Pd(II) and Au(III) Complexes of Some 4-Glycopyranosylamino-5-nitroso-6-oxo-pyrimidine Derivatives

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Six Pd(II) and Au(III) complexes of 4-glycopyranosylamino-5-nitroso-6-oxo-pyrimidine derivatives were prepared. On the basis of their ^{1}H-NMR and IR spectra, it has been found that the coordination sites are the 5-nitroso and the 6-oxo substituents. Likewise, the thermal behaviour of the complexes has also been studied.

(Keywords: Pd(II) complexes; Au(III) complexes; ^{1}H-NMR; Thermal studies)

Komplexe des Pd(II) *und* Au(III) *mit einigen Derivaten des 4-Glycopyranosylamino-5-nitroso-6-oxo-pyrimidins*

Sechs Pd(II)- und Au(III)-Komplexe mit 4-Glycopyranosylamino-5-nitroso-6-oxo-pyrimidin-Derivaten wurden hergestellt. Auf der Basis ihrer ^{1}H-NMR und IR-Spektren wurde herausgefunden, daß die Substituenten 5-nitroso und 6-oxo die Koordinationsstellen sind. Das thermische Verhalten der Komplexe wurde ebenfalls untersucht.

Introduction

It is well known that some metal complexes of pyrimidines and their nucleotides play an essential role in many biochemical systems[1—4]. For this reason research into the interactions of metal ions with the abovementioned compounds has grown considerably over the last few years. An important part of this research consists in determining the coordination positions of the ligands to the central ion[5,6]. Here we report the

preparation of some Pd(II) and Au(III) complexes with 4-glucopyrano-sylamino and 4-xylopyranosylamino pyrimidine derivatives (Scheme 1).

Scheme 1

	R_1	X	R_2
A	H	O	CH_2OH
B	H	S	H
C	H	S	CH_2OH
D	CH_3	S	H
E	CH_3	S	CH_2OH
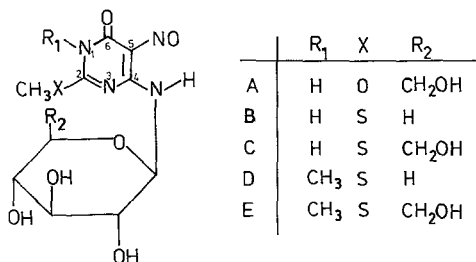
All the complexes were characterized on the basis of their ^{1}H-NMR and IR spectra. Likewise, their thermal behaviour was studied via the ATG and DSC curves.

Experimental

The 4-glycopyranosylamino pyrimidine derivatives were obtained according to previously reported methods[7].

The Pd(II) and Au(III) complexes were isolated as follows:

a) Palladium(II) complexes

An aqueous solution of $Na_2[PdCl_4]$ (2.4 mmol) was added slowly with stirring to a hot (40 °C) saturated aqueous solution of the respective ligand (1.2 mmol). All the complexes precipitated almost immediately, except $[Pd(D^-)_2] \cdot 4 H_2O$, which did so after diluting the initial volume of the mixture (40 ml) with ethanol from one to five volumes. The complexes were filtered off by suction, washed with hot water and ethanol and dried in a desiccator containing P_4O_{10}.

It must be pointed out that a solid precipitated in the Pd(II)/E system in aqueous solution, which would appear to be a mixture of different complexes impossible to obtain separately.

b) Gold(III) complexes

$Au(C^=)Cl \cdot H_2O$ was prepared by adding slowly and with stirring a concentrated aqueous solution of $H[AuCl_4]$ (0.4 mmol) to a concentrated aqueous solution of the C compound at 40 °C (0.2 mmol). To this mixture 0.1 N NaOH was immediately added drop by drop up to $pH = 6.5$. The complex precipitated immediately.

[$AuDCl_3$] was obtained by the addition of a concentrated aqueous solution of $H[AuCl_4]$ (1 mmol) to a concentrated aqueous solution of the ligand (0.5 mmol) heated to 40 °C. The solid precipitated immediately.

The two Au(III) complexes were filtered by suction, washed and dried by the same method as the Pd(II) complexes.

The Au(III)/A, Au(III)/B, and Au(III)/C systems precipitated solids consisting probably of mixtures of the respective complex (which was confirmed by IR spectroscopy) and metallic gold, but whose individual components could not be obtained separately due to their insolubility.

