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THERMAL STUDIES ON PURINE COMPLEXES. III. PALLADIUM COMPLEXES OF XANTHINE AND SOME XANTHINE DERIVATIVES

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ABSTRACT

Some complexes $|PdL_2Cl_2|$ (where L = xanthine, theophylline, theobromine, 3,8-dimethylxanthine, caffeine and 1,3,8-trimethylxanthine) have been prepared in acid medium. Their structure has been established from IR and ^{1}H-NMR data. The thermal behaviour of these complexes has been studied by TG, DTG and DSC techniques. Heats of dehalogenation have been calculated from the DSC curves.

INTRODUCTION

Metal complexes formed by interaction of free purinic bases with salts of a wide variety of metal ions have been studied quite extensively in recent years [1–3]. However, to our knowledge, no investigation of the thermal behaviour of these complexes has been reported.

Following our recent thermal studies on some 3*d* metal complexes of xanthine (2,6-dioxopurine) and xanthine derivatives [4,5], in the present paper we report the synthesis, characterization and thermal behaviour of six new complexes of Pd(II) with the purinic bases: xanthine (XH), theophylline

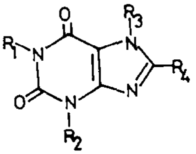

Fig. 1. R_1, R_2, R_3, R_4 = H (xanthine); R_1, R_2 = CH_3; R_3, R_4 = H (theophylline); R_2, R_3 = CH_3; R_1, R_4 = H (theobromine); R_2, R_4 = CH_3; R_1, R_3 = H (3,8-dimethylxanthine); R_1, R_2, R_3 = CH_3; R_4 = H (caffeine); R_1, R_2, R_4 = CH_3; R_3 = H (1,3,8-trimethylxanthine).

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(TH), theobromine (TBH), 3,8-dimethylxanthine (DMH), caffeine (C) and 1,3,8-trimethylxanthine (TMH) (Fig. 1).

EXPERIMENTAL

Materials

$PdCl_2$, theophylline, theobromine and caffeine were purchased from Carlo Erba, and xanthine was obtained from Merck. 3,8-Dimethylxanthine and 1,3,8-trimethylxanthine were synthesized using methods described previously [6,7]. After recrystallization using water, the products were obtained as white crystalline needles.

Methods

Microanalyses of C, H and N were carried out in a Carlo Erba microanalyzer model 1106; palladium was determined gravimetrically.

The spectra of solids were obtained as KBr or polyethylene pellets on a Beckmann 4250 spectrometer. The ^{1}H-NMR spectra were taken with a Hitachi–Perkin-Elmer model R-600 FT-NMR spectrometer. DMSO-d_6 was used as solvent and TMS as internal reference.

TG studies were made using pure air with a flow rate of 100 ml min^{-1} on a Mettler thermobalance model TG 50 at a heating rate of 10°C min^{-1}; whereas DSC runs were carried out on a Mettler differential scanning calorimeter model DSC 20 at a heating rate of 5°C min^{-1}, in the temperature

TABLE 1

Elemental analysis for the PdL_2Cl_2 complexes

Compound	Colour	Analysis (%)					
			C	H	N	Cl	Pd
$Pd(XH)_2Cl_2 \cdot 2\ H_2O$	Yellow	Calcd.	23.27	2.31	21.72	13.77	20.63
		Found	22.90	2.03	21.41	13.85	19.72
$Pd(TH)_2Cl_2$	Yellow	Calcd.	31.26	2.98	20.84	13.21	19.80
		Found	31.40	2.84	20.88	13.52	19.20
$Pd(TBH)_2Cl_2$	Yellow	Calcd.	31.26	2.98	20.84	13.21	19.80
		Found	30.78	3.01	20.69	13.52	19.40
$Pd(DMH)_2Cl_2$	Yellow	Calcd.	31.26	2.98	20.84	13.21	19.80
		Found	30.28	2.89	20.27	12.80	19.80
$Pd(C)_2Cl_2$	Yellow	Calcd.	33.95	3.54	19.81	12.56	18.82
		Found	33.92	3.42	19.60	13.05	18.71
$Pd(TMH)_2Cl_2 \cdot 2\ H_2O$	Yellow	Calcd.	31.92	3.99	18.62	11.80	17.70
		Found	32.34	3.96	18.17	11.70	18.20

