Inorganic Reaction Mechanisms

Chem421

Inorganic Reaction Mechanisms

Course Name	Inorganic Reaction Mechanisms
Course Number	Chem421
Credit Hours (Lecture+ Lab)	2+0
Pre-requisite	Chem322
Level	Eight

Evaluations:

Assessments	Credit	Time
Quizzes/ Home Works	10	During the semester
Mid 1	20	6th week
Mid 2	20	12th week
Final	50	16th week

Cyano
chloro

أمثلة تحسيبية :

$Ca[CO(CN)_4Cl_2]SO_4$

$2 + Co + (-4) + (-2) = +2$

$Co = +6$

Calcium dichlorotetracyanocobaltate (VI) Sulphate

② $NH_4[Fe(CO)_6]$

$1 + Fe = 0 \Rightarrow Fe = -1$

ammoniumhexacarbonylferrate (-I)

$[CO(CN)_4Cl_2]SO_4$

① يمثل كما هو

② يمثل كما هو

④ تبدأ تسمية الليجندات السالبة مع إضافة مقطع (o) في نهاية الاسم ثم الليجندات المتعادلة في حالة تشابه الليجندات (بالهرون الأبجدي)

③ كتابة اسم الفلز كما هو ماعدا في حالتين يضاف مقطع ate في نهاية اسم الفلز في حالة
أ) وهيدروكسيد
ب) وهيدروشحنة سالبة على المعقد

⑤ كتابة عدد الأكسدة

Chapter 1: Introduction to Coordination Compounds

③ $Mg[Cu(H_2O)_2(en)_2]NO_3$

$2 + Cu + (0) + (0) = +1 \Rightarrow Cu = -1$

magnesium diaquabis(ethylenediamine) cuprate (-I) nitrite

④ $K_2[Ag(NH_3)_2]$

$2 + Ag + 0 = 0 \Rightarrow Ag = -2$

potassium diammine Argentate (-II)

$Ca[Co(CN)_4(Cl)_2]SO_4$

① lewis acid Co^{+6}

② lewis base CN and Cl

③ counter ion SO_4

④ charge of the comlex zero neutral

⑤ geometry octahedral

⑥ electron configuration of the metal $Co_{27}: [Ar]_{18}4s^2 3d^7$, $Co^{+6}: [Ar]_{18}3d^3$



⑦ magnetic property paramagnetic

⑧ magnetic moment $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM

⑨ colored or colorless colored

$NH_4[Fe(CO)_6]$

① lewis acid Fe^{-1}

② lewis base CO

③ counter ion

④ charge of the comlex zero neutral

⑤ geometry octaheral

⑥ electron configuration of the metal $Fe_{26}: [Ar]_{18}4s^2 3d^6$ $Fe^{-1}: [Ar]_{18}4s^2 3d^7$



⑦ magnetic property paramagnetic

⑧ magnetic moment $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM

⑨ colored or colorless colored

$Mg^{+2}[Cu(H_2O)_2(en)_2]^{+1}NO_3^{-1}$

① lewis acid Cu^{-1}

② lewis base H_2O and ethylene diamine

③ counter ion NO_3

④ charge of the comlex

⑤ geometry octahedral

⑥ electron configuration of the metal $Cu_{29}: [Ar]_{18}4s^2 3d^9$ $Cu^{-1}_{29}: [Ar]_{18}4s^2 3d^{10}$

⑦ magnetic property diamagnetic

⑧ magnetic moment

⑨ colored or colorless colorless

$K_2[Ag(NH_3)_2]$

① lewis acid Ag^{-2}

② lewis base

③ counter ion

④ charge of the comlex

⑤ geometry

⑥ electron configuration of the metal

⑦ magnetic property

⑧ magnetic moment

⑨ colored or colorless

What Are Coordination Compounds?

- Coordination compounds are substances formed by the coordination of a central metal atom or ion with surrounding molecules or ions called ligands. These compounds play key roles in biological, chemical, and industrial processes.

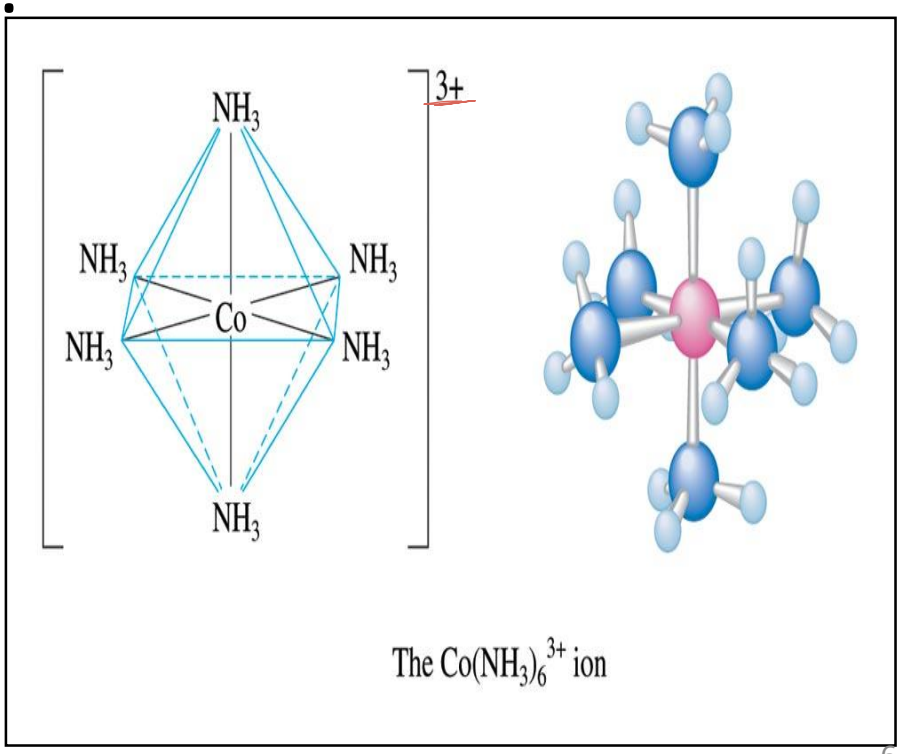
Components of a Coordination Compound

- - Central metal ion (e.g., Fe^{2+}, Cu^{2+})
- - Ligands: molecules or ions that donate electron pairs (e.g., NH_3, Cl^-)
- - Coordination number: number of ligand atoms bonded to the metal
- - Coordination sphere: metal and ligands within brackets [ ]

Structure Example: $[Co(NH_3)_6]^{3+}$

- This complex shows a central cobalt(III) ion surrounded by six ammonia ligands in an octahedral geometry.

- Geometry: Octahedral
- Coordination Number: 6



The $Co(NH_3)_6^{3+}$ ion

Types of Ligands

- Ligand defined as neutral molecule or ion having a lone electron pair that can be used to form a bond to a metal ion.

- Monodentate ligands have only one point of attachment to the metal ion
- Multi-dentate ligands (also called chelate ligand) have two or more points of attachment to the metal ion.
- Multidentate may be bidetate, tridentate, tetradentate, ….etc
- Bidentate ligand (chelate ligand) – two bonds to a metal ion
  - Polydentate ligand – more than two bonds to a metal ion

2: bi-dentate

3: tri-dentate

4: tetra-dentate

5: penta-dentate

6: hexa-dentate

monodentate ⟸ $NO_2 - SCN$

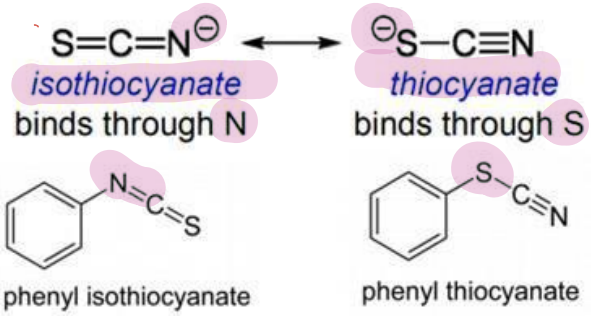
N-Nitrito S-

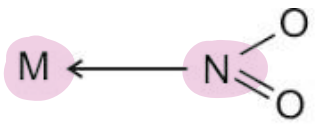
O-Nitrito N-

Ambidentate Ligand

Some ligands have the ability to bind to the central atom via the atoms of two different elements.

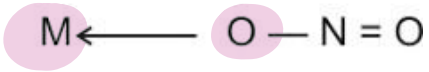
For example, the SCN– ion can bind to a ligand via the nitrogen atom or via the sulfur atom. Such ligands are known as ambidentate ligands.





Nitrito – N

and

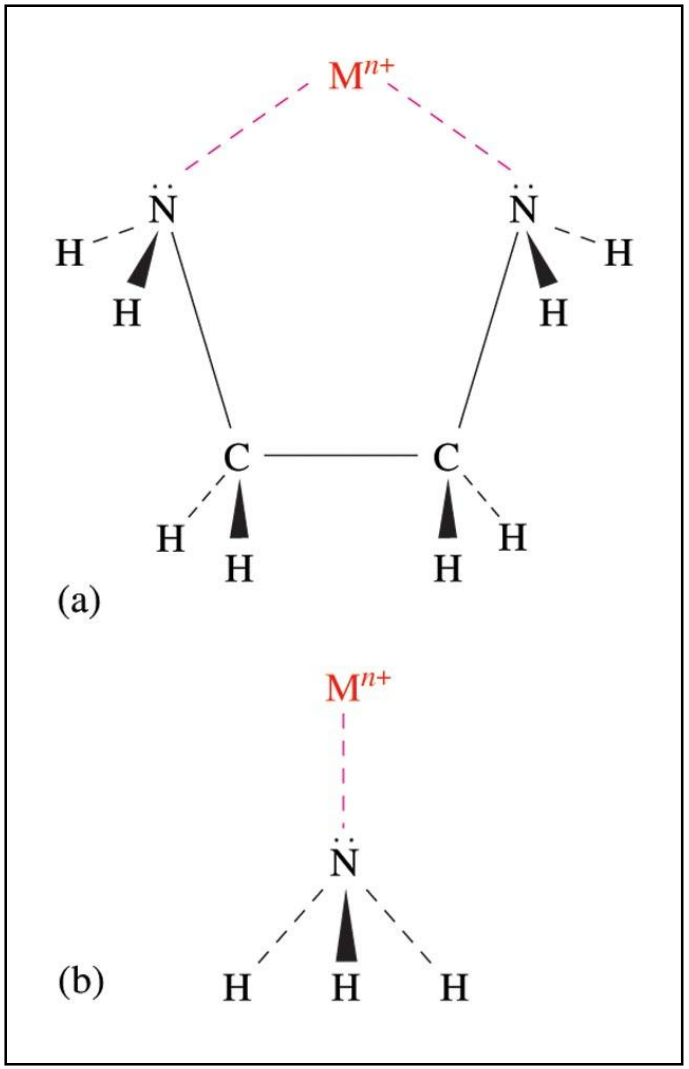


Nitrito – O

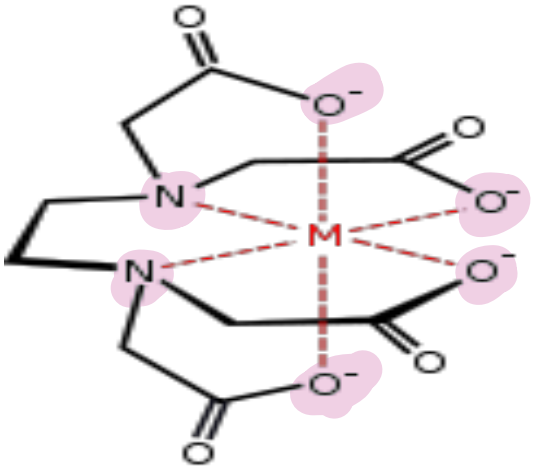
UCI 2018

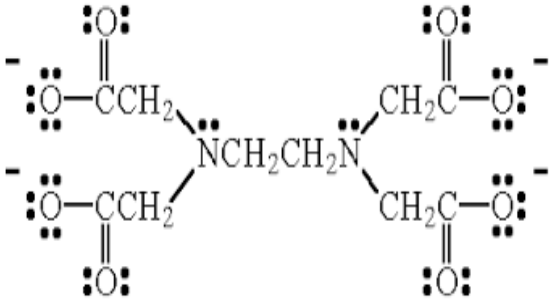
The Bidentate ligand (Ethylenediamine)

the Monodentate ligand (Ammonia)



The Coordination of EDTA with a M^{3+} Metal ion





EDTA(Ethylediamine tetraacetic acid) ion bounded M, if M=Co^{+3} , Co^{+3} bounded by six donors in $[CoEDTA]^-$

EDTA(Ethylediamine tetraacetic acid) ion ($EDTA^{4-}$)

Types of Coordination Compounds

1. Based on the Charge of the Complex

- Cationic Complexes: Complexes with an overall positive charge (e.g., $[Co(NH_3)_6]^{3+}$).
- Anionic Complexes: Complexes with an overall negative charge (e.g., $[Fe(CN)_6]^{4-}$).
- Neutral Complexes: Complexes with no net charge (e.g., $[Ni(CO)_4]$).

2- Based on the Nature of the Ligand

- Monodentate Complexes: Ligands that bind to the central metal atom through a single donor atom (e.g., NH_3, H_2O, Cl^-).
- Polydentate Complexes: Ligands that bind through multiple donor atoms, forming chelate complexes:
  - Bidentate ligands: Bind at two sites (e.g., ethylenediamine (en)).
  - Tridentate and higher ligands: Bind at three or more sites (e.g., EDTA binds at six sites).

3. Based on the Nature of the Central Metal Atom

- Homoleptic Complexes: All ligands are of the same type (e.g., $[Co(NH_3)_6]^{3+}$).
- Heteroleptic Complexes: Different types of ligands are attached to the metal (e.g., $[Pt(NH_3)_2Cl_2]$).

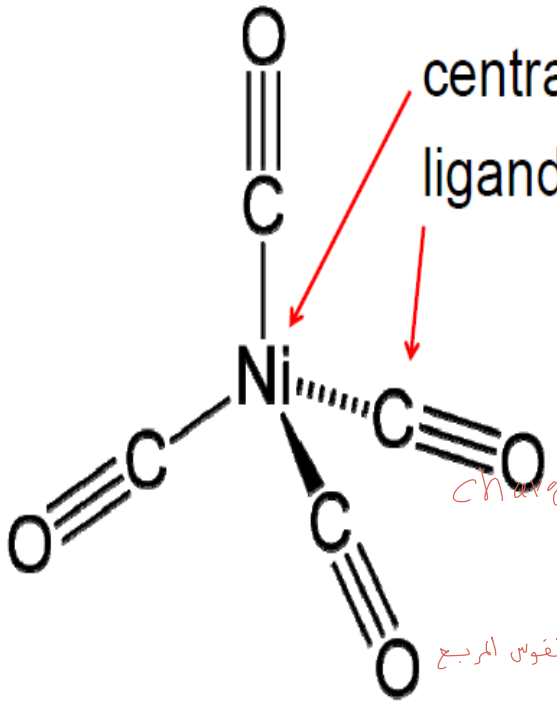
4. Based on the Coordination Number

- Coordination Number 2: Usually linear geometry (e.g., $[Ag(NH_3)_2]^{+}$).
- Coordination Number 4: Can have tetrahedral (e.g., $[NiCl_4]^{2-}$) or square planar geometry (e.g., $[PtCl_4]^{2-}$).
- Coordination Number 6: Typically octahedral geometry (e.g., $[Cr(H_2O)_6]^{3+}$).

5. Based on the Geometry

- Linear: Found in complexes with a coordination number of 2 (e.g., $[CuCl_2]^{-}$).
- Tetrahedral: Common with a coordination number of 4 (e.g., $[NiCl_4]^{2-}$).
- Square Planar: Common in d^8 metals (e.g., $[PtCl_4]^{2-}$).
- Octahedral: Common for a coordination number of 6 (e.g., $[Fe(CN)_6]^{3-}$).

عبارة عن الحديد + الشحنه Lewis acid
عبارة عن الجذات Lewis base



central metal M: Ni^0

ligands L: CO (carbonyl)

Each ligand has at least one lone pair of electrons with which to coordinate to the metal.

- Metal acts as Lewis acid.
- Ligands act as Lewis bases.

charge الشحنه

The ligands directly attached to the metal are its ***first coordination sphere***.

داخل القوس المربع

tetracarbonylnickel: $Ni(CO)_4$

- pale yellow liquid (m.p. -17°C, b.p. 43°C)
- tetrahedral compound
- synthesized in 1890 by Mond
- extremely poisonous

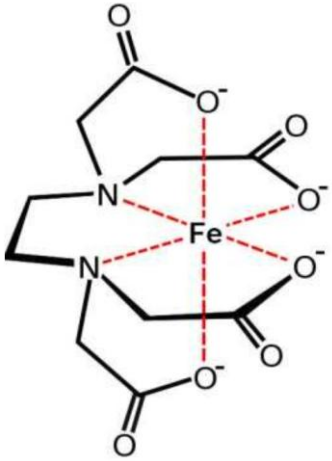
The ***coordination number*** of the metal is the number of coordinate bonds to the metal (CN = 4 in this case).

second or بدا القوس

Chelate complexes more stable than mono dentate.

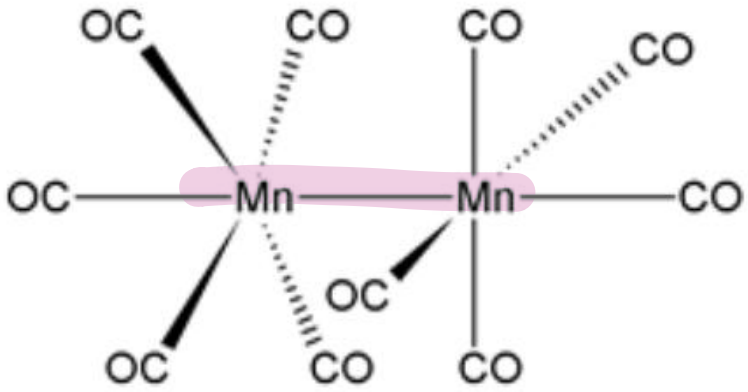
6. Chelate Complexes

Formed when a polydentate ligand binds to a metal through multiple donor atoms creating a ring-like structure (e.g., $[Fe(EDTA)]^{-}$).



7. Bridged Complexes

Contain ligands that connect two or more metal centers (e.g., $[Mn_2(CO)_{10}]$).



