CO-ORDINATION CHEMISTRY

Stability of complexes :

Considering the reaction

$$M^{n+} + nL \rightleftharpoons [ML_n]^{n+}$$ the equilibrium

constant K is given by,

$$K = \frac{[ML_n]^{n+}}{[M^{n+}][L]^n}$$

K is called formation constant of stability constant. If the Value of K is more, the stability of the complex will be more. [The reciprocal of K is known as instability constant].

The studying the formation of complex compounds in aqueous solution, two kinds of stabilities have to be taken into account. They are

(i) Thermodynamic stability

(ii) Kinetic stability.

Thermodynamic stability :

It deals with properties such as bond energies, stability constants and redox potentials, which affect the equilibrium conditions.

Kinetic stability :

It deals with the rates of reaction complexes in solution, the mechanism of chemical reaction, formation of intermediate complexes, related

activation energies etc,.

Factors affecting stability of complexes:

The stability of complexes depends on the for following factors,

(i) Properties of central metal ions,

(ii) Properties of the ligand

(iii) Chelate effect.

(i) Properties of central metal ion:

a) Size of central metal ion:

For a given ligand the stability of the complexes of the metallic ions having the same charge on them decreases with the increase of the size of the central metal ion.

Eg: The stability of hydroxide complexes of alkali-metal ions is in the order.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

b) Charge on the central metal ion:

For a given ligand the stability of the complexes of the metallic ions having almost the same size but different charges on them increases with increase of the charge on them.

Eg: The stability of complexes of some metal ion is as follows:

$Co^{3+} > Co^{2+}$; $Fe^{3+} > Fe^{2+}$

c) Electronic configuration of the central metal ion:

For metallic ions which have the same ionic potential,

Eg: Na^+ and Cu^+;

Ca^{2+} and Cd^{2+};

Sc^{3+} and Ga^{3+};

The stability also depends on the number of electrons present in inner d orbitals.

(ii) Properties of the ligand:

a) Size and charge of ligand:

If a ligand is small it can approach the metal ion more closely forming a stable bond. Similarly, a highly charged ligand forms a strong bond with the metal. Thus high charge and small size of the ligand leads to the formation of stable complexes.

Eg:

The stability of the complexes of a given metal ion with halide ligands is in the order,

$$F^- > Cl^- > Br^- > I^-$$

b) Dipole moment of ligands:

For neutral ligands the larger the magnitude of permanent dipole moment, the greater is the stability of the complexes.

Eg:

The order of stability of complexes for formed

by some neutral ligand is :

ammonia > ethylamide > diethylamine > triethyl amine

c) Basic character of ligand :

The more basic is the ligand is more easily it can donate electron pairs to the central ion and hence more easily it can form complexes of greater stability. Thus F^- should form more stable complexes than Cl^-, Br^-, or I^- NH_3 should be a better ligand than HP, which in turn should be better than HF.

d) P-bonding capacity of ligands :

The ligands like CN^-, CO etc which are capable of forming p-bonds with transition metal ions give more stable complexes.

e) Steric hindrance :

When a bulky group is attached to the donor atom or if it is present near the donor atom of a ligand, the repulsive forces between the bulky group and the donor atom weaken the metal-ligand bond. The complexes become less stable. The effect of the presence of bulky group on the stability of complex is commonly called steric hindrance.

(iii) Chelate effect:

When all the donor atoms of a polydentate ligand get co-ordinated with same metal ion we get a complex compound which contains one or more rings in its structure. Such a complex is called a chelate or a chelated complex. The process of a formation of a chelate is called chellation.

Eg:

$$[Co(H_2O)_6]^{2+} + 3en \rightarrow \underset{\text{Chelate}}{[Co(en)_3]^{2+}} + 6H_2O$$

Chelates are more stable than similar non-chelated complexes of the same metal ion, greater stability of chelated complexes means that there will be lesser dissociation of the chelated complex into its components in a given solvent. The enhanced stability of a chelated complex as compared to that of a non-chelated complex is due to to the increase in entropy.

Eg: Formation of $[Co(H_2O)_6]^{2+}$ and $[Co(en)_2]^{2+}$ chelated complex form $[Co(H_2O)]^{2+}$.

