Synthesis, IR, and multinuclear NMR spectroscopic studies of complexes of the type *cis*- and *trans*-Pt(amine)$_2$(NO$_3$)$_2$

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Abstract: Compounds of the types *cis*- and *trans*-Pt(amine)$_2$NO$_3$)$_2$ have been synthesized and characterized by IR and multinuclear (^{195}Pt, ^{13}C, and ^{1}H) NMR spectroscopies. The nitrato IR bands were compared for the two isomers. The ^{195}Pt NMR resonances of the trans complexes were observed at lower fields (avg. –1570 ppm for primary amines) than the cis analogues (avg. –1698 ppm) for an average $\Delta\delta$ value of 124 ppm. The complexes containing a secondary amine were observed at about the same field for the cis isomers (avg. –1682 ppm) and surprisingly at much higher fields for the trans compounds (avg. –1638 ppm). In ^{1}H NMR, the coupling constants $^2J(^{195}\text{Pt-}^1\text{HN})$ are larger for the cis isomers (avg. 67 Hz) than for the trans compounds (avg. 58 Hz). The $^3J(^{195}\text{Pt-}^1\text{H})$ are also larger for the cis complexes (avg. 40 vs. 33 Hz). In ^{13}C NMR, the coupling constants are also geometry dependent. The $^3J(^{195}\text{Pt-}^{13}\text{C})$ are larger for the cis isomers (avg. 37 Hz) than for the *trans* compounds (avg. 28 Hz). The $^2J(^{195}\text{Pt-}^{13}\text{C})$ are much smaller (avg. 18 Hz for the cis complexes and 16 Hz for the trans isomers).

Key words: platinum, amine, nitrato, NMR, IR.

Résumé : Des composés de types *cis*- et *trans*-Pt(amine)$_2$(NO$_3$)$_2$ ont été synthétisés et caractérisés par spectroscopies infrarouge et de résonance magnétique multinucléaire (^{195}Pt, ^{13}C et ^{1}H). Les vibrations des ligands nitrato ont été comparées dans les deux isomères. Les signaux en RMN du ^{195}Pt ont montré des résonances à plus hauts champs pour les composés cis (moy. –1698 ppm pour les amines primaires) que pour les analogues trans (moy. –1570 ppm). La valeur moyenne de $\Delta\delta$ est 124 ppm. Les complexes contenant des amines secondaires ont été observés à environ le même champ pour les isomères cis (moy. –1682 ppm) et à plus haut champ pour les composés trans (moy. –1638 ppm). En RMN du ^{1}H, les constantes de couplage $^2J(^{195}\text{Pt-}^1\text{HN})$ sont plus grandes pour les isomères cis (moy. 67 Hz) que pour les composés trans (moy. 58 Hz). Les couplages $^3J(^{195}\text{Pt-}^1\text{H})$ sont aussi plus importants pour les complexes cis (moy. 40 vs. 33 Hz). En RMN du ^{13}C, les constantes de couplage dépendent aussi de la géométrie. Les valeurs $^3J(^{195}\text{Pt-}^{13}\text{C})$ sont plus grandes pour les isomèrs cis (moy. 37 Hz) que pour les composés trans (moy. 28 Hz). Les constantes $^2J(^{195}\text{Pt-}^{13}\text{C})$ sont beaucoup plus petites (moy. 18 Hz pour les complexes cis et 16 Hz pour les isomères trans).

Mots clés : platine, amine, nitrato, IR, RMN.

Introduction

The antitumor compound *cisplatin* (*cis*-Pt(NH$_3$)$_2$Cl$_2$) is the most widely used anticancer drug today. Its mechanism of action involves its hydrolysis inside the cells, where the pH is neutral and the chloride ion concentration is low. In these conditions, *cis*-Pt(NH$_3$)$_2$Cl$_2$ becomes aquated, producing different ionic species that can bind to DNA (1) leading to the eventual destruction of the cell. One of these species is the diaqua complex *cis*-[Pt(NH$_3$)$_2$(OH$_2$)$_2$]$^{2+}$, which, because of the neutral pH inside the cells, will exist predominantly in the form *cis*-[Pt(NH$_3$)$_2$(OH)(OH$_2$)]$^+$ (2). The latter species has been shown in laboratories to produce different oligomeric species, which have been characterized by ^{195}Pt NMR (3–5) and by crystallographic methods (6–10). Some of these species are toxic and could be partially responsible for the toxicity of cisplatin in humans. Therefore, it is important to study the hydrolysis reactions of a complex before its development as an anticancer drug.

Platinum complexes with amines are potent antitumor agents. Some compounds have shown much better antitumor properties than *cis*-Pt(NH$_3$)$_2$Cl$_2$, but several are too insoluble to become useful drugs.

Our research group has undertaken a systematic study of complexes of the types *cis*- and *trans*-Pt(amine)$_2$I$_2$. The compounds have been studied by various spectroscopic techniques and by crystallography (11). We have characterized these products to study their hydrolysis reactions. However, the solubility of these complexes in water is very low. Substitution of the halides by nitrato ligands leads to a much greater solubility in water. A method for the synthesis of Pt(amine)$_2$(NO$_3$)$_2$ has been published for a few amines (12), but the complexes were characterized only by elemental analysis, IR spectroscopy, and by ^{1}H NMR.

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Several complexes of the types *cis*- and *trans*-Pt(amine)$_2$(NO$_3$)$_2$ have now been synthesized in our laboratories and the compounds were studied by IR and multinuclear NMR (^{195}Pt, ^{1}H, and ^{13}C) spectroscopies. The study of the hydrolysis and aquation reactions of these cis and trans dinitrato compounds is underway and the results will be published in a subsequent paper.

Experimental

Potassium tetrachloroplatinate(II) was purchased from Johnson Matthey and was recrystallized in water before use. The amine ligands were obtained from Aldrich, while silver nitrate was purchased from Anachemia. Deuterated acetone was acquired from CDN Isotopes.

The IR spectra were recorded between 4000 and 270 cm^{-1} as KBr pellets, on a PerkinElmer 783 grating spectrometer. The decomposition points were measured on a Fisher-Johns instrument. The NMR spectra were measured on a Varian Gemini 300BB in acetone. The fields were 300.075, 75.460, and 64.395 MHz for ^{1}H, ^{13}C, and ^{195}Pt, respectively. The acetone peaks were used as an internal standard for ^{1}H NMR (2.04 ppm) and ^{13}C NMR (29.8 ppm). For the ^{195}Pt spectra, K$_2$[PtCl$_4$] (in D$_2$O with KCl, adjusted at –1628 ppm from K$_2$[PtCl$_6$] whose δ(Pt) = 0 ppm) was the external standard.

Synthesis

The complexes Pt(amine)$_2$I$_2$ were synthesized as recently published (11). The dinitrato complexes were prepared according to a modified version of a published method described for other ligands (12). The complexes Pt(amine)$_2$I$_2$ (0.5 mmol) were dissolved in a minimum quantity of acetone (8 mL). A slight excess of AgNO$_3$ was added and the mixture was stirred in the dark and at lower temperature (5 °C) until a colorless solution (with a yellow precipitate) was obtained. The precipitate was filtered out and the solution was evaporated to dryness. The white residue was dissolved in 5 mL of acetone and filtered again to remove the last traces of AgI and AgNO$_3$. Diethyl ether was added and the mixture was cooled several hours until precipitation was complete. The precipitate was filtered, washed with diethylether, and dried under vacuum.

