Ligand Substitution Dynamics

Substitution of a ligand in an inner sphere complex by an outside group is the most fundamental reaction in metal ion chemistry

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Of the 103 known elements, 83 are classified as metals. Much of the chemistry of this very large and diverse family of elements is the chemistry of metals as ions in solution. This includes some of those most familiar of all chemical reactions that we meet in our first introduction to chemistry: the precipitation of halides as their silver salts for identification; the changes of color of copper ion solution as ammonia is added; and many more. Metal ions in solution are always bound to other molecules or negative ions. Species capable of good binding to metal ions are referred to as ligands and may be solvent molecules or other good coordinating groups. The metal plus the most firmly bound ligands make up an aggregate species called an inner sphere complex. Species immediately outside the inner sphere complex are in the "outer sphere" environment.

Such complex compounds of metals play key roles in important chemical processes. Hemoglobin, the oxygen carrier of blood, is an iron complex. The green pigment of plants, chlorophyll, is a similar compound of magnesium. Vitamin B_{12} contains a cobalt ion bound to another elaborate ligand system. Many catalysts important to chemical synthesis are metal ion complexes, and metal complexes intervene in most electroplating processes.
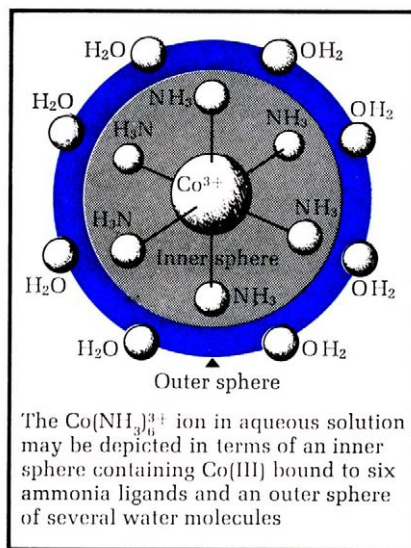
If we are to understand and control the chemistry of metal ions in solution, we must understand the processes by which their complexes are formed and interconverted. This is most often a matter of the replacement of one coordinated ligand by another. *The substitution of a ligand in the inner sphere (leaving group) by an outside group (entering group) is the most fundamental of the reactions in metal ion chemistry.* In fact, all discussions of reactions of metal complexes hinge on an understanding of the dynamics of their ligand substitution process, since it is an ever present possibility.

To attempt a general theory of ligand substitution dynamics seems a formidable task, since so many elements of such diverse properties fall within the scope of the undertaking. However, substantial progress has been made, especially in recent years, because of a fascinating convergence of:

• Results of studies of certain model systems by traditional methods for analysis of rate and mechanism.

• Results over a broad time range made available by application of new fast reaction techniques developed largely by Prof. Manfred Eigen and his collaborators in West Germany.

• Results of applications of improved electronic structural models for metal complexes to give added power to theoretical correlations.

In this article we outline some recent advances in the understanding of ligand substitution dynamics to reveal the effectiveness of the interplay of new and old techniques with fresh theoretical insights.

The $Co(NH_3)_6^{3+}$ ion in aqueous solution may be depicted in terms of an inner sphere containing Co(III) bound to six ammonia ligands and an outer sphere of several water molecules

Mechanistic language

To approach an understanding of ligand substitution processes, it is first necessary to catalog the kinds of experiments which are available in the armamentarium of the "chemical dynamicist" interested in these problems and to consider what sorts of information these experiments provide. Commonly, a student of chemical dynamics studies reaction rates. But such studies may be approached from two points of view. First, it is possible to analyze the rate law for a reaction, which is the differential equation relating rate to reactant concentrations. This allows determination of the species which are present in the transition state of the reaction. Second, if it is assumed that a series of reactions proceeds by related mechanisms, the rates of the reactions may be compared and the energetic factors in activation inferred. In other words, it may be possible to consider the role of a variable entering group in a substitution and determine from the observed rates whether the entering group plays a role in determining the activation energy for substitution. Reaction mechanisms for substitution processes may be classified with respect to these types of experiments. A useful classification which considers reaction types that can be defined "operationally" is constructed readily when classification with respect to each of the two types of experiments is approached separately.

