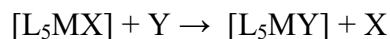# Substitution reactions in octahedral complexes

Octahedral complexes, that is, complexes with six ligands disposed at the corners of a figure approximating an octahedron, are probably the most common in the literature of coordination chemistry. Two factors are common to all octahedral systems that point to differences between their reactions and those of the square-planar systems. First, a steric factor has been introduced. The two open faces of the square complex have been filled by the fifth and sixth ligands. Thus, for comparable ligands, octahedral complexes should be more crowded and ligand-ligand repulsions should be larger. Second, octahedral complexes are not unsaturated in their σ-bonding systems. The p_z orbital that is available for involvement in σ bonding during the reactions of d^8 a square-planar complexes is already so employed in the octahedral ground state. The lone family of octahedral complexes for which adequate data are now available is the Co(III) family, notably the substituted cobalt-amine systems.

Ligand Displacement Reactions in Octahddral Complexes :

A general equation for a ligand displacement reaction in octahedral complexes is

$$[L_5MX] + Y \rightarrow [L_5MY] + X$$

Octahedral substitution reactions are mainly dissociative in character. They have been most thoroughly studied in aqueous solution using non-labile Co(III) and Cr(III) complexes. In aqueous solution the special case in which Y is H_2O (or OH^-) is of overwhelming importance. It appears that there are few, if any, reactions in which X is not first replaced by H_2O, and only then does the other ligand Y, enter the complex by displacing H_2O. The simple substitution reaction in aqueous solution is really a two step process involving prior displacement of X by H_2O followed by displacement of H_2O by Y. Consequently, in aqueous media the only reactions which can easily be studied are acid and base hydrolysis and anation.

Substitution reactions in octahedral complexes

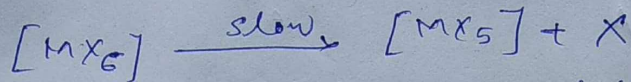## Substitution Reaction in octahedral complexes

① Nucleophilic substitution reaction —
Nucleophile is involved in the reaction

② Electrophilic substitution reaction —
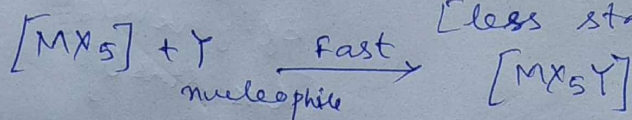Electrophiles are involved in the reaction

$$[MX_6] + Y \longrightarrow [MX_5Y] + X$$

X is substitutes by Y

① unimoleculer nucleophilic susstitution reaction or SN^1 reaction or dissociative SN^1 reaction

$$[MX_6] \xrightarrow{\text{slow}} [MX_5] + X$$

Intermediate
five coordinated
[less stable]

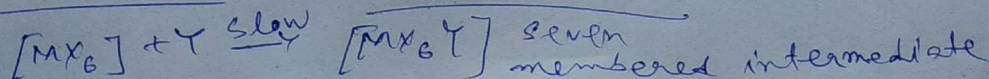$$[MX_5] + Y \xrightarrow[\text{nucleophile}]{\text{fast}} [MX_5Y]$$

octahederal complex
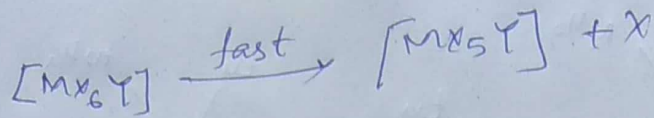
$$\boxed{Rate = k[MX_6]}$$

Completely depend on the conc. of reactiing moleculer.

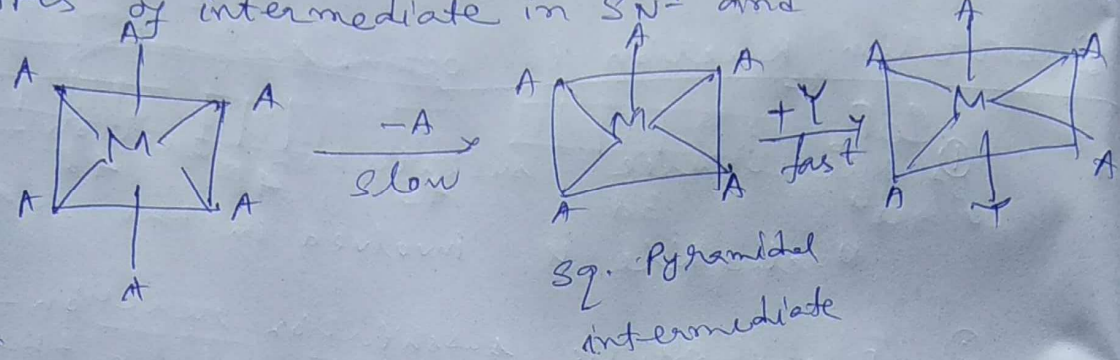② Bimoleculer nucleophilic substitution (SN^2) reaction or associative reaction

