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Synthesis and Characterization of Platinum(II) Complexes with Adamantanamine Derivatives and Related Ligands

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Monosubstituted anionic complexes of the type $[Pt(amine)Cl_3]^-$ with methylamine, ethylamine, cyclobutylamine, cyclopentylamine, dimethylamine, 1-adamantanamine, 2-adamantanamine, and (1-adamantylmethyl)amine have been synthesized and characterized mainly by ^{195}Pt NMR spectroscopy. The $\delta(Pt)$ resonances of the compounds were observed between −1822 and −1865 ppm in DMF solution. Disubstituted complexes $Pt(amine)_2X_2$ where X = Cl and I with the same amines were also studied. The ^{195}Pt NMR signals of the dichloro compounds were observed around −2200 ppm while those of the diiodo complexes were found between −3211 and −3354 ppm. The results on the adamantanamine (adam) complexes have shown that the previously reported compounds *cis*-$Pt(adam)_2Cl_2$, which do not have any antitumor properties, were not pure and contained about 65% impurities. The ^{195}Pt NMR spectra indicate that the chloro/1- and chloro/2-adamantanamine complexes are mixtures of cis and trans isomers, while (1-adamantylmethyl)amine produces only one isomer, presumably the cis isomer. A few mixed-ligand complexes, $Pt(amine)(adam)X_2$, have been prepared with X = Cl and I, and these compounds were studied by IR, Raman, and NMR spectroscopy. In the chloro series, only one isomer was observed in the ^{195}Pt NMR spectra. The IR and Raman spectroscopic results suggest that these complexes have cis geometry. For the iodo series, the ^{195}Pt NMR spectra indicate the presence of two isomers for a few compounds and only one isomer for others. Some IR and Raman data for the iodo complexes in the $\nu(Pt–I)$ region are reported.

Introduction

cis-$Pt(NH_3)_2Cl_2$ (cisplatin) is now well established as an antitumor drug. However, there are still difficulties in its widespread administration because of its numerous side effects and toxicity. Replacement of the NH_3 groups by cyclic amines reduces the toxicity of the platinum compounds, especially for large rings like cyclopentylamine.[2] The use of amines more compatible to the human system might possibly be another way of surmounting these problems. One such amine is the polycyclic cage molecule adamantanamine, which has been demonstrated to exhibit both antiviral[3–5] and antitumor activity.[6] 1-Adamantanamine and 2-adamantanamine inhibit the multiplication of certain strains of influenza virus by slowing or blocking the penetration of the virus into the host cells.[5] It seems that the pK_a of the nitrogen atom, rather than the lipophilicity of the molecule, is the major factor in the antiviral activity of this class of compounds. In addition to the virucidal properties, the antitumor activities of adamantanamine derivatives have been studied.[6] 1-Adamantanamine is a good antitumor agent against angiocarcinoma and pancreatic carcinoma.[7] Platinum(II) complexes containing 1,2-diaminoadamantane, of the general formula Pt(1,2-diaminoadamantane)X_2 where X = halide, NO_3^-, OH^-, and SO_4^{2-} have been synthesized.[8] These complexes exhibit good antitumor activity but have no antiviral properties. The dichloro complex is currently being used in Japan for treatment of human cancer,[8] as is the commercially-licenced drug cisplatin. The complexes *cis*-Pt(1- and 2-adamantanamine)$_2Cl_2$ have been synthesized, and the biological tests have unexpectedly shown that these complexes have no antitumor properties.[9] The inert nature of these two complexes was suggested to arise from their low solubilities. On the basis of these results, we decided to investigate the syntheses of these complexes. The results of this study will be discussed as part of this paper.

Mono(amine)platinum(II) complexes are important molecules because they are convenient precursors to mixed-ligand complexes, $PtLL'X_2$. Most of the known active antitumor agents are cis-disubstituted compounds containing two identical amine ligands. If complexes containing two different ligands could be systematically synthesized, the screening range of platinum complexes could be greatly extended, and the antitumor activity, toxicity, and solubility could be significantly modified. Rochon and Kong have already reported a new method for the synthesis of mixed-ligand complexes, from the cleavage of the iodo-bridged oligomer,[10] but the method is not applicable to adamantanamine ligands. Four methods have been reported for the preparation of monoamine complexes, and $K[Pt(NH_3)Cl_3]$[11,12] and K[Pt(pyridine)Cl_3][13,14] have been known for many years. The synthesis of K[Pt(L)Cl_3] where L is a primary amine has been reported for bulky amines like *tert*-butylamine[15] and for less crowded amines like methylamine, ethylamine, and others.[16] We have applied these methods to the synthesis of Pt–adamantanamine complexes and have now synthesized and characterized several complexes of the types [Pt(adamantanamine)Cl_3]$^-$, Pt(adamantanamine)$_2X_2$, and Pt(amine)(adamantanamine)X_2 with X = Cl and I. The results of this study are reported below.

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[1] (a) Université du Québec à Montréal. (b) McGill University.
[2] Cleare, M. J.; Hydes, P. C.; Malerbi, B. W.; Watkins, D. M. *Biochimie* **1978**, *60*, 835.
[3] Hay, A. J.; Wolstenholme, A. J.; Skihel, J. J.; Smith, M. H. *EMBO J.* **1985**, *4*, 3021.
[4] Widell, A.; Hansson, B. G.; Oberg, B.; Nordenfelt, E. *Antiviral Res.* **1986**, *6*, 103.
[5] Fletcher, R. D.; Hirschfield, J. E.; Forbes, M. *Nature* **1965**, *207*, 664.
[6] Ho, Y. K.; Hakala, M. T.; Zakrsewski, S. F. *Cancer Res.* **1972**, *32*, 1023.
[7] Klimova, N. V.; Arendaruk, A. P.; Baranova, M. A.; Vasetchenkova, N. I.; Shnar'yan, M. I.; Skoldinov, A. P. *Khim. Farm. Zh.* **1970**, *4*, 14.
[8] Shionogi and Co. Ltd. Jpn Kokai Tokkyo Koho JP58 79994, 1983.
[9] Braddock, P. D.; Connors, T. A.; Jones, M.; Khokhar, A. R.; Melzack, D. H.; Tobe, M. L. *Chem. Biol. Interact.* **1975**, *11*, 145.
[10] Rochon, F. D.; Kong, P. C. *Can. J. Chem.* **1986**, *64*, 1894.
[11] Cossa, A. *Gazz. Chim. Ital.* **1890**, *20*, 725.
[12] Jeannin, Y. P.; Russell, D. R. *Inorg. Chem.* **1970**, *9*, 778.
[13] Werner, A.; Fassbender, F. Z. *Z. Anorg. Allg. Chem.* **1897**, *15*, 123.
[14] Kong, P. C.; Rochon, F. D. *Can. J. Chem.* **1978**, *56*, 441.
[15] Rochon, F. D.; Fleurent, L. *Inorg. Chim. Acta* **1988**, *143*, 81.
[16] Rochon, F. D.; Melanson, R.; Doyon, M. *Inorg. Chem.* **1987**, *26*, 3065.

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Experimental Section

K_2PtCl_4 was purchased from Johnson Matthey and Co. and was recrystallized from water before use. Methylamine ($MeNH_2$, 40% in water), ethylamine ($EtNH_2$, 70% in water), cyclobutylamine (cba), cyclopentylamine (cpa), dimethylamine (Me_2NH, 40% in water), 1-adamantanamine (1-adam), 2-adamantanamine (2-adam), and (1-adamantylmethyl)amine (1-Meadam) were obtained from Aldrich or Eastman Chemical Co. and were used without further purification. All the synthesized compounds were dried in a drying pistol under P_4O_{10}.

