

Coordination Chemistry IV: Reactions and Mechanisms

A

Studying chemical kinetics → Understanding reaction mechanism → Finding ways of facilitating the reaction

+ **B**
$$\rightarrow$$
 C + **D**
 $Rate = k[A]^{m}[B]^{n} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$ $k = \text{rate constant}$

Requirements of reaction mechanism

- 1. Sum of elementary reactions must be the balanced overall reaction.
- 2. Reaction mechanism should explain the experimentally-determined rate law.

 $NO_{2}(g)+CO(g) \rightarrow NO(g)+CO_{2}(g)$ Experimentally, $Rate = k[NO_{2}]^{2}$ Possible mechanism $NO_{2}(g)+NO_{2}(g) \rightarrow NO_{3}(g)+NO(g)$ \leftarrow rate-determining step $\frac{NO_{3}(g)+CO(g) \rightarrow NO_{2}(g)+CO_{2}(g)}{NO_{2}(g)+CO(g) \rightarrow NO(g)+CO_{2}(g)}$ $Rate = \frac{\Delta[NO_{3}]}{\Lambda t} = k_{1}[NO_{2}]^{2} \implies Rate = \frac{\Delta[NO]}{\Lambda t} = \frac{\Delta[CO_{2}]}{\Lambda t} = k_{1}[NO_{2}]^{2}$

Principle of microscopic reversibility:

- •In a reversible reaction, the mechanism in one direction is exactly the reverse of the mechanism in the other direction. This does not apply to reactions that begin with a photochemical excitation.
- •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.





Parameters obtained from the kinetic experiments:

- •Order of the reaction, Rate constant
- •Free energy of activation, Enthalpy (or heat) of activation, Entropy of activation
- Volume of activation

 $A + B \rightarrow C + D$

$$Rate = k[A]^{m}[B]^{n} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$$

k = rate constant

•Sometimes, we use **steady-state approximation** for deriving the rate law.

The concentration of the **intermediate** is assumed to be small and essentially unchanging during much of the reaction



Understanding the mechanism





Reaction types of transition metal complexes



Inert and Labile Compounds

Examples of substitution reactions	These reactions are fast. Complexes, which react rapidly, are called labile.
$[N_1(H_2O)_6]^{2+} + 6 NH_3 \implies [N_1(NH_3)_6]^{2+} + 6 H_2O$ green blue	Taube's criterion $-t_{1/2} \le 1 \min$
$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5(SCN)]^{2+} + H_2O$ very pale violet red	Labile ◄► Inert (Robust) <== kinetic term
Successive addition of HNO ₃ , NaCl, H ₃ PO ₄ , KSCN, NaF to aq. soln of $Fe(NO_3)_3 \bullet 9H_2O$	Be careful! : thermodynamically, kinetically
$[Fe(H_2O)_5(OH)]^{2+} + H^+ \longrightarrow [Fe(H_2O)_6]^{3+}$ yellow colorless (very pale violet)	[Fe(H ₂ O) ₅ (F)] ²⁺ : thermodynamically stable, but kinetically labile
$[Fe(H_2O)_6]^{3+} + Cl^- \longrightarrow [Fe(H_2O)_5(Cl)]^{2+} + H_2C$ yellow	$(C_0(NH_3)_6)^{3+} + 6 H_3O^+$
$[Fe(H_2O)_5(Cl)]^{2+} + PO_4^{3-} \longrightarrow Fe(H_2O)_5(PO_4) + Cl^-$ colorless	Thermodynamically unstable, but kinetically inert
$Fe(H_2O)_5(PO_4) + SCN^- \longrightarrow [Fe(H_2O)_5(SCN)]^{2+} + Po_{red}$	O ₄ ³⁻
$[Fe(H_2O)_5(SCN)]^{2+} + F^- \longrightarrow [Fe(H_2O)_5(F)]^{2+} + SCN$ colorless	• Inert compound is easier to be studied.

Inert and Labile Compounds

In general, those Number of d Electrons 1 2 3 4 5 6 7 8 9 10	e with h LFSE (Δ_0) $-\frac{2}{5}$ $-\frac{4}{5}$ $-\frac{6}{5}$ $-\frac{3}{5}$ $-\frac{4}{5}$ $-\frac{6}{5}$ $-\frac{4}{5}$ $-\frac{6}{5}$ $-\frac{3}{5}$ $-\frac{6}{5}$ $-\frac{3}{5}$ $-\frac{6}{5}$ 0	higher LF LFSE (Δ_0) $-\frac{2}{5}$ $-\frac{4}{5}$ $-\frac{6}{5}$ $-\frac{10}{5}$ $-\frac{12}{5}$ $-\frac{9}{5}$ $-\frac{9}{5}$ $-\frac{9}{5}$ $-\frac{9}{5}$ $-\frac{6}{5}$ $-\frac{9}{5}$ $-\frac{9}{5}$ $-\frac{6}{5}$ $-\frac{9}{5}$	SE are inert. Werner was lucky because his compounds were Co(III), Cr(III), Pt(II) which are inert. In other words, he was careful for choosing his complexes.	These reactions are fast. Comp rapidly, are called labile . Taube's criterion $- t_{1/2} \le 1$ min Labile \checkmark Inert (Robust) Be careful!: thermodynamically [Fe(H ₂ O) ₅ (F)] ²⁺ : thermodynamically stable. [Co(NH ₃) ₆] ³⁺ + 6 H ₃ O ⁺ \downarrow \Longrightarrow [Co(H ₂ O) ₆] ³⁺ Thermodynamically unstable.	elexes, which react <== kinetic term , kinetically , but kinetically labile $+ 6 \text{ NH}_4^+ (\Delta G^\circ < 0)$ le, but kinetically inert
Slow Reaction	ns (Ine	ert)	Intermediate	Fast Reactions (Labile)	• Inert compound
d^3 , low-spin d^4 , Strong-field d^8 (so	d ⁵ , an quare p	d d ⁶ blanar)	Weak-field d ⁸	d^{1} , d^{2} , high-spin d^{4} , d^{5} , and d^{6} d^{7} , d^{9} , d^{10}	is easier to be studied.