$$[MX_6] + Y \xrightarrow{\text{slow}} [MX_6Y]$$ seven membered intermediate

Substitution reactions in octahedral complexes
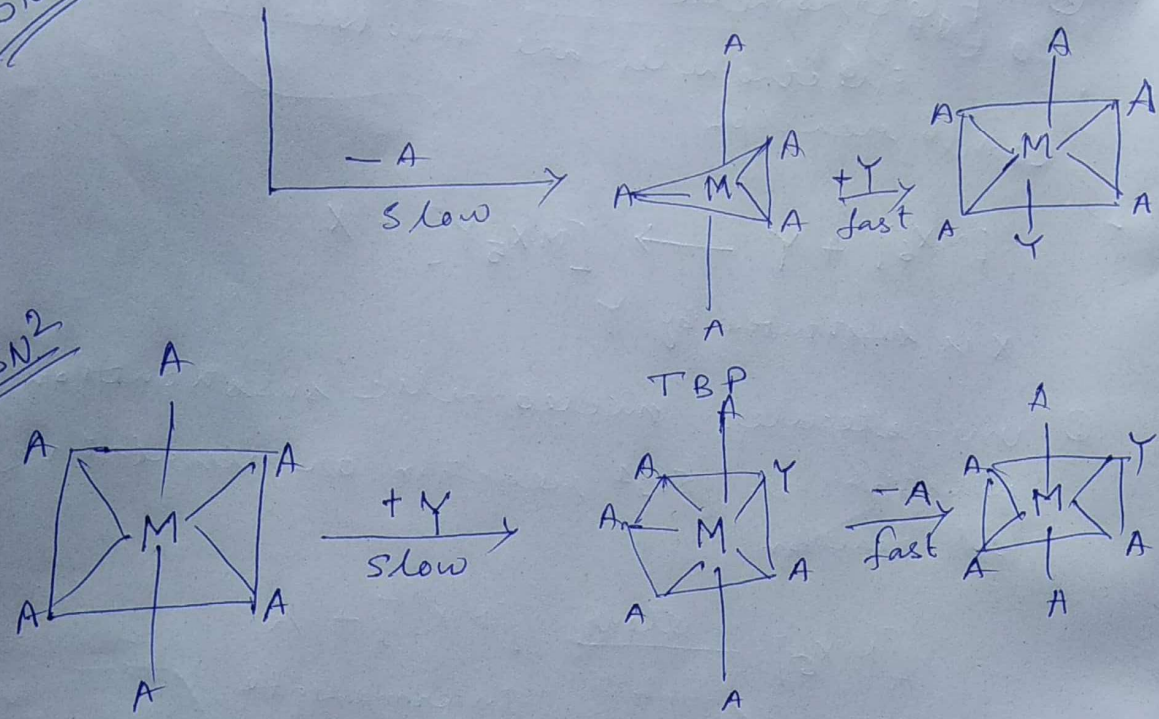
$$[MX_6Y] \xrightarrow{\text{fast}} [MX_5Y] + X$$

