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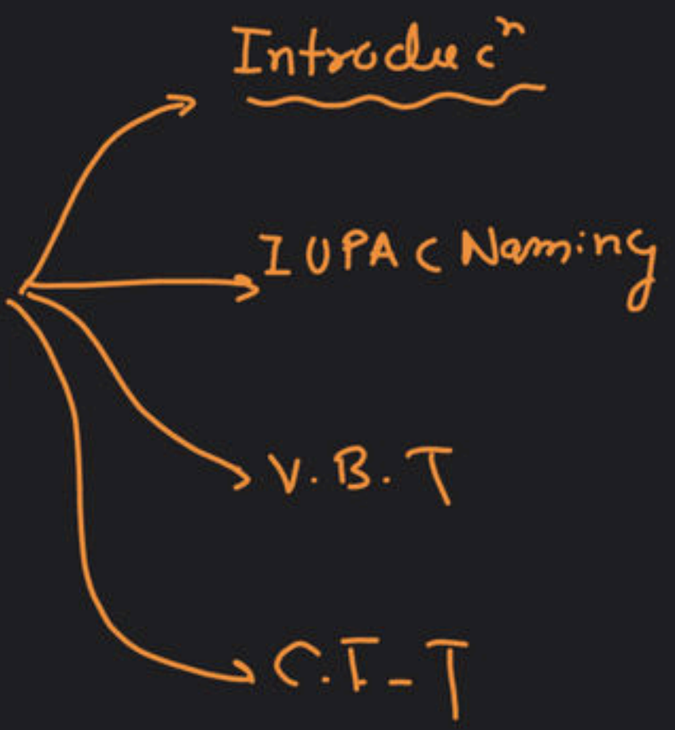
Coordination Compound 01

Chemistry Extra Class



Rahul Kumar Gupta • Lesson 2 • Feb 24, 2026

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Co-ordination compound

Addition Compounds

Double Salts

(3) $KCl + MgCl_2$

(3) Ex:- $KCl \cdot MgCl_2 \cdot 6H_2O$

- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
- $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$

Co-ordination compound

(3) $KCN + Fe(CN)_2$

- $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$ (1) complex ion
- $K_3[Fe(CN)_6]$
- $[Cu(NH_3)_4]SO_4$ etc.

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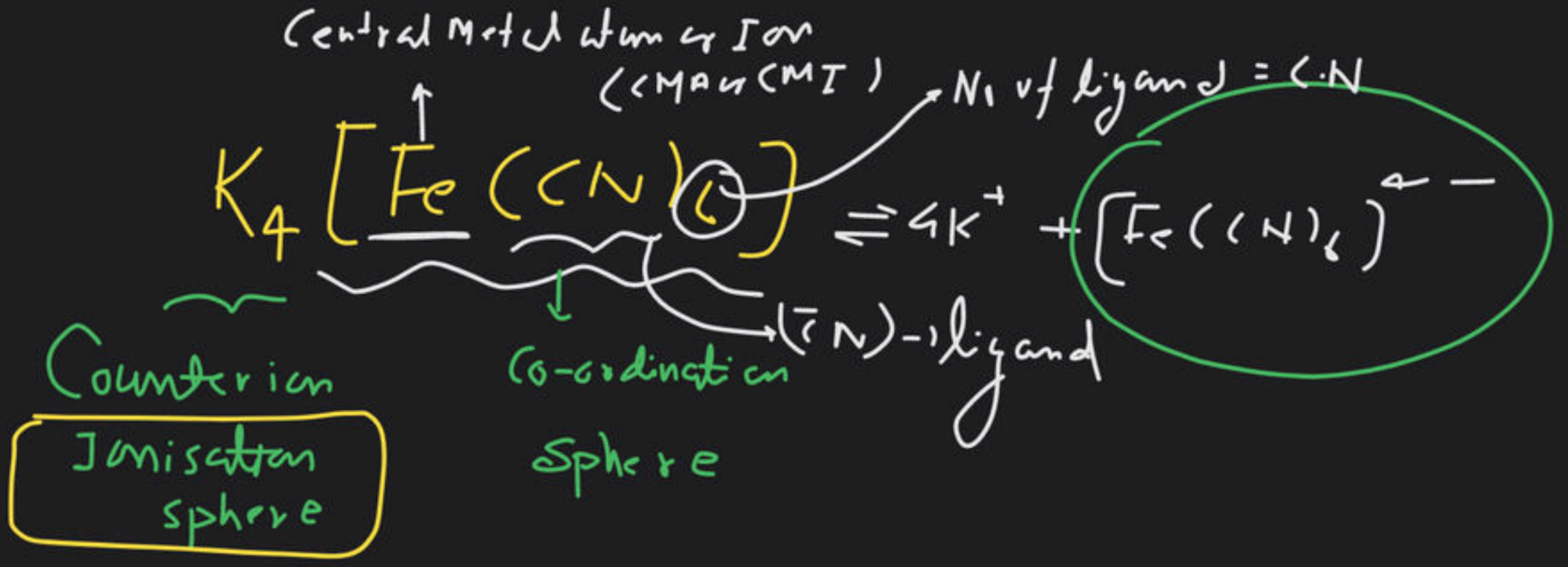
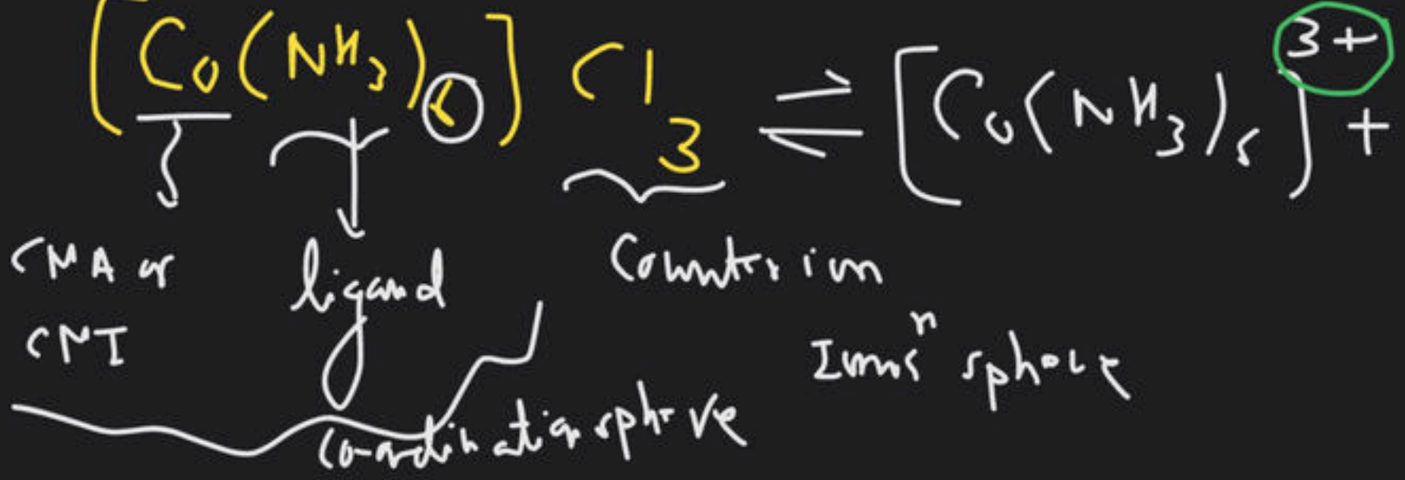

Central Metal atom or Ion
(CMA or CMI)
No of ligand = C.N
$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$
(CN)- ligand
Counterion
Co-ordination
Sphere
Ionisation sphere


$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$
CMA or CMI
ligand
Counterion
Co-ordination sphere
Ionisn sphere

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Classifi^{n} of Complex compound :-

(A) On the basis of charge on complex

Cationic Complex	Anionic complex	Neutral complex
$[Cu(NH_3)_4]^{+2}SO_4^{-2}$	$K_3[Fe(CN)_6]^{3-}$	$[Ni(CO)_4]$
$[Ni(H_2O)_6]^{+2}Cl_2$	$K_4[Fe(CN)_6]^{4-}$	$[Mn(CO)_5]$
		$[Co(NH_3)_3Cl_3]$

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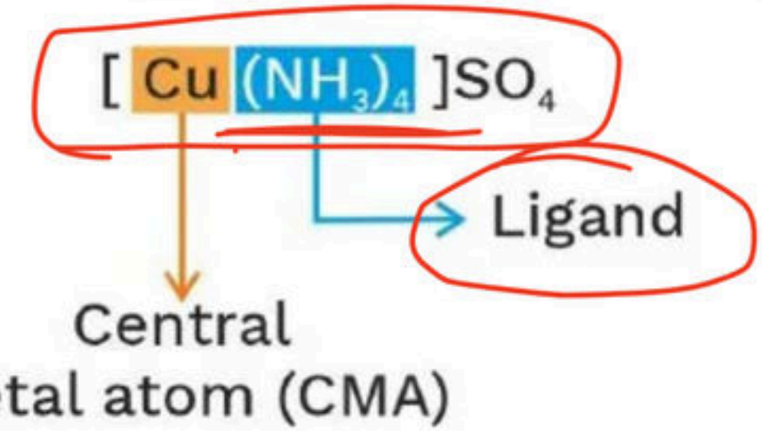
Classification of Complex Compound

1. **On basis of type of ligands**

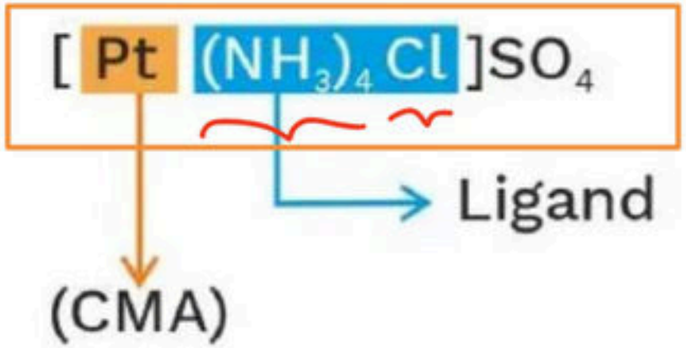
(i) **Homoleptic complex: -** Same type of ligands

Ex.



Heteroleptic

(ii) ~~Heteropoietic~~ **Complex: -** Different type of ligands



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2. On the basis of degree of dissociation

(i) Perfect complex compound : Relatively more stable and its aqueous solution doesn't give test of its all constitutive ions.

$$3KCN + CuCN \xrightarrow[\text{Solution}]{\text{Aqueous}} K_3[Cu(CN_4)] \xrightarrow[\text{Solution}]{\text{Aqueous}} 3K^+ + [Cu(CN_4)^{-3}]$$

Perfect Complex compound complexion

$[Cu^+]\,[S^{-2}] < Ksp$ No. ppt. $\xleftarrow[\text{gas}]{H_2S}$ $Cu^+ + 4CN^-$

less conc.

(ii) Imperfect complex compound: - Relatively less stable and its aqueous solution gives test of its all constitute ions.

$$2KCN + Cd(CN)_2 \longrightarrow K_2[Cd(CN)_4] \xrightarrow[\text{Solution}]{\text{Aqueous}} 2K^+ + [Cd(CN)_4]^{-2}$$ less stable

Imperfect complex compound — Complexion

More ionisation

$$Cds \xleftarrow[\text{gas}]{H_2S} Cd^{+2} + 4CN^-$$

yellow ppt

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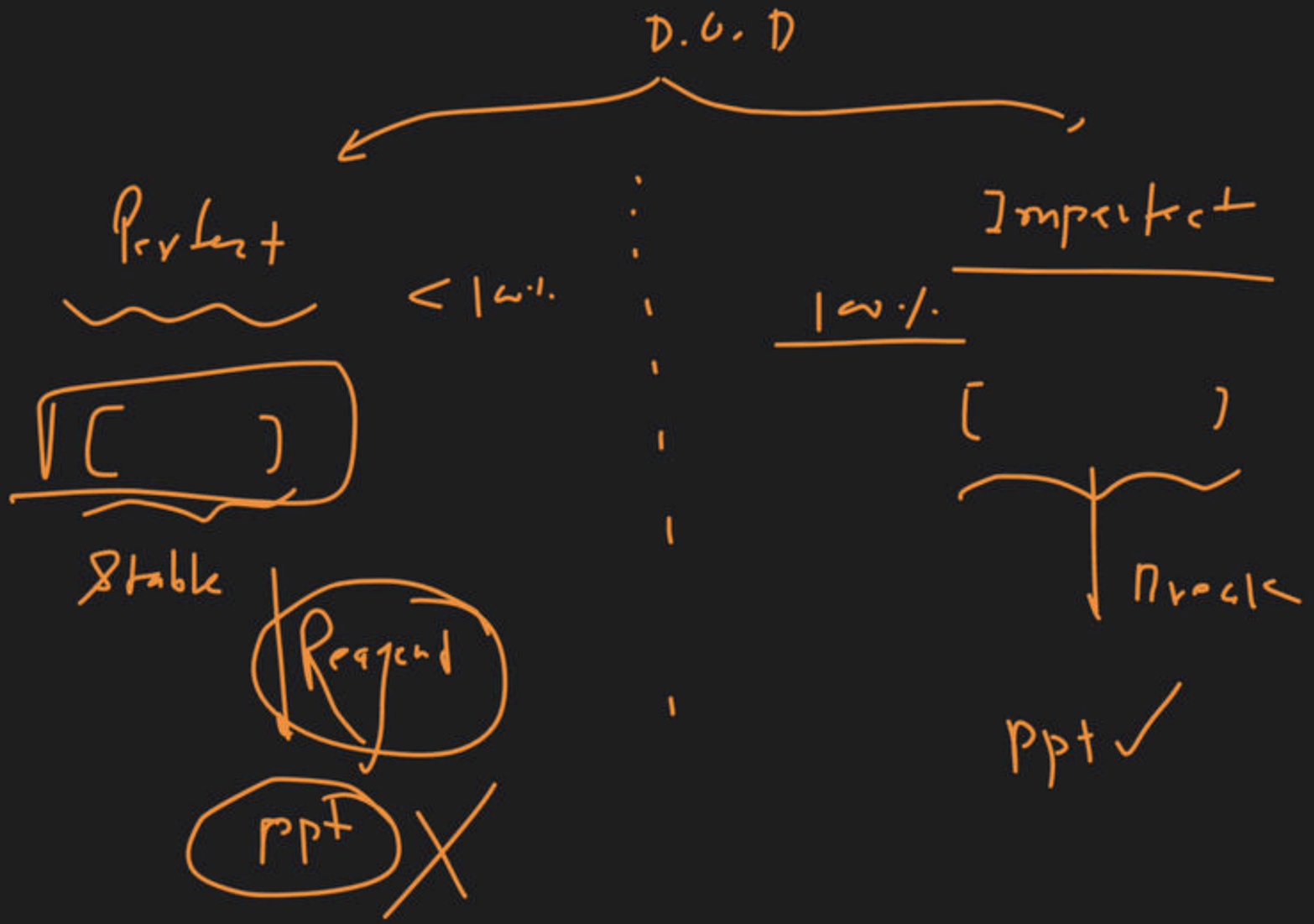
D.C.D
Perfect
<100%
Imperfect
100%
Stable
Regard
ppt
X
Oracle
ppt ✓

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- Imperfect complex compound which undergoes 100% ionisation is known as double salt.
- There is no sharp line between perfect and imperfect complex compound.
- Complex forming tendency decreases down a group in s-block because size increases.