(i) $[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$

Number of particles $1+6=7$ $1+6=7$

(ii) $[Co(H_2O)_6]^{2+} + 3en \rightleftharpoons [Co(en)_3]^{2+} + 6H_2O$

Number of particles $1+3=4$ $1+6=7$

Application of chelate formation:

1. Estimation of Ni^{3+} by dimethyl glyoxime involves chelate formation.
2. Estimation of Mg^{2+} and Ca^{2+} ions by EDTA involves chelate formation.
3. In water softening this principle is used, $EDTAH_4$ is used for softening water which forms soluble chelates with Ca^{2+} and Mg^{2+} ions, which impart hardness to water.

Unimolecular and bimolecular nucleophilic substitution reactions:

The nucleophilic substitution reactions of co-ordination compounds proceed by two mechanisms. They are

(i) S_N1 (unimolecular nucleophilic substitution)

(ii) S_N2 (bimolecular nucleophilic substitution)

S_N1 mechanism:

1. step:

$$ML_n \longrightarrow ML_{n-1} + L \quad \text{(slow)}$$

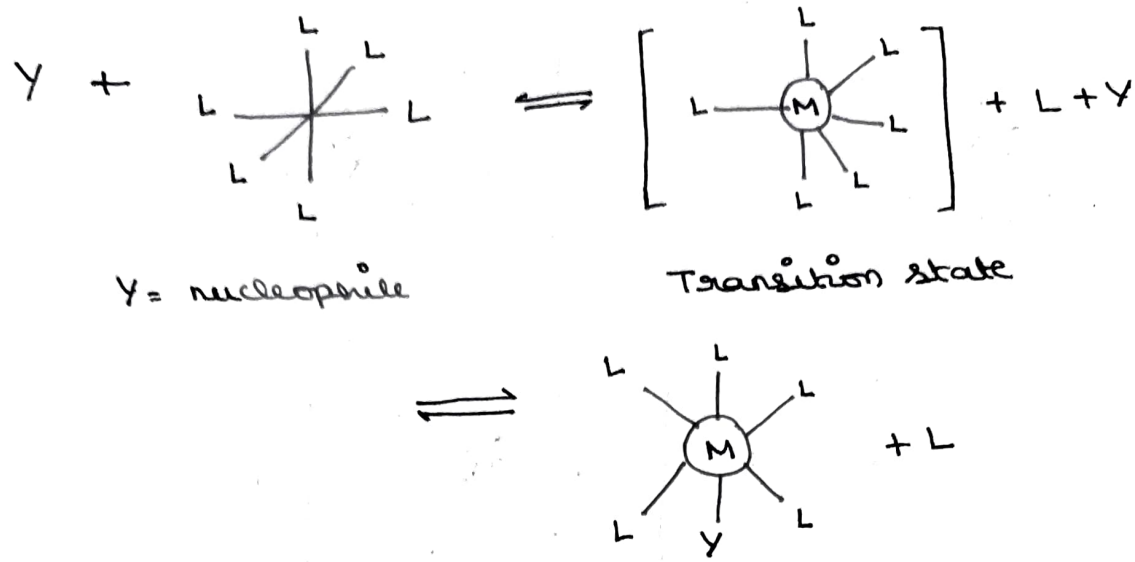
2. Step:

$$ML^{n-1} + Y \longrightarrow ML_{n-1}Y \quad \text{(Fast)}$$

(M = Metal,

Ln = Number of Ligands

Y = Nucleophile)



