

# **Electron Transfer Reaction in Oh Complexes**

**M. Sc. 402 - I**

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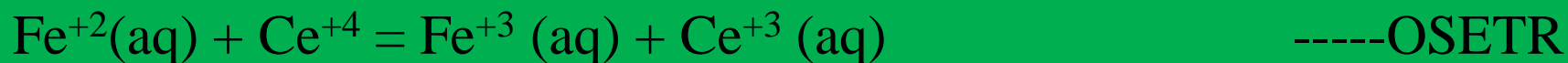
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# Electron-Transfer reaction(ETR)

## Redox reaction

Change in O.N. by transfer of electron  
from one atom to other atom.

ETR is the reaction in which transfer  
of e from one complex to other  
or within the complex



## **Types of ETR in Oh complexes.**

**In 1950 Taube identified two types of electron transfer reaction for metal complexes & proposed mechanism for these type of reaction known as**

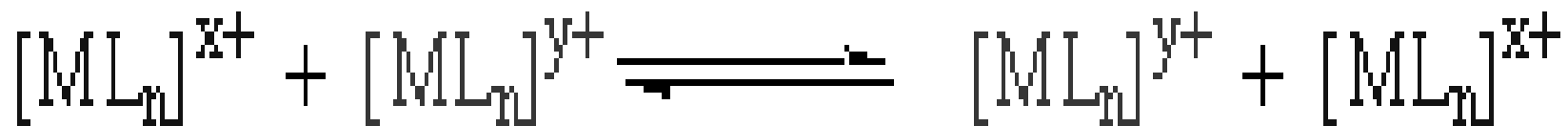
**(A) Outer sphere Electron Transfer Reaction (OSETR)**

**(A) Inner Sphere Electron Transfer Reaction (ISETR)**

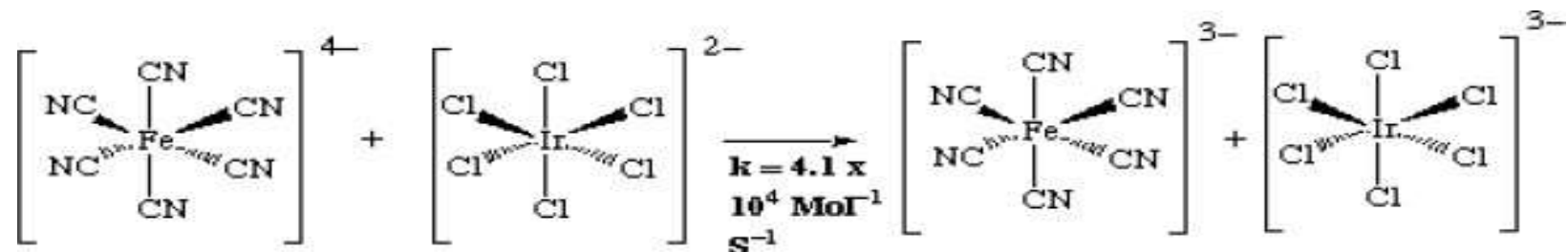
**We have to discuss mechanism of both type of reaction one by one**

## **Outer Sphere Electron Transfer Reaction (OSETR)**

It consists No substitution of ligand/No net change in reaction/it is out of change of ligands in sphere. It consists no sharing of ligand. It is out of covalent linkage between the reactants.



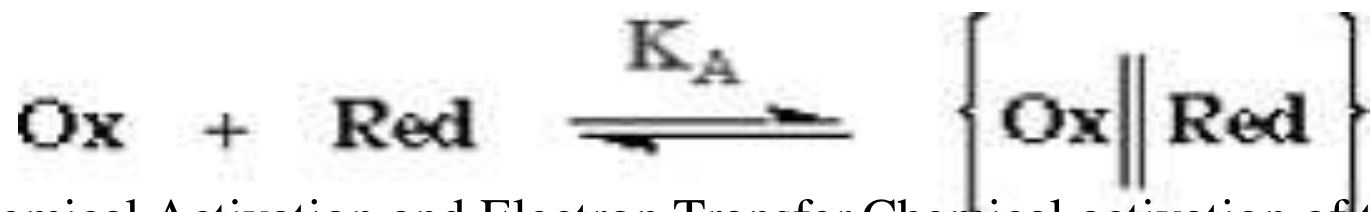
For examples.



