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INFRARED AND THERMAL STUDIES OF PLATINUM(II) HALIDE COMPLEXES WITH 1-HEXANAMINE

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ABSTRACT

The complexes *cis*-$PtHea_2X_2$, *trans*-$PtHea_2X_2$, $[PtHea_3X]X$, $[PtHea_3Cl]Cl \cdot Hea$, $[PtHea_4]X_2$ (Hea ≙ 1-hexanamine; X = Cl, Br) have been prepared and characterized in the solid state by elemental analysis, IR spectra and TG, DTG, DTA measurements.

The best methods of preparing pure samples with good yields are discussed. The IR spectra presented are, in several regions, characteristic of geometry and stoichiometry. The thermal analysis data of all the complexes are reported; degradation of the 1:3 and 1:4 derivatives gives *trans*-$PtHea_2X_2$ species as intermediates.

INTRODUCTION

The wide interest given to platinum(II) halide complexes with ammonia and amines (Am) depends mainly on the current use of *cis*-$Pt(NH_3)_2Cl_2$ as an antitumor drug and on the encouraging results obtained on various complexes with amines. Although there have been plenty of studies in this field (see, e.g., recent reviews [1,2]) the meaning of the particular activity of some compounds and the type of biochemical reactions involved are still an unsolved problem. The antitumor properties depend on the configuration of the complexes, the *cis* isomer being generally the active species; therefore, much effort has been expended towards synthesis and activity tests of *cis*- and *trans*-$PtAm_2Cl_2$, in order to determine the influence of small variations in the molecular structure of the ligand on the toxicity and therapeutic index of the drug. The compound *cis*-$PtHea_2Cl_2$ (Hea = 1-hexanamine) has been tested, along with several aliphatic amine complexes, on mice bearing ADJ (PC 6A) [3,4] and S180 [5,6] sarcomas, and its preparation has been reported in several Patents [4]; moreover, both *cis*- and *trans*-$PtHea_2Cl_2$ have been isolated by the reaction of $PtCl_2$ with Hea in dichloromethane [7].

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Particular attention must be paid to the purity of the drug, because biological tests can be strongly affected by traces of secondary products, either present as impurities or formed in recrystallization processes [8–10]; it is then of importance to select reaction conditions, which allow the isolation of one of the isomers [11–13], and to ascertain the role of the solvent, which can react with the compound and can assist isomerization [14–18].

The interest given to platinum(II) amino-derivatives is not limited to the $PtAm_2Cl_2$ isomers, but also concerns the higher stoichiometry complexes. In fact, the quite different activity of *cis* and *trans* species could be due to their different ability to interact with the DNA coordination sites: in this way reactions of *cis*-$Pt(NH_3)_2Cl_2$ with various model molecules (L) to give $[Pt(NH_3)_2LX]^+$ and $[Pt(NH_3)_2L_2]^{2+}$ have been reported [19–24]. A number of aliphatic amines were then taken into account in order to prepare either the 1:2 platinum halide derivatives or the higher stoichiometry complexes with the same amine and with other nitrogen and sulfur donors.

In this paper the preparation of the PtX_2 (X = Cl, Br) complexes with 1-hexanamine and their characterization in the solid state by IR and thermal analysis data are reported.

EXPERIMENTAL

Reagents were PtX_2 (X = Cl, Br; Ventron), K_2PtCl_4 (Fluka), K_2PtBr_4, 1-hexanamine (C. Erba). When not specified otherwise, the reactions were carried out at room temperature.

Preparation of the complexes

$[PtHea_4]X_2$ (X = Cl, Br)

The chloro-derivative was prepared by adding an aqueous solution of Hea (8.7 mmol in 2 ml) to aqueous K_2PtCl_4 (1.45 mmol in 3 ml). The red solution became colourless and a small amount of white solid separated out (*cis*-$PtHea_2Cl_2$ plus an unidentified product by IR); the mixture was then heated until dissolution of the solid and formation of a pale yellow oil which was insoluble in H_2O. The white crystals formed overnight ($\simeq 5°C$) were filtered and kept at room temperature under reduced pressure, in order to eliminate additional Hea and H_2O. In this way hydrated species, containing one or two H_2O molecules (by thermogravimetry), were obtained, which, by gentle heating in vacuo ($\simeq 60°C$), gave the anhydrous product (yield, $\simeq 74\%$). By operating at higher molar ratios (up to 11:1) the yields lowered. $[PtHea_4]Br_2$ was prepared either with the same method (yield, $\simeq 78\%$) or by dissolving $PtBr_2$ in a benzene solution of Hea (molar ratio 1:4) and evaporating the solvent in air (fume hood). The solid, containing generally one water molecule, was dried in vacuo ($\simeq 60°C$).

