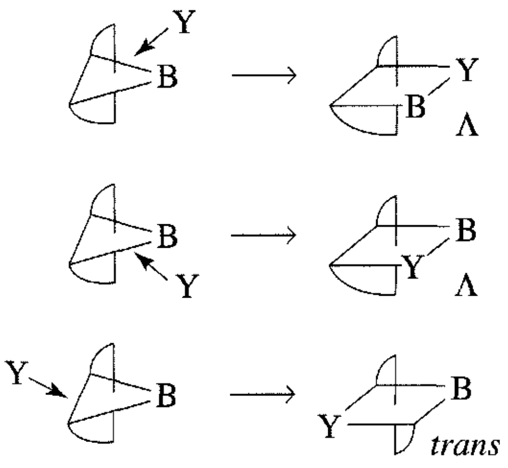
CHAPTER

12

Coordination Chemistry IV: Reactions and Mechanisms



Reactions of coordination compounds share some characteristics with reactions of other molecules, both organic and inorganic, so an understanding of coordination compound reactions can draw on some familiar concepts. However, the chemistry of coordination compounds has some additional features because the molecules have more complex geometries and more possibilities for rearrangement, the metal atoms exhibit more variability in their reactions, and different factors influence the course of reactions.

Reactions of coordination complexes can be conveniently divided into substitution reactions at the metal center, oxidation-reduction reactions, and reactions of the ligands that do not change the attachments to the metal center. Reactions that include more elaborate rearrangements of ligand structures are more often observed in organometallic compounds; description of these reactions is given in Chapter 14.

12-1

HISTORY AND PRINCIPLES

Synthesis of coordination compounds has always been a major part of chemistry. Although the early chemists did not know the structures of the compounds they worked with, they did learn how to make many of them and described them according to the style of the time. The synthetic work done by Werner, Jørgensen, and others that established the current picture of coordination geometry began the systematic development of reactions for specific purposes. Many years of experimentation and consideration of possible reaction pathways have led to the ideas described in this chapter, and even now these ideas must be considered tentative and provisional in many cases. The unification of reaction theory is still a goal of chemists, whether they work with organic, inorganic, coordination, organometallic, polymeric, solid-state, liquid, or gaseous compounds, but the goal is still far in the future. The discovery of new reactions outruns the explanations, but correlation of these reactions with theoretical explanations gradually extends our knowledge. Although the ability to predict products and choose appropriate reaction conditions to obtain the desired products is still a matter of art as well as science, the list of known reactions is now long enough to provide considerable guidance.

The goals of those studying reaction kinetics and mechanisms vary, but a major underlying reason for such studies is to understand the electronic structure of the compounds and their interactions. The information from these studies also allows more control of reactions and the design of reaction steps that may be useful for synthesis. A by-product of synthetic and kinetic studies is the esthetic pleasure of seeing the colors that are characteristic of many coordination compounds and how they change with changes in ligands and metal ions.

We will first review some of the background needed to understand reaction mechanisms, then consider the major categories of such mechanisms, and finally describe some of the results of these mechanistic studies.

In general, chemical reactions move from one energy minimum (the reactants) through a higher energy structure (the transition state) to another energy minimum (the products). In simple cases, the energies and bond distances can be shown as a three-dimensional surface, with two different bond distances along the base-plane axes and free energy as the vertical dimension. The reaction $MX + Y \longrightarrow MY + X$ begins at a point representing the short M—X distance of the bond to be broken and the longer distance between the two reactants MX and Y. As the M—X bond breaks and the M—Y bond forms, the reaction point moves to represent the short M—Y bond distance and the longer distance between the two products MY and X. The free energy surface usually has a saddle shape, much like a mountain pass between two valleys. For more complex reactions, such a visual representation is difficult or impossible, but the path between the reactants and the products is always the lowest energy pathway and must be the same regardless of the direction of the reaction. This is the **principle of microscopic reversibility**, frequently described by the mountain pass analogy; the lowest pass going in one direction must also be the lowest pass going in the opposite direction.

If the reaction is such that the conversion from reactants to products takes place with no hesitation at the transition point as in Figure 12-1(a), the structure at that state is called the **transition state**. If there is a structure that lasts a bit longer as in Figure 12-1(b), and particularly if it is detectable by some experimental means, it is called an **intermediate**. Frequently, the kinetic equations include intermediates, even if they remain undetected. Their presence allows treatment by a **steady-state approximation**, in which the concentration of the intermediate is assumed to be small and essentially unchanging during much of the reaction. Details of this approach are described later.

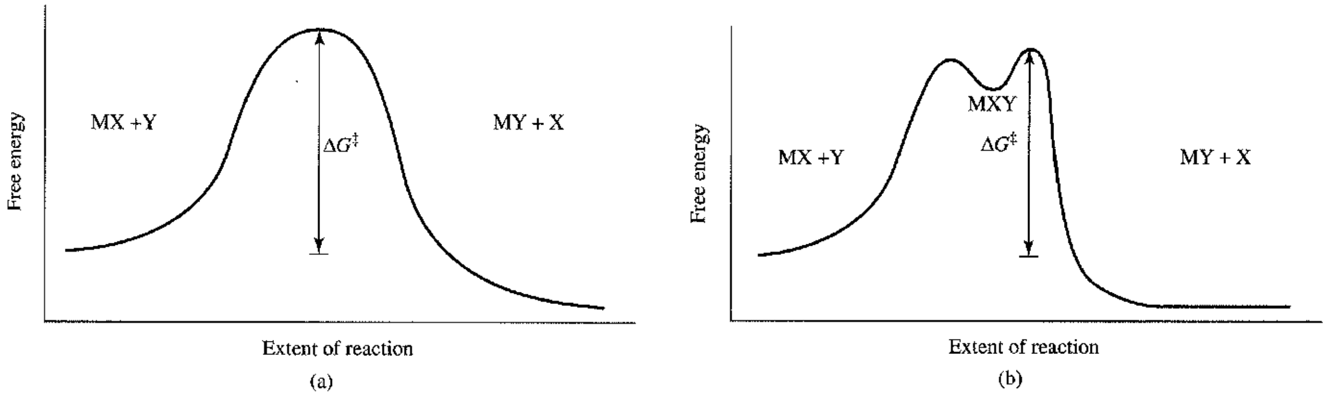


FIGURE 12-1 Energy Profiles and Intermediate Formation. (a) No intermediate. The activation energy is the energy difference between the reactants and the transition state. (b) An intermediate is present at the small minimum at the top of the curve. The activation energy is measured at the maximum point of the curve.

A number of different parameters can be obtained from kinetics experiments. First, the **order** of the reaction, indicated by the power of the reactant concentration in the differential equation that describes it, can be determined, together with the **rate constant** that describes the speed of the reaction. By studying a reaction at different temperatures, the **free energy of activation** and the **enthalpy** (or **heat**) and **entropy of activation** can be found. These allow further interpretation of the mechanism and the energy surface. A somewhat more recent inclusion of pressure dependence provides the **volume of activation**, which offers insight into whether the transition state is larger or smaller than the reactants.

12-2 SUBSTITUTION REACTIONS

12-2-1 INERT AND LABILE COMPOUNDS

Many synthetic reactions require substitution, or replacing one ligand by another; this is particularly true when the starting material is in aqueous solution, where the metal ion is likely to be in the form $[M(H_2O)_m]^{n+}$. Some simpler reactions of this type produce colored products that can be used to identify metal ions:

$$\underset{\text{blue}}{[Cu(H_2O)_6]^{2+}} + 4\,NH_3 \rightleftharpoons \underset{\text{much more intense blue}}{[Cu(NH_3)_4(H_2O)_2]^{2+}} + 4\,H_2O$$

$$\underset{\text{very pale violet}}{[Fe(H_2O)_6]^{3+}} + SCN^- \rightleftharpoons \underset{\text{red}}{[Fe(H_2O)_5(SCN)]^{2+}} + H_2O$$

These reactions, and others like them, are very fast and form species that can undergo a variety of reactions that are also very fast. Addition of $HNO_3(H^+)$, $NaCl(Cl^-)$, $H_3PO_4(PO_4^{3-})$, $KSCN(SCN^-)$, and $NaF(F^-)$ successively to a solution of $Fe(NO_3)_3\cdot 9\,H_2O$ shows this very clearly. The initial solution is yellow because of the presence of $[Fe(H_2O)_5(OH)]^{2+}$ and other "hydrolyzed" species containing both water and hydroxide ion. Although the exact species formed in this series depend on solution concentrations, the products in the reactions given here are representative:

$$\underset{\text{yellow}}{[Fe(H_2O)_5(OH)]^{2+}} + H^+ \longrightarrow \underset{\text{colorless (very pale violet)}}{[Fe(H_2O)_6]^{3+}}$$

$$[Fe(H_2O)_6]^{3+} + Cl^- \longrightarrow \underset{\text{yellow}}{[Fe(H_2O)_5(Cl)]^{2+}} + H_2O$$

$$[Fe(H_2O)_5(Cl)]^{2+} + PO_4^{3-} \longrightarrow \underset{\text{colorless}}{Fe(H_2O)_5(PO_4)} + Cl^-$$

$$Fe(H_2O)_5(PO_4) + SCN^- \longrightarrow \underset{\text{red}}{[Fe(H_2O)_5(SCN)]^{2+}} + PO_4^{3-}$$

$$[Fe(H_2O)_5(SCN)]^{2+} + F^- \longrightarrow \underset{\text{colorless}}{[Fe(H_2O)_5(F)]^{2+}} + SCN^-$$

Compounds such as these that react rapidly are called **labile** (lā′-bil). In many cases, exchange of one ligand for another can take place in the time of mixing the solutions. Taube[1] has suggested a reaction half-life (the time of disappearance of half the initial compound) of one minute or less as the criterion for lability. Compounds that

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[1] H. Taube, *Chem. Rev.*, **1952**, *50*, 69.

react more slowly are called **inert** or **robust** (a term used less often). An inert compound is not inert in the usual sense that no reaction can take place; it is simply slower to react. These kinetic terms must also be distinguished from the thermodynamic terms **stable** and **unstable**. A species such as $[Fe(H_2O)_5(F)]^{2+}$ is very stable (has a large equilibrium constant for formation), but it is also labile. On the other hand, hexaaminecobalt(3+) is thermodynamically unstable in acid and can decompose to the equilibrium mixture on the right

$$[Co(NH_3)_6]^{3+} + 6\,H_3O^+ \rightleftharpoons [Co(H_2O)_6]^{3+} + 6\,NH_4^+\ (\Delta G^\circ < 0)$$

but it reacts very slowly (has a very high activation energy) and is therefore called inert or robust. The possible confusion of terms is unfortunate, but no other terminology has gained general acceptance. One possibility is to call the compounds **substitutionally** or **kinetically labile** or **inert**, but these terms are not in general use at this time.

Werner studied cobalt(III), chromium(III), platinum(II), and platinum(IV) compounds because they are inert and can be more readily characterized than labile compounds. This tendency has continued, and much of the discussion in this chapter is based on inert compounds because they can be more easily crystallized from solution and their structures determined. Labile compounds have also been studied extensively, but their study requires techniques capable of dealing with very short times (stopped flow or relaxation methods, for example, temperature or pressure jump, nuclear magnetic resonance).

Although there are exceptions, general rules can be given for inert and labile electronic structures. Inert octahedral complexes are generally those with high ligand field stabilization energies (described in Chapter 10), specifically those with d^3 or low-spin d^4 through d^6 electronic structures. Complexes with d^8 configurations generally react somewhat faster, but slower than the d^7, d^9, or d^{10} compounds. With strong-field ligands, d^8 atoms form square-planar complexes, many of which are inert. Compounds with any other electronic structures tend to be labile. Summarizing, we get:

Slow Reactions (Inert)	*Intermediate*	*Fast Reactions (Labile)*
d^3, low-spin d^4, d^5, and d^6		d^1, d^2, high-spin d^4, d^5, and d^6
Strong-field d^8 (square planar)	Weak-field d^8	d^7, d^9, d^{10}

12-2-2 MECHANISMS OF SUBSTITUTION

Langford and Gray[2] have described the range of possibilities for substitution reactions, listed in Table 12-1. At one extreme, the departing ligand leaves and a discernible intermediate with a lower coordination number is formed, a mechanism labeled ***D*** for **dissociation**. At the other extreme, the incoming ligand adds to the complex and an intermediate with an increased coordination number (discernible either by kinetic or analytical methods) is formed in a mechanism labeled *A* for **association**. Between the two extremes is **interchange, *I***, in which the incoming ligand is presumed to assist in the reaction but no detectable intermediates appear. When the degree of assistance is small and the reaction is primarily dissociative, it is called **dissociative interchange, I_d**. When the incoming ligand begins forming a bond to the central atom before the departing ligand bond is weakened appreciably, it is called **associative interchange, I_a**. Many reactions are described by I_a or I_d mechanisms rather than by *A* or *D* when the kinetic evidence points to association or dissociation but detection of intermediates is not possible. Langford and Gray call these categories the **stoichiometric mechanisms**; the distinction between activation processes that are associative and dissociative is called the

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[2] C. H. Langford and H. B. Gray, *Ligand Substitution Processes*, W. A. Benjamin, New York, 1966.

TABLE 12-1
Classification of Substitution Mechanisms

	Stoichiometric Mechanism		
Intimate Mechanism	*Dissociative 5-Coordinate Transition State for Octahedral Reactant*		*Associative 7-Coordinate Transition State for Octahedral Reactant*
Dissociative activation	*D*	I_d	
Associative activation		I_a	*A*
	Alternative Labels		
S_N1 lim (limiting first-order nucleophilic substitution)			S_N2 lim (limiting second-order nucleophilic substitution)

intimate mechanism. The energy profiles for associative and dissociative reactions are shown in Figure 12-2. The clear separation of these two mechanisms in the figure should not be taken as an indication that the distinction is easily made. In many cases, there is no clear-cut evidence to distinguish them, and inferences must be made by using the available evidence.

Kinetic experiments are frequently carried out with large excess of the incoming reagent, Y. This simplifies the analysis of the progress of the reaction for each kinetic run, but requires a number of runs at different concentrations of Y to determine the order of the reaction with respect to Y.

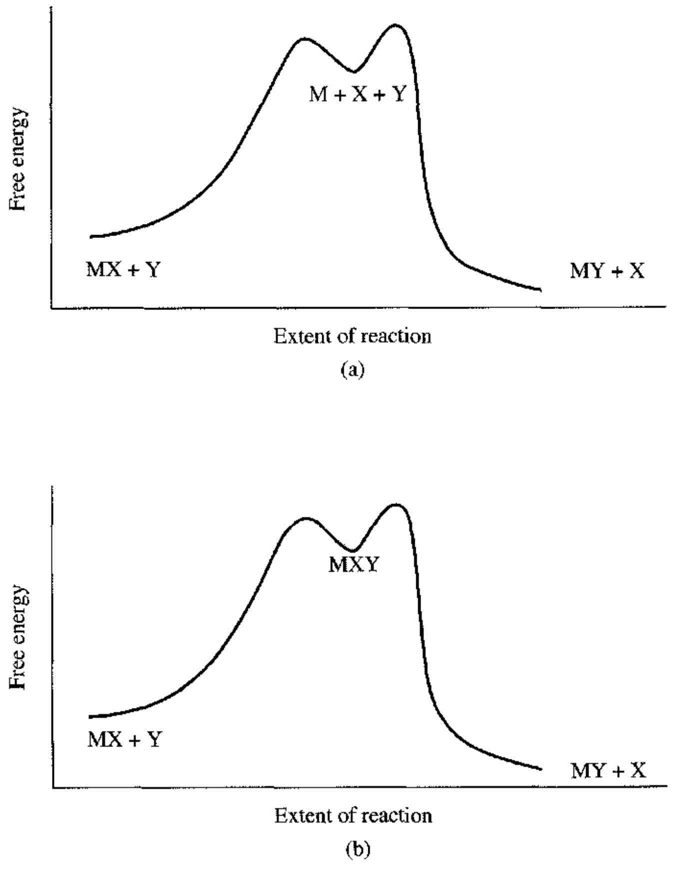

FIGURE 12-2 Energy Profiles for Dissociative and Associative Reactions. (a) Dissociative mechanism. The intermediate has a lower coordination number than the starting material. (b) Associative mechanism. The intermediate has a higher coordination number than the reactant.