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Representation of complex ion

Coordination sphere: –

$$[Mlx]^{\pm n}$$

↙

A/T alphabet order

Outside region: –

- Ionisation sphere
- Free ion
- Cation

Naming of ligands

- —O—suffix provided to the name of anionic ligands.
- —ium suffix provided to the name of cationic ligands.

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

Ligands whose names end in -ite or -ate become -ito or -ato, i.e., by replacing the ending -e with -o.

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* Anionic ligands :-

ide ⟶ ido (Cl^- : Chlorido)

ite ⟶ ito (NO_2^- : Nitrito)

ate ⟶ ato (SO_4^{-2} : Sulphato)

* Cationic ligand

Add (ium) as suffix.

NO^+ : Nitrosonium

Definition of Ligand

(e⁻-rich) → l.p donor ⟶ (CMA) & CMI

The neutral molecules; cations or anions which are directly linked with the centred metal atom or ion in complex ion are called ligands.

Classification of Ligands :-

A) One the basis of denticity

* Monodentate Ligand

mono
bidentate

The ligands that have one donar atom i.e. they only donate one electron pair to central metal atom or ion are known as monodentate ligands.

C.N
Type of ligand

C.N : n × (1)
: 6 × 1
: 6

ph

$[Co(en)_3]^{+3}$
C.N : 3 × 2 : 6

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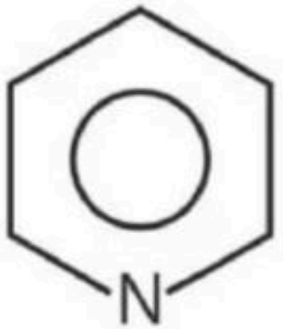
1. Monodentate ligand

(i) Neutral ligands

H_2O	aqua	PH_3	Phosphene
NH_3	Ammine	$P(Ph)_3$	Triphenyl phosphene
CO	Carbonyl	O_2	Dioxygen
CS	Thiocabonyl	N_2	Dinitrogen
NO	Nitrosyl		Pyridine(Py)

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(ii) Cationic ligand: -

O_2^+	Oxygenium
NO^+	Nitrosylium or Nitrosonium
$H_2N-\overset{+}{N}H_3$	Hydrazinium

(iii) Anionic ligands

F^-	Flurido Or fluro	S^{-2}	Sulphido Or sulpho
Cl^-	Chlorido Or chloro	OH^-	hydroxide Or hydroxo
Br^-	Bromido Or bromo	CH_3O^-	Methoxido Or methoxo
I^-	Iodido Or Ido	O_2^-	Superoxido Or superoxo
O^{-2}	Oxido	O_2^{-2}	Peroxido Or peroxo
NO_2^-	Nitro	N^{-3}	Nitrido
N_3^-	Azido	NH_2^-	Amido
H^-	Hydrido		

O_2 O_2^{+1} O_2^- O_2^{-2}

NH_3

H_2O

CO

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Previous Year's Questions

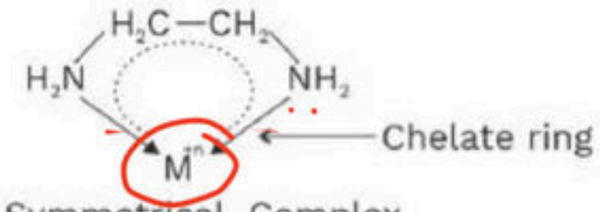
Which of these cannot act as a ligand?

[AIPMT]

(1) NH_3
(2) H_2O
(3) CO
(4) NH_4^+

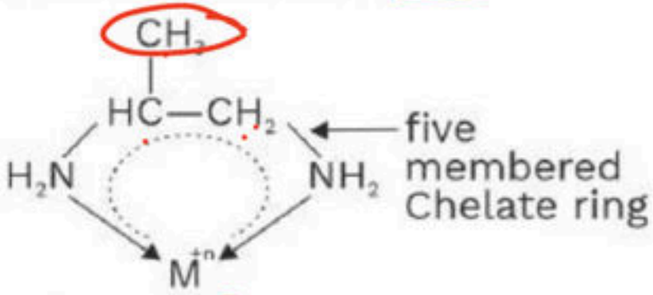
2. Bidentate ligands

(i) Ethylene diamine (en)
Or (ethane 1, 2–diamine)

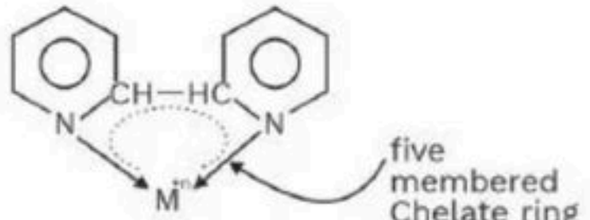


Symmetrical Complex

(ii) Propane 1,2–diamine
Or propylene diamine (Pn)

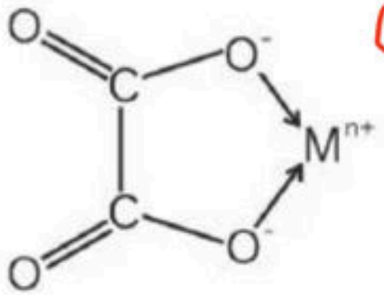


(iii) Dipyridyl (dipy)

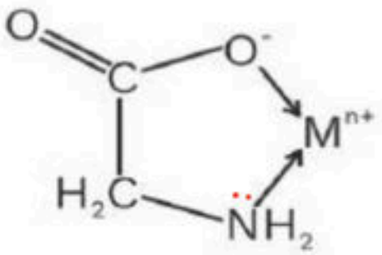


Symmetrical Complex

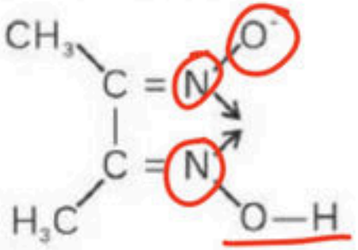
(iv) Oxalato (OX)$^{-2}$



(v) Glycenato (gly)$^{-}$



(vi) Dimethyl glyoximato (dmg)$^{-}$



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3. Polydentate ligands

All bidentate and polydentate ligand are chelating ligands.

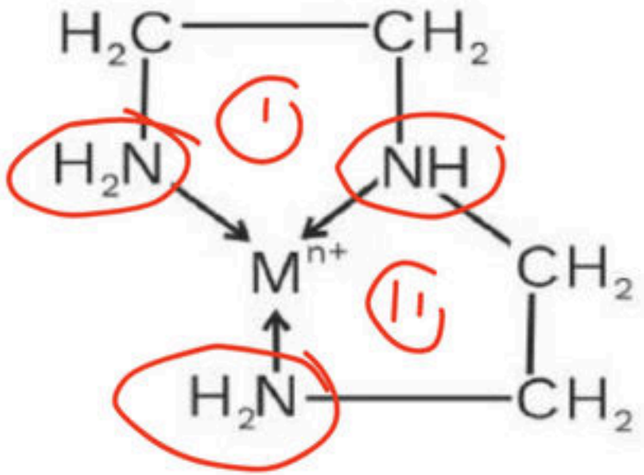
No of chelate ring = Denticity – 1

(i) Diethylenetriamine (dien)

Denticity = 3

No. of rings = 2

Neutral



R.P

en → 2 (N)

dien → 3 (N)

trien → 4 (N)

(ii) (trien) – Triethylene tetramine

Denticity = 4

Chelate rings = 3

Neutral

(iii) Terpyridine

Denticity = 3

Chelate rings = 2

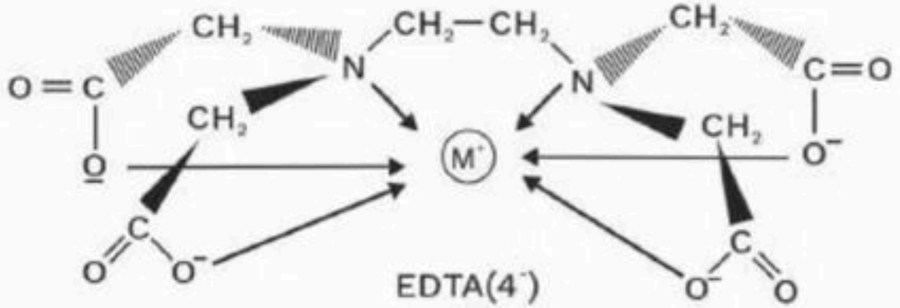
Neutral

(iv) Ethylenediamine tetracetato (EDTA)$^{-4}$

2N 4(O)

Denticity = 6

Chelate rings = 5



(v) Ethylenediamine triacetato (EDTA)$^{-3}$

Denticity = 5

Chelate rings = 4

Note:-

Chelating ligands form more stable complexes than the unidentate analogs. This is called chelating effect.

Chelation

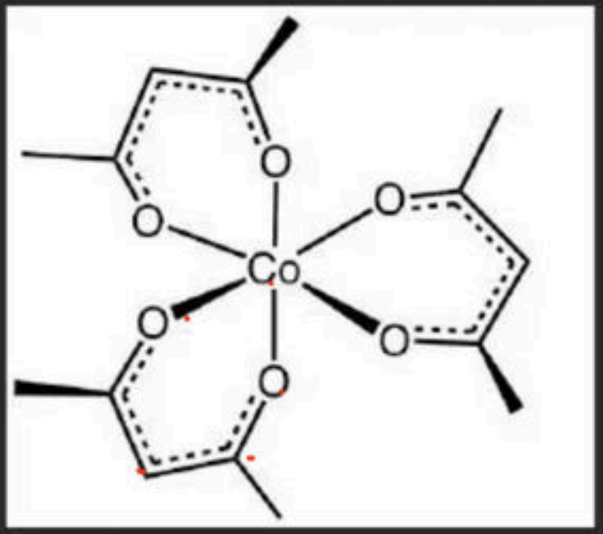
denticity

Previous Year's Questions

The anion of acetylacetone (acac) forms $Co(acac)_3$ chelate with Co^{3+}. The rings of the chelate are

[NEET-2013]

(1) five membered
(2) four membered
(3) six membered
(4) three membered



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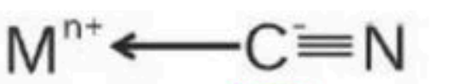
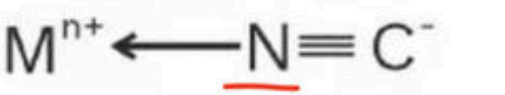
4. Ambidentate ligands

- Ligands which have two different donor atoms but at time of coordination such ligand can be coordinate CMA by either of two donor atoms.

(a)

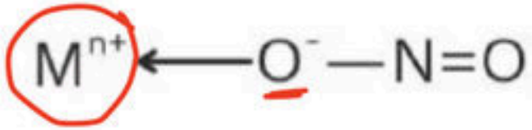


Cynido (CN)
Cynido—C

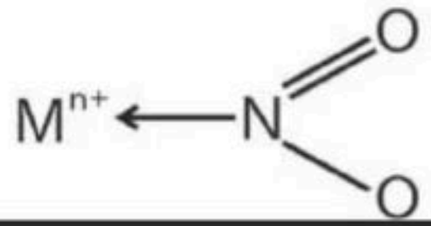


Isocynido (NC)
Cynido — N

(b) ^{-}ONO & NO_2^{-}



Nitrito-O



Nitrito-N

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Cyanate ion

Isocyanate ion

cyanato-O

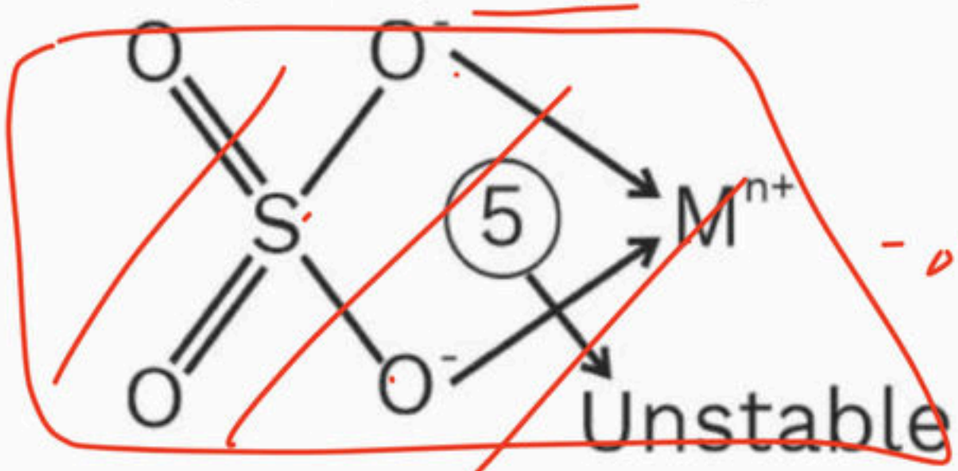
cyanato-N

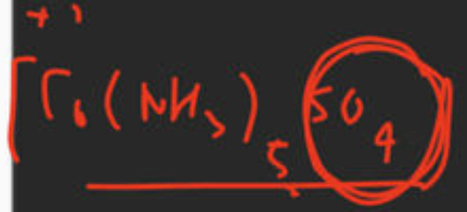
$(SCN)^-$ & $(NCS)^-$

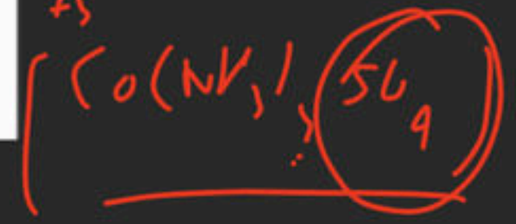
5. Flexi dentate → Polydentate

Ligands which can change their denticity

Ex. $CO_3^{-2}, PO_4^{-3}, SO_4^{-2}, CH_3 - COO^-, NO_3^-$ etc.







