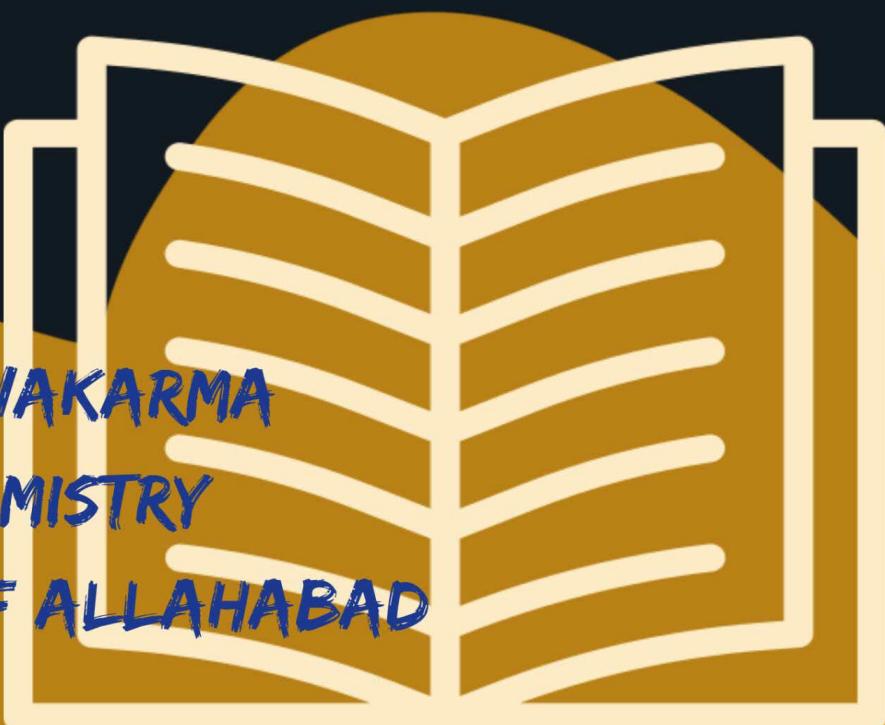


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# B.Sc. Chemistry Handwritten Notes

For 2nd Year Students



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# Chemistry of Element of

## First Transition Series

### Transition Element

The transition element are those in which element or ion have partially filled electron  $(n-1)d$  orbitals is called transition element. They are also called d-block element.

According to definition, Cu, Ag, Au and their monovalent cation should not be considered to transition element. Similarly, Zn Cd, Hg and their bivalent cation should not be considered to be d-block element.

There are three complex series transition element ( $3d$ ,  $4d$ ,  $5d$ ) of 10 element and incomplete  $4^{th}$  series ( $6d$ ) of three element

### Position in periodic table

d-block element have been placed in between s- and p-block element in the

long form of periodic table. They occurs in 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup> and 7<sup>th</sup> of periodic table. In 4<sup>th</sup> transition series i.e. 3d, 4d 5d and 6d series each series start from IIIb group and end at IIb group of the periodic table.

Periods    IIIB    IVB    VIB    VIIB    VIIIB    IB    IIB

4 (3d-series) Sc   Ti   V   Cr   Mn   Fe   Co   Ni   Cu   Zn

5 (4d-series) Y   Zr   Nb   Mo   Tc   Ru   Rh   Pd   Ag   Cd

6 (5d-series)

7 (6d-series)

First transition series or 3d-series

First transition series lie in 4<sup>th</sup> period from Sc to Zn. Since the energy of 4s-orbital is lower than the 3d-orbital. The additional electron would enter the 3d-orbital after the complete of 4s-orbital.

These have 10 elements are also called 3d-series element.

## Properties of first transition series

1-

### Electronic configuration

The electronic configuration of element of 3d-series is given below. In this series element generally contain two electrons in their ns-orbital except Cr and Cu.

21 Sc -  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$

সংক্ষ

22 Ti -  $[Ar] 4s^2, 3d^2$   
টীচর

23 V -  $[Ar] 4s^2, 3d^3$   
বে

24 Cr -  $[Ar] 4s^1, 3d^5$   
ক্র

25 Mn -  $[Ar] 4s^2, 3d^5$   
মিন

26 Fe -  $[Ar] 4s^2, 3d^6$   
ফের

27 Co -  $[Ar] 4s^2, 3d^7$   
কো

28 Ni -  $[Ar] 4s^2, 3d^8$   
নাই

29 Cu -  $[Ar] 4s^1, 3d^{10}$   
কু

30 Zn -  $[Ar] 4s^2, 3d^{10}$   
জিন

Q- Atomic radii —

The atomic radii of first transition series generally decrease with increase in the atomic number. This is due to increase in nuclear charge.

A.g. Sc	T <sup>o</sup> V Cr Mn Fe Co Ni Cu Zn
in Å <sup>-1</sup> 1.67 1.47 1.34 1.25 1.26 1.16 1.16 1.15 1.24 9.738	1.67 1.47 1.34 1.25 1.26 1.16 1.16 1.15 1.24 9.738

3- Ionic radii —

Like atomic radii, ionic radii also decrease with increase in atomic number across a series.

4 - Ionisation potential —

The value of ionisation potential of first transition element lie in between s-block and p-block element. The ionisation potential generally increases with moving from left to right across a first transition series.

I.P. Sc	T <sup>o</sup> V Cr Mn Fe Co Ni Cu Zn
I- 6.5 6.8 6.7 6.74 7.4 7.9 7.06 7.63 7.72 9.37	6.5 6.8 6.7 6.74 7.4 7.9 7.06 7.63 7.72 9.37
II- 12.8 13.5 14.6 16.4 15.6 16.1 17.01 18.1 20.3 18.0 (in eV)	12.8 13.5 14.6 16.4 15.6 16.1 17.01 18.1 20.3 18.0 (in eV)

## 5- Oxidation state -

Most of transition element show several oxidation state in their compound. This is due to fact that in addition to using electron of ns-orbital in the compound formation, a variable number of  $(n-1)$  d electrons can be used to this purpose.

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

## 6 - Metallic character -

All these transition element are hard malleable and ductile metals. They have relatively high density, melting and boiling point. These property indicate the atom in these elements are held together by strong metallic bond these are good conductor of heat and electricity.

## Catalytic properties —

Most of the first transition elements and its compound act as catalyst in various reaction due to incomplete of d-orbitals.

Example — In Habour process the formation of  $\text{NH}_3$ , Fe acts as catalyst.

## Magnetic properties —

When a magnetic field applied the substance mainly two types of magnetic properties is produced. These are either paramagnetic or diamagnetic.

### Paramagnetic substance —

A paramagnetic substance is attract in a magnetic field. The paramagnetic behavior is arises due to one or more unpaired electron in the orbital. The magnetic behavior of transition metal is expressed in term of magnetic movement. The magnetic movement of the transition element can be calculated by

Following formula -

$$M = Jn(n+2) \text{ B.M.}$$

Diamagnetic substance -

Diamagnetic substance repelled by the magnetic field because they have paired electron. Diamagnetic substance does not exist the absence of magnetic field. The magnetic movement produce by the one electron is cancelled by that produce by another electron because each electron has equal and opposite magnetic movement. Hence the magnetic movement of diamagnetic is zero.

Formation of complex -

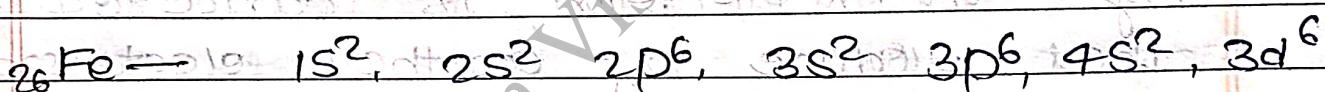
Transition element form complex compound due to presence of unpaired electron and small size and highly charge ion with vacant orbital in

complex compound Legand molecule donot a pair of electron to vacant orbital of central metal

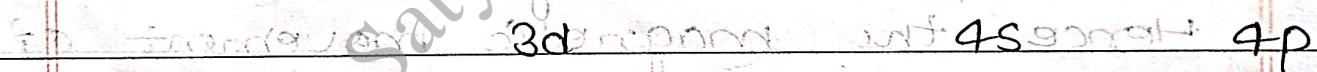
atom and form co-ordinate bond between central metal atom and ligand. The number of co-ordinate in complex compound is called co-ordinate number.

Example -  $K_4 [Fe(CN)_6]$

where Fe is the central metal atom which have +2 oxidation number. Fe<sup>2+</sup> and Fe<sup>++</sup> electronic configuration is given below -



transition	1V	1	1	1	1	1V		
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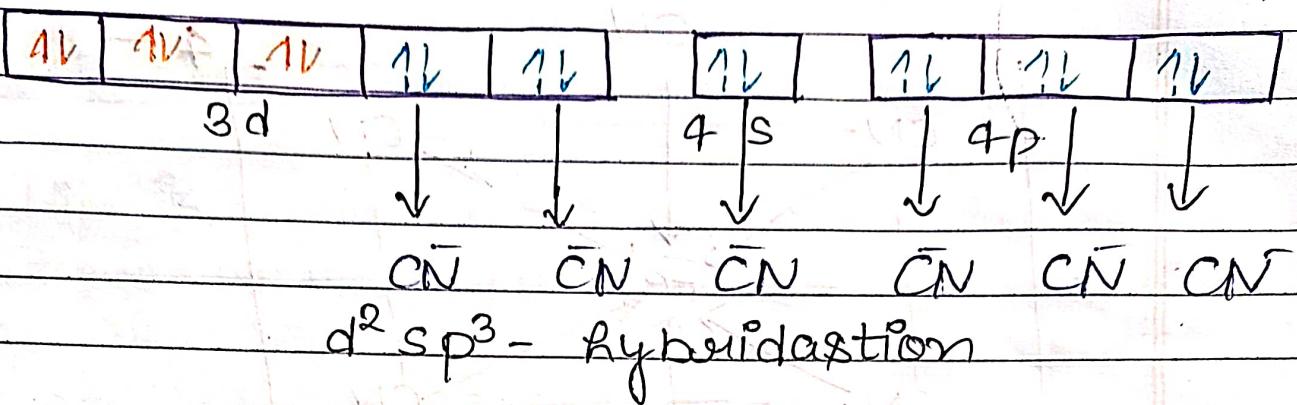


transition	1V	1	1	1	1			
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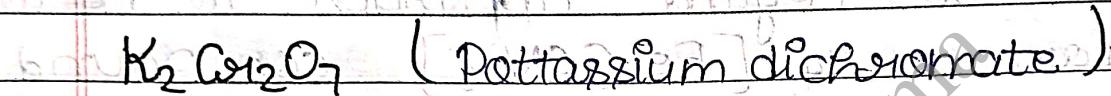
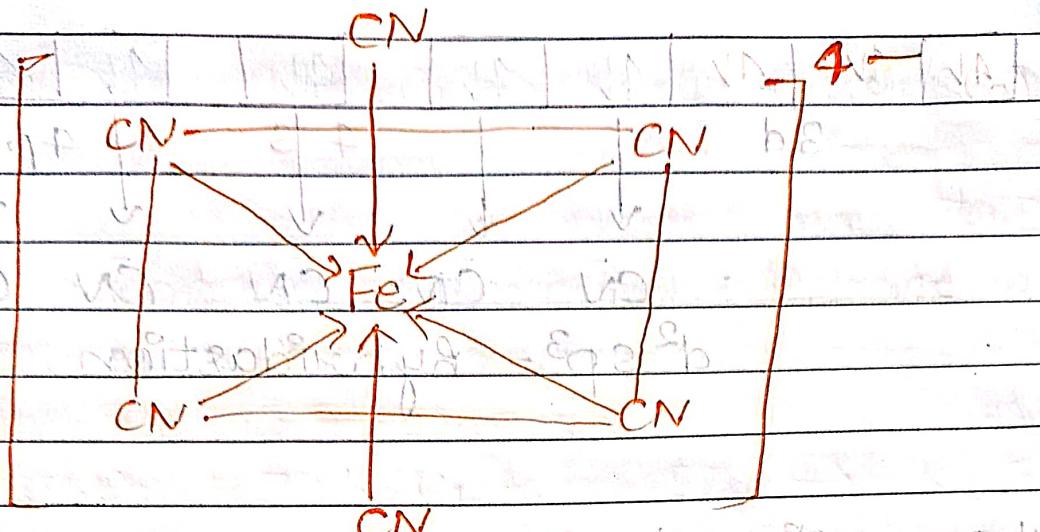
In pairing form -

1V	1V	1V					
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formation of  $[Fe^{++}(CN)_6]$



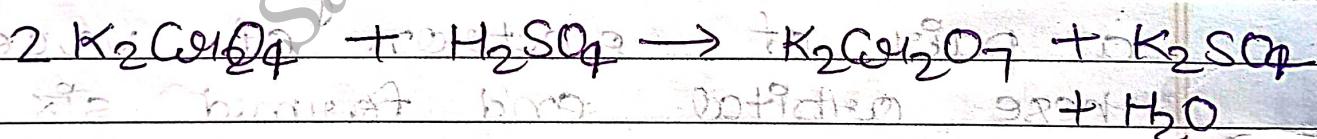
When six ligand approach to  $\text{Fe}^{2+}$  ion to form  $\text{K}_4[\text{Fe}(\text{CN})_6]$  compound the unpaired electron of  $\text{Fe}^{2+}$  are forced to paired by these ligand and form six empty orbitals for hybridization.  $\text{K}_4[\text{Fe}(\text{CN})_6]$  molecule shows  $d^2\text{sp}^3$ - hybridization. These form  $\text{Fe}^{2+}$  ion having six  $d^2\text{sp}^3$ - hybrid orbitals. The  $\text{CN}^-$  ligand donate a pair of electron of valence these orbital and formed six co-ordinate bond. The shape of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  molecule is octahedral. It have no unpaired electron so, it is show diamagnetic behavior in magnetic field. The shape of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  molecule is given below—



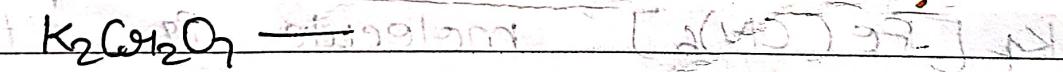
Method of preparation

i] Laboratory method

By reacting  $aq.$  potassium chromate with conc.



ii] Conversion of sodium dichromate into



By adding  $aq.$   $KCl$  sol. to sodium dichromate solution.



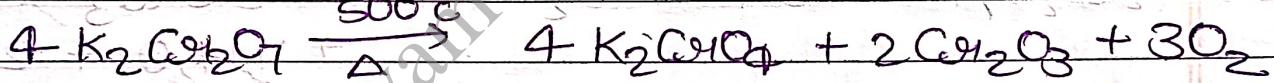
## Properties —

- i) It is orange red crystal solid.  
It is soluble in water but insoluble in alcohol. It has melting point  $396^{\circ}\text{C}$ .

## Chemical properties —

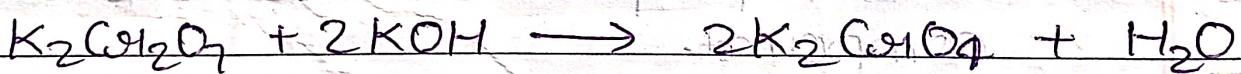
### Action of heat —

It decompose at  $500^{\circ}\text{C}$  to form  $\text{K}_2\text{CrO}_4$ , chromic oxide and oxygen.



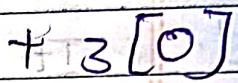
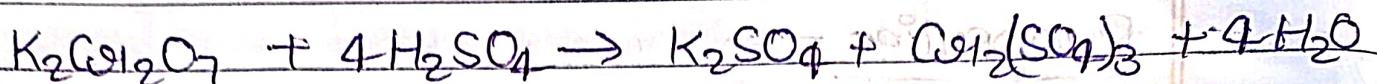
### Reaction with alkalis —

$\text{K}_2\text{Cr}_2\text{O}_7$  react with alkalis it changes to  $\text{K}_2\text{CrO}_4$ .