12-3 KINETIC CONSEQUENCES OF REACTION PATHWAYS

Although the kinetic rate law is helpful in determining the mechanism of a reaction, it does not always provide sufficient information. In cases of ambiguity, other evidence must be used to find the mechanism. This chapter will describe a number of examples in which the rate law and other experimental evidence have been used to find the mechanism of a reaction. Our goal is to provide two related types of information: (1) the type of information that is used to determine mechanisms, and (2) a selection of specific reactions for which the mechanisms seem to be fairly completely determined. The first is the more important, because it enables a chemist to examine data for other reactions critically and to evaluate the proposed mechanisms. The second is also helpful, because it provides part of the collection of knowledge that is required for designing new syntheses. Each of the substitution mechanisms is described with its required rate law.[3]

12-3-1 DISSOCIATION (*D*)

In a dissociative (*D*) reaction, loss of a ligand to form an intermediate with a lower coordination number is followed by addition of a new ligand to the intermediate:

$$\mathrm{ML_5X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_5 + X}$$

$$\mathrm{ML_5 + Y} \xrightarrow{k_2} \mathrm{ML_5Y}$$

The stationary-state (or steady-state) hypothesis assumes a very small concentration of the intermediate, $\mathrm{ML_5}$, and requires that the rates of formation and reaction of the intermediate must be equal. This in turn requires that the rate of change of $[\mathrm{ML_5}]$ be zero during much of the reaction. Expressed as a rate equation,

$$\frac{d[\mathrm{ML_5}]}{dt} = k_1[\mathrm{ML_5X}] - k_{-1}[\mathrm{ML_5}][\mathrm{X}] - k_2[\mathrm{ML_5}][\mathrm{Y}] = 0$$

Solving for $[\mathrm{ML_5}]$,

$$[\mathrm{ML_5}] = \frac{k_1[\mathrm{ML_5X}]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

and substituting into the rate law for formation of the product,

$$\frac{d[\mathrm{ML_5Y}]}{dt} = k_2[\mathrm{ML_5}][\mathrm{Y}]$$

leads to the rate law:

$$\frac{d[\mathrm{ML_5Y}]}{dt} = \frac{k_2k_1[\mathrm{ML_5X}][\mathrm{Y}]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

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[3] In the reactions of this chapter, X will indicate the ligand that is leaving a complex, Y the ligand that is entering, and L any ligands that are unchanged during the reaction. In cases of solvent exchange, all (X, Y, and L) may be chemically the same species, but in the more general case they may all be different. Charges will be omitted in the general case, but remember that any of the species may be ions. The general examples will usually be 6-coordinate, but other coordination numbers could be chosen and the discussion would be similar.

One criterion for this mechanism is that the intermediate, ML_5, be detectable during the reaction. Direct detection at the low concentrations expected is a very difficult experimental challenge, and there are very few clear-cut dissociative reactions. More often, the evidence is indirect, but no intermediate has been found. Such reactions are usually classified as following an interchange mechanism.

12-3-2 INTERCHANGE (*I*)

In an interchange (*I*) reaction, a rapid equilibrium between the incoming ligand and the 6-coordinate reactant forms an ion pair or loosely bonded molecular combination. This species, which is not described as having an increased coordination number and is not directly detectable, then reacts to form the product and release the initial ligand.

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5X{\cdot}Y$$

$$ML_5X{\cdot}Y \xrightarrow{k_2} ML_5Y + X$$

When $k_2 \ll k_{-1}$, the reverse reaction of the first step is fast enough that this step is independent of the second step, and the first step is an equilibrium with $K_1 = k_1/k_{-1}$.

Applying the stationary-state hypothesis:

$$\frac{d[ML_5X{\cdot}Y]}{dt} = k_1[ML_5X][Y] - k_{-1}[ML_5X{\cdot}Y] - k_2[ML_5X{\cdot}Y] = 0$$

If [Y] is large compared with $[ML_5X]$ (a common experimental condition), the concentration of the unstable transition species may be large enough to significantly change the concentration of the ML_5X, but not that of Y. For this reason, we must solve for this species in terms of the total initial reactant concentrations of ML_5X and Y, which we will call $[M]_0$ and $[Y]_0$:

$$[M]_0 = [ML_5X] + [ML_5X{\cdot}Y]$$

Assuming that the concentration of the final product, $[ML_5Y]$, is too small to change the concentration of Y significantly, then

$$[Y]_0 \cong [Y]$$

From the stationary-state equation,

$$k_1([M]_0 - [ML_5X{\cdot}Y])[Y]_0 - k_{-1}[ML_5X{\cdot}Y] - k_2[ML_5X{\cdot}Y] = 0$$

The final rate equation then becomes

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5X{\cdot}Y] = \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0 + (k_2/k_{-1})} \cong \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0}$$

where k_2/k_{-1} is very small and can be omitted because $k_2 \ll k_{-1}$ is required for the first step to be an equilibrium.

K_1 can be measured experimentally in some cases and estimated theoretically in others from calculation of the electrostatic energy of the interaction, with fair agreement in cases in which both methods have been used.

Two variations on the interchange mechanism are I_d (dissociative interchange) and I_a (associative interchange). The difference between them is in the degree of bond formation in the first step of the mechanism. If bonding between the incoming ligand and the metal is more important, it is an I_a mechanism. If breaking the bond between the leaving ligand and the metal is more important, it is an I_d mechanism. The distinction between them is subtle, and careful experimental design is required to determine which description fits a given reaction.

As can be seen from these equations, both *D* and *I* mechanisms have the same mathematical form for their rate laws. (If both the numerator and the denominator of the *D* rate law are divided by k_{-1}/k_{-1}, the equations have the similar forms shown here.)

$$\text{Rate} = \frac{k[\text{M}][\text{Y}]}{[\text{X}] + k'[\text{Y}]} \qquad\qquad \text{Rate} = \frac{k[\text{M}]_0[\text{Y}]_0}{1 + k'[\text{Y}]_0}$$

At low [Y], the denominator simplifies to [X] for the dissociative and to 1 for the interchange equation. Both then are second order (first order in M and Y, rate $= k[\text{M}]_0[\text{Y}]_0$ or $k[\text{M}]_0[\text{Y}]_0/[\text{X}]$), with the rate of the dissociative reaction slowing as more free X is formed.

At high [Y], a common condition in kinetic experiments, the second term in the denominator is larger, $[\text{X}] + k'[\text{Y}] = k'[\text{Y}]$ and $1 + k'[\text{Y}]0 = k'[\text{Y}]0$, and [Y] cancels, making the reaction first order in complex and zero order in Y (rate $= (k/k')[\text{M}]_0$).

The change from one rate law to the other depends on the specific values of the rate constants. The similarity of the rate laws limits their usefulness in determining the mechanism and requires other means of distinguishing between different mechanisms.

12-3-3 ASSOCIATION (*A*)

In an associative reaction, the first step, forming an intermediate with an increased coordination number, is the rate-determining step. It is followed by a faster reaction in which the leaving ligand is lost:

$$\text{ML}_5\text{X} + \text{Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{ML}_5\text{XY}$$

$$\text{ML}_5\text{XY} \xrightarrow{k_2} \text{ML}_5\text{Y} + \text{X}$$

The same stationary-state approach used in the other rate laws results in the rate law

$$\frac{d[\text{ML}_5\text{Y}]}{dt} = \frac{k_1 k_2[\text{ML}_5\text{X}][\text{Y}]}{k_{-1} + k_2} = k[\text{ML}_5\text{X}][\text{Y}]$$

This is a second-order equation regardless of the concentration of Y.

EXERCISE 12-1

Show that the preceding equation is the result of the stationary-state approach for an associative reaction.

As with the dissociative mechanism, there are very few clear examples of associative mechanisms in which the intermediate is detectable. Most reactions fit better between the two extremes, following associative or dissociative interchange mechanisms. The next section summarizes the evidence for the different mechanisms.

12-4 EXPERIMENTAL EVIDENCE IN OCTAHEDRAL SUBSTITUTION

12-4-1 DISSOCIATION

Most substitution reactions of octahedral complexes are believed to be dissociative, with the complex losing one ligand to become a 5-coordinate square pyramid in the transition state and the incoming ligand filling the vacant site to form the new octahedral product. Theoretical justification for the inert and labile classifications of Section 12-2-1 comes from ligand field theory, with calculation of the change in LFSE between the octahedral reactant and the presumed 5-coordinate transition state, either square-pyramidal or trigonal-bipyramidal in shape. Table 12-2 gives the **ligand field activation energy** (LFAE), calculated as the difference between the LFSE of the square-pyramidal transition state and the LFSE of the octahedral reactant. LFAEs calculated for trigonal-bipyramidal transition states are generally the same or larger than those for square-pyramidal transition states. These calculations provide estimates of the energy necessary to form the transition state. When combined with the general change in enthalpies of formation described in Section 10-6, and particularly Figure 10-27, the activation energies of the square-pyramidal transition state match the experimental facts (d^3 and d^8 complexes are inert in both the strong- and weak-field cases, and d^6 strong-field complexes are inert). Examination of these numbers shows that the activation energies of the square-pyramidal transition state match the experimental facts (d^3, low-spin d^4 through d^6, and d^8 are inert). Therefore, the calculation of LFAE supports a square-pyramidal geometry (and a dissociative mechanism) for the transition state. However, all these numbers assume an idealized geometry not likely to be found in practice, and the LFAE is only one factor that must be considered in any reaction.

TABLE 12-2
Ligand Field Activation Energies Calculated by Angular Overlap

	Strong Fields (units of e_σ)			*Weak Fields (units of e_σ)*		
System	*LFSE Octahedral*	*LFSE Square pyramidal*	***LFAE***	*LFSE Octahedral*	*LFSE Square pyramidal*	***LFAE***
d^0	−12	−10	2	−12	−10	2
d^1	−12	−10	2	−12	−10	2
d^2	−12	−10	2	−12	−10	2
d^3	−12	−10	2	−12	−10	2
d^4	−12	−10	2	−9	−8	1
d^5	−12	−10	2	−6	−5	1
d^6	−12	−10	2	−6	−5	1
d^7	−9	−8	1	−6	−5	1
d^8	−6	−5	1	−6	−5	1
d^9	−3	−3	0	−3	−3	0
d^{10}	0	0	0	0	0	0

NOTE: For a square-pyramidal transition state, LFAE = LFSE (sq. pyr.) − LFSE (oct.), for σ donor only.

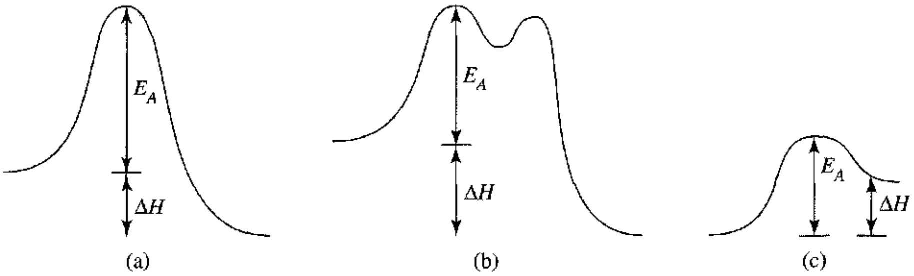

FIGURE 12-3 Activation Energies and Reaction Enthalpies. (a), (b), Large E_a, slow reaction. (c) Small E_a, fast reaction. (a), (b), $\Delta H < 0$, large equilibrium constant; (c) $\Delta H > 0$, small equilibrium constant. In (b), the intermediate is potentially detectable.

Even for thermodynamically favorable reactions, a large activation energy means that the reaction will be slow. For thermodynamically unfavorable reactions, even a fast reaction (with small activation energy) would be unlikely to occur. The rate of reaction depends on the activation energy, as in the Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = \ln A - \frac{E_a}{RT}$$

Some of the possible energy relationships for reactions are shown in Figure 12-3. In (a) and (b), the reaction is exothermic ($\Delta H < 0$), and the equilibrium constant is large (entropy effects could be important, but are ignored for this discussion). In (a), the reaction is spontaneous ($\Delta H < 0$), but E_a is large, so few molecules have enough energy to get over the barrier and the reaction is slow. In (b), the reaction is spontaneous, with an intermediate at the dip near the top of the activation energy curve. Intermediates of this sort are frequently described, but can be detected and identified in only a few cases. In (c), the reaction can go quickly because of the low activation energy, but has a small equilibrium constant because the overall enthalpy change is positive.

When s and p orbital influences are added, the results are similar to those of the thermodynamic case of enthalpy of hydration shown in Figure 10-7, with long half-lives for d^3 and d^8 and short half-lives for d^0, d^4, d^9, and as shown in Figure 12-4.

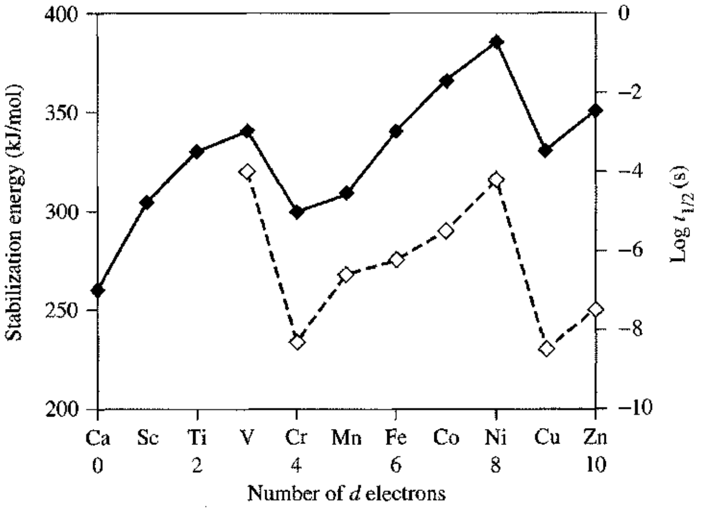

FIGURE 12-4 Stabilization Energy and Experimental Half-Lives for Water Exchange. (Angular overlap data (*solid line*) from J. K. Burdett, *J. Chem. Soc. Dalton*, **1976**, 1725. Half-lives for water exchange (*dashed line*) from F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., John Wiley & Sons, New York, 1967, p. 155.)

Other metal ion factors that affect reaction rates of octahedral complexes include the following (relative rates for ligand exchange are indicated by the inequalities):

1. *Oxidation state of the central ion.* Central ions with higher oxidation states have slower ligand exchange rates.

$$\underset{3+}{[AlF_6]^{3-}} > \underset{4+}{[SiF_6]^{2-}} > \underset{5+}{[PF_6]^{-}} > \underset{6+}{SF_6}$$

$$\underset{1+}{[Na(H_2O)_n]^{+}} > \underset{2+}{[Mg(H_2O)_n]^{2+}} > \underset{3+}{[Al(H_2O)_6]^{3+}}$$

2. *Ionic radius.* Smaller ions have slower exchange rates.

$$\underset{112\text{ pm}}{[Sr(H_2O)_6]^{2+}} > \underset{99\text{ pm}}{[Ca(H_2O)_6]^{2+}} > \underset{66\text{ pm}}{[Mg(H_2O)_6]^{2+}}$$

Both effects can be attributed to a higher electrostatic attraction between the central atom and the attached ligands. A strong attraction between the two will slow the reaction, because reaction is presumed to require dissociation of a ligand from the complex. Figure 12-4 shows the half-lives for exchange of water molecules on aquated 2+ transition metal ions. All the ions in the figure are labile, with half-lives for the aqua complexes shorter than 1 second; measurement of such fast reactions is done by indirect methods, particularly relaxation methods[4] (including temperature jump, pressure jump, and NMR). The monovalent alkali metal cations have very short half-lives (10^{-9} second or less); of the common 2+ metal ions, only Be^{2+} and V^{2+} have half-lives as long as 0.01 second. Al^{3+} has a half-life approaching 1 second, and Cr^{3+} has a half-life of 40 hours, the only inert aquated transition metal ion.

The evidence for dissociative mechanisms can be grouped as follows:[5, 6, 7, 8]

1. The rate of reaction changes only slightly with changes in the incoming ligand. In many cases, **aquation** (substitution by water) and **anation** (substitution by an anion) rates are comparable. If dissociation is the rate-determining reaction, the entering group should have no effect at all on the reaction rate. Although there is no specific criterion for this, changes in rate constant of less than a factor of 10 are generally considered to be insignificant for this purpose.
2. Decreasing negative charge or increasing positive charge on the reactant complex decreases the rate of substitution. Larger electrostatic attraction between the positive metal ion and the negative ligand should slow the dissociation.
3. Steric crowding on the reactant complex increases the rate of ligand dissociation. When ligands on the reactant are crowded, loss of one of the ligands is made easier. On the other hand, if the reaction has an A or I_a mechanism, steric crowding interferes with the incoming ligand and slows the reaction.

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[4] F. Wilkinson, *Chemical Kinetics and Reactions Mechanisms*, Van Nostrand-Reinhold, New York, 1980, pp. 83–91.

[5] F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., John Wiley & Sons, New York, 1967, pp. 158–170.

[6] R. G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Allyn and Bacon, Boston, 1974, pp. 193–196.

[7] J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole, Monterey, CA, 1985, pp. 82–83.

[8] C. H. Langford and T. R. Stengle, *Ann. Rev. Phys. Chem.*, **1968**, *19*, 193.

