# Class 12th

→ d f Block
→ coordination comp
4-5
Tg

# Complete INORANIC CHEMISTRY



## In Detail

Notes
Imp. Ques.


Break
15 min
↓
2:40
class will
Resume

# d-Block

→ 40 elements

1 → 1s 1 2

2 → 2s Li Be

3 → 3s Na Mg

4 → 4s K Ca

5 → 5s Rb Sr

6 → 6s Cs Ba

7 → 7s Fr Ra

S-block

90% Ques

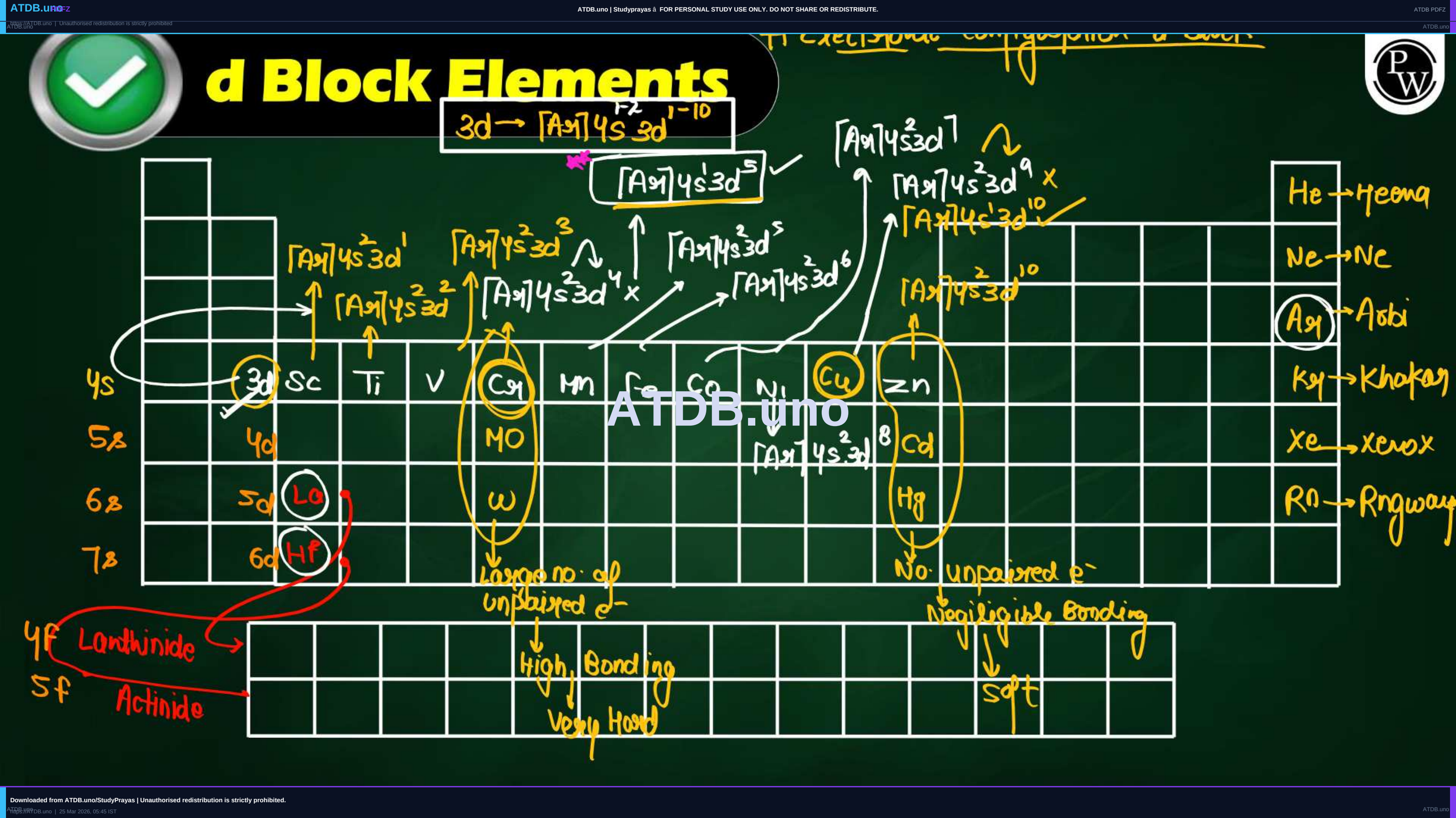
Ru belongs to which d-series?

(A) 3d (B) 4d (C) 2d (D) 5d

| | 3 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sky | T | V | Cromepati | Mna | Fe | Co | Ni | Cu | Zncte |
| 3d | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn |
| 4d | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd |
| 5d | 57 La | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg |
| 6d | 89 Ac | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 Cn |

12

d-block



Que Which of the following shows exceptional behav. in Electronic Config ?

(A) Zn, Cr

(B) Cu, Fe

(C) Cu, Cr

(D) None of these

APM A|B|C|D

# General E.C of d-block

$$[\,]ns^{1-2}(n-1)d^{1-10}$$

ATDB.uno

# d Block Elements


- **d-block** → Elements in d-block represent change or transition in properties from most electropositive s-block elements to most electronegative p-block elements. Therefore, these elements are called "Transition elements".

- **Transition Elements** → Elements whose outermost shell is partially filled d orbitals either in ground state or in ionic form are only called as Transition Elements, that's why Zn, Cd, Hg are not transition metals or called as Pseudo Transition metals.



Account for the following:
Zn, Cd, Hg are considered as d-block elements but not as transition elements. (1/5, 2020)

→ This is due to the reason that they do not have partially filled d-orbitals in their ground or ionic state.

APM

# Some Important Basic points


- Half/fully filled orbitals are more stable as compared to generally filled.
- **No. of Unpaired e-** → Partially filled orbitals (unpaired e⁻)

3d

| | Unpaired |
|---|---|
| Sc → $4s^2 3d^1$ | 1 ✓ |
| Ti → $4s^2 3d^2$ | 2 ✓ |
| V → $4s^2 3d^3$ | 3 ✓ |
| Cr → $4s^1 3d^5$ | 6 ✓ |
| Mn → $4s^2 3d^5$ | 5 ✓ |
| Fe → $4s^2 3d^6$ | 4 ✓ |
| Co → $4s^2 3d^7$ | 3 ✓ |
| Ni → $4s^2 3d^8$ | 2 ✓ |

Cu → $4s^1 3d^{10}$ 1 ✓

Zn → $4s^2 3d^{10}$ 0 ✗

Not a Transition element

$Cu^+ \rightarrow 4s^0 3d^{10}$

$Cu^{2+} \rightarrow 4s^0 3d^9$

$Zn^{2+} \rightarrow 4s^0 3d^{10}$ ✗

d-block

Fully filled → $d^{10}$

Half filled → $d^5$

Gen. Filled → $d^3/d^4$...

$d^5 / d^{10} > d^3 / d^4$ ✓

| | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| Z | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
| 5s | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 2 |
| 4d | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 10 | 10 |

# Metallic Character

- All the d-block elements are metals, have High M.P. and B.P. are good conductors of electricity, are hard ductile and Malleable (Hg is an exception).
  → Liq at room Temp
- d-block elements shows both metallic and Covalent bonding.

APM

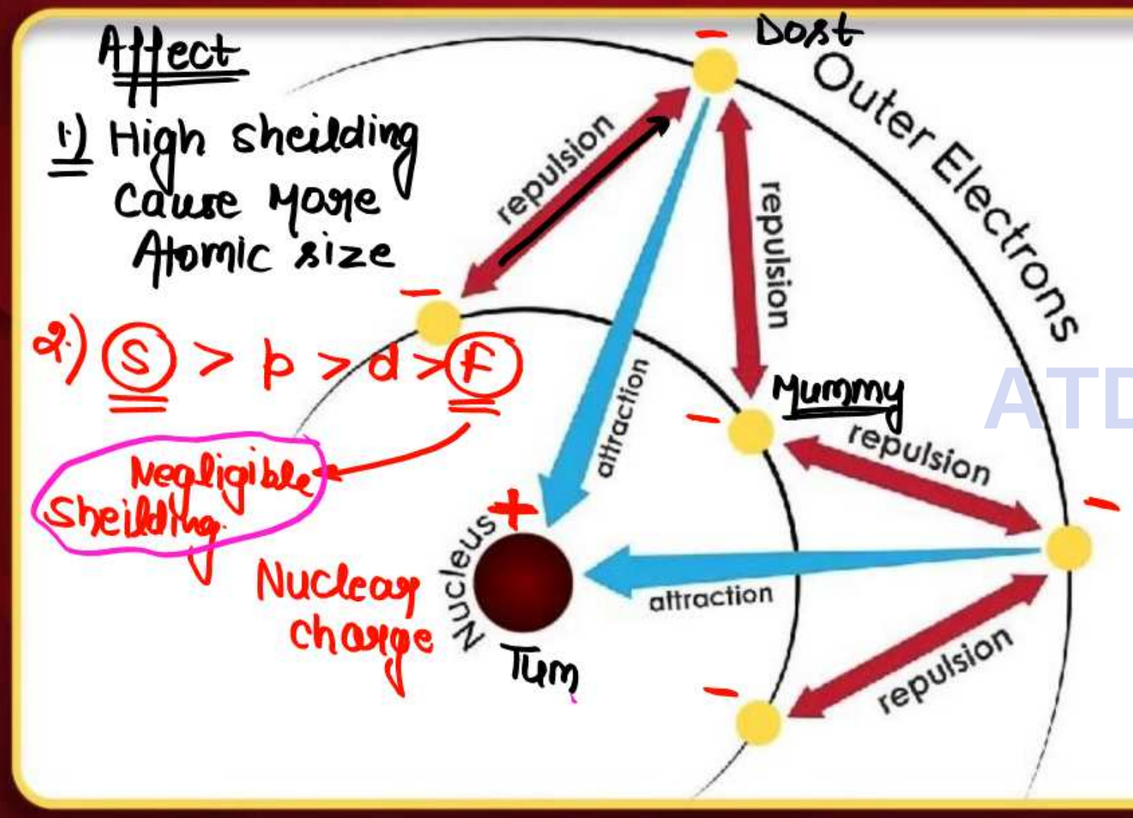


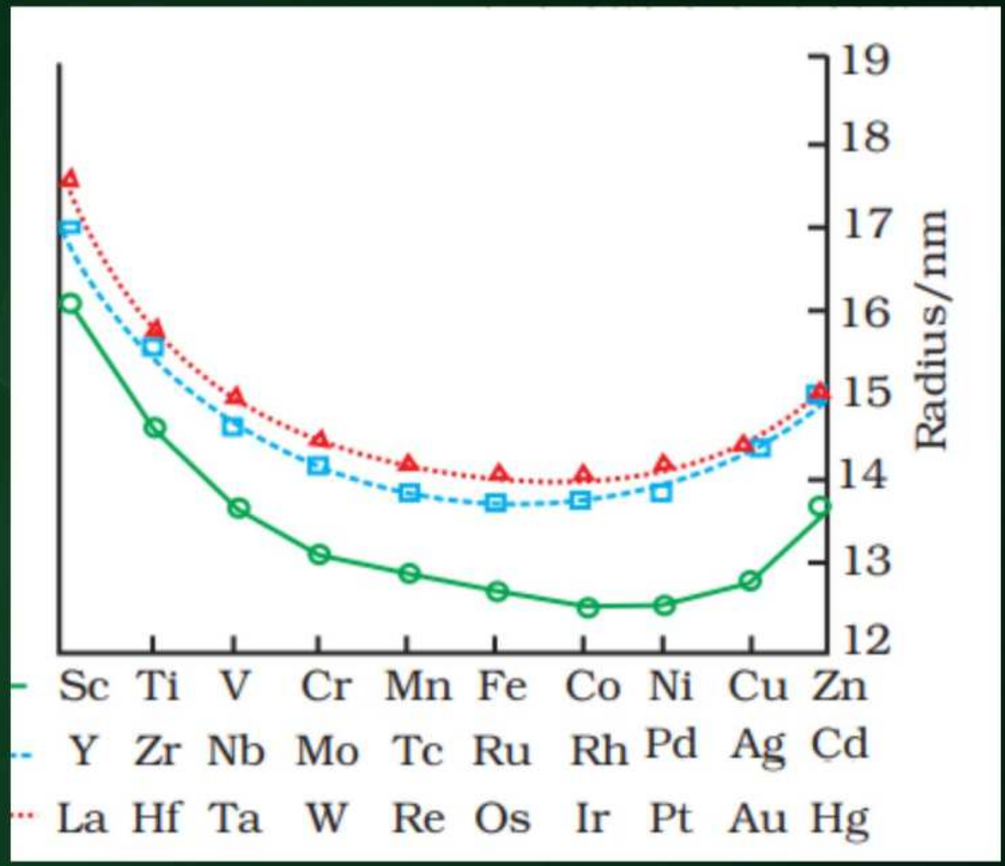
Metallic → It is due to the presence of valence e⁻ in outermost shell

Covalent → It is due to the presence of partially filled d-orbital

- More unpaired e in d orbitals → More Covalent/Metallic Bonding
  ↓
  Hard will be the Metal
- Cr, Mo and W are very hard . due to large no. of unpaired e⁻
- Zn, Cd, Hg are very soft due to absence of unpaired e⁻ in d-orbitals.
- Metallic character inc. down the group.

# SHIELDING EFFECT



# Atomic Radii

APM

- **Left → Right**

As we move left to right in d-block, firstly size decreases due to increase nuclear charge but from midway when screening due (n – 1)d also increases the effect of inc. nuclear charge got overshadowed by screening effect and then further no change in atomic radii. but at the end due to more S.E in Zn Atomic radii inc.



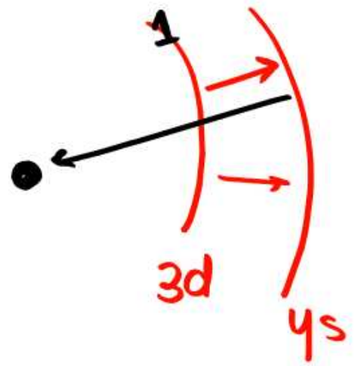
**Ex.** $4s^2 3d^1 > 4s^2 3d^2 > 4s^2 3d^3 > 4s^1 3d^5 \sim 4s^2 3d^5 \sim 4s^2 3d^6 \sim 4s^2 3d^7 \sim 4s^2 3d^8 \sim 4s^1 3d^{10} < 4s^2 3d^{10}$

$Sc_{21} > Ti_{22} > V_{23} > Cr_{24} \sim Mn \sim Fe \sim Co \sim Ni \sim Cu < Zn$

144 132 122 117 117 117 116 115 117 125

dec. constant Inc.

| Nuclear Charge > Screening | N.C = S.E | N.C < S.E |
|---|---|---|



# Lanthanide Contraction

**Top → Bottom**

**The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction.**

No. of shell inc.
Nuclear charge inc
Screening eff. inc
As a result size inc 3d → 4d

No. of shell inc. ✓
Nuclear charge inc. ✓
Negligible ↑EX
As a result atomic size remains cons. from 4d → 5d

3d $4s^2 3d^1$
4d $3d^{10} 5s^2 4d^1$
5d $6s^2 4f^{14} 5d$
6d

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Mn | 27 Co | 28 Ni | 29 Cu | 30 Zn |
| 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd |
| 57 La | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg |
| 89 Ac | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 Cn |

f block



**The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties**

They are hard to seperate.

**2. two statements are given - one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below. (2024)**

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.



**Assertion (A) :** Separation of Zr and Hf is difficult.

**Reason (R) :** Zr and Hf have similar radii due to lanthanoid contraction.

# Melting/Boiling Point**

M·P/ B·P ⟹ more ⟹ Larger no of unpaired e⁻ ⇓ High Bonding

- As we move Left → Right,

M.P. / B.P. first inc. and then decreases this is due to the fact that initially unpaired e⁻ in d-orbitals inc. Therefore, more covalent/Metallic bonding Hence strong bond but then further pairing up of d-orbitals taking place. Hence less Metallic bonding & low M.P.

M.P. ⇒ Sc < Ti < V < Cr > Mn > Fe > Co > Ni > Cu > Zn

1 2 3 6 5 4 3 2 1 0

E.C of Mn ⇒ 4s² 3d⁵

Due to its Half filled configuration it is Highly stable

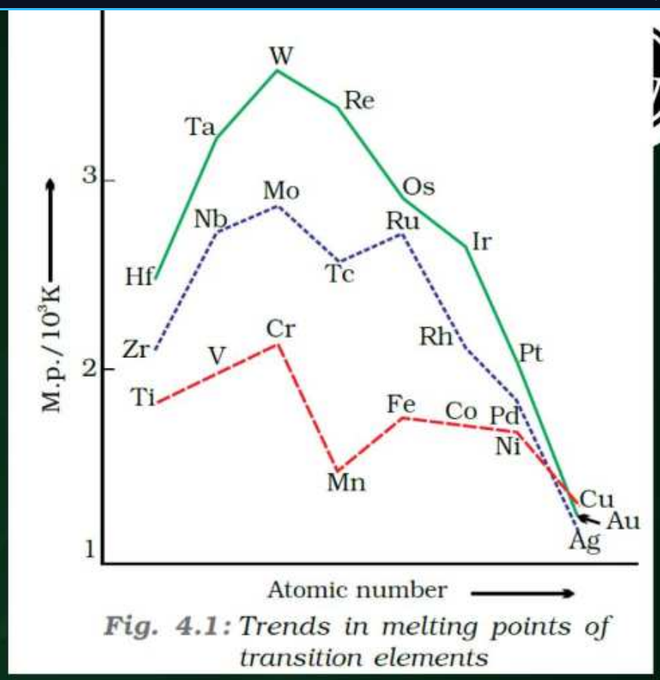



Fig. 4.1: Trends in melting points of transition elements

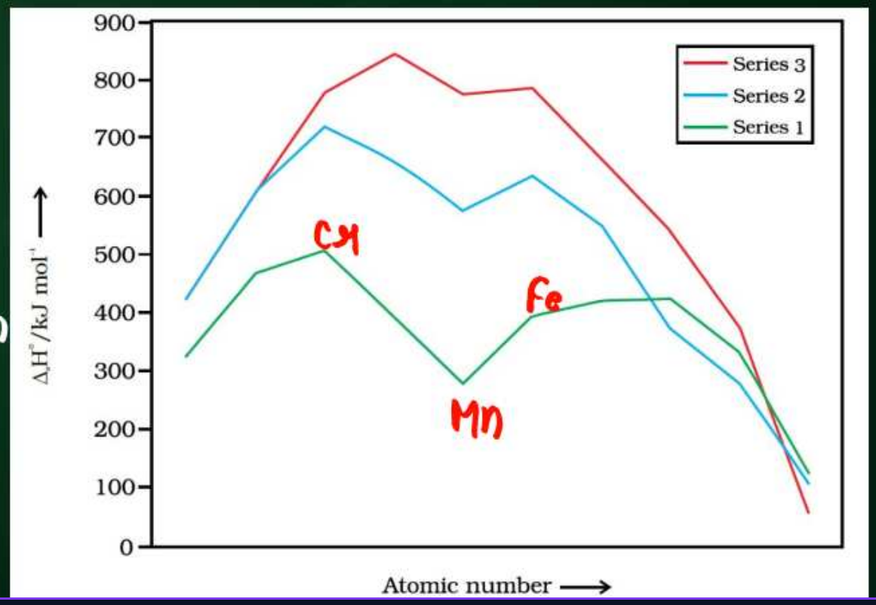
# Enthalpy of Atomisation**

In general, greater the number of valence electrons, stronger is the resultant bonding and Hence higher will be the enthalpy of atomization.

No. of unpaired e⁻ ⇒ High Bonding ⇒ High ΔHatom

M(s) ⟶ M(g)

ΔHatom.



Qu Which of the following has least $\Delta H_{atom}$?

PYQ 2024

(A) Mn

(B) Cu

(C) Sc

(D) Zn

# Ionization Energies

It can be defined as the minimum energy required to remove an $e^-$ from outermost shell of an isolated gaseous atom.

- As we move left to right, I.E. values increases but not regularly.

Atomic size dec.

3d

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| 631 | 656 | 650 | 652 | 717 | 762 | 758 | 737 | 745 | 906 |

Mn: $4s^2 3d^5$ / Half filled

Zn: $4s^2 3d^{10}$ fully filled.