Mechanisms of Substitution

Dissociative (D) Mechanism $ML_nX \rightarrow ML_n + X \rightarrow ML_nY + X$

The departing ligand leaves, and a discernable intermediate with a lower coordination number is formed. Rate is independent of Y, and is determined by the breaking of the M-X bond (analogous to S_N 1).

Associative (A) Mechanism $ML_nX + Y \rightarrow ML_nXY \rightarrow ML_nY + X$

The incoming ligand adds to the complex, and an intermediate with a increased coordination number is formed. (analogous to $S_N 2$).

Interchange (I) Mechanism

 $\begin{array}{ccc} ML_nX+Y & \rightarrow & ML_nY+X \\ & &$





The incoming ligand is presumed to assist in the reaction, but no detectable intermediates appear. \rightarrow dissociative interchange (I_d) and associative interchange (I_a)

TABLE 12.1 Classification of Substitution Mechanisms				
	Stoichiome	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	А	
	Alternative Labels			
S _N 1 lim (limiting first-order nucleophilic substitution)			S _N 2 lim (limiting second-order nucleophilic substitution)	

Kinetic Aspects of Reaction Pathways

Dissociative (D) Mechanism $ML_nX \rightarrow ML_n + X \rightarrow ML_nY + X$

The departing ligand leaves, and a discernable intermediate with a lower coordination number is formed. Rate is independent of Y, and is determined by the breaking of the M-X bond (analogous to S_N 1).

Mechanism

$$ML_5 X \xrightarrow{l}{k_{-1}} ML_5 + X$$
$$ML_5 + Y \xrightarrow{k_2} ML_5 Y$$

k,

Steady-state approximation

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

[ML₅] = $\frac{k_1[ML_5X]}{k_{-1}[X] + k_2[Y]}$

Rate law

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5][Y] = \frac{k_2k_1[ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$



Extent of reaction

Kinetic Aspects of Reaction Pathways

Associative (A) Mechanism $ML_nX + Y \rightarrow ML_nXY \rightarrow ML_nY + X$

The incoming ligand adds to the complex, and an intermediate with a increased coordination number is formed. (analogous to $S_N 2$).

Mechanism $ML_5X + Y \xleftarrow{k_1}{k_{-1}} ML_5XY \longleftarrow$ rate determining step $ML_5XY \xrightarrow{k_2} ML_5Y + X$



Extent of reaction

Steady-state approximation

$$\frac{d[ML_5XY]}{dt} = k_1[ML_5X][Y] - k_{-1}[ML_5XY] - k_2[ML_5XY] = 0$$
$$[ML_5XY] = \frac{k_1[ML_5X][Y]}{k_{-1} + k_2}$$

Rate law

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5XY] = \frac{k_1k_2[ML_5X][Y]}{k_{-1} + k_2} = k[ML_5X][Y]$$
2nd order

Kinetic Aspects of Reaction Pathways

Interchange (I) Mechanism

$$ML_nX + Y \longrightarrow ML_nY + X$$

$$V \longrightarrow Y \longrightarrow ML_nY + X$$

The incoming ligand is presumed to assist in the reaction, but no detectable intermediates appear. \rightarrow dissociative interchange (I_d) and associative interchange (I_a)



Mechanism 1 $ML_5X + Y \xrightarrow{k_1} ML_5Y + X$

Rate law 1

$$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = k_{1}[\mathrm{ML}_{5}\mathrm{X}][\mathrm{Y}]$$

or

Mechanism 2 $ML_5X + Y \rightleftharpoons_{k_{-1}}^{k_1} ML_5Y + X$

Rate law 2

$$-\frac{d[ML_5X]}{dt} = \frac{d[ML_5Y]}{dt} = k_1[ML_5X][Y] - k_1[ML_5Y][X]$$
$$-\frac{d[ML_5X]}{dt} = \frac{d[ML_5Y]}{dt} = k_1[ML_5X] - k_1[ML_5Y] \quad \text{if [X] and [Y] are large}$$

Kinetic Aspects of Reaction Pathways

MX +Y

Y----ML_n----X

 ΔG^{\ddagger}

MY + X

Interchange (I) Mechanism

The incoming ligand is presumed to assist in the reaction, but no detectable intermediates appear. \rightarrow dissociative interchange (I_d) and associative interchange (I_a)