$$Rate = K [MX_6][Y]$$

Types of intermediate in SN^1 and SN^2 reaction

Sq. Pyramidal intermediate
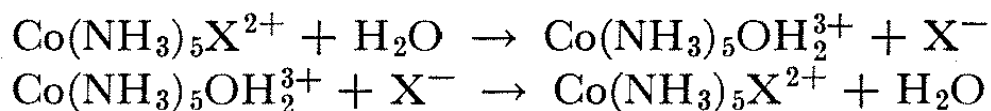
SN^1

TBP

SN^2
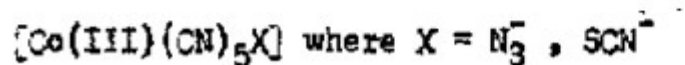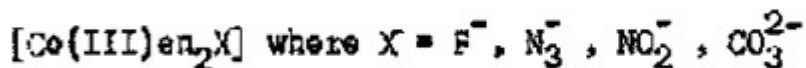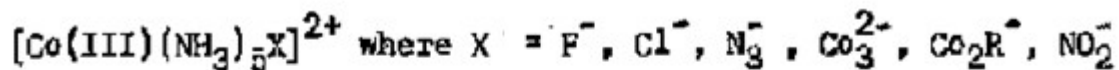

Pentagonal bipyramid [less stable]

Substitution reactions in octahedral complexes

Acid hydrolysis: The most common reaction of a metal complex is the reaction between the complex and the solvent water.

$$Co(NH_3)_5X^{2+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + X^-$$
$$Co(NH_3)_5OH_2^{3+} + X^- \rightarrow Co(NH_3)_5X^{2+} + H_2O$$

The reactions of these complexes with water in acid solution show that the reactions proceed in two steps. First, the original anionic ligand is replaced by a water molecule; then, in a second step, the water molecule is replaced by the entering anionic ligand. The first step is rate-determining.

In these reactions the aquo completes are formed by acid hydrolysis. An alternative term to acid hydrolysis is aquation. In acid solution, with a pH less than about 3, such reactions are referred to as acid hydrolysis reactions. Kinetic studies show that these reactions are pseudo-fi'rst-order. Since the concentration of the solvent does not change during the reaction, the kinetic order does not show the dependence of the rate of hydrolysis on water. Attempts to determine the role played by water making use of non-aqueous solvents containing varying amounts of water have, as yet, not been successful. Acid catalysed hydrolysis usually occurs when the leaving group can be protonated as far strongly-basic ligands or those forming hydrogen bonds. Examples which undergo this sort of reaction are :

$[Co(III)(NH_3)_5X]^{2+}$ where $X = F^-$, Cl^-, N_3^-, CO_3^{2-}, CO_2R^-, NO_2^-

$[Co(III)en_2X]$ where $X = F^-$, N_3^-, NO_2^-, CO_3^{2-}

$[Co(III)(CN)_5X]$ where $X = N_3^-$, SCN^-

Two alternatives are possible in the primary steps of acid hydrolysis

Substitution reactions in octahedral complexes

$$[M - X]^{n+} + H_2O \longrightarrow [M - OH]^{n+} + XH$$

$$[M - X]^{n+} + H_2O \longrightarrow [M - OH_2]^{(n-1)+} + X^-$$
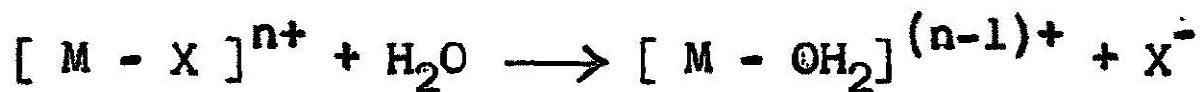
The rate of aquation reactions are usually first-order and the form of the rate law of reaction is

$$\text{rate} = k[Co(NH_3)_5Cl^{2+}]$$

Regardless of mechanism, such a pseudo first-order rate law is obtained whenever the concentration of one of the reactants is so large as to remain essentially constant during reaction. For aquation reactions, where the solvent water is also the reagent, its role in the transition state cannot be obtained by direct kinetic studies. These results favor reactions by an SN^I mechanism. For example, the rates of reaction decrease with increased positive charge on the metal ion. This is best illustrated by similar low-spin d^6 complexes which decrease in reactivity in the order Fe(II) > Co (III) > Pt(IV). Furthermore, the entering group, except for the special case of hydroxide ion has no effect on the rate of reaction of cobalt (III) complexes. The ratio of the rates of aquation of $[Co(NH_3)_5X]^{2+}$ for X = Cl^-:Br^-:I^- is 1 : 3.8 : 5 , which shows an increase in rate with increasing size of the leaving group. The rate of acid hydrolysis of trans-$[Co(NH_3)_4Cl_2]^+$ is approximately 103 times faster than that of $[Co(NH_3)_5Cl]^{2+}$. This may result from the negative charge of the second chloro group which enhances the separation of charges in a dissociative process. All these observations are consistent with a dissociation (SN^I) mechanism.