Stable & I.E

APM



**Note :** III[rd] I.E. of Mn is very high because third $e^-$ is to be removed from a stable configuration ($Mn^{2+}$, $3d^5$) i.e half filled 3d-subshell.

$Mn - 1e^- \xrightarrow{I.E_1} Mn^+ - 1e^- \xrightarrow{I.E_2} Mn^{2+} - 1e^- \xrightarrow{I.E_3} Mn^{+3}$

$4s^2 3d^5$ $\quad 4s^1 3d^5$ $\quad 4s^0 3d^5$

**Note :** II[nd] I.E. of Cu and Cr is very high as compared to neighbouring elements. This is because of the stable or fully filled or half filled configurations.

$Cu - 1e^- \longrightarrow Cu^+ (3d^{10}) - 1e^- \xrightarrow{I.E_2}$

$4s^1 3d^{10}$

$Cr^+ (3d^5) - 1e^- \xrightarrow{I.E_2}$

Cr

$4s^1 3d^5$

# Top to Bottom-

From 4d to 5d or from 5d to 6d series where differentiating $e^-$ enters into f-subshell which causes negligible screening effect (i.e Lanthanide contraction)
Hence due to More Nuclear charge I.E increases.

Size inc.
I.E dec

Size constant
Negligible S.E
High N.C
I.E inc

| | | | | |
|---|---|---|---|---|
| 3d | 21 Sc | 22 Ti | 23 V | 24 Cr |
| 4d | 39 Y | 40 Zr | 41 Nb | 42 Mo |
| 5d | 57 La | 72 Hf | 73 Ta | 74 W |
| | 89 Ac | 104 Rf | 105 Db | 106 Sg |

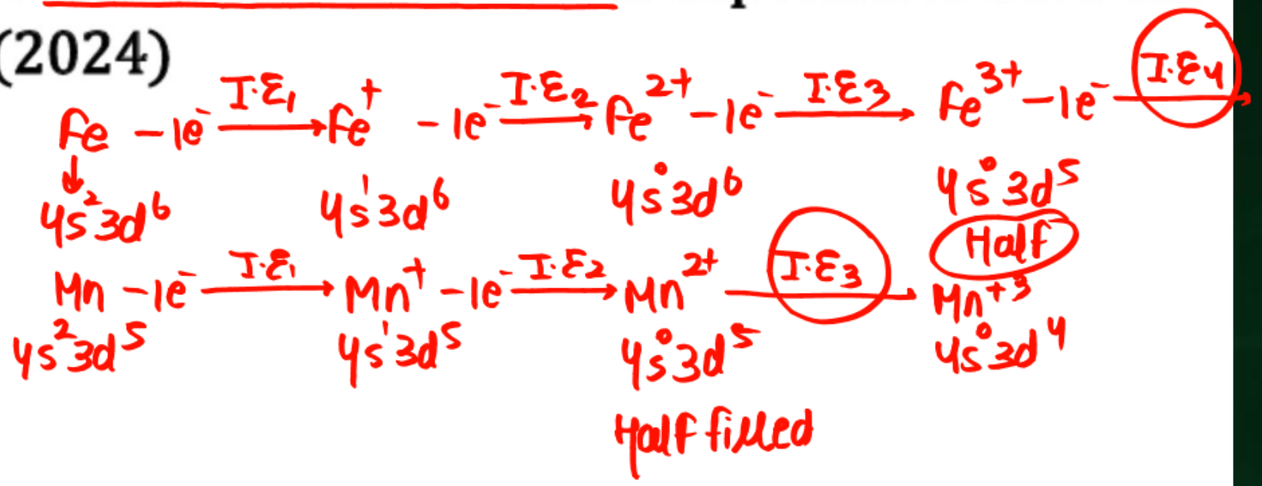
1. Which one of the following first row transition elements is expected to have the highest third ionization enthalpy ? (2024)

(A) Iron (Z = 26) X

(B) Manganese (Z = 25)

(C) Chromium (Z = 24)

(D) Vanadium (Z = 23)



# Why d-block elements shows variable Oxidation State

Transition elements shows variable oxidation states is due to the involvement of (n-1)d and outer ns electrons in Bonding as the energy of ns and (n-1)d subshell are nearly equal.

The lower oxidation state is generally shown when only ns elections participate in Bonding and higher oxidation states are exhibited when ns and (n-1)d electrons Both take part in Bonding.

$4s^2 3d^1$ $4s^2 3d^2$ $4s^2 3d^3$ $4s^1 3d^5$ $4s^2 3d^5$ $4s^2 3d^6$ $4s^2 3d^7$ $4s^2 3d^8$ $4s^1 3d^{10}$ $4s^2 3d^{10}$

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| +3 | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +1 | +2 |
| | +3 | +3 | +3 | +3 | +3 | +3 | +3 | +2 | |
| | +4 | +4 | +4 | +4 | +4 | +4 | +4 | | |
| | | +5 | +5 | +5 | | | | | |
| | | | +6 | +6 | +6 | | | | |
| | | | | +7 | | | | | |

Bold → High stable

Note PYQ

Sc & Zn doesn't show variable Oxidation State.

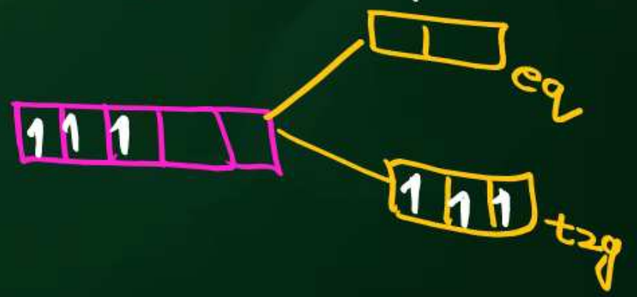
**Why some of the Oxi. State are more stable**

1) Due to half filled $d^5$ config. $Fe^{3+}$, $Mn^{+2}$
2) Due to fully filled $d^{10}$ config. $Zn^{2+}$
3) Due to inert electronic config. $Cr^{+6}$ $Mn^{+7}$
4) Due to half filled $t_{2g}$ config. $Cr^{+3}$

$Cr^{+3}$

$Cr \rightarrow 4s^1 3d^5$

$Cr^{+3} \rightarrow 4s^0 3d^3$



## Oxidation state

(i) Higher O.S (+4 , +5, +6, +7, +8) (shown by fluorides and oxyfluoride)

(ii) Common O.S (+2 , +3,) (shown by chlorides and sulphides)

(iii) Lower O.S (0, +1) (shown by Metal carbonyl (CO) complex compound



$MnO_4^{(-)}$

$Mn + 4 \times O = -1$

$Mn + 4(-2) = -1$

$Mn - 8 = -1$

$Mn = -1 + 8$

$\boxed{Mn = +7}$

**Why Fluorine has ability to show higher oxidation state?**

The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy or higher bond enthalpy terms for the higher covalent compounds.

**Why Oxygen has higher ability to stablises higher oxidation state than fluorine?**

This is due the reason that Oxygen can make multiple bonds to stablise higher oxidation state while fluorine can't.

# Standard reduction Potential

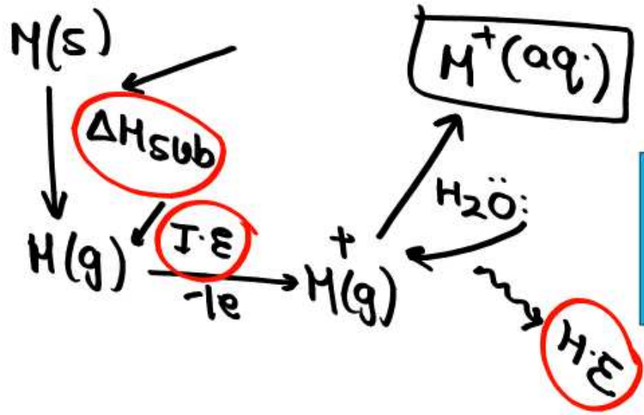
- Tendency of an element to get oxidized is called as Oxidation Potential. / Loss of $e^-$
- Tendency of an element to get reduced is called as Reduction Potential. / Gain of $e^-$

D-Block Elements ⟹ Metals ⇒ Oxidation ⇒ $E_{ox}$ ↑

Red. Potential ⇒ $E_{Red}$ ⇒ Negative



This Reduction Potential is used to measure the stability of ions in aqueous form.




$M(s) \rightarrow M^+(aq) + e^-$ $\quad \Delta H_T = \Delta H_{sub.} + I.E. - H.E.$

Process Forward ⟹ Stability ⇒ Low in Energy

Oxi. ⇒ T.E ↓

Sub/I.E ↓

H.E ↑

$E_{Red}$ ↓ (−)

# • The values of $E^0$ for Mn, Zn and Ni are more negative than expected. This is due to extra stability of half filled or fully filled d-subshell of $Mn^{2+}$ and $Zn^{2+}$.

(1) $Mn \rightleftharpoons Mn^{2+}$

$4s^2 3d^5$ $\quad$ $4s^0 3d^5$

I.E ↓ $\quad$ H.E ↑ $\quad$ ΔT.E ↓

$E_{Red} = -$ ✗

(2) $Zn \rightleftharpoons Zn^{2+}$

$4s^2 3d^{10}$ $\quad$ $4s^0 3d^{10}$

I.E ↓ $\quad$ H.E ↑ $\quad$ T.E ↓

$E_{Red} = (-)$

(3) $Cu(s) > Cu^{2+}(aq)$

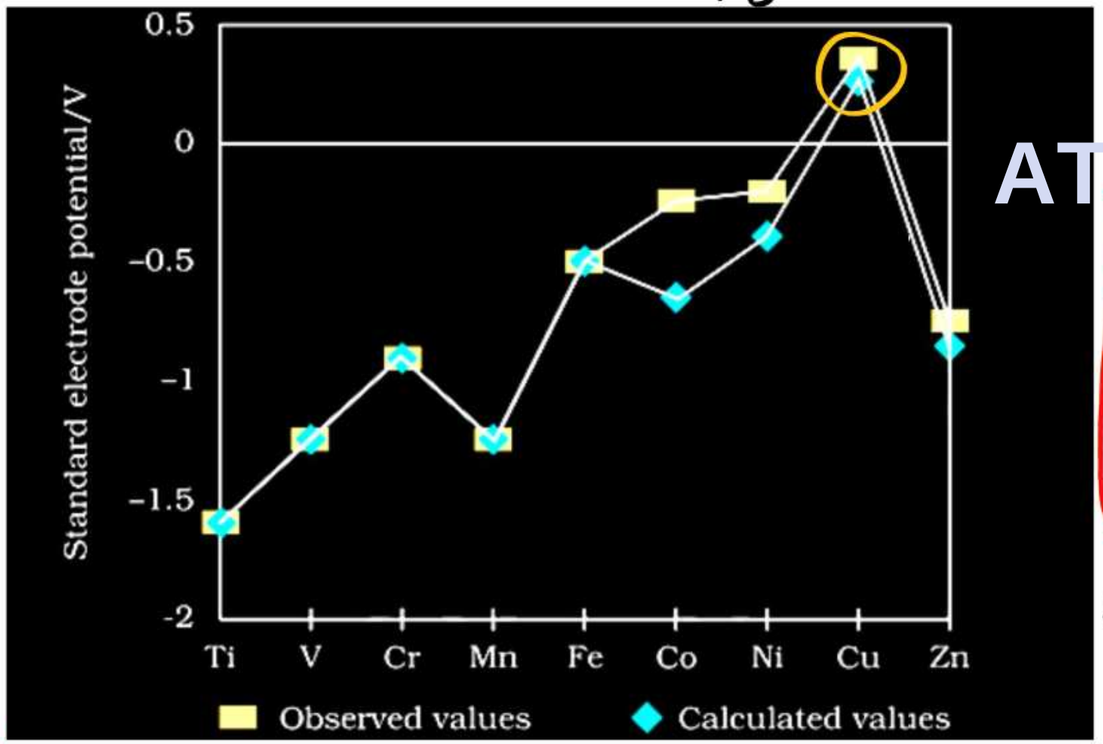
$4s^1 3d^{10}$ $\quad$ $4s^0 3d^9$

I.E ↑ $\quad$ H.E ↑ $\quad$ $E_{Red} = (+)$

(4) $Cu^+(aq) < Cu^{2+}(aq)$

$4s^0 3d^{10}$ $\quad$ $4s^0 3d^9$

I.E ↑ $\quad$ H.E ↑






The high energy to transform Cu(s) to $Cu^{2+}(aq)$ is not balanced/compensated by its hydration enthalpy.

The high energy to transform $Cu^+(aq)$ to $Cu^{2+}(aq)$ is balanced compensated by its hydration enthalpy.

* Why Cu has (+) $E_{Red}$ potential while other d-block elements have (−) $E_{Red}$ potential.

**4. The elements of 3d transition series are given as:** (3 Marks) (2025)

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Reducing agent → Oxidation

**Answer the following:**

**(a)** Copper has exceptionally positive $E^{\circ}_{M^{2+}/M}$ value, why ?

APM ♥

Ans

$Cu^{+2} \rightarrow Cu^{+3}$ (X) Oxi

High Red.

**(b)** Which element is a strong reducing agent in +2 oxidation state and why?

$Cu^{+3}$

**(c)** $Zn^{2+}$ salts are colourless. Why? → Due to Absence of unpaired e⁻

# QUESTION

## Why do the Transition elements exhibit higher enthalpies of atomization ?

Transition elements exhibit higher enthalpies of atomization due the presence of High no. of unpaired electrons which results in high bonding.

# QUESTION

**In the series Sc to Zn, the enthalpy of atomization of Zn is the lowest. Why ?**

Since Zn has 0 unpaired electrons that's why it has lowest Enthalpy of atomistion.

# Magnetic Properties

**Paramagnetic Substances-** A Paramagnetic substance is one which is weakly attracted into a magnetic field.

↳ Due to the presence of unpaired $e^-$

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

$n$ = unpaired $e^-$

**Diamagnetic Substances-** A Diamagnetic substance is one which is repelled by a magnetic field.

↳ Due to absence of unpaired $e^-$

Substances which are attracted very strongly are said to be ferromagnetic. In fact, ferromagnetism is an extreme form of paramagnetism.



$Cr \rightarrow 4s^1 3d^5$

$Cr^{+3} \rightarrow 4s^0 3d^3$

↑ ↑ ↑

1. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of $Cr^{3+}$ ion (Atomic no. : Cr = 24) is _____. (1 Marks) (2025)

(A) 2.87 B.M.

(B) 3.87 B.M.

(C) 3.47 B.M.

(D) 3.57 B.M.

$n = 3$

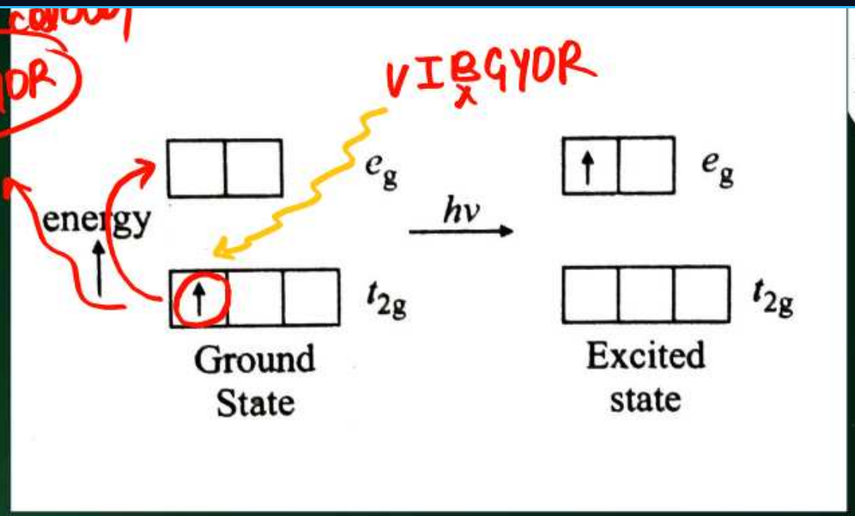
$\mu = \sqrt{3(3+2)}$

$\mu = \sqrt{15}$

# Colour

When an $e^-$ from a lower energy d-orbital is excited to a higher energy d-orbital, the energy of excitation corresponds to a particular frequency of light absorbed And rest of the frequencies are passed giving complimentary colour.

This is called as d-d transition




| Config. | Example | Colour |
|---|---|---|
| $3d^0$ | $Sc^{3+}$ | Colourless |
| $3d^0$ | $Ti^{4+}$ | Colourless |
| $3d^1$ | $Ti^{3+}$ | Purple |
| $3d^1$ | $V^{4+}$ | Blue |
| $3d^2$ | $V^{3+}$ | Green |
| $3d^3$ | $V^{2+}$ | Voilet |
| $3d^3$ | $Cr^{3+}$ | Voilet |
| $3d^4$ | $Cr^{2+}$ | Blue |

| Config. | Example | Colour |
|---|---|---|
| $3d^4$ | $Cr^{2+}$ | Blue |
| $3d^4$ | $Mn^{3+}$ | violet |
| $3d^5$ | $Fe^{3+}$ | Yellow |
| $3d^6$ | $Fe^{2+}$ | Green |
| $3d^7/3d^6$ | $CO^{2+}/CO^{3+}$ | Blue pink |
| $3d^8$ | $Ni^{2+}$ | Green |
| $3d^9$ | $Cu^{2+}$ | Blue |
| 3d10 | $Zn^{2+}$ | Colurless |

# APM Trick on TOP

$V^{2+}$ ⟶ Voilet — Very

$Cr^{2+}$ ⟶ Blue — Beautiful

$Mn^{2+}$ ⟶ Pink — Pinky

$Fe^{2+}$ ⟶ Goreen — G

$Co^{2+}/Co^{3+}$ ⟶ Blue pink — Beautiful like pineapple

$Ni^{2+}$ ⟶ Green — Hara h

$Cu^{2+}$ ⟶ Blue — Bolo ko

$Zn^{2+}$ ⟶ Colourless — Colour apka

Sc ⟶ Colourless — Colour kyaa

$Ti^{3+}$ ⟶ Purple — Parlour jaa

$V^{3+}$ ⟶ Green — Hara is

$Cr^{3+}$ ⟶ Voilet — Very

$Mn^{3+}$ ⟶ Yellow — Yummy

# Tendency to form complexes

# Formation of Interstitial compounds

- d-block elements have a marked ability to from complex compounds. This is due to their :-

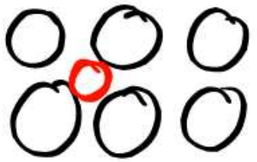
1. Small size
2. High nuclear charge
3. No. of vacant d-orbitals which can accommodate lone pair of ligands.

Ex. $Fe(CO)_5$, $Ni(CO)_4$, $[Cr(NH_3)_6]Cl_3$

- Interstitial compounds are those which are formed when small atoms like H, C, B or N are trapped inside the crystal lattice of metal.

They are neither ionic nor covalent.

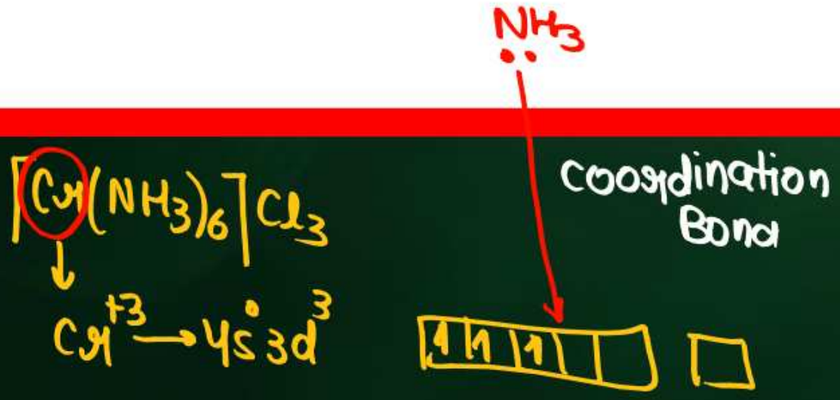
Ex. TiC, $Mn_4N$, $Fe_3H$, $TiH_{1.7}$ etc.



Charteristics :-

1. They have high M.P. that of pure metals.
2. They are very hard.
3. They are chemically inert





The incorrect statement about interstitial compounds is

(a) they are chemically reactive.

