Inorganic chemistry

Transition Metal

D-block elements :- last e⁻ enters in the d-orbital.

→ All transition metals are d-block but all d-block elements are not transition metal.

Sc (21)

Zn (30) – d-block.

→ d- block elements $\xrightarrow{\text{d-orbitals partially filled. } (d^1\text{-}d^9)}$ → elemental form (Sc, Ti, V) → called Transition metals.
→ in a common oxidation state (Cu^{+2})

$Sc(21) \rightarrow (4s^2 3d^1)$ – T.M. – – – $Ni(28) \rightarrow 4s^2 3d^8$ – T.M.

$Cu(29) \rightarrow 4s^1 3d^{10}$ – not T.M.
∴ $Cu^{+2} \rightarrow 4s^0 3d^9$ – T.M.

$Zn(30) \rightarrow 3d^{10}4s^2$ – not T.M
$Zn^{+2} \rightarrow 3d^{10}$ – not T.M.
d-block but not Transition met

$Cd \rightarrow 4d^{10}5s^2$.
$Cd^{+2} \rightarrow 4d^{10}$.

$Hg \rightarrow 5d^{10}6s^2$
$Hg^{+2} \rightarrow 5d^{10}$.
– also not T.M.

→ d-orbitals are partially filled from Sc to Ni — so, they are transition metals. — also called typical T.M. — exhibit properties of T.M.

→ d-orbitals are full-filled from Cu to Zn — so, they are d-block but not transition metals.
— also called non-typical T.M.
— do not exhibit properties of T.M.

T.M →
- variable oxdn state
- colored compounds
- complex compounds
- paramagnetism
- catalytic properties.

– but (for not T.M.) — non-typical T.M को छोड़कर।

Abhishek

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Properties of transition Metal

① Variable oxdn states :- two or more oxdn state.

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

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

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

└ more stable due to half filled d-orbital.

(n-1) n

Valance shell electronic configuration → $(n-1)d^{1-10}\,ns^{1-2}$ (3d, 4s)

→ almost same energy.

∴ e^-s from both (n-1)d & ns orbitals participate in bonding.

→ so, exhibit variable oxdn state.

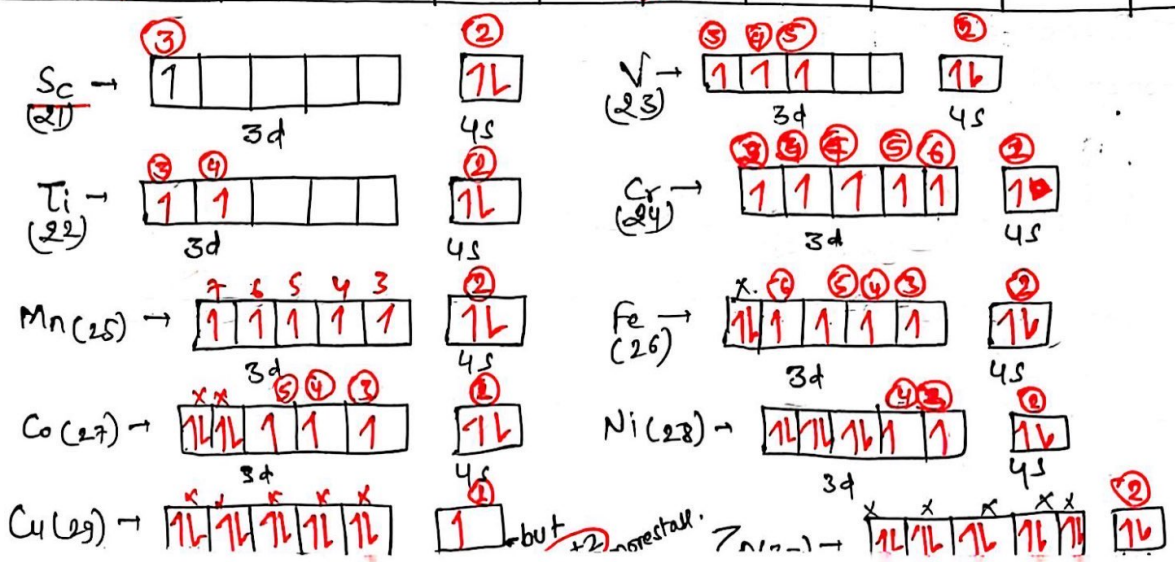
Ni → ?

