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Inorganica Chimica Acta 360 (2007) 461–472

Inorganica Chimica Acta

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Study of Pt(II)-aromatic amines complexes of the types *cis*- and *trans*-$Pt(amine)_2I_2$, $[Pt(amine)_4]I_2$ and $I(amine)Pt(\mu\text{-}I)_2Pt(amine)I$

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Received 20 July 2006; accepted 28 July 2006
Available online 12 August 2006

Abstract

Pt(II) complexes of the types *cis*- and *trans*-$Pt(amine)_2I_2$ with amines containing a phenyl group were synthesized and studied mainly by IR and multinuclear (^{195}Pt, ^{1}H and ^{13}C) magnetic resonance spectroscopies. The compounds are not very soluble. In ^{195}Pt NMR spectroscopy, the *cis* isomers were observed at slightly lower fields than the *trans* analogues (average $\Delta\delta = 11$ ppm) in acetone. In ^{1}H NMR, the NH groups were also found at slightly lower fields in the *cis* isomers. The coupling constants $^{2}J(^{195}Pt–^{1}HN)$ varied from 53 to 85 Hz and seem slightly smaller in the *trans* configuration. The ^{13}C NMR spectra of most of the complexes were measured. No coupling constants $J(^{195}Pt–^{13}C)$ were detected due to the low solubility of the compounds. The *cis* isomers containing a phenyl group on the N atom could not be isolated except for $Ph\text{-}NH_2$ which was shown to be a mixture of isomers in acetone. The tetrasubstituted ionic compounds $[Pt(amine)_4]I_2$ for the less crowded ligands were also studied mainly by NMR spectroscopy in aqueous solution. The ^{195}Pt chemical shifts vary between −2855 and −2909 ppm. The coupling constants $^{3}J(^{195}Pt–^{1}H)$ are about 40 Hz. The iodo-bridged dinuclear species I(amine)-$Pt(\mu\text{-}I)_2Pt(amine)I$ were also synthesized and characterized. Two isomers are present in acetone solution for most of the compounds. Their δ(Pt) signals were observed at about −4000 ppm and their coupling constants $^{2}J(^{195}Pt–^{1}HN)$ are around 69 Hz.

Keywords: Platinum; Aromatic amine; Iodo; NMR; IR; X-ray crystal structure; Dimers

1. Introduction

The antitumor properties of Pt(II) compounds have been known for several decades. The commercial compound *cisplatin* (*cis*-$Pt(NH_3)_2Cl_2$) is still one of the most widely used drugs in chemotherapy. A good review of the influence of the structure on the activity of Pt drugs has been published [1]. When the ligand NH_3 in *cisplatin* is replaced by primary amines, the antitumor properties can increase, especially with cyclic amines [2–5], but the latter compounds have often a more limited activity spectrum. Furthermore, several of the most active compounds are quite insoluble [6]. In the amine system, the most active compounds usually have the *cis* geometry, although a few *trans* compounds have been shown to possess some antitumor properties. Our research group has recently undertaken a systematic study on complexes of the types *cis*- and *trans*-$Pt(amine)_2I_2$ with different aliphatic amines [7,8]. We have transformed these complexes into *cis*- and *trans*-$Pt(amine)_2(NO_3)_2$, which have also been studied in the solid state by IR and in solution by ^{195}Pt, ^{1}H and ^{13}C NMR spectroscopy [8,9]. Conductivity measurements in acetone have shown that the dinitrato complexes are not dissociated. We have also recently reported Pt(II) complexes with primary amines and dicarboxylate ligands using a new method involving a Ag-dicarboxylato intermediate compound [10].

We have now started a similar study on Pt(II)-aromatic amine compounds. There are very few of these complexes reported in the literature. We have first synthesized the *cis* and *trans* diiodo compounds which were characterized by IR and by multinuclear magnetic resonance spectroscopies

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doi:10.1016/j.ica.2006.07.098

in order to determine the purity of the compounds. Two series of primary amines were studied. The first series, correspond to the amines containing a linear alkyl group between the phenyl and the amine group and are of the type Ph–X–NH$_2$ (X = methyl, ethyl, *n*-propyl and *n*-butyl). The second series include aniline (PhNH$_2$) and its *para* derivatives. A secondary amine PhNHMe was also investigated. The ligands of the second series are sterically more demanding around the N bonding atom than the first, while the steric hindrance is the greatest for the secondary amine PhNHMe.

The complexes *trans*-Pt(amine)$_2$I$_2$ with the less crowded ligands were synthesized from the tetrasubstituted intermediate complex [Pt(amine)$_4$]$^{2+}$. The latter were also characterized by NMR. The tetrasubstituted compounds cannot be isolated with the more bulky ligands. Therefore, only the complexes containing the amines of the first series could be studied.

The diiodo-bridged dimers I(amine)Pt(μ-I)$_2$Pt(amine)I are important molecules since they can be the starting material for many different compounds, especially the mixed-amines complexes [11,12]. For example, *cis*-Pt(NH$_3$)(2-picoline)Cl$_2$ was found quite active and it is currently in clinical trials [13,14]. The dinuclear species can also be the intermediate for the preparation of the monoamine compounds [Pt(amine)Cl$_3$]$^-$ [15]. The dimers are usually synthesized from Pt(amine)$_2$I$_2$ and the two types of complexes are very insoluble. Therefore, the reacting time must be very long (2–3 weeks). Furthermore, it is not easy to determine the end of the reaction. The diiodo-bridged dimers are usually brownish while the starting material is yellow, but the color of the mixture is not always a good criterion. We have now synthesized the dinuclear species with aromatic amines and their characterization and their purity are discussed below.

2. Experimental

K$_2$[PtCl$_4$] was purchased from Johnson–Matthey and was recrystallized in water before use. The amines were bought from Aldrich. D$_2$O and CD$_3$COCD$_3$ were obtained from CDN Isotopes.

The NMR spectra were measured on a Varian Gemini 300BB. The fields were 300.070, 75.460 and 64.311 or 64.267 MHz for ^{1}H, ^{13}C and ^{195}Pt, respectively. For the ^{195}Pt NMR spectra, K[Pt(DMSO)Cl$_3$] (−2998 ppm in D$_2$O) or *cis*-Pt(tetramethylenesulfoxide)$_2$Cl$_2$ (−3450 ppm in CDCl$_3$) were the external standards. The NMR spectra of the diiodo complexes and the iodo-bridged dimers were measured in CD$_3$COCD$_3$, while the tetrasubstituted compounds were studied in D$_2$O.

2.1. *cis-Pt(amine)$_2$I$_2$*

The compounds *cis*-Pt(amine)$_2$I$_2$ were synthesized as described in our recent publication on aliphatic amines [7,8], but with slight modifications. Since the amines are not soluble in water, they were dissolved in ethanol and the reactions were performed in a mixture of H$_2$O and ethanol.

cis-Pt(PhMeNH$_2$)$_2$I$_2$: Yield: 90%, m.p. 208–211 °C (dec.). IR (cm^{-1}): ν(N–H) 3255w, 3207m, 3190m, ν(=C–H) 3060w, ν(C–H) 2940vs, δ(N–H) 1569vs, other bands 1602s, 1493m, 1354m, 1219w, 1207w; 1197m, 1162w, 1155m, 1071m, 1028w, 1002w, 972s, 920m, 911m, 822w, 807w, 752s, 699s, 616w, 560w, 491w, 473m, 342w, 303w. NMR (δ(ppm)): ^{1}H: NH 4.827(s + d) $^2J(^{195}$Pt–N^{1}H) = 63 Hz, H$_1$ 3.994t, H$_2$–H$_3$–H$_4$ 7.283m; ^{13}C: C$_1$ 51.34, C$_2$ 139.17, C$_3$ 129.58, C$_4$ 129.78, C$_5$ 128.91.

cis-Pt(PhEtNH$_2$)$_2$I$_2$: Yield: 86%, m.p. 183–217 °C (dec.). IR (cm^{-1}): ν(N–H) 3263s, 3205m, 3189s, 3108w, ν(=C–H) 3024m, ν(C–H) 2982vs, 2908w, 2874w, 2845w, δ(N–H) 1561vs, other bands 1600w, 1561w, 1493s, 1454s, 1386w, 1330w, 1206m, 1181w, 1140w, 1074w, 1032s, 987s, 905w, 749w, 716m, 697s, 622w, 590w, 524w, 432w, 353w, 312w. NMR (δ(ppm)): ^{1}H: NH 4.525(s + d) $^2J(^{195}$Pt–N^{1}H) = 65 Hz, H$_1$ 3.238qt, H$_2$ 3.033t, H$_3$–H$_4$–H$_5$ 7.261m; ^{13}C: C$_1$ 48.85, C$_2$ 38.01, C$_3$ 138.96, C$_4$ 129.47, C$_5$ 129.62, C$_6$ 127.42.

