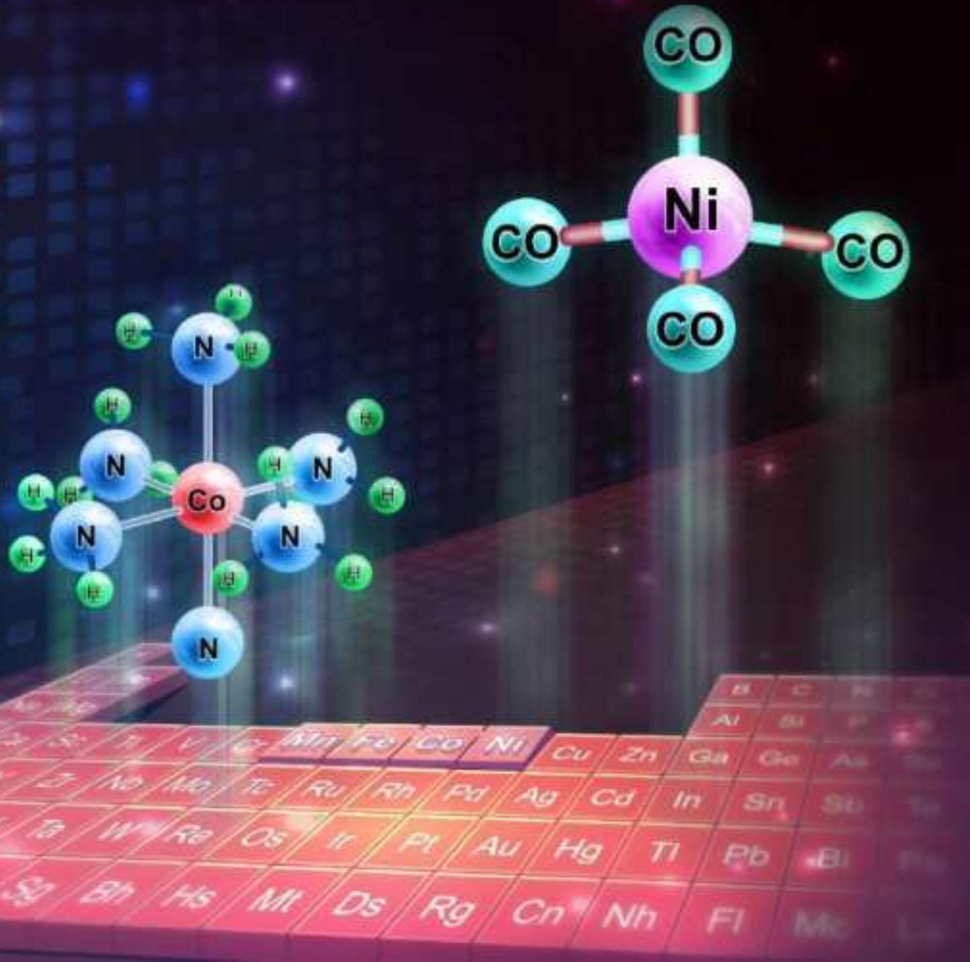
Welcome to

Aakash + BYJU'S LIVE

Coordination Compounds



Salt and its Classification

An ionic compound that contains **a cation** (basic radical) and **an anion** (acidic radical)

Salt

- Simple salt
- Double salt
- Complex salt

Simple Salt

A simple salt is formed by the **neutralisation of an acid and a base**.

$$\mathrm{NaOH} + \mathrm{HCl} \longrightarrow \underset{\substack{\big\downarrow \\ \text{Simple salt}}}{\mathrm{NaCl}} + \mathrm{H_2O}$$

Click to add text

Double Salt

It is formed by the combination of **two or more stable compounds** in a stoichiometric ratio.

It **dissociates into simple ions** completely when dissolved in water.

$$KCl + MgCl_2 + 6H_2O \longrightarrow \underbrace{KCl.MgCl_2.6H_2O}_{\textbf{Carnallite}}$$

Double Salt

EXAMPLE

$$Fe_2SO_4 + (NH_4)_2SO_4 + 6H_2O \longrightarrow \underbrace{Fe_2SO_4.(NH_4)_2SO_4.6H_2O}_{\text{Mohr's salt}}$$

Ferrous sulphate + Ammonium sulphate = Mohr's salt

Double Salt

$FeSO_4.(NH_4)_2SO_4.6H_2O$

When dissolved in water

The solution shows the properties of **Fe^{2+}, NH_4^+, and SO_4^{2-}** ions.

$KCl.MgCl_2.6H_2O$

When dissolved in water

The solution shows the properties of **K^+, Mg^{2+}, and Cl^-** ions.

Double Salt

$K_2SO_4.Al_2(SO_4)_3.24H_2O$

When dissolved in water

The solution shows the properties of **K^+, Al^{3+} and SO_4^{2-}** ions.

Note!!

On qualitative analysis, a solution of double salt gives the **test for each individual constituent ions.**

Generally, a double salt contains **same anion** but **different cations.**

Complex Salt

$Fe(CN)_2.4KCN$

When dissolved in water

The solution **does not** show the properties of **Fe^{2+}** and **CN^-**

$CuSO_4.4NH_3.H_2O$

When dissolved in water

The solution shows the properties of **SO_4^{2-}** but **does not** show for **NH_3**

Complex Salt

$$CuSO_4 + 4NH_3 + H_2O \longrightarrow CuSO_4.4NH_3.H_2O$$

Tetraamminecopper(II)
sulphate monohydrate

It is formed by the combination of **two or more stable compounds** in a stoichiometric ratio. However, it **does not dissociate** into simple ions when dissolved in water.

$[Cu(NH_3)_4]SO_4.H_2O$

Exists as a
distinct entity

Gives test for SO_4^{2-}

Complex salts
are
generally **coordination compounds.**

Complex Salt

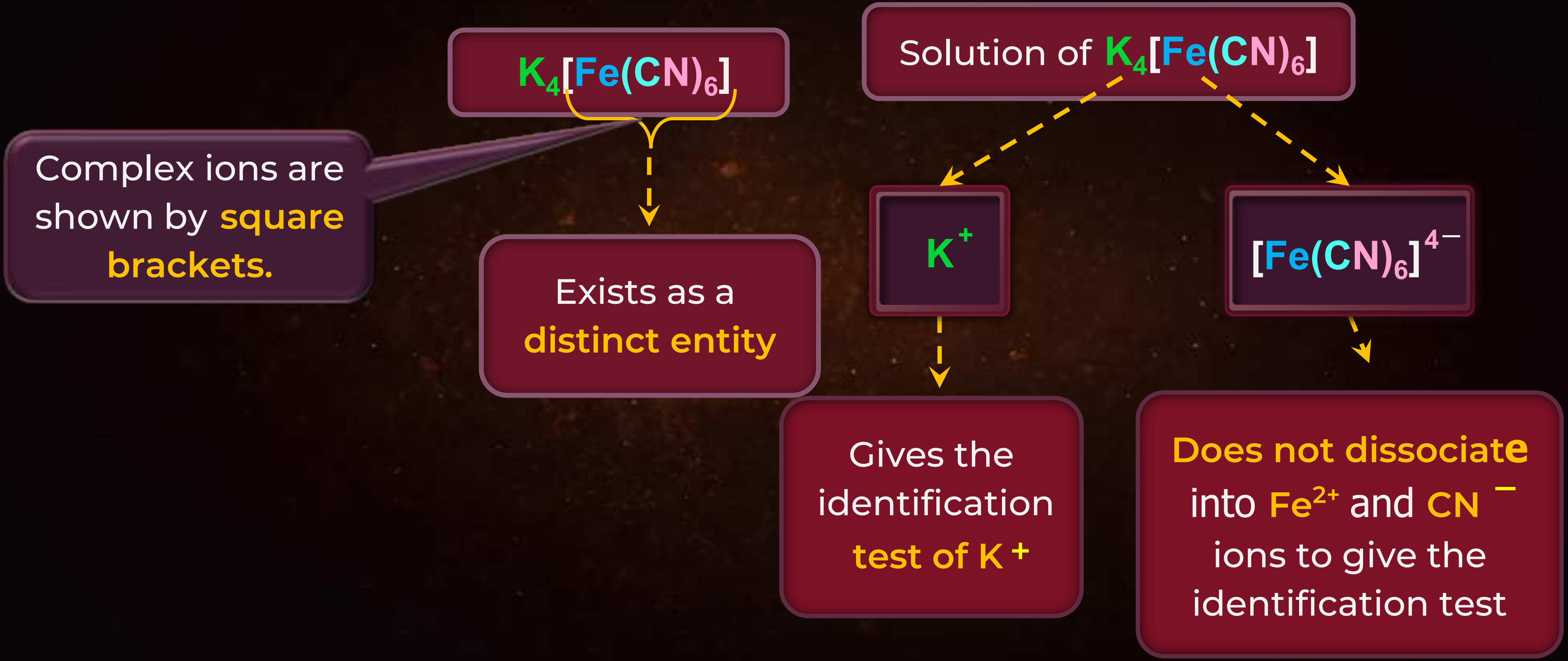
$$Fe(CN)_2 + 4KCN \longrightarrow \underbrace{Fe(CN)_2.4KCN}_{\textbf{Potassium ferrocyanide}}$$

$Fe(CN)_2.4KCN$

When dissolved in water

The solution **does not** show the properties of Fe^{2+} and CN^{-}.

Complex Salt



$K_4[Fe(CN)_6]$

Complex ions are shown by **square brackets.**

Exists as a **distinct entity**

Solution of $K_4[Fe(CN)_6]$

K^+

$[Fe(CN)_6]^{4-}$

Gives the identification **test of K^+**

Does not dissociate into **Fe^{2+}** and **CN^-** ions to give the identification test

Coordination Compounds

The addition compounds that **retain their identity** (i.e., **do not lose** their **identity**) in solutions are known as **coordination compounds.**

Metal atom or ion is attached to group of neutral molecules/ions by **coordinate covalent** bonds.

Example: $K_4[Fe(CN)_6]$

Coordination Compounds

General formula

$[M(L)_n]^{a+}\ X^{a-}$

$$\underbrace{[M(L)_n]}_{\text{Coordination entity}}{}^{a+}\ X^{a-}$$

The **central atom/ion** and the **ligands** attached to it are enclosed in **square brackets** along with **electrical charge** on it, collectively termed as the **coordination entity.**

Coordination Entity

$\underbrace{[\mathrm{Co(NH_3)_6}]}_{\text{Coordination entity}}{}^{3+}\ 3\mathrm{Cl}^-$

M

↓

Central atom

↓

Generally, **metals**

Central Atom

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a **definite geometrical arrangement** around it, is known as the **central atom or ion.**

Also referred to as **Lewis acids**

[**Co**$(NH_3)_6]Cl_3$

Central metal atom/ion

Coordination Compounds

General formula

$[M(\mathbf{L})_n]^{a+} X^{a-}$

Ligand

The electron-rich species **bound to the central atom/ion** inside the square bracket are known as **ligands.**

Ligand

Behaves as **Lewis base**

In general, **donates** the **electron** to the central metal atom

$[Co(\mathbf{NH_3})_6]Cl_3$

Ligand

Ligands

Ligand

Behaves as **Lewis base**

In general, **donates** the **electron** to the central metal atom

$[Co(\mathbf{NH_3})_6]Cl_3$

Ligand

Coordination Compound

General formula

$[M(L)_n]^{a+} X^{a-}$

Charge on the coordination entity

$[Co(NH_3)_6]^{3+} 3Cl^-$

Charge on the coordination entity

Coordination Compound

General formula

$[M(L)_n]^{a+} X^{a-}$

Coordination sphere

$[Co(NH_3)_6]^{3+} 3Cl^-$

Coordination sphere

The central atom/ion and the ligands attached to it are enclosed in **square brackets** termed as the coordination sphere.

Coordination Entity vs Coordination Sphere

Coordination sphere	Coordination entity
Collection of a **central atom** and the **ligands** surrounding the atom	**Coordination entity** given with the **electrical charge** of the coordination compound

Coordination Compounds

General formula

$[M(L)_n]^{a+}\ \mathbf{X}^{a-}$

Counter ion

$[Co(NH_3)_6]^{3+}\ \mathbf{3Cl}^{-}$

Counter ion

Counter Ion as Complex Compound

When there are two **coordination** spheres joined together by an **ionisation** sphere

$[Ag(NH_3)_2]^{1+}[Ag(CN)_2]^{1-}$

$[Cr(NH_3)_6]^{3+}[Co(CN)_6]^{3-}$

Ionisation Sphere

The molecule or ionic species **present outside the coordination sphere** constitute the **ionisation sphere.**

In $K_4[Fe(CN)_6]$, the ionisation sphere is K^+.

Coordination Compounds

General formula

$[M(L)_n]^{a+} X^{a-}$

Coordination number

$[Co(NH_3)_6]^{3+} 3Cl^-$

Coordination number

The coordination number (CN) of a metal ion in a complex can be defined as

The number of ligand donor atoms to which the metal is **directly bonded.**

Coordination Number

$[Pt(Cl)_6]^{2-}$

Coordination number of Pt = 6

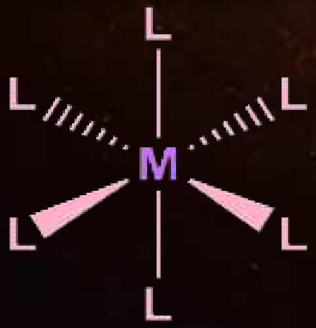
$[Ni(NH_3)_4]^{2+}$

Coordination number of Ni = 4

Coordination Polyhedron

The **spatial arrangement** of the ligand atoms that are directly attached to the central atom/ion defines a coordination **polyhedron** about the central atom.

The most common coordination polyhedral are **octahedral, square planar,** and **tetrahedral**.



Octahedral

Tetrahedral

Square planar

Oxidation Number of Central Metal Atom

The **charge** that a metal would carry if all the **ligands are removed along with the electron pairs** that are shared with the central atom

$[Cu(CN)_4]^{3-}$

$x \quad -1$

$x + 4(-1) = -3$

$x = +1$

Oxidation number of **Cu**

Classification of complex

- Based upon the charge on the coordination sphere
- Based upon the type of the donor group

Classification of Complex

Based on the charge on the coordination sphere

- Positive
- Neutral
- Negative

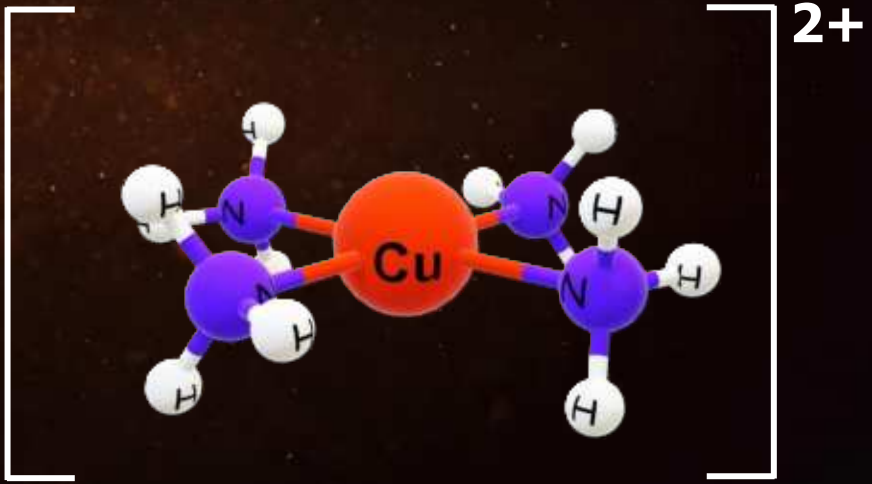
Positively Charged Coordination Complex

Charge on the coordination sphere: **Positive**

Cationic complex

EXAMPLE

$[Cu(NH_3)_4]^{2+}$



Neutral Coordination Sphere

Neutral complex

Charge on the coordination sphere: **Absent or no charge**

$[Ni(CO)_4]$

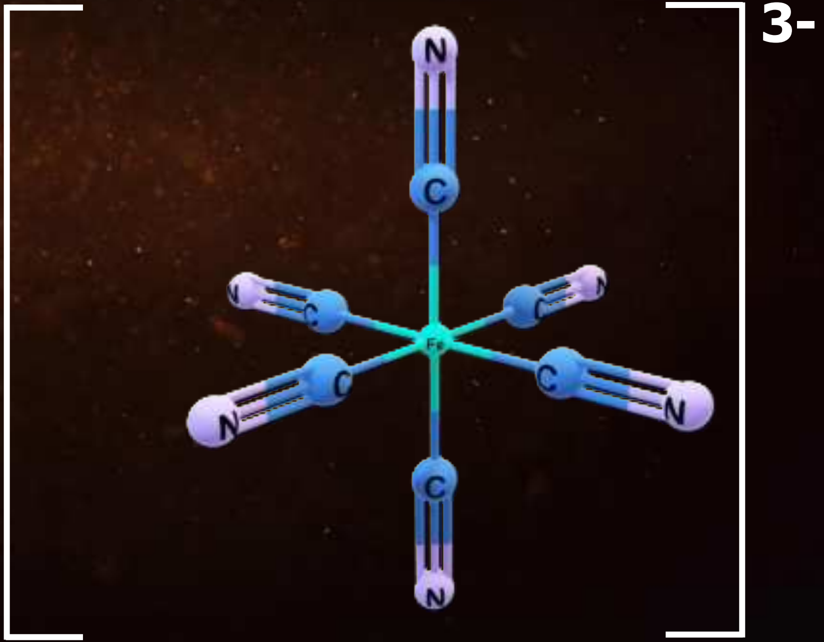
Negatively Charged Coordination Sphere

Anionic complex

Charge on the coordination sphere: **Negative**

EXAMPLE

$[Fe(CN)_6]^{3-}$



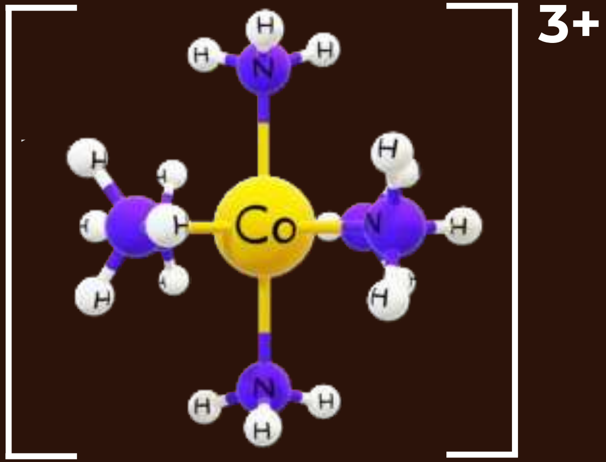
Classification of Complex

- Based on the type of the donor group
  - Homoleptic
  - Heteroleptic

Homoleptic Complex

A metal is bound to only one kind of donor group.

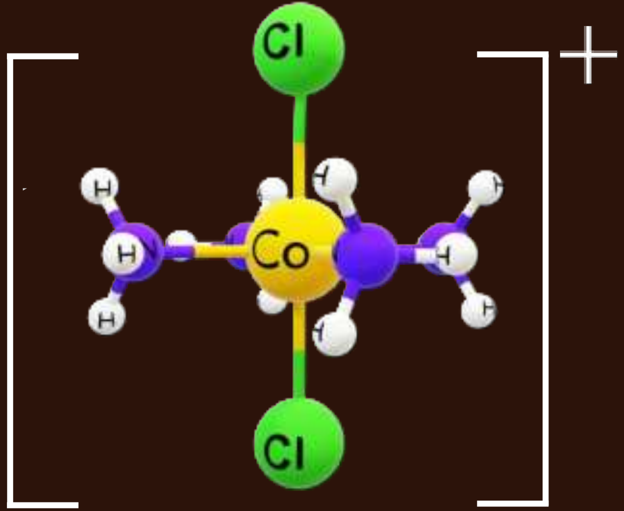
Example: $[Co(NH_3)_6]^{3+}$

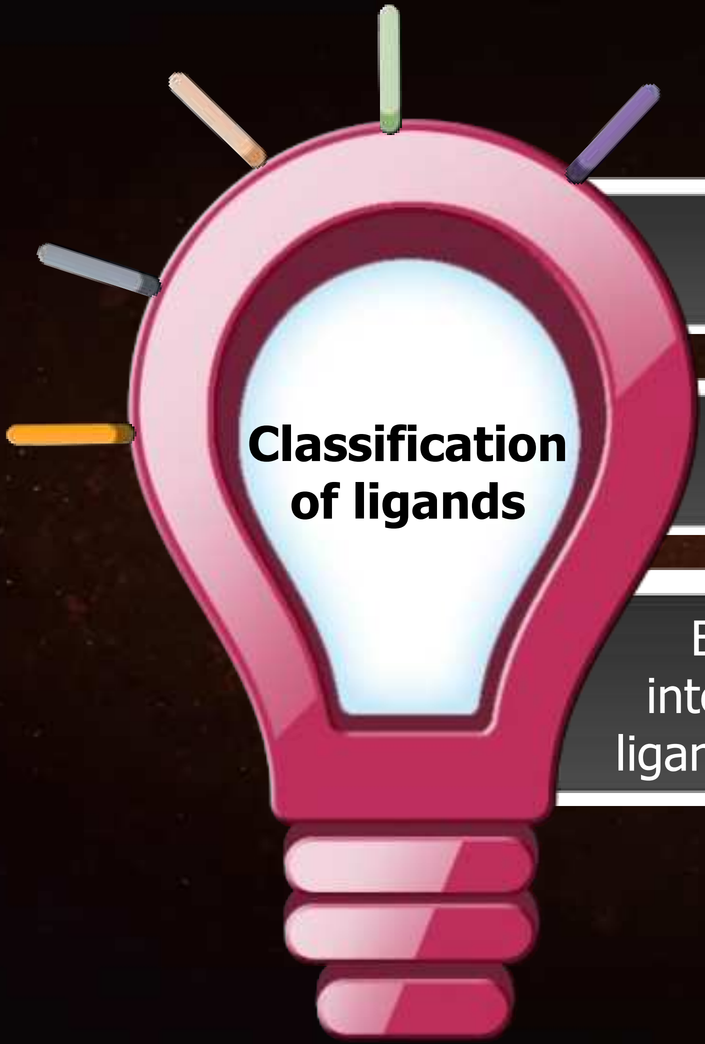


Heteroleptic Complex

A metal is bound to **more than one** kind of **donor groups.**

Example: $[Co(NH_3)_4Cl_2]^+$





Classification of ligands

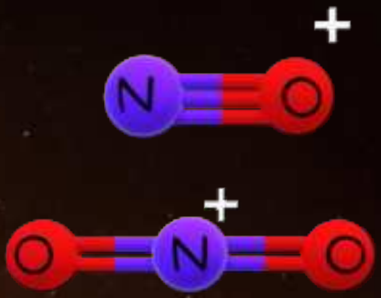
- Based on the charge
- Based on the denticity
- Based upon bonding interactions between the ligand and the central atom

Classification of Ligands

Based on their charge, ligands can be classified as

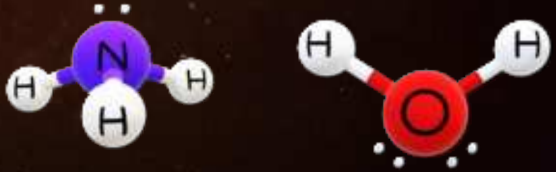
Positive

Examples:
NO^+, NO_2^+



Neutral

Examples:
H_2O, NO, CO, NH_3, etc.



Negative

Examples:
Cl^-, OH^-, CN^-, etc.

Denticity

The number of donations **accepted by a central atom** from a particular ligand is known as the denticity of the ligand.

Classification based upon denticity of ligand

- Monodentate
- Bidentate
- Polydentate

Monodentate Ligand

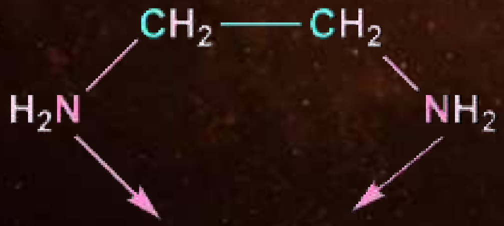
Only **one donation** is accepted from the ligand.

EXAMPLE

H_2O, NO, CO, NH_3, Cl^-, etc.

Bidentate Ligand

Two donations are accepted from the ligand.



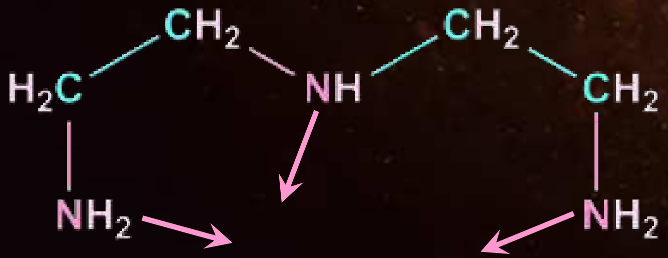
en: Ethylenediamine

Ox^{2-} : Oxalate

Polydentate Ligand

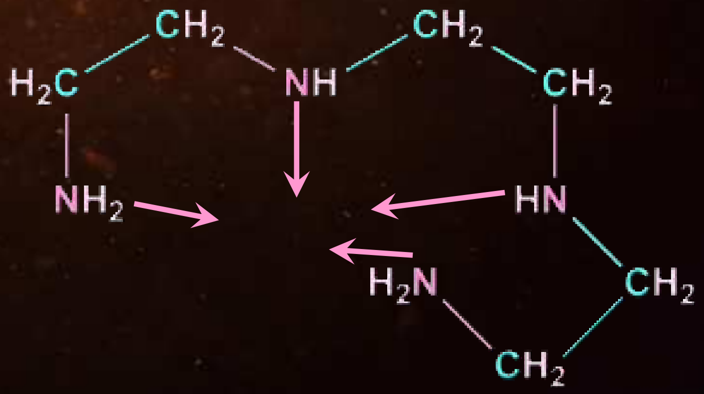
More than two donations are accepted from the ligand.

Tridentate Ligand



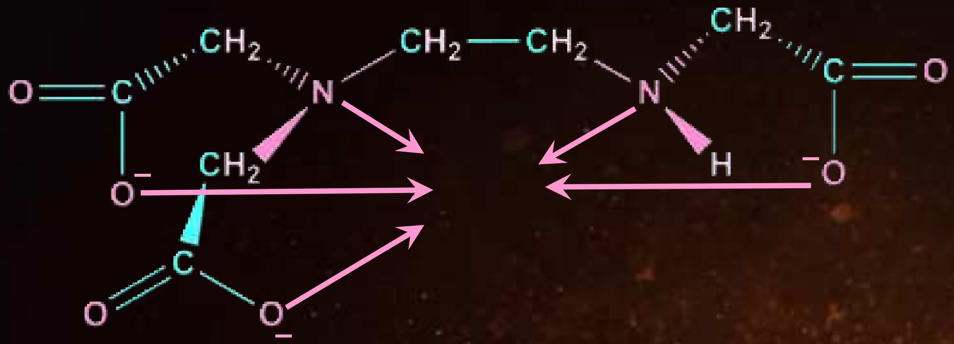
dien: Diethylenetriamine

Tetradentate Ligand



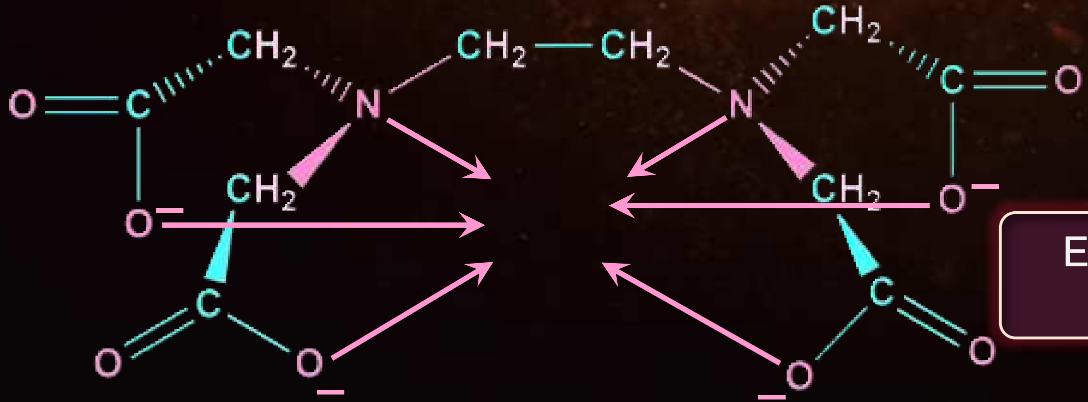
trien: Triethylenetetraamine

Pentadentate Ligand



Ethylenediaminetriacetate

Hexadentate Ligand



Ethylenediaminetetraacetate
(EDTA)

Classification of Ligands

Types of ligands

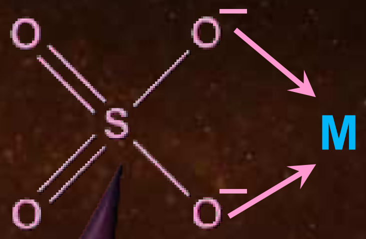
- Flexidentate ligand
- Ambidentate ligand
- Chelating ligand

Flexidentate Ligand

A ligand that shows **flexible denticity**

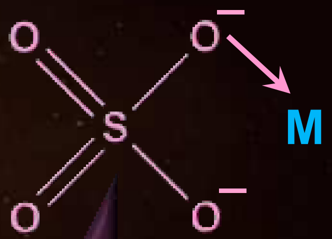
Examples: $S_2O_3^{2-}$, CH_3COO^-, NO_3^-, SO_4^{2-}, etc.

Didentate ligand



Flexidentate ligand behaving as **didentate**

Monodentate ligand

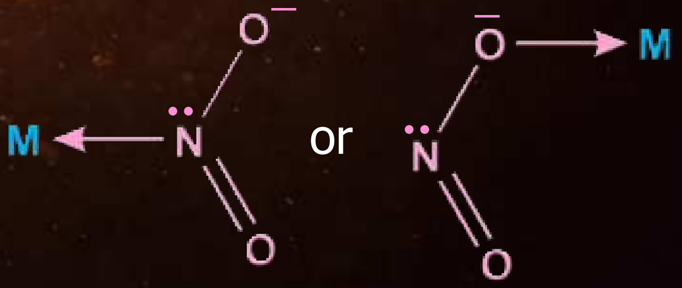


Flexidentate ligand behaving as **monodentate**

Ambidentate Ligand

A ligand that has **two different donor atoms** and either of the two ligates/donates in the complex

$\ddot{N}O_2^-$



$^-C\ddot{N}$

$M \leftarrow \bar{C}\equiv\ddot{N}$ or $\bar{C}\equiv\ddot{N} \rightarrow M$

Chelating Ligand

When a ligand uses **two or more of its donor atoms** simultaneously to **bind a single metal** ion and produces a ring

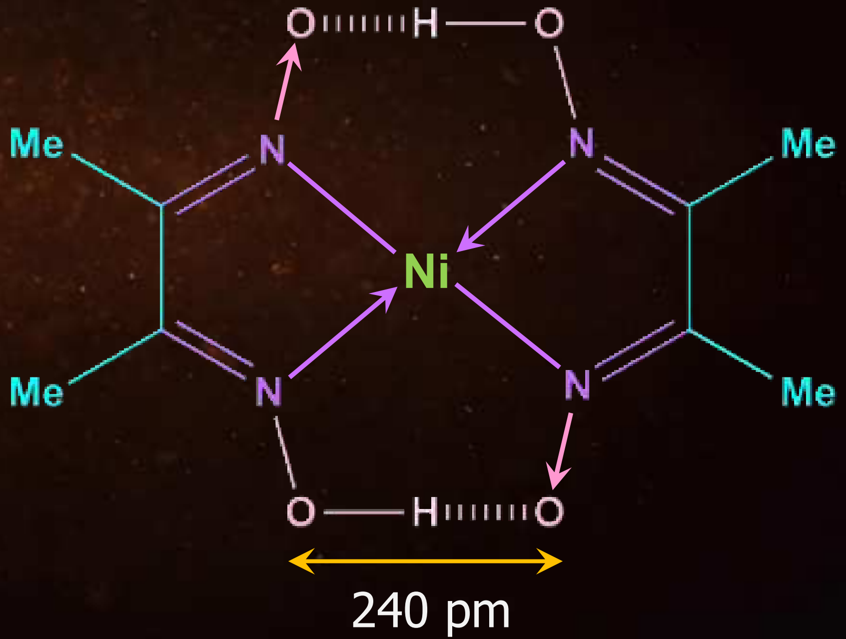
The complex formed is referred to as a **chelate complex.**

The process of **chelate formation** is known as **chelation.**

Chelating Ligand

EXAMPLE

dmg



Points to Remember!

More than **two donor sites**

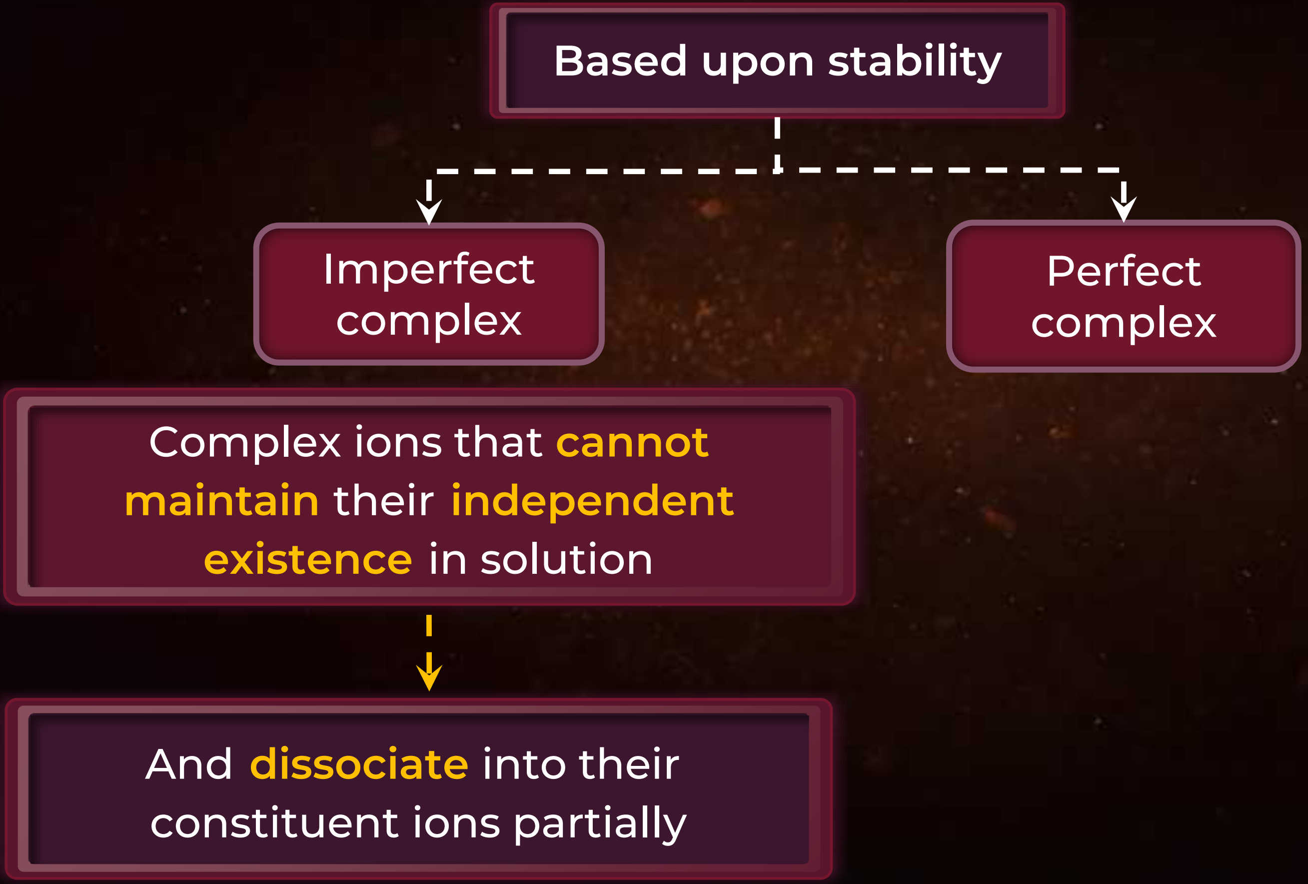
All **polydentate ligands** are examples of **chelating ligands** and they can form **chelate complexes**.

Note!!

A complex is perfect or imperfect will **depend upon the reagent** by which that complex is reacted.

Stability of the complex will **depend** upon the **reagent** by which that complex is reacted.