[PtHea$_3$Cl]Cl

To a suspension of $PtCl_2$ in benzene (3.7 mmol in 5 ml) a benzene solution of Hea (18.5 mmol in 10 ml) was added with stirring. The exothermal reaction gave initially a white solid and a yellow solution; a further 5 ml of benzene were added and after ≃ 30 min only a small amount of unreacted $PtCl_2$ was still present. By evaporating the filtered solution in air a white yellowish solid, identified as $[PtHea_3Cl]Cl \cdot Hea$, was obtained. The additional Hea molecule was eliminated by prolonged heating at ≃ 95°C and subsequent washing with *n*-hexane (yield, 95%); $[PtHea_3Cl]Cl$ could also be prepared by evaporating a benzene solution of $[PtHea_4]Cl_2$. The first product was generally $[PtHea_3Cl]Cl \cdot H_2O$ (by IR and thermal analysis), which easily gave the anhydrous form on gentle heating in vacuo (60°C).

[PtHea$_3$Br]Br

Prepared, as the analogous chloro-derivative, by reacting $PtBr_2$ and Hea in benzene (molar ratio 1 : 3.1). The white solid, obtained after evaporation of the benzene solution in air, was mainly the 1 : 3 complex with traces of the 1 : 4 complex; the latter, slightly soluble in *n*-hexane, was removed by abundant washings with this solvent (yield ≃ 98%). Differing from the 1 : 3 chloro-complex, the bromo-analogue could not be prepared by evaporating a benzene solution of $[PtHea_4]Br_2$; in fact, the last compound showed no tendency to release Hea in benzene.

trans-*PtHea$_2$Cl$_2$*

$[PtHea_3Cl]Cl$, kept under reduced pressure, was gradually heated (oil bath) and its thermal decomposition followed by IR spectrometry. Up to 165°C the solid formed was essentially the 1 : 3 complex, whereas the first melted mixture (170°) also contained *trans*-$PtHea_2Cl_2$ (≃ 20%). The mixture was cooled and ground, then heated to 175°C (mixture richer in *trans*) and, after successive grindings, up to 180°C, obtaining a green liquid containing a small amount of a black solid. The mixture was dissolved in acetone. After separating the black residue, the yellow solution was evaporated obtaining the pure *trans* species (yield, ≃ 90%) which could be recrystallized from benzene/*n*-hexane. Nujol mulls should not be kept between CsI discs, owing to the progressive formation of *trans*-$PtHea_2I_2$.

trans-*PtHea$_2$Br$_2$*

Prepared in a quantitative yield by the thermal decomposition of $[PtHea_3Br]Br$, which melts at about 145°C with the immediate release of Hea. The optimum temperature for obtaining the pure product is ~ 170°C; at ~ 190°C a black solid begins to form. Purification and recrystallization were performed as for the 1 : 2 chloro-derivative.

cis-*PtHea$_2$Cl$_2$*

The exothermal reaction of $PtCl_2$ (2.3 mmol in 3 ml of acetone) with Hea

(4.8 mmol in 4 ml of acetone) gave a white solid, which was kept, with stirring, overnight, then filtered and washed with methanol to remove traces of the 1 : 3 complex (yield, ≃ 52%). The compound can be prepared with a ≃ 42% yield by carrying out the reaction in benzene (molar ratio 1 : 2.2; reaction time, 72 h); in CH_2Cl_2 the yield was lower and the product not pure. A very pure sample was obtained with a scarce yield (≃ 10%) by reaction of K_2PtCl_4 and Hea in H_2O (molar ratio, 1 : 2). The solids obtained with the methods described have identical IR spectra but their melting points are in the range 178–190°C.

cis-$PtHea_2Br_2$

A suspension of $PtBr_2$ in a benzene solution of Hea (molar ratio 1 : 2.1), with stirring (4 days), gave a yellow complex (impure for $PtBr_2$) which was filtered and recrystallized from benzene (yield, ≃ 45%). By the addition of *n*-hexane to the initial benzene solution, crystals of *trans*-$PtHea_2Br_2$, containing traces of the 1 : 3 complex, separated (yield, ≃ 35%). The compound could also be prepared by reacting K_2PtBr_4 and Hea in H_2O (molar ratio 1 : 2; yield, ≃ 54%); after filtration the yellow solid was washed with diethyl ether.

Measurements

The IR spectra were registered by Perkin-Elmer spectrophotometers (Models 580B and 683), as Nujol and Voltalef 10S (Ugine Kuhlmann) mulls between KBr and polythene discs.

The TG, DTG and DTA curves were obtained by the Netzch STA429 thermoanalytical equipment. Tests were performed in a nitrogen atmosphere (flux rate, 250 ml min^{-1}; heating rate, 5°C min^{-1}); some tests were carried out in air flux, to show the influence of oxygen on the thermal processes. In the DTA measurements neutral Al_2O_3 (C. Erba) was used as reference material.

