Inorg. Chem. **1994,** *33,* 4485−4493

Synthesis of Pt(amine)(DMF)Cl_2 and $[Pt(amine)X_2]_n$ (X = Cl, I) and Crystal Structure of *cyclo*-Tris(μ-chloro)tris[chloro(dimethylamine)platinum(II)]

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Received December 27, 1993[⊗]

Chloro-bridged oligomers of the type $[Pt(amine)Cl_2]_n$ have been synthesized and characterized by IR and ^{1}H- and ^{195}Pt-NMR spectrometry. These compounds are believed to consist of mostly dimers in the solid state. Heating the oligomers in dichloromethane solution favors the formation of trimers. The crystal structure of the dimethylamine chloro-bridged trimer was determined by X-ray diffraction. The crystals belong to the trigonal (hexagonal cell) $R\bar{3}$ space group, with a = 15.463(6) Å, c = 13.984(5) Å, and Z = 6. The results have shown that the compound is a cyclic six-membered chloro-bridged trimer with a 3-fold axis in the center of the ring. The terminal Pt—Cl bond is 2.274(3) Å, significantly shorter than the bridging bonds which are 2.332(3) and 2.319(3) Å. The Pt_3Cl_3 ring assumes a "crown" conformation with C_3 symmetry. The internal angles are Cl—Pt—Cl′ = 90.5(1)° and Pt—Cl—Pt′ = 93.9(2)°. The oligomers are rapidly cleaved in DMF to form first *cis*-Pt(amine)(DMF)Cl_2, which isomerize to the *trans* isomers. On standing in acetone or dichloromethane solution, the DMF complexes are partly rearranged to the chloro-bridged oligomers. A few iodo-bridged oligomers were characterized by ^{195}Pt NMR. The resonances of these species were observed around −4000 ppm. Contrary to the chloro-bridged compounds, the iodo complexes are not cleaved by DMF.

Introduction

Halo-bridged complexes of platinum are of special interest since they are often excellent starting materials for the synthesis of mixed-ligand Pt(II) complexes. Several methods for the synthesis of chloro-bridged dimers have been reported with different kinds of ligands[2−10] but not with normal primary amines, except for the bulky amine *tert*-butylamine.[10] Chloro-bridged compounds with pyridine derivatives have been prepared in our laboratory. Molecular weight measurements showed that these compounds are dimers in chloroform solution at room temperature.[8] More recently iodo-bridged dimers (or oligomers) with aliphatic amines have been reported.[11,12] These compounds, prepared from *cis*-Pt$(amine)_2I_2$ in acid solution, are excellent starting materials for the synthesis of mixed-ligand compounds[11,13] or $[Pt(amine)Cl_3]^-$ complexed ions.[14] Chloro-bridged compounds with aliphatic amines cannot be prepared by a similar method.

Although several chloro- and hydroxo-bridged dimers have been reported, the presence of chloro-bridged trimeric species has never been confirmed even if the existence of oligomers with iodo bridges has been suggested.[12] A few hydroxo-bridged trimers have been characterized by X-ray diffraction.[15−18] The crystal structures of a few tetramers have also been reported.[19−21]

The chloro-bridged dimers, discussed above, can be cleaved by nucleophiles such as pyridine, ethylene, acetonitrile, and DMF. Dimethylformamide is a commonly used organic solvent whose interaction with metals is not well-known. Examination of the orbital energy diagram of DMF shows two possible donor orbitals available for the coordination to a metal ion: the nonbonding orbital containing the free electron doublet of nitrogen and the nonbonding orbital containing the free electron doublet of oxygen. Although platinum usually shows a preference for N-donor ligands, bonding through nitrogen is unknown in transition metal DMF complexes and all published data have shown that the binding site is the oxygen atom.[8,22−24] DMF possesses a resonance structure of two mesomeric forms, and the ionic form is more favored as shown by the planar structure of DMF.[25] A brief survey of several DMF crystal structure

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

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0020-1669/94/1333-4485$04.50/0

determinations has shown that DMF has almost the same structure, whether it is free, coordinated to a metal, or uncomplexed as a molecule of crystallization.[24]

Few platinum(II) complexes with DMF are known in the literature. DMF complexes with piperidine and pyridine derivatives were reported[8,10] but not with aliphatic amines. The crystal structure of *trans*-Pt(DMF)(2,6-lutidine)Cl_2 was published.[24] Bonding through the oxygen atom can be determined from IR spectroscopy, by a lowering of the stretching C=O vibration, and by ^{1}H-NMR spectroscopy, from the coupling of the aldehydic proton with platinum No ^{195}Pt coupling with the methyl groups of DMF was observed.

Primary aliphatic amine complexes of platinum(II) with DMF are not yet known. We have now developed a new and general method for the preparation of such compounds. This method is based on the cleavage of halo-bridged oligomers as reported for pyridine complexes.[8] We have synthesized a series of complexes of the type Pt(amine)(DMF)Cl_2 with methylamine, ethylamine, cyclobutylamine (cba), cyclopentylamine (cpa), and dimethylamine. All the compounds were characterized by proton- and platinum-NMR and by IR spectroscopy.

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), and dimethylamine (Me_2NH, 40% in water) 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 decomposition points were measured on a Fisher-Johns instrument. The IR spectra were recorded on a Perkin-Elmer 783 or a Digilab FT-50 spectrometer (CsI beamsplitter, resolution 1 cm^{-1}). 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). K_2PtCl_4 was used as an external standard adjusted to −1628 ppm from Na_2PtCl_6 ($\delta = 0$ ppm). ^{1}H-NMR spectra were measured on a Varian XL-200, Gemini-200, XL-300, or Gemini-300 spectrometer in DMF-d_7, acetone-d_6, CD_2Cl_2, or D_2O solutions.

[Pt(amine)Cl_2]$_n$. The compounds were synthesized as already reported for pyridine ligands.[8] Compounds with methylamine, ethylamine, cyclobutylamine, cyclopentylamine, and dimethylamine were synthesized.

[Pt(CH_3NH_2)Cl_2]$_n$: Yield 77%; dec pt 183−191 °C. Anal. Calc: C, 4.04; H, 1.70; Cl, 23.86; N, 4.71. Found: C, 4.16; H, 1.66; Cl, 23.38; N, 4.95. IR (cm^{-1}): 3270 m, 3222 m ν(NH), 1560 m δ(NH_2), 1578 m, 1412 m, 1260 m, 1090 s, 1085 s, 695 w, 340 s ν(Pt−Cl)$_t$, 308 m (ν(Pt−Cl)$_b$ (trans to Cl), 293 m ν(Pt−Cl)$_b$ (trans to amine).

[Pt($C_2H_5NH_2$)Cl_2]$_n$: Yield 84%; dec pt 175−184 °C. Anal. Calc: C, 7.72; H, 2.67; Cl, 22.78; N, 4.50. Found: C, 7.75; H, 2.19; Cl, 22.23; N, 4.76. IR (cm^{-1}): 3245 s, 3220 m ν(NH), 1561 s δ(NH_2), 1395 w, 1237 m, 1221 m, 1078 s, 1036 s, 695 s, 338 s ν(Pt−Cl)$_t$, 309 m ν(Pt−Cl)$_b$ (trans to Cl), 291 m ν(Pt−Cl)$_b$ (trans to amine).

[Pt($C_4H_7NH_2$)Cl_2]$_n$: Yield 37%; dec pt 180−187 °C. IR (cm^{-1}): 3276 s, 3126 m, 3105 m ν(NH), 1569 m δ(NH_2), 1242 w, 1218 w, 1155 w, 1095 m, 338 s ν(Pt−Cl)$_t$, 305 m ν(Pt−Cl)$_b$ (trans to Cl), 295 m ν(Pt−Cl)$_b$ (trans to amine).

[Pt($C_5H_9NH_2$)Cl_2]$_n$: Yield 61%; dec pt 150−165 °C. IR (cm^{-1}): 3239 s, 3190 s, 3119 m ν(NH), 1571 s δ(NH_2), 1220 w, 1137 w, 978 m, 340 s ν(Pt−Cl)$_t$, 325 m ν(Pt−Cl)$_b$ (trans to Cl), 305 m ν(Pt−Cl)$_b$ (trans to amine).

