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SPECTROSCOPIC AND THERMAL STUDIES ON PLATINUM(II) IODIDE COMPLEXES WITH PRIMARY AMINES

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ABSTRACT

The complexes *cis*- and *trans*-$[PtL_2I_2]$, $[PtBua_3I]I$ and $[PtL_4]I_2$, where L = butan-1-amine (Bua) or hexan-1-amine (Hea), have been prepared and characterized by elemental analyses, IR and ^1H NMR spectra and TG, DTG, DTA measurements. Thermal degradation of the 1:3 and 1:4 species yields the corresponding *trans* complexes as intermediates. Moreover, the *cis* species isomerize to *trans* without decomposition. In the ^1H NMR spectra of the 1:2 and 1:4 derivatives, the NH_2 proton signal is characteristic of the stoichiometry and geometry, whereas $[PtBua_3I]I$ decomposes in most solvents, releasing one of the ligand molecules to give *trans*-$[PtBua_2I_2]$ solutions.

INTRODUCTION

In the past few years we have reported on various platinum(II) halide complexes with hexan-1-amine (Hea) and propan-1-amine (Pra) having the formulae *cis*- and *trans*-$[PtL_2X_2]$, $[PtL_3X]X$ and $[PtL_4]X_2$ (X = Cl or Br), which were characterized either in the solid state (IR and thermal analysis) or in solution (^1H NMR spectra) [1,2]. We extended the study to the iodo-derivatives [3], due to their use as intermediates in the preparation of drugs for anti-tumour tests [4,5]. When aquo-ion solutions are used in biological tests particular attention must be paid to the purity of the starting platinum iodide amino complexes. In this line, a recent paper reports the preparation of pure *cis*-$[Pt(NH_3)_2I_2]$ through formation of solvates with formamides and its behaviour in aqueous KI and HI solutions [6].

In this paper we report the preparation of the PtI_2 complexes with hexan-1-amine and butan-1-amine (Bua) and their characterization by IR, ^1H NMR and thermal analysis data.

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EXPERIMENTAL

The reagents used were PtI_2 (Johnson Matthey), $K_2[PtCl_4]$ (Fluka), hexan-1-amine (C. Erba) and butan-1-amine (Janssen). The reactions were generally carried out at room temperature.

Preparation of the complexes

trans-*[PtHea₂I₂]*

The complex was prepared by reacting PtI_2 (0.7 mmol) with Hea (1.6 mmol) in benzene (5 cm^3) with stirring (6 h). The resultant yellow solid was filtered, washed with *n*-pentane and dried in vacuo. Further fractions of product were obtained by partial evaporation of the residual benzene solution and subsequent addition of *n*-pentane (yield, 80%). The compound can be recrystallized from benzene/*n*-pentane. The melting point range was 110–112 °C and the experimental composition was: C, 22.2; H, 4.7; N, 4.3% (calculated (for $C_{12}H_{30}I_2N_2Pt$): C, 22.1; H, 4.7; N, 4.3%). It was also prepared in a nearly quantitative yield by stirring (4 h) a PtI_2 (0.5 mmol) suspension in a Et_2O solution of Hea (1.1 mmol in 5 cm^3). The reaction went on in heterogeneous phase, yielding the slightly soluble *trans* isomer. Pure samples were also obtained by evaporation to dryness of carefully filtered acetone solutions of the crude product and by heating $[PtHea_4]I_2$ under reduced pressure (ca. 80 °C).

cis-*[PtHea₂I₂]*

Aqueous KI (3.7 mmol in 2.0 cm^3 of H_2O) was added to an aqueous solution of $K_2[PtCl_4]$ (0.9 mmol in 5 cm^3). The dark red solution was carefully filtered from a yellow undissolved residue. Addition of Hea (1.8 mmol) with vigorous stirring yielded a pinkish solid, which was filtered, washed with H_2O and dried under reduced pressure. The solid, washed with Et_2O, was recrystallized from benzene/*n*-hexane and finally washed with Et_2O (yield, 60%, m.p., 102–103 °C; found: C, 22.1; H, 4.7; N, 4.3%).