The elemental analyses were performed by Galbraith Laboratories, Inc. The melting or decomposition points were measured on a Fisher-Johns instrument. The IR spectra were recorded on a Perkin-Elmer 783 or a Dililab FT-50 spectrometer (CsI beamsplitter, resolution 1 cm^{-1}, 256 scans). The Raman spectra were recorded (below 400 cm^{-1}) on a U-1000 Ramanor spectrometer equipped with a Nachet optical microscope, by using the 514.5-nm line of an argon ion laser for excitation (200 mW), with slit width 300 μm, 20–40 scans, and nine-point smoothing. The ^{195}Pt NMR spectra were obtained on a Bruker WH-400 FT instrument operating at 85.832 MHz (spectral window 1000 ppm) or on a Varian XL-300 instrument operating at 64.374 MHz (spectral window 1500 ppm). The spectra were recorded in DMF, acetone, or CH_2Cl_2 solutions with a D_2O external tube for lock purposes and K_2PtCl_4 as an external standard adjusted to −1628 ppm from Na_2PtCl_6. ^{1}H-NMR spectra were measured on a Varian XL, a Gemini-200, or a Gemini-300 spectrometer in DMF-d_7, acetone-d_6, or D_2O solutions.

K[Pt(L)Cl$_3$]. The complexes with L = $MeNH_2$, $EtNH_2$, cba, cpa, and Me_2NH were prepared as described in the literature.[16]

K[Pt(adam)Cl$_3$]. These compounds were synthesized in DMF according to the method published for preparing the similar pyridine complexes.[14] Only K[Pt(1-adam)Cl$_3$] could be isolated. The other complexes decomposed in air. The ^{195}Pt-NMR spectra of K[Pt(2-adam)Cl$_3$] and K[Pt(1-Meadam)Cl$_3$] were recorded after concentrating the DMF solution obtained before isolating the compounds. The spectra showed that the two concentrated solutions contained mixtures of mono- and disubstituted compounds. K[Pt(1-adam)Cl$_3$]: yield 12%; dec pt 195–210 °C. Anal. Calc: C, 24.4; H, 3.5; Cl, 21.6; N, 2.9. Found: C, 24.4; H, 4.0; Cl, 20.7; N, 3.1. ^{1}H-NMR (ppm in $CDCl_3$): δ(ligand) = 1.591 s (1.529 s), 1.688 m (1.590 m), 2.179 m (2.057 m). IR (cm^{-1}): 3230 w, 3200 m, 3125 w, δ(N–H) 1570 m, 555 w, ν(Pt–Cl) 330 m.

[N(CH$_3$)$_4$][Pt(adam)Cl$_3$]. A cation-exchange resin (Dowex 50W-X8, H$^+$, 20–50 mesh) was used to change 1 mmol of K_2PtCl_4 to H_2PtCl_4, which was then neutralized with $[N(CH_3)_4]OH$. The resulting salt, $[N(CH_3)_4]_2[PtCl_4]$, was then isolated and dried. The reactions of the salt with adamantanamine ligands were peformed as described above for the K$^+$ salt. The two compounds [N(CH$_3$)$_4$][Pt(adam)Cl$_3$] where adam = 2-adam and 1-Meadam were identified from the similarity of their spectroscopic properties with those of the K$^+$ salts. [N(CH$_3$)$_4$][Pt(2-adam)CL$_3$]: yield 26%; dec pt 163–266 °C. IR (cm^{-1}): 3282 m, 3190 w, 3132 w, δ(N–H) 1582 m, 1560 w, 508 w, ν(Pt–Cl) 332 s, 312 m. The compound [N(CH$_3$)$_4$][Pt(1-Meadam)Cl$_3$] was contaminated with Pt(1-Meadam)$_2$Cl$_2$. Attempts were made to separate the two compounds using different solvents, but these were unsuccessful.

[2-adamH][Pt(EtNH$_2$)Cl$_3$]. One millimole of K[Pt(EtNH$_2$)Cl$_3$] and 1.1 mmol of 2-adam were stirred together in 10 mL of water for 90 min. HCl (10 mL, 0.1M) was then added to the mixture, which was stirred for another 10 min. The yellow precipitate which formed was filtered off, and the filtrate was evaporated to dryness. The yellow residue was dissolved with acetone, and the solution was filtered. The filtrate was again evaporated to dryness and the residue washed with ether and dried over P_4O_{10}: yield 65%; dec pt 140–160 °C. The crystal structure of this compound was recently reported.[17]

[adamH]$_2$[PtCl$_4$]. The compounds containing 1-adam, 2-adam, and 1-Meadam were prepared from the reaction of aqueous K_2PtCl_4 with aminoadamantane hydrochloride in a 1:2 proportion. The pink precipitates were filtered off and washed with water.

Pt(L)(adam)Cl$_2$. One millimole of adamantanamine was added to an aqueous solution (5 mL) of 1 mmol of K[Pt(L)Cl$_3$], and the mixture was stirred at room temperature for 2–3 h. The insoluble product was filtered off, and the free adam ligand was removed by washing with water. After drying briefly in air, the residue was washed with ether and left under vacuum in a drying pistol containing P_4O_{10} for 12 h. Pt(MeNH$_2$)(1-adam)Cl$_2$: yield 60%; dec pt 205–217 °C. Anal. Calc: C, 29.5; H, 4.9; N, 6.3. Found: C, 28.5; H, 4.8; N, 6.0. IR (cm^{-1}): 3276 w, 3231 s, 3196 s, 3144 w, 3124 w, 1569 s, 555 m, 462 w, 325 s. Raman (ν(Pt–Cl), cm^{-1}): 324 s. Pt(EtNH$_2$)(1-adam)Cl$_2$: yield 47%; dec pt 195–220 °C. Anal. Calc: C, 31.2; H, 5.2; Cl, 15.3; N, 6.1. Found: C, 31.3; H, 5.7; Cl, 14.5; N, 6.2. IR (cm^{-1}): 3224 s, 3195 s, 3129 s, 1577 s, 555 w, 462 w, 329 m, 314 s. Raman (cm^{-1}): 325 s, 311 m. Pt(cba)(1-adam)Cl$_2$: yield 90%; dec pt 206–225 °C. Anal. Calc: C, 34.4; H, 5.4; Cl, 14.4; N, 5.7. Found: C, 34.1; H, 5.7; Cl, 13.8; N, 5.7. IR (cm^{-1}): 3260 w, 3213 s, 3122 s, 1575 s, 550 w, 462 w, 323 s. Raman (cm^{-1}): 322 s. Pt(cpa)(1-adam)Cl$_2$: yield 16%; dec pt 195–217 °C. Anal. Calc: C, 35.9; H, 5.6; Cl, 14.1; N, 5.6. Found: C, 34.1; H, 5.6; Cl, 13.3; N, 5.3. IR (cm^{-1}): 3215 s, 3188 s, 3121 s, 1590 w, 1563 s, 550 w, 322 s. Raman (cm^{-1}): 322 s. Pt(MeNH$_2$)(2-adam)Cl$_2$: yield 65%; dec pt 192–212 °C. Anal. Calc: C, 29.5; H, 4.9; Cl, 15.8; N, 6.3. Found: C, 29.9; H, 4.9; Cl, 15.9; N, 6.2. IR (cm^{-1}): 3273 m, 3237 s, 3214 s, 3145 s, 1590 s, 1571 s, 525 w, 505 w, 329 s. Raman (cm^{-1}): 328 s. Pt(EtNH$_2$)(2-adam)Cl$_2$: yield 24%; dec pt 170–192 °C. Anal. Calc: C, 31.2; H, 5.2; Cl, 15.3; N, 6.1. Found: C, 31.0; H, 5.2; Cl, 15.1; N, 5.9. IR (cm^{-1}): 3265 w, 3197 s, 3131 m, 1570 m, 555 w, 498 m, 328 s, 313 m. Raman (cm^{-1}): 327 s, 311 m. Pt(MeNH$_2$)(1-Meadam)Cl$_2$: yield 44%; dec pt 195–209 °C. Anal. Calc: C, 31.2; H, 5.2; N, 6.1. Found: C, 31.8; H, 4.8; N, 5.6. IR (cm^{-1}): 3287 s, 3238 s, 3214 s, 3141 m, 3118 m, 1586 s, 1576 s, 545 w, 515 w, 326 s. Raman (cm^{-1}): 338 s, 327 m.