[Pt((CH_3)$_2$NH)Cl_2]$_2$: Yield 42%; dec pt 170−178 °C. Anal. Calc: C, 7.72; H, 2.67; Cl, 22.78; N, 4.50. Found: C, 7.86; H, 2.26; Cl, 22.72; N, 4.62. IR (cm^{-1}): 3210 s ν(NH), 1268 m, 1090 s, 1008 m, 898 m, 350 m ν(Pt−Cl)$_t$, 320 m ν(Pt−Cl)$_b$ (trans to Cl), 303 m ν(Pt−Cl)$_b$ (trans to amine).

[Pt((CH_3)$_2$NH)Cl_2]$_3$. A 1 mmol amount of K[Pt((CH_3)$_2$NH)Cl_3], synthesized by the method already reported,[14] was stirred in 10 mL of perchloric acid for 10 min. The solution was then concentrated under reduced pressure at 30 °C until an orange compound precipitated. The compound was filtered off and dissolved in dichloromethane. The solution was placed in a beaker and sealed off with wax paper. Crystals were obtained by slow evaporation of the solvent with slight warming (40 °C). One of these crystals was chosen for X-ray diffraction studies: Yield 48%; dec pt 160−168 °C. IR (cm^{-1}): 3198 s ν(NH), 1390 w, 1273 w, 1125 m, 1088 s, 1005 m, 896 s, 520 w, 341 s ν(Pt−Cl)$_t$, 312w ν(Pt−Cl)$_b$ (trans to Cl), 294 m ν(Pt−Cl)$_b$ (trans to amine).

Pt(amine)(DMF)Cl_2. A 1 mmol amount of the chloro dimer or oligomer was dissolved in DMF, and the solution was evaporated to dryness under reduced pressure. The resulting product was washed with ether and filtered off. The complex Pt(CH_3NH_2)(DMF)Cl_2 must be isolated under nitrogen atmosphere since it decomposes in air. The products were dried over P_4O_{10}. The proton NMR chemical shifts for the free ligands are as follows: DMF (acetone-d_6), 2.82 s, 2.98 s, 8.01 s; CH_3NH_2 ($CDCl_3$), 2.25 s; $C_2H_5NH_2$ ($CDCl_3$), 0.97 t, 2.59 q; cba ($CDCl_3$), 1.27 m, 1.872 m, 3.053 m; cpa ($CDCl_3$), 1.064 m, 1.563 m, 3.132 m; (CH_3)$_2$NH ($CDCl_3$), 1.85 d.

Pt(CH_3NH_2)(DMF)Cl_2: Yield 33%; dec pt 74−104 °C. Anal. Calc: C, 12.98; H, 3.27; Cl, 19.15; N, 7.57. Found: C, 11.78; H, 2.97; Cl, 19.89; N, 6.91. IR (KBr pellet, cm^{-1}): ν(NH) 3259 ms, 3218 ms, 3121 m, ν(C=O) 1645 s, δ(NH_2) 1595 m, 1582 ms, 1420 w, 1375 m, 1280 w, 1249 w, 1122 s, 1089 s, 1061 w, 1049 w, 990 m, δ(OCN) 721 m, ν(Pt−N), ν(Pt−O) 442 w, 402 mw, and ν(Pt−Cl) 341 ms. ^{1}H-NMR (δ (ppm), acetone-d_6): *trans*, 2.36 (t + dt), ^3J(^{195}Pt−^{1}H) = 48 Hz, 4.49 (NH), 2.88 (s), 3.16 (s), 8.13 (s + d), ^3J(^{195}Pt−^{1}H) = 23 Hz; *cis*, 2.32 (t + dt), 4.70 (NH), 2.85 (s), 3.13 (s), 8.09 (s + d).

Pt($C_2H_5NH_2$)(DMF)Cl_2: Yield 30%; dec pt 78−98 °C. Anal. Calc: C, 15.63; H, 3.67; Cl, 18.45; N, 7.29. Found: C, 13.69; H, 3.07; Cl, 19.45; N, 6.27. ^{1}H-NMR (δ (ppm), acetone-d_6): 1.29 (t), 2.66 (m), ^3J(^{1}H−^{1}H) = 7 Hz, 2.90 (s), 3.18 (s), 8.15 (s + d), ^3J(^{195}Pt−^{1}H) = 23 Hz. ^{1}H-NMR (δ (ppm), CD_2Cl_2): 1.26 (t), 2.77 (m), ^3J(^{1}H−^{1}H) = 7 Hz, 3.82 (NH), 2.93 (s), 3.06 (s), 8.23 (s + d), ^3J(^{195}Pt−^{1}H) = 22 Hz. IR (KBr pellet, cm^{-1}): ν(NH) 3245 ms, 3220 m, 3198 m, 3140 mw, ν(C=O) 1650 s, δ(NH_2) 1592 ms, 1570 ms, 1430 m, 1378 m, 1250 m, 1121 m, 1090 w, 1080 m, 1060 w, 1040 w, δ(OCN) 723 m, ν(Pt−N), ν(Pt−O) 442 w, 397 mw, and ν(Pt−Cl) 342 ms.

Pt(cba)(DMF)Cl_2: Yield 14%; dec pt 92−101 °C. ^{1}H-NMR (δ (ppm) acetone-d_6): 3.51 (m), 2.30 (m), ^3J(^{1}H−^{1}H) = 8 Hz, 2.06 (m), 1.66 (m), 4.68 (NH), 2.89 (s), 3.17 (s), 8.13 (s + d), ^3J(^{195}Pt−^{1}H) = 22 Hz. IR (KBr pellet, cm^{-1}): ν(NH) 3305 ms, 3278 m, 3121 m, ν(C=O) 1640 s, δ(NH_2) 1587 m, 1485 m, 1432 m, 1355 w, 1245 s, 1230 m, 1161 w, 1125 s, 1100 s, 978 w, δ(OCN) 720 m, ν(Pt−N), ν(Pt−O) 444 w, 400 mw, and ν(Pt−Cl) 341 ms.

Pt(cpa)(DMF)Cl_2: Yield 17%; dec pt 98−123 °C. ^{1}H-NMR (δ (ppm) acetone-d_6): 3.41 (m), 2.06 (m), ^3J(^{1}H−^{1}H) = 8 Hz, 1.81 (m), 1.57 (m), 4.48 (NH), 2.90 (s), 3.18 (s), 8.15 (s + d), ^3J(^{195}Pt−^{1}H) = 22 Hz. IR (KBr pellet, cm^{-1}): ν(NH) 3240 m, 3208 m; 3130 mw, ν(C=O) 1642 s, δ(NH_2) 1570 m, 1140 w, 975 w, δ(OCN) 721 m, ν(Pt−N), ν(Pt−O) 442 w, 398 mw, and ν(Pt−Cl) 338 ms.

Pt((CH_3)$_2$NH)(DMF)Cl_2: Yield 78%: dec pt 115−122 °C. Anal. Calc. C, 15.63; H, 3.67; Cl, 18.45; N, 7.29. Found: C, 14.79; H, 3.38; Cl, 19.06; N, 7.13. ^{1}H-NMR (δ (ppm), acetone-d_6): 2.53 (d + dd), ^3J(^{195}Pt−^{1}H) = 38 Hz, 5.20 (NH), 2.88 (s), 3.17 (s), 8.09 (s + d), ^3J(^{195}Pt−^{1}H) = 23 Hz. ^{1}H-NMR (δ (ppm), CD_2Cl_2): 2.60 (d + dd), ^3J(^{195}Pt−^{1}H) = 38 Hz, 5.05 (NH), 2.92 (s), 3.05 (s), 8.14 (s + d), ^3J(^{195}Pt−^{1}H) = 24 Hz. IR (KBr pellet, cm^{-1}): ν(NH) 3219 m, ν(C=O) 1641 s, 1432 m, 1420 w, 1375 m, 1280 w, 1248 w, 1135 w, 1120 m, 1095 s, 1015 m, 905 m, δ(OCN) 718 m, ν(Pt−N), ν(Pt−O) 443 w, 392 mw, and ν(Pt−Cl) 343 ms.