cis-Pt(PhPrNH$_2$)$_2$I$_2$: Yield: 79%, m.p. 142–203 °C (dec.). IR (cm^{-1}): ν(N–H) 3253s, 3192m, 3161w, 3118w, ν(=C–H) 3078w, 3057w, 3021w, ν(C–H) 2970w, 2943w, 2918w, 2880w, 2856w, δ(N–H) 1569m, other bands 1601w, 1493m, 1462m, 1453m, 1374w, 1271w, 1203m, 1075w, 1027m, 1001w, 989s, 805w, 753s, 736m, 719s, 702m, 620w, 586m, 490m, 375w, 352w. NMR (δ(ppm)): ^{1}H: NH 4.447(s + d) $^2J(^{195}$Pt–N^{1}H) = 70 Hz, H$_1$ 2.967qt, H$_3$–H$_4$–H$_5$ 7.222m; ^{13}C: C$_1$ 58.78, C$_2$ 33.50, C$_3$ 47.57, C$_4$ 142.43, C$_5$ 129.29, C$_6$ 129.31, C$_7$ 126.87.

cis-Pt(PhBuNH$_2$)$_2$I$_2$: Yield: 65%, m.p. 177–201 °C (dec.). IR (cm^{-1}): ν(N–H) 3264m, 3229w, 3190s, 3111w, ν(=C–H) 3082w, 3058w, 3022w, ν(C–H) 2965w, 2929m, 2954w, δ(N–H) 1562w, other bands 1601w, 1582w, 1496m, 1452m, 1381w, 1178w, 1081w, 1041w, 1030w, 998m, 751s, 719s, 700s, 608w, 562w, 495w, 377w, 348w. NMR (δ(ppm)): ^{1}H: NH 4.450(s + d) $^2J(^{195}$Pt–N^{1}H) = 77 Hz, H$_1$ 3.003t, H$_2$–H$_3$ 1.696m, H$_4$ 2.634, H$_5$–H$_6$–H$_7$ 7.218m; ^{13}C: C$_1$ 59.10, C$_2$ 36.02, C$_3$ 31.58, C$_4$ 47.84, C$_5$ 143.04, C$_6$ 129.16, C$_7$ 129.30, C$_8$ 126.63.

cis-Pt(PhNH$_2$)$_2$I$_2$: Yield: 88%, m.p. 108–197 °C (dec.). IR (cm^{-1}): ν(N–H): 3219m, 3191m, 3121m, ν(=C–H) 3036w, δ(N–H): 1574s, other bands 1597m, 1561m, 1491s, 1463m, 1338w, 1209m, 1186s; 1156s, 1145s, 1067m, 1027m, 1004w, 974w; 906w, 800m, 753s, 722m, 685w, 618w, 575m, 558w, 538m, 437m, 365w, 302w. This compound is not stable in acetone.

2.2. *[Pt(amine)$_4$]I$_2$*

The tetrasubstituted compounds were synthesized by a slight variation of the Kauffman [16] method and more recently described by our group [7]. They were obtained only with the less sterically demanding ligands (series 1).

$[Pt(PhMeNH_2)_4]I_2$: Yield: 65%, m.p. 81–118 °C (dec.). IR (cm^{-1}): ν(N–H) 3145m, ν(=C–H) 3076s, 3044s, ν(C–H) 2933w, δ(N–H) 1584w, other bands 1603w, 1498w, 1358w, 1243m, 1204w, 1169w; 1155w, 1078w, 1026w, 1002w, 1028w, 1002w, 976m, 922w, 814w, 753w, 699s, 631w, 585w, 486w, 464w. 355w. NMR (δ(ppm)): ^1H: H_1 4.067s, $^3J(^{195}Pt–H_1) = 40$ Hz, $H_2–H_3–H_4$ 7.392m.

$[Pt(PhEtNH_2)_4]I_2$: Yield: 72%, m.p. 155–163 °C (dec.). IR (cm^{-1}): ν(N–H) 3163m, 3099vs, ν(=C–H) 3061vs, ν(C–H) 2948w, 2854s, δ(N–H) 1572m, other bands 1599m, 1495m, 1341w, 1222m, 1177w, 1157w; 1076w, 1027w, 1001w, 753s, 731w, 699s, 618w, 540m, 432w, 348w. NMR (δ(ppm)): ^1H: NH 4.92, H_1 3.195t (7.2 Hz), H_2 2.960t (7.2 Hz), $H_3–H_4–H_5$ 7.286m.

$[Pt(PhPrNH_2)_4]I_2$: Yield: 65%, m.p. 138–152 °C (dec.). IR (cm^{-1}): ν(N–H) 3147w, 3082vs, ν(=C–H) 3024vs, ν(C–H) 2932m, 2856w, δ(N–H) 1602m, other bands 1496s, 1452s, 1356w, 1204w, 1176w, 1154w; 1080w, 1031m, 1006w, 990w, 912w, 752s, 733m, 599w, 586w, 556w, 536w, 493w, 474w, 348w. NMR (δ(ppm)): ^1H: H_1 3.334t, H_2 1.281m, H_3 2.208t, $H_4–H_5–H_6$ 7.360m.

$[Pt(PhBuNH_2)_4]I_2$: Yield: 42%, m.p. 119–128 °C (dec.). IR (cm^{-1}): ν(N–H) 3144s, 3082s, ν(=C–H) 3036m, ν(C–H) 2934m, 2855m, δ(N–H) 1602m, other bands 1496m, 1452m, 1378w, 1218w, 1154w, 1080w, 1048w, 1027w, 1002w, 974w, 747s, 699s, 613w, 570w, 507w, 352w. NMR (δ(ppm)): ^1H: H_1 2.982t, H_2 1.269m, H_3 1.675m, H_4 2.675t, $H_5–H_6–H_7$ 7.340m.

2.3. $I(amine)Pt(\mu\text{-}I)_2Pt(amine)I$

The diiodo-bridged complexes were synthesized by slight variations of the published method [11,12,17]. The complex *cis*-PtL_2I_2 (0.2 mmol) was added to 5 mL ethanol and 1.5 mL of 0.67 M perchloric acid and mixed until the formation of a brown or orange precipitate (around two weeks). The yellow color of the starting material must have disappeared completely. The brownish product was filtered, washed with water and cold ethanol and dried under vacuum in a desiccator. The compound with the secondary amine PhNHMe was synthesized directly from the reaction of $K_2[PtI_4]$ with an excess of amine in water, as already described to synthesize *cis*-$Pt(amine)_2I_2$ [7,17]. The isolated product was a mixture of the *trans* monomer and the dimer. There are usually two isomers of the dinuclear species, the *cis* and the *trans* compounds. Furthermore, the $PhMeNH_2$ complex was contaminated with the *cis* monomer (60%). The ^1H NMR spectra of the mixtures were measured but they were difficult to interpret.

$I(amine)Pt(\mu\text{-}I)_2Pt(amine)I$: The total yields were 73% for $PhMeNH_2$, 57% for $PhEtNH_2$, 48% for $PhPrNH_2$, 37% for $PhBuNH_2$, 67% for $PhNH_2$ and 53% for PhNHMe. The ^1H and ^{195}Pt NMR spectra were measured and the chemical shifts are discussed in the text.

2.4. *trans*-$Pt(amine)_2I_2$

2.4.1. amine = $PhMeNH_2$, $PhEtNH_2$, $PhPrNH_2$, and $PhBuNH_2$

The complexes $[Pt(amine)_4]I_2$ are suspended in ethanol and the mixture is heated while stirring until a clear yellow solution is obtained. The solution is placed in an ice bath until complete precipitation of the *trans* complex occur. The crystals are filtered, washed with water and then cold ethanol and dried in a desiccator under vacuum.

trans-$Pt(PhMeNH_2)_2I_2$: Yield: 15%, m.p. 209–216 °C (dec.). IR (cm^{-1}): ν(N–H) 3245w, 3201m, 3148m, ν(=C–H) 3076s, 3047m, ν(C–H) 2954w, 2879w, δ(N–H) 1559vs, other bands 1602w, 1496w, 1453m, 1340w, 1204m, 1158w, 1075w, 1028w, 982m, 911w, 847w, 811w, 754s, 697vs, 631w, 587w, 479w, 350w. NMR (δ(ppm)): ^1H: NH 4.343(s + d) $^2J(^{195}Pt–N^1H) = 53$ Hz, H_1 3.996t, $H_2–H_3–H_4$ 7.399m; ^{13}C: C_1 52.87, C_2 139.17, C_3 129.43, C_4 129.55, C_5 128.84.

trans-$Pt(PhEtNH_2)_2I_2$: Yield: 61%, m.p. 178–194 °C (dec.). IR (cm^{-1}): ν(N–H) 3244m, 3210m, 3123w, ν(=C–H) 3082w, 3023w, ν(C–H) 2972w, 2935w, 2873w, 2851w, δ(N–H) 1572vs, other bands 1601w, 1493w, 1455m, 1388w, 1329w, 1261w, 1206m, 1175w, 1153w, 1140m, 1075w, 1033w, 1002w, 825w, 789w, 756s, 697s, 620w, 592w, 542w, 489w, 351w. NMR (δ(ppm)): ^1H: NH 4.044(s + d) $^2J(^{195}Pt–N^1H) = 60$ Hz, H_1 3.012t, H_2 3.414m, $H_3–H_4–H_5$ 7.229m.

