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

by

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Abstract

Cis-$Pt(NH_3)_2Cl_2$ is now well established as an antitumor drug. There are still difficulties in its widespread administration, however, because of its numerous side effects and toxicity. Replacement of the NH_3 groups by amines more compatible to the human system might possibly be a way of surmounting these problems. One such amine is 1–adamantanamine which has been demonstrated to exibit both antiviral and anticancer activity.

New platinum(II) complexes of the type $[Pt(A')Cl_3]^-$, $Pt(A)(A')Cl_2$ and $Pt(A)(A')I_2$, where A = methylamine, ethylamine, cyclobutylamine and cyclopentylamine and A' = 1-adamantanamine, 2-adamantanamine and 1-methyladamantanamine have been synthesized. The structure of $[2\text{-adamH}][Pt(EtNH_2)Cl_3]$ complex has been determined by X-ray diffraction.

The synthesis of platinum(II) complexes containing the dimethylformamide ligand (DMF) was undertaken to study the reactivity of DMF with chloro-bridged dimers and trimers. When platinum complexes of the type $[Pt(A)Cl_3]^-$ were stirred in perchloric acid, oligomeric species were formed which can be cleaved by O-donor ligands such as DMF, water or acetone. A series of complexes of the type $[Pt(A)Cl_2]_n$ and $[Pt(A)(DMF)Cl_2]$, where A = methylamine, ethylamine, cyclobutylamine, cyclopentylamine, dimethylamine and DMF has been synthesized. The crystal structure of a cyclic trimer, cyclo-tri-μ-chloro-tri-[chloro(dimethylamine)platinum(II)] was determined. All the compounds have been characterized by infrared and Raman spectroscopy, by ^{195}Pt- and ^{1}H-NMR spectroscopy (when soluble) and occasionally by X-ray diffraction when suitable crystals could be obtained.

Résumé

Cis-$Pt(NH_3)_2Cl_2$ est actuellement le médicament le plus utilisé en chimiothérapie. Cependant, son administration à grande échelle est limitée par ses nombreux effets secondaires et par sa toxicité. Le remplacement des groupements NH_3 par des amines plus compatibles avec le corps humain pourrait être un moyen de surmonter ces problèmes. Une de ces amines est l'adamantanamine-1, qui possède un activité antivirale en plus d'une activité antitumorale.

De nouveaux complexes de platine du type $[Pt(A')Cl_3]^-$, $Pt(A)(A')Cl_2$ et $Pt(A)(A')I_2$, où A = méthylamine, éthylamine, cyclobutylamine et cyclopentylamine et A' = 1-adamantanamine, 2-adamantanamine et 1-méthyladamantanamine ont été synthétisés. La majorité de ces complexes n'a pas encore été rapportée dans la littérature. La structure du complexe 2-adamH$[Pt(EtNH_2)Cl_3]$ a été déterminée par diffraction des rayons-X.

La synthèse de complexes de platine avec le ligand diméthylformamide (DMF) a été entreprise en vue d'étudier la réaction du diméthylformamide avec les dimères ou trimères à ponts chlorés. Lorsque les complexes de platine du type $[Pt(A)Cl_3]^-$ sont mis en présence d'acide perchlorique, ils forment des oligomères qui peuvent s'ouvrir en présence d'un ligand oxygéné, tel le DMF, l'eau ou l'acétone. Une série de complexes du type $[Pt(A)Cl_2]_n$ et $[Pt(A)(DMF)Cl_2]$, où A = méthylamine, éthylamine, cyclobutylamine, cyclopentylamine et diméthylamine a été synthétisée. La diffraction des rayons-X a mis en évidence une espèce trimère à ponts chlorés avec la diméthylamine. Tous les produits ont été caractérisés par spectroscopie infrarouge et Raman, par résonance magnétique nucléaire du ^{195}Pt et ^{1}H (lorsque solubles) et de temps en temps par diffraction des rayons-X lorsque des cristaux adéquats ont pu être obtenus.

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List of Symbols and Abbreviations

A	amine ligand
A'	amine ligand different from A
Å	angstrom (1×10^{-10} m)
adam	adamantanamine derivative
1-adam	1-adamantanamine
2-adam	2-adamantanamine
2-adamH	2-adamantylammonium ion
asym	asymmetric
B_o	applied magnetic field
CBA	cyclobutylamine
CBDCA	1,1-cyclobutanedicarboxylate
CPA	cyclopentylamine
δ	deformation vibration
δ(Pt)	platinum chemical shift
d	distance between 2 planes in a unit cell
D_c	calculated density
DMF	N, N-dimethylformamide
DMNH	dimethylamine
DMSO	dimethylsulfoxide
DNA	deoxyribonucleic acid
E	energy
$EtNH_2$	ethylamine
h	Planck constant (6.626×10^{-34} Js)

I	angular momentum
I_{hkl}	intensity of reflection hkl
IR	infrared
K_a	acidity constant
L	ligand but not amine ligand
λ	lambda (wavelength)
LD_{50}	lethal dose which kills 50% of the animals
1- Madam	1- methyladamantanamine
$MeNH_2$	methylamine
mg/m^{-2}	dosage given as milligram per square meter surface area
MHz	megahertz
μ	reduced mass or magnetic moment
μ_D	dipole moment
μm	micron
mM	millimolar
M_w	molecular weight
mW	milliwatt
$\mathcal{N}$	Avogadro number
nm	nanometer (1×10^{-9} m)
ν	frequency or stretching vibration
NMe_4	tetramethylammonium
NMR	nuclear magnetic resonance
pK_a	- log K_a
py	pyridine or substituted pyridine ligand
R	residual index

S	solvent molecule
$\sigma(I)$	standard deviation of intensity data
SW	spectral window
sym	symmetric
TI	therapeutic index
TO	transmittor offset
tu	thiourea [$S = C(NH_2)_2$]
U_{eq}	equivalent thermal parameter
V	volume of a unit cell
wR	weighted residual index
X	monodentate anionic ligand
Y	entering ligand
Z	number of molecules in a unit cell

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CHAPTER 1

Introduction

1.1 Platinum Chemistry

Platinum is a noble metal which exists naturally in association with small traces of iridium, osmium, palladium, rhodium and ruthenium. This metal has numerous applications, e.g., in catalysis, jewellery and cancer chemotherapy. Its ground state electronic structure is $[Xe]4f^{14}5d^{9}6s^{1}$. Although platinum exibits oxidation states ranging from 0 to 6, the divalent state is the most common in aqueous systems. Platinum(II) has the electronic configuration $[Xe]4f^{14}5d^{8}$. The most common type of complex involving a d^8 configuration has coordination number 4 with square-planar geometry resulting in low-spin diamagnetic complexes. In term of crystal field theory, the d^8 electrons occupy the low-energy d_{yz}, d_{xz}, d_z2 and d_{xy} orbitals while the high-energy $d_x2\text{-}y2$ orbital remains unoccupied (1, 2). The crystal field stabilization energy is thus normally high, as shown by examination of the relative energies of the d orbitals in different coordination environments given in Figure 1 (2).

Square-planar platinum(II) complexes are relatively kinetically inert and they form stable compounds with both σ- and π-electron donating ligands. The ligands are generally anionic or neutral and the relative affinity of ligands for Pt(II) follows the trend $CN^- > NH_3 \approx RNH_2 \approx OH^- > I^- > SCN^- > Br^- > Cl^- >> F^- \approx H_2O \approx MeOH$. Platinum(II) shows a preference for nitrogen (in amines and NO_2^-), halides, cyanide and heavy donor atoms (e.g., P, As, S, Se) and relatively low affinity for fluoride and oxygen donating ligands unless it is deprotonated as in the carboxylate anion. Ammonium or alkali metal (Na or K) salts of the halide anions $[PtX_4]^{2-}$ are common starting materials for the synthesis of Pt(II) complexes. The red $[PtCl_4]^{2-}$ ion is made by reduction of $[PtCl_6]^{4-}$ with oxalic acid (1).

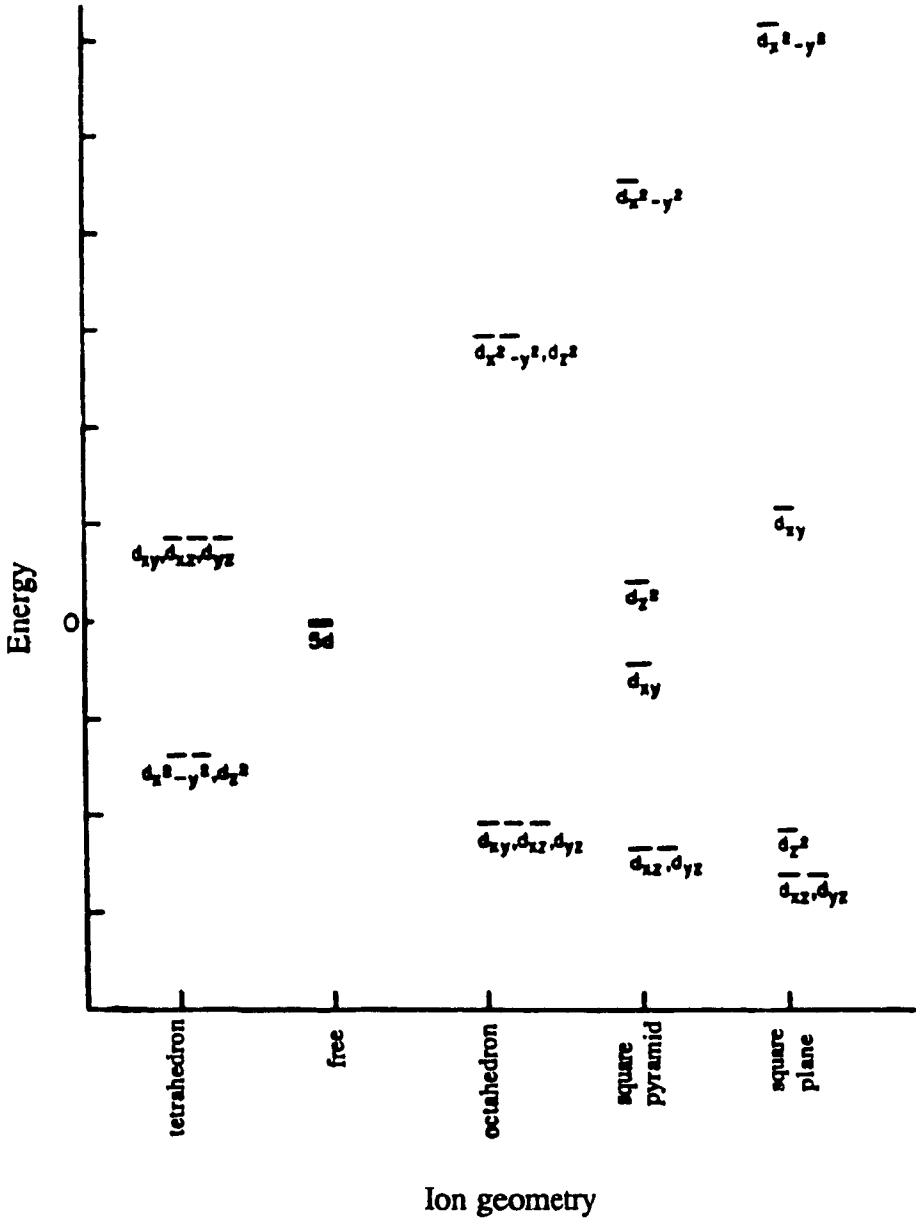


Figure 1. Relative energies of the d orbitals in differer t coordination environments (adapted from ref. 2).

1.2 Antitumor Properties of Platinum Complexes

The antitumor activity of platinum(II) complexes was discovered accidentally by Rosenberg and his collaborators over 20 years ago (3, 4). Since that time, efforts are being made by many research groups to understand the inorganic and biological properties of platinum complexes that exibit antitumor properties.

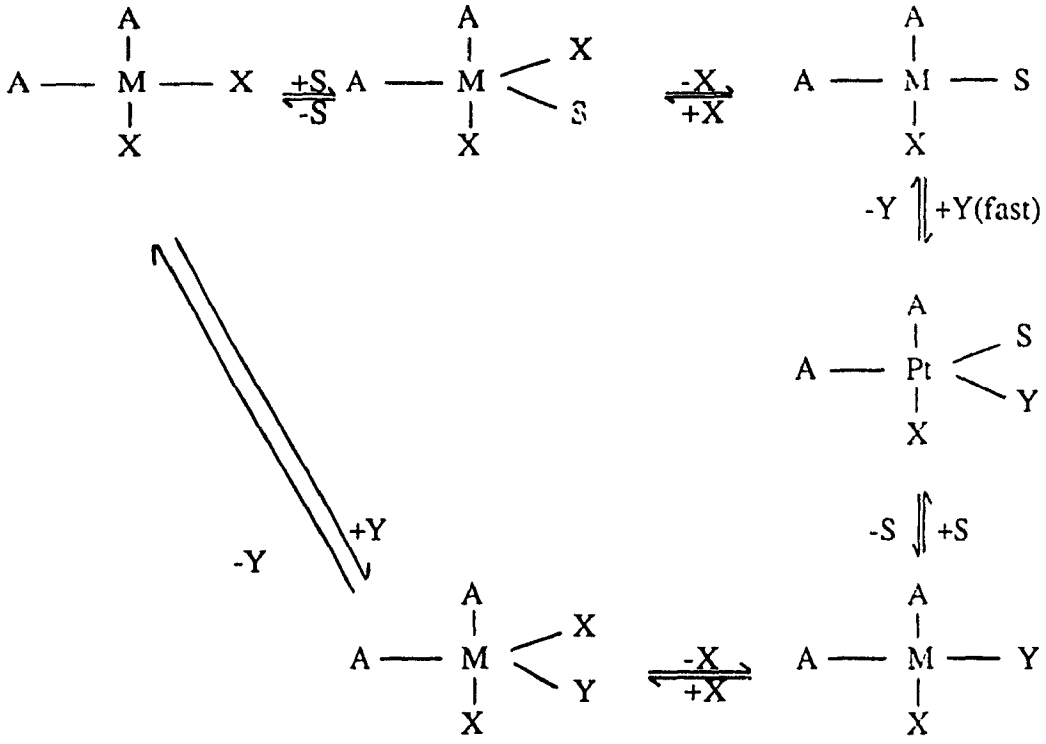
Antitumor activity usually requires neutral square-planar platinum complexes with two leaving groups in a *cis* configuration, PtA_2X_2, where A is NH_3 or an amine ligand. Even though both *cis* and *trans* isomers inhibit replication, very few case of activity in a *trans* compound has been reported (5, 6). The leaving ability of the X ligands is important and two main classes have been found successful: monodentate anionic ligands, mainly Cl^- , also Br^- to a lesser extent and bidentate carboxylate ligands (e.g., oxalate, malonate). As an example, the 1,1-cyclobutanedicarboxylato analogue, $Pt(CBDCA)(NH_3)_2$ shows a similar activity to "*cisplatin*" (% T/C = 205) but has a better solubility (17 mg/ml compared to 1 mg/ml for *cisplatin*) and a lower toxicity (LD_{50} = 130 mg/kg compared to 13 mg/kg for *cisplatin*) (7, 8). The % T/C is the mean survival time of treated mice over the mean survival time of untreated mice (significant when $\geq$ 150 %) (9, 10). The lethal dose, LD_{50} , is the dose required to kill 50% of the animal population.

The geometry of the amine ligands (A) is also important in the antitumor property. Lower alkyl substitution of the H atoms in NH_3 seems to diminish activity against the tumour, while heterocyclic and alicyclic amines show an increase in the activity, mostly due to lowered toxicities. The toxicity of the ammine complexes is thought to be due to an increase in hydrogen bonding with the DNA (10-12).

The complex actually used in chemotherapy is *cisplatin*, *cis*-$Pt(NH_3)_2Cl_2$. It is active against two major types of malignant tumors: solid tumors (e.g., solid Sarcoma

180) and disseminated tumors (e.g., leukemia L1210). Comparison with other established and clinically-used drugs shows that *cisplatin* has a wider spectrum of activity than adriamicin or 5-fluorouracil (10). When these molecules are used in combination with *cisplatin*, a marked synergy is shown.

Platinum complexes of the type *cis*-$Pt(A)_2Cl_2$ can react with other ligands according to a bimolecular SN_2 substitution mechanism that follows a two-path mechanism in aqueous solution (11). The upper-half pathway involves the replacement of the X group by a solvent molecule (water) generating a solvated intermediate with trigonal bipyramidal geometry. The solvent molecule is then replaced by the incoming group Y. This process is entirely stereospecific: *cis* and *trans* starting materials lead, respectively, to *cis* and *trans* products.



where S = solvent, Y = entering ligand and X = leaving group

An alternative route, the lower-half pathway, involves the direct replacement of the leaving group by the nucleophile Y without participation of the solvent.

The most important factors that can influence the substitution reactions in platinum(II) complexes are the type of entering and leaving groups, the solvent effects and the *trans* and *cis* effects. The kinetic *trans* or *cis* effect differs from the thermodynamic *trans* and *cis* influence (1) which is the tendency of a ligand to weaken the bond *trans* or *cis* to itself in the metal complex. It reflects the ground state of a complex. The *trans* and *cis* effects involve a reaction transition state or intermediate, assumed to have a trigonal bipyramidal structure. The *trans* influence determines which ligand is less strongly bonded while the *trans* effect determines how quickly the designated ligand will depart. The order of *trans* labilizing ability is H_2O, OH^-, NH_3, amine, py < Cl^-, Br^- < SCN^-, I^-, NO_2^-, $C_6H_5^-$ < $SC(NH_2)_2$, CH_3^- < H^-, PR_3 < C_2H_4, CN^-, CO (1).

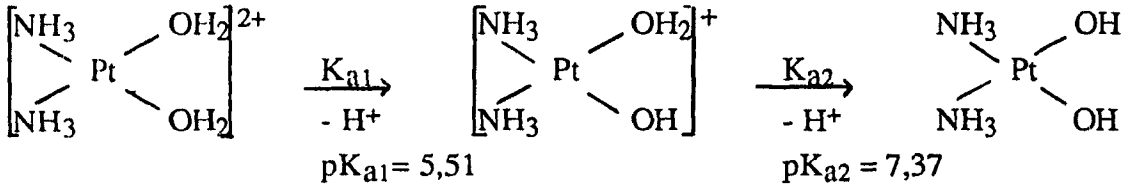
In aqueous solution, $Pt(NH_3)_2Cl_2$ complexes undergo hydrolysis to form a variety of hydrolyzed species. Both *cis* and *trans* isomers, in aqueous solution, exchange only two of their ligands, the chloride ions, for incoming groups such as H_2O, OH^-, RNH_2, RS^- or $RSCH_3$, which are abundant in a biological milieu (13). Aside from the formation of these hydrolyzed species, hydroxo-bridged oligomers are also formed at neutral pH when the chloride concentration is low and contributes to increase the toxicity of these species.

Patients are treated with intravenous injection of *cisplatin*. In the plasma, the neutral, dichloro form is maintained because the concentration of the chloride ions is sufficiently high enough (≈ 104 mM). After passive diffusion across the lipid membrane, the concentration of the chloride ion decreases sharply (to ≈ 4 mM) and promotes the hydrolysis of the labile chloride ligands (13). In aqueous solution, the following two equilibria are set up:

$$Pt(NH_3)_2Cl_2 + H_2O \longrightarrow [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$$

$$[Pt(NH_3)_2Cl(H_2O)]^+ + H_2O \longrightarrow [Pt(NH_3)_2(H_2O)_2]^{2+} + Cl^-$$

Aqua species, such as $[Pt(NH_3)_2(H_2O)_2]^{2+}$, can undergo loss of protons to form the monoaquamonohydroxo and dihydroxo species.



Thus, at physiologic pH, the active species is the monoaquamonohydroxo compound. These aquated species can subsequently react with a variety of intracellular components, including DNA. At this pH, hydroxo-bridged oligomers are also formed rapidly and these have been shown to be toxic.

The possible modes of binding by common drugs and metal complexes to DNA are intercalation, outer-sphere binding, inner-sphere binding and strand breakage (10). Platinum(II) complexes prefer inner-sphere binding and Figure 2 shows three possible models of the interaction between DNA and platinum complexes.

Cisplatin might inhibit DNA replication by chelation at N_7-O_6 site of guanine (Figure 2a), by formation of interstrand crosslink between adenine units (Figure 2b) or by formation of intrastrand crosslinks with two adjacent guanine bases (Figure 2c). Models a and b are not good models. It is believed now that the activity of *cisplatin* is due to the adducts formed by intrastrand crosslink with two guanosine nucleosides on the same strand (model c) which cannot be formed by the *trans* isomer due to stereochemical reasons (15, 16). This kind of binding seems to explain the difference between the

activity of the *cis* and *trans* isomers of $Pt(NH_3)_2Cl_2$. The local disruption caused by *cisplatin* is lethal for the cell because it inhibits replication and eludes the repair enzymes especially in cancer cells where the repair mechanism is repressed. The *trans* isomer, binding to purines (guanine and adenine) separated by one or two other bases, does not cause DNA to bend by 30-40° as does *cisplatin*. The inactivity of the *trans* isomer is explained by the fact that the lesions caused by the *trans* complex are more readily repaired than those caused by *cisplatin* (17).

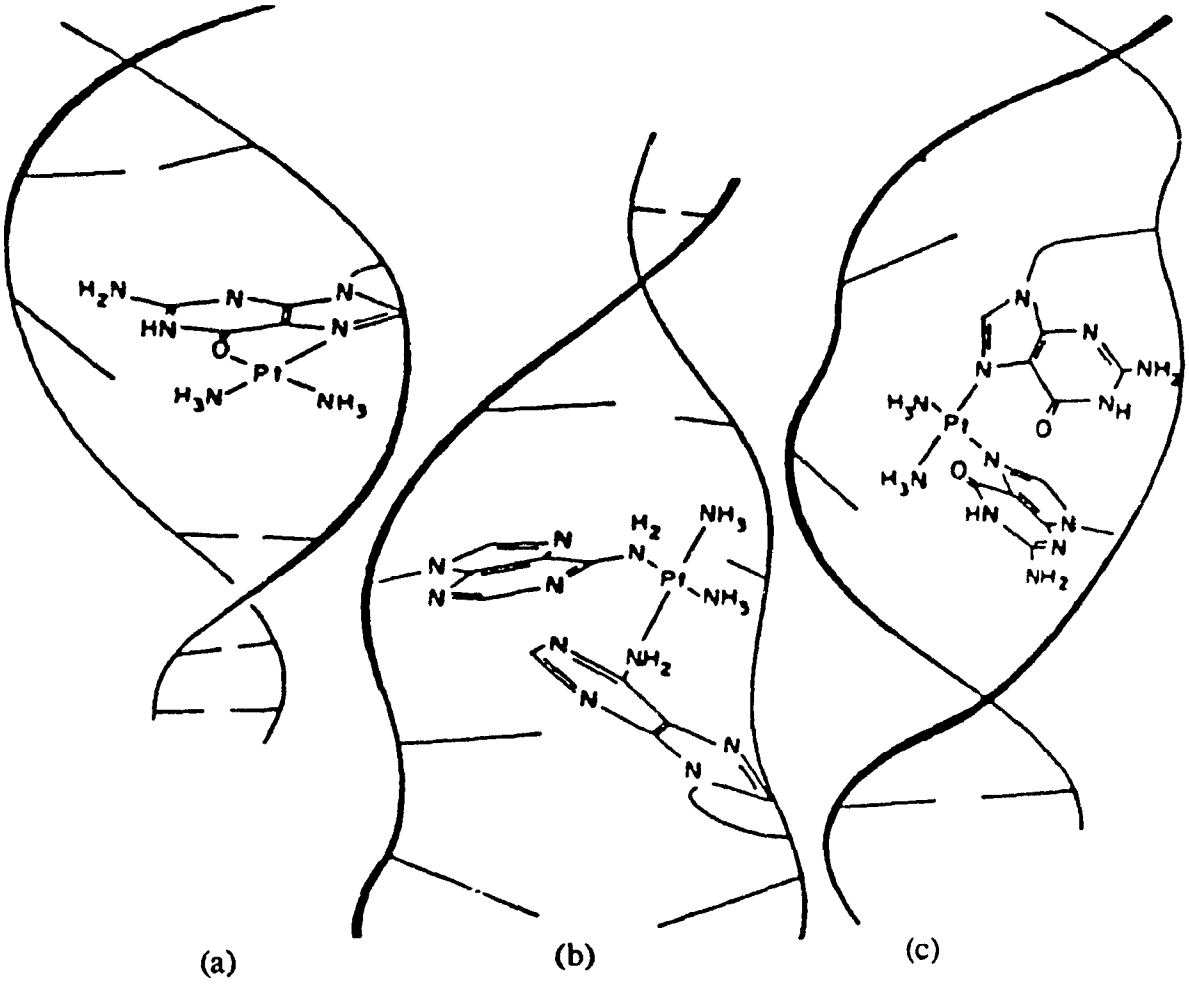


Figure 2. Possible models for the interaction of *cisplatin* with DNA (adapted from refs. 13, 14).

Platinum complexes are not selective. They react with normal cells as well as tumor cells, but the DNA repair mechanism is different in the two cases. In normal cells, the DNA repair mechanism is rapid enough and *cisplatin* lesions are repaired before replication, while in cancer cells, where there is a deficiency in this repair process, the lesions are not repaired before replication and this leads to the death of the cells. But, because platinum complexes are not selective, they cause serious side-effects.

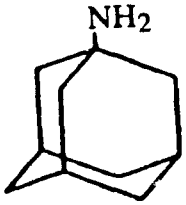
The most severe side-effect is due to damage to the kidney function, in particular to the proximal convoluted tubules. This damage causes a decrease in the filtering capacity of the kidney, thus an elevation of the blood-urea nitrogen and a decrease in the creatinine clearance. To limit the toxic effects of the metal in the kidney, the patients are treated at weekly intervals and/or with low doses in combination with other drugs more compatible with the body system. Other agents, all sulfur nucleophiles, such as sulfiram or thiourea, are also used in spite of the fact that they often reduce the activity of *cisplatin.* These compounds inhibit *cisplatin* nephrotoxicity probably because they react as competitive agents with the renal SH groups (10). Another way is to force or induce diuresis; the anticancer activity of platinum compounds does not decrease but the kidney toxicity is decreased. While doses around 50 mg/m^{-2} (dosage given as milligram per square meter surface area) are significantly toxic in normal conditions, with these techniques, doses around 120 mg/m^{-2} can be given.

Since the action of *cisplatin* is due to inhibition of DNA synthesis, tissues with a high rate of cellular proliferation like hair follicules are also affected (10). Nausea and vomiting are also severe, thus antiemetic drugs are used in treatment (11).

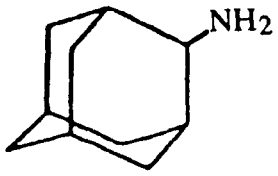
1.3 Complexes with Adamantanamine Derivatives

The studies with aminoadamantane derivatives are interesting for several reasons. The first reason is that adamantane itself and its derivatives have attracted some attention due to their globular structure and the possibility for them to form plastic crystalline phases (18-20). The second is the fact that homoconjugated $[NHN]^+$ cations in salts of 2:1 ratio, present an interesting type of strong hydrogen bonding (21, 22). The third one, which we are interested in, is their biological activity.

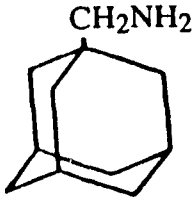
1-Adamantanamine is a stable, colorless, crystalline amine with a symmetrical cage structure. 2-Adamantanamine is a similar amine which is commercially available as its hydrochloride salt. 1-Methyladamantanamine is a colorless liquid.



1-adamantanamine



2-adamantanamine



1-methyladamantanamine

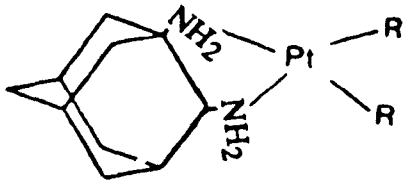
The direct inactivation of virus is not a major factor in the activity of the adamantane compounds in tissue culture (23). 1-Adamantanamine and 2-adamantanamine have been reported to inhibit the multiplication of certain strains of influenza virus by slowing or blocking the penetration of virus into the host cells (24). Studies by electron microscopy show that intact influenza particles are taken into the cells by phagocytosis. This engulfment process is prevented by NH_4Cl and various amines. The fact that this effect can be eliminated by a simple washing of the cells suggests that the compounds may interfere with the penetration process by causing ionic changes at the cell surface. In the presence of one of the compounds, the viruses do not penetrate the cell and thus remain susceptible to inactivation by antibodies (23). The failure of the agents to

block a virus of influenza type B, indicates that viruses of type A and B may penetrate the cells at different sites or differ in their tolerance of changes in ionic conditions (24). It seems that the pK_a of the nitrogen atom rather than its lipophilicity, is the major factor in the antiviral activity of this class of compounds.

Metal ions are important in many biological processes and, depending on their concentration, may either contribute towards the health of the organism or cause toxicity (25). Many research groups (25-28) have investigated the effects of metal complexes of several amines structurally related to 1-adamantanamine on virus replication. They found a considerable increase in antiviral activity when the metal complexes, rather than the uncomplexed ligands, were used. This situation may be due to enhanced lipid solubility of the metal complexes.

In addition of virucidal properties, the antitumor activities of adamantanamine derivatives have been determined by Ho, Hakala and Zakrsewski (29). Since 1-adamantanamine is also reported to have antitumor activity by itself against angiocarcinoma and pancreatic carcinoma (30), it would be interesting to examine the addition of adamantanamino ligands, which are polycyclic molecules, to platinum(II) to see if the antitumoral activity could be enhanced.

Platinum(II) complexes containing 1,2-diaminoadamantane of the general formula R_2Pt(1,2-diaminoadamantane) where R= halides, NO_3^-, OH^-, SO_4^{2-} have been synthesized by Shionogi and Co. Ltd (31). These compounds exibit antitumor activity, but have no antiviral properties. The complex 1,2-diaminoadamantane(dichloro)-platinum(II), is actually used in Japan for treatment of human cancers as is *cisplatin* (31).



Other complexes $Pt(1\text{-adam})_2Cl_2$ and $Pt(2\text{-adam})_2Cl_2$ have been synthesized by Braddock et al. (32) and they show no antitumor activity. According to these authors, the lack of anticancer properties is probably due to their low solubility but, as will be discussed later, we have some doubt about their method of synthesis.

1.4 Geometrical Isomerism in Platinum Complexes

Neutral square-planar complexes of the general formula MA_2X_2 where A is an amine and X is a halide, exhibit *cis-trans* isomerism and these isomers can be differentiated by the presence of a dipole moment (μ_D) in the *cis* isomer but none in the *trans* isomer (33).

Another way to distinguish *cis* and *trans* isomer in platinum complexes PtA_2X_2 is the Kurnakov test (33). The addition of **thiourea** (tu) to the *cis* complex results in complete replacement of the X ligands according to the following reaction:

$$cis\text{-}Pt(A)_2X_2 \xrightarrow{tu} [Pt(tu)_4]^{2+}$$

whereas for the *trans* isomer, the replacement stops after the two halide ions have been replaced since the *trans* amine ligands does not labilize each other:

$$trans\text{-}Pt(A)_2X_2 \xrightarrow{tu} [Pt(A)_2(tu)_2]^{2+}$$

1.5 Objectives of the Thesis Project

The main objective of the thesis was the synthesis of new platinum(II) complexes with adamantanamine derivatives. The characterization of these complexes was achieved by infrared and Raman spectroscopy, multinuclear NMR spectroscopy and X-Ray diffraction when suitable crystals were obtained. The different experimental methods are discussed in Chapter II.

Chapter III deals with the synthesis and characterization of the starting materials $[Pt(A)Cl_3]^-$ and $[Pt(adam)Cl_3]^-$.

Chapter IV presents the synthesis of the mixed-amine compounds of the type $Pt(A)(adam)X_2$ (X = Cl, I). In this chapter, a comparison is made with data for complexes already published in the literature. A few compounds screened for antitumor properties by the group of Braddock (32) lead us to the conclusion that there are some ambiguities in their published results.

Chapter V concerns the synthesis of complexes of the type $Pt(A)(DMF)Cl_2$ and $Pt(A)Cl_2]_n$, and cleavage of the choro-bridged oligomers $[Pt(A)Cl_2]_n$.

1.6 References

1. F. A. Cotton and G. Wilkinson. Advanced Inorganic Chemistry, 3rd ed. John Wiley and Sons, Inc. (1972).
2. M. E. Howe-Grant and S. J. Lippard. Metal Ions in Biological Systems, Ed. H. Sigel, Marcel Dekker Inc., N.Y. (1980).
3. B. Rosenberg, L. Van Camp and T. Krigas. Nature, **205**, 698 (1965).
4. B. Rosenberg, L. Van Camp, J. E. Trosko and H.V. Mansour. Nature, **222**, 385 (1969).
5. W. I. Sundquist, D. P. Bancroft and S. J. Lippard. J. Am. Chem.Soc. **112**, 1590 (1990).
6. C. A. Lepre, L. Chassot, C. E. Costello and S. J. Lippard. Biochem. **29**, 811 (1990).
7. F. H. Lee, R. Canetta, B. F. Isell and L. Lenaz. Cancer Treat. Rev. **10**, 39 (1983).
8. L. S. Hollis, M. M. Roberts and S. J. Lippard. Inorg. Chem. **22**, 3637 (1983).
9. J. P. Macquet and J. L. Butour. J. Nat. Cancer Inst. **70**(5), 899 (1983).
10. N. Farrell. Transition Metal Complexes as Drugs and Chemotherapeutic Agents. Kluwer Academic Publishers, Dordrecht, Boston, London (1989).
11. M.J. Cleare and P.C. Hydes. Metal Ions in Biological Systems, Ed. H. Sigel, Publ. Marcel Dekker Inc., N.Y. (1980).
12. M.J.Cleare. Platinum Coordination Complexes in Cancer Chemotherapy, T. A. Connors and J. J. Roberts Ed. N.Y.12 (1974).
13. A. L. Pinto and S. J. Lippard. Bioch.Bioph. Acta, **780**, 167 (1985).

14. J. P. Caradona and S. J. Lippard. Platinum coordination Compounds in Cancer Chemotherapy. M. P. Hacker, E. B. Douple and I.H. Krakoff eds. Martinus Nijhoff, Boston (1984).

15. A. L. Pinto, L. J. Naser, J. M. Essigmann and S. J. Lippard. J. Am. Chem. Soc. **108**, 7405 (1986).

16. S. E. Shermann, D. Gibson, A. H. J. Wang and S. J. Lippard. Science, **230**, 412 (1985).

17. S. J. Lippard. Platinum Metals Review, **34** (4), 213 (1990).

18. S. D. Hamann. High Temperature-High Pressure. **10**, 445 (1978).

19. P. J. Wu, J.L. Hsu and D. A. Dows. J. Chem. Phys. **51**, 2714 (1971).

20. P. D. Harvey, D. F. R. Gilson and I. S. Butler. Can. J. Chem. **65**, 1757 (1987).

21. E. Grech, Z. Malarski and L. Sobczyk. Pol. J. Chem. **52**, 131 (1978).

22. E. Grech, Z. Malarski and L. Sobczyk. J. Mol. Struct. **115**, 327 (1984).

23. W. L. Davies, R. R. Grunert, R. F. Haff, J. W. McGahen, E. M. Newmayer, M. Paulshock, J. C. Watts, T. R. Wood, E. C. Hermann and C. E. Hoffmann. Science, **144**, 862 (1964).

24. R. D. Fletcher, J. E. Hirschfield and M. Forbes. Nature, **207**, 664 (1965).

25. J. T. H. Roos and D. R. Williams. J. Inorg. Nucl. Chem. **39**, 1294 (1977).

26. B. D. Korant, J. C. Kauer and B. E. Butterworth. Nature, **248**, 588 (1974).

27. H. F. Maassab and K. W. Cochran. Science, **145**, 1443 (1964).

28. J. S. Wishnok. J. Chem. Ed. **50**(11), 781 (1973).

29. Y. K. Ho, M. T. Hakala and S. F. Zakrsewski. Cancer Research, **32**, 1023 (1972).

30. N. V. Klimova, A. P. Arendaruk, M. A. Baranova, N. I. Vasetchenkova, M. I. Shmar'yan and A. P. Skoldinov. Khim. Farm. Zh. **4**, 14 (1970) abstract.

31. Shionogi and Co. Ltd. Jpn Kokai Tokkyo Koho JP 58 79994 (1983).

32. P. D. Braddock, T. A. Connors, M. Jones, A. R. Khokhar, D. H. Melzack and M. L. Tobe. Chem. Biol. Interactions, **11**, 145 (1975).

33. J. E. Huheey. Inorganic Chemistry 2rd. ed. M. Wasserman Ed. N. Y. (1978).

CHAPTER 2

Experimental and Instrumentation

2.1 Experimental

The platinum salt, $K_2[PtCl_4]$, 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 (DMNH, 40% in water), 1-adamantanamine (1-adam), 2-adamantanamine (2-adam), 1-methyladamantanamine (1-Madam) and N,N-dimethylformamide (DMF) were obtained from Aldrich and Eastman and were used without further purification. All the complexes were dried in a drying pistol under P_2O_5.

The microanalyses were done by Galbraith Laboratories, Inc. The melting points were measured on a Fisher-Johns instrument. The IR spectra were recorded on a Perkin-Elmer 783 or Digilab FT50 spectrometer (CsI beamsplitter with a resolution of 1 cm^{-1}, 256 scans). The Raman spectra were measured on a U-1000 Ramanor spectrometer equipped with a microscope, with the argon-ion green line (514.5 nm), with a slit width of 300 μm and a power of 200 mW, 20 scans were accumulated (40 for best resolution) and 9-point smoothing was done. The ^{195}Pt nuclear magnetic resonance spectra were taken on a Bruker WH-400 FT NMR spectrometer at 85.832 MHz, spectral window 1000 ppm, in DMF, acetone or CH_2Cl_2 (conc: 30-60 mg / 3 ml) with a D_2O external tube for lock purposes and $K_2[PtCl_4]$ as an external reference adjusted at -1628 ppm relative to $Na_2[PtCl_6]$ or on a Varian XL–300 FT NMR spectrometer at 64.374 MHz, spectral window 1500 ppm, in DMF, acetone, D_2O or CH_2Cl_2. The spectrometer was locked on D_2O and $K_2[PtCl_4]$ was used as an external standard adjusted at -1628 ppm. Proton nuclear magnetic resonance spectra were taken on a Varian XL- or Gemini-200 or on a XL- or Gemini-300 FT NMR spectrometer, in DMF-d_7, acetone-d_6, CD_2Cl_2 or D_2O.

2.2 Instrumentation

2.2.1 X-Ray Diffraction

X-ray crystallography is one of the best methods to determine the precise composition and atomic arrangement in a molecule. The packing of the molecules into the crystal defines the symmetry of the electron density distribution and the size of the unit cell.

The parameters of a unit cell are defined by the axes a, b, c and the angles are α, β, γ. The volume, V, may be used to calculate the density, D_c, of the crystal according to the following formula:

$$D_c = \frac{Z M_w}{V \mathcal{N}}$$

where Z is the number of formula weights in the unit cell, M_w is the molecular weight and $\mathcal{N}$ is Avogadro's number. The selection rule for X-ray diffraction is given by Bragg's law defined as:

$$2d\sin\theta = n\lambda$$

One of the methods used to obtain information on a single crystal is the precession method (1). The unit cell parameters and space group can be determined by this method. The data collection then can be made by a diffractometer. The observed intensity (I_{hkl}) of the measured reflections, is defined by the equation:

$$I_{hkl} = \frac{[I_{int} - (B_l - B_r)]\ v}{R\ \tau}$$

where I_{int} = integrated intensity

B_l = contribution of the left background

B_r = contribution of the right background

v = scan rate

R = ratio of total background measurement time over scan time (0.5 in our model)

τ = transmission coefficient

The standard deviation $\sigma(I)$ is obtained by:

$$\sigma^2(I_{hkl}) = \{[I_{int} + (B_l + B_r) / R^2] v^2 + (C I_{hkl})^2\} / \tau$$

where C is the instability factor of the measurement system (0.02 in our model).

After the data collection on the diffractometer, a data reduction program transforms the intensity data into F_{obs} values, making corrections for the Lorentz and polarization terms of the observed intensity (I_{hkl}) of the hkl reflections as follows:

$$|F_{hkl}|^2 = \frac{KI_{hkl}}{Lp}$$

The Lorentz correction depends on the measurement technique. It can be defined for a diffractometer by the equation: $L = 1/\sin 2\theta$. The polarization correction is a simple function of 2θ ($p = (1 + \cos^2 2\theta)/2$) and is independent of the method used for the data collection. The K parameter is a constant depending upon the properties of the data collection system, such as crystal size, beam intensity and a number of fundamental constants. The K term is taken care of by a scale factor which is varied in the least-squares refinement program (2). The resulting F_{hkl} value is called the observed structure factor amplitude. This is the absolute value of the structure factor, F_{obs}, and in solving a crystal structure, the F_{obs} values are compared with the F_{calc} values that are calculated from an assumed arrangement of atoms in the unit cell.

When a system contains a heavy atom, the structure solution can be obtained by the heavy atom (or Patterson) method. The metal atom is the first atom localized in the unit cell model. In this method, it is assumed that the unit cell contains only the heavy atoms. After refinement of the coordinates and isotropic thermal factors of these atoms by a least-squares program, an electron density map of the residual atoms can be obtained from difference Fourier map calculations. The program used is a Fourier program that can be used to calculate the Patterson function, F_{obs} electron density maps, or $|F_{obs}| - |F_{calc}|$ density maps. Since each peak in the electron density map corresponds to an atomic position, it is simple to pick out the locations of the atoms from the Fourier and Fourier difference maps. The least-squares refinement program varies the parameters of all atoms and the scale factor to obtain the best agreement between the F_{obs} and F_{calc} values. This program is also responsable for calculating structure factors for use in the Fourier program. The goodness of the model is judged by the R factor, which can be written as $R = \Sigma||Fo| - |Fc|| / \Sigma w|Fo|$ and a weighted residual $wR = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma(|Fo|)^2]^{1/2}$ ($w = 1/\sigma^2(I_{hkl})$). In general, the values of R or wR should be nearly the same at the end of refinement, and as low as possible for a good model.

Several problems may occur during refinement of a structure. The problem arising from the existence of two different orientations of a lattice in what is often apparently one crystal is called *twinning* and causes all reflections to be doubled. *Absorption* is another problem. Corrections are usually made based on the equation of the crystal faces. When the faces can be well described, the absorption correction can be made with fairly good precision; for irregular shapes, the correction is less precise. No correction is needed if the absorption coefficient is very small. *Disorder*, when it is found, is often a very difficult

problem. The difficulty arises when some atoms in the unit cell or in different cells can be placed in two (or more) positions (3).

2.2.2 Infrared and Raman Spectroscopy

In recent years, dispersive, i.e. prism and grating, infrared spectrophotometers have been replaced by Michelson interferometers equipped with minicomputers for performing fast Fourier transforms of the resulting interferograms. The latter development has added high spectral resolution (0.06-1.0 cm^{-1}) and good time resolution (4). The advantages of Fourier transform spectroscopy over prism and grating techniques can be summarized as following:

1) Felgett's advantage: the information is recorded throughout the IR spectrum simultaneously at all frequencies; thus a single interferogram covering 4000 to 200 cm^{-1} can be recorded in a few seconds.

2) Jacquinot's advantage concerns the improvement of the optical throughput. In a dispersive spectrometer, radiation reaching the detector is attenuated by the entrance and exit slits of the monochromator (which must be very narrow for high-resolution spectra), while with an interferometer, there is no such limitation, except the size of the mirrors.

3) Connes' advantage concerns the accuracy of the frequency determination. This is possible by using a He-Ne laser interferometer to reference the position of the moving mirror.

In addition to these optical advantages, the Fourier transform spectrometers have very important data processing advantages. The minicomputer used to do the Fourier transform is also used in manipulating and displaying the spectra (4). Both IR and Raman

spectroscopy provide information about molecular vibrations, but the selection rules are quite different. For IR activity, there must be a change in the dipole moment derivative, $(\partial\mu/\partial Q)_0 \neq 0$, where μ is the dipole moment and Q is the normal coordinate that describes the relative motions of the atoms in the molecule during the vibration. For Raman activity, on the other hand, there must be a change in the molecular polarizability derivatives, $(\partial\alpha/\partial Q)_0 \neq 0$, during the vibration. An important consequence of these selection rules in the case of centrosymmetric systems is the rule of mutual exclusion, which states that molecular vibrations that are Raman active are IR inactive and vice versa. The non-coincidence of IR and Raman peaks in the spectra of a compound is thus good evidence for the presence of a center of symmetry. This could be applied to platinum(II) complexes to determine the isomerism of the synthesized compounds. *Cis* and *trans* platinum(II) complexes can usually be determined by this method (5). The patterns of the ν(Pt-Cl) vibrations are quite characteristic for a molecule containing three chloride bonds (as in $[Pt(A)Cl_3]^-$ complexes), two chloride bonds in *cis* or *trans* position (as in *cis*- and *trans*-PtA_2X_2, X = Cl, I) or $Pt(A)(DMF)Cl_2$ or bridging and terminal chloride (as in oligomers species, $[Pt(A)Cl_2]_n$). An example of each of these patterns is presented in Figure 3 and the group theory (6) is given in Appendix I.

C_{2v}
3ν(Pt-Cl)

cis C_{2v}
6ν(Pt-Cl)

trans C_{2h}
3ν(Pt-Cl)

$K[Pt(A)Cl_3]$ **trans-** $[Pt(A)Cl_2]_2$

cis C_{2v}
2ν(Pt-Cl)

trans D_{2h}
1ν(Pt-Cl)

cis-$Pt(A)_2Cl_2$ **trans-**$Pt(A)_2Cl_2$

Figure 3. Infrared spectra in the ν(Pt-Cl) region for different platinum(II) complexes.

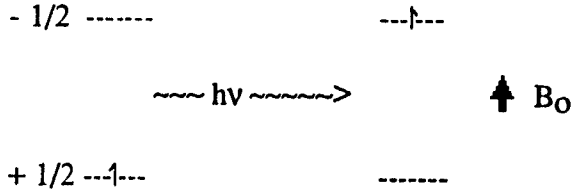
2.2.3 Nuclear Magnetic Resonance Spectroscopy

Nuclei having spin = 0 cannot experience magnetic resonance, while nuclei having spin different from 0 can produce a NMR spectrum. Spin states are not of equivalent energy in an applied magnetic field (B_o) and any charged particule generates a magnetic field of its own. Thus a nucleus has a magnetic moment (μ) generated by its spin. In an applied magnetic field, all nuclei will have their μ (magnetic moment) aligned or opposed to it (7).

- 1/2 higher state E↑ opposed with the field

+1/2 lower state E↓ aligned with the field

When nuclei aligned with an applied field are induced to absorb energy and change their spin orientation with respect to the applied field, NMR occurs . The energy absorption is a quantized process and is equal to the energy difference between the two states involved.



Spin 1/2 nuclei have an angular momentum (I) which is quantized in units of h (Planck constant)/2π:

$I = \sqrt{I(I+1)}\ h/2\pi$ where I refers to the nuclear spin quantum number of nuclear spin

^{195}Pt is an isotope with a natural abundance of 33.7%, with a nuclear spin I = 1/2 and can be studied by nuclear magnetic resonance spectroscopy. This is a powerful method of identifying different platinum complexes. The studies in the past fifteen years have

produced an accumulation of ^{195}Pt-NMR measurements, so that some qualitative generalizations (8) have been made. The chemical shift (δPt) of the platinum complexes are influenced by the presence of all the ligands in the coordination sphere of the metal and resonances move to high field in the order P > As > S > N > Cl^- > O. Thus the anions $[Pt(H_2O)Cl_3]^-$, $[Pt(NMe_3)Cl_3]^-$ and $[Pt(PMe_3)Cl_3]^-$ are observed at -1180, -1715 and –3500 ppm, respectively. The resonances of Pt(II) complexes appear at higher field than those of Pt(IV) compounds. By convention, the platinum chemical shifts are defined relative to $Na_2[PtCl_6]$ which is fixed at 0 ppm. The higher field resonances have negative signs. As an example $K_2[PtCl_4]$ appears at -1628 ppm relative to $Na_2[PtCl_6]$ fixed at 0 ppm. There is a dependence of δ^{195}Pt on complex geometry. For PtX_2L_2 types, where X is a relatively hard ligand such as Cl^-, and L= PR_3 or AsR_3, the *cis* complex is upfield of the *trans* analog by 400-500 ppm. Where X and L are not so markedly different (X = Cl^- and L = H_2O), the difference is smaller, about 10-20 ppm. Substitution of a group by another one (on the same donor atom) or simply lengthening an alkyl chain produces small variations in the δ^{195}Pt. Interestingly, if the ligand becomes sterically larger, there is a marked downfield shift of the platinum signal. This has been explained by solvent effects. If steric hindrance around the platinum atom is large, solvent molecules cannot "bind" to platinum atom and there is no net change in the chemical shift. If there is no steric hindrance, the solvent molecule can approach the platinum and there is a shift towards higher field, because the electronic density around the nucleus increases. Therefore, the solvent is very important for comparison purposes. Both solvent and temperature affect the δ^{195}Pt signal. Even in the octahedral dianion complex $[PtCl_6]^{2-}$, a spread of 400 ppm has been observed on going from H_2O to DMSO with the latter appearing at higher field. A change in temperature of 100° C could result in a 40-50 ppm effect.

Fold over

To represent the frequency of a signal correctly, the sampling rate must be greater than or equal to twice the signal frequency (Nyquist theorem). If a signal lies outside the selected range, it can appear in the spectrum but at a wrong frequency and it will be distorted in phase compared to the rest of the spectrum. Depending upon the implementation of the Fourier transform algorithm used, the aliased signal will appear on the same side of the spectrum or be flipped across and appear on the other side (9-12). Quadrature data may be collected in two different ways. In the first method, two data points are collected simultaneously at each sampling interval (Varian); in the second, the two quadrature signals are sampled sequentially (Bruker). Aliasing is caused by sampling the data too slowly, i.e., at a rate which violates the Nyquist theorem. Thus, aliased peaks arise from regions which lie outside the chosen spectral width, SW. When simultaneous acquisition is used (Varian), the aliased signals are zoned or wrapped around the SW to appear at the opposite end of the spectral width from their real position; but when alternate acquisition (Bruker) is used the aliased signal are folded about the nearest end of SW.

The best method to distinguish between aliased and real signals is to change the SW. Movement of TO (transmitter offset position) will only distinguish between a real signal and an aliased one if alternate acquisition is used (Bruker). If simultaneous acquisition is used (Varian), distinguishing aliased peaks needs a change of SW. The phase properties of aliased lines also change with the sampling scheme. Thus, an aliased line may appear out of phase with the rest of the spectrum. A peak whose real position is ΔW beyond the edge of the SW will appear aliased as a peak at ΔW inside (but at the opposite end) the spectral width when simultaneous acquisition is used (Varian). If alternate acquisition is used, an aliased peak will appear folded about the nearest end of SW (Bruker).

As an example, if we define SW from -1000 to -1500 ppm on a Bruker spectrometer, the aliased peak whose real position is at -1700 ppm will appear at -1300 ppm. If we move the window from -900 to -1400 ppm, the aliased peak will now appear at -1100 ppm indicating that it is not a real peak. Thus, moving the window (change TO) is enough to detect a fold over (Figure 4).

Now, if we define the same spectral window on a Varian spectrometer, the aliased peak (whose real position is also at -1700 ppm) will appear at -1200 ppm. If we move the SW from -900 to -1400 ppm, the aliased peak will again appear at -1200 ppm. Thus, moving the window (change TO) is not enough to detect a fold over on a Varian spectrometer, changing the window is a better procedure (change SW). If we change SW from -1000 to -1400 ppm, the aliased peak will now appear at -1300 ppm, indicating that it is not a real peak.

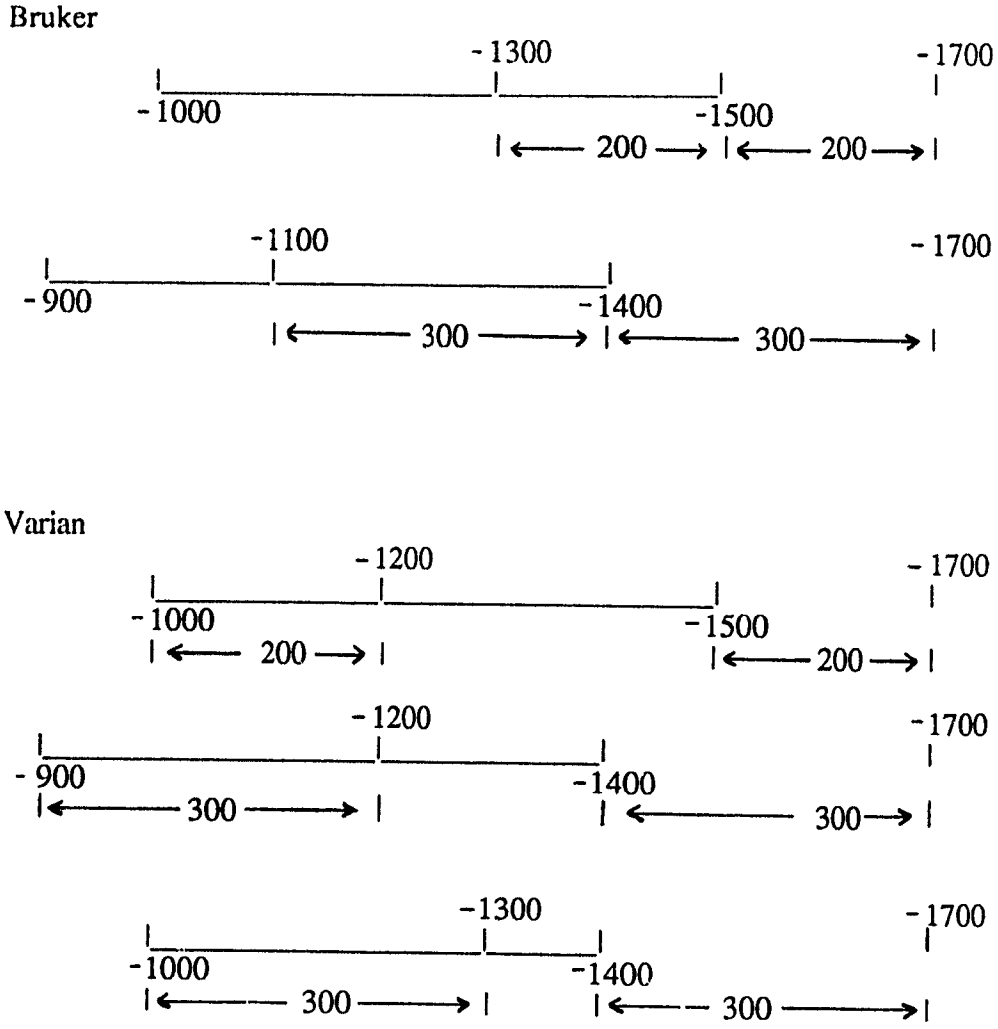


Figure 4. Comparison between a Bruker and a Varian spectrometer for the detection of aliased peaks (values in ppm).

2.3 References

1. M. J. Buerger. The Precession Method in X-ray Crystallography, John Wiley and Sons, Inc. (1964).
2. G. H. Stout and L. H. Jensen.X-ray Structure Determination. Macmillan Publishing Co. Inc. (1968).
3. R. S. Drago. Physical Methods in Chemistry. W. B. Saunders Company (1977).
4. J. R. Ferraro and L. J. Basile. Fourier Transform Infrared Spectroscopy, Vol.2, Academic Press, New York. (1979).
5. K. Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds. 3rd edition. John Wiley and Sons Inc. (1978).
6. F. A. Cotton. Chemical application of group theory. 3rd. ed. N.Y. Wiley (1990)
7. J. K. M. Sanders and B. K. Hunter. Modern NMR Spectroscopy. Oxford University Press. (1987).
8. P. S. Pregosin. Coord. Chem. Rev. **44**, 247 (1982).
9. C. J. Turner and H. D. W. Hill. J. Magn. Reson. **66**, 410 (1986).
10. A. G. Redfield and S. D. Kunz..J. Magn. Reson. **19**, 250 (1975).
11. R. T. Pajer and I. M. Armitage. J. Magn. Reson. **21**, 365 (1976).
12. G. Bodenhausen, R. Freeman, G. A. Morris, R. Niedermeyer and D. L. Turner. J. Magn. Reson. **25**, 559 (1977).

CHAPTER 3

Synthesis of $[Pt(amine)Cl_3]^-$ Complexes

and

Crystal Structure of 2-Adamantylammonium Trichloro(ethylamine)platinate(II)

3.1 Introduction

The classic, square-planar, platinum(II) complex, $K[Pt(NH_3)Cl_3]$, was first discovered in 1890 by Cossa (1). It is best prepared nowadays by refluxing a mixture of *cis*-$Pt(NH_3)_2Cl_2$ and KCl in N,N-dimethylformamide (2). Related complexes of the type $K[Pt(py)Cl_3]$ have since been synthesized by reacting $K_2[PtCl_4]$ with pyridine or pyridine derivatives (py) in DMF solution (3-4). These methods are not appropriate, however, for the preparation of monoamine platinum(II) complexes. In 1988, Rochon and Fleurent (5) reported a synthetic route to such compounds involving the reaction of $K_2[PtCl_4]$ with a monoamine and an excess of KCl in aqueous solution. Although this method is useful for bulky amine ligands such as tert-butylamine and isopropylamine, it is totally unsuited for smaller amines, owing to the rapid formation of unwanted disubstituted complexes. A successful synthesis of small monoamine platinum(II) complexes has been achieved recently that involves cleavage of iodo-bridged amine dimers with aqueous $AgNO_3$ and subsequent reaction with KCl (6). These specific reactions will be discussed in more detail in section 3.3.1.

Monoamine platinum(II) complexes are important because they are convenient precursors to mixed-ligand complexes $Pt(A)(L)Cl_2$ (A = amine and L = monodentate ligand). Many of the currently known, active anti-tumor agents are square-planar platinum(II) complexes with *cis* stereochemistry containing two identical primary amine ligands. Platinum(II) complexes with secondary amines and pyridine derivatives are less active. Cyclic primary amines complexes seem to be more active as the ring size increases (7), although complexes with two adamantanamine derivatives showed no activity presumably because of their low solubility in biological media (8). If complexes containing two different amine 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 synthesized complexes of the type $Pt(A)(A')Cl_2$, but not with adamantanamine derivatives (9). The cage molecule 1-adamantanamine ($C_{10}H_{15}NH_2$) has been the subject of some attention lately, chiefly because of its own antiviral (10-12) and antitumor activity (13).

