Reaction Kinetics and Mechanism

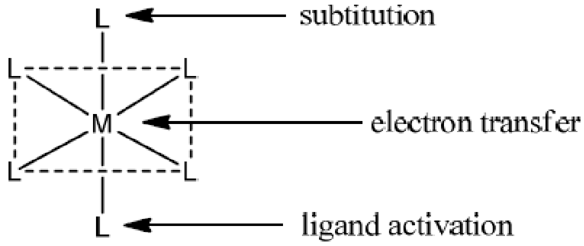
Mechanism describes the reaction pathway through which the reactants convert to products. Several methods are used to understand the mechanism of a reaction. These are (i) ascertaining the stoichiometry of a reaction, (ii) isolation of intermediate, (iii) study with isotopes, (iv) measurements of rates of the reactions under suitably designed condition. (v) the structure of starting and end product etc. Four general classes of reaction are important for a metal complex in a given geometry. These are –

(i) Substitution: Replacement of one coordinated ligand by another ligand

(ii) Electron transfer: Change in oxidation state of the metal

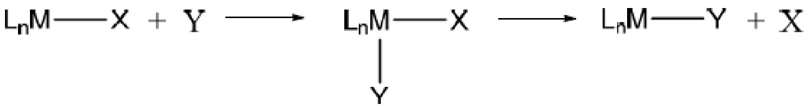
(iii) Activation of ligand: Attack at a ligand

(iv) Isomerism: Cis-trans and racemisation



Ligand substitution reactions generally occur in three mechanistic ways.

(i) Associative (A): The entering group binds to the metal before any bond weakening of the leaving group takes place. The reaction profile consists a single intermediate and two transition state.

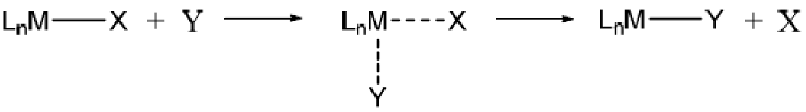


$$L_nM{-}X + Y \longrightarrow \begin{array}{c} L_nM{-}X \\ | \\ Y \end{array} \longrightarrow L_nM{-}Y + X$$

(ii) Dissociative (D): Leaving group has left before any interaction of the incoming group with metal ion. This reaction profile also consists a single intermediate and two transition state.

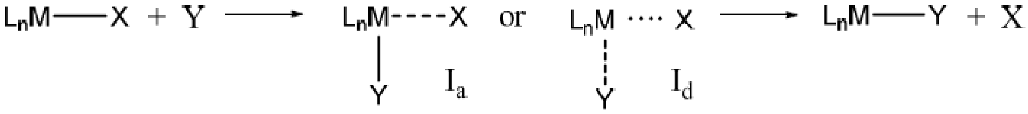
$$L_nM{-}X + Y \longrightarrow L_nM + X + Y \longrightarrow L_nM{-}Y + X$$

(iii) Interchange (I): The leaving and entering group exchange in a single step by forming an activated complex but not a true intermediate. As the entering group approaches to the metal, the leaving group responds in a concerted manner and progressively leaving the site. The reaction profile consists only one transition state.

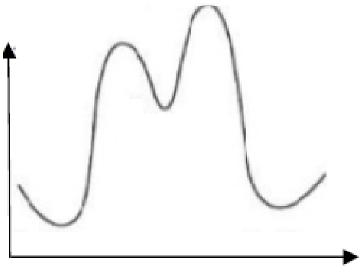


$$L_nM{-}X + Y \longrightarrow \begin{array}{c} L_nM{\cdots}X \\ \vdots \\ Y \end{array} \longrightarrow L_nM{-}Y + X$$

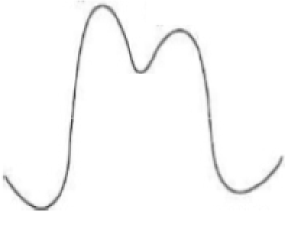
In reality, dissociation of leaving group and association of entering group do not occur with same intensity. There is two possibility of binding nature of leaving and entering group with metal centre. In one case the out leaving group is reluctant to leave its hold with the approach of entering group and retains its attachment right upto when the entering group bound completely to the metal site, assigned as I_a(interchange association). In other case, leaving group is very sensitive to the approach of the entering group and practically loses its hold even before the incoming group is tightly bound assigned as I_d(interchange dissociation).



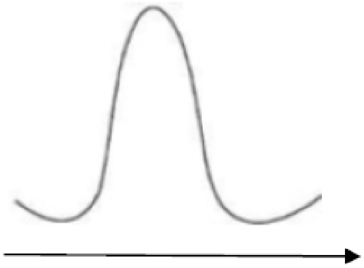
$$L_nM{-}X + Y \longrightarrow \underset{Y}{L_nM{\cdots}X}\ \ I_a \ \text{or}\ \underset{Y}{L_nM\cdots X}\ \ I_d \longrightarrow L_nM{-}Y + X$$



Reaction coordinate
Associative (A)



Reaction coordinate
Dissociative (D)



Reaction coordinate
Interchange(I)

Parameters to determine the mechanistic paths of the reaction

(i) The rate of the reaction is affected by change of temperature, pressure, solvents etc.

(ii) It is also affected by variation in structural and electronic factors like overall charge on the complex, steric crowding at reaction centre, nature of the leaving and entering group, nature of the central metal ion etc. For example, rate is independent on the nature of entering group but largely dependent on the leaving group suggests it undergoes on dissociative path.

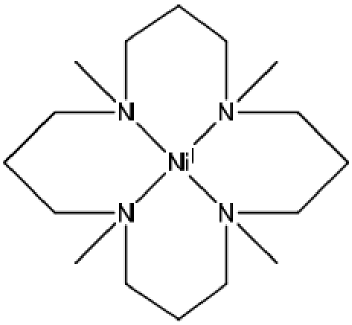
(iii) The activation parameter like $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ also provide important mechanistic information. For example, a negative $\Delta S^{\ddagger}$ indicates an associative mechanism and a dissociative process cause $\Delta S^{\ddagger}$ to increase. Again, if the formation of intermediate or activated complex is accompanied by net increase of charge then solvent molecule becomes more ordered that lowers $\Delta S^{\ddagger}$.

(iv) The change of volume in the formation of an activated complex has also important in study of reaction mechanism. The molar volume of activation $\Delta V^{\ddagger}$ is the difference in molar volume between the initial reactant and the activated complex. In a dissociative path, a ligand leaves the primary coordination sphere of metal and the $\Delta V^{\ddagger}$ become positive whereas, in negative. Generally, reactions are studied under high pressure to estimate $\Delta V^{\ddagger}$ of the reaction.

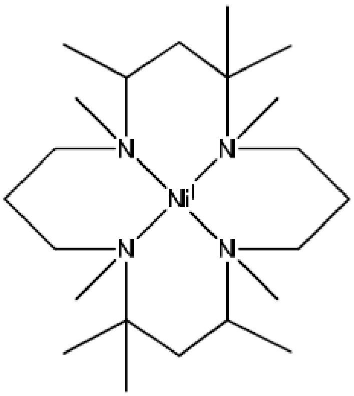
$$[M(CH_3OH)_6]^{2+} + CH_3O^*H \rightarrow [M(CH_3OH)_5(CH_3O^*H)]^{2+} + CH_3OH$$

Metal ion	$\Delta S^{\ddagger}$ (J mol^{-1}K^{-1})	$\Delta V^{\ddagger}$ (cc mol^{-1})
Ni^{2+}	+33.5	+11.4
Co^{2+}	+30.1	+8.9
Fe^{2+}	+12.6	+0.4
Mn^{2+}	-50.2	-5.0

With the increase of the volume (bulk) of the metal ion association process (A) increases.



I



II

$K_I/K_{II} = 5 \sim 6$ oxidation by Co(III) complex and $K_I/K_{II} = 10^2$ oxidation by peroxide (organic reagent)

Greater sensitivity towards steric hindrance in this oxidation reaction by peroxide is due to coordination effect of peroxide. It oxidizes the metal centre only after the coordination. Since, complex II is more sterically hindered, coordination is less favourable. But, oxidation by any complex like Co(III) complex, does not need any coordination to acts as oxidizing agent.

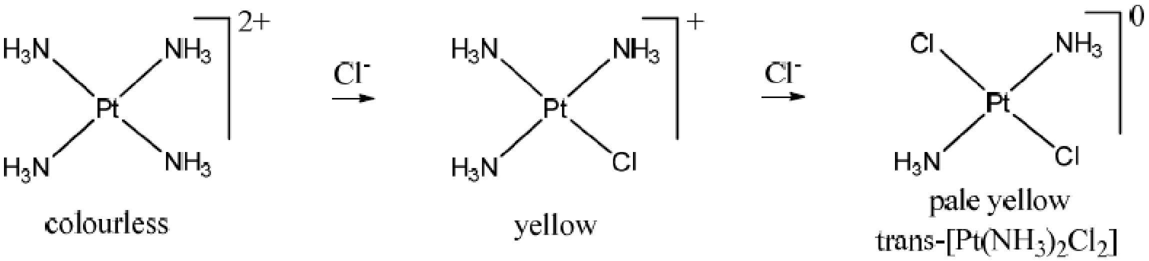
Trans effect:

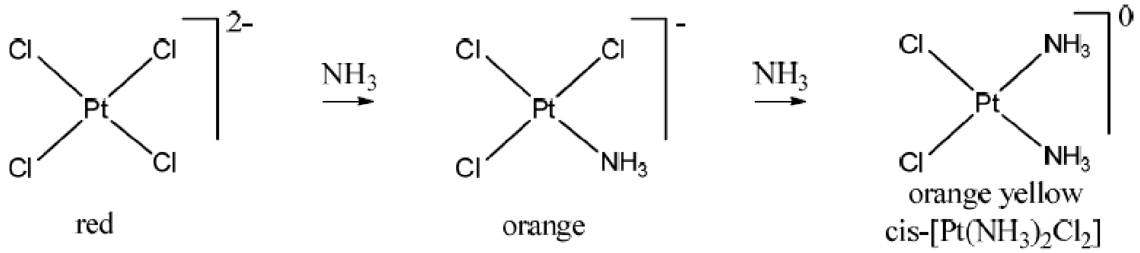
Chernyaev first introduced the trans effect from the observation on substitution reaction at platinum(II) complex. It is observed that certain ligands facilitate the substitution of the ligand that is in trans position to them. For example, ligands trans to chloride are more easily replaced than those trans to ammonia that means chloride has a stronger *trans* effect than ammonia. The trans effect is defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it in a metal complex. It is possible to arrange different ligands in a series according to their trans effect ability.