Measurements

A Radiometer TTT-60 automatic titrator fitted with glass and calomel electrodes was used to obtain the potentiometric titration curves of the solutions of the respective ligands. In each of the cases, solutions $5 \cdot 10^{-4} M$ and with an ionic strength $0.1 M$ of NO_3K of the respective ligand (25 ml) were used.

The chemical analyses of C, H, N, Cl, and S were carried out by microanalytical methods at the Institute of Bio-Organic Chemistry of the CSIC (Barcelona) and at the Department of Inorganic Chemistry of the University of Extremadura.

The determination of Pd in the complexes was carried out gravimetrically using dimethylglyoxime[8]. To determine gold in the complexes, a fixed quantity of the corresponding complex was mineralized using a 1 : 1 mixture of SO_4H_2/NO_3H. The residue was dissolved using water slightly acidified with NO_3H as solvent. An excess of *Mohr*'s salt was then added to the resulting solution. The precipitate of metallic gold was calcinated and then weighed.

The infrared spectra were recorded using KBr pellets (for the 4000–200 cm^{-1} range) and polyethylene pellets (for the 650–200 cm^{-1} range) on a Beckman 4250 spectrophotometer.

The ^{1}H-NMR spectra were recorded on a Hitachi Perkin-Elmer R-600 FT-NMR spectrometer, using *DMSO-d_6* as solvent and *TMS* as internal standard.

The TG studies were carried out in a dynamic air atmosphere (100 ml · min^{-1}) on a Mettler TG-50 thermobalance, at a heating rate of 10 deg · min^{-1}, while the DSC runs were obtained using a Mettler DSC-20 differential scanning calorimeter in the 35–550 °C temperature range at a heating rate of 10 deg · min^{-1}. The weight of the samples used varied between 11.80 and 1.40 mg.

Results and Discussion

Ligands

The compounds used as ligands can exist either in keto-amino, hydroxy-imino or keto-oxime forms; when $R_1 = H$, apart from these forms, 6-hydroxy-5-amino and 6-hydroxy-5-hydroxy-imino structures are also possible[9]. Nevertheless, the fact that $v(C=O)$, $v(N=O)$ and $v(N-H)$ were identified in the IR spectra of all the compounds in the 1 675–1 700, 1 480–1 540 and 2 600–3 310 cm^{-1} ranges, respectively, proves that all the compounds are to be found as solids in the keto-amino tautomeric form[10].

The values of the constants of acid dissociation, K_1 (in mol · l^{-1}), in aqueous solution (ionic strength $0.1 M$ of NO_3K), calculated by *Speakman*'s method[11], at a working temperature of 40 °C, were as follows: $K_A = 1.07 \cdot 10^{-6}$; $K_B = 1.07 \cdot 10^{-6}$; $K_C = 1.99 \cdot 10^{-6}$; $K_D = 6.76 \cdot 10^{-11}$ and $K_E = 2.88 \cdot 10^{-11}$.

K_A, K_B, and K_C values correspond to the ionization of N_1—H groups and are similar to that given in the literature for 4-amino-1, 6-dihydro-2-methylthio-5-nitroso-6-oxo-pyrimidine[12].

K_1 values for the D and E compounds correspond to the ionization of C_4—NH groups and are slightly lower than those of their analogous 4-amino-1,6-dihydro-1-methyl-2-methylthio-5-nitroso-6-oxo-pyrimidine[13]. This fact could presumably be due to a decrease in the polarity of the C_4N—H bond arising from the inductive effect of the glycosidic residue on the nitrogen atom of the said group.

On the other hand, the K_2 values for the A, B and C compounds due to the ionization of the NH groups substituted in C_4 were: $K_{2A} = 3.16 \cdot 10^{-11}$; $K_{2B} = 1.74 \cdot 10^{-11}$, and $K_{2C} = 2.82 \cdot 10^{-11} \, mol \cdot l^{-1}$. These values suggest the possibility of the occurrence of a certain ionization of the afore-mentioned NH bond in the neutral or basic solutions of these compounds.

Complexes

Analytical and colour data of the complexes are given in Table 1. The results of elemental analysis are in close agreement with the proposed formulae. In Table 1 it can be seen that all the Pd(II) complexes have a stoichiometric ratio value [ligand]/[Metal] of 2/1, while in the Au(III) complexes this ratio is 1/1.