Careful study of the reaction rate law leads to identification of the reactant species which are components in the transition state or participate in reaction steps preceding the transition state. In reasonably favorable circumstances, this leads, in turn, to identification of the number of elementary steps necessary for the accomplishment of the overall reaction. Substitutions may follow one of three distinct, simple patterns: dissociative (D), associative (A), and interchange (I). The dissociative reaction is a two-step substitution involving the initial formation of an intermediate of reduced coordination number. The associative substitution proceeds in two steps through initial formation of an intermediate of increased coordination number. The interchange pattern is a substitution in a single step.
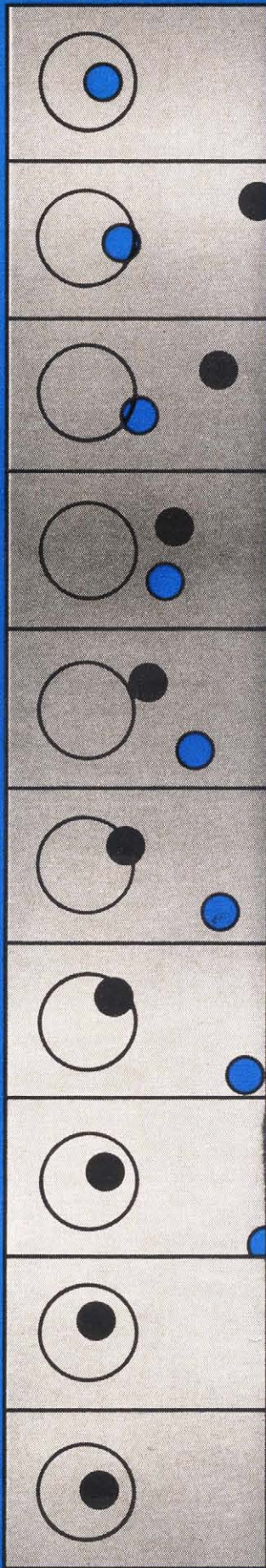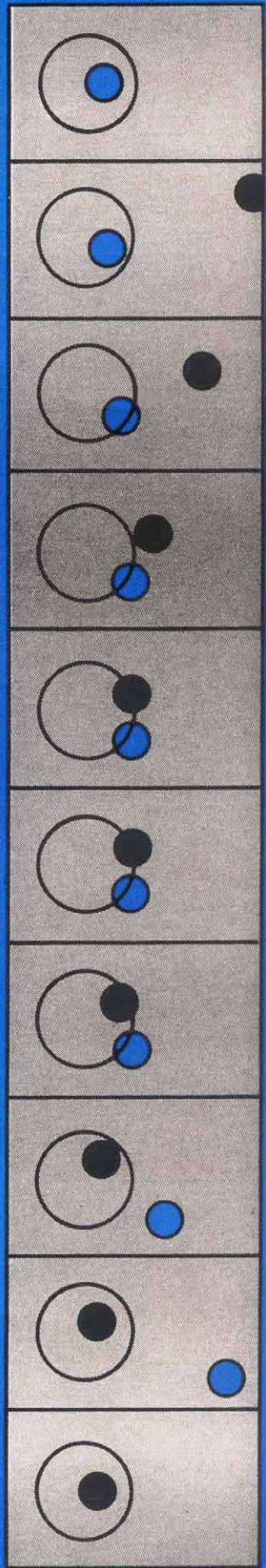
ENERGY

HIGH ← → LOW
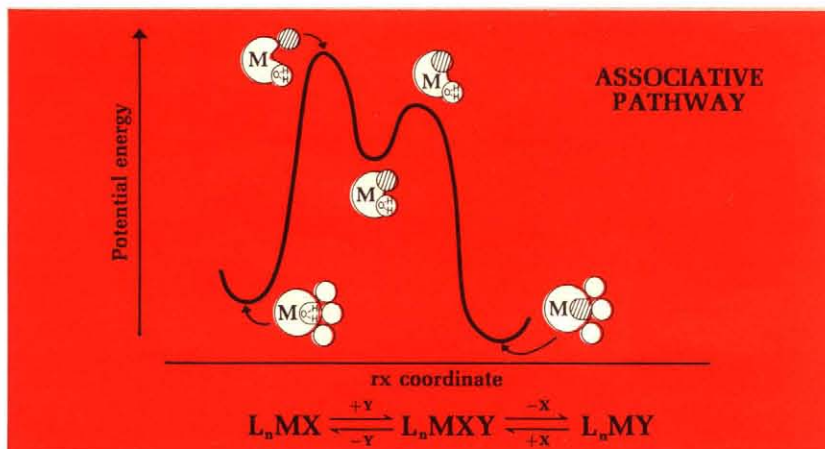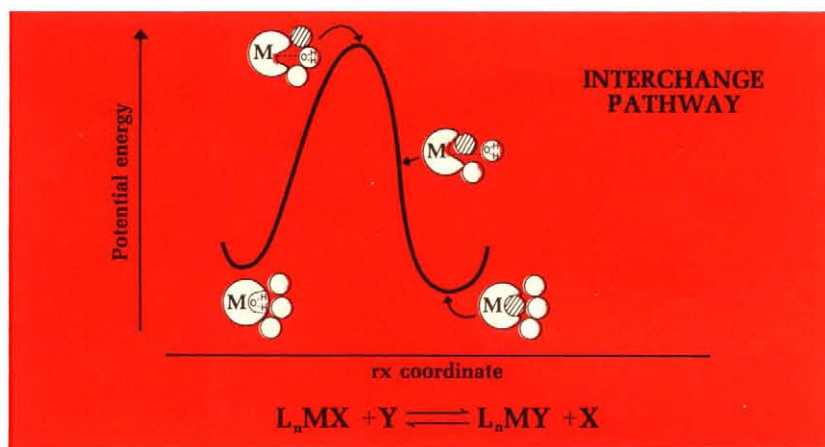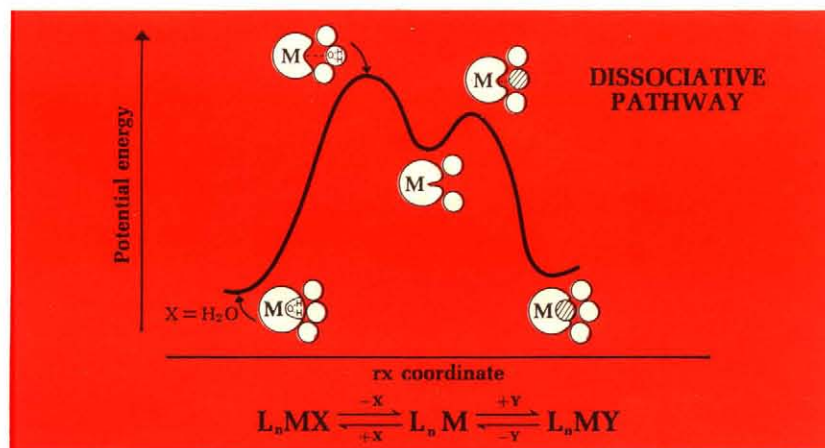
DISSOCIATIVE PATHWAY
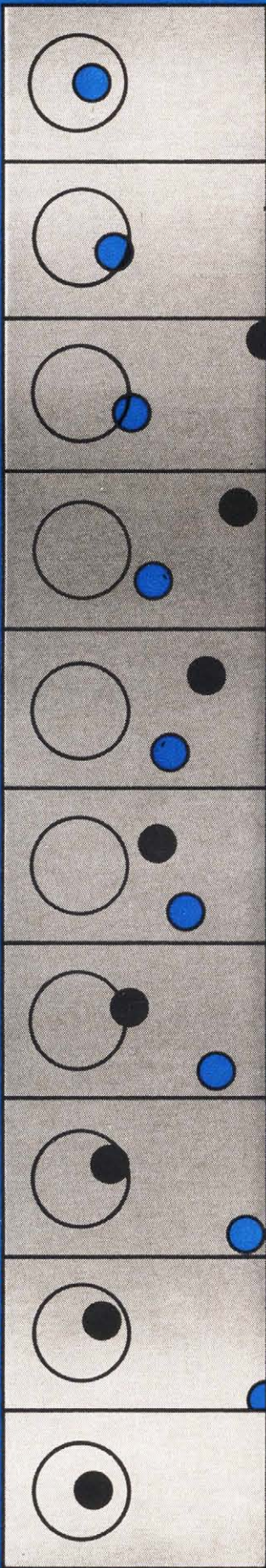
INTERCHANGE PATHWAY

