



# Coordination Compounds

RAKESH SIR

"CULTIVATING EXCELLENCE IN EVERY STUDENT"  
9814516618



## Concept Ladder



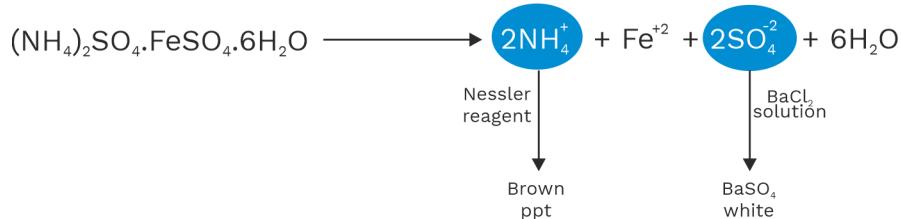
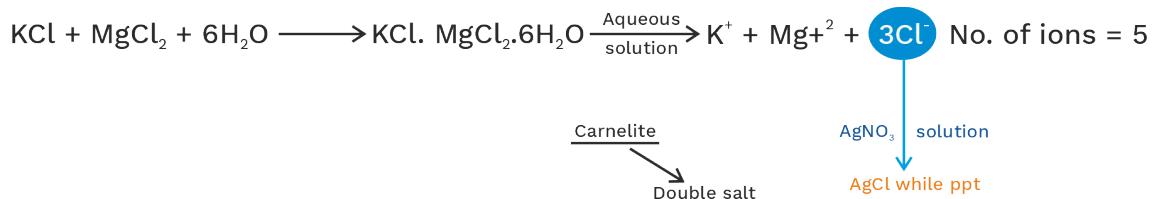
The concept of coordination compounds originates from the tendency for complex formation of transition elements.

## Addition Compounds

When two or more than two simple salts are allowed to chemically combine in a fix ratio then addition compound is formed.

On the basis of behaviour in aqueous solution they are of the following two types.

- Double salt:** - Addition compound in which simple salts don't loss their identity and its aqueous solution give test of its all constitute ions.
- Double salts loss their identity in aqueous solution.



- All Alums are double salt.
- Complex compound:** - Addition compound in which simple salts loss their identity and it's aqueous solution doesn't give test of its all constitute ions.
- Complex compound don't loss their identify in aqueous solution.



Does not ionize to give  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions

## Rack your Brain



State whether the given complexes are double salt or complex compound

- $\text{K}_4[\text{Fe}(\text{CN})_6]$
- $\text{NaCl} \cdot \text{NaF} \cdot 2\text{Na}_2\text{SO}_4$

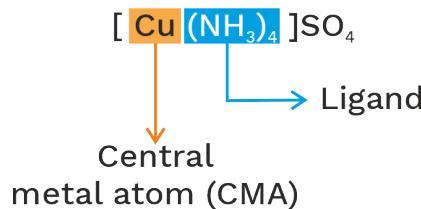


### Classification of Complex Compound

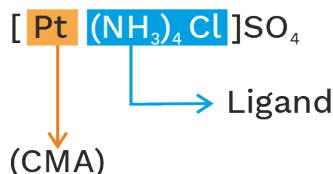
#### 1. On basis of type of ligands

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

Ex.



(ii) **Heteropietic Complex:** - Different type of ligands



#### Concept Ladder



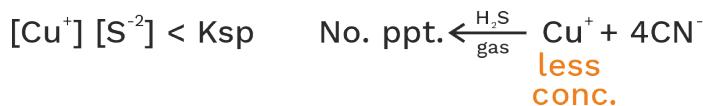
First coordination compound is **Prussian blue**, which was accidentally prepared in 1704 by a Berlin colour maker, prepared by strong heating animal waste and sodium carbonate in an iron container.

#### 2. On the basis of degree of dissociation

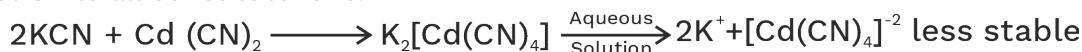
(i) **Perfect complex compound :** Relatively more stable and its aqueous solution doesn't give test of its all constitutive ions.



#### Perfect Complex compound complexion



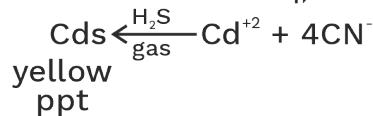
(ii) **Imperfect complex compound:** - Relatively less stable and its aqueous solution gives test of its all constitute ions.



#### Imperfect complex compound

#### Complexion

$\updownarrow$   
More ionisation

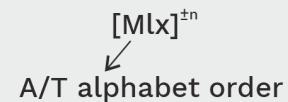




- Imperfect complex compound which undergoes 100% ionisation is known as double salt.
- There is no sharp line between perfect and imperfect complex compound.
- Complex forming tendency decreases down a group in s-block because size increases.

### Representation of complex ion

**Coordination sphere:** -



**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.

### Concept Ladder



d-Block metals have strong complex forming tendency due to smaller size, high charge and presence of vacant orbitals.



### Definitions

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

**Q.1**

Green colour of leaves is due to presence of chlorophyll which is a complex compound. Which metal is present in it?

**A.1**

Magnesium



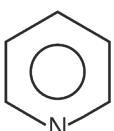
### Classification of ligands

#### (a) On the basis of denticity

##### 1. Monodentate ligand

###### (i) Neutral ligands

H <sub>2</sub> O	aqua	PH <sub>3</sub>	Phosphene
NH <sub>3</sub>	Ammine	p(Ph) <sub>3</sub>	Triphenyl phosphene
CO	Carbonyl	O <sub>2</sub>	Dioxygen
CS	Thiocarbonyl	N <sub>2</sub>	Dinitrogen

NO	Nitrosyl		Pyridine(Py)
CH <sub>3</sub> NH <sub>2</sub>	Methyl Amine		Urea

H<sub>2</sub>N—NH<sub>2</sub> Hydrazine

- Hydrazine never acts as bidentate ligand.

###### (ii) Cationic ligand: -

O <sub>2</sub> <sup>+</sup>	Oxygenium
NO <sup>+</sup>	Nitrosylgium
Or	Nitrosonium
H <sub>2</sub> N—NH <sub>3</sub>	Hydrazinium

###### (iii) Anionic ligands

F <sup>-</sup>	Flurido	S <sup>-2</sup>	Sulphido
	Or fluro		Or sulpho
Cl <sup>-</sup>	Chlorido	OH <sup>-</sup>	hydroxide
	Or chloro		Or hydroxo
Br	Bromido	CH <sub>3</sub> O <sup>-</sup>	Methoxido
	Or bromo		Or methoxo
I <sup>-</sup>	Iodido	O <sub>2</sub> <sup>-</sup>	Superoxido
	Or Ido		Or superoxol
O <sup>-2</sup>	Oxido	O <sub>2</sub> <sup>-2</sup>	Peroxido
			Or peroxy
NO <sub>2</sub> <sup>-</sup>	Nitro	N <sup>-3</sup>	Nitrido
N <sub>3</sub> <sup>-</sup>	Azido	NH <sub>2</sub> <sup>-</sup>	Amido
H <sup>-</sup>	Hydrido		

### Definitions

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



### Concept Ladder



Denticity of the ligands is termed as the number of coordinating or ligating groups present in a ligand.



### Previous Year's Questions

Which of these cannot act as a ligand?

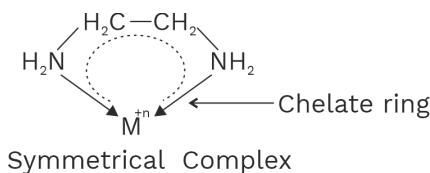
[AIPMT]

- (1) NH<sub>3</sub>      (2) H<sub>2</sub>O  
 (3) CO      (4) NH<sub>4</sub><sup>+</sup>

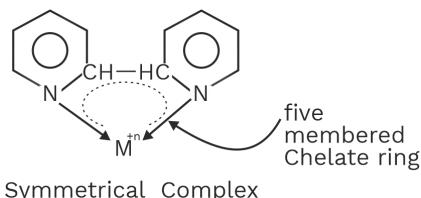


## 2. Bidentate ligands

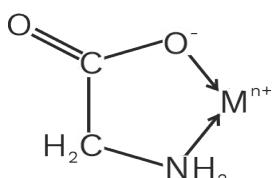
(i) Ethylene diamine (en)  
Or (ethane 1, 2-diamine)



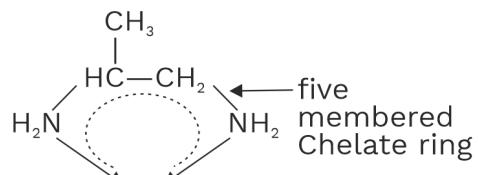
(iii) Dipyridyl (dipy)



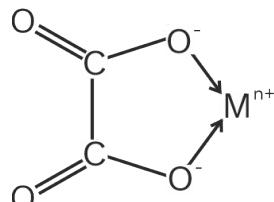
(v) Glycenate (gly)<sup>-</sup>



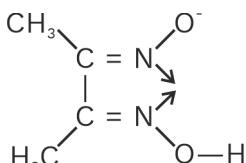
(ii) Propane 1,2-diamine  
Or propylene diamine (Pn)



(iv) Oxalato (OX)<sup>-2</sup>



(vi) Dimethyl glyoximato (dmg)<sup>-</sup>



## 3. Polydentate ligands

All bidentate and polydentate ligand are chelating ligands.

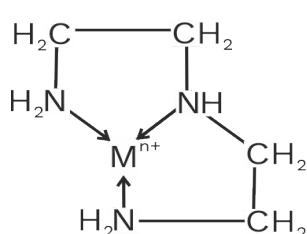
No of chelate ring = Denticity – 1

(i) Diethylenetriamine (dien)

Denticity = 3

No. of rings = 2

Neutral



### Previous Year's Questions



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

[NEET-2013]

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



**(ii) (trien) – Triethylene tetramine**

Denticity = 4

Chelate rings = 3

Neutral

**(iii) Terpyridine**

Denticity = 3

Chelate rings = 2

Neutral

**(iv) Ethylenediamine tetracetato (EDTA)<sup>-4</sup>**

2N                    4(O)

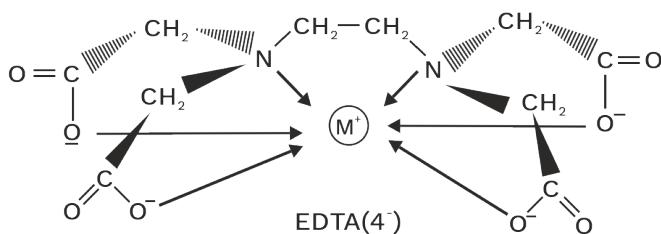
Denticity = 6

Chelate rings = 5

**Concept Ladder**



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



**Rack your Brain**



Explain how dithiocoxalate behaves as ambidentate ligand.