$AgNO_3$

Classic Monodentate Ligands

Common Name	IUPAC Name	Formula
hydrido	hydrido	H^-
fluoro	fluoro	F^-
chloro	chloro	Cl^-
bromo	bromo	Br^-
iodo	iodo	I^-
nitrido	nitrido	N^{3-}
azido	azido	N_3^-
oxo	oxido	O^{2-}
cyano	cyano	CN^-
thiocyano	thiocyanato-*S* (S-bonded)	SCN^-
isothiocyano	thiocyanato-*N* (N-bonded)	NCS^-

(continues)

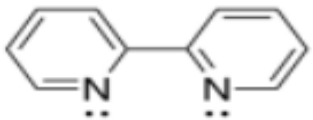
Common Name	IUPAC Name	Formula
hydroxo	hydroxo	OH^-
aqua	aqua	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO^+
nitro	nitrito-*N* (N-bonded)	NO_2^-
nitrito	nitrito-*O* (O-bonded)	ONO^-
methyl isocyanide	methylisocyanide	CH_3NC
phosphine	phosphane	PR_3
pyridine	pyridine (abbrev. py)	C_5H_5N
ammine	ammine	NH_3
methylamine	methylamine	$MeNH_2$
amido	azanido	NH_2^-
imido	azanediido	NH^{2-}

polydentate

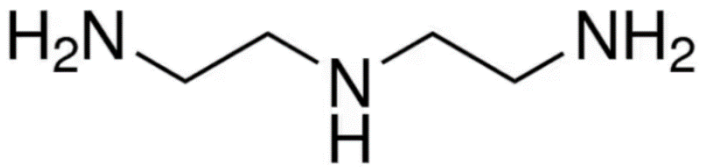
Chelating Points	Common Name	IUPAC Name	Abbrev.	Formula
bidentate	ethylenediamine	1,2-ethanediamine	en	$NH_2CH_2CH_2NH_2$
tridentate	diethylenetriamine	1,4,7-triazaheptane	dien	$NH_2CH_2CH_2NHCH_2CH_2NH_2$
bidentate	2,2'-bipyridine	2,2'-bipyridyl	bipy	$C_{10}H_8N_2$



ethylenediamine
(en)



bipyridyl
(bpy)



diethylenetriamine

IUPAC Nomenclature of Coordination Compounds

Rules For Naming Coordination Compound

A. When naming coordination compounds, always name the cation before the anion. This rule holds regardless of whether the complex ion is the cation or the anion. (This is just like naming an ionic compound.)

1. Name the ligands first, in alphabetical order, and then name the metal atom or ion.
   Note: The metal atom or ion is written before the ligands in the chemical formula.
   e.g $[Co(NH_3)_6]\ (NO_3)_3$ Hexaamminecobalt(III) nitrate
   $K_2\ [PtCl_6]$ Potassium hexachloroplatinate(IV)

Anionic ligands end in "-o." For anions that end in "-ide"(e.g. chloride, hydroxide), "-ate" (e.g. sulfate, nitrate), and "-ite" (e.g. nirite), change the endings as follows: -ide to -o; e.g., chloride to chloro and hydroxide to hydroxo
-ate to -ato; e.g., sulfate to sulfato and nitrate to nitrato
-ite to -ito; e.g., nitrite to nitrito ·
For neutral ligands, the common name of the molecule is used (e.g. $H_2NCH_2CH_2NH_2$ (ethylenediamine)). Important exceptions: water is called 'aqua', ammonia is called 'ammine', carbon monoxide is called 'carbonyl', and the N2 and O2 molecules are called 'dinitrogen' and 'dioxygen'.

Table 1. Names of Some Common Ligands

Anionic Ligands	Names
Br^-	bromo
F^-	fluoro
O^{2-}	oxo
OH^-	hydroxo
CN^-	cyano
$C_2O_4^{2-}$	oxalato
CO_3^{2-}	carbonato
CH_3COO^-	acetato

Neutral Ligands	Names
NH_3	ammine
H_2O	aqua
NO	Nitrosyl
CO	Carbonyl
O_2	dioxygen
N_2	dinitrogen
C_5H_5N	pyridine
$H_2NCH_2CH_2NH_2$	ethylenediamine

3. The Greek prefixes di-, tri-, tetra-, etc. are used to designate the number of each type of ligand in the complex ion. If the ligand already contains a Greek prefix (e.g. ethylenediamine) or if it is a polydentate ligand (i.e. it can attach at more than one coordination site), the prefixes bis-, tris-, tetrakis-, and pentakis- are used instead (See examples 3 and 4).

The numerical prefixes are listed in Table 2.

Table 2. Numerical Prefixes

Number	Prefix	Number	Prefix	Number	Prefix
1	mono	5	penta (pentakis)	9	nona (ennea)
2	di (bis)	6	hexa (hexakis)	10	deca
3	tri (tris)	7	hepta	11	undeca
4	tetra (tetrakis)	8	octa	12	dodeca

4. After naming the ligands, name the central metal.

- If the complex ion is a cation or neutral, the metal is named the same as the element.

$[Ni(CO)_4]$ Tetracarbonylnickel , $[Co(NH_3)_3(NO_3)_3]$ (Triaminetrinitrocobalt (III)

Co in a complex cation or neutral is called cobalt and Pt is called platinum.

$[Fe(H_2O)_6]SO_4$ Hexaaquairon (II) sulfate (Also, see examples 1-4.)

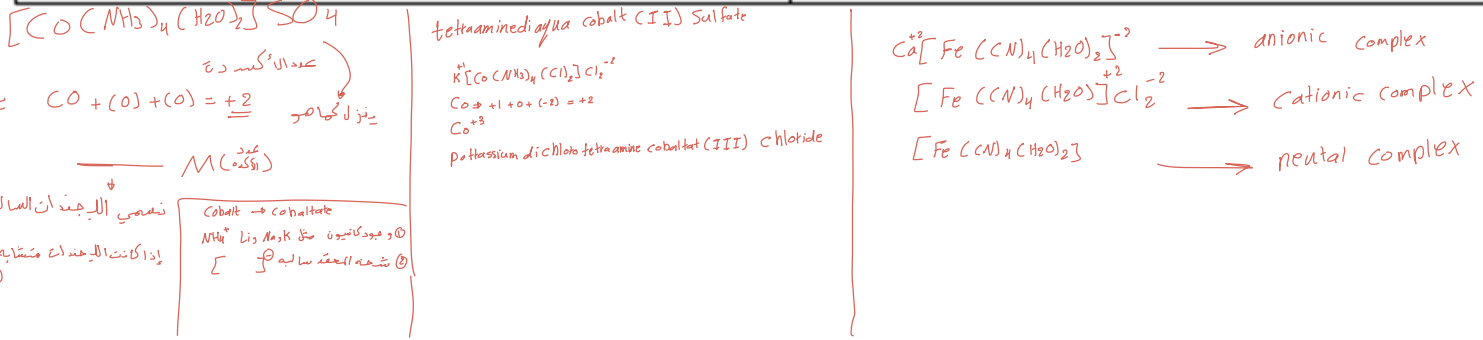
- If the complex ion is an anion, the name of the metal ends with the suffix –ate.

$Ca_2[Fe(CN)_6]$ Calcium hexacyanoferrate(II) (Also, see examples 5 and 6.)

For example, Co in a complex anion is called cobaltate and Pt is called platinate. For some metals, the Latin names are used in the complex anions (e.g. Fe is called ferrate and not ironate).

Table 3: Name of Metals in Anionic Complexes

Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

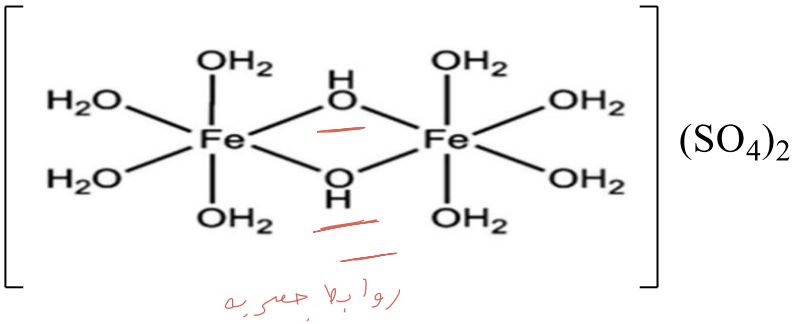


5. To name bridging ligands between two metal ions, the prefix μ is used before the name of each of the ligands.

$[(NH_3)_4Co(OH)(NH_2)Co(NH_3)_4](NO_3)_4$

Octaammine-μ-amido-μ-hydroxodicobalt(III) nitrate

If a complex has two similar bridging ligands, μ-di is used for its name.



octaaqua-μ-dihydroxo diiron(III) sulphate

$[(H_2O)_4Fe(OH)(OH)Fe(H_2O)_4]\ (SO_4)_2$

$[Co(NH_3)_4(H_2O)_2]SO_4$

① lewis acid → M^+ Co^{+2}

② lewis base: NH_3 / H_2O

③ C.N. = 6

④ First coordination sphere: $[Co(NH_3)(H_2O)]$

⑤ Second " " : SO_4

⑥ neutral and monodentate ligand

⑦ Heteroleptic

⑧ charge of the complex = $[Co(NH_3)_4(H_2O)]^{+2}$

④ magnetic property

Co_{27} : $[Ar]_{18}\ 4s^2\ 3d^7$

Co^{+2} : $[Ar]_{18}\ 3d^7$

paramagnetic

⑦ magnetic moment

$\mu = \sqrt{n(n+2)}$

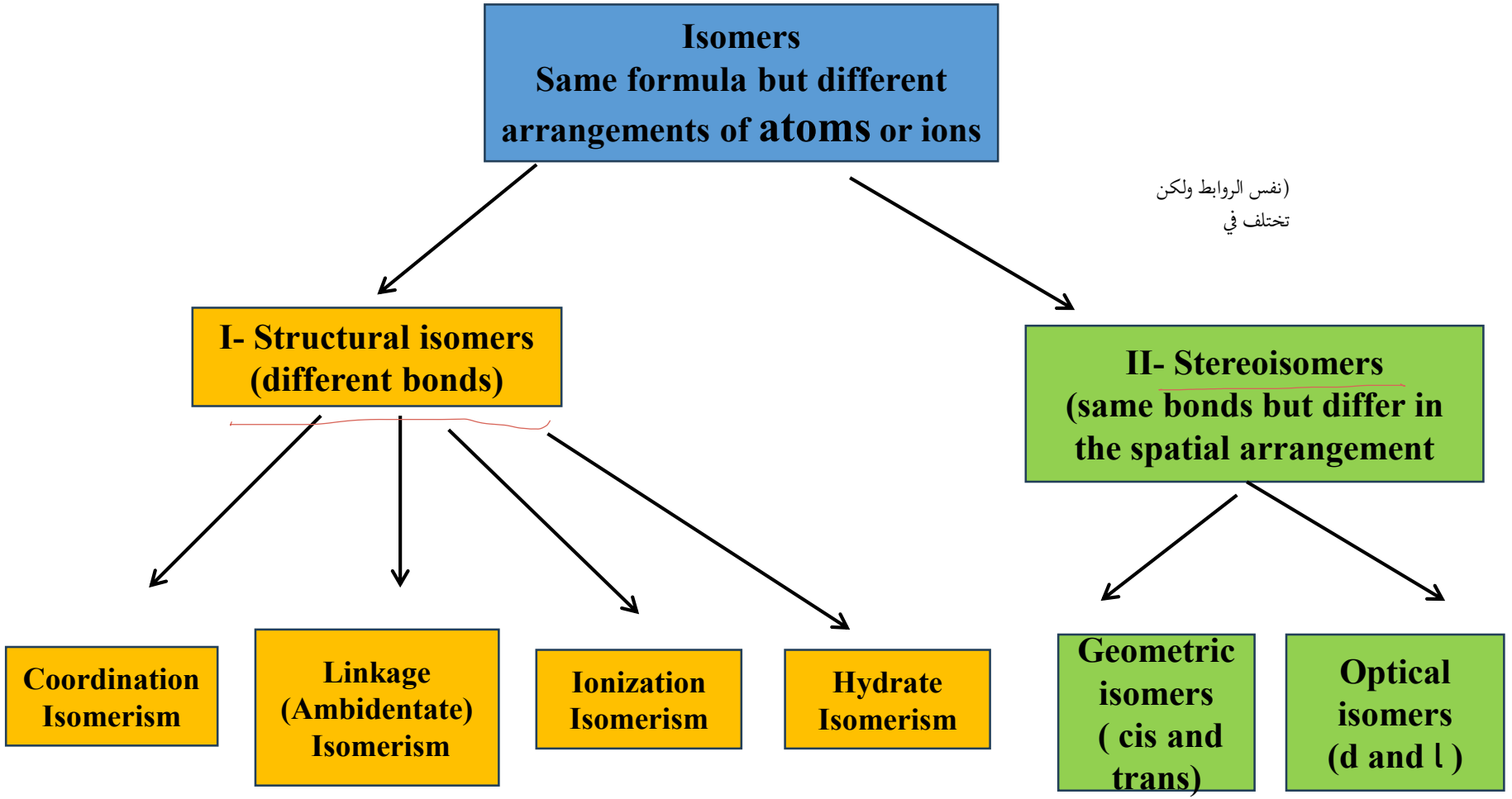
عدد الإلكترونات الغير مزدوجة

$\mu = \sqrt{3(3+2)} = \sqrt{15} =$ BM

الوحدة

⑪ octahedral الشكل الهندسي

Some Classes of Isomers



Some Classes of Isomers

In coordination chemistry, **isomerism** refers to the phenomenon where coordination compounds with the same chemical formula have different arrangements of atoms or ions, leading to different properties. The main types of isomerism are classified into two categories:

I- **Structural isomers;** There are several types of Structural isomerism. The most common types are

Linkage (Ambidentate) Isomerism

Coordination Isomerism

Ionization Isomerism

Hydrate Isomerism

II- Stereoisomers; Contains two types;

Geometrical isomerism (cis and trans)

Optical isomerism (d and l)

I-Structural (or constitutional) Isomerism

Structural Isomerism

Structural isomers have different arrangements of atoms or ligands but the same chemical formula. The types of structural isomerism are:

1- Coordination Isomerism:

Definition: Occurs when there is an exchange of ligands between cationic and anionic parts of a coordination compound.

Requires at least two different metal ions in the coordination compound

$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

Hexaamminecobalt(III) hexacyanochromate(III) and Hexaamminechromium(III) hexacyanocobalate(III)

2- Linkage (Ambidentate) Isomerism:

Definition: Occurs when a ligand can bind to the central metal through different donor atoms.

$[Co(NH_3)_4(NO_2)Cl]Cl$

Tetraamminechloronitrocobalt(III) chloride

(yellow)

$[Co(NH_3)_4(ONO)Cl]Cl$

Tetraamminechloronitritocobalt(III) chloride

(red)

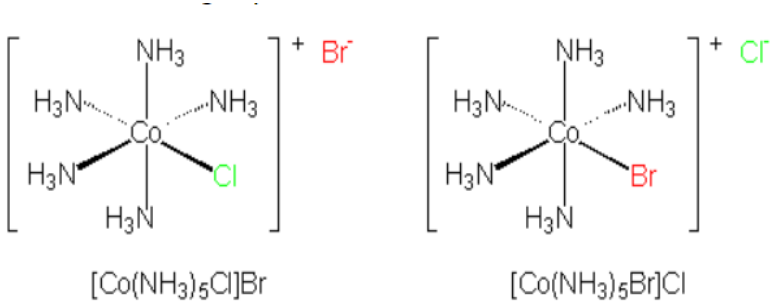
3- Ionization Isomerism

Definition: Arises when a counter ion in the coordination compound can replace a ligand, producing isomers that yield different ions in solution.

Example:

$[Pt(NH_3)_3Br]Cl$ and $[Pt(NH_3)_3Cl]Br$

$[Cr(NH_3)_5SO_4]Br$ and $[Cr(NH_3)_5Br]SO_4$



4- Hydrate Isomerism

Definition: Occurs when water molecules are present either inside or outside the coordination sphere, leading to isomers.

$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ (two water outside the sphere)

$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ (one water outside the sphere)

$[Cr(H_2O)_6]Cl_3$ (all water as ligands)

II-Stereoisomerism

تُعرَّف بأنها مركبات تناسقية يمكن فيها للذرات أو مجموعات
الذرات أن تتخذ مواقع مختلفة حول حلقة صلبة أو رابطة .

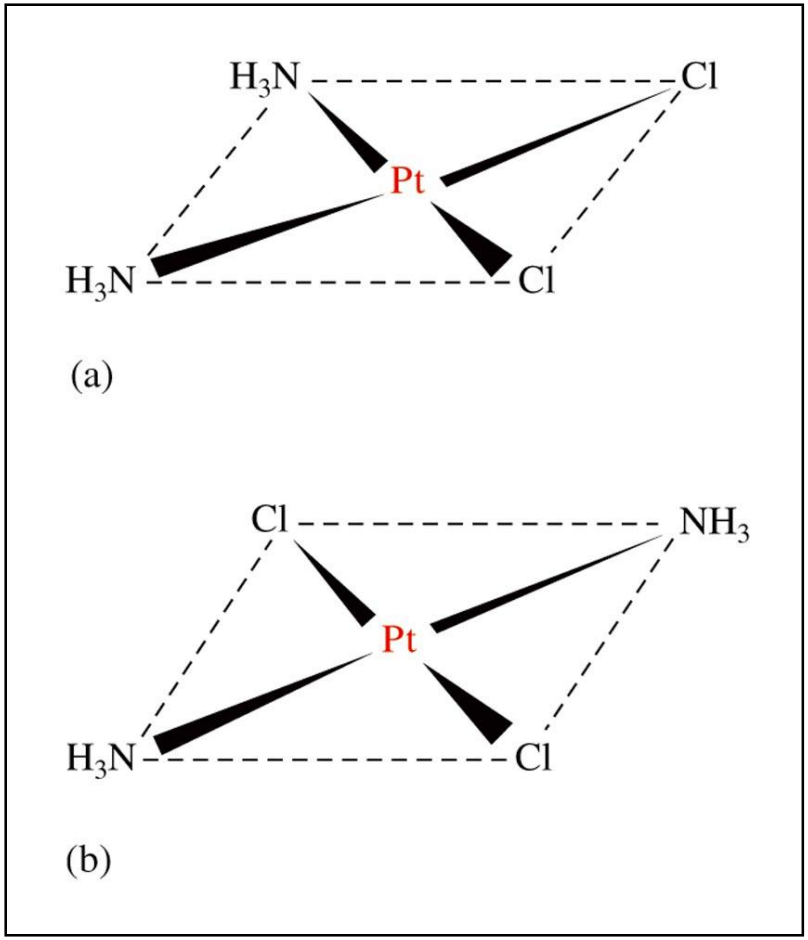
1- Geometrical Isomerism (*cis-trans*):

Defined as, coordination compounds in which atoms or groups of atoms can assume different positions around a rigid ring or bond.

