

Faculty:	Science
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Course:	M.Sc.
Semester:	II
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Unit:	4
Topic:	Substitution Reaction in Square Planar Complexes

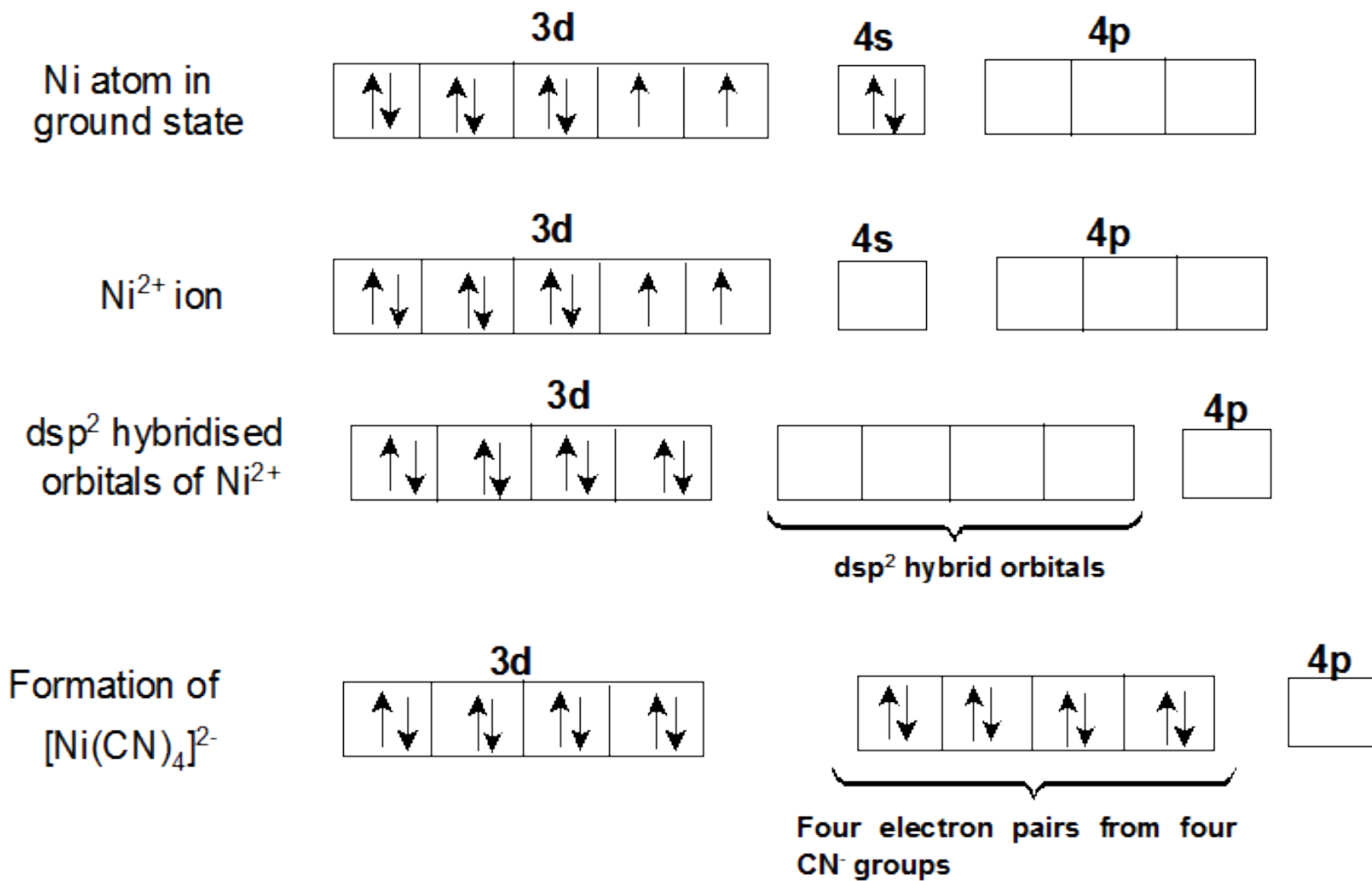
Reaction Mechanism in Transition Metal Complexes