On the other hand, the IR and ^{1}H-NMR spectral studies of the complexes enable us to establish the assignments summarized in Tables 2 and 3 respectively. These tables also include the data corresponding to the free ligands which have been discussed in previous papers[10, 14].

a) Palladium(II) Complexes

The analysis of the ^{1}H-NMR data of the Pd(II) complexes of A, B, and C (R_1 = H) compounds shows three significant features: 1) the signals due to the N_1—H groups are lost, which proves that the ligands coordinate to the central ion in the monoanionic form; 2) the signals due to the C_4—NH groups shift to higher field values. This fact may indicate that the 5-NO groups intervene in the coordination to the central ion, acting upon and weakening the hydrogen bridge between 5-NO and C_4—NH groups[10]; 3) the signals due to C_1—H, C_2—O—Me and C_2—S—Me groups appear at equivalent or similar resonance values as in the respective free ligands.

With regard to the IR spectral data of the A, B, and C complexes of Pd(II), the most significant facts concerning the high frequency range are the loss of the $v(C=O)$ stretching vibration band and the shift of the $v(N=O)$ bands to lower wavenumber values. In the low frequency range, between 650 and 200 cm^{-1}, a new, weak band was observed in all three

Table 1. *Colour and analytical data (theoretical values in parentheses)*

Complex	Colour	C	H	N	Cl	S	M
Pd(A⁻)₂·4H₂O	orange	30.22 (31.41)	4.23 (4.52)	13.51 (13.33)	—	—	12.72 (12.66)
Pd(B⁻)₂·4H₂O	red brown	29.33 (29.54)	4.03 (4.18)	13.64 (13.79)	—	8.05 (7.88)	13.32 (13.10)
Pd(C⁻)₂·4H₂O	dark brown	29.85 (30.26)	4.15 (4.36)	12.77 (12.84)	—	7.16 (7.34)	12.51 (12.19)
Pd(D⁻)₂·2H₂O	orange	31.58 (32.82)	4.12 (4.23)	13.45 (13.92)	—	7.91 (7.96)	13.62 (13.23)
AuC=Cl·H₂O	light yellow	21.95 (22.13)	2.98 (2.68)	9.20 (9.39)	5.79 (5.95)	5.12 (5.36)	34.51 (33.02)
AuECl₃	pale yellow	21.64 (21.63)	2.75 (2.70)	8.27 (8.42)	15.02 (16.00)	4.62 (4.81)	30.00 (29.60)

complexes (see Table 2), which was assigned to v(Pd—N) stretching vibrations. This band appears for *trans*-[$(py)_2$PdX_2$] square-planar complexes (where py = pyridine and X = Cl, Br, I) in the 305–310 cm^{-1} range[15].

All the above-mentioned data allow us to assume that in the three complexes the ligands are coordinated to the Pd(II) ions as 6-oxy anionic forms, via the N atoms of the 5-NO groups and the O atoms of the 6-oxy groups (Scheme 2).

Scheme 2
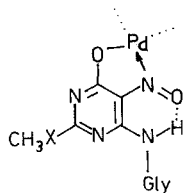
The ^{1}H-NMR spectral data of the solid complex obtained in the Pd(II)/D system in aqueous solution show the loss of the C_4-NH signal, while the C_1-H and C_2—S—*Me* signals appear at practically the same value of chemical shift as in the D compound spectrum. These data demonstrate, therefore, both that D acts, in this complex, as a monoanion, and that the C_2—S—*Me* group does not participate in the coordination.

The most significant features of the IR spectral data of this complex are the following: 1) the loss of the bands due to the v(N—H) and v(C=O) stretching vibrations; 2) the appearance of a new band of medium intensity (centred at 1 675 cm^{-1}), assigned to the v(C_4=N) stretching vibration. According to literature data, the relatively high wavenumber of this band may indicate the low conjugation of the ring[16,17]; 3) the shift of the band corresponding to the v(N=O) stretching vibration to a lower wavenumber; 4) the appearance in the low frequency range (650–200 cm^{-1}) of a new, weak band at 360 cm^{-1}, which was assigned, following the literature[15], to a v(Pd—N) stretching vibration.