The notation of Nakamoto (13) was used for the IR assignments of the nitrato ligands.

cis-Pt(MeNH$_2$)$_2$(NO$_3$)$_2$

Yield: 75%; dec 132–150 °C. IR (cm^{-1}): ν(N-H) 3280s, 3255s, 3230s, ν(C-H) 2995w, 2950m, δ(N-H) 1603m, ν_4(NO$_3$) 1502s, δ(C-H) 1420w, 1395m, 1363m, ν_2(NO$_3$) 1261s, ν(C-N) 1103m, 1095s, ν_1(NO$_3$) 965s, ν_6(NO$_3$) 785m, ν_5(NO$_3$) 703m, ν(Pt-N) 535w, 515f, ν(Pt-O) 335m; other band: 990s, 755m. ^{1}H NMR (ppm) δ: NH 5.177s+d, ^2J(^{195}Pt-NH) = 69 Hz, H$_1$ 2.466t+d, ^3J(^{1}H-^{1}H) = 6.3 Hz, ^3J(^{195}Pt-H$_1$) = 47 Hz. ^{13}C NMR (ppm) δ: C$_1$ 34.460, ^2J(^{195}Pt-C$_1$) = 25 Hz. Anal. calcd. (%): C 6.30, H 2.64, N 14.70; found (%): C 6.47, H 2.78, N 14.73.

cis-Pt(EtNH$_2$)$_2$(NO$_3$)$_2$

Yield: 73%; dec 108–132 °C. IR (cm^{-1}): ν(N-H) 3260s, 3245s, 3150m, ν(C-H) 2965s, 2925m, 2865m, δ(N-H) 1585m, ν_4(NO$_3$) 1512s, δ(C-H) 1475m, 1455s, 1360w, ν_2(NO$_3$) 1263s, ν(C-N) 1112s, 1072m, ν_1(NO$_3$) 965F, ν_6(NO$_3$) 783s, ν_5(NO$_3$) 702m, ν(Pt-N) 530w, 460m, ν(Pt-O) 330m; other bands: 1335w, 1315w, 1045w, 996m, 742s. ^{1}H NMR (ppm) δ: NH 5.164s+d, ^2J(^{195}Pt-NH) = 68 Hz, H$_1$ 2.763tq, ^3J(^{1}H-^{1}H) = 7.2 Hz and 6.6 Hz, H$_2$ 1.308t, ^3J(^{1}H-^{1}H) = 6.9 Hz. ^{13}C NMR (ppm) δ: C$_1$ 43.172, ^2J(^{195}Pt-C$_1$) = 24 Hz, C$_2$ 15.776, ^3J(^{195}Pt-C$_2$) = 42 Hz.

cis-Pt(*n*-PrNH$_2$)$_2$(NO$_3$)$_2$

Yield: 78%; dec 107–123 °C. IR (cm^{-1}): ν(N-H) 3260s, 3220s, ν(C-H) 2965s, 2925m, 2865w, δ(N-H) 1575m, ν_4(NO$_3$) 1515s, δ(C-H) 1465s, 1365s, ν_2(NO$_3$) 1270s, ν(C-N) 1160m, 1110m, 1080w, ν_1(NO$_3$) 962s, ν_6(NO$_3$) 783m, ν_5(NO$_3$) 702w, ν(Pt-N) 435m, ν(Pt-O) 332m; other bands: 1000s, 820s, 390w. ^{1}H NMR (ppm) δ: NH 5.160s+d, ^2J(^{195}Pt-NH) = 68 Hz, H$_1$ 2.682tt, ^3J(^{1}H-^{1}H) = 7.5 Hz, 6.9 Hz, H$_2$ 1.774tq, ^3J(^{1}H-^{1}H) = 7.5 Hz, 7.2 Hz, H$_3$ 0.933t, ^3J(^{1}H-^{1}H) = 7.2 Hz. ^{13}C NMR (ppm) δ: C$_1$ 50.017, ^2J(^{195}Pt-C$_1$) = 20 Hz, C$_2$ 24.336, ^3J(^{195}Pt-C$_2$) = 40 Hz, C$_3$ 11.177.

cis-Pt(*n*-BuNH$_2$)$_2$(NO$_3$)$_2$

Yield: 72%; dec 99–110 °C. IR (cm^{-1}): ν(N-H) 3280s, 3245s, 3145m, ν(C-H) 2955s, 2925m, 2880w, δ(N-H) 1590m, ν_4(NO$_3$) 1513s, δ(C-H) 1480s, 1465s, 1395w, ν_2(NO$_3$) 1265s, ν(C-N) 1115m, 1075m, 1050m, ν_1(NO$_3$) 965s, ν_6(NO$_3$) 786m, ν_5(NO$_3$) 703w, ν(Pt-N) 530w, 465m, ν(Pt-O) 330m; other bands: 1000s, 900w, 885m, 745m. ^{1}H NMR (ppm) δ: NH 5.153s+d, ^2J(^{195}Pt-NH) = 66 Hz, H$_1$ 2.719tt, ^3J(^{1}H-^{1}H) = 7.2 Hz, 6.6 Hz, H$_2$ 1.745tt, ^3J(^{1}H-^{1}H) = 7.2 Hz, 6.9 Hz, H$_3$ 1.376tq, ^3J(^{1}H-^{1}H) = 7.5 Hz, 7.2 Hz, H$_4$ 0.900t, ^3J(^{1}H-^{1}H) = 7.2 Hz. ^{13}C NMR (ppm) δ: C$_1$ 48.028, ^2J(^{195}Pt-C$_1$) = 21 Hz, C$_2$ 33.199, ^3J(^{195}Pt-C$_2$) = 39 Hz, C$_3$ 20.344, C$_4$ 13.970.

cis-Pt(*i*-PrNH$_2$)$_2$(NO$_3$)$_2$

Yield: 73%; dec 136–151 °C. IR (cm^{-1}): ν(N-H) 3260s, 3215s, 3150w, ν(C-H) 2965s, 2920m, 2870w, δ(N-H) 1580m, ν_4(NO$_3$) 1518s, δ(C-H) 1467s, 1395m, 1370m, ν_2(NO$_3$) 1270s, ν(C-N) 1155m, 1110s, 1085w, ν_1(NO$_3$) 960s, ν_6(NO$_3$) 782m, ν_5(NO$_3$) 702m, ν(Pt-N) 440m, ν(Pt-O) 330m; other bands: 1350w, 1000s, 820m, 392w. ^{1}H NMR (ppm) δ: NH 5.088s+d, ^2J(^{195}Pt-NH) = 67 Hz, H$_1$ 2.993thept, ^3J(^{1}H-^{1}H) = 6.6 Hz, 6.3 Hz, ^3J(^{195}Pt-H$_1$) = 39 Hz, H$_2$ 1.397d, ^3J(^{1}H-^{1}H) = 6.3 Hz. ^{13}C NMR (ppm) δ: C$_1$ 50.123, ^2J(^{195}Pt-C$_1$) = 22 Hz, C$_2$ 23.198, ^3J(^{195}Pt-C$_2$) = 30 Hz. Anal. calcd. (%): C 16.48, H 4.15, N 12.81; found (%): C 16.95, H 4.23, N 12.38.