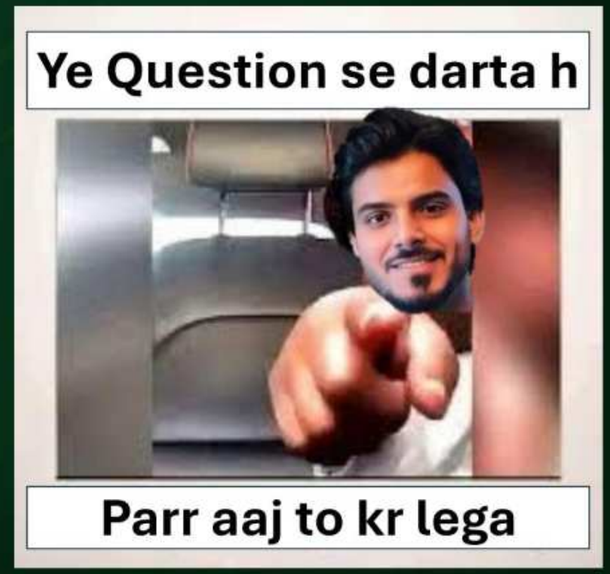
(b) they are very hard.

(c) they retain metallic conductivity.

(d) they have high melting point.

(2020)





# Catalytic Properties

- The transition metals and their compounds are known for catalytic activity.
- Catalyst at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst.

Since transition metal ions can change their oxidation state they become more effective or catalyst or they can utilize (n –1)d orbitals and use Multiple oxidation state in Bonding.



| Catalyst | Process |
|---|---|
| Fe | Haber's process |
| Ni | Addition Reaction |
| $V_2O_3$ | Contact process ($H_2SO_4$ formation) |
| Co salt | Bleaching power Decomposition |

| Catalyst | Used as |
|---|---|
| Ziegler's Natta catalyst $TiCl^{4+}$ $Al(C_2H_5)$ | Production of polythene |
| $PdCl_2$ | In wacker process $C_2H_4 \rightarrow CH_3CHO$ |
| Pt/Rh | Making of $HNO_3$ in Ostwald process |

# Important Compounds

$K_2Cr_2O_7$

$K_2CrO_4$

$K_2MnO_4$

$KMnO_4$

## (A) Potassium Dichromate ($K_2Cr_2O_7$) :

Prep: Chromite ore

$$FeO \cdot Cr_2O_3 + O_2 + Na_2CO_3 \longrightarrow Fe_2O_3 + Na_2CrO_4$$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 \quad Na_2SO_4$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$



$K_2CrO_4$ $K_2Cr_2O_7$

**The chromate and dichromate are interconvertible in aqueous solution depending upon pH of the solution.**

2024 PYQ

$K_2Cr_2O_7$ Dichromate $\xrightarrow{\text{Basic } |OH^-| \ pH>7}$ $K_2CrO_4$ Chromate

$K_2CrO_4$ Chromate $\xrightarrow{\text{Acidic } |H^+| \ pH<7}$ $K_2Cr_2O_7$ Dichromate

# Structure of Chromate and Dichromate

APM

**Chromate/$CrO_4^{2-}$** **Dichromate** / $Cr_2O_7^{2-}$ (+6)

$Cr O_4^{2-}$

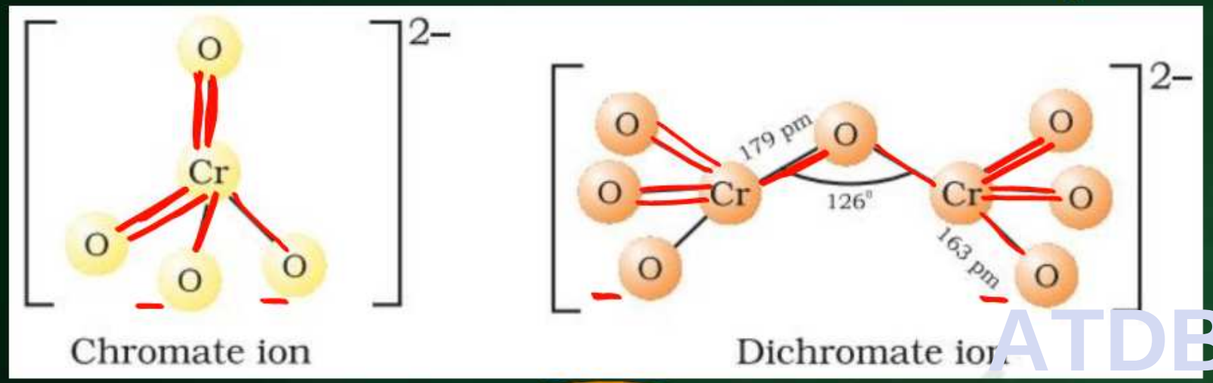
$Cr + 4 \times O = -2$

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

$Cr - 8 = -2$

$Cr = -2 + 8$

$Cr = +6$






**$K_2Cr_2O_7$ will oxidize Iodide to Iodine, Sulphides to Sulphur, $sn^{2+}$ to $sn^{4+}$ and $Fe^{2+}$ to $Fe^{3+}$**

$$\overset{+6}{I^-} + Cr_2O_7^{2-} \longrightarrow \underline{Cr^{+3}} + I_2^0$$

$$\overset{-2}{H_2S} + \overset{+6}{Cr_2O_7^{2-}} \longrightarrow Cr^{+3} + S^0$$

$$Fe^{2+} + \overset{+6}{Cr_2O_7^{2-}} \longrightarrow Cr^{3+} + Fe^{+3}$$

**Note** $Cr^{+6}$ is less stable than $Cr^{+3}$

$Cr^{+6} < Cr^{+3}$

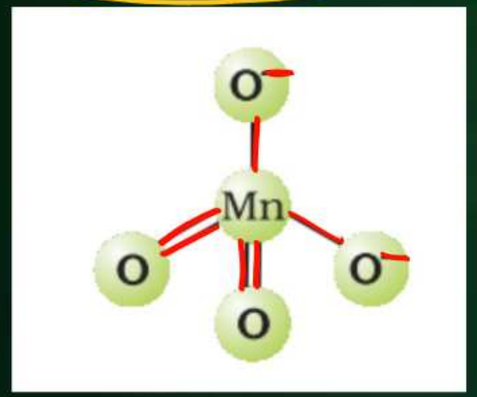
Reduction

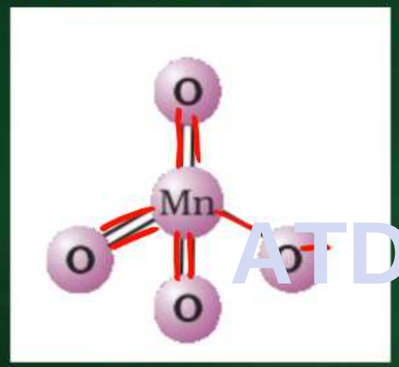
Oxidising agent

# Manganate and Permanganate

(B)

| Manganate | Permanganate |
|---|---|
| $(MnO_4^{2-})$ | $(MnO_4^-)$ |




$MnO_4^{2-}$

$Mn + 4 \times O = -2$

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

$Mn - 8 = -2$

$Mn = -2 + 8$

$Mn = +6$



$MnO_4^{2-}$ is only stable in strong alkaline solution. If $MnO_4^{2-}$ present is acidic/less basic/Neutral sol. It undergoes disproportionation.

$$\overset{+6}{MnO_4^{2-}} \xrightarrow{H^+} \overset{+7}{MnO_4^-} + \overset{+4}{MnO_2}$$

Green → Purple + Brown

# Preparation of Manganate

$K_2MnO_4$

**Pyrolusite**

$$MnO_2 \xrightarrow[\text{Boil}]{KOH + O_2} K_2MnO_4$$

# Laboratory preparation of $KMNO_4$



$$MnO_4^{2-} \xrightarrow[\text{alkaline solution}]{\text{Electrolytic oxidation in}} MnO_4^-$$

manganate — permanganate ion

# Preparation of Permanganate

$$K_2MnO_4 + H_2SO_4 \longrightarrow KMnO_4 + MnO_2$$

# Oxidising Properties of $MnO_4^-$ (In acidic Medium)

| | |
|---|---|
| (1) | $\overset{+7}{MnO_4^-} + Fe^{+2} \rightarrow Mn^{2+} + Fe^{3+}$ |
| (2) | $\overset{+7}{MnO_4^-} + I^- \rightarrow Mn^{2+} + I_2$ |
| (3) | $\overset{+7}{MnO_4^-} + H_2O_2 \rightarrow Mn^{2+} + O_2$ |
| (4) | $\overset{+7}{MnO_4^-} + \overset{+4}{SO_2} \rightarrow Mn^{2+} + \overset{+6}{H_2SO_4}$ |
| (5) | $MnO_4^- + NO_2^- \rightarrow Mn^{2+} + NO_3^-$ |
| (6) | $MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$ |
| (7) | $MnO_4^- + H_2S \rightarrow Mn^{2+} + S\downarrow$ |
| (8) | $MnO_4^- + SO_3^{2-} \rightarrow Mn^{2+} + SO_4^{2-}$ |

## Oxidising Behaviour of $Mn^{+7}$

$Mn^{+7}$ is less stable than $Mn^{+2}$

$Mn^{+7} < Mn^{2+}$

Red.

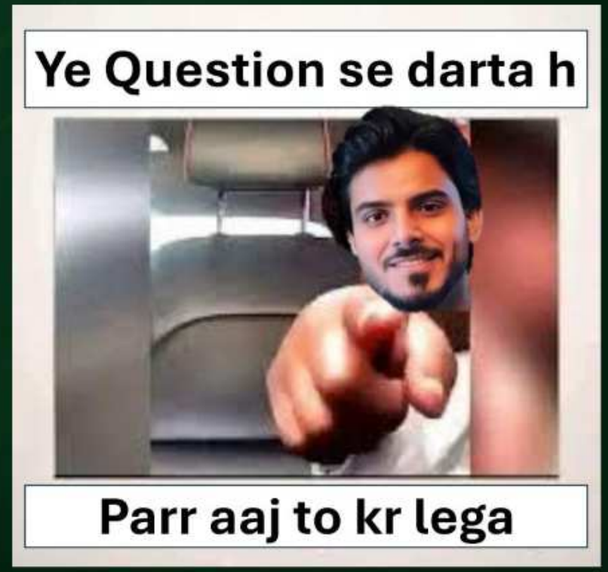
Oxidizing agent

## 3. Complete and balance the following chemical equations: (2 Marks) (2025)

(a) $2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \longrightarrow 2Mn^{+2} + 5I_2 + 8H_2O$

(b) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_2O$





# F-Block Elements

General e⁻ : $[\text{noble gas}]\, ns^2 (n-1)d^{0-1} (n-2)f^{1-14}$

28 elements from 58 to 71 and from atomic no. 90 to 103, These elements are collectively called as f-block element as the last or differentiating electrons of these elements enters into f- orbital.

Electrons in f-orbital always present in Anti pen-ultimate shell ie. (n -2)f.



Cerium

Lutetium

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4f | 58 Ce 140.12 | 59 Pr 140.91 | 60 Nd 144.24 | Pm (144.91) | 62 Sm 150.36 | 63 Eu 151.97 | 64 Gd 157.25 | 65 Tb 158.93 | 66 Dy 162.50 | 67 Ho 164.93 | 68 Er 167.26 | 69 Tm 168.93 | 70 Yb 173.04 | 71 Lu 174.97 |
| 5f | 90 Th 232.04 | 91 Pa 231.04 | 92 U 238.03 | Np (237.05) | Pu (244.06) | Am (243.06) | Cm (247.07) | Bk (247.07) | Cf (251.08) | Es (252.08) | Fm (257.10) | Md (258.10) | No (259.10) | Lr (262.11) |

Thorium

Lawrencium

Ce → Cerium

Pr → Praseodymium

Nd → Neodymium

Pm → Presmothium

Sm → samarium

Eu → europium

Gd → Gadolinium

Tb → Terbium

Dy → Dysprosmium

Ho → Holium

Er → Erbium

Tm → Thulium

Yb → Ytterbium

Lu → lutetium

can → 58 → [Xe] $4f^1 5d^1 6s^2$

Put → 59 → $4f^3 6s^2$

Needle → 60 → $4f^4 6s^2$

Properly in → 61 → $4f^5 6s^2$

Slot → 62 → $4f^6 6s^2$

Every → 63 → $4f^7 6s^2$

Gu[illegible] → 64 → $4f^7 5d^1 6s^2$

Tries → 65 → $4f^9 6s^2$

Daily → 66 → $4f^{10} 6s^2$

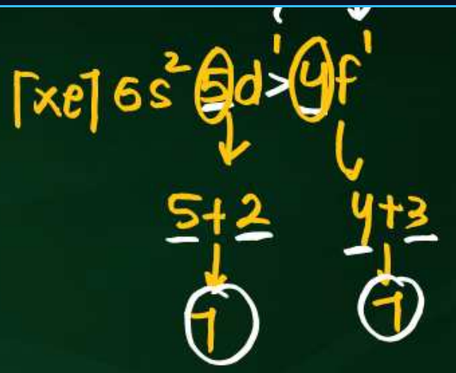
However → 67 → $4f^{11} 6s^2$

Every → 68 → $4f^{12} 6s^2$

Time → 69 → $4f^{13} 6s^2$

you → 70 → $4f^{14} 6s^2$

Loose → 71 → $4f^{14} 5d^1 6s^2$




S=0
P=1
d=2
f=3

# Electronic configurations

# Actinides

$Th \rightarrow 90 \rightarrow [Rn]6d^2 7s^2$ — $d^2$

$Pa \rightarrow 91 \rightarrow [Rn]5f^2 6d^1 7s^2$ — $d^1$

$U \rightarrow 92 \rightarrow [Rn]5f^3 6d^1 7s^2$ — $d^1$

$Np \rightarrow 93 \rightarrow [Rn]\ 5f^4 6d^1 7s^2$ — $d^1$

$Pu \rightarrow 94 \rightarrow [Rn]\ 5f^6 7s^2$

$Am \rightarrow 95 \rightarrow [Rn]\ 5f^7 7s^2$

$Cm \rightarrow 96 \rightarrow [Rn]\ 5f^7 6d^1 7s^2$

$Bk \rightarrow 97 \rightarrow [Rn]5f^9 7s^2$

$Cf \rightarrow 98 \rightarrow [Rn]5f^{10} 7s^2$

$Es \rightarrow 99 \rightarrow [Rn]5f^{11} 7s^2$

$Fm \rightarrow 100 \rightarrow [Rn]5f^{12} 7s^2$

$Md \rightarrow 101 \rightarrow [Rn]5f^{13} 7s^2$

$No \rightarrow 102 \rightarrow [Rn]5f^{14} 7s^2$

$Lr \rightarrow 103 \rightarrow [Rn]5f^{14} 6d^1 7s^2$

Thorium → Th → Thor

Protoactinium → Pa → Protect

Uranium → U → Uranium

Neptunium → NP → Neptune

Plutonium → Pu → Pluto

Americium → Am → American

Curium → Cm → Computer/chemistry

Berkelium → Bk → Book lm

Californium → Cf → California explains

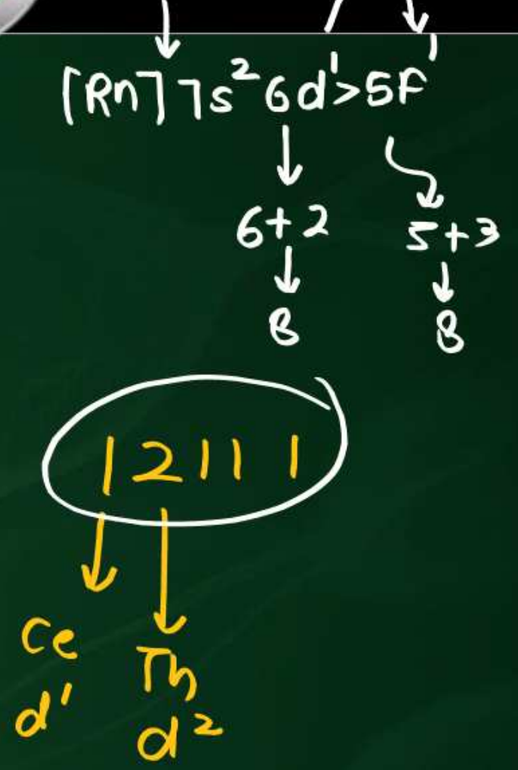
Einsteinium → Es → Einstein

Fermium → Fm → Fermi

Mendeleevium → Md → Maded

Nobelium → No → Noble gas

Lawrencium → Lr → Laws



| Lanthanoids | Actinoids |
|---|---|
| Differentiating electron eneters in 4f orbital | Differentiating electron eneters in 5f orbital |
| Binding energy of 4f orbitals are higher | Binding energy of 5f orbitals are lower |
| They show less tendency to form complexes | They show greater tendency to form complexes |
| Besides +3 oxidation states lanthanoids show +2 and +4 oxidation states in few cases. | Besides +3 oxidation states actinoids show higher oxidation states such as +4, +5, +6 and +7. |



## Why Actinoid contraction is greater than Lanthanide Contraction ?

Actinoid contraction is greater than Lanthanide contraction because the 5f electrons in Actinoid provides much poor shielding of nuclear charge as compared to 4f electrons of Lanthanide.

# Lanthanides

Rare Earth Metals

# Actinides

Radioactive elements

The best single use of the lanthanoids is for the production of alloy steels for plates and pipes.

A well known alloy is misch metal which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of misch metal is used in Mg-based alloy to produce bullets, shell and lighter flint.

CH-2

Board supremacy < APM supremacy

# Coordination Compounds

# Molecular Or Addition Compounds

When solution containing two or more simple stable compounds in molecular proportions are allowed to evaporate, crystals of new substance are obtained. These substance are termed as molecular or Addition compounds.

Ex.

$KCl + MgCl_2 + 6H_2O \rightarrow KCl \cdot MgCl_2 \cdot 6H_2O$

$K_2SO_4 + Al_2(SO_4)_3 + 24H2O \rightarrow$

$FeSO_4 + (NH_4)_2SO_4 + 6H2O \rightarrow$

Cognallity
Alum
Mohr's salt

Salt I + Salt II + Salt III

## 1 Double Salts Or Lattice Compounds

The addition comp. which are stable but broken down into individual constituents when dissolved in water. Their solutions have the same proportions as the mixture of individual comp. Ex. Mohr's salt

$FeSO_4.(NH_4)_2SO_4.6H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2NH_4^+ + 6H_2O$

## 2 Coordination Or Complex Compounds

The addition comp. in which some of the constituent ions or molecules retain their identity & when dissolved in water they do not break up completely into individual ions.

Ex- $CuSO4.4NH3 \rightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$

# Important Terminology

**Ligands :-** The neutral molecules, anions or cations which are directly linked with the central metal atom or ion in a complex are called ligands. They behave as an electron donor due to the presence of Lone pair.

**Central Metal atom/ion :-** These are the metal atom/ions which behave as an electron acceptor due to the absence of empty d orbital or positive charge.



