

Semester II

CHE-RC/HG-2016 :CHEMISTRY2

*Section A:*

Topic: Coordination Chemistry

# Coordination Compounds

**Definition:** Coordination compounds are composed of a **metal atom** or **ion** and **one or more ligands (atoms, ions, or molecules)** that donate electrons to the metal. This definition includes compounds with metal–carbon bonds, or organometallic compounds

❑ **Coordination compound** comes from the coordinate covalent bond, which refers to donation of a pair of electrons from one atom to another.

❑ The donors are usually called the **ligands** and the acceptors are the **metals**.

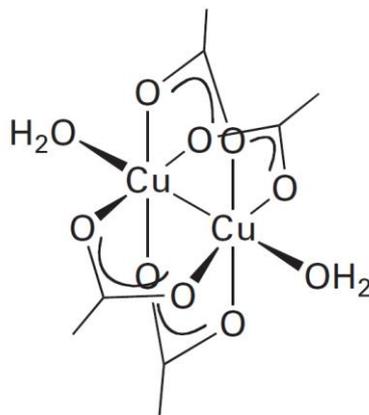
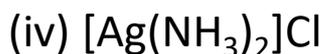
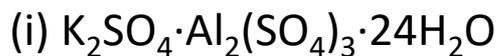
❑ Complexes/complex ions are shown using **square brackets**.

❑ Coordination compounds are examples of **acid–base adducts**.

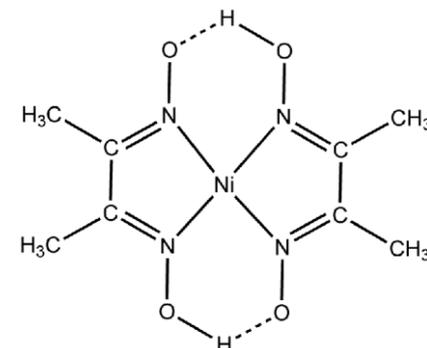
❑ They are frequently called **complexes** or, if charged, **complex ions**.

❑ **Homoleptic** complexes  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , and **heteroleptic** complexes:  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

**Examples:**



Copper(II) acetate dihydrate



Nickel bis(dimethylglyoximate)

# Werner's Coordination Theory



Coordination compounds have been used as pigments and dyes

For e.g.:

(i) Prussian blue of  $(KFe[Fe(CN)_6])$

(ii) Aureolin  $(K_3[Co(NO_2)_6] \cdot 6H_2O)$ , yellow

(iii) Royal blue color of  $[Cu(NH_3)_4(H_2O)_2]^{2+}$

Alfred Werner (1866–1919)

*In 1893, Werner proposed a theory to explain the structures and formation of coordination complexes (first inorganic chemistry to be awarded Nobel prize in 1913 in inorganic chemistry)*

Werner postulated that metal exhibits two types of valencies:

**(i) Primary valencies:** correspond to the valency of the central atom (now known as oxidation state/number)

*E.g.:* 1.  $[Co(NH_3)_6]Cl_3$  exists as  $[Co(NH_3)_6]^{3+}$  and  $3Cl^-$

2.  $[Co(NH_3)_4Cl_2]Cl$  exists as  $[Co(NH_3)_4Cl_2]^+$  and  $Cl^-$

**(ii) Secondary valencies:** corresponds to the number of ligands coordinated to the metal (called the coordination number)

*E.g.:*  $[Co(NH_3)_6]Cl_3$  the secondary valency corresponds to six  $NH_3$  ligands.

# Werner's Coordination Theory

Compounds		Colour	Old Name	No. of Charges on Complex Ion	No. of Ions		
Old Formulae	New Formulae				Cation	Anion	Total
(a) $\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Yellow	Luteo complex	+3	1	3	4
(b) $\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Purple	Purpureo complex	+2	1	2	3
(c) $\text{CoCl}_3 \cdot 4\text{NH}_3$	<i>Trans-</i> $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	Green	Praseo complex	+1	1	1	2
(d) $\text{CoCl}_3 \cdot 4\text{NH}_3$	<i>cis-</i> $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	Violet	Violeo complex	+1	1	1	2
(e) $\text{CoCl}_3 \cdot 3\text{NH}_3$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	Blue green	—	—	—	—	—

Werner postulated that metal exhibits two types of valencies:

**(i) Primary valencies:** correspond to the valency of the central atom (now known as oxidation state/number)

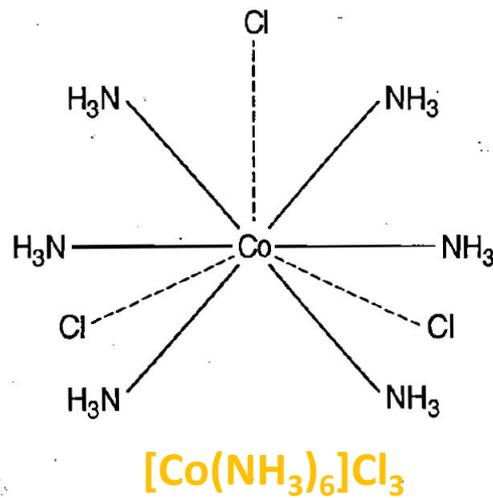
E.g.: 1.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  exists as  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $3\text{Cl}^-$

2.  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  exists as  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $\text{Cl}^-$

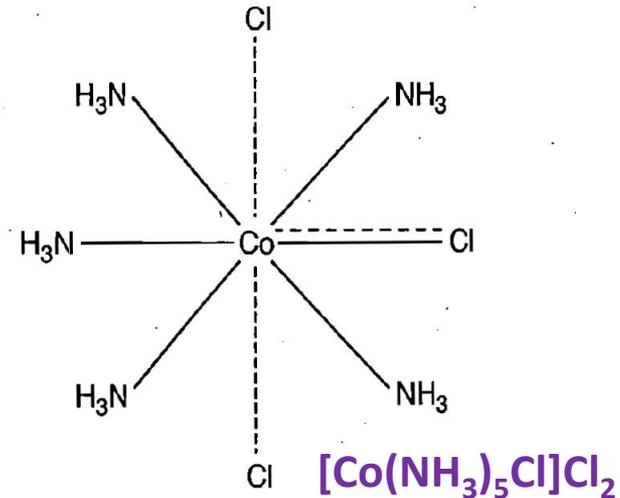
**(ii) Secondary valencies:** corresponds to the number of ligands coordinated to the metal (called the coordination number)

E.g.:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  the secondary valency corresponds to six  $\text{NH}_3$  ligands.

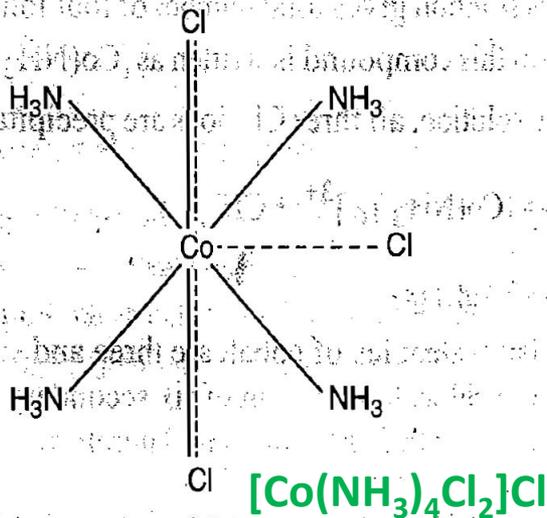
# Werner's Coordination Theory



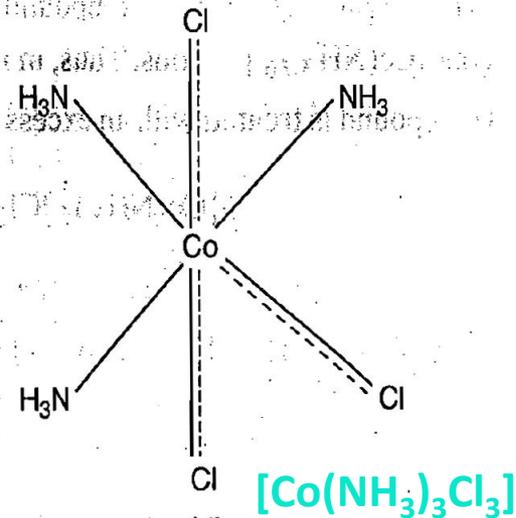
(a)



(b)



(c)



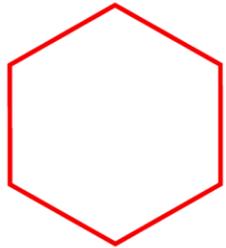
(d)

# Werner's Coordination Theory

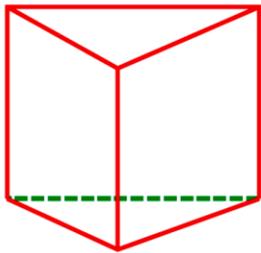
Werner also attempted to predict the shapes of the complexes

**Table:** Number of isomers predicted and actually found

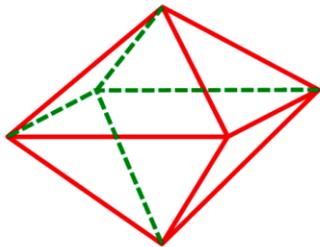
Complex	Observed	Predicted		
		Octahedral	Planar hexagon	Trigonal prism
$[MX_6]$	1	1	1	1
$[MX_5Y]$	1	1	1	1
$[MX_4Y_2]$	2	2	3	3
$[MX_3Y_3]$	2	2	3	3



