

IOC Mega Revision

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1st March - 13th March



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Prateek Gupta Sir
eSaral Chemistry Faculty



- **IIT Bombay, Metallurgy**
- **Online Creativity & Visualization Expert**
- **Mentored Lakhs of Students**





Saransh Gupta Sir eSARAL Physics HoD

Phy
Mega Revision

- IIT Bombay, CS
- AIR-41 IIT-JEE
- Air-71 AIEEE (JEE Main)
- AIR-4 NSO
- 1% In Top INPHO
- 8+ Years of Teaching Experience
- Mentored Lakhs of Students



N.K. Gupta Sir eSaral Math Faculty & Master Planner

- IIT Kanpur, Mechanical
- Ex **Vice President & Academic Head**, Allen, Kota
- Mentored many of **Rank 1 & Top 100** Students
- **30+** years of Teaching Experience
- Mentored over **3,00,000** Students



Dr. Anshuman Agarwal eSaral Biology Faculty

- MBBS, MD, FIPM
- **AIR-196**, AIPMT(NEET)
- **ARR-46**, RPMT
- **NTSE Scholar**
- **Ex HoD Biology**, Resonance, Kota
- **10+ years** of Teaching Experience
- **Mentored** over thousands of doctors

Master Planners & Faculties

A portrait of Dr. Kushika Taneja, a woman with dark hair, wearing a dark blue polo shirt with the eSara! logo. She has her arms crossed and is smiling slightly.

Dr. Kushika Taneja eSara! Biology Faculty

- **Ex-HoD Biology**, Pace IIT and Medical, Indore
- Biology faculty at Rao Academy, Kota
- **7+ years** of Teaching Experience
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① Chemistry ③
Samjho, dekho & yaad karo

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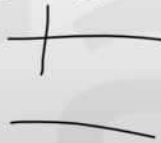
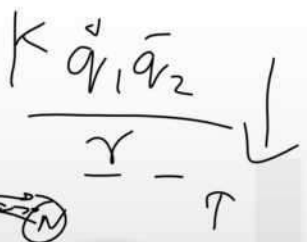
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Why Bonding?

X Octet rule

X Overlapping

X Hybridisation



What is a Coordination Compound ?





(A) Double Salts ✓

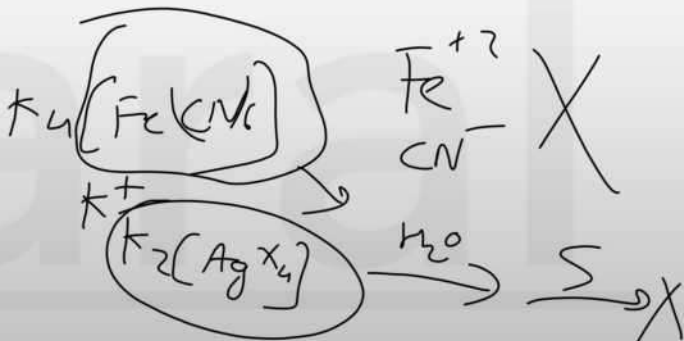
Break down into simpler ions.

Paani ✓



(B) Coordination Compounds

Retain their identity in solution.



(I) Perfect Complexes

(II) Imperfect Complexes





Classification of Ligands

(A) Based on charge

(i) Neutral ligands

H_2O , NO , CO , C_6H_6 etc.

(ii) Positive ligands NO^+ , $N_2H_5^+$

(iii) Negative ligands

Cl^- , NO_2^- , CN^- , OH^-

zn
tn
pn
bn
ox
EDTA

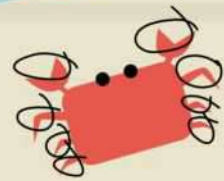
MLG





(B) Based on **denticity** → teeth/claws

The number of electron pairs donated to central metal by ligands is known as DENTICITY. Depending on number of electron pairs donated, these are classified in following categories.





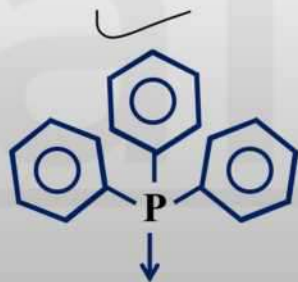
(a) Unidentate/monodentate ligands

Ligands which donate one pair of electron to the central metal are called unidentate ligands.

X^- , CN^- , NO_2^- , NH_3 , Pyridine, OH^- , NO_3^- , H_2O , SO_3^{2-} , CO , NO , O^{2-} , $(C_6H_5)_3P$, CH_3CO^- etc.



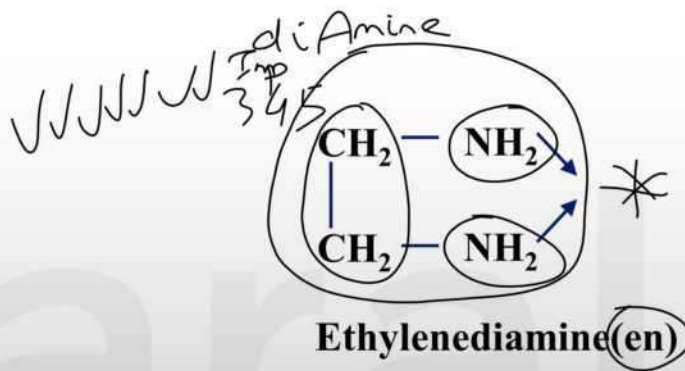
Pyridine (Py)



Triphenyl phosphine
(PPh_3)



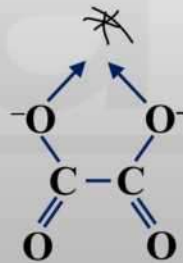
(b) Bidentate ligands



Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.

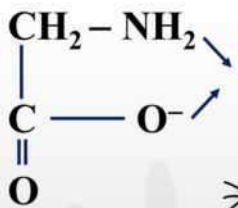


**1, 10-Phenanthroline
(O-phen)**

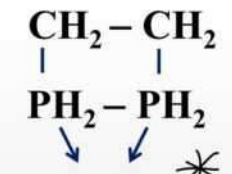


Oxalate (ox)

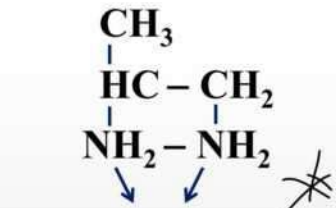




Glycinato (Gly)

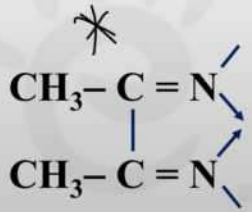


ethylene diphosphene (diphos)

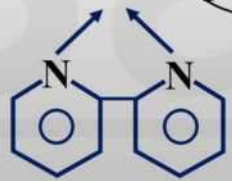


Propylene diamine

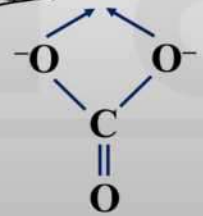
or
1,2- diamino propane (pn)



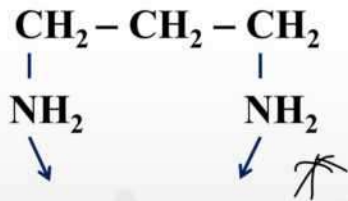
Dimethyl glyoximion (DMG)



2, 2'-Dipyridyl (Dipy)



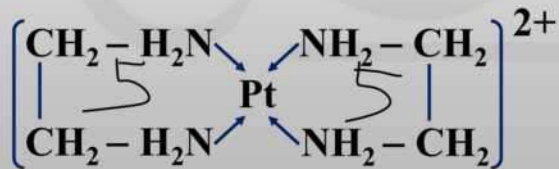
Carbonate



1,3 diamino propane
or
trimethylene diamine

(tn)

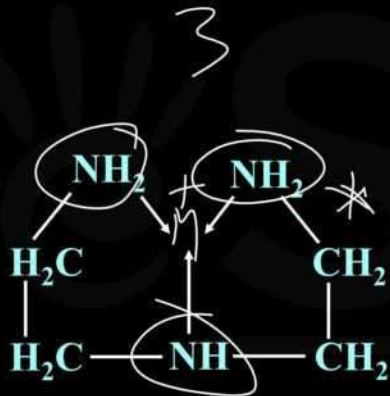
chelation



Super stable



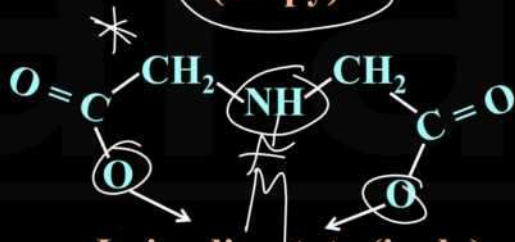
(c) Tridentate ligands



Diethylene triamine (Dien)

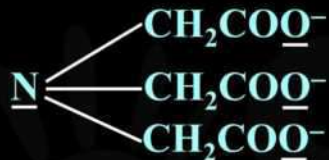


2,2',2''-Terpyridine
(Terpy)

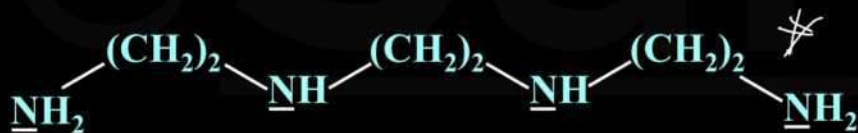


Iminodiacetate (imda)

(d) Tetradentate ligands



Nitrilotriacetato (nta^{3-})



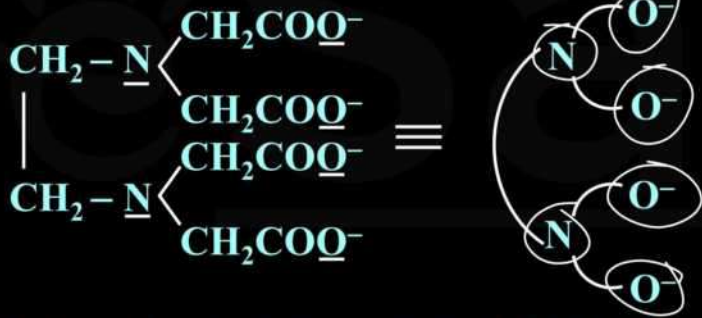
**Triethylene tetra amine
(trien)**

(f) Hexadentate ligands

Super stable

Most Important Ligand

5 membered
6 " Rings



Ethylenediaminetetraacetato (EDTA)⁻⁴



(h) Ambidentate ligands

1 site only
1 lp

No imaan dharm

Ligands which can ligate through two different atoms present in it are called ambidentate ligands. At a time only one atom can donate.





(C) Based upon bonding interaction between the ligand and the central atom.

(i) Classical or simple ligand

These ligands only donate the lone pair of electrons to the central atom.

Ex. O^{2-} , OH^- , F^- etc.





(ii) Non classical or π -acid or π -acceptor ligand

lp

\uparrow
 π

These ligand not only donate the lone pair of electrons to central metal but also accept the electron cloud from central atom.





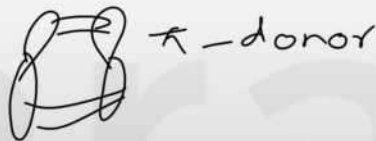
On the basis of nature of donating electron cloud these ligands are following types.

Trick



(a) σ donor π acceptor

Ex. CO, CN^- , NO^+ , PF_3 , PR_3 etc.



(b) π donor π acceptor

Non-classical ligand
Aromatic, Anti-Aromatic can never be σ acceptor

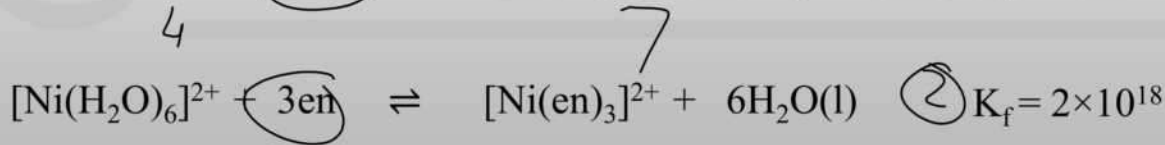
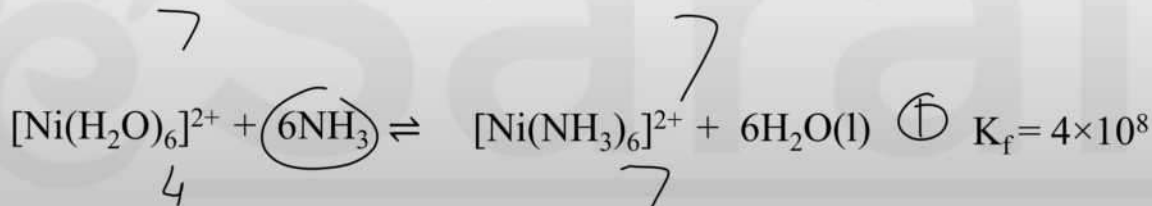
Ex. C_2H_4 , C_6H_6 , C_5H_5^- etc.