4. The rate of reaction correlates with the metal-ligand bond strength of the leaving group, in a linear free energy relationship (LFER, explained in the next section).
5. Activation energies and entropies are consistent with dissociation, although interpretation of these parameters is difficult. Another activation parameter now being measured by experiments at increased pressure is the volume of activation, the change in volume on forming the activated complex. Dissociative mechanisms generally result in positive values for ΔV_{act} because one species splits into two, and associative mechanisms result in negative ΔV_{act} values because two species combine into one, with a presumed volume smaller than the total for the reactants. However, caution is needed in interpreting volume effects because solvation effects, particularly for highly charged ions, may be larger than the difference expected for the reaction otherwise.

12-4-2 LINEAR FREE ENERGY RELATIONSHIPS

Many kinetic effects can be related to thermodynamic effects by a **linear free energy relationship (LFER)**.[9] Such effects are seen when, for example, the bond strength of a metal-ligand bond (a thermodynamic function) plays a major role in determining the dissociation rate of that ligand (a kinetic function). When this is true, a plot of the logarithm of the rate constants (kinetic) for different leaving ligands versus the logarithm of the equilibrium constants (thermodynamic) for the same ligands in similar compounds is linear. The justification for this correlation is found in the Arrhenius equation for temperature dependence of rate constants and the equation for temperature dependence of equilibrium constants. In logarithmic form, they are

$$\underset{\text{kinetic}}{\ln k = \ln A - \frac{E_a}{RT}} \quad \text{and} \quad \underset{\text{thermodynamic}}{\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}}$$

If the pre-exponential factor, A, and the entropy, ΔS°, are nearly constant and the activation energy, E_a, depends on the enthalpy of reaction, ΔH°, there will be a linear correlation between $\ln k$ and $\ln K$. A straight line on such a log-log plot is indirect evidence for a strong influence of the thermodynamic parameter, ΔH°, on the activation energy of the reaction. In molecular bonding terms, a stronger bond between the metal and the leaving group results in a larger activation energy, a logical connection for a dissociative mechanism. Figure 12-5 shows an example from the hydrolysis of $[Co(NH_3)_5X]^{2+}$:

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$$

From this evidence, Langford[10] argued that the X^- group is essentially completely dissociated and acts as a solvated anion in the transition state of acid hydrolysis and that water is at most weakly bound in the transition state. Another example from reactions of square-planar platinum complexes is given in Section 12-6-2.

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[9] J. W. Moore and R. G. Pearson, *Kinetics and Mechanism*, 3rd ed., John Wiley & Sons, New York, 1981, pp. 357–363.

[10] C. H. Langford, *Inorg. Chem.*, **1965**, *4*, 265.

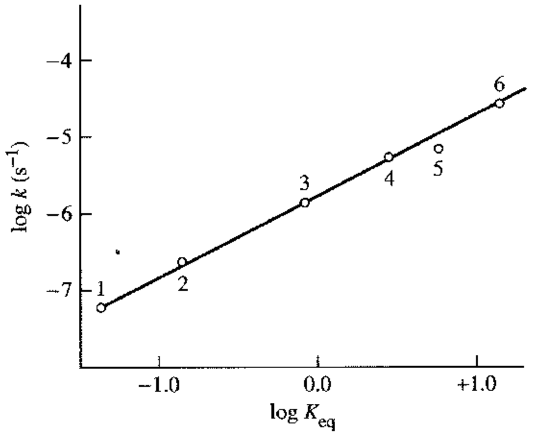

FIGURE 12-5 Linear Free Energy and $[Co(NH_3)_5X]^{2+}$ Hydrolysis. The log of the rate constant is plotted against the log of the equilibrium constant for the acid hydrolysis reaction of $[Co(NH_3)_5X]^{2+}$ ions. Measurements were made at 25.0°C. Points are designated as follows: 1, $X^- = F^-$; 2, $X^- = H_2PO_4^-$; 3, $X^- = Cl^-$; 4, $X^- = Br^-$; 5, $X^- = I^-$; 6, $X^- = NO_3^-$. (Reproduced with permission from C. H. Langford, *Inorg. Chem.*, **1965**, *4*, 265. Data for F^- from S. C. Chan, *J. Chem. Soc.*, **1964**, 2375, and for I^- from R. G. Yalman, *Inorg. Chem.*, **1962**, *1*, 16. All other data from A. Haim and H. Taube, *Inorg. Chem.*, **1964**, *3*, 1199.)

Examples of the effect (or lack of effect) of incoming ligand are given in Tables 12-3 and 12-4. In Table 12-3, the data are for the first-order region (large [Y]). The k_1 column gives the rate constants for anion exchange; the $k_1/k_1(H_2O)$ shows the ratio of k_1 to the rate for water exchange. The rate constants are all relatively close to that for water exchange, as would be expected for a dissociative mechanism. Table 12-4 gives

TABLE 12-3
Limiting Rate Constants for Anation or Water Exchange of $[Co(NH_3)_5H_2O]^{3+}$ at 45°C.

$$[Co(NH_3)_5H_2O]^{3+} + Y^{m-} \longrightarrow [Co(NH_3)_5Y]^{(3-m)+} + H_2O$$

Y^{m-}	k_1 (10^{-6} s^{-1})	$k_1/k_1(H_2O)$	Reference
H_2O	100	1.0	a
N_3^-	100	1.0	b
SO_4^{2-}	24	0.24	c
Cl^-	21	0.21	d
NCS^-	16	0.16	d

SOURCES: [a] W. Schmidt and H. Taube, *Inorg. Chem.*, **1963**, *2*, 698.
[b] H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **1958**, *75*, 1463.
[c] T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **1969**, *8*, 1604.
[d] C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, **1967**, *89*, 3141.

TABLE 12-4
Rate Constants for Substitution on $[Ni(H_2O)_6]^{2+}$

Y	k_0K_0 (10^3 M^{-1} s^{-1})	K_0 (M^{-1})	k_0 (10^4 s^{-1})
$CH_3PO_4^{2-}$	290	40	0.7
CH_3COO^-	100	3	3
NCS^-	6	1	0.6
F^-	8	1	0.8
HF	3	0.15	2
H_2O			3
NH_3	5	0.15	3
C_5H_5N, pyridine	~4	0.15	~3
$C_4H_4N_2$, pyrazine	2.8	0.15	2
$NH_2(CH_2)_2NMe_3^+$	0.4	0.02	2

SOURCE: Adapted with permission from R. G. Wilkins, *Acc. Chem. Res.*, **1970**, *3*, 408; $C_4H_4N_2$ data are from J. M. Malin and R. E. Shepherd, *J. Inorg. Nucl. Chem.*, **1972**, *34*, 3203.

data for the second-order region for anation of $[Ni(H_2O)_6]^{2+}$. The second-order rate constant, k_0K_0, is the product of the ion pair equilibrium constant, K_0, and the rate constant, k_0:

$$Ni{-}OH_2 + L \rightleftharpoons Ni{-}OH_2{\cdot}L \qquad K_0$$

$$Ni{-}OH_2{\cdot}L \longrightarrow Ni{-}L + H_2O \qquad k_0$$

K_0 is calculated from an electrostatic model that provides good agreement with the few cases in which experimental evidence is also available. The rate constant, k_0, varies by a factor of 5 or less and is close to the rate constant for the exchange of water. The close agreement for the wide variety of different ligands shows that the effect of the incoming ligand on the second step is minor, although the difference in ion pair formation is significant. Both these reactions are consistent with D or I_d mechanisms, with ion pair formation likely as the first step in the nickel reactions.

12-4-3 ASSOCIATIVE MECHANISMS

Associative reactions are also possible in octahedral substitution, but are much less common.[11] Table 12-5 gives data for both dissociative and associative interchanges for similar reactants. In the case of water substitution by several different anions in $[Cr(NH_3)_5(H_2O)]^{3+}$, the rate constants are quite similar (within a factor of 6), indicative of an I_d mechanism. On the other hand, the same ligands reacting with $[Cr(H_2O)_6]^{3+}$ show a large variation in rates (more than a 2000-fold difference), indicative of an I_a mechanism. Data for similar Co(III) complexes are not conclusive, but their reactions generally seem to have I_d mechanisms.

Reactions of Ru(III) compounds frequently have associative mechanisms and those of Ru(II) compounds have dissociative mechanisms. The entropies of activation for substitution reactions of $[Ru(III)(EDTA)(H_2O)]^-$ are negative, indicating association as part of the transition state. They also show a very large range of rate constants

TABLE 12-5
Effects of Entering Group and *cis*-Ligands on Rates

	Rate Constants for Anation	
Entering Ligand	$[Cr(H_2O)_6]^{3+}$ $k\ (10^{-8}\ M^{-1}\ s^{-1})$	$[Cr(NH_3)_5H_2O]^{3+}$ $k\ (10^{-4}\ M^{-1}\ s^{-1})$
NCS^-	180	4.2
NO_3^-	73	—
Cl^-	2.9	0.7
Br^-	1.0	3.7
I^-	0.08	—
CF_3COO^-	—	1.4

SOURCE: Reproduced with permission from J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Books/Cole, Monterey, CA, 1985, p. 85; data from D. Thusius, *Inorg. Chem.*, **1971**, *10*, 1106; T. Ramasami and A. G. Sykes, *Chem. Commun. (Cambridge)*, **1978**, 378.

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[11] Atwood, *Inorganic and Organometallic Reaction Mechanisms*, p. 85.

TABLE 12-6
Rate Constants for $[Ru(III)(EDTA)(H_2O)]^-$ Substitution

Ligand	$k_1 (M^{-1}\ s^{-1})$	$\Delta H^\ddagger$ $(kJ\ mol^{-1})$	$\Delta S^\ddagger$ $(J\ mol^{-1}\ K^{-1})$
Pyrazine	20,000 ± 1,000	5.7 ± 0.5	−20 ± 3
Isonicotinamide	8,300 ± 600	6.6 ± 0.5	−19 ± 3
Pyridine	6,300 ± 500		
Imidazole	1,860 ± 100		
SCN^-	270 ± 20	8.9 ± 0.5	−18 ± 3
CH_3CN	30 ± 7	8.3 ± 0.5	−24 ± 4

SOURCE: T. Matsubara and C. Creutz, *Inorg. Chem.*, **1979**, *18*, 1956.

TABLE 12-7
Rate Constants for $[Ru(II)(EDTA)(H_2O)]^{2-}$ Substitution

Ligand	$k_1 (M^{-1}\ s^{-1})$
Isonicotinamide	30 ± 15
CH_3CN	13 ± 1
SCN^-	2.7 ± 0.2

SOURCE: T. Matsubara and C. Creutz, *Inorg. Chem.*, **1979**, *18*, 1956.

depending on the incoming ligand (Table 12-6), as required for an I_a mechanism, but those of Ru(II) (Table 12-7) are nearly the same for different ligands, as required for an I_d mechanism. The reasons for this difference are not certain. Both complexes have a free carboxylate (the EDTA is pentadentate, with the sixth position occupied by a water molecule). Hydrogen bonding between this free carboxylate and the bound water may distort the shape sufficiently in the Ru(III) complex to open a place for entry by the incoming ligand. Although similar hydrogen bonding may be possible for the Ru(II) complex, the increased negative charge may reduce the $Ru—H_2O$ bond strength enough to promote dissociation.

12-4-4 THE CONJUGATE BASE MECHANISM

Other cases in which second-order kinetics seemed to require an associative mechanism have subsequently been found to have a **conjugate base mechanism**[12] (called S_N1CB, for substitution, nucleophilic, unimolecular, conjugate base in Ingold's notation[13]). These reactions depend on amine, ammine, or aqua ligands that can lose protons to form amido or hydroxo species that are then more likely to lose one of the other ligands. If the structure allows it, the ligand *trans* to the amido or hydroxo group is frequently the one lost.

$$[Co(NH_3)_5X]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4(NH_2)X]^+ + H_2O \quad \text{(equilibrium)} \qquad (1)$$

$$[Co(NH_3)_4(NH_2)X]^+ \longrightarrow [Co(NH_3)_4(NH_2)]^{2+} + X^- \quad \text{(slow)} \qquad (2)$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(OH)]^{2+} \quad \text{(fast)} \qquad (3)$$

Overall,

$$[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$$

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[12] Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*, pp. 207–210; Basolo and Pearson, *Mechanisms of Inorganic Reactions*, pp. 177–193.

[13] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, NY, 1953, Chapters 5 and 7.

In the third step, addition of a ligand other than water is also possible; in basic solution, the rate constant is k_{OH} and the equilibrium constant for the overall reaction is K_{OH}.

Additional evidence for the conjugate base mechanism has been provided by several related studies:

1. Base-catalyzed exchange of hydrogen from the amine groups takes place under the same conditions as these reactions.
2. The isotope ratio ($^{18}O/^{16}O$) in the product in ^{18}O-enriched water is the same as that in the water regardless of the leaving group ($X^- = Cl^-, Br^-, NO_3^-$). If an incoming water molecule had a large influence (an associative mechanism), a higher concentration of ^{18}O should be in the product, because the equilibrium constant $K = 1.040$ for the reaction
$$H_2{}^{16}O + {}^{18}OH^- \rightleftharpoons H_2{}^{18}O + {}^{16}OH^-$$
3. RNH_2 compounds (R = alkyl) react faster than NH_3 compounds, possibly because steric crowding favors the 5-coordinate intermediate formed in Step 2.
4. The rate constants and dissociation constants for these compounds form a linear free energy relationship (LFER), in which a plot of ln k_{OH} versus ln K_{OH} is linear.
5. When substituted amines are used, and there are no protons on the nitrogens available for ionization, the reaction is very slow or nonexistent.

Reactions with $[Co(tren)(NH_3)Cl]^{2+}$ isomers show that the position *trans* to the leaving group is the most likely deprotonation site for a conjugate base mechanism.[14] The reaction in Figure 12-6(a) is 10^4 times faster than that in Figure 12-6(b). In addition, most of the product in both reactions is best explained by a trigonal-bipyramidal intermediate or transition state with the deprotonated amine in the trigonal plane. The reaction in Figure 12-6(a) can form this state immediately; the reaction in Figure 12-6(b) requires rearrangement of an initial square-pyramidal structure.

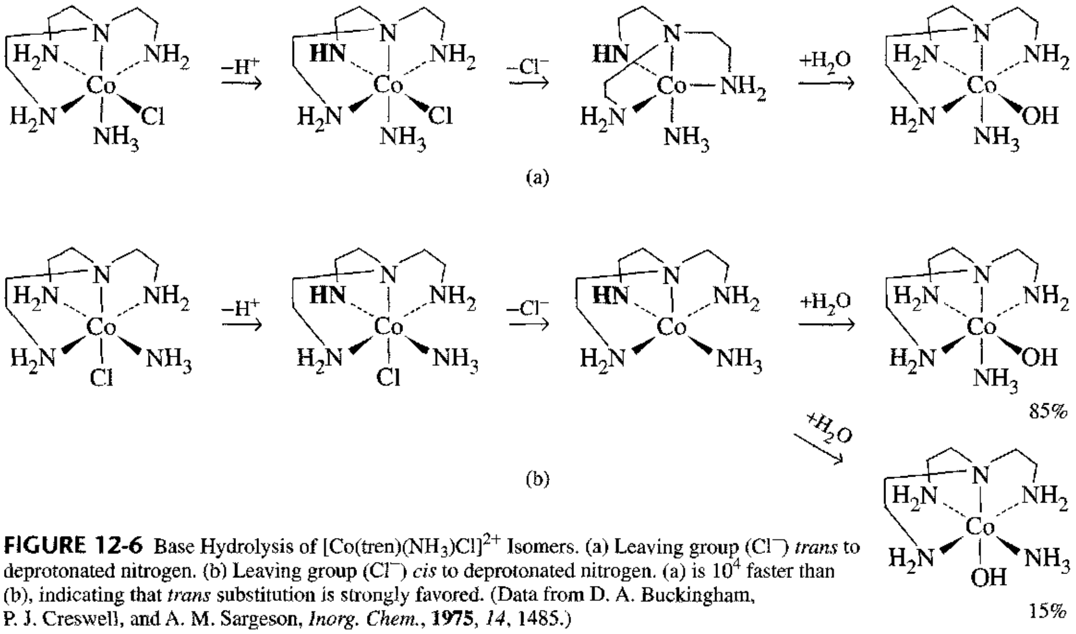

FIGURE 12-6 Base Hydrolysis of $[Co(tren)(NH_3)Cl]^{2+}$ Isomers. (a) Leaving group (Cl^-) *trans* to deprotonated nitrogen. (b) Leaving group (Cl^-) *cis* to deprotonated nitrogen. (a) is 10^4 faster than (b), indicating that *trans* substitution is strongly favored. (Data from D. A. Buckingham, P. J. Creswell, and A. M. Sargeson, *Inorg. Chem.*, **1975**, *14*, 1485.)

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[14] D. A. Buckingham, P. J. Cressell, and A. M. Sargeson, *Inorg. Chem.*, **1975**, *14*, 1485.