Planar hexagon

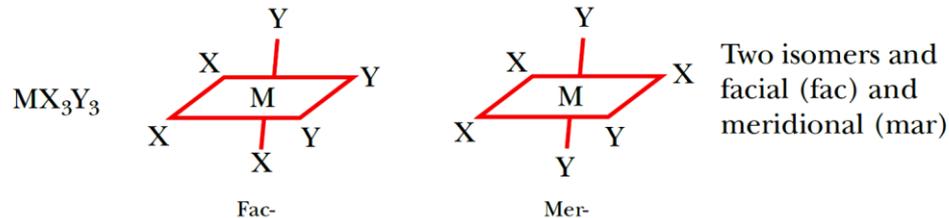
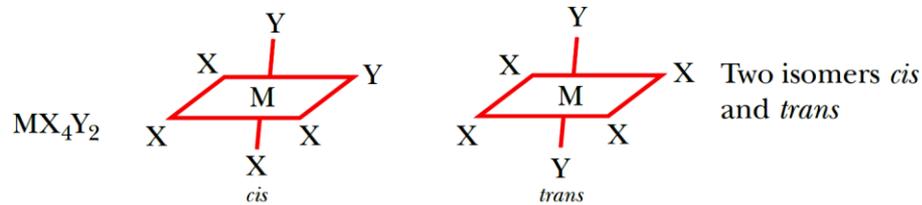
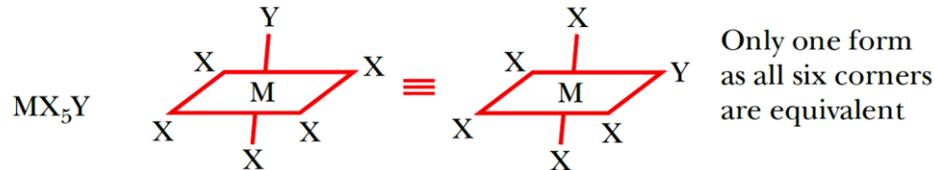
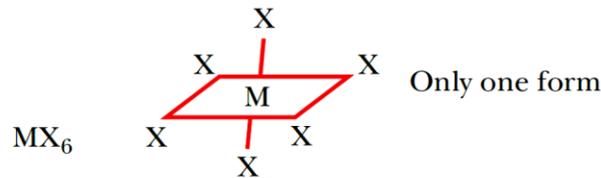


Trigonal prism



Octahedron

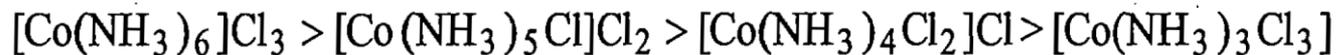
Possible geometric shapes for six-coordination



Isomers in Octahedral Complexes

# Evidence in favour of Warner's Theory

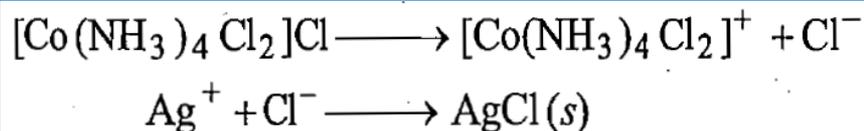
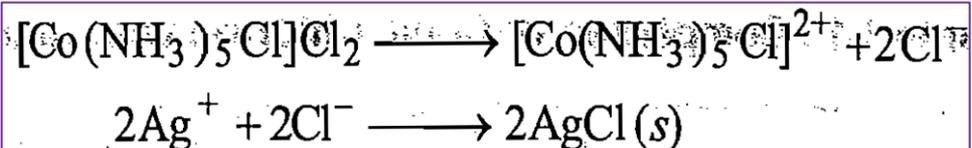
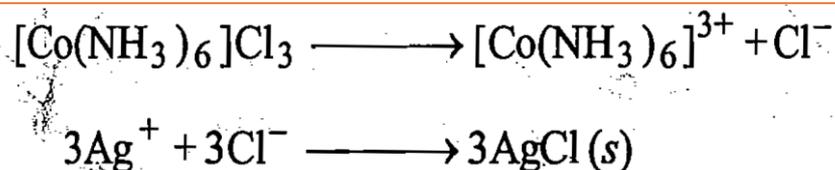
**1. Electrical Conductance Measurement:** The decreasing order of molar conductance



**2. Cryoscopic Measurement:** The no. of particles in aqueous solution was obtained from the *depression of freezing point data*. Depression in freezing point is a colligative property that depend on then no. of particles in solution.

Compound	No of Particles
$\text{CoCl}_3 \cdot 6\text{NH}_3$	4
$\text{CoCl}_3 \cdot 5\text{NH}_3$	3
$\text{CoCl}_3 \cdot 4\text{NH}_3$	2
$\text{CoCl}_3 \cdot 3\text{NH}_3$	1

**3. Precipitation Reactions:**



# Modern Techniques and Theories

## Modern Experimental Techniques:

- (i) **UV-Vis spectroscopy:** information about energies of orbitals, shapes of complexes
- (ii) **X-ray crystallography:** information about structure of complex with bond length and angles
- (iii) **Magnetic measurements:** information about shapes of complexes

## Theories of Coordination Complexes

- ❑ **Lewis theory** with eight electrons around metal atom is **obsolete** as even expanding the valence shell to 10 or 12 electrons does not work.
- ❑ Some complexes show extreme stability with a total of 18 electrons. Therefore, **18-electron rule (EAN)** simply accounts for the bonding in many coordination compounds. This approach is applied to **organometallic compounds**.
- ❑ **Pauling** used his **valence bond approach** to explain differences in magnetic behavior among coordination compounds by use of either metal ion 3d or 4d orbitals.
- ❑ **Griffith and Orgel** developed **ligand field theory (LFT)**, derived from the **crystal field theory (CFT)** of **Bethe and Van Vleck** on the behavior of metal ions in crystals and from the **molecular orbital treatment** of **Van Vleck**.

# CLASSIFICATION OF LIGANDS

## 1. Based upon charges:

(i) **Neutral ligands:**  $\text{H}_2\text{O}$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{NH}_3$  etc.

(ii) **Positive ligands:**  $\text{NO}^+$ , etc.

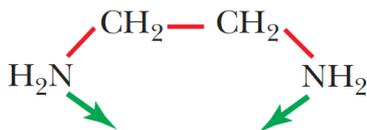
(iii) **Negative ligands:**  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ , etc.

**2. Based upon denticity of the ligand:** (The number of donations accepted by a central atom from a particular ligand is known as the denticity of the ligand)

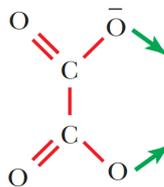
(i) **Monodentate:**  $\text{H}_2\text{O}$ ,  $\text{CN}^-$ ,  $\text{CO}$ ,  $\text{NO}^+$  etc.