1 qp
2 qp
3 qp

rate \uparrow
 $\Delta G = \Delta H - T\Delta S$

floridentate ΔS no of molecules \uparrow





Sidgwick Theory or Effective Atomic Number Concept (EAN)

Polynuclear CE

no of e^- in the molecule

Noble gas



EAN = (atomic number of the metal – oxidation state of central metal) +
number of electrons gained from the donor atoms of the ligands.

no of e^-

no of e^- lost

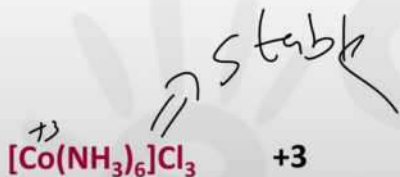




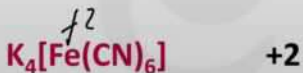
Q) Determine the effective atomic number of the metal atom in the following

Fail

Complex oxidation state of the metal Effective atomic number (EAN)



$$\overset{24}{(27 - 3)} + \overset{NH_3}{(6 \times 2)} = 36 \text{ (kr)}$$



$$\overset{24}{(26 - 2)} + (6 \times 2) = 36 \text{ (kr)}$$





Q) Find value of x

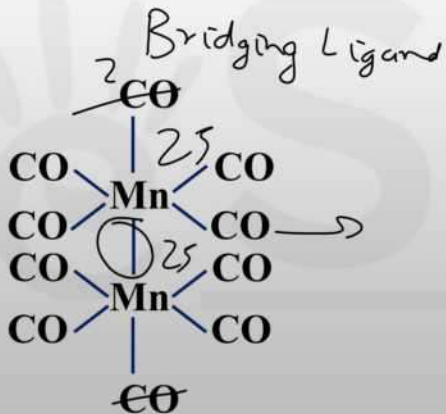
$[\text{Mn}_2(\text{CO})_x]$ Mn-Mn linkage is present and no bridge ligand is present.

Sol. $\text{Mn}_2(\text{CO})_{12}$ Mn

$$\frac{72}{2} = 36$$

to

$$\frac{68}{2} = 34$$





Werner's Co-ordination Theory

Legendary

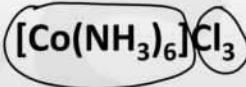
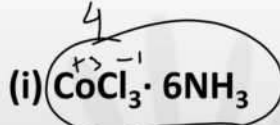
Q) Old

New

primary 4 ions

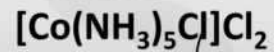
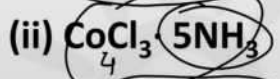
No. of Cl⁻ ions precipitate

Total No. of ions ↑ Cond ↑



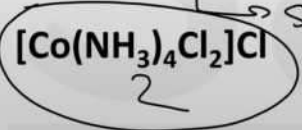
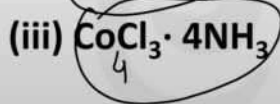
3 primary valency

4



2 secondary valency

3



2

Sol. Order of electrical conductivity of aq. solution. (i) > (ii) > (iii)



Synergic Bonding



\checkmark Imp



$$BO = 1$$

$$BO > 1$$

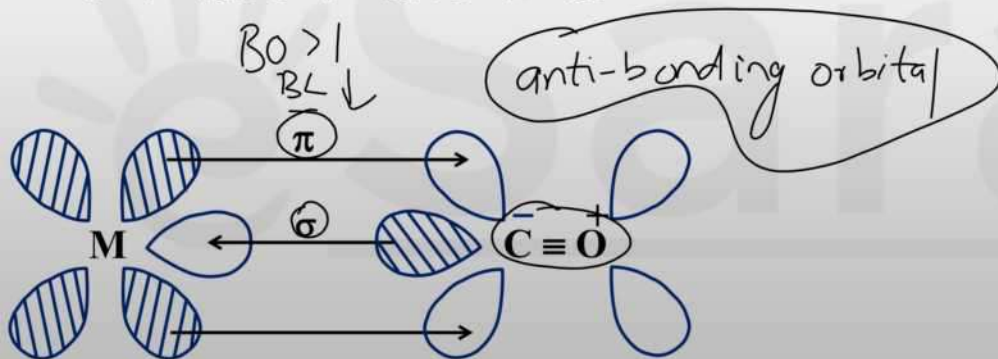
Due to presence of π acceptor ligands special type of bonding takes place in coordination compounds. It is known as synergic bonding.





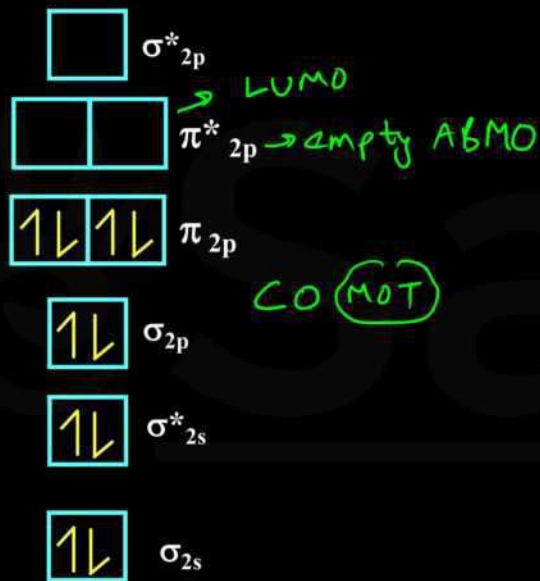
1. Bonding in metal carbonyl

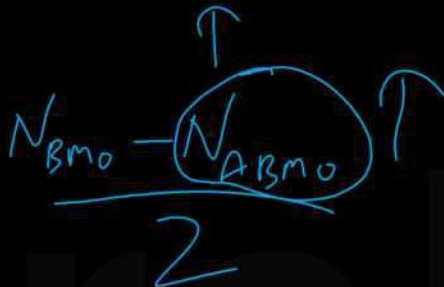
Ex. $[\text{Fe}(\text{CO})_5]$; $[\text{Ni}(\text{CO})_4]$; $[\text{Cr}(\text{CO})_6]$



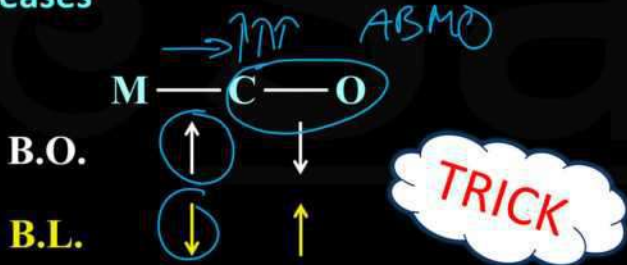
σ - donor , π - acceptor



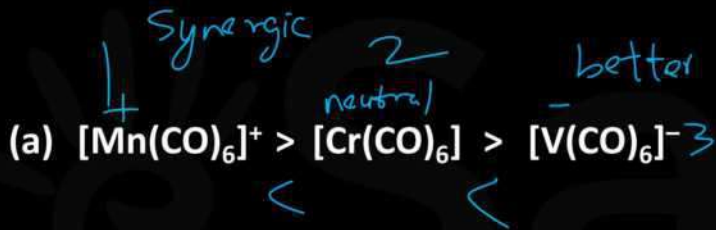
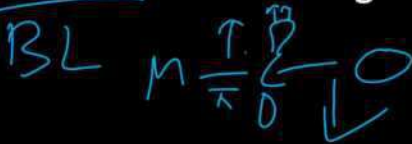




As Bond order increases, bond length decreases



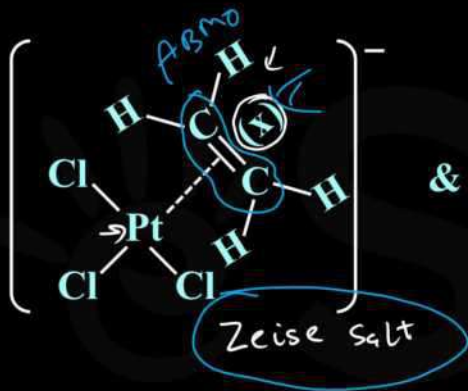
Q) Order of carbon oxygen bond order in following metal carbonyls.



For isoelectronic species as negative charge on center metal atom/ion increases extent of back bonding increases.



Q)



Sol. $y > x$ (bond length)



WORK HARDER

1 minute motivation

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करेगा!



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SECOND ROUND

99%

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IUPAC nomenclature of coordination compounds

Imp Part

(a) Like simple salts, the positive part of the coordination compound is named first.

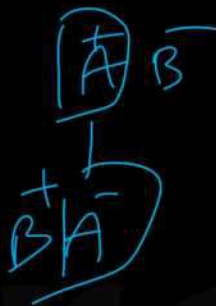
Ex. $K_4[Fe(CN)_6]$ the naming of this complex starts with potassium.

$[Cr(NH_3)_6]Cl_3$ the naming of this complex starts with name of complex ion.

(b) Naming of coordination sphere



X → name



The names of ligands along with their numerical prefixes (to represent their no.) are written first, followed by the name of central metal.

(c) The ligands can be neutral, anionic or cationic.

(i) The neutral ligands are named as the molecule

C_5H_5N [pyridine]

$(C_6H_5)_3P$ [Triphenyl phosphine]

$H_2N-CH_2-CH_2-NH_2$ [ethylene diamine]

CH_3NH_2 [methyl amine]

Me_2O [diethyl ether]



The neutral ligands which are not named as the molecule are

CO [carbonyl]

CS [thiocarbonyl]

NO [nitrosyl]

H₂O [aqua]

NH₃ [ammine]



o/ido
chloride

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chloro/Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo/Peroxido
CN^-	Cyano/Cyanido	O_2H^-	Perhydroxo/Perhydroxido
O^{2-}	Oxo/Oxido	S^{2-}	Sulphido
OH^-	Hydroxo/Hydroxido	NH^{2-}	Imido
H^-	Hydrido	NH_2^-	Amido

Symbol	Name as ligand	Symbol	Name as ligand
CO_3^{2-}	Carbonato	SO_3^{2-}	Sulphito
$\text{C}_2\text{O}_4^{2-}$	Oxalato	CH_3COO^-	Acetato
SO_4^{2-}	Sulphato	ClO_3^-	Chlorate
NO_3^-	Nitrato		
$\text{S}_2\text{O}_3^{-2}$	Thiousulphate		



(iii) Positive ligand naming ends in 'ium'

gmp

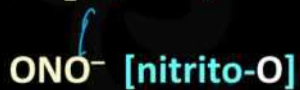
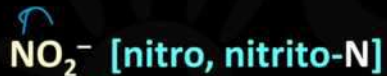
$\text{NH}_2 - \text{NH}_3^+$ [Hydrazinium]

NO_2^+ [nitronium]

NO^+ [nitrosonium/nitrosylium]



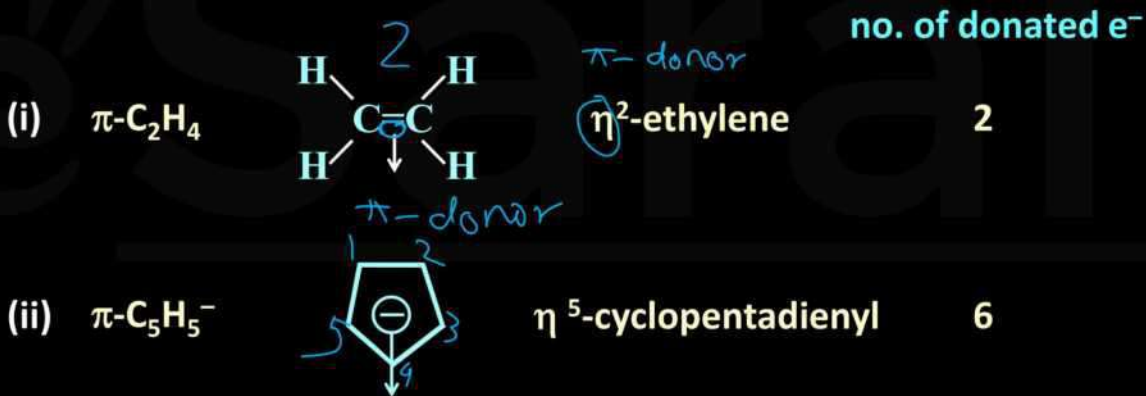
(iv) Ambidentate ligands



(v) π -donor and π -acceptor ligands

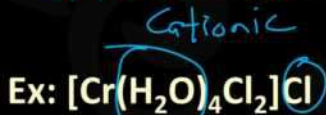
Prefix of Greek letter η^x (ita) is repeated before the name of each different kind of π -donor, π -acceptor ligand.