APM

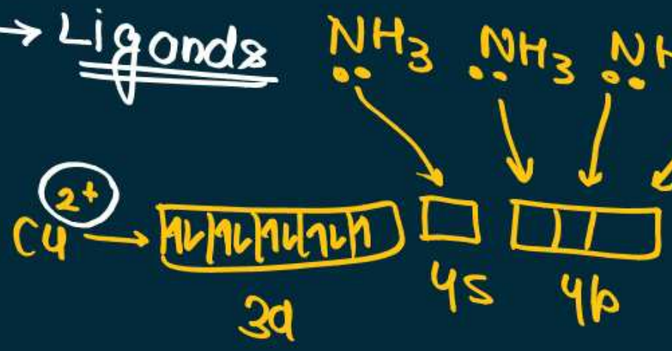
$[Cu(NH_3)_4]^{2+}$

Ligands → $NH_3$ $NH_3$ $NH_3$ $NH_3$

Central Metal atom/ion → $Cu^{2+}$

$Cu \rightarrow 4s^1 3d^{10}$

$Cu^{2+} \rightarrow 4s^0 3d^9$



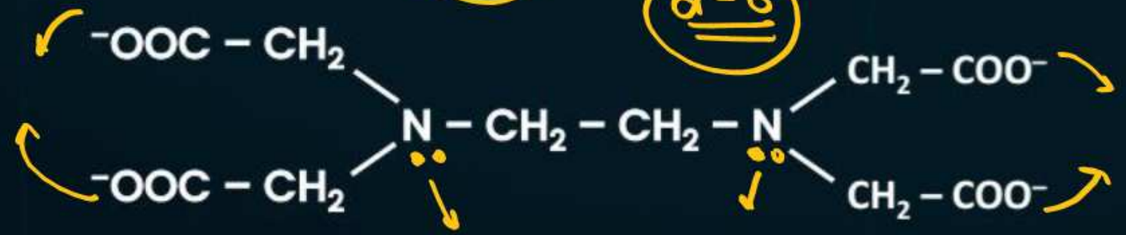

→ Coordination Bond → Coordination comp

## On the basis of charge

- **Negative ligands**
  $CN^-$, $F^-$, $Cl^-$, $NO_2^-$, $NO_3^-$, $OH^-$, $O^{2-}$
- **Positive ligands**
  $NO_2^+$, $NO^+$, $N_2H_5^{5+}$
- **Neutral ligands**
  $H_2O$, $NH_3$, CO, $NH_2OH$, $CH_3NH_2$

## On the basis of number of donor sites

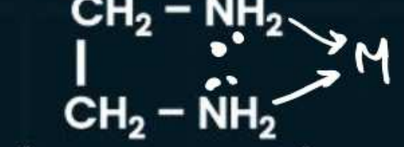
- **Monodentate :** (d=1)
  Only one donor site
  e.g., $H_2O$, $NH_3$, $F^-$, $Cl^-$
- **Bidentate :** Two donor site (d=2)
  e.g., $(COO^-)_2$ (Oxalato), $CH_2(NH_2)-CH_2(NH_2)$ (Ethylenediamine) (en)
- **Polydentate:** More than two donor sites e.g.,
  EDTA (Hexadentate) (d=6)




## On the basis of bonding

An atom can only donate a single lone pair.
Denticity ⇒ No. of Donor atoms

- **Chelating ligands:** A bidentate or polydentate ligand which forms more than one coordinate bonds in such a way that a ring formed.




(Ethylenediamine)

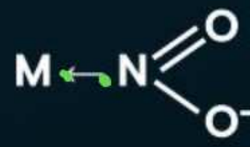

Chleation ∝ Stable

- **Ambidentate ligands:** Monodentate ligand which contains more than one coordinating atom (or donor atom). (d=1)

M ← $O^- - N = O$, or

M ← SCN, or

M ← CN or




M ← NCS

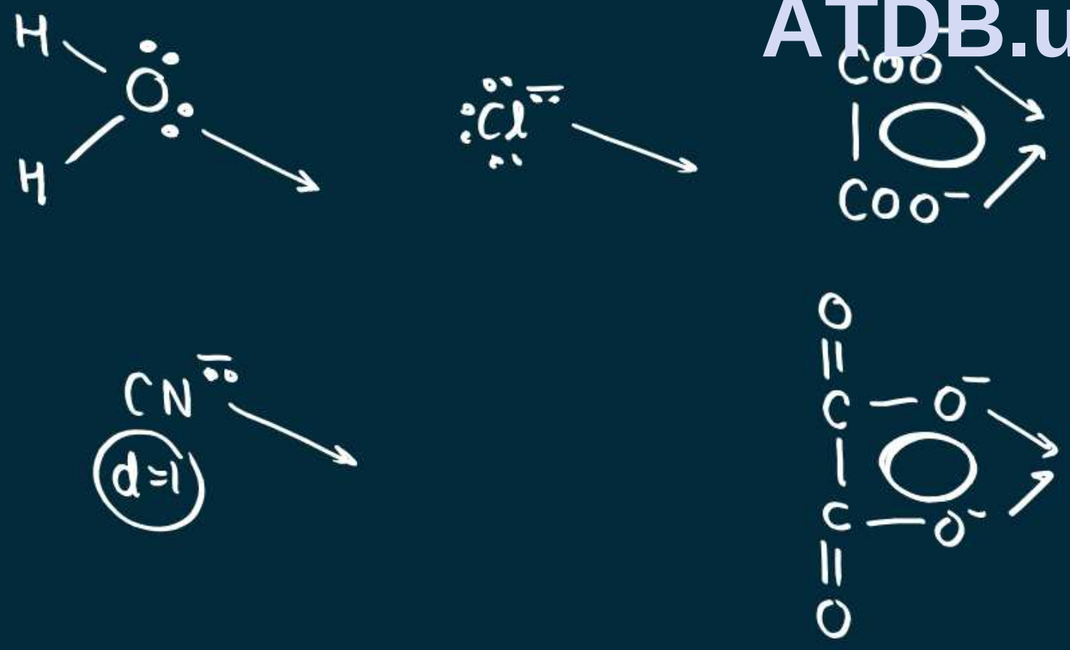
M ← NC

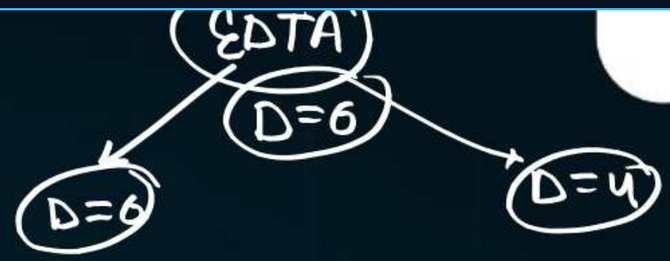
# QUESTIONS

Which of the following ligands form a 'chelate' complex with metal ion?

(2021C)

1. $H_2O$
2. $CN^-$
3. $C_2O_4^{2-}$
4. $Cl^-$



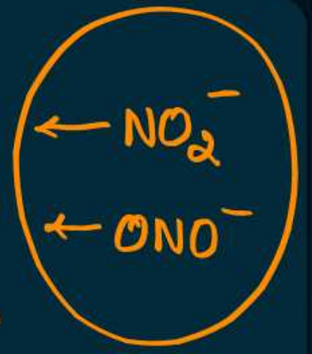


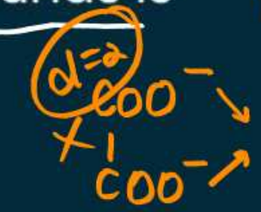

# Types of Ligands

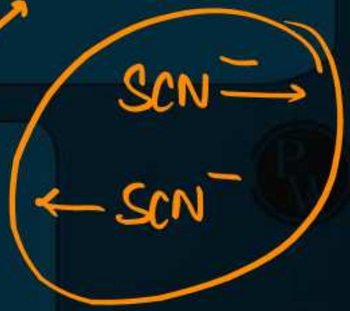
**Flexidentate Ligand –**

A ligand which show variable denticity in different coordination compounds is called as Flexidentate Ligand.

Ex– $SO_4^{2-}$, EDTA.




## QUESTIONS

**The set which does not have ambidentate ligand(s) is:**

JEE

**(2023, 11 April Shift – I)**

1. $NO_2^-$, $C_2O_4^{2-}$, $EDTA^{4-}$
2. $EDTA^{4-}$, $NCS^-$, $C_2O_4^{2-}$
3. $C_2O_4^{2-}$, $NO_2^-$, $NCS^-$
4. $C_2O_4^{2-}$, ethylene diamine, $H_2O$

# Coordination Number

Ligand ... Metal ke Baraboor Me Hone chiye

The no. of atoms of the ligands that are directly bound to the central metal atom or ion by coordinate bond is known as the coordination no. of the metal ion.

Ex. $[Cu(NH_3)_4]^{2+}$ = (4)

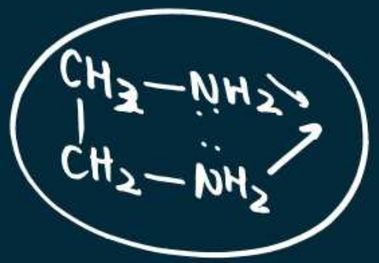
$[Cu(en)_3]^{3+}$ = 3 × 2 = (6)

Most common coordination no. are 2, 4, & 6.

**C.N. = No. of ligands × Dentate charc. of ligands.**



$\ddot{N}H_3$ (d=1)




$CN^-$ d=1
$Cl^-$ d=1
$NH_3$ d=1
edta = 6
CO = d=1
$F^-$ d=1

**Example :-**

~~$K_4[Fe(CN)_6]$~~ ⇒ 6×1 = 6

$[Ag(CN)_2]$ ⇒ 2×1 = 2

$[Pt(NH_3)_2(Cl)_2]$ = 2×1 + 2×1 = 4

$[Ca(edta)]$ = 1×6 = 6

$Fe(CO)_5$ = 5×1 = 5

$[Ni(CN)_5]^{3-}$ = 5×1 = 5

$[ZrF_7]^{3-}$ = 7×1 = 7

# Coordination Sphere

Ex $K_4[Fe(CN)_6]$

Ionisation sphere

↳ coordination sphere

The central atom or ion and the ligands that are directly attached to it are enclosed in a square bracket.

This has been called coordination entity or coordination sphere.

Any ion present outside this sphere is separated form the complex when dissolved in water.

Ex. $K_4[Fe(CN)_6]$ → $4K^+$ + $[Fe(CN)_6]^{4-}$



Charge on the complex ion :- O. No of metal + charge on the ligand

$CN^-$

$Fe + 6CN = -4$

$Fe + 6(-1) = -4$

$Fe - 6 = -4$

$Fe = -4 + 6$

$Fe = +2$ ★

$4K + Fe + 6CN = 0$

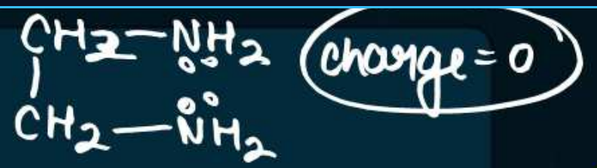
$4(+1) + Fe + 6(-1) = 0$

$4 + Fe - 6 = 0$

$Fe - 2 = 0$

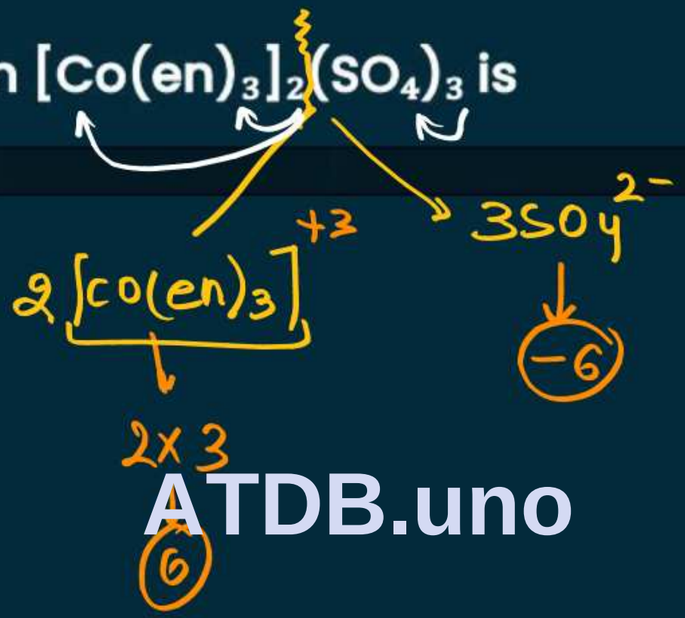
$Fe = +2$

# QUESTIONS




The oxidation number of Co in $[Co(en)_3]_2(SO_4)_3$ is

AIA PYQ
(2021C)




1. +2
2. +3
3. +4
4. +6

$Co + 3en = +3$

$Co + 3(0) = +3$

$Co = +3$

$2Co + 6en + 3SO_4 = 0$

$2Co + 6x0 + 3(-2) = 0$

$2Co + 0 - 6 = 0$

$2Co = +6$

$Co = \frac{+6}{2} = +3$

## QUESTIONS

2025

(PYQ)

The oxidation state Cr in $[Cr(NH_3)_4Cl_2]^{+}$ is

1. 0
2. +1
3. +2
4. +3

$Cr + 4NH_3 + 2Cl = +1$

$Cr + 4(0) + 2(-1) = +1$

$Cr + 0 - 2 = +1$

$Cr = +1 + 2 = +3$

Coordin. NO / Lxd



## QUESTIONS

(2019, 12 April Shift-II)

The coordination numbers of Co and Al in $[CoCl(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$, respectively, are

1. 5 and 3
2. 3 and 3
3. 6 and 6
4. 5 and 6

$1 \times 1 + 2 \times 2$

$1 + 4$

5

$3 \times 2$

6

COO⁻ / COO⁻

# Homoleptic and Heteroleptic Complexes

2024

**Homoleptic** → Complexes in which a metal is bound to only one kind of donor group.

Ex. → $[Cr(NH_3)_6]^{3+}$ , $[Fe(CN)_6]^{3-}$

**Heteroleptic** → Complexes in which a metal is bound to diff. kind of donor group.

Ex. → $[Co(en)_2Cl_2]^{+}$ , $[Cr(NH_3)_4Cl_2]^{+}$

## QUESTIONS 2024



Which of the following is an example of homoleptic complex? (PYQ)

1. $[Co(NH_3)_6]Cl_3$
2. $[Pt(NH_3)_2Cl_2]$
3. $[Co(NH_3)_4Cl_2]$
4. $[Co(NH_3)_5Cl]_2$

# Nomenclature of Coordination Compounds

IUPAC

## Name of the Ligands-

a) Anionic ligands ending with -ide are named by replacing- ide with suffix -o or replacing -e by - o.

b) Ligands whose names ends in –ite or –ate become –ito or –ato i.e by replacing the ending –e with -o.



| Anion | | Ligand Name | Anion | | Ligand Name |
|---|---|---|---|---|---|
| Chloride | $Cl^-$ | Chlorido | Carbonate | $CO_3^{2-}$ | Carbonato |
| Bromide | $Br^-$ | Bromido | Oxalate | $C_2O_4^{2-}$ | Oxalato |
| Cyanide | $CN^-$ | Cyano | Sulphate | $SO_4^{2-}$ | Sulphato |
| Oxide | $O^{2-}$ | Oxo | Nitrate | $NO_3^-$ | Nitrato |
| Sulphide | $S^{2-}$ | Sulphido | Nitrite | $NO_2^-$ | Nitrito |

# Nomenclature of Coordination Compounds

c) Neutral ligands are called with the same names as their neutral molecules or with their special names.

| | | | |
|---|---|---|---|
| $H_2O$ | Aqua | $NH_3$ | Ammine |
| CO | carbonyl | NO | Nitrosyl |
| CS | Thio carbonyl | NS | Thio Nitrosyl |

$M(NH_3)_2$ diammine

$[MCl_2]$ dichlorido

$M(en)_2$ bis ethylenediamine

d) If the number of a particular ligand is more than one in the complex ion, then the Number used as di, tri, tetra, penta, hexa, etc. But when the name of the ligands Includes a number Ex- Diamine, then bis, tris, tetrakis will be used.



e) Complex positive ions and neutral coordination compounds have no special ending but complex negative ions always ends with suffix- ate.

f) Oxidation state of the central metal is shown by Roman numeral in bracket following its name.

# IUPAC Nomenclature

Complex → Ligand (Alphabetical) + Metal

Oxidation No

1. $[Co(NH_3)_4H_2O(Cl)]Cl_2$ → Tetraammine, aqua, chloride cobalt ( ) Chloride

2. $[Cu(en)_2]SO_4$ → Bisethylenediamine copper ( ) sulphate

3. $[Cr(H_2O)_4Cl_2]^+$

4. $[Fe(H_2O)_4(C_2O_4)]_2SO_4$ → Tetraaqua Oxalato Iron ( ) sulphate

5. $[Ag(NH_3)_2]Cl$ → Diammine Silver ( ) chloride

6. $K_3[Fe(CN)_6]$ → Potassium Hexacyano ferrate(III)

7. $Na[Ag(CN)_2]$

$3K + Fe + 6(CN) = 0$

$3(+1) + Fe + 6(-1) = 0$

$3 + Fe - 6 = 0$

$Fe - 3 = 0$

$Fe = +3$

| ⊕/Neutral | ⊖ |
|---|---|
| Cobalt | Cobaltate |
| Iron | Ferrate |
| Silver | Argentate |
| Chromium | Chromate |
| Platinum | Platinate |
| Copper | cuprate |

# IUPAC Nomenclature

**(PYQ)**

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

2. $[Ag(NH_3)_2][Ag(CN)_2]$



| Metal | C.N. |
|---|---|
| $Ag^{+}$ | 2 |

| Metal | C.N. |
|---|---|
| $Fe^{3+}$ | 6 |
| $Co^{3+}$ | 6 |
| $Zn^{2+}$ | 4 |

| Metal | C.N. |
|---|---|
| $Sc^{3+}$ | 6 |
| $Cr^{3+}$ | 6 |
| $Pt^{2+}$ | 4 |
| $Pt^{4+}$ | 6 |

## QUESTIONS

The correct IUPAC name of $[Pt(NH_3)_2Cl_2]^{2+}$ is

diammine dichlorido platinum(IV) ion

PYQ (2025)

$Pt + 2NH_3 + 2Cl = +2$

$Pt + 2\times0 + 2(-1) = +2$

$Pt + 0 - 2 = +2$

$Pt = +2+2 = +4$

1. Diamminedichloridoplatinum (II)
2. Diamminedichloridoplatinum (IV)
3. Diamminedichloridoplatinum (0)
4. Diamminedichloridoplatinate (IV)



## QUESTIONS

The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]Cl_2$ is

(PYQ) 2024

$Co + NO_2 + 5NH_3 + 2Cl = 0$

$Co + (-1) + 5\times0 + 2(-1) = 0$

$Co - 1 + 0 - 2 = 0$

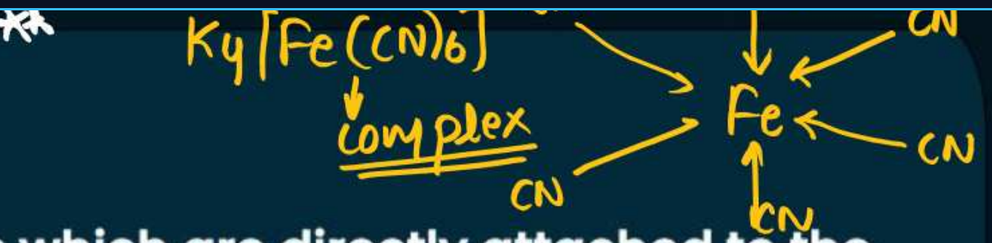
$Co = +3$

$2+$ $2Cl^-$

1. ~~nitrito-N-pentamminecobalt (III) chloride~~
2. ~~nitrito-N-pentamminecobalt (II) chloride~~
3. pentammine nitrito-N-cobalt(II) chloride
4. pentammine nitrito-N-cobalt(III) chloride

# Coordination polyhedron

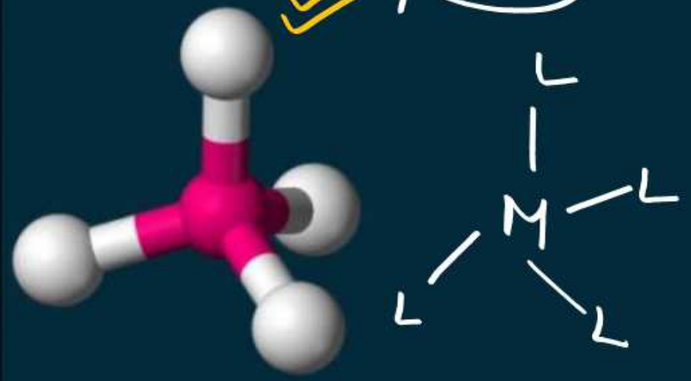
$K_4[Fe(CN)_6]$ → complex




The spatial arrangement of the ligand atoms which are directly attached to the central ion or atom is called coordination polyhedron.