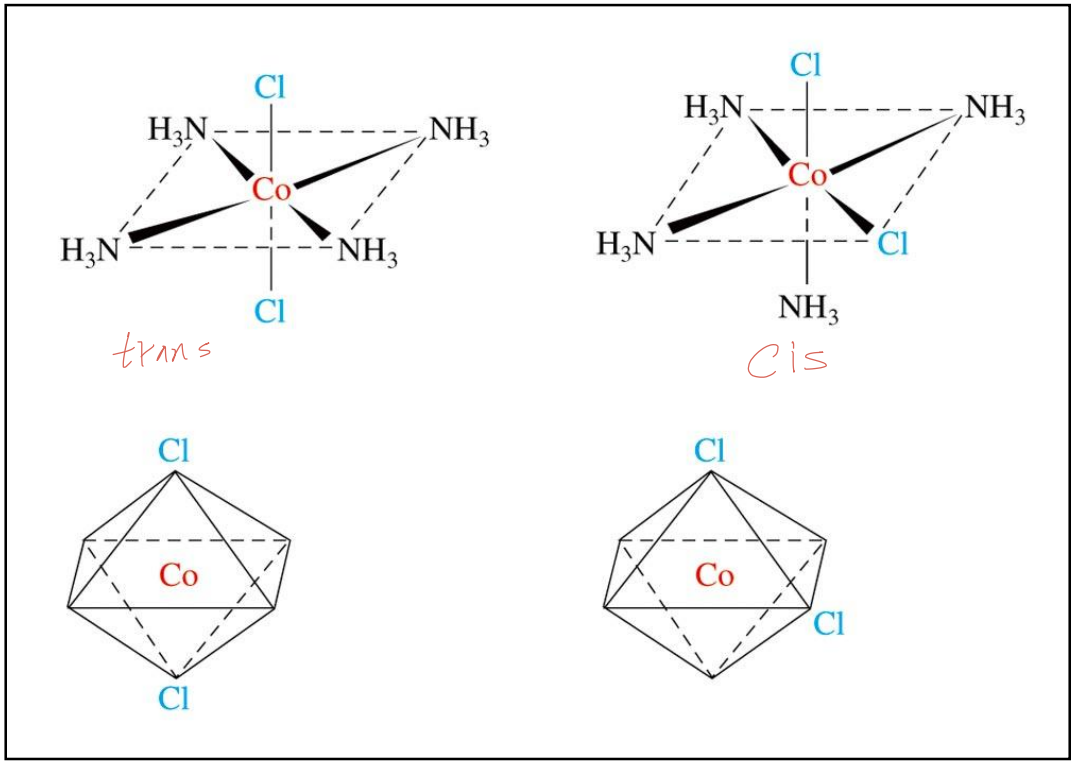
- *Cis* – same side (next to each other)
- *Trans* – opposite sides (across from each other)

Geometrical (*cis-trans*) Isomerism for a Square Planar Compound

(a) *cis* isomer (b) *trans* isomer



Geometrical (*cis-trans*) Isomerism for an Octahedral Complex Ion



Determine Which of these compounds is ci and which is trans?

II- Stereoisomerism

2- Optical Isomerism:

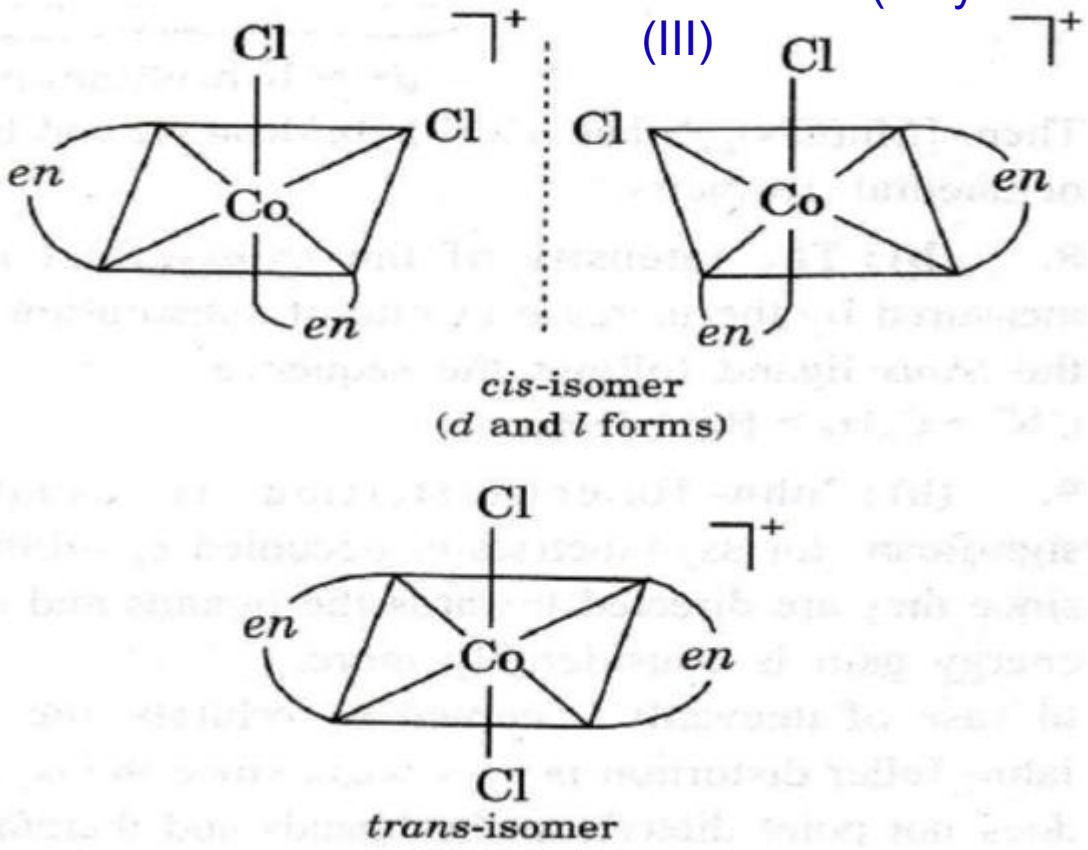
Defined as, coordination compounds in which isomers have opposite effects on plane-polarized light.

Optical Activity

- Exhibited by molecules that have nonsuperimposable mirror images (chiral molecules).
- Enantiomers – isomers of nonsuperimposable mirror images.

Delta- dichlorobis(ethylenediamine) cobalt (III)

Lamda- dichlorobis(ethylenediamine) cobalt (III)



The *trans* isomer of dichlorobis(ethylenediamine) cobalt (III) ion and its mirror image are identical. They are not optical isomers in it.

Electron Configurations

- Example
  - V: [Ar]$4s^2 3d^3$
  - Fe: [Ar]$4s^2 3d^6$
- Exceptions: Cr and Cu
  - Cr: [Ar]$4s^1 3d^5$
  - Cu: [Ar]$4s^1 3d^{10}$

Exercise: Analyze the Complex

- Given the complex $[Cr(en)_2Cl_2]^+$

- 1. Identify the central metal and its oxidation state.
- 2. Name the ligands, their type, and charge.
- 3. Determine the coordination number.
- 4. Predict the geometry of the complex.

Suggested Answers

- 1. Central metal: Chromium (Cr^{3+})
- 2. Ligands: en (bidentate), Cl^- (monodentate)
- 3. Coordination number: 6
- 4. Geometry: Octahedral

C.N = 4 ← توجد لها تفاعلات استبدال

Chapter 2: Substitution Reactions of Octahedral Complexes

Objectives

2.1 Mechanism and kinetics of complex reactions.
2.2 Catalysts and catalysis.
2.3 Reaction kinetics and reaction mechanics.
2.4 Mechanism of Ligand Reactions
2.6 Factors affecting reaction mechanics.
2.7 General substitution reactions in octahedral complexes.
2.8 Reactions with S_N1 mechanics (substitution on octahedral complexes).
2.9 Reactions with S_N2 mechanics (substitution on octahedral complexes).

تتضمن بعض التفاعلات المعقدة تغيرات في بنية مجال التناسق ؛ ويحدث ذلك عندما تتفاعل الليغاندات مع أيونات الفلزات — التي تكون عادةً مميهة (أي محاطة بجزيئات الماء) عندما تكون في حالة حرة . وتُعرف قدرة المركب التناسقي على استبدال واحد أو أكثر من الليغاندات المكونة له بليغاندات جديدة باسم "نشاط المركب التناسقي" .

Substitution Reactions of Octahedral Complexes

2.1 Mechanism and kinetics of complex reactions.

Some complex reactions involve changes in the structure of the coordination field. This happens when ligands react with metal ions — which, when free, are usually hydrated (surrounded by water molecules).The ability of a complex to replace one or more of its ligands with new ones is called "complex activity."

- If this replacement happens quickly, the complex is called active.
- If it happens slowly or not at all, it's called inactive.

⚠ Note:"**Active/inactive**" refers to reaction rate, which is related to the **kinetics of the reaction**, not the stability.

Stability is described by terms like "**stable" or "unstable**," which are related to **thermodynamics**, not reaction rates.

وُجد أن المعقد الأيوني $[Co(NH_3)_6]^{+3}$ يمكن أن يبقى لعدة أيام في وسط حمضي دون أن يتفكك ، وذلك نظراً لخموله الحركي (أي كونه مركباً مستقراً) ، رغم أنه يُعد معقداً غير مستقر من وجهة نظر الديناميكا الحرارية ، كما يتضح من ثابت الاتزان التالي :

It was found that the ionic complex $[(Co(NH_3)_6]^{+3}$ can remain for several days in an **acidic medium** without breaking down due to its kinetic inactivity or lack of activity (stable compound), although from a thermodynamic point of view it is considered an unstable complex, as evidenced by the following equilibrium constant:

لاحظ أن ثابت الاتزان للتفاعل الأمامي كبير (وهذا يعني أن التفاعل مع الحمض ممكن من الناحية الديناميكية الحرارية ، ولكنه لا يحدث فعلياً ، كما أن المركب $[Co(NH_3)_6]^{+3}$ لا يتأثر بالأحماض) .

$$[\ Co(NH_3)_6]^{3+} + 6\ H_3O+ \longrightarrow [Co(H_2O)_6]^{3+} + 6\ NH^{4+} \quad K = 10^{25}$$

Note that the forward equilibrium constant is large (this means **that thermodynamically the reaction with acid happens**, but actually does not happen, and the compound $[\ Co(NH_3)_6]^{3+}$ is not affected by acids

In contrast, the $[Ni(CN)_4]^{2-}$ complex is very stable.

$$[Ni(CN)_4]^{2-} \longrightarrow Ni^{2+} + 4\ CN \qquad K \approx 10^{-22}$$

stable (thermodynamic)

Thermodynamically, the reaction does not happen. However, the rate of substitution of cyanide ions with numbered cyanide ions is rapid.

من الناحية الديناميكية الحرارية ، لا يحدث التفاعل ؛ ومع ذلك ، فإن معدل استبدال أيونات السيانيد بأيونات سيانيد مرقمة

kinetic

بالنسبة لمعظم الفلزات الانتقالية من الصف الأول ذات المعقدات ثمانية السطوح ، يحدث الاستبدال بسرعة ، خاصة مع روابط مثل الماء . تُسمى هذه المعقدات بالمعقدات غير المستقرة ، أي أنها تتفاعل بسرعة ، وأحيانًا بشكل فوري .

For most first-row transition metals with octahedral complexes, the substitution happens quickly, especially with ligands like water. These are called **labile complexes**, meaning they react fast, sometimes instantly.

- However, complexes of chromium Cr (III) and cobalt Co (III) are not labile. Their substitution reactions are slow, taking hours, days, or even weeks at room temperature (25°C).

Because of their slow reactions, **Cr (III) and Co (III) complexes are useful for studying reaction mechanisms in detail**.

Important Definitions:

1. Labile and inert describe how fast a reaction happens → this is called kinetics.

- **Labile =** reacts quickly
- **Inert =** reacts slowly or not at all

2. Stable and unstable describe how strong or weak a complex is → this is called thermodynamics.

- **Stable =** hard to break
- Unstable = easy to break

3. Reaction mechanism means the step-by-step process of how a reaction happens at the molecular level.

3 . تشير آلية التفاعل إلى العملية التي توضح ،

In kinetics, we use an equation called the rate law to describe how fast a reaction happens.

- **The reaction rate (R) depends on:**

- The concentration of the reactants (how much of each substance is present).

- The temperature and the type of medium (like water or air).

There's also a number called K (rate constant) in the equation.

K changes with temperature and tells us how fast the reaction goes.

تتضمن المعادلة أيضاً قيمة تُعرف بـ K (ثابت السرعة) ؛ وتتغير قيمة K بتغير درجة الحرارة ،

Example of a Rate Law:

For the reaction: A + B → C + D (Products)

The rate law is:

علاوةً على ذلك ، ونظراً لوجود علاقة بين $[H^+]$ و$[OH^-]$ (إذ يؤدي ارتفاع أحدهما إلى انخفاض الآخر) ، فإن هذا يعني أن أيون الهيدروكسيد

$$R = K_a[A] + K_{ab}[A][B] + K_{ab}[A][B][H^+]$$

This means the reaction can happen in three different ways:

1. The first step depends only on the amount of A.
2. Second step depends on the amounts of both A and B.
3. The third step depends on A, B, and H^+ (acidity)

So the pH affects the reaction.

💡 Also, since $[H^+]$ and $[OH^-]$ are related (if one goes up, the other goes down), this means OH^- can also take part in forming the intermediate complex before the final products are made.

Most chemical reactions happen **in more** than one step.

- Because of that, we can't find the rate just by looking at the balanced equation.
- Only simple (one-step) reactions allow us to calculate the rate directly.

تتحكم هذه الخطوة الأبطأ في سرعة التفاعل

- In multi-step reactions, one step is usually slower than the others. This slowest step controls how fast the whole reaction goes.
- This slow step is called the rate-determining step.

$NO_2 + CO \rightarrow NO + CO_2$

This reaction looks simple, but in reality, it occurs in two steps:

⚙ Step-by-Step Mechanism:

Step 1 (slow):

$NO_2 + NO_2 \rightarrow NO + NO_3$ → intermediate

- This is the slow step, and it involves two NO_2 molecules.
- Because it's slow, it controls the speed of the overall reaction.
- So it is the rate-determining step (RDS).

Step 2 (fast):

$NO_3 + CO \rightarrow NO_2 + CO_2$

- This step is faster and happens after the first step.
  - It uses the NO_3 formed in Step 1 and reacts it with CO.

📌 Key Observations:

- The intermediate NO_3 is formed in Step 1 and used in Step 2.
- Intermediates do not appear in the final overall equation.
- The slow step (Step 1) determines the overall rate of the reaction.

That's why it's called the rate-determining step.

Rate Law:

Since the slow step involves:

$NO_2 + NO_2 \rightarrow NO + NO_3$ the rate depends on the concentration of NO_2 squared:

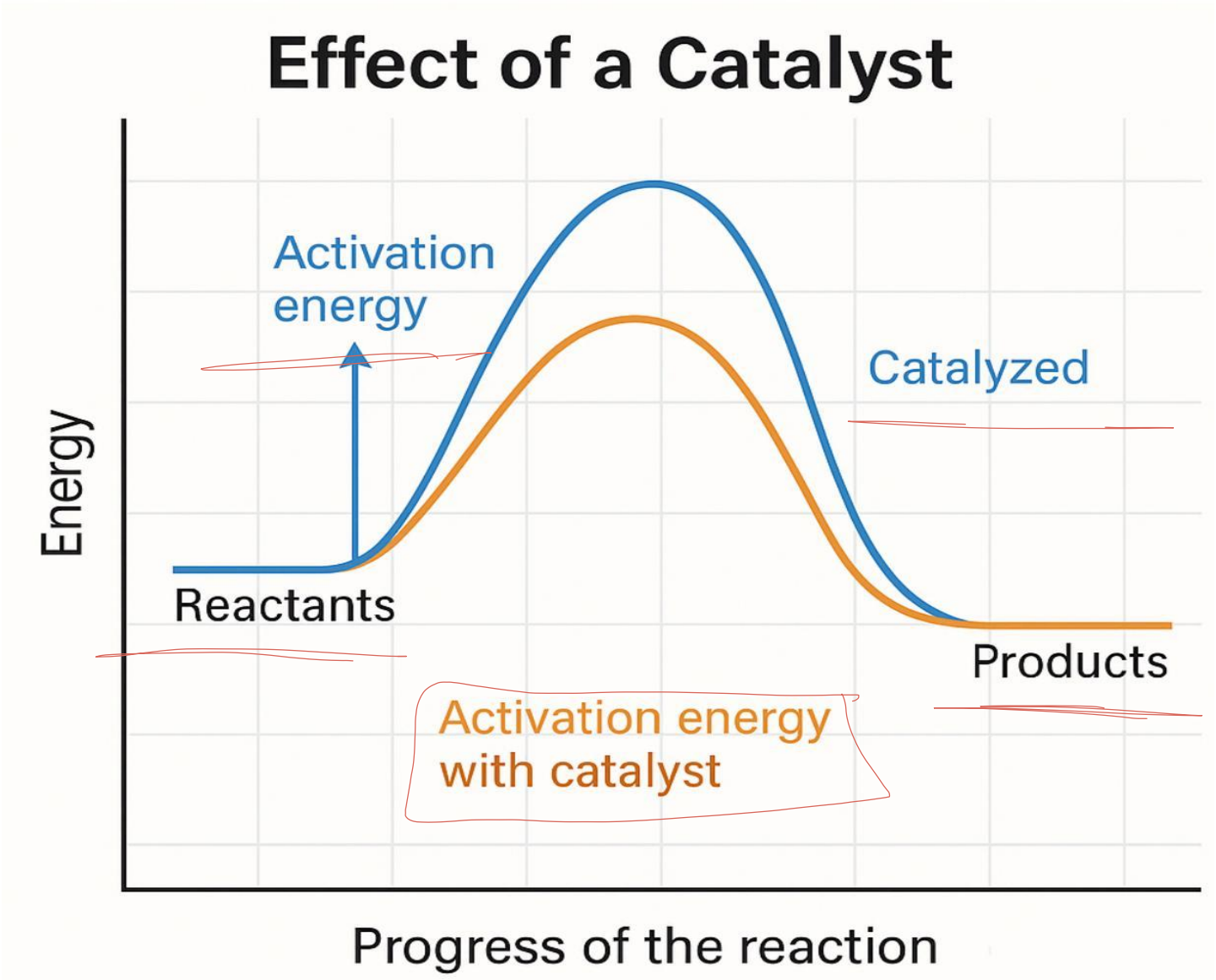
✓ Rate = $k [NO_2]^2$

Notice:

- CO is not in the rate law, because it only appears in the fast step.
- We only use reactants from of the slow step to write the rate law.

2. 2. Catalysts and catalysis :

- A catalyst is a substance that changes the speed of a chemical reaction — usually by making it faster.
- It does not get used up in the reaction.
- For example, manganese dioxide (MnO_2) helps potassium chlorate ($KClO_3$) break down faster to produce oxygen gas (O_2).
- A catalyst works by giving the reaction a different path that needs less energy to start. This is called lowering the activation energy.


