

Substitution reactions in octahedral complexes

Base hydrolysis in octahedral complexes

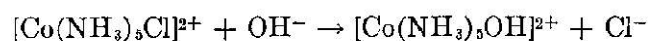
Whereas the acid hydrolysis is occurred for reactions of metal complexes with water at $\text{pH} < 3$, base hydrolysis occurs in basic solutions (at $\text{pH} > 10$). For intermediate pH ranges the reaction is referred to as just hydrolysis.

Hydroxide ion is a privileged nucleophile in aqueous solution. . It is the only one that can penetrate the second coordination sphere of the complex by the proton transfer conduction mechanism. Thus, it need not displace a water molecule. The rate of solvolysis of chloroammincobalt(III) complexes in alkaline solution is extremely rapid. For example, the release of chloride ion from a given complex at pH 13 may be from 10^4 to 10^8 times faster than at pH 2. This is a unique behavior of OH^- , for it is known that other substances such as NO_2^- , NCS^- , and NH_3 do not affect the rate of chloride ion release. OH^- is a strong base as well as a good nucleophile.

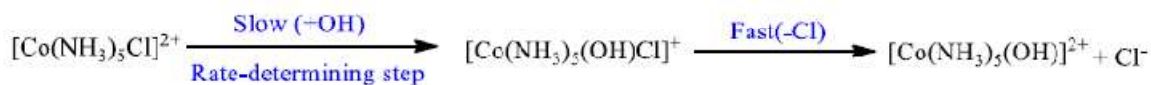
Two types of mechanisms are followed for base hydrolysis in octahedral complexes. (i) $\text{S}_{\text{N}}2$ or Associative mechanism. (ii) $\text{S}_{\text{N}}1\text{CB}$ or Dissociation mechanism.

$\text{S}_{\text{N}}1\text{CB}$ Mechanism is more favored than $\text{S}_{\text{N}}2$ Mechanism.

A base hydrolysis reaction can be discussed using $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$



$\text{S}_{\text{N}}2$ or Associative mechanism:

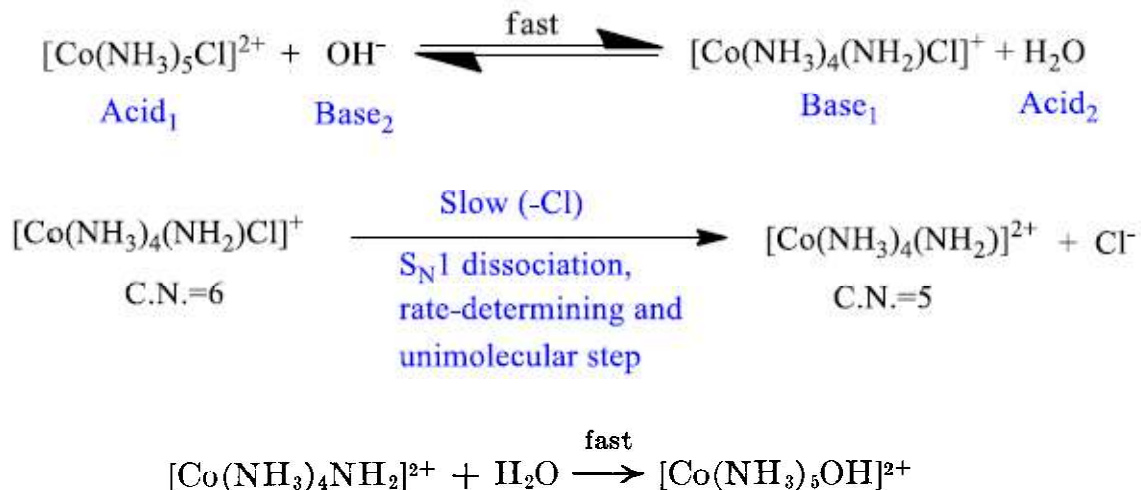


$$\text{Rate} = k[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} [\text{OH}^-]$$

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S_N1CB or Dissociation mechanism (Substitution, nucleophilic, unimolecular, conjugate base):

Acid-Base properties of the complexes are more important than the nucleophilic properties of OH⁻ in S_N1CB Mechanism. Reactions occurring in non hydroxylic solvents like Dimethyl sulphoxide, can be explained by S_N1CB mechanism but not by S_N2.