(ii) **Bidentate:**

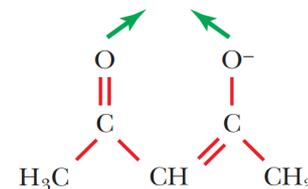
en: ethylenediamine



ox<sup>2-</sup>: oxalate



acac<sup>-</sup>: acetylacetonate

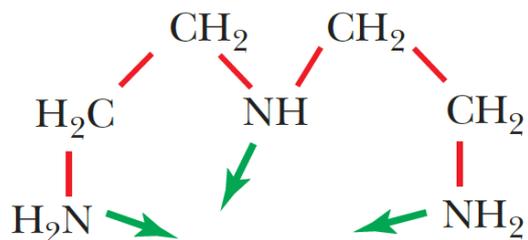


The word *denticity* is derived from *dentis*, the Latin word for tooth

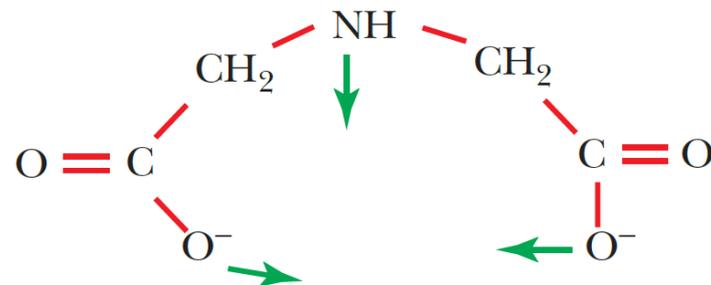
# CLASSIFICATION OF LIGANDS

## (iii) Tridentate:

(i) dien: diethylenetriamine

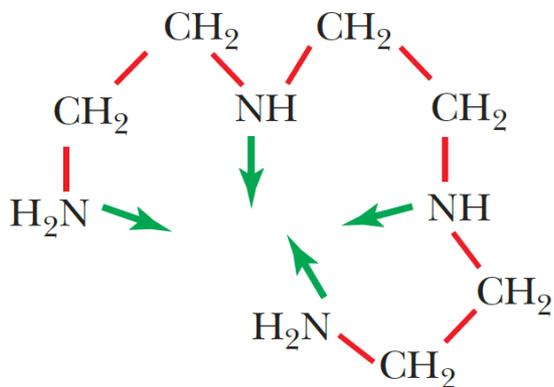


(ii) imda<sup>2-</sup>: iminodiacetate

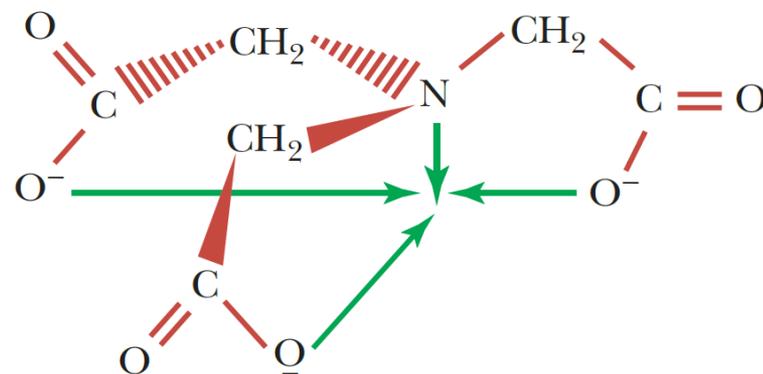


## (iv) Tetradentate:

(i) trien: triethylenetetraamine



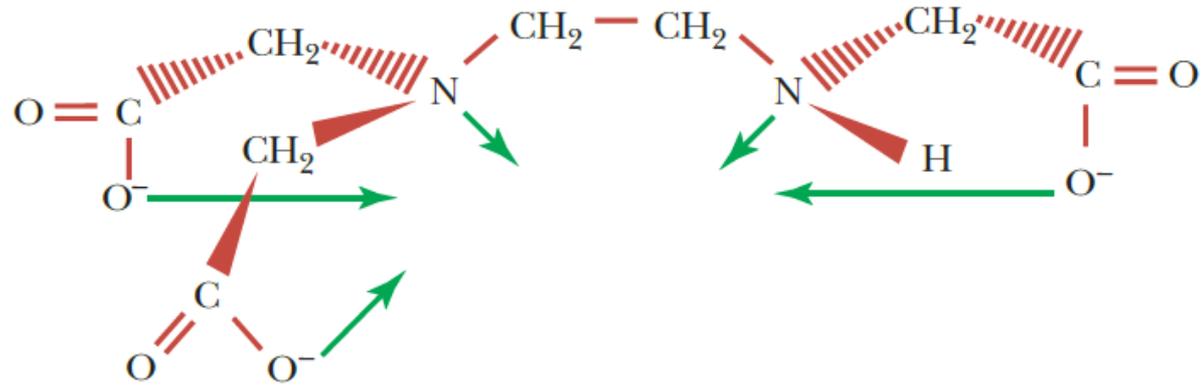
(ii) NTA<sup>3-</sup>: nitrilotriacetate



# CLASSIFICATION OF LIGANDS

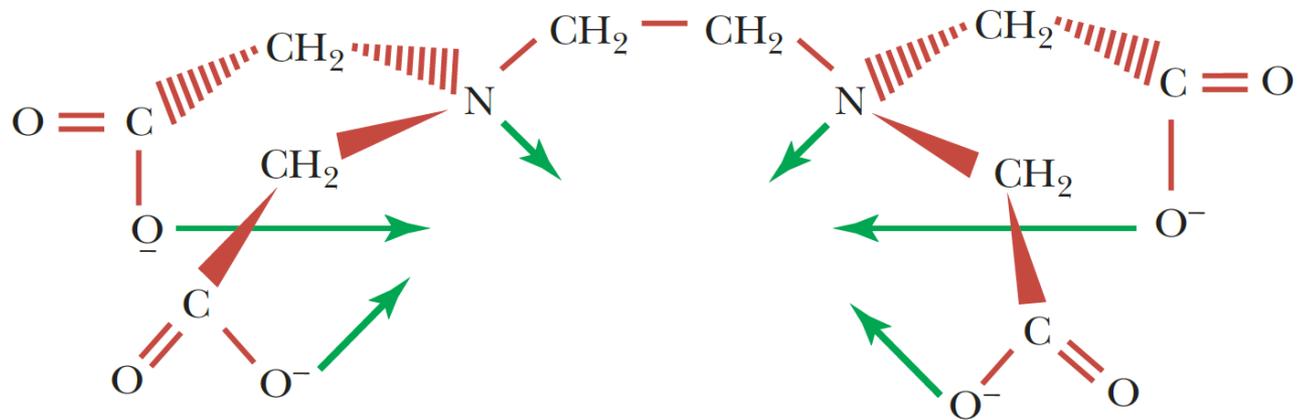
## (v) Pentadentate:

EDTA<sup>3-</sup>: ethylenediamine triacetate



## (iv) Hexadentate:

EDTA<sup>4-</sup>: ethylenediamine tetracetate

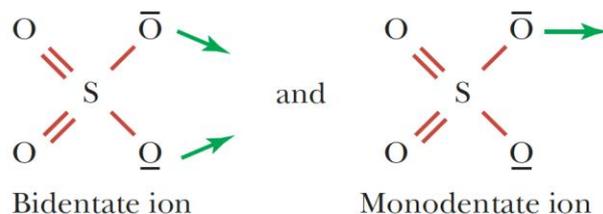


# CLASSIFICATION OF LIGANDS

## Note:

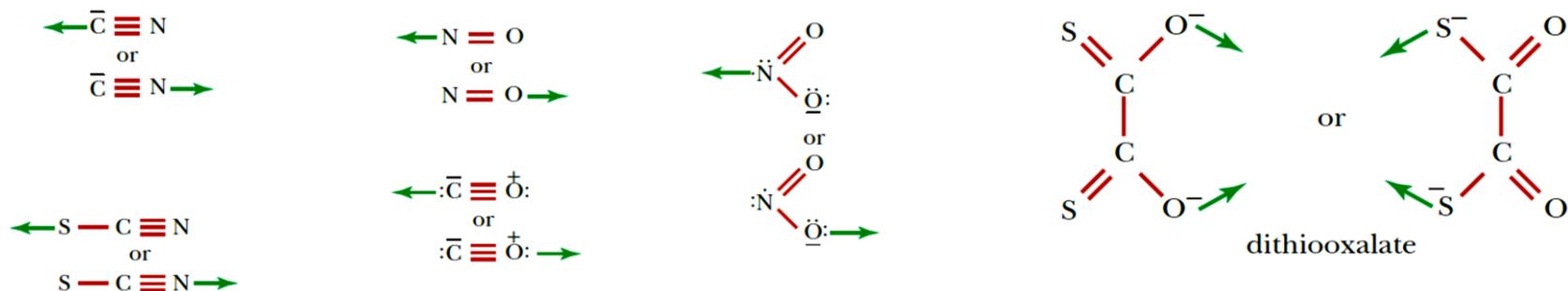
**1. Flexidentate ligands:** A ligand which shows variable denticity. For e.g.:

(i)



**2. Chelation:** A ligand that can form a ring structure with the central atom is called a chelating ligand. E.g.: All polydentate ligands.

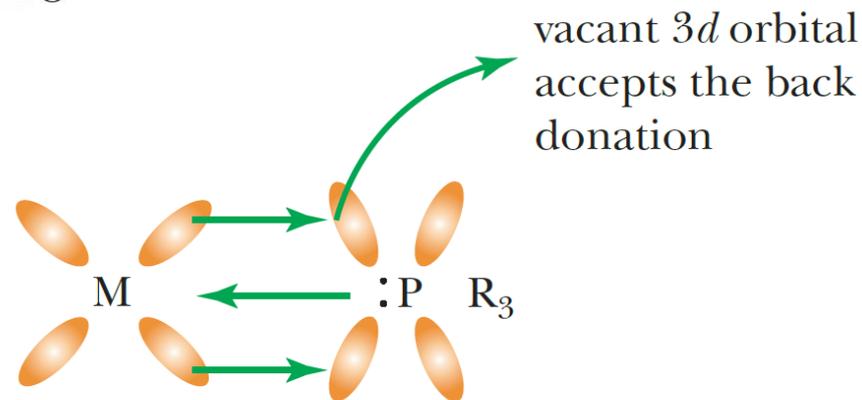
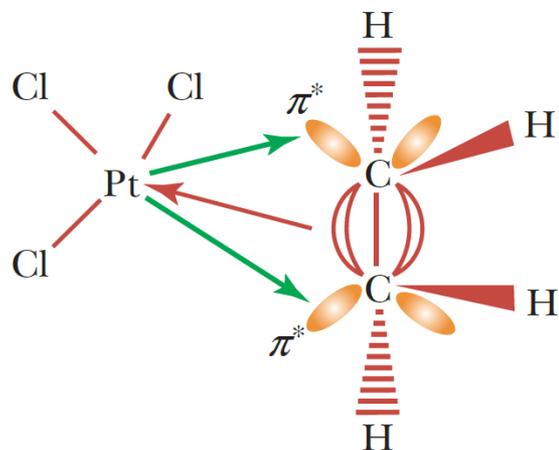
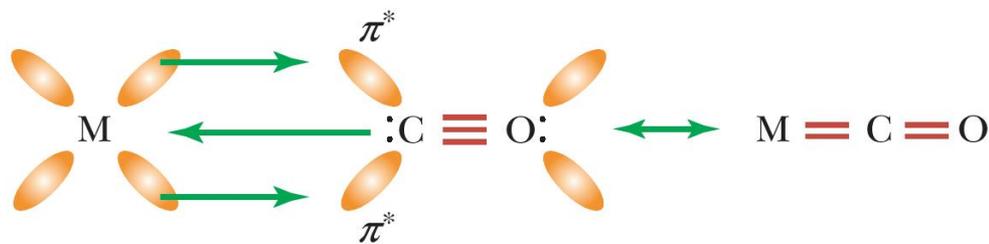
**3. Ambidentate ligand:** A ligand that may have more than one kind of donor sites but at a time only one kind of donor site is utilized for donation is called as ambidentate ligand. For e.g.:



# CLASSIFICATION OF LIGANDS

## 3. Bonding interaction between the ligand and the central atom

- Classical or simple donor ligand:** These ligands only donate the lone pair of electrons to the central atom. For example,  $O^{2-}$ ,  $OH^-$ ,  $F^-$ ,  $NH_2^-$ ,  $NH_3$ ,  $N^{3-}$ , etc.
- Non-classical or  $\pi$  - acid or  $\pi$  - acceptor ligand:** These ligands not only donate the lone pair of electrons to the central atom but also accept the electron cloud from the central atom in their low-lying vacant orbitals. This kind of back donation is known as 'synergic effect' or 'synergic bonding'.  $CO$ ,  $CN^-$ ,  $NO^+$ ,  $PF_3$ ,  $PR_3$  ( $R = H, Et, Ph, \dots$ ),  $C_2H_4$ ,  $C_2H_2$ ,  $CO_2$ , etc.