TABLE 2

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

Compound	ν(OH)	ν(N–H)	ν(C=O)	ν(C=C)	ν(C=N)	ν(Pd–Cl)	ν(Pd–N)
Xanthine		3200–2700	1700, 1650	1615	1570		
$Pd(XH)_2Cl_2 \cdot 2\,H_2O$	3540 3470	3200–2700	1720, 1700	1615	1570	350	260
Theophylline		3120	1715, 1665	1605	1560		
$Pd(TH)_2Cl_2$		3100	1715, 1660	1615	1560	340	250
Theobromine		3120	1700, 1675	1600	1550		
$Pd(TBH)_2Cl_2$		3120	1700, 1675	1600	1550	345	255, 240
3,8-Dimethylxanthine	3470	3150, 3040	1705, 1660	1600	1565		
$Pd(DMH)_2Cl_2$		3180, 3070	1705, 1680	1640	1570	340	252
Caffeine			1700, 1650	1595	1540		
PdC_2Cl_2			1710, 1660	1605	1550	340	260
1,3,8-Trimethylxanthine		3180	1700, 1630	1590	1550		
$Pd(TMH)_2Cl_2 \cdot 2\,H_2O$	3630 3535	3110	1710, 1665	1615	1570	335	

TABLE 3

^1H-NMR chemical shifts for PdL_2Cl_2 complexes

Values given in ppm.

Proton	XH	$Pd(XH)_2Cl_2 \cdot 2\,H_2O$	TH	$Pd(TH)_2Cl_2$	TBH	$Pd(TBH)_2Cl_2$	DMH	$Pd(DMH)_2Cl_2$	C	$Pd(C)_2Cl_2$	TMH	$Pd(TMH)_2Cl_2 \cdot 2\,H_2O$
C_8–H	7.90	8.30	7.95	8.05	7.97	7.97			7.95	7.95		
C_8–CH_3							2.35	2.70			2.40	2.40

range 40–550°C. The thermolytic reactions were made with samples varying in weight from 2.390 to 12.884 mg.

PREPARATION OF THE COMPLEXES

Preparation of the six new Pd(II) complexes involved the same procedure: 8.5×10^{-4} mole of palladium chloride dissolved in 50 ml of 0.25N HCl were added to 100 ml of a 1.7×10^{-2} M solution of purinic base. The mixture was stirred and heated at 60°C. A yellow precipitate was formed, which was filtered, successively washed with water and ethanol and dried with ether. The chloro complexes prepared, along with their elemental analysis and colour are presented in Table 1.

RESULTS AND DISCUSSION

In order to establish the molecular structures of the palladium complexes prepared, we used elemental analysis, IR and ^{1}H-NMR spectroscopy. In Tables 2 and 3 we have collected the most significant IR and ^{1}H-NMR bands for the complexes isolated. These assignations have been made on the basis of the empirical band assignments for the free xanthine and some xanthine derivatives [8–12].

As regards the IR evidence (Table 2), the new palladium complexes of xanthine and 1,3,8-trimethylxanthine, show the characteristic ν(OH) band of water, as well as the ν(N–H) mode of neutral XH or TMH. The latter band is present in the remaining Pd(II) complexes isolated, except for the palladium(II) caffeine complex (the caffeine does not have free N–H groups), and suggests that coordination of the purinic bases to Pd(II) takes place in molecular form through the N_9 atom [except in $Pd(XH)_2Cl_2$, where the

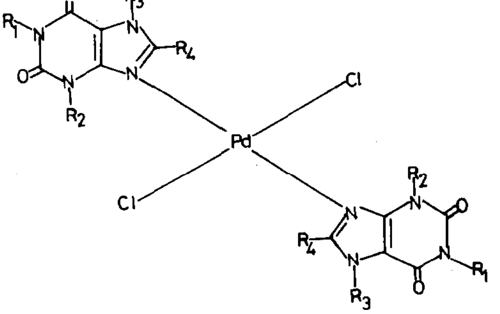

Fig. 2. Possible structure of PdL_2Cl_2 (where L = xanthine, theophylline, 3,8-dimethylxanthine, caffeine and 1,3,8-trimethylxanthine).