Where x is the number of carbon atoms to which donated electron cloud is bounded. x is known as **heptacity** of ligand.



Alphabetical

(d) If ligands are present more than once, then their number is indicated by prefixes like di, tri, tetra etc.



Cationic

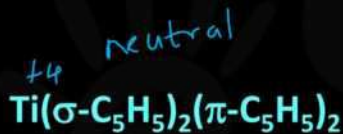
Roman numerals

Tetraaquadichlorochromium(III)Chloride

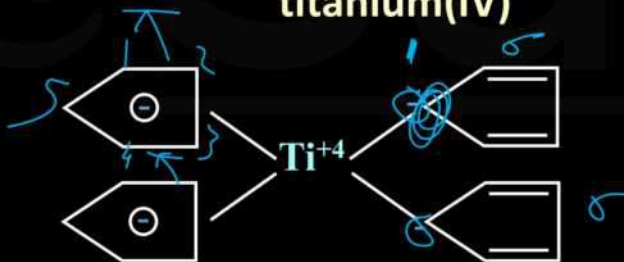
(e) If words like di, tri, tetra are already used in the naming of ligand, or if it is polydentate ligand or organic ligand, the prefixes bis-, tris-, tetrakis-, pentakis- etc. are used to specify their number.



Example



Bis(η^1 -cyclopentadienyl)bis(η^5 -cyclopentadienyl)
titanium(IV)



If the complex is the part of anion then
some of center metal atom/ion is named as

Al – aluminate

Pt – Platinate

Mo – Molybdate

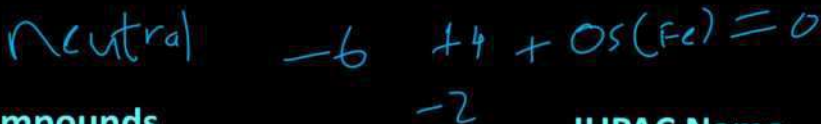
Ni – Nickelate

Fe – Ferrate

Mn – Manganate



Q) The naming of some of the complexes is done as follows (as per IUPAC)



Complex Compounds

IUPAC Name

(i) $K_4[Fe(CN)_6]$ (anionic complex)

so suffix 'ate' is added with metal name

Potassium hexacyanoferrate(II)

(ii) $K_2[PtCl_6]$

Potassium hexachloroplatinate(IV)

(iii) $[Co(NH_3)_6]Cl_3$ (Cationic complex)

so metal is without any suffix

Hexaminecobalt (III) Chloride

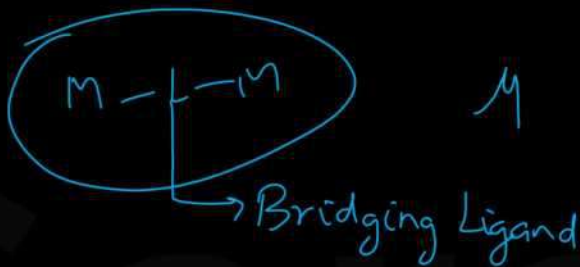


20. Which of the following name formula combinations is not correct?

[J-MAIN-2014, Online]

Formula	Name
(1) $K[Cr(NH_3)_2Cl_4]$	Potassium diammine Tetrachlorochromate (III)
(2) $[Co(NH_3)_4(H_2O)I]SO_4$	Tetraammine aquaiodo cobalt (III) sulphate
(3) $[Mn(CN)_5]^{2-}$	Pentacyanomagnate (II) ion
(4) $K_2[Pt(CN)_4]$	Potassium tetracyanoplatinate(II)

Ans 3

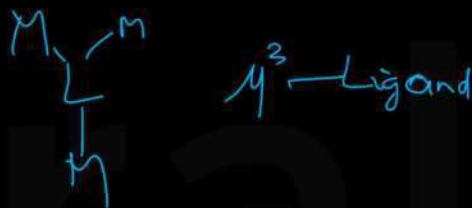


(i) If a complex ion has two metal atoms then it is termed polynuclear.

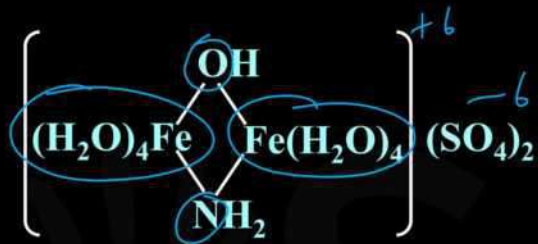
The ligand which connects the two metal ions is called as **Bridging ligand** or **Bridge group**.

A prefix of Greek letter μ^x is repeated before the name of each different kind of bridging group.

Where x is number of center metal atom/ion joined by one bridge ligand. The value of x is only mentioned when it is more than two.



Q)

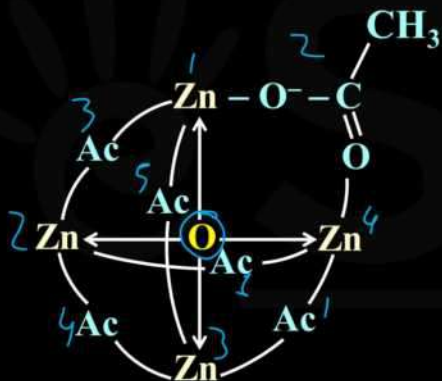


Ans. Tetraaquairon(III)- μ -amido- μ -hydroxotetraaquairon(III)sulphate



$$-2 - 6 + 4(05) = 0$$

Sol. Hexa- μ -acetato - μ^4 -oxido - tetrazinc(II)



Ac : CH_3COO^-



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1 minute motivation

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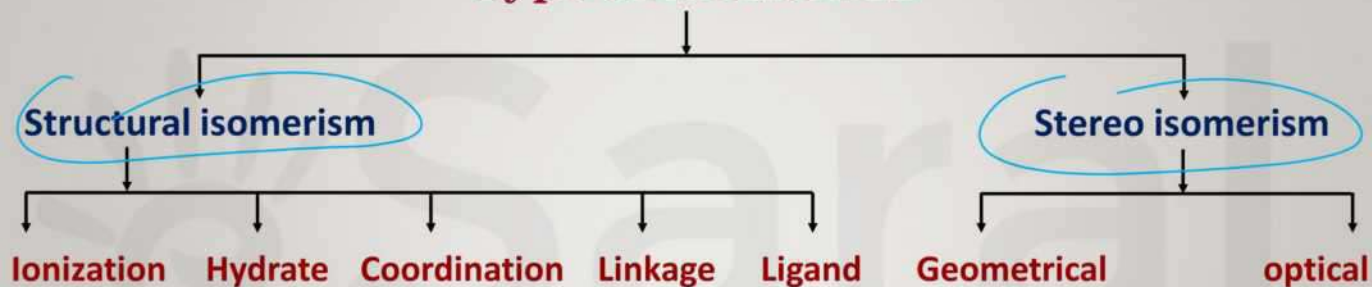


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Classification of Isomerism



Type of isomerism



(A) Structural Isomerism



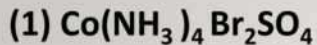
It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.





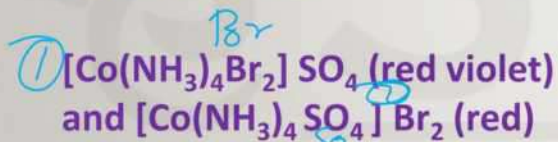
(a) Ionisation isomerism

Q) Find the ionisation isomers of the following



Sol.

$\text{Co}(\text{NH}_3)_4\text{Br}_2\text{SO}_4$ can be represented as:-



These complexes give sulphate ion and bromide ion respectively





(b) Hydrate isomerism

Q) Find the hydrate/solvate isomers of $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$ Compound.

Sol. $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$ has four possible structures

(i) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ violet

(ii) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ green

(iii) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ dark green

(iv) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ dark green

Water of
hydration



(c) Linkage isomerism

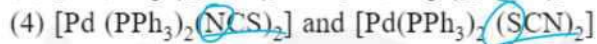
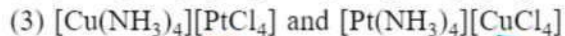
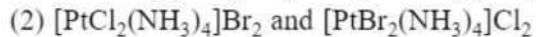
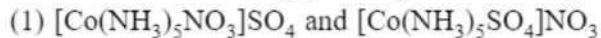


(i) This type of isomerism arises due to presence of ambidentate ligands like NO_2^- , CN^- and SCN^-



1. Which of the following pairs represents linkage isomers ?

[AIEEE – 2009]



+4



Sol. 4



(d) Coordination isomerism

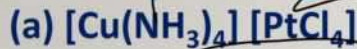


- (i) This type of isomerism is exhibited when the complex has two complex ions in it - **'Cationic and anionic'**.



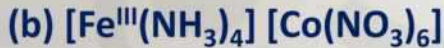
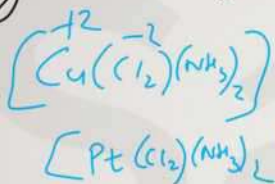


Q) Find total number of Coordination isomers of the following



Neutral

Ans. 4



Ans. 6

Total cases - 1



(e) Ligand isomerism



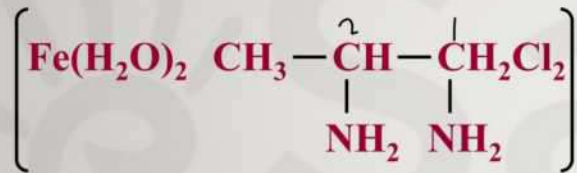
It is arising due to possible isomerism within a particular ligand.



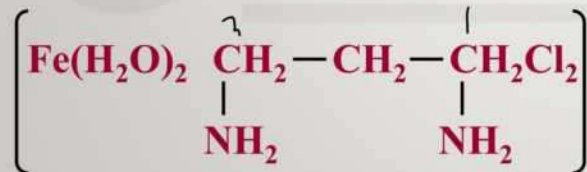
Q) Find the ligand isomers of $[\text{Fe}(\text{H}_2\text{O})_2 \text{C}_3\text{H}_6(\text{NH}_2)_2\text{Cl}_2]$



Sol. It has two different ligand structures



and



(f) Co-ordination Position Isomerisation



It is shown by polynuclear complexes, due to interchange of ligands between the different metal nuclei.



(B) Stereo Isomerism



They have **same molecular formula**, **same constitution**, they differ only with respect to the **spatial orientation of ligands** in space around the metal ion.



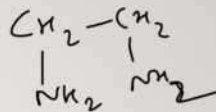
(a) Geometrical Isomerism



(i) The ligands occupy different positions around the central metal ion.