Classification of Complex



Based upon stability

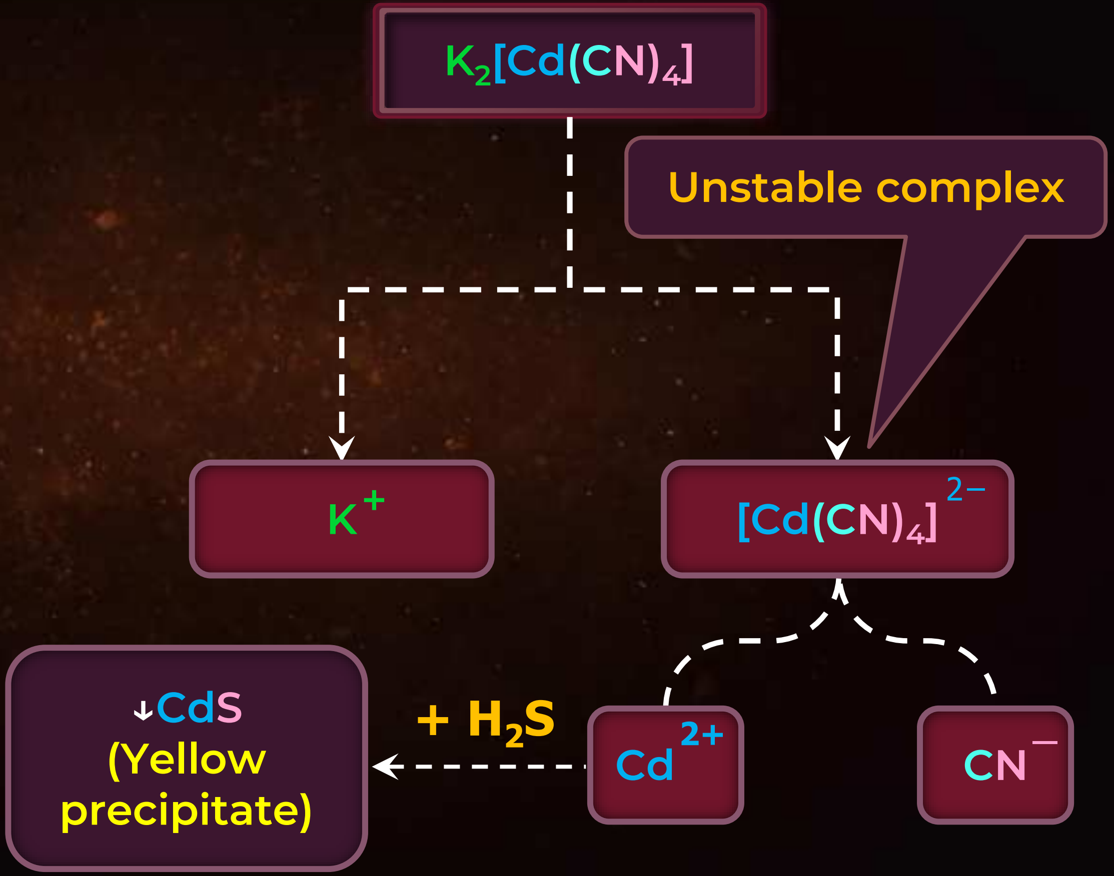
Imperfect complex

Perfect complex

Complex ions that **cannot maintain** their **independent existence** in solution

And **dissociate** into their constituent ions partially

Imperfect Complex



$K_2[Cd(CN)_4]$

Unstable complex

K^+

$[Cd(CN)_4]^{2-}$

Cd^{2+}

CN^-

$+ H_2S$

$\downarrow CdS$ (Yellow precipitate)

Classification of Complex

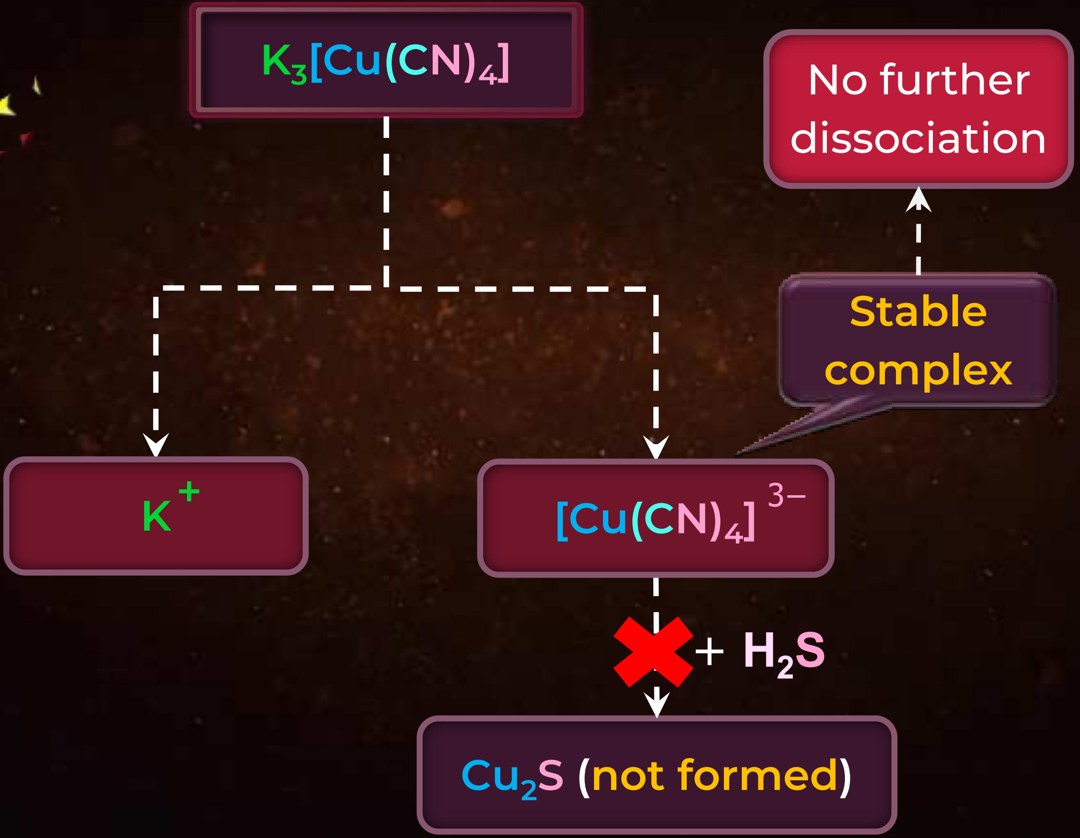
Based upon stability

Imperfect complex

Perfect complex

Complex ions that exhibit very **less degree of dissociation** in solution

Perfect Complex



$K_3[Cu(CN)_4]$

K^+

$[Cu(CN)_4]^{3-}$

Stable complex

No further dissociation

$+ H_2S$

Cu_2S (not formed)

Stability Due to Chelation

Chelated complexes are **more stable than** similar complexes with **monodentate ligands** as **dissociation of the complex** involves **breaking of more bonds** rather than one.

Condition for Chelation

Chelating ligands prefer forming 5 or 6 membered ring complexes with metal compared to other ring sizes.

Stability Due to Chelation

EXAMPLE

$Co^{3+}(aq) + 6\ NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{3+}$ ①

$Co^{3+}(aq) + 3\ en(aq) \rightleftharpoons [Co(en)_3]^{3+}$ ②

$Co^{3+}(aq) + 2\ dien(aq) \rightleftharpoons [Co(dien)_2]^{3+}$ ③

Stability Order : 3 > 2 > 1

Chelate Effect

The **greater affinity of chelating ligands** for a **metal ion** than that of similar nonchelating (monodentate) ligands for the same metal is known as **Chelate Effect.**

$$[Co(NH_3)_6]^{3+}(aq) + 3\,en(aq) \rightleftharpoons [Co(en)_3]^{3+} + 6\,NH_3(aq)$$

Naming of Mononuclear Coordination Compounds

Given by **IUPAC**

The **names** of coordination compounds are **derived** by the following **principles** of nomenclature.

Rules

1

The **cation is named first** in both **positively** and **negatively** charged coordination entities.

Naming of Mononuclear Coordination Compounds

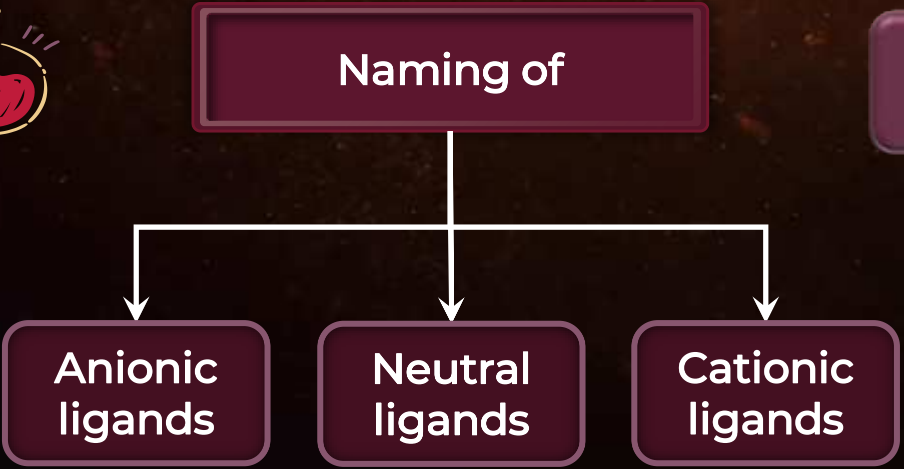
Rules

2

The ligands are **named** in an **alphabetical order** before the name of the central atom/ion.

Multiplicative prefixes are not considered.

3



Naming of

Anionic ligands

Neutral ligands

Cationic ligands

Naming of Anionic Ligands

The **names** of **anionic ligands** end with **‘o’**.

NO_3^- --→ Nitrate --→ Nitrato

Ligand	Name
NO_3^-	Nitrato
CO_3^{2-}	Carbonato
$MeCO_2^-$	Acetato or Ethanoato
$acac^-$	Acetylacetonato
SO_4^{2-}	Sulphato
$S_2O_3^{2-}$	Thiosulphato

Naming of Anionic Ligands

b

Ligand names ending with **‘ite’** are changed to **‘ito’.**

Ligand	Name
SO_3^{2-}	Sulphito
ClO_2^-	Chlorito
OCl^-	Hypochlorito
NO_2^-	Nitrito
HSO_3^-	Hydrogensulphito

c

Ligand names ending with **‘ide’** are changed to **‘ido’.**

Ligand	Name
F^-	Fluorido
Cl^-	Chlorido
Br^-	Bromido
I	Iodido

Naming of Anionic Ligands

Ligand	Name
CN^-	Cyanido
NC^-	Isocyanido
H^-	Hydrido
OH^-	Hydroxido
OD^-	Duterido
NH_2^-	Amido
NH^{2-}	Imido

Ligand	Name
N^{3-}	Nitrido
N_3^-	Azido
O^{2-}	Oxido
O_2^{2-}	Peroxido
O_2^-	Superoxido
S^{2-}	Sulphido
HS^-	Hydrosulphido

Naming of Anionic Ligands

EXAMPLE

Ambidentate ligands

Serial number	Ligand	Name
1	^{-}CN	Cyanido/Cyanido-C
	NC^{-}	Isocyanido/Cyanido-N
2	$^{-}NO_2$	Nitro/Nitrito-N
	ONO^{-}	Nitrito/Nitrito-O

Naming of Anionic Ligands

Ambidentate ligands

Serial number	Ligand	Name
3	^{-}OCN	Cyanato/cyanato-O
	^{-}NCO	Isocyanato/cyanato-N
4	^{-}SCN	Thiocyanato/thiocyanato-S
	^{-}NCS	Isothiocyanato/thiocyanato-N

Naming of Neutral Ligands

The names of **neutral ligand** have **no specific endings.**

Ligand	Name
H_2O	Aqua
NH_3	Ammine
CO	Carbonyl
NO	Nitrosyl
$MeCONH_2$	Acetamide

Ligand	Name
$MeNH_2$	Methanamine
$MePH_2$	Methylphosphine
C_6H_6	Benzene
CH_3NC	Methyl isocyanide
PPh_3	Triphenylphosphine
C_5H_5N	Pyridine

Naming of Cationic Ligands

Rules 3

The name of **cationic ligands** end with **‘ium’.**

Ligand	Name
NO^+	Nitrosonium
$H_2N—NH_3^+$	Hydrazinium
NO_2^+	Nitronium

π-Donor Ligands

The **π-donor ligands** are the **unsaturated organic compounds** that can **donate** the electron pair to the metal atom/ion.

Examples

Alkenes, alkynes and benzene

Naming of Anionic π -donors

For the **π -donor** ligands

↓

Prefix like "η^x" is used.
Where, η : **Hapticity** of the ligand
x : **Number of atoms** attached
to the metal atom/ion.

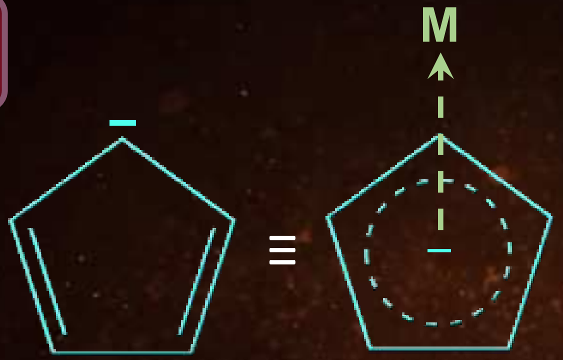
Hapticity

The **number of carbon** atoms of a ligand which are **directly attached** to (or closely associated with) the **metal** in a compound is called as the **hapticity.**

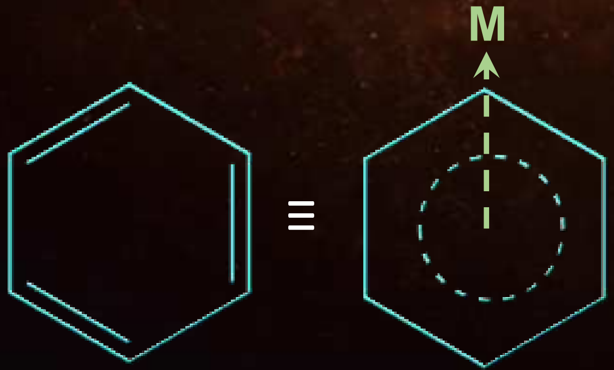
$\pi\text{-}C_5H_5^-$	η5- cyclopetadienyl
$\pi\text{-}C_6H_6$	η6- benzene
$\pi\text{-}C_3H_5^-$	η3- allyl

Examples of structures of Hapticity

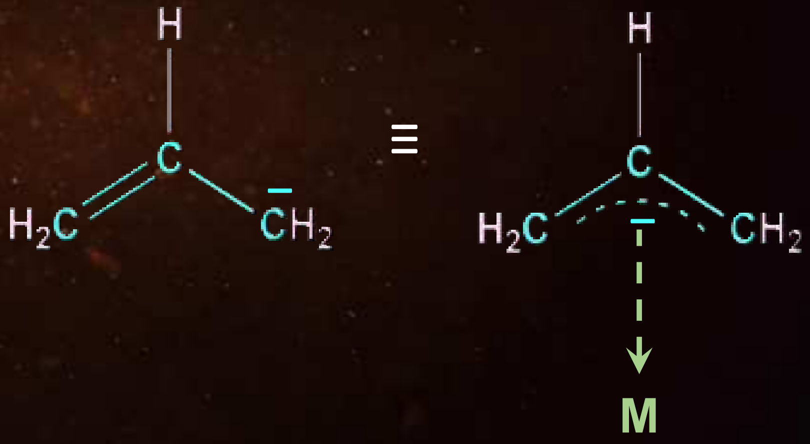
η^5 - $C_5H_5^-$



η^6 -C_6H_6



η^3 – allyl



Naming of Mononuclear Coordination Compounds

Rules

4

If a number of same ligands are present, then a prefix is used.

Prefixes

- 2-di
- 3-tri
- 4-tetra
- 5-penta
- 6-hexa
- 7-hepta

Naming of Mononuclear Coordination Compounds

Rules

5

When the **name of a ligand** already includes terms like **di, tri, tetra,** etc., then a **second set of prefix** is used.

The ligand's name is **kept within brackets** to avoid **ambiguity.**

Prefixes

- 2-bis
- 3-tris
- 4-tetrakis
- 5-pentakis
- 6-hexakis
- 7-heptakis

Naming of Mononuclear Coordination Compounds

$(en)_2$	bis-(ethylenediamine)
Me_2NH	dimethylamine
$(NH_2Me)_2$	bis-(methylamine)

To make it **distinct** from dimethyl amine

Naming of Mononuclear Coordination Compounds

Rules

6

There is **no deletion** of **vowels** or use of a **hyphen.**

Example: $(NH_3)_4$ → Tetraammine

Naming of Mononuclear Coordination Compounds

For **anionic complexes,** the names of metal **end** with **-ate.**

Aluminium	Aluminate	Nickel	Nickelate
Platinum	Platinate	Cobalt	Cobaltate
Molybdenum	Molybdate	Iron	Ferrate
Zinc	Zincate	Manganese	Manganate

Note!!

For **cationic** and **neutral complexes,** the metal is **named as the element.**

Example: **Co**: Cobalt

Example: **Pt**: Platinum

Naming of Mononuclear Coordination Compounds

Rules

8

The **oxidation state** of the **metal** in a cation, anion, or neutral coordination entity is indicated by a **Roman numeral in brackets.**

Examples:

(II), (-I), (V)

Naming of Mononuclear Coordination Compounds

Rules

9

If there is **water of crystallisation,** it is to be **included** in the name.

Example:

$[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Tetraaquadichloridochromium(III) chloride dihydrate

10

No space is left between the **names** that refer to the **same coordination entity.**

Note!!

For coordination complexes, we **don't indicate** the **number** of **cations and anions** in the IUPAC nomenclature.

Rules for Writing Formulas from the Names

Rules for Writing Formulas

RULE 1

The central atom is listed first.

RULE 2

The ligands are then listed in an alphabetical order.

The placement of a ligand in the list does not depend on its charge.

Rules for Writing Formulas

RULE 3

Polydentate ligands are also listed **alphabetically**.

In case of an abbreviated ligand, the **first letter** of the abbreviation is used to determine the **position of the ligand** in the alphabetical order.

RULE 4

Formula for the **entire coordination entity**

Charged

Uncharged

Enclosed in square brackets

Rules for Writing Formulas

RULE 5

When ligands are polyatomic, their formulas are **enclosed in parentheses.**

Examples:
(CN^-), (H_2O)

Ligand **abbreviations** are also enclosed in parentheses.

Examples:
(en), (ox)

RULE 6

There should be **no space between** the **ligands** and the **metal** within a coordination sphere.

Rules for Writing Formulas

RULE 7

When the formula of a **charged coordination entity** is to be written **without** that of the counter ion

The charge is indicated **outside the square brackets** as a right superscript with the **number before the sign.**

Examples:
$[Co(CN)_6]^{3-}$,
$[Cr(H_2O)_6]^{3+}$, etc.

RULE 8

The charge of the **cation(s)** is **balanced** by the charge of the **anion(s).**

Rules for Writing Formulas

EXAMPLE

Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride

$[CoCl_2(en)_2]Cl$

Hexaamminechromium(III)hexacyanido cobaltate(III)

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

Bonding in coordination compounds

- Werner’s theory
- Valence bond theory (VBT)
- Crystal field theory (CFT)

Werner’s Theory

1893

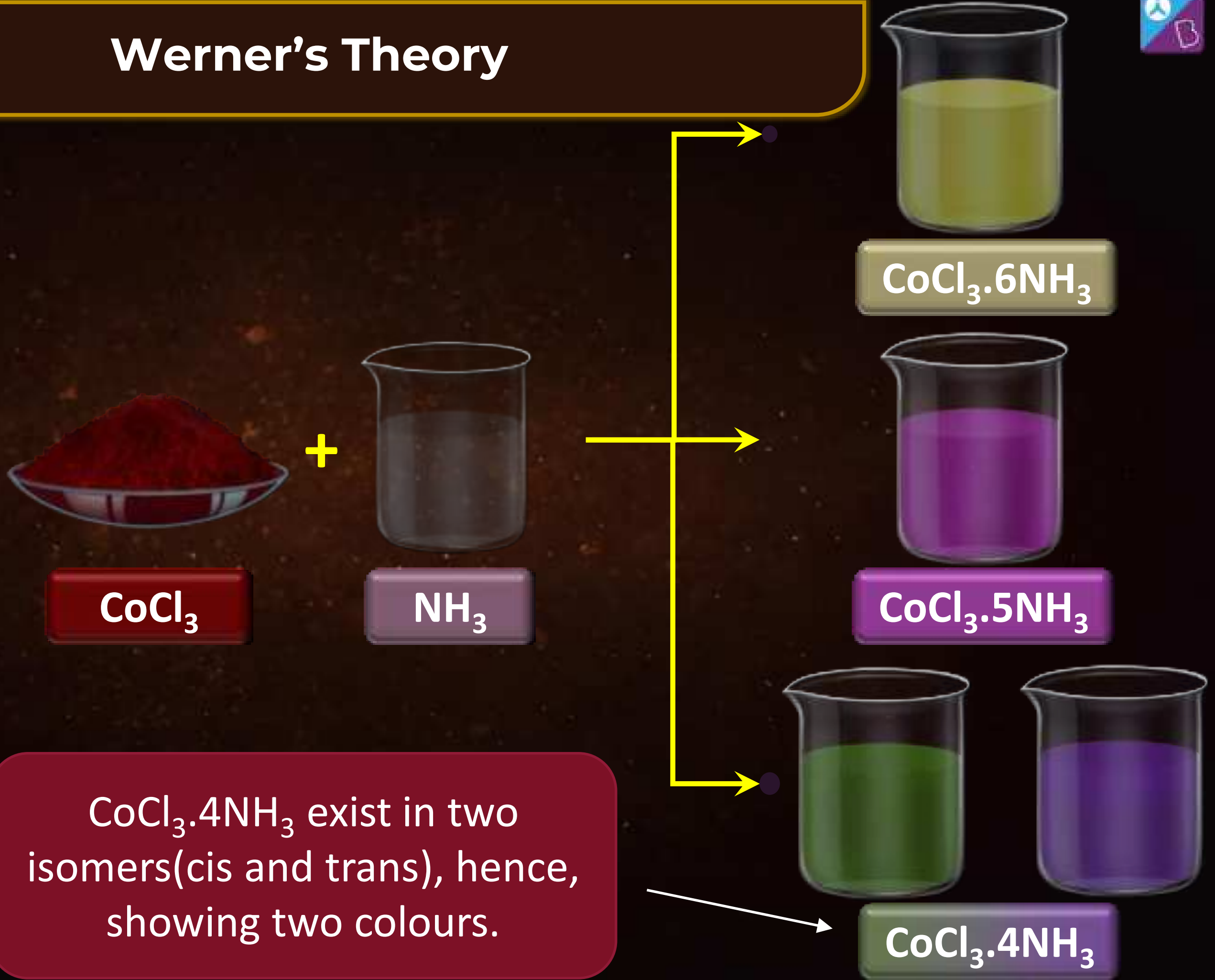
Werner’s coordination theory was the **first attempt** to explain the **bonding** in coordination compounds.

While adding **excess of $AgNO_3$** solution in a series of compounds of **Co(III) chloride with NH_3,** the following results were found:

Werner's Theory

Experiment

A series of compounds formed by $CoCl_3$ and NH_3



$CoCl_3.4NH_3$ exist in two isomers(cis and trans), hence, showing two colours.

Werner’s Theory

$CoCl_3.6NH_3$ + $AgNO_3$ $\longrightarrow$ $3AgCl\downarrow$

1 mol | Excess | 3 mol

Why this gives 3 mol AgCl

Because it has an **ionisable valency** of **3**

The series of compounds formed by $CoCl_3$ and NH_3 after reacting with excess $AgNO_3$ gives different number of AgCl.

Werner’s Theory

$CoCl_3.5NH_3 + AgNO_3 \longrightarrow 2AgCl \downarrow$

1 mol

Excess

2 mol

Why this gives 2 mol AgCl

Because it has an **ionisable valency** of **2**

Werner's Theory

$$CoCl_3.4NH_3 + AgNO_3 \rightarrow AgCl\downarrow$$

1 mol, (green)

Excess

1 mol

Why this gives 1 mol AgCl

Because it has an **ionisable valency** of **1**

Werner's Theory

$$\underset{\text{1 mol, (violet)}}{CoCl_3.4NH_3} + \underset{\text{Excess}}{AgNO_3} \longrightarrow \underset{\text{1 mol}}{AgCl \downarrow}$$

Why this gives
1 mol AgCl

Because it has an
ionisable valency of **1**

Conductance

A series of compounds formed by $CoCl_3$ and NH_3 show different conductance values which confirms the presence of ionisable and non-ionisable valencies.

$CoCl_3.6NH_3$

$CoCl_3.5NH_3$

$CoCl_3.4NH_3$

$CoCl_3.4NH_3$

Conclusion of Werner's Experiment

The atoms **within the square brackets** form a single entity and **do not dissociate** under the reaction conditions.

Colour	Formula	Solution conductivity corresponds to
Yellow	$[Co(NH_3)_6]^{3+}3Cl^-$	1:3 electrolyte
Purple	$[CoCl(NH_3)_5]^{2+}2Cl^-$	1:2 electrolyte
Green	$[CoCl_2(NH_3)_4]^+Cl^-$	1:1 electrolyte
Violet	$[CoCl_2(NH_3)_4]^+Cl^-$	1:1 electrolyte

Isomers

Have identical molecular formula, but **distinct properties**

Werner's Theory

Metals in coordination compounds show **two types of valencies/linkages**

- Primary or ionisable
- Secondary or non-ionisable

Primary Valency

The primary valencies are **normally ionisable** and are satisfied by **negative ions.**

$[Mn(H_2O)_6]Cl_2$

Primary valency

Secondary Valency

The secondary valencies are **non-ionisable**. These are satisfied by **neutral** molecules or **negative** ions.

A secondary valency is **equal to the coordination number** and is **fixed** for a metal.

$[Mn(H_2O)_6]Cl_2$

Secondary valency

Secondary Valency

Primary valency	Secondary valency
It is equal to the **oxidation number** of central atom.	It is equal to the **coordination number.**
It is **non-directional.**	It is **directional** in nature.
It is **ionisable.**	It is **non-ionisable.**

Limitations of Werner's Theory

Werner could not explain :

1. Why only **certain elements** possess the remarkable property of **forming coordination compounds**?
2. Why the bonds in coordination compounds have **directional properties**?
3. Why coordination compounds have characteristic **magnetic and optical properties**?

Valence Bond Theory

The **valence bond theory, VBT,** was extended to coordination compounds by **Linus Pauling.**

In 1931

Valence Bond Theory

Postulate 1

The **formation** of complex involves a **reaction** between a **Lewis base** (ligand) and a **Lewis acid** (metal or metal ion)

With the **formation of a coordinate covalent** (or dative) bonds.

Postulate 2

In order to form a bond, VBT utilises the **concept of hybridisation,** in which (n-1)d, ns, np or ns, np, nd orbitals of a metal atom or ion are hybridised to yield a set of equivalent orbitals of definite geometry.

Note!!

Sometimes, the unpaired (n-1)d electrons pair up as fully as possible prior to hybridisation, thus making some **(n-1)d** orbitals **vacant** for hybridisation.

Valence Bond Theory

Postulate 3

These **hybrid orbitals** are allowed to overlap with **ligand orbitals** that can **donate electron** pairs for bonding.

Consequently, these bonds are of **equal strength** and are **directional** in nature.

Postulate 4

The number of **unpaired electrons** measured by the **magnetic moment** of the compounds determines **which d-orbitals are used.**

Valence Bond Theory

The **hybridisation** and **shape** of the complexes
can be predicted with the help of some known properties.

Magnetic moment

Hybridisation of Coordination Compounds

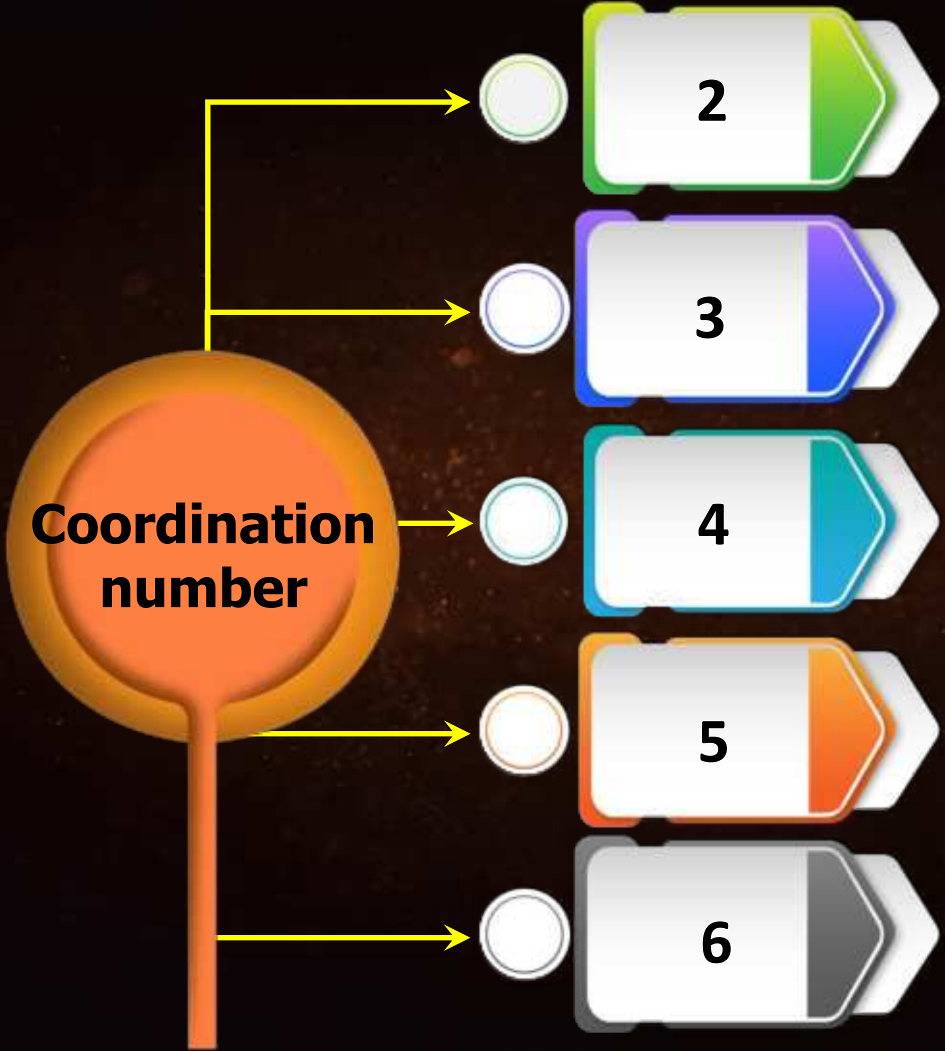
C.N. of metal	2	3
Type of hybridisation	sp	sp^2
Shape of complex	Linear	Trigonal planar
Type of d-orbital	-	-

C.N. of metal	4	4	4
Type of hybridisation	sp^3	dsp^2	d^3s
Shape of complex	Tetrahedral	Square planar	Tetrahedral
Type of d-orbital	-	$d_{x^2-y^2}$	d_{xy}, d_{yz}, d_{xz}

Hybridisation of Coordination Compounds

C.N. of metal	5	5
Type of hybridisation	sp^3d	dsp^3
Shape of complex	Trigonal bipyramidal	Square pyramidal
Type of d-orbital	d_{z^2}	$d_{x^2-y^2}$

C.N. of metal	6	6
Type of hybridisation	sp^3d^2	d^2sp^3
Shape of complex	Octahedral	Octahedral
Type of d-orbital	$d_{x^2-y^2}$, d_{z^2}	$d_{x^2-y^2}$, d_{z^2}



Coordination number

2

3

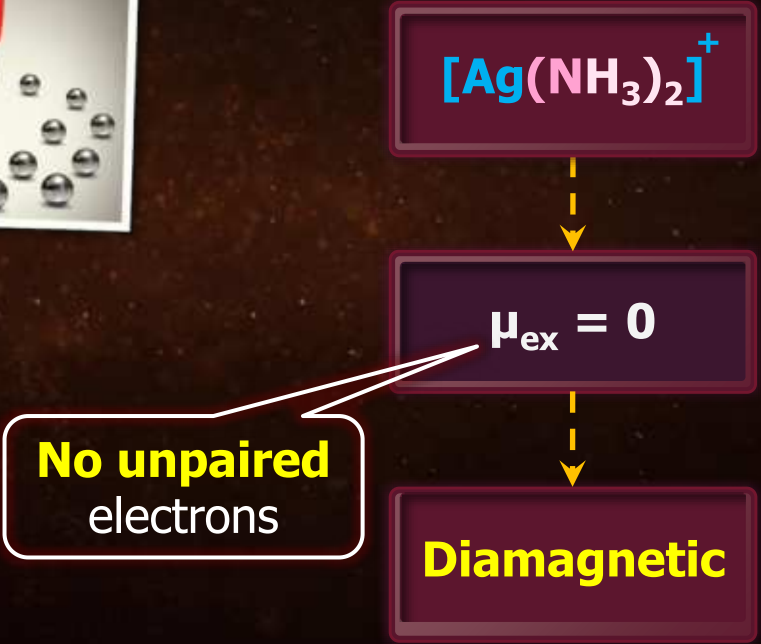
4

5

6

Coordination Number = 2

EXAMPLE



$[Ag(NH_3)_2]^+$

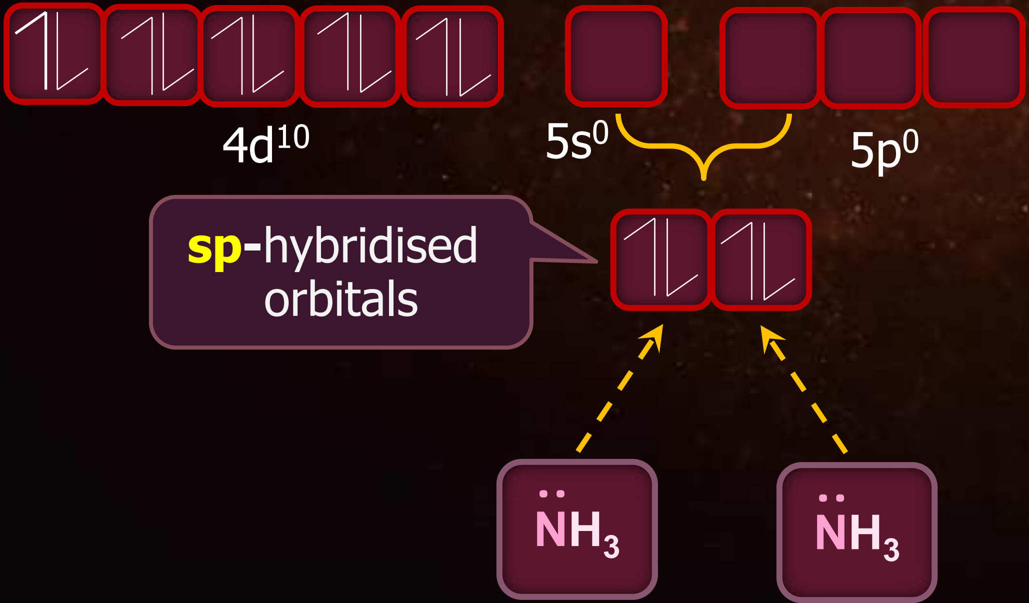
$\mu_{ex} = 0$

No unpaired electrons

Diamagnetic

Coordination Number = 2

Ag^+ = $4d^{10}\ 5s^0\ 5p^0$



$4d^{10}$

$5s^0$

$5p^0$

sp-hybridised orbitals

$\ddot{N}H_3$

$\ddot{N}H_3$

$[Ag(NH_3)_2]^+$

Hybridisation = **sp**

Shape = **Linear**

Coordination Number = 3

EXAMPLE

$[Hg(CN)_3]^-$

$\mu_{ex} = 0$

No unpaired electron

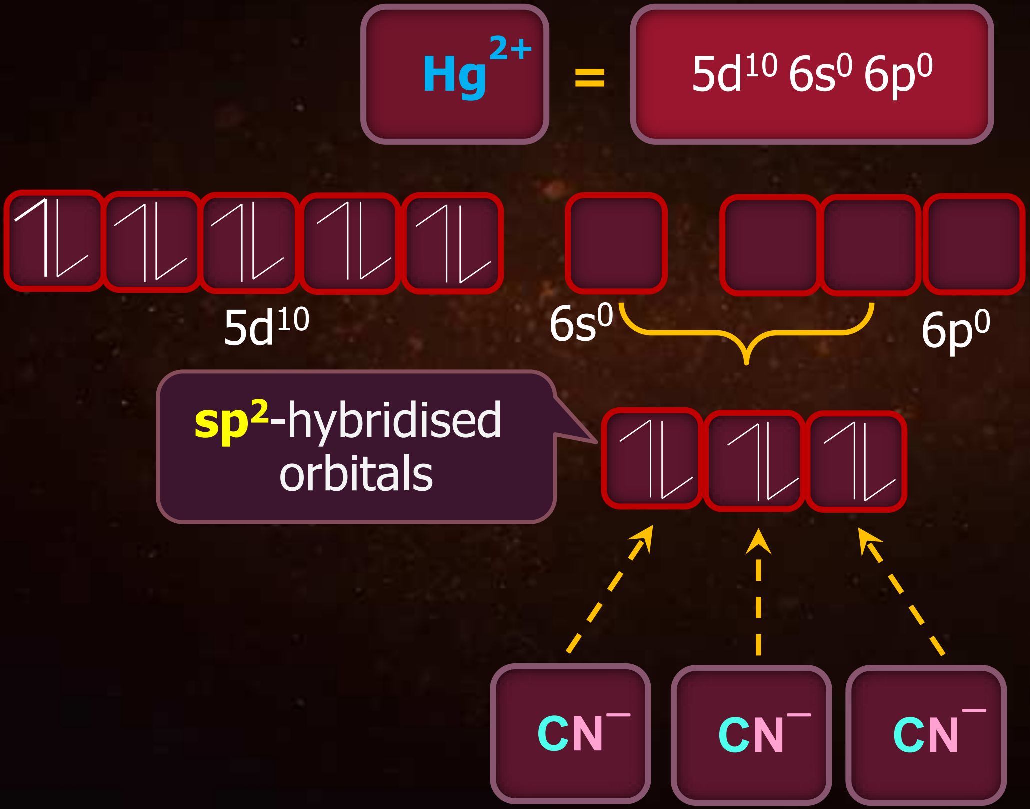
Diamagnetic

$[Hg(CN)_3]^-$

Hybridisation = sp^2

Shape = **Trigonal planar**

Coordination Number = 3



Hg^{2+} = $5d^{10}\,6s^{0}\,6p^{0}$

sp^2-hybridised orbitals

Coordination Number = 4

$[Ni(Cl)_4]^{2-}$

μ_{ex} = 2.5 BM

2 unpaired electrons

Paramagnetic

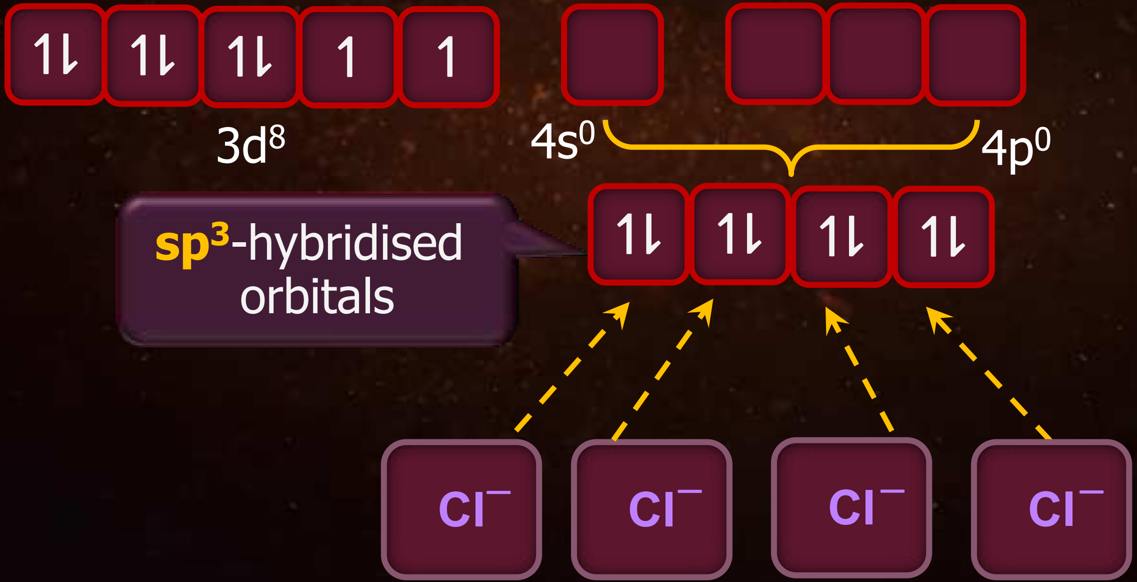
$[Ni(Cl)_4]^{2-}$

Hybridisation = **sp^3**

Shape = **Tetrahedral**

Coordination Number = 4

Ni^{2+} = $3d^8\,4s^0\,4p^0$



sp^3-hybridised orbitals

Coordination Number = 4

$[Ni(CN)_4]^{2-}$

$\mu_{ex} = 0$

Diamagnetic

No unpaired electron

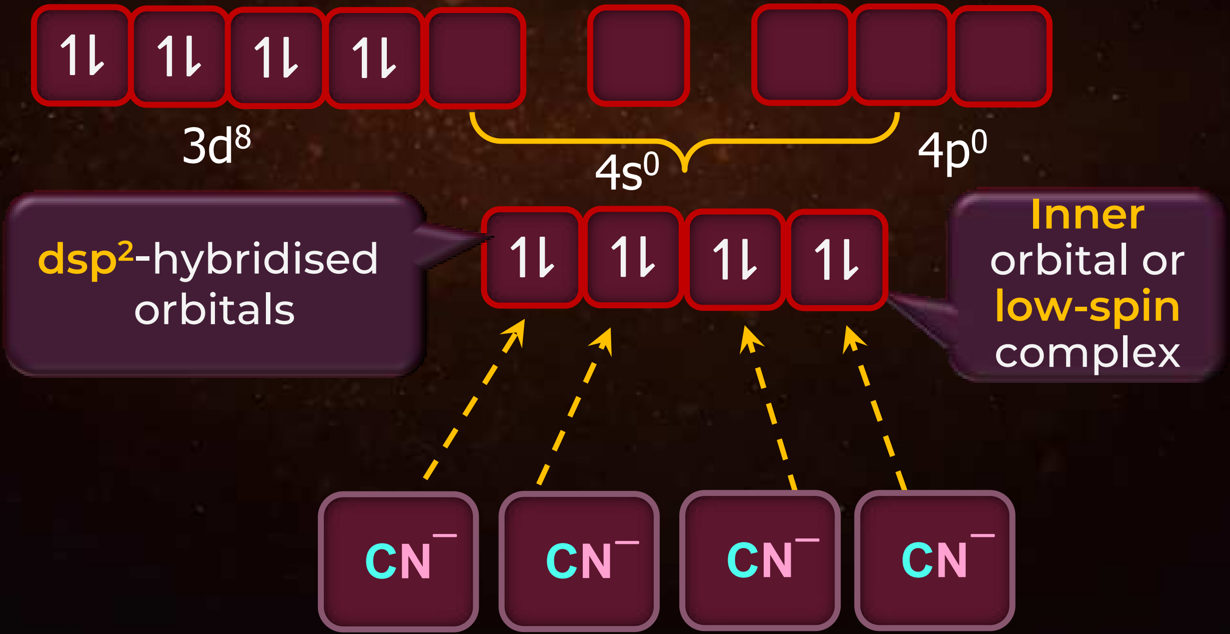
Hybridisation = dsp^2

Shape

Square planar

Coordination Number = 4

Ni^{2+} = $3d^8\ 4s^0\ 4p^0$



dsp^2-hybridised orbitals

Inner orbital or **low-spin** complex

Inner Orbital and Outer Orbital Complex

In the complex formation, the **inner d-orbitals** are used in the hybridisation.