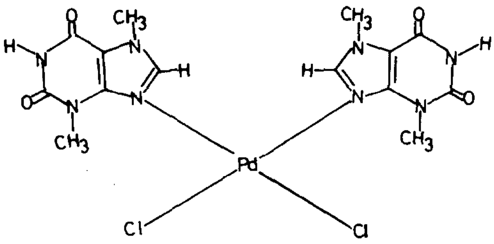

Fig. 3. Possible structure of Pd(TBH)$_2$Cl$_2$.

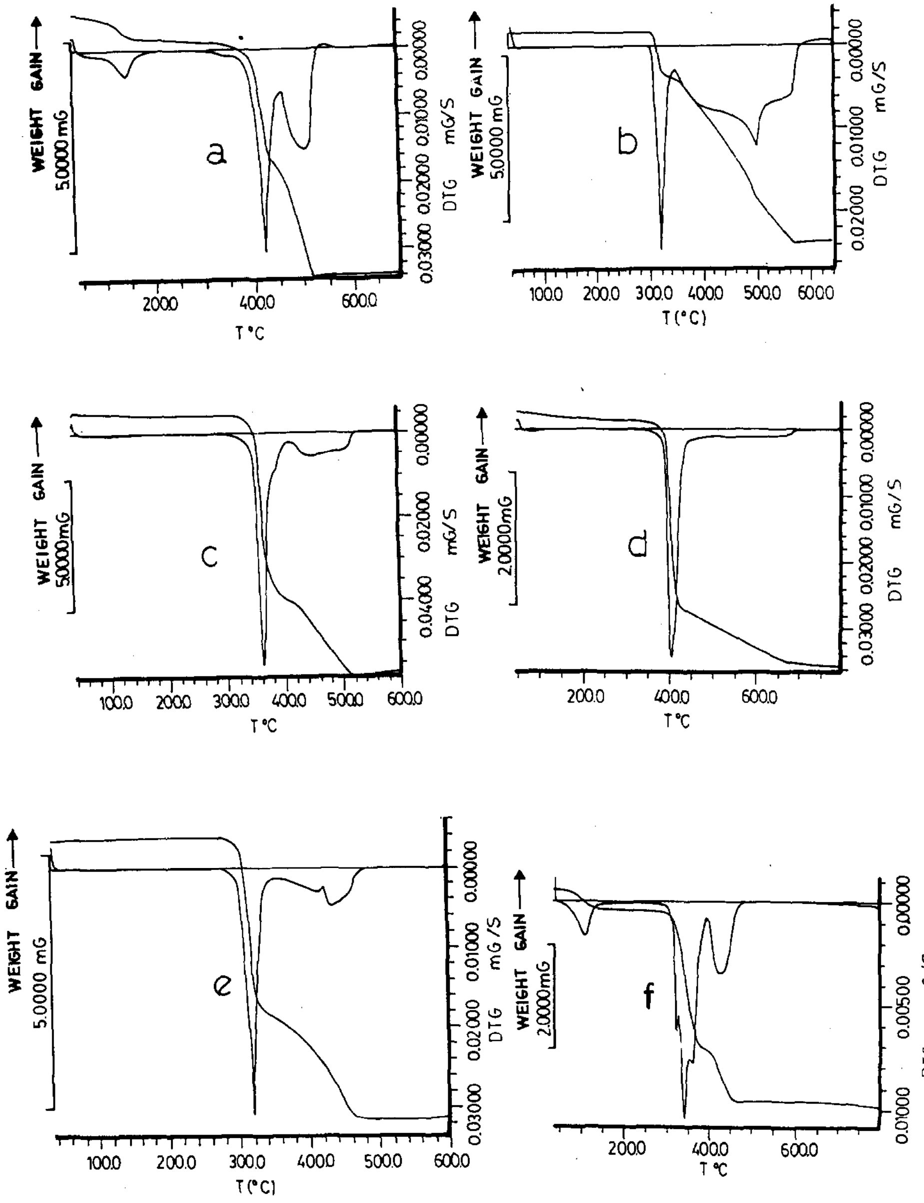

Fig. 4. TG curves for: a, xanthine; b, theophylline; c, theobromine; d, 3,8-dimethylxanthine; e, caffeine; f, 1,3,8-trimethylxanthine.

binding is established through the N_7 atom]. ^{1}H-NMR data for $Pd(XH)_2Cl_2$, $Pd(TH)_2Cl_2$ and $Pd(DMH)_2Cl_2$ are in agreement with the foregoing IR data.

With regard to the six palladium(II) complexes isolated, a square-planar configuration is valid, as suggested by magnetic measurements (the six