 $\begin{array}{ccc} ML_nX+Y & \rightarrow & ML_nY+X \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$

Mechanism

Rate law

$$ML_{5}X + Y \xrightarrow{k_{1}} ML_{5}X \cdot Y$$

$$ML_{5}X \cdot Y \xrightarrow{k_{2}} ML_{5}Y + X$$

$$A rapid equilibrium betwee reactant to form an ion provide the second second$$

pid equilibrium between the incoming ligand and the 6-coordinate tant to form an ion pair or **preassociation complex**

Free energy

$$K_1 = \frac{k_1}{k_{-1}} \quad k_2 << k_{-1}$$

Steady-state approximation

$$\frac{d[ML_{5}X \cdot Y]}{dt} = k_{1}[ML_{5}X][Y] - k_{-1}[ML_{5}X \cdot Y] - k_{2}[ML_{5}X \cdot Y] = 0$$

$$[M]_{0} = [ML_{5}X] + [ML_{5}X \cdot Y] \quad \text{and} \quad [Y]_{0} \cong [Y]$$

$$\frac{d[ML_{5}X \cdot Y]}{dt} = k_{1}([M]_{0} - [ML_{5}X \cdot Y])[Y]_{0} - k_{-1}[ML_{5}X \cdot Y] - k_{2}[ML_{5}X \cdot Y] = 0$$

$$[ML_{5}X \cdot Y] = \frac{k_{1}[M]_{0}[Y]_{0}}{k_{-1} + k_{1}[Y]_{0} + k_{2}}$$

$$\frac{d[ML_{5}Y]}{dt} = k_{2}[ML_{5}X \cdot Y] = \frac{k_{1}k_{2}[M]_{0}[Y]_{0}}{k_{-1} + k_{1}[Y]_{0} + k_{2}} = \frac{\frac{k_{1}}{k_{-1}}k_{2}[M]_{0}[Y]_{0}}{1 + \frac{k_{1}}{k_{-1}}} \cong \frac{K_{1}k_{2}[M]_{0}[Y]_{0}}{1 + K_{1}[Y]_{0}}$$

Kinetic Aspects of Reaction Pathways

	Dissociative (D) Mechanism	Interchange (I) Mechanism (Preassociation Complex)	Associative (A) Mechanism
	$\frac{d[ML_{5}Y]}{dt} = \frac{k_{2}k_{1}[ML_{5}X][Y]}{k_{-1}[X] + k_{2}[Y]}$	$\frac{d[ML_{5}Y]}{dt} = \frac{K_{1}k_{2}[M]_{0}[Y]_{0}}{1 + K_{1}[Y]_{0}}$	$\frac{d[ML_{5}Y]}{dt} = \frac{k_{1}k_{2}[ML_{5}X][Y]}{k_{-1} + k_{2}}$
	$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = \frac{k[\mathrm{ML}_{5}\mathrm{X}][\mathrm{Y}]}{[\mathrm{X}] + k'[\mathrm{Y}]}$	$\frac{d[ML_{5}Y]}{dt} = \frac{k[M]_{0}[Y]_{0}}{1 + k'[Y]_{0}}$	$\frac{d[ML_5Y]}{dt} = k[ML_5X][Y]$
When [Y] is low	$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = \frac{k[\mathrm{ML}_{5}\mathrm{X}][\mathrm{Y}]}{[\mathrm{X}]}$	$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = k[\mathrm{M}]_{0}[\mathrm{Y}]_{0}$	$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = k[\mathrm{ML}_{5}\mathrm{X}][\mathrm{Y}]$
	1 st order for M, 1 st order for Y	1 st order for M, 1 st order for Y	1 st order for M, 1 st order for Y
When [Y] is high	$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = k''[\mathrm{ML}_{5}\mathrm{X}]$	$\frac{d[\mathbf{ML}_{5}\mathbf{Y}]}{dt} = k''[\mathbf{M}]_{0}$	$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = k[\mathrm{ML}_{5}\mathrm{X}][\mathrm{Y}]$
	1 st order for M	1 st order for M	1 st order for M, 1 st order for Y

There is no clear-cut to distinguish the mechanisms from the kinetic aspects. Need more experimental evidences to distinguish

Dissociative (*D*) Mechanism : Most substitution reactions are dissociative.

Evidence 1. Correlation between inert, labile complexes and Ligand Field Activation Energy (LFAE)

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

LFAE: Difference in LFSEs of the octahedral reactant and the presumed 5-coordinate transition state



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Strong-field d^8 (square planar)	Weak-field d^8	d ⁷ , d ⁹ , d ¹⁰

LFAE: Difference in LFSEs of the octahedral reactant and the presumed 5-coordinate transition state