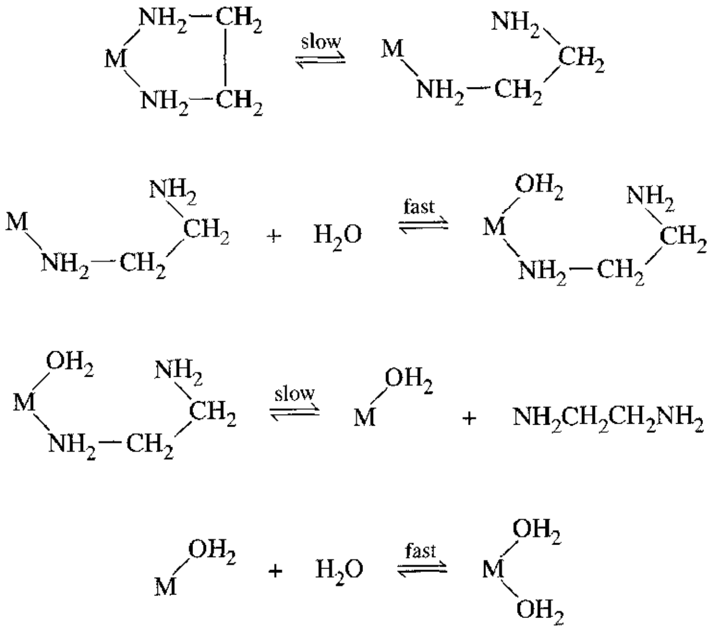
Explanations of the promotional effect of the amido group center on its basic strength, either as a σ donor or because of ligand to metal π interaction. The π interaction is most effective when the amido group is part of the trigonal plane in a trigonal-bipyramidal geometry, but there is at least one case in which this geometry is not necessarily achieved.[15]

12-4-5 THE KINETIC CHELATE EFFECT

The thermodynamic chelate effect, which causes polydentate complexes to be thermodynamically more stable than their monodentate counterparts,[16] was described in Section 10-1-1. The difference in the attachment and dissociation of the second (and third or higher numbered) point of attachment for the ligand is also observed kinetically.

Substitution for a chelated ligand is generally a slower reaction than that for a similar monodentate ligand. Explanations for this effect center on two factors, the increased energy needed to remove the first bound atom and the probability of a reversal of this first step.[17]

The reaction must have two dissociation steps for a bidentate ligand, one for each bound atom (the addition of water in Steps 2 and 4 is likely to be fast, because of its high concentration):



(1)

(2)

(3)

(4)

The first dissociation (1) is expected to be slower than a similar dissociation of ammonia because the ligand must bend and rotate to move the free amine group away from the metal. The second dissociation (3) is likely to be slow because the concentration of the intermediate is low and because the first dissociation can readily reverse. The

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[15] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **1969**, *8*, 1595.

[16] Basolo and Pearson, *Mechanisms of Inorganic Reactions*, pp. 27, 223; G. Schwarzenbach, *Helv. Chim. Acta*, **1952**, *35*, 2344.

[17] D. W. Margerum, G. R. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, "Kinetics of Complex Formation and Ligand Exchange," in A. E. Martell, ed., *Coordination Chemistry*, Vol. 2, American Chemical Society Monograph 174, Washington, DC, 1978, pp. 1–220.

uncoordinated nitrogen is held near the metal by the rest of the ligand, making reattachment more likely. Overall, this kinetic chelate effect reduces the rates of aquation reactions by factors from 20 to 10^5.

12-5

STEREOCHEMISTRY OF REACTIONS

A common assumption is that reactions with dissociative mechanisms are more likely to result in random isomerization or racemization and associative mechanisms are more likely to result in single-product reactions; however, the evidence is much less clear-cut. Dissociative mechanisms can lead to single-product reactions with either retention of configuration or a change of configuration, depending on the circumstances. For example, base hydrolysis of Λ-*cis*-$[Co(en)_2Cl_2]^+$ in dilute (<0.01 M) hydroxide yields Λ-*cis*-$[Co(en)_2(OH)_2]^+$, but in more concentrated (>0.25 M) hydroxide it gives Δ-*cis*-$[Co(en)_2(OH)_2]^+$ (Tables 12-8 and 12-9 and Figure 12-7).[18] A conjugate base mechanism is expected in both cases, with the hydroxide removing a proton from an ethylenediamine nitrogen, followed by loss of the chloride *trans* to the deprotonated nitrogen. In the more concentrated base, the higher concentration of ion pairs ($[Co(en)_2Cl_2]^+ \cdot OH^-$) is assumed to result in a water molecule (from the OH^- and the H^+ removed from ethylenediamine) positioned for easy addition with inversion of the chiral center.

A similar change in product, this time dependent on temperature, takes place in the substitution of ammonia for both chlorides in $[Co(en)_2Cl_2]^+$.[19] At low temperatures (−33° C or below, in liquid ammonia), there is inversion of configuration; at higher temperatures (above 25° C in liquid ammonia, alcohol solution, or solid exposed to gaseous ammonia), there is retention. In both cases, there is also a small fraction of the *trans* isomer.

Although not a complete explanation of these reactions, all the reported inversion reactions occur under conditions in which a conjugate base mechanism is possible.[20] The orientation of the ligand entering the proposed trigonal-bipyramidal intermediate

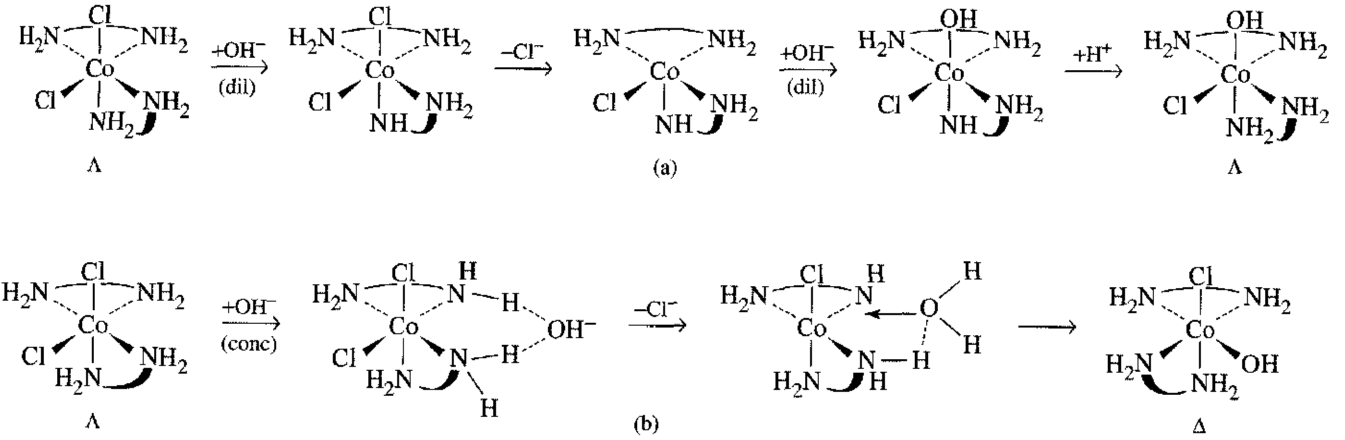

FIGURE 12-7 Mechanisms of Base Hydrolysis of Λ-*cis*-$[Co(en)_2Cl_2]^+$. (a) Retention of configuration in dilute hydroxide. (b) Inversion of configuration in concentrated hydroxide.

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[18] L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **1964**, *86*, 3656.

[19] J. C. Bailar, Jr., J. H. Haslam, and E. M. Jones, *J. Am. Chem. Soc.*, **1936**, *58*, 2226; E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **1966**, *88*, 1125.

[20] Basolo and Pearson, *Mechanisms of Inorganic Reactions*, p. 272.

TABLE 12-8
Stereochemistry of Acid Aquation

$$[Co(en)_2LX]^{n+} + H_2O \longrightarrow [Co(en)_2LH_2O]^{(1+n)+} + X^-$$

cis-L	*X*	*% cis Product*	*trans-L*	*X*	*% cis Product*
OH^-	Cl^-	100	OH^-	Cl^-	75
OH^-	Br^-	100	OH^-	Br^-	73
Br^-	Cl^-	100	Br^-	Cl^-	50
Cl^-	Cl^-	100	Br^-	Br^-	30
Cl^-	Br^-	100	Cl^-	Cl^-	35
N_3^-	Cl^-	100	Cl^-	Br^-	20
NCS^-	Cl^-	100	NCS^-	Cl^-	50–70
NCS^-	Br^-	100	NH_3	Cl^-	0
NO_2^-	Cl^-	100	NO_2^-	Cl^-	0

SOURCE: Data from F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., J. Wiley & Sons, New York, 1967, p. 257.

TABLE 12-9
Stereochemistry of Base Substitution

$$[Co(en)_2LX]^{n+} + OH^- \longrightarrow [Co(en)_2LOH]^{n+} + X^-$$

		% cis Product					
cis-L	*X*	Δ	*Racemic*[a]	Λ	*trans-L*	*X*	*% cis Product*
OH^-	Cl^-	61		36	OH^-	Cl^-	94
OH^-	Br^-		96		OH^-	Br^-	90
Cl^-	Cl^-	21		16	Cl^-	Cl^-	5
Cl^-	Br^-		30		Cl^-	Br^-	5
Br^-	Cl^-		40		Br^-	Cl^-	0
N_3^-	Cl^-		51		N_3^-	Cl^-	13
NCS^-	Cl^-	56		24	NCS^-	Cl^-	76
NH_3	Br^-	59		26	NCS^-	Br^-	81
NH_3	Cl^-	60		24	NH_3	Cl^-	76
NO_2^-	Cl^-	46		20	NO_2^-	Cl^-	6

SOURCE: Data from F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., J. Wiley & Sons, New York, 1967, p. 262.

NOTE: The total % *cis* product is the sum of Δ and Λ obtained from the Δ-*cis* starting material. The optically inactive *trans* isomer will yield racemic *cis*; % *trans* = 100% − % *cis*.

[a] Racemic reactant, so the product is also racemic.

then dictates the configuration of the product. In some cases, a preferred orientation of the other ligands may dictate the product. For example, the β form of trien complexes is more stable than the α form; both are shown in Figure 9-18.

12-5-1 SUBSTITUTION IN *TRANS* COMPLEXES

Substitution of Y for X in *trans*-$[M(LL)_2BX]$ (LL = a bidentate ligand such as en) can proceed by three different pathways. If dissociation of X from the reactant leaves a square-pyramidal intermediate that then adds the new ligand directly into the vacant site, the result is retention of configuration and the product, like the reactant, is *trans*, shown in Figure 12-8(a). A trigonal-bipyramidal intermediate with B in the trigonal plane leads to a mixture of *trans* and *cis*, as shown in Figure 12-8(b). The incoming

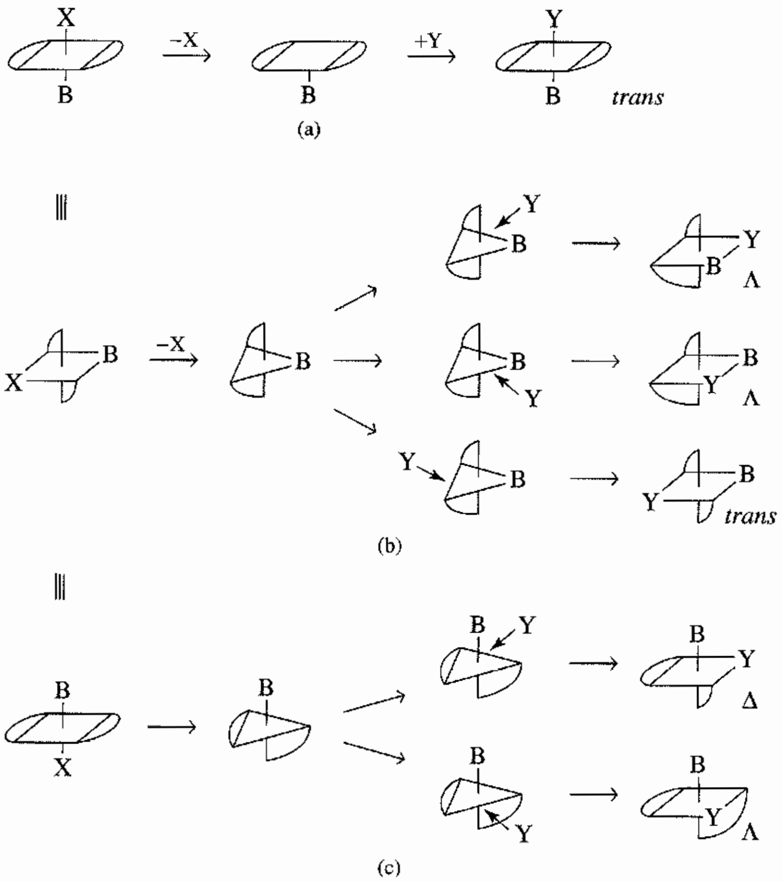
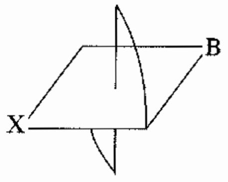


FIGURE 12-8 Dissociation Mechanism and Stereochemical Changes for *trans*-[$M(LL)_2BX$]. (a) Square-pyramidal intermediate (retention of configuration). (b) Trigonal-bipyramidal intermediate (three possible products). (c) Less likely trigonal-bipyramidal intermediate (two possible products.)

ligand can enter along any of the three sides of the triangle, resulting in two *cis* possibilities and one *trans* possibility. Dissociation to form a trigonal pyramid with B in an axial position, Figure 12-8(c), allows two positions for attack by Y, both of which give *cis* products (the third side of the triangle is blocked by an LL ring). An intermediate with an axial B is less likely than one with an equatorial B, because an axial B requires more rearrangement of the ligands (a 90° change by one nitrogen and 30° changes by two others, in contrast to two 30° changes for the equatorial B) as well as a larger stretch for the LL ring in the equatorial plane. As a result, the statistical probability of a change from *trans* to *cis* is two thirds for a trigonal-bipyramidal intermediate.

EXERCISE 12-2

Starting with the structure on the right, follow the example of Figure 12-8(b) and show that the first two products would be Δ rather than Λ.



(Experimentally, the two chiral forms are equally likely, because how we draw the structures has no effect on the experimental result.)

In fact, experimental results indicate that the statistical distribution is seldom followed. With *trans* reactants, both acid aquation and base substitution reactions result in a mixture of isomers; the fractions of *cis* and *trans* depend on the retained ligand and range from 100% *trans* to 94% *cis*, as shown in Tables 12-8 and 12-9. Of course, any

TABLE 12-10
Rate Constants for Reactions of $[Co(en)_2(H_2O)X]^{n+}$ at 25°C, k $(10^{-5}\ s^{-1})$

X	*cis* ⟶ *trans*	*trans* ⟶ *cis*	*Racemization*	H_2O *Exchange*
OH^-	200	300	—	160
Br^-	5.4	16.1	—	—
Cl^-	2.4	7.2	2.4	—
N_3^-	2.5	7.4	—	—
NCS^-	0.0014	0.071	0.022	0.13
H_2O	0.012	0.68	~0.015	1.0
NH_3	<0.0001	0.002	0.003	0.10
NO_2^-	0.012	0.005	—	—

Source: Adapted with permission from R. G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Allyn and Bacon, Boston, 1974, p. 344. Data from M. L. Tobe, in J. H. Ridd, ed., *Studies in Structure and Reactivity*, Methuen, London, 1966, and M. N. Hughes, *J. Chem. Soc., A*, **1967**, 1284.

cis isomer produced from the optically inactive *trans* reactants will be a racemic mixture of Λ and Δ. For both the axial and equatorial types of trigonal-bipyramidal intermediates, the chiral form of the product is determined by which square plane becomes trigonal in the intermediate; Δ and Λ products are equally likely.

Other factors, such as the leaving ligand, X, can strongly influence the mechanism and the outcome, making the products deviate further from statistical probability. Data on several reactions for $[Co(en)_2(H_2O)X]^{n+}$ are shown in Table 12-10. For $X = Cl^-$, SCN^-, and H_2O, racemization and *cis* ⟶ *trans* conversion are nearly equal in rate, making it likely that they have identical intermediates. Water exchange is faster than the other reactions for all but the hydroxide complex; simple exchange with the solvent requires no rearrangement of the ligands and the high concentration of water makes it more likely. For $X = NH_3$, racemization and *trans* ⟶ *cis* conversion are faster than *cis* ⟶ *trans* conversion. The reasons for this difference are not clear.

12-5-2 SUBSTITUTION IN *CIS* COMPLEXES

Substitution in *cis* complexes can proceed by the same three intermediates as in the *trans* complexes. Again, a square-pyramidal intermediate results in retention of configuration, providing a *cis* product in this case. If dissociation of X forms a trigonal bipyramid with B in the trigonal plane, there are three possible locations for the addition of Y, all in the same trigonal plane. Two of these result in *cis* products and one in a *trans* product. The less likely trigonal bipyramid with an axial B, whether derived from a *cis* or a *trans* reactant, produces two *cis* products that are half Δ and half Λ. These possibilities are all shown in Figure 12-9.