Platinum(II) complexes containing the related 1,2-diaminoadamantane ligand (14) apparently possess antitumor activity comparable to that of the commercially-licensed drug, cisplatin, *cis*-$Pt(NH_3)_2Cl_2$ (15). The development of a new method for the synthesis of $K[Pt(A)Cl_3]$ complexes (6) has led to a convenient synthetic route to mixed-ligand platinum(II) complexes of the type *cis*-$Pt(A)(L)Cl_2$. Compounds with L = alkene or acetylenic glycol have been recently reported (16) and it was felt that it would be worthwhile attempting to synthesize similar complexes with various adamantanamine ligands. The ultimate hope is that such synthetic combinations might result in compounds with enhanced antitumor activity and reduced toxicity.

3.2 Experimental

[AdamH]$_2$[PtCl$_4$] One equivalent of $K_2[PtCl_4]$ was dissolved in water and the filtered solution was treatedwith two equivalents of aminoadamantane hydrochloride in water. The insoluble pale pink chloroplatinite of the protonated amine was filtered off, washed with water and dried.

K[Pt(A)Cl$_3$] The K[Pt(A)Cl$_3$] complexes (A = methylamine ($MeNH_2$), ethylamine ($EtNH_2$) cyclobutylamine (CBA), cyclopentylamine (CPA) and dimethylamine (DMNH)) were synthesized by the literature procedure (6). This method did not prove suitable for adamantanamine ligands.

K[Pt(adam)Cl$_3$] Since adamantanamine derivatives are bulkier than the amines mentioned above, the compounds were synthesized as reported for lutidine ligands (4). The same method was used for 1-adamantanamine (1-adam), 2-adamantanamine (2-adam) and 1-methyladamantanamine (1-Madam). Only K[Pt(1-adam)Cl$_3$] was successfully isolated; the other complexes decomposed on contact with water.

K[Pt(1-adam)Cl$_3$] Yield: 12 %; dec. pt: 195-210°C; Anal. Calcd: 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.

[NMe$_4$][Pt(adam)Cl$_3$] An exchange resin (Dowex 50W-X8, H^+, 20-50 mesh) was used to change one mmole of potassium tetrachloroplatinate(II) to the H^+ form (H_2PtCl_4), which was neutralized with tetramethylammonium hydroxide. The resulting salt, tetramethylammonium tetrachloroplatinate(II), was then isolated and dried. The reactions of $[NMe_4]_2[PtCl_4]$ with the adamantanamine ligands were performed as described above for the synthesis of K[Pt(adam)Cl$_3$], starting with one mmole of $[NMe_4]_2[PtCl_4]$. They were identified by the similarity of their spectroscopic properties with the K[Pt(1-adam)Cl$_3$] complex.

$[NMe_4][Pt(2\text{-}adam)Cl_3]$ Yield: 26%; dec. pt: 163-266°C

$[NMe_4][Pt(1\text{-}Madam)Cl_3]$ Yield: 72%; dec. pt: 212-265°C

$[2\text{-}C_{10}H_{15}NH_3][Pt(EtNH_2)Cl_3]$ One mmole (0.385 g) of $K[Pt(EtNH_2)Cl_3]$, synthesized by the method already reported (6), and 1.1 mmole (0.168 g) of 2–adamantanamine ($2\text{-}C_{10}H_{15}NH_2$) were stirred in a minimum quantity of water (10 ml) for 90 min. Then, 10 ml of 0.1N HCl was added to the solution and the mixture was stirred for a further 10 min. The resulting yellow precipitate was filtered off and the filtrate was evaporated to dryness. The yellow residue was dissolved in acetone and filtered to remove KCl and $Pt(EtNH_2)(2\text{-}C_{10}H_{15}NH_2)Cl_2$. The filtrate was again evaporated to dryness and the residue was washed in ether, filtered and dried over P_2O_5. The crystals used for the crystallographic work were recrystallized by slow evaporation of an acetone solution. Yield: 65%; dec. pt. 140-160 °C

3.3 Results and Discussion

3.3.1 Synthesis of $[Pt(amine)Cl_3]^-$ complexes

The syntheses of the starting materials $K[Pt(A)Cl_3]$ were done according to a method recently developed in our laboratories (6). The different steps of the synthesis are as follows :

$$K_2[PtCl_4] + 4\,KI \xrightarrow{H_2O} K_2[PtI_4] + 4\,KCl$$

$$K_2[PtI_4] + 2A \xrightarrow{H_2O} \textit{cis}\text{-}Pt(A)_2I_2 + 2\,KI$$

$$2\,\textit{cis}\text{-}Pt(A)_2I_2 \xrightarrow{HClO_4} \begin{matrix} A & & I & & I \\ & \diagdown & \diagup\diagdown & \diagup & \\ & Pt & & Pt & \\ I & \diagup & \diagdown I & \diagup & A \end{matrix}$$

$$[Pt(A)I_2]_2 \xrightarrow[-AgI]{AgNO_3} \text{hydrolysed species} \xrightarrow[-KNO_3]{KCl} 2\ K[Pt(A)Cl_3]$$

Complexes with A = methylamine, ethylamine, cyclobutylamine, cyclopentylamine and dimethylamine were synthesized. They have already been studied by infrared spectroscopy, X-ray diffraction and proton-NMR spectroscopy (6) but not by ^{195}Pt-NMR spectroscopy. The ^{195}Pt-NMR spectra were measured as part of this thesis and the results will be discussed in Section 3.3.2. The method used to synthesize the $K[Pt(A)Cl_3]$ complexes could not be applied to the preparation of the adamantanamine derivatives, because the dimerization does not occur, probably due to the low aqueous solubility of the $Pt(adam)_2I_2$ complexes.

New complexes of the type $K[Pt(adam)Cl_3]$ were synthesized by a method previously reported for lutidine ligands (4), according to the following reaction:

$$K_2[PtCl_4] + 1\ adam \xrightarrow{DMF} K[Pt(adam)Cl_3] + KCl$$

One equivalent of adamantanamine derivative is added to one equivalent of potassium tetrachloroplatinate(II) in 100 ml of DMF and stirred for 3 h at 80°C. The 2–adamantanamine, commercially available as the hydrochloride salt was neutralized with one equivalent of sodium hydroxide before the reaction. If an excess of ligand is added, the disubstituted complexes $Pt(adam)_2Cl_2$ are rapidly formed. If the ligand is added too slowly, there is formation of impurities due to decomposition of DMF (17). Complexes with adam = 1-adamantanamine, 2-adamantanamine and 1-methyladamantanamine were prepared. The complex $K[Pt(1\text{-}adam)Cl_3]$ is stable, but was isolated only in a very low yield (12%); the results of its elemental analysis are excellent. This compound was

characterized by its ^{195}Pt-NMR and infrared spectra, which will be discussed in Section 3.3.2 and 3.3.3. The complexes K[Pt(2-adam)Cl_3] and K[Pt(1-Madam)Cl_3] were not isolated because they decomposed readily on contact with water. Therefore, the DMF solutions were concentrated as much as possible, cooled to ~0°C, and the KCl was filtered off. The ^{195}Pt-NMR spectra of these solutions were measured at room temperature.

In an attempt to isolate the [Pt(adam)Cl_3]$^-$ complexes with 2-adam and 1–Madam, the larger cation, $[NMe_4]^+$ was employed. The $[NMe_4]_2[PtCl_4]$ complex was prepared according to the following reaction:

$$K_2[PtCl_4] \xrightarrow{resinH^+} H_2PtCl_4 \xrightarrow{2[NMe_4]OH} [NMe_4]_2[PtCl_4]$$

A Dowex 50W-X8,H^+, 20-50 Mesh resin, was used to change the potassium ions to H^+ ions, which in the presence of tetramethylammonium hydroxide, NMe_4OH, gave tetramethylammonium tetrachloroplatinate(II), $[NMe_4]_2[PtCl_4]$, which was isolated and dried. The adam ligand was then added to $[NMe_4]_2[PtCl_4]$ dissolved in DMF:

$$[NMe_4]_2[PtCl_4] + \text{adam} \xrightarrow{DMF} [NMe_4][Pt(adam)Cl_3] + NMe_4Cl$$

The experimental conditions were the same as those used for K[Pt(adam)Cl_3], starting with one mmole of $[NMe_4]_2[PtCl_4]$ and one mmole of 2-adamantanamine or 1-methyladamantanamine. The complexes formed were appreciably more stable and could be isolated. The complex with 2-adam is water soluble, but the one with 1-Madam is much less soluble. These compounds have been characterized by NMR and IR spectroscopy and these data will be discussed in Section 3.3.2 and 3.3.3, respectively.

3.3.2 ^{195}Pt- and ^{1}H- NMR Spectra

Natural platinum contains three main isotopes: 194, 195 and 196. The only one with non-zero nuclear spin is ^{195}Pt. It has I = 1/2 and reasonable abundance (33.7%) and sensitivity (9.94×10^{-3}) for an equal number of nuclei at constant field (18), and is amenable to study by nuclear magnetic resonance spectroscopy. The ^{195}Pt resonances for the complexes $[Pt(A)Cl_3]^-$ and $[Pt(adam)Cl_3]^-$ are given in Table I, together with the chemical shifts of some $[PtCl_4]^{2-}$ complexes with different counterions. The reference was an external standard, $K_2[PtCl_4]$ in D_2O, which has a resonance of -1628 ppm, relative to $Na_2[PtCl_6]$. From Table I, the chemical shifts are solvent dependent, since the resonance of $K_2[PtCl_4]$ appears at 202 ppm lower field in DMF than in D_2O, while the $[Pt(L)Cl_3]^-$ resonances appear only 19-35 ppm higher in acetone than in DMF. The large difference observed between DMF and D_2O for $[PtCl_4]^{2-}$ and the small difference between DMF and acetone for $[Pt(A)Cl_3]^-$ might be explained by the degree of ionization of these compounds in the different solvents. In general, protic solvents can solvate an anion by hydrogen bonding to it while aprotic solvents cannot stabilize any anion by hydrogen bonding. Since these compounds are ionic complexes, they are totally dissociated in D_2O, whereas in organic solvents, the dissociation is much less and might be similar for DMF and acetone. Studies by Pesek and Mason (19) have shown similar features for $((\underline{n}\text{–}C_4H_9)_4N)_2[PtCl_4]$. An important downfield shift has been observed from water (–1624 ppm) to organic solvents, while very little difference was observed between the chemical shift of this species in acetone (-1388), acetonitrile (-1384) or DMSO (-1372 ppm). This difference was explained by the increasing possibility of ion pairing in organic solvents for the tetra-n-butylammonium cation. There is also a small dependence on the counterion. In water, the difference is relatively small, but in DMF

there is a 39 ppm downfield shift when the potassium ions in $K_2[PtCl_4]$ (-1426 ppm) are replaced by tetramethylammonium ions (-1387 ppm). This observation is in agreement with a similar study reported by Freeman et al. (18) who observed a comparable difference in the position of δ(Pt) for the $[Ph_4P]_2[PtCl_4]$ (-1461) compared to $[Bu_4N]_2[PtCl_4]$ (-1437 ppm) in CH_2Cl_2. They explained this difference by a less efficient pairing of the ions in $[Ph_4P]_2[PtCl_4]$, due to a more diffuse positive charge located on the P atoms, which are larger than the nitrogens in $[Bu_4N]_2[PtCl_4]$. No difference was observed between the chemical shift of $Na_2[PtCl_4]$ (-1618 ppm) and $K_2[PtCl_4]$ (-1618) in water (18), even though there is a significant size difference between Na and K. The cations are so strongly solvated in water that the anion is completely independent of the cation and the resonance of $[PtCl_4]^{2-}$ is unchanged. In Table I, there is a 29 ppm upfield shift in DMF when K is replaced by hydrogen, and a 46-62 ppm upfield shift when it is replaced by an adamantylammonium derivative. In the potassium and tetraalkylammonium salts, there is no possibility of hydrogen bonding between the cations and the solvent, or between the different ions. In $H_2[PtCl_4]$ or $[adamNH_3)]_2[PtCl_4]$, the presence of hydrogen bonds between the solvent and the cations might result in a less efficient pairing of the ions, thus a better solvation of the anions, which results in a upfield shift. The same trend is observed in the $[Pt(L)Cl_3]^-$ complexes but the range is smaller, the ionicity being smaller due to the smaller formal negative charge on the complexes. When K is replaced by $[NMe_4]$, there is a 8-9 ppm downfield shift, while the replacement of K by an adamantylammonium group leads to a 5 ppm upfield shift.

Table I. ^{195}Pt resonances for $[PtCl_4]^{2-}$, $[Pt(A)Cl_3]^-$ and $[Pt(adam)Cl_3]^-$ complexes and pK_a of some of the amine ligands in water.

Compounds	$\delta^{195}Pt(\pm 5ppm)$ D_2O	acetone	DMF	pK_a of A
$K_2[PtCl_4]$	-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	
$[1\text{-MadamH}]_2[PtCl_4]$			-1472	
$K[Pt(D_2O)Cl_3]$	-1194			
	-1180 (18)			
$K[Pt(MeNH_2)Cl_3]$			-1842	10.66(20)
$K[Pt(EtNH_2)Cl_3]$			-1850	10.81(20)
K[Pt(CBA)Cl$_3$]		-1875	-1852	
K[Pt(CPA)Cl$_3$]		-1866	-1847	
K[Pt(1-adam)Cl$_3$]			-1822	9.92(21)
K[Pt(2-adam)Cl$_3$]			-1859	
K[Pt(1-Madam)Cl$_3$]			-1865	
[NMe$_4$][Pt(2-adam)Cl$_3$]			-1851	
[NMe$_4$][Pt(1-Madam)Cl$_3$]			-1856	
$[2\text{-adamH}][Pt(EtNH_2)Cl_3]$			-1855	
K[Pt(DMNH)Cl$_3$]		-1860	-1825	10.73(20)

There is also a dependence on the concentration of the species in solution. The chemical shift for $K[Pt(D_2O)Cl_3]$ in D_2O is located at -1194 ppm in our reference spectrum. Freeman et al. (18) have observed that the resonance of this solvolysis species lies between 1180 and -1194 ppm depending on the concentration of the aqua or

tetrachloro ion in solution, and moves to higher field with increasing concentration. In concentrated solution, the resonance appears at -1194 ppm, while the peak at -1180 ppm is obtained for a dilute solution of $K_2[PtCl_4]$.

The platinum resonances are therefore dependent on several factors such as solvent effects, the presence of different counterions and concentrations of species in solution. Nevertheless, when they are measured under similar conditions, some valid comparisons can be made. All the chemical shifts of the $[Pt(A)Cl_3]^-$, $[Pt(adam)Cl_3]^-$ and $[PtCl_4]^{2-}$ complexes have been measured in DMF, and a few have been measured in D_2O or acetone. The resonances appear between -1822 and -1875 ppm for $[Pt(A)Cl_3]^-$ and $[Pt(adam)Cl_3]^-$, in good agreement with the chemical shifts observed at -1826 ppm for $K[Pt(NH_3)Cl_3]$ in water and at -1863 ppm for $[NPr_4][Pt(DMNH)Cl_3]$ in CH_2Cl_2 (22). All the $[Pt(A)Cl_3]^-$ and $[Pt(adam)Cl_3]^-$ anions show only one resonance except $K[Pt(2–adam)Cl_3]$ and $K[Pt(1\text{-}Madam)Cl_3]$ and $[NMe_4][Pt(1\text{-}Madam)Cl_3]$. The spectra of the complexes $K[Pt(2\text{-}adam)Cl_3]$ and $K[Pt(1\text{-}Madam)Cl_3]$, which have not been isolated, showed other peaks around –2200 ppm, which were attributed to the disubstituted species $Pt(adam)_2Cl_2$. The spectrum of $[NMe_4][Pt(1\text{-}Madam)Cl_3]$ also showed another peak at –2242 ppm, which was assigned to the disubstituted species $Pt(1\text{-}Madam)_2Cl_2$.

Besides solvent effects, the platinum chemical shift is highly sensitive to the kind of ligands coordinated to the platinum atom. According to a rule suggested first by Kift et al. (23), an increase in the electron density on the platinum atom upon coordination (thus an increase in basicity of the ligand) should lead to a chemical shift towards higher frequency. In a study on *trans*-$Pt(py)(C_2H_2)Cl_2$ (py = pyridine or substituted pyridine), Motchi et al. (24) noted the opposite trend: an increase in basicity of the ligand led to a

downfield shift (max. $\Delta\delta$ = 116 ppm). This effect has also been observed in a study on *cis* and *trans*-Pt(py)(DMSO)Cl_2 (25). The authors found a slight linear dependence of chemical shift on pKa for pyridine or 4-substituted pyridines ranging in pKa from 1.9 to 9.7. For the *trans* series, increasing basicity of the ligand led to a downfield shift (max. $\Delta\delta$ = 135 ppm) as observed for *trans*-Pt(py)(C_2H_2)Cl_2, while in the *cis* series, upfield shifts were observed with increasing basicity of the ligands (max. $\Delta\delta$ = 261 ppm).

We tried to see if in our study some correlations could be made between the pK_a of the ligands and the δ(Pt) chemical shifts of the platinum complexes. As seen in Figure 5a, for $EtNH_2$ (pK_a = 10.81), $MeNH_2$ (pK_a = 10.66) and 1-adamantanamine (pK_a = 9.92), the chemical shifts of the platinum complexes respectively at –1850, –1842 and –1822 ppm, apparently showed a linear relationship. When a secondary amine, dimethylamine, (pK_a = 10.73) is considered in the data (Figure 5b), the chemical shift of the platinum complex (–1825 ppm) is very similar to the chemical shift of the complex containing the 1–adamantanamine ligand. The only pK_a values in water available in the literature are for methylamine, ethylamine, dimethylamine and 1-adamantanamine (20-21). These data are sufficient to show that besides the basicity of the amine, other factors like steric hindrance or solvent effects could affect the chemical shifts of the platinum complexes. A study by Pregosin (26) showed that steric hindrance also played a role in δ(Pt) and a downfield shift was observed when the ligand became sterically larger. When one methyl group of the dimethylamine ligand in Pt(DMNH)(C_2H_4)Cl_2 (-3074 ppm) was replaced by an isopropyl group, a 44 ppm downfield shift was observed. Replacement of one hydrogen on the nitrogen of the methylamine ligand by one methyl group lead to more steric hindrance around the platinum atom. This could explain why the chemical shift of the dimethylamine platinum complex is in the same region as that for the

1-adamantanamine platinum complex, even though the basicity of the ligand is much higher.

It would be interesting to plot the δ(Pt) values of the complexes against the proton affinity of the ligands determined in the gas phase, which are intrinsic measures of the basicity of the ligands (27). This 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/mole) and $EtNH_2$ ($\Delta G°_{25°C}$ = -9.8 kcal/mole) (27), are not available in the literature.

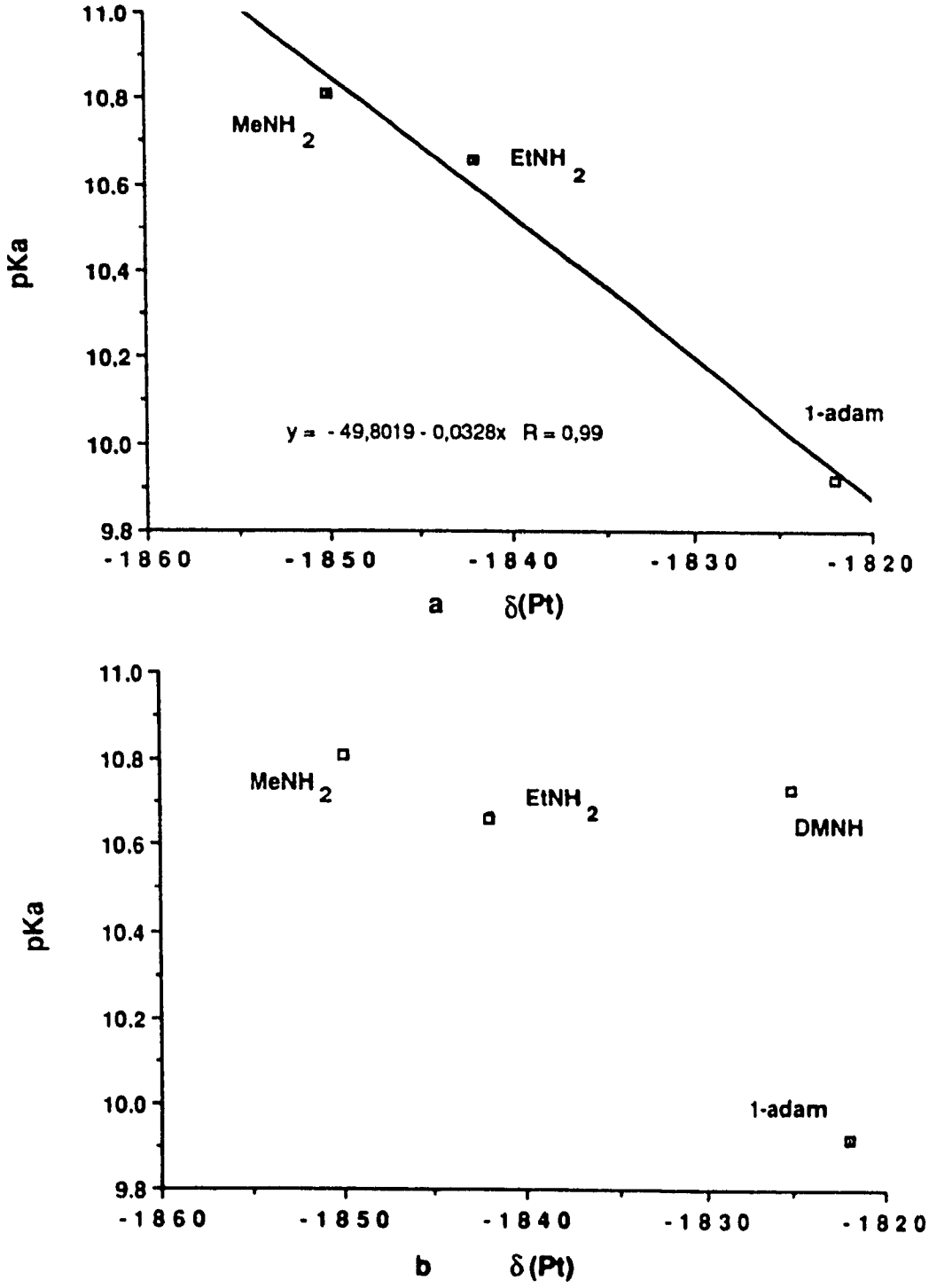
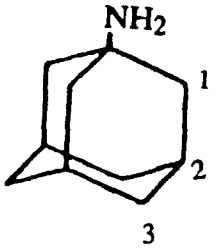


Figure 5. The pKa of the ligands as a function of the ^{195}Pt chemical shifts (in ppm): (a) methylamine, ethylamine and 1-adamantanamine (b) including dimethylamine.

The proton-NMR spectrum of $K[Pt(1\text{-adam})Cl_3]$ has been measured in $CDCl_3$ on a Varian XL 200-MHz spectrometer and the resonances of the protons were detected at lower fields when coordinated (Table II). The protons of the amine group were not observed and no coupling constant with platinum could be obtained, but this is probably due to the very low solubility of the complex. The proton-NMR spectra of the other complexes were not measured because of their low solubilities in the available deuterated organic solvents.

Table II. ^1H-NMR resonances for $K[Pt(1\text{-adam})Cl_3]$ complex.

Compounds	H_1	H_2	H_3
1-adam	2.057	1.590	1.529
$K[Pt(1\text{-adam})Cl_3]$	2.179	1.688	1.591



3.3.3 Infrared Spectra

The infrared spectra of the free adamantanamine ligands are typical of primary aliphatic amines with a rich structure of bands due to the vibrations of the adamantane cage. We have observed the stretching ν(NH) bands of 1-adamantanamine at 3342 (ν asym) and 3265 (ν sym) with an additional band at 3172 cm^{-1} attributable to Fermi resonance. The $\delta(NH_2)$ bending mode is located at 1608 cm^{-1}. The observed values are comparable to those found by Gretch et al. (28) for 1-adamantanamine where the corresponding vibrations appear at 3340, 3270, 3170 and 1605 cm^{-1}. The very low intensity of the ν(NH) vibration has to be emphasized and has been linked by Grech et al. (28) to a considerable freedom of reorientational motion. These vibrations are also at lower frequencies than for the other primary amine ligands used in this work, but this is normal since the spectra of the latter are usually measured in the gas phase or as neat liquids. For example, for free gaseous methylamine, the ν(NH) frequencies appear between 3470 and 3360 cm^{-1} (29), which is a much higher range than for the adamantanamine derivatives measured in the solid state. The values for 1-adam are similar to those found for the secondary amine DMNH, which displays only a single band at 3335 cm^{-1}.

Table III lists the stretching vibrations ν(N-H) and ν(Pt-Cl), as well as the deformation vibrations $\delta(NH_2)$ observed for the $[Pt(adam)Cl_3]^-$ complexes. In the infrared spectra of the $[Pt(adam)Cl_3]^-$ complexes, the presence of the amine is confirmed by three ν(N-H) vibrations between 3120 and 3282 cm^{-1} and by the $\delta(NH_2)$ vibrations between 1560 and 1586 cm^{-1}. Only one deformation band is present in the spectrum of $K[Pt(1\text{-}adam)Cl_3]$, while two bands are observed for $[NMe_4][Pt(2\text{-}adam)Cl_3]$. The spectrum of $K[Pt(MeNH_2)Cl_3].xH_2O$ published by Kharitivov et al. displayed two bands

in this region, attributed to the $\delta(NH_2)$ vibration (30), while in our spectrum for the same complex, only one band appears in this region at 1581 cm^{-1} (6). For the $[NMe_4][Pt(1-Madam)Cl_3]$ complex, the presence of two bands in the same region is probably due to the presence of $Pt(1\text{-}Madam)_2Cl_2$, since the ^{195}Pt-NMR spectrum showed two resonances. These sharp bands, characteristic of stretching and deformation vibrations for primary amines, are shifted to lower frequencies by about 26 to 177 cm^{-1}, indicating that coordination with platinum takes place via the nitrogen atom. Upon coordination to platinum, the N-H bond is weakened and so the force constant of the bond is reduced. In addition, the amine groups are often involved in hydrogen bonding with the chloride ligands which weakens the bonds and this also contributes in lowering the energy of the ν(NH) vibrations (5). These results are in good agreement with our earlier work on $[Pt(A)Cl_3]^-$ complexes (6). The spectra of all these complexes, except $K[Pt(DMNH)Cl_3]$, showed at least three peaks between 3120 and 3280 cm^{-1}, characteristic of ν(NH) vibrations for primary amines, which are slighltly higher in energy than for the adamantanamine complexes. The complex $K[Pt(DMNH)Cl_3]$ showed only one ν(NH) vibration at 3208 cm^{-1}, in the same region as for the adamantanamine complexes. This is in good agreement with a study on *trans*-$Pt(L)(RR'NH)Cl_2$ complexes ($L = C_2H_4$, PEt_3) where a decrease in the frequency of the NH stretching vibrations was observed with increasing bulkiness of the R group, R' being a hydrogen or an alkyl group (31-32). For the $K[Pt(A)Cl_3]$ complexes (6), there was also one vibration between 1568 and 1581 cm^{-1} for the N-H deformation mode. In addition to these bands, there are two sharp bands for each complex between 3522 and 3600 cm^{-1} and another band between 1590 and 1597 cm^{-1} (6). Similar values were found in the spectrum of $K[Pt(MeNH_2)Cl_3].xH_2O$ published by Kharitivov et al. (30). These bands have been assigned to stretching and deformation vibrations of water of hydration in the

complexes. The crystal structure of two of these complexes, $K[Pt(isoPr)Cl_3]\cdot 1/2H_2O$ and $K[Pt(CPA)Cl_3]\cdot 1/2H_2O$ (6,33) have confirmed the presence of one half molecule of water per platinum atom. It seems that the complexes with adamantanamine derivatives do not crystallize with water of hydration since these bands are absent in the IR spectra of the $[Pt(adam)Cl_3]^-$ complexes.

Table III. Main infrared bands of the ligands and $[Pt(adam)Cl_3]^-$ complexes in the solid state (cm^{-1}).

Compounds	ν(NH)	δ(NH_2)	ν(Pt-Cl)
1-adam	3342(m), 3265(m) 3172(w)	1608 (m)	-
2-adam	3350(m), 3285(w) 3184 (w)	1608 (m)	-
1-Madam	3389 (m) 3278(m)	1612 (m)	-
$K[Pt(1\text{-adam})Cl_3]$	3230(w), 3200(m) 3125 (w)	1570(m)	330(m)
$[NMe_4][Pt(2\text{-adam})Cl_3]$	3282(m), 3190(w) 3132(w)	1582(m) 1560(w)	332(s) 312(m)
$[NMe_4][Pt(1\text{-Madam})Cl_3]$*	3212(w), 3198(m) 3120(w)	1586(m) 1572(sh)	328(s)

m: medium; w: weak; sh: shoulder; s: strong
* contains 50% of $Pt(1\text{-Madam})_2Cl_2$

If L is considered as a point mass in space, the skeleton symmetry for a complex of the type $[Pt(L)Cl_3]^-$ (25) is C_{2v} and the group theory (Appendix 1) 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. From Table III, two bands are observed for $[NMe_4][Pt(2\text{-adam})Cl_3]$ at 312 and 332 cm^{-1}, while only one large band was observed for the two other complexes. The infrared spectrum of $[NMe_4][Pt(1\text{–}Madam)Cl_3]$ represents the superposition of this complex with the disubstituted amine compound $Pt(1\text{–}Madam)_2Cl_2$, since the ^{195}Pt-NMR spectrum showed the presence of the two compounds in approximately equal amounts. Group theory also predicts one infrared-active ν(Pt-N) vibration (A_1) in the spectra of the $[Pt(A)Cl_3]^-$ complexes. In a study on methylamine complexes by Kharitinov et al. (30), the ν(Pt-N) vibration has been located at 523 cm^{-1} for $K[Pt(MeNH_2)Cl_3]\cdot xH_2O$. In the spectra of $K[Pt(1\text{–adam})Cl_3]$ and $[NMe_4][Pt(2\text{-adam})Cl_3]$, there is one band for each complex in this region, at 555 and 508 cm^{-1}, respectively, but they are very low in intensity and it is difficult to assign them definitely to ν(Pt-N) vibrations. The spectrum of $[NMe_4][Pt(2\text{–adam})Cl_3]$ shows no band in this region.

3.3.4 Crystal Structure of [2-adamH][Pt(EtNH$_2$)Cl$_3$]

This crystal has been obtained from the filtrate of the reaction of K[Pt(EtNH$_2$)Cl$_3$] with 2-adam, which contained HCl from the washing of Pt(EtNH$_2$)(2–adam)Cl$_2$. It was apparently synthesized according to the following reactions:

$$K[Pt(EtNH_2)Cl_3] + 2\text{-adam} \xrightarrow{H_2O} Pt(EtNH_2)(2\text{-adam})Cl_2$$

$$Pt(EtNH_2)(2\text{-adam})Cl_2 + HCl \longrightarrow [2\text{-adamH}][Pt(EtNH_2)Cl_3]$$

Reaction of K[Pt(EtNH$_2$)Cl$_3$] with 2-adamantanamine (2-adam) yield the mixed-amine complex Pt(EtNH$_2$)(2-adam)Cl$_2$ but, upon treatment with dilute HCl during the work-up of the product, yellow crystals of the (2–adamH)$^+$[Pt(EtNH$_2$)Cl$_3$]$^-$ salt are also produced. This complex is probably the result of displacement of the coordinated adamantanamine ligand by Cl$^-$ and subsequent quaternization of the amine group. This compound was characterized by X-ray diffraction and the results have been published recently (34).

The structure of a crystal of [2-C$_{10}$H$_{15}$NH$_3$][Pt(EtNH$_2$)Cl$_3$] was first determined in the space group P2$_1$/c by X-ray diffraction with MoKα (λ= 0.71069 Å) radiation. From the 4698 reflections measured, only 1558 (I>2.5σ(I)) reflections were observed and used for the structure determination. The intensities were corrected for Lorentz and polarization factors, but no correction for absorption was applied. Usually, correction for absorption gives better results but, in our case, the results were worse after applying this correction. The crystal data in this space group are presented in Table IV.

The X-ray diffraction study revealed significant distortion of the adamantane ring as seen by the high thermal factors resulting in high e.s.d.'s in the bond distances and angles. The C-C distances for the adamantanamine varied between 1.32(8) and 1.73(3)Å for an average C-C of 1.55(12)Å. The C-C-C angles varied between 88(6)° and 128(6)° with a mean value of 108°. It was not possible to refine the structure lower than R = 0.099, which was unacceptable.

Table IV. Crystallographic data for the $[C_{10}H_{15}NH_3][Pt(EtNH_2)Cl_3]$ complex.

	First crystal	Second crystal
Space group	$P2_1/c$	$P2_1/n$
Formula	$PtCl_3N_2C_{12}H_{25}$	$PtCl_3N_2C_{12}H_{25}$
Molecular weight	498.80 g/mol	498.80 g/mol
Crystalline system	monoclinic	monoclinic
Cell parameters	a = 12.411(15)Å	a = 12.401(10)Å
	b = 6.845(7)Å	b = 6.859(15)Å
	c = 25.545(30)Å	c = 20.199(15)Å
	β = 129.07(6)°	β = 100.72(6)°
Volume	1685(3) $Å^3$	1688(2) $Å^3$
Z	4	4
Calculated density	1.973 Mg/m^3	1.962 Mg/m^3
F(000)	960	960
Wavelenght λ(MoKα)	0.71069 Å	0.71069 Å
R	0.099	0.060
wR	0.100	0.049

A second crystal of superior quality was then studied. It was hoped that better data would be obtained and that the thermal factors of the atoms would be reduced. In order to reduce the correlation factors, the non-standard $P2_1/n$ space group was chosen.

The crystal data of 2-adamantylammonium trichloro(ethylamine)platinate(II) in this space group are presented in Table IV.

The difference between the two unit cells is that the glide plane is along the diagonal of the unit cell (which was the c axis of the unit cell defined by the space group $P2_1/c$) (Figure 6.) In Figure 6, the cell parameters for the space group $P2_1/c$ are defined by a, b, c and $\beta = 129°$ while the corresponding values for the space group $P2_1/n$ are a',b', c' and $\beta' = 101°$.

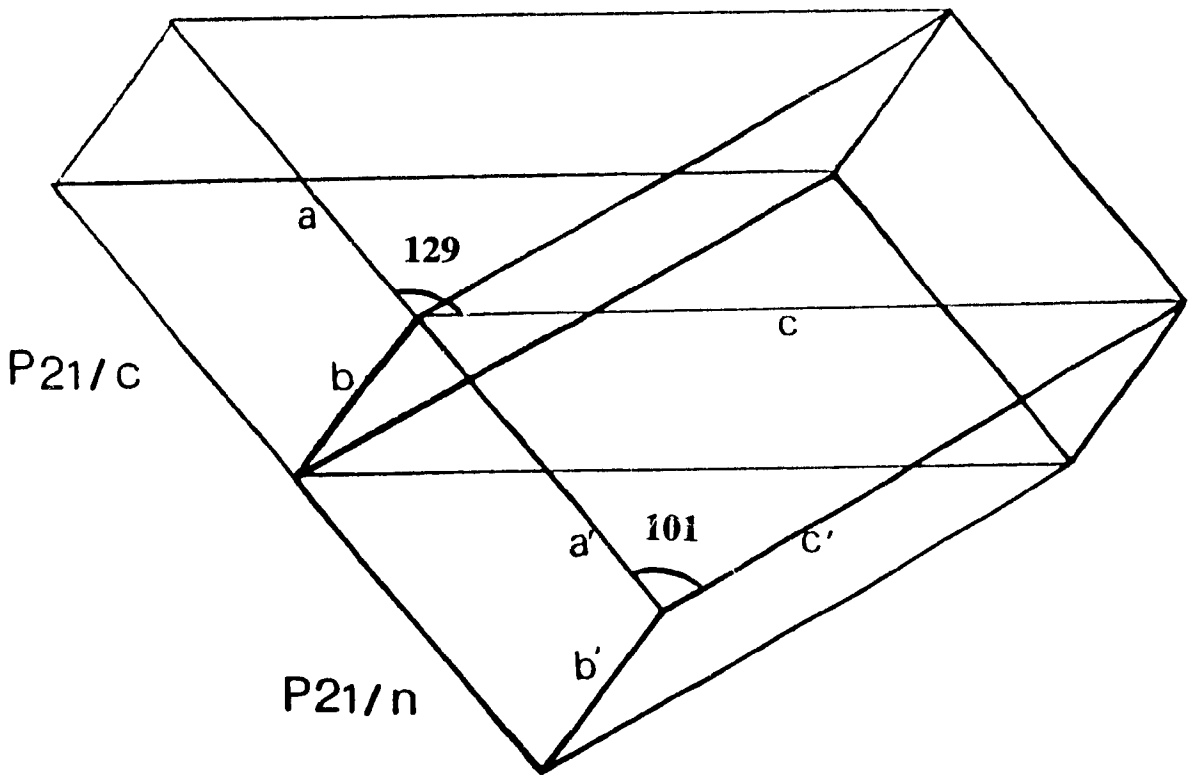


Figure 6. Differences between the cells defined by the space group $P2_1/c$ and $P2_1/n$.

The faces and dimensions (mm) of the yellow crystal are: $10\bar{1}$-$\bar{1}01$ (0.120), $10\bar{3}$-$\bar{1}03$ (0.100), 101-$\bar{1}0\bar{1}$ (0.192), $1\bar{1}1$-$\bar{1}1\bar{1}$ (0.366) and 111-$\bar{1}\bar{1}\bar{1}$ (0.366). The intensity data were measured on a Syntex $P\bar{1}$ diffractometer with graphite-monochromatized MoKα radiation. The space group was determined from a set of precession photographs and the cell parameters were determined from the refined angles of 15 centered reflections (2θ = 7.28-23.91°). From the 4236 independent reflections measured up to $2\theta < 55°$ by a 2θ-θ scan technique (range of hkl: h = 0 → 16, k = 0 → 8, l = -26 → 25), 1801 unique observed reflections ($I_{net} > 2.5\ \sigma(I)$) were used to solve the structure. The scan rate and the $\sigma(I)$ were calculated as in Melanson et al. (35). The standard reflections used were 5, 1, -1; 1, 3, 1 and 0, 0, 6, with variations less than 2.0%. Absorption correction (μ(MoKα) = 8.86 mm^{-1}) was based on the equations of the crystal faces (transmission factors from 0.242 to 0.465) and the data were corrected for Lorentz and polarization effects.

The position of Pt was determined from the three-dimensional Patterson map and the other non-hydrogen atoms were located by structure-factor and Fourier-map calculations. The H atoms were fixed at the calculated positions (C–H = 0.95Å and N–H = 0.85Å) with isotropic Ueq = 0.076, except for $-CH_3$ (H could not be located). One H atom in the NH_3^+ group was located and the other two H were calculated. The refinement was done by full matrix least-squares calculations minimizing $\Sigma w(|F_o|-|F_c|)^2$ and the ratio of maximum least-squares shift to e.s d. in the final refinement cycle was <0.9 for C(2) and <0.5 for the other atoms. The isotropic secondary extinction corrections were done according to Coppens and Hamilton (36). The scattering curves used were those from Cromer and Waber (37) for Pt, Cl, N, C and of Stewart, Davidson and Simpson (38), for H. The anomalous dispersion terms of Pt and Cl from Cromer (39) were included in the

calculations, which were done on a Cyber 830 with programs already described (35). The individual weights were calculated according to $w = 1/\sigma^2(F)$. The maximum residual peak was close to the platinum atom in its final Fourier synthesis with $\Delta\rho_{max}$ = 1.0 eÅ^{-3}. The goodness of fit was 1.36; the residual index, R = 0.060 and the weighted residual index, wR = 0.049.

The refined atomic parameters are given in Table V. A labeled diagram of the complex [2-$C_{10}H_{15}NH_3$][Pt($EtNH_2$)Cl_3] is shown in Figure 7. As expected, the platinum complexed ion has a square-planar geometry and the angles around the Pt atom are close to 90 and 180°. The weighted best coordination plane was calculated through the five atoms and the deviations are: Pt, -0.0005(5); Cl(1), 0.018(4); Cl(2), 0.021(4); Cl(3), -0.005(4) and N(2), -0.05(1)Å.

The bond lengths and angles are listed in Table VI. The Pt-Cl bonds are 2.281(4), 2.278(4) for the *cis* bonds and 2.301(4) Å for the *trans* bond. The two Pt-Cl bonds *cis* to the amine ligand seem slightly shorter than the *trans* bond. The values found in [Pt(NH_3)Cl_3]$^-$ are 2.288 (27), 2.280 (14)Å for the *cis* bonds and 2.317(7) Å for the *trans* bond (40). In [Pt(isopropylamine)Cl_3]$^-$, the corresponding values are 2.296(4), and 2.299(3) for the *cis* bonds and 2.320(3)Å for the *trans* bond (6), while in [Pt(cyclopentylamine)Cl_3]$^-$ they are 2.311(4), 2.302(4) and 2.315(4) (33). In K[Pt(t–butylamine)Cl_3], the *cis* bonds are 2.299(2) and 2.314(2) while the *trans* bond is 2.317(2)Å (41). In [Pt(NH_3)$_4$][Pt(isopropylamine)Cl_3]$_2$, the corresponding values are 2.301(3), 2.300(4) and 2.321(4) Å (41). In most of these compounds, the *trans* bond seems slightly longer but the difference might not be significant. The slight lengthening may be due to a higher *trans* influence of amines or to the fact that in these compounds the *trans* chloride ligand is usually more involved in the hydrogen bonding system than are

the other chloride ligands. The Pt-N bond is 2.03(1)Å and agrees well with the published values for aminechloroplatinum(II) complexes (6, 33, 42-44) The organic ligand is normal with bond distances N(2) - C(11) = 1.47(2) and C(11) - C(12) = 1.49(2) Å and angles Pt - N(2) - C(11) = 116.9(9) and N(2) - C(11) - C(12) = 117(1)°.

Table V. Atomic coordinates (x 10^4 for Pt, Cl and x 10^3 for C, N) with their e.s.d.'s. and thermal parameters Ueq (x 10^4 for Pt, Cl, N and 10^3 for C).
$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}\, a_i^* a_j^* a_i.a_j$

	x	y	z	U_{eq}
Pt	1103.9(4)	2265.4(8)	1753.5(3)	440
Cl(1)	1847(3)	-362(5)	1311(2)	678
Cl(2)	417(3)	4878(6)	2235(2)	708
Cl(3)	354(3)	3385(6)	694(2)	746
N(1)	551(1)	275(2)	416(1)	824
N(2)	171(1)	128(2)	270(1)	535
C(1)	758(2)	322(5)	467(1)	129
C(2)	673(6)	413(12)	431(2)	503
C(3)	667(2)	473(5)	357(2)	206
C(4)	754(3)	624(3)	380(2)	137
C(5)	867(3)	552(5)	408(3)	219
C(6)	834(3)	454(8)	479(2)	289
C(7)	810(6)	211(6)	433(2)	407
C(8)	820(2)	234(5)	360(2)	222
C(9)	717(2)	319(6)	330(1)	184
C(10)	903(2)	394(6)	384(1)	141
C(11)	97(1)	13(2)	303(1)	82
C(12)	135(1)	-33(3)	376(1)	85

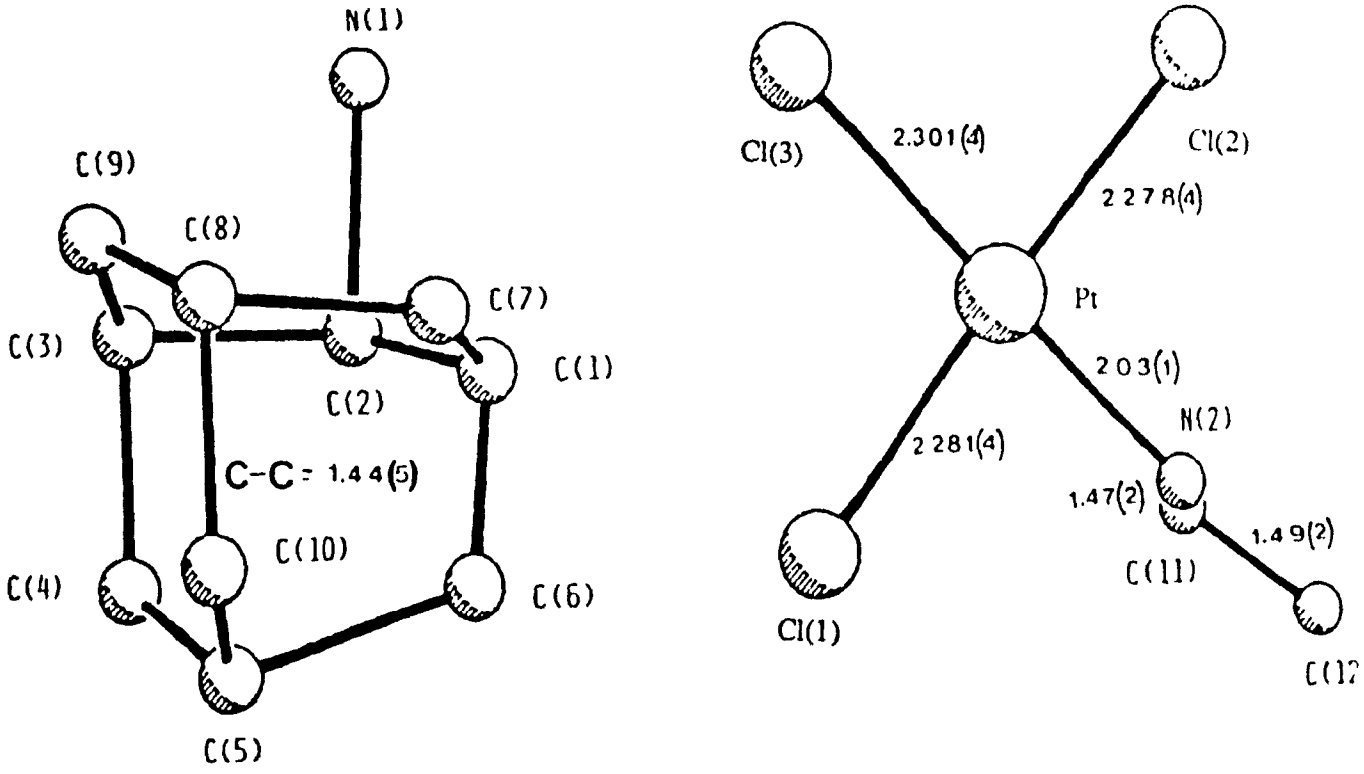


Figure 7. Structure of the complex $[C_{10}H_{15}NH_3][Pt(EtNH_2)Cl_3]$ with the atomic numbering (the H atoms are absent).

Most of the carbon atoms in the 2-adamantylammonium cage are disordered as evidenced by the high thermal factors especially those of C(2) and C(7), resulting in very high e.s.d.'s in the bond distances and angles. It was not possible to resolve the disorder. The C - C bond distances vary from 1.28(6) to 1.72(6) Å with an average value of 1.44 Å, while the C - C - C angles range from 89(3) to 127(4)° (average = 108°).

Table VI. Bonds distances(Å) and angles(°).

Atom-atom	Distance (Å)	Atom-atom	Distance (Å)
Pt-Cl(1)	2.281(4)	C(4)-C(5)	1.49(5)
Pt-Cl(2)	2.278(4)	C(5)-C(6)	1.72(6)
Pt-Cl(3)	2.301(4)	C(5)-C(10)	1.29(5)
Pt-N(2)	2.03(1)	C(7)-C(8)	1.51(5)
C(1)-C(2)	1.32(7)	C(8)-C(9)	1.44(4)
C(1)-C(6)	1.30(5)	C(8)-C(10)	1.52(4)
C(1)-C(7)	1.28(6)	C(11)-C(12)	1.49(2)
C(2)-C(3)	1.54(6)	N(1)-C(2)	1.75(8)
C(3)-C(4)	1.50(4)	N(2)-C(11)	1.47(2)
C(3)-C(9)	1.38(5)		

Atom-atom-atom	Angle (°)	Atom-atom-atom	Angle (°)
Cl(1)-Pt-Cl(2)	177.6(1)	C(2)-C(1)-C(7)	115(4)
Cl(1)-Pt-N(2)	89.9(3)	C(2)-C(3)-C(4)	89(3)
Cl(1)-Pt-Cl(3)	91.3(1)	C(2)-C(3)-C(9)	104(4)
Cl(2)-Pt-N(2)	87.9(3)	C(3)-C(4)-C(5)	117(3)
Cl(2)-Pt-Cl(3)	90.9(1)	C(3)-C(9)-C(8)	124(3)
Cl(3)-Pt-N(2)	178.1(3)	C(4)-C(3)-C(9)	108(3)
Pt-N(2)-C(11)	116.9(9)	C(4)-C(5)-C(6)	95(3)
N(1)-C(2)-C(1)	114(5)	C(4)-C(5)-C(10)	120(3)
N(1)-C(2)-C(3)	95(4)	C(5)-C(10)-C(8)	118(3)
N(2)-C(11)-C(12)	117(1)	C(6)-C(1)-C(7)	95(3)
C(1)-C(2)-C(3)	123(5)	C(6)-C(5)-C(10)	98(3)
C(1)-C(6)-C(5)	113(3)	C(7)-C(8)-C(9)	104(3)
C(1)-C(7)-C(8)	127(4)	C(7)-C(8)-C(10)	87(3)
C(2)-C(1)-C(6)	104(4)	C(9)-C(8)-C(10)	115(3)

From previous work on adamantane derivatives (45-46), disorder of the adamantane ring system was expected at room temperature. Our values can be compared to those obtained for the disordered room-temperature phase of 1-adamantanecarboxylic acid, where the C - C bonds range from 1.453(16) to 1.602(16) Å and the C - C - C angles from 103.1(9) to 116.0 (11)°. The corresponding values for the ordered low-temperature phase of the acid are 1.527(4) to 1.548(3)Å and 108.4(2) to 111.3(2)° (46). Adamantane ($C_{10}H_{16}$) itself and many of its derivatives are well known to undergo order-disorder phase transitions (47) over a wide temperature range and with a large variation in entropy of the transition. With the exception of 1–adamantanol, $C_{10}H_{15}OH$ (48), the phase transitions occur below room temperature and the room-temperature phases are usually disordered (45-46, 49-50). The calculated torsion angles of the adamantyl-ammonium cage in $[2\text{-}C_{10}H_{15}NH_3][Pt(EtNH_2)Cl_3]$, listed in Table VII, indicate distortion from the expected perfect chair conformation. The overall mean torsion angle of 52(5)° is not very close to the expected value of 60° for a perfectly staggered chair conformation with tetrahedral bond angles. Figure 8 shows the packing of the molecules in the unit cell. It consists of layers of anions and cations parallel to the diagonal plane (101). The crystal structure is stabilized by hydrogen bonding and the distances and angles between atoms involved in hydrogen bonds are shown in Table VIII. The hydrophilic moiety of $[2\text{-}C_{10}H_{15}NH_3]^+$ is oriented towards the chloride ligands of the Pt complexed anions. All the H atoms of the $-NH_3^+$ group are involved in hydrogen bonds with the chloride ligands. Two of these are shown in Figure 8, the third one is downward along the b axis. One of the H atoms of the ethylamine ligand is also involved in hydrogen bonding with Cl(1). The N ··· Cl distances vary from 3.12(2) to 3.34(1) Å. Apart from these hydrogen bonds, there are no other short contacts. In contrast to similar complexes (6, 33), this molecule crystallizes without water of

hydration. The hydrogen bonds formed between the large cation and the chloride ligands might be sufficient to stabilize the crystal. This suggestion is supported by the absence of water molecules in the crystal structure of $[Pt(NH_3)_4][Pt(isopropylamine)Cl_3]_2$ (41). The anisotropic thermal parameters (Table IX), the equation and deviations from the best weighted least-squares plane (Table X) and the calculated H coordinates (Table XI) are shown in Appendix 2.

Table VII. Torsion angles (°) for the adamantylammonium cage in the crystal $[C_{10}H_{15}NH_3][Pt(EtNH_2)Cl_3]$.

Atom-atom-atom-atom	angle(°)	Atom-atom-atom-atom	angle(°)
C1-C2-C3-C4	-70(6)	C3-C4-C5-C10	34(5)
C2-C3-C4-C5	69(4)	C4-C5-C10-C8	-33(5)
C3-C4-C5-C6	-69(4)	C5-C10-C8-C9	36(4)
C4-C5-C6-C1	59(4)	C10-C8-C9-C3	-46(4)
C5-C6-C1-C2	-59(5)	C8-C9-C3-C4	46(4)
C6-C1-C2-C3	73(6)	C9-C3-C4-C5	-35(4)
C1-C7-C8-C10	77(5)	C1-C2-C3-C9	38(6)
C7-C8-C10-C5	-67(4)	C2-C3-C9-C8	-48(5)
C8-C10-C5-C6	67(4)	C3-C9-C8-C7	45(4)
C10-C5-C6-C1	-62(4)	C9-C8-C7-C1	-33(5)
C5-C6-C1-C7	58(4)	C8-C7-C1-C2	28(7)
C6-C1-C7-C8	-80(5)	C7-C1-C2-C3	-30(7)

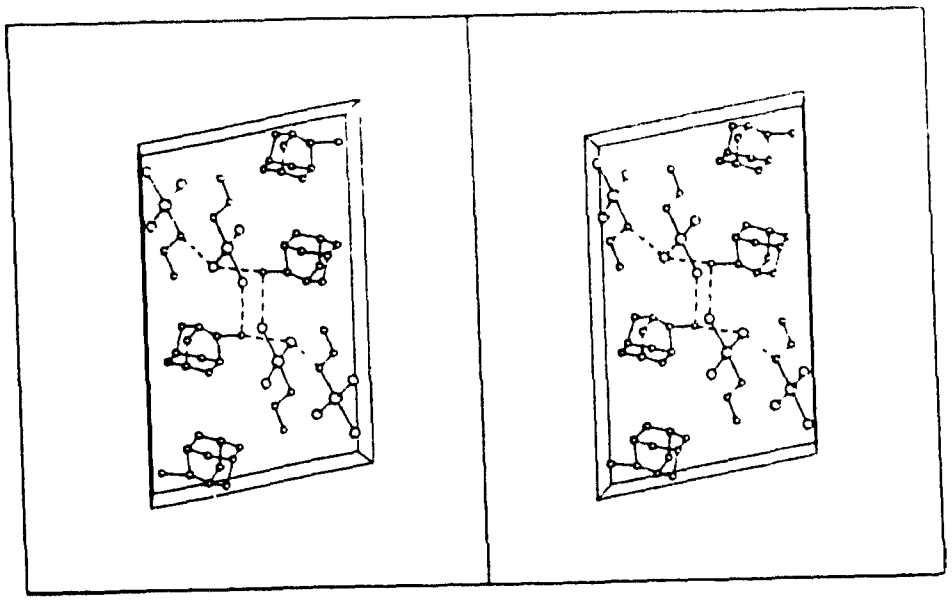


Figure 8. Stereoscopic view of the packing in the unit cell (c axis horizontal, down b axis; dashed lines correspond to H bonds).

Table VIII. Distances (Å) and angles (°) of atoms involved in possible hydrogen bonds

Atom-atom	Distance (Å)	Atom-atom-atom	Angle (°)
N(1)-H···Cl(1)[a]	3.18(1)	C(2)-N(1)···Cl(1)	123(2)
N(1)-H···Cl(3)[b]	3.23(2)	C(2)-N(1)···Cl(3)	99(2)
N(1)-H···Cl(3)[a]	3.12(2)	C(2)-N(1)···Cl(3)	141(2)
N(2)-H···Cl(1)[a]	3.34(1)	Pt-N(2)···Cl(1)	113.5(4)
		C(11)-N(2)···Cl(1)	114.2(8)

a) -x + 1/2, y + 1/2, -z + 1/2

b) x + 1/2, -y + 1/2, z + 1/2

3.4 References

1. A. Cossa. Gazz. Chim. Ital. **20**, 725 (1890).
2. Y.P. Jeannin and D.R. Russell. Inorg. Chem. **9**, 778 (1970).
3. A. Wemer and F.Z.Z. Fassbender. Anorg. Chem. **15**, 123 (1897).
4. P.C. Kong and F.D. Rochon. Can. J. Chem. **56**, 441 (1978).
5. F.D. Rochon and L. Fleurent. Inorg. Chim. Acta, **143**, 81 (1988).
6. F.D. Rochon, R. Melanson and M. Doyon. Inorg. Chem. **26**, 3065 (1987).
7. M.J. Cleare. Platinum Coordination Complexes in Cancer Chemotherapy, T. A. Connors and J. J. Roberts Ed. 12 (1974).
8. P.D. Braddock, T.A. Connors, M.Jones, A.R. Khokhar, D.H. Melzack and M.L. Tobe. Chem.-Biol. Interactions, **11**, 145 (1975).
9. F.D.Rochon and P.C. Kong. Can. J. Chem. **64**, 1894 (1986).
10. A.J. Hay, A.J. Wolstenholme, J.J. Shehel and M.H. Smith. The EMBO Journal, **4** (11), 3021 (1985).
11. A. Widell, B.G. Hansson, B. Oeberg and E. Nordenfelt. Antiviral Research, **6**(2), 103 (1986).
12. R.D. Fletcher, J.E. Hirschfield and H. Forbes. Nature, **207**, 664 (1965).
13. Y.K. Ho, M. T. Hakala and S.F. Zakrsewski. Cancer Research, **32**, 1023 (1972).
14. Shionogi and Co Ltd. Jpn Kokai Tokkio Koho JP 58 79994 (1983).
15. B. Rosenberg, L. Van Camp, J.E. Trosko and V.H. Mansour. Nature, **222**, 385 (1969).
16. F.D. Rochon, R. Melanson and M. Doyon. Can. J. Chem.. **67**, 2209 (1989).
17. C. Bensimon, Ph.D. Thesis, Université de Montréal (1990).