Lecture I

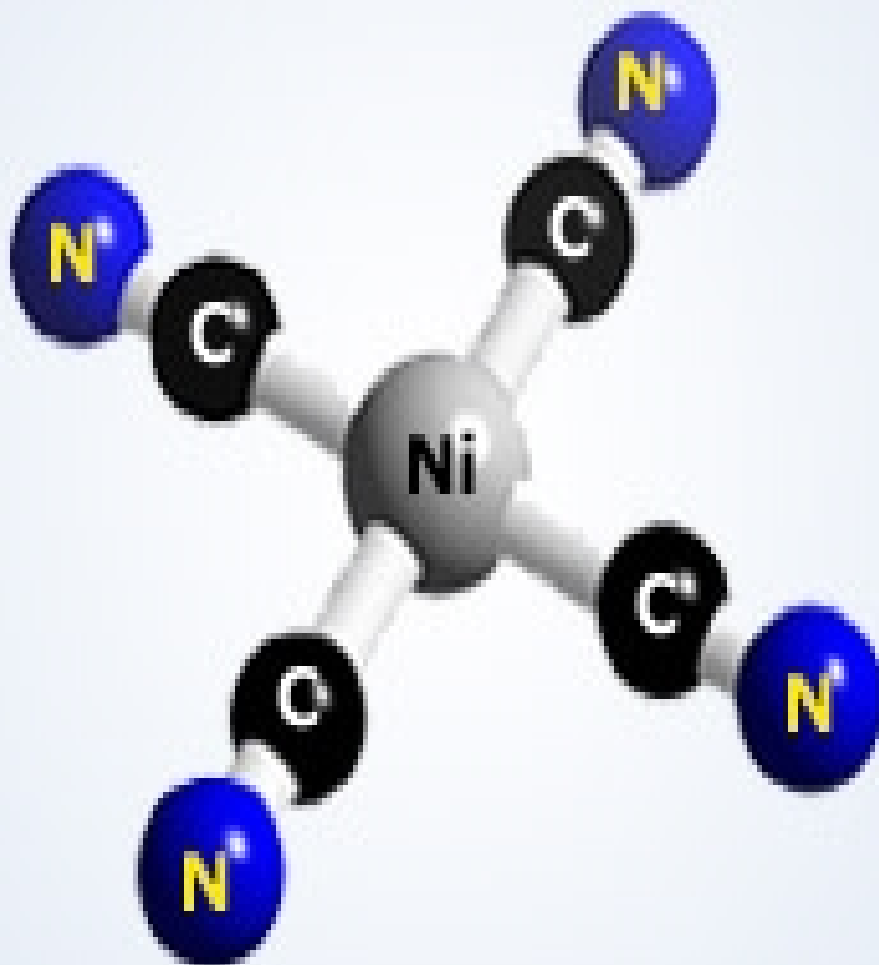
Substitution Reaction in Square Planar Complexes