Effect of a Catalyst
Activation energy
Catalyzed
Energy
Reactants
Products
Activation energy with catalyst
Progress of the reaction

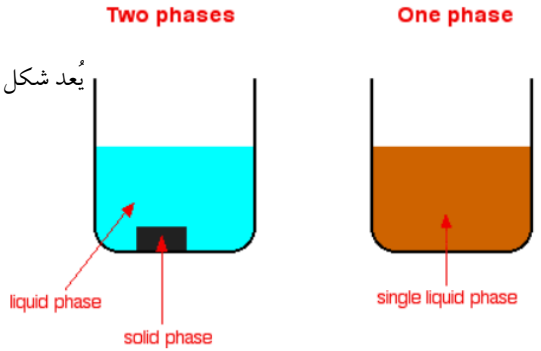
Types of Catalysts:

1. Homogeneous Catalysts:

The catalyst and reactants are in the same phase (like all in a liquid phase, or all reactants in a solid phase, etc.).

- Example: Catalyst and reactants are both dissolved in water (liquid phase).

يُعد شكل الإنزيم بالغ الأهمية لكي يعمل



2. Heterogeneous Catalysts:

The catalyst and reactants are in different phases.

- Example: A solid catalyst with gas reactants.

Enzymes (Biological Catalysts):

- Enzymes are special catalysts found in living things.

$$\text{Starch} \xrightarrow{\text{Amylase}} \text{Gloucose}$$

- They speed up reactions in the body by using their active sites (special regions on their surface).
- The shape of the enzyme is very important for it to work properly.
  - This shape is held together by intermolecular forces like:

  - Hydrogen bonds
  - Dipole-dipole forces
  - London dispersion forces

2.3. Reaction Kinetics & Reaction Mechanism

• تفسر هذه النظرية كيف تمر التفاعلات عبر

Transition State Theory (TST):

- This theory explains how reactions go through a high-energy transition state before forming products.

• توجد الحالة الانتقالية في حالة توازن مؤقت مع

- The transition state is in temporary equilibrium with the reactants.

• لا تنطبق نظرية الحالة الانتقالية (TST) على التفاعلات التي تتحكم فيها سرعة حركة الجسيمات (التفاعلات المحدودة بالانتشار) .

- TST does not apply to reactions that are controlled by how fast particles move (diffusion-limited reactions).

✓ For a reaction to happen easily:

مزيد من الفوضى

- It should have higher entropy ΔS^{+} (more disorder)
- And lower activation energy Δs^{act} (less energy needed to start the reaction)

2.4. Rate measurements of reactions.

لقياس سرعة حدوث التفاعلات ، ننظر إلى عمر النصف (أي المدة التي تبقى فيها الجزيئات قبل أن تتفاعل) .

To measure how fast reactions happen, we look at the half-life (how long the molecules last before reacting)

1. Chemically Inert Molecules:

تتفاعل هذه الجزيئات ببطء (يبلغ عمر النصف أكثر من دقيقة

• يمكننا قياسها باستخدام طرق بصرية واحدة(مثل امتصاص الضوء) أو عن طريق رصد التغيرات في الأس الهيدروجيني (pH) .

- These molecules react slowly (half-life more than 1 minute).
- We can measure them using optical methods (like light absorption) or by checking pH changes.

2. Unstable Molecules:

نستخدم تقنيات "التدفق المتوقف" (التي تمزج المواد المتفاعلة بسرعة فائقة) لقياسها ، وذلك في إطار التحليل الطيفي السريع .

- These react faster (half-life between 1 minute and 0.001 seconds).
- We use stopped-flow techniques (which mix reactants very quickly) to measure them, Fast Spectroscopy.

عندما يقل عمر النصف عن جزء من الألف من الثانية (1 مللي ثانية) . وفي هذه الحالة ، يمكن استخدام طرق الاسترخاء (مطيافية السرعة

جزيئات سريعة التفاعل كيميائياً

3) Molecules chemically fast

when their half-life is less than one thousandth of a second (ms 1 > (1/2). In this case, relaxation methods (fast spectroscopy) such as nuclear magnetic resonance (NMR) can be used.

• آلية تفاعلات الرُبيطات :

2.5. Mechanism of Ligand Reactions:

في المعقدات ثمانية السطوح (سداسية التناسق) ، يمكن استبدال الليغاندات بطريقتين رئيسيتين : آليتي $SN1$ و$SN2$.

In octahedral (hexacoordinated) complexes, ligands can be replaced in two main ways. SN1 and SN2 Mechanisms

• يغادر الرابطد القديم أولاً ، كاسراً رابطته مع

• يؤدي هذا إلى تكوين مركب وسيط مؤقت خماسي الرابطة (خماسي التناسق) يحتوي على فراغ .

☞ First Type: SN1 Mechanism

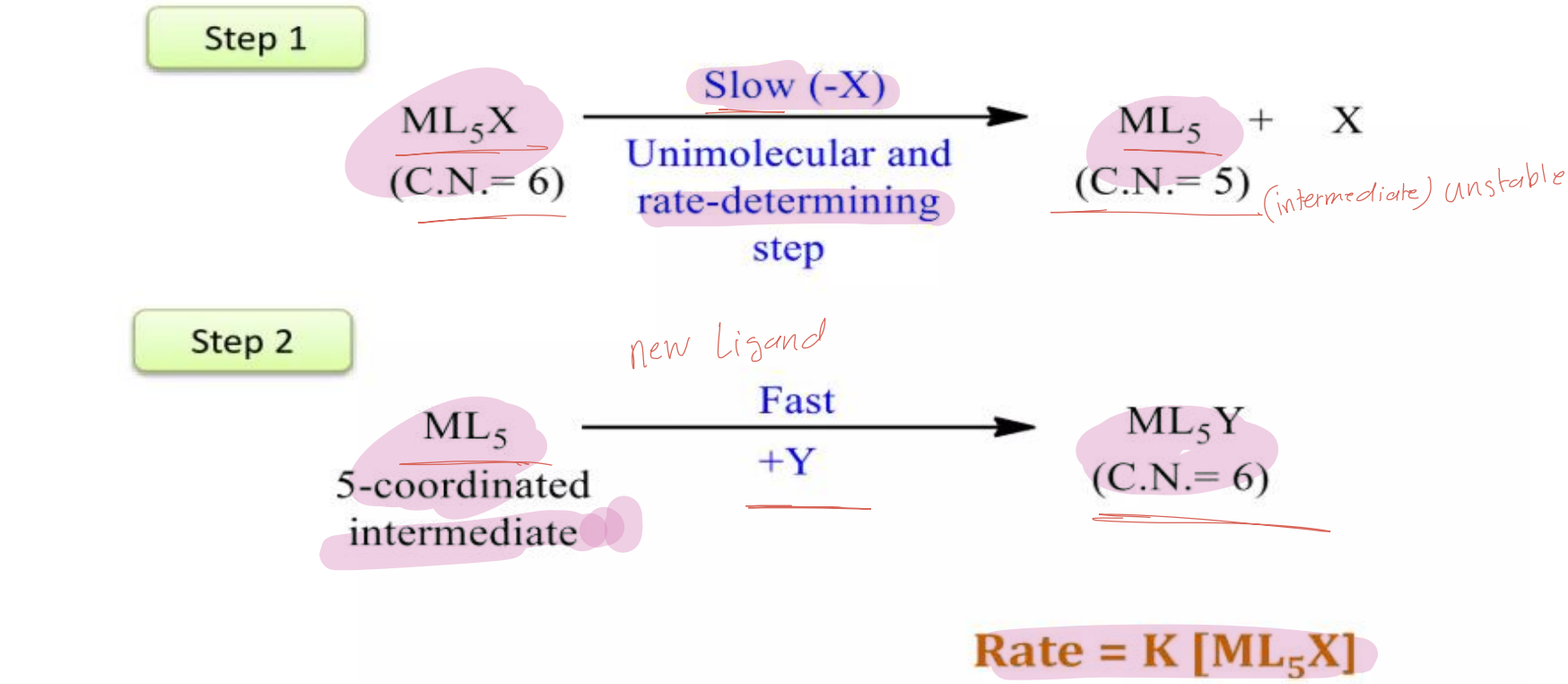
- The old ligand leaves first, breaking its bond with the metal.

هذه الخطوة الأولى بطيئة وتتحكم في سرعة

- This creates a temporary 5-ligand (pentacoordinated) intermediate, which has an empty space.
- This first step is slow and controls the reaction rate.
- Then, the new ligand quickly enters and fills the empty space — this second step is very fast.

• بعد ذلك ، يدخل الرابط الجديد بسرعة ويملأ

📌 This is called an SN1 reaction (unimolecular nucleophilic substitution).



The first step is the slow step and hence it is also the rate-determining step for the process.

The overall rate is: Rate = k [ML_5X]

في هذا النوع ، يرتبط الليغاند الجديد بالمعدن

The Second Type: S_N2 Mechanism

يُشكّل هذا مركباً وسطياً سباعي التناسق (بسبع

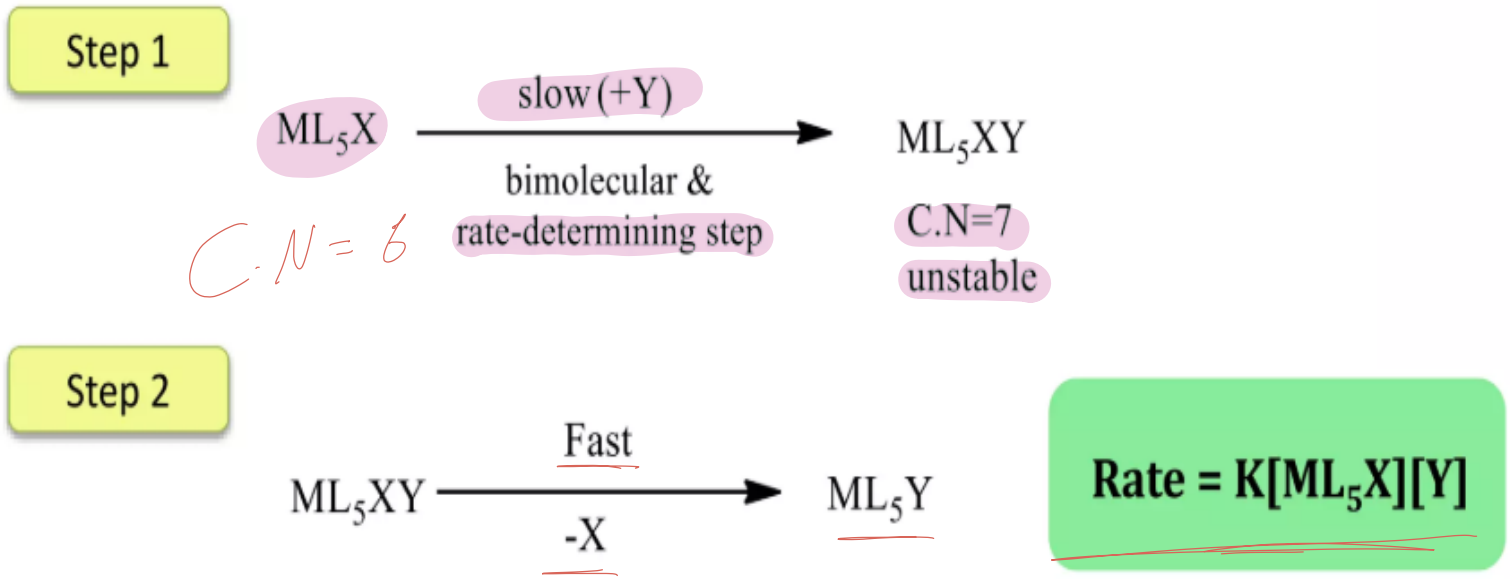
- In this type, the new ligand attaches to the metal first.
- This forms a 7-ligand (heptacoordinated) intermediate.
- This first step is slow, because it's crowded around the metal.

• تتسم هذه الخطوة الأولى بالبطء بسبب

- Then, the old ligand quickly leaves in the second step, which is fast.

📌 This is called an S_N2 reaction (bimolecular nucleophilic substitution).

• بعد ذلك ، يغادر الرابط القديم بسرعة في



The first step is the slow step and hence it is also the rate-determining step for the process.

The overall rate is Rate = k [MA_5L] [Y]

آلية الانفصال (آلية D)

Dissociative Mechanism (D mechanism)

تشبه هذه الآلية آلية SN1 ، إلا أن قانون السرعة مختلف .

- This mechanism is similar to SN1, but the rate law is different.

1. The old ligand (L) leaves the metal, forming a 5-ligand (pentacoordinated) intermediate. يوجد هذا المركب الوسطي منفرداً لفترة وجيزة ،
2. This intermediate briefly exists alone, surrounded by:
   - The old ligand (L)
   - The new ligand (L)
   - Solvent molecules (S)
3. Then, the new ligand attaches to the metal.

Important Notes:

- The reaction rate does NOT depend on the concentration of the new ligand.
- The M–L bond fully breaks before a new bond forms.

$$ML6 \underset{K\text{-}1}{\overset{k1}{\rightleftharpoons}} ML5 + L$$

$$ML5 + L^- \underset{}{\overset{k2}{\rightleftharpoons}} ML5L^-$$

The rate of the reaction is given by this equation:

$R = (K_1K_2 [ML_6] [L']) / (K_{-1} + K_2 [L])$

$[ML_6]$ = the metal complex with its original ligands

[L'] = the new ligand coming in

[L] = the original (leaving) ligand

تعتمد سرعة التفاعل (R) على كمية الربيطة

K_1, K_2, K_{-1} = rate constants

تقريبا، التركيز

The speed of the reaction (R) depends on how much of the leaving ligand [L] is present.

ولكن إذا كانت [L] عالية جداً ، فإن K- تصبح صغيرة للغاية ويمكن إهمالها .

But if [L] is very high, then K_{-1} becomes very small and can be ignored.

- So, the equation becomes simpler: When [L] is very high

→ $R = K_1 [ML_6]$

لماذا تم إهمال L في المعادلة ؟

تتميز هذه الآلية بتكوين المعقد بأكمله على هيئة
مركب وسطي سباعي التناسق (ML5L) ،

The associative mechanism (A mechanism)

تتبع SN2

This mechanism is characterized by the formation of the entire complex as a seven-coordinate intermediate 'ML5L‘ which is followed by a dissociation step to give the product complex.

$$ML6 + L' \rightleftharpoons ML6L'$$

unstable

$$ML6L' \rightleftharpoons ML5L' + L$$

The reaction rate law can be calculated from the equation: $R = K_1 [ML_6] [L']$

إلى هنا الاختبار

The Interchange Mechanisms

• تبدأ إحدى روابط M–L (رابطة فلز–

In this reaction mechanism:

- One of the M–L bonds (metal-ligand) starts to stretch, but it doesn't fully break.

• وفي الوقت ذاته ، يبدأ ربيطة جديدة (L')

- At the same time, a new ligand (L') begins to lightly interact with the metal.

This forms a weak, temporary complex called ML·L', where:

- The new ligand (L') is starting to attach,
- And the old ligand (L) is starting to leave.

$$ML_6 + L' \xrightarrow{K1} ML6{\cdot}L' \xrightarrow{K2} [L5M.....L, L'] \longrightarrow ML5{\cdot}L' + L$$

2.6 Factors affecting reaction mechanics.

2.6.1. – Effect of Solvent

تحدث العديد من تفاعلات الاستبدال في المركبات المعقدة في الماء ، الذي يُعدّ بحد ذاته ربيطة ، ويتواجد بتركيز عال وثابت (55. 5 مولار) . وبالتالي ، سيُلاحظ قانون المعدل في المعادلة (1) R=K [LsMX] حتى لو كان التفاعل الحقيقي

Many substitution reactions in complexes take place in water, which itself is a ligand and is present at a high and constant concentration (55.5M). Thus the rate law in Equation (1) $R=K\,[L_5MX]$ will be observed even if the real reaction is

$$[L_5MX] + H_2O \rightarrow [L_5MH_2O] + X$$
$$[L_5MH_2O] + Y \rightarrow [L_5MY] + H_2O$$

It cannot be determined whether the reaction proceeds according to the S2, SN1 mechanism from the law Rate only.

لا يمكن تحديد ما إذا كان التفاعل يسير وفقاً لآلية (SN_2) أم (SN_1) بالاعتماد على

explain ?

2-Formation of ionic pairs

2- تكوين الأزواج الأيونية

عندما يكون معقد المتفاعلات كاتيوناً وتكون المجموعة الداخلة أنيوناً – لا سيما إذا كان لأحدهما أو لكليهما شحنة عالية – فإن ذلك يؤدي إلى تكوين أزواج أيونية ، وهو ما يُعرف أحياناً بمركبات التناسق الخارجية .

When the reactant complex is a cation and the entering group is an anion, and especially when one or both of them has a high charge, then in this case ion pairs will be formed, or sometimes called outer coordination compound. They have a constant K

general equation

$$[L_5MX]^{n+} + Y^{m-} \leftrightarrow \{[L_5MX]Y\}^{n-m}$$

عندما يكون تكوين هذا الأيون المزدوج هو السبيل الوحيد لتفاعل $Y^m- $ مع $[LMX]^{+n}$ بمعدل مقبول ، فإن قانون السرعة سيتخذ الصيغة التالية :

When the formation of this double ion is the only way Y^{m-} reacts with $[L_5MX]^{n+}$ at a reasonable rate, the rate law will take the form:

$$R = K' K [L_5MX] [y] = K'' [L_5MX] [y]$$

But in the end we will find that the rate law is the rate law mentioned in equation (2) which expresses a reaction that follows the SN2 mechanism. Therefore, additional experiments must be conducted.

ولكن في النهاية ، سنجد أن قانون السرعة هو القانون المذكور في المعادلة (2) ، والذي يعبّر عن تفاعل يتبع ميكانيكية SN2 .

$$(2)\ R=K [L_6MX] [L]'$$

يتبع SN2

عندما تتضمن معادلة سرعة التفاعل تركيز أيونات الهيدروكسيل [$^-$OH] ، يثور تساؤل حول ما إذا كانت مجموعة الهيدروكسيل تهاجم المعدن مباشرةً — وهو ما يمثل تفاعلاً من النمط (SN2) — أم أنها تظهر في معادلة سرعة التفاعل لأنها تتفاعل أولاً مع أحد الليجاندات المرتبطة بذرة المعدن (في تفاعل سريع) لانتزاع بروتون منه ، مما يؤدي إلى تكوين القاعدة المرافقة (CB) ؛ والتي بدورها تدخل في التفاعلات الموضحة أدناه :

تكوين القاعدة المرافقة : (القاعدة المرافقة (CB)

3- Formation of the accompanying base: (Conjugate base (CB)

When the rate law includes the concentration of hydroxyl ions [OH], the question arises as to whether the hydroxyl group actually attacks the metal, which is an SN2 reaction, or whether the hydroxyl group appears in the rate law because it first reacts with one of the ligands attached to the metal atom (a fast reaction) to remove a proton from it, forming the conjugate base (CB).Which in turn react as shown in the following reactions:

$$[Co(NH_3)_3Cl]^{2+} + OH^- \leftrightarrow [Co(NH_3)_4(NH_2)Cl]^+ + H_2O$$

$$[Co(NH_3)_4\ (NH_2)Cl]^{2+} + L^- \leftrightarrow [Co(NH_3)_4(NH_2)L]^+ + Cl^-$$

في الحالات التي يحدث فيها التفاعل البطيء عبر آلية $ S_N1 $ ، يُطلق على آلية التفاعل الكلية –الممثلة بالمعادلتين

$$[Co(NH_3)_4(NH_2)L]^+ + H^+ \rightarrow [Co(NH_3)_5L]^{2+}$$

In cases where the slow reaction takes place using the Sx1 mechanism, it is called the overall reaction mechanism represented by the two previous equations using the SN1-CB mechanism.