In the complex formation, the **outer d-orbitals** are used in the hybridisation.

Coordination Number = 4

VO_4^{3-}

↓

$\mu_{ex} = 0$

↓

Diamagnetic

No unpaired electron

Hybridisation = d^3s

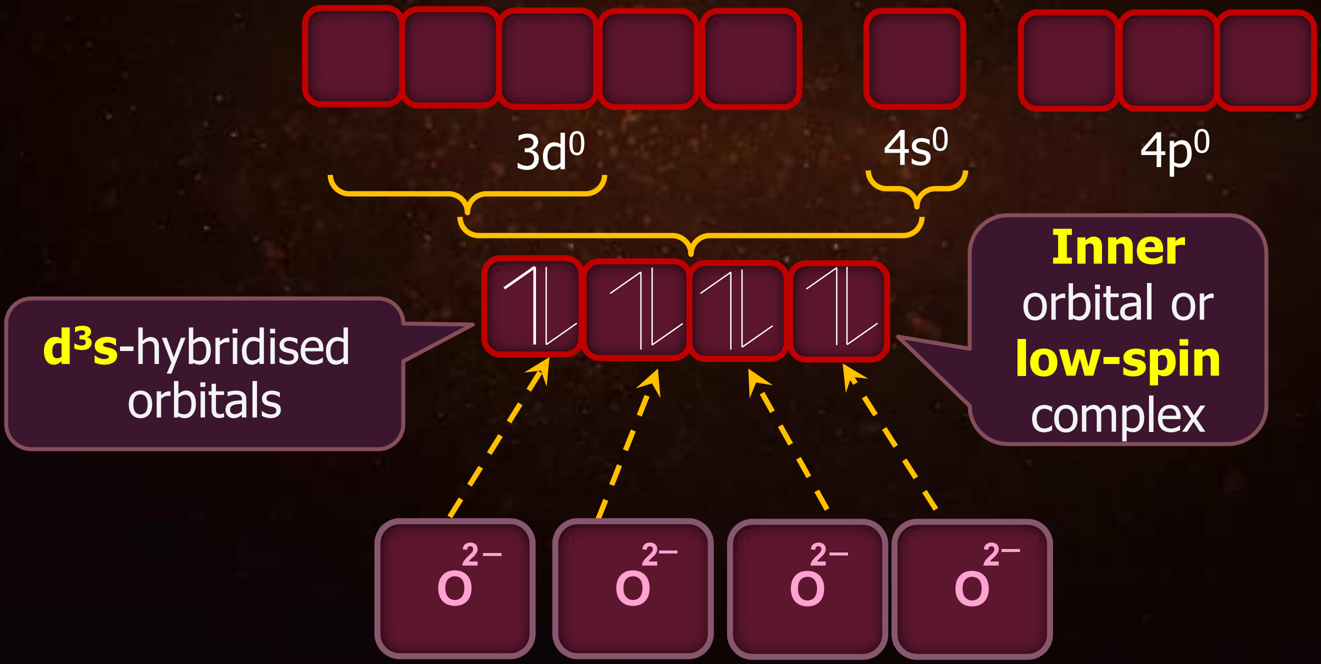
Shape = Tetrahedral

Another example = $KMnO_4$ & $K_2Cr_2O_7$

Coordination Number = 4

VO_4^{3-}

V^{5+} = $3d^0\ 4s^0\ 4p^0$



$3d^0$ $4s^0$ $4p^0$

d^3s-hybridised orbitals

Inner orbital or **low-spin** complex

O^{2-} O^{2-} O^{2-} O^{2-}

Coordination Number = 5

EXAMPLE

$Fe(CO)_5$

↓

$\mu_{ex} = 0$

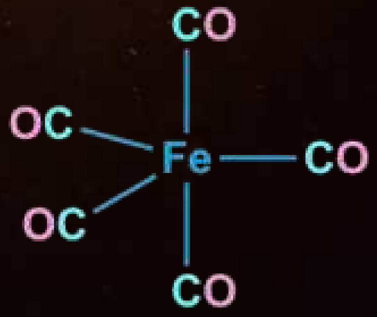
↓

Diamagnetic

No unpaired electron

Hybridisation = **dsp^3**

Shape = **Trigonal bipyramidal**



Coordination Number = 5

Fe^{0} = $3d^6\,4s^2\,4p^0$

$3d^6$

$4s^0$

$4p^0$

dsp^3-hybridised orbitals

Inner orbital or **low-spin** complex

Electron pairs from **CO**

Coordination Number = 6

$[Co(CN)_6]^{3-}$

$\mu_{ex} = 0$

Diamagnetic

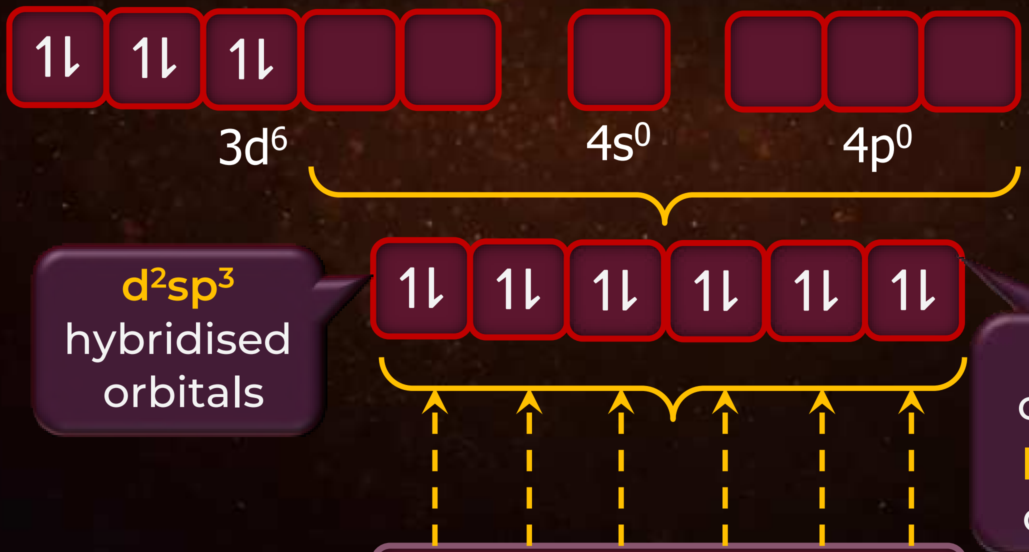
No unpaired electron

Hybridisation = d^2sp^3

Shape = **Octahedral**

Coordination Number = 6

Co^{3+} = $3d^6\ 4s^0\ 4p^0$



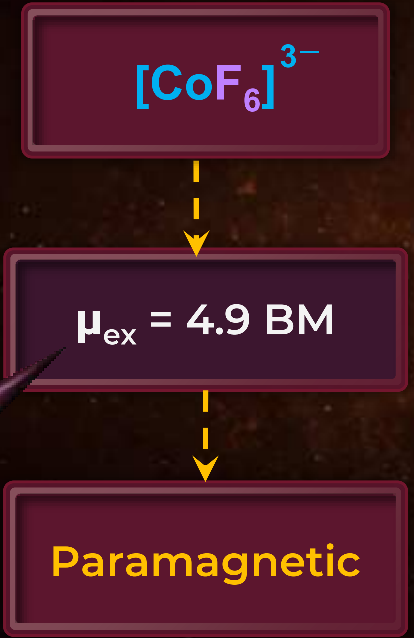
d^2sp^3 hybridised orbitals

Inner orbital or **low-spin** complex

Electron pairs from **CN^-**

Coordination Number = 6

EXAMPLE



$[CoF_6]^{3-}$

μ_{ex} = 4.9 BM

4 unpaired electrons

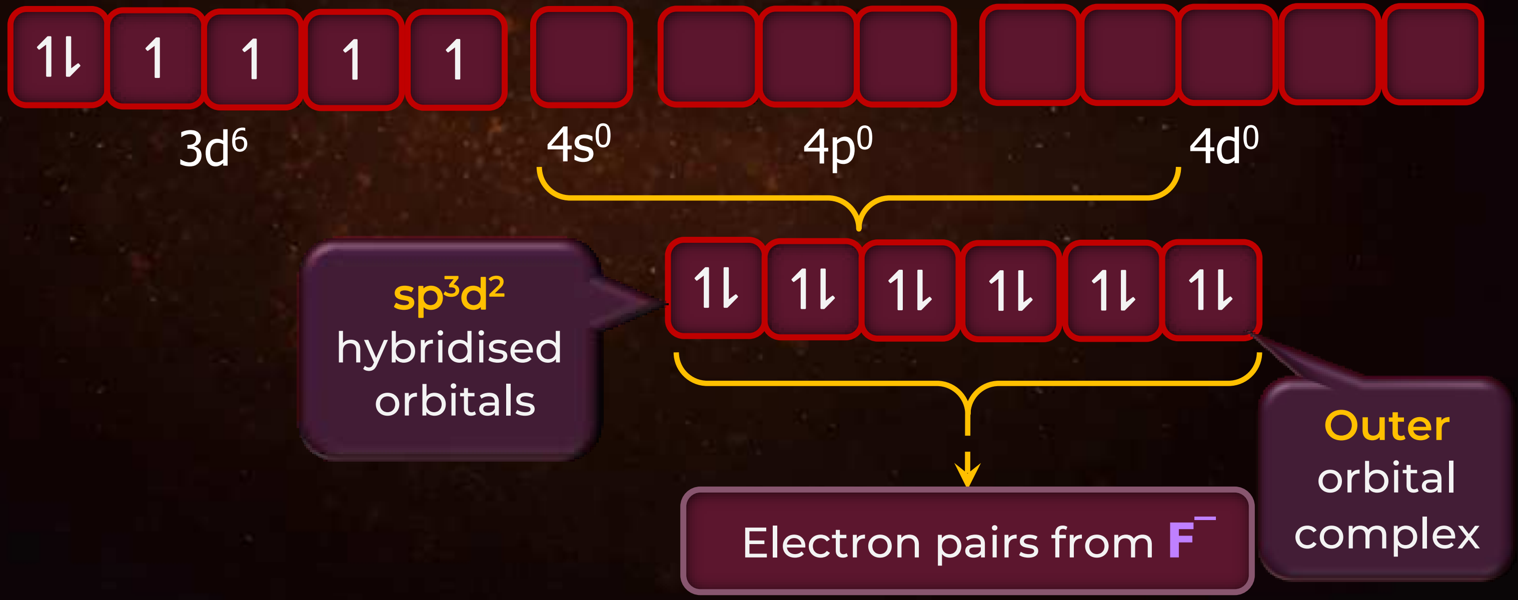
Paramagnetic

Hybridisation = sp^3d^2

Shape = Octahedral

Coordination Number = 6

Co^{3+} = $3d^6 4s^0 4p^0$



$3d^6$ $4s^0$ $4p^0$ $4d^0$

sp^3d^2 hybridised orbitals

Electron pairs from F^-

Outer orbital complex

Limitations of Valence Bond Theory

1. It involves a number of **assumptions.**
2. It **does not** give quantitative interpretation of **magnetic data.**
3. It **does not explain the colour** exhibited by the coordination compounds.
4. It **does not** give a quantitative interpretation of the **thermodynamic or kinetic stabilities** of coordination compounds.
5. It **does not** make exact predictions regarding the **tetrahedral** and **square planar** structures of 4-coordinate complexes.
6. It **does not distinguish** between weak and strong ligands.

Crystal Field Theory

The crystal field theory (CFT) is an **electrostatic model.**

Assumption 1

According to the electrostatic model, the **metal-ligand** bond has to be **ionic** and the interactions are considered as **purely electrostatic**.

Crystal Field Theory

Assumption 2

The **transition metal** that is present as the central atom in the complex is considered as a **positive point charge.**

Assumption 3

When the **ligands** are

- Anions
  - **Point charges**
- Neutral molecules
  - **Point dipoles**

Crystal Field Theory

The arrangement of ligands around the central metal ion is such that the **repulsions** between these points are **minimum**.

Assumption 4

It **considers** the effect of ligands on the **relative energies** of the d-orbitals of the central metal atom/ion.

Crystal Field Theory

Assumption 5

In an **isolated gaseous** metal ion

Five d-orbitals are **degenerate.**

Orbitals that are **identical** in **energy**

Degenerate d-orbitals
(Free metal atom/ion)

Crystal Field Theory

Assumption 6

This degeneracy is still **maintained.** If a **spherically symmetrical field** of ligands **surrounds** the metal atom/ion

Average energy

Degenerate d-orbitals
(Free metal atom/ion)

Overall **energy increased** due to **spherical field** of ligands

Crystal Field Theory

Either **anions** or the negative **ends** of dipolar molecules like **NH_3** and **H_2O**

When there is a negative field **due to ligands** in a complex. It becomes **asymmetrical** and the **degeneracy** of the d-orbitals is **lost**

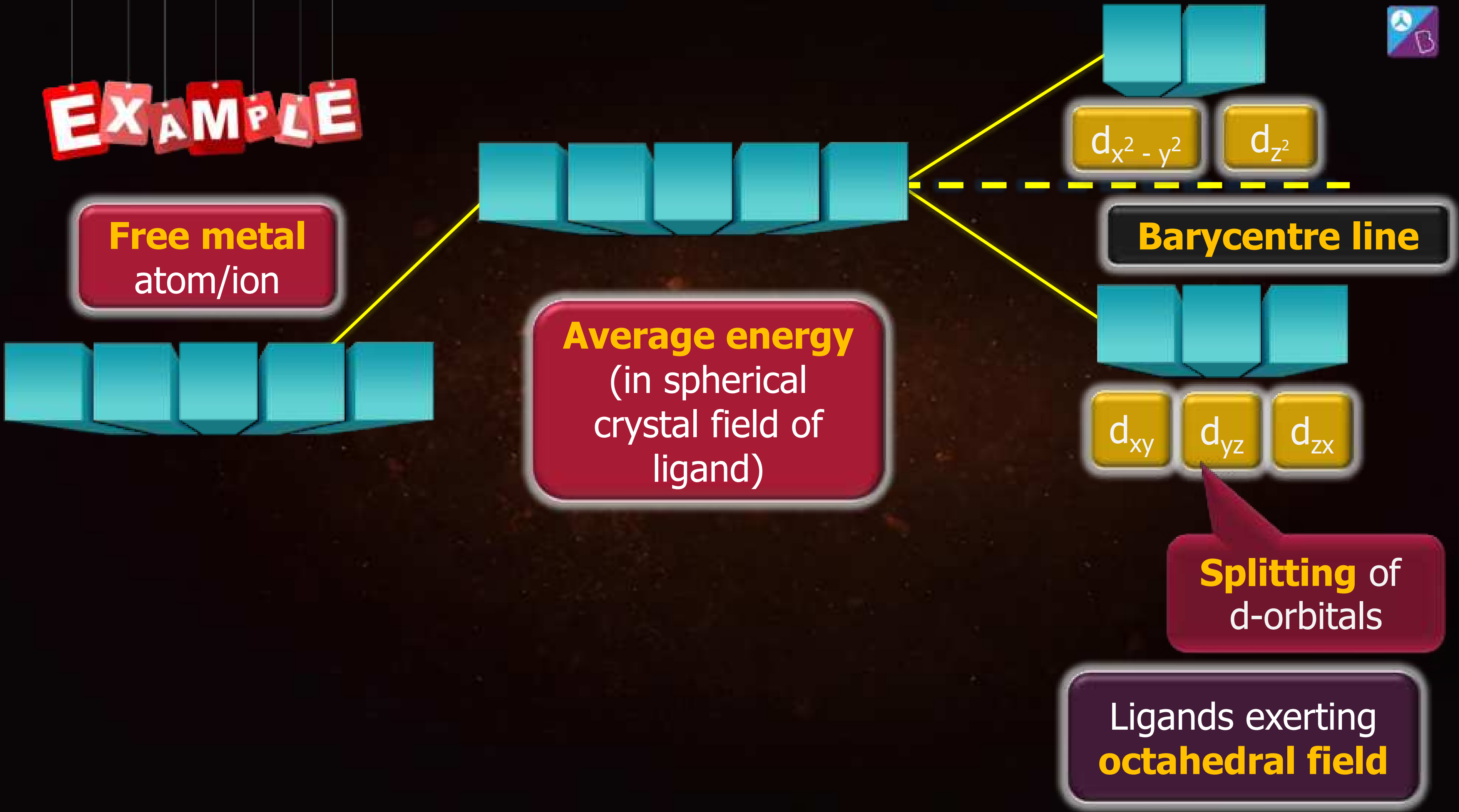
Results in **splitting of d-orbitals**

Crystal Field Theory

The pattern of the splitting depends upon the **nature of the crystal field** exerting its influence on the central metal atom/ion.

For both t_{2g} and e_g orbitals, the d-electrons occupy the orbitals **singly** in accordance with **Hund's rule.**

EXAMPLE



Free metal atom/ion

Average energy (in spherical crystal field of ligand)

$d_{x^2-y^2}$ d_{z^2}

Barycentre line

d_{xy} d_{yz} d_{zx}

Splitting of d-orbitals

Ligands exerting **octahedral field**

Crystal Field Theory

CFT gives an idea about the **electronic distribution** of the central metal ion in the given complex.

Properties like **electronic spectra, colour,** and **magnetic moment** can be determined.

The crystal field **splitting depends** upon the **field** produced by

- Ligand
- Metal ion

Crystal Field Theory

Ligands are able to produce

Strong field

Splitting will be **larger**

Weak field

Splitting will be **smaller**

Generally, ligands can be arranged in a series of **increasing field strength.**

Such a series is termed as **spectrochemical series.**

Spectrochemical Series

Experimentally determined series

I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- <
^-OH < EtOH < Oxalate < H_2O < EDTA <
NH_3 and pyridine < Ethylenediamine < Dipyridyl <
o-phenanthroline < NO_2^- < CN^- < CO

Spectrochemical Series

I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- <

^-OH < EtOH < Oxalate < H_2O < EDTA <

NH_3 and pyridine < Ethylenediamine < Dipyridyl <

o-phenanthroline < NO_2^- < CN^- < CO

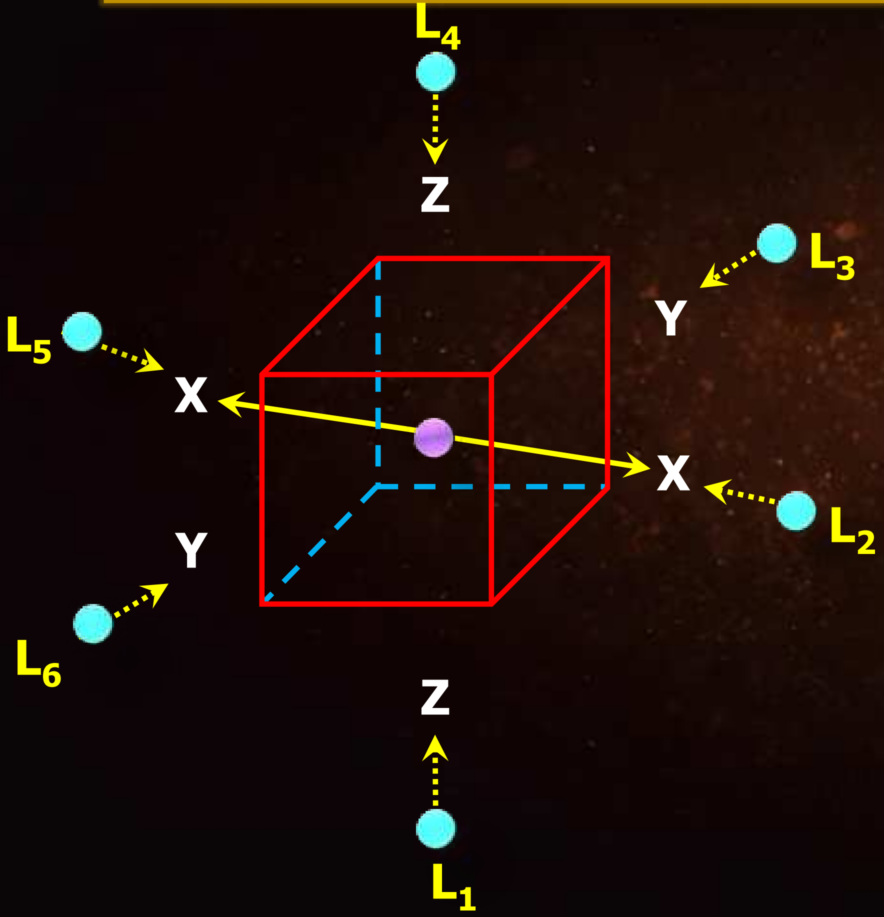
Generally, **strong field** ligands

Spectrochemical Series

Generally, **weak field** ligands

I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- <
^-OH < EtOH < Oxalate < H_2O < EDTA <
NH_3 and pyridine < Ethylenediamine < Dipyridyl <
o-phenanthroline < NO_2^- < CN^- < CO

Approach of Ligands in Octahedral Complex



Ligands approach from/towards the axes.

The orbitals present towards the axes are repelled greater than the orbitals present between the axes.

As a result, the energies of $d_{x^2-y^2}$ and d_{z^2} are increased, and d_{xy}, d_{yz}, and d_{xz} are decreased relative to the average energy in the spherical crystal field.

Splitting in Octahedral Complex

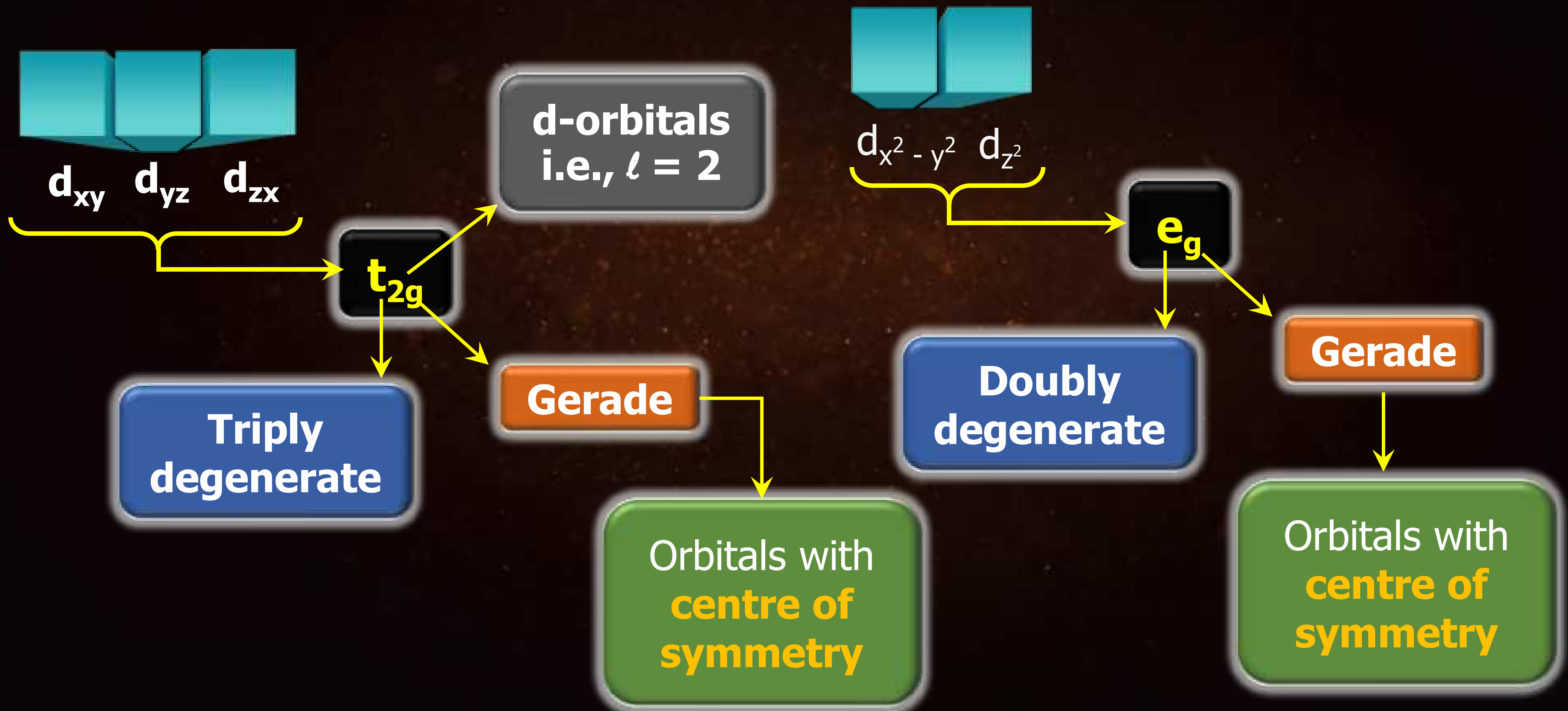
Results

Degeneracy of the d-orbitals is lost due to

Ligand's electron-metal electron repulsions in the octahedral complex

Yield three orbitals of lower energy (t_2g) and two orbitals of higher energy (e_g)

Splitting in Octahedral Complex



d_{xy} d_{yz} d_{zx}

t_{2g}

d-orbitals
i.e., $\ell = 2$

Triply degenerate

Gerade

Orbitals with **centre of symmetry**

$d_{x^2-y^2}$ d_{z^2}

e_g

Doubly degenerate

Gerade

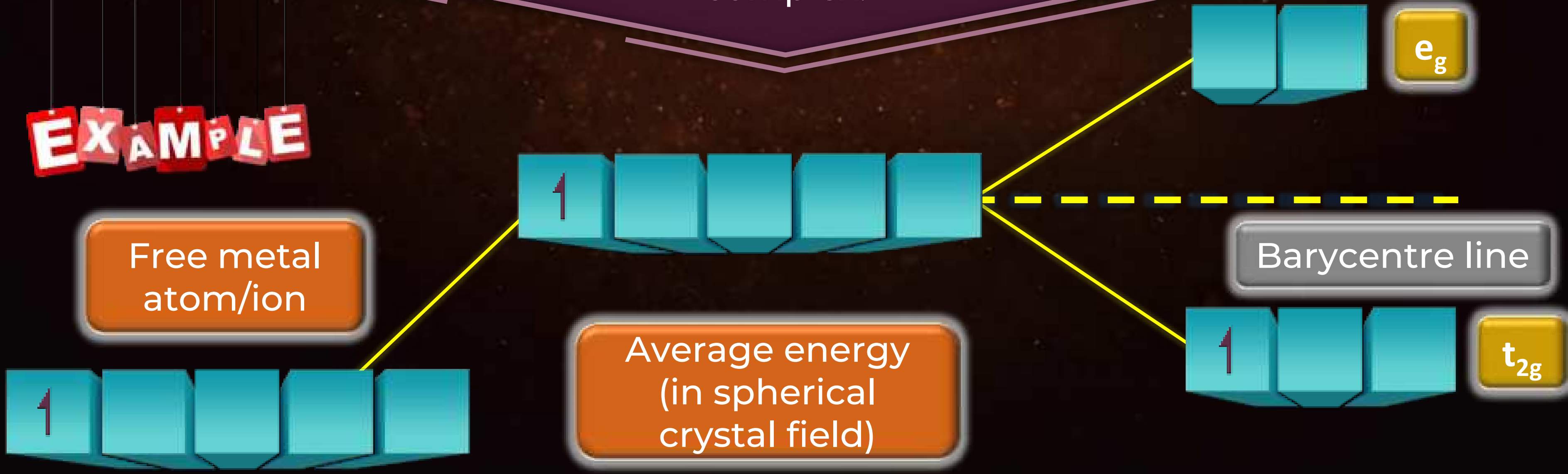
Orbitals with **centre of symmetry**

d-orbital splitting in an octahedral crystal

Splitting in an Octahedral Complex

The energy of **separation** between **e_g** and **t_2g** is known as **crystal field splitting energy (Δo)** in an octahedral complex.

EXAMPLE



Free metal atom/ion

Average energy (in spherical crystal field)

Barycentre line

e_g

t_{2g}

Trick to Remember

Pattern of **increasing sigma donation**

Halide donors < O donors < N donors < C donors

Splitting in Octahedral Complex

In an octahedral coordination entity with **six ligands** surrounding the metal atom/ion, there will be **repulsion** between

1. **Electrons** in metal’s **d-orbitals**

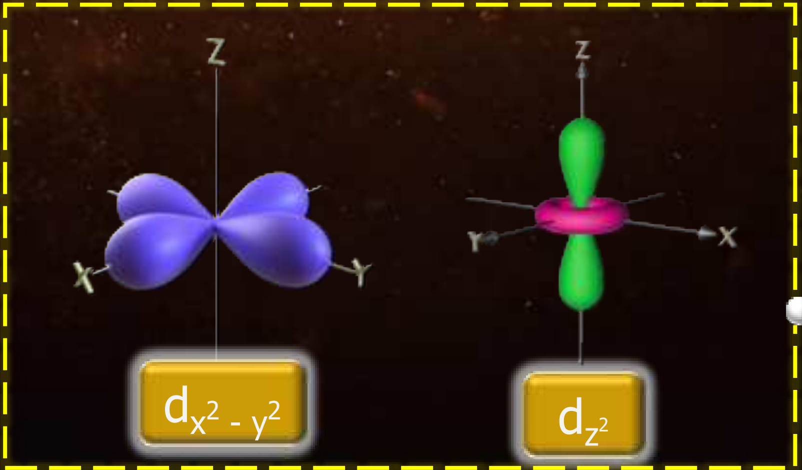
← →

2. **Electrons** (or negative charge) of the **ligands**

To understand the **shift of energy** of orbitals, let’s first see the **structures of d-orbitals.**

Directed between the axes

d_{xy} d_{zx} d_{yz}



$d_{x^2-y^2}$ d_{z^2}

Directed along the axes

Splitting in an Octahedral Complex

For **t_2g** orbitals, the **d-electrons occupy** the orbitals **singly** in accordance with **Hund's rule.**

For **d^4**-configuration, **two** possible **e^- distributions** are

4th electron will singly **occupy e_g orbital**

4th electron will undergo **pairing in t_{2g} orbital**

Splitting in an Octahedral Complex

Two possibilities

$\Delta_o < P$

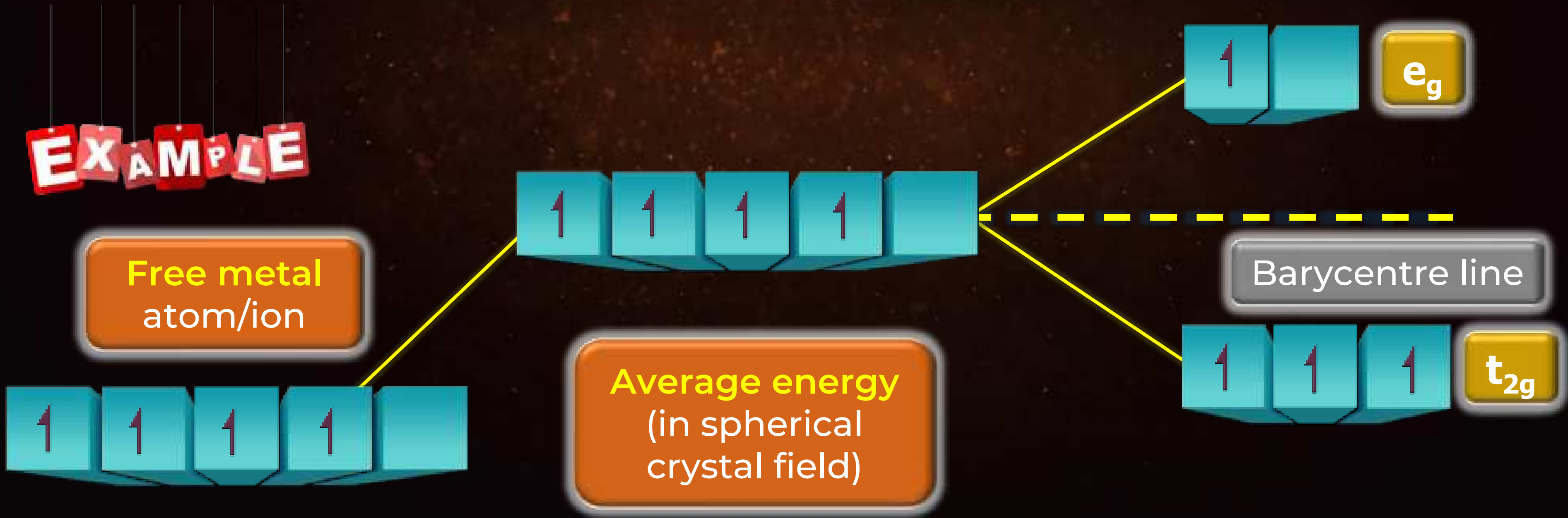
$\Delta_o > P$

Pairing Energy(P)
The energy
required
for **electron
pairing**
in a single orbital

Splitting in an Octahedral Complex

The 4th **electron** enters one of the e_g orbitals

Giving the configuration $t_{2g}^{3}\,e_{g}^{1}$



e_g

Barycentre line

t_{2g}

Free metal atom/ion

Average energy (in spherical crystal field)

Splitting in an Octahedral Complex

Ligands with **$\Delta_o < P$**

Weak field ligands

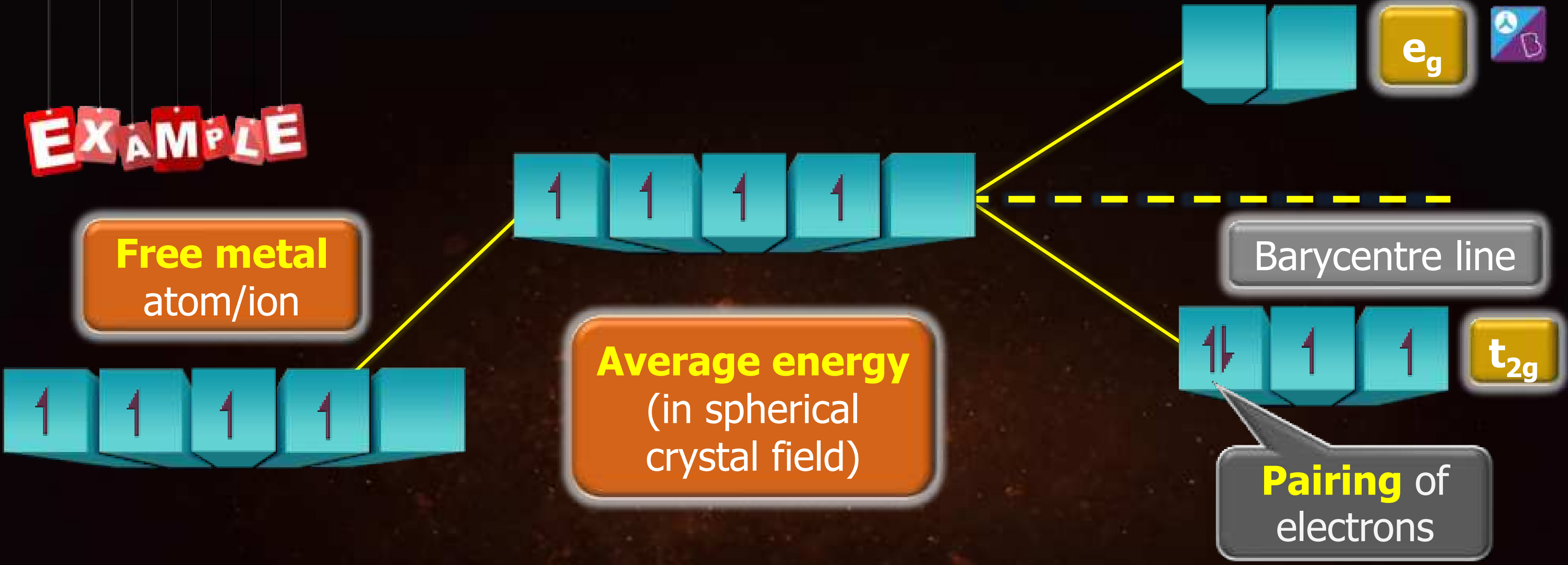
Generally, ligands form a **high-spin complex.**

Ligands with **$\Delta_o > P$**

The **4th** electron becomes **energetically more favourable** to occupy

t_{2g} orbital with configuration **$t_{2g}^4\ e_g^0$**

EXAMPLE



Free metal atom/ion

Average energy (in spherical crystal field)

e_g

Barycentre line

t_{2g}

Pairing of electrons

Splitting in an Octahedral Complex

Ligands with $\Delta_o > P$

Strong field ligands

Generally, ligands form a **low-spin complex.**

Similarly, calculations are done for d^5, d^6, and d^7 configurations.