**(v) Ethylenediamine triacetato (EDTA)<sup>-3</sup>**

Denticity = 5

Chelate rings = 4

**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)

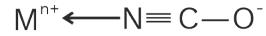
Cynido—N

**(b)**



Cynido (OCN)

Cynido—O



Isocynido (NCO)

Cynido—N

**(c)**



Nilito (ONO)

Nitrilo—O



Nilito (NO<sub>2</sub>)

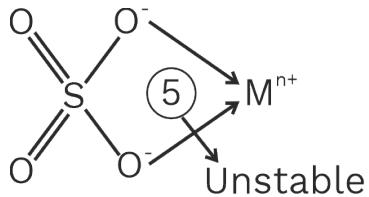
Nitrilo—N



## 5. Flexi dentate

Ligands which can change their denticity

**Ex.**  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3 - \text{COO}^-$ ,  $\text{NO}_3^-$  etc.



**Ex.**  $[\text{Co}(\text{NH}_3)_5 \text{SO}_4]\text{Cl}$

$$\begin{aligned} X + 0 - 2 &= 0 & X &\Rightarrow +3 \\ && C.N &\Rightarrow 6 \end{aligned}$$

5 by  $\text{NH}_3$  + 1 by  $\text{SO}_4$

Monodentate

### (b) On the basis of $e^-$ donating and $e^-$ accepting nature

#### 1. Normal Or classical ligands

Ligands which only donate  $e^-$  pair to CMA and form coordinate  $\sigma$  bond.

**Ex.**  $\text{NH}_2^-$ ,  $\text{OH}^-$ ,  $\text{N}^{3-}$ ,  $\text{Cl}^-$ ,  $\text{O}^{2-}$

#### 2. Non classical or $\pi$ acid or $\pi$ acceptor ligands

Ligands which donate  $e^-$  pair to CMA and form coordinate bond but simultaneously they accept  $e^-$  pair from CN through back bonding (synergic bonding)

**Ex.**  $\text{CO}$ ,  $\text{NO}^+$ ,  $\text{CN}^-$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_5\text{H}_5^-$ ,  $\text{C}_2\text{H}_4$

### Concept Ladder



Coordination number  
 $= \Sigma$  number of ligands  
 $\times$  Dentate character of ligands



### Rack your Brain



Why CO is a stronger ligand than  $\text{NH}_3$  for many metals?

**Q.2** Why only transition metals are known to form  $\pi$  complexes?

**A.2** Transition metals/ions have empty d-orbitals into which the electron-pairs can be donated by ligands containing  $\pi$  electron-pairs can be donated by ligands containing p electrons, i.e., electrons in their  $\pi$  molecular orbitals, e.g.,  $\text{CH}_2=\text{CH}_2$ ,  $\text{C}_5\text{H}_5$ ,  $\text{C}_6\text{H}_6$  etc.

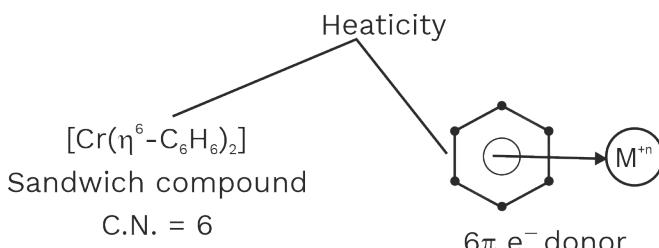


### 3. $\pi$ donor and $\pi$ acceptor ligand

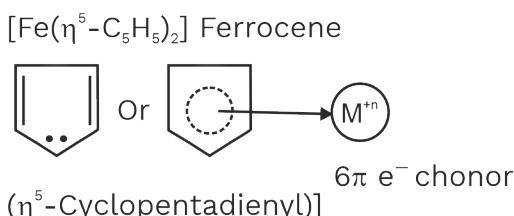
Ligands which donate  $\pi e^-$  to CMA and also accept  $e^-$  density from CMA though synergic bonding.

**Ex.**  $C_6H_6$ ,  $C_5H_5^-$

(i)



(ii)



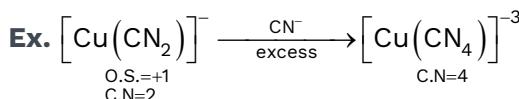
#### Coordination Number

Total no of  $e^-$  pair accepted by CMA

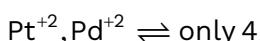
1.  $[\text{Ni}(\text{dmg})_2]$  = 4
2.  $[\text{Pt}(\text{trien})]\text{Cl}_2$  = 4
3.  $[\text{Fe}(\text{EDTA})]^{2-}$  = 6
4.  $[\text{Co}(\text{en})_2\text{Ox}]\text{Cl}$  = 6

#### Some important points

1. Generally C.N of monovalent cation is two and four except



2. Generally C.N of bivalent cation is four and six except.



3. Generally C.N. of trivalent cation is six except some exceptions.

#### Concept Ladder



As per VBT and MOT, it is implicit that the bond order of C—O bond decreases but the C—O bond length increases due to synergic effect.

#### Definitions

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.



#### Previous Year's Questions

Coordination number of Ni in  $[\text{Ni}(\text{C}_2\text{O}_4)_3]^{4-}$  is

**[AIPMT]**

- |       |       |
|-------|-------|
| (1) 3 | (2) 6 |
| (3) 4 | (4) 2 |



4. C.N of tetravalent cation is 6.
5. C.N of CMA depends upon charge of CMA, size of CMA of ligands and concentration of ligand.

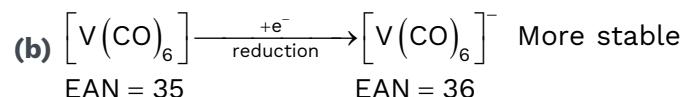
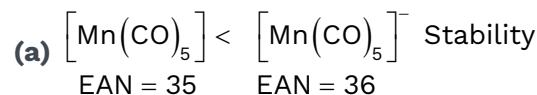
#### Effective Atomic Number (EAN)

Total number of  $e^-$  of CMA after accepting  $e^-$  pair from ligands  
 $ENA = Z - (0.5) + 2 \times C.N.$

1.  $K_4[Fe(CN)_6] \Rightarrow 26 - (+2) + 2 \times 6 \Rightarrow 36 [Kr]$   
O.S. = +2, C.N. = 6
2.  $K_3[Fe(CN)_6] \Rightarrow 26 - (+3) + 2 \times 6 \Rightarrow 35 [Kr]$   
O.S. = +3, C.N. = 6
3.  $[Fe(\eta^5-C_5H_5)_2] \Rightarrow 26 - (+2) + 2 \times 6 \Rightarrow 36 [Kr]$   
O.S. = +2, C.N. = 6

#### Sidgwick rule

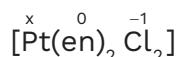
- If EAN of CMA in metal carbonyl is equal to Atomic number of nearest inert gas then the stability of metal is high.



- Sidgwick rule is applicable only for metal carbonyl.

**Q.3** Write the coordination number and oxidation state of Platinum in the complex  $[Pt(en)_2Cl_2]$ .

**A.3** As en is bidentate ligand, coordination number of Pt = 6



$$\therefore x - 2 = 0, x = +2$$

Oxidation state of Pt = 2

#### Concept Ladder



The effective atomic number generally coincides with the atomic number of next inert gas in some cases.



#### Rack your Brain

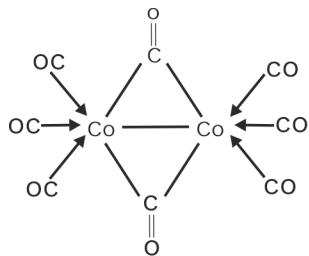
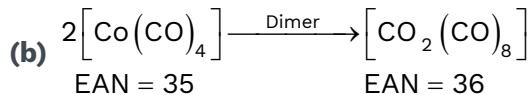
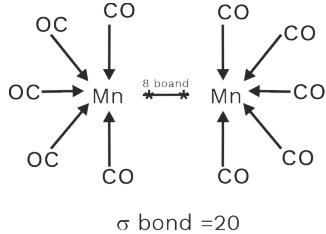
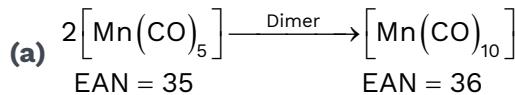


Calculate the EAN of the metal atom in the following

- (i)  $[Cr(CO)_6]$
- (ii)  $[Ni(NH_3)_6]^+$



### EAN Of Polynuclear Metal Carbonyl



### FORMULA AND IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

#### 1. Formula of a Complex

- (a) In formulas of both simple and complex salts, cation precedes the anion. Nonionic compounds are written as single units.
- (b) Complex ions are written inside square brackets without any space between the ions.
- (c) Metal atom and ligands are written in the following order:
  - (i) In the complex part, the metal atom is written first followed by ligands in the order, anionic  $\rightarrow$  neutral  $\rightarrow$  cationic.
  - (ii) If more than one ligand of one type (anionic, neutral or cationic) are present, then they are arranged in English alphabetical order, e.g. between  $\text{H}_2\text{O}$  and  $\text{NH}_2$ ,  $\text{H}_2\text{O}$  should be written first. Similarly, order of  $\text{NO}_2^-$ ,  $\text{SO}_3^{2-}$  and  $\text{OH}^-$  will be  $\text{NO}_2^-$

#### Concept Ladder



In the old system, (i) the ligands are named in the order of negative, neutral and positive without separation by hyphens.  
 (ii) when there are several ligands of same kind, these are listed alphabetically.





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- (iii) When ligands of the same type have similar name for the first atom, then the ligand with less number of such atoms is written first. Sometimes the second atom may be used to decide the order. When number of atoms are also same e.g., Out of  $\text{NO}_2^-$ ,  $\text{NH}_2^-$  will be written first. In  $\text{H}_3$  and  $\ddot{\text{N}}_2$ ,  $\ddot{\text{N}}\text{H}_3$  will be written first as it contains only one N-atom.
- (iv) Polyatomic ligands and abbreviations for ligands are always written in lower case letters. e.g. (en), (py), etc.
- (v) Charge of a complex ion is represented as over script or square bracket.

#### Examples,

$\text{K}_4[\text{Fe}(\text{CN})_6]$  — First cation and then anion

$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Br}$ — $\text{Cl}^-$  (negative ligand) before  $\text{H}_2\text{O}$

#### Q.4

Write the formulae of the following:

- (i) bis (acetylacetonato) oxovanadium (IV)
- (ii) dichloridoplatinum (IV) tetrachloridoplatinate (II)

#### A.4

- (i)  $[\text{V}(\text{acac})_2\text{O}]$
- (ii)  $[\text{PtCl}_2][\text{PtCl}_4]$

#### Q.5

Give the IUPAC names of the complexes

- (i)  $\text{K}[\text{BF}_4]$
- (ii)  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$
- (iii)  $[\text{Mn}_3(\text{CO})_{12}]$

#### A.5

- (i) potassium tetrafluoridoborate (III)
- (ii) bis (cyclopentadienyl) iron
- (iii) dodecacarbonyl trimagnaese (0)

#### Previous Year's Questions



The name of complex ion,  $[\text{Fe}(\text{CN})_6]^{3-}$  is

[NEET-2015]

- (1) hexacyanitoferate (III) ion
- (2) tricyanoferrate (III) ion
- (3) hexacyanidoferate (III) ion]
- (4) hexacyanoiron (III) ion



## 2. Nomenclature of Coordination Compounds

Mononuclear coordination compounds are named by following these rules:

- In both the positively and negatively charged coordination compounds, the cation is named first followed by the anion.
- The name of the central atom/ion is written after the ligands are named in alphabetical order. (This procedure is reversed in writing its formula).
- Names of the anionic ligands end in -o.