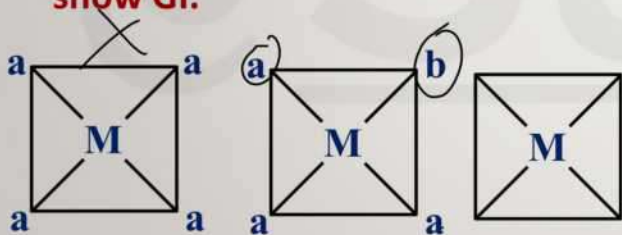
Geometrical isomers with coordination number = 4 (Square planar complexes)



AA

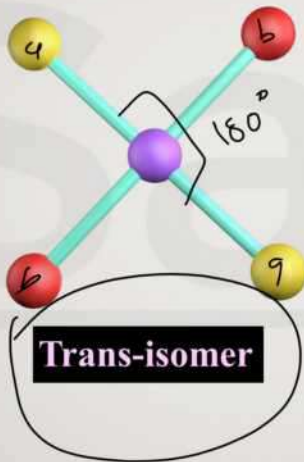
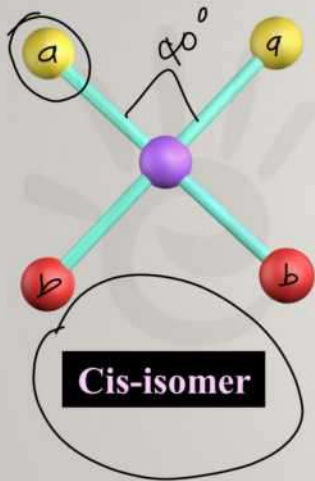
a, b → monodentate

(i) ~~Ma_4 , Ma_3b~~ , $\text{M}(\text{AA})_2$, $\text{M}(\text{AA})\text{a}_2$, $\text{M}(\text{AA})\text{ab}$, $\text{M}(\text{AB})\text{a}_2$, $\text{M}(\text{AA})(\text{AB})$, $\text{M}(\text{AA})(\text{BB})$ can't show GI.

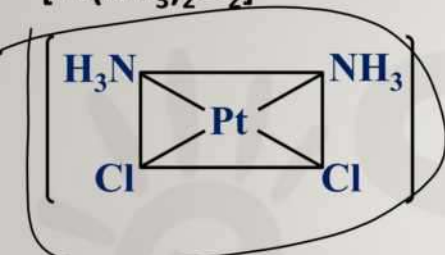




(i) Complexes with general formula, Ma_2b_2
(where both a and b are monodentate)
can have Cis-and trans isomers.



Complex Ma_2b_2



Cis(Cis-platin) anti cancer

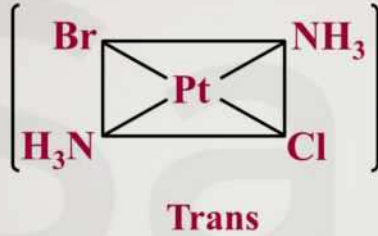
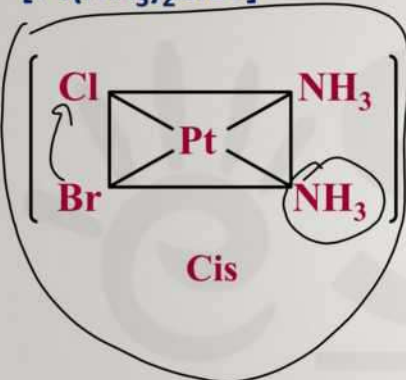
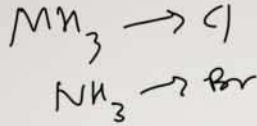
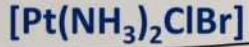


Trans

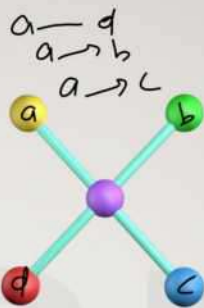
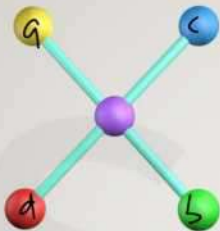
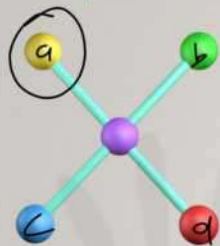




Complex Ma_2bc



Complex Mabcd



3





10. The complex ion

$[\text{Pt}(\text{NO}_2)(\text{Py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$ will give :-

[J-MAIN-2012, Online]

- (1) 4 isomers (Geometrical) (2) 2 isomers (Geometrical)
(3) 3 isomers (Geometrical) (4) 6 isomers (Geometrical)

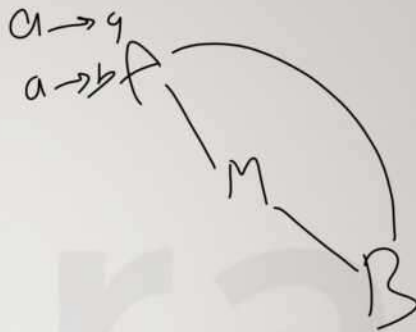
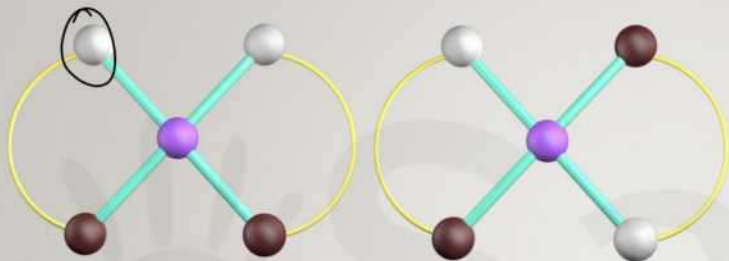
Mabcd

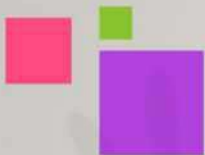
Sol. 3

eSaral



$M(AB)_2$

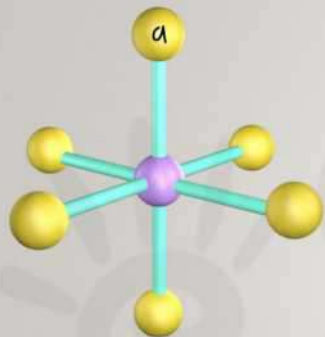




Stereoisomerism In Octahedral Complexes



M_a_6



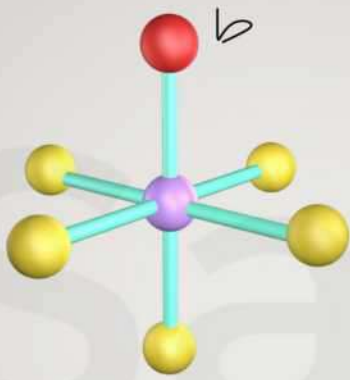
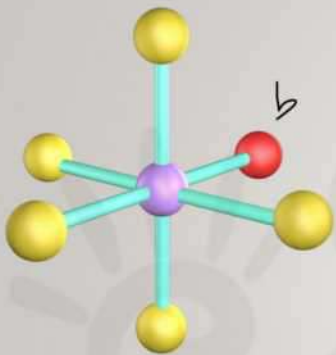
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Ma_5b

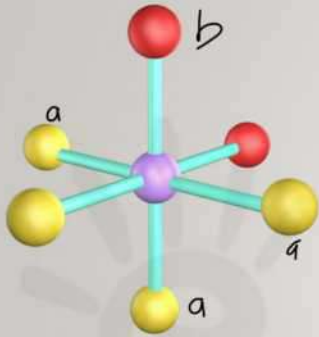


no isomerism





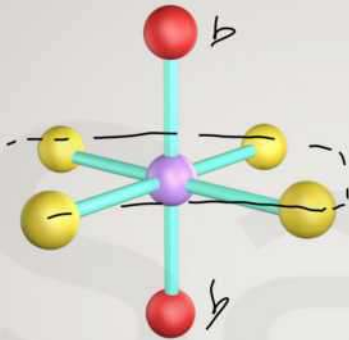
Ma_4b_2



For Octahedral
2 isomers

2 same species
in trans position

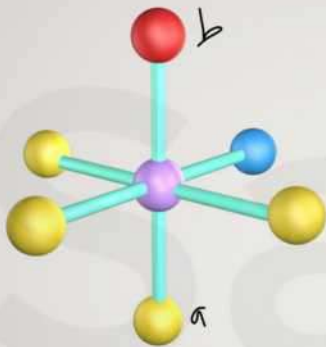
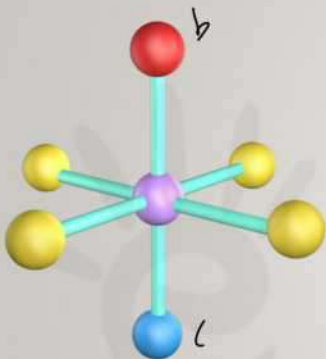
no OI

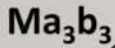


Ma_4bc

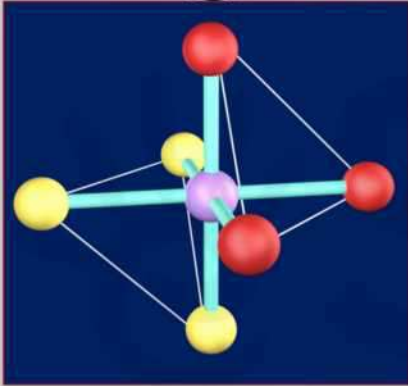


2 ISOMERS

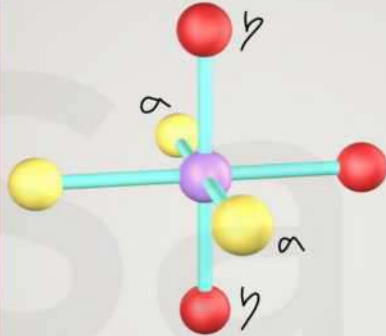




fac

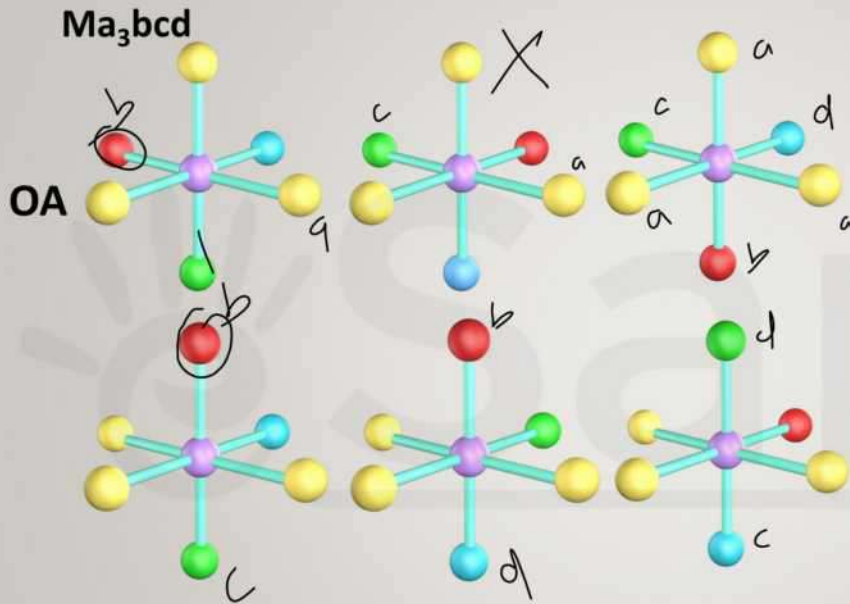


mer



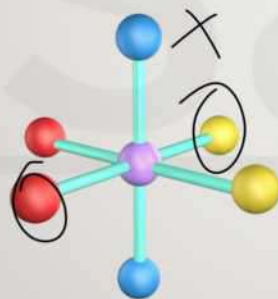
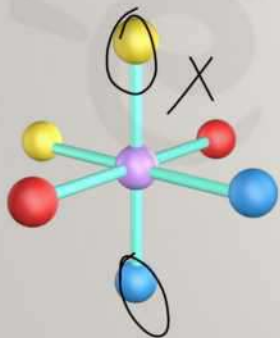
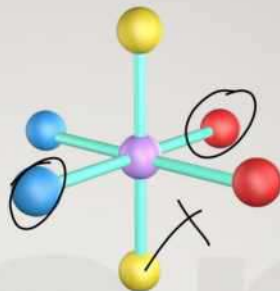
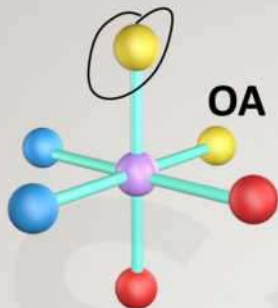
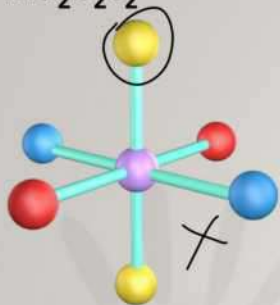
2 Isomers