An optically active *cis* complex can yield products that retain the same configuration, convert to *trans* geometry, or create a racemic mixture. Statistically, the product of substitution of a *cis*-$[M(LL)_2BX]$ complex through a trigonal-bipyramidal intermediate should be 1/6 *trans* if both intermediates were equally likely and 1/3 *trans* if the axial B form is not formed at all. Experimentally, aquation of *cis*-$[M(LL)_2BX]$ in acid results in 100% *cis* isomer (Table 12-9), indicating a square-pyramidal transition state. Substitution of optically active *cis* complexes in base gives products ranging from 95% to 30% *cis*, with about 2:1 retention of chiral configuration (Table 12-9). (Four of the reactants listed in Table 12-9 are racemic, so the product is also a racemic *cis* mixture.)

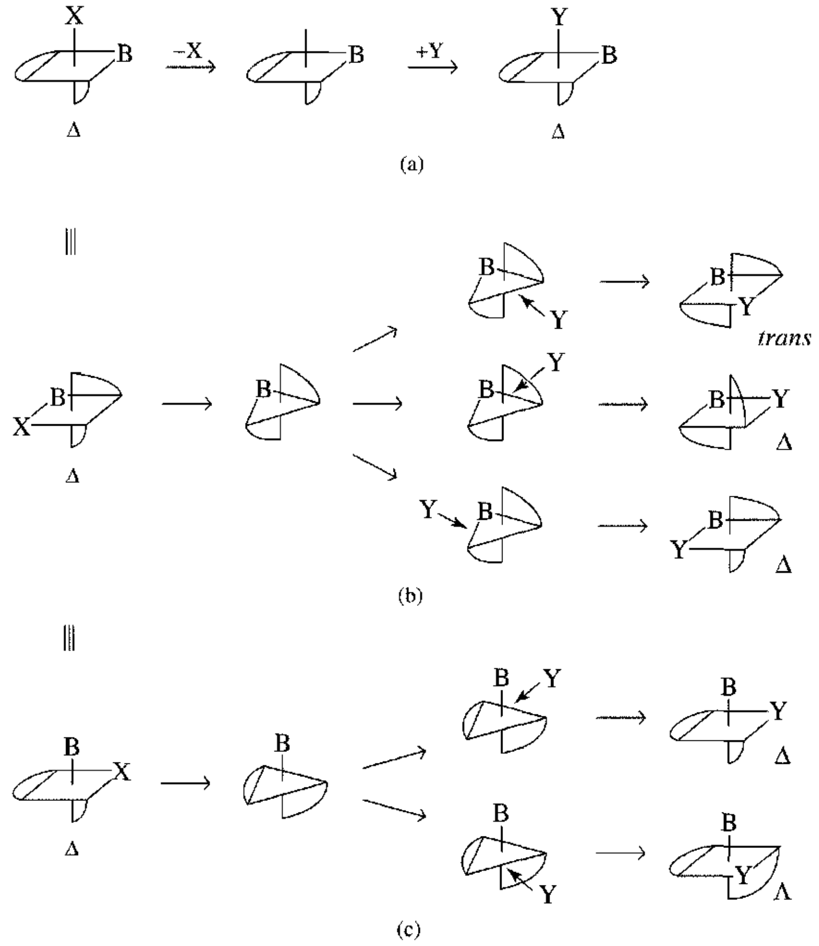


FIGURE 12-9 Dissociation Mechanism and Stereochemical Changes for *cis*-$[M(LL)_2BX]$.
(a) Square-pyramidal intermediate (retention of configuration).
(b) Trigonal-bipyramidal intermediate (three possible products). (c) Unlikely trigonal bipyramidal intermediate (two possible products).

Among the compounds that retain their optical activity and geometry on hydrolysis are $[M(en)_2Cl_2]^+$ with M = Co, Rh, and Ru.[21] As a general rule, *cis* reactants retain their *cis* configuration, but *trans* reactants are more likely to give a mixture of *cis* and *trans* products.

12-5-3 ISOMERIZATION OF CHELATE RINGS

Isomerization has been described previously for a number of complexes with monodentate ligands or with two bidentate ligands. Similar reactions with three bidentate ligands or with more complex ligands can follow two types of mechanism. In some cases, one end of a chelate ring dissociates and the resulting 5-coordinate intermediate rearranges before reattachment of the loose end. This mechanism does not differ appreciably from the substitution reactions described in Sections 12-5-1 and 12-5-2; the ligand that dissociates in the first step is the same one that adds in the final step, after rearrangement.

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[21] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **1963**, *85*, 1741; J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **1969**, *8*, 2124.

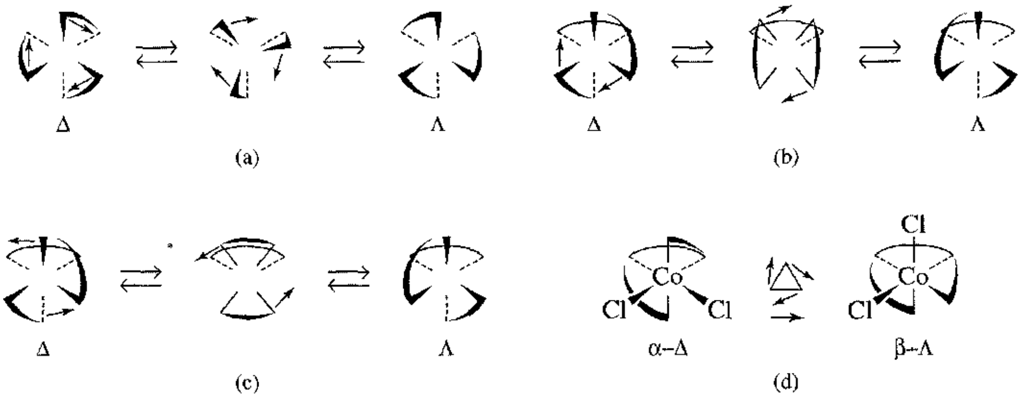

FIGURE 12-10 Twist Mechanisms for Isomerization of $M(LL)_3$ and $[Co(trien)Cl_2]^+$ Complexes. (a) Trigonal twist. The front triangular face rotates with respect to the back triangular face. (b) Twist with perpendicular rings. The back ring remains stationary as the front two rings rotate clockwise. (c) Twist with parallel rings. The back ring remains stationary as the front two rings rotate counterclockwise. (d) $[Co(trien)Cl_2]^+$ α-β isomerization. The connected rings limit this isomerization to a clockwise trigonal twist of the front triangular face.

Pseudorotation

Other isomerization mechanisms involving compounds containing chelating ligands are different types of twists. A number of twist mechanisms have been described, with different movements of the rings; those most commonly considered are shown in Figure 12-10.

The trigonal, or Bailar, twist, Figure 12-10(a), requires twisting the two opposite trigonal faces through a trigonal prismatic transition state to the new structure. In the tetragonal twists, one chelate ring is held stationary while the other two are twisted to the new structure. The first one illustrated, Figure 12-10(b), has a transition state with the stationary ring perpendicular to those being twisted. The second tetragonal twist, Figure 12-10(c), requires twisting the two rings through a transition state with all three rings parallel. There have been attempts to determine which of these mechanisms is applicable, but the complexity of the reactions and the indirect means of measurement leave them subject to different interpretations. NMR study of tris(trifluoroacetylacetonato) metal(III) chelates shows that a trigonal twist mechanism is not possible for M = Al, Ga, In, and *fac*-Cr, but leaves it a possibility for *fac*-Co.[22] The multiple-ring structure of *cis*-α-$[Co(trien)Cl_2]^+$ allows only a trigonal twist in its conversion to the β isomer, as shown in Figure 12-10(d).

12-6

SUBSTITUTION REACTIONS OF SQUARE-PLANAR COMPLEXES

The products of substitution reactions of square-planar complexes [platinum(II) complexes are the primary examples] have the same configuration as the reactants, with direct replacement of the departing ligand by the new ligand. The rates vary enormously, and different compounds can be formed, depending both on the entering and the leaving ligands. This section and Section 12-7 describe some of these effects.

12-6-1 KINETICS AND STEREOCHEMISTRY OF SQUARE-PLANAR SUBSTITUTIONS

Square-planar substitution reactions frequently show two term rate laws, of the form

$$\text{Rate} = k_1[\text{Cplx}] + k_2[\text{Cplx}][\text{Y}]$$

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[22] R. C. Fay and T. S. Piper, *Inorg. Chem.*, **1964**, *3*, 348.

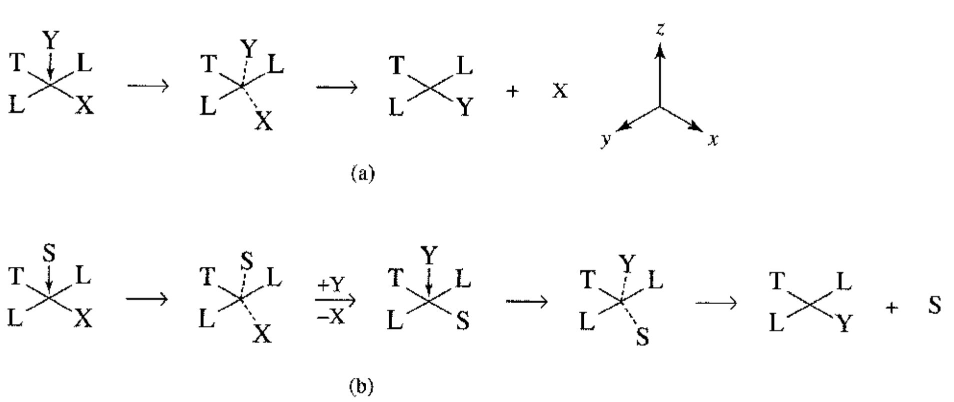
where [Cplx] = concentration of the complex and [Y] = concentration of the incoming ligand. Both pathways (both terms in the rate law) are considered to be associative, in spite of the difference in order. The k_2 term easily fits an associative mechanism in which the incoming ligand Y and the reacting complex form a 5-coordinate transition state. The accepted explanation for the k_1 term is a solvent-assisted reaction, with solvent replacing X on the complex through a similar 5-coordinate transition state, and then itself being replaced by Y. The second step of this mechanism is presumed to be faster than the first (Figure 12-11), and the concentration of solvent is large and unchanging, so the overall rate law for this path is first order in complex.

Because many of the reactions studied have been with platinum compounds, we will use the simplified reaction $\text{T—Pt—X} + \text{Y} \longrightarrow \text{T—Pt—Y} + \text{X}$, where T is the ligand *trans* to the departing ligand X and Y is the incoming ligand. We will also designate the plane of the molecule the xy plane and the Pt axis through T—Pt—X the x axis. The other two ligands, L, are of lesser importance and will be ignored for the moment.

12-6-2 EVIDENCE FOR ASSOCIATIVE REACTIONS

It is generally accepted that reactions of square-planar compounds are associative, although there is doubt about the degree of association, and they are classified as I_a. The two mechanisms, both associative, are shown in Figure 12-11. The incoming ligand approaches along the z axis. As it bonds to the Pt, the complex rearranges to approximate a trigonal bipyramid with Pt, T, X, and Y in the trigonal plane. As X leaves, Y moves down into the plane of T, Pt, and the two L ligands. This same general description will *fit whether the incoming ligand bonds strongly to Pt before the departing ligand bond is* weakened appreciably (I_a) or the departing ligand bond is weakened considerably before the incoming ligand forms its bond (I_d). The solvent-assisted mechanism follows the same pattern, but requires two associative steps for completion.

The evidence for a 5-coordinate intermediate is very strong, including isolation of several 5-coordinate complexes with trigonal-bipyramidal geometry ($[\text{Ni(CN)}_5]^{3-}$, $[\text{Pt(SnCl}_3)_5]^{3-}$, and similar complexes), although Basolo and Pearson argue that the transition state may well be 6-coordinate, with assistance from solvent.[23] The highest energy transition state may be either during the formation of the intermediate or as the leaving ligand dissociates from the intermediate.



(a)

(b)

FIGURE 12-11 The Interchange Mechanism in Square-Planar Reactions. (a) Direct substitution by Y. (b) Solvent-assisted substitution.

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[23] Basolo and Pearson, *Mechanisms of Inorganic Reactions*, pp. 377–379, 395.

TABLE 12-11
Rate Constants and LFER Parameters for Entering Groups

$trans\text{-}PtL_2Cl_2 + Y \longrightarrow trans\text{-}PtL_2ClY + Cl^-$

	$k\ (10^{-3}\ M^{-1}\ s^{-1})$		
Y	$L = py\ (s = 1)$	$L = PEt_3\ (s = 1.43)$	η_{Pt}
PPh_3	249,000		8.93
SCN^-	180	371	5.75
I^-	107	236	5.46
Br^-	3.7	0.93	4.18
N_3^-	1.55	0.2	3.58
NO_2^-	0.68	0.027	3.22
NH_3	0.47		3.07
Cl^-	0.45	0.029	3.04

SOURCE: Rate constants from U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **1965**, *87*, 241; PPh_3 and η_{Pt} data from R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.*, **1968**, *90*, 319.

NOTE: *s* and η are nucleophilic reaction parameters explained in the text.

This mechanism explains naturally the effect of the incoming ligand. A strong Lewis base is likely to react readily, but the hard-soft nature of the base has an even larger effect. Pt(II) is generally a soft acid, so soft ligands react more readily with it. The order of ligand reactivity depends somewhat on the other ligands on the Pt, but the order for the reaction

$$trans\text{-}PtL_2Cl_2 + Y \longrightarrow trans\text{-}PtL_2ClY + Cl^-$$

for different Y in methanol was found to be as follows (examples are in Table 12-11):

$$PR_3 > CN^- > SCN^- > I^- > Br^- > N_3^- > NO_2^- > py > NH_3 \sim Cl^- > CH_3OH$$

A similar order, with some shuffling of the center of the list, is found for reactants with ligands other than chloride as T. The ratio of the rate constants for the extremes in the list is very large, with $k(PPh_3)/k(CH_3OH) = 9 \times 10^8$. Because T and Y have similar positions in the transition state, it is reasonable for them to have similar effects on the rate, and they do. Discussion of this ***trans*** **effect** is in the next section.

By the same argument, the leaving group X should also have a significant influence on the rate, and it does (Table 12-12).[24] The order of ligands is nearly the reverse of that given above, with hard ligands such as Cl^-, NH_3, and NO_3^- leaving quickly. Soft ligands with considerable π bonding such as CN^- and NO_2^- leave reluctantly; in the reaction

$$[Pt(dien)X^+] + py \longrightarrow [Pt(dien)(py)]^{2+} + X^-$$

the rate increases by a factor of 10^5 with H_2O as compared with $X^- = CN^-$ or NO_2^- as the leaving group. The bond-strengthening effect of the metal-to-ligand π bonding reduces the reactivity of these ligands significantly. In addition, π bonding to the leaving group uses the same orbitals as those bonding to the entering group in the trigonal plane. These two effects result in the slow displacement of metal-to-ligand π-bonding ligands when compared with ligands with only σ bonding or ligand-to-metal π bonding.

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[24] Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*, p. 231.

TABLE 12-12
Rate Constants for Leaving Groups

$[Pt(dien)X]^+ + py \longrightarrow [Pt(dien)py]^{2+} + X^-$
$(\text{Rate} = (k_1 + k_2[py])[Pt(dien)X^+])$

X^-	$k_2\ (M^{-1}\ s^{-1})$
NO_3^-	very fast
Cl^-	5.3×10^{-3}
Br^-	3.5×10^{-3}
I^-	1.5×10^{-3}
N_3^-	1.3×10^{-4}
SCN^-	4.8×10^{-5}
NO_2^-	3.8×10^{-6}
CN^-	2.8×10^{-6}

SOURCE: Calculated from data in F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **1960**, *82*, 4200.

Good leaving groups (those that leave easily) show little discrimination between entering groups. Apparently, the ease of breaking the Pt—X bond takes precedence over the formation of the Pt—Y bond. On the other hand, for complexes with less reactive leaving groups, the other ligands have a significant role; the softer PEt_3 and $AsEt_3$ ligands show a large selective effect when compared with the harder dien or en ligands. The LFER equation[25] for this comparison is

$$\log k_Y = s\,\eta_{Pt} + \log k_S$$

where k_Y = rate constant for reaction with Y

k_S = rate constant for reaction with solvent

s = **nucleophilic discrimination factor** (for the complex)

η_{Pt} = **nucleophilic reactivity constant** (for the entering ligand)

The parameter s is defined as 1 for *trans*-$[Pt(py)_2Cl_2]$ and has values from 0.44 for the hard $[Pt(dien)H_2O]^{2+}$ to 1.43 for the soft *trans*-$[Pt(PEt_3)_2Cl_2]$. Values of η_{Pt} are found by the equation $\eta_{Pt} = \log(k_Y/k_S)$, where k_S refers to reaction with *trans*-$[Pt(py)_2Cl_2]$ in methanol at 30° C. Table 12-11 shows both these factors. For $L = PEt_3$, the change in rate constant is greater than for L = py because of the larger s value, and the increase in rate constants parallels the increase in η_{Pt}. Each of the parameters s and η_{Pt} may change by a factor of 3 from fast reactions to slow reactions, allowing for an overall ratio of 10^6 in the rates.