$CO \sim CN^- \sim C_2H_4 > PR_3 \sim H^- > CH_3^- \sim SC(NH_2)_2 > C_6H_5^- > NO_2^- \sim SCN^- \sim I^- > Br^- > Cl^- >$ py, $NH_3 > OH^- > H_2O$

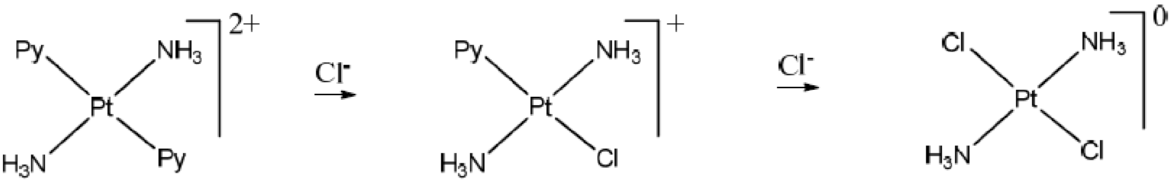
Application of trnas effect:

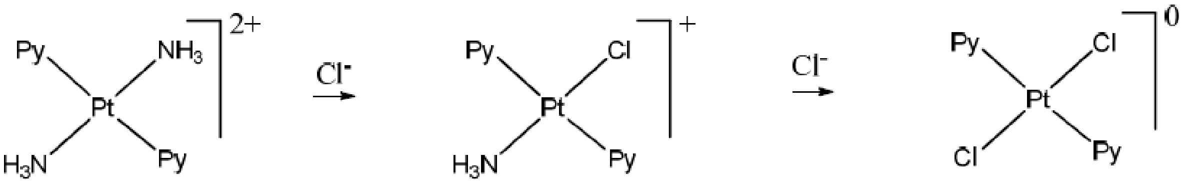
I) The trans effect allows the formation of isomeric Pt complex and formation of cis- and trans complex.

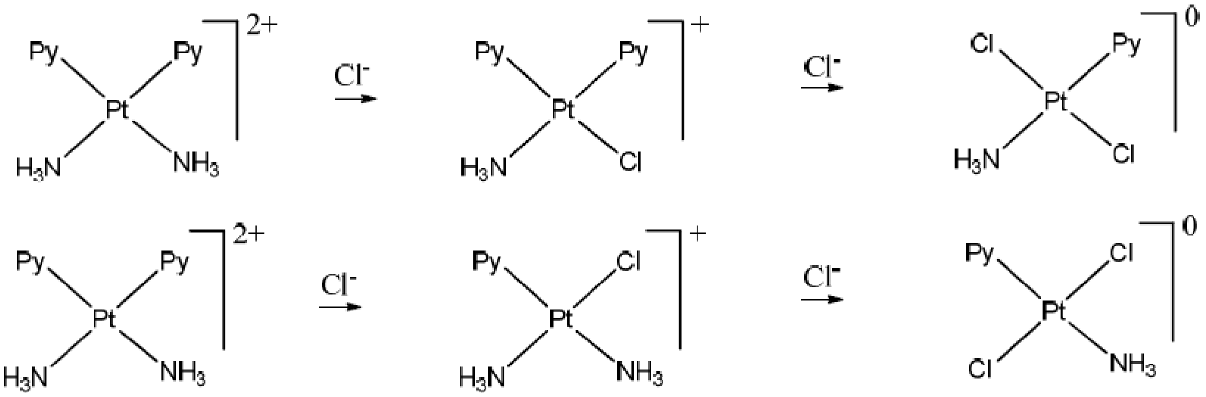


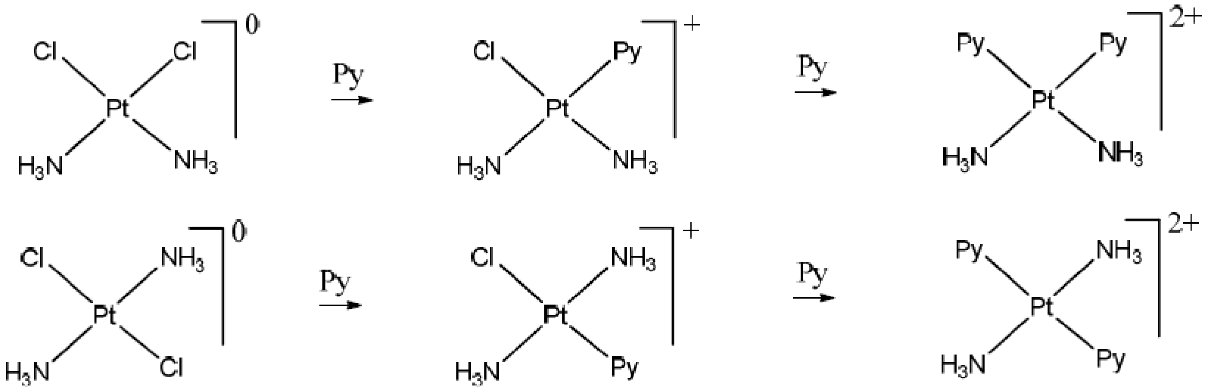


In both cases, the greater trans-directing power of Cl^- over NH_3 determines the geometry of the final product in the second step. Chloride ions trans to each other are mole labile than the chloride ions trans to NH_3.