For d^8, d^9, d^{10} configurations, the d-electrons occupy the e_g orbitals in accordance with **Hund's rule.**

Crystal Field Stabilisation Energy

The energy released by which a complex is **stabilised** (compared to the **free ion**) due to the **splitting** of the **d-orbitals**

$$\text{CFSE} = [-0.4(n)\ t_{2g} + 0.6(n')\ e_g]\Delta_o + n^{*}P$$

Where,

n: Number of e– occupying t_2g orbital

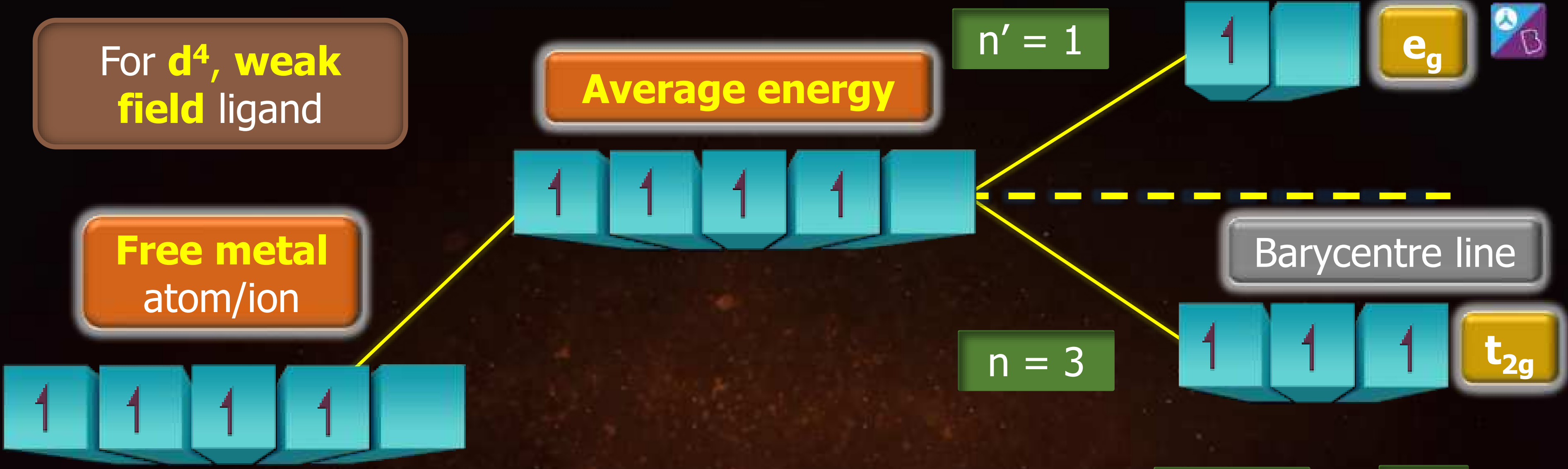
n': Number of e– occupying e_g orbital

Δo: Ligand field splitting energy

n*: Number of extra electron pairs

P: Spin-pairing energy

For **d^4, weak field** ligand



Free metal atom/ion

Average energy

$n' = 1$

e_g

Barycentre line

$n = 3$

t_{2g}

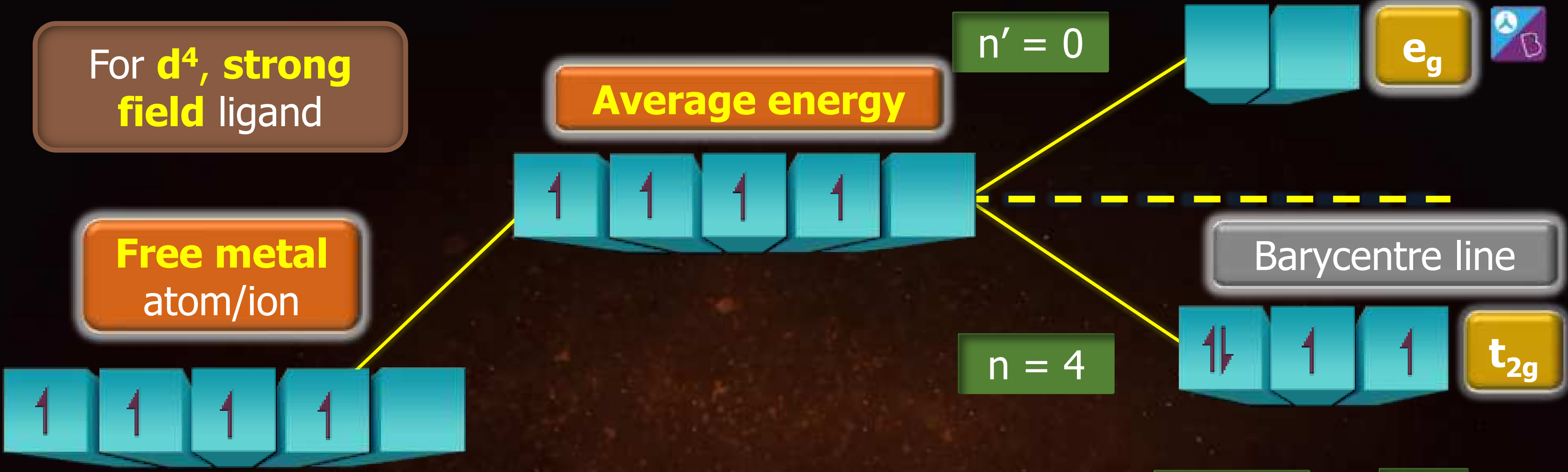
Pairing **does not** occur

$n^* = 0$

$$\text{CFSE} = [-0.4(3) + 0.6(1)]\Delta_o + 0 \times P$$

$$\text{CFSE} = -0.6\Delta_o$$

For d^4, **strong field** ligand



Free metal atom/ion

Average energy

$n' = 0$

e_g

Barycentre line

$n = 4$

t_{2g}

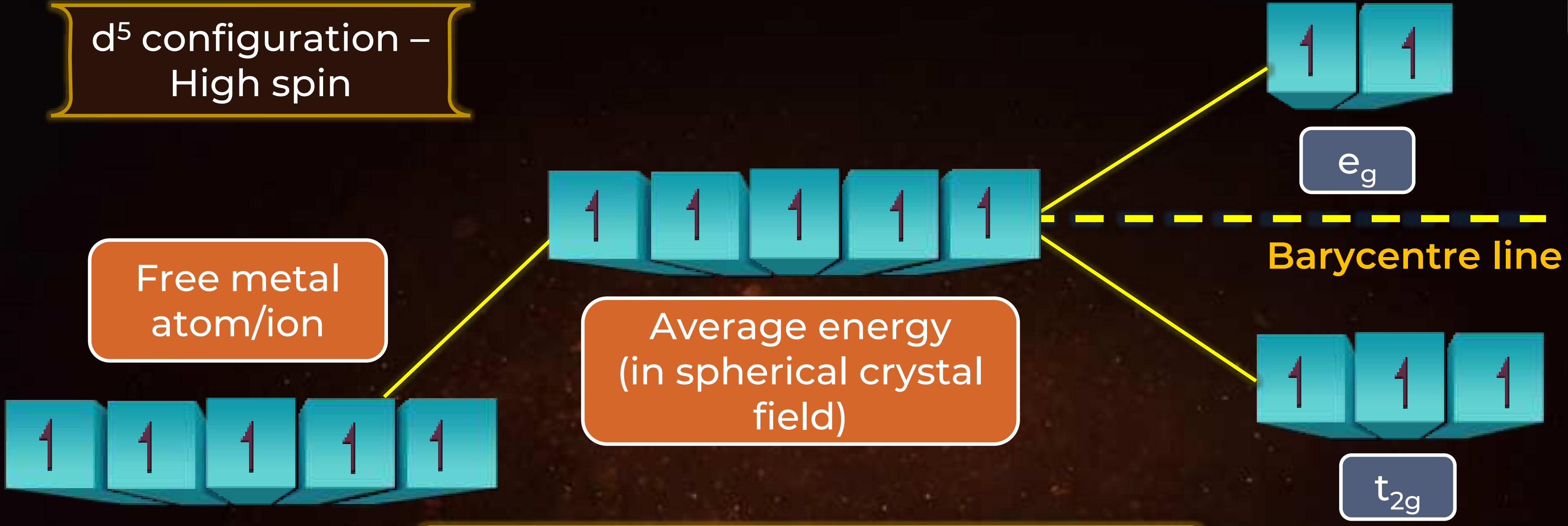
$n^* = 1$

One extra **paired e^-**

CFSE = $[-0.4(4) + 0.6(0)]\Delta_o + 1 \times P$

CFSE = $-1.6\Delta_o + P$

d^5 configuration – High spin



Free metal atom/ion

Average energy (in spherical crystal field)

e_g

Barycentre line

t_{2g}

CFSE $= [\, 0.6(n')e_g - 0.4(n)t_{2g}]\Delta_o + n^*P$

$= [0.6 \times 2 - 0.4 \times 3]\ \Delta_o$

$= 0$

d^5 configuration – Low spin

Free metal atom/ion

Average energy (in spherical crystal field)

Barycentre line

e_g

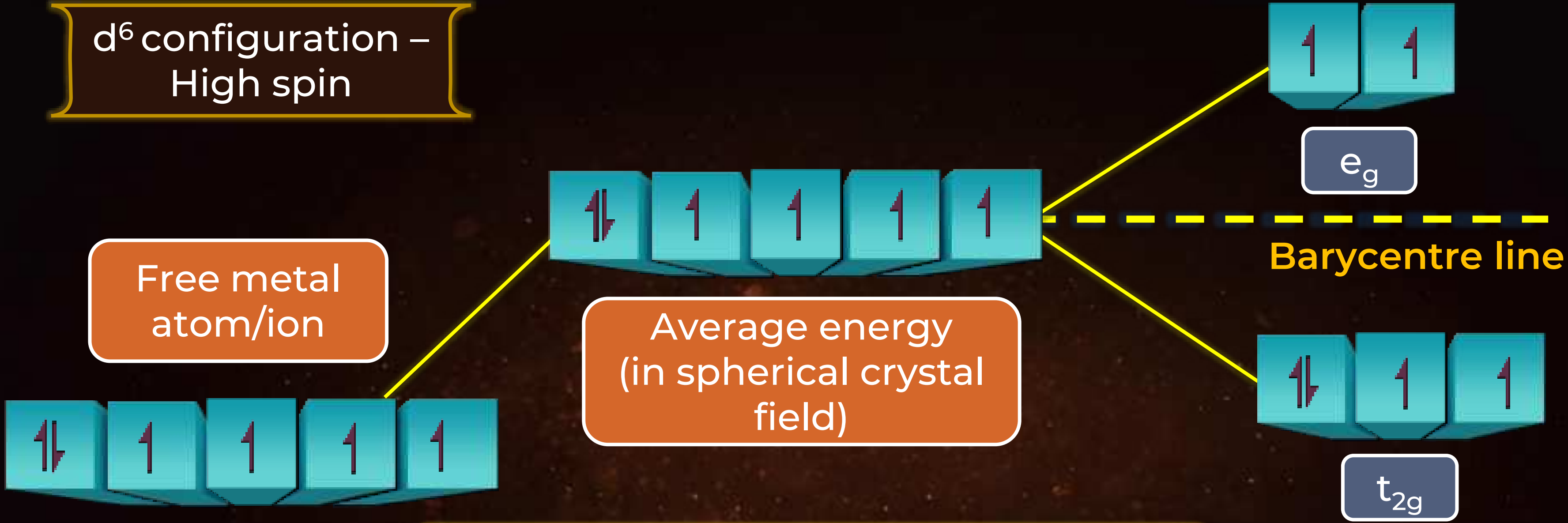
t_{2g}

$$\textbf{CFSE} = [0.6(n')e_g - 0.4(n)t_{2g}]\Delta_o + n^*P$$

$$= [-0.4 \times 5]\,\Delta_o + 2P$$

$$= 2(P - \Delta_o)$$

d^6 configuration – High spin



Free metal atom/ion

Average energy (in spherical crystal field)

e_g

Barycentre line

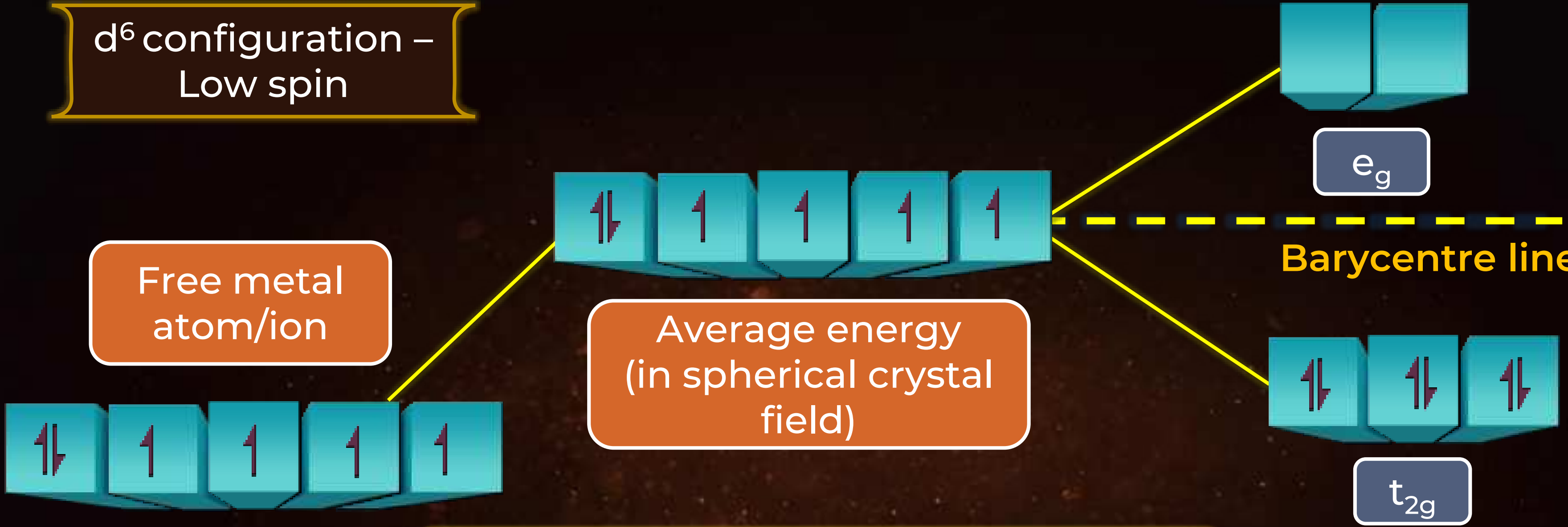
t_{2g}

CFSE $= [0.6(n')e_g - 0.4(n)t_{2g}]\Delta_o + n^*P$

$= [0.6 \times 2 - 0.4 \times 4]\ \Delta_o$

$= -0.4\ \Delta_o$

d^6 configuration – Low spin



Free metal atom/ion

Average energy (in spherical crystal field)

e_g

Barycentre line

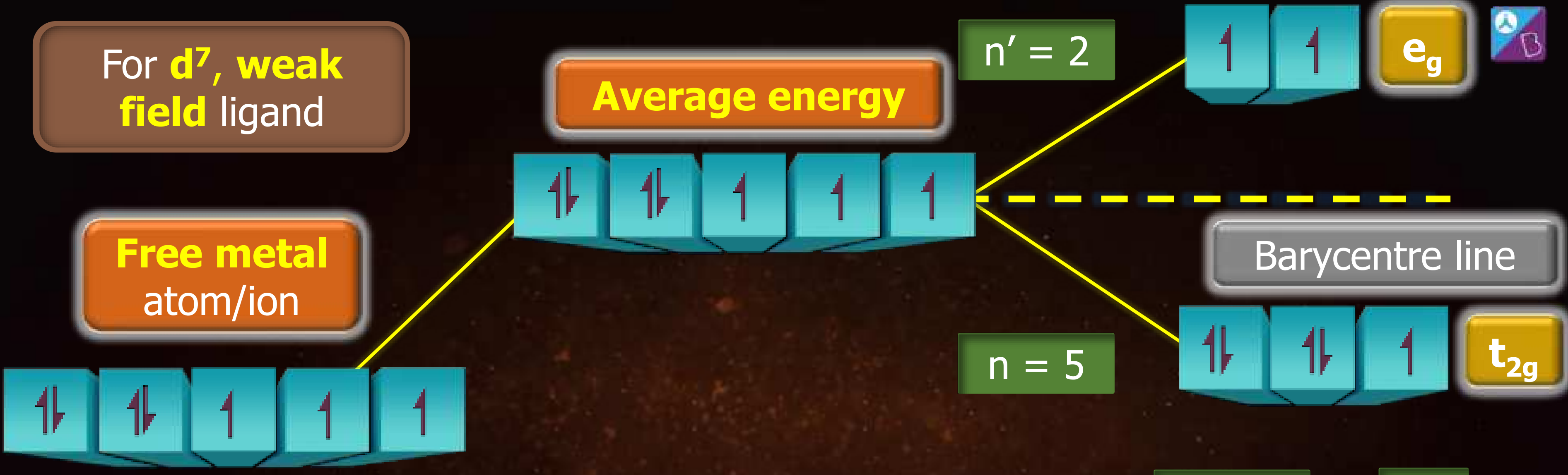
t_{2g}

$$\textbf{CFSE} = [0.6(n')e_g - 0.4(n)t_{2g}]\Delta_o + n^*P$$

$$= [-0.4 \times 6]\ \Delta_o + 2P$$

$$= -2.4\ \Delta_o + 2P$$

For **d^7, weak field** ligand



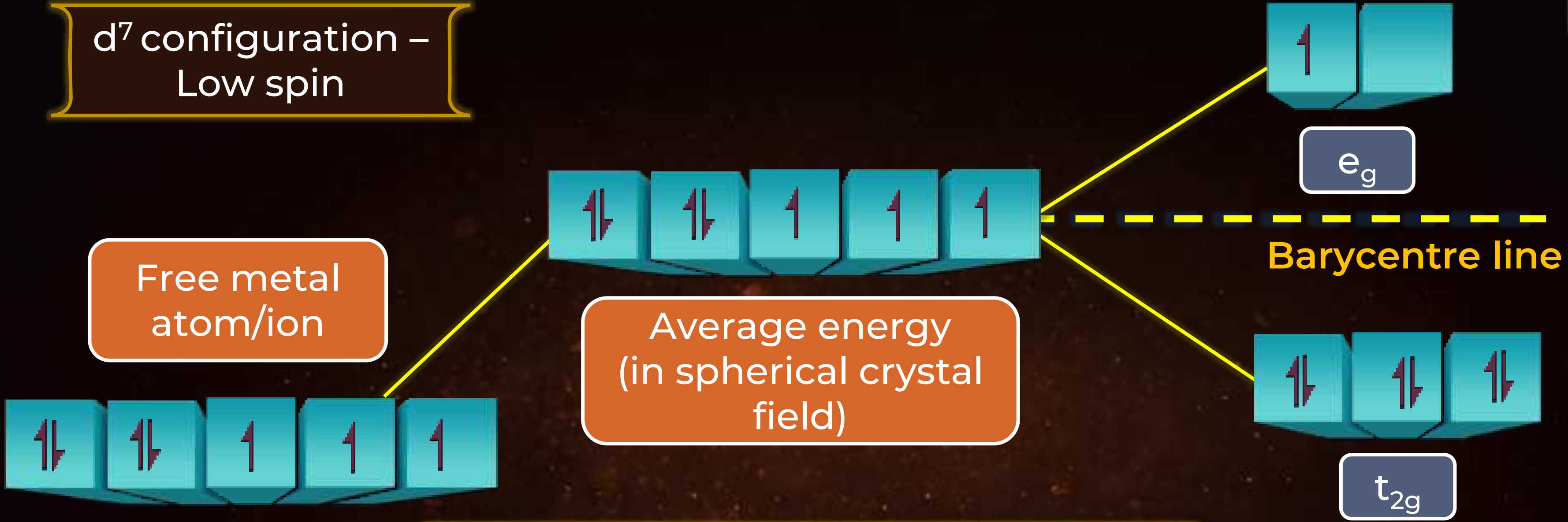
n* = 0

Pairing **does not** occur

CFSE = $[-0.4(5) + 0.6(2)]\Delta_o + 0 \times P$

CFSE = $-0.8\Delta_o$

d^7 configuration – Low spin



Free metal atom/ion

Average energy (in spherical crystal field)

Barycentre line

e_g

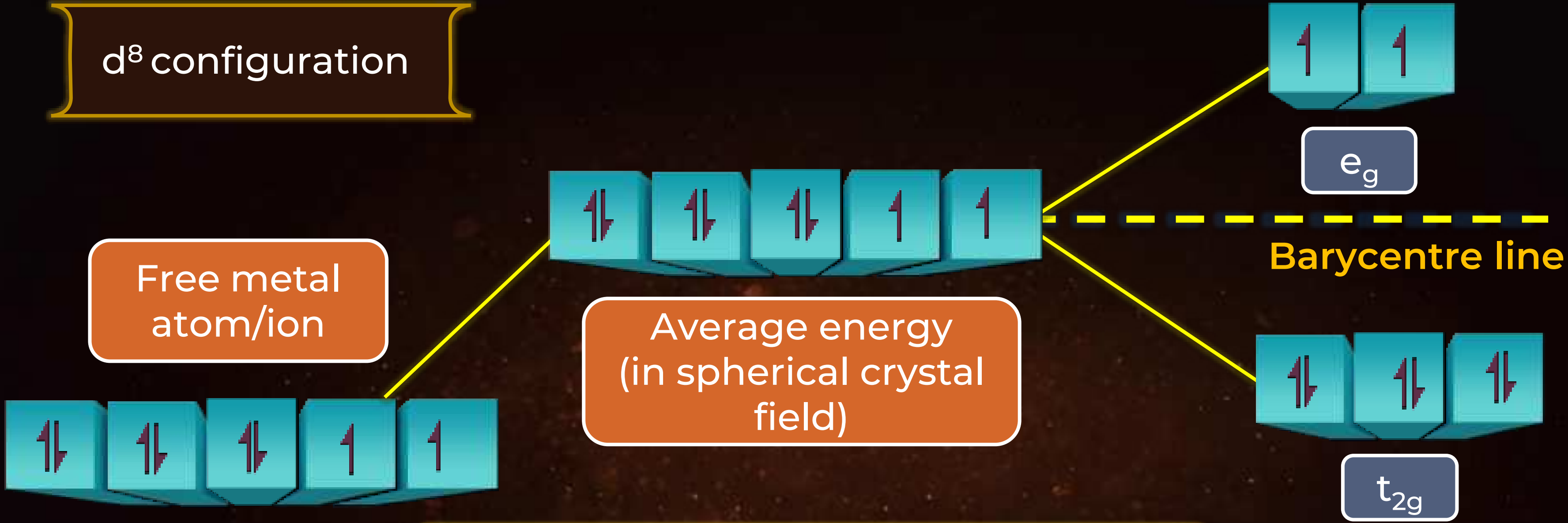
t_{2g}

CFSE $= [0.6(n')e_g - 0.4(n)t_{2g}]\Delta_o + n^*P$

$= [0.6 \times 1 - 0.4 \times 6]\ \Delta_o + P$

$= -1.8\ \Delta_o + P$

d^8 configuration



Free metal atom/ion

Average energy (in spherical crystal field)

e_g

Barycentre line

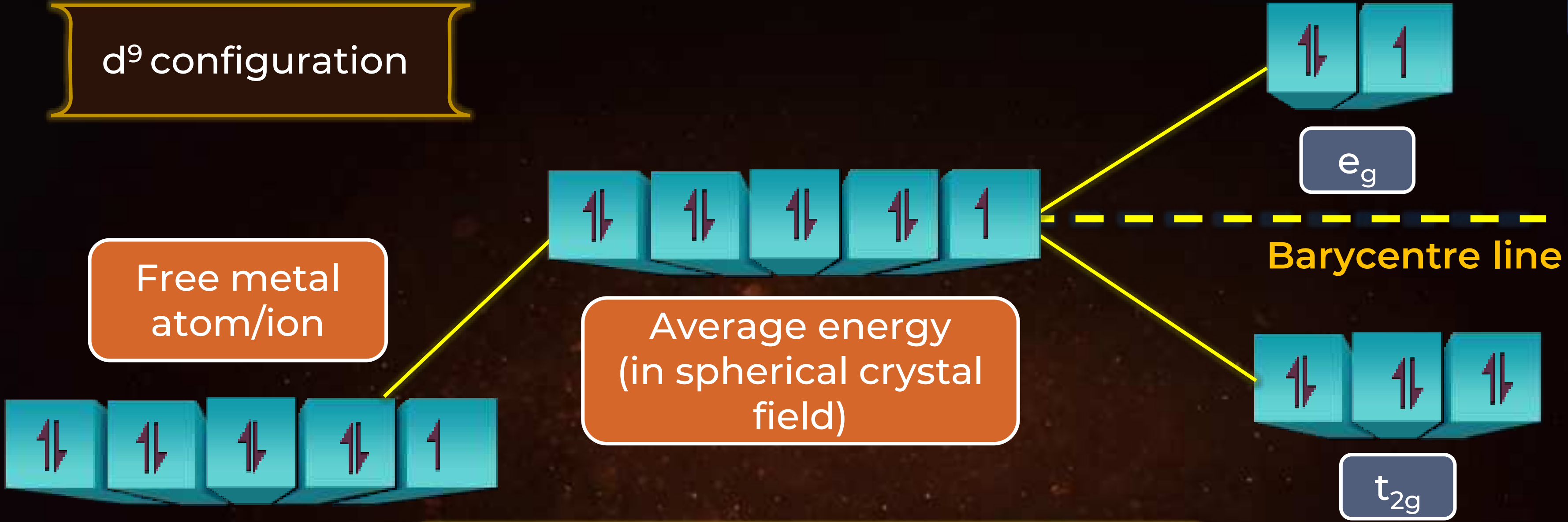
t_{2g}

$$\text{CFSE} = [0.6(n')e_g - 0.4(n)t_{2g}]\Delta_o + n^*P$$

$$= [0.6 \times 2 - 0.4 \times 6]\ \Delta_o$$

$$= -1.2\ \Delta_o$$

d^9 configuration



Free metal atom/ion

Average energy (in spherical crystal field)

Barycentre line

e_g

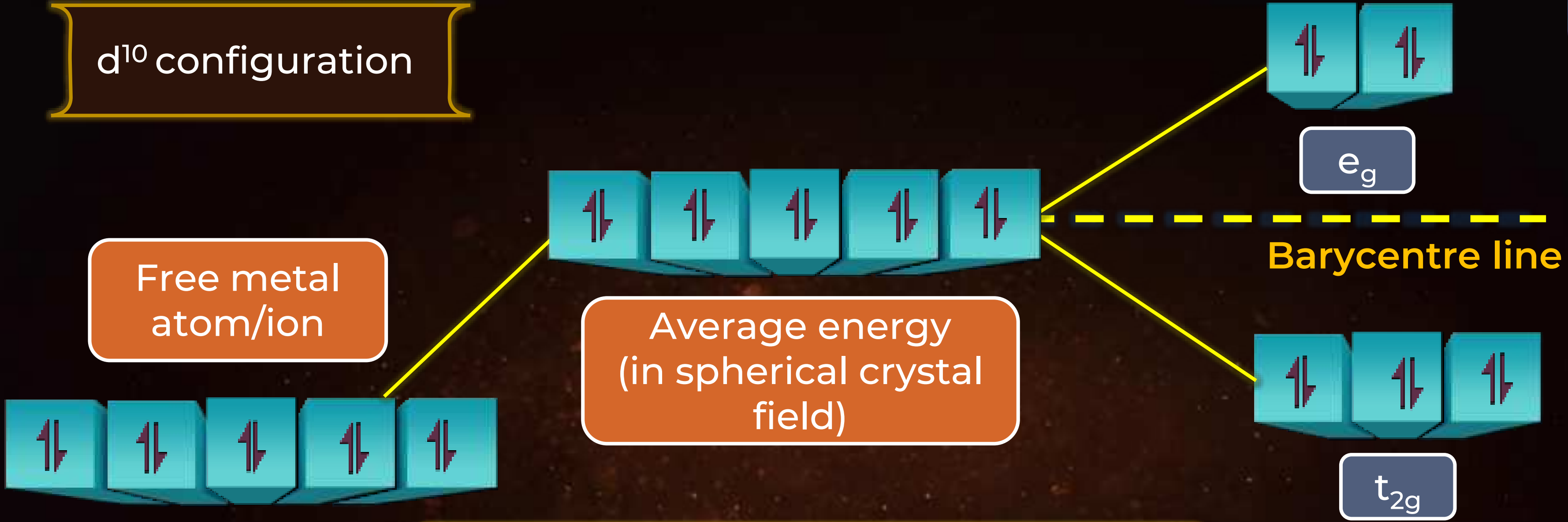
t_{2g}

CFSE $= [0.6(n')e_g - 0.4(n)t_{2g}]\Delta_o + n^*P$

$= [0.6 \times 3 - 0.4 \times 6]\ \Delta_o$

$= -0.6\ \Delta_o$

d^{10} configuration



Free metal atom/ion

Average energy (in spherical crystal field)

e_g

Barycentre line

t_{2g}

CFSE $= [0.6(n')e_g - 0.4(n)t_{2g}]\Delta_o + n^*P$

$= [0.6 \times 4 - 0.4 \times 6]\ \Delta_o$

$= 0$

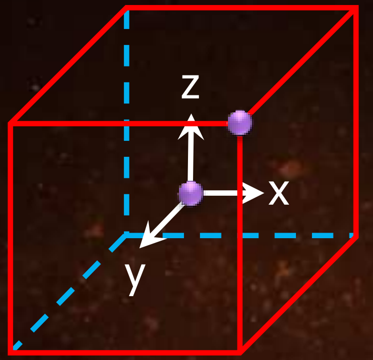
Calculation of CFSE

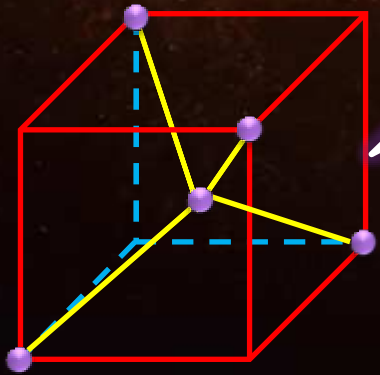
CFSE of **d^4, d^5, d^6, and d^7** electronic configurations in the presence of **WFL** and **SFL**

Electronic configuration	CFSE of WFL	CFSE of SFL
d^4	$-0.6\Delta_o$	$-1.6\Delta_o$
d^5	0	$-2.0\Delta_o$
d^6	$-0.4\Delta_o$	$-2.4\Delta_o$
d^7	$-0.8\Delta_o$	$-1.8\Delta_o$

Calculations show that **d^4** to **d^7** coordination entities are **more stable** for a **strong field** as compared to a **weak field.**

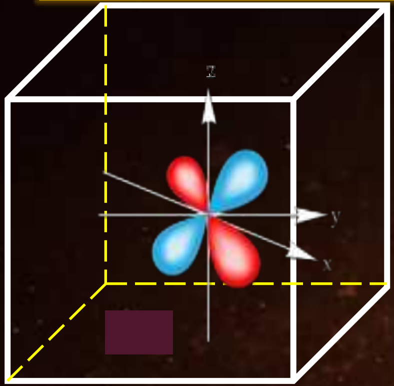
Relation of a Tetrahedron with a Cube



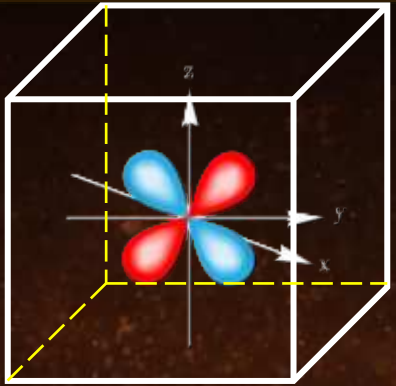


Tetrahedral geometry in a cube

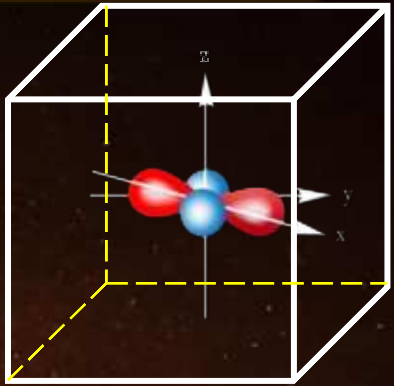
Orientation of d-Orbitals Relative to a Cube



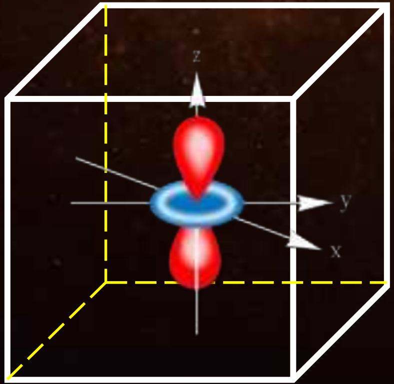
d_{xz}



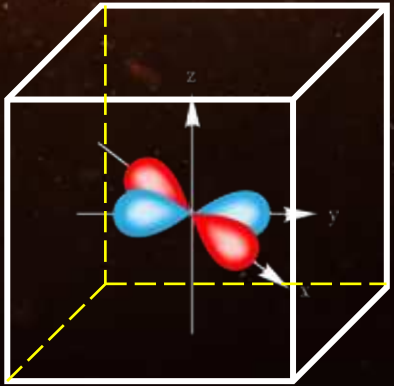
d_{yz}



d_{xy}



d_{z^2}



$d_{x^2-y^2}$

Splitting in Tetrahedral Complexes

In the **splitting** of tetrahedral complexes, the **direction of approach** of the ligands **does not coincide** exactly with either the **e_g** or the **t_{2g} orbitals.**

t_2-Orbitals	e-Orbitals
Nearer to the **ligand's approach** direction	**Away** from the **ligand's approach** direction
Raised in energy in the crystal field of ligands	**Energy raised** but **lower** than t_2 orbitals
Example: d_{xy}, d_{yz}, d_{xz}	Example: $d_{x^2-y^2}$, d_{z^2}

Note!!

The crystal field **splitting** in a **tetrahedral** complex is in the **opposite way** to that in an **octahedral** complex.

d-orbital splitting in a tetrahedral crystal

The crystal field **splitting** in a **tetrahedral** complex is in the **opposite way** to that in an **octahedral** complex.