cis-Pt(*i*-BuNH$_2$)$_2$(NO$_3$)$_2$

Yield: 73%; dec 105–124 °C. IR (cm^{-1}): ν(N-H) 3280s, 3250m, 3230s, 3135w, ν(C-H) 2970m, 2930m, 2880w, δ(N-H) 1590m, ν_4(NO$_3$) 1503s, δ(C-H) 1460w, 1360m, ν_2(NO$_3$) 1263s, ν(C-N) 1100m, 1050w, ν_1(NO$_3$) 949s, ν_6(NO$_3$) 780m, ν_5(NO$_3$) 710s, ν(Pt-O) 335m; other bands: 1015w, 833w, 698m, 613w. ^{1}H NMR (ppm) δ: NH 5.157s+d, ^2J(^{195}Pt-NH) = 65 Hz, H$_1$ 2.594td, ^3J(^{1}H-^{1}H) = 7.5 Hz, 6.9 Hz, ^3J(^{195}Pt-H$_1$) = 37 Hz, H$_2$ 2.096thept, ^3J(^{1}H-^{1}H) = 6.9 Hz, 6.6 Hz, H$_3$ 0.953d, ^3J(^{1}H-^{1}H) = 6.6 Hz. ^{13}C NMR (ppm) δ: C$_1$ 55.693, ^2J(^{195}Pt-C$_1$) = 21 Hz, C$_2$ hidden by the solvent, C$_3$ 20.101.

***cis*-Pt(*sec*-BuNH$_2$)$_2$(NO$_3$)$_2$**

Yield: 79%; dec 101–118 °C. IR (cm^{-1}): ν(N-H) 3225s, 3145m, ν(C-H) 2960s, 2915m, 2870w, δ(N-H) 1600m, ν_4(NO$_3$) 1509s, δ(C-H) 1470s, 1380s, ν_2(NO$_3$) 1278s, ν(C-N) 1140w, 1115m, 1075m, ν_1(NO$_3$) 965s, ν_6(NO$_3$) 788m, ν_5(NO$_3$) 702w, ν(Pt-N) 460w, 430w, ν(Pt-O) 335m; other bands: 1000m, 895w, 835w. ^{1}H NMR (ppm) δ: NH 5.117s+d, $^2J(^{195}\text{Pt-NH})$ = 65 Hz, H$_1$ 2.712ttq, $^3J(^1\text{H-}^1\text{H})$ = 7.2 Hz, 6.9 Hz, 6.6 Hz, $^3J(^{195}\text{Pt-H}_1)$ = 35 Hz, H$_2$ 1.543dq, $^3J(^1\text{H-}^1\text{H})$ = 7.2 Hz, 6.6 Hz, H$_{2'}$ 1.404d, $^3J(^1\text{H-}^1\text{H})$ = 6.6 Hz, H$_3$ 0.941t, $^3J(^1\text{H-}^1\text{H})$ = 7.2 Hz. ^{13}C NMR (ppm) δ: C$_1$ 55.405, $^2J(^{195}\text{Pt-C}_1)$ = 20 Hz, C$_2$ hidden by the solvent, C$_{2'}$ 20.101, $^3J(^{195}\text{Pt-C}_{2'})$ = 29 Hz, C$_3$ 10.631.

***cis*-Pt(Me$_2$NH)$_2$(NO$_3$)$_2$**

Yield: 72%; dec 121–147 °C. IR (cm^{-1}): ν(N-H) 3280s, 3225s, 3135w, ν(C-H) 2930s, 2865s, δ(N-H) 1585m, ν_4(NO$_3$) 1503s, δ(C-H) 1460m, 1370s, ν_2(NO$_3$) 1260s, ν(C-N) 1170m, 1125m, ν_1(NO$_3$) 949s, ν_6(NO$_3$) 780s, ν_5(NO$_3$) 710s, ν(Pt-N) 440w, 405w, ν(Pt-O) 342m; other bands: 1030m, 830w, 820w, 603w. ^{1}H NMR (ppm) δ: NH 5.998s+d, $^2J(^{195}\text{Pt-NH})$ = 69 Hz, H$_1$ 2.650d+d, $^3J(^1\text{H-}^1\text{H})$ = 5.7 Hz, $^3J(^{195}\text{Pt-H}_1)$ = 40 Hz. ^{13}C NMR (ppm): C$_1$ 44.553, $^2J(^{195}\text{Pt-C}_1)$ = 25 Hz.

***cis*-Pt(Et$_2$NH)$_2$(NO$_3$)$_2$**

This compound was not synthesized from *cis*-Pt(Et$_2$NH)$_2$I$_2$ as the other *cis*-dinitrato complexes. The compound *trans*-Pt(Et$_2$NH)$_2$I$_2$ contained about 30% of the cis isomer. A mixture of the cis and trans isomers of Pt(Et$_2$NH)$_2$(NO$_3$)$_2$ was obtained. ^{1}H NMR for the cis isomer (ppm) δ: NH 5.836s+d, $^2J(^{195}\text{Pt-NH})$ = 67 Hz, H$_1$ 3.046tq, $^3J(^1\text{H-}^1\text{H})$ = 7.2 Hz, 6.6 Hz, H$_2$ 1.368t, $^3J(^1\text{H-}^1\text{H})$ = 6.6 Hz. ^{13}C NMR for the cis isomer: C$_1$ 51.350, $^2J(^{195}\text{Pt-C}_1)$ = 22 Hz, C$_2$ 15.220, $^3J(^{195}\text{Pt-C}_2)$ = 39 Hz.

***trans*-Pt(MeNH$_2$)$_2$(NO$_3$)$_2$**

Yield: 80%; dec 137–163 °C. IR (cm^{-1}): ν(N-H) 3260s, 3240s, 3150s, ν(C-H) 2985w, 2940m, 2890w, δ(N-H) 1595s, ν_4(NO$_3$) 1503s, δ(C-H) 1455m, 1420w, 1355m, ν_2(NO$_3$) 1251s, ν(C-N) 1095s, 1055s, ν_1(NO$_3$) 966s, ν_6(NO$_3$) 775s, ν_5(NO$_3$) 709s, ν(Pt-N) 505m, ν(Pt-O) 350m; other bands: 1020m. ^{1}H NMR (ppm) δ: NH 4.737s+d, $^2J(^{195}\text{Pt-NH})$ = 57 Hz, H$_1$ 2.327 t+d, $^3J(^1\text{H-}^1\text{H})$ = 6.6 Hz, $^3J(^{195}\text{Pt-H}_1)$ = 32 Hz. ^{13}C NMR (ppm) δ: C$_1$ 32.380, $^2J(^{195}\text{Pt-C}_1)$ = 20 Hz.

***trans*-Pt(EtNH$_2$)$_2$(NO$_3$)$_2$**

Yield: 83%; dec 120–157 °C. IR (cm^{-1}): ν(N-H) 3280s, 3240s, 3150m, ν(C-H) 2960m, 2930w, 2870w, δ(N-H) 1585s, ν_4(NO$_3$) 1512s, δ(C-H) 1485m, 1470m, 1380m, ν_2(NO$_3$) 1268s, ν(C-N) 1115m, 1075w, 1050w, ν_1(NO$_3$) 967s, ν_6(NO$_3$) 785w, ν_5(NO$_3$) 705w, ν(Pt-N) 465w, ν(Pt-O) 333m; other bands: 1000s, 885w, 740m. ^{1}H NMR (ppm) δ: NH 4.764s+d, $^2J(^{195}\text{Pt-NH})$ = 59 Hz, H$_1$ 2.665tq, $^3J(^1\text{H-}^1\text{H})$ = 7.5 Hz, 7.2 Hz, H$_2$ 1.321t, $^3J(^1\text{H-}^1\text{H})$ = 7.2 Hz. ^{13}C NMR (ppm) δ: C$_1$ 41.229, $^2J(^{195}\text{Pt-C}_1)$ = 19 Hz, C$_2$ 15.487, $^3J(^{195}\text{Pt-C}_2)$ = 30 Hz. Anal. calcd. (%): C 11.74, H 3.45, N 13.69; found: C 11.69, H 3.32, N 13.06.