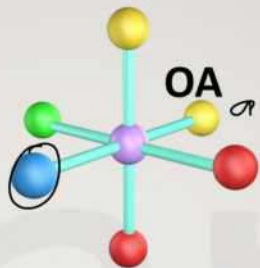
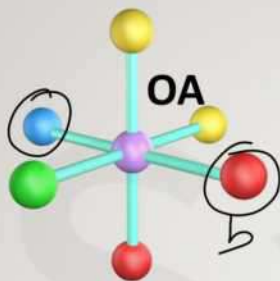
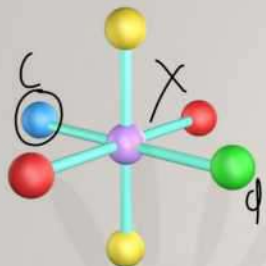




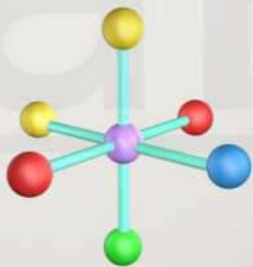
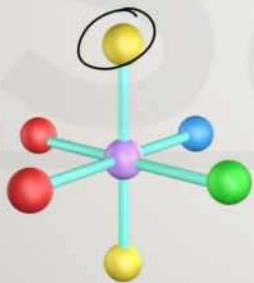
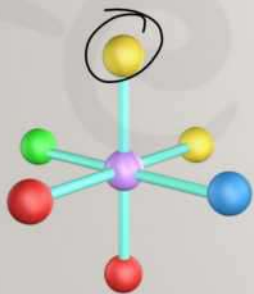
$Ma_2b_2c_2$



Ma_2b_2cd



EP
2

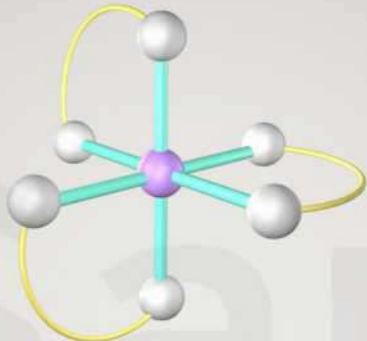
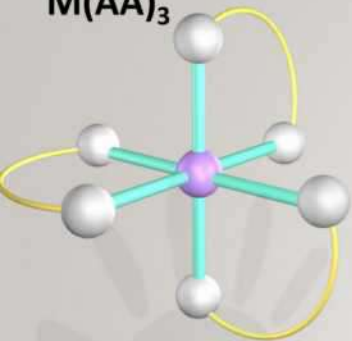




General formula	GI	Pairs of Enantiomers	Total
Ma_6	1	0	1
Ma_5b	1	0	1
Ma_4b_2	2	0	2
Ma_4bc	2	0	2
Ma_3b_3	2	0	2
Ma_3b_2c	3	0	3
Ma_3bcd	4	1	5
$Ma_2b_2c_2$	5	1	6
Ma_2b_2cd	6	2	8
Ma_2bcde	9	6	15
$Mabcdef$	15	15	30



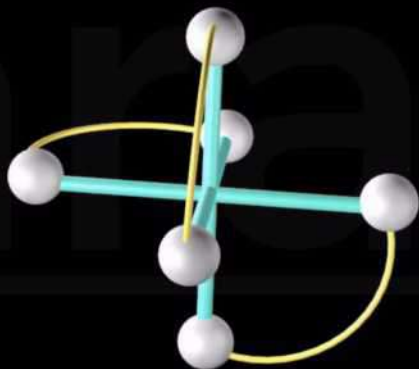
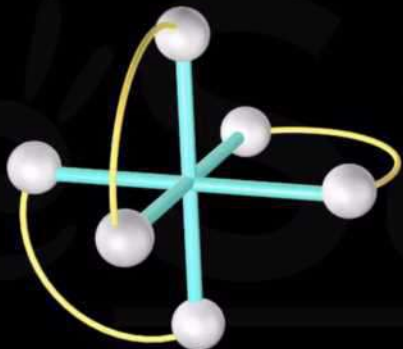
$M(AA)_3$



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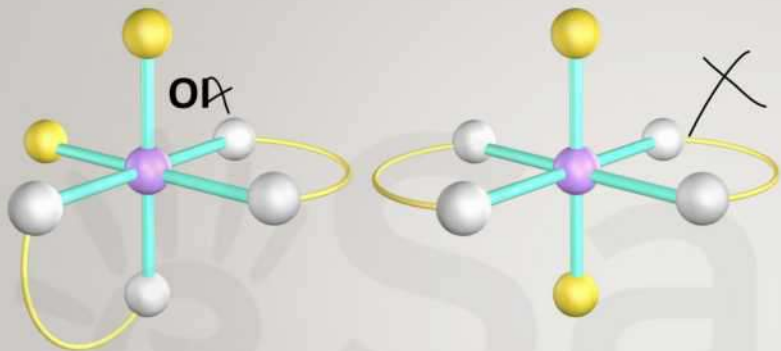


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$M(AA)_2a_2$

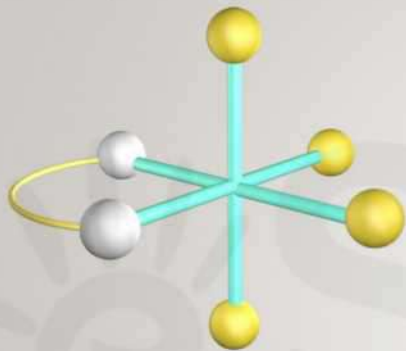


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$M(AA)a_4$

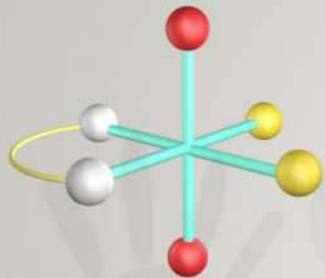


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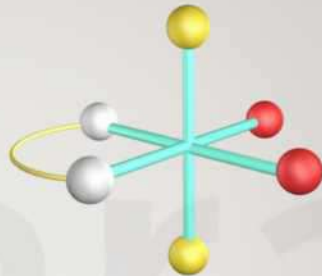
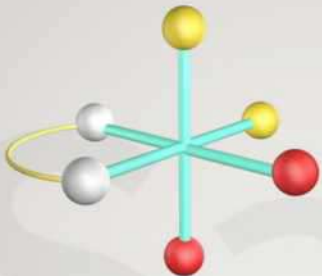


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$M(AA)_2b_2$



OA



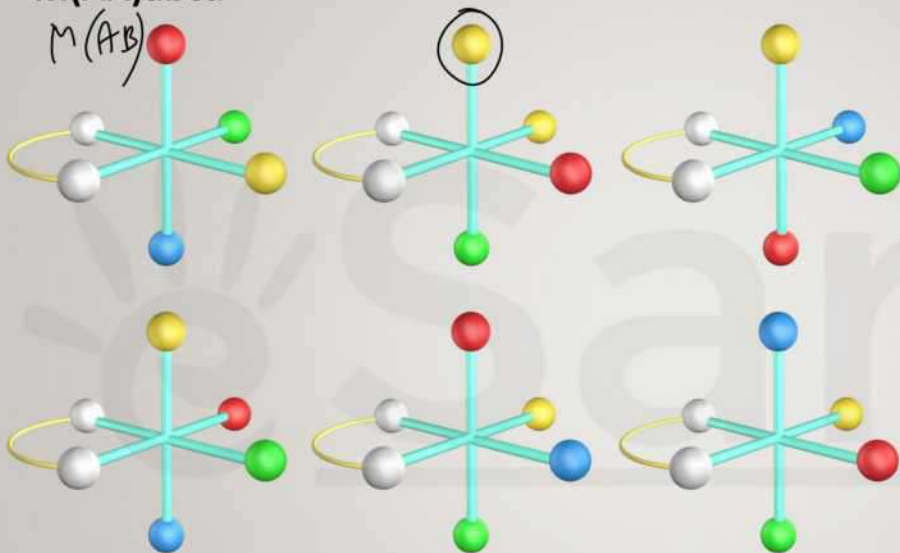
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$M(AA)abcd$

$M(AB)$



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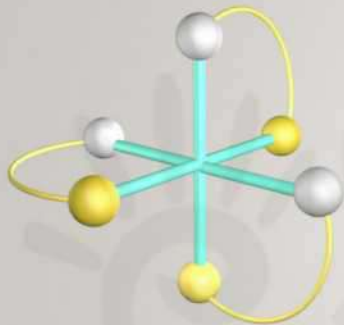


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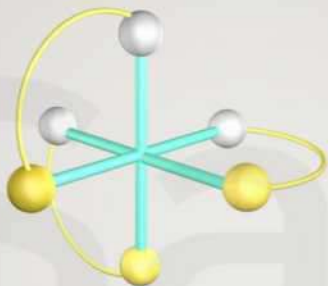
$M(AB)_3$



OA



OA



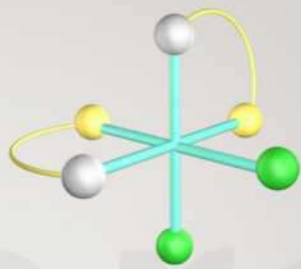
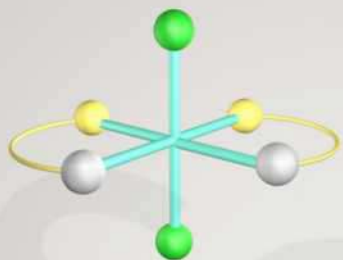
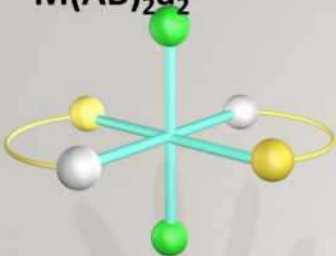
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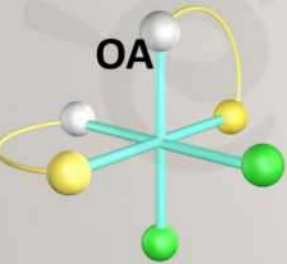


$M(AB)_2a_2$

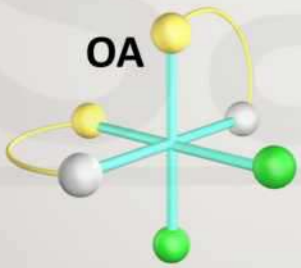


OA

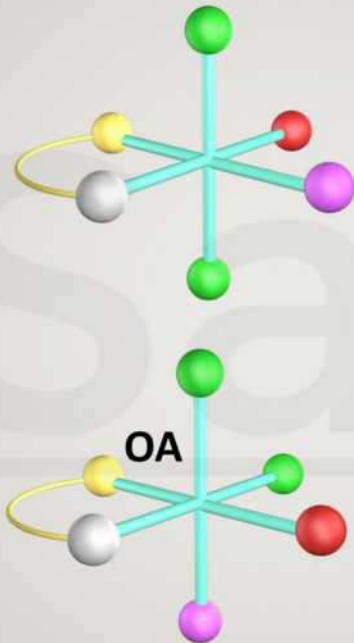
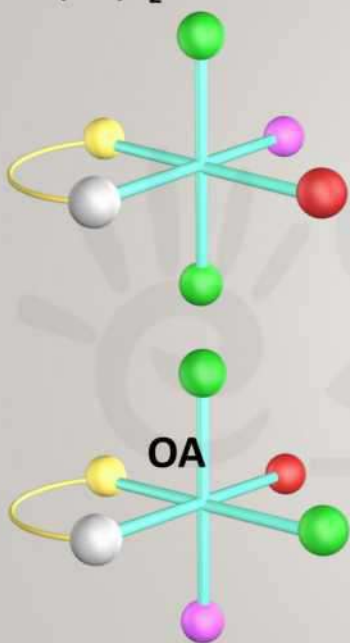
OA



OA



$M(AB)a_2bc$

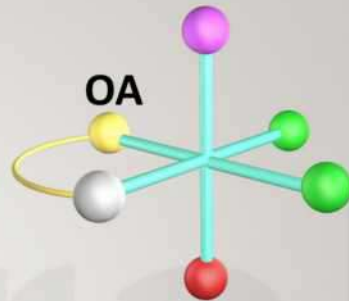
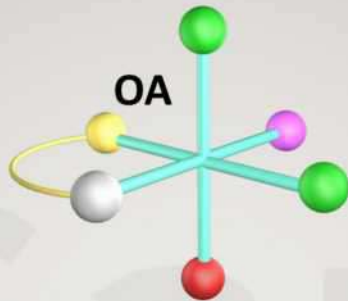
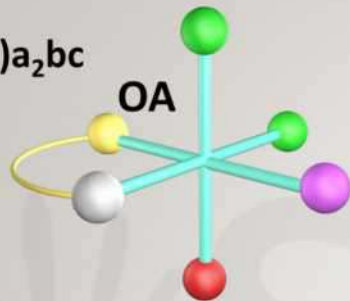


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$M(AB)_2bc$



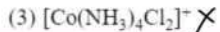
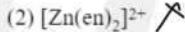
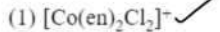
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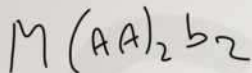
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11. Which of the following complex ions will exhibit optical isomerism?