RESULTS AND DISCUSSION

The prepared compounds and their approximate solubilities in various solvents are reported in Table 1. Along with $[PtHea_4]X_2$ (X = Cl, Br), the 1 : 3 adducts have also been isolated, which, by thermal decomposition, give the corresponding *trans*-$PtHea_2X_2$ species in a very high yield. The compounds *cis*-$PtHea_2X_2$, prepared by reaction of PtX_2 and Hea in acetone (X = Cl) and in benzene (X = Br) were obtained with a yield of 40–50%, owing to the simultaneous formation of the *trans* species, which are more soluble in acetone, benzene and dichloromethane than the corresponding *cis* complexes (Table 1). The general insolubility of the complexes in water does

TABLE 1

Analytical data (calculated values in parentheses) and solubilities[a] in various solvents[b]

Compound	Colour	M.p.(°C)	C%	H%	N%	MeOH	EtOH	Acetone	CH_2Cl_2	Benzene
cis-$PtHea_2Cl_2$[c]	yellowish white	186–190	30.80	6.50	5.94	i	sls	sls	sls	i
			(30.77)	(6.46)	(5.98)					
trans-$PtHea_2Cl_2$	bright yellow	121–122	30.80	6.38	5.92	sls[d]	sls[d]	vs	vs	vs
$[PtHea_3Cl]Cl$[e]	white	170–171	37.52	8.19	7.15	sls	sls	i	i	i
			(37.96)	(7.96)	(7.38)					
$[PtHea_4]Cl_2$[f]	white	86–89	43.01	9.20	8.26	s	s	sls	s	vs
			(42.97)	(9.02)	(8.35)					
cis-$PtHea_2Br_2$	pale yellow	159–161[g]	25.83	5.52	5.01	i	i	s	s	s
			(25.86)	(5.42)	(5.03)					
trans-$PtHea_2Br_2$	yellow	115–116	26.12	5.44	5.09	sls	i	vs	vs	vs
$[PtHea_3Br]Br$	white	143–146	32.95	6.98	6.48	s	i	sls	s	sls
			(32.83)	(6.89)	(6.38)					
$[PtHea_4]Br_2$	white	93–96	37.38	7.86	7.35	s	s	s	s	s
			(37.95)	(7.96)	(7.38)					

[a] At room temperature; i, insoluble; s, soluble, sls, slightly soluble; vs, very soluble.

[b] All the complexes are soluble in dimethylsulfoxide; insoluble in *n*-hexane (except for $[PtHea_4]Br_2$, slightly soluble in this solvent) and in water.

[c] Cl%, 15.20 (15.14).

[d] in this solvent, as in *iso*-PrOH, the compound dissolves slightly and the residual solid is white.

[e] Cl%, 12.63 (12.45).

[f] Cl%, 10.51 (10.57).

[g] By fast heating of a fresh crystalline sample; if heating is slow, progressive isomerization to *trans* occurs.

TABLE 2

IR bands in the 3400–3000, 1650–1500 and 550–200 cm^{-1} regions [a]

Compound	3400–3000 cm^{-1}				1650–1500 cm^{-1}		
cis-$PtHea_2Cl_2$		3240sh	3208sbr	3125m		1578s	
trans-$PtHea_2Cl_2$		3245s	3218s	3142m		1587s	
$[PtHea_3Cl]Cl$		3230sh	3178sbr	3100m	1615vw	1580ms	
$[PtHea_3Cl]Cl \cdot Hea$	3320mbr	3230sh	3180sbr	3100m	1635shbr	1580ms	1565sh
$[PtHea_4]Cl_2$		3190sh	3130sh	3080sbr	1612s	1600sh	
cis-$PtHea_2Br_2$	3235sh	3215sh	3199s	3120m		1570s	
trans-$PtHea_2Br_2$		3258m	3220s	3140m		1582s	
$[PtHea_3Br]Br$		3220sh	3182s	3100m		1578s	
$[PtHea_4]Br_2$	≈ 3200sh		3130sh	3080sbr	1615mbr	1590sh	

[a] sh, shoulder, br, broad; s, strong; ms, moderately strong; m, medium; w, weak; vw, very

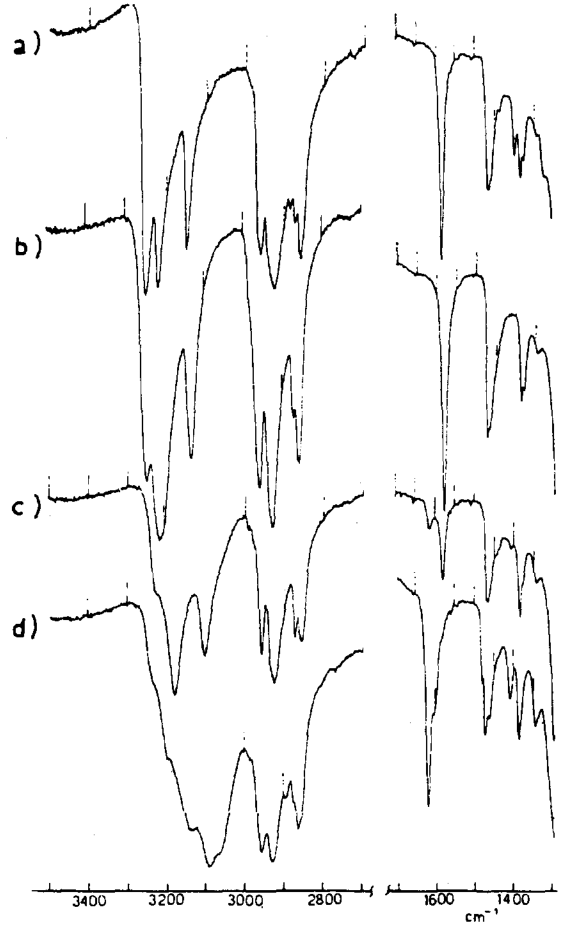

Fig. 1. Infrared spectra: (a) *trans*-$PtHea_2Cl_2$; (b) *cis*-$PtHea_2Cl_2$; (c) $[PtHea_3Cl]Cl$; (d) $[PtHea_4]Cl_2$.