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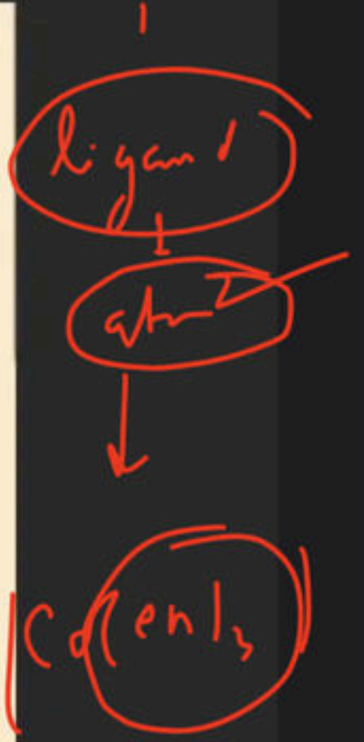
Co-ordination Number :-

The number of atoms in a ligand that directly bonded to the central metal atom or ion by coordinate bond is called coordination number of metal atom or ion.



ligand

atom

$Co(en)_3$

C.N = n_L × denticity.

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Coordination number
= Σ number of ligands
× Dentate character of ligands

C.N = N_l × denticity

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Total no of e^- pair accepted by CMA

1. $[Ni(dmg)_2]$ 2×2 = 4
2. $[Pt(trien)]Cl_2$: 1×4 = 4
3. $[Fe(EDTA)]^-$ 6×1 = 6
4. $[Co(en)_2Ox]Cl$ = 6

$2 \times 2 + 1 \times 2 = 6$

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Previous Year's Questions

Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is

[AIPMT]

(1) 3

(2) 6

(3) 4

(4) 2

IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The present system of nomenclature derived from the suggestions of **Alfred Werner** and recommended by the Inorganic Nomenclature Committee of the I.U.P.A.C. The main rules of naming of complexes are -

(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.

(b) In the naming of complex ion, ligands are to be named before the naming of central metal ion.

(c) If no. of ligands are more than one then their presence is indicated by prefixes like di, tri, tetra etc. but in case of polydentate ligands different prefixes such as bis, tris are used.

(d) When more than one type of ligand is present in the complex, then the ligands are named in the alphabetical order.

(e) If the complex is neutral or cationic then the central metal ion is to be named as it is.

If the complex is anionic complex then the name of central metal ion ends in 'ate'

(f) After the naming of central metal ion, oxidation state of central metal ion is written in Roman numeral.

	Complex Compounds	IUPAC Name
(i)	$K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate (II)
(ii)	$K_2[HgI_4]$	Potassium tetraiodidomercurate (II)
(iii)	$[Co(NH_3)_6]Cl_3$	Hexamminecobalt (III) chloride
(iv)	$[Cr(H_2O)_4Cl_2]Cl$	Tetraaquadichlorochromium (III) chloride
(v)	$[Pt(NH_3)_2Cl_4]$	Diammine tetrachloroplatinum (IV)
(vi)	$[Co(NH_3)_3Cl_3]$	Triamminetrichlorocobalt (III)
(vii)	$K_3[Co(NO_2)_6]$	Potassium hexanitrocobaltate (III)
(viii)	$Na_2[Fe(CN)_5NO]$	Sodium pentacyanonitrosoniumferrate (II)
(ix)	$[NiCl_4]^{-2}$	Tetrachloronickelate (II) ion
(x)	$[Ru(NH_3)_5Cl]^{+2}$	Pentamminechlororuthenium (III) ion
(xi)	$[Fe(en)_3]Cl_3$	Tris (ethylenediamine) iron (III) chloride
(xii)	$[Ni(Gly)_2]$	Bis (glycinato) nickel (II)

BONDING IN COORDINATION COMPOUNDS

WERNER'S THEORY

This was postulated by **Alfred Werner** in 1893. The postulates of Werner's theory of complexes are –

According to Werner central metal atom in a complex compound have 2 types of valencies :

Primary valencies	Secondary valencies
(i) Equal to oxidation state of CMA	(i) Equal to coordination number of CMA
(ii) Satisfied by anions	(ii) satisfied by ligands
(iii) Non directional	(iii) Directional
(iv) Ionisable	(iv) Non-ionisable
(v) not helpful in geometry prediction of complex ion	(v) helpful in geometry prediction of complex ion

Effective atomic Number

Effective atomic number (EAN) – Total no. of e^- associated with central metal ion in a complex is equal to effective atomic number.

EAN = Atomic number – (Oxidation state) + (2 × Coordination number)

Examples :

Complex	Metal (Oxidation State)	Atomic Number of Metal	Coordination number	Effective atomic number (E.A.N.)
$[Cu(NH_3)_4]SO_4$	+2	29	4	(29 – 2) + (4 × 2) = 35
$[Co(NH_3)_6]Cl_3$	+3	27	6	(27 – 3) + (6 × 2) = 36
$K_2[HgI_4]$	+2	80	4	(80 – 2) + (4 × 2) = 86
$[Ag(NH_3)_2]Cl$	+1	47	2	(47 – 1) + (2 × 2) = 50

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The IUPAC name of $Fe(CO)_5$ is

(1) Pentacarbonyl ferrate (0)

(2) Pentacarbonyl Ferrate (III)

(3) Pentacarbonyl Iron (0)

(4) Pentacarbonyl Iron (II)

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The compound $Na_2[Fe(CN)_5NO]$ is called

(1) Sodium pentacyanonitrosonium ferrate (II)

(2) Sodium nitroprusside

(3) Sodium nitrosoferrocyanide

(4) 1 & 2 both

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The Effective atomic number of Cr in $Cr(CO)_6$ is

(1) 36 (2) 38 (3) 28 (4) 54

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Which complex is chelating complex ?

(1) Diammine dichloroplatinum (II)

(2) Bis (ethylene diamine) copper (II)

(3) Tetra carbonyl nickel (0)

(4) Hexacyanoferrate (III) ion

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The Effective atomic number of iron in $K_4[Fe(CN)_6]$ is :

(1) 35 (2) 34 (3) 36 (4) 38

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Which of the following does not follow EAN rule ?

(1) $[Ni(CO)_4]$ (2) $[Fe(CO)_5]$ (3) $[Cr(CO)_6]$ (4) $[Mn(CO)_5]$

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VALENCE BOND THEORY

This theory was mainly developed by **Linus Pauling**. The main features of this theory are -

(a) Metal ion when it forms a complex compound undergoes formation of coordinate bond.

(b) During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals according to its coordination number.

(c) **Ex.** In the formation of $[Fe(NH_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.

In $[Cu(NH_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

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(d) These vacant orbitals undergo hybridisation before bond formation with ligands.

(e) The vacant hybrid orbitals of metal ion get overlapped with orbitals of ligands containing lone pair of electrons.

(f) If in a complex strong ligand is present then it will cause pairing of unpaired e^- in (n−1)d orbitals of central metal ion and if (n−1)d orbitals are involved in hybridisation then inner orbital complex is formed.

(g) If in the complex weak ligand is present then there will be no pairing of unapaired e^- in (n−1)d orbitals and if nd orbitals are involved in hybridisation, outer orbital complex is formed.

(h) If unpaired e^- is present in the complex then it will be paramagnetic otherwise it will be diamagnetic.

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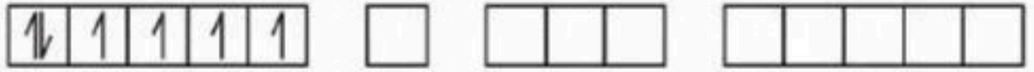
Applications of valence bond Theory

(a) 6-coordinated complexes :

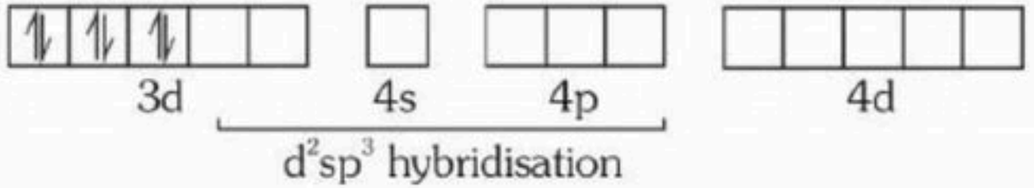
$[Co(NH_3)_6]^{3+}$

e^- configuration of $_{27}Co$ = [Ar] $3d^7\ 4s^2$ So, Co^{+3} = [Ar] $3d^6\ 4s^\circ\ 4p^\circ\ 4d^\circ$

Co^{3+}



Due to presence of strong ligand unpaired electrons get paired up so metal ion provides vacant '3d' orbitals for hybridisation.



- This is a **diamagnetic complex.**
- As inner 'd' orbitals are involved in hybridisation, hence it is an **inner orbital complex**.

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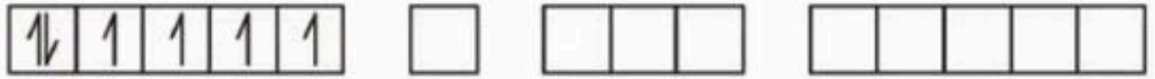
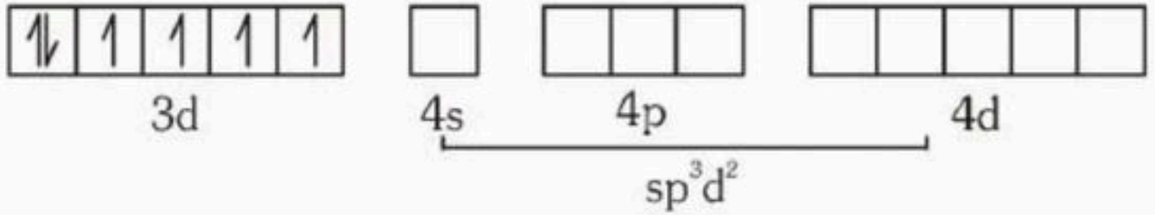
- **$[CoF_6]^{3-}$**

  e^- configuration of Co_{27} = [Ar] $3d^7 4s^2$ ∴ Co^{+3} = [Ar] $3d^6\ 4s^0\ 4p^0\ 4d^0$

  Co^{3+} ion



  ∵ F^- is a weak ligand, so unpaired e^- do not get paired up and vacant 4d orbitals involved in hybridisation.



- This is a **paramagnetic** complex.
- The outer 'd' orbitals are involved in hybridisation, hence it is an **outer orbital** complex.

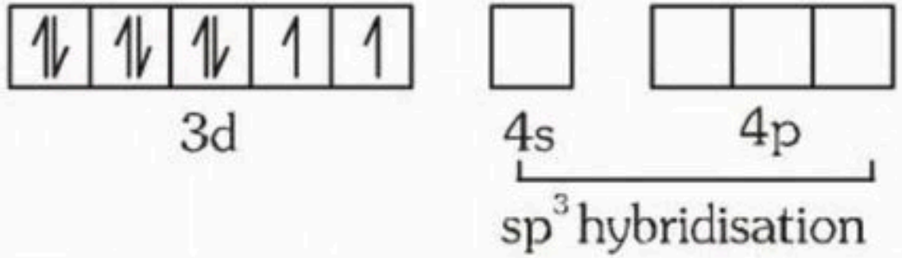
4-coordinated complexes :

- **$[NiCl_4]^{2-}$**

  e^- configuration of $_{28}Ni = [Ar]\ 3d^8\ 4s^2$

  $\therefore \quad Ni^{+2} = [Ar]\ 3d^8\ 4s^0\ 4p^0$

- There will be no pairing of unpaired e^- in 3d orbitals.



- $[NiCl_4]^{2-}$ has **tetrahedral geometry**.
- It is a paramagnetic complex.

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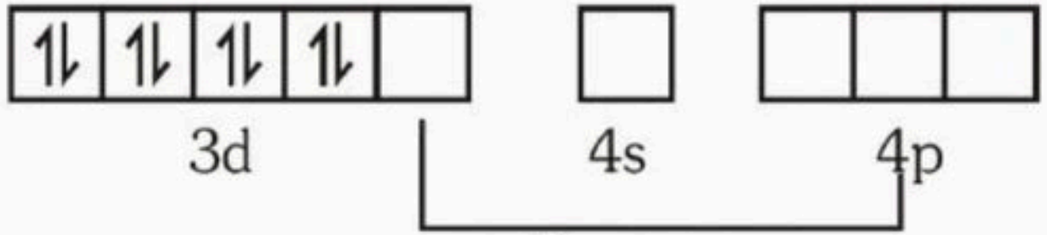
$[Ni(CN)_4]^{2-}$

$_{28}Ni = [Ar]\ 3d^8 4s^2$ $\quad Ni^{+2} = [Ar]\ 3d^8 4s^0 4s^0$

CN^- is a strong ligand so unpaired e^- in 3d orbitals get paired up



dsp^2 hybridisation

$[Ni(CN)_4]^{2-}$ has square planer geometry and diamganetic in nature.

