

Coordination compounds - Stability

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1 Labile and inert complexes

1.1 Labile complex

In these complexes, the rate of substitution of ligands is relatively high.

Example:

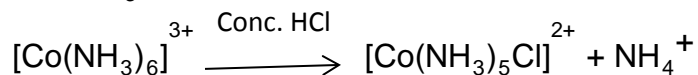
$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is labile. Its aqueous solution is blue in color. When concentrated hydrochloric acid is added to this solution, the blue solution immediately turns green giving $[\text{CuCl}_4]^{2-}$.

1.2 Inert complex

In this case, ligands are not exchanged easily. The rate of exchange is very slow.

Example:

$[\text{Co}(\text{NH}_3)_6]^{3+}$ reacts slowly. When this complex is treated with concentrated HCl, no reaction takes place. Only when it is heated with 6M HCl for many hours, one NH_3 is substituted by Cl^- .



1.3 Factors affecting the labile/inert nature of complexes

1. Size of the central metal ion

Smaller the size of the metal ion, greater will be the inertness because the ligands are held tightly by the metal ion.

2. Charge on the central metal ion

Greater the charge on the metal ion, greater will be the inertness of the complex.

3. d-electron configuration

If electrons are present in the antibonding e_g^* orbitals, the

complex will be labile because the ligands will be weakly bonded to the metal and hence can be substituted easily.

If the complex contains empty t_{2g} orbitals, then it will be labile because ligands can approach easily without much repulsion. In short, if the complex contains less than three d-electrons, it will be labile. Or, if one or more e_g electrons are present, it will be labile.

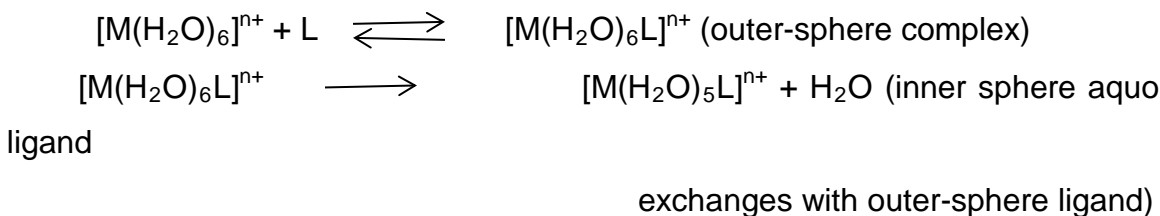
No. of d electrons & electron configuration	Nature		Example
d^0	Labile		$[\text{CaEDTA}]^{2-}$
$d^1; t_{2g}^1 e_g^0$	Labile		$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
$d^2; t_{2g}^2 e_g^0$	Labile		$[\text{V}(\text{phen})_3]^{3+}$
$d^3; t_{2g}^3 e_g^0$		Inert	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$
d^4 (high-spin); $t_{2g}^3 e_g^1$	Labile		$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
d^4 (low-spin); $t_{2g}^4 e_g^0$		Inert	$[\text{Cr}(\text{CN})_6]^{4-}$
d^5 (high-spin); $t_{2g}^3 e_g^2$	Labile		$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
d^5 (low-spin); $t_{2g}^5 e_g^0$		Inert	$[\text{Mn}(\text{CN})_6]^{4-}$
d^6 (high-spin); $t_{2g}^4 e_g^2$		Inert	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
d^6 (low-spin); $t_{2g}^6 e_g^0$		Inert	$[\text{Fe}(\text{CN})_6]^{4-}$
d^7, d^8, d^9, d^{10}	Labile		

1.4 Mechanisms

1. In an aquo complex, the rate of substitution of aquo ligand does not depend on the nature of the incoming ligand.
2. Exchange of aquo ligand by another ligand is always faster than the substitution of one ligand by another.

Explanation

The above observations suggest that the reaction should proceed in two steps.

