

Multinuclear NMR study and crystal structures of complexes of the types *cis*- and *trans*-Pt(amine)₂I₂

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Abstract

Complexes of the types *cis*- and *trans*-Pt(amine)₂I₂ were studied by spectroscopic methods, especially by multinuclear NMR spectroscopy. In ¹⁹⁵Pt NMR, the *cis* diiodo compounds with primary amines were observed between –3342 and –3357 ppm in acetone, while the *trans* compounds were found between –3336 and –3372 ppm. For the secondary amines, the chemical shifts were observed at lower fields. In ¹H NMR, the *trans* complexes were observed at higher fields than the *cis* compounds, while in ¹³C NMR, the reverse was observed. The ²J(¹⁹⁵Pt–¹H) and ³J(¹⁹⁵Pt–¹H) coupling constants are larger for the *cis* compounds (ave. 67 and 45 Hz, respectively) than for the *trans* isomers (ave. 59 and 38 Hz). In ¹³C NMR, the values of ²J(¹⁹⁵Pt–¹³C) and ³J(¹⁹⁵Pt–¹³C) were also found to be larger for the *cis* complexes (ave. 17 and 39 Hz versus 11 and 28 Hz). There seems to be a slight dependence of the pK_a values of the protonated amines or the proton affinity in the gas phase with the δ(Pt) chemical shifts. The crystal structures of eight diiodo complexes were determined. These compounds are *cis*-Pt(CH₃NH₂)₂I₂, *cis*-Pt(*n*-C₄H₉NH₂)₂I₂, *cis*-Pt(Et₂NH)₂I₂, *trans*-Pt(*n*-C₃H₇NH₂)₂I₂, *trans*-Pt(*iso*-C₃H₇NH₂)₂I₂, *trans*-Pt(*n*-C₄H₉NH₂)₂I₂, *trans*-Pt(*t*-C₄H₉NH₂)₂I₂ and *trans*-Pt(Me₂NH)₂I₂. The Pt–N bond distances located in *trans* position to the iodo ligands were compared to those located in *trans* position to the amines. The Pt–N bond in *cis*-Pt(Et₂NH)₂I₂ are much longer than the others, probably caused by the steric hindrance of the two very bulky ligands located in *cis* positions.

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1. Introduction

The anti-tumor complex *cisplatin*, *cis*-Pt(NH₃)₂Cl₂, has been known for several decades. Its chemistry has been studied by many authors. The compound is now one of the most widely used anti-cancer drug. A good review of the influence of structure on the activity of Pt drugs has been published [1]. It has been observed that when NH₃ is replaced by primary amines, the anti-tumor activity can sometimes increase, especially for cyclic amines [2–5], but these compounds have generally a more limited activity spectrum. Furthermore, some of the most active complexes with amines are too insoluble to be useful anti-cancer drugs [6].

Several earlier studies on the mechanism of action of *cisplatin* have been reported [7–11]. Most of the early work postulated that the main species present in the cells were the aqua-hydroxo species. More recently, House and co-workers [12–20] have published a series of papers on the hydrolysis of *cisplatin* in different chloride concentrations. They calculated, with various rate constants, the proportion of the different species inside the cells and in the plasma. At pH 7.4 and [Cl[–]] = 0.1 M (concentration in the plasma), the main species are *cis*-Pt(NH₃)₂Cl₂ (68%), *cis*-Pt(NH₃)₂(OH)Cl (24%) and *cis*-[Pt(NH₃)₂(H₂O)Cl]⁺ (7%). At [Cl[–]] = 0.004 M (concentration inside the cell), the main species are *cis*-Pt(NH₃)₂Cl₂ (31%), *cis*-Pt(NH₃)₂(OH)Cl (32%), *cis*-[Pt(NH₃)₂(H₂O)Cl]⁺ (28%) and *cis*-[Pt(NH₃)₂(H₂O)(OH)]⁺ (7%). The method used by these authors to detect the different species did not permit the observation of oligomeric species, which are

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known to exist. Indeed, it has been shown, mainly by ^{195}Pt NMR and crystallographic methods, that at neutral pH, several hydroxo-bridged oligomers are formed [21–27]. Some of these species have been found to be toxic for humans and may be partly responsible for the toxicity of *cisplatin* [28,29]. Therefore, it seems important to study the hydrolysis reactions of the Pt complexes at neutral pH, prior to the development of new anti-tumor agents.

The objective of this project was to study the hydrolysis reactions of the complexes *cis* and *trans* diamine Pt(II) complexes, which will be the subject of a subsequent paper. The starting materials are usually the dihalo complexes, which have been known for a long time and most of them have been characterized mainly by IR spectroscopy. A few dichloro and diiodo diamine complexes have also been characterized by NMR techniques (mainly ^1H), in DMF or DMSO [30–36], solvents which are known to react with these complexes.

In this paper, we report a systematic and detailed study of the multinuclear (^1H , ^{13}C and ^{195}Pt) NMR spectra of the complexes *cis*- and *trans*-Pt(amine) $_2\text{I}_2$ in acetone- d_6 (the compounds decompose in CDCl_3), a solvent which is relatively inert. Complexes with different amines were studied. Amines cannot accept electron density from the metal. Therefore, the σ bonds should cause a deshielding effect on the ligand and a shielding effect on the metal. The strength of the σ bond should be related to the $\text{p}K_a$ value of the protonated ligand or the proton affinity of the ligand, although few of the latter values have been reported in the literature. We also report in this paper, the crystal structures of eight diiodo complexes in an attempt to gain information on the nature of the Pt–amine bond and on the relative *trans* influence of the ligands. The results were compared to those obtained recently on similar dipyridine complexes [37,38].

2. Experimental

$\text{K}_2[\text{PtCl}_4]$ was obtained from Johnson Matthey and was recrystallized in water before use. The amines were bought from Aldrich. CD_3COCD_3 and 1.101DMF- d_7 were purchased from CDN Isotopes.

The infrared spectra were measured from 4000 to 280 cm^{-1} as KBr pellets using a Perkin–Elmer 783 grating spectrometer. The decomposition points were measured on a Fisher–Johns instrument and are not corrected. The NMR spectra were measured on a Varian Gemini 300BB in CD_3COCD_3 . For comparison purposes, a few spectra were repeated in DMF- d_6 . The fields were 300.075, 75.462 and 64.311 MHz, respectively, for ^1H , ^{13}C and ^{195}Pt . The acetone peak was used as an internal standard for ^1H (2.04 ppm) and ^{13}C (29.8 ppm). The external reference used for ^{195}Pt was $\text{K}[\text{Pt}(\text{DMSO})\text{Cl}_3]$ (in D_2O), adjusted at -2998 ppm from $\text{K}_2[\text{PtCl}_6]$ ($\delta(\text{Pt}) = 0$ ppm).

2.1. Crystallographic measurements and structure resolution

The crystals were selected after examination under a polarizing microscope for homogeneity. The unit cell parameters were obtained by least-squares refinement of the angles 2θ , ω and χ for well-centered reflections on a Siemens P4 diffractometer using graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data collections were done at room temperature using the XSCANS program [39]. The background time to scan time ratio was 0.5. The crystal data and the experimental details are listed in Tables 1 and 2. All the calculations were done using the SHELXTL system [39]. The coordinates of the Pt atoms were determined from Patterson map calculations or by direct methods and the positions of all the other non-hydrogen atoms were found by the usual Fourier methods. The refinement of the structures was done on F_o^2 using all the reflections. The H atoms were fixed at their calculated positions (riding model) with $U_{\text{eq}} = 1.2$ (or 1.5 for methyl groups) $\times U_{\text{eq}}$ of the C atom to which they are bonded. The intensity data were corrected for absorption (Gaussian integration for crystals **I** and **VII** and semi-empirical for the others) and for the effects of Lorentz and polarization. In *cis*-Pt(*n*BuNH $_2$) $_2\text{I}_2$ (**II**) one butyl chain is disordered while in *trans*-Pt(*t*BuNH $_2$) $_2\text{I}_2$ (**VII**) there are two positions for all the terminal CH $_3$ groups. The refinement of the scale factor, coordinates and anisotropic temperature factors of all the non-hydrogen atoms converged to the R_1 and wR_2 values shown in Tables 1 and 2. The most intense residual peaks were found in the close environment of the Pt atom.

2.2. Synthesis

2.2.1. *cis*-Pt(amine) $_2\text{I}_2$

These complexes were synthesized by a modified version of Dhara's method [40]. An excess of amine (Pt:amine = 4.6) was used and added very slowly. The mixture was stirred for 6–8 h. The precipitate was filtered, washed with water and ethanol and dried. For the amine *t*BuNH $_2$, the *cis* compound does not form. A brown compound, probably the iodo-bridged dimer was obtained. For Et $_2$ NH, a brown product was also formed and ^{195}Pt NMR has shown the presence of the iodo-bridged dimers (70%) and another compound, which was assumed to be *cis*-Pt(Et $_2$ NH) $_2\text{I}_2$ (30%).

cis-Pt(MeNH $_2$) $_2\text{I}_2$: Yield = 86%, m.p. = 138–203 °C (dec). IR (cm^{-1}): $\nu(\text{N–H})$ 3265s, 3195s, 3115w, $\nu(\text{C–H})$ 2963s, 2925m, $\delta(\text{N–H})$ 1580s, 1565s, $\delta(\text{C–H})$ 1475s, 1453m, 1396s, 1380s, $\nu(\text{C–N})$ 1280s, 1195s, 1170s, $\nu(\text{Pt–N})$ 470w, 420m, other bands: 1338m, 1025m, 925w, 880m, 740m, 355m. NMR (δ (ppm)): ^1H : NH 4.459s+d, $^2J(^{195}\text{Pt–NH}) = 69$ Hz, H_1 2.628t+dt, $^3J = 6.3$ Hz, $^3J(^{195}\text{Pt–H}_1) = 49$ Hz, ^{13}C : C_1 33.792, $^2J(^{195}\text{Pt–C}_1) = 21$ Hz.