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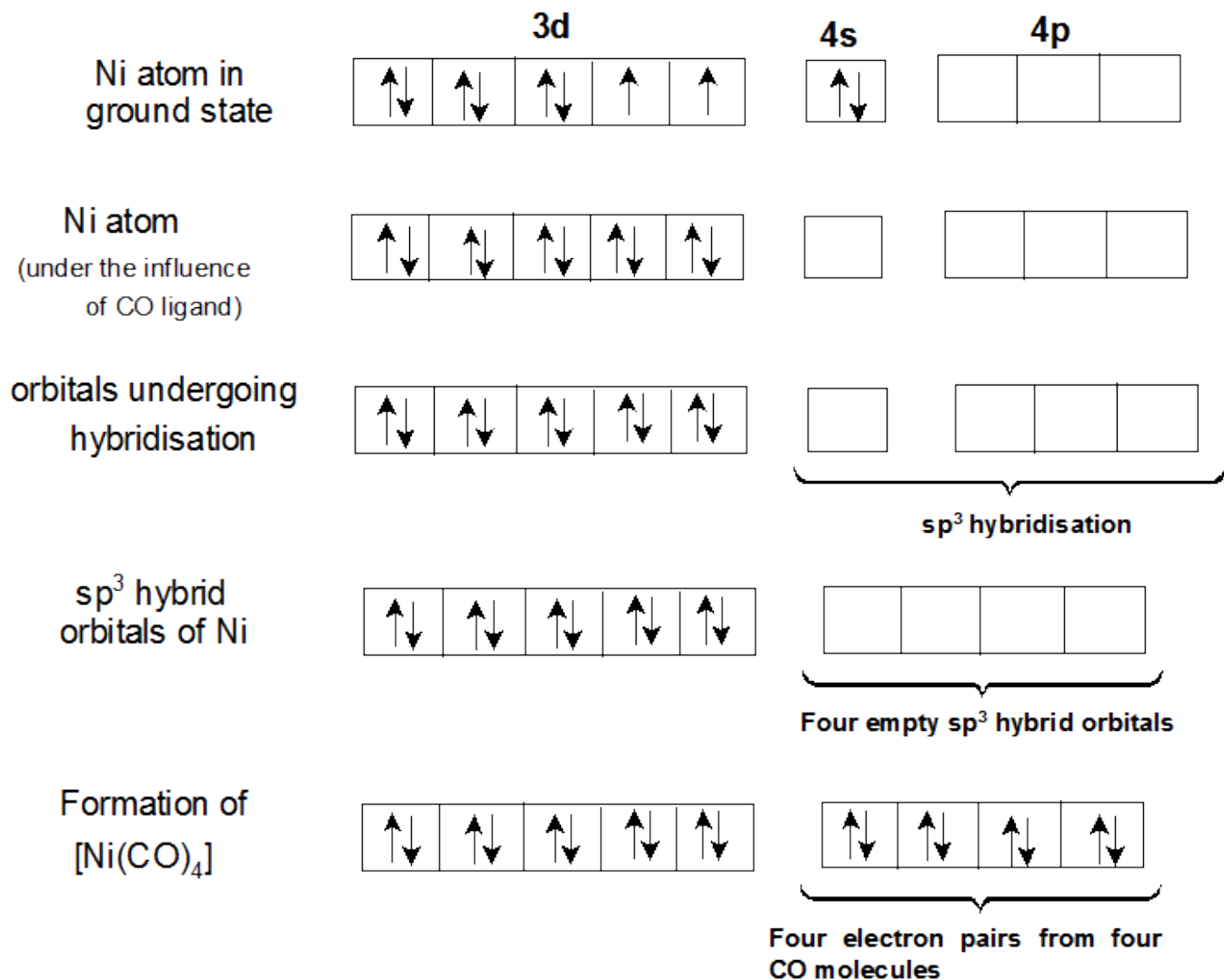
Formation of Square Planar Complex



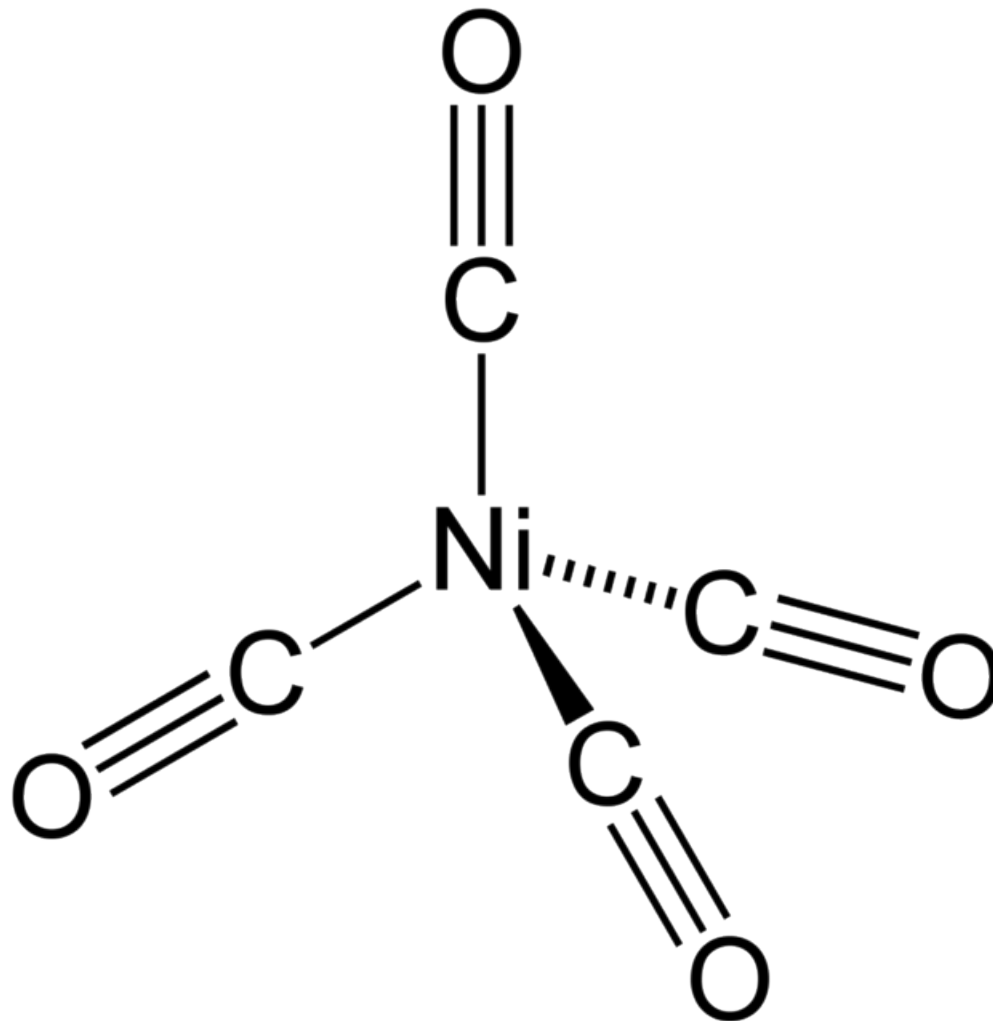
Square Planar Complex $[\text{Ni}(\text{CN})_4]^{2-}$