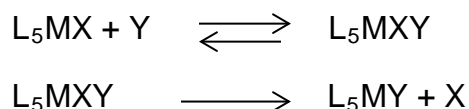


Of these two steps, the rate determining step mainly involves the breaking of M-OH₂ bond and the influence of the entering ligand is negligible.

1.4.1 Associative and dissociative mechanisms for ligand substitution reactions

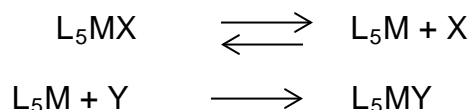
1.4.1.1 Associative mechanism

Here, the bond formation between the central metal ion and the entering ligand is important. This determines the magnitude of activation energy and hence the rate of reaction. The steps can be represented as follows:



1.4.1.2 Dissociative mechanism

In the first step, the already attached ligand to the metal breaks and in the second step, the new ligand forms a bond with the central metal ion. The steps are:

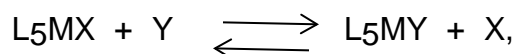


In this mechanism, the breaking of the bond between the metal and the already present ligand is important and the magnitude of activation energy depends on this step.

2 Substitution in octahedral complexes

2.1 Intimate and stoichiometric mechanisms

Let us consider the following reaction:



where X is the leaving group and Y is the entering

These reactions can be explained in two ways: (1) intimate mechanism and (ii) stoichiometric mechanism

Dissociative and associative activations are known as intimate mechanism. In dissociative activation, breaking of the bond between the metal and the leaving group is important and in associative activation, bond formation between the metal and the entering ligand is important.

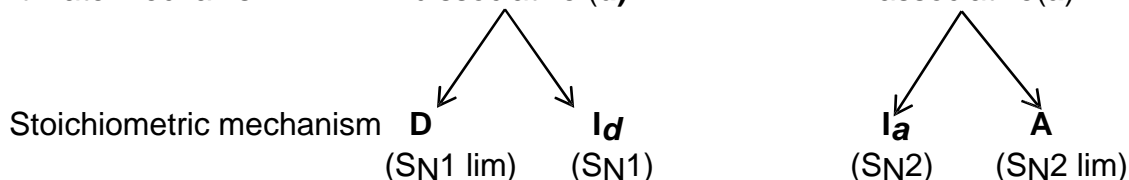
The sequence of elementary steps from reactants to products is called stoichiometric mechanism.

2.1.1 Relation between intimate and stoichiometric reaction mechanisms

Intimate mechanism

dissociative (d)

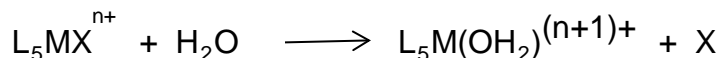
associative(a)



2.2 Intimate mechanism

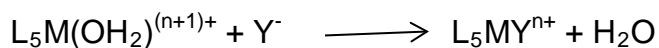
2.2.1 Aquation (acid hydrolysis) reaction

Here already existing ligand is substituted by aquo ligand.



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2.2.2 Anation reaction



2.3 Factors affecting these reactions

2.3.1 Nature of the entering or leaving group

Let us consider the complex, $[Co(NH_3)_5X]^{n+}$. The rates of aquation for this complex very much **depends on the nature of the leaving group, X**

As an example, for the complex, $[Co(NH_3)_5(NO_3)]^{2+}$, k is of the order of $10^{-5} s^{-1}$.

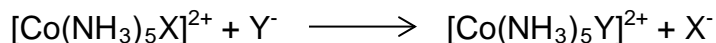
When I^- is present instead of NO_3^- , the rate decreases and is of the order of $10^{-6} s^{-1}$ for the complex, $[Co(NH_3)_5I]^{2+}$. Both NO_3^- and I^- are leaving groups. The

reaction slows down when the leaving group is I^- . In the case of the complex, $[Co(NH_3)_5F]$, the rate is the order of 10^{-8} . That is, the reaction further slows down. Thus it is proved that **M-X bond breaking is very much important in aquation reactions** than bond formation.