	-	-				
Strong Fields (units of Δ_{o})			Weak Fields (units of Δ_o)			
System	Octahedral LFSE	Square-Pyramidal LFSE	LFAE	Octahedral LFSE	Square-Pyramidal LFSE	LFAE
d^0	0	0	0	0	0	0
d^1	-0.400	-0.457	-0.057	-0.400	-0.457	-0.057
d^2	-0.800	-0.914	-0.114	-0.800	-0.914	-0.114
d^3	-1.200	-1.000	0.200	-1.200	-1.000	0.200
d^4	-1.600	-0.914	0.686	-0.600	-0.914	-0.314
d^5	-2.000	-1.371	0.629	0	0	0
d^6	-2.400	-1.828	0.572	-0.400	-0.457	-0.057
d^7	-1.800	-1.914	-0.114	-0.800	-0.914	-0.114
d^8	-1.200	-1.828	-0.628	-1.200	-1.000	0.200
ď ⁹	-0.600	-0.914	-0.314	-0.600	-0.914	-0.314
d^{10}	0	0	0	0	0	0

TABLE 12.3 Ligand Field Activation Energies

For a square-pyramidal transition state, LFAE = square pyramid LFSE – Octahedral LFSE, for σ donor only.

Experimental Evidences in Octahedral Substitution

Dissociative (*D*) Mechanism : Most substitution reactions are dissociative.

Evidence 2. Oxidation state of the central ion

Rate
$$[AIF_6]^{3-} > [SiF_6]^{2-} > [PF_6]^{-} > SF_6$$

$$3+ 4+ 5+ 6+$$

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

$$1+ 2+ 3+$$

Evidence 3. Ionic radius

Rate
$$\begin{bmatrix} Sr(H_2O)_6 \end{bmatrix}^{2+} > [Ca(H_2O)_6]^{2+} > [Mg(H_2O)_6]^{2+} \\ 112 \text{ pm} & 99 \text{ pm} & 66 \text{ pm} \end{bmatrix}$$

Evidence 4. Decreasing negative charge or increasing positive charge on the reactant compound decreases the rate of substitution.

Evidence 5. Steric crowding on the reactant complex increases the rate of ligand dissociation.

Evidence 6. Activation energies and entropies are consistent with dissociation. And volume of activation (ΔV_{act}) is positive.

Experimental Evidences in Octahedral Substitution

Dissociative (*D*) Mechanism : Most substitution reactions are dissociative.

Evidence 7. The rate of reaction changes only slightly with changes in the incoming ligand.

Dissociative (D) Mechanism

Associative (A) Mechanism

$\frac{d[M]}{d}$	$\frac{L_{5}Y]}{t} = \frac{k_{2}k_{1}[ML_{5}X][Y]}{k_{-1}[X] + k_{2}[Y]}$	$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} =$	$=\frac{k_1k_2[ML_5X][Y]}{k_{-1}+k_2}$
When [Y] is high	$\frac{d[ML_5Y]}{dt} = k''[ML_5X]$	$\frac{d[ML_5Y]}{dt}$	$= k[ML_5X][Y]$ M. 1 st order for Y

TABLE 12.3	Limiting Rate Constants for Anation or Water Exchange of
$[Co(NH_3)_5H_2C]$	0] ³⁺ at 45 °C.

	$\longrightarrow [Co(NH_3)_5Y]^{(3-m)+} + H_2O$	
Y ^{<i>m</i>-}	$k_1 (10^{-6} s^{-1})$	k ₁ /k ₁ (H ₂ O)
H ₂ O	100	1.0
N_3^-	100	1.0
SO4 ²⁻	24	0.24
CI^-	21	0.21
NCS ⁻	16	0.16

Not much effect of incoming ligand

Experimental Evidences in Octahedral Substitution

Dissociative (*D*) Mechanism : Most substitution reactions are dissociative.

Evidence 7. The rate of reaction changes only slightly with changes in the incoming ligand.

On the other hand	Interchange (I) Mechanism (Preassociation Complex)	When [Y] is high	$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = k''[\mathrm{M}]_{0}$
	$\frac{d[ML_5Y]}{dt} = \frac{K_1k_2[M]_0[Y]_0}{1 + K_1[Y]_0}$		1 st order for M

TABLE 12.5 Rate Constants for $[Ni(H_2O)_6]^{2+}$ Substitution Reactions

Y	$k_2 K_1 (10^3 M^{-1} s^{-1})$	$K_1(M^{-1})$	k ₂ (10 ⁴ s ⁻¹)
CH ₃ PO 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 ₂ O			3
NH ₃	5	0.15	3
C ₅ H ₅ N, pyridine	~4	0.15	~3
C ₄ H ₄ N ₂ , pyrazine	2.8	0.15	2
NH ₂ (CH ₂) ₂ NMe ₃ ⁺	0.4	0.02	2

$$[\operatorname{Ni}(\operatorname{H}_{2}\operatorname{O})_{6}]^{2+} + \operatorname{L}^{n} \rightleftharpoons [\operatorname{Ni}(\operatorname{H}_{2}\operatorname{O})_{6} \cdot \operatorname{L}]^{2+n}$$
$$[\operatorname{Ni}(\operatorname{H}_{2}\operatorname{O})_{6} \cdot \operatorname{L}]^{2+n} \longrightarrow [\operatorname{Ni}(\operatorname{H}_{2}\operatorname{O})_{5}\operatorname{L}]^{2+n} + \operatorname{H}_{2}\operatorname{O}$$

Incoming ligand: not much effect on k_2 significant effect on K_1

→ Predissociation complex mechanism

Experimental Evidences in Octahedral Substitution

Dissociative (*D*) Mechanism : Most substitution reactions are dissociative.