Table 1
Crystallographic data for crystals I–IV

Crystal	I	II	III	IV
Name	<i>cis</i> -Pt(MeNH ₂) ₂ I ₂	<i>cis</i> -Pt(<i>n</i> BuNH ₂) ₂ I ₂	<i>cis</i> -Pt(Et ₂ NH) ₂ I ₂	<i>trans</i> -Pt(<i>n</i> PrNH ₂) ₂ I ₂
Chemical formula	C ₂ H ₁₀ I ₂ N ₂ Pt	C ₈ H ₂₂ I ₂ N ₂ Pt	C ₈ H ₂₂ I ₂ N ₂ Pt	C ₆ H ₁₈ I ₂ N ₂ Pt
Molecular weight	511.01	595.17	595.17	567.11
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> <i>c</i> (No. 7)
<i>a</i> (Å)	6.928(2)	24.477(5)	9.060(3)	8.958(3)
<i>b</i> (Å)	8.021(3)	8.979(2)	13.151(4)	7.748(2)
<i>c</i> (Å)	16.236(5)	24.232(5)	13.024(4)	9.571(2)
β (°)	99.02(2)	114.468(10)	105.62(3)	90.16(2)
Volume (Å ³)	891.0(5)	4847(2)	1494.5(8)	664.3(3)
<i>Z</i>	4	12	4	2
ρ_{calc} (g cm ⁻³)	3.809	2.447	2.645	2.835
$\mu(\text{Mo K}\alpha)$ (cm ⁻¹)	22.594	12.478	13.491	15.168
<i>F</i> (000)	880	3216	1072	504
Measured reflections	1888	14 526	13 390	7544
Independent reflections (<i>R</i> _{int})	1742 (0.0442)	3802 (0.1044)	3426 (0.0640)	3906 (0.0851)
Observed reflections (<i>I</i> > 2 σ (<i>I</i>))	1291	2271	2802	3207
<i>R</i> ₁ (<i>F</i> > 2 σ (<i>I</i>))	0.0399	0.0699	0.0542	0.0440
<i>wR</i> ₂ (all data)	0.1144	0.1816	0.1304	0.1187
<i>S</i>	1.056	1.072	1.083	1.067

$$R_1 = \sum(|F_o - F_c|)/|F_o|, wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}.$$

Table 2
Crystallographic data for crystals V–VIII

Crystal	V	VI	VII	VIII
Name	<i>trans</i> -Pt(<i>iso</i> PrNH ₂) ₂ I ₂	<i>trans</i> -Pt(<i>n</i> BuNH ₂) ₂ I ₂	<i>trans</i> -Pt(<i>t</i> BuNH ₂) ₂ I ₂	<i>trans</i> -Pt(Me ₂ NH) ₂ I ₂
Chemical formula	C ₆ H ₁₈ I ₂ N ₂ Pt	C ₈ H ₂₂ I ₂ N ₂ Pt	C ₈ H ₂₂ I ₂ N ₂ Pt	C ₄ H ₁₄ I ₂ N ₂ Pt
Molecular weight	567.11	595.17	595.17	539.06
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	11.805(2)	10.346(3)	8.841(3)	8.2029(13)
<i>b</i> (Å)	12.312(2)	16.092(4)	9.131(2)	7.0033(9)
<i>c</i> (Å)	9.252(2)	9.903(3)	19.785(5)	10.2556(14)
β (°)	98.72(2)	110.26(2)	97.16(2)	112.329(11)
Volume (Å ³)	1329.1(4)	1546.7(8)	1584.6(7)	544.98(13)
<i>Z</i>	4	4	4	2
ρ_{calc} (g cm ⁻³)	2.834	2.556	2.495	3.285
$\mu(\text{Mo K}\alpha)$ (cm ⁻¹)	15.162	13.035	12.723	18.479
<i>F</i> (000)	1008	1072	1072	472
Measured reflections	9243	13859	14106	4085
Independent reflections (<i>R</i> _{int})	3532 (0.0587)	3548 (0.1057)	3645 (0.0399)	1071 (0.0465)
Observed reflections (<i>I</i> > 2 σ (<i>I</i>))	2592	2743	3009	1017
<i>R</i> ₁ (<i>F</i> > 2 σ (<i>I</i>))	0.0407	0.0417	0.0307	0.0283
<i>wR</i> ₂ (all data)	0.0917	0.0925	0.0653	0.0698
<i>S</i>	1.052	1.044	1.054	1.058

$$R_1 = \sum(|F_o - F_c|)/|F_o|, wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}.$$

cis-Pt(EtNH₂)₂I₂: Yield = 82%, m.p. = 130–196 °C (dec.). IR (cm⁻¹): ν (N–H) 3200s, 3150w, ν (C–H) 2900m, 2870m, 2830m, δ (N–H) 1580w, δ (C–H) 1465s, 1420m, 1395m, ν (C–N) 1270s, 1220m, 1135m, 1080s, ν (Pt–N) 495w, 450w, other bands: 1015s, 895s. NMR (δ (ppm)): ¹H: NH 4.455s+d, ²*J*(¹⁹⁵Pt–NH) = 68 Hz, H₁ 3.022tq, ³*J* = 7.5 Hz, 6.9 Hz, H₂ 1.270t, ³*J* = 7.2 Hz, ¹³C: C₁ 42.747, ²*J*(¹⁹⁵Pt–C₁) = 18 Hz, C₂ 16.823, ³*J*(¹⁹⁵Pt–C₂) = 48 Hz.

cis-Pt(*n*PrNH₂)₂I₂: Yield = 88%, m.p. = 129–192 °C (dec.). IR (cm⁻¹): ν (N–H) 3240m, 3200s, 3120m, ν (C–H)

2950s, 2920m, 2840m, δ (N–H) 1565s, δ (C–H) 1460m, 1440m, 1385w, ν (C–N) 1205m, 1095m, other bands: 1320w, 1045m, 980m, 945m, 885w, 748w, 700m, 645w, 560w. NMR (δ (ppm)): ¹H: NH 4.462s+d, ²*J*(¹⁹⁵Pt–NH) = 68 Hz, H₁ 2.935tt, ³*J* = 7.5, 7.2 Hz, H₂ 1.711tq, ³*J* = 7.5, 7.2 Hz, H₃ 0.930t, ³*J* = 7.2 Hz, ¹³C: C₁ 49.683, ²*J*(¹⁹⁵Pt–C₁) = 17 Hz, C₂ 25.156, ³*J*(¹⁹⁵Pt–C₂) = 45 Hz, C₃ 11.222.

cis-Pt(*n*BuNH₂)₂I₂: Yield = 91%, m.p. = 117–169 °C (dec.). IR (cm⁻¹): ν (N–H) 3245s, 3210s, 3110w, ν (C–H) 2965s, 2920w, 2890w, δ (N–H) 1586s, 1577s, 1568s,

$\delta(\text{C-H})$ 1455m, 1396m, 1380m, $\nu(\text{C-N})$ 1225s, 1205s, 1085s, 1065s, $\nu(\text{Pt-N})$ 485w, other bands: 1365m, 1035s, 885w, 805w, 725m, 680w, 565w, 385w. NMR (δ (ppm)): ^1H : NH 4.443s+d, $^2J(^{195}\text{Pt-NH}) = 65$ Hz, H_1 2.978tt, $^3J = 7.5, 7.2$ Hz, $^3J(^{195}\text{Pt-H}_1) = 43$ Hz, H_2 1.682tt, $^3J = 7.5, 6.9$ Hz, H_3 1.380tq, $^3J = 7.5, 7.2$ Hz, H_4 0.908t, $^3J = 7.2$ Hz, ^{13}C : C_1 47.679, $^2J(^{195}\text{Pt-C}_1) = 18$ Hz, C_2 34.050, $^3J(^{195}\text{Pt-C}_2) = 43$ Hz, C_3 20.344, C_4 13.970.

cis-Pt(*iso*PrNH₂)₂I₂: Yield = 83%, m.p. = 142–177 °C (dec.). IR (cm⁻¹): $\nu(\text{N-H})$ 3200m, 3115s, 3080s, $\nu(\text{C-H})$ 2950s, 2925m, 2880m, $\delta(\text{N-H})$ 1590m, 1575s, $\delta(\text{C-H})$ 1460m, 1390s, 1375s, $\nu(\text{C-N})$ 1275m, 1255s, after 1155s 1120s, 1075s, $\nu(\text{Pt-N})$ 450m, other bands: 1340m, 940m, 830m, 795s, 780m, 600m, 395w. NMR (δ (ppm)): ^1H : NH 4.383s+d, $^2J(^{195}\text{Pt-NH}) = 66$ Hz, H_1 3.553thept, $^3J = 7.2, 6.9$ Hz, H_2 1.356d, $^3J = 6.9$ Hz, ^{13}C : C_1 49.774, $^2J(^{195}\text{Pt-C}_1) = 13$ Hz, C_2 23.987, $^3J(^{195}\text{Pt-C}_2) = 30$ Hz.