550–200 cm^{-1}									
					345sh	320s		271w	220vwbr
521vw	508vw		445w		348sh	330s		278m	
538vvw	496sh	485w	448vvw	422vvw	348w	≃330sh	300mbr		230wbr
535vw	496vw	487vw	440vw	420vw	348sh	≃330sh	300mbr		230wbr
535w		487vw		425vw	345sh	323mbr	287mbr		220shbr
				407vvw	340vvw	325vvw		268w	220ms
		472w		403vw	339w			268w	228s
535vvw		483w	435vvw	403vvw	340sh	≃320sh	295mbr		230m
	495vvw	470vw		405w	340sh		303mbr		225wbr

weak; vvw, extremely weak. ν(Pt–Hal) are underlined.

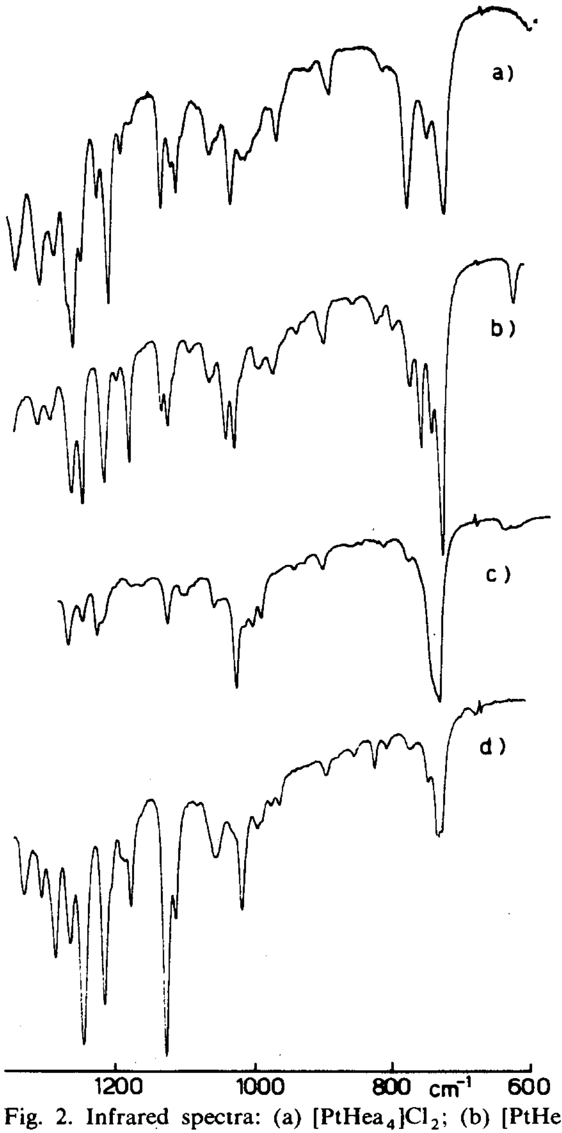

Fig. 2. Infrared spectra: (a) [PtHea$_4$]Cl$_2$; (b) [PtHea$_3$Cl]Cl; (c) *cis*-PtHea$_2$Cl$_2$; (d) *trans*-PtHea$_2$Cl$_2$.

not prevent the study of their biological activity; in fact, long-chain ligands improve liposolubility, which is of great importance in their interactions with membranes. The bromo-derivatives are generally more soluble than the chloro-analogues in organic solvents and a study of their behaviour in solution is now in progress. All the complexes dissolve in DMSO, a coordinating solvent which probably displaces the Hea molecules forming various species, as observed for *cis*-$Pt(NH_3)_2Cl_2$ [17]. The IR spectra (Table 2) allow the characterization of the complexes; in particular, ν(NH) (3300–3000 cm^{-1}) and $\delta(NH_2)$ (1620–1550 cm^{-1}) are indicative of the different stoichiometries, as already observed for the 1 : 2 and 1 : 4 complexes with methanamine [25], ethanamine [26] and propanamine [27]. The spectra of the chloro-derivative series in the above reported regions are presented in Fig. 1. The *trans* species present three well-separated bands beyond 3000 cm^{-1}; the *cis* species show a strong broad absorption (with shoulders) around 3200 cm^{-1} and a medium one around 3120 cm^{-1}. In the $\delta(NH_2)$ region the isomers have a strong peak, whose position depends on the geometry (for