This complex is an **inner orbital complex**

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

$Zn = [Ar]\ 4s^2\ 3d^{10}$

$\therefore \quad Zn^{+2} = [Ar]\ 3d^{10}4s^0 4p^0$

$\because \quad Zn^{+2}$ has d^{10} configuration

So there is no possibility of pairing

3d

4s

4p

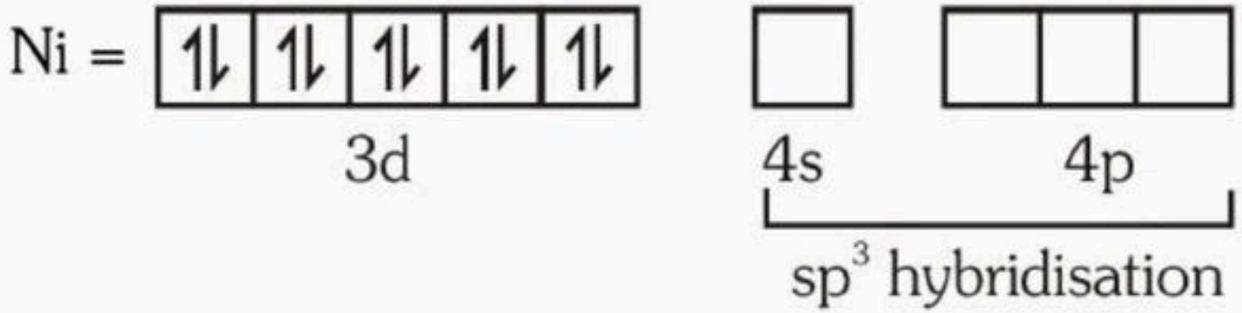
sp^3

Because the complex is formed by sp^3 hybridisation, hence it has **tetrahedral geometry**.

Since all electrons are paired, hence it is **diamagnetic**

$[Ni(CO)_4]$ Ni = [Ar] $3d^8\ 4s^2\ 4p^0$

$\because$ CO is a strong ligand so unpaired e^- in (n−1)d orbitals get paired up.



Complex has sp^3 hybridisation

It has tetrahedral geometry.

It is diamagnetic complex as unpaired e^- is absent.

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

$_{29}Cu = [Ar]\ 4s^1\ 3d^{10}$ $\quad \therefore\ Cu^{+2} = [Ar]\ 3d^9\ 4s^0\ 4p^0$

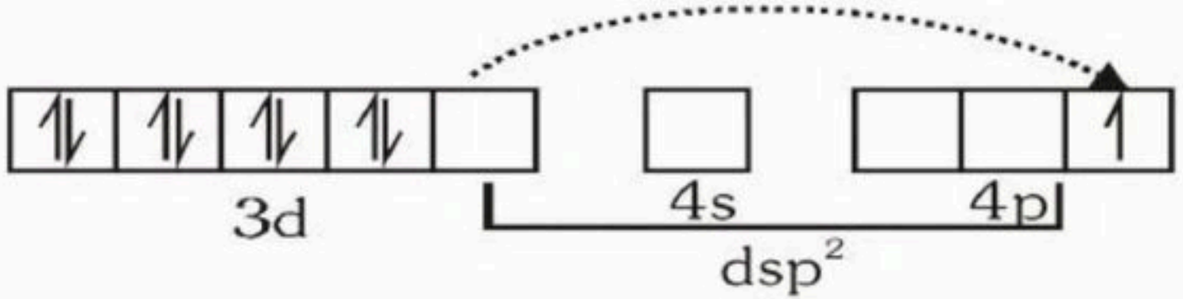
$\because$ NH_3 is a strong ligand so after rearrangement

Complex has dsp^2 hybridsation

It is inner orbital complex

It has square planer geometry

It is paramagenetic



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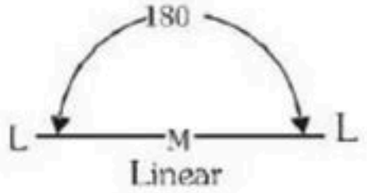
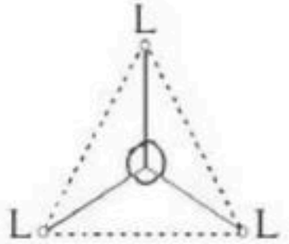
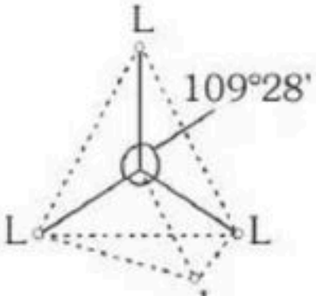
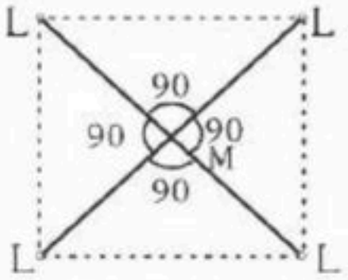
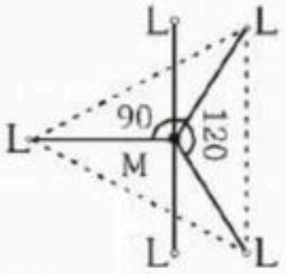
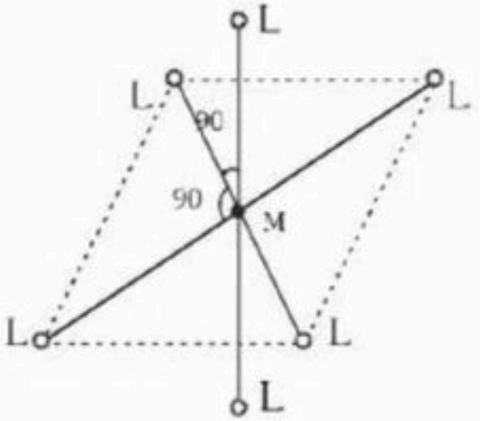
Series which shows the relative strength of ligands

$$I^-(\text{weakest}) < Br^- < SCN^- < Cl^- < S^{-2} > F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^-$$

$$< edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO(\text{strongest})$$

Coordination Number	Hybridised orbital	Geometrical shape of the Complex	Examples of Complex
2	sp	 Linear	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
3	sp^2	 Trigonal planer	$[HgI_3]^-$
4	sp^3	 Tetrahedral	$[CuCl_4]^{-2}$ $[ZnCl_4]^{-2}$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{+2}$

4	dsp^2 $(d_{x^2-y^2}\text{orbital})$	 Square plannar	$[PdCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{+2}$ $[Cu(NH_3)_4]^{+2}$ $[PtCl_4]^{2-}$
5	dsp^3/sp^3d	 Trigonal bipyramidal	$[Fe(CO)_5]$

6	d^2sp^3 When d-orbitals are (n - 1)d-orbitals (Inner orbital comlexes) or sp^3d^2 When d-orbitals are nd orbitals (Outer orbital complexes) In both cases d-orbitals are d_{z^2} and $d_{x^2-y^2}$ orbitals	 Octahedral	$[Cr(NH_3)_6]^{+3}$ $[Ti(H_2O)_6]^{+3}$ $[Fe(CN)_6]^{-3}$ $[Co(NH_3)_6]^{+3}$ $[PtCl_6]^{-2}, [CoF_6]^{-3}$

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Complex ion having square planar geometry is :-

(1) $[Ni(CN)_4]^{2-}$ (2) $[Cu(CN)_4]^{-2}$ (3) $[Cu(NH_3)_4]^{+2}$ (4) All

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In the complex ion $[FeF_6]^{-3}$, according to valence bond theory, the magnetic properties of the complex ion corresponds to how many unpaired electrons ?

(1) 0 (2) 5 (3) 2 (4) 3

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Among $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ and $[Ni(Cl)_4]^{2-}$:

(1) $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic

(2) $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[Ni(CO)_4]$ is paramagnetic

(3) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2-}$ is paramagnetic

(4) $[Ni(CO_4)]$ is diamagnetic and $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic

Match list - I with list - II and choose the correct answer from the code given below

List - I (complex)	**List - II (geometry)**
(A) $[Ni(CN)_4]^{-2}$	(a) Octachedral
(B) $[Pt(NH_3)_6]^{+4}$	(b) Squareplanar
(C) $[Ag(NH_3)_2]^{+}$	(c) Tetrahedral
(D) $[Zn(NH_3)_4]^{+2}$	(d) Linear

	A	**B**	**C**	**D**
(1)	b	a	d	c
(2)	a	b	c	d
(3)	c	d	b	a
(4)	b	c	d	a

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Which pair of complexes has inner orbital complexes ?

(1) $[Fe(CN)_6]^{-3}$ & $[FeF_6]^{-3}$

(2) $[CoF_6]^{-3}$ & $[CoCl_6]^{-3}$

(3) $[Zn(NH_3)_6]^{+2}$ & $[Zn(H_2O)_6]^{+2}$

(4) $[Fe(CN)_6]^{-3}$ & $[Fe(CN)_6]^{-4}$

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Which is not related with complex $[Ni(CO)_4]$:-

(1) It has sp^3 hybridisation

(2) It has tetrahedral geometry

(3) It is paramagnetic

(4) It is diamagnetic

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Crystal field theory

Crystal Field Theory : This is a model of electronic structure of transition-metal complexes that considers how the energies of the d-orbitals of a metal ion are affected by the electric field of the ligand. According to this theory.

(a) Central metal ion is considered as a positive point charge, anionic ligand as a negative point charge, neutral ligand as a point dipole and attraction between metal ion and ligand is electrostatic in nature.

(b) In the electric field of ligands, the five d orbitals of the metal atom no longer have exactly same energy while they are splitted into different energy levels. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

(c) The extent of splitting of metal d-orbitals depends upon the nature and number of ligands surrounding it and the charge on the central metal ion.

(d) The extent of splitting of metal d-orbitals determines the magnetic and spectroscopic properties of the complexes.

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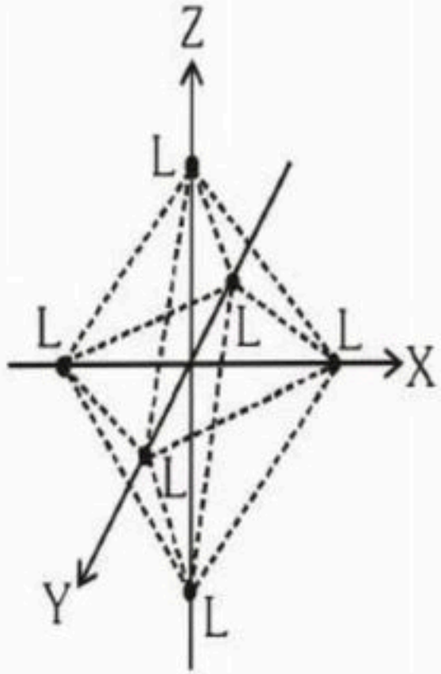
SPLITTING IN OCTAHEDRAL COMPLEXES

In a octahedral complex, the co-ordination number is 6. The metal ion is at the centre and the ligands occupy the six corners of the octahedron as shown in figure.

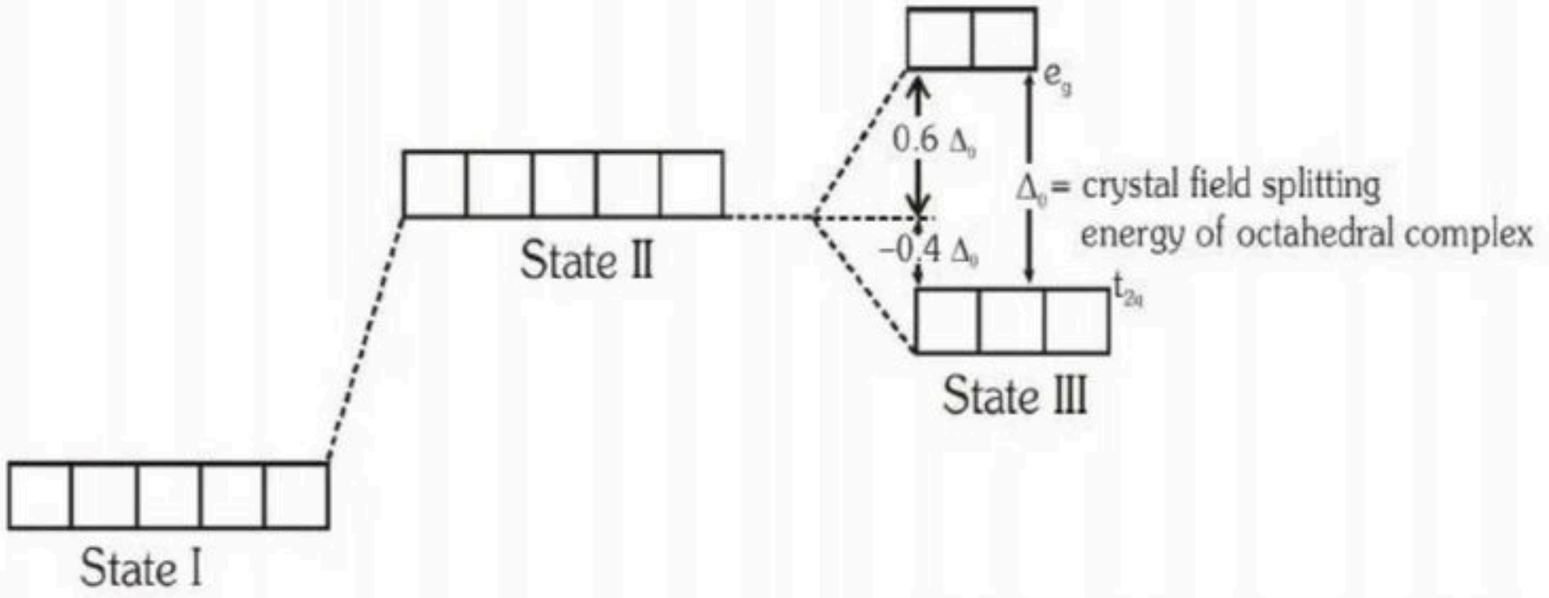
We know that two orbitals, $d_{x^2-y^2}$ and d_{z^2} are oriented along the axis while the remaining three orbitals, viz., d_{xy}, d_{yz} and d_{zx} are oriented in between the axis.



The two orbtials $d_{x^2-y^2}$ and d_{z^2} are designated as e_g orbitals while the three orbitals d_{xy}, d_{yz} and d_{zx} are designated as t_{2g} orbitals. As the six ligands approach the central ion along the axis hence e_g orbitals, is repelled more by the ligand than the t_{2g} orbitals.

In other words, the energy of the eg orbitals increases much more than the energy of the t_{2g} orbitals.