cis-Pt(*iso*BuNH₂)₂I₂: Yield = 87%, m.p. = 119–142 °C (dec.). IR (cm⁻¹): $\nu(\text{N-H})$ 3250s, 3210s, 3110m, $\nu(\text{C-H})$ 2955s, 2865m, $\delta(\text{N-H})$ 1565s, $\delta(\text{C-H})$ 1470s, 1390m, 1370m, $\nu(\text{C-N})$ 1200s, 1170m, 1120s, 1080w, $\nu(\text{Pt-N})$ 450w, other bands: 1315w, 1005s, 945m, 890w, 825w, 715s, 590m, 395w, 370w. NMR (δ (ppm)): ^1H : NH 4.425s+d, $^2J(^{195}\text{Pt-NH}) = 66$ Hz, H_1 2.823dt, $^3J = 7.2, 6.9$ Hz, H_2 1.930thept, $^3J = 6.9, 6.6$ Hz, H_3 0.965d, $^3J = 6.6$ Hz, ^{13}C : C_1 55.405, $^2J(^{195}\text{Pt-C}_1) = 18$ Hz, C_2 hidden by the solvent, C_3 20.162.

cis-Pt(*sec*BuNH₂)₂I₂: Yield = 76%, m.p. = 110–141 °C (dec.). IR (cm⁻¹): $\nu(\text{N-H})$ 3240m, 3195s, 3120m, $\nu(\text{C-H})$ 2960s, 2930m, 2870m, $\delta(\text{N-H})$ 1570s, $\delta(\text{C-H})$ 1465s, 1385m, 1365m, $\nu(\text{C-N})$ 1230m, 1140w, 1115s, 1065w, $\nu(\text{Pt-N})$ 430w, other bands: 1030w, 965w, 895w, 815w, 775w, 725w, 598w. NMR (δ (ppm)): ^1H : NH 4.369s+d, $^2J(^{195}\text{Pt-NH}) = 67$ Hz, H_1 3.309ttq, $^3J = 7.2, 6.9, 6.6$ Hz, H_2 1.493dq, $^3J = 6.9, 6.6$ Hz, H_2' 1.370d, $^3J = 6.3$ Hz, H_3 0.938t, $^3J = 7.2$ Hz, ^{13}C : C_1 55.132 and 55.071, C_2 31.257 and 31.090, $^3J(^{195}\text{Pt-C}_2) = 32$ and 32 Hz, C_2' 20.830 and 20.693, $^3J(^{195}\text{Pt-C}_2') = 25$ and 23 Hz, C_3 10.646.

cis-Pt(Me₂NH)₂I₂: Yield = 92%, m.p. = 132–158 °C (dec.). IR (cm⁻¹): $\nu(\text{N-H})$ 3180s, $\nu(\text{C-H})$ 2900m, 2870s, 2830s, $\delta(\text{C-H})$ 1460s, 1455s, 1430m, 1390m, $\nu(\text{C-N})$ 2830m, 1105s, 1065m, $\nu(\text{Pt-N})$ 495m, 465m, other bands: 1005s, 885s. NMR (δ (ppm)): ^1H : NH 4.920s+d, $^2J(^{195}\text{Pt-NH}) = 70$ Hz, H_1 2.793d+dd, $^3J = 5.7$ Hz, $^3J(^{195}\text{Pt-H}_1) = 43$ Hz, ^{13}C : C_1 43.870, $^2J(^{195}\text{Pt-C}_1) = 14$ Hz.

cis-Pt(Et₂NH)₂I₂: This compound was not obtained pure. The product of the reaction contained 70% of the iodo-bridged dimers. NMR (δ (ppm)): ^1H : NH 4.604s+d, $^2J(^{195}\text{Pt-NH}) = 68$ Hz, H_1 3.119tq, $^3J = 7.2, 6.9$ Hz, H_2 1.358t, $^3J = 6.9$ Hz, ^{13}C : C_1 50.487, $^2J(^{195}\text{Pt-C}_1) = 13$ Hz, C_2 14.683, $^3J(^{195}\text{Pt-C}_2) = 34$ Hz.

2.2.2. *trans*-Pt(amine)₂I₂

These compounds were synthesized from the tetra-substituted compounds [Pt(amine)₄]I₂ similarly to

Kauffman's method [41], except for Et₂NH and *t*BuNH₂. A large excess of amine (amine:Pt = 20) was added very slowly to K₂[PtI₄] and the yellow mixture was stirred for several days until a colorless solution was obtained. With a few ligands, slight heating was necessary. The solution was concentrated until a white precipitate was observed. The latter was filtered and washed with very cold water and dried. The compound [Pt(amine)₄]I₂ was suspended in ethanol and the mixture was heated (40–50 °C) with stirring until a dark yellow solution was obtained. The solution was filtered and the filtrate was left in air several hours to concentrate until crystallization was complete. The precipitate was filtered, recrystallized in ethanol, washed with water and then with cold ethanol and finally dried. For the ligands Me₂NH and *sec*BuNH₂, the *trans* complexes were isolated by concentration in air of the colorless aqueous solutions.

trans-Pt(MeNH₂)₂I₂: Yield = 76%, m.p. = 175–218 °C (dec.). IR (cm⁻¹): $\nu(\text{N-H})$ 3240s, 3205s, 3125m, $\nu(\text{C-H})$ 2955s, 2920m, 2870m, $\delta(\text{N-H})$ 1575s, $\delta(\text{C-H})$ 1452m, 1390m, 1375m, $\nu(\text{C-N})$ 1275m, 1238s, 1215s, 1145w, 1115s, 1075m, $\nu(\text{Pt-N})$ 465w, other bands: 1325m, 1030m, 965w, 900w, 825w, 770w, 605w, 345w. NMR (δ (ppm)): ^1H : NH 3.920s+d, $^2J(^{195}\text{Pt-NH}) = 61$ Hz, H_1 2.468t+dd, $^3J = 6.3$ Hz, $^3J(^{195}\text{Pt-H}_1) = 35$ Hz, ^{13}C : C_1 34.733, $^2J(^{195}\text{Pt-C}_1) = 15$ Hz.

trans-Pt(EtNH₂)₂I₂: Yield = 69%, m.p. = 188–217 °C (dec.). IR (cm⁻¹): $\nu(\text{N-H})$ 3235s, 3190s, 3110m, $\nu(\text{C-H})$ 2965s, 2925m, 2860w, $\delta(\text{N-H})$ 1563s, $\delta(\text{C-H})$ 1460m, 1386m, 1375m, 1368m, $\nu(\text{C-N})$ 1230m, 1155s, 1100s, 1055m, $\nu(\text{Pt-N})$ 433w, other bands: 932m, 805m, 735m, 595w, 385w. NMR (δ (ppm)): ^1H : NH 3.951s+d, $^2J(^{195}\text{Pt-NH}) = 58$ Hz, H_1 2.842tq, $^3J = 7.2, 6.9$ Hz, H_2 1.200t, $^3J = 7.2$ Hz, ^{13}C : C_1 43.748, $^2J(^{195}\text{Pt-C}_1) = 12$ Hz, C_2 16.929, $^3J(^{195}\text{Pt-C}_2) = 36$ Hz.

trans-Pt(*n*PrNH₂)₂I₂: Yield = 58%, m.p. = 185–209 °C (dec.). IR (cm⁻¹): $\nu(\text{N-H})$ 3240m, 3210s, 3125m, $\nu(\text{C-H})$ 2960s, 2920m, 2860w, $\delta(\text{N-H})$ 1573s, $\delta(\text{C-H})$ 1465m, 1450m, 1375w, $\nu(\text{C-N})$ 1218s, 1195w, 1095m, other bands: 1315m, 1050m, 1008m, 965w, 600w, 405w. NMR (δ (ppm)): ^1H : NH 3.931s+d, $^2J(^{195}\text{Pt-NH}) = 59$ Hz, H_1 2.765tt, $^3J = 7.5, 6.9$ Hz, H_2 1.649tq, $^3J = 7.5, 7.2$ Hz, H_3 0.912t, $^3J = 7.2$ Hz, ^{13}C : C_1 50.700, $^2J(^{195}\text{Pt-C}_1) = 10$ Hz, C_2 25.004, $^3J(^{195}\text{Pt-C}_2) = 36$ Hz, C_3 11.253.

trans-Pt(*n*BuNH₂)₂I₂: Yield = 61%, m.p. = 131–176 °C (dec.). IR (cm⁻¹): $\nu(\text{N-H})$ 3200s, 3120s, 3060s, $\nu(\text{C-H})$ 2945s, 2920s, 2860m, $\delta(\text{N-H})$ 1568s, 1550s, $\delta(\text{C-H})$ 1413s, 1405m, $\nu(\text{C-N})$ 1235w, 1210m, 1110m, 1065m, $\nu(\text{Pt-N})$ 445w, other bands: 1322m, 1020w, 972m, 945w, 890w, 732m, 710m, 597w. NMR (δ (ppm)): ^1H : NH 3.910s+d, $^2J(^{195}\text{Pt-NH}) = 58$ Hz, H_1 2.805tt, $^3J = 7.5, 6.9$ Hz, H_2 1.621tt, $^3J = 7.5, 7.2$ Hz, H_3 1.367tq, $^3J = 7.5, 7.2$ Hz, H_4 0.902t, $^3J = 7.2$ Hz, ^{13}C : C_1 48.575, $^2J(^{195}\text{Pt-C}_1) = 12$ Hz, C_2 33.837, $^3J(^{195}\text{Pt-C}_2) = 34$ Hz, C_3 20.284, C_4 13.939.