The above data allow us to assume that in the [Pd(D$^-$)$_2$] 2 H$_2$O complex, D acts as a 6-oxy monoanion which is linked to the central ion, Pd(II), via the 6-oxy group and the N atom of the 5-NO group (Scheme 3).
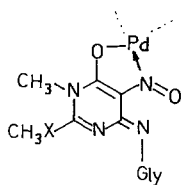
Scheme 3

Table 2. ^{1}H-*NMR data*

Compound	N$_1$-H	N$_1$-CH$_3$	C$_2$-O*Me*	C$_2$-S*Me*	C$_4$-NH	C$_1'$-H
A	12.70 s	—	4.00 s	—	12.70 d	5.20 m
B	13.00 s	—	—	2.60 s	12.60 d	5.35 m
C	12.60 s	—	—	2.60 s	12.60 d	5.30 m
D	—	3.50 s	—	2.65 s	12.30 d	5.40 m
E	—	3.50 s	—	2.60 s	12.25 d	5.40 m
Pd(A$^-$)$_2$·4H$_2$O	—	—	3.90 s	—	9.80 d	5.30 m
Pd(B$^-$)$_2$·4H$_2$O	—	—	—	2.60 s	10.05 d	5.40 m
Pd(C$^-$)$_2$·4H$_2$O	—	—	—	2.60 s	10.00[1] d 9.80 d	5.40 m
Pd(D$^-$)$_2$·2H$_2$O	—	3.30[2]	—	2.60[2]	—	5.40–6.00[3] m
Au(C$^=$)Cl·H$_2$O	—	—	—	2.60[2]	—	5.00–5.60[3] m
Au(E)Cl$_3$	—	3.50 s	—	2.50 s	11.40 w	5.80 d

d: doublet, $J = 8.2$ Hz.
m: multiplet.
s: singlet.
[1] $J = 9$ Hz.
[2] two singlets.
[3] two multiples.
w: weak.

On the basis of the spectroscopic data and bearing in mind the non-paramagnetic character of the four above-mentioned Pd(II) complexes, we propose square-planar structures in which the coordination of each ligand molecule to the Pd(II) ions occurs in the 6-oxy anionic form, via the O atom of the 6-oxy group and the N atom of the 5-NO group.

It is of interest to point out the splitting of the signal from the C$_4$-NH group in the ^{1}H-NMR spectrum of the [Pd(C$^-$)$_2$]·4H$_2$O complex,

and of the C_2—S—*Me* and $C_{1'}$-H signals in the ^{1}H-NMR spectrum of the $Pd(D^-)_2 2 H_2O$ complex. Several different phenomena could be discussed as the cause of this splitting. However, given that the complexes precipitated almost immediately, it seems probable that the isolated solids are a mixture of the *cis* and *trans* isomers of the complexes, in which the magnetic environments of the hydrogen atoms are different[18—21].

b) Gold(III) Complexes

The ^{1}H-NMR data of the complex obtained in the C/Au(III) system show the loss of the N_1-H and C_4-NH signals, indicating that C acts as a bianion. This is logical if we have in mind the fact that the solution in which the complex was obtained had been neutralized with a 0.1 *N* NaOH solution.

The study of the IR spectrum of this complex reveals the loss of the $v(C=O)$ stretching vibration band; on the other hand, there also appears a new, wide band of medium intensity at $1\,695\,\text{cm}^{-1}$, which was assigned to the $v(C_4=N)$ stretching vibration. In the low frequency range there appear two new and relatively strong bands at $345\,\text{cm}^{-1}$ and $360\,\text{cm}^{-1}$, which were assigned to $v(Au—Cl)$ stretching vibrations.

On the basis of the spectroscopic data obtained, it would seem that D is coordinated to the central Au(III) ion as a bianion via the O atom of the 6-oxy group and via the negatively charged O atom of the $C_5 = N$—O^- group, as shown in Scheme 4.

Scheme 4
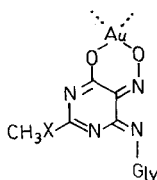
On the other hand, the low value of the dehydration enthalpy of the complex under examination (see Table 4) probably indicates that the H_2O molecule is not coordinated. Moreover, the non-paramagnetic character of this complex is in accordance with a probable square-planar arrangement of the ligands around the central ion Au(III). As an explanation of these facts we would propose a dimeric structure with two atoms as a halogen bridge, whose formula would be $[(AuC^=Cl)_2] \cdot 2 H_2O$; a similar structure with two atoms as halogen bridges has been observed in some dialkylgold halide complexes with the formula $[(AuRX)_2] \cdot 2 H_2O^{22}$. Nonetheless, further research, in which the spectral study of the com-

pound in the far IR range would be involved, is necessary to prove this hypothesis[15, 23].