trans-$Pt(PhPrNH_2)_2I_2$: Yield: 42%, m.p. 144–202 °C (dec.). IR (cm^{-1}): ν(N–H) 3278w, 3250m, 3231m, 3210m, 3125w, ν(=C–H) 3082w, 3060w, 3024w, ν(C–H) 2969w, 2921w, 2855w, δ(N–H) 1574w, other bands 1602w, 1496m, 1453m, 1369w, 1273w, 1226w, 1197w, 1185w, 1077w, 1029m, 879m, 751m, 729w, 700s, 582w, 418w, 367w. NMR (δ(ppm)): ^1H: NH 4.038(s + d) $^2J(^{195}Pt–N^1H) = 70$ Hz, H_1 2.866m, H_2 1.999m, H_3 2.717t, $H_4–H_5–H_6$ 7.215m; ^{13}C: C_1 48.62, C_2 33.39, C_3 33.61, C_4 142.45, C_5 129.16, C_6 129.23, C_7 126.68.

trans-$Pt(PhBuNH_2)_2I_2$: Yield: 66%, m.p. 177–207 °C (dec.). IR (cm^{-1}): ν(N–H) 3243m, 3209s, 3128m, ν(=C–H) 3082w, 3060w, 3023w, ν(C–H) 2922w, 2950w, δ(N–H) 1574s, other bands 1601w, 1495w, 1465w, 1453w, 1373w, 1250w, 1191m, 1045w, 1028w, 977w, 789w, 745m, 698s, 611w, 510w, 493w, 351w. NMR (δ(ppm)): ^1H: NH 3.962(s + d) $^2J(^{195}Pt–N^1H) = 67$ Hz, $H_2–H_3$ 1.689m, H_4 2.628t, $H_5–H_6–H_7$ 7.206m; ^{13}C: C_1 48.62, C_2 31.34, C_3 29.17, C_4 35.97, C_5 143.06, C_6 129.07, C_7 129.26, C_8 126.51.

2.4.2. *trans*-$Pt(amine)_2I_2$ (amine = 4-$EtPhNH_2$, 4-iso-$PrPhNH_2$, 4-t-$BuPhNH_2$ and 4-$BuPhNH_2$)

$K_2[PtCl_4]$ (0.5 mmol) are dissolved in 5 mL of water. KI (4.0 mmol) are added to the solution which is stirred for 10 min. The amine (10–12 mmol) is dissolved in ethanol and the $K_2[PtI_4]$ solution is added to the amine solution. The mixture is stirred until the formation of a precipitate. It is then heated and filtered. The yellow precipitate is washed with water and cold ethanol. It is dried in air and then under vacuum in a desiccator.

trans-Pt(4-EtPhNH$_2$)$_2$I$_2$: Yield: 50%, m.p. 121–165 °C (dec.). IR (cm^{-1}): ν(N–H) 3250w, 3226w, 3193m, 3121w, ν(C–H) 2960m, 2925w, 2867w, δ(N–H) 1575vs, other bands 1595vs, 1565s, 1509vs, 1452w, 1370w, 1199m, 1187s, 1173s, 1155m, 1019w, 828s, 764w, 736w, 638w, 571m, 536m, 454w, 356w. NMR (δ(ppm)): ^{1}H: NH 6.389(s + d) $^2J(^{195}\text{Pt–N}^1\text{H}) = 70$ Hz, H$_1$ 7.476d, H$_2$ 7.091d, H$_3$ 2.565q, H$_4$ 1.165t; ^{13}C: C$_1$ 142.30, C$_2$ 124.25, C$_3$ 128.59, C$_4$ 140.31, C$_5$ 28.75, C$_6$ 15.88.

trans-Pt(4-*iso*-PrPhNH$_2$)$_2$I$_2$: Yield: 58%, m.p. 164–196 °C (dec.). IR (cm^{-1}): ν(N–H) 3219m, 3184m, 3115m, ν(=C–H) 3057w, 3038w, ν(C–H) 2955m, 2865w, δ(N–H) 1571vs, other bands 1608w, 1599w, 1507s, 1461m, 1433m, 1381w, 1201s, 1178s, 1105w, 1052m, 1017m, 832vs, 813w, 767m, 641w, 574s, 543w, 515m, 357w. NMR (δ(ppm)): ^{1}H: NH 6.391(s + d) $^2J(^{195}\text{Pt–N}^1\text{H}) = 64$ Hz, H$_1$ 7.491d, H$_2$ 7.129d, H$_3$ 2.825h, H$_4$ 1.190d; ^{13}C: C$_1$ 146.91, C$_2$ 124.22, C$_3$ 127.18, C$_4$ 140.36, C$_5$ 34.26, C$_6$ 24.20.

trans-Pt(4-*t*-BuPhNH$_2$)$_2$I$_2$: Yield: 48%, m.p. 149–236 °C (dec.). IR (cm^{-1}): ν(N–H) 3223m, 3187m, 3116w, ν(=C–H) 3064w, ν(C–H) 2961vs, 2864w, δ(N–H) 1571s, other bands 1597w, 1509s, 1461w, 1364m, 1325w, 1196m, 1182m, 1072w, 1016w, 830s 818w, 765w, 641w, 575m, 552w, 375w. NMR (δ (ppm)): ^{1}H: NH 6.403(s + d) $^2J(^{195}\text{Pt–N}^1\text{H}) = 69$ Hz, H$_1$ 7.500d, H$_2$ 7.290d, H$_3$ 1.279s; ^{13}C: C$_1$ 153.03, C$_2$ 123.78, C$_3$ 126.16, C$_5$ 34.93, C$_6$ 31.55.

trans-Pt(4-BuPhNH$_2$)$_2$I$_2$: Yield: 85%, m.p. 152–183 °C (dec.). IR (cm^{-1}): ν(N–H) 3264w, 3213m, 3118w, ν(=C–H) 3038w, ν(C–H) 2952m, 2923w, 2867w, 2854w, δ(N–H) 1567vs, other bands 1595w, 1509s, 1468w, 1458w, 1428w, 1367w, 1206w, 1173w, 1158vs, 1067w 1019w 831m 816w, 789w, 757w, 641w, 573m, 554w, 420wm, 383w. NMR (δ(ppm)): ^{1}H: NH 6.383(s + d) $^2J(^{195}\text{Pt–N}^1\text{H}) = 66$ Hz, H$_1$ 7.472d, H$_2$ 7.083d, H$_3$ 2.547t, H$_4$ 1.554qt, H$_5$ 1.339s, H$_6$ 0.903t; ^{13}C: C$_1$ 140.95, C$_2$ 124.22, C$_3$ 129.14, C$_4$ 140.34, C$_5$ 35.55, C$_6$ 34.54, C$_7$ 22.94, C$_8$ 14.12.

2.4.3. *trans-Pt(PhNH$_2$)$_2$I$_2$*

The compound was synthesized by a method very similar to the one used to prepare *cis*-Pt(amine)$_2$I$_2$. About 2.3 mmol of PhNH$_2$ dissolved in ethanol are added to 0.5 mmol of K$_2$[PtI$_4$] in 5 mL of water. The solution is stirred for several hours while heating. The precipitate is then filtered, washed with water and cold ethanol. The compound is dried in air and then in a desiccator under vacuum. The yield is 81%.

This complex can also be synthesized from the isomerization of the *cis* complex dissolved in DMF. The solution is heated, filtered and the filtrate is evaporated to dryness.

trans-Pt(PhNH$_2$)$_2$I$_2$: m.p. 173–177 °C (dec.). IR (cm^{-1}): ν(N–H) 3218s, 3190s, 3173w, 3121m, ν(=C–H) 3072m, 3050w, 3037w, δ(N–H) 1576vs, other bands 1596m, 1465m, 1340w, 1198w, 1174s; 1149w, 1069w, 1026m, 840w; 804w, 775w, 751vs, 685vs, 617w, 575s, 558m, 444m, 365m. NMR (δ(ppm)): ^{1}H: NH 6.497s, H$_1$ 7.568d, H$_2$ 7.258dd, H$_3$ 7.138d; ^{13}C: C$_1$ 143.62, C$_2$ 126.36, C$_3$ 129.59, C$_4$ 129.23.

2.4.4. *trans-Pt(PhNHMe)$_2$I$_2$*

The iodo-bridged dimer was suspended in a water–ethanol mixture. A small excess of ligand was added and the mixture was stirred for 2 days with slight heating. The precipitate was filtered out and washed with water, ethanol and finally with ether. The product was dried in a desiccator under vacuum.

trans-Pt(PhNHMe)$_2$I$_2$: Yield: 53%, m.p. = 64–234 °C (dec.). IR (cm^{-1}): ν(N–H) 3196m, ν(=C–H) 3033w, ν(C–H) 2941w, δ(NH$_2$) 1595m, other bands 1493s, 1464m, 1448m, 1198m, 1175m, 1074m, 1055s, 1030m, 1007m, 818w, 776m, 761tF, 693w, 616w, 569m, 480w, ν(Pt–N) 352w. NMR (δ(ppm)): ^{1}H: NH 6.773s + d $^2J(^{195}\text{Pt–NH}) = 85$ Hz, H$_1$ 3.099t $^3J(^{195}\text{Pt–H}_1) = 32$ Hz, H$_2$ 7.167mult, H$_3$ 7.518mult, H$_4$ 7.321mult; ^{13}C: C$_1$ 45.706, C$_{1'}$ 165.777, C$_2$ 126.740, C$_3$ 129.169, C$_4$ 122.991.