# IUPAC Nomenclature

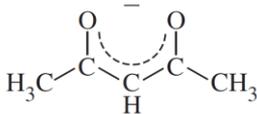
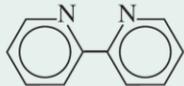
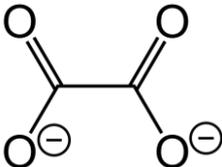
**Table: IUPAC name of common monodentate ligands**

Common Name	IUPAC Name	Formula
hydrido	hydrido	$\text{H}^-$
fluoro	fluoro	$\text{F}^-$
chloro	chloro	$\text{Cl}^-$
bromo	bromo	$\text{Br}^-$
iodo	iodo	$\text{I}^-$
nitrido	nitrido	$\text{N}^{3-}$
azido	azido	$\text{N}_3^-$
oxo	oxido	$\text{O}^{2-}$
cyano	cyano	$\text{CN}^-$
thiocyano	thiocyanato- <i>S</i> (S-bonded)	$\text{SCN}^-$
isothiocyano	thiocyanato- <i>N</i> (N-bonded)	$\text{NCS}^-$
hydroxo	hydroxo	$\text{OH}^-$
amido	azanido	$\text{NH}_2^-$

*Contd.*

# IUPAC Nomenclature

**Table: IUPAC name of multidentate ligands with abbreviation**

Common Name	IUPAC Name	Abbreviation	Formula and Structure
acetylacetonato	2,4-pentanediono	acac	$\text{CH}_3\text{COCHCOCH}_3^-$ 
2,2'-bipyridine	2,2'-bipyridyl	bipy	$\text{C}_{10}\text{H}_8\text{N}_2$ 
1,10-phenanthroline, <i>o</i> -phenanthroline	1,10- diaminophenanthrene	phen, <i>o</i> -phen	$\text{C}_{12}\text{H}_8\text{N}_2$ 
Pyridine		py	
Oxalato		ox	

# IUPAC Nomenclature

## Ligands with common names

Neutral Ligands	Names
$N_2$	dinitrogen
$O_2$	dioxygen
$C_5H_5N$	pyridine
bpy	bipyridyl
$CH_3NH_2$	methylamine
$(CH_3)_2NH$	dimethylamine
$NH_2 - NH_2$	hydrazine
$NH_2OH$	hydroxylamine

## For ambidentate ligands

### Name and Mode of Attachment

- $-NO_2^-$ , nitrito – N or nitro
- $-ONO^-$ , nitrito – O or nitrito
- $-SCN^-$ , thicyanato – S or thicyanato
- $-NCS^-$ , thicyanato – N or isothiocyanato

## Ligands with special names

Neutral Ligands	Name
$NH_3$	ammine
CO	carbonyl
CS	thiocarbonyl
$H_2O$	aqua
NO	nitrosyl

## For anionic complex replace –ium with -ate

Metal	Anion Name
aluminium	aluminate
scandium	scandate
titanium	titanate
vanadium	vanadate
chromium	chromate
zirconium	zirconate
palladium	palladate
rhodium	rhodate
rhenium	rhenate

# IUPAC Nomenclature

## Rules:

1. The cation comes first, followed by the anion.

**Examples:** diamminesilver(I) chloride,  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

potassium hexacyanoferrate(III),  $\text{K}_3[\text{Fe}(\text{CN})_6]$

2. The inner coordination sphere is enclosed in square brackets. Although the metal is provided first within the brackets, the ligands within the coordination sphere are written before the metal in the formula name.

**Examples:** tetraamminecopper(II) sulfate,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

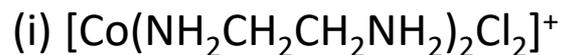
hexaamminecobalt(III) chloride,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

3. The number of ligands of each kind is indicated by prefixes (in margin). In simple cases, the prefixes in the second column are used. If the ligand name already includes these prefixes or is complicated, it is set off in parentheses, and prefixes in the third column (ending in *-is*) are used.

# IUPAC Nomenclature

Rules:

Examples:



dichlorobis(ethylenediamine)cobalt(III)



tris(2,2'-bipyridine)iron(II)

## Table of Prefixes

2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	heptakis
8	octa	octakis
9	nona	nonakis
10	deca	decakis

4. Ligands are generally written in alphabetical order

-according to the ligand name, not the prefix.



tetraamminedichlorocobalt(III)

*(tetraammine is alphabetized by a and dichloro by c, not by the prefixes)*



amminebromochloromethylamineplatinum(II)

# IUPAC Nomenclature

## Rules:

5. Anionic ligands are given an *o* suffix. Neutral ligands retain their usual name. Coordinated water is called aqua and coordinated ammonia is called ammine.

## 6. Two systems exist for designating charge or oxidation number:

a. The *Stock system* puts the calculated oxidation number of the metal as a Roman numeral in parentheses after the metal name (**most common**)

b. The *Ewing-Bassett system* puts the charge on the coordination sphere in parentheses after the name of the metal.

***(In either case, if the charge is negative, the suffix -ate is added to the name)***

**Examples:** (i)  $[\text{Pt}(\text{NH}_3)_4]^{2+}$

tetraammineplatinum(II) **or** tetraammineplatinum(2+)

(ii)  $[\text{PtCl}_4]^{2-}$

tetrachloroplatinate(II) **or** tetrachloroplatinate(2-)

(iii)  $[\text{PtCl}_6]^{2-}$

hexachloroplatinate(IV) **or** hexachloroplatinate(2-)

# IUPAC Nomenclature

## Rules:

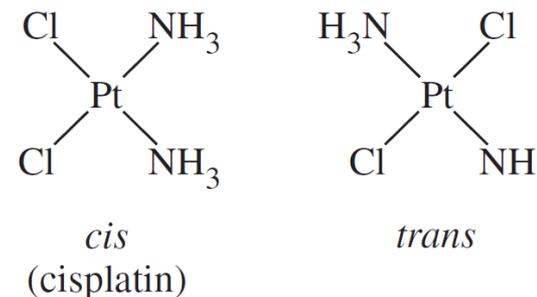
7. Prefixes designate adjacent (*cis* -) and opposite (*trans* -) geometric locations.

**Examples:** (i)  $[\text{PtCl}_2(\text{NH}_3)_2]$

*cis* - and *trans* -diamminedichloroplatinum(II)

(ii)  $[\text{CoCl}_2(\text{NH}_3)_4]^+$

*cis* - and *trans* -tetraamminedichlorocobalt(III)

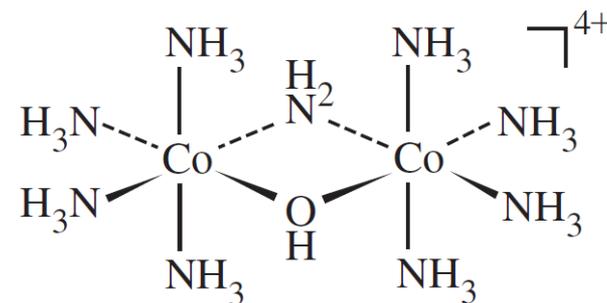


8. Bridging ligands between two metal ions have the prefix,  $\mu$

## Examples :



$\mu$ -amido- $\mu$ -hydroxobis(tetramminecobalt)(4+)



9. When the complex is negatively charged, the names for these metals are derived from the sources of their symbols:

**Examples:** (i)  $[\text{FeCl}_4]^-$

iron (Fe)	ferrate	lead (Pb)	plumbate	tetrachloroferrate(III) or tetrachloroferrate(1-)
silver (Ag)	argentate	tin(Sn)	stannate	(ii) $[\text{Au}(\text{CN})_2]^-$
gold (Au)	aurate	Pt	platinate	dicyanoaurate(I) or dicyanoaurate(1-)

# IUPAC Nomenclature

## Examples:



sodium pentacyanonitrosylferrate(II)



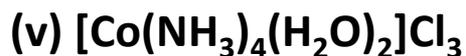
dichlorobis(urea)copper(II)



tetracarbonylnickel(0)



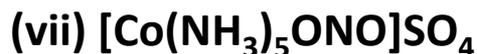
bis(cyclopentadienyl)iron(II)



tetraaminediaquacobalt(III) chloride



tris(ethylenediamine)cobalt(III) chloride



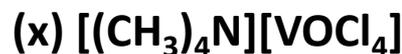
pentaaminenitrito-Ocobalt(III) sulfate



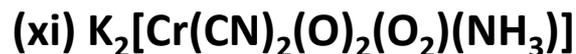
pentaaminesulfatocobalt(III) chloride



iron hexacyanoferrate(II)



tetramethylammonium tetrachlorooxovanadate(IV)



potassium aminedicyanodioxoperoxochromate (VI)



tetraamineplatinum(II) tetrachloroplatinate(II)