Thus, in octahedral complexes, the five d-orbitals split up into two sets : one set consisting of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) of higher energy (e_g orbitals) and the other set consisting of three orbitals (d_{xy}, d_{yz} and d_{zx}) of lower energy (t_{2g} orbitals).



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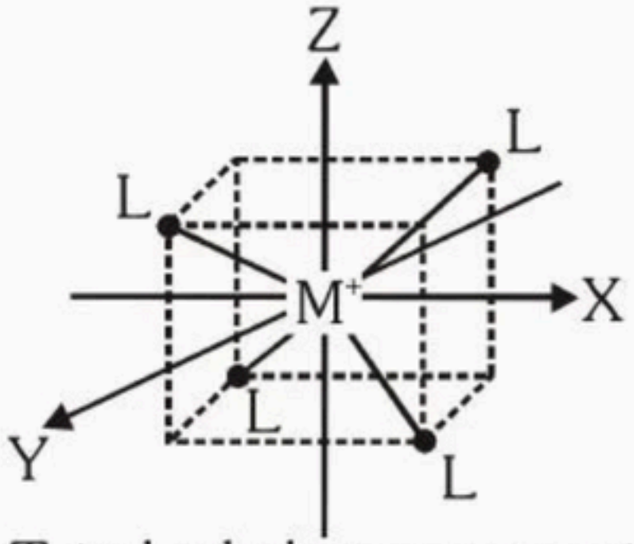
Splitting in tetrahedral complex

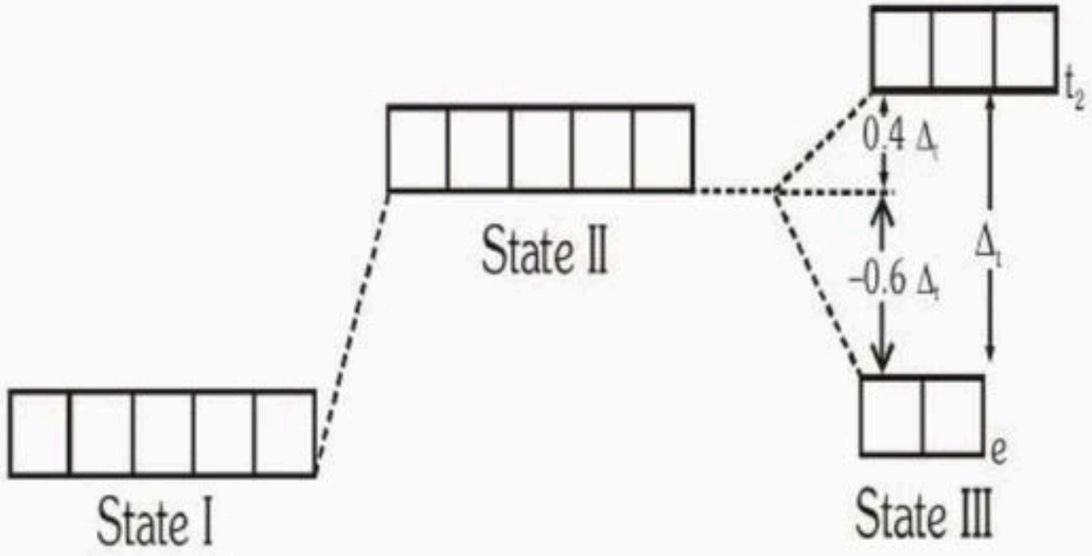
The co-ordination number for tetrahedral complexes is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands at the alternate corners of a cube, as shown in figure.



Tetrahedral arrangement of four lignads

It can be shown that in a tetrahedral structure, none of the d-orbitals points exactly towards the ligands. When ligand approaches it is more close d_{xy}, d_{yz}, d_{xz} in comparision of $d_{x^2-y^2}$ and d_{z^2} because d_{xy}, d_{yz}, d_{zx} are between the axis and d_{z^2} and $d_{x^2-y^2}$ are along the axis. So d_{xy}, d_{yz}, d_{zx} feels more repulsion as compare to d_{z^2} and $d_{x^2-y^2}$.

Thus, the d orbitals are also splitted into two groups but in a reverse order of octahedral complex. The three orbitals, d_{xy}, d_{yz} and d_{xz}, designated are now have higher energy than the two orbitals $d_{x^2-y^2}$ and d_{z^2}.



= Spitting energy of tetrahedral complex

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Calculation of crystal field stablizing energy (CFSE)

For octahedral complex CFSE $= \left[-0.4\left(n_{t_{2g}}\right)+0.6\left(n_{eg}\right)\right]\Delta_0$ + Pairing energy **(P.E.)**

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

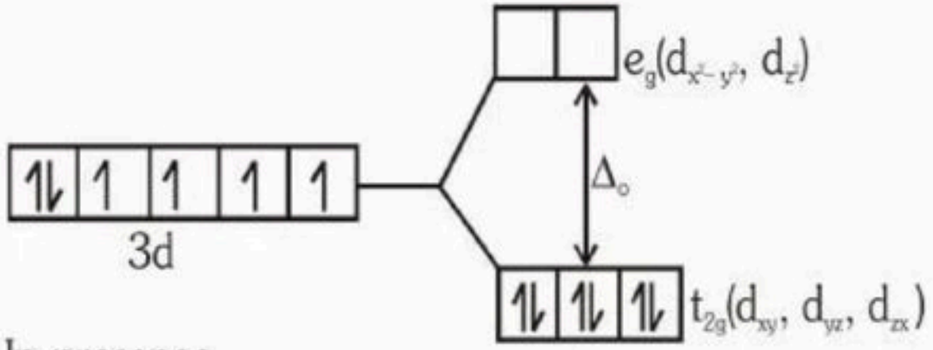
n_{eg} = number of electron in eg orbitals

Δ_0 = crystal field **splitting** energy

Example **Explain the formation of $Na_4[Fe(CN)_6]$ and $Na_4[FeF_6]$? Show which is low spin and which is high spin complex and also calculate the Crystal field stablisation energy (CFSE) ?**

Solution In given compounds CN^- is strong field ligands and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d^6 configuration.

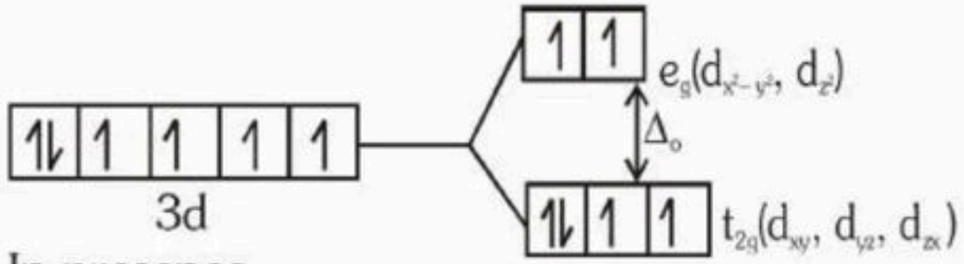
So in $Na_4[Fe(CN)_6]$



In presence of ligand

$\because$ in presence of CN^- (SFL) Δ_0 is high than pairing energy, so unpaired e^- get paired and it is a low spin complex

$Na_4[FeF_6]$



In presence of ligand

in presence of F^- (WFL) Δ_0 is less than pairing energy so unpaired e^- do not get paired and it is a high spin complex

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Factors affecting splitting energy (Δ)

(i) Strength of ligand — [C.F.S.E. is more in case of S.F.L. as compared to W.F.L.]

(ii) Oxidation state of central metal ion — [C.F.S.E. $\propto$ oxidation state]

(iii) Transition series (d-series) — [C.F.S.E. , 5d > 4d > 3d]

(iv) Geometry (number of ligands). — [$\Delta_{sq} > \Delta_0 > \Delta_t$]

$$\Delta_{sp} = \frac{4}{3}\Delta_0 \quad ; \quad \Delta_t = \frac{4}{9}\Delta_0$$

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Spectro-chemical series for ligands

Series which shows the relative strength of ligands

I^-(weakest) < Br^- < SCN^- < Cl^- < S^{-2} > F^- < OH^- < $C_2O_4^{2-}$ < H_2O < NCS^-

< $edta^{4-}$ < NH_3 < en < NO_2^- < CN^- < CO(strongest)

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APPLICATION OF CRYSTAL FIELD THEORY

Applications of C.F.T are

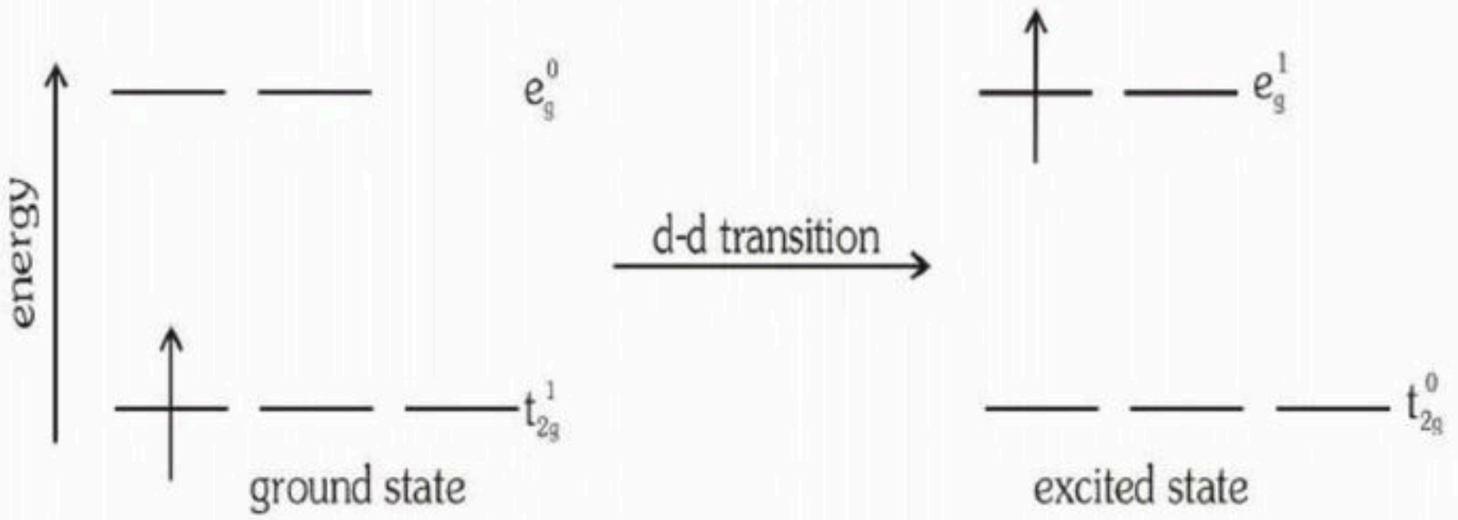
(i) To explain weather complex is high spin or low spin complex.

(ii) To explain colour property

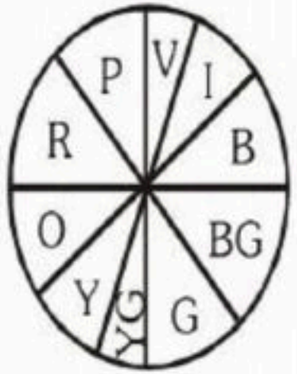
(iii) To explain stability of complex

COLOUR PROPERTY OF COMPLEX COMPOUNDS :

Reason for colour in complexes is due to d-d-transition



Complentary colour wheel



For example complementry colour of red is blue green.

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Example. **$[Ti(H_2O)_6]^{+3}$ is violet in colour explain using CFT.**

Solution In $[Ti(H_2O)_6]^{3+}$, d-orbitals of Ti^{3+} lost their degeneracy in the presence of octahedral ligand field and produce t_{2g^1} & eg^0 orbital of different energy, complex absorbs visible light for excitation of electron from t_{2g} to eg which is corresponding to green yellow colour and show its complimentry violet colour.

Example. **How the complex compounds show the colour?**

Solution When d-electrons absrobs energy from visible region they will get excited. Absorbed energy is related to a particular wavelength.

$$E_{\underset{(\Delta)}{absorbed}} = \frac{hc}{\lambda_{absorbed}}$$

when electrons fall into lower energy level it will show colour whose wavelength (λ) is the complimentary of absorbed wavelength ($\lambda_{absorbed}$).

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Example. **Why violet coloured $[Ti(H_2O)_6]Cl_3$ becomes colourless when heated ?**

Solution When $[Ti(H_2O)_6]Cl_3$ is heated water molecules are removed and in the absence of ligand crystal field splitting does not occur and hence the substance is colourless due to no d–d transition.

Example. **$[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ show different colours. Why ?**

Solution Due to difference in strength of ligands splitting energy will be different due to which $\lambda_{absorbed}$ and $\lambda_{emitted}$ will be diffrent for both complexes.

Example. **What will be the correct order for the wavelengths of absorption in the visible region for the following : $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?**

Solution $[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$

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Important points :-

- Red colour of ruby is due to presence of small amount of Cr^{+3} in atmosphere of Al_2O_3
- Green colour of emerald is due to presence of Cr^{+3} in atmosphere of $Be_3Al_2Si_6O_{18}$ [beryl]
- Complex become colourless in absence of ligand field because in absence of ligand d-d-transition does not occur.
- $[Ti(H_2O)_6]^{3+}$ become colourless on heating due to removal of water molecules.
- Anhydrous $CuSO_4$ which is colourless but hydrated $CuSO_4$ is blue in presence of moisture.
- Halogens are coloured due to the HOMO-LUMO transition.
- $KMnO_4$, $K_2Cr_2O_7$, CrO_2Cl_2 are coloured due to charge transfer spectrum.

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STABILITY OF CO-ORDINATION COMPOUNDS

According to thermodynamic stability, the reaction between a metal ion and the ligands may be considered as a Lewis acid base reaction. If the equilibrium constant is high then the complex obtained is theromodynamically stable. The reaction can be written as follows : $M + nL \rightleftharpoons [ML_n]$

The stability constant K, of the complex $[ML_n]$ is given by the relation, $K = \frac{[ML_n]}{[M][L]^n}$. The greater the value of K, more stable is the complex.

The stability of a complex ion also depends upon –

(i) Higher charge of the central metal ion.

