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Synthesis and study of Pt(II)-aromatic amines complexes of the types *cis*- and *trans*-Pt(amine)$_2$(NO$_3$)$_2$ and *cis*-Pt(amine)$_2$(R(COO)$_2$)

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Abstract

Complexes of the types *cis*- and *trans*-Pt(amine)$_2$(NO$_3$)$_2$ with amines containing a phenyl group were synthesized and studied mainly by IR and multinuclear magnetic resonance spectroscopies. The *cis* complexes could be synthesized pure only with the amines of the type Ph–R–NH$_2$ (R = alkyl), while pure *trans* compounds were synthesized with all the studied amines. In ^{195}Pt NMR spectroscopy, the dinitrato complexes of the amines Ph–R–NH$_2$ were observed around −1700 ppm for the *cis* isomers and at about −1580 for the *trans* complexes. For the other amines, where a phenyl ring is directly attached to the amino group, the signals were observed at lower fields, −1528 ppm for *cis*-Pt(PhNH$_2$)(NO$_3$)$_2$ and around −1450 ppm for all the *trans* isomers. There is a linear relationship between the δ(Pt) of the Pt(amine)$_2$(NO$_3$)$_2$ complexes and the pK_a of the protonated amines. The coupling constants $^2J(^{195}\text{Pt}–^1\text{HN})$ are larger in the *cis* compounds (ave. 76 Hz) than in the *trans* isomers (ave. 63 Hz). The complexes *cis*-Pt(amine)$_2$(R(COO)$_2$) with bidentate dicarboxylato ligands were also synthesized and characterized mainly by IR spectroscopy. The compounds apparently decompose in DMF and are too insoluble in other solvents for solution studies.

Keywords: Platinum; Aromatic amine; Nitrato; Carboxylato; NMR; IR

1. Introduction

The antitumor drug *cisplatin* (*cis*-Pt(NH$_3$)$_2$Cl$_2$) is still one of the most widely used drugs in chemotherapy. Its mechanism of action has been studied by several authors, but there are still many uncertainties, since its reactions are extremely complex [1,2]. The drug remains mostly unchanged in the plasma in the presence of a high chloride concentration (103 mM) and can cross the cell membrane because of its neutrality. The chloride ion concentration is much lower inside the cells (4 mM) and in these conditions, *cis*-Pt(NH$_3$)$_2$Cl$_2$ produces different ionic species, which can bind to DNA [3] leading to the eventual cell death. Its mechanism of action involves aquation or hydrolysis reactions, which have been studied in a few laboratories.

A good review of the influence of the structure on the activity of Pt drugs has been published [4]. When the ligands NH$_3$ in *cisplatin* are replaced by primary amines, the antitumor properties can increase, especially with cyclic amines [5–7], but the latter compounds have often a more limited activity spectrum. Furthermore, several of the most active compounds are quite insoluble [8]. 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)$_2$X$_2$ (X = I or Cl) with different aliphatic amines [9,10]. These complexes have been known for a long time, but their purity has not been well investigated. We have found that multinuclear magnetic resonance spectroscopy is an excellent technique to determine the purity of the

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complexes and also their geometry. The purity of the isomers is important since in the amine system, the antitumor properties are related to the isomeric form of the compound. 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 acetone solution by ^{195}Pt, ^1H and ^{13}C NMR spectroscopy [10,11]. Conductivity measurements in acetone have shown that the dinitrato complexes are not dissociated.

We have now started to extend the study to aromatic amines. We have recently reported the results on complexes of the types *cis*- and *trans*-$Pt(amine)_2I_2$ with different types of amines containing a phenyl group [12]. The compounds were characterized by IR and by multinuclear magnetic resonance spectroscopies in order to determine the purity of the compounds. Most compounds were pure, except for *cis*-$Pt(PhNH_2)_2I_2$, which contained some *trans* isomers when dissolved in acetone. But it was not possible to isolate *cis* complexes with other amines containing a phenyl group directly on the binding N atom because of steric hindrance. We have now transformed these diiodo compounds into the dinitrato complexes. The latter compounds are not very stable in air, but they could be characterized by IR and multinuclear magnetic resonance spectroscopies.

We have also prepared the compounds $Pt(amine)_2(R\text{-}(COO)_2)$ with the same amines. Three dicarboxylate ligands were chosen to form bidentate complexes. These ligands are 1,1-cyclopropyldicarboxylate (1,1-CPDCA), 1,1-cyclobutyldicarboxylate (1,1-CBDCA) and 1,2-cyclobutyldicarboxylate (1,2-CBDCA). Therefore only *cis* compounds were isolated. The latter are very insoluble in most solvents. Therefore solution NMR studies were not possible. The IR spectra were measured in the solid state. The results on these aromatic amines Pt(II) complexes are described 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, while silver nitrate was purchased from Analar. D_2O and CD_3COCD_3 were obtained from CDN Isotopes.

The NMR spectra were measured on a Varian Gemini 300BB. The fields were 300.070, 75.460 and 64.395 MHz for ^1H, ^{13}C and ^{195}Pt, respectively. For the ^{195}Pt NMR spectra, $K_2[PtCl_4]$ (−1628 ppm in D_2O with KCl) was the external standard. The NMR spectra of the dinitrato complexes were measured in CD_3COCD_3, while the carboxylato compounds were studied particularly in D_2O and DMF. Other organic solvents were tried for the latter compounds without success.

2.1. $Pt(amine)_2(NO_3)_2$

The compounds *cis*- and *trans*-$Pt(amine)_2I_2$ were prepared as described in our recent publication on aromatic amines [12]. The dinitrato complexes *cis*- and *trans*-$Pt(amine)_2(NO_3)_2$ were synthesized by slight variations of the methods described for aliphatic amines [10,11]. The compounds $Pt(amine)_2I_2$ (0.5 mmol) were dissolved in a minimum quantity of acetone (EtOH: $CHCl_3$ 1:1 for *cis*-$Pt(PhNH_2)_2I_2$). A slight excess of silver nitrate (1.05 mmol, 178.4 mg) was added and the mixture was stirred in the dark and at low temperature (5 °C) until the reaction was complete (clear colorless solution and a yellow precipitate of AgI). The mixture was filtered and the filtrate was evaporated to dryness. The product was dried under vacuum in a dessicator.

cis-$Pt(PhMeNH_2)_2(NO_3)_2$: IR (cm^{-1}): $\nu_4(NO_3)$ 1512 m, $\nu_2(NO_3)$ 1274w, $\nu_1(NO_3)$ 980s, $\nu_6(NO_3)$ 783w, $\nu_5(NO_3)$ 722m, ν(Pt–N) 385w, ν(Pt–O) 350w, 347w. NMR (δ(ppm)): ^1H: NH, 5.612s + d $^2J(^{195}Pt\text{–}NH) = 73$ Hz, H_1 4.036t, H_2–H_3–H_4 7.430mult.

trans-$Pt(PhMeNH_2)_2(NO_3)_2$: IR (cm^{-1}): $\nu_4(NO_3)$ 1508w, $\nu_2(NO_3)$ 1268m, $\nu_1(NO_3)$ 976m, $\nu_6(NO_3)$ 758m, $\nu_5(NO_3)$ 722vs, ν(Pt–N) 369w, ν(Pt–O) 352w. NMR (δ(ppm)): ^1H: NH, 5.400s, $^2J(^{195}Pt\text{–}NH) = 63$ Hz, H_1 3.848t, H_2–H_3–H_4 7.429mult.