12-7 THE *TRANS* EFFECT

In 1926, Chernyaev[26] introduced the concept of the ***trans* effect** in platinum chemistry. In reactions of square-planar Pt(II) compounds, ligands *trans* to chloride are more easily replaced than those *trans* to ligands such as ammonia; chloride is said to have a stronger *trans* effect than ammonia. When coupled with the fact that chloride itself is more easily replaced than ammonia, this *trans* effect allows the formation of isomeric

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[25] Atwood, *Inorganic and Organometallic Reaction Mechanisms*, pp. 60–63.

[26] I. I. Chernyaev, *Ann. Inst. Platine USSR.*, **1926**, *4*, 261.

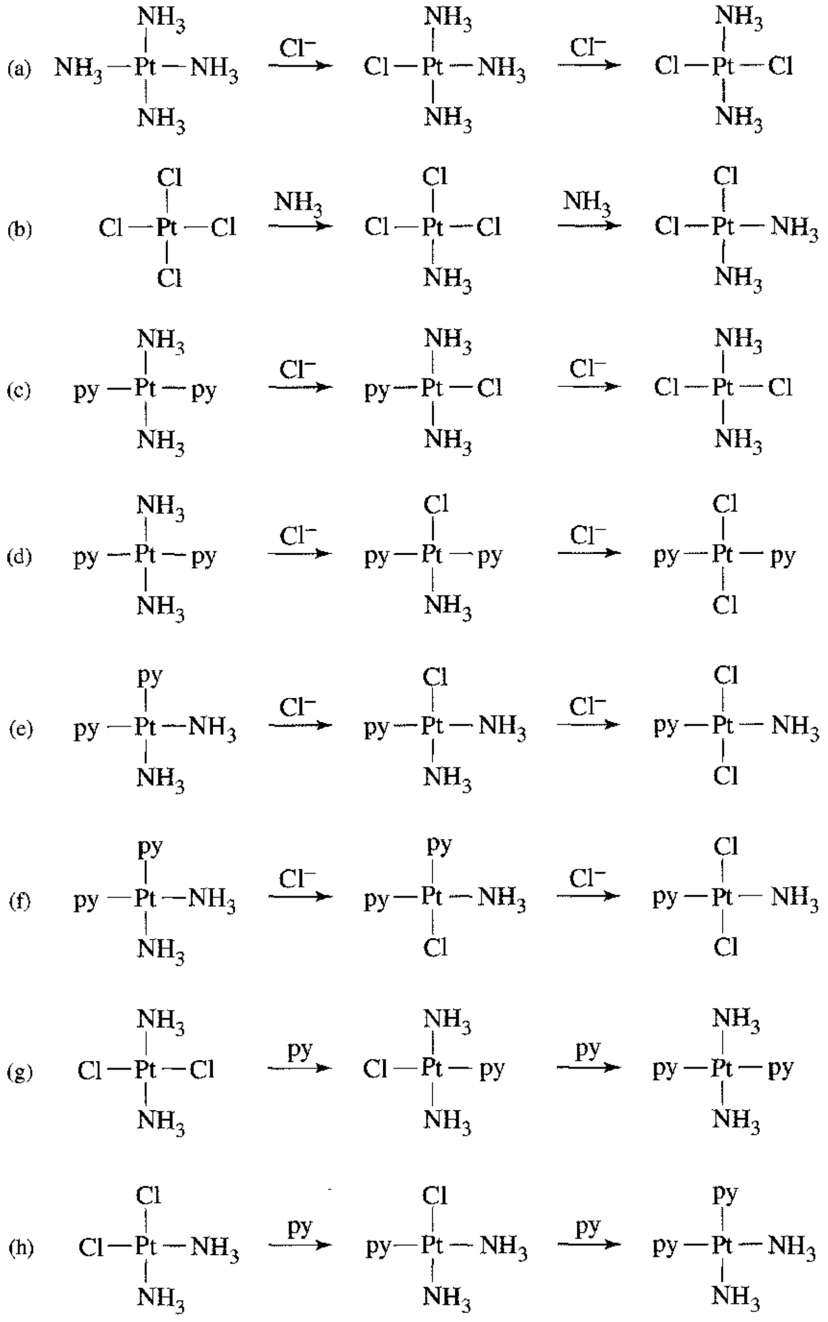

FIGURE 12-12 Stereochemistry and the *trans* Effect in Pt(II) Reactions. Charges have been omitted for clarity. In (a) through (f), the first substitution can be at any position, with the second controlled by the *trans* effect. In (g) and (h), both substitutions are controlled by the lability of chloride.

Pt compounds, as shown in the reactions of Figure 12-12. In reaction (a), after the first ammonia is replaced, the second replacement is *trans* to the first Cl^-. In reaction (b), the second replacement is *trans* to Cl^- (replacement of ammonia in the second reaction is possible, but then the reactant and product are identical). The first steps in reactions (c) through (f) are the possible replacements, with nearly equal probabilities for replacement of ammonia or pyridine in any position. The second steps of (c) through (f) depend on the *trans* effect of Cl^-. Both steps of (g) and (h) depend on the greater lability of chloride. By using reactions such as these, it is possible to prepare specific isomers with different ligands. Chernyaev and coworkers did much of this, preparing a wide variety of compounds and establishing the order of *trans* effect ligands:

$$CN^- \sim CO \sim C_2H_4 > PH_3 \sim SH_2 > NO_2^- > I^- > Br^- > Cl^- > NH_3 \sim py > OH^- > H_2O$$

EXERCISE 12-3

Predict the products of these reactions (there may be more than one product when there are conflicting preferences).

$[PtCl_4]^{2-} + NO_2^- \longrightarrow$ (a) $\qquad$ (a) $+ NH_3 \longrightarrow$ (b)

$[PtCl_3NH_3]^- + NO_2^- \longrightarrow$ (c) $\qquad$ (c) $+ NO_2^- \longrightarrow$ (d)

$[PtCl(NH_3)_3]^+ + NO_2^- \longrightarrow$ (e) $\qquad$ (e) $+ NO_2^- \longrightarrow$ (f)

$[PtCl_4]^{2-} + I^- \longrightarrow$ (g) $\qquad$ (g) $+ I^- \longrightarrow$ (h)

$[PtI_4]^- + Cl^- \longrightarrow$ (i) $\qquad$ (i) $+ Cl^- \longrightarrow$ (j)

12-7-1 EXPLANATIONS OF THE *TRANS* EFFECT[27]

Sigma-bonding effects

Two factors dominate the explanations of the *trans* effect, weakening of the Pt—X bond and stabilization of the presumed 5-coordinate transition state. The energy relationships are given in Figure 12-13, with the activation energy the difference between the reactant ground state and the first transition state.

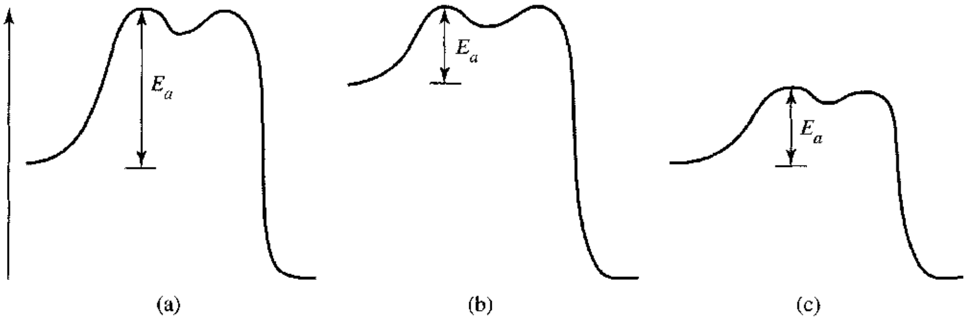

FIGURE 12-13 Activation Energy and the *trans* Effect. The depth of the energy curve for the intermediate and the relative heights of the two maxima will vary with the specific reaction. (a) Poor *trans* effect, low ground state, high transition state. (b) σ-Bonding effect, higher ground state (*trans* influence). (c) π-Bonding effect, lower transition state, (*trans* effect).

The Pt—X bond is influenced by the Pt—T bond, because both use the Pt p_x and $d_{x^2-y^2}$ orbitals. When the Pt—T σ bond is strong, it uses a larger part of these orbitals and leaves less for the Pt—X bond (Figure 12-14). As a result, the Pt—X bond is weaker and its ground state (sigma-bonding orbital) is higher in energy, leading to a smaller activation energy for the breaking of this bond [Figure 12-13(b)]. This ground state effect is sometimes called the ***trans* influence** and applies primarily to the leaving group. It is a thermodynamic effect, contributing to the overall kinetic result by changing the reactant ground state. This part of the explanation predicts the order for the *trans* effect based on the relative σ-donor properties of the ligands:

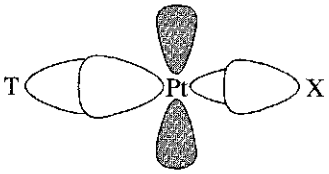

FIGURE 12-14 Sigma-Bonding Effect. A strong σ bond between Pt and T weakens the Pt—X bond.

$$H^- > PR_3 > SCN^- > I^- \sim CH_3^- \sim CO \sim CN^- > Br^- > Cl^- > NH_3 > OH^-$$

The order given here is not quite correct for the *trans* effect, particularly for CO and CN^-, which have strong *trans* effects.

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[27] Atwood, *Inorganic and Organometallic Reactions Mechanisms*, p. 54; Basolo and Pearson, *Mechanisms of Inorganic Reactions*, p. 355.

Pi-bonding effects

The additional factor needed is π bonding in the Pt—T bond. When the T ligand forms a strong π-acceptor bond with Pt, charge is removed from Pt and the entrance of another ligand to form a 5-coordinate species is more likely. In addition to the charge effect, the $d_{x^2-y^2}$ orbital, which is involved in σ bonding in the square-planar geometry, and both the d_{xz} and d_{yz} orbitals can contribute to π bonding in the trigonal-bipyramidal transition state. Here, the effect on the ground state of the reactant is small, but the energy of the transition state is lowered, again reducing the activation energy [Figure 12-13(c)]. The order of π-acceptor ability of the ligands is

$$C_2H_4 \sim CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$$

The expanded overall *trans* effect list is then the result of the combination of the two effects:

$$CO \sim CN^- \sim C_2H_4 > PR_3 \sim H^- > CH_3^- \sim SC(NH_2)_2 > C_6H_5^- >$$

$$NO_2^- \sim SCN^- \sim I^- > Br^- > Cl^- > py, NH_3 \sim OH^- \sim H_2O$$

Ligands highest in the series are strong π acceptors, followed by strong σ donors. Ligands at the low end of the series have neither strong σ-donor nor π-acceptor abilities. The *trans* effect can be very large; rates may differ as much as 10^6 between complexes with strong *trans* effect ligands and those with weak *trans* effect ligands.

EXERCISE 12-4

It is possible to prepare different isomers of Pt(II) complexes with four different ligands. Predict the products expected if 1 mole of $[PtCl_4]^{2-}$ is reacted successively with the following reagents (e.g., the product of reaction a is used in reaction b):

a. 2 moles of ammonia

b. 2 moles of pyridine [see Reactions (g) and (h) in Figure 12-12]

c. 2 moles of chloride

d. 1 mole of nitrite, NO_2^-

12-8 OXIDATION-REDUCTION REACTIONS

Oxidation-reduction reactions of transition metal complexes, like all redox reactions, involve the transfer of an electron from one species to another—in this case, from one complex to another. The two molecules may be connected by a common ligand through which the electron is transferred, in which case the reaction is called a bridging or **inner-sphere reaction**, or the exchange may occur between two separate coordination spheres in a nonbridging or **outer-sphere reaction**.

The rates have been studied by many different methods, including chemical analysis of the products, stopped-flow spectrophotometry, and the use of radioactive and stable isotope tracers. Taube's research group has been responsible for a large amount of the data, and their reviews cover the field.[28]

The rate of reaction for electron transfer depends on many factors, including the rate of substitution in the coordination sphere of the reactants, the match of energy levels of the two reactants, solvation of the two reactants, and the nature of the ligands.

[28] T. J. Meyer and H. Taube, "Electron Transfer Reactions," in G. Wilkinson, R. D. Gillard, and J. A. McCleverty, eds., Pergamon, *Comprehensive Coordination Chemistry*, Vol. 1, London, 1987, pp. 331–384; H. Taube, *Electron Transfer Reactions of Complex Ions in Solution*, Academic Press, New York, 1970; *Chem. Rev.*, **1952**, *50*, 69; *J. Chem. Educ.*, **1968**, *45*, 452.

12-8-1 INNER- AND OUTER-SPHERE REACTIONS

When the ligands of both reactants are tightly held and there is no change in the coordination sphere on reaction, the reaction proceeds by outer-sphere electron transfer. Examples of these reactions are given in Table 12-13 with their rate constants.

TABLE 12-13
Rate Constants for Outer-Sphere Electron Transfer Reactions[a]

	Reductants	
Oxidant	$[Cr(bipy)_3]^{2+}$	$[Ru(NH_3)_6]^{2+}$
$[Co(NH_3)_5(NH_3)]^{3+}$	6.9×10^2	1.1×10^{-2}
$[Co(NH_3)_5(F)]^{2+}$	1.8×10^3	
$[Co(NH_3)_5(OH)]^{2+}$	3×10^4	4×10^{-2}
$[Co(NH_3)_5(NO_3)]^{2+}$		3.4×10^1
$[Co(NH_3)_5(H_2O)]^{3+}$	5×10^4	3.0
$[Co(NH_3)_5(Cl)]^{2+}$	8×10^5	2.6×10^2
$[Co(NH_3)_5(Br)]^{2+}$	5×10^6	1.6×10^3
$[Co(NH_3)_5(I)]^{2+}$		6.7×10^3

SOURCE: $[Cr(bipy)_3]^{2+}$ data from J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **1964**, *86*, 1019. $[Ru(NH_3)_6]^{2+}$ data from J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **1964**, *86*, 1686.
NOTE: [a]Second-order rate constants in $M^{-1}\,s^{-1}$ at 25°C.

The rates show very large differences, depending on the details of the reactions. Characteristically, the rates depend on the ability of the electrons to tunnel through the ligands. This is a quantum mechanical property whereby electrons can pass through potential barriers that are too high to permit ordinary transfer. Ligands with π or p electrons or orbitals that can be used in bonding (as described in Chapter 10 for π-donor and π-acceptor ligands) provide good pathways for tunneling; those like NH_3, with no extra lone pairs and no low-lying antibonding orbitals, do not.

In outer-sphere reactions, where the ligands in the coordination sphere do not change, the primary change on electron transfer is a change in bond distance. A higher oxidation state on the metal leads to shorter σ bonds, with the extent of change depending on the electronic structure. The changes in bond distance are larger when e_g electrons are involved, as in the change from high-spin Co(II) ($t_{2g}{}^5\,e_g{}^2$) to low-spin Co(III) ($t_{2g}{}^6$). Because the e_g orbitals are antibonding, removal of electrons from these orbitals results in a more stable compound and shorter bond distances. A larger ligand field stabilization energy makes oxidation easier. Comparing water and ammonia as ligands, we can see that the stronger field of ammonia makes oxidation of Co(II) relatively easy. $[Co(NH_3)_6]^{3+}$ is a very weak oxidizing agent. The aqueous Co(III) ion, on the other hand, has a large enough potential to oxidize water:

$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad \mathscr{E}^\circ = +0.108\text{ V}$$

$$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq) \qquad \mathscr{E}^\circ = +1.808\text{ V}$$

Inner-sphere reactions also use the tunneling phenomenon, but in this case a single ligand is the conduit. The reactions proceed in three steps: (1) a substitution reaction that leaves the oxidant and reductant linked by the bridging ligand, (2) the actual transfer of the electron (frequently accompanied by transfer of the ligand), and (3) separation of the products:[29]

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[29] J. P. Candlin and J. Halpern, *Inorg. Chem.*, **1965**, *4*, 766.

$$\underset{\text{Co(III) oxidant}}{[Co(NH_3)_5(Cl)]^{2+}} + \underset{\text{Cr(II) reductant}}{[Cr(H_2O)_6]^{2+}} \longrightarrow \underset{\text{Co(III)}\ \ \text{Cr(II)}}{[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+}} + H_2O \tag{1}$$

$$\underset{\text{Co(III)}\ \ \text{Cr(II)}}{[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+}} \longrightarrow \underset{\text{Co(II)}\ \ \text{Cr(III)}}{[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+}} \tag{2}$$

$$[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+} + H_2O \longrightarrow [(NH_3)_5Co(H_2O)]^{2+} + [(Cl)Cr(H_2O)_5]^{2+} \tag{3}$$

In this case, these are followed by a reaction made possible by the labile nature of Co(II):

$$[(NH_3)_5Co(H_2O)]^{2+} + 5\,H_2O \longrightarrow [Co(H_2O)_6]^{2+} + 5\,NH_3$$

The transfer of chloride to the chromium in these reactions is easy to follow experimentally because Cr(III) is substitutionally inert and the products can be separated by ion exchange techniques and their composition can be determined. When this is done, all the Cr(III) appears as $CrCl^{2+}$. The $[Cr(H_2O)_6]^{2+}$-$[Cr(H_2O)_5Cl]^{2+}$ exchange reaction (which results in no net change) has also been studied, using radioactive ^{51}Cr as a tracer.[30] All the chloride in the product came from the reactant, with none entering from excess Cl^- in the solution. The rate of the reaction could also be determined by following the amount of radioactivity found in the $CrCl^{2+}$ at different times during the reaction.