***trans*-Pt(*n*-PrNH$_2$)$_2$(NO$_3$)$_2$**

Yield: 79%; dec 138–152 °C. IR (cm^{-1}): ν(N-H) 3260s, 3230s, 3210s, ν(C-H) 2980s, 2930m, 2880w, δ(N-H) 1580m, ν_4(NO$_3$) 1508s, δ(C-H) 1430w, 1385s, ν_2(NO$_3$) 1261s, ν(C-N) 1100w, 1080m, 1055w, ν_1(NO$_3$), 965s, ν_6(NO$_3$) 785m, ν_5(NO$_3$) 700w, ν(Pt-N) 410w, ν(Pt-O) 338m; other bands: 1025m, 885w, 835w, 760w. ^{1}H NMR (ppm) δ: NH 4.759s+d, $^2J(^{195}\text{Pt-NH})$ = 57 Hz, H$_1$ 2.584tt, $^3J(^1\text{H-}^1\text{H})$ = 7.5 Hz, 6.9 Hz, H$_2$ 1.805 tq, $^3J(^1\text{H-}^1\text{H})$ = 7.5 Hz, 7.2 Hz, H$_3$ 0.938t, $^3J(^1\text{H-}^1\text{H})$ = 7.2 Hz. ^{13}C NMR (ppm) δ: C$_1$ 48.241, $^2J(^{195}\text{Pt-C}_1)$ = 16 Hz, C$_2$ 24.048, $^3J(^{195}\text{Pt-C}_2)$ = 29 Hz, C$_3$ 11.329.

***trans*-Pt(*n*-BuNH$_2$)$_2$(NO$_3$)$_2$**

Yield: 83%; dec 135–146 °C. IR (cm^{-1}): ν(N-H) 3240s, 3140m, ν(C-H) 2960s, 2930m, 2870m, δ(N-H) 1595s, ν_4(NO$_3$) 1510s, δ(C-H) 1480s, 1385s, ν_2(NO$_3$) 1260s, ν(C-N) 1150w, 1115w, 1075w, ν_1(NO$_3$) 962s, ν_6(NO$_3$) 788w, ν_5(NO$_3$) 702w, ν(Pt-N) 460w, ν(Pt-O) 337w; other bands: 1000s, 895w, 830w. ^{1}H NMR (ppm) δ: NH 4.746s+d, $^2J(^{195}\text{Pt-NH})$ = 56 Hz, H$_1$ 2.622tt, $^3J(^1\text{H-}^1\text{H})$ = 7.5 Hz, 6.9 Hz, H$_2$ 1.787tt, $^3J(^1\text{H-}^1\text{H})$ = 7.5 Hz, 7.2 Hz, H$_3$ 1.385tq, $^3J(^1\text{H-}^1\text{H})$ = 7.5 Hz, 7.2 Hz, H4 0.910t, $^3J(^1\text{H-}^1\text{H})$ = 7.2 Hz. ^{13}C NMR (ppm) δ: C$_1$ 46.146, $^2J(^{195}\text{Pt-C}_1)$ = 16 Hz, C$_2$ 32.942, $^3J(^{195}\text{Pt-C}_2)$ = 26 Hz, C$_3$ 20.466, C4 14.030. Anal. calcd. (%): C 20.65, H 4.77, N 12.04; found: C 21.09, H 5.17, N 12.03.

***trans*-Pt(*i*-PrNH$_2$)$_2$(NO$_3$)$_2$**

Yield: 80%; dec 144–163 °C. IR (cm^{-1}): ν(N-H) 3305s, ν(C-H) 3080w, 3060w, 3010m, δ(N-H) 1575s, ν_4(NO$_3$) 1510s, δ(C-H) 1475w, 1450m, 1395w, ν_2(NO$_3$) 1266s, ν(C-N) 1170m, 1130s, 1090w, 1055s, ν_1(NO$_3$) 961s, ν_6(NO$_3$) 795m, ν_5(NO$_3$) 700w, ν(Pt-N) 550m, ν(Pt-O) 375m; other bands: 1000s, 930m, 750m. ^{1}H NMR (ppm) δ: NH 4.738s+d, $^2J(^{195}\text{Pt-NH})$ = 59 Hz, H$_1$ 2.933thept, $^3J(^1\text{H-}^1\text{H})$ = 7.2 Hz, 6.6 Hz, H$_2$ 1.380d, $^3J(^1\text{H-}^1\text{H})$ = 6.6 Hz. ^{13}C NMR (ppm) δ: C$_1$ 48.514, $^2J(^{195}\text{Pt-C}_1)$ = 15 Hz, C$_2$ 23.076, $^3J(^{195}\text{Pt-C}_2)$ = 26 Hz.

***trans*-Pt(*i*-BuNH$_2$)$_2$(NO$_3$)$_2$**

Yield: 78%; dec 128–141 °C. IR (cm^{-1}): ν(N-H) 3280s, 3250s, 3150w, ν(C-H) 2970m, 2930m, 2880w, δ(N-H) 1585m, ν_4(NO$_3$) 1510s, δ(C-H) 1480m, 1465m, 1385s, ν_2(NO$_3$) 1266s, ν(C-N) 1115m, 1070w, ν_1(NO$_3$) 965m, ν_6(NO$_3$) 785w, ν_5(NO$_3$) 700w, ν(Pt-N) 470w, ν(Pt-O) 345m, other bands: 1045w, 1000s, 880w, 830w, 745m. ^{1}H NMR (ppm) δ: NH 4.714s+d, $^2J(^{195}\text{Pt-NH})$ = 57 Hz, H$_1$ 2.481td, $^3J(^1\text{H-}^1\text{H})$ = 6.9 Hz, 6.3 Hz, H$_2$ 2.131thept, $^3J(^1\text{H-}^1\text{H})$ = 6.6 Hz, 6.3 Hz, H$_3$ 0.962d, $^3J(^1\text{H-}^1\text{H})$ = 6.6 Hz. ^{13}C NMR (ppm) δ: C$_1$ 55.948, $^2J(^{195}\text{Pt-C}_1)$ = 15 Hz, C$_2$ hidden by the solvent, C$_3$ 20.223.

