AQUEOUS SUBSTITUTION BEHAVIOUR OF THE CHLOROTRIS(1,3,5-TRIAZA-7-PHOSPHAADAMANTANE) PLATINUM(II) ION

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by

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ABBREVIATIONS AND SYMBOLS

δ	Chemical shift
θ_T	Tolman cone angle
θ_E	Effective cone angle
$\theta/_2$	Half-angle
Ac	Acetyl
Bu	Butyl
CO	Carbonyl
cod	Cyclooctadiene
Cy	Cyclohexyl
d	Doublet
dd	Doublet of doublets
dien	Diethylenetriammine
DNA	Deoxyribonucleic acid
Et	Ethyl
h	Planck's constant
$h\nu$	Photochemical light
^{i}Pr	Isopropyl
IR	Infrared spectroscopy
K_a	Acid dissociation constant
k_B	Boltzmann's constant
k_{ab}	Rate constant for the reaction proceeding from a to b
k_{obs}	Observed pseudo first-order rate constant
L	Neutral ligand
Me	Methyl
$^{n}J_{x\text{-}y}$	n^{th}-order coupling between nuclei x and y
NMR	Nuclear magnetic resonance spectroscopy
OEt	Ethoxy
o-tolyl	*ortho*-tolyl

PGM	Platinum group metal
Ph	Phenyl
pH	-log [H^+]
pK_a	-log K_a
ppm	Unit of chemical shift – parts per million
PTA	1,3,5-triaza-7-phosphaadamantane
py	pyridine
R	Monoanionic ligand (R = H^-, Me^- or Ph^-)
S	Solvent
SMe_2	Dimethyl sulphide
T	Temperature
t	Triplet
td	Triplet of doublets
Triflic acid	Trifluoromethanesulphonic acid
tt	Triplet of triplets
UV-Vis	Ultraviolet-visible

1 INTRODUCTION AND AIM

1.1 INTRODUCTION[1]

The chemistry of platinum has been studied for many years. The metal has numerous uses in catalysis, jewellery and electrical applications, and the study of its complexes has been pivotal in the development of coordination chemistry. The substitution chemistry of platinum(II) was also of early significance: for example, the *trans* effect was discovered and formulated by carrying out substitution reactions on platinum(II) complexes[2]. These studies have been extensively used for the specific synthesis of *cis* and *trans* platinum(II) complexes. Recently, platinum complexes having non-integral oxidation states have been studied because of their electrical conductivity, and the discovery of *cis*-$[PtCl_2(NH_3)_2]$ as a chemotherapeutic agent has led to the development of platinum chemistry with significant biological application.

With the development of NMR, platinum, of which 33.7% is present in nature as the ^{195}Pt isotope and has a nuclear spin of 1/2, has been attractive because of the possibility of observing coupling between the metal and other nuclei[3]. The presence or absence of such coupling provides important information on which structural conclusions are based as well as enabling mechanistic suggestions for the reactions of organoplatinum complexes. In its compounds platinum shows a definite preference for three oxidation states namely 0, +II and +IV. Lately, an increased number of platinum complexes in the +I oxidation state have been described. Compounds in the +III and +V oxidation states are rare and those in the +VI oxidation state are only known when platinum has coordinated oxygen or fluorine ligands.

Platinum complexes are relatively easily oxidised or reduced in two-electron processes between the three main oxidation states so that oxidative addition and reductive elimination reactions are facile. Since the most influential geometry for the +II state is square planar and that for the +IV state is octahedral, oxidative addition accompanied by the addition of two fragments to the platinum(II) and reductive elimination accompanied by the loss of two fragments from platinum(IV) are particularly favourable. Although platinum(0) displays a wider range of geometries than the other two states, the loss of ligands to form two-coordinate platinum(0) complexes is relatively facile. This enables platinum(0) ⇌ platinum(II) oxidative additions and reductive eliminations to be accompanied by the respective addition or loss of two fragments.

The principal uses of platinum[4] are in jewellery, chemical, petroleum and electrical industries and the largest single use is in autocatalysts. A wide variety of platinum complexes are of catalytic interest. These include the hydrosilylation of olefins catalysed by chloroplatinic acid and the platinum(II)-tin(II) catalysts for the selective hydrogenation of polyolefins to monoolefins. In the chemical industry platinum is widely used in the oxidation of ammonia to nitric acid (as a platinum-rhodium gauze) and transforming of low octane naphthas to high quality petroleum products. The metal has also been used in the selective hydrogenation and dehydrogenation catalysts for chemical intermediates in the plastic, man-made fibre, rubber, pesticide, dyestuff and pharmaceutical industries. However, a large advantage in organoplatinum chemistry is the possibility of isolating stable complexes of the corresponding and more labile, *e.g.* Pd and Rh analogues.

The new three way catalysts based on platinum and rhodium have reduced the consumption of palladium to the extent that overall, significantly more platinum than palladium is used in the motor industry compared to a few years ago. Three way catalysts not only oxidise carbon monoxide, hydrogen and any unburnt hydrocarbons, but they also reduce the oxides of nitrogen[5].

1.2 AIM OF THIS RESEARCH

The 1,3,5-triaza-7-phosphaadamantane (PTA) ligand was first prepared by Daigle[6] and further investigations were later conducted by the groups of Darensbourg[7] and Joó[8]. This ligand has attracted much interest due to its remarkable and interesting characteristics since it is air stable, water-soluble and has a low steric demand (cone angle of 118°, similar to PMe_3[9]). It finds use as a neutral, water-soluble P-donor ligand by hydrogen bonding to the tertiary amine nitrogen atoms. The interest in this ligand is primarily from, in addition to its potential catalytic employment, possible medical applications[9,10].

The Wilkinson catalyst $[RhCl(PPh_3)_3]$ has been widely used in catalysis[11] including the hydrogenation of olefins, in hydrosilylation of C=C and C=O bonds and in the hydrogenation[12] of carbon dioxide. Research was expanded into using water-soluble phosphines in homogeneous catalysis and work done by Wilkinson[13] and Beck[14] showed that water-soluble triphenylphosphine derivatives had potential in aqueous phase homogeneous catalysis. Later, the interest for organometallic reactions done in water grew stronger, triggered then by the discovery that the rate of certain reactions was strongly increased by utilising water as a solvent[15]. The increased interest also involved preparation of new water-soluble ligands such as PTA. Water-soluble analogues of the Vaska's complex[16], *trans*-$[IrCl(CO)(PPh_3)_2]$, have been prepared using the water-soluble ligands TPPMS (*meta*-monosulphonated triphenylphosphine) and PTA and these have catalytic implications[17].

Based on the above, it is without doubt the Wilkinson-type analogues with water-soluble phosphine ligands that have potential applications in homogeneous catalysis and the basic reactions and behaviour of selected Pt(II) complexes with PTA as a ligand will be investigated.

Prior to the experimental investigation a complete literature survey, covering different aspects to be investigated, was done and is reported in **Chapters 2** and **4**.

The main aims of this study are summarised as follows:

1. Preparation of the platinum(II) analogue of the Wilkinson catalyst, $[PtCl(PTA)_3]Cl$.

2. Study of the aqueous solution behaviour including stability and kinetic reactivity of the $[PtCl(PTA)_3]Cl$ with various halides and pseudo-halides.

3. Study of the effects of pH on the $[PtCl(PTA)_3]Cl$ complex.

4. Characterisation of the starting complex together with the products formed by use of IR and UV-Vis spectrophotometry, by ^{1}H, ^{31}P, ^{195}Pt, ^{35}Cl NMR and by X-ray crystallography.

5. Suggestion of a complete mechanism for the aqueous solution behaviour of the $[PtCl(PTA)_3]^{+}$ complex in the presence of halides and pseudo-halides.

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2 THEORETICAL ASPECTS OF PLATINUM COMPLEXES

2.1 INTRODUCTION

Since early history, transition metal complexes have been icons used as pharmaceutical agents, but since they have found uses in other fields such as chemotherapy, catalysis and so forth. Organometallic chemistry has been studied for a long time and today the applications have a valuable impact on the world economy.

The organometallic complex containing a transition group element that is considered the cornerstone of the subject, is what is known as Zeise's[1] complex, $K[PtCl_3(C_2H_4)]\cdot H_2O$. Ever since its discovery almost 200 years ago, platinum has played an indispensable part in organometallic chemistry since it forms a wide range of complexes that are stable enough for isolation and characterisation.

Platinum is the longest known and probably the most studied of the platinum group metals (PGM's), because of its abundance and consequent availability. It was first discovered in the sixteenth century in the Choco district of Columbia[2]. Platinum occurs naturally as the element, generally with small amounts of other PGM's and it was used as a silver substitute by Colombian Indians who called it 'platina del Pinto' ('little silver of the Pinto river')[3].

Platinum is one of the key materials whose electrical and thermal properties are used internationally as the basis for calibration and reference. The choice of platinum is a consequence of its stability and inertness and it is readily available in high purity.

Its chemical properties include the fact that it is less attacked by oxygen compared to other platinum group metals, is unaffected by acids except aqua regia in which it readily dissolves and it reacts with molten caustic potash at 500 °C.

The metal has numerous uses in catalysis, while its study has been pivotal in the development of coordination chemistry. Platinum metal catalysts are thermally stable and are known to function at low temperatures; also the metal acts as a catalyst in the oxidation of alkanes. Platinum thermocouples are widely used for temperature determination. The metal has also been used in jewellery and in the glass making industry: most types of special glass such as camera and some optical fibres are melted and processed in platinum apparatus. Glass fibres used for reinforcements and insulation have also placed considerable demands on the platinum industry since the new fibre-optic cables for telecommunications depend critically upon the use of special high purity platinum equipment. More recently the discovery of cisplatin, *cis*-$[PtCl_2(NH_3)_2]$, as a chemotherapeutic agent has led to the development of platinum chemistry with medical applications. The chemistry of platinum revolves around three oxidation states namely, 0, II and IV, and representative complexes are shown in **Fig. 2.1**.

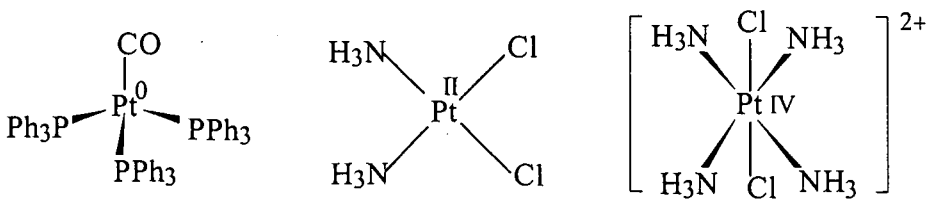


Figure 2.1: Representative platinum complexes of the 0, II, and IV oxidation states.

Although the transition elements display a range of oxidation states, platinum is a little unusual since it has three oxidation states differing by two electrons each. Platinum complexes are easily oxidised or reduced in two-electron processes between the three main oxidation states so that oxidative addition and reductive elimination reactions are facile.

Complexes of platinum(0) are few and may be two-, three- or four-coordinate. Many of these compounds have been shown to display catalytic activity and some are clusters of the metal.

Platinum(IV) complexes are d^6 complexes with a hexacoordinate, octahedral structure. The preparations of these complexes are usually done by the oxidative addition from platinum(II) complexes or by ligand exchange. These complexes also form neutral, cationic and anionic complexes and a very distinctive characteristic about them is their kinetic stability.

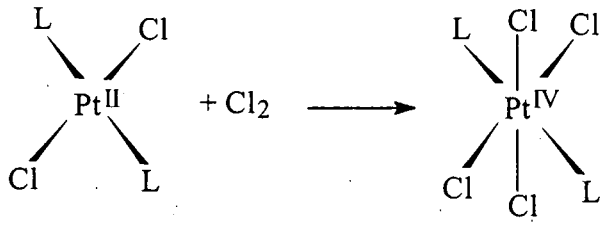


Figure 2.2: Preparation of Pt(IV) complexes by oxidative addition.

Platinum(II) complexes are the most abundant and mechanistic studies on these complexes have been fundamental in understanding substitution reactions at square planar metal centres. These studies have also led to the identification of associative and dissociative pathways in these replacement reactions, the effect of entering and leaving groups and the development of the ligand nucleophilicity concept to platinum. These complexes are four-coordinate planar complexes which have a coordinately unsaturated 16-electron d^8 platinum centre. The gateway to platinum(II) chemistry is often through the halides, for example M_2PtCl_4 and PtX_2, as starting materials and compounds of the type $PtCl_2L_2$ are also important both historically and as starting materials.

2.2 PLATINUM AND CHEMOTHERAPY

2.2.1 General aspects of chemotherapy

The term chemotherapy is defined as the use of drugs to combat an invading organism with limited damage to the host. There have been developments in chemotherapy[4] and the use of any substance as a chemotherapeutic agent will clearly depend on how its action favours the host over the invading organism. Chemotherapy uses toxicity and requires an essentially irreversible process: cell death. Normally a different organism is attacked, a virus, bacterium, or a parasite but in cancer treatment the host's own malignant cells are attacked. The requirement for an irreversible process distinguishes chemotherapeutic agents from drugs which modify biological responses or alter biochemistry reversibly in the organism without necessary killing the cell.

Cancer is a disease that is caused by the uncontrolled growth of abnormal cells. These cells have the ability to multiply themselves by DNA replication, thus invading healthy tissue and organs in the body and can therefore spread throughout the whole body.

There are various ways of treating cancer including removal of the cancer cells by surgery, X-ray radiation and chemotherapy. Anticancer treatments should be safe enough, have a limited number of side effects and be very specific in their action.

Surgical removal of the tumour cell has been the most effective method of treatment, but the problem encountered is that it can damage the patient where the cancer has developed and it offers no help if the cancer has advanced throughout the body.

Irradiation by X- or gamma rays kills the cancer cells, without harming the unaffected cells since they recover much quicker from radiation, and it causes less trauma to the patient as compared to surgery. This method also cannot treat advanced cancer since radiation of the whole body can cause damage to unaffected delicate tissues.

Chemotherapy involves administration of drugs, which can be taken orally[5,6] or injected in the blood. After years of introduction of cisplatin, orally applicable platinum drugs played a small role in cancer treatment and this can be explained by the fact that they had to be soluble in water, neutral, lipophillic and be able to survive the acidic and alkaline media of the gastric environment.

Anticancer drugs have side effects, like renal toxicity for cisplatin, which then restrict them to limited doses. Damage to bone marrow causes anaemia, which is an inability to fight infections and a tendency to internal bleeding. Other side effects include vomiting, diarrhoea, nausea, hair loss and neurological complications. Another drawback that can be encountered in using drugs is the fact that the tumour can develop resistance to other drugs after the first administration.

2.2.2 Antitumour activity of platinum complexes

The initial discovery of the antitumour activity of platinum complexes was made by Barnett Rosenberg's[7] research group in the 1960's. They were studying the effects of an electric current passed over platinum electrodes immersed in a solution containing *Escherichia coli* cells that were growing in the presence of an ammonium chloride buffer. Interesting enough was that cell growth continued but division of the cells was greatly inhibited. It was found from tests that followed that the platinum had reacted with NH_4Cl to form an active compound, *cis*-$[PtCl_2(NH_3)_2]$ (cisplatin) of which the synthesis[8] and structure were well known at the time.

Antitumour screening revealed that only the *cis* isomer of the complex was the active agent and not the *trans* isomer. This platinum complex inhibited cell division without killing the bacteria, and this suggested that it could cease cell division in tumour cells with no damage to the host.

Tests were done on cisplatin proving that it has beneficial effects on the treatment of cancer[9,10]. The biological activity results from binding to the DNA, thus inhibiting replication. Today, cisplatin is used in combination with other anticancer agents and is effective against testicular and ovarian carcinomas, bladder cancer and tumours of the head and neck. There are a number of side effects experienced with cisplatin including kidney and liver toxicity, nausea, neurotoxicity and vomiting.

There are certain prerequisites that are essential in the so-called 'active' platinum complexes and they include:

- There must be two ammine groups in a *cis* configuration.
- The complex must be uncharged.
- There should be good leaving groups like chloride or the carboxylate ion in a *cis* configuration.

These findings have implied that specific chemical reactions responsible for antitumour activity need bifunctional attachment to biological molecules. Further, the chemical interactions unique to the *cis* isomer should suggest a guide to details of the molecular mechanism of action of the drug.

2.2.3 Mechanism of action of cisplatin

Since the classic discovery of *cis*-$[PtCl_2(NH_3)_2]$ and its antitumour activity by Rosenberg, continuous research was done to determine its mechanism of action and to account for the fact that only the *cis* isomer was active.

Cisplatin cannot be taken orally due to the hydrolysis action of the gastric juices in the stomach and therefore it is injected in the blood where it is bound to plasma protein. Some is excreted renally and some is transported in the blood as uncharged $[PtCl_2(NH_3)_2]$ molecules which pass through the cell wall unchanged. It is believed that cisplatin is not active in its normal form, therefore once through the cell wall it is converted to the actual drug.

$[PtCl_2(NH_3)_2]$ undergoes hydrolysis to *cis*-$[PtCl(NH_3)_2(H_2O)]^+$ and more slowly to *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ owing to the lower intracellular Cl^- concentrations as compared to the higher chloride concentration outside the cell. The hydrolysis of the chloride is outlined in **Eq. 2.1** and **2.2** followed by deprotonation (**Eq. 2.3** and **2.4**).

$$\textit{cis}\text{-}[PtCl_2(NH_3)_2] + H_2O \rightarrow Cl^- + \textit{cis}\text{-}[PtCl(NH_3)_2(H_2O)]^+ \quad (2.1)$$

$$\textit{cis}\text{-}[PtCl(NH_3)_2(H_2O)]^+ + H_2O \rightarrow Cl^- + \textit{cis}\text{-}[Pt(NH_3)_2(H_2O)_2]^{2+} \quad (2.2)$$

$$\textit{cis}\text{-}[Pt(NH_3)_2(H_2O)_2]^{2+} \rightleftharpoons \textit{cis}\text{-}[Pt(OH)(NH_3)_2(H_2O)]^+ + H^+ \quad (2.3)$$

$$\textit{cis}\text{-}[Pt(OH)(NH_3)_2(H_2O)]^+ \rightleftharpoons \textit{cis}\text{-}[Pt(OH)_2(NH_3)_2] + H^+ \quad (2.4)$$

The platinum complex is more reactive when it looses the chloride because water is a better leaving group than Cl^-. Coordination of water to platinum lowers its p*K*a, thereby causing the hydroxo products to form as well[11,12]. Since the hydroxo groups in the above-mentioned complexes are not reactive towards substitution, it is believed that the aqua species reacts with DNA.

In addition, the rate of hydrolysis of the first chloro ligand in *trans*-$[PtCl_2(NH_3)_2]$ is expected to be much more rapid than that of the second. The positively charged platinum complexes are electrostatically attracted to the negatively charged DNA helix. The surface of the DNA double helix is characterised by major and minor grooves of which the backbone of each strand is made up of deoxy-ribose phosphodiester units. Cisplatin has been known to form interesting adducts with DNA mainly by forming intrastrand cross-links by joining two adjacent guanine groups or adjacent guanine and adenine groups, which occupy the *cis* position, formerly filled with Cl^-.

The need to replace two Cl^- ligands explains why species like chlorodiethylenetriammineplatinum(II), ($[PtCl(dien)]^+$, **Fig. 2.3**), with only one labile chloride are inactive. Because of the different geometry of *trans*-$[PtCl_2(NH_3)_2]$ molecules, they bind to DNA differently from cisplatin through interstrand cross-links.

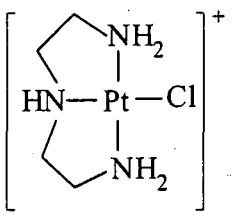


Figure 2.3: Structure of chlorodiethylenetriammineplatinum(II).

There are other ways of cisplatin binding to DNA namely interstrand cross-links and DNA-protein cross-links, **Fig. 2.4**.

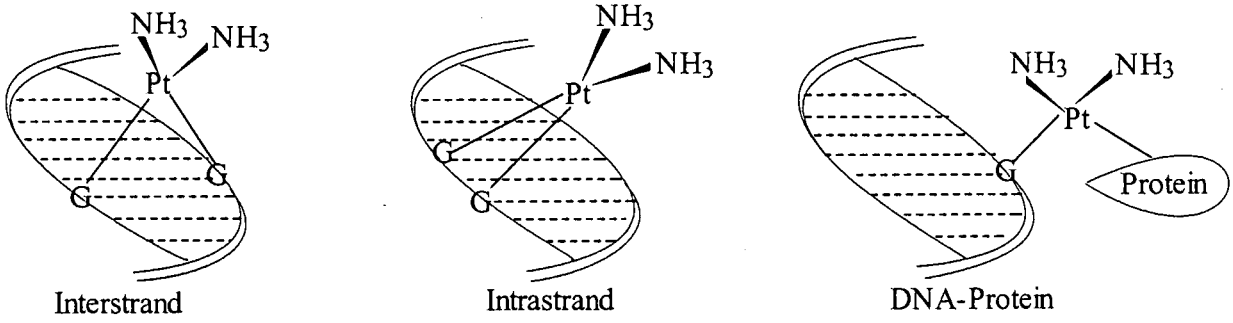


Figure 2.4: Possible ways of binding of *cis*-$[PtCl_2(NH_3)_2]$ to DNA.

Binding of cisplatin to the N7 atoms of the two neighbouring guanosine nucleosides in the DNA, when it forms the 1,2-intrastrand cross-links, disrupts the orderly stacking of the bases thus bending the DNA helix and causing it to unwind by some degree resulting in the distortion of the helix. These cross-links are believed to block DNA replication and this results in the death of the tumour cell.

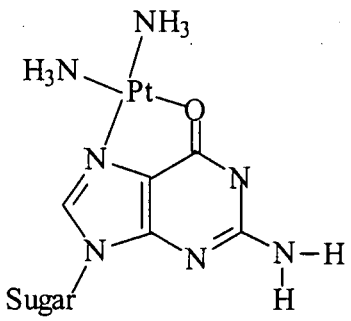
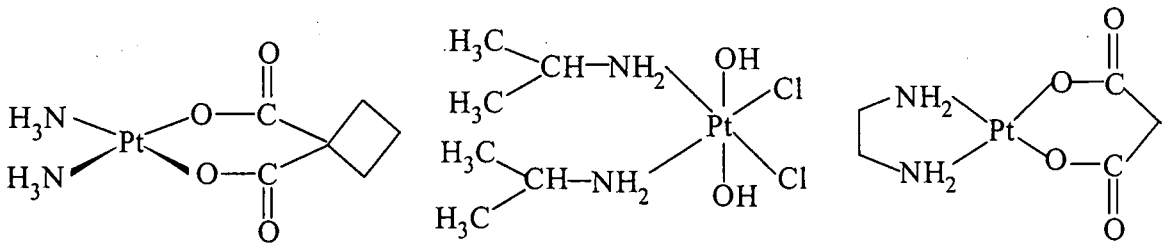


Figure 2.5: Bifunctional binding of cisplatin to guanine.

Figure 2.5 shows another way of coordination of cisplatin to the DNA, where it binds to the same guanine molecule, although this form of binding is of little significance. It is very fascinating to suggest that this mode of binding is important to the antitumour activity of cisplatin since the *trans* isomer cannot form such a closed ring chelate involving the guanine N(7)-O(6) positions while cisplatin can. The alkylation at the O(6) site has also been postulated as the most relevant in causing mutation in cells when alkylating agents are employed.

The study and the understanding of these mechanisms involved in the binding of platinum complexes to DNA is very important in designing better and more effective metal based drugs with less side effects. This goes for more than chemotherapy and includes treatment of other diseases like arthritis.

Other platinum complexes[13] that are known as second generation platinum antitumour drugs are illustrated in **Fig. 2.6**.



I **II** **III**

Figure 2.6: Platinum compounds studied for antitumour activity. **I**, Carboplatin; **II**, *cis*-dichloro-*trans*-dihydroxy-*cis*-bis(isopropylamine)platinum(IV), (Iproplatin); **III**, Malonatoplatinum.

Carboplatin, (*cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II)), displays similar activity to that of cisplatin but is less toxic and is used to treat ovarian tumours. Although it causes less nausea, it has a side effect of lowering platelet levels. Iproplatin contains platinum (IV) in an octahedral coordination sphere and is an example of a platinum complex containing organic ligands but lacks carbon-metal bonds.

Several complexes containing metals other than platinum have also been studied[14], these include auranofin (**Fig. 2.7**, which is the gold(I) species active against primary chronic polyarthritis), iron compounds and some ruthenium derivatives. Main group metal compounds like gallium(III) nitrate[15], have been known to have antiproliferative activity. Titanium and vanadium compounds such as metallocenes[16], *e.g.* $[(C_5H_5)_2TiCl_2]$, have also shown antitumour activity.

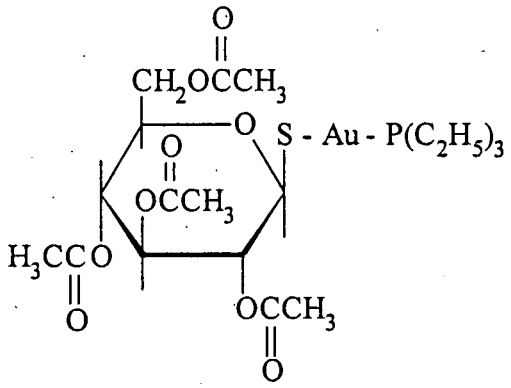


Figure 2.7: Structure of (2,3,4,6-tetra-O-acetyl-1-thio-1-β-D-glucopyranosato)(triethylphosphine)gold(I) complex, (Auranofin).

Interestingly enough, is that platinum complexes known as 'platinum blue complexes' have been found to be antitumour active[17]. Although first formulated as $[Pt(CH_3CONH_2)]\cdot H_2O$[18], this was modified later and the first X-ray structural study revealed an α-pyridonate-bridged platinum blue complex, $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5\cdot 2H_2O$. They were first discovered as a result of studies on the interaction of *cis*-$[PtCl_2(NH_3)_2]$ and its aquated products with pyrimidines which produced dark-blue compounds. The platinum-pyrimidine blues, derived from cisplatin are an interesting class of complexes with antitumour activity. The results of antitumour screening on these blue complexes indicated activity characterised by high aqueous solubility and low toxicity[19]. The studies conducted on these complexes have elucidated the principal structural and chemical features of these species, a good example where interest in biological activity has led to the development of new platinum coordination chemistry.

2.3 SUBSTITUTION REACTIONS IN PLATINUM(II) COMPLEXES

2.3.1 Introduction

The main objective of this section is to introduce and discuss substitution reactions; reactions wherein ligand-metal bonds are broken and new ones are formed *via* various mechanisms. Substitution involves the replacement of the ligand coordinated to a metal by a free ligand in solution or the replacement of a coordinated metal ion by a free metal ion. There is no change in the oxidation state of the metal, but a change may take place as a result of substitution. The focus will also be on the replacement reactions at four-coordinate planar reaction centres.

The most studied square planar complexes are those based on transition metal ions with low spin d^8 electron configurations, mainly the platinum group metals.

Table 2.1: Examples of d^8 metal centres.

Co(I)	Ni(II)	Au(III)
Rh(I)	Pd(II)	
Ir(I)	Pt(II)	

Of these, the substitution reactions of platinum(II) have been the most intensively studied since it has the following useful properties:

- Pt (II) is more stable to oxidation as compared to Pd(II), Rh(I) or Ir(I).
- The platinum(II) substitution reactions proceed at rates convenient for the application of classical monitoring techniques.
- Complexes of platinum(II) are always square planar, unlike Ni(II) complexes which can often be tetrahedral, especially with weak ligands.

Platinum(II) complexes are therefore representatives of this geometry, much as the Co(III) complexes epitomize the octahedral behaviour particularly for the same reasons that they have been well studied and characterised. The chemistry of platinum and palladium complexes has been reviewed in deeper details[20].

2.3.2 Important factors in square planar substitution

A deeper understanding of substitution reactions of square planar platinum complexes is of importance to various fields of chemistry such as homogeneous catalysis, electron transfer reactions and chemotherapy.

Substitution reactions of X for Y in $PtXL_3$ (**Eq. 2.5**) follow a two-term rate law which is represented by **Eqs. 2.6** and **2.7**,

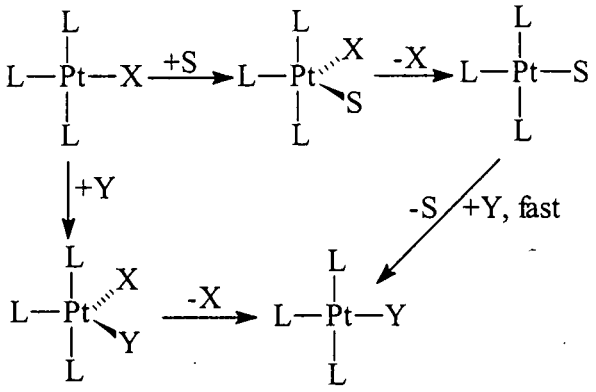
$$PtXL_3 + Y \longrightarrow PtYL_3 + X \qquad (2.5)$$

$$\text{Rate} = \{k_S + k_Y[Y]\}[PtXL_3] \qquad (2.6)$$

$$k_S = k[\text{Solvent}] \qquad (2.7)$$

where k_S is the first-order rate constant for the solvolytic pathway and k_Y is the second-order rate constant for a direct bimolecular substitution pathway. This rate law is typical for square planar complexes and it has been rationalised in terms of two parallel pathways both involving an associative mechanism.

This rate law requires a two-path reaction mechanism and the pathway is represented in **Scheme 2.1**.



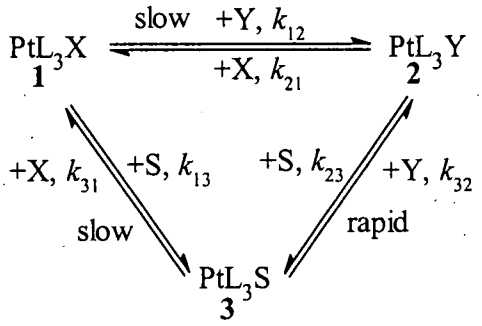
Scheme 2.1: Two parallel reaction pathways involved in square planar substitution reactions.

In the k_Y pathway, the ligand Y attacks the metal complex and the reaction proceeds *via* a five-coordinate transition state which is generally taken as having a trigonal bipyramidal stereochemistry. The associative mechanism also implies a labile five-coordinate intermediate, which is formed in the rate determining step. The existence of stable five-coordinate complexes[21] of platinum(II), nickel(II) and palladium(II) is in mutual agreement with an associative mechanism.

Since the geometry of the original complex is retained, that is the ligands *cis* and *trans* to the replaced ligand remain in the same arrangement to the entering groups, the entering and leaving groups and the ligand originally *trans* to the leaving groups must lie in the trigonal plane. A similar mechanism also applies in the k_S pathway but the solvent is the entering group and is then displaced by the ligand Y in a rapid consecutive associative process.

During the early years of systematic investigation on the reaction mechanisms of inorganic systems, substitution mechanisms at octahedral sites were dominated by studies on Co(III) complexes while substitution mechanisms at square planar sites featured Pt(II) complexes.

It has been proven that, in general, square planar substitution reactions occur *via* an associative mode of activation almost without exception, although some examples do follow dissociative mechanism. The rate laws for square planar substitution reactions are more complicated when equilibria are present. A schematic representation of such a square planar substitution reaction is given in **Scheme 2.2**.



Scheme 2.2: Representation of a square planar substitution reaction involving full reversibility in all steps.

In **Scheme 2.2** S refers to the solvent and the solvent concentration is included in the rate constants k_{13} and k_{23}. Complete reversibility is considered in all the reactions resulting in the following expression for the observed pseudo first-order rate constant given in **Eq. 2.8**.

$$k_{obs} = k_{12}[Y] + \frac{k_{12}}{K_{eq}}[X] + \frac{\frac{k_{13}}{K_{eq}}\frac{k_{32}}{k_{31}}k_{31}[X] + k_{32}k_{13}[Y]}{k_{31}[X] + k_{32}[Y]} \qquad (2.8)$$

In the more traditional form, if all reactions are considered non-reversible (large equilibrium constants in all cases), the expression simplifies to **Eq. 2.9**.

$$k_{obs} = k_{12}[Y] + k_{13} \qquad (2.9)$$

As portrayed in the scheme there are two possible reaction routes, first being the direct attack by the entering ligand on the metal centre resulting in a five-coordinate intermediate (k_{12} route). The second route involves a concurrent bimolecular attack by the solvent forming the solvento intermediate which is followed by the attack of the entering ligand to yield the final products (k_{13} route).

Important factors in square planar substitution reactions are:

- The nature of the entering group.
- The effect of other groups in the complex *e.g.* ligands that are *cis* or *trans* to the leaving group.
- The nature of the leaving group and of the central metal ion.
- The nature of the solvent.

For Pt(II) complexes, these factors have been arranged in order of decreasing dominance, although this is not always the case for the other d^8 metal ions. One of the consequences of an associative mechanism is the importance of all the ligands, entering, leaving and non-labile, on the rate of the substitution reaction.

This arises because all the ligands involved are present in the five-coordinate activated complex and can therefore affect its stability and the activation energy for its production. This feature points out the difference in square planar substitution reactions as compared to octahedral substitution.