1 – معدلات تبادل الماء : نود الإشارة إلى أن جميع التفاعلات التي تتضمن تبادل الماء وتكوين معقدات للأيونات المميأة (hydrated ions) هي تفاعلات سريعة . وكحالة خاصة ، سندرس المعدلات التي تتبادل بها الأيونات المميأة جزيئات الماء ؛ ففي وجود الماء كمذيب ، تُعد جميع هذه التفاعلات سريعة ، باستثناء بعض التفاعلات الخاصة .

2.7 General substitution reactions in octahedral complexes.

Most of the substitution reactions of octahedral complexes are of the following types:

1- Water-exchange rates: We would like to point out that all reactions that involve the exchange of water and the formation of complexes of hydrated ions are all fast reactions. As a special case we will study the rates at which hydrated ions exchange water molecules With water as a solvent, all these reactions are rapid except for special reactions.

THE COMPLEX $[Cr(H_2O)_6]^{+3}$, $[Rh(H_2O)_6]^{+3}$ which are relatively slow.

The half-life of the hydrated chromium(III) ion is ~105×3.5 sec), which is illustrated by the diagram in Figure (1).

The effect of size and charge on the alkali and alkaline earth ions can also be observed. We find that within each group, the replacement rate is observed to be It increases with increasing size

يمكن أيضًا ملاحظة تأثير الحجم والشحنة على أيونات الفلزات القلوية والقلوية الترابية . وجدنا أنه ضمن كل مجموعة ، يزداد معدل الاستبدال مع ازدياد الحجم .

This prompts us to ask: What are the factors that affect the reaction rates of similar and different complexes of metal ions? In this case, labeled water (H2O)* is used, i.e. it contains, for example, the oxygen isotope (^{18}O), where the formation of The following equilibrium:

وهذا يدفعنا إلى التساؤل : ما هي العوامل التي تؤثر على معدلات

$$[M(H_2O)_6]^{m+} + H_2O^* \qquad [M(H_2O)_5(H_2O)^*]^{m+} + H_2O$$

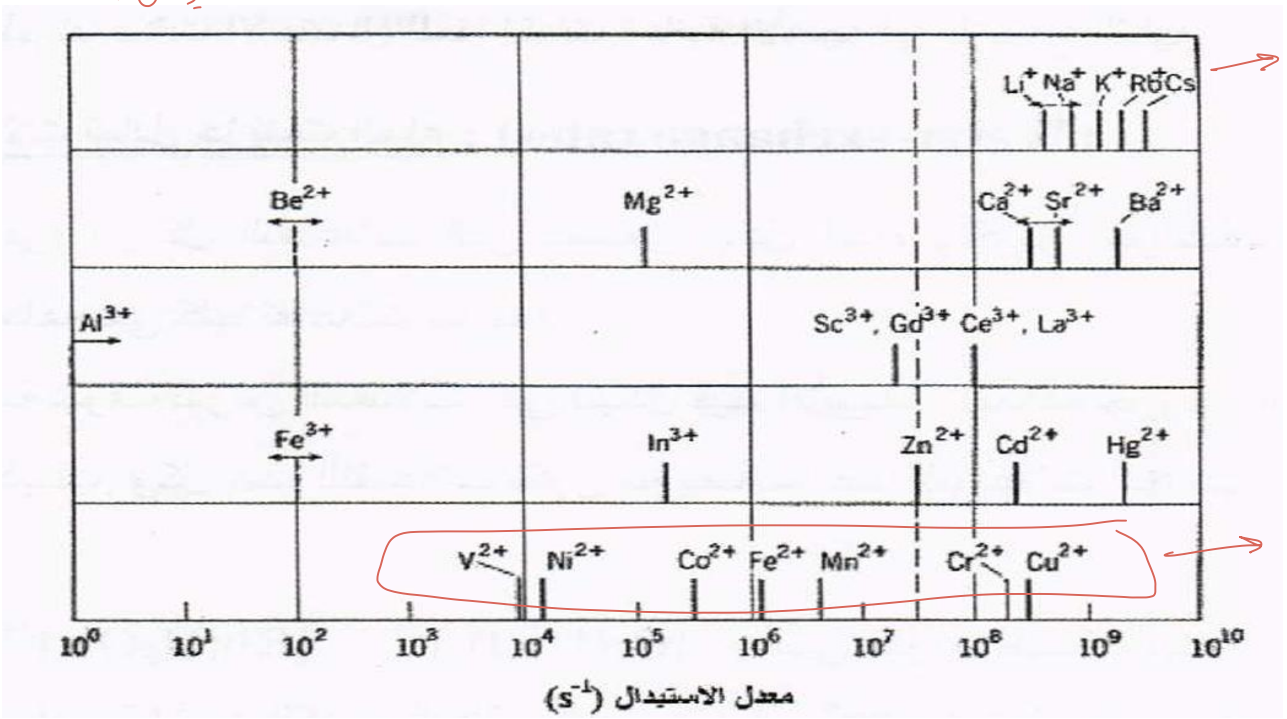


Figure (2-3) shows the rate constants (seconds) for the replacement of water by different hydrated ions.

أظهرت الدراسات الحركية أنه ضمن مجموعة واحدة في الجدول الدوري :

Kinetic studies showed that within a single group in The periodic table:

يزداد معدل تبادل جزيئات الماء مع زيادة حجم ذرة المعدن .

** The rate of exchange of water molecules increases with the increase in the size of the metal atom.

** For ions M^{+1}, M^{2}, M^{3} which have the same size, it was found that the ion that The one that carries the least charge is the one that exchanges the fastest.

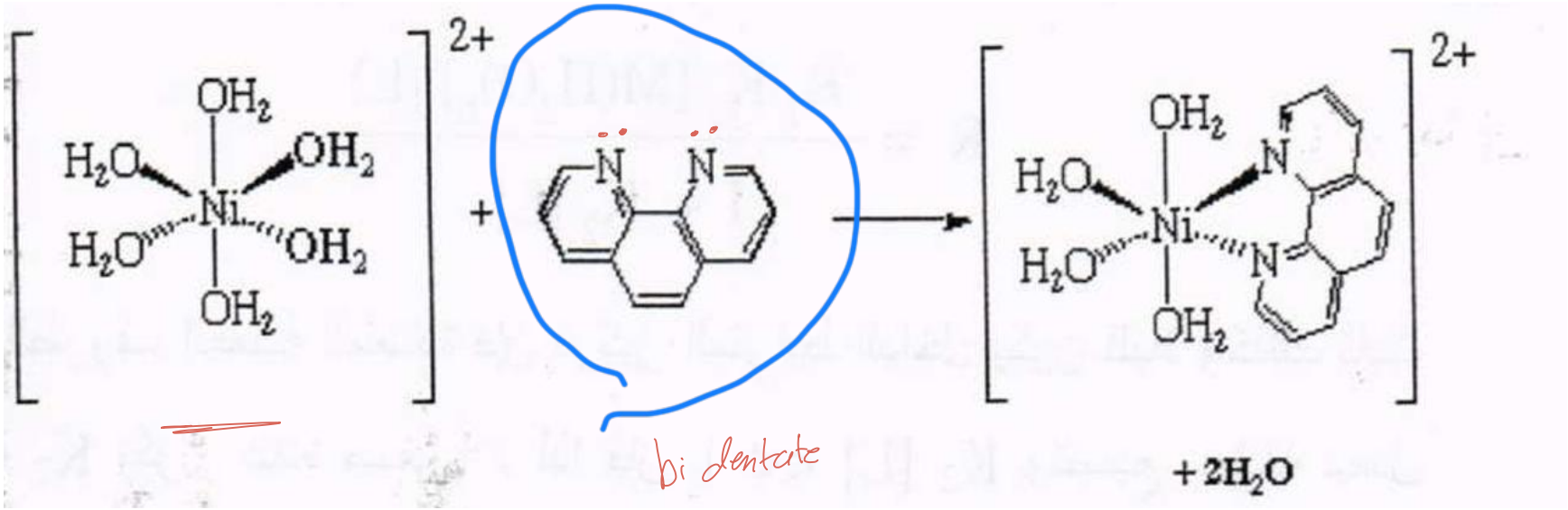
Since the strength of the bond between the metal atom and the water molecule M-OH_2 increases with the increase in charge and the size of the metal ion decreases, it has been suggested that the transition state of the water exchange reaction must first contain a step of breaking the M-OH bond that is highly present before the formation of the new bond, i.e. it is a reaction with a dissociation mechanism of the type D-type

explain one example

يتمثل ذلك في استبدال جزيء مذيب مرتبط بذرة فلز (مثل جزيء الماء) بربيطة (Ligand) من النوع L . ولعل معظم التفاعلات المدروسة من هذا النمط تؤدي إلى تكوين معقد أيوني لأيون فلزي مُميَّه في المحلول . مثال :

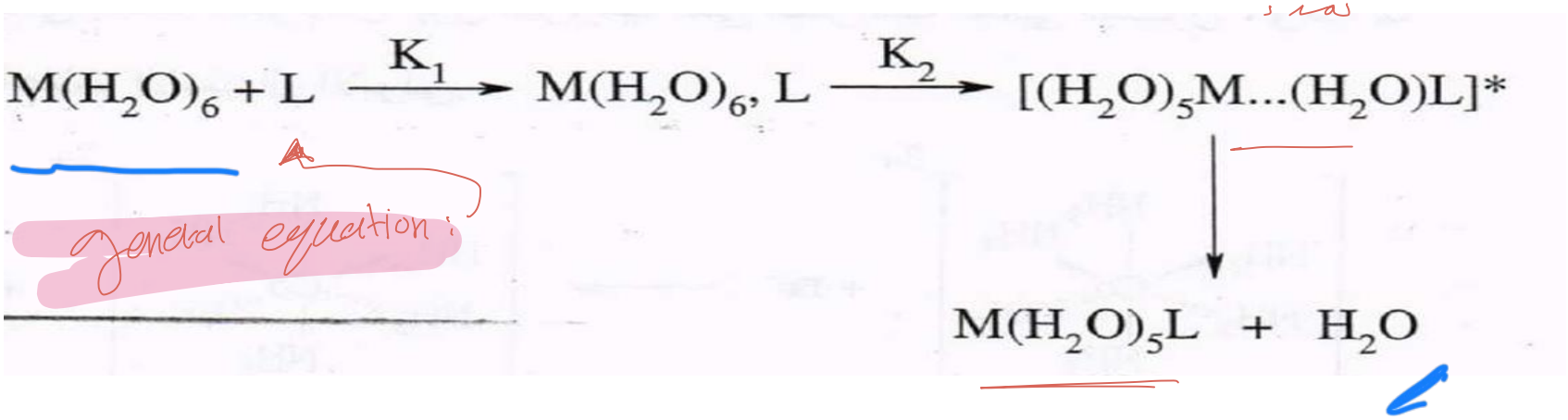
2- Formation of complexes of aqueous metal ions:

It is the replacement of a coordinated solvent molecule with a metal atom (such as a water molecule) by an L-ligand. Perhaps most of the reactions studied of this type lead to the formation of an ionic complex of an aqueous metal ion in solution. Example:



يتم التفاعل عبر خطوتين . في الخطوة الأولى ، يتكون معقد "خارجي النطاق" (outer-sphere complex) بين الأيون المعدني المميّه (المحاط بجزيئات الماء) والربيطة (ligand) . تلي ذلك خطوة ثانية تتمثل في إزالة جزيء ماء من الأيون المميّه ، وذلك على غرار عملية تبادل جزيئات الماء ؛ أي أن آلية التفاعل تتبع نمط التفكك المتبادل (آلية Ia) .

The reaction proceeds in two steps. In the first step, an aqua ion-ligand outer-sphere complex is formed between the hydrated metal ion and the ligand. This is followed in a second step by the removal of a water molecule from the hydrated ion in the same way as the exchange of water molecules, i.e.,The reaction mechanism is of the mutual dissociation type Ia mechanism



في هذه الحالة ، تكون المجموعة الداخلة عبارة عن أيون ؛ فعلى سبيل المثال ، استبدال

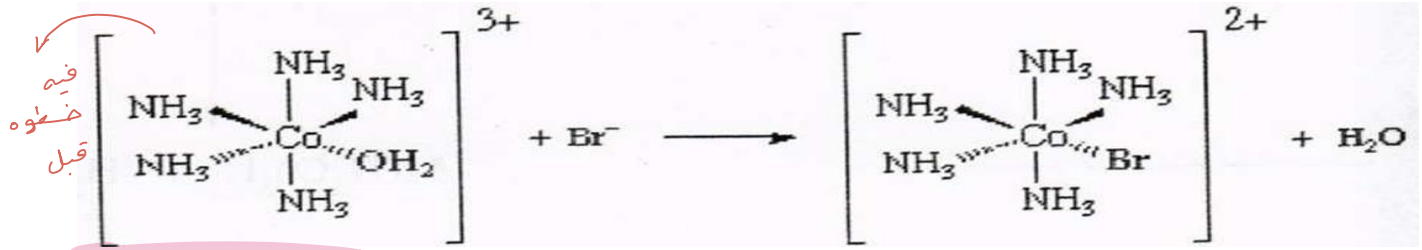
3-Ionic substitution reactions

In this case the entering group is an ion, for example replacing an ammonia molecule with a bromide ion in an aqueous solution.

$$[Co(NH_3)_6]^{3+} + Br \rightarrow [Co(NH_3)_5Br]^{2+} + NH_3$$

It appears that the reaction does not proceed in one step as shown in the previous equation, but in aqueous solutions, an ammonia molecule first emerges and is replaced by a water molecule, which subsequently causes an attack by the bromide ion on the aqueous complex formed.

This is what is called ionic substitution reactions.



general equation:

$$[L_nMX] + H_2O \rightleftharpoons [L_nM(H_2O)] + X$$

$$[L_nM(H_2O)] + Y \longrightarrow [L_nMY] + H_2O$$

في بعض التفاعلات المعروفة ، لا يحدث استبدال الرابطة (الليجاند) عن طريق كسر الروابط بين ذرة المعدن والروابط (الليجاندات) ، بل عن طريق كسر الروابط داخل الروابط (الليجاندات) نفسها وإعادة تكوينها .

4-Attack interactions on the interconnected:

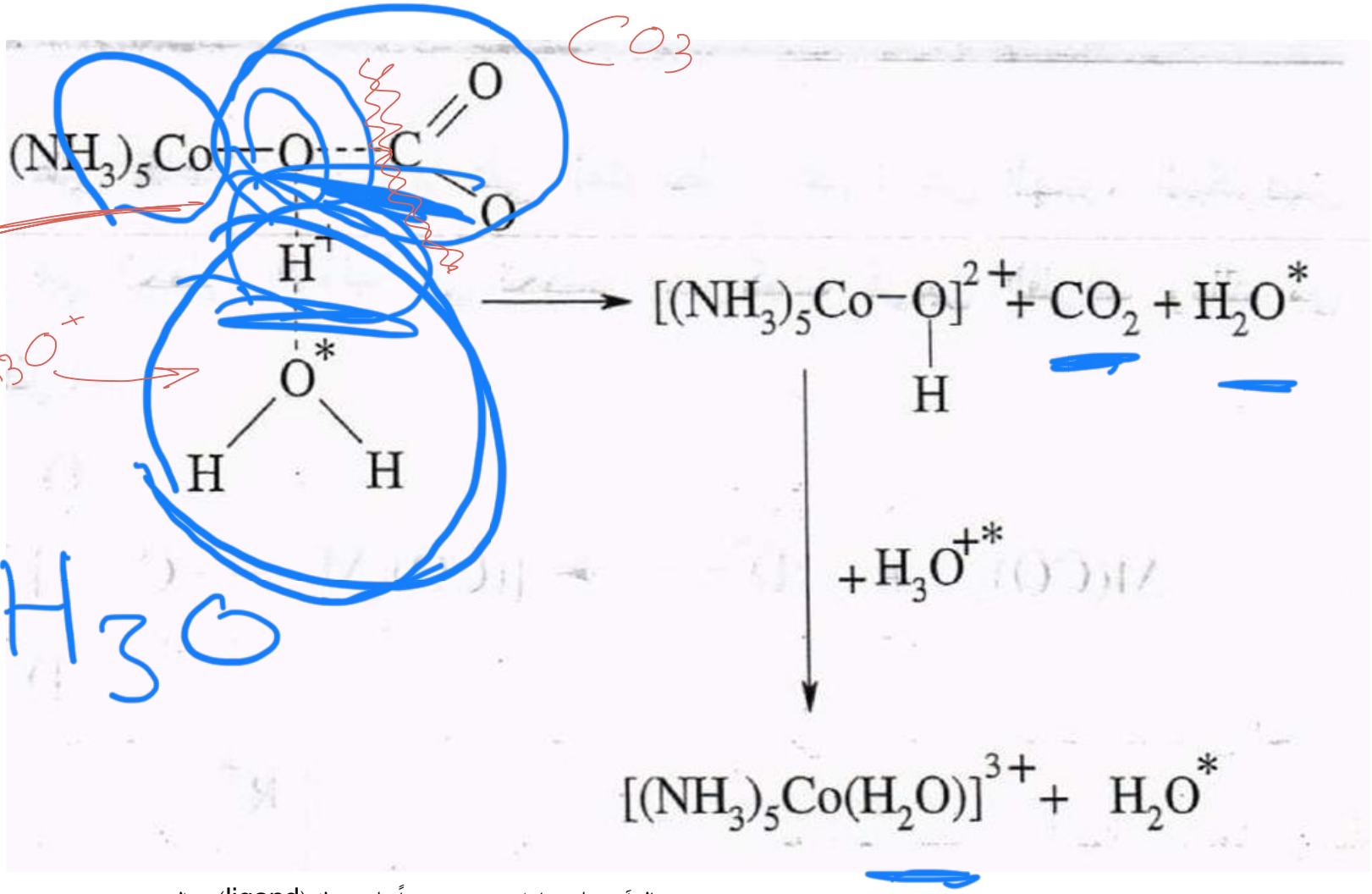
In some known reactions, the replacement of the ligand occurs not by breaking the bonds between the metal atom and the ligands, but by breaking the bonds of the ligands themselves and re-forming them.