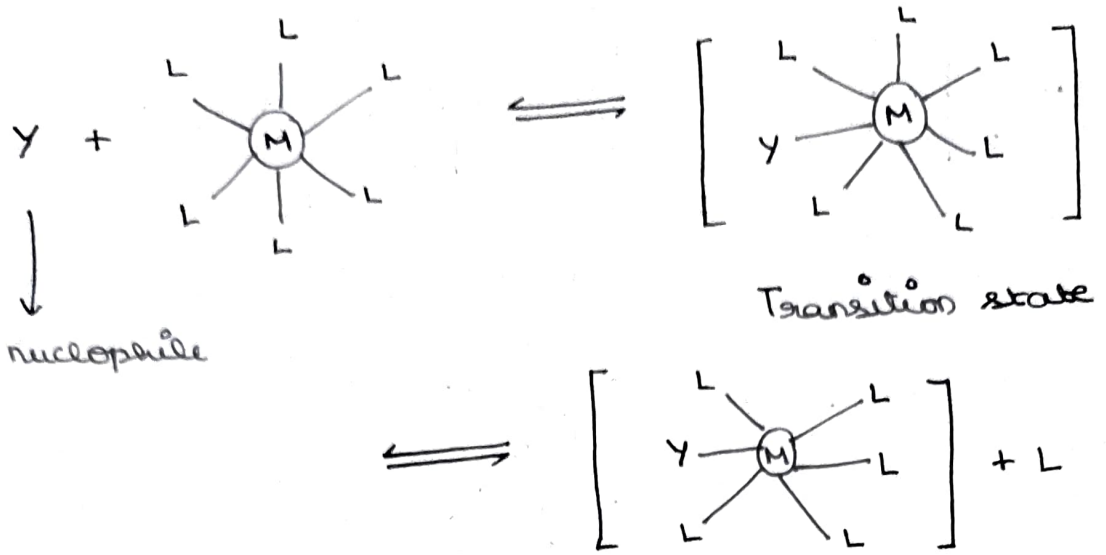
ML_n is the only one species involved in the formation of transitional state complex ML_{n-1}. Hence, it is termed unimolecular reaction. The reaction is nucleophilic since incoming ligand seeks a positive center, the metal ion. During the formation of the activated complex (ML_{n-1}) the co-ordination number of the metal is reduced. The rate determining step of S_N1 reaction the bond breaking step that forms an electron deficient intermediate. Thus S_N1 mechanism is characterized by bond breaking.

S_N2 mechanism:

Step 1: $ML_n + Y \longrightarrow ML_nY$ (slow)

Step 2: $ML_nY \longrightarrow ML_{n-1}Y + L$ (fast)

The rate of the reaction depends on both $[ML_n]$ and $[Y]$ and hence it is termed bimolecular reaction



During the formation of an activated complex in S_N2 reaction the co-ordination number of the metal is increased. In an S_N2 reaction, the rate is controlled by entry of the new ligand rather than leaving of the old ligand. Thus S_N2 mechanisms are characterised by bond making.

In Octahedral Complexes:

The most extensively studied octahedral complexes are those of Co(III) and Cr(III). Octahedral substitution reactions have been studied in aqueous solutions.

Example:

The acid hydrolysis of $[Co(NH_3)_5Cl]^{2+}$. This involves replacement of the Cl by H_2O, a process known as aquation or acid hydrolysis.

$$[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + Cl^-$$

(i) Effect of charge on the complex:

The rate of hydrolysis of complex depends on the charge of metal ion.

Eg: The hydrolysis of $[Co(NH_3)_5H_2O]^{3+}$ is found to be slower than the hydrolysis of cis or trans $[Co(NH_3)_5Cl]^{2+}$. Increased charge on a complex may strengthen metal-ligand bonds and hence retard metal-ligand bond cleavage. It may also attract incoming ligands and aid displacement reactions. But, since a decrease in rate is observed as the charge on the complex increases, a dissociation (S_N1) mechanism seems to be operative.

(ii) Effect of substitution on ethylenediamine:

The complexes containing the substituted diamines react more rapidly that the ethylene diamine complex. The replacement of H by CH_3 increases the bulk of the ligands. This makes it more difficult and attacking ligand to approach the metal atom. This steric crowding may retard an S_N2 mechanism reaction, This suggests that S_N2 dissociation mechanism is involved and the increases in rate is due to the formation of a five co-ordinated transition state which relieves steric strain.

(iii) Nature of leaving group :

The rate of hydrolysis of $[Co(NH_3)_5X]^{2+}$ depends on the nature of the leaving group X, this is because bond breaking is of great importance in the rate determining step. The order of reactivity of X^- is

$HCO_3^- > NO_3^- > I^- > Br^- > Cl^- > SO_2^{2-} > F^- > CH_3COO^- > SCN^- > NO_2^-$.