A. The effect of the entering group on substitution reactions

There have been extensive studies on the influence of a ligand on its rate of entry into a Pt(II) complex[22,23]. When the reaction proceeds *via* an associative mechanism, the rate must then in a way depend on the character of the entering group. Evaluating the entering group effects is as much the same as ascribing a nucleophilicity order to the incoming ligand. This order depends on both the nucleophile and the electrophile[24] and the nucleophilicity of the reactant is the normal referred parameter in substitution reactions of this type. Nucleophilicity is a concept which refers to the ability of a Lewis base to act as the entering group thereby influencing the rate of the reaction in a nucleophilic substitution, hence it is a kinetic term.

Important factors determining the reactivity of nucleophilic reagents are basicity, polarisability and the presence of unshared pairs of electrons on the atom adjacent to the nucleophilic atom. The relationship of basicity and nucleophilic character is implicit in the fact that substitution reactions are generalised acid-base reactions. In these reactions, the nucleophilic ligand is interacting most directly with the electrophilic atom which, in the ground state, is bonded to the leaving group and has a net negative charge.

However, in the transition state the electrophilic atom has acquired a positive charge of some sort since the leaving group would remove the negative charge from it. Therefore, there should be a relationship between the occurrences in the transition state and the rate of substitution reactions.

The reasons for the effect of high polarisability on the rate are not quite well understood but the polarisation of non-bonding electrons on the nucleophilic atom away from the electrophilic one reduces the electrostatic repulsion between the nucleophilic atom and the leaving group.

There were attempts made to predict and calculate the nucleophilicity of the entering group[25] and one of the earliest discoveries relating nucleophilicity and reactivity was that made by Swain and Scott[26]. From this study it was formulated that the nucleophilicity parameter for ligands attacking platinum(II) complexes is defined by **Eq. 2.10**,

$$\log(k_Y/k_S) = sn_{Pt} \qquad (2.10)$$

where k_Y is the rate constant for the reaction of the nucleophile and the Pt(II) complex and k_S denotes the rate constant of the solvent reaction with the complex, the parameter s is the nucleophilic discrimination factor and n_{Pt} is the nucleophilicity reactivity constant.

Table 2.2: Nucleophilicity constants[27] for various ligands to *trans*-$[PtCl_2(py)_2]$.

Nucleophile	n_{Pt}	Nucleophile	n_{Pt}
$CH_3CO_2^-$	< 2.4	$(PhCH_2)_2Se$	5.39
Cl^-	3.04	I^-	5.42
NH_3	3.06	$(CH_3)_2Se$	5.56
NO_2^-	3.22	SCN^-	6.65
N_3^-	3.58	Ph_3Sb	6.65
NH_2OH	3.85	Ph_3As	6.75
Br^-	4.18	Ph_3P	8.79
$(CH_2)_5S$	4.88	Et_3P	8.85

In the various studies done in determining the nucleophilicity parameters using the classical *trans*-$[PtCl_2(py)_2]$[22] complex, it was noted that the nucleophilicity of the halide ions decreases in the order, $I^- > Br^- > Cl^- >> F^-$. The Group 15 donors decrease their nucleophilicity in the order, phosphines > arsines > stibines >> amines. It was also concluded that sulphur donors are better nucleophiles than oxygen ones. These observations can be of major importance in the synthesis of complexes. Recently the complex $[PtCl(NH_3)en]^+$ (en = ethylenediamine) has been used as a reference to determine nucleophilicity constants with the same nucleophiles[28,29,30].

B. The influence of the ligands *trans* or *cis* to the leaving group

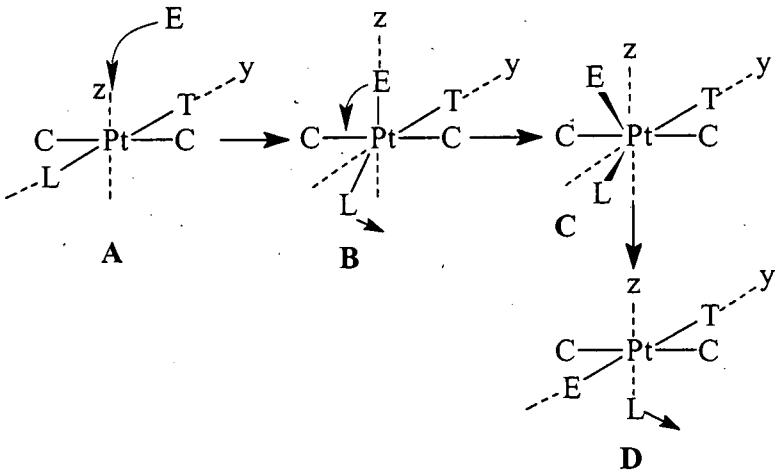
The nature of the ligand *trans* to the leaving group in square planar Pt(II) complexes plays a vital role on the course of substitutions and it may be used to explain if any stereochemistry is involved. The primary factor to be considered when interpreting kinetic data for these complexes is the *trans* effect.

The *trans* effect may be defined as the effect of the coordinated ligand upon the rate of substitution of a ligand coordinated *trans* to it. Therefore in square planar Pt(II) complexes certain groups can, more quickly than others, influence elimination and substitution of groups *trans* to themselves. Further examination and comparison of the reactions of Pt(II) complexes has led to the qualitative development of the *trans* influence. The *trans* influence considers the behaviour at the ground state level, whereas the *trans* effect is important in the transition state level since it is a measure of the relative substitution rates.

From the definitions above it can be seen that the *trans* effect is a kinetic phenomenon and the *trans* influence a thermodynamic phenomenon. Considering Pt(II) complexes, the *trans* effect is in the order[27]: CN^-, C_2H_4 > PR_3, H^- > Me^-, $SC(NH_2)_2$ > Ph^-, NO_2^-, I^-, SCN^- > Br^-, Cl^- > pyridine > NH_3, OH^-, H_2O.

The groups with the greatest ability to *trans* labilise are replaced the least easily and are the more powerful nucleophiles. This might be anticipated since in the five-coordinate intermediate, (**Scheme 2.3**), the entering nucleophile E, the *trans* ligand T, and the leaving group L all occupy positions in the trigonal plane and all may influence the energy relations of the transition state in similar ways. The *trans* effect partly depends on the nature of the entering ligand and also the effects of the *trans* ligands and the entering groups cannot be neatly divided.

Square planar substitution reactions proceed *via* a trigonal bipyramidal transition state as shown in **Scheme 2.3** below.

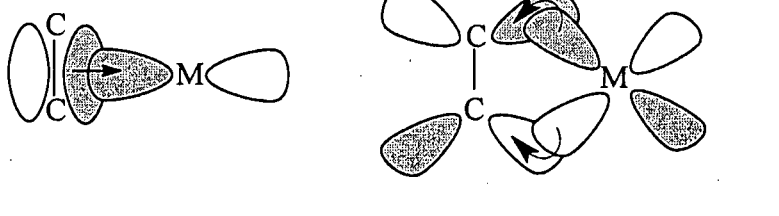


Scheme 2.3: Illustration of the entering ligand approach.

As the entering ligand (E) approaches the complex, the symmetry of its donor orbital is in line for overlap with the unoccupied metal p_z orbital (**A**). From this point the entering ligand can replace any of the four ligands present in the complex but the preferred direction will be to move towards the leaving group and away from the strongly bound *trans* ligand (**B**). This shows a connection between the *trans* effect and the *trans* influence as some ligands weaken the bond to the *trans* ligand hence causing it to leave and this happens with the molecule in the ground state.

The transition state is a trigonal bipyramid where the leaving group must move away from the y-axis faster than the entering ligand approaches the y-axis. The overall effect will be that the overlap of E and L in the p_y orbital is less than the overlap of L with the orbital in the Pt(II) complex. This results in the occupation of T with the p_y orbital to increase, especially if T is an effective σ-donor such as CH_3^- causing greater stabilisation in the transition state, particularly with more strongly bonding T groups thus enhancing the reaction rate.

This remarkable explanation of the transition state stabilisation can also be applied to olefins in labilising *trans* ligands and to explain by π-bonding why they are high in the series. The two ways that an olefin binds to a metal are by a donation of π electrons in the olefin to the metal σ orbital and the back-donation of metal electron density from the metal π orbital into the olefin π^* orbital, which are illustrated in **Fig. 2.8**.



Olefin to metal electron transfer

Metal to ligand electron transfer

Figure 2.8: Illustration of the bonding of an olefin to a metal.

In substitution reactions, the approach of the entering ligand causes the electron density on the metal to increase and this density is removed by the metal-*trans* ligand atomic orbital interaction ($d\pi$-π^*). This stabilises the transition state hence facilitating the reaction, and increasing the rate.

With comprehensive research the *trans* influence order has been determined as Si > σ-R ~ H^- ≥ carbenes ~ PR_3 ≥ AsR_3 > CO ~ RNC ~ C=C ~ Cl^- ~ NH_3. In associative mechanisms the question arises if bond weakening destabilises the ground state more or less as it does in the transition state. If a pair of atoms sharing the same *p* orbital greatly differ in electronegativity, then the less electronegative atom will form its covalent bond at the expense of the more electronegative atom. This means that the bond between the metal and the leaving group will be strong if the *trans* ligand is more electronegative.

Highly electronegative donors have a low bond strengthening effect and in the transition state which is trigonal bipyramidal, the competition between the two *trans* groups is relieved since they no longer compete for the same orbital in such a manner. Much information has been provided on the effect of the ligands, which are *cis* to the leaving group, on the rate of substitution reactions. This usually happens if the entering group is a poor nucleophile and the ability of the ligands to act as *trans* labilisers is the same as ability to act as *cis* labilisers although to a lesser extent.

The *cis* effect is less observed than the *trans* effect and is more observed in *o*-tolyl and mesityl ligands[31], which lead to a slow reaction due to steric hindrance influenced by the *o*-methyl substituents. It is also known that the *cis* effect is dependent upon the nature of the entering group. The order of the *cis* effect is PEt_3 < $AsEt_3$ < pyridine < piperidine when the incoming ligand is a poor nucleophile (*e.g.* NO_2^-) but the trend changes to piperidine < pyridine < PEt_3 < $AsEt_3$ for good nucleophiles such as $SeCN^-$ and thiourea. This inversion of trend has been explained in terms of *cis* ligands labilising the metal-leaving group bond and in determining the electron density at the reaction centre. Ligands that weaken bonds *trans* to themselves also weaken *cis* metal-ligand bonds and this depends only on one orbital, d_{x2-y2}. Therefore, bond breaking in the transition state is easier for good *cis* directors and this enhances the rate of the reaction although not as much as if the *cis* ligand were in the *trans* position.

C. The effect of the leaving group and the central metal on substitution

The nature of the leaving group can also have an effect on the rate of substitution reactions[32]. An example studied was of the complex $[PtX(dien)]^+$ where X was replaced by pyridine to give $[Pt(dien)(pyridine)]^{2+}$ with a range of leaving groups[33]. The effect of the leaving group on the reactivity order was determined as $NO_3^- > H_2O > Cl^- > Br^- > N_3^- > SCN^- > CN^-$.

The central metal atom also plays a role in square planar substitution reactions. It is found that the tendency to undergo substitution decreases in the order: Ni(II) > Pd(II) >> Pt(II) and this is the same with the formation of five-coordinate complexes. The formation of this intermediate complex leads to stabilisation and thereby speeding up the rate of the reaction.

D. Other important factors in substitution reactions

Since substitution reactions follow a two-term rate law it would be obvious that the solvent effects are very noteworthy. The solvent is the reaction medium and therefore by solvating the ground and the activated states it will influence the energy levels of the activation process. Weakly coordinating solvents include organic solvents such as benzene and carbon tetrachloride and strongly coordinating are water, DMSO, lower alcohols *etc.*

Steric effects are very useful in exploring mechanisms of square planar substitution reactions. Much work has been done[34,35] to obtain three-coordinate intermediates by using bulky ligands to prevent bond formation while simultaneously facilitating dissociation due to steric crowding around the central metal atom. In these studies comparison of the reaction rates of diethylenetriamine platinum(II) and palladium(II) complexes with those of N-alkyl substituted analogues was done. Crowding around the metal ion is expected to retard the rates of reactions that occur *via* an associative mechanism and to accelerate the rates occurring *via* a dissociative mechanism.

Increased steric hindrance caused by alkyl substitution on the terminal nitrogens of a coordinated diethylenetriamine ligand brought a dramatic decrease in both the nucleophile dependent and the nucleophile independent rate constants. In most sterically hindered systems the rate of substitution was greatly controlled by the solvent pathway. In most sterically hindered systems the effect of the nucleophile independent rate constant disappears leaving the rate of halide substitution controlled by the solvolytic pathway. However, this does not provide enough evidence of a dissociative mechanism involving a three-coordinate intermediate. In systems like these the substrate molecule cannot make a distinction between different entering ligands and the solvent remains as the nucleophile of choice. The sterically hindered aqua complexes $[M(R_5\text{-dien})(H_2O)]^{2+}$ (R = alkyl substituent, M = Pt(II) or Pd(II)), were found to exhibit discrimination between the entering nucleophiles while the solvolytic pathway was kinetically undetectable[36].

The effect of charge is also important in substitution reactions of platinum(II) complexes. A neutral ligand will react faster with a negatively charged complex than a negatively charged ligand would. With all other things held constant an increased positive charge should make bond breaking between the ligand and the metal more difficult. Hence it is expected that the rate will decrease with increasing positive charge for dissociative activation. For a metal ion in a given oxidation state, there is no way to vary the overall charge on the complex without introducing differently charged ligands which leads to a change in σ- and π-bonding. Even so, an increase in the rate as the positive charge decreases has been accepted as proof of a dissociative activation. Exactly the opposite holds for an associative mechanism in that, reactivity increases with increase in positive charge. This causes a more favoured entrance for the nucleophiles due to electronic attraction.

2.3.3 Dissociative substitution mechanism

The normal mode of activation for substitution at square planar d^8 metal centres is associative. However, as mentioned earlier, bulky *cis* groups such as *o*-tolyl or mesityl lead to slow substitution rates due to steric hindrance thus preventing the coordination of the fifth ligand. For a dissociative pathway the following is noted:

- Reaction rates are independent of the entering group concentrations even when good nucleophiles such as SCN^-, I^-, PhS^-, $S_2O_3^{2-}$ are employed at high concentrations.
- Steric hindrance on the complex should increase the rate.
- Large enthalpies of activation, positive volumes- and entropies of activation.

A dissociative mechanism in the case of ligand substitution would be where the activation energy is determined primarily by the energy required to break the bond to the leaving group. Two elementary steps are possible in the dissociative mechanism. First, the complex accumulates enough energy to completely break the metal-leaving group bond, leaving a three-coordinate intermediate. Second, this intermediate reacts with the entering group, which could be a solvent, from the second coordination sphere.

Extensive research has been done[37, 38,39] to indicate that some platinum(II) complexes undergo substitution *via* a dissociative mode of activation. Complexes investigated were of the type, *cis*-$[PtR_2S_2]$ (R = Me or Ph; S = R_2S, Me_2SO) which when reacted with nitrogen chelating ligands (L-L) yield $[PtR_2(L\text{-}L)]$ products in non-polar solvents. The facile dissociation is derived essentially from the strong σ-donor power of the *trans* methyl or phenyl groups, which lengthen and weaken the Pt-S bond. Elding and Wendt[40] also obtained similar results when they showed that substitution of the phosphine ligands in *cis*-$[Pt(SiMePh_2)_2(PMe_2Ph)_2]$ by the bidentate phosphine ligand bis(diphenylphosphino)ethane follows a dissociative mode of activation.

It was found that the silyl ligands are more effective in blocking associative attack, in accordance with the higher *trans* influence thereof. For a dissociative mechanism, the rate of the reaction is independent of the nature of the entering ligand and the large positive values of the enthalpies- and entropies of activation gives strong support of ligand dissociation as the dominant pathway[38].

The rate also tends to be independent of the concentration of the entering ligand as the concentration of the free sulphur donor ligand is increased. The normal bimolecular attack is displayed by the stronger entering nucleophiles such as the dithioethers and bisphosphines, therefore, a reaction scheme having both associative and dissociative pathways can be proposed and the associative pathway is not considered for ligands with weak donor atoms such as nitrogen.

Sulphoxides are ambidentate ligands that can bind to metals through sulphur or oxygen. The normal mode of bonding to the platinum(II) complex is through sulphur except in cases where the ligand is forced into a sterically crowded surroundings. In platinum complexes containing sulphoxides, it was noted that there is discrimination between the different entering nucleophiles. The stabilised 14-electron transition state, which is three-coordinate, is formed through the interaction of the sulphoxide oxygen atom with the empty coordination site. In this way, the three-coordinate intermediate is stabilised giving it a lifetime long enough to discriminate between the different entering nucleophiles.

In principle, it should be possible to promote a dissociative mechanism by increasing bond weakening in the platinum-leaving group bond by using strong σ-donor *trans*-activating ligands that stabilise the three-coordinate intermediate. The use of good leaving groups like nitrate, acetate and solvent molecules helps in dissociation as well.

2.4 PHOSPHINE COMPLEXES OF PLATINUM

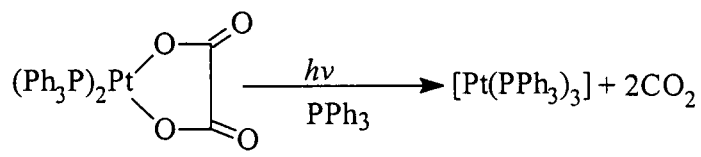
2.4.1 Introduction

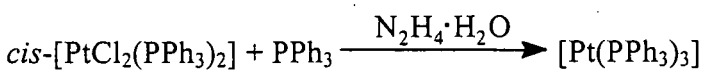
Phosphines are of significant importance as ligands in platinum chemistry. Trivalent phosphorus donor ligands[41], PR_3 (R = aryl, *O*-alkyl, *O*-aryl, F, Cl, H, alkyl) have played an important role in the development of coordination and organometallic chemistry.

Studies have also been conducted[42] in tertiary phosphines, (PR_nQ_{3-n}, R = Me, Et, ^{t}Bu or Ph and Q = CH_2OCOMe, CH_2OH), with the halides of metals of group VIII and their applications in catalysis in reactions such as the isomerisation and the hydrogenation of olefins and acetylenes. Tertiary phosphines have also been involved in substitution and isomerisation reactions in platinum(II) complexes[43].

2.4.2 Platinum(0) phosphine complexes

The most known simple platinum(0) complex is $[Pt(PPh_3)_3]$ and its synthesis and chemistry was already done in the late 60's[44]. This complex was synthesised by photochemical decomposition of the oxalato complex in the presence of alkynes (C_2R_2) or triphenylphosphine or by the reduction of *cis*-$[PtCl_2(PPh_3)_2]$ with hydrazine or ethanolic potassium hydroxide as illustrated in **Scheme 2.4**.



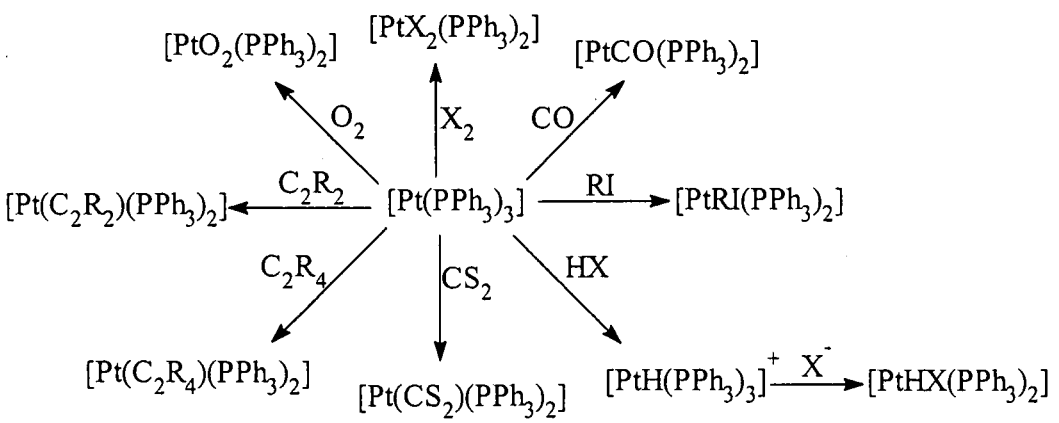


Scheme 2.4: Methods of synthesis of $[Pt(PPh_3)_3]$.

Addition of additional PPh_3 to a solution containing this complex forms $[Pt(PPh_3)_4]$ as proved by ^{31}P NMR spectroscopy. The exact coordination number for these platinum complexes is influenced by both steric and electronic factors. A similar arsine complex can also be prepared as a colourless solid. The triethylphosphine complex, $[Pt(PEt_3)_4]$, can be prepared by the reaction of $PtCl_2$, PEt_3 and potassium in THF solvent giving high yields of the complex. This synthesis is carried out in dry nitrogen atmosphere because of the air sensitivity of the complex and the PEt_3 ligand.

There are numerous reactions that the tris(triphenylphosphine)platinum(0) complex can undergo including oxidative addition reactions with the halides to give *cis*-$[PtX_2(PPh_3)_2]$ (X = Br, I). The *trans* isomers can be obtained if the complex is reacted with the excess of the halide for a short time. The excess halogen oxidises the free triphenylphosphine but short reaction times prevent the formation of large amounts of $[PtX_4(PPh_3)_2]$.

Other reactions of $[Pt(PPh_3)_3]$ include addition of HX or RX giving $[PtHXL_2]$ and $[PtRXL_2]$, respectively. Replacement of a phosphine ligand with carboranes, alkenes and alkynes (L^*) to give PtL_2L^* complexes and protonation reactions to give $PtHL_3^+$ are also known. A summary of the commonest reactions is given in **Scheme 2.5**.



Scheme 2.5: Summary of $[Pt(PPh_3)_3]$ reactions.

Platinum(0) complexes with tertiary phosphines are known to have numerous applications in catalysis. The heterogeneously catalysed water-gas shift reaction requires high temperature, thus homogeneous catalysts active at lower temperatures are of considerable interest. With $[Pt(PPh_3)_4]$ no reaction occurs but with the complex $[Pt(P^iPr_3)_3]$, the turnover numbers are high when the temperature is high and acetone is used as a solvent.

A reaction mixture of the water-gas shift reaction catalysed by $[Pt(PEt_3)_3]$ in acetone contained a water adduct, $[PtH(PEt_3)_3]OH$, which was isolated as the salt in considerable amounts. The catalytic activity of these PtL_3 complexes decreases in the order $P(^iPr)_3 > PEt_3 >> PPh_3$.

The fact that no catalytic activity is shown by $[Pt(PPh_3)_3]$ can be due to the incapability of water adduct formation. When the bulky phosphine substituents are used, the platinum(0) complexes become two-coordinate and these complexes have received a vast amount of interest. The stabilisation of such complexes depends on the steric bulk of the phosphine. Complexes such as $[Pt(P^tBu_3)_2]$ and other analogues can be prepared by sodium reduction of $[PtCl_2L_2]$ complexes or by the substitution of the cyclooctadiene ligand in $[Pt(cod)_2]$ by any of the phosphine ligands.

Another method of preparing these two-coordinate complexes[45] is by treating the methoxy-bridged binuclear platinum complex, $[Pt(\mu\text{-}OCH_3)(C_8H_{12}OCH_3)]_2$, with two equivalents of the phosphine in an alcoholic solvent such as methanol. These reactions proceed rapidly at normal temperatures and under an inert atmosphere to give the corresponding bis(tertiary phosphine)platinum(0) complexes. Complexes of this type oxidise readily in air or when reacted with oxygen to form the dioxygen platinum(II) complexes, $[PtO_2(R_3P)_2]$, (R_3P = Cy_3P, $^tBuPh_2P$, $^tBu_2MeP$, $^tBu_2{}^nBuP$). However when tri-t-butyl phosphine was used, no dioxygen complex was obtained but only the bisphosphine complex was regained in almost quantitative yields, perhaps because of the bulkiness of the phosphine which prevented the oxidation process.

Tertiary phosphite platinum(0) complexes can be prepared by the hydrazine reduction of $[PtCl_2\{P(OR)_3\}_2]$ or by the replacement of triphenylphosphine in $[Pt(PPh_3)_3]$. These reactions are given in **Scheme 2.6** and a detailed synthesis of $[Pt\{P(OEt)_3\}_4]$ from K_2PtCl_4 and triethyl phosphite with KOH has been reported[46].

$$[PtCl_2\{P(OR)_3\}_2] + 2P(OR)_3 \xrightarrow{N_2H_4} [Pt\{P(OR)_3\}_4]$$

$$[Pt(PPh_3)_3] + nP(OR)_3 \longrightarrow [Pt\{P(OR)_3\}_n] + 3PPh_3$$

$$K_2PtCl_4 + 5P(OEt)_3 + 2KOH \longrightarrow [Pt\{P(OEt)_3\}_4] + OP(OEt)_3 + 4KCl + H_2O$$

Scheme 2.6: Synthesis of platinum(0) phosphite complexes.

2.4.3 Platinum(IV) phosphines

Platinum(IV) is a familiar oxidation state invariably found in six-coordinate environments and with octahedral or distorted octahedral geometry. The chemistry of platinum(IV) complexes is less pronounced than that of the other two main oxidation states of platinum. Platinum(IV) complexes can be prepared by the halogenation of platinum(II) phosphine or phosphite complexes (**Eq. 2.11**).

$$\mathbf{[PtCl_2(P\,^nPr_3)_2] + Cl_2 \longrightarrow [PtCl_4(P\,^nPr_3)_2]} \qquad \mathbf{(2.11)}$$

The following complexes can be prepared by the similar method, *trans*-$[PtX_4(PEt_3)_2]$ (X = Cl, Br, I), *cis*-$[PtX_4(PEt_3)_2]$ (X = Cl, Br), *cis*- and *trans*-$[PtCl_4(P^nBu_3)_2]$ and *cis*-$[PtCl_4(PPh(CH_3)_2)_2]$. A rare example of a phosphine oxide complex of a high valent metal centre is found in $[PtBr_4L]$ (L = 2-pyridyldiphenylphosphine oxide)[47].

2.4.4 Platinum(II) phosphines

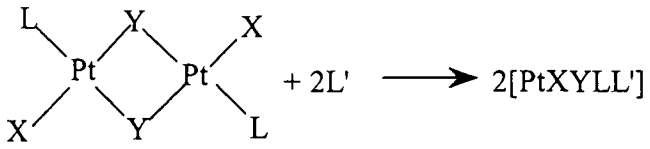
Tertiary phosphines, PR_3, form a wide variety of complexes of the type $[PtX_2(PR_3)_2]$ (X = halide, pseudo-halide; R = alkyl, aryl, or mixed alkylaryl). The increasing utility of substituted phosphine complexes of platinum(II) as starting compounds in preparative chemistry and as homogeneous catalysts makes the search for new convenient synthesis of these complexes more interesting. These tertiary phosphines react with PtX_4^{2-} to give $[PtX_2(PR_3)_2]$ complexes. When R is a lower alkyl group the initially formed ionic complex only slowly converts to the final product[48]. If the *cis* and *trans* isomers are formed, it may be possible to separate the isomers by fractional crystallisation[49].

Platinum(II) complexes have also been prepared from $H_2PtCl_6 \cdot H_2O$ and the *cis* complexes $[PtCl_2(PPh_3)_2]$ or $[PtCl_2(P\text{-}P)]$ (P-P = $Ph_2P(CH_2)_nPPh_2$; n = 1, 2, 4) are prepared by addition of excess phosphine using ethanol as a solvent. To prepare the *trans*-$[PtCl_2(PPh_3)_2]$ complex aqueous formaldehyde is added to the solution. However, there can be a substantial amount of the platinum metal that may be deposited.

The most used reaction for the preparation of complexes with mixed phosphine ligands is by bridge cleavage (**Scheme 2.7**). The strength of the bridge bonds increases in the series $Cl^- < Br^- < I^-$ and $Cl^- < Et_2PO^- < RS^- < R_2P^-$. The weaker bridges can be broken by phosphine ligands L' to give monomeric phosphine complexes of platinum(II). The bridge cleavage reaction can be reversed by fusion of the monomeric complex $[PtCl_2L_2]$ with $PtCl_2$. This cleavage method can also be used to prepare complexes with different phosphine ligands and also complexes of platinum(II) with halogenated Group 7 ligands giving *cis*-$[PtX_2LL']$ (L' = PPh_2Cl, PEt_2Cl, $AsPh_2Cl$, $As(CH_3)_2Cl$).

$$2PtCl_4^{2-} + 4PR_3 \longrightarrow [Pt(PR_3)_4][PtCl_4] \longrightarrow 2[PtCl_2(PR_3)_2]$$

$$3PtCl_2 + 4PX_3 \longrightarrow [PtCl_2(PX_3)_2] + [PtCl_2(PX_3)]_2 \ (X = F, Cl)$$



Scheme 2.7: Synthetic reactions of platinum(II) phosphine complexes.

2.4.5 Water-soluble phosphines

Most water-soluble phosphines have ligands with hydrophilic functional groups and are mainly used in the field of catalysis. The development of transition metal reagents for use in aqueous solvent systems offers advantages for a wide variety of chemical processes ranging from large scale industrial processes to fine organic synthesis. The low water-solubility of most organometallic compounds has confined the study of their chemistry to organic media[50]. The use of water-soluble reagents for chemical manufacture can simplify catalyst-product separation and is also interesting because of the economy and the safety of using water as a solvent.

Water has a variety of properties that set it apart from most organic solvents, and hence it is possible that one might observe very different chemistry in aqueous solution. Therefore, there has been interest in the water-solubilisation of organometallic compounds. This is generally achieved *via* coordination of hydrophilic ligands usually functionalised tertiary phosphines.

A variety of hydrophilic moieties that have been employed include $-NR_3^+$, -COOH, $-SO_3^-$ and -OH groups which either act as separate units or as polymers containing one of these groups. Of these the sulphonic acid group, $-SO_3^-$, is used most frequently since it can be easily attached to already available phosphines containing phenyl groups. There has been a review article[51] that describes a large number of compounds prepared from such phosphines, in some cases comparing catalytic activities of their complexes with those of the more typical, non-functionalised phosphines. Unfortunately, hydroxyl group-containing ligands often do not exhibit greatly enhanced water-solubility while phosphines containing amino or carboxyl groups are soluble only in acidic or basic media respectively.

The amount of impurities from oxidation products can be kept low with the new developed methods of sulphonation[52]. Compounds containing sulphonated triphenylphosphines have been studied extensively[53].

These ligands containing the sulphonic acid moiety can therefore be grouped together with those that contain a charge like the quaternary ammonium ions (Amphos) or phosphonium ions as hydrophilic functional groups. The indefinite charged functional groups induce high water-solubility to the ligands and this high water-solubility makes sulphonated ligands very versatile in aqueous/organic biphasic catalysis. The problem of catalyst separation still exists however, if substrates with low solubility in the organic phase are used.

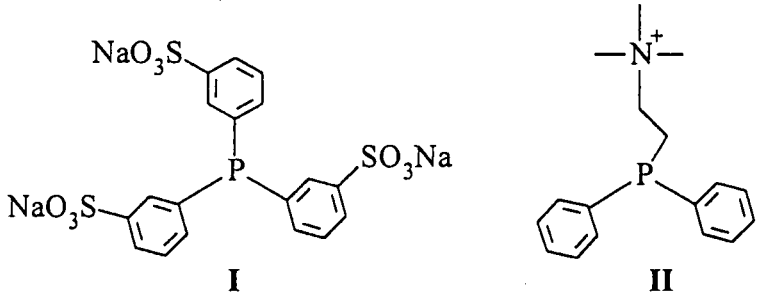


Figure 2.9: Examples of water-soluble phosphines: **I**, TPPTS and **II**, Amphos.

An example of a cationic water-soluble phosphine that has been synthesised and characterised is (2-diphenylphosphinoethyl)trimethylammonium iodide, amphos iodide[54]. Its metal carbonyl substitution complexes include iron, molybdenum and tungsten complexes as iodide salts, showing greatly enhanced solubility in polar solvents. Amphos acts as a typical tertiary phosphine, its electron donor properties are slightly lower than those of $P(CH_3)Ph_2$ and PPh_3. Amphos iodide is synthesised in high yields from 2-dimethylaminethyldiphenylphosphine, ($Ph_2PCH_2CH_2N(CH_3)_2$), by oxidation to the phosphine oxide with hydrogen peroxide, alkylation at nitrogen with CH_3I followed by reduction with $HSiCl_3$ to give the air stable phosphine.

The sulphonated phosphines namely $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS) and $Ph_2P(m\text{-}C_6H_4SO_3Na)_3$ (TPPMS) afford water-soluble complexes with metals. Owing to its higher solubility in water (1100g/1*l* water), TPPTS is generally the ligand of choice for carrying out commercial reactions in aqueous media and indeed has been incorporated into several important industrial processes. Examples are the hydroformylation[55] of propylene by [RhCl(TPPTS)$_3$], the telomerisation[56] of dienes with [Pd(TPPTS)$_4$] and the functionalisation of dienes[57] by *cis*-[$PtCl_2$(TPPTS)$_2$]. It has been shown that the $-SO_3^-$ substituents in the *m*-position have only a minor electronic influence on the nature of the metal-phosphorus bond[58,59,60,61]. However, there are steric significant differences between TPPTS and $P(C_6H_5)_3$[62]. A process which has been used lately is the selective hydrogenation of the aldehyde group in α,β-unsaturated aldehydes using Ru(II) TPPMS as a water-soluble catalyst[63].

One of the most important discoveries in the area of water-soluble phosphine ligands was that of 1,3,5-triaza-7-phosphaadamantane, (PTA, **Fig. 2.10**), first prepared by Daigle[64] and co-workers. The interest shown in this ligand is mainly from its catalytic utilisation and in addition, also possible medical applications[65].