trans-Pt(*iso*PrNH₂)₂I₂: Yield = 82%, m.p. = 220–233 °C (dec.). IR (cm⁻¹): ν(N–H) 3240m, 3200s, 3100m, ν(C–H) 2960s, 2930m, 2830w, δ(N–H) 1582s, 1565s, δ(C–H) 1465m, 1390m, 1366m, ν(C–N) 1232s, 1153m, 1095m, 1065m, ν(Pt–N) 435m, other bands: 1040w, 930m, 860w, 805m, 755w, 590w, 385w. NMR (δ (ppm)): ¹H: NH 3.896s+d, ²J(¹⁹⁵Pt–NH) = 60 Hz, H₁ 3.415tsept, ³J = 7.2, 6.6 Hz, H₂ 1.282d, ³J = 6.6 Hz, ¹³C: C₁ 51.428, ²J(¹⁹⁵Pt–C₁) = 11 Hz, C₂ 24.412, ³J(¹⁹⁵Pt–C₂) = 22 Hz.

trans-Pt(*iso*BuNH₂)₂I₂: Yield = 74%, m.p. = 123–144 °C (dec.). IR (cm⁻¹): ν(N–H) 3260s, 3225m, 3120w, ν(C–H) 2960s, 2950m, 2870m, δ(N–H) 1577s, δ(C–H) 1475m, 1465m, 1390m, 1370m, ν(C–N): 1212w, 1200s, 1167m, 1120s, 1080w, ν(Pt–N) 445w, other bands: 1335m, 1307m, 1015s, 808w, 600w, 395w. NMR (δ (ppm)): ¹H: NH 3.862s+d, ²J(¹⁹⁵Pt–NH) = 59 Hz, H₁ 2.633dt, ³J = 7.5, 6.9 Hz, H₂ 1.928tsept, ³J = 6.9, 6.6 Hz, H₃ 0.931d, ³J = 6.6 Hz, ¹³C: C₁ 56.376, ²J(¹⁹⁵Pt–C₁) = 14 Hz, C₂-hidden by the solvent, C₃ 20.071.

trans-Pt(*sec*BuNH₂)₂I₂: Yield = 74%, m.p. = 132–148 °C (dec.). IR (cm⁻¹): ν(N–H) 3240s, 3200s, 3165m, ν(C–H) 2955s, 2930m, 2870w, δ(N–H) 1575s, δ(C–H) 1455s, 1378w, ν(C–N) 1275w, 1235s, 1215s, 1150w, 1115s, 1070m, ν(Pt–N) 465w, other bands: 1325w, 1030m, 960w, 900w, 770w, 600w. NMR (δ (ppm)): ¹H: NH 3.908 and 3.828, H₁ 3.214ttq, ³J = 7.2, 6.6, 6.3 Hz and 3.206ttq, ³J = 7.2, 6.6, 6.3 Hz, H₂ 1.448dq, ³J = 7.5, 7.2 Hz and 1.451dq, ³J = 7.2, 6.9 Hz, H_{2'} 1.288d, ³J = 6.6 Hz, H₃ 0.929t, ³J = 7.2 Hz, ¹³C: C₁ 56.665, ²J(¹⁹⁵Pt–C₁) = 10 Hz, C₂ 31.029, ³J(¹⁹⁵Pt–C₂) = 28 Hz, C_{2'} 21.270, ³J(¹⁹⁵Pt–C_{2'}) = 21 Hz, C₃ 10.281.

trans-Pt(Me₂NH)₂I₂: Yield = 80%, m.p. = 194–211 °C (dec.). IR (cm⁻¹): ν(N–H) 3170s, 3075s, ν(C–H) 2980m, 2910m, δ(N–H) 1570s, δ(C–H) 1445s, 1415m, ν(C–N) 1273s, 1255s, 1080s, 1065s, ν(Pt–N) 475m, other bands: 1325w, 1035s, 1010s, 980s, 775s, 755m, 730s, 695w. NMR (δ (ppm)): ¹H: NH 4.439s+d, ²J(¹⁹⁵Pt–NH) = 62 Hz, H₁ 2.630d+dd, ³J = 6.6 Hz, ³J(¹⁹⁵Pt–H₁) = 37 Hz, ¹³C: C₁ 46.374, ²J(¹⁹⁵Pt–C₁) = 10 Hz.

The *trans*tBuNH₂ and Et₂NH compounds were synthesized from the iodo-bridged dimer as described above for the synthesis of the *cis* isomers. An excess of amine (amine:Pt = 15) was added to the dimers suspended in water and heated until the brown color changed to bright yellow. The precipitate was filtered, recrystallized in ethanol, washed with water and then with cold ethanol and finally dried. The Et₂NH compound contained 30% of the *cis* isomer.

trans-Pt(*t*BuNH₂)₂I₂: Yield = 71%, m.p. = 171–192 °C (dec.). IR (cm⁻¹): ν(N–H) 3240s, 3210s, 3135m, ν(C–H) 2970s, 2925m, 2890w, δ(N–H) 1578s, δ(C–H) 1460w, 1440m, 1380m, ν(C–N) 1235s, 1075s, other bands: 1345m, 1035s, 885w, 820m, 600w. NMR (δ (ppm)): ¹H: NH 4.197s+d, ²J(¹⁹⁵Pt–NH) = 58 Hz, H₁ 1.450s, ¹³C: C₁ 55.420, ²J(¹⁹⁵Pt–C₁) = 9 Hz, C₂ 32.608, ³J(¹⁹⁵Pt–C₂) = 17 Hz.

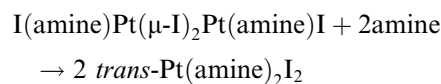
trans-Pt(Et₂NH)₂I₂: Yield = 59% (contained 30% of the *cis* isomer), m.p. = 152–176 °C (dec.). NMR (δ (ppm)): ¹H: NH 4.285s+d, ²J(¹⁹⁵Pt–NH) = 60 Hz, H₁ 2.968tq, ³J = 7.5, 6.9 Hz, H₂ 1.327t, ³J = 6.9 Hz, ¹³C: C₁ 53.750, ²J(¹⁹⁵Pt–C₁) = 9 Hz, C₂ 15.199, ³J(¹⁹⁵Pt–C₂) = 22 Hz.

3. Results and discussion

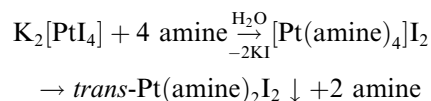
3.1. Synthesis

Complexes of the type *cis*-Pt(amine)₂I₂ with amine = methylamine (MeNH₂), ethylamine (EtNH₂), *n*-propylamine (*n*PrNH₂), *n*-butylamine (*n*BuNH₂), *iso*-propylamine (*iso*PrNH₂), *iso*-butylamine (*iso*BuNH₂), *sec*-butylamine (*sec*BuNH₂) and dimethylamine (Me₂NH) were synthesized by a modified Dhara's method [40]. A slight excess of the amine was used to maximize the yields, which varied between 76% and 92%. Similar reactions with *t*-butylamine (*t*BuNH₂) and diethylamine (Et₂NH) produced the iodo-bridged dimers I(amine)Pt(μ-I)₂Pt(amine)I. The product obtained with Et₂NH contained also about 30% of another compound which we have assigned to *cis*-Pt(Et₂NH)₂I₂. The ligand *t*-butylamine is too bulky to form a *cis* compound.

The equivalent *trans*-Pt(amine)₂I₂ complexes were prepared by two different methods. For the most sterically demanding amines (*t*BuNH₂ and Et₂NH), the compounds were prepared from the reaction of the iodo-bridged dimers with a large excess of amine in water. Slight heating is necessary to reduce the time of reaction



The iodo-bridged dimers were synthesized by the reported method [42] or as mentioned above. The other *trans* compounds were prepared from the tetrasubstituted intermediates similarly to Kauffman's method [41]



For Me₂NH and *sec*BuNH₂, the colorless aqueous solutions were concentrated until precipitation of the *trans* compounds occurred. For the six other amines, the tetrasubstituted complexes were dissolved in ethanol and the solutions were heated until precipitation occurred. The yields (from K₂[PtCl₄]) are lower than those for the *cis* compounds due to the difficulty to obtain the tetrasubstituted compound in quantitative yields, especially for the bulkier amines. They varied between 59% (Et₂NH) and 82%.

The decomposition points of the compounds $\text{Pt}(\text{amine})_2\text{I}_2$ are shown in Section 2. In general, the *cis* complexes start to decompose at lower temperatures than the corresponding *trans* compounds. A few *cis* complexes probably isomerize to the *trans* isomer as the temperature is increased. Thermal isomerization of the *cis* complexes with MeNH_2 , EtNH_2 and $n\text{BuNH}_2$ has already been reported [43,44]. All the diido complexes were characterized by IR (except *cis* and *trans*- $\text{Pt}(\text{Et}_2\text{NH})_2\text{I}_2$ which were not obtained pure) and multinuclear NMR spectroscopies.

3.2. IR spectroscopy

The main IR bands are listed in Section 2. The spectra of the disubstituted complexes have shown the presence of two or three bands in the stretching $\nu(\text{N}-\text{H})$ region at slightly lower energies ($3075\text{--}3260\text{ cm}^{-1}$) than in the free amines. The deformation bands $\delta(\text{N}-\text{H})$ were also observed at lower frequencies ($1560\text{--}1585\text{ cm}^{-1}$) in the coordinated ligands. The vibration frequencies of the Pt–N bonds were assigned based on published works [36,45–52]. These bands are usually weak and are quite difficult to assign. Some of these vibrations might also couple with others, which increases the assignment difficulties. Attempts have been made to interpret these vibrations and the results are shown in Table 3, along with some published results. All the *trans* compounds have shown only one band, while one or two bands are reported for the *cis* complexes. This is in agreement with group theory, when idealized C_{2v} (2 bands) and D_{2h} (1

band) symmetries are considered for the *cis* and *trans* complexes, respectively [53]. The energy of the $\nu(\text{Pt}-\text{N})$ vibrations seems to be dependent on the halo ligand. For example, for the *cis*- $\text{Pt}(\text{NH}_3)_2\text{X}_2$ complexes, the two bands were reported at 520 and 508 cm^{-1} for $\text{X}=\text{Cl}$ [47,49], at 513 and 499 cm^{-1} for $\text{X}=\text{Br}$ [48] and at 491 and 477 cm^{-1} for $\text{X}=\text{I}$ [48]. Our values are also slightly lower than those of a few published dichloro compounds [45,46] and a few diido complexes with more crowded ligands [36].