Anation reactions do not depend very much **on** the nature of the **entering group, Y^-** . Instead, it is very much dependent on the nature of the bond being broken. Experimental data show that the rate is of the order 10^{-6} for the different entering groups (Y^-), N_3^- , SO_4^{2-} , Cl^- or NCS^- clearly indicating that the rate is independent of the nature of the entering group.

Another important experimental support for this observation is that ligand exchange reactions do not take place directly but instead takes place through aquation and then anation.

Example:



In this reaction, X^- is not directly substituted by Y^- . In the first step, aquation takes place, that is, X^- is substituted by H_2O to give $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ and then anation reaction takes place in which H_2O is substituted by Y^- .

This indicates that the Co-X bond breaking is very much significant and then whatever species is present at a higher concentration will add in anation reaction. Thus, nature of Y^- is not important.

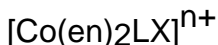
2.3.2 Steric effects of inert (non-leaving) ligands

When the non-leaving ligands are bulky, they will be crowding the central metal ion and hence, the incoming ligand will find it difficult to approach the central metal ion slowing down the rate of reaction taking place by associative mechanism. Instead, if the reaction takes place by dissociative mechanism, (that is, one ligand breaks first and then a new ligand approaches), the rate of the reaction will increase because the crowding around the metal ion is reduced.

2.3.3 Electronic effects of inert ligands

If the existing ligand is capable of π -donation to the metal and stabilize the transition state, the reaction will be fast. When a reaction takes place by dissociative mechanism, when a ligand leaves, the metal becomes electron deficient. If there is a *cis*-ligand and if it is capable of donating electrons by forming π -bond with the electron deficient metal, then it stabilizes the transition state by lowering the energy and hence the reaction takes place faster

Example:



If L is cis to the leaving group X, and if it is a good π -donor, the reaction is fast. For example, the rate of the reaction is of the order 10^{-3} s^{-1} in the case of *cis*- $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ and is of the order of 10^{-4} s^{-1} in the case of *trans*- $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$.

If the ligand is not capable of π -bonding but only a σ -donor such as NH_3 , then the reaction will be slow. For example, in the case of *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, the rate is of the order 10^{-4} s^{-1} and in the case of *cis*- $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$, the rate is of the order of 10^{-7} s^{-1} .

2.3.4 Effect of charge

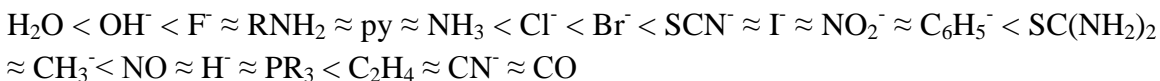
The increase in positive charge decreases the rate of reaction following a dissociative mechanism because the breaking the metal-ligand bond becomes difficult.

3 Substitution reactions in square planar complexes

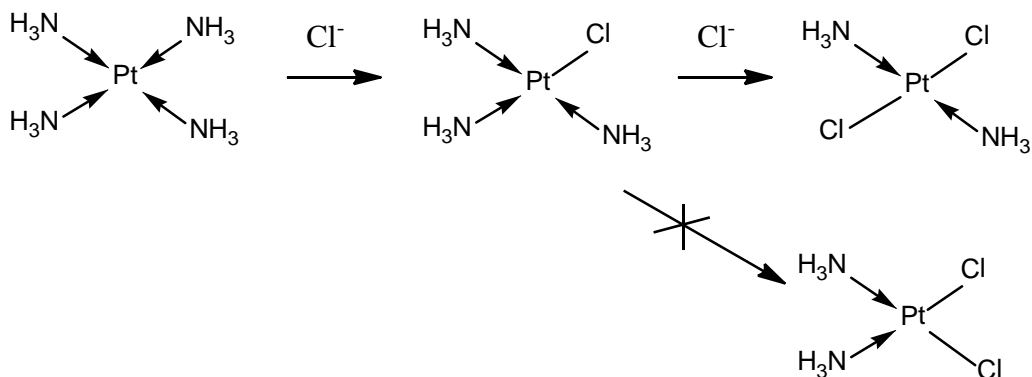
3.1 Ligand substitution reactions – Trans effect

Trans effect is the influence of a ligand on the substitution of another ligand trans to it. This is very much useful in the synthesis of square planar complexes.