Pt(adam)$_2$Cl$_2$. One millimole of K$_2$[PtCl$_4$] and 2 mmol of the adamantanamine ligand were heated in DMF solution at 80 °C for 3 h. The DMF solution was concentrated as much as possible and cooled to ~0 °C, and the KCl which had formed was filtered off. The ^{195}Pt-NMR spectrum of the solution was recorded at room temperature. The mixture was then evaporated to dryness, and the yellow residue was washed sequentially with ether, acetone, and water, to remove DMF, K[Pt(adam)Cl$_3$], and KCl, respectively. After drying briefly in air, the residue was washed with ether and dried. Pt(1-adam)$_2$Cl$_2$: yield 65%; dec pt 180–205 °C. IR (cm^{-1}): 3208m , 3122 m, 1595 sh, 1572 m, 550 w,461 w, 329 m. Raman (cm^{-1}): 342 w, 337 mw, 323 s, 318 m. Pt(2-adam)$_2$Cl$_2$: yield 72%; dec pt 185–215 °C. IR (cm^{-1}): 3305 m, 3279 w, 3261 w, 3238 m, 3190 s, 3123 s, 1578 s, 503 mw, 335 m. Raman (cm^{-1}): 329 s, 322 m. Pt(1-Meadam)$_2$Cl$_2$: yield 68%; dec pt 195–225 °C. IR (cm^{-1}): ν(Pt–Cl) 341 m, 325 m. Raman (cm^{-1}): 334 s, 325 m.

Pt(L)$_2$I$_2$. The compounds with L = methylamine, ethylamine, cyclobutylamine, cyclopentylamine, and dimethylamine were synthesized as already described in the literature.[10] Pt(MeNH$_2$)$_2$I$_2$: ^{1}H-NMR (δ (ppm) in acetone) 2.65 (t+dt), ^3J(Pt–CH$_3$) = 49 Hz, 4.50 (NH). Pt(EtNH$_2$)$_2$I$_2$: ^{1}H-NMR (δ (ppm) in acetone) 1.29 (t), 3.04 (m), 3.24 (NH); ^{1}H-NMR (in DMF) 1.21 (t), 2.95 (m), 4.45 (NH). Pt(cba)$_2$I$_2$: ^{1}H-NMR (δ (ppm) in DMF) 1.64 (m), 1.94 (m), 2.30 (m), 3.73 (m) 3.48 (NH). Pt(cpa)$_2$I$_2$: ^{1}H-NMR (δ (ppm) in DMF): 1.68 (m), 2.11 (m), 3.61 (m), 4.34 (NH), ^2J(Pt–NH) = 70 Hz. Pt(Me$_2$NH$_2$)$_2$I$_2$: ^{1}H-NMR (δ (ppm) in acetone): 1.85 (d+dd), ^3J(Pt–CH$_3$) = 43 Hz, 4.97 (NH).

Pt(adam)$_2$I$_2$. These compounds were prepared by an adapted version of Dhara's method.[18] Pt(1-adam)$_2$I$_2$: dec pt 164–279 °C. Anal. Calc: C, 32.0; H, 4.6. Found: C, 32.5; H, 4.8. IR (cm^{-1}): 3262 m, 3200 s, 3112 w, 1565 s, 1552 s, 580 w, 455 w. ^{1}H NMR (δ(ppm) in $CDCl_3$): 1.59 m, 1.98 m, 2.11 m, 3.61 (NH), ^2J(Pt–NH): 68 Hz. Pt(2-adam)$_2$I$_2$: dec pt 250–295 °C. Anal. Calc: C, 32.0; H, 4.6. Found: C, 33.0; H, 4.5. IR (cm^{-1}): 3288s, 3202 s, 3118 w, 1572 s, 500 w.

Pt(L)(adam)I$_2$. The adamantanamine ligand (1.5 mmol) was added to an aqueous solution of 1 mmol of [Pt(L)I$_2$]$_2$, and the mixture was stirred for 2–3 h. The insoluble product was filtered off, and the free adam ligand was removed by washing with water. After drying briefly in air, the residue was washed with ether and dried over P_4O_{10}. The yields were almost quantitative. Pt(MeNH$_2$)(1-adam)I$_2$: dec pt 160–175 °C. IR (cm^{-1}): 3290 m, 3250 m, 3198 s, 3120 w, 1565 s, 590 w, 480 w. ^{1}H-NMR (δ (ppm) in DMF): 1.55 (m), 1.99 (m), 2.12 (m), 2.61 (t), 3.63 (NH), 3.80 (NH). Pt(EtNH$_2$)(2-adam)I$_2$: dec pt 140–170 °C. Anal. Calcd: C, 22.3; H, 3.8. Found: C, 22.8; H, 3.6. IR (cm^{-1}): 3262 m, 3201 s, 3119 w, 1575 s, 495 w. Pt(MeNH$_2$)(2-adam)I$_2$: dec pt 171–195°C. Pt(cba)(2-adam)I$_2$: dec pt 185–200 °C. Anal. Calc: C, 25.1; H, 3.9. Found: C, 26.6; H, 4.2. IR (cm^{-1}): 3292 m, 3279 w, 3246 m, 3204 s, 3125 w, 1576 s, 500 w. Pt(cpa)(2-adam)I$_2$: dec pt 186–212 °C. Anal. Calc: C, 26.3; H, 4.1. Found: C, 26.6; H, 4.4. IR (cm^{-1}): 3295 m, 3272 w, 3202 s, 3122 m, 1565 s. Pt(MeNH$_2$)(1-Meadam)I$_2$: dec pt 130–168 °C. IR (cm^{-1}): 3379 m, 3332 m, 3310 s, 1580 s, 1561 sh, 528

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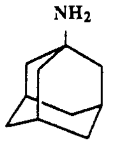
(17) Rochon, F. D.; Melanson, R.; Doyon, M.; Butler, I. S. *Acta Crystallogr.* **1990**, *C46*, 584.

(18) Dhara, S. C. *Indian J. Chem.* **1970**, *8*, 193.

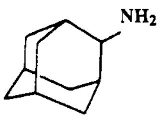
w. $Pt(EtNH_2)(1\text{-}Meadam)I_2$: dec pt 205–240 °C. IR (cm^{-1}): 3295 w, 3335 m, 1562 s, 460 w.

Results and Discussion

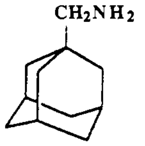
Monosubstituted Platinum(II) Complexes. The complexes $K[Pt(L)Cl_3]$ where L = $MeNH_2$, $EtNH_2$, cyclobutylamine (cba), cyclopentylamine (cpa), and Me_2NH were synthesized by cleavage of the iodo-bridged dimer $[Pt(L)I_2]_2$ with a silver salt, followed by reaction with KCl.[16] All these complexes have previously been studied by IR and ^{1}H-NMR spectroscopy, a few of them by X-ray diffraction, but none by ^{195}Pt-NMR spectroscopy. The method used to prepare these compounds was investigated, and several attempts were made to synthesize mono(adamantanamine)platinum(II) complexes, but the method proved unsuitable. The iodo-bridged dimers are usually prepared from the reaction of $Pt(L)_2I_2$ in perchloric acid. For adamantanamine derivatives, the dimerization process is very slow, probably due to the low aqueous solubility of the starting material $Pt(adam)_2I_2$.