2.5. *Crystal structures*

The crystal structures of the compounds *trans*-Pt(4-EtPhNH$_2$)I$_2$ (**1**) and *trans*-Pt(4-*iso*-PrPhNH$_2$)I$_2$ (**2**) were determined by X-ray diffraction methods. The data sets were obtained from a Enraf-Nonius CAD-4 diffractometer (graphite-monochromatized Mo Kα radiation) under the control of the CAD-4 software [18]. The reduced cell was initially determined from 25 spots located on a preliminary

Table 1
Crystal data

Crystal	**1**	**2**
Chemical formula	C$_{16}$H$_{22}$N$_2$I$_2$Pt	C$_{18}$H$_{26}$N$_2$I$_2$Pt
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Molecular weight	691.25	719.30
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (Å)	6.018(3)	29.680(10)
b (Å)	17.736(10)	8.484(4)
c (Å)	9.075(5)	8.746(6)
β (°)	102.22(4)	97.87(4)
Volume (Å^3)	946.7(9)	2182(2)
Z	2	4
ρ_{calc} (g cm^{-3})	2.425	2.190
Crystal size (mm)	0.41 × 0.06 × 0.05	0.64 × 0.53 × 0.05
μ (mm^{-1})	10.668	9.264
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Temperature (K)	293(2)	293(2)
Reflections collected	27170	11763
Ranges of h, k, l	$-7 \leqslant h \leqslant 7$, $-22 \leqslant k \leqslant 22$, $-11 \leqslant l \leqslant 11$	$-37 \leqslant h \leqslant 37$, $-10 \leqslant k \leqslant 10$, $-10 \leqslant l \leqslant 11$
Independent reflections (R_{int})	1876 (0.083)	2265 (0.150)
R_1[a] (observed)	0.0312	0.0515
wR_2[a] (all data)	0.0542	0.1129
S (all data)[a]	0.650	0.957

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $S = \{\sum[w(F_o^2 - F_c^2)^2]/(N_{\text{reflns}} - N_{\text{params}})\}^{1/2}$.

rotation photograph and centered in the detector aperture. Accurate cell parameters were then determined from the positions of 25 high-angle reflections centered with the SETANG and DETTH procedures. The intensities were recorded over the whole sphere by $\omega/2\theta$ scans and five standard reflections were measured every hour. An absorption correction based on the crystal geometry was applied using NRCVAX [19]. The data were finally corrected for the effects of Lorentz and polarization.

The SHELXTL package [20] was used for all calculations. The starting model was obtained from either a Patterson synthesis or direct methods with SHELXS [21]. The positions of all other non-hydrogen atoms were found by the standard Fourier technique and the structures were refined on F_o^2 using all reflections with SHELXL [22]. All non-hydrogen atoms were refined anisotropically. Hydrogens were added to the model at idealized positions with standard C, N–H distances. Their isotropic displacement factors U_{iso} were adjusted to 20–50% above the value for the bonded atom. At the end of the refinement, the VOID routine of PLATON [23] was used to check for the presence of holes in the structure. The crystal data are summarized in Table 1.

3. Results and discussion

3.1. Syntheses of the different complexes

The *cis* diiodo compounds were synthesized by a modified version of the published method [7,8,16] from the aqueous reaction of $K_2[PtI_4]$ with the amine dissolved in ethanol. Compounds with phenylamine ($PhNH_2$), phenylmethylamine ($PhMeNH_2$), phenylethylamine ($PhEtNH_2$), phenylpropylamine ($PhPrNH_2$) and phenylbutylamine ($PhBuNH_2$) were isolated. A large excess of amine dissolved in ethanol was used to maximize the yields which varied between 65% and 90%. The presence of ethanol is required since the amines are quite insoluble in water. The *cis* compounds with the other amines could not be synthesized because of the steric hindrance close to the binding site.

The tetrasubstituted compounds $[Pt(amine)_4]I_2$ were synthesized by a modified version of Kauffman's method [7,16], from the aqueous reaction of $K_2[PtI_4]$ with the amine (20 equiv.) dissolved in ethanol. The mixture was stirred for 3–4 days until a colorless solution and a white precipitate is obtained. Slight heating was used to accelerate the reaction. The yields from $K_2[PtCl_4]$ were between 42% and 72%. Because of the important steric hindrance of several ligands, only the tetrasubstituted complexes with the following amines could be isolated: $PhMeNH_2$, $PhEtNH_2$, $PhPrNH_2$ and $PhBuNH_2$.

The *trans* compounds containing $PhMeNH_2$, $PhEtNH_2$, $PhPrNH_2$ and $PhBuNH_2$ were prepared by heating the tetrasubstituted compound in ethanol. The yields (from $K_2[PtCl_4]$) are lower (between 15% and 66%), since it is difficult to obtain the tetrasubstituted compounds quantitatively.

$$[Pt(amine)_4]I_2 \rightarrow \textit{trans}\text{-}Pt(amine)_2I_2 \downarrow + 2amine$$

For the other primary amines (second series), the *trans* disubstituted compounds were prepared from the method described above for the tetrasubstituted compounds. The yields varied between 48% and 85%. The compound *trans*-$Pt(PhNH_2)_2I_2$ can also be obtained from the isomerization of the *cis* isomer in hot DMF.

$$\textit{cis}\text{-}Pt(PhNH_2)_2I_2 \underset{\Delta}{\overset{DMF}{\rightarrow}} \textit{trans}\text{-}Pt(PhNH_2)_2I_2$$

Finally, *trans*-$Pt(PhNHMe)_2I_2$ was obtained from the cleavage of the diiodo-bridged dimer with the amine. The reaction took about 2 days with slight heating in a H_2O–EtOH mixture.

$$I(PhNHMe)Pt(\mu\text{-}I)_2Pt(PhNHMe)I + PhNHMe \xrightarrow[\Delta]{H_2O/EtOH} \textit{trans}\text{-}Pt(PhNHMe)_2I_2$$

The iodo-bridged dimers were prepared following the published procedure for aliphatic amines [11,17] from the reaction of *cis*-$Pt(amine)_2I_2$ and perchloric acid in a water–ethanol mixture. The brownish diiodo-bridged dimers are obtained after one to three weeks of vigorous stirring. For the ligand PhNHMe, the iodo-bridged dimer was isolated following the procedure to synthesize *cis*-$Pt(amine)_2I_2$. The yields (from $K_2[PtCl_4]$) vary between 37% and 73%.

The $PhMeNH_2$ dinuclear compound contained some *cis* monomer (the reaction was not complete), while the secondary amine dimer contained some *trans* monomer. The diiodo dimers can exist in two isomeric forms, the *cis* and the *trans* compounds. The crystal structures of the *n*-$BuNH_2$ and Et_2NH compounds were determined by X-ray diffraction methods [17] and have shown a *trans* configuration. The latter is probably thermodynamically more stable.

3.2. Characterization of the complexes

3.2.1. $Pt(amine)_2I_2$

The *cis*- and *trans*-$Pt(amine)_2I_2$ complexes have been characterized mostly by IR and multinuclear magnetic resonance spectroscopies. The two isomers will be discussed together in order to determine if these spectroscopic methods are good indicators to determine the geometry of the compounds. The ν(Pt–Cl) bands in IR spectroscopy are usually a good criterion to determine the *cis* or *trans* configuration of the dichloro complexes, but the ν(Pt–I) bands are below 200 cm^{-1} and special instrumentation is required for the study of these vibrations.

The decomposition points of the diiodo complexes are shown in Section 2. Some of the *cis* compounds seem to isomerize to the *trans* isomers when heated, since the final decomposition points of the two isomers are often very similar. Although these compounds were not studied, it has been shown by DSC that other similar *cis* disubstituted amine complexes isomerize to the *trans* compounds when heated [8].

3.2.1.1. IR spectroscopy. The IR spectra of the complexes were measured in the solid state and the observed bands are shown in Section 2. Most *cis* compounds (C_{2v} symmetry for the squeleton PtN_2I_2) have shown two bands in the far IR region and these were assigned to ν(Pt–N) vibrations between 302 and 377 cm^{-1}, while the *trans* analogues (D_{2h} symmetry) have shown only one band between 350 and 383 cm^{-1} (Table 2). These results are as expected from group theory [24]. The ν(Pt–N) vibrations of *cis*- and *trans*-$Pt(PhNH_2)I_2$ were reported at 300 and 350 cm^{-1} for the *cis* isomer and at 366 cm^{-1} for the *trans* compound [25]. These values for aromatic amines are at lower energy that the corresponding vibrations for the aliphatic amine complexes, which were reported between 433 and 585 cm^{-1} [7,8]. The ν(Pt–N) bands have low intensity and these vibrations might not be pure since they may couple with other vibrations. The ν(Pt–N) bands are usually difficult to interpret and are probably not reliable to determine the geometry of the complexes.