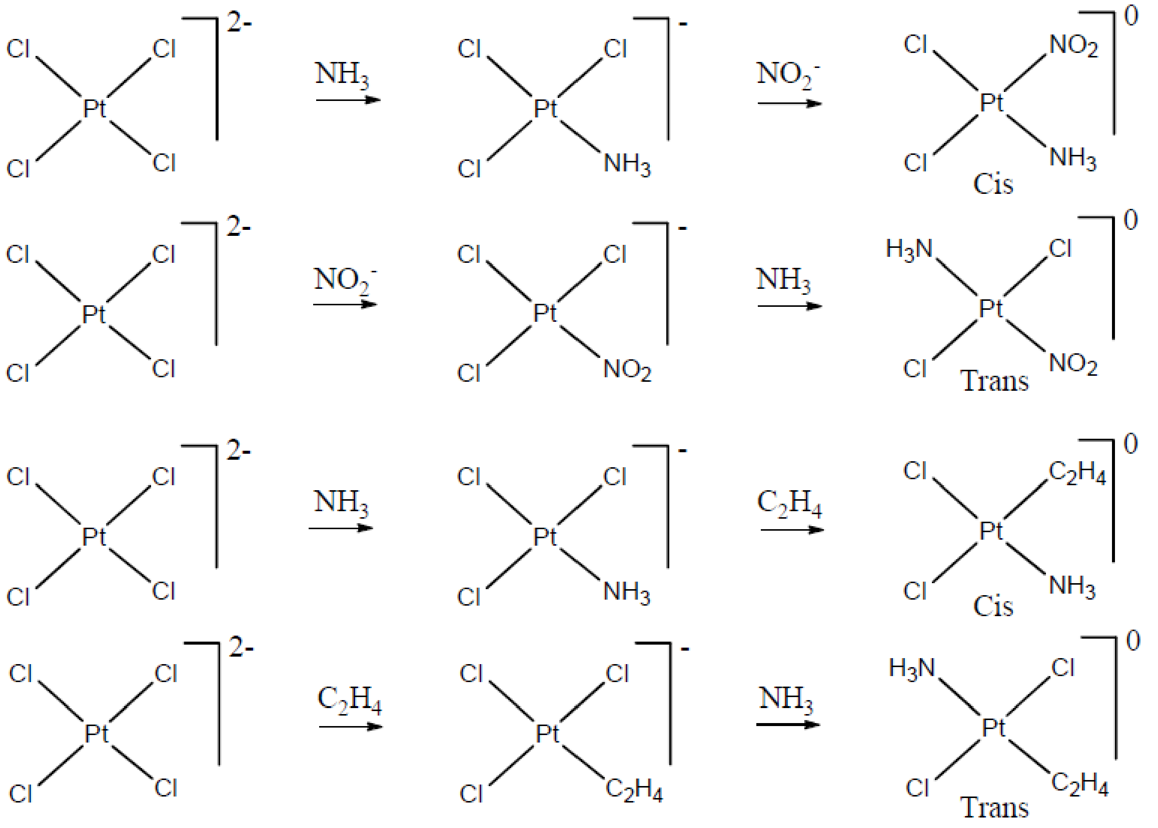


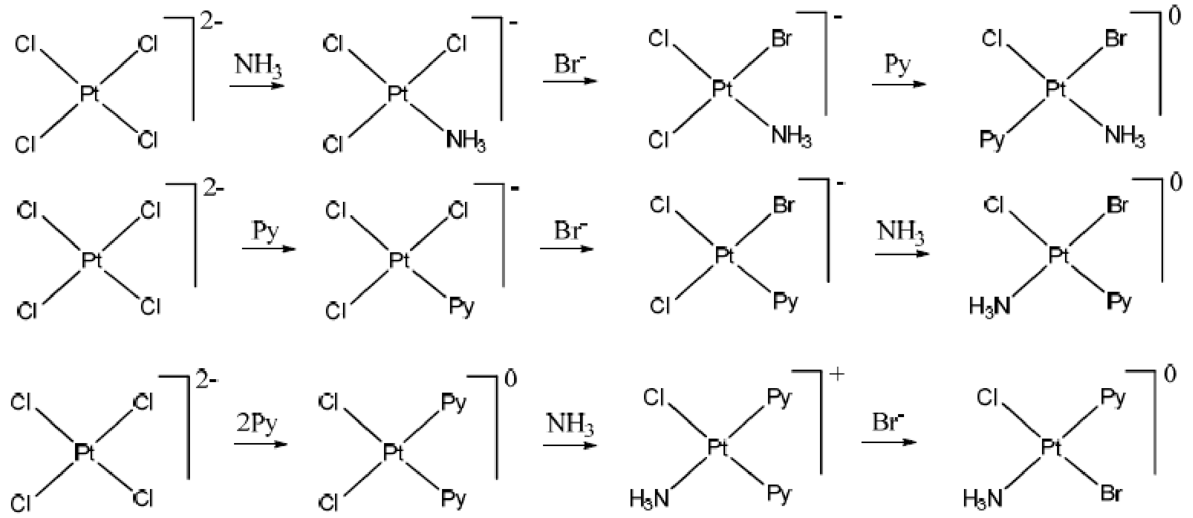






Inherent lability of Pt-Cl bond drives the reaction





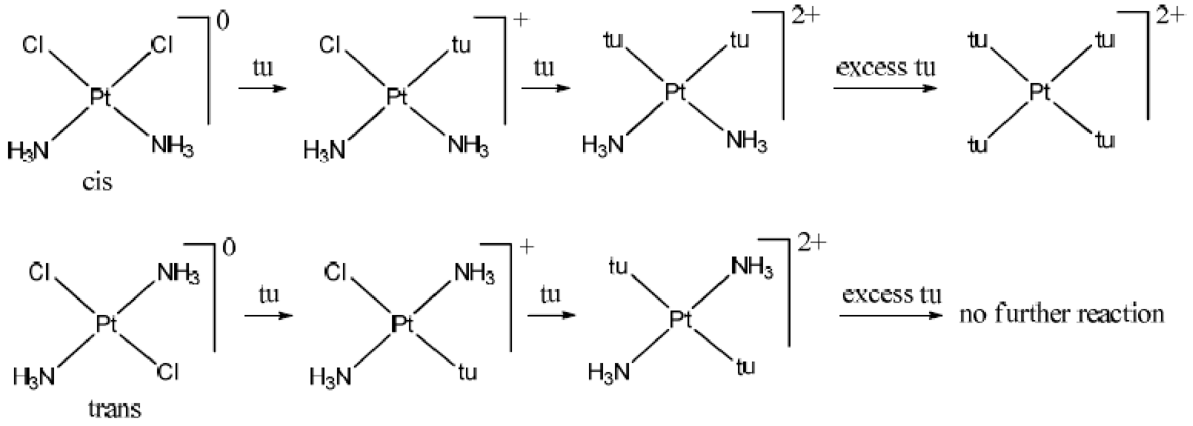
The trans effect merely gives an empirical guideline on the expected geometry of the product in a substitution process of known stoichiometric reaction. It does not foretell the nature of the product i.e., which ligand is going to be replaced. Thus, both trans effect and order of bond strength have significant role in the synthesis of different isomer.

Trans effect: Br > Cl > py > NH_3 and

Bond strength: Pt-NH_3 > Pt-py > Pt-Br > Pt-Cl

II) Trans effect has also used to distinguish cis and trans isomer Pt complex

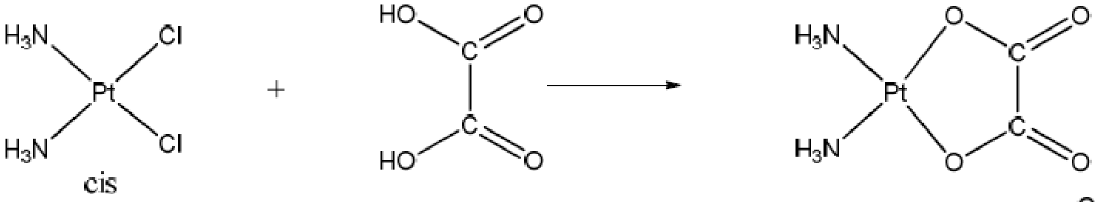
For example, reaction with thiourea (tu), cis-$[Pt(NH_3)_2Cl_2]$ gives yellow $[Pt(tu)_4]^{2+}$ where as trans-$[Pt(NH_3)_2Cl_2]$ gives white $[Pt(tu)_2(NH_3)_2]^{2+}$

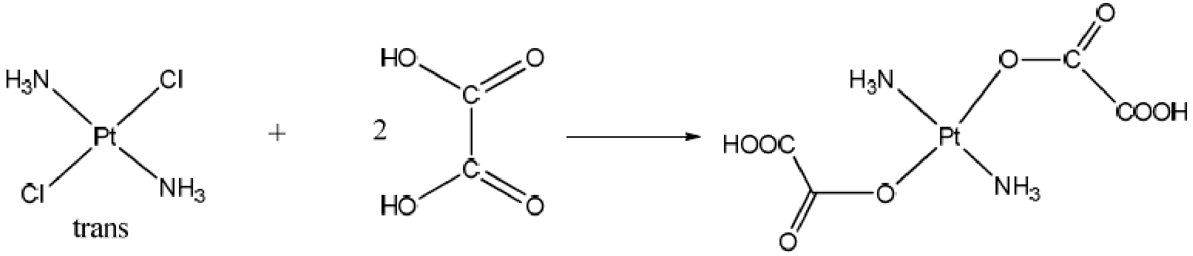


The cis isomer first, tu replaces two Cl producing cis-$[Pt(NH_3)_2(tu)_2]$. In the second step, due to strong trans effect of tu, two NH_3 become labile and replaced by tu. But, in trans isomer, replacement of two Cl by tu producing trans-$[Pt(NH_3)_2(tu)_2]$ that means two each tu and NH3 are trans to each other. Therefore, NH_3 is not labile enough to be replaced by tu. This test is known as Kurnakov test.

Grinberg's method:

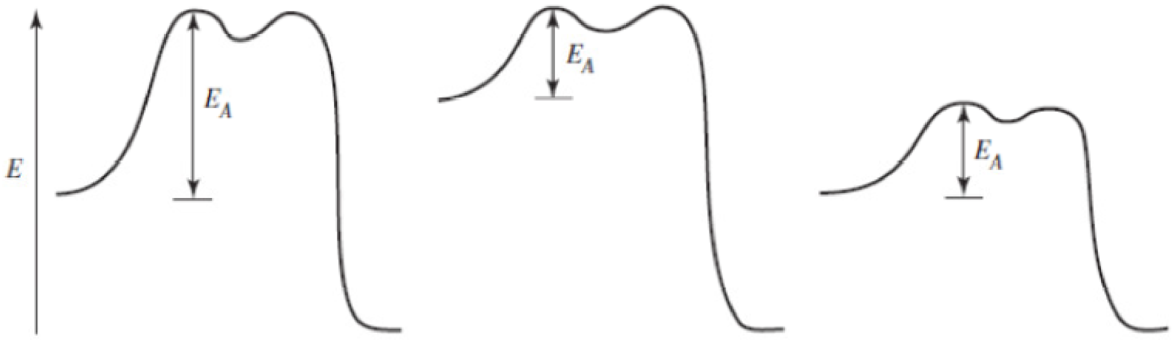
When complex of type MY_2X_2 is treated with di-dentate ligand then two labile ligands in cis-position is replaced by one di-dented ligand forming a chelating complex. But in trans complex, two labile ligand is replaced by two di-dentate ligand and do not form any chelating ring i.e., entering ligand acts as a mono dentate ligand. Generally, oxalic acid, glycine, ethylenediamine are used as di-dentate ligands.





Theories of Trans effect:

The trans effect series of the ligand shows that simple σ-donor ligand like NH_3 and H^-, and similarly π-acceptor ligand PPh_3 and py have widely different trans effect. The role of these ligands is enhancing the rate of substitution of their trans ligand. A higher rate of substitution implies a lower activation energy barrier. This may possible in either of two ways: (i) the ground state may be raised in energy(destabilized) and (ii) transition state may be stabilized. In fact, both of these effects may operate simultaneously with many trans directing ligands.



Normal energy state

Destabilizing ground state

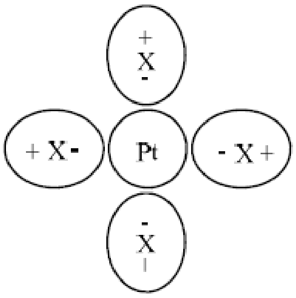
Stabilizing transition state

E_A = activation energy of the reaction

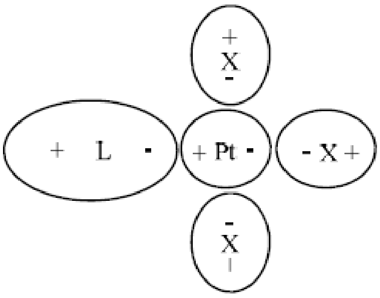
Mainly two theories are helpful to understand the trans effect. These are (i) σ-bonding theory or polarization theory (Ground state effect) (ii) π-bonding theory (Transition state effect)

(i) σ-bonding theory or polarization theory (Ground state effect):

Grinberg first proposed polarisation of the bond to explain the trans effect. This theory explains the ground state destabilization by weakening of the bond at trans position of pure or stronger σ-donors such as hydride and alkyl. These ligands are strongly polarizing and pull electron density towards themselves, thereby depriving the other bond particularly trans bond. This effect can be understood by considering a symmetrical complex, PtX_4 and a unsymmetrical complex PtX_3L.



PtX_4



PtX_3L

In case of PtX_4, the central platinum ion polarizes the four ligands equally. Therefore, induced dipole moment trans to each other will be cancelled and resultant dipole become zero. Thus, none of the four ligands shows trans effect. But, in PtX_3L, where L is more polarizable than X, the platinum induces a dipole on L and this may, in turn, induce a net polarization on the metal in a manner that positive charge on the metal opposite to L is reduced or negative charge arises. Hence, attraction of X by Pt is reduced and the bond becomes weakened. This weakening of the Pt-X bond trans to L facilitates the substitution process. Due to weakening of the Pt-X bond, ground state of PtX_3L becomes destabilized and has higher energy. This in turn, lowers the activation energy of substitution reaction. This thermodynamic effect is called **trans influence** rather than trans effect. According to this theory,

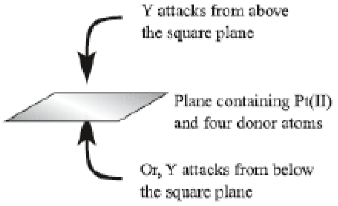
(i) The more polarizable ligands have strong trans direction power. This is consistent with the observed trends $H^- > I^- > Br^- > Cl^-$; $NH_3 > H_2O$

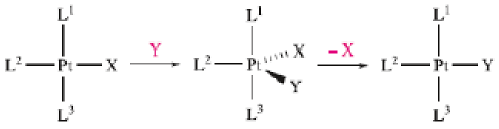
(ii) The trans effect will be significant only when the metal ion itself is polarizable. In fact, trans effect is not significant when the metal is less polarizable e.g., Pd(II), Pt(IV).