18. W. Freeman, P.S. Pregosin, S.N. Sze and L.M. Venanzi. J. Magn. Res. **22**, 473 (1976).

19. J.J. Pesek and W.R. Mason. J. Magn. Res. 25, 519 (1977).

20. CRC Handbook of Chemistry and Physics, 70th Edition R.C. Weast Editor, CRC Press Inc. D-161-2 (1990).

21. G.L. Grunewald, A.M. Warner, S.J. Hays, S.J. Bussel and M.K. Seals. J. Med. Chem. **15**, 747 (1972).

22. R.G. Kidd and R.J. Goodfellow in F.K. Harris and B. Nann (Eds). NMR and the Periodic Table, Academic Press, London (1978).

23. F.J. Kift, G. W. Canters, J.H.H. Den Hartog, A.T.M. Marcelis and J.J. Reedijk. J. Am. Chem. Soc. **106**, 3644 (1984).

24. H. Motchi, S.N. Sze and P.S. Pregosin. Helv. Chim. Acta, **62**, 2086 (1979).

25. L.G. Marzilli, Y.Hayden and M.D. Reily. Inorg. Chem., 25, 974 (1986).

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

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

28. E. Grech, Z. Malrski and L. Sobczyk. J. Molecular Structure, **115**, 327 (1984).

29. L.J. Bellamy. "The Infrared Spectra of Complex Molecules", Methuen and Co. Ltd, 250, (1966).

30. Y.Y. Kharitinov, I.K. Dymina and T.N. Leonova. Russ. J. Inorg. Chem. **13** (5), 709 (1968).

31. J. Chatt, L. A. Duncanson and L. M. Venanzi. J. Chem. Soc. 2712 (1956).

32. L. A. Duncanson and L.M. Venanzi. J. Chem. Soc. 3841 (1960).

33. C. Dion, A. Beauchamp, F.D. Rochon and R. Melanson. Acta Cryst. **C45**, 852 (1989).

34. F.D. Rochon, R. Melanson, M. Doyon and I.S. Butler. Acta Cryst. **C46**, 584 (1990).

35. R. Melanson and F.D. Rochon. Can. J. Chem. **53**, 2371 (1975).

36. P. Coppens and W.C. Hamilton. Acta Cryst. **A26**, 71 (1970).

37. D.T. Cromer and J.T. Waber. Acta Cryst. **18**, 104 (1965).

38. R.F. Stewart, E.R. Davidson and W.T. Simpson. J. Chem. Phys. **42**, 3175 (1965).

39. D.T. Cromer. Acta Cryst. **18**, 17 (1965).

40. Y.P. Jeannin and D.R. Russell, Inorg. Chem. **9**(4), 778 (1970).

41. F.D. Rochon and R. Melanson. Acta Cryst. (1991) in press.

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

43. R. Melanson and F.D. Rochon. Acta Cryst. **C40**, 793 (1984).

44. R. Melanson and F.D. Rochon. Acta Cryst. **C41**, 350 (1985).

45. F. Belanger-Gariepy, F. Brisse, P.D. Harvey, I.S. Butler and D.F.R. Gilson. Acta Cryst. **C43**, 756 (1987).

46. F. Belanger-Gariepy, F. Brisse, P.D. Harvey, I.S. Butler and D.F.R. Gilson. Acta Cryst. Can. J. Chem. 68, 1163 (1990).

47. J. Donohue and S.H. Goodman. Acta Cryst. **22**, 352 (1967).

48. P.D. Harvey, D.F.R. Gilson and I.S. Butler. Can. J. Chem. **65**, 1757 (1987).

49. G..H. Wahl, R.L. Greene and J. Bordner. J.C.S. Chem. Comm. 927 (1973).

50. K.K. Chacko and R. Zand. Acta Cryst. **B29**, 2681 (1973).

CHAPTER 4.

Synthesis

of

$Pt(adam)_2X_2$ and $Pt(A)(adam)X_2$ (X = Cl, I) Complexes

4.1 Introduction

The screening range, antitumor activity, toxicity and solubility of platinum complexes would be greatly expanded if *cis* mixed-ligand square-planar complexes could be systematically synthesized. It is already known that platinum amine complexes with cyclic amines have better antitumor activity than does cisplatin, *cis*-$Pt(NH_3)Cl_2$, or other non-cyclic amine complexes (1). The changes in therapeutic index are structure related and are caused by a decrease in toxicity as the ring size increases . The low toxicity is thought to be due to the greater flexibility of the larger rings, which permits orientation of these rings so that they protect the axial positions above and below the platinum plane, thereby preventing coordination to the sulfur atoms in the kidney tubules (2). Some mixed-amine platinum(II) complexes of the type $Pt(NH_3)$(cycloalkylamine)Cl_2 have been synthesized and their antitumor activities and toxicities compared to those of cisplatin and Pt(cycloalkylamine)$_2Cl_2$ (3, 4). It seems that the toxicities of the mixed-amine compounds are much greater than those of the corresponding Pt(cycloalkylamine)$_2Cl_2$. The toxicity values for the mixed-amine complexes vary from 6 to 20 mg kg^{-1} compared to 57 to 3200 mg kg^{-1} for the complexes with two cyclic amines (1-4). The mixed-amine complexes have similar toxicities to that of cisplatin (13 mg kg^{-1}).

The choice of adamantanamine derivatives as ligands for platinum(II) has been guided by their biological activity (5-9). Indeed, the aminoadamantane derivatives in general (particularly 1-adamantanamine) show antiviral activity against influenza A. This antiviral activity is due to an ionic change at the cell surface that blocks the penetration of the virus into the cell, which thus remains susceptible to inactivation by antibodies (10). This inhibiting effect increases when a metal is added to the amine due to the enhanced lipid solubility of the metal complexes (11). 1-adamantanamine also has antitumor

activity by blocking DNA replication. When adamantanamine is bonded to the substrate, it increases the lipid solubility of the new molecule formed which can then bind to the receptor more easily (12, 13). Shionogi and Co. Ltd (14) have synthesized platinum(II) complexes with 1,2-diaminoadamantane and these complexes exibit antitumor activity similar to that of platinum(II) complexes with two cyclopentylamine ligands. Braddock et al. (1) have studied the antitumor activity of $Pt(adam)_2Cl_2$ (adam = 1-adamantanamine and 2-adamantanamine) (Table XII).

Table XII. Characterization and antitumor activity of platinum(II) complexes with two adamantanamine ligands (from ref. 1).

		Elemental analysis				Infrared	Anutumor activity	
		%C	%H	%N	%Cl	ν(Pt-Cl)	LD_{50}	ID_{90}
$Pt(1\text{-adam})_2Cl_2$	calc	42.2	6.0	4.9	12.5			
	exp	42.1	5.9	4.7	-	328,324	>625	>625
$Pt(2\text{-adam})_2Cl_2$	calc	42.2	6.0	4.9	12.5			
	exp	42.1	6.0	4.8	-	331,312	>800	>800

The compounds are inactive with respect to the PC6, Walker and L1210 tumor systems (1) . The authors claimed that: " ...with the three fused six-mernbered rings,... the generally inert nature of these complexes may arise from their low solubility" (1). We have repeated the synthesis of the compound with 1-adamantanamine and we found that their synthetic method is inadequate. These results will be discussed later in this chapter.

The development of a new method for the synthesis of monoamine platinum complexes, K[Pt(A)Cl_3] (15), has opened the door for the rational preparation of mixed-amine complexes. Since 1-adamantanamine has been reported to have antitumor activity against angiocarcinoma and pancreatic carcinoma, it was felt that it would be interesting to examine the coordination of adamantanamine derivatives, which are polycyclic molecules, to platinum(II) to see if the antitumor activity of the resulting complexes would be enhanced, and concomitantly increase the screening range of these potential antitumor agents. A series of mixed-amine platinum(II) complexes, Pt(A)(adam)X_2 (X = Cl, I ; A = methylamine, ethylamine, cyclobutylamine, cyclopentylamine and adam = 1–adamantanamine, 2-adamantanamine and 1-methyladamantanamine) has been synthesized. Our aim was also to extend the chemistry of platinum complexes in order to have, in the future, some clues to the identification of the structure of new platinum complexes.

4.2 Experimental

Pt(A)(adam)Cl_2 One mmole of adamantanamine was added to an aqueous solution (5 ml) of one mmole of K[Pt(A)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_2O_5 for 12 h.

Compounds	Yield	Dec. pt (°C)		Elemental analysis % C	% H	% Cl	% N
Pt($MeNH_2$)(1-adam)Cl_2	60%	205-217	Calcd:	29.5	4.9	15.8	6.3
			Found:	28.5	4.8	14.2	6.0
Pt($EtNH_2$)(1-adam)Cl_2	47%	195-220	Calcd:	31.2	5.2	15.3	6.1
			Found:	31.3	5.7	14.5	6.2
Pt(CBA)(1-adam)Cl_2	90%	206-225	Calcd:	34.4	5.4	14.4	5.7
			Found:	34.1	5.7	13.8	5.7
Pt(CPA)(1-adam)Cl_2	16%	195-217	Calcd	35.9	5.6	14.1	5.6
			Found:	34.1	5.6	13.3	5.3
Pt($MeNH_2$)(2-adam)Cl_2	65%	192-212	Calcd:	29.5	4.9	15.8	6.3
			Found:	29.9	4.9	15.9	6.2
Pt($EtNH_2$)(2-adam)Cl_2	24%	170-192	Calcd:	31.2	5.2	15.3	6.1
			Found:	30.9	5.2	15.1	6.2
Pt($MeNH_2$)(1-Madam)Cl_2	44%	195-209	Calcd:	31.2	5.2	15.3	6.1
			Found:	31.8	4.8	13.5	5.6

Pt(adam)$_2Cl_2$ One mmole (0.514 g) of K_2[$PtCl_4$] and 2 mmoles of the adamantanamine ligand were heated in DMF solution at 80°C for 3 h. The DMF solutions were concentrated as much as possible, cooled to ~0°C, and the KCl which had formed

was filtered off. The ^{195}Pt-NMR spectra of the solutions were measured at room temperature. The mixtures was then evaporated to dryness and the yellow residues were washed sequentially with ether, acetone and water, to remove DMF, K[Pt(adam)Cl_3] and KCl, respectively. After drying briefly in air, the residues were washed with ether and dried over P_2O_5.

Compounds	Yield	Dec. pt (°C)
Pt(1-adam)$_2Cl_2$	65%	180-205
Pt(2-adam)$_2Cl_2$	72%	185-215
Pt(1-Madam)$_2Cl_2$	68%	195-225

Pt(A)$_2I_2$, Pt(adam)$_2I_2$ and [Pt(A)I_2]$_2$ The compounds with methylamine, ethylamine, cyclobutylamine, cyclopentylamine, dimethylamine, 1-adamantanamine, 2-adamantanamine and 1-methyladamantanamine were synthesized as already described in the literature (3, 16).

Compounds	Dec. pt (°C)	Elemental analysis	% C	% H
Pt(1-adam)$_2I_2$	164-279	Calcd:	32.0	4.6
		Found	32.5	4.8
Pt(2-adam)$_2I_2$	250-295	Calcd:	32.0	4.6
		Found	33.4	4.5
Pt(1-Madam)$_2I_2$	188-295	Calcd:	33.9	4.9
		Found:	36.5	5.5

Pt(A)(adam)I_2 The requisite adamantanamine ligand (1.5 mmole) was added to an aqueous solution of 1 mmole of $[Pt(A)I_2]_2$ 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 under P_2O_5. The yields were almost quantitative.

Compounds	Dec. pt (°C)	Elemental analyses	% C	% H
$Pt(MeNH_2)$(1-adam)I_2	160-175	Calcd:	20.9	3.5
		Found:	24.3	3.7
$Pt(MeNH_2)$(2-adam)I_2	171-195	Calcd:	20.9	3.5
		Found:	23.1	3.8
$Pt(EtNH_2)$(2-adam)I_2	140-170	Calcd:	22.3	3.8
		Found:	22.8	3.6
Pt(CBA)(2-adam)I_2	185-200	Calcd:	25.0	3.9
		Found:	26.6	4.2
Pt(CPA)(2-adam)I_2	186-212	Calcd:	26.3	4.1
		Found:	26.6	4.4
$Pt(EtNH_2)$(1-Madam)I_2	205-240	Calcd:	23.7	4.0
		Found:	34.8	5.2
$Pt(MeNH_2)$(1-Madam)I_2	130-168	Calcd:	22.3	3.6
		Found:	26.5	4.1

4.3 Results and Discussion

4.3.1 Synthesis of $Pt(adam)_2X_2$ and $Pt(A)(adam)X_2$ Complexes

The $Pt(A)(adam)Cl_2$ complexes were synthesized according to the following reaction:

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

The complexes with A = $MeNH_2$, $EtNH_2$, CBA, CPA and adam = 1-adam, 2-adam and 1-Madam were prepared. In water, the *cis* isomers should be formed first since the *trans* effect of chloride is greater than the *trans* effect of amines but other factors like the bulkiness of the ligands might lead to the formation of the *trans* isomers. The compounds were first washed with dilute HCl to get rid of the free adamantanamine ligand. This explains the second peak in ^{195}Pt-NMR spectra in the region of $[Pt(A)Cl_3]^-$ and will be discuss later in section 4.3.2. From the moment it was demonstrated that HCl reacts with coordinated adamantanamine, washing with HCl was replaced by washing with a large quantity of water. The presence of the second peak in ^{195}Pt-NMR spectra was then eliminated.

All the products isolated are insoluble in water, but they are soluble in DMF and DMSO. For the complexes $Pt(MeNH_2)(2\text{-adam})Cl_2$, $Pt(EtNH_2)(2\text{-adam})Cl_2$, $Pt(EtNH_2)(1\text{-adam})Cl_2$ and $Pt(CBA)(1\text{-adam})Cl_2$, the elemental analyses are very good. For the complexes $Pt(MeNH_2)(1\text{-adam})Cl_2$, $Pt(CPA)(1\text{-adam})Cl_2$ and $Pt(MeNH_2)(1\text{-Madam})Cl_2$, the results show the presence of impurities. The chloride values are lower than expected, probably due to the presence of free adamantanamine ligand, since there is only one species detected by ^{195}Pt-NMR spectroscopy. These new compounds were

characterized by their NMR, IR and Raman spectra and the results will be discussed in Sections 4.3.2 and 4.3.3.

The $Pt(adam)_2Cl_2$ complexes were synthezised according to the following reaction:

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

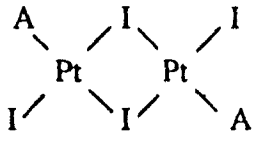
The compounds were isolated immediately after recording their ^{195}Pt-NMR spectra. The DMF solutions were concentrated as much as possible, cooled to ~0°C and the KCl was filtered off. The ^{195}Pt-NMR spectra of the solutions were measured at room temperature (see Section 4.3.2). The DMF solvent was then evaporated off and the resulting yellow residues were washed with ether to remove DMF and unreacted ligands. Further washing with acetone and water eliminated the $[Pt(L)Cl_3]^-$ complex and KCl. The yields varied from 65 to 72 %. The different compounds were characterized by IR and Raman spectroscopy (see Section 4.3.3).

The disubstituted iodo and the iodo-bridged complexes, $Pt(A)_2I_2$, $Pt(adam)_2I_2$ and $[Pt(A)I_2]_2$, were synthesized as described previously (3, 16). The different steps in the preparation are:

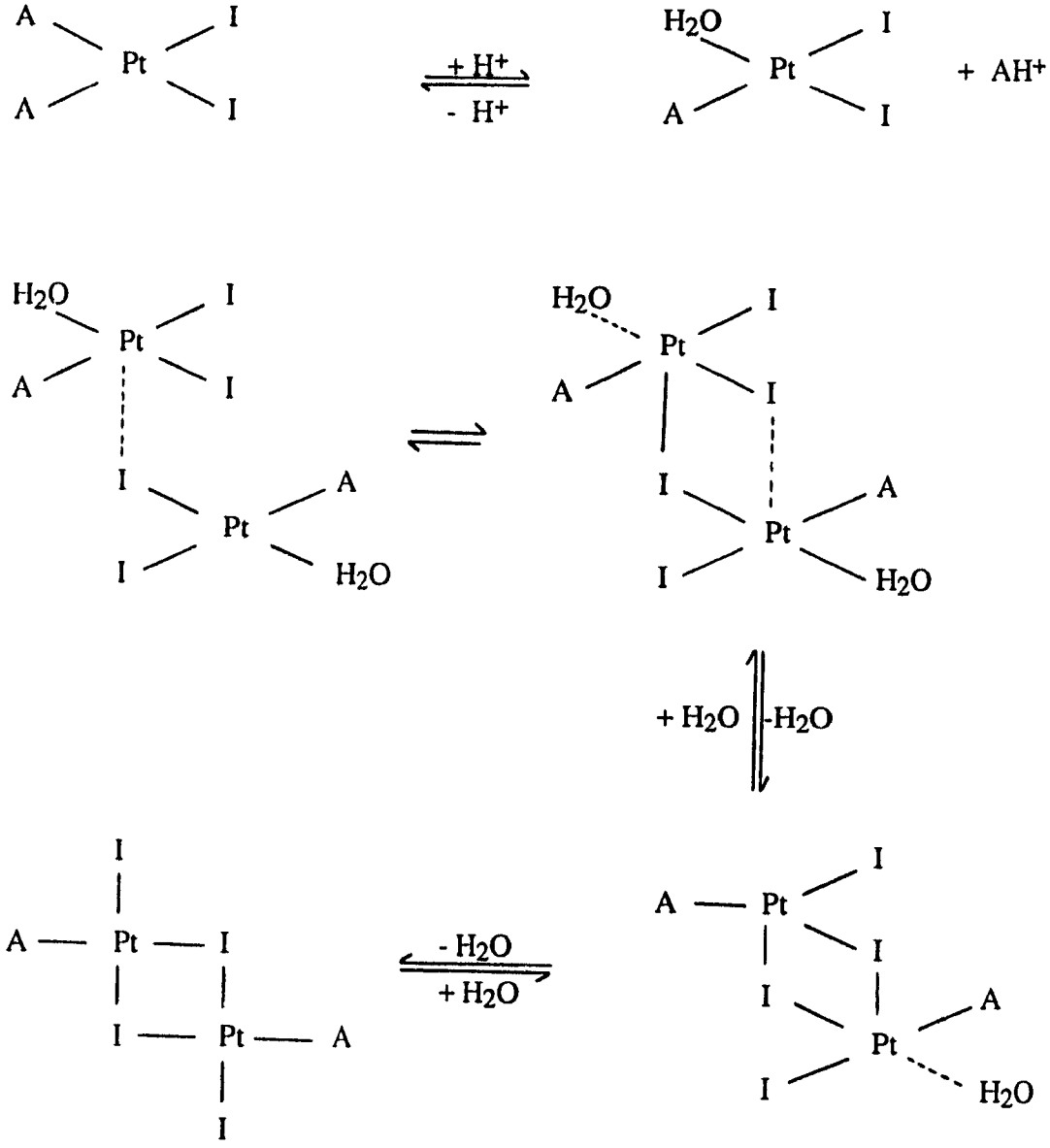
$$K_2[PtCl_4] + 4\,KI \xrightarrow{H_2O} K_2[PtI_4] + 4\,KCl$$

$$K_2[PtI_4] + 2A \xrightarrow{H_2O} cis\text{-}Pt(A)_2I_2 + 2\,KI$$

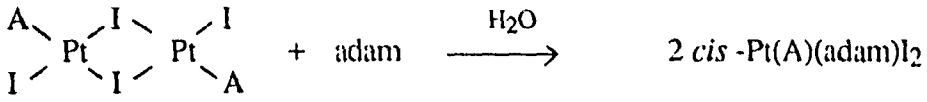
$$2\,cis\text{-}Pt(A)_2I_2 \xrightarrow{HClO_4}$$



According to the earlier work of Elding and Olsson (17), the mechanism of dimerization of *cis*-Pt A_2I_2 in acidic media could be:



The iodo-bridged dimer is a good starting material for the synthesis of mixed-ligands complexes (3). It can be cleaved by another amine to give the mixed-amine iodo complex $Pt(A)(adam)I_2$ according to the following equation:



The synthesis of iodo complexes is important since they are more soluble in organic solvents than are the chloro compounds. The ^{1}H-NMR spectra could be measured because they are soluble in $CDCl_3$ and this solvent does not interfere with the resonances of the ligands. Far-IR measurements in solution are also possible and these data can be compared with the results obtained for solids. Raman data can also be recorded in the same way for the solids and in solution. The ^{195}Pt-NMR spectra were measured in DMF and compared to the chloro series. DMF was chosen in order to compare the chemical shifts of the iodo complexes with the chloro compounds. The same trend would be expected if steric and/or solvent effects are responsible for the observed chemical shifts.

The iodo complexes could also be good starting materiels for many other interesting compounds. The mixed amine iodo complexes $Pt(A)(adam)I_2$ can be treated with silver nitrate and KCl to complete the chloro series. The disubstituted iodo complexes can also be treated with silver nitrate and then with adamantanecarboxylate derivative. This might be useful since carboxylate complexes are less toxic than the chloro complexes.

4.3.2 ^{195}Pt- and ^{1}H-NMR Spectra

The ^{195}Pt-NMR chemical shifts are very sensitive to the nature of the ligands in the coordination sphere, and the platinum resonances move to lower field in the ligating atom order I > P > As > S > N > Cl > O (18). These shifts have been related to a decrease in covalence in going from iodide to oxygen and this has been interpreted in terms of covalency effects in the σ_p contribution to the shielding (19, 20). As an example, in a series of $[Pt(L)Cl_3]^-$ complexes where L = NH_3, Cl and H_2O, the chemical shifts in water are, respectively, –1826, –1628 and –1180 ppm (18). Changing three chloride ligands to iodide leads to an extremely large upfield shift, e.g., $[NR_4][Pt(DMNH)Cl_3]$ (R = Pr^n or Bu^n) at –1863 and $[NR_4][Pt(DMNH)I_3]$ at –4004 ppm in CH_2Cl_2 solution (21). Changing one chloride ligand to a nitrogen ligand is also important: $K[Pt(NH_3)Cl_3]$ is observed at –1826, $Pt(NH_3)_2Cl_2$ at –2097, $[Pt(NH_3)_3Cl]Cl$ at –2354 ppm (18) and $[Pt(NH_3)_4]Cl_2$ at –2560 ppm (20).

The ^{195}Pt-NMR spectra of the different complexes studied in this chapter were measured in DMF solution (unless otherwise mentioned) and the results are given in Table XIII. The compounds were expected to exhibit resonances between those for the ammine complex, $Pt(NH_3)_2Cl_2$ (–2048 ppm in DMF; –2097 ppm in DMSO; –2168 in H_2O) (18, 22) and the ethylenediamine complex $Pt(en)Cl_2$ (–2345 ppm in DMSO) (23).

All the spectra of the diaminodichloro complexes displayed resonances between -2141 and -2242 ppm, in good agreement with the values observed in DMF solution by O'Halloran (24) for $Pt(MeNH_2)_2Cl_2$ at -2222 ppm and by Dion for *cis*- and *trans*-$Pt(CBA)_2Cl_2$ at -2235 and -2225 ppm, respectively (25).

Table XIII. ^{195}Pt-NMR for disubstituted amine complexes.

Compounds	δ^{195}Pt (±5ppm)	Other peaks observed
$Pt(MeNH_2)_2Cl_2$	-2222 (24)	
cis- $Pt(CBA)_2Cl_2$	-2235 (25)	
trans- $Pt(CBA)_2Cl_2$	-2225 (25)	
cis -$Pt(DMNH)_2Cl_2$	-2188	
trans -$Pt(DMNH)_2Cl_2$	-2181	
$Pt(iso\text{-}PrNH_2)_2Cl_2$	-2224	
$Pt(2,6\text{-}CH_2OHPy)_2Cl_2$	-2095	
$Pt(1\text{-adam})_2Cl_2$	-2141 (*trans*, 52%), -2184 (*cis*, 19%)	-1823 (29%)
$Pt(2\text{-adam})_2Cl_2$	-2193 (*trans*, 27%) -2230 (*cis*, 13%)	-1851(60%)
$Pt(1\text{-Madam})_2Cl_2$	-2242 (*cis*, 71%)	-1861(29%)
$Pt(MeNH_2)(1\text{-adam})Cl_2$	-2213	
$Pt(EtNH_2)(1\text{-adam})Cl_2$	-2208	
$Pt(CBA)(1\text{-adam})Cl_2$	-2199	
$Pt(CPA)(1\text{-adam})Cl_2$ (washed with HCl)	-2188 (56%)	-1842 (44%)
$Pt(MeNH_2)(2\text{-adam})Cl_2$(washed with HCl)	-2219 (97%)	-1828 (3%)
$Pt(MeNH_2)(2\text{-adam})Cl_2$	-2219	
$Pt(EtNH_2)(2\text{-adam})Cl_2$(washed with HCl)	-2222 (98%)	-1851 (2%)
$Pt(EtNH_2)(2\text{-adam})Cl_2$	-2223	
$Pt(EtNH_2)(2\text{-adam})Cl_2$ (reaction with HCl)	-2225 (26%)	-1854 (74%)
$Pt(MeNH_2)(1\text{-Madam})Cl_2$	-2235	

For several of the adam complexes, two resonances were displayed in the $Pt(L)_2Cl_2$ region. The upfield resonance was assigned to the *cis* isomer, the other to the *trans* isomer. Similar assignments have been reported by other research groups. The

values observed (26) for the $Pt[CH_3(CH_2)_5{}^{15}NH_2]_2Cl_2$ complexes are -2130 ppm in $CDCl_3$ for the *trans* isomer and -2215 in DMSO-d_6 for the *cis* isomer. For similar complexes with cyclobutylamine, the observed values are -2225 ppm (*trans*) and -2235 ppm (*cis*) in DMF (25).

For the *cis* complex with the secondary amine, DMNH, the δ(Pt) resonance appears at lower field (-2188 ppm) than do those for the other diamine complexes. The same trend is found for the *cis* complexes with two 1-adamantanamine ligands (–2184 ppm) but not for the complexes with two 2-adamantanamine (–2230 ppm) or two 1–methyladamantanamine (-2242 ppm) ligands. Pregosin (18) has noticed a downfield shift of the platinum signal when the ligand becomes sterically larger. In the case of the complex with 1-methyladamantanamine, the $-CH_2-$ group between the amine and the bulky adamantane ring is sufficient to relieve the steric hindrance and this compound resonates in the same region as other less bulky primary amine complexes. The same trend is observed for the mixed-ligand complexes of 1-adamantanamine. There is a downfield shift from $MeNH_2$ to the CPA ligand and the CPA ligand apparently creates a similar steric environment as do two DMNH ligands.

In addition to the resonances of the disubstituted complexes, the ^{195}Pt-NMR spectra of many of the compounds with adamantanamine derivatives showed a low intensity peak in the -1850 ppm region (Figure 9a) which we attribute to $[adamH][Pt(A)Cl_3]$.

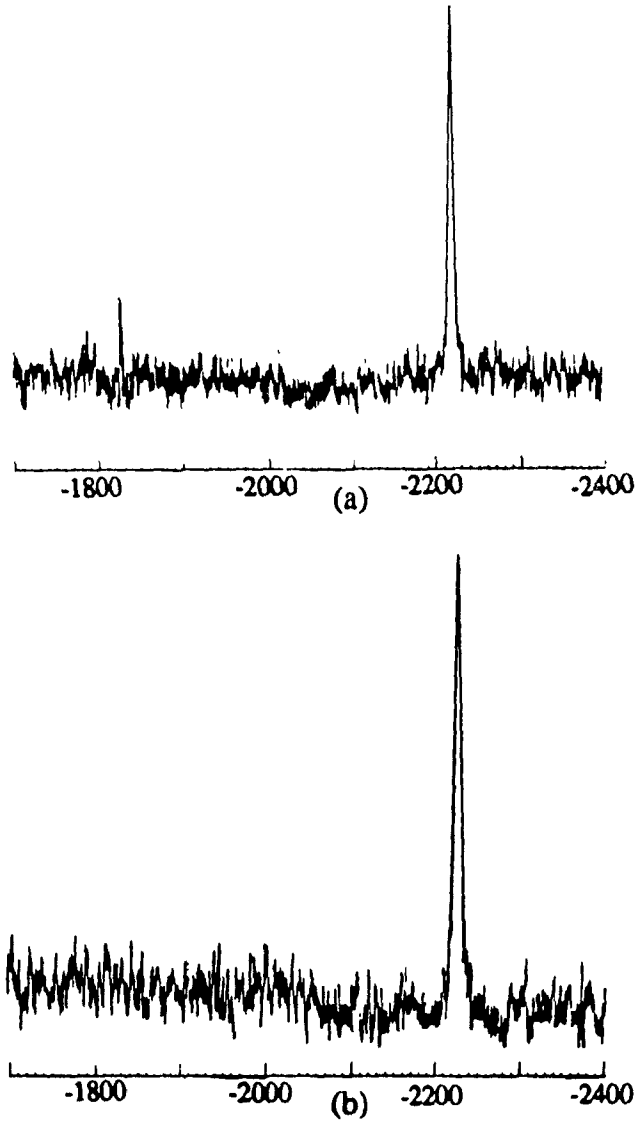


Figure 9. Typical ^{195}Pt-NMR spectrum of Pt(A)(adam)Cl_2: (a) washed with dilute HCl and (b) without washing with dilute HCl.

The presence of the resonance due to the K[Pt(A)Cl_3] starting materials in the spectra was initially surprising. Since these complexes are very soluble in water, they should have been eliminated during the synthetic work up. This dilemma was resolved by determining the crystal structure of the complex obtained from the washings during the treatment of Pt($EtNH_2$)(2-adam)Cl_2 with dilute HCl (27). The washing was done to

eliminate any free adamantanamine ligand. The δ(Pt) resonance at -1854 ppm is assigned to the ionic complex [2-adamH][Pt($EtNH_2$)Cl_3], the crystal structure of which was discussed in Chapter 3. The ^{195}Pt-NMR spectra of the complexes prepared without washing with dilute HCl showed no peak in this region (Figure 9b).

After determining the crystal structure of 2-adamantylammonium trichloro(ethylamine)platinate(II), which was the result of displacement of the coordinated adamantanamine ligand by Cl^- and subsequent quaternization of the amine group, we decided to look more closely at the structures of the adamantanamine platinum(II) complexes, Pt(1-adam)$_2Cl_2$ and Pt(2-adam)$_2Cl_2$, tested by Braddock et al. since these authors used concentrated HCl for washing. We had washed our compounds only with dilute HCl and had observed a small quantity of [adamH][Pt(A)Cl_3]. We therefore decided to repeat Braddock et al.'s synthetic work (1) and measured the ^{195}Pt-NMR spectra of the products in order to verify the authenticity of the compounds.

If we look at the values reported by Braddock et al. (1) for the elemental analyses of the Pt(adam)$_2Cl_2$ (Table XII), the calculated and found C, N and H values are in good agreement but no Cl analysis is given. For the complexes Pt(adam)$_2Cl_2$ and [adamH][Pt(adam)Cl_3], the calculated analyses are C, 42.2; N, 6.0; H, 4.9; Cl, 12.5 and C, 39.7; N, 4.6; H, 5.8; Cl, 17.6, respectively. The differences (ΔC, 2.5, ΔN, 1.4; ΔH, 0.9) between calculated values for C, N and H are small. The greater difference expected for the chloride analysis (ΔCl, 5.1) would have afforded more information about the empirical formula of the complex. If the proportion of the ionic complex is small, a mixture of the two compounds (three if we assume the presence of *cis*- and *trans*-Pt(adam)$_2Cl_2$) would give similar analysis for C, N and H. There is a similar problem

with the IR data. For the IR-active ν(Pt-Cl) vibrations, the results are not conclusive since a mixture of complexes would give the same results.

The synthesis of $Pt(1\text{-adam})_2Cl_2$ was therefore repeated, exactly as published in the literature by Braddock et al. (1) and the ^{195}Pt-NMR spectrum of the product was measured in DMF. The compounds $Pt(1\text{-adam})_2Cl_2$ was prepared as follows. One equivalent of $K_2[PtCl_4]$ was dissolved in water and the filtered solution was treated with two equivalents of aminoadamantane hydrochloride in water. The insoluble pale pink chloroplatinite of the protonated amine was filtered off and washed with water. The complex $(adamH)_2[PtCl_4]$ was suspended in water with two equivalents of sodium hydroxyde and the mixture was stirred overnight. The pale yellow product was filtered off, washed with concentrated HCl, water, methanol and then ether and finally dried under vacuum. The ^{195}Pt-NMR spectrum of the product obtained dissolved in DMF is shown in Figure 10a. Three peaks were observed, the most intense peak (-1822 ppm) being assigned to [1-adamH][Pt(1-adam)Cl_3]. Although [1-adamH][Pt(1-adam)Cl_3] is not believed to be very soluble in water (otherwise it would have been eliminated during the workup), it is surely more soluble than the $Pt(1\text{–adam})_2Cl_2$ complex. The compound that was tested by Braddock et al. (1) for antitumor activity was more likely a mixture containing the ionic complex and the *cis* and *trans* disubstituted species. It was normal that the results of the biological tests were negative since only *cis* complexes have any significant antitumor activity. In order to compare the ^{195}Pt-NMR spectra, complexes of the type K[Pt(1-adam)Cl_3] and $Pt(1\text{-adam})_2Cl_2$ were also synthesized by another method. The spectrum obtained for the latter before isolation also showed three δ(Pt) peaks in the same region, the most intense being attributed to the *trans* isomer. The NMR spectra are compared in Figure 10. The resonances appear at -2190 (38%), -2155 (11%) and -1822

(51%) for Braddock's compound compared to -2184 (19%), -2141 (52%) and -1823 (29%) ppm for our 1-adam compound.

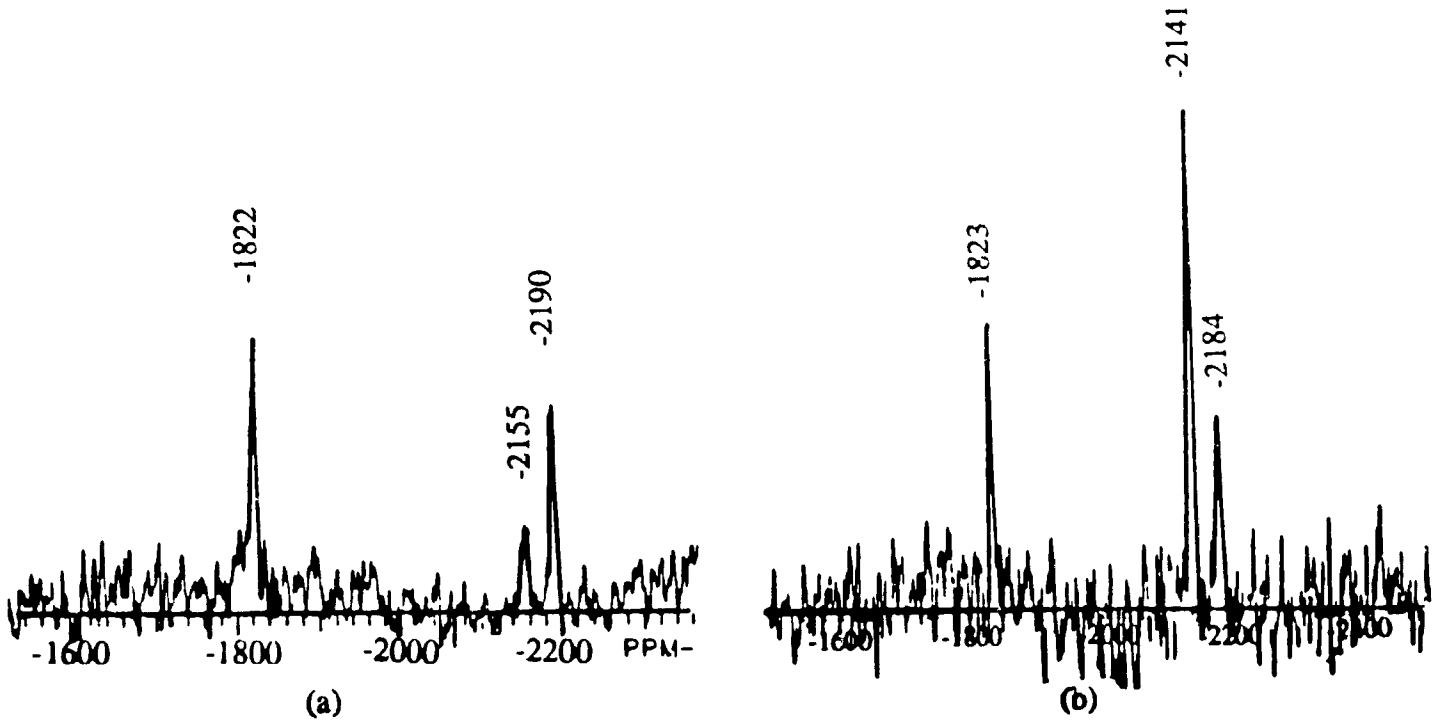


Figure 10. Comparison of the ^{195}Pt-NMR spectra for the Pt(1-adam)$_2$Cl$_2$ complex (a) prepared by the method described by Braddock et al. (1) and (b) by our method.

As we have already seen, Pt(EtNH$_2$)(2-adam)Cl$_2$ gives only one resonance, at -2223 ppm, when it is not washed with HCl. To prove that the resonance at -1823 ppm belongs to [adamH][Pt(adam)Cl$_3$], the Pt(EtNH$_2$)(2-adam)Cl$_2$ complex was stirred in HCl and the ^{195}Pt-NMR spectrum of the mixture was recorded (Figure 11), and compared to the spectrum of Pt(A)(adam)Cl$_2$ (Figure 9a) following washing with dilute HCl.

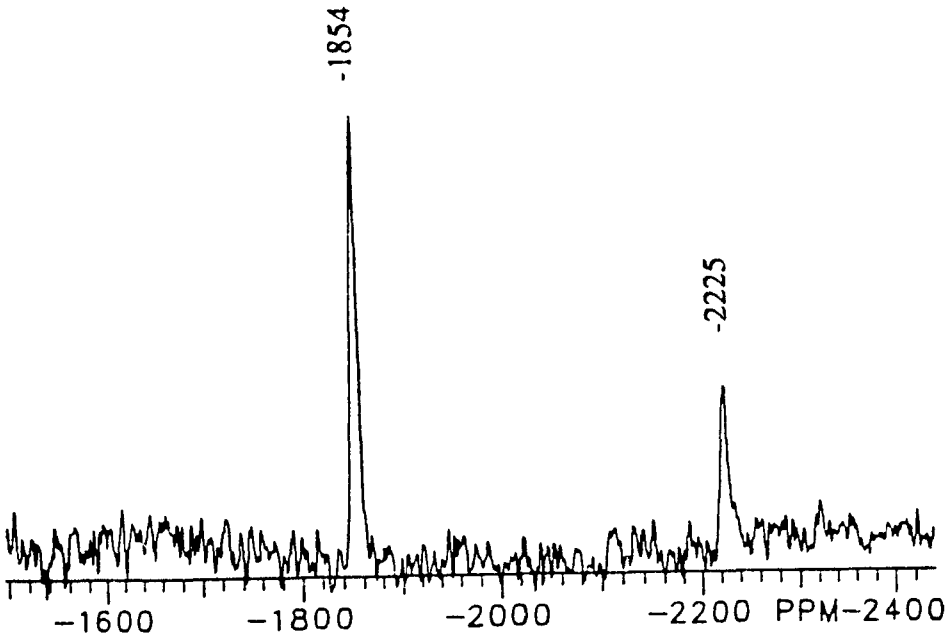


Figure 11. ^{195}Pt-NMR spectrum of $Pt(EtNH_2)(2\text{-adam})Cl_2$ after stirring in HCl for 10 min.

The spectrum shows a new intense resonance at -1854 ppm which can be attributed to [2-adamH][$Pt(EtNH_2)Cl_3$]. This is in the same region as that for the least intense peak in Figure 9a, thereby confirming that when concentrated HCl is used to wash the disubstituted amines complexes, species of the type [adamH][$Pt(A)Cl_3$] are produced. Indeed, when these complexes are in contact with HCl, the acid reacts with the coordinated adamantanamine and the Cl^- replaces the amine in the coordination sphere. It is now important to find a new synthetic route to the pure *cis* complexes in order to eventually examine the potential antitumor properties of these complexes.

Similar complexes with two iodo ligands were synthesized and the ^{195}Pt-NMR spectra were measured in DMF. The results are listed in Table XIV.

Table XIV. ^{195}Pt resonances for the iodo complexes.

Compounds	^{195}Pt(+5ppm)
$Pt(en)I_2$	-3462 (28)
$Pt(NH_3)_2I_2$	-3264 (28)
$Pt(MeNH_2)_2I_2$	-3327
$Pt(EtNH_2)_2I_2$	-3330
$Pt(CBA)_2I_2$	-3346
$Pt(CPA)_2I_2$	-3302
$Pt(DMNH)_2I_2$	-3211
$Pt(1\text{-adam})_2I_2$	-3331 (*trans*, 63%)
	-3364 (*cis*, 37%)
$Pt(2\text{-adam})_2I_2$	-3333
$Pt(1\text{-Madam})_2I_2$	-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
$Pt(2\text{-adam})(CPA)_2$	-3328
$Pt(2\text{-adam})(CBA)I_2$	-3358 (*trans*, 86%)
	-3387 (*cis*, 14%)
$Pt(MeNH_2)(1\text{-Madam})I_2$	-3336 (*trans*, 75%)
	-3389 (*cis*, 25%)
$Pt(EtNH_2)(1\text{-Madam})I_2$	-3388

A 1000-ppm upfield shift is observed going from two chloro to two iodo ligands. Lippard has already synthesized such complexes with NH_3 and ethylenediamine ligands (28). The resonances for $Pt(NH_3)_2I_2$ and $Pt(en)I_2$ were observed at –3264 and

-3462 ppm respectively, in DMF solutions, i.e., 1167 and 1117 ppm to high field compared to the values for the chloro analogs. It was expected that our compounds would display resonances between these two values since, in the chloro series, the diamino complexes showed resonances between the ammine and the ethylenediamine complexes, as discussed previously. All the complexes, except $Pt(DMNH)_2I_2$ showed a resonance between -3302 and -3389 ppm. The $Pt(DMNH)_2I_2$ complex resonates at lower field (–3211 ppm) than does the ammine complex (–3264 ppm) and, in this case, steric hindrance might possibly be the predominant factor.

In the proton-NMR spectra, there is no solvent problem for the iodo complexes because they are usually soluble in most common organic solvents. In our case, $CDCl_3$ or acetone-d_6 were chosen and the results are shown in Table XV. The electronic density is drained toward the platinum atom upon coordination and there are downfield shifts for the protons of the coordinated ligands when compared to those of the free ligands. For $Pt(MeNH_2)_2I_2$, a triplet is observed at 2.65 ppm (Figure 12a) for the methyl group due to coupling with the amine protons (^3J(H-H) = 6 Hz) with the two triplet satellites due to coupling with platinum-195 isotope ($^3J(^{195}Pt\text{-}H)$ = 49 Hz). The resonance of the amine protons appears at 4.50 ppm for $Pt(MeNH_2)_2I_2$ and no coupling is observed with platinum-195. For the dimethylamine complex, the same trend is observed and the resonance of the methyl groups is found at 2.80 ppm as a doublet plus a doublet of doublets with coupling constants ^3J(H-H) = 6 Hz and $^3J(^{195}Pt\text{-}H)$ = 43 Hz. For $Pt(1\text{–adam})_2I_2$ (Figure 12b) and $Pt(CPA)_2I_2$ complexes , in addition to the expected peaks for the ligands, the resonances of the amine protons at 3.61 and 4.34 ppm with coupling constants $^2J(^{195}Pt\text{-}NH)$ = 68 and 70 Hz, respectively, could be detected.

Table XV. ^1H resonances (ppm) for the ligands and the iodo complexes (in $CDCl_3$ solution).

Compounds	H1	H2	H3	NH	J(Pt-NH) Hz	J(Pt-CH) Hz
$MeNH_2$	2.25(s)			not obsd		
$Pt(MeNH_2)_2I_2$ [a]	2.65(t+dt)			4.50	not obsd	49
$EtNH_2$	0.97(t)	2.59(q)		not obsd		
$Pt(EtNH_2)_2I_2$	1.21(t)	2.95(m)		4.45	not obsd	not obsd
[a]	1.29	3.04		3.24	not obsd	not obsd
CBA	1.297(m)	1.872(m)	3.053(m)	not obsd		
$Pt(CBA)_2I_2$	1.94(m)	2.30(m)	3.73(m)	3.48	not obsd	not obsd
	1.64(m)					
CPA	1.064(m)	1.563(m)	3.132(m)	not obsd		
$Pt(CPA)_2I_2$	1.68(m)	2.11(m)	3.61(m)	4.34	70	not obsd
1-adam	1.529(s)	1.590(m)	2.057(m)	not obsd		
$Pt(1\text{-adam})_2I_2$	1.59(m)	1.98(m)	2.11(m)	3.61	68	not obsd
DMNH	1.85(d)					
$Pt(DMNH)_2I_2$ [a]	2.80(d+dd)			4.97	not obsd	43
$Pt(MeNH_2)(1\text{-adam})I_2$	2.61(t)			3.80	not obsd	not obsd
	1.55(m)	1.99(m)	2.12(m)	3.63	not obsd	not obsd

[a] In acetone-d_6 solution

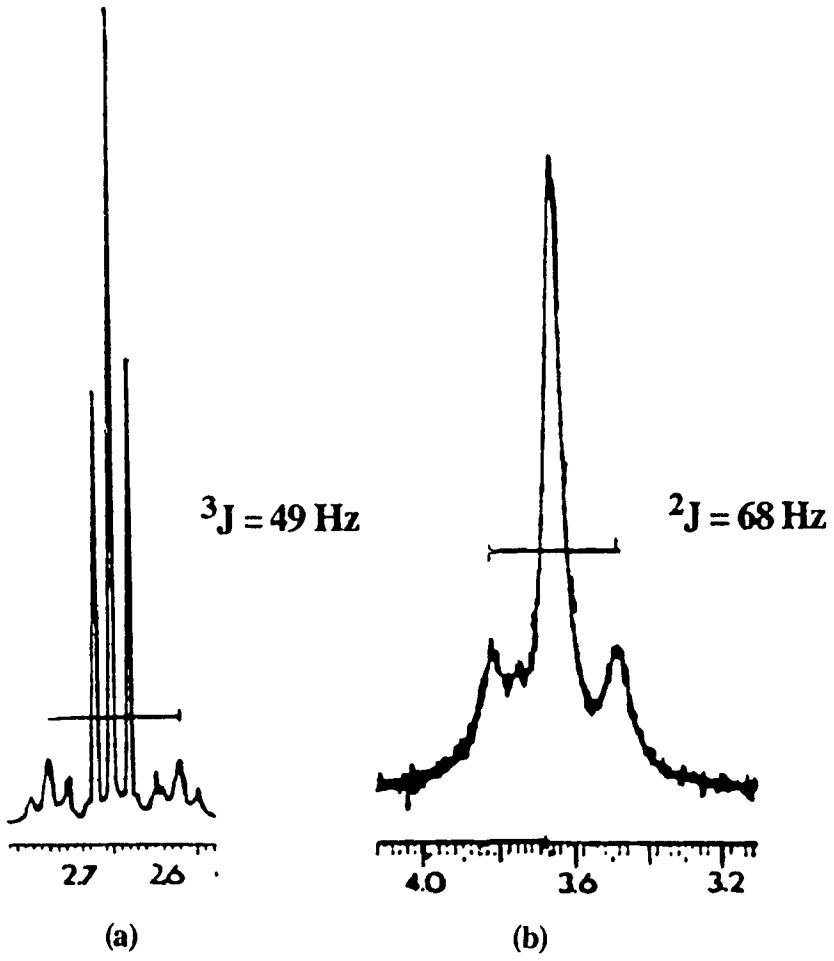


Figure 12. ^{1}H-NMR spectra for (a) $Pt(MeNH_2)_2I_2$ in acetone-d_6 and (b) $Pt(1\text{-adam})_2I_2$ in $CDCl_3$.

4.3.3 Infrared and Raman Spectra

The IR (4000-250 cm^{-1}) and Raman (500-200 cm^{-1}) spectra of the $Pt(A)(adam)Cl_2$ and $Pt(adam)_2Cl_2$ complexes were recorded in the solid state. Table XVI lists the $\nu(NH)$, $\delta(NH_2)$ and $\nu(Pt\text{-}N)$ vibrations from the IR measurements. The IR- and Raman-active $\nu(Pt\text{-}Cl)$ bands are listed in Table XVII. The complexes used for the vibrational studies were those synthesized without washing with dilute HCl and we assume that the ionic complexes were not formed on the basis of the ^{195}Pt-NMR spectra of the $Pt(MeNH_2)(2\text{-adam})Cl_2$ and $Pt(EtNH_2)(2\text{-adam})Cl_2$ complexes (Section 4.3.1). For the complexes with two adamantanamine derivatives, the IR and Raman spectra were recorded after the work-up to eliminate the $K[Pt(adam)Cl_3]$ complex. The IR spectra were obtained on a FT 50 DIGILAB spectrometer, 256 scans at 1 cm^{-1} resolution. The Raman spectra were measured on a U-1000 Ramanor spectrometer and using an argon-ion laser on the green line (514.5 nm) equipped with a Nachet microscope (4X objective). The assignments given have been made according to the group theory and by comparison with the results published by other workers on similar complexes (3, 29-32). The IR spectra of the $K[Pt(amine)Cl_3]\cdot 1/2H_2O$ complexes exhibit two sharp $\nu(OH)$ bands between 3600 and 3480 cm^{-1} and one $\delta(OH)$ between 1597 and 1590 cm^{-1} due to water of hydration (15). These bands are absent in the mixed-ligand complexes.

The IR spectra of the $Pt(adam)_2Cl_2$ complexes are very similar to those of the $K[Pt(adam)Cl_3]$ complexes. The amine bands are shifted to lower energies by about 65 to 120 cm^{-1}, due to coordination to platinum. For the mixed-amine complexes, additional bands due to the presence of the second amine are observed. This is particularly true in the region of the stretching vibrations of the amine group. The spectra of all the mixed-amine complexes show three-to-five $\nu(NH)$ vibrations between 3287 and 3118 cm^{-1}. As

an example, the ν(NH) vibrations in K[Pt(1-adam)Cl_3] were located at 3125, 3200 and 3230 cm^{-1} while in K[Pt($MeNH_2$)Cl_3] the corresponding vibrations were observed a little higher at 3140, 3245 and 3270 cm^{-1}. The spectrum of Pt($MeNH_2$)(1-adam)Cl_2 shows almost a superposition of these bands. Five ν(NH) bands are observed between 3276 and 3124 cm^{-1}. The complexes show one or two IR-active δ(NH_2) vibrations between 1595 and 1563 cm^{-1}, lowered by about 25 to 60 cm^{-1}, compared to absorption bands of the free ligand. The platinum-nitrogen stretching vibrations are located between 555 and 455 cm^{-1}. Except for Pt(CPA)(1-adam)Cl_2 and Pt(2-adam)$_2Cl_2$ which show only one band, all the other spectra exhibit two bands in this region. These assignments for the ν(Pt-N) vibrations are based on previous work (29-31).

The above spectral observations correlate well with the published values for similar complexes. An IR study on Pt(en)Cl_2 showed two ν(Pt-N) vibrations at 545 and 464 cm^{-1} (31). Kharitinov et al have already reported the IR absorption spectra of several methylamine complexes (29). They observed that the general nature of the spectra is retained even if there is one, two or four methylamine ligands coordinated to the platinum atom. They did not observe any band splitting as the result of solid-state effects or due to the presence of several molecules of methylamine in the complex. For all the compounds, the ν(Pt-N) modes appear between 526 and 490 cm^{-1}; these vibrations are shifted to lower energies by about 30 cm^{-1} upon isotopic substitution at the amino group. For example, the ν(Pt-N) vibrations of Pt($MeNH_2$)$_2Cl_2$ have been assigned to 523 cm^{-1} for the *trans* isomer and to 517 and 505 cm^{-1} for the *cis* isomer. For the latter, the lower energy band, which is the most intense in the IR spectrum, has been assigned to the antisymmetric and the other to the symmetric ν(Pt-N) vibration. The same authors (29) also observed two δ(NH_2) at 1598 and 1577 cm^{-1} for the *cis* isomer, while only one band

was observed at 1596 cm^{-1} for the *trans* isomer. These complexes have also been studied by Watt, Hutchison and Klett (30) who assigned the ν(Pt-N) vibrations to 518 cm^{-1} (*trans*) and 506 and 517 cm^{-1} (*cis*). Only one $\delta(NH_2)$ deformation vibration was observed at 1594 cm^{-1} for the *trans* compound while three bands appear in the same region at 1596, 1581 and 1575 cm^{-1} for the *cis* isomer. The same is true for *cis*-and *trans*-$Pt(CBA)_2Cl_2$ which were studied by Lock and Zvagulis (32). For the *cis* compound, the $\delta(NH_2)$ vibrations are located at 1662, 1586 and 1562 cm^{-1} and for the *trans* isomer at 1591 cm^{-1}. In a study on *cis*-mixed ligand complexes, reported by Rochon and Kong (3), all the compounds except one showed two or more $\delta(NH_2)$ vibrations between 1642 and 1525 cm^{-1}. In these publications, the presence of a lower $\delta(NH_2)$ deformations of the amino group for the *trans* isomer is always mentioned, but never discussed. If there is still D_{2h} "local" symmetry (ignoring the nature of the amine), there will be an "in-phase" and "out-of-phase" $\delta(NH_2)$ vibration. Since it is centrosymmetric, the "in-phase" motion will be Raman active only while the other motion will be IR active only (Rule of Mutual Exclusion). For the *cis* compounds (C_{2v} symmetry), both motions will be IR and Raman-active.

Cis- and *trans*-$Pt(A)_2Cl_2$ complexes can often be distinguished by IR spectroscopy. The local skeleton symmetry for the Pt-Cl bonds is C_{2v} for the *cis* isomer and D_{2h} for the *trans* isomer. Group theory predicts two IR-active ν(Pt-Cl) bands (a_1+b_2) for a *cis* isomer and one (b_{2u}) for the *trans* isomer (see Appendix I)

Table XVI Main IR bands for Pt(A)(adam)Cl_2 and Pt(adam)$_2Cl_2$ complexes in nujol mulls (cm^{-1}).

Compounds	ν(NH)	δ(NH_2)	ν(Pt-N)
Pt($MeNH_2$)(1-adam)Cl_2	3276 (w), 3231 (s) 3196 (s), 3144 (w) 3124 (w)	1569 (s)	555 (m), 462(w)
Pt($EtNH_2$)(1-adam)Cl_2	3224 (s), 3195 (s) 3129 (s)	1577 (s)	555 (w), 462(vw)
Pt(CBA)(1-adam)Cl_2	3260 (w), 3213 (s) 3122 (s)	1575 (s)	550(vw),462(vw)
Pt(CPA)(1-adam)Cl_2	3215 (s), 3188 (s) 3121 (s)	1590 (w), 1563 (s)	550(w)
Pt($MeNH_2$)(2-adam)Cl_2	3273 (m), 3237 (s) 3214 (s), 3145 (s)	1590 (s), 1571 (s)	525(w), 505(w)
Pt($EtNH_2$)(2-adam)Cl_2	3265 (w), 3197 (s) 3131 (m)	1570 (m)	555 (w), 498(m)
Pt($MeNH_2$)(1-Madam)Cl_2	3287 (s), 3238 (s) 3214 (s), 3141 3118 (m)	1586 (s), 1576 (s)	545(w), 515(w)
Pt(1-adam)$_2Cl_2$	3208(m), 3122(m)	1572(m) 1595(sh)	550(w), 461(w)
Pt(2-adam)$_2Cl_2$	3305(m), 3279(w) 3261(w), 3238(m) 3190(s), 3123(s)	1578(s)	503(mw)
Pt(1-Madam)$_2Cl_2$	3298(m), 3235(s) 3218(s), 3142(s)	1571(w) 1594(m)	545(vw), 455(w)

The ν(Pt-Cl) stretching vibrations, both symmetric and antisymmetric, are expected to absorb in the 400-300 cm^{-1} region (32). For the *cis* complex, both modes should be active in the Raman spectra, while for the *trans* isomer, only the symmetric mode (a_g) will be Raman active. The symmetric M-Cl stretch which gives the least intense IR peak, affords the strongest Raman band. The antisymmetric mode often provides the most intense M-X stretching band in the IR but is generally weak and often not observable in the Raman spectrum. The corresponding mode in *trans*-ML_2X_2 is Raman inactive. Sometimes the two vibrations of a *cis* complex have very close energies and only one band (slightly broader) 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 at around 320-315 cm^{-1}, while the *trans* complex absorb at higher energies (around 340-335 cm^{-1}) (32). For complexes with two different amines, approximations can be made and, very often, two ν(Pt-Cl) bands are observed in both the IR and Raman spectra of a *cis* complex while only one band is detected for a *trans* isomer. In the study on mixed-amine complexes by Rochon and Kong (3), some compounds exibited two bands between 327-308 cm^{-1} while others showed one large band between 320-310 cm^{-1}. The *cis* isomerism was confirmed by x-ray diffraction for two complexes, $Pt(CBA)(NH_3)Cl_2$ and $Pt(CPA)(NH_3)Cl_2 \cdot 1/4\ H_2O$, which showed only one band in the IR spectrum (4, 33).

In our case, on the basis of the IR and Raman data (Table XVII), it seems that the complexes $Pt(EtNH_2)(1\text{-adam})Cl_2$ and $Pt(EtNH_2)(2\text{-adam})Cl_2$ are *cis* isomers since they have two bands coincident in the IR and Raman spectra in the Pt-Cl stretching region. In the Raman spectra, the peak at higher wavenumber is the most intense, indicating that this is the symmetric stretching mode. The other mixed-amine complexes

$Pt(MeNH_2)(1\text{-}adam)Cl_2$, $Pt(CBA)(1\text{-}adam)Cl_2$, $Pt(CPA)(1\text{-}adam)Cl_2$ and $Pt(MeNH_2)(2\text{-}adam)Cl_2$ show only one band around 325 cm^{-1} which is closer to the value for a *cis* complex and since these bands are coincident both in IR and Raman, we have assigned them as *cis* isomers. For the complex $Pt(MeNH_2)(1\text{-}Madam)Cl_2$, there is one additional band in Raman and the compound may be a *cis* isomer with an unresolved peak in IR. The compound is not a mixture of isomers since only one peak was observed in its ^{195}Pt-NMR spectrum.