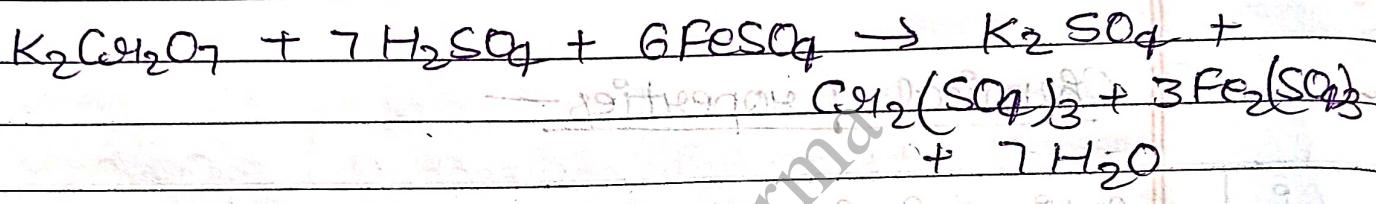


### Oxydising property —

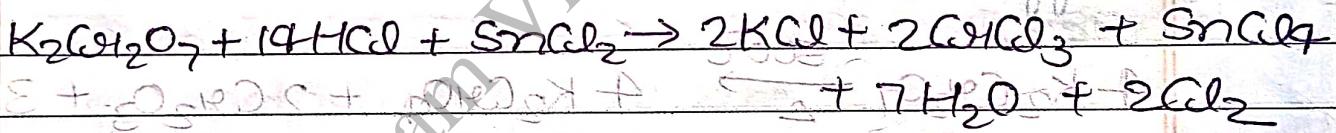
In acidic medium it act as powerful oxydising agent. It is used with conc.  $\text{H}_2\text{SO}_4$  in many reaction.



a - It oxidised ferrous sulphate to ferric sulphate.



b - Stannous chloride is oxidised to stannic chloride.



### uses -

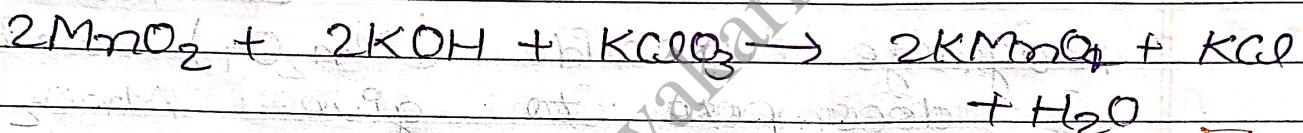
- i] As an oxidising agent.
- ii] In the preparation various chromium compound.
- iii] In the preparation of ethyl alcohol, acetylhyde etc.
- iv] In textile industry.
- v] In manufacture of alloys, explosives and synthetic perfume.

## KMnO<sub>4</sub> - (Potassium permanganate)

### Method of preparation -

#### Lab method -

By  $MnO_2$  + into a fuse mixture of KOH and  $KClO_3$  then they form  $KMnO_4$ .



#### Physical property -

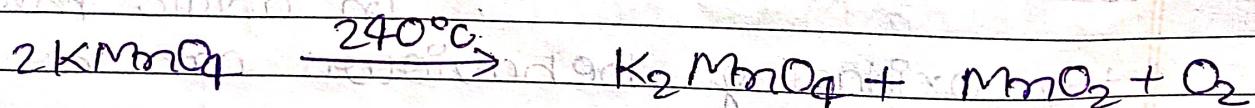
It is dark purple crystalline substance.

It is readily soluble in water but insoluble in organic solvent.

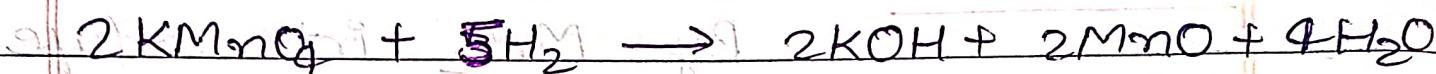
#### Chemical property -

##### i) Action of heat -

$KMnO_4$  decompose on heating upto  $240^\circ C$



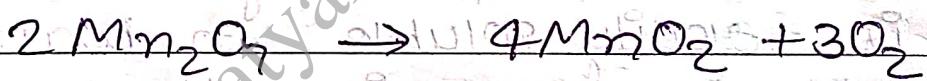
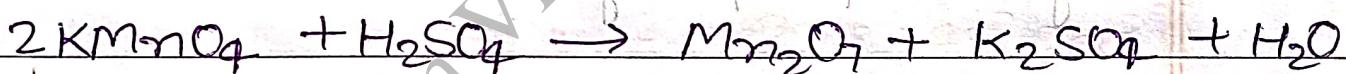
Reaction with hydrogen — On heating in the stream of hydrogen it form KOH, MnO and H<sub>2</sub>O



Reaction with conc. H<sub>2</sub>SO<sub>4</sub> →

It form

magnize heptooxide (Mn<sub>2</sub>O<sub>7</sub>) which is decompose to give MnO<sub>2</sub> and O<sub>2</sub>.

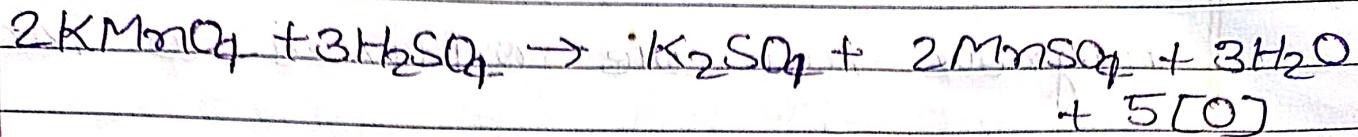


Oxidasing property —

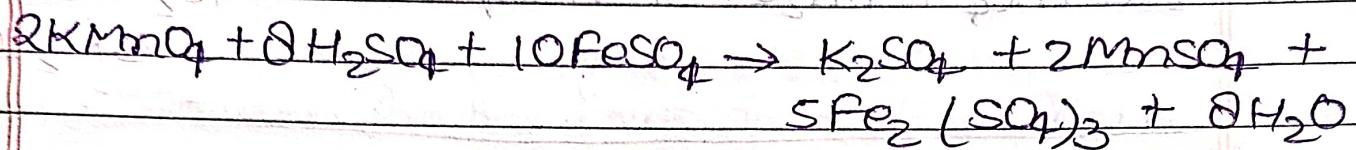
KMnO<sub>4</sub> is a strong oxidasing agent in acidic alkiline and nutral medium.

In acidic medium —

In acidic medium the oxidasing behaviour can be represented below —

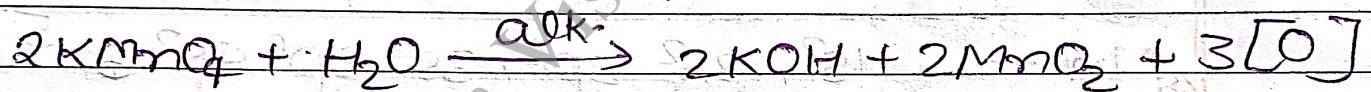


ferrous salt oxidized to ferric salt.



In alkylne medium —

In alkylne medium the oxidasing action of  $\text{KMnO}_4$  is given by the following equation —

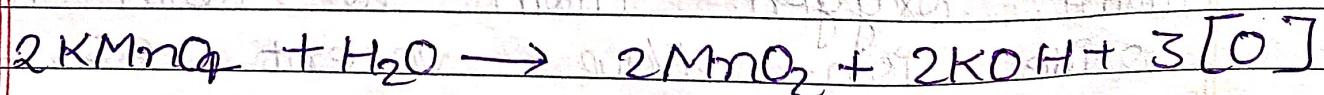


KI is oxidased to potassium iodate.

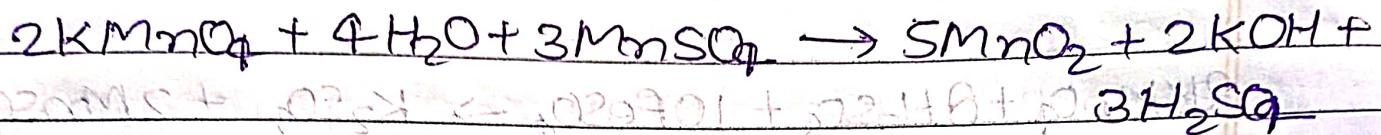
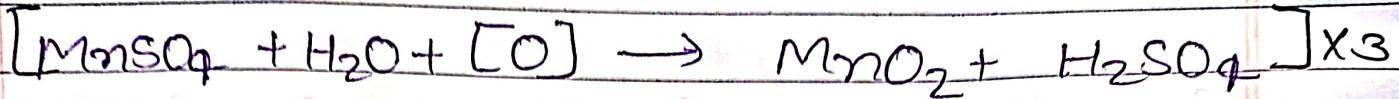


In neutral medium —

$\text{KMnO}_4$  directly reduce to  $\text{MnO}_2$ .

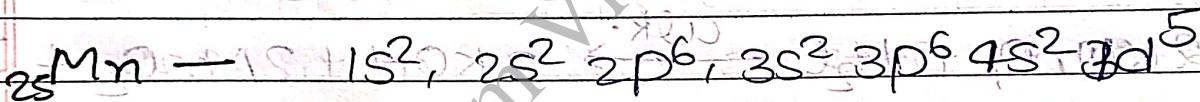


magnous salt are oxidised to  $MnO_2$

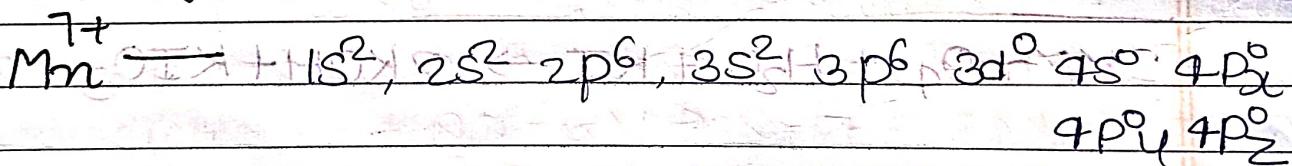


### Structure —

In  $KMnO_4$ , Mn is central metal atom. The electronic configuration in ground state —



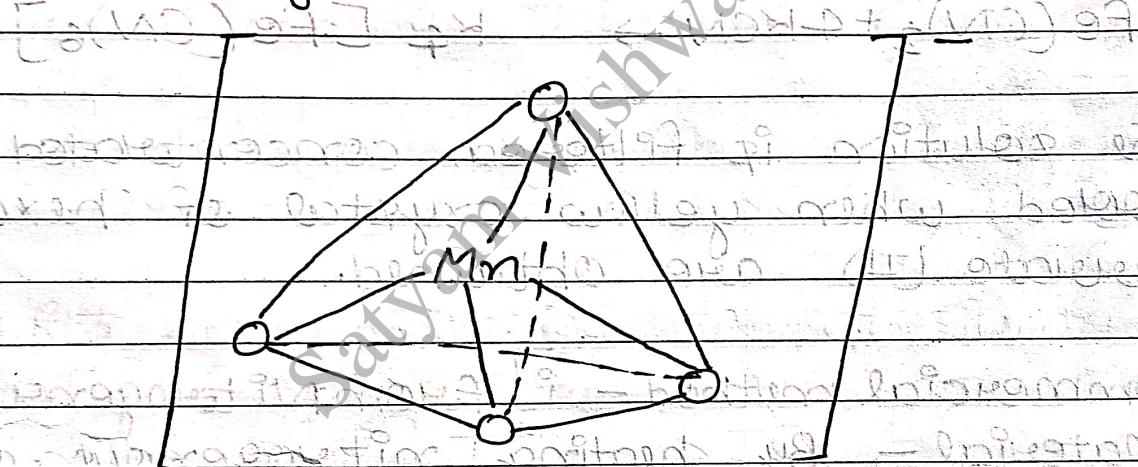
The oxidation number of Mn in  $KMnO_4$  is +7 hence its electronic configuration is —



One electron from K and seven electrons from Mn atoms i.e. eight electrons in all are taken by four oxygen atom to form four oxide ion. Now ← vacant  $4S^0, 4P^0$

$4P_y$ ,  $4P_z$  are hybridised to form four equivalent  $sp^3$ -hybrid orbital. Each oxide ion donates one lone pair of electron to central  $Mn^{7+}$  vacant orbital.

These electrons are accommodated in four  $sp^3$ -hybrid orbital. Thus the shape of  $KMnO_4$  is tetrahedral and the complex is diamagnetic.



### Uses

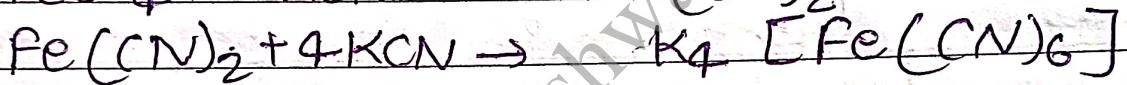
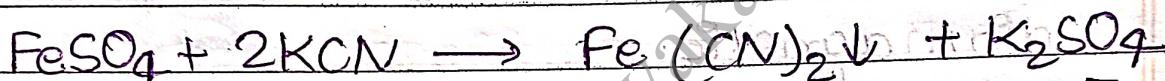
- As an oxidising agent in lab and industry.
- In the purification of water.
- As a volumetric reagent.
- In qualitative analysis for the detection of oxalates, chlorides, bromide, iodide and in controlling air pollution.

## Potassium Hexacyano ferrate (II) $K_4[Fe(CN)_6]$

### Preparation

### Laboratory method

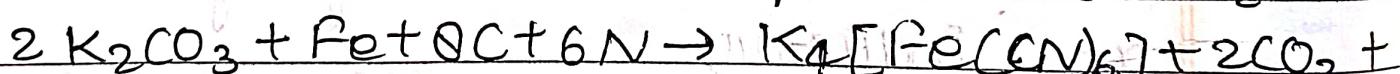
By mixing gradually solution of ferrous Sulphate with a solution of KCN until small amount of precipitate remains undissolved.



The solution is filtered, concentrated and cooled when yellow crystal of hexacyano ferrate (II) are obtained.

### Commercial method - i] from Nitrogenous organic material

Material - By heating nitrogenous organic material like horns, blood clots, leather scrap etc. with iron an KOH or  $K_2CO_3$ .



### Physical property

It is pale yellow crystalline solid. It is soluble in water but insoluble in alcohol.

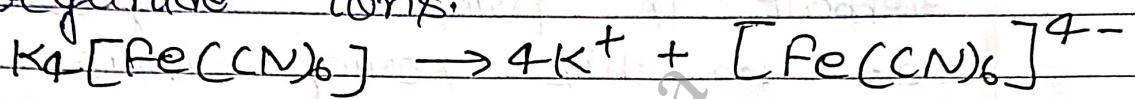
## chemical properties -

### Action of heat -

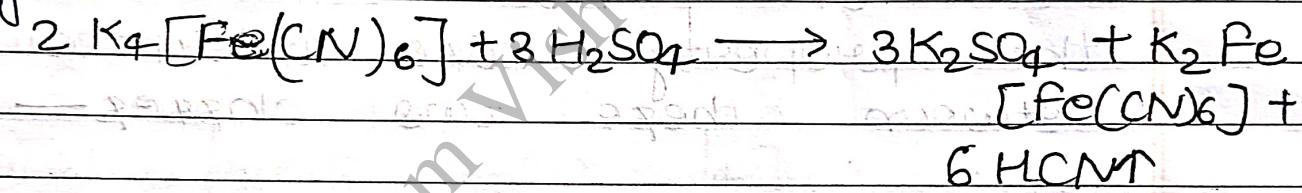
- a- It loses water of crystallization at  $140^{\circ}\text{C}$
- b- On strong heating it decomposes as -



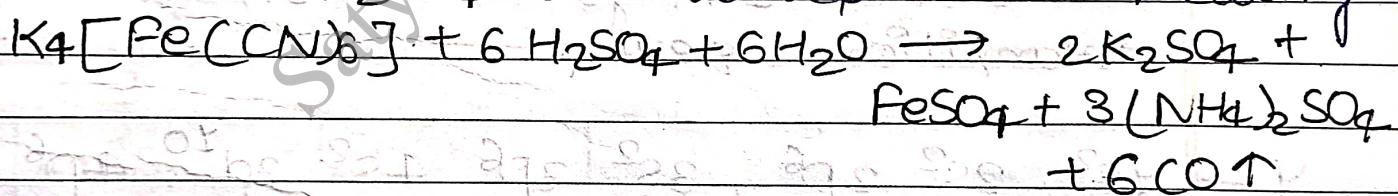
- c- Ionisation - when dissolved in water, it ionises to give potassium and ferrocyanide ions.