[PtHea₄]I₂

PtI_2 (0.5 mmol) was allowed to dissolve in a Et_2O solution of Hea (2.2 mmol in 5 cm^3; 4 h). Slow evaporation of the filtered yellow solution yielded white crystals of the compound, which were washed with *n*-pentane. The compound can be purified by evaporation of solutions in *n*-hexane, in which the complex is slightly soluble (yield, 90%; m.p., 84–85 °C; C, 33.7; H, 7.2; N, 6.6%; calculated (for $C_{24}H_{60}I_2N_4Pt$): C, 33.8; H, 7.1; N, 6.6%).

trans-*[PtBua₂I₂]*

The yellow solution obtained by reacting PtI_2 (0.4 mmol) and Bua (0.8 mmol) in benzene (3 cm^3) was filtered from the small undissolved residue (a mixture of *cis* and 1 : 3 species from IR spectra). The first solid fraction obtained after addition of *n*-hexane was discarded (*cis–trans* mixture). Further addition of *n*-hexane gave the yellow compound. It can be recrystallized from benzene/*n*-hexane (yield, 70%; m.p., 140–142 °C; C, 16.2; H, 3.7; N, 4.7%; calculated (for $C_8H_{22}I_2N_2Pt$): C, 16.1; H, 3.7; N, 4.7%). The compound can be easily obtained by thermal decomposition of the corresponding 1 : 3 and 1 : 4 complexes under reduced pressure (ca. 130 °C).

cis-*[PtBua*$_2$*I*$_2$*]*

Prepared by the method used for *cis*-[PtHea$_2$I$_2$]. The yellow solid was recrystallized from benzene (yield, 60%; m.p., 140–142 °C; C, 16.1; H, 3.7; N, 4.7%).

[PtBua$_3$*I]I*

The reaction of PtI_2 (0.4 mmol) with Bua (1.3 mmol) in Et_2O yielded (6 h, with stirring) a white solid and a yellow solution. The solid, filtered and washed with Et_2O, was [PtBua$_4$]I$_2$ impure for the 1 : 3 complex (by IR spectra). The residual Et_2O solution, kept at ca. − 20 °C, yielded greenish-white crystals of the compound, which were filtered, washed with small fractions of cold Et_2O (in order to eliminate traces of the *trans* species) and finally with *n*-pentane (yield, 50%; C, 21.7; H, 5.1; N, 6.3%; calculated (for $C_{12}H_{33}I_2N_3Pt$): C, 21.6; H, 5.0; N, 6.3%).

[PtBua$_4$*]I*$_2$

A suspension of PtI_2 (0.6 mmol) in a Et_2O solution of Bua (2.9 mmol in 5 cm^3) yielded, overnight with stirring, a white solid, which was filtered and washed with Et_2O and *n*-pentane. It was recrystallized from benzene/*n*-pentane (yield, 80%; m.p., 127–129 °C; C, 26.0; H, 6.1; N, 7.5%; calculated (for $C_{16}H_{44}I_2N_4Pt$): C, 25.9; H, 6.0; N, 7.6%).

Measurements

The IR spectra were recorded by using either a Perkin Elmer 580B spectrophotometer (4000–400 cm^{-1}) or a Bruker FT IR instrument (450–100 cm^{-1}) as Nujol mulls between KBr and polyethylene discs. The ^{1}H NMR spectra were obtained using a Jeol FX 90 Q spectrometer. The TG, DTG, and DTA curves in dinitrogen (flux rate, 250 cm^3 min^{-1}; heating rate, 5 °C min^{-1}) were recorded on a Netzsch STA 429 thermoanalytical instrument (reference material, neutral Al_2O_3).