3.2.1.2. NMR spectroscopy. The solubility of these compounds are quite low. The NMR spectra of all the diiodo complexes were measured in CD_3COCD_3. Several of these compounds are slightly soluble in normal chloroform but they decompose quite rapidly in $CDCl_3$. Similar problems were observed with CD_2Cl_2. DMSO reacts rapidly with the compounds and was rapidly eliminated. DMF reacts more slowly and isomerization of some of the *cis* compounds is possible. Acetone was chosen, since no reaction was observed over a longer period of time, even if it is not a completely inert solvent. No solvolysis was observed in acetone for the aliphatic amines system [8]. The *cis* dichloro compounds can isomerize to the *trans* compounds in acetone, especially when heated but no isomerization was observed for the diiodo complexes after one week of standing in CD_3COCD_3.

The ^{195}Pt NMR signals of the *trans* diiodo compounds were observed between −3363 and −3375 ppm (average −3369 ppm) for the four ligands of the first series and between −3355 and −3367 ppm (average −3358 ppm) for the corresponding *cis* isomers (Table 3). The four *cis* complexes were observed at slightly lower fields and the $\Delta\delta$ values vary between 6 and 20 ppm. The *trans* complexes of the second series were observed at lower fields (−3233 and −3247 ppm) than the *trans* analogues of the first series. The *trans* complex containing the secondary amine (PhNHMe) was observed at much lower fields (−2947 ppm) as expected for more hindered ligands. This observation is due to the solvent effect. In solution, the molecules of solvents can normally approach the Pt atom on both sides of the coordination plane, which increases the electron density in the immediate environment of the Pt atom. When the binding atom of the ligand is sterically more demanding, the molecules of solvent cannot approach the Pt atom as easily and the electron density in the close environment of the Pt atom is reduced. The chemical shifts of secondary amines complexes have been observed at lower fields than primary amines compounds. For example, the δ(Pt) for *cis*- and *trans*-$Pt(MeNH_2)I_2$ were reported at −3342 and −3360 ppm, respectively, while it was found at −3247 and −3057 ppm for *cis*- and *trans*-$Pt(Me_2NH)I_2$ [7]. The solvent effect is probably also responsible for the lower field shifts of the *trans* complexes of the second series of ligands compared to the amines of the first series. The solvent effect is more important for solvents containing donor atoms like water and acetone.

The ^{195}Pt NMR spectrum of *cis*-$Pt(PhNH_2)I_2$, has shown the presence of three species at −3141, −3183 and −3247 ppm. The most shielded signal is caused by the presence of the *trans* isomer. The complexes with $PhNH_2$ are much less soluble in acetone than the other compounds. Long accumulation times were required especially for the *cis* isomer. Therefore, the complex *cis*-$Pt(PhNH_2)I_2$ was probably pure when placed in the NMR tube, and isomerized during the measurement. A few other solvents were tried, but the solubility were even lower. DMF is probably a better solvent, but isomerization should be faster than in acetone. The *cis*-$PhNH_2$ complex is sterically more demanding than the other *cis* isomers, which contain amines of the first series only. The two other signals were observed at lower fields −3141 and −3183 ppm than the

Table 2
ν(Pt–N) (cm^{-1}) for the complexes *cis*- and *trans*-$Pt(amine)_2I_2$

amine	*cis*	*trans*
$PhMeNH_2$	342, 303	350
$PhEtNH_2$	353, 312	351
$PhPrNH_2$	375, 352	367
$PhBuNH_2$	377, 348	351
$PhNH_2$	365, 302	365
4-$BuPhNH_2$		383
4-*t*-$BuPhNH_2$		375
4-*iso*-$PrPhNH_2$		357
4-$EtPhNH_2$		356
PhNHMe		352

Table 3
$\delta(^{195}Pt)$ and $\Delta\delta = \delta_{cis} - \delta_{trans}$ (ppm) of the complexes $Pt(amine)_2I_2$ and $I(amine)Pt(\mu\text{-}I)_2Pt(amine)I$ (in CD_3COCD_3) and $[Pt(amine)_4]I_2$ (in D_2O)

amine	pK_a [28]	Proton affinity	*cis*	*trans*	$\Delta\delta$
$PhMeNH_2$	9.62	913	−3355	−3375	20
$PhEtNH_2$	9.83	936	−3367	−3373	6
$PhPrNH_2$	10.28[a]		−3355	−3363	8
$PhBuNH_2$	10.66[a]		−3355	−3363	8
$PhNH_2$	4.603	883	−3141, −3183	−3247	106, 64
4-$BuPhNH_2$	4.90[a]			−3240	
4-*t*-$BuPhNH_2$	4.93[a]			−3233	
4-*iso*-$PrPhNH_2$	5.01[a]			−3242	
4-$EtPhNH_2$	5.09[a]			−3242	
PhNHMe	4.85	917		−2947	

[a] These values were calculated with the software Solaris V4.67 [29].

trans compound, with $\Delta\delta$ of 106 and 64 ppm (Table 3). These values are at much lower fields than the other *cis* complexes. $PhNH_2$ is a weaker base (pK_a of 4.603) than the other ligands of the first series (pK_a around 9–10) and the δ(Pt) of *cis*-$Pt(PhNH_2)I_2$ should be expected at lower fields. The compounds *cis*-$Pt(NH_3)_2I_2$ and *cis*-Pt(pyridine)$_2$I$_2$ were reported in the same region (−3198 ppm in DMF [26] and −3199 ppm in CD_2Cl_2 [27], respectively). The two signals observed for *cis*-$Pt(PhNH_2)I_2$ at −3141 and −3183 ppm ($\Delta\delta$ of 42 ppm) could be caused by the presence of rotamers in solution. The two phenyl rings could be on the same side of the coordination place or on different sides. Rotamers have been observed for *cis*-Pt(2-picoline)$_2$I$_2$ (at −3281 and −3312 ppm, $\Delta\delta$ of 31 ppm) and for *cis*-Pt(2,4-lutidine)$_2$I$_2$ (at −3261 and −3288 ppm, $\Delta\delta$ of 27 ppm) in chloroform [27].

The ^{195}Pt chemical shifts observed for the complexes Pt(amine)$_2$I$_2$ containing aromatic amines from the first series (δ_{average} −3363 ppm) are very similar to those published on aliphatic amines ($\delta_{\text{average}} \sim -3356$ ppm [7,8]). These ligands contain an alkyl group between the aromatic ring and the amine group. The results on the complexes of the second series resemble those published for the pyridine ligand, which is an aromatic molecule, but quite different in nature. The *cis* compounds containing pyridine derivatives were reported at slightly higher fields than the *trans* corresponding complexes, which might suggest that π-bonding is present. Ligands like sulfoxides which contain empty π^* orbitals can accept electron density from platinum, which reduces the electron density on the metallic center. For these compounds, the *cis* isomers are more stable than the *trans* compounds, since π-bonding is much more efficient in the *cis* geometry. Pyridines also contains empty π^* orbitals which can form π-bonds with platinum, but to a much smaller extent. Therefore, the *cis* compounds with pyridine are observed at slightly higher fields than the trans. Amines cannot accept π back-donation and the *trans* compounds are more stable than the *cis* analogues. For the amine systems, the *trans* isomers are observed at higher fields than the *cis*, but the difference is small for primary amine complexes. For secondary amines, the difference is larger due to the solvent effect as discussed above.

For the ligands of the second series, the aromatic ring is a phenyl group attached directly to a NH_2 group. The ligands should contain empty π^* orbitals, but π-bonding with platinum is probably absent, because of the presence of the amine group between the phenyl ring and the Pt atom. But these amines present a larger steric hindrance around the Pt atom, and their ^{195}Pt chemical shifts are at lower fields than the complexes of the first series. For the *cis* compounds of the second series, the chemical shifts are at much lower fields, at least for the only compound isolated (*cis*-$Pt(PhNH_2)_2I_2$). For the first series, the results show that the value $\Delta\delta$ ($\delta_{cis} - \delta_{trans}$) is small (average 11 ppm), as observed for aliphatic primary amines complexes [7,8]. For the second series, the *cis* compound was isolated only with $PhNH_2$, but the $\Delta\delta$ is larger (average for the two rotamers, 85 ppm). For the other ligands, the *cis* isomers could not be isolated because of steric hindrance.

The strength of the σ Pt–N bond should be related to the basicity of the ligand. The formation of the σ bond (amine → Pt) should transfer some electron density from the amine to the platinum atom, resulting in a shielding on the Pt atom and a deshielding effect on the ligands (^{1}H and ^{13}C signals). We have found a relatively good relation between the pK_a values [28] of the protonated amines and the δ(Pt) of the *trans* complexes containing the primary amines (Fig. 1) as expected. For the *cis* compounds, there are not enough data available and other factors due to the steric hindrance are more important factors. The pK_a values are measured in a solvent (water or alcohol) and are influenced by the presence of the substituents on the protonated N atom. The proton affinity value, which is measured in the gas phase is probably a better indicator of basicity, but these values are still not common in the literature. A few data are available and are shown in Table 3. For the *cis* isomers, only three values are available and the δ(Pt) of the complexes are in accordance with the basicity of the three protonated amines. There is also a linear correlation between the δ(Pt) of the complexes and the published proton affinity values for the three *trans* isomers containing primary amines. The *trans* secondary amine complex is alone in its category and is very influenced by the solvent effect as already discussed.