The [AuECl$_3$] complex is not easily soluble in *DMSO-d$_6$*. Moreover, these solutions are unstable, yielding, after a few minutes, the free ligand. This fact prevented us from obtaining the corresponding ^{1}H-NMR spectrum with sufficient resolution. In spite of this, two facts became clear as a result of the ^{1}H-NMR data obtained: 1) all the signals of the neutral molecule E are present, which indicates that E is to be found in the complex as a neutral molecule; 2) the signal due to C$_4$-NH appears at 11.40 ppm, which leads us to assume that the ligand E is coordinated to the Au(III) ion via the 5-NO group. The fact that E acts as a neutral molecule is not surprising since the complex was obtained in a relatively strong acid medium (*pH* = 2.5).

The most significant feature of the IR spectrum of this complex, as shown in Table 3, are that the $v(C = O)$ stretching vibration is practically unmodified, whereas the $v(N = O)$ band is shifted by 60 cm^{-1} to a lower wavenumber in comparison with its value in the free ligand. In the 650–200 cm^{-1} range the IR spectrum shows two new bands at 345 cm^{-1} and 355 cm^{-1}, which were assigned to the v_{asym} (Au—Cl) stretching vibrations envisaged for neutral complexes of the [Au*LX$_3$*] type[15, 23]. On the other hand, in the 340–200 cm^{-1} range none of the bands predicted for v(Au—N) vibrations in [Au*LX$_3$*] complexes were observed[15], but a new, weak band was observed at 505 cm^{-1}, which could be assigned to a v(Au—O) stretching vibration.

Taking into account all the above data, we would suggest that in the [AuECl$_3$] complex the ligand E is coordinated to the Au(III) ions as a neutral molecule via the N atom of the 5-NO group, as shown in Scheme 5. Finally, the non-paramagnetic character of the complex is in accordance with a square-planar arrangement of the ligands around the central ion Au(III).

Scheme 5
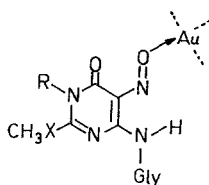
Thermal Studies

The TG and DSC plots of the six compounds obtained are shown in Figs. 1 and 2 respectively. From these figures we obtained the dehydration

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Table 3. *IR*

Compound	v(O—H)	v(N—H)	v(C—H)	v(C=O)
A	3 430 s	3 330 s	2 970 w 2 940 w 2 915 w 2 890 w	1 700 s
B	3 400 m	3 250 m	2 920 w 2 890 w	1 685 s
C	3 460 s	3 310 s	2 940 m 2 905 m	1 685 s
D	3 500–3 300 s	3 500–3 300 s	2 920 w 2 850 w	1 680 m
E	3 420 s	3 200 m	2 960 w 2 930 w 2 895 w 2 870 w	1 675 s
Pd(A⁻)₂·4 H₂O	3 400 s, wi	3 300 s 2 920 w 2 880 w	2 880 s 2 920 w 2 945 w	—
Pd(B⁻)₂·4 H₂O	3 400 s, wi	3 280 s	2 920 w 2 850 w	—
Pd(C⁻)₂·4 H₂O	3 400 s, wi	3 270 s	2 870 w	—
Pd(D⁻)₂·2 H₂O	3 420 s, wi	—	2 920 w 2 840 w	—
Au(C⁼)ClH₂O	3 400 s, wi	—	2 920 w 2 840 w	—
AuECl₃	3 480 m	3 340 m 3 200 m	2 920 w	1 680 s

s: strong, m: medium, w: weak, wi: wide.

and decomposition temperatures, the observed weight losses and the weight losses of the samples calculated on the hypothesis of the formation of either PdO or Au°, as well as the dehydration energies. The corresponding results are summarized in Table 4.