This is not to say that aquation reactions of all cobalt (III) complexes proceed by an SN^I process. For example, it does appear that water plays an increasingly important role in the hydrolysis of a complex containing an electron-withdrawing group such as nitrite ion. The presence of such a group would make the metal more positive and result in more energy being required to break the metal-ligand bond. Thus the rate of a reaction proceeding by a dissociation process would be slower. Instead it has been found that trans-$[Co(en)_2NO_2Cl]^+$ aquates more rapidly than does trans$[Co(en)_2Cl_2]^+$ and that the cis isomers react at approximately the same rate. This suggests

Substitution reactions in octahedral complexes

that the SN^I mechanism assigned the dichloro system is not strictly applicable to the chloronitro complex. This difference and other observations are adequately explained in terms of π bonding.

The effect of changes in ligand L on the rate of aquation of $[Co(en)_2LCl]^{n+}$ as well as its effect on the stereochemical changes accompanying with the reaction have been studied

$$[Co(en)_2LCl]^{n+} + H_2O \rightarrow [Co(en)_2LH_2O]^{(n+1)+} + Cl^-$$
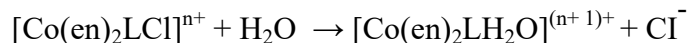
The kinetic and stereochemical data are given in the Table (below) and the kinetic data are shown graphically in the Figure (below). An examination of ligand L in terms of its capacity to π-bond with cobalt (III) reveals that there are four different types of ligands: (1) ligands containing additional electron pairs which can be delocalized ligand $\rightarrow$ metal e.g. NH_2^-, OH^-, Cl^-; (2) ligands with vacant orbitals permitting delocalization of metal electron pairs towards the ligand e.g., NO_2^-; (3) ligands with resonance structures such that π bonding of either type (1) or (2) is possible, e.g., NCS^-, N_3^-; (4) ligands that cannot π-bonds, e.g., NH_3 . Let us now consider the probable effect of these two different types of π bonding on the reaction processes.

RATES AND STEREOCHEMISTRY OF THE REACTION[a]

$$[Co(en)_2LCl]^{n+} + H_2O \xrightarrow{25°C} [Co(en)_2LH_2O]^{(n+1)+} + Cl^-$$
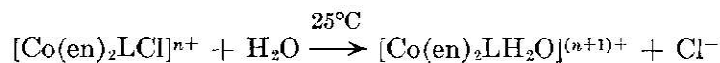
Isomer	Ligand	k (sec^{-1})	% cis product
Trans	OH	1.4×10^{-3}	75
Trans	Cl	3.2×10^{-5}	35
Trans	N$_3$	2.4×10^{-4}	20
Trans	NCS	5.0×10^{-8}	50 70
Trans	NH$_3$	4.0×10^{-7}	0
Trans	NO$_2$	1.0×10^{-3}	0
Cis	OH	1.3×10^{-2}	100
Cis	Cl	2.4×10^{-4}	100
Cis	N$_3$	2.5×10^{-4}	100
Cis	NCS	1.1×10^{-5}	100
Cis	NH$_3$	5.0×10^{-7}	100
Cis	NO$_2$	1.1×10^{-4}	100

[a] Data from Tobe (1960).

Substitution reactions in octahedral complexes

For this we can use, as specific examples of the two types, the ligands OH^- and NO_2^-. With the compound containing coordinated OH^- there is a flow of electrons toward Co (III) which makes it easier to break the Co-Cl bond. In addition, the π bonding tends to stabilize the five-coordinated intermediate which then means that OH^- tends to promote an SN^I mechanism,