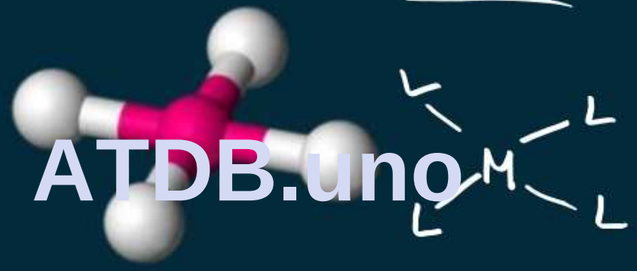
## Tetrahedral

CN = 4




## Square Planar

C.NO = 4

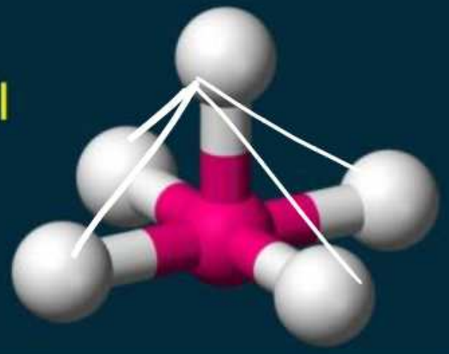



## Octahedral

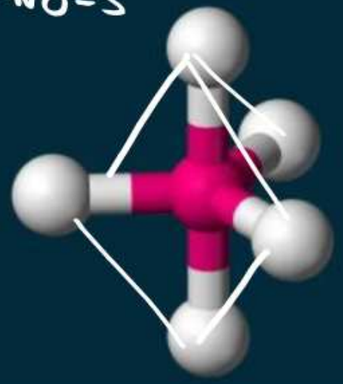
CN = 6


## Square Pyramidal

CN = 5 ✗



C.NO = 5



✗ Trigonal Bipyramidal

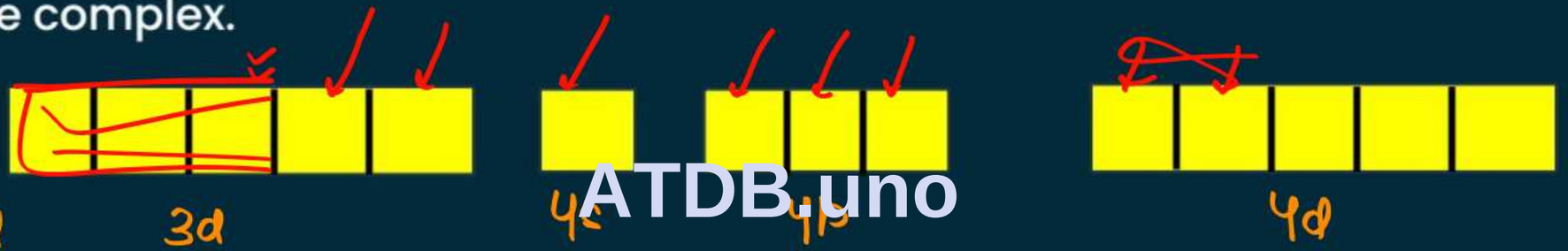
Bonding

# (A) Valence Bond Theory

- This theory describes the bonding in terms of hybridized orbitals of the central metal atom or ion.
- The theory mainly deals with the geometry (shape) and magnetic properties of the complex.

d-block

3d 4s 4p 4d






| Coordination number | Type of hybridisation | Distribution of hybrid orbitals in space |
|---|---|---|
| 4 | $sp^3$ | Tetrahedral |
| 4 | $dsp^2$ | Square planar |
| 5 | $sp^3d$ | Trigonal bipyramidal |
| 6 | $sp^3d^2$ | Octahedral (Outer) |
| 6 | $d^2sp^3$ | Octahedral (Inner) |

# Postulates

1. The central atoms loses a requisite no. of electrons to form the ion. The no of electrons lost is the valency of the resulting cation.
2. The central metal ion or atom makes available a no. of empty s, p & d orbitals equal to its coordination no.

WFL

**(i) $[NiCl_4]^{2-}$**

$Ni + 4Cl = -2$

$Ni + 4(-1) = -2$

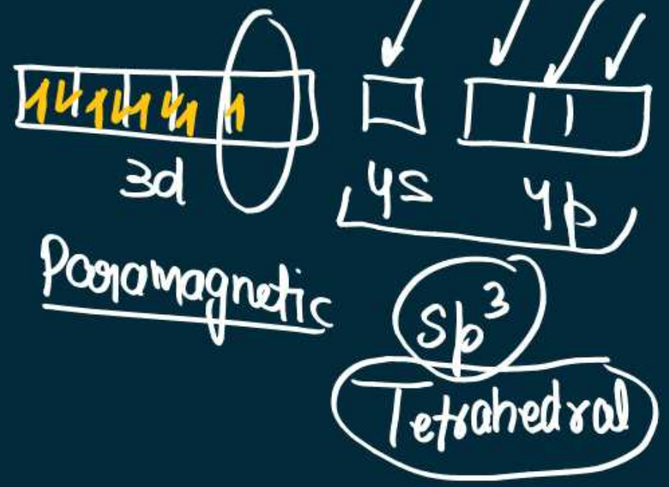
$Ni - 4 = -2$

$Ni = -2 + 4$

$\boxed{Ni = +2}$

$Ni \rightarrow 4s^2 3d^8$

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




SFL

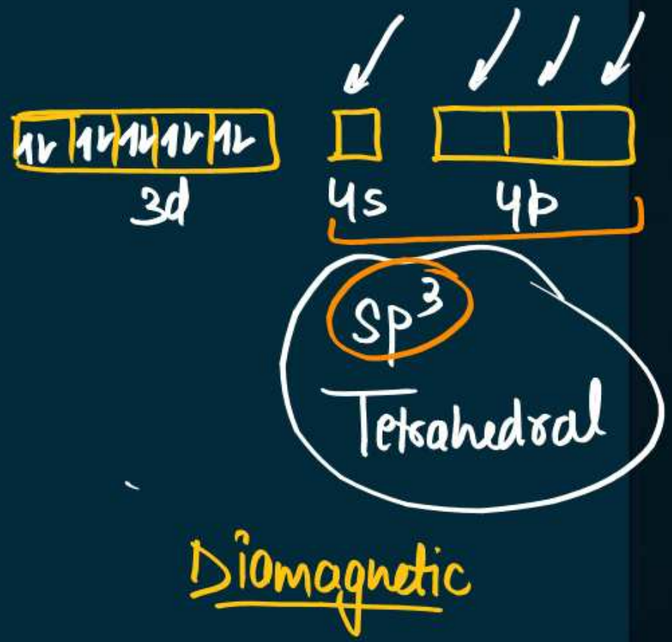
**(i) $[Ni(CO)_4]$**

$Ni + 4 \times CO = 0$

$Ni + 4 \times 0 = 0$

$Ni = 0$

$Ni \rightarrow 4s^2 3d^8$




Diamagnetic

# Complex with C.No ⟹ 4

WFL

## (i) $[CuCl_4]^{2-}$

$Cu + 4Cl = -2$

$Cu + 4(-1) = -2$

$Cu - 4 = -2$

$Cu = -2 + 4$

$Cu = +2$

$Cu \rightarrow 4s^1 3d^{10}$

$Cu^{+2} \Rightarrow 4s^0 3d^9$

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

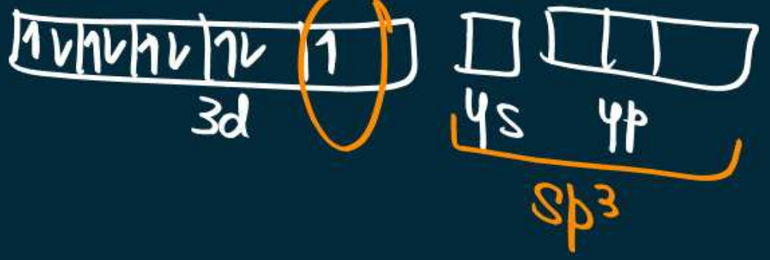
$n = 1$

$\mu = \sqrt{1*(1+2)}$

$\sqrt{3}$

Tetrahedral

Paramagnetic




SFL

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

$Ni + 4CN = -2$

$Ni + 4(-1) = -2$

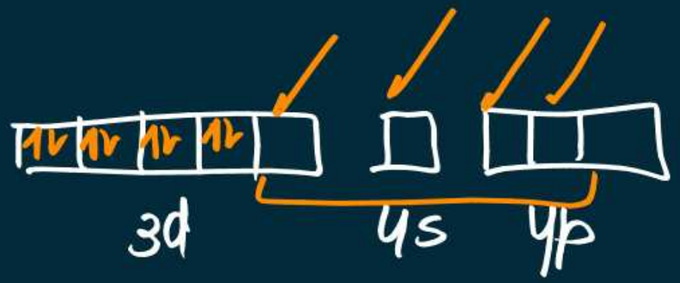
$Ni - 4 = -2$

$Ni = -2 + 4$

$Ni = +2$

$Ni \rightarrow 4s^2 3d^8$

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




$dsp^2$

Square planar

Diamagnetic

## QUESTIONS

Atomic number: Ni = 28

The magnetic moment of $[NiCl_4]^{2-}$ is

(2023)

1. 1.82 B.M.
2. 2.82 B.M.
3. 4.42 B.M.
4. 5.46 B.M.



## QUESTIONS

Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. no.: Cr = 24, Co = 27, Ni = 28)

(NCERT Intext, 1/3, AI 2014)

# Complex with C.No ⟹ 6

They posses two type of complexes:

(i) Inner orbital octahedral complexes ⟶ These are formed by $d_2sp_3$ hybridized involving strong ligands. These are also known as Low spin complexes (less unpaired $e^-$)

(ii) Outer orbital octahedral complexes ⟶ These are formed by $sp_3d_2$ hybridization involving weak ligands. These are also known as high spin complexes. (More unpaired $e^-$)



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

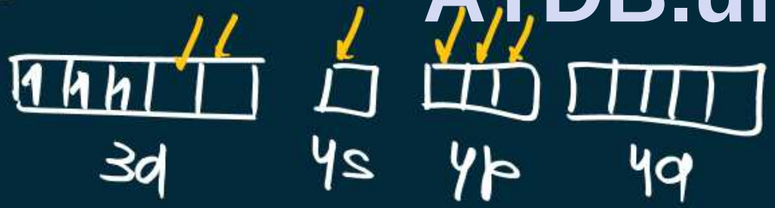
WFL

$Cr + 6NH_3 = +3$

$Cr + 6 \times 0 = +3$

$Cr = +3$

$Cr^{+3} \equiv 4s^0 3d^3$




$d^2sp^3$

Inner octahedral

$n = 3$

Paramagnetic

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

WFL

$Fe + 6H_2O = +3$

$Fe + 6 \times 0 = +3$

$Fe + 0 = +3$

$Fe = +3$

$Fe^{+3} \rightarrow 4s^0 3d^5$

$Sp^3d^2$

Outer octahedral

Paramagnetic

# Limitations of VBT

1. This theory doesn't after any explanation about spectra of complex (Colour of the complex)
2. This theory was failed to explain why at one time the electron are rearranged against the Hund's rule and other time electronic configuration is not disturbed.
3. This theory doesn't after any explanation for the existence of inner and outer orbital complexs.
4. $NH_3 \rightarrow$ SFL $\rightarrow$ For higher C.NO i.e $Co^{+3}$

   $NH_3 \rightarrow$ WFL $\rightarrow$ For lower C.NO. i.e $Ni^{+2}$

# Crystal Field Theory

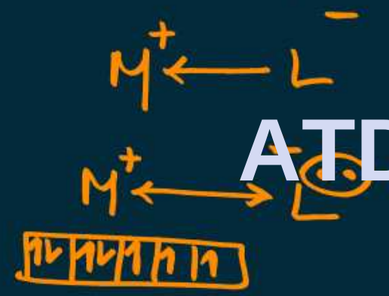
APM

According Crystal Field theory the bonding in complex is not covalent or by overlapping of orbitals but it is purely electrostatic.

There are two types of Force exist between Metal ion and Ligand–

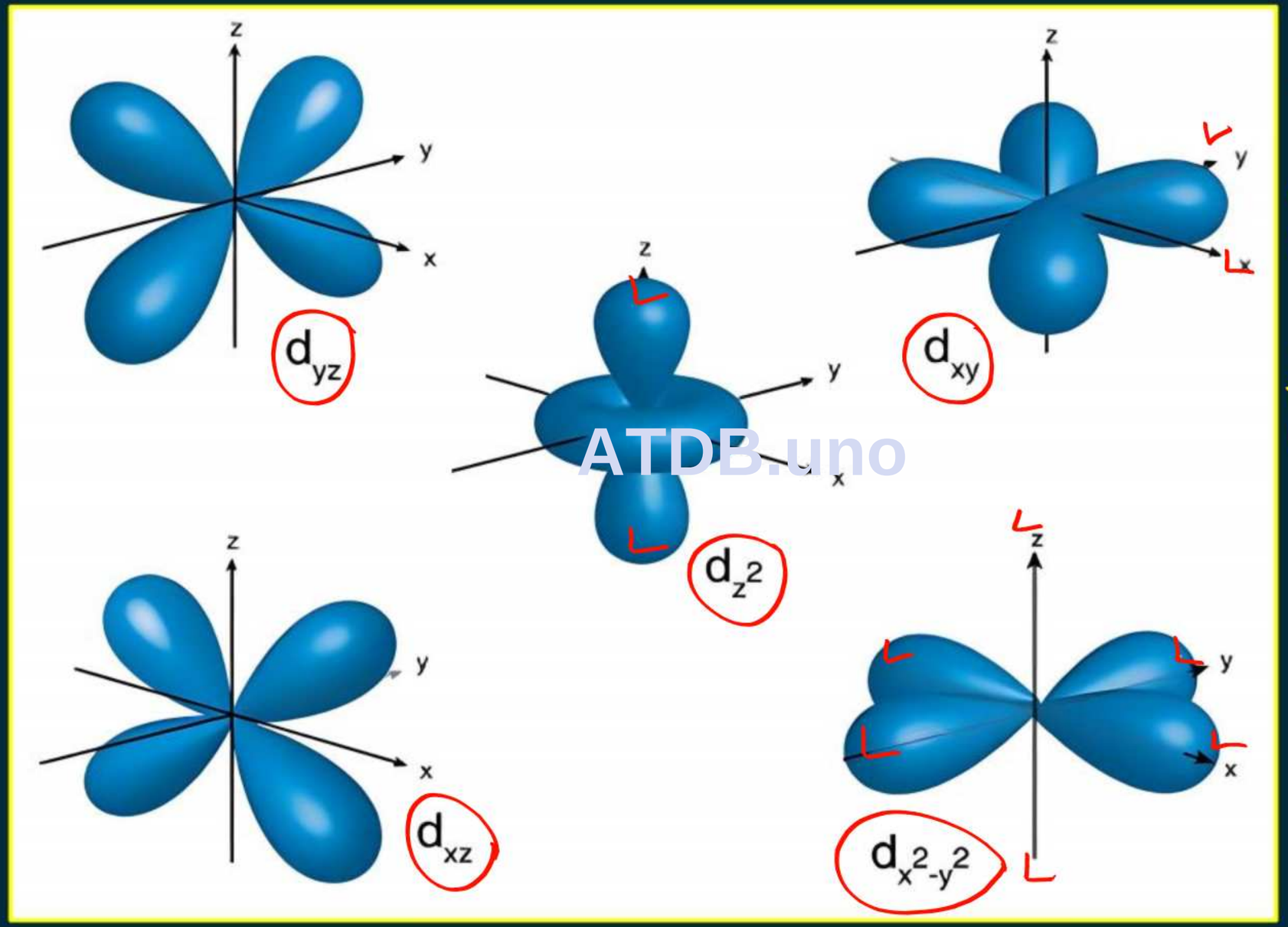
1) Force of attraction

2) Force of Repulsion





Crystal field theory mainly focus on the Force of Repulsion between Lone pair of ligands and Electrons in d orbital of Metal ion.






dxy dyz dzx $d_{z^2}$ $d_{x^2-y^2}$

B/w the axis

double dumbell

on the axis

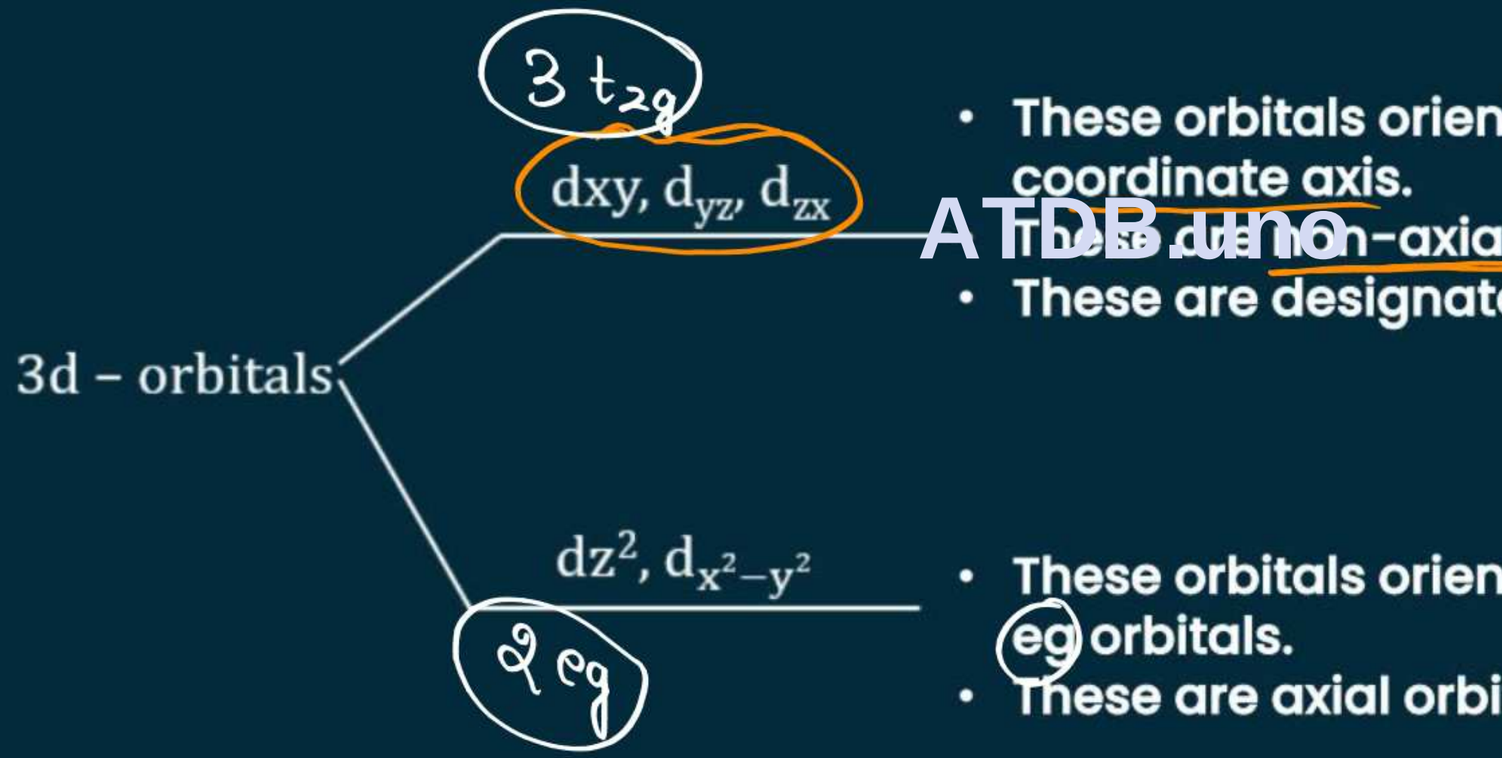
# Crystal Field Theory

C.NO = 4 / Tetrahedral

C.NO = 6 / Octahedral

In a free transition metal or ion, there are 5d-oribtals which are designated as dxy, dyz, dzx $dx^2-y^2$, $dz^2$.