(ii) Greater strength of the ligand.

(iii) Ring formation (chelation) in structure of complexes.

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For the $t_{2g}^6 e_g^2$ system, the value of magnetic moment (μ) is :

(1) 2.83 B.M. (2) 1.73 B.M. (3) 3.87 B.M. (4) 4.92 B.M.

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The stability constants of the complexes formed by a metal ion M^{2+} with NH_3, CN^-, H_2O are of the order of 10^{15}, 10^{27}, 10^{11} respectively. Then :-

(1) NH_3 is the strongest ligand

(2) CN^- is the strongest ligand

(3) These values cannot predict the strength of the ligand

(4) All the ligands are equally strong

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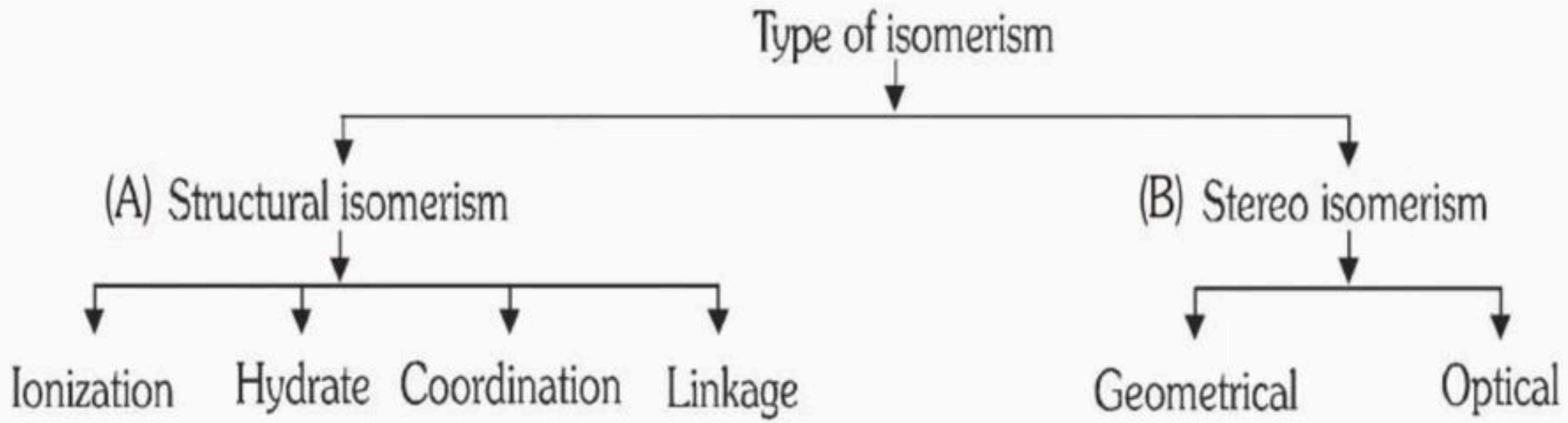
ISOMERISM IN COMPLEXES

Compounds which have the same molecular formula, but differ in their properties due to the difference in their structure are called as **Isomers**.

Classification of isomerism :



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(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.

(i) Ionisation Isomerism

Compounds having same molecular formula but give different type of ions in their aqueous solution are known as ionisation isomer.

Due to exchange of ions between coordination sphere and ionisation sphere different ionisation isomers are formed. So they are ionisation isomers.

Ex. (a) $CoBrSO_4 \cdot 5NH_3$ can represent

(i) $[Co(NH_3)_5Br]\,SO_4$ (red violet)

(ii) $[Co(NH_3)_5\,SO_4]\,Br$ (red).

These complexes give sulphate ion and bromide ion respectively

(b) $[Pt(NH_3)_4Cl_2]\,Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

(c) $[Co(NH_3)_4(NO_3)_2]SO_4$ and $[Co(NH_3)_4SO_4](NO_3)_2$

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(ii) Hydrate Isomerism

This type of isomerism is due to presence of different number of water molecules inside the complex ion.

Ex. (a) $Cr(H_2O)_6Cl_3$ has three possible hydrate isomers.

(i) $[Cr(H_2O)_6]Cl_3$ (violet)

(ii) $[Cr(H_2O)_5Cl]\,Cl_2.H_2O$ (green)

(iii) $[Cr(H_2O)_4Cl_2]Cl\,.\,2H_2O$ (dark green)

These complexes differ from one another with respect to the number of water molecules acting as ligands.

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(iii) Linkage Isomerism

(a) This type of isomerism arises due to presence of ambidentate ligands

(b) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

Ex. $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5 ONO]Cl_2$

In NO_2^- ligand, the donor site is nitrogen while in ONO^- ligand donor site is oxygen.

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(iv) Coordination Isomerism

(a) This type of isomerism is exhibited when in complex compound both cation as well as anion is complex.

(b) This type of isomerism is caused by the interchange of ligands between the two complex ions of a complex compound.

Ex. **(i)** $[Zn(NH_3)_4][ZnCl_4]$

(ii) $[Zn(NH_3)_3Cl][ZnCl_3(NH_3)]$

} Coordination isomers

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(B) Stereo Isomerism

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

(b) The two types of stereo isomers which are possible are - Geometrical and optical.

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(i) Geometrical Isomerism

(a) Due to change in relative positions of ligands around central metal ion, different forms are obtained which are known as GI.

(b) When two identical ligands are coordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).

(c) If the two identical ligands are coordinated to the metal ion from opposite side then it is **Trans isomer** (in Latin, Trans means across).

(d) These geometrical isomers differ in physical as well as in chemical properties.

(e) Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.

(f) 4-coordinated complexes with tetrahedral geometry do not exhibit cis- Trans isomerism, because relative position of ligands remain same for each other.

(g) It is exhibited by 4-coordinated complexes with square planar geometry.

Note : There are only 5 possible cases which shows geometrical isomerism in square planar complex.

such as Ma_2b_2, Ma_2bc, Mabcd, $M(AB)_2$, M(AB)cd

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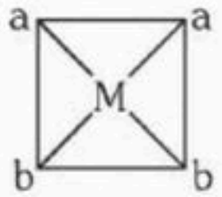
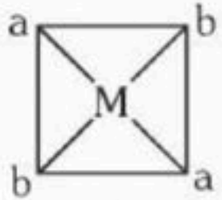
Geometrical Isomers With Coordination Number = 4 (Square Planar Complexes)

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

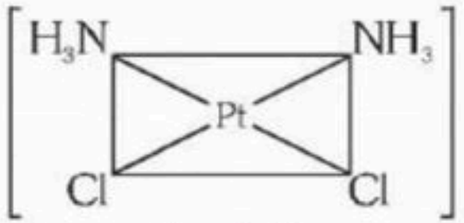


Cis-isomer

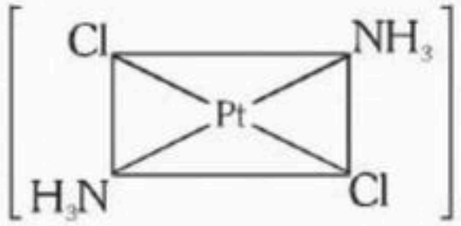


Trans-isomer

Ex. $[Pt(NH_3)_2Cl_2]$



cis-platin
(used as a anti cancer)



Trans – platin

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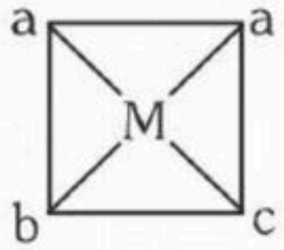
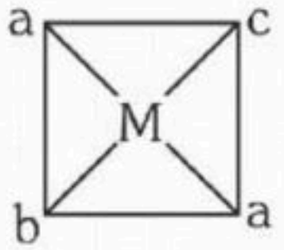
(ii) Complexes with general formula $\mathbf{Ma_2bc}$ can have Cis - and trans-isomers.

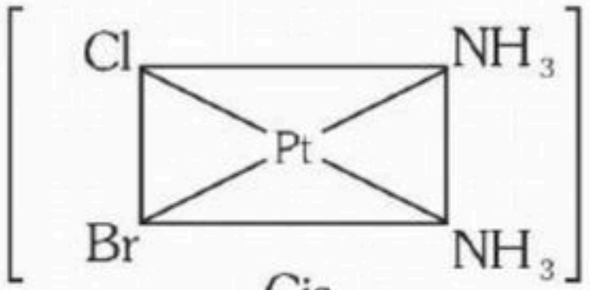


Cis

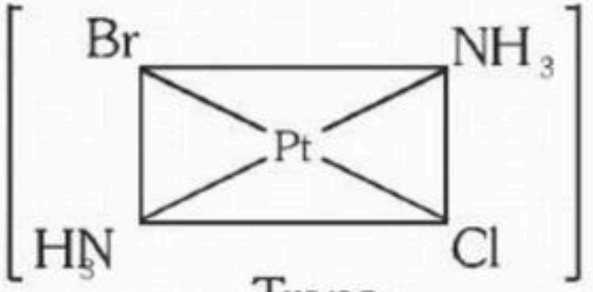


trans

eg. $\mathbf{[Pt(NH_3)_2ClBr]}$

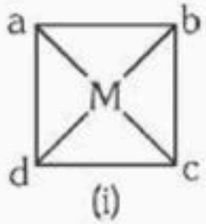


Cis

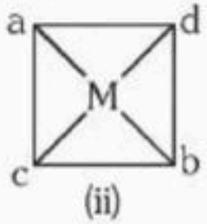


Trans

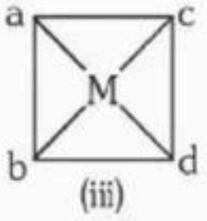
(iii) Complexes with general formula, **Mabcd** can have three geometrical isomers.



(i)



(ii)

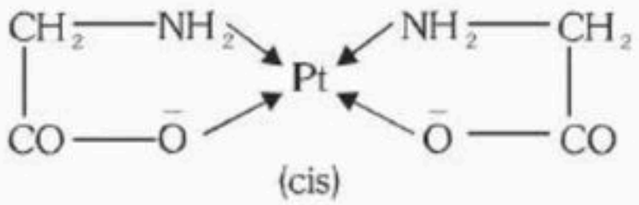


(iii)

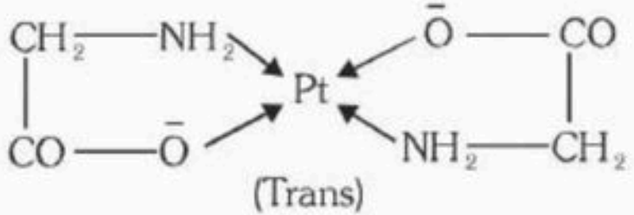
eg. $[Pt(NH_3)(Py)ClBr]$

(iv) Complex with general formula $[M(AB)_2]$ have 2 geometrical isomers (Where AB is unsymmetrical Bidentate ligand)

eg. $[Pt(gly)_2]$



(cis)

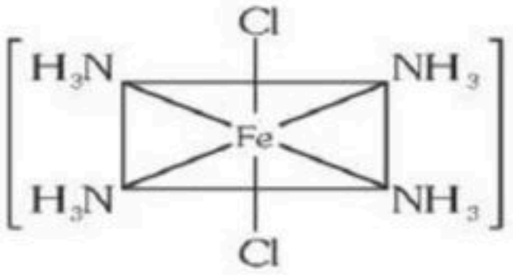


(Trans)

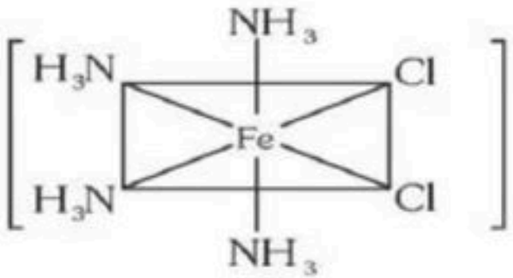
Geometrical isomers with Coordination number = 6 (Octahedral complex)

(i) $[Ma_4b_2]$ has 2 geometrical isomers

eg. $[Fe(NH_3)_4Cl_2]$



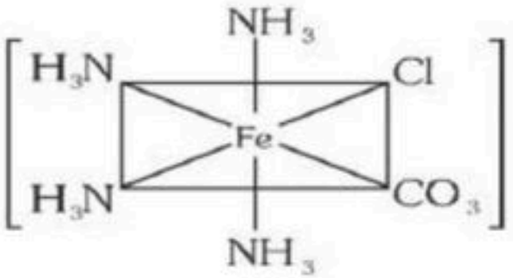
Trans



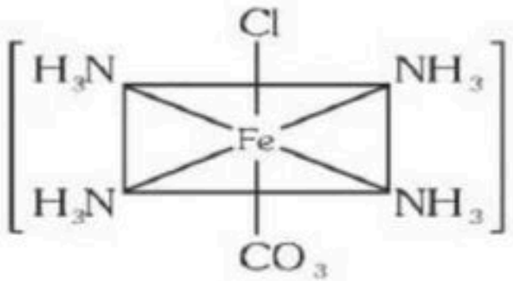
Cis

(ii) $[Ma_4bc]$ has 2 geometrical isomers

eg. $[Fe(NH_3)_4ClCO_3]$



Cis



Trans

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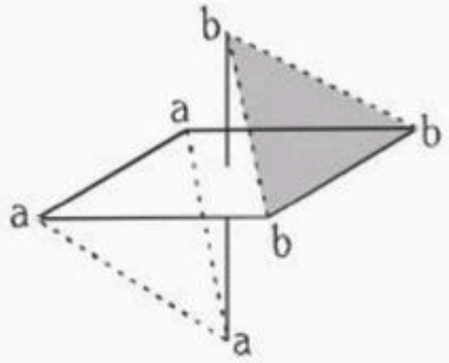
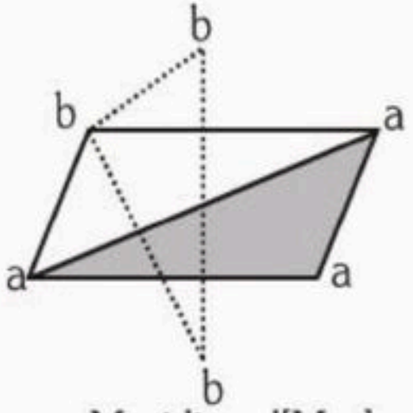
(iii) Facial and Meridional isomerism (Ma_3b_3)



Facial (fac)



Meridional[Mer]

eg. $[Cr(NH_3)_3(H_2O)_3]^{+3}$

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Other examples of geometrical isomers in octahedral complexes.