(Pt exhibits oxidation states of +2 (C.N. = 4) and +4

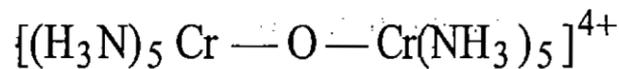
(C.N. = 6)



potassium pentacyanonitrosylferrate(II) dihydrate

# IUPAC Nomenclature

Examples: (A)

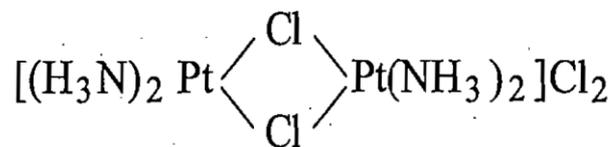


$\mu$ - oxo *bis* [pentaammine chromium (III)]

OR pentaammine chromium (III) -  $\mu$  - oxopentaammine chromium (III)

OR  $\mu$  - oxodecaammine dicobalt (III) ion

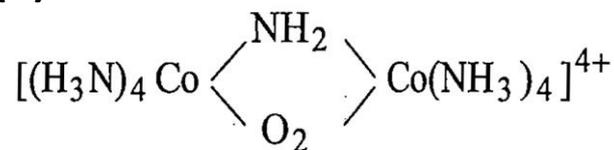
(B)



di -  $\mu$  chloro *bis* [diammine platinum (II)] Chloride

OR diammine platinum (II) - di-  $\mu$  - chloro diammine platinum (II) chloride

(C)

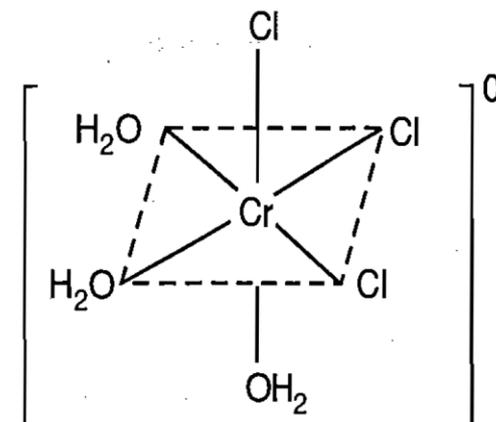


$\mu$  - amido -  $\mu$  - superoxo *bis* [tetraamminecobalt (III)]

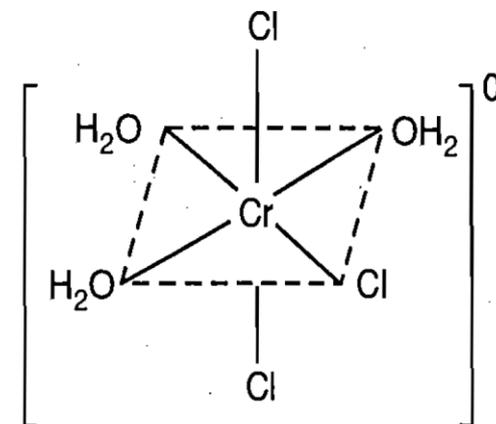
OR  $\mu$  - amido -  $\mu$  - superoxooctaamminedicobalt (III).

OR tetraammine cobalt (III) -  $\mu$  - amido -  $\mu$  - superoxotetraammine cobalt (III)

(D)



*fac*-triaquatrichlorochromium (III)

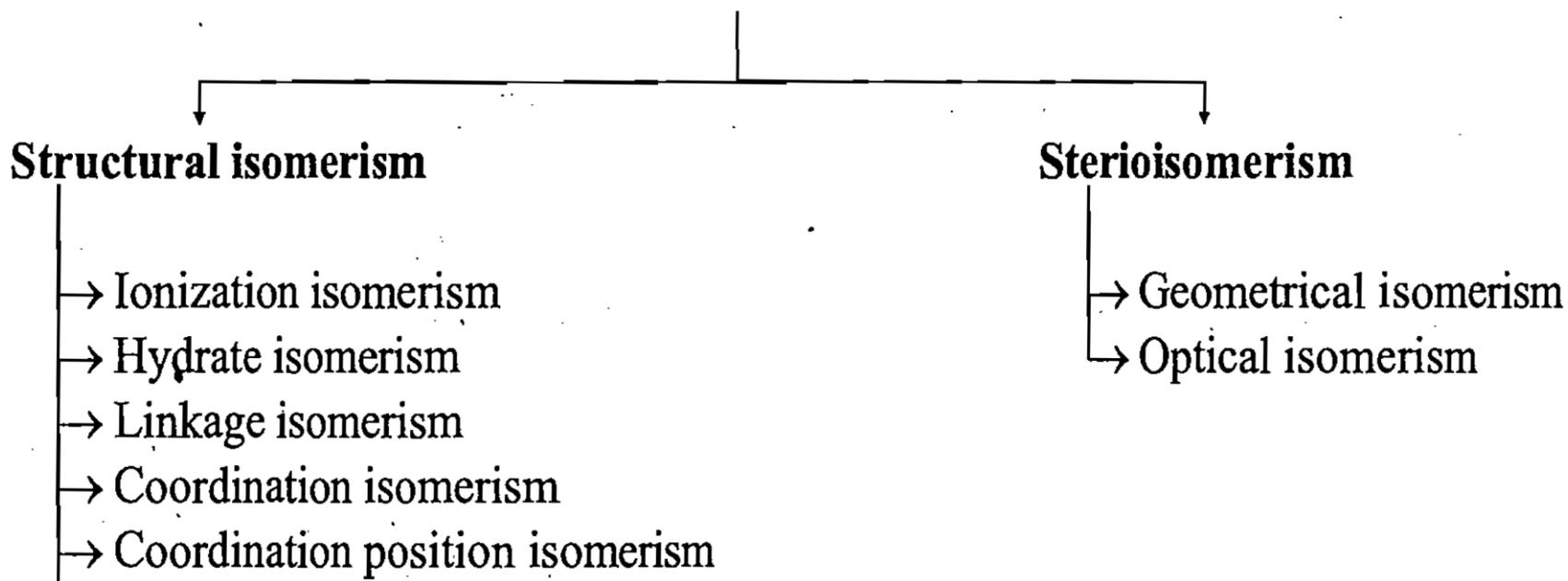


*mer*-triaquatrichlorochromium (III)

# Isomerism

**Definition:** Two or more molecules with identical formulas. The phenomenon of existence of isomers is called isomerism.

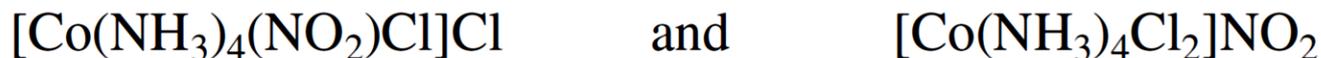
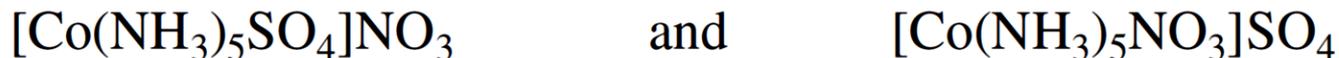
## Isomerism



- ❑ Isomers are different compounds therefore differ in reactivity and physical properties.
- ❑ Structural isomers arise due to different bond connectivity between the metal and ligands.
- ❑ Stereoisomers arise due to same bond connectivity between the metal and ligands but different orientations in space.

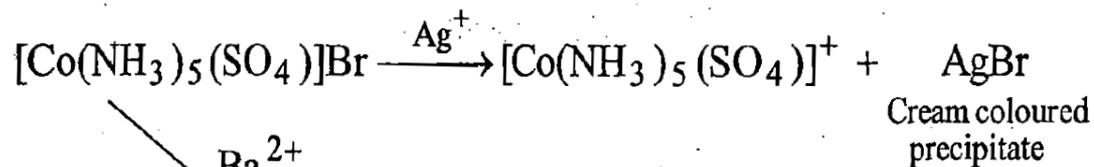
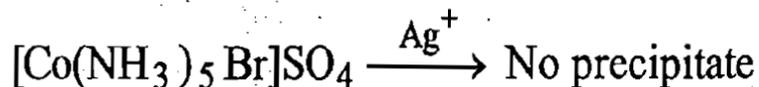
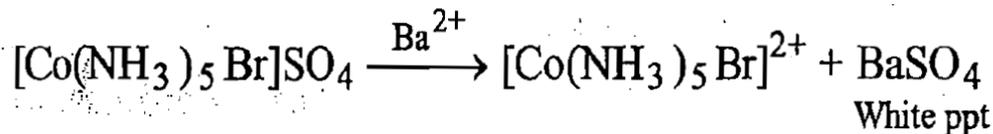
# Structural Isomerism

**1. Ionization Isomerism:** Compounds with the same formula, but which give different ions upon dissociation, exhibit ionization isomerization. For example:



**Physical property:** The complex  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  is *red-violet* while  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  is *red*. Both are ionization isomers.

**Chemical property:**



No Precipitate

# Structural Isomerism

**2. Hydrate Isomerism:** Hydrate isomerism requires water to play two roles, as (i) a ligand and as (ii) solvate within the crystal structure. (Solvent isomerism is a broader definition. For e.g:

(a)  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  is a classic example.