- d- Action of sulphuric acid - with dil.  $\text{H}_2\text{SO}_4$  - it evolves hydrogen cyanide gas.

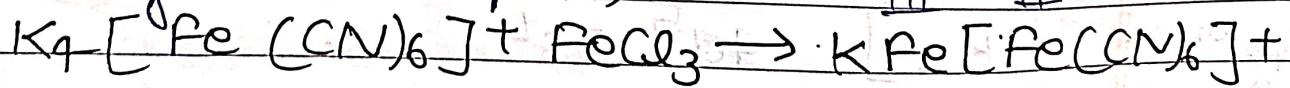


With conc.  $\text{H}_2\text{SO}_4$  it evolves CO on heating.



### 4 action of salts:-

- i] With ferric salts, it gives dark blue precipitate called prussian blue (Pot. ferric ferrocyanide complex)



- ii]  $\text{K}_4[\text{Fe}(\text{CN})_6] + 2\text{CuSO}_4 \rightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] + 3\text{KCl} + 2\text{K}_2\text{SO}_4$

## Chemistry of element of II<sup>nd</sup> Transition element

Second transition series consist of element from Y to Cd. It is also known as 4d-series. In this series no element is present they are Y to Cd. In this series their filling is regular filling in 4d-orbital of these electronic configurations. This element is separated in between the s-block and p-block element. Therefore the property also intermediate between these two classes.

### Electronic configuration of II<sup>nd</sup> transition series

$Y = [Ar] 4s^2, 2s^2 2p^6, 3s^2 3p^6 4s^2 3d^{10}, 4p^6 5s^2 4d^1$

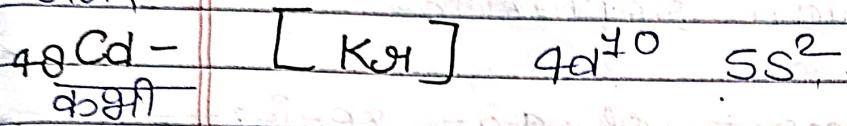
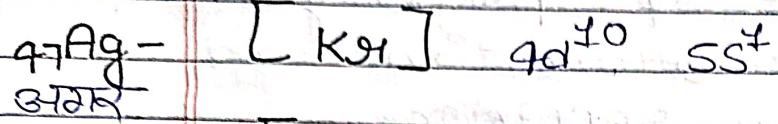
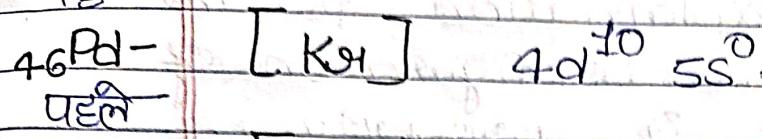
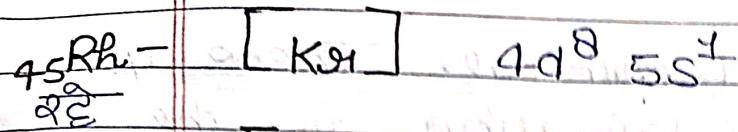
$Zr = [Ar] 4s^2, 2s^2 2p^6, 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$

$Nb = [Kr] 4d^4 5s^1$

$Mo = [Kr] 4d^5 5s^1$

$Tc = [Kr] 4d^5 5s^2$

$Ru = [Kr] 4d^7 5s^1$



Trick -

	1	2	3	4	5	6	7	8	9	10
Electron	+1	2	4	5	5	7	8	10	10	10

In  $4d$ -

1	2	3	4	5	6	7
$^{40}\text{K}$ [Kr]	$^{41}\text{Nb}$ [Kr]	$^{42}\text{Mo}$ [Kr]	$^{43}\text{Tc}$ [Kr]	$^{44}\text{Ru}$ [Kr]	$^{45}\text{Rh}$ [Kr]	
$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^7 5s^1$	$4d^8 5s^1$
8	9	10				
$^{46}\text{Pd}$ [Kr]	$^{47}\text{Ag}$ [Kr]	$^{48}\text{Cd}$ [Kr]				
$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$				

In the II<sup>nd</sup> transition series six elements mainly Nb, Mo, Ru, Rh, Pd, Ag have irregular electronic configuration. The change in the electronic configuration of these elements in the case of stability associated with half

filled and full-filled orbital. There is no responsible explanation for the irregular electronic configuration of other element. It is property nucleus electron attraction and inner electronic repulsion.

### Property of element of 3d-series

#### Metallic property-

All the element of II<sup>nd</sup> transition series are metal because it have one or two electron in outer most shell. All the element of which is easily losses, these metals are good conductors of heat and electricity.

The atom exist two type of bond i.e. metallic bond and covalent bond. Covalent is responsible for conductivity of heat and electricity.

#### Atomic radii-

The atomic radii gradually decreases from U to Mo but from Ru to Pd these value remains nearly constant in II<sup>nd</sup> transition element.

## Ionisation potential

We know that, when we move from left to right in a series, then the ionisation potential increases due to the  $Z_{eff}$  increases.

But when increase the electrons the shielding effect of the nucleus is also increases than IP decreases.

## Oxidation state

Most of the transition element show several oxidation state in their compound. The oxidation number of  $^{II}$  transition element are given below -

	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	+3	+2	+2	+2	+2	+2	+1	+2
+4	+3	+3	+4	+3	+3	+3	+3	+2
	+4	+4	+6	+4	+4	+4	+4	+3
	+5	+5	+7	+5	+6	+6	+5	+4

## Catalytic properties —

Most of the element of the  $3^{\text{rd}}$  transition series are good conductor catalyst i.e. Mo, Pd, Ag, etc used as catalyst in various chemical reaction.

The transition element act as catalyst due to the irregularity of configuration and its unsaturation and they are provide large surface area for the reactant to be absorbed and thus comes closer to another for the reaction occurs readily on the surface of catalyst.

## Formation of complex compound —

—  $3^{\text{rd}}$  transition element form complex compound due to the smaller size and highly charged ion with valent orbital. During the formation of complex compound the ligand donate a pair of electron to valent orbital of central metal atom and form co-ordinate bond. The total number of co-ordinate bond in complex compound is called co-ordinate number.

Example -  $\text{Na}_3[\text{ZrF}_7]$ ,  $[\text{Mo}(\text{CN})_8]$

Magnetic property —

Second transition series element are metal show magnetic property in magnetic field. The element which have unpaired in d-orbital they are weakly attract in magnetic field. are called paramagnetic. The electron which d-orbital are completely filled and they are repelled in magnetic field are called diamagnetic.

## Chemistry of element of Third transition series

The element of this series have been placed in 6th period of the long periodic table. This series includes  $\text{La}$  and  $\text{Hf}$  to  $\text{Hg}$ . In these electron enters  $5d$ -orbital after the completion of  $6s$ -orbital. These 10 elements are called  $sd$ -series element. The 10 elements are —

$\text{La}$     $\text{Hf}$     $\text{Ta}$     $\text{W}$     $\text{Re}$     $\text{Os}$     $\text{Ir}$     $\text{Pt}$   
 $\text{Au}$     $\text{Hg}$

### Properties —

#### 1— Electronic configuration —

The electronic configuration of these element are as follows — Aufbau principle except  $\text{Pt}$  and  $\text{Au}$ . The general valence shell electronic configuration of element of  $\text{III}^{\text{rd}}$  transition series may be written as —  $n\text{s}^{1-10}$  and  $(n-1)d$

### Trik -

1 2 3 4 5 6 7 8 9 10

Electron 1 2 3 4 5 6 7 8 9 10  
in - 5d

57 La - [Xe]  $5d^1 6s^2$

लात्टी

72 Hf - [Xe]  $(4f^1 5d^2) 6s^2$

हफ्रन

73 Ta - [Xe]  $4f^3 5d^3 6s^2$

तात्टी

74 W - [Xe]  $4f^4 5d^4 6s^2$

वरना

75 Re - [Xe]  $4f^5 5d^5 6s^2$

रेहान

76 Os - [Xe]  $4f^{14} 5d^6 6s^2$

अस्मान

77 Ir - [Xe]  $4f^{14} 5d^7 6s^2$

इरफन

78 Pt - [Xe]  $4f^{14} 5d^9 6s^1$

पिंटो

79 Au - [Xe]  $4f^{14} 5d^{10} 6s^1$

आँख पड़ीसी

80 Hg - [Xe]  $4f^{14} 5d^{10} 6s^2$

हँसी

## 2- Atomic Radii —

Atomic radii decrease

gradually from La to Os and then increase upto Hg. For the elements from La to Re the atomic radii decrease due to the fact that increased nuclear charge pulls the electron cloud inward. upto Re ( $5d^2 6s^2$ ) electron-electron repulsions do not take place because there is no pairing of electrons in  $sd$ -orbital. However in case of the element from Os to Hg, the pairing of electrons in  $sd$ -orbitals takes place. This produces electron-electron repulsions which make the atom to expand while the nuclear charge makes it to shrink in size. In the element from Os to Hg these opposing effects counterbalance each other and hence there is no major change in size on going from Os to Hg.

## 3- Ionisation potential —

The values of first ionisation potential of the

Elements of the third transition series increase as we move from left to right across a period but the increase is slow. The reason for the slow increase is as below:

We know that the nuclear charge increases as we move from left to right in the series. The increased nuclear charge would attract  $6s^2$  electrons with greater force and hence ionisation potential are expected to increase at each step. However, as the electron is added to  $5d$ -orbital at each step the  $6s^2$  electrons are shielded more and more. The effect of increasing nuclear charge is opposed by the additional screening effect of the nucleus and consequently the ionisation potential increase slowly along the series.

#### 4- Oxidation states -

The element shows several oxidation states in their compounds. This is due to the following reasons:

The energies of 5d and 6s orbitals are almost the same and hence electrons can be removed from 5d orbitals easily as they cannot be removed from 6s orbital.

The core or inner kernel of these elements is unstable and hence can lose one or more electrons resulting in the formation of cations having different oxidation states. The various oxidation states shown by the elements of third transition series.

	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	+3 (+2)	+2 (+2)							
+4				+3 (+3)	+3 (+3)	+3 (+3)	+3 (+3)	+3 (+3)	+3 (+3)
				+4 (+4)	+4 (+4)	+4 (+4)	+4 (+4)	+4 (+4)	+4 (+4)
				+5 (+5)	+5 (+5)	+6 (+6)	+6 (+6)	+6 (+6)	+6 (+6)
				+6	+6	+8	+8	+8	+8
				+7	+7				

### 5- Magnetic properties

The elements of ions which possess all the paired electrons are diamagnetic in nature. On the other hand the

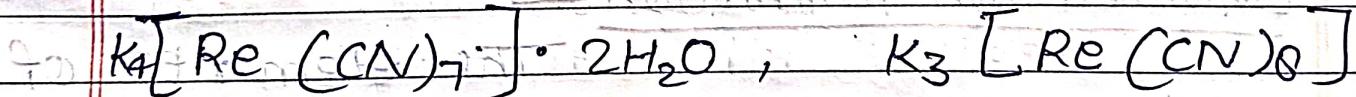
elements in ions which contain unpaired electrons, are paramagnetic in nature.

### 6- Complex formation

The cations of elements of third transition series form a number of complex compound with certain ligands due to the following reasons:

- i- They have high charge density so that they can easily accept lone pairs of electrons from ligands.
- ii- They have vacant  $5d$ - orbitals to accommodate lone pairs of electrons.
- iii- They show variable oxidation states and hence can form complexes in different oxidation states.

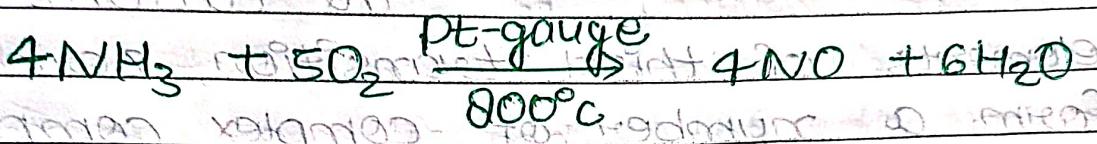
for example:-  $\text{Na}[\text{HF}_7]$ ,  $[\text{W}(\text{CN})_8]$ ,



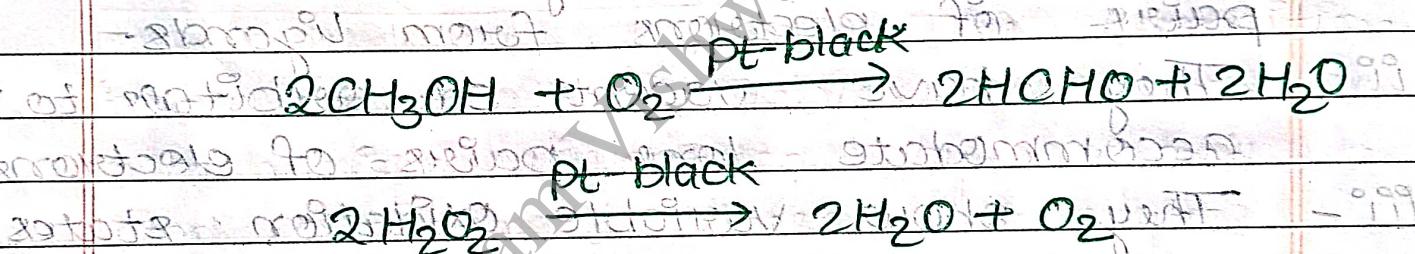
### 7- Catalytic properties

Most of the elements of third transition series are good catalysts e.g.  $\text{Co}^{2+}$  and  $\text{Ti}^{4+}$  are good catalysts.

i— Platinum gauge is used as a catalyst in the oxidation of  $\text{gaseous NH}_3$  to  $\text{NO}$  required for the manufacture of  $\text{HNO}_3$  by Ostwald's process.



ii— Platinum black is used as a catalyst in the preparation of formaldehyde from methanol and in the decomposition of  $\text{H}_2\text{O}_2$ .



iii— Colloidal platinum is used as a catalyst in the decomposition of  $\text{H}_2\text{O}_2$ .

### Q— Coloured ion formation —

The elements of  $\text{D}_{\text{II}}$  series form coloured compounds due to incomplete  $5d$ -orbital. The compound which have vacant  $5d$ -orbital ( $5d^0$ ) or have full filled  $5d$ -orbital ( $5d^{10}$ ) are colourless because  $d-d$  transitions are not possible.

## Colour of some compounds of 3rd-series

Compound	Colour
TaBr <sub>3</sub>	Dirty green
TaBr <sub>5</sub>	Yellow
W <sub>2</sub> O <sub>3</sub>	Brown
WBri <sub>3</sub>	Dark brown
WBri <sub>6</sub>	Bluish black
WTi <sub>2</sub>	Brown
ReCl <sub>3</sub>	Purple
ReBr <sub>3</sub>	Green
ReF <sub>7</sub>	Yellow
PtF <sub>6</sub>	Red

## Co - coordination compound

Complex compound or co-ordination compound —

The complex in which the central metal atom directly bonded to ligand through co-ordination bond is called complex or co-ordination compound.