$\boxed{\text{No of oxdn state} \propto \text{no. of unpaired } e^- \text{ in d-orbitals.}}$

Elements	Sc(21)	Ti(22)	V(23)	Cr(24)	Mn(25)	Fe(26)	Co(27)	Ni(28)	Cu(29)	Zn(30)
				exp. of Afbau p.					exp. of Afbau p.	
V.S. Econfi	$3d^{1}4s^{2}$	$3d^{2}4s^{2}$	$3d^{3}4s^{2}$	$3d^{5}4s^{1}$	$3d^{5}4s^{2}$	$3d^{6}4s^{2}$	$3d^{7}4s^{2}$	$3d^{8}4s^{2}$	$3d^{10}4s^{1}$	$3d^{10}, 4s^{2}$
				1	2	2	2	2	1	2
oxdn states	2	2	2	2	3	3	3	3	2	
	3	3	3	3	4	4	4	4	3	
		4	4	4	5	5	5			
			5	5	6	6				
				6	7					

oxdn state ↑es. upto Mn.

oxdn state ↓es. from Mn to Zn.



Note:-

(i) Zn doesnot exhibit variable valency / Transition state.
(ii) only Cr & Cu exihibit lowest oxdn states → (+1).
(iii) Highest oxdn state of Mn → +7.
(iv) except → $\overset{+6}{O_s}O_4$ → Os → (+8) oxdn state.
$\overset{+8}{R_u}O_4$, $\overset{+8}{X_e}O_4$ → xenon.

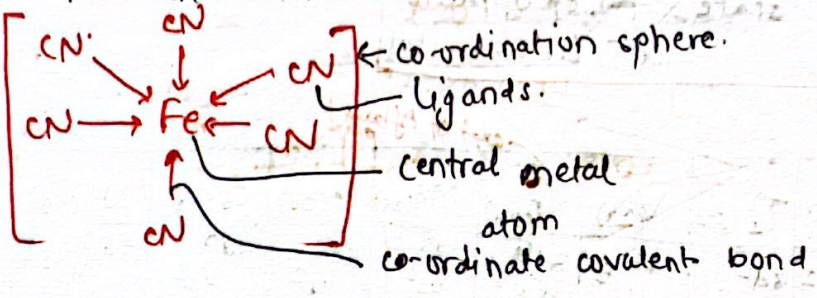
Formation of complexes (complex compounds) coordination compound

→ $Fe(CN)_2$, $Fe(CN)_3$, $ZnCl_2$ → Normal compounds.

→ $K_4[Fe(CN)_6]$ (co-ordination no.), $Fe(CO)_5$ (co-ordination no.), $[ZnCl_4]^{2-}$ → Complex compounds

· $K_4(Fe(CN)_6)$ →

Fe → central metal atom



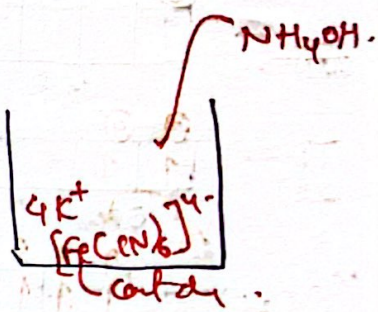
→ Those compounds having a central metal atom co-ordinated with ligands within co-ordination sphere.