Rate = k₁[CB]; where CB= Conjugate Base ,

$$[\text{CB}] = \frac{K [\text{Co(NH}_3\text{)}_5\text{Cl]}^{2+} [\text{OH}^-]}{[\text{H}_2\text{O}]}$$

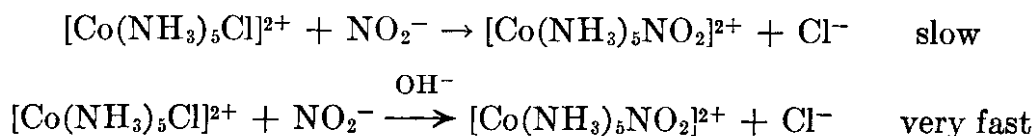
The rate-determining step is the rate of dissociation of the conjugate base, Since its concentration depends on the concentration of the complex and of OH⁻, it follows that the rate law should be first-order in each of these species.

Several things can be done to test the validity of an S_N¹CB mechanism. It is observed that an S_N¹CB mechanism is favored over an S_N² displacement process. The conjugate base process requires that the acid-base equilibration would be fast compared with the rate of base hydrolysis but that the concentration of conjugate base would be small even at pH 13.

Substitution reactions in octahedral complexes

If this S_N^1CB mechanism is responsible for the unique effectiveness of OH^- , then it would not be such a good reagent for analogous cobalt (III) complexes containing no "acid" N—H bonds. It is shown that the complexes of the type $trans-[Co(py)_4Cl_2]^+$ (py = pyridine) and $[Co(CN)_5X]^{3-}$ ($X^- = Cl^-, Br^-, I^-$) undergo hydrolysis at rates that are independent of hydroxide ion concentration. The most direct evidence in support of an S_N^1CB mechanism would be to establish the formation of a five-coordinated intermediate. This intermediate would be extremely reactive and therefore very difficult to detect.

This was demonstrated by experiments showing that the reaction of $[Co(NH_3)_5Cl]^{2+}$ with NO_2^- is catalyzed by hydroxide ion.



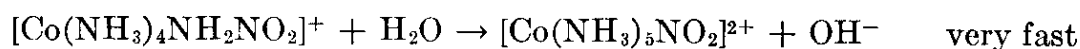
If the hydroxide ion were reacting by an S_N^2 process, it would first enter the complex forming $[Co(NH_3)_5OH]^{2+}$ which in turn would have to react rapidly with NO_2^- to form the nitro product.



However this reaction is found to be very slow, which means that such a reaction path cannot be used to explain the OH^- catalysis. If, instead, the role of OH^- is to generate an active intermediate, such as $[Co(NH_3)_4NH_2]^{2+}$, the latter could react rapidly with the nitrite ion.



A rapid proton transfer, gives the final product and regenerates the OH^- needed in equilibrium, such that only catalytic amounts of OH^- are necessary.



Since this is an S_N^1CB mechanism, it follows that the rate of the catalyzed reaction is determined by the rate of dissociation of the conjugate base.

Substitution reactions in octahedral complexes

Experiments do show that the rate of reaction at the same OH^- concentration does not depend on the concentration of NO_2^- and that it is the same for the entry of other nucleophilic reagents such as NCS^- and N_3^- . Furthermore, other bases such as piperidine also act as catalysts.

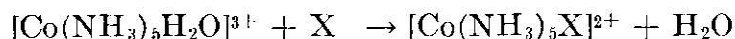
why the rate of dissociation of the conjugate base is so much more rapid than that of the parent compound, e.g., $[\text{Co}(\text{NH}_3)_4\text{NH}_2\text{Cl}]^+ \gg \gg [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. It is to be expected that the separation of charge (chloride ion from cationic complex) will be easier for the smaller the charge on the cation. This favors a more rapid reaction for the conjugate base, but its rate is so much faster than other mono valent cobalt (III) cationic complexes that it would not appear to be just a matter of cationic charge. A better explanation is afforded by the extreme π bonding of the amido group ($\text{Co} - \text{NH}_2$) which stabilizes the transition state, thus promoting dissociation.

Base hydrolysis reactions of cobalt (III) complexes generally proceed with stereochemical rearrangement.

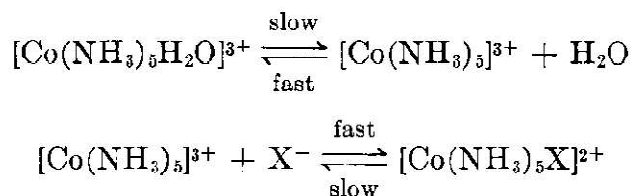
Anation Reactions

In these reactions a coordinated solvent molecule, such as H_2O is replaced by another ligand, often anionic that means aquo ligand or H_2O molecules from an aquo complex is replaced from the coordination shell by some anion. It is the reverse of acid-hydrolysis.