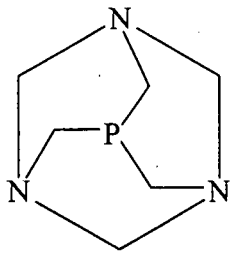
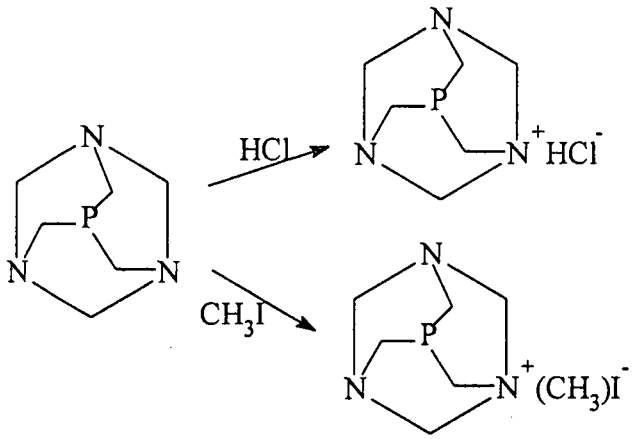


Figure 2.10: The PTA ligand.

This air-stable PTA ligand has attracted much interest due to its unique characteristics. The solubility of this compound in water and the difficulty of oxidation make this ligand an unusual aliphatic phosphine. The small cone angle of 118° suggests that this phosphine should be a good substitute for trimethylphosphine[66]. The ability of this phosphine to form stable organic derivatives[67], which leave the donor ability of the phosphorus intact, suggests that fine tuning of useful properties of metal complexes such as charge effects may be possible. This ligand is also of interest due to its ability to form hydrogen bonds with both counter-ions and water molecules and in addition, PTA can be either protonated by HX or methylated at one of the nitrogen sites to form [PTAH]X and $[(CH_3)PTA]I$[68], respectively.



Scheme 2.8: Protonation and methylation of PTA.

Rhodium(I) carbonyl complexes containing the methylated PTA, [RhI(CO)(PTA$^+$ MeI$^-$)] and [RhI(CO)(PTA$^+$MeI$^-$)$_3$]·4H$_2$O, have been prepared[69]. These complexes are stable in air in the solid state but when in solution they are oxidised with the loss of the carbonyl ligand and formation of water-insoluble complexes. The carbonyl stretching frequencies of these complexes suggest that the methylated PTA ligand possess stronger π-acceptor properties than most alkyl- and aryl-phosphines. These rhodium complexes were also found to be active catalysts for the water-gas shift reaction and they catalyse hydroformylation and carboxylation of alkenes as well as the hydrogenation of aldehydes and compounds containing a C=C bond[70].

Complexes containing the methylated PTA ligand display very strong hydrophilic properties and therefore their concentrations in the organic phase are very low in comparison with complexes containing PTA. Thus it can be concluded that they are better catalysts for two-phase catalytic reactions than PTA complexes.

Research studies on gold(I) [71,72] and mercury(II) complexes[73]complexes with PTA or functionalised PTA have been conducted. Wide and interesting research was done on platinum, palladium and nickel complexes containing PTA and these investigations were spear-headed mainly by the groups of Darensbourg[74] and Joó[75]. The coordination chemistry of the PTA ligand with these metals is closely parallel to that of other basic, sterically unhindered phosphine ligands such as PMe_3 with the added property of facilitating water-solubility in both neutral and acidic aqueous media.

Complexes of the type *cis*-$[MCl_2(PTA)_2]$ (M = Pt, Pd), *cis*-$[PtCl_2(PTAH)_2]Cl_2$, zero-valent complexes of platinum, palladium and nickel were isolated and characterised. The bisphosphine complexes of platinum and palladium were found to have a slightly distorted square planar geometry. $[M(PTA)_4]$ (M = Pt, Pd, Ni) complexes are all slightly distorted tetrahedra which do not undergo facile phosphine dissociation in solution. These complexes are often protonated at one nitrogen atom of the PTA ligand using an acid, with no products of oxidative addition such as $[M(H)Cl(PTA)_2]$ being formed. Because PTA has the advantage of resisting oxidation, these Group 10 water-soluble phosphine complexes, like the $P(CH_2OH)_3$ derivatives[76], display properties for serving as catalysts or precursors for a large variety of reactions catalysed by organometallic complexes.

A quite novel five-coordinate $[Pt(I)_2(PTA)_3]$ complex was isolated from the reaction mixture of $[PtCl(PTA)_3]Cl$ and NaI in aqueous methanol[66]. This complex was found to be five-coordinate both in the solid state and solution and only a few of these platinum(II) complexes are reported in the literature[77,78,79]. The solid state geometry of $[Pt(I)_2(PTA)_3]$ is a severely distorted square pyramid with one iodo and the three PTA ligands occupying the equatorial plane and with the second iodo ligand in the apical position.

Water-soluble ruthenium(II) and rhodium(I) phosphine complexes catalyse the hydrogenation of aqueous HCO_3^- to HCO_2^- under mild conditions. PTA has also been employed in ruthenium complexes, $[RuCl_2(PTA)_4]$ together with $[RuCl_2(m\text{-}TPPMS)_2]_2$ and $[RhCl(m\text{-}TPPMS)_3]$ complexes. These are precursors that have shown catalytic activity, in the hydrogenation of CO_2 and bicarbonate in aqueous solutions or in water/$CaCO_3$ suspensions in the absence of amine or other additives and under mild conditions[80].

2.5 CATALYTIC ACTIVITY OF THE PLATINUM GROUP METALS

2.5.1 Introduction

The word 'catalysis' is derived from the Greek words, *kata* meaning 'down' and *lysein* meaning 'to break'. It is thus related to analysis ('to break apart'), hydrolysis ('to break with water') and the many other words ending in lysis that are familiar to chemists. A German scientist Wilhelm Ostwald, rendered the first modern definition of the catalysis concept in 1865 as 'a substance that changes the rate of the reaction without itself appearing in the product'. Today the most widely accepted definition of a catalyst is a substance that increases the rate of approach to equilibrium of a chemical reaction, without being substantially consumed in the reaction[81].

This definition suggests that a catalyst can never change the thermodynamic equilibrium of a reaction and only the rate by which the equilibrium is reached is changed. The acceleration of the rate is possible since the catalyst allows for a new reaction pathway. The overall reaction is categorised into several individual steps of which the rate-determining step has lower activation energy than the uncatalysed reaction, hence the increased reaction rate. This definition also indicates that a catalyst must not be consumed in the reaction thus, an ideal catalyst would be efficient endlessly or should be recycled in the reaction.

Therefore, for a substance to be classified as a catalyst these criteria must be met:

- It should increase the rate of the catalysed reaction which should be thermodynamically favourable.
- It should not be consumed in the reaction.
- The equilibrium constant of a reaction is not affected.
- It must have selectivity towards the desired product and a small quantity must be able to affect the rate for a large amount of the reactant.

The power of transition metals to catalyse different kinds of organic transformations has led to the rapid development of organometallic chemistry over the past years[82]. Organometallic chemistry has successfully led to the development of homogeneous catalysis, which has been among the most dynamic disciplines in chemistry and widely covered in literature[83,84].

Before Otto Roelen discovered the hydroformylation reaction, the research on homogeneous catalysis received little attention[85,86]. It was only the work of Adkins and Krsek[87], Storch *et al.*[88], Berty and Markó[89] and Natta[90] that ratified oxo catalysts to be homogeneous in nature. The distinction between homogeneous, heterogeneous and enzymatic catalysis lies only in the extent of differentiation between the phases of the catalyst and the reactants. Thus, if the catalyst is not separated from the reactants by a phase boundary, one may speak of homogeneous catalysis.

A heterogeneous catalyst operates in a phase which is separate from the substrate. Enzymes differ from homogeneous catalysts in their size, since they do not form normal solutions but are described as colloidal dispersions.

Homogeneous catalysts offer some advantages as compared to heterogeneous ones, including:

- They show high activity relative to the metal content and have a high selectivity towards a certain reaction.
- They offer far better mechanistic understanding of the microscopic processes involved.
- Variation of steric and electronic properties of a catalyst is possible.
- Reaction conditions used are mild but the service life of a catalyst is variable.

Despite these advantages, heterogeneous catalysts are important in more than 80% of industrial processes[91] such as the synthesis of sulphuric acid, nitric acid and ammonia, for which there are no good homogeneous alternatives. They are also used in the production of fine chemicals. They are generally more stable at higher temperatures where these reactions are performed, can be regenerated and present easy separation from the products.

Large-scale processes involving homogeneous catalysts include the Monsanto acetic acid synthesis, the hydroformylation reaction of higher olefins using cobalt and rhodium catalysts, the Rhône-Poulenc process for the production of butanal from propene and the Shell Higher Olefin Process for the production of detergent range alcohols. These industrial processes also address different solutions to the problem of catalyst separation.

2.5.2 Homogeneous and heterogeneous catalysis reactions

The influence of homogeneous catalysis on industrial processes has developed since 1960 to the same extent as organometallic chemistry has developed as a science. Homogeneous catalysis has many commercial applications and the examples that can be mentioned are the cobalt-based BASF process (hydroformylation of propene or higher olefins), the Exxon process (hydroformylation of olefins in the C_6-C_{12} range) and the Shell process (process to hydroformylate olefins of medium chain length C_7-C_{14}).

The rhodium-based processes include the Union Carbide Corporation process, the Ruhrchemie/Rhône-Poulenc process (applying water-soluble rhodium complexes as catalysts for the hydroformylation reaction) and the BASF process which also makes use of a gas recycle step to separate aldehydes and catalyst solution with the rhodium complex dissolved therein.

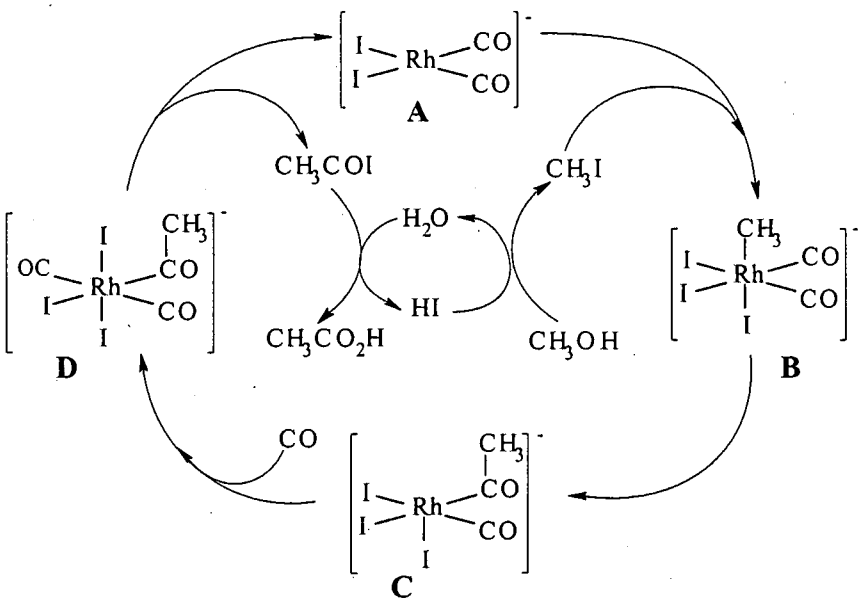
New research done on the structure and reactivity of organometallic compounds has brought new catalytic processes in industry into existence and has improved older ones. These are seen in the replacement of cobalt with rhodium in processes like methanol carbonylation and hydroformylation. Of these many catalytic processes only a few are discussed in this section.

One of the most important industrial processes utilising homogeneous transition-metal catalysis is the rhodium and iodide promoted carbonylation of methanol to acetic acid.

$$CH_3OH + CO \xrightarrow[150\text{-}200\ ^oC,\ 30\text{-}60\ bar]{Rh,\ CH_3I} CH_3COOH \qquad (2.12)$$

Acetic acid is an important building block[92] in the manufacturing of acetate esters like cellulose acetates and monochloroacetic acid and also as a solvent in the manufacturing of terephthalic acid[93]. Its most important derivative, vinyl acetate monomer, is the largest and fastest growing precursor for the production of acetic acid.

Nowadays acetic acid is widely produced by this rhodium-catalysed carbonylation process, (The Monsanto process) (**Scheme 2.9**).

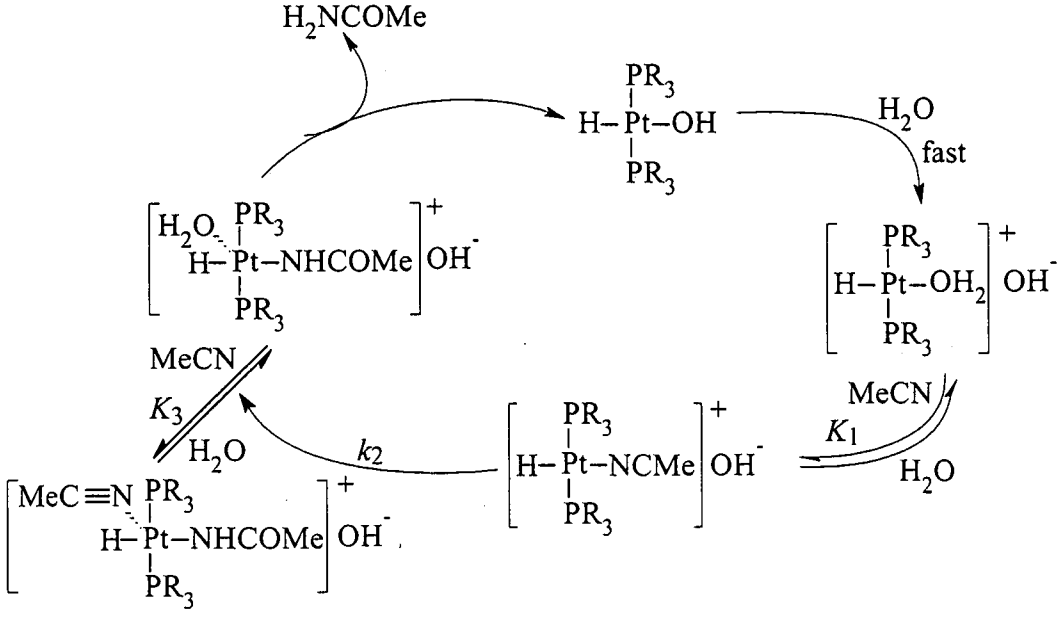


Scheme 2.9: The Monsanto acetic acid cycle[94].

Extensive research[95,96] has indicated that the active catalyst precursor is the square planar rhodium(I) complex, $[RhI_2(CO)_2]^-$, (**A**). In this cycle the step that determines the overall reaction rate is the oxidative addition of CH_3I to $[RhI_2(CO)_2]^-$ to form the octahedral Rh(III) intermediate complex $[RhI_3(CH_3)(CO)_2]^-$, (**B**). Following this step is the methyl migration, (C-C bond formation), step **B** to **C**.

Subsequent CO insertion into the *cis* CH_3-Rh bond gives a five-coordinate acetyl complex, **C**. This monocarbonyl acetyl complex decomposes by the loss of methyl iodide rather than the acetyl iodide. Addition of CO leads to the formation of a six-coordinate complex **D**. Subsequent reductive elimination of HI by the species **D** regenerates complex **A** and the HI that is eliminated reacts with the next methanol molecule to form iodomethane and the cycle restarts. The first step (reaction of methanol with HI to give methyl iodide) and the last (reaction of acetyl iodide with H_2O to give acetic acid and regenerate HI) are purely organic. Kinetic measurements showed that the rate of the overall reaction is first-order in both [Rh] and [CH_3I] but zero-order in [CO] and [CH_3OH][94].

Metal hydrides are implicated in many important catalytic reactions. The *trans*-[$PtHCl(PR_3)_2$] (R = Me, Et) complex reacts with sodium hydroxide in water/acetonitrile solution to produce a system that catalyses the hydration of acetonitrile or acrylonitrile. For the acetonitrile case $[PtH(H_2O)(PEt_3)_2]^+$, $[PtH(MeCN)(PEt_3)_2]^+$ and $[PtH(NHCOMe)(PEt_3)_2]$ have been characterised spectroscopically and the catalytic cycle shown in **Scheme 2.10** has been proposed[97].



Scheme 2.10: Hydrolysis of acetonitrile to acetamide catalysed by a platinum hydride complex.

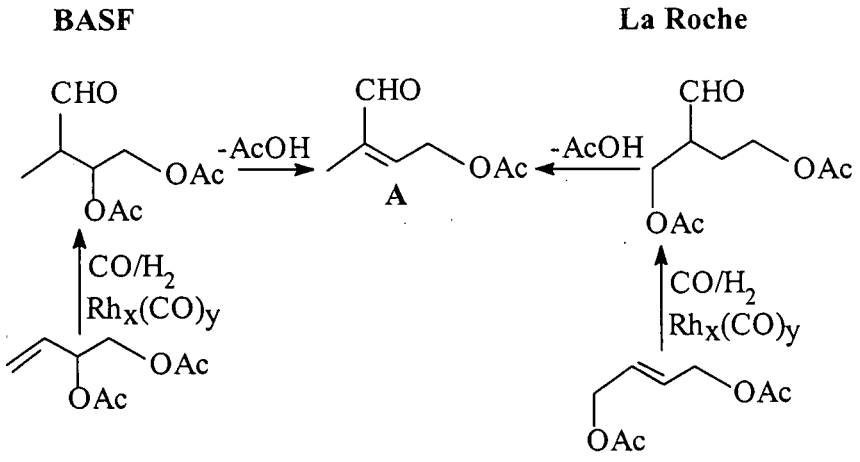
Platinum as such is not that widely utilised in catalysis but other platinum group metals and organometallic complexes of other metal centres have excelled themselves in a number of important processes, both as homogeneous and heterogeneous catalysts.

Some of the best known catalytic processes which feature organometallic complexes, PGM's and square planar complexes are:

- Hydroformylation (Co or Rh catalyst) and hydrogenation ($[RhCl(PPh_3)_3]$ – Wilkinson's catalyst) of olefins.
- Oxidation of olefins to aldehydes and ketones (Pd catalyst – Wacker process).
- Polymerisation of propylene to form stereoregular polymers (Al/Ti catalyst – Ziegler-Natta catalyst).
- Olefin isomerisation (Ni catalyst).
- Cyclooligomerisation of acetylenes using nickel catalysts (Reppe's or Wilke's catalysts).

Hydroformylation was discovered by Otto Roelen[85] when he passed a mixture of ethylene and synthesis gas over a cobalt-containing catalyst at 150 °C and at 100 bar pressure. Adkins[87] later modified the hydroformylation reaction. The reaction between the olefinic double bonds and the mixture of hydrogen and carbon monoxide (synthesis gas) leads to linear and branched aldehydes as primary products. The first generation of hydroformylation processes (by BASF, ICI, Kuhlmann, Ruhrchemie) was exclusively based on cobalt as the catalyst metal and the second generation processes combined the advantages of ligand modification with the transition from cobalt to rhodium as the catalyst metal.

An example of the application[98] of hydroformylation is in the synthesis of vitamin A (**Scheme 2.11**).



Scheme 2.11: The hydroformylation step in the synthesis of vitamin A precursor (**A**).

2.5.3 Conclusion

The above processes show that a wide range of organometallic complexes is important in modern catalysis. Square planar substitution reactions are also important in a wide rage of catalytic processes involving other metals of the platinum group metals such as rhodium, iridium and palladium. Further research in the area of homogeneous catalysis is not only focused on the changes to the metal but also on the ligands surrounding these metal centres[99,100,101]. Square planar substitution reactions can be used in studying the effects brought about by ligand systems frequently used in catalysis by varying the steric and electronic parameters of the metal centre by changing one metal to another, for example, from Pt(II) to Pd(II) or Co(I) to Rh(I).

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3 SYNTHESIS AND CHARACTERISATION OF COMPLEXES

3.1 INTRODUCTION

Organometallic complexes containing phosphine ligands, such as 1,3,5-triaza-7-phosphaadamantane (PTA), are currently widely under investigation for their chemical behaviour[1,2,3,4]. The discovery and synthesis of PTA, which was done in 1974[5], geared a wide investigation into this tetrabasic ligand. PTA has a cone angle of 118° (similar to that of PMe_3)[6] thus has a low steric demand and by taking advantage of this reduced steric hindrance, stable platinum(II) complexes containing this ligand can be prepared.

The PTA ligand is also of interest due to its solubility in aqueous media and ability to form hydrogen bonds with both counter-ions and water molecules. This ligand has been receiving much attention because of its remarkable characteristics since it is neutral, water-soluble, and is stable in air. Investigations on various transition elements containing these ligands are of importance in numerous fields, for example in catalysis[7], possible medical applications[8] *etc.*

In this chapter, the experimental details and the characterisation of the ligands and the complexes prepared are described. Characterisation was done using IR and NMR spectroscopy as well as X-ray crystallography which will be discussed in more detail later in this chapter (**Section 3.4**).

3.2 CHEMICALS AND INSTRUMENTAL

All chemicals used in the preparations were of reagent grade. The following chemicals were commercially available: K_2PtCl_4 (Next Chimica); SMe_2 (Merk); $P(CH_2OH)_4Cl$ (Fluka); Hexamine (Merck). These reagents were used without further purification.

Infrared spectra were recorded as KBr disks between 4000-250 cm^{-1} using a Hitachi 270-50 instrument. The complexes were further identified using ^1H and ^{31}P NMR (Bruker spectrometer operating at 300 and 121.497 MHz respectively). The NMR spectra were recorded in D_2O or $CDCl_3$, while the ^1H spectra were calibrated relative to the residual H_2O (4.60 ppm) or $CHCl_3$ peak (7.24 ppm) as applicable. The ^{31}P NMR spectra were calibrated relative to 85% H_3PO_4 as an internal standard in a capillary at 0 ppm. The UV-Vis spectra were obtained on either a Hitachi UV-Vis Model 150-20 or a CARY 50 CONC UV-Vis spectrophotometer with cell holders which were thermostated to within 0.1 °C.

3.3 SYNTHESIS OF COMPLEXES

3.3.1 1,3,5-triaza-7-phosphaadamantane

The procedure described is as according to that of Daigle[9].

To a beaker containing ice (12.4 g) and tetrakis(hydroxymethyl)phosphonium chloride (80% solution in water, 17 ml, 95 mmol), a solution of NaOH (50% w/w, 6.39 g) was slowly added while manually stirring.

After the resulting clear colourless solution reached room temperature, formaldehyde (37%, 45 g, 0.55 mol) was added, followed by hexamethylenetetraamine (14 g, 99.9 mmol) that was dissolved in the solution, which was subsequently allowed to stand overnight. The solution was then transferred to a large evaporating dish and placed in a hood for evaporation. It was allowed to stand until the solution became approximately 80% solid. The solid was then filtered in a Büchner funnel, washed with several volumes of cold ethanol and allowed to dry in air giving the desired product (6.0 g, 38%).

IR (KBr): 1620 (w), 1438 (w), 1416 (w), 1368 (w), 1302 (m), 1242 (s), 1106 (w), 1014 (s), 970 (s) cm^{-1}.

^{1}H NMR: δ 3.8 (d, 6H, $^2J_{H-H}$ = 9 Hz), 4.35 (dd, 6H, $^2J_{P-H}$ = 13.5 Hz).

3.3.2 $[PtCl_2(SMe_2)_2]$

K_2PtCl_4 (1.01 g, 2.43 mmol) was dissolved in the minimum volume of distilled water (25 ml). SMe_2 (1.5 ml) was added to the solution with stirring and the flask was sealed with a stopper. The reaction mixture became pink in colour indicating the formation of the Magnus salt $[PtCl_4][Pt(SMe_2)_4]$. This was heated until a yellow colour developed indicating the formation of $[PtCl_2(SMe_2)_2]$. After cooling, the solution was extracted with several portions of chloroform (8 x 5 ml) until the organic phase was colourless. The chloroform portions were combined and dried over anhydrous magnesium sulphate. After filtration and slow evaporation of the solvent, the yellow crystalline product was obtained as a mixture of the *cis* and *trans* isomers (796 mg, 84%).

IR (KBr): 1432 (s), 1414 (w), 1318 (m), 1032 (m), 982 (s), 342 (m) cm^{-1}.

^{1}H NMR: *trans* isomer: δ 2.45 (t, 12H, $^3J_{Pt-H}$ = 42 Hz), *cis* isomer: δ 2.55 (t, 12H, $^3J_{Pt-H}$ = 51 Hz).

3.3.3 $[PtCl(PTA)_3]Cl$

A mixture of *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ (400 mg, 1.03 mmol) was dissolved in minimum volume of hot distilled water (5 ml). PTA (509 mg, 3.07 mmol) was added in small portions. Addition of the first portion of PTA gave a dense milky solution indicating the formation of *cis*-$[PtCl_2(PTA)_2]$. Further addition dissolved the *cis*-$[PtCl_2(PTA)_2]$ complex thus producing a yellow solution, which was allowed to evaporate in the fume hood. After evaporation, recrystallisation of the solid from methanol gave white crystals (157 mg, 21%).

IR (KBr): 1290 (s), 1240 (s), 1098 (m), 1012 (m), 968 (s), 944(m), 804 (m), 736 (m), 390 (w) cm^{-1}.

^{31}P NMR: δ -51.2 (td, due to the phosphorus atoms of the PTA ligands *cis* to the chloride, $^1J_{Pt-P}$ = 2242 Hz), -48.5 (tt, due to the phosphorus atom of the PTA *trans* to the chloride, $^1J_{Pt-P}$ = 3345 Hz).

3.3.4 $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$

To an aqueous solution of $[PtCl(PTA)_3]Cl$ (20 mg, 0.027 mmol), 1.5 equivalents of NaSCN (3.3 mg, 0.041 mmol) were added. The solution was evaporated under hood and the yellow solid obtained was recrystallised from water to give crystals suitable for X-ray analysis (8.4 mg, 40%, see **Section 3.5.3** for the structural determination).

IR (KBr): 2080 (s), 1286 (m), 1242 (m), 1098 (m), 1012 (m), 972 (s), 946 (s), 576 (m) cm^{-1}.

^{31}P NMR: δ -58.05 (broad peak).

3.3.5 $[Pt(N_3)(PTA)_3]N_3$

$[PtCl(PTA)_3]Cl$ (37.5 mg, 0.051 mmol) was dissolved in distilled water (3 ml) and NaN_3 (19.5 mg, 0.3 mmol) also dissolved in water (3 ml) was added. The solution was stirred for a few minutes and placed in a cool room to crystallise. Within 24 hours slightly yellowish crystals were formed (13.5 mg, 35%). However, the crystals decomposed and they were not suitable for X-ray crystallographic investigation.

IR (KBr): 2040 (s), 1278 (m), 1240 (m), 1096 (m), 1014 (m), 574 (m) cm^{-1}.

3.3.6 $[Pt(Br)(PTA)_3]Br$

$[PtCl(PTA)_3]Cl$ (20 mg, 0.027 mmol) was dissolved in distilled water (3 ml), 1.5 equivalents of NaBr (4.2 mg, 0.041 mmol) were added. The solution was evaporated under hood and the white solid obtained was recrystallised from water. However, the crystals were not suitable for X-ray crystallographic investigation.

IR (KBr): 1638(s), 1618(s), 1286(m), 1240(m), 1012(m), 974(s), 950(m), 806(m), 740(m), 578(m) cm^{-1}.

^{31}P NMR: δ -57.88 (t, $^1J_{Pt-P}$ = 1971 Hz), -48.70 (t, $^1J_{Pt-P}$ = 3309 Hz).

3.4 X-RAY CRYSTALLOGRAPHY

3.4.1 Introduction

X-ray crystallography is important in studying crystal structures. It involves the use of X-rays to determine how atoms or molecules are built into regular three-dimensional patterns, which is the basic concept in the development of solid state science.

To solve the crystal structure of a chemical compound, the following procedures are followed[10]:

- The determination of the crystal system and unit cell parameters.
- The tests for group intensities are done systematically.
- The determination of the space group.
- The heavy atom position is determined from a Patterson function or direct methods are applied to solve the structure.
- The determination of the positions of the other atoms and the refinement of the structure through consecutive least-square cycles.

Crystallography[11] deals mainly with the laws governing the crystalline state of solid materials, their chemical and physical properties, together with the arrangement of atoms in that particular crystal. Thus a crystal can be described as a homogeneous, periodic cluster of atoms, ions or molecules arranged in three-dimensions. The arrangement of these atoms, ions or molecules constitutes a crystal structure.

The consideration of some properties of such a repetition of a periodic pattern can be simplified by replacing an atom, an ion or a molecule by a point, which then leads to a crystal lattice. The lattice is therefore an infinite set of points that may be generated from a single starting point by the infinite repetition of a set of fundamental translations that characterise the lattice. In a lattice each point has the same properties as any other lattice point. From this a unit cell can be described as the group of particles in a crystal that is repeated systematically in three-dimensions. The size and shape of a unit cell are specified by means of the lengths a, b, and c of the three independent sides and the three angles α, β, and γ between these sides. The angle α is between sides b and c, β is between a and c and γ between a and b.

In addition to lattice translations, there are repetition operations, such as rotations and reflections, which are called symmetry operations. When a symmetry operation has a 'locus' that is a point, a line, or a plane that is left unchanged by the operation, this locus is called a symmetry element. Examples are the rotation axis, a mirror plane and the inversion centre.

There are seven crystal systems as outlined in **Table 3.1.**

Table 3.1: Different crystal systems with the various conditions.

Crystal system	Axis relationship	Angle relationship
(i) Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$
(ii) Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^0 \neq \beta$
(iii) Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$
(iv) Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$
(v) Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$
(vi) Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0, \gamma = 120^0$
(vii) Trigonal	$a = b \neq c$	$\alpha = \beta = \gamma \neq 90^0$

A point group is defined as a set of symmetry elements, all of which pass through a single fixed point, and the symmetry operations of a point group must leave at least one point unmoved. A space group is then a combination of point symmetry elements and the translations of a crystal, and there are 230 space groups. Space groups represent the distinct ways of arranging identical objects on one of the fourteen Bravais lattices by the use of certain symmetry operations. The Bravais lattices represent the only fourteen ways in which it is possible to fill space by a three-dimensional periodic array of points.

3.4.2 X-ray Diffraction by Crystals

X-ray diffraction is a tool for the study of the arrangement of matter in a crystalline solid. The information contained in the radiation scattered by an object cannot, in the case of X-rays, be displayed directly in a magnified image but can only be extracted by the use of monochromatic radiation and complicated mathematical analysis.

The incident and diffracted beams obey the ordinary laws of reflection from the set of planes (hkl), but in addition reflection occurs when the condition $n\lambda = 2d\sin\theta$ which is known as Bragg's law is satisfied. λ is the wavelength of the scattered radiation, θ is the angle between the incident beam and the set of planes responsible for the diffraction and d is the perpendicular distance between the layers of planes. The X-ray radiation scattered by one unit cell of a structure in any direction in which there is a diffraction maximum has a particular combination of amplitude and phase known as the structure factor and is symbolised by F(hkl).

The structure factor expresses the scattering of X-rays for all atoms in the unit cell compared to that of a single electron and its amplitude, $|F(hkl)|$, is measured in electrons. The intensity of the scattered radiation is proportional to the square of the amplitude, $|F|^2$, and is generally expressed as:

$$\mathbf{I = K|F|^2(L_p)(T_v)(Abs)} \qquad \mathbf{(3.1)}$$

where K is a scale factor, (L_p) is an abbreviation for the geometric factors, (T_v) is an abbreviation for the correction factor for "thermal vibration" and (Abs) is the absorption factor. The amplitude of the scattered wave is proportional to the scattering factor f_n (which depends on the atomic number of the scattering atom and the Bragg angle for the reflection hkl) and the phase α_n with respect to the origin of the unit cell.

The contribution of the atom n to the structure factor is expressed as:

$$f_n e^{i\alpha_n} = f_n \, e^{2\pi i(hx_n + ky_n + lz_n)} \qquad (3.2)$$

For N waves F_{hkl} takes the form

$$F_{hkl} = \Sigma \, f_n e^{2\pi i(hx_n + ky_n + lz_n)} \qquad (3.3)$$

3.4.3 Fourier Transform Theory

The theory of the interrelation between the scattering phenomena and the structure of the scattering material is better understood by employing the principle of Fourier transformation[12].

The electron density at any point x,y,z is expressed as the following,

$$p(x,y,z) = 1/V \; \Sigma\Sigma\Sigma \; F(hkl) \; e^{-2\pi i(hx + ky + lz)} \qquad (3.4)$$

V is the volume of the unit cell and F(hkl) is the structure factor for the particular set of indices h, k and l. Thus if the structure factor amplitude, $|F|$, and the phase angles are known then p, for all values of x, y and z, could be calculated and the values obtained would be plotted to give a three-dimensional electron density map. However, only the structure factor amplitudes can be obtained directly from the experimental measurements and not the phase angles. This problem of estimating the phase angles so that an image of the scattering matter can be calculated is called the 'phase problem'.