cis-$Pt(PhEtNH_2)_2(NO_3)_2$: yield = 11%, m.p. = 123–169 °C (dec). IR (cm^{-1}): ν(N–H) 3229m, 3136w, ν(=C–H) 3060w, ν(C–H) 2938w, δ NH_2 1586s, $\nu_4(NO_3)$ 1507m, $\nu_2(NO_3)$ 1270s, $\nu_1(NO_3)$ 958m, $\nu_6(NO_3)$ 775w, $\nu_5(NO_3)$ 701s, other bands 1495m, 1455w, 1180w, 1156w, 1086w, 1028s, 1001s, 751vs, 701s, 613w, 547w, 591w, 438w, ν(Pt–N) 374w, ν(Pt–O) 342w. NMR (δ(ppm)): ^1H: NH 5.468s + d, $^2J(^{195}Pt\text{–}NH) = 72$ Hz, H_1 4.045t, H_2 3.116t, H_3–H_4–H_5 7.285mult.

trans-$Pt(PhEtNH_2)_2(NO_3)_2$: yield = 48%, m.p. = 106–157 °C (dec). IR (cm^{-1}): ν(N–H) 3279w, 3234m, 3126w, ν(=C–H) 3043m, ν(C–H) 2941w, 2852w, δ NH_2 1576m, $\nu_4(NO_3)$ 1524m, $\nu_2(NO_3)$ 1279m, $\nu_1(NO_3)$ 959w, $\nu_6(NO_3)$ 763m, $\nu_5(NO_3)$ 701s, other bands 1496 s, 1454vs, 1176m, 1052w, 1077w, 1032m, 833m, 804w, 751s, 592w, 549w, 438w, ν(Pt–N) 358w, ν(Pt–O) 325w. NMR (δ(ppm)): ^1H: NH 4.468s + d $^2J(^{195}Pt\text{–}NH) = 65$ Hz, H_1 4.350mult, H_2 2.628mult, H_3–H_4–H_5 7.045mult.

cis-$Pt(PhPrNH_2)_2(NO_3)_2$: yield 78%, m.p. = 100–112 °C (dec). IR (cm^{-1}): ν(N–H) 3283w, 3254m, 3221m, 3200m, 3125w, ν(=C–H) 3085w, 3062w, 3025w, ν(C–H) 2923w, 2887w, 2855w, δNH_2 1584m, $\nu_4(NO_3)$ 1519m, $\nu_2(NO_3)$ 1271m, $\nu_1(NO_3)$ 988m, $\nu_6(NO_3)$ 780w, $\nu_5(NO_3)$ 731m, other bands 1602m, 1496m, 1455w, 1474w, 1382s, 1353vs, 1206w, 966m, 746m, 698s, 576w, ν(Pt–N) 494w, 462w, ν(Pt–O) 325w. NMR (δ(ppm)): ^1H: NH 5.240s + d $^2J(^{195}Pt\text{–}NH) = 80$ Hz, H_1 2.711mult, H_2 2.089mult, H_3 2.686mult, H_4-H_5-H_6 7.232mult.

trans-$Pt(PhPrNH_2)_2(NO_3)_2$: yield 69%, m.p. = 108–161 °C (dec). IR (cm^{-1}): ν(N–H) 3282m, 3250m, 3170w, ν(=C–H) 3082w, 3060w, 3024w, ν(C–H) 2946w, 2924w, 2860w, δNH_2 1582w, $\nu_4(NO_3)$ 1502s, $\nu_2(NO_3)$ 1259s, $\nu_1(NO_3)$ 960s, $\nu_6(NO_3)$ 794w, $\nu_5(NO_3)$ 715w, other bands 1601w, 1528s, 1453m, 1362m, 1286m, 1205m, 1379m, 1174w, 1153w, 1078w, 1030m, 847w, 759m, 704s, 777w, 579w, ν(Pt–N) 362w, ν(Pt–O) 332f. NMR (δ(ppm)): ^1H:

NH 4.846s + d $^2J(^{195}$Pt–NH) = 67 Hz, H_1 2.717mult, H_2 2.138q, H_3, 2.691mult, H_4–H_5–H_6 7.220mult.

cis-Pt$(PhBuNH_2)_2(NO_3)_2$: yield = 43%, m.p. = 97–111 °C (dec). IR (cm^{-1}): ν(N–H) 3261m, 3236m, 3157w, ν(=C–H) 3083w, 3061w, 3023w, ν(C–H) 2933w, 2858w, δ NH_2 1587w, $\nu_4(NO_3)$ 1507m, $\nu_2(NO_3)$ 1275s, $\nu_1(NO_3)$ 988m, $\nu_6(NO_3)$ 793w, $\nu_5(NO_3)$ 722w, other bands 1603f, 1495s, 1454w, 1216w, 1465w, 1354vs, 1180w, 1155w, 1084w, 1028w, 976m, 833w, 743m, 698m, 580w, ν(Pt–N) 376w, ν(Pt–O) 352w, 328w. NMR (δ(ppm)): ^{1}H: NH 5.172s + d, $^2J(^{195}$Pt–NH) = 77 Hz, H_1 2.748q, H_2 1.689mult, H_3 1.780mult, H_4 2.620t, H_5–H_6–H_7 7.202mult.

trans-Pt$(PhBuNH_2)_2(NO_3)_2$: yield 25%, m.p. = 132–162 °C (dec). IR (cm^{-1}): ν(N–H) 3266s, 3244s, 3173m, ν(=C–H) 3082w, 3057w, 3021w, ν(C–H) 2971w, 2953w, 2932w, 2894w, 2863w, δNH_2 1600s, $\nu_4(NO_3)$ 1498s, $\nu_2(NO_3)$ 1267vs, $\nu_1(NO_3)$ 967vs, $\nu_6(NO_3)$ 784m, $\nu_5(NO_3)$ 717m, other bands 1487s, 1456m, 1400w, 1356w, 1383m, 1205m, 1154m, 1080w, 1031w, 1094w, 747m, 691m, 520w, ν(Pt–N) 390w, ν(Pt–O) 344w. NMR (δ(ppm)): ^{1}H: NH 4.779s + d, $^2J(^{195}$Pt–NH) = 57 Hz, H_1–H_4, 2.634mult, H_2 1.697tt, H_3 1.847tt, H_5–H_6–H_7 7.186mult.

cis-Pt$(PhNH_2)_2(NO_3)_2$: yield: 53%, m.p. = 92–118 °C (dec). IR (cm^{-1}): ν(N–H) 3256m, 3240m, ν(=C–H): 3044w, δ NH_2 1599vs, $\nu_4(NO_3)$ 1510m, $\nu_2(NO_3)$ 1260w, $\nu_1(NO_3)$ 970m, $\nu_6(NO_3)$ 784w, $\nu_5(NO_3)$ 716w, other bands1612s, 1494m, 1467w, 1393m, 1193w, 1178w, 1070w, 1027w, 922w, 832m, 802s, 756s, 732w, 689w, 619w, 577w, 554w, 447m, ν(Pt–N) 386w, ν(Pt–O) 338m, 330w. NMR (δ(ppm)): ^{1}H: H_1–H_2–H_3, 7.278mult.