Formation of Tetrahedral Complex



Tetrahedral Complex $[\text{Ni}(\text{CO})_4]$



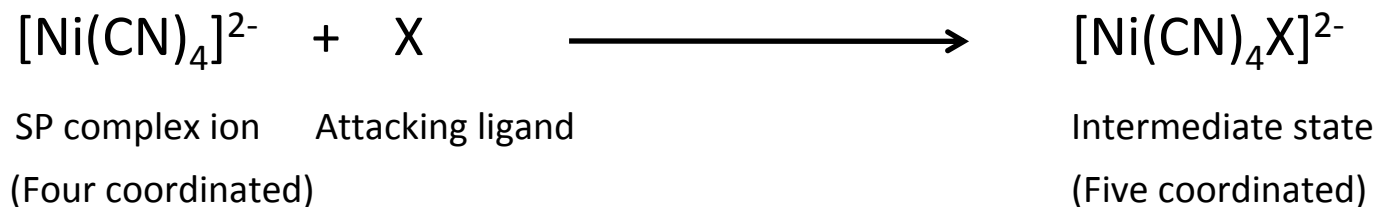
Formation of Square Planar Complex

- Most of the studies of substitution reaction in SP complexes have been done in SP complexes of Pt(II) because they are slow in substitution and hence can be easily studied.
- ***The mechanism of substitution reaction in SP complexes appears to follow associative S_N^2 rather than S_N^1 mechanism.***
- This can be concluded on the basis of the following:

Mechanism of substitution in Square Planar Complex via S_N² mechanism

1. In case of SP complexes of Ni(II), Pd(II) and Pt(II), there are five degenerate vacant orbitals (**one d, one s, three p**) available for sigma bonding with groups in the coordination sphere.

Since only four ligands approach the CMI in SP complex, one of these orbitals remains vacant and can easily accommodate the electrons from the attacking ligand; i.e. a five coordinated intermediate or an “**activated complex**” gets formed from a four coordinated SP complex through associative S_N² mechanism.



Mechanism of substitution in Square Planar Complex via S_N^2 mechanism

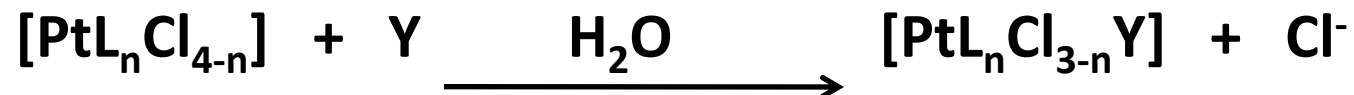
2. The rate of substitution reactions of SP complexes also dependent on the nature of the reacting complex and the central metal ion.

Ni(II) can expand its coordination number with greater ease than Pt(II) and Pd(II), therefore Ni(II) SP complexes are much more reactive towards formation of a five coordinated activated complex through associative S_N^2 mechanism.

Expanding its CN = Moving from four coordinated SP complex to five coordinated intermediate or activated complex.

Formation of Square Planar Complex

Consider the reaction of the type:



where L = monodentate ligand

n = 0 to 3

The above complexes $[\text{PtL}_n\text{Cl}_{4-n}]$ & $[\text{PtL}_n\text{Cl}_{3-n}\text{Y}]$ may be neutral or charged depending upon the nature of Ligand 'L'.