(en = 1, 2-diamine ethane)



man b₂





WORK HARDER

1 minute motivation

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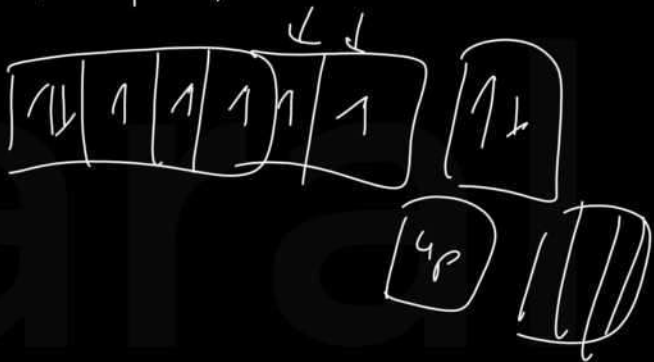
Valence Bond Theory

(a) The metal ion under the influence of ligands can use its vacant $d(n-1)$, ns , np , nd orbitals for hybridisation.

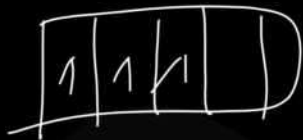
In the formation of $[\text{Fe}(\text{NH}_3)_6]^{3+}$, Fe^{3+} ion provides six vacant orbitals.

In $[\text{Cu}(\text{NH}_3)_4]^{2+}$, Cu^{2+} ion provides four vacant orbitals.

$4s, 4p, 2(4d)$



Points To Remember In VBT

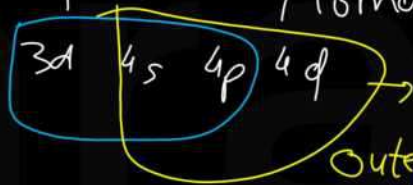


high spin

low spin

inner orbital complex

Magnetic Moment



outer orbital complex

(i) In octahedral complexes with CM having d^0 , d^1 , d^2 , d^3 configuration, pairing of e^- don't take place, no matter what the ligand is.

And all such complexes are inner orbital complexes with

$$\mu = 0, \sqrt{3}, \sqrt{8}, \sqrt{15}$$

respectively (d^2sp^3 configuration)

d^0 Diamagnetic

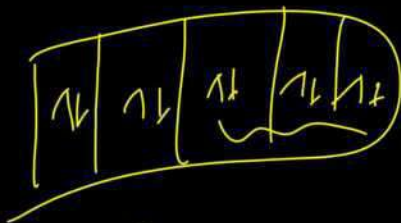
d^1, d^2, d^3 Paramagnetic

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4s 4p 4d



d^8

(ii) In octahedral complexes with CM having d^8, d^9, d^{10} configuration pairing of e^- doesn't take place, whatever be the ligand, and all such complexes are outer orbital complex (sp^3d^2) with $\mu = \sqrt{8}, \sqrt{3}, 0$ BM respectively.

$d^2 sp^3$

(iv) All the octahedral complex of Co^{3+} are inner orbital complexes ($d^2 sp^3$) irrespective of nature of ligands and all such complex are diamagnetic except $[CoF_6]^{3-}$ and $[Co(H_2O)_3F_3]$ are outer orbital complex, $sp^3 d^2$, $\mu = \sqrt{24}$ BM

(v) All the above points are written considering that ligand is not paramagnetic. (important)

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Example



is paramagnetic due to paramagnetic nature of O_2^- (superoxido)



$\phi \rightarrow$ poor shielding

(vi) In all the octahedral complexes of 4d and 5d series metal ions with configuration d^4 , d^5 , d^6 and d^7 , pairing of e^- takes place whatever may be the ligand.

Q) For $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ (Brown ring complex), μ

$= \sqrt{15}$ B.M. Select the correct statement(s)

NO⁺

Learn

(A) oxidation state of Fe is +1

(B) geometry is octahedral

(C) hybridisation of Fe is sp^3d^2

(D) NO is neutral ligand

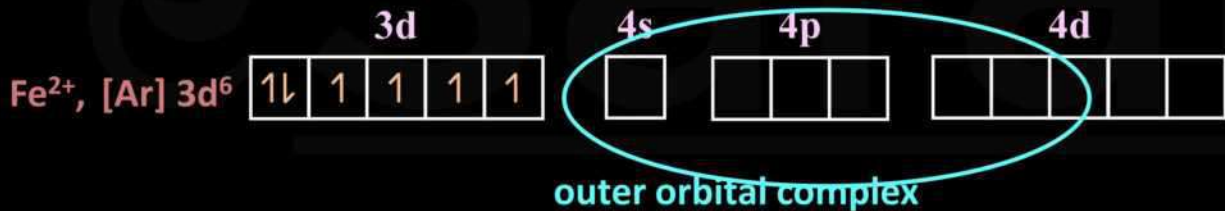
Ans. A, B, C

Q) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is paramagnetic while $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic.

VBTX

$d^4 - d^7$
Ligand strength

Sol. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ involves sp^3d^2 hybridization.



Crystal Field Theory

The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate.

This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion.

Most important

Average energy of 'd' orbitals in spherical crystal field



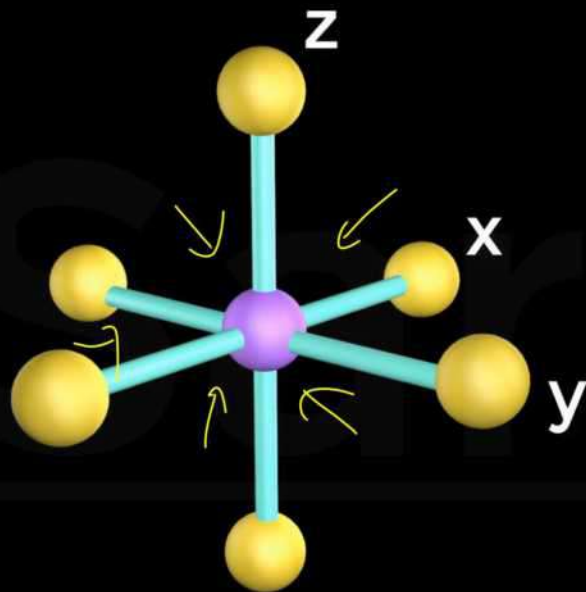
Five degenerate d-orbitals on the free central metal cation



However, when this negative field is due to ligands in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost.

It results in splitting of the d orbitals.



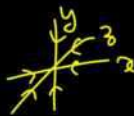


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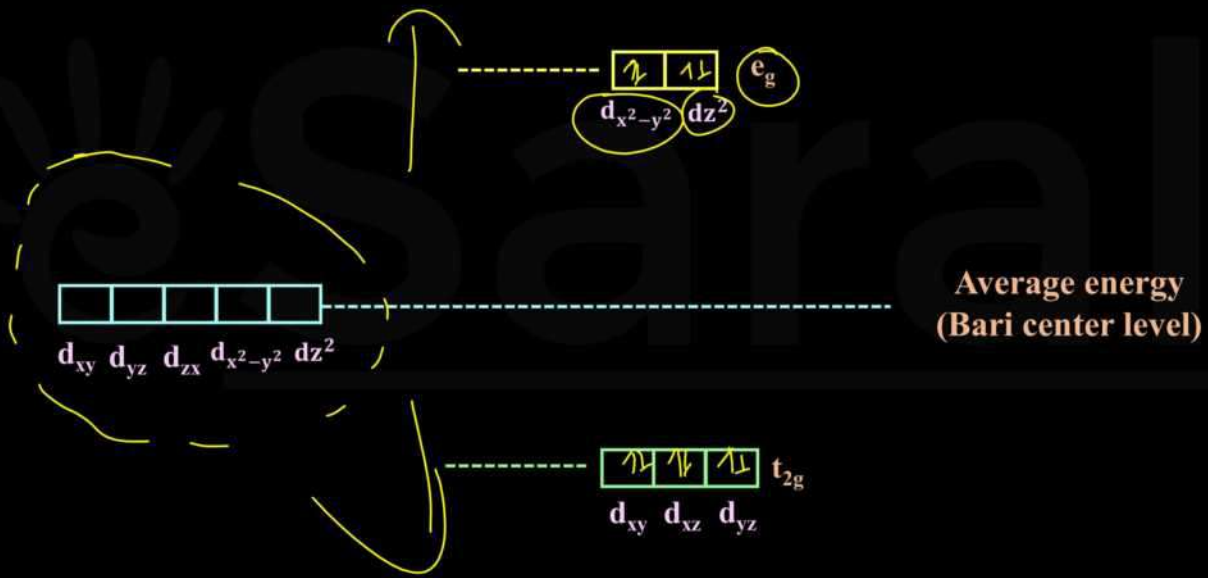


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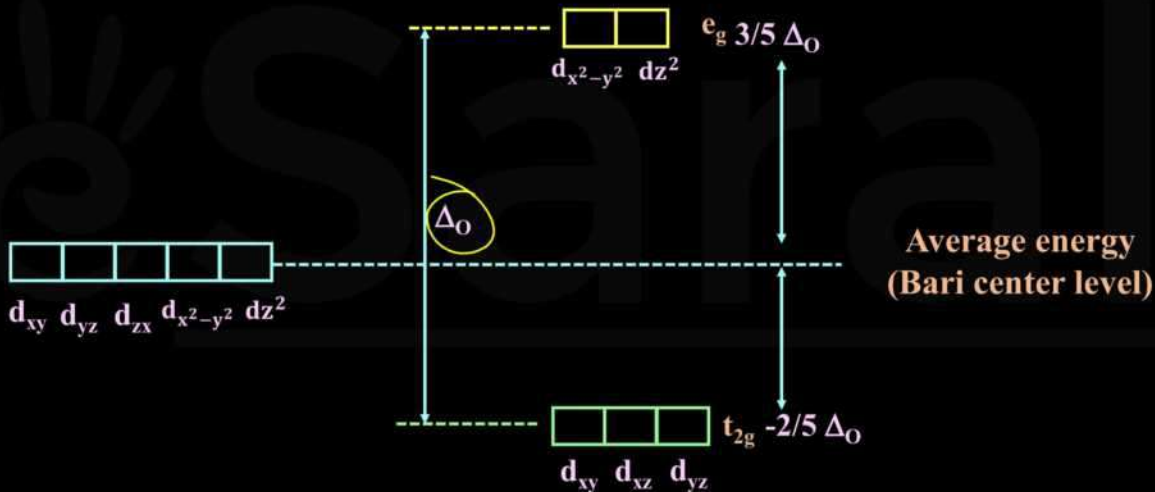
Crystal field splitting for octahedral complex



$d^4 - d^7$



Crystal field splitting for octahedral complex

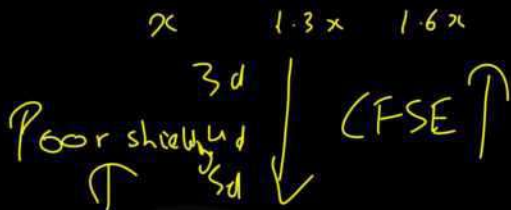


CFSE depends upon the following factors

+ve charge \uparrow
CFSE \uparrow

- 1. Higher the charge on the metal ion higher will be CFSE.**





2. It depends upon the nature of metal ion, that is the metal ion is of which transition series.

It has been observed that as we go down from first transition state to second to third CFSE increases by 30% at each step.



LS ↑ Δo ↑



3. It depends upon the nature of ligand.

Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals.



CFSE depends upon the following factors

- 1. Higher the charge on the metal ion higher will be CFSE.**



2. It depends upon the nature of metal ion, that is the metal ion is of which transition series.

It has been observed that as we go down from first transition state to second to third CFSE increases by 30% at each step.