Central metal atom —

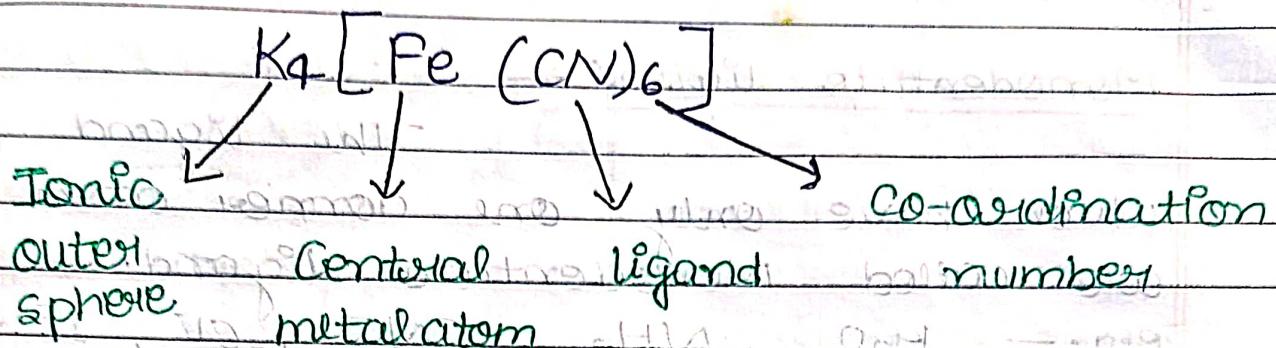
The transition metal atom in complex compound which is surrounded by ligand and bonded to these through co-ordination bond is called central metal atom.

Co-ordination number —

The total number of co-ordination bond in complex compound is called co-ordination number.

OR

The total number of monodentate ligand in complex compound is called co-ordination number.



### Ligands —

The ions, groups or molecule which are attached to the central metal ion are through co-ordination number are called ligand.

Ligand donate a pair of electron to central metal atom in complex compound.

### Types of Ligands —

On the basis of number of atom which donate a pair of electron to central metal atom in complex compound. Ligands may be following type—

- i - Monodentate or Unidentate
- ii - Bidentate
- iii - Tridentate
- iv - Tetradentate
- v - Polydentate

## Monodentate ligand —

The ligand which have only one donor atom are called Monodentate ligand.

e.g. —  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{I}^-$  etc.

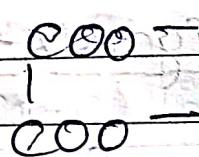
## Bidentate ligand —

The ligand which have two donor atom are called bidentate ligand.

e.g. — ethylene diamine



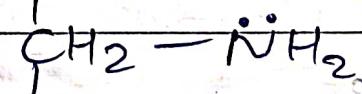
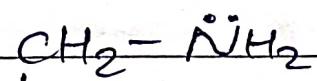
## Oxylate ion —



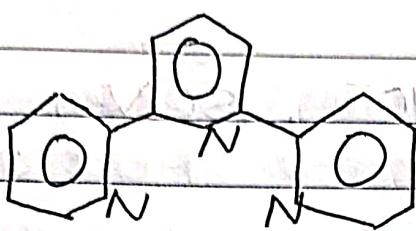
## Tridentate ligand —

The ligand which have three donor atom are called tridentate ligand.

e.g. —



Tri amine propane



Tetra pyridine

giving titanium as metal bidentate ligament

Tetra dentate ligand —

the ligand which have four donor atom.

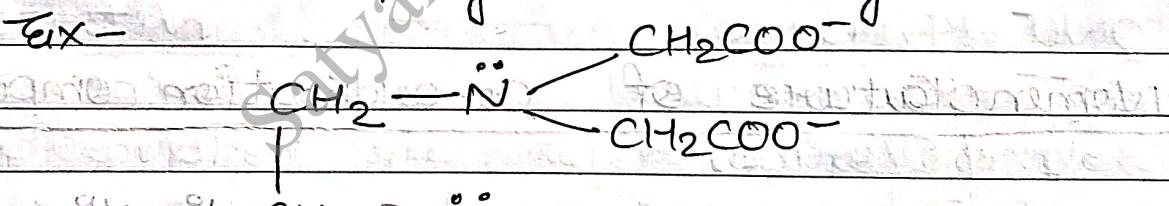
Ex —  $(\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2)_3\text{N}$  - bromine

Tetra (2-aminoethyl) amine

Polydentate ligand —

The ligand which have more than four donor atom is called polydentate ligand.

Ex —



Ethylenediamine tetraacetate ion  
 $(\text{EDTA}^{4-})$

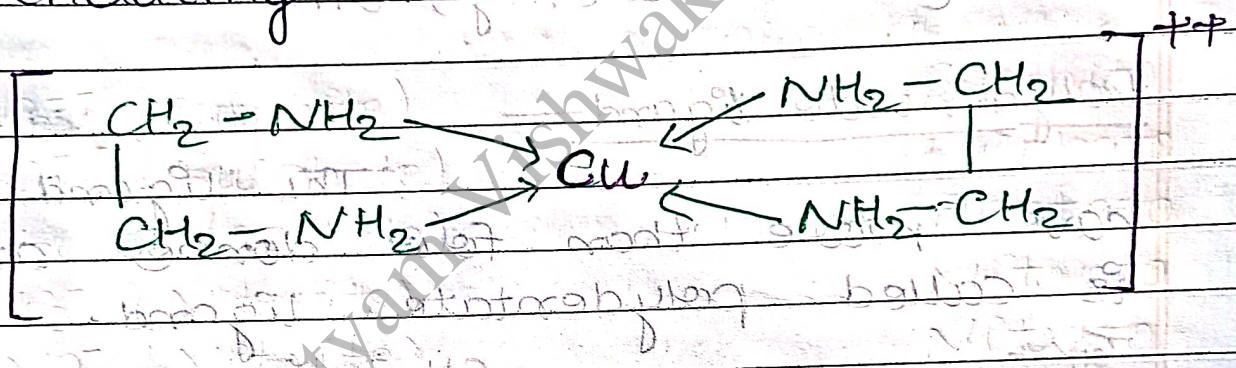
Ambidentate ligand —

The ligand which may be co-ordinate to the central metal ion through more than one donor atom are called ambidentate ligand.

Ex-  $\text{NO}_2^-$ ,  $\text{ONO}^-$ ,  $\text{SCN}^-$ ,  $\text{NCS}$

### Chelate compound—

The cyclic complex formed when a multidentate ligand attach through two or more atom to the same central metal atom are called chelate compound. The multidentate ligand chelating dentate.

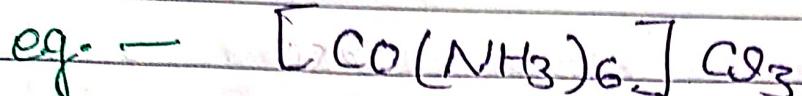


### Nomenclature of co-ordination compound—

Co-ordination compound are name I.U.P.A.C system.  
In this system of nomenclature  
the following rules are observed.

#### Order of naming

In Ionic complex  
the cation is named first followed  
by the anion.



Hexammine cobalt (III) chloride

### Naming of co-ordination sphere

In naming of co-ordination sphere the ligand are named first and then central metal ion.

### Order of naming ligand

The order of naming ligand is negative neutral positive with separation of hyphens.

### Naming of negative ligand

In general if anion names end in -ide then it

is replaced by (o)no-

### Name of Negative ligand (Replace of 'ide')

#### Negative ligand

$\text{F}^-$

$\text{Cl}^-$

$\text{Br}^-$

$\text{OH}^-$

$\text{CN}^-$

$\text{NO}_2^-$

Name

fluoro

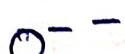
chloro

bromo

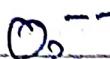
hydrox

ciano

nitro



Oxo



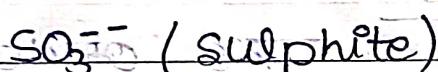
Peroxo

Name of negative ligand (Replace of 'ate')

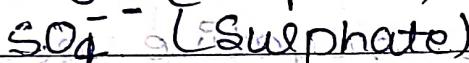
In general if anion names end in 'ite' or 'ate' it is the final 'e' is replaced by 'o'

Negative ligand

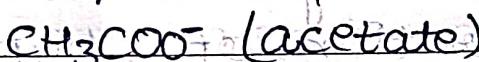
Name



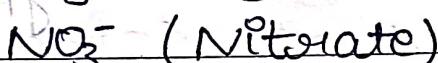
Sulphito



Sulphato



Acetato



Nitrato



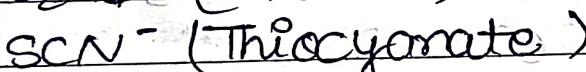
Nitrito



Carbonato



Oxalato



Thiocyanato



Thiosulphato

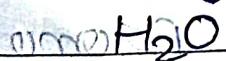
Naming of Neutral ligand

Neutral ligand

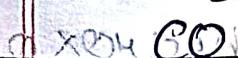
Name



Amine



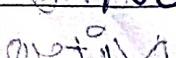
Aqua



Carbonyl



Nitrosyl



ON

CS

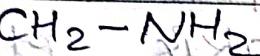
Thiocarbonyl

NS

Thio Nitrosyl



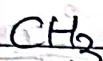
Aminium



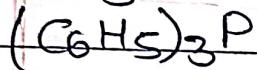
Ethylene diamine (en)



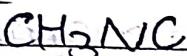
Phenyl



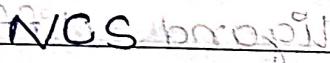
Methyl



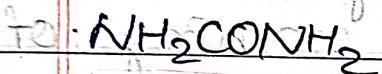
Triphenyl phosphine



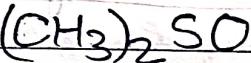
Methyl isocyanate



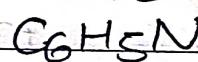
Thiocyanate



Urea



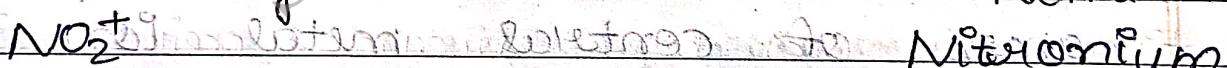
Dimethyl sulphoxide



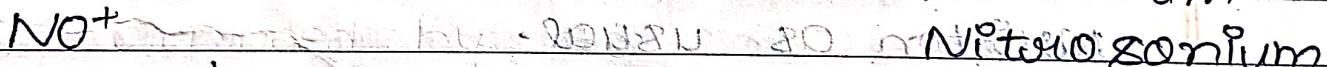
Pyridine

### Naming of positive ligand

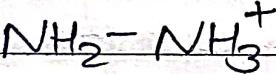
positive ligand has bnd. IUPAC name



Nitronium



Nitrosonium



Hydrazinium



Pyridinium

### Number of ligand

The number of simple ligand is indicated by greek prefix di, tri, tetra, penta; Hexa etc.

If the ligand have complex name such as (en, trialkyl phosphine etc) Their numbers 2, 3, 4, 5, 6 etc. are indicated by prefix bis, tris, tetraakis, pentakis etc.

Naming of the central metal ion -

It is named after naming all the ligand different rule are observed the naming of different complex -

i- For anionic complex the name of central metal ion 'ium' is replaced by 'ate'

ii- For neutral and cationic complex the names of central metal ions written as usual.

Oxidation state of the central metal ion -

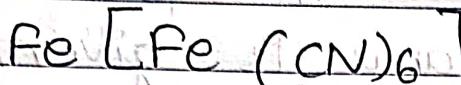
It is indicated by

roman number like as - I, II, III,

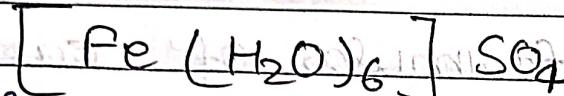
IV etc after naming of central metal atom.

oxH ; oxOH ; oxO ; metat ; met ; in ;

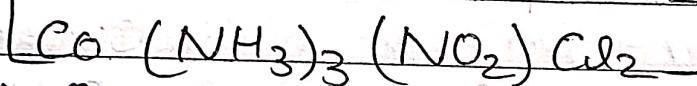
Example —



Iron hexacyanoferrate (III)



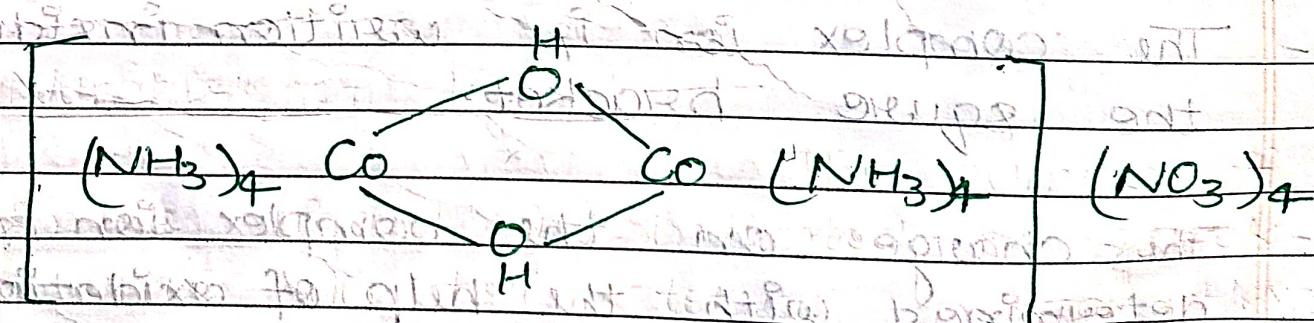
hexaaqua ferrionium (II) sulphate



triamine dichloro nitro cobalt (III)

Naming of bridge complex compound —

If the complex containing two or more metal ion is called polynuclear complex. The ligand which link the two metal atoms are called bridge group and are separated from rest of the complex by hyphens and denoted by greek letter 'μ'.



Octa amine-16-dihydroxo dicobalt (III) nitrate.

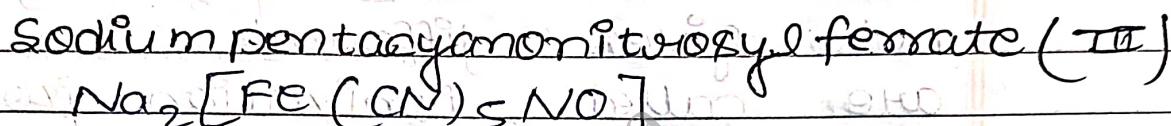
## Written formula of complex compound →

The formula of compound if its name is given, the following points are given below—

- i - First write the formula of cation followed by anion present in the complex compound.
- ii - Simple cation or anion are written as the anion obtained from the simple salt.
- iii - Write the formula of complex ion or molecule, ligand and metal ion are written in reverse order i.e., first write symbol of metal and then ligand. The ligand are written in the order positive, neutral, negative.
- iv - The complex ion is written inside the square bracket.
- v - The charge on the complex ion is determined with the help of oxidation number of the metal and charge of the ligand.

vi - Cation and anion are multiplied by such a whole number so that positive and negative charge become equal.

Example - Sodium pentacyanomonitrosoyl ferrate (II)



Pentaamminenitrito cobalt (III) sulphate  
 $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$

### Isomerism in co-ordination compound

The compound having same molecular formula but different structures and properties are called isomers and this phenomenon is called isomerism.