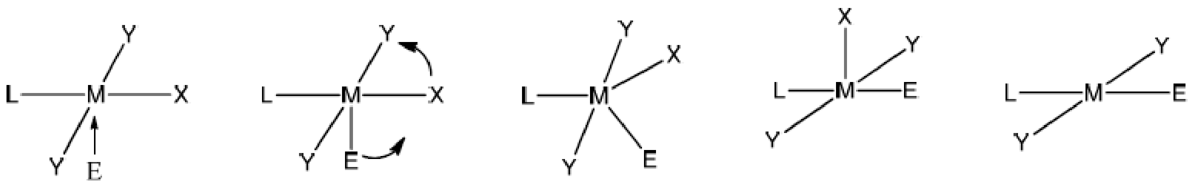
(ii) π-bonding theory (Transition state effect)

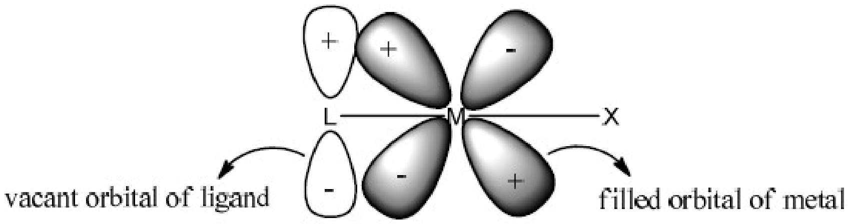
Chatt and Orgel independently proposed π-bonding theory to rationalize the trans effect. According to this theory, when the ligand, L engages in a strong π-acceptor (back bonding) interaction with metal, charge is removed from metal, rendering the metal center more electrophilic and more susceptible to nucleophilic attack. This is necessary for formation of the 5-coordinate intermediate with a relatively strong M—Nu bond, that stabilizes the intermediate. It is noteworthy that π–back bonding between M and L also stabilizes the intermediate by partially compensating the increase in energy due to weakening the M—X bond. The energy of the transition state will be lowered due to stabilization through strong π-interaction between L and M. Thus, the activation energy will be decreased.

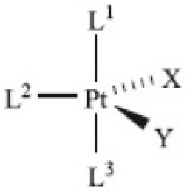
It may be noted that in such π-bonding, the vacant π or π* orbitals of the ligands accept electron from the filled d-orbitals (d_{xz} or d_{yz}) of the metal. The substitution reactions of square planar complex are thought to proceed through a trigonal bipyramidal transition state. In trigonal bipyramidal state, the leaving group, entering group and the trans directing ligand occupy the equatorial position because for better π-bonding it is necessary to positioned the trans ligand at equatorial plane. Generally, the entering group approaches to the metal away from the strongly bound ligand (trans directing ligand) and close to the least strongly bound ligand (leaving ligand).



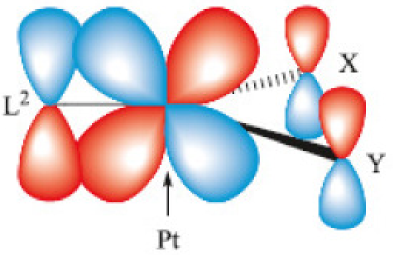








Trigonal bipyramidal transition state or intermediate



π-Bonding in the trigonal plane

The order of ligand π-acceptor ability is $C_2H_4 \sim CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$

The overall *trans* effect list is the result of the combination of the two effects:

$CO \sim CN^- \sim C_2H_4 > PR_3 \sim H^- > CH_3^- \sim SC(NH_2)_2 > C_6H_5^- > NO_2^- \sim SCN^- \sim I^- > Br^- > Cl^- >$ py, $NH_3 > OH^- > H_2O$

Ligands highest in the series are strong π acceptors, followed by strong σ donors. Ligands at the low end of the series have neither strong σ-donor nor π-acceptor abilities.

Kinetics and Mechanism of substitution reaction in square planar complex

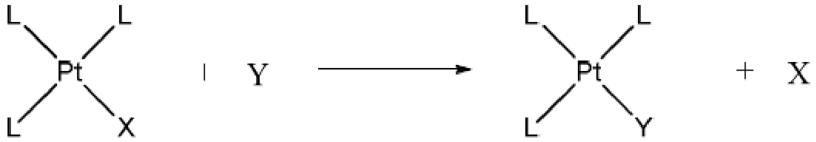
The square planar complexes are formed by transition metal ions with d^8 configuration, e.g., Ni(II), Pd(II), Pt(II), Rh(I), Ir(I), Au(III). But substitution reactions of Pt(II) complex has been greatly studied because,

i) Pt(II) complex is more stable towards oxidation than Rh(I), Ir(I)

ii) Pt(II) complex is always square planar unlike Ni(II) complex which can often be tetrahedral

iii) Rate of substitution of Pt(II) complex is much slow (10^6 times) than Ni(II) complex helps to follow-up the reaction.

A general substitution reaction of square planar Pt(II) complex can be written as:

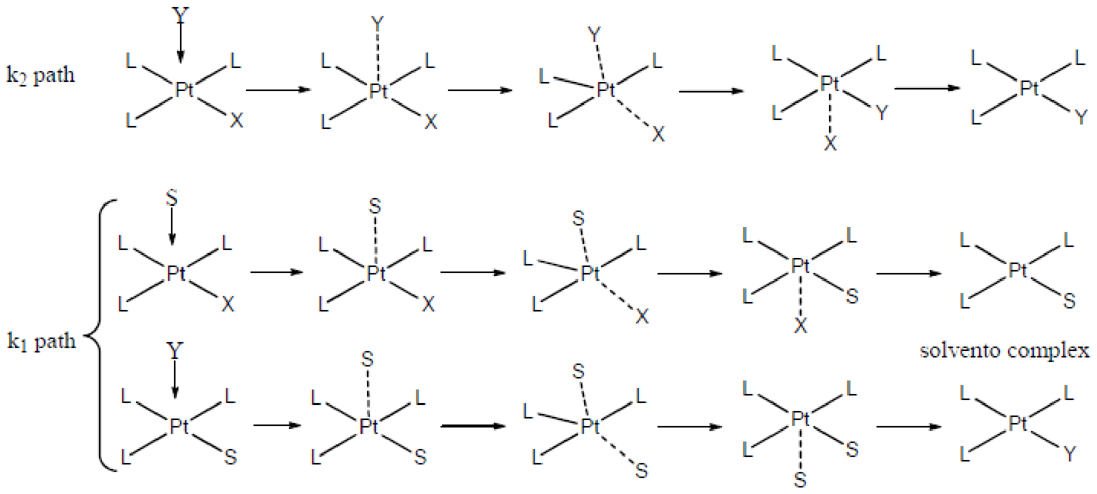


Available kinetic data of such substitution reaction is solution suggest reaction passes through association mechanism forming a 5-coordinate transition state or intermediate. The typical kinetic features of such reactions are two term rate law,

$$\text{Rate} = k_1[\text{complex}] + k_2[\text{Ligand-Nu}][\text{complex}]$$

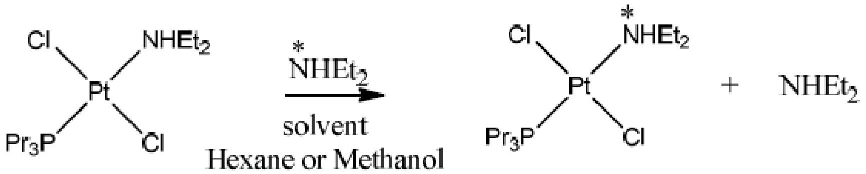
i) Rate equation suggests it is a combination of two parallel processes. The k_2 path is first order with respect to both ligand nucleophile and complex where the nucleophile Y attacks the metal complex. The k_1 path is first order with respect to complex but independent of nucleophile where solvent molecule acts as nucleophile that means $k_1 = k_s[\text{solvent}]$. Since, solvent concentration is large in the reaction medium, so its concentration remains constant.

The pathway of the substitution of square planar complex generally shown as:

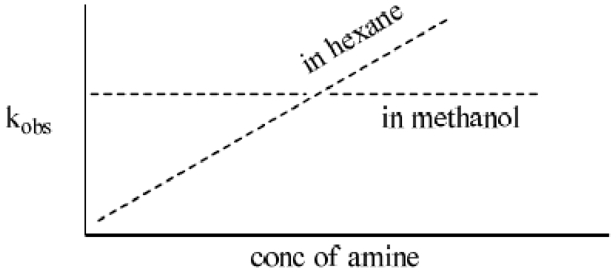


ii) Rate strongly depends on the nature of incoming nucleophile, leaving group and even the spectator (non leaving) ligand. A significant rate enhancing effect of the trans ligand is observed called trans effect.

iii) Rate of the substitution is strongly dependent on the solvent. In polar solvent k_1 path is contribute significantly towards the overall rate but if solvent has less nucleophilic character then rate depends on ligand nucleophile.

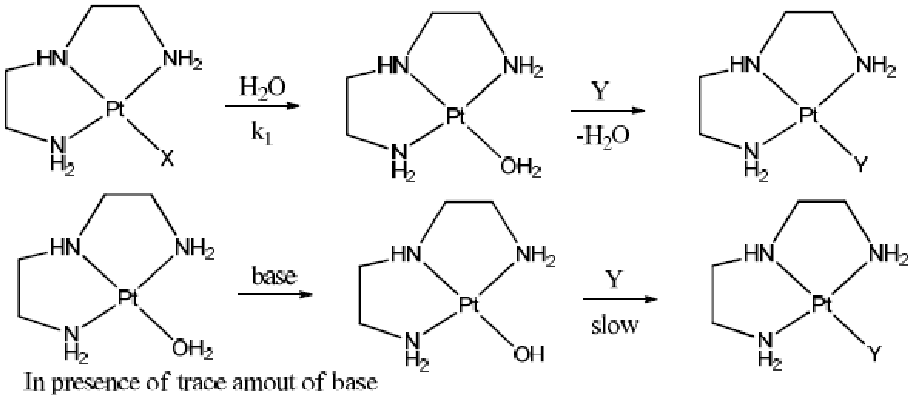


Hexane is non coordinating solvent. So, in hexane reaction should proceeds through solvent independent pathway, that is k_2 path. In methanol, however, the reaction should proceeds through the solvent-dependent path that is k_1 path. In fact, as there is no amine-dependent contribution to the observed rate in methanol. We can correlate the fact with the plot of k_{obs} vs. Concentration of amine (nucleophile). In hexane, the intercept of the plot is effectively zero means $k_1 = 0$ and in methanol slope is zero means $k_2 = 0$.