1-adamantanamine



2-adamantanamine



(1-adamantylmethyl)amine

New monosubstituted complexes of the type $K[Pt(adam)Cl_3]$ (adam = 1-adamantanamine (1-adam), 2-adamantanamine (2-adam), and (1-adamantylmethyl)amine (1-Meadam)) were synthesized by a method similar to the one reported for pyridine ligands[14] from the reaction with $K_2[PtCl_4]$ in DMF. Not more than 1 equiv of adam should be used, since the disubstituted compounds are rapidly formed. The complex $K[Pt(1\text{-}adam)Cl_3]$ is fairly stable and was isolated in low yield. The compound was characterized by elemental analysis and by ^{195}Pt- and ^{1}H-NMR and IR spectroscopy. The complexes with 2-adam and 1-Meadam could not be isolated since they are not stable in air. Therefore, the DMF solutions were concentrated and cooled close to ~0 °C, and the KCl was filtered off. The ^{195}Pt-NMR spectra of these solutions were recorded at room temperature. The results have shown the presence of two species in the concentrated DMF solutions, $[Pt(adam)Cl_3]^-$ and $Pt(adam)_2Cl_2$.

In an attempt to isolate the $[Pt(adam)Cl_3]^-$ complexes with 2-adam and 1-Meadam, a larger cation was employed. $[N(CH_3)_4]_2[PtCl_4]$ was synthesized according to the reaction

$$K_2[PtCl_4] \xrightarrow{\text{resin } H^+} H_2[PtCl_4] \xrightarrow{2N(CH_3)_4OH} [N(CH_3)_4]_2[PtCl_4]$$

$[N(CH_3)_4]_2[PtCl_4]$ was isolated and dried, and its reaction with adamantanamine in DMF gave $[N(CH_3)_4][Pt(adam)Cl_3]$. The complex with 2-adam is water soluble while the one with 1-Meadam is much less soluble. The two products were characterized by NMR and IR spectroscopy. The ^{195}Pt-NMR spectra displayed only one resonance for the $[Pt(2\text{-}adam)Cl_3]^-$ complex, but two signals corresponding to $[Pt(1\text{-}Meadam)Cl_3]^-$ and $Pt(1\text{-}Meadam)_2Cl_2$ were observed. Since $[N(CH_3)_4][Pt(1\text{-}Meadam)Cl_3]$ is quite insoluble, it was not possible to separate it completely from the disubstituted compound.

Table I. ^{195}Pt-NMR Resonances for the Monosubstituted Pt(II) Complexes and Related Compounds and pK_a of Some of the Amines in Water

compd	δ(^{195}Pt) (ppm) D$_2$O	δ(^{195}Pt) (ppm) acetone	δ(^{195}Pt) (ppm) DMF	pK_a of amine
$K_2[PtCl_4]$	−1628		−1426	
$H_2[PtCl_4]$			−1455	
$[NMe_4]_2[PtCl_4]$	−1614		−1387	
$[1\text{-}adamH]_2[PtCl_4]$			−1486	
$[2\text{-}adamH]_2[PtCl_4]$			−1482	
$[1\text{-}MeadamH]_2[PtCl_4]$			−1472	
$K[Pt(D_2O)Cl_3]$	−1194 (−1180[20])			
$K[Pt(MeNH_2)Cl_3]$			−1842	10.66[24]
$K[Pt(EtNH_2)Cl_3]$			−1850	10.81[24]
$K[Pt(cba)Cl_3]$		−1875	−1852	
$K[Pt(cpa)Cl_3]$		−1866	−1847	
$K[Pt(1\text{-}adam)Cl_3]$			−1822	9.92[25]
$K[Pt(2\text{-}adam)Cl_3]$			−1859	
$K[Pt(1\text{-}Meadam)Cl_3]$			−1865	
$[NMe_4][Pt(2\text{-}adam)Cl_3]$			−1851	
$[NMe_4][Pt(1\text{-}Meadam)Cl_3]$		−1856		
$[2\text{-}adamH][Pt(EtNH_2)Cl_3]$		−1855	−1854	
$K[Pt(Me_2NH)Cl_3]$		−1860	−1825	10.73[24]

The ^{195}Pt-NMR chemical shifts of all the monosubstituted complexes are given in Table I. The resonances of some $[PtCl_4]^{2-}$ complexes with different counterions are also listed in the same table. The chemical shifts are solvent dependent, especially for the $[PtCl_4]^{2-}$ salts. For the K$^+$ salt, the signal is observed at lower field (202 ppm) in DMF than in D_2O. These compounds are totally dissociated in water, whereas in organic solvents, the dissociation is much reduced and is probably similar for DMF and acetone. Studies on $[NBu_4]_2[PtCl_4]$[19] have shown an important downfield shift from water (−1624 ppm) to organic solvents, while very little differences were observed between the resonances of the compound in acetone (−1388 ppm), acetonitrile (−1384 ppm), or DMSO (−1372 ppm). The authors explained the difference by the increasing possibility of ion pairing in organic solvents compared to water. Table I shows also a slight dependence of the chemical shifts on the counterion. In water, the difference is small, but in DMF, it is more important. This observation is in agreement with a similar study[20] where $[PPh_4]_2[PtCl_4]$ was observed at −1461 ppm and $[NBu_4]_2[PtCl_4]$ at −1437 ppm in CH_2Cl_2. The authors expained the difference by a less efficient pairing of the ions in $[PPh_4]_2[PtCl_4]$, due to a more diffuse positive charge located on the P atoms, compared to the smaller N atoms in $[NBu_4]_2[PtCl_4]$. In water, the cations are so strongly solvated that the chemical shift of $[PtCl_4]^{2-}$ is independent of the cation. Another factor which might be important in DMF is hydrogen bonding. K$^+$ and $[NMe_4]^+$ cannot form H bonds with the solvent or the anions, while H$^+$ or adamH$^+$ cations will form strong H bonds with the solvent, resulting in a less efficient pairing of the ions and thus a better solvation of the anions, leading to an upfield shift.

For the $[Pt(L)Cl_3]^-$ complexes, a similar trend is observed, but the influence of the solvent is smaller. When K$^+$ is replaced by $[NMe_4]^+$, a slight downfield shift (~9 ppm) is observed, while replacing K$^+$ by adamH$^+$ leads to a very small upfield shift of ~5 ppm. The chemical shifts of the monoamine complexes are observed in DMF between −1822 and −1865 ppm. These values agree with those reported for $K[Pt(NH_3)Cl_3]$ (−1826 ppm in water) and $[NPr_4][Pt(Me_2NH)Cl_3]$ (−1863 ppm in CH_2Cl_2).[21] The ^{195}Pt-NMR spectra of all the monoamine complexes except those of $K[Pt(2\text{-}adam)Cl_3]$, $K[Pt(1\text{-}Meadam)Cl_3]$, and $[NMe_4][Pt(1\text{-}Meadam)Cl_3]$ showed only one signal. The two K$^+$ salts with 2-adam and 1-Meadam, which were not isolated before recording the NMR spectra, contained some disubstituted compound as seen by a signal around −2200 ppm. The spectrum of $[NMe_4][Pt(1\text{-}Meadam)Cl_3]$ also contained a resonance around −2200 ppm since the complexed salt is not very soluble in water and could not be well separated from the disubstituted complex.

The ^{195}Pt chemical shifts are usually dependent on the ligands. An increase in the electron density on the platinum atom (thus

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(19) Pesek, J. J.; Mason, W. R. *J. Magn. Reson.* **1977**, *25*, 519.

(20) Freeman, W.; Pregosin, P. S.; Sze, S. N.; Venanzi, L. M. *J. Magn. Reson.* **1976**, *22*, 473.