3.3. NMR

The NMR spectra of all the complexes $\text{Pt}(\text{amine})_2\text{I}_2$ were measured in CD_3COCD_3 . Although several compounds are soluble in normal CHCl_3 , they decompose quite rapidly to produce iodine. Attempts to purify CDCl_3 were not successful. We also encountered similar problems with CD_2Cl_2 . DMSO reacts quite rapidly with these compounds and was rapidly eliminated. DMF reacts more slowly, but since our ^{13}C NMR spectra were accumulated for at least overnight, we have found that deuterated acetone was the best solvent, even if it is not a very inert solvent. In order to determine if solvolysis could occur in acetone, the spectra of *cis*- and *trans*- $\text{Pt}(\text{amine})_2\text{I}_2$ (amine = EtNH_2 and *sec* BuNH_2) were recorded in CD_3COCD_3 in the presence of 0, 2, 5 and 10 meq of KI. But no difference was observed in the spectra measured with and without KI. We have also verified if the *cis* complexes could isomerize to the *trans* compounds as reported for a few dichloro complexes [54]. The NMR spectra of fresh solutions of the *cis* complexes were identical after one week of standing in CD_3COCD_3 .

Table 3
 $\nu(\text{Pt}-\text{N})$ vibrations (cm^{-1}) for the complexes *cis*- and *trans*- PtL_2X_2 and some examples from the literature

Complex	<i>cis</i>		<i>trans</i>	Ref.
	ν_s	ν_{as}	ν_{as}	
$\text{Pt}(\text{NH}_3)_2\text{Cl}_2$	517	508	509	[47]
	523	507	538	[49]
			506	[51]
			505	[50]
$\text{Pt}(\text{NH}_3)_2\text{Br}_2$	513	499	502	[48,50]
$\text{Pt}(\text{NH}_3)_2\text{I}_2$	491	477	498	[48]
$\text{Pt}(\text{MeNH}_2)_2\text{Cl}_2$	565	506	518	[45]
$\text{Pt}(\text{cycloPrNH}_2)_2\text{Cl}_2$	595			[46]
$\text{Pt}(\text{MeNH}_2)_2\text{I}_2$	495	485		[36]
$\text{Pt}(\text{EtNH}_2)_2\text{I}_2$	578	498		[36]
$\text{Pt}(\text{cycloBuNH}_2)_2\text{I}_2$	568			[36]
$\text{Pt}(\text{cycloPeNH}_2)_2\text{I}_2$	585	530		[36]
$\text{Pt}(\text{2-adamNH}_2)_2\text{I}_2$		500		[36]
$\text{Pt}(\text{Me}_2\text{NH})_2\text{I}_2$	502	478		[36]
$\text{Pt}(\text{MeNH}_2)_2\text{I}_2$	470	420	465	
$\text{Pt}(\text{EtNH}_2)_2\text{I}_2$	495	450	433	
$\text{Pt}(n\text{BuNH}_2)_2\text{I}_2$	485		445	
$\text{Pt}(iso\text{PrNH}_2)_2\text{I}_2$		450	435	
$\text{Pt}(iso\text{BuNH}_2)_2\text{I}_2$		450	445	
$\text{Pt}(sec\text{BuNH}_2)_2\text{I}_2$		430	465	
$\text{Pt}(\text{Me}_2\text{NH})_2\text{I}_2$	495	465	475	

3.3.1. ^{195}Pt NMR

The $\delta(\text{Pt})$ chemical shifts of all the compounds are listed in Table 4. The signals of the *cis* diido complexes with primary amines were observed between -3342 and -3357 ppm and between -3345 and -3372 ppm for the *trans* analogues. The $\Delta\delta$ between the two isomers are very small. These results are quite surprising, since in the pyridine (Ypy) series, the difference between the *cis* and *trans* isomers were larger. The *cis* diido pyridine complexes were observed in CDCl_3 between -3199 and -3312 ppm , while the *trans* analogues were observed at lower field, between -3122 and -3264 ppm [37], with $\Delta\delta$ values (*cis*–*trans*) $\approx -70\text{ ppm}$. Our results on amine complexes show $\Delta\delta$ (*cis*–*trans*) values between -10 and 18 ppm . We have repeated these spectra several times and the results were always almost identical ($\pm 2\text{ ppm}$). For *isoPrNH}_2 and *secBuNH}_2, the *cis* complexes were observed at slightly higher fields than the *trans* isomers as expected. For the other ligands, the *trans* compounds were observed at higher fields (although the $\Delta\delta$ values are not very large) which is contrary to all published values on similar compounds. With ligands capable of**

Table 4
Chemical shifts $\delta(^{195}\text{Pt})$ and $\Delta\delta(\delta_{cis}-\delta_{trans})$ (ppm) of the complexes PtL_2I_2 in CD_3COCD_3

L	PA	pK _a	<i>cis</i>	<i>trans</i>	$\Delta\delta$
MeNH ₂	914	10.62	-3342	-3360	18
			-3324 ^a	-3348 ^a	24 ^a
EtNH ₂	930	10.63	-3354	-3368	14
			-3328 ^a	-3353 ^a	25 ^a
<i>n</i> PrNH ₂	933	10.69	-3350	-3363	13
<i>n</i> BuNH ₂	924	10.61	-3349	-3363	13
<i>iso</i> PrNH ₂		10.63	-3352	-3345	-7
<i>iso</i> BuNH ₂		10.72	-3357	-3372	15
<i>sec</i> BuNH ₂		10.56	-3346	-3336	-10
			-3309,	-3322 ^a	13 ^a
			-3321 ^a (65%)	(35%)	
<i>t</i> BuNH ₂		10.68		-3369	
Me ₂ NH		10.73	-3247	-3057	-190
Et ₂ NH		11.04	-3302 ^b	-3128	-174

^a In DMF-d₇.

^b See text.

accepting π -electrons like sulfoxides, the *cis* compounds are observed at lower fields, since the π -bonding is much more efficient in the *cis* geometry compared to the *trans* isomer. The *cis* compounds are also more stable than the *trans* analogues in the sulfoxide system. But amines cannot accept back π -donation and the *trans* amine compounds are thermodynamically more stable. Pyridine ligands contain empty π^* orbitals capable of accepting electron density from platinum. This back-donation will reduce the electron density on the metallic center, resulting in a deshielding in the Pt chemical shifts. For pyridine ligands, it does not seem very important, since the *trans* compounds are observed at lower fields than the *cis* as mentioned above.

A few results on diiodo complexes were reported by our research group several years ago on some *cis* diamine complexes, and also with slightly more bulky amines (mainly adamantamine derivatives) [36]. These have been measured in DMF and some of the results are shown in Table 5. All these compounds were synthesized as to produce *cis* compounds. The more bulky ligands showed two signals in ¹⁹⁵Pt NMR and we have assumed partial isomerization of the *cis* to the *trans* complexes. Based on data published in the literature, we had suggested that the resonance of the *cis* isomers were at higher fields than the corresponding *trans* compounds ($\Delta\delta$ (*cis-trans*) between -29 and -53 ppm). But these assignments might have been inverted. DMF is a reasonably good solvent to isomerize such compounds, especially those with bulkier ligands.

For comparison purposes, we have remeasured our *cis* and *trans* MeNH₂, EtNH₂ and *sec*BuNH₂ compounds in DMF. The chemical shifts are shown in Table 4 along with our results in CD_3COCD_3 . With MeNH₂, and EtNH₂ in DMF, there was only one signal for the *cis* and *trans* compounds. The ¹⁹⁵Pt NMR spectrum of *trans*-

Table 5
Chemical shifts $\delta(^{195}\text{Pt})$ and $\Delta\delta(\delta_{cis}-\delta_{trans})$ (ppm) of the complexes PtL_2X_2 in the literature

Complex	<i>cis</i>	<i>trans</i>	$\Delta\delta$	Ref.
Pt(NH ₃) ₂ I ₂	-3264			[31] ^a
	-3198			[32] ^c
Pt(MeNH ₂) ₂ I ₂	-3327			[36] ^c
Pt(EtNH ₂) ₂ I ₂	-3330			[36] ^c
Pt(Me ₂ NH) ₂ I ₂	-3327			[36] ^c
Pt(1-adam) ₂ I ₂	-3364	-3331	-33	[36] ^c
Pt(2-adam) ₂ I ₂	-3333			[36] ^c
Pt(cpa) ₂ I ₂	-3302			[36] ^c
Pt(cba) ₂ I ₂	-3346			[36] ^c
Pt(cba)(2-adam)I ₂	-3387	-3358	-29	[36] ^c
Pt(MeNH ₂)(1-Me-adam)I ₂	-3389	-3336	-53	[36] ^c
Pt(py) ₂ I ₂	-3199	-3133	-66	[37,38] ^a
Pt(Ypy) ₂ I ₂ (δ_{ave})	-3235	-3161	-74	[31,38] ^a [37] ^{a,b}
Pt(NH ₃) ₂ Cl ₂	-2104	-2101	-3	[30] ^c
	-2100	-2101	1	[32] ^c
	-2097			[35] ^d
Pt(MeNH ₂) ₂ Cl ₂	-2222			[36] ^c
Pt(Me ₂ NH) ₂ Cl ₂	-2188	-2181	-7	[36] ^c
Pt(<i>iso</i> PrNH ₂) ₂ Cl ₂	-2224			[36] ^c
Pt(C ₆ H ₁₁ NH ₂) ₂ Cl ₂	-2215 ^d	-2130 ^a	-85	[34]
Pt(cba) ₂ Cl ₂	-2235			[36] ^c
Pt(1-adam) ₂ Cl ₂	-2184	-2141	-43	[36] ^c
Pt(2-adam) ₂ Cl ₂	-2230	-2193	-37	[36] ^c
Pt(1-Meadam) ₂ Cl ₂	-2242			[36] ^c
Pt(py) ₂ Cl ₂	-2014	-1960	-54	[37] ^a
Pt(Ypy) ₂ Cl ₂ (δ_{ave})	-2009	-1957	-52	[37] ^a

^a CDCl₃.