3.4.4 The Patterson Function

In 1934, Patterson reported a new Fourier series, which could be calculated directly from the experimental intensity data. However, because phase information is not required in the Patterson series, the results cannot be interpreted as a set of atomic positions but rather as a collection of interatomic vectors, all taken to a common origin. This function requires a presence of one or two heavy, crystallographically different atoms which are phase determining. Patterson defined a function, which was very useful in solving the phase problem,

$$P(u,v,w) = V \int\int\int p(x,y,z)\, p(x+u, y+v, z+w)\, dx\, dy\, dz. \qquad (3.5)$$

This Patterson function shows that the electron density at x, y, z is multiplied by the electron density at x + u, y + v, z + w. Integration is done over the unit cell volume and the whole function is multiplied by the cell volume. This function is defined by the following equation[13],

$$P(u,v,w) = 1/V \sum\sum\sum |F|^2 \cos 2\pi (hu, kv, lw). \qquad (3.6)$$

P(u,v,w) will show a maximum only where there is electron density for all the interatomic vectors. The Patterson function is a series where only the indices and the $|F|^2$ value of each of the diffracted beams are needed. These are directly derivable from the experimental quantities, which are the angular positions and the intensities of the diffracted beams. The Patterson maps have proved to be the most important method for getting the trial structure information especially when a heavy atom is present. However, it can be difficult to understand the map so as to solve the structure, particularly if the chemical formula is not known.

Since there are N^2 vector peaks in a unit cell containing N atoms, there can be a large number of interatomic vectors as there are N^2 - N peaks other than the original peak. This creates a problem with the Patterson maps because when N becomes large, vector peaks overlap one another and it becomes difficult to resolve, especially for the atoms with smaller masses.

3.4.5 Structure Refinement

Trial structures can be refined by the method of least-squares approximation which can be performed in cycles using high-speed computer programs. One can calculate an approximation to the true electron density by a three-dimensional Fourier summation of the observed structure factor amplitudes, $|F_o|$, with the calculated phases.

The fit between the model and data is normally given by the reliability index, R, defined as:

$$R = \frac{\Sigma \| F_o | - | F_c \|}{\Sigma | F_c |} \qquad (3.7)$$

An R value of 0.10 or less is essentially acceptable and can be quoted for the most reliably determined structures, provided that a large number of reflections were used, whereas an R value smaller than 0.05 indicates a good agreement between the model and the data. In updated versions of crystallographic programs[14], the principle of refinement against F^2 is considered:

$$wR_2 = \frac{\Sigma \left[w \left(F_o^2 - F_c^2 \right)^2 \right]}{\Sigma \left[w \left(F_o^2 \right)^2 \right]^{\frac{1}{2}}} \qquad (3.8)$$

3.5 STRUCTURE DETERMINATIONS

3.5.1 Introduction

The complex formed when reacting $[PtCl(PTA)_3]Cl$ with thiocyanate in water was characterised by means of X-ray crystallography and the results are presented below.

3.5.2 Experimental

A simple method of determining the crystal system and the space group is by using the Weissenberg technique. An oscillation photo is obtained by keeping the camera stationary and rotating the crystal through an angle of approximately 15°. Zero and first layer photographs are obtained when only the zero or first layer lines are allowed to reach the film when the crystal is rotated through approximately 200° while the film is placed parallel to the rotating axis.

The experimental density of the crystal was determined by flotation in a solution of diiodomethane and benzene. The reflection data were collected at 293(2) K on a Siemens Smart CCD diffractometer using Mo K_α radiation (λ = 0.71073Å). The structure was solved by the heavy atom method and was refined through full matrix least squares approximations using the SHELXS-97[15] and SHELXL-97[14] programs with F^2 being minimised. All non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were constrained to parent sites, using a riding model. The graphics were performed with the DIAMOND[16] computer program.

A summary of the general crystal data and refinement parameters is presented in **Table 3.2** and the supplementary material containing the complete lists of atomic coordinates, bond distances and angles, anisotropic displacement parameters as well as hydrogen coordinates is given in the **Appendix**.

The effective (θ_E) and Tolman (θ_T) cone angles of the PTA ligands were determined according to the Tolman model[17] and the results are presented in **Table 3.5**. The average values of θ_E = 115.8° and θ_T = 116.2° deviate quite significantly from the previously reported value of 102°[18]. During the study the values for the individual half-angles were determined using the graphics program DIAMOND[16]. In each case the largest half-angle to an atom (hydrogen in all cases) on the individual substituents was used in the calculations. As the angles were measured from a point (2.28 Å from P, as per definition) to the point of the hydrogen atom, thus not touching the Van der Waals radius, a correction was applied using **Eq. 3.9**.

$$(^{\theta}/_{2})_T(P_n) = (^{\theta}/_{2})_i(P_n) + sin^{-1}(^{1.2}/_{d}) \qquad (3.9)$$

$(^{\theta}/_{2})_T(P_n)$ = Total half-angle for substituent n.

$(^{\theta}/_{2})_i(P_n)$ = Initial half-angle for substituent n.

n = 1-3.

1.2 Å = Van der Waals radius of hydrogen[14].

d = distance from point to hydrogen.

By substituting these values for the total half-angles into **Eq. 3.10** the Tolman cone angle for the PTA ligand could be calculated.

$$\theta_T = {}^{2}/_{3}\,\Sigma(^{\theta}/_{2})_T(P_n) \qquad (3.10)$$

Table 3.2: Crystallographic data for the complex, $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

Identification code	**$\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$**
Empirical formula	$C_{60}\ H_{118}\ N_{33}\ O_5\ S_6\ P_9\ Pt_3$
Formula weight	2438.2
Temperature (K)	293(2)
Crystal system	Triclinic
space group	$P\bar{1}$
a / b / c (Å)	14.9135(2) / 15.2532(2) / 22.7413(3)
α / β / γ (°)	73.2012(6) / 78.5067(6) / 61.7241(6)
V (Å^3)	4349.52(10)
Z	2
D_m (g.cm^{-3})	1.835
D_c (g.cm^{-3})	1.862
μ (mm^{-1})	5.189
F(000)	2428
Crystal size (mm)	0.11 x 0.25 x 0.25
Theta range (°)	1.88 to 27.53
Index ranges	$0 \leq h \leq 19$ $-16 \leq k \leq 18$ $-28 \leq l \leq 29$
Reflections collected / unique	17534 / 17534 [R_{int} = 0.0000]
Data / restraints / parameters	17534 / 0 / 1080
Goodness-of-fit on F^2	1.011
Final R indices [I>2(σ)(I)]	R_1 = 0.0367, wR_2 = 0.0671
R indices (all data)	R_1 = 0.0649, wR_2 = 0.0755
ρ_{max} and ρ_{min} (e.Å^{-3})	1.554 and –1.021

3.5.3 The crystal structure of $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$

3.5.3.1 INTRODUCTION

The crystal structure of $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ was investigated to determine if the 'bis' (two PTA ligands) or the 'tris' complex (three PTA ligands) would form when the $[PtCl(PTA)_3]Cl$ complex is reacted with sodium thiocyanate in aqueous medium as was the case with the Pd(II) systems[19] which formed 'bis' complexes. Another motivation for the structure determination was to establish whether, if any substitution of the chloride ion by the thiocyanate ligand occurs, the bonding mode of the ligand is through the nitrogen or the sulphur donor atom. The preparation of this complex and growth of the crystals used for collection of the intensity data were reported in **Section 3.3.4**. A molecular diagram showing the numbering scheme of the complex is presented in **Fig. 3.1**, the packing in the unit cell is shown in **Fig. 3.2** and selected bond distances and angles in **Tables 3.3** and **3.4**, respectively.

3.5.3.2 RESULTS

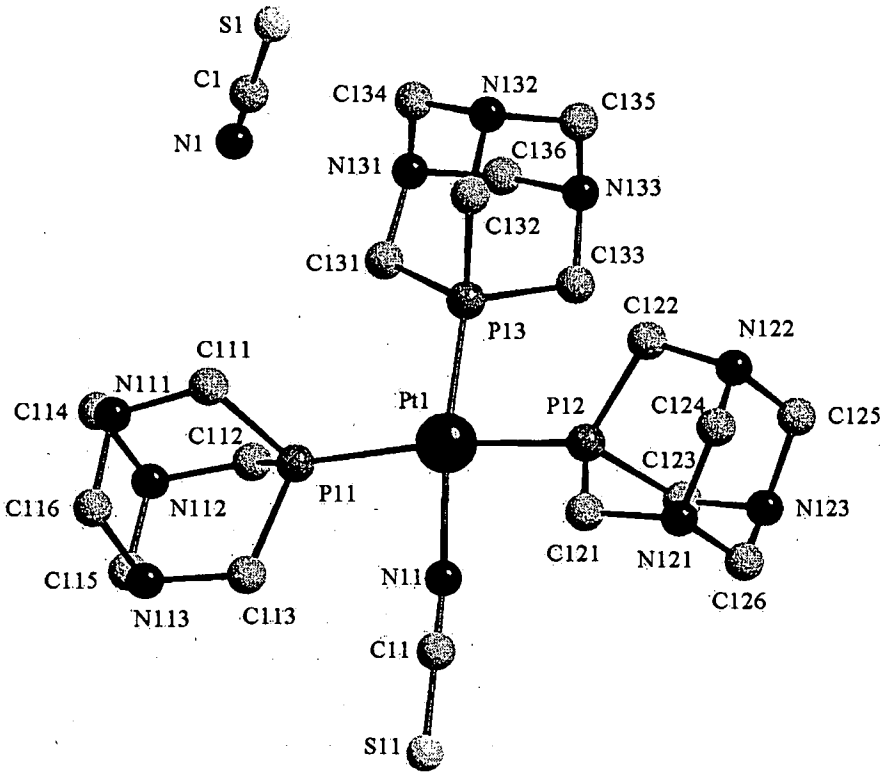

Figure 3. 1: Molecular drawing of molecule 1 of $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ showing the numbering scheme and thermal ellipsoids (30% probability). Molecules 2 and 3 are similar. Hydrogen atoms and water molecules are omitted for clarity. In the numbering scheme the first digit refers to the number of the molecule and the second one to the number of the atom in the molecule.

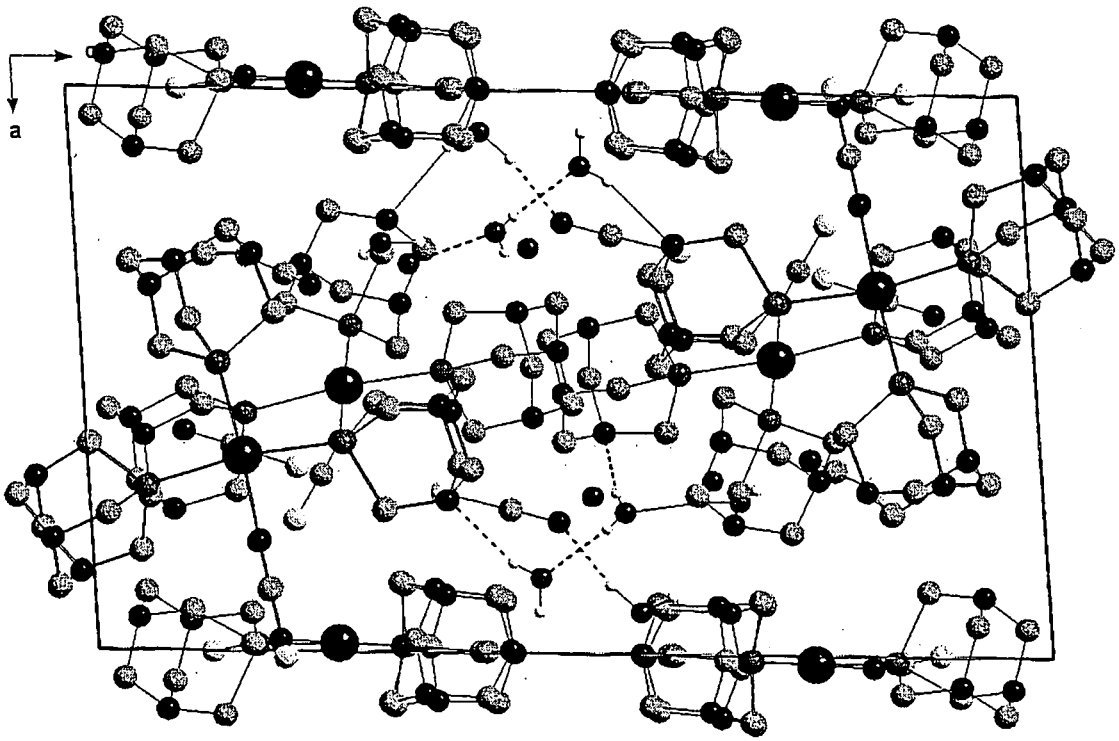

Figure 3.2: Molecular drawing of $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ showing the packing in the unit cell, hydrogen bonding and thermal ellipsoids (30% probability). Hydrogen atoms, except for water molecules, are omitted for clarity.

Table 3.3: Selected bond lengths (Å) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

Molecule 1		Molecule 2		Molecule 3	
Pt(1)-P(11)	2.3215(13)	Pt(2)-P(21)	2.3090(13)	Pt(3)-P(31)	2.3283(14)
Pt(1)-P(12)	2.2972(13)	Pt(2)-P(22)	2.3361(13)	Pt(3)-P(32)	2.3495(15)
Pt(1)-P(13)	2.2407(13)	Pt(2)-P(23)	2.2359(13)	Pt(3)-P(33)	2.2407(13)
P(11)-C(111)	1.843(5)	P(21)-C(211)	1.841(5)	P(31)-C(311)	1.839(5)
Pt(1)-N(11)	2.036(4)	Pt(2)-N(21)	2.052(4)	Pt(3)-N(31)	2.043(4)
P(11)-C(111)	1.843(5)	P(21)-C(211)	1.841(5)	P(31)-C(311)	1.839(5)
P(11)-C(112)	1.863(5)	P(21)-C(212)	1.849(5)	P(31)-C(312)	1.859(5)
P(11)-C(113)	1.844(5)	P(21)-C(213)	1.848(5)	P(31)-C(313)	1.829(5)
P(12)-C(121)	1.846(5)	P(22)-C(221)	1.849(5)	P(32)-C(321)	1.841(5)
P(12)-C(122)	1.842(5)	P(22)-C(222)	1.845(5)	P(32)-C(322)	1.857(5)
P(12)-C(123)	1.831(5)	P(22)-C(223)	1.859(5)	P(32)-C(323)	1.858(5)
P(13)-C(131)	1.833(5)	P(23)-C(231)	1.835(5)	P(33)-C(331)	1.840(5)
P(13)-C(132)	1.850(5)	P(23)-C(232)	1.850(5)	P(33)-C(332)	1.840(5)
P(13)-C(133)	1.843(5)	P(23)-C(233)	1.840(5)	P(33)-C(333)	1.843(5)
N(11)-C(11)	1.153(6)	N(21)-C(21)	1.159(6)	N(31)-C(31)	1.150(6)
S(11)-C(11)	1.618(5)	S(21)-C(21)	1.617(5)	S(31)-C(31)	1.619(6)

Table 3.4: Selected bond angles (°) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

Molecule 1		Molecule 2		Molecule 3	
(11)-Pt(1)-P(11)	86.66(12)	N(21)-Pt(2)-P(21)	87.55(12)	N(31)-Pt(3)-P(31)	86.61(13)
(11)-Pt(1)-P(12)	83.83(12)	N(21)-Pt(2)-P(22)	80.89(12)	N(31)-Pt(3)-P(32)	81.30(13)
(11)-Pt(1)-P(13)	170.97(13)	N(21)-Pt(2)-P(23)	179.08(12)	N(31)-Pt(3)-P(33)	178.92(13)
(12)-Pt(1)-P(11)	166.94(5)	P(21)-Pt(2)-P(22)	168.43(5)	P(31)-Pt(3)-P(32)	167.61(5)
(13)-Pt(1)-P(11)	96.84(5)	P(23)-Pt(2)-P(21)	91.61(5)	P(33)-Pt(3)-P(31)	92.49(5)
(11)-N(11)-Pt(1)	171.2(4)	C(21)-N(21)-Pt(2)	160.5(4)	C(31)-N(31)-Pt(3)	169.6(4)
(11)-C(11)-S(11)	179.4(5)	N(21)-C(21)-S(21)	178.5(5)	N(31)-C(31)-S(31)	179.1(5)

Table 3.5: Calculated steric angles (°) for PTA ligands in $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

θ_E P(11)	116.0	θ_T P(11)	117.1
θ_E P(12)	116.0	θ_T P(12)	116.5
θ_E P(13)	116.9	θ_T P(13)	115.8
θ_E P(21)	115.7	θ_T P(21)	116.6
θ_E P(22)	115.8	θ_T P(22)	117.3
θ_E P(23)	116.1	θ_T P(23)	114.8
θ_E P(31)	115.1	θ_T P(31)	116.4
θ_E P(32)	114.8	θ_T P(32)	116.7
θ_E P(33)	115.6	θ_T P(33)	114.5

3.5.3.3 DISCUSSION

The $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ compound crystallises in the triclinic space group $P\bar{1}$ with three platinum complexes, three thiocyanate counter-ions and five water solvent molecules in the asymmetric unit. Each platinum complex consists of three PTA ligands, bonded through the phosphorus atom, and a thiocyanate ligand bonded through the nitrogen atom. The three platinum complexes are thus chemically equivalent, but they are however crystallographically different due to small variations in their packing modes.

The crystallisation modes of the three independent molecules in the asymmetric unit are thus almost identical with only some deviations in the bond lengths and angles of the coordination sphere. For all three molecules the P-Pt-P angles deviate significantly from the expected 180° at 166.94(5), 168.43(5) and 167.61(5)°, respectively suggesting that there is a steric hindrance imposed by the PTA ligands. The N(21)-Pt(2)-P(23) and N(31)-Pt(3)-P(33) bond angles are 179.08(12) and 178.92(13)° respectively, and these differ significantly from the N(11)-Pt(1)-P(13) bond angle which is 170.97(13)°. This suggests that molecules 2 and 3 are more similar, but different from molecule 1. Since the bond distances between the nitrogen atom of the free thiocyanate and the platinum (Pt(1)-N(1) = 5.494(6), Pt(2)-N(2) = 6.057(8), Pt(3)-N(3) = 5.758(6) Å respectively), and the distance between the sulphur end of the free thiocyanate and platinum (S(1)-Pt(1) = 7.413(4), S(2)-Pt(2) = 4.645(3), S(3)-Pt(3) = 4.194(2) Å respectively) are large, there is no interaction between them. However, there are interactions between the thiocyanate counter-ion and water molecules (N(1)-H(4A) = 2.06(7) Å) and between the nitrogen atom of PTA ligands and the solvent molecules (N(232)-H(2A) = 2.20(6), N(223)-H(3B) = 2.09(9) Å respectively). An interesting observation was that the thiocyanate ligand coordinated through the nitrogen atom and this depends upon the nature of other ligands present in the complex. This form of coordination of the thiocyanate ion, can also be due to either electronic or steric effects[20]. The Pt-N bond distances range from 2.036(4) to 2.052(4) Å and Pt-P distances from 2.2359(13) to 2.3495(15) Å.

The structure of $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ shows the Pt moiety to be distorted square planar with two PTA ligands *trans* to each other occupying the equatorial plane and the other PTA ligand coordinated *trans* to the nitrogen atom of the coordinated thiocyanate ligand. The Pt-P bond distances of the phosphorus atoms of the PTA ligands *trans* to each other are longer (average Pt-P distance = 2.3236(13) Å) than the Pt-P distances (average Pt-P distance = 2.2391(13) Å) of the phosphorus *trans* to the nitrogen atom (See **Table 3.3** and **Fig. 3.1**). This is probably due to the combination of the large *trans* influence of the PTA ligands as compared to that of the nitrogen.

It is clear from **Table 3.6** that in Pt(II) and Pd(II) complexes with the thiocyanate ligand, *trans*-[PtPh(NCS)(PPh_3)$_2$], {[Pt(NCS)(PTA)$_3$]NCS}$_3$·5H_2O and *trans*-[Pd(SCN)$_2$($PTAH$)$_2$](SCN)$_2$, the M-P bond lengths are comparable to each other. These M-P bond lengths range from 2.294(1) to 2.3236(13) Å and are approximately of normal length of 2.33 Å. However, for the reasons mentioned earlier, in {[Pt(NCS)(PTA)$_3$]NCS}$_3$·5H_2O the Pt-P bond distance *trans* to the thiocyanate ligand is quite short. The average Pt-P bond length of 2.323(2) Å for the *trans* phosphine ligands in [PtCl(PTA)$_3$]Cl is significantly longer than the one *trans* to the chloride atom. This is attributed to the stronger *trans* influence of PTA as compared to that of the Cl^-. This is also the case with [Pt(I)$_2$(PTA)$_3$]·CH_3OH where the Pt-P bond lengths for the *trans* phosphine ligands are longer than the one sharing the equatorial plane with the iodo atoms. Comparing the three complexes, {[Pt(NCS)(PTA)$_3$]NCS}$_3$·5H_2O, [PtCl(PTA)$_3$]Cl and [Pt(I)$_2$(PTA)$_3$]·CH_3OH the Pt-P bonds *trans* to the X ligand are comparable to each other (Pt-P = 2.2391(13), 2.233(2) and 2.2514 Å respectively). In [PdCl(PTA)$_3$]Cl the Pd-P bond lengths for the phosphine ligands *trans* to each other are of normal length and the Pd-P bond *trans* to the chloride is quite short.

There are little changes induced in the M-X bond when interchanging one metal with another. The M-X bond distances are approximately the same when changing the platinum metal centre, (Pt-X bond in [PtCl(PTA)$_3$Cl] and *cis*-[PtCl$_2$($PTAH$)$_2$]Cl$_2$ = 2.371(2) and 2.358(5) Å respectively), to palladium (Pd-X bond in [PdCl(PTA)$_3$]Cl and *trans*-[PdBr$_2$(PTA)$_2$] = 2.375(3) and 2.427(1) Å respectively). The slight differences are due to the size of the Cl and Br atoms. Comparing the platinum complexes, {[Pt(NCS)(PTA)$_3$]NCS}$_3$·5H_2O and *trans*-[PtPh(NCS)(PPh_3)$_2$] (Pt-X bond = 2.044(2) and 2.046(15) Å respectively) and the palladium complex *trans*-[Pd(SCN)$_2$($PTAH$)$_2$](SCN)$_2$ (Pd-X = 2.351(1)) an increase in the M-X bond lengths is observed. In the three complexes listed, *trans*-[PdBr$_2$(PTA)$_2$], [ReBr(PTA)$_2$(CO)$_3$] and [Pt(I)$_2$(PTA)$_3$]·CH_3OH containing the larger halogens Br^- and I^- it is observed that the M-X bond is much longer than the M-NCS bond which can be due to steric crowding.

Comparing *trans*-[PtPh(NCS)(PPh_3)$_2$], {[Pt(NCS)(PTA)$_3$]NCS}$_3$·5H_2O, *trans*-[Pt(CN)$_2$(PTA)$_2$] and [Pt(CN)$_2$(*cis*-dppen)] complexes, the M-CN bond lengths are shorter than the M-NCS bonds. The differences are as a result of the size of the C atoms as compared to the N atoms. The M-CN bond in the nickel complex, [Ni(CN)$_2$(PTA)$_3$] is also quite short. A good σ-donor ligand like CN^- will cause increased electron density on the metal centre thus forming strong bonds with the metal. In [Pt(I)$_2$(PTA)$_3$]·CH_3OH the Pt-I bonds lengths of 2.7192(3) and 3.2369(3) Å are exceptionally long due to the combination of the large *trans* influence of the PTA ligand and the steric crowding experienced in the equatorial plane.

Table 3.6: Comparative table of bond lengths for this study with other platinum phosphine and metal-PTA complexes.

Complex	**Bond distances (Å)**[a]		
X = NCS^-, Cl^-, I^-, CN^-, Br^-	**M-P**	**M-X**	**Ref**
trans-[PtPh(NCS)(PPh_3)$_2$]	2.3064(19)	2.046(15)	**21**
{[Pt(NCS)(PTA)$_3$]NCS}$_3$·5H_2O	2.3236(13)[b,c]	2.044(2)	This study
	2.2391(13)[b,d]		
trans-[Pt(CN)$_2$(PTA)$_2$]	2.305(2)	1.975(9)	**22**
trans-[Pd(SCN)$_2$($PTAH$)$_2$](SCN)$_2$[e]	2.294(1)	2.351(1)	**19**
[PtCl(PTA)$_3$]Cl	2.326(2)[c]	2.371(2)	**23**
	2.233(2)[d]		
	2.320(2)[c]		
{*cis*-[PtCl$_2$(PTA)$_2$]}$_2$·H_2O	2.2263(14)	2.3585(13)	**21**
cis-[PtCl$_2$($PTAH$)$_2$]Cl$_2$	2.218(5)	2.358(5)	**4**
[Pt(I)$_2$(PTA)$_3$]·CH_3OH	2.3133(11)[c]	2.7192(3)	**21**
	2.2514(11)[d]	3.2369(3)	
	2.3214(11)[c]		
trans-[PtI$_2$(PTA)$_2$]	2.3128(12)	2.6022(6)	**24**

Table 3.6: Comparative table of bond lengths for this study with other platinum phosphine and metal-PTA complexes (continued).

Complex	Bond distances (Å)		
X = NCS^-, Cl^-, I^-, CN^-, Br^-	M-P	M-X	Ref
$[PdCl(PTA)_3]Cl$	2.330(2) [c]	2.375(3)	25
	2.238(3) [d]		
	2.338(2) [c]		
trans-$[PdBr_2(PTA)_2]$	2.320(1)	2.427(1)	19
$[Ni(CN)_2(PTA)_3]$	2.197(3)	1.868(15)	26
	2.234(3)	1.841(14)	
	2.227(3)		
$[Pt(CN)_2$(*cis*-dppen)$]$ [f]	2.2655(13)	2.018(5)	27
	2.2721(13)	2.002(5)	
$[Ir(PTA)_4(CO)]Cl{\cdot}3H_2O$	2.3229(10)		28
	2.3188(9)		
	2.3187(10)		
	2.3378(9)		
$[ReBr(PTA)_2(CO)_3]$	2.447(2)	2.6549(8)	29
	2.427(2)		

[a] Average lengths for chemically equivalent ligands, [b] Average of distances in three independent molecules, [c] M-P distances *trans* to each other, [d] M-P distances *trans* to X, [e] PTAH = Protonated form of PTA, [f] *cis*-dppen = *cis*-1,2-bis(diphenylphosphino)ethene.

Introduction of strong π-acceptor ligands like CO in the iridium complex listed in **Table 3.6** causes the M-P bond to be shorter and changing the metal centre to rhenium elongates the M-P bonds. Electron withdrawing substituents decrease the σ-donating ability of the phosphine resulting in less electron density on the metal centre available for π-back bonding to the carbonyl.

In conclusion, it was shown by this crystallographic study that several factors, including a change in the ligands coordinated to the metal, account for the variations in the M-P and M-X bond distances observed in structure determinations. The extensive hydrogen bonding network (see **Fig. 3.2**) was also pointed out and contributes to the solubility in aqueous solution. The characterisation of the title complex was very important to aid in the elucidation of the complex stoichiometric mechanism, which is discussed in the next chapter.

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4 KINETIC STUDY OF THE SUBSTITUTION OF THE CHLORIDE IN COMPLEXES OF PLATINUM(II)

4.1 INTRODUCTION

Chemical reactions are processes in which a substance or substances (reactants) are transformed into other substances (products). Chemistry is all about the study of reactions, so the knowledge of the rates at which they occur is of central and practical importance. Complex processes in which substances undergo a series of stepwise changes, each consisting of a reaction of its own, are much common. The overall mechanism is then made up of contributions from all such reactions. Thus the study of chemical kinetics is a fundamental part of chemistry and it often provides the only convenient approach towards the unravelling of the reaction mechanism.

Kinetics therefore, is the study of the rates of chemical reactions[1,2], which involves accurate measurements of the variation of concentration of the reacting species with time. Measurements are usually done to investigate the effects of temperature, pressure, concentrations of additional species, pH, isotopic substitution, solvent, salt concentration and so forth. The most fundamental and important variables[3] are time, concentration and temperature. The rate of conversion of one substance into another is studied with respect to the concentration of the reactants and different reactions display differences in concentration dependence.

While thermodynamics is only concerned with the initial and final states of a system, it has the limitation of not expressing the rate nor explaining the details of a chemical reaction involved. Chemical kinetics however deals with the analysis of the dynamics of a chemical reaction, and the data collected in chemical kinetics indicate the measurement of a reaction rate and is used to explain these rates in terms of a complete reaction mechanism. This is the most universal way of determining the mechanism of a reaction, therefore the measured rate shows the statistical average state[4,5] of the molecules taking part in the reaction. Chemical kinetics provides no information on the energetic or on the stereochemical state of the individual molecules but it does have the desired potential to break down complex mechanisms into sequences of simple reactions.

No matter how thorough, a kinetic study does not really determine a mechanism in the same sense that X-ray diffraction measurements determine a structure. The reaction mechanism is a scientific postulate that is open to revision where new data and theories of reactivity emerge. It defines the progression of events from the reactants to the products and it shows whether a given chemical reaction occurs in a single molecular process (an elementary reaction) or in several processes. If several steps exist, the experiments will define whether they enter as concurrent competing alternatives or in succession along a single pathway. If several steps do occur in a sequence the concept of reaction intermediates is considered. Using tests for substituents, stereochemistry and especially reactivity the composition and structure of the proposed intermediates can be determined.

The study and understanding of the mechanisms of the reactions is never enough as refined resolution of the mechanisms may be obtained with further study. The rates and mechanisms of the electron transfer reactions, nucleophilic substitution, hydrolysis and other reactions have long been studied experimentally and theoretically but the research continues as issues of finer detail and broader importance are examined.

A mechanism is never really 'proven', but sufficient definitive experiments may eliminate some alternatives as being impossible or unlikely, therefore leaving but one convincing mechanism remaining. Lewis pointed out that the subject of reaction mechanisms deserve no special reprimand for no model or hypothesis in science, which has been advanced to explain a set of observations is ever proved[6]. The best one does is to consider the proposal from every possible viewpoint and try to design tests of a critical nature; tests that will probe every assumption and every assertion.

The substitution behaviour of square planar d^8 metal complexes, especially Pt(II) has been widely investigated[7]. The manipulation of the intimate mechanism through which these reactions take place and the current knowledge regarding the *trans* effect, for instance, was brought into being by this research. In **Chapter 2** a brief outline was given on some of the most important results that have been obtained in this regard.

In this study, different mechanistic investigations were conducted to explain the intrinsic mechanism of the reaction pathway and the solution behaviour of the water-soluble PTA systems, which included:

- Determination of the equilibrium constants for $[PtCl(PTA)_3]Cl$ and the reactivity of this complex with different halides and pseudo-halides.
- Effect of pH on the $[PtCl(PTA)_3]Cl$ complex.
- Preliminary study of the chloride exchange in $[PtCl(PTA)_3]Cl$.

4.2 PRINCIPLES OF KINETICS

In this section some relevant rate expressions and kinetic principles, as well as activation parameters are briefly discussed[2,8].

4.2.1 Basic concepts

The rate of a reaction can be defined as the change in the concentration of a reactant or the product per unit time. For a general reaction (**Eq. 4.1**),

$$A + B \xrightarrow{k_1} C \qquad (4.1)$$

the reaction rate is represented by:

$$R = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} \qquad (4.2)$$

[] indicates concentration and the negative signs the disappearance of A and B with the formation of C.

The rate of the reaction is nearly always dependent on the reactant concentrations and, for reversible reactions, product concentrations. The interpretation of the kinetic data is largely based on an empirical discovery called the Law of Mass Action which states that in dilute solutions the rate of a one-step reaction is proportional to the indices of their stoichiometric coefficients, and independent of other concentrations and reactions[9]. Thus **Eq. 4.2** can be written as **Eq. 4.3**:

$$R = k_{obs}[A]^a[B]^b \qquad (4.3)$$

with k as a proportionality constant (rate constant) that relates the rate of change to the reagent concentrations.

The values a and b represent the order of the reaction with respect to A and B respectively, and their sum is equal to the overall order of the rate law or the total reaction. The order is the way in which the rate varies with a change in the concentration of one or both of the reacting species and the units of the rate constant depend on the overall reaction order. The values can be determined experimentally but this is often difficult. This problem can be overcome by using pseudo first-order conditions where the condition [B] >> [A] is allowed, then **Eq. 4.3** reduces to,

$$\mathbf{R} = k_{obs}[\mathbf{A}]^{a} \qquad (4.4)$$

with the observed pseudo first-order rate constant being:

$$k_{obs} = k_1[\mathbf{B}]^{b} \qquad (4.5)$$

Pseudo first-order conditions (with [B] at least ten times in excess of [A]) resulting in **Eq. 4.5** help in obtaining the rate constant by determining k_{obs} using different concentrations of B. It can also be used to simplify second-order reactions. If the value of b = 1, then the reaction is first-order in B and a graph of k_{obs} *versus* [B] is a straight line with a zero intercept to indicate that there is no second reaction occurring. If a second reaction was taking place,

$$\mathbf{A} \xrightarrow{k_2} \mathbf{P} \qquad (4.6)$$

with a = b = 1, then the rate would be given by:

$$\mathbf{R} = k_1[\mathbf{A}][\mathbf{B}] + k_2[\mathbf{A}] \qquad (4.7)$$

and under pseudo first-order conditions, k_{obs} is represented by **Eq. 4.8**,

$$k_{obs} = k_1[\mathbf{B}] + k_2 \qquad (4.8)$$

Eq. 4.8 also holds for a reaction at equilibrium (**Eq. 4.9**) and k_2 denotes the reverse reaction.