Crystal Structure of [Pt((CH_3)$_2$NH)Cl_2]$_3$. The crystals were obtained by heating slowly (40 °C) a dichloromethane solution of the orange powder (containing probably mainly dimers) obtained by the method described above. A red crystal was selected after examination under a polarizing microscope for homogeneity. The unit cell parameters were obtained by least-squares refinement of the angles of 15 well-centered reflections on a Syntex P$\bar{1}$ diffractometer using

Table 1. Experimental Details of the X-ray Diffraction Study of $[Pt((CH_3)_2NH)Cl_2]_3$

compd	$C_6H_{21}N_3Cl_6Pt_3$
M_w	933.24
cryst system	trigonal (hexagonal cell)
space group	$R3$
a (Å)	15.463(6)
b (Å)	15.463(5)
c (Å)	13.984(5)
α (deg)	90.0
β (deg)	90.0
γ (deg)	120.0
V (Å^3)	2895(2)
Z	6
$F(000)$	2484
ϱ_{calcd} (Mg m^{-3})	3.211
λ(Mo Kα) (Å)	0.710 69
μ(Mo Kα) (mm^{-1})	22.75
cryst faces and dimens (mm)	$(101)-(\bar{1}0\bar{1})$ (0.172), $(\bar{1}11)-(1\bar{1}\bar{1})$ (0.134), $(0\bar{1}1)-(01\bar{1})$ (0.192)
transm factor range	0.049−0.122
2θ max (deg)	52
quadrants measd	$h,k,\pm l$
h,k,l	$0\rightarrow16$, $0\rightarrow16$, $-17\rightarrow17$
scan technique	$2\theta/\theta$
std reflcns (dev)	300, 030, $00\bar{6}$ (<2%)
T (K)	295
no. of indep reflcns	1627
no. of obsd reflcns ($I > 2.5\sigma(I)$)	1054
no. of params refined	56
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.031
Δ/σ	<0.1
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum\|F_o\|^2]^{1/2}$	0.029
S (std dev, unit weight)	1.16

graphite-monochromatized Mo Kα radiation. From the systematic extinctions, the possible space groups were $R3$, $R\bar{3}$, $R32$, $R\bar{3}m$, and $R3m$. Successful refinement of the structure, showed that $R\bar{3}$ was the correct space group. Crystal data and other information are summarized in Table 1. The background-to-scan time ratio was 0.5. Scan rates (from 2 to 24°/min depending on the intensity of the reflection) and data treatment have already been described.[26] The $\sigma(I)$ was calculated as described previously.[26] The intensity data were corrected for absorption (Gaussian integration) and for the effects of Lorentz and polarization.

The coordinates of the Pt atom were determined from a three-dimensional Patterson synthesis, and the positions of all the other non-hydrogen atoms were obtained by structure factor and Fourier-map calculations. One H atom from each methyl group was located, and the positions of the other H atoms were calculated with C—H = 0.95 Å and N—H = 0.85 Å. The positions of these atoms were fixed with isotropic $U = 0.076$ Å^2. The refinement of the structure was done by using full-matrix least-squares calculations minimizing $\sum w(F_o - F_c)^2$. Isotropic secondary-extinction corrections[27] were included in the calculations. Individual weights $w = 1/\sigma^2(F)$ were applied. The scattering curves of Cromer and Waber[28] were used for Pt, Cl, N, and C, and those of Stewart, Davidson, and Simpson[29] were used for H. The anomalous dispersion terms of Pt and Cl were included in the calculations.[30] The refinement of the scale factor, coordinates, and anisotropic temperature factors of all non-hydrogen atoms converged to $R = 0.031$ and $R_w = 0.029$. The ratio of maximum least-squares shifts to esd in the final refinement cycle was <0.1. There were a few residual peaks (<0.4 e Å^{-3}) in the close environment of the Pt atom. The calculations were performed on a Cyber 830 using the programs already described.[26]

Table 2. ^{195}Pt Resonances ($\delta \pm 5$ ppm) of the Pt(amine)(DMF)Cl_2 Complexes in Different Solvents

amine	DMF	acetone	CH_2Cl_2
$Pt(CH_3NH_2)(DMF)Cl_2$	−1560	−1559	
$Pt(C_2H_5NH_2)(DMF)Cl_2$	−1571	−1567	−1569
After heating at 35 °C for 5 min			−1569 (83%), −1715 (17%)
Pt(cba)(DMF)Cl_2	−1578	−1576	−1588
Pt(cpa)(DMF)Cl_2	−1566	−1565	
$Pt((CH_3)_2NH)(DMF)Cl_2$	−1515	−1514	−1522
old solution (1 month)			−1524 (55%), −1576 (5%), −1700 (40%)

Results and Discussion

Pt(amine)(DMF)Cl_2 Complexes. Complexes of the type Pt(RNH_2)(DMF)Cl_2 are not yet known. The reactions of DMF with the monoamine complexes $K[Pt(RNH_2)Cl_3]$ in aqueous solution or in DMF solution do not produce the mixed-ligands complexes. There is no reaction with DMF under these conditions, as established by ^{195}Pt-NMR spectroscopy. The spectrum of a DMF solution of $K[Pt(CH_3NH_2)Cl_3]$, heated at 50 °C over a 3-week period, exhibited only a resonance at −1847 ppm, at the position of the $K[Pt(CH_3NH_2)Cl_3]$ complex.[31] The synthetic method which we have now developed is based on the cleavage of chloro-bridged oligomers as reported for the pyridine complexes.[8] The oligomers, which will be discussed later in this publication, can be easily cleaved by DMF.

$$[\mathrm{Pt(amine)Cl_2}]_n \xrightarrow{\mathrm{DMF}} n\mathrm{Pt(amine)(DMF)Cl_2}$$

A series of complexes of the type Pt(amine)(DMF)Cl_2, where amine = methylamine, ethylamine, cyclobutylamine (cba), cyclopentylamine (cpa), and dimethylamine, have been synthesized. The results of the elemental analyses have shown that a few compounds contain a small quantity of chloro-bridged oligomers.

The ^{195}Pt- and ^{1}H-NMR spectra of the Pt(amine)(DMF)Cl_2 compounds have been measured in different solvents, and the results are presented in Table 2 (^{195}Pt) and the Experimental Section (^{1}H). There is no solvent difference for the ^{195}Pt-NMR spectra of these complexes measured in acetone or DMF and maybe a small upfield shift (10 ppm) in CH_2Cl_2. Fresh solutions of the complexes show only one ^{195}Pt resonance in the different solvents. The proton-NMR spectra of the fresh solutions showed only one series of resonances for the amine and the bonded DMF ligand with integrations of one to one. The methyl groups of the DMF ligands are not equivalent and were observed as two singlets around 3.0 ppm, while the aldehyde proton resonance was found around 8.1 ppm with the coupling constant ^3J(Pt—H) ≈ 23 Hz, in acetone or dichloromethane. The presence of coupling of this proton with platinum confirmed the coordination through the oxygen atom. This coupling constant is close to the values found by Courtot et al. for complexes of the type *trans*-Pt(py)(DMF)Cl_2 (py = 4-methylpyridine, 2-methylpyridine, and 2,4,6-trimethylpyridine), where the aldehyde resonances were observed at 8.30 ppm with coupling constants of 27 Hz in chloroform solution.[10] Coupling constants $^3J(^{195}Pt—^1H)$ were also observed with CH_3NH_2 (48 Hz) and with $(CH_3)_2NH$ (38 Hz). The NH resonance were observed between 4.48 and 4.70 ppm in acetone for the primary amines and at 5.20 ppm for $(CH_3)_2NH$.

The ^{195}Pt chemical shifts for the mixed-ligand complexes were observed between −1559 and −1588 ppm and at slighly lower

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fields for the secondary amine (−1514 to −1522 ppm). These values are close to that reported for the $[Pt(N-O)Cl_2]^-$ (N−O = glycinate) complex at −1602 ppm.[32]

The IR spectra of the $Pt(amine)(DMF)Cl_2$ complexes were measured in the solid state. The main absorption bands are listed in the Experimental Section. A normal-coordinate analysis for DMF has indicated that the ν(CO), ν(CN), and δ(CH) modes are coupled significantly and are not really good vibrations for frequency shift comparisons.[33] Nevertheless, valence bond considerations predict that oxygen coordination should result in a decrease in ν(CO) and an increase in ν(CN). The spectra of the complexes have shown ν(CO) vibrations around 1640 cm^{-1}, 18−28 cm^{-1} lower than the ν(CO) value for the free ligand (1670 cm^{-1}). The O−C−N bending mode, found at 660 cm^{-1} in free DMF, is not coupled to other vibrations and might be a better choice for frequency shift comparisons. An increase in wavenumber is expected for this vibration when the coordination is through the oxygen atom, and it was observed between 718 and 723 cm^{-1} in our spectra. These values are close to those observed for $Pt(py)(DMF)Cl_2$, where py is a pyridine derivative.[8,10] The amine ν(N−H) vibrations were observed between 3121 and 3305 cm^{-1}, and $\delta(NH_2)$ vibrations, around 1580 cm^{-1}.