### Rack your Brain



Write the name for iron metal when it is used as complex anion?

Symbol	Name as ligand	Symbol	Name as ligand
$\text{N}^{3-}$	Azido	$\text{OH}^-$	Hydroxo
$\text{Cl}^-$	Chloro	$\text{CO}_3^{2-}$	Carbonato
$\text{O}^{2-}$	Peroxo	$\text{C}_2\text{O}_4^{2-}$	Oxalato
$\text{Br}^-$	Bromo	$\text{SO}_4^{2-}$	Sulphato
$\text{O}_2\text{H}^-$	Perhydroxo	$\text{NO}_3^-$	Nitrato
$\text{CN}^-$	Cyano	$\text{SO}_3^{2-}$	Sulphito
$\text{S}^{2-}$	Sulphido	$\text{CH}_3\text{COO}^-$	Acetato
$\text{O}_2^{2-}$	Peroxo	$\text{NO}_2^-$	(Bonded through oxygen) nitrite
$\text{NH}_2^-$	Amido		(Bonded through nitrogen) nitro

- Names of neutral and cationic ligands are the same except for aqua for  $\text{H}_2\text{O}$ , ammine for  $\text{NH}_3$ , carbonyl for  $\text{CO}$  and nitrosyl for  $\text{NO}$ . These are placed within parentheses ( ).

Symbol	Name as ligand	Symbol	Name as ligand
$\text{H}_2\text{O}$	Aqua	$\text{NO}$	Nitrosyl
$\text{NH}_3$	Ammine	$\text{CS}$	Thiocarbonyl
$\text{CO}$	Carbonyl		



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(e) Positive ligands are named as:

Symbol	Name as ligand
$\text{NH}^{+4}$	
$\text{NO}^+$	Nitrosylum
$\text{NH}_2\text{NH}_3^+$	Hydrazinium

(f) Oxidation state of the metal in a cation, anion or a neutral coordination compound is indicated by a Roman numeral in parenthesis.

(g) When the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. In an anion, Co is called cobaltate. For some metals, their Latin names are used in the complex anions, e.g. ferrate for Fe.

(h) Nomenclature of a neutral complex molecule is done in the similar way as that of a complex cation.

The following examples illustrate the nomenclature for coordination compounds:

- $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$  is named as: Triaminetriaquachromium (III) chloride
- $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]_2\text{SO}_4$  is named as: Tris(ethane-1, 2-diammine) cobalt (III) sulphate
- $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$  is named as: Diamminesilver (I) dicyanoargentate (I)

(i) Ligands which join two metals are known as 'Bridge ligands' and they are prefixed by 'μ' (mu).

E.g.  $\left[ (\text{NH}_3)_4\text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \\ \diagdown \\ \text{NH}_2 \end{array} \text{Co}(\text{NH}_3)_4 \right] (\text{NO}_3)_4$ , in this

complex.

### Concept Ladder



- Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands in a coordination compound.
- When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, and the ligand to which they refer is placed in parentheses.

### Rack your Brain

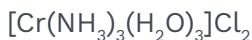


Explain with an example how the name of the metal differs in cation and anion even though they contain the same metal ions.



### 3. Nomenclature of Complexes

#### (I) Cationic Complex



triaminetriaquachromium (III) chloride

- (i) The number of the individual ligands are indicated by prefix like mono, di, tri, etc. and ligands are named in an alphabetical order.
- (ii) Central metal atom and oxidation state indicated by Roman numeral in parenthesis.
- (iii) Name of ionisable anion.

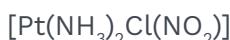
#### (II) Anionic Complex



Potassium hexacyanoferrate (III)

- (i) Name of ionisable metal and oxidation state
- (ii) Name of ligand in an alphabetical order
- (iii) Central metal atom + ate and oxidation state

#### (III) Neutral Complex



Diammine chloronitrito-N-platinum (II)

- (i) Name of ligands in an alphabetical order
- (ii) Central metal atom and oxidation states.

**Q.6**

Give the IUPAC names of the complexes

- |                                       |  |
|---------------------------------------|--|
| (i) $\text{K}[\text{BF}_4]$           | (ii) $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ |
| (iii) $[\text{Mn}_3(\text{CO})_{12}]$ |  |

**A.6**

- (i) potassium tetrafluoridoborate (III)
- (ii) bis (cyclopentadienyl) iron
- (iii) dodecacarbonyl trimagnaese (0)

#### Concept Ladder



Polyatomic ligands are enclosed in parentheses but all ligands are formulated without any space in between.



#### Previous Year's Questions



The hypothetical complex chlorodiaquatriammine cobalt (III) chloride can be represented as

**[AIPMT]**

- (1)  $[\text{CoCl}(\text{NH}_3)_3(\text{H}_2\text{O})_2]\text{Cl}_2$
- (2)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_3]$
- (3)  $[\text{Co}(\text{NH}_2)_3(\text{H}_2\text{O})_2\text{Cl}]$
- (4)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$



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### Magnetic Nature

**Ferromagnetic :** Fe, Co, NO<sub>2</sub>

Spin magnetic moment = ( $\mu$ ) =  $\sqrt{n(n+2)}$  B.M.

$$n = 1 \quad \mu = 1.73$$

$$n = 2 \quad \mu = 2.83$$

$$n = 3 \quad \mu = 3.87$$

$$n = 4 \quad \mu = 4.90$$

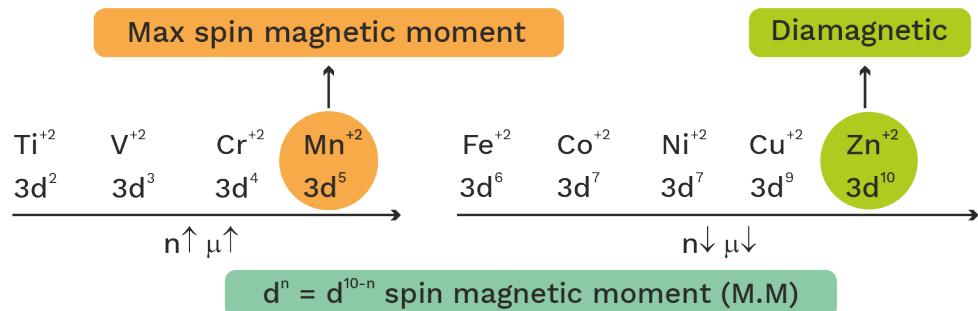
$$n = 5 \quad \mu = 5.92$$

### Concept Ladder



The magnetic property depends upon oxidation state of central metal atom or ion and nature of ligand.

### Spin magnetic moment of bivalent cation of 3d series



### Spin magnetic moment of trivalent lanthanoids

- 'Na' (Neodymium) has max. M.M. among lanthanoids due to sum of spin magnetic moment + orbital magnetic moment.

### Bonding in complex compound

#### 1. Werner's Theory

According to Werner, central metal atom has two types of valencies

#### Primary valency

Equal to O.S. of CMA

Satisfied by anions

Non directional and ionisable

Not helpful in geometry prediction

#### Secondary Valency

Equal to C.N. of CMA

Satisfied by ligands

Directional and non ionisable

Helpful in geometry prediction



- All secondary valencies have specific arrangement according to C.N.

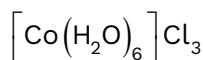
CN = 2 → Linear

CN = 3 → Trigonal planar

CN = 4 → Tetrahedral or square planar

CN = 5 → TBP or square pyramidal

CN = 6 → Octahedral



O.S. ⇒ +3CN = 6

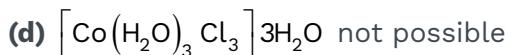
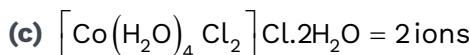
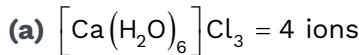
Primary valency =+3

Secondary valency =6

Satisfied by 3Cl Satisfied by 6H<sub>2</sub>O

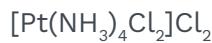
- Possible complex of CaCl<sub>3</sub>. 6H<sub>2</sub>O

O.S = +3 C.N. = 6



- Pt Cl<sub>4</sub>. 4NH<sub>3</sub>  $\xrightarrow{\text{AgNO}_3 \text{ solution}}$  2 mol AgCl ppt

O.S = +4 C.N. = 6



- Pt Cl<sub>4</sub>. 2HCl  $\xrightarrow{\text{AgNO}_3 \text{ Solution}}$  No. ppt

O.S = +4 C.N = 6



Hexachloro platinic (IV) acid

- Pt Cl<sub>2</sub>. 4NH<sub>3</sub>  $\xrightarrow{\text{AgNO}_3 \text{ Solution}}$  2 mole AgCl ppt

O.S = +2 C.N. = 4



### Concept Ladder



In 1898, Werner proposed the concept of a primary valence and a secondary valence for a metal ion.

### Rack your Brain



What are the limitation of Werner's theory?

### Previous Year's Questions



Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?

[AIPMT-2012]

- (1)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- (2)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$
- (3)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- (4)  $[\text{Co}(\text{NH}_3)_6]^{3+}$



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### Valence Bond Theory

- Central metal atom releases  $e^-$  according to its O.S.
- Central metal atom will provide vacant orbitals according to its coordination number.
- These vacant orbital undergo histrion and form coordinate  $\sigma$  bond with donor atoms.
- Hybridisation state of central metal atom depends upon C.N. and nature of ligand M.M. dipole moment, isomerism etc. are also helpful in hybridisation prediction.

C.N = 2 sp linear

C.N = 3  $sp^2$  Trigonal planar

C.N = 4  $sp^3$  Tetrahedral

$dsp^2$  square planar

C.N = 5  $sp^3d$  TBP

$dsp^3$  (i) TBP

(ii) Square pyramidal ( $dx^2y^2$ )

C.N = 6  $sp^3d^2$  Octahedral (SBP)

$d^2sp^3$  Octahedral (SBP)

- In presence of strong field ligand (SFL), the pairing of  $(n-1)d$   $e^-$  is possible before hybridisation but this pairing is not possible in presence of WFL.

S or S-donor

O-donor

N-donor

C-donor

$I^- < Br^- < SN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA < NH_3 < en < NO_2^- < CN^- < CO$

X or S-donor < O-donor

WFL

N – Donor < C-donor

SFL

For 3d series Metal

- All ligands acts as SFL with 4d and 5d series metal ions.
- $P^-$  acts as SFL with  $Ni^{+4}$
- $H_2O$  and  $C_2O_4^{2-}$  acts as SFL with  $CO^{+3}$
- $NH_3$  act as WFL with  $Fe^{+2}$  and  $Mn^{+2}$ .
- $H_2O$  act as SFL with  $Cu^{+2}$  (C.N = 4)

### Rack your Brain



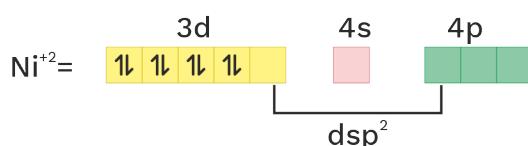
Name the type of spin complex involved for hybridisation of inner  $(n - 1)d$  orbital.