It is two type -

i - Structural isomerism

ii - Stereo isomerism

### Structural isomerism

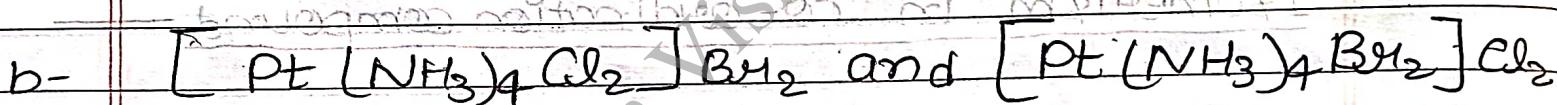
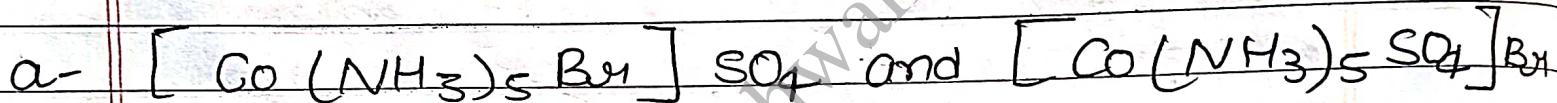
The isomers which have same molecular formula but different structural arrangement

of atom are called structural isomerism.

### i- Ionisation isomerism-

The complex

which have same molecular formula but gives different ion in solution are called ionization isomers and this phenomenon is called ionization isomerism.

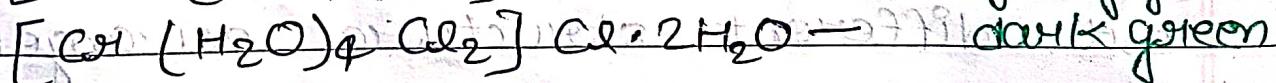
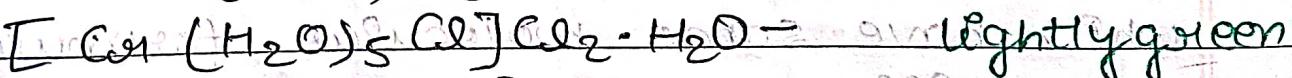
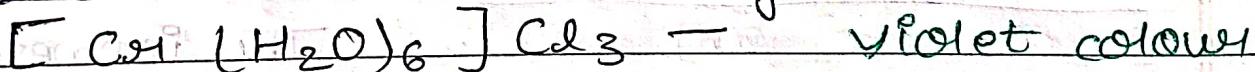


### ii- Hydrated isomerism

The isomers obtained by replacing a co-ordinated group by water of hydration are called hydrated isomers and this phenomenon is known as hydrated isomerism.

Example -

Three isomers of  $\text{Cr}(\text{Cl}_3(\text{H}_2\text{O}))_6$  are known which is given below -

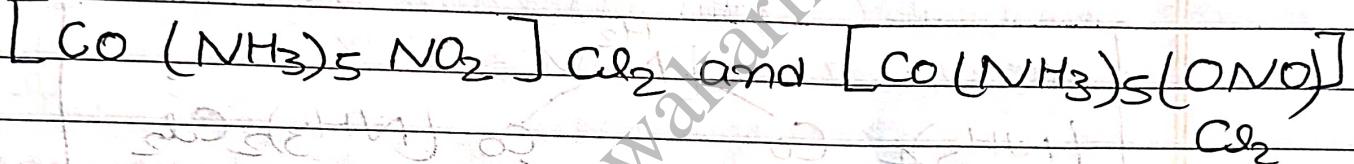


iii-

### Linkage Isomerism

This type of isomerism occurs when more than one single atom in a co-ordinated group may act as donor. This type of isomerism is called linkage isomerism.

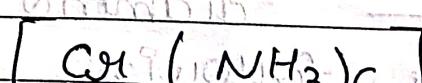
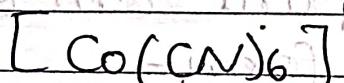
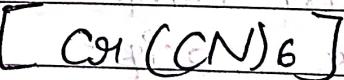
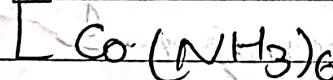
Example—



iv- Co-ordination Isomerism —

When both cation and anion are complex isomerism is possible due to the interchange of the ligand between the two complex ion this type of isomerism is called co-ordination isomerism.

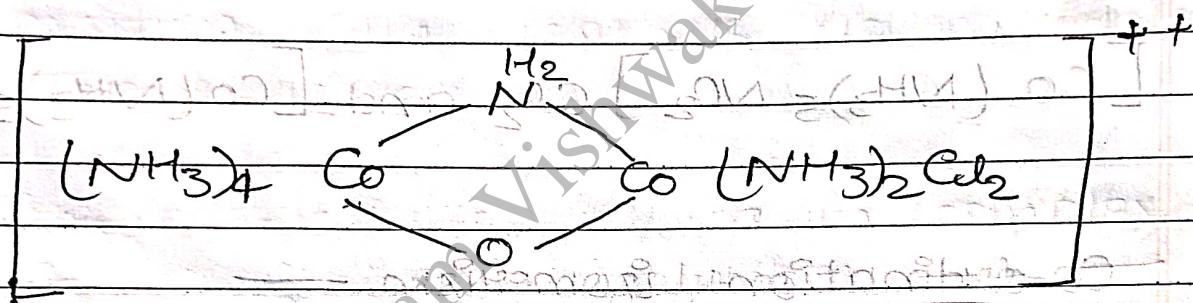
Example—



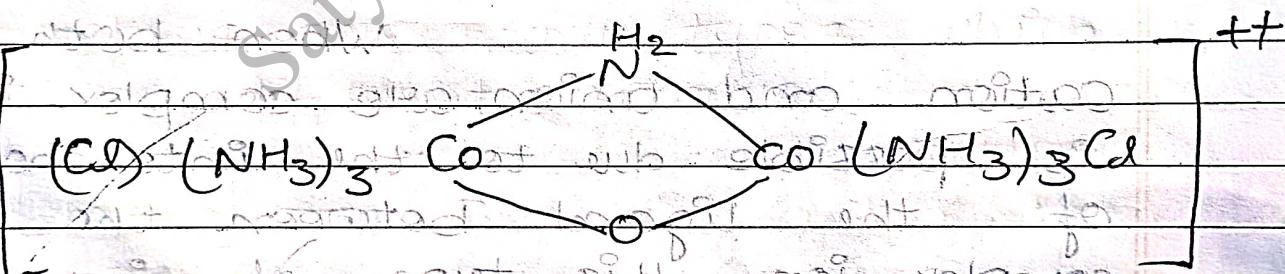
## Co-ordination position isomerism

This isomerism occurs in polynuclear complex in which ligand may be exchange their position between the different metal nuclei.

Example —



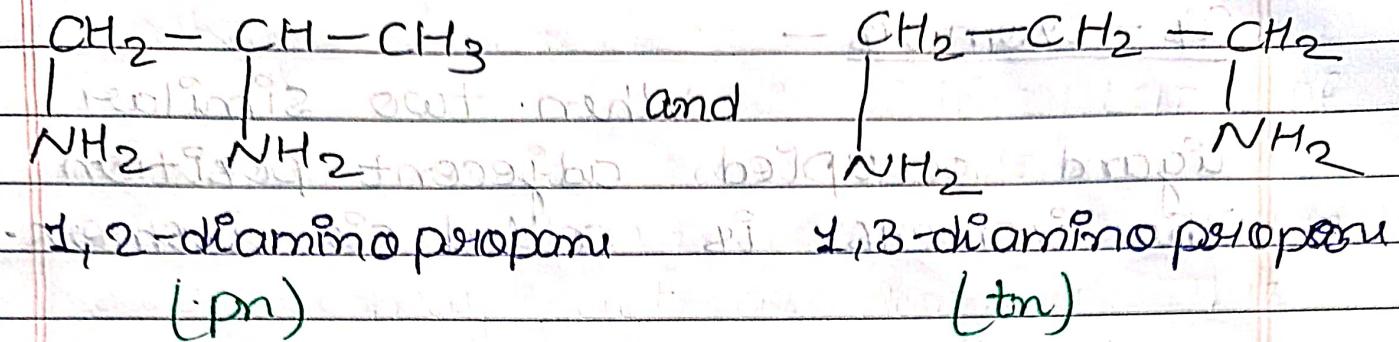
and



## Ligand isomerism —

This type of isomerism is found in complex in which ligand themselves exist as isomers.

Example — diamino propane can exist in the following two form —



### Stereo Isomerism

This isomerism is due to the difference in the arrangement of ligand in space in a molecule.

The different arrangement are known as stereo isomers and this phenomenon is called stereo isomerism. It is of two type —

i- Geometrical Isomerism

ii- Optical Isomerism

### Geometrical Isomerism

The compound having empirical formula but different physical and chemical properties due to the different arrangement of ligand are called geometrical isomers and thus isomerism is called geometrical isomerism.

geometrical isomerism are two form —

### Cis - Isomers -

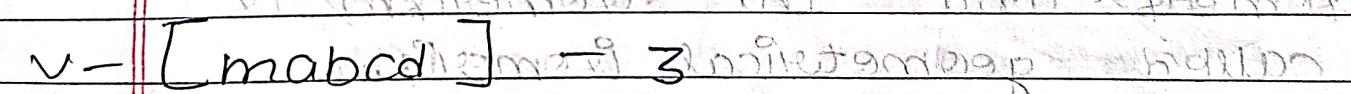
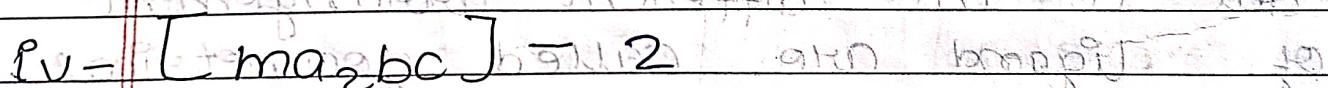
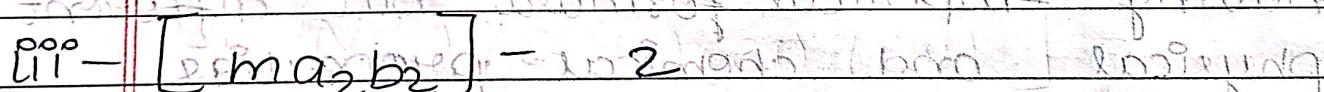
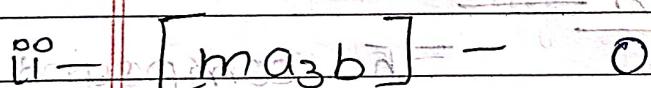
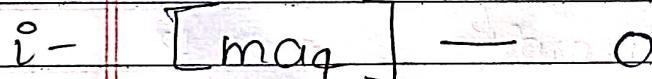
When two similar ligand occupied adjacent position  
The isomer is called cis - Isomers.

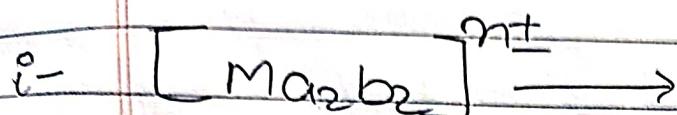
### Trans - Isomers -

When two similar ligand occupied diagonally opposite position. The isomer is called Trans - Isomers.

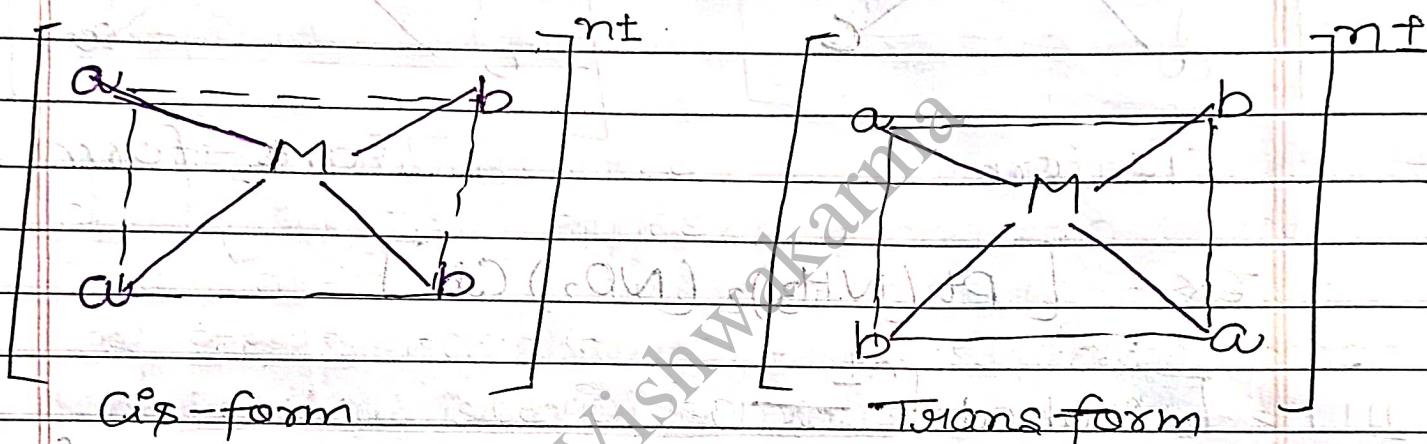
Geometrical isomerism in complex of co-ordination number 4

four co-ordination numbers are many types which gives different isomers.

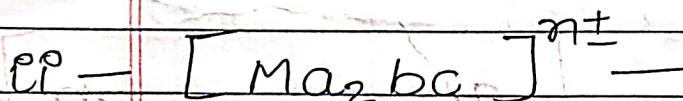
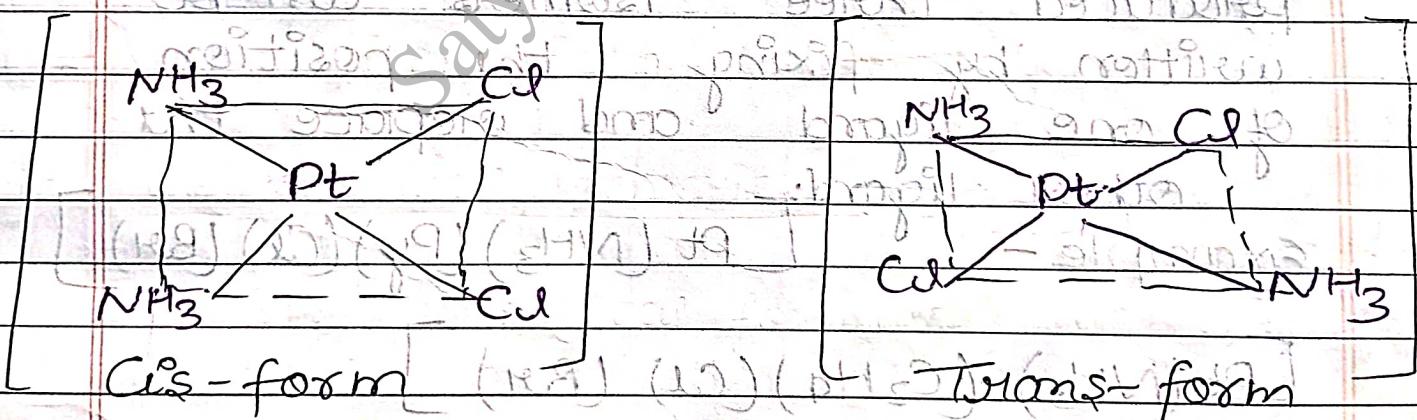




This type of complex compound shows two geometrical isomerism which is first is cis and second is trans isomers.