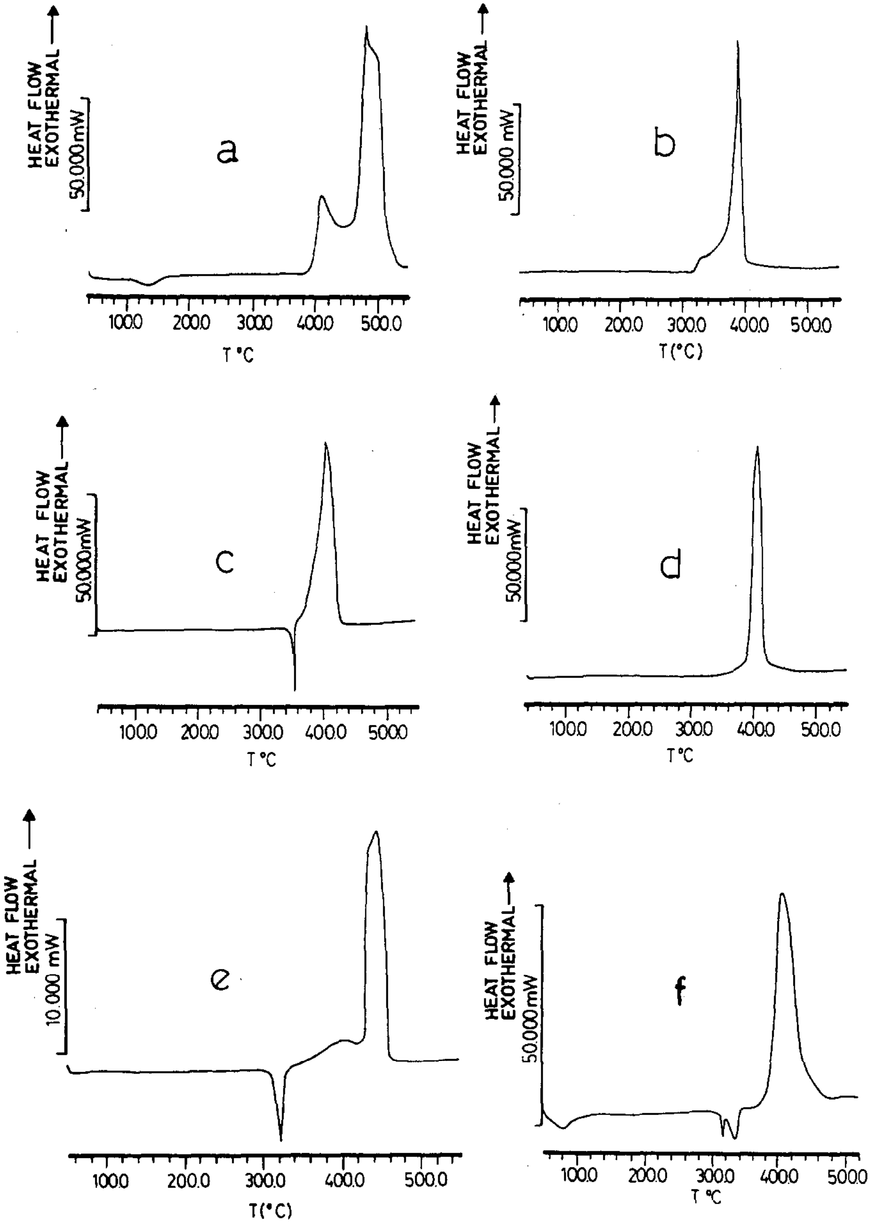

Fig. 5. DSC curves for: a, xanthine; b, theophylline; c, theobromine; d, 3,8-dimethylxanthine; e, caffeine; f, 1,3,8-trimethylxanthine.

TABLE 4

TG data for the decomposition of isolated palladium complexes

Complex	Decomposition temperature range (°C)	Weight residue	
		Found (%)	Calcd. (%)
$Pd(XH)_2Cl_2 \cdot 2\ H_2O$	370–540	23.5	23.65
$Pd(TH)_2Cl_2$	290–580	23.9	22.77
$Pd(TBH)_2Cl_2$	310–530	22.9	22.77
$Pd(DMH)_2Cl_2$	380–530	21.4	22.86
$Pd(C)_2Cl_2$	270–480	21.9	21.65
$Pd(TMH)_2Cl_2 \cdot 2\ H_2O$	290–460	19.6	20.35

complexes are diamagnetic) and IR interpretation. Thus the band at 340–350 cm^{-1} is due to stretching vibrations of Pd–Cl bonds, which suggests that the chlorine atoms are at the *trans* position [13], while those at 250–260 cm^{-1} are due to vibrations of Pd–N bonds [14]. The $Pd(TBH)_2Cl_2$ compound presents two bands at 255 and 240 cm^{-1}. These bands are assigned a Pd–N stretching vibration, which suggests that this compound has *cis* configuration [14]. Based on these data, we suggest the structures shown in Figs. 2 and 3, respectively, for these complexes.