ASSOCIATIVE PATHWAY

Classification of ligand substitution mechanisms

|	Stoichiometric mechanism		
Mode of activation	Intermediate of increased coordination number	One-step process	Intermediate of reduced coordination number
Associative activation	A	I_a	
Dissociative activation		I_d	D

Ligand substitutions may follow one of three mechanisms

X is the leaving ligand, Y the entering ligand, M the metal atom, and L designates other ligands not involved in substitution.

DISSOCIATIVE PATHWAY

Potential energy

$X = H_2O$

rx coordinate

$$L_nMX \underset{+X}{\overset{-X}{\rightleftharpoons}} L_nM \underset{-Y}{\overset{+Y}{\rightleftharpoons}} L_nMY$$

INTERCHANGE PATHWAY

Potential energy

rx coordinate

$$L_nMX + Y \rightleftharpoons L_nMY + X$$

ASSOCIATIVE PATHWAY

Potential energy

rx coordinate

$$L_nMX \underset{-Y}{\overset{+Y}{\rightleftharpoons}} L_nMXY \underset{+X}{\overset{-X}{\rightleftharpoons}} L_nMY$$

Turning to comparison of rates of related substitution reactions, the most important single issue is the effect of the entering group. If the rate of a substitution is dependent upon the nature of the entering group, clearly the process of breaking the bond to the leaving group is assisted by the newly forming bond. If the rate of substitution is quite insensitive to the nature of the entering group, it is difficult to imagine that binding of the entering group is assisting substitution. In the second case, the complex must accumulate sufficient energy by thermal fluctuations to "dissociate" the leaving group. Because these two types of activation processes occur in the A and D paths, respectively, they are designated the *a* and *d* modes of activation. Interchange processes may employ either activation model I_a or I_d.

An alternative approach to classifying substitutions which differs from the present scheme (see table) is the scheme borrowed from discussion of nucleophilic substitution reactions of organic chemistry. The D process may be designated S_N1 (substitution, nucleophilic, unimolecular) and the A process S_N2 (substitution, nucleophilic, bimolecular). This classification is widely used but may be argued to be infelicitous for some I reactions. All I reactions are "bimolecular" in the sense that both the substrate complex and the entering group must be participants in the transition state. But the bimolecularity may be quite accidental. An I_d process is analogous to a D process in that the transition state is achieved by breaking the bond to the leaving group. If the residual moiety left behind when the bond is broken is noticeably stable, an intermediate is formed which may survive long enough to react selectively and a two-step D reaction is observed. If, however, the residual moiety left after dissociation is highly energetic, it may not be able to survive long enough to react with any ligand except those in its immediate outer sphere "solvation" shell. An I_d reaction which is "accidentally" bimolecular is the result. The close analogy between the D and I_d processes in terms of mode of activation is preserved in the S_N1-S_N2 classification scheme only by redefining the concept of molecularity to make it correspond to the number of species changing covalency in the reaction step. Then D and I_d reactions are S_N1. The price of this maneuver is to make molecularity a nonoperational concept. Molecularity then may no longer be determined from rate laws. In this article we will employ the scheme shown in the table because mechanisms on the D-I_d borderline have turned out to be extremely common in ligand substitutions.

