitumor activity of these complexes [4]. For this reason, and following our studies on the thermal behaviour of metal complexes of xanthine derivatives [10], in this paper we wish to report the synthesis and thermal studies of



Scheme 1

some Pd(II) complexes of 8-alkyltheophyllines: ethyl (ETH), propyl (PRH), isopropyl (IPH) and pentyl (PH) (Scheme 1).

EXPERIMENTAL

$PdCl_2$ was purchased from Carlo Erba. The alkyltheophylline derivatives were synthesized according to the method described by Speer [11]. After

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TABLE 1

Elemental analysis for the PdL_2Cl_2 complexes

Compound	Colour		Analysis (%)			
			C	H	N	Pd
$Pd(ETH)_2Cl_2$	Yellow	Calcd.	36.40	4.04	18.87	17.93
		Found	36.59	3.65	19.57	17.70
$Pd(PRH)_2Cl_2$	Yellow	Calcd.	38.62	4.50	18.02	17.12
		Found	39.23	4.56	17.69	16.25
$Pd(IPH)_2Cl_2$	Yellow	Calcd.	38.62	4.50	18.02	17.12
		Found	38.45	4.63	18.38	16.02
$Pd(PH)_2Cl_2$	Yellow	Calcd.	42.51	5.31	16.53	15.71
		Found	41.90	4.99	15.49	16.70

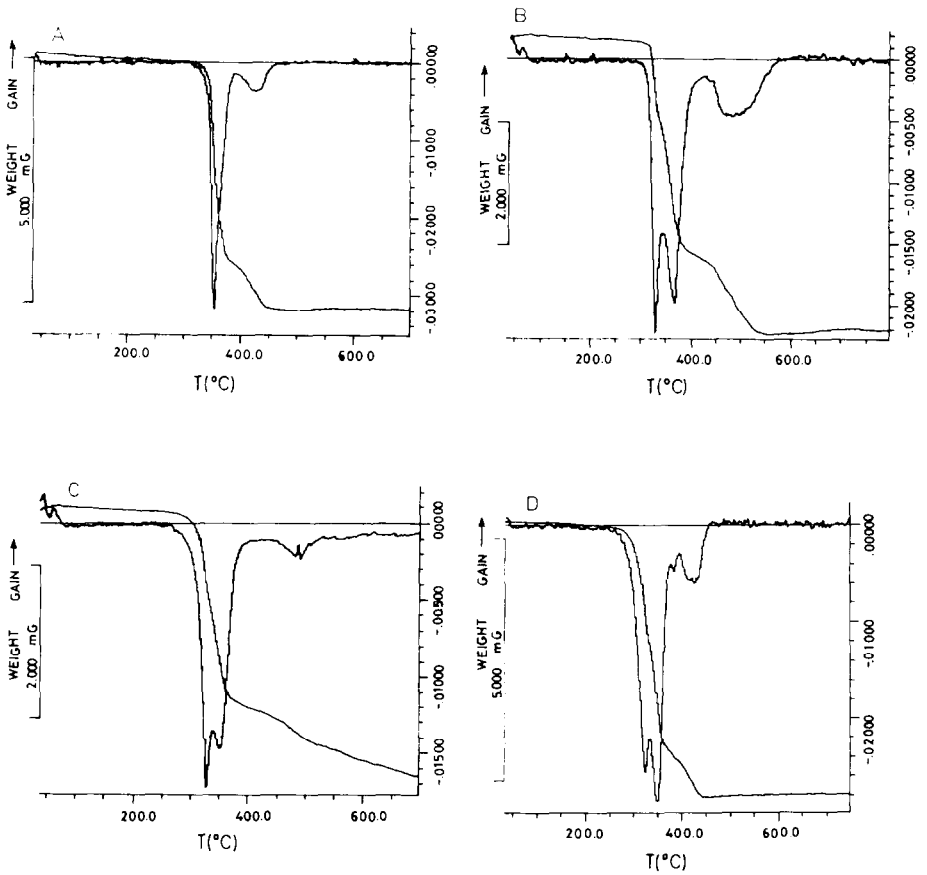

Fig. 1. TG curves for $Pd(ETH)_2Cl_2$ (A); $Pd(PRH)_2Cl_2$ (B); $Pd(IPH)_2Cl_2$ (C) and $Pd(PH)_2Cl_2$ (D).

recrystallization using ethanol–water mixtures, the products were obtained as white crystalline needles.

The synthetic conditions for the Pd(II) complexes were the same as those employed in a previous work [12].

Carbon, hydrogen and nitrogen contents were determined by elemental analysis (at the Institute of Bio-organic Chemistry of Barcelona). Palladium was determined gravimetrically. The complexes prepared, along with their elemental analysis and colour, are presented in Table 1.