RESULTS AND DISCUSSION

The compounds (Table 1) were generally prepared in organic media by reaction of platinum iodide and amine in the appropriate molar ratio, except

TABLE 1

Solubilities [a] and infrared frequencies in the 3500–3000 cm^{-1} and 1650–1500 cm^{-1} regions

Compound	Solubility					Frequency (cm^{-1})	
	MeOH	C_6H_6	Me_2CO	Et_2O	CH_2Cl_2	ν(NH)	$\delta(NH_2)$
trans-$[PtHea_2I_2]$	~ i	vs	vs	sls	vs	3243(s), 3208(s), 3130(m)	1578(s)
cis-$[PtHea_2I_2]$	s	vs	vs	~ i	vs	3228(sh), 3203(sbr), 3118(w)	1565(s)
$[PtHea_4]I_2$	sls	s	s	s	s	3190(sh), 3130(sh), 3075(sbr)	1608(wbr), 1590(sh)
trans-$[PtBua_2I_2]$	s	vs	vs	s	vs	3248(m), 3212(s), 3132(m)	1578(s)
cis-$[PtBua_2I_2]$	sls	sls	vs	i	s	3230(sh), 3202(sbr), 3115(w)	1565(s)
$[PtBua_3I]I$	s	s	vs	sls	vs	3205(sh), 3180(sbr), 3110(m)	1574(s)
$[PtBua_4]I_2$	vs	s	vs	i	vs	3200(sh), 3140(sbr), 3080(sbr)	1610(wbr), 1590(sh)

[a] At room temperature: i, insoluble; s, soluble, sls, slightly soluble; vs, very soluble. The complexes are insoluble in H_2O (except for $[PtBua_4]I_2$, sls) and in *n*-hexane (except for $[PtHea_4]I_2$, sls). All the complexes are soluble in DMSO and in DMF.

for *cis* derivatives, which were prepared by reaction of $[PtI_4]^{2-}$ and amine in water. The *trans* isomers were also obtained by thermal decomposition of the higher stoichiometry derivatives and by thermal isomerization of the parent *cis* species. Owing to their solubility in organic solvents (Table 1) the complexes can be easily purified, except for $[PtBua_3I]I$, which generally releases one ligand molecule, yielding yellow solutions of *trans*-$[PtBua_2I_2]$. Since the process is slow in diethylether, the compound has been prepared in this solvent by reaction of platinum iodide and Bua (molar ratio 1 : 3.1) and stored at about 5 °C. In analogous conditions, the 1 : 3 Hea derivative was isolated in a low yield and impure form for $[PtHea_4]I_2$. Attempts to recrystallize $[PtHea_3I]I$ were unsuccessful, owing to its easy decomposition and to its solubility, very close to that of the parent 1 : 4 complex.

The trend of the infrared absorptions in the $\nu(NH)$ and $\delta(NH_2)$ regions (Table 1) is strictly related to stoichiometry and geometry and, apart for small halide-dependent shifts, it is very close to that of the chloro- and bromo-derivatives [1]. The *trans* species show, beyond 3000 cm^{-1}, three sharp absorptions, whereas the *cis* species and $[PtBua_3I]I$ present a strong, broad band at 3200 cm^{-1} and 3180 cm^{-1}, respectively. Owing to the presence of strong hydrogen bonds with iodides, the 1 : 4 complex absorptions are at lower energy (ca. 3100 cm^{-1}), the corresponding bending mode bands being at 1610 cm^{-1}. The halide-dependent $\delta(NH_2)$ absorptions shift in the *trans*-$[PtHea_2X_2]$ series from 1587 ($X = Cl$) to 1582 cm^{-1} ($X = Br$) and 1578 cm^{-1} ($X = I$) and in the analogous *cis* series from 1578 ($X = Cl$) to 1570 cm^{-1} ($X = Br$) and 1565 cm^{-1} ($X = I$). A similar behaviour was observed for the parent platinum halide complexes with Pra. The platinum–iodine stretching frequencies (Table 2) are as expected. The *cis* isomers present a strong band at ca. 177 cm^{-1}, shifted to higher frequencies in the *trans* isomers (191 cm^{-1}). The compound $[PtBua_3I]I$ exhibits, together with $\nu(Pt\text{–}I)$ at 188 cm^{-1}, a strong absorption at 278 cm^{-1}, common to the 1 : 4 species (289 cm^{-1}), probably to be assigned to Pt–N stretching [7–10].