The formation of metal complexes in water solution requires the replacement of coordinated water by some other ligand; this replacement, therefore, is a very common and very important reaction.

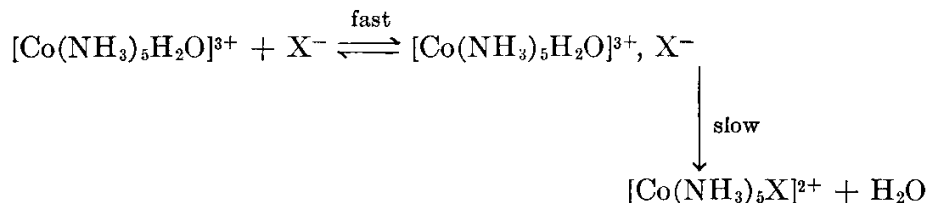


The rate of this reaction depends both on the concentration of the complex and on that of the entering ligand X^- . This may suggest a bimolecular displacement process ($\text{S}_{\text{N}}2$), but an alternative dissociative mechanism ($\text{S}_{\text{N}}1$) is equally in accord with the kinetic results.

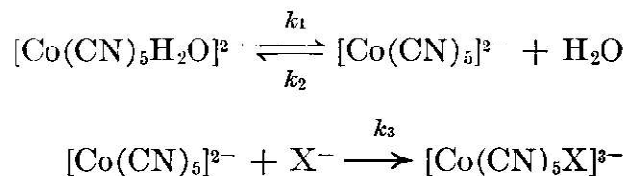


Substitution reactions in octahedral complexes

Thus there is a competition between H_2O and X^- for the five-coordinated species, which means that the rate of formation of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ depends on the concentration of X^- . This mechanism requires that, at some high concentration of X^- , the rate no longer depend on its concentration and that it be the same as the rate of dissociation of the coordinated water. This occurs because with increasing X^- concentration cationic complexes make ion pair with X^- .



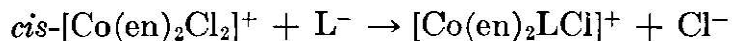
This difficulty has recently been avoided by using the anionic complex $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$. Its reaction with thiocyanate and with azide ions conforms to the S_{NI} mechanisms.



The same approximate values of k_1 were estimated from kinetic data where $\text{X} = \text{NCS}^-$ or N_3^- .

Reactions in Nonaqueous Systems

A detailed study of the reaction of $\text{cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ with a variety of reagents L, was made using methanol as the solvent.



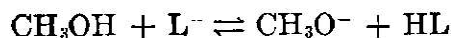
It was observed that for $\text{L} = \text{NCS}^-, \text{NO}_3^-, \text{Br}^-$ and Cl^- the rate of reaction is the same and is independent of the concentration of L.

These results can be explained on the basis of a dissociation process yielding a symmetrical active intermediate $[\text{Co}(\text{en})_2\text{Cl}]^{2+}$. These results can be explained on the basis of a dissociation process yielding a symmetrical active intermediate $[\text{Co}(\text{en})_2\text{Cl}]^{2+}$.

Substitution reactions in octahedral complexes

However the same reaction for $L = \text{CH}_3\text{O}^-$, NO_2^- , N_3^- , and $\text{C}_2\text{H}_3\text{O}_2^-$ was found to be much faster, to differ for each of these reagents, and to depend on their concentrations. A rather obvious explanation is that, compared with the previous group of L's, these reagents are better nucleophiles and the reactions proceed by an $\text{S}_{\text{N}}2$ mechanism.

Further investigation has shown that the more rapid reaction observed for NO_2^- , N_3^- and $\text{C}_2\text{H}_3\text{O}_2^-$ is almost entirely due to the methoxide ion generated in solution by these basic anions,



The CH_3O^- , analogous to OH^- in water as the solvent, is believed to react by an $\text{S}_{\text{N}}1\text{CB}$ mechanism.