(21) Kidd, F. J., Goodfellow, R. J., Harris, F. K., Nann, B., Eds. *NMR and the Periodic Table*; Academic Press: London, 1978.

an increase in basicity of the ligand) should lead to higher field chemical shifts as observed for *cis*-Pt(py)(DMSO)Cl_2 (py = pyridine derivatives, pK_a of py ranging from 1.9 to 9.7).[22] But opposite trends have also been observed for *trans*-Pt(py)(C_2H_4)Cl_2[23] and *trans*-Pt(py)(DMSO)Cl_2.[22] We examined the possibility of a correlation between the chemical shifts of the monoamine complexes and the pK_a values of the amines in water. There is a linear relationship for the three primary amines $EtNH_2$ (pK_a = 10.81), $MeNH_2$ (pK_a = 10.66), and 1-adam (pK_a = 9.92)[24,25] with δ(Pt) of −1850, −1842, and −1822 ppm, respectively. The other pK_a values in water are not available in the literature. For the secondary amine Me_2NH, with a pK_a of 10.73,[24] its chemical shift is out of line, because of steric factors close to the binding site of the amine. Its chemical shift (−1825 ppm) is very close to that of the 1-adam complex (−1822 ppm). This observation is in agreement with the results obtained by Pregosin,[26] who observed a downfield shift when the ligand became sterically larger close to the binding atom. Proton affinities of the ligands (determined in the gas phase) are intrinsic measures of the basicity of ligands and could bring a better understanding of how steric hindrance and solvent effects are related to the chemical shifts. Unfortunately, the proton affinities of the ligands used in this work, except for $MeNH_2$ ($\Delta G°_{25 °C} = -11.0$ kcal/mol) and $EtNH_2$ ($\Delta G°_{25 °C} = -9.8$ kcal/mol),[27] are not available in the literature.

The IR spectra of the adamantanamine complexes K[Pt(1-adam)Cl_3] and [NMe_4][Pt(2-adam)Cl_3] ([NMe_4][Pt(1-Meadam)Cl_3] was contaminated with Pt(1-Meadam)$_2Cl_2$ and will not be discussed) were recorded. The crystal structures of K[Pt(isopropylamine)Cl_3][7] and K[Pt(cpa)Cl_3][28] have been reported, and the results have shown that the compounds crystallize with water molecules which could be detected by IR spectroscopy. These bands were absent in the IR spectra of the three adam complexes, confirming that these compounds do not crystallize with water of hydration.

The skeleton symmetry for $[Pt(adam)Cl_3]^-$ is C_{2v}, and group theory predicts three infrared-active ν(Pt–Cl) stretching vibrations ($2A_1 + B_2$ modes). Sometimes, the vibrations are very close in energy and fewer bands are observed. Two bands were observed for [NMe_4][Pt(2-adam)Cl_3] at 332 and 312 cm^{-1}, while only one wide band was detected for K[Pt(1-adam)Cl_3] at 330 cm^{-1}. Group theory also predicts one infrared-active ν(Pt–N) vibration (A_1) in the spectra of these complexes. In a study of K[Pt($MeNH_2$)Cl_3]·xH_2O, the ν(Pt–N) mode was located at 523 cm^{-1}.[29] The spectra of K[Pt(1-adam)Cl_3] and [NMe_4][Pt(2-adam)Cl_3] each showed one very weak band at 555 and 508 cm^{-1}, respectively, which can be tentatively assigned to the ν(Pt–N) vibrations.

Pt(adam)$_2Cl_2$ and Pt(L)(adam)Cl_2 Complexes. Two types of disubstituted compounds were prepared, Pt(adam)$_2Cl_2$ and Pt(L)(adam)Cl_2 where L = $MeNH_2$, $EtNH_2$, cba, and cpa and adam = 1-adam, 2-adam, and 1-Meadam. The bis(adamantanamine) compounds were prepared according to the following equation:

$$K_2[PtCl_4] + 2adam \xrightarrow{DMF, \Delta} Pt(adam)_2Cl_2 + 2KCl$$

After being heated for 3 h, the DMF solution was concentrated and cooled to ~0 °C, and the KCl was filtered off. The ^{195}Pt-NMR spectrum of the solution was then recorded. The spectra of the three solutions indicated the presence of Pt(adam)$_2Cl_2$ and K[Pt(adam)Cl_3]. After the ^{195}Pt-NMR spectra were recorded, the DMF solvent was evaporated off and the residues were washed with ether (to remove excess ligand and DMF) and acetone and water [to remove K[Pt(adam)Cl_3] and KCl]. The yields of Pt(adam)$_2Cl_2$ varied from 65 to 72%. The isolated complexes were characterized by IR and Raman spectroscopy.

Table II. ^{195}Pt-NMR Resonances for the Disubstituted Chloro Complexes (in DMF)

compd	$\delta(^{195}Pt)$ (ppm)
Pt($MeNH_2$)$_2Cl_2$	−2222[30]
cis-Pt(cba)$_2Cl_2$	−2235[31]
trans-Pt(cba)$_2Cl_2$	−2225[31]
cis-Pt(Me_2NH)$_2Cl_2$	−2188
trans-Pt(Me_2NH)$_2Cl_2$	−2181
Pt(*i*-$PrNH_2$)$_2Cl_2$	−2224
Pt(1-adam)$_2Cl_2$	−2184 (*cis*, 28%), −2141 (*trans*, 72%)
Pt(2-adam)$_2Cl_2$	−2230 (*cis*, 33%), −2193 (*trans*, 67%)
Pt(1-Meadam)$_2Cl_2$	−2242
Pt($MeNH_2$)(1-adam)Cl_2	−2213
Pt($EtNH_2$)(1-adam)Cl_2	−2208
Pt(cba)(1-adam)Cl_2	−2199
Pt(cpa)(1-adam)Cl_2	−2188
Pt($MeNH_2$)(2-adam)Cl_2	−2219
Pt($EtNH_2$)(2-adam)Cl_2	−2223
Pt($MeNH_2$)(1-Meadam)Cl_2	−2235

The mixed-ligand complexes were prepared as follows:

$$K[Pt(L)Cl_3] + adam \xrightarrow{H_2O} Pt(L)(adam)Cl_2 + KCl$$

The yields varied from 16 to 90%. The complexes were first washed with dilute HCl to remove the excess adam ligands which are not very soluble in water. ^{195}Pt-NMR spectroscopy showed the presence of [adamH][Pt(L)Cl_3], produced from the reaction of HCl with the coordinated ligand. A crystal obtained from the HCl filtrate of Pt($EtNH_2$)(1-adam)Cl_2 was identified as [1-adamH][Pt($EtNH_2$)Cl_3] by X-ray diffraction.[17] Later, HCl washing was replaced by washing with a large quantity of water. The signal of the monosubstituted Pt compound then disappeared in the ^{195}Pt-NMR spectrum, leaving only one signal in the region expected for disubstitued compounds.