trans-Pt$(PhNH_2)_2(NO_3)_2$: yield = 19%, m.p. = 133–173 °C (dec). IR (cm^{-1}): ν(N–H): 3256m, 3162m,ν(=C–H): 3037w, δ NH_2 1599s, $\nu_4(NO_3)$ 1508Fs, $\nu_2(NO_3)$ 1276w, $\nu_1(NO_3)$ 970s, $\nu_6(NO_3)$ 784w, $\nu_5(NO_3)$ 716w, other bands 1613s, 1493s, 1466m, 1383m, 1197w, 1167w, 1069w, 1027w, 1152w, 833w, 802w, 756vs, 688sv, 626w, 556w, 578s, 448m, ν(Pt–N) 387m, ν(Pt–O) 347m. NMR (δ(ppm)): ^{1}H: H_1–H_2–H_3, 7.260mult.

trans-Pt$(4\text{-}EtPhNH_2)_2(NO_3)_2$: yield 58%, m.p. = 107–170 °C (dec). IR (cm^{-1}): ν(N–H) 3256s, 3238s, 3166s, ν(=C–H) 3074w, 3042w, ν(C–H) 2969m, 2929w, 2874w, 2841w, δNH_2 1593m, $\nu_4(NO_3)$ 1512s, $\nu_2(NO_3)$ 1273s, $\nu_1(NO_3)$ 975s, $\nu_6(NO_3)$ 786m, $\nu_5(NO_3)$ 716m, other bands 1608s, 1484w, 1452m, 1442m, 1374m, 1228s, 1208s, 1157w, 1113w, 1047w, 1019w, 942s, 830s, 636w, 580s, 540w, 486m, 457w, ν(Pt–N) 384w, ν(Pt–O) 346m. NMR (δ(ppm)): ^{1}H: H_1 7.225d, H_2 7.133d, H_3 2.571q, H_4 1.180t.

trans-Pt(4-*iso*PrPhNH$_2$)$_2$(NO$_3$)$_2$: yield 56%, m.p. = 108–253 °C (dec). IR (cm^{-1}): ν(N–H) 3243vs, 3204s, 3134s, ν(=C–H) 3042m, ν(C–H) 2957m, 2888w, δNH_2 1599s, $\nu_4(NO_3)$ 1512m, $\nu_2(NO_3)$ 1278m, $\nu_1(NO_3)$ 978s, $\nu_6(NO_3)$ 780m, $\nu_5(NO_3)$ 719w, other bands 1488s, 1440m, 1381m, 1363m, 1290s, 1258s, 1183m, 1144w, 1053w, 1019m, 883m, 841m, 735w, 639w, 584s, 549w, 459w, ν(Pt–N) 392w, ν(Pt–O) 352w. ^{1}H NMR (δ(ppm)): NH 7.120s + d, $^2J(^{195}$Pt–NH) = 57 Hz, H_1 7.231d, H_2 7.171d, H_3 2.842h, H_4 1.204d.

trans-Pt(4-*t*BuPhNH$_2$)$_2$(NO$_3$)$_2$: yield 59%, m.p. = 84–144 °C (dec). IR (cm^{-1}): ν(N–H) 3240s, 3214m, 3137m, ν(=C–H) 3056w, ν(C–H) 2957m, 2866w, δNH_2 1598s, $\nu_4(NO_3)$ 1513m, $\nu_2(NO_3)$ 1277m, $\nu_1(NO_3)$ 974m, $\nu_6(NO_3)$ 780w, $\nu_5(NO_3)$ 716w, other bands 1492vs, 1353vs, 1256s, 1204w, 1189w, 1018w, 836s, 802w, 740w, 700w, 584m, 530w, 451w, ν(Pt–N) 369w, ν(Pt–O) 353w. ^{1}H NMR (δ(ppm)): NH 7.134s + d, $^2J(^{195}$Pt–NH) = 62 Hz, H_1 7.339d, H_2 7.227d, H_3 1.284s.

trans-Pt(4-*t*BuPhNH$_2$)$_2$(NO$_3$)$_2$: yield 59%, m.p. = 84–144 °C (dec). IR (cm^{-1}): ν(N–H) 3240s, 3214m, 3137m, ν(=C–H) 3056w, ν(C–H) 2957m, 2866w, δNH_2 1598s, $\nu_4(NO_3)$ 1513m, $\nu_2(NO_3)$ 1277m, $\nu_1(NO_3)$ 974m, $\nu_6(NO_3)$ 780w, $\nu_5(NO_3)$ 716w, other bands 1492vs, 1353vs, 1256s, 1204w, 1189w, 1018w, 836s, 802w, 740w, 700w, 584m, 530w, 451w, ν(Pt–N) 369w, ν(Pt–O) 353w. ^{1}H NMR (δ(ppm)): NH 7.134s + d, $^2J(^{195}$Pt–NH) = 62 Hz, H_1 7.339d, H_2 7.227d, H_3 1.284s.

trans-Pt$(4\text{-}BuPhNH_2)_2(NO_3)_2$: yield 59%, m.p. = 96–190 °C (dec). IR (cm^{-1}): ν(N–H) 3249s, 3161m, ν(=C–H) 3054w, 3022w, ν(C–H) 2958w, 2920m, 2872w, 2855w, δNH_2 1605s, $\nu_4(NO_3)$ 1513m, $\nu_2(NO_3)$ 1273m, $\nu_1(NO_3)$ 973vs, $\nu_6(NO_3)$ 782w, $\nu_5(NO_3)$ 716w, other bands 1492s, 1451w, 1361m, 1261s, 1207m, 1164w, 1090w, 1021w, 823s, 802w, 760w, 574m, 544w, 472m, ν(Pt–N) 371w, ν(Pt–O) 344m. ^{1}H NMR (δ(ppm)): H_1 7.219d, H_2 7.119d, H_3 2.551t, H_4 1.568tt, H_5 1.344qt, H_6 0.904t.

trans-Pt$(PhNHMe)_2(NO_3)_2$: yield 66%, m.p. = 97–116 °C (dec). IR (cm^{-1}): ν(N–H) 3226s, 3183s, ν(=C–H) 3038w, ν(C–H) 2944w, δNH_2 1600s, $\nu_4(NO_3)$ 1525m, $\nu_2(NO_3)$ 1261s, $\nu_1(NO_3)$ 965s, $\nu_6(NO_3)$ 780m, $\nu_5(NO_3)$ 712w, other bands 1493w, 1470w, 1407m, 1355m, 1181w, 1156w, 1130m, 1066m, 1076m, 1066m, 1032w, 832w, 761w, 690m, 617w, 576w, 420w, ν(Pt–N) 351w, ν(Pt–O) 326w. ^{1}H NMR (δ(ppm)): NH 7.631s + d, $^2J(^{195}$Pt–NH) = 71 Hz, H_1 2.850s + d, $^3J(^{195}$Pt–H_1) = 24 Hz, H_2–H_3–H_4 7.291m.

2.2. $Ag_2R(COO)_2$

These compounds were synthesized by the recently published method (13).

Ag_2(1,1-CBDCA): yield 71%, dec. 199–300. IR (cm^{-1}) ν(C=O) 1596, ν(C–O) 1345.

Ag_2(1,2-CBDCA): yield quantitative, dec. 228–300. IR (cm^{-1}) ν(C=O) 1556, ν(C–O) 1396.

Ag_2(1,1-CPDCA): yield 45%, dec. 194–300. IR (cm^{-1}) ν(C=O) 1589, 1569, ν(C–O) 1391, 1373.