This order corresponds to the order of decreasing thermodynamic stability of the complexes of these groups.

The results of the various investigation are consistent with an S_N1 mechanism.

The base hydrolysis of $[Co(NH_3)_5Cl]^{3+}$.

The replacement of ligands by OH is referred to as base hydrolysis, the base hydrolysis is much faster than the acid hydrolysis and the reaction is second order, first order in complex and first order in OH^-. The reaction involves the following steps.

$$[Co(NH_3)_5Cl]^{2+} + OH^- \xrightleftharpoons{Fast} \underset{\text{Conjugate base}}{[Co(NH_3)_4NH_2Cl]^+} + H_2O$$

$$[Co(NH_3)_4NH_2Cl]^+ + H_2O \xrightarrow{Slow} [Co(NH_3)_4NH_2] + Cl^-$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{Fast} [Co(NH_3)_4OH]^{2+}$$

The first step involves the removal of a proton by OH^- to give a complex ion of lower charge which then loses a Cl. The last mechanism step is relatively fast so the second step is rate determing. This mechanism is referred to a S_N1CB mechanism, indicating that it involves an S_N1 reaction of the conjugate base of the starting complex.

The rate law for the base hydrolysis is

$$\text{Rate} = K[\text{complex}][\text{Base}].$$

In square planar complexes:

Square planar complexes undergo substitution reaction by an associative (S_N2) mechanism. The four co-ordinated Pt(II) complexes are most thoroughly studied. The rate law is given in general form as,

$$\text{Rate} = K[\text{complex}] + K'[Y][\text{complex}]$$

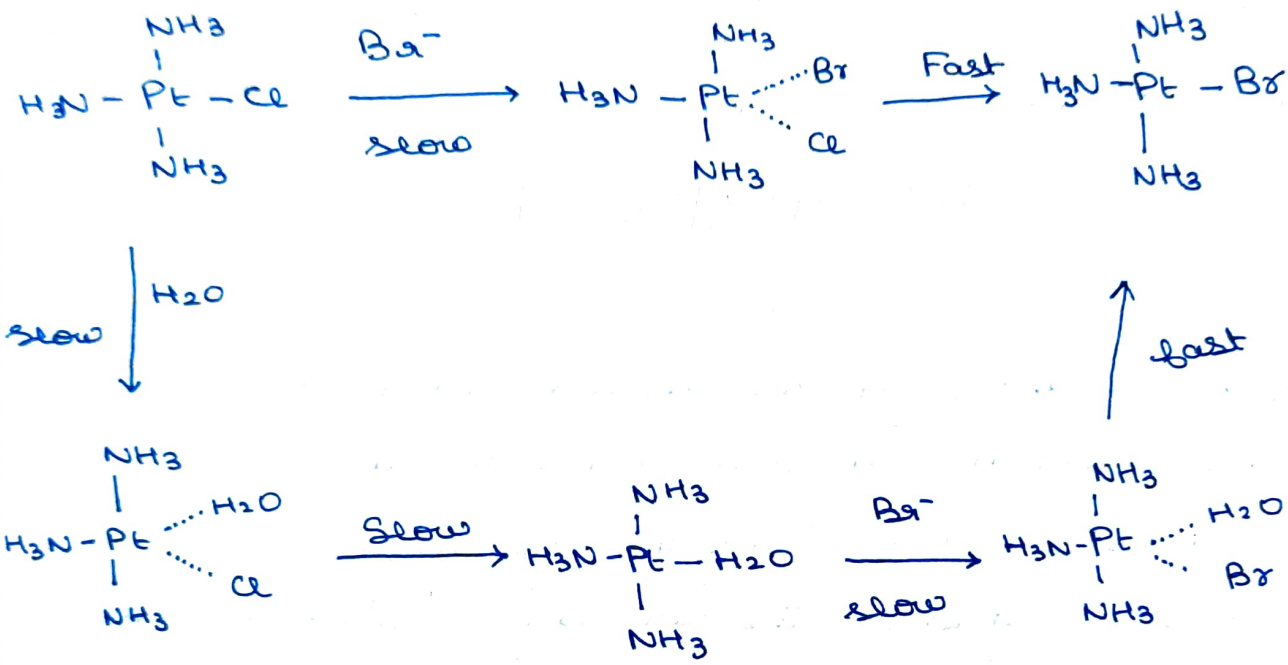
Here K is first order rate constant for an S_N2 reaction between complex and solvent and -K' is the second order rate constant for the reaction with Y. Thus reaction of ligand displacement may proceed by two paths, both supporting associative mechanism. The first path involves solvent and the second involves the entering ligand Y.