The ^{195}Pt-NMR spectra of all the disubstituted complexes displayed signals between −2141 and −2242 ppm (Table II). These values are close to those reported for Pt($MeNH_2$)$_2Cl_2$ (−2222 ppm[30]), for *cis*- and *trans*-Pt(cba)$_2Cl_2$ (−2235 and −2225 ppm[31] in DMF), and for *cis*- and *trans*-Pt($C_6H_{13}{}^{15}NH_2$)$_2Cl_2$ (−2215 ppm in DMSO-d_6 and −2130 ppm in $CDCl_3$,[32] respectively). In water, the cis isomers are first formed since the trans effect of Cl^- is greater than that for the amines. Other factors like bulkiness of the ligands might lead to isomerization to trans isomers. The ^{195}Pt-NMR spectrum of Pt(1-Meadam)$_2Cl_2$ showed only one signal at −2242 ppm while its IR spectrum has two ν(Pt–Cl) stretching vibrations at 341 and 325 cm^{-1}. The Raman spectrum also showed two ν(Pt–Cl) bands at 334 and 325 cm^{-1}. It appears that this compound has cis geometry. For Pt(1-adam)$_2Cl_2$ and Pt(2-adam)$_2Cl_2$, two ^{195}Pt resonances were observed at −2141, −2184 cm^{-1} and −2193, −2230 cm^{-1}, respectively. The upfield resonances are attributed to the cis isomers, while the lower field signals correspond to the trans isomers as reported for Pt(cba)$_2Cl_2$[31] and Pt($C_6H_{13}NH_2$)$_2Cl_2$.[32] From the intensity pattern of the ^{195}Pt-NMR spectra, the trans isomers are formed in greater quantity than are the cis isomers. For Pt(1-adam)$_2Cl_2$, the proportions are 72:28 while, for Pt(2-adam)$_2Cl_2$, the proportions are 67:33. The cis–trans mixtures were probably at equilibrium, since measurements were repeated several times and the compositions

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(22) Marzilli, L. G.; Hayden, Y.; Reiley, M. D. *Inorg. Chem.* **1986**, *25*, 974.

(23) Motchi, S. N.; Sze, S. N.; Pregosin, P. S. *Helv. Chim. Acta* **1979**, *62*, 2086.

(24) *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed. CRC Press: Boca Raton, FL, 1990; p D-161-2.

(25) Grunewald, G. L.; Warner, A. M.; Hays, S. J.; Bussel, S. J.; Nann, B. *J. Med. Chem.* **1972**, *15*, 747.

(26) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.

(27) Arnett, E. M. *J. Chem Educ.* **1985**, *62*, 385.

(28) Dion, C.; Beauchamp, A. L.; Rochon, F. D.; Melanson, R. *Acta Crystallogr.* **1989**, *C45*, 852.

(29) Kharitinov, Y. Y.; Dymina, I. K.; Leonova, T. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1968**, *13*, 709.

(30) O'Halloran, T. Ph.D. Thesis, Massachusetts Institute of Technology, 1987; Chapter 6.

(31) Rochon, F. D.; Dion, C.; Beauchamp, A. L. To be published.

(32) Motschi, M.; Pregosin, P. S.; Venanzi, L. M. *Helv. Chim. Acta* **1979**, *62*, 667.

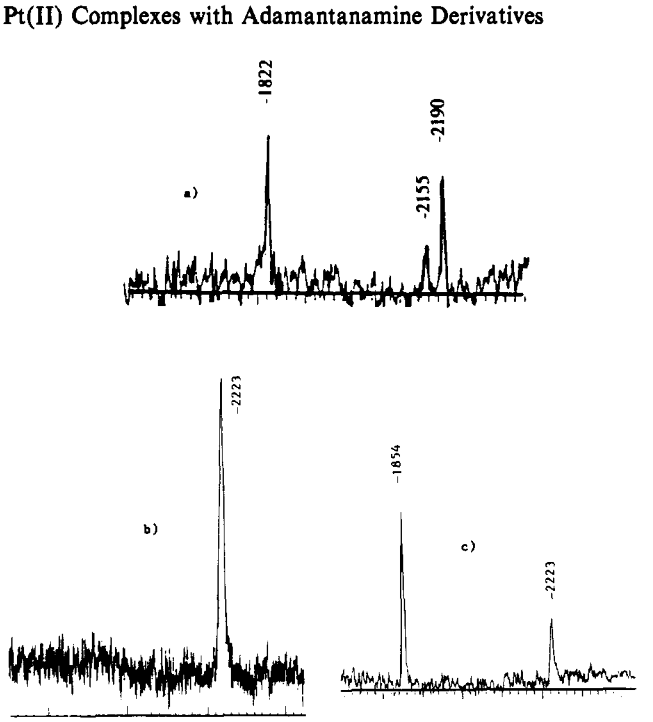

Figure 1. ^{195}Pt-NMR spectra of (a) Pt(1-adam)$_2$Cl$_2$ prepared according to ref 9, (b) Pt(EtNH$_2$)(2-adam)Cl$_2$ before washing with HCl, and (c) Pt(EtNH$_2$)(2-adam)Cl$_2$ after washing with HCl.

were very similar. The trans isomers are presumably produced in order to reduce the steric hindrance, which is quite important in the cis isomers of 1- and 2-adam. For 1-Meadam, the binding site is far from the bulk of the molecule and no isomerization occurs. If we compare the chemical shifts for the three *cis*-Pt(adam)$_2$Cl$_2$ complexes, the values are in agreement with the work of Pregosin.[26] The signal for the complex with the bulkiest ligand 1-adam, where the amine group is attached to a tertiary C atom, is observed at the lowest field, -2184 ppm, close to that for Pt(Me$_2$NH)$_2$Cl$_2$ (-2188 ppm), while that for the compound with 2-adam is observed at an intermediate field at -2230 ppm. For the complex with 1-Meadam, the -CH$_2$- group between the amine and the bulky adamantane ring is sufficient to relieve the steric hindrance and the compound resonates in the same field as other complexes with less bulky primary amines (-2242 ppm).

In 1975, the antitumor activities of *cis*-Pt(1-adam)$_2$Cl$_2$ and *cis*-Pt(2-adam)$_2$Cl$_2$ were studied,[9] and the compounds were found to be inactive. The authors characterized their compounds by elementary analysis (only C, H, and N) and IR spectroscopy. Two ν(Pt-Cl) bands were reported. The authors had washed their product with concentrated HCl in order to remove the excess of ligands which were not very soluble in water. After we observed the formation of [adamH][Pt(L)Cl$_3$] by washing Pt(adam)(L)Cl$_2$ with dilute HCl, we decided to repeat the synthesis reported by these authors with 1-adam. The ^{195}Pt-NMR spectrum of the product obtained by the method used by these authors, recorded in DMF solution, showed the presence of three signals (Figure 1a), corresponding to [Pt(1-adam)Cl$_3$]$^-$, 50% (-1822 ppm), *trans*-Pt(1-adam)$_2$Cl$_2$, 15% (-2155 ppm), and *cis*-Pt(1-adam)$_2$Cl$_2$, 35% (-2190 ppm). The product tested by these authors[9] was therefore probably a mixture of the ionic monosubstituted complex [1-adamH][Pt(1-adam)Cl$_3$], and the cis- and trans-disubstituted species. A chloride analysis, which was not reported by the research group, would probably have indicated the presence of an important quantity of monosubstituted compound. IR spectroscopy in not an adequate method to detect mixtures of chloro compounds. In order to confirm the hypothesis of the reaction of the disubstituted complex with HCl to produce the monosubstituted compound, we stirred *cis*-Pt(EtNH$_2$)(2-adam)Cl$_2$ (which exhibited only one Pt signal (Figure 1b) at -2223 ppm) with HCl. After isolation of the product, its ^{195}Pt NMR spectrum showed two signals (Figure 1c) at -1854 (~75%) and -2223 ppm (~25%). The lower field resonance, due to [2-adamH][Pt(EtNH$_2$)Cl$_3$], was very close to our value of -1850 ppm observed for K[Pt(EtNH$_2$)Cl$_3$]. We can therefore conclude that the biological tests done by these authors were not reliable, especially since the main impurity [Pt(adam)Cl$_3$]$^-$ (~50%) is much more soluble than the disubstituted compound. The diamine compounds should be retested.