Metal ions in aqueous solution may be placed into four arbitrary classes

Decreasing rate, sec.⁻¹ → 10^8 10^4 1 10^{-8}

I   II   III   IV
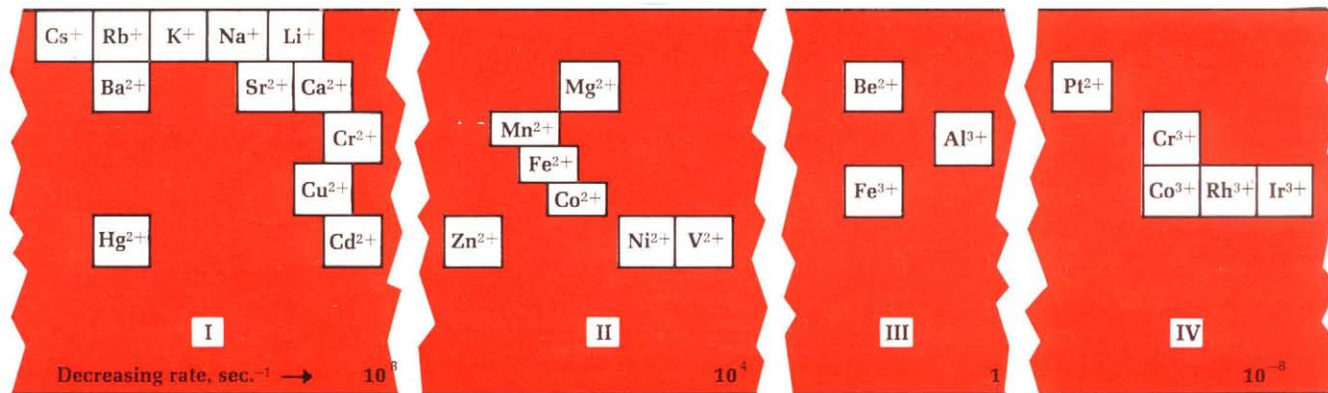
Substitution time scale

Metal ions in aqueous solution may be placed into four arbitrary classes based on the magnitudes of the rate constants for substitutional processes involving their complexes. For this discussion we are concerned with reactions where the leaving group X = H_2O, the solvent is water, and the other inner sphere ligands (L_n) are also H_2O molecules. Four categories on a time scale are defined as:

• Class I. Exchange of water is very fast; most, even "fast," kinetic techniques are not applicable. First order rate constants are about 10^8 sec.⁻¹ or greater. Included in this group are the alkali metal ions and the alkaline earth metal ions except Mg^{2+} and Be^{2+}.

• Class II. The first order rate constant for water exchange is 10^4 to 10^8 sec.⁻¹ Dipositive transition metal ions plus the tripositive rare earth ions are in this class, along with Mg^{2+}. Most ions display characteristic rates independent of the entering group.

• Class III. First order rate constants here are 1 to 10^4 sec.⁻¹ Most of the tripositive transition metal ions such as Fe^{3+} are in this class as are Be^{2+} and Al^{3+}.

• Class IV. Complexes of Class IV ions are relatively inert; first order rate constants are commonly between 10^1 and 10^{-9} sec.⁻¹ Prominent members include Co^{3+}, Cr^{3+}, and Pt^{2+}.

Before turning to finer mechanistic

details, we will examine the reasons for the dramatic differences in substitutional reactivity of the metal ions. For example, a factor of some 10^{16} in rate separates $K(H_2O)_x^+$ and Cr-$(H_2O)_6^{3+}$. Most of the large differences can be explained on the basis of a simple electrostatic model of binding, because there is a rough correlation between the charge-to-size ratio of the ion and its position in the reactivity table. Other factors being equal, we should expect that small, highly charged cations should firmly bind a relatively nonpolarizable ligand such as water. Moreover, the higher the charge, the stronger the binding should be. Thus, Class I consists of *all* the monopositive and several large dipositive ions. Class II is composed mainly of the smaller dipositive ions and several large tripositive ones. Class III includes the very small Be^{2+} and two small tripositive ions, Fe^{3+} and Al^{3+}. The very low reactivity of the Class IV ions cannot be understood in terms of this simple model. However, we recognize the ions in this class as those having specially stable d^n ground-state electronic structures in octahedral and square planar coordination environments. In octahedral structures, the d^n configurations d^3 and d^6 (low spin) have special stability, d^8 (low spin) is a notably stable ground state for square planar coordination. Class IV ions, then, all have extra ligand-field ground-state stabilization and a resulting low substitutional reactivity.