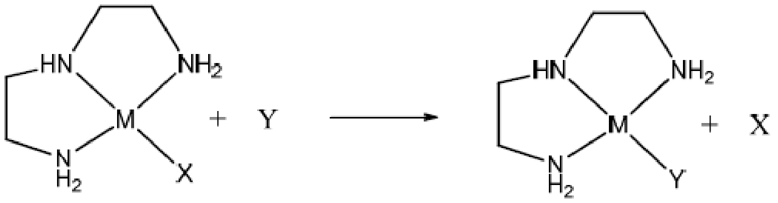
$$k_{obs} = k_1 + k_2 [Y]$$

Evidence in favour of solvent complex:



Pt-OH bond is stronger than the Pt-OH_2 bond. Therefore, in presence of base good leaving group H_2O is converted to bad leaving group and rate becomes slower, practically inhibits the substitution.

iv) Increasing steric crowding at the metal or reaction centre k_1 and k_2 both decreases. Therefore, both path of substitution reaction follows similar association (A) path.



If the H-atoms of the ligand are replaced by the ethyl group, the rate of the reaction is decreased by 10^5 times. It suggests reaction passes through association mechanism.

Association and dependence on entering group:

It has been observed that rate of substitution by Y, a nucleophilic ligand, in a given complex dependence on entering group, Y and the increase of rate constant is seen in an order as follows for the Pt(II) complex: $H_2O < NH_3 \sim Cl^- < py < Br^- < I^- < CN^- < PR_3$. This order is called nucleophilicity sequence for substitution in Pt(II) complex. According to this sequence one can calculate the nucleophilicity parameter, n_{Pt}, of different entering group for a particular substitution reaction of Pt(II) complex by the following relation.

$$n_{Pt} = \log k_2 - \log k_2' \text{ where } k_2' \text{ rate constant with } Y = MeOH$$

For example, n_{pt} value for the reaction trans-$[PtCl_2(py)_2] + Y \rightarrow$ trans-$[PtCl(py)_2Y] + Cl^-$ are:

ligand	Cl^-	NH_3	py	Br^-	I^-	CN^-	PPh_3
n_{Pt}	3.04	3.07	3.19	4.18	5.46	7.14	8.93

The experiment suggests rate is differ with variation of the entering group and it authenticates substitution proceed through association mechanism.

Dependence on leaving group:

It is seen that the leaving group has significant influence of the rate of substitution. The hard ligand Cl^-, NH_3, and NO_3^- are leaving relatively quickly whereas the soft ligands with considerable metal to-ligand p bonding, such as CN^- and NO_2^-, leaves relatively slowly. For example:

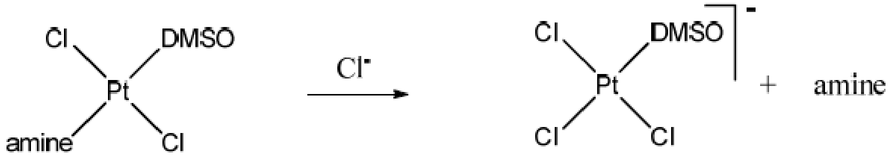
$$[Pt(dien)X]^+ + py \rightarrow [Pt(dien)(py)]^{2+} + X^-$$

In the reaction the rate increases by a factor of 10^5 with X = H_2O as compared with X = CN^- or NO_2^- as the leaving group. Metal-to-ligand p bonding to X reduces the reactivity of square planar platinum complexes significantly towards substitution of these ligands; the M—X bonds are strengthened as a result of this p interaction. In addition π-back bonding to X uses the same orbitals as those bonding to the entering group in the trigonal plane. The extension of the HOMO from the Pt(II) center is reduced, decreasing the accessibility of this orbital towards incoming nucleophiles. These two effects result in the slow displacement of ligands that participate in metal-to-ligand π-bonding compared to ligands with only σ-bonding or ligand-to-metal π-bonding capability.

$$[Pt(dien)X]^+ + py \rightarrow [Pt(dien)(py)]^{2+} + X^-$$

X	NO_3^-	Cl^-	Br^-	I^-	SCN^-	NO_2^-	CN^-
$K_2(M^{-1}s^{-1})$	very fast	5.3×10^{-3}	3.5×10^{-3}	1.5×10^{-3}	4.8×10^{-5}	3.8×10^{-6}	2.8×10^{-6}

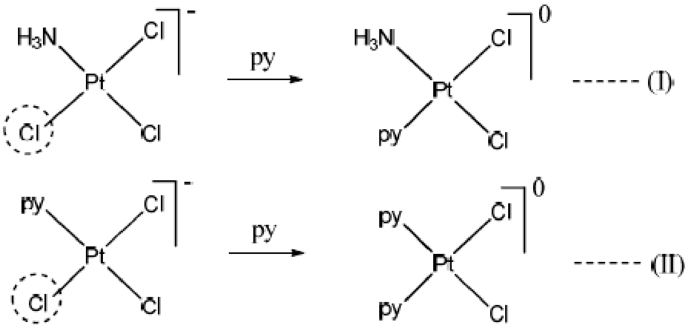
ii)



The displacement of amines was found to proceed through both the k_2 and k_1 paths. But, the rate constant k_1 is more sensitive to the basicity of the leaving group than k_2, In fact, there was an excellent correlation between the pK_a of the leaving group and log k_1, as the basicity of the amine increases, its replacement becomes more difficult. This could imply that bond breaking is important in the rate determining step.

Cis effect:

Substitution reaction in square planar complex may also be effected by cis group. Though such effect does exist for a few platinum complexes, is not as strong as trans effect.



It has been observed that reaction II is about 40% faster than reaction I. This is attributed greater cis effect of py over NH_3 in labilizing the groups cis to themselves. Similar effect is observed for substitution of Cl cis to NH_3 20% faster in comparison to cis to NO_2. Thus, order of cis effect is py > NH_3 > NO_2

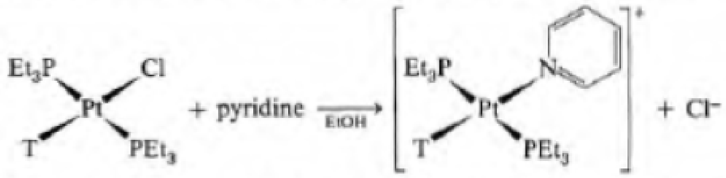
Characteristic values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$

In case of associative path, the values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ are negative. These values are in the range -50 to -180 J mol^{-1} K^{-1} for $\Delta S^{\ddagger}$ and -6.0 to -15.0 cc mol^{-1} for $\Delta V^{\ddagger}$.

Reaction	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta V^{\ddagger}$ cc mol^{-1}
$[Pt(dien)Cl]^+ + H_2O$	+84	-63	-10
$[Pt(dien)Cl]^+ + N_3^-$	+65	-71	-8.5
trans-$[PtCl_2(PEt_3)_2]^+$ + py	+14	-25	-14
trans-$[PtCl(NO_2)(py)_2]^+$ + py	+12	-24	-9
trans-$[Pt(PEt_3)_2(R)Br] + I^-$	+59	-115	-16
trans-$[Pt(PEt_3)_2(R)Br] + SC(NH_2)_2$	+43	-130	-11

R = 2,4,6-$Me_3C_6H_2$

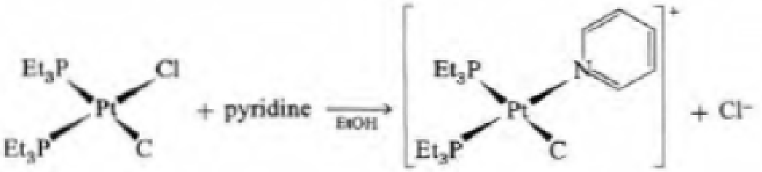
In cases where a relatively poor nucleophile acts as the entering group, the relative ability of ligands to act as *trans* labilizers is the same as their ability to act as *cis* labilizers, but the effect is less marked. For example, in the reaction[44]



the relative ordering of *trans* labilizing effects, measured against T = Cl as the standard case, is given by

$$\begin{array}{lcccc} T = & H^- & > CH_3^- & > C_6H_5^- & > Cl^- \\ \dfrac{k_Y(T)}{k_Y(Cl)} = & >10^4 & 1700 & 400 & 1.0 \end{array}$$

In contrast, the *cis* effect of these same ligands is in the same order but is considerably less.[44]



$$\begin{array}{lccc} C = & CH_3^- & > C_6H_5^- & > Cl^- \\ \dfrac{k_Y(C)}{k_Y(Cl)} = & 3.6 & 2.3 & 1.0 \end{array}$$

The most likely explanation for this observation is that the *cis* effect is similar in origin to the *trans* effect. Indeed, molecular orbital calculations show that ligands that weaken bonds *trans* to themselves also weaken *cis* M—L bonds, but not by as large an amount.[45] (This is presumably due to the fact that there is direct communication between *trans* ligands *via* the metal p_y and $d_{x^2-y^2}$ orbitals, whereas *cis* ligand communication depends only on one orbital, $d_{x^2-y^2}$.) Therefore, bond breaking in the transition state becomes somewhat easier for good *cis* directors, and the reaction rate increases, although not quite as much as if the *cis* ligand were in the *trans* position.

Thermodynamic and Kinetic stability

Stability of the metal complexes towards substitution reaction is associated with two term (i) Thermodynamic stability (ii) Kinetic stability. **Thermodynamic stability** of the complex is measured by equilibrium constant (K) of the reaction, where $\Delta G = - RT\ln K$. That provides whether the complex is stable or unstable that means whether the complex retain or lose its identity in solution. **Kinetic stability** is measured by term lability and inertness. It means how quickly a complex undergoes substitution reaction or not.

Labile means substitution of the ligands occurs very rapidly where **inert** means rate of the reaction is very slow.

Definition: According to Taube, the complexes which react completely within about one minute at 25°C are considered labile and those that take longer are considered inert.

Labile and inertness is also classified as: at ordinary temperature for a 0.1 (M) solution of metal complex undergoes substitution reaction with half life < 30 sec is called labile. If half life is greater than 30 sec or reaction is too slow to measure or slow enough to follow by conventional techniques is classified as inert.