One of the known reactions of this type is the hydration of carbonato complexes. When we carry out a hydration reaction of the complex using labeled water (H_2O) containing the oxygen isotope $^{18}(O)$, we find that there is no evidence of the presence of the oxygen isotope 18 in the coordination range of the ion during the hydration process.

تُعدّ عملية تميؤ معقدات الكربونات إحدى التفاعلات المعروفة من هذا النوع . فعند

$$[Co(NH_3)_5OCO_2]^+ + 2H_3O^{+*} \longrightarrow Co(NH_3)_5(H_2O)]^{3+} + CO_2 + 2H_2O^*$$

The most accepted mechanism for this reaction involves a proton (H) attack on the oxygen atom attached to the cobalt atom followed by the step of expelling a carbon dioxide molecule



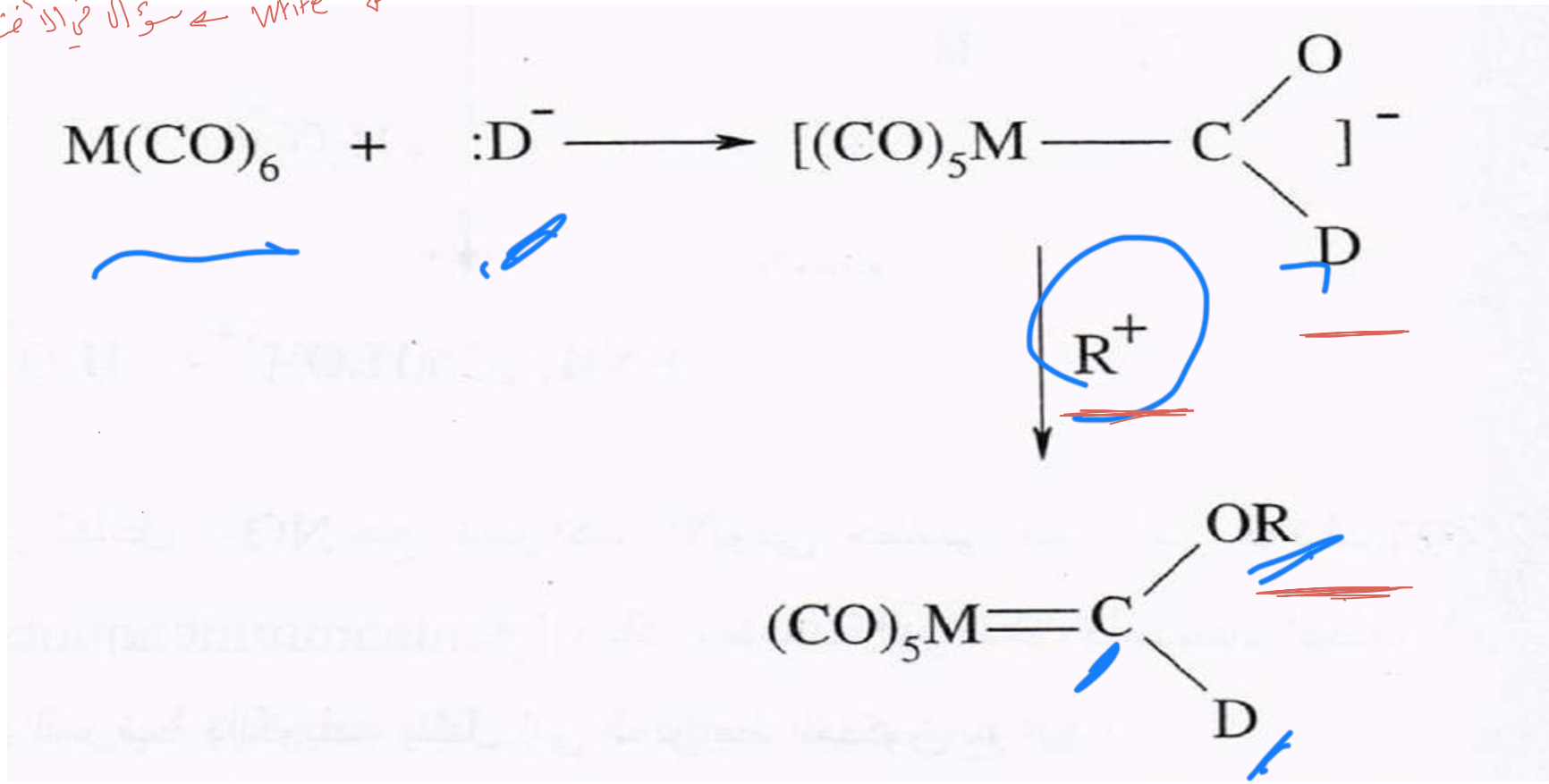
مثال آخر على تفاعل يتضمن هجوماً على ربيطة (ligand) هو الهجوم النيوكليوفيلي الذي يحدث في الخطوة الأولية لتحضير معقدات الكربين المعدنية (metal carbene complexes) انطلاقاً من الكربونيلات المعدنية (carbonyl metals) .

مثال أخر على تفاعلات الهجوم

Write

Another example of a ligand-attack reaction is the nucleophilic attack involved in the initial step in the preparation of metal carbene complexes.Carbonyl metals.

سؤال في الامتحان ← Write



What is Hydrolysis Reactions

The substitution reactions in which a ligand is replaced by a H_2O molecule or by OH^- groups are called hydrolysis reactions.

They are of two types

(a) when an aqua complex is formed by the replacement of a ligand by H_20 molecules are called acid hydrolysis

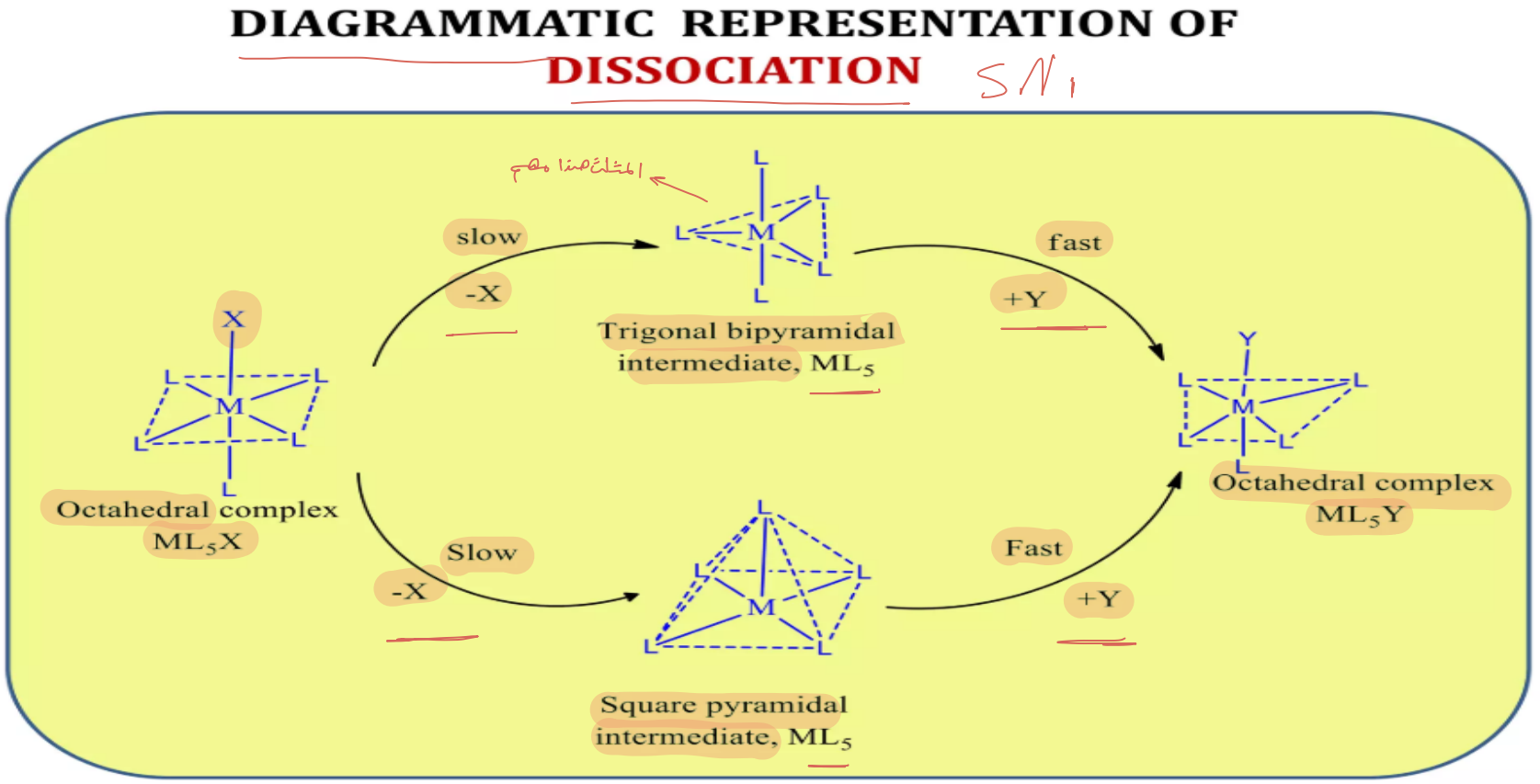
(b) the reactions, in which a hydroxo complex is formed by the replacement of a ligand by OH^- group are called base hydrolysis reactions.

NOTE-Acid hydrolysis reactions occur in neutral and acidic solutions and basic hydrolysis I basic medium.

Ex- $[Co^{III}(NH_3)5Cl]^{2+} + H_2O \rightarrow [Co^{III}(NH_3)_5(H_2O)]^{3+} + Cl$ → acid hydrolysis

$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^-$ → base hydrolysis

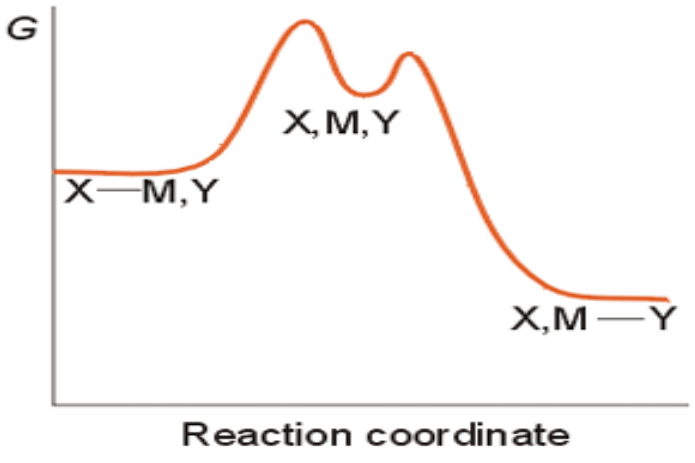
2.8 Reactions with S_N1 mechanics (substitution on octahedral complexes).

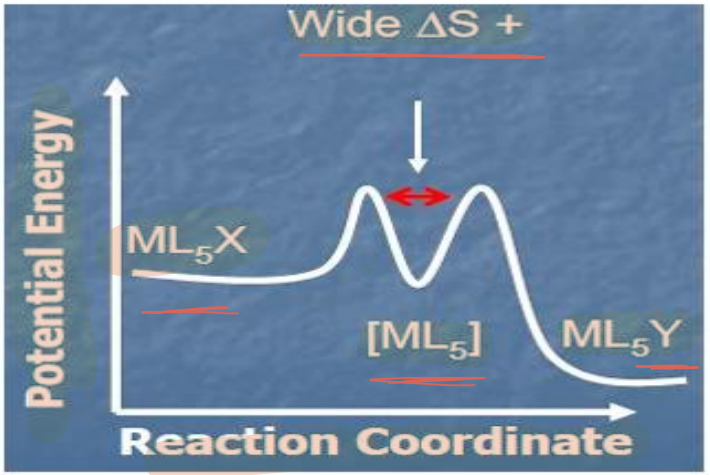


The typical reaction coordinate diagram for ligand displacement reactions in octahedral metal complexes through S_N1 mechanism reaction.

صخطط الطاقه SN1

واسع و الإنتروبي





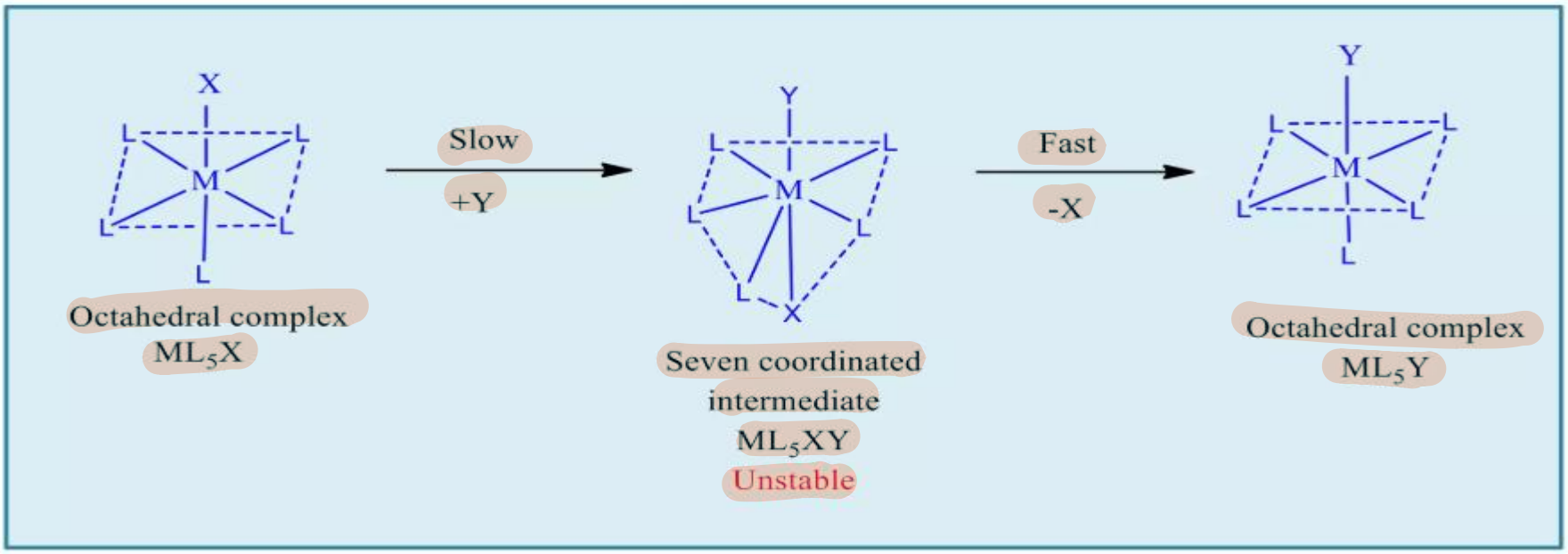
- **Two step mechanism:**

Formation of intermediate: $ML_5X \rightarrow ML_5 + X$ (Slow)

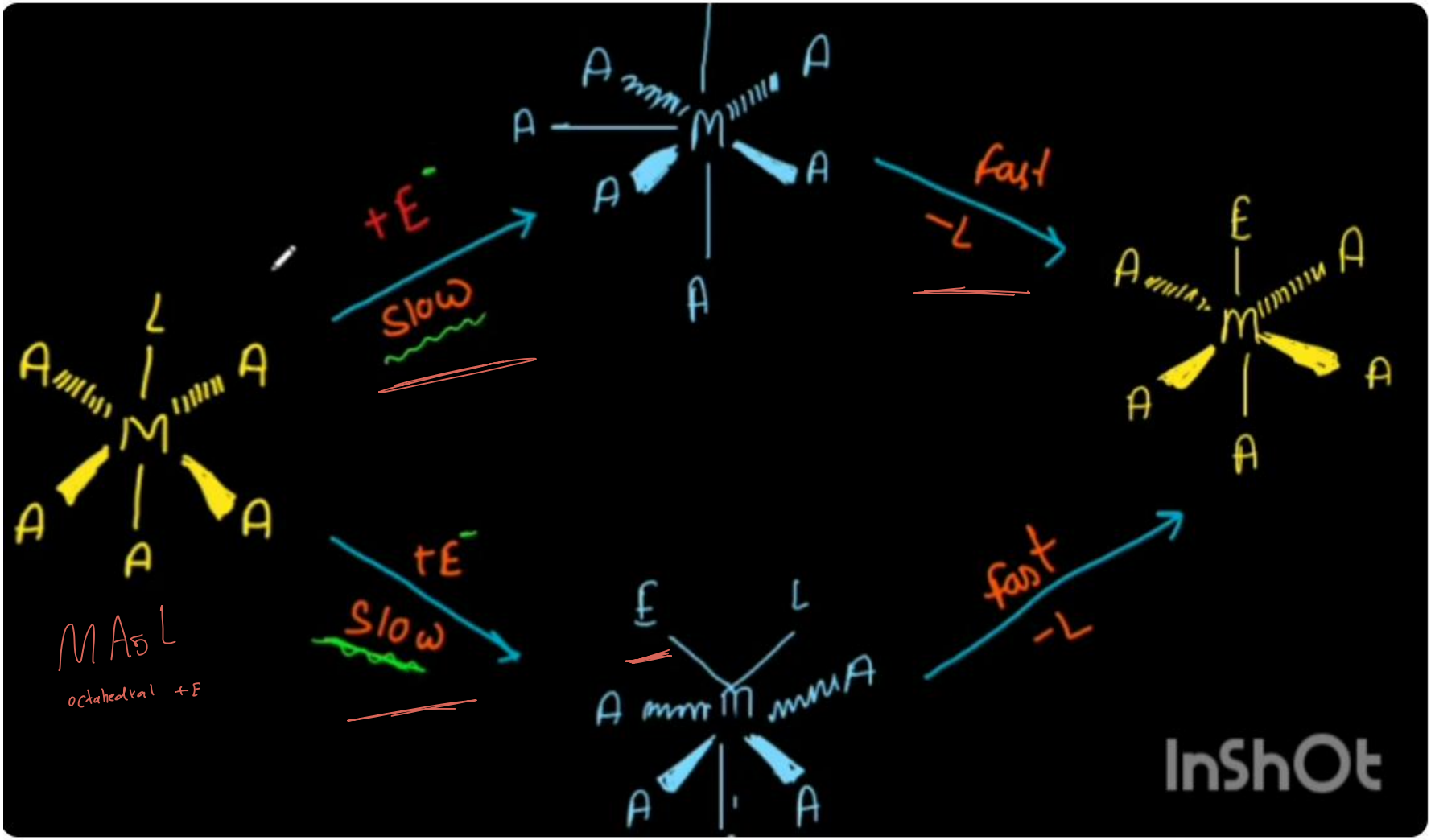
Attack of incoming group: $ML_5 + Y \rightarrow ML_5Y$ (Fast)

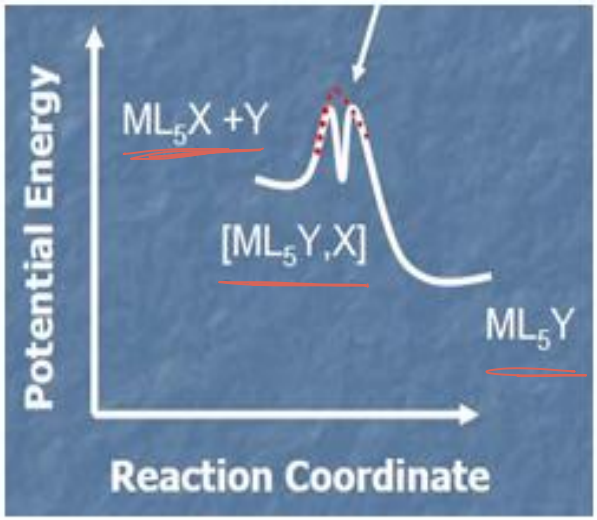


2.9 Reactions with S_N2 mechanics (substitution on octahedral complexes).

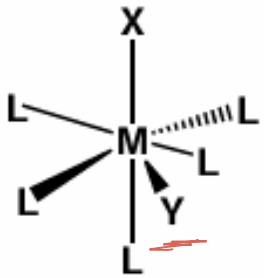


The typical reaction coordinate diagram for ligand displacement reactions in octahedral metal complexes through the S_N2 mechanism.