The TG and DSC plots of all the Pd(II) complexes are very alike. The weight losses due to the water of hydration began between 50 °C for [Pd(C⁻)₂]·4 H₂O, and 60 °C for [Pd(A⁻)₂]·4 H₂O, and ended at 135 °C, corresponding to the number of water molecules predicted in the respective formulae. The expected endothermic behaviour for these

spectral data

$\nu(C_4=N)$	$\nu(C=C)$ + $\nu(C=N)$	$\nu(N=O)$	$\nu(M-O)$	$\nu(M-Cl)$	$\nu(M-N)$
—	1 585 s 1 540 m	1 495 m	—	—	—
—	1 580 m 1 555 s	1 480 m	—	—	—
—	1 590 s 1 540 s	1 495 m	—	—	—
—	1 580 s 1 530 m	1 480 m	—	—	—
—	1 570 s 1 550 s	1 540 s	—	—	—
—	1 540–1 570 s	1 460 m	—	—	305 w
—	1 540–1 585 s	1 435 m	—	—	340 w
—	1 540–1 585 s	1 435 m	—	—	320 w
1 675 m	1 520–1 560 s	1 430 m	—	—	360 w
1 695 m	1 520–1 550 s	—	—	345 s 360 s	—
—	1 585 s 1 520 s	1 480 s	505 w	345 s 355 s	—