Stereochemistry of Substitution Reactions

Consider first a **dissociation process**. There are two plausible reaction paths. The D mechanism includes a five-coordinate intermediate, and the most probable geometries are those of known five-coordinate complexes - the square pyramid and the trigonal bipyramid. Consider first the intermediates derived from $\text{trans}[\text{Co}(\text{en})_2(\text{A})\text{X}]^+$. In one, the five remaining ligands stay in essentially their original positions so that the intermediate has a square pyramid structure and reaction takes place with retention of configuration. The square-pyramidal intermediate has an open face where the leaving group was located and is expected to yield 100 per cent trans product by addition of the new group on the open face. If instead, as the leaving group departs, two of the adjacent ligands move in to fill this space, the five coordinated intermediate has a trigonal bipyramid structure. Assuming that the entering group enters in the trigonal plane, it follows that this path may permit rearrangement to occur. The trigonal-bipyramidal intermediate has three nearly equivalent directions for addition of the entering group, between N(2) and N(4), between N(2) and A, or between N(4) and A. The two adjacent to A yield cis products, whereas the third yields a trans product.

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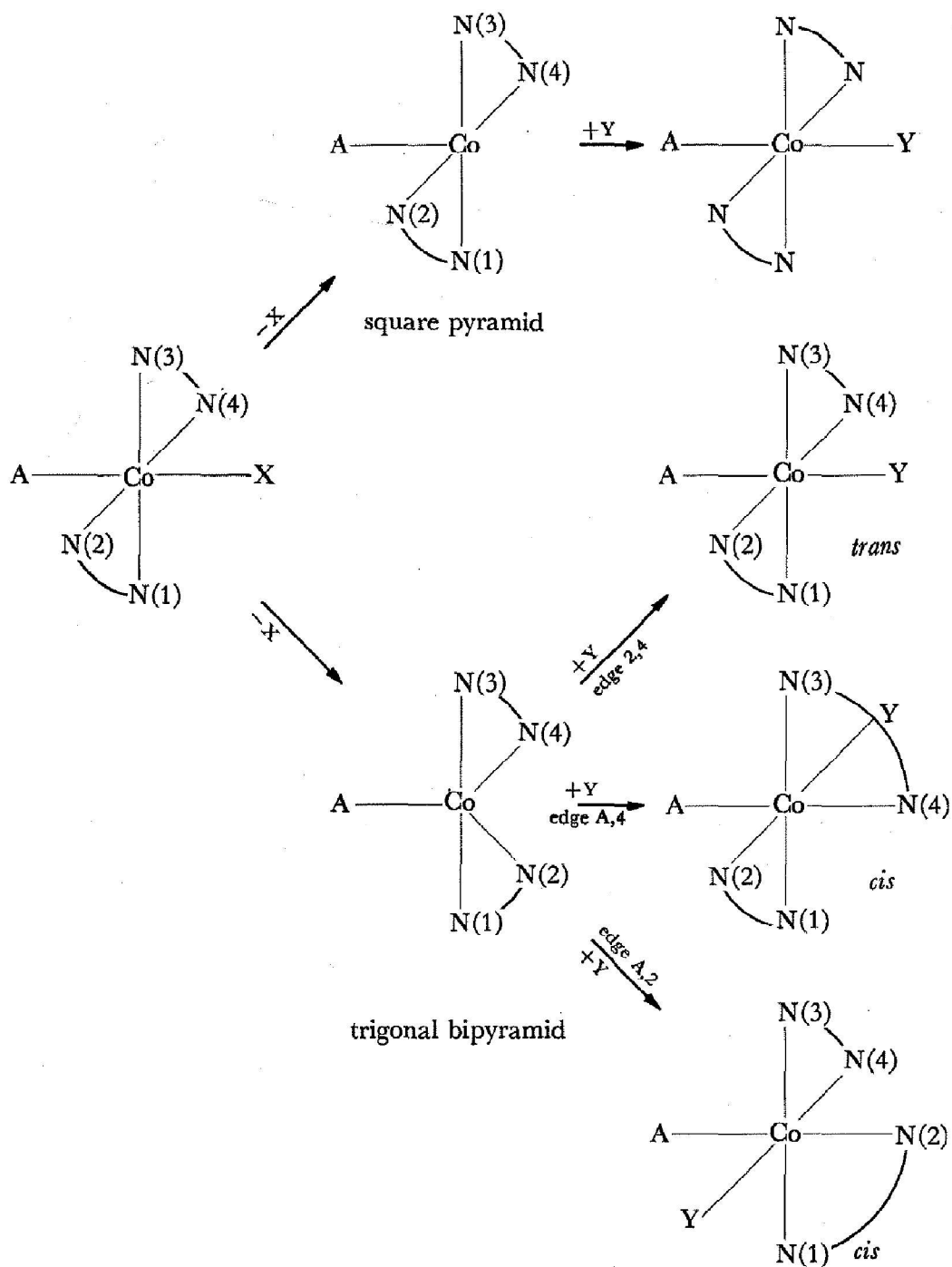