Figures 4 and 5 present TG and DSC plots of palladium(II) complexes of xanthine, theophylline, theobromine, 3,8-dimethylxanthine, caffeine and 1,3,8-trimethylxanthine.

Under the experimental conditions used in the present work, the dehydration of $Pd(XH)_2Cl_2 \cdot 2\ H_2O$ and $Pd(TMH)_2Cl_2 \cdot 2\ H_2O$ occurs in one step in the temperature ranges 100–150 and 70–150°C, respectively. The observed weight losses in these temperature ranges (6.9 and 6.4%) are in good agreement with theoretical values (6.95 and 5.99%) calculated, for the elimination of two water molecules in both complexes. The expected endo-

TABLE 5

Dehalogenation enthalpies and decomposition temperature peaks for PdL_2Cl_2 complexes

Complex	ΔH, dehal ($kJ\ mole^{-1}$)	Decomp. peak (°C)
$Pd(XH)_2Cl_2 \cdot 2\ H_2O$		Exo 410 Exo 486
$Pd(TH)_2Cl_2$		Exo 392
$Pd(TBH)_2Cl_2$	120.4	Exo 412
$Pd(DMH)_2Cl_2$		Exo 414
$Pd(C)_2Cl_2$	228.4	Exo 451
$Pd(TMH)_2Cl_2 \cdot 2\ H_2O$	144.3	Exo 410

thermic behaviour for the dehydration process associated with these complexes has been observed from DSC curves. The dehydration enthalpies calculated are 70.4 kJ mole^{-1} for $|Pd(XH)_2Cl_2| \cdot 2\ H_2O$ and 94.7 kJ mole^{-1} for $|Pd(TMH)_2Cl_2| \cdot 2\ H_2O$.