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet);  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (blue-green);  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$  (dark green)

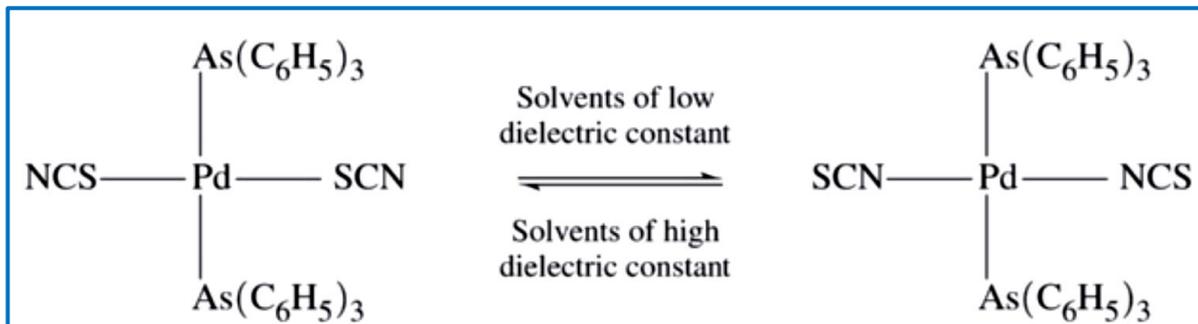
(b)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$

(c)  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$  and  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

**3. Linkage(Ambidentate) Isomerism:** It arises when an *ambidentate ligand* coordinates to metal cation through either of the two different donor atoms.

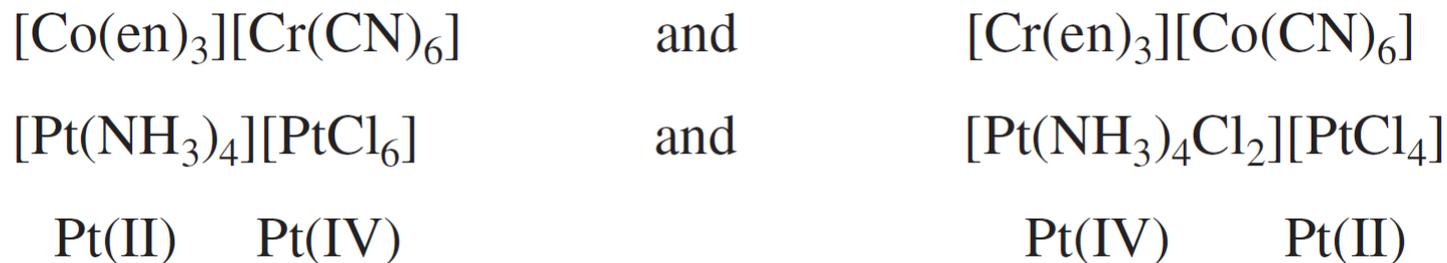
(i)  $[\text{Co}(\text{NH}_3)_5(\text{SCN})]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$

(ii)  $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$  and  $[\text{Co}(\text{en})_2(\text{ONO})_2]^+$

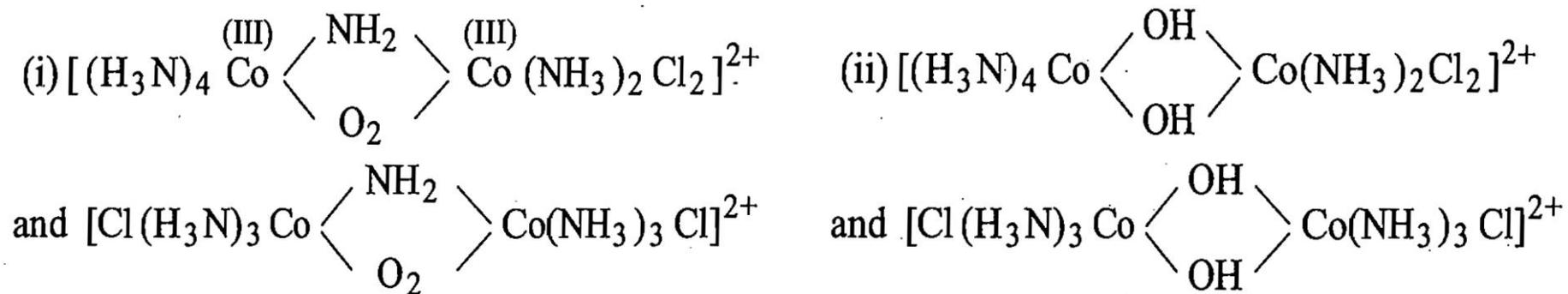


# Structural Isomerism

**4. Coordination Isomerism:** The coordination isomers requires at least two metals. Both the metals may be same or different. The ligand:metal ratio remains the same, but the ligands attached to a specific metal ion changes. For example:



**5. Coordination Position Isomerism:** It occurs in bridging complexes. An exchange of non bridging ligands between two metal ions gives rise to coordination position isomerism. For e.g.:



# Geometrical Isomerism

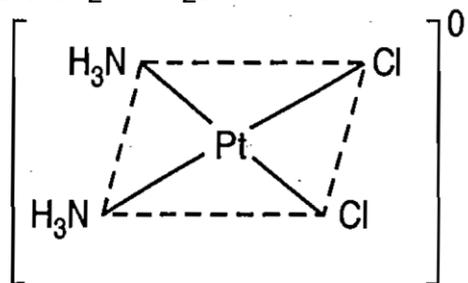
## 4-Coordinate complexes

**A. Tetrahedral complexes:** These complexes do not exhibit geometrical isomerism.

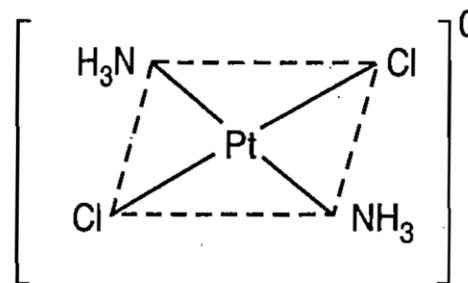
### B. Square planar complexes:

Type I:  $[Ma_2b_2]^{n\pm}$ -type complexes: These type of complexes show *cis* and *trans* isomerism. For

e.g:  $[(NH_3)_2PtCl_2]$ ,  $[(py)_2PtCl_2]$ , etc.



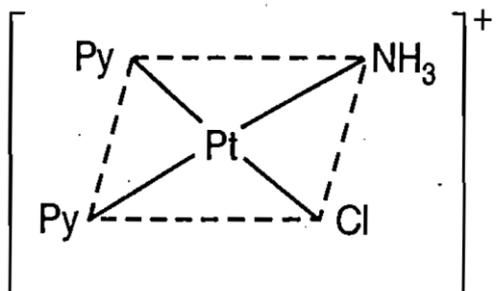
*cis-isomer*



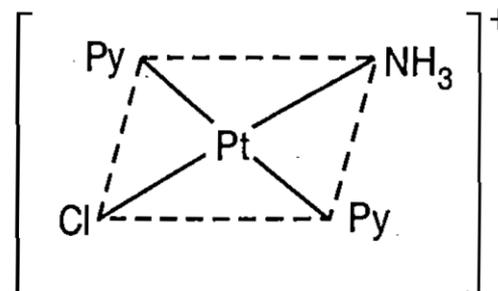
*trans-isomer*

Type II:  $[Ma_2bc]^{n\pm}$ -type complexes: These type of complexes show *cis* and *trans* isomerism. For

e.g:  $[Pt(NH_3)_2pyCl]$ ,  $[Pt(NH_3)_2(NO_2)Cl_2]$ , etc.



*cis-isomer*



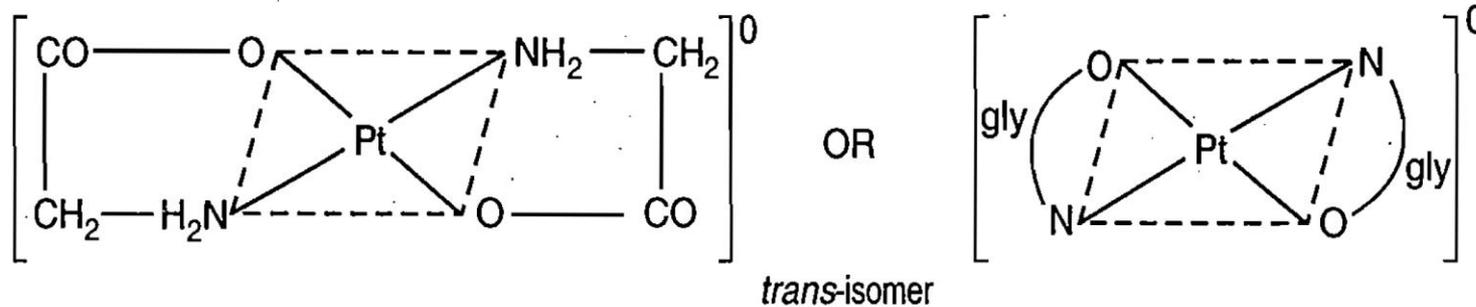
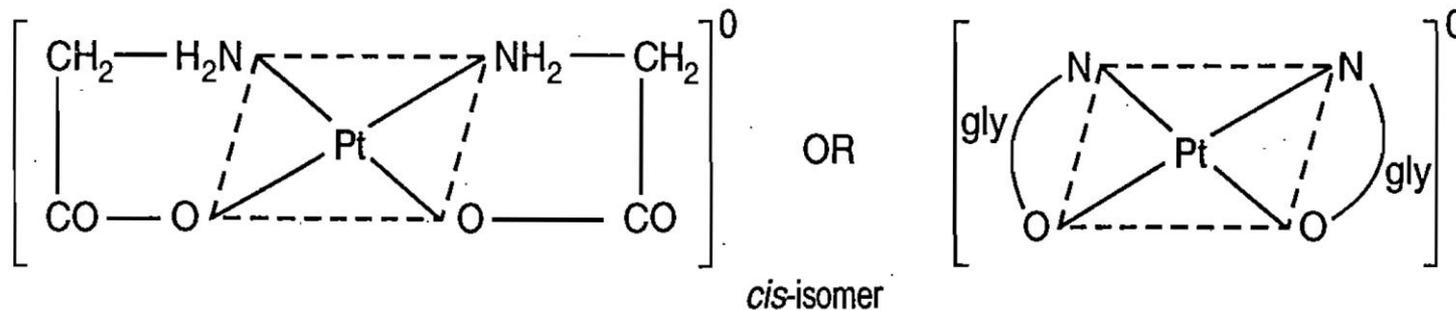
*trans-isomer*

# Geometrical Isomerism

## 4-Coordinate complexes

Type III:  $[M(AB)_2]^{n+}$  -type complexes: These type of complexes show *cis* and *trans* isomerism. For

e.g:  $[Pt(gly)_2]$ ,  $[Cu(gly)_2]$ , etc.