The ^{1}H NMR spectra are shown in Section 2. Most of the spectra are very complicated due to the multiplicity of the signals. The amino group chemical shifts and the coupling constants $^2J(^{195}\text{Pt}–^1\text{HN})$ are shown in Table 4. The chemical shifts of the *cis* compounds are found at lower fields (between 4.45 and 4.83 ppm) than those of the *trans* analogues in the first series (between 3.96 and 4.34 ppm). These results are similar to those observed for the aliphatic amines complexes [7,8]. The NH signal in the complexes containing a phenyl ring directly bonded to the N atom was observed at much lower fields (6.4–6.8 ppm). In the latter free amines, the amino groups are not very different ($\delta(^1\text{HN}) = 4.3–4.8$ ppm) from those of the free amines of the first series ($\delta(^1\text{HN}) = 3.1–4.4$ ppm).

For the compounds of the first series, the $\delta(^1\text{HN})$ values are shifted slightly to higher fields as the number of C atoms between the phenyl and the amine groups is increased (average *cis*–*trans*, 4.575–4.097 ppm) contrary to the expected results. The basicity of the ligands should increase as the number of C atoms increases. The pK_a values for $PhMeNH_2$ and $PhEtNH_2$ are 9.62 and 9.83 [28]. For $PhPrNH_2$ and $PhBuNH_2$ the values were calculated using the software Solaris V4.67 [29] (Table 3). As the basicity of the ligand is increased, the σ bond should transfer a greater electron density to the metal. Therefore, a larger deshielding should be observed on the ligands as the pK_a increases. For the aliphatic amines, the NH_2 signal is almost constant in the $MeNH_2$, $EtNH_2$, *n*$PrNH_2$, and

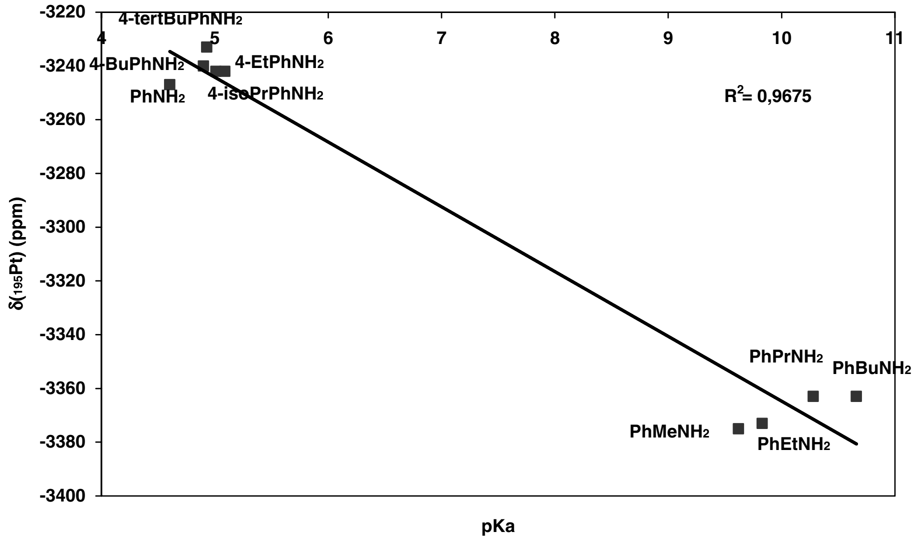


Fig. 1. $\delta(^{195}Pt)$ (ppm) of the complexes *trans*-$Pt(amine)_2I_2$ vs. the pK_a of the protonated amines.

Table 4
$\delta(^1H)$, $\Delta\delta$ ($\delta_{complex} - \delta_{amine}$) ppm and $^2J(^{195}Pt–^1HN)$ (Hz) for $Pt(amine)_2I_2$ in CD_3COCD_3

amine		NH	$\Delta\delta$	$^2J(^{195}Pt–^1HN)$
$PhMeNH_2$	*cis*	4.827	0.402	63
	trans	4.343	−0.082	53
$PhEtNH_2$	*cis*	4.525	0.839	65
	trans	4.044	0.358	60
$PhPrNH_2$	*cis*	4.499	1.384	70
	trans	4.038	0.923	69
$PhBuNH_2$	*cis*	4.450	[a]	73
	trans	3.962	[a]	67
$PhNH_2$	*trans*	6.497	2.175	
$4-BuPhNH_2$	*trans*	6.383	2.070	66
4-*t*-$BuPhNH_2$	*trans*	6.403	2.059	69
4-*iso*-$PrPhNH_2$	*trans*	6.391	2.088	64
$4-EtPhNH_2$	*trans*	6.389	2.048	70
PhNHMe	*trans*	6.773	1.967	84

[a] NH_2 of free $BuPhNH_2$ hidden by CH_2.

n$BuNH_2$ complexes [7]. But for aromatic amines of the first series, opposite results are observed for both isomers.

But if we consider the $\Delta\delta$ ($\delta_{complex} - \delta_{free\ amine}$) values, the difference is larger as the length of the chain is increased as expected. The ^1H NMR spectra of the free amines were measured in acetone, in order to evaluate the real $\Delta\delta$ values, which are shown in Table 4. The signal of the $–NH_2$ group in $PhBuNH_2$ was hidden under the peak of the most deshieded $–CH_2$ group. For the three amines of the first series, the $\Delta\delta$ values vary between 0.402 and 1.384 ppm for the *cis* isomers and between −0.082 and 0.923 ppm for the *trans* compounds. Therefore, the electron donation from the amine (σ bond) to Pt increases as the C chain between the Ph and the NH_2 group increases as expected. The $\Delta\delta$ values are larger in the *cis* geometry as observed for other reported aliphatic amines [7,8]. Acetone is not an inert solvent for amines and these values might not be theoretically significant.

For the amines of the second series, the pK_a values are much smaller, 4.603 for $PhNH_2$ and between 4.90 and 5.09 (calculated) for its *para* derivatives. For the *trans* compounds of the *para* derivatives of aniline, the $\Delta\delta(NH_2)$ values are very uniform (2.05–2.09 ppm), while it is 2.18 ppm for *trans*-$Pt(PhNH_2)_2I_2$. For the secondary amine PhNHMe, the $\Delta\delta$ value is 1.97 ppm.

For the amines of the first series, the coupling constants $^2J(^{195}Pt–^1HN)$ are larger for the *cis* compounds (average 68 Hz) than for the *trans* complexes (average 62 Hz) as observed for the aliphatic amines system [7,8]. For the other *trans* complexes, the coupling constants $^2J(^{195}Pt–^1HN)$ are 64–70 Hz for the primary amines and 85 Hz for the secondary amine (Table 4). Only one coupling constant $^3J(^{195}Pt–^1H)$ could be calculated because all the other signals are multiplets of lower intensity. In *trans*-$Pt(PhNHMe)_2I_2$ the coupling constant of the methyl group is 32 Hz, in agreement with published values for aliphatic amines [7,8].

The ^{13}C NMR spectra of the diiodo complexes were also studied in acetone and the results are shown in Section 2. The spectra of the free amines were also measured in acetone for comparison. Several $\Delta\delta$ values ($\delta_{complex} - \delta_{free\ amine}$) are shown in Table 5. The interpretation of the signals was not always evident, since some of the signals have very low intensity due to the low solubility of most of the complexes. The results shown on Table 5 can be considered as a tentative assignment and they are not easy to interpret. For the complexes containing amines of the first series, most of the C atoms located in *ortho*, *meta* and *para* positions on the aromatic ring are all deshielded upon coordination as expected. The *cis* compounds are slightly more deshielded than the *trans* isomers and the deshielding decreases as the length of the alkyl group between the amine and phenyl groups is increased. The chemical shifts of the C atom in the phenyl group attached to the alkyl group in the complexes is always shielded compared to

Table 5
$\Delta\delta(^{13}C)$ ($\delta_{complex} - \delta_{amine}$) ppm for $Pt(amine)_2I_2$ in CD_3COCD_3

amine		C–NH	C(Ph)	C_{ortho}	C_{meta}	C_{para}
$PhMeNH_2$	*cis*	−4.068	−2.565	1.153	0.987	2.019
	trans	−2.535	−2.565	1.002	0.759	1.943
$PhEtNH_2$	*cis*	−4.720	−2.656	0.569	0.076	0.941
	trans	−3.339	−2.489	0.508	−0.061	0.835
$PhPrNH_2$	*cis*	−3.448	−0.913	0.311	0.129	0.539
	trans	−2.462	−0.891	0.182	0.046	0.439
$PhBuNH_2$	*cis*	−3.665	−0.406	0.231	0.220	0.345
	trans	−2.883	−0.387	0.136	0.171	0.224
$PhNH_2$	*trans*		−3.342	11.247	−0.045	11.762
4-$BuPhNH_2$	*trans*		−5.859	8.970	−0.410	8.833
4-*t*$BuPhNH_2$	*trans*		6.481	8.875	−0.183	3.613
4-*iso*-$PrPhNH_2$	*trans*		0.364	9.970	−0.213	2.626
4-$EtPhNH_2$	*trans*		−4.538	8.940	−0.326	7.285
PhNHMe	*trans*	15.264	14.858	14.039	−0.501	6.131

the free amine and the shielding decreases as the length of the alkyl chain is increased. The aromatic ring is an electron attracting group which should decrease the strength of the σ-bond (amine → Pt), but its influence should decrease as the length of the alkyl group increases between the amine and the phenyl groups. The results on *trans*-$Pt(PhNH_2)_2I_2$ show that the *ortho* and *para* H atoms are much more affected by coordination than the proton in *meta* position as expected. For the complexes of the second series, no pattern was detected. These results on Pt(II) compounds with amines containing an aromatic group are quite different from those containing aliphatic amines. Therefore, the presence of the phenyl ring has a very important influence on the electronic system in these molecules.