***trans*-Pt(*sec*-BuNH$_2$)$_2$(NO$_3$)$_2$**

Yield: 85%; dec 132–148 °C. IR (cm^{-1}): ν(N-H) 3260s, 3230s, 3160m, ν(C-H) 2960s, 2940m, 2870w, δ(N-H) 1600m, ν_4(NO$_3$) 1502s, δ(C-H) 1455m, 1370s, ν_2(NO$_3$) 1255s, ν(C-N) 1150w, 1122m, 1075m, ν_1(NO$_3$) 967s, ν_6(NO$_3$) 788w, ν_5(NO$_3$) 710w, ν(Pt-N) 470w, ν(Pt-O) 345m; other bands: 1035w, 900w, 830w. ^{1}H NMR (ppm) δ: NH 4.720s+d, $^2J(^{195}\text{Pt-NH})$ = 58 Hz, H$_1$ 2.662ttq, $^3J(^1\text{H-}^1\text{H})$ =

7.2 Hz, 6.6 Hz, 6.3 Hz, H$_2$ 1.596dq, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.9 Hz, 6.6 Hz, H$_{2'}$ 1.381d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6,6 Hz, H$_3$ 0.951t, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.9 Hz. ^{13}C NMR (ppm) δ: C$_1$ 54.008, $^2J(^{195}\mathrm{Pt}\text{-}\mathrm{C}_1)$ = 15 Hz, C$_2$ hidden by the solvent, C$_{2'}$ 20.041, $^3J(^{195}\mathrm{Pt}\text{-}\mathrm{C}_{2'})$ = 27 Hz, C$_3$ 10.585.

trans-Pt(*t*-BuNH$_2$)$_2$(NO$_3$)$_2$

Yield: 76%; dec 111–134 °C. IR (cm^{-1}): ν(N-H) 3270s, 3250s, 3170m, ν(C-H) 2980m, 2930w, 2880w, δ(N-H) 1600s, ν_4(NO$_3$) 1495s, δ(C-H) 1455w, 1380m, 1355m, ν_2(NO$_3$) 1265s, ν(C-N) 1080s, ν_1(NO$_3$) 970s, ν_6(NO$_3$) 783s, ν_5(NO$_3$) 710w, ν(Pt-O) 345m; other bands: 1030s, 880w, 740w, 605w. ^{1}H NMR (ppm) δ: NH 4.808s+d, $^2J(^{195}\mathrm{Pt}\text{-}\mathrm{NH})$ = 59 Hz, H$_2$ 1.385s, $^4J(^{195}\mathrm{Pt}\text{-}\mathrm{H}_2)$ = 15 Hz. ^{13}C NMR (ppm) δ: C$_1$ 55.721, $^2J(^{195}\mathrm{Pt}\text{-}\mathrm{C}_1)$ = 11 Hz, C$_2$ 31.763, $^3J(^{195}\mathrm{Pt}\text{-}\mathrm{C}_2)$ = 19 Hz.

trans-Pt(Me$_2$NH)$_2$(NO$_3$)$_2$

Yield: 86%; dec 132–159 °C. IR (cm^{-1}): ν(N-H) 3225s, 3200s, ν(C-H) 2980w, 2940m, 2920m, δ(N-H) 1540m, ν_4(NO$_3$) 1512s, δ(C-H) 1465s, 1430w, 1395w, 1355s, ν_2(NO$_3$) 1260s, ν(C-N) 1140m, 1095s, 1080s, ν_1(NO$_3$) 960s, ν_6(NO$_3$) 778s, ν_5(NO$_3$) 703m, ν(Pt-N) 510m, ν(Pt-O) 347m; other bands: 1015s, 935s, 890s, 835w. ^{1}H NMR (ppm) δ: NH 5.500s+d, $^2J(^{195}\mathrm{Pt}\text{-}\mathrm{NH})$ = 58 Hz, H$_1$ 2.478d+d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.0 Hz, $^3J(^{195}\mathrm{Pt}\text{-}\mathrm{H}_1)$ = 33 Hz. ^{13}C NMR (ppm) δ: C$_1$ 42.883, $^2J(^{195}\mathrm{Pt}\text{-}\mathrm{C}_1)$ = 18 Hz.

trans-Pt(Et$_2$NH)$_2$(NO$_3$)$_2$

This compound was found to be a cis–trans mixture. Yield: 80%; dec 124–143 °C. IR (cm^{-1}): ν(N-H) 3280s, 3175m, ν(C-H) 2980m, 2885m, δ(N-H) 1575s, ν_4(NO$_3$) 1510s, δ(C-H) 1475m, 1455w, 1375m, ν_2(NO$_3$) 1267s, ν(C-N) 1210m, 1065w, ν_1(NO$_3$) 964s, ν_6(NO$_3$) 780w, ν_5(NO$_3$) 705w, other bands: 1005s, 865w, 755w. ^{1}H NMR of the trans isomer (ppm) δ: NH 5.519s+d, $^2J(^{195}\mathrm{Pt}\text{-}\mathrm{NH})$ = 58 Hz, H$_1$ 2.955tq, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 7.5 Hz, 6.9 Hz, H$_2$ 1.344t, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H})$ = 6.9 Hz. ^{13}C NMR of the trans isomer (ppm) δ: C$_1$ 50.834, $^2J(^{195}\mathrm{Pt}\text{-}\mathrm{C}_1)$ = 14 Hz, C$_2$ 15.099, $^3J(^{195}\mathrm{Pt}\text{-}\mathrm{C}_2)$ = 28 Hz.

Results and discussion

The dinitrato complexes were prepared by the reaction of the diiodo complexes with a slight excess (10%) of silver nitrate in acetone similar to a published method (12).

$$\mathrm{Pt(amine)_2I_2 + 2AgNO_3 \rightarrow Pt(amine)_2(NO_3)_2 + 2AgI\downarrow}$$

The diiodo complexes dissolved in acetone resulting in a yellow solution. Silver nitrate is only slightly soluble in acetone. The reaction was performed in the dark and at a lower temperature in ice, to reduce decomposition. The published method (12), which was used for other ligands, required 5–20 min of stirring time. The reaction time for our ligands varied between a few hours to 2 days depending on the amine. After filtration and the purification process, the white dinitrato complexes were isolated and characterized. The cis or trans geometry was retained during the reaction. The cis and trans compounds with amine = methylamine (MeNH$_2$), ethylamine (EtNH$_2$), *n*-propylamine (*n*-PrNH$_2$), *n*-butylamine (*n*-BuNH$_2$), *iso*-propylamine (*i*-PrNH$_2$), *iso*-butylamine (*i*-BuNH$_2$), *sec*-butylamine (*sec*-BuNH$_2$), dimethylamine (Me$_2$NH), and trans compounds with *tert*-butylamine (*t*-BuNH$_2$) and diethylamine (Et$_2$NH) were synthesized.

The use of a slight excess of silver nitrate increased the yields. When the reactions were performed at room temperature, oily compounds were obtained and the products decomposed quite rapidly. The yields were also very low. Most dinitrato complexes are stable when kept in the dark and at lower temperature. Even in these conditions, a few compounds decomposed fairly rapidly to a black material. The complex *cis*-Pt(*i*-BuNH$_2$)$_2$(NO$_3$)$_2$ decomposed after a few hours. All the IR and NMR spectra were measured on fresh samples. The compound *trans*-Pt(Et$_2$NH)$_2$(NO$_3$)$_2$ was not pure, since two series of signals were observed in NMR (^{1}H, ^{13}C, and ^{195}Pt) spectroscopy. The second compound was assumed to be the cis analogue, since the starting material *trans*-Pt(Et$_2$NH)$_2$I$_2$ contained some cis isomers as described in a previous paper (11).

IR spectroscopy

The IR spectra of the complexes were recorded and are listed in the *Experimental* section. The notation of Nakamoto (13) was used for the bands involving the nitrato ligands.