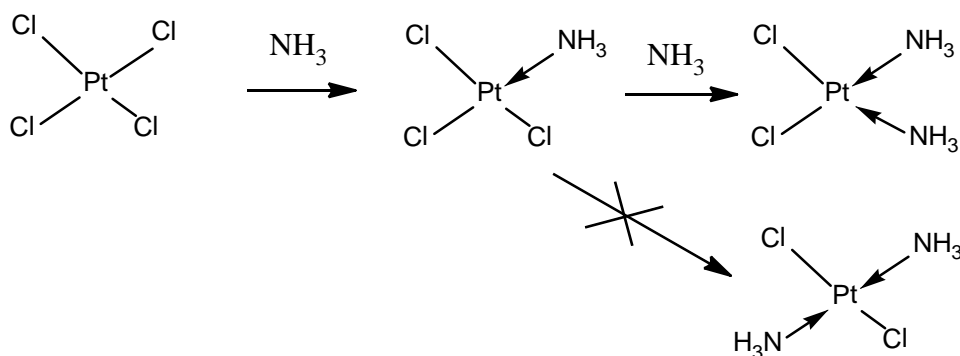
The ligands are arranged in the increasing order of trans effect as follows:



Example – Synthesis of isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$



Since Cl^- has a stronger trans effect than NH_3 , the second NH_3 goes to the position trans to Cl^- rather than trans to NH_3 .



3.2 Theories of trans effect

Trans effect can be explained based on polarization or σ -donor capacity.

According to polarization theory, a strong trans-directing ligand will be easily polarizable and forms an ionic bond with the metal. Then the dipole repels the ligand trans to it weakening the bond between the metal and the trans ligand.

Thus, this could explain why H^- and CH_3^- occupy high in the trans effect series

According to the second theory, a ligand which is a strong σ -donor, repels the metal – ligand bond trans to it and weakens it. A strong σ -donor will take maximum share of the metal σ -orbital and thus gives only a small share of the bond to the trans ligand.

In other words, strong trans directing ligands are those capable of forming strong back bonding (π -acceptors), for example, CO, CN^- , olefins etc. or strong σ -donors such as CH_3^- , H^- , PR_3 etc. Strong π -donors such as H_2O , OH^- , NH_2^- , etc. are weak in their trans directing properties.

3.3 Thermodynamic and kinetic stability

Stable and unstable are thermodynamic terms, while labile and inert are kinetic terms. As a rule of thumb, those complexes which react completely within about one minute at 25°C are considered labile and those complexes which take longer time than this to react are considered inert.

$[\text{Ni}(\text{CN})_4]^{2-}$ is thermodynamically stable but kinetically inert because it rapidly exchanges ligands.

$[\text{Co}(\text{NH}_3)_6]^{3+}$ is thermodynamically unstable but kinetically inert. We may expect the complex to decompose in presence of acid immediately because the complex is thermodynamically unstable.

The rate is of the order of 10^{25} for the decomposition in acidic solution. Hence, it is thermodynamically unstable. However, nothing happens to the complex when it is kept in acidic solution for several days.

While considering the stability of a complex, always the condition must be specified. That is, under what condition, the complex is stable or unstable must be specified such as acidic or basic condition, temperature, reactant etc.

A complex may be stable with respect a particular condition but with respect to another. In brief, a stable complex need not be inert and similarly, an unstable complex need not be labile.

4 References

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