Model systems

Class IV complexes have been studied extensively because the rates are slow enough to permit using conventional kinetic techniques. Rate constants for exchange of water at 25° C. in three exemplary cases are:

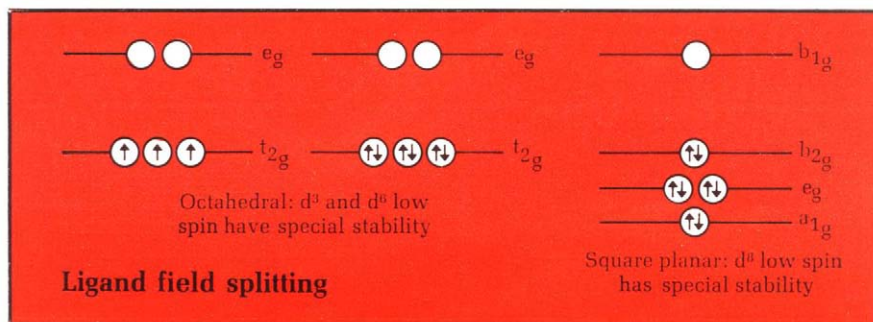• Octahedral d^6 low spin; Co-$(NH_3)_5OH_2^{3+}$; $k = 6 \times 10^{-6}$ sec.⁻¹

• Octahedral d^3; $Cr(OH_2)_6^{3+}$; $6k = 2 \times 10^{-5}$ sec.⁻¹

• Square planar d^8 low spin; Pt-$(dien)OH_2^{2+}$; $k = 1 \times 10^{-3}$ sec.⁻¹

The ligand "dien" is diethylenetri-amine:

$$NH_2-(CH_2)_2-\underset{\underset{NH_2.}{|}}{N}-(CH_2)_2-NH_2.$$

We shall now explore the types of experiments which have led to detailed understanding of cobalt(III) and platinum(II) reactions like the ones above, because it is emerging that the octahedral complexes of cobalt(III) and the square planar complexes of platinum(II) have functioned admirably *as models for the development of key concepts and experiments for understanding ligand substitution processes in general.*

Activation modes

The mode of activation may be deduced from studies of the rate dependence on the nature of the entering group. In cobalt(III) substitutions, it is a very general result that, excluding hydroxide ion, variation of the entering group does not significantly change the rate of reaction. Rate laws commonly are strictly first order, reflecting the fact that, in the absence of entering group effects, the most populous entering group—the solvent— usually enters. Other ligands appear in the rate law only if a solvent molecule is the leaving group. This behavior clearly indicates failure to discriminate among entering groups and is characteristic of the dissociative mode of activation.

Octahedral: d^3 and d^6 low spin have special stability

Square planar: d^8 low spin has special stability

Ligand field splitting

In contrast, rates of platinum(II) substitutions are strongly dependent on the entering group. A reaction which has received much attention recently is:
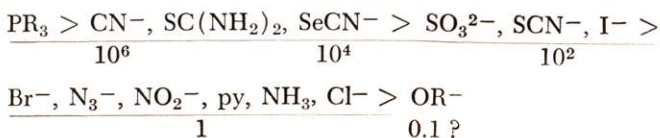
$$trans\text{-}Pt(pip)_2Cl_2 + Y^- \rightarrow$$
$$trans\text{-}Pt(pip)_2(Cl)(Y) + Cl^-$$

where pip = piperidine
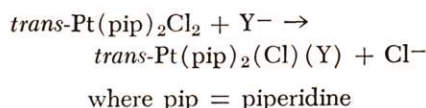
The rate law for this reaction has the form:

$$Rate = (k_1 + k_2[Y])\,[substrate]$$

The second order term (k_2) is what we would expect for an associative mode of activation. All evidence suggests that the first order term (k_1) does not indicate a concurrent dissociative mechanism, rather another associative process involving the solvent. The following are values of k_2 for various entering groups for the substrate trans-dichloropiperidineplatinum(II) in ethanol at 30° C., taken from very recent work by Prof. Umberto Belluco and his coworkers of Padcva, Italy:

Y	$k_2 \times 10^3$, M^{-1} sec.$^{-1}$
$^{36}Cl^-$	0.9
Br^-	6.9
SCN^-	400
$SeCN^-$	3300
$SC(NH_2)_2$	4600

These rate data may be considered definitive for an associative mode of activation. The magnitude of the rate constant k_2 is influenced profoundly by the nature of Y. Experiments of this type have led to an ordering of entering groups for platinum(II) substitutions on a generalized relative rate scale:

$$\underset{10^6}{PR_3} > \underset{10^4}{CN^-,\ SC(NH_2)_2,\ SeCN^-} > \underset{10^2}{SO_3{}^{2-},\ SCN^-,\ I^-} >$$

$$\underset{1}{Br^-,\ N_3{}^-,\ NO_2{}^-,\ py,\ NH_3,\ Cl^-} > \underset{0.1\ ?}{OR^-}$$

In both a and d modes of activation the bond to the leaving group must be "perturbed" in the transition state. In the dissociative mode, the effect should be most dramatic (and independent of the entering group). But for associative activation, the leaving group effect should be variable, being of great importance for poor entering groups.