The thermal analysis data are summarized in Table 3. The *trans* species melt without decomposition (Hea, 115 °C; Bua, 143 °C) and their degradation starts at ca. 190 °C. The thermograms of *cis*-$[PtBua_2I_2]$ (Fig. 1) clearly show the isomerization exotherm at 122 °C, followed by the melting endotherm of the *trans* species, as observed for *cis*-$[PtPra_2I_2]$ (isomerization exotherm 125 °C; melting exotherm, 203 °C). The isomerization process starts in *cis*-$[PtHea_2I_2]$ (Fig. 2) at 90 °C, then melting of the *cis–trans* mixture takes place (100 °C) followed by further isomerization in the melt (107 °C). At higher temperatures the thermograms coincide with those of the *trans* derivatives, as for the 1 : 4 complexes after releasing of two ligand molecules. The thermal behaviour of $[PtBua_3I]I$ differs from that of $[PtPra_3I]I$, which releases one ligand molecule in a single step (109 °C) to give *trans*-$[PtPra_2I_2]$. As is shown in Fig. 3, the release of the first ligand

TABLE 2

Infrared frequencies (450–100 cm^{-1}; ν(Pt–I) are underlined) and ^{1}H NMR data in $CDCl_3$ (ppm; T, ca. 25 ° C)

Compound	Infrared frequency (cm^{-1})	NMR chemical shift (ppm)		
		NH_2[a,b]	αCH_2[b]	βCH_2
trans-[$PtHea_2I_2$]	403(vw), 339(w), 267(mw), 224(vw), $\underline{191}$(s), 88(w)	3.25	2.9	1.4[c]
cis-[$PtHea_2I_2$]	401(vw), 327(vw), 254(vw), $\underline{178}$(m)	4.35	2.9	1.7
[$PtHea_4$]I_2	405(vw), 342(vw), 289(sbr), $\underline{225}$(wbr), 135(wbr)	5.65	2.7	1.85
trans-[$PtBua_2I_2$]	346(w), 265(mw), $\underline{191}$(s), 89(w)	3.25	2.9	1.4[c]
cis-[$PtBua_2I_2$]	331(vw), 253(vw), $\underline{176}$(m)	4.35	2.9	1.65
[$PtBua_3I$]I	443(vw), 433(vw), 278(sbr), 228(vw), $\underline{188}$(m)	5.6w–3.2[d]	2.7–2.9	
[$PtBua_4$]I_2	455(wbr), 430(vw), 347(w), 289(sbr), 180(wv)	5.65	2.7	1.80

[a] Coupling with ^{195}Pt (J ca. 60 Hz) is observed.

[b] Broad signals.

[c] Superimposed on the signals of the other CH_2 groups.

[d] The solution, initially colourless, turns to yellow in 5 min, owing to formation of the *trans* species.

TABLE 3

Thermal data of the complexes (in dinitrogen)

Compound	Decomposition interval (° C)	TG weight loss (%)		DTA peak temperature (° C) [a]
		Experimental	Calculated	
trans-[PtHea$_2$I$_2$]	195–370	68.6	70.0 (2Hea + 2I)	115(m), 220(ex), 345(d)
cis-[PtHea$_2$I$_2$]	185–370	68.7	70.0(2Hea + 2I)	95(iso), 100(m), 107(iso), 222(ex), 345(d)
[PtHea$_4$]I$_2$	80–190	23.6	23.7(2Hea)	95(m), 137(d)
	190–370	52.4	53.4(2Hea + 2I)	225(ex), 345(d)
trans-[PtBua$_2$I$_2$]	190–370	66.8	67.2(2Bua + 2I)	143(m), 216(ex), 345(d)
cis-[PtBua$_2$I$_2$]	190–370	66.4	67.2(2Bua + 2I)	122(iso), 143(m), 216(ex), 345(d)
[PtBua$_3$I]I	55–140	11.0	10.9(1Bua)	90(d), 135(shd), 143(m)
	180–370	59.2	59.9(2Bua + 2I)	216(ex), 345(d)
[PtBua$_4$]I$_2$	95–145	19.7	19.7(2Bua)	134(d), 143(m)
	175–370	52.8	54.0(2Bua + 2I)	216(ex), 345(d)

[a] ex, exotherm; m, melting endotherm; d, decomposition endotherm; iso, isomerization exotherm.