Anhydrous $Pd(XH)_2Cl_2$ is stable from 170 to 370°C. Above 370°C the TG curve of this complex shows a strong decomposition in two steps, which finishes at 540°C. At this point, the residual weight is 23.5% of the original weight, which closely corresponds with the theoretical value required for PdO (23.65%).

TG curves for the other five palladium complexes are analogous to that of $Pd(XH)_2Cl_2$. The decomposition temperature ranges, observed weight losses and calculated weight losses for the residue of the pyrolysis (PdO in all cases) are indicated in Table 4.

On the bases of their initial decomposition temperatures, the thermal stability of these complexes follows the order: $Pd(DMH)_2Cl_2 > Pd(XH)_2Cl_2 > Pd(TBH)_2Cl_2 > Pd(TH)_2Cl_2 \simeq Pd(TMH)_2Cl_2 > Pd(C)_2Cl_2$.

Finally, from TG and DSC data a scheme of thermal decomposition has been proposed for these Pd(II) square-planar complexes. This scheme is composed by two steps: (i) dehalogenation and (ii) decomposition of the dehalogenated compounds to PdO.

In the DSC curve for $Pd(TMH)_2Cl_2$, the endothermic effect centred at 315.3°C corresponds with the melting of the complex. The fusion enthalpy calculated from the area due to the endothermic effect was 26.3 kJ mole^{-1}.

Dehalogenation processes are visible from DSC curves (Fig. 5) for $Pd(TBH)_2Cl_2$, $Pd(C)_2Cl_2$ and $Pd(TMH)_2Cl_2$ as endothermic effects centred at 335, 320 and 325°C, respectively. However, for $Pd(XH)_2Cl_2$, $Pd(TH)_2Cl_2$ and $Pd(DMH)_2Cl_2$, the dehalogenation process was not observed due to the overlapping of endothermic effects with the exothermic effects corresponding to pyrolysis of the organic moiety. Dehalogenation enthalpies and decomposition temperature peaks are summarized in Table 5.

REFERENCES

1 R.M. Izzat, J.J. Christensen and J.H. Rytting, Chem. Rev., 71 (1971) 439.
2 D.J. Hodgson, Prog. Inorg. Chem., 23 (1977) 211.
3 L.G. Marzilli, Prog. Inorg. Chem., 23 (1977) 255.
4 J.M. Salas-Peregrin, E. Colacio-Rodriguez and J.D. Lopez-Gonzalez, Thermochim. Acta, 63 (1983) 145.
5 E. Colacio-Rodriguez, J.M. Salas–Peregrin, M.P. Sanchez-Sanchez and A. Mata-Arjona, Thermochim. Acta, in press.
6 H. Bredereck, I. Henning, W. Pfleiderer and G. Weber, Chem. Ber., 86 (1953) 333.
7 J.H. Speer and A.L. Raymond, J. Am. Chem. Soc., 75 (1953) 114.
8 E.R. Blount and M. Fields, J. Am. Chem. Soc., 72 (1950) 479.
9 J.R. Lacher, J.L. Bitner, D.J. Emery, M.E. Seffe and J.D. Park, J. Phys. Chem., 59 (1955) 615.

10 C.P. Beetz, Jr. and G. Ascarelli, Spectrochim. Acta, 36 (1980) 299.
11 D. Lichtenberg, F. Bergman and Z. Neiman, J. Chem. Soc. C, (1971) 1939.
12 L.M. Twanmoh, H.B. Wood, Jr. and J.S. Driscoll, J. Heterocycl. Chem., 10 (1973) 187.
13 Pi-Chang Kong and F.D. Rochon, Can. J. Chem., 57 (1979) 526.
14 J.R. Ferraro, Low-Frequency Vibration of Inorganic and Coordination Compounds, Plenum Press, New York, 1971.