For cobalt(III) substrates, there are enough equilibrium and rate data available to show a linear free energy correlation (log k vs. log K) for the substitution reaction:

$$Co(NH_3)_5X^{2+} + H_2O \rightleftharpoons$$
$$Co(NH_3)_5OH_2{}^{3+} + X^-$$
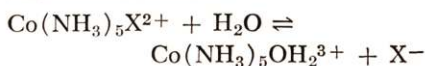
In the expression $\Delta\Delta G^{\ddagger} = \beta\Delta(\Delta G°)$, $\beta = 1.0$, supporting dissociative activation.
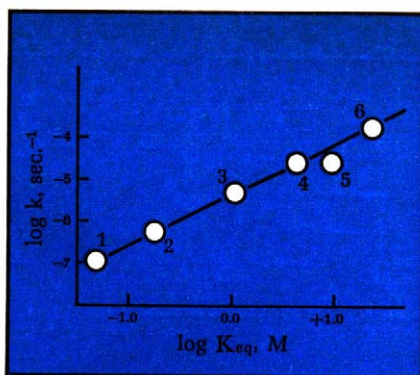
This plot of log rate constant vs. log of equilibrium constant is for the acid hydrolysis reaction of $[Co(NH_3)_5X]^{2+}$ ions. Measurements were made at 25.0° C. Points are: 1, $X^- = F^-$; 2, $X^- = H_2PO_4{}^-$; 3, $X^- = Cl^-$; 4, $X^- = Br^-$; 5, $X^- = I^-$; and 6, $X^- = NO_3{}^-$. The log of a rate or equilibrium constant is proportional to a free energy change. Note that each change of 1.0 kcal. in the overall free energy change for the reaction is paralleled by a 1.0-kcal. change in the free energy required for activation. It is only the leaving anion that is being varied. As the leaving anion is varied, the only significant change in the overall reaction is the change in the solvated anion produced as a product. The linear free energy relationship implies that the transition state **resembles closely** the product with respect to this variation. It follows that the leaving group must be functioning very nearly as a solvated anion in the transition state; that is, effective dissociation has occurred

We'd like to comment now on the electronic theory of the modes of activation under scrutiny here. In the case of cobalt(III) substrates, there is a close correlation between the ligand field strength and inertness of the ligand as a leaving group. For example, we have the rate order for leaving groups:
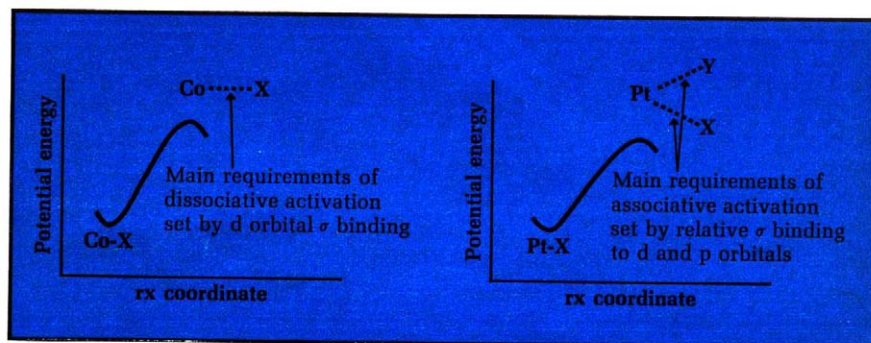
$$I^- > Br^- > Cl^- > F^- > CN^-$$

and the ligand field strength order:

$$CN^- > F^- > Cl^- > Br^- > I^-$$
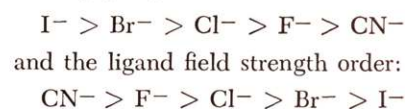
The ligand field splitting is a measure of binding to metal d orbitals. Recent research indicates that the order reflects increasing σ binding to d orbitals, with π orbital effects in a distinctly secondary role. With this in mind, we propose, other things being equal, that the electronic mode of activation at cobalt(III) involves breaking a σ bond to a metal d orbital [in $Co(NH_3)_5X^{2+}$ this would be d_{z^2}].

In platinum(II) substitutions, there is no similar correlation of ligand field strength and inertness of leaving groups. For example, the halides depart in opposite order to that observed for cobalt(III):

$$Cl^- \sim Br^- > I^-$$

And, in general, for platinum(II) it appears that heavier donor atoms are more inert than lighter members of an analogous series. This indicates that binding to d orbitals alone cannot explain the reactivity pattern. Specifically, this suggests an important role for the platinum(II) 6p orbitals. Strong binding to the large 6p orbitals would benefit the heavier donor atoms with more expanded valence orbitals. This would provide the simplest explanation for the anticorrelation of ligand field splitting and ligand inertness. There are other strong indicators for the role of 6p orbitals in platinum(II) substitutions, which we will discuss shortly.

The entering and leaving group effects establish the cobalt(III) substrates as models for dissociative activation and platinum(II) substrates as models for associative activation. In terms of potential energy profiles, we suggest the details of activation shown below:

Main requirements of dissociative activation set by d orbital σ binding

Main requirements of associative activation set by relative σ binding to d and p orbitals

Other relative rate studies are consistent with different modes of activation for the model cobalt(III) and platinum(II) substrates. Two of particular interest which may be acceptable for general use are steric effects and substrate-charge effects. Generally, steric crowding due to substituents on the nonlabile ligands rapidly accelerates cobalt(III) substitutions, where the transition state is *less crowded*. In platinum(II) cases, however, crowding in the ground state slows the reaction enormously, consistent with associative activation in the *unhindered* cases. Indeed, the most sterically hindered platinum(II) and palladium(II) complexes may be forced into dissociative activation. This is presumably the case for the complex $Pd(Et_4dien)Cl^+$ [Et_4dien is $(C_2H_5)_2N\text{-}(CH_2)_2\text{-}N(H)\text{-}(CH_2)_2\text{-}N(C_2H_5)_2$], which reacts 10^4 times slower than unhindered $Pd(dien)Cl^+$ in water, and at least 10^5 times slower in dimethylsulfoxide. Interestingly, the rates for $Pd(Et_4dien)Cl^+$ are about the same as those for analogous rhodium(III) substitutions.

