

❖ Electrophilic Attack on Ligands

There is a special class of ligand substitution reactions in which ligand displacement occurs without the breaking of metal-ligand bonds. Experimental studies suggested that these reactions take place via an electrophilic attack on the ligand already attached to the metal center. Consider the preparation of $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ complex from $[(\text{NH}_3)_5\text{Co}-\text{CO}_3]^+$ cationic species:



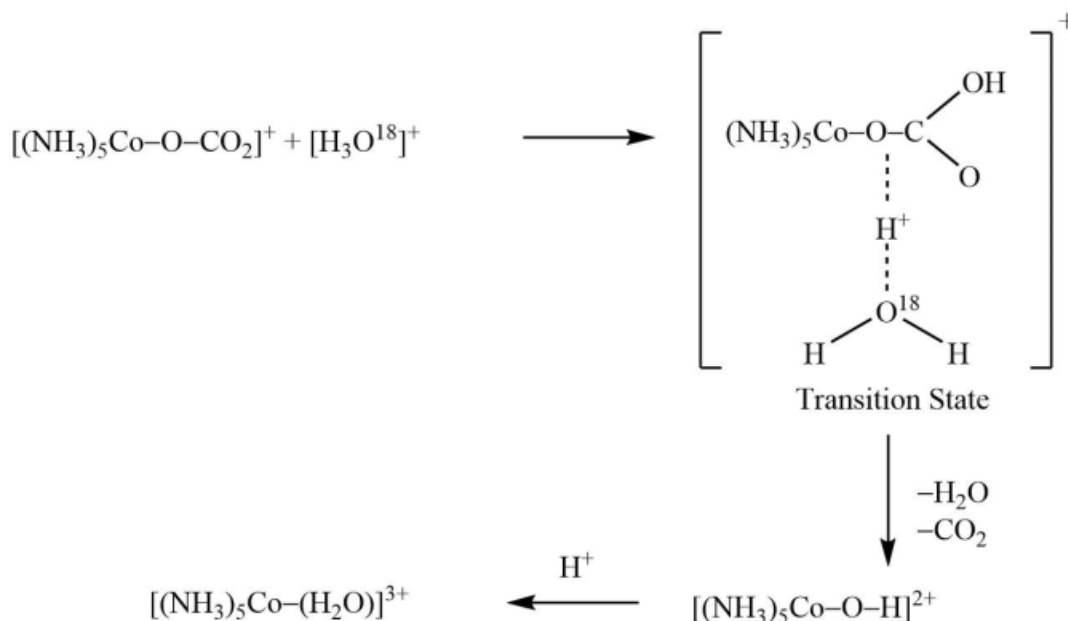
Carbonate Complex

Aquo Complex

It has been observed that the no isotopically labeled oxygen is found in the aquo complex which indicates that no metal-ligand bond-breaking has actually been taken place during the course of the whole substitution process.

Mechanism: The whole process can be summed up into the following steps

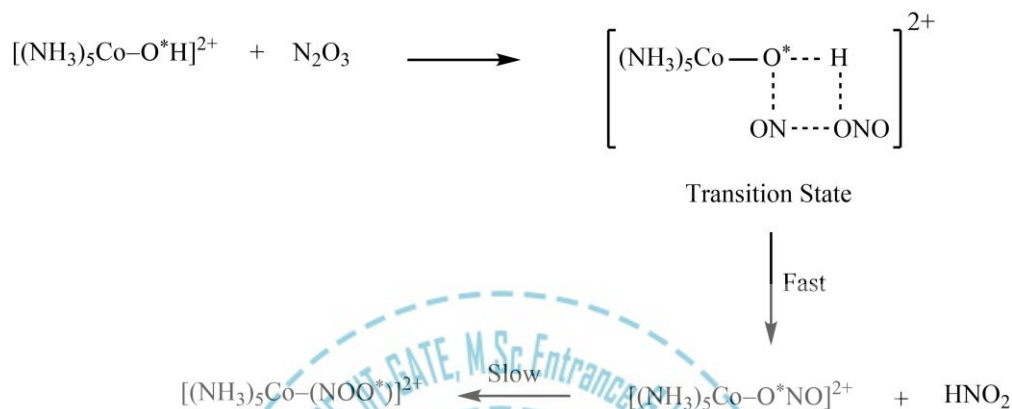
- (1) Electrophilic or the proton attack on the oxygen atom of the ligand bonded to the trivalent cobalt.
- (2) Expulsion of CO_2 and H_2O to form hydroxo complex.
- (3) Protonation of the hydroxo complex.



It is also worthy to mention that the reaction described above is a decarboxylation rather than the acid hydrolysis.

The similar behavior can be observed in the reaction of NO_2^- group with pentaammineaquocobalt(III) ion. When the studies involving isotopic labelling were carried out, we came to know that show that the oxygen

of bound water is actually the same to what is used by NO_2^- to bind with metal centre. This unusual result can be explained by the following mechanism.



Hence, in both of the reactions given above, the displacement of previously attached ligand octahedral complexes occurs without metal-ligand bond breaking.



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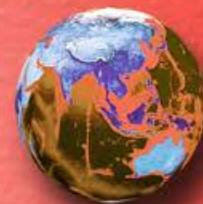
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Volume I

MANDEEP DALAL



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