The approximate skeleton symmetries for *cis* and *trans* complexes with amine ligands are C_{2v} and D_{2h}, respectively. For the dichloro compounds, group theory predicts two ν(Pt−Cl) IR active vibrations for the *cis* isomer and only one for the *trans* isomer. For complexes containing two neutral ligands with different donor atoms like DMF and amine ligands, the approximate symmetry is at best C_s for the two isomers and group theory predicts two ν(Pt−Cl) IR active vibrations (2A′) and one ν(Pt−O) (A′) and one ν(Pt−N)(A′) mode for both complexes. The ν(Pt−Cl) vibrations of the complexes $Pt(amine)(DMF)Cl_2$ were observed as a single intense band at ≈340 cm^{-1}. In the literature, most *trans* dichloro compounds with two different ligands display only one ν(Pt−Cl) band, while *cis* compounds usually have two bands or a single broadened one.[11,34−36] For these reasons, we suggest that the compounds have a *trans* configuration.

Since platinum−oxygen and platinum−nitrogen stretching vibrations are of similar energy and of the same symmetry, coupling of the two vibrations is very likely and could lead to mixed character. Thus, even though the ν(Pt−N) is expected at slightly higher frequency than the ν(Pt−O) band, these two IR active vibrations have not been separated and are located between 392 and 444 cm^{-1} with the higher band belonging chiefly to the ν(Pt−N) vibration.

The complex *trans*-$Pt(CH_3NH_2)(DMF)Cl_2$ decomposes in acetone or methylene chloride solutions as shown by NMR spectroscopy. The proton spectrum (Figure 1) of an old solution of the complex in acetone shows, in the region around 8 ppm, two Pt−DMF species (δ = 8.13 and 8.09 ppm, with satellites) and free DMF at δ = 7.96 ppm. The loss of DMF suggests a possible rearrangement of *trans*-$Pt(CH_3NH_2)(DMF)Cl_2$ to the chloro-bridged dimers and other oligomeric species, as already noted by other workers in noncoordinating solvents.[2,8,9,37] As an example, the complex $Pt(2,6\text{-lutidine})(DMF)Cl_2$ was synthesized and dissolved in CH_2Cl_2. Six weeks later, red crystals, which proved to be the chloro-bridged dimer $[Pt(2,6\text{-lutidine})Cl_2]_2$, were obtained at room temperature.[9] The aldehydic signal observed for the old solution at 8.13 ppm is assigned to *trans*-$Pt(CH_3NH_2)(DMF)Cl_2$. The new aldehyde resonance observed at 8.09 ppm and the corresponding resonances for the methyl groups of DMF at 3.13 and 2.85 ppm were assigned to *cis*-$Pt(CH_3NH_2)(DMF)Cl_2$, which is formed from the reaction of chloro-bridged oligomers with free DMF. We will see later that the ^{195}Pt-NMR spectrum of a fresh solution of chloro-bridged dimers (or oligomers) measured in DMF produced two resonances corresponding to the presence of *cis*- and *trans*-$Pt(CH_3NH_2)(DMF)Cl_2$. *Cis* to *trans* isomerization is common in solvents like acetone, but *trans* to *cis* isomerization is not frequent for these types of ligands. In this particular case, we suggest that *trans*-$Pt(CH_3NH_2)(DMF)Cl_2$ decomposes to chloro-bridged oligomers releasing DMF. The oligomers will then react with free DMF to produce first *cis*-$Pt(CH_3NH_2)(DMF)Cl_2$. In the cleavage reaction of chloro-bridged oligomers, which will be discussed later, we suggest that the *cis* compound is first formed and the *trans* compound is obtained from subsequent isomerization of the *cis* isomer. This equilibrium will be seen only in solution, since, in the solid state, we believe that only *trans*-$Pt(CH_3NH_2)(DMF)Cl_2$ was isolated.

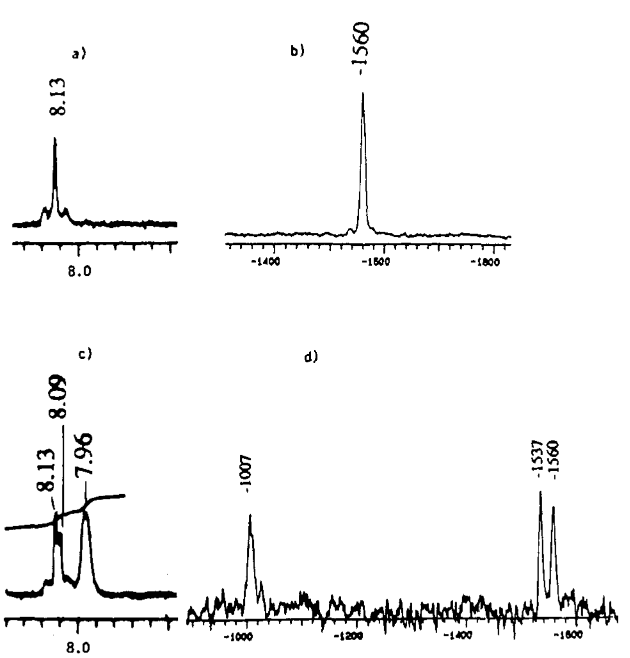

Figure 1. (a) ^{1}H- and (b) ^{195}Pt-NMR spectra of a fresh solution of *trans*-$Pt(CH_3NH_2)(DMF)Cl_2$ in acetone, (c) ^{1}H-NMR spectrum of an old solution in acetone, and (d) ^{195}Pt-NMR spectrum of an old solution in DMF.

Since the resonance of the aldehydic proton in the *cis* isomer appears at higher field compared to that in the *trans* isomer, we should expect the ^{195}Pt resonance for the *cis* species at lower field. The ^{195}Pt-NMR spectrum of an old sample, showed two resonances at −1560 and −1537 ppm. The signal observed at −1560 ppm is due to *trans*-$Pt(MeNH_2)(DMF)Cl_2$, while the −1537 ppm resonance is due to the corresponding *cis* isomer, which is observed at lower field as expected. An old sample measured in DMF has shown a third peak at −1007 ppm which might be assigned to a species containing three DMF ligands and one amine ligand. This is a reasonable chemical shift, since substitution of one chloride ligand for DMF in $K[Pt(amine)Cl_3]$ results in a downfield shift of approximately 280 ppm. Substitution of a second and third chloride should lead to a resonance at ≈−1000 ppm close to the −1007 ppm value in our spectrum. Other calculated values have been found close

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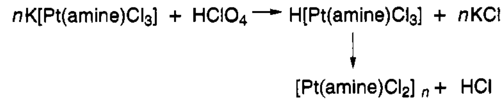
(32) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.
(33) Kaufmann, G.; Leroy, N. J. F. *Bull. Soc. Chim. Fr.* **1967**, 402.
(34) Rochon, F. D.; Fleurent, L. *Inorg. Chim. Acta* **1988**, *143*, 81.
(35) Lock, C. J. L.; Zvagulis, M. *Inorg. Chem.* **1981**, *20*, 1817.
(36) Howard-Lock, H. E.; Lock, C. J. L.; Turner, G.; Zvagulis, M. *Can. J. Chem.* **1981**, *59*, 2737.
(37) Gloria, J. M.; Susz, B. P. *Helv. Chim. Acta.* **1971**, *54* (7), 2251.

to the observed platinum chemical shifts, assuming that the effects of substitutions are additive.[38]

The *trans*-Pt($C_2H_5NH_2$)(DMF)Cl_2 complex decomposed more rapidly in acetone than did the CH_3NH_2 analog. A small quantity of free DMF could be observed after a few minutes of spectral accumulation in the proton-NMR spectrum. The corresponding ^{195}Pt-NMR spectrum showed only one resonance at −1567 ppm. The ^{1}H-NMR spectrum of the Pt($C_2H_5NH_2$)(DMF)Cl_2 complex, measured after slight heating in dichloromethane, showed intense free DMF peaks. No new resonances for bonded DMF ligand are detectable, but new resonances for the ethylamine ligand are apparent suggesting the rearrangement to chloro-bridged dimers or oligomers. The ^{195}Pt-NMR spectrum after heating for 5 min (≈40 °C) in CD_2Cl_2 showed a new resonance at −1715 ppm in the region of the chloro-bridged trimer. No *cis*-Pt($C_2H_5NH_2$)(DMF)Cl_2 is observed, since the oligomers seem quite stable in dichloromethane.