Eg:

$$[Pt(NH_3)_3Cl]^+ + Br^- \xrightarrow{H_2O} [Pt(NH_3)Br]^+ + Cl^-$$

$$\text{Rate} = k[Pt(NH_3)_3Cl^-]^+ + k'[Pt(NH_3)_3Cl^-]^+ + Br^-$$

The reaction occurs by two paths, but only one involves Br^- in the rate determining step. The solvent HP replaces Cl^- in the slow step and H_2O is subsequently replaced in a rapid step by Br^-. The sequence of reactions can be written as,



groups like phosphines, SCN^- and I^- react rapidly with pt(II) complexes. Amines, Br^- and Cl^- react at an intermediate rate H_2O and OH^- react slowly. It shows that OH^- is a poor nucleophile towards Pt(II). The order of reactivity is related to the ease with which the entering ligand releases its electrons to Pt(II). Iodide ion is a better releasing agent than Cl^- ion.

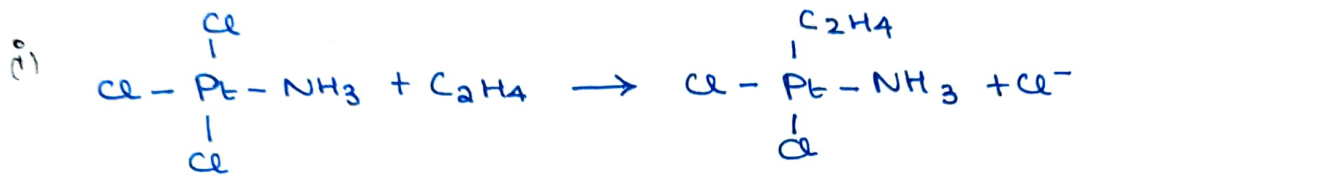
TRANS EFFECT:

It is an important feature of square planar substitution. Certain ligands already present cause

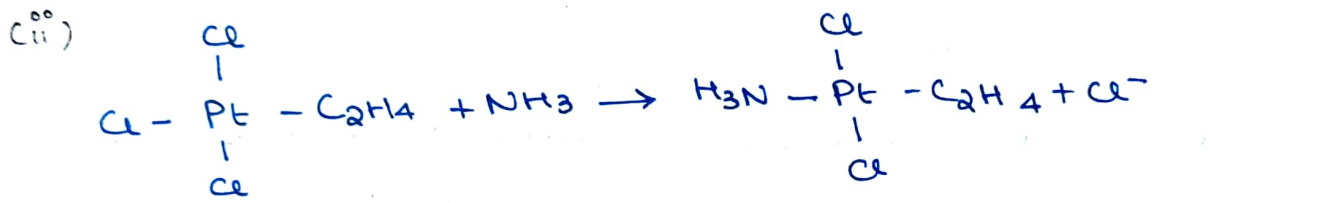
the groups across from them in the square planner to be replaced easily. These groups are known as Trans directing groups. The property of these groups due to which the groups lying trans to them are replaced fare more easily by the entering ligand is called trans-effect.

Explanation with an example:

(i)



(ii)



In the first reaction chloride trans to chloride is replaced. In the second reaction chloride trans to ethylene is replaced. This shows that ethylene has a greater trans effect than chloride and chloride a greater trans effect than ammonia.