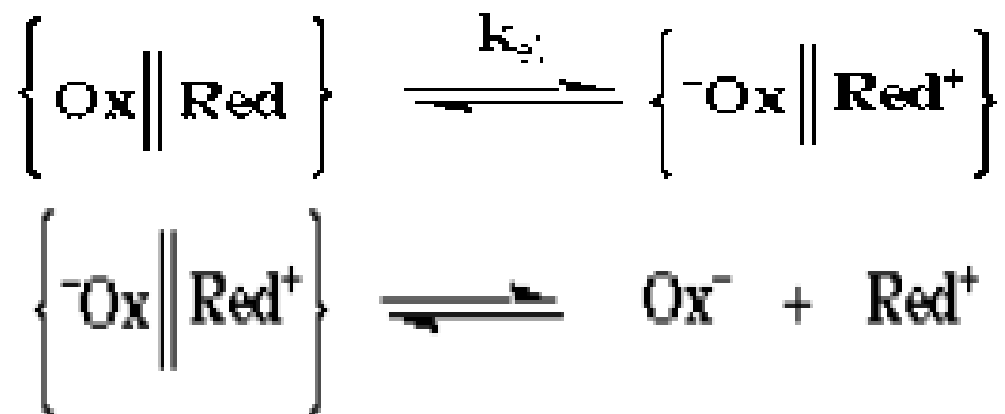
## Mechanism

Mechanism of this OSETR involves transfer of electron from the reductant to the oxidant, with the coordination shells or spheres of each staying intact. i.e. One reactant becomes involved with outer sphere or second coordination sphere of the other reactant. Such reactions are observed in electron-transfer reactions of substitutionally inert complexes. It is out of net chemical change. It is neither breaking of bond nor formation of bond in complexes.

**Step 1.**Formation of the Precursor Complex.This step is always considered to be fast,



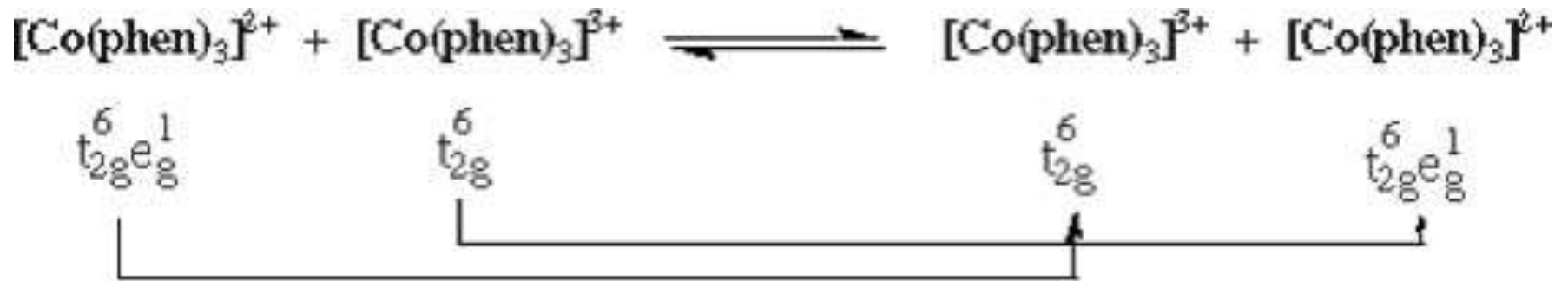
**Step 2.**Chemical Activation and Electron Transfer.Chemical activation of the precursor and electron transfer and relaxation of the successor complex. Dissociation to the separated products.



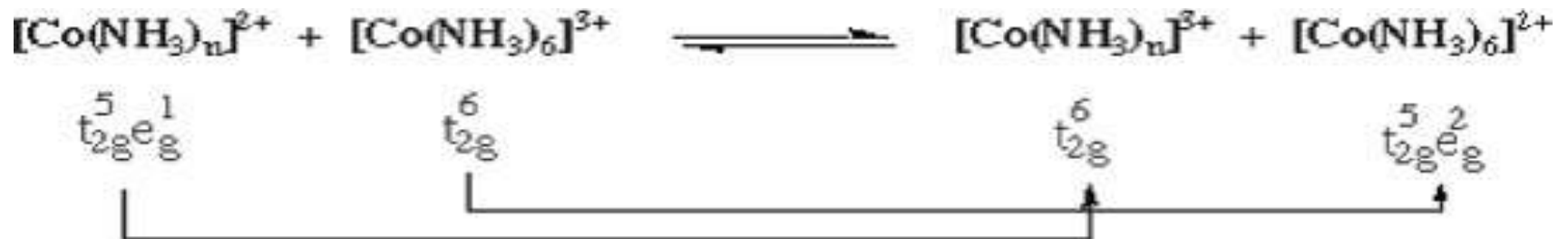
Here  $k_{\text{obs}} = K_A k_{\text{el}}$ .

An outer sphere electron transfer rate of  $1.1 \text{ M}^{-1} \text{ sec}^{-1}$ , simply requires the transfer of electron