2.3. *cis*-Pt(amine)$_2$(R(COO)$_2$)

The two compounds *cis*-Pt(amine)$_2I_2$ and $Ag_2R(COO)_2$ were mixed together in acetone in a 1:1.15 proportion. The mixture is stirred in the dark until the formation of AgI is complete (several hours). The yellow precipitate is filtered out and the filtrate is evaporated to dryness and the residue is dried in a dessicator under vacuum.

cis-Pt(PhMeNH$_2$)$_2$(1,1-CBDCA): yield 41%, m.p. = 138–157°C. IR (cm^{-1}): ν(N–H) 3209m 3115w, ν(=C–H) 3063w 3031w, ν(C–H) 2942w 2855w ν(C=O) 1608vs, ν(C–O) 1360s, other bands 1497w, 1455m, 1224w, 1116w, 1156w, 1077w, 1029w, 988w, 842w, 751m, 698s, 619w, 576w, ν(Pt–O) 481w, ν(Pt–N) 357w, 329w.

cis-Pt(PhMeNH$_2$)$_2$(1,2-CBDCA): yield 19%, m.p. = 92–171 °C. IR (cm^{-1}): ν(N–H) 3202m, 3111w, ν(=C–H) 3062w 3030w, ν(C–H) 2943w 3871w, ν(C=O) 1604s, ν(C–O) 1368m, other bands 1496m, 1454m, 1293w, 1267w, 1225w, 1177w, 1076w, 1029w, 983w, 752s, 699vs, 621w, 575w, ν(Pt–O) 480w, ν(Pt–N) 354w, 326w.

cis-Pt(PhMeNH$_2$)$_2$(CPDCA): yield 51%, m.p. = 103–149 °C. IR (cm^{-1}): ν(N–H) 3208m 3111m, ν(=C–H) 3064w 3030w, ν(C–H) 2949w 2878w, ν(C=O) 1619s, ν(C–O) 1377s, other bands 1497w, 1455w, 1197m, 1077w, 1030w, 973w, 916w, 808w, 751s, 698vs, 619w, 530w, ν(Pt–O) 480w, ν(Pt–N) 374w, 326w.

cis-Pt(PhEtNH$_2$)$_2$(1,1-CBDCA): yield 41%, m.p. = 112–139 °C. IR (cm^{-1}): ν(N–H) 3210m 3125fw, ν(=C–H) 3087w 3062w 3027w, ν(C–H) 2943w 2855w, ν(C=O) 1621s 1604s, ν(C–O) 1360m, other bands 1496m, 1454m, 1220w, 1180w, 1157w, 1078w, 1033w, 1002w, 904w, 749w, 699m, 552w, ν(Pt–O) 470w, ν(Pt–N) 352w, 323w.

cis-Pt(PhEtNH$_2$)$_2$(1,2-CBDCA): yield 24%, m.p. = 103–124 °C. IR (cm^{-1}): ν(N–H) 3206m 3122w, ν(=C–H) 3086w, 3062w, 3027w, ν(C–H) 2945w, 2855w, ν(C=O) 1604s, ν(C–O) 1370m, other bands 1496m, 1454w, 1265w, 1225w, 1178, 1156w, 1079w, 1032w, 748m, 699s, 619w, 550w, ν(Pt–O) 494w, ν(Pt–N) 345w, 327w.

cis-Pt(PhEtNH$_2$)$_2$(CPDCA): yield 57%, m.p. = 96–163 °C. IR (cm^{-1}): ν(N–H) 3204m 3123m, ν(=C–H) 3026w, ν(C–H) 2918m, 2850w, ν(C=O) 1619s 1591s, ν(C–O) 1398s, other bands 1496w, 1454w, 1421m, 1227w, 1195w, 1157w, 1079w, 1033w, 964w, 933w, 770w, 747m, 699m, 558w, 530w, ν(Pt–O) 488w, ν(Pt–N) 366w, 326w.

cis-Pt(PhPrNH$_2$)$_2$(1,1-CBDCA): yield 62%, m.p. = 122–157 °C. IR (cm^{-1}): ν(N–H) 3213m, ν(=C–H) 3086w 3062w 3026w, ν(C–H) 2941m 2856w, ν(C=O) 1619s 1604s, ν(C–O) 1360m, other bands 1496m, 1454m, 1220w, 1157w, 1082w, 1029m, 1115w, 908w, 746m, 699m, 581w, 565w, ν(Pt–O) 470w, ν(Pt–N) 352w, 323w.

cis-Pt(PhPrNH$_2$)$_2$(1,2-CBDCA): yield 37%, m.p. = 97–141 °C. IR (cm^{-1}): ν(N–H) 3207m 3121w, ν(=C–H) 3085w 3061w 3025w, ν(C–H) 2941m, 2858w, (C=O) 1604vs, ν(C–O) 1399m 1373m, other bands 1495m, 1453w, 1225w, ν(C–N) 1178w, 1155w, 1082w, 1029w, 910w, 746m, 699s, 620w, 563w, ν(Pt–O) 494w, ν(Pt–N) 364w, 330w.

cis-Pt(PhPrNH$_2$)$_2$(CPDCA): yield 62%, m.p. = 108–153 °C. IR (cm^{-1}): ν(N–H) 3213m, ν(=C–H) 3085w 3061w 3025w, ν(C–H) 2939m 2857w, ν(C=O) 1617s 1603s, ν(C–O) 1362m, other bands 1495m, 1454m, 1245tw, 1220w, 1157w, 1082w, 1029w, 1114w, 746m, 698m, 566w, ν(Pt–O) 468w, ν(Pt–N) 353w, 321w.

cis-Pt(PhBuNH$_2$)$_2$(1,1-CBDCA): yield 49%, m.p. = 122–211 °C. IR (cm^{-1}): ν(N–H) 3213m, ν(=C–H) 3086w 3062w 3026w, ν(C–H) 2937m 2857w, ν(C=O) 1617s 1604s, ν(C–O) 1364m, other bands 1496w, 1454w, 1221w, 1158w, 1085w, 1029w, 1116w, 905w, 748m, 699m, 569w, ν(Pt–O) 469w, ν(Pt–N) 352w, 329w.

cis-Pt(PhBuNH$_2$)$_2$(1,2-CBDCA): yield 39%, m.p. = 93–121 °C. IR (cm^{-1}): ν(N–H) 3208m 3122w, ν(=C–H) 3085w 3061w 3025w, ν(C–H) 2933m 2855w, ν(C=O) 1604s, ν(C–O) 1373m, other bands 1495w, 1453w, 1227w, 1178w, 1155w, 1083w, 1046w, 1029w, 912w, 748m, 699m, 619w, 569w, ν(Pt–O) 462w, ν(Pt–N) 351w, 328w.

cis-Pt(PhBuNH$_2$)$_2$(CPDCA): yield 52%, m.p. = 110–142 °C. IR (cm^{-1}): ν(N–H) 3214m, ν(=C–H) 3086w 3062w 3025w, ν(C–H) 2932m 2857w, ν(C=O) 1621s 1604s, ν(C–O) 1380m, other bands 1496w, 1453w, 1239w, 1197w, 1085w, 1030w, 972w, 810w, 748m, 699m, 612w, 530w, 570w, ν(Pt–O) 496w, ν(Pt–N) 366w, 325w.

cis-Pt(PhNH$_2$)$_2$(1,1-CBDCA): yield 38%, m.p. = 102–147 °C (dec.). IR (cm^{-1}): ν(N–H) 3191m, ν(=C–H) 3046m, ν(C–H) 2990m 2944m 2868w, ν(C=O) 1619s 1600s, ν(C–O) 1352m, other bands 1494vs, 1225w, 1469w, 1199w, 1156w, 1072w, 1028w, 904w, 801w, 756m, 690s, 620w, 550w, 593w, ν(Pt–O) 458w, ν(Pt–N) 353w, 303w.