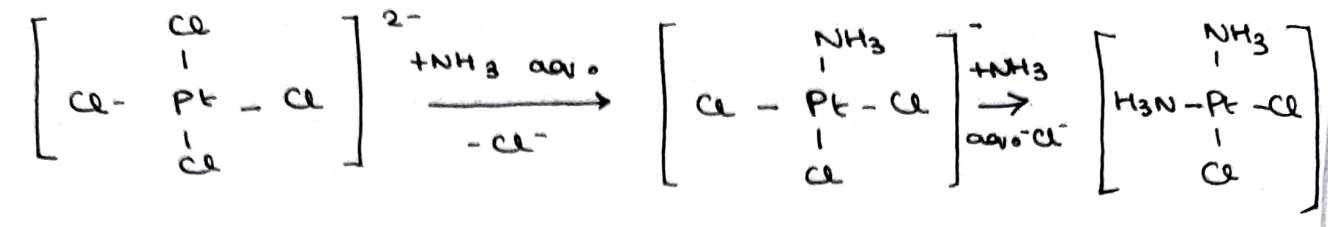
The trans effect of ligand decrease in the order,

$CN^- > CO > C_2H_4 > NO^{2-} > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O$

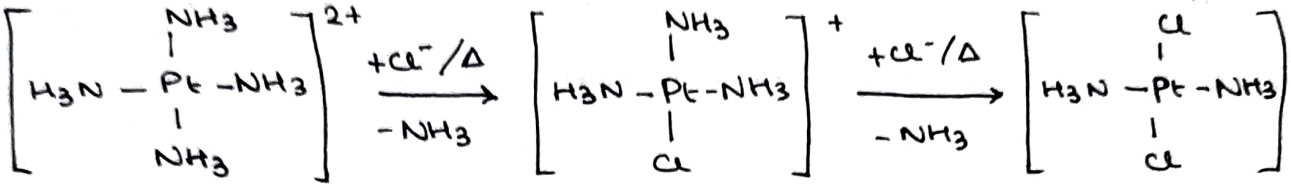
Applications:

1. Synthesis of cis and Trans $[Pt\,a_2b_2]^0$ type complexes:

Using the trans effect cis and trans $[Pt(NH_3)_2Cl_2]$ can be synthesised as follows:



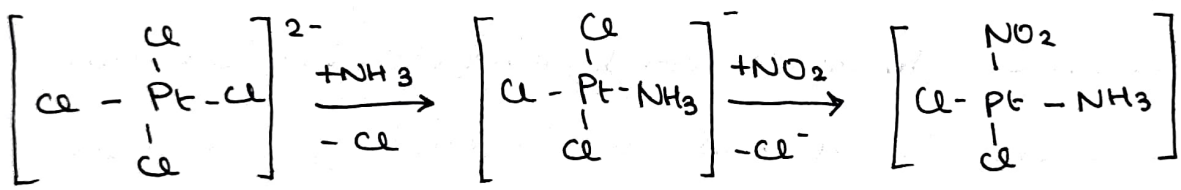
(yellow) cis



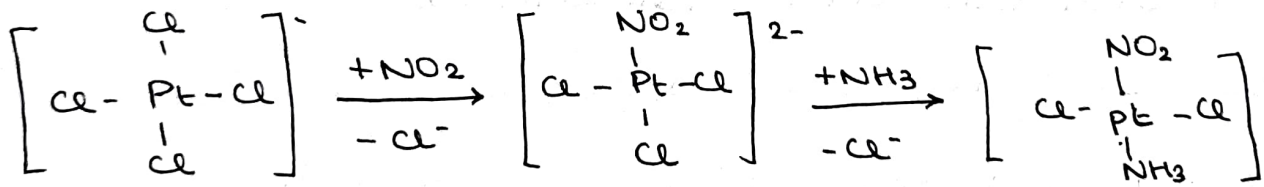
(yellow) Trans

2. Synthesis of cis and Trans $[Pta_2bc]$ type complexes, where a and b are negative ligands and c is a neutral ligand.

Using trans-effect, cis-trans $[PtCl_2(NH_3)NO_2]^-$ can be synthesised from $[PtCl_4]^{2-}$ as follows:



cis-product

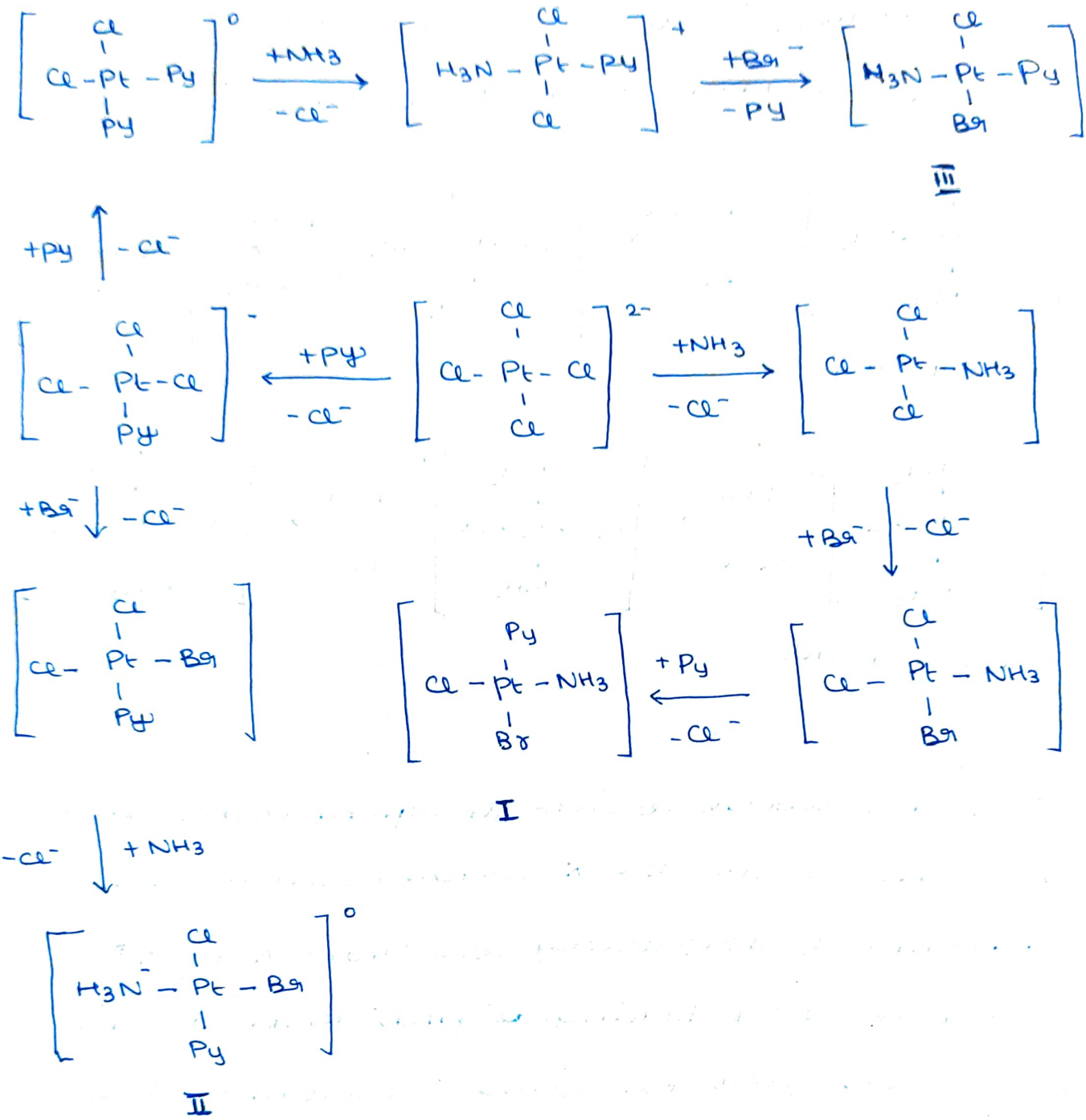


trans-product

3. Synthesis of isomers of $[Pt(py)(NH_3)BrCl]$:

This complex exists in three isomeric forms I, II, and III. These are prepared using the fact that the trans-directing capacity of these four ligands are in the order $NH_3 < py < Cl^- < Br^-$ and Pt-N bond