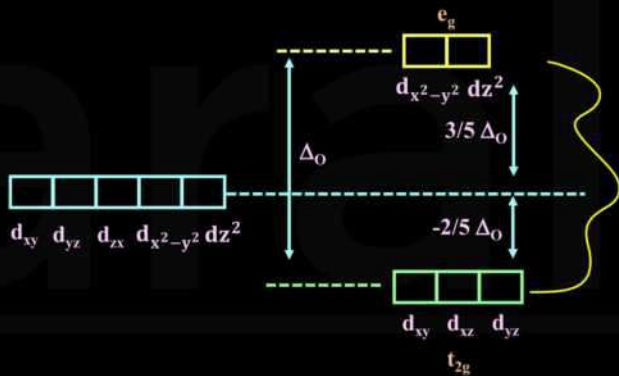
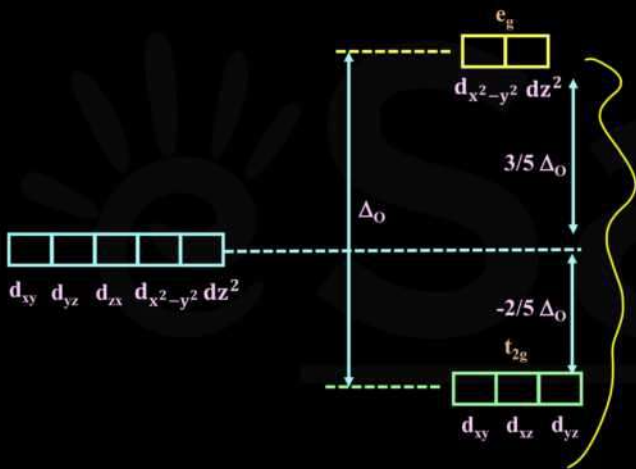
3. It depends upon the nature of ligand.

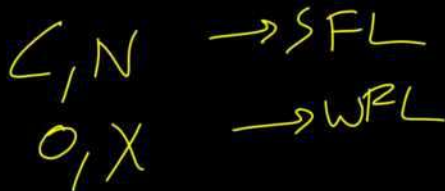
Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals.



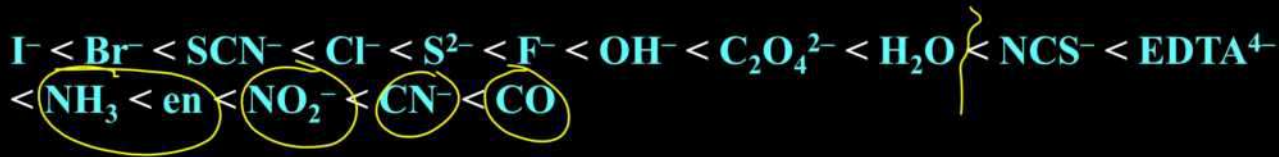
SFL

WFL





In general, ligands can be arranged in a series in the order of increasing field strength as given below



3. It depends upon geometry.

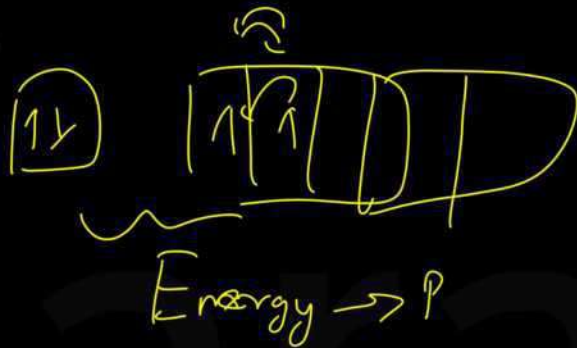
$$\Delta_{sp} > \Delta_o > \Delta_t$$

$$\Delta_{sp} > 1.3\Delta_o$$

$$\Delta_t > 4/9\Delta_o$$



Mean pairing energy (P)



It is the energy required for electron pairing in a single orbital. And it is defined per pair.

The two possibilities are-

- (i) If $\Delta_o < P$, the fourth electron enters in one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.
- (ii) Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.



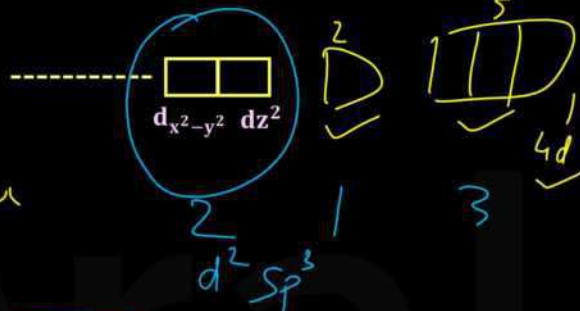
SFL Pairing ✓
WFL " X

(ii) If $\Delta_o > P$, it becomes energetically more favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$.

Ligands which produce this effect are known as strong field ligands and form low spin complexes.

SFL $\rightarrow d^2 sp^3$
 WFL $\rightarrow sp^3 d^2$

Outer orbital complex



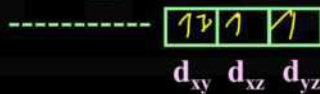
d^4, d^5, d^6, d^7

WFL \rightarrow ~~$d^2 sp^3$~~ $sp^3 d^2$

SFL \rightarrow ~~$sp^3 d^2$~~ $d^2 sp^3$

Inner orbital complex

d^7 will shift its 7th e- to the higher energy level



WFL + SFL

Can't be predicted unless the relationship b/w Δ_o & P is directly or indirectly given.

Q) $[\text{Co}(\text{NH}_3)_6]^{2+}$ & $[\text{Co}(\text{NO}_2)_6]^{4-}$ are very much prone towards oxidation. Explain.

+7 +7 SFL $\frac{1 \uparrow 1 \uparrow}{3d}$ \curvearrowright 4d

$\left. \begin{matrix} \text{NH}_3 \\ \text{NO}_2 \end{matrix} \right\}$ SFL | Can shift an e^- to the higher energetic level



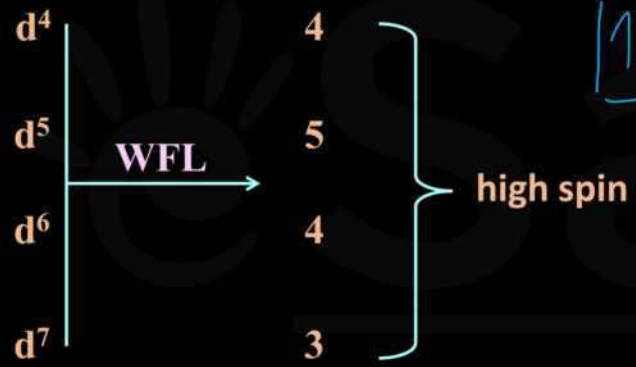


Since the last e^- is already in the higher energy status. Room temp or visible light is sufficient to remove it oxidation.



WFL \rightarrow high spin 

No. of up e



	No. of upe	
d^4	2	} Low Spin
d^5	1	
d^6	0	
d^7	1	

SFL



Crystal Field Stabilising Energy In Octahedral Field (CFSE)

not important

Formula

$$\text{CFSE} = [-0.4 (n) t_{2g} + 0.6 (n') e_g] \Delta_0 + *mP.$$

where n & n' are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex $*m$ represents the number of electron pairs formed.

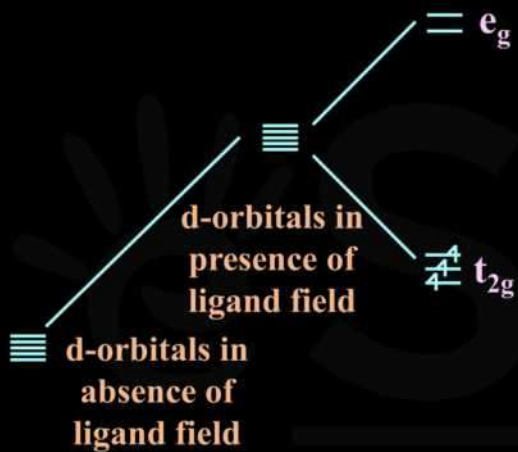


Q) For each of the following complexes, draw a crystal field energy-level diagram, assign the electrons to orbitals, and predict the number of unpaired electrons



Ans. F^- is weak field ligand. Cr^{3+} , $3d^3$





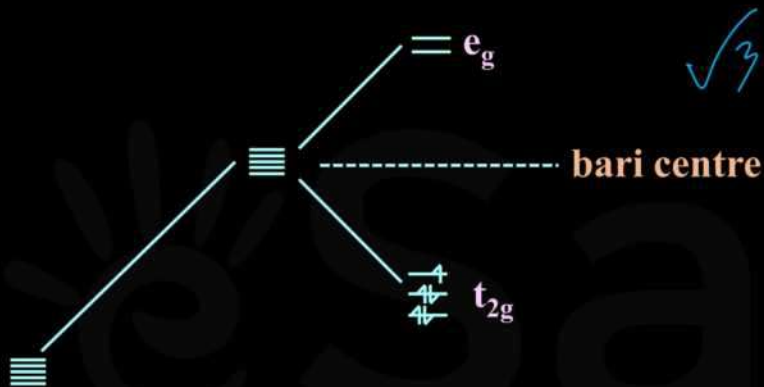
3 unpaired
 $\sqrt{15}$

So number of unpaired electrons = 3



Ans. CN^- is strong field ligand. Fe^{3+} , $3d^5$





So number of unpaired electron = 1.

Q) $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$ has a magnetic moment of 3.83 B.M. The correct distribution of 3d electrons in Chromium is?

- (A) $3d_{xy}^1, 3d_{yz}^1, 3d_{z^2}^1$ (B) $(3d_{x^2-y^2})^1, 3d_{z^2}^1, 3d_{xz}^1$
- (C) $3d_{xz}^1 (3d_{x^2-y^2})^1, 3d_{yz}^1$ (D) $3d_{xy}^1, 3d_{yz}^1, 3d_{xz}^1$

Ans. (D)

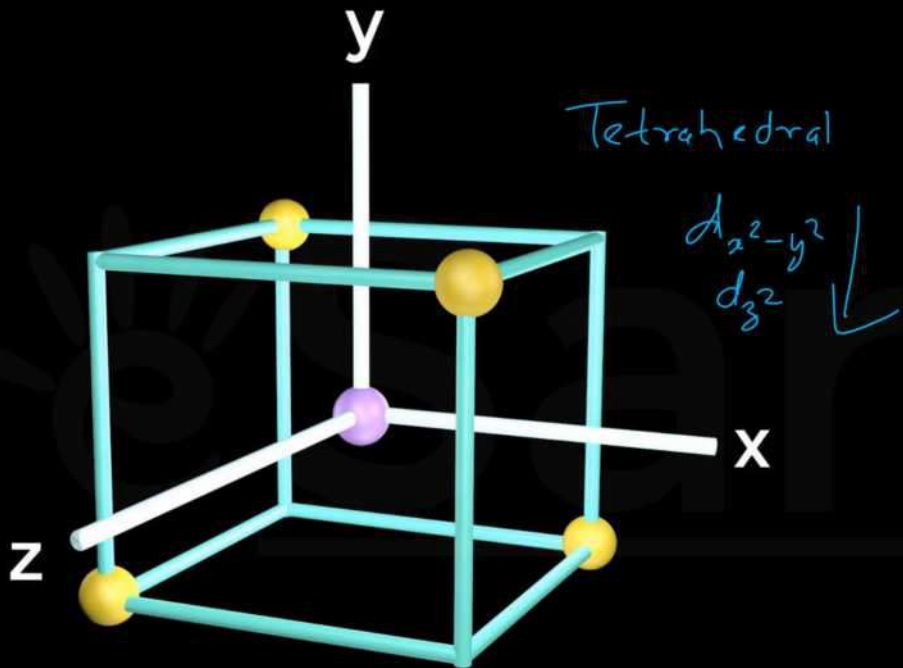


Crystal Field Splitting In Tetrahedral Coordination Entities

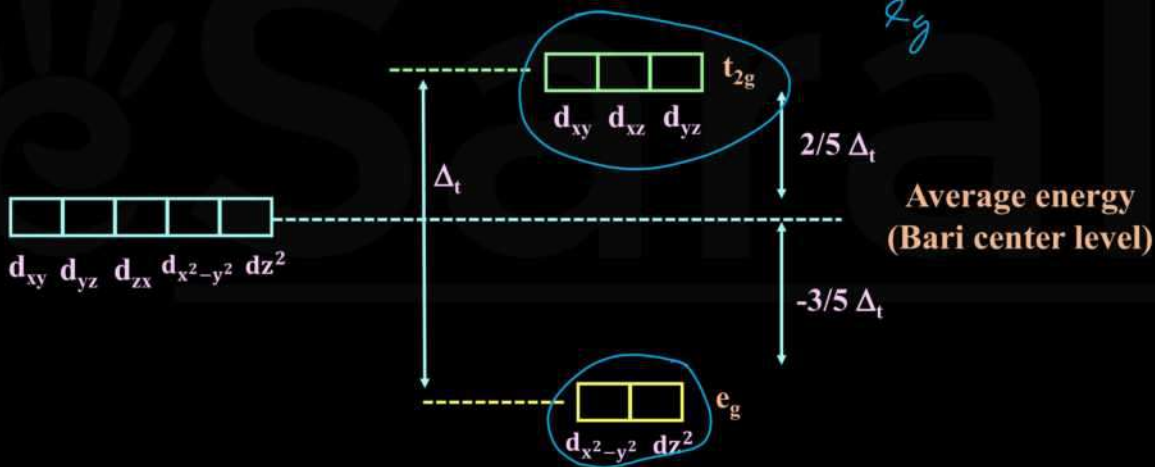
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Crystal field splitting for tetrahedral complex