^c DMF-d₇.

^b CD₂Cl₂.

^d DMSO.

Pt(*sec*BuNH₂)₂I₂ showed one signal at -3322 ppm, while the *cis* compound showed two peaks (-3309 and -3321 ppm), indicating that some isomerization has taken place. If we compare the values in DMF with those in CD_3COCD_3 , the values in DMF were observed at slightly lower fields than those in acetone (12–37 ppm). But all the *cis* compounds were observed in DMF at lower fields than the corresponding *trans* isomers. The $\Delta\delta$ (*cis-trans*) vary between 13 and 25 ppm. The difference seems to be slightly more important in DMF (ave. $\Delta\delta$ 21 ppm) than in CD_3COCD_3 (ave. $\Delta\delta$ 7 ppm) for these three amines.

For the secondary amine Me₂NH, the difference between the *cis* and *trans* isomers is much larger and is as expected. The *cis* compound is observed at higher field and the $\Delta\delta$ (*cis-trans*) is -190 ppm. For Et₂NH, a similar value ($\Delta\delta = -174$ ppm) was observed, although we were not certain of the identification of the *cis* compound as discussed above.

There are not many ¹⁹⁵Pt NMR data in the literature on Pt(amine)₂X₂ (X = Cl or I) systems. These data are shown in Table 5. For the chloro system, the chemical shifts of *cis*- and *trans*-Pt(NH₃)₂Cl₂ have been reported in DMF [30,32,33]. The data are identical for the two isomers. The *cis* compound was also reported at -2097

ppm in DMSO [35] ppm. For $\text{NH}_2(\text{CH}_2)_5\text{CH}_3$, ($X = \text{Cl}$) the difference is larger, -2215 (*cis* in DMSO) and -2130 ppm (*trans* in CDCl_3) [34], although the solvents are different. In the iodo system, the chemical shift of *cis*- $\text{Pt}(\text{NH}_3)_2\text{I}_2$ was reported in DMF at -3198 ppm [32] and at -3264 ppm in CDCl_3 [31], but no data are available for the *trans* isomer. The other studies [36–38] have been discussed above.

The ^{195}Pt chemical shifts depend on many factors and can be described by modified versions of Ramsey's equation [55–57]. One of the factor is the metallic character of the different d orbitals of the platinum atom. Therefore, the chemical shifts can give information of the degree of covalency of the bonding between the metal and the ligands. Strong σ -donors should increase the electron density on the metal resulting in a shielding in ^{195}Pt NMR. The basicity of the ligands can be evaluated by the $\text{p}K_a$ values of the protonated amines. We have attempted to correlate the $\text{p}K_a$ values [58,59] with the ^{195}Pt NMR signals. Figs. 1 and 2 show the relation between $\delta(\text{Pt})$ versus $\text{p}K_a$ values for the *cis* and *trans* primary amine compounds, respectively. Fig. 3 shows a few results on secondary amines. For the primary amines, the maximum difference in $\text{p}K_a$ and in $\delta(\text{Pt})$ values are very small and the experimental errors are not negligible. Therefore, there

seems to be a linear relationship as expected, but the dispersion around the straight line is fairly large. Furthermore, some of the amines in the list are quite different in bulkiness. For the two secondary amines, the $\delta(\text{Pt})$ values are more different, but more data are needed to confirm the linear relationship.

The basicity of a ligand can also be evaluated by its proton affinity in the gas phase. There are not many such values available in the literature. Fig. 4 shows the $\delta(\text{Pt})$ versus the published proton affinity of the amines [60–64]. The linear relationship is much better and seems to indicate that the proton affinity value in the gas phase is a better basicity indicator than the $\text{p}K_a$ values. The latter are measured in a solvent which usually participates in the reaction and the results depend on many factors like the bulkiness around the protonated atom.

3.3.2. ^1H and ^{13}C NMR

The ^1H and ^{13}C NMR signals are listed in Section 2 with the proposed assignments. No free ligand was detected in the spectra. The NMR spectra of the free amines were also measured and compared with those of the complexes. Three of the ligands are commercially available as aqueous solutions, since they are gases at room temperature. The chemical shifts of the free amines vary

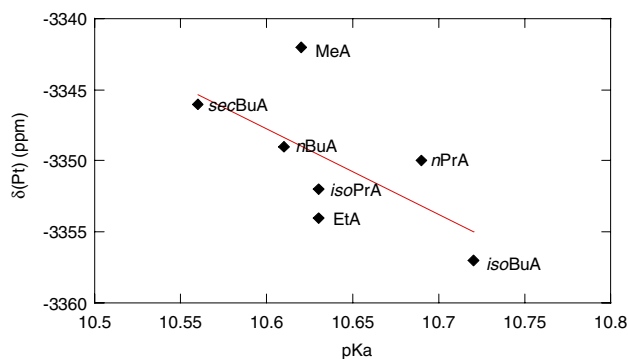


Fig. 1. $\delta(^{195}\text{Pt})$ vs $\text{p}K_a$ of the protonated amines for *cis*- PtL_2I_2 ($L = \text{primary amine}$).

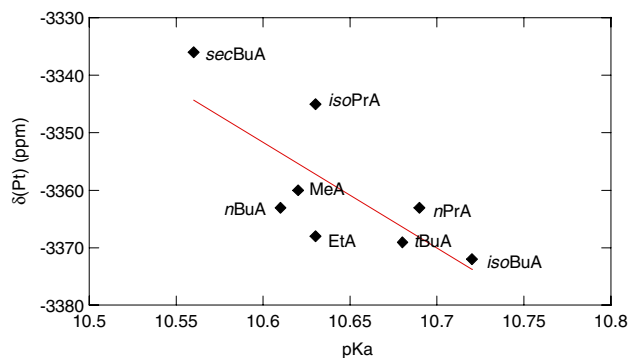


Fig. 2. $\delta(^{195}\text{Pt})$ vs $\text{p}K_a$ of the protonated amines for *trans*- PtL_2I_2 ($L = \text{primary amine}$).

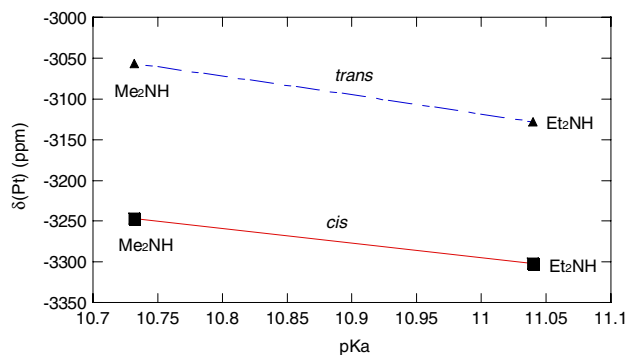


Fig. 3. $\delta(^{195}\text{Pt})$ vs $\text{p}K_a$ of the protonated amines for *cis*- and *trans*- PtL_2I_2 ($L = \text{secondary amine}$).

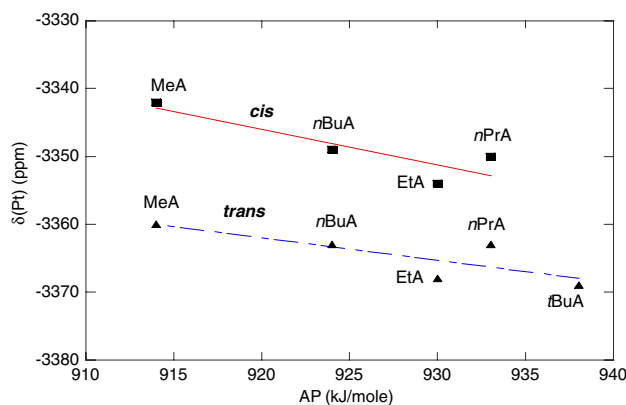


Fig. 4. $\delta(^{195}\text{Pt})$ vs proton affinity (PA) of the amines for *cis*- and *trans*- PtL_2I_2 .

with the solvents. For example, the chemical shift of MeNH₂ is observed at 2.927 ppm in CD₃COCD₃ (containing water from the dissolved amine) and at 2.245 ppm in pure D₂O. Therefore, the spectra of the three aqueous amines were not recorded in pure acetone. For this reason, it is difficult to discuss the $\Delta\delta$ values ($\delta_{\text{complex}} - \delta_{\text{amine}}$). Furthermore, acetone is not an inert solvent for amines. We have measured the ¹H and ¹³C NMR spectra of the free amines in CD₃COCD₃, CDCl₃, and D₂O and calculated the $\Delta\delta$ values. In acetone (complexes and free amines), these values are not very informative, but in CDCl₃ or D₂O (complex in acetone, amine in CDCl₃ or D₂O), the values decrease as the distance from the bonding atom increase, as expected [65]. In ¹H NMR, the $\Delta\delta$ values are smaller for the *trans* isomers, indicating that they are more shielded upon coordination than the *cis* compounds. In ¹³C NMR, the $\Delta\delta$ values are smaller for the *cis* isomers, indicating that the latter are more shielded upon coordination than the corresponding *trans* compounds.