The substitution of Cl⁻ by 'Y' may have two independent pathways.

Formation of Square Planar Complex

First Pathway: $r = k_1 (\text{conc. of } [\text{PtL}_n\text{Cl}_{4-n}] \times [\text{Y}])$

Indicating that the **slower rate** determining step is bimolecular and an associative S_N^2 mechanism is involved.

Second Pathway: $r = k_2 (\text{conc. of } [\text{PtL}_n\text{Cl}_{4-n}])$

Indicating that the step involving the attack of the ligand Y is the **fast step** and therefore does not constitute the rate determining Step of the pathway.

Formation of Square Planar Complex

The second pathway is a slow aquation reaction as follows:



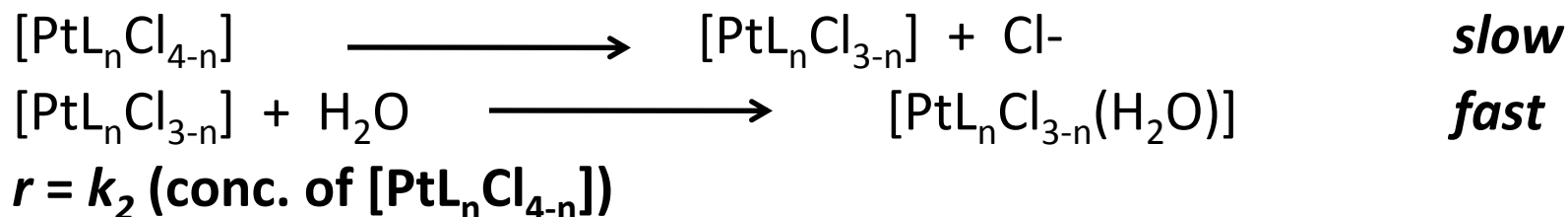
This is followed by a fast replacement of coordinated H_2O by the ligand Y as below:



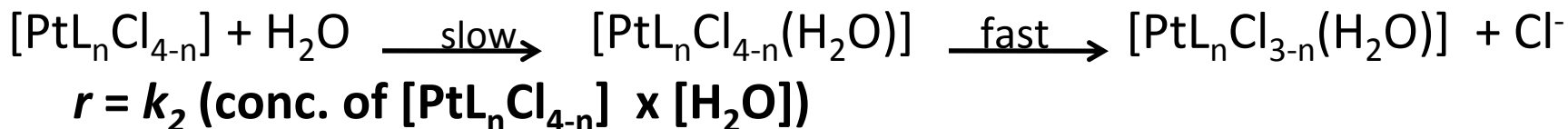
Therefore the first step is the rate determining step

Formation of Square Planar Complex

- Suppose the reaction follows the S_N^1 mechanism:



- Suppose the reaction follows the S_N^2 mechanism:



Since H_2O is present in large excess so the conc. of H_2O may be taken to be constant, hence the rate of reaction would then be