Table XVII. Infrared and Raman ν(Pt-Cl) bands for $Pt(A)(adam)Cl_2$ and $Pt(adam)_2Cl_2$ complexes (cm^{-1}).

Compounds	IR ν(Pt-Cl)	RAMAN ν(Pt-Cl)
$Pt(MeNH_2)(1\text{-}adam)Cl_2$	325(s)	324(s)
$Pt(EtNH_2)(1\text{-}adam)Cl_2$	329(m), 314(s)	325(s), 311(m)
$Pt(CBA)(1\text{-}adam)Cl_2$	323(s)	322(s)
$Pt(CPA)(1\text{-}adam)Cl_2$	322(s)	322(s)
$Pt(MeNH_2)(2\text{-}adam)Cl_2$	329(s)	328(s)
$Pt(EtNH_2)(2\text{-}adam)Cl_2$	328(s) , 313 (m)	327(s), 311(m)
$Pt(MeNH_2)(1\text{-}Madam)Cl_2$	326(s)	338(s), 327(m)
$Pt(1\text{-}adam)_2Cl_2$	329(m)	342(w), 337(mw)
		323(s), 318(m)
$Pt(2\text{-}adam)_2Cl_2$	335(m)	329(s), 322(m)
$Pt(1\text{-}Madam)_2Cl_2$	341(m), 325(m)	334(s), 325(m)

For the complexes with two adamantanamine derivatives, $Pt(1\text{-}adam)_2Cl_2$ and $Pt(2\text{-}adam)_2Cl_2$ each shows only one band at 329 and 335 cm^{-1}, respectively in the IR. In the Raman, these bands are split to four and two components, respectively, and are not

coincident. The compounds is a mixture of isomers, since the ^{195}Pt-NMR spectra display two peaks in the $Pt(adam)_2Cl_2$ region. The complex with 1-Madam also exibits two bands in IR and Raman. Since there is an additional resonance in ^{195}Pt-NMR in the region of $[Pt(adam)Cl_3]^-$, these bands are probably due to a mixture of $[Pt(1\text{-}Madam)Cl_3]^-$ and $Pt(1\text{-}Madam)_2Cl_2$.

Another problem may arise in the IR and Raman spectra of platinum(II) complexes. In a study by Hendra (34), the Raman spectrum of *trans*-$Pt(NH_3)_2Cl_2$ showed two ν(Pt-Cl) vibrations at 335 and 318 cm^{-1} and two ν(Pt-N) vibrations at 540 and 528 cm^{-1}, while the infrared spectrum showed only one band for each of the two vibrations, at 330 and 506 cm^{-1} respectively. The splitting of the bands in the Raman spectrum was attributed to an intermolecular coupling (Factor group splitting). This phenomenon might explain the four bands observed in the Raman spectra of $Pt(1\text{-}adam)_2Cl_2$. The two lower energy vibrations could be assigned to the *cis* isomer. The two higher bands could be assigned to the *trans* isomer, and the vibration, being split by intermolecular effects, appears as a doublet.

Because our spectra were recorded in the solid state, splitting of the bands may occur and it could be difficult to identify whether or not the two bands observed in the ν(Pt-Cl) region are the bands expected for a *cis* compound or are due to factor group splitting. Thus, it would be important to run the spectra in solution to know if factor group splitting has an effect on the IR and the Raman spectra in the solid state. Since the compounds are soluble only in DMF and DMSO, solution IR or Raman spectroscopy is not easy. Subtraction of the solvent peaks would be possible using the modern computer software. Unfortunately, in certain conditions, both DMF and DMSO can react with Pt(II) to form DMF and DMSO complexes. An alternative suggestion would be to synthesize

the analogous iodo complexes, which are more soluble in organic solvents, and then to study the ν(Pt–I) vibrations. For this reason, a series of mixed-amine platinum(II) complexes, $Pt(A)(adam)I_2$, were prepared, where A = methylamine, ethylamine, cyclobutylamine, cyclopentylamine and adam = 1-adamantanamine, 2-adamantanamine and 1–methyladamantanamine. The main IR bands for the aminodiiodo complexes measured in the solid state are listed in Table XVIII and the IR and Raman ν(Pt-I) bands are compared in Table XIX. All IR spectra between 400 and 110 cm^{-1} were recorded on a single-beam, evacuated grating spectrometer using samples as Nujol mulls squeezed between rigid polyethene sheets. With the exception of $Pt(1\text{-adam})_2I_2$, $Pt(2\text{-adam})(CBA)I_2$ and $Pt(MeNH_2)(1\text{-Madam})I_2$, all the other complexes exibited only one peak in their ^{195}Pt-NMR spectra.

The general appearance of the spectra is retained when the 4000-600 cm^{-1} region for the chloro and iodo complexes are compared. For the $Pt(adam)_2I_2$ complexes, the spectra are very similar to those of the $K[Pt(adam)Cl_3]$ and $Pt(adam)_2Cl_2$ complexes. As for the chloro analogs, all the amine bands are shifted to lower energies conforming amine coordination to platinum. In the mixed-amine complexes, additional bands due to the presence of the second amines are present in the IR spectra. One or two $\delta(NH_2)$ vibrations are observed between 1595 and 1563 cm^{-1} (lowered by about 25 to 60 cm^{-1}, compared to the free ligands). There are fewer literature values available for metal-iodide and metal-nitrogen stretching modes than for the analogous chloro vibrations (31, 34-35).

Table XVIII. Main IR bands for the diaminodiiodo complexes measured in the solid state in nujol mulls (cm^{-1}).

Compounds	ν(NH)	δ(NH_2)	ν(Pt-N)
$Pt(MeNH_2)_2I_2$	3113(m), 3169(s) 3212(s), 3251(s)	1591(vw) 1565(s)	485(w) 495(m)
$Pt(EtNH_2)_2I_2$	3119(w), 3218(s) 3250(m)	1580(s), 1569(sh) 1590(sh)	498(vw) 578(w)
$Pt(CBA)_2I_2$	3125(s), 3190(s)	1568(s), 1558(sh) 1579(sh)	568(m)
$Pt(CPA)_2I_2$	3118(m), 3192((s) 3240(m)	1570(s)	530(vw) 585(w)
$Pt(DMNH)_2I_2$	3195(s)	-	478(m) 502(w)
$Pt(1\text{-adam})_2I_2$	3112(w), 3200(s) 3262(m)	1552(s) 1565(s)	455(vw) 580(vw)
$Pt(2\text{-adam})_2I_2$	3118(w), 3202(s) 3288(s)	1572(s)	500(vw)
$Pt(MeNH_2)(1\text{-adam})I_2$	3120(w), 3198(s) 3250(m), 3262(vw) 3290(m)	1565(s)	480(vw) 590(vw)
$Pt(EtNH_2)(2\text{-adam})I_2$	3119(w), 3201(s) 3262(m)	1575(s)	495(w)
$Pt(CBA)(2\text{-adam})I_2$	3125(w), 3204(s) 3246(m), 3279(w) 3292(m)	1576(s)	500(w)
$Pt(CPA)(2\text{-adam})I_2$	3122(w), 3202(s) 3272(w), 3295(m)	1565(s)	-
$Pt(MeNH_2)(1\text{-Madam})I_2$	3379(m), 3332(m) 3310(s)	1580(s) 1561(sh)	485(vw) 528(vw)
$Pt(EtNH_2)(1\text{-Madam})I_2$	3235(m), 3295(mw)	1562(s)	460(vw)

In the Raman spectrum of *trans*-$Pt(NH_3)_2I_2$, the ν(Pt-I) vibration has been reported at 153 cm^{-1} and the ν(Pt-N) at 532 cm^{-1} (34). Similarly, in the IR spectrum of $Pt(en)I_2$, the ν(Pt-I) vibrations have been observed at 192 and 181 cm^{-1}, while the ν(Pt-N) modes were observed at 524 and 444 cm^{-1} (31). Extensive studies on *cis*- and *trans*-$Pt(L)_2X_2$ complexes (L = SMe_2, SEt_2, $AsEt_3$, PPh_3 PMe_3, $AsMe_3$ and X = Cl, Br and I) have been performed by Duddell, Goggin, Goodfellow, Norton and Smith (35) and Park and Hendra (36). These two groups are not in agreement for the ν(Pt-I) assignments however. For example, the symmetric ν(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. The corresponding antisymmetric mode which should be strong in the IR has been assigned to a peak at 206 cm^{-1} eventhough it is very weak. The same vibrations for the $Pt(PMe_3)_2I_2$ and $Pt(AsMe_3)_2I_2$ complexes have been assigned by Park and Hendra (36) to 189 and 169 cm^{-1}, respectively, in the IR spectra. The argument of Duddell et al. (35) against Park and Hendra's (36) assignment is that the frequency difference between the two classes of compounds (Cl → I) is too great since metal-halogen frequencies are relatively insensitive to changes in the accompanying neutral ligand. For the only *cis*-diiodo complex obtained by Duddell et al. (35), $Pt(PMe_3)_2I_2$, the symmetric and antisymmetric ν(Pt-I) bands were assigned at 148 and 133 cm^{-1} in Raman with coincident IR bands at 146 and 137 cm^{-1}, respectively.

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 between 590 and 455 cm^{-1} have been assigned to the platinum-nitrogen stretching vibrations. There is no such general agreement for the platinum-iodide stretching frequencies in the literature. The following assignments are only tentative (Table XIX)

and are made by comparison with published work on similar complexes. It seems that IR spectroscopy does not provide characteristic band criteria for the iodides in the same way that it generally can for the chlorides (35). The only assignment which seems conclusive is for the symmetric ν(Pt-I) vibration around 150 cm^{-1} in the Raman spectra. Since our Raman spectra all exibit a strong band in this region, we have assigned it to the symmetric ν(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 ν(Pt-I) vibration, is more difficult to locate.

Table XIX. Infrared and Raman ν(Pt-I) bands for diaminodiiodo complexes in the solid state(cm^{-1}).

	IR	Raman
Compounds	ν(Pt-I)	ν(Pt-I)
$Pt(MeNH_2)_2I_2$	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)
$Pt(1\text{-adam})_2I_2$	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)
$Pt(CBA)(2\text{-adam})I_2$	193(s), 178(s)	149(s)
$Pt(CPA)(2\text{-adam})I_2$	184(s), 151(w)	147(s)
$Pt(MeNH_2)(1\text{-Madam})I_2$	183(s), 151(w)	181(m), 149(s)
$Pt(EtNH_2)(1\text{-Madam})I_2$	192(s), 153(w)	150(s)

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 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 (37).

In conclusion, it was difficult to obtain good IR and Raman spectra even in the solid state for these complexes and the results presented in Table XIX are tentative. Systems containing iodine present greater difficulty since their vibration frequencies are at low energy and it is difficult to distinguish between intramolecular and lattice modes. In addition, in IR spectroscopy, the absorption of the ν(Pt-I) vibration is in a region where there are problems with water absorptions. Nevertheless, the appearance of two ν(Pt-I) and two ν(Pt-N) peaks in most cases is strongly suggestive of *cis* isomers.

4.4 References

1. P D. Braddock, T. A. Connors, M. Jones, A. R. Khokhar, D. H. Melzack and M. L. Tobe. Chem. Biol. Interactions, **11,** 145 (1975).
2. C. J. L. Lock, R. A. Speranzini and M. Zvagulis. Acta Cryst. **B36**, 1783 (1980).
3. F. D. Rochon and P. C. Kong. Can. J. Chem., **64**, 1894 (1986).
4. F. D. Rochon and P. C. Kong. Acta Cryst. **C42**, 1291 (1986).
5. A. J. Hay, A. J. Wolstenholme, J. J. Skihel and M. H. Smith. The EMBO Journal, **4** (11), 3021(1985).
6. A. Hermann, P. Lentzsch, G. Lassmann, A. M. Ladhoff and E. Donath. Biochim. Biophys. Acta, **82**, 27 (1985).
7. J. S. Wishnok. J. Chem. Ed. **50** (11), 780 (1973).
8. H. F. Maassab and K W. Cochran. Science, **145**, 1443 (1964).
9. A. Widell, B. G. Hansson, B. Oberg and E. Nordenfelt. Antiviral Research, **6,** 103 (1986).
10. R. D. Fletcher, J. E. Hirschfield and M. Forbes. Nature, **207**, 664 (1965).
11. J. T. H. Roos and D. R. Williams. J. Inorg. Nucl. Chem. **39**, 1294 (1977).
12. Y. K. Ho, M. T. Hakala and S. F. Zakrsewski. Cancer Research, **32**, 1023 (1972).
13. N. V. Klimova, A. P. Arendaruk, M. A. Baranova, N. I. Vasetchenkova, M. I. Shnar'yan and A. P. Skoldinov. Khim. Farm. Zh. **4**, 14 (1970) abstract.
14. Shionogi and Co. Ltd. Jpn Kokai Tokkyo Koho, JP58 79994, 1983.
15. F. D. Rochon, R. Melanson and M. Doyon. Inorg. Chem. **26**, 3065 (1987).
16. S. C. Dhara. Indian J. Chem. **8**, 193 (1970).
17. L. I. Elding and L. F. Olsson. Inorg. Chem. **16** (11), 2789 (1977).

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

19. P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor and R. H. Marshall. J. Chem. Soc. Dalton, 459 (1976).

20. J. J. Pesek and W. R. Mason. J. Magn. Res. **25**, 519 (1977).

21. R. J. Kidd and R. J. Goodfellow in R. K. Harris and B. Mann (Eds), NMR and the Periodic Table, Academic Press, London, 249 (1978).

22. I.M. Ismail and P. S. Sadler. Platinum, Gold and Other Metal Chemotherapeutic Agents, American Chemical Society, Washington, 183 (1983).

23. S. J. S. Kerrison and P. J. Sadler. Inorg. Chim. Acta, **104**, 197 (1985).

24. T. O'Halloran. Ph. D. Thesis. Massachusetts Institute of Technology, Ch. 6 (1987)

25. C. Dion. Thèse de doctorat. Université de Montréal. (1986)

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

27. F. D. Rochon, R. Melanson, M. Doyon and I. S. Butler. Acta Cryst. **C46**, 584 (1990).

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

29. Y. A. Kharitivov, L. K. Dymina and T. N. Leonova. Russ. J. Inorg. Chem. **13**(5), 709 (1968).

30. G. W. Watt, B. B. Hutchison and D. S. Klett. J. Am. Chem. Soc. **89**(9), 2007 (1967)

31. R. W. Berg and K. Rasmussen. Spect. Acta, **29 A**, 319(1973).

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

33. C. Dion, A. L. Beauchamp, F. D. Rochon and R. Melanson. Acta Cryst. **C45**, 852 (1989).

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

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

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

37. D. M. Adams and D. M. Morris. J. Chem Soc. A, 765 (1969).

CHAPTER 5

Synthesis of $Pt(A)(DMF)Cl_2$ and $[Pt(A)Cl_2]_n$ (A = amine; X = Cl, I)

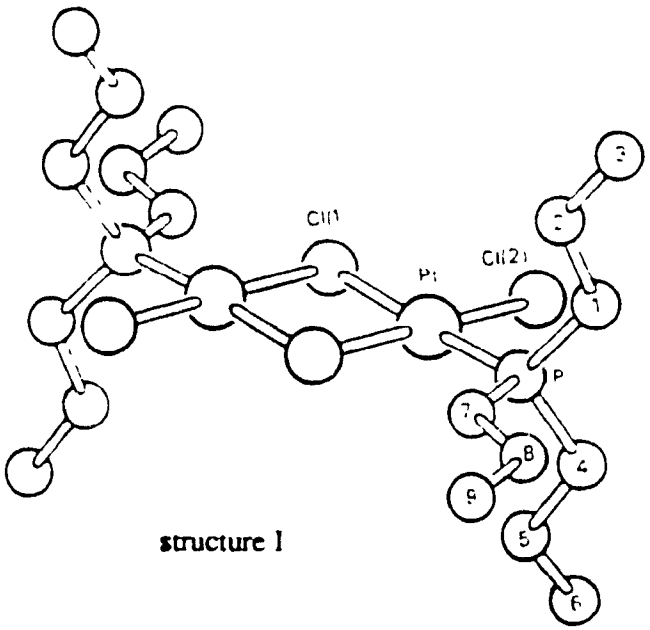
and

Crystal Structure of Cyclo-tri-μ-chloro-tri-

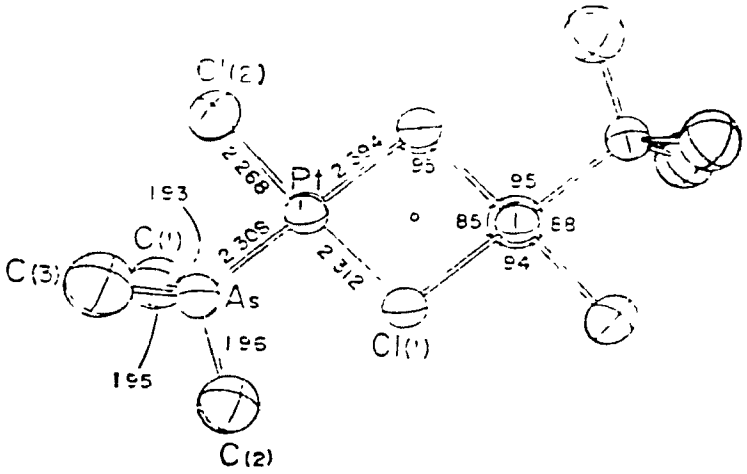
[chloro(dimethylamine)platinum(II)]

5.1 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. Halo bridged palladium and platinum compounds have been known since 1868 (1), but these complexes are not typical and the methods of synthesis are not generally applicable. Chatt and Venanzi have reviewed the different available methods and have developed a new more general synthesis (1). Their method gives chloro-bridged dimers $[Pt(L)Cl_2]_2$ with ligands containing as donor atoms, nitrogen (pyridine derivatives), phosphorus, sulphur, arsenic, selenium, antimony and tellurium (1-2). Further investigations by other workers (3-9) yielded chloro-bridged dimers with similar ligands but not with normal primary amine ligands. The crystal and molecular structures of *trans*-di-μ-chloro-dichloro-bis(tripropylphosphine)diplatinum(II) (structure I) (3), di-μ-chloro-dichlorobis(tri-methylarsine)diplatinum(II) (structure II) (4) and *trans*-di-μ-chloro-bis(phenylazophenyl-2)diplatinum(II) (structure III) (5) have been determined by X-ray diffraction. Complexes of the type $[Pt(L)X(\mu\text{-}X)]_2$ with L = sulphoxide and X = Cl, Br and I have been reported (6). Chloro-bridged compounds of the type $[Pt(L)Cl_2]_2$ (L = pyridine, picoline and lutidine) have been prepared in our laboratory. Molecular weight measurements showed that these compounds are dimers in chloroform solution at room temperature (7). The crystal structure of di-μ-chloro-dichlorobis(2,6-lutidine) diplatinum(II) dichloromethane solvate (structure IV) has been determined and showed a *trans* configuration (8). Courtot, Rumin, Perron and Girault (9 and references therein) have studied complexes of the type $[PtCl(L)(\mu\text{-}Cl)]_2$ (L = methylpyridine, *tert*-butylamine, piperidine). The compound with the bulky amine *tert*-butylamine is the only one reported in the literature for a chloro-bridged dimer with an aliphatic primary amine.



structure I



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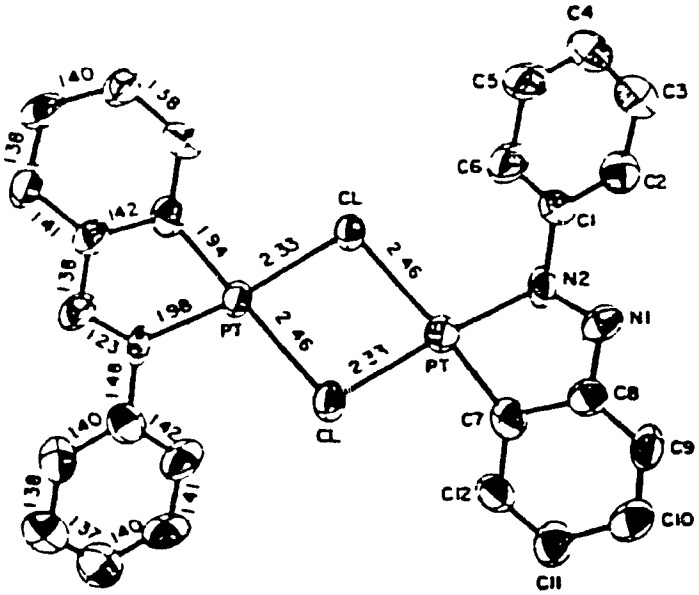
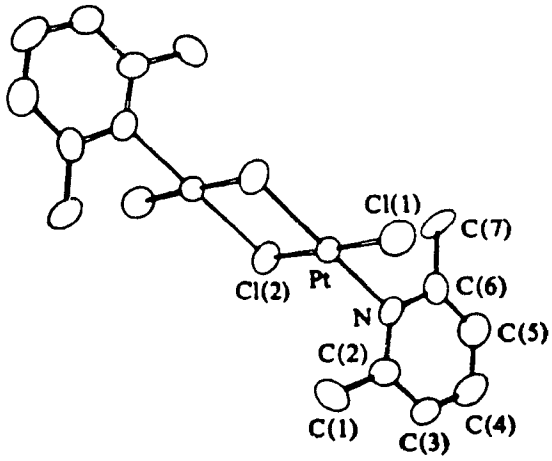


structure III



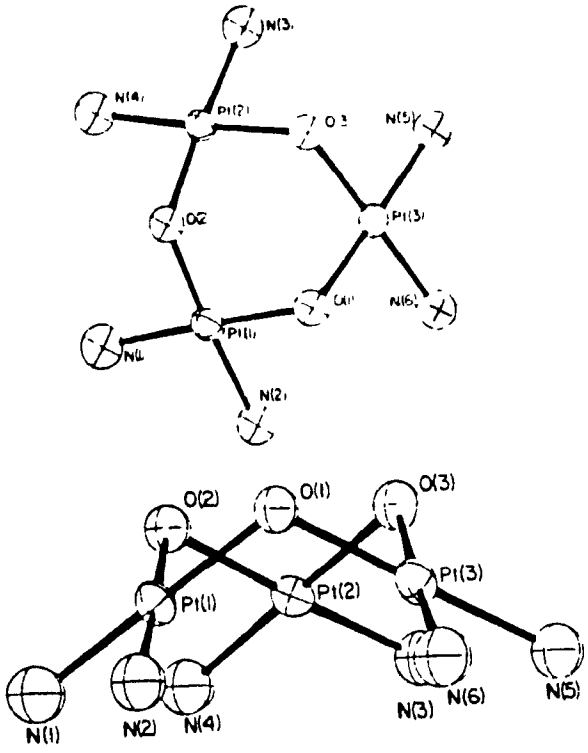
structure IV

Structures adapted from refs.. 3, 4, 5 and 8, respectively.

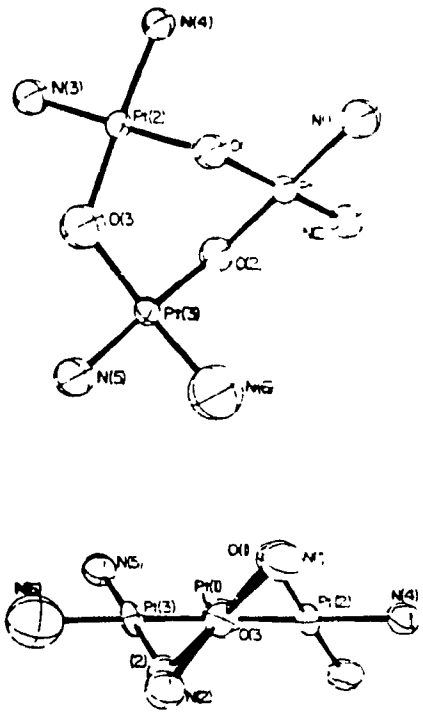
More recently iodo-bridged dimers with aliphatic amines have been reported (10, 11). These dimers are prepared from *cis*-Pt(amine)$_2$I$_2$ in acid solution and are excellent starting materials for the synthesis of mixed-ligand compounds (10, 12) or [Pt(amine)Cl$_3$]$^-$ complexed ions (13). Chloro-bridged dimers with alphatic 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 have never been confirmed even if the existence of oligomers with iodo bridges has been suggested (11) A few hydroxo-bridged trimers have been characterized in the literature. The crystal structure of bis-[cyclo-tri-μ-hydroxo-tris(*cis*-diammineplatinum(II))] trisulfate hexahydrate (structure V) (14), cyclo-tri-μ-hydroxo-tris[*cis*-diammineplatinum(II) nitrate (structure VI) (15), bis[cyclo-tri-μ-hydroxo-tris(*trans*-1,2-diaminocyclohexane)platinum(II))] trisulfate (struc-ture VII) (16) and cyclo-tri-μ-hydroxo-(trinitroargentio)tris[(ethylenediammine) platinum(II)] nitrate (structure VIII) (17) have been determined by X-ray diffraction. The crystal structures of two cyclic hydroxo-bridged tetramers have also been reported (18-19).

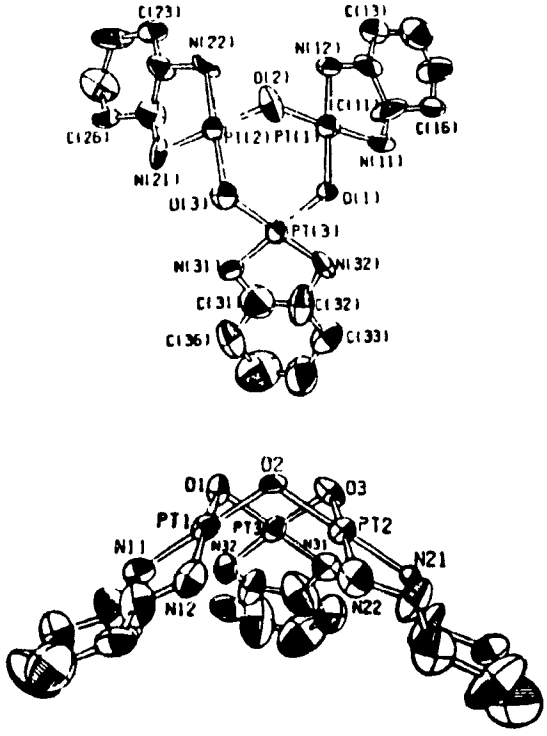
The chloro-bridged dimers, discussed above, can be cleaved by nucleophiles such as pyridine, ethylene, acetonitrile and DMF. Dimethylformamide is a commonly used organic solvent whose interaction with metals is not well known. Examination of the orbital energy diagram of DMF shows two possible donor 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.



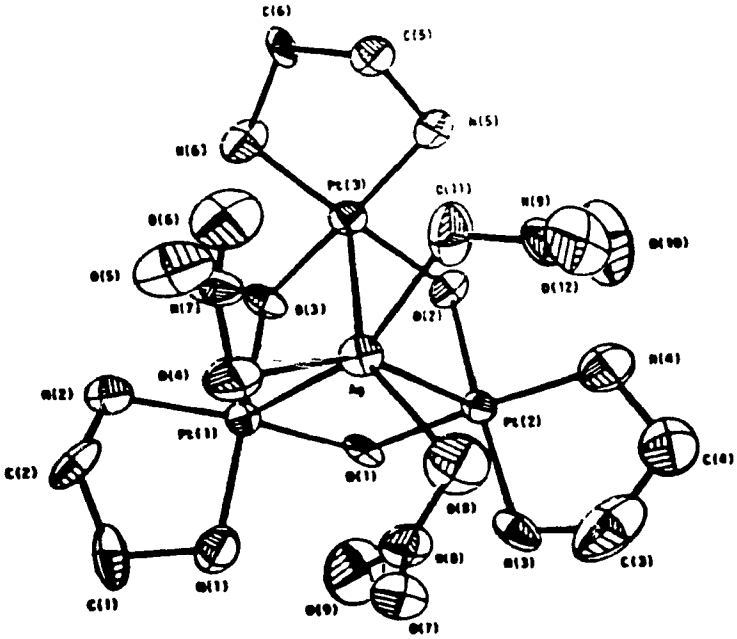
Structure V



Structure VI



Structure VII



Structure VIII

Structures adapted from refs. 14, 15, 16 and 17, respectively.

Although platinum usually shows a preference for N-donor ligands, bonding through nitrogen is unknown in transition metal DMF complexes and all published structures have shown that the binding site in DMF complexes is the oxygen atom (7, 20-22). It has been postulated that coordination via oxygen is more favored due to steric hindrance at the substituted nitrogen atom. In addition, DMF possesses a resonance structure of two mesomeric forms:

Because of its ionic structure, DMF will bind platinum trough its oxygen atom easier than with its nitrogen atom. Since the ionic form is favored when DMF is coordinated to a metal, a more pronounced decrease in multiplicity of the C - O bond along with an increase of multiplicity of the C - N bond would be expected. But it is interesting to observe that a brief survey of several DMF crystal structure 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 (22). The structure of DMF in the gas phase was determined in 1962 by electron diffraction (23). The molecule is planar and the C - O bond length was fixed at 1.20 Å while the N - C distance was found to be 1.34(4) Å. The results of the brief survey (22 and references therein) have shown that in the crystal structures where DMF is a solvent molecule of crystallization, the C - O bond distances varied from 1.211 to 1.30 Å (in some structures, the standard deviations were very high due to disorder), while the N - C bond distances were from 1.30 to 1.41 Å. In the metal-bonded DMF structures, the corresponding distances varied from 1.222 to 1.32 Å and from 1.28 to 1.35 Å, respectively. In all the published structures, bonded and

non-bonded DMF has a planar geometry. These results seem to indicate that the ionic form in free DMF is important.

Few platinum(II) complexes with DMF has been reported in the literature. Chatt and Venanzi (1, 2, 24) published a general method for the synthesis of $PtLL'Cl_2$ complexes, from the cleavage of chloro-bridged dimers of the type $[PtLCl_2]_2$, where L and L' = C_2H_4, pyridine, PR_3, AsR_3, SeR_2, TeR_2. Depending on the ligands, the authors obtained mixtures of *cis-trans* isomers or pure *trans*-isomers. The authors were unable to synthesize mixed-complexes with aliphatic amines or DMF ligands. Courtot et al. (9) have studied complexes of the type $Pt_2Cl_4(L)_2$ (L = methylpyridine, tert-butylamine, piperidine) and their cleavage by various ligands including DMF. They have observed the formation of *trans*-$Pt(L)(DMF)Cl_2$ with L = 4-methylpyridine, 2-methylpyridine and 2,4,6-trimethylpyridine, but not with tert-butylamine. Kong and Rochon have also synthesized by a different method chloro-bridged dimers $[Pt(L)Cl_2]_2$ (L = pyridine, picoline and lutidine) and investigated the cleavage of these molecules with dimethylformamide. The authors believed that *cis* and *trans*-$Pt(L)(DMF)Cl_2$ complexes were obtained but were unable to prove the existence of *cis* isomers (7). The crystal structure of the complex *trans*-Pt(2,6-lutidine)$(DMF)Cl_2$ was determined and DMF was shown to be bonded through its oxygen atom as expected (22). Bonding through the oxygen atom was confirmed by 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. One objective of this thesis was to develop a method to synthesize $Pt(A)(DMF)Cl_2$ (A = primary amine) compounds. This method is based on the cleavage of halo-bridged

oligomers as reported for pyridine complexes (7). We have now synthesized a series of complexes of the type $Pt(A)(DMF)Cl_2$ where A= methylamine, ethylamine, cyclobutylamine, cyclopentylamine and dimethylamine. All the compounds were characterized by proton- and platinum-NMR and IR spectroscopy.

5.2 Experimental

$[Pt(A)Cl_2]_2$. The compounds were synthesized as already reported for pyridine ligands (7). Compounds with methylamine, ethylamine, cyclobutylamine, cyclopentylamine and dimethylamine were synthesized. The elemental analyses were determined for the methylamine, ethylamine and dimethylamine complexes. The composition of the other compounds were assumed identical because of the similarity of their spectroscopic properties.

Compounds	Yield	Dec. pt.		Elemental analysis %C	%H	%Cl	%N
$[Pt(MeNH_2)Cl_2]_2$	77%	183-191°C	calc.	4.04	1.70	23.86	4.71
			exp.	4.16	1.66	23.38	4.95
$[Pt(EtNH_2)Cl_2]_2$	84%	175-184°C	calc.	7.72	2.67	22.78	4.50
			exp.	7.75	2.19	22.23	4.76
$[Pt(CBA)Cl_2]_2$	37%	180-187°C					
$[Pt(CPA)Cl_2]_2$	61%	150-165°C					
$[Pt(DMNH)Cl_2]_2$	42%	170-178°C	calc.	7.72	2.67	22.78	4.50
			exp.	7.86	2.26	22.72	4.62

$[Pt(DMNH)Cl_2]_3$. One mmole of $K[Pt(DMNH)Cl_3]$, synthesized by the method already reported (13), 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. $[Pt(DMNH)Cl_2]_3$ Yield: 48%, dec. pt.: 160-168°C.

$Pt(A)(DMF)Cl_2$. One mmole of the chloro dimer 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 $Pt(MeNH_2)(DMF)Cl_2$ must be isolated under nitrogen atmosphere since it decomposes in air. The products were dried over P_2O_5. The elemental analyses were determined for the methylamine, ethylamine and dimethylamine complexes. The structures of the other compounds were established by the similarity of their spectroscopic properties.

Compound	Yield	Dec.pt.(°C)		Elemental Analysis %C	%H	%Cl	%N
$Pt(MeNH_2)(DMF)Cl_2$	33%	74-104	calc.	12.98	3.27	19.15	7.57
			exp.	10.73	2.97	19.89	6.91
$Pt(EtNH_2)(DMF)Cl_2$	29%	78-98	calc.	15.63	3.67	18.45	7.29
			exp.	12.69	3.07	19.45	6.27
$Pt(CBA)(DMF)Cl_2$	14%	92-101					
$Pt(CPA)(DMF)Cl_2$	17%	98-123					
$Pt(DMNH)(DMF)Cl_2$	78%	115-122	calc.	15.63	3.67	18.45	7.29
			exp.	14.79	3.38	19.06	7.13

5.3 Results and Discussion

5.3.1 Synthesis of $Pt(A)(DMF)Cl_2$ Complexes

Primary aliphatic amine complexes of platinum(II) with DMF are not yet known. One objective of this thesis was to develop a method to synthesize $Pt(A)(DMF)Cl_2$ (A = primary amine) compounds. The first attempt involved the simple reaction of DMF with the monoamine complex $K[Pt(A)Cl_3]$ in aqueous solution or in DMF solution.

$$K[Pt(A)Cl_3] \xrightarrow[DMF/D_2O]{\text{DMF or}} Pt(A)(DMF)Cl_2$$

This method, which works very well with nitrogen donor ligands to produce the mixed-ligands complex is not adequate for DMF. There was no reaction with DMF under these conditions, as established by ^{195}Pt-NMR spectroscopy. The spectrum of a DMF solution of $K[Pt(MeNH_2)Cl_3]$, heated at 50°C over a 3-week period, exhibited only a resonance at -1847 ppm, at the position of the $K[Pt(MeNH_2)Cl_3]$ complex (see Chapter III).

The second synthetic method that we tried was more successful. It is based on the cleavage of halo-bridged oligomers as reported for the pyridine complexes (7). The oligomers which will be discussed later in this chapter, can be easily cleaved by DMF.

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

A series of complexes of the type $Pt(A)(DMF)Cl_2$ where A = methylamine, ethylamine, cyclobutylamine, cyclopentylamine and dimethylamine has been synthesized. The results of the elemental analyses have shown that a few compounds, especially $Pt(EtNH_2)(DMF)Cl_2$, contains a small quantity of chloro-bridged oligomers. All the compounds were characterized by proton- and platinum-NMR and IR spectroscopy.

5.3.1.1 ^{195}Pt- and ^{1}H NMR spectra

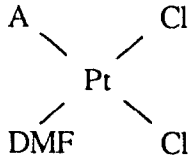
The ^{195}Pt- and ^{1}H-NMR spectra of the compounds Pt(A)(DMF)Cl_2 have been measured in different solvents and the results are presented in Tables XX and XXI, respectively. There is no solvent difference for the ^{195}Pt-NMR spectra of these complexes in acetone and DMF and maybe a slight upfield shift (10 ppm) in CH_2Cl_2. Each complex shows only one ^{195}Pt resonance in the different solvents.

Table XX. ^{195}Pt resonances (δ ±5ppm) of the Pt(A)(DMF)Cl_2 complexes.

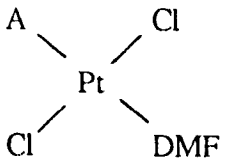
Solvent Compound	DMF		Acetone	CH_2Cl_2
Pt($MeNH_2$)(DMF)Cl_2	-1560	-1559	-	
Pt($EtNH_2$)(DMF)Cl_2	-1571	-1567	-1569	
(after heating at 35° for 5 min.)			-1569, -1715 83% 17%	
Pt(CBA)(DMF)Cl_2	-1578	-1576	-1588	
Pt(CPA)(DMF)Cl_2	-1566	-1565	-	
Pt(DMNH)(DMF)Cl_2	-1515	-1514	-1522	
old solution (1 month)			-1524, -1576, -1700 55% 10% 35%	

There are several possible complexes that could be formed when the oligomers $[Pt(A)Cl_2]_n$ react with DMF. The most probable are the *cis* (I) and *trans* (II) monomers with one DMF and one amine ligand, since terminal chloro ligands form stronger bonds with Pt than DMF. There are other less likely possibilities like the *cis* (III) and *trans* (IV) disubstituted DMF monomers and the trisubstituted DMF monomer (V). Partially cleaved

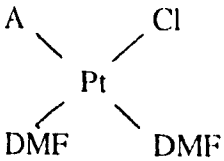
species containing a single chloro bridge such as compounds *cis* (VI) and *trans* (VII) dimers are also possible. Other partially-cleaved oligomers (e.g., trimers) might possibly be present, but not very likely. Such species would produce more than one resonance in the ^{195}Pt-NMR spectra. Structure VII (*trans* isomer) would also produce two different resonances and therefore these structures were eliminated.



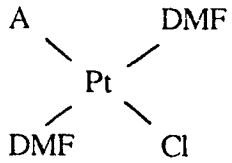
I



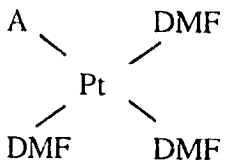
II



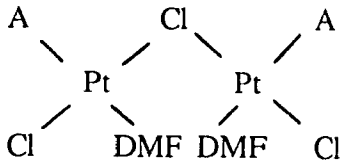
III



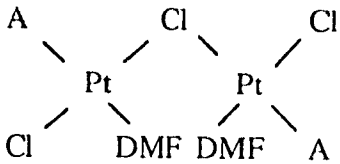
IV



V



VI



VII

The ^{1}H-NMR spectra, measured on fresh solutions in acetone or dichloromethane (Figure 13, 15 and 17), showed only one series of resonances for the amine and the bonded DMF ligands. Therefore, structures III (two DMF ligands in the *cis*

positions) and V (three DMF ligands) must be eliminated. Only four possible species remain: I, II IV and VI. On the basis of the integration measurements, the species with two DMF ligands (IV) can be rejected since the DMF resonances should be two times more intense than the amine resonance. The integration measurements give one DMF ligand for one amine ligand. This leaves three possible species: the *cis* (I) and *trans* (II) monomers with one DMF and one amine, and the partially-cleaved *cis* dimers. Since the partially-cleaved dimer is not a strong possibility, the most likely products, are either the *cis* and the *trans* monomers with one DMF and one amine ligand.

The ^{195}Pt chemical shifts are observed at about -1550 ppm, in an acceptable region for a platinum environment consisting of one amine, one O-bonded ligand and two chloro ligands. This is very close to the value reported for $[Pt(\overset{\frown}{N\ O})Cl_2]^-$ ($\overset{\frown}{N\ O}$ = glycinate) complex at -1602 ppm (25).

The presence of bonded DMF has been confirmed by ^1H-NMR spectroscopy of the $Pt(A)(DMF)Cl_2$ complexes. The aldehyde proton was observed around 8.1 ppm as a singlet + doublet, with a coupling constant $^3J(Pt\text{-}H) \approx 23$ Hz, in acetone. The presence of coupling of this proton with platinum confirmed the coordination through the oxygen atom since the methyl resonances should have shown a coupling with platinum if the bonded site was the nitrogen atom. This $^3J(^{195}Pt\text{-}^1H)$ 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 found at 8.30 ppm with coupling constants of 27 Hz in chloroform solution (9). Similarly, Kong and Rochon reported for complexes $Pt(L)(DMF)Cl_2$ (L = pyridine, 2-picoline, 4-picoline, 2,4-lutidine and 2,6-lutidine) an aldehyde chemical shift

between 8.15 and 8.35 ppm in chloroform with coupling constants of about 40 Hz. (7). These coupling constants are higher than our values and those reported by Courtot et al with similar ligands (9).

The ^{1}H-NMR spectrum of a fresh acetone-d_6 solution of $Pt(MeNH_2)(DMF)Cl_2$, shows only one species and the corresponding ^{195}Pt-NMR spectrum gives only one resonance at -1559 ppm (Figure 13a and 13b). The methyl group of the methylamine ligand appears as a triplet, centered at 2.36 ppm, resulting from the coupling of these hydrogens with the hydrogens of the nitrogen with $^{3}J(CH\text{-}NH) = 6$ Hz. A doublet of triplets can be observed on each side of this signal resulting from the coupling of these hydrogens with platinum with a coupling constant $^{3}J(Pt\text{-}CH) = 48$ Hz. The hydrogens of the nitrogen atom are observed at 4.49 ppm. The methyl groups of the DMF ligands are not equivalent and appear respectively at 3.16 and 2.88 ppm while the aldehyde proton resonance appears as a singlet plus doublet at 8.13 ppm with the coupling constant $^{3}J(Pt\text{-}H) = 23$ Hz.

The results of the NMR study indicate that the products of the reaction of the chloro-bridged dimers (or higher oligomers) with DMF are $Pt(A)(DMF)Cl_2$, but it does not give us any information on the isomer produced. IR spectroscopy is a better method to determine the geometry of such compounds and will be discussed later in this chapter. But since it is important at this stage to know the geometry of the isomers formed, we will accept the fact that these compounds are *trans*-isomers.

Table XXI. ^{1}H-NMR resonances of DMF and the Pt(A)(DMF)Cl_2 complexes in acetone-d_6 [δ(ppm) and coupling constants J(Hz)]

	amine							DMF		
	H_1	J(H-H)	^{3}J(Pt-H_1)	H_2	J(H-H)	$H_{2'}$+H_3	NH	CH_3	H	J(Pt-H)
DMF								2.82(s) 2.98(s)	8.01(s)	
trans-Pt($MeNH_2$)(DMF)Cl_2	2.36 (t+dt)		48	-			4.49	2.88(s) 3.16(s)	8.13(s+d)	23
cis-Pt($MeNH_2$)(DMF)Cl_2	2.32(t+dt)		-	-			4.70	2.85(s) 3.13(s)	8.09(s+d)	
Pt($EtNH_2$)(DMF)Cl_2(acetone)	2.66(m)	7		1.29(t)	7		-	2.90(s) 3.18(s)	8.15(s+d)	23
(CD_2Cl_2)	2.77(m)	7		1.26(t)	7	-	3.82	2.93(s) 3.06(s)	8.23(s+d)	22
Pt(CBA)(DMF)Cl_2	3.51(m)	8		2.30(m)	8	2.06(m)	4.68	2.89(s) 3.17(s)	8.13(s+d)	22
						1.66(m)				
Pt(CPA)(DMF)Cl_2	3.41(m)	8		2.06(m)	8	1.81(m)	4.48	2.90)s) 3.18(s)	8.15(s+d)	22
						1.57(m)				
Pt(DMNH)(DMF)Cl_2 (acetone)	2.53(d+dd)		38	-			5.20	2.88(s) 3.17(s)	8 09(s+d)	23
(CD_2Cl_2)	2.60(d+dd)		38	-			5.05	2.92(s) 3.05(s)	8.14(s+d)	24

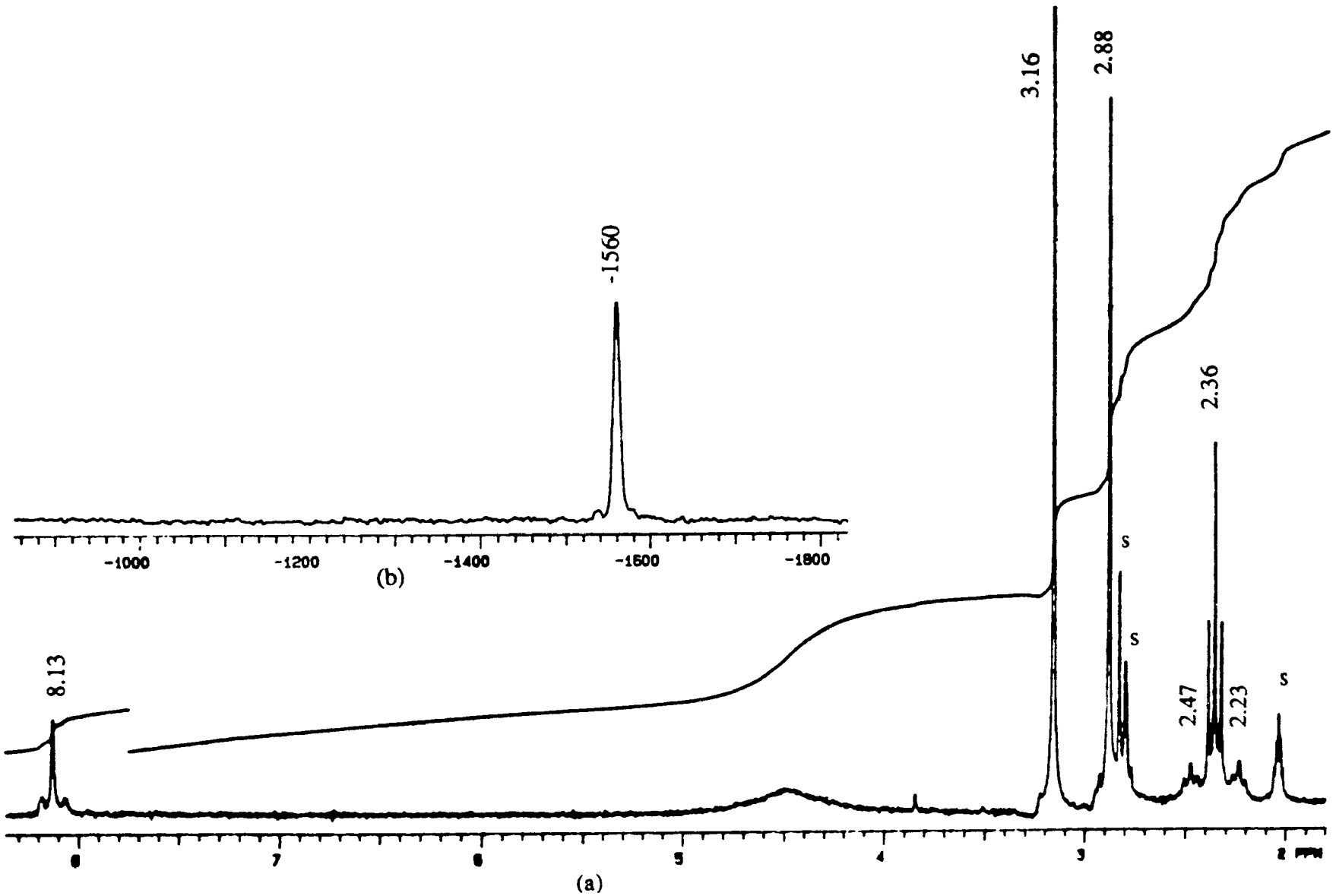


Figure 13 (a)^{1}H- and (b) ^{195}Pt-NMR spectra of a fresh solution of *trans*-Pt(MeNH$_2$)(DMF)Cl$_2$ in acetone

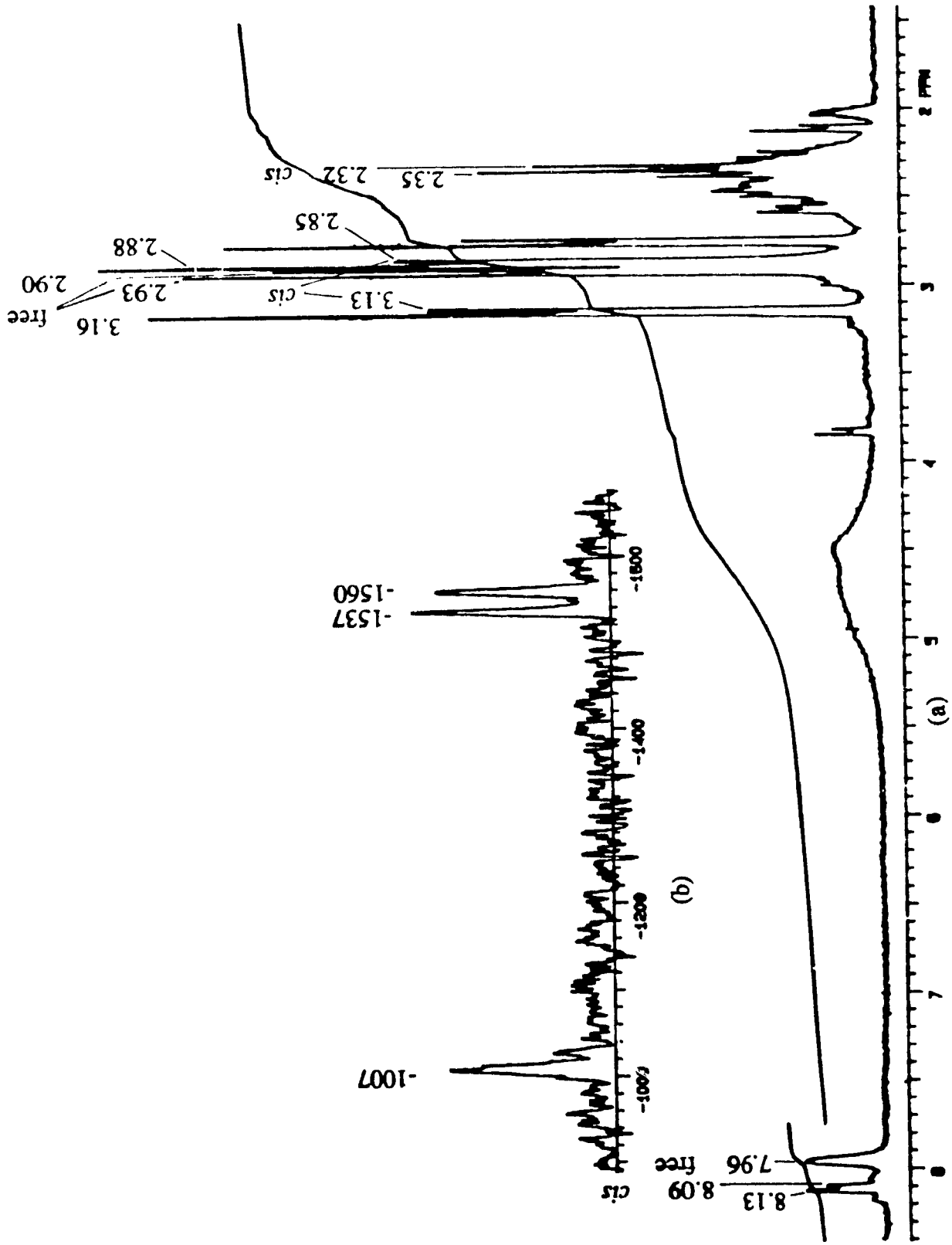


Figure 14. (a) ^{1}H- and (b) ^{195}Pt-NMR spectra of an old solution of $Pt(MeNH_2)(DMF)Cl_2$.

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 14a) of an old solution of the complex in acetone shows in the region around 8 ppm the presence of 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 non-coordinating solvents (1,7, 8, 26). As an example, the complex Pt(2,6–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-lutidine)Cl_2]$_2$, were obtained at room temperature (8). The aldehydic signal observed for the old solution at 8.13 ppm is assigned to *trans*-Pt($MeNH_2$)(DMF)Cl_2. In addition to oligomeric species, a new aldehyde resonance is observed at 8.09 ppm with corresponding resonances for the methyl groups of DMF at 3.13 and 2.85 ppm. These new signals are assigned to *cis*-Pt($MeNH_2$)(DMF)Cl_2 which is formed from the reaction of chloro-bridged oligomers with free DMF. We will see later in this section 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($MeNH_2$)(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, *trans*-Pt($MeNH_2$)(DMF)Cl_2 decomposes to chloro-bridged oligomers releasing DMF. The oligomers will react with free DMF to produce first *cis*-Pt($MeNH_2$)(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 isomerisation of the *cis* isomer. This equilibrium

will be seen in solution, since in the solid state, we believe that only *trans*-$Pt(MeNH_2)(DMF)Cl_2$ was isolated.

Since the resonance of the aldehydic proton in the *cis* isomer appears at higher field compared to the *trans* isomer, we should expect the ^{195}Pt resonance for the *cis* species at lower field. The ^{195}Pt-NMR of an old sample which was measured in DMF, exhibits three resonances: at -1560, -1537 and -1012 ppm. It is difficult to compare exactly this spectrum to the proton one, since in this case, the acetone solvent was evaporated to dryness. DMF was added to the residue and the ^{195}Pt-NMR spectrum was measured. The signal observed at -1560 is *trans*-$Pt(MeNH_2)(DMF)Cl_2$, while the -1537 ppm resonance is the corresponding *cis* isomer, which is observed at lower field as expected. Oligomeric species are not observed since they are cleaved in DMF. The resonance at -1012 ppm 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 for DMF in $K[Pt(A)Cl_3]$ results in a downfield shift of approximately 280 ppm. Substitution of a second chloride in these complexes will result in a resonance at ≈-1280 ppm and substitution of a 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 to the observed platinum chemical shifts by assuming that the effects of substitutions are additive (27). As an example, Appleton et al., calculated values of –2126 and –1544 ppm for the complexes $Pt(NH_3)_2Cl_2$ and $Pt(NH_3)_2(OH)_2$ while the observed values were –2100 and –1572 ppm.

The ^1H-NMR spectrum of $Pt(EtNH_2)(DMF)Cl_2$ complex has been measured in acetone-d_6 and dichloromethane. Both spectra were very similar except for the position

of the different peaks due to solvent effects. The ^{195}Pt- and ^{1}H-NMR spectra of a fresh solution of this complex in CD_2Cl_2 show only one species (Figure 15) which is assigned to *trans*-Pt($EtNH_2$)(DMF)Cl_2. The methyl and methylene groups of the ethylamine ligand appear, respectively, as a triplet centered at 1.26 ppm and a multiplet at 2.77 ppm suggesting possible coupling of the methylene protons with platinum. The methyl groups of the DMF ligand are at 3.06 and 2.93 ppm, while the aldehydic resonance appears as a singlet plus a doublet at 8.23 ppm with a coupling constant of 22 Hz. Some free DMF can be observed even after 2 min. of spectral accumulation indicating that these compounds decompose very rapidly in acetone. The corresponding ^{195}Pt-NMR spectrum shows only one resonance at -1569 ppm.

The ^{1}H-NMR spectrum of Pt($EtNH_2$)(DMF)Cl_2 complex measured after slight heating in dichloromethane, shows an intense free DMF peak in the aldehyde region (Figure 16a). No new aldehydic or methyl resonances for the 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°) in CD_2Cl_2 (Figure 16b) shows a new resonance at -1715 ppm in the region of the chloro-bridged trimer. No *cis*-Pt($EtNH_2$)(DMF)Cl_2 is observed, since the oligomers are quite stable in dichloromethane.

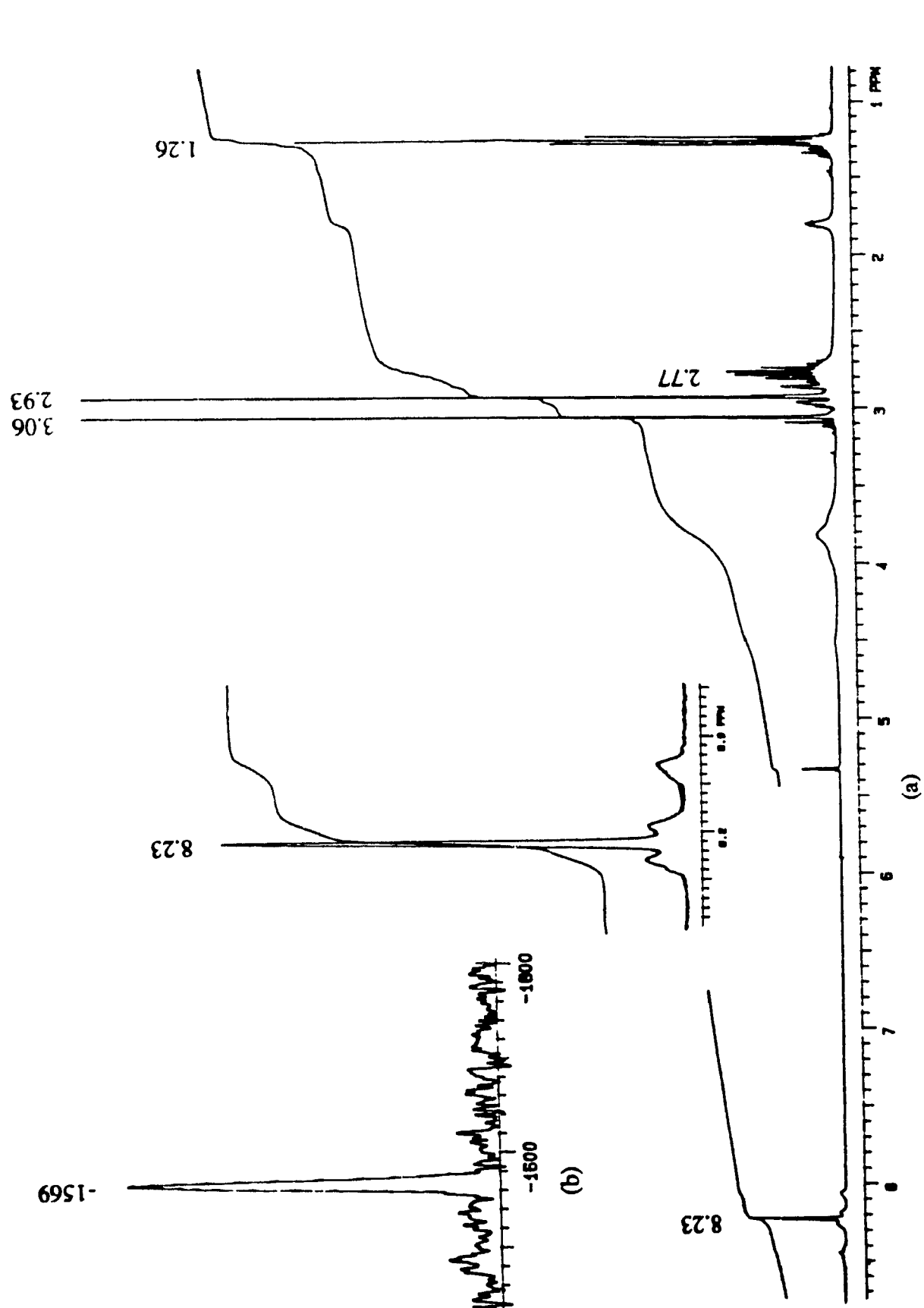


Figure 15. (a) ^{1}H- and (b) ^{195}Pt-NMR spectra of a fresh solution of *trans*-$Pt(EtNH_2)(DMF)Cl_2$ in CD_2Cl_2.