The symmetry of the free nitrate ion is D_{3h}, with a bond order of 1 1/3. However, in the monodentate-coordinated nitrato ligand, the N—O(Pt) bond order is close to 1. The π electronic density is then delocalized on only two N—O bonds resulting in a bond order of 1 1/2 for the two bonds. The approximate symmetry of coordinated NO$_3^-$ is C_{2v}. The reduction in the N—O(Pt) bond order is clearly observed by comparing the stretching band ν_1 (13) in free NO$_3^-$ (1049 cm^{-1}) with the one observed in CH$_3$ONO$_2$ (854 cm^{-1}), a purely covalent compound (14). It has been suggested that the position of the ν_1 band gives important information on the covalent character of the Pt—O bond (15). Because of the reduction in symmetry of the coordinated nitrato ligand, some of the vibration modes, which were degenerate in the free ion, will be split. This is the case for the ν_3 stretching mode in D_{3h} (E), which will separate into the ν_2 (A$_1$) and ν_4 (B$_2$) stretching modes in C_{2v} symmetry (13). The energy difference between the two latter modes ($\Delta = \nu_4 - \nu_2$) should also give additional information on the covalent character of the Pt—O bond (14, 15). For ionic nitrate Δ is 0 cm^{-1}, while it is 385 cm^{-1} in CH$_3$ONO$_2$.

The values of Δ as well as the energy difference ($\Delta\nu_1$) between the ν_1 band for free nitrate and the coordinated nitrato ligands are shown in Table 1. The average value $\Delta(\nu_4 - \nu_2)$ is 243 cm^{-1} in the *cis* complexes and 246 cm^{-1} in the trans isomers. The difference is not significant. We have calculated this $\Delta(\nu_4 - \nu_2)$ value for a few dinitrato complexes reported in the literature. These values for *cis*-PtA$_2$(NO$_3$)$_2$ are 230 cm^{-1} for A = NH$_3$ (16), 227 cm^{-1} for NH$_2$CH$_3$ (12), 214 cm^{-1} for NH$_2$(C$_6$H$_{11}$) (12), 226 cm^{-1} for 4-hydroxymethylpyridine (12), and 238 cm^{-1} for NH$_2$(CH$_2$Ph) (12), and 245 cm^{-1} for A$_2$ = bipy and 240 cm^{-1} for phen (14). These results are close to our values. In a study on *cis*- and *trans*-Pt(Ypy)$_2$NO$_3$)$_2$, (Ypy = pyridine derivative) the average value for $\Delta(\nu_4 - \nu_2)$ was found to be higher in the

Table 1. $\Delta(\upsilon_4 - \upsilon_2)$ and $\Delta\upsilon_1$ (cm^{-1}) (as defined in the text) of the complexes of $Pt(amine)_2(NO_3)_2$.

	cis-$Pt(amine)_2(NO_3)_2$		*trans*-$Pt(amine)_2(NO_3)_2$	
Amine	$\Delta(\upsilon_4 - \upsilon_2)$	$\Delta\upsilon_1$	$\Delta(\upsilon_4 - \upsilon_2)$	$\Delta\upsilon_1$
$MeNH_2$	241	84	252	83
$EtNH_2$	249	84	244	82
n-$PrNH_2$	245	87	247	84
n-$BuNH_2$	248	84	250	87
i-$PrNH_2$	248	89	244	88
i-$BuNH_2$	240	100	244	84
sec-$BuNH_2$	231	84	247	82
t-$BuNH_2$			230	79
Me_2NH	243	100	252	89

Table 2. υ(Pt-O) (cm^{-1}) vibrations in $Pt(amine)_2(NO_3)_2$ and some examples from the literature.

Amine	cis	trans	Reference
NH_3	330		18
$MeNH_2$	332		19
$C_6H_{11}NH_2$	334, 340	345	19
$PhCH_2NH_2$	350, 360		19
2,2′-Bipyridine	340, 350		19
4-Hydroxymethylpyridine	338, 346		19
Pyridine	341, 325	360	17
4-Picoline	338	350	19
	338	353	17
2-Picoline	340, 350	330	17
3-Picoline	330, 339	349	17
2,4-Lutidine	343	340	17
3,5-Lutidine	330, 337	351	17
$MeNH_2$	335	350	
$EtNH_2$	330	333	
n-$PrNH_2$	332	338	
n-$BuNH_2$	330	337	
i-$PrNH_2$	330	375	
i-$BuNH_2$	335	345	
sec-$BuNH_2$	335	345	
t-$BuNH_2$		345	
Me_2NH	342	347	
Et_2NH		340 (Mixture)	

trans compounds (264 cm^{-1}) than in the cis isomers (233 cm^{-1}) (17).

The position of ν_1 for our compounds is also not very different in the two geometries (avg. $\Delta\upsilon_1$ 89 cm^{-1} for cis and 84 cm^{-1} for trans). For the compounds *cis*- and *trans*-$Pt(Ypy)_2NO_3)_2$, the ν_1 band was found to be less energetic in the trans complexes (avg. $\Delta\upsilon_1$ = 120 vs. 90 cm^{-1} for the cis isomers), suggesting a more covalent character for the Pt—O bonds in the trans geometry (17). Our results on the amine system seem to indicate that the covalency of the Pt—O bonds in the cis and trans compounds are not very different.

The stretching energy of a more covalent bond should increase and these results can be compared with the energies of the ν(Pt-O) vibrations. The skeletal symmetry around the platinum atom is C_{2v} for the cis complexes and D_{2h} for the trans isomers. Two ν(Pt-O) bands are expected for the cis compounds and one for the trans complexes, according to group theory. Our assignment of the υ(Pt-O) bonds was made according to some published works (17–19). These bands are shown in Table 2 along with the results published in the literature. Some of the published work on the cis complexes have shown two ν(Pt-O) absorption bands, while others have shown only one. We have observed only one band for both isomers. The position of the band is not very different for the different isomers, although it appears slightly larger for the trans compounds (avg. 346 vs. 333 cm^{-1}). These results seem to agree with our conclusion reached above from the study of the nitrato ν_1 band and $\Delta(\nu_4 - \nu_2)$ values. There seems to be no important difference between the two isomers. These ν(Pt-O) vibrations are not very energetic and are close to the ν(Pt-Cl) vibrations. They are difficult to assign with certainty, since they are quite weak. It is also possible that they are not pure and might couple with other vibrations.

The ν(Pt-N) bands were assigned based on some published works (13, 19–22). Two vibration modes are expected for the cis compounds and only one for the trans isomers. Our assignments are shown in Table 3. For most complexes, two bands were observed for the cis complexes while only one was shown by the trans isomers. The energies of these bands are slightly higher than those of the corresponding iodo complexes (11), suggesting that the covalency of the Pt—N bonds are greater in the dinitrato compounds than in the diiodo analogues. The reduced polarizability of the nitrato ligand compared to the iodo ligand could increase the energy of the ν(Pt-N) vibrations. The trans influence of the iodo ligand is larger than the one of the nitrato ligand, which should also increase the energy of the ν(Pt-N) vibrations in the *cis*-dinitrato complexes. The trans compounds with *tert*-butylamine and diethylamine and the *cis*-*iso*-butylamine compound did not show any band in the ν(Pt-N) region.