Study of exchange reaction by labelled cyanide (^{14}CN)

$$[M(CN)_n]^{m-} + n\,^{14}CN^- \rightarrow [M(^{14}CN)_n]^{m-} + n\,CN^-$$

Cyanide complexes	Formation constant (β)	Exchange rate ($t_{½}$)
$[Ni(CN)_4]^{2-}$	10^{30}	$t_{½} \approx 30$ sec
$[Mn(CN)_6]^{3-}$	$> 10^{20}$	$t_{½} \approx 1$ h
$[Cr(CN)_6]^{3-}$	$> 10^{20}$	$t_{½} \approx 24$ days

These complexes are extremely stable from thermodynamic point of view, but differ kinetically. The measurement of the rate of exchange of radio carbon labelled cyanide shows that despite of thermodynamic stability $[Ni(CN)_4]^{2-}$ exchange cyanide ligands very rapidly that is labile while $[Mn(CN)_6]^{3-}$ is moderately labile and $[Cr(CN)_6]^{3-}$ exchange cyanide very slowly can be considered as inert.

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \rightarrow [Co(H_2O)_6]^{3+} + 6NH_4^+ \qquad K_{eq} \sim 10^{25}$$

Very high value of equilibrium constant suggests on acidification reaction will occur very fast but fact is that on acidification there is no immediate change and several days are required for degradation of the complex despite of favourable thermodynamics. So, $[Co(NH_3)_6]^{3+}$ is thermodynamically unstable but kinetically inert in acid medium. It authenticates the inertness arises due to the absence of suitable low energy pathway for the acid hydrolysis reaction.

Prediction of lability and inertness

H. Taube was first pointed out that electronic structure of a complex has relation with the lability. It is expecting in an octahedral complex with electrons in the antibonding e_g level, the ligands will be relatively weakly bound and hence may be displaced easily. This implies that a substitution via a five-coordinate activated complex (D-process) will be favoured. Again, when a complex has less than three electrons, it will have one or two t_{2g} orbitals vacant. The ligand can be approached to metal along to these vacant t_{2g} orbitals with relatively less electronic repulsion. This implies that a substitution via a seven-coordinate activated complex (A-process) will be favoured.

Labile complex (vacant t_{2g} or e_g electron)		Inert complex	
d^0, (t_{2g}^0 e_g^0)	$[Ca(edta)]^{2-}$, $[TiCl_6]^{2-}$	d^3, (t_{2g}^3 e_g^0)	$[Cr(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{2+}$
d^1, (t_{2g}^1 e_g^0)	$[Ti(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$	d^4,(LS) (t_{2g}^4 e_g^0)	$[Cr(CN)_6]^{4-}$, $[Mn(CN)_6]^{3-}$
d^2, (t_{2g}^2 e_g^0)	$[V(phen)_3]^{3+}$	d^5, (LS) (t_{2g}^5 e_g^0)	$[Mn(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$
d^4, (t_{2g}^3 e_g^1)	$[Cr(H_2O)_6]^{2+}$	d^6, (LS) (t_{2g}^6 e_g^0)	$[Fe(CN)_6]^{4-}$, $[Co(NO_2)_6]^{3-}$,
d^5, (t_{2g}^3 e_g^2)	$[Mn(H_2O)_6]^{2+}$	d^6, (LS) (t_{2g}^6 e_g^0)	$[PtCl_6]^{2-}$
d^6, (t_{2g}^4 e_g^2)	$[Fe(H_2O)_6]^{2+}$		
d^7, (t_{2g}^5 e_g^2)	$[Co(NH_3)_6]^{2+}$		
d^8, (t_{2g}^6 e_g^2)	$[Ni(en)_3]^{2+}$		
d^9, (t_{2g}^6 e_g^3)	$[Cu(NH_3)_4(H_2O)_2]^{2+}$		

i) $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$: Ferrocyanide and ferricyanide species although contain cyanide ion these are non-poisonous. Because of their inertness the cyanide ions are not ionisable.

ii) $[V(H_2O)_6]^{3+}$ *vs.* $[V(H_2O)_6]^{2+}$: In between aqueous V^{3+} and V^{2+} ion, it is expected the V^{3+} will be inert because of the high charge, metal will strongly bind the existing ligand. But, reverse is true. The electronic factor is predominant over the charge factor. V^{3+} (d^2, t_{2g}^2 e_g^0) has vacant t_{2g} orbital, but t_{2g} orbitals are filled in V^{2+} (d^3, t_{2g}^3 e_g^0).

iii) $[Cr(H_2O)_6]^{3+}$ *vs.* $[Cr(H_2O)_6]^{2+}$: In between Cr^{2+} and Cr^{3+}, Cr^{3+} will be inert due to higher charge and absence of vacant t_{2g} orbital or presence of e_g electron. Here, charge factor and electronic factor are parallel.

Lability and LFSE

Though absolute value of LFSE can't measure activation energy or rate of the reaction but the loss of LFSE upon formation of activated complex may be measure activation energy. The greater loss of LFSE, the complex will be more inert. The difference of LFSE between the initial octahedral complex and activated intermediate complex either seven coordinated pentagonal bipyramid or five coordinated trigonal bipyramid or square pyramid is called crystal field activation energy (CFAE).

Basolo and Pearson have calculate CFAE for strong and weak field for square pyramid (C.N. = 5) and pentagonal bipyramid (C.N. = 7) intermediates.

System	High Spin		Low Spin	
	C.N = 5	C.N. = 7	C.N. = 5	C.N. = 7
d^0	0	0		
d^1	+0.57	+1.28		
d^2	+1.14	+2.56		
d^3	-2.00	-4.26		
d^4	+3.14	-1.07	-1.43	-2.98
d^5	0	0	-0.86	-1.70
d^6	+0.57	+1.28	-4.00	-8.52
d^7	+1.14	+2.56	+1.14	-5.34
d^8	-2.00	-4.26		
d^9	+3.14	-1.07		
d^{10}	0	0		

Conclusion:

i) Positive ΔE_a implies that a better LFSE will be obtained by distorting the octahedron. In such cases the original state is a distorted octahedral.

ii) d^3, d^8 and low spin d^6 complexes shows large loss of LFSE by both reaction pathway i.e. Inert.

iii) d^0, d^1, d^2, d^{10} do not loss LFSE by either mechanism predicting to reacts fast compare to those having positive ΔE_a .

iv) In strong field ligand, reaction of d^0, d^1, d^2 are predicted to be fast while d^3, d^4, d^5, d^6 are slow with the rates decreasing in the order, $d^5 > d^4 > d^3 > d^6$ (ΔE_a increases) by either mechanism.

v) In weak field ligand, d^3, and d^8 are predicted to be slow by either mechanism while d^1, d^2, high spin d^4, d^5, d^6, d^7, d^9 system are fast.

Kinetics and Mechanism of substitution reaction in octahedral complex

Substitution at an octahedral metal site in an aqueous medium is mainly concerned with (i) replacement of coordinated water by other ligand (de-aquation), including exchange of water molecule and (ii) substitution of other ligands by water (hydrolysis).

The exchange of water between the coordinated water and solvent water has been studied using isotopically labelled water. Reaction may be represented as:

$$[M(H_2O)_6]^{n+} + H_2O^* \rightleftharpoons [M(H_2O)_5(H_2O^*)]^{n+} + H_2O$$

Water exchange rate constants (k) vary widely as a function of the metal ion and correlated to the electronic configuration of the starting complex.

Complex	K (s^{-1}) at 298 K	Electronic configuration	
$[Ti(H_2O)_6]^{3+}$	1.8×10^5	d^1	t_{2g}^1
$[V(H_2O)_6]^{3+}$	5.0×10^2	d^2	t_{2g}^2
$[V(H_2O)_6]^{2+}$	8.7×10^1	d^3	t_{2g}^3
$[Cr(H_2O)_6]^{3+}$	2.4×10^{-6}	d^3	t_{2g}^3
$[Cr(H_2O)_6]^{2+}$	$> 10^8$	d^4	$t_{2g}^3e_g^1$
$[Fe(H_2O)_6]^{3+}$	1.6×10^2	d^5	$t_{2g}^3e_g^2$
$[Fe(H_2O)_6]^{2+}$	4.4×10^6	d^6	$t_{2g}^4e_g^2$
$[Co(H_2O)_6]^{2+}$	3.2×10^6	d^7	$t_{2g}^5e_g^2$
$[Ni(H_2O)_6]^{2+}$	3.2×10^4	d^8	$t_{2g}^6e_g^2$
$[Cu(H_2O)_6]^{2+}$	4.4×10^9	d^9	$t_{2g}^6e_g^3$
$[Zn(H_2O)_6]^{2+}$	$> 10^7$	d^{10}	$t_{2g}^6e_g^4$

The values of rate constant reveals that electronic factor along with small extent of electrostatic interaction is reponsible for such exchange reaction. Because, $[V(H_2O)_6]^{3+}$ lose water rapidly than $[V(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ lose water molecule 10^{13} faster than $[Cr(H_2O)_6]^{3+}$ can be explained on basis their electronic configuration. Metal ions with vacant t^{2g} orbital or electron in e_g orbital undergoes rapid exchange reaction.

These exchange reaction can occur through either associative or dissociative mechanism. The data reveals that water exchange reactions mainly undergoes dissociative pathway.

The values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ of these exchange process for different metal ions as follows:

	V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
$\Delta H^{\ddagger}$ (kJmol^{-1})	62	33	41	47	57
$\Delta S^{\ddagger}$ (J mol^{-1}K^{-1})	-0.4	+6	+21	+37	+32
$\Delta V^{\ddagger}$ (cc mol^{-1})	-4.1	-5.4	+3.7	+6.1	+7.2

	Ti^{3+}	V^{3+}	Cr^{3+}	Fe^{3+}
$\Delta H^{\ddagger}$ (kJmol^{-1})	43	49	109	64
$\Delta S^{\ddagger}$ (J mol^{-1}K^{-1})	+1.0	-29	+12	+12
$\Delta V^{\ddagger}$ (cc mol^{-1})	-12.1	-8.9	-9.6	-5.4

A negative value of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ corresponds to an associative process while a positive value indicates dissociative process. From left to right there is a change of A to D mechanism irrespective to the oxidation state of the metal ions. This can be rationalized considering the approach of the H_2O molecule to an octahedral complex. A water molecule must attack the metal site from the directions which are least protected by the existing ligands. In octahedral complex, the approach of the H_2O must be along the direction of metal t_{2g} orbital that is one of the C_3 symmetry axes. When the t_{2g} orbitals are empty, they are in position to accept the attacking nucleophile offering associative path. But on moving towards right along the transition series, t_{2g} orbitals gets filled gradually and repulsion with the incoming ligand/water will increase that favours a dissociative pathway for substitution.