Properties

① $K_4[Fe(CN)_6] \xrightarrow{aq.} 4K^+ + [Fe(CN)_6]^{4-}$
($4K^+$ → simple ion; $[Fe(CN)_6]^{4-}$ → complex ion)

- Donot dissociate completely in solution (Metal & Ligands donot dissociate].

② $NH_4OH + Fe^{++} \longrightarrow Fe(OH)_2\downarrow\downarrow$
(Fe^{++} → cant diss.)



- Donot give test of all individual species in complex.
- central metal atom & ligand doesnt give test (chemical).

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Q. Which of the following doesn't give $AgNO_3$ test?

(a) $CaCl_2$ → Cl^- (b) $AlCl_3$ → Cl^- (c) $[Co(NH_3)_6]Cl_3$ → Cl^- (d) $K_2[NiCl_4]$ → Cl^- (ligand) (cauli dissoi)

• Ligands :-

Ligand : + C. Metal atom ⟶ L → M (co-ordinate covalent bond.)

Ligand : → lone pair donor → lewis base

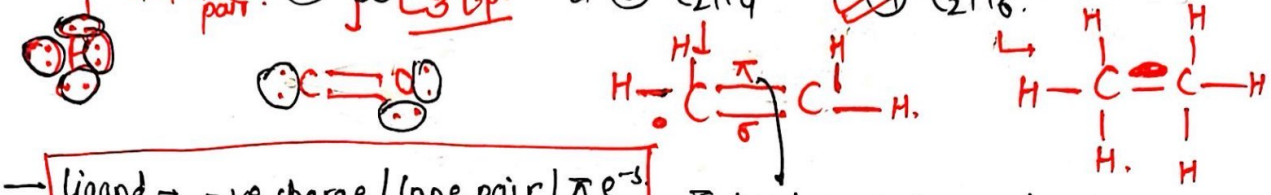
C. Metal atom → lone pair acceptor → lewis acid

→ Any lewis base which is co-ordinated to the central metal atom in a complex → ligands.

e.g. F^-, Cl^-, NO_3^-, $:NH_3$, $H_2\ddot{O}$, NO^+, NO_2^+.

Q. Which of the following cannot form complexes? (cauli act as ligand.)

(a) F^- → 4 lone pair. (b) CO → 3 l.p. (c) C_2H_4 (d) C_2H_6 → no lone pair.



→ $\boxed{\text{ligand} \rightarrow \text{-ve charge / lone pair / } \pi e^-\text{s}}$

π-bond → eq. to lone pair.

• Shape of complex ion

→ Using valance bond theory (VBT).

$-\overset{|}{\underset{|}{C}}- \Rightarrow$ [↑↓] [↑|↑|↑] → sp^3 — 0+4 = 4.
2s 2p

$-\overset{|}{\underset{|}{A}} \Rightarrow$ [↑L] [↑|↑|↑] sp^3 — $-\overset{|}{B}- \Rightarrow$ [↑L] [↑L|↑|↑] — sp^3
2s 2p 2s 2p

1+3 = 4. 2+2 ⇒ 4.
l.p. bond pair.

• Sum → 2 → sp
3 → sp^2
4 → sp^3
→ Hybridization.

→ L → M.
Filled orbital, Vacant orbital.

→ M ← L L L L. 0+4=4. sp^3.
4 का orbital vacant हुन पर्‍यो।
for 4 ligands.

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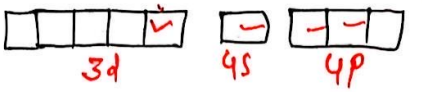
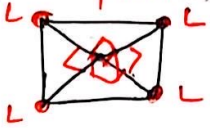
→ only vacant atomic orbitals of central metal atom participate hybridization.