Mixed-amine Pt(II) compounds with adamantanamine ligands have not been reported previously. For most of the complexes prepared in the present work, the elemental analyses are very good. For a few complexes, like Pt(cpa)(1-adam)Cl$_2$, the results may indicate the presence of a small quantity of impurities, but only one species was detected by ^{195}Pt-NMR spectroscopy. The Pt resonances of all the mixed-amine complexes were observed between -2188 and -2235 ppm (Table II). Only one signal was observed for each complex, indicating the compounds are isomerically pure. The ^{195}Pt chemical shifts of the complexes Pt(L)(1-adam)Cl$_2$ were slightly dependent on the size of L, as was observed for the bis(adamantanamine) complexes. The resonances gradually move toward lower fields as the size of L increases, with δ(Pt) = -2213, -2208, -2199, and -2188 ppm for MeNH$_2$, EtNH$_2$, cyclobutylamine, and cyclopentylamine, respectively. The compound with cpa apparently creates a similar steric environment as do two Me$_2$NH ligands (-2188 ppm).

The IR (4000–250 cm^{-1}) and Raman (500–200 cm^{-1}) spectra of all the chloro-disubstituted complexes were recorded in the solid phase. The IR spectra of the complexes Pt(adam)$_2$Cl$_2$ are similar to those of K[Pt(adam)Cl$_3$]. The amine bands are shifted to lower energies by about 65–120 cm^{-1}, and for the mixed-amine complexes, additional bands due to the presence of the second amine are observed. The complexes show one or two IR-active δ(NH$_2$) vibrations between 1595 and 1563 cm^{-1}, lowered by about 25–60 cm^{-1}, compared to the absorption bands of the free ligands. The ν(Pt-N) vibrations are located between 555 and 455 cm^{-1}. Except for those of Pt(cpa)(1-adam)Cl$_2$ and Pt(2-adam)$_2$Cl$_2$, which show only one band, all the other spectra exhibit two bands in this region. These assignments are based on previous work.[29,33,34]

cis- and *trans*-Pt(L)$_2$Cl$_2$ complexes can often be characterized by vibrational spectroscopy. Group theory predicts two IR- and Raman-active ν(Pt-Cl) bands for the cis isomer and one band (IR, b_{2u}; Raman, a_g) for the trans isomer. Sometimes the two vibrations of a cis complex have very close energies and only one band is observed. In this case, the geometrical isomerism of the complexes can sometimes be determined by the position of the band. The cis complexes absorb around 315–320 cm^{-1}, while the trans compounds absorb at higher energies, around 335–340 cm^{-1}.[35] In a study reported on mixed-amine complexes, some of the cis complexes showed two bands between 327 and 308 cm^{-1} (IR), while others showed one large band between 310 and 320 cm^{-1}.[10] The cis isomerism was confirmed by X-ray diffraction studies of a few crystals.[28,36] For the Pt(L)(adam)Cl$_2$ complexes, the compounds Pt(EtNH$_2$)(1-adam)Cl$_2$ and Pt(EtNH$_2$)(2-adam)Cl$_2$ are cis isomers since they exhibit two ν(Pt-Cl) bands, which are coincident in the IR and Raman spectra. The other mixed-amine complexes Pt(MeNH$_2$)(1-adam)Cl$_2$, Pt(cba)(1-adam)Cl$_2$, Pt(cpa)(1-adam)Cl$_2$, and Pt(MeNH$_2$)(2-adam)Cl$_2$ show only one band around 325 cm^{-1}, and since these bands are coincident in both IR and Raman spectra, we have assigned them as cis isomers. For Pt(MeNH$_2$)(1-Meadam)Cl$_2$, two bands were observed in the Raman and only one was observed at 326 cm^{-1} in the IR spectrum. This compound is also believed to be a cis

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(33) Watt, G. W.; Hutchison, B. B.; Klett, D. S. *J. Am. Chem. Soc.* **1967**, *89*, 2007.

(34) Berg, R. W.; Rasmussen, K. *Spectrochim. Acta* **1973**, *29A*, 319.

(35) Lock, C. J. L.; Zvagulis, M. *Inorg. Chem.* **1981**, *20*, 1817.

(36) Rochon, F. D.; Melanson, R. *Acta Crystallogr.* **1986**, *C42*, 1291.

Table III. ^{195}Pt NMR Resonances for the Diiodo Complexes (in DMF)

compd	$\delta(^{195}Pt)$ (ppm)
$Pt(en)I_2$	-3462^{38}
$Pt(NH_3)_2I_2$	-3264^{38}
$Pt(MeNH_2)_2I_2$	−3327
$Pt(EtNH_2)_2I_2$	−3330
$Pt(cba)_2I_2$	−3346
$Pt(cpa)_2I_2$	−3302
$Pt(Me_2NH)_2I_2$	−3211
$Pt(1\text{-}adam)_2I_2$	−3364 (*cis*, 37%), −3331 (*trans*, 63%)
$Pt(2\text{-}adam)_2I_2$	−3333
$Pt(1\text{-}Meadam)_2I_2$	−3354
$Pt(MeNH_2)(1\text{-}adam)I_2$	−3336
$Pt(MeNH_2)(2\text{-}adam)I_2$	−3328
$Pt(EtNH_2)(2\text{-}adam)I_2$	−3327
$Pt(cba)(2\text{-}adam)I_2$	−3387 (*cis*, 14%), −3358 (*trans*, 86%)
$Pt(cpa)(2\text{-}adam)I_2$	−3328
$Pt(MeNH_2)(1\text{-}Meadam)I_2$	−3389 (*cis*, 25%), −3336 (*trans*, 75%)
$Pt(EtNH_2)(1\text{-}Meadam)I_2$	−3388

isomer with an unresolved peak in the IR spectrum. These compounds are probably not mixtures of isomers, since only one resonance was observed in the ^{195}Pt-NMR spectra. For the $Pt(adam)_2Cl_2$ complexes, ^{195}Pt NMR has shown that the compounds with 1-adam and 2-adam were mixtures of isomers, while the complex with 1-Meadam is probably the cis isomer.

$Pt(adam)_2I_2$ and $Pt(amine)(adam)I_2$ Complexes. The disubstituted $Pt(adam)_2I_2$ complexes were synthesized by Dhara's method.[18] The mixed-ligand compounds were prepared by cleavage of the amine iodo-bridged dimers by the adamantanamine ligands, as described previously for mixed-amine ligands.[10]

$$cis\text{-}Pt(amine)_2I_2 \xrightarrow{HClO_4} [Pt(amine)I_2]_2$$

$$[Pt(amine)I_2]_2 + 2adam \xrightarrow{H_2O} 2Pt(amine)(adam)I_2$$

The dimers were prepared from the reaction of $Pt(amine)_2I_2$ with perchloric acid. A mechanism involving dimerization of *cis*-$Pt(L)_2I_2$ in acidic media has been suggested by Elding and Olsson.[37] Adamantanamine iodo-bridged dimers are difficult to prepare probably because of the low solubility of the $Pt(adam)_2I_2$ complexes.

The synthesis of iodo complexes is important since they are more soluble in organic solvents than are the chloro analogues. The ^1H-NMR spectra of the diiodo complexes were recorded in $CDCl_3$ solution. For the complexes *cis*-$Pt(cpa)_2I_2$ and $Pt(1\text{-}adam)_2I_2$, ^{195}Pt couplings with the amine protons were observed with $^2J(Pt-H) = 70$ and 68 Hz, respectively. The amine protons were observed between 3.61 and 4.97 ppm, while ^{195}Pt couplings with the methyl protons were detected for $Pt(MeNH_2)_2I_2$ and $Pt(Me_2NH)_2I_2$ with $^3J(Pt-H) = 49$ and 43 Hz, respectively.