With the basis of experimental data it is worth mentioning that, an associative process appears to operate for second and third row metal ions that are consistent with the idea of larger metal centres may facilitate association with the entering ligand.

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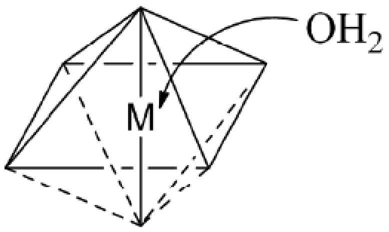
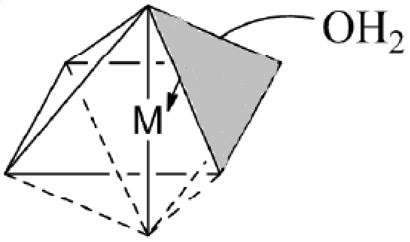




Substitution reaction of non-transition elements:

(i) Rate of substitution depends on the oxidation state of the central ion. Central atoms with higher oxidation states have slower ligand exchange rates because central atoms will binds the ligand more tightly with increasing oxidation state of it. For example:

(a) $[AlF_6]^{3-} > [SiF_6]^{2-} > [PF_6]^{-} > SF_6$ (b) $[Na(H_2O)_n]^{+} > [Mg(H_2O)_n]^{2+} > [Al(H_2O)_n]^{3+}$

+3 +4 +5 +6

(ii) Rate of substitution depends on the ionic radius of the central ion. Smaller ions have slower exchange rates. Ions with same and different size have different ionic potential (ϕ). Ion with greater ionic potential binds the existing ligand more strongly that the ions having lesser ionic potential. At the same time, the ions with larger size are capable to expand coordination number in the intermediate state but it is sterically unfavourable for smaller ions. For example: $[Sr(H_2O)_6]^{2+} > [Ca(H_2O)_6]^{2+} > [Mg(H_2O)_6]^{2+}$

112 pm 99 pm 66 pm

Substitution of a ligand by H_2O:

Substitution reactions in aqueous solution appear to proceed always the intermediate formation of an aqua-complex, e.g.,

$$[MX_5Y]^{n+} + H_2O \rightleftharpoons [MX_5(H2O)]^{n+} + Y$$

This process can take place either in acid medium (pH $\leq$ 4) often called acid hydrolysis or in base medium called base hydrolysis. In base medium generally a hydroxo complex is formed.

$$[MX_5Y]^{n+} + H_2O \xrightleftharpoons{OH^-} [MX_5(OH)]^{(n-1)+} + Y$$

Steric hindrance favours dissociative path:

$$[Co(RNH_2)_5X]^{2+} + H_2O \rightarrow [Co(RNH_2)_5(H_2O)]^{3+} + X^-$$

When R = H, rate constant is k_1 and for R = t_{Bu}, rate constant is k_2

It is observed that $k_2 > k_1$ that authenticates substitution by H_2O occur through dissociative path. With replacement of H by bulky t_{Bu} group steric crowding at the reaction centre is increased that facilitates the dissociation of leaving group and rates becomes faster.

Dependence on leaving group:

(i) The rate of ligand substitution usually depends on the nature of leaving ligand.

For example: $[Co(NH_3)_5X]^{2+}$ (I) and $[Co(CN)_5X]^{3-}$ (II) (X = halides) undergo substitution reaction of X^- by H_2O show different reaction rate. For (I), observed rate follows the order F < Cl < Br < I whereas (II) shows reverse order I < Br < Cl < F

$$[Co^{III}(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + X^- \text{ ....I}$$

$$[Co^{III}(CN)_5X]^{3-} + H_2O \rightarrow [Co(CN)_5H_2O]^{2-} + X^- \text{ ....II}$$

In complex (I), cobalt(III) is coordinated by amine which is hard ligand. In amine coordination sphere, Co^{III} becomes hard. So, it is expected that Co^{III} binds tightly with F^- another hard ligand. Therefore, expected reaction rate will be in order of F < Cl < Br < I.

In case of complex (II), cobalt(III) is coordinated by soft ligand CN^-, a π-acid. In this CN^- coordination atmosphere, Co^{III} becomes soft and it bounds soft I^- more strongly than hard F^-. So, expected rate substitution reaction will be the order of I < Br < Cl < F.

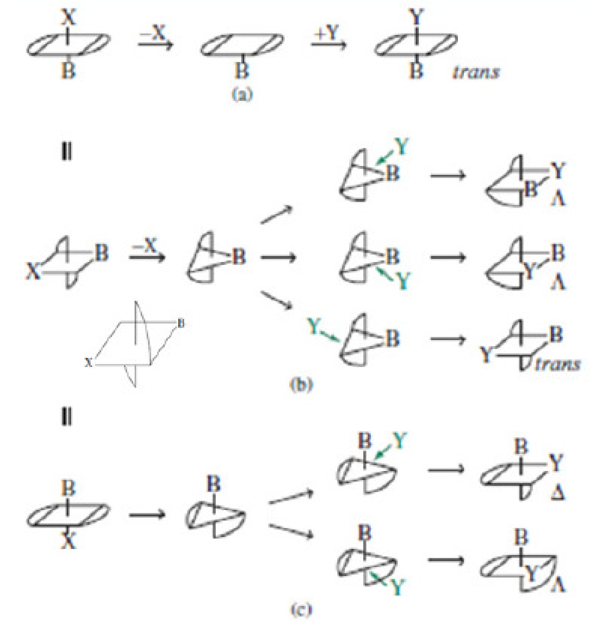
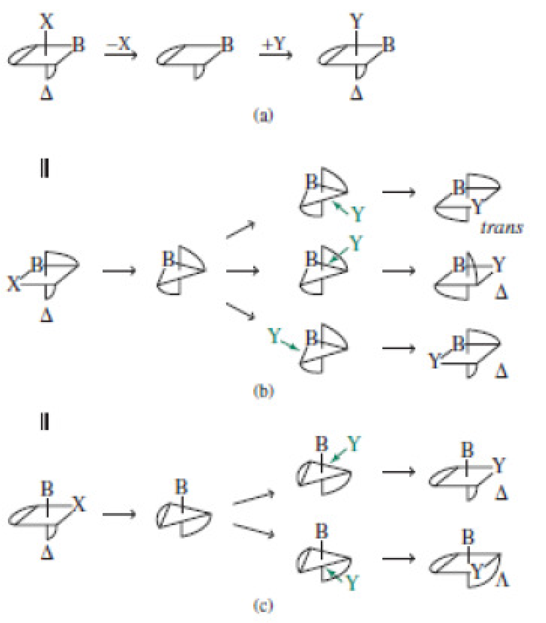
That means the nature or rate of substitution is guided by symbiotic phenomenon.

(ii) $[Co^{III}(NH_3)_5X]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5H_2O]^{3+} + X^-$. For this complex, the rate of substitution increases with X^- in the following order: $OH^- < N_3^- \sim NCS^- < MeCO_2^- < Cl^- < Br^- < I^- < NO_3^-$. This trend correlates with the M-X bond strength that means the stronger the bond, the slower the rate. The observation is predicted that the rate-determining step involving bond breaking in a dissociative step.

Stereochemistry substitution reaction:

Substitution reactions in octahedral complex generally involved D or I_d pathways. In dissociative mechanism involves a five coordinate species have either square pyramidal or trigonal bipyramidal geometry.

It was experimentally found that stereochemistry of substitution of Co(III) complex is independent of leaving group but depends on the structure of the intermediate. For example, starting with cis-$[Co(en)_2BX]^+$, it is seen that a square pyramidal intermediate leads to retention of stereochemistry but with trigonal bipyramidal intermediate, the entering group can attack at one of three positions between pairs of ligands in the equatorial plane that results mixture of cis and trans products in an approximately 2:1 ratio. That means hydrolysis of Co(III) octahedral complex occur with different extent of rearrangement.

trans-[M(LL)$_2$BX]	*cis*-[M(LL)$_2$BX]
	
(a) Square-pyramidal intermediate (retention of configuration). (b) Trigonal-bipyramidal intermediate a racemic mixture of *cis* isomers (Λ and Δ) and trans form [only Λ cis-isomers is shown] (c) Less likely trigonal-bipyramidal intermediate (two possible products).	(a) Square-pyramidal intermediate (retention of configuration). (b) Trigonal-bipyramidal intermediate. (c) Unlikely trigonal bipyramidal intermediate.

cis-$[CoX(en)_2Y]^+ + H_2O \rightarrow [Co(OH_2)(en)_2Y]^{2+} + X^-$			*trans*-$[CoX(en)_2Y]^+ + H_2O \rightarrow [Co(OH_2)(en)_2Y]^{2+} + X^-$		
Y^-	X^-	% of *cis*-product[†]	Y^-	X^-	% of *trans*-product[‡]
$[OH]^-$	Cl^-	84	$[OH]^-$	Cl^-	30
$[OH]^-$	Br^-	85	$[OH]^-$	Br^-	29
Cl^-	Cl^-	75	Cl^-	Cl^-	74
Br^-	Br^-	73.5	Br^-	Br^-	84.5
$[N_3]^-$	Cl^-	86	$[N_3]^-$	Cl^-	91
$[N_3]^-$	Br^-	85	$[N_3]^-$	Br^-	91
$[NO_2]^-$	Cl^-	100	$[NO_2]^-$	Cl^-	100
$[NO_2]^-$	Br^-	100	$[NO_2]^-$	Br^-	100
$[NCS]^-$	Cl^-	100	$[NCS]^-$	Cl^-	58.5
$[NCS]^-$	Br^-	100	$[NCS]^-$	Br^-	57

[†] Remaining % is *trans*-product.
[‡] Remaining % is *cis*-product.
[Data: W.G. Jackson and A.M. Sargeson (1978) *Inorg. Chem.*, vol. 17, p. 1348; W.G. Jackson (1986) in *The Stereochemistry of Organometallic and Inorganic Compounds*, ed. I. Bernal, Elsevier, Amsterdam, vol. 1, Chapter 4, p. 255.]