The spectra of solids were obtained as KBr or polyethylene pellets on a Beckman 4250 spectrometer. TG studies were made in a dynamic atmosphere of pure air (100 ml min^{-1}) in a Mettler TG-50 thermobalance, using samples varying in weight from 7.27 to 4.33 mg and a heating rate of 10°C min^{-1}. The DSC curves were recorded on a Mettler differential scanning calorimeter (DSC-20) at a heating rate of 5°C min^{-1}, in the temperature range 40–560°C, using samples varying in weight from 3.70 to 1.81 mg.

RESULTS AND DISCUSSION

$PdCl_2$ reacts with 8-alkyltheophylline derivatives in water to give compounds which, according to the results of the elemental analyses (Table 1),

TABLE 2

Infrared data for the PdL_2Cl_2 complexes (cm^{-1})

Compound	ν(N–H)	ν(C=O)	ν(C=C)	ν(C=N)	ν(Pd–Cl)	ν(Pd–N)
ETH	3160	1710				
		1660	1605	1565	—	—
$Pd(ETH)_2Cl_2$ (**I**)	3140	1725	[a]	1565	335	250
		1670			330	
PRH	3180	1715	[a]	1560	—	—
		1630 [b]				
$Pd(PRH)_2Cl_2$ (**II**)	3205	1720	[a]	1560	325	[c]
	3175	1670				
IPH	3220	1725	1605	1560	—	—
		1635				
$Pd(IPH)_2Cl_2$ (**III**)	3135	1715	[a]	1560	335	255
		1660			330	
PH	3190	1720	[a]	1560	—	—
		1635 [b]				
$Pd(PH)_2Cl_2$ (**IV**)	3210	1715	[a]	1560	330	[c]
	3180	1670				

[a] Not observed due to the overlapping with the ν(C=O) band.

[b] Wide band.

[c] Not observed.

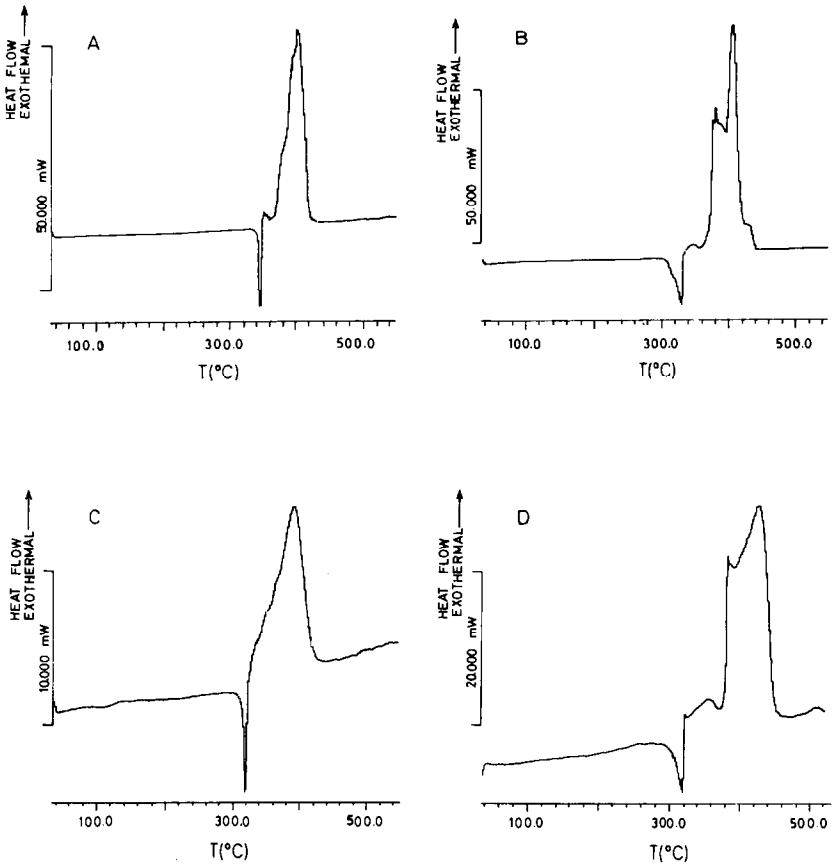

Fig. 2. DSC curves for $Pd(ETH)_2Cl_2$ (A); $Pd(PRH)_2Cl_2$ (B); $Pd(IPH)_2Cl_2$ (C) and $Pd(PH)_2Cl_2$ (D).

show the experimental formula PdL_2Cl_2. The compounds are not ionic and their IR spectra show some M–X stretching bands. Since palladium(II) usually forms four-coordinated compounds, this formula suggests that the ligands act in monodentate form.

