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| Chemistry | Paper No. 3: Inorganic Chemistry-I (Stereochemistry, Metal-Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes) |
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## 1. Learning Outcomes

After learning and grasping the module, you will be able to know:

- Background of crystal field theory behind lability and inertness of the complexes
- Crystal field theory for the explanation of Inertness and lability of the complexes
- Crystal field activation energy and its applications

## 2. Background of Crystal Field Theory

Explanation provided by valence bond theory for lability and inertness of the complexes was incomplete and had limitations. So, a better explanation was needed which was provided by the crystal field theory.

Explanation given by crystal field theory was based on following observations:

**2.1** ***Geometry of intermediate of nucleophilic substitution reaction are different than that of reactant or product molecule***

Since, geometry of both reactant and intermediates different and therefore, crystal field splitting pattern for both will differ. As we know, rate depends on activation energy of the reaction and therefore rate can be correlated with the energy of transition state.

Unfortunately, transition state exists for that much small time that structure of reactant and transition state cannot be correlated. One of the factors that include activation energy of the reaction is crystal field activation energy, which is difference of crystal field stabilization energy of intermediate and that of reactant.

***2.2 In dissociative nucleophilic substitution reaction for octahedral complexes, intermediate is of square pyramidal in shape***

Dissociative nucleophilic substitution reaction involves two steps, in which a leaving ligand break first from the reactant to provide square pyramidal intermediate.

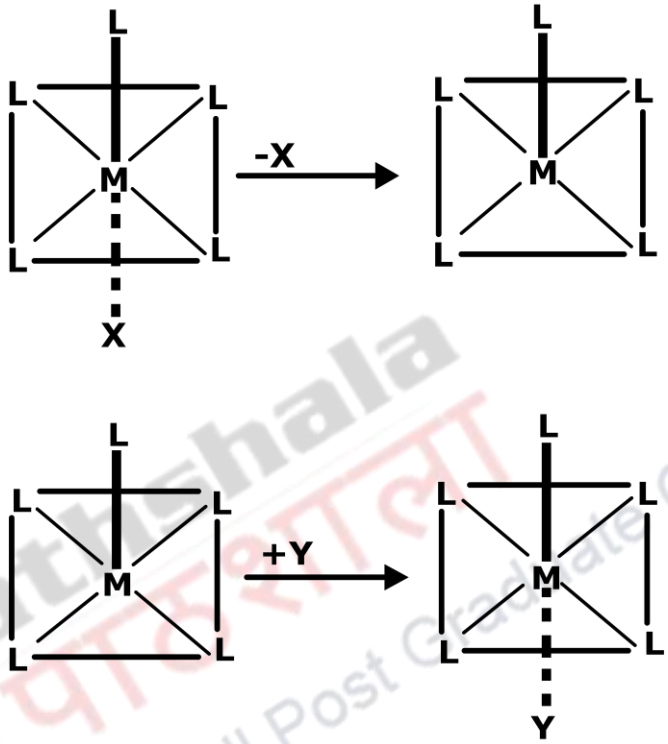


Figure 1: Pictorial diagram for the Dissociative nucleophilic Substitution reaction

***2.3 In associative nucleophilic substitution reaction for octahedral complexes, intermediate is of octahedral wedge shape***

Associative nucleophilic substitution reaction involves two steps, in which attacking ligand attach with the metal ion before detachment of leaving ligand. In the process octahedral wedge shaped intermediate use to form.