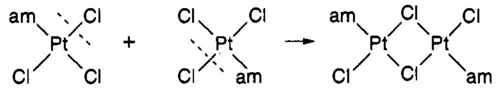
The ^{1}H-NMR spectrum of an old CD_2Cl_2 solution of the *trans*-Pt(($CH_3)_2$NH)(DMF)Cl_2 complex indicated that the free DMF aldehydic signal was about twice as intense as the bonded DMF signal. The loss of DMF suggests a rearrangement of *trans*-Pt(($CH_3)_2$NH)(DMF)Cl_2 to chloro-bridged oligomeric species [Pt(($CH_3)_2$NH)Cl_2]$_n$, whose methyl resonances appear as a doublet centered at 2.78 ppm with a coupling constant of J(CH−NH) = 6 Hz. These resonances are close to those of the trimeric species (2.73 ppm) measured in CD_2Cl_2 (discussed later). The ^{195}Pt-NMR of the old sample exhibited two main resonances at −1524 and −1700 ppm and a very minor peak (∼5%) at −1576 ppm. These signals were assigned to *trans*-Pt(($CH_3)_2$NH)(DMF)Cl_2, the chloro-bridged trimer, and to *cis*-Pt(($CH_3)_2$NH)(DMF)Cl_2 (aldehydic proton hidden under two other species), respectively.

Chloro-Bridged Oligomers [Pt(amine)X$_2$]$_n$. The chloro-bridged compounds were synthesized by a method similar to that reported previously for pyridine ligands.[8] The ionic complex K[Pt(amine)Cl_3], synthesized by the cleavage of the iodo-bridged dimers, as described previously,[14] forms the chloro-bridged oilgomers in the presence of perchloric acid, according to the following equation:



$$n\mathrm{K[Pt(amine)Cl_3]} + \mathrm{HClO_4} \rightarrow \mathrm{H[Pt(amine)Cl_3]} + n\mathrm{KClO_4}\downarrow$$
$$\downarrow$$
$$\mathrm{[Pt(amine)Cl_2]}_n + \mathrm{HCl}$$

$KClO_4$ is removed by filtration, and on evaporation to dryness, the oligomer is formed. The method is believed to produce mainly *trans* dimers, since the *trans* effect of chloride is greater than the *trans* effect of an amine.



trans isomer

The crystal structure of the chloro-bridged dimer with 2,6-lutidine has confirmed the *trans* configuration.[9] Other oligomeric cyclic species can also be formed.

Complexes of the type [Pt(amine)Cl_2]$_n$ with methylamine, ethylamine, cyclobutylamine, cyclopentylamine, and dimethylamine have been synthesized. All these complexes were characterized by proton- and platinum-NMR and IR spectroscopy. The isolated compounds are believed to be mainly chloro-bridged dimers in the solid state. These compounds were isolated as orange to brownish-red powders. Slight heating (≈40 °C for a few hours) of a methylene chloride solution containing the oligomers (mainly dimers) with dimethylamine produced, on standing, red crystals which were suitable for X-ray diffraction analysis. The crystal structure of one of these crystals was determined, and the results have shown that the compound is a chloro-bridged trimer.

Table 3. Atomic Coordinates (×10^5 for Pt and ×10^4 for Cl, N, C) with their Esd's and Thermal Parameters U_{eq} (×10^4)^a

	x	y	z	U_{eq}
Pt	71889(3)	47711(3)	10440(3)	380
Cl(1)	8072(2)	4234(2)	1974(2)	550
Cl(2)	6318(2)	5309(2)	153(3)	667
N	8458(5)	5587(5)	255(6)	408
C(1)	8303(9)	5463(9)	−801(8)	647
C(2)	8998(8)	6650(8)	518(8)	570

^{a} $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

$$\mathrm{[Pt((CH_3)_2NH)Cl_2]_2} \xrightarrow[\Delta]{\mathrm{CH_2Cl_2}} \mathrm{[Pt(Me_2NH)Cl_2]_3}$$

The red trimeric crystals were also studied by IR and proton- and ^{195}Pt-NMR spectroscopy and the data compared to those of the dimers. These results will be discussed later.

Crystal Structure of [Pt(($CH_3)_2$NH)Cl_2]$_3$. Although the crystal structures of several chloro- and hydroxo-bridged dimers and a few hydroxo-bridged trimers have been reported in the literature, there is no example of a chloro-bridged platinum trimer containing amine ligands. Our X-ray diffraction study of the structure of the trimer, *cyclo*-tris(μ-chloro)tris[chloro-(dimethylamine)platinum(II)], provided evidence of such a complex.

The refined atomic parameters of the structure are listed in Table 3. Labeled diagrams of the molecules are shown in Figure 2. The bond distances and angles are reported in Table 4. The results of the crystal structure determination have shown that the compound is a cyclic six-membered chloro-bridged trimeric species with a 3-fold axis in the center of the ring. The coordination around each Pt atom is square-planar. The best weighted plane was calculated through the five atoms. The deviations from this plane (Å) are as follows: Pt, −0.0006(4); Cl(1), 0.014(3); Cl(2), 0.017(3); Cl(1)′, 0.001(3) and N, 0.014(8). The angles around the Pt atom are close to the expected 90 and 180°. The internal angles Cl(1)−Pt−Cl(1)′ and Pt−Cl(1)−Pt′ are 90.5(1) and 93.9(2)°, respectively.

The terminal Pt−Cl(2) bond distance is 2.274(3) Å, significantly shorter than the bridging Pt−Cl(1) bond distances which are 2.332(3) and 2.319(3) Å. No chloro-bridged trimer has been reported yet in the literature, but our Pt−Cl values are similar to those observed for the 2,6-lutidine chloro-bridged dimer, where the terminal bond was 2.272(3) Å and the bridged bonds were 2.321(3) and 2.320(3) Å.[9] Our values also agree with those found in other chloro-bridged dimers.[4−6] The bridging Pt−Cl(1)′ (2.332(3) Å) which is located in a *trans* position to the amine ligand seems slightly longer than the bridging Pt−Cl(1) (2.319(3) Å) located in *trans* position to the terminal chloro ligand, but we do not know at the moment if the difference is significant. For the chloro-bridged dimer with 2,6-lutidine, the two bridging bonds are identical (2.321(3) and 2.320(3) Å).[9] For monomers of the type [Pt(amine)Cl_3]$^-$, several crystal structures have shown a slightly longer Pt−Cl distance for the bond located in *trans* position to the amine ligand.[14,31,39,40] The *trans* influence of amines might be slightly

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(39) Rochon, F. D.; Melanson, R. *Acta Crystallogr.* **1991**, *C47*, 2300.

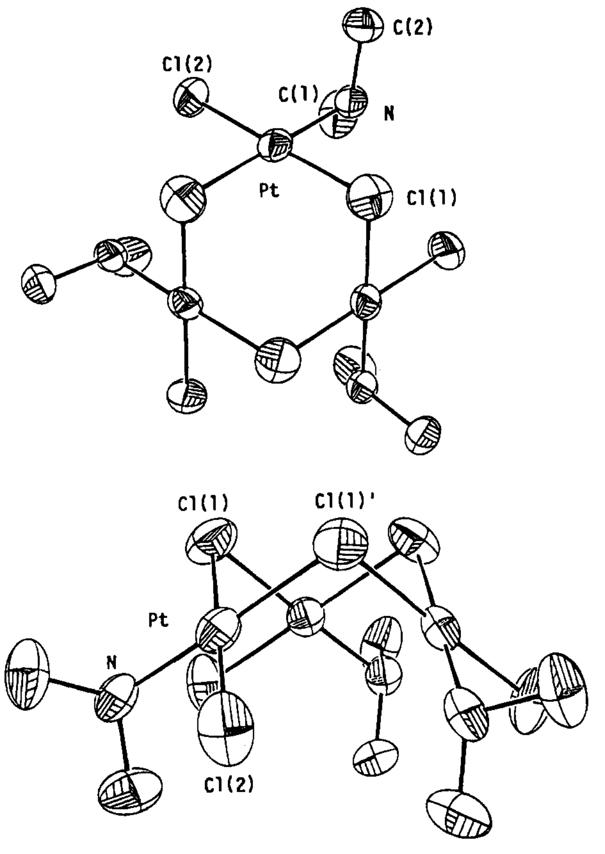


Figure 2. Structure of the complex $[Pt((CH_3)_2NH)Cl_2]_3$ with the atomic numbering.