These are divided into two sets:



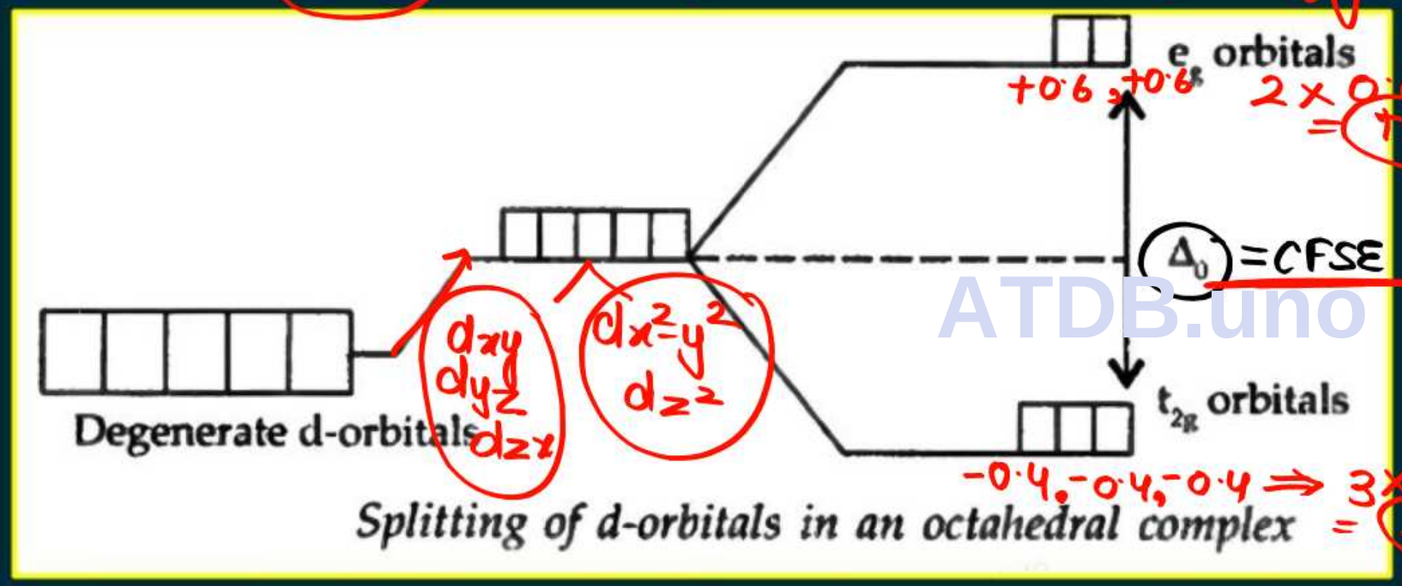

- These orbitals orient in the region between the coordinate axis.
- These are non-axial orbitals
- These are designated as t2g orbitals

- These orbitals orient along the axes are called eg orbitals.
- These are axial orbitals.

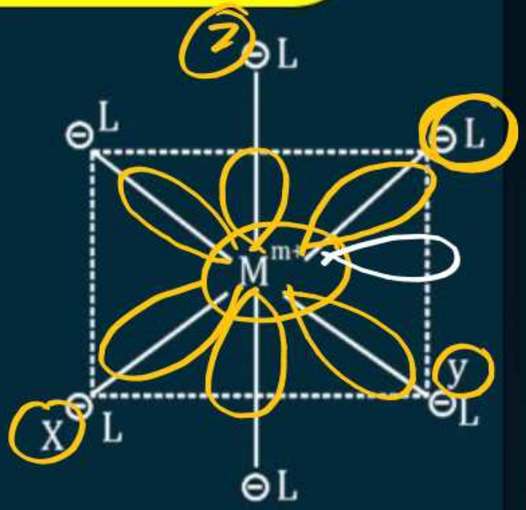
# # Splitting or d-orbitals in octahedral complex

$[ML_6]^{n+}$ → CN = 6

CFSE → Crystal field splitting energy




Splitting of d-orbitals in an octahedral complex

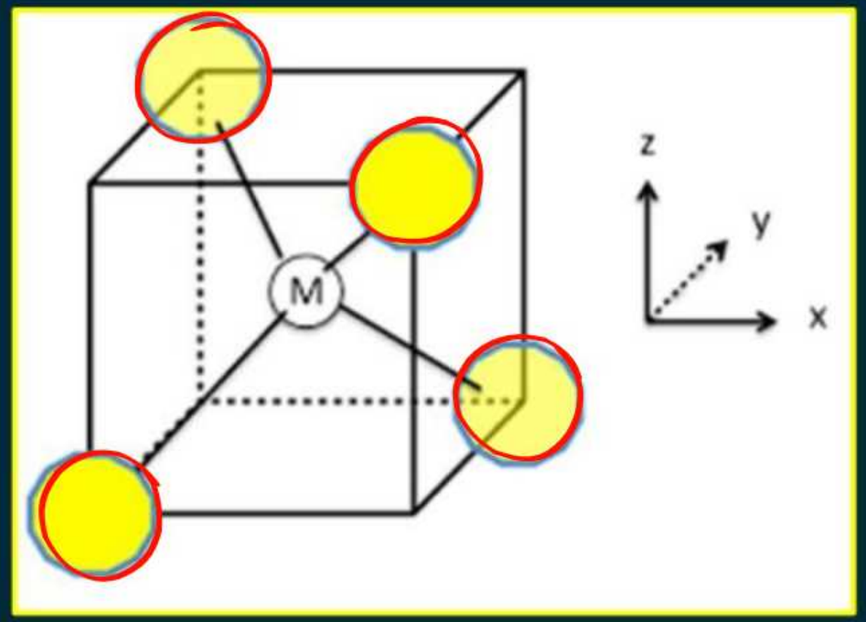


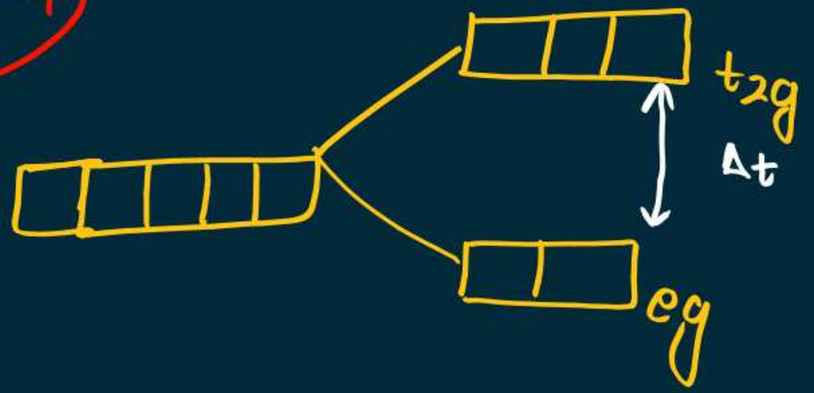

$d_{x^2-y^2}$

# Splitting or d-orbitals in Tetrahedral complex

(N=4

$[ML_4]^{n+}$




$\Delta_t < \Delta_o$

$\Delta_o = \frac{4}{9}\Delta_t$

More ligands ⇒ More splitting
Less ligands ⇒ Less splitting



In this case, three d-orbitals i.e t2g orbitals are close to the approaching ligands. As a result of this, t2g electrons suffer more repulsion than eg electron.

# Spectrochemical series

For any given metal cation, the magnitude of crystal field splitting energy depends on the nature of the ligands.
The greater the ease with which the ligand can approach the metal ion, the greater will be the splitting caused by it.

CFSE $L_{S.F}$ > $L_{W.K}$ CFSE

## Strong Field Ligand

Ligands which can approach the central metal ion with ease and cause High repulsion thus high splitting.



## Weak Field Ligand

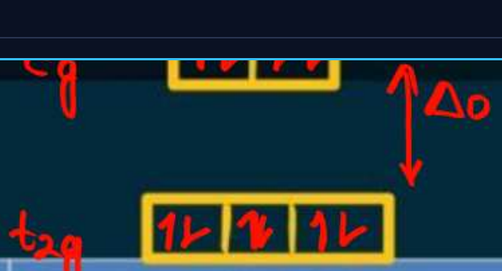
Ligands which can't approach the central metal ion with ease and cause Low repulsion thus less splitting.

I Brought some Colourful sweets from office containing water Nancy

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < O^{2-} < C_2O_4^{2-} < H_2O < NCN^-$

ate Nine in Canteen corridor

EDTA < $NH_3$ < en < $CN^-$ CO





APM ❤

| Configure | No. of unpaired e⁻ | C.F.S.E | Config. | No. of unpaired | CFSE |
|---|---|---|---|---|---|
| $d^1 \rightarrow t_{2g}^1$ | 1 | $CFSE = 1 \times (-0.4\Delta_0) + 0 = -0.4\Delta_0$ | $d^1 \rightarrow t_{2g}^1$ | 1 | |
| $d^2 \rightarrow t_{2g}^2$ | 2 | | $d^2 \rightarrow t_{2g}^2$ | 2 | |
| $d^3 \rightarrow t_{2g}^3$ | 3 | | $d^3 \rightarrow t_{2g}^3$ | 3 | |
| $d^4 \rightarrow t_{2g}^4$ | 2 | | $d^4 \rightarrow t_{2g}^3 e_g^1$ | 4 | |
| $d^5 \rightarrow t_{2g}^5$ | 1 | | $d^5 \rightarrow t_{2g}^3 e_g^2$ | 5 | |
| $d^6 \rightarrow t_{2g}^6$ | 0 | | $d^6 \rightarrow t_{2g}^4 e_g^2$ | 4 | |
| $d^7 \rightarrow t_{2g}^6 e_g^1$ | 1 | $CFSE = 6 \times (-0.4\Delta_0) + 1 \times (0.6\Delta_0) = -2.4\Delta_0 + 0.6\Delta_0 = -1.8\Delta_0$ | $d^7 \rightarrow t_{2g}^5 e_g^2$ | 3 | |
| $d^8 \rightarrow t_{2g}^6 e_g^2$ | 2 | | $d^8 \rightarrow t_{2g}^6 e_g^2$ | 2 | |
| $d^9 \rightarrow t_{2g}^6 e_g^3$ | 1 | | $d^9 \rightarrow t_{2g}^6 e_g^3$ | 1 | |
| $d^{10} \rightarrow t_{2g}^6 e_g^4$ | 0 | | $d^{10} \rightarrow t_{2g}^7 e_g^4$ | 0 | |

# Calculation of CFSE

Octahedral

$$C.F.S.E = \text{No. of } e^- \text{ in } t_{2g} \times (-0.4\Delta_o) + \text{No. of } e^- \text{ in } e_g \times (+0.6\Delta_o)$$

## QUESTIONS



(a) On the basis of crystal field theory, write the electronic configuration for $d^4$ with a strong field ligand for which $\Delta_0 > P$.

SFL

$t_{2g}^4 e_g^0$

(b) A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CO)_4]$ is colourless. Explain.

PYQ (2023)

## QUESTIONS

The crystal field splitting energy for octahedral ($\Delta_0$) and tetrahedral ($\Delta_t$) complexes is related as

PYQ (2020)

1. $\Delta_t = 2/9\ \Delta_0$
2. $\Delta_t = 5/9\ \Delta_0$
3. $\Delta_t = 4/9\ \Delta_0$
4. $\Delta_t = 2\Delta_0$

# Werner's coordination Theory

Werner proposed coordination theory to explain properties and structure of various coordination compounds.

**Primary valency** corresponds to oxidation state of the central metal.
It is satisfied by the negative ions. This is also called principle, Ionisable or Ionic valency.
Its attachment to the metal is shown by dotted lines.



- **Secondary valency** is satisfied by neutral molecules or negative ions.
- It represents the coordination no. of the metal
- This valency is non-ionic or non-ionizable. The atoms of the ligands which satisfy the coordination number are directly attached to the metal atom and shown by thick lines.

Example

$COCl_3.6NH_3$

+3

$[CO(NH_3)_6]Cl_3$

P·V=3 S·V=6


P·V = 3
S·V = 6

## QUESTIONS

(2023, 24 Jan Shift-I)

The primary and secondary valencies of cobalt respectively in $[Co(NH_3)_5Cl]Cl_2$ are

P.V = 3

S.V = 6

$Co + 5NH_3 + Cl + 2Cl = 0$

$Co + 5(0) + (-1) + 2(-1) = 0$

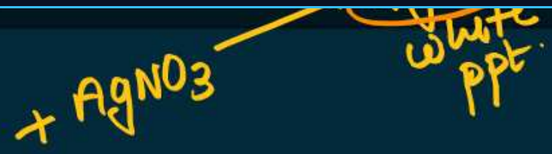
$Co + 0 - 1 - 2 = 0$

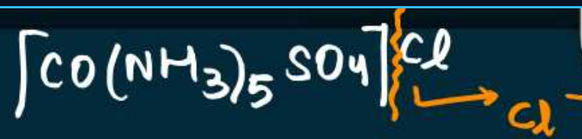
$Co - 3 = 0$

$Co = +3$

1. 3 and 6
2. 2 and 6
3. 3 and 5
4. 2 and 8

## QUESTIONS




**Assertion:** $[Co(NH_3)_5SO_4]Cl$ gives a white precipitate with silver nitrate solution.
**Reason:** The complex dissociates to give $Cl^-$ and $SO_4^{2-}$ ions.

(PYQ) 2024

1. Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
2. Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
3. Assertion (A) is correct, but Reason (R) is incorrect statement
4. Assertion (A) is incorrect, but Reason (R) is correct statement.

# QUESTIONS

One mole of $CrCl_3 \cdot 6H_2O$ compound reacts with excess $AgNO_3$ solution to yield two moles of $AgCl(s)$.

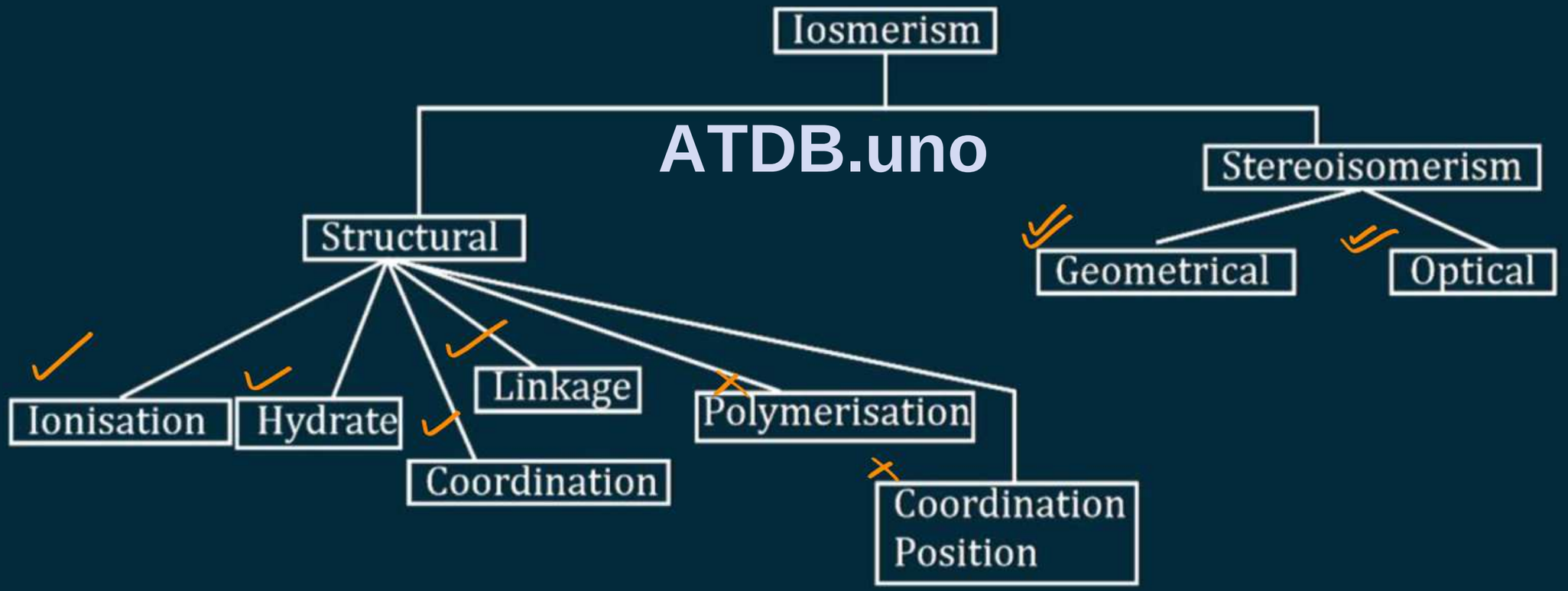
The structural formula of the compound is:

(PYQ) 2023

1. $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
2. $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$
3. $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
4. $[Cr(H_2O)_6]Cl_3$

# Isomerism in coordination compounds

The compounds have same molecular formula but different physical and chemical properties on account of different structures or spatial arrangement are called isomers.



# Structural

## (i) Ionisation

When the coordination compound having same empirical formula give different ions in solution .

$[Co(NH_3)_5SO_4]Br$ → Yellow AgBr

$[Co(NH_3)_5Br]SO_4$ → White $BaSO_4$

## (ii) Hydrate Isomerism

When the empirical formula of coordination comp. is same but have different no. water molecules inside and outside the coordination sphere

**Example:**

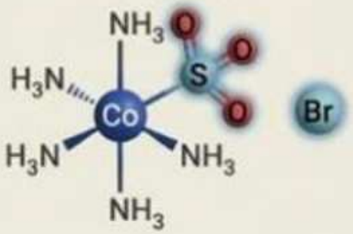
$[Cr(H_2O)_6]Cl_3$ → Voilet

$[Cr(H_2O)_5Cl]Cl_2.H_2O$ → Green

$[Cr(H_2O)_4Cl_2]Cl.\ 2H_2O$ → Green



Red-violet
$[Co(NH_3)_5(SO_4)]Br$

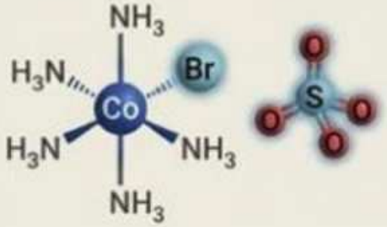



In solution, this yields the bromide ion ($Br^-$).

Test with $BaCl_2$ → No Precipitate

Test with $AgNO_3$ → AgBr Precipitate

Red
$[Co(NH_3)_5Br]SO_4$




In solution, this yields the sulphate ion ($SO_4^{2-}$).

Test with $BaCl_2$ → $BaSO_4$ Precipitate

Test with $AgNO_3$ → No Precipitate

# Coordination Isomerism

When the empirical formula of coordination compound is same but both having both cationic and anionic complex ion.

Then Ligands are interchanged in both cationic and anionic ions to form isomers.

Example

$[Pt(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][PtCl_4]$

$[Cr(NH_3)_6][Co(C_2O_4)_3]$ and $[Co(NH_3)_6][Cr(C_2O_4)_3]$

# Linkage Isomerism

This type of isomerism occurs in complex compound. Which contain ambidentate ligands like $NO^-_2$ , $SCN^-$, $S_2O^{2-}_3$ and CO. These ligands have two donor atoms but at a time only 1 atoms is directly linked to the central metal of the complex.

Example: $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$



## QUESTIONS

The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(Br)(NH_3)_5]SO_4$ represent: (PYQ) 2022

1. Optical isomerism
2. Linkage isomerism
3. Ionisation isomerism
4. Coordination isomerism

## QUESTIONS

Assertion (A): Linkage isomerism arises in coordination compounds because of ambidentate ligand.
Reason (R): Ambidentate ligand like $NO_2$ has two different donor atoms i.e., N and O.

2024 (PYQ)

1. Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).



2. Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

3. Assertion (A) is correct, but Reason (R) is incorrect statement

4. Assertion (A) is incorrect, but Reason (R) is correct statement.

# Stereoisomerism

## 1. Geometrical isomerism

The isomerism is due to ligands occupying different position around the central metal atom or ion. The ligands occupy positions either adjacent or opposite to one another.

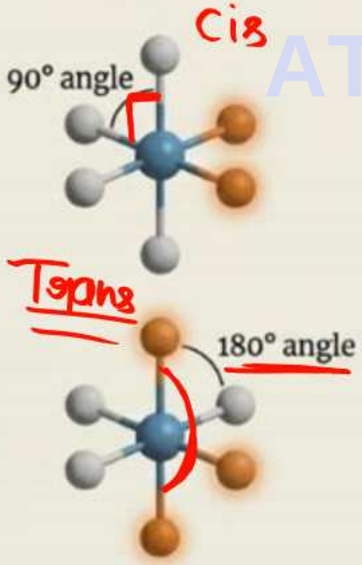
This type of isomerism is called as Cis-trans isomerism

$MO_2b_2$

### Cis-Trans

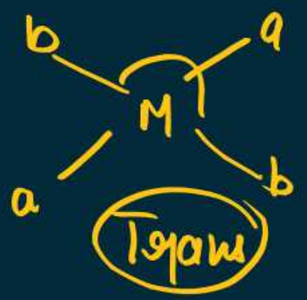
*cis*: Ligands are adjacent (e.g., at 90° in an octahedron).