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

O.S. = +2 C.N = 4 ligand = SFL

Ni =  $3d^84s^2$



square planar  
diamagnetic

(2)  $[\text{Ni}(\text{Cl}_4)]^{-2}$  or  $[\text{Ni}(\text{SCN})_4]^{-2}$

O.S. = +2 C.N = 4 ligand = WFL

Ni =  $3d^84s^2$



$\text{sp}^3$

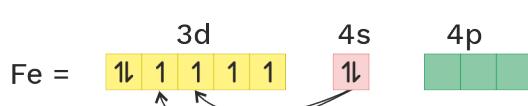
Tetrahedral  
paramagnetic

$$\mu = \sqrt{8}$$

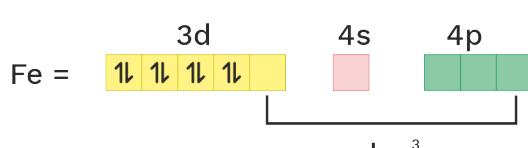
(3)  $[\text{Fe}(\text{CO})_5]$  D.M. = 0

O.S. = 0 C.N. = 5

Ligand = SFL



s-e shifting  
(not depends on strength of ligand)



diamagnetic  
 $\mu = 0$  so Trigonal Bipyramidal  
inner orbital complex  
low spin complex

### Concept Ladder



The number of unpaired electrons in the complex, determines the geometry of the complex as well as hybridization of the central metal ion and vice-versa.

### Rack your Brain



Find the value of magnetic moment for  $[\text{CuCl}_4]^{-2}$ .

### Previous Year's Questions



The geometry and magnetic behaviour of the complex  $[\text{Ni}(\text{CO})_4]$  are

[NEET-2018]

- (1) square planar geometry and diamagnetic
- (2) tetrahedral geometry and diamagnetic
- (3) square planar geometry and paramagnetic
- (4) tetrahedral geometry and paramagnetic



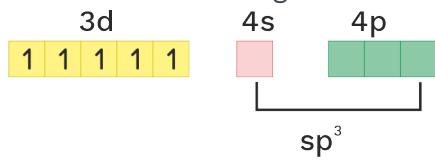
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O.S. = +2 C.N. = 4 Ligand = WFL



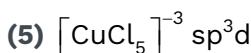
Tetrahedral paramagnetic

$$\mu = \sqrt{35}$$

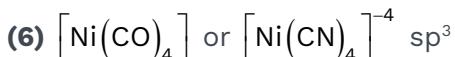
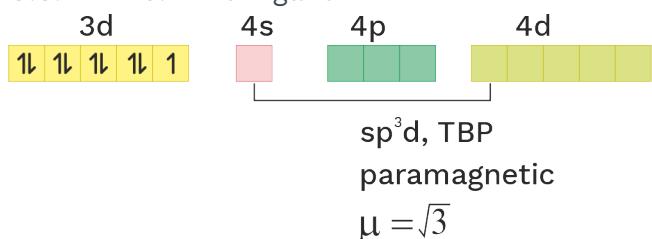
### Concept Ladder



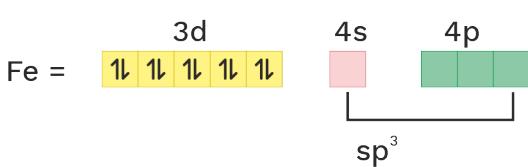
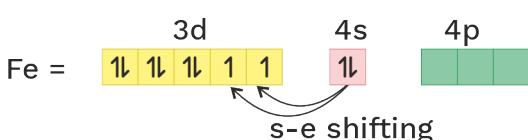
Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity.



O.S. = +2 C.N. = 5 Ligand = WFL



O.S. = 0 C.N. = 4 Ligand = SFL



Tetrahedral diamagnetic

### Rack your Brain



Find hybridization of  $[\text{Ni}(\text{CN})_5]^{-3}$  compound.

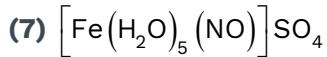
### Previous Year's Questions



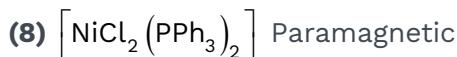
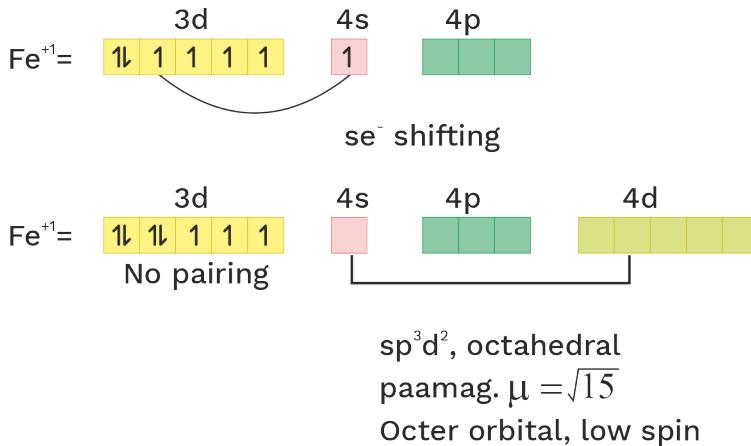
Aluminium chloride in acidified aqueous solution forms a complex 'A', in which hybridisation state of Al is 'B'. What are 'A' and 'B', respectively?

[NEET-2019]

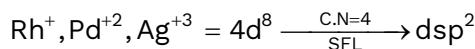
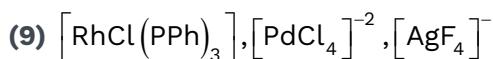
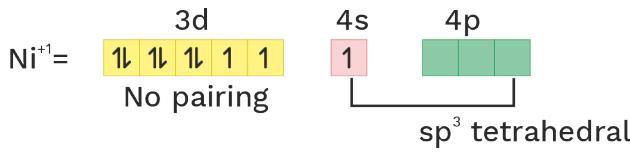
- (1)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , sp<sup>3</sup>d<sup>2</sup>
- (2)  $[\text{Al}(\text{H}_2\text{O})_4]^{3+}$ , sp<sup>3</sup>
- (3)  $[\text{Al}(\text{H}_2\text{O})_4]^{3+}$ , d<sup>2</sup>sp<sup>2</sup>
- (4)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , d<sup>2</sup>sp<sup>3</sup>



O.S = +1 CN = 6 Ligand = WFL



O.S = +2 CN = 4 Ligand = WFL = No pairing



$\text{Co}^+, \text{Ni}^{+2}, \text{Cu}^{+3} = 3\text{d}^8$
$\text{Rh}^+, \text{Pd}^{+2}, \text{Ag}^{+3} = 4\text{d}^8$
$\text{Ir}^+, \text{Pt}^{+2}, \text{Au}^{+3} = 5\text{d}^8$

↓

CN = 4  
 dsp<sup>2</sup>, square planar  
 diamag.

### Previous Year's Questions

Pick out the correct statement with respect to  $[\text{Mn}(\text{CN})_6]^{3-}$

[NEET-2017]

- (1) It is  $\text{sp}^3\text{d}^2$  hybridised and tetrahedral
- (2) It is  $\text{d}^2\text{sp}^3$  hybridised and octahedral
- (3) It is  $\text{dsp}^2$  hybridised and square planar
- (4) It is  $\text{sp}^3\text{d}^2$  hybridised and octahedral



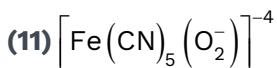
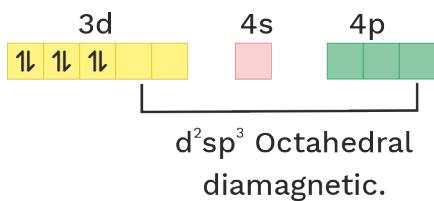
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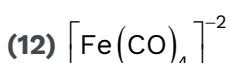
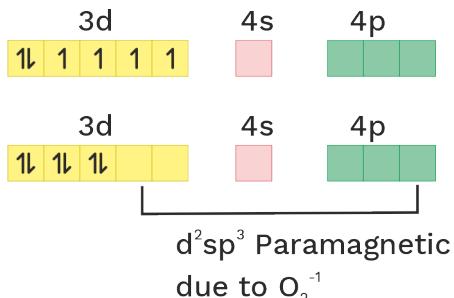
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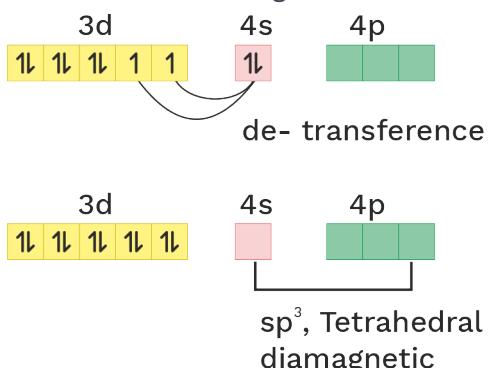
O.S. = +4 CN = 6



O.S. = +2 CN = 6 Ligand = AFL



O.S. = -2 CN = 4 Ligand = SPL



### Drawbacks of VBT

- (1) It can't explain stability of complex compound
- (2) It can't explain colour of complex compound
- (3) It can't explain d e⁻ transference
- (4) It can't explain pairing of (n-1)d e⁻
- (5) It doesn't give any criteria for classification of AFL and WFL.

### Concept Ladder



Pt(II) and Au(III) always form square planar complexes irrespective of their ligands being strong or weak.

### Rack your Brain



What is the shape of  $[\text{Co}(\text{NH}_3)_6]^{+2}$  compound?

### Previous Year's Questions



A magnetic moment at 1.73 BM will be shown by one among the following options

[NEET-2013]

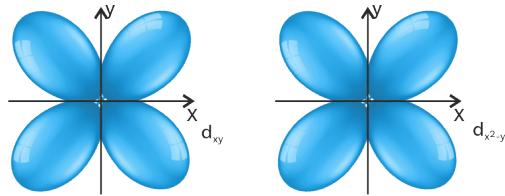
- (1)  $\text{TiCl}_4$
- (2)  $[\text{CoCl}_6]^{4-}$
- (3)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$
- (4)  $[\text{Ni}(\text{CN})_4]^{2-}$



### CFT for octahedral complex

$$d_{xy}, d_{yz}, d_{zx} = t_{2g}$$

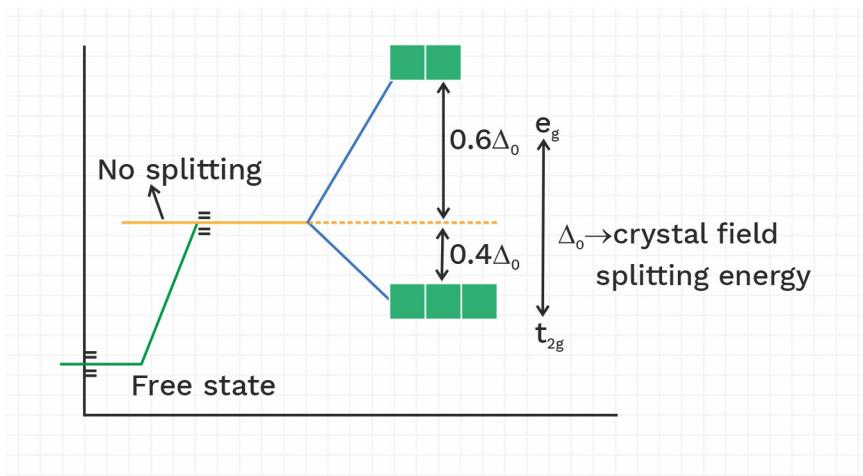
$$d_{z^2}, d_{x^2-y^2} = e_g$$



### Concept Ladder



CFT is an electrostatic model which considers the metal ligand bond to be ionic occurring purely due to the electrostatic interaction between the metal ion and the ligand.