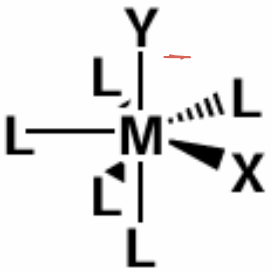

E
A
A
A
M
A
A
+E
slow
fast
-L
L
A
A
M
A
A
A
E
A
A
M
A
A
+E
slow
fast
-L
MA5L
octahedral +E
E
L
A
M
A
A
A
InShOt



Narrow, ΔS –ve
For short lived
Intermediate or
TS



Capped Oct.



Penta bipy medal

- Two step mechanism:

Formation of intermediate: $ML_5X + Y \rightarrow ML_5XY$ (Slow; Int. rarely isolatable)

Release of leaving group : $ML_5XY \rightarrow ML_5Y + X$ (Fast)

Chapter 3: *Substitution Reactions of Square Planner Complexes and the Trans Effect*

المواضيع

Square Planar Complexes

1. Mechanism of ligand substitution for square planar complexes
2. Berry Pseudorotation
3. The trans-effect
4. Square planar Pt(II) anticancer drugs

Substitution reactions of square planar complexes

Square planar is the common geometry for the following d^8 metal ions.

Co^{+}	Ni^{2+}	Cu^{3+}
Rh^{+}	Pd^{2+}	Ag^{3+}
Ir^{+}	Pt^{2+}	Au^{3+}

Kinetics – Ligand Substitution Reactions

Recall: Octahedral $ML_5X + Y \longrightarrow ML_5Y + X$ dissociative mechanism

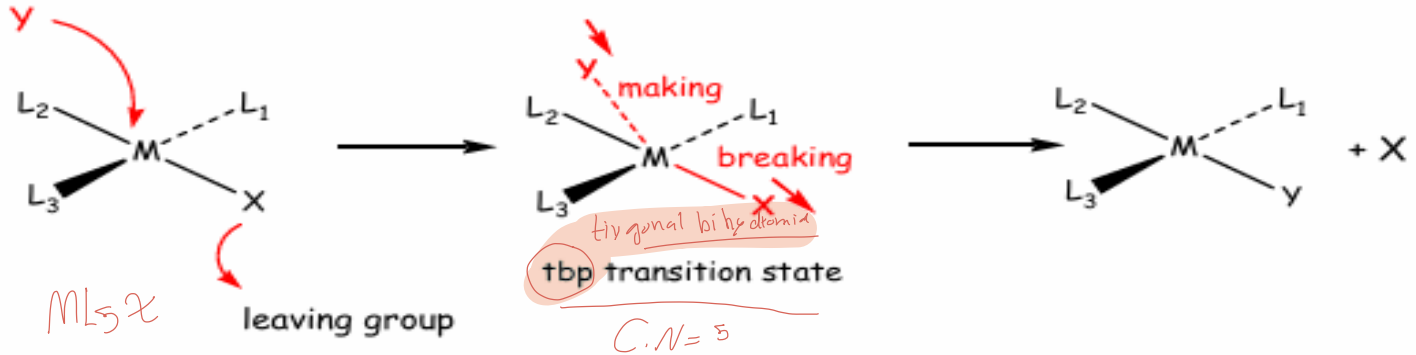
- For Square Planar $ML_3X + Y \longrightarrow ML_3Y + X$

  X and Y can be any pair of ligands.
- Rate = $k[ML_3X][Y]$ i.e. second order kinetics so it depends on the nature of both the leaving group X and the entering group Y.
- Steric crowding slows down the reaction.
- Evidence for an **associative mechanism**.

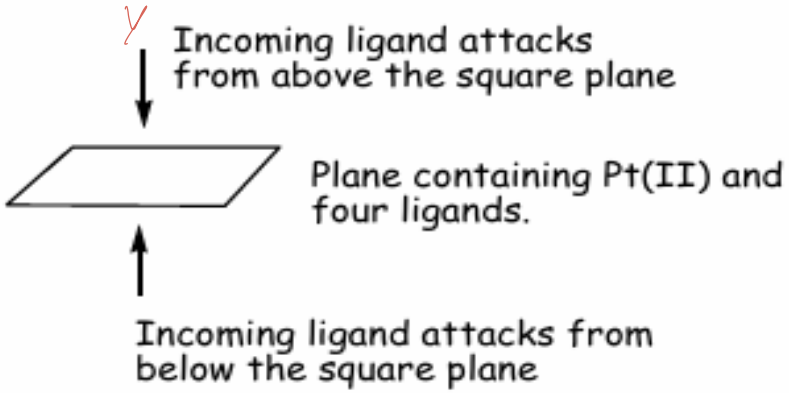
1. Mechanism for Square Planar Ligand Substitution

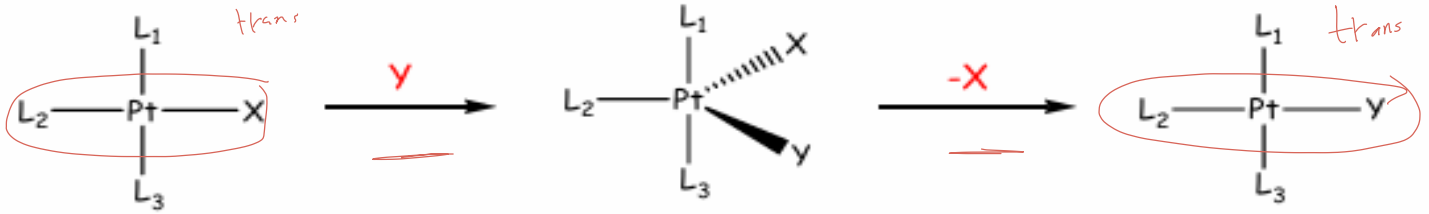
- For square planar **BOTH bond-breaking and bond making are important** in the reaction mechanism (i.e. an associative mechanism).

entering group can approach from top or bottom since sq. planar is easy to get into



- **Stereospecific** – X (leaving group) is trans to L_2 and so is Y (entering group)

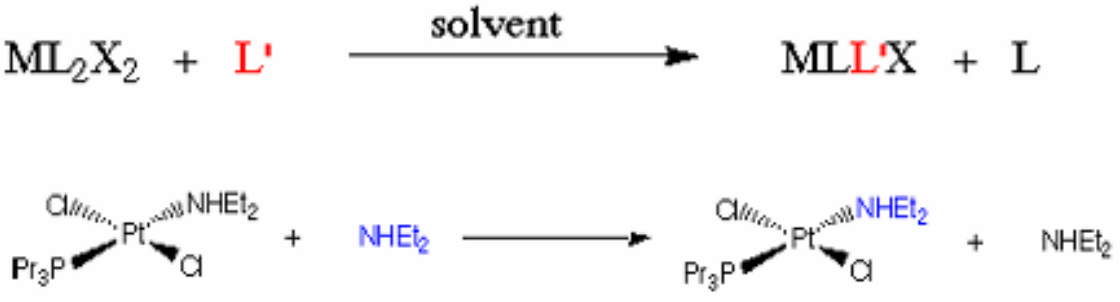




Initial attack by the entering group at a square planar Pt(II) centre is **from above or below the plane**. Nucleophile Y then coordinates to give a **trigonal bipyramidal intermediate species** which loses X with **retention of stereochemistry**.

Square Planar Substitution Reactions

Examples:



Factors Which Affect The Rate Of Substitution

i). Role of the Entering Group

ii). The Role of The Leaving Group

iii). The Nature of the Other Ligands in the Complex

iv). Effect of the Metal Centre

i). Role of the Entering Group

- The rate of substitution is proportional to the nucleophilicity of entering group
- i.e. for most reactions of Pt(II), the rate constant increases in the order: H_2O < NH_3 = py < Br^- < I^- < CN^-
- The ordering is consistent with **Pt(II)** being a **soft metal centre**.

ii). The Role Of The Leaving Group

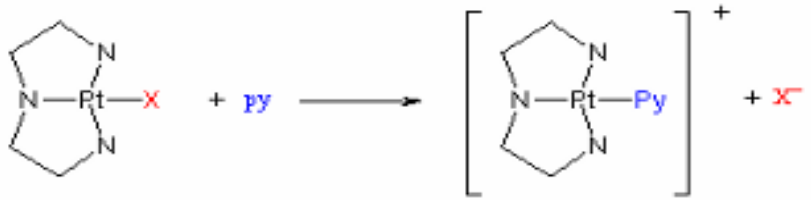
For the reaction

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

in H_2O at 25^0C the sequence of lability is;

H_2O > Cl^- >Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-

with a spread of over 10^6 in rate across series.



- the leaving group does not affect the nucleophilic discrimination factors only the intrinsic reactivity.
- the series tend to parallel the strength of the Metal-L bond.

iii). The Nature of other Ligands in the Complex

3. The trans effect

Definition;

- The *trans effect* is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.

  Or The ability of a ligand in a square planar complex to direct the replacement if the ligand trans to it.

- The trans effect is given as the following series:

$$CN^- > NO_2^- > I^- = SCN^- > Br^- > Cl^- > py > NH_3 > H_2O$$

The Trans Effect in Practice

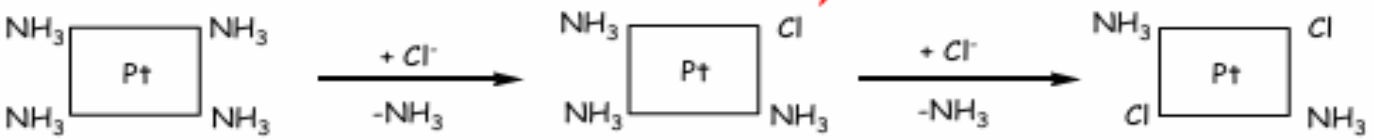
1. $[Pt(NH_3)_4]^{2+} \xrightarrow{2Cl^-} [Pt(NH_3)_2Cl_2]$ TRANS

2. $[Pt(Cl)_4]^{2-} \xrightarrow{2NH_3} [Pt(NH_3)_2Cl_2]$ CIS

why the different isomers ?

Reaction 1

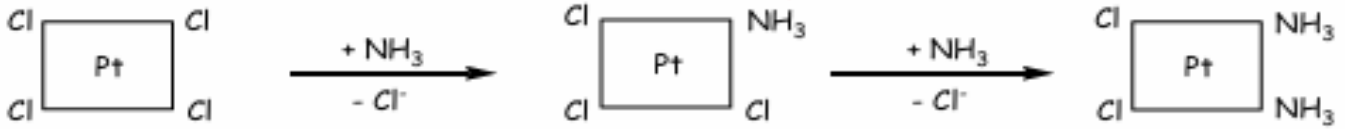
very good at directing next Cl- trans to it



TRANS

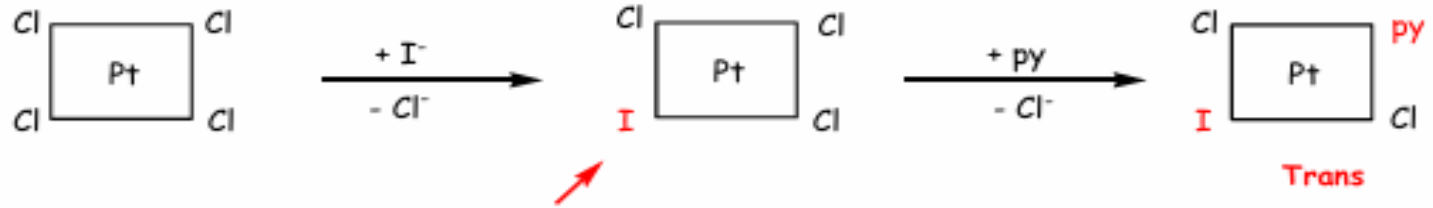
Reaction 2

less trans directing ability than Cl^-



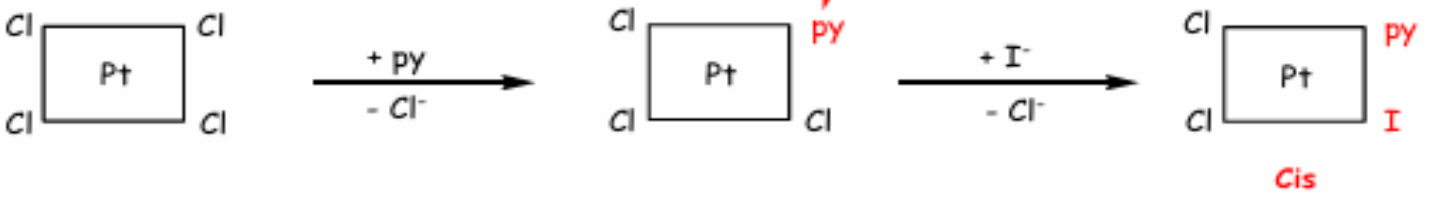
CIS

- Conclusion: Cl^- has a **greater trans directing** effect than NH_3.
- Trans directing series $Cl^- > NH_3$
- Depends on order in which the reagents are added as to which geometric isomer is formed so has uses for devising synthesis of Pt(II) complexes.
- e.g. consider the preparation of cis and trans $PtCl_2I(py)$ from $PtCl_4^{2-}$, I^- and py.



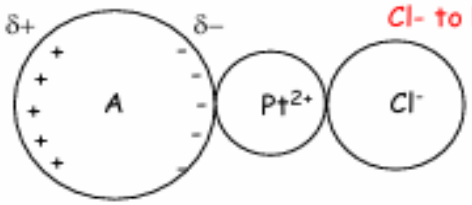
higher than Cl^- in the trans directing series, directs py trans to it

lower than Cl^- in the trans directing series, Cl- directs I trans to py

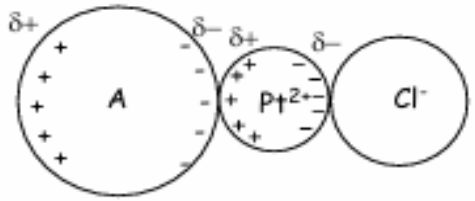


Polarization Theory

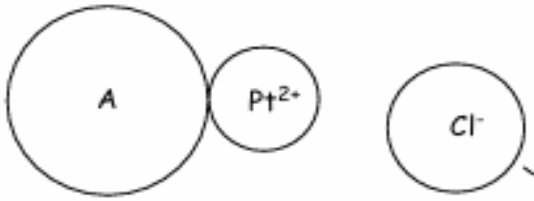
For explaining the kinetic trans effect in square planar Pt(II) complexes



The Pt(II) cation induces a dipole in the polarizable trans-directing ligand A.



The induced dipole in ligand A induces a dipole in the polarizable Pt(II) cation.

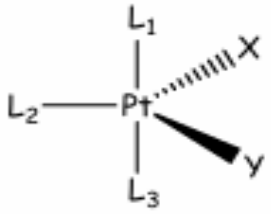


The chloride anion trans to A is more easily released due to the extra repulsive forces between its negative charge and the induced dipole of the Pt(II) cation.

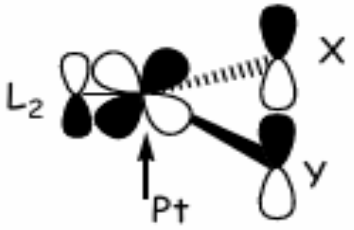
- Support for this theory is demonstrated by looking at the trans-directing series.
- The more polarizable ligands such as SCN^-, and I^- and the ligands containing π-clouds e.g. CN^- are high in the series, whereas less polarizable ligands such as ammonia or water are lower in the series.
- Additional support comes from the observation that Pt(II) complexes demonstrate a more pronounced trans effect than those of the less polarizable Pd(II) and Ni(II) cations.

Other contributing factors to the trans-effect

- In the trigonal plane of the 5-coordinate transition state or intermediate, a π-bonding interaction can occur between a metal d-orbital (e.g. d_{xy}) and suitable orbitals (p atomic orbitals, or molecular orbitals of p-symmetry) of ligand L_2 (the ligand trans to the leaving group) and Y (the entering group).
- These 3 ligands and the metal centre can communicate electronically through π-bonding only if they all lie in the same plane in the transition state or intermediate.
- **This implies the 5-coordinate species must be trigonal pyramidal.**



trigonal bipyramidal
transition state or intermediate



π-bonding in the trigonal plane

Rules:

- It is easier to replace Cl^- than most other ligands.
- If you want to displace some other ligands with Cl^- you must use a huge excess of Cl^-
- If there is more than one possibility for replacing the Cl^-, the one that is replaced is the one **trans to the ligand higher in the series**.
- Part of the general order for the trans effect (the ability of ligands to direct trans-substitution) is shown below:

  $CN^- > NO_2^- > I^- > SCN^- > Br^- > Cl^- > py > NH_3 > H_2O$

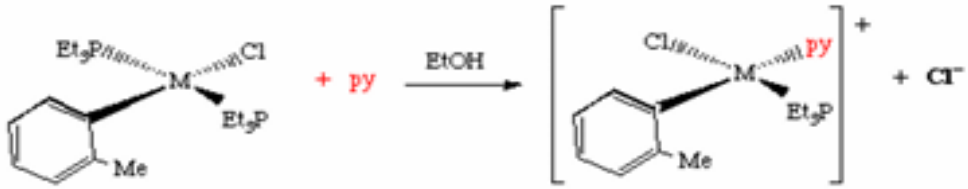
- A strong π-acceptor e.g. CN^- will stabilize the transition state by accepting electron density that the incoming nucleophile donates to the metal centre, and will **thereby facilitate substitution at the site trans to it.**

iv). Effect of the Metal Centre

- The order of reactivity of a series of isovalent ions is;

  Ni(II) > Pd(II) >> Pt(II)

- This order of reactivity is the same order as the tendency to form 5-coordinate complexes.
- More ready the formation of a 5-coordinate intermediate complex, the greater the stabilization of the transition state and so the greater the bimolecular rate enhancement.