^{195}Pt NMR spectroscopy

The ^{195}Pt NMR spectra of the dinitrato complexes were measured in acetone and the chemical shifts are listed in Table 4 as well as the pK_a of the protonated ligands (23) and the proton affinity of the amines (24–27). To determine if the nitrato ligands are partly dissociated in acetone, the conductivity of several cis and trans complexes were measured in acetone. The results have shown that there is no appreciable solvolysis of the compounds. The molar conductivity values varied between 0.03 and 0.06 S cm^2/mol. The corresponding values for several cesium salts were much larger. Therefore, the chemical shifts in Table 4 correspond to those of the dinitrato complexes.

The cis isomers were observed at higher fields than their trans analogues. The complex *trans*-$Pt(Et_2NH)_2(NO_3)_2$ contained a second compound, which we have assigned to the cis isomer, since the starting material *trans*-$Pt(Et_2NH)_2I_2$ was shown to contain some cis compound (11). The signal observed at higher field was assumed to be the cis compound as observed for the other ligands. The difference between the cis and trans isomers is larger for the primary amines (avg. 125 ppm) than for the secondary amines (avg.

Table 3. υ(Pt-N) (cm^{-1}) bands for the complexes of Pt(amine)$_2$(NO$_3$)$_2$.

Amine	cis		trans
	ν_s	ν_{as}	ν_{as}
NH$_3$ (28)	562	558	
MeNH$_2$	535	515	505
EtNH$_2$	530	460	465
n-PrNH$_2$		435	410
n-BuNH$_2$	530	465	460
i-PrNH$_2$		440	550
i-BuNH$_2$			470
sec-BuNH$_2$	460	430	470
Me$_2$NH	440	405	510

Table 4. δ(^{195}Pt) and $\Delta\delta = \delta_{cis} - \delta_{trans}$ (ppm) of the complexes of Pt(amine)$_2$(NO$_3$)$_2$. (PA = proton affinity, kJ/mole).

Amine	PA	pK_a	cis	trans	$\Delta\delta$
NH$_3$ (DMF)	854	9.25	–1592 (28)	–1413 (28)	–179
MeNH$_2$	914	10.62	–1713	–1608	–105
EtNH$_2$	930	10.67	–1707	–1579	–128
n-PrNH$_2$	933	10.71	–1694	–1577	–117
n-BuNH$_2$	924	10.78	–1699	–1574	–125
i-PrNH$_2$		10.63	–1698	–1558	–140
i-BuNH$_2$		10.72	–1694	–1572	–122
sec-BuNH$_2$		10.56	–1683	–1548	–135
t-BuNH$_2$		10.68		–1540	
Me$_2$NH		10.73	–1696	–1675	–21
Et$_2$NH		11.04	–1668*	–1601	–67

Note: PA is the proton affinity (kJ/mol).
*Indicates an impurity in the trans compound (see text).

44 ppm). Our results are in agreement with those of the NH$_3$ complexes (28).

Surprisingly, the trans isomers of the complexes containing the secondary amines were observed at higher fields than the compounds containing the primary amines, while the cis compounds were observed at about the same fields. For square-planar complexes, the molecules of solvent can normally approach and weakly bind to the Pt atom on both sides of the coordination plane. For complexes containing more bulky ligands close to the binding site, the molecules of solvent cannot approach the Pt atom easily, resulting in a decrease of the electronic density around the Pt nucleus. This solvent factor is very important for solvents like water that can coordinate to platinum. However, the dinitrato complexes were measured in deuterated acetone, a solvent that could coordinate to Pt, but not as easily as water. Therefore the solvent effect should be considerably reduced. Furthermore, the reduced solvation for crowded ligands is less important in trans compounds, where the two ligands are far from each other.

Nitrato ligands are more bulky than iodo or chloro ligands. Therefore, the presence of the nitrato ligands should have an influence of the solvation of the Pt atom. There are two Pt NMR studies in the literature on dinitrato compounds. The results for the NH$_3$ (28) complexes are shown in Table 4. NH$_3$ complexes are usually observed at lower fields than amine complexes. The other published paper is on a series of pyridine complexes (17). In these compounds, the cis compounds were observed between –1485 and –1532 ppm, while the trans isomers were reported between –1402 and –1481 ppm, with $\Delta\delta$ (cis–trans) = –43 to –83 ppm. The compounds with ortho substituents were observed at lower fields than the others, probably because of reduced solvation around the Pt atom, due to a more limited rotation of the pyridine ligand around the Pt—N bond (17). The ortho substituents are mainly located on top of the Pt atom and prevent the approach of the molecules of solvent. Our results on the diamine complexes have shown values of $\Delta\delta$ (cis–trans) from –105 to –140 ppm for the primary amines. The difference is larger than those published for the pyridine complexes (17), but smaller than the one for the NH$_3$ compounds (28), where it is 179 ppm. Our values for the secondary amines (avg. 44 ppm) are closer to those reported for the pyridine system (17).

There seems to be a slight deshielding effect on the Pt atom as the bulkiness on the primary amine is increased. This is probably due to a reduction in the solvation of the metal centre. The difference in chemical shifts is smaller in the cis compounds (30 ppm) than in the trans isomers (68 ppm) for the complexes containing primary amines.

Attempts were made in the literature (29–31) to correlate the ^{195}Pt chemical shifts with the basicity of the amine ligands to study the nature of the Pt–amine bond. Contrary to pyridine, amines cannot accept π electron density from the metal. Therefore, in the formation of the σ(amine $\rightarrow$ Pt) bond, electron density is transferred from the amine ligand to the platinum nucleus, resulting in a shielding on the ^{195}Pt nucleus and a deshielding effect on the ligands (^{1}H and ^{13}C NMR signals). A weak relation between δ(^{195}Pt) and the basicity of the ligands was reported for complexes of the type *cis*- and *trans*-Pt(Ypy)$_2$X$_2$ (X = Cl$^-$ or I$^-$) (29), but the dispersion around the straight line was fairly large. For pyridine derivatives, the ^{195}Pt chemical shifts seem to depend more on the position of the CH$_3$ substituents then on the basicity of the ligand. To verify the influence of the basicity of the amine on the δ(Pt) values, the latter were plotted vs. the pK_a of the protonated amines. No correlation could be observed for the cis or the trans compounds. The pK_a values were measured in a solvent (water or alcohol) and are influenced by the presence of the substituents on the protonated N atom. The errors on the pK_a values are not negligible, especially for the primary amines where the pK_a values do not vary very much (from 10.62 to 10.78). The proton affinity values of the amines that are measured in the gas phase, might represent better the basicity of the ligands. But these values are not as common as the pK_a values. Figure 1 shows the relation between the δ(Pt) and the published proton affinity of the amines (24–27) for the cis and trans complexes. The ^{195}Pt chemical shift seems to increase slightly as the proton affinity increases. But the difference is small, close to the experimental errors. More data are needed to reach a sound conclusion.