The signals of the amine groups in the complexes could be detected in CD₃COCD₃. Furthermore, an approximate value of the ²J(¹⁹⁵Pt–¹H) coupling constants could be calculated and are shown in Table 6. These vary between 65 and 70 Hz (ave. 67 Hz) for the *cis* compounds and between 58 and 62 Hz (ave. 59 Hz) for the *trans* isomers. A few ³J(¹⁹⁵Pt–¹H) coupling constants were also observed. The average values are 45 Hz for the *cis* compounds and 36 Hz for the *trans* complexes. Therefore, these coupling constants are larger in the *cis* isomers as observed in other related compounds [37].

In ¹³C NMR, the ²J(¹⁹⁵Pt–¹³C) and ³J(¹⁹⁵Pt–¹³C) coupling constants are also shown in Table 6. The ³J values (*cis*: ave. 38 Hz, *trans*: ave. 27 Hz) are similar to those observed in similar complexes [37,66,67]. For *sec*BuNH₂, the ³J(¹⁹⁵Pt–¹H) coupling constant on the terminal C atom is smaller (*cis*: 24 Hz, *trans*: 21 Hz) than the other ³J(¹⁹⁵Pt–¹H) constant (*cis*: 32 Hz, *trans*: 28 Hz). The ²J are much smaller than expected, probably because of inadequate orientation of the orbitals. The average values are 17 Hz (*cis*) and 11 Hz (*trans*).

The ligand *sec*-butylamine is a chiral molecule. Its complexes have shown a single resonance in ¹⁹⁵Pt NMR. In ¹H NMR, the *trans* isomer has shown two series of peaks, while only one was observed for the *cis* complex. Surprisingly in ¹³C NMR, the reverse was observed. The *cis* isomer has shown two series of peaks, while only one series of signals was observed for the *trans* compound. The separation between the two series becomes negligible as the distance from the bonding atom increases.

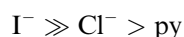
3.4. Crystal structures and the *trans* influence

The crystal structures of three *cis* (crystals I–III) and five *trans* diamine complexes (crystals IV–VIII) were determined. The crystallographic details are shown in Tables 1 and 2. The crystallographic results were compared with those obtained on the diiodo complexes with pyridine ligands [37]. The data on pyridine derivatives seemed to indicate that the *trans* influence of the chloro ligand is

Table 6
Coupling constants with ¹⁹⁵Pt of the complexes

Amine	Isomer	² J(¹⁹⁵ Pt– ¹ H)	³ J(¹⁹⁵ Pt– ¹ H)	² J(¹⁹⁵ Pt– ¹³ C)	³ J(¹⁹⁵ Pt– ¹³ C)
MeNH ₂	<i>cis</i>	69	49	21	
	<i>trans</i>	61	35	15	
EtNH ₂	<i>cis</i>	68		18	48
	<i>trans</i>	58		12	36
<i>n</i> PrNH ₂	<i>cis</i>	68		17	45
	<i>trans</i>	59		10	36
<i>n</i> BuNH ₂	<i>cis</i>	65	43	18	43
	<i>trans</i>	58		12	34
<i>iso</i> PrNH ₂	<i>cis</i>	66		13	30
	<i>trans</i>	60		11	22
<i>iso</i> BuNH ₂	<i>cis</i>	66		18	
	<i>trans</i>	59		14	
<i>sec</i> BuNH ₂	<i>cis</i>	67			32, 24
	<i>trans</i>			10	28, 21
<i>t</i> BuNH ₂	<i>trans</i>	58		9	17
Me ₂ NH ₂	<i>cis</i>	70	43	14	
	<i>trans</i>	62	37	10	
Et ₂ NH ₂	<i>cis</i>	68		13	34
	<i>trans</i>	60		9	22

larger than the one of pyridine, although the difference might be small. The *trans* influence of the iodo ligand seemed much larger than the one of the chloro ligand. The order of the *trans* influence series was found to be [37]



For the dipyridine isomers, the difference in $\delta(^{195}\text{Pt})$ between the two isomers is greater for the diiodo complexes (average 65 ppm) than for the dichloro complexes (45 ppm) [37]. McFarlane [68] has proposed for the *cis* and *trans* isomers of the type PtL_2X_2 , that $\Delta\delta(^{195}\text{Pt})$ is greater when the ligands L and X are far from each other in the *trans* influence series, since the energy difference (ΔE terms in Ramsey equation) between the two isomers would be larger. Contrary to the *trans* effect series which is relatively well known, the *trans* influence series is not known with certainty. In order to compare the results obtained in the pyridine system with the diamine system, we have studied several diamine complexes by X-ray diffraction methods.

The crystal structures of the *cis* diiodo complexes with MeNH_2 (**I**), $n\text{BuNH}_2$ (**II**) and Et_2NH (**III**) and of the *trans* compounds containing the ligands $n\text{PrNH}_2$ (**IV**), isoBuNH_2 (**V**), $n\text{BuNH}_2$ (**VI**), $t\text{BuNH}_2$ (**VII**) and Me_2NH (**VIII**) were determined. In *cis*- $\text{Pt}(n\text{BuNH}_2)_2\text{I}_2$ (**II**), there are two independent molecules, one is located on a twofold axis, while the second is in general position. In *trans*- $\text{Pt}(\text{MeNH}_2)_2\text{I}_2$ (**VIII**), the Pt atom is located on an inversion centre. Labeled diagrams of a few structures are shown in Figs. 5–8.

The Pt–I and Pt–N bond distances are listed in Table 7. The Pt–I like the Pt–Cl bond distances usually do not vary very much with the *trans* ligand, but the Pt–N bond distances are usually more sensitive to its *trans* ligand. The Pt–I average bond distance in the *cis* structures (in *trans* position to an amine) is 2.598 Å, while it is 2.604 Å in the *trans* isomers (*trans* to iodide). The latter seems slightly

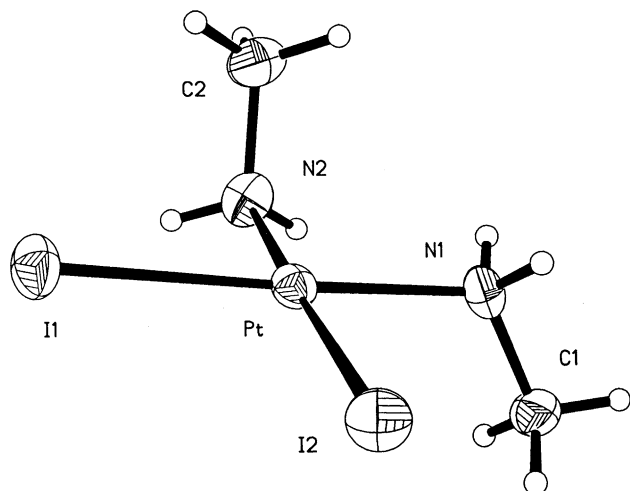


Fig. 5. Labeled diagram of *cis*- $\text{Pt}(\text{MeNH}_2)_2\text{I}_2$ (**I**).

larger, although the difference might not appear significant. The average Pt–N bond distance in the *trans* complexes is 2.062 Å. In the *cis* isomers, the bonds are very similar for crystals **I** and **II** (ave. 2.054 Å), but it is very different in crystal **III**. The latter crystal contains two bulky secondary amines (Et_2NH) located in *cis* position

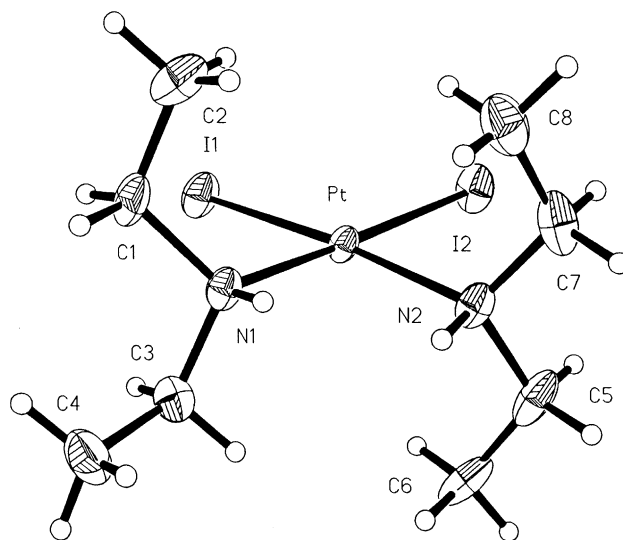


Fig. 6. Labeled diagram of *cis*- $\text{Pt}(\text{Et}_2\text{NH})_2\text{I}_2$ (**III**).

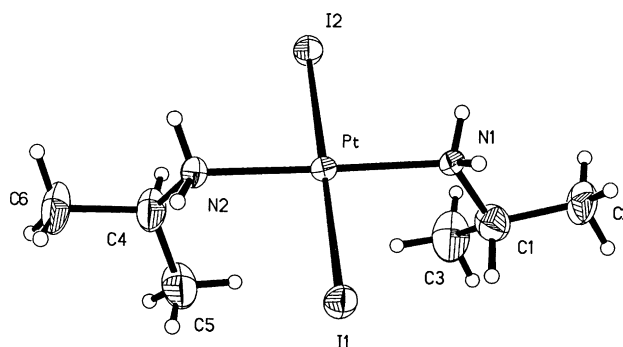


Fig. 7. Labeled diagram of *trans*- $\text{Pt}(\text{isoPrNH}_2)_2\text{I}_2$ (**V**).