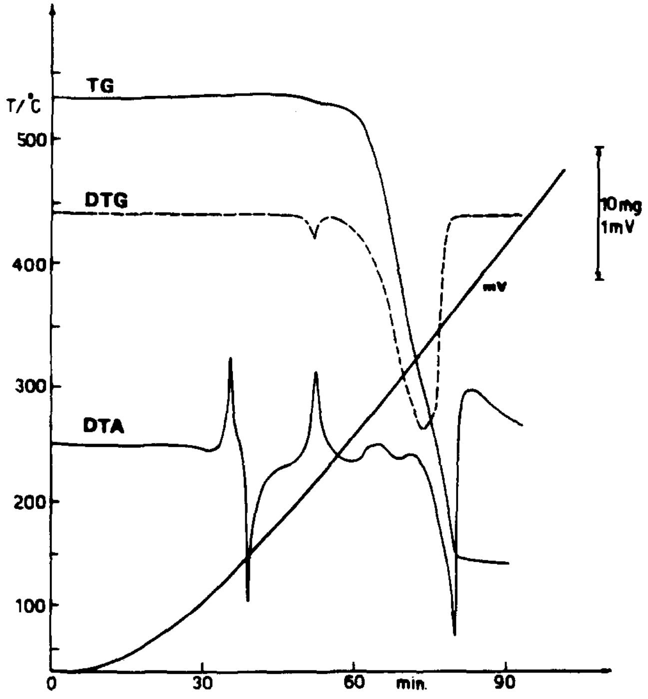

Fig. 1. Thermograms of *cis*-[PtBua$_2$I$_2$] (56.42 mg).

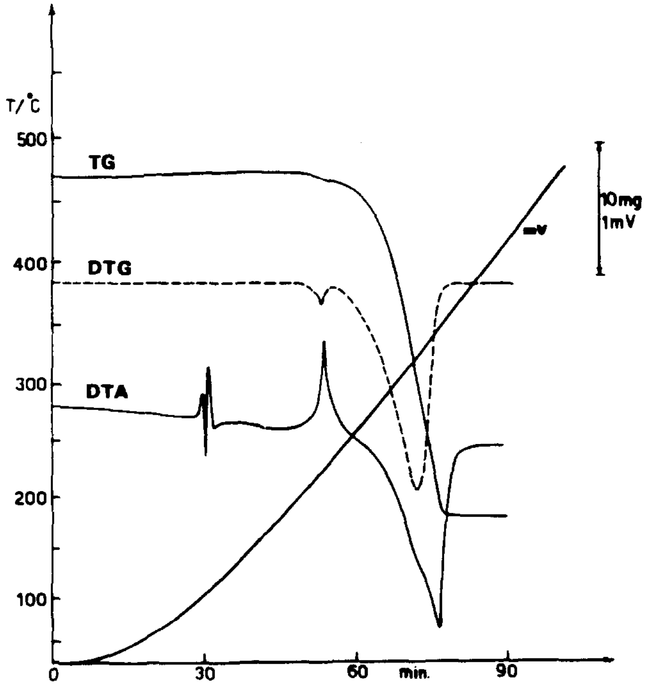

Fig. 2. Thermograms of *cis*-[PtHea$_2$I$_2$] (39.04 mg).