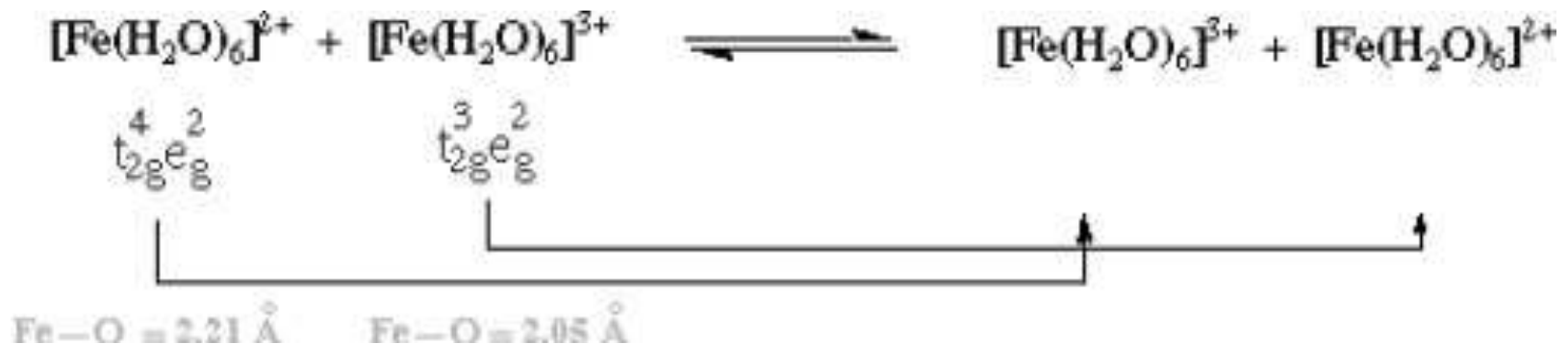
from  $e_g$  orbital of one Co to the other.



The reaction is very slow  $k = 10^{-9} \text{ M}^{-1} \text{ sec}^{-1}$  requires a change of spin multiplicity as well.



In addition the oxidant and reductant must structurally reorganise themselves before electron transfer so that the energies of their transition states are equal.

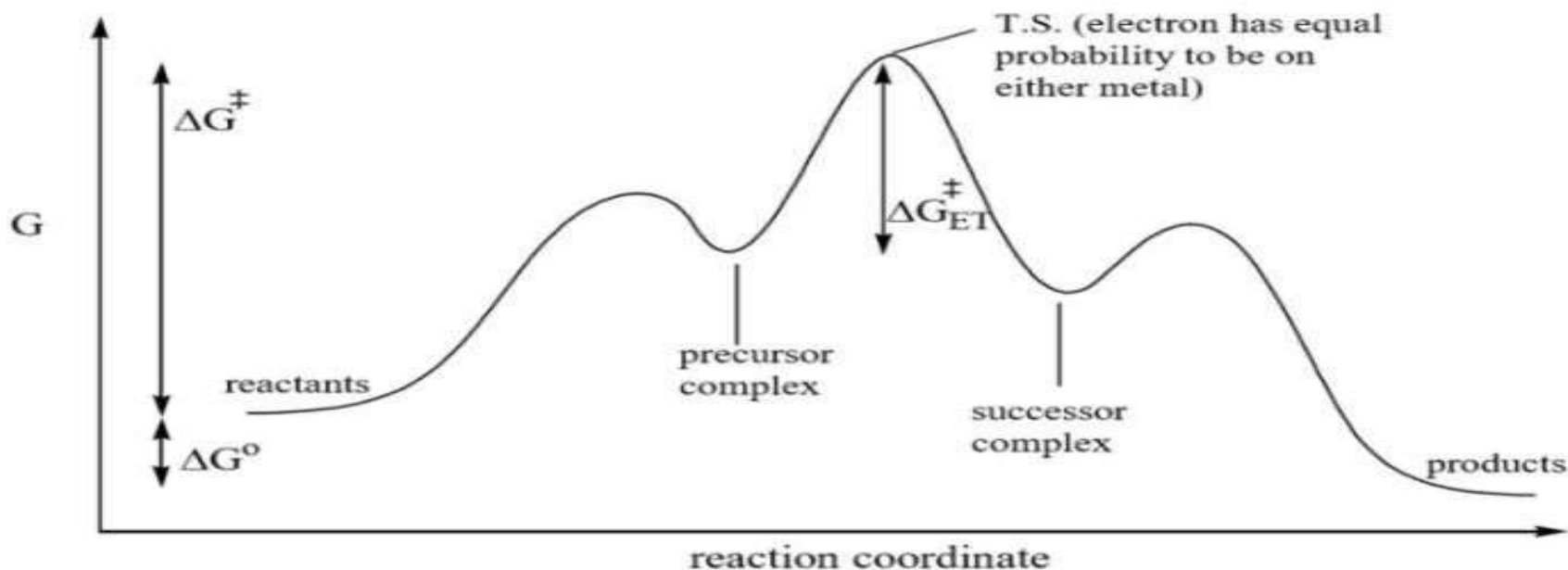


## Marcus-Hush equation $k_{12} = (k_{11} k_{22} K_{12} f_{12})$

Where  $k$  = rate constants,  $K_{12}$  = equilibrium constant for cross-reaction,  $\log f = (\log K_{12})^2 / 4 \log k_{11} k_{22} / Z^2$

$Z$  = effective collision frequency in solution

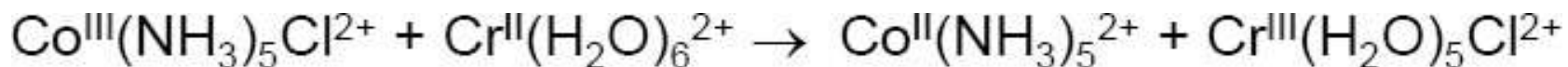
If the value of  $k_{12}$  calculated from the Marcus-Hush equation agrees with the experimental value, this provides strong evidence that the cross-reaction proceeds by an outer-sphere mechanism. If the Marcus-Hush equation is not fully filled, this indicates that another mechanism (e.g. inner-sphere mechanism) is probably operative.