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \qquad (4.9)$$

The integration of **Eq. 4.3** between time = 0 and t respectively, gives **Eq. 4.10** (expressed in terms of C in **Eq. 4.1**),

$$[C]_t = [C]_0 e^{-k_{obs} t} \qquad (4.10)$$

According to Beer-Lambert law:

$$A = \varepsilon c l \qquad (4.11)$$

with A = absorbance, ε = molar absorptivity, c = concentration and l = light path length.

Combining **Eq. 4.11** and **Eq. 4.10** (with $\frac{[C]_t}{[C]_0} = \frac{A_\infty - A_t}{A_\infty - A_0}$ where ∞, t and 0 are times at infinity, t and 0 respectively) and then manipulated, the following equation results:

$$A_t = A_\infty - (A_\infty - A_0) e^{k_{obs} t} \qquad (4.12)$$

Infinity is the time at which the reaction is complete for all practical reasons, and k_{obs} can then be determined by the least-squares fit using the absorbance *vs.* time data for the first-order reaction.

4.2.2 Activation enthalpy and entropy[10]

The transition state theory states that an activated complex or transition state is in equilibrium ($K^{\neq}$ = equilibrium constant) with the reactants before the reaction takes place and that the rate is given by the decomposition rate, k, of the activated complex to yield the products:

$$A + B \overset{K^{\neq}}{\rightleftharpoons} (AB)^{\neq} \xrightarrow{k} C \qquad (4.13)$$

The rate of which is given by:

$$k = \frac{k_B T}{h} K^{\neq} \qquad (4.14)$$

where k_B = Boltzmann's and h = Planck's constants.

From the basic thermodynamics it follows that:

$$K^{\neq} = e^{\frac{-\Delta G^{\neq}}{RT}} \qquad (4.15)$$

with $\Delta G^{\neq}$ = standard Gibbs free energy of activation and R = universal gas constant.

Substituting **Eq. 4.15** into **Eq. 4.14** and the fact that $\Delta G^0 = \Delta H^0 - T\Delta S^0$ yields **Eq. 4.16** which is known as the Eyring equation.

$$k = T\frac{k_B}{h} e^{\left[\left(\frac{\Delta S^{\neq}}{R}\right) - \left(\frac{\Delta H^{\neq}}{RT}\right)\right]} \qquad (4.16)$$

Eq. 4.16 is generally written in a logarithmic form as shown below in **Eq. 4.17**:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^{\neq}}{R}\right) - \left(\frac{\Delta H^{\neq}}{RT}\right) \qquad (4.17)$$

The graph of $\ln \frac{k}{T}$ *versus* $\frac{1}{T}$ will have a slope of $-\Delta H^{\neq}/R$, with $\Delta H^{\neq}$ = standard enthalpy of activation and the y-intercept giving $\frac{\Delta S^{\neq}}{R} + \ln\left(\frac{k_B}{h}\right)$, with $\Delta S^{\neq}$ the standard entropy of activation.

4.2.3 Equilibrium and stability constants

The thermodynamic stability of a complex can be expressed in terms of an equilibrium constant relating to its concentration and the concentration of other species present when the system has reached equilibrium. Equilibrium is dynamic with reactions proceeding in both forward and reverse directions, but with equal rates so that the equilibrium concentrations are maintained. The kinetic stability of a species refers to the speed with which transformations leading to the beginning of equilibrium will occur.

If in a solution containing solvated metal ions (M) and the unidentate ligands (L), only soluble mononuclear complexes are formed, the following equations and constant may represent the system at equilibrium.

$$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML \qquad (4.18)$$

$$K_1 = \frac{[ML]}{[M][L]} \qquad (4.19)$$

There will be N such equilibria, where N represents the maximum coordination number of the metal ion (M) for the ligand (L) and L may vary from one ligand to another. An example of such an equilibrium reaction is the isomerisation equilibrium between *cis*- and *trans*-3-phenyl-propenonitrile,

$$cis\text{-}C_6H_5CH{=}CHCN \underset{k_r}{\overset{k_f}{\rightleftharpoons}} trans\text{-}C_6H_5CH{=}CHCN \qquad (4.20)$$

at equilibrium

$$K = \frac{r_f}{r_r} = \frac{k_f\ trans\text{-}[C_6H_5CH{=}CHCN]_{eq}}{k_r\ cis\text{-}[C_6H_5CH{=}CHCN]_{eq}} \qquad (4.21)$$

where r_f and r_r are the rates of the forward and the reverse reactions, the subscript (eq) refers to conditions at equilibrium and K is the equilibrium constant.

4.2.4 Square planar substitution

Studies on the substitution reactions of square planar platinum complexes are of importance in understanding the kinetics involved in these reactions. Substitution reactions of X for Y in $PtXL_3$ (**Eq. 4.22**) in general follow a two-term rate law which is represented by **Eqs. 4.23** and **4.25**.

$$PtXL_3 + Y \longrightarrow PtYL_3 + X \qquad (4.22)$$

$$\text{Rate} = \{k_S + k_Y[Y]\}[PtXL_3] \qquad (4.23)$$

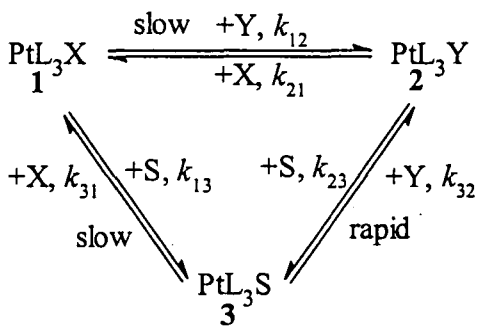
with

$$k_{obs} = k_S + k_Y[Y] \quad ([Y] >> [Pt]) \qquad (4.24)$$

$$k_S = k[\text{Solvent}] \qquad (4.25)$$

k_S is the first-order rate constant for the solvolytic pathway and k_Y is the second-order rate constant for a direct bimolecular substitution pathway. This rate law is typical for square planar complexes and it has been rationalised in terms of two parallel pathways both involving an associative mechanism. The first step in the pathways involves a direct attack of the entering nucleophile on the complex forming the product. The second pathway is the concurrent bimolecular attack of the solvent forming an intermediate that can quickly react with the entering nucleophile to form the final product.

It has been proven that, in general, square planar substitution reactions occur *via* an associative mode of activation almost without exception, although some examples do follow a dissociative mechanism. The rate laws for square planar substitution reactions are more complicated when different equilibria are present. A schematic representation of such a more general square planar substitution reaction is given in **Scheme 4.1**.



Scheme 4.1: Representation of the two parallel pathways of a square planar substitution reaction. The subscripts in the rate constants denote the numbers of the species involved in the specific reaction and the solvent, S, concentration is included in the rate constants, k_{13} and k_{23}.

When the concentrations of the chloride (X) and the entering nucleophile, Y, are considered to be much greater than the platinum(II) complex, the following expression for the observed pseudo first-order rate constant given in **Eq. 4.26** is obtained.

$$k_{obs} = k_{12}[Y] + \frac{k_{12}}{K_{eq}}[X] + \frac{\frac{k_{13}}{K_{eq}}\frac{k_{32}}{k_{31}}k_{31}[X] + k_{32}k_{13}[Y]}{k_{31}[X] + k_{32}[Y]} \quad (4.26)$$

If in **Eq. 4.26** the equilibrium constant, K_{eq}, is considered to be large and pseudo first-order conditions are ensured, then this equation simplifies to the well known rate law for square planar reactions (**Eq. 4.27**), which is identical to **Eq. 4.24**.

$$k_{obs} = k_{12}[Y] + k_{13} \quad (4.27)$$

4.3 CHEMICAL EXCHANGE AS STUDIED BY NMR

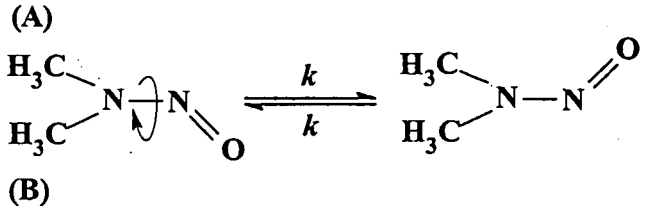
4.3.1 Introduction

Nuclear magnetic resonance spectroscopy is an enormously powerful and versatile technique for investigating the structure and dynamics of molecules. It is the single most important tool for obtaining detailed information on chemical systems at the molecular level. Spectroscopy may be defined as the interaction between matter and electromagnetic radiation when energy is absorbed or emitted according to the Bohr frequency condition, $\Delta E = h\nu$. ΔE is the energy difference (normally quantised) between the initial and final states of the matter, h is the Planck's constant and ν is the frequency of the electromagnetic radiation.

The energy difference (ΔE) depends on the strength of the interaction between the magnetic nucleus of an atom and the magnetic field or in other words, on the size of the nuclear magnetic moment and the strength of the magnetic field. For a given field strength, the energy gap, ΔE, and therefore the resonance frequency, are determined principally by the nuclide observed, because every nuclide (*e.g.* ^{1}H, ^{2}H, ^{31}P, ^{13}C, ^{14}N, ^{37}Cl, *etc.*) has a characteristic magnetic moment. Since there are several nuclei that can be determined one can have, for example, proton, phosphorus, chloride NMR spectra of a specific complex, which conveniently aid in studying different aspects of the system.

4.3.2 Chemical exchange

Chemical exchange[11,12] is concerned with somewhat slower motions which nonetheless cause reversible changes, a typical case of dynamic equilibrium where a molecule is converting between two conformations of equal energy. A process of mutual exchange occurs when two magnetic sites (two different environments for a given nuclide) are interchanged, as is the case for the methyl protons of dimethylnitrosamine (A and B, **Eq. 4.28**) when internal rotation occurs.



(4.28)

The skeleton of the molecule is planar, due to the partial double-bond character of the N-N bond, but not rigid. The nitroso group can undergo 180° rotations, so interconverting the two degenerate forms. At low temperatures, the internal rotation is slow and the ^{1}H spectrum consists of two equally intense resonances from the methyl groups *cis* and *trans* to the oxygen.

At high temperatures the nitroso group flips at a reasonable rate such that the chemical shifts of the two sets of the methyl protons are interchanged. If the two resonance frequencies are considered to be ν_{cis} and ν_{trans}, then the resonance frequency of each group of protons is interchanged with the other with an average time of $\tau = 1/k$ (τ = mean lifetime, k = rate constant). Such processes are known as chemical exchange.

There are two types of chemical exchange, the symmetrical and unsymmetrical two-site exchange. In a symmetrical exchange a simple A .B exchange with equal forward and backward rates is considered. When the exchange is very slow, two equally intense, narrow peaks at the resonance frequencies (ν_A and ν_B) of the two sites are seen. As the rate constant is increased, the two lines first broaden, shift towards one another and further broadening until they merge into a single, wide resonance. Further increase in the exchange rate produces a sharp resonance at the average frequency $1/2(\nu_A + \nu_B)$. Slow exchange is a process where the separate resonances are broadened but are still at frequencies ν_A and ν_B. The increase in linewidth (width of the specific signal at half its height) is given by **Eq. 4.29**.

$$\Delta\nu = k/\pi = 1/(\tau\pi) \qquad \textbf{(4.29)}$$

This indicates that the faster the exchange, the wider the linewidth. Fast exchange is when the two lines have merged to form a single and broadened resonance at the mean frequency. The extra linewidth due to chemical exchange is given by,

$$\Delta\nu = \frac{\pi(\delta\nu)^2}{2k} = 1/2\ (\delta\nu)^2\ \tau \qquad \textbf{(4.30)}$$

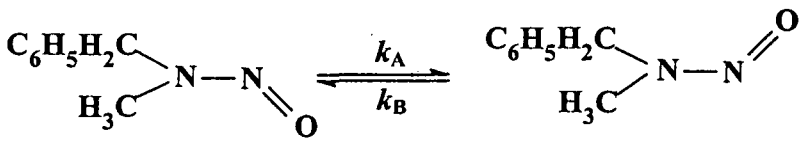
where $\delta\nu = \nu_A - \nu_B$. Contrary to the slow exchange, the single line observed in fast exchange becomes narrower as the rate increases.

In the intermediate exchange the separate resonances are combined. The condition when the two resonances just merge into a single line is indicated in **Eq. 4.31**.

$$k = \frac{\pi(\delta\nu)}{\sqrt{2}} \approx 2.2\ \delta\nu \tag{4.31}$$

A single line is observed at the mean resonance frequency when k is larger than the right hand side of **Eq. 4.31** and when k is smaller two separate resonances should be observed.

An example of unsymmetrical two-site exchange is when a benzyl group replaces one methyl group in dimethylnitrosamine. The two conformers no longer have the same energy and the forward and the reverse rates also differ.



(4.32)

If the fractional populations of the two sites are p_A and p_B, $p_A + p_B = 1$ and the two first-order rate constants are k_A and k_B then $p_A k_A = p_B k_B$ at equilibrium. The average lifetimes of the two sites are $\tau_A = 1/k_A$ and $\tau_B = 1/k_B$. In the slow exchange limit, the lifetime broadenings are $\Delta\nu_A = k_A/\pi = 1/\pi\tau_A$ and $\Delta\nu_B = k_B/\pi = 1/\pi\tau_B$. For fast exchange, a single resonance is observed at the weighted average frequency (**Eq. 4.33**),

$$\nu_{av} = p_A\nu_A + p_B\nu_B \tag{4.33}$$

with a line broadening of

$$\Delta\nu = \frac{4\pi p_A p_B (\delta\nu)^2}{k_A + k_B}. \tag{4.34}$$

The above expressions reduce to formulae for the symmetrical exchange when $p_A = p_B = 1/2$ and $k_A = k_B = k$.

4.3.3 Spin relaxation

Chemical exchange, chemical shifts and spin-spin couplings are the important factors that determine the appearance of a NMR spectrum, but more to it are the two relaxation processes known as spin-lattice relaxation and spin-spin relaxation which allow nuclear spins to return to equilibrium following some disturbance.

Relaxation can be defined as the way that the signal looses its magnetisation after it has been exposed to the magnetic field. Before a sample is put into the magnetic field when taking a NMR spectrum, the 2I+1 energy levels of a spin-I nucleus are degenerate and their populations are equal. When the sample is introduced into the magnetic field, the spin states split apart because of energy and the populations cannot adjust to the applied field and therefore remain equal. Spin-lattice relaxation enables the spins to flip among the energy levels so as to secure the Boltzmann population differences needed for a successful NMR experiment. As the nuclei approach equilibrium, the energy released is dissipated in the surroundings (the lattice). These changes in populations are characterised by a time T_1, which is the spin-lattice relaxation time and the rate of these processes is T_1^{-1}.

Considering a disordered molecular solid in which all motions are frozen out, every nucleus has several neighbours to each of which it has a dipolar coupling. The NMR line of every spin is therefore split many times over by these dipolar interactions with neighbouring spins each with different radius and angle. The spin-spin relaxation time T_2 is defined as the parameter,

$$\frac{1}{\pi T_2} = \Delta\nu \qquad (4.35)$$

where $\Delta\nu$ is the linewidth associated with the relaxation process.

Another relaxation process is called quadrupolar relaxation. A nucleus with a spin quantum number greater than 1/2 possesses an electric quadrupole moment in addition to its magnetic dipole moment. Nuclei in low symmetry environments experience non-zero electric field gradients which depend on the orientation of the molecule in the magnetic field. Two negative charges at a fixed distance from a quadrupolar nucleus have a more favourable Coulombic interaction when they lie on the spin axis (close to the poles of the non-spherical nucleus) than when they are in the equatorial plane. This anisotropic interaction produces splittings in the spectra of single crystals and broad lines for powders and solids.

Many nuclei with spin quantum number greater than 1/2 in low symmetry environments have large quadrupolar interactions and therefore more achieved spin relaxation. In the slow exchange limit, the transverse relaxation rate is given in **Eq. 4.36** where τ is the mean lifetime and $T_{2Q}{}^{b}$ is the quadrupolar relaxation time.

$$1/T_2{}^{b} = 1/\tau + 1/T_{2Q}{}^{b} \qquad (4.36)$$

4.4 EXPERIMENTAL

4.4.1 General considerations

The preparation, spectroscopic characterisation and crystallographic characterisation of the complexes kinetically investigated were described in **Chapter 3**. Unless stated otherwise, all chemicals were used without further purification and reagents were of analytical grade, distilled water was used in all the experiments and all measurements were carried out in air.

4.4.2 Kinetic measurements

UV-Vis investigations were carried out on either a Hitachi 150-20 or a Cary 50 Conc spectrophotometer, while stopped-flow investigations were done on an Applied Photophysics instrument attached to a J&M diode array detection unit. All apparatus were equipped with constant temperature water baths which regulate temperature within ± 0.1 °C.

The equilibrium constant and the influence of pH experiments were all conducted using freshly prepared $[PtCl(PTA)_3]Cl$ and NaCl solutions, in aqueous media and at 25°C. The platinum solutions contained a ten-fold excess NaCl, to ensure pseudo first-order conditions.

For equilibrium constant determinations the platinum solutions were mixed with the different concentrations of the various halide solutions and the final concentrations for Pt(II), Cl^- and halide were thus 0.075, 1.0 and 0.025 – 20 mM respectively. The absorbance spectra were recorded in the wavelength range of 200 – 500 nm using 1 cm quartz cuvettes. At a selected wavelength the absorbance values were plotted against halide concentrations in order to obtain equilibrium constants. Data analysis was conducted by means of Microsoft Excel 97 and the observed equilibrium constants were obtained from the absorbance versus concentration traces using the least-squares program Scientist[13] for the UV data.

The chloride exchange NMR studies were performed on a 300 MHz Bruker spectrometer operating at 29.4078 MHz for ^{35}Cl. Experiments were done with different platinum, chloride concentrations and at different pH values.

4.5 REACTION MECHANISM

In order to construct a complete mechanistic scheme, the following points were utilised as obtained from preliminary measurements, characterisation studies and literature:

1. The starting complex, $[PtCl(PTA)_3]Cl$ ('tris' complex), was successfully synthesised and characterised (see **Section 3.3.3**).

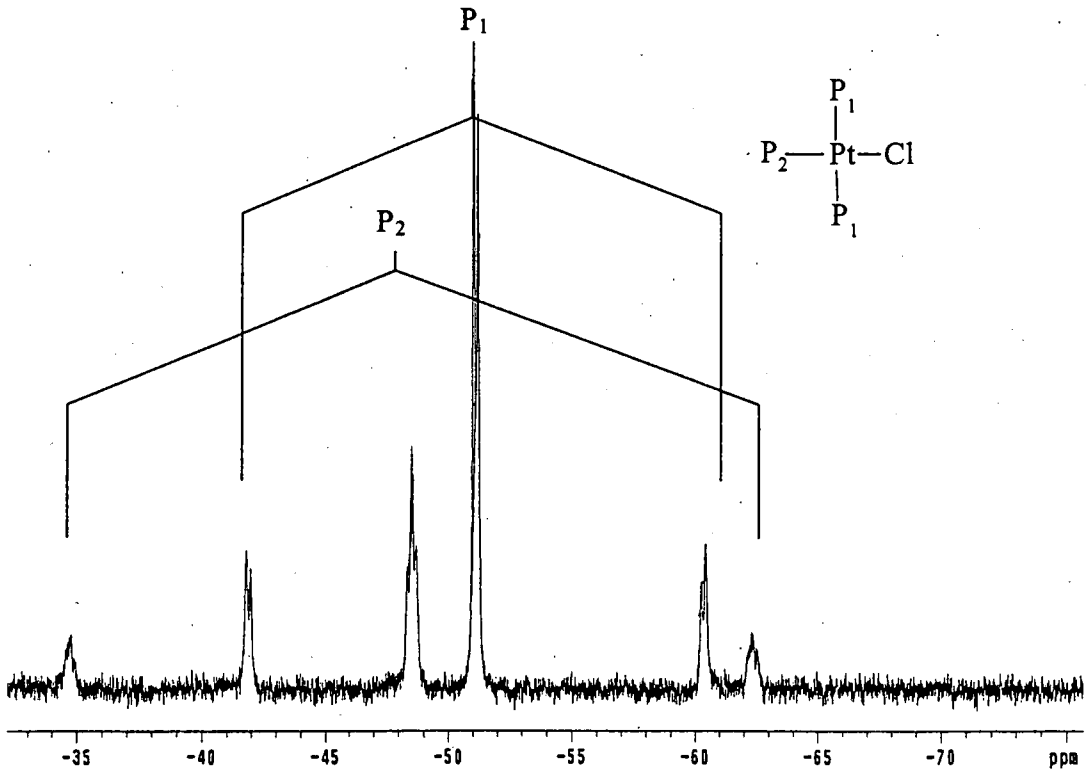


Figure 4.1: ^{31}P NMR spectrum of the complex $[PtCl(PTA)_3]Cl$ showing the coupling between Pt and P with the subscripts 1 and 2 denoting the different sites in the complex. P_1 = -51.2 ppm (triplet of doublets), $^1J_{Pt\text{-}P1}$ = 2242 Hz; P_2 = -48.5 ppm (triplet of triplets), $^1J_{Pt\text{-}P2}$ = 3345 Hz.

2. (a) The products were synthesised and $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ was characterised by X-ray crystallography (see **Section 3.5**).

(b) The $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ complex was also characterised by ^{31}P NMR (see **Section 3.3.4**, a broad peak was observed at δ = -58.05 ppm).

3. The stability of the $[PtCl(PTA)_3]^+$ complex in aqueous medium was evaluated. There was significant decomposition of the complex when dissolved in neat aqueous medium (pH = 5.6) over a three-hour period (**Fig. 4.2a**). When the complex was dissolved in aqueous NaCl (10 mM, pH = 5.6), the spectra collected over a period of three hours were subsequently identical (**Fig. 4.2b**).

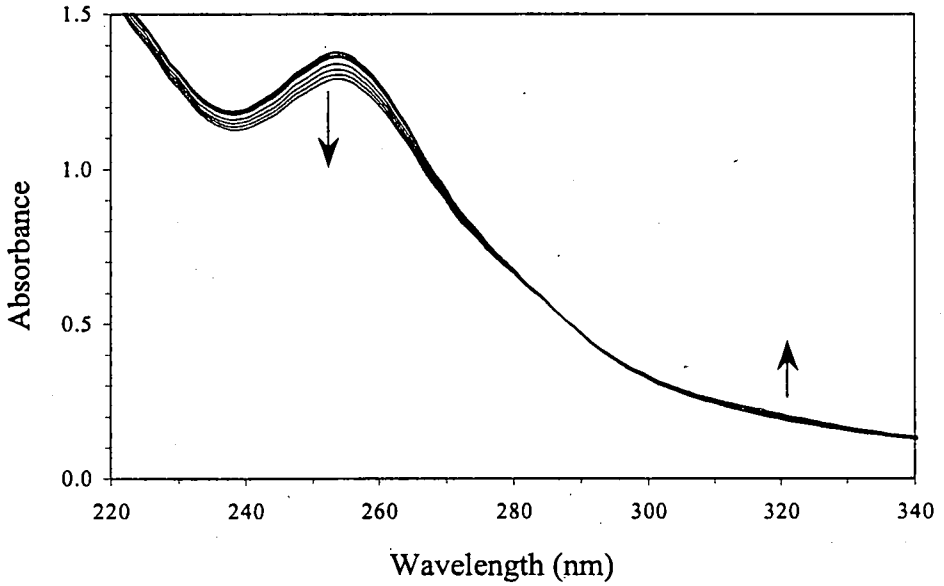


Figure 4.2a: UV-Vis spectrum of $[PtCl(PTA)_3]Cl$ when only dissolved in H_2O at 25 °C. Scans were taken at 5 minute intervals for a period of 3 hours. [Pt] = 0.075 mM, pH = 5.6.

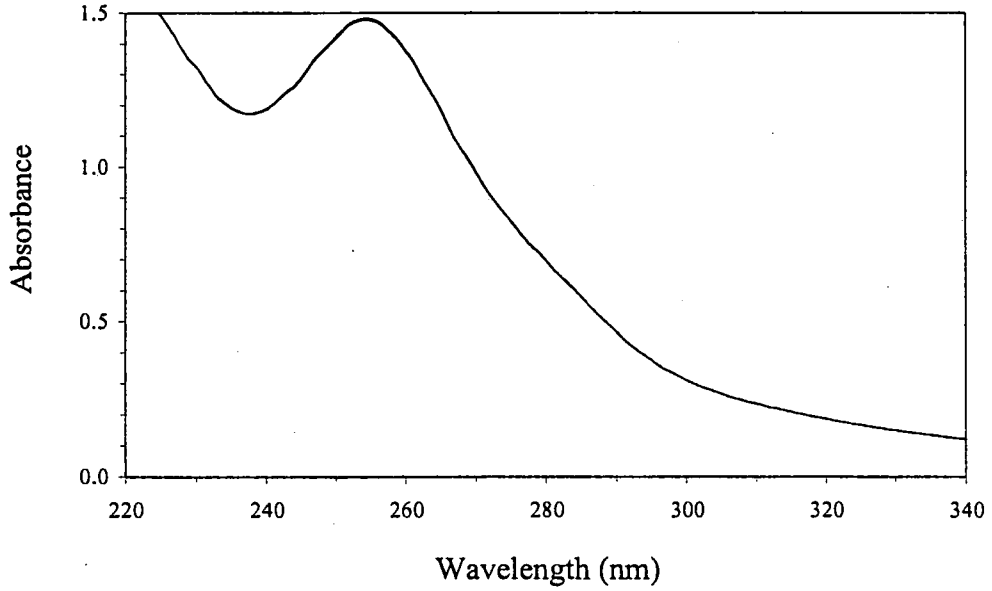


Figure 4.2b: UV-Vis spectrum of $[PtCl(PTA)_3]Cl$ when dissolved in aqueous NaCl at 25 °C. Scans were taken at 5 minute intervals for a period of 3 hours. [Pt] = 0.075 mM, $[Cl^-]$ = 10 mM, pH = 5.6.

4. The equilibrium constants obtained from reacting $[PtCl(PTA)_3]Cl$ with various halides and pseudo-halides ($Y = Br^-$, SCN^-, N_3^-) were well determined. **Fig. 4.3** illustrates the absorbance *versus* wavelength scans when $[PtCl(PTA)_3]Cl$ is reacted with thiocyanate. The equilibrium reaction for the process is given as **Eq. 4.37**.

$$[PtCl(PTA)_3]^+ + Y \underset{}{\overset{K}{\rightleftharpoons}} [PtY(PTA)_3]^+ + Cl^- \quad (4.37)$$
(II, Scheme 4.2)

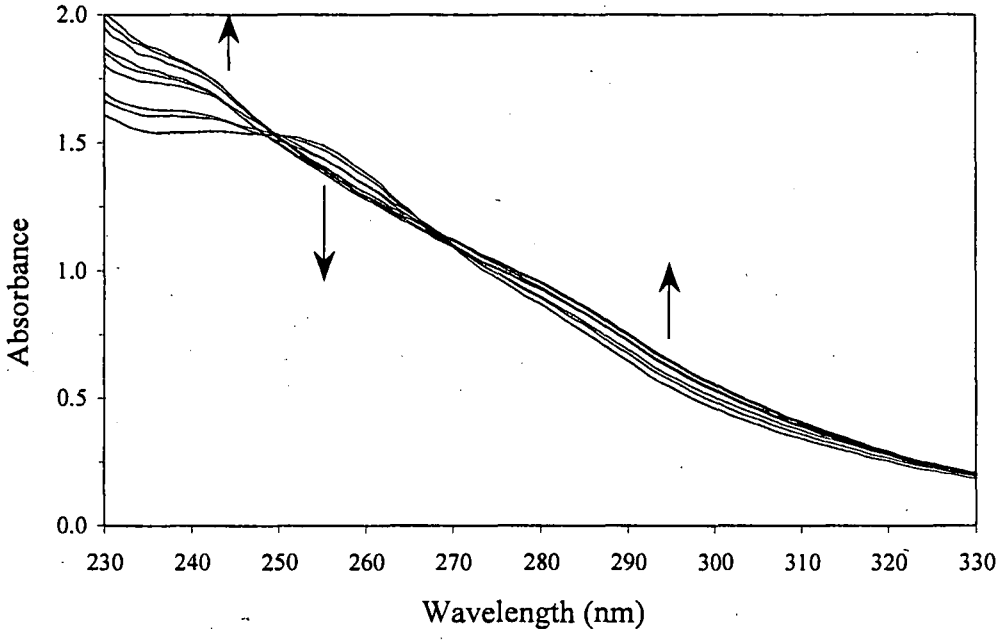


Figure 4.3: UV-Vis spectrum of $[PtCl(PTA)_3]Cl + SCN^-$ at 25 °C. Scans were taken for a period of 4.5 h. The final concentrations of Pt and the excess Cl^- (as NaCl) added were 0.075 and 1 mM respectively. $[SCN^-]$ = 0-1 mM, pH = 5.6.

5. There was an observed proton catalysis of PTA substitution to form *cis*-$[PtCl_2(PTA)_2]$ when different concentrations of triflic acid were added to the 'tris' complex. See **Fig. 4.4**.

$$[PtCl(PTA)_3]^+ + H \rightleftharpoons [PtCl(PTA)_2(PTAH)]^{2+} \rightleftharpoons cis\text{-}[PtCl_2(PTA)_2] \quad (4.38)$$
(I)

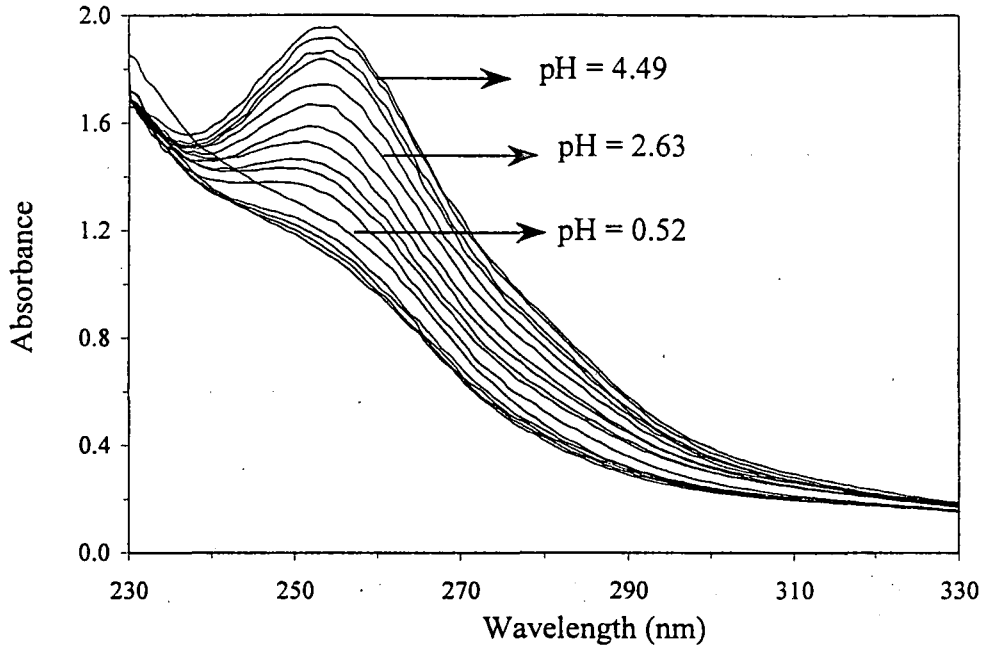


Figure 4.4: UV-Vis spectrum showing the protonation behaviour of $[Pt(PTA)_3Cl]Cl$ at different pH values. The final concentrations of Pt and the excess Cl^- added were 0.075 and 20 mM respectively. pH was varied from 5.65 (no acid added) - 0.52, T = 25 °C.

6. Upon addition of a halide or pseudo-halide, Y, in a neutral to slight acidic solution (pH = 5-6.5), the chloride in **I** (**Eq. 4.38** and **Scheme 4.2**) is rapidly substituted to form **II** (**Eq. 4.37**). In palladium systems this complex (**II**) rapidly converts to the *trans* 'bis Y' complex **IV** (**Eq. 4.39** and **Scheme 4.2**, *cis-trans* equilibrium)[14].

$$[PdY(PTA)_3]^+ + Y \xrightarrow{-PTA} cis\text{-}[PdY_2(PTA)_2]^{2+} \longrightarrow \underset{(IV)}{trans\text{-}[PdY_2(PTA)_2]} \quad (4.39)$$

7. It is postulated that in a more acidic solution the 'bis Y' complex is further converted to the protonated PTA complex (see **Scheme 4.2**).

$$cis\text{-}[PtCl_2(PTA)_2]+H^+ \rightleftharpoons cis\text{-}[PtCl_2(PTA)(PTAH)]^+ \rightleftharpoons cis\text{-}[PtCl_2(PTAH)_2]^{2+} \quad (4.40)$$

8. The rate of the chloride substitution by Y is very fast. This was checked by the stopped-flow spectrophotometry (reaction with half-lives greater than 1 ms accessible) allowing to estimate only a lower limit for the substitution rate. The rate of substitution was too fast even to detect under the conditions employed (T = 18 °C, [Y] = 0.5 mM, pH = 5.65) *i.e.* the half-life of the substitution reaction is thus smaller than 1 ms or the rate constants are greater than 700 s^{-1}.

9. The existence of a five-coordinate iodide complex, $[Pt(I)_2(PTA)_3]$ in solution has been presented previously[15].

10. Since the substitution reactions were too fast to be followed on a stopped-flow instrument, the chloride exchange process was studied by ^{35}Cl NMR, also at different pH values (**Fig. 4.5**), platinum and excess chloride concentrations. Significant line broadening on the free Cl^- peak was observed, indicative of the system being in fast exchange. It seemed that the effect of pH was not significant in terms of the rate of the Cl^- exchange, and this was not pursued further in this study.