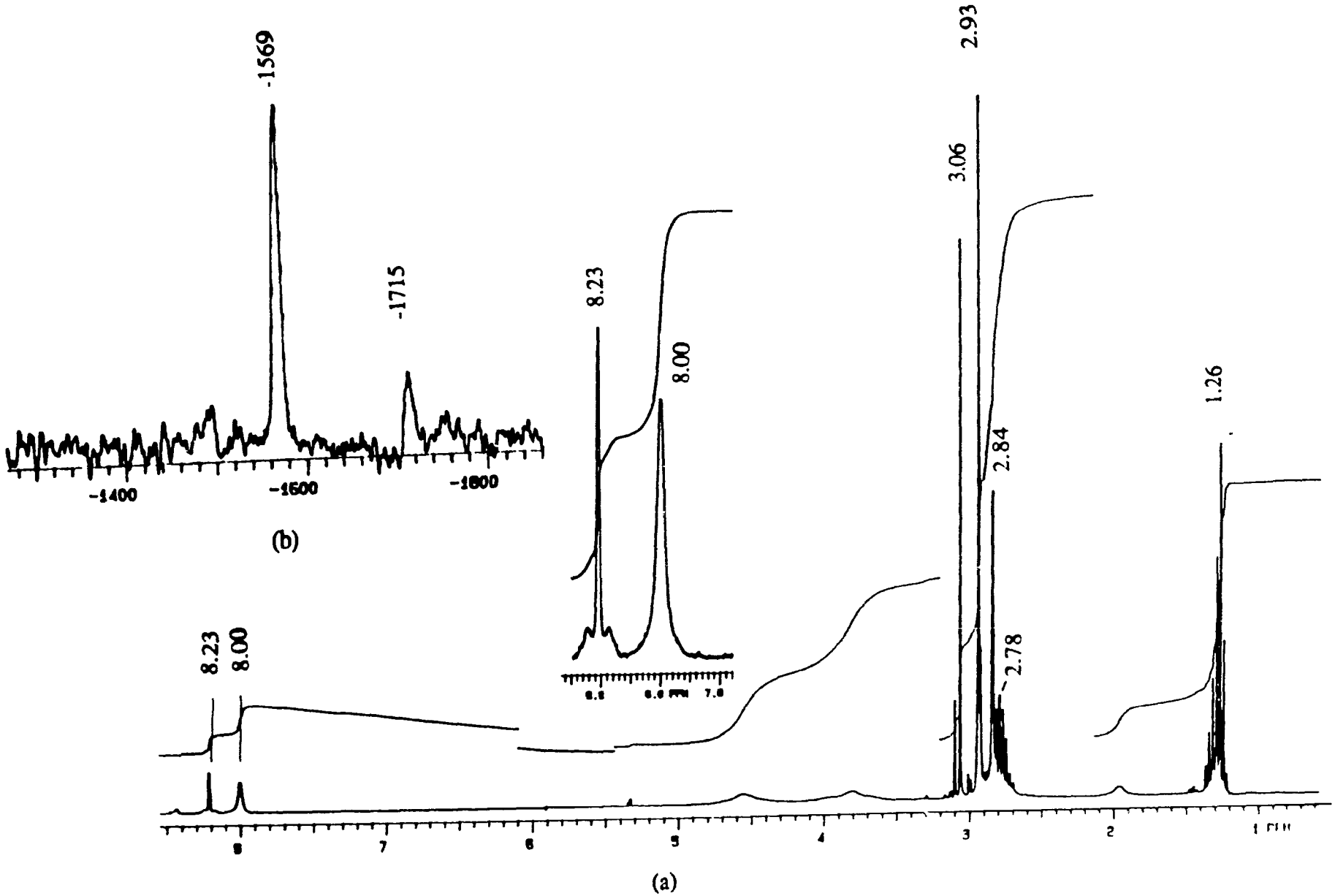


Figure 16. (a) ^{1}H- and (b) ^{195}Pt-NMR spectra of an old solution of $Pt(EtNH_2)(DMF)Cl_2$ in CD_2Cl_2

The NMR spectra of fresh solutions of the compounds Pt(CBA)(DMF)Cl_2 and Pt(CPA)(DMF)Cl_2 show the presence of only one species. The ^{195}Pt resonances are in the same region as the other amine-DMF compounds, suggesting similar structures. The coupling constants of the aldehydic proton of DMF with ^{195}Pt is 22 Hz for both complexes. No $^3J(^{195}Pt\text{-}^1H)$ was observed for the amines, since the signals are multiplets of weak intensity.

The ^1H-NMR spectrum of a fresh CD_2Cl_2 solution containing *trans*-Pt(DMNH)(DMF)Cl_2, shows only one species and the corresponding ^{195}Pt-NMR spectrum gives only one resonance at -1522 ppm (Figure 17). The methyl groups of the dimethylamine ligand appear as a doublet, centered at 2.60 ppm, showing the coupling of these hydrogens with the hydrogens of the nitrogen with $^3J(CH\text{-}NH) = 6$ Hz. A doublet of doublet can be observed on each side of this signal resulting from the coupling of these hydrogens with platinum with a coupling constant $^3J(Pt\text{-}CH) = 38$ Hz. The hydrogens of the nitrogen are observed at 5.05 ppm. The methyl groups of the DMF ligands are not equivalent and appear respectively at 3.05 and 2.92 ppm while the aldehyde proton resonance appears as a singlet plus doublet at 8.14 ppm with a coupling constant $^3J(Pt\text{-}H) = 24$ Hz.

The proton spectrum of the old CH_2Cl_2 solution of the same complex, shows that the free DMF aldehydic signal is almost twice as intense as the bonded DMF (Figure 18). The loss of DMF suggests a rearrangement of *trans*-Pt(DMNH)(DMF)Cl_2 to chloro-bridged oligomeric species $[Pt(DMNH)Cl_2]_n$, whose methyl resonances appear as a doublet centered at 2.78 ppm with a coupling constant of $J(CH\text{-}NH) = 6$ Hz. These resonances are close to those of the trimeric species (2.73 ppm) measured in CD_2Cl_2 (Figure 23c , next section). Since this resonance is observed at lower field in the ^1H-

NMR spectra, the ^{195}Pt resonance is expected at higher field The ^{195}Pt-NMR of the old sample exibits three resonances: at -1524, -1576 and -1700 ppm corresponding to the resonances of *trans*-, *cis*-Pt(DMNH)(DMF)Cl_2 and the chloro-bridged trimer, respectively (see section 5.3.2.2).

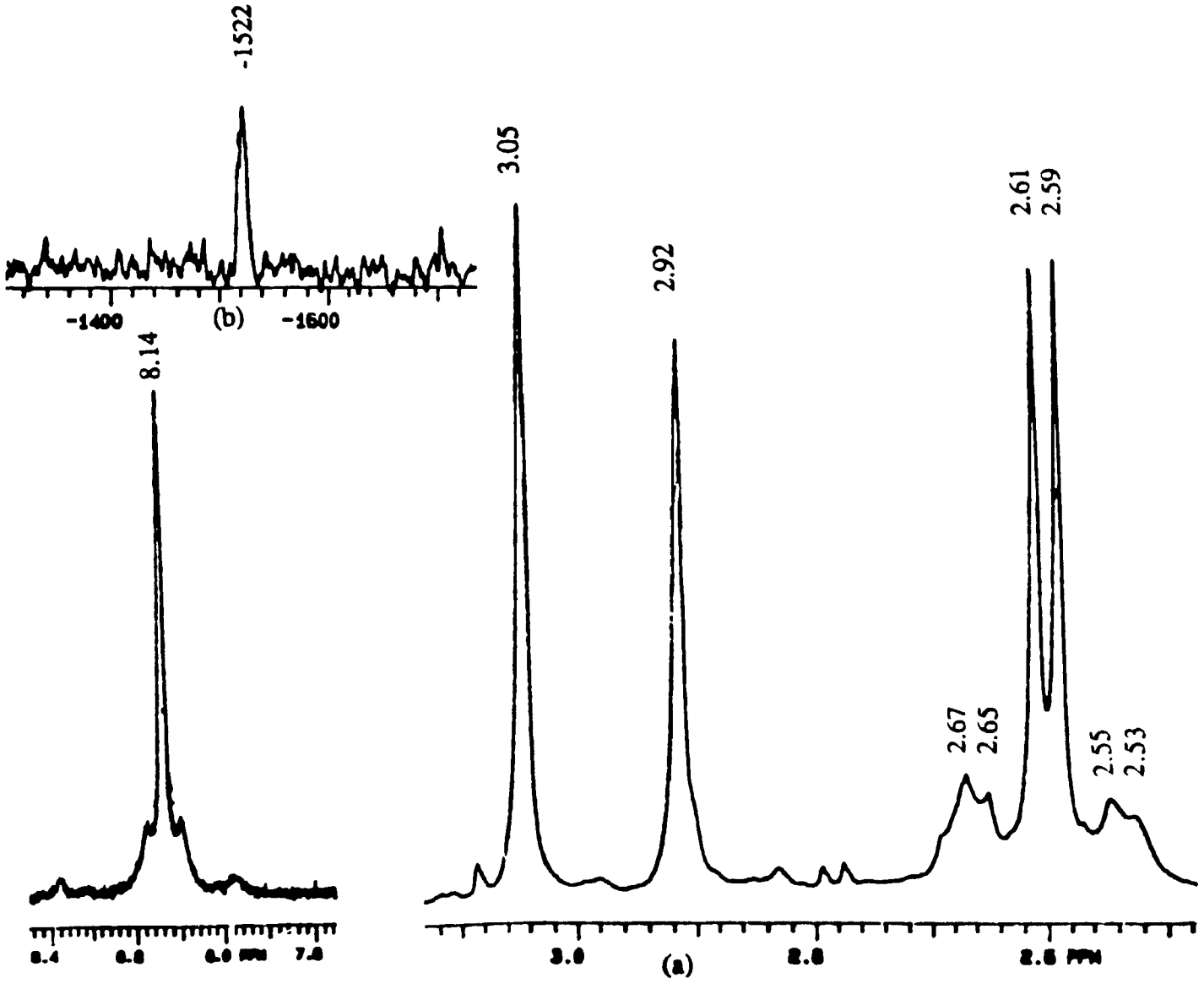


Figure 17. (a) ^{1}H- and (b) ^{195}Pt-NMR spectra of a fresh solution of *trans*-Pt(DMNH)(DMF)Cl_2 in methylene chloride.

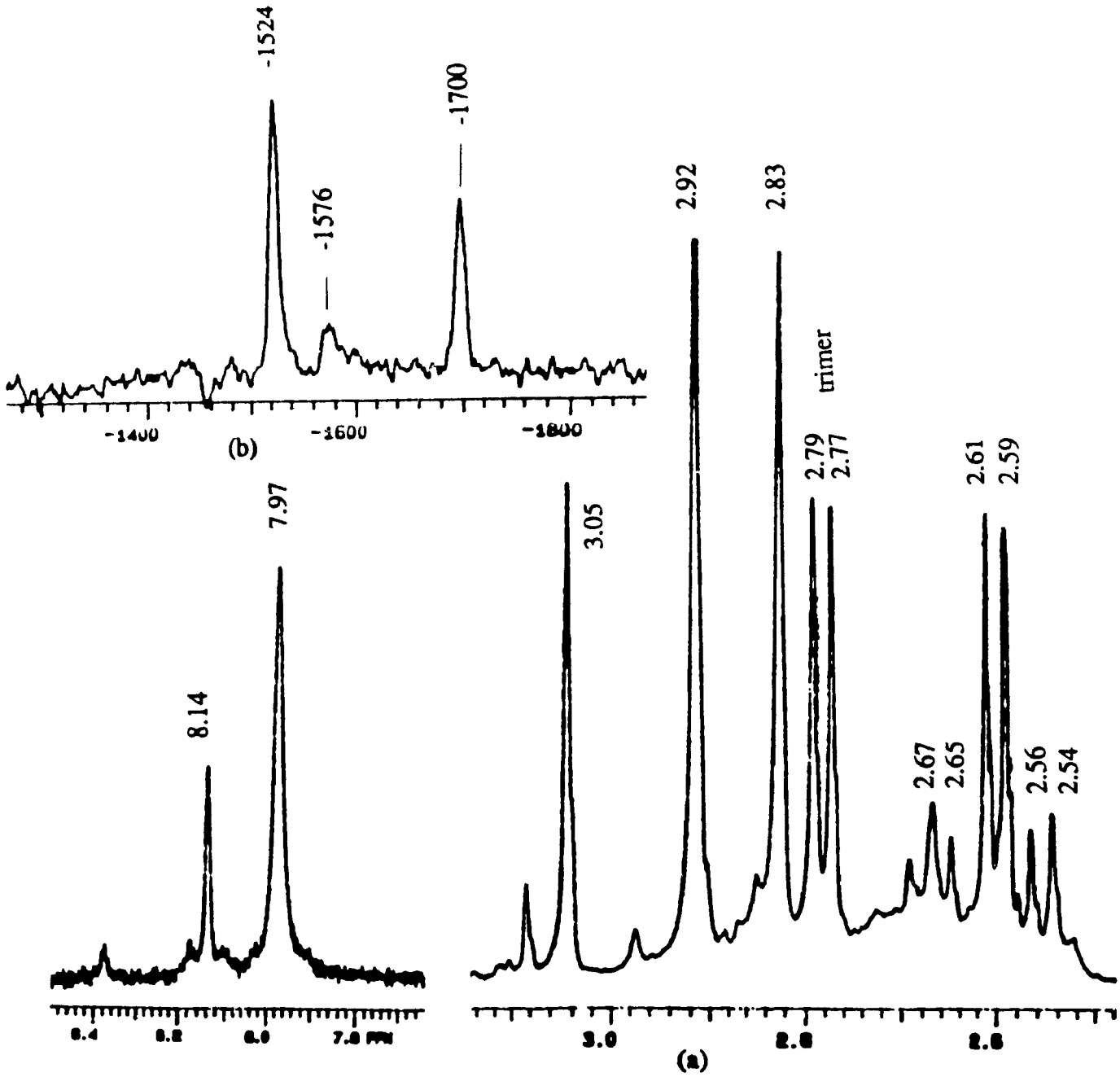


Figure 18. (a) ^{1}H- and (b) ^{195}Pt-NMR spectra of an old solution of $Pt(DMNH)(DMF)Cl_2$ in methylene chloride.

5.3.1.2 Infrared Spectra

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 (28). 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 Pt(A)(DMF)Cl_2 complexes have shown ν(CO) vibrations around 1640 cm^{-1}, 18 - 28 cm^{-1} lower than the ν(CO) for the free ligand (1670 cm^{-1}) indicating coordination through the oxygen atom for the DMF ligand. 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 comparison. An increase in wavenumber is expected for this vibration if the coordination is through the oxygen atom and we observe this vibration between 718 and 723 cm^{-1} in our spectra. The presence of the coordinated amine is confirmed by lower ν(N-H) vibrations between 3121 and 3305 cm^{-1} and δ(NH_2) vibrations around 1580 cm^{-1} (except for the dimethylamine complex where the latter band is often too weak to be observed). These values are close to those observed for Pt(py)(DMF)Cl_2 where py is a pyridine derivative (7, 9).

The approximate skeleton symmetries for *cis* and *trans* complexes with two amine ligands are C_{2v} and D_{2h} respectively. For dichloro compounds, group theory predicts two ν(Pt-Cl) 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 (see Appendix 1) predicts two ν(Pt-Cl) vibrations (2A'), one ν(Pt-O) (A') and one ν(Pt-N) (A') modes for both complexes.

Table XXII. Main IR bands (cm^{-1}) of the $Pt(A)(DMF)Cl_2$ complexes in the solid state (KBr pellets).

Compounds	ν(NH)	ν(C=O)	δ(NH_2)	δ(OCN)	ν(Pt-N) ν(Pt-O)	ν(Pt-Cl)
$Pt(MeNH_2)(DMF)Cl_2$	3121(m) 3218(ms) 3259(ms)	1645(s)	1582(ms) 1595(m)	721(m)	442(w) 402(mw)	341(ms)
$Pt(EtNH_2)(DMF)Cl_2$	3140(mw) 3198(m) 3220(m) 3245(ms)	1650(s)	1570(ms) 1592(ms)	723(m)	442(w) 397(mw)	342(ms)
$Pt(CBA)(DMF)Cl_2$	3121(mw) 3278(m) 3305(ms)	1640(s)	1587(m)	720(m)	444(w) 400(mw)	341(ms)
$Pt(CPA)(DMF)Cl_2$	3130(w) 3208(m) 3240(m)	1642(s)	1570(m)	721(m)	442(w) 398(mw)	338(ms)
$Pt(DMNH)(DMF)Cl_2$	3219(m)	1641(s)	-	718(m)	443(w) 392(mw)	343(m)

When the chloro-bridged dimers react with DMF, the ν(Pt-Cl) modes of the products are observed at ≈340 cm^{-1}. The intensity of this band is strong, when compared to those of the dimer. A weak band observed around 280 cm^{-1} for all the complexes (except $Pt(EtNH_2)DMF)Cl_2$) was assigned to a ligand vibration. On the basis of C_s symmetry, both the *cis* and *trans* isomers should show two ν(Pt-Cl) vibrations in the IR. The difference between the two vibrations should be smaller for the *trans* isomer. 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

(10, 29-31). For these reasons, we can conclude 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, in all the spectra (Figure 19) even though the ν(Pt-N) is expected at slightly higher frequency than the ν(Pt-O) band, these two 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.

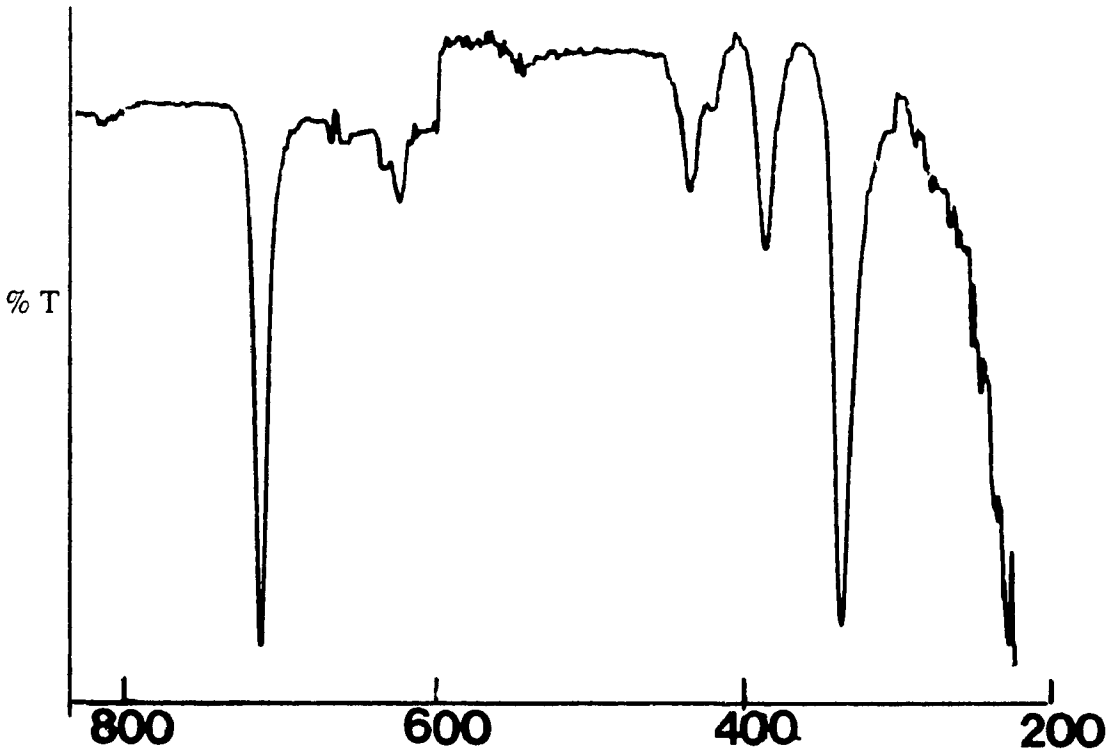


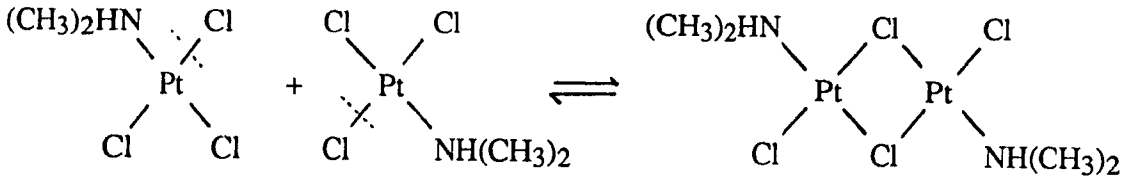
Figure 19. Typical IR spectrum for $Pt(A)(DMF)Cl_2$ complexes in the 800-250 cm^{-1} region (A = DMNH).

5.3.2 Synthesis of $[Pt(A)X_2]_n$

The chloro-bridged compounds were synthesized as already reported for pyridine ligands (7). The starting material $K[Pt(A)Cl_3]$ was synthesized by the cleavage of the iodo-bridged dimers as described recently (13). The chloro-bridged oligomers are formed from the reaction of the complexes $K[Pt(A)Cl_3]$ in the presence of perchloric acid according to the following equation:

$$nK[Pt(A)Cl_3] + HClO_4 \longrightarrow [Pt(A)Cl_2]_n + KClO_4 + KCl$$

The $KClO_4$ salt is removed by filtration after cooling the solution to about 0°C. The oligomers precipitate when the solution is concentrated close to dryness. The method is believed to produce *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 shown a *trans* configuration (8).

Complexes of the type $[Pt(A)Cl_2]_n$ where A = 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 thought to be mainly chloro-bridged dimers in the solid state. These compounds were isolated as orange to brownish-red powders. Slight heating (≈40°, for a few hours) of a methylene chloride solution containing the oligomer (mainly dimers) with dimethylamine, produced on standing red crystals which were suitable for X-ray diffraction methods. The crystal structure of one of these crystals was determined and the results have shown that the compound is a chloro-bridged trimer.

$$[Pt(DMNH)Cl_2]_2 \xrightarrow[\Delta]{CH_2Cl_2} [Pt(DMNH)Cl_2]_3$$

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 in this chapter.

5.3.2.1. Crystal Structure of $[Pt(DMNH)Cl_2]_3$

Although the crystal structure 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-tri-μ-chloro-tri[chlorodimethylamineplatinum(II)], provided evidence of such a complex. The results of this study are discussed below.

The crystals were obtained by heating slowly (40°) a dicloromethane solution of the orange powder (containing 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 2θ, ω and χ for 15 well-centered reflections on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized MoKα radiation. The 2θ range of the reflections was 10 - 25°. From the systematic extinctions, the possible space groups were R3, $R\bar{3}$, R32, R3m and $R\bar{3}m$. Successful refinement of the structure, showed that $R\bar{3}$ was the correct space group. Crystal data and other information are summarized in Table XXIII. 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 (32). The σ(I) was calculated as described previously (32). The intensity data were corrected for absorption (based on the equations of the crystal faces) and Lorentz-polarization effects.

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. The refinement of the structure was done by using full-matrix least-squares calculations minimizing $\Sigma w(|F_o|-|F_c|)^2$. Isotropic secondary-extinction corrections (33) were included in the calculations. Individual weights $w = 1/\sigma^2(F)$ were applied. The scattering curves of Cromer and Waber (34) were used for Pt, Cl, N and C and those of Stewart, Davidson and Simpson (35) were used for H. The anomalous dispersion terms of Pt and Cl were included in the calculations (36). The refinement of the scale factor, coordinates and anisotropic temperature factors of all non-hydrogen atoms converged to R = 0.031 and wR = 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 (32). A listing of the final observed and calculated structure factors is available from the author.

Table XXIII. Experimental details of the X-ray diffraction studies of $[Pt(DMNH)Cl_2]_3$.

Compound	$C_6H_{21}N_3Cl_6Pt_3$
M_w	933.24
Crystalline system	trigonal (hexagonal cell)
Space group	$R\bar{3}$
a (Å)	15.463(6)
b (Å)	15.463(5)
c (Å)	13.984(5)
α (°)	90.0
β (°)	90.0
γ (°)	120.0
Volume ($Å^3$)	2895(2)
Z	6
F(000)	2484
ρ_{calcd} (Mg m^{-3})	3.211
λ(MoKα) (Å)	0.71069
μ(MoKα) (mm^{-1})	22.75
Crystal faces and dimensions (mm)	$(10\bar{1})$-$(\bar{1}0\bar{1})$ (0.172) $(\bar{1}11)$-$(1\bar{1}\bar{1})$ (0.134) $(0\bar{1}1)$-$(01\bar{1})$ (0.192)
Transmission factor range	0.049 · 0.122
2θ max (°)	52
Quadrants measured	h, k, ±ℓ
h, k, l	0→16, 0→16, -17→17
Scan technique	2θ/θ
Standard reflections (dev.)	300, 030, 00-6 (2%)
T(°)	295
no. of independent reflections	1627
no. of observedd reflections ($I > 2.5\sigma(I)$)	1054
$R = \sum\|\|F_o\| - \|F_c\|\| / \sum\|F_o\|$	0.031
Δ/σ	<0.1
$wR = [\sum w(\|F_o\| - \|F_c\|)^2 / \sum\|F_o\|^2]^{1/2}$	0.029
S (standard deviation, unit weight)	1.16

The refined atomic parameters of the structure are listed in Table XXIV. Labelled diagrams of the molecules are shown in Figure 20. The bond distances and angles are reported in Table XXV. The results of the crystal structure determination have shown that the compound is a 6-membered chloro-bridged cyclic trimeric species with a three-fold axis in the center of the ring.

Table XXIV. Atomic coordinates ($x10^5$ for Pt and $x10^4$ for Cl, N, C) with their e.s.d.'s and thermal parameters Ueq ($x10^4$). $Ueq = 1/3\Sigma_i\Sigma_j U_{ij}\, a^*_i a^*_j a_i.a_j$.

	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

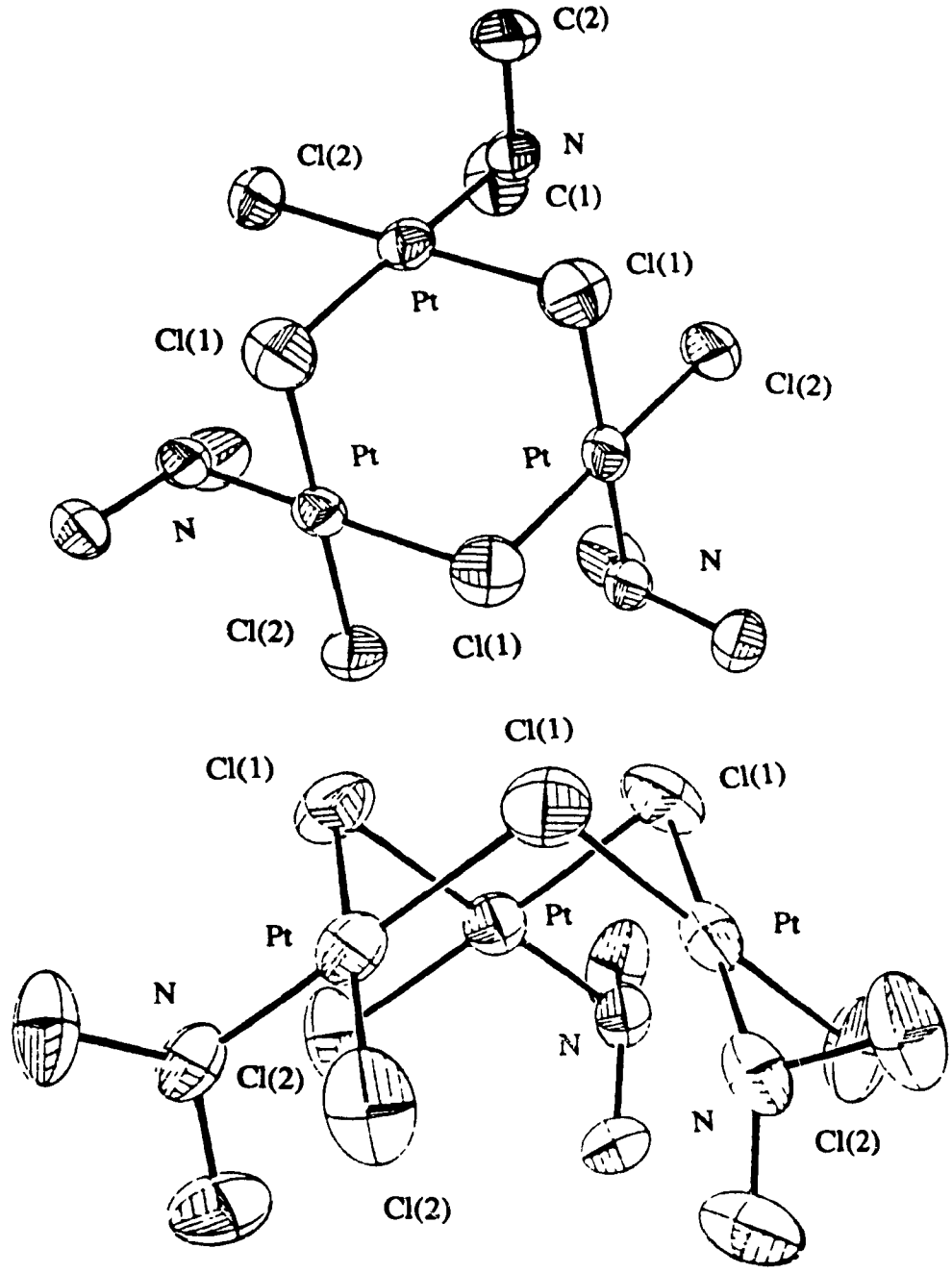


Figure 20. Structure of the complex $[Pt((CH_3)_2NH)Cl_2]_3$ with the atomic numbering.

The coordination around each Pt atom is square-planar. The best weighted plane was calculated through the five atoms. The deviations from this plane are: Pt, -0.0006(4); Cl(1), 0.014(3); Cl(2), 0.017(3); Cl(1)', 0.001(3) and N, 0.014(8) Å. 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.

Table XXV. Bonds distances(Å) and angles(°).

Bond	Distance (Å)
Pt-Cl(1)	2.319(3)
Pt-Cl(1')	2.332(3)
Pt-Cl(2)	2.274(3)
Pt-N	2.046(9)
N-C(1)	1.494(15)
N-C(2)	1.470(12)

Bonds	Angle (°)	Bonds	Angle (°)
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)

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. 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 2.321(3) and 2.320(3) Å.(8). Our values also agree with those found in other chloro-bridged dimers (3-5). The bridging Pt - Cl(1)' (2.332(3) Å) which is located in *trans* position to the amine ligand is slightly longer that the bridging Pt - Cl(1) (2.319(3) Å) located in *trans* position to the terminal chloro ligand. For the chloro-bridged dimer with 2,6-lutidine, the two bridging bonds are identical (2.321(3) and 2.320(3) Å) (8). 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 (37-40). The *trans* influence of amines might be slightly larger than the one of chloro ligands. But this slight 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 (see Chapter 3)

The Pt - N bond length is 2.046(9) Å, close to the values found in other Pt-amine complexes (53-56). 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 the tetrahedral value as observed in other Pt-amine compounds (37-40). The angle C(1) - N - C(2) is normal [110.8(9)°].

The conformation of the molecule is similar to that of the hydroxo-bridged trimers $[(Pt(\mu\text{-}OH)(NH_3)_2)_3]_2(SO_4)_3\cdot 6H_2O$ (14) and $[(Pt(\mu\text{-}OH)(trans\text{-}dach))_3]_2(SO_4)_3\cdot 14H_2O$ (16). The average value for the torsion angles (Table XXVI) in the Pt_3Cl_3 ring of the $[Pt(DMNH)Cl_2]_3$ 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. This clearly indicates similar conformation in the three complexes. 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 20, 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 (15). where one oxygen atom of the Pt_3O_3 ring is almost on the plane of the three platinum atoms (0.02Å), 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-twofold axis symmetry.

Table XXVI. The torsion angles for the $[Pt(DMNH)Cl_2]_3$ complex.

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

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 21. It consists of layers of cyclic trimeric 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. The the Pt atoms are located in the center. There are two such layers in each 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 weak H bonds between the amine and the terminal chloro ligands, increasing the stability of the crystal. The N ··· Cl(2) = 3.417(9) Å and the angles Pt - N ··· Cl(2) and C - N ··· Cl(2) are reasonable (Table XXVII).

The anisotropic thermal parameters (Table XXVIII), the calculated H coordinates (Table XXIX), the equation and deviations from the weighted best plane (Table XXX) are listed in Appendix 3.

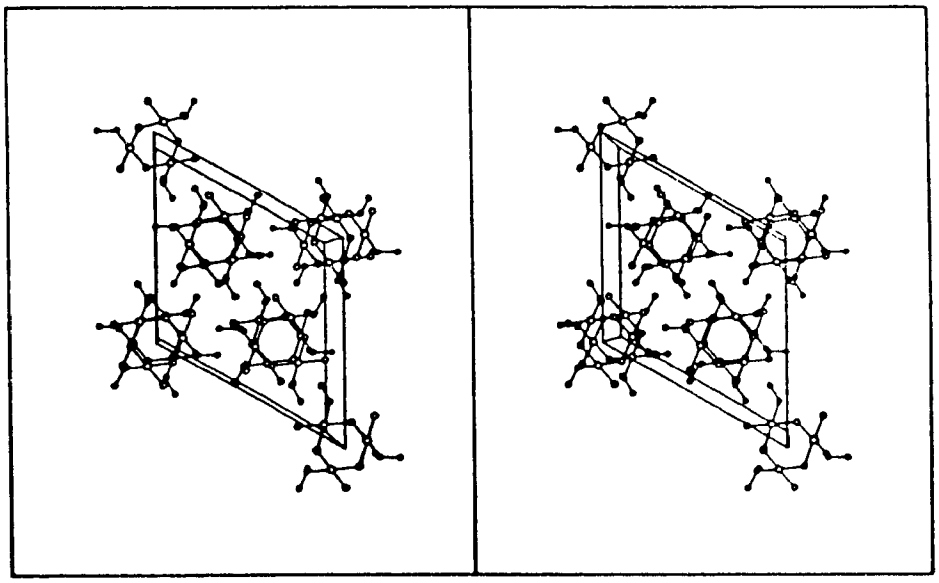


Figure 21. Stereoscopic view of the packing in the $[[Pt((CH_3)_2NH)Cl_2]_3$ crystal (b axis horizontal, view down c axis).

Table XXVII. Distances (Å) and angles (°) between atoms involved in possible hydrogen bonds.

Atoms	distance	Atoms	angles
N-H ··· Cl(2)[1]	3.417(9)	Pt - N ··· Cl(2)	93.9(3)
		C(1) - N ··· Cl(2)	87.1(6)
		C(2) - N ··· Cl(2)	137.6(6)

1) 1+y-x, 1-x, z

5.3.2.2 ^{195}Pt- and ^{1}H-NMR Spectra

The chloro-bridged platinum oligomers have been studied by proton- and ^{195}Pt-NMR spectroscopy. The chemical shifts δ(Pt) obtained in different solvents are presented in Table XXXI. These reddish orange compounds are soluble in several 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 with DMF.

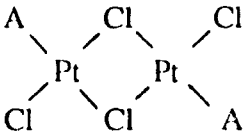
Table XXXI. ^{195}Pt resonances for $[Pt(A)Cl_2]_n$ complexes in different solvents.

A	δ^{195}Pt(±5ppm) DMF	Acetone	CH_2Cl_2	D_2O
$MeNH_2$	-1537c, -1560t 42% 58%	-1622a	-	-
$EtNH_2$	-1532c, -1568t 47% 53%	-	-1713tr	-
CBA	-1531c, -1574t 35% 65%	-1601w, -1630a 53% 47%	-1711tr	-
CPA	-1530c, -1563t 18% 82%	-1584w, -1623a 66% 34%	-1700tr	-
DMNH(powder)	-1513t, -1553c 30% 70%	-1570w	-1703tr, -1570w 27% 73%	-1563w
DMNH(crystals)	-1514t, -1553c 31% 69%	-1567w	-1700tr, -1565w 85% 15%	-

c: *cis*, t: *trans*, a: acetone complex, w: aqua complex, tr: trimer

For the chloro-bridged oligomeric complexes, the ^{195}Pt resonances are expected at slightly lower field than those of $[Pt(A)Cl_3]^-$, whose average value is -1848 ppm in DMF (see chapter III). The spectra of the oligomers dissolved in DMF showed two resonances between -1530 and -1574 ppm. These values are at lower fields than expected for chloro-bridged species and we suggest than the oligomers are cleaved by DMF to produce compounds of the type $Pt(A)(DMF)Cl_2$ as discussed previously.

All the ^{195}Pt-NMR spectra of the $[Pt(A)Cl_2]_n$ complexes with primary amines shows a first resonance around -1535 ppm in DMF. After a few minutes of accumulation, a second signal appears around -1570 ppm which becomes the most intense resonance after one hour. In each case, this last peak corresponds to the monomeric species *trans*-$Pt(A)(DMF)Cl_2$ obtained from the cleavage of the oligomer with DMF as seen in the previous section (5.3.1.1). The first signal is believed to be the *cis* isomer which is first produced upon cleavage, because of the larger trans effect of chloride compared to the one of amines.

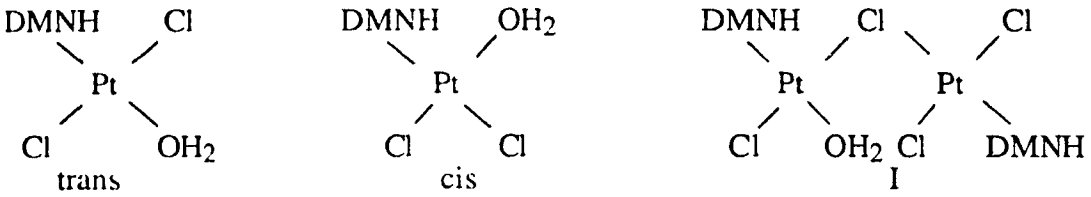


$$\xrightarrow{DMF} 2cis\text{-}Pt(A)(DMF)Cl_2 \xrightarrow{DMF} 2trans\text{-}Pt(A)(DMF)Cl_2$$

The complex with a secondary amine, $[Pt(DMNH)Cl_2]_n$ does not react in the same manner as the primary amine complexes. The ^{195}Pt-NMR spectrum of the $[Pt(DMNH)Cl_2]_n$ complex shows two resonances at -1513 and -1553 ppm in DMF. The first peak to appear in this case is the higher frequency one at -1553 ppm, while the lower frequency one now corresponds to the peak obtained by reaction of this oligomer with DMF (see section 5.3.1.1). We suggest that the first compound observed at -1553 ppm, is *cis*-$Pt(DMNH)(DMF)Cl_2$, while the second compound is the *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 $[Pt(DMNH)Cl_2]_n$ is agitated for several days, solubility occurs as seen by its proton and platinum NMR spectra in deuterated water (Figure 22). The other complexes with primary amine ligands are much less soluble under the same conditions. The ^{1}H-NMR spectrum of $[Pt(DMNH)Cl_2]_n$ measured on a 60-MHz spectrometer 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 in fact 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 ($DN(CH_3)_2$), while the doublet centered at 2.41 ppm is for the methyl groups of the bonded non-deuterated dimethylamine ligand. The latter protons are coupled with the hydrogen of the nitrogen atom with a coupling constant ^2J(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) than the signal of the non-deuterated amine (2.41 ppm). In the spectrum of the same sample taken on a 300-MHz spectrometer, the singlet at 2.40 ppm on the 60-MHz spectrometer, is resolved and appears as two singlets 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 only one resonance at -1583 ppm. Several possibilities were examined in order to interpret these spectra. The proton spectrum could be explained by the presence of a mixture of *cis*- and *trans*-$Pt(DMNH)(H_2O)Cl_2$ monomers, if the two isomers are present in equal amounts. The presence of a *trans* dimer partially cleaved by water, $(DMNH)Cl(H_2O)Pt(\mu\text{-}Cl)Pt(H_2O)Cl(DMNH)$, would give a similar spectrum, since the methyl groups of the dimethylamine ligand being in a different environment, would give two different signals of equal intensity. But this last possibility is not very probable, since

there would be free chloride ions which are stronger bonding ligands than are aqua ligands. Other partially-cleaved species like structure I would give two very different Pt signals and therefore were eliminated.



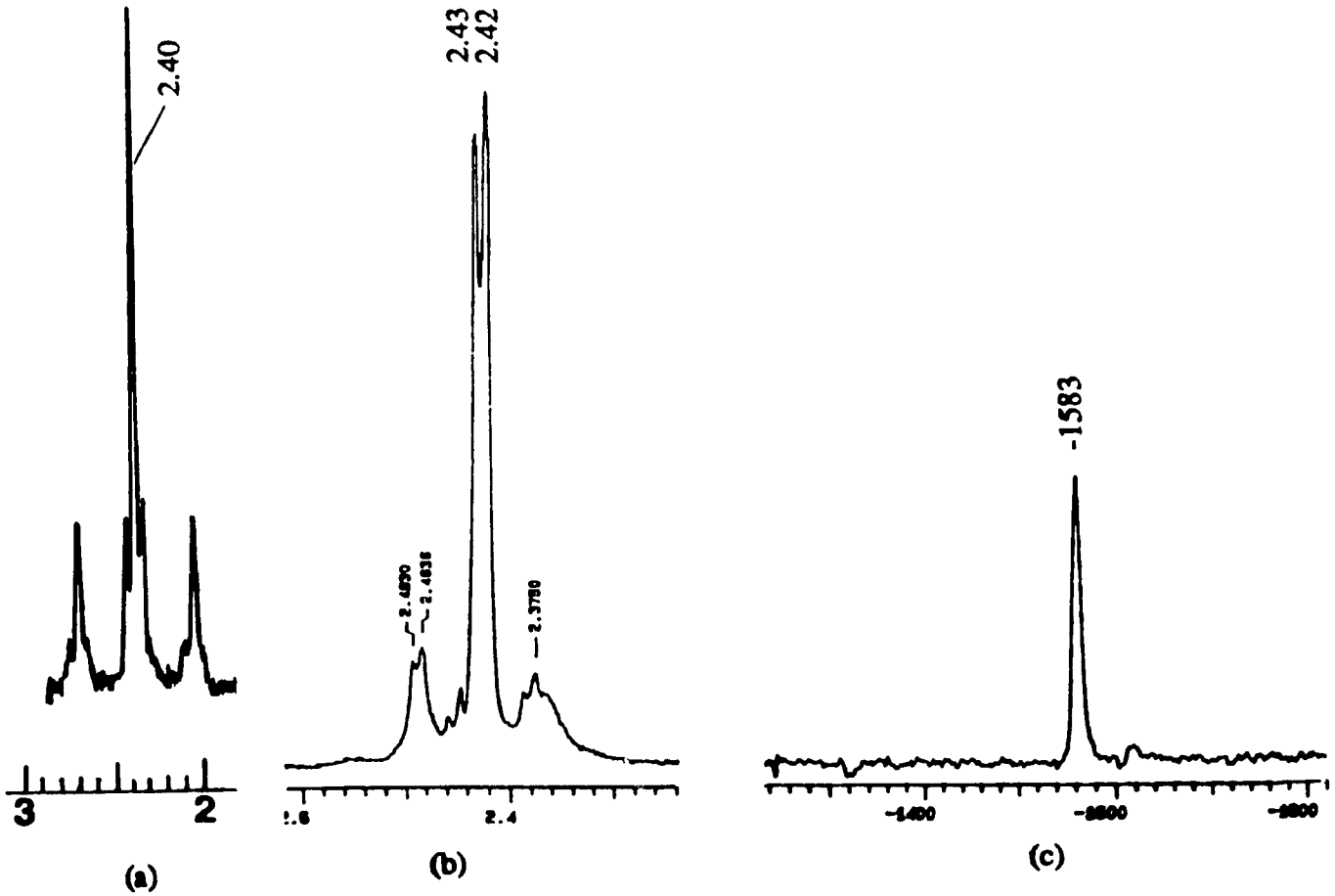


Figure 22. (a) ^{1}H-NMR spectrum of $[Pt(DMNH)Cl_2]_n$ in D_2O (on a 60-MHz spectrometer), (b) same sample on a 300-MHz spectrometer, (c) corresponding ^{195}Pt-NMR spectrum (value in ppm).

We suggest that the first compound observed when the chloro-bridged oligomer with dimethylamine is cleaved with water, is the *cis* isomer since the *trans* effect of chloride is larger than the one of amines. The *cis* compound might then isomerize partially to the *trans* isomer. The difference between the two isomers would be too small to be observed by ^{195}Pt-NMR. The doublet assigned to the coupling for the non-deuterated compound on the 60-MHz spectrometer appears also as a pair of two singlets on the 300-MHz instrument, and are seen only on the left side of the two main singlets. The other part of this signal is hidden under the right part of the two main singlets.

Although there are some complexes with acetone as a ligand known in the literature (41), the isolation of Pt compounds containing acetone has not yet been reported and was also unsuccessful in our case. Platinum is a soft metal and does not form strong bonds with O-donor ligands, unless they are deprotonated. This does not mean however that acetone cannot act as a ligand for platinum when 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 resonance for the oligomer with DMNH in acetone was observed at -1570 ppm, very close to the value of -1563 ppm observed for the compound in water. We therefore suggest the presence of the same species in the two solvents, Pt(DMNH)(H_2O)Cl_2. For the CBA and CPA oligomers, which are quite insoluble in water, two signals were observed in acetone. One signal is thought to belong to a species produced from the cleavage of the oligomer with water, Pt(A)(H_2O)Cl_2 (-1601 and -1584 ppm, respectively), and the second is obtained from the cleavage of the dimers with

acetone, Pt(A)(acetone)Cl_2 (-1630 and -1623 ppm, respectively). The spectrum of the $MeNH_2$ oligomer in acetone showed only one resonance at -1622 ppm, which was assigned to a cleaved product with acetone, Pt(CH_3NH_2)(acetone)Cl_2, since this dimer is very insoluble in water and the resonance is close to the values assigned to the acetone complex for the other ligands.

In dichloromethane, the DMNH oligomer showed two signals at -1570 ppm corresponding to the cleaved product with H_2O, discussed above, while the second resonance at -1700 ppm is assigned to the chloro-bridged trimer. In non-coordinating 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 (7, 8). 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 be the chloro-bridged *trans* dimer [Pt(2,6-lutidine)Cl_2]$_2$ (8). In the same study, measurements of molecular weights have also indicated that the compounds were dimers in chloroform solution at room temperature. We also believe that at room temperature, the chloro-bridged oligomeric species are mostly dimers while slight heating results in trimer formation. The ^{1}H- and ^{195}Pt-NMR spectra of the oligomer with dimethylamine have been measured and are presented in Figure 23. The orange powder obtained from the reaction:

$$nK[Pt(A)Cl_3] \xrightarrow{HClO_4} [Pt(A)Cl_2]_n$$

has been dissolved in CH_2Cl_2 and the ^{195}Pt-NMR spectrum is shown in Figure 23a. Two signals were observed, the most intense at -1570 and a weaker one at -1703 ppm. This solution was heated with hot water for 10 min. and the spectrum measured again

(Figure 23b). The same two resonances were observed, but now the signal at -1700 is much more intense. The red crystals isolated from the reaction:

$$[Pt(A)Cl_2]_2 \xrightarrow[\Delta]{CH_2Cl_2} [Pt(A)Cl_2]_3$$

have been dissolved in deuterated CH_2Cl_2 and the ^1H- and ^{195}Pt-NMR spectra are shown in Figure 23c and 23d respectively. The spectra 23b and 23d are almost identical. Since the crystal isolated for structure analysis and identified as a cyclic chloro-bridged trimer was taken from a solution after slight heating, we believe that this species is favored under such conditions and the most intense peak around -1700 ppm should be assigned to the cyclic chloro-bridged trimeric species. It was not possible to isolate only the trimers, since the two species are soluble in CH_2Cl_2. The red crystals have been taken out one by one under the microscope, but some powder sticks on them. The ^1H-NMR spectrum of these crystals (Figure 23c) shows a doublet for the DMNH ligand centered at 2.73 ppm with its coupling with platinum $^3J(Pt\text{-}H) = 42$ Hz. Two other weak resonances at the right of the first one 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, i.e., 85/15. From these NMR studies, we can assign the $\delta(Pt)$ peak at -1700 ppm to the trimer. All the other complexes, except $[Pt(MeNH_2)Cl_2]_n$, show only one resonance in the -1700 ppm region and can be similarly assigned to the trimeric species. The spectrum of $[Pt(MeNH_2)Cl_2]_n$ was not measured because this complex is not sufficiently soluble in CH_2Cl_2. The peak at -1570 ppm was first assigned to the dimer, but after the synthesis of the $Pt(A)(DMF)Cl_2$ complexes whose resonances are observed in the same region, this idea has been reconsidered. It is not logical to find the resonance for a dimer with an environment

consisting of three Cl and one N donor atoms in the same region as a monomer with one N, one O and two Cl donor atoms. The proton-NMR spectrum of dichloromethane has shown the presence of a small quantity of water which can cleave the dimeric species to produce an aqua complex whose resonance appears at -1570 ppm. This aqua species would be the same as that produced when the DMNH oligomers are cleaved by water. This also concurs with the fact that when the dimers are rearranged to trimers, there must be some cleavage of one of the bridged bonds.

The ^{195}Pt-NMR spectra of the oligomeric species containing $EtNH_2$, CBA and CPA showed only one resonance around -1710 ppm corresponding to the presence of the chloro-bridged trimers. 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 CH_2Cl_2 (Figure 24). This spectrum exhibits only one resonance at -1711 ppm. When one drop of DMF is added, this peak disappears and a new resonance appears around at -1587 ppm, which is assigned to $Pt(CBA)(DMF)Cl_2$, taking into account a 10 ppm highfield shift for the effect of solvent on going from DMF (-1574 ppm) to CH_2Cl_2.

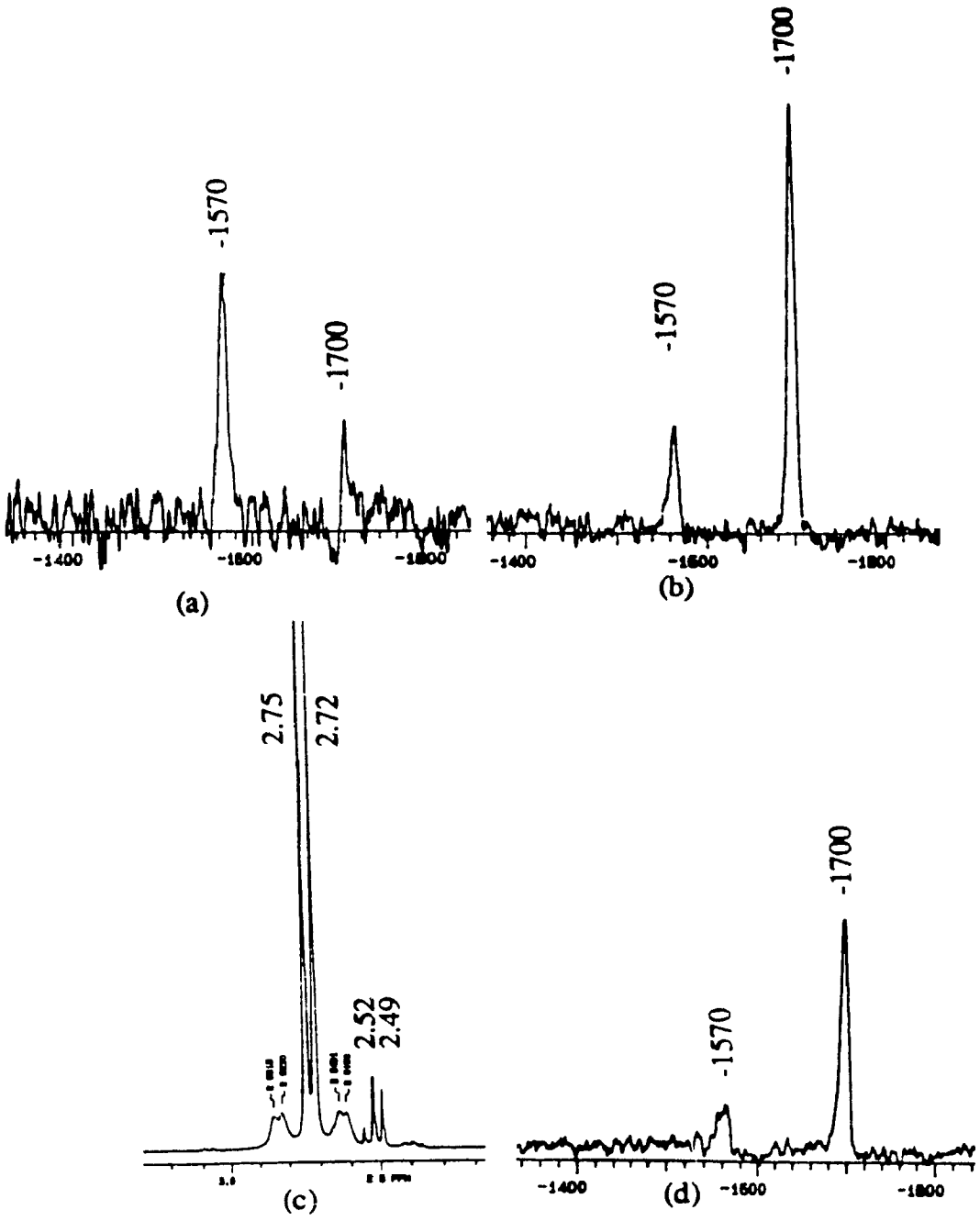


Figure 23. Comparison of the NMR spectra of the trimer and dimer with dimethylamine (a) ^{195}Pt-NMR spectrum of powder in methylene chloride before heating (b) ^{195}Pt-NMR spectrum powder in methylene chloride after heating (c) ^{1}H-NMR spectrum of crystals in CD_2Cl_2 and (d) ^{195}Pt-NMR spectrum of crystals in CD_2Cl_2.

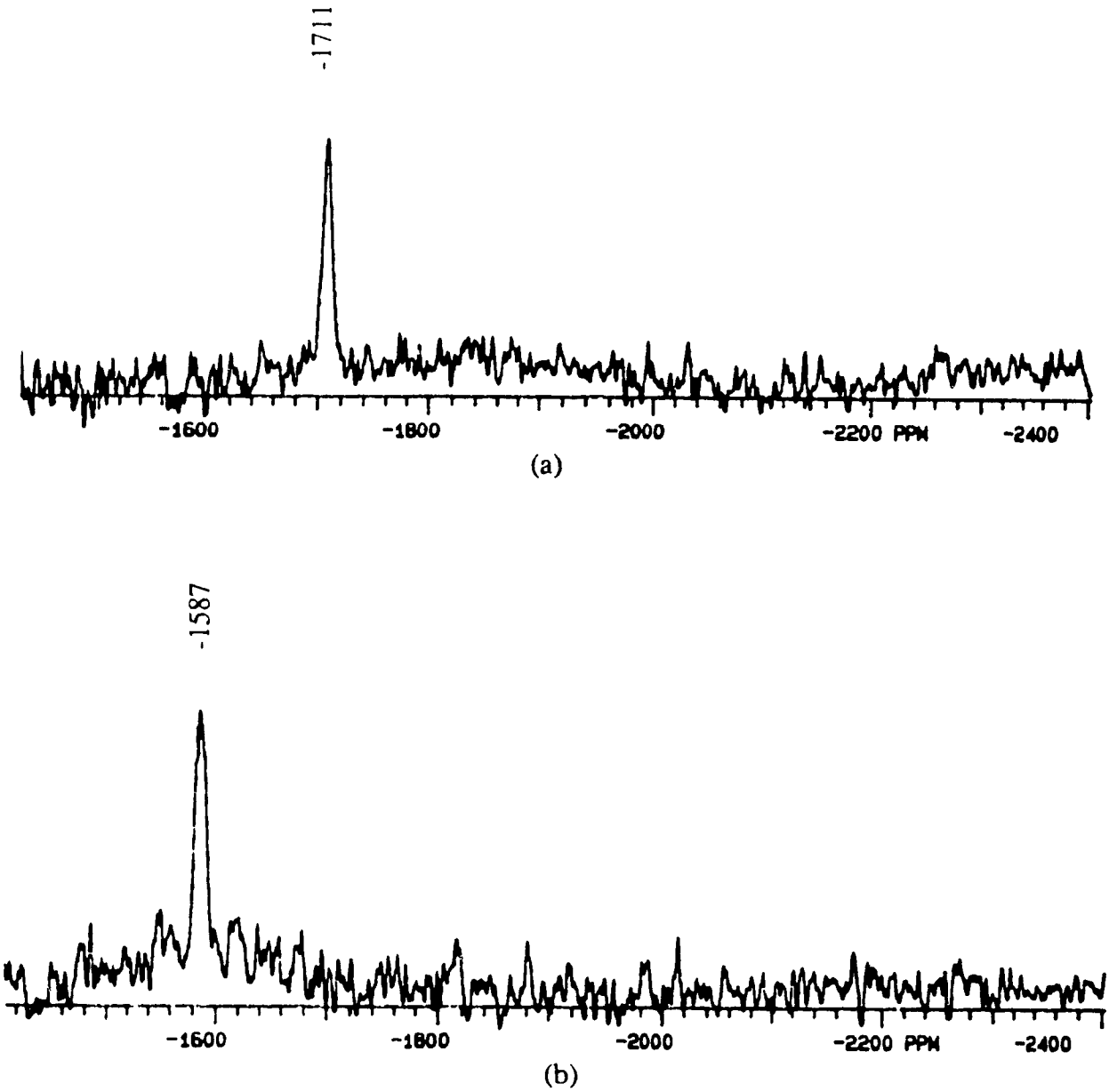


Figure 24. (a) ^{195}Pt-NMR spectrum of the $[Pt(CBA)Cl_2]_2$ complex in CD_2Cl_2 (b) one drop of DMF is added in the solution.