**Q.7**

Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for  $d^4$  ion if  $\Delta_0 < P$ .

**A.7**

In a free transition metal ion, all the five d-orbitals are degenerate but when it is involved in a complex formation, the degeneracy is split into two sets of d-orbitals. This is called crystal field splitting.

The difference of energy between the two sets of d-orbitals is called crystal field splitting energy (CFSE).

The lower energy set of three d-orbitals is called  $t_{2g}$  and the higher energy set of two d-orbitals is called  $e_g$ . The three electrons first enter into  $t_{2g}$ , one in each orbital. If  $\Delta_0 < P$ , the 4th electron will enter  $e_g$ . Hence, the configuration will be  $t_{2g}^3 e_g^1$ .



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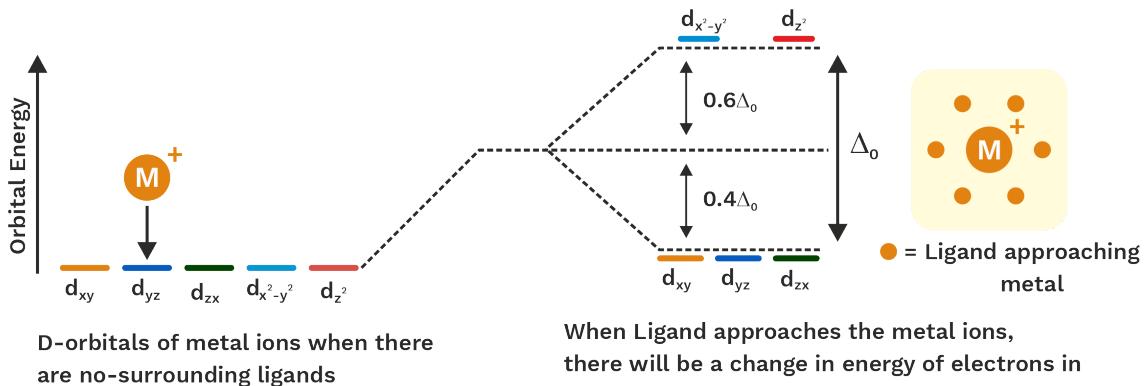
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## CRYSTAL FIELD THEORY

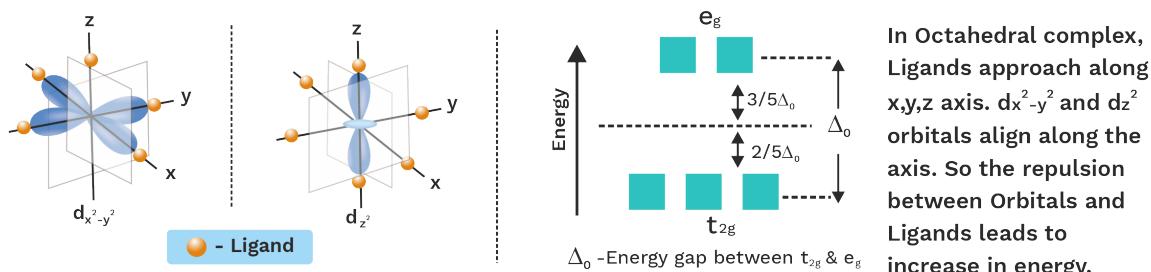
In crystal field theory bonding between metal and ligands is purely electrostatic.

Ligands are considered as negative point charges.

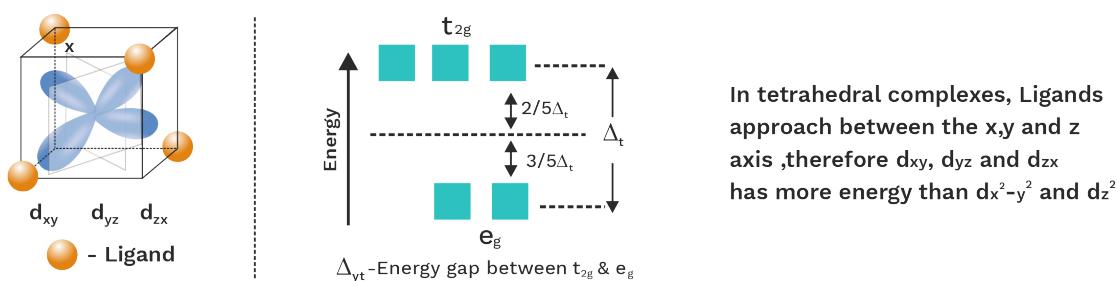
### What Happens When Ligands Approach A Metal



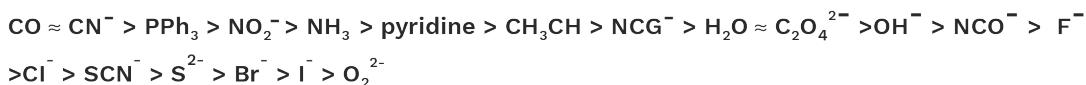
### Orbital Splitting In Octahedral Complexes



### Orbital Splitting In Tetrahedral Complexes



### Strength Of Ligands





### D<sup>n</sup> system

Electronic configuration of (n-1) d<sup>-</sup> of CMA (after splitting) depends upon 2 type of energies are :

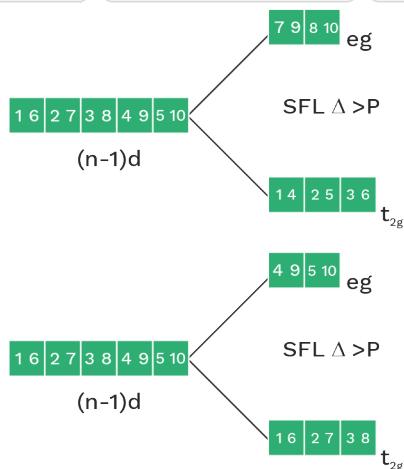
(1)  $\Delta_{0(2)}$  Pairing energy (P)

There are two conditions

(1) In presence of SFL  $\Delta_0 > P$

(2) In presence of WFL  $\Delta_0 < P$

D <sup>n</sup>	Presence of SFL	Presence of WFL
D <sup>1</sup>	t <sub>2g</sub> <sup>1</sup> eg <sup>0</sup>	t <sub>2g</sub> <sup>1</sup> eg <sup>0</sup>
D <sup>2</sup>	t <sub>2g</sub> <sup>2</sup> eg <sup>0</sup>	t <sub>2g</sub> <sup>2</sup> eg <sup>0</sup>
D <sup>3</sup>	t <sub>2g</sub> <sup>3</sup> eg <sup>0</sup>	t <sub>2g</sub> <sup>3</sup> eg <sup>0</sup>
D <sup>4</sup>	t <sub>2g</sub> <sup>4</sup> eg <sup>0</sup>	t <sub>2g</sub> <sup>3</sup> eg <sup>1</sup>
D <sup>5</sup>	t <sub>2g</sub> <sup>5</sup> eg <sup>0</sup>	t <sub>2g</sub> <sup>3</sup> eg <sup>2</sup>
D <sup>6</sup>	t <sub>2g</sub> <sup>6</sup> eg <sup>0</sup>	t <sub>2g</sub> <sup>4</sup> eg <sup>2</sup>
D <sup>7</sup>	t <sub>2g</sub> <sup>6</sup> eg <sup>1</sup>	t <sub>2g</sub> <sup>5</sup> eg <sup>2</sup>
D <sup>8</sup>	t <sub>2g</sub> <sup>6</sup> eg <sup>2</sup>	t <sub>2g</sub> <sup>6</sup> eg <sup>2</sup>
D <sup>9</sup>	t <sub>2g</sub> <sup>6</sup> eg <sup>3</sup>	t <sub>2g</sub> <sup>6</sup> eg <sup>3</sup>
D <sup>10</sup>	t <sub>2g</sub> <sup>6</sup> eg <sup>4</sup>	t <sub>2g</sub> <sup>6</sup> eg <sup>4</sup>



### Concept Ladder



Complexes possessing d<sup>0</sup> or d<sup>10</sup> configuration of a metal ion are always diamagnetic.



### Rack your Brain



Explain how d-d transition is responsible for the colour of transition metal complexes?

### Concept Ladder



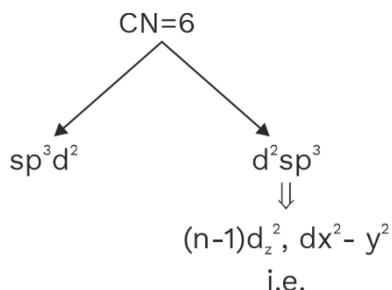
Complexes like CrO<sub>4</sub><sup>2-</sup>, CrO<sub>7</sub><sup>2-</sup> and MnO<sub>4</sub><sup>-</sup> have d<sup>0</sup> configuration of the metal ion but still exhibit intense colour. Here the colour is caused by the charge transfer spectra (CT) and not by the d-d transition.





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### Hybridisation State and Magnetic Nature

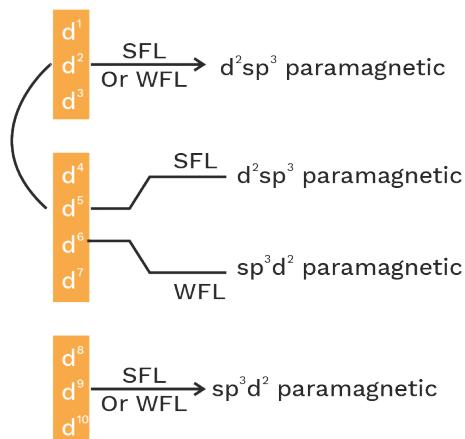


### Concept Ladder



It is observed that the higher the charge on the central metal atom (or oxidation state), higher is the value for CFSE.

### Configuration of metal in



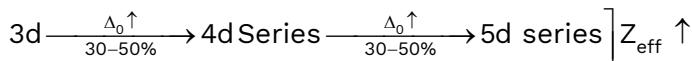
### Rack your Brain



Write the assumption made for Crystal Field theory?