No coupling constant could be measured because of the low solubility of the compounds. The accumulation times were quite long, but the background was still too important to evaluate the $J(^{195}Pt–^{13}C)$ coupling constants.

3.2.1.3. Crystal structures. The crystal structures of the complexes *trans*-$Pt(4\text{-}EtPhNH_2)I_2$ (**1**) and *trans*-Pt(4-*iso*-$PrPhNH_2)I_2$ (**2**) were determined by X-ray diffraction methods. The results have confirmed the *trans* geometry of the complexes. Labelled diagrams of the two crystals are shown in Figs. 2 and 3. Both crystals belong to a centrosymmetric space group and the Pt atom is located on an inversion center. Selected bond distances and angles are shown in Table 6.

The Pt–I bonds are 2.597(1) and 2.591(1) Å, and the Pt–N bond lengths are 2.060(7) Å for the 4-$EtPhNH_2$ compound and 2.029(11) Å for the 4-*iso*-$PrPhNH_2$ complex. The *cis* angles vary between 89.2(2)° and 90.8(2)°, while the *trans* angles are 180° by symmetry. The Pt(II) coordination plane is perfectly planar by symmetry. Since the Pt atom is on an inversion center, the two amine ligands in both crystals are on opposite sides of the Pt plane. This conformation of the molecule should be the thermodynamically most stable. The Pt–N–C angles are 116.6(6)° (**1**) and 116.3(7)° (**2**).

The dihedral angles between the Pt(II) coordination plane and the aromatic plane are 112.6° for **1** and 72.6° for **2**. The torsion angle of the 4-ethyl group with the

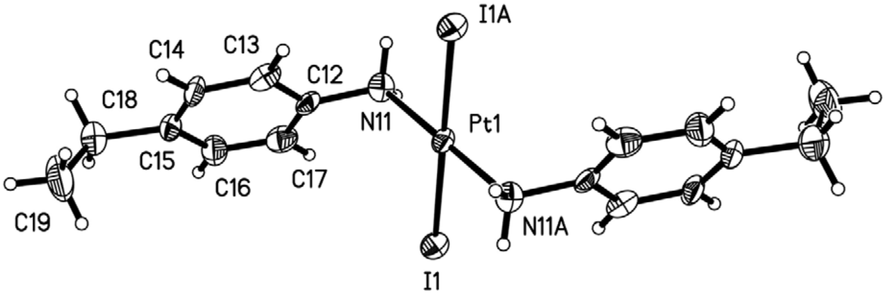


Fig. 2. Labelled diagram of the molecule *trans*-$Pt(4\text{-}EtPhNH_2)I_2$ in crystal **1** (the ellipsoids correspond to a 30% probability).

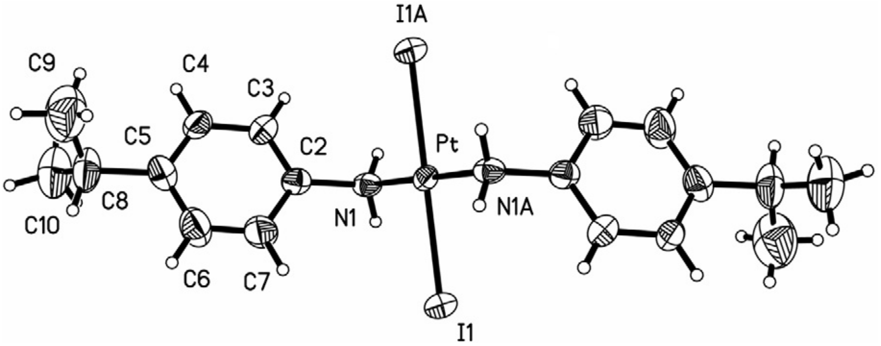


Fig. 3. Labelled diagram of the molecule *trans*-Pt(4-*iso*-$PrPhNH_2)I_2$ in crystal **2** (the ellipsoids correspond to a 30% probability).

Table 6
Selected bond lengths (Å) and angles (°) for crystals **1** and **2**

Crystal	1	2
Pt–I	2.5968(12)	2.5907(13)
Pt–N	2.060(7)	2.029(11)
N–C	1.487(11)	1.498(17)
C–C (average aromatic)	1.390(13)	1.37(2)
Other C–C (average)	1.520(13)	1.47(2)
I–Pt–I′	180	180
N–Pt–N′	180	180
I–Pt–N	90.8(2)	89.7(3)
I–Pt–N′	89.2(2)	90.3(3)
Pt–N–C	116.6(6)	116.3(7)

aromatic ring is ~60°, while the dihedral angle between the isopropyl group and the phenyl ring is 86.9°. The bond distances and angles in the amine ligands are normal.

The crystal structures are stabilized by intermolecular H-bonds between the amine groups and the iodo ligands. In **1**, the distances N–I′ and H–I′ are 3.684(7) and 2.85 Å with an N–H–I angle of 154.1°. In crystal **2**, these distances are 3.802(10) and 2.92 Å with an N1–H1A–I′ angle of 168.4°, and 3.719(9) and 2.94 Å with an N1–H1B–I′ angle of 145.9°.

3.2.2. $[Pt(amine)_4]I_2$

The tetrasubstituted complexes have usually been reported in the literature as starting materials for the synthesis of *trans* disubstituted compounds. Only the Pt(II) complexes with the ligands $PhMeNH_2$, $PhEtNH_2$, $PhPrNH_2$, and $PhBuNH_2$ (first series) could be isolated. The other ligands are too sterically hindered close to the N atom to form stable tetrasubstituted compounds. The measurements of the decomposition points have shown that all the white complexes, except $[Pt(PhEtNH_2)_4]I_2$ decompose to the yellow *trans*-$Pt(amine)_2I_2$ compounds. The experimental conditions for the synthesis of *trans*-$Pt(PhEtNH_2)_2I_2$ from $[Pt(PhEtNH_2)_4]I_2$ was quite different from the other amines, since a much longer heating time in ethanol solution was required.

The four complexes were characterized by IR spectroscopy. One ν(Pt–N) band is expected for the D_{4h} PtN_4 skeleton and two normal deformation modes. The latter two modes could not be observed on our instrument. One band observed between 348 and 355 cm^{-1} was assigned to the ν(Pt–N) vibration (Table 7). These values are close to those observed for the diiodo complexes discussed above. There are no published values in the literature on Pt-aromatic amines compounds. These values are at lower energies than those reported for aliphatic amines [30–34].

The tetrasubstituted compounds were studied by nuclear magnetic resonance spectroscopy in aqueous solution. The $PhPrNH_2$ and $PhBuNH_2$ complexes are much less soluble than the two others in water and their accumulation times in NMR were much longer. The $\delta(^{195}Pt)$ vary between −2855 and −2909 ppm (Table 7). There is no correlation between the δ(Pt) and the basicity of the ligands. These data can be compared to those determined on aliphatic amines [35] which have shown δ(Pt) values of about −2750 ppm. Our values on aromatic amines are at higher fields. The phenyl group is an electron-attracting group, which should decrease the strength of the σ-bond compared to aliphatic amine complexes. Our values are not in agreement with this statement. In the aliphatic system, the δ(Pt) values are slightly shifted towards lower fields as the length of the C chain is increased (−2769 for $MeNH_2$ to −2743 for *n*-$BuNH_2$), contrary to the basicity of the protonated amines. Our results on the aromatic amines are almost identical for the $PhMeNH_2$, $PhEtNH_2$ and $PhPrNH_2$ compounds (−2860 ppm) and slightly at higher field for the $PhBuNH_2$ complex (−2909 ppm) as expected for the most basic amine. Therefore, other factors like steric hindrance and the solvent effects (especially water) must have a greater influence on the ^{195}Pt chemical shifts than the electronic factors. Steric hindrance is a very important factor in complexes of the type $[Pt(amine)_4]^{2+}$.