Table 4. Bonds Distances (Å) and Angles (deg)

Pt—Cl(1)	2.319(3)	Pt—N	2.046(9)
Pt—Cl(1')	2.332(3)	N—C(1)	1.494(15)
Pt—Cl(2)	2.274(3)	N—C(2)	1.470(12)
Cl(1)—Pt—Cl(2)	179.1(1)	Pt—N—C(1)	114.3(7)
Cl(1)—Pt—N	88.2(3)	Pt—N—C(2)	112.9(7)
Cl(1)—Pt—Cl(1)'	90.5(1)	Pt—Cl(1)—Pt'	93.9(2)
Cl(2)—Pt—N	92.3(3)	C(1)—N—C(2)	110.8(9)
Cl(1)'—Pt—N	178.6(3)	Cl(2)—Pt—Cl(1)'	89.1(1)

larger than the one for chloro ligands. But this small lengthening might also be due to hydrogen bonding. In these structures, the *trans* chloro ligand is usually much more involved in the hydrogen bonding system than are the *cis* chloro ligands. In the chloro-bridged trimer, Cl(1) is not involved in hydrogen bonds.

The Pt—N bond length is 2.046(9) Å, close to the values found in other Pt—amine complexes. The dimethylamine ligand is normal with N—C(1) = 1.49(1) and N—C(2) = 1.47(1) Å. The Pt—N—C angles are slightly larger (114.3(7) and 112.9(7)°) than is the tetrahedral value as observed in other Pt—amine compounds.[14,31,39–41] The C(1)—N—C(2) angle is normal (110.8(9)°).

The conformation of the molecule is similar to those of the hydroxo-bridged trimers $[(Pt(\mu\text{-}OH)(NH_3)_2)_3]_2(SO_4)_3{\cdot}6H_2O$[15] and $[(Pt(\mu\text{-}OH)(\textit{trans}\text{-}1,2\text{-diaminocyclohexane}))_3]_2(SO_4)_3{\cdot}14H_2O$.[17] The average value for the torsion angles (Table 5) in the Pt_3Cl_3 ring of the $[Pt((CH_3)_2NH)Cl_2]_3$ complex is 88.2(1)°, not very far from the values found for the Pt_3O_3 rings in the above complexes, 80.6 and 83.6°, respectively. The Pt_3Cl_3 ring assumes a "crown" conformation with C_3 symmetry. All the bridging chlorides lie on the same side of the three platinum plane as seen in Figure 2, with a distance between the two planes of 1.300(3) Å. This is in contrast to the NH_3 hydroxo-bridged trimer with nitrate anions,[16] where one oxygen atom of the Pt_3O_3 ring is almost on the plane of the three platinum atoms (0.02 Å), while the two other oxygen atoms lie on each side of this plane, at 1.16 and 1.02 Å, respectively, leading to a pseudo-2-fold axis symmetry.

Table 5. Torsion Angles (deg) for the $[Pt((CH_3)_2NH)Cl_2]_3$ Complex[a]

Pt^i—Cl^i—Pt—Cl	−88.3(1)	Cl(2)—Pt—N—C(1)	−49.0(8)
Cl^i—Pt—Cl—$Pt(1)^{ii}$	88.0(1)	Cl(1)—Pt—N—C(2)	−100.3(7)
Cl(1)—Pt—N—C(1)	131.8(7)	Cl(2)—Pt—N—C(2)	78.9(7)

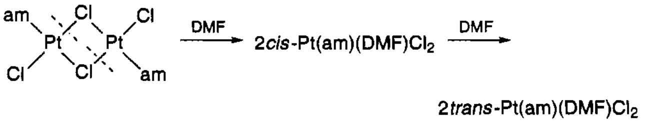
[a] Key: (i) $1 - y, x - y, z$; (ii) $1 + y - x, 1 - x, z$.

A stereoscopic view of the packing of the molecules in the unit cell is shown in Figure 3. It consists of layers of molecules parallel to the *ab* plane. Each layer contains on one side the chloro-bridged atoms and on the other side the amine and terminal chloro ligands, with the Pt atoms in the center. There are two such layers per unit cell, and the molecules are superimposed on top of each other with a 60° rotation. Furthermore each layer is reversed to form pairs (with the amine and terminal chloro ligands facing each other) which are bonded by H bonds between the amine and the terminal chloro ligands, increasing the stability of the crystal. The distance N···Cl(2) = 3.417(9) Å and the angles Pt—N···Cl(2) (93.9(3)°), C(1)—N···Cl(2) (87.1(6)°), and C(2)—N···Cl(2) (137.6(6)°) are reasonable.

NMR Spectra. The chloro-bridged platinum oligomers have been studied by proton- and ^{195}Pt-NMR spectroscopy. The δ(Pt) chemical shifts obtained in different solvents are presented in Table 6. The reddish-orange compounds are soluble in common organic solvents such as acetone, DMF, and methylene chloride. Solubility in coordinating solvents is probably due to the cleavage of the platinum oligomers since these solvents can be considered as weak donor ligands for platinum. This is in fact the best way to obtain mixed-ligand complexes with weak donor atoms, as seen in the previous section for DMF.

For the chloro-bridged oligomeric complexes, the ^{195}Pt resonances are expected at very slightly lower fields than those for $[Pt(amine)Cl_3]^-$ derivatives, whose average value is about −1850 ppm in DMF.[31] The spectra of the oligomers dissolved in DMF showed two resonances between −1530 and −1574 ppm. These values are at much lower fields than expected for chloro-bridged species, and we suggest that the oligomers are cleaved by DMF to produce compounds of the type $Pt(amine)(DMF)Cl_2$, as discussed earlier in this publication.

All the ^{195}Pt-NMR spectra of the $[Pt(amine)Cl_2]_n$ complexes with primary amines show a first resonance around −1535 ppm in DMF. After a few minutes of data accumulation, a second signal appears around −1570 ppm which becomes the most intense resonance after 1 h. This second peak corresponds to the monomeric species *trans*-$Pt(amine)(DMF)Cl_2$ obtained from the cleavage of the oligomer with DMF, as discussed in the previous section. The first signal is believed to be the *cis* isomer which is produced first upon cleavage, because of the larger *trans* effect of the chloride ligand compared to that of an amine.



The secondary amine complex, $[Pt((CH_3)_2NH)Cl_2]_n$, does not react in the same way as do the primary amine complexes. The

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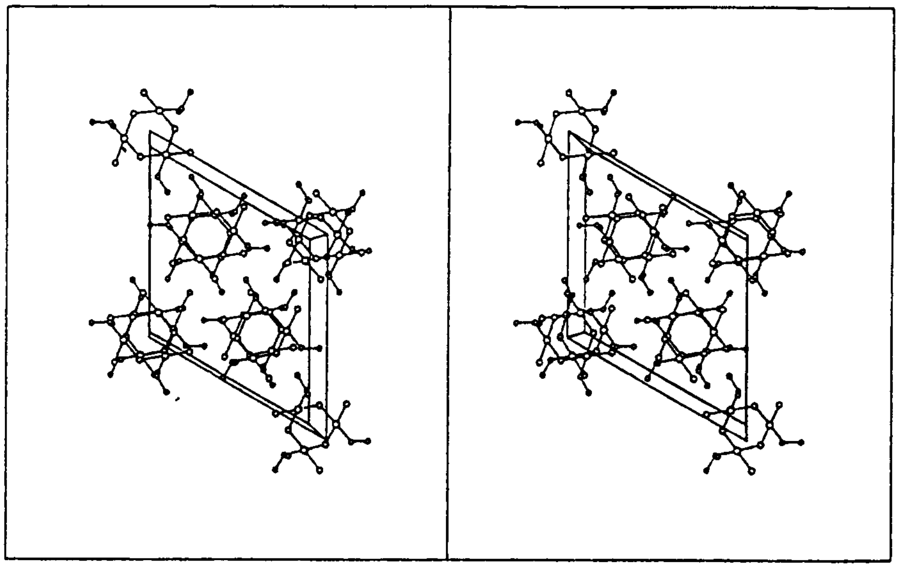

Figure 3. Stereoscopic view of the packing in the [Pt((CH$_3$)$_2$NH)Cl$_2$]$_3$ crystal (*a* axis vertical, down *c* axis).