$$r = k_2 (\text{conc. of } [\text{PtL}_n\text{Cl}_{4-n}])$$

Hence S_N^1 and S_N^2 yield the same expression for rate constant

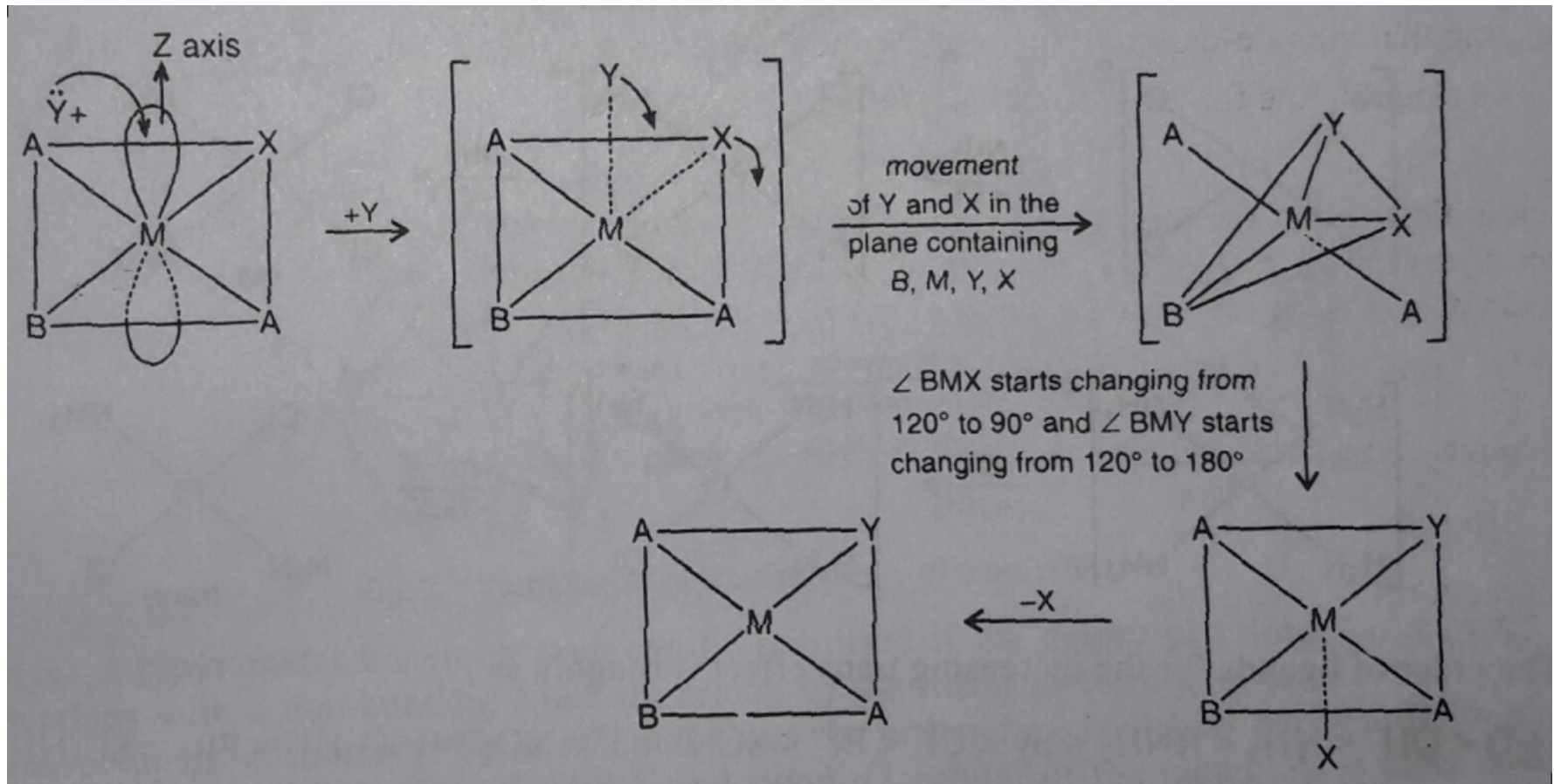
Formation of Square Planar Complex

- It has been observed that there is very *little variation* in the rate of aquation (removal of outgoing ligand and addition of H₂O) of complexes viz. [PtCl₄]²⁻, [PtCl₃(NH₃)]⁻, [PtCl₂(NH₃)₂] and [PtCl(NH₃)₃]⁺¹.
- If aquation of these complexes proceeds through S_N¹ mechanism, it would involve breaking of the Pt – Cl bond which would become more and more difficult as the +ve charge on the complex increases from -2 to +1.
- Hence rate of aquation should decrease in complexes on going from lower positive charge to higher positive charge. **However, this is contrary to the experimental observation, therefore SN¹ mechanism is ruled out.**

Formation of Square Planar Complex

- Increase in positive charge of the complex would make the breaking of Pt – Cl bond difficult but it would make the formation of Pt – OH₂ bond easier (*the lone pair of O atom would be greatly attracted to such a complex hence facilitating the formation of Pt – OH₂ bond*).
- It also means that the rate of aquation reaction would be the same for viz. [PtCl₄]²⁻, [PtCl₃(NH₃)]⁻, [PtCl₂(NH₃)₂] and [PtCl(NH₃)₃]⁺¹ irrespective of the charge on the complex.
- The above observation indicates that the aquation reaction in square planar complexes would proceed through SN² mechanism.

Formation of Square Planar Complex



The incoming ligand 'Y' attacks on the z-axis forming a five coordinate Square Pyramidal intermediate which transforms to a TBP intermediate and later reforms to a Square Pyramidal intermediate which later forms the substituted Square Planar Complex.