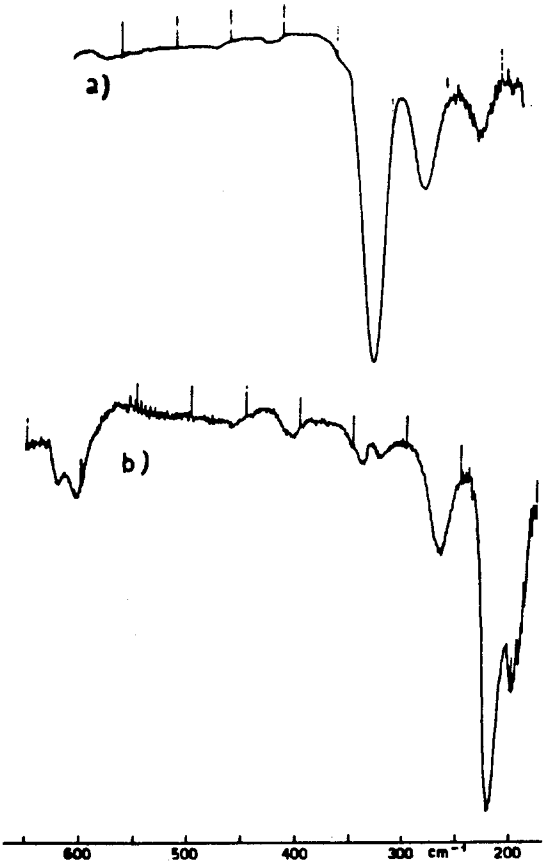

Fig. 3. Far-infrared spectra of *cis*-$PtHea_2X_2$: (a) X = Cl; (b) X = Br.

trans about 11 cm^{-1} above *cis*) and on the halide (shifting to lower frequencies from chloro to bromo species of equal geometry). Both 1 : 3 complexes present a band characteristic of this stoichiometry at about 3180 cm^{-1}, whereas the 1 : 4 species absorption has a maximum at a lower frequency (3080 cm^{-1}). The hydrated 1 : 3 and 1 : 4 complexes show the water absorptions at 3450 and 1630 cm^{-1}; the additional Hea molecule in $[PtHea_3Cl]Cl \cdot Hea$ produces the broad band at 3320 cm^{-1}. The bands of all the compounds in the 3000–2800 cm^{-1} region are due to the stretching of the aliphatic chain C–H bonds. Some bands in the 1200–800 cm^{-1} region (Fig. 2), characteristic of stoichiometry and geometry, whatever the halide is, characterize the side products in syntheses performed by different methods and the species formed in the thermal processes (either decomposition or isomerization). The *trans* isomers present a band at 1120 cm^{-1}, absent in the *cis* species, whose characterizing group of bands is around 1000 cm^{-1}; the 1 : 3 complexes show the sequence 721 s, 740 sh, 750 m, 770 w, the 1 : 4 complexes show two bands of comparable intensity at 721 and 778 cm^{-1}.

In the far IR region the isomers *cis*-$PtHea_2X_2$ show (Fig. 3) broad bands

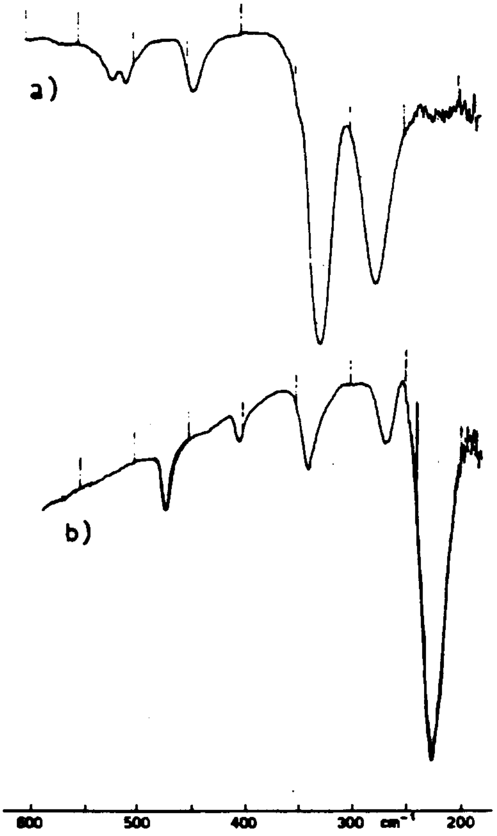

Fig. 4. Far-infrared spectra of *trans*-$PtHea_2X_2$: (a) X = Cl; (b) X = Br.