3. Results and discussion

3.1. Pt(amine)$_2$(NO$_3$)$_2$

3.1.1. Synthesis of the compounds

The dinitrato compounds were synthesized from the diiodo complexes. Two series of primary amines were studied in this project. The amines of the first series are of the type Ph–R–NH$_2$, with an alkyl group between the phenyl and amine groups. The second series includes PhNH$_2$ and 4-R–PhNH$_2$ (R = Et, *iso*Pr, *tert*-Bu and *n*-Bu in *para* position). A secondary amine (PhNHMe) was also included in the study. The amines of the second series contain a phenyl group on the binding atom and are more sterically hindered than the amines of the first series. The secondary amine is the most sterically demanding ligand.

The compounds Pt(amine)$_2$I$_2$ with these ligands were synthesized as recently reported [12]. The *cis* diiodo isomers were synthesized only with the amines of the first series and PhNH$_2$. The diiodo complexes containing the other amines could not be synthesized because of steric hindrance. Therefore the compounds *cis*-Pt(amine)$_2$(NO$_3$)$_2$ were synthesized only with the amines of the first series and PhNH$_2$.

The dinitrato complexes were prepared by the reaction (in the dark around 5 °C) of the diiodo complexes with a slight excess (10–15%) of silver nitrate in acetone, as reported for aliphatic amines [10,11].

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

The time of reaction varied between 4 and 8 h. For the *cis* PhNH$_2$ compound, the reaction was performed in a 1:1 mixture of ethanol and chloroform, since the *cis* compound isomerizes in acetone. Souchard et al. [14] have reported the compound *cis*-Pt($PhNH_2$)$_2$(NO_3)$_2$ which was synthesized in acetone. We have repeated their procedure and we have found by NMR spectroscopy that *cis* and *trans* complexes were present. The reported compound was not characterized by NMR by the authors [14]. Following our procedure, only the *cis* isomer was detected when the preparation was performed in a 1:1 mixture of ethanol and chloroform.

These dinitrato complexes are not very stable at room temperature. For the $PhMeNH_2$ compound, all the manipulations were done in the cold, the solution was evaporated at 5 °C and kept below this temperature to avoid decomposition.

The *cis* dinitrato complexes were synthesized with the amines of the first series Ph–R–NH where R = CH_3, C_2H_5, *n*-C_3H_7, and *n*-C_4H_9 and also with $PhNH_2$. The *trans* dinitrato compounds were prepared with all the studied amines. The yields varied between 11% and 78%. In general, the decomposition points (shown in the Section 2) of the *cis* complexes are lower than those of the *trans* isomers and also than the corresponding diiodo analogues.

3.1.2. IR spectroscopy

The compounds were characterized in the solid state in KBr pellets by IR spectroscopy. The main bands were assigned based on published work on similar compounds [15–19] and are shown in Section 2. The notation of Nakamoto [20] was used for the bands involving the nitrato ligands. The symmetry of the free nitrate ion is D_{3h} with a bond order of $1\frac{1}{3}$, while in the monodentate coordinated nitrato ligand, the N–O(Pt) bond order is close to 1. The π electron density is then delocalized on only two N–O bonds resulting in a bond order of $1\frac{1}{2}$ for the two latter bonds. The approximate symmetry of coordinated NO_3^- (monodentate) is C_{2v}. It has been suggested that the position of the ν_1 band (at 1049 cm^{-1} [20] in free NO_3^-) gives important information on the covalent character of the Pt–O bond [21]. 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 $\nu_2(A_1)$ and $\nu_4(B_2)$ stretching modes in C_{2v} symmetry [20]. 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 [21,22]. For ionic nitrate $\Delta = 0$ cm^{-1}, while it is 385 cm^{-1} in CH_3ONO_2 a totally covalent compound [22].

The Δ values 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 $\Delta(\nu_4 - \nu_2)$ was calculated using the five complexes for which the two isomers could be measured. These values are 241 cm^{-1} (*cis*) and 238 cm^{-1} (*trans*). For the aliphatic amines system [11], the values were 252 cm^{-1} (*cis*) and 238 cm^{-1} (*trans*) and for cyclic amines, they were 227 cm^{-1} (*cis*) and 240 cm^{-1} (*trans*) [10]. In this study on aromatic amines, the difference between the *cis* and *trans* isomers does not seem very significant.

Table 1
$\Delta(\nu_4 - \nu_2)$ and $\Delta\nu_1$ (cm^{-1}) in the complexes *cis*- and *trans*-Pt(amine)$_2$(NO_3)$_2$

Amine	*cis*-Pt(amine)$_2$(NO_3)$_2$		*trans*-Pt(amine)$_2$(NO_3)$_2$	
	$\Delta(\nu_4 - \nu_2)$	$\Delta\nu_1$	$\Delta(\nu_4 - \nu_2)$	$\Delta\nu_1$
$PhMeNH_2$	237	69	240	73
$PhEtNH_2$	237	91	245	90
$PhPrNH_2$	248	61	243	89
$PhBuNH_2$	232	61	231	82
$PhNH_2$	250	79	232	79
4-$EtPhNH_2$			239	74
4-*i*$PrPhNH_2$			234	71
4-*t*$BuPhNH_2$			236	75
4-$BuPhNH_2$			240	76
PhNHMe			264	84

The position of ν_1 for our compounds is slightly different in the two geometries (ave. $\Delta\nu_1$ 72 cm^{-1} for *cis* and 83 cm^{-1} for *trans*, using only the five complexes whose spectra of both isomers are available). For cyclic amines, these values are 71 and 86 cm^{-1} [10]. For the compounds *cis* and *trans*-Pt(pyridine derivative)$_2$(NO_3)$_2$, the ν_1 band was also found less energetic in the *trans* complexes (ave. $\Delta\nu_1 = 90$ cm^{-1} (*cis*), 120 cm^{-1} (*trans*)), suggesting a more covalent character of the Pt–O bonds in the *trans* geometry [19]. For amines, the difference is smaller than in pyridine complexes. Our previous results on the aliphatic amines system seemed to indicate that the covalency of the Pt–O bonds in the *cis* and *trans* compounds is not very different in the two isomers [10,11]. The aromatic amines studied here, seem very similar to the results obtained on aliphatic and cyclic amines complexes.

The stretching energy of a slightly more covalent bond should increase and these results can be compared to the energies of the ν(Pt–O) vibrations. For the *cis* complexes, two ν(Pt–N) and two ν(Pt–O) bands are expected from group theory for the skeleton PtN_2O_2 (C_{2v} symmetry), while one ν(Pt–N) and one ν(Pt–O) are predicted for the *trans* analogues (20). A study on *cis*-Pt(NH_3)$_2$(NO_3)$_2$ has shown that these vibrations are often coupled with other vibrations [23]. The bands assigned to these vibrations are shown in Table 2. Only one band was observed for the ν(Pt–O) vibrations in the *trans* compounds, between 325 and 353 cm^{-1}, while one or two bands were observed in the range 325–352 cm^{-1} in the *cis* configuration. The energy of these vibrations are quite low and close to the energy of ν(Pt–Cl) vibrations, but they are difficult to assign with certainty, since the intensity of the bands are weak. They are probably not pure and might couple with other vibrations. Similar results were reported for dinitrato aliphatic amines complexes [10,11].