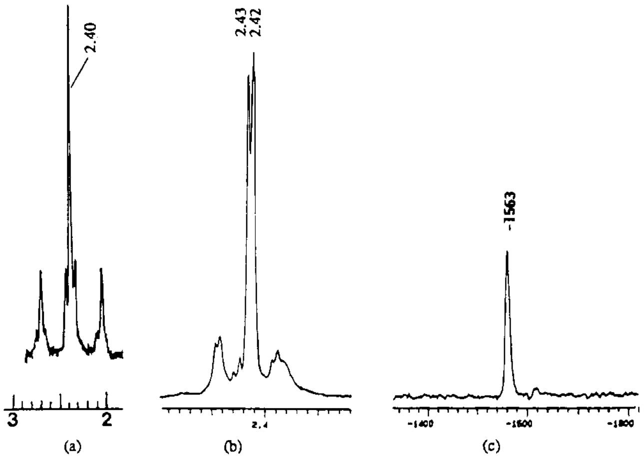

Figure 4. (a) ^{1}H-NMR spectrum of [Pt((CH$_3$)$_2$NH)Cl$_2$]$_n$ in D$_2$O measured on a 60-MHz spectrometer, (b) same sample on a 300-MHz spectrometer, and (c) corresponding ^{195}Pt-NMR spectrum (values in ppm).

^{195}Pt-NMR spectrum of the [Pt((CH$_3$)$_2$NH)Cl$_2$]$_n$ complex shows two resonances at −1513 and −1553 ppm in DMF. The first peak to appear is the higher frequency one (−1553 ppm), while the lower frequency one corresponds to the peak (−1515 ppm) obtained by reaction of this oligomer with DMF, as discussed already. We suggest that the first compound is *cis*-Pt((CH$_3$)$_2$NH)(DMF)Cl$_2$, while the second is the corresponding *trans* isomer.

All the oligomers are insoluble in aqueous acidic solution since they are isolated as precipitates from perchloric acid solution. When a water suspension containing the oligomeric species [Pt((CH$_3$)$_2$NH)Cl$_2$]$_n$ is agitated for several days, it dissolves sufficiently for its proton and platinum-NMR spectra to be measured (Figure 4). The other complexes with primary amine ligands are not soluble under the same conditions. The ^{1}H-NMR spectrum of [Pt((CH$_3$)$_2$NH)Cl$_2$]$_n$, recorded on a 60-MHz spectrometry, shows a triplet plus a doublet of triplets centered at 2.40 ppm with a coupling constant ^3J(Pt—H) = 39 Hz. The central triplet is probably a superposition of a singlet and a doublet. The singlet observed at 2.40 ppm is caused by the resonance of the −CH$_3$ groups in the bonded deuterated amine [(CH$_3$)$_2$ND], while the doublet centered at 2.41 ppm corresponds to the methyl groups of the bonded nondeuterated dimethylamine ligand. The latter protons are coupled with the hydrogen of the nitrogen atom with a coupling constant ^3J(NH—CH) = 6 Hz. In deuterated water, the amine proton is partly exchanged by the deuterium of water and the signal of the deuterated amine is observed at slightly higher field (2.40 ppm) that is the signal of the nondeuterated amine (2.41 ppm). In the spectrum of the same sample taken on a 300-MHz spectrometer, the singlet observed on the 60-MHz spectrometer appears as two peaks (slightly enlarged) of almost equal intensity at 2.42 and 2.43 ppm with a coupling constant ^3J(Pt—H) = 38 Hz. The corresponding ^{195}Pt-NMR spectrum shows one main resonance at −1563 ppm. A very small peak (<5%) can also be detected near −1620 ppm. Several possibilities were examined in order to interpret these spectra. The high-field ^{1}H-NMR spectrum could be explained by the presence of a mixture of *cis*- and *trans*-Pt((CH$_3$)$_2$NH)(D$_2$O)Cl$_2$ monomers, if the two isomers are present almost in equal amounts. But this is not confirmed by Pt-NMR, unless the two species would appear at the same chemical shifts. The presence of a *trans* dimer partially cleaved by water, ((CH$_3$)$_2$NH)Cl(D$_2$O)Pt(μ-Cl)Pt(D$_2$O)Cl((CH$_3$)$_2$NH), would give a similar spectrum, since the methyl groups of the two dimethylamine ligands are in a different environment, resulting in two different signals of equal intensity. The two peaks would not be resolved at low field. Partially cleaved species of the type (am)$_2$Pt(H$_2$O)(μ-OH)(Pt(H$_2$O)(am)$_2$ are stable in solution and have been reported with other amines.[42-44] Another possibility is the chloro- and hydroxo-bridged dimer ((CH$_3$)$_2$NH)ClPt(μ-Cl)(μ-OH)Pt((CH$_3$)$_2$NH)Cl (*cis* or *trans*), which would show only one ^{195}Pt resonance, but seems to us less probable because the pH is not basic. Other partially-cleaved species like [(CH$_3$)$_2$NH]Cl(D$_2$O)Pt(μ-Cl)PtCl$_2$[(CH$_3$)$_2$NH] would give two very different Pt signals (of equal intensity) and therefore were eliminated. If we assume that the main species observed at −1563 ppm is [(CH$_3$)$_2$NH]Cl(D$_2$O)Pt(μ-Cl)Pt(D$_2$O)Cl[(CH$_3$)$_2$NH], the small peak at −1620 ppm could be caused by the presence of a small quantity of Pt[(CH$_3$)$_2$NH](D$_2$O)Cl$_2$.

Although there are a few complexes with the acetone ligand

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Table 6. ^{195}Pt Resonances (±5 ppm) for $[Pt(amine)Cl_2]_n$ Complexes in Different Solvents

amine	DMF	acetone	CH_2Cl_2	D_2O
CH_3NH_2	−1537 (42%), −1560 (58%)	−1622		
$C_2H_5NH_2$	−1532 (47%), −1568 (53%)		−1713	
cba	−1531 (35%), −1574 (65%)	−1601 (53%), −1630 (47%)	−1711	
cpa	−1530 (18%), −1563 (82%)	−1584 (66%), −1623 (34%)	−1700	
$(CH_3)_2NH$ (powder)	−1513 (30%), −1553 (70%)	−1570	−1703 (27%), −1570 (73%)	−1563 (>95), −1620 (<5)
$(CH_3)_2NH$ (cryst)	−1514 (31%), −1553 (69%)	−1567	−1700 (85%), −1565 (15%)	

reported in the literature,[45] the isolation of such Pt compounds has yet to be confirmed. Our trials were also not successful. Platinum(II) is a soft metal and does not form strong bonds with O-donor ligands, unless they are deprotonated. Acetone can probably act as a ligand for platinum(II) in solution. This ligand will be easily lost by evaporation of the solvent. The ^{195}Pt-NMR spectra of the oligomers measured in acetone have shown that the compounds are cleaved to produce complexes of the type $Pt(amine)(solvent)Cl_2$. Acetone always contains a small quantity of water which is probably a better ligand for platinum than is acetone. The oligomers of cyclobutylamine and cyclopentylamine showed two resonances when dissolved in acetone. These could be caused by the two isomers of $Pt(amine)(acetone)Cl_2$ (the higher field signals would be produced by the *trans* isomers) or only one isomer would be produced and the second peak would be caused by $Pt(amine)(D_2O)Cl_2$. For the methylamine and dimethylamine oliogmers, only one resonance was observed. These could be assigned to the acetone complexes. Some aqua species might also be present, but the signals are too close to those of the acetone species to be observed separately.