Base catalyzed hydrolysis:

$[Co(NH_3)_5Cl]^{2+}$ undergoes base catalysed hydrolysis reaction generates $[Co(NH_3)_5(OH)]^{2+}$.

$$\text{Rate equation is, rate} = k_B[\{Co(NH_3)_5Cl\}^{2+}]\,[OH^-]$$

Apparently, it was thought that the process proceeds through S_N^2 process where OH^- acts as nucleophile. Therefore, it is right to expect the rate of the substitution will be faster with strong nucleophile CN^-. But, fact that rate is not increased. So, nucleophilicity is not the determining factor.

Same experimental result was obtained with OOH^- which is stronger nucleophile than OH^- but weaker base. Again, $[Co(CN)_5Cl]^{3-}$ does not undergoes base hydrolysis with OH^-.

Therefore, it can be concluded that substrate must have at least one acidic hydrogen to undergo base hydrolysis reaction.

Mechanism:

(i) Rapid and reversible deprotonation of a coordinated ammonia molecule.

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4(NH_2)X]^+ + H_2O$$

(ii) Slow, rate determining loss of X^- from the amido complex, which is the conjugate base of the starting complex.

$$[Co(NH_3)_4(NH_2)X]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4(NH_2)]^{2+} + X^-$$

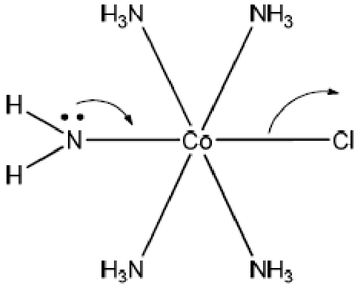
(iii) The five coordinate amido complex now readily captures a water molecule and finally intramolecular H-transfer between basic NH_2^- and H_2O.

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_4(NH_2)(H_2O)]^{2+} + X^-$$

$$[Co(NH_3)_4(NH_2)(H_2O)]^{2+} \longrightarrow [Co(NH_3)_5(OH)]^{2+}$$

This mechanism is said to be S_N1CB (substitution, nucleophilic, Unimolecular conjugate base) or DCB (dissociative conjugate base).

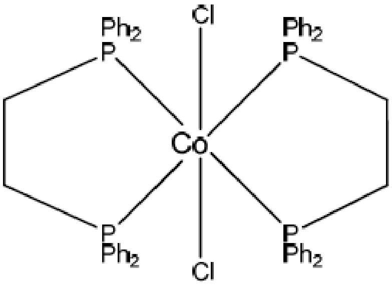
The conjugate base presumably loses the X^- ion more easily owing to electron donation from NH_2 group and consequently weakening the Co^{III}-X bond.



Evidence in favour of mechanism:

(i) If the complex does not have any proton then base hydrolysis is not observed. For example, $[Co(CN)_5Cl]^{3-}$ does not undergo hydrolysis in presence of OH^-.

One can say that due high negative charge density the complex $[Co(CN)_5Cl]^{3-}$, approach of the nucleophile OH^- is hindered to some extent. But the complex $[Co(Ph_2PCH_2CH_2PPh_2)_2Cl_2]^+$ also has no catalytic effect. So, charge density is not the controlling factor, presence of acidic hydrogen is the primary condition.



(ii) Since the first step of the mechanism is reversible acid-base reaction, then if we use D_2O as solvent, deuterium (D) may be incorporate in NH_3. Actually, this has been observed.

(iii) The value of $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ of these kind of reaction was found in the range +(43 – 19) ml mol^{-1} and +(160 - 80) $JK^{-1}mol^{-1}$ respectively. This data also supports dissociation mechanism.

(iv) Base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ in the presence of N_3^-, a competing nucleophile, produces $[Co(NH_3)_5(OH)]^{2+}$ and $[Co(NH_3)_5(N_3)]^{2+}$ in relative proportions that are independent of the concentration of OH^-, at a fixed concentration of N_3^-. This result is consistent with the facts that in the hydrolysis reaction, the nucleophile is H_2O and that OH^- acts as a base.

(v) Base hydrolysis of $[Co(NH_3)_5X]^{2+}$ ($X = Cl, Br, NO_3$) with a fixed concentration of OH^- is carried out in a mixture of H_2O and H_2O^*, it is found that the ratio of $[Co(NH_3)_5(OH)]^{2+}$ to $[Co(NH_3)_5(^*OH)]^{2+}$ is constant and independent of X^-. This provides strong evidence that the entering group is H_2O, and not OH^-, at least in the cases of the leaving groups being Cl^-, Br^- and NO_3^-.

Acid catalysed hydrolysis

Through Generation of better leaving group:

$[Co(en)_2F_2]^+$ is hydrolysed in slower rate but in presence of aqueous acid rate become fast. The observation can be explained through formation of good leaving group HF instead of F.

$$\begin{tikzcd}
{[Co(en)_2F_2]^+} \arrow[r, "H_2O", "slow"'] \arrow[d, shift left, "H^+"] & {[Co(en)_2(H_2O)F]^{2+}} \\
{[Co(en)_2(HF)F]^{2+}} \arrow[u, shift left] \arrow[r, "-HF", "fast"'] & {[Co(en)_2F]^{2+}} \arrow[u, "H_2O"']
\end{tikzcd}$$

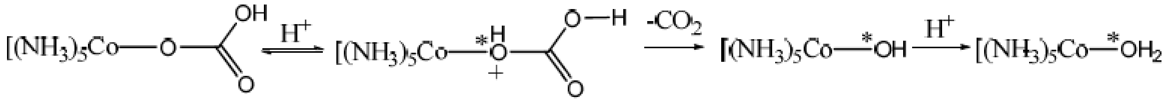
Interestingly, $[Co(en)_2I_2]^+$ does not show catalytic reaction in aqueous acidic medium. It can be explained considering the hard-soft principle. H^+ is hard can combine strongly with hard F^- but not with soft I^-. But, in presence of Hg^{2+}, $[Co(en)_2I_2]^+$ undergoes catalyzed hydrolysis.

$$[Co(en)_2I_2]^+ \xrightleftharpoons{Hg^{2+}} [Co(en)_2(HgI)I]^{2+} \xrightarrow[\text{fast}]{-HgI/+H_2O} [Co(en)_2(H_2O)I]^{2+}$$

(ii) $[Co(NH_3)_5(HCO_3)]^{2+}$ shows slower rate of hydrolysis in H_2O but faster rate in aqueous acid.

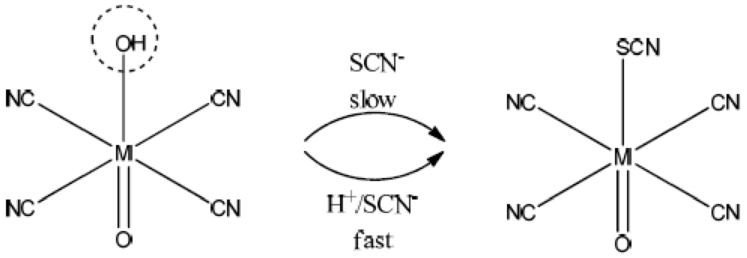
$$\begin{tikzcd}
{[Co(NH_3)_5(HCO_3)]^{2+}} \arrow[r, bend left, "H_2O \\ slow"] \arrow[r, bend right, "H^+/H_2O \\ fast"'] & {[Co(NH_3)_5(H_2O)]^{3+}}
\end{tikzcd}$$

Mechanism:



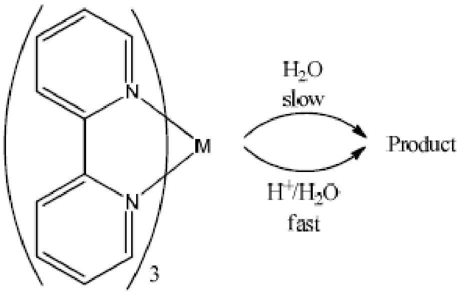
Since, isotopic oxygen retain its position so, reaction does not involve any metal-ligand bond breaking.

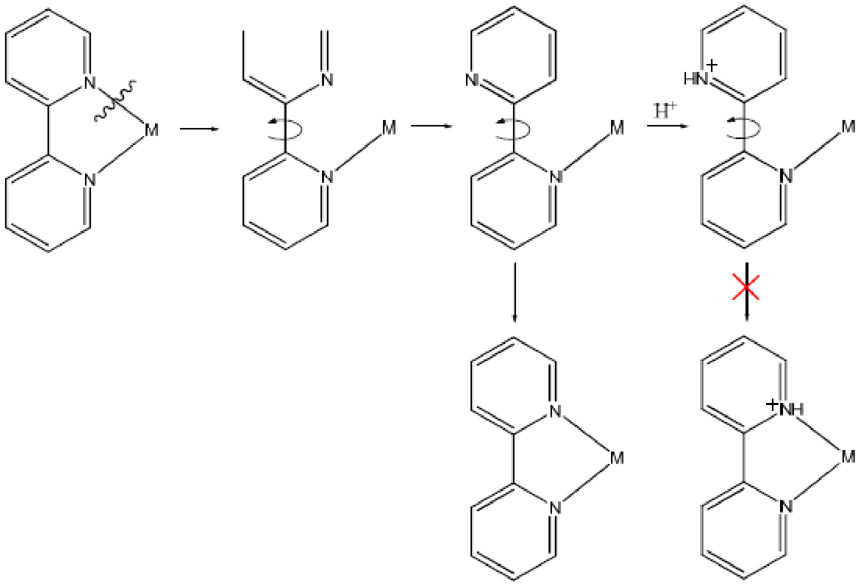
(iii)



In presence of aqueous acid, good leaving group H_2O is generates and rate becomes faster.

(iii)





In aqueous medium, pyridine-N remains bonding distance to the metal. Therefore, further formation of bond has higher probability. So, the attacking of H_2O as nucleophile becomes hindered. But acid medium, pyridine-N becomes protonated that deny any chances of further attacking pyridine-N to metal centre. Now, H_2O can attack to the metal centre easily.

This mechanism is further supported by the reaction below: Here, phenanthroline-N will present always bonding distance to metal because no free rotation is accessible and aquation will be very difficult even in acid medium.