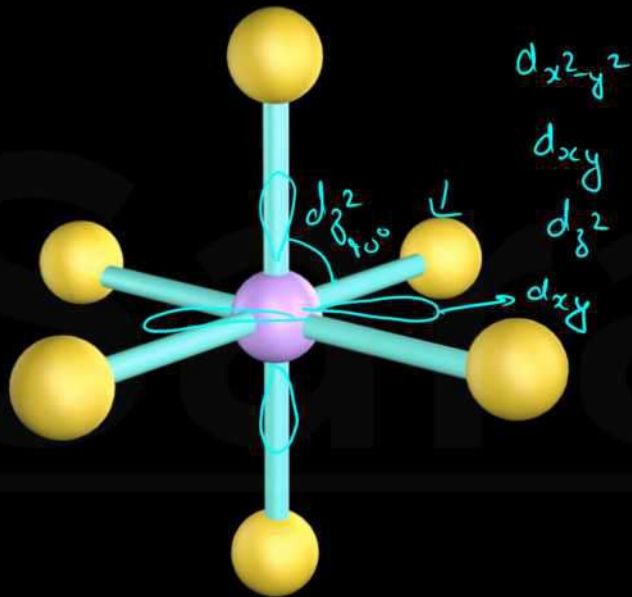


Crystal Field Splitting in Square Planar Coordination Entities

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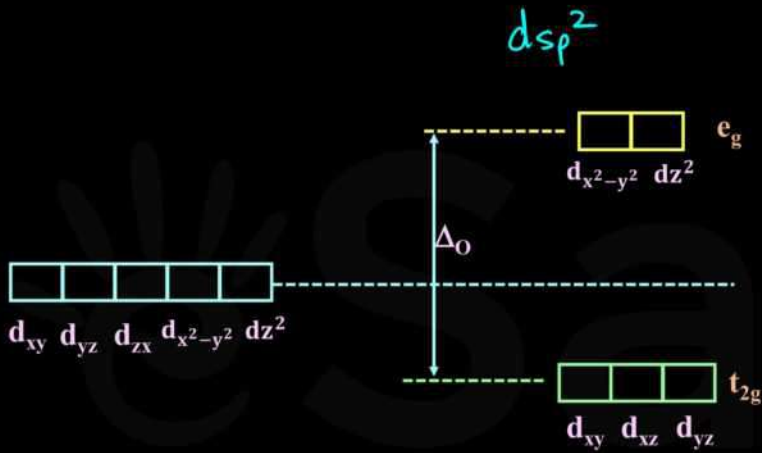


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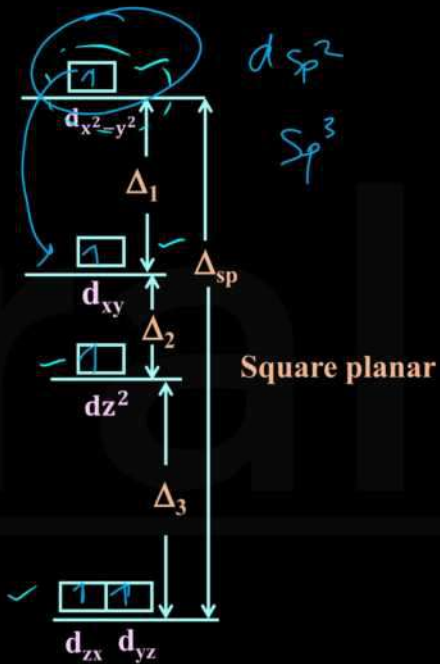


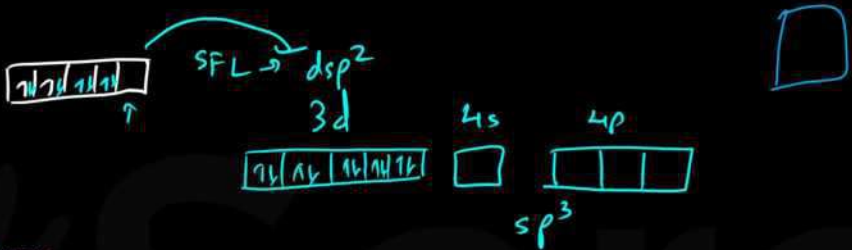
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Crystal field splitting for square planar complex



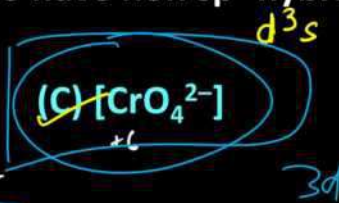
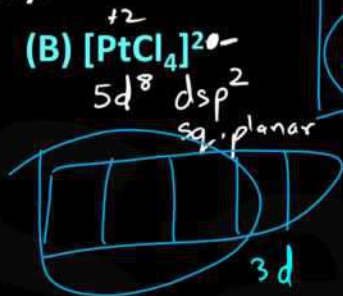
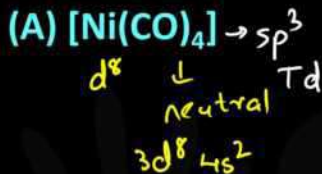
$\Delta_{sp} > \Delta_0$





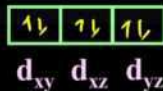
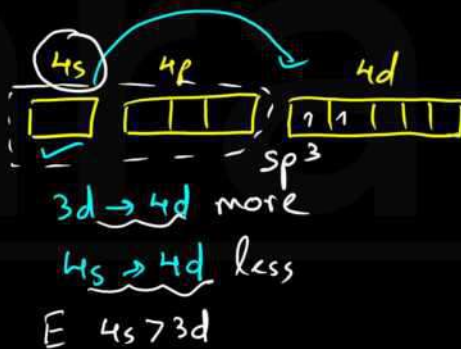
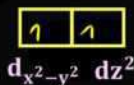
CN = 4
 WFL → **sp^3 (outer orbital complex)**
 SFL → **dsp^2 (inner orbital complex)**
Not valid for d^{10}

Q) Which of the following are expected to have non sp^3 hybridisation but tetrahedral geometry?



Sol. Since this is a d^0 system.

Ans. (C)



Q) The magnetic moments of following, arranged in increasing order will be
(atomic number of Co = 27) *Revsion*

(1) Co^{3+} (octahedral complex with a strong field ligand) $d^6 \rightarrow 0 \text{ upe}$ *LS*

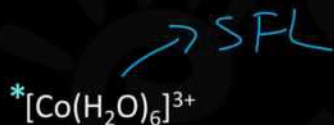
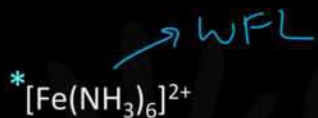
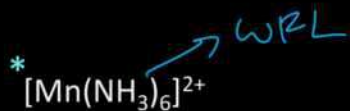
(2) Co^{3+} (octahedral complex with a weak field ligand, F^-) $d^6 \rightarrow 4 \text{ upe}$ *HS*

(3) Co^{2+} (tetrahedral complex) $d^7 \rightarrow 3 \text{ upe}$ *WFL*

(4) Co^{2+} (square planar complex) 2 upe *SFL*

(A) $1 > 2 > 3 > 4$ (B) $2 > 3 > 4 > 1$ (C) $3 > 2 > 4 > 1$ (D) $2 > 4 > 3 > 1$

Ans is B



Q) The magnetic moment of $[\text{NiCl}_4]^{2-}$ is?

d^8

(A) ~~2.82~~ BM

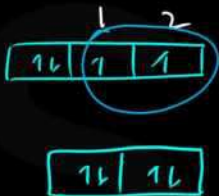
(B) 1.41 BM

(C) 1.82 BM

(D) 5.46 BM



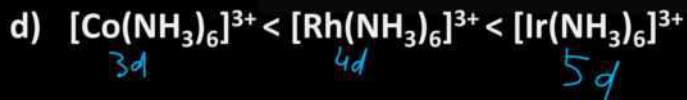
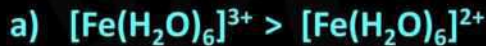
Ans A



(F) Factors Influencing the Magnitude of CFSE

1. Higher the CFSE value higher will be the stability of complex

+3

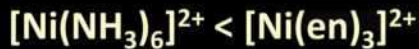


Stability Factors

Strong Ligand ↑
Stability



2. Chelated complexes are more stable than non-chelated complexes given the donor atoms are same

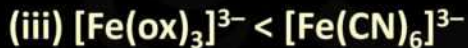


no of rings \uparrow stability \uparrow



2 rings

3 rings



3. Same charges on the cation but the number of d-electrons is different

The magnitude of CFSE increases with the increase of the number of d-electrons.



e.g., $[\text{Co}(\text{H}_2\text{O})_6]^{2+} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+}$





Colour In Coordination Compounds

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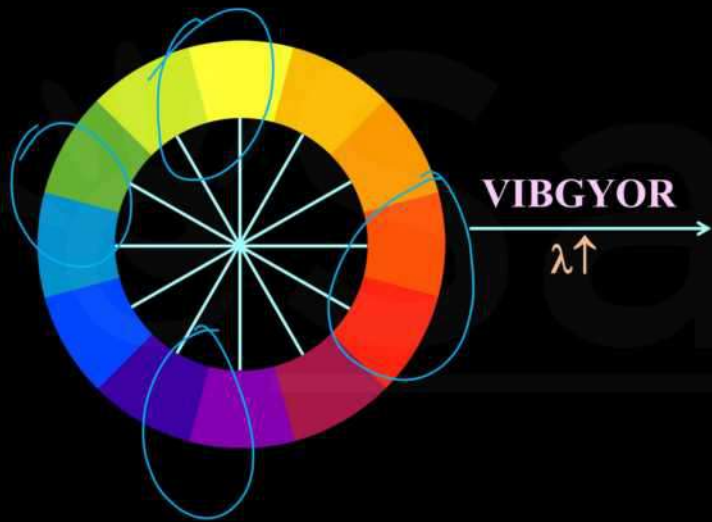
According to the crystal field theory
the colour of coordination compound
is due to **d-d transition of electron**

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Colour wheel

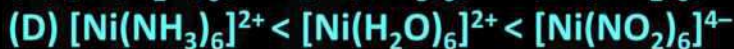
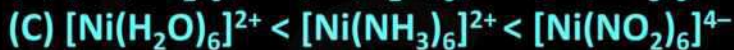
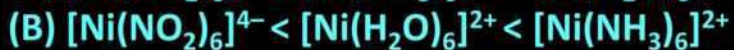


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Q) The correct order for the wavelength of absorption in the visible region is



$\lambda \propto \frac{1}{E}$
CFSE

$$E = \frac{hc}{\lambda}$$

$$E = h\nu$$

Ans. (A)



The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1 , L_2 , L_3 and L_4 absorb wavelength in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is: [J-MAIN-2014]

(1) $L_3 < L_2 < L_4 < L_1$

(2) $L_1 < L_2 < L_4 < L_3$

(3) $L_4 < L_3 < L_2 < L_1$

(4) $L_1 < L_3 < L_2 < L_4$

VIBGYOR
→ $\lambda \uparrow$
EL

L_4, L_2, L_3, L_1

Ans. 4

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