The ν(Pt–N) bands assignments are based on some published works [9–11,20,23–25]. We have assigned only one band for the *cis* isomers (ν_s) and only one band (ν_{as}) for the *trans* compounds around 380 cm^{-1} (Table 2). The

Table 2
ν(Pt–O) and ν(Pt–N) (cm^{-1}) for the complexes Pt(amine)$_2$(NO$_3$)$_2$

Amine	ν(Pt–O)		ν(Pt–N)	
	cis	*trans*	*cis*	*trans*
PhMeNH$_2$	350, 347	352	385	369
PhEtNH$_2$	342	325	374	358
PhPrNH$_2$	325	332		362
PhBuNH$_2$	352, 328	344	376	390
PhNH$_2$	338, 330	347	386	387
4-EtPhNH$_2$		346		384
4-*i*PrPhNH$_2$		352		392
4-*t*BuPhNH$_2$		353		369
4-BuPhNH$_2$		344		377
PhNHMe		326		351

second band for the *cis* complexes is probably hidden by the ν(Pt–O) bands. The ν(Pt–N) vibrations are observed at similar or slightly higher energies than in the corresponding diiodo compounds [12].

3.1.3. NMR spectroscopy

The complexes Pt(amine)$_2$(NO$_3$)$_2$ were characterized by ^{195}Pt and ^{1}H magnetic resonance in acetone. The complexes were pure and are not dissociated in acetone as shown by conductivity measurements of the cyclic amine complexes [10].

The ^{195}Pt chemical shifts of the dinitrato complexes are listed in Table 3. The nitrato ion is a weak ligand and its polarisability is smaller than the one of the iodo ligand. Therefore the Pt d orbital coefficient in the Ramsey equation is larger for the dinitrato complex and the Pt signals will be observed at much lower field than for the diiodo compounds. The *cis* dinitrato isomers of the complexes containing the amines of the first series were observed at higher fields (ave. −1702 ppm) than their *trans* analogues (ave. −1582 ppm). The difference ($\Delta\delta$) between the *cis* and *trans* isomers (ave. 120 ppm) is quite constant for the different ligands and it is much larger than the value (ave. 10 ppm [12]) published for the corresponding diiodo compounds. The results on these dinitrato compounds are similar to those reported for aliphatic and cyclic primary amines (around −1695 (*cis*) and −1570 (*trans*) ppm) [10,11]. The ^{195}Pt chemical shifts of the other compounds were observed at lower fields. The *cis*-Pt(PhNH$_2$)$_2$(NO$_3$)$_2$ was found at lower fields than the other *cis* compounds (about 75 ppm), probably due to the solvent effect. In the complexes of the amines of the first series, there is an alkyl group separating the phenyl group from the binding atom. Steric hindrance close to the binding side is thus reduced, permitting the approach of molecules of solvents close to the Pt atom, which increases the electron density on the Pt atom. In the *cis* PhNH$_2$ complex, the two phenyl groups are very close to the metal atom, which hinders the approach of molecules of solvent towards the Pt atom. The electron density on the Pt atom will thus be reduced and its δ(^{195}Pt) will be shifted towards lower fields. The chemical shifts of the *trans* compounds of the second series and of the secondary amines are more uniform (−1436 to −1484 ppm) and are observed at lower fields than the *trans* complexes of the first series also because of the solvent effect.

Table 3
δ(^{195}Pt) and $\Delta\delta = \delta_{cis} - \delta_{trans}$ (ppm) of the complexes Pt(amine)$_2$(NO$_3$)$_2$ in CD$_3$COCD$_3$

Amine	pK_a	Proton affinity (kJ/m)	*cis*	*trans*	$\Delta\delta$
PhMeNH$_2$	9.62	913	−1691	−1571	−120
PhEtNH$_2$	9.83	936	−1703	−1582	−121
PhPrNH$_2$	10.28[a]		−1706	−1587	−119
PhBuNH$_2$	10.66[a]		−1708	−1589	−119
PhNH$_2$	4.603	883	−1528	−1436	−92
4-EtPhNH$_2$	5.09[a]			−1451	
4-*i*PrPhNH$_2$	5.01[a]			−1449	
4-*t*BuPhNH$_2$	4.93[a]			−1441	
4-BuPhNH$_2$	4.90[a]			−1462	
PhNHMe	4.85	917		−1484	

[a] These values were calculated [27].

The solvent effect is an important factor in these studies, especially for solvents like water or acetone which can coordinate to platinum in solution. The dinitrato complexes were measured in deuterated acetone, a solvent which can coordinate to Pt, but not as easily as water. Therefore the solvent effect should be reduced compared to water, but it should still be an important factor. 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 electron density around the Pt nucleus. 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 a few studies published in the literature on dinitrato complexes. For the NH$_3$ dinitrato [26] complexes, the $\Delta\delta$ value between the *cis* and *trans* isomers is −179 ppm (in DMF), for primary amines [10,11] the ave. reported value is −125 ppm (in acetone), for secondary amines [11] $\Delta\delta_{\text{ave}} = -44$ ppm (in acetone) and for pyridine derivatives [19] $\Delta\delta_{\text{ave}} = -59$ ppm (in CDCl$_3$ or CD$_2$Cl$_2$). Therefore the $\Delta\delta$ values seem to depend on the solvent and the N-ligands. Our values are close to those reported on the aliphatic amines and cyclic amines [10,11].

The δ(^{195}Pt) of the complexes of the first series shift slightly towards higher fields as the length of the alkyl chain increases for both isomers. This is again explained by the solvent effect. For the PhMeNH$_2$ ligand, the phenyl group is closer to the binding site than in PhBuNH$_2$ ligand. The proximity of the phenyl groups close to the Pt atom reduces the approach of the molecules of solvent in the close environment of the metal centre. Therefore the electron density on the Pt atom is reduced when the phenyl groups are close to the binding atom. In ^{195}Pt NMR, the chemical shifts will be observed at lower fields (lower electron density of the Pt atom) when the alkyl chain is shorter.

For the four ligands of the first series, the difference is about 18 ppm between R = Me and R = Bu for both isomers.

Attempts were made to correlate the $\delta(^{195}Pt)$ of the complexes with the basicity of the protonated amines. These ligands cannot accept electron density from the Pt atom. Therefore, in the formation of the σ(amine → Pt) bond, electron density is transferred from the amine ligand to the metal atom, resulting in a shielding on the Pt nucleus (^{195}Pt NMR) and a deshielding effect on the ligand (^{1}H NMR). The pK_a values of the ligands are not all available. A few were calculated using the software SOLARIS V4.67 [27] and are shown in Table 3. The δ(Pt) values were plotted *versus* the pK_a of the protonated amines and a very good correlations could be observed, especially with the *cis* compounds. The relation is shown in Fig. 1. For the *trans* complexes, there is also a good relation, especially if we do not include the secondary amine compound. Therefore the δ(Pt) values of these complexes are influenced by the basicity of the ligands. For the aliphatic amines systems, the correlations were poor [10,11]. For the latter compounds, better correlations were observed with the proton affinity values, which are measured in the gas phase. But these values are not very common in the literature. A few values for aromatic amines are known and are shown in Table 3. For the primary amines, only three values are available and there seems to be a good correlation for both the *cis*- and *trans*-Pt(amine)$_2$(NO$_3$)$_2$ complexes.