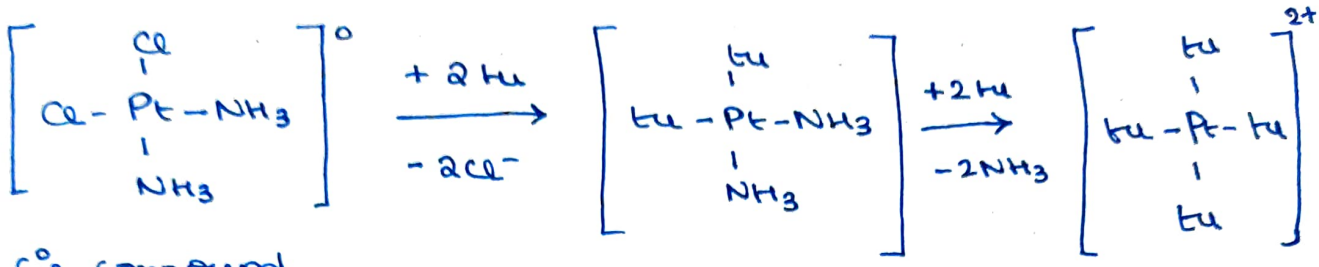
strength greater than Pt – Cl bond strength.



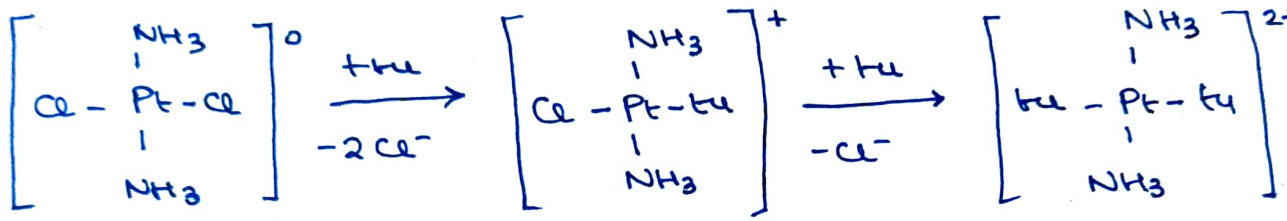
4. To distinguish between Cis- and Trans- isomers of $[Pt a_2 b_2]^0$ type complexes:

In addition to its use in the synthesis of dissolved Pt(II) complexes the trans effect is used to distinguish between the cis and trans isomers of complexes of the type $[Pt a_2 b_2]^0$. [Here a = NH_3; b = a negative group]. This is illustrated taking

$[Pt(NH_3)_2Cl_2]^0$ as an example. C is $[Pt(NH_3)_2Cl_2]^0$ gives $[Pt(tu)_4]^{2+}$ [tu - thio urea $CS(NH_2)_2$] while the trans compound gives $[Pt\,tu_2(NH_3)_2]^{2+}$



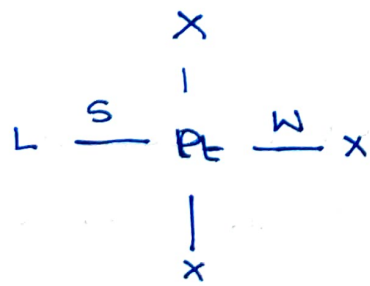
cis compound



trans compound

Theories of trans effect:

There are several theories to explain trans effect. We shall discuss the π - bonding theory here. According to this theory the vacant π or π* orbital of the p-bonding ligands accepts a pair of electrons from the filled d- orbitals of the metal d_{xz} or d_{yz} orbital to form metal ligand π bond ($d_\pi - d_\pi$ or $d_\pi - p_\pi$ bond)



S = strengthened

W = weakened

In the case of Pt(II) square planar complex, PtX_3L (where L is the bonding ligand) the d_{yz} orbital of pt (II) with a pair of electrons overlaps with the empty p_z orbital of L to form $d\pi - p\pi$ bonds between pt (II) and L and that in the direction of X trans to L decreases. In other words the pt-X bonds trans to L weakens. So it is replaced which is the trans effect.