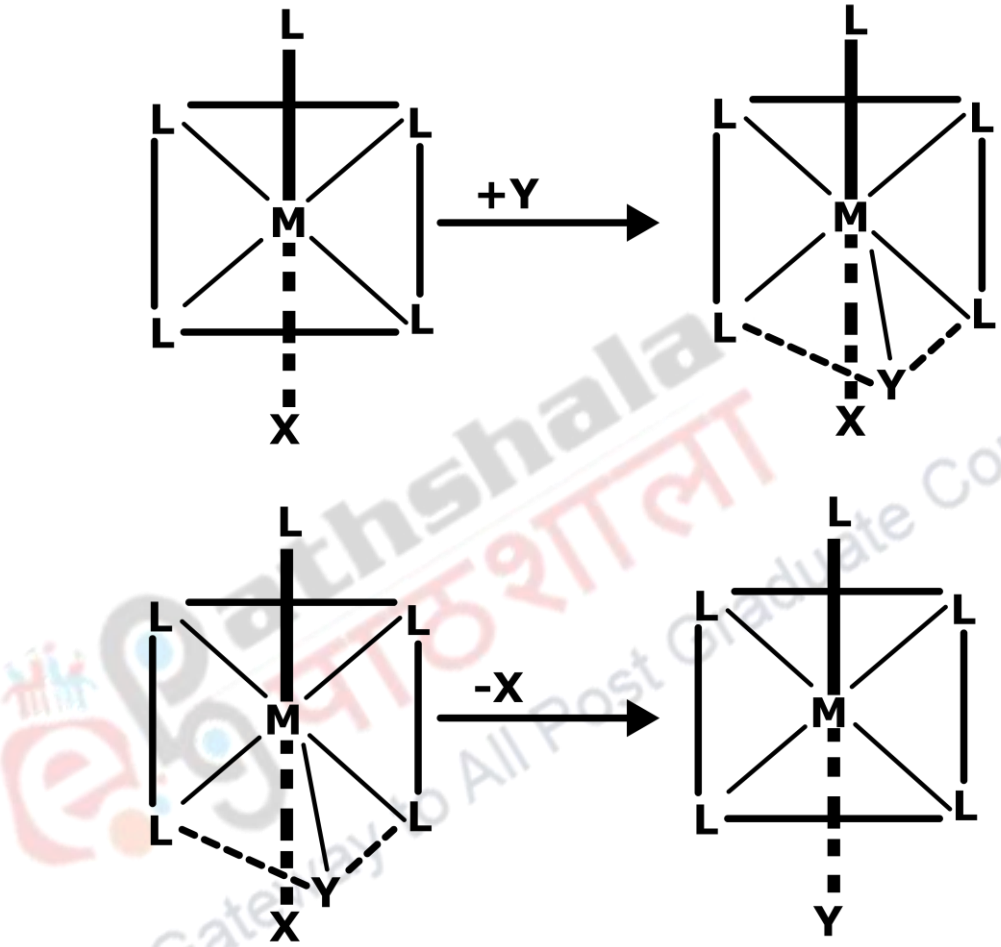


**Figure 2: Pictorial diagram for Associative nucleophilic substitution reaction**

***2.4 Crystal field activation energy can decide about feasibility of formation of intermediate***

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The difference of crystal field stabilization energy of intermediate and reactant is called crystal field activation energy. Crystal field activation energy is one of the important factor among the various that can decide activation barrier of the reaction. Since, activation barrier is directly related to rate of reaction, CFAE can be treated as a deciding factor behind lability and inertness of the complexes.

## 3. Explanation of Crystal Field Theory

For better understanding of theory behind lability and inertness, lets discuss Dissociative and associative nucleophilic substitution one by one:

### 3.1 *Dissociative Nucleophilic Substitution Reaction*

Figure 1, represent dissociative nucleophilic substitution that involve square pyramidal complex as an intermediate. Crystal field splitting pattern for octahedral (in right side of the diagram) and square pyramidal (in left side of the diagram) is shown below. For convenience $d^1$ system is shown here.

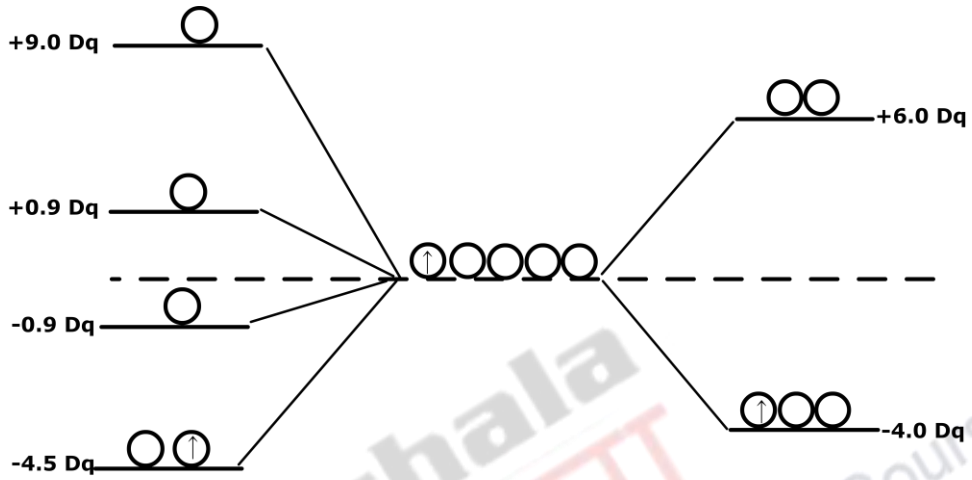


**Figure 3: Crystal field splitting pattern for octahedral (in right side) and square pyramidal (in left side)**

Now, on the basis of different factors that effect crystal field splitting energy, the formed complex may either be high spin or low spin. CFAE will decide about lability and inertness of the complexes. More negative the value of CFAE more will be the chances for formation of intermediate and therefore, more labile complex will be. The crystal field stabilization energy for octahedral and square pyramidal arrangement for high spin complex is summarized in Table 1, while Table 2 represent crystal field stabilization energy for a low spin complex.