The ^{195}Pt-NMR spectra of some iodo dimers, $[Pt(A)I_2]_2$, or oligomers have been measured in DMF and in CH_2Cl_2 and the results are presented in Table XXXII. The observed chemical shifts vary from -3901 to -4084 ppm. Since the four-membered ring is less strained than in the chloro compounds due to the longer Pt-I bonds, the resonances of these species are expected to be closer to those for $[Pt(A)I_3]^-$ complexes. The value found by Kidd and Goodfellow for $NR_4[Pt(DMNH)I_3]$ (R = Pr^n or Bu^n) is -4004 ppm in CH_2Cl_2 (42), very close to our values.

Attempt to isolate species of the type $Pt(A)(DMF)I_2$ by reaction of $[Pt(A)I_2]_2$ with DMF was not successful but again this does not mean that these weak donor molecules cannot act as ligands when in solution. A DMF solution containing $[Pt(A)I_2]_2$ was heated during 3h and then the DMF was evaporated. The IR spectra of the isolated compounds were measured and the spectra were identical to those of the dimeric species. No C=O band was detectable in the IR spectra indicating the absence of bonded DMF. When the solutions were heated overnight, decomposition occurred.

Table XXXII. ^{195}Pt resonances for $[Pt(A)I_2]_n$ complexes in different solvents.

A	DMF	CH_2Cl_2
$MeNH_2$	-3984, -3999	not measured
$EtNH_2$	-3996	-4032
CBA	-4014, -4030	-4046
CPA	-3992, -4006	-4022
DMNH(powder)	-3905, -3934	-3924, -3946
	-3901, -3929 (acetone)	-3920, -3942 (Bruker)
1-adam	-4068, -4084	not measured
2-adam	-4030	not measured

5.3.2.3 Infrared spectra

The IR spectra of the $[Pt(A)Cl_2]_n$ oligomers have been measured and the most important vibrations are listed in Table XXXIII. These spectra are the most simple spectra actually presented in this work 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*–$Pt_2A_2Cl_4$ is C_{2h} (C_{2v} for a *cis* isomer) and group theory predicts three ν(Pt-Cl) ($3B_u$ modes) vibrations in the IR. Table XXXIII presents the results for these complexes. There is one $\nu(Pt\text{-}Cl)_t$ (t = terminal) and two $\nu(Pt\text{-}Cl)_b$ (b = bridged bonds). From the latter two, there is one $\nu(Pt\text{-}Cl)_b$ *trans* to the chloride, at a higher frequency, and one $\nu(Pt\text{-}Cl)_b$ *trans* to the amine group at a lower frequency (43). The spectra of the complexes have shown one $\nu(Pt\text{-}Cl)_t$ vibration between 340-350 cm^{-1}, one $\nu(Pt\text{-}Cl)_b$ vibration *trans* to the chloride ligand between 308-325 cm^{-1}, and one $\nu(Pt\text{-}Cl)_b$ vibration *trans* to the amine ligand between 291-305 cm^{-1}. An example of a typical spectrum is presented in Figure 3 (Experimental part, Chapter 2). The IR spectra of the $[Pt(A)Cl_2]_2$ complexes give the pattern expected for a *trans* isomer but because the bands are large enough and show some shoulders, the possibility of having a *cis* isomer cannot be rejected. The presence of the amine ligand is confirmed by the ν(NH) vibrations between 3105-3276 cm^{-1} and the $\delta(NH_2)$ vibration between 1560-1571 cm^{-1}.

Table XXXIII. Main IR Bands (cm^{-1}) for $[Pt(A)Cl_2]_2$ complexes.

Compounds	ν(NH)	δ(NH_2)	ν(Pt-Cl)$_t$	ν(Pt-Cl)$_b$ *trans* to Cl	ν(Pt-Cl)$_b$ *trans* to A
$[Pt(MeNH_2)Cl_2]_2$	3222(m) 3270(m)	1560(m)	340(s)	308(m)	293(m)
$[Pt(EtNH_2)Cl_2]_2$	3220(sh) 3245(s)	1561(s)	338(s)	309(m)	291(m)
$[Pt(CBA)Cl_2]_2$	3105(m) 3126(m) 3276(s)	1569(m)	338(s)	305(m)	295(m)
$[Pt(CPA)Cl_2]_2$	3119(m) 3190(s) 3239(s)	1571(s)	340(s)	325(m)	305(m)
$[Pt(DMNH)Cl_2]_2$	3210(s)	-	350(m)	320(m)	303(m)
$[Pt(DMNH)Cl_2]_3$	3198(s)	-	341(s)	312(w)	294(m)

For the cyclic trimer, there are minor differences compared to the chloro dimer For the trimeric species, $[Pt(DMNH)Cl_2]_3$, we observed the ν(N-H) vibration at slightly lower wavenumber than for the corresponding dimer. The ν(N-H) vibration at 3210 cm^{-1} is shifted to 3198 cm^{-1} in the trimer. The ν(Pt-Cl) vibrations are shifted to lower frequencies and the band shapes are not the same. The ν(Pt-Cl)$_t$ 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 at 525, 1037, 1392, 1417, 1430, 1441, 1451, 2999 and 3022 cm^{-1} and are designated by a "x" on the IR spectrum of the complex shown in Figure 25.

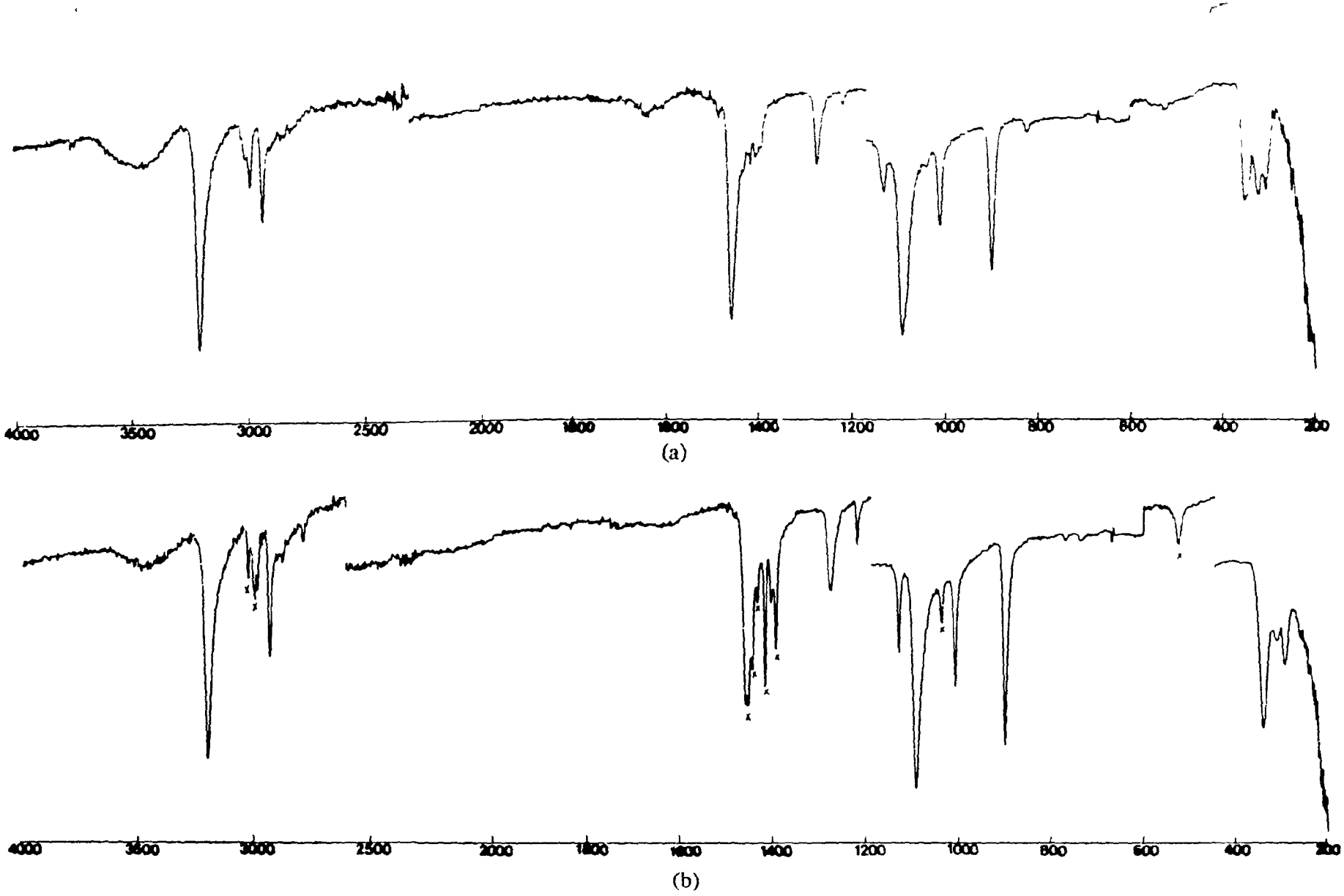


Figure 25. Comparison of the IR spectra of (a) powdered $[Pt(DMNH)Cl_2]_n$ and (b) crystalline $[Pt(DMNH)Cl_2]_3$.

5.4 References

1. J. Chatt and L. M Venanzi. J. Chem. Soc. 2787 (1955) and references therein.
2. J. Chatt and L. M. Venanzi. J. Chem. Soc. 652 (1951).
3. M. Black, R. H. B. Mais and P. G. Owston. Acta Cryst. **B25**, 1760 (1969).
4. S.F. Watkins. J.Chem.Soc.A, 168 (1970).
5. R. C. Elder, R. D. P. Cruea and R. F. Morisson. Inorg.Chem. **15**(7), 1623 (1976).
6. P. C. Kong and F. D. Rochon. Inorg. Chim. Acta. **37**, L457 (1979).
7. P. C. Kong and F. D. Rochon. Can. J. Chem. **57**, 682 (1979).
8. F. D. Rochon and R. Melanson. Acta Cryst. **B37**, 690 (1981).
9. P. Courtot, R. Rumin, A. Perron and J. P. Girault. J. Organomet. Chem. **145**, 343 (1978) and references therein.
10. F. D. Rochon and P. C. Kong. Can. J. Chem. **64**, 1894, (1986).
11. F. D. Rochon and P. C. Kong. USA Patent No. 4, **533**, 502 (1985).
12. F. D. Rochon and R. Melanson. Acta Cryst. **C42**, 1291 (1986).
13. F. D. Rochon, R. Melanson and M. Doyon. Inorg. Chem. **26**, 3065 (1987).
14. R. Faggiani, B. Lippert, C. J. L. Lock and B. Rosenberg. Inorg. Chem. **7**, 1941 (1978).
15. R. Faggiani, B. Lippert, C. J. L. Lock and B. Rosenberg. Inorg. Chem. **16**(5), 1192 (1977).
16. J. P. Macquet, S. Cros and A. L. Beauchamp. J. Inorg. Biochem. **25**, 197 (1985).
17. F. D. Rochon and R. Melanson. Acta Cryst. **C44**, 474 (1988).
18. H. S. Preston, J. C. Mills and C. H. L. Kennard. J. Organomet. Chem. **14**, 447 (1968); R. E. Rundle and J. H. Sturdivant. J. Am. Chem Soc. 69, 1561 (1947).
19. F. D. Rochon, A. Morneau and R. Melanson. Inorg. Chem. **27**(1), 10 (1988).

20. M. A. M. Meester, D. J. Stufcens and K. Vrieze. Inorg. Chim. Acta, **16**, 191 (1976).

21. F. Conti, M.Donati and G.F. Pregaglia. J. Organometal. Chem. **30**, 421 (1971).

22. F.D. Rochon, P.C. Kong and R. Melanson. Can. J. Chem. **58**, 97 (1980).

23. L. V. Vilkov, P. A. Akishin and V. M. Presnyakova. J. Struct. Chem. **3**, 3 (1962).

24. J. Chatt and L. M. Venanzi. J. Chem. Soc. 3858 (1955).

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

26. J. M. Gloria and B. P. Susz. Helv. Chim. Acta. **54** (7), 2251 (1971).

27. T. G. Appleton, J. R. Hall and S. F. Ralph. Inorg. Chem. **24**, 4685 (1985).

28. G. Kaufmann and N.J. F. Leroy. Bull. Soc. Chim. France, 402 (1967).

29. F. D. Rochon and L. Fleurant. Inorg. Chim. Acta, **143**, 81 (1988).

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

31. H. E.Howard-Lock, C. J. L. Lock, G. Turner and M. Zvagulis. Can. J. Chem. **59**, 2737 (1981).

32. R. Melanson and F. D. Rochon. Can. J. Chem. **53**, 2371 (1975).

33. P. Coppens and W. C. Hamilton. Acta Cryst. **A26**, 71 (1970).

34. D. T. Cromer and J. T. Waber. Acta Cryst. **18**, 104 (1965).

35. R.F. Stewart, E. R. Davidson and W. T. Simpson. J. Chem. Phys. **42**, 3175 (1965).

36. D. T. Cromer. Acta Cryst. **18**, 17 (1965).

37. F. D. Rochon and R. Melanson. Acta Cryst. (1991) in press.

38. F. D. Rochon, R. Melanson and M. Doyon. Inorg. Chem. 26, 3065 (1987).

39. F. D. Rochon, R. Melanson, M. Doyon. and I. S. Butler. Acta Cryst. C46, 584 (1990).

40. C. Dion, A. L. Beauchamp, F. D. Rochon and R. Melanson Acta Cryst. C45, 852(1989).

41. A.G. Thayer and N.C. Payne Acta Cryst. **C42**, 1302 (1986).

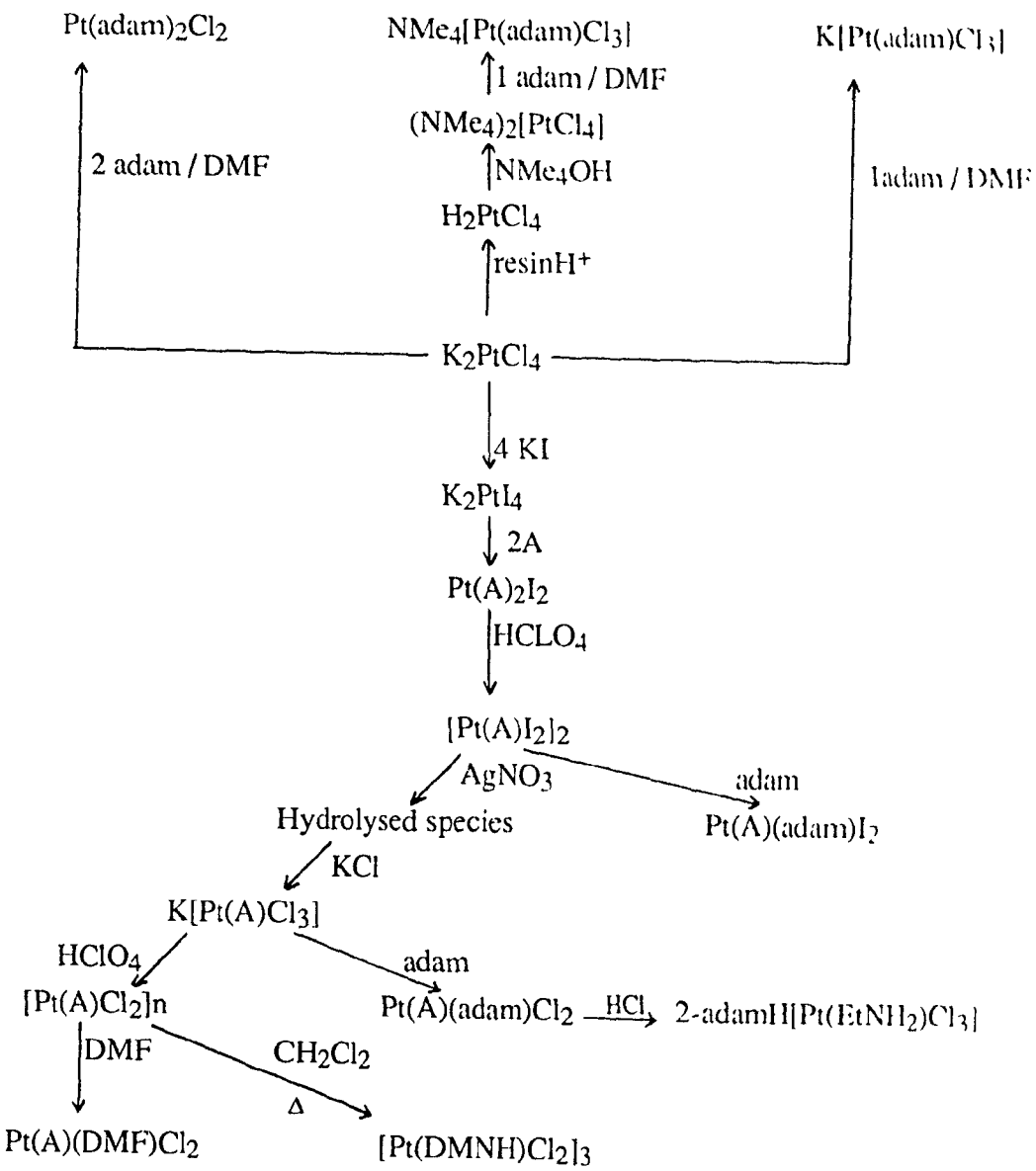
42. R.G. Kidd and R. G. Goodfellow. NMR of the Periodic Table, Academic Press London 252 (1978).

43. K. Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds. 3rd edition. John Wiley and Sons Inc. 322-3 (1978).

CHAPTER 6.

Contributions to knowledge

The various steps for the different syntheses can be summarized by to the following scheme:



New complexes of the type $K[Pt(A')Cl_3]$ (A' = 1-adamantanamine, 2-adamantanamine and 1-methyladamantanamine) have been synthesized. These complexes with 2-adam and 1-Madam were not stable enough and needed the presence of a larger cation, NMe_4, in order to be isolated. The ^{195}Pt resonances for the $[Pt(A)Cl_3]^-$ complexes where A = methylamine, ethylamine, cyclobutylamine, cyclopentylamine, dimethylamine and the $[Pt(A')Cl_3]^-$ complexes appear between -1822 and -1865 ppm. With the exception of $[NMe_4][Pt(1\text{-}Madam)Cl_3]$, all the complexes showed only one resonance, which is a good indication of the purity of the compounds. The second resonance observed for $[NMe_4][Pt(1\text{-}Madam)Cl_3]$ at -2242 ppm was assigned to the disubstituted species $Pt(1\text{–}Madam)_2Cl_2$. The platinum resonances were found to be dependent on solvent effects, the presence of different counterions and the concentrations of the species in solution. No direct correlation between the pKa of the amine ligands and the ^{195}Pt chemical shifts was found.

The structure of $[2\text{-}C_{10}H_{15}NH_3][Pt(EtNH_2)Cl_3]$ has been determined by X-ray diffraction. Contrary to similar complexes of the type $K[Pt(A)Cl_3].1/2H_2O$, this molecule does not crystallize with water of hydration. In the case of the $K[Pt(A)Cl_3]$ species, water molecules play an important role in stabilizing the complexes. In the $[2\text{-}C_{10}H_{15}NH_3][Pt(EtNH_2)Cl_3]$ complex, the larger cation in able to form hydrogen bonds with the chloride ligands and this is sufficient to stabilize the crystal. This is in agreement with the crystal structure of $[Pt(NH_3)_4][Pt(isopropylamine)Cl_3]_2$ which crystallizes without water of hydration.

Mixed-ligand complexes of the type $Pt(A)(A')Cl_2$ have been synthesized from the reaction of $K[Pt(A)Cl_3]$ with the appropriate adamantanamine ligands in water. ^{195}Pt-NMR measurements on these species obtained after washing with dilute HCl showed the

presence of a peak in the region expected for $[Pt(A)Cl_3]^-$ complexes. This resonance has been attributed to species of the type [adamH][$Pt(A)Cl_3$] which are formed by displacement of the coordinated adamantanamine ligand by Cl^- and subsequent quaternization of the amine group This result lead to some doubt about the real nature of $Pt(1\text{-adam})_2Cl_2$ and $Pt(2\text{-adam})_2Cl_2$ tested for antitumor activity by Braddock et al., since the authors washed their compounds with concentrated HCl. ^{195}Pt-NMR measurements confirm the presence of three species when this method is used and so the compounds tested might be a mixture of the three species, [adamH][$Pt(adam)Cl_3$, *cis* and *trans*-$Pt(adam)_2Cl_2$.

The IR and Raman spectra of the mixed-ligand complexes, $Pt(A)(adam)Cl_2$, showed that most of the species were *cis* isomers while the disubstituted compounds, $Pt(adam)_2Cl_2$, were found to be a mixture of isomers.

For the corresponding iodide complexes, it was difficult to obtain good far-IR and Raman spectra and the results presented are only tentative, even for the solid state. Systems containing iodides present greater difficulty since their vibrational frequencies are at low energy and it is difficult to distinguish intramolecular and lattice modes. In addition, in IR spectroscopy, the absorption of the ν(Pt-I) vibration is in a region where there are problems with water absorptions. Nevertheless, the appearance of two ν(Pt-I) and two ν(Pt-N) peaks in most cases is strongly suggestive of *cis* isomers. The symmetric ν(Pt-I) vibration was easier to locate and has been assigned at 150 cm^{-1}. The antisymmetric mode, more difficult to locate, was assigned to a band around 200-180 cm^{-1}, close to the value of 180 cm^{-1} reported for this vibration in the $[PtI_4]^{2-}$ ion

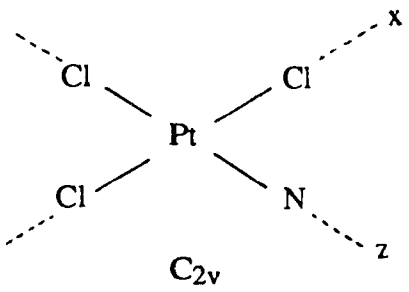
In Chapter 5, we have shown that the reaction of oligomeric species of the type $[Pt(A)Cl_2]n$ with DMF produces $Pt(A)(DMF)Cl_2$, which from the IR results probably have a *trans* configuration in the solid state. When $Pt(A)(DMF)Cl_2$ is dissolved in a solvent like DMF, acetone or dichloromethane, the structure is retained and only one species was observed by ^{195}Pt- and ^{1}H-NMR spectroscopy. But on standing, these compounds are partially rearranged to chloro-bridged oligomers, probably mainly dimers and trimers. In DMF, the oligomers are rapidly cleaved to produce first the *cis*-isomer which isomerized to the *trans* compound. In dichloromethane, the chloro-bridged species are more stable and the presence of trimers was detected by ^{195}Pt-NMR spectroscopy. The decomposition of *trans*-$Pt(C_2H_5NH_2)(DMF)Cl_2$ was faster than the corresponding methylamine and dimethylamine DMF complexes.

APPENDIX 1

The number of active vibrations in the IR and Raman spectra can be calculated from the following equation:

$$a_i = \frac{1}{h} \sum_{R} \chi(R) \; \chi i \; R$$

where a_i = number of times the i-th irreducible representation appears
h = order of the point group
$\chi(R)$ = character of the R-th operation in the reducible representation
χi = character of the R-operation in the i-th irreducible representation.



C_{2v}

C_{2v}	I	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_{Pt\text{-}Cl}$	3	1	3	1
$\Gamma_{Pt\text{-}N}$	1	1	1	1

$\Gamma_{Pt\text{-}Cl}$

$$nA_1 = \frac{1}{4}[(3)(1)(1)+(1)(1)(1)+(3)(1)(1)+(1)(1)(1)] = 2$$

$$nA_2 = \frac{1}{4}[(3)(1)(1)+(1)(1)(1)+(3)(1)(-1)+(1)(1)(-1)] = 0$$

$$nB_1 = \frac{1}{4}[(3)(1)(1)+(1)(1)(-1)+(3)(1)(1)+(1)(1)(-1)] = 1$$

$$nB_2 = \frac{1}{4}[(3)(1)(1)+(1)(1)(-1)+(3)(1)(-1)+(1)(1)(1)] = 0$$

$$\Gamma_{Pt\text{-}Cl} = 2A_1 + 1B_1$$
IR/R IR/R

$\Gamma_{Pt\text{-}N}$

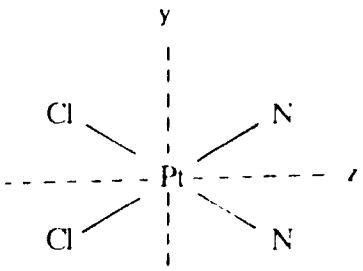
$$nA_1 = \frac{1}{4}[(1)(1)(1)+(1)(1)(1)+(1)(1)(1)+(1)(1)(1)] = 1$$

$$nA_2 = \frac{1}{4}[(1)(1)(1)+(1)(1)(1)+(1)(1)(-1)+(1)(1)(-1)] = 0$$

$$nB_1 = \frac{1}{4}[(1)(1)(1)+(1)(1)(-1)+(1)(1)(1)+(1)(1)(-1)] = 0$$

$$nB_2 = \frac{1}{4}[(1)(1)(1)+(1)(1)(-1)+(1)(1)(-1)+(1)(1)(1)] = 0$$

$$\Gamma_{Pt\text{-}N} = A_1$$
IR/R



cis

C_{2v}

For the *cis* isomer

C_{2v}	I	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_{Pt\text{-}Cl}$	2	0	0	2
$\Gamma_{Pt\text{-}N}$	2	0	0	2

$$n\ A_1 = \frac{1}{4}[(2)(1)(1) + 0 + 0 + (2)(1)(1)] = 1$$

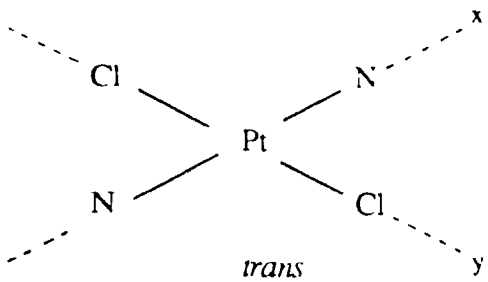
$$n\ A_2 = \frac{1}{4}[(2)(1)(1) + 0 + 0 + (2)(1)(-1)] = 0$$

$$n\ B_1 = \frac{1}{4}[(2)(1)(1) + 0 + 0 + (2)(1)(-1)] = 0$$

$$n\ B_2 = \frac{1}{4}[(2)(1)(1) + 0 + 0 + (2)(1)(1)] = 1$$

$$\Gamma_{Pt\text{-}Cl} = A_1 + B_2 \ (IR/R)$$

$$\Gamma_{Pt\text{-}N} = A_1 + B_2 \ (IR/R)$$



trans

D_{2h}

For the *trans* isomer.

D2h	I	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_v(xy)$	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_{Pt\text{-}Cl}$	2	0	2	0	0	2	0	2
$\Gamma_{Pt\text{-}N}$	2	0	0	2	0	2	2	0

$\Gamma_{Pt\text{-}Cl}$:

$$n\,A_g = \frac{1}{8}[(2)(1)(1) + 0 + (2)(1)(1) + 0 + 0 + (2)(1)(1) + 0 + (2)(1)(1)] = 1$$

$$n\,B_{1g} = \frac{1}{8}[(2)(1)(1) + 0 + (2)(1)(-1) + 0 + 0 + (2)(1)(1) + 0 + (2)(1)(-1)] = 0$$

$$n\,B_{2g} = \frac{1}{8}[(2)(1)(1) + 0 + (2)(1)(1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(-1)] = 0$$

$$n\,B_{3g} = \frac{1}{8}[(2)(1)(1) + 0 + (2)(1)(-1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(1)] = 0$$

$$n\,A_u = \frac{1}{8}[(2)(1)(1) + 0 + (2)(1)(1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(-1)] = 0$$

$$n\,B_{1u} = \frac{1}{8}[(2)(1)(1) + 0 + (2)(1)(-1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(1)] = 0$$

$$n\,B_{2u} = \frac{1}{8}[(2)(1)(1) + 0 + (2)(1)(1) + 0 + 0 + (2)(1)(1) + 0 + (2)(1)(1)] = 1$$

$$n\,B_{3u} = \frac{1}{8}[(2)(1)(1) + 0 + (2)(1)(-1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(1)] = 0$$

$$\Gamma_{Pt\text{-}Cl} = A_g + B_{2u}$$

R IR (because of rule of mutual exclusion)

$\Gamma_{Pt\text{-}N}$:

n $A_g = \frac{1}{8}[(2)(1)(1) + 0 + 0 + (2)(1)(1) + 0 + (2)(1)(1) + (2)(1)(1) + 0] = 1\ A_g$

n $B_{1g} = \frac{1}{8}[(2)(1)(1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(1) + (2)(1)(-1) + 0] = 0$

n $B_{2g} = \frac{1}{8}[(2)(1)(1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(-1) + (2)(1)(1) + 0] = 0$

n $B_{3g} = \frac{1}{8}[(2)(1)(1) + 0 + 0 + (2)(1)(1) + 0 + (2)(1)(-1) + (2)(1)(-1) + 0] = 0$

a $A_u = \frac{1}{8}[(2)(1)(1) + 0 + 0 + (2)(1)(1) + 0 + (2)(1)(-1) + (2)(1)(-1) + 0] = 0$

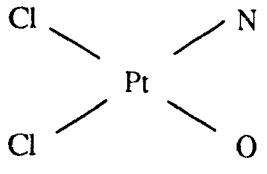
a $B_{1u} = \frac{1}{8}[(2)(1)(1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(-1) + (2)(1)(1) + 0] = 0$

a $B_{2u} = \frac{1}{8}[(2)(1)(1) + 0 + 0 + (2)(1)(-1) + 0 + (2)(1)(1) + (2)(1)(-1) + 0] = 0$

a $B_{3u} = \frac{1}{8}[(2)(1)(1) + 0 + 0 + (2)(1)(1) + 0 + (2)(1)(1) + (2)(1)(1) + 0] = 1$

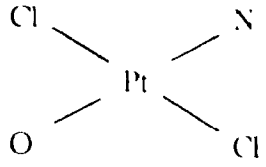
$\Gamma_{Pt\text{-}N} = A_g + B_{3u}$

R IR (because of rule of mutual exclusion)



cis

Cs



trans

Cs

For the *cis* or *trans* isomer:

Cs	I	σ_h
ΓPt-Cl	2	2
ΓPt-O	1	1
ΓPt-N	1	1

ΓPt-Cl:

$$nA' = \frac{1}{2}[(2)(1)(1)+(2)(1)(1)] = 2$$

$$nA'' = \frac{1}{2}[(2)(1)(1)+(2)(1)(-1)] = 0$$

ΓPt-Cl = 2A' (IR/R)

ΓPt-O and ΓPt-N.

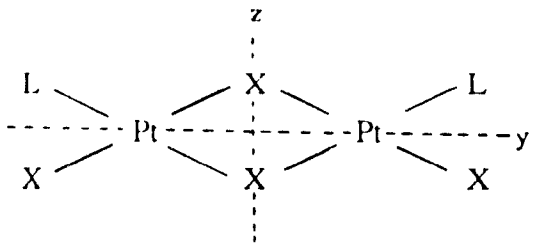
$$nA' = \frac{1}{2}[(1)(1)(1)+(1)(1)(1)] = 1$$

$$nA'' = \frac{1}{2}[(1)(1)(1)+(1)(1)(-1)] = 0$$

ΓPt-O = 1A' (IR/R)

ΓPt-N = 1A' (IR/R)

For the *cis* dimer



cis

C_{2v}

C_{2v}	I	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_{Pt\text{-}X_t}$	2	0	0	2
$\Gamma_{Pt\text{-}X_b}$	4	0	0	4

$\Gamma_{Pt\text{-}X_t}$

$a A_1 = \frac{1}{4}[(2)(1)(1)+ 0 + 0 + (2)(1)(1)] = 1$

$a A_2 = \frac{1}{4}[(2)(1)(1) + 0 + 0 +(2)(1)(-1)] = 0$

$a B_1 = \frac{1}{4}[(2)(1)(1)+ 0 + 0 +(2)(1)(-1)] = 0$

$a B_2 = \frac{1}{4}[(2)(1)(1)+ 0 + 0 + (2)(1)(1)] = 1$

$\Gamma_{Pt\text{-}X_t} = 1A_1 + 1B_1$

IR/R IR/R

$\Gamma_{Pt\text{-}X_b}$

$a A_1 = \frac{1}{4}[(4)(1)(1)+ 0 + 0 + (4)(1)(1)] = 2$

$a A_2 = \frac{1}{4}[(4)(1)(1)+ 0 + 0 + (4)(1)(-1)] = 0$

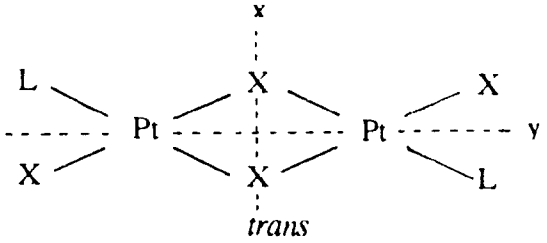
$a B_1 = \frac{1}{4}[(4)(1)(1)+ 0 + 0 + (4)(1)(-1)] = 0$

$a B_2 = \frac{1}{4}[(4)(1)(1)+ 0 + 0 + (4)(1)(1)] = 1$

$\Gamma_{Pt\text{-}X_b} = 2A_1 + 2B_2$

IR/R IR/R

For the *trans* dimer:



C_{2h}

C_{2h}	I	$C_2(z)$	i	$\sigma_h(xy)$
$\Gamma_{Pt\text{-}Xt}$	2	0	0	2
$\Gamma_{Pt\text{-}Xb}$	4	0	0	4

$\Gamma_{Pt\text{-}X_t}$

$a\,A_g = \frac{1}{4}[(2)(1)(1)+0+0+(2)(1)(1)] = 1$

$a\,B_g = \frac{1}{4}[(2)(1)(1)+0+0+(2)(1)(-1)] = 0$

$a\,A_u = \frac{1}{4}[(2)(1)(1)+0+0+(2)(1)(-1)] = 0$

$a\,B_u = \frac{1}{4}[(2)(1)(1)+0+0+(2)(1)(1)] = 1$

$\Gamma_{Pt\text{-}X_b}$

$a\,A_g = \frac{1}{4}[(4)(1)(1)+0+0+(4)(1)(1)] = 2$

$a\,B_g = \frac{1}{4}[(4)(1)(1)+0+0+(4)(1)(-1)] = 0$

$a\,A_u = \frac{1}{4}[(4)(1)(1)+0+0+(4)(1)(-1)] = 0$

$a\,B_u = \frac{1}{4}[(4)(1)(1)+0+0+(4)(1)(1)] = 2$

$\Gamma_{Pt\text{-}X_t} = 1A_g + 1B_u$

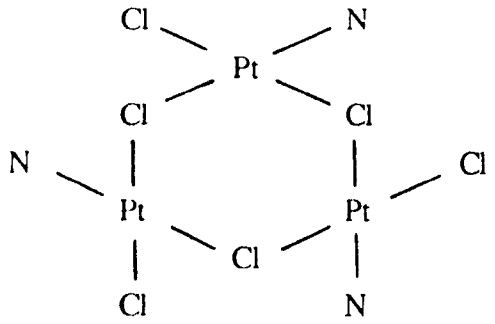
R IR

$\Gamma_{Pt\text{-}X_b} = 2A_g + 2B_u$

R IR

(because of rule of mutual exclusion)

For the trimer



C_3	I	C_3	C_3^2
$\Gamma_{Pt\text{-}Cl_t}$	3	0	0
$\Gamma_{Pt\text{-}Cl_b}$	6	0	0

$\Gamma_{Pt\text{-}Cl_b}$

$aA = \frac{1}{3}[(6)(1)(1) + 0 + 0] = 2$

$aE = \frac{1}{3}[(6)(1)(1) + 0 + 0] = 2$

$\Gamma_{Pt\text{-}Cl_b} = 2A + 2E$

1R/R 1R/R

$\Gamma_{Pt\text{-}Cl_t}$

$aA = \frac{1}{3}[(3)(1)(1) + 0 + 0] = 1$

$aE = \frac{1}{3}[(3)(1)(1) + 0 + 0] = 1$

$\Gamma_{Pt\text{-}Cl_t} = 1A + 1E$

1R/R 1R/R

APPENDIX 2

Table IX. Anisotropic thermal parameters ($x10^4$ for Pt, Cl; $x10^3$ for N, C except C(2) and C(7): $x10^2$) of atoms in 2-adamH[$Pt(EtNH_2)Cl_3$].

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	417(3)	509(4)	424(3)	-25(4)	28(2)	56(4)
Cl(1)	825(27)	684(26)	538(22)	172(23)	44(19)	-6(21)
Cl(2)	812(27)	764(28)	627(24)	272(23)	138(21)	73(22)
Cl(3)	907(28)	904(32)	488(21)	189(24)	24(20)	136(21)
N(1)	57(7)	104(11)	94(11)	-2(9)	20(7)	1(10)
N(2)	41(6)	65(8)	57(7)	1(6)	1(5)	3(6)
C(1)	70(12)	289(36)	45(9)	-41(19)	1(9)	47(17)
C(2)	51(9)	106(16)	17(4)	51(11)	26(5)	34(6)
C(3)	111(21)	161(27)	270(38)	73(21)	-111(24)	-96(27
C(4)	168(26)	68(15)	207(30)	-8(17)	67(23)	18(17)
C(5)	84(21)	112(25)	474(74)	-48(19)	34(32)	-3(32)
C(6)	102(22)	550(75)	179(31)	-163(37)	37(21)	-133(40)
C(7)	91(15)	28(5)	22(4)	33(7)	37(7)	12(4)
C(8)	63(13)	224(31)	314(41)	40(20)	6(19)	-180(34)
C(9)	122(21)	284(41)	112(17)	-77(26)	18(15)	-108(23)
C(10)	67(14)	261(36)	100(16)	20(21)	35(12)	-18(21)
C(11)	83(12)	83(12)	89(13)	-17(11)	16(10)	8(11)
C(12)	99(13)	129(15)	47(9)	18(12)	9(9)	46(10

Table X. Equation and deviations from the best weighted least-squares plane passing through Pt, Cl(1), Cl(2), Cl(3) and N(2) for crystal 2-adamH[Pt(EtNH$_2$)Cl$_3$].

Equation: 0.8552x + 0.5177y - 0.0247z = 1.3263

Atom-to-plane distance (Å)			
Pt	-0.0005(5)	C(11)	-1.38(2)
Cl(1)	0.018(4)	C(12)	-1.40(2)
Cl(2)	0.021(4)		
Cl(3)	-0.005(4)		
N(2)	-0.05(1)		

Table XI. Calculated H coordinates ($x10^3$) for crystal 2-adamH[Pt(EtNH$_2$)Cl$_3$].

Atom	x	y	z
H1C1	729	266	504
H1C2	653	487	459
H1C3	604	520	327
H1C4	760	704	342
H2C4	731	701	413
H1C5	919	653	405
H1C6	807	553	505
H2C6	896	394	505
H1C7	866	229	457
H2C7	788	87	439
H1C8	834	129	333
H1C9	666	217	323
H2C9	729	364	287
H1C10	934	428	346
H2C10	957	338	418
H1C11	30	83	299
H1C11	84	-108	280
H1N2	227	58	267
H2N2	191	227	294
H1N1(located)	480	280	400
H2N1	563	204	384
H3N1	540	195	448

APPENDIX 3

Table XXVIII. Anisotropic thermal parameters(x 10^4) for crystal $[Pt(DMNH)Cl_2]_3$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	464(2)	415(2)	515(2)	254(2)	-55(2)	-131(2)
Cl(1)	720(18)	675(17)	611(15)	357(14)	-278(14)	-113(13)
Cl(2)	553(15)	582(16)	1232(26)	366(13)	-46(16)	149(16)
N(1)	484(44)	437(42)	555(50)	252(36)	-109(38)	-190(37)
C(1)	867(82)	1041(92)	608(79)	574(76)	9(64)	-230(68)
C(2)	552(61)	531(61)	909(85)	284(52)	-14(56)	-169(56)

Table XXIX. Atomic H coordinates (x 10^4)for crystal $[Pt(DMNH)Cl_2]_3$.

Atom	x	y	z
H(1)C(1)	8080	5980	-920
H(2)C(1)	8020	4870	-980
H(3)C(1)	8960	5770	-1080
H(1)C(2)	9220	6810	1140
H(2)C(2)	8420	6850	340
H(3)C(2)	9670	7070	180
H(1)N(1)(calc)	8458	5587	255

Table XXX. Equation and deviations from the best weighted least-squares plane passing through Pt, Cl(1), Cl(1)', Cl(2) and N in $[Pt(DMNH)Cl_2]_3$.

Equation: 0.1234x - 0.7811y - 0.6120z = 4.9684

Atom-to-plane distance (Å)			
Pt	0.0006(4)	C(1)	1.00(1)
Cl(1)	-0.014(3)	C(2)	-1.35(1)
Cl(1)'	-0.001(3)	H(1)N	0.2098
Cl(2)	-0.017(3)		
N	-0.014(8)		

Calculated Structure Factor Amplitudes

for

[2-adamH][Pt(EtNH$_2$)Cl$_3$]

H	K	L	FOBS	FCAL
0	0	2	111	115
0	0	4	103	107
0	0	6	152	146
0	0	8	[illegible]	170
0	0	10	1	[illegible]
0	0	12	195	196
0	0	14	7	13
0	0	16	53	[illegible]
0	0	18	55	55
0	0	0	113	116
0	0	[illegible]	42	41
0	[illegible]	4	14	11*
0	1	1	87	[illegible]
0	1	[illegible]	157	[illegible]
[illegible]	1	3	44	11
0	1	4	1	9
0	1	5	45	11
0	1	6	81	81
0	1	7	127	130
0	1	8	114	113
0	1	9	51	47
0	1	10	208	13
0	1	11	1	8*
0	1	12	81	82
0	1	13	[illegible]	[illegible]
0	1	14	[illegible]	28
0	1	15	[illegible]	*
0	1	16	77	75
0	1	17	1	7*
0	1	18	88	11
[illegible]	1	19	[illegible]	10*
0	1	20	13	7*
0	1	21	13	1*
0	1	[illegible]	46	43
0	1	[illegible]	17	13*
0	1	4	41	41
0	1	5	17	1*
0	2	0	132	171
0	2	1	10	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	50
[illegible]	[illegible]	[illegible]	[illegible]	57
0	[illegible]	4	[illegible]	57
0	2	[illegible]	52	53
0	2	6	[illegible]	177
0	2	7	15	[illegible]
0	2	8	07	211
0	2	9	9	11*
0	2	10	15	1*
0	2	11	16	13*
0	2	12	[illegible]	151
0	2	13	53	58
0	2	14	130	[illegible]
0	2	15	17	27*
0	2	16	31	32
0	[illegible]	17	[illegible]	18*

H	K	L	FOBS	FCAL
0	2	18	40	41
0	2	19	13	[illegible]
0	[illegible]	0	59	54
0	2	21	13	[illegible]
0	[illegible]	2	13	3*
0	2	23	14	6*
0	2	4	14	8*
0	2	25	17	11*
0	3	[illegible]	15	[illegible]
0	3	2	130	14
0	3	3	71	[illegible]
0	3	4	[illegible]	1
0	3	5	100	1
0	3	6	43	43
0	3	7	9	*
0	3	8	70	[illegible]
0	3	9	9	13
0	3	10	112	116
0	3	11	47	55
0	3	12	68	71
0	3	13	12	9*
0	3	14	23	15*
0	3	15	63	52
0	3	16	77	75
0	3	17	25	27*
0	3	18	66	64
0	3	19	30	2
0	3	20	21	7*
0	3	21	22	12*
0	3	[illegible]	17	30
0	3	[illegible]	3	22*
0	3	24	41	14
0	4	0	158	155
0	4	1	91	94
0	4	2	104	102
0	4	3	20	20*
0	4	4	38	10
0	4	5	85	[illegible]
0	4	6	[illegible]	122
0	4	7	57	59
0	4	8	[illegible]	[illegible]
0	[illegible]	9	[illegible]	1*
0	4	10	16	6*
0	4	11	11	13*
0	4	12	49	47
0	4	13	42	42
0	4	14	53	68
0	4	15	35	9
0	4	16	16	22*
0	4	17	14	7*
0	4	18	33	29
0	4	19	25	1*
0	4	20	46	43
0	4	21	25	[illegible]
0	4	22	22	7*

H	K	L	FOBS	FCAL
0	4	23	19	[illegible]
0	5	1	27	35
0	5	2	45	45
0	5	3	[illegible]	78
0	5	4	92	98
0	5	5	40	42
0	5	6	45	44
0	5	7	34	31
0	5	8	36	33
0	5	9	61	67
0	5	10	[illegible]	61
[illegible]	5	11	[illegible]	[illegible]
0	[illegible]	12	[illegible]	[illegible]
0	5	13	14	[illegible]
0	5	14	3	13*
0	5	15	35	33
0	5	16	54	49
0	5	17	29	31*
0	5	18	24	[illegible]
0	5	19	21	13*
0	5	20	27	5*
0	5	21	20	11*
0	6	0	3	37
0	6	1	40	45
0	6	2	29	28
0	6	3	12	11*
0	6	4	24	16*
0	6	5	37	40
0	6	6	51	57
0	6	7	63	[illegible]
0	6	8	30	[illegible]
0	6	9	35	34
0	6	10	13	[illegible]
0	6	11	23	33*
0	6	12	38	23
0	6	13	50	52
0	6	14	37	39
0	6	15	[illegible]	[illegible]
0	6	16	22	[illegible]
0	6	17	15	7*
0	6	18	11	5*
0	6	19	22	22*
0	7	1	31	29
0	7	2	28	[illegible]
0	7	3	58	54
0	7	4	35	32
0	7	5	13	1
0	7	6	13	*
0	7	7	16	[illegible]
0	7	8	13	18*
0	7	9	[illegible]	[illegible]
0	7	10	22	[illegible]
0	7	11	33	31
0	7	12	25	20*
0	7	13	27	*

H	K	L	FOBS	FCAL
0	7	14	16	5*
0	7	15	19	23*
0	7	16	27	12*
0	8	0	31	20
0	8	1	41	40
0	8	2	21	15*
0	8	3	13	2*
0	8	4	16	1*
0	8	5	19	27*
0	[illegible]	6	15	11*
0	8	7	15	31
0	8	8	18	[illegible]
0	8	9	15	11*
0	8	10	17	5*
0	8	11	14	11*
1	0	-25	18	8*
1	0	-23	59	52
1	0	-21	89	82
1	0	-19	16	15*
1	0	-17	92	95
1	0	-15	115	114
1	0	-13	84	84
1	0	-11	69	69
1	0	-9	192	195
1	0	-7	43	46
1	0	-5	33	19
1	0	-3	330	369
1	0	-1	[illegible]	317
1	0	1	26	10
1	0	3	101	95
1	0	5	242	243
1	0	7	138	140
1	0	9	106	103
1	0	11	139	142
1	0	13	41	41
1	0	15	11	7*
1	0	17	77	77
1	0	19	96	94
1	0	21	20	15*
1	0	23	29	29*
1	0	25	22	48
1	1	-25	34	33
1	1	-24	14	13*
1	1	-23	26	25*
1	1	-22	13	3*
1	1	-21	29	21
1	1	-20	13	6*
1	1	-19	95	93
1	1	-18	12	3*
1	1	-17	69	65
1	1	-16	23	13*
1	1	-15	12	15*
1	1	-14	44	42
1	1	-13	111	113
1	1	-12	19	10*

H	K	L	FOBS	FCAL
1	1	-11	182	188
1	1	-10	15	21*
1	1	-9	60	59
1	1	-8	30	30
1	1	-7	171	174
1	1	-6	19	22*
1	1	-5	209	212
1	1	-4	90	84
1	1	-3	139	133
1	1	-2	55	54
1	1	-1	77	70
1	1	0	7	9*
1	1	1	367	357
1	1	2	12	5*
1	1	3	187	130
1	1	4	44	41
1	1	5	8	17*
1	1	6	120	126
1	1	7	193	200
1	1	8	33	37
1	1	9	211	214
1	1	10	9	[illegible]
1	1	11	33	3*
1	1	12	10	[illegible]
1	1	13	74	70
1	1	14	11	19*
1	1	15	119	118
1	1	[illegible]	12	15*
1	1	17	56	58
1	1	18	12	14*
1	1	19	47	39
1	1	20	13	5*
1	1	21	66	61
1	1	22	13	11*
1	1	23	25	36*
1	1	24	14	1*
1	1	25	14	4*
1	2	-25	[illegible]	5*
1	2	-24	11	11*
1	2	23	[illegible]	36*
1	2	-22	[illegible]	12*
1	2	-21	[illegible]	44
1	2	-20	14	12*
1	2	-19	15	12*
1	2	-18	17	13*
1	2	-17	49	[illegible]
1	2	-16	26	27*
1	2	-15	94	95
1	2	-14	43	13
1	2	-13	59	67
1	2	-12	11	[illegible]
1	2	-11	87	71
1	2	10	19	[illegible]
1	2	-9	217	[illegible]
1	2	8	35	1

H	K	L	FOBS	FCAL
1	2	-7	156	157
1	2	-6	59	60
1	2	-5	14	12*
1	2	-4	120	120
1	2	-3	195	194
1	2	-2	41	47
1	2	-1	188	182
1	2	0	29	30
1	2	1	37	35
1	2	2	50	51
1	2	3	99	105
1	2	4	39	39
1	2	5	144	147
1	2	6	30	34
1	2	7	127	127
1	2	8	10	15*
1	2	9	72	72
1	2	10	10	13*
1	2	11	181	189
1	2	12	69	71
1	2	13	121	122
1	2	14	26	20*
1	2	15	13	6*
1	2	16	40	38
1	2	17	76	78
1	2	18	12	16*
1	2	19	62	65
1	2	20	13	13*
1	2	21	13	5*
1	2	22	21	5*
1	2	23	14	19*
1	2	24	16	13*
1	3	-24	14	13*
1	3	-23	15	18*
1	3	-22	20	8*
1	3	-21	30	26
1	3	-20	18	12*
1	3	19	60	62
1	3	-18	37	35
1	3	-17	52	49
1	3	-16	33	49
1	3	-15	21	24*
1	3	-14	12	21*
1	3	-13	84	87
1	3	-12	56	57
1	3	-11	95	75
1	3	10	18	44
1	3	9	31	37
1	3	-8	10	1*
1	3	7	98	100
1	3	6	85	84
1	3	-5	175	175
1	3	[illegible]	10	15
1	3	[illegible]	111	113
[illegible]	[illegible]	[illegible]	7	1

H	K	L	FOBS	FCAL
1	3	-1	36	40
1	3	0	54	52
1	3	1	191	196
1	3	2	98	107
1	3	3	141	145
1	3	4	72	76
1	3	5	38	38
1	3	6	24	25
1	3	7	134	143
1	3	8	37	43
1	3	9	102	107
1	3	10	49	50
1	3	11	24	21*
1	3	12	12	7*
1	3	13	55	57
1	3	14	57	53
1	3	15	89	93
1	3	16	12	12*
1	3	17	45	47
1	3	18	13	17*
1	3	19	13	15*
1	3	20	13	25*
1	3	21	50	43
1	3	22	23	25*
1	3	23	40	34
1	3	24	24	3*
1	4	-23	26	32*
1	4	-22	30	28*
1	4	-21	27	32*
1	4	-20	22	22*
1	4	-19	13	7*
1	4	-18	17	2*
1	4	-17	49	48
1	4	-16	41	43
1	4	-15	82	82
1	4	-14	41	43
1	4	-13	32	35
1	4	-12	16	6*
1	4	-11	34	40
1	4	-10	33	24
1	4	-9	67	73
1	4	-9	58	59
1	4	-7	71	69
1	4	-6	44	47
1	4	-5	19	14*
1	4	4	47	52
1	4	-3	115	122
1	4	-2	85	87
1	4	-1	129	136
1	4	0	76	76
1	4	1	41	[illegible]
1	4	2	11	[illegible]
1	4	3	[illegible]	[illegible]
1	4	4	[illegible]	[illegible]
1	[illegible]	[illegible]	11	1

H	K	L	FOBS	FCAL
1	4	6	63	67
1	4	7	55	57
1	4	8	12	14*
1	4	9	12	19*
1	4	10	30	38
1	4	11	57	55
1	4	12	46	49
1	4	13	50	49
1	4	14	27	11*
1	4	15	23	7*
1	4	16	26	15*
1	4	17	52	42
1	4	18	22	25*
1	4	19	50	44
1	4	20	20	22*
1	4	21	27	19*
1	4	22	22	6*
1	5	-21	17	15*
1	5	-20	27	18*
1	5	-19	23	27*
1	5	-18	23	29*
1	5	-17	39	35
1	5	-16	22	13*
1	5	-15	13	4*
1	5	-14	32	30
1	5	-13	52	53
1	5	-12	52	53
1	5	-11	49	49
1	5	-10	36	32
1	5	-9	16	10*
1	5	-8	14	9*
1	5	-7	67	68
1	5	-6	66	66
1	5	-5	87	92
1	5	-4	78	82
1	5	-3	11	13*
1	5	-2	70	23*
1	5	-1	39	38
1	5	0	47	51
1	5	1	64	71
1	5	2	73	72
1	5	3	88	84
1	5	4	14	10*
1	5	5	14	1*
1	5	6	59	62
1	5	7	64	63
1	5	8	61	67
1	5	9	59	64
1	5	10	40	34
1	5	11	28	31*
1	5	12	19	20*
1	5	13	45	30
1	5	14	48	35
1	[illegible]	15	[illegible]	[illegible]
1	[illegible]	15	[illegible]	31*

H	K	L	FOBS	FCAL
1	5	17	23	15*
1	5	18	14	7*
1	5	19	23	8*
1	5	20	17	17*
1	5	21	15	22*
1	6	-19	15	1*
1	6	-18	14	3*
1	6	-17	14	18*
1	6	-16	22	27*
1	6	-15	24	31*
1	6	-14	41	41
1	6	-13	13	7*
1	6	-12	15	11*
1	6	-11	34	28
1	6	-10	46	47
1	6	-9	42	46
1	6	-8	66	67
1	6	-7	44	46
1	6	-6	20	24*
1	6	-5	12	6*
1	6	-4	44	35
1	6	-3	51	48
1	6	-2	56	58
1	6	-1	38	37
1	6	0	32	33
1	6	1	12	14*
1	6	2	12	14*
1	6	3	27	32*
1	6	4	45	52
1	6	5	38	51
1	6	6	47	50
1	6	7	18	20*
1	6	8	20	9*
1	6	9	14	13*
1	6	10	45	43
1	6	11	48	44
1	6	12	46	51
1	6	13	43	41
1	6	14	14	12*
1	6	15	14	2*
1	6	16	20	24*
1	6	17	15	16*
1	6	18	27	10*
1	7	-16	15	14*
1	7	-15	14	12*
1	7	-14	25	11*
1	7	-13	24	23*
1	7	-12	32	35
1	7	-11	13	15*
1	7	-10	13	26*
1	7	-9	13	5*
1	7	-8	15	13*
1	7	-7	[illegible]	15*
1	7	-6	30	41
1	[illegible]	-5	[illegible]	[illegible]

H	K	L	FOBS	FCAL
1	7	-4	49	43
1	7	-3	22	19*
1	7	-2	12	6*
1	7	-1	12	8*
1	7	0	52	48
1	7	1	24	32*
1	7	2	56	54
1	7	3	25	27*
1	7	4	21	21*
1	7	5	38	9
1	7	6	18	19*
1	7	7	17	25*
1	7	8	33	42*
1	7	9	33	19*
1	7	10	15	22*
1	7	11	20	9*
1	7	12	15	13*
1	7	13	15	9*
1	7	14	16	27*
1	7	15	25	16*
1	8	-11	21	8*
1	8	-10	33	21
1	8	-9	25	12*
1	8	-8	24	27*
1	8	-7	14	6*
1	8	-6	13	12*
1	8	-5	13	8*
1	8	-4	17	16*
1	8	-3	27	18*
1	8	-2	39	41
1	8	-1	13	14*
1	8	0	35	29
1	8	1	24	5*
1	8	2	14	14*
1	8	3	14	7*
1	8	4	35	38
1	8	5	23	14*
1	8	6	49	31
1	8	7	17	11*
1	8	8	20	1*
1	8	9	17	1*
1	8	10	17	23*
1	8	11	32	10*
2	0	-26	34	19
2	0	-24	39	43
2	0	-22	57	51
2	0	-20	13	22*
2	0	-18	113	110
2	0	-16	100	100
2	0	-14	25	32*
2	0	-12	122	124
2	0	-10	137	142
2	0	-8	43	44
2	0	[illegible]	13	[illegible]
2	0	[illegible]	156	157