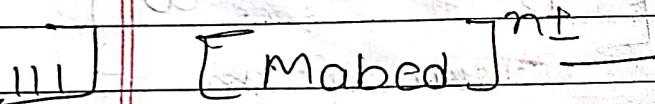
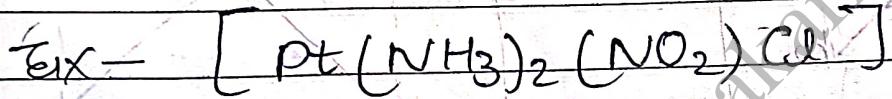
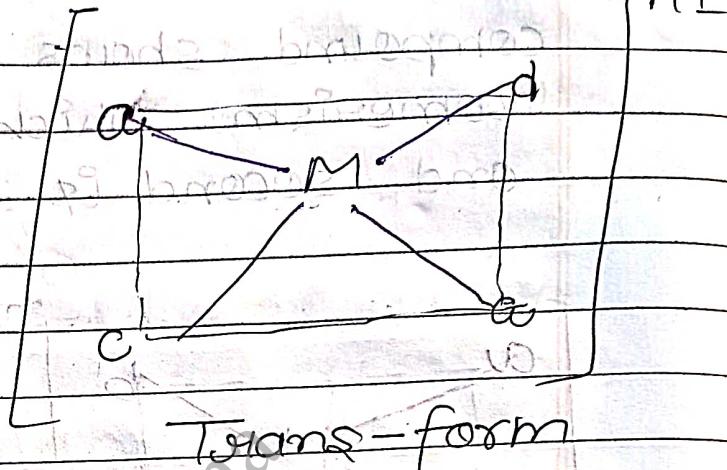
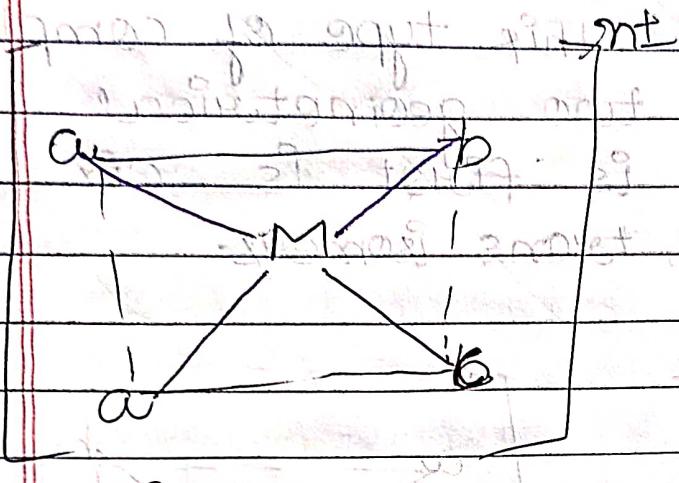


Example -  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^{n\pm}$  (bodum)

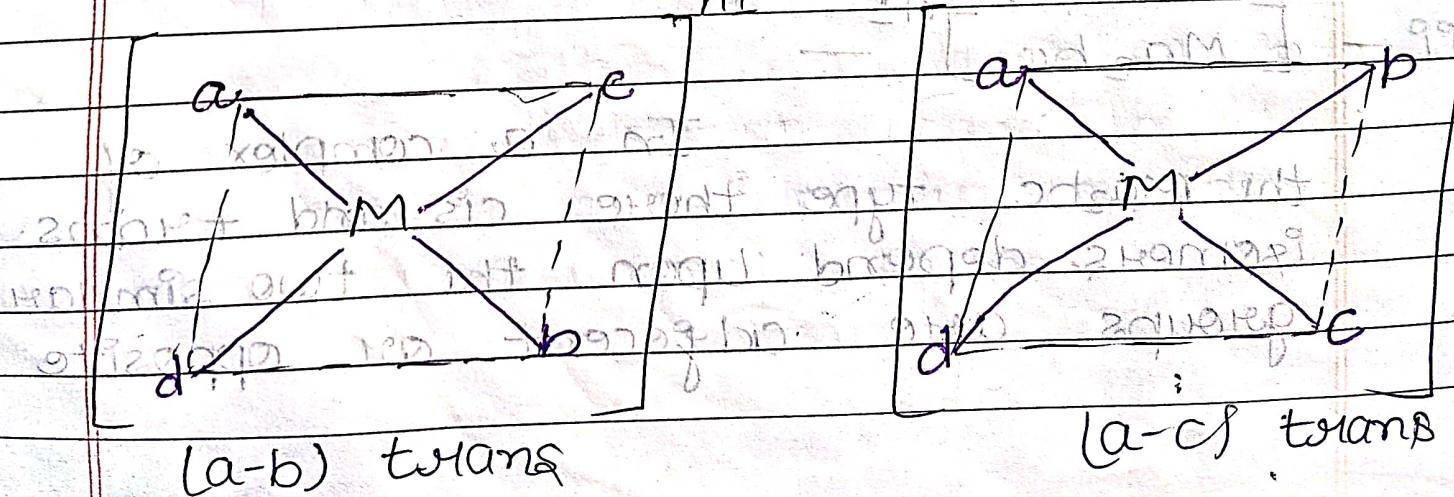
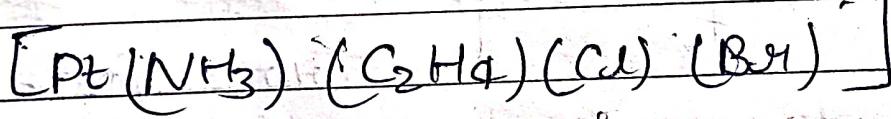
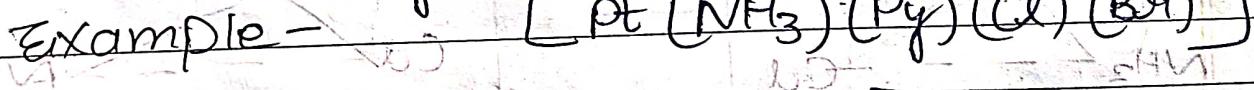


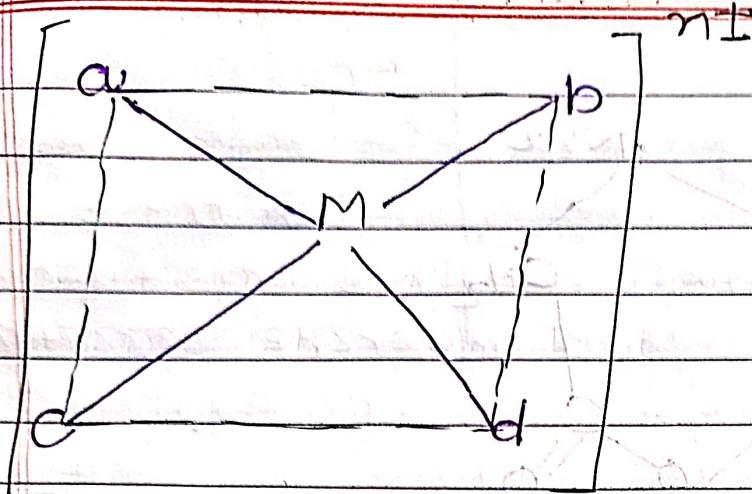
In a complex of the  $\text{M}_2\text{bc}$  type there cis and trans isomers depend upon the two similar groups are adjacent or opposite

to another.



In the complex of  $[\text{Mabcd}]$  type is square planar produced three isomers can be written by fixing the position of one ligand and replace the other ligand.

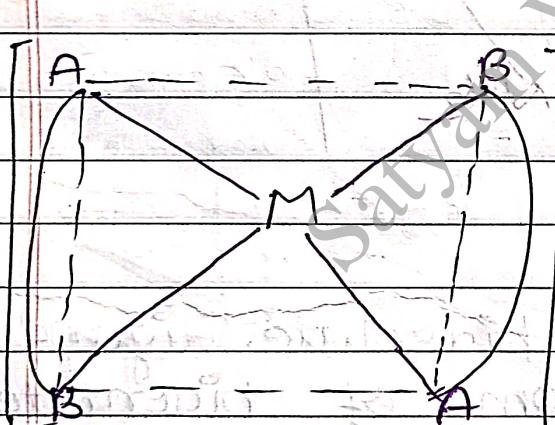




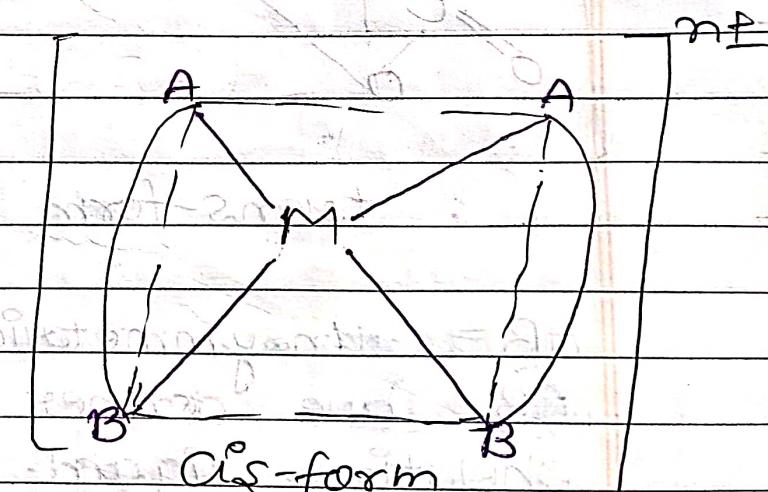
(a-d) trans

$[M(AB)_2]$  - type complex

Such type  
of complex shows that cis and  
trans isomerism which is —



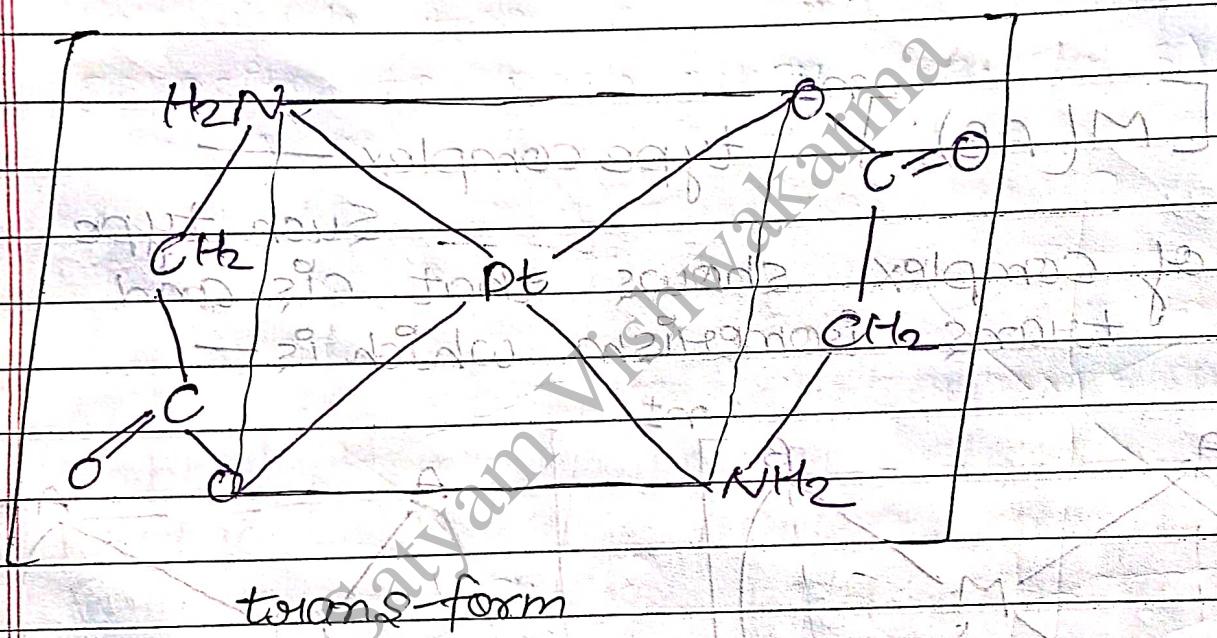
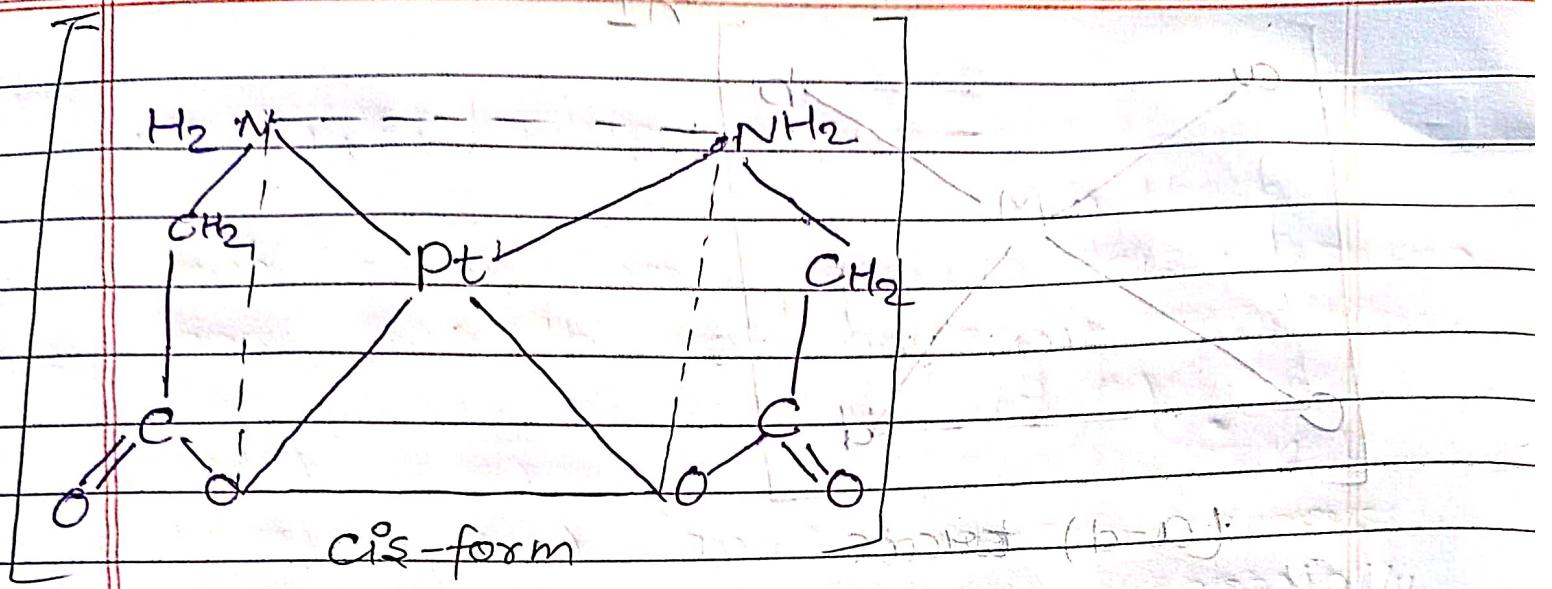
trans-form