→ Co-ordination no. of central metal atom determines hybridization

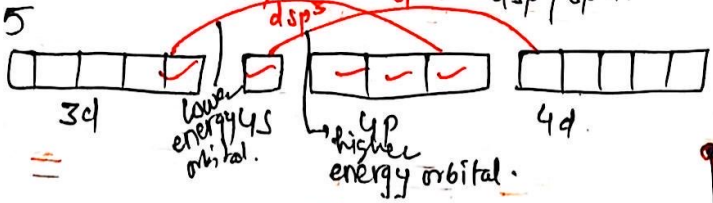
shape ← determines

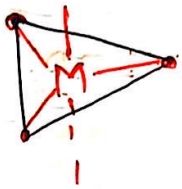
Co-ordination no.	Hybr.	shape
2	sp	Linear (180°)
3	sp^2	Trigonal planar (120°)
4	sp^3	tetrahedral (109.5°)
4	dsp^2	Square planar (90°)



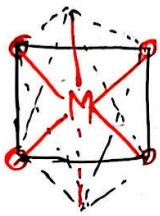


5 — dsp^3, sp^3d, dsp^3/sp^3d — Trigonal Bipyramid (120°; 90°)

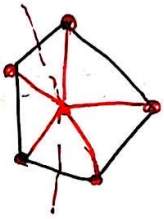




6 — d^2sp^3 / sp^3d^2 — square bipyramid / octahedral (90°).



7. — sp^3d^3 — pentagonal bipyramid (72°; 90°)



$\frac{360}{5}$

#Spectrochemical series

F^-, Cl^-, Br^-, I^-, OH^-, NO_3^-, $C_2O_4^{--}$, H_2O, NH_3, NO_2^-, CN^-, CO

weak filled ligand @ (X, O-donor) — Strong filled ligand @ (C, N-donor)

M = 1 1 1 1 1

↳ no pairing of e^- (unchanged) ← weak ligand → 1 1 1 1 1

M = 1 1 1 1 1

strong ligand → 1L 1L 1

• Complexes having C.N = 4 → sp^3 / dsp^2

Paramagnetic → one or more unpaired e⁻s.

Diamagnetic → No unpaired e⁻

eg. ① $[Ni^{+2}Cl_4]^{2-}$ (Cl⁻ = weak ligand)

$Ni(28) = 3d^8 4s^2$

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

Ni^{+2} → | 3d: ↿⇂ ↿⇂ ↿⇂ 1 1 | 4s: ☐ | 4p: ☐ ☐ ☐ | 4d: ☐ ☐ ☐ ☐ ☐ |

(4s + 4p → sp^3)

ligand → weak so, no pairing of e⁻

So, · Hybridization → sp^3 (vacant). d-orbital is not vacant so, not dsp^2.

· Shape → Tetrahedral.

· No. of unpaired e⁻ (n) ⇒ 2.

∴ Magnetic property → paramagnetic

· Magnetic moment → $\sqrt{n(n+2)}$

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

$= \sqrt{8} = 2\sqrt{2}$ (Bohr's magneton)

② $[Ni^{+2}(CN)_4]^{2-}$ (x + 4 = −2, x = +2.)

Strong ligand.

$Ni(28) \rightarrow 3d^8 4s^2$

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

Ni^{+2} → | 3d: ↿⇂ ↿⇂ ↿⇂ 1 1 | 4s: ☐ | 4p: ☐ ☐ ☐ |

Ni^{+2} paired state → (due to strong ligand) | 3d: ↿⇂ ↿⇂ ↿⇂ ↿⇂ ✓ | 4s: ✓ | 4p: ✓ ✓ X | (dsp²)

C.N = 4

∴ Hybridization → dsp^2.

Shape → Square planar

No. of unpaired e⁻ (n) → Zero.

Magnetic property → Diamagnetic

Magnetic Moment → $\sqrt{n(n+2)}$

$= 0.$

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Complexes with C.N → 6.

↳ always octahedral shape.

sp^3d^2 d^2sp^3

e.g. (i) $[Fe^{+2}(CN)_6]^{4-}$

↳ strong ligand.