### Factor affecting splitting energy

- (1)  $\Delta_0 \propto$  charges of central metal atom
- (2)  $\Delta_0 \propto Z_{\text{eff}}$  of central metal atom



- (3)  $\Delta_0 \propto$  strength of ligand
- (4) Geometry of complex

$$\Delta_{\text{sp}} > \Delta_0 > \Delta_t$$

$$\Delta_t = \frac{4 \Delta_0}{9}$$

### Previous Year's Questions

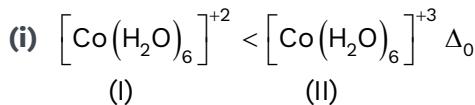


The crystal field stabilisation energy (CFSE) for  $[\text{CoCl}_6]^{4-}$  is  $18000 \text{ cm}^{-1}$ . The CFSE for  $[\text{CoCl}_4]^{2-}$  will be  
**[NEET-2019]**

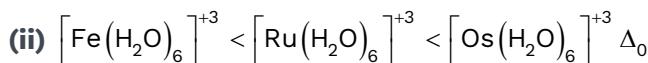
- (1)  $6000 \text{ cm}^{-1}$
- (2)  $16000 \text{ cm}^{-1}$
- (3)  $18000 \text{ cm}^{-1}$
- (4)  $8000 \text{ cm}^{-1}$



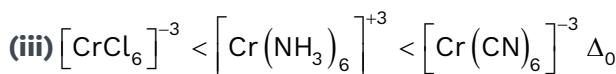
### Examples,



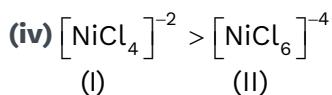
$\text{H}_2\text{O}$  acts as strong ligand with  $\text{Co}^{+3}$ , so splitting energy for (II) is higher than (I)



Fe is a 3d series element whereas Ru and Os are 4d and 5d transition elements, so  $\text{H}_2\text{O}$  is weaker ligand but it acts as strong ligand with higher d series transition element.



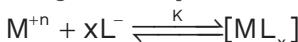
Ligand strength for  $\text{CN}^- > \text{NH}_3 > \text{Cl}^-$



(I) is tetrahedral and (II) is octahedral complex

$$\Delta_t > \Delta_o$$

### Stability of complex compound

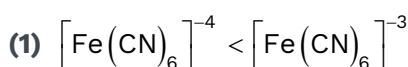


$$(\text{formation constant}) K = \frac{[\text{ML}_x]}{[\text{M}^{+n}] [\text{L}^-]^x}$$

$K \uparrow$ , stability  $\uparrow$

Stability	$\propto$	charge of CMA
	$\propto$	$Z_{\text{eff}}$ of CMA
	$\propto$	Strength of ligand
	$\propto$	chelation effect
	$\propto$	$\frac{1}{\text{size of CMA}}$

### Stability order :



$$\text{O.S.} = +2 \quad \text{O.S.} = +3$$

### Concept Ladder



Complexes normally exhibit two kinds of stabilities viz. thermodynamic and kinetic.

- Thermodynamic stability deals with the metal-ligand bond energy, stability constants etc that affect the equilibrium.
- Kinetic stability deals with the rates of reaction of complexes in a solution.

### Previous Year's Questions

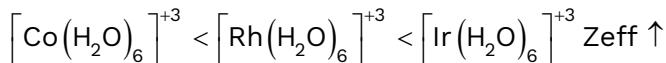


Crystal field splitting energy for high spin d<sup>4</sup> octahedral complex is  
**[NEET-2013]**

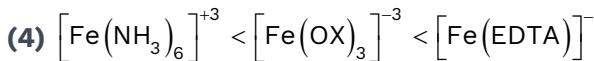
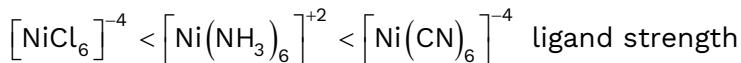
- |                      |                      |
|----------------------|----------------------|
| (1) – 1.2 $\Delta_0$ | (2) – 0.6 $\Delta_0$ |
| (3) – 0.8 $\Delta_0$ | (4) – 1.6 $\Delta_0$ |



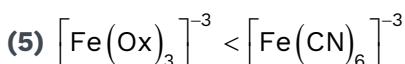
(2)



(3)

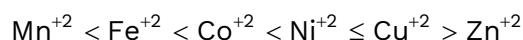


No chelation    3 chelate    5 chelate rings



Chelation synergic bonding

(6) Irving williams series



### C.F.S.E. (Crystal field stabilisation energy)

Extra stabilisation (released energy) due to splitting in comparison to no splitting

### Concept Ladder



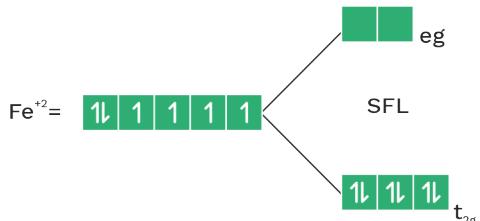
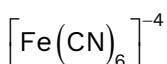
Weak ligands favor high spin complexes because they cannot pair up the electrons against Hund's rule while strong ligands favor low spin complexes.

**Q.8**

Calculate CFS for the given compound :



**A.8**

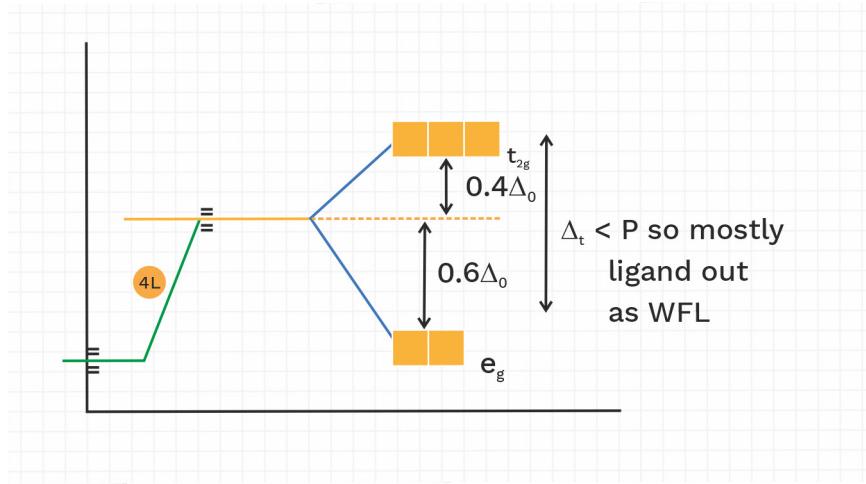


Priority to 2P = N, New pairs  
 $\text{CFS} = -0.4\Delta_0 \times 6 + 0.6\Delta_0 \times 0$   
 $= -2.4\Delta_0$   
 Total pairs



$$CFSE = 0.4\Delta_0 n_{t_{2g}} + 0.6\Delta_0 n_{e_g} + xp = \text{new pairs}$$

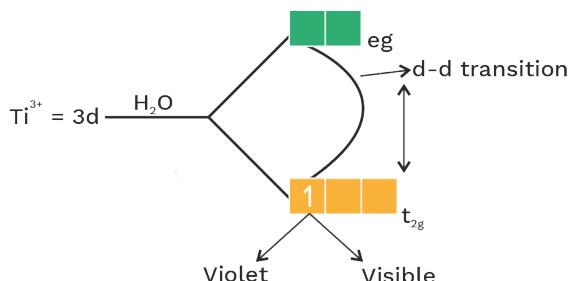
**CFT for Tetrahedral complex**



### Colour

#### (a) d-d Transition

- Colour of complex compound is due to d-d transition
- Ag. Solution of  $Ti^{+3}$  is violet .



- Colour of complex compound depends upon splitting energy.
- Complex become colourless in absence of ligand filled (no ligand, no splitting, no transition)
- Colour of f-block compounds is due to f-f transition.

#### Rack your Brain



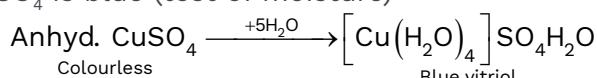
What is the difference between inner and outer orbital complexes?



**Examples,**

(a)  $[\text{Ti}(\text{H}_2\text{O})_6]^+$  become colourless on heating due to removal of water molecules.

(b) Anhydrous  $\text{CuSO}_4$  is colourless but hydrated  $\text{CuSO}_4$  is blue (test of moisture)



**(b) Charge transfer**

Colour of some compound is due to charge transfer ( $e^-$  transition) from anion to metal ion.

$\text{KMnO}_4$	purple	$\text{Mn}^{+3}$ or $\text{Cr}^{+6} = 3\text{d}^0$ (no d – d transition)
$\text{K}_2\text{Cr}_2\text{O}_7$	Orange	
$\text{Na}_2\text{CrO}_4$	Yellow	
$\text{CrO}_2\text{Cl}_2$	Blood Red	

**(c) Polarisation**

- Colour of same compound can be explained on the basis of polarisation.
- Polarisation increase, possibility of finding colour increase

**Examples,**

- (1)  $\text{AgF}$  colourless but  $\text{AgI}$  yellow.
- (2)  $\text{PbF}_2$  colourless but  $\text{PbI}_2$  yellow.
- (3)  $\text{HgF}_2$  colourless but  $\text{HgI}_2$  Red.
- (4)  $\text{ZnS}$  colourless but  $\text{CdS}$  yellow.  $\text{HgS}$  Black

**Concept Ladder**



In many complexes the d-orbital split takes place in the two sets  $t_{2g}$  and  $e_g$ , which possess different energies. the difference in energies of  $t_{2g}$  and  $e_g$  lies in the visible region of the spectrum and their helps transisition metal complexes to absorbe color.



**Rack your Brain**



Why  $\text{SnF}_4$  is colourless besides  $\text{SnI}_2$  is red in colour?

**Q.9**

On the basis of crystal field theory, write the electronic configuration for  $\text{d}^4$  ion if  $\Delta_0 > P$ .

**A.9**

In this case, the 4th electron will enter into  $t_{2g}$ , i.e., pairing in one of the  $t_{2g}$  orbitals will take place. Hence, electronic configuration will be  $t_{2g}^4$ .



# Colour of Co-ordination compounds

What is **Colour** Wheel ?

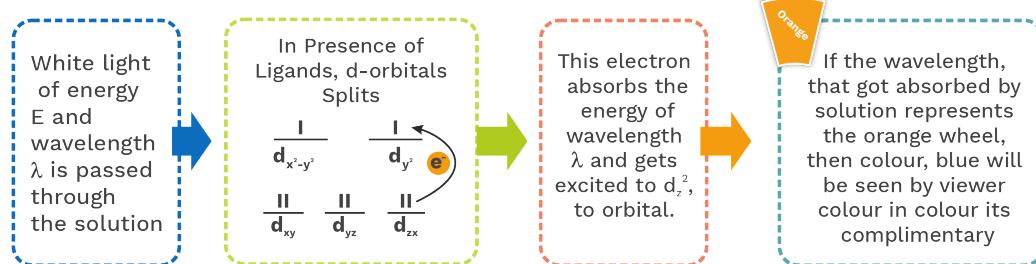


Generally white light is a mix of two opposite colors on colour wheel. These two colour are called component colours.