Evidence 8. Linear Free-Energy Relationship (LFER)

metal-ligand bond strength ⇔ dissociation rate of the ligand equilibrium constant (thermodynamic function) ⇔ rate constant (kinetic function)

$$\ln k = \ln A - \frac{E_a}{RT} \Leftrightarrow \ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

$$[\operatorname{Co}(\operatorname{NH}_3)_5 X]^{2^+} + \operatorname{H}_2 O \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_5 (\operatorname{H}_2 O)]^{3^+} + X^-$$



Indirect evidence for strong influence of the thermodynamic parameters, ΔH , on the activation energy, E_a .

 \Rightarrow A stronger bond between the metal and the leaving group results in a larger activation energy.

Langford argued a complete dissociation of X⁻.

Experimental Evidences in Octahedral Substitution

 2.7 ± 0.2

Associative (A) Mechanism : Associative substitution is less common.

			TABLE 12	TABLE 12.5 Effects of Entering Group on Rates Rate Constants for Anation			
			Entering L	igand [Cr(i k (10 ⁻	H ₂ O) ₆] ³⁺ ⁸ M ⁻¹ s ⁻¹)	[Cr(NH ₃) ₅ H ₂ O] ³⁺ k (10 ⁻⁴ M ⁻¹ s ⁻¹)	
			NCS ⁻	18	0	4.2	
			NO ₃ -	7	3	_	
			CI-	I	2.9	0.7	
			Br	- <i>a</i>	1.0	⁻ <i>a</i> 3.7	
TABLE 12.6 Rate	Constants for [Ru(III)(EI	OTA)(H ₂ O)] [–] Substituti	on		0.08	_	
Ligand	$k_1(M^{-1}s^{-1})$	ΔH^{\ddagger} (kJ mol ⁻¹)	ΔS^{\ddagger} (J mol ⁻¹ K ⁻¹)	-	_	1.4	
Pyrazine	20,000 ± 1,000	$5.7~\pm~0.5$	-20 ± 3	-			
Isonicotinamide	8,300 ± 600	$6.6~\pm~0.5$	-19 ± 3				
Pyridine	6,300 ± 500	I					
Imidazole	$1,860 \pm 100$	1 <i>a</i>					
SCN ⁻	270 ± 20	8.9 ± 0.5	-18 ± 3				
CH ₃ CN	30 ± 7	$8.3~\pm~0.5$	-24 ± 4				
			TABLE 12.7	Rate Constants for	[Ru(II)(EDTA)(H ₂ O)] ²⁻ Substitution	
			Ligand		k ₁ (M⁻	$^{-1} s^{-1}$)	
			Isonicotinamide	9	30 =	£ 15	
			CH ₃ CN		<i>I</i> _d 13 =	£ 1	

 SCN^{-}

Conjugate Base Mechanism (S_N1CB): A reaction pathway by which many metal amine complexes undergo substitution. Typically, the reaction entails reaction of a polyamino metal halide with aqueous base to give the corresponding polyamine metal hydroxide. Second-order rate law.

 $[\operatorname{Co}(\operatorname{NH}_3)_5 X]^{2+} + \operatorname{OH}^- \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{OH})]^{2+} + X^-$

 $Rate = k([Co(NH_3)_5X]^{2+})[OH^-]$

looks like associative, but ...

 $[\operatorname{Co}(\operatorname{NH}_3)_5 X]^{2+} + \operatorname{OH}^- \rightleftharpoons [\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2)X]^+ + \operatorname{H}_2 O \quad (\text{equilibrium}) \quad (1)$ $[\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2)X]^+ \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2)]^{2+} + X^- \quad (\text{slow}) \quad (2)$ $[\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2)]^{2+} + \operatorname{H}_2 O \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{OH})]^{2+} \quad (\text{fast}) \quad (3)$

Conjugate base mechanism (Dissociative !!)

 $H_2O + OH^- \longrightarrow OH^- + H_2O$

Conjugate acid-base

Experimental Evidences in Octahedral Substitution

Conjugate Base Mechanism (S_N1CB):

$$[\operatorname{Co}(\operatorname{NH}_3)_5 X]^{2+} + \operatorname{OH}^- \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{OH})]^{2+} + X^- \qquad Rate = k([\operatorname{Co}(\operatorname{NH}_3)_5 X]^{2+})[\operatorname{OH}^-]$$

$[\operatorname{Co}(\operatorname{NH}_3)_5 X]^{2+} + \operatorname{OH}^- \rightleftharpoons [\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2) X]^+ + \operatorname{H}_2 \operatorname{O}$	(equilibrium)	(1)
$[\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2)X]^+ \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2)]^{2+} + X^-$	(slow)	(2)
$[\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2)]^{2+} + \operatorname{H}_2\operatorname{O} \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{OH})]^{2+}$	(fast)	(3)

Experimental observations supporting S_N1CB:

- 1. Base-catalyzed exchange of hydrogen from the amine groups takes place under the same conditions as these reactions.
- The isotope ratio (¹⁸O/¹⁶O) in the product in ¹⁸O-enriched water is the same as that in the water regardless of the leaving group. [If associative (incoming water has big influence), the isotope ratio (¹⁸O/¹⁶O) in the product would be higher. Because equilibrium isotope fractionation for

 $H_2^{16}O + {}^{18}OH^- \longrightarrow {}^{16}OH^- + H_2^{18}O$ is K = 1.042. ???] 3. RNH₂ (R = alkyl) complexes react faster than NH₃ complexes. (steric crowding) 4. A plot of $\ln(k_{OH})$ versus $\ln(K_{OH})$ is linear regardless of the leaving group. (LFER) 5. When substituted amines with no protons are used, the reaction is very slow or nonexistent.