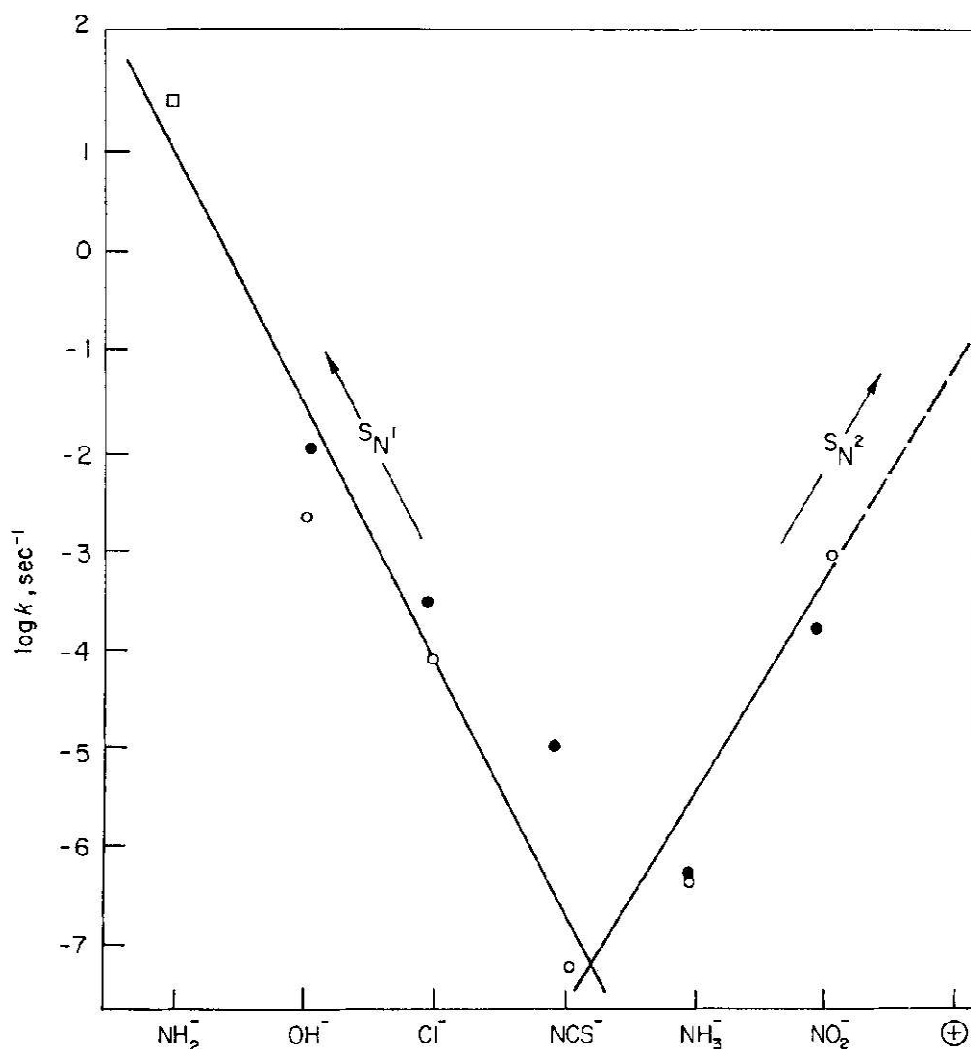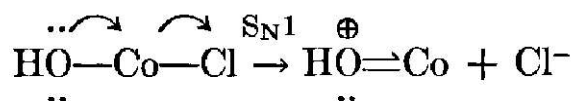$$HO{-}Co{-}Cl \xrightarrow{\;S_N1\;} HO{=}Co^{\oplus} + Cl^-$$

Figure. Rates of aquation of Co(en)$_2$LCl]$^{n+}$ as a function of L. The ascending curves indicate increasing SN^I character (left branch) and increasing SN^2 character (right branch) in the reaction mechanism. ⬤, *cis* isomer; O, *trans* isomer; ⊐, unknown structure; L, ⊕ is hypothetical analogous Ni(IV) complex.

Substitution reactions in octahedral complexes

In contrast to this, the nitro group removes electrons from Co (III), making it more difficult to break the Co—CI bond but promoting nucleophilic attack or an SN^2 mechanism.
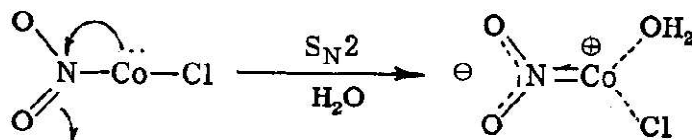
Two other significant points evolve on further scrutiny of the data in the above Table . One is that for ligands promoting an S_N^I reaction the *cis* isomer reacts more rapidly than does the *trans,* whereas the reverse is true for the ligands that promote an S_N^2 process. The second point is that S_N^I reactions proceed with retention of configuration for the *cis* isomers but rearrangement for the *trans,* whereas there is retention in both cases for S_N^2 reactions. These results were not anticipated but they can be nicely explained in terms of π bonding, paying particular attention to the geometries of the orbitals involved.