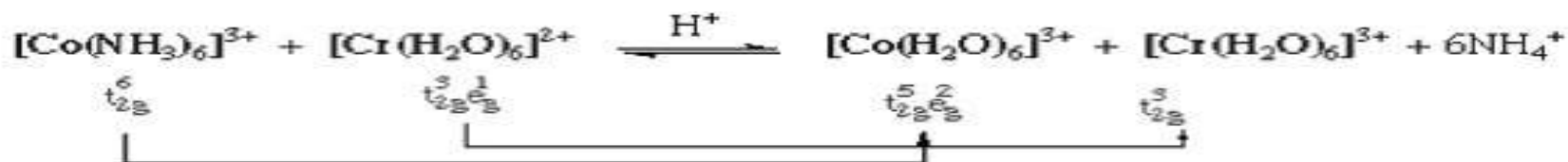
From thermodynamics, Driving force  $\Delta G^0 = -nF\Delta E^0$

# Inner Sphere Electron Transfer (ISETR)

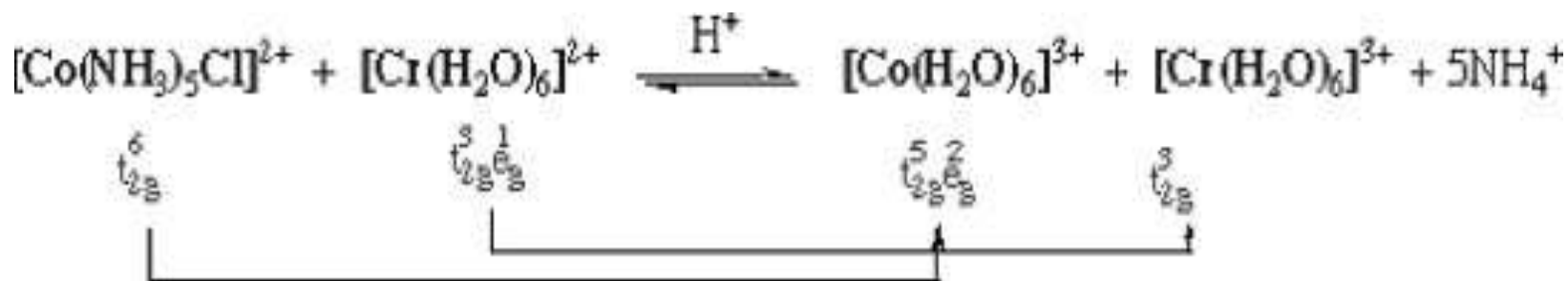
An inner sphere mechanism is one in which the reactant and oxidant share a ligand in their inner or primary coordination spheres the electron being transferred across a bridging group. In an inner-sphere mechanism, electron transfer occurs via a **covalently bound bridging ligand**. It is net change in reaction & it involves substitution one or more ligand.



Reduction of hexa amminecobalt(<sup>3+</sup>) by hexa aquochromium(<sup>2+</sup>) occurs slowly ( $k = 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$ ) by an outer sphere mechanism.



However, if one ammonia ligand on Co(III) is substituted by Cl<sup>-</sup>, reaction now occurs with a substantially greater rate ( $k = 6 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ )

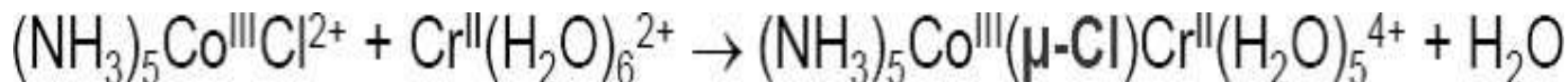




One reactant (usually the oxidant) possesses at least one ligand capable of binding simultaneously to two metal ions. The other reactant is substitutionally labile; i.e. one ligand must be replaced by the bridging ligand. Ligand transfer is not a requirement for inner sphere mechanism.