The ^{1}H NMR chemical shifts of the complexes are listed in Section 2. There are very few dinitrato complexes studied by NMR in the literature. For the complexes of the amines of the first series, the NH signals of the *cis* complexes were observed at lower fields (5.2–5.6 ppm) than those of the *trans* isomers (4.8–5.4 ppm) as shown in Table 4. This observation is in agreement with the δ(Pt) values, 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 (δ(H) at lower field) should be associated with a greater electron density on the platinum atom (δ(Pt) at higher field). The NH$_2$ signals of the PhNH$_2$, 4-EtPhNH$_2$ and 4-BuPhNH$_2$ were hidden by other resonances.

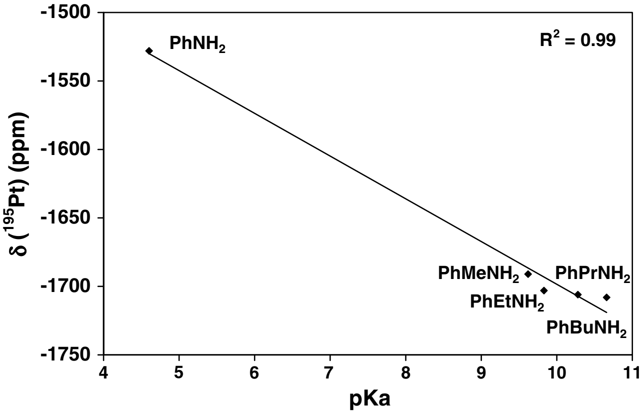

Fig. 1. $\delta(^{195}Pt)$ (ppm) of the complexes *cis*-Pt(amine)$_2$(NO$_3$)$_2$ vs. pK_a of the protonated amines.

Table 4
$\delta(^{1}HN)$, $\Delta\delta(\delta_{complex} - \delta_{free\ amine})$ (ppm) and $^{2}J(^{195}Pt–^{1}HN)$ (Hz) of Pt(amine)$_2$(NO$_3$)$_2$ in CD$_3$COCD$_3$ (for a few complexes, the NH$_2$ signal was hidden by other signals)

Amine		NH	Δδ(NH)	$^{2}J(^{195}Pt–^{1}HN)$	$^{3}J(^{195}Pt–^{1}H_3C)$
PhMeNH$_2$	*cis*	5.612	1.187	73	
	trans	5.400	0.974		
PhEtNH$_2$	*cis*	5.468	1.782	72	
	trans	4.468	0.782	65	
PhPrNH$_2$	*cis*	5.240	2.125	80	
	trans	4.846	1.731	67	
PhBuNH$_2$	*cis*	5.172	[a]	77	
	trans	4.779	[a]	57	
4-*i*PrPhNH$_2$	*trans*	7.120	2.817	57	
4-*t*BuPhNH$_2$	*trans*	7.134	2.790	62	
PhNHMe	*trans*	7.631	2.825	71	24

[a] δ(NH$_2$) of free amine hidden by other signal.

The ^{1}H NMR spectra of the free amines were also measured in acetone and the $\Delta\delta$ ($\delta_{complex} - \delta_{amine}$) values calculated (shown in Table 4) in order to evaluate the effect of platinum coordination on the ligands. As already mentioned, the values for the NH signals are larger in the *cis* geometry. The $\delta(^{1}H)$ of the NH$_2$ resonance shifts towards higher fields as the lengths of the alkyl chain increases in the complexes of the first series (5.61 and 5.40 ppm for *cis*- and *trans*-Pt(PhMeNH$_2$)(NO$_3$)$_2$ to 5.17 and 4.78 ppm for *cis*- and *trans*-Pt(PhBuNH$_2$)(NO$_3$)$_2$), which might appear surprising since PhBuNH$_2$ should be a better donor than PhMeNH$_2$. But if the $\Delta\delta$ values are considered, these data seem to increases as the length of the alkyl chain increases in the complexes of the first series (Table 4). For the other *trans* compounds, the value seems more uniform (~2.8 ppm).

The $^{2}J(^{195}Pt–^{1}HN)$ coupling constants are shown in Table 4. They are larger in the *cis* configuration with an average value of 76 Hz compared to 63 Hz (ave.) for the *trans* isomers. The average values were found to be 68 Hz (*cis*) and 62 Hz (*trans*) for the corresponding diiodo complexes [12]. In the dinitrato primary aliphatic amines these values were 67 (*cis*) and 58 (*trans*) Hz [11].

The $^{3}J(^{195}Pt–^{1}H)$ coupling constants usually also depend on the geometry of the complex. They are difficult to observe in these complexes because of the multiplicity of the signals. But it was observed for *trans*-Pt(PhNHMe)$_2$(NO$_3$)$_2$ (24 Hz) since the –CH$_3$ signal is a singlet. In the aliphatic and cyclic amines systems, these values were 35–47 Hz for the *cis* compounds and 27–33 Hz for the *trans* isomers [10,11].

3.2. cis-Pt(amine)$_2$(R(COO)$_2$)

3.2.1. Synthesis of the compounds

A few methods have been reported for the synthesis of Pt(II)-carboxylato complexes. The different methods have been summarized recently along with our new method published recently [13]. This new synthetic procedure is more rapid and produces pure compounds contrary to most of the other published methods. In this method, the silver dicarboxylate compound is first synthesized and reacted with *cis*-Pt(amine)$_2$I$_2$ and the reaction is performed in acetone. We have used only bidentate carboxylate ions in this study, therefore all the Pt(II) complexes have the *cis* geometry. Three dicarboxylate ligands were studied: 1,1-cyclopropyldicarboxylate, 1,1-cyclobutyldicarboxylate and 1,2-cyclobutyldicarboxylate.

$$\begin{aligned} &cis\text{-Pt(amine)}_2\text{I}_2 + \text{Ag}_2(\text{R(COO)}_2) \\ &\quad \rightarrow cis\text{-Pt(amine)}_2(\text{R(COO)}_2) + 2\text{AgI}\downarrow \end{aligned}$$

The crystal structure of one of the silver intermediate Ag$_2$(1,1-CBDCA) was recently published [13]. The yields of *cis*-Pt(amine)$_2$(R(COO)$_2$) varied between 19% and 62%. They are quite low, because the preparations were done on a micro scale. They were the lowest with 1,2-CBDCA, since this ligand forms a 7-membered chelate ring with the Pt atom, which reduces its stability compared to the other carboxylates, which form the more stable 6-membered chelates. The decomposition points of the complexes are also the lowest with the 1,2-CBDCA ligand (experimental section) showing the importance of the chelate effect in the stability of the Pt complexes.

The *cis*-Pt(amine)$_2$(R(COO)$_2$) complexes were prepared with the four amines of the first series. We have shown that the complex *cis*-Pt(PhNH$_2$)$_2$I$_2$ partly isomerizes in acetone [12]. Therefore its reaction was studied in chloroform and it seems that with the ligand 1,1-CBDCA, the compound was formed. With other carboxylates, the *cis*-Pt(PhNH$_2$)$_2$I$_2$ solution decomposed.

The dicarboxylato compounds are very insoluble and could not be characterized in solution by NMR spectroscopy. DMF seemed the best solvent, but the spectra of the solution indicated that the complexes were decomposed. There are several products formed, since the ^{1}H NMR spectra contained a great number of new signals. Furthermore, the signals were very large probably caused by the presence of solid particles in suspension.