H	K	L	FOBS	FCAL
2	0	[illegible]	222	[illegible]
2	0	0	6	17*
2	0	2	323	315
2	0	4	263	237
2	0	6	98	100
2	0	8	216	212
2	0	10	177	178
2	0	12	37	30
2	0	14	20	17*
2	0	16	101	75
2	0	18	53	59
2	0	20	13	12*
2	0	22	48	47
2	0	24	51	49
2	1	-26	17	23*
2	1	-25	15	14*
2	1	-24	14	5*
2	1	-23	14	4*
2	1	-22	48	45
2	1	-21	13	6*
2	1	-20	82	79
2	1	-19	13	16*
2	1	-18	23	24*
2	1	-17	14	7*
2	1	-16	55	50
2	1	-15	34	41
2	1	-14	124	124
2	1	-13	11	3*
2	1	-12	150	150
2	1	-11	57	57
2	1	-10	56	54
2	1	-9	10	5*
2	1	-8	219	227
2	1	[illegible]	23	25
2	1	-6	176	127
2	1	-5	97	90
2	1	-4	34	27
2	1	-3	78	71
2	1	-2	251	241
2	1	-1	18	6*
2	1	0	315	297
2	1	1	178	154
2	1	2	80	84
2	1	3	8	5*
2	1	4	76	95
2	1	5	58	58
2	1	6	224	224
2	1	7	15	13*
2	1	8	157	150
2	1	9	32	39
2	1	10	34	33
2	1	11	15	[illegible]
2	1	12	[illegible]	[illegible]
2	1	13	[illegible]	[illegible]
2	1	[illegible]	11	[illegible]

H	K	L	FOBS	FCAL
2	1	15	12	7*
2	1	16	12	1*
2	1	17	12	10*
2	1	18	25	12
2	1	19	13	3*
2	1	20	72	67
2	1	21	13	17*
2	1	22	17	0*
2	1	[illegible]	3	1*
2	1	24	14	17*
2	2	-25	31	12*
2	2	-24	33	3
2	2	-23	14	14*
2	2	-22	35	33
2	2	-21	13	4*
2	2	-20	13	10*
2	2	-19	13	3*
2	2	-18	58	62
2	2	-17	13	25*
2	2	-16	67	62
2	2	-15	12	20*
2	2	-14	12	6*
2	2	-13	23	23*
2	2	-12	115	118
2	2	-11	35	31
2	2	-10	138	192
2	2	-9	77	79
2	2	-8	91	94
2	2	-7	10	12*
2	2	-6	107	105
2	2	-5	99	67
2	2	-4	270	271
2	2	-3	24	25
2	2	-2	209	201
2	2	-1	43	35
2	2	0	45	37
2	2	1	12	11*
2	2	2	138	133
2	2	3	94	92
2	2	4	136	132
2	2	5	3	0*
2	2	6	30	47
2	2	7	19	45
2	2	8	133	136
2	2	9	11	35
2	2	10	158	154
2	2	11	59	54
2	2	12	53	71
2	2	13	10	5*
2	2	14	32	37
2	2	15	40	10
2	2	16	115	115
2	2	17	17	1*
2	2	[illegible]	3	55
2	2	[illegible]	1	1*

H	K	L	FOBS	FCAL
2	2	20	19	13*
2	2	21	33	13
2	2	22	40	16
2	2	23	19	16*
2	2	24	31	27*
2	3	-24	14	7*
2	3	-23	12	15
2	3	-22	30	14*
2	3	-21	14	1*
2	3	-20	53	[illegible]
2	3	-19	14	7*
2	3	-18	13	*
2	3	-17	23	1*
2	3	-16	[illegible]	55
2	3	-15	38	32
2	3	-14	97	91
2	3	-13	59	50
2	3	-12	57	59
2	3	-11	43	47
2	3	-10	43	37
2	3	-9	11	9*
2	3	-8	127	134
2	3	-7	73	78
2	3	-6	152	157
2	3	-5	19	11*
2	3	-4	44	47
2	3	-3	111	117
2	3	-2	119	115
2	3	-1	74	70
2	3	0	185	181
2	3	1	59	59
2	3	2	86	87
2	3	3	9	1*
2	3	4	98	101
2	3	5	54	67
2	3	6	161	[illegible]
2	3	7	[illegible]	[illegible]
2	3	8	0	72
2	3	9	48	37
2	3	10	23	2*
2	3	11	13	13*
2	3	12	87	91
2	3	13	50	55
2	3	14	85	83
2	3	15	13	*
2	3	16	17	13*
2	3	17	37	33
2	3	18	39	34
2	3	19	12	*
2	3	20	45	[illegible]
2	3	21	14	1*
2	3	22	31	[illegible]
2	3	23	11	*
2	4	-23	[illegible]	*
2	4	-22	17	1*

H	K	L	FOBS	FCAL
2	4	-21	14	9*
2	4	-20	15	17*
2	4	-19	19	14*
2	4	-18	65	58
2	4	-17	55	49
2	4	-16	72	67
2	4	-15	32	30
2	4	-14	12	3*
2	4	-13	29	6
2	4	-12	55	51
2	4	-11	13	41
2	4	-10	61	64
2	4	-9	46	53
2	4	-8	46	41
2	4	-7	12	9*
2	4	-6	52	52
2	4	-5	63	64
2	4	-4	108	112
2	4	-3	62	63
2	4	-2	66	63
2	4	-1	40	38
2	4	0	35	33
2	4	1	46	43
2	4	2	143	140
2	4	3	123	125
2	4	4	144	147
2	4	5	46	44
2	4	6	[illegible]	30
2	4	7	42	41
2	4	8	67	66
2	4	9	53	55
2	4	10	77	79
2	4	11	44	47
2	4	12	27	12
2	4	13	12	17*
2	4	14	36	35
2	4	15	32	35
2	4	16	50	50
2	4	17	22	19*
2	4	18	12	31
2	4	19	13	9*
2	4	20	14	1*
2	4	21	25	13*
2	4	22	44	30
2	5	-21	15	20*
2	5	-20	14	21*
2	5	-19	17	25*
2	5	-18	14	15*
2	5	-17	13	1*
2	5	-16	14	21*
2	5	-15	43	17
2	5	-14	51	53
2	5	-13	40	41
2	5	-12	38	40
2	5	-11	12	5*

H	K	L	FOBS	FCAL
2	5	-10	13	9*
2	5	-9	45	41
2	5	-8	76	81
2	5	-7	79	82
2	5	-6	80	81
2	5	-5	61	65
2	5	-4	13	17*
2	5	-3	12	7*
2	[illegible]	[illegible]	65	68
2	5	-1	63	63
2	5	0	68	71
2	5	1	56	55
2	5	2	19	35*
2	5	3	24	3*
2	5	4	45	42
2	5	5	75	66
2	5	6	61	67
2	5	7	57	58
2	5	8	54	55
2	5	9	13	10*
2	5	10	13	19*
2	5	11	41	44
2	5	12	55	51
2	5	13	50	54
2	5	14	57	54
2	5	15	25	24*
2	5	16	13	4*
2	5	17	14	7*
2	5	18	23	6*
2	5	19	23	[illegible]
2	5	20	29	[illegible]
2	6	-19	17	17*
2	6	-18	11	17*
2	6	-17	10	[illegible]
2	6	-16	14	1*
2	6	-15	20	3*
2	6	-14	1	11*
2	6	-13	3	6*
2	6	-12	17	16
2	6	-11	52	48
2	6	-10	38	10
2	6	-9	[illegible]	[illegible]
2	6	-8	13	24*
2	6	-7	12	1*
2	6	-6	31	13
2	6	-5	67	59
2	6	-4	50	51
2	6	-3	50	56
2	6	-2	11	15
2	6	-1	17	11*
2	6	0	17	*
2	6	1	17	[illegible]
2	6	[illegible]	40	11
2	6	[illegible]	[illegible]	[illegible]
2	6	4	51	[illegible]

H	K	L	FOBS	FCAL
2	6	5	20	27*
2	6	6	17	3*
2	6	7	19	11*
2	6	8	35	28
2	6	9	46	46
2	6	10	44	43
2	6	11	29	39*
2	6	12	36	27
2	6	13	14	5*
2	6	14	14	14*
2	6	15	33	35
2	6	16	22	26*
2	6	17	33	32*
2	6	18	15	19*
2	7	-16	17	16*
2	7	-15	19	21*
2	7	-14	15	22*
2	7	-13	30	34*
2	7	-12	32	4
2	7	-11	31	16
2	7	-10	23	12*
2	7	-9	17	21*
2	7	-8	21	22*
2	7	-7	33	41
2	7	-6	20	22*
2	7	-5	33	28
2	7	-4	19	4*
2	7	-3	19	18*
2	7	-2	19	16*
2	7	-1	59	56
2	7	0	32	34
2	7	1	35	39
2	7	2	26	24*
2	7	3	13	4*
2	7	4	15	18*
2	7	5	33	38*
2	7	6	22	29*
2	7	7	42	46
2	7	8	15	13*
2	7	9	15	12*
2	7	10	15	4*
2	7	11	37	24
2	7	12	20	18*
2	7	13	27	28*
2	7	14	32	15*
2	7	15	15	14*
2	8	-11	21	26*
2	8	-10	15	10*
2	8	-9	14	21*
2	8	-8	18	2*
2	8	-7	14	1*
2	8	-6	14	10*
2	8	-5	11	23*
2	[illegible]	-4	11	14*
2	[illegible]	-3	4	35*

H	K	L	FOBS	FCAL
2	8	-2	29	6*
2	8	-1	13	14*
2	8	0	13	4*
2	8	1	26	26*
2	8	2	27	14*
2	8	3	45	40
2	8	4	15	15*
2	8	5	21	23*
2	8	6	18	5*
2	8	7	27	17*
2	8	8	17	6*
2	8	9	37	31*
2	8	10	16	13*
3	0	-25	32	31
3	0	-23	20	25*
3	0	-21	56	50
3	0	-19	97	99
3	0	-17	62	54
3	0	-15	39	39
3	0	-13	155	160
3	0	-11	148	155
3	0	-9	19	11*
3	0	-7	116	118
3	0	-5	165	169
3	0	-3	95	90
3	0	-1	297	279
3	0	1	292	262
3	0	3	223	220
3	0	5	46	39
3	0	7	312	310
3	0	9	180	181
3	0	11	10	6*
3	0	13	61	66
3	0	15	93	92
3	0	17	30	24
3	0	19	53	47
3	0	21	52	54
3	0	23	40	36
3	1	-26	14	4*
3	1	-25	14	12*
3	1	-24	30	2*
3	1	-23	50	50
3	1	-22	19	10*
3	1	-21	55	55
3	1	-20	13	25*
3	1	-19	16	10*
3	1	-18	27	9*
3	1	-17	73	72
3	1	-16	35	32
3	1	-15	100	104
3	1	-14	12	7*
3	1	13	70	68
3	1	[illegible]	10	17
3	1	-11	[illegible]	113
3	1	[illegible]	11	11*

H	K	L	FOBS	FCAL
3	1	-9	165	174
3	1	-8	45	45
3	1	-7	98	99
3	1	-6	10	10*
3	1	-5	13	25*
3	1	-4	10	21*
3	1	-3	280	266
3	1	-2	20	26*
3	1	-1	262	254
3	1	0	170	152
3	1	1	36	34
3	1	2	105	103
3	1	3	164	164
3	1	4	57	55
3	1	5	180	178
3	1	6	8	8*
3	1	7	90	89
3	1	8	63	60
3	1	9	105	105
3	1	10	49	55
3	1	11	138	141
3	1	12	12	15*
3	1	13	87	85
3	1	14	32	25
3	1	15	12	13*
3	1	16	12	5*
3	1	17	103	98
3	1	18	12	4*
3	1	19	60	58
3	1	20	13	20*
3	1	21	13	2*
3	1	22	14	4*
3	1	23	42	10
3	1	24	14	5*
3	2	-25	46	33
3	2	-24	15	10*
3	2	-23	14	17*
3	2	-22	14	2*
3	2	-21	35	33
3	2	-20	13	4*
3	2	-19	68	61
3	2	-18	17	25*
3	2	-17	38	41
3	2	-16	13	4*
3	2	-15	13	18*
3	2	-14	17	27*
3	2	-13	113	115
3	2	-12	17	34*
3	2	-11	133	137
3	2	-10	38	34
3	2	-9	13	7*
3	2	-8	11	3*
3	2	-7	171	162
3	2	-6	92	85
3	2	-5	257	[illegible]

H	K	L	FOBS	FCAL
3	2	-4	48	48
3	2	-3	98	95
3	2	-2	17	19*
3	2	-1	144	140
3	2	0	57	53
3	2	1	164	155
3	2	2	52	52
3	2	3	80	80
3	2	4	36	33
3	2	5	33	32
3	2	6	28	31
3	2	7	143	148
3	2	8	10	24*
3	2	9	94	98
3	2	10	38	48
3	2	11	11	5*
3	2	12	14	16*
3	2	13	94	92
3	2	14	33	40
3	2	15	124	122
3	2	16	12	9*
3	2	17	43	39
3	2	18	12	4*
3	2	19	33	37
3	2	20	17	10*
3	2	21	46	50
3	2	22	14	16*
3	2	23	14	25*
3	3	-24	15	15*
3	3	-23	39	34
3	3	-22	24	16*
3	3	-21	49	42
3	3	-20	13	10*
3	3	-19	13	1*
3	3	-18	13	7*
3	3	-17	66	67
3	3	-16	45	47
3	3	-15	79	82
3	3	-14	38	18
3	3	-13	13	14*
3	3	-12	17	23*
3	3	-11	86	87
3	3	-10	25	12*
3	3	-9	128	134
3	3	-8	88	91
3	3	-7	67	63
3	3	-6	11	4*
3	3	-5	30	34
3	3	-4	105	124
3	3	-3	123	118
3	3	-2	57	67
3	3	-1	156	161
3	3	0	11	25
3	3	1	11	11
3	3	[illegible]	[illegible]	7

H	K	L	FOBS	FCAL
3	3	3	149	146
3	3	4	99	97
3	3	5	169	166
3	3	6	24	37
3	3	7	52	53
3	3	8	30	27
3	3	9	75	78
3	3	10	23	23*
3	3	11	112	112
3	3	12	62	65
3	3	13	56	51
3	3	14	12	2*
3	3	15	12	21*
3	3	16	28	29
3	3	17	54	52
3	3	18	16	26*
3	3	19	45	46
3	3	20	13	10*
3	3	21	28	13*
3	3	22	30	20*
3	4	-23	15	3*
3	4	-22	14	1*
3	4	-21	25	25*
3	4	-20	14	22*
3	4	-19	59	53
3	4	-18	28	41*
3	4	-17	42	10
3	4	-16	13	12*
3	4	-15	36	31
3	4	-14	43	38
3	4	-13	71	73
3	4	-12	46	50
3	4	-11	61	61
3	4	-10	37	36
3	4	-9	12	5*
3	4	-8	12	15*
3	4	-7	72	79
3	4	-6	60	57
3	4	-5	90	94
3	4	-4	42	43
3	4	-3	17	10*
3	4	-2	12	14*
3	4	-1	72	6*
3	4	0	62	63
3	4	1	141	139
3	4	2	107	105
3	4	3	112	108
3	4	4	10	2*
3	4	5	38	37
3	4	6	60	62
3	4	7	102	106
3	4	8	58	56
3	4	9	83	91
3	4	10	[illegible]	1*
3	4	11	[illegible]	13*

H	K	L	FOBS	FCAL
3	4	[illegible]	[illegible]	[illegible]
3	4	11	[illegible]	[illegible]
3	4	14	4	[illegible]
3	4	15	47	50
3	4	16	[illegible]	14*
3	4	17	13	13*
3	4	18	13	1*
3	4	17	14	15*
3	4	[illegible]	14	[illegible]
3	4	1	37	33
3	5	1	8	[illegible]
3	5	[illegible]	14	[illegible]
3	5	17	14	6*
3	5	18	14	4*
3	5	17	32	33
3	5	16	30	19*
3	5	15	42	13
3	5	14	15	11
3	5	13	[illegible]	17*
3	5	1	27	15*
3	5	1	33	4
3	5	10	56	56
3	5	9	76	9
3	5	8	55	68
3	5	7	58	53
3	[illegible]	6	17	0
3	5	5	17	42
3	5	4	38	47
3	5	3	76	[illegible]
3	5	[illegible]	71	67
3	5	1	57	[illegible]
3	5	0	52	58
3	5	1	14	10*
3	5	[illegible]	12	17
3	[illegible]	3	67	[illegible]
3	[illegible]	4	68	9
3	[illegible]	[illegible]	36	45
3	[illegible]	6	33	30
3	[illegible]	7	33	31
3	5	[illegible]	15	20*
3	5	[illegible]	13	11*
3	5	10	[illegible]	60
3	5	11	21	1
3	5	12	41	13
3	5	13	50	46
3	[illegible]	14	13	1*
3	5	15	18	9*
3	5	16	[illegible]	23*
3	5	17	[illegible]	33*
3	5	18	14	[illegible]
3	5	19	17	7
3	6	17	5	1*
3	6	1[illegible]	15	1*
3	6	1[illegible]	[illegible]	1*
3	6	1[illegible]	[illegible]	1*

H	K	L	FOBS	FCAL
3	6	15	14	10*
3	6	14	14	16*
3	6	13	27	3*
3	6	12	40	45
3	6	11	30	25
3	6	10	29	30*
3	6	9	15	7*
3	6	8	37	[illegible]
3	6	7	45	52
3	6	6	76	71
3	6	5	[illegible]	[illegible]
3	6	4	53	53
3	6	3	26	17*
3	6	2	12	12*
3	6	1	28	19*
3	6	0	56	58
3	6	1	46	47
3	6	2	51	49
3	6	3	34	29
3	6	4	12	12*
3	6	5	12	18*
3	6	6	12	26*
3	6	7	32	31
3	6	8	43	45
3	6	9	33	30
3	6	10	26	22*
3	6	11	13	[illegible]
3	6	12	34	22
3	6	13	27	18*
3	6	14	46	40
3	6	15	17	29*
3	6	16	21	27*
3	6	17	23	16*
3	7	16	37	27
3	7	15	15	15*
3	7	14	28	27*
3	7	13	14	7*
3	7	12	14	0*
3	7	11	29	21*
3	7	-10	35	31
3	7	-9	14	21*
3	7	8	41	35
3	7	7	13	7*
3	7	6	13	11*
3	7	5	13	12*
3	7	4	37	30
3	7	3	34	24
3	7	2	14	47
3	7	1	10	32
3	7	0	13	11*
3	7	1	12	1*
3	7	2	22	[illegible]
3	7	3	11	[illegible]
3	[illegible]	4	[illegible]	[illegible]
3	[illegible]	[illegible]	[illegible]	[illegible]

H	K	L	FOBS	FCAL
3	7	6	35	40
3	7	7	19	8*
3	7	8	14	3*
3	7	9	14	14*
3	7	10	14	12*
3	7	11	20	23*
3	7	12	15	25*
3	7	13	15	9*
3	7	14	15	7*
3	8	11	15	8*
3	8	10	15	11*
3	8	-9	16	1*
3	8	-8	14	11*
3	8	-7	14	11*
3	8	-6	14	26*
3	8	-5	14	10*
3	8	-4	34	26
3	8	-3	14	2*
3	8	-2	14	1*
3	8	-1	20	13*
3	8	0	19	32*
3	8	1	18	17*
3	8	2	39	33
3	8	3	14	9*
3	8	4	25	9*
3	8	5	17	2*
3	8	6	21	25*
3	8	7	16	11*
3	8	8	30	34*
3	8	9	18	15*
4	0	-26	15	19*
4	0	-24	23	4*
4	0	-22	52	51
4	0	-20	73	73
4	0	-18	17	10*
4	0	-16	97	97
4	0	-14	162	170
4	0	-12	78	131
4	0	-10	86	19
4	0	-8	111	115
4	0	-6	122	126
4	0	-4	10	5*
4	0	-2	219	209
4	0	0	227	213
4	0	2	78	78
4	0	4	184	171
4	0	6	283	287
4	0	8	117	114
4	0	10	53	57
4	0	12	99	75
4	0	14	81	81
4	0	16	12	7*
4	0	18	69	57
4	0	20	50	[illegible]
4	0	22	13	2*

H	K	L	FOBS	FCAL
4	1	26	15	22*
4	1	-25	15	6*
4	1	24	45	44
4	1	-23	14	10*
4	1	-22	38	32
4	1	-21	25	2*
4	1	-20	47	38
4	1	19	23	6*
4	1	-18	76	71
4	1	17	30	23
4	1	-16	74	72
4	1	15	13	5*
4	1	14	21	10*
4	1	-13	16	15*
4	1	-12	139	144
4	1	-11	11	21*
4	1	-10	156	158
4	1	-9	17	12*
4	1	-8	38	38
4	1	-7	63	63
4	1	-6	115	112
4	1	-5	47	43
4	1	-4	276	270
4	1	-3	32	30
4	1	-2	144	143
4	1	-1	87	83
4	1	0	130	125
4	1	1	12	13*
4	1	2	170	152
4	1	3	34	26
4	1	4	163	154
4	1	5	19	14
4	1	6	9	13*
4	1	7	30	27
4	1	8	174	174
4	1	9	42	44
4	1	10	132	133
4	1	11	14	5*
4	1	12	45	48
4	1	13	46	44
4	1	14	55	56
4	1	15	14	22*
4	1	16	103	104
4	1	17	20	5*
4	1	18	33	40
4	1	19	17	10*
4	1	20	15	19*
4	1	21	13	1*
4	1	22	48	44
4	1	23	27	4*
4	2	-25	15	3*
4	2	-24	15	7*
4	2	-23	31	3*
4	2	22	43	50
4	2	-21	14	7*

H	K	L	FOBS	FCAL
4	2	-20	61	52
4	2	-19	28	19*
4	2	-18	13	14*
4	2	-17	16	2*
4	2	-16	41	40
4	2	-15	27	29*
4	2	14	88	84
4	2	-13	35	30
4	2	12	59	57
4	2	11	32	15
4	2	-10	[illegible]	63
4	2	-9	24	25*
4	2	-8	178	182
4	2	-7	90	87
4	2	-6	165	166
4	2	-5	18	19*
4	2	-4	34	37
4	2	-3	46	43
4	2	-2	218	203
4	2	-1	43	42
4	2	0	163	155
4	2	1	70	72
4	2	2	67	68
4	2	3	19	17*
4	2	4	84	83
4	2	5	37	33
4	2	6	148	145
4	2	7	19	31*
4	2	8	55	57
4	2	9	28	35
4	2	10	44	46
4	2	11	27	28
4	2	12	113	115
4	2	13	45	37
4	2	14	100	97
4	2	15	12	4*
4	2	16	11	2*
4	2	17	12	11*
4	2	18	60	65
4	2	19	23	25*
4	2	20	55	53
4	2	21	13	14*
4	2	22	24	17*
4	2	23	17	10*
4	3	24	34	29
4	3	-23	15	10*
4	3	-22	14	22*
4	3	-21	14	1*
4	3	-20	27	20*
4	3	-19	31	30
4	3	19	21	[illegible]
4	3	17	40	[illegible]
4	3	15	[illegible]	[illegible]
4	3	15	11	[illegible]
4	3	14	24	11*

H	K	L	FOBS	FCAL
4	3	11	13	9*
4	3	12	97	100
4	3	-11	44	42
4	3	-10	106	101
4	3	-9	90	86
4	3	-8	22	16*
4	3	7	12	7*
4	3	6	84	82
4	3	5	64	67
4	3	4	150	152
4	3	3	49	45
4	3	2	102	96
4	3	-1	10	5*
4	3	0	60	60
4	3	1	85	80
4	3	2	164	157
4	3	3	80	77
4	3	4	133	131
4	3	5	10	9*
4	3	6	10	5*
4	3	7	10	13*
4	3	8	102	103
4	3	9	45	45
4	3	10	101	99
4	3	11	55	58
4	3	12	19	19*
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4	4	-14	77	78
4	4	13	35	41
4	4	12	31	36
4	4	11	19	1*
4	4	10	27	31*
4	4	9	41	11
4	4	[illegible]	47	22
4	4	[illegible]	54	51
4	[illegible]	[illegible]	[illegible]	[illegible]
4	[illegible]	[illegible]	[illegible]	[illegible]

H	K	L	FOBS	FCAL
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4	4	-3	16	16*
4	4	-2	75	70
4	4	-1	65	67
4	4	0	115	112
4	4	1	75	70
4	4	2	37	38
4	4	3	32	26
4	4	4	96	93
4	4	5	79	79
4	4	6	115	115
4	4	7	62	64
4	4	8	61	64
4	4	9	14	7*
4	4	10	25	16*
4	4	11	55	54
4	4	12	67	70
4	4	13	39	40
4	4	14	36	45
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4	5	-20	15	17*
4	5	-19	19	14*
4	5	-18	29	36*
4	5	-17	39	35
4	5	-16	30	25*
4	5	-15	19	19*
4	5	-14	14	10*
4	5	-13	14	20*
4	5	-12	40	38
4	5	-11	47	48
4	5	-10	59	63
4	5	-9	45	40
4	5	-8	24	25*
4	5	-7	25	20*
4	5	-6	58	53
4	5	-5	68	66
4	5	-4	78	74
4	5	-3	68	65
4	5	-2	42	33
4	5	-1	30	24*
4	5	0	40	42
4	5	1	42	42
4	5	2	94	92
4	5	3	70	65
4	5	4	46	43
4	[illegible]	5	27	25
4	[illegible]	[illegible]	[illegible]	7*
4	[illegible]	7	[illegible]	27*

H	K	L	FOBS	FCAL
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4	5	9	55	58
4	5	10	62	61
4	5	11	12	25*
4	5	12	22	26*
4	5	13	17	24*
4	5	14	33	22
4	5	15	36	36
4	5	16	42	35
4	5	17	27	27*
4	5	18	18	23*
4	5	19	14	4*
4	6	-19	16	16*
4	6	-18	15	2*
4	6	-17	15	1*
4	6	-16	28	22*
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4	6	-11	14	8*
4	6	-10	23	18*
4	6	-9	50	38
4	6	-8	50	51
4	6	-7	64	61
4	6	-6	31	36
4	6	-5	35	33
4	6	-4	18	9*
4	6	-3	20	33*
4	6	-2	27	36*
4	6	-1	71	71
4	6	0	57	54
4	6	1	34	37
4	6	2	20	17*
4	6	3	13	17*
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4	6	5	21	39*
4	6	6	33	31
4	6	7	31	38
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4	7	-13	15	11*
4	7	-12	15	22*
4	7	11	44	16
4	7	-10	[illegible]	10*
4	7	9	21	27*

H	K	L	FOBS	FCAL
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4	7	-7	14	2*
4	7	-6	35	25
4	7	-5	31	34*
4	7	-4	24	24*
4	7	-3	41	40
4	7	-2	22	17*
4	7	-1	16	1*
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4	7	1	36	41*
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4	7	3	45	49
4	7	4	27	25*
4	7	5	26	22*
4	7	6	13	3*
4	7	7	13	20*
4	7	8	13	19*
4	7	9	32	36
4	7	10	14	23*
4	7	11	15	20*
4	7	12	20	2*
4	7	13	14	3*
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4	8	-3	20	13*
4	8	-2	15	14*
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4	8	0	15	12*
4	8	1	29	21*
4	8	2	22	1*
4	8	3	13	5*
4	8	4	21	8*
4	8	5	40	33
4	8	6	13	14*
4	8	7	37	31
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5	0	-9	118	153
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H	K	L	FOBS	FCAL
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5	0	9	135	134
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5	0	15	37	47
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5	0	19	37	31
5	0	21	21	3*
5	0	23	31	33*
5	1	-25	37	34
5	1	-24	14	6*
5	1	-23	14	8*
5	1	-22	22	0*
5	1	-21	52	49
5	1	-20	18	6*
5	1	-19	63	64
5	1	-18	24	20*
5	1	-17	34	39
5	1	-16	13	11*
5	1	-15	53	54
5	1	-14	17	8*
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5	1	-12	17	11*
5	1	-11	88	95
5	1	-10	12	19*
5	1	-9	30	28
5	1	-8	73	67
5	1	-7	130	132
5	1	-6	51	48
5	1	-5	215	216
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5	1	-3	44	43
5	1	-2	13	18*
5	1	-1	183	175
5	1	0	9	4*
5	1	1	166	163
5	1	2	47	49
5	1	3	108	106
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5	1	7	195	199
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5	1	9	95	95
5	1	10	21	9*
5	1	11	11	5*
5	1	12	13	34
5	1	13	71	89
5	1	14	11	17*
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5	1	17	1[illegible]	1[illegible]*
5	1	18	1[illegible]	1[illegible]

H	K	L	FOBS	FCAL
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5	1	20	17	7*
5	1	21	53	45
5	1	2	14	4*
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5	2	4	14	11*
5	2	[illegible]	60	51
5		22	0	11*
5	[illegible]	[illegible]	41	4[illegible]
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5	2	18	20	13*
5	2	17	58	54
5	2	16	25	33*
5	2	-15	55	58
5	2	14	13	5*
5	2	-13	24	13*
5	2	-12	13	17*
5	2	11	78	79
5	2	-10	28	24
5	2	-9	129	135
5	2	-8	44	45
5	2	-7	79	83
5	2	6	20	17*
5	2	5	103	105
5	2	-4	51	52
5	2	3	155	[illegible]
5	2		87	[illegible]
5	2	1	105	[illegible]
5	2	0	48	44
5	2	1	27	21
5	2	2	71	58
5	2	3	164	166
5	2	4	41	43
5	2	5	121	110
5	2	6	7	5*
5	[illegible]		10	1*
5	2	8	10	[illegible]
5	2	9	67	71
5	2	10	34	32
5	2	11	5	9[illegible]
5	2	12	13	1*
5	2	13	65	61
5	2	14	11	11*
5	2	15	31	37
5	2	16	13	15*
5	2	17	77	80
5	2	18	11	29
5	2	19	32	4
5	2	20	13	5*
5	2	21	13	1*
5	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

H	K	L	FOBS	FCAL
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5	3	20	14	[illegible]*
5	3	19	59	[illegible]
5	3	18	28	24*
5	3	17	32	15
5	3	16	18	11*
5	3	15	29	[illegible]
5	3	14	34	31
5	3	13	101	[illegible]
5	3	12	54	[illegible]
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5	3	10	59	55
5	3	-9	44	34
5	3	8	13	11*
5	3	-7	115	121
5	3	-6	47	54
5	3	-5	111	109
5	3	-4	33	30
5	3	3	21	11*
5	3	-2	11	15*
5	3	-1	103	99
5	3	0	72	73
5	3	1	147	143
5	3	2	55	55
5	3	3	93	90
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5	3	5	41	42
5	3	6	55	53
5	3	7	117	116
5	3	8	61	60
5	3	9	78	[illegible]
5	3	10	31	30
5	3	11	14	19*
5	3	12	12	1*
5	3	13	75	[illegible]
5	3	14	12	21*
5	3	15	58	58
5	3	16	16	1*
5	3	17	28	8
5	3	18	11	[illegible]*
5	3	19	13	[illegible]3*
5	3	20	10	[illegible]
5	3	21	35	18
5	4	-23	15	1*
5	4	-22	25	1*
5	4	-21	19	17*
5	4	20	15	1*
5	4	19	14	1[illegible]*
5	4	-19	17	1*
5	4	17	41	[illegible]7
5	4	15	[illegible]	13
[illegible]	4	1[illegible]	51	[illegible]
[illegible]	[illegible]	1[illegible]	11	*
[illegible]	4	11	11	*
[illegible]	[illegible]	1[illegible]	14	1*

H	K	L	FOBS	FCAL
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5	4	-9	106	105
5	4	8	52	54
5	4	-7	49	4
5	4	6	14	8*
5	4	5	47	[illegible]
5	4	4	[illegible]	11*
5	4	3	38	[illegible]
5	4	-2	54	[illegible]
5	4	-1	59	[illegible]3
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5	4	5	95	95
5	4	6	44	42
5	4	7	32	25
5	4	8	18	17*
5	4	9	53	53
5	4	10	62	70
5	4	11	91	87
5	4	12	31	36
5	4	13	38	32
5	4	14	21	11*
5	4	15	24	19*
5	4	16	25	20*
5	4	17	29	3[illegible]*
5	4	18	27	2[illegible]*
5	4	19	14	22*
5	4	20	14	1*
5	5	-21	25	20*
5	5	-20	31	22*
5	5	-19	14	30
5	5	18	[illegible]7	31*
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5	5	-16	15	7*
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5	5	12	41	40
5	5	-11	48	38
5	5	-10	14	14*
5	5	-9	14	4*
5	5	8	41	4[illegible]
5	5	-7	58	68
5	5	-6	71	71
5	5	5	70	67
5	5	-4	42	35
5	5	-3	27	11*
5	[illegible]	[illegible]	14	14*
[illegible]	[illegible]	1	5	7
[illegible]	5	0	1	[illegible]
[illegible]	[illegible]	1	17	[illegible]

H	K	L	FOBS	FCAL
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5	5	5	[illegible]9	1*
5	5	6	[illegible]	1
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5	5	8	41	[illegible]
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5	5	13	8	15*
5	5	14	39	40
5	5	15	35	14
5	5	16	19	16*
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5	6	-18	32	1[illegible]*
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5	6	15	24	1[illegible]*
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5	6	[illegible]1	18	*
5	6	10	5[illegible]	1*
5	6	9	15	17
5	6	8	4[illegible]	4[illegible]
5	6	7	[illegible]	11*
5	6	6	15	1*
5	6	5	19	30*
5	6	4	5[illegible]	51
5	6	3	51	51
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5	6	0	11	11*
5	6	1	2	1*
5	6	[illegible]	44	17
5	6	3	[illegible]	4[illegible]
5	6	4	[illegible]1	11
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5	6	6	22	*
5	6	7	12	*
5	6	8	12	1*
5	6	9	15	*
5	6	10	30	32
5	6	11	17	34*
5	6	12	31	5
5	6	13	25	11*
5	6	14	11	14
5	6	15	14	18
[illegible]	[illegible]	15	1[illegible]	1*
5	[illegible]	16	57	5
[illegible]	[illegible]	11	[illegible]	17*
[illegible]	[illegible]	1	[illegible]	14*

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6	0	10	141	143
6	0	12	31	31
6	0	14	91	90
6	0	16	80	77
6	0	18	18	15*
6	0	20	13	18*
6	0	22	24	34*
6	1	-25	15	2*
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6	1	-22	50	50
6	1	-21	14	11*
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6	1	-19	18	25*
6	1	-18	13	3*
6	1	-17	17	4*
6	1	-16	71	67
6	1	-15	13	19*
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6	1	-13	18	11*
6	1	-12	37	41
6	1	-11	12	0*
6	1	-10	69	71
6	1	-9	31	36
6	1	-8	142	142
6	1	-7	18	6*
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6	1	-5	26	26
6	1	-4	65	63
6	1	-3	20	14*
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6	1	-1	54	51
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6	1	4	150	148
6	1	5	11	5*
6	1	6	164	154
6	1	7	33	32
6	1	8	37	42
6	1	9	25	15
6	1	10	54	54
6	1	11	17	27*
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6	1	13	11	5*
6	1	14	73	73
6	1	15	12	15*
6	1	16	21	21*
6	1	17	12	14*
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[illegible]	1	17	[illegible]	11*
[illegible]	1	[illegible]	[illegible]	[illegible]

H	K	L	FOBS	FCAL
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6	1	22	19	10*
6	2	-25	15	11*
6	2	-24	53	41
6	2	-23	25	11*
6	2	-22	35	16
6	2	-21	14	6*
6	2	-20	39	39
6	2	-19	23	20*
6	2	-18	67	67
6	2	-17	13	17*
6	2	-16	46	51
6	2	-15	14	2*
6	2	-14	18	24*
6	2	-13	13	4*
6	2	-12	91	88
6	2	-11	29	31
6	2	-10	78	81
6	2	-9	34	30
6	2	-8	17	7*
6	2	-7	30	30
6	2	-6	129	125
6	2	-5	49	47
6	2	-4	206	198
6	2	-3	64	58
6	2	-2	100	96
6	2	-1	10	15*
6	2	0	108	106
6	2	1	56	63
6	2	2	182	174
6	2	3	36	34
6	2	4	109	107
6	2	5	15	13*
6	2	6	41	39
6	2	7	15	11*
6	2	8	88	87
6	2	9	31	39
6	2	10	55	56
6	2	11	11	8*
6	2	12	12	12*
6	2	13	12	14*
6	2	14	54	57
6	2	15	12	13*
6	2	16	69	71
6	2	17	23	21*
6	2	18	30	30
6	2	19	13	1*
6	2	20	26	21*
6	2	21	14	15*
6	3	-2[illegible]	22	15*
6	3	-23	1[illegible]	[illegible]*
6	3	-22	[illegible]	35
[illegible]	[illegible]	21	[illegible]	11*
[illegible]	1	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	1[illegible]	1[illegible]	11[illegible]

H	K	L	FOBS	FCAL
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6	3	-17	24	25*
6	3	-16	64	54
6	3	-15	29	34*
6	3	-14	79	78
6	3	-13	24	31*
6	3	-12	23	25*
6	3	-11	39	29
6	3	-10	59	67
6	3	-9	18	18
6	3	-8	113	113
6	3	-7	59	58
6	3	-6	73	70
6	3	-5	33	29
6	3	-4	43	49
6	3	-3	16	12*
6	3	-2	126	121
6	3	-1	83	79
6	3	0	113	111
6	3	1	10	8*
6	3	2	32	27
6	3	3	75	71
6	3	4	86	86
6	3	5	55	61
6	3	6	121	118
6	3	7	47	43
6	3	8	47	47
6	3	9	11	3*
6	3	10	49	48
6	3	11	33	40
6	3	12	80	84
6	3	13	18	26*
6	3	14	46	43
6	3	15	12	11*
6	3	16	25	13*
6	3	17	13	6*
6	3	18	42	39
6	3	17	25	25*
6	3	20	37	34
6	4	-22	15	4*
6	4	21	17	8*
6	4	-20	35	21
6	4	-19	13	17*
6	4	-13	46	44
6	4	-17	41	35
6	4	-16	27	27*
6	4	-15	14	14*
6	4	-14	14	21*
6	4	-13	27	29*
6	4	12	70	77
6	4	-11	61	64
6	4	-10	14	34
5	4	[illegible]	11	15
5	4	[illegible]	11	*
[illegible]	[illegible]	[illegible]	[illegible]	11*

H	K	L	FOBS	FCAL
6	4	-6	69	66
6	4	-5	59	53
6	4	-4	57	56
6	4	-3	47	40
6	4	-2	27	23*
6	4	-1	12	9*
6	4	0	53	51
6	4	1	43	4[illegible]
6	4	2	102	99
6	4	3	49	44
6	4	4	55	51
6	4	5	11	21*
6	4	6	18	15*
6	4	7	26	31
6	4	8	81	81
6	4	9	66	69
6	4	10	86	83
6	4	11	15	20*
6	4	12	12	7*
6	4	13	29	24
6	4	14	37	38
6	4	15	17	30*
6	4	16	37	36
6	4	17	21	19*
6	4	18	14	15*
6	4	19	14	5*
6	5	-20	15	17*
6	5	-19	15	22*
6	5	-18	21	8*
6	5	-17	24	3*
6	5	-16	33	33
6	5	-15	27	29*
6	5	-14	37	30
6	5	-13	37	33
6	5	-12	21	14*
6	5	-11	14	1*
6	5	-10	14	29*
6	5	-9	52	51
6	5	-8	23	70
6	5	-7	50	47
6	5	-6	36	45
6	5	-5	15	11*
6	5	-4	15	4*
6	5	-3	44	38
6	5	2	58	63
6	5	1	75	73
6	5	0	67	56
6	5	1	39	43
6	5	2	11	8*
6	5	3	12	7*
6	5	4	25	54
6	5	5	17	11
[illegible]	[illegible]		1[illegible]	14
[illegible]	[illegible]		11	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	1[illegible]

PAGE [illegible]

H	K	L	FOBS	FCAL
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6	5	10	21	25*
6	5	11	44	41
6	5	12	45	44
6	5	13	29	31*
6	5	14	31	28
6	5	15	17	4*
6	5	16	14	5*
6	5	17	[illegible]	[illegible]*
6	6	-18	34	24*
6	6	17	15	25*
6	6	16	15	9*
6	6	15	15	10*
6	6	14	17	11*
6	6	13	15	17*
6	6	-12	36	26
6	6	-11	43	34
6	6	10	29	24*
6	6	9	26	26*
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6	6	1	14	9*
6	6	0	30	3*
6	6	1	48	57
6	6	2	56	48
6	6	3	53	53
6	6	4	12	24*
6	6	5	23	1[illegible]*
6	6	6	1	2*
6	6	7	20	20
6	6	8	1[illegible]	2[illegible]*
6	6	9	[illegible]	1[illegible]*
6	6	10	13	2[illegible]*
6	6	11	1*	13*
6	6	12	13	[illegible]*
6	6	13	14	7*
6	6	14	14	15*
6	7	-14	15	15*
6	7	13	39	24
6	7	-12	15	3*
6	7	11	15	1*
6	7	10	[illegible]1	1[illegible]*
6	7	[illegible]	20	[illegible]*
6	7	8	15	[illegible]*
6	7	7	[illegible]	31*
6	7	[illegible]	15	3*
[illegible]	7	5	[illegible]	11*
[illegible]	[illegible]	1		1[illegible]*
[illegible]	7	1	[illegible]	*
[illegible]	7		[illegible]	*

H	K	L	FOBS	FCAL
6		1	41	37
6			1	0*
6	[illegible]	1	4	19*
6	7		11	3*
6	[illegible]	1	4	12*
6	7	4	11	14*
6	[illegible]	[illegible]	4	
6	7		5	[illegible]4*
6		[illegible]	34	9
6	7	1	11	16*
6		7	11	3*
6	[illegible]	10	14	7*
6	7	11	18	[illegible]4*
6	8	7	17	10*
6	8	6	17	10*
6	8	5	17	8*
6	8	4	17	11*
6	8	3	17	20*
6	8	2	19	*
6	8	1	17	*
6	8	0	17	11*
6	8	1	15	10*
6	8	2	1	11*
6	8	3	5	25*
6	8	4	14	4*
7	0	5	15	7*
7	0	1	14	[illegible]*
7	[illegible]	1	7	13*
7	0	17	13	16
7	0	1[illegible]	4	15*
7	0	15	3	56
7	0	13	13[illegible]	145
7	0	11	[illegible]	31
7	0	7	6[illegible]	58
7	0	7	175	17[illegible]
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7	0	3	15	[illegible]1*
7	0	1	1[illegible]1	110
7	0	1	1[illegible]7	105
7	0	3	48	17
7	0	5	114	113
7	0	7	[illegible]	1[illegible]9
7	0	7	87	70
7	0	11	[illegible]1	[illegible]5*
7	0	13	173	104
7	0	1[illegible]	65	70
7	0	17	12	7*
7	0	1[illegible]	[illegible]3	15*
7	0	1	31	33
7	1	5	25	0*
7	1	4	14	1*
7	1	1	7	15
7	1		14	7*
7	1	1		*
	1		1	1*

H	K	L	FOBS	FCAL
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7	1	18	11	1*
7	1	17	[illegible]4	72
7	1	16	11	16*
7	1	15	70	81
7	1	14	35	34
7	1	13	24	17*
7	1	12	13	11*
7	1	11	91	87
7	1	10	17	8*
7	1	9	116	11[illegible]
7	1	8	14	16*
7	1	7	60	61
7	1	-6	53	56
7	1	5	119	120
7	1	-4	30	24
7	1	-3	172	171
7	1	-2	12	15*
7	1	-1	87	87
7	1	0	10	5*
7	1	1	24	33
7	1	2	10	3*
7	1	3	149	151
7	1	4	20	20*
7	1	5	132	132
7	1	6	39	41
7	1	7	11	17*
7	1	8	14	6*
7	1	9	82	81
7	1	10	18	24*
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7	1	15	47	54
7	1	16	20	15*
7	1	17	65	67
7	1	18	13	17*
7	1	19	46	33
7	1	20	14	3*
7	2	24	15	[illegible]*
7	2	23	14	5*
7	2	22	13	1*
7	2	21	53	48
7	2	20	25	21*
7	2	-19	59	61
7	2	-18	14	16*
7	2	-17	30	21
7	2	-16	13	7*
7	2	15	11	17
7	2	-14	21	17*
7	2	13	12	34
7	2	12	[illegible]	[illegible]*
7	2	11	12	41
7	2	1[illegible]	3	1[illegible]*

H	K	L	FOBS	FCAL
7	2	9	35	35
7	2	8	23	5*
7	2	7	102	104
7	2	6	45	36
7	2	5	119	119
7	2	-4	37	34
7	2	3	21	6*
7	2	-2	11	3*
7	2	1	15[illegible]	14
7	2	0	[illegible]5	5[illegible]
7	2	1	1[illegible]3	1[illegible]
7	2	2	22	15*
7	2	3	50	53
7	2	4	22	13*
7	2	5	88	87
7	2	6	23	28*
7	2	7	101	100
7	2	8	43	41
7	2	9	51	48
7	2	10	11	4*
7	2	11	35	28
7	2	12	13	15*
7	2	13	71	57
7	2	14	18	12*
7	2	15	51	50
7	2	16	19	11*
7	2	17	17	3*
7	2	18	13	6*
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7	3	-22	15	17*
7	3	-21	17	19*
7	3	-20	14	5*
7	3	19	14	15*
7	3	-18	37	27
7	3	-17	54	57
7	3	16	20	1*
7	3	-15	47	57
7	3	-14	14	10*
7	3	-13	13	7*
7	3	-12	23	11*
7	3	-11	73	77
7	3	-10	62	58
7	3	-9	99	99
7	3	-8	36	41
7	3	-7	15	15*
7	3	-6	13	8*
7	3	5	90	79
7	3	-4	33	3
7	3	-3	95	97
7	3	-2	[illegible]1	55
7	3	1	5	5
7	3	[illegible]	11	7*
7	3	1	[illegible]8	[illegible]9

H	K	L	FOBS	FCAL
7	3	2	57	57
7	3	3	115	113
7	3	4	42	41
7	3	5	96	97
7	3	6	15	15*
7	3	7	15	8*
7	3	8	72	24*
	3	9	69	71
	3	10	40	51
7	3	11	84	83
7	3	12	12	1[illegible]*
7	3	13	12	20*
7	3	14	15	3*
7	3	15	38	34
7	3	16	22	14*
7	3	17	44	43
7	3	18	33	22
7	3	19	23	21*
7	4	-22	15	1*
7	4	-21	22	2[illegible]*
7	4	-20	20	19*
7	4	-19	43	30
7	4	-18	22	23*
7		-17	14	2*
7	4	-16	21	1*
7	4	-15	31	36*
7	4	-14	28	27*
7	4	13	65	55
7	4	-12	47	46
7	4	11	29	45*
7	4	-10	19	1[illegible]*
7	4	-9	29	32*
7	4	8	55	50
7	4	-7	84	85
7	4	-6	61	52
7	4	-5	72	67
7	4	-4	25	23*
7	4	-3	13	1*
7	4	-2	13	11*
7	4	-1	78	75
7	4	0	55	53
7	4	1	74	75
7	4	2	33	33
7	4	3	18	11*
7	4	4	17	2*
7	4	5	36	30
7	4	6	36	41
7	4	7	75	75
7	4	8	18	51
7	4	9	50	53
7	4	10	12	1*
7	4	11	12	10*
	4	12	31	31
7	4	13	[illegible]1	[illegible]
7	4	14	[illegible]5	33

H	K	L	FOBS	FCAL
7	4	15	24	36*
7	4	16	11	14*
7	4	17	14	5*
7	4	18	15	14*
7	5	-20	16	9*
7	5	-19	29	17*
7	5	-18	15	13*
7	5	17	15	32*
7	5	-16	37	30
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7	5	-9	52	51
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7	5	16	27	5*
7	6	-17	15	1*
7	6	16	15	3*
7	6	-15	27	15*
	5	14	31	25*
7	6	-13	25	23*
7	6	-12	20	27*
7	6	-11	15	11*
7	6	-10	28	11*
7	6	-9	2[illegible]	21*
7	6	8	15	17
7	6	-7	11	1[illegible]
7	5	5	1[illegible]	1[illegible]
7	[illegible]	5	11	[illegible]
7	6	1	[illegible]	*

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H	K	L	FOBS	FCAL
7	6	3	15	1*
7	6	-2	30	27*
7	6	1	40	39
7	6	0	60	57
7	6	1	45	44
7	6	2	38	39
7	6	3	12	13*
7	6	4	12	6*
7	6	5	21	14*
7	6	6	33	40
7	6	7	33	31
7	6	8	14	27*
7	6	9	22	17*
7	6	10	13	2*
7	6	11	13	12*
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7	7	-6	27	2*
7	7	-5	33	20*
7	7	4	29	29*
7	7	3	18	[illegible]0*
7	7	[illegible]	33	31*
7	7	1	15	9*
7	7	0	14	4*
7	7	1	14	10*
7	7	[illegible]	19	24*
7	7	3	20	17*
7	7	4	40	37
7	7	5	13	20*
7	7	6	24	15*
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8	0	20	17	27*
8	0	18	[illegible]0	5*
8	0	16	72	77
8	0	14	90	93
8	0	12	11	5*
8	0	10	85	83
8		1	111	1[illegible]4
8		5	1	1

H	K	L	FOBS	FCAL
8	0	-4	70	65
8	0	2	122	121
8	0	0	79	78
8	0	2	17	17*
8	0	4	110	111
8	0	6	100	105
8	0	8	24	26*
8	0	10	59	55
8	0	12	99	103
8	0	14	53	52
8	0	16	26	32*
8	0	18	49	46
8	0	20	39	32
8	1	24	30	33*
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8	1	-15	24	24*
8	1	-14	53	46
8	1	-13	13	8*
8	1	-12	94	94
8	1	-11	13	18*
8	1	10	79	80
8	1	-9	13	5*
8	1	-8	23	12*
8	1	-7	30	30
8	1	-6	136	136
8	1	-5	27	22
8	1	-4	139	139
8	1	-3	20	2*
8	1	-2	36	35
8	1	-1	22	29*
8	1	0	79	78
8	1	1	35	30
8	1	2	156	162
8	1	3	11	10*
8	1	4	72	72
8	1	5	23	23*
8	1	6	70	75
8	1	7	22	14*
8	1	8	93	95
8	1	9	32	20
8	1	10	71	75
8	1	11	11	6*
8	1	12	11	8*
8	1	13	20	3*
8	1	14	63	57
8	1	15	12	11*
8	1	1[illegible]	[illegible]	1
	1	1[illegible]	1	1*

H	K	L	FOBS	FCAL
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8	1	19	13	9*
8	2	-24	15	17*
8	2	-23	15	5*
8	2	-22	42	44
8	2	-21	23	16*
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8	2	-19	14	6*
8	2	-18	14	6*
8	2	-17	14	15*
8	2	-16	63	64
8	2	-15	13	19*
8	2	-14	73	74
8	2	-13	13	28*
8	2	-12	14	6*
8	2	-11	26	7*
8	2	-10	44	53
8	2	-9	25	35*
8	2	-8	86	88
8	2	-7	28	16*
8	2	-6	49	47
8	2	-5	12	10*
8	2	-4	68	70
8	2	-3	25	16*
8	2	-2	138	135
8	2	-1	51	52
8	2	0	110	112
8	2	1	11	5*
8	2	2	19	6*
8	2	3	26	30
8	2	4	110	114
8	2	5	46	44
8	2	6	116	119
8	2	7	32	33
8	2	8	11	22*
8	2	9	11	7*
8	2	10	44	53
8	2	11	18	24*
8	2	12	66	69
8	2	13	12	6*
8	2	14	26	26*
8	2	15	12	4*
8	2	16	12	21*
8	2	17	13	12*
8	2	18	48	41
8	2	19	14	15*
8	3	-23	28	1[illegible]*
8	3	22	17	2*
8	3	21	14	4*
8	3	-20	20	29*
8	3	-19	25	22*
8	3	18	47	49
8	3	17	17	1*
8	3	15	11	5*
8	3	1[illegible]	1	3*

H	K	L	FOBS	FCAL
8	3	-14	18	25*
8	3	-13	31	31
8	3	-12	80	78
8	3	-11	45	41
8	3	-10	73	71
8	3	-9	28	13*
8	3	-8	22	13*
8	3	-7	13	8*
8	3	-6	92	90
8	3	-5	37	38
8	3	-4	77	84
8	3	-3	65	67
8	3	-2	16	6*
8	3	-1	12	16*
8	3	0	82	79
8	3	1	42	45
8	3	2	105	103
8	3	3	12	23*
8	3	4	44	45
8	3	5	22	2*
8	3	6	12	27*
8	3	7	46	46
8	3	8	70	77
8	3	9	37	40
8	3	10	63	65
8	3	11	12	3*
8	3	12	12	3*
8	3	13	12	12*
8	3	14	48	47
8	3	15	25	20*
8	3	16	39	39
8	3	17	20	19*
8	3	18	17	6*
8	4	-21	15	19*
8	4	-20	23	17*
8	4	-19	17	12*
8	4	-18	23	9*
8	4	-17	14	10*
8	4	-16	37	37
8	4	-15	28	25*
8	4	-14	38	34
8	4	-13	30	33*
8	4	-12	14	8*
8	4	-11	14	7*
8	4	-10	56	60
8	4	-9	55	57
8	4	-8	86	86
8	4	-7	41	44
8	4	-6	36	39
8	4	-5	14	6*
8	4	-4	[illegible]5	20*
8	4	-3	17	43
8	4	[illegible]	79	[illegible]5
8	4	1	58	51
8	4	0	17	30

H	K	L	FOBS	FCAL
8	4	1	14	12*
8	4	2	12	15*
8	4	3	12	18*
8	4	4	45	48
8	4	5	38	37
8	4	6	53	53
8	4	7	38	33
8	4	8	18	16*
8	4	9	12	14*
8	4	10	45	43
8	4	11	34	38
8	4	12	50	55
8	4	13	33	26
8	4	14	30	29
8	4	15	13	2*
8	4	16	13	7*
8	5	-19	22	19*
8	5	-18	26	26*
8	5	-17	15	25*
8	5	-16	15	2*
8	5	-15	15	12*
8	5	-14	15	21*
8	5	-13	14	18*
8	5	-12	37	38
8	5	-11	30	37*
8	5	-10	15	28*
8	5	-9	15	17*
8	5	-8	15	12*
8	5	-7	22	24*
8	5	-6	46	41
8	5	-5	50	47
8	5	-4	55	50
8	5	-3	26	30*
8	5	-2	13	24*
8	5	-1	34	25
8	5	0	38	42
8	5	1	58	51
8	5	2	50	59
8	5	3	42	42
8	5	4	21	21*
8	5	5	12	14*
8	5	6	27	21*
8	5	7	30	27
8	5	8	47	45
8	5	9	27	34*
8	5	10	32	25
8	5	11	11	10*
8	5	12	11	5*
8	5	13	11	14*
8	5	14	13	18*
8	6	-16	20	20*
8	6	-15	17	25*
8	6	-14	12	10*
8	6	-11	24	[illegible]1*
8	6	-12	1[illegible]	0*

H	K	L	FOBS	FCAL
8	6	11	15	34*
8	6	10	15	24*
8	6	9	[illegible]	28*
8	6	8	19	24*
8	6	7	19	32*
8	6	6	15	4*
8	6	5	15	7*
8	6	4	30	19*
8	6	3	22	3*
8	6	2	37	43
8	6	1	41	47
8	6	0	23	30*
8	6	1	20	20*
8	6	2	13	4*
8	6	3	25	24*
8	6	4	26	26*
8	6	5	49	44
8	6	6	31	33
8	6	7	13	23*
8	6	8	13	9*
8	6	9	23	11*
8	6	10	27	18*
8	6	11	32	24
8	7	-11	24	28*
8	7	-10	16	12*
8	7	-9	24	15*
8	7	-8	31	8*
8	7	-7	15	12*
8	7	-6	34	23*
8	7	-5	30	32*
8	7	-4	22	15*
8	7	-3	15	21*
8	7	-2	15	4*
8	7	-1	15	5*
8	7	0	27	13*
8	7	1	24	26*
8	7	2	14	15*
8	7	3	25	3*
8	7	4	13	17*
8	7	5	23	1*
8	7	6	[illegible]	[illegible]
8	7	7	14	26*
9	0	-19	13	14*
9	0	-17	25	30
9	0	-15	41	23
9	0	-13	13	25*
9	0	-11	35	21
9	0	-9	114	117
9	0	-7	24	21*
9	0	-5	123	123
9	0	-3	[illegible]	[illegible]
9	0	-1	17	12
9	0	1	[illegible]	[illegible]
9	[illegible]	[illegible]	[illegible]	[illegible]
9	[illegible]	[illegible]	[illegible]	[illegible]

H	K	L	FOBS	FCAL
9	0	7	26	25
9	0	9	76	77
9	0	11	85	90
9	0	13	19	10*
9	0	15	52	51
9	0	17	55	52
9	1	20	14	7*
9	1	19	47	45
9	1	18	14	4*
9	1	17	13	4*
9	1	16	13	[illegible]
9	1	15	52	62
9	1	-14	19	6*
9	1	13	78	78
9	1	12	28	27*
9	1	11	23	30*
9	1	-10	14	13*
9	1	-9	48	52
9	1	-8	26	13*
9	1	-7	125	125
9	1	-6	18	19*
9	1	-5	80	84
9	1	-4	18	6*
9	1	3	24	24*
9	1	2	34	37
9	1	-1	101	101
9	1	0	19	22*
9	1	1	118	119
9	1	2	11	7*
9	1	3	11	3*
9	1	4	13	13*
9	1	5	81	85
9	1	6	12	8*
9	1	7	87	71
9	1	8	12	2*
9	1	9	15	41
9	1	10	13	13*
9	[illegible]	11	11	1
9	1	12	12	1*
9	1	13	74	71
9	1	14	12	11*
9	1	15	32	30
9	1	16	13	3*
9	1	17	13	7*
9	1	18	15	1*
9	2	-20	11	1*
9	2	-19	27	27*
9	2	18	14	20*
9	2	-17	72	73
9	2	16	76	17*
9	2	15	17	15
[illegible]	2	14	11	11*
[illegible]	[illegible]	13	[illegible]	*
[illegible]	[illegible]	1	[illegible]	4*
9	[illegible]	11	3	[illegible]