The cobalt (III) complexes are low-spin d^6 systems meaning that the nonbonding orbitals d_{xy}, d_{xz}, and d_{yz} each contain a pair of electrons, as do also the bonding d^2sp^3 hybrid orbitals. It is assumed that for effective π bonding some of these orbitals of relatively low energy are utilized.

For the *p* orbital electrons on oxygen of coordinated OH^- to be donated in π bonding requires a simultaneous departure of an electron pair from a filled d^2sp3 hybrid orbital, in other words the departure of the leaving group Cl^-. For a *cis* isomer the orbital overlap is reasonably good without extensive rearrangement (Fig. 1). This then is in accord with the observation that these *cis* isomers react with retention of configuration. Furthermore, since there is no rearrangement, the reactions require less energy and are faster than reactions which proceed with rearrangement. The latter seems to be the case for analogous *trans* isomers found to react more slowly than the *cis* form and to yield a mixture of *cis* and *trans* products.
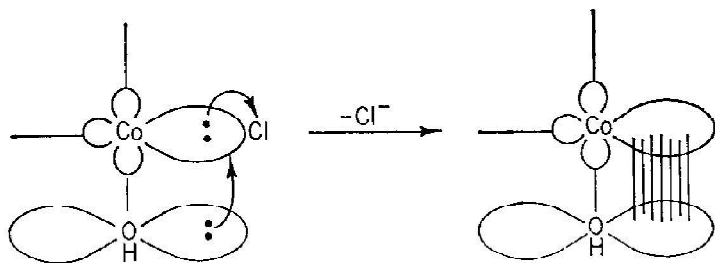
FIig.1. Dissociation mechanism for the replacement of Cl^- from cis - $[Co(en)_2OHCl]^+$. Without rearrangement, π bonding of the *p* orbital with the vacated $d2sp3$ orbital is possible.
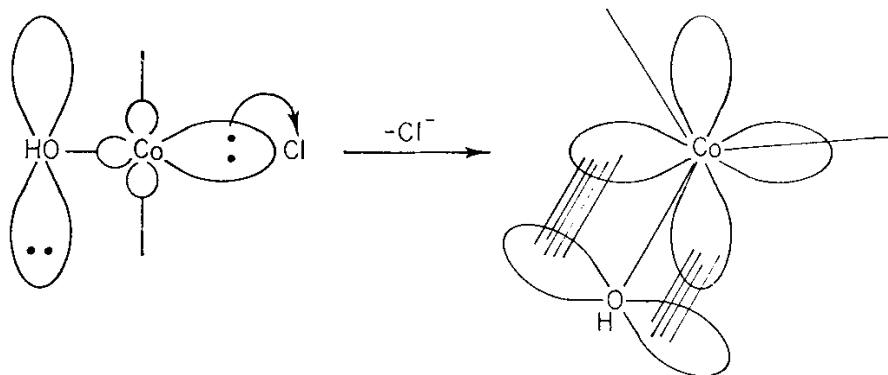
Substitution reactions in octahedral complexes

Fig.2. Dissociation mechanism for the replacement of Cl$^-$ from trans-[Co(en)$_2$OHCl]$^+$. Rearrangement to a trigonal bipyramid structure is required to permit π bonding of the p orbital with the vacated dx^2-y^2 orbital.

The schematic in Fig. 2 shows that for the *trans* isomer the filled p orbital on oxygen of the coordinated OH$^-$ cannot overlap the vacated d^2sp^3 orbital without extensive rearrangement, e.g., trigonal bipyramid dsp^3 structure giving a vacant dx^2-y^2 orbital. Assuming that the entering group (water for aquation reactions) comes in the trigonal plane, then it follows that if it enters the position opposite OH$^-$ a *trans* product results, but if it comes in at one of the two positions adjacent to OH$^-$ then a *cis* product is formed. Thus, as stated earlier, this π bonding hypothesis does adequately explain the experimental results.