cis-form

Ex -  $[Pt(\text{gly})_2]$

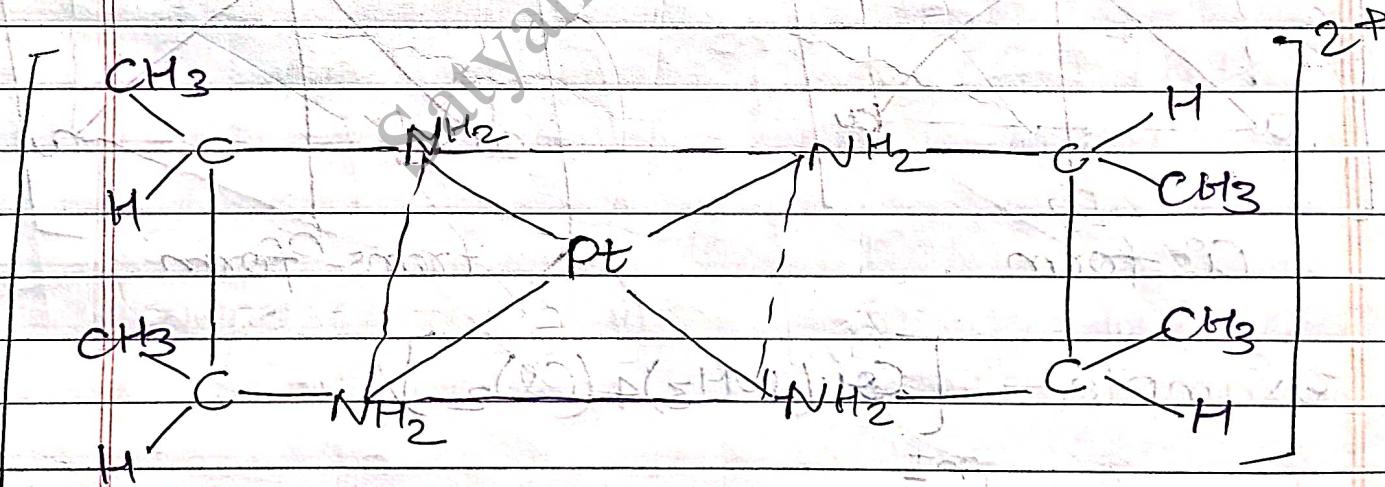
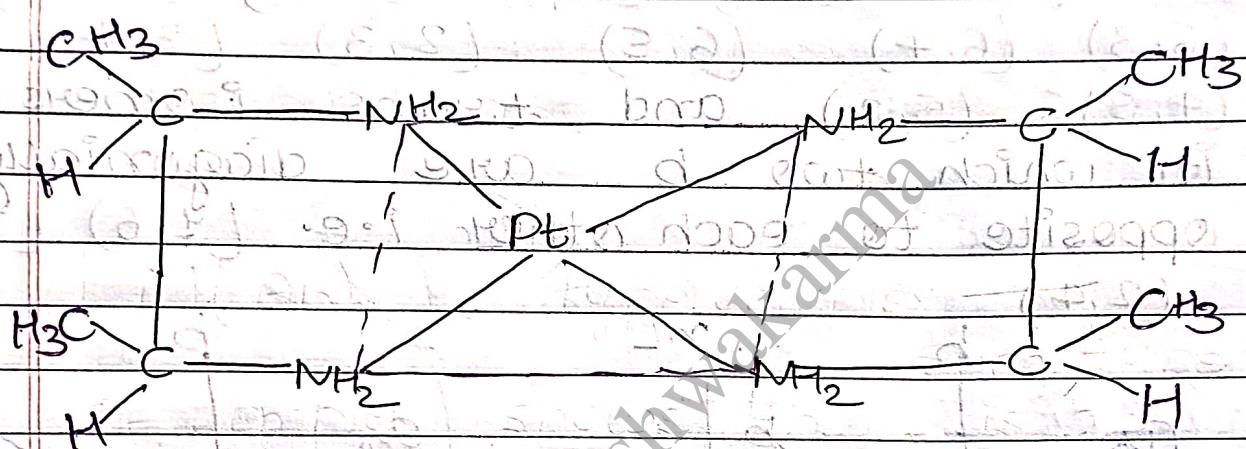
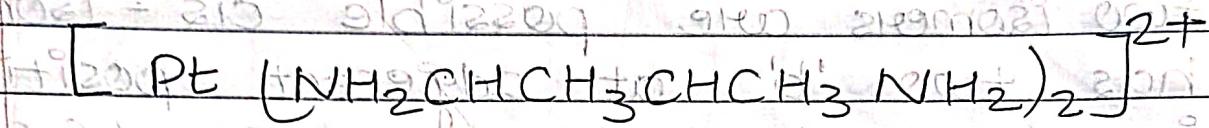
diaquat and homocitrate anions



$AB =$  unsymmetrical bidentate ligand  
 $AB$  are donor atom of bidentate chelating ligand.

$[M(LAA)_2]^{n+}$  type complex  
 where AA is the symmetrical bidentate ligand in which A and A are donor atom of bidentate chelating ligand.

Such type of complex also shows cis and trans isomers.



### Co-ordination Number - 6 —

The following of octahedral complex shows geometrical isomerism.

i)  $[M a_4 b_2]^{n+}$  type complex —

In these complex two isomers are possible cis - isomers has two 'b' at adjacent position.

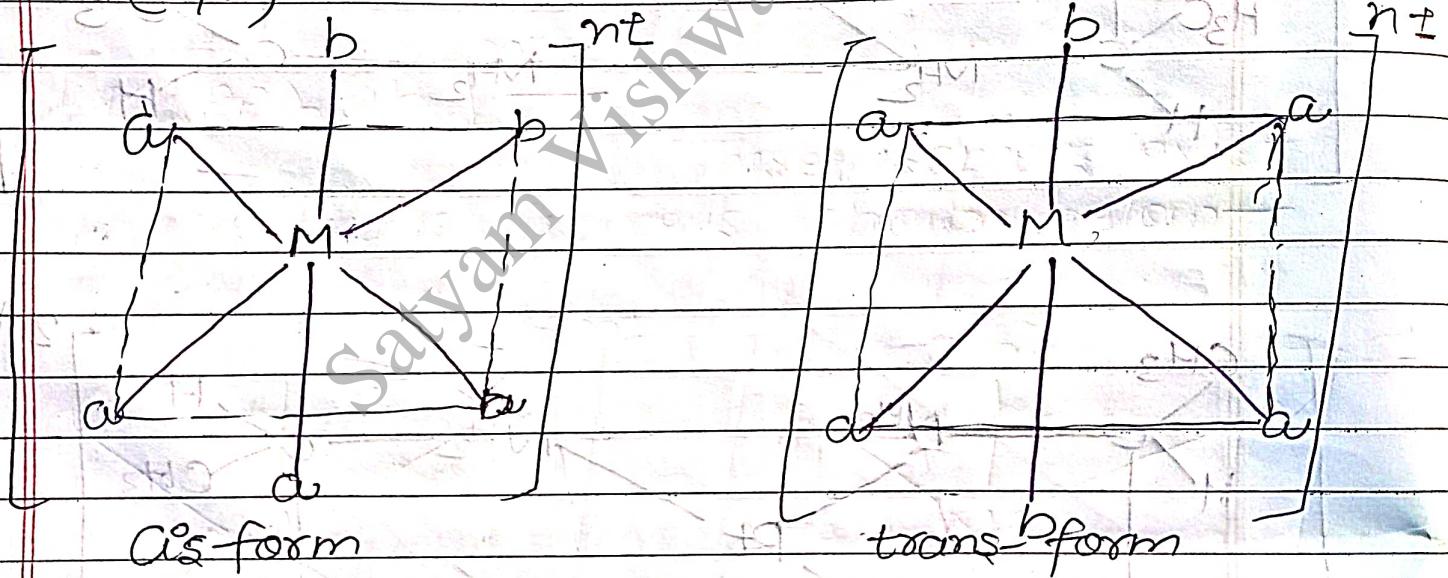
i.e. (1,2) (1,3) (1,4) (1,5) (6,2)

(6,3) (6,4) (6,5) (2,3) (3,4)

(4,5) (5,2) and trans isomers

In which two 'b' are diagonally opposite to each other i.e. (1,6) (3,5)

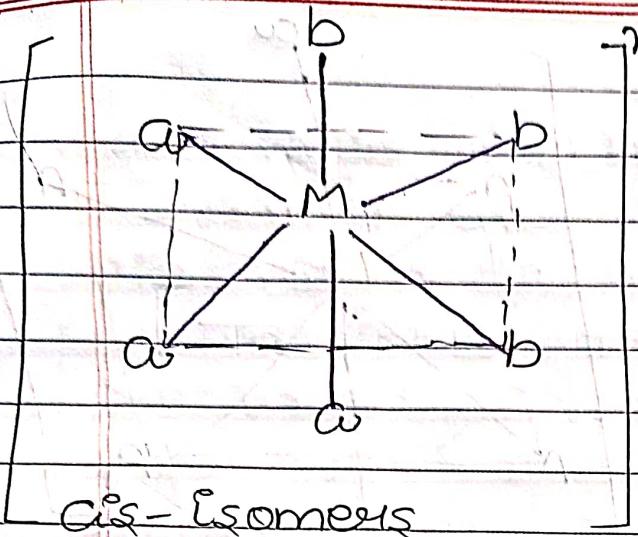
(2,4)



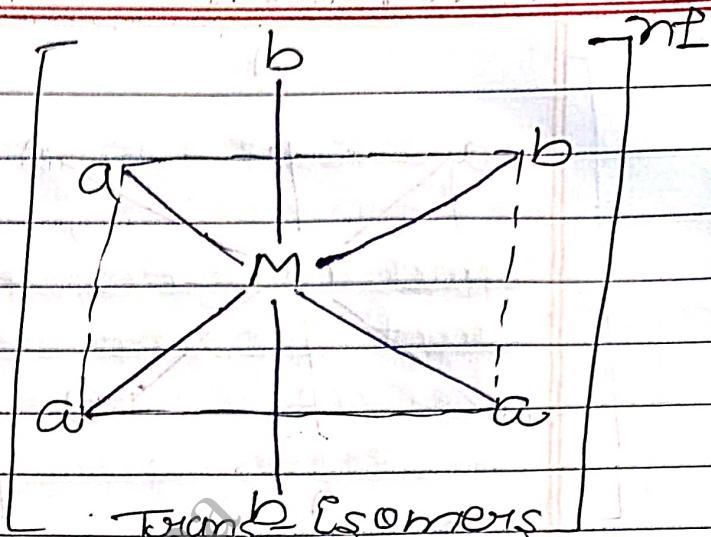
Example -  $[Co(NH_3)_4(Cl)_2]$

ii)  $[M a_2 b_3]^{n+}$  type complex —

In these complex two isomers are possible cis - isomers occupied (1,2,3) and trans isomers - (1,2,6)



cis - Isomers

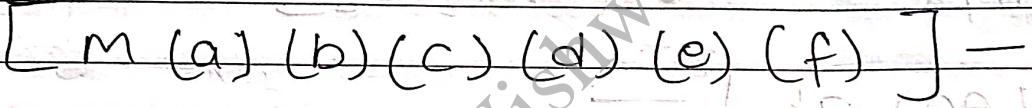


trans - Isomers

Example -



iii



such type of complex exist in 15 different geometrical form however the only one compound of this type.

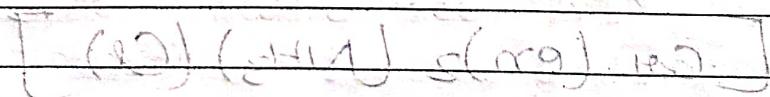
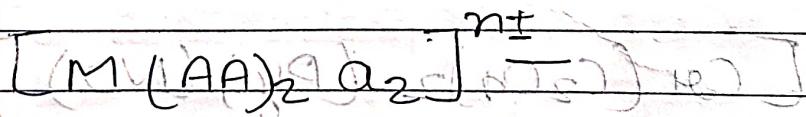


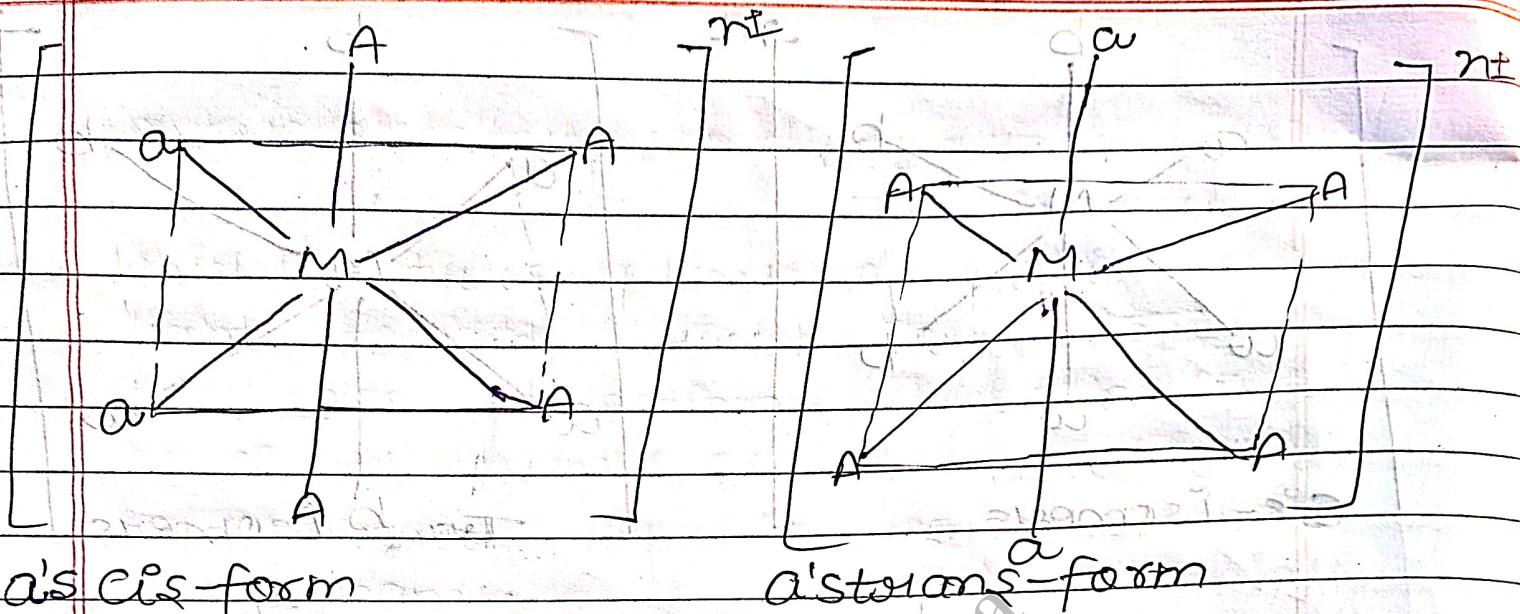
The geometrical isomers are 15 type.

Octahedral complex containing monodentate and symmetrical bidentate chelating ligand

These complex

exist in cis and trans isomers.