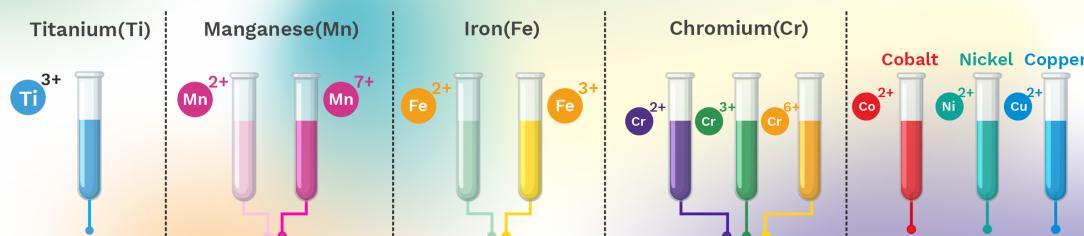


Why we are seeing **Blue**, Why Not **Red or Green** ?

Let's see what happens inside the solution containing co-ordination compound when we cast a white light, on it



## Colours shown by metals in various oxidation states





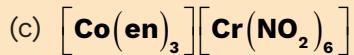
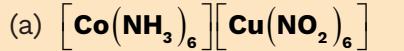
### Structural Isomerism

- Same molecular formula but different structural formula

#### (1) Coordination Isomerism

It arises due to exchange of ligands between complex cation and complex anion.

**Q.10** How many Coordination isomers are there in the given compounds?



**A.10** (a)

$\text{Co}^{+3}$	$\text{Cu}^{+3}$
$\text{NH}_3 : \text{NO}_2^-$	$\text{NH}^3 : \text{NO}_2^-$
6 : 0	0 : 6
5 : 1	1 : 5
4 : 2	2 : 4
3 : 3	Netural
2 : 4	4 : 2
1 : 5	5 : 1
0 : 6	6 : 0

Total no. of Coordination Isomers = 6

(b)

$\text{Pt}^{+2}$	$\text{Pt}^{+2}$
$\text{NH}_3 : \text{Cl}^-$	$\text{NH}_3 : \text{Cl}^-$
4 : 0	0 : 4
3 : 1	1 : 3
2 : 2	Netural
1 : 3	3 : 1
0 : 4	4 : 0

Total no. of Coordination Isomers = 2



(c)

Co	Cr <sup>+6</sup>
en : NO <sub>2</sub>	NO <sub>2</sub> : en
3 : 0	6 : 0
2 : 2	4 : 1
1 : 4	2 : 2
0 : 6	0 : 3

Total no. of Coordination Isomers = 4

(d)

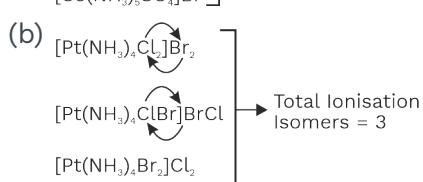
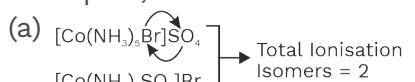
Pt <sup>+2</sup>	Zn
NH <sub>3</sub> : Cl	Cl : NH <sub>3</sub>
4 : 0	4 : 0
3 : 1	3 : 1
2 : 2	2 : 2
1 : 3	1 : 3

Total no. of Coordination Isomers = 4

## (2) Ionisation Isomerism

- Structural isomer which give differ ions in aqueous solution
- Ionization isomerism is the result of the exchange of groups or ions between the coordinating sphere and the ionization sphere.

Examples,



### Previous Year's Questions



The type of isomerism shown by the complex  $[\text{CoCl}_2(\text{en})_2]$  is]

**[NEET-2018]**

- (1) geometrical isomerism
- (2) coordination isomerism
- (3) ionization isomerism
- (4) linkage isomerism



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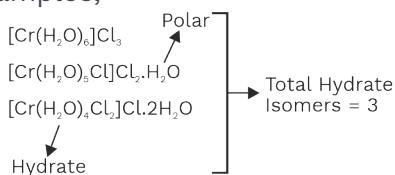
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### (3) Hydrate Isomerism

- It is a special type of ionisation isomerism in which number of water molecules differ in coordination sphere/outside region.

Examples,



### Concept Ladder

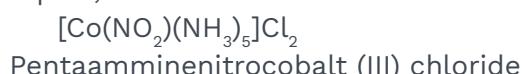


Complexes of formula  $MA_2B_2$  and  $MA_2BC$  types have two geometrical isomers, whereas  $MA_4$ ,  $MA_3B$  and  $MAB_3$  do not show geometrical isomerism when A & B are monodentate ligands.

### (4) Linkage Isomerism

- It arises due to presence of ambidentate ligand.

Examples,



### (5) Polymerisation Isomerism

- Complexes which have different molecular formula but have same empirical formula. It is not a true isomerism.

Example,



### Rack your Brain

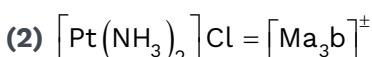
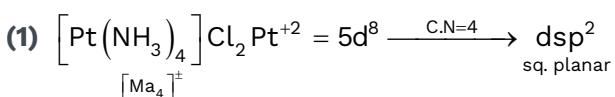


Can in a complex compound water molecules behave in two ways? Explain in brief.

### Geometrical Isomerism in square planar complexes

- Tetrahedral complexes don't show 'Geometrical Isomerism'.
- Square planar complexes can show 'Geometrical Isomerism'.
- Any two identical ligands at  $180^\circ$  show Trans.
- All identical ligands at  $90^\circ$  show Cis.

Examples,



(aa) (ab) No G.I.

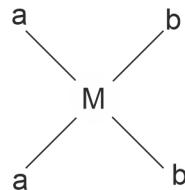
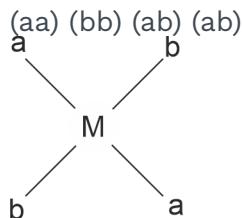
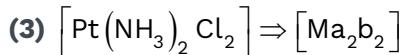
### Previous Year's Questions



The complexes  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  are the examples of which type of isomerism?

[NEET-2011]

- Linkage isomerism
- Ionization isomerism
- Coordination isomerism
- Geometrical isomerism

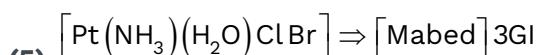


Is  $[\text{Pt}(\text{NH}_3)_2 \text{Cl}_2]$  — it is used as anticancer agent.



(aa) (bc) (bc) (ac)

Trans cis

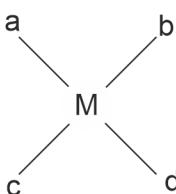
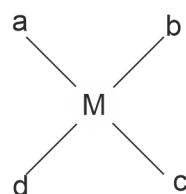
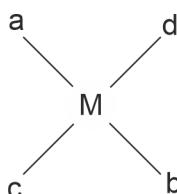


(ab) (cd), (ac) (bd), (ad)(bc) 2cis+1 trans

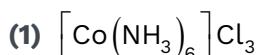
### Concept Ladder



Complexes of type  $\text{MA}_4\text{R}_2$  exist in cis and trans forms and both forms are optically inactive due to plane of symmetry whereas complexes of type  $\text{MA}_3\text{B}_2$  exist in facial and meridional form but both are optically inactive.

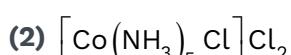


- Geometrical and Optical Isomerism in octahedral complexes



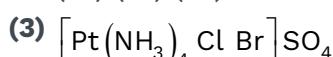
$[\text{Ma}_6]^{\pm}$  optically inactive

(aa) (aa) (aa) No GI



$[\text{Ma}_5\text{b}]^{\pm}$

(aa) (aa) (ab) No GI



$[\text{Ma}_4\text{bc}]^{\pm}$  2GI

(aa) (aa) (bc) (aa) (ab) (ac) O-inactive

### Previous Year's Questions



The complex,  $[\text{Pt}(\text{py})(\text{NH}_3)\text{BrCl}]$  will have how many geometrical isomers?

[NEET-2011]

- (1) 3  
 (3) 0

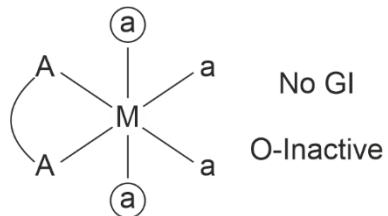
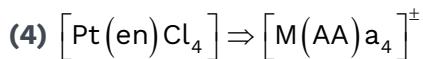
- (2) 4  
 (4) 2



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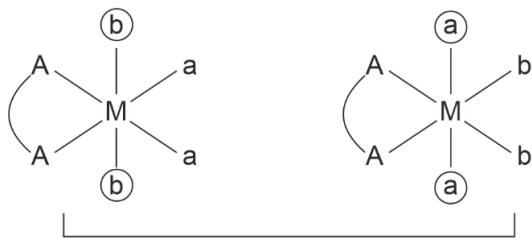
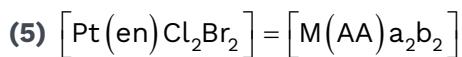
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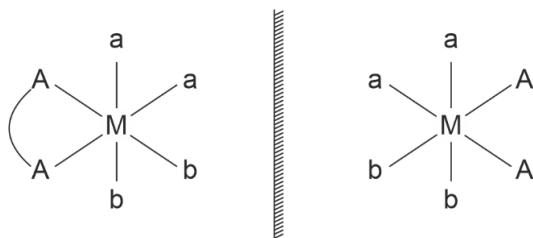
### Rack your Brain



How many geometrical isomers are possible for the  $[\text{Ni}(\text{NH}_3)_4]^{+2}$ ?



Trans, O-Inactive

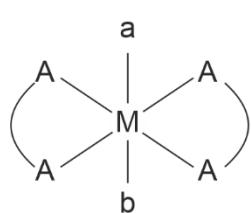
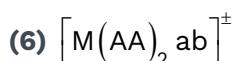


Cis, O-active  
(Ab) (Aa) (ab)

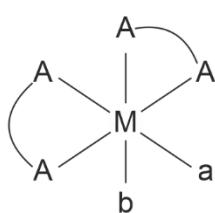
GI = 3

O-active = 3

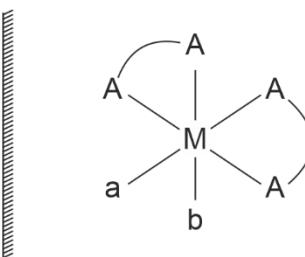
S.I. = 4



Trans



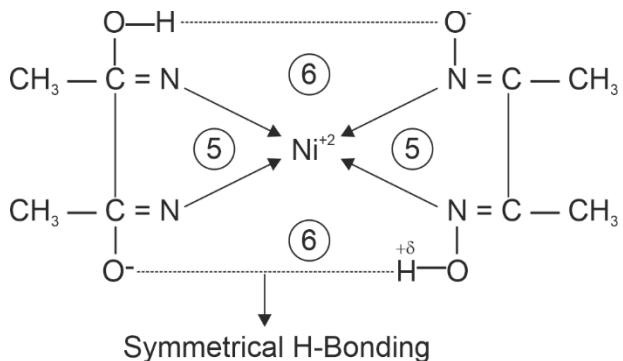
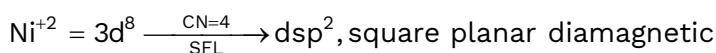
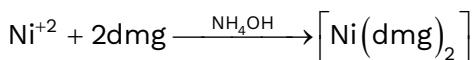
Cis, O-Inactive