$Fe(26) \rightarrow 3d^6 4s^2$

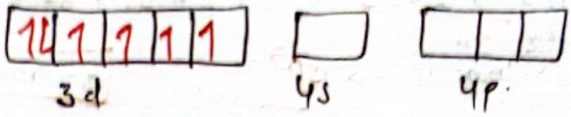
$Fe^{+2} \rightarrow 3d^6 4s^0 4p^0 4d^0$

inner ↳ outer.

Fe^{+2} state →

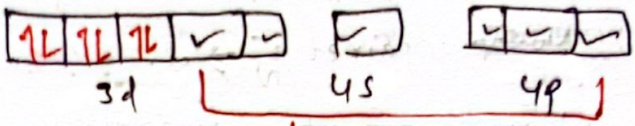
3d	4s	4p
↑↓ ↑ ↑ ↑ ↑		

Fe^{+2} state in paired (strongli.) →



3d	4s	4p
↑↓ ↑↓ ↑↓ ✓ ✓	✓	✓ ✓ ✓

↳ d^2sp^3.



Hybridization → d^2sp^3.

shape → octahedral / Sq. Bipyramidal (inner orbital complex).

No. of unpaired $e^-(n)$ ⇒ zero

Mag. property → Diamagnetic

Mag. moment → $\sqrt{n(n+2)} = 0$ BM.

(ii) $[Fe^{+3}F_6]^{3-}$

↳ weak ligand. ↳ no pairing

$Fe(26) \rightarrow 3d^6 4s^2$

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

(CN) - 6. (coord. no.)

Fe^{+3} state →

3d	4s	4p	4d
↑ ↑ ↑ ↑ ↑	✓	✓ ✓ ✓	✓ ✓ ✓

↳ sp^3d^2.



Hybridization → sp^3d^2.

shape → octahedral. (outer orbital complex).

no. of unpaired $e^-(n)$ → 5.

Mag. property → paramagnetic

Mag. moment → $\sqrt{n(n+2)} = \sqrt{5\times 2} = \sqrt{35}$ BM.

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→ $[\overset{+3}{Co}(NH_3)_6]Cl_3$.

└ strong ligand.

(27) └ $3d^7 4s^2$ → Co^{+3} → $3d^6 4s^0$

└ [↑↓|↑↓|↑↓|–|–] [–] [–|–|–]

3d. 4s 4p.

└ d^2sp^3.

n=0. └ octahedral.

- $[\overset{+2}{Zn}(CN)_4]^{2-}$

Zn_{30} → $3d^{10}4s^2$

Zn^{+2} → $3d^{10}$ ← [↑↓|↑↓|↑↓|↑↓|↑↓] [–] [–|–|–]

3d. 4s 4p.

└ sp^3.

also, for $[ZnCl_4]^{2-}$ → same.

Shape of d-orbital

$l = 2$

$m = +2, +1, 0, -1, -5$.

$= 5$ values.

└ 5 types of spatial orientation.

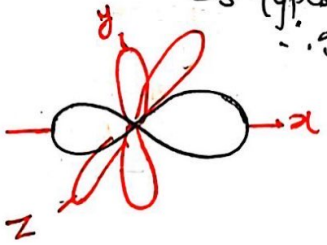
∴ 5 orbitals.

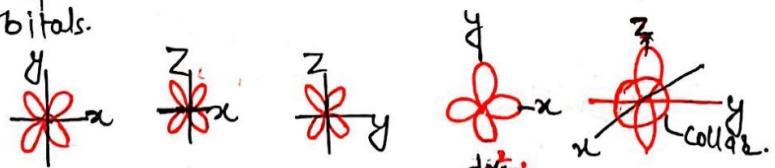
no-orientation

P → subshell

P_x → orbital.

└ orientation ↑↓.





d_{xy} d_{xz} d_{yz}. $d_{x^2-y^2}$ d_{z^2}.

└ non-axial d-orbital.

└ t_{2g} → orbitals.

└ axial d-orbitals

e_g-orbitals.