processes of dehydration was observed in the DSC curves in the same temperature range. The dehydration energy calculated for these effects varied between 47.2 kJ · mol^{-1} (for [Pd(D$^-$)$_2$] · 2 H$_2$O) and 30.0 kJ · mol^{-1} (for [Pd(B$^-$)$_2$] · 4 H$_2$O). The anhydrous compounds were stable up to 230 °C. This temperature is similar to that of the decomposition of the free ligands[24], suggesting that the decomposition of the anhydrous complexes begins with the pyrolysis of the ligands. Weight loss continued without interruption up to approximately 500 °C, at which temperature the weight of the residue in the crucible was in accordance with that calculated for
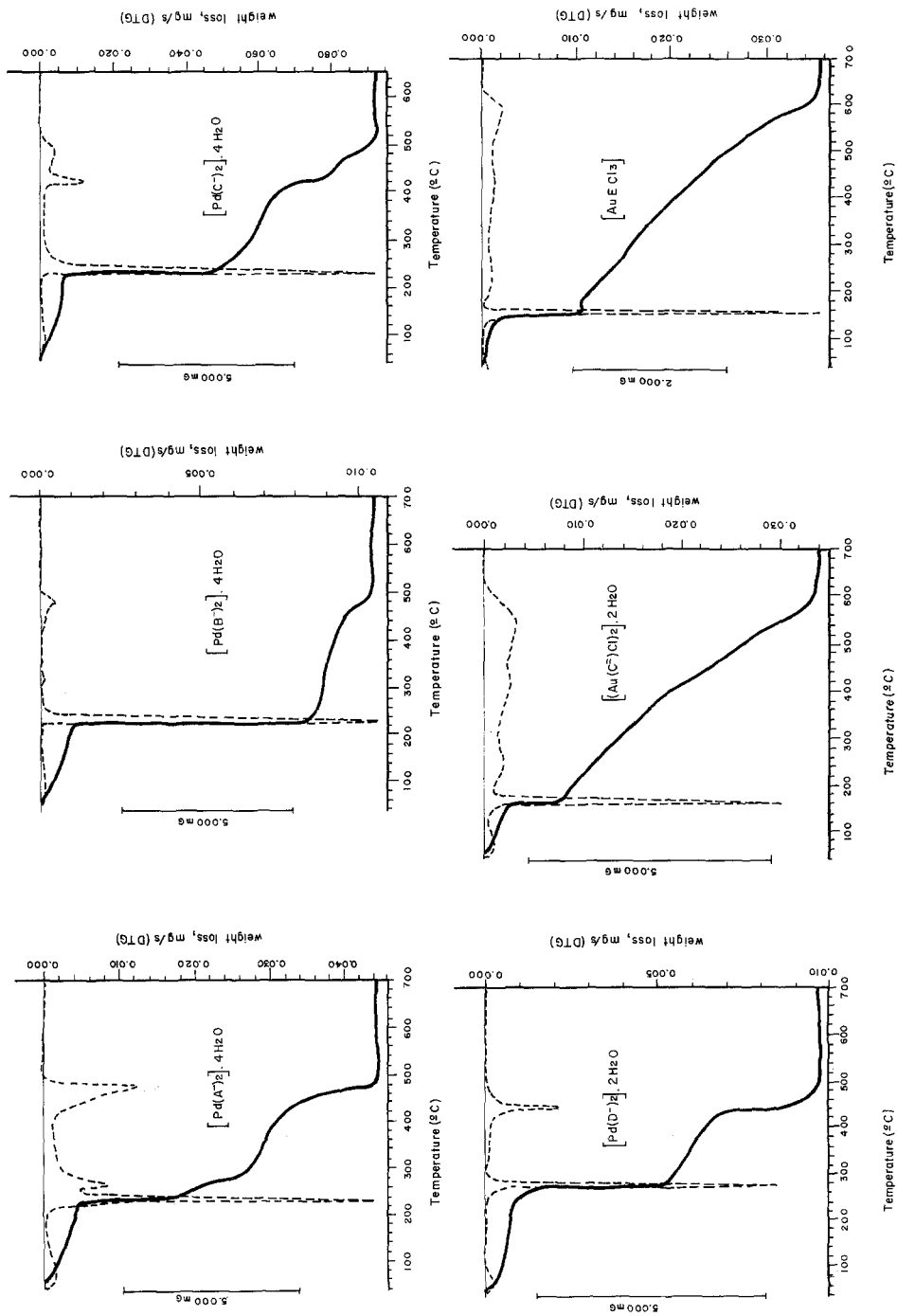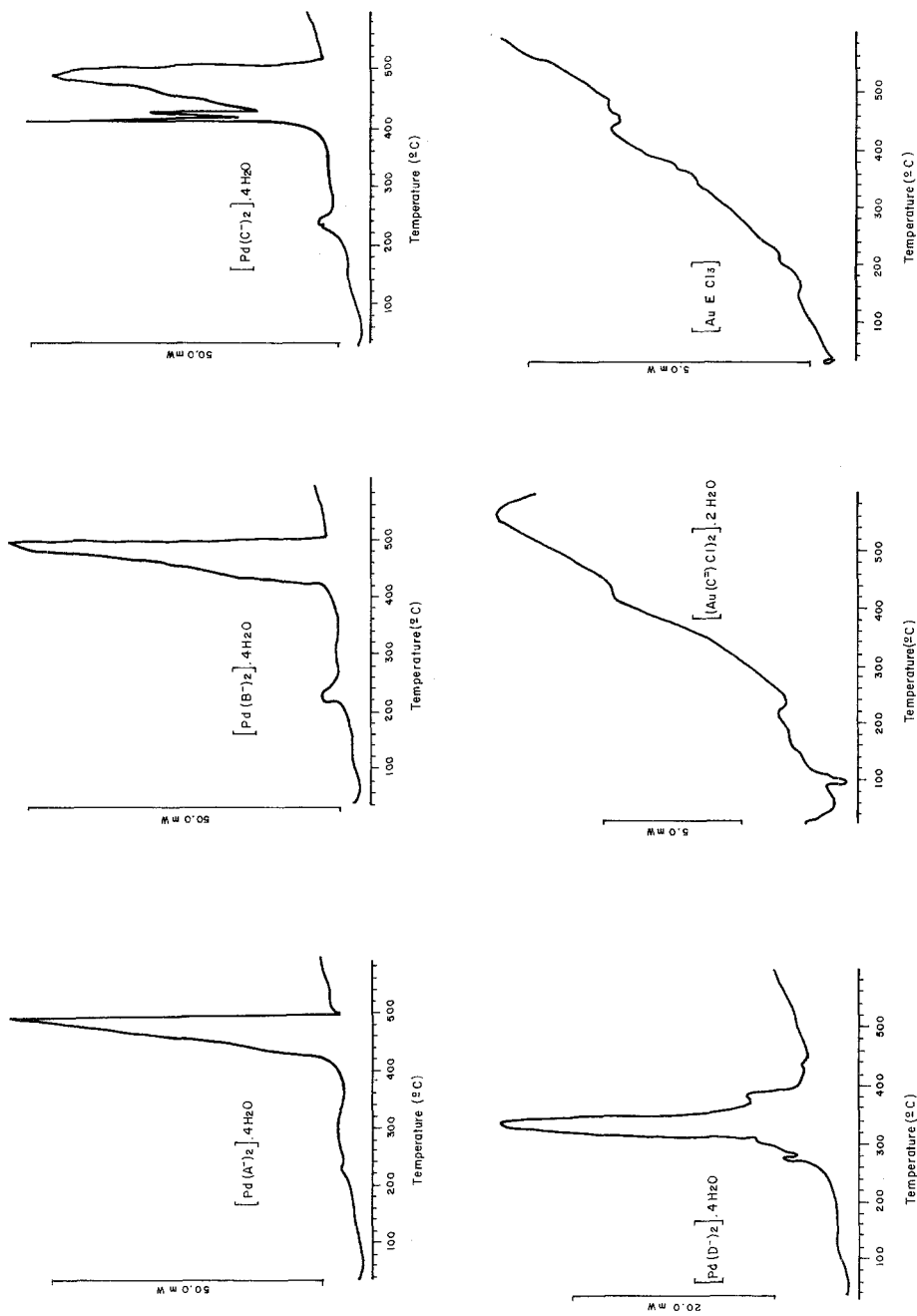
Fig. 1. TG and DTG curves