**Table 1: Summarized table for lability and inertness of complexes undergoing $SN^1$ reaction in their high spin state**

| d electronic configuration | CFSE for $O_h$ (in Dq) | CFSE for S.P. (in Dq) | CFAE (in Dq) | Labile/ Inert |
|---|---|---|---|---|
| $d^1$ | -4.0 | -4.5 | -0.5 | Labile |
| $d^2$ | -8.0 | -9.0 | -1.0 | Labile |
| $d^3$ | -12.0 | -9.9 | +2.1 | Inert |
| $d^4$ | -6.0 | -9.0 | -3.0 | Labile |
| $d^5$ | 0 | 0 | 0 | Labile |
| $d^6$ | -4.0 | -4.5 | -0.5 | Labile |
| $d^7$ | -8.0 | -9.0 | -1.0 | Labile |
| $d^8$ | -12.0 | -9.9 | +2.1 | Inert |
| $d^9$ | -6.0 | -9.0 | -3.0 | Labile |
| $d^{10}$ | 0 | 0 | 0 | Labile |

**Table 2: Summarized table for lability and inertness of complexes undergoing $SN^1$ reaction in their low spin state**

| d electronic configuration | CFSE for $O_h$ (in Dq) | CFSE for S.P. (in Dq) | CFAE (in Dq) | Labile/ Inert |
|---|---|---|---|---|
| $d^1$ | -4.0 | -4.5 | -0.5 | Labile |
| $d^2$ | -8.0 | -9.0 | -1.0 | Labile |
| $d^3$ | -12.0 | -9.9 | +2.1 | Inert |
| $d^4$ | -16.0 | -14.4 | +1.6 | Inert |
| $d^5$ | -20.0 | -18.9 | +1.1 | Inert |
| $d^6$ | -24.0 | -19.8 | +4.2 | Inert |
| $d^7$ | -18.0 | -18.9 | -0.9 | Labile |
| $d^8$ | -12.0 | -9.9 | +2.1 | Inert |
| $d^9$ | -6.0 | -9.0 | -3.0 | Labile |
| $d^{10}$ | 0 | 0 | 0 | Labile |

*$O_h$ = octahedral, S.P. = Square pyramidal, CFSE: Crystal field stabilization energy

From the above table, it is clear that complexes containing metal ion with $d^3$ and $d^8$ arrangement are inert, while $d^4$, $d^5$ and $d^6$ arrangements are inert in low spin states only.

**3.2 Associative Nucleophilic Substitution Reaction:** Associative nucleophilic substitution reaction involves octahedral wedge intermediate (C.N. 7) as shown in Figure 2. Table 3 shows, crystal activation energy for $SN^2$ reaction for complexes containing metal ion in their high spin and predict about lability and inertness of complexes.

**Table 3: Summarized table for lability and inertness of complexes undergoing $SN^2$ reaction in their high spin state**

| d electronic configuration | CFSE for $O_h$ (in Dq) | CFSE for OW (in Dq) | CFAE (in Dq) | Labile/ Inert |
|---|---|---|---|---|
| $d^1$ | -4.0 | -5.3 | -1.3 | Labile |
| $d^2$ | -8.0 | -10.6 | -2.6 | Labile |
| $d^3$ | -12.0 | -7.75 | +4.25 | Inert |
| $d^4$ | -6.0 | -4.9 | +1.1 | Inert |
| $d^5$ | 0 | 0 | 0 | Labile |
| $d^6$ | -4.0 | -5.28 | -1.3 | Labile |
| $d^7$ | -8.0 | -10.56 | -2.6 | Labile |
| $d^8$ | -12.0 | -7.74 | +4.25 | Inert |
| $d^9$ | -6.0 | -4.93 | +1.1 | Inert |

| | | | | |
|---|---|---|---|---|
| $d^{10}$ | 0 | 0 | 0 | Labile |

*OW = Octahedral Wedge (C.N. 7)

CFAE for complexes undergoing $SN^2$ reaction in their low spin are intentionally left as a task for the reader (both can be drawn by the use of above table).

## 4. Summary

- Crystal field theory explains concept of lability and inertness on the basis of crystal field activation energy, which is difference of crystal field stabilization energy of intermediate and reactant.
- For $SN^1$ reaction, complexes containing metal ion with $d^3$ and $d^8$ arrangement are inert in both their low and high spin state, while $d^4$, $d^5$ and $d^6$ arrangements are inert in low spin state only.
- For associative nucleophilic substitution reaction, complexes containing metal ion with $d^3$, $d^4$, $d^8$ and $d^9$ arrangement are inert, while $d^3$ to $d^9$ configurations are inert for low spin complexes.