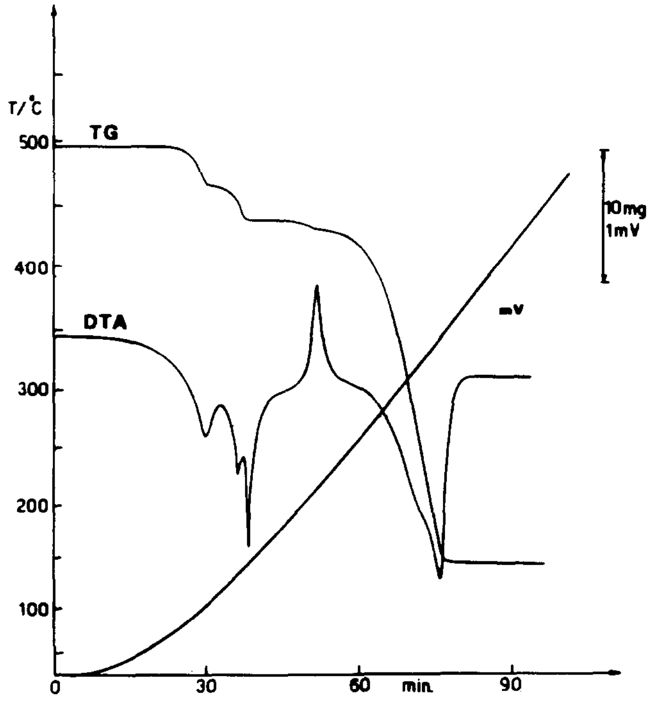

Fig. 3. Thermograms of $[PtBua_3I]I$ (45.54 mg).

molecule takes place in two steps, the related DTA peaks being at 90 ° C and 135 ° C. IR and ^1H NMR spectra of $[PtBua_3I]I$ samples heated up to 90 ° C are in accordance with the formation of *trans*-$[PtBua_2I_2]$ and, in part, of $[PtBua_4]I_2$. Both species are absent in the starting product, whose IR spectrum shows an absorption minimum below 3100 cm^{-1}, where the 1 : 4 complex absorbs strongly. The relative intensity of the steps depends on the amount of substance in the crucible. If a few milligrams are used, the second step is minimized.

The ^1H NMR data in deuterated chloroform are reported in Table 2. Whereas the αCH_2 and βCH_2 resonances are quite close for all complexes, the NH_2 proton signal is affected by stoichiometry and geometry (Fig. 4). For the *trans* species it is observed upfield (3.25 ppm) with respect to the corresponding signal in the *cis* isomer (4.35 ppm), allowing the detection of *cis* to *trans* isomerization processes in solution. The NH_2 resonances of the 1 : 4 complexes are downfield with respect to those of the 1 : 2 complexes, as observed previously for analogous halides. The ^1H NMR spectrum of a solution of $[PtBua_3I]I$ is initially similar to those of the chloro- and bromo-homologues and presents two NH_2 signals, due to the different environment of the ligand molecules in the square planar $[PtBua_3I]^+$ moiety. In a short time the solution turns from colourless to yellow and the downfield signal

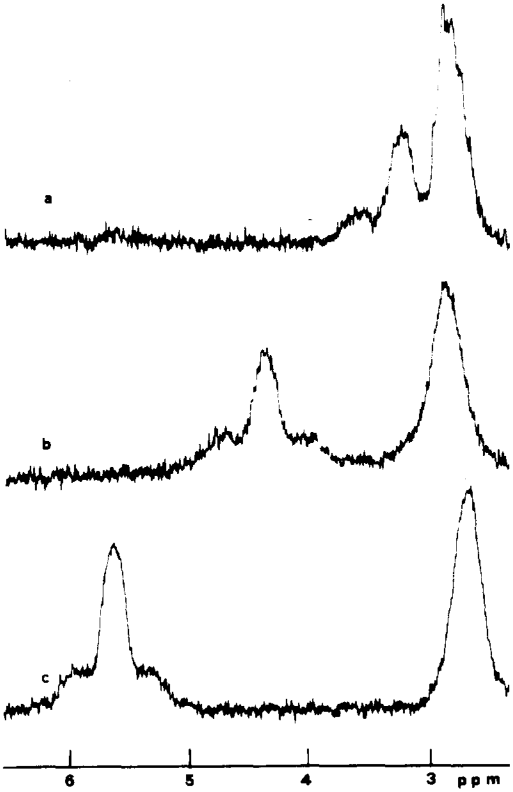

Fig. 4. ^1H NMR spectra in $CDCl_3$: a, *trans*-$[PtHea_2I_2]$; b, *cis*-$[PtHea_2I_2]$; c, $[PtHea_4]I_2$.

decreases progressively, the final spectrum coinciding with that of *trans*-$[PtBua_2I_2]$. In conclusion, either the *cis* species or $[PtBua_3I]I$ present a low stability in solution. Among the complex series prepared, the bromo-derivatives seem to be the more useful intermediates in the preparation of aquo-ion solutions and compounds of biochemical interest, owing to the easy purification and the solubility and stability characteristic.

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