General formula	Total No. of geometrical isomers
Mabcdef	15
Ma_2bcde	9
Ma_2b_2cd	6
$Ma_2b_2c_2$	5
Ma_3bcd	4
Ma_3b_2c	3
Ma_3b_3	2
Ma_4bc	2
Ma_4b_2	2
Ma_5b	Nil
Ma_6	Nil

Here M = central atom ; a, b, c, d, e, f = Monodentate ligands

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(B) Optical Isomers

(a) Compounds which are mirror image of each other but non superimposable, are known as optical isomers.

(b) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.

(c) The complex which rotates plane polarised light to left hand side is **laevo rotatory i.e. 'ℓ' or '–'** and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory 'd' or '+'.**

(d) Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.

(e) The 'd' and 'ℓ' isomers of a compound are called as **Enantiomers**.

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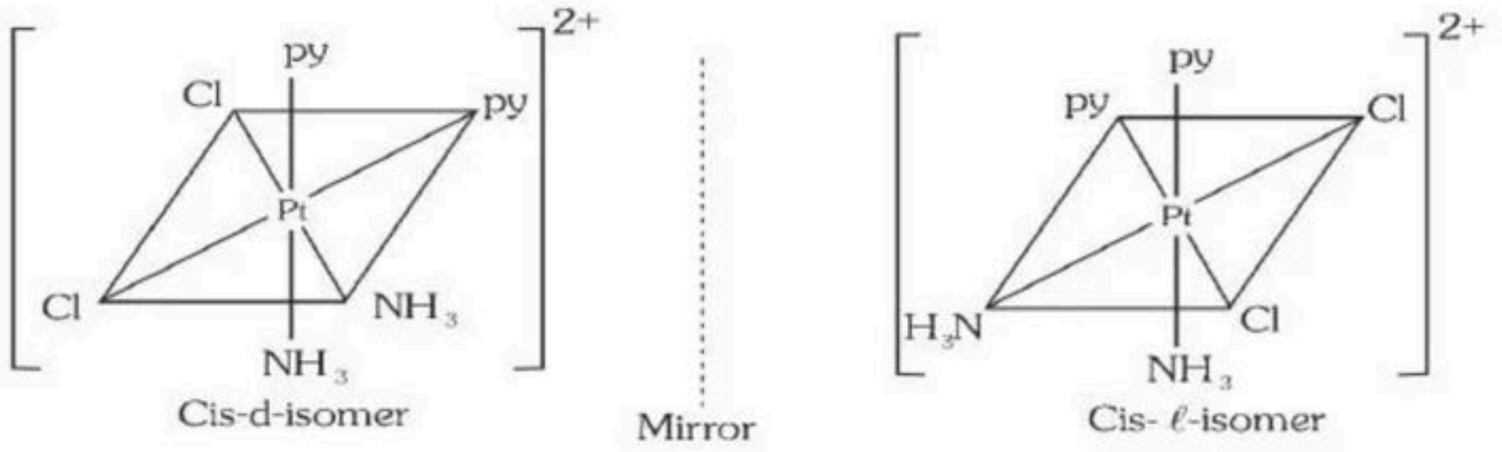
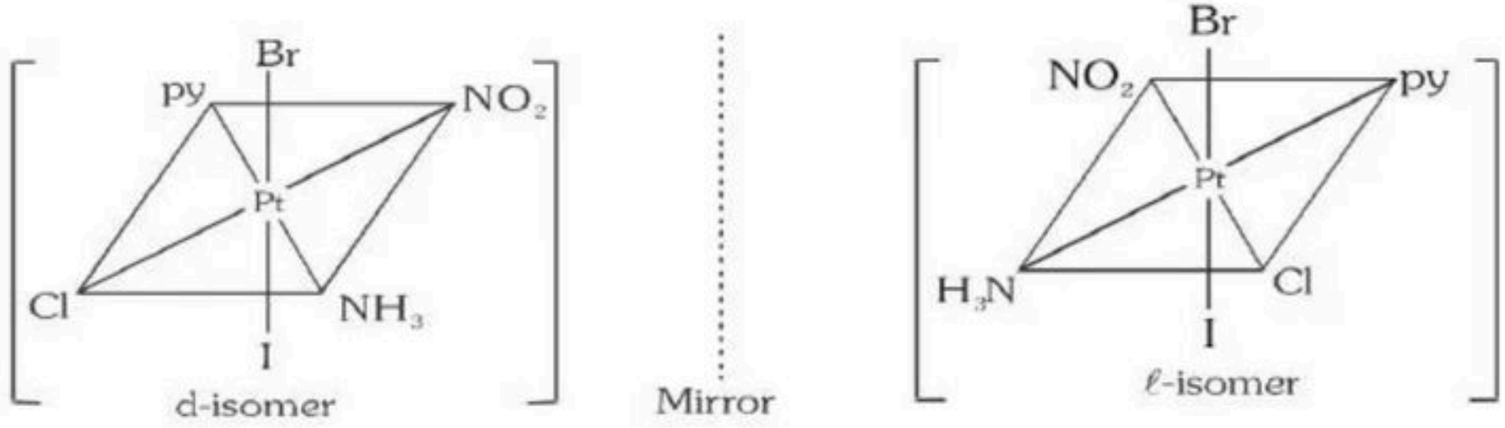
Optical isomers with Coordination number = 6

(i) $[Ma_2b_2c_2]^{n+} \rightarrow [Pt(py)_2(NH_3)_2Cl_2]^{2+}$



(ii) $[Mabcedf] \rightarrow [Pt(py)NH_3NO_2ClBrI]$



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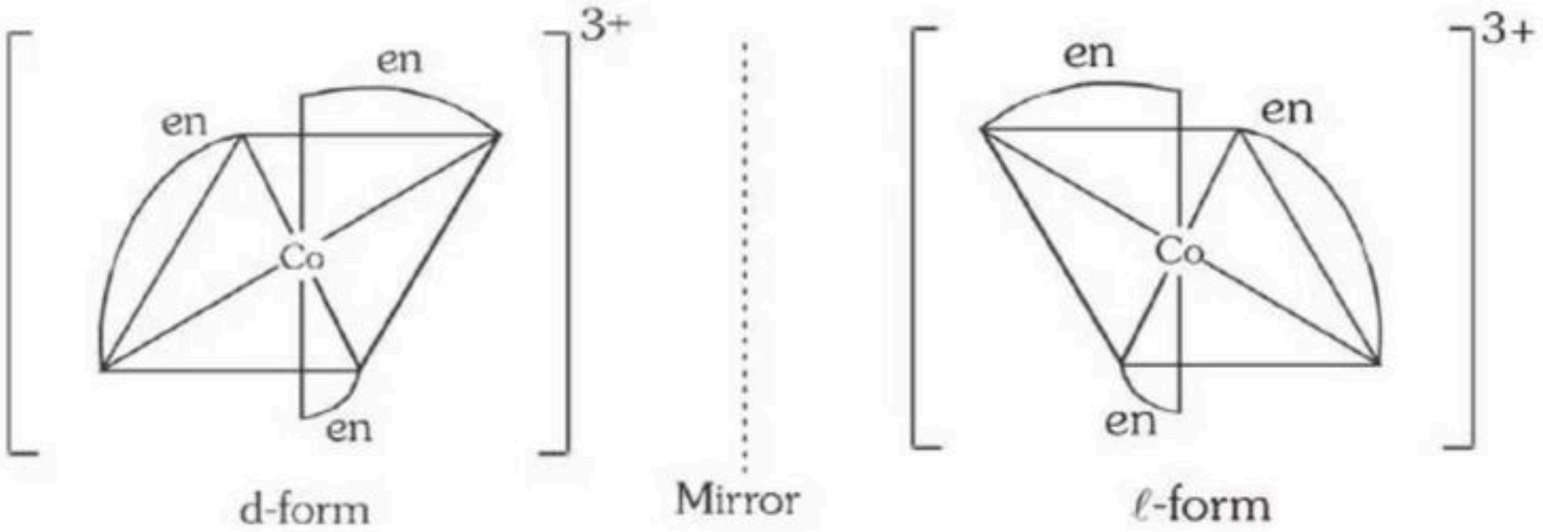
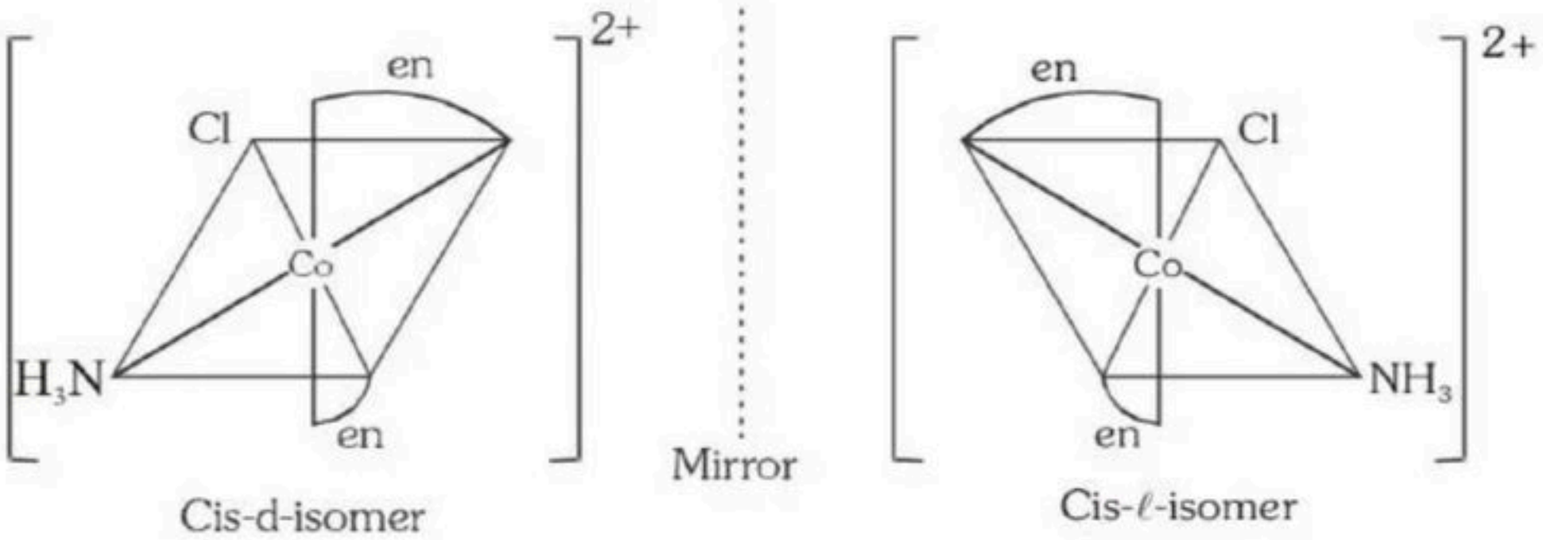
(iii) $[M(AA)_3]^{n+} \rightarrow [Co(en)_3]^{3+}$



(iv) $[M(AA)_2ab]^{n+} \rightarrow [Co(en)_2NH_3Cl]^{2+}$



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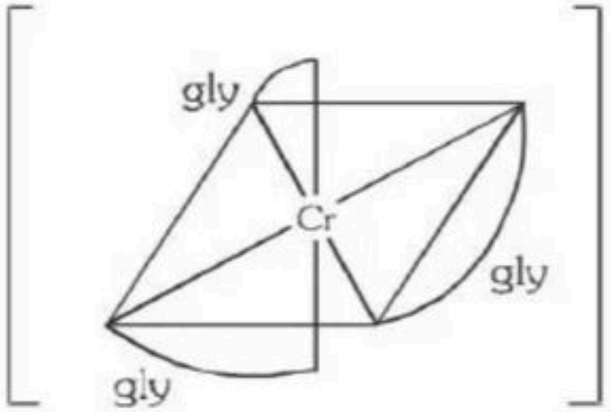
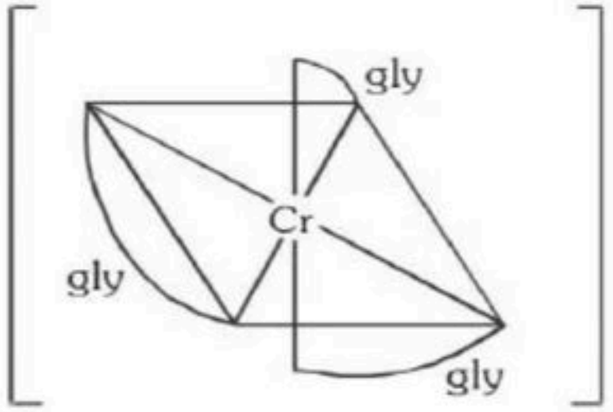
(v) $[M(AB)_3] \rightarrow [Cr(gly)_3]$