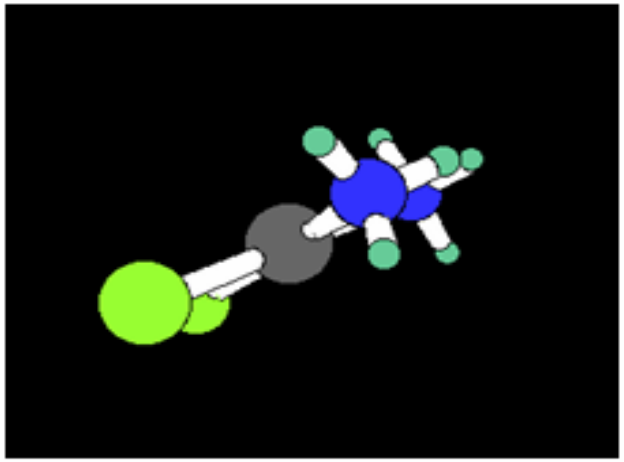
- M (II) Ni k = 33 M^{-1} sec^{-1}

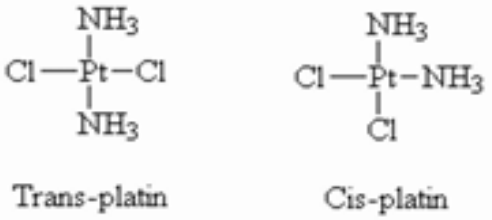
  Pd k = 0.58 M^{-1} sec^{-1}

  Pt k = 6.7 x 10^{-6} M^{-1} sec^{-1}

4. Square Planar Pt(II) anticancer drugs

- **Cisplatin** and its analogs are heavy metal complexes containing a Pt(II) central atom surrounded by 2 Cl and 2 NH_3 in the cis position.

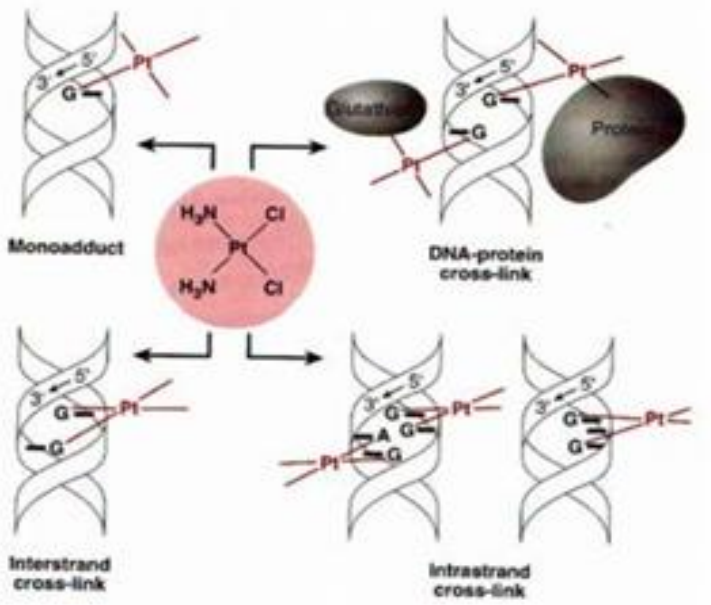




- Cisplatin was first synthesized by M. Peyrone in 1884.
- Sometimes referred as Peyrone's chloride.
- Rosenberg (1970s) is recognized as the discoverer of cisplatin through a series of studies on E.Coli and the effects of Pt(II) compounds in cell division.

DNA Binding - Crosslinking in DNA

- **Cisplatin** has biochemical properties that allow it to produce interstrand and intrastrand **cross-linking in DNA.**
- **Transplatin is an inactive isomer** because it cannot form the 1,2-intrastrand crosslink.
- In the 1,2-intrastrand crosslink the DNA is unwound and bent toward the major groove.
- Essentially when cisplatin binds to DNA it "kinks" the DNA an prevents it from unwinding.
- Thus the (cancerous) cell cannot reproduce itself.
- Cancerous cells reproduce faster than other cells.

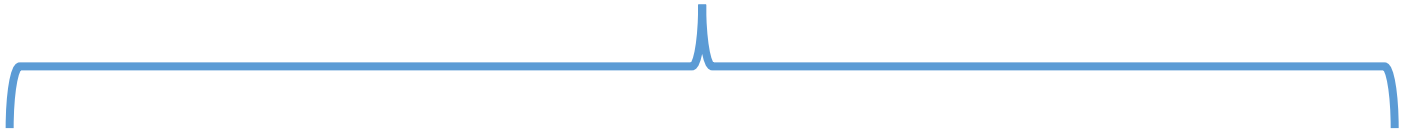


- Although **cisplatin** is also able to interact with many types of proteins vital to replication and cell division, its **primary target is DNA.**
- Cisplatin **alters the physical structure of DNA** when it is bound to it, but the overall structure remains intact.
- It is believed that the **alterations of the DNA structure prevents replication and thus activation of cellular repair mechanisms.**
- Cisplatin is a **chemotherapy drug used as therapy against**:
  - Testicular – most effective
  - Ovarian
  - Head
  - Neck
  - Bladder
  - Cervical
  - Lymphomas

Chapter 4: Oxidation Reduction Reactions and Inner and Outer Sphere Processes

Oxidation-reduction reactions and inner- and outer sphere

There are two mechanisms by which inorganic complexes transfer electrons.



1. Outer sphere mechanism When electron transfer occurs between complexes that do not undergo substitution. No new bonds are broken or formed.

2. Inner sphere mechanism When Electron transfer occurs between complexes via a bridging ligand. At least one of the complexes needs to be labile to allow the bridge to form. Bonds are broken and formed.

Out-of-coordination mechanism Contains an electron transfer from the reducing agent to the oxidizing agent with the coordination spheres not connected.This occurs when one of the reactants meets the "second" outer coordination sphere of the other reactant, and then a flow of electrons occurs from the reducing agent to the oxidizing agent. These mechanisms occur when a rapid electron transfer occurs between complexes that are inert in terms of substitution.

1. Outer sphere mechanism: In this mechanism one reactant is reduced and other is oxidized by involving three steps

Outer sphere electron transfer



$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$

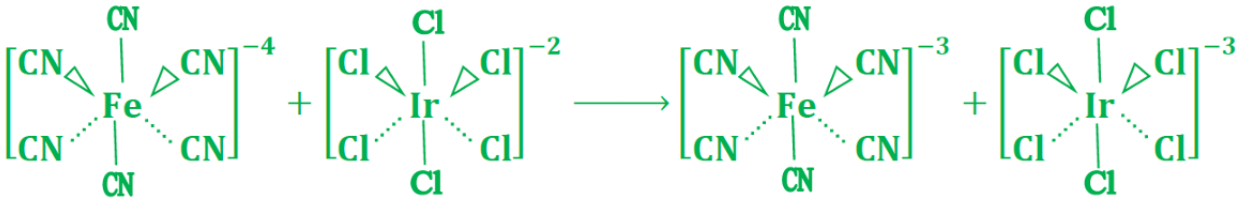
These are of two types:

Self Electron Transfer. Both species involved are similar, same metal ions and same ligands/ ligand framework, only differ in oxidation states.

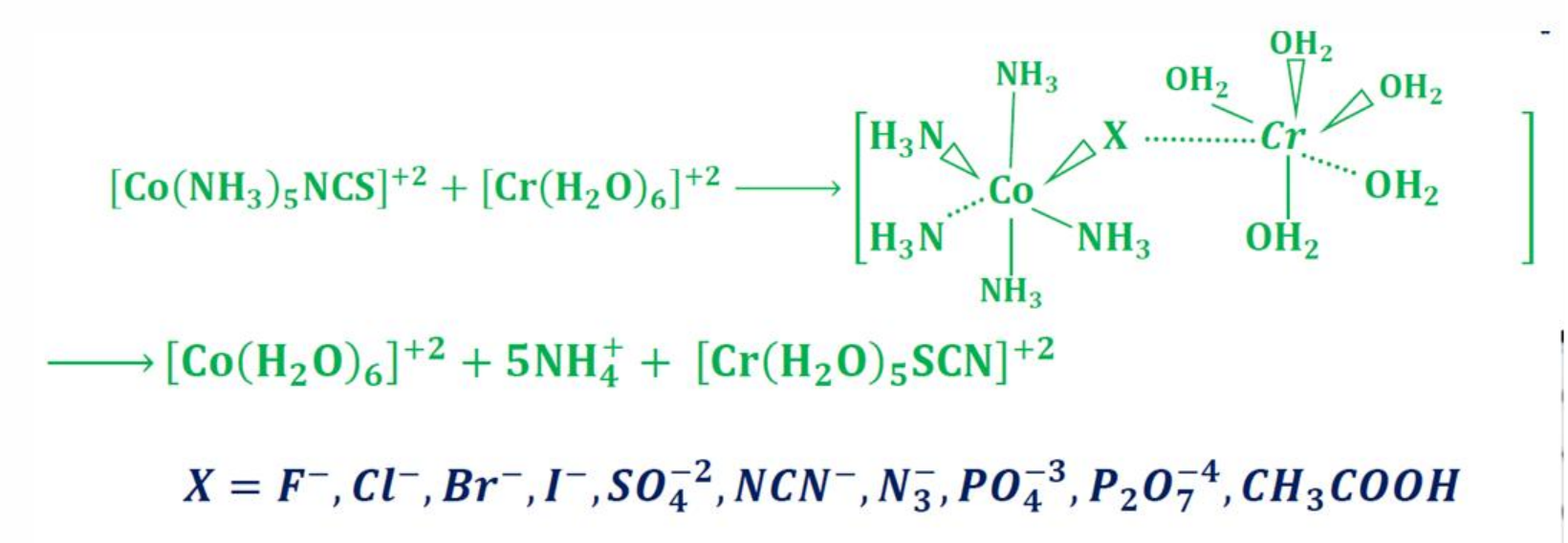
$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \longrightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$

Crossed Electron Transfer: Both species involved are different i.e. either different metals or different ligands or both. Crossed electron transfer is faster than Self Electron

$[Fe(CN)_6]^{4-} + [Mo(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_6]^{4-}$



Inner-coordination sphere "bridged" mechanism: Inner-coordination field electron transfer reactions occur when both the reducing agent and the oxidizing agent share a single ligand in the first "internal" coordination field of the two complexes, and the electron transfers throughthe ligand.



$$[Cr(H_2O)_5X]^{+2} + [Co(NH_3)_5X]^{+2} = [(H_2O)_5Cr(X)\ Co(NH_3)_5]^{+4}$$

electron transfers

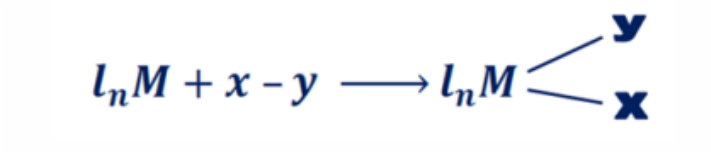
$$[Cr(H_2O)_5X]^{+2} + [Co(NH_3)_5(H_2O)]^{+2} = [(H_2O)_5Cr(X)Co(NH_3)_5]^{+4}$$

H^+, H_2O

$$[Co(H_2O)_6]^{+2} + 5NH_4^+$$

Addition and Oxidation Reactions

The general equation for this reaction



For these reactions to occur, several reaction must occur

1- in order to increase the oxidation number of the metal, the metal atom must contain at least two electrons in the subshell by +2

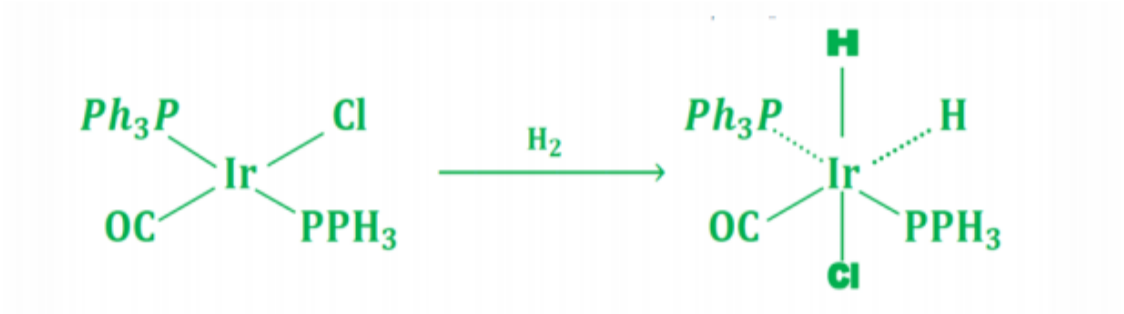
$$M^{+n} \longrightarrow M^{(n+2)+}$$
$$d^n \longrightarrow M^{n-2}$$

2- The metal atom must be coordination unsaturated, so the coordination number of the metal can be increased by 2

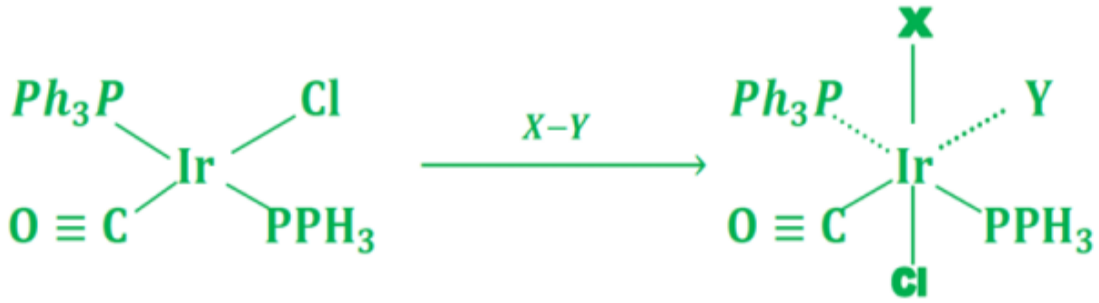
3- The metal atom must contain empty orbitals that can accept the added bonding electrons

Some examples

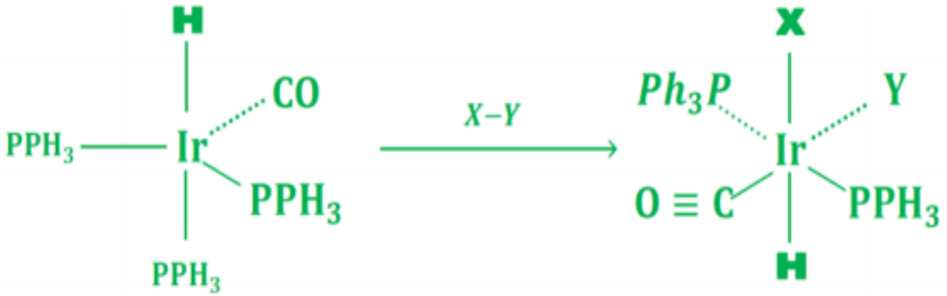
1-Addition of hydrogen complex iridium



2-oxidation addition reactions on the bonded of ***XY*** on the complex [*Ir Cl(CO)(PPh$_3$)$_2$*] in the square planar case



3-oxidation addition reactions on the bonded of ***XY*** on the complex [*Ir H(CO)(PPh$_3$)$_3$*] in the square planar case



Mechanisms of Addition-Oxidation Reactions:

There are three main types of mechanisms, which depend on the amount of reactants and the reaction conditions:

1. The coordinated mechanism:

The properties of this mechanism are:

1. The reaction contains a tri centric transition state and the approach of the inner part from the side.

2. The -molecule bonds to the reaction center, and then the electrons are spontaneously rearranged in a sequential (XY) TO M-X, MY

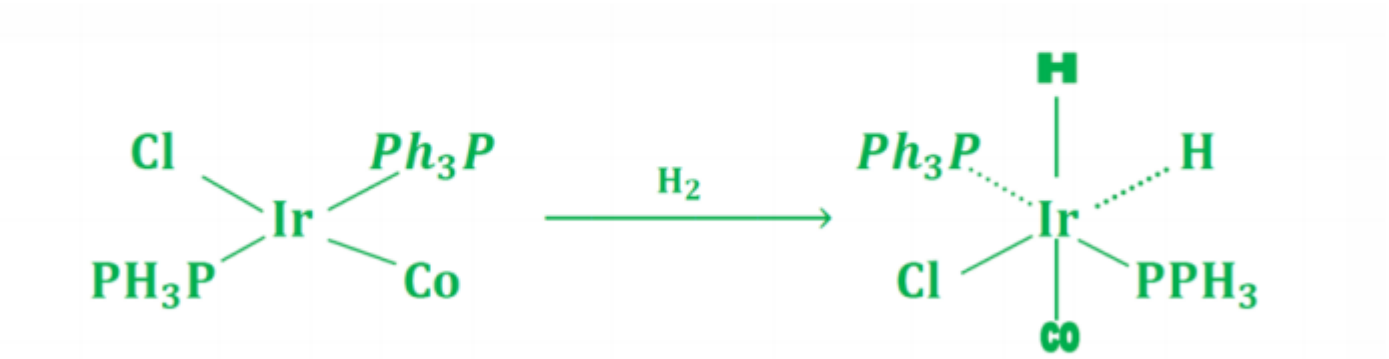


General features of the coordinated mechanism:

1-The reactant molecule is coordination-unsaturated.

2-The reaction is common when the bond is slightly polar, such as RSi - (H2)....

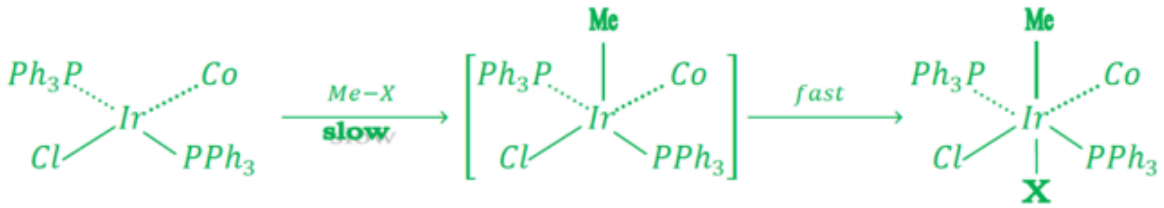
3-The reaction is stereoselective, and the addition of compound (X) is of the cis type.



2- Addition reactions with oxidation by addition of a nucleopile

General Features

1- The addition to the complex is in the trans position.
2-The reaction rate is sensitive to the nature of the other ligands in the complex



The distinctive properties of this reaction are

1- The greater the electron –donating property of the phosphine group, the greater the addition rate.
2-The greater the number of ligands in the complex, the slower the addition rate, due to the crowding of grous in the transition state.