The $\delta(N^1H)$ groups were not observed in D_2O. The $^3J(^{195}Pt–^1H)$ coupling constant could be calculated only for the $PhMeNH_2$ complex, which was found to be 40 Hz. We can compare with the value (42 Hz) determined for $[Pt(MeNH_2)_4]I_2$ [35] in D_2O.

Table 7
ν(Pt–N) (cm^{-1}), δ(Pt) ppm and $^3J(^{195}Pt–^1H)$ (Hz) for $[Pt(amine)_4]I_2$ in D_2O

amine	ν(Pt–N)	$\delta(^{195}Pt)$	$^3J(^{195}Pt–^1H)$
$PhMeNH_2$	355	−2868	40
$PhEtNH_2$	348	−2855	
$PhPrNH_2$	348	−2858	
$PhBuNH_2$	352	−2909	

3.2.3. $(amine)IPt(\mu\text{-}I)_2PtI(amine)$

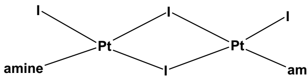
The iodo-bridged dimers were isolated with the four amines of the first series and also with $PhNH_2$ and the secondary amine PhNHMe.

The compounds were characterized by ^{195}Pt and ^1H NMR spectroscopy. The spectra have shown the presence of more than one species in acetone solution. The reported paper on iodo-bridged dimers on aliphatic amines has shown for many ligands the presence of three compounds, the disubstituted compound (cis or trans) and the two isomers of the iodo-bridged dimers, which seem reasonably stable in acetone. In ^{195}Pt NMR, the two isomeric dimers were reported at about −4000 ppm and are separated by about 12 ppm for the aliphatic primary amines and by 26 ppm for two secondary amines [17]. In the present study, two Pt(II) compounds were present in solution for the five ligands shown in Table 8. The *trans* disubstituted compound was observed in ^{195}Pt NMR for the secondary amine PhNHMe at −2947 ppm (see results above) in a 80% proportion. The iodo-bridged dimers are observed at much higher fields (around −4000 ppm) and therefore, they can easily be differentiated. The $\delta(^{195}Pt)$ of the studied compounds are shown in Table 8. For four amines, the two

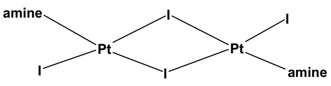
Table 8
$\delta(^{195}Pt)$ (ppm) and $^2J(^{195}Pt–^1HN)$ (Hz) of $I(amine)Pt(\mu–I)_2Pt(amine)I$ in CD_3COCD_3

amine	$\delta(^{195}Pt)$		$\Delta\delta(cis - trans)$	$^2J(^{195}Pt–^1HN)$	
	trans	*cis*		*trans*	*cis*
$PhMeNH_2$	too insoluble				
$PhEtNH_2$	−4016	−4002	14	64	54
$PhPrNH_2$	−4010	−3999	11	72	75
$PhBuNH_2$	−4008	−3996	12	71	77
$PhNH_2$	−3973	−3915	58		
PhNHMe	−3848				

isomers of the iodo-bridged dimers were observed, while for the secondary amine, PhNHMe, only one isomer was detected. The structures of the two isomers are shown below.



cis



trans

In a previous paper on iodo-bridged dimers with aliphatic amines, we have assigned the higher field isomer to the *trans* compound, especially because it was present in much greater concentration. In this study, the proportions of the two isomers are more equal and it is not possible at the moment to make definite assignments, but we suggest again that the signal at higher field is the *trans* isomer. We will therefore assume these configurations in the remaining discussion.

The $PhEtNH_2$, $PhPrNH_2$, and $PhBuNH_2$ dimeric complexes were observed around −4000 ppm, and the separation $\Delta\delta$ between the two isomers is about 12 ppm, very close to the results reported for primary amine complexes [17]. The $PhNH_2$ dimers were observed at slightly lower fields (average −3945 ppm), close to the values reported for secondary amines [17], and the $\Delta\delta$ is larger (58 ppm). For the secondary aromatic amine, PhNHMe, only one dimer was observed at even lower field as expected (−3848 ppm). It is not possible to determine which isomer is present. The product isolated with the ligand $PhMeNH_2$ was not sufficiently soluble in acetone to measure its ^{195}Pt NMR spectrum. After 24 h of accumulations, no signal was evident.

The ^1H NMR spectra of the products were measured, but because of the presence of two to three species, most of the assignments could not be determined. The assignments of the two iodo-bridged dimers were particularly difficult, since their proportions are almost equal. The signals are also in the same regions as those of the disubstituted compound, which is present for two ligands. The ^1H NMR spectrum of the $PhMeNH_2$ product was measured and showed the presence of three species including the presence of *cis*-$Pt(PhMeNH_2)_2I_2$ in ~60% proportion. The other two species are probably the two isomers of the dimer. The *cis* disubstituted compound is the intermediate in the synthesis of the iodo-bridged dimer and the reaction was probably stopped too rapidly. For the secondary amine, PhNHMe complexes, the *trans* disubstituted complex was observed in large concentration and the dimer was observed in much smaller proportion as observed in ^{195}Pt NMR.

The coupling constants $^2J(^{195}Pt–^1HN)$ for three complexes could be measured. They vary between 54 and 77 Hz (Table 8). The values are not different for the two isomers. In monomers, the *cis* isomers have usually larger coupling constants than the trans. But the iodo-bridged compounds are very different, since the two amine ligands are located on two different Pt atoms. Therefore, their $^2J(^{195}Pt–^1HN)$ coupling constants cannot be compared to those of monomers. For aliphatic amines, the $^2J(^{195}Pt–^1HN)$ in the iodo-bridged dimers were slightly larger for the *trans* compounds (average 68 Hz) than those in the *cis* configuration (average 56 Hz) [17].

4. Conclusions

The *cis*- and *trans*-$Pt(amine)_2I_2$ complexes with amines containing a phenyl ring have been synthesized and characterized mainly by IR and multinuclear magnetic resonance spectroscopies. Two *trans* isomers have also been characterized by crystallographic methods. In ^{195}Pt NMR, the *trans* compounds were observed at higher fields than the *cis* isomers. For the primary amines of the first series, the $\Delta\delta$ ($\delta cis - \delta trans$) is small, but it is larger for $PhNH_2$. For the latter *cis* compound, two signals were observed, which were assigned to the presence of rotamers in solution. For the other amines containing a phenyl group attached to the amine group, no *cis* complexes could be isolated probably because of steric hindrance close to the binding atom. The $\delta(^{195}Pt)$ of the *cis*-$PhNH_2$ compound were observed at lower fields than the one of the other *cis* complexes. The *trans*-$PhNH_2$ isomer was observed in the same region as the other *trans* compounds containing amines of the second series. The *trans* complex containing the secondary amine was observed at much lower field, because of the solvent effect.

The coupling constants $^2J(^{195}Pt–^1HN)$ are larger in the *cis* isomers than in the *trans* analogues. Multinuclear magnetic resonance spectroscopy seems a good criterion to evaluate the purity of the disubstituted compounds. For example, *cis*-$Pt(PhNH_2)I_2$ was shown to contain some *trans* compound. The geometry of the isomer can be evaluated by the coupling constants $^2J(^{195}Pt–^1HN)$ and sometimes by $^3J(^{195}Pt–^1H)$. The study of these complexes in solution is hindered by their very low solubility.

The tetrasubstituted ionic complexes $[Pt(amine)_4]I_2$ could be synthesized only with the four amines of the first series, due again to steric hindrance. These compounds are observed at lower fields than the disubstituted compounds, at $\delta(^{195}Pt) = -2873$ ppm (average in D_2O). The molecules were used as starting material for the synthesis of the *trans* disubstituted complexes.

The iodo-bridged dinuclear species of the type described in this paper are important molecules for the synthesis of several types of compounds, especially those containing mixed-ligands. The preparation of mixed-amines Pt(II) complexes is particularly important in the synthetic field of new potential antitumor compounds. The cleavage of the iodo-bridged dimers in water has been shown to produce only the *cis* isomers unless the ligands are very sterically hindered. The products can be easily transformed in the *cis* dichloro species. The dimers have also been used as intermediates in the preparation of the monosubstituted ionic complex $K[Pt(amine)Cl_3]$, which can be the starting material for the synthesis of all kinds of mixed ligands complexes. We have also used the dimers as intermediates for the synthesis of the *trans* disubstituted complexes with bulky ligands. The normal method to prepare *trans* compounds from the reaction of the tetrasubstituted compounds cannot be used for sterically more demanding ligands.

The purity of these dimers is important especially in the field related to chemotherapy. We have shown that they might contain some $Pt(amine)_2I_2$. The latter compounds will be an impurity in the preparation of the mixed-ligands complexes. It is therefore essential to develop methods to verify the purity of the complexes. ^{195}Pt NMR seems an excellent method to identify the purity of the different compounds. Iodo-bridged dimers have two geometric isomers which can both be observed around −4000 ppm, far from the $Pt(amine)_2I_2$ compounds (around −3300 ppm).

5. Supplementary material

The CIF tables for the two crystals have been deposited to the Cambridge Data File Centre. The deposit numbers are: CCDC Nos. 615207–615208.

Acknowledgements

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of the project and a NSERCC undergraduate summer scholarship to C.B.

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