Experimental Evidences in Octahedral Substitution

Conjugate Base Mechanism (S_N1CB): A reaction pathway by which many metal amine complexes undergo substitution. Typically, the reaction entails reaction of a polyamino metal halide with aqueous base to give the corresponding polyamine metal hydroxide. Second-order rate law.





Base catalyzed hydrolysis of [Co(III)L]

Pseudo-aminate mechanism through deprotonation of methylene groups

If structurally allowed, the position *trans* to the leaving group is usually deprotonated. (a) is faster $(x10^4)$ than (b). ((b) needs rearrangement)

Experimental Evidences in Octahedral Substitution

Kinetic Chelate Effect: Substitution for a chelate ligand is generally slower reaction than that for a similar monodentate ligand. ($20 \sim 10^5$ times slower)



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.



TABLE 12.9	Stereoch	emistry of [Co(en) ₂ LX] ⁿ⁺ Acid H	ydrolysis	* [% cis produ	uct
	[Co	$(en)_2 LX]^{n+} + H_2 O$ —	\rightarrow [Co(en) ₂ L(H ₂	$_{2}O)]^{(1+n)+} + X^{-}$	(Dissociative)	
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	



= sum of two optical isomers]

TABLE 12.10 Stereochemistry of Base Substitution

* [% cis products = sum of two optical isomers]

	$[Co(en)_2 LX]^{n+} + OH^- \longrightarrow [Co(en)_2 LOH]^{n+} + X^-$			(Dissociative or S _N 1		
		% cis Pr	oduct			% cis Product
∆ <i>-cis</i> -L	X	Δ	Λ	trans-L	Х	
OH^-	Cl^{-}	61	36	OH^-	Cl^{-}	94
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





Sterochemistry depends on many factors such as mechanism, reaction rate, concentration, and temperature.

Stereochemistry



Ш

Mechanical aspect: Substitution in *trans* Complexes

) ₂ LX] ⁿ⁺ Acid Hy	drolysis		itution		
\rightarrow [Co(en) ₂ L(H ₂	O)] ⁽¹⁺ⁿ⁾⁺ + X ⁻		[Co(en) ₂ LOH] ⁿ⁺ + X ⁻	
trans-L	х	% cis Product			% cis Product
OH-	Cl^-	75	trans-L	Х	
OH^-	Br ⁻	73	OH-	Cl^{-}	94
Br ⁻	Cl^{-}	50	NCC ⁻	C1-	76
Br ⁻	Br ⁻	30	NCS	CI	/0
CI-	Cl-	35	NCS ⁻	Br^{-}	81
Cl-	Br^{-}	20	NH ₃	Cl^{-}	76
NCS ⁻	Cl^{-}	50-70	NO_2^-	Cl^-	6

Dissociation mechanism and stereochemical change

- (a) sq. py. intermediate: retention of geometry
- (b) tr. bipy. intermediate, eq. B:
- (c) tr. bipy. intermediate, ax. B:

Statistical expectation(through tr. bipy) $trans \rightarrow trans \ \frac{1}{3}$ $trans \rightarrow cis \ \frac{2}{3}$ (overall) $trans \rightarrow trans \ ?$ $trans \rightarrow cis \ ?$



Stereochemistry



 $\|$

Less likely because of bigger

rearrangement than in eq. B

Mechanical aspect: Substitution in *cis* Complexes

TABLE 12.9 Stereochemistry of [C TABLE 12.10 Stereochemistry of Base Subst

	[Co	(en) ₂ LX] ^{<i>n</i>+} + H	[Co(en) ₂ LX] ^{<i>n</i>+} + OH ⁻			- OH⁻>
cis-L	х	% cis Prod			% cis Pr	oduct
OH^-	CI	100	Δ -cis-L	Х	Δ	Λ
OH-	Br ⁻	100	OH^-	Cl-	61	36
Br ⁻	Cl-	100	NCS ⁻	C1 ⁻	56	24
Cl ⁻	Cl-	100	NU	Dr ⁻	50	26
CI-	Br ⁻	100	INH3	DI	59	20
N_3^-	C1	100	NH ₃	CI	60	24
NCS ⁻	Cl^{-}	100	NO_2^-	Cl^{-}	46	20

Dissociation mechanism and stereochemical change

- (a) sq. py. intermediate: retention of configuration
- (b) tr. bipy. intermediate, eq. B:
- (c) tr. bipy. intermediate, ax. B:

Statistical expectation Acid hydrolysis: square (through tr. bipy) pyramidal intermediate $cis(\Delta) \rightarrow cis(\Delta)$ 2/3pathway $cis(\Delta) \rightarrow trans$ 1/3(overall) $cis(\Delta) \rightarrow cis(\Delta)$? $cis(\Delta) \rightarrow trans$ 2