In many cases, the choice between inner- and outer-sphere mechanisms is difficult. In the examples of Table 12-13, the outer-sphere mechanism is required by the reducing agent. $[Ru(NH_3)_6]^{2+}$ is an inert species and does not allow formation of bridging species fast enough for the rate constants observed. Although $[Cr(bipy)_3]^{2+}$ is labile, the parallels in the rate constants of the two species strongly suggest that its redox reactions are also outer-sphere. In other cases, the oxidant may dictate an outer-sphere mechanism. In Table 12-14, $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ have outer-sphere mechanisms because their ligands have no lone pairs with which to form bonds to the reductant. The other reactions are less certain, although Cr^{2+}(aq) is usually assumed to react by inner-sphere mechanisms in all cases in which bridging is possible.

TABLE 12-14
Rate Constants for Aquated Reductants[a]

	Cr^{2+}	Eu^{2+}	V^{2+}
$[Co(en)_3]^{3+}$	$\sim 2 \times 10^{-5}$	$\sim 5 \times 10^{-3}$	$\sim 2 \times 10^{-4}$
$[Co(NH_3)_6]^{3+}$	8.9×10^{-5}	2×10^{-2}	3.7×10^{-2}
$[Co(NH_3)_5(H_2O)]^{3+}$	5×10^{-1}	1.5×10^{-1}	$\sim 5 \times 10^{-1}$
$[Co(NH_3)_5(NO_3)]^{2+}$	$\sim 9 \times 10^{1}$	$\sim 1 \times 10^{2}$	
$[Co(NH_3)_5(Cl)]^{2+}$	6×10^{5}	3.9×10^{2}	~ 5
$[Co(NH_3)_5(Br)]^{2+}$	1.4×10^{6}	2.5×10^{2}	2.5×10^{1}
$[Co(NH_3)_5(I)]^{2+}$	3×10^{6}	1.2×10^{2}	1.2×10^{2}

SOURCE: Data from J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **1964**, *86*, 1019; data for Cr^{2+} reactions with halide complexes from J. P. Candlin and J. Halpern, *Inorg. Chem.*, **1965**, *4*, 756; data for $[Co(NH_3)_6]^{3+}$ reactions with Cr^{2+} and V^{2+} from A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **1961**, *83*, 793.

[a] Rate constants in $M^{-1}\,s^{-1}$.

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[30] D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **1958**, *80*, 1091.

$V^{2+}(aq)$ reactions appear to be similar to those of $Cr^{2+}(aq)$, although the range of rate constants is smaller than that for Cr^{2+}. This seems to indicate that the ligands are less important and makes an outer-sphere mechanism more likely. This is reinforced by comparison of the rate constants for the reactions of $[Cr(bipy)_3]^{2+}$ (outer-sphere, Table 12-13) and V^{2+} (Table 12-14) with the same oxidants. V^{2+} may have different mechanisms for different oxidants, just as Cr^{2+} does.

$Eu^{2+}(aq)$ is an unusual case. The rate constants do not parallel those of either the more common inner- or outer-sphere reactants, and the halide data are in reverse order from any others. The explanation offered for these rate constants is that the thermodynamic stability of the EuX^+ species helps drive the reaction faster for F^-, with slower rates and stabilities as we go down the series. Because of the smaller range of rate constants, Eu^{2+} reactions are usually classed as outer-sphere reactions.

When $[Co(CN)_5]^{3-}$ reacts with Co(III) oxidants ($[Co(NH_3)_5X]^{2+}$) that have potentially bridging ligands, the product is $[Co(CN)_5X]^{2+}$, evidence for an inner-sphere mechanism. Rate constants for a number of these reactions are given in Table 12-15. The reaction with hexamminecobalt(III) must be outer-sphere, but has a rate constant similar to the others. The reactions with thiocyanate or nitrite as bridging groups also show interesting behavior. With N-bonded $[(NH_3)_5CoNCS]^{2+}$, it reacts by bonding to the free S end of the ligand, because the cyanides soften the normally hard Co^{2+} ion. With S-bonded $[(NH_3)_5CoSCN]^{2+}$, it reacts initially by bonding to the free N end of the ligand and then rearranges rapidly to the more stable S-bonded form. In a similar fashion, a transient O-bonded intermediate is detected in reactions of $[(NH_3)_5Co(NO_2)]^{2+}$ with $[Co(CN)_5]^{3-}$.[31]

TABLE 12-15
Rate Constants for Reactions with $[Co(CN)_5]^{3-}$

Oxidant	*k* ($M^{-1}\ s^{-1}$)
$[Co(NH_3)_5(F)]^{2+}$	1.8×10^3
$[Co(NH_3)_5(OH)]^{2+}$	9.3×10^4
$[Co(NH_3)_5(NH_3)]^{3+}$	8×10^{4}[a]
$[Co(NH_3)_5(NCS)]^{2+}$	1.1×10^6
$[Co(NH_3)_5(N_3)]^{2+}$	1.6×10^6
$[Co(NH_3)_5(Cl)]^{2+}$	$\sim 5 \times 10^7$

SOURCE: Data from J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **1963**, *85*, 2517.

NOTE: [a] Outer-sphere mechanism caused by the oxidant. Complexes with other potential bridging groups (PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, and several carboxylic acids) also react by an outer-sphere mechanism, with constants ranging from 5×10^2 to 4×10^4.

Other reactions that follow an inner-sphere mechanism have been studied to determine which ligands bridge best. The overall rate of reaction usually depends on the first two steps (substitution and transfer of electron), and in some cases it is possible to draw conclusions about the rates of the individual steps. For example, ligands that are reducible provide better pathways, and their complexes are more quickly reduced.[32] Benzoic acid is difficult to reduce, but 4-carboxy-N-methylpyridine is relatively easy to

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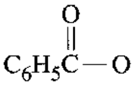
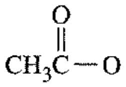
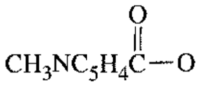
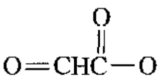
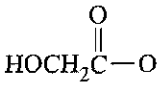
[31] J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **1965**, *87*, 3002, J. L. Burmeister, *Inorg. Chem.*, **1964**, *3*, 919.

[32] Taube, *Electron Transfer Reactions of Complex Ions in Solution*, pp. 64–66; E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **1964**, *86*, 1318.

TABLE 12-16
Ligand Reducibility and Electron Transfer

Rate constants for the reaction

$[(NH_3)_5CoL]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow Co^{2+} + 5\,NH_3 + [Cr(H_2O)_5L]^{2+} + H_2O$

L	$k_2\ (M^{-1}\,s^{-1})$	*Comments*
 $C_6H_5\overset{\overset{O}{\Vert}}{C}{-}O$	0.15	Benzoate is difficult to reduce
 $CH_3\overset{\overset{O}{\Vert}}{C}{-}O$	0.34	Acetic acid is difficult to reduce
 $CH_3NC_5H_4\overset{\overset{O}{\Vert}}{C}{-}O$	1.3	N-methyl-4-carboxypyridine is more reducible
 $O{=}CH\overset{\overset{O}{\Vert}}{C}{-}O$	3.1	Glyoxylate is easy to reduce
 $HOCH_2\overset{\overset{O}{\Vert}}{C}{-}O$	7×10^3	Glycolate is very easy to reduce

SOURCE: H. Taube, *Electron Transfer Reactions of Complex Ions in Solution*, Academic Press, New York, 1970, pp. 64–66.

reduce. The rate constants for the reaction of the corresponding pentammine Co(III) complexes of these two ligands with Cr(II) differ by a factor of 10, although both have similar structures and transition states (Table 12-16). For both ligands, the mechanism is inner-sphere, with transfer of the ligand to chromium, indicating that coordination to the Cr(II) is through the carbonyl oxygen. The substitution reactions should have similar rates, so the difference in overall rates is a result of the transfer of electrons through the ligand. The data of Table 12-16 show these effects and extend the data to glyoxylate and glycolate, which are still more easily reduced. The transfer of an electron through such ligands is very fast when compared with similar reactions with ligands that are not reducible.

Remote attack on ligands with two potentially bonding groups is also found. Isonicotinamide bonded through the pyridine nitrogen can react with Cr^{2+} through the carbonyl oxygen on the other end of the molecule, transferring the ligand to the chromium and an electron through the ligand from the chromium to the other metal. The rate constants for different metals are shown in Table 12-17. The rate constants for the cobalt pentammine and the chromium pentaaqua complexes are much closer than usual. The rate for Co compounds with other bridging ligands is frequently as much as 10^5 larger than the rate for corresponding Cr compounds, primarily because of the greater oxidizing power of Co(III). With isonicotinamide compounds, the rate seems to depend more on the rate of electron transfer from Cr^{2+} to the bridging ligand, and the readily reducible isonicotinamide makes the two reactions more nearly equal in rate. The much faster rate found for the ruthenium pentammine has been explained as the result of the transfer of an electron through the π system of the ligand into the t_{2g} levels of Ru(III) (low-spin Ru(III) has a vacancy in the t_{2g} level). A similar electron transfer to Co(III) or Cr(III) places the incoming electron in the e_g levels, which have σ symmetry.[33]

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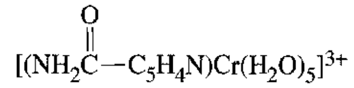
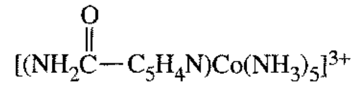
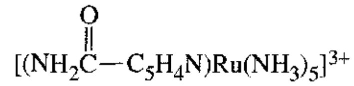
[33] H. Taube and E. S. Gould, *Acc. Chem. Res.*, **1969**, 2, 321.

TABLE 12-17
Rate Constants for Reduction of Isonicotinamide (4-Pyridine Carboxylic Acid Amide) Complexes by $[Cr(H_2O)_6]^{2+}$

Oxidant	*k_2 (M^{-1} s^{-1})*
 $[(NH_2\overset{\overset{O}{\|}}{C}-C_5H_4N)Cr(H_2O)_5]^{3+}$	1.8
 $[(NH_2\overset{\overset{O}{\|}}{C}-C_5H_4N)Co(NH_3)_5]^{3+}$	17.6
 $[(NH_2\overset{\overset{O}{\|}}{C}-C_5H_4N)Ru(NH_3)_5]^{3+}$	5×10^5

Source: H. Taube, *Electron Transfer Reactions of Complex Ions in Solution*, Academic Press, New York, 1970, pp. 66–68.

12-8-2 CONDITIONS FOR HIGH AND LOW OXIDATION NUMBERS

The overall stability of complexes with different charges on the metal ion depends on many factors, including LFSE, bonding energy of ligands, and redox properties of the ligands. When other factors are more or less equal, the hard and soft character of the ligands also has an effect. For example, all the very high oxidation numbers for the transition metals are found in combination with hard ligands, such as fluoride and oxide. Examples include MnO_4^-, CrO_4^{2-}, and FeO_4^{2-} with oxide, and AgF_2, RuF_5, PtF_6, and OsF_6 with fluoride. At the other extreme, the lowest oxidation states are found with soft ligands, with carbon monoxide being one of the most common. Zero is a common formal oxidation state for carbonyls; $V(CO)_6$, $Cr(CO)_6$, $Fe(CO)_5$, $Co_2(CO)_8$, and $Ni(CO)_4$ are examples. All these are stable enough for characterization in air, but some react slowly with air or decompose easily to the metal and CO. Their structures and reactions are explained further in Chapters 13 and 14.

Reactions of copper complexes show these ligand effects. Table 12-18 lists some of these reactions and their electrode potentials. If the reactions of the aquated Cu(II)

TABLE 12-18
Electrode Potentials of Cobalt and Copper Species

Cu(II)-Cu(I) Reactions	*$\mathcal{E}^\circ$ (V)*
$Cu^{2+}(aq) + 2\,CN^- + e^- \rightleftharpoons [Cu(CN)_2]^-(aq)$	+1.103
$Cu^{2+}(aq) + I^- + e^- \rightleftharpoons CuI(s)$	+0.86
$Cu^{2+}(aq) + Cl^- + e^- \rightleftharpoons CuCl(s)$	+0.538
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.153
$[Cu(NH_3)_4]^{2+} + e^- \rightleftharpoons [Cu(NH_3)_2]^+ + 2\,NH_3$	−0.01
Cu(II)-Cu(0) Reactions	*$\mathcal{E}^\circ$ (V)*
$Cu^{2+}(aq) + 2\,e^- \rightleftharpoons Cu(s)$	+0.337
$[Cu(NH_3)_4]^{2+} + 2\,e^- \rightleftharpoons Cu(s) + 4\,NH_3$	−0.05
Co(III)-Co(II) Reactions	*$\mathcal{E}^\circ$ (V)*
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.808
$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$	+0.108
$[Co(CN)_6]^{3-} + e^- \rightleftharpoons [Co(CN)_6]^{4-}$	−0.83

Source: T. Moeller, *Inorganic Chemistry*, Wiley-Interscience, New York, 1982, p. 742.

and Cu(I) are taken as the basis for comparison, it can be seen that complexing Cu(II) with the hard ligand ammonia reduces the potential, stabilizing the higher oxidation state as compared with either Cu(I) or Cu(0). On the other hand, the soft ligand cyanide favors Cu(I), as do the halides (increased potentials). The halide cases are complicated by precipitation, but still show the effects and also show that the soft iodide ligand makes Cu(I) more stable than the harder chloride.

In other cases, almost any ligand can serve to stabilize a particular species, and competing effects will have different results. Perhaps the most obvious example is the Co(III)-Co(II) couple, mentioned earlier in Section 12-8-1. As the hydrated ion (or aqua complex), Co(III) is a very strong oxidizing agent, reacting readily with water to form oxygen and Co(II). However, when coordinated with any ligand other than water or fluoride, Co(III) is kinetically stable, and almost stable in the thermodynamic sense as well. Part of the explanation is that Δ_o is quite large with any ligand, leading to an easy change from the high-spin Co(II) configuration $t_{2g}^5\, e_g^2$ to the low-spin Co(III) configuration t_{2g}^6. This means that the reverse reduction is much less favorable, and the complex ions have little tendency to oxidize other species. The reduction potentials (Table 12-18) for Co(III)-Co(II) with different ligands are in the order $H_2O > NH_3 > CN^-$, the order of increasing Δ_o and decreasing hardness. The increasing LFSE change is strong enough to overcome the usual effect of softer ligands stabilizing lower oxidation states.

12-9 REACTIONS OF COORDINATED LIGANDS

The reactions described to this point are either substitution reactions or oxidation-reduction reactions. Other reactions are primarily those of the ligands; in these reactions, coordination to the metal changes the ligand properties sufficiently to change the rate of a reaction or to make possible a reaction that would otherwise not take place. Such reactions are important for many different types of compounds and many different conditions. Chapter 14 describes such reactions for organometallic compounds and Chapter 16 describes some reactions important in biochemistry. In this chapter, we describe only a few examples of these reactions; the interested reader can find many more examples in the references cited.

Organic chemists have long used inorganic compounds as reagents. For example, Lewis acids such as $AlCl_3$, $FeCl_3$, $SnCl_4$, $ZnCl_2$, and $SbCl_5$ are used in Friedel-Crafts electrophilic substitutions. The labile complexes formed by acyl or alkyl halides and these Lewis acids create positively charged carbon atoms that can react readily with aromatic compounds. The reactions are generally the same as without the metal salts, but their use speeds the reactions and makes them much more useful.