Splitting in Tetrahedral Complex

The **'g'** subscript is used for the **octahedral** complexes that have **centre of symmetry.**

Since **tetrahedral** complexes **lack symmetry, 'g'** subscript is **not used** with energy levels.

The **magnitude** of the crystal field splitting **(Δ_t) in tetrahedral** complexes is considerably **less than** in **octahedral** fields.

$$\Delta_t = \frac{2}{3} \times \frac{2}{3} \Delta_o \approx \frac{4}{9} \Delta_o$$

Splitting in Tetrahedral Complexes

$$\Delta_t = \mathbf{\frac{2}{3}} \times \frac{2}{3}\Delta_o = \frac{4}{9}\Delta_o$$

There are **only four ligands** instead of six. So, the **ligand field** is only **two-third** the size.

Hence, the ligand field **splitting** is also **two-thirds** the size.

$$\Delta_t = \frac{2}{3} \times \mathbf{\frac{2}{3}}\Delta_o = \frac{4}{9}\Delta_o$$

The **direction** of the **orbitals does not coincide** with the direction of the **ligands.**

This **reduces** the crystal field splitting by roughly a further **two-third.**

Splitting in Tetrahedral Complexes

Strong field ligands cause a **bigger energy difference** between t_{2g} and e_g than weak field ligands.

Tetrahedral splitting Δ_t is always **much smaller than** octahedral splitting Δ_o.

Results

It is **never energetically favourable** to pair electrons.

All tetrahedral complexes are **high-spin.**

CFSE In Tetrahedral Complexes

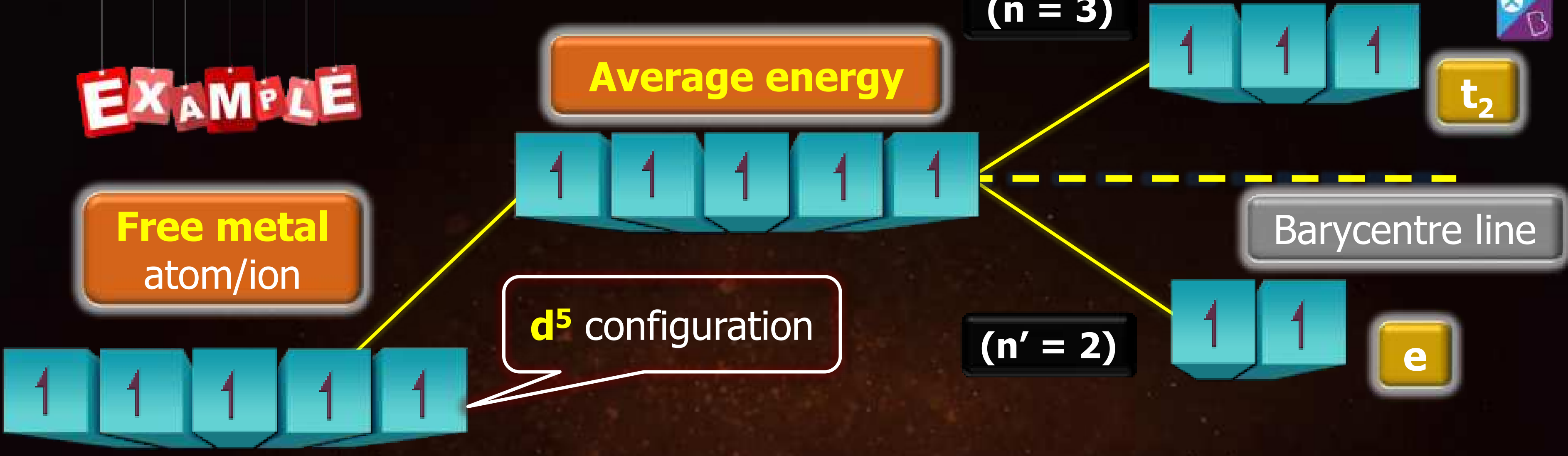
CFSE = $[\ 0.4(n)\ t_2 - 0.6(n')\ e\ ]\Delta_t$

Where,

n: Number of electrons occupying **t_2** orbital

n': Number of electrons occupying **e** orbital

Δ_t: Ligand field splitting energy



EXAMPLE

Free metal atom/ion

d^5 configuration

Average energy

(n = 3)

t_2

Barycentre line

(n′ = 2)

e

CFSE in Tetrahedral Complexes

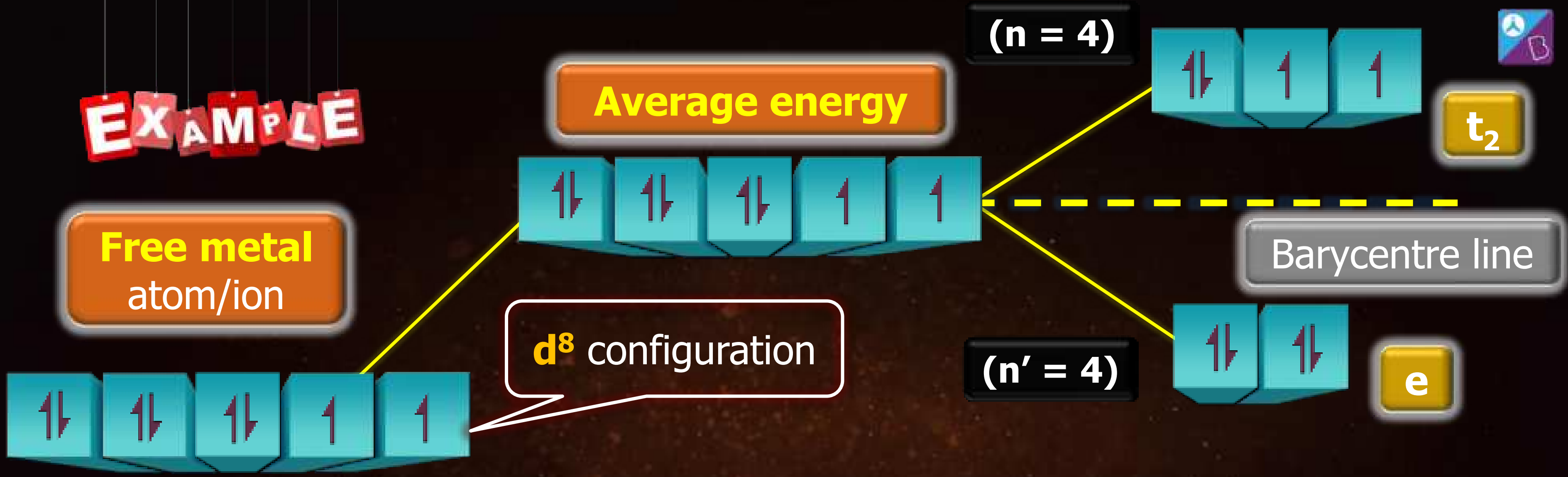
CFSE = $[0.4(n)\ t_2 - 0.6(n')\ e]\Delta_t$

= $[0.4 \times 3 - 0.6 \times 2]\Delta_t$

= $[1.2 - 1.2]\Delta_t$

= **0**

EXAMPLE



Free metal atom/ion

d^8 configuration

Average energy

(n = 4)

t$_2$

Barycentre line

(n′ = 4)

e

CFSE in Tetrahedral Complexes

$$\text{CFSE} = [\,0.4(n)\,t_2 - 0.6(n')\,e\,]\Delta_t$$

$$= [\,0.4 \times 4 - 0.6 \times 4\,]\Delta_t$$

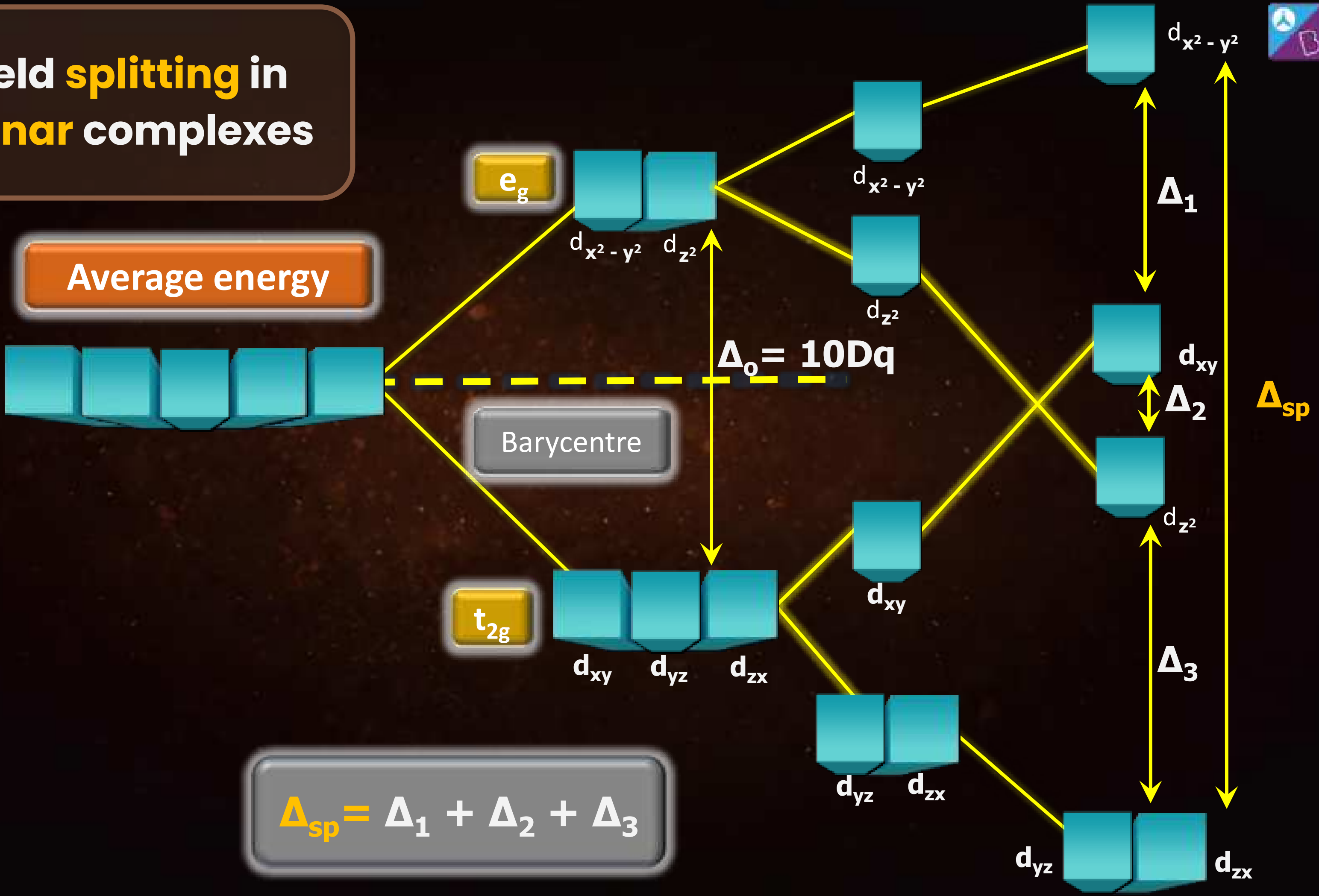
$$= [\,1.6 - 2.4\,]\Delta_t$$

$$= \mathbf{-0.8\Delta_t}$$

Square Planar Complexes

The **square planar** arrangement of ligands is derived from octahedral ligand field by **removing two trans ligands** located along the **z-axis.**

Crystal field splitting in square planar complexes



$$\Delta_{sp} = \Delta_1 + \Delta_2 + \Delta_3$$

Conclusion

More repulsion

d-orbitals

- $d_{x^2-y^2}$ → Along the axis → Greater energy
- d_{xy} → Between the axes → Energy raised, but lower than $d_{x^2-y^2}$
- d_{z^2} → Along the axis → Lower energy than d_{xy}
- d_{xz} & d_{yz} → Between the axes → Least energy

CFSE in Square Planar Complexes

Δ_{sp} > Δ_o

Because d_{xz} and d_{yz} orbitals interact with **only two ligands** in **square planar** complexes, but in **octahedral** complexes, interaction takes place with **four ligands**

Δ_{sp} = $1.3\Delta_o$

Factors Affecting Stability of Complexes

Stability of a complex $\propto$ CFSE $\propto$ CFS

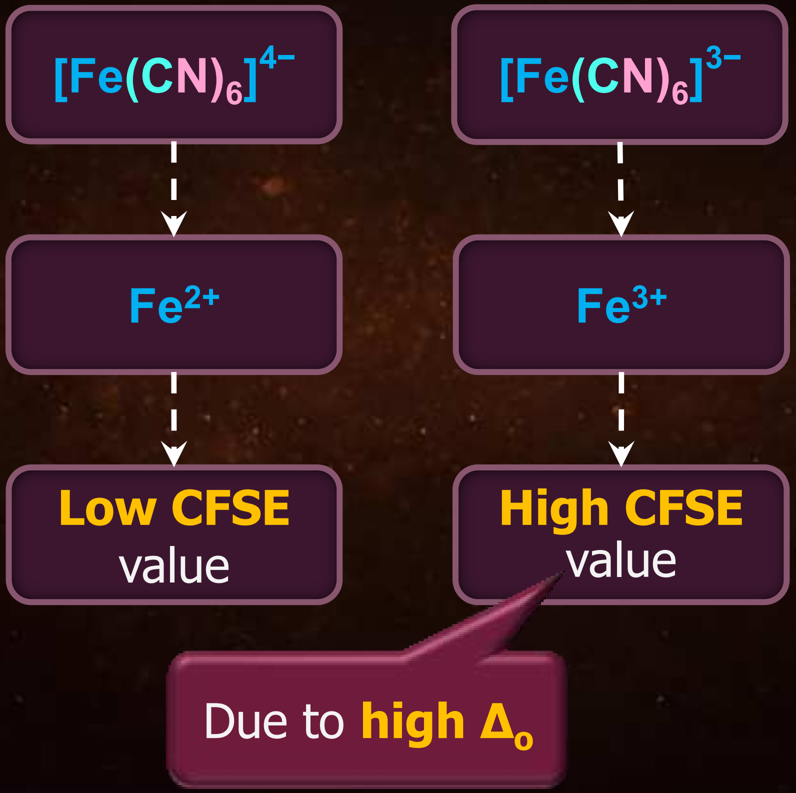
1 **Oxidation state** of central atom

CFSE $\propto$ Oxidation state

For the **same metal** ion, **same ligand,** and **fixed** coordination number

Factors Affecting Stability of Complexes

EXAMPLE



$[Fe(CN)_6]^{4-}$ → Fe^{2+} → **Low CFSE** value

$[Fe(CN)_6]^{3-}$ → Fe^{3+} → **High CFSE** value

Due to **high Δ_o**

Factors Affecting Stability of Complexes

2 Nature of ligand

Strong field ligand **(SFL)** → **More CFSE** value

Weak field ligand **(WFL)** → **Less CFSE** value

Because the **strength of ligand** can vary the **Δ** of the complex

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

SFL

↓

More CFSE value

$[CoF_6]^{3-}$

WFL

↓

Less CFSE value

Factors Affecting Stability of Complexes

3 Geometry of complex

Order of CFSE/CFS

Square planar > Octahedral > Tetrahedral

$[Ni(CN)_6]^{4-}$ → Octahedral

$[Ni(Cl)_4]^{2-}$ → Tetrahedral

$[Ni(CN)_4]^{2-}$ → Square planar

Order of CFSE

$[Ni(CN)_4]^{2-}$ > $[Ni(CN)_6]^{4-}$ > $[Ni(Cl)_4]^{2-}$

Factors Affecting Stability of Complexes

4 Nature of metal cation

CFSE ∝ Size of metal cation

For the same ligand and oxidation state, i.e., 3d < 4d < 5d

Down the group

Order of CFSE

$Co^{3+} < Rh^{3+} < Ir^{3+}$

$Ni^{2+} < Pd^{2+} < Pt^{2+}$

$Cu^{+} < Ag^{+} < Au^{+}$

Factors Affecting Stability of Complexes

5 Formation constant **(K_f)** or stability constant **(K_s)**

Stability $\propto$ **K_f** or **K_s**

For the **same metal** ion, **same ligand,** and **fixed** coordination number

Factors Affecting Stability of Complexes

General reaction

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$$

$$K_s = K_f = \frac{[ML_n]}{[M(H_2O)_n]\,[L]^n}$$

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

$$K_s = K_f = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}]\,[NH_3]^4}$$

Note!!

Greater the value of K_f/K_s, **more** is the thermodynamic **stability** of a complex.

Factors Affecting Stability of Complex

6 **Chelation**

Stability $\propto$ Number of **rings** in a **chelate** complex

A **chelating complex** would be generally **more stable.**

Magnetic Moment of a Complex

Generally,

Coordination compounds have **partially filled** d-orbitals.

Due to this, they show a **characteristic magnetic property.**

Formula

Spin-only magnetic moment

$$\mu = \sqrt{n(n+2)}\ \text{B.M.}$$

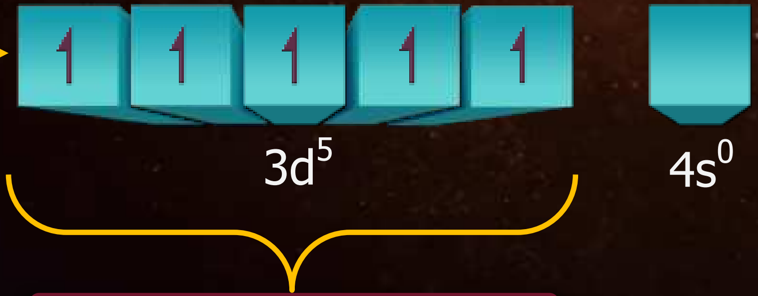
Where, **n** is the number of **unpaired electrons.**

Magnetic Moment of a Complex

EXAMPLE

$[FeF_6]^{3-}$

Fe^{3+}



5 unpaired electrons

$\mu = \sqrt{5(5+2)}$ B.M.

$\mu = \sqrt{35}$ B.M.

$\mu = 5.91$ B.M.

Limitations of CFT

Limitation 1

It considers only the metal ion **d-orbitals.**

It gives **no consideration** at all to other metal orbitals (**s, p_x, p_y, and p_z** orbitals).

Limitation 2

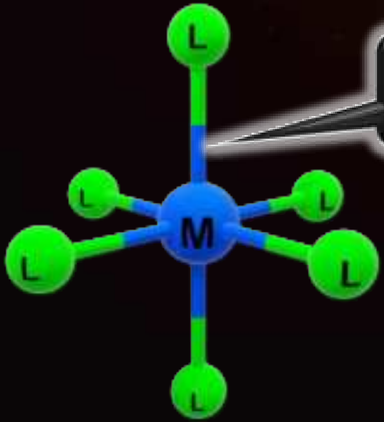
It is unable to explain the relative **strengths of ligands**.

For example, it gives **no explanations** regarding why **H_2O** is a **stronger ligand** than **OH^-** in the spectrochemical series.

Limitations of CFT

Limitation 3

The CFT **could not** explain the **π-bonding** in complexes.

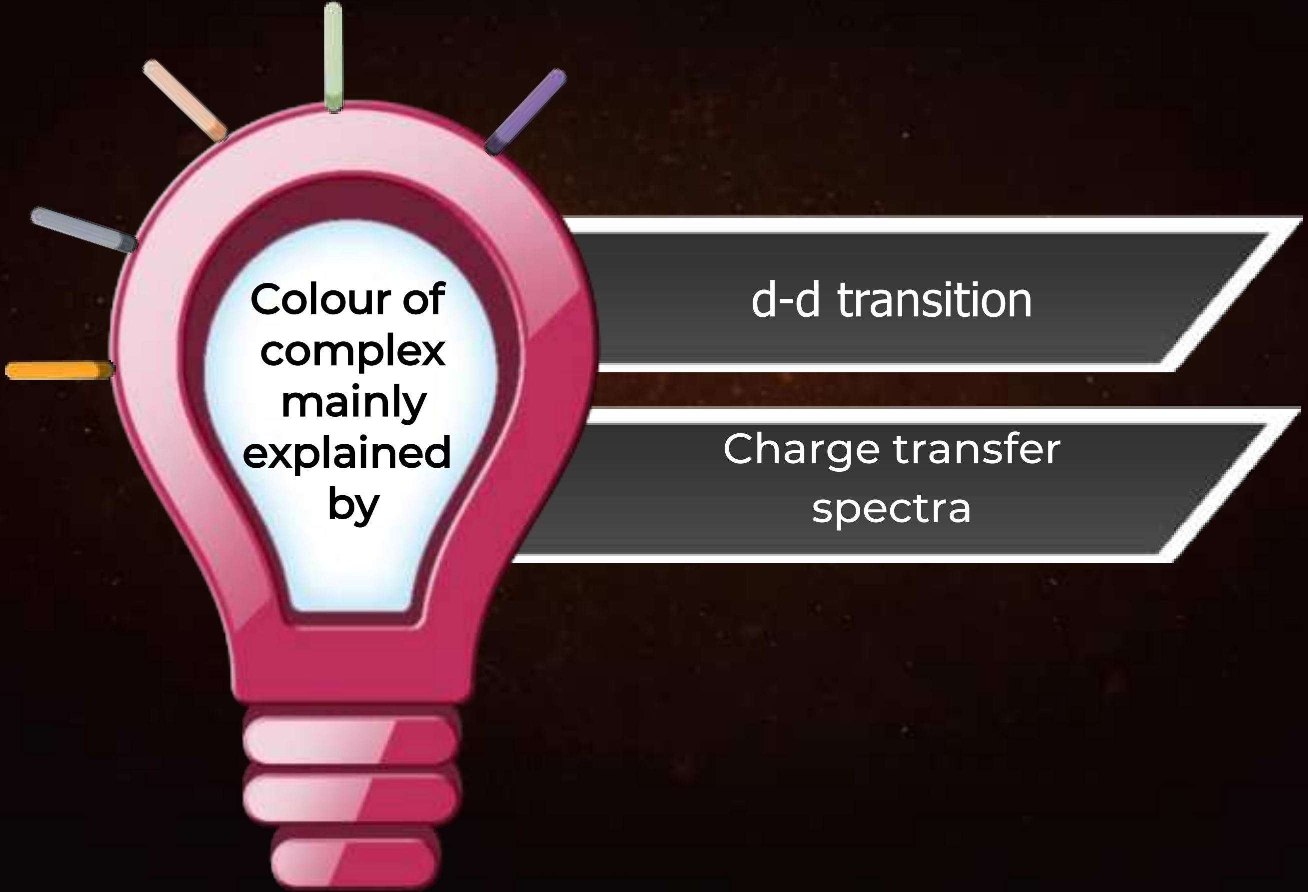


Partial covalent character of bonding

Limitation 4

According to this theory, the **bonds** between the **metal** and **ligands** are **purely ionic**. It gives **no account** on the **partially covalent nature** of the metal-ligand bonds.

Colour in Coordination Compounds

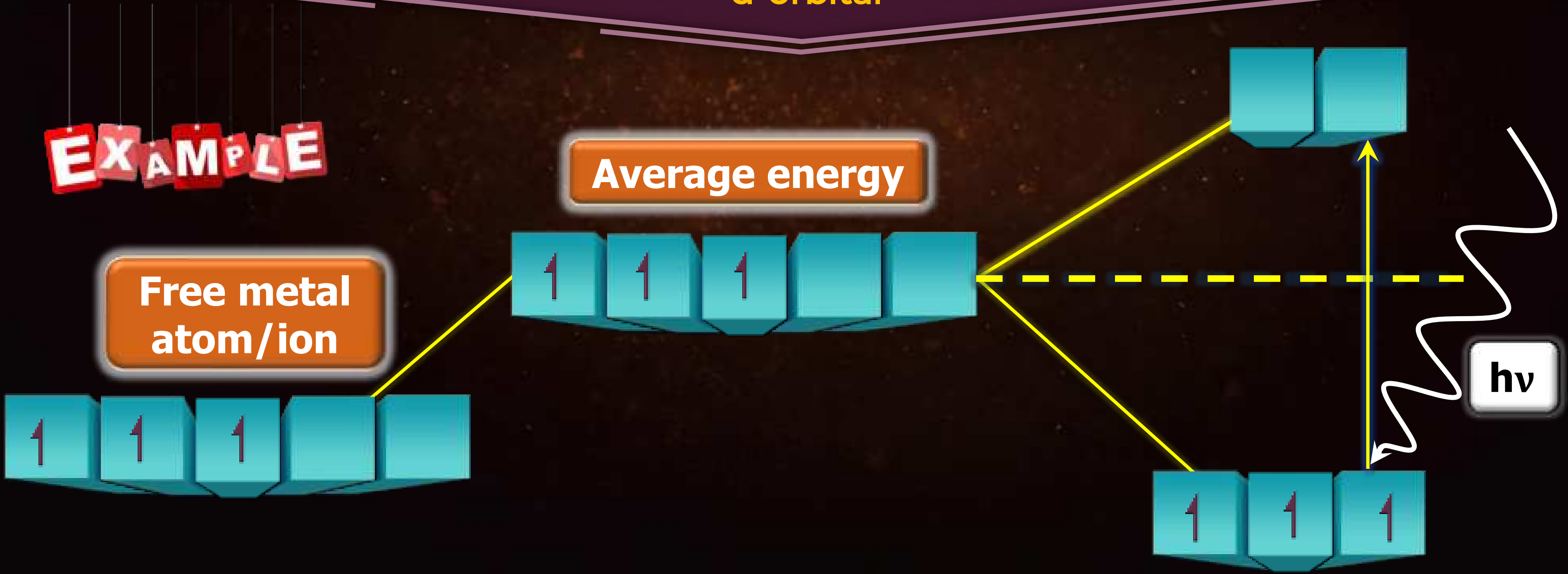


Colour of complex mainly explained by

- d-d transition
- Charge transfer spectra

Colour of Coordination Compounds

When an electron from a lower energy d-orbital is excited to a higher energy d-orbital



Note!!

A metal complex must contain an **unpaired electron** for a **d-d transition** to occur.

Colour in Coordination Compounds

Due to the absorption of light at a **specific wavelength** in the **visible region**

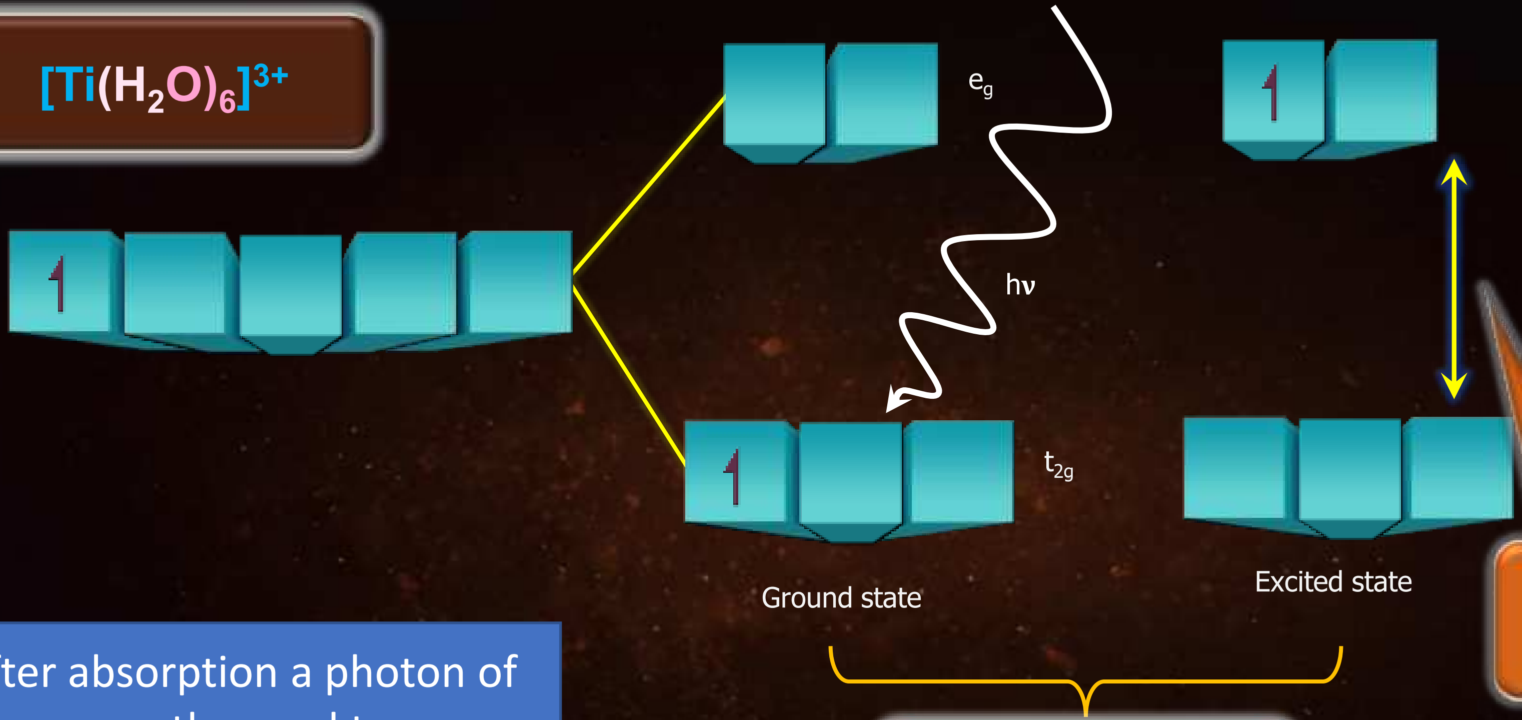
400 to **700** nm

And the **transmission** or **reflection** of the light with **rest** of the wavelengths

An object that **absorbs all visible** light appears **black.**

Absorption and Transmission Process in Complexes

$[Ti(H_2O)_6]^{3+}$



d-d transition

Δ_o or $E_{absorbed}$

After absorption a photon of energy exactly equal to energy difference between t_{2g} and e_g, the electron does a transition from t_{2g} to e_g.

Colour in Coordination Compounds

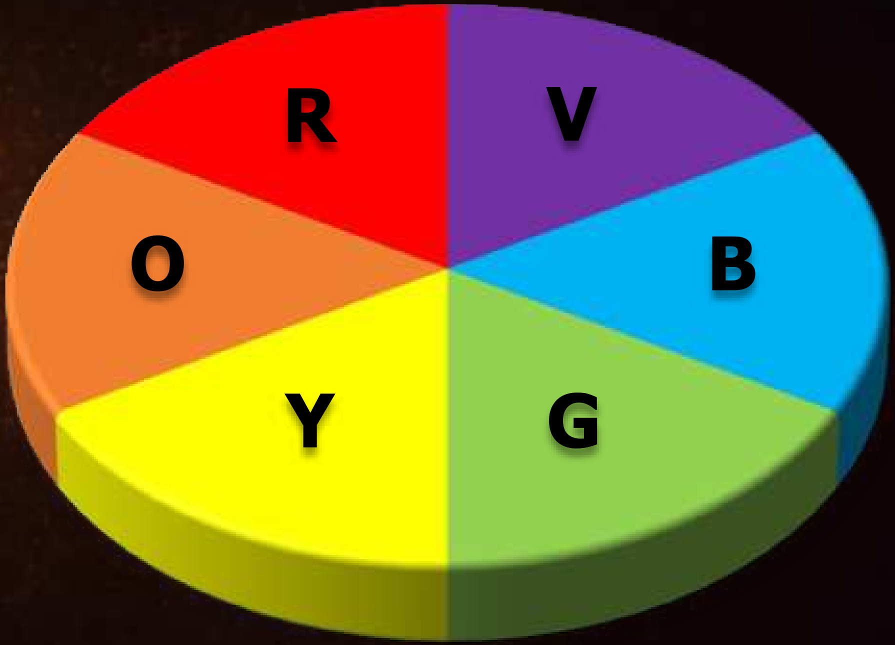
Due to the absorption of light at a specific wavelength in the visible region

Corresponding wavelength gives complementary colour

And **transmission or reflection** of the light with rest of the wavelengths

Complementary Colour

The **complementary colour** is generated from the **wavelength left over.**



Colour in Coordination Compounds

In the **absence** of a ligand

Crystal field splitting does not occur as all five d-orbitals are degenerate.

No d-d transition

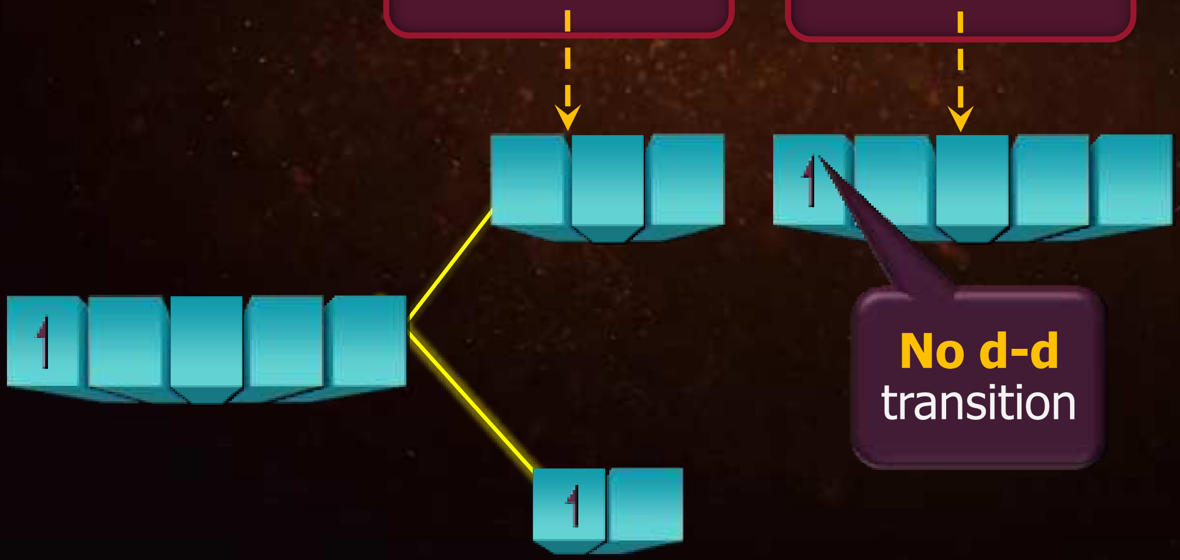
Hence, the substance is **colourless.**

Colour in Coordination Compounds

$$[Ti(H_2O)_6]Cl_3 \xrightarrow{\Delta} TiCl_3 + 6H_2O$$

Violet

Colourless



Degenerate orbitals

No d-d transition

Charge Transfer Spectra

The transition in which an electron is transferred from one atom or group to another one

Charge transfer transitions are also considered as internal redox reactions.

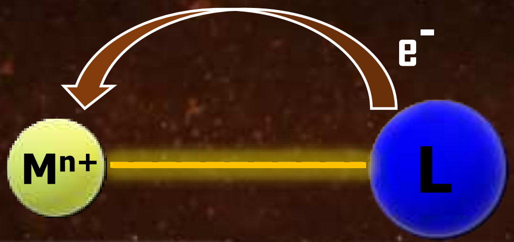
Charge Transfer Transitions

Charge transfer transitions are mainly of three types

- Ligand to metal charge transfer (LMCT)
- Metal to ligand charge transfer (MLCT)
- Metal to metal charge transfer (MMCT)

LMCT

Ligand to metal charge transfer



Electron acceptor

Electron donor

Ligand To Metal Charge Transfer

Charge transfer occurs from the **ligand's** filled molecular orbitals to the **metal's empty or partially filled** d-orbitals.

Generally, metals having **high oxidation state** (+5,+6,+7) with π donor ligands **show LMCT**.

Ligand To Metal Charge Transfer

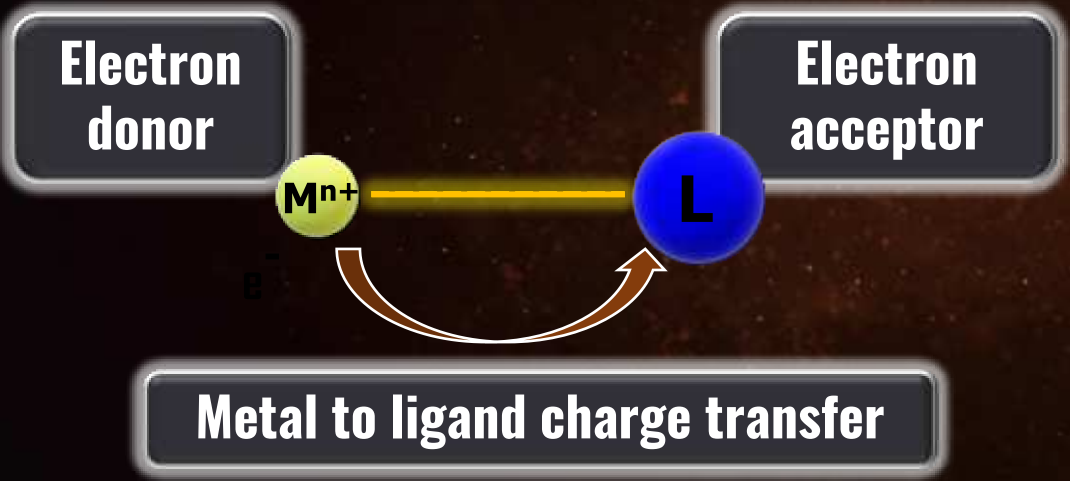
MnO_4^- → Deep purple

MnO_4^{2-} → Green

$Cr_2O_7^{2-}$ → Orange

CrO_4^{2-} → Yellow

MLCT



Electron donor

Electron acceptor

Metal to ligand charge transfer

Charge transfer occurs from the **metal's filled orbitals** to the **empty orbital of ligand**.

Note!!

Generally, metals having **low oxidation state** (0,+1,+2) with π acceptor ligands **show LMCT**.