### **Steps and Rate Expression for the Inner Sphere Mechanism**

Formation of a precursor complex (bridge formation)



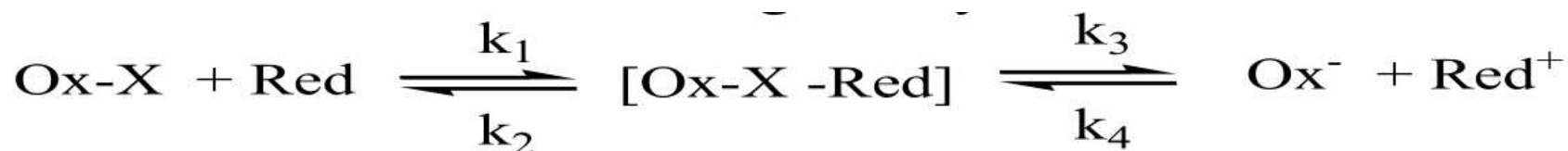
Activation of the precursor, and electron transfer via bridge



Dissociation to the separated products



# The overall reaction can be given by



$$k_{\text{obs}} = \frac{k_1 k_3}{k_2 + k_3} [\text{Ox-X}] [\text{Red}]$$

$k_1$  is rate limiting, formation of the precursor complex (usually substitution of the bridging ligand for  $\text{H}_2\text{O}$  on the Red complex).  $k_3$  is rate determining, electron transfer within the complex, or fission of the successor complex. Both extremes give 2 order kinetics. Most inner-sphere processes exhibit second order kinetics. Any of the three steps (bridge formation, electron transfer, bridge cleavage) can be rate-determining.

If the reaction is carried out in the presence of free  $^*\text{Cl}$ , labelled Cl is not incorporated into the product complex. The transferred Cl must have been bound to both metal centres during the reaction.

Common bridging ligands in inner-sphere mechanisms: halides,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{NCS}^-$ .

## Isomerization And Racemization Of Octahedral Complexes

Formation of isomers or racemers is called isomerization or racemization in Oh complex.

Tris-chelate complexes exist in enantiomeric configurations L and D about the metal atom and when the chelating ligand is unsymmetrical.

There are also geometrical isomers, cis and trans. Each geometrical isomer exists in enantiomeric forms.

So there are four different molecules.

In the case of tris complexes with symmetrical ligands, the process of inversion (inter conversion of enantiomers) is of considerable interest. When the metal ions are of the inert type, it is possible to resolve the complex; then the process of racemization can be followed by measurement of optical rotation as a function of time. Possible paths of racemization fall into two broad classes, those without bond rupture and those with bond rupture.

There are two pathways without bond rupture that have been widely discussed. One is the trigonal, or Bailar twist and the other is rhombic, or Ray – Dutt Twist.

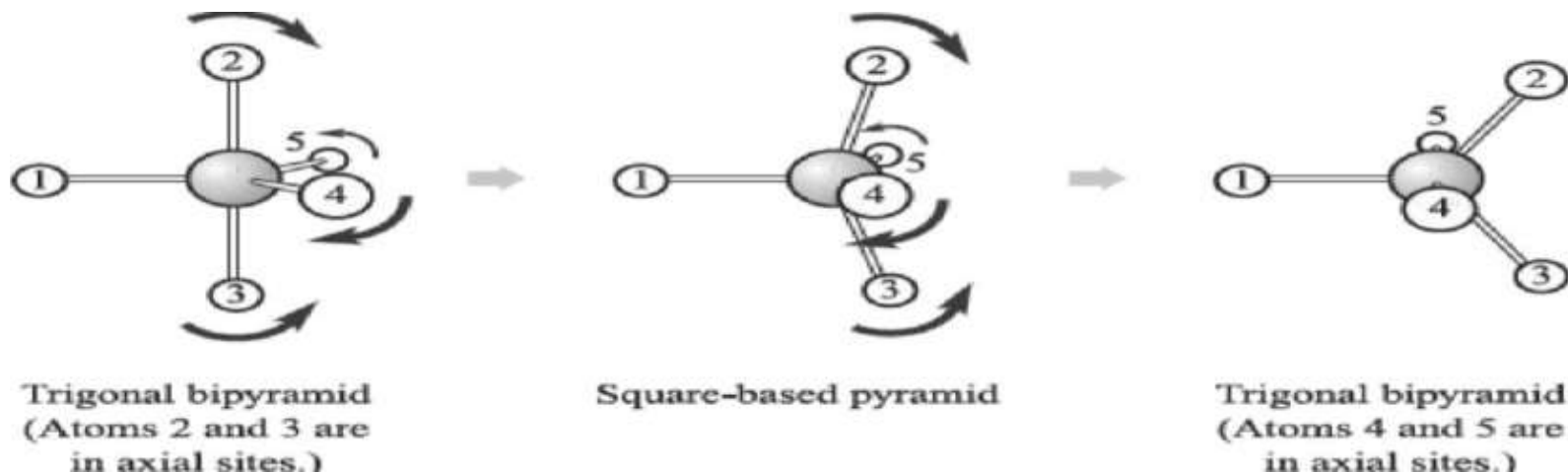
Twist processes are of course, not confined to chelate complexes. It has already been noted that some cis –  $M(CO)_4(PR_3)_2$  complexes are believed to isomerize in this way.

Let us consider some of the data and deductions for the system  $Co[CH_3COCHCOCH(CH_3)_2]_3$  measured in  $C_6H_5Cl$ . It was found that both the isomerization and the racemization are intra molecular processes, which occur at approximately the same rate and with activation energies that are identical within experimental errors. It thus appears likely that the two processes have the same transition state. This excludes the twist mechanism as the principal pathway for racemization.