As usual, it is easier to study reactions of inert compounds, such as those of Co(III), Cr(III), Pt(II), and Pt(IV), in which the products remain complexed to the metal and can be isolated for more complete study. However, useful catalysis requires that the products be easily separated from the catalyst, so relatively rapid dissociation from the metal is a desirable feature. Although many of the reactions described here do not have this capability, those with biological significance do, and chemists studying ligand reactions for synthetic purposes try to incorporate it into their reactions.

12-9-1 HYDROLYSIS OF ESTERS, AMIDES, AND PEPTIDES

Amino acid esters, amides, and peptides can be hydrolyzed in basic solution, and the addition of many different metal ions speeds the reactions. Labile complexes of Cu(II), Co(II), Ni(II), Mn(II), Ca(II), and Mg(II), as well as other metal ions, promote the reactions. Whether the mechanism is through bidentate coordination of the α-amino group and the carbonyl, or only through the amine, is uncertain, but seems to depend on the relative concentrations. Because the reactions depend on complex formation and hydrolysis as separate steps, their temperature dependence is complex, and interpretation of all the effects is difficult.[34]

Co(III) complexes promote similar reactions. When four of the six octahedral positions are occupied by amine ligands and two *cis* positions are available for further reactions, it is possible to study not only the hydrolysis itself, but the steric preferences of the complexes. In general, these compounds catalyze the hydrolysis of N-terminal amino acids from peptides, and the amino acid that is removed remains as part of the complex. The reactions apparently proceed by coordination of the free amine to cobalt, followed either by coordination of the carbonyl to cobalt and subsequent reaction with OH^- or H_2O from the solution (path A in Figure 12-15) or reaction of the carbonyl carbon with coordinated hydroxide (path B).[35] As a result, the N-terminal amino acid is removed from the peptide and left as part of the cobalt complex in which the α-amino nitrogen and the carbonyl oxygen are bonded to the cobalt. Esters and amides are also hydrolyzed by the same mechanism, with the relative importance of the two pathways dependent on the specific compounds used.

Other compounds such as phosphate esters, pyrophosphates, and amides of phosphoric acid, are hydrolyzed in similar reactions. Coordination may be through only one oxygen of these phosphate compounds, but the overall effect is similar.

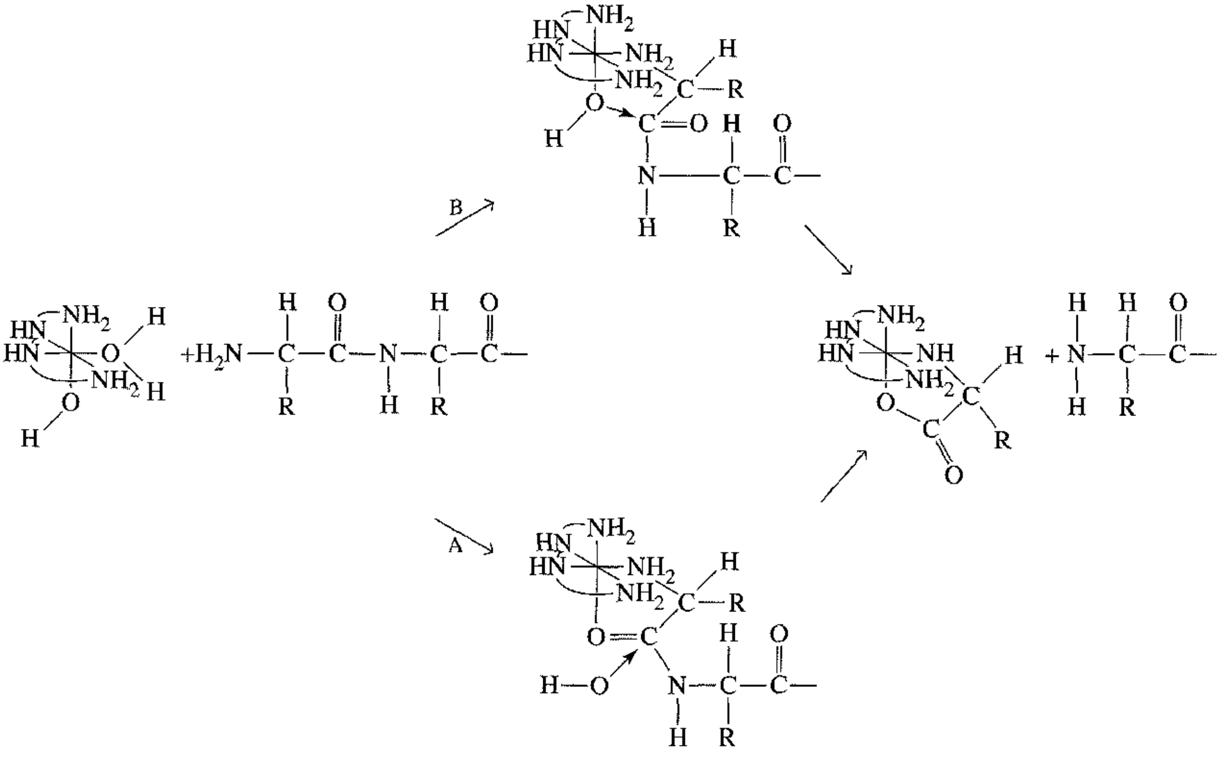


FIGURE 12-15 Peptide Hydrolysis by $[Co(trien)(H_2O)(OH)]^{2+}$. (Data from D. A. Buckingham, J. P. Collman, D. A. R. Hopper, and L. G. Marzilli, *J. Am. Chem. Soc.*, **1967**, *89*, 1082).

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[34] M. M. Jones, *Ligand Reactivity and Catalysis*, Academic Press, New York, 1968. Chapter III summarizes the arguments and mechanisms.

[35] J. P. Collman and D. A. Buckingham, *J. Am. Chem. Soc.*, **1963**, *85*, 3039; D. A. Buckingham, J. P. Collman, D. A. R. Hopper, and L. G. Marzelli, *J. Am. Chem. Soc.*, **1967**, *89*, 1082.

12-9-2 TEMPLATE REACTIONS

Template reactions are those in which formation of a complex places the ligands in the correct geometry for reaction. One of the earliest was for the formation of phthalocyanines, shown in Figure 12-16. Although the compounds were known earlier, their study really began in 1928 after discovery of a dark blue impurity in phthalimide prepared by reaction of phthalic anhydride with ammonia in an enameled vessel. This impurity was later discovered to be the iron phthalocyanine complex, created from iron released into the mixture by a break in the enamel surface. A similar reaction takes place with copper, which forms more useful pigments. The intermediates shown in Figure 12-16 have been isolated. Phthalic acid and ammonia first form phthalimide, then 1-keto-3-iminoisoindoline, and then 1-amino-3-iminoisoindolenine. The cyclization reaction then occurs, probably with the assistance of the metal ion, which holds the chelated reactants in position. This is confirmed by the lack of cyclization in the absence of the metals.[36] Other reagents can be used for this synthesis, but the essential feature of all these reactions is the formation of the cyclic compound by coordination to a metal ion.

More recently, similar reactions have been used extensively in the formation of macrocyclic compounds. Imine or Schiff base complexes ($R_1N{=}CHR_2$) have been extensively studied. In this case, the compounds can be formed without complexation, but the reaction is much faster in the presence of metal ions. An example is shown in Figure 12-17. In the absence of copper, benzothiazoline is favored in the final step rather than the imine; very little of the Schiff base is present at equilibrium.

A major feature of template reactions is geometric; formation of the complex brings the reactants into close proximity with the proper orientation for reaction. In addition, complexation may change the electronic structure sufficiently to promote the reaction. Both are common to all coordinated ligand reactions, but the geometric factor is

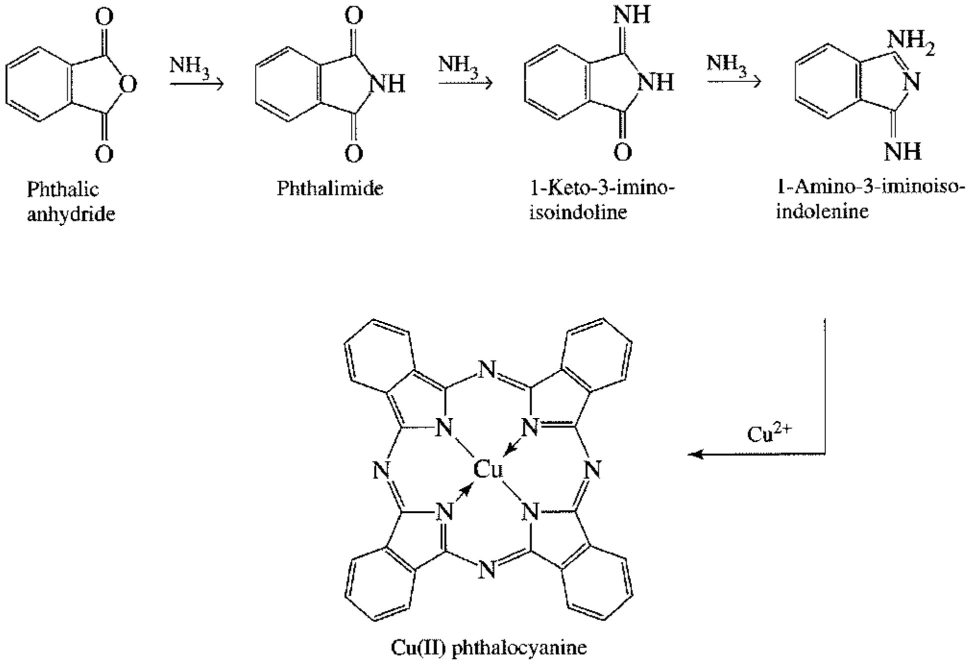

FIGURE 12-16 Phthalocyanine Synthesis.

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[36] R. Price, "Dyes and Pigments," in G. Wilkinson, R. D. Gillard, and J. A. McCleverty, eds., *Comprehensive Coordination Chemistry*, Vol. 6, Pergamon Press, Oxford, 1987, pp. 88–89.

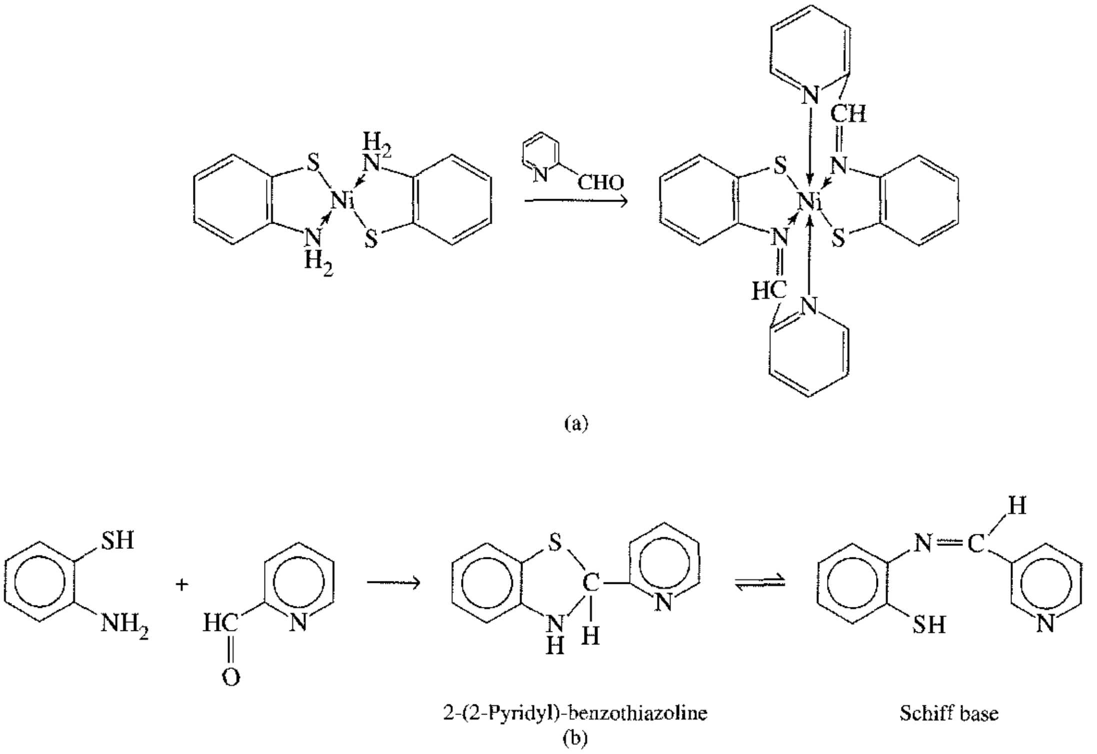


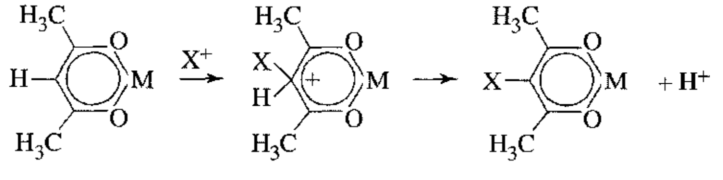
FIGURE 12-17 Schiff Base Template Reaction. (a) The Ni(II)-*o*-aminothiophenol complex reacts with pyridine-1-carboxaldehyde to form the Schiff base complex. (b) In the absence of the metal ion, the product is benzthiazoline; very little of the Schiff base is formed. (From L. F. Lindoy and S. E. Livingstone, *Inorg. Chem.*, **1968**, *7*, 1149.)

more obvious in these; the final product has a structure determined by the coordination geometry. Template reactions have been reviewed and a large number of reactions and products described.[37]

12-9-3 ELECTROPHILIC SUBSTITUTION

Acetylacetone complexes are known to undergo a wide variety of reactions that are at least superficially similar to aromatic electrophilic substitutions. Bromination, nitration, and similar reactions have been studied.[38] In all cases, coordination forces the ligand into an enol form and promotes reaction at the center carbon by preventing reaction at the oxygens and concentrating negative charge on carbon 3. Figure 12-18 shows the reactions and a possible mechanism.

FIGURE 12-18 Electrophilic Substitution on Acetylacetone Complexes. X = Cl, Br, SCN, SAr, SCl, NO_2, CH_2Cl, $CH_2N(CH_3)_2$, COR, CHO.



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[37] D. St. C. Black, "Stoichiometric Reactions of Coordinated Ligands," in Wilkinson, Gillard, and McCleverty, *Comprehensive Coordination Chemistry*, pp. 155–226.

[38] J. P. Collman, *Angew. Chem., Int. Ed.*, **1965**, *4*, 132.

GENERAL REFERENCES

The general principles of kinetics and mechanisms have been described by J. W. Moore and R. G. Pearson, *Kinetics and Mechanism*, 3rd ed., Wiley-Interscience, New York, 1981, and F. Wilkinson, *Chemical Kinetics and Reaction Mechanisms*, Van Nostrand-Reinhold, New York, 1980. The classic for coordination compounds is F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., John Wiley & Sons, New York, 1967. More recent books are by J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole, Monterey, CA, 1985, and D. Katakis and G. Gordon, *Mechanisms of Inorganic Reactions*, Wiley-Interscience, New York, 1987. The reviews in G. Wilkinson, R. D. Gillard, and J. A. McCleverty, eds., *Comprehensive Coordination Chemistry*, Pergamon Press, Elmsford, New York, 1987, provide a more comprehensive collection and discussion of the data. Volume 1, *Theory and Background*, covers substitution and redox reactions, and Volume 6, *Applications*, is particularly rich in data on ligand reactions.

PROBLEMS

12-1 The high-spin d^4 complex $[Cr(H_2O)_6]^{2+}$ is *labile*, but the low-spin d^4 complex ion $[Cr(CN)_6]^{4-}$ is *inert*. Explain.

12-2 Why is the existence of a series of entering groups with different rate constants evidence for an associative mechanism (A or I_a)?

12-3 Predict whether these complexes would be labile or inert and explain your choices. The magnetic moment is given in Bohr magnetons (μ_B) after each complex.

Ammonium oxopentachlorochromate(V)	1.82
Potassium hexaiodomanganate(IV)	3.82
Potassium hexacyanoferrate(III)	2.40
Hexammineiron(II) chloride	5.45

12-4 Consider the half-lives of substitution reactions of the pairs of complexes:

Half-Lives Shorter than 1 Minute	*Half-Lives Longer than 1 Day*
$[Cr(CN)_6]^{4-}$	$[Cr(CN)_6]^{3-}$
$[Fe(H_2O)_6]^{3+}$	$[Fe(CN)_6]^{4-}$
$[Co(H_2O)_6]^{2+}$	$[Co(NH_3)_5(H_2O)]^{3+}$ (H_2O exchange)

Interpret the differences in half-lives in terms of the electronic structures.

12-5 The general rate law for substitution in square-planar Pt(II) complexes is valid for the reaction

$$[Pt(NH_3)_4]^{2+} + Cl^- \longrightarrow [Pt(NH_3)_3Cl]^+ + NH_3$$

Design the experiments needed to verify this and to determine the rate constants. What experimental data are needed, and how are the data to be treated?