EXAMPLE

HgO

$[Fe(phen)_3]^{3+}$

$[Fe(acac)_3]$

Metal To Metal Charge Transfer

Intervalence charge transfer

The excitation and subsequent transfer of electrons from a **lower O.S cation** to neighbouring **cation of a higher O.S**

Prussian blue complex

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$

Oxidation state

$$\overset{III}{Fe_4}[\overset{II}{Fe}(CN)_6]_3$$

Metal To Metal Charge Transfer

Turnbull's blue complex

$$3FeCl_2 + 2K_3[Fe(CN)_6] \longrightarrow Fe_3[Fe(CN)_6]_2 + 6KCl$$

Turnbull's blue

Oxidation state

$$\overset{II}{Fe_3}[\overset{III}{Fe}(CN)_6]_2$$

Now, Let’s See the Different Types of Charge Transfer Transitions in Gemstones!

Gemstones

Gemstones

Ruby

Emerald

Ruby is aluminium oxide **(Al_2O_3)**

Containing about **0.5-1 % Cr^{3+} ions** (d^3).

Randomly distributed in **Al^{3+}** positions

The **colour shown** by ruby is

Due to the **d-d transitions**

Emerald

Emerald

Green

It **transmits light** in the **green** region. Here also the colour is due to impurities in crystal.

Organometallic Compounds

Organometallic compounds are the compounds that contain carbon-metal bond.

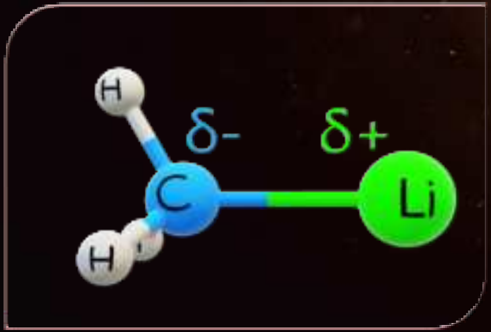
Metal carbonyls are the transition metal complexes of **carbon monoxide** containing **metal-carbon (M-C) bonds.**

Metal carbonyls have simple, **well-defined structures.**

Organometallic Compounds

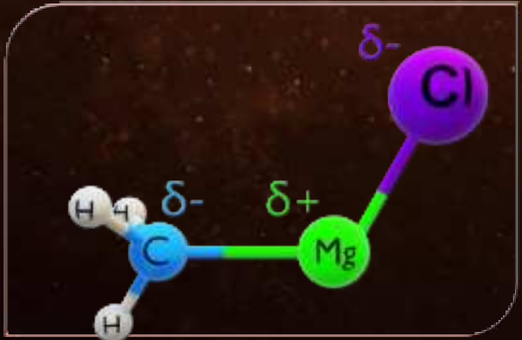
Example

Organolithium Compound



$\overset{\delta-}{CH_3} — \overset{\delta+}{Li}$

Organomagnesium compound



$\overset{\delta-}{CH_3} — \overset{\delta+}{Mg} — \overset{\delta-}{Cl}$

Metal Carbonyls

$Fe(CO)_5$

Bonding in Metal Carbonyls

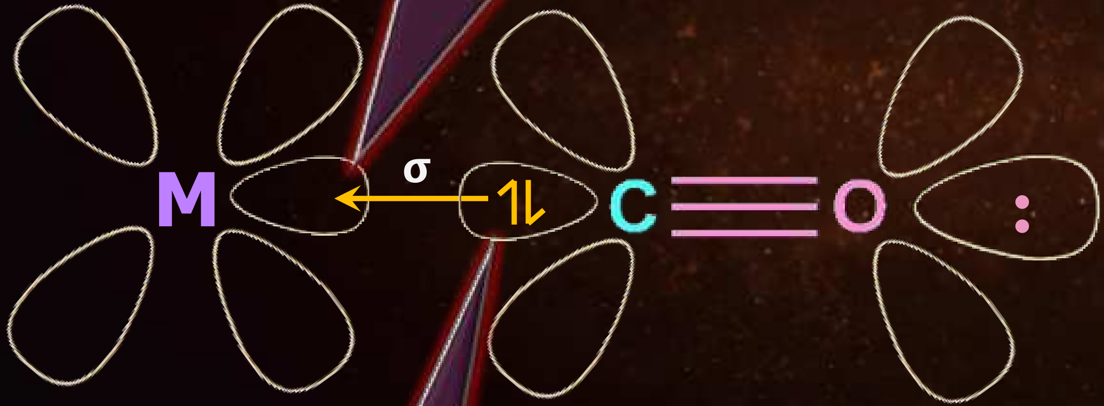
Metal–carbon bond in metal carbonyls possesses

- σ-character
- π-character

M–C **σ–bond** is formed by

The donation of lone pair of electrons of **carbonyl carbon into vacant d-orbital** of metal

σ-Bonding in Metal Carbonyls



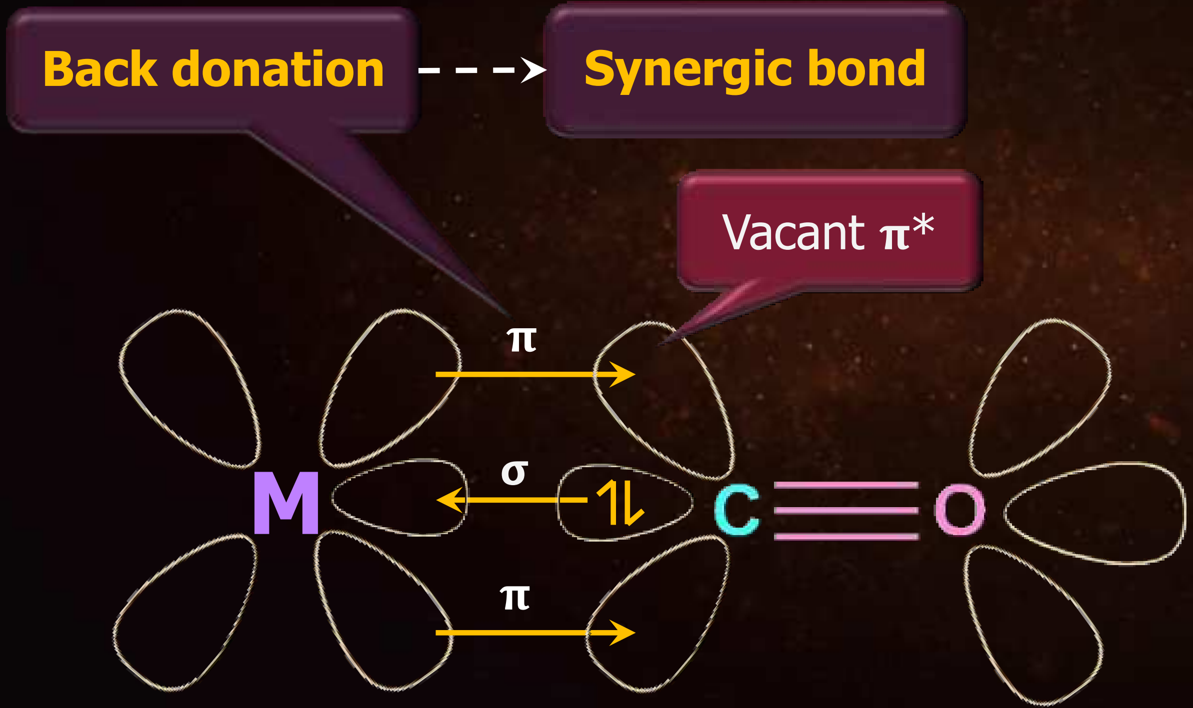
Empty **d-orbital** of metal

NBMO

M–C **π–bond** is formed by

The donation of lone pair of electrons from **filled d-orbital** of **metal** to **vacant π* orbital** of CO

π–Bonding in Metal Carbonyls



Back donation - - -> **Synergic bond**

Vacant π*

Bonding in Metal Carbonyls

Metal–carbon bond in metal carbonyls possesses

- σ-character
- π-character

M–C **σ–bond** is formed by

↓

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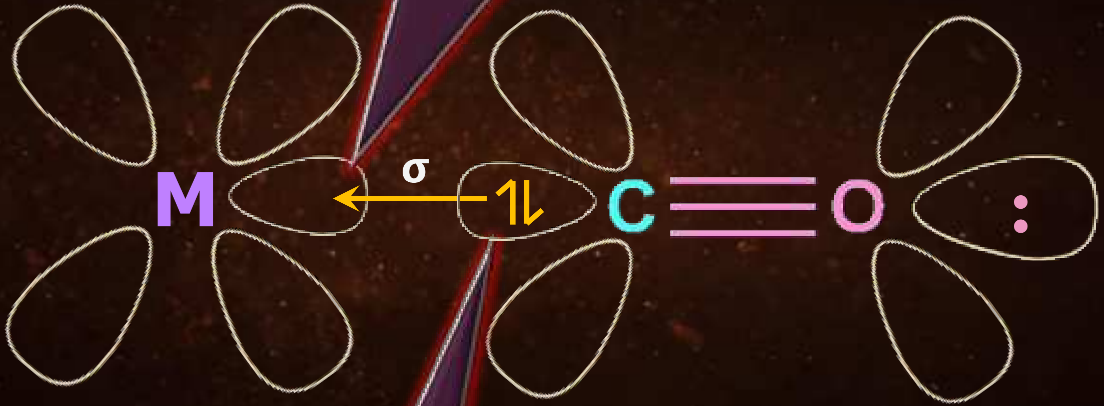
σ-Bonding in Metal Carbonyls



Empty **d-orbital** of metal

NBMO

π–Bonding in Metal Carbonyls

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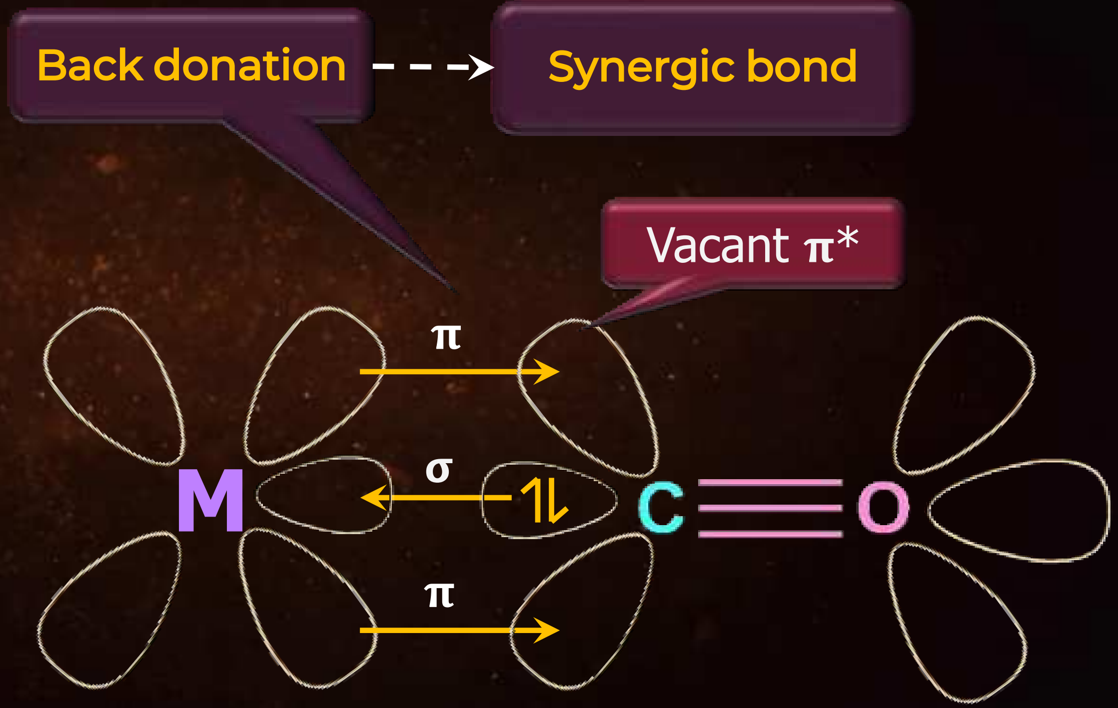
The donation of lone pair of electrons from **filled d-orbital** of **metal** to **vacant π* orbital** of CO



Synergic Bond

The **π-bond** formed between a **metal atom/ion** and a **ligand** by **back donation** of a metal atom/ion is known as a **synergic bond.**

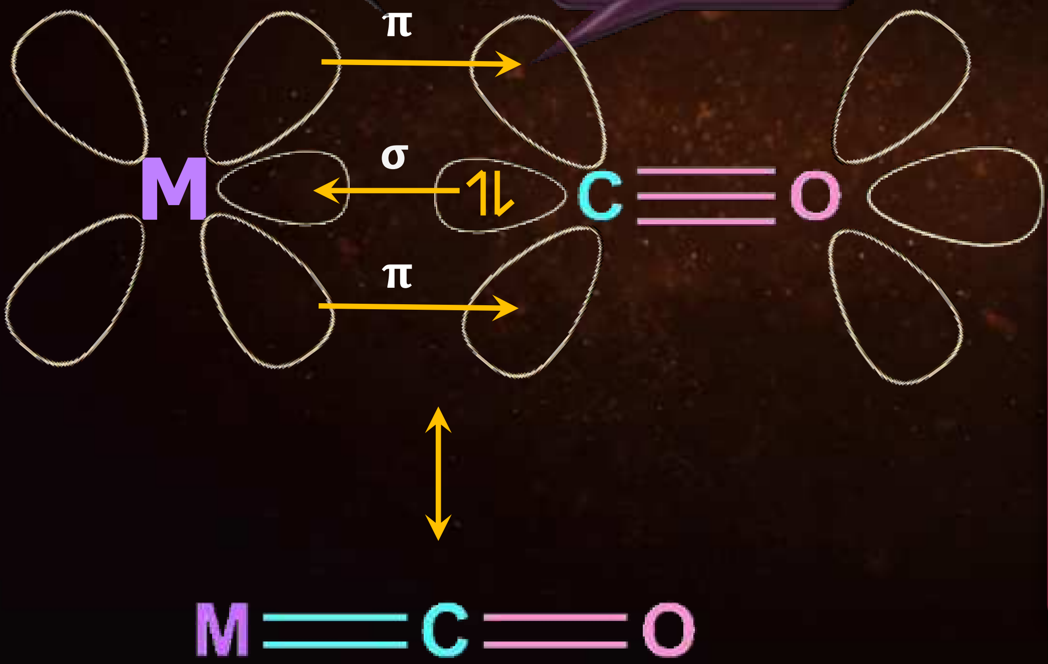
Synergic effect is due to a **self-strengthening bond,** which involves **transference** of electrons from

1. Ligand to metal
2. Metal’s filled orbitals to vacant orbitals of ligand

Synergic Effect

Back bond/
Synergic bond

Vacant **π***



CO is a **non-classical** ligand.

Those ligands which not only donate the lone pair of electrons but **also accept the electron cloud** from the central metal atom/ion in their low-lying vacant orbitals.

Synergic Effect

The **length** of the **internal bond** of a ligand and the **length** of the **metal–ligand bond vary** due to the synergic bonding. This effect is known as **synergic effect.**

Because electrons are coming in **π^* orbitals** of **CO**

Bond order of the **C–O** bond **decreases**

BUT →

The length of C–O bond **increases**

Synergic Bonding

More electron rich the metal, i.e., lower the oxidation state of metal

↓

More the donation of electrons from metal to ligands

↓

More the increase in C–O bond length

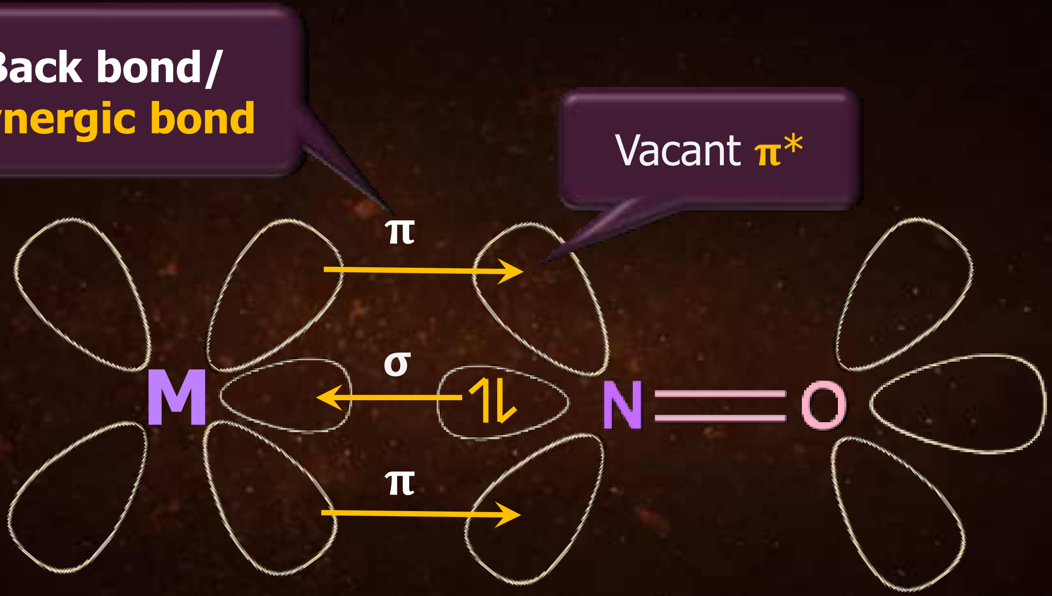
Synergic Bonding

Synergic bonding in case of

- Metal nitrosyls
- Metal phosphenes
- Alkenes

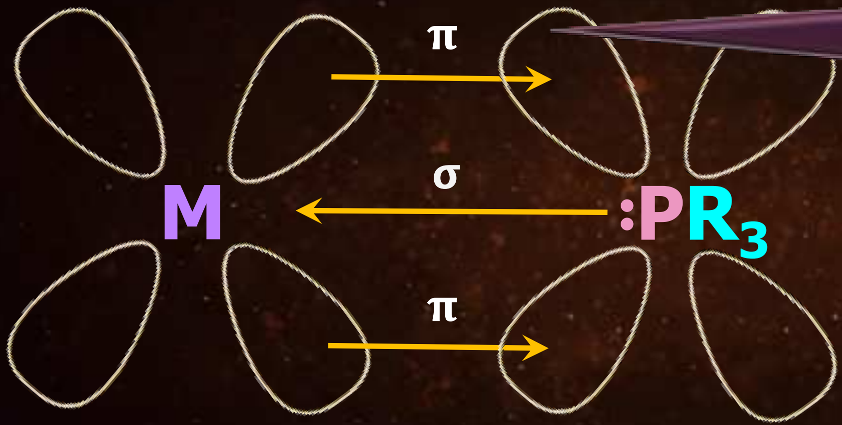
Example: $[Fe(H_2O)_5NO]^{2+}$

π-Bonding in Metal Nitrosyls



Formation of M⟶NO⁺ bond by back donation in metal nitrosyls

Synergic Bonding in Metal Phosphenes



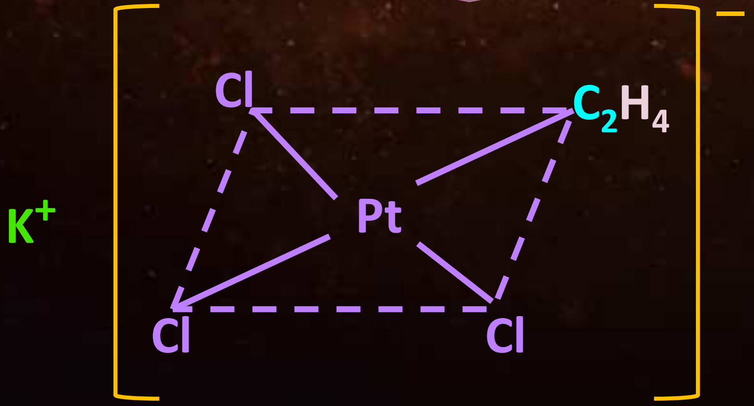
Vacant **3d** orbital **accepts** the **back donation**

Wilkinson’s catalyst

Synergic Bonding in Alkenes

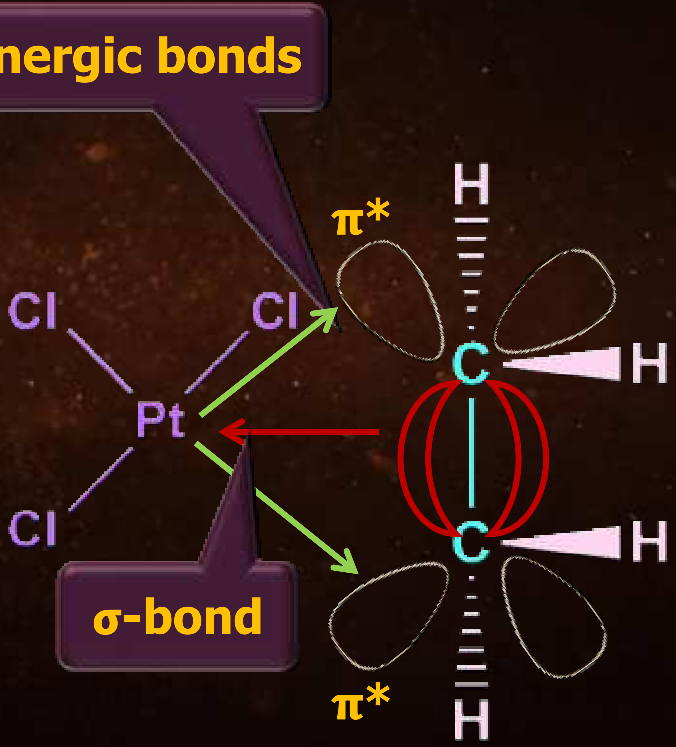
The **filled d-orbitals** of metal **overlap** with **vacant π*** molecular orbital of ethylene molecule and forms **π-bond/backbond/ synergic bond.**

Zeise's salt



$K[PtCl_3(\eta^2\text{-}C_2H_4)]$

Synergic Bonding in Alkenes


Synergic bonds

σ-bond

Stability of Organometallic Compounds

Rules

18 electron rule

Proposed by **Irving Langmuir**

EAN rule

Proposed by **Sidgwick**

18 Electron Rule

When the central metal atom or ion of a complex **acquires** an outer shell electronic configuration of **$(n-1)d^{10}ns^2np^6$**

There will be **18 electrons** in the valence shell

And the electronic configuration will be **closed** and **stable**

Total valence electron = Contribution of metal ion + Contribution of ligand ± Charge on coordination sphere

Counting the Number of Electrons

Two **conventions** for **counting the number of electrons** in a complex

Neutral atom (Covalent model)

We will study only this

Oxidation state (Ionic model)

Electron count of metal ion = Group number of metal

Scandium → Group number = 3 → Electron count = 3

Cobalt → Group number = 9 → Electron count = 9

Electron Count of Ligand

Ligand classification

- Anionic
- Neutral
- Organic

Electron count of anionic ligand = Charge on anion

H^- → Electron count = 1

Cl^- → Electron count = 1

O^{2-} → Electron count = 2

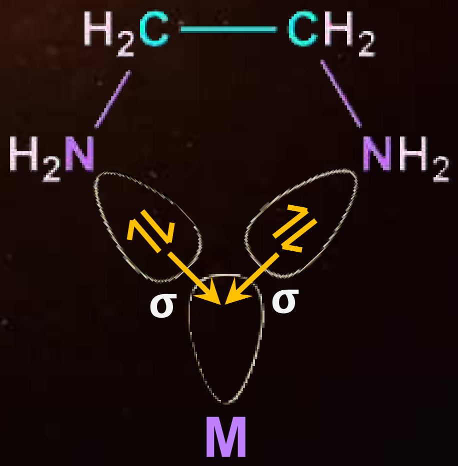
Neutral Ligand

Electron count of neutral ligand = Number of electron donated

CO → Electron count = 2

NH_3 → Electron count = 2

Ethylene diamine → Electron count = 4



Organic Ligand

Organic ligands are ligands having **unsaturated bond**.

Electron count of organic ligand = Hepacity of ligand

Allyl ion → Electron count = Heptacity = 3

cyclopentadiene → Electron count = Heptacity = 5

Counting of Number of Electrons

EXAMPLES

Ferrocene

Covalent model

Fe → 8 electrons

$2C_5H_5^-$ → 10 electrons

Total electrons = 18 electrons

Counting of Number of Electrons

$(CO)_5Mn — CH_3$

Covalent model

Mn → 7 electrons

$5CO$ → 10 electrons

CH_3^- → 1 electron

Total electrons = 18 electrons

Limitations of 18-Electron Rule

1

The 18-Electron rule **is not a hard** and **fast rule** and is **not** always **strictly obeyed.**

There are number of stable complexes in which the electron count is not equal to 18.

Examples in which the number of **electrons ≠ 18**

$[Cr(H_2O)_6]^{2+}$

16 electrons

$[Zn(NH_3)_6]^{2+}$

22 electrons

Both the complexes **exist** and are **stable**.

Limitations of 18-Electron Rule

The **transition metal ions** on the left side of the periodic table have a **lower** number of **valence electrons.**

$[Ti(F)_6]^{2-}$

12 electrons

$[V(Cl)_6]^{3-}$

14 electrons

Such transition metals **cannot** acquire **18 electrons** in their valence shell.

Complexes of these transition metals have less than 18 electrons in their valence shell

Both the complexes exist and are **stable**.

Effective Atomic Number Rule (EAN)

The **sum** of **electrons** on the central metal atom or ion and electrons donated from the ligand is known as **effective atomic number**.

Generally, **EAN** is equal to the **atomic number** of the **nearest noble gas** to the central metal atom.

Proposed by **Sidgwick**

Krypton (Kr)	**36**
Xenon (Xe)	**54**
Radon (Rn)	**86**

Effective Atomic Number Rule

Mathematically → $\text{EAN} = \underbrace{Z - \text{O.S}} + 2(\text{C.N})$

Number of electrons in the **central metal atom or ion**

Number of electrons donated by **ligands**

EAN = Number of **electrons** in the **central metal** atom or ion + Number of **electrons donated** by ligands

Effective Atomic Number Rule

$[Cr(CO)_6]$

O.S of **Cr** = 0

Electrons in **Cr** atom = **Atomic number** of **Cr**

24

Number of electrons **donated** by **6CO**

2 X 6 = 12

36

Obeys EAN rule

Note!!

Some complexes can be **stabilised** by following **EAN rule.**

Applications of the EAN Rule

1

The **number** of CO molecules attached in mononuclear carbonyls **can be predicted**.

$Fe(CO)_x$

5

$Ni(CO)_y$

4

$Cr(CO)_z$

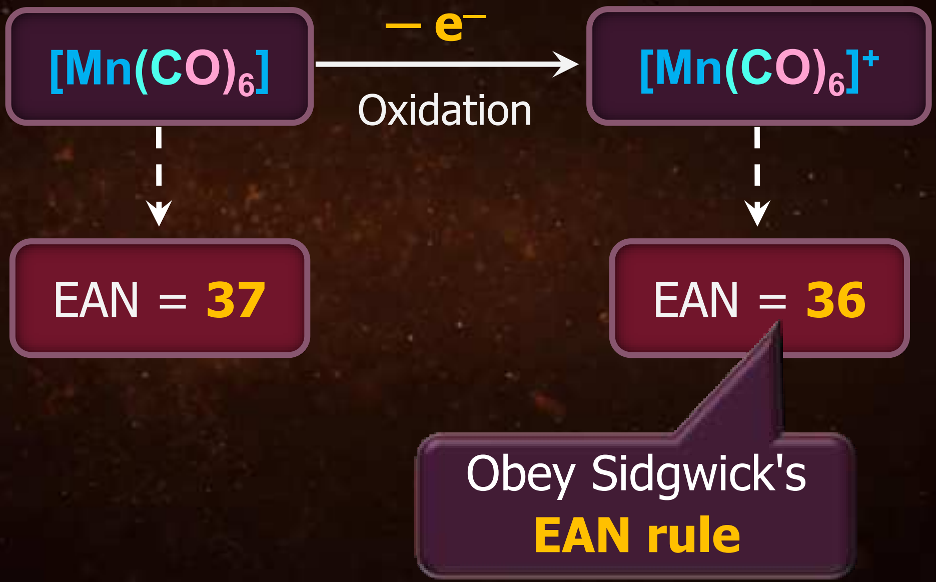
6

2

Some complexes can act as reducing agents by losing electron.

To attain the **noble gas configuration**

Applications of the EAN Rule



$$[Mn(CO)_6] \xrightarrow[\text{Oxidation}]{-\,e^-} [Mn(CO)_6]^+$$

EAN = **37**

EAN = **36**

Obey Sidgwick's
EAN rule

Applications of the EAN Rule

3

Some complexes can act as **oxidising agents** by **gaining electrons.**

To attain the **noble gas configuration**

$$[V(CO)_6] \xrightarrow[\text{Reduction}]{+\ e^-} [V(CO)_6]^-$$

EAN = **35**

EAN = **36**

Obey Sidgwick's **EAN rule**

Applications of the EAN Rule

4

Some complexes undergo **dimerisation.**

To attain the **noble gas configuration**

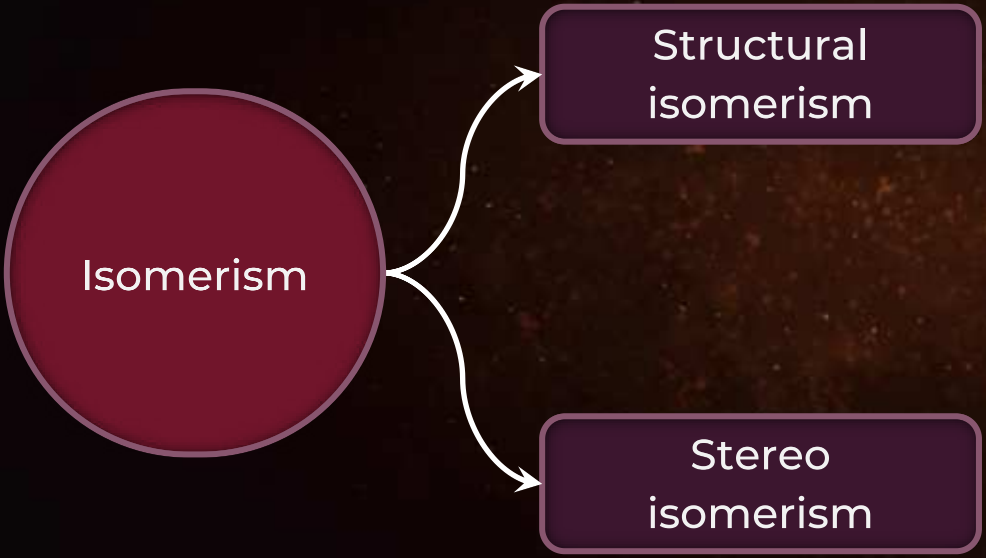
$$2[Mn(CO)_5] \longrightarrow [Mn_2(CO)_{10}]$$

EAN = **35**

EAN = **36**

Obey Sidgwick's **EAN rule**

Isomerism in Coordination Compounds



Isomerism

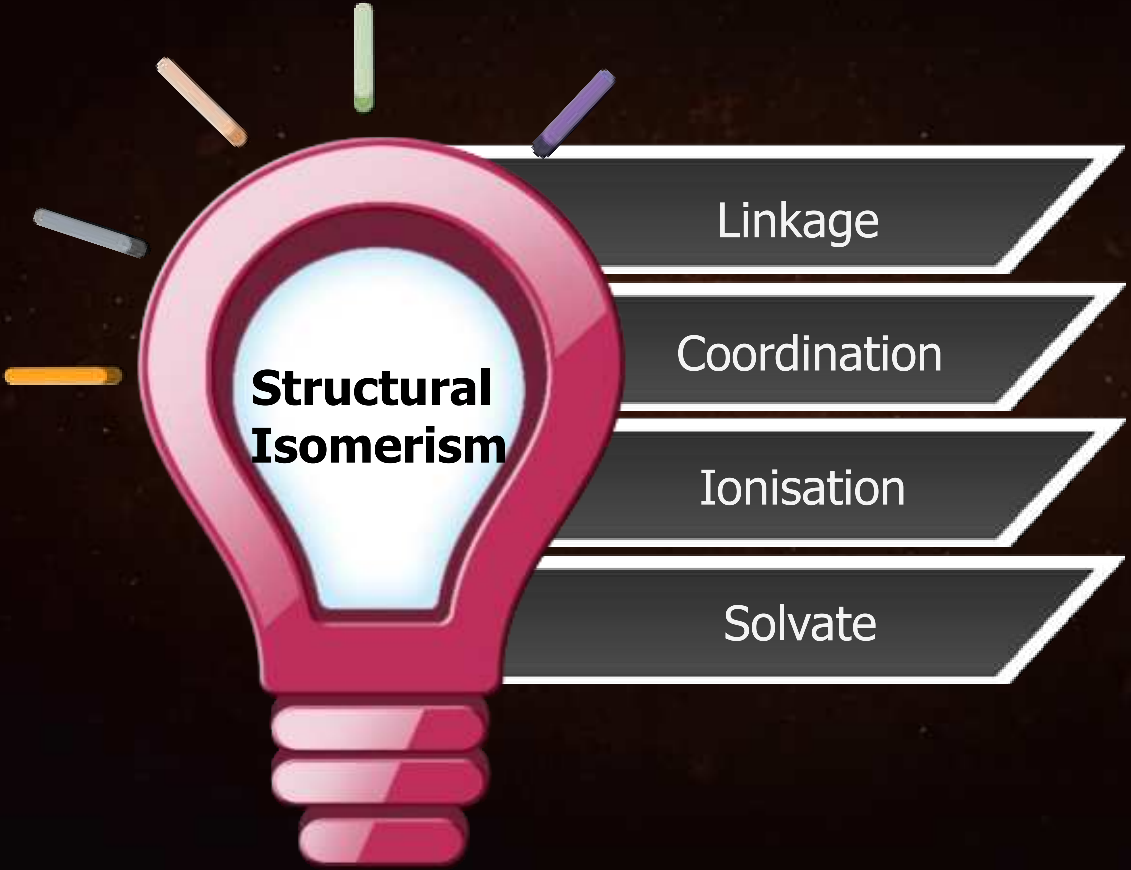
Structural isomerism

Stereo isomerism

Structural isomerism

An isomer in which molecules with the **same molecular formula** have **different bonding patterns**

Structural Isomerism



Structural Isomerism

- Linkage
- Coordination
- Ionisation
- Solvate

Linkage Isomerism

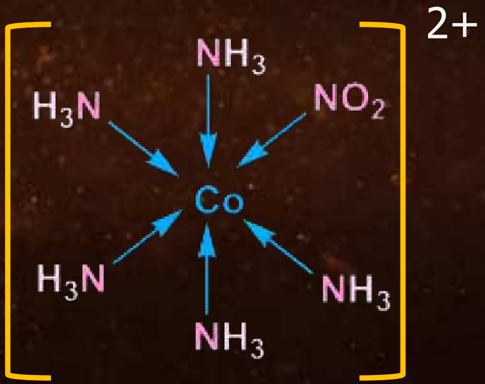
CN^-, NO_2^-, SCN^-, etc.

The isomers formed when **ambidentate ligands** use **different coordinating atoms/ sites** for binding metal ions

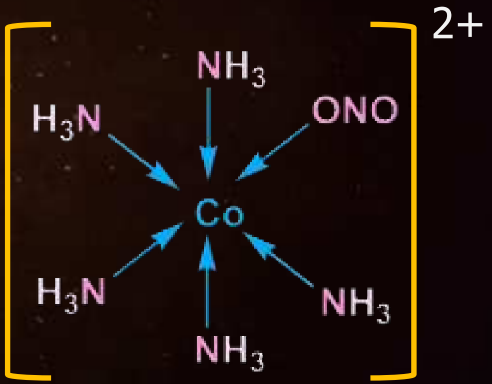
Ligands that can ligate through **two different sites** present in them.

Linkage Isomerism

$[Co(NH_3)_5NO_2]Cl_2$



Nitropentammine-cobalt(III) ion

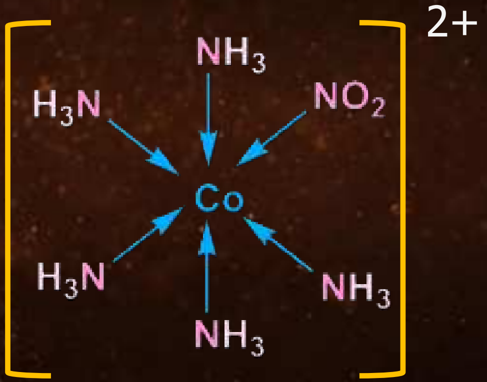


Nitritopentammine-cobalt(III) ion

Linkage Isomerism

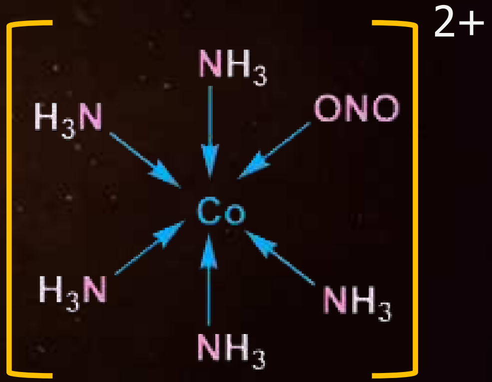
Jorgensen observed the difference in **colour** of the two isomers.