- [| | | |]

d_{xy} d_{xz} d_{yz} $d_{x^2-y^2}$ d_{z^2}. └ dumbell.

└ t_{2g} └ e_g

└ not double dumbell

Crystal field Theory (CFT) – for octahedral complexes.

└ colored compound.

co-ordination no. → 6.

M^{+n} → [| | | |] e_g t_{2g}

isolated state or non-bonded state

degenerate d-orbitals

└ (5-orbitals having same energy)

ligand field.

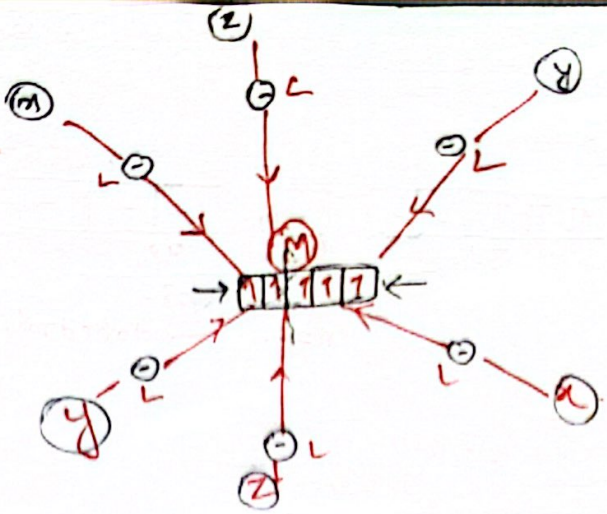
repulsion b/w -ve charge on ligands & e^- in d-orbitals.

→ [|] e_g

[| |] t_{2g}.

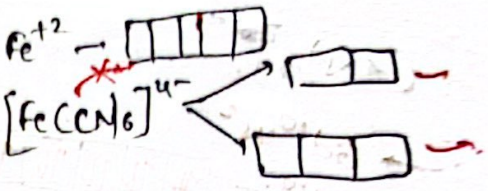
E

splitting of d-orbitals called



Ligand = 6 — dif ener.

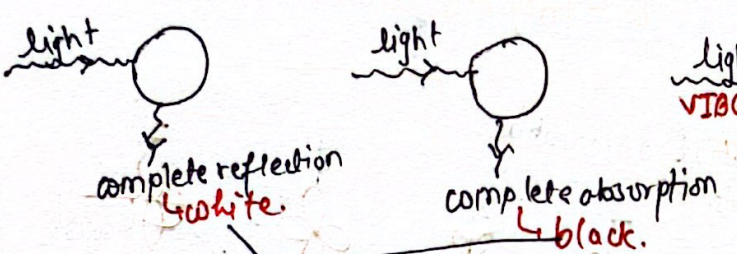
5 → d-orbital.



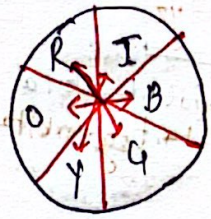
→ Formation of colored compounds

→ T.M ion / compound are usually colored.
→ color arises due to d-d transition.

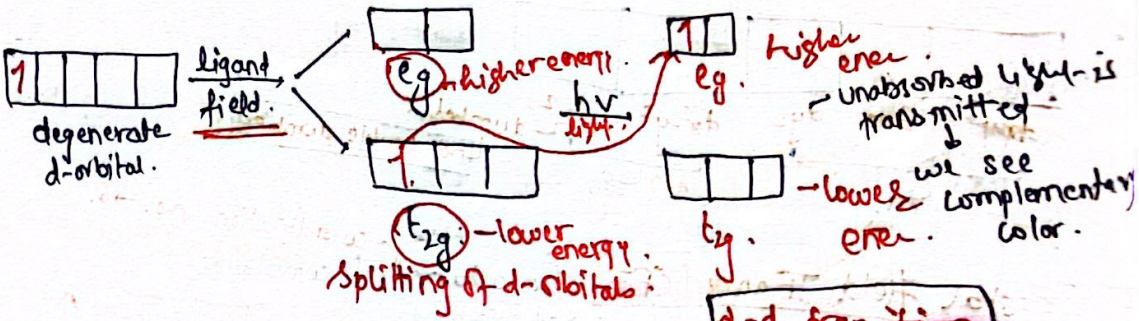
Note :- compounds of- representative elements → colorless / white
↳ s & p-block except Noble gas.