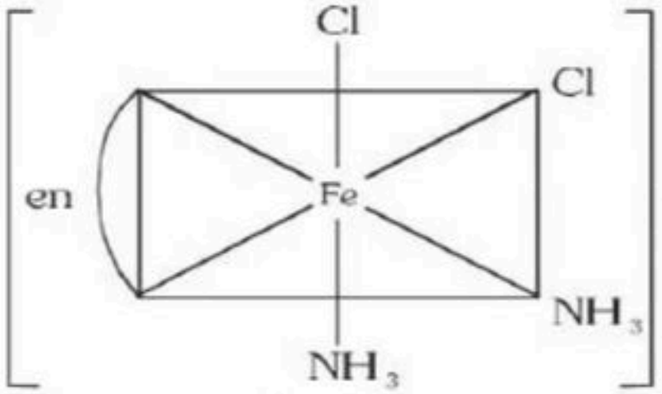
Cis or trans-d-isomer

Mirror



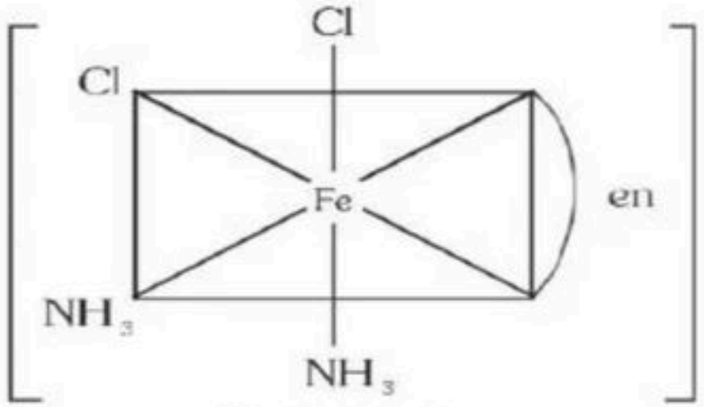
Cis or trans-ℓ-isomer

(vi) $[Fe(NH_3)_2(en)Cl_2]$



Cis–d-isomer

Mirror



Cis-ℓ-isomer

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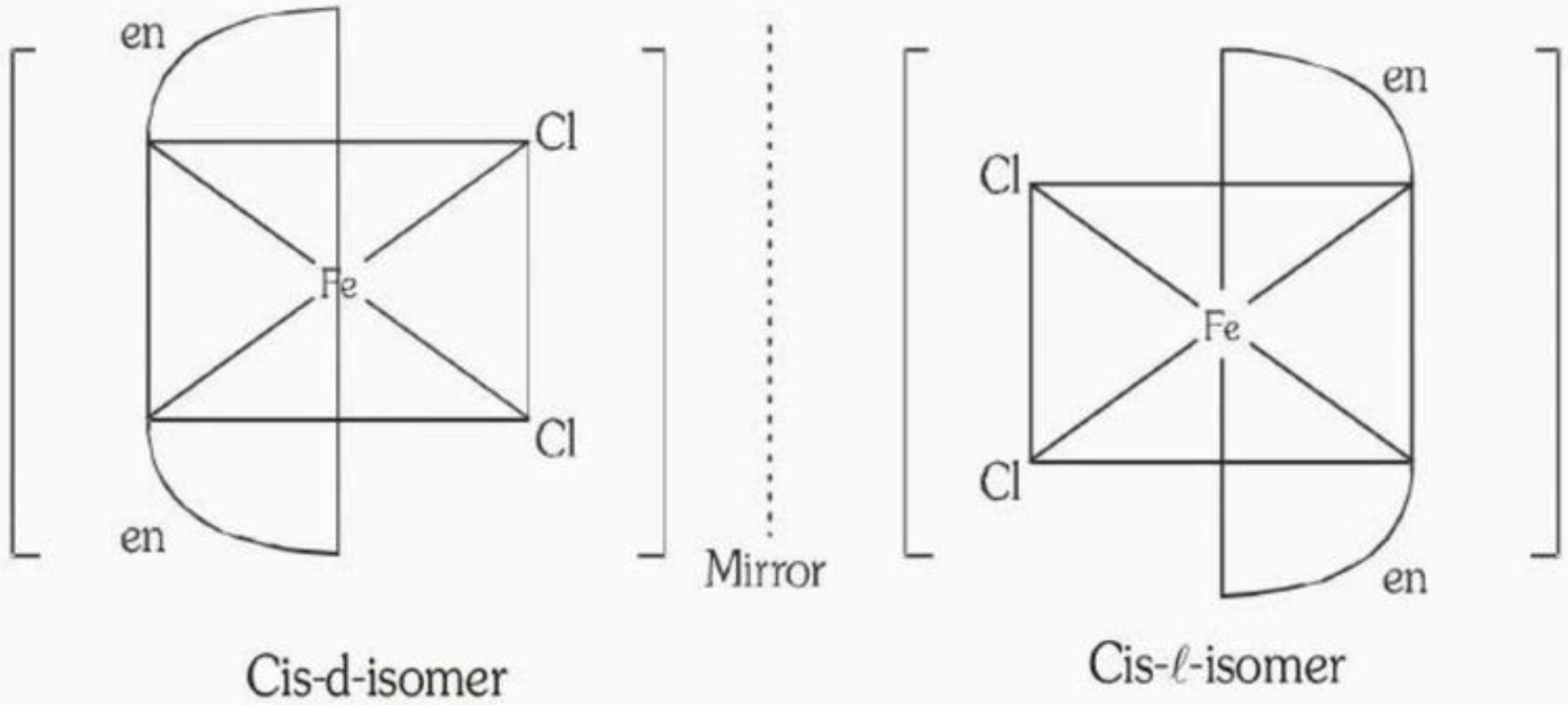
(vii) $[Fe(en)_2Cl_2]$



Cis-d-isomer

Cis-ℓ-isomer

Which of the following sets is/are example of co-ordination isomerism in complexes ?

(1) $[Co(NH_3)_6]\,[Cr(CN)_6]$ and $[Co(CN)_6]\,[Cr(NH_3)_6]$

(2) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

(3) $[Co(NH_3)_5Br]SO_4$ and $[Cr(NH_3)_5SO_4]Br$

(4) $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4]\,[PtCl_4]$

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The number of geometrical isomers of $[Co(NH_3)_3(NO_3)_3]$ are :

(1) 0 (2) 2 (3) 3 (4) 4

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The number of isomeric forms in $[Co(NH_3)_4Cl_2]^{1+}$ ion will be :-

(1) 2 (2) 3 (3) 4 (4) 1

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The complexes $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(ONO)(NH_3)_5]Cl_2$ are the examples of

(1) Coordination isomerism

(2) Ionisation isomerism

(3) Geometrical isomerism

(4) Linkage isomerism

The type of isomerism exhibited in complex $[Pt(NH_3)_4Cl_2]Br_2$ is/are

(1) Linkage isomerism

(2) Ionisation isomerism

(3) Geometrical isomerism

(4) 2 and 3 both

Match the following and choose correct option

Complexes	**e^- configuration**
(P) $[CoCl_6]^{3-}$	(a) $t_{2g}^5\ eg^0$
(Q) $[Co(OX)_3]^{3-}$	(b) $t_{2g}^6\ eg^0$
(R) $[Co(H_2O)_6]^{2+}$	(c) $t_{2g}^5\ eg^2$
(S) $[Fe(CN)_6]^{-3}$	(d) $t_{2g}^4\ eg^2$

	P	Q	R	S
(1)	b	a	c	d
(2)	d	a	b	c
(3)	d	b	c	a
(4)	d	a	c	b

Which order is correct

(1) $[NiCl_6]^{4-} > [NiCl_4]^{2-}$ splitting energy Δ_0

(2) $[Cr(en)_3]Cl_3 > [Cr(H_2O)_6]Cl_3$ crystal field stabilisation energy

(3) $[Co(CN)_6]^{4-} > [Co(CN)_6]^{3-}$ reducing behaviour

(4) All of these

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The complex exhibit lowest energy absorption bond is

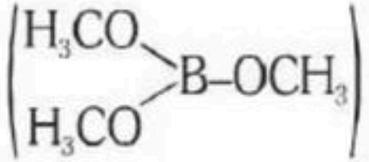
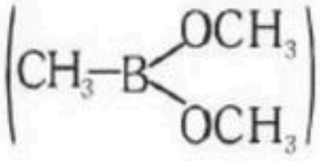
(1) $[NiCl_4]^{2-}$ (2) $[Ni(CO)_4]$ (3) $[Ni(CN)_4]^{2-}$ (4) $[Ni(H_2O)_6]^{2+}$

ORGANOMETALLIC COMPOUNDS

Compound in which C atom of a hydrocarbon or a ligand is directly bonded with a metal/metalloid/non metal like B, P ets is known as organometallic compounds.

eg. R – Zn – R dialkyl zinc (Frankland reagent)
R – Mg – X Alkyl Magnesium halide (Grignards reagent) } OMC

Sodium acetate	$CH_3-\overset{\overset{O}{\|\|}}{C}-ONa$	These are not organometallic compounds because in these compounds metal is not directly attached with carbon atom.
Sodium ethoxide	C_2H_5-O-Na	
Sodium Mercaptide	H_3C-SNa	

$B(OCH_3)_3$  is not OMC and $CH_3B(OCH_3)_2$  is OMC

Carbides and carbonates are not considered OMC because in these compounds metal carbon bond has ionic nature.

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Classification of Organometallic Compounds

OMC can be classified into three main categories–

σ - bonded OMC : These compounds are formed mostly by non transition and metalloid elements.

Ex. R – Mg – X (Grignard's reagent)

$(CH_3)_2Zn$ (Dimethyl zinc or Frankland's reagent)

R_2Cd (dialkyl cadmium)

$(C_2H_5)_4Pb$ (Tetra ethyl lead) – used as antiknocking agent in petrol.

$(C_2H_5)_3Al+TiCl_4$ (Ziegler natta catalyst) – Heterogeneous catalyst, used in polymerisation of alkene.

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π - bonded OMC : These are usaully formed by transition metals.

Ex. Ferrocene $[Fe(\eta^5 - C_5H_5)_2]$

Zeise's salt $K[PtCl_3(\eta^2 - C_2H_4)]$

Chromocene $[Cr(\eta^6 - C_6H_6)_2]$

σ and π - bonded OMC : Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC. The carbonyl compounds of these metals have both σ and π bonds.

Ex. $[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Mn_2(CO)_{10}]$ etc.

The order of energy absorbed which is responsible for the color of complexes

(A) $[Ni(H_2O)_2(en)_2]^{2+}$

(B) $[Ni(H_2O)_4(en)]^{2+}$ and

(C)$[Ni(en)_3]^{2+}$

is

[NEET(UG) 2022]

(1) (A) > (B) > (C)

(2) (C) > (B) > (A)

(3) (C) > (A) > (B)

(4) (B) > (A) > (C)

Match list-I with List-II **[NEET(UG) 2021]**

List-I		**List-II**	
(a)	$[Fe(CN)_6]^{3-}$	(i)	5.92 BM
(b)	$[Fe(H_2O)_6]^{3+}$	(ii)	0 BM
(c)	$[Fe(CN)_6]^{4-}$	(iii)	4.90 BM
(d)	$[Fe(H_2O]_6]^{2+}$	(iv)	1.73 BM

Choose the **correct** answer from the option given below

(1) (a)→(iv); (b)→(ii); (c)→(i); (d)→(iii)

(2) (a)→(ii); (b)→(iv); (c)→(iii); (d)→(i)

(3) (a)→(i); (b)→(iii); (c)→(iv); (d)→(ii)

(4) (a)→(iv); (b)→(i); (c)→(ii); (d)→(iii)

Ethylene diaminetetraacetate (EDTA) ion is

[NEET(UG) 2021]

(1) Hexadenate ligand with four “O” and two “N” donor atoms

(2) Unidenatate ligand

(3) Bidenate ligand with two “N” donor atoms

(4) Tridenate ligand with three “N” donor atoms

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Which of the following is the correct order of increasing field strength of ligands to form coordination compounds ?

[NEET(UG) 2020]

(1) $CN^- < C_2O_4^{2-} < SCN^- < F^-$

(2) $SCN^- < F^- < C_2O_4^{2-} < CN^-$

(3) $SCN^- < F^- < CN^- < C_2O_4^{2-}$

(4) $F^- < SCN^- < C_2O_4^{2-} < CN^-$

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The Crystal Field Stabilisation Energy (CFSE) for $[CoCl_6]^{4-}$ is 18000 cm^{-1}. The CFSE for $[CoCl_4]^{2-}$ will be-

[NEET(UG) 2019 (ODISHA)]

(1) 6000 cm^{-1}

(2) 16000 cm^{-1}

(3) 18000 cm^{-1}

(4) 8000 cm^{-1}

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What is the correct electronic configuration of the central atom in $K_4[Fe(CN)_6]$ based on crystal field theory?

[NEET(UG) 2019]

(1) $t_{2g}^4 e_g^2$

(2) $t_{2g}^6 e_g^0$

(3) $e^3 t_2^3$

(4) $e^4 t_2^2$

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Iron carbonyl, $Fe(CO)_5$ is **[NEET(UG) 2018]**

(1) tetranuclear

(2) mononuclear

(3) trinuclear

(4) dinuclear

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The geometry and magnetic behaviour of the complex $(Ni(CO)_4)$ are

[NEET(UG) 2018]

(1) square plane geometry and diamagnetic

(2) tetrahedral geometry and diamagnetic

(3) square planar geometry and paramagnetic

(4) tetrahedral geometry and paramagnetic

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The type of isomerism shown by the complex $[COCl_2(en)_2]$ is **[NEET(UG) 2018]**

(1) Geometrical isomerism

(2) Coordination isomerism

(3) Lonization isomerism

(4) Linkage isomerism

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Pick out the correct statement with respect to $[Mn(CN)_6]^{3-}$: **[NEET-2017]**

(1) It is sp^3d^2 hybridised and tetrahedral

(2) It is d^2sp^3 hybridised and octahedral

(3) It is dsp^2 hybridised and square planar

(4) It is sp^3d^2 hybridised and octahedral

The correct order of the stoichiometries of AgCl formed when $AgNO_3$ in excess is treated with the complexes: $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$ respectively is :

[NEET 2017]

(1) 1AgCl, 3AgCl, 2AgCl
(2) 3AgCl, 1AgCl, 2AgCl
(3) 3AgCl, 2AgCl, 1AgCl
(4) 2AgCl, 3AgCl, 1AgCl

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The sum of coordination number and oxidation number of the metal M in the complex $[M(en)_2(C_2O_4)]Cl$ (where en is ethylenediamine) is- **[Re-AIPMT 2015]**

(1) 7 (2) 8 (3) 9 (4) 6

The hybridization involved in complex $[Ni(CN)_4]^{2-}$ is (At. No. NI = 28)

[Re-AIPMT 2015]

(1) d^2sp^2

(2) d^2sp^3

(3) dsp^2

(4) sp^3

Which of these statements about $[Co(CN)_6]^{3-}$ is true: **[AIPMT 2015]**

(1) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration

(2) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a high spin configuration

(3) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a high-spin configuration

(4) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration

A magnetic moment of 1.73 BM will be shown by one among the following:

[NEET-UG 2013]

(1) $[CoCl_6]^{4-}$

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

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

(4) $TiCl_4$