$[Co(NH_3)_5NO_2]Cl_2$



Nitropentammine-cobalt(III) ion

Yellow

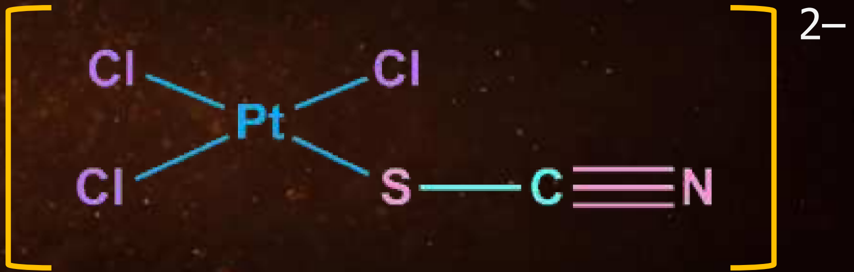


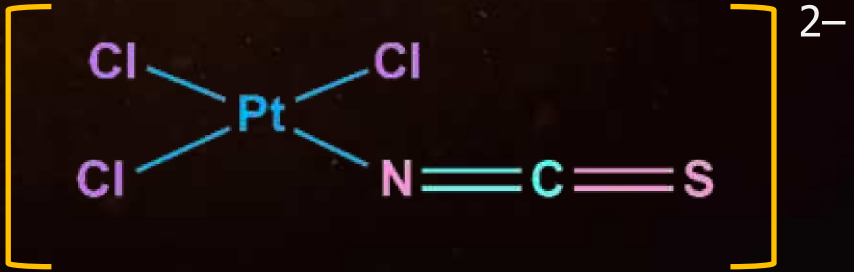
Nitritopentammine-cobalt(III) ion

Red

Linkage Isomerism

$[PtCl_3(SCN)]^{2-}$





Coordination Isomerism

It arises due to an **interchange** of ligands between **cationic** and **anionic** entities of **different metal ions** present in the complex.

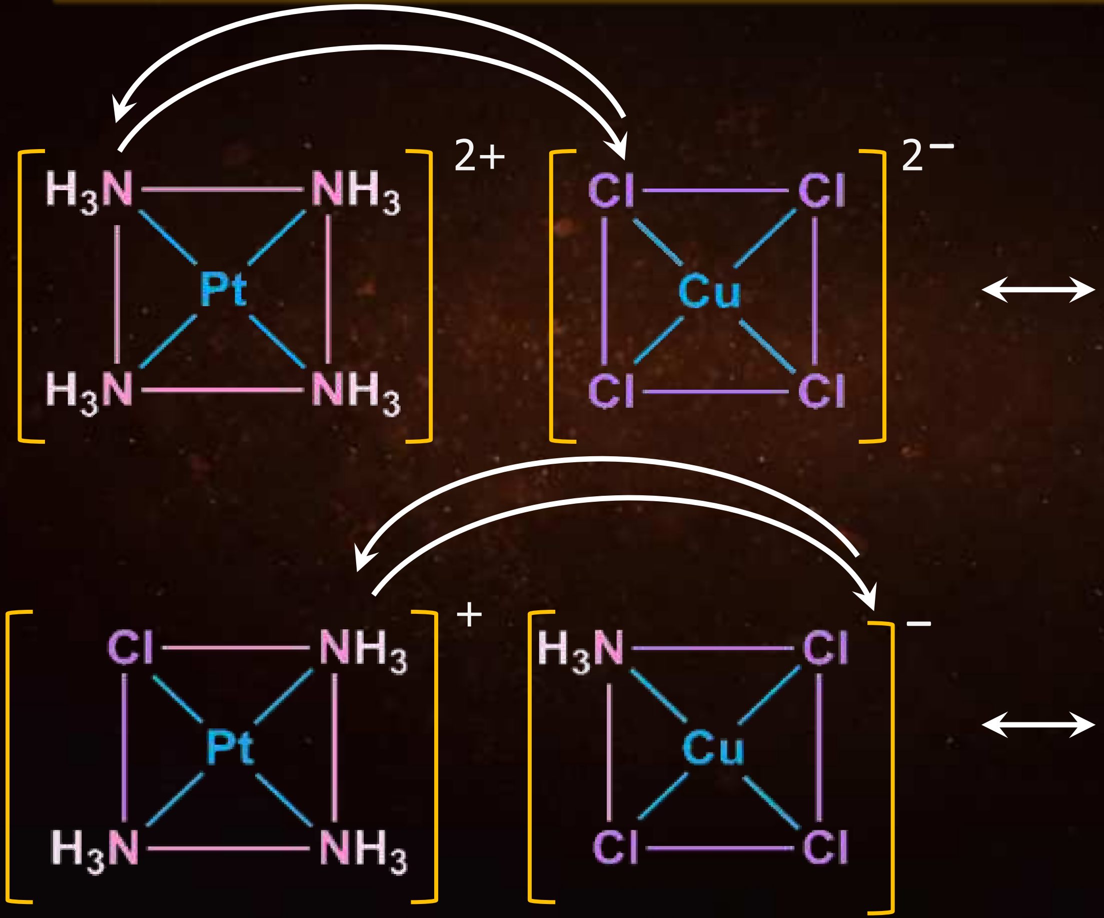
$[Pt(NH_3)_4]^{2+}[CuCl_4]^{2-}$

$\updownarrow$

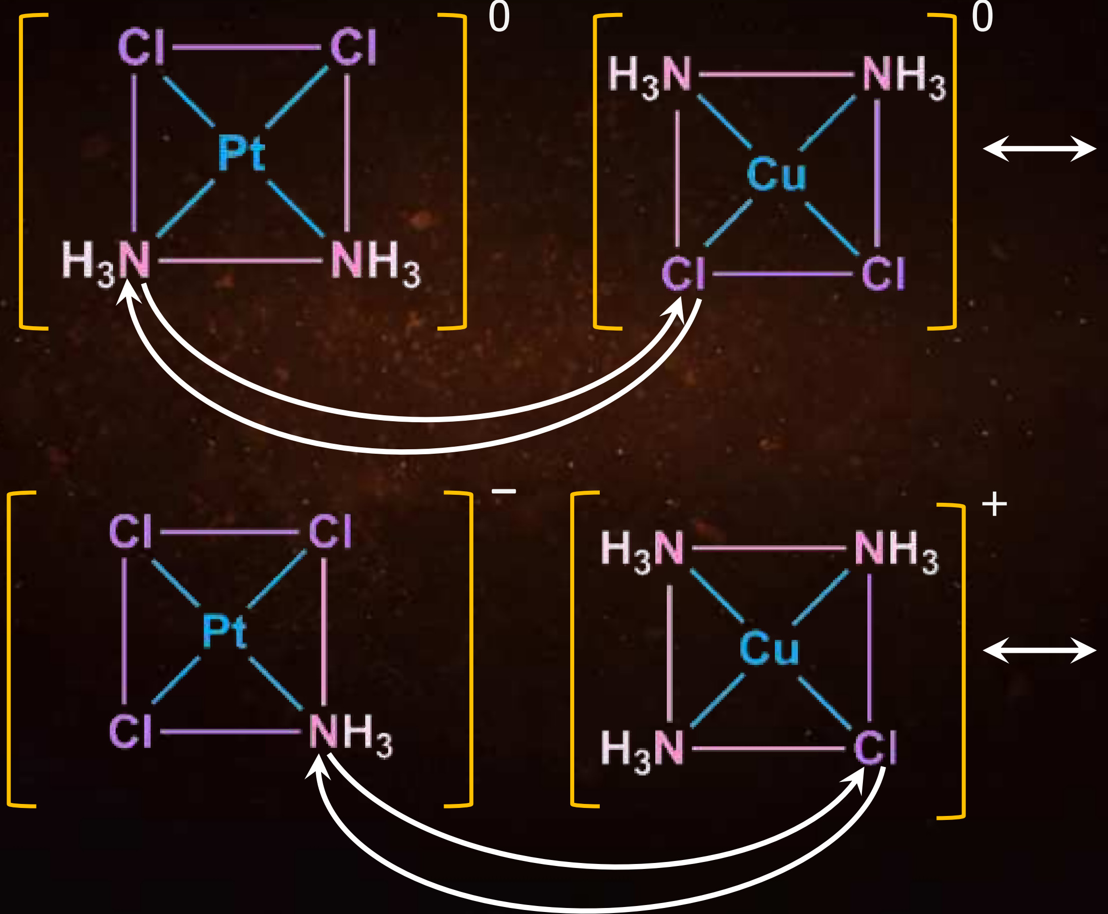
$[PtCl_4]^{2-}[Cu(NH_3)_4]^{2+}$

Coordination isomer

Coordination Isomerism



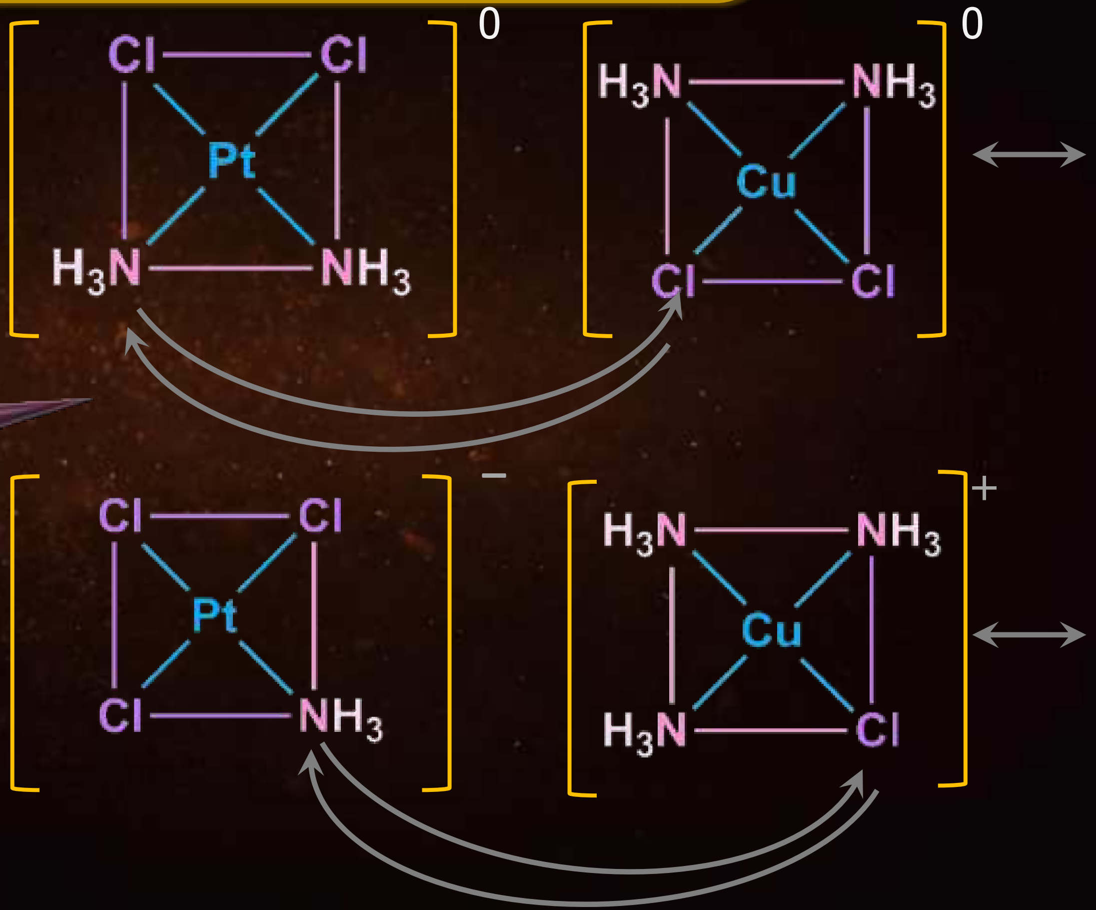
Coordination Isomerism



Coordination Isomerism

Total coordination isomers = 4

Coordination Isomerism



This is
not considered
as a coordination
isomers.

Points to Remember!

If the **coordination entity** becomes **neutral**, then it is **not** considered as a coordination complex and it **exists as a free entity** in the solution.

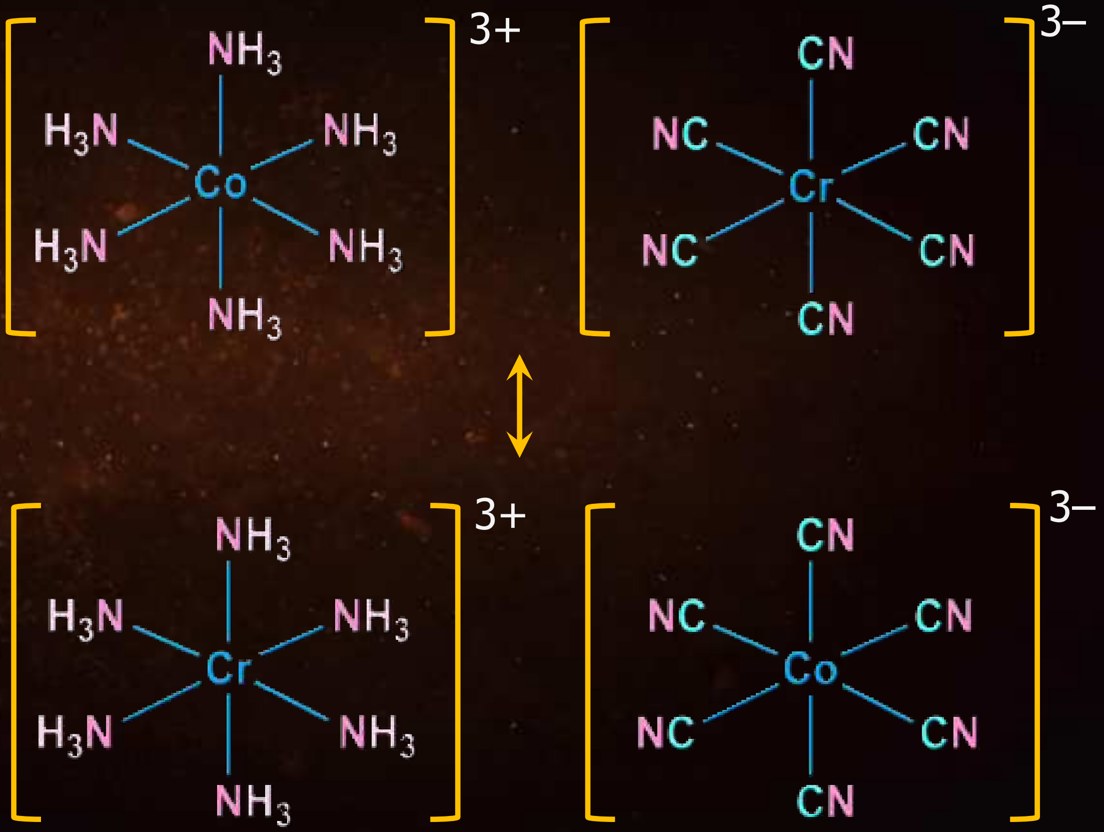
Coordination Isomerism

$[Co(NH_3)_6]^{3+}\,[Cr(CN)_6]^{3-}$

↕

$[Cr(NH_3)_6]^{3+}\,[Co(CN)_6]^{3-}$

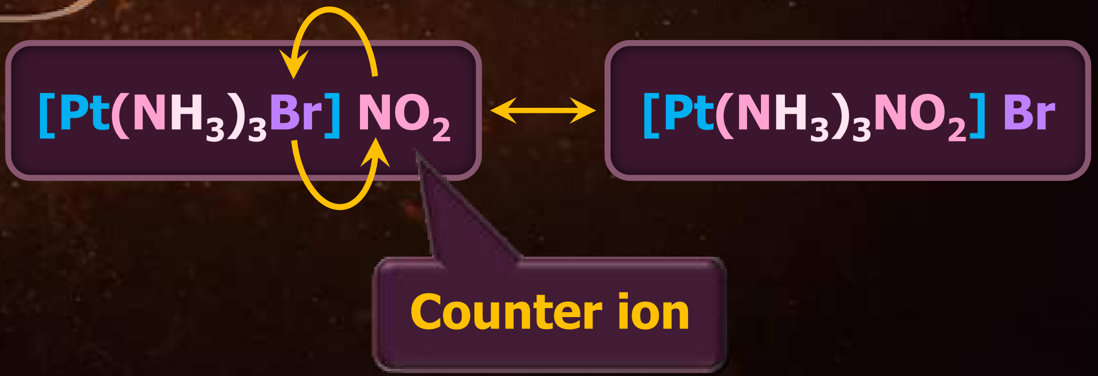
Coordination isomer



Ionisation Isomerism

It arises when a **counter ion** in a complex salt itself is a **potential ligand.**

So, it can **displace** an actual **ligand,** which can then become a **counter ion.**



$$[Pt(NH_3)_3Br]\,NO_2 \longleftrightarrow [Pt(NH_3)_3NO_2]\,Br$$

Counter ion

Note!!

Ionisation isomers produce **different ions** in **aqueous solutions.**

$$[Co(NH_3)_5(SO_4)]Br \xrightleftharpoons{H_2O} [Co(NH_3)_5(SO_4)]^{+} + Br^{-}$$

Red

$$[Co(NH_3)_5Br]SO_4 \xrightleftharpoons{H_2O} [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$$

Violet

Solvate Isomerism

Isomers that differ with respect to the number of **solvent ligand molecules** as well as **counter ions**

1. Ammonia **(NH_3)**
2. Water **(H_2O)**

Hydrate Isomerism

When **water** is present as a **solvent**, the solvate isomerism is known as **hydrate isomerism.**

$CrCl_3.6H_2O$

$[Cr(H_2O)_6]Cl_3$

Violet

Produces $3Cl^-$

$[Cr(H_2O)_5Cl]Cl_2.H_2O$

Bright blue green

Produces $2Cl^-$

$[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Dark green

Produces $1Cl^-$

Note!!

Solvate and **hydrate** isomerism are types of **ionisation isomerism.**

Polymerisation Isomerism

A **special case** of **coordination** isomerism but **not a true** isomerism

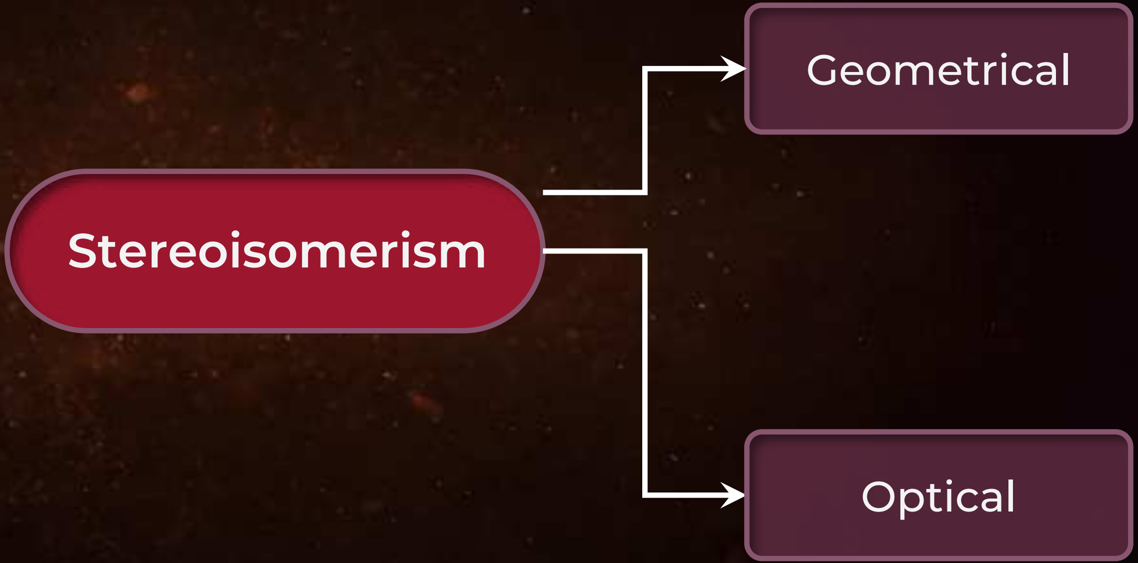
In which compounds **differ** from each other in **molecular formula & molecular weight.**

$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4][PtCl_4]$

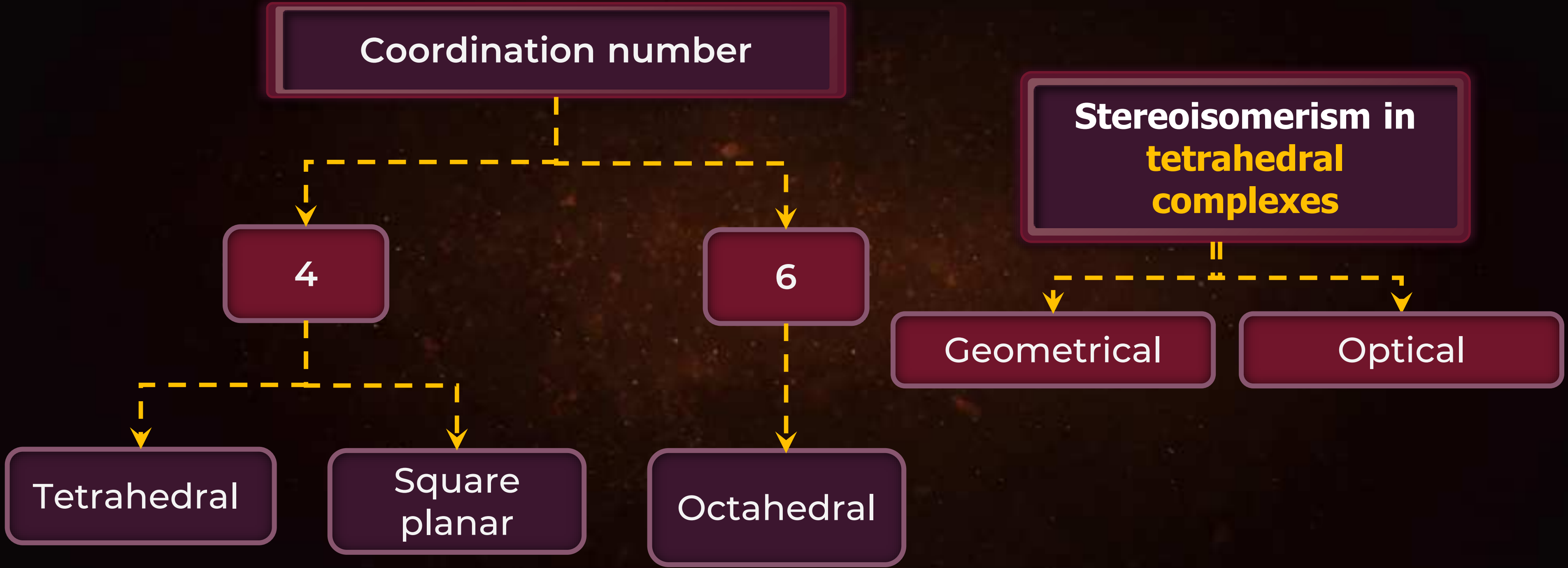
$[Pt(NH_3)_4][Pt(NH_3)_2Cl_3]_2$ and $[Pt(NH_3)_3Cl]_2[PtCl_4]$

Stereoisomerism

Isomerism due to different **spatial arrangements** of atoms or groups **(ligands)** about the **central metal** atom or ion



Geometrical and Optical Isomerism



Coordination number

4

6

Tetrahedral

Square planar

Octahedral

Stereoisomerism in tetrahedral complexes

Geometrical

Optical

Geometrical Isomerism in Tetrahedral Complexes

Generally, **GI** is **not possible** in tetrahedral complexes.

↓

$[Ma_4]$, $[Ma_2b_2]$, or $[Mabcd]$

The **arrangement** of every **ligand** around the **central metal atom/ion** in space is **equivalent** in every respect.

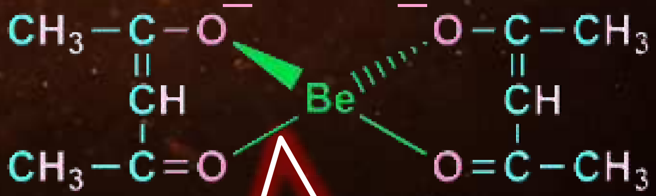
Optical Isomerism in Tetrahedral Complexes

A complex can show **optical isomerism** only when the attached **4 ligands** are **different.**

But **POS and COS must be absent**

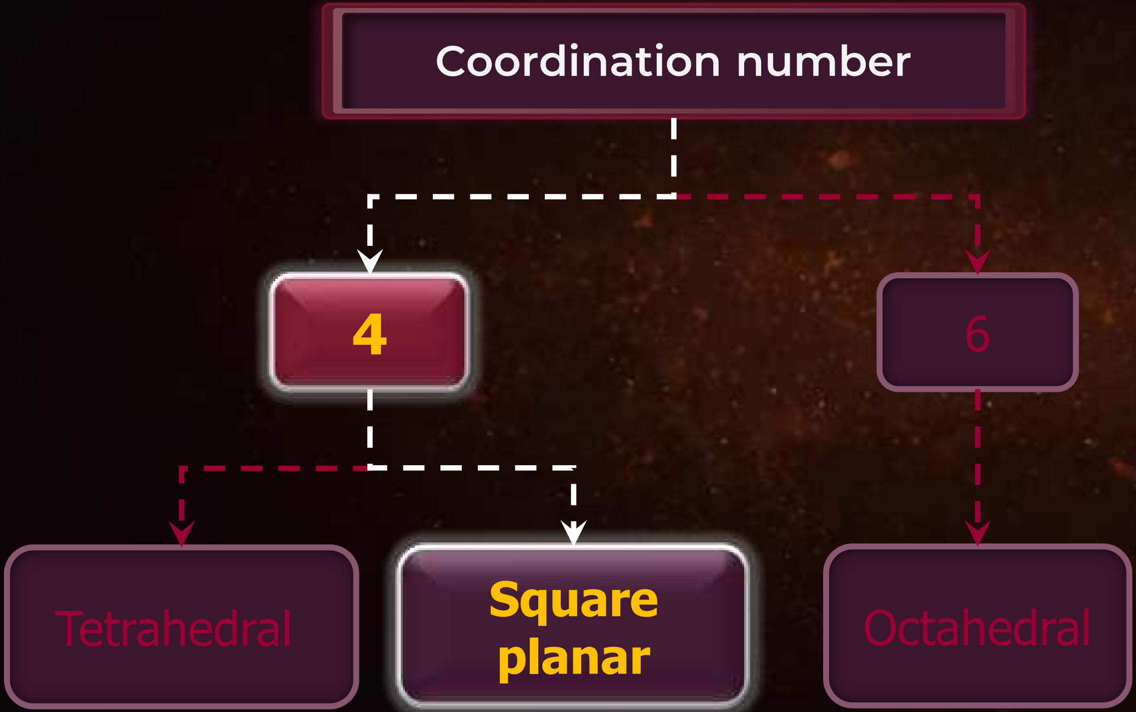
$[Be(acac)_2]$

acetylacetonato



Optically inactive due to POS

Geometrical and Optical Isomerism



Coordination number

4

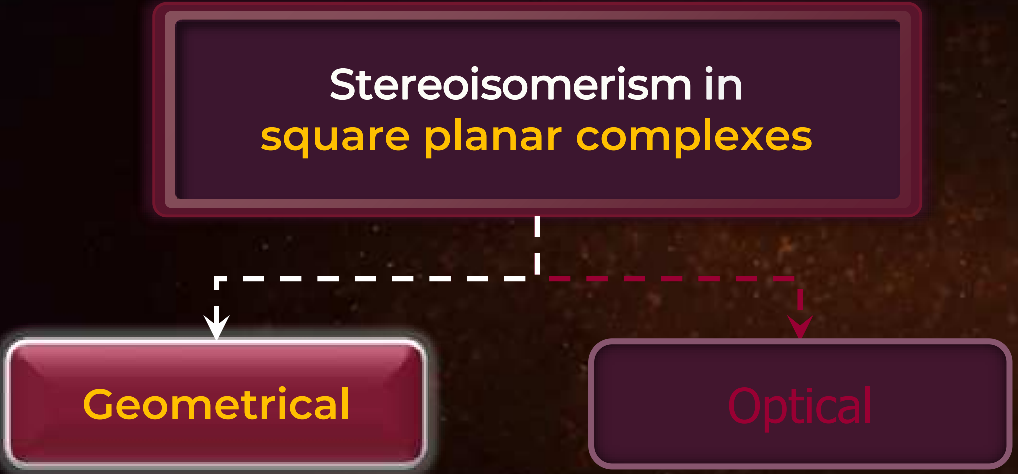
6

Tetrahedral

Square planar

Octahedral

Geometrical and Optical Isomerism



Stereoisomerism in square planar complexes

Geometrical

Optical

- $[Ma_4]^{n\pm}$
- $[M(AB)a_2]^{n\pm}$
- $[Ma_3b]^{n\pm}$
- $[Ma_2b_2]^{n\pm}$
- $[M(AA)_2]^{n\pm}$
- $[Ma_2bc]^{n\pm}$
- $[M(AA)a_2]^{n\pm}$
- $[Mabcd]^{n\pm}$

GI in Square Planar Complexes

Where

a, b, c, d	Simple **monodentate** ligands	CN^-, Br^-, NH_3, etc.
AA	**Symmetrical bidentate** ligand	en, oxalato, etc.
AB	**Unsymmetrical bidentate** ligand	Glycinato

$[Ma_4]^{n\pm}$

$[Ma_3b]^{n\pm}$

$[M(AA)_2]^{n\pm}$

$[M(AA)a_2]^{n\pm}$

$[M(AB)a_2]^{n\pm}$

$[Ma_2b_2]^{n\pm}$

$[Ma_2bc]^{n\pm}$

$[Mabcd]^{n\pm}$

GI in Square Planar Complexes

Does not show geometrical isomerism

$[Ma_4]^{n\pm}$

$[Ma_3b]^{n\pm}$

$[M(AA)_2]^{n\pm}$

$[M(AA)a_2]^{n\pm}$

$[M(AB)a_2]^{n\pm}$

$[Ma_2b_2]^{n\pm}$

$[Ma_2bc]^{n\pm}$

$[Mabcd]^{n\pm}$

Reason

Since **only one** geometry is **possible**

Simple **monodentate** ligand

Symmetrical bidentate ligand

Unsymmetrical bidentate ligand

GI in Square Planar Complexes

$[Ma_4]^{n\pm}$	$[M(AB)a_2]^{n\pm}$
$[Ma_3b]^{n\pm}$	$[Ma_2b_2]^{n\pm}$
$[M(AA)_2]^{n\pm}$	$[Ma_2bc]^{n\pm}$
$[M(AA)a_2]^{n\pm}$	$[Mabcd]^{n\pm}$

Shows geometrical isomerism

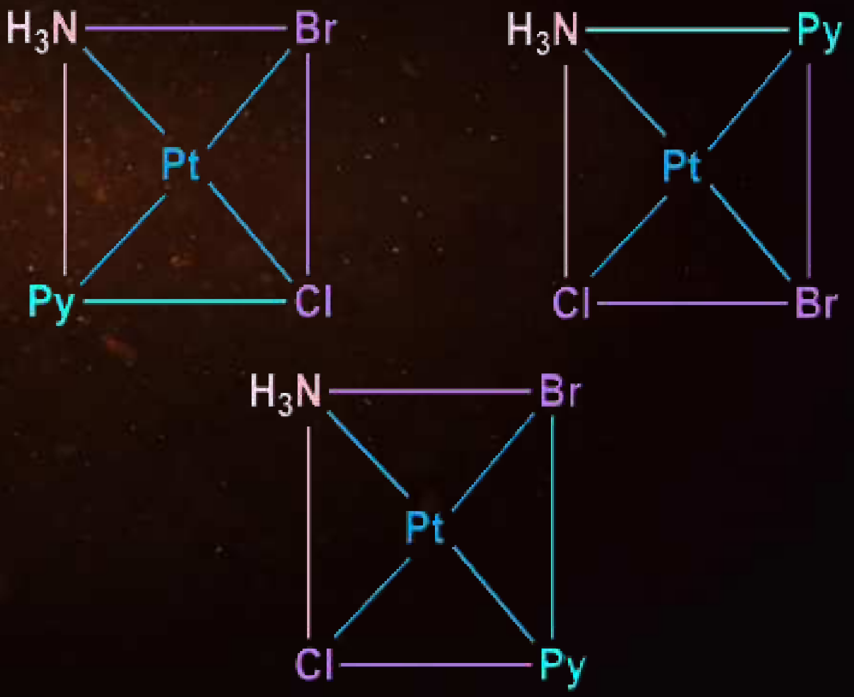
GI in Square Planar Complexes

EXAMPLE

$[Mabcd]^{n\pm}$

Total possible isomers: 3

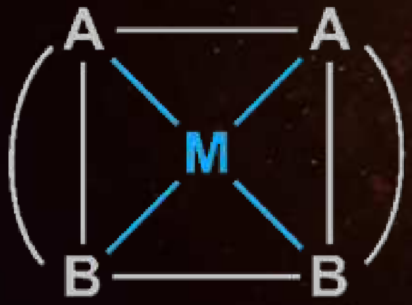
$[Pt(NH_3)BrCl(py)]$

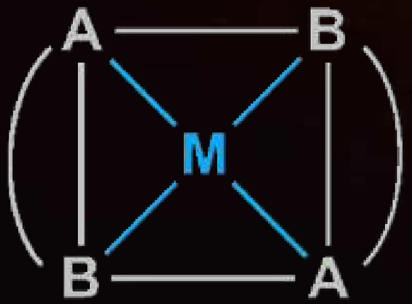


GI in Square Planar Complexes

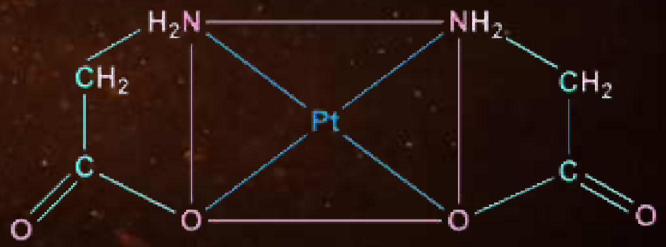
EXAMPLE

$[M(AB)_2]^{n\pm}$

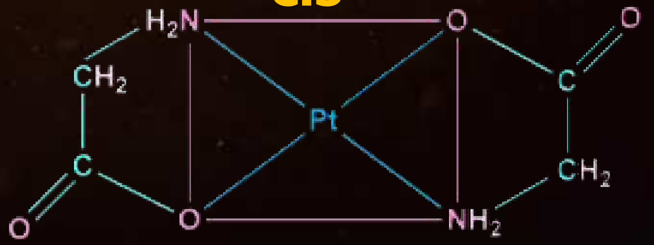




$[Pt(gly)_2]$



cis

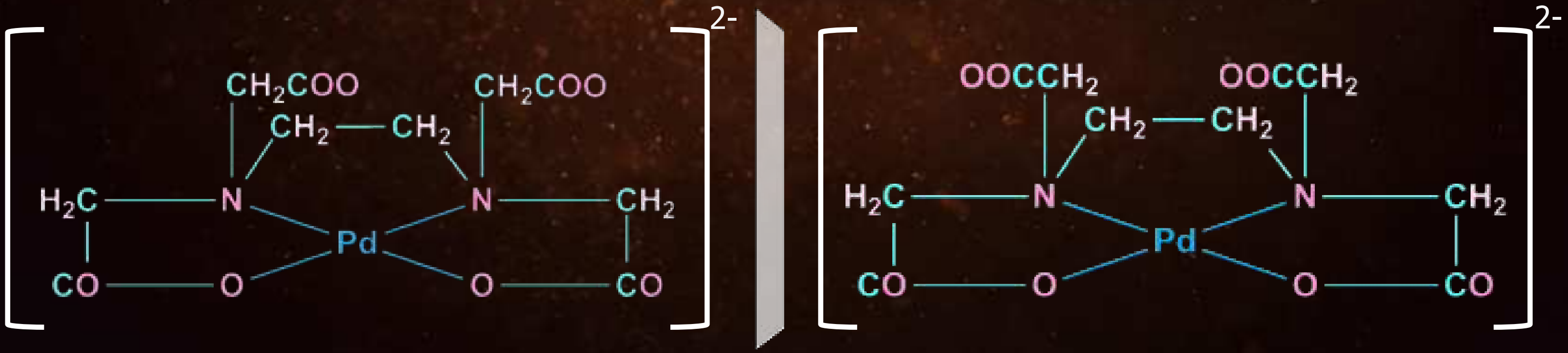


trans

Optical Isomerism in Square Planar Complexes

$[Pd(EDTA)]^{2-}$

Acts as a
tetradentate ligand



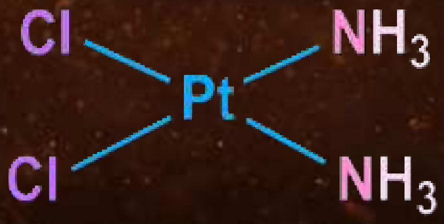
Mirror

Optically active compounds

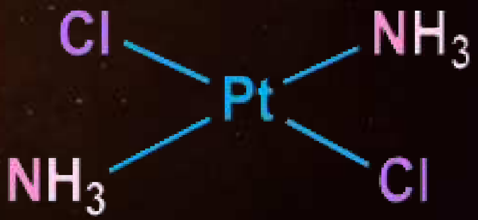
GI in Square Planar Complexes

EXAMPLE

$[Pt(NH_3)_2(Cl)_2]$



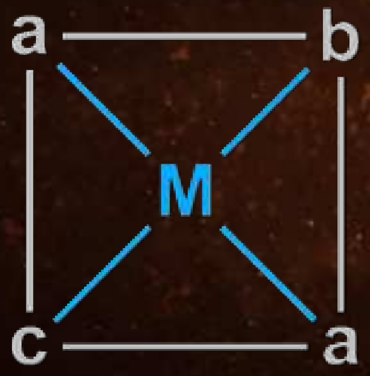
cis



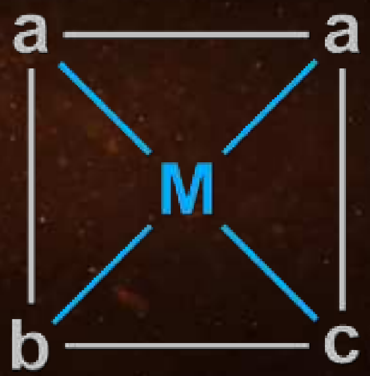
trans

GI in Square Planar Complexes

$[Ma_2bc]^{n\pm}$



Same group
opposite side
(trans)



Same group
same side
(cis)

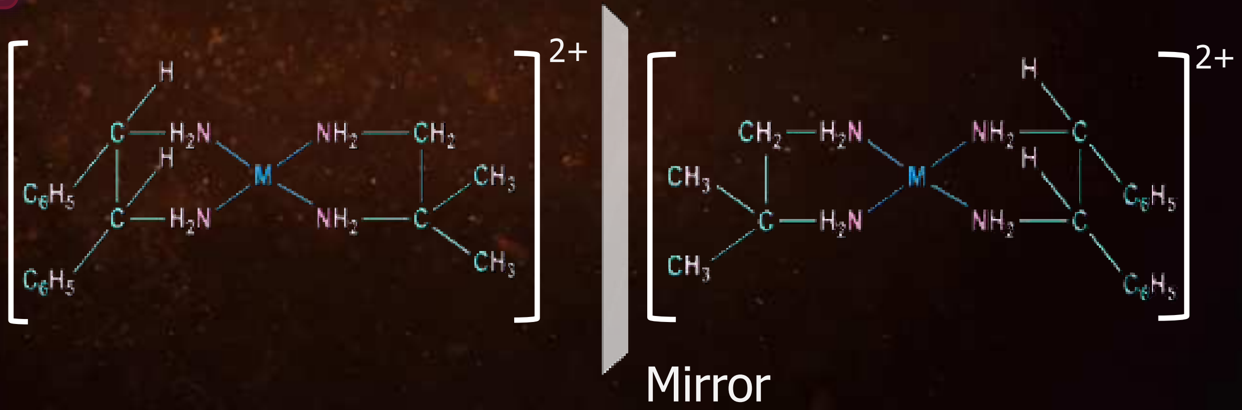
Optical Isomerism in Square Planar Complexes

Generally, square planar complexes **do not show** optical isomerism.