at 320 cm^{-1} (X = Cl) and 220 cm^{-1} (X = Br) assigned as ν(Pt–X), shifted to higher frequencies (about 10 cm^{-1}) in the corresponding *trans* species; the absorption around 270 cm^{-1} is generally weak, except for *trans*-PtHea$_2$Cl$_2$, which has a band of appreciable intensity at 278 cm^{-1}. The shape of the spectrum (Fig. 4a) could lead to an erroneous assignment of the geometry, if the full series of 1 : 2 complexes is not considered. Both 1 : 3 species present a strong absorption around 300 cm^{-1} (Fig. 5); the [PtHea$_3$Br]Br medium band at 230 cm^{-1} is assigned as ν(Pt–Br). Along with [Pt(NH$_3$)$_3$Cl]Cl [28] a number of complexes containing one chlorine atom in the coordination sphere have been isolated [19,29–32] whose Pt–Cl stretching frequency is in the 320–345 cm^{-1} range. In this zone [PtHea$_3$Cl]Cl presents a weak band at 348 cm^{-1}, common to all the chloro-derivatives, and a shoulder around 330 cm^{-1}, common to the 1 : 3 bromo complex; the ν(Pt–Cl) could be below 320 cm^{-1}, when it would be included in the broad band at 300 cm^{-1}. However, we intend to examine 1 : 3 derivatives of various aliphatic amines to verify an eventual presence of coordinated water, leading to species such as [PtAm$_3$H$_2$O]Cl$_2$. Absorptions assignable to water are absent in the spectrum of the compound under study, except for a weak band at 1615 cm^{-1}.

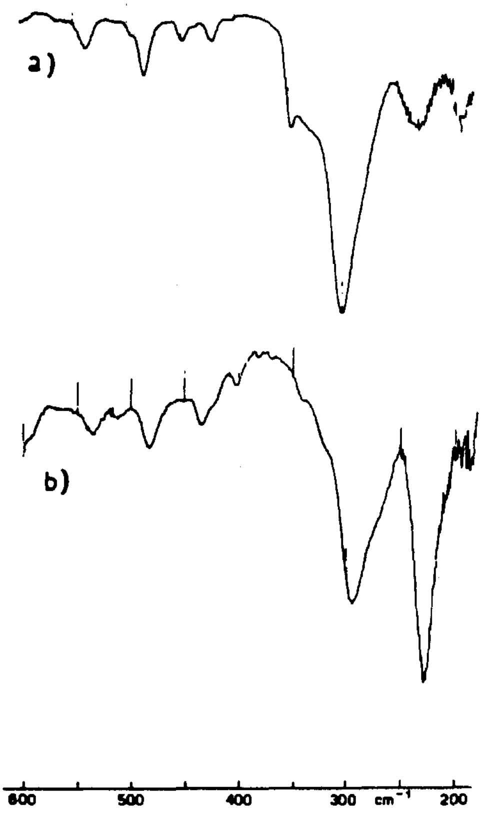

Fig. 5. Far-infrared spectra of [PtHea$_3$X]X: (a) X = Cl; (b) X = Br.

TABLE 3

Thermal data of the complexes (in nitrogen)

Compound	Decomposition interval (°C)	TG weight loss (%)		DTA peak temp. (°C) [a]
		Found	Calcd.	
cis-$PtHea_2Cl_2$	190–320	57.2	58.3 (2 Hea + 2 Cl)	184m, 197ex, 258d, 290d
trans-$PtHea_2Cl_2$	200–320	57.8	58.3 (2 Hea + 2 Cl)	90en, 115ensh, 121m, 217ex, 282d
cis-$PtHea_2Br_2$	210–360	64.7	65.0 (2 Hea + 2 Br)	88en, 158m, 218ex, 306d, 353d
trans-$PtHea_2Br_2$	220–360	64.6	65.0 (2 Hea + 2 Br)	61en, 120m, 225ex, 306d, 338d
$[PtHea_3Cl]Cl$ [b]	150–190	18.8	17.8 (Hea)	47en, 87en, 154end, 181md
	190–320	46.2	48.0 (2 Hea + 2 Cl)	261d, 281d
$[PtHea_3Cl]Cl \cdot Hea$	49–90	15.2	15.1 (Hea)	47en [c], 86en [c], 100d
	130–190	15.8	15.1 (Hea)	185md
	190–320	39.4	40.7 (2 Hea + 2 Cl)	265d, 288 d
$[PtHea_3Br]Br$	150–190	15.9	15.4 (Hea)	123en, 148m, ≈160d, 188ex
	220–360	54.4	55.0 (2 Hea + 2 Br)	245dsh, 334d
$[PtHea_4]Cl_2^b$	140–190	30.6	30.2 (2 Hea)	101m, 183d
	190–320	40.2	40.7 (2 Hea + 2 Cl)	254d, 278d
$[PtHea_4]Br_2^b$	130–190	26.2	26.6 (2 Hea)	52en, 103m, 175d
	190–360	48.1	47.7 (2 Hea + 2 Br)	250dsh, 334d

[a] en, weak endotherm without weight loss; ex, exotherm (see text); m, melting endotherm; d, decomposition endotherm; sh, shoulder. [b] The corresponding hydrates lose H_2O in the 40–80°C region. [c] Weak shoulders of the decomposition endotherm (100°C) relative to the release of the additional Hea molecule.