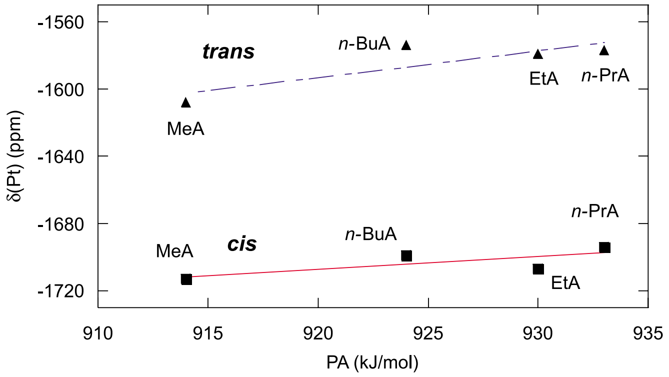
The δ(Pt) does not seem to be very influenced by the basicity of the ligands. Acetone is not an inert solvent for platinum, and solvation around the Pt atom is probably a more

Table 5. $\delta(^1H)$ (ppm) and $J(^{195}Pt\text{-}H_1)$ (Hz) of $Pt(amine)_2(NO_3)_2$ in CD_3COCD_3.

Amine		NH	H_1	H_2	H_3	H_4 or $H_{2'}$	$^2J(^{195}Pt\text{-}NH)$	$^3J(^{195}Pt\text{-}H_1)$
$MeNH_2$	cis	5.177	2.466				69	47
	trans	4.737	2.327				57	32
EtH_2	cis	5.164	2.763	1.308			68	
	trans	4.764	2.665	1.321			59	
n-$PrNH_2$	cis	5.160	2.682	1.774	0.933		68	
	*	4.600	2.700	1.700	0.940		65*	
	trans	4.759	2.584	1.805	0.938		57	
	*	3.850	2.700	1.750	0.960		65*	
n-$BuNH_2$	cis	5.153	2.719	1.745	1.376	0.900	66	
	trans	4.746	2.622	1.787	1.385	0.910	56	
i-$PrNH_2$	cis	5.088	2.993	1.397			67	
	trans	4.738	2.933	1.380			59	
i-$BuNH_2$	cis	5.157	2.594	2.096	0.953		65	37
	trans	4.714	2.481	2.131	0.962		57	
sec-$BuNH_2$	cis	5.117	2.712	1.543	0.941	1.404	65	35
	trans	4.720	2.662	1.596	0.951	1.381	58	
Me_2NH	cis	5.998	2.650				69	40
	trans	5.500	2.478				58	33
t-$BuNH_2$	trans	4.808		1.385			59	
Et_2NH	cis‡	5.836	3.046	1.368			67	
	trans	5.519	2.955	1.344			58	

*In $CDCl_3$ (32).
‡See text.

Fig. 1. $\delta(^{195}Pt)$ vs. proton affinity (PA) of the amine for the complexes of $Pt(amine)_2(NO_3)_2$.



important factor in determining the NMR chemical shifts. The trans complexes with secondary amines have shown resonances at higher fields than those with primary amines, but more complexes with secondary amines are needed before any conclusion can be reached.

^1H and ^{13}C NMR spectroscopy

The ^1H NMR chemical shifts are listed in Table 5 as well as the published values on $Pt(n\text{-}PrNH_2)_2(NO_3)_2$ measured in $CDCl_3$ (32). These authors have also measured their compounds in CD_3COCD_3, but only the $-NH_2$ are reported at 5.2 (cis) and 4.7 (trans) ppm (32). These values agree with ours. There are not many data in the literature on dinitrato amine complexes. The NH and H_1 chemical shifts of the cis compounds are more deshielded than the corresponding values for the trans isomers. These results are in agreement with the δ(Pt), where the cis compounds were observed at higher fields than the corresponding trans isomers. A larger reduction of electron density on the ligand in the cis compounds should be associated with a larger electron density on the platinum atom (δ(Pt) at higher fields). Therefore, the σ bonds seem stronger in the cis compounds than in the trans isomers.

For the chiral ligand, *sec*-butylamine, only one series of signals was observed in the ^1H NMR for both isomers. For the compound identified as *trans*-$Pt(Et_2NH)_2(NO_3)_2$, two series of signals were observed as in ^{195}Pt NMR. The second series was assigned to the cis isomer as discussed above.

All the NH $^2J(^{195}Pt\text{-}^1H)$ coupling constants could be calculated. They are larger in the cis configuration where the average value is 67 Hz compared to 58 Hz (avg.) for the trans isomers. These values were found to be 67 Hz (cis) and 59 Hz (trans) for the corresponding diiodo complexes (11). The $^3J(^{195}Pt\text{-}^1H)$ coupling constants also depend on the geometry of the complex. They range between 35 and 47 Hz for the cis complexes and between 32 and 33 Hz for the trans compounds. These values are difficult to measure, since the signals are often multiplets of low intensity. These values agree with those reported for other similar complexes (11, 12, 17, 29, 33). One $^4J(^{195}Pt\text{-}^1H_2)$ coupling constant for *trans*-$Pt(t\text{-}BuNH_2)_2(NO_3)_2$ could be measured (15 Hz).

The ^{13}C NMR chemical shifts as well as the $J(^{195}Pt\text{-}^{13}C)$ coupling constants are listed in Table 6. The ^{13}C NMR signals of C_1 and C_2 are more deshielded for the cis complexes than those of the trans analogues. This is consistent with the more upfield ^{195}Pt chemical shifts observed for the cis complexes and with the results obtained in ^1H NMR.

The $^2J(^{195}Pt\text{-}^{13}C)$ and $^3J(^{195}Pt\text{-}^{13}C)$ coupling constants are also dependent on the geometry of the compounds. For the

Table 6. $\delta(^{13}C)$ (ppm) and $J(^{195}Pt\text{-}^{13}C)$ (Hz) of $Pt(amine)_2(NO_3)_2$ in CD_3COCD_3.

Amine		C_1	C_2	C_3	C_4 or $C_{2'}$	$^2J(^{195}Pt\text{-}C_1)$	$^3J(^{195}Pt\text{-}C_2)$
$MeNH_2$	cis	34.460				25	
	trans	32.380				20	
$EtNH_2$	cis	43.172	15.776			24	42
	trans	41.229	15.487			19	30
n-$PrNH_2$	cis	50.017	24.336	11.177		20	40
	trans	48.241	24.084	11.329		16	29
n-$BuNH_2$	cis	48.028	33.199	20.344	13.970	21	39
	trans	46.146	32.942	20.466	14.030	16	26
i-$PrNH_2$	cis	50.123	23.198			22	30
	trans	48.514	23.076			15	26
i-$BuNH_2$	cis	55.693	*	20.101		21	
	trans	55.948		20.223		15	
sec-$BuNH_2$	cis	55.405	*	10.631	20.101	20	29
	trans	54.008		10.585	20.041	15	27
Me_2NH	cis	44.553				25	
	trans	42.883				18	
t-$BuNH_2$	trans	55.721	31.763			11	19
Et_2NH	cis‡	51.350	15.220			22	39
	trans	50.834	15.099			14	28

*Hidden by the solvent.
‡See text.

^3J the average value is 37 Hz for the cis complexes and 28 Hz for the trans isomers. The $^2J(^{195}Pt\text{-}^{13}C)$ coupling constants are smaller, probably because of inadequate orientation of the orbitals (30) as reported for other similar compounds. The average values are 18 Hz (cis) and 16 Hz (trans).

For the compound identified as *trans*-$Pt(Et_2NH)_2(NO_3)_2$, two series of signals were observed as in ^{195}Pt and ^1H NMR. The second series was assigned to the cis isomer as discussed above. For the chiral ligand, *sec*-butylamine, only one series of signals was observed in ^{13}C NMR for both isomers. For the diiodo analogues, some spectra with this ligand have shown two series of signals (11).

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