The substrate-charge effect for cobalt(III) and platinum(II) systems is:

| Substrate (charge)	k_1 (H$_2$O), sec.$^{-1}$ (25° C.)	Ratio, $\dfrac{n^+}{(n+1)^+}$
trans-Pt(NH$_3$)$_2$Cl$_2$	9.8×10^{-5}	3.8
Pt(NH$_3$)$_3$Cl$^+$	2.6×10^{-5}	
trans-Co(NH$_3$)$_4$Cl$_2^+$	1.8×10^{-3}	2.7×10^2
Co(NH$_3$)$_5$Cl^{2+}	6.7×10^{-6}	

The much larger effect of substrate charge is consistent with dissociative activation in the cobalt(III) case.

The models cobalt(III) and platinum(II) allow us to extract some useful generalizations concerning relative rates expected for the two different modes of activation. These generalizations are:

| Mode of activation | Influence of | | | |
	Entering group	Leaving group	Steric crowding	Substrate charge
Associative	Large	Variable	Very large decrease in rate	Generally small
Dissociative	Negligible	Large	Moderate to large increases in rate	Generally large

Trans effect in Pt(II) substitutions

A particularly significant influence on rates due to nonlabile ligands is the trans effect in platinum(II) substitutions. The presence of this effect allows us to say more about the structure of the transition state. From experiments, we know that in platinum(II) substitutions the rate of reaction depends strongly on the nature of the ligand in trans position to the leaving group. Conversely, there is little or no influence from the two cis ligands. From this result we can extend the mechanism of associative activation to include a definite structural arrangement of ligands in the transition state. A particularly attractive model assumes trigonal bipyramidal structure for the transition state:
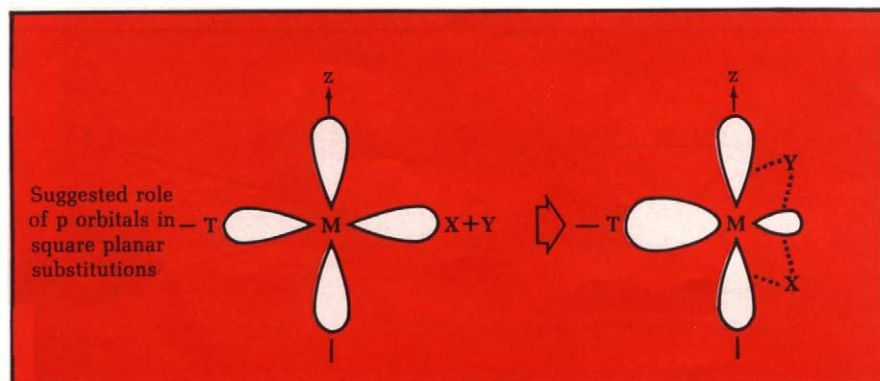

Transition state
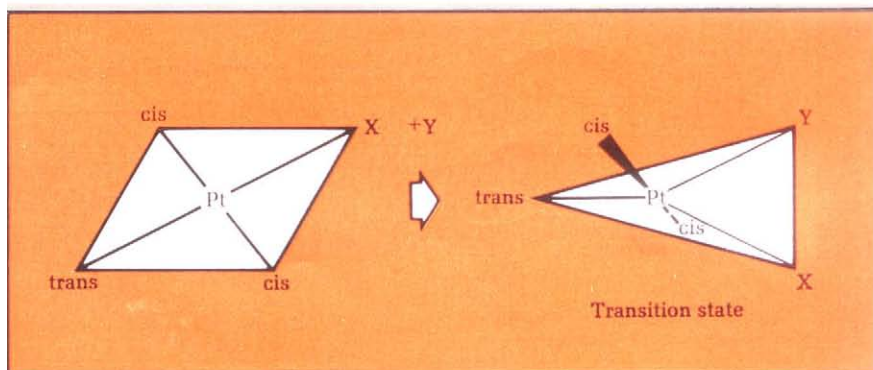
The advantage of this model is that it allows an understanding of large effects due to entering, leaving, and trans groups and relatively small effects due to the cis groups. Specifically, there are large orbital changes in going from the ground state for the *three ligands present in the trigonal plane*.

The observed trans-effect order of ligands, on a relative rate scale, is set out below. Two factors are of possibly major importance in giving this effect.
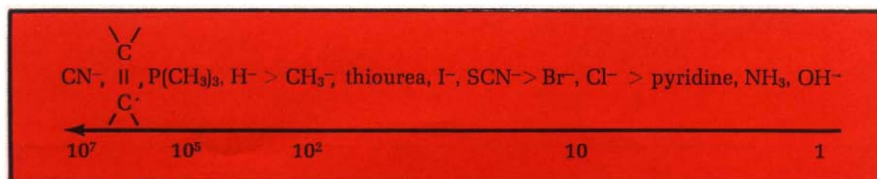
Trans-labilizing order of ligands