The thermal decomposition of all the complexes has been studied by means of TG, DTG and DTA (Table 3); when measurements were carried out in a nitrogen atmosphere, the final product was platinum. Thermal degradation of *cis*-$PtHea_2Cl_2$ (Fig. 6) immediately follows the melting process (184°C), whereas *trans*-$PtHea_2Cl_2$ melts at 121°C and begins to decompose around 200°C (Fig. 7); both *cis* and *trans* bromo-derivatives melt without decomposition at 158 and 120°C, respectively, and their degradation starts around 210°C. By heating *cis*-$PtHea_2Br_2$ slightly above its melting point, a slow isomerization to *trans* occurs; in the same conditions *cis*-$PtHea_2Cl_2$ decomposes and only traces of the *trans* species are formed. $[PtHea_3Cl]Cl$ (Fig. 8) shows two close weight-loss steps, it melts at 181°C releasing one Hea molecule with formation of *trans*-$PtHea_2Cl_2$, whose preparation requires a careful temperature control (see Experimental) to avoid massive decomposition. On the contrary $[PtHea_3Br]Br$ easily gives *trans*-$PtHea_2Br_2$ in a quantitative yield; in fact, it melts at 148°C and then releases Hea forming the *trans* species well below its decomposition tempera-

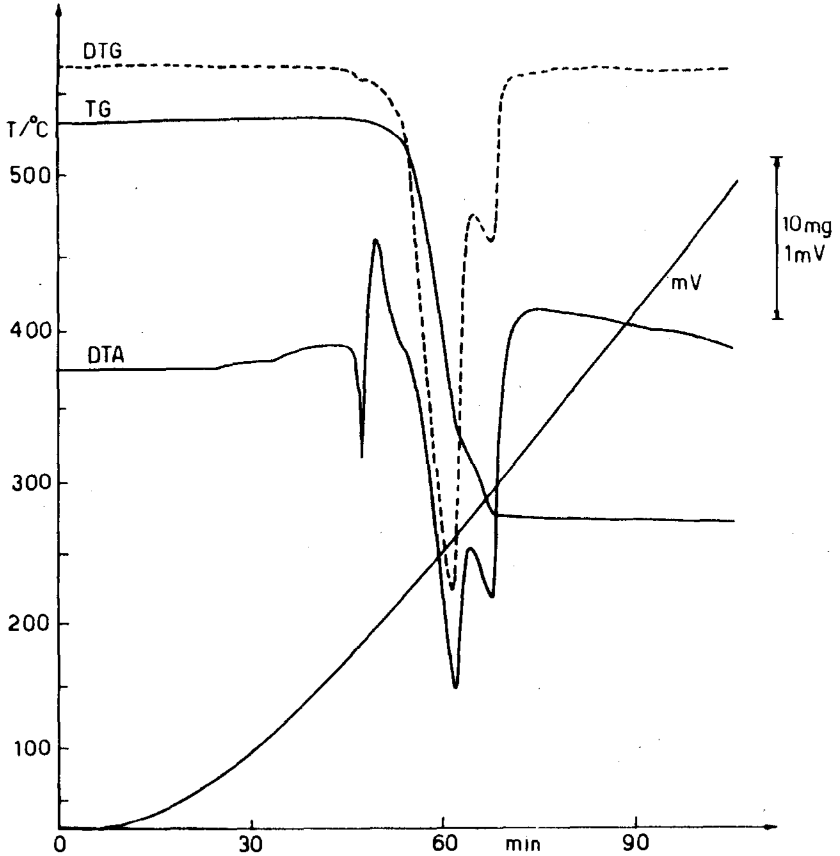

Fig. 6. Thermograms of *cis*-$PtHea_2Cl_2$ (46.00 mg).