3.2.2. IR spectroscopy

All the isolated complexes were characterized by IR spectroscopy and the results are shown in the experimental section. The carboxylate region is of special interest for this type of compounds. For the carboxylate ions, the ν(C=O) vibrations absorb between 1595 and 1565 cm^{-1}, while the ν(C–O) vibrations range between 1410 and 1330 cm^{-1}. The difference between the two vibration modes ($\Delta\nu$) is smaller in the carboxylates (≈180 cm^{-1}) than in the acids (≈400 cm^{-1}), where the resonance is much reduced.

The ν(C=O) and ν(C–O) vibrations modes of the *cis* dicarboxylato Pt(II) complexes are shown in Table 5. A few bands are split. The ν(C=O) vibrations absorb around 1610 cm^{-1}, while the ν(C–O) mode was observed around 1370 cm^{-1}. The $\Delta\nu$ values were calculated and they vary between 218 and 263 cm^{-1}. These values agree with the results reported in the literature [28–31]. For comparison, two of these reports [32] are also shown in Table 5. The $\Delta\nu$ values are larger than in the free carboxylates, but much lower than in the acids. These bonds are usually involved in H-bonding and these will influence the energy of the carboxyl vibrations.

Table 5
ν_{sym}C=O, ν_{asym}C–O and $\Delta(\nu_{\text{sym}} - \nu_{\text{asym}})$ (cm^{-1}) in *cis*-Pt(amine)$_2$(R(COO)$_2$)

Amine	R(COO)$_2$	ν_{sym}C=O	ν_{asym}C–O	Δ[a]
PhNH$_2$	1,1-CBDCA	1619, 1600	1352	263
PhMeNH$_2$	1,1-CPDCA	1619	1377	242
	1,1-CBDCA	1608	1360	248
	1,2-CBDCA	1604	1368	236
PhEtNH$_2$	1,1-CPDCA	1619	1398	221
	1,1-CBDCA	1621, 1604	1360	253
	1,2-CBDCA	1604	1370	234
PhPrNH$_2$	1,1-CPDCA	1617, 1603	1362	248
	1,1-CBDCA	1619, 1604	1360	252
	1,2-CBDCA	1604	1399, 1373	218
PhBuNH$_2$	1,1-CPDCA	1621, 1604	1380	233
	1,1-CBDCA	1617, 1604	1364	247
	1,2-CBDCA	1604	1373	231
NH$_3$ [32]	1,1-CBDCA	1610	1378, 1360	241
EtNH$_2$ [32]	1,1-CBDCA	1620	1365	255

[a] When two bands, the average value was used.

The ν(Pt–N) and ν(Pt–O) vibrations are usually weak bands which are difficult to assign. There are very few examples in the literature found on this type of complex. A few metallic complexes with glycine have been reported. For Pt(glycine)$_2$, the ν(Pt–N) and ν(Pt–O) vibrations have been located at 549 and 415 cm^{-1}, respectively, [20]. In a few examples with 1,1-CBDCA the authors have assigned the ν(Pt–O) vibrations between 460 and 480 cm^{-1} [33–35]. In these *cis* compounds, only one ν(Pt–O) band was observed, although theoretically, there should be two. These vibrations seem to be very dependent on the metal and are affected by intermolecular interactions. We have used these references to make tentative assignments for the ν(Pt–N) and ν(Pt–O) vibrations in our complexes and these are shown in Table 6. One weak band observed between 458 and 496 cm^{-1} was assigned to the ν(Pt–O) vibrations, while two weak bands observed between 303 and 374 cm^{-1} were assigned to the ν(Pt–N) modes. Two bands were observed for the latter vibrations as expected for *cis* compounds. The ν(Pt–N) vibrations seem to absorb at quite low energy, in the same region as the ν(Pt–Cl) vibrations, but similar values were reported for the compounds Pt(amine)$_2$I$_2$ with the same amines [12] and for the Pt(amine)$_2$(NO$_3$)$_2$ compounds discussed in the above section. It seems that the ν(Pt–N) vibrations absorb at lower energy for amines containing an aromatic group compared to aliphatic amines, where these vibration modes are observed at higher energy [9,10].

Table 6
Tentative ν(Pt–O) and ν(Pt–N) vibrations (cm^{-1}) in the complexes *cis*-Pt(amine)$_2$(R(COO)$_2$)

Amine	R(COO)$_2$	ν(Pt–O)	ν(Pt–N)
PhNH$_2$	1,1-CBDCA	458	353, 303
PhMeNH$_2$	1,1-CPDCA	480	374, 326
	1,1-CBDCA	481	357, 329
	1,2-CBDCA	480	354, 326
PhEtNH$_2$	1,1-CPDCA	488	366, 326
	1,1-CBDCA	490	350, 326
	1,2-CBDCA	490	345, 327
PhPrNH$_2$	1,1-CPDCA	468	353, 321
	1,1-CBDCA	470	352, 323
	1,2-CBDCA	494	364, 330
PhBuNH$_2$	1,1-CPDCA	496	366, 325
	1,1-CBDCA	469	352, 329
	1,2-CBDCA	462	351, 328

4. Conclusion

The complexes *cis*- and *trans*-Pt(amine)$_2$(NO$_3$)$_2$ with aromatic amines were synthesized from the diiodo complexes and were characterized in the solid state by IR spectroscopy and in acetone solution by ^{195}Pt and ^{1}H NMR spectroscopy. The complexes are pure and are not dissociated in acetone as shown by conductivity measurements. These dinitrato compounds are not very stable and it was not possible to prepare crystals adequate for crystallographic studies.

IR spectroscopy has confirmed that the NO$_3$$^-$ ligands are coordinated in a monodentate fashion. The *trans* isomers have shown only one ν(Pt–O) and one ν(Pt–N) bands, while most of the *cis* isomers have two ν(Pt–O) bands, but only one ν(Pt–N) band. These bands are weak bands and they are not easy to detect.

In^{195}Pt NMR, the *cis* isomers were observed at higher fields than the *trans* compounds, while in ^{1}H NMR, the signals of the NH groups of the *cis* complexes were observed at lower fields than their *trans* analogues. The $J(^{195}$Pt–^{1}H) coupling constants of the *cis* compounds are larger than those of the corresponding *trans* isomers. Therefore multinuclear magnetic resonance spectroscopy is a good technique to identify the geometry of the isomers.

The *cis*-Pt(amine)$_2$(R(COO)$_2$) were synthesized with bidentate carboxylato ligands. The IR spectra have shown the expected bands for the bidentate carboxylato ligands. The compounds have shown two ν(Pt–N) bands as expected for a *cis* geometry, but only one stretching ν(Pt–O) band was tentatively assigned.

The bidentate carboxylato complexes are very insoluble in all the solvents normally used in NMR. Most neutral Pt(II) complexes with amines containing aromatic groups are extremely insoluble in water and other organic solvents. Although some of the compounds seem slightly soluble in warm DMF-d_7, most of the ^{1}H NMR signals were very large. It was first believed to contain solid particles in suspension, but no change was observed after filtering. It might be caused by the presence of paramagnetic species. Furthermore, there were more signals than expected, suggesting the presence of decomposition products. Therefore, the solution NMR study was not pursued for the moment. Efforts were made to obtain crystals of good quality for X-ray diffraction studies, but again without success.

Monodentate carboxylato ligands might produce slightly more soluble Pt(II) complexes. The research project is continuing along this line, but isomerization of the *cis* compounds usually occur in organic solvents, especially when slightly heated, which is usually required to slightly dissolve these species.

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