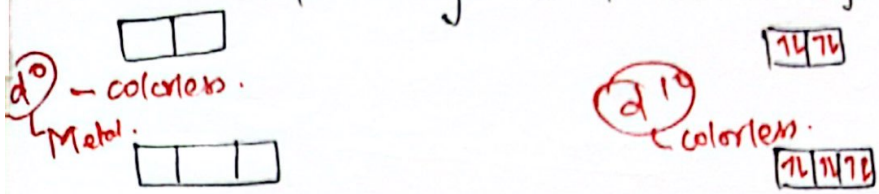
Red
chl
green.
violet → yellow green



d-d transition

energy absorbed by sunlight

→ Substance is exposed in light.
- e^- absorb light ⟷ e^- promote from lower energy d-orbital to higher energy d-orbital. This is called d-d transition.
- d-d transition takes place by absorbtion of light in visible region. VIBGYOR.
- Unabsorbed light is transmitted which gives color to the substance.
- We see complementary color of absorbed light.



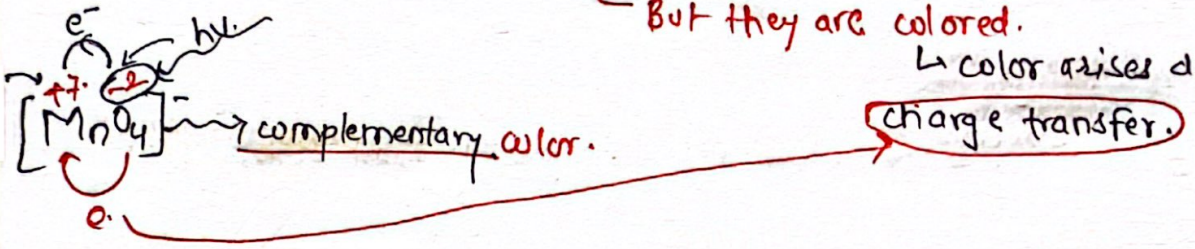
- T.M having d^0 (e.g. Sc^{+3}, Ti^{+4}, etc) & d^{10} (eg Cu^+, Zn^{++}, etc) electronic configuration donot exihibit dd transition. So, they are colourless (white.

exception

$KMnO_4$ → $3d^5 4s^2 \xrightarrow{+7} 3d^0$.

$K_2Cr_2O_7$ → $3d^5 4s^1 \xrightarrow{+6} 3d^0$.

But they are colored.
↳ color arises due to charge transfer.



→ d^1 — d^9 → colored due to d-d transition.

- d^0 & d^{10} → Usually colorless – No d-d transition
  → rarely colored → due to charge transfer.
  eg. $KMnO_4$ & $K_2Cr_2O_7$.

e.g. $Ti \rightarrow 3d^2 4s^2$

$TiCl_4$ (+4) → $3d^0$ ↳ colorless.

$TiCl_3$ (+3) → $3d^1$ ↳ colored.

$Cu^+ \rightarrow 3d^{10}$ ↳ colorless.

$Cu^{+2} \rightarrow 3d^9$ ↳ colored (blue).

$Zn^{++} \rightarrow 3d^{10}$ ↳ colorless. (white vitriol).

$NiSO_4$ (+2) → $3d^8$ ↳ colored.
28.

$Fe^{+2} \rightarrow 3d^6$ ↳ colored.

$Fe^{+3} \rightarrow 3d^5$ ↳ colored.

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