(c)



Stereochemistry

Example of concentration effect

- Base hydrolysis of Λ -cis-[Co(en)₂Cl₂]⁺ (S_N1CB)
- (a) In dilute OH⁻ : retention of configuration (sq. py intermediate)
- (b) In concentrated OH⁻ : inversion of configuration (tr. bipy intermediate)



Example of temperature effect

 $[\operatorname{Co}(en)_2\operatorname{Cl}_2]^+ + 2\operatorname{NH}_3 \rightarrow [\operatorname{Co}(en)_2(\operatorname{NH}_3)_2]^+ + 2\operatorname{Cl}^-$

- (a) $T < -33^{\circ}C$: inversion of configuration (in liquid ammonia)
- (b) $T > 25^{\circ}C$: retention of configuration (in liquid ammonia, alcohol solution, or gaseous ammonia)

Stereochemistry

Isomerization of Chelate Rings (Pseudorotation)

Strictly speaking, this is not a substitution reaction. Dissociation of one of the donor atom => Rearrangement => Association of the dissociated atom



Stereochemistry

Isomerization of Chelate Rings

Strictly speaking, this is not a substitution reaction.

Dissociation of one of the donor atom => Rearrangement => Association of the dissociated atom



Square-Planar Complexes

Kinetics and Stereochemistry



Experimentally observed $Rate = k_1[ML_3X] + k_2[ML_3X][Y]$



Square-Planar Complexes

Evidence for Associative Mechanism

- Many five coordinate transition metal complexes with trigonal bi-pyramidal geometry are known, e.g., Fe(CO)₅, [Pt(SnCl)₃]⁺, [Ni(CN)₅]³⁻.
- 2. Rate law is consistent with associative mechanism.



Square-Planar Complexes

Evidence for Associative Mechanism

2. Rate law is consistent with associative mechanism.



	trans-PtL ₂ Cl ₂ + Y —	\rightarrow trans-PtL ₂ ClY + 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
Ι_	107	236	5.46
$ m Br^-$	3.7	0.93	4.18
3	1.55	0.2	3.58
$\mathrm{MO_2}^-$	0.68	0.027	3.22
NH ₃	0.47		3.07
CI-	0.45	0.029	3.04

TABLE 12.13 Rate Constants for Leaving Groups

$[Pt(dien)X]^+ + py \longrightarrow [Pt(dien)py]^{2+} + X^-$ $(Rate = (k_1 + k_2[py])[Pt(dien)X]^+)$			
X −	$k_2 (M^{-1} s^{-1})$		
NO_3^-	very fast		
Cl^{-}	5.3×10^{-3}		
Br ⁻	3.5×10^{-3}		
Ι-	1.5×10^{-3}		
N_3^-	1.3×10^{-4}		
SCN ⁻	$4.8 imes 10^{-5}$		
NO_2^-	$3.8 imes 10^{-6}$		
CN^{-}	$2.8 imes 10^{-6}$		

Reactivity toward to Pt(II)

Square-Planar Complexes

The Trans Effect

The effect of a coordinated ligand upon the rate of substitution of ligands opposite to it

For Pt(II) complexes, the order of the trans effect is generally: kinetic effect !!

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

$$\begin{array}{c} \overset{\mathrm{NH}_{3}}{\underset{\mathrm{NH}_{3}}{\overset{\mathrm{Pr}}{\underset{\mathrm{NH}_{3}}{\overset{\mathrm{Pr}}{\underset{\mathrm{NH}_{3}}{\overset{\mathrm{CI}}{\underset{\mathrm{NH}_{3}}{\underset{\mathrm{NH}_{3}}{\overset{\mathrm{CI}}{\underset{\mathrm{NH}_{3}}{\overset{\mathrm{CI}}{\underset{\mathrm{NH}_{3}}{\overset{\mathrm{CI}}{\underset{\mathrm{NH}_{3}}{\underset{N}{\underset{NH}_{3}}{\overset{\mathrm{CI}}{\underset{N}{\underset{N}}{\underset{N}}{\underset{N}}{\underset{N}}{\underset{N}}{\overset{\mathrm{CI}}{\underset{N}}{$$

Square-Planar Complexes

The Trans Effect [Explanation]

1. σ -bonding effect

Good σ -bases (e.g., alkyl-, H-) are donating electron density to the metal d orbital which is shared with the leaving group. This weakens the M-X bond in the ground state. (Thermodynamic effect)



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



Square-Planar Complexes

The Trans Effect [Explanation]

2. π -bonding effect

•The simultaneous coordination of X and Y in the 5-coordinate transition

→ increase of electron density at the metal • π -back donation to the trans ligand → decrease of electron density at the metal during the transition state. → stabilizing the transition state (Kinetic effect)



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



 σ -bonding effect + π -bonding effect

 $CO \sim CN^{-} \sim C_2H_4 > PR_3 \sim H^{-} > CH_3^{-} \sim SC(NH_2)_2 > C_6H_5^{-} >$ $NO_2^{-} \sim SCN^{-} \sim I^{-} > Br^{-} > CI^{-} > py, NH_3 \sim OH^{-} \sim H_2O$