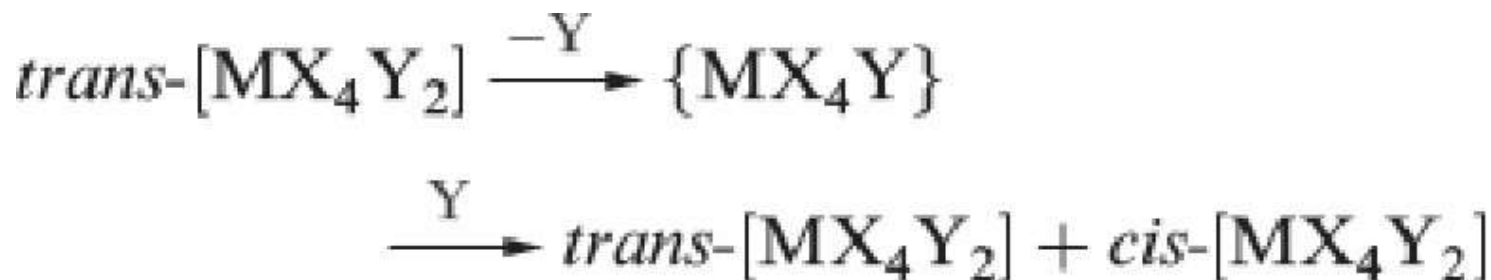
Moreover, it was found that isomerization occurs mainly with inversion of configuration. This imposes a considerable restriction on the acceptable pathways. Detailed consideration of the stereo chemical consequences of the various dissociative pathways, and combinations thereof, leads to the conclusion that for this system the major pathway is through a *tdp* intermediate with the dangling ligand in an axial position.

Evidence for the trigonal twist mechanism has been obtained in a few complexes in which the size of the ligand is small, thus causing the ground state configuration to have a small twist angle. A twist Mechanism is preferred in these cases because the structure is distorted away from an octahedral configuration of sulfur atoms towards a trigonal prismatic configuration. Thus the transition state, which is trigonal prismatic, is probably more energetically accessible than it would be if the complex had an essentially regular octahedral ground configuration. The three possible modes of intramolecular racemization of a trischelate complex.

**Example :** Octahedron is stereo chemically rigid, loss of a ligand gives a 5-coordinate species which can undergo Berry pseudorotation.

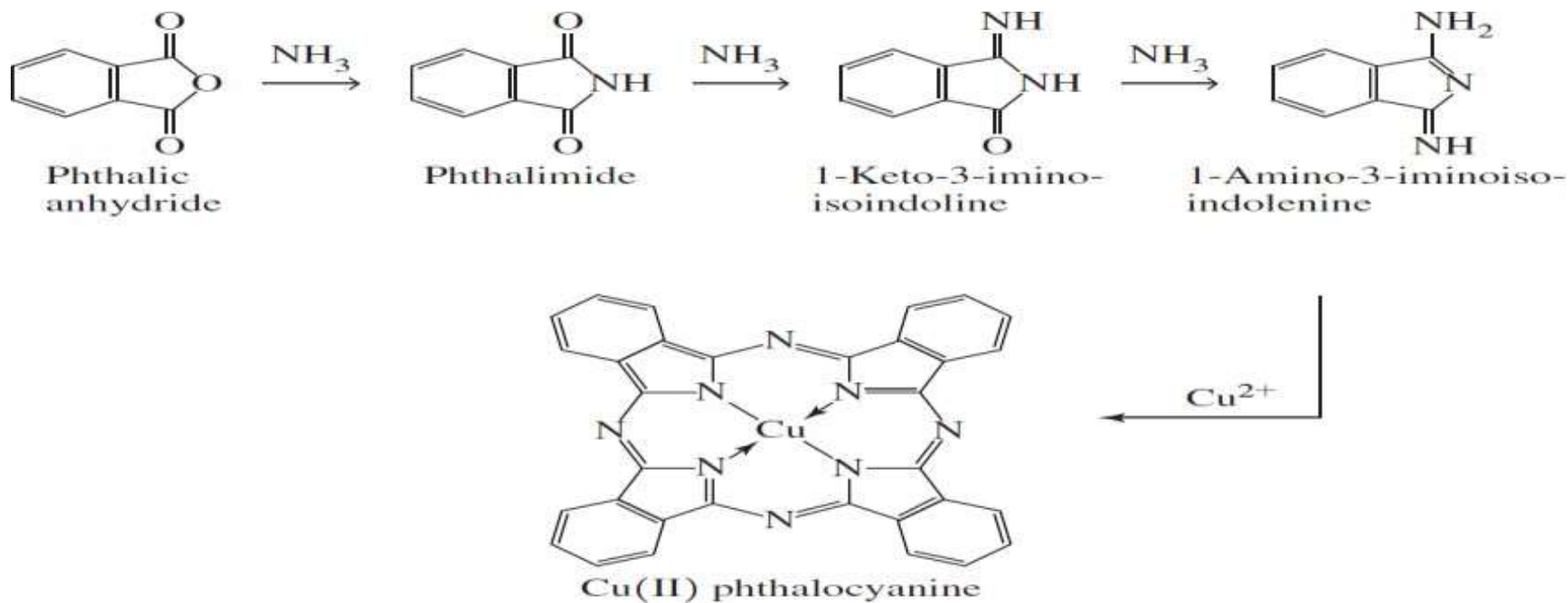


If the lifetime of the intermediate is long enough, it provides a mechanism for isomerization,