*trans*: Ligands are opposite (e.g., at 180° in an octahedron).









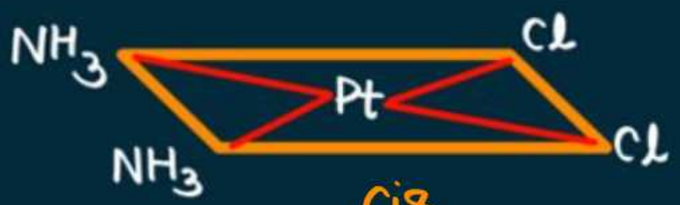
# Square planar complexes

Square Planar
Tetra X
C.N = 6
Octahedral

(a) $Ma_2b_2$, Where a and b both are monodentate.

PYQ ***

$[Pt(NH_3)_2(Cl_2)]$




Cis


Trans



(b) $Ma_2bc$, where a, b, c are monodentate

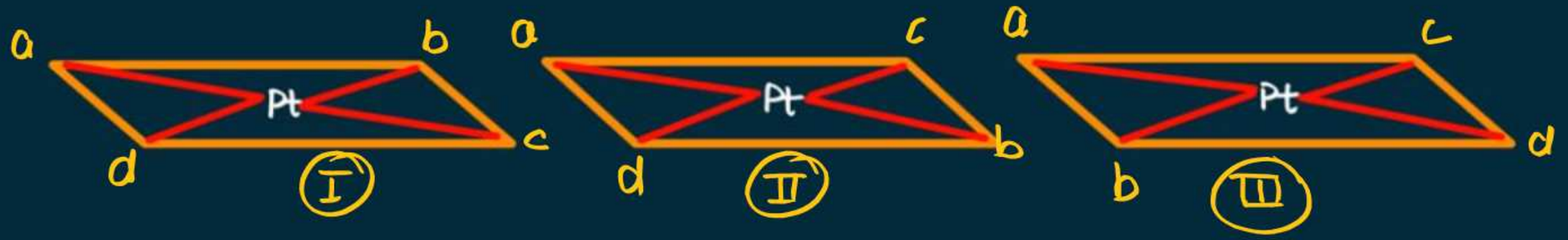
$[Pt(NH_3)_2(Cl)NO_2]$


Cis


Trans

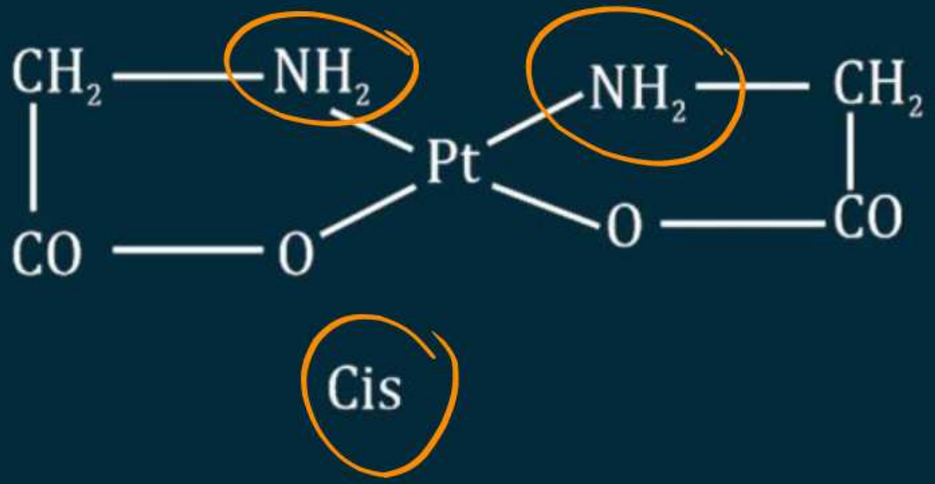
(c) Mabcd, Where a, b, c, d are monodentate

$[Pt(NH_3)(NH_2OH)(NO_2)(Py)]NO_2$

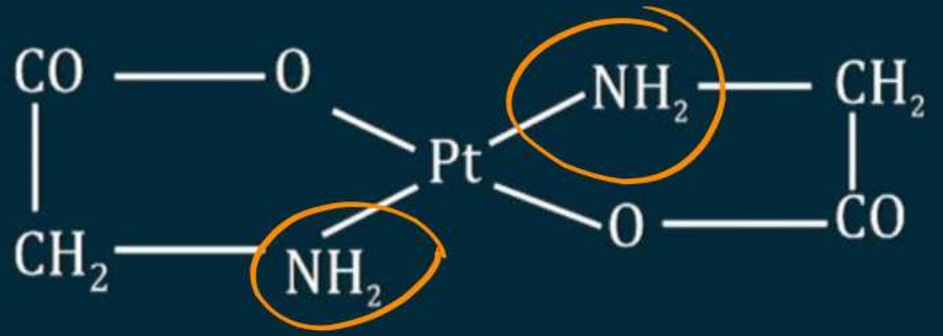



(d) Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism.






Cis

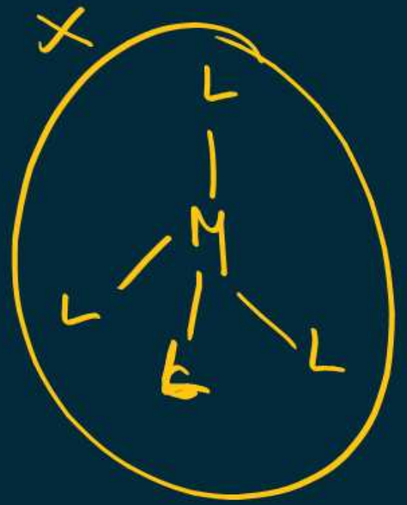


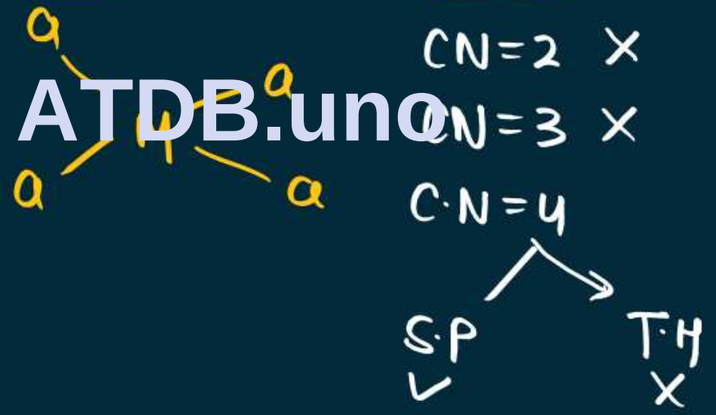

Trans.

# Important notes

square planar

1. Geometrical isomerism is not observed in complexes of C.No. 2 and 3
2. Square planner of type $Ma_4$, $Ma_3b$ and $Mab_3$ do not show geometrical isomerism
3. Geometrical isomerism is not observed in complex of C.NO. 4 of tetrahedral geometry. All positions are adjacent to one another.






$Ma_2bc \rightarrow 2$

$Ma_2b_2 \rightarrow 2$

$Mabcd \rightarrow 3$

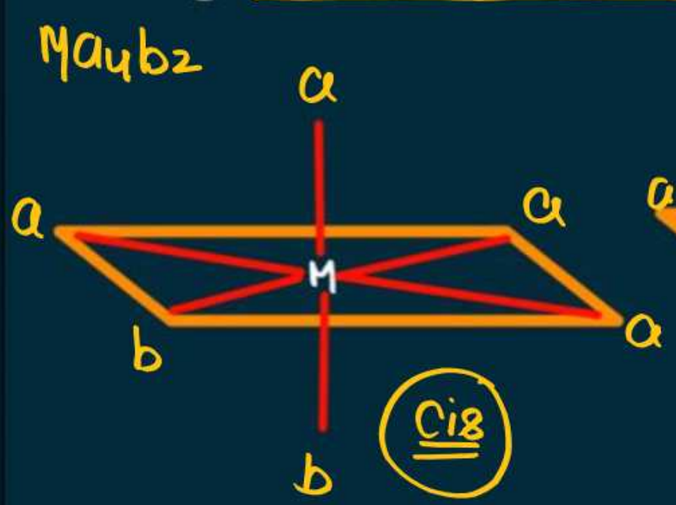
$Ma_4 \rightarrow 0$

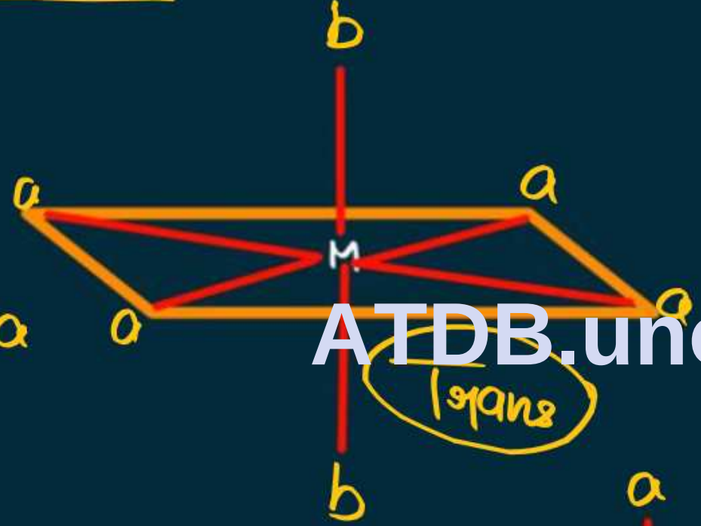
$Ma_3b \rightarrow 0$

$Mab_3 \rightarrow 0$

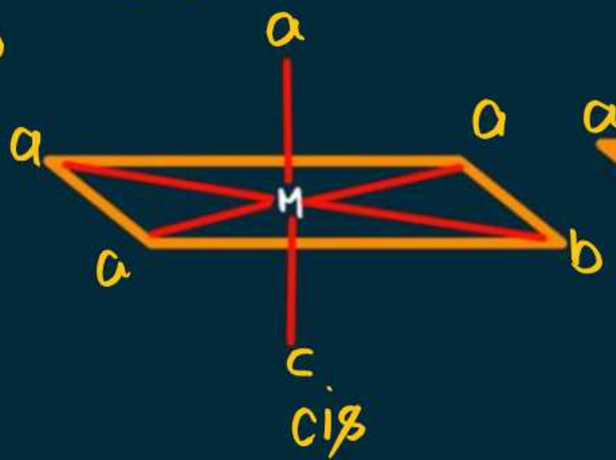
# Octahedral Complexes (C.No = 6)

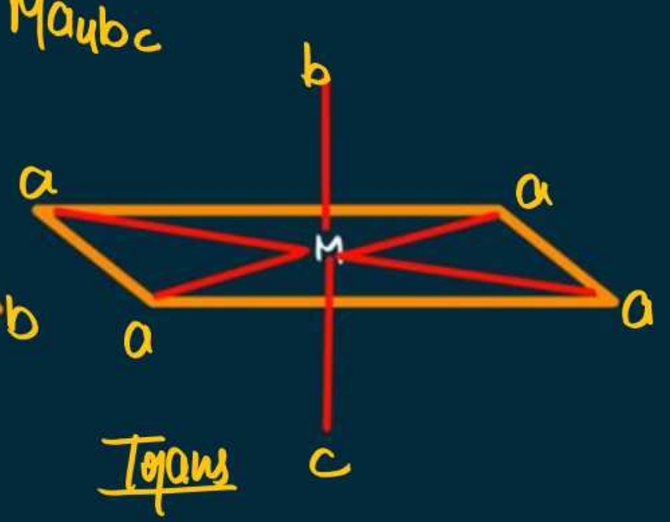
**(a) Octahedral complexes of the type $Ma_4B_2$, $Ma_2B_4$, $Ma_4bc$ and $Ma_3b_3$ exhibit geometrical isomerism**






**Ex. $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_3Cl_3]$**

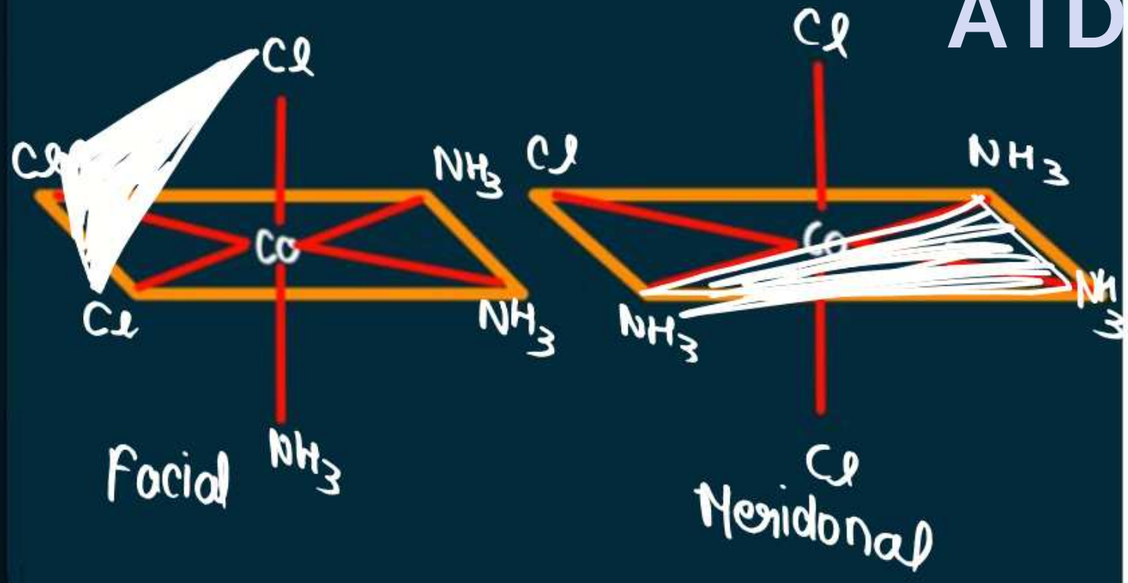
cis-Trans

**Note :**

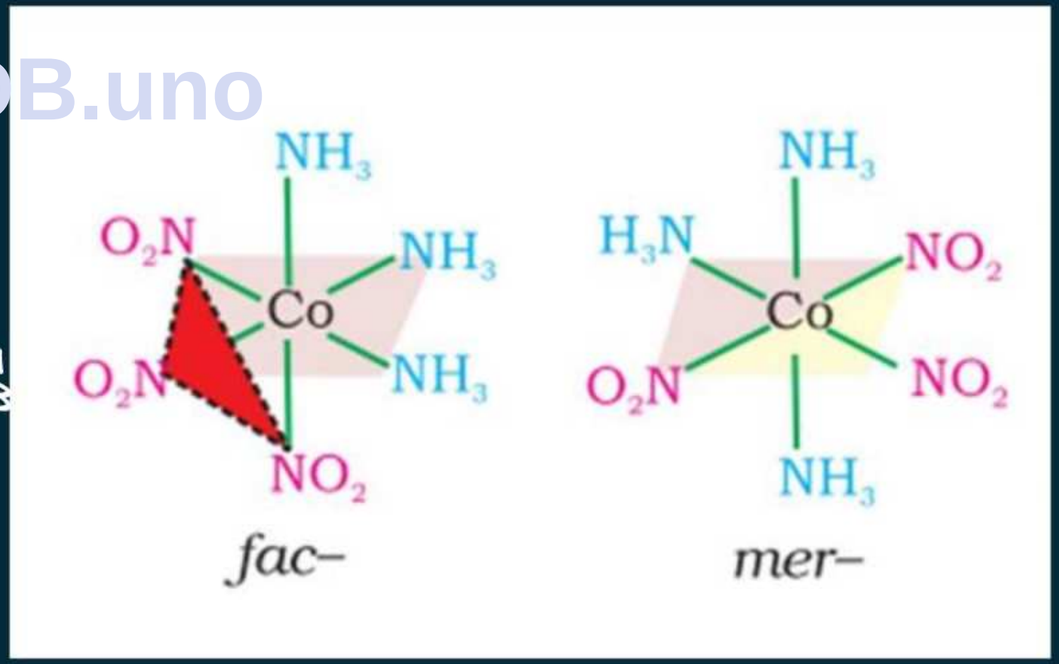
$Ma_3b_3$ type octahedral complex do not exhibit cis and trans isomerism, they exhibit facial and meridional isomerism.

**Example**

$[CO(NH_3)_3Cl_3]$ and $[CO(NH_3)_3(NO_3)_3]$



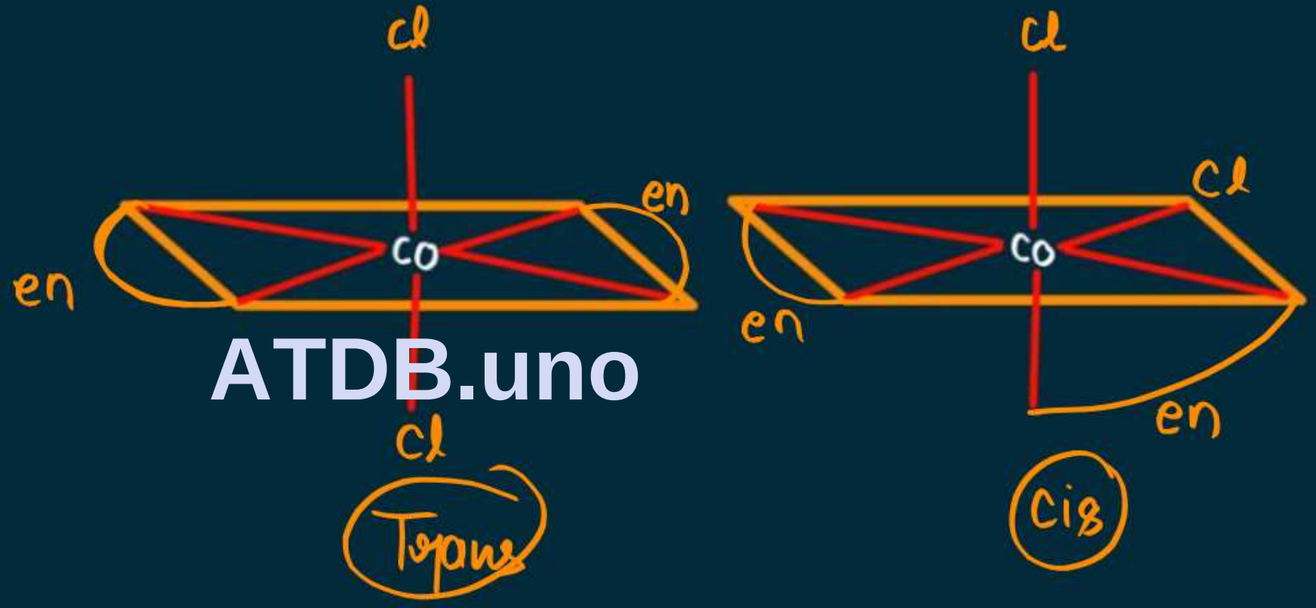


(b) Octahedral complexes having bidentate ligands of the type $M(aa)_2b_2$ or $M(aa)_2bc$ can also exist in cis-trans isomers where aa is symmetrical bidendate ligands

**Example**

PYQ $[Co(en)_2Cl_2]^+$






**QUESTIONS**

(2019)

Write IUPAC name of the complex $[Pt(en)_2Cl_2]$.

Draw structures of geometrical isomers for this complex.

# Optical Isomerism

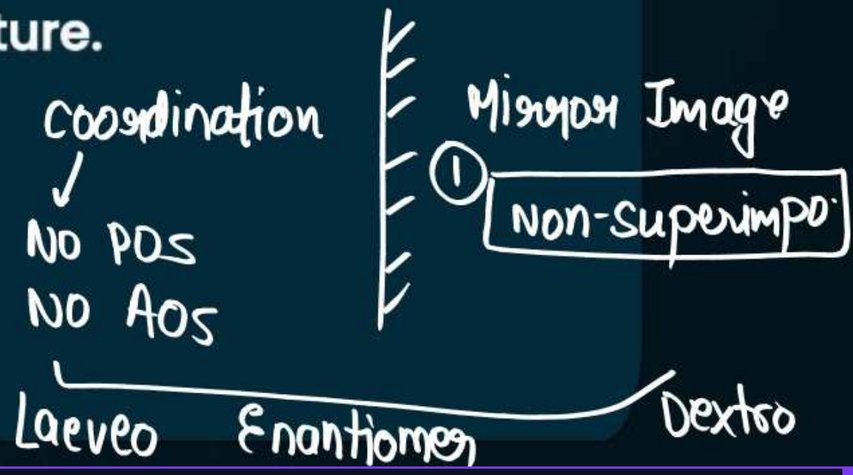
- A coordination compound which can rotate the plane of polarized light is said to be optically active.