Fig: Stereochemical changes accompanying the displacement of X by Y in $\text{trans-}[\text{Co}(\text{en})_2(\text{A})\text{X}]^+$ by a dissociation ($\text{S}_{\text{N}}1$) mechanism through either a tetragonal pyramidal or a trigonal bipyramidal intermediate

Substitution reactions in octahedral complexes

There are also two plausible seven-coordinated intermediates available to **displacement reactions**. The more probable one seems to be that which results from a *cis* attack (sometimes called non-edge displacement). Here the attack is at the face of the octahedron adjacent to the departing group. It is pictured as having a synchronous motion into the opposite face from that of the entering group, and thus in the transition state both groups occupy identical positions with respect to the rest of the complex. The net result is no ligand motion other than the departing and entering groups and, consequently, no change in configuration. The other possibility of *trans* attack (sometimes called edge displacement) does require ligand motion and is therefore believed less likely.

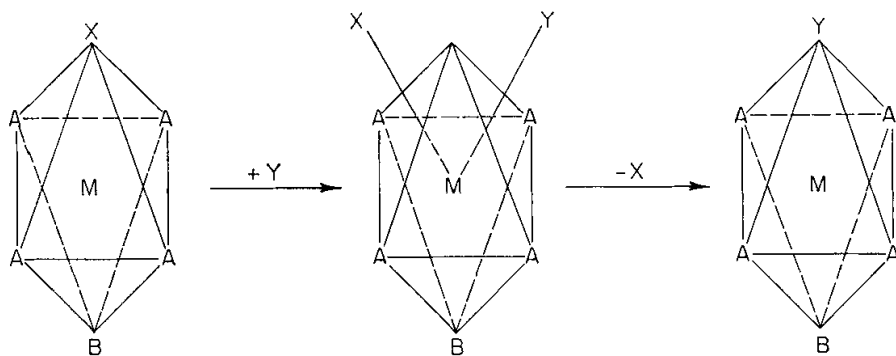


Fig: Retention of configuration during the displacement of X by Y in *trans*-[MA₄BX] by a *cis* attack S_N2 process

Now take the example of hydrolysis of [Co(en)₂LCl]ⁿ⁺ complexes. First decide the label S_N1 or S_N2 for the reaction then it is possible to interpret the stereochemical results on the basis of the active intermediates. The S_N1 reactions of *cis*-[Co(en)₂LCl]⁺ proceed with retention of configuration by presumably a tetragonal pyramid intermediate, whereas the *trans* isomer reacts with rearrangement via a trigonal bipyramid. These structures permit stabilization of the five-coordinated intermediate by π bonding with electron flow ligand to metal, L → M. On the other hand, S_N2 reactions of both *cis*- and *trans*- [Co(en)₂LCl]ⁿ⁺ proceed with retention of configuration. This is in keeping with a *cis* attack mechanism being of lower energy than *trans* attack which would result in rearrangement. The π bonding contribution of metal to ligand, M → L is observed for these reactions.

Substitution reactions in octahedral complexes

Interchange mechanism: We speak generally about associative and dissociative reaction mechanisms, the terms A and D are reserved for situations where 7 and 5 coordinate intermediates have actually been isolated and positively identified. If no intermediates have been isolated or identified the designations associative (I_a) or dissociative (I_d) are more appropriate. The interchange mechanism is similar to the associative and dissociative pathways, except that no distinct ML_nY or ML_{n-1} intermediate is formed. This concerted mechanism can be thought of as analogous to nucleophilic substitution via the S_N2 pathway at a tetrahedral carbon atom. The interchange mechanism associative (I_a) or dissociative (I_d) depends on the relative importance of M-Y and M-L bonding in the transition state. If the transition state is characterized by the formation of a strong M-Y bond, then the mechanism is I_a . Conversely, if weakening of the M-L bond is more important in reaching the transition state, then the mechanism is I_d .

An example of the I_a mechanism is the interchange of bulk and coordinated water in $[V(H_2O)_6]^{2+}$. In contrast, the slightly more compact ion $[Ni(H_2O)_6]^{2+}$ ion exchanges water via the I_d mechanism.

As Y begins to bond and X begins to leave. i.e. the bond making to Y and bond breaking to X occur simultaneously (organic S_N2).