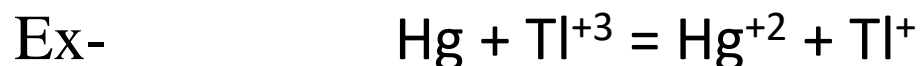
# Template Effect and Synthesis of Macrocyclic Ligands

Template reactions are those in which formation of a complex places the ligands in the correct geometry for reaction. One of the earliest was for the formation of phthalocyanines. Phthalic acid and ammonia first form phthalimide, then 1-keto-3-iminoisoindoline, and then 1-amino-3-iminoisoindolenine. The cyclization reaction then occurs, probably with the assistance of the metal ion, which holds the chelated reactants in position. This is confirmed by the lack of cyclization in the absence of the metals. The essential feature of these reactions is the formation of the cyclic compound by coordination to a metal ion.



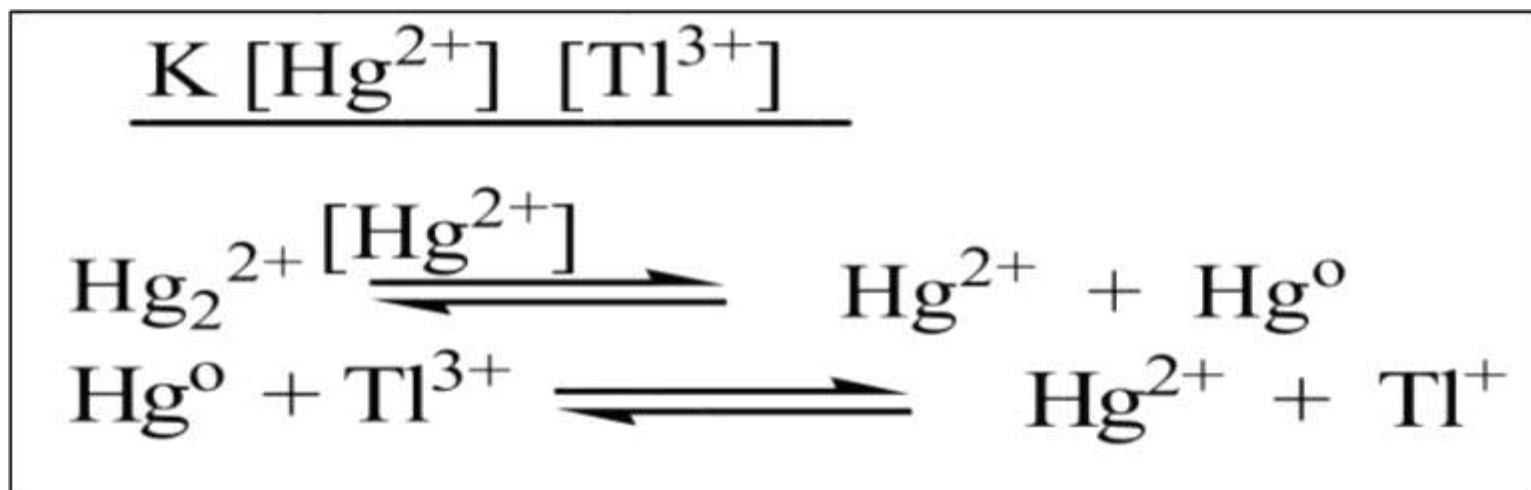
# Complementary and Non-Complementary Reactions

Reactions in which number of electrons gained by one species is equal to number of electrons lost by the other are called Complementary reactions.



Here, two electron transfer occurs.

Two electron transfers have been suggested for the oxidation of  $\text{Hg}_2^{2+}$  by  $\text{Tl}^{3+}$  and for the  $\text{Tl}^{3+}$ . In the latter case, the formation of  $\text{Tl}^{2+}$  is also possible, but the rate law for the former reaction.