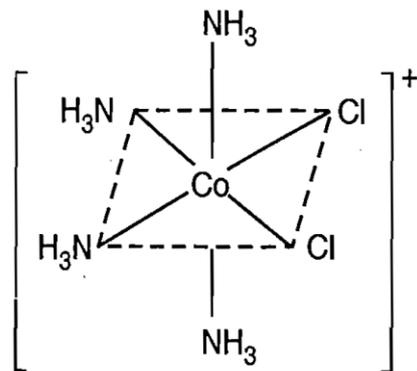
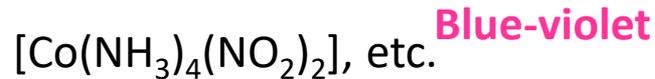
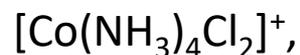
# Geometrical Isomerism

## 6-Coordinate complexes

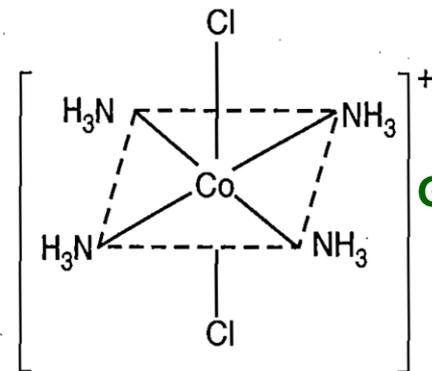
### A. Octahedral complexes:

Type I:  $[\text{Ma}_4\text{b}_2]^{n\pm}$  -type complexes: These type of complexes show *cis* and *trans* isomerism.

For e.g:



*cis*-isomer

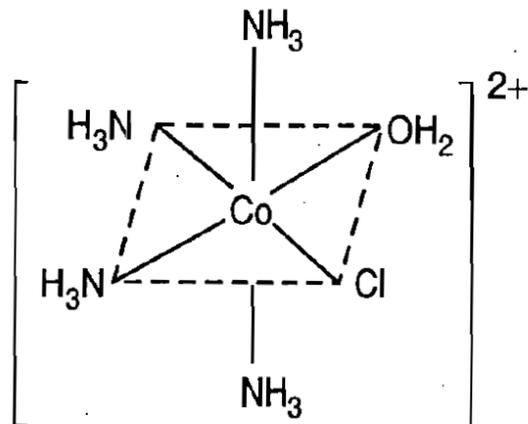
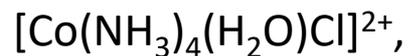


Green

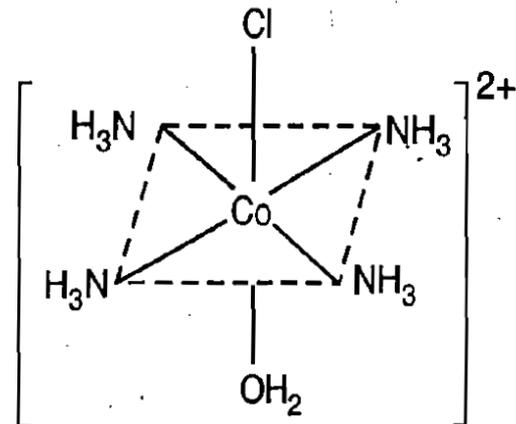
*trans*-isomer

Type II:  $[\text{Ma}_4\text{bc}]^{n\pm}$  -type complexes: These type of complexes show *cis* and *trans* isomerism.

For e.g:



*cis*-isomer



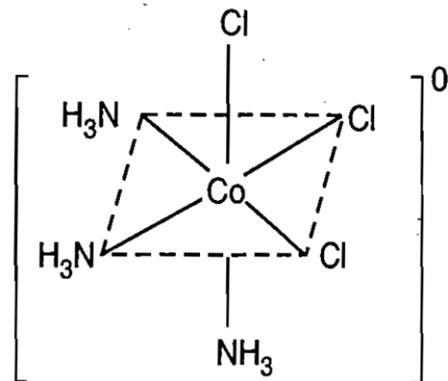
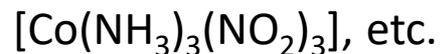
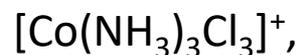
*trans*-isomer

# Geometrical Isomerism

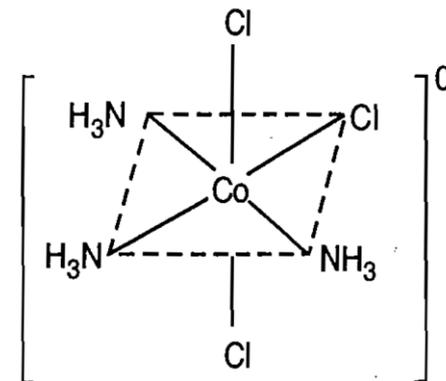
## 6-Coordinate complexes

Type III:  $[\text{Ma}_3\text{b}_3]^{n\pm}$  -type complexes: These type of complexes show *facial* and *meridional* isomerism.

For e.g:

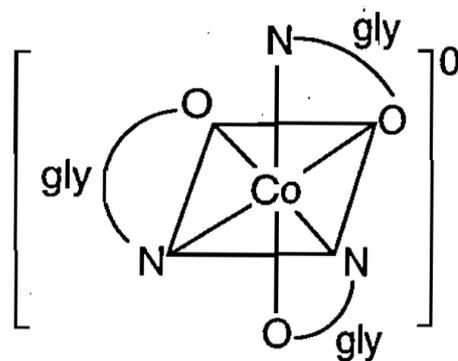
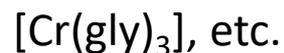


*facial-isomer*

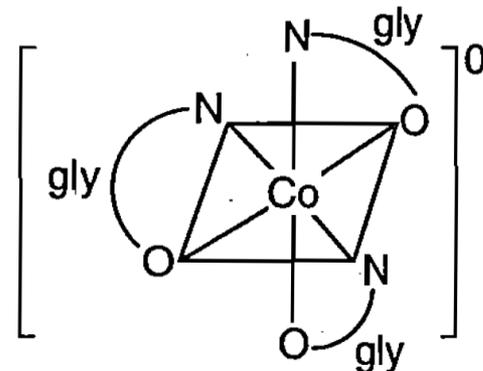


*meridional-isomer*

Type IV:  $[\text{M}(\text{AB})_3]^{n\pm}$  -type complexes: These type of complexes show *facial* and *meridional* isomerism.



*fac-isomer*



*mer-isomer*

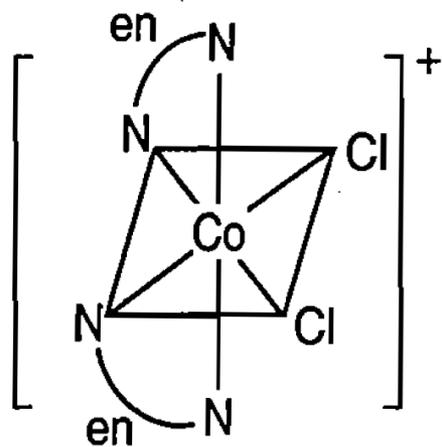
**Note:** *facial isomer has three L–M–L connection at 90° angle; meridional isomer has two 90° and one 180° L–M–L connections*

# Geometrical Isomerism

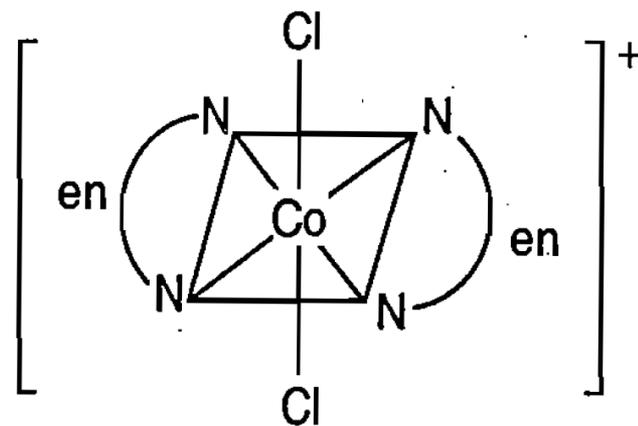
## 6-Coordinate complexes

Type V:  $[M(AA)_2a_2]^{n\pm}$  -type complexes: These type of complexes show *cis and trans* isomerism.

For e.g:  $[Co(en)_2Cl_2]^+$ ,  $[Rh(ox)_2Cl_2]^{3-}$ , etc.