For the nitro ligand which promotes an S$_N$^{2} reaction, it is seen that both isomers react with retention of configuration but that the *trans* form reacts more rapidly than does the *cis*. If the entering group attacks an octahedral face near the departing ligand *(cis attack)*, it follows that substitution takes place without rearrangement. Furthermore, attack on the *trans* isomer is facilitated by the back-donation of nonbonding d orbital electrons on cobalt (III) to the vacated p orbital of the nitro group (Fig. 3). Because of the geometry of the d orbitals, the electron density is lowered in only one of the octahedral faces for the *cis* isomer (Fig. 4). This means there is a greater stabilization of the transition state for the *trans* isomer compared to the *cis,* which in turn may account for the more rapid rate of reaction of the *trans* isomer.
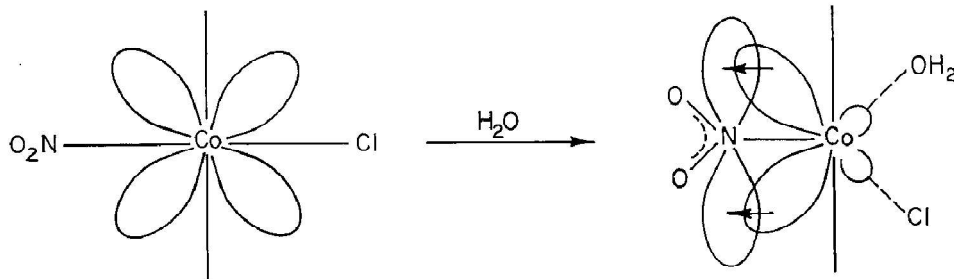
Substitution reactions in octahedral complexes

Fig. 3. Bimolecular displacement reaction of trans-$[Co(en)_2NO_2Cl]^+$. The electron withdrawal capacity of NO_2^- by π bonding decreases the electron density in the opposite octahedral faces and promotes an S_N^2 process.
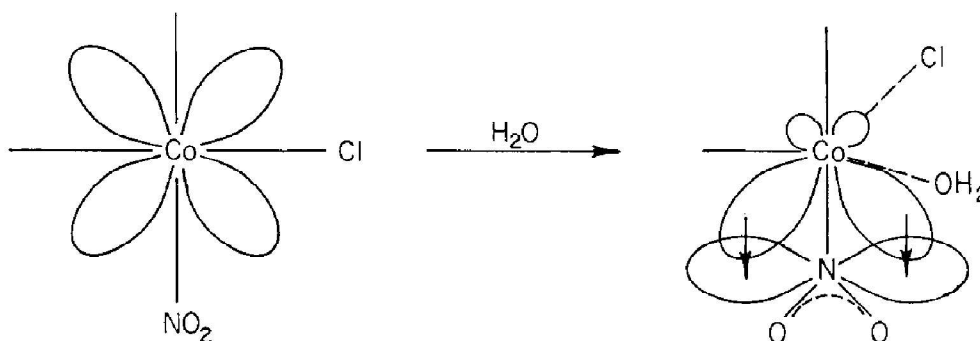

Fig. 4. Bimolecular displacement reaction of a cis-$[Co(en)_2NO_2Cl]^+$. The electronwithdrawal capacity of NO_2^- by π bonding decreases the electron density in the opposite octahedral faces but increases it in the adjacent faces; both are involved in an S_N^2 reaction.

Summarizing, aquation reactions of chloroamminecobalt(III) complexes appear to take place by an S_N^I mechanism except for systems containing ligands capable of electron withdrawal from the cobalt by π bonding. Preliminary studies suggest an S_N^2 mechanism for substitution reactions of chloroamminerhodium(III) complexes. Such a result seems reasonable on the basis of rhodium (III) having a larger size and larger effective ionic charge than cobalt (III).

Substitution reactions in octahedral complexes

The evidence for dissociative mechanism :

1. The rate of reaction changes only slightly with changes in the incoming ligand. (rate constant of less than a factor of 10)

2. Decreasing negative charge or increasing positive charge on the reactant compound decreases the rate of substitution.

3. Steric crowding on the reactant complex increases the rate of ligand dissociation.

4. The rate of reaction correlates with the metal-ligand bond strength of the leaving group, in a linear free energy relationship (LFER).

5. Activation energies and entropies are consistent with dissociation.