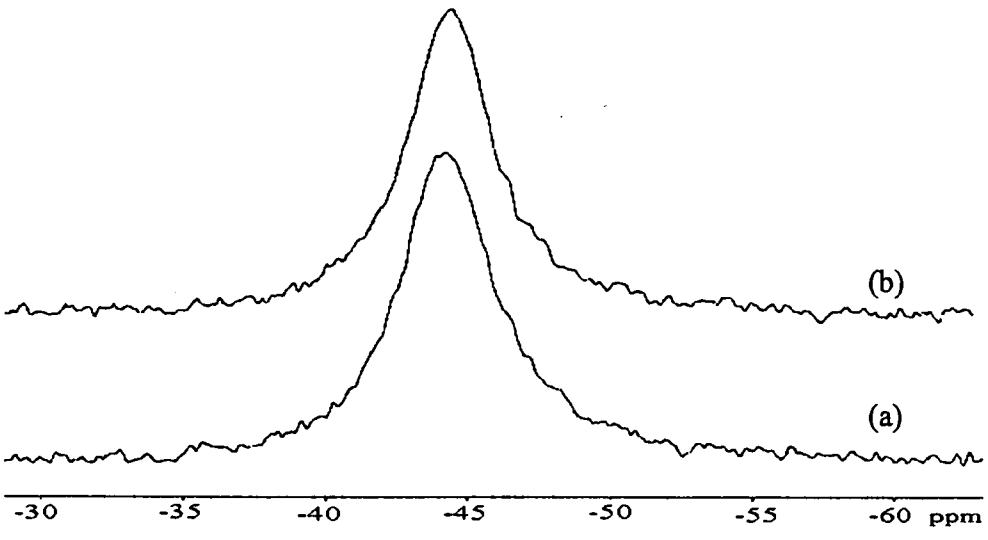
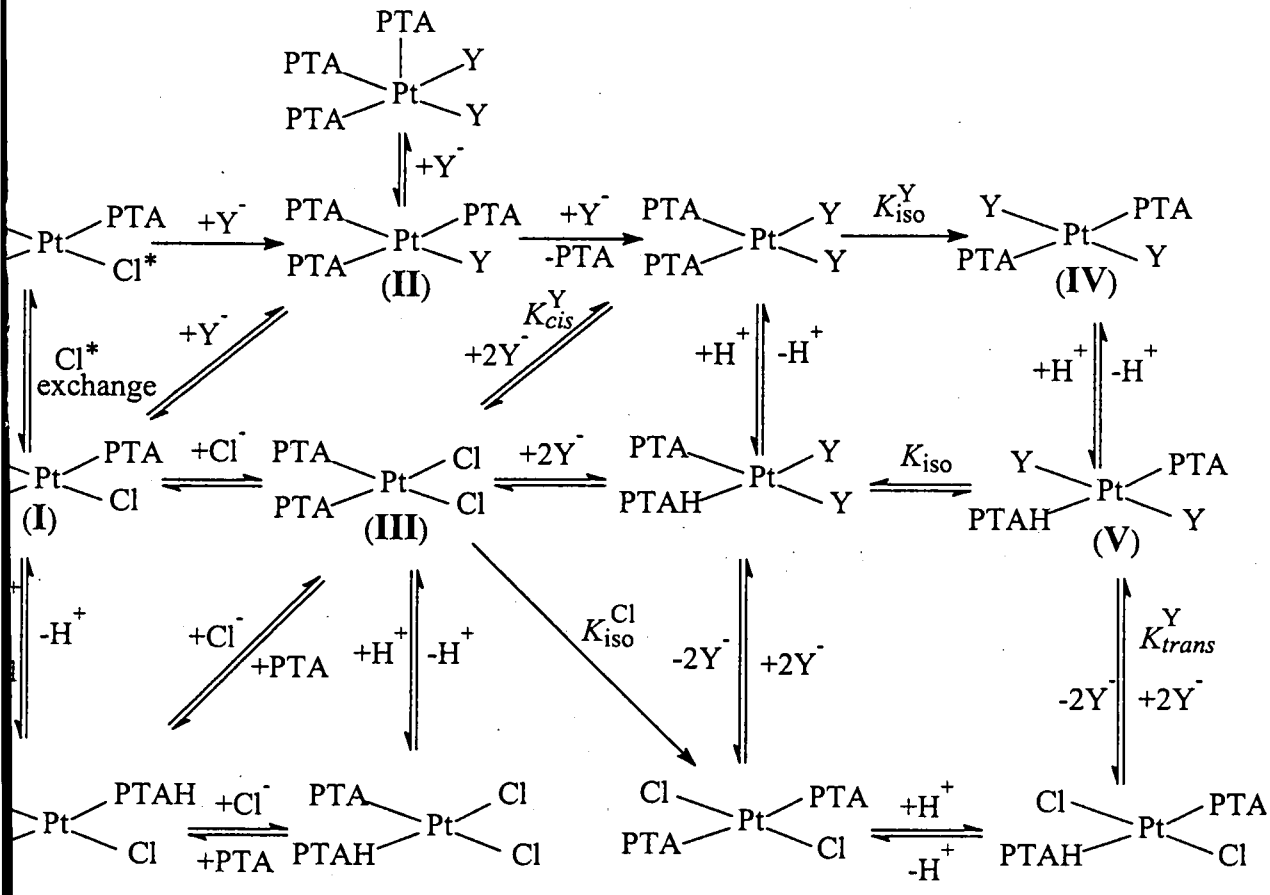


Figure 4.5: ^{35}Cl NMR spectra for the exchange of $[PtCl(PTA)_3]^+$ (2.26 mM) with excess Cl^- (as NaCl) at different pH values. $[Cl^-]$ = 2 M, T = 22 °C, (a) indicates pH at 5.65 and (b) at 6.5 respectively.

11. With the above in mind, the following complete reaction scheme for the substitution behaviour of the $[PtCl(PTA)_3]^+$ complex in aqueous solution is postulated:

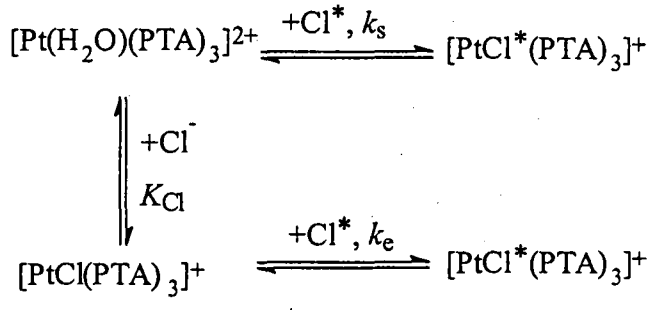


Scheme 4.2: Proposed scheme of the reaction mechanism; all the charges of the complexes are omitted for simplification. $PTAH^+$ = protonated PTA and iso = isomerisation.

4.6 RATE LAWS

Equations for the chloride exchange rate law are derived as follows:

Considering **Scheme 4.3**



Scheme 4.3: Representation of the mechanism for chloride exchange of the $PtCl(PTA)_3]^+$ complex. K_{Cl} is the hydrolysis equilibrium constant, k_e the exchange rate constant, k_s the rate constant for the solvent substitution and Cl* is the free chloride in the exchange process.

A complete derivation of the rate law is given in the **Appendix**.

The rate for the Cl^- exchange is given by

$$R = (k_s[[Pt(H_2O)(PTA)_3]Cl] + k_e[[PtCl(PTA)_3]Cl])[Cl^-] \quad \textbf{(4.41)}$$

$$K_{Cl} = [[PtCl(PTA)_3]Cl] / ([[Pt(H_2O)(PTA)_3]Cl] \times [Cl^-]) \quad \textbf{(4.42)}$$

Rearranging **4.42** and substitution in **4.41** gives **4.43**,

$$R = (k_s + k_e K_{Cl}[Cl^-] / (1 + K_{Cl}[Cl^-]))[Cl^-][Pt]_T \quad \textbf{(4.43)}$$

The rate constant observed (as a function of the linewidth) on the free Cl^- peak is given by:

$$d[PtCl]/dt[Cl^-] = (k_{obs})_{Cl} = (k_s + k_e K_{Cl}[Cl^-] / (1 + K_{Cl}[Cl^-]))[Pt]_T \quad \textbf{(4.44)}$$

If $K_{Cl} = 1/K_{Cl(R)}$ ($K_{Cl(R)}$ = hydrolysis equilibrium constant defined in reverse direction) is substituted in **4.43** and after reorganisation then

$$(k_{obs})_{Cl} = (k_e + k_s K_{Cl(R)} /[Cl^-] / (1 + K_{Cl(R)}[Cl^-]))[Pt]_T \quad \textbf{(4.45)}$$

When $[Cl^-] >> K_{Cl(R)}$ then

$$(k_{obs})_{Cl} / [Pt] = (k_{obs})' = k_e + k_s K_{Cl(R)}/[Cl^-] \quad \textbf{(4.46)}$$

4.7 RESULTS

4.7.1 Equilibrium studies

Typical UV-Vis spectra of $[PtCl(PTA)_3]Cl$ with other different ligands (Br^-, N_3^-) at different concentrations are shown in **Fig. 4.6a-b**.

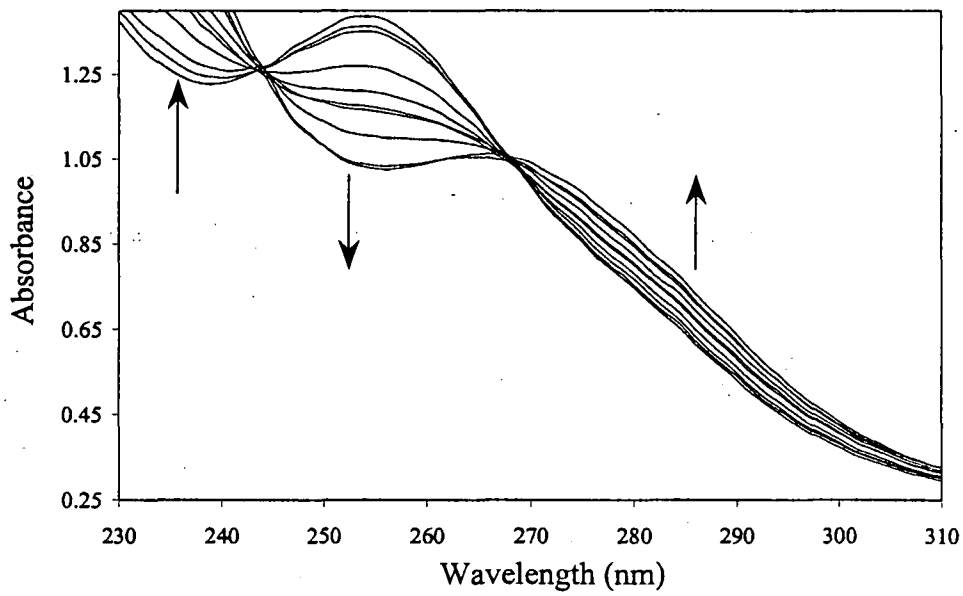


Figure 4.6a: UV-Vis spectrum of $[PtCl(PTA)_3]Cl$ with Br^- at 25 °C. Scans were taken over a period of 2.5 h. The final concentrations of Pt and the excess Cl^- (as NaCl) added were 0.075 and 1 mM respectively. $[Br^-]$ = 0-20 mM, pH = 5.6.

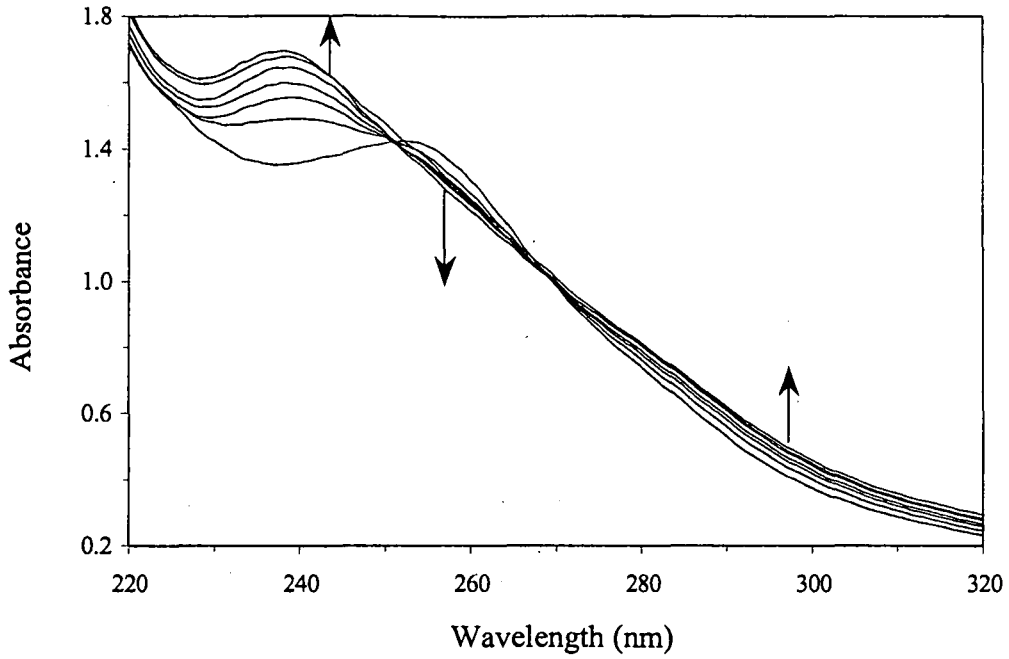


Figure 4.6b: UV-Vis spectrum showing the aqueous solution behaviour of $[PtCl(PTA)_3]Cl + N_3^-$ (as NaN_3) at 25 °C. Scans were taken over a period of 2.5 h. The final concentrations of Pt and the excess Cl^- (as NaCl) added were 0.075 and 1 mM respectively. $[N_3^-]$ = 0-20 mM, pH = 5.6.

The $[PtCl(PTA)_3]Cl$ complex was reacted with various halides and pseudo-halides as shown by **Eq. 4.47**.

$$[PtCl(PTA)_3]^+ + Y \underset{}{\overset{K}{\rightleftharpoons}} [PtY(PTA)_3]^+ + Cl^- \quad (Y = SCN^-, Br^-, N_3^-) \qquad (4.47)$$

For the determination of the equilibrium constants **Eq. 4.48** (derived in the **Appendix**) was used to fit the absorbance *vs.* [Y] data.

$$Abs = \frac{A_R[Cl^-] + (A_P)K[Y]}{[Cl^-] + K[Y]} \qquad (4.48)$$

Abs = Total absorbance

A_R = Absorbance of the pure reactant

A_P = Absorbance of the pure product

$[Cl^-]$ = Concentration of added Cl^-

K = Equilibrium constant

[Y] = Concentration of added halide or pseudo-halide.

Data was fitted to **Eq. 4.48** and the graphs as shown in **Fig. 4.7a-c** were obtained.

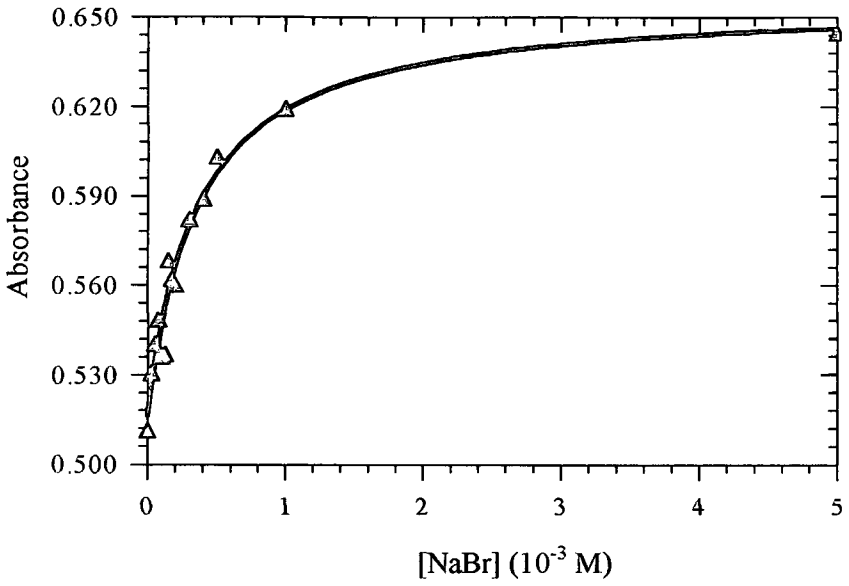


Figure 4.7a: Absorbance changes when $[Br^-]$ (as NaBr) is varied in an aqueous solution of $[PtCl(PTA)_3]Cl$ + excess Cl^- (as NaCl). Wavelength = 290 nm, [Pt] = 0.075 mM, $[Cl^-]$ = 1 mM, $[Br^-]$ = 0-5 mM, T = 25 °C.

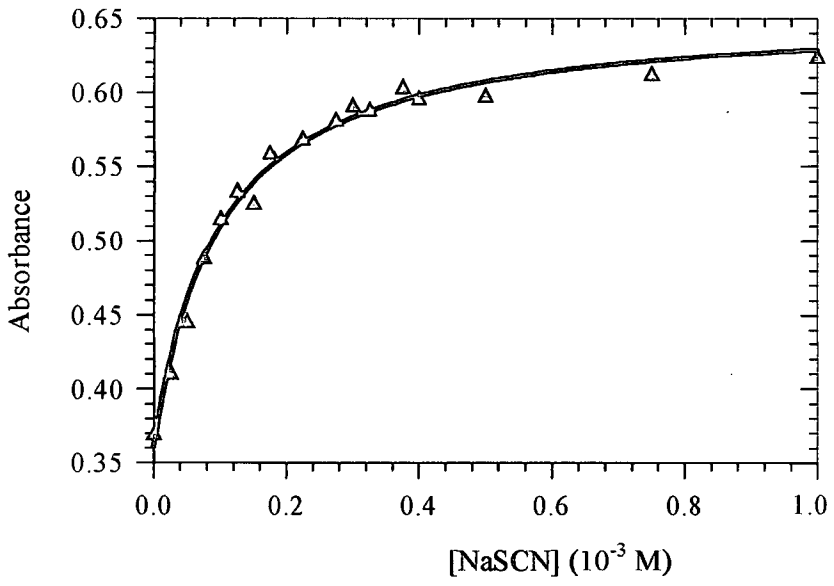


Figure 4.7b: Absorbance changes when $[SCN^-]$ (as NaSCN) is varied in an aqueous solution of $[PtCl(PTA)_3]Cl$ + excess Cl^- (as NaCl). Wavelength = 298 nm, [Pt] = 0.075 mM, $[Cl^-]$ = 1 mM, $[SCN^-]$ = 0-1 mM, T = 25 °C.

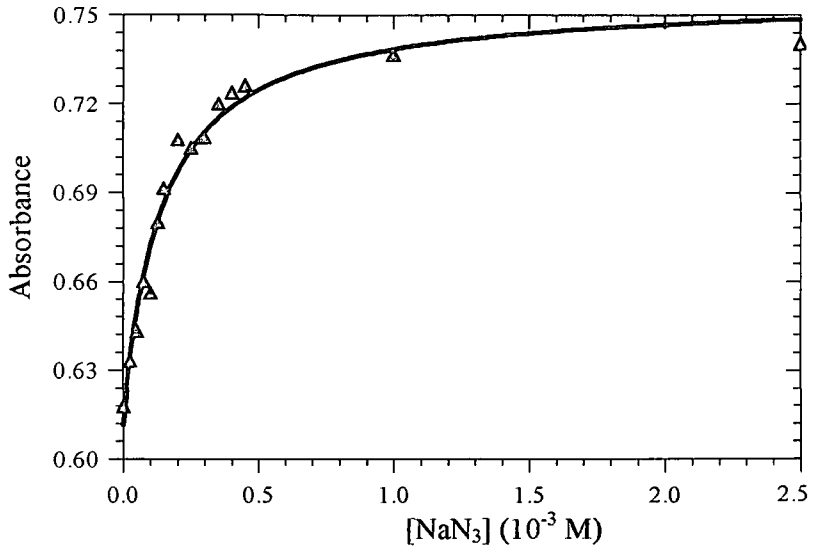


Figure 4.7c: Absorbance changes when $[N_3^-]$ (as NaN_3) is varied in an aqueous solution of $[PtCl(PTA)_3]Cl$ + excess Cl^- (as NaCl). Wavelength = 285 nm, [Pt] = 0.075 mM, $[Cl^-]$ = 1 mM, $[N_3^-]$ = 0-2.5 mM, T = 25 °C.

The equilibrium constant values obtained from the graphs above are summarised and given in **Table 4.1**.

Table 4.1: Equilibrium constant values obtained for the reaction $[PtCl(PTA)_3]Cl$ + Y (Y = SCN^-, N_3^-, Br^-) at 25 °C. The values were determined at a wavelength of 298, 285 and 290 nm for SCN^-, N_3^- and Br^- respectively.

Y	K $(M^{-1})^a$
SCN^-	10(1)
N_3^-	7(1)
Br^-	2.8(5)

[a] Defined in **Eq. 4.47**

4.7.2 Influence of pH on [PtCl(PTA)$_3$]Cl

Absorbance values from the UV-Vis spectral changes (**Fig 4.4**) at different wavelengths were plotted against pH values (**Appendix**) and to obtain pK_a values **Eq. 4.49**[16] was used to fit the plots.

$$A_{obs} = \frac{A_1[H^+]^2 + A_2K_{a_1}[H^+] + A_3K_{a_1}K_{a_2}}{[H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2}} \qquad (4.49)$$

The absorbance *versus* pH values were fitted to **Eq. 4.49** and the result is illustrated in **Fig. 4.8**.

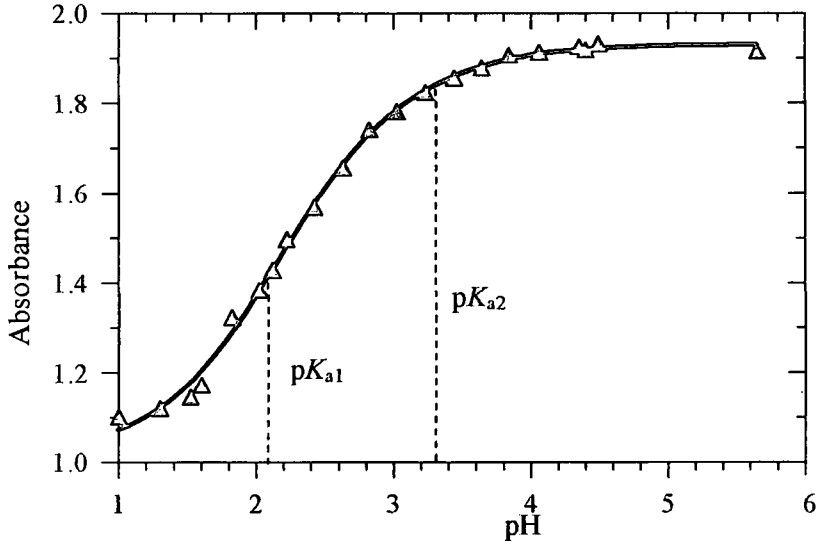


Figure 4.8: Absorbance *vs.* pH graph for [PtCl(PTA)$_3$]Cl with triflic acid at 254.6 nm. The final concentrations of Pt and added Cl^- were 0.075 and 20 mM respectively. The pH values plotted vary from 1-6.

Table 4.2: pK_a values obtained at wavelengths of 254.6 and 275.5 nm.

	λ = 254.6 nm	λ = 275.5 nm
pK_{a1}	2.1(1)	2.13(7)
pK_{a2}	3.3(8)	3.7(6)

4.7.3 Chloride exchange

The rates of substitution reactions were too fast to monitor by the conventional stopped-flow instrument. However, this enabled the study of the rapid chloride exchange process by NMR since significant line broadening was observed. The only signal observed was the free ^{35}Cl peak and the linewidth in the absence of exchange is only 20 Hz. The ^{35}Cl NMR spectra obtained are shown in **Fig. 4.9** and **4.10** (spectra with the variation of the platinum and chloride concentrations, respectively).

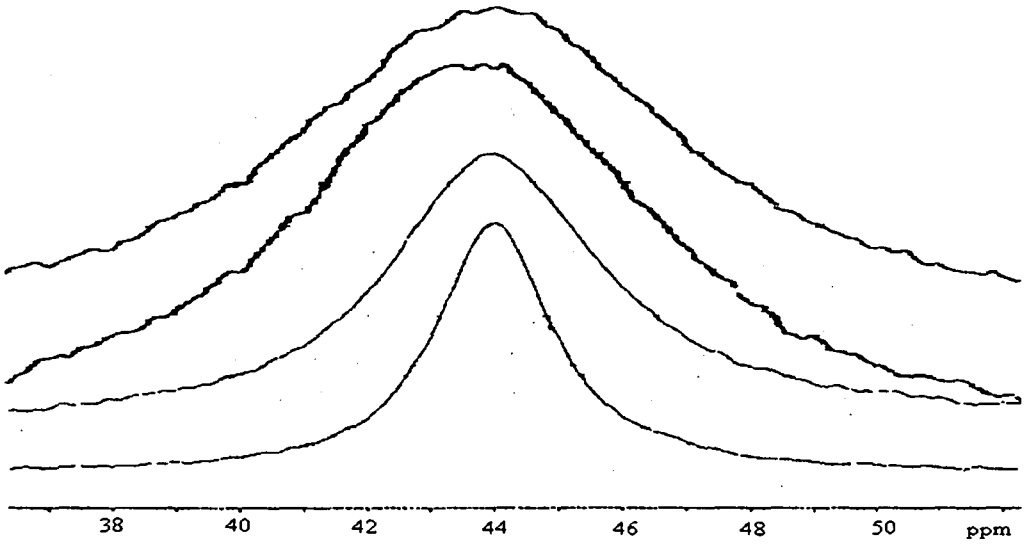


Figure 4.9: ^{35}Cl NMR spectra for the Cl^- exchange between $[PtCl(PTA)_3]^+$ (2.26, 4.52, 6.78, 9.04 mM respectively) and free Cl^- (as NaCl). $[Cl^-]$ = 4 M, T = 22 °C and pH = 5.6.

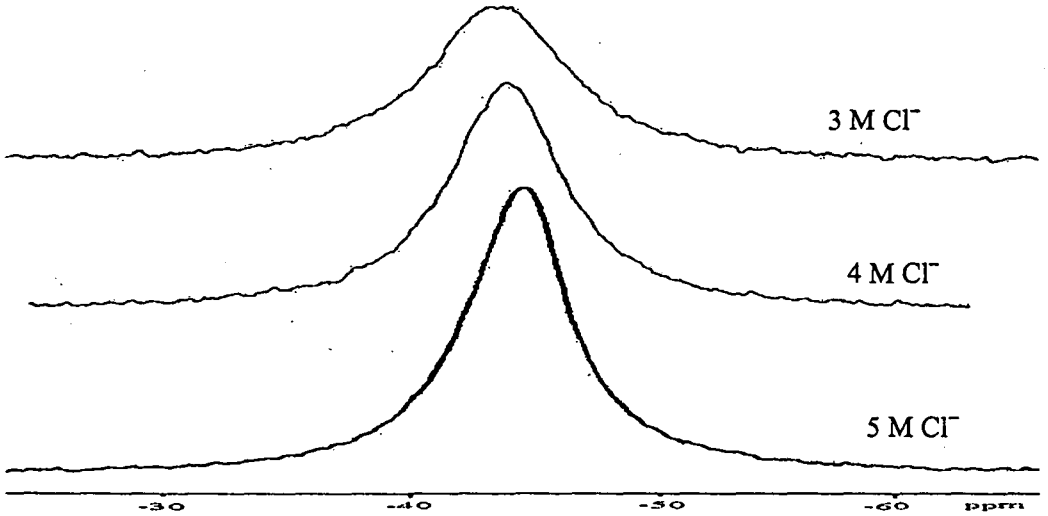


Figure 4.10: ^{35}Cl NMR spectra for the Cl^- exchange between $[PtCl(PTA)_3]^+$ (6.78 mM) and free Cl^- (as NaCl). $[Cl^-]$ = 3, 4 and 5 M as indicated, T = 22 °C and pH = 5.6.

From the NMR spectra the observed line broadening due to exchange was calculated using **Eq. 4.50**,

$$\Delta\nu_{exch} = \Delta\nu_{obs} - \Delta\nu_{no\ exch} \qquad (4.50)$$

and the observed rate constant by employing **Eq. 4.51**.

$$k_{obs} = \Delta\nu_{exch} \times \pi \qquad (4.51)$$

The observed rate constants $(k_{obs})_{Cl}$ calculated for specific $[Cl^-]$ with different $[PtCl(PTA)_3]^+$ concentrations at 22 °C are reported in **Table 4.3**.

Table 4.3: Observed rate constants $(k_{obs})_{Cl}$, calculated for the rapid chloride exchange observed for $[PtCl(PTA)_3]^+ + Cl^-$ on ^{35}Cl NMR. T = 22 °C, pH = 5.65.

$[PtCl(PTA)_3]^+$ concentration (mM)	$(k_{obs})_{Cl}$ (s^{-1}) for different $[Cl^-]$			
	2 M	3 M	4 M	5 M
2.26	312	190	140	-
4.52	600	401	284	-
6.78	882	573	437	370
9.04	1180	800	606	505
11.30	1500	1000	750	640
13.56	-	-	900	755
15.82	-	-	1050	880

The calculated $(k_{obs})_{Cl}$ values (data in **Table 4.3**) were plotted against platinum and chloride concentration and were fitted to **Eqs 4.45** and **4.46** using the least-squares program Scientist[13], and are illustrated in the following graphs.

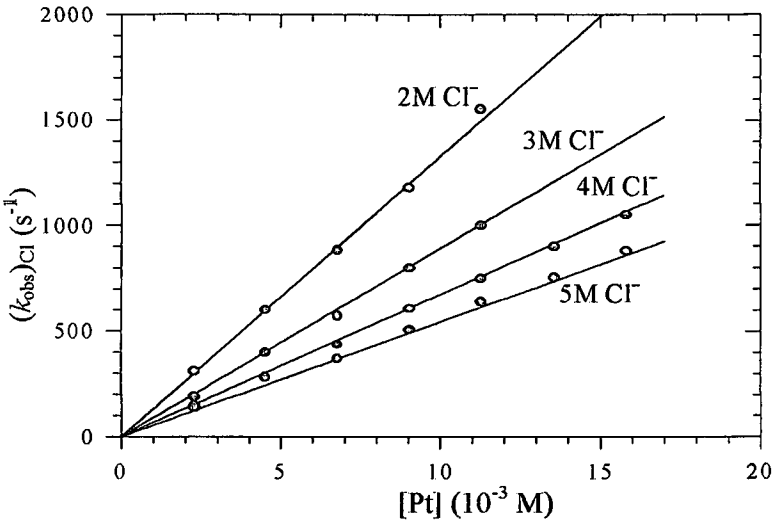


Figure 4.11: Graphs of $(k_{obs})_{Cl}$ *vs.* platinum concentration (**Table 4.3**) at different Cl^- concentrations (indicated on the figure) for the exchange of free Cl^- with $[PtCl(PTA)_3]^+$, T = 22 °C. This graph clearly shows a direct linear relationship between $(k_{obs})_{Cl}$ and [Pt] and has an intercept = 0 (See **Eq. 4.45**).

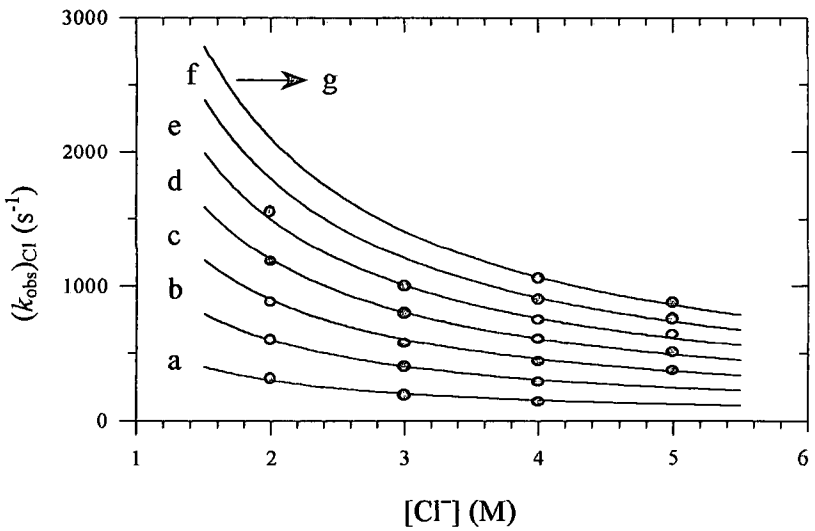


Figure 4.12: Graphs of $(k_{obs})_{Cl}$ *vs.* Cl^- concentration (2, 3 and 4 M) at different platinum concentrations (a: 2.26, b: 4.52, c: 6.78, d: 9.04, e: 11.3, f: 13.56 and g: 15.82 mM) for the exchange of free Cl^- with $[PtCl(PTA)_3]^+$, T = 22 °C. This graph shows an inverse relationship between $(k_{obs})_{Cl}$ and [Cl^-] (See **Eq. 4.46**).

The inverse relationship (**Eq. 4.46**) between the observed rate constant and [Cl^-] is further illustrated by plotting $(k_{obs})_{Cl}$ *vs.* 1/[Cl^-] as shown by **Fig. 4.13**. The intercept is therefore given by k_e[Pt] and the slope by $(k_s K_{Cl(R)})$[Pt] as determined in the derivation of the rate law in **Section 4.6**.