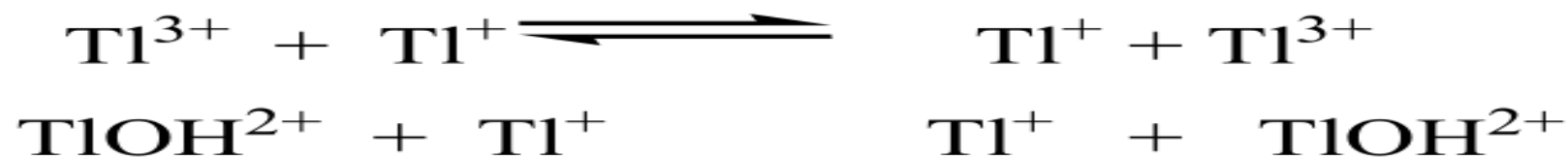




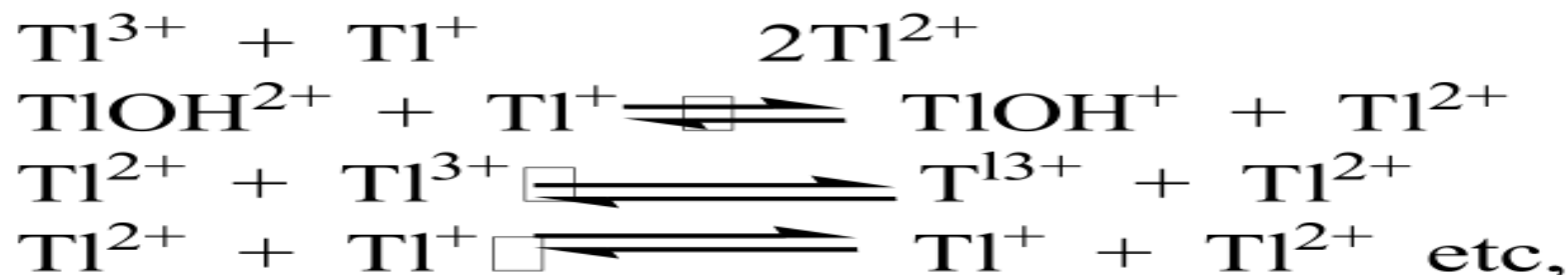
The exchange reaction of  $Tl^+ - Tl^{3+}$  which has been extensively studied is considered. Nevertheless, there is still not agreement as to whether the reaction occurs in a single two – electron transfer step or in a series of steps with unstable  $Tl^{2+}$  as an intermediate. The extreme sensitivity which  $Tl^{2+}$  shows that the exchange goes by this intermediate. The hydrolysis reaction,



introduces a pH dependence for the rate. The mechanism would be

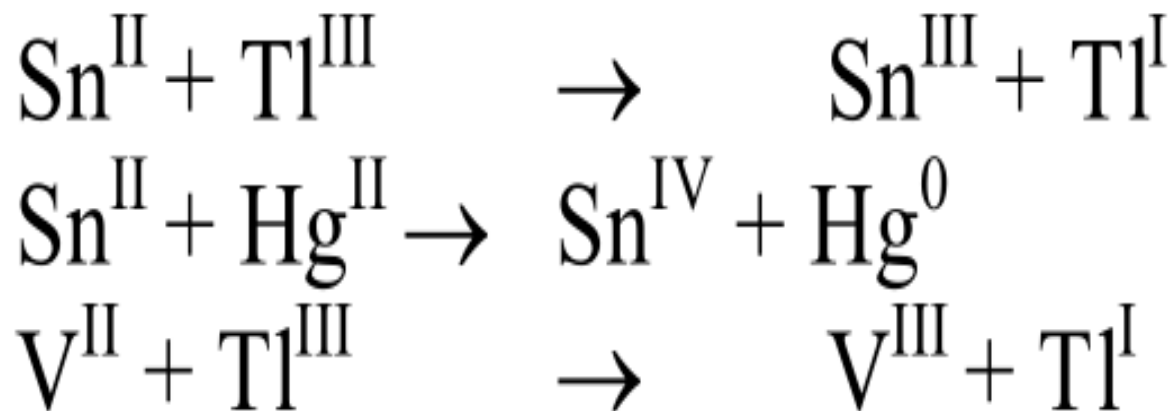


or



In the presence of other anions more complicated rate laws are found, indicating that two – electron transfers occurs through various  $\text{Tl}^{3+}$  complexes.

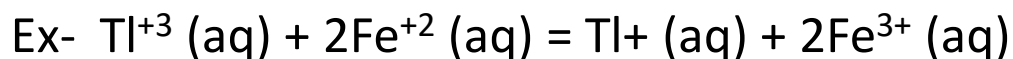
A number of other redox reactions also appear to proceed by two electron transfers, examples are,



All these reactions are complementary meaning that in the overall stoichiometry the oxidant gains and the reductant loses two electrons.

# Non – Complementary Reactions

Reactions in which the number of electrons gained by one ion of one species is not equal to the number lost by the other ion are called non-complementary reactions. In this reaction multistep mechanisms occurs,



since ternary activated complexes are not likely and are not supported by an experimental evidence. This, in turn, means that some relatively unstable intermediate must be generated. For eg, the overall reaction of  $\text{Fe}^{2+}$  with  $\text{Tl}^{3+}$  (eqn1) might have as its initial step either a one – electron transfer to generate  $\text{Fe}^{3+}$  and the unstable  $\text{Tl}^{2+}$  or a two – electron transfer to generate  $\text{Tl}^{+}$  and the unstable  $\text{Fe}^{4+}$ . It has been reported that the addition of  $\text{Fe}^{3+}$  reduces the rate of reaction, but the addition of  $\text{Tl}^{+}$  is without effect. This indicates that the mechanism would be that of eqn2 and 3.