IR (Table 2), ^1H NMR and magnetic studies of the compounds PdL_2Cl_2

TABLE 3

TG data for the decomposition of isolated palladium complexes

Complex	Decomp. temp. range (°C)	Weight residue	
		Found (%)	Calcd. (%)
$Pd(ETH)_2Cl_2$	315–475	20.37	20.63
$Pd(PRH)_2Cl_2$	300–550	18.70	19.70
$Pd(IPH)_2Cl_2$	250–700	18.43	19.70
$Pd(PH)_2Cl_2$	225–475	19.21	18.07

[13] show them to be mononuclear, square-planar molecules, containing N_7-bonded 8-alkyltheophylline. $Pd(ETH)_2Cl_2$ (**I**) and $Pd(IPH)_2Cl_2$ (**III**) complexes seem to have a *cis* geometry, whilst for $Pd(PRH)_2Cl_2$ (**II**) and $Pd(PH)_2Cl_2$ (**IV**) a *trans* geometry is suggested [13].

Figures 1 and 2 present TG and DSC plots of the complexes. The TG curves show that the thermal decomposition of these complexes is very similar. All the complexes are anhydrous, and on the basis of their initial decomposition temperatures, the thermal stability follows the order $Pd(ETH)_2Cl_2 > Pd(PRH)_2Cl_2 > Pd(IPH)_2Cl_2 > Pd(PH)_2Cl_2$. The thermal stability decreases with length and orientation of the alkyl group in position 8, probably due to the increase of the steric hindrance. Likewise, TG curves show that the decomposition of these complexes takes place in two steps (except for **I**, which occurs in only one step). At the end of the decomposition, PdO was obtained as a residue. The decomposition temperature ranges, observed weight losses and calculated weight losses for the residue are given in Table 3.

From DSC curves, it is possible to propose the following scheme for the thermal decomposition of the complexes

$$PdL_2Cl_2 \underset{\text{endo}}{\rightarrow} PdL_2 + Cl_2$$

$$PdL_2 \underset{\text{exo}}{\rightarrow} PdO + \text{pyrolysis products}$$

The dehalogenation process can be observed in the DSC curves as a strong endothermic effect. The dehalogenation enthalpies and peak temperatures are given in Table 4.

As can be observed from Table 4, the order of the dehalogenation enthalpy follows the order of the thermal stability, which are analogous to those found for the complexes PdL_2Cl_2 (where L = 3-methyl-8-ethylxanthine, 1,3,8-trimethylxanthine and caffeine) [12,14].

Once dehalogenated, the complexes decompose showing one strong exothermic effect in the DSC curves. This must be attributed to the combustion of the organic matter. The decomposition peak temperatures are also given in Table 4.

TABLE 4

DSC data for PdL_2Cl_2 complexes

Complex	ΔH Dehal. (kJ mol^{-1})	Peak Temp. (°C)	Decomp. peak (°C)
$Pd(ETH)_2Cl_2$	208.2	344.7	406
$Pd(PRH)_2Cl_2$	203.7	328.5	380
			410
$Pd(IPH)_2Cl_2$	171.9	318.6	390
$Pd(PH)_2Cl_2$	161.0	319.1	390
			430

REFERENCES

1 W.M. Beck, J.C. Calabrese and N.D. Kottmair, Inorg. Chem., 18 (1979) 176.
2 E.H. Griffith and E.L. Amma, J. Chem. Soc., Chem. Commun., (1979) 322.
3 N.H. Abnew, T.G. Appleton, J.R. Hall, G.F. Kilmister and I.J. McMahon, J. Chem. Soc., Chem. Commun., (1979) 324.
4 R.E. Cramer, D.M. Ho, W.V. Doorne, J.A. Ibers, T. Norton and M. Kashiwagi, Inorg. Chem., 20 (1981) 2457.
5 J.O. Orbell, K. Wilkowski, B. de Castro, L.G. Marzilli and T.J. Kistenmacher, Inorg. Chem., 21 (1982) 813.
6 J.R. Lusty and P.F. Lee, Inorg. Chim. Acta, 91 (1984) L47.
7 D.M.L. Goodgame, P.B. Hafman, R.T. Riley and D.J. Williams, Inorg. Chim. Acta, 91 (1984) 89.
8 G. Pneumatikakis, Inorg. Chim. Acta, 93 (1984) 5.
9 D.J. Hodgson, Prog. Inorg. Chem., 23 (1977) 211.
10 J.M. Salas-Peregrin, E. Colacio-Rodríguez, F. Girela-Vilchez and M. Roldán-Medina, Thermochim. Acta, 80 (1984) 323 and references therein.
11 J.H. Speer and A.L. Raymond, J. Am. Chem. Soc., 75 (1953) 114.
12 J.M. Salas-Peregrin, E. Colacio-Rodríguez, M.A. Romero-Molina and M.P. Sánchez-Sánchez, Thermochim. Acta, 69 (1983) 313.
13 E. Colacio and J.M. Salas, Inorg. Chim. Acta, submitted.
14 J.M. Salas-Peregrin, E. Colacio-Rodríguez and E. Sánchez-Martínez, Thermochim. Acta, 86 (1985) 189.