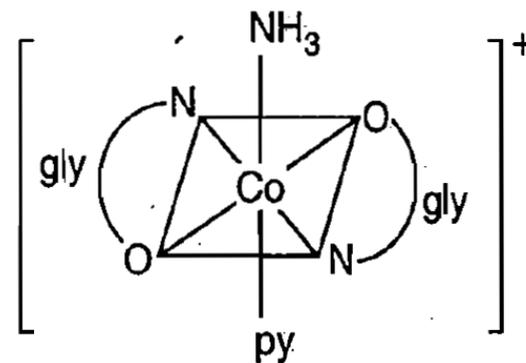
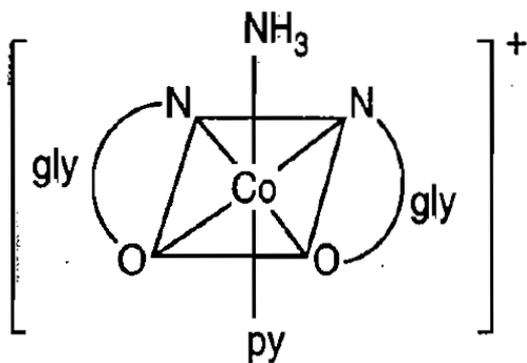
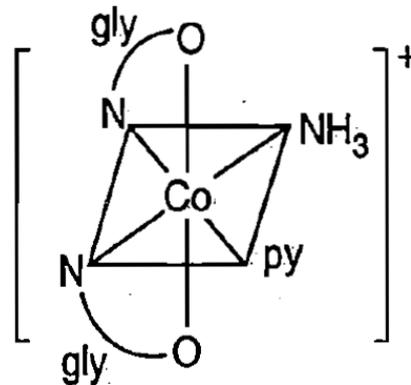
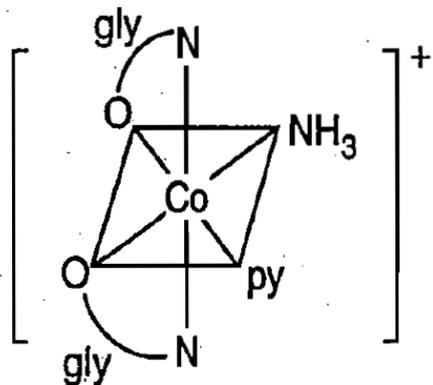
*cis-isomer*



*trans-isomer*

# Geometrical Isomerism

## 6-Coordinate complexes



Experimental methods of distinguishing *cis*- and *trans*- isomers

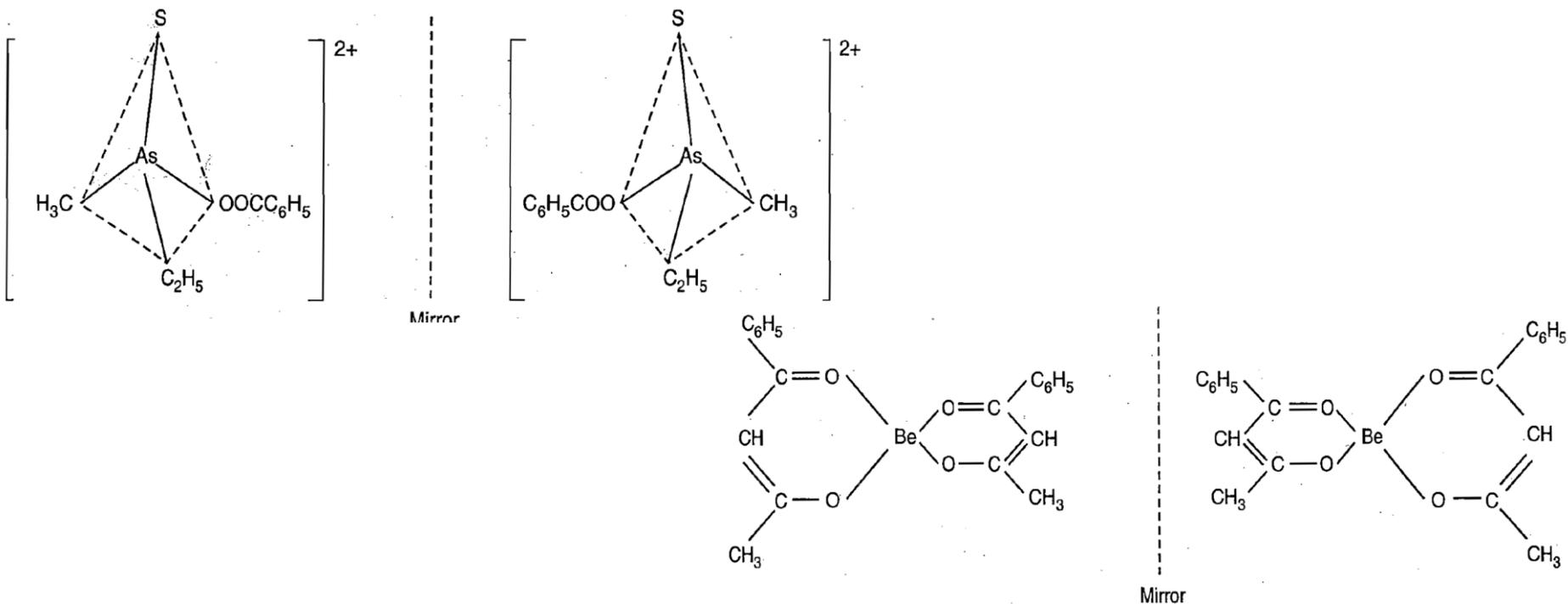
i. Dipole moment measurements

ii. IR-Spectroscopy

# Optical Isomerism

- ❑ Optical isomers (enantiomers) are pair of molecules or ions with non superimposable mirror images.
- ❑ Optical isomers are called chiral. They may be d (or + or  $\Delta$ ), l (or - or  $\Lambda$ ) and a racemate (equimolar mixture of d and l isomers)
- ❑ Molecules having inversion center, or a plane of symmetry are achiral.
- ❑ Molecules whose mirror image superimposes on 180-degree rotation are achiral.

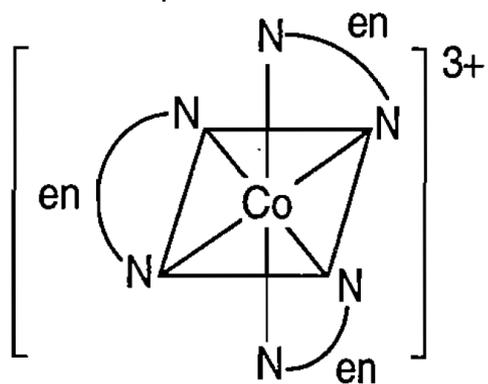
## Optical isomerism in tetrahedral complexes



# Optical Isomerism

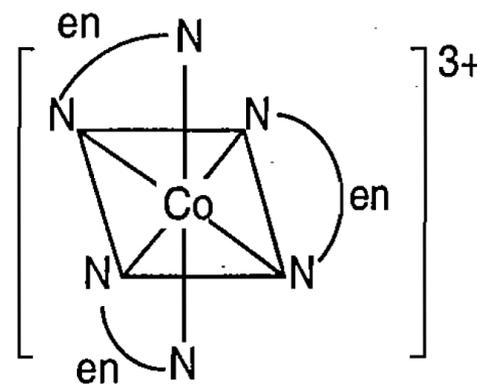
## Optical isomerism in octahedral complexes

Type II:  $[M(AA)_3]^{n\pm}$  -type complexes: These type of complexes are chiral. It is to be noted that octahedral complex with three chelate rings are always chiral. For e.g.:  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Cr}(\text{ox})_3]^{3-}$

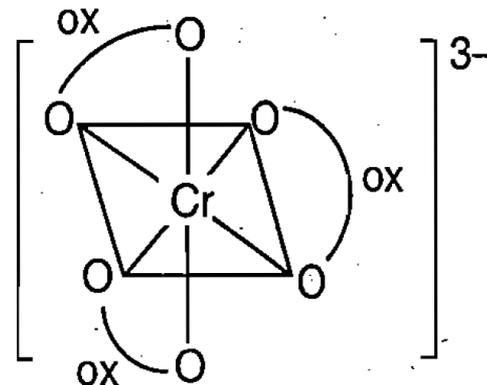
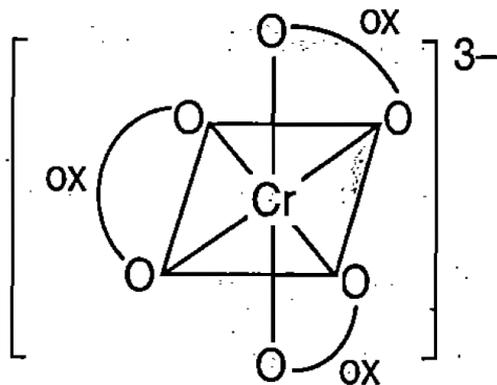


*d*-isomer

Mirror



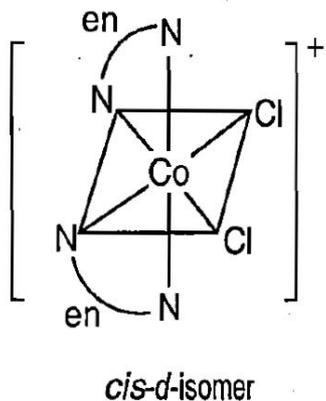
*l*-isomer



# Optical Isomerism

## Optical isomerism in octahedral complexes

Type III:  $[M(AA)_2a_2]^{n\pm}$  -type complexes: These type of complexes are chiral. It is to be noted that octahedral complex with three chelate rings are always chiral. For e.g.:  $[Co(en)_2Cl_2]^+$



Mirror