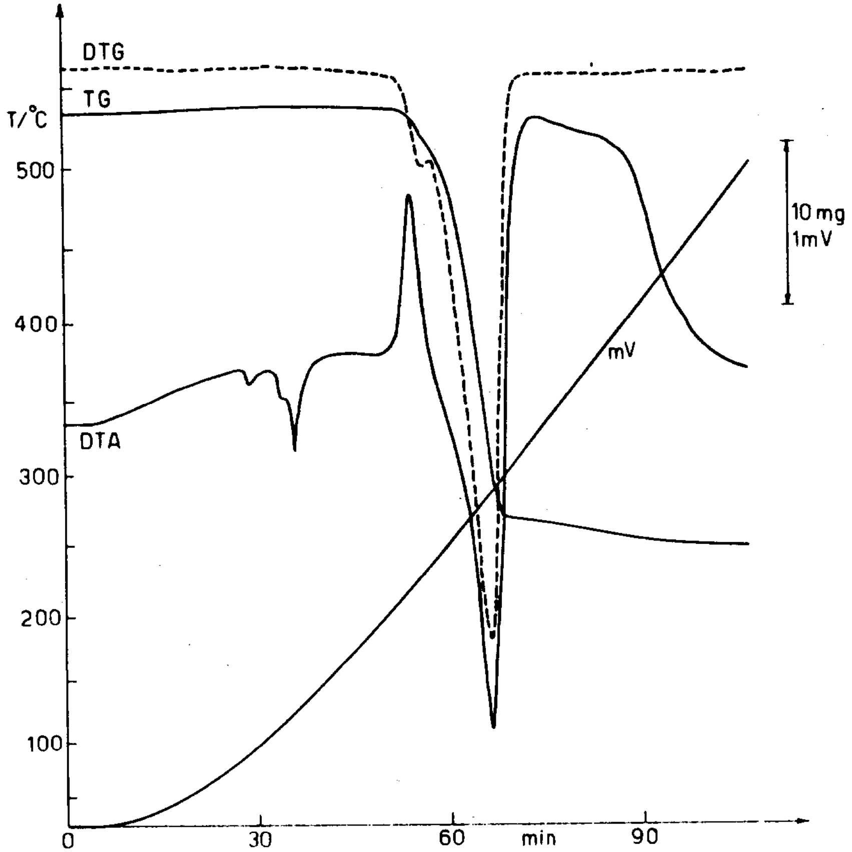

Fig. 7. Thermograms of *trans*-$PtHea_2Cl_2$ (45.25 mg).

ture. The TG curve of $[PtHea_3Cl]Cl \cdot Hea$ presents three steps, the first one (below 110°C) concerning loss of the additional Hea molecule; at higher temperatures all the curves match those of $[PtHea_3Cl]Cl$. The 1 : 4 complexes melt without decomposition at around 100°C with a first step related to the release of two Hea molecules and a second one due to the decomposition of the 1 : 2 intermediates. The main product in samples heated to 180°C is the *trans* isomer, along with an unidentified product and traces of the corresponding 1 : 3 species; the *trans* yields are significantly lower than those of the 1 : 3 thermal degradation. The hydrated 1 : 4 species firstly lose water (40–80°C), as for $[Pt(NH_3)_4]Cl_2$ [33], then their thermograms resemble those of the 1 : 4 species. Perfectly anhydrous samples are obtained by melting the hydrated forms under reduced pressure; they should be stored in nitrogen, owing to a slow water absorption with time. The weak endothermal peaks observed for most compounds below the melting temperature are probably due to rearrangements in the solid state; e.g., $[PtHea_4]Br_2$ presents a weak endotherm at 52°C: if a powdered sample is heated in a capillary tube, formation of transparent needles takes place in the 50–60°C region.

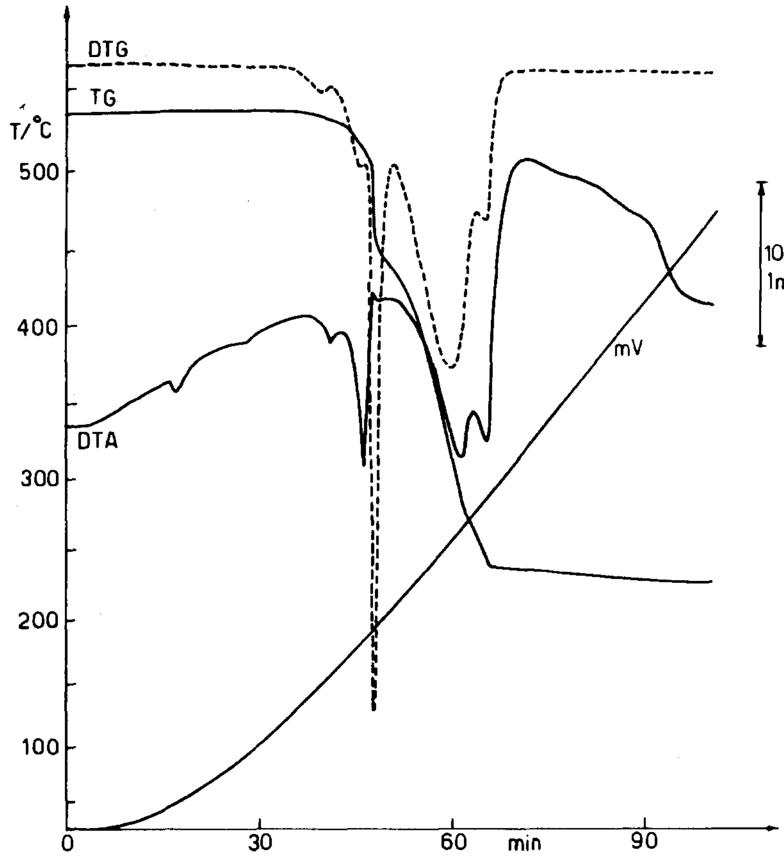

Fig. 8. Thermograms of [PtHea$_3$Cl]Cl (44.32 mg).

When thermal analyses are carried out in an air flow, the decomposition of the 1 : 2 species produces a strong exothermal peak; at lower temperatures the DTA curves are identical to those of tests in nitrogen. The exothermal peaks observed at the beginning of the 1 : 2 species degradation (see Table 3 and Figs. 6 and 7) are then probably due to reaction of the first decomposition products with traces of oxygen left in the furnace; in [PtHea$_3$Cl]Cl and [PtHea$_4$]X$_2$ the endothermal release of ligand, close to the 1 : 2 intermediate decomposition, possibly overcomes the thermal effects of such a reaction.

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