Inner-sphere reaction - include atom transfer processes

- a ligand is shared in a bridged intermediate activated complex

1. Substitution reaction followed by linking the oxidant and reductant

 $[\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{Cl})]^{2+} + [\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_6]^{2+} \rightarrow [(\operatorname{NH}_3)_5\operatorname{Co}(\operatorname{Cl})\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_5]^{4+} + \operatorname{H}_2\operatorname{O}_{\operatorname{III}}$ III II II II

2. Electron transfer

$$[(\mathrm{NH}_3)_5\mathrm{Co}(\mathrm{Cl})\mathrm{Cr}(\mathrm{H}_2\mathrm{O})_5]^{4+} \rightarrow [(\mathrm{NH}_3)_5\mathrm{Co}(\mathrm{Cl})\mathrm{Cr}(\mathrm{H}_2\mathrm{O})_5]^{4+}$$

$$\underset{\mathrm{III}}{\mathrm{III}} \qquad \underset{\mathrm{III}}{\mathrm{III}} \qquad \underset{\mathrm{III}}{\mathrm{III}}$$

3. Separation

 $[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+} + H_2O \rightarrow [(NH_3)_5Co(H_2O)]^{2+} + [(Cl)Cr(H_2O)_5]^{2+}$ II III III III III



Outer-sphere reaction - simple electron transfer without ligand sharing

- non labile ligand spheres
- faster than ligand substitution

TABLE 12.13 Rate Constants	TABLE 12.13 Rate Constants for Outer-Sphere Electron Transfer Reactions ^a				
	Reduc	tants			
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			
$[Co(NH_3)_5(CI)]^{2+}$	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}			

The rates show very large differences depending on the ability of the electrons to tunnel through the ligands.

Inner-sphere and outer-sphere reactions

	TABLE 12.14 Rate Cons	tants for Aquated Red	uctants ^a	
		Cr ²⁺	Eu ²⁺	V ²⁺
outer ←	[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
	$[Co(NH_3)_5(NO_3)]^{2+}$	$\sim 9 \times 10^{-1}$	$\sim 1 \times 10^2$	
	$[Co(NH_3)_5(CI)]^{2+}$	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}
		Usually inner	Usually outer	Likely outer

Inner-sphere and outer-sphere reactions

		TABLE 12.15 Rate Constants for Real	actions 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}
outer ←	←	$[Co(NH_3)_5(NH_3)]^{3+}$	8×10^{4a}
		$[Co(NH_3)_5(NCS)]^{2+}$	1.1×10^{6}
		$[Co(NH_3)_5(N_3)]^{2+}$	1.6×10^{6}
	$[Co(NH_3)_5(CI)]^{2+}$	\sim 5 \times 10 ⁷	

Inner (products $[Co(CN)_5(X)]^{3-}$ are found)

Condition for High and Low Oxidation numbers

The overall stability of complexes with different charges on the metal ion depends on LFSE, bonding energy of ligands, redox properties of ligands

TABLE 12.18 Electrode Potentials of Cobalt and Copper Species in Aqueou	is Solution
Cu(II)-Cu(I) Reactions	€° (V)
$Cu^{2+} + 2 CN^{-} + e^{-} \Longrightarrow [Cu(CN)_2]^{-}$	+1.103
$Cu^{2+} + I^- + e^- \Longrightarrow Cul(s)$	+0.86
$Cu^{2+} + Cl^- + e^- \Longrightarrow CuCl(s)$	+0.538
$Cu^{2+} + e^- \Longrightarrow Cu^+$	+0.153
$[Cu(NH_3)_4]^{2+} + e^- \Longrightarrow [Cu(NH_3)_2]^+ + 2 NH_3$	-0.01
Cu(II)-Cu(0) Reactions	€° (V)
$Cu^{2+} + 2e^{-} \Longrightarrow Cu(s)$	+0.337
$[Cu(NH_3)_4]^{2+} + 2 e^- \Longrightarrow Cu(s) + 4 NH_4$	-0.05
Co(III)-Co(II) Reactions	€° (V)
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.808
$[Co(NH_3)_6]^{3+} + e^- \Longrightarrow [Co(NH_3)_6]^{2+}$	+0.108
$[Co(CN)_6]^{3-} + e^- \rightleftharpoons [Co(CN)_6]^{4-}$	-0.83

The properties of organic ligands changes significantly by coordination to metal ion. Slow reactions in organic conditions can be promoted in inorganic conditions.

Hydrolysis of Esters, Amides, and Peptides



Peptide hydrolysis by [Co(trien)(H₂O)(OH)]²⁺

Template Reactions – Formation of a complex places the ligands in the correct geometry for reaction



Template Reactions – Formation of a complex places the ligands in the correct geometry for reaction



Template Reactions – Formation of a complex places the ligands in the correct geometry for reaction



Electrophilic Substitution



Metal coordination of acetylacetone

- \Rightarrow Forcing enol form of the ligand, preventing reactions on the oxygens, concentrating negative charge on the central carbon
- \Rightarrow Making electrophilic substitution easier (similar to electrophilic aromatic substitution)