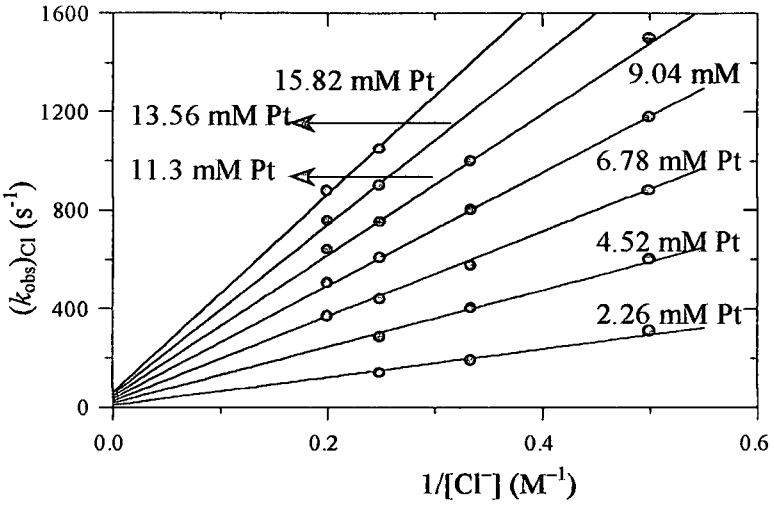


Figure 4.13: Graphs of $(k_{obs})_{Cl}$ *vs.* 1/Cl^- concentration at different platinum concentrations (**Table 4.3**) for the exchange of free Cl^- with $[PtCl(PTA)_3]^+$. T = 22 °C.

The complete rate law is illustrated by **Fig. 4.14**, which gives a three-dimensional representation of the observed Cl^- exchange rate constant as a function of both [Cl^-] and [Pt].

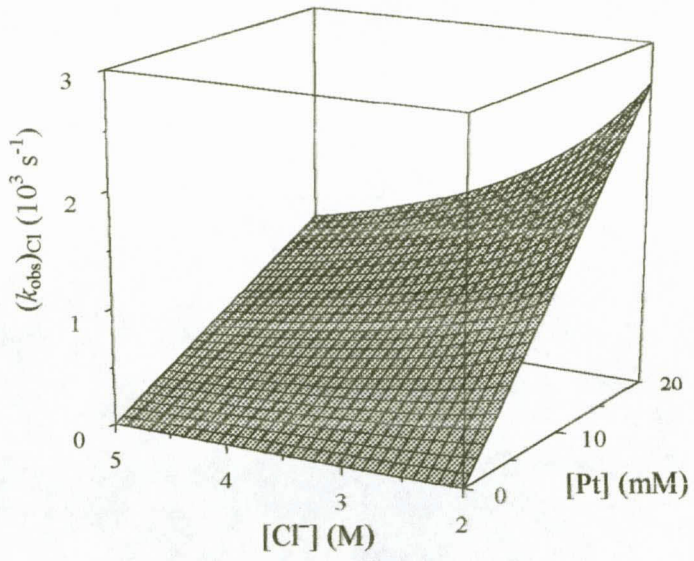


Figure 4.14: 3D representation of the graphs of $(k_{obs})_{Cl}$ *vs.* [Cl⁻] *vs.* [Pt] for the exchange of free Cl⁻ with $[PtCl(PTA)_3]^+$. T = 22 °C.

The results of the rate constants obtained from the above figures are reported in **Table 4.4**. Unfortunately $k_s K_{Cl(R)}$ is only obtained as a combined constant, (could only be determined for different nucleophiles Br^-, N_3^- and SCN^-).

Table 4.4: Overall rate constants for the Cl⁻ exchange with $[MCl(PTA)_3]^+$, pH = 5.6, T = 22 °C.

M	k_e ($M^{-1}s^{-1}$)	$k_s K_{Cl(R)}$ (s^{-1})
Pt[a]	3.7(9) x 10^3	2.54(3) x 10^5
Pt[b]	2(1) x 10^3	2.61(4) x 10^5
Pd[17]	1.64(8) x 10^5	5.7(2) x 10^5

[a]From **Fig. 4.13** [b]From **Fig. 4.14.**

However, if it is assumed that K will be comparable to the values obtained for Br^-, N_3^- and SCN^- (See **Table 4.1** and using the average value of 3,7 and 10 ≈ 6 M^{-1}), an estimated value of k_s = (2.6 x 10^5 s^{-1} x 6 M^{-1}) = 1.5 x 10^6 $M^{-1}s^{-1}$ is obtained.

4.8 DISCUSSION

From the results presented above, it can be concluded that the platinum(II) analogue of the Wilkinson catalyst, $[PtCl(PTA)_3]^+$, the starting complexes and the products prepared were characterised and the solution behaviour of this complex in aqueous medium was explored which indicated the complex mechanism (**Scheme 4.2**). The ^{31}P NMR spectrum of the $[PtCl(PTA)_3]Cl$ complex consisted of a triplet of doublets at δ -51.2 ppm due to the phosphorus atoms of the two PTA ligands *cis* to the chloride and a triplet of triplets at δ –48.5 ppm due to the phosphorus atom of the PTA *trans* to the chloride (**Fig. 4.1**).

When the $[PtCl(PTA)_3]Cl$ complex is dissolved in water, it was observed that it is unstable and hydrolyses, therefore an addition of excess chloride (as NaCl) was essential. For the purpose of this study it was assumed that the complex is stable in an excess of the Cl^- (**Fig. 4.2b**) and in all the UV-Vis experiments, equilibrium constant determination and in the study of the influence of pH on the complexes, an excess of NaCl was added to the aqueous solutions to prevent hydrolysis and consequent decomposition of the $[PtCl(PTA)_3]Cl$ complex.

When the $[PtCl(PTA)_3]^+$ complex was reacted with several halides and pseudo-halides ($Y = Br^-$, SCN^-, N_3^-), well defined equilibria were observed, thus forming the final products (**Eq. 4.37**). The addition of the halide or pseudo-halide to the $[PtCl(PTA)_3]^+$ complex results in the rapid substitution of the chloride in the complex thereby forming $[PtY(PTA)_3]^+$. The isolated crystal structure of $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ provides evidence for the formation of these final products. This coordination compound shows a distorted square planar geometry with the monosubstituted thiocyanate ion bonded through the nitrogen atom.

The equilibrium constants determined for the reaction of $[PtCl(PTA)_3]^+$ and a range of entering ligands Y are presented in **Table 4.1**. From this table it is noted that the equilibrium constants for the SCN^- and N_3^- are comparable, since in the structure isolated the SCN^- ligand is N-coordinated and this could be due to steric or electronic effects. During the study of the equilibrium reactions it was observed that the reactions are fast and there is probably more than one reaction occurring that could not be investigated, and therefore only the overall reactions were studied. It was found in these systems that complex solution behaviour exists and for this study the equilibrium constants determined can be considered as overall equilibrium constants for the reaction **(Eq. 4.37)**.

UV-Vis experiments done to investigate the protonation behaviour of $[PtCl(PTA)_3]^+$ revealed that there is indeed a pH dependence for the complex. Two pK_a values were determined using **Eq. 4.49** yielding the first $pK_a = 2.12$ (average pK_a) and the second 3.5 (average pK_a). Addition of the acid resulted in one of the PTA ligands in the complex to be protonated **(Eq. 4.38)** resulting in the first pK_a value and in the presence of Cl^- converted $[PtCl(PTA)_3]^+$ to the protonated *cis*-$[PtCl_2(PTAH)_2]^{2+}$ complex **(Eq. 4.40)** which indicates the second pK_a value obtained. Extensive research has been done to investigate the effect of pH in water-soluble ruthenium(II) and rhodium(I) complexes and it was found that it has implications in organometallic catalysis[18,19,20]. It is clear that more detailed research is also needed in future to quantify the effect of pH in this $[PtCl(PTA)_3]^+$ system.

As shown in **Scheme 4.3** the chloride exchange process consists of two steps, a direct substitution of the chloride by the solvent forming $[Pt(H_2O)(PTA)_3]^{2+}$ (the aqua complex) and the direct chloride exchange pathway. From **Figs. 4.11-4.14** it can be seen that when the chloride concentration is increased the exchange rate constant decreases and when the platinum concentration is increased the rate increases. This confirms that there are two species involved in the kinetic process that are in equilibrium *i.e.* the $[PtCl(PTA)_3]^+$ and $[Pt(H_2O)(PTA)_3]^{2+}$ complexes.

The $[Pt(H_2O)(PTA)_3]^{2+}$ complex is more reactive towards aqua substitution and when the chloride concentration is increased the equilibrium is shifted towards the less reactive $[PtCl(PTA)_3]^+$ complex. The exchange process therefore occurs between the chloride present in this complex and the free chloride and is slower than the substitution of the chloride in the aqua complex by the free chloride. In fact, based on the estimated values reported above, the direct aqua substitution on the $[Pt(H_2O)(PTA)_3]^{2+}$ complex (k_s = 1.5 x 10^6 $M^{-1}s^{-1}$) is almost three orders-of-magnitude faster than the Cl^- exchange process (k_e = 3 x 10^3 $M^{-1}s^{-1}$). This is to be expected for pure associative processes since the entering of Cl^- on the dicationic $[Pt(H_2O)(PTA)_3]^{2+}$ complex is expected to be more rapid than on the $[PtCl(PTA)_3]^+$ complex. The exchange rates on platinum(II) species were found to be slower than those of the corresponding palladium(II) analogues (**Table 4.4**). This is in agreement with what is normally observed when the exchange of ligands on the two metal centres are compared.

Ligand substitution reactions occurring at transition metal centres have been probed largely by examining concentration and temperature dependence of the reaction rate, substituent effects in the complex, changes of solvent and medium and the changes in the nature of the entering ligands. The studies conducted by changing these parameters can make a significant contribution in deciphering the intimate nature of substitution mechanisms. For associative substitution reactions on square planar complexes there is a complicated interaction between the metal centre and the *trans* and entering ligands and these are mainly important in determining the overall reaction rate[21].

The effect of ligand size on the rate of substitution is evident for complexes of the type $[PtL_4]^+$ (L = MeCN, H_2O) [22]. Ligands with these hard donor atoms have similar exchange rates (k = 6.2, 7.1 $M^{-1}s^{-1}$). In contrast, softer ligands like Me_2S and MeNC have higher substitution rates indicating that in the absence of steric effects, ligand nucleophilicity and the *trans* effect determine reactivity. This is due to the stabilisation of the five-coordinate transition state or intermediate by π back-bonding from the metal to the ligand and the isolation of the five-coordinate platinum(II) intermediate has been possible[23]. In this study, the difference between the Pt(II) and Pd(II) systems is approximately 20 times, typical of systems wherein significant π ligands (PTA) are present.

Since line broadening can be from the chloride exchange or quadrupolar effects of the platinum(II) centre, for the purpose of this study it was assumed that the exchange is due to the exchange process. However more extended studies and wider temperature variations have to be done to explain these effects in the interesting chloride exchange process.

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5 EVALUATION AND FUTURE ASPECTS

The evaluation and results of this study are briefly discussed (**Section 5.1**) in terms of the aims presented in **Chapter 1** while some future aspects of the research are outlined in **Section 5.2**.

5.1 SCIENTIFIC EVALUATION

The platinum(II) analogue of the Wilkinson catalyst, $[PtCl(PTA_3)]Cl$, the starting complexes and the products were successfully prepared. However, the preparation of some complexes, *e.g.* $[Pt(N_3)(PTA)_3]N_3$, required higher concentrations of the platinum complex and that of the ligand. These complexes were characterised with UV-Vis spectrophotometry, IR and multi-nuclear NMR spectroscopy. The complexes needed to be recrystallised repeatedly in water or methanol to remove the excess PTA and the 'bis' complex, *cis*-$[PtCl_2(PTA)_2]$.

The aqueous equilibrium studies on $[PtCl(PTA_3)]Cl$ with different halides and pseudo-halides (Y = SCN^-, Br^-, N_3^-) were done successfully. The general equilibrium reaction for the process is given as **Eq. 5.1**.

$$[PtCl(PTA)_3]^+ + Y \underset{}{\overset{K}{\rightleftharpoons}} [PtY(PTA)_3]^+ + Cl^- \qquad (5.1)$$

The equilibrium reactions could not be studied in neat aqueous medium as the $[PtCl(PTA_3)]Cl$ complex was not stable when dissolved in water (**Eq. 5.2**). Therefore, to increase the stability of this complex a large excess of the chloride ion (in the form of NaCl) was required to prevent hydrolysis.

$$[PtCl(PTA)_3]^+ + H_2O \underset{}{\overset{K}{\rightleftharpoons}} [Pt(H_2O)(PTA)_3]^+ + Cl^- \qquad (5.2)$$

From the results presented in **Chapter 4** it was noted that the equilibrium constants for the SCN^- and N_3^- are similar since it was proved in the structure characterised (**Section 3.5.3.3**) that the thiocyanate ligand bonded through the nitrogen atom.

X-ray crystallography was used for the characterisation of complexes when the 'tris' complex is reacted with the various ligands (SCN^-, Br^-, and N_3^-). The structure of $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ shows that the coordination compound exhibits a distorted square planar geometry with monosubstituted thiocyanate ion bonded through the nitrogen atom and three PTA ligands bonded *via* the phosphorus atoms. The crystal structure determinations of the complexes of bromide and azide were unsuccessful since the crystals decomposed. In an attempt to overcome this, a high concentration of several counter-ions like $NaClO_4$, $Na(BPh_4)$ and NH_4PF_6 was added in the synthesis of the complexes but the decomposition still persisted.

UV-Vis experiments of the effect of addition of chloride, and the pH dependence on the $[PtCl(PTA)_3]Cl$ complex was also done. Addition of acid resulted in one of the PTA ligands in the complex to be protonated and in the presence of Cl^- converted $[PtCl(PTA)_3]^+$ to the protonated *cis*-$[PtCl_2(PTA)_2]$ complex which is defined by a second pK_a value.

As the kinetic reactions were too fast to be followed on a stopped-flow instrument, preliminary studies on the chloride exchange using ^{35}Cl NMR were done which showed that there is significant line broadening due to the very rapid chloride exchange process. The chloride exchange was studied in the slow exchange regime. Variations of platinum and added chloride concentrations were done to study this effect on the line broadening. Significant temperature variations could not be done as the NMR instrument was limited in this respect and a wide variation of the temperature is needed to determine whether the exchange is due to line broadening or to quadrupolar effects.

In general, the study has been successful since the starting complexes were successfully synthesised, adequately characterised and a definite contribution towards elucidating the complex aqueous solution behaviour was made.

5.2 FUTURE ASPECTS

Since the rate of the substitution of the chloride in $[PtCl(PTA)_3]^+$ was too fast to be monitored on a stopped-flow instrument, the investigations should be extended by changing the solvent from water to methanol or using a range of organic solvents. The systems should then be investigated at lower temperatures. PTA was used in this study but other compounds like $P(NMe_2)_3$ and bidentate ligands could also be introduced. These modifications will help with the solubility of the complexes in various solvents and to enable the employment of the ionic salts (NaSCN, NaN_3, NaBr *etc.*) as nucleophiles to investigate the chloride substitution.

Further aspects that can be investigated by isolating crystals and solving structures of the azide and bromide complexes include using other counter-ions, higher platinum and halide concentrations and operating at low temperatures. The research done with the complexes containing the water-soluble PTA and other modified phosphine ligands should be continued since it can be a gateway to the synthesis of new water-soluble chemotherapeutic drugs.

Platinum(II) complexes containing PTA, and/or other ligands like TPPMS (monosulphonated triphenylphosphine) or tris(*m*-sulphonatophenyl)phosphine (TPPTS) have catalytic implications as well. These include the catalytic hydrogenation and deuteration of phospholipid model membranes, hydrogenation and selective isomerisation of olefins, *etc*. Further studies could also be extended by changing the metal centre to Rh, Pd, Ru and Ir analogues.

The preliminary NMR experiments indicated chloride exchange between $[PtCl(PTA)_3]^+$ and additional chloride, which was assumed in this study to be in the slow exchange regime. However, more temperature and pH variations should be performed in future studies to determine whether line broadening is due to the chloride exchange or perhaps due to quadrupolar effects. This then provides a broad future study of the interesting and complex reactivity and thermodynamics of the $[PtCl(PTA)_3]^+$ aqueous system.

APPENDIX

A: Crystallographic data for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

Table A.1: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

olecule 1					Molecule 2				
	x	y	z	U(eq)		x	y	z	U(eq)
(1)	6523(1)	273(1)	1613(1)	18(1)	Pt(2)	5266(1)	4674(1)	2719(1)	15(1)
11)	6263(1)	-128(1)	2679(1)	19(1)	P(21)	4986(1)	4011(1)	3749(1)	16(1)
12)	7079(1)	721(1)	606(1)	19(1)	P(22)	5762(1)	5000(1)	1668(1)	16(1)
13)	4877(1)	1036(1)	1413(1)	19(1)	P(23)	4198(1)	6265(1)	2821(1)	16(1)
1)	2985(1)	5631(1)	1785(1)	37(1)	S(2)	722(2)	6926(2)	2163(1)	82(1)
11)	10093(1)	-1510(1)	1937(1)	36(1)	S(21)	7652(1)	1584(1)	2119(1)	33(1)
1)	3483(4)	3617(5)	2426(2)	45(2)	N(2)	6099(6)	8126(5)	1023(4)	93(3)
11)	8040(3)	-595(3)	1733(2)	24(1)	N(21)	6250(3)	3207(3)	2639(2)	22(1)
111)	5609(3)	675(3)	3700(2)	26(1)	N(211)	5792(3)	2312(3)	4682(2)	23(1)
112)	5697(3)	-1035(3)	3820(2)	23(1)	N(212)	4620(3)	3934(3)	4987(2)	20(1)
113)	7279(3)	-853(3)	3730(2)	22(1)	N(213)	3929(3)	3054(4)	4583(2)	25(1)
121)	8617(3)	1082(4)	-143(2)	25(1)	N(221)	5883(3)	6077(3)	478(2)	18(1)
122)	6942(3)	1875(3)	-571(2)	22(1)	N(222)	7489(3)	4636(3)	874(2)	18(1)
123)	8026(3)	6(4)	-427(2)	27(1)	N(223)	6169(3)	4292(3)	608(2)	20(1)
131)	2941(3)	1234(4)	1833(2)	27(1)	N(231)	3810(3)	7829(3)	3351(2)	19(1)
132)	3087(3)	2660(3)	1028(2)	21(1)	N(232)	2324(3)	7564(3)	3267(2)	20(1)
133)	3517(3)	1030(3)	762(2)	25(1)	N(233)	3128(3)	8312(3)	2343(2)	22(1)
1)	3291(4)	4453(5)	2167(3)	31(2)	C(2)	6355(6)	7674(7)	1508(4)	61(2)
11)	8896(4)	-976(4)	1815(2)	20(1)	C(21)	6845(4)	2528(4)	2426(2)	19(1)
olecule 3									
3)	9847(1)	3969(1)	2503(1)	16(1)	N(313)	9423(3)	6022(3)	440(2)	22(1)
31)	9887(1)	5241(1)	1650(1)	17(1)	N(321)	8860(4)	1289(4)	3538(2)	32(1)
32)	9877(1)	2483(1)	3203(1)	21(1)	N(322)	10735(4)	397(4)	3379(2)	40(1)
33)	9895(1)	4792(1)	3159(1)	18(1)	N(323)	9944(4)	1097(3)	4305(2)	30(1)
)	7160(1)	4734(1)	3670(1)	36(1)	N(331)	8979(3)	6497(3)	3638(2)	23(1)
1)	10004(1)	1943(1)	1186(1)	35(1)	N(332)	10868(3)	5697(4)	3492(2)	25(1)
3)	7653(4)	3749(4)	4888(3)	46(2)	N(333)	9998(3)	4874(3)	4332(2)	22(1)
31)	9788(3)	3243(3)	1894(2)	23(1)	C(3)	7444(4)	4158(5)	4386(3)	30(2)
311)	11067(3)	5800(3)	680(2)	20(1)	C(31)	9870(4)	2706(4)	1600(2)	22(1)
312)	9465(3)	7183(3)	977(2)	22(1)					
1)	8670(4)	8393(5)	4656(2)	57(2)					
2)	748(3)	7662(4)	4301(2)	45(1)					
3)	2510(4)	2337(5)	4412(2)	61(2)					
4)	2713(5)	2197(5)	3198(3)	76(2)					
5)	3083(9)	332(10)	3478(6)	107(4)					
6)	2810(7)	9801(6)	4735(4)	52(3)					

Table A.2: Bond lengths (Å) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

Molecule 1		Molecule 2		Molecule 3	
Pt(1)-P(11)	2.3215(13)	Pt(2)-P(21)	2.3090(13)	Pt(3)-P(31)	2.3283(14)
Pt(1)-P(12)	2.2972(13)	Pt(2)-P(22)	2.3361(13)	Pt(3)-P(32)	2.3495(15)
Pt(1)-P(13)	2.2407(13)	Pt(2)-P(23)	2.2359(13)	Pt(3)-P(33)	2.2407(13)
Pt(1)-N(11)	2.036(4)	Pt(2)-N(21)	2.052(4)	Pt(3)-N(31)	2.043(4)
P(11)-C(111)	1.843(5)	P(21)-C(211)	1.841(5)	P(31)-C(311)	1.839(5)
P(11)-C(112)	1.863(5)	P(21)-C(212)	1.849(5)	P(31)-C(312)	1.859(5)
P(11)-C(113)	1.844(5)	P(21)-C(213)	1.848(5)	P(31)-C(313)	1.829(5)
P(12)-C(121)	1.846(5)	P(22)-C(221)	1.849(5)	P(32)-C(321)	1.841(5)
P(12)-C(122)	1.842(5)	P(22)-C(222)	1.845(5)	P(32)-C(322)	1.857(5)
P(12)-C(123)	1.831(5)	P(22)-C(223)	1.859(5)	P(32)-C(323)	1.858(5)
P(13)-C(131)	1.833(5)	P(23)-C(231)	1.835(5)	P(33)-C(331)	1.840(5)
P(13)-C(132)	1.850(5)	P(23)-C(232)	1.850(5)	P(33)-C(332)	1.840(5)
P(13)-C(133)	1.843(5)	P(23)-C(233)	1.840(5)	P(33)-C(333)	1.843(5)
S(1)-C(1)	1.635(7)	S(2)-C(2)	1.604(10)	S(3)-C(3)	1.645(7)
S(11)-C(11)	1.618(5)	S(21)-C(21)	1.617(5)	S(31)-C(31)	1.619(6)
N(1)-C(1)	1.158(7)	N(2)-C(2)	1.147(10)	N(3)-C(3)	1.155(7)
N(11)-C(11)	1.153(6)	N(21)-C(21)	1.159(6)	N(31)-C(31)	1.150(6)
N(111)-C(111)	1.456(6)	N(211)-C(211)	1.471(6)	N(311)-C(311)	1.469(6)
N(111)-C(114)	1.469(6)	N(211)-C(216)	1.470(6)	N(311)-C(314)	1.460(6)
N(111)-C(116)	1.460(7)	N(211)-C(214)	1.472(6)	N(311)-C(316)	1.467(6)
N(112)-C(112)	1.466(6)	N(212)-C(212)	1.458(6)	N(312)-C(312)	1.468(6)
N(112)-C(114)	1.484(6)	N(212)-C(214)	1.467(6)	N(312)-C(314)	1.479(6)
N(112)-C(115)	1.457(6)	N(212)-C(215)	1.458(6)	N(312)-C(315)	1.458(6)
N(113)-C(113)	1.468(6)	N(213)-C(213)	1.489(6)	N(313)-C(313)	1.457(6)
N(113)-C(115)	1.476(6)	N(213)-C(215)	1.486(6)	N(313)-C(315)	1.475(6)
N(113)-C(116)	1.472(6)	N(213)-C(216)	1.469(7)	N(313)-C(316)	1.468(6)
N(121)-C(121)	1.477(6)	N(221)-C(221)	1.475(6)	N(321)-C(321)	1.457(6)
N(121)-C(124)	1.466(7)	N(221)-C(224)	1.472(6)	N(321)-C(324)	1.484(7)
N(121)-C(126)	1.459(6)	N(221)-C(226)	1.474(6)	N(321)-C(326)	1.466(7)
N(122)-C(122)	1.470(6)	N(222)-C(222)	1.473(6)	N(322)-C(322)	1.461(7)
N(122)-C(124)	1.451(6)	N(222)-C(224)	1.464(6)	N(322)-C(324)	1.454(8)
N(122)-C(125)	1.462(7)	N(222)-C(225)	1.476(6)	N(322)-C(325)	1.468(7)
N(123)-C(123)	1.469(6)	N(223)-C(223)	1.481(6)	N(323)-C(323)	1.468(7)
N(123)-C(125)	1.466(7)	N(223)-C(225)	1.472(6)	N(323)-C(325)	1.463(6)
N(123)-C(126)	1.470(6)	N(223)-C(226)	1.471(6)	N(323)-C(326)	1.475(7)
N(131)-C(131)	1.463(6)	N(231)-C(231)	1.480(6)	N(331)-C(331)	1.477(6)
N(131)-C(134)	1.471(7)	N(231)-C(234)	1.468(6)	N(331)-C(334)	1.471(6)
N(131)-C(136)	1.462(7)	N(231)-C(236)	1.465(6)	N(331)-C(336)	1.463(6)
N(132)-C(132)	1.466(6)	N(232)-C(232)	1.473(6)	N(332)-C(332)	1.469(6)
N(132)-C(134)	1.465(6)	N(232)-C(234)	1.478(6)	N(332)-C(334)	1.475(7)
N(132)-C(135)	1.484(6)	N(232)-C(235)	1.478(6)	N(332)-C(335)	1.466(6)
N(133)-C(133)	1.460(6)	N(233)-C(233)	1.468(6)	N(333)-C(333)	1.465(6)
N(133)-C(135)	1.471(7)	N(233)-C(235)	1.467(6)	N(333)-C(335)	1.467(6)
N(133)-C(136)	1.467(6)	N(233)-C(236)	1.458(6)	N(333)-C(336)	1.469(6)

Table A.3: Bond angles (°) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

Molecule 1		Molecule 2		Molecule 3	
N(11)-Pt(1)-P(11)	86.66(12)	N(21)-Pt(2)-P(21)	87.55(12)	N(31)-Pt(3)-P(31)	86.61(13)
N(11)-Pt(1)-P(12)	83.83(12)	N(21)-Pt(2)-P(22)	80.89(12)	N(31)-Pt(3)-P(32)	81.30(13)
N(11)-Pt(1)-P(13)	170.97(13)	N(21)-Pt(2)-P(23)	179.08(12)	N(31)-Pt(3)-P(33)	178.92(13)
P(12)-Pt(1)-P(11)	166.94(5)	P(21)-Pt(2)-P(22)	168.43(5)	P(31)-Pt(3)-P(32)	167.61(5)
P(13)-Pt(1)-P(11)	96.84(5)	P(23)-Pt(2)-P(21)	91.61(5)	P(33)-Pt(3)-P(31)	92.49(5)
P(13)-Pt(1)-P(12)	93.89(5)	P(23)-Pt(2)-P(22)	99.95(5)	P(33)-Pt(3)-P(32)	99.63(5)
C(111)-P(11)-Pt(1)	114.80(17)	C(211)-P(21)-Pt(2)	113.05(15)	C(311)-P(31)-Pt(3)	116.20(18)
C(112)-P(11)-Pt(1)	128.48(17)	C(212)-P(21)-Pt(2)	127.75(17)	C(312)-P(31)-Pt(3)	127.38(15)
C(113)-P(11)-Pt(1)	112.26(15)	C(213)-P(21)-Pt(2)	114.79(17)	C(313)-P(31)-Pt(3)	112.94(18)
C(121)-P(12)-Pt(1)	114.30(17)	C(221)-P(22)-Pt(2)	129.71(15)	C(321)-P(32)-Pt(3)	112.72(18)
C(122)-P(12)-Pt(1)	126.11(16)	C(222)-P(22)-Pt(2)	111.57(16)	C(322)-P(32)-Pt(3)	114.07(18)
C(123)-P(12)-Pt(1)	114.07(17)	C(223)-P(22)-Pt(2)	114.69(16)	C(323)-P(32)-Pt(3)	130.01(18)
C(131)-P(13)-Pt(1)	117.43(17)	C(231)-P(23)-Pt(2)	116.52(16)	C(331)-P(33)-Pt(3)	117.63(17)
C(132)-P(13)-Pt(1)	124.62(17)	C(232)-P(23)-Pt(2)	117.60(17)	C(332)-P(33)-Pt(3)	117.79(15)
C(133)-P(13)-Pt(1)	114.13(16)	C(233)-P(23)-Pt(2)	121.85(15)	C(333)-P(33)-Pt(3)	120.66(17)
C(11)-N(11)-Pt(1)	171.2(4)	C(21)-N(21)-Pt(2)	160.5(4)	C(31)-N(31)-Pt(3)	169.6(4)
N(1)-C(1)-S(1)	177.4(6)	N(2)-C(2)-S(2)	173.1(9)	N(3)-C(3)-S(3)	179.4(5)
N(11)-C(11)-S(11)	179.4(5)	N(21)-C(21)-S(21)	178.5(5)	N(31)-C(31)-S(31)	179.1(5)

Table A.4: Anisotropic displacement parameters ($Å^2$ x 10^3) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11 + ... + 2hka^*b^*U12]$.

	U11	U22	U33	U23	U13	U12
Pt(1)	15(1)	18(1)	15(1)	-1(1)	0(1)	-5(1)
P(11)	18(1)	17(1)	16(1)	0(1)	-1(1)	-6(1)
P(12)	17(1)	20(1)	15(1)	-2(1)	0(1)	-7(1)
P(13)	16(1)	17(1)	20(1)	-2(1)	-1(1)	-7(1)
S(1)	30(1)	42(1)	49(1)	-15(1)	-5(1)	-20(1)
S(11)	19(1)	48(1)	35(1)	2(1)	-5(1)	-15(1)
N(1)	42(3)	47(4)	46(4)	-12(3)	0(3)	-19(3)
N(11)	23(3)	23(3)	18(2)	0(2)	-2(2)	-6(2)
N(111)	25(2)	25(3)	25(3)	-6(2)	-1(2)	-8(2)
N(112)	21(2)	26(3)	17(2)	0(2)	1(2)	-10(2)
N(113)	24(2)	23(3)	18(2)	-2(2)	-3(2)	-10(2)
N(121)	22(2)	32(3)	23(3)	-2(2)	0(2)	-18(2)
N(122)	23(2)	25(3)	17(2)	4(2)	-1(2)	-13(2)
N(123)	33(3)	28(3)	23(3)	-9(2)	5(2)	-16(2)
N(131)	24(2)	31(3)	32(3)	-2(2)	-3(2)	-20(2)
N(132)	15(2)	20(3)	24(3)	2(2)	-4(2)	-6(2)
N(133)	29(3)	21(3)	31(3)	-3(2)	-13(2)	-12(2)
C(1)	19(3)	45(5)	32(4)	-21(3)	5(3)	-13(3)
C(11)	25(3)	15(3)	16(3)	-1(2)	5(2)	-10(2)
C(111)	25(3)	13(3)	21(3)	0(2)	-1(2)	-6(2)
C(112)	23(3)	22(3)	24(3)	2(3)	-5(2)	-11(2)
C(113)	17(3)	19(3)	18(3)	2(2)	-2(2)	-8(2)
C(114)	28(3)	27(4)	22(3)	-1(3)	2(2)	-10(3)
C(115)	34(3)	26(4)	14(3)	2(3)	3(2)	-11(3)
C(116)	47(4)	19(4)	22(3)	-6(3)	-1(3)	-16(3)

Table A.4: Anisotropic displacement parameters ($Å^2$ x 10^3) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11 + ... + 2hka^*b^*U12]$ (continued).