- When the coordination compounds have same formula but differ in their abilities to rotate directions of the plane of polarized light are said to be exhibit optical isomers and molecules are optical isomers.



- The optical isomers are pair of molecules which are non-superimposable mirror images of each other.
- The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure.

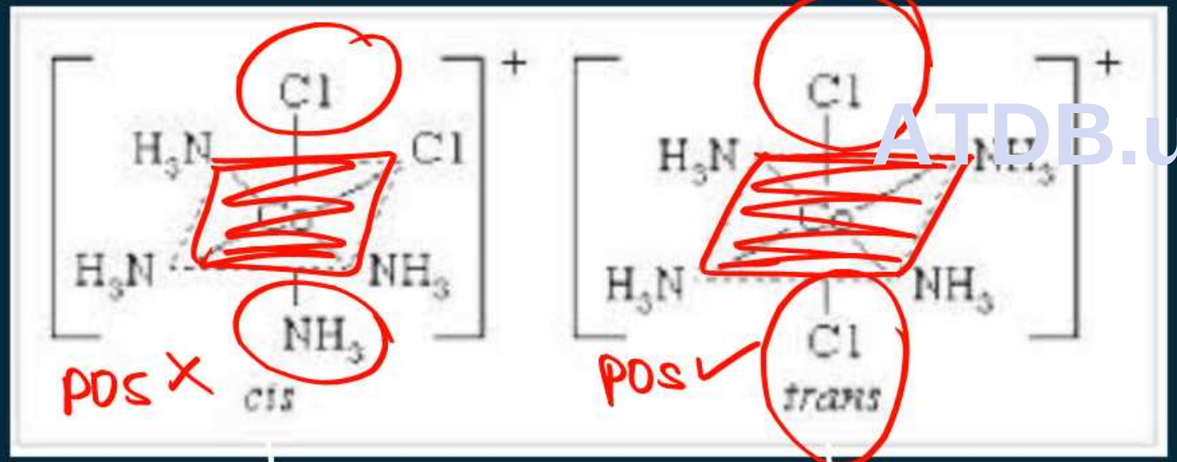
Axis of Symmetry



## Note : -

**Plane of symmetry** → Plane that divides the structure into 2 equal/superimposable /halves or 2 parts are mirror images of each other.

**Axis of symmetry** → Axis (line) that divides the structure into 2 equal/superimposable structure/halves.

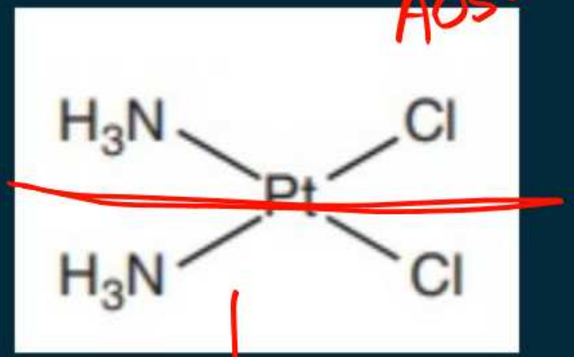



POS ✗

Optical isomers

POS ✓

No optical iso.




AOS ✓

Square planar

AOS ✓

No optical isomerism.

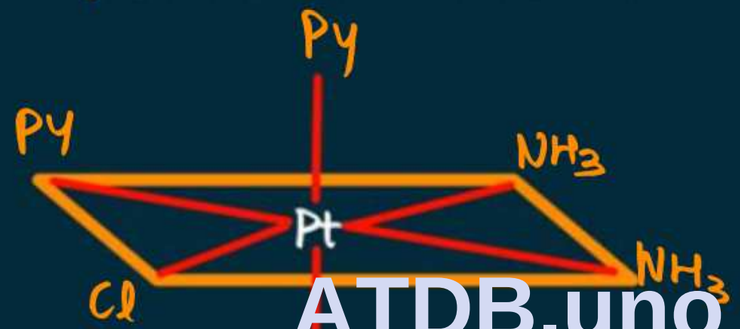
- Optical isomers rarely occurs in square planar complexes on account of the presence of axis of symmetry

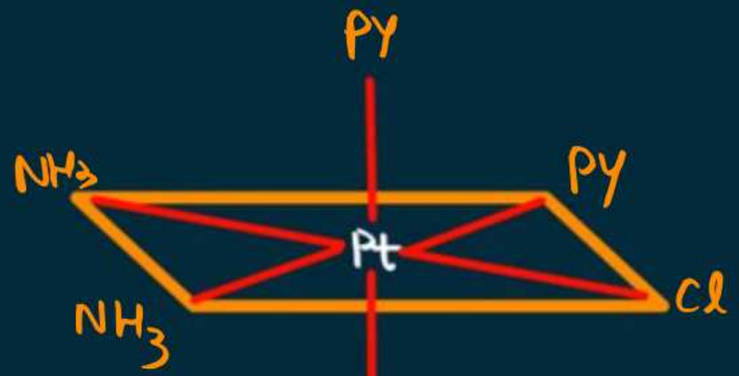
## Examples of octahedral complex shows Isomerism.

Ex.

$[Pt(Py)_2(NH_3)_2Cl_2]$

Cis Trans (X)

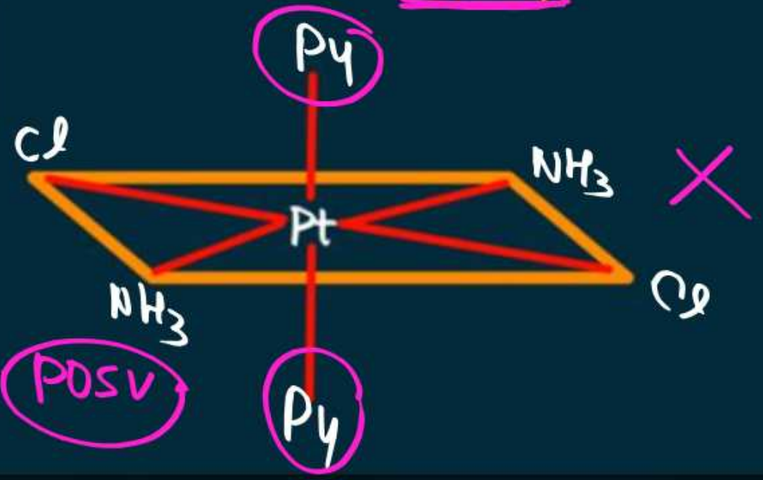


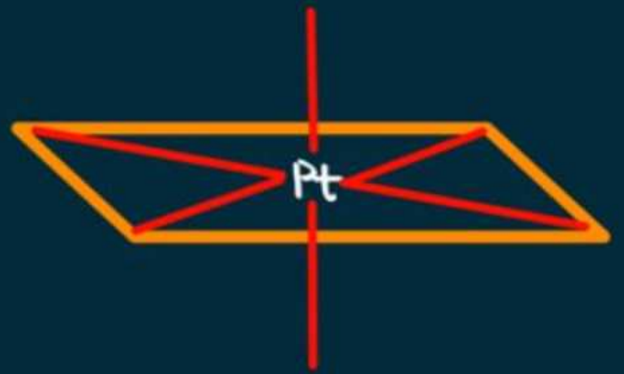





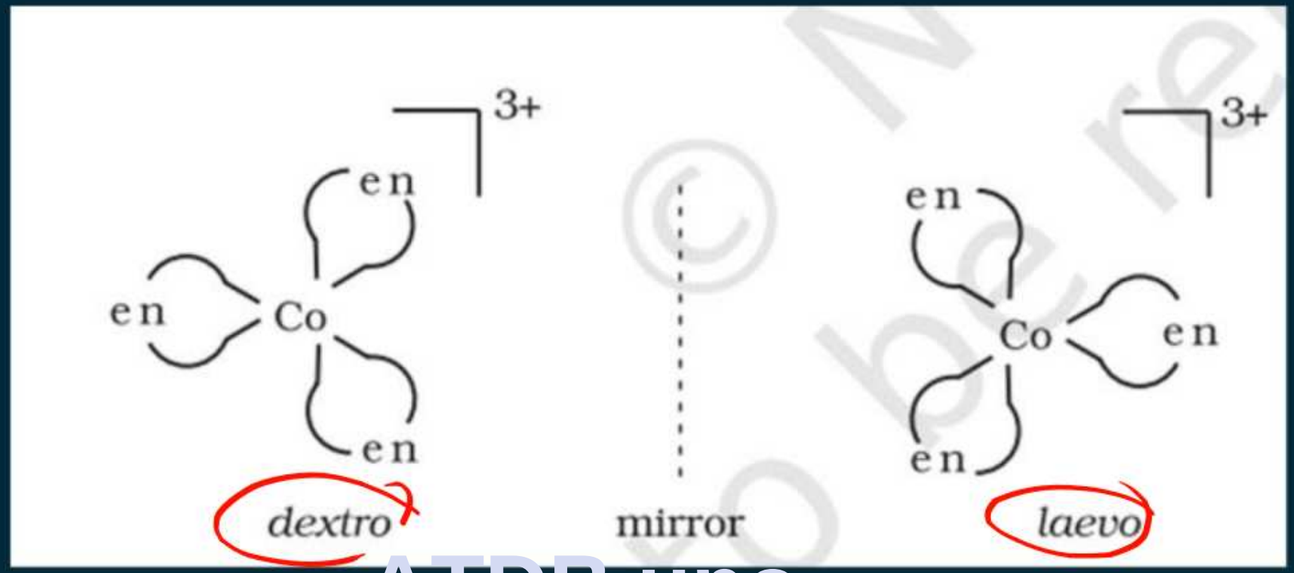

Cl Cis (-)

Cl Cis (+)



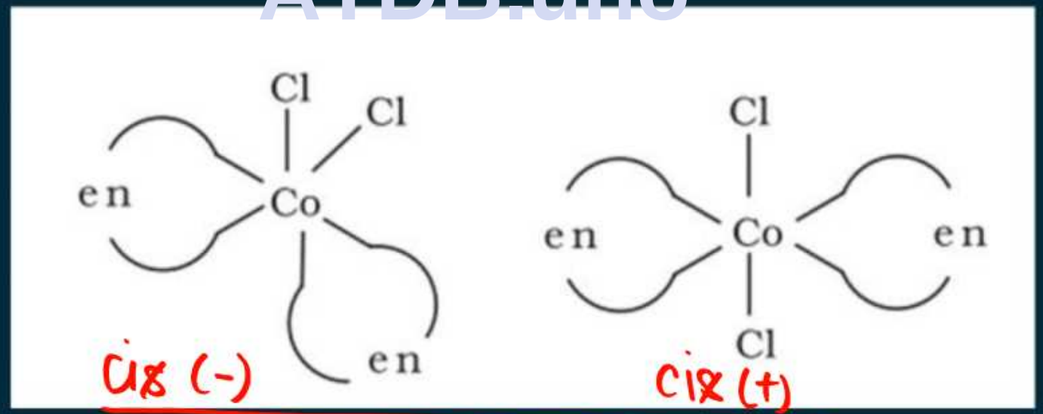
$[Co(en)_3]^{3+}$




APM

$[Co(en)_2Cl_2]^{+}$

cis Trans ✗



# Colour of coordination compound

Some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white.

The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over.



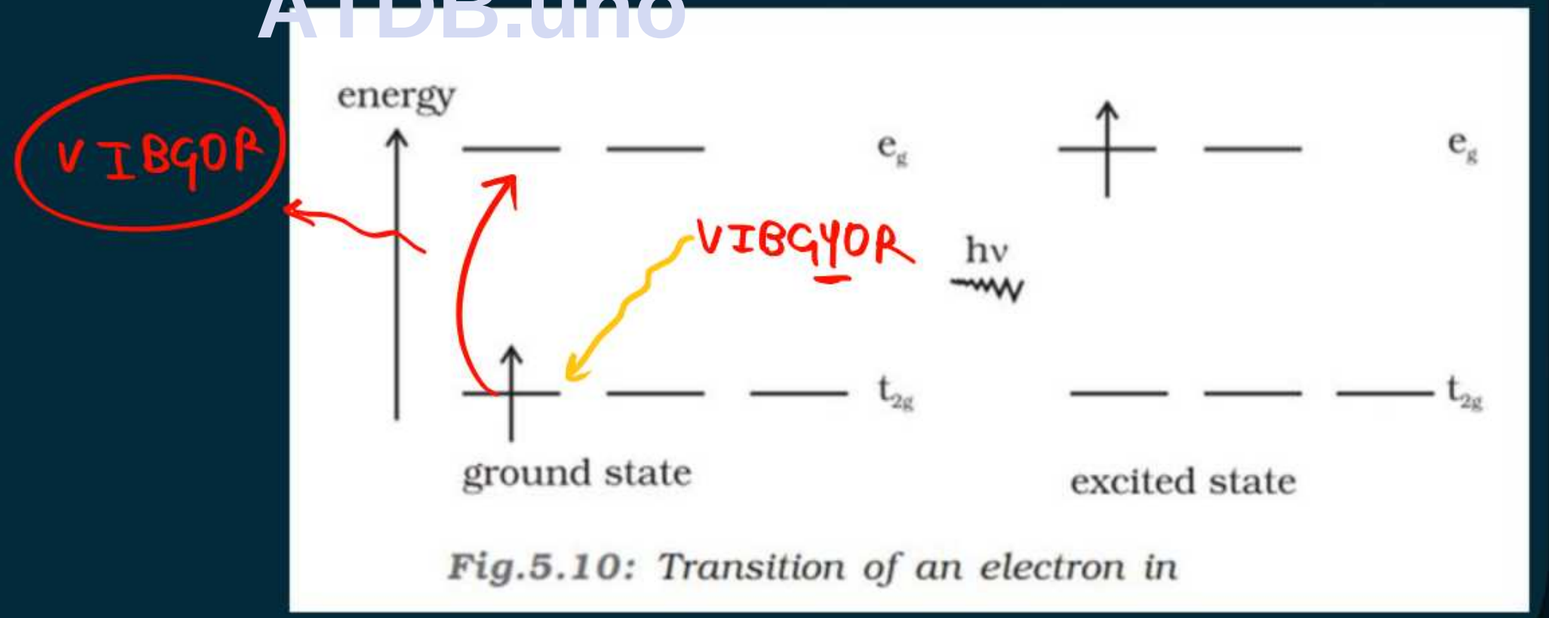



*Fig.5.10: Transition of an electron in*

| Coordinaton entity | Wavelength of light absorbed (nm) | Colour of light absorbed | Colour of coordination entity |
|---|---|---|---|
| $[CoCl(NH_3)_5]^{2+}$ | 535 | Yellow | Violet |
| $[Co(NH_3)_5(H_2O)]^{3+}$ | 500 | Blue Green | Red |
| $[Co(NH_3)_6]^{3+}$ | 475 | Blue | Yellow Orange |
| $[Co(CN)_6]^{3-}$ | 310 | Ultraviolet | Pale Yellow |
| $[Cu(H_2O)_4]^{2+}$ | 600 | Red | Blue |
| $[Ti(H_2O)_6]^{3+}$ | 498 | Blue Green | Violet |

Not in visible region



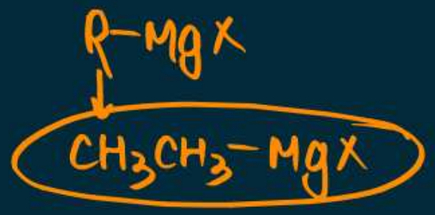
It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4 .5H_2O$ is blue in colour.

# Organometallic compounds

Compounds that contain at least one carbon-metal bond are called organometallic compound.

Ex.

Grignard reagent (RMgx), [Fe(CO)4]



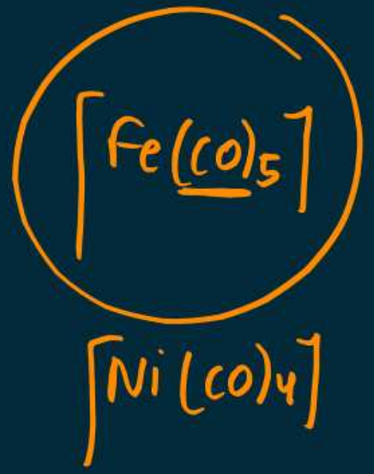

Organometallic compounds may be classified into 3 classes

(A) Sigma (σ) bonded complexes

(B) Pi (π) bonded complexes

(C) Complex containing both σ and π → Metal carbonyl

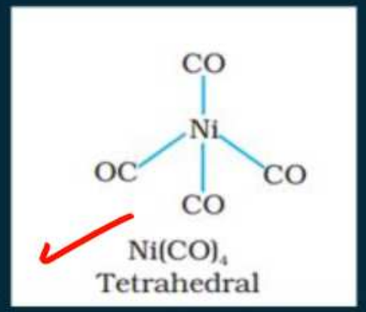




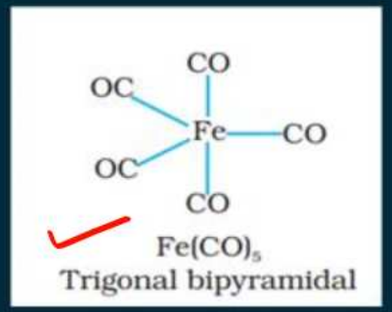
# Metal carbonyl

## The Homoleptic carbonyls are formed by most of the transition metal

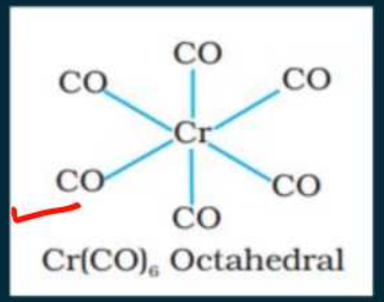
**Tetra carbonyl Nickel** **Pentacarbonyl Iron**



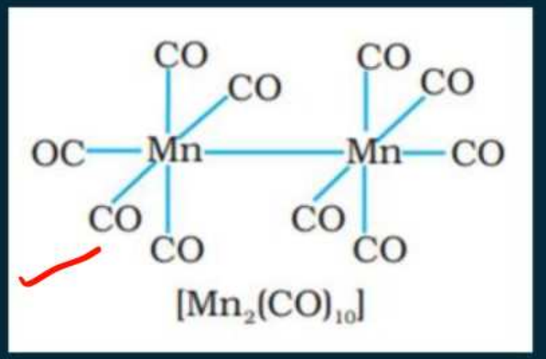

$Ni(CO)_4$
Tetrahedral




$Fe(CO)_5$
Trigonal bipyramidal

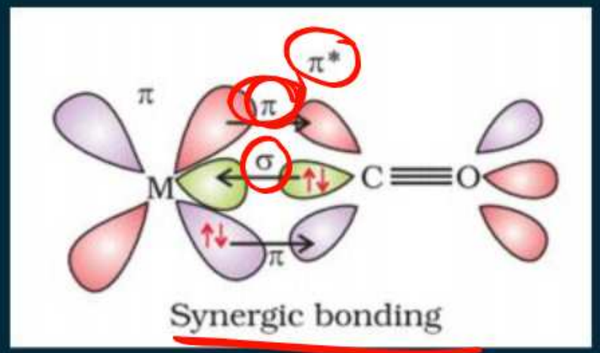



$Cr(CO)_6$ Octahedral




$[Mn_2(CO)_{10}]$






Synergic bonding

- The metal –carbon bond in metal carbonyl posses both σ and π character.
- The M-C σ bond is formed by the donation of lone pair of $e^-$ of the carbonyl carbon into vacant orbital of the metal
- The M–C π bond is formed by the donation of a pair electron from a filled d-orbital of metal into the vacant antibonding π* orbital of CO.

# Samaj Aaya ?

Compend OC

Sample paper

High weightage

# APM




# Thank You