Fig. 2. DSC curves

Table 4. *TG and DSC data (the analytical data in parentheses are theoretical values)*

Complex	Dehydration			Other effects		Residue	
	T (°C)	Wt loss (%)	ΔH kJ·mol⁻¹	T (°C)	ΔH kJ·mol⁻¹	Wt loss (%)	T (°C)
$Pd(A^-)_2 \cdot 4H_2O$	75	8.4 (8.6)	134.6	230 (exo) (w) 280 (exo) (w) 490 (exo)	— —6 558.2ᵃ	87.7 (85.4)	500
$Pd(B^-)_2 \cdot 4H_2O$	75	8.8 (8.9)	120.2	230 (exo) 310 (exo) (w) 495 (exo)	—251.5 —6 733.2	86.0 (84.9)	520
$Pd(C^-)_2 \cdot 4H_2O$	75	7.6 (7.9)	153.3	238 (exo) 310 (exo) (w) 412 (exo) (w) 440 (exo) (w) 490 (exo)	—470.5 — } —7 190.9	85.5 (85.9)	520
$Pd(D^-)_2 \cdot 2H_2O$	70	4.6 (4.5)	94.4	275 (exo) (w) 305 (exo) (w) 330 (exo) 380 (exo) (w) 440 (exo) (w)	} —6 535.5	81.9 (84.7)	520
$Au(C^=)Cl \cdot H_2O$	100	3.2 (3.0)	24.0	160 (exo) (w) 228 (exo) (w) 412 (exo) 560 (exo)	— — } —2 916.7ᵃ	35.4 (33.0)	620
$AuECl_3$	—	—	—	145 (exo) (w) 210 (exo) (w) 460 (exo)	} —922.2ᵃ	30.0 (29.6)	650

ᵃ Integration of only a half peak has been possible.

PdO, this being confirmed by IR spectroscopy. At 820 °C the reduction of PdO to Pd occurred in accordance with the literature data[25].

The $[(Au(C^=)Cl)_2] \cdot 2\,H_2O$ complex became totally dehydrated in the 80–115 °C range. At this temperature the observed weight loss corresponded to two water molecules per mol of compound. The dehydration enthalpy was $24.0\,kJ \cdot mol^{-1}$, which indicates that the water was probably not coordinated. The pyrolytic decomposition of the remaining anhydrous complex began at 145 °C, a lower temperature than that of the thermal decomposition of the C compound[24]. The complex underwent an initial abrupt weight loss (11.6%) which ceased at 155 °C. The IR spectrum of a sample of the complex obtained after heating to 155 °C did not present the $v(Au—Cl)$ bands, which shows that the pyrolysis begins by dehalogenation. Nonetheless, the weight loss observed was greater than that calculated for total dehalogenation, which indicates that the process overlaps with the probable pyrolysis of the ligand. From a temperature of 155 °C onwards the decomposition of the complex into metallic gold took place in two further stages as can be seen from its ATG curve. The accumulated weight loss at 625 °C was in close agreement with the quantity of metallic gold residue in the crucible. This fact was confirmed by the absence of the $v(Au—O)$ band in the IR spectrum of the said residue.

The DSC curve of the $(AuECl_3)$ complex reveals its anhydrous character. The pyrolytic decomposition of the compound began at 140 °C with an abrupt weight loss which ended at 160 °C. The IR spectrum of a sample of the complex heated to this temperature showed the loss of $v(Au—Cl)$ bands in the same way as in the aforementioned Au(III) complex. In this case also there was a considerable difference between the observed weight loss and that calculated for total dehalogenation (20.1%), which suggests that this process overlaps with the beginning of pyrolysis of the ligand. From 160 °C onwards decomposition continued slowly and was complete at 625 °C, at which temperature the residue in the crucible was metallic gold. The total accumulated weight loss at this temperature was in accordance with the calculated one.

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