According to the π-bonding theory, the trans-labilizing order parallels the order of π-electron accepting ability of the labilizing ligand. This was reasoned on the basis of the idea that upon forming the trigonal bipyramidal intermediate from the square planar structure four rather than three d orbitals would then have the proper symmetry for π interaction with the ligands. A trans group with empty, reasonably stable π-symmetry orbitals would then lower the energy of the transition state simply by accommodating the excess electronic charge around the central metal atom due to the entering ligand. The finding that groups such as PR_3, H^-, and CH_3^- are good trans-labilizing ligands suggests that other factors are also at play. Here again we infer a role for platinum(II) 6p orbitals. If the trans group has strong σ interaction with the metal p orbital (which H^- and CH_3^- should have from overlap considerations), then the bond to the leaving group will be relatively weak in the square planar structure. In the transition state the leaving and entering groups share the previously unoccupied $6p_z$ orbital; the driving force of the reaction is provided by the tendency of the trans ligand (T) to own as much of its own p orbital as possible. This is shown by:

Suggested role of p orbitals in square planar substitutions

Thus far we have not looked beyond the transition state in either cobalt(III) or platinum(II) substitutions. The most difficult area of mechanistic study involves characterization of the number of elementary steps leading to products. In the cobalt(III) case, three studies may be singled out as exemplary in the establishment of *stoichiometric* mechanism.

In the case of $Co(NH_3)_5OH_2^{3+}$ as substrate, rates of water replacement by ligands Y reach limiting values when the $[Co(NH_3)_5OH_2^{3+},Y^-]$ ion pair forms. These limiting rates *do not depend significantly on the nature* of Y, and, furthermore, they are *lower* than the rate of $^{18}OH_2$ exchange. A satisfactory picture emerges by assuming that one of perhaps eight positions in the outer sphere is occupied by Y and, therefore, $k(Y) \cong 1/8k(H_2O)$ for an I_d mechanism. If the reactions were D, the limiting rates would have to reach the water exchange rate.

Two studies have emerged as models for D mechanisms. The substitutions of $Co(CN)_5OH_2^{2-}$ and $Co(SO_3)(NH_3)_5^+$ by various entering groups may be fit to rate laws appropriate to two-step D reactions. *Selective* reactivity of the five-coordinate intermediate is observed. Furthermore, the rate of H_2O exchange in $Co(CN)_5OH_2^{2-}$ is known with fair precision and is consistent with the two-step D process.

In the platinum(II) substitutions, there is strong evidence *external* to rate studies in support of the stable five-coordinate intermediates required along two-step A pathways. The evidence is the existence of several stable trigonal bipyramidal platinum(II), palladium(II), and nickel(II) complexes. Two complexes of relevance are $Ni(CN)_5^{3-}$ and $Pt(SnCl_3)_5^{3-}$.

Finally, then, we may come to strong conclusions with respect to the modes of activation in cobalt(III) and platinum(II) systems. There is more uncertainty with respect to stoichiometric mechanism: A mechanisms are a solid choice for platinum(II) systems, but cobalt(III) systems are so near the D-I_d borderline that crossover has been observed and future cases will need to be judged on an individual basis. Considering ions more generally, it appears that modes of activation may be assigned with some confidence now. Square planar complexes in general appear to employ the *a* mode. The reactions of the Class II ions (water exchange characteristic time 10^{-4} to 10^{-8} sec.), which are entering group insensitive, strongly suggest the *d* mode. Work on the analysis of stoichiometric mechanism in fast reactions is just beginning.

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Suggestions for further reading

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HARRY B. GRAY *was born in Woodburn, Ky., in 1935. He received a B.S. from Western Kentucky University in 1957. He held Dow and National Science Foundation fellowships at Northwestern University, where he received a Ph.D. in 1960. His research was carried out in physical inorganic chemistry under the direction of Prof. Ralph G. Pearson and Prof. Fred Basolo.*

Dr. Gray was a National Science Foundation postdoctoral fellow in the University of Copenhagen during 1960–61. In Copenhagen, he was associated with Prof. Carl J. Ballhausen. In 1961, he joined the chemistry staff at Columbia University as assistant professor, in 1963 was promoted to associate professor, and 1965 to professor. In 1966, he joined the staff of the California Institute of Technology as professor of chemistry.

Dr. Gray has published approximately 90 papers and four books. His fifth book, "Chemical Dynamics," coauthored with J. Dence and G. S. Hammond, will be published this year. He is a member of numerous honorary and professional organizations. His recent honors include an Alfred P. Sloan research fellowship, the E. C. Franklin Memorial Award, the Reilly Lectureship at the University of Notre Dame, the Venable Lectureship at the University of North Carolina, the Franklin Lectureship at the University of Kansas, and the Sloan Lectureship at the University of Alaska. At present, Dr. Gray is serving as chairman of the freshman committee on the Advisory Council of College Chemistry and as associate editor of Inorganica Chimica Acta.

His current research interests include inorganic reaction mechanisms, the preparation and characterization of new inorganic substances, and the interpretation of spectral and magnetic properties of transition metal complexes in terms of modern quantum mechanical theories of electronic structure.
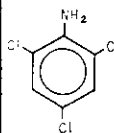
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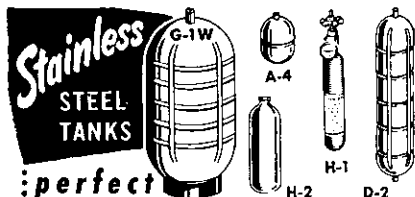**PENINSULAR CHEMRESEARCH INC.**
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