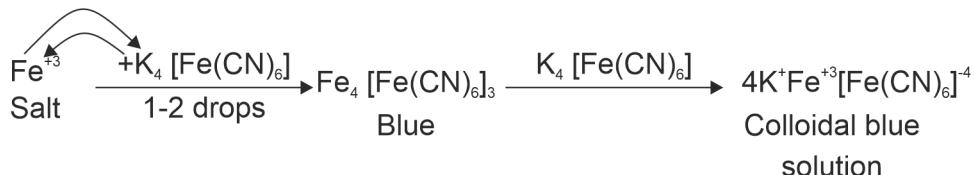
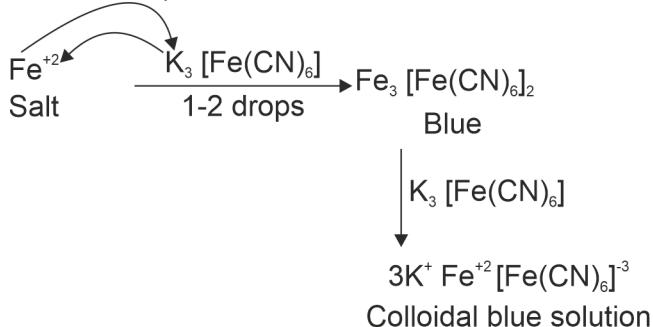
GI=2  
O-Active = 2  
SI = 3

## **Application of Complex compound**

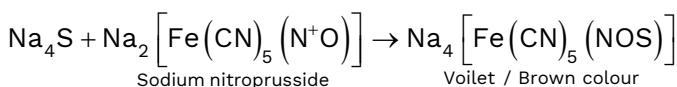
### (1) Test of Ni<sup>2+</sup>



## (2) Test of $\text{Fe}^{+2}$ , $\text{Fe}^{+3}$ and $\text{Cu}^{+2}$



### (3) Test of sulphide ion

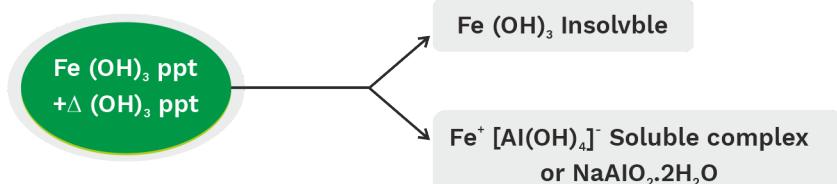


Rack your Brain



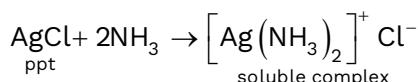
Explain in brief how by forming complexes, silver and gold can be extracted from metals.

#### (4) Separation of hydroxides or oxides

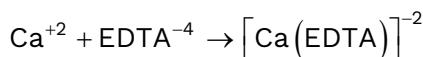


(5) If excess amount of KCN is added into  $\text{CuSO}_4$  solution then insoluble CuCN is formed which later into soluble complex.

(6) AgCl or AgBr ppt (not AgI) are soluble in NH<sub>3</sub> or NH<sub>4</sub>OH



(7)  $[\text{EDTA}]^{-4}$  is used for estimation and removal of hardness of  $\text{H}_2\text{O}$ .



(8) Wilkinson catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  is used for hydrogenation of alkene.

(9) Biological importance: -

- (a) Chlorophyll → Mg  
(b) Vit-B<sub>12</sub> → Co  
(c) Carboxypeptidase → Zn  
(d) Plastocyanin → Cu  
(e) Insulin → Zn  
(f) Haemoglobin → Fe<sup>+2</sup>  
(g) Hboglobin → Fe<sup>+2</sup>



Light blue colour of aq. solution of  $\text{CuSO}_4$  term into dark blue in presence of ammonia or  $\text{NH}_4\text{OH}$  but in presence of acid there is no colour change.

**Q.11** Describe with an example of each, the role of coordination compounds in :  
(i) Biological system      (ii) Analytical chemistry  
(iii) Medicinal chemistry

**A.11** (i) Vit. B-12, it is a antipernicious anemia factor.  
(ii) Determining and estimation of metal  
(iii) EDTA is used in lead poisoning.



### Organometallic Compound

Compounds in which carbon atom of hydrocarbon part is directly bonded with metal or metalloid.

OMC	Not OMC
R-MgX	$\text{Cu}_3\text{-COO}^-\text{Na}^+$
R-Zn-R	$\text{C}_6\text{H}_5\text{O}^-\text{Na}^+$
Frankland reagent	$\text{CaCO}_3$
R-Cd-R	$\text{CaC}_2$
$(\text{Cu}_3)_3\text{As}$	NaCN
$(\text{R}_2\text{SiO})_n$	$\text{Ti}(\text{OC}_6\text{H}_5)_4$
$[\text{Ni-(CO)}_4]$	

### Types

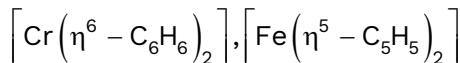
#### (1) $\sigma$ Bonded OMC

$(\text{C}_2\text{H}_5)_4\text{Pb}$  T.E.L used as anti knocking agent

$[\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}]$  Ziggler natta catalyst (Heterogenous catalyst) = used for polymerisation of alkene.

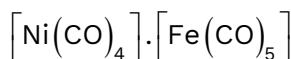
#### (2) $\pi$ Bonded OMC

Presence of  $\pi$  donor ligand

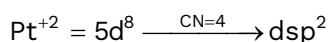
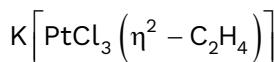


#### (3) $\sigma$ and $\pi$ bonded OMC

Presence of synergic bonding



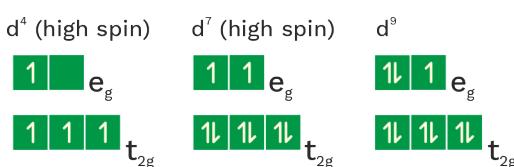
### Trans effect



square planar diamagnetic

### John Teller effect

Distortion in octahedral geometry due to unsymmetrical  $e^-$  cloud in eg set of orbitals.



### Definitions

The compounds in which carbon forms a bond with an atom (metal/non-metal) which is less electronegative than carbon, then the compound as organometallic compound.

### Rack your Brain



Why compounds like alkoxides, carbides and cyanides are not termed as organometallic compounds?

### Previous Year's Questions



An example of a sigma bonded organometallic compound is

**[NEET-2017]**

- (1) Grignard's reagent
- (2) ferrocene
- (3) cobaltocene
- (4) ruthenocene



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**Q.12** A coordination compound  $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$  precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write the structural formula of the compound and name it.

**A.12** The structural formula will be  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ . Tetraquaquadichlorido chromium(III) chloride is the name of this compound.

**Q.13** Why are low spin tetrahedral complexes not formed?

**A.13** The crystal field splitting energy of tetrahedral complexes is too low. It is lower than pairing energy so, the pairing of electrons is not favoured and therefore the complexes cannot form low spin complexes.

**Q.14** Explain why  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has a magnetic moment value of 5.92 BM whereas  $[\text{Fe}(\text{CN})_6]^{3-}$  has a value of only 1.74 BM.

**A.14**  $\text{H}_2\text{O}$  is a weak field ligand for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , won't cause pairing of electrons, therefore there are 5 unpaired electrons.  $\text{CN}^-$  is a strong field ligand for  $[\text{Fe}(\text{CN})_6]^{3-}$  so,  $\text{Fe}^{3+}$  has six unpaired electrons which will cause pairing of all the electrons. So, the electrons will start pairing leaving behind one unpaired electron.

**Q.15** Name the type of isomerism when ambidentate ligands are attached to a central metal ion. Give two examples of ambidentate ligands.

**A.15** Ambidendate ligands are those having different two binding sites.

Examples: Isothiocyanato Thiocyanato and Nitrite-N Nitrito-O

The type of isomerism when ambidentate ligands are attached to a central metal ion is called linkage isomerism because they only differ in the atom that is linked to the central metal ion.



**Q.16**  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is blue while  $\text{CuSO}_4$  is colourless. Why?

**A.16** In  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  molecule is a ligand. Whereas, in  $\text{CuSO}_4$ , there are no  $\text{H}_2\text{O}$  molecules to act as ligands, so no crystal field splitting happens and for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as electrons will excite to higher d-orbital and show colour.

**Q.17** Why do compounds having similar geometry have a different magnetic moment?

**A.17** They differ in the number of paired and unpaired electrons. A strong field ligand will cause pairing of electrons while a weak field ligand will not cause pairing. Pairing or not pairing will change the number of unpaired electrons, which affects the magnetic moment.

**Q.18** Why are low spin tetrahedral complexes not formed?

**A.18** For tetrahedral complexes, the crystal field splitting energy is too low. It is lower than pairing energy so, the pairing of electrons is not favoured and therefore the complexes cannot form low spin complexes.

**Q.19** Based on crystal field theory explain why Co(III) forms a paramagnetic octahedral complex with weak field ligands whereas it forms a diamagnetic octahedral complex with strong field ligands.

**A.19** The electronic configuration will be  $t_{2g}^4 e_g^2$ . It has 4 unpaired electron and paramagnetic. With weak ligand  $\Delta_0 < p$ . The configuration with strong field ligand will be  $t_{2g}^6 e_g^0$ , the  $\Delta_0 > p$  and there won't be any unpaired electron therefore diamagnetic.



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## Summary



- In coordination compounds - central atom acts as lewis acid and ligands act as lewis base.
- Trans isomer does not show optical isomerism due to presence of symmetry. Only Cis isomer show optical isomerism due to presence of unsymmetry.
- Geometrical isomerism is not possible for complexes of type  $MA_4$  and  $MA_3B$ .
- $MA_2X_2Y_2$  type of complexes show both optical and geometrical isomerism.
- (i) Octahedral complexes of type  $MA_3B_3$  from 2 isomeric forms.  
(ii) Octahedral complexes of type MABCDEF from 15 isomeric forms.
- $CO$ ,  $CN^-$  and  $NO_2^-$  ligands cause passing of  $e^-$  in central metal atom.
- Zeisse's salt  $K[PtCl_3(\eta^2-C_2H_4)]$   
Ferrocene  $[Fe(\eta^2-C_5H_5)_2]$ .
- Cis platin – cis  $[PtCl_2(NH_3)_2]$  is used in treatment of cancer.
- (i) Zegler - Natta Catalyst is  $(PH_3P)_3RhCl$  is use in hydrogenation of alkenes.  
(ii) Wilkinson's catalyst  $(Ph_3P)_3RhCl$  is used in hydrogenation of alkenes.
- Bleaching powder is mixed salt –  $CaOCl_2$ ,  $Ca^{2+} + Cl^- + OCl^-$ .
- Effectivfe atomic no. (EAN rule) by Sidgwick :  
 $EAN = Z - (O.N.) + 2 \times (C.N.)$   
where  $Z$  = At. no. of central atom.  
 $O.N.$  = Oxidation no. of central atom.  
 $C.N.$  = Co-ordination of central metal atom.
- EDTA is hexadentate ligand — It has six donar atoms; 2 nitrogen atoms and 4 oxygen atoms.
- CO is called  $\pi$  acid ligand due to back bonding present in it.
- In  $CuSO_4 \cdot 5H_2O$  (solid), Copper is co-ordinated to 4 water molecules.