This is because all the **four ligands** and **metal** cations exist in the **same plane.**

Have **POS**

(Isobutylenediamine) (meso-diphenylethylenediamine) Palladium(II) or **Platinum(II)** complex



Where **M** = Pd(II) or Pt(II)

Geometrical and Optical Isomerism

Stereoisomerism in octahedral complexes

- Geometrical
- Optical

Geometrical Isomerism in Octahedral Complexes

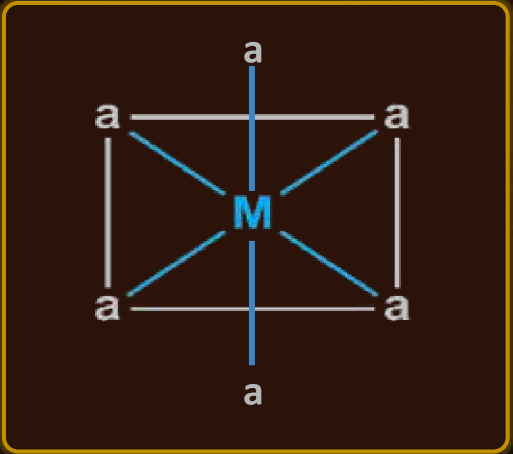
Octahedral complexes where **ligands** are

- Monodentate
  - Having **no chiral centre**
- Symmetrical bidentate and monodentate type
- Unsymmetrical bidentate and monodentate type

Octahedral Complexes with Monodentate Ligands

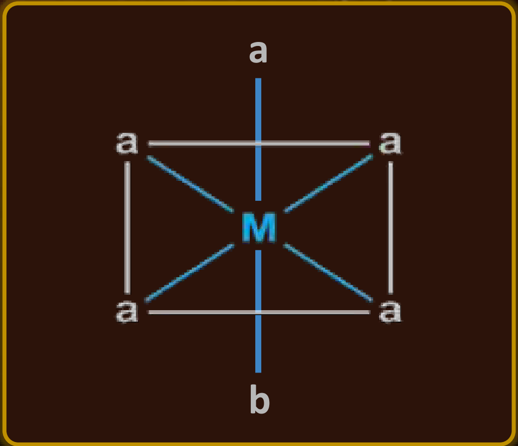
Case 1(a)

- $[M(a_6)]^{n\pm}$
- Does not show Geometrical Isomerism



Case 1(b)

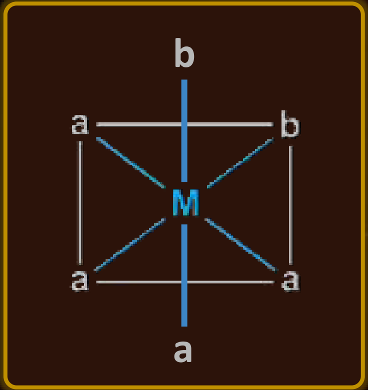
- $[M(a_5b)]^{n\pm}$
- Does not show Geometrical Isomerism

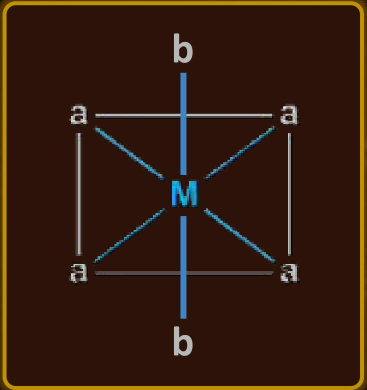


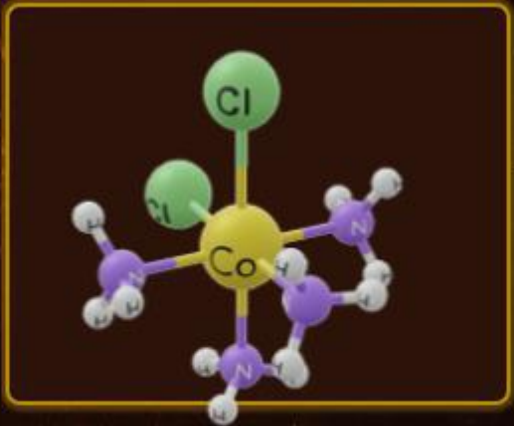
Octahedral Complexes with Monodentate Ligands

Case 1(c)

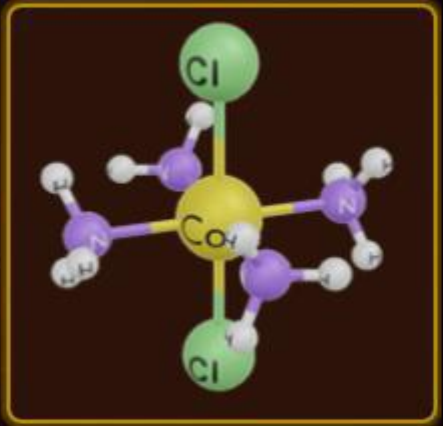
Example







Cis



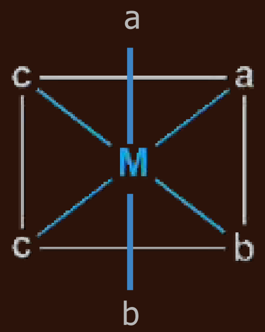
Trans

- $[M(a_4b_2)]^{n\pm}$
- Cis form

- $[M(a_4b_2)]^{n\pm}$
- Trans form

Octahedral Complexes with Monodentate Ligands

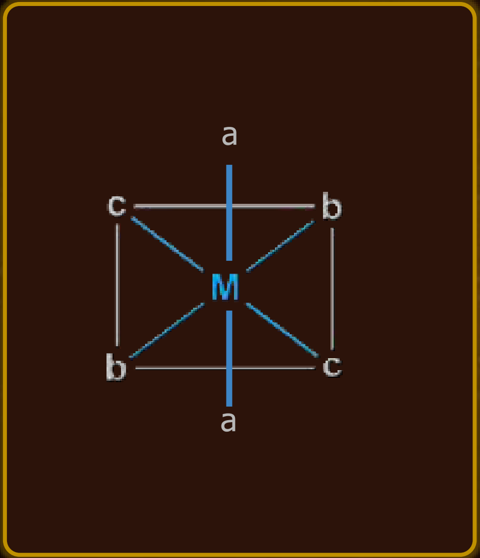
Case 1(d)



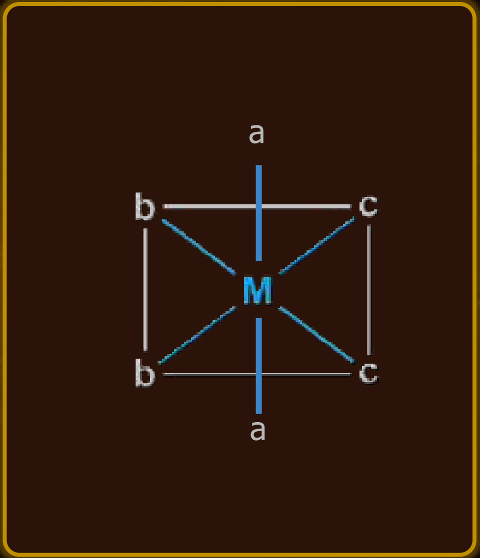
$[Ma_2b_2c_2]^{n\pm}$

Octahedral Complexes with Monodentate Ligands

Case 1(d)



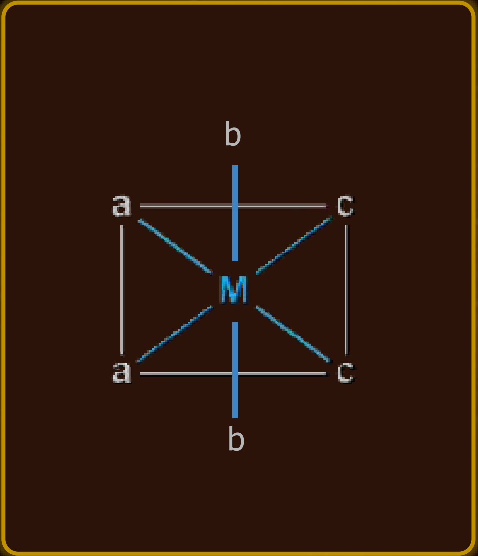
$[Ma_2b_2c_2]^{n\pm}$

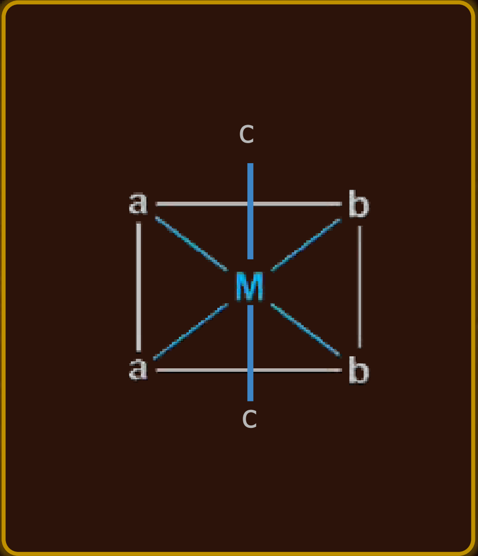


$[Ma_2b_2c_2]^{n\pm}$

Octahedral Complexes with Monodentate Ligands

Case 1(d)





$[Ma_2b_2c_2]^{n\pm}$

$[Ma_2b_2c_2]^{n\pm}$

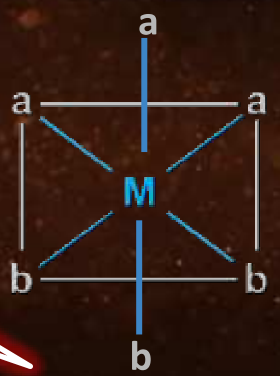
Possible number of geometrical isomers = 5

Octahedral Complexes Having Monodentate Ligands

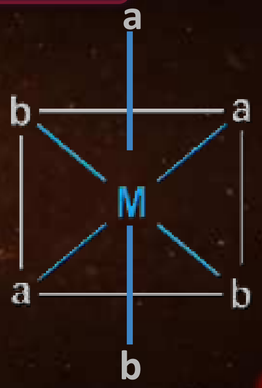
Case **1(e)**

$[Ma_3b_3]^{n\pm}$

Have **three** identical ligands on **one triangular face**



Facial (fac)



Meridional (mer)

Have **three** identical ligands in a plane **bisecting** the **molecule**

Possible number of **geometrical** isomers = **2**

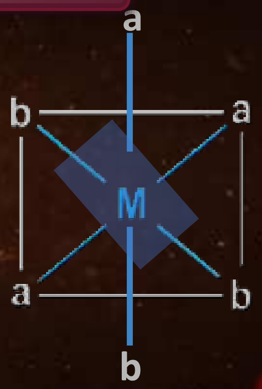
Octahedral Complexes Having Monodentate Ligands

Case **1(e)**

$[Ma_3b_3]^{n\pm}$

Have **three** identical ligands on **one** **triangular face**

Facial (fac)

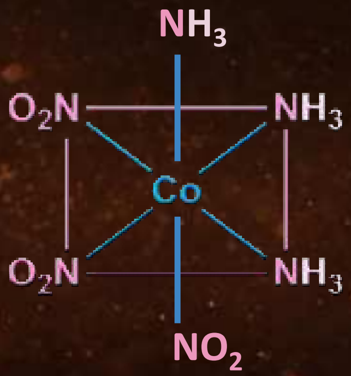


Meridional (mer)

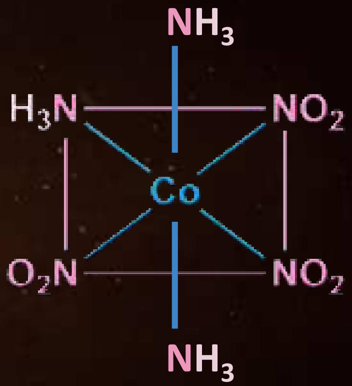
Have **three** identical ligands in a plane **bisecting** the **molecule**

Possible number of **geometrical** isomers = **2**

Octahedral Complexes Having Monodentate Ligands



Facial **(fac)**



Meridional **(mer)**

Octahedral Complexes Having Monodentate Ligands

Case **1(f)**

$[M(abcdef)]^{n\pm}$

Possible number of **geometrical** isomers = **15**

Geometrical Isomerism in Octahedral Complexes

Octahedral complexes where **ligands** are

Monodentate

Symmetrical bidentate and monodentate type

Unsymmetrical bidentate and monodentate type

Symmetrical Bidentate and Monodentate Ligands

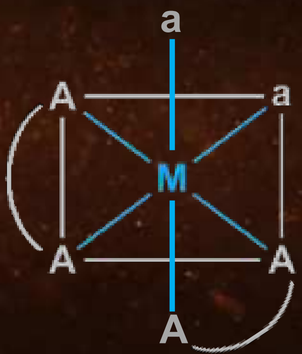
Case **2(a)**

$[M(AA)_3]^{n\pm}$

Does not show GI but chiral

Case **2(b)**

$[M(AA)_2a_2]^{n\pm}$



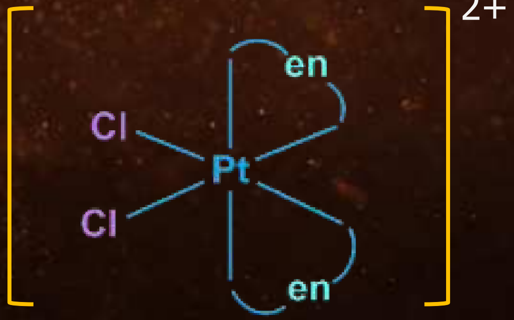
cis

trans

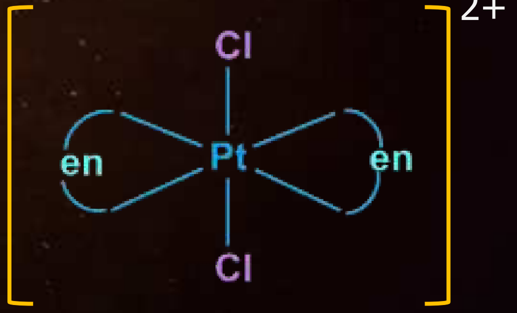
Possible number of **geometrical** isomers = **2**

Symmetrical Bidentate and Monodentate Ligands

$[Pt(en)_2Cl_2]^{2+}$



cis

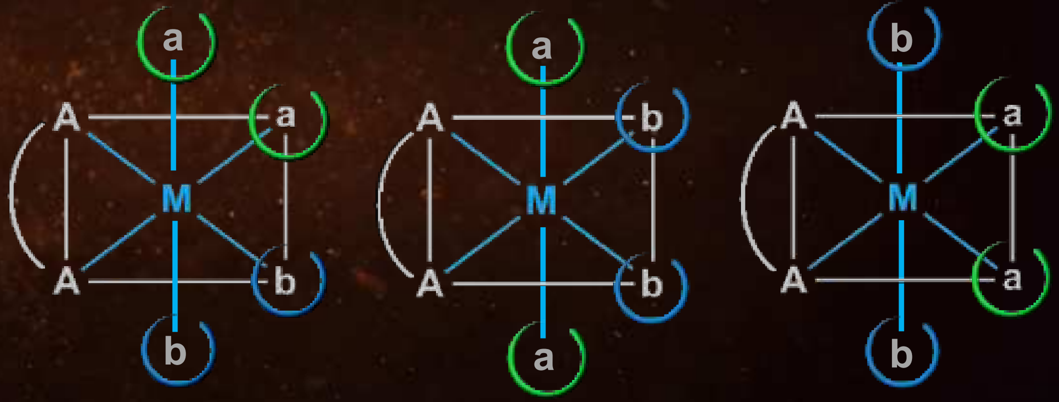


trans

Symmetrical Bidentate and Monodentate Ligands

Case **2(c)**

$[M(AA)a_2b_2]^{n\pm}$

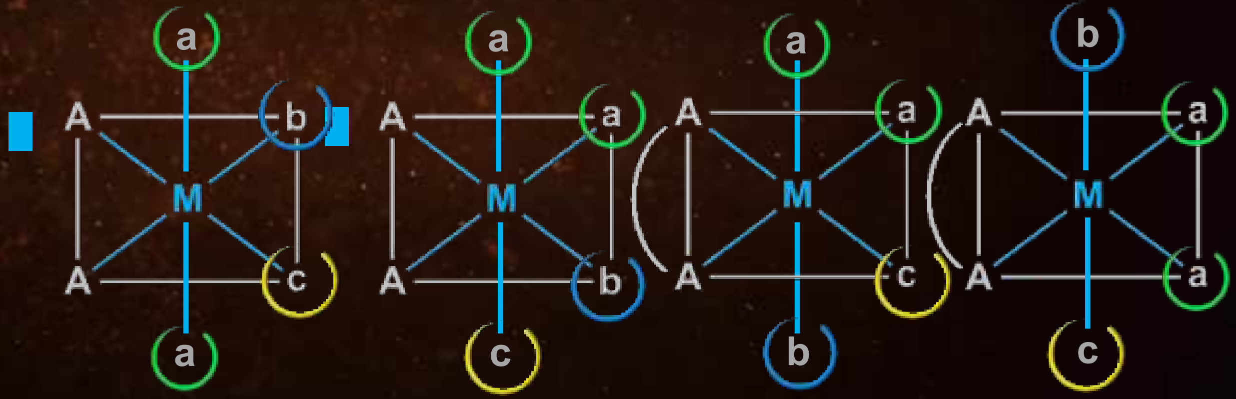


Possible number of **geometrical** isomers = **3**

Symmetrical Bidentate and Monodentate Ligands

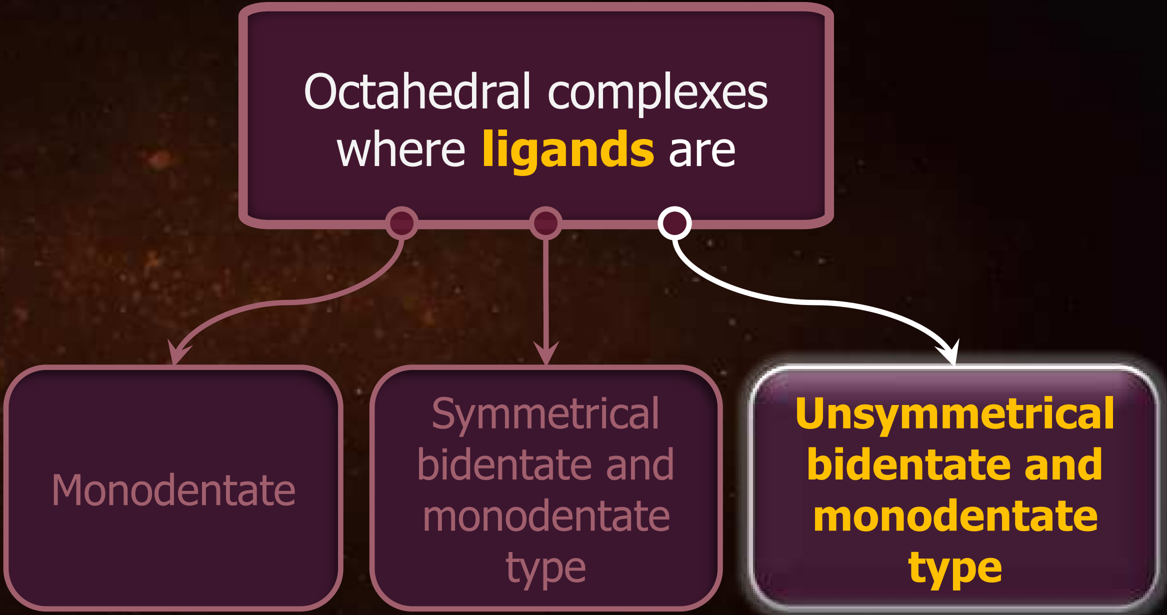
Case **2(d)**

$[M(AA)a_2bc]^{n\pm}$



Possible number of **geometrical** isomers = **4**

Optical Isomerism in Octahedral Complexes



Octahedral complexes where **ligands** are

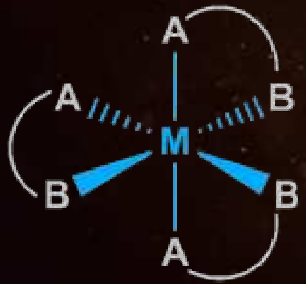
- Monodentate
- Symmetrical bidentate and monodentate type
- **Unsymmetrical bidentate and monodentate type**

Unsymmetrical Bidentate and Monodentate Ligands

Case **3(a)**

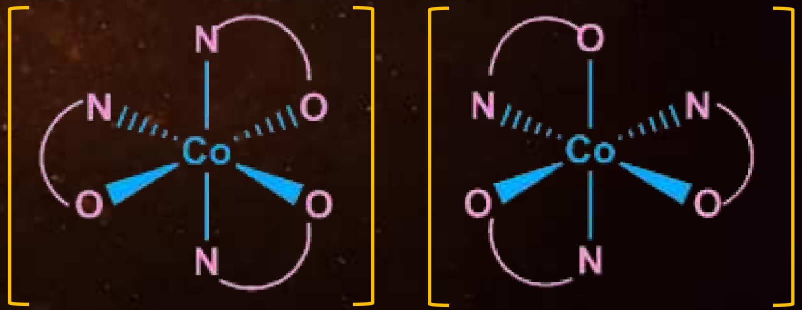
$[M(AB)_3]^{n\pm}$

$[Co(gly)_3]$



mer-isomer

fac-isomer



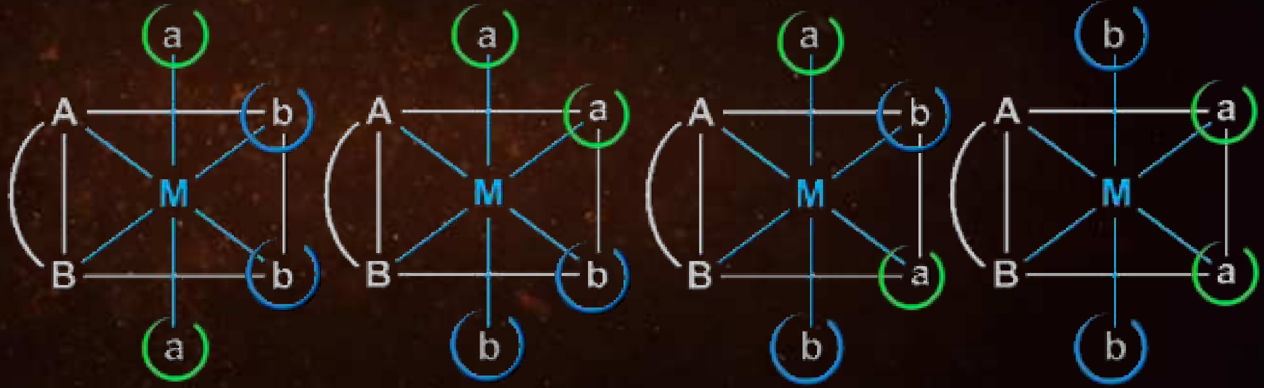
Possible number of **geometrical** isomers = 2

Possible number of **geometrical** isomers = 2

Unsymmetrical Bidentate and Monodentate Ligands

Case **3(b)**

$[M(AB)_2a_2b_2]^{n\pm}$



Possible number of **geometrical** isomers = **4**

Optical Isomerism in Octahedral Complexes

Octahedral compounds where **ligands** are

- Monodentate
- Symmetrical bidentate and monodentate
- Unsymmetrical bidentate and monodentate

Octahedral Complexes Having Monodentate Ligands

Case **1(a)**

$[M(a_4b_2)]^{n\pm}$

Does not show optical isomerism

Possible number of **enantiomers** = **0**

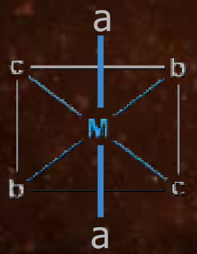
Octahedral Complexes Having Monodentate Ligands

Case 1(b)

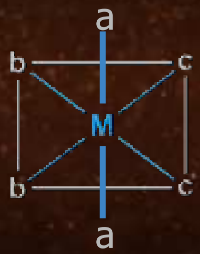
$[M(a)_2(b)_2(c)_2]^{n\pm}$

All possible GI's

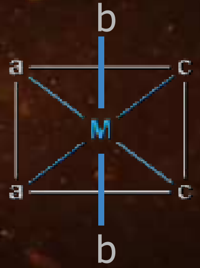
Optically active



Optically inactive



Optically inactive



Optically inactive

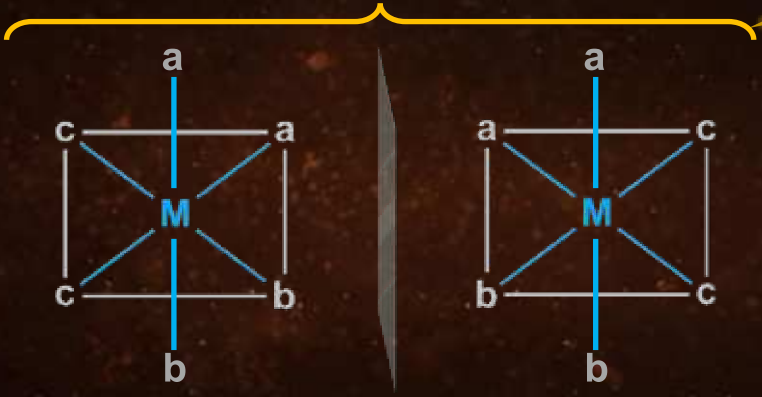
Optically inactive

Octahedral Complexes Having Monodentate Ligands

Case 1(b)

$[M(a)_2(b)_2(c)_2]^{n\pm}$

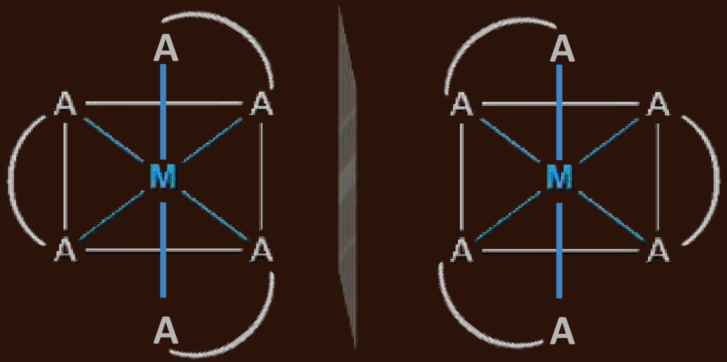
Optical isomer



Possible number of enantiomeric pairs	=	1
Total possible stereoisomers	=	6

Symmetrical Bidentate and Monodentate Ligands

Case 2(a) : $[M(AA)_3]^{n\pm}$



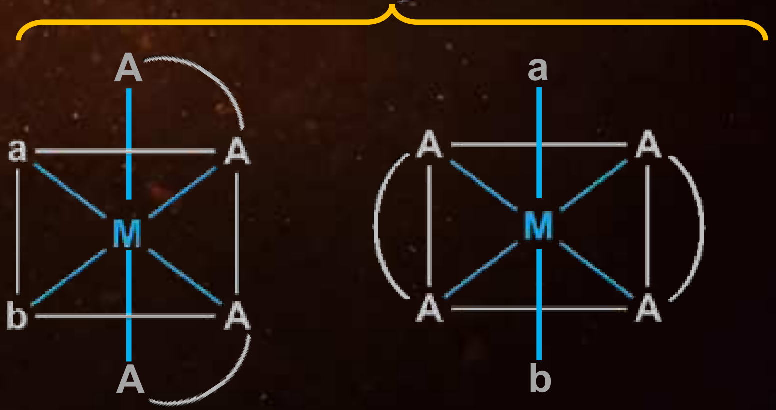
- Possible number of **Enantiomeric pairs = 1**
- Total number of **stereoisomers = 2**

Symmetrical Bidentate and Monodentate Ligands

Case **2(b)**

$[M(AA)_2ab]^{n\pm}$

Possible **GI's**



Optically active

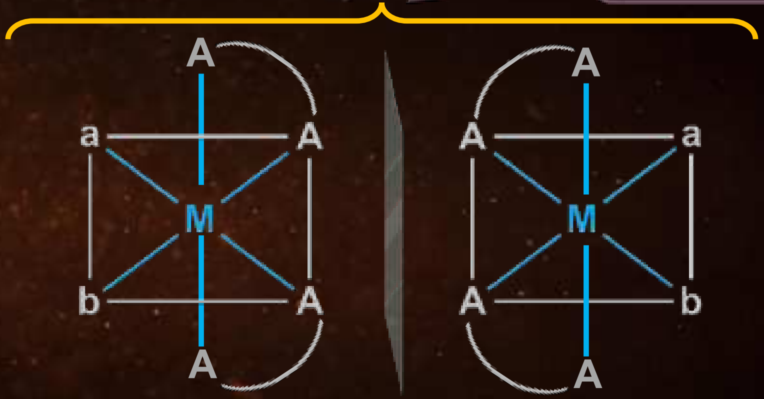
Optically inactive

Symmetrical Bidentate and Monodentate Ligands

Case **2(b)**

$[M(AA)_2ab]^{n\pm}$

Optical isomers



Possible number of **enantiomeric pairs** = **1**

Total **possible stereoisomers** = **3**

Unsymmetrical Bidentate and Monodentate Ligands

Case **3(a)**

$[M(AB)_3]^{n\pm}$

Possible **GI's**

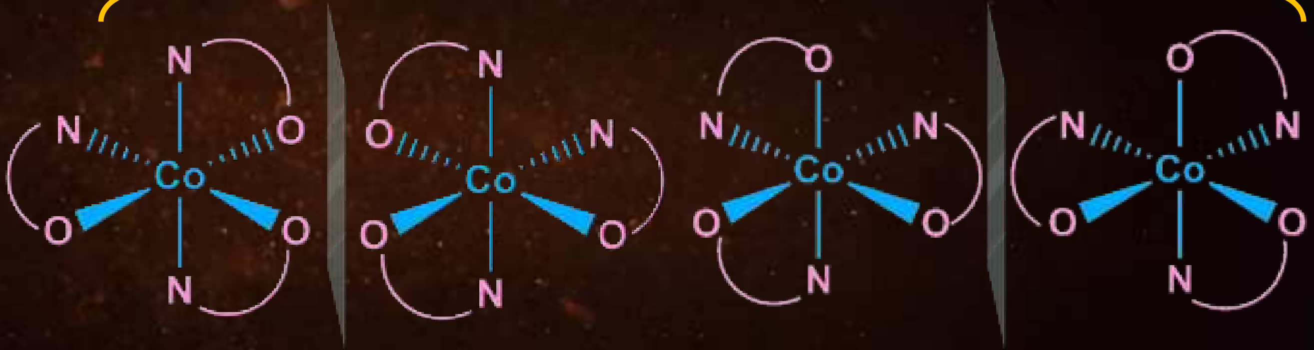
Optically active

Optically active

Unsymmetrical Bidentate and Monodentate Ligands

$[Co(gly)_3]$

Optical isomers



Possible number of **enantiomeric pairs** = **2**

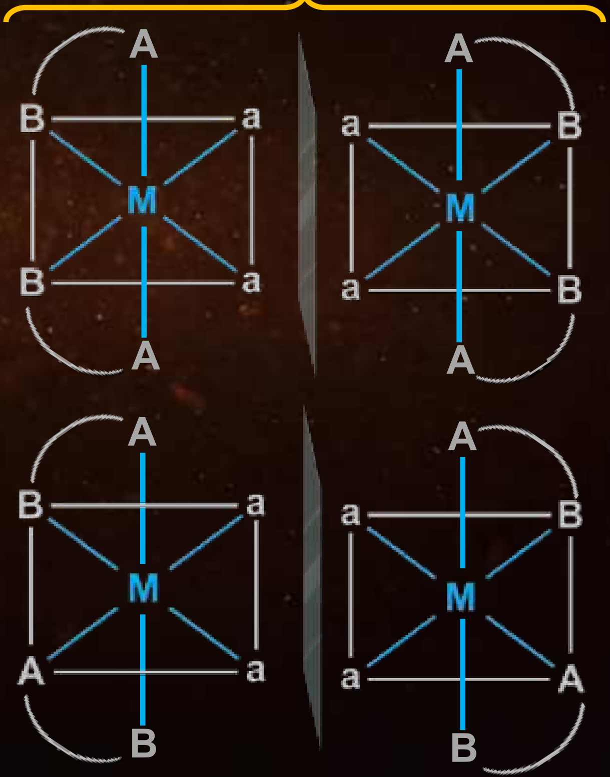
Total **possible stereoisomers** = **4**

Unsymmetrical Bidentate and Monodentate Ligands

Case **3(b)**

$[M(AB)_2a_2]^{n\pm}$

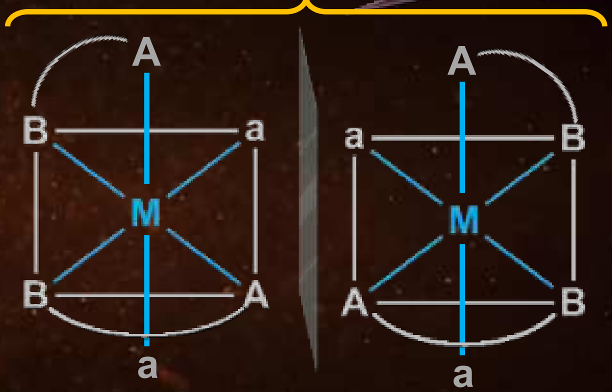
Optical isomers



Unsymmetrical Bidentate and Monodentate Ligands

Case **3(b)**

Optical isomers



Possible number of **enantiomeric pairs** = **3**

Total **possible stereoisomers** = **8**

Applications and importance of coordination chemistry in

- Analytical chemistry
- Metallurgy
- Biological systems
- As Catalysts
- Medicinal chemistry
- Other industrial applications

Applications in Analytical Chemistry

1

Detection and **estimation** of a **metal**

Due to the colour produced by the metal when it reacts with a **ligand**

Chelating ligands such as **EDTA, DMG,** etc.

Applications in Analytical Chemistry

2

In estimation of **hardness of water**

Done by **titration** with **Na_2EDTA**

Because **Ca^{2+}** and **Mg^{2+}** ions form **stable** complexes with **EDTA**

	$\log K_f$
$Ca^{2+} + EDTA \rightleftharpoons Ca(EDTA)^{2-}$	10.69
$Mg^{2+} + EDTA \rightleftharpoons Mg(EDTA)^{2-}$	8.79

Selective estimation due to the difference in **stability constants**

Coordination Chemistry in Metallurgy

In **extraction of metals**

Examples: **Au, Ag**

Roasted gold ore $+ CN^- + H_2O \xrightarrow{O_2} [Au(CN)_2]^- + OH^-$

In **aqueous solution**

Coordination Chemistry in Metallurgy

Purification of metals

By **formation** and **subsequent decomposition** of their coordination compounds

$$\underset{\text{Impure}}{Ni + 4CO} \xrightarrow{330\text{–}350\ K} Ni(CO)_4 \xrightarrow{450\text{–}470\ K} \underset{\text{Pure}}{Ni} + CO\uparrow$$

Coodination Chemistry in Biological System

Name	Metal involved	Function
Chlorophyll	Mg	Photosynthesis
Haemoglobin	Fe	Carries Oxygenated blood
Vitamin B12 (Cyanocobalamin)	Co	Anti-pernicious anaemia factor
Carboxypeptidase A Carbonic anhydrase	Zn	Enzymes

Used as Catalysts

Coordination compounds are used as catalysts in industrial process.

Example

Wilkinson's Catalyst → Hydrogenation of alkene

$(Ph_3P)_3RhCl$

$$H_2C = CH_2 + H_2 \xrightarrow{(Ph_3P)_3RhCl} H_3C - CH_3$$

Application in Medicinal Chemistry

When **metal** is present in **toxic proportion** in **plants/animals**

Excess metal is removed using chelating ligand which is known as **Chelating therapy**

Cis-platin and related compounds effectively **inhibit the growth** of a **tumour.** Hence, it is used in the **treatment** of **cancer.**

Application in Medicinal Chemistry

Excess Metal	Chelating ligand used in removal
Cu	D - penicillamine
Fe	Desferrioxamine B
Pb poisoning	EDTA

Other Industrial Applications

Electroplating

Articles electroplated by silver $[Ag(CN)_2]^-$ and gold $[Au(CN)_2]^-$

Even and smoother solutions of other metal.

Other Industrial Applications

Black and white photography.

Developed film is fixed and washed with hypo ($Na_2S_2O_3$)

Dissolves undecomposed AgBr to form $[Ag(S_2O_3)_2]^{3-}$