	U11	U22	U33	U23	U13	U12
C(121)	29(3)	37(4)	24(3)	-6(3)	-5(2)	-18(3)
C(122)	23(3)	23(3)	25(3)	1(3)	4(2)	-8(3)
C(123)	29(3)	22(3)	23(3)	-7(3)	6(2)	-12(3)
C(124)	32(3)	23(4)	18(3)	0(3)	2(2)	-13(3)
C(125)	39(3)	45(4)	18(3)	-9(3)	0(3)	-26(3)
C(126)	16(3)	32(4)	25(3)	1(3)	7(2)	-5(3)
C(131)	26(3)	21(3)	21(3)	7(3)	-7(2)	-14(3)
C(132)	24(3)	15(3)	28(3)	-7(3)	5(2)	-12(2)
C(133)	25(3)	18(3)	28(3)	-4(3)	-6(2)	-6(2)
C(134)	16(3)	26(4)	30(3)	-5(3)	-3(2)	-7(3)
C(135)	25(3)	35(4)	26(3)	-1(3)	-10(2)	-12(3)
C(136)	32(3)	31(4)	45(4)	1(3)	-7(3)	-24(3)
Pt(2)	17(1)	13(1)	14(1)	-2(1)	1(1)	-8(1)
P(21)	20(1)	16(1)	14(1)	-3(1)	1(1)	-10(1)
P(22)	17(1)	18(1)	15(1)	-2(1)	0(1)	-9(1)
P(23)	16(1)	14(1)	18(1)	-4(1)	-1(1)	-7(1)
S(2)	55(1)	159(3)	65(2)	-57(2)	23(1)	-68(2)
S(21)	39(1)	22(1)	35(1)	-14(1)	13(1)	-13(1)
N(2)	92(6)	30(5)	135(8)	-15(5)	6(6)	-17(4)
N(21)	31(3)	14(3)	20(2)	-2(2)	4(2)	-12(2)
N(211)	30(3)	19(3)	16(2)	-1(2)	1(2)	-10(2)
N(212)	28(2)	20(3)	16(2)	-2(2)	0(2)	-16(2)
N(213)	34(3)	29(3)	19(3)	-5(2)	6(2)	-23(2)
N(221)	18(2)	21(3)	15(2)	-4(2)	-3(2)	-8(2)
N(222)	20(2)	18(3)	13(2)	2(2)	0(2)	-11(2)
N(223)	24(2)	18(3)	21(2)	-3(2)	0(2)	-12(2)
N(231)	23(2)	16(3)	19(2)	-6(2)	-1(2)	-10(2)
N(232)	18(2)	19(3)	22(2)	-7(2)	-2(2)	-5(2)
N(233)	28(2)	19(3)	18(2)	-4(2)	-5(2)	-8(2)
C(2)	49(5)	50(6)	87(7)	-18(5)	21(5)	-34(5)
C(21)	27(3)	20(3)	18(3)	0(3)	0(2)	-19(3)
C(211)	24(3)	16(3)	21(3)	0(2)	4(2)	-11(2)
C(212)	25(3)	17(3)	14(3)	-4(2)	3(2)	-14(2)
C(213)	28(3)	29(4)	22(3)	-9(3)	2(2)	-19(3)
C(214)	34(3)	35(4)	15(3)	2(3)	-7(2)	-20(3)
C(215)	30(3)	28(4)	17(3)	-7(3)	8(2)	-19(3)
C(216)	49(4)	29(4)	14(3)	-1(3)	4(3)	-29(3)
C(221)	24(3)	19(3)	15(3)	-3(2)	-1(2)	-12(2)
C(222)	25(3)	16(3)	16(3)	0(2)	-6(2)	-11(2)
C(223)	24(3)	18(3)	28(3)	-6(3)	-3(2)	-16(2)
C(224)	19(3)	19(3)	20(3)	-2(2)	4(2)	-12(2)
C(225)	22(3)	22(3)	21(3)	-7(3)	1(2)	-10(2)
C(226)	23(3)	34(4)	12(3)	-6(3)	-5(2)	-10(3)
C(231)	19(3)	20(3)	20(3)	-6(2)	-1(2)	-10(2)
C(232)	19(3)	25(3)	19(3)	-8(3)	-1(2)	-12(2)
C(233)	27(3)	17(3)	20(3)	-5(2)	1(2)	-9(2)
C(234)	28(3)	19(3)	19(3)	-4(3)	-1(2)	-8(3)
C(235)	21(3)	23(3)	22(3)	-10(3)	-4(2)	-4(2)
C(236)	33(3)	12(3)	22(3)	0(3)	-3(2)	-12(3)

Table A.4: Anisotropic displacement parameters ($Å^2$ x 10^3) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11 + ... + 2hka^*b^*U12]$ (continued).

	U11	U22	U33	U23	U13	U12
Pt(3)	18(1)	16(1)	17(1)	-4(1)	1(1)	-9(1)
P(31)	18(1)	18(1)	16(1)	-2(1)	-2(1)	-10(1)
P(32)	23(1)	15(1)	23(1)	-3(1)	3(1)	-8(1)
P(33)	18(1)	18(1)	18(1)	-5(1)	1(1)	-10(1)
S(3)	30(1)	35(1)	44(1)	-6(1)	0(1)	-17(1)
S(31)	45(1)	31(1)	35(1)	-17(1)	1(1)	-18(1)
N(3)	35(3)	45(4)	44(4)	-5(3)	2(3)	-12(3)
N(31)	32(3)	17(3)	23(3)	-5(2)	-1(2)	-13(2)
N(311)	20(2)	24(3)	19(2)	-4(2)	1(2)	-13(2)
N(312)	27(2)	17(3)	22(3)	-4(2)	0(2)	-11(2)
N(313)	31(3)	22(3)	20(2)	2(2)	-7(2)	-19(2)
N(321)	48(3)	24(3)	29(3)	1(2)	4(2)	-26(3)
N(322)	59(4)	18(3)	34(3)	-8(3)	13(3)	-15(3)
N(323)	39(3)	15(3)	29(3)	-1(2)	4(2)	-10(2)
N(331)	29(3)	21(3)	16(2)	-4(2)	-2(2)	-10(2)
N(332)	30(3)	33(3)	22(3)	-12(2)	3(2)	-21(2)
N(333)	31(3)	27(3)	16(2)	-6(2)	-4(2)	-17(2)
C(3)	19(3)	19(4)	54(4)	-12(3)	5(3)	-10(3)
C(31)	26(3)	20(3)	19(3)	1(3)	2(2)	-14(3)
C(311)	23(3)	24(3)	18(3)	-8(3)	2(2)	-11(2)
C(312)	27(3)	19(3)	16(3)	-6(2)	5(2)	-12(2)
C(313)	33(3)	34(4)	22(3)	2(3)	-12(2)	-21(3)
C(314)	28(3)	24(4)	23(3)	0(3)	-2(2)	-25(3)
C(315)	19(3)	27(4)	24(3)	-3(3)	-4(2)	-7(3)
C(316)	31(3)	21(3)	16(3)	-3(3)	-2(2)	-12(3)
C(321)	34(3)	17(3)	25(3)	-6(3)	2(2)	-11(3)
C(322)	34(3)	20(4)	29(3)	-8(3)	9(3)	-5(3)
C(323)	29(3)	24(4)	17(3)	-3(3)	-1(2)	-8(3)
C(324)	66(5)	21(4)	33(4)	-3(3)	2(3)	-28(3)
C(325)	49(4)	9(3)	33(4)	3(3)	3(3)	-4(3)
C(326)	49(4)	23(4)	36(4)	-1(3)	15(3)	-22(3)
C(331)	23(3)	23(3)	22(3)	-4(3)	-1(2)	-9(2)
C(332)	25(3)	34(4)	22(3)	-14(3)	6(2)	-19(3)
C(333)	21(3)	25(3)	18(3)	-1(3)	-6(2)	-12(2)
C(334)	44(4)	28(4)	26(3)	-8(3)	1(3)	-20(3)
C(335)	27(3)	31(4)	24(3)	-11(3)	-6(2)	-13(3)
C(336)	26(3)	24(3)	21(3)	-10(3)	4(2)	-12(3)
O(1)	33(3)	117(5)	25(3)	-13(3)	-3(2)	-40(3)
O(2)	31(3)	69(4)	35(3)	-14(3)	3(2)	-23(2)
O(3)	74(4)	104(5)	33(3)	0(3)	-3(3)	-71(4)
O(4)	117(5)	100(5)	42(3)	-5(4)	-8(3)	-79(4)
O(5)	54(6)	40(6)	45(6)	-6(5)	-14(5)	-5(5)
O(6)	87(9)	122(11)	130(11)	-49(9)	-3(8)	-52(9)

Table A.5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

Molecule 1					Molecule 2				
	x	y	z	U(eq)		x	y	z	U(eq)
H(11A)	5860	1460	2867	22(1)	H(21A)	6222	2316	3785	22(1)
H(11B)	4858	1332	2934	22(1)	H(21B)	6646	2881	4047	22(1)
H(11C)	4965	-671	3068	22(1)	H(21C)	5275	4772	4412	22(1)
H(11D)	6032	-1632	3078	22(1)	H(21D)	4098	5244	4349	22(1)
H(11E)	7878	-1422	2972	22(1)	H(21E)	3301	4210	3851	22(1)
H(11F)	7844	-351	2895	22(1)	H(21F)	4053	3174	3661	22(1)
H(11G)	4448	311	3823	22(1)	H(21G)	5495	2603	5524	22(1)
H(11H)	5049	-101	4412	22(1)	H(21H)	6125	3135	5073	22(1)
H(11I)	7123	-2139	3879	22(1)	H(21I)	3160	4344	4903	22(1)
H(11J)	6717	-1630	4445	22(1)	H(21J)	3645	3365	5424	22(1)
H(11K)	6636	67	4323	22(1)	H(21K)	5032	1727	4414	22(1)
H(11L)	6990	588	3684	22(1)	H(21L)	4822	1730	5115	22(1)
H(12A)	8067	1518	664	22(1)	H(22A)	4606	6497	1049	22(1)
H(12B)	8756	337	751	22(1)	H(22B)	5448	6707	1215	22(1)
H(12C)	5722	1803	-29	22(1)	H(22C)	7320	5034	1674	22(1)
H(12D)	6125	2459	159	22(1)	H(22D)	7510	3901	1767	22(1)
H(12E)	8076	-915	415	22(1)	H(22E)	5903	3511	1452	22(1)
H(12F)	7014	-428	139	22(1)	H(22F)	4909	4453	1187	22(1)
H(12G)	7636	2561	-354	22(1)	H(22G)	7310	5701	90	22(1)
H(12H)	8161	2102	-934	22(1)	H(22H)	7105	6129	677	22(1)
H(12I)	7571	1050	-1210	22(1)	H(22I)	7599	3921	228	22(1)
H(12J)	6683	852	-799	22(1)	H(22J)	7554	3280	899	22(1)
H(12K)	9366	-411	-114	22(1)	H(22K)	4991	5590	250	22(1)
H(12L)	9242	264	-785	22(1)	H(22L)	6005	5367	-172	22(1)
H(13A)	4212	79	2198	22(1)	H(23A)	4724	6346	3700	22(1)
H(13B)	3932	1111	2365	22(1)	H(23B)	5229	6825	3108	22(1)
H(13C)	4090	2783	1434	22(1)	H(23C)	2547	6363	2953	22(1)
H(13D)	4452	2665	752	22(1)	H(23D)	2971	6039	3600	22(1)
H(13E)	4957	742	442	22(1)	H(23E)	4430	7407	1930	22(1)
H(13F)	4874	-162	958	22(1)	H(23F)	3493	7239	1875	22(1)
H(13G)	1830	2623	1519	22(1)	H(23G)	2384	8478	3726	22(1)
H(13H)	2570	2644	1910	22(1)	H(23H)	2976	7317	4029	22(1)
H(13I)	2408	2421	446	22(1)	H(23I)	1889	8092	2400	22(1)
H(13J)	3503	2314	193	22(1)	H(23J)	1695	8964	2712	22(1)
H(13K)	2256	1011	1259	22(1)	H(23K)	3171	9221	2804	22(1)
H(13L)	3256	47	1489	22(1)	H(23L)	4249	8519	2539	22(1)

Table A.5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ (continued).

Molecule 3									
	x	y	z	U(eq)		x	y	z	U(eq)
H(31A)	11545	5107	1535	22(1)	H(32K)	8939	525	4419	22(1)
H(31B)	11519	4363	1191	22(1)	H(32L)	8415	1712	4343	22(1)
H(31C)	8604	6891	1737	22(1)	H(33A)	8708	6491	2804	22(1)
H(31D)	9653	6754	1885	22(1)	H(33B)	8190	5946	3351	22(1)
H(31E)	9572	4643	916	22(1)	H(33C)	11598	4520	3073	22(1)
H(31F)	8561	5536	1108	22(1)	H(33D)	10959	5556	2628	22(1)
H(31G)	10621	7302	383	22(1)	H(33E)	9397	4060	4147	22(1)
H(31H)	10903	6891	1070	22(1)	H(33F)	10593	3561	4052	22(1)
H(31I)	8995	7531	142	22(1)	H(33G)	9924	7053	3702	22(1)
H(31J)	8250	7274	674	22(1)	H(33H)	9867	7040	3025	22(1)
H(31K)	10829	5014	209	22(1)	H(33I)	10934	5436	4400	22(1)
H(31L)	10574	6139	-151	22(1)	H(33J)	11499	4437	4150	22(1)
H(32A)	8153	2815	3344	22(1)	H(33K)	8481	5717	4380	22(1)
H(32B)	8661	2363	2758	22(1)	H(33L)	9068	6227	4543	22(1)
H(32C)	10885	1312	2572	22(1)	H(2A)	1030(5)	7680(5)	3960(3)	56(8)
H(32D)	11552	1194	3070	22(1)	H(4A)	2940(5)	2630(5)	3010(3)	56(8)
H(32E)	10609	2032	4141	22(1)	H(1A)	9270(5)	8190(5)	4620(3)	56(8)
H(32F)	9416	2599	4244	22(1)	H(2B)	1220(5)	7180(5)	4610(3)	56(8)
H(32G)	9751	-189	3508	22(1)	H(1B)	8420(5)	8560(6)	4380(3)	56(8)
H(32H)	9709	560	2865	22(1)	H(4B)	2710(5)	2140(5)	3600(3)	56(8)
H(32I)	10801	-364	4261	22(1)	H(3A)	2210(6)	2160(6)	4610(3)	56(8)
H(32J)	11424	272	4091	22(1)	H(3B)	2870(5)	2580(5)	4500(3)	56(8)

Table A.6: Torsion angles (°) for $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$.

Molecule 1	(°)	Molecule 2	(°)	Molecule 3	(°)
N(11)-Pt(1)-P(11)-C(111)	123.3(2)	N(21)-Pt(2)-P(21)-C(211)	24.5(2)	N(31)-Pt(3)-P(31)-C(311)	-86.9(2)
N(11)-Pt(1)-P(11)-C(112)	-110.6(3)	N(21)-Pt(2)-P(21)-C(212)	146.5(2)	N(31)-Pt(3)-P(31)-C(312)	146.8(2)
N(11)-Pt(1)-P(11)-C(113)	10.7(2)	N(21)-Pt(2)-P(21)-C(213)	-88.2(2)	N(31)-Pt(3)-P(31)-C(313)	26.3(2)
N(11)-Pt(1)-P(12)-C(121)	-40.1(2)	N(21)-Pt(2)-P(22)-C(221)	177.4(3)	N(31)-Pt(3)-P(32)-C(321)	-58.3(2)
N(11)-Pt(1)-P(12)-C(122)	-161.9(3)	N(21)-Pt(2)-P(22)-C(222)	-60.7(2)	N(31)-Pt(3)-P(32)-C(322)	53.2(2)
N(11)-Pt(1)-P(12)-C(123)	72.7(2)	N(21)-Pt(2)-P(22)-C(223)	52.0(2)	N(31)-Pt(3)-P(32)-C(323)	178.0(3)
N(11)-Pt(1)-P(13)-C(131)	96.0(8)	N(21)-Pt(2)-P(23)-C(231)	43(7)	N(31)-Pt(3)-P(33)-C(331)	31(7)
N(11)-Pt(1)-P(13)-C(132)	-139.8(8)	N(21)-Pt(2)-P(23)-C(232)	-75(7)	N(31)-Pt(3)-P(33)-C(332)	-89(7)
N(11)-Pt(1)-P(13)-C(133)	-17.8(8)	N(21)-Pt(2)-P(23)-C(233)	163(7)	N(31)-Pt(3)-P(33)-C(333)	151(7)

B: Supplementary material reported for Chapter 4.

Table B.1: Absorbance values plotted against ligand concentration used in the determination of the equilibrium constant for the aqueous reaction of $[PtCl(PTA)_3]Cl$ with Y (Br^-, SCN^- or N_3^-) at 25 °C, [Pt] = 0.075 mM and [Cl^-] (as NaCl) added = 1 mM.

[Br^-] (mM)	A^{290}	[SCN^-] (mM)	A^{298}	[N_3^-] (mM)	A^{285}
0.000	0.511	0.000	0.370	0.000	0.618
0.025	0.531	0.025	0.411	0.025	0.633
0.050	0.540	0.050	0.447	0.050	0.643
0.075	0.548	0.075	0.489	0.075	0.660
0.100	0.536	0.100	0.516	0.100	0.656
0.125	0.537	0.125	0.534	0.125	0.680
0.150	0.568	0.150	0.526	0.150	0.692
0.175	0.562	0.175	0.560	0.200	0.708
0.200	0.560	0.225	0.570	0.250	0.705
0.300	0.582	0.275	0.582	0.300	0.709
0.400	0.589	0.300	0.592	0.350	0.720
0.500	0.603	0.325	0.589	0.400	0.724
1.000	0.619	0.375	0.604	0.450	0.726
5.000	0.645	0.400	0.597	1.000	0.737
		0.500	0.599	2.500	0.740
		0.750	0.613		
		1.000	0.625		

Derivation of Eq. 4.48 used in the fitting of absorbance *vs.* concentration data for the determination of equilibrium constants.

$$PtClP_3 + Y \underset{}{\overset{K}{\rightleftharpoons}} PtYP_3 + Cl^- \quad (Y = Br^-, SCN^-, N_3^-) \qquad (1)$$

The equilibrium constant (K) is defined as

$$K = \frac{[PtYP_3]\,[Cl^-]}{[PtClP_3]\,[Y]} \qquad (2)$$

At any given time, the total Pt concentration is given by

$$[Pt]_T = [PtClP_3] + [PtYP_3] \qquad (3)$$

From **(2)**

$$[PtClP_3] = \frac{[PtYP_3]\,[Cl^-]}{K[Y]} \quad \textbf{(4)}$$

Also

$$[PtYP_3] = \frac{K[PtClP_3][Y]}{[Cl^-]} \quad \textbf{(5)}$$

Substitution of **(4)** into **(2)** and after multiplication by $K[Y]/K[Y]$ gives

$$[PtYP_3] = \frac{[Pt]_T\,K[Y]}{[Cl^-] + K[Y]} \quad \textbf{(6)}$$

Also substitution of **(5)** into **(2)** and after multiplication by $[Cl^-]/[Cl^-]$ gives

$$[PtClP_3] = \frac{[Pt]_T[Y]}{[Cl^-] + K[Y]} \quad \textbf{(7)}$$

The total absorbance observed at equilibrium is

$$A_{obs} = A_{PtClP_3} + A_{PtYP_3}$$

$$= \varepsilon_{PtClP_3}\,[PtClP_3] + \varepsilon_{PtYP_3}\,[PtYP_3]$$

$$= \varepsilon_{PtClP_3}\,\frac{[Pt]_T[Cl^-]}{[Cl^-] + K[Y]} + \varepsilon_{PtYP_3}\,\frac{[Pt]_T\,K[Y]}{[Cl^-] + K[Y]} \text{ (from } \textbf{Eq. 6} \text{ and } \textbf{7)} \quad \textbf{(8)}$$

Since $A = \varepsilon cl$ then absorbance observed for the reactants (A_R) and absorbance for the products (A_P) is given by

$A_R = \varepsilon_{PtClP_3}\,[PtClP_3]$ and $A_P = \varepsilon_{PtYP_3}\,[PtYP_3]$ respectively.

Therefore from **Eq. 8**

$$A_{obs} = \frac{A_R[Cl^-] + A_P K[Y]}{[Cl^-] + K[Y]}$$

Table B.2: pH and absorbance values obtained for the reaction of $[PtClPTA)_3]Cl$ with triflic acid at different wavelengths of 254.6 and 275.5 nm respectively. [Pt] = 0.075 mM, $[Cl^-]$ (as NaCl) added = 20 mM and T = 25 °C.

pH	Absorbance (254.6 nm)	Absorbance (275.5 nm)
5.65	1.915	1.007
4.49	1.931	1.019
4.40	1.918	1.003
4.35	1.925	1.005
4.06	1.914	0.996
3.84	1.907	0.986
3.64	1.880	0.975
3.44	1.856	0.958
3.23	1.824	0.936
3.02	1.782	0.922
2.82	1.741	0.888
2.63	1.656	0.840
2.42	1.568	0.779
2.22	1.497	0.744
2.12	1.429	0.703
2.02	1.383	0.677
1.82	1.323	0.620
1.60	1.172	0.537
1.52	1.144	0.522
1.30	1.119	0.508
1.00	1.100	0.497

Derivation of the observed exchange rate constant, $(k_{obs})_{Cl}$, (Eq. 4.45 and 4.46) using the mechanism presented in Scheme 4.3.

The rate is given as

$$R = (k_s[[Pt(H_2O)(PTA)_3]Cl] + k_e[[PtCl(PTA)_3]Cl])[Cl^-] \quad \textbf{(A)}$$

$$K_{Cl} = [[PtCl(PTA)_3]Cl] / ([[Pt(H_2O)(PTA)_3]Cl] \times [Cl^-]) \quad \textbf{(B)}$$

Rearranging **B** gives **C**,

$$[Pt(H_2O)(PTA)_3]Cl] = [[PtCl(PTA)_3]Cl] / K_{Cl}[Cl^-] \quad \textbf{(C)}$$

and

$$[PtCl(PTA)_3]Cl] = [[Pt(H_2O)(PTA)_3]Cl] [Cl^-] K_{Cl} \quad \textbf{(D)}$$

APPENDIX

The total platinum concentration, $[Pt]_T$, is given by **E**.

$$[Pt]_T = [[PtCl(PTA)_3]Cl] + [[Pt(H_2O)(PTA)_3]Cl] \quad \textbf{(E)}$$

Substitution of **C** and **D** into **E** results in

$$[[Pt(H_2O)(PTA)_3]Cl] = [Pt]_T / (1 + K_{Cl}[Cl^-]) \quad \textbf{(F)}$$

and

$$[[PtCl(PTA)_3]Cl] = [Pt]_T K_{Cl}[Cl^-] / (1 + K_{Cl}[Cl^-]) \quad \textbf{(G)}$$

Replacing **F** and **G** in **A** gives

$$R = (k_s + k_e K_{Cl}[Cl^-] / (1 + K_{Cl}[Cl^-]))[Cl^-][Pt]_T \quad \textbf{(H)}$$

The rate constant observed (as a function of the linewidth) on the free Cl^- peak is given by:

$$d[PtCl]/dt[Cl^-] = (k_{obs})_{Cl} = (k_s + k_e K_{Cl}[Cl^-] / (1 + K_{Cl}[Cl^-]))[Pt]_T \quad \textbf{(I)}$$

If $K_{Cl} = 1/K_{Cl(R)}$ ($K_{Cl(R)}$ = hydrolysis equilibrium constant defined in reverse direction) is substituted in **I** and after multiplication with $K_{Cl(R)}/[Cl^-]$ then

$$(k_{obs})_{Cl} = (k_e + k_s K_{Cl(R)} /[Cl^-] / (1 + K_{Cl(R)}[Cl^-]))[Pt]_T \quad \textbf{(J)}$$

When $[Cl^-] >> K_{Cl(R)}$ then

$$(k_{obs})_{Cl} = (k_e + k_s K_{Cl(R)}/[Cl^-])[Pt] \quad \textbf{(K)}$$

$$(k_{obs})_{Cl} / [Pt] = (k_{obs})' = k_e + k_s K_{Cl(R)}/[Cl^-] \quad \textbf{(L)}$$

SUMMARY

The aim of this study was to prepare, characterise and investigate the interesting reactivity and substitution behaviour of the platinum(II) analogue of the Wilkinson catalyst, $[PtCl(PTA)_3]^+$, in aqueous medium. The water-soluble ligand 1,3,5-triaza-7-phosphaadamantane (PTA) was employed in the synthesis of the various complexes in this study. This title complex was reacted with various halides and pseudo-halides like SCN^-, Br^-, N_3^- to form products, which could be characterised, and also to investigate the aqueous substitution behaviour of these. Characterisation of the complexes that were synthesised was done by the use of multi-nuclear NMR, IR, UV-Vis techniques and X-ray crystallography.

X-ray crystallography was utilised to study the crystal structure of $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$ which crystallises in a triclinic space group, $P\bar{1}$; and was refined to a final R value of 3.67%. The structure of this compound showed that the Pt(II) centre displays a well defined square planar geometry but it crystallised with three platinum complexes, three thiocyanate counter-ions and five water solvent molecules in the asymmetric unit. The three platinum complexes are chemically equivalent, but are crystallographically slightly different due to small variations in their packing modes.

The above-mentioned substitution reactions were investigated by means of UV-Vis spectrophotometry and stopped-flow techniques. Since the $[PtCl(PTA)_3]^+$ complex was not stable in aqueous medium, (represented in the scheme below), an excess of the chloride ion concentration (as NaCl) was added in all investigations done with the complex.

$$[PtCl(PTA)_3]^+ + Y \underset{}{\overset{K}{\rightleftharpoons}} [PtY(PTA)_3]^+ + Cl^- \quad (Y = SCN^-, Br^-, N_3^-)$$

$$\Big\Vert \; H_2O$$

$$[Pt(H_2O)(PTA)_3]^{2+} + Cl^-$$

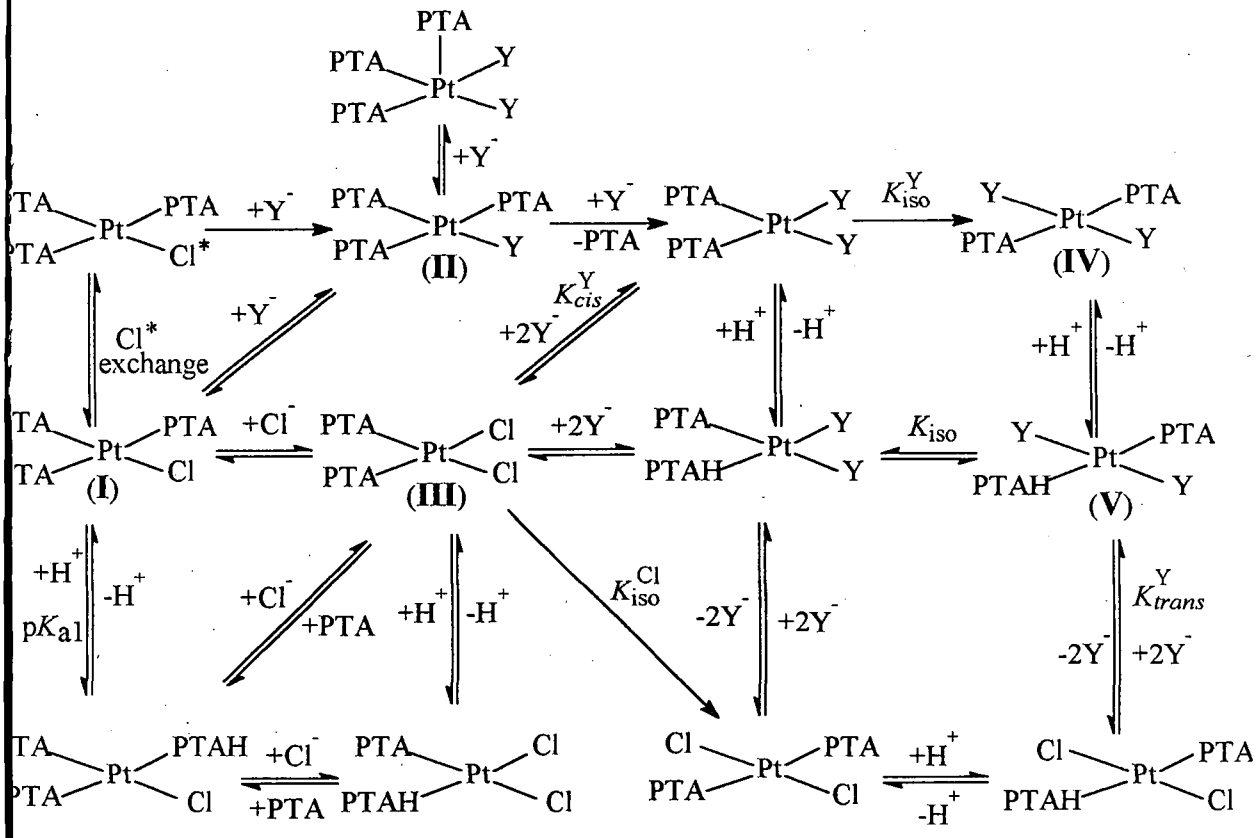
SUMMARY

The equilibrium studies of $[PtCl(PTA)_3]^+$ were done by the addition of halides and pseudo-halides, Y (Br^-, N_3^-, SCN^-) which resulted in the rapid substitution of the chloride to form $[PtY(PTA)_3]^+$ as the final product. The equilibrium constants obtained were 10(1), 7(1) and 2.8(5) M^{-1} for SCN^-, N_3^- and Br^- respectively.

The protonation behaviour of the $[PtCl(PTA)_3]^+$ complex was also investigated and it was found that it subsequently converts to the *cis*-$[PtCl_2(PTA)_2]$. Two pK_a values, pK_{a1} = 2.1(1) and pK_{a2} = 3.3(8) which are assumed to represent the protonation of the $[PtCl(PTA)_3]Cl$ and *cis*-$[PtCl_2(PTA)_2]$ complexes respectively, were determined.

The rates of substitution reactions were too fast to monitor by time-resolved spectroscopy, which enabled the study of the rapid chloride exchange process by ^{35}Cl NMR since significant line broadening was observed. From the experiments done it was noted that increased concentration of the chloride resulted in slower rates of the chloride exchange. The chloride exchange rate constant for the $[PtCl(PTA)_3]^+$ at 22 °C was determined to be 2(1) x 10^3 $M^{-1}s^{-1}$.

The complex aqueous solution behaviour of the $[PtCl(PTA)_3]^+$ complex can be represented in the scheme below, where the charges of the complexes have been omitted for simplicity, $PTAH^+$ = protonated PTA ligand, and iso = isomerisation.



OPSOMMING

Die doel van hierdie studie was om die reaktiwiteit en substitusiegedrag van die wateroplosbare Pt(II)-analoog van die Wilkinsonkatalis, $[PtCl(PTA)_3]^+$, in waterige medium te ondersoek. Die wateroplosbare ligand, 1,3,5-triaza-7-phosphaadamantaan (PTA) is gebruik vir die sintese van die verskillende komplekse. Die titelkompleks is met verskeie haliede en pseudohaliede, naamlik SCN^-, Br^-, N_3^-, gereageer. Karakterisering van die gevormde produkte is gedoen met behulp van multikern KMR, IR, UV-Sigbare tegnieke en X-straalkristallografie.

X-straalkristallografie is spesifiek gebruik om die struktuur van $\{[Pt(NCS)(PTA)_3]NCS\}_3 \cdot 5H_2O$, wat in die trikliniese ruimtegroep $P\bar{1}$ kristalliseer, op te klaar en te verfyn tot 'n R-waarde van 3.67%. Hierdie struktuur het getoon dat die Pt(II)-metalkern 'n tipiese vierkantig-planêre geometrie vertoon, maar dat dit as drie onafhanklike Pt(II)-katione, drie tiosianaatione en vyf watermolekule in die asimmetriese eenheid uitkristalliseer. Die drie Pt(II) metaalsentra is almal chemies ekwivalent maar vertoon klein verskille as gevolg van pakkingseffekte.

Die bogenoemde substitusiesreaksies is met UV-Sigbare spektrofotometrie en stopvloeitegnieke bestudeer. Aangesien die $[PtCl(PTA)_3]^+$ kompleks onstabiel in suiwer waterige medium is (sien skema hieronder), moes 'n oormaat vry $[Cl^-]$ (as NaCl) in alle eksperimente bygevoeg word om hidroliese te minimiseer.

$$[PtCl(PTA)_3]^+ + Y \underset{}{\overset{K}{\rightleftharpoons}} [PtY(PTA)_3]^+ + Cl^- \quad (Y = SCN^-, Br^-, N_3^-)$$

$$\downarrow\uparrow H_2O$$

$$[Pt(H_2O)(PTA)_3]^{2+} + Cl^-$$

Die ewewigstudies op $[PtCl(PTA)_3]^+$ is gedoen deur die byvoeging van die betrokke halied of pseudohalied Y (Br^-, N_3^-, SCN^-), wat die vinnige substitusie van die chloroligand tot gevolg gehad het met die vorming van die $[PtY(PTA)_3]^+$ komplekse as finale produkte. Die ewewigskonstantes is spektrofotometriese as 10(1), 7(1) en 2.8(5) M^{-1} vir SCN^-, N_3^- en Br^- onderskeidelik bepaal.

Die protoneringsgedrag van die $[PtCl(PTA)_3]^+$ kompleks is ondersoek en daar is gevind dat daar twee pK_a waardes bestaan wat uiteindelik veroorsaak dat die *cis*-$[PtCl_2(PTA)_2]$ kompleks gevorm word. Huidige getuienis dui aan dat hierdie twee waardes pK_{a1} = 2.1(1) en pK_{a2} = 3.3(8) die protonering van die $[PtCl(PTA)_3]^+$ en die *cis*-$[PtCl_2(PTA)_2]$ onderskeidelik verteenwoordig.

Die tempo van chloriedsubstitusie deur die verskillende inkomende ligande was te vinnig om dit met behulp van tydafhanklike volspektrumanalise te monitor, maar was nietemin geskik om die chlorieduitruiling met behulp van ^{35}Cl KMR, aangesien betekenisvolle lynverbreding waargeneem is, te ondersoek. Dit het volgens die eksperimente geblyk dat 'n toename in vrye cloriedkonsentrasie 'n afname in die tempo van chlorieduitruiling tot gevolg het, en die chlorieduitruilingstempokonstante van die $[PtCl(PTA)_3]^+$ kompleks by 22 °C is as 2(1) x 10^3 $M^{-1}s^{-1}$ bepaal.

Die komplekse oplossingsgedrag van die $[PtCl(PTA)_3]^+$ kompleks word in die volgende skema voorgestel, waar ladings eenvoudigheidshalwe uitgelaat is, $PTAH^+$ die geprotoneerde PTA ligand, en iso isomerisasie voorstel.