In dichloromethane, the $(CH_3)_2NH$ oligomer showed two signals. The first peak at −1570 ppm is close to the cleaved product in D_2O and in acetone discussed above, while the second resonance at −1700 ppm is assigned to the chloro-bridged oligomer, probably the trimer. In noncoordinating solvents like CH_2Cl_2, it is believed that the oligomeric species are favored, even in the presence of a small quantities of weak nucleophiles as shown by similar studies done in our laboratory.[8,9] Red crystals obtained from a dichloromethane solution of Pt(2,6-lutidine)(DMF)Cl_2, after standing at room temperature for several weeks, were shown, by X-ray diffraction, to contain the chloro-bridged *trans* dimer [Pt(2,6-lutidine)$Cl_2]_2$.[9] We believe that, in the solid state at room temperature, the chloro-bridged oligomeric species of $(CH_3)_2NH$ are mostly dimers, while slight heating results in trimer formation. The orange powder obtained from the reaction of $K[Pt((CH_3)_2NH)Cl_3]$ with perchloric acid was dissolved in CH_2Cl_2, and the ^{195}Pt-NMR spectrum was measured. Two signals were observed, the most intense at −1570 (73%) and a weaker one (27%) at −1703 ppm. This solution was heated with hot water for 10 min, and the ^{195}Pt-NMR spectrum showed the same two resonances, but now the signal at −1700 ppm is much more intense (85%). The NMR spectra of the red crystals isolated from a heated (40 °C) dichloromethane solution for the purposes of X-ray diffraction and picked one by one under a microscope measured in CD_2Cl_2 showed the same spectra as the heated sample. Since the results of the structure analysis have shown a cyclic chloro-bridged trimer, we believe that the trimeric species is favored under such conditions and, accordingly, the most intense peak around −1700 ppm has been assigned to the cyclic chloro-bridged trimeric species. The ^{1}H-NMR spectrum of the red crystals (containing mostly trimers) showed a doublet for the $(CH_3)_2NH$ ligand centered at 2.73 ppm with its coupling with platinum $^3J(Pt-H)$ = 42 Hz. Two other weak resonances centered at 2.51 ppm are also observed. The integration is 88/12 for the proton spectra, in good agreement with the integration of the corresponding platinum resonances for the same solution (85/15). The peak at −1570 ppm could be assigned to some hydrolyzed complex, resulting from the cleavage of the dimeric species, which would be much more reactive toward cleavage than the trimeric species. The proton-NMR spectrum of dichloromethane has shown the presence of a small quantity of water which could cleave the dimeric species to produce the aqua complex as observed when the $(CH_3)_2NH$ oligomers are cleaved by water. This also concurs with the fact that when the dimers are rearranged to trimers in dichloromethane, there must be some cleavage of one of the bridged bonds. In the solid state, the $(CH_3)_2NH$ oligomers would contain trimers and dimers, and in CH_2Cl_2 solution only the dimers would be cleaved, because of the significantly greater strain in the four-membered-ring dimer. For the primary amine oligomers, only one resonance (assigned to the cyclic oligomers) was observed in the −1710 ppm region. No hydrolyzed species were observed with these ligands, since the oligomers are much more insoluble in water than is the dimethylamine comlex, as mentioned earlier. The spectrum of $[Pt((CH_3)NH_2)Cl_2]_n$ was not measured because the complex is not sufficiently soluble in CH_2Cl_2. Additional evidence for the oligomeric nature of these species is afforded by the ^{195}Pt-NMR spectra of the $[Pt(cba)Cl_2]_n$ complex in CD_2Cl_2. This spectrum exhibits only one resonance at −1711 ppm. When one drop of DMF is added and the mixture well mixed, the peak disappears and a new resonance appears at −1587 ppm, which is assigned to Pt(cba)(DMF)Cl_2, taking into account a small high-field shift for the effect of changing the solvent from DMF to CH_2Cl_2.

Infrared Spectra. The IR spectra of the $[Pt(amine)Cl_2]_n$ oligomers are very simple and suggest a high symmetry. For the chloro dimers, the synthesis usually gives the *trans* isomers, since the *trans* effect of the chloride is greater than the *trans* effect of the amine. The skeleton symmetry for a complex *trans*-$Pt_2am_2Cl_4$ is C_{2h} (C_{2v} for a *cis* isomer), and group theory predicts three $\nu(Pt-Cl)$ ($3B_u$ modes) vibrations in the IR. There are one $\nu(Pt-Cl)_t$ (t = terminal) and two $\nu(Pt-Cl)_b$ (bridging bonds). From the latter two, there are one $\nu(Pt-Cl)_b$ *trans* to the chloride, at a higher frequency, and one $\nu(Pt-Cl)_b$ *trans* to the amine group at a lower frequency.[46] The spectra of the complexes (Experimental Section) have shown one $\nu(Pt-Cl)_t$ vibration between 340 and 350 cm^{-1}, one $\nu(Pt-Cl)_b$ vibration *trans* to the chloride ligand between 308 and 325 cm^{-1}, and one $\nu(Pt-Cl)_b$ vibration *trans* to the amine ligand between 291 and 305 cm^{-1}. The IR spectra of the amine complexes showed the expected pattern for a *trans* isomer, but the bands are quite large and show some shoulders. The $\nu(NH)$ vibrations appear between 3105 and 3276 cm^{-1}, and the $\delta(NH_2)$ vibration appears between 1560 and 1571 cm^{-1}.

The IR spectrum of the powdered complex with $(CH_3)_2NH$ (which we will assume to contain mainly dimers) is quite different from that of the red crystals, containing mainly trimeric

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Table 7. ^{195}Pt Resonances for [Pt(amine)I$_2$]$_n$ Complexes in Different Solvents[a]

amine	DMF	CH$_2$Cl$_2$
CH$_3$NH$_2$	−3984, −3999	
C$_2$H$_5$NH$_2$	−3996	−4032
cba	−4014, −4030	−4046
cpa	−3992, −4006	−4022
(CH$_3$)$_2$NH	−3905, −3934	−3924, −3946
	−3901,[b] −3929[b]	−3920,[c] −3942[c]
1-adamantanamine	−4068, −4084	
2-adamantanamine	−4030	

[a] Measured on a Varian 300 MHz spectrometer. [b] Measured in acetone. [c] Measured on a Bruker 400 MHz instrument to confirm the chemical shifts.

species. The ν(N—H) and ν(Pt—Cl) vibrations are shifted to lower frequencies, and the band shapes are different. The ν(Pt—Cl)$_t$ band is stronger in the trimer spectrum, while the ν(Pt—Cl)$_b$ vibration *trans* to the chloride ligand is stronger in the dimer spectrum. Some additional bands are also observed in the spectrum of the trimer, indicating a change in molecular structure. These weak-to-medium intensity bands are located at 525, 1037, 1392, 1417, 1430, 1441, 1451, 2999, and 3022 cm^{-1}.

[Pt(amine)I$_2$]$_n$. The ^{195}Pt-NMR spectra of several iodo-bridged oligomers were measured in DMF and in CH$_2$Cl$_2$, and the results are presented in Table 7. The observed chemical shifts vary from −3901 to −4084 ppm. Since the four-membered ring in iodo-bridged dimers is less strained than in the chloro compounds due to the longer Pt—I bonds, the chemical shifts of these species are expected to be closer to those observed for [Pt(amine)I$_3$]$^-$ complexes. The value reported for NR$_4$[Pt{(CH$_3$)$_2$NH}I$_3$] (R = Pr^n or Bu^n) is −4004 ppm in CH$_2$Cl$_2$,[47] while the NH$_3$ iodo-bridged dimer was reported at −3995 ppm in DMF,[48] which confirm our assignments. One or two species were observed for the oligomers. These are assigned to different isomers (e.g., *cis* or *trans* dimers) or different oligomers. Work in this area is in progress.

Attempts to isolate species of the type Pt(amine)(DMF)I$_2$ by reaction of [Pt(amine)I$_2$]$_n$ with DMF were not successful. A DMF solution containing [Pt(amine)I$_2$]$_n$ was heated for 3 h, and then the DMF was evaporated off. The IR spectrum of the material isolated was identical to those of the oligomeric species. No C═O band was detected indicating the absence of bonded DMF. When the solutions were heated overnight, decomposition occurred. The great stability of the iodo-bridged oligomers in DMF (compared to the chloro-bridged oligomers) is quite surprising. We were unable to grow crystals suitable for X-ray diffraction. This study is being continued.

Acknowledgment. The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support and to the Ministère de l'Education (Québec) for a Ph.D. scholarship (M.D.).

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated H coordinates, and the equation and deviations from the weighted best plane (2 pages). Ordering information is given on any current masthead page.

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