H	K	L	FOBS	FCAL
9	2	-10	33	24
9	2	-9	72	68
9	2	-8	13	7*
9	2	7	15	9*
9	2	6	13	5*
9	2	5	82	79
9	2	4	23	27*
9	2	3	119	111
9	2	[illegible]	17	11
9	2	1	47	1
9	2	0	17	9*
9	2	1	51	57
9	2	2	43	40
9	2	3	135	137
9	2	4	26	27*
9	2	5	80	81
9	2	6	12	17*
9	2	7	17	19*
9	2	8	23	20*
9	2	9	64	68
9	2	10	23	20*
9	2	11	53	58
9	2	12	12	2*
9	2	13	18	7*
9	2	14	11	2*
9	2	15	35	34
9	2	16	17	15*
9	2	17	43	38
9	3	-20	23	12*
9	3	19	33	9*
9	3	-18	14	12*
9	3	-17	14	3*
9	3	-16	14	7*
9	3	15	38	39
9	3	14	25	25*
9	3	13	71	68
9	3	-12	17	3*
9	3	11	34	31
9	3	10	21	7*
9	3	-9	48	14
9	3	-8	37	35
9	3	7	49	33
9	3	-6	43	37
9	3	5	44	43
9	3	-4	14	43
9	3	-3	27	8
9	3	2	15	10*
9	3	1	46	87
9	3	0	41	37
9	3	1	74	5
9	3	2	17	1*
9	3	3	5	*
9	[illegible]	[illegible]	1	11*
9	[illegible]	5	15	1
9	3	5	11	11

H	K	L	FOBS	FCAL
9	3	7	69	71
9	3	8	11	7*
9	3	9	33	40
9	3	10	24	19*
9	3	11	21	4*
9	3	12	24	15*
9	3	13	54	*
9	3	14	[illegible]	17*
9	3	15	38	31
9	3	16	14	11*
9	4	20	15	1*
9	4	19	15	15*
9	4	18	17	13*
9	4	17	31	30*
9	4	16	27	[illegible]
9	4	15	14	10*
9	4	14	10	19*
9	4	-13	14	15*
9	4	12	15	10*
9	4	11	54	59
9	4	10	49	46
9	4	-9	62	[illegible]
9	4	-8	17	22*
9	4	7	14	10*
9	4	-6	14	17*
9	4	5	47	50
9	4	4	49	45
9	4	3	64	71
9	4	[illegible]	41	41
9	4	1	26	5*
9	4	0	15	2*
9	4	1	32	33
9	4	[illegible]	38	[illegible]
9	4	3	51	50
9	4	4	38	31
9	4	5	40	37
9	4	6	17	11*
9	4	7	15	5*
9	4	8	12	21*
9	4	9	53	55
9	4	10	23	17*
9	4	11	37	14
9	4	12	23	1*
9	4	13	21	11*
9	4	14	13	7*
9	4	15	20	21*
9	5	11	15	17*
9	5	-17	15	1*
9	5	-15	15	1*
9	5	15	8	25*
9	[illegible]	14	11	27
9	[illegible]	13	71	1*
9	[illegible]	17	15	57
9	[illegible]	11	11	*
9	[illegible]	10	15	7*

H	K	L	FOBS	FCAL
9	5	9	15	17*
9	5	8	19	7*
9	5	7	19	19
9	5	6	19	40
9	5	5	17	10
9	5	4	17	9*
9	5	1	14	14*
9	[illegible]	[illegible]	11	17
[illegible]	[illegible]	1	[illegible]	[illegible]
9	5	0	[illegible]	42
9	[illegible]	1	45	10
9	[illegible]	[illegible]	3	0*
9	5	1	19	9*
9	5	4	10	*
9	5	5	11	17
9	5	6	6	16*
9	5	7	4	41
9	5	8	18	28*
9	5	9	13	10*
9	5	10	13	*
9	5	11	[illegible]	0*
9	5	12	16	10*
9	5	13	14	1
9	6	15	15	11*
9	6	14	1	7*
9	6	13	6	7*
9	6	12	15	1*
9	6	11	15	4*
9	6	10	4	11*
9	6	9	15	15*
9	6	8	17	10*
9	6	7	15	5*
9	6	6	15	4*
9	6	[illegible]	30	4
9	6	4	15	1
9	6	3	55	5
9	6	[illegible]	13	[illegible]
9	6	1	17	7*
9	6	[illegible]	13	1*
9	6	1	3	*
9	6	[illegible]	41	15
9	6	1	7	11*
9	6	4	41	19
9	6	5	[illegible]	[illegible]
9	6	6	[illegible]	7*
9	6	7	13	1*
9	6	8	11	[illegible]
9	[illegible]	7	1	*
9	7	7	[illegible]	1*
9	7	8	[illegible]	*
9	7	[illegible]	1	17*
9	[illegible]	5	[illegible]	*
[illegible]	[illegible]	[illegible]	1	1*
9	[illegible]	1	1	11*
9	[illegible]	1	1	1*

H	K	L	FOBS	FCAL
9	7	-2	31	15*
9	7	-1	15	17*
9	7	0	39	26
9	7	1	23	7*
9	7	2	22	17*
9	7	3	14	2*
9	7	4	18	9*
10	0	-20	28	27*
10	0	-18	52	48
10	0	-16	14	13*
10	0	-14	49	41
10	0	-12	66	68
10	0	-10	59	59
10	0	-8	38	38
10	0	-6	141	141
10	0	-4	99	100
10	0	-2	16	2*
10	0	0	72	75
10	0	2	106	106
10	0	4	12	19*
10	0	6	44	48
10	0	8	63	72
10	0	10	54	54
10	0	12	12	22*
10	0	14	65	64
10	0	16	42	46
10	1	-20	25	23*
10	1	-19	14	3*
10	1	-18	14	14*
10	1	-17	14	9*
10	1	-16	65	61
10	1	-15	27	12*
10	1	-14	58	56
10	1	-13	22	21*
10	1	-12	13	2*
10	1	-11	23	10*
10	1	-10	[illegible]	70
10	1	-9	13	3*
10	1	-8	99	97
10	1	-7	14	12*
10	1	-6	23	23*
10	1	-5	13	5*
10	1	-4	25	54
10	1	-3	31	21
10	1	-2	109	[illegible]
10	1	-1	13	1*
10	1	0	[illegible]	75
10	1	1	17	15*
10	1	2	23	31*
10	1	3	11	20*
10	1	4	[illegible]	13[illegible]
10	1	5	[illegible]	17*
10	1	6	[illegible]	[illegible]
10	1	[illegible]	[illegible]	1*
10	1	[illegible]	[illegible]	*

H	K	L	FOBS	FCAL
10	1	9	12	4*
10	1	10	51	57
10	1	11	12	4*
10	1	12	63	67
10	1	13	13	7*
10	1	14	13	14*
10	1	15	13	2*
10	1	16	19	23*
10	1	17	14	11*
10	2	-20	34	35
10	2	-19	25	14*
10	2	-18	58	53
10	2	-17	15	12*
10	2	-16	28	13*
10	2	-15	14	6*
10	2	-14	40	44
10	2	-13	14	19*
10	2	-12	72	71
10	2	-11	32	23
10	2	-10	40	44
10	2	-9	13	1*
10	2	-8	34	20
10	2	-7	23	13*
10	2	-6	83	80
10	2	-5	13	23*
10	2	-4	56	58
10	2	-3	36	29
10	2	-2	21	3*
10	2	-1	18	11*
10	2	0	79	75
10	2	1	30	27
10	2	2	105	104
10	2	3	12	21*
10	2	4	32	32
10	2	5	15	5*
10	2	6	45	17
10	2	7	33	31
10	2	8	75	76
10	2	9	12	17*
10	2	10	40	41
10	2	11	19	3*
10	2	12	20	15*
10	2	13	13	9*
10	2	14	42	41
10	2	15	13	11*
10	2	16	38	30
10	3	-20	15	14*
10	3	-19	25	7*
10	3	-18	21	1*
10	3	-17	11	7*
10	3	-16	45	15
10	[illegible]	15	11	*
10	[illegible]	14	1	[illegible]
10	[illegible]	1	1	1*
10	[illegible]	1	11	*

H	K	L	FOBS	FCAL
10	3	-11	33	26
10	3	-10	53	55
10	3	-9	35	35
10	3	-8	68	67
10	3	-7	14	25*
10	3	-6	15	26*
10	3	-5	18	7*
10	3	-4	44	15
10	3	-3	31	29
10	3	-2	85	87
10	3	-1	19	32*
10	3	0	42	42
10	3	1	12	12*
10	3	2	29	28
10	3	3	19	14*
10	3	4	63	63
10	3	5	33	36
10	3	6	55	55
10	3	7	12	17*
10	3	8	12	8*
10	3	9	26	25*
10	3	10	40	44
10	3	11	25	24*
10	3	12	41	49
10	3	13	16	14*
10	3	14	27	10*
10	3	15	14	1*
10	4	-19	15	15*
10	4	-18	16	20*
10	4	-17	26	16*
10	4	-16	15	3*
10	4	-15	15	8*
10	4	-14	25	25*
10	4	-13	19	17*
10	4	-12	43	47
10	4	-11	32	33*
10	4	-10	42	30
10	4	-9	14	9*
10	4	-8	31	22
10	4	-7	26	2[illegible]*
10	4	-6	[illegible]7	62
10	4	-5	47	48
10	4	-4	52	55
10	4	-3	15	27*
10	4	-2	13	2*
10	4	-1	32	5
10	4	0	52	[illegible]
10	4	1	34	11
10	4	2	46	18
10	4	3	2[illegible]	[illegible]*
10	4	4	13	11*
10	4	5	12	*
10	4	[illegible]	[illegible]	10
10	4	[illegible]	[illegible]	*
10	4	[illegible]	17	11

H	K	L	FOBS	FCAL
10	4	9	25	25*
10	4	10	21	26*
10	4	11	13	5*
10	4	12	13	7*
10	4	13	14	16*
10	5	-17	21	13*
10	5	-16	34	21*
10	5	-15	31	25*
10	5	14	16	17*
10	5	-13	31	20*
10	5	-12	15	8*
10	5	-11	15	5*
10	5	-10	41	34
10	5	-9	43	26
10	5	-8	26	27*
10	5	-7	32	27*
10	5	-6	15	8*
10	5	-5	19	2*
10	5	-4	25	23*
10	5	-3	42	37
10	5	-2	55	49
10	5	-1	41	37
10	5	0	32	31
10	5	1	20	5*
10	5	2	13	3*
10	5	3	31	26
10	5	4	39	34
10	5	5	41	35
10	5	6	35	32
10	5	7	13	14*
10	5	8	13	4*
10	5	9	25	10*
10	5	10	25	2[illegible]*
10	5	11	24	20*
10	6	-13	27	23*
10	6	12	23	24*
10	6	11	16	25*
10	6	-10	16	10*
10	6	-9	16	10*
10	6	-8	15	12*
10	6	-7	16	14*
10	6	-6	22	2[illegible]*
10	6	-5	30	28
10	6	-4	33	16*
10	6	3	15	17*
10	6	2	18	7*
10	6	1	11	11*
10	6	0	11	21
10	6	1	16	11
10	6	2	[illegible]	24*
10	6	3	[illegible]	[illegible]*
10	6	4	11	1*
10	[illegible]	[illegible]	11	7*
10	[illegible]	[illegible]	14	1*
10	[illegible]	[illegible]	1	*

H	K	L	FOBS	FCAL
11	0	-19	11	30*
11	0	17	14	6*
11	0	-15	38	42
11	0	-13	46	18
11	0	11	13	18*
11	0	-9	57	62
11	0	-7	111	116
11	0	-5	55	54
11	0	1	13	27
11	0	-1	90	94
11	0	1	79	83
11	0	3	12	14*
11	0	5	58	63
11	0	7	59	56
11	0	9	24	16*
11	0	11	30	38
11	0	13	56	58
11	0	15	30	27*
11	1	-20	20	7*
11	1	19	33	27
11	1	-18	14	6*
11	1	-17	54	54
11	1	-16	20	9*
11	1	-15	28	27*
11	1	-14	21	13*
11	1	-13	33	26
11	1	-12	13	2*
11	1	-11	70	67
11	1	10	25	10*
11	1	-9	59	59
11	1	-8	11	13*
11	1	-7	13	8*
11	1	-6	13	4*
11	1	-5	31	80
11	1	4	25	11*
11	1	3	85	67
11	1	-2	12	*
11	1	1	19	0*
11	1	0	17	3*
11	1	1	62	64
11	1	2	18	1*
11	1	3	71	73
11	1	4	12	11*
11	1	5	31	40
11	1	6	12	3*
11	1	7	12	17*
11	1	8	17	1*
11	1	7	12	*
11	1	10	11	*
11	1	11	45	15
11	1	1[illegible]	13	*
11	1	11	[illegible]	*
11	[illegible]	14	1	*
11	1	1	11	1[illegible]
11	[illegible]	[illegible]	11	11*

[illegible]

H	K	L	FOBS	FCAL
12	4	9	14	9*
12	5	-12	28	23*
12	5	-11	33	22*
12	5	-10	16	4*
12	5	-9	15	6*
12	5	8	15	17*
12	5	-7	22	15*
12	5	6	22	27*
12	5	-5	22	24*
12	5	-4	15	19*
12	5	-3	20	10*
12	5	-2	17	8*
12	5	-1	14	16*
12	5	0	20	26*
12	5	1	29	29*
12	5	2	27	29*
12	5	3	21	17*
12	5	4	23	10*
12	5	5	14	11*
13	0	-19	39	26
13	0	17	42	34
13	0	-15	14	15*
13	0	-13	14	21*
13	0	-11	31	52
13	0	9	29	30*
13	0	-7	19	21*
13	0	-5	59	60
13	0	-3	50	60
13	0	-1	13	9*
13	0	1	59	62
13	0	3	63	64
13	0	5	32	24
13	0	7	13	22*
13	0	9	48	49
13	0	11	14	24*
13	1	-18	15	2*
13	1	17	17	11*
13	1	-16	15	5*
13	1	15	47	37
13	1	-14	14	8*
13	1	-13	33	35
13	1	-12	14	6*
13	1	-11	14	5*
13	1	-10	16	1*
13	1	-9	42	48
13	1	8	17	5*
13	1	7	59	60
13	1	6	13	17*
13	1	-5	13	22*
13	1	4	29	8*
13	1	3	40	33
13	1	2	13	5*
13	1	1	[illegible]	[illegible]
13	1	[illegible]	11	*
13	1	1	[illegible]	[illegible]

H	K	L	FOBS	FCAL
13	1	2	13	1*
13	1	3	16	15*
13	1	4	23	10*
13	1	5	40	53
13	1	6	13	9*
13	1	7	43	44
13	1	8	15	2*
13	1	9	26	4*
13	1	10	11	1*
13	1	11	42	34
13	2	-18	15	8*
13	2	-17	38	30
13	2	-16	15	12*
13	2	-15	15	13*
13	2	-14	15	1*
13	2	-13	17	27*
13	2	-12	14	12*
13	2	-11	46	54
13	2	-10	14	14*
13	2	-9	47	35
13	2	-8	14	8*
13	2	-7	14	15*
13	2	-6	14	7*
13	2	-5	38	47
13	2	-4	26	18*
13	2	-3	47	43
13	2	-2	13	7*
13	2	-1	14	2*
13	2	0	22	7*
13	2	1	33	44
13	2	2	13	14*
13	2	3	44	47
13	2	4	13	18*
13	2	5	27	20*
13	2	6	13	2*
13	2	7	34	23
13	2	8	19	12*
13	2	9	40	47
13	2	10	22	10*
13	3	-14	23	2*
13	3	-15	29	29*
13	3	-14	15	16*
13	3	-13	30	27*
13	3	12	15	7*
13	3	-11	16	2*
13	3	-10	22	10*
13	3	9	35	11
13	3	-8	14	20*
13	3	-7	46	47
13	3	-6	17	17*
13	3	5	14	17*
13	3	4	21	1*
13	3	[illegible]	[illegible]	[illegible]
13	3	[illegible]	[illegible]	[illegible]
13	3	[illegible]	[illegible]	17

H	K	L	FOBS	FCAL
13	3	0	23	21*
13	3	1	30	29
13	3	2	14	11*
13	3	3	13	14*
13	3	4	19	8*
13	3	5	28	41*
13	3	6	23	19*
13	3	7	43	33
13	3	8	14	6*
13	4	-13	21	18*
13	4	-12	15	12*
13	4	-11	15	25*
13	4	-10	19	19*
13	4	-9	15	12*
13	4	-8	15	10*
13	4	-7	15	13*
13	4	-6	15	14*
13	4	-5	41	37
13	4	-4	29	27*
13	4	-3	33	37
13	4	-2	19	12*
13	4	-1	19	3*
13	4	0	19	8*
13	4	1	24	26*
13	4	2	26	25*
13	4	3	37	33
13	4	4	32	20
13	4	5	17	12*
13	4	6	14	2*
13	5	-8	16	17*
13	5	-7	16	21*
13	5	-6	16	20
13	5	-5	15	4*
13	5	-4	15	2*
13	5	-3	14	20
13	5	-2	27	17*
13	5	-1	17	26*
13	5	0	[illegible]	22*
13	5	1	15	15*
14	0	-16	19	1*
14	0	-14	32	29*
14	0	-12	18	34
14	0	-10	18	10*
14	0	-8	25	31*
14	0	-6	50	52
14	0	-4	30	35
14	0	-2	14	21*
14	0	0	55	66
14	0	2	53	16
14	0	4	13	1*
14	0	6	12	35
14	0	7	10	31*
14	1	[illegible]	[illegible]	11*
14	1	15	9	[illegible]
14	1	[illegible]	[illegible]	[illegible]

H	K	L	FOBS	FCAL
14	1	-13	15	3*
14	1	-12	27	14*
14	1	11	14	4*
14	1	-10	60	49
14	1	-9	15	7*
14	1	8	34	39
14	1	-7	[illegible]	13*
14	1	-6	14	5*
14	1	-5	15	5*
14	1	-4	48	12
14	1	-3	16	5*
14	1	-2	50	46
14	1	-1	13	5*
14	1	0	33	16
14	1	1	22	4*
14	1	2	18	33*
14	1	3	15	10*
14	1	4	46	48
14	1	5	14	7*
14	1	6	34	27
14	1	7	14	5*
14	1	8	14	12*
14	2	-15	20	2*
14	2	-14	21	31*
14	2	-13	25	12*
14	2	-12	33	39*
14	2	-11	15	9*
14	2	-10	16	12*
14	2	-9	14	7*
14	2	-8	14	28*
14	2	-7	17	13*
14	2	-6	43	45
14	2	5	16	15*
14	2	-4	14	27*
14	2	-3	14	1*
14	2	-2	14	18*
14	2	-1	74	6*
14	2	0	41	43
14	2	1	13	15*
14	2	2	16	30*
14	2	3	14	11*
14	2	4	13	2*
14	2	5	14	5*
14	2	6	27	13*
14	2	7	28	10*
14	3	-13	16	1*
14	3	-12	15	11*
14	3	11	25	7*
14	3	-10	41	32
14	3	-9	15	17*
14	3	-8	74	[illegible]
14	3	[illegible]	11	10*
14	3	6	[illegible]	[illegible]
14	3	[illegible]	[illegible]	[illegible]
14	[illegible]	[illegible]	[illegible]	[illegible]

H	K	L	FOBS	FCAL
14	3	-3	20	22*
14	3	2	41	41
14	3	-1	14	11*
14	3	0	22	12*
14	3	1	15	1*
14	3	2	17	23*
14	3	3	14	13*
14	3	4	23	[illegible]
14	3	[illegible]	11	1*
14	4	-9	15	3*
14	4	-8	15	17*
14	4	-7	17	14
14	4	-6	12	30*
14	4	-5	37	17
14	4	-4	31	18*
14	4	-3	31	4*
14	4	-2	15	12*
14	4	-1	15	15*
14	4	0	28	31*
14	4	1	16	[illegible]
15	0	-13	24	24*
15	0	-11	24	6*
15	0	-9	16	3*
15	0	-7	38	14
15	0	-5	22	9*
15	0	-3	27	33*
15	0	-1	40	49
15	0	1	28	24*
15	0	3	14	16*
15	0	5	29	13*
15	1	13	30	22*
15	1	-12	15	7*
15	1	-11	42	37
15	1	-10	15	5*
15	1	-7	31	17*
15	1	-8	14	3*
15	1	-7	17	18*
15	1	-6	14	1*
15	1	-5	30	33
15	1	-4	14	6*
15	1	-3	[illegible]	13
15	1	-2	14	1*
15	1	1	25	7*
15	1	0	14	1*
15	1	1	37	12
15	1	2	14	4*
15	1	3	40	[illegible]
15	1	4	[illegible]	1*
15	[illegible]	[illegible]	15	4*
15	2	11	17	*
15	2	10	[illegible]	[illegible]
15	[illegible]	[illegible]	[illegible]	11
15	[illegible]	1	[illegible]	[illegible]
15	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	11	[illegible]

H	K	L	FOBS	FCAL
15	2	-5	15	7*
15	2	-4	14	3*
15	2	-3	18	28*
15	2	-2	17	11*
15	2	-1	43	36

H	K	L	FOBS	FCAL
15	2	0	14	10*
15	2	1	14	15*
15	2	2	23	4*
15	2	3	27	14*
15	3	-8	16	4*

H	K	L	FOBS	FCAL
15	3	-7	15	15*
15	3	-6	24	12*
15	3	-5	24	33*
15	3	-4	35	14
15	3	-3	22	26*

H	K	L	FOBS	FCAL
15	3	-2	15	4*
15	3	-1	18	2*
16	0	-8	15	22*
16	0	-6	32	7*
16	0	-4	32	32*

H	K	L	FOBS	FCAL
16	0	-2	29	32*
16	1	-6	40	31
16	1	-5	24	6*
16	1	-4	16	14*

Calculated Structure Factor Amplitudes

for

$[Pt(DMNH)Cl_2]_3$

H	K	L	FOBS	FCAL
0	0	3	101	104
0	0	6	517	5[illegible]
0	0	9	451	45[illegible]
0	0	12	4[illegible]	388
0	0	15	191	19[illegible]
0	1	16	86	79
0	1	13	286	281
0	1	10	108	107
0	1	7	399	400
0	1	4	575	577
0	1	1	220	206
0	1	2	1089	1125
0	1	5	331	331
0	1	8	307	310
0	1	11	461	472
0	1	14	86	82
0	1	17	97	96
0	2	17	38	148
0	2	14	123	100
0	2	11	167	174
0	2	8	9[illegible]	82
0	2	5	478	478
0	2	2	329	321
0	2	1	80	80
0	2	4	313	315
0	2	7	97	100
0	2	10	136	138
0	2	13	114	100
0	2	16	29	58
0	3	15	60	708
0	3	12	180	180
0	3	-9	25	258
0	3	-6	440	440
0	3	-3	437	437
0	3	0	317	324
0	3	3	534	539
0	3	6	244	242
0	3	9	157	160
0	3	12	126	141
0	3	15	29	78
0	4	-16	91	93
0	4	-13	124	126
0	4	-10	423	421
0	4	-7	85	92
0	4	-4	658	657
0	4	1	488	499
0	4	2	341	336
0	4	5	903	925
0	4	8	207	212
0	4	11	236	235
0	4	14	253	245
0	5	-14	139	136
0	5	-11	131	137
0	5	-8	653	650
0	5	-5	324	329

H	K	L	FOBS	FCAL
0	5	[illegible]	395	400
0	5	1	848	899
0	5	4	20	28
0	5	7	50[illegible]	499
0	5	10	221	221
0	5	13	105	99
0	5	16	162	160
0	6	15	91	91
0	6	12	143	108
0	6	-9	86	88
0	6	-6	420	417
0	6	3	277	276
0	6	0	256	267
0	6	3	494	501
0	6	6	228	228
0	6	9	158	155
0	6	12	154	155
0	6	15	61	258
0	7	13	65	60
0	7	-10	24	238
0	7	-7	40	458
0	7	-4	155	157
0	7	-1	95	99
0	7	2	104	110
0	7	5	58	42
0	7	8	24	48
0	7	11	31	238
0	7	14	47	28
0	8	14	103	93
0	8	-11	94	93
0	8	-8	189	189
0	8	-5	276	278
0	8	-2	74	77
0	8	1	318	327
0	8	4	141	146
0	8	7	112	118
0	8	10	173	174
0	8	13	29	158
0	9	-12	111	115
0	9	-9	142	141
0	9	-6	158	155
0	9	-3	447	449
0	9	0	156	156
0	9	3	263	260
0	9	6	347	353
0	9	9	45	218
0	9	12	150	143
0	10	-13	47	418
0	10	-10	56	708
0	10	-7	143	139
0	10	-4	49	228
0	10	-1	221	220
0	10	2	228	218
0	10	5	58	65
0	10	8	204	189

H	K	L	FOBS	FCAL
0	10	11	125	120
0	11	11	27	458
0	11	8	25	178
0	11	-5	27	98
0	11	-2	165	161
0	11	1	26	158
0	11	4	28	438
0	11	7	97	109
0	11	10	53	38
0	12	-9	26	248
0	12	-6	55	588
0	12	-3	139	138
0	12	0	32	178
0	12	3	139	112
0	12	6	125	124
0	12	9	54	598
0	13	-10	44	258
0	13	-7	80	74
0	13	-4	25	178
0	13	-1	126	130
0	13	2	87	99
0	13	5	30	388
0	13	8	126	114
0	14	-8	57	148
0	14	-5	48	468
0	14	-2	71	61
0	14	1	26	158
0	14	4	26	488
0	14	7	59	788
0	15	-6	28	288
0	15	-3	47	528
0	15	0	27	278
0	15	3	115	108
0	15	6	28	348
0	16	-4	29	328
0	16	-1	132	130
0	16	2	90	79
1	0	-17	93	96
1	0	-14	94	82
1	0	-11	469	472
1	0	-8	319	310
1	0	-5	338	333
1	0	-2	1154	1125
1	0	1	218	206
1	0	4	582	577
1	0	7	393	400
1	0	10	111	106
1	0	13	281	281
1	0	16	67	79
1	1	-15	87	79
1	1	-12	28	88
1	1	-9	272	278
1	1	-6	332	336
1	1	-3	308	304
1	1	0	647	634

H	K	L	FOBS	FCAL
1	1	3	471	46[illegible]
1	1	6	221	222
1	1	9	300	307
1	1	12	72	65
1	1	15	68	82
1	2-16		30	258
1	2-13		29	208
1	2-10		26	68
1	2	-7	147	146
1	2	-4	158	151
1	2	-1	149	151
1	2	2	112	111
1	2	5	35	518
1	2	8	23	198
1	2	11	46	218
1	2	14	63	8
1	2	17	39	58
1	3-14		52	448
1	3-11		140	159
1	3	-8	256	254
1	3	-5	148	143
1	3	-2	463	464
1	3	1	217	212
1	3	4	25	348
1	3	7	270	273
1	3	10	74	75
1	3	13	112	115
1	3	16	77	80
1	4-15		73	81
1	4	-12	115	125
1	4	-9	129	126
1	4	-6	473	466
1	4	-3	268	270
1	4	0	455	450
1	4	3	601	615
1	4	6	129	127
1	4	9	235	231
1	4	12	167	173
1	4	15	52	238
1	5-16		75	46
1	5-13		34	288
1	5-10		141	138
1	5	-7	95	88
1	5	-4	166	165
1	5	-1	336	336
1	5	2	22	128
1	5	5	329	331
1	5	8	273	274
1	5	11	63	64
1	5	14	122	122
1	6	-14	58	498
1	6	-11	61	62
1	6	-8	30	248
1	6	-5	240	243
1	6	-2	81	73

H	K	L	FOBS	FCAL
1	6	1	43	43
1	6	4	299	297
1	6	7	35	318
1	6	10	112	117
1	6	13	81	85
1	7-15		66	37
1	7-12		31	248
1	7	-9	107	103
1	7	-6	195	197
1	7	-3	77	70
1	7	0	239	242
1	7	3	285	287
1	7	6	107	112
1	7	9	175	180
1	7	12	28	498
1	7	15	64	598
1	8-13		59	368
1	8-10		97	93
1	8	-7	31	108
1	8	-4	198	197
1	8	-1	98	90
1	8	2	57	69
1	8	5	230	229
1	8	8	75	79
1	8	11	75	77
1	8	14	81	86
1	9-14		28	78
1	9-11		26	168
1	9	-8	65	39
1	9	-5	56	56
1	9	-2	21	198
1	9	1	65	45
1	9	4	126	122
1	9	7	24	278
1	9	10	53	578
1	9	13	29	588
1	10-12		56	478
1	10	-9	25	168
1	10	-6	125	129
1	10	-3	114	104
1	10	0	227	230
1	10	3	164	161
1	10	6	23	148
1	10	9	149	151
1	10	12	44	308
1	11-10		136	136
1	11	-7	63	70
1	11	-4	224	221
1	11	-1	192	192
1	11	2	94	87
1	11	5	284	298
1	11	8	94	100
1	11	11	118	111
1	12-11		71	39
1	12	-8	200	200

H	K	L	FOBS	FCAL
1	12	-5	144	134
1	12	-2	127	135
1	12	1	244	247
1	12	4	60	60
1	12	7	151	148
1	12	10	116	115
1	13	-9	79	54
1	13	-6	109	106
1	13	-3	94	91
1	13	0	79	69
1	13	3	107	122
1	13	6	65	63
1	13	9	27	88
1	14	-7	116	101
1	14	-4	40	288
1	14	-1	26	398
1	14	2	72	91
1	14	5	72	57
1	14	8	41	398
1	15	-5	187	174
1	15	-2	86	71
1	15	1	119	136
1	15	4	123	121
1	16	0	83	90
2	0	-16	29	58
2	0	-13	105	100
2	0	-10	135	138
2	0	-7	110	100
2	0	-4	316	315
2	0	-1	78	80
2	0	2	330	321
2	0	5	480	478
2	0	8	83	82
2	0	11	181	174
2	0	14	106	100
2	0	17	30	148
2	1	-17	30	288
2	1	-14	101	84
2	1	-11	40	578
2	1	-8	275	274
2	1	-5	263	256
2	1	-2	42	48
2	1	1	502	494
2	1	4	83	74
2	1	7	149	149
2	1	10	190	185
2	1	13	42	58
2	1	16	76	72
2	2-15		70	398
2	2-12		89	96
2	2	-9	238	234
2	2	-6	81	78
2	2	-3	541	512
2	2	0	494	491
2	2	3	290	284

H	K	L	FOBS	FCAL
2	2	6	352	354
2	2	9	119	117
2	2	12	105	111
2	2	15	86	74
2	3-14		60	468
2	3-13		84	94
2	3-10		26	108
2	3	-7	193	192
2	3	-4	116	109
2	3	-1	84	80
2	3	2	446	457
2	3	5	20	178
2	3	8	146	153
2	3	11	162	155
2	3	14	30	68
2	4	-14	30	38
2	4	-11	27	328
2	4	-8	46	78
2	4	-5	33	378
2	4	-2	17	28
2	4	1	91	91
2	4	4	19	238
2	4	7	22	178
2	4	10	91	95
2	4	13	29	48
2	4	16	31	178
2	5	-15	44	488
2	5	-12	41	78
2	5	-9	180	182
2	5	-6	162	157
2	5	-3	320	320
2	5	0	388	399
2	5	3	103	99
2	5	6	310	314
2	5	9	125	136
2	5	12	42	468
2	5	15	100	86
2	6	-13	172	183
2	6	-10	129	126
2	6	-7	274	272
2	6	-4	378	374
2	6	-1	111	116
2	6	2	605	623
2	6	5	226	230
2	6	8	232	231
2	6	11	298	300
2	6	14	57	428
2	7	-14	48	468
2	7	-11	260	259
2	7	-8	217	215
2	7	-5	217	207
2	7	-2	528	526
2	7	1	102	109
2	7	4	278	272
2	7	7	267	267

H	K	L	FOBS	FCAL
2	7	10	59	30
2	7	13	159	166
2	8	-12	63	59
2	8	-9	164	165
2	8	-6	148	141
2	8	-3	198	194
2	8	0	264	254
2	8	3	123	122
2	8	6	111	108
2	8	9	134	137
2	8	12	29	348
2	9-13		36	18
2	9-10		141	141
2	9	-7	91	97
2	9	-4	79	74
2	9	-1	239	233
2	9	2	86	83
2	9	5	114	116
2	9	8	109	104
2	9	11	76	67
2	10-11		64	67
2	10	-8	311	306
2	10	-5	171	170
2	10	-2	210	213
2	10	1	348	359
2	10	4	24	88
2	10	7	256	259
2	10	10	107	102
2	11	-9	26	428
2	11	-6	372	373
2	11	-3	189	191
2	11	0	163	163
2	11	3	476	480
2	11	6	103	99
2	11	9	155	141
2	12-10		143	148
2	12	-7	26	258
2	12	-4	215	221
2	12	-1	172	172
2	12	2	92	94
2	12	5	238	242
2	12	8	97	94
2	13	-8	75	81
2	13	-5	34	518
2	13	-2	112	110
2	13	1	64	65
2	13	4	46	428
2	13	7	26	288
2	14	-6	28	58
2	14	-3	156	157
2	14	0	101	107
2	14	3	69	74
2	14	6	114	103
2	15	-4	53	18
2	15	-1	188	191

H	K	L	FOBS	FCAL
2	15	2	128	117
3	0	-15	29	78
3	0	-12	141	141
3	0	-9	164	160
3	0	-6	243	242
3	0	-3	339	329
3	0	0	332	324
3	0	3	426	437
3	0	6	435	440
3	0	9	48	258
3	0	12	180	180
3	0	15	76	70
3	1	-16	148	156
3	1	-13	134	132
3	1	-10	214	211
3	1	-7	321	321
3	1	-4	60	52
3	1	-1	901	874
3	1	2	328	340
3	1	5	328	328
3	1	8	642	659
3	1	11	126	128
3	1	14	146	161
3	2	-14	212	216
3	2	-11	215	220
3	2	-8	205	201
3	2	-5	765	783
3	2	-2	292	294
3	2	1	363	356
3	2	4	569	584
3	2	7	50	448
3	2	10	340	342
3	2	13	117	124
3	2	16	30	708
3	3	-15	31	278
3	3	-12	155	159
3	3	-9	134	136
3	3	-6	264	264
3	3	-3	325	328
3	3	0	256	254
3	3	3	285	290
3	3	6	307	312
3	3	9	52	398
3	3	12	94	80
3	3	15	73	48
3	4	-16	32	88
3	4	-13	128	124
3	4	-10	151	153
3	4	-7	83	79
3	4	-4	345	342
3	4	-1	35	318
3	4	2	260	261
3	4	5	294	300
3	4	8	137	138
3	4	11	118	125

H	K	L	FOBS	FCAL
3	4	14	29	418
3	5-14		29	408
3	5-11		348	346
3	5	-8	244	243
3	5	-5	246	243
3	5	-2	718	713
3	5	1	140	141
3	5	4	450	456
3	5	7	313	317
3	5	10	141	138
3	5	13	226	231
3	6-15		141	137
3	6-12		32	188
3	6	-9	428	429
3	6	-6	315	320
3	6	-3	251	253
3	6	0	989	1017
3	6	3	221	222
3	6	6	306	302
3	6	9	418	426
3	6	12	49	248
3	6	15	131	136
3	7-13		171	170
3	7-10		35	138
3	7	-7	271	265
3	7	-4	315	315
3	7	-1	122	127
3	7	2	511	514
3	7	5	208	208
3	7	8	157	163
3	7	11	263	266
3	7	14	71	65
3	8-11		118	117
3	8	-8	42	348
3	8	-5	233	228
3	8	-2	110	110
3	8	1	81	78
3	8	4	114	120
3	8	7	24	328
3	8	10	26	528
3	8	13	28	168
3	9-12		144	141
3	9	-9	25	208
3	9	-6	239	237
3	9	-3	230	234
3	9	0	113	116
3	9	3	282	292
3	9	6	100	98
3	9	9	117	113
3	9	12	72	68
3	10-10		234	229
3	10	-7	69	41
3	10	-4	297	296
3	10	-1	261	268
3	10	2	105	105

H	K	L	FOBS	FCAL
3	10	5	412	426
3	10	8	102	101
3	10	11	110	124
3	11	-11	83	83
3	11	-8	265	271
3	11	-5	106	90
3	11	-2	181	184
3	11	1	335	333
3	11	4	26	78
3	11	7	206	208
3	11	10	112	121
3	12	-9	89	77
3	12	-6	144	163
3	12	-3	65	65
3	12	0	120	115
3	12	3	175	172
3	12	6	79	66
3	12	9	37	538
3	13	-7	98	77
3	13	-4	51	538
3	13	-1	72	60
3	13	2	31	538
3	13	5	27	188
3	14	-5	131	128
3	14	-2	28	318
3	14	1	116	122
3	14	4	79	81
4	0	-14	261	265
4	0	-11	239	235
4	0	-8	210	212
4	0	-5	940	925
4	0	-2	343	336
4	0	1	495	499
4	0	4	641	647
4	0	7	88	92
4	0	10	429	421
4	0	13	123	126
4	0	16	81	93
4	1	-15	32	119
4	1	-12	320	314
4	1	-9	342	339
4	1	-6	240	244
4	1	-3	1407	1388
4	1	0	335	325
4	1	3	429	431
4	1	6	885	911
4	1	9	117	124
4	1	12	244	245
4	1	15	157	151
4	2	-16	128	139
4	2	-13	76	73
4	2	-10	222	220
4	2	-7	415	417
4	2	-4	63	59
4	2	-1	753	745

H	K	L	FOBS	FCAL
4	2	2	3 c	365
4	2	5	326	330
4	2	8	554	553
4	2	11	116	111
4	2	14	129	129
4	3	-14	95	93
4	3	-11	27	268
4	3	-8	254	253
4	3	-5	148	148
4	3	-2	60	61
4	3	1	324	318
4	3	4	76	75
4	3	7	114	109
4	3	10	69	84
4	3	13	26	28
4	3	16	71	44
4	4	-15	106	114
4	4	-12	45	378
4	4	-9	251	248
4	4	-6	293	286
4	4	-3	122	123
4	4	0	521	535
4	4	3	331	326
4	4	6	198	199
4	4	9	230	230
4	4	12	27	118
4	4	15	52	758
4	5	-13	237	236
4	5	-10	84	93
4	5	-7	319	318
4	5	-4	435	436
4	5	-1	101	104
4	5	2	709	739
4	5	5	248	249
4	5	8	217	221
4	5	11	348	349
4	5	14	69	54
4	6	-14	92	75
4	6	-11	311	310
4	6	-8	172	166
4	6	-5	218	224
4	6	-2	652	634
4	6	1	92	92
4	6	4	374	375
4	6	7	275	276
4	6	10	44	488
4	6	13	189	192
4	7	-12	70	64
4	7	-9	196	196
4	7	-6	119	109
4	7	-3	160	162
4	7	0	356	347
4	7	3	164	158
4	7	6	153	156
4	7	9	170	164

H	K	L	FOBS	FCAL
4	7	12	70	58
4	8	-13	45	238
4	8	-10	85	82
4	8	-7	103	95
4	8	-4	97	99
4	8	-1	93	95
4	8	2	23	148
4	8	5	61	58
4	8	8	24	338
4	8	11	26	178
4	9	-11	91	81
4	9	-8	182	174
4	9	-5	95	86
4	9	-2	192	190
4	9	1	212	203
4	9	4	25	348
4	9	7	175	179
4	9	10	31	478
4	10	-9	79	69
4	10	-6	220	225
4	10	-3	118	112
4	10	0	144	153
4	10	3	301	294
4	10	6	54	518
4	10	9	121	112
4	11	-10	43	473
4	11	-7	24	158
4	11	-4	118	115
4	11	-1	122	120
4	11	2	24	308
4	11	5	139	138
4	11	8	114	106
4	12	-8	27	128
4	12	-5	60	448
4	12	-2	30	208
4	12	1	24	158
4	12	4	79	80
4	12	7	41	78
4	13	-6	62	578
4	13	-3	28	298
4	13	0	57	348
4	13	3	103	95
4	13	6	28	188
4	14	-1	58	658
4	14	2	29	68
5	0	-16	145	160
5	0	-13	110	99
5	0	-10	219	221
5	0	-7	507	499
5	0	-4	20	78
5	0	-1	918	899
5	0	2	404	400
5	0	5	316	320
5	0	8	436	650
5	0	11	129	137

H	K	L	FOBS	FCAL
5	0	14	342	336
5	1	-14	222	222
5	1	-11	162	167
5	1	-8	187	183
5	1	5	755	746
5	1	-2	301	292
5	1	1	433	434
5	1	4	565	562
5	1	7	31	68
5	1	10	343	348
5	1	13	136	131
5	1	16	78	64
5	2	15	32	238
5	2	-12	134	139
5	2	-9	126	126
5	2	-6	144	140
5	2	-3	456	449
5	2	0	239	241
5	2	3	229	234
5	2	6	300	302
5	2	9	131	149
5	2	12	102	95
5	2	15	76	86
5	3	-13	82	54
5	3	-10	57	63
5	3	-7	118	111
5	3	-4	77	70
5	3	-1	41	228
5	3	2	99	100
5	3	5	52	45
5	3	8	23	338
5	3	11	25	68
5	3	14	46	148
5	4	-14	43	478
5	4	-11	172	172
5	4	-8	129	117
5	4	-5	273	278
5	4	-2	328	327
5	4	1	19	68
5	4	4	268	279
5	4	7	129	123
5	4	10	110	109
5	4	13	112	111
5	5	-12	31	548
5	5	-9	222	215
5	5	-6	169	171
5	5	-3	231	223
5	5	0	478	485
5	5	3	157	154
5	5	6	189	191
5	5	9	245	253
5	5	12	36	238
5	6	-13	54	518
5	6	-10	26	398
5	6	-7	103	97

H	K	L	FOBS	FCAL
5	6	4	154	153
5	6	1	32	208
5	6	2	229	231
5	6	5	272	221
5	6	8	53	43
5	6	11	143	136
5	6	14	95	83
5	7	-11	26	208
5	7	8	67	75
5	7	-5	23	258
5	7	2	44	43
5	7	1	188	190
5	7	4	53	24
5	7	7	31	69
5	7	10	103	105
5	7	13	27	18
5	8	12	27	108
5	8	9	95	87
5	8	-6	24	248
5	8	-3	73	82
5	8	0	192	196
5	8	3	34	398
5	8	6	118	120
5	8	9	63	61
5	8	12	61	468
5	9	10	26	178
5	9	-7	67	69
5	9	-4	89	84
5	9	-1	35	118
5	9	2	144	157
5	9	5	75	70
5	9	8	26	308
5	9	11	63	75
5	10	-8	26	138
5	10	-5	32	218
5	10	-2	25	298
5	10	1	77	61
5	10	4	25	128
5	10	7	60	29
5	10	10	85	74
5	11	-6	54	478
5	11	-3	81	74
5	11	0	85	91
5	11	3	34	278
5	11	6	125	126
5	12	-7	67	72
5	12	-4	117	111
5	12	-1	27	68
5	12	2	179	171
5	12	5	69	81
5	13	-2	132	130
5	13	1	29	528
5	13	4	65	72
6	0	-15	63	258
6	0	-12	152	156

H	K	L	FOBS	FCAL
6	0	-9	149	155
6	0	-6	228	228
6	0	-3	516	501
6	0	0	272	267
6	0	3	277	276
6	0	6	410	417
6	0	9	90	88
6	0	12	136	108
6	0	15	90	91
6	1	-13	30	578
6	1	-10	33	418
6	1	-7	147	138
6	1	-4	74	72
6	1	-1	200	201
6	1	2	327	332
6	1	5	21	108
6	1	8	198	202
6	1	11	161	166
6	1	14	28	158
6	2	-14	66	288
6	2	-11	77	82
6	2	-8	96	103
6	2	-5	112	99
6	2	-2	281	281
6	2	1	97	99
6	2	4	42	438
6	2	7	233	237
6	2	10	24	208
6	2	13	102	99
6	3	-15	52	188
6	3	-12	106	104
6	3	-9	28	258
6	3	-6	154	158
6	3	-3	299	301
6	3	0	120	120
6	3	3	238	233
6	3	6	157	149
6	3	9	69	77
6	3	12	92	89
6	3	15	29	18
6	4	-13	28	128
6	4	-10	79	78
6	4	-7	109	117
6	4	-4	31	58
6	4	-1	288	284
6	4	2	20	178
6	4	5	57	59
6	4	8	136	131
6	4	11	51	378
6	4	14	28	318
6	5	-14	32	198
6	5	-11	26	28
6	5	-8	24	308
6	5	-5	23	48
6	5	-2	29	338

H	K	L	FOBS	FCAL
6	5	1	54	60
6	5	4	23	138
6	5	7	127	129
6	5	10	25	208
6	5	13	28	238
6	6	-12	27	408
6	6	-9	77	78
6	6	-6	54	44
6	6	-3	213	209
6	6	0	135	124
6	6	3	251	255
6	6	6	144	152
6	6	9	25	278
6	6	12	116	123
6	7	-10	88	88
6	7	-7	205	204
6	7	-4	40	308
6	7	-1	309	313
6	7	2	180	182
6	7	5	128	134
6	7	8	254	258
6	7	11	39	578
6	8	-11	104	104
6	8	-8	81	75
6	8	-5	260	262
6	8	-2	107	108
6	8	1	149	149
6	8	4	221	218
6	8	7	39	18
6	8	10	123	125
6	9	-9	80	66
6	9	-6	101	94
6	9	-3	102	114
6	9	0	73	64
6	9	3	76	82
6	9	6	73	80
6	9	9	48	218
6	10	-7	36	208
6	10	-4	162	143
6	10	-1	24	58
6	10	2	93	91
6	10	5	100	88
6	10	8	78	68
6	11	-5	74	79
6	11	-2	231	228
6	11	1	44	48
6	11	4	163	174
6	11	7	106	100
6	12	-3	30	728
6	12	0	268	259
6	12	3	78	71
7	0	-14	39	28
7	0	-11	38	238
7	0	-8	32	48
7	0	5	52	42

H	K	L	FOBS	FCAL
7	0	-2	815	810
7	0	1	101	99
7	0	4	157	157
7	0	7	23	458
7	0	10	43	238
7	0	13	47	608
7	1	-15	56	388
7	1	-12	93	99
7	1	-9	24	358
7	1	-6	294	284
7	1	-3	219	220
7	1	0	358	343
7	1	3	384	394
7	1	6	24	368
7	1	9	239	241
7	1	12	83	95
7	1	15	60	618
7	2	-13	84	68
7	2	-10	273	269
7	2	-7	100	103
7	2	-4	387	396
7	2	-1	333	332
7	2	2	188	188
7	2	5	514	534
7	2	8	146	150
7	2	11	167	172
7	2	14	155	163
7	3	-14	102	105
7	3	-11	81	78
7	3	-8	331	344
7	3	-5	202	205
7	3	-2	221	224
7	3	1	452	450
7	3	4	22	88
7	3	7	252	254
7	3	10	130	139
7	3	13	83	65
7	4	-12	41	728
7	4	-9	110	107
7	4	-6	166	171
7	4	-3	113	108
7	4	0	213	207
7	4	3	174	174
7	4	6	36	298
7	4	9	51	628
7	4	12	59	44
7	5	-13	83	89
7	5	-10	26	238
7	5	-7	207	204
7	5	-4	57	63
7	5	-1	166	162
7	5	2	217	221
7	5	5	113	114
7	5	8	136	137
7	5	11	52	618

H	K	L	FOBS	FCAL
7	6	-11	132	136
7	6	-8	89	90
7	6	-5	411	417
7	6	-2	154	148
7	6	1	281	287
7	6	4	289	288
7	6	7	47	68
7	6	10	222	221
7	7	-9	165	170
7	7	-6	97	100
7	7	-3	467	484
7	7	0	149	154
7	7	3	173	174
7	7	6	359	348
7	7	9	26	548
7	8	-10	104	116
7	8	-7	165	175
7	8	-4	68	73
7	8	-1	244	249
7	8	2	137	136
7	8	5	113	108
7	8	8	185	193
7	9	-8	119	121
7	9	-5	42	608
7	9	-2	82	86
7	9	1	89	89
7	9	4	58	22
7	9	7	34	448
7	10	-6	140	140
7	10	-3	45	368
7	10	0	200	205
7	10	3	98	92
7	10	6	91	86
7	11	-4	149	143
7	11	-1	34	208
7	11	2	235	235
7	11	5	94	91
8	0	-13	29	158
8	0	-10	178	174
8	0	-7	113	118
8	0	-4	153	144
8	0	-1	318	327
8	0	2	83	77
8	0	5	277	278
8	0	8	193	189
8	0	11	93	93
8	0	14	93	93
8	1	-14	122	123
8	1	-11	96	83
8	1	-8	487	494
8	1	-5	217	218
8	1	-2	320	325
8	1	1	550	558
8	1	4	40	48
8	1	7	377	378

H	K	L	FOBS	FCAL
8	1	10	168	170
8	1	13	100	100
8	2	-12	175	179
8	2	-9	72	74
8	2	-6	580	583
8	2	-3	265	262
8	2	0	252	250
8	2	3	747	753
8	2	6	146	147
8	2	9	222	230
8	2	12	208	213
8	3	-13	85	104
8	3	-10	204	208
8	3	-7	32	478
8	3	-4	325	323
8	3	-1	232	231
8	3	2	168	170
8	3	5	391	387
8	3	8	108	108
8	3	11	114	121
8	4	-11	125	126
8	4	-8	83	95
8	4	-5	116	105
8	4	-2	200	200
8	4	1	47	498
8	4	4	95	93
8	4	7	75	75
8	4	10	29	178
8	4	13	39	468
8	5	-12	99	102
8	5	-9	170	169
8	5	-6	25	318
8	5	-3	331	324
8	5	0	219	212
8	5	3	126	133
8	5	6	249	248
8	5	9	24	418
8	5	12	99	85
8	6	-10	138	133
8	6	-7	268	256
8	6	-4	25	88
8	6	-1	376	374
8	6	2	217	207
8	6	5	123	120
8	6	8	312	314
8	6	11	69	71
8	7	-8	106	112
8	7	-5	306	303
8	7	-2	80	69
8	7	1	203	203
8	7	4	252	235
8	7	7	26	78
8	7	10	161	154
8	8	-9	27	228
8	8	-6	80	97

H	K	L	FOBS	FCAL
8	8	1	161	160
8	8	0	55	57*
8	8	3	80	100
8	8	6	121	115
8	8	9	64	51
8	9	[illegible]	61	55*
8	9	4	76	79
8	9	1	28	21*
8	9	[illegible]	76	66
8	9	[illegible]	27	41*
8	10	5	91	95
8	10	[illegible]	141	137
8	10	1	28	11*
8	10	4	131	115
8	11	0	143	157
9	0	12	143	143
9	0	-9	26	21*
9	0	-6	351	353
9	0	-3	255	260
9	0	0	162	156
9	0	3	432	449
9	0	6	147	155
9	0	9	141	141
9	0	12	110	115
9	1	-13	110	104
9	1	-10	266	271
9	1	-7	47	39*
9	1	-4	412	406
9	1	1	329	338
9	1	2	148	145
9	1	5	541	549
9	1	8	157	157
9	1	11	135	132
9	1	14	181	178
9	2	11	91	99
9	2	-8	339	348
9	2	-5	157	156
9	2	-2	243	244
9	2	1	443	439
9	2	4	48	44*
9	2	7	274	275
9	2	10	162	154
9	2	13	49	40*
9	3	-12	28	23*
9	3	-9	92	88
9	3	-6	183	192
9	3	-3	79	83
9	3	0	130	134
9	3	3	214	210
9	3	6	121	128
9	3	9	105	98
9	3	12	105	97
9	4	-10	76	63
9	4	-7	89	84
9	4	-4	44	54*

H	K	L	FOBS	FCAL
9	4	1	114	106
9	4	[illegible]	58	70
9	4	5	24	24*
9	4	8	58	44
9	4	11	26	24*
9	[illegible]	11	28	56*
9	5	8	126	131
9	5	5	184	193
9	5	2	42	44*
9	5	1	168	166
9	5	4	146	147
9	5	7	25	47*
9	5	10	96	105
9	6	9	70	67
9	6	6	94	90
9	6	-3	244	244
9	6	0	120	116
9	6	3	112	122
9	6	6	208	215
9	6	9	43	42*
9	7	7	54	37*
9	7	-4	29	17*
9	7	1	106	118
9	7	2	108	111
9	7	5	41	13*
9	7	8	95	92
9	8	-5	55	38*
9	8	-2	75	63
9	8	1	26	5*
9	8	4	38	8*
9	8	7	76	77
9	9	-3	90	84
9	9	0	27	15*
9	9	3	28	46*
9	10	-1	65	68
10	0	-11	122	120
10	0	-8	185	189
10	0	-5	24	65*
10	0	-2	217	218
10	0	1	214	220
10	0	4	42	22*
10	0	7	140	139
10	0	10	64	70
10	0	13	29	41*
10	1	-12	57	55*
10	1	-9	96	92
10	1	-6	229	237
10	1	-3	175	172
10	1	0	163	167
10	1	3	337	337
10	1	6	98	106
10	1	9	89	93
10	1	12	123	129
10	2	-10	31	33*
10	2	-7	25	37*

H	K	L	FOBS	FCAL
10	2	-4	115	104
10	2	1	134	136
10	2	2	49	33*
10	2	5	129	135
10	2	8	156	160
10	2	11	26	2*
10	3	-11	26	28*
10	3	-8	64	57
10	3	5	106	98
10	3	2	24	34*
10	3	1	32	37*
10	3	4	154	[illegible]
10	3	7	26	19*
10	3	10	85	74
10	4	-9	26	26*
10	4	-6	131	132
10	4	-3	31	6*
10	4	0	84	92
10	4	3	118	124
10	4	6	54	37*
10	4	9	60	66
10	5	-10	61	59
10	5	-7	26	6*
10	5	-4	97	104
10	5	-1	25	32*
10	5	2	39	14*
10	5	5	94	82
10	5	8	66	42
10	6	-8	27	14*
10	6	5	30	3*
10	6	-2	61	38
10	6	1	31	6*
10	6	4	76	69
10	6	7	45	34*
10	7	-6	58	73*
10	7	-3	67	68
10	7	0	107	110
10	7	3	105	100
10	7	6	49	5*
10	8	-4	117	102
10	8	-1	129	110
10	8	2	28	33*
10	8	5	144	151
10	9	1	118	120
11	0	-10	42	3*
11	0	-7	108	109
11	0	-4	46	43*
11	0	-1	24	15*
11	0	2	161	161
11	0	5	45	9*
11	0	8	33	17*
11	0	11	26	45*
11	1	-11	52	8*
11	1	-8	26	24*
11	1	-5	60	46

H	K	L	FOBS	FCAL
11	1	-2	57	54
11	1	1	62	56
11	1	4	81	76
11	1	7	45	29*
11	1	10	78	81
11	2	-9	89	89
11	2	-6	109	102
11	2	-3	131	128
11	2	0	228	224
11	2	3	60	57
11	2	6	196	194
11	2	9	103	96
11	3	-10	57	81*
11	3	-7	114	126
11	3	-4	206	204
11	3	-1	25	38*
11	3	2	283	285
11	3	5	117	122
11	3	8	129	121
11	4	-8	102	105
11	4	-5	76	93
11	4	-2	229	234
11	4	1	36	23*
11	4	4	136	130
11	4	7	105	109
11	4	10	28	39*
11	5	-6	58	52
11	5	-3	107	107
11	5	0	78	72
11	5	3	25	5*
11	5	6	41	48*
11	6	-7	66	6*
11	6	-4	57	57*
11	6	-1	132	141
11	6	2	26	42*
11	6	5	106	107
11	7	-5	86	91
11	7	-2	115	116
11	7	1	184	187
11	7	4	28	1*
11	8	0	88	85
12	0	-9	55	59*
12	0	-6	124	124
12	0	-3	111	112
12	0	0	23	17*
12	0	3	135	138
12	0	6	56	58
12	0	9	25	24*
12	1	-10	99	89
12	1	-7	38	54*
12	1	-4	203	203
12	1	-1	31	5*
12	1	2	194	194
12	1	5	138	135
12	1	8	79	88

H	K	L	FOBS	FCAL
12	1	11	113	96
12	2	-8	127	128
12	2	-5	129	126
12	2	-2	344	344
12	2	1	39	54*
12	2	4	241	234
12	2	7	179	166
12	2	10	62	63*
12	3	-9	203	199
12	3	-6	147	149
12	3	-3	119	119
12	3	0	386	389
12	3	3	95	93
12	3	6	145	143
12	3	9	200	190
12	4	-7	127	131
12	4	-4	115	123
12	4	-1	83	82
12	4	2	188	188
12	4	5	86	74
12	4	8	84	82
12	5	-5	99	110
12	5	-2	27	22*
12	5	1	86	84
12	5	4	63	57
12	6	-3	133	114
12	6	0	41	55*
12	6	3	170	170
13	0	-8	116	114
13	0	-5	58	38
13	0	-2	87	99
13	0	1	134	130
13	0	4	54	17*
13	0	7	58	74*
13	0	10	28	25*
13	1	-9	157	151
13	1	-6	124	136
13	1	-3	79	59
13	1	0	274	274
13	1	3	110	120
13	1	6	98	98
13	1	9	128	129
13	2	-7	150	162
13	2	-4	194	196
13	2	-1	49	37*
13	2	2	294	302
13	2	5	126	124
13	2	8	79	81
13	3	-5	98	111
13	3	-2	217	215
13	3	1	35	41*
13	3	4	160	151
13	3	7	138	129
13	4	-6	28	5*
13	4	-3	55	70*

H	K	L	FOBS	FCAL
13	4	0	98	105
13	4	3	62	47
13	4	6	71	70
13	5	-4	78	66
13	5	-1	55	53*
13	5	2	52	3*
14	0	-7	73	78
14	0	-4	57	48*
14	0	-1	26	15*

H	K	L	FOBS	FCAL
[illegible]	0	2	61	61
14	0	5	27	46*
14	0	8	27	14*
14	1	-8	29	39*
14	1	-5	107	108
14	1	-2	137	142
14	1	1	26	22*
14	1	4	100	100
14	1	7	71	63

H	K	L	FOBS	FCAL
14	2	-6	28	62*
14	2	-3	82	65
14	2	0	171	174
14	2	3	67	80
14	2	6	53	56*
14	3	-4	45	33*
14	3	-1	45	26*
14	3	2	85	74
14	3	5	93	89

H	K	L	FOBS	FCAL
14	4	-2	34	33*
14	4	1	68	62
15	0	-6	50	34*
15	0	-3	103	108
15	0	0	27	27*
15	0	3	61	52
15	0	6	30	20*
15	1	-4	27	11*
15	1	-1	77	71

H	K	L	FOBS	FCAL
15	1	2	27	6*
15	1	5	28	15*
15	2	-2	37	5*
15	2	1	28	50*
15	2	4	29	19*
16	0	-2	77	79
16	0	1	135	130
16	0	4	29	32*
16	1	0	86	78