The ^{195}Pt-NMR spectra were recorded in DMF solution, and the results were compared to those obtained for the chloro series. The same trends would be expected for the chemical shifts of the iodo and chloro complexes, if steric and/or solvent effects are responsible for the observed chemical shifts. The ^{195}Pt resonances of the iodo complexes are shown in Table III. The signals of the compounds were observed between −3302 and −3389 ppm for the primary amines and at −3211 ppm for Me_2NH. A slight steric hindrance resulting from the presence of secondary amines might possibly be an important chemical shift factor for these complexes. The measured values agree with those reported for *cis*-$Pt(NH_3)_2I_2$ (−3264 ppm) and $Pt(en)I_2$ (−3462 ppm) in DMF.[38] Two signals were observed for $Pt(1\text{-}adam)_2I_2$, $Pt(cba)(2\text{-}adam)I_2$, and $Pt(MeNH_2)(1\text{-}Meadam)I_2$, indicating that the three compounds were mixtures of cis and trans isomers, with the trans compound being in greater concentration. All the other complexes exhibited only one ^{195}Pt signal. The chemical shifts of all the complexes are very similar (except for the secondary amine Me_2NH) and are not very dependent on the ligands, as observed for the dichloro series. For example, $Pt(MeNH_2)(2\text{-}adam)I_2$, $Pt(EtNH_2)(2\text{-}adam)I_2$, and $Pt(cpa)(2\text{-}adam)I_2$ all have the same chemical shifts.

Table IV. Infrared and Raman Bands for the Diamino Diiodo Complexes in the Solid State (cm^{-1})

compd	IR	Raman
$Pt(MeNH_2)_2I_2$	150 (m), 140 (mw)	149 (mw), 137 (m)
$Pt(EtNH_2)_2I_2$	148 (w), 142 (m) 177 (s), 164 (m)	154 (w), 140 (m)
$Pt(cba)_2I_2$	178 (s), 142 (w)	179 (m), 147 (s)
$Pt(cpa)_2I_2$	180 (s), 152 (w)	176 (ms), 149 (s)
$Pt(1\text{-}adam)_2I_2$ (63% *trans*, 37% *cis*)	161 (vw), 142 (w) 201 (sh), 195 (s)	165 (w), 152 (s)
$Pt(2\text{-}adam)_2I_2$	151 (ms), 141 (s) 203 (vs), 179 (vs)	152 (m), 149 (s)
$Pt(MeNH_2)(1\text{-}adam)I_2$	150 (m), 142 (mw) 191 (vs), 168 (mw)	150 (s), 140 (w) 167 (w)
$Pt(EtNH_2)(2\text{-}adam)I_2$	163 (w), 150 (w) 181 (s)	162 (m), 147 (w) 178 (s)
$Pt(cba)(2\text{-}adam)I_2$ (86% *trans*, 14% *cis*)	193 (s), 178 (s)	149 (s)
$Pt(cpa)(2\text{-}adam)I_2$	184 (s), 151 (w)	147 (s)
$Pt(MeNH_2)(1\text{-}Meadam)I_2$ (75% *trans*, 25% *cis*)	183 (s), 151 (w)	181 (m), 149 (s)
$Pt(EtNH_2)(1\text{-}Meadam)I_2$	192 (s), 153 (w)	150 (s)

The IR and Raman spectra of the complexes were recorded in the solid state. The general appearance of the IR spectra is retained when the 4000–600-cm^{-1} regions for the chloro and iodo complexes are compared. There are fewer data available in the literature for metal–iodide and metal–nitrogen stretching modes than for the analogous chloro vibrations.[34,39,40] In the Raman, the $\nu(Pt-I)$ and the $\nu(Pt-N)$ vibrations has been reported at 153 and 532 cm^{-1}, respectively, for *trans*-$Pt(NH_3)_2I_2$.[39] For $Pt(en)I_2$, the $\nu(Pt-I)$ vibrations have been attributed to Raman peaks at 192 and 181 cm^{-1}, while the $\nu(Pt-N)$ modes were observed at 524 and 444 cm^{-1} in the IR.[34] Extensive studies on *cis*- and *trans*-$Pt(L)_2X_2$ complexes ($L = SMe_2, SEt_2, AsEt_3, PPh_3, PMe_3, AsMe_3$; $X = Cl, Br, I$) have been reported by Duddell et al.[40] and by Park and Hendra.[41] These two research groups did not agree in the assignments of the $\nu(Pt-I)$ vibrations. For example, the symmetric $\nu(Pt-I)$ stretching frequency for *trans*-$Pt(PMe_3)_2I_2$ complexes has been located in the Raman at 150 cm^{-1} because it is extremely intense and polarized in solution.[40] The corresponding antisymmetric mode, which should be strong in the IR, has been assigned to a weak peak at 206 cm^{-1}. The same vibrations for the $Pt(PMe_3)_2I_2$ and $Pt(AsMe_3)_2I_2$ complexes have been assigned by Park and Hendra[41] at 189 and 169 cm^{-1}, respectively, in the IR spectra. For the only *cis*-diiodo complex obtained by Duddell et al.,[40] $Pt(PMe_3)_2I_2$, the symmetric and antisymmetric $\nu(Pt-I)$ bands were assigned at 148 and 133 cm^{-1} in the Raman with coincident IR bands at 146 and 137 cm^{-1}, respectively.

It seems that IR spectroscopy does not provide characteristic band criteria for the iodides in the same way that it generally does for the chlorides.[40] The only assignment in the literature which seems conclusive is for the symmetric $\nu(Pt-I)$ vibration around 150 cm^{-1} in the Raman spectra. Since our Raman spectra all exhibit a strong band in this region, we have assigned it to the symmetric $\nu(Pt-I)$ vibration. In most of the complexes, this band has a counterpart in the IR spectra, which is a good indication of cis complexes. The second band, the antisymmetric $\nu(Pt-I)$ vibration, is more difficult to locate. On the basis of the chloro spectra, this mode should be at a lower frequency than the symmetric mode and should be weak in the Raman and strong

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(37) Elding, L. I.; Olsson, L. F. *Inorg. Chem.* **1977**, *16*, 2789.

(38) Lippard, S. J. *J. Mol. Biol.* **1987**, *194*, 705.

(39) Hendra, P. J. *Spectrochim. Acta* **1967**, *23A*, 1275.

(40) Duddell, D. A.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Smith, J. G. *J. Chem. Soc. A* **1970**, 545.

(41) Park, P. J. D.; Hendra, P. J. *Spectrochim. Acta* **1969**, *25A*, 909.

in the IR. In general, there is a weaker band at lower frequency in the Raman spectra, which has also a counterpart in the IR spectrum, but this band is also very weak. On the other hand, in many cases, there is a strong band around 200–180 cm^{-1} in the IR spectrum which has in many compounds no counterpart in the Raman spectra. Since it is known that this vibration is generally weak in the Raman and often cannot be observed, we have assigned this band to the antisymmetric ν(Pt–I) vibration. This is close to the value of 180 cm^{-1} reported for the $[PtI_4]^{2-}$ ion.[42] These bands are listed in Table IV.

There seems to be agreement for the platinum–ligand frequencies, and these are located in the same region as those of the chloro complexes. On this basis, the bands which we have observed between 590 and 455 cm^{-1} have been assigned to the platinum–nitrogen stretching vibrations (see Experimental Section).

Systems containing iodide ligands present greater difficulties than do the chloro analogues, since their vibrational frequencies are at lower energies and it is difficult to distinguish between internal and lattice modes. In addition, in IR spectroscopy, the ν(Pt–I) absorptions are in a region where there are problems with water absorptions. Nevertheless, the appearence of two ν(Pt–I) and two ν(Pt–N) peaks in most cases is suggestive of cis isomers, except for the complexes which have been shown to be mixtures of isomers by ^{195}Pt-NMR spectroscopy. Those have been identified in Table IV.

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[42] Adams, D. M.; Morris, D. M. *J. Chem Soc. A* **1969**, 765.