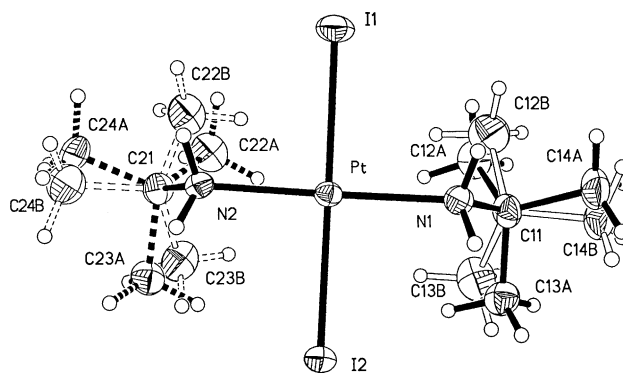


Fig. 8. Labeled diagram of *trans*- $\text{Pt}(t\text{BuNH}_2)_2\text{I}_2$ (**VII**). The terminal methyl groups are disordered on two positions.

Table 7
Selected bond distances (Å) for the complexes Pt(amine)₂X₂

Complex	Pt–N	Pt–I
<i>cis</i> -Pt(MeNH ₂) ₂ I ₂ (I)	2.047(12), 2.070(10)	2.5938(13), 2.5973(13)
<i>cis</i> -Pt(<i>n</i> BuNH ₂) ₂ I ₂ (II)	2.042(18), 2.042(18)	2.604(2), 2.604(2)
	2.059(21), 2.054(18)	2.595(2), 2.596(2)
<i>cis</i> -Pt(Et ₂ NH) ₂ I ₂ (III)	2.112(10), 2.113(10)	2.5967(13), 2.6011(13)
<i>trans</i> -Pt(<i>n</i> PrNH ₂) ₂ I ₂ (IV)	2.024(8), 2.096(9)	2.594(2), 2.599(2)
<i>trans</i> -Pt(<i>iso</i> PrNH ₂) ₂ I ₂ (V)	2.054(6), 2.069(6)	2.6049(9), 2.6062(9)
<i>trans</i> -Pt(<i>n</i> BuNH ₂) ₂ I ₂ (VI)	2.051(7), 2.058(8)	2.5972(9), 2.5977(9)
<i>trans</i> -Pt(<i>t</i> BuNH ₂) ₂ I ₂ (VII)	2.068(6), 2.062(5)	2.6098(7), 2.6072(7)
<i>trans</i> -Pt(Me ₂ NH) ₂ I ₂ (VIII)	2.070(5)	2.6104(6)

to each other, resulting in very long Pt–N bonds (2.113(10) Å). Therefore, these distances are not only influenced by its *trans* ligand, but also by the substituents on the N donor atoms. In *trans*-Pt(Et₂NH)(NH=C(NEt₂)₂)I₂ [69], the Pt–N bond was also longer (2.095(9) Å), although the bulkiness is slightly reduced in a *trans* compound. In the iodo-bridged dimer (Et₂NH)IPt(μ-I)₂Pt(Et₂NH)I [70], the Pt–N bonds are normal (2.065(9) Å), probably because the steric hindrance is reduced by the smaller angle inside the four-membered ring, which increases the other angles. The *cis* ligand is also monoatomic. The influence of the bulkiness of the amine can also be seen by comparing the results on the crystals containing *n*BuNH₂ (VI) and *t*BuNH₂ (VII). The Pt–N and Pt–I bonds are slightly longer in the *t*BuNH₂ crystal (2.054(8) and 2.5974(9) Å for VI and 2.065(6) and 2.6085(7) Å for VII). In the reported structure *trans*-Pt(*t*BuNH₂)₂Cl₂, the average Pt–N bond was 2.047(6) Å [71]. In *trans*-Pt(Me₂NH)₂I₂ (VIII), the Pt–I bonds are the longest observed in this study, (2.6104(6) Å). The presence of two methyl groups on the bonding atom probably increases this distance. The Pt–N bonds are also slightly long (2.070(5) Å). These values are identical to those observed in *trans*-Pt(*t*BuNH₂)₂I₂ (VII), another bulky amine. These results seem to indicate that the bulkiness of the amine is an important factor in the Pt–N bond distances, probably more important than its *trans* influence. Nevertheless, the data on less bulky amines can give an indication of their *trans* influence.

In the diiodo dipyridine series (Ypy), the Pt–N bonds located in *trans* position to the iodo ligand were found longer (ave. 2.052(12) Å) than those in *trans* position to pyridine (ave. 2.020(12) Å) [37]. The latter value is smaller than the corresponding distance in the diamine series. These results indicate that the *trans* influence of amines is larger than the one of pyridine ligands, although it is smaller than the one of iodo ligands. It might be comparable to the one of chloro ligands. There are a few structures in the literature on *cis*- and *trans*-Pt(amine)₂Cl₂ [54,72–76]. For example in *cis*-Pt(MeNH₂)₂Cl₂, the average Pt–N bonds is 2.046 Å [72], while it is 2.057(12) Å in the iodo analogue (I). These data seem to indicate that the Pt–N bonds in *trans* po-

sition to a primary amine is similar to the one in *trans* position to a chloro ligand

I[−] > Cl[−] ≈ Amines > Ypy

These results support the previous discussion on the ¹⁹⁵Pt chemical shifts observed in NMR. This *trans* influence series might explain why the NMR chemical shifts δ(Pt) of *cis*- and *trans*-Pt(amine)₂I₂ are quite similar, while the ones of *cis* and *trans*-Pt(Ypy)₂I₂ are very different. In the chloro analogues, the amine complexes have identical chemical shifts, while the pyridine compounds have slightly different δ(Pt). The crystallographic results seem to support the suggestion of McFarlane [68] mentioned above.

The crystal structure of *cis*-Pt(MeNH₂)₂Cl₂ was reported [72]. Two crystallographic forms were observed. In form A, the two MeNH₂ ligands are located on the same side of the Pt plane, while form B contains three types of units. Two of these look like form A, while in the third unit, one of the methyl groups is above the plan, while the other one is located below the Pt plane. Fig. 5 shows the diagram of the diiodo analogue (crystal I). The two methyl groups are located on different sides of the Pt plane.

It is interesting to observe that a few *trans* crystals were obtained from the isomerization of the *cis* isomers during the recrystallizing process in organic solvents. Therefore, this method is an effective alternate method to synthesize *trans* compounds, especially with sterically more demanding ligands.

4. Conclusions

Complexes of the type *cis*- and *trans*-Pt(amine)₂I₂ were characterized by multinuclear NMR in a relatively inert solvent, acetone. In ¹⁹⁵Pt NMR, the diiodo complexes were observed at much higher fields than the dichloro analogues. Contrary to the pyridine analogues, the *cis* and *trans* diiodo diamine compounds were observed at similar fields. This difference was related to the relative order of iodo, amine and pyridine ligands in the *trans* influence series.

There seems to be a dependence of the $\delta(\text{Pt})$ on the $\text{p}K_{\text{a}}$ of the protonated ligand, but the dispersion about the linear relation is quite large. The $\text{p}K_{\text{a}}$ values of the protonated amines were measured in water or alcohol and they are influenced by the presence of molecules of solvent close to the protonated site (N atom). The intrinsic basicity of the amines can be evaluated from the gas phase protonic affinities or by the Hammett constants, but these values are not easily accessible. Some results on the gas phase protonic affinities indicate a linear relationship with the ^{195}Pt chemical shifts. As these values become more available, they might bring further information on the nature of the metal–amine bond.

The $^3J(^{195}\text{Pt}-^1\text{H})$ coupling constants in the $\text{Pt}(\text{amine})_2\text{X}_2$ complexes are larger for the *cis* isomers (45 Hz) than for the *trans* compounds (36 Hz), which might be a relatively simple method to differentiate between the two different isomers. The $^2J(^{195}\text{Pt}-^1\text{H})$ coupling constants of the amine protons are also larger in the *cis* complexes (67 versus 59 Hz). The $^3J(^{195}\text{Pt}-^{13}\text{C})$ are also geometry dependent. The average values are 38 and 27 Hz for the *cis* and *trans* compounds, respectively. The $^2J(^{195}\text{Pt}-^{13}\text{C})$ are small, 17 (*cis*) and 11 (*trans*) Hz.

The crystal structures of eight diiodo complexes were determined and the results have shown that the iodo ligand has a slightly larger *trans* influence than amines, which in turn have a larger *trans* influence than pyridine derivatives. This fact explained the smaller difference in $\delta(^{195}\text{Pt})$ between the *cis* and *trans* isomers for the diiodo diamine complexes when compared to the diiodo dipyridine compounds. The Pt–N bonds in *cis*- $\text{Pt}(\text{Et}_2\text{NH})_2\text{I}_2$ are very long caused by steric factors.

Finally, the crystal structure analysis of *trans*- $\text{Pt}(\text{Me}_2\text{NH})_2\text{I}_2$, which was isolated from the isomerization of the *cis* analogues in ethanol, confirmed the *cis* *trans* isomerization in organic solvents.

5. Supplementary material

The CIF tables for the eight crystals have been deposited to the Cambridge Data File Centre. The deposit numbers are: CCDC 224779–224786.

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