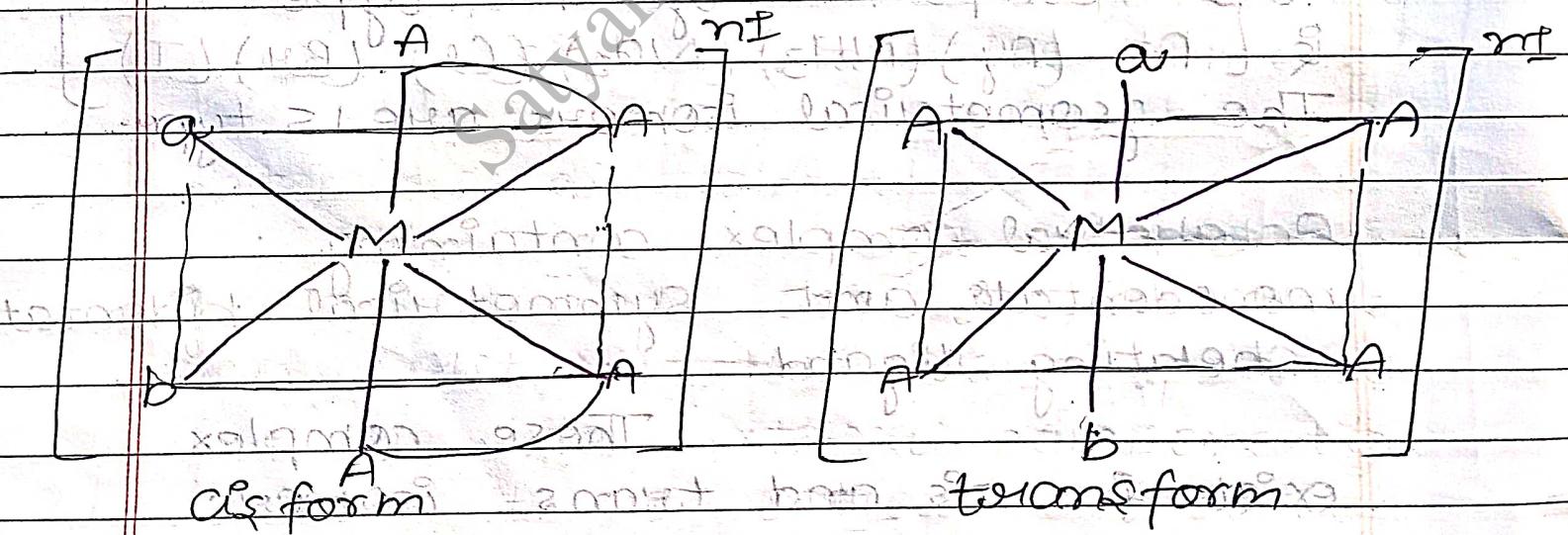




Example -  $[Co(en)_2Cl_2]$

ii)  $[M(AA)_2ab]$  —

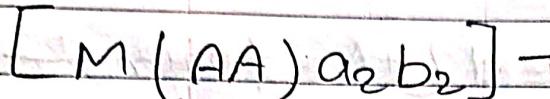
These isomers exist in a's trans isomers shown below—



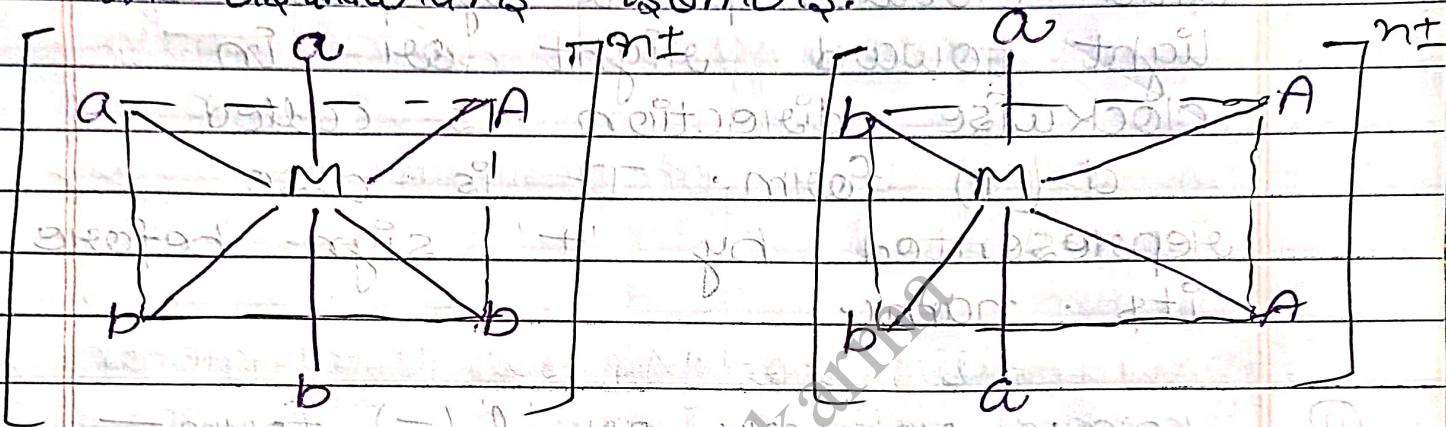
Example -  $[Co(C_2O_4)_2(PY)(NO)]$

$[Co(en)_2(NH_3)(Cl)]$

PIP



These complex exist  
in cis-and-trans isomers.



cis - isomers

trans - isomers

### Optical Isomerism

The compound which both molecular formula and structural formula both are similar but behave of ligand on mirror is different called optical isomers and this phenomenon known as optical isomerism.

29ab - +F - L TOR

The compound which rotate rapidly in plane polarised light called optical active compound.

Optical active compound exist in the following type-

① Dextro rotatory or 'd' (+) form —

The isomers which rotates plane of polarise light toward right or in clockwise direction is called d (+) form. It is also represented by '+' sign before its name.

② Laevo rotatory or 'l' (-) form —

The isomers which rotates the plane polarise light towards left or anticlockwise direction is called Laevo rotatory or 'l' form. It is represented by '-' sign before its name.

③ Racemic or 'dl' form —

It is the mixture of 50% 'd' and 50% 'l'. It does not rotate the plane polarise light due to external compensation hence it is optically inactive.

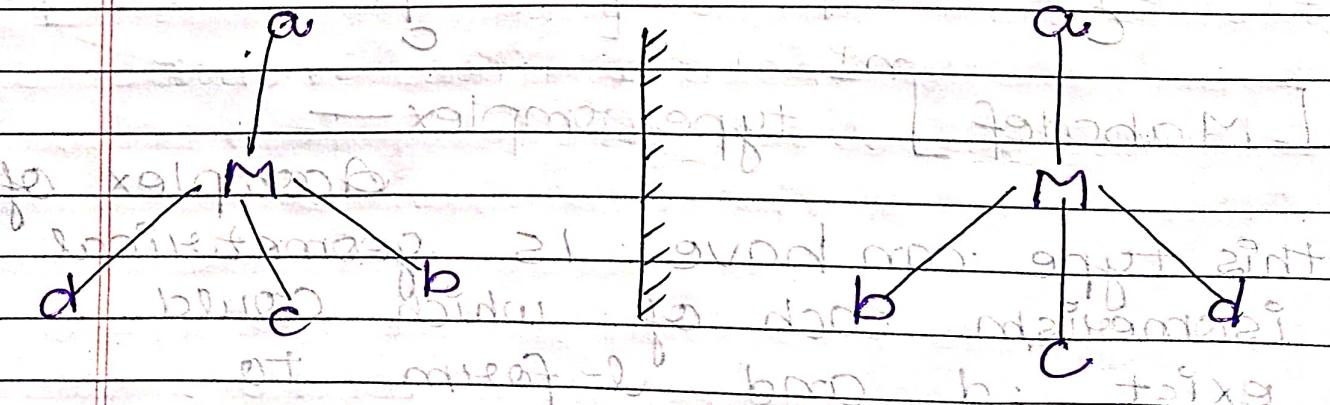
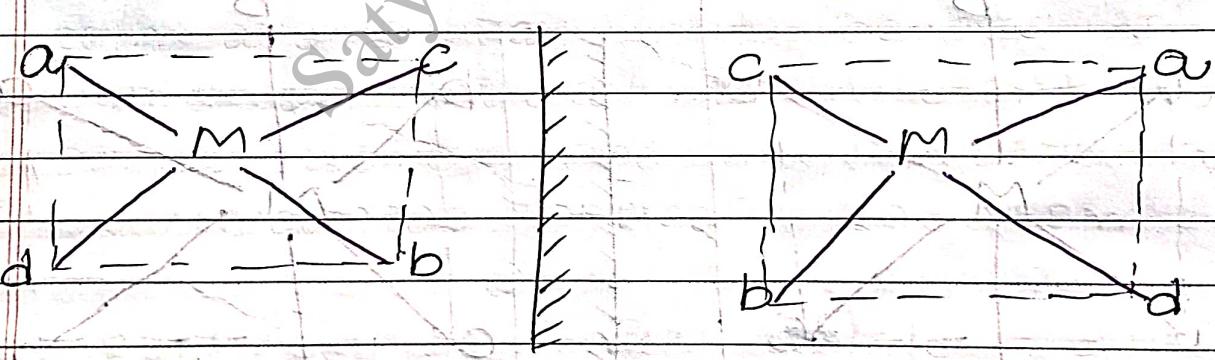
④ Meso form —

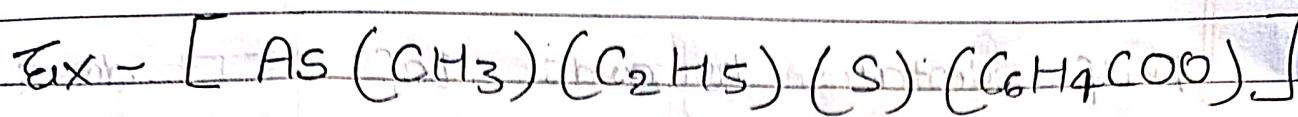
In meso form the half molecules rotates plane polarise light towards right while other

half rotates towards left. It does not rotates the plane polarise light due to internal compensation hence it is optically inactive.

Optical Isomerism in co-ordination No-4 →

Optical isomerism is not possible with square planar and tetrahedral complex of type -  $[ma_4]^{n\pm}$ ,  $[ma_3b]^{n\pm}$  and  $[mab_3]^{n\pm}$  but  $[mabcd]^{n\pm}$  shows the 2 optical isomers.



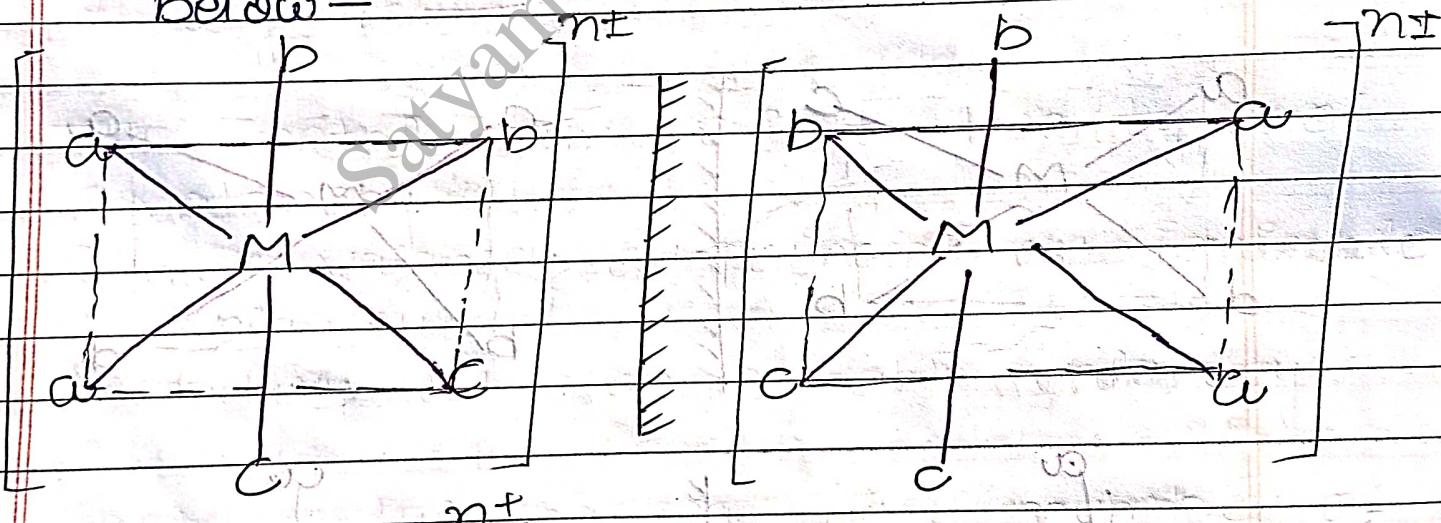


Optical Isomerism in complex with six co-ordination number —

optical isomerism in octahedral complex is following types —

Octahedral complex containing only monodentate ligand

a)  $[ma_2b_2c_2]^{n\pm}$  type complex — Such complex having two optical isomerism shown below —



b)  $[Mabcdef]^{n\pm}$  type complex —

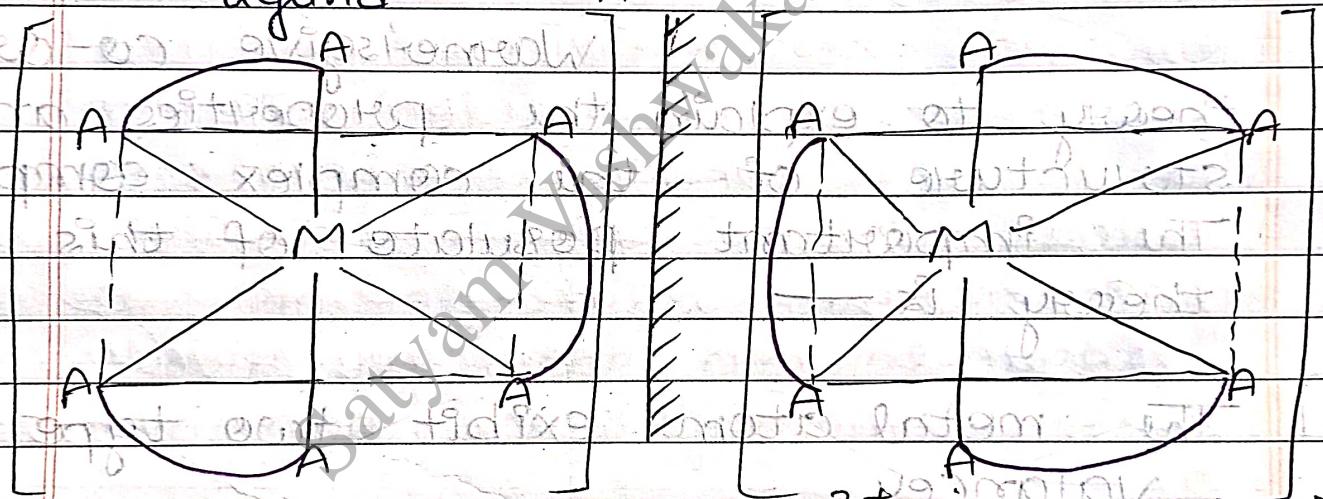
A complex of this type can have 15 geometrical isomerism each of which could exist d and l-form to

give a total 30 optical isomers.

Octahedral complex containing by symmetrical bidentate chelating ligand -

i)  $[M(AA)_3]$  type complex -

AA - symmetrical bidentate chelating ligand.

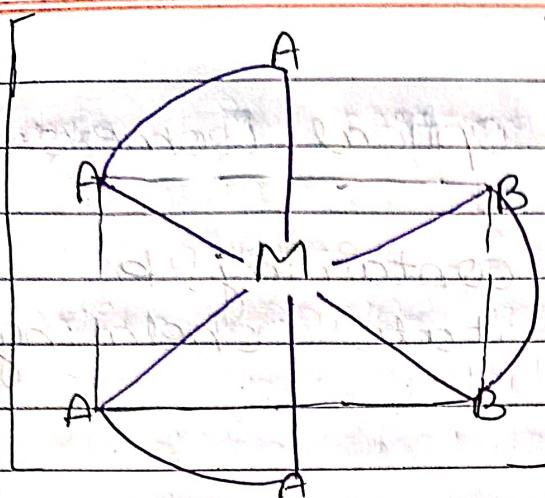
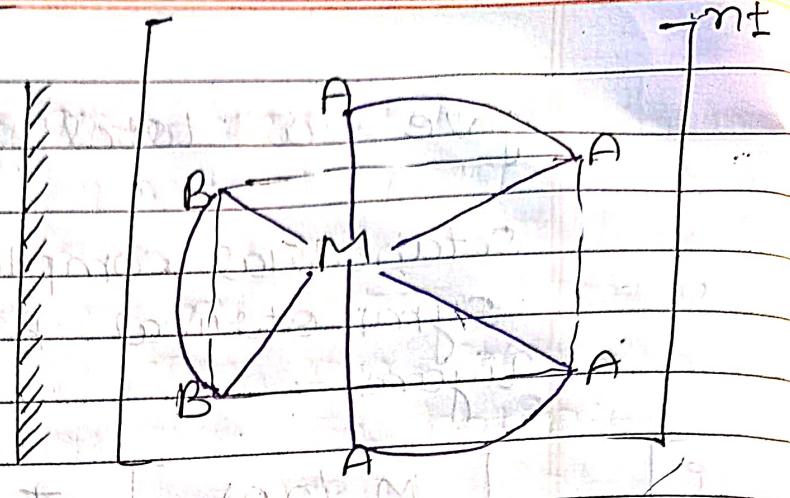


example -  $[Co(en)_3]$ ,  $[Co(Pn)_3]$

ii)  $[M(AA)_2(BB)]$  type complex -

where AA and BB

are two different unsymmetrical bidentate chelating ligand.

n<sup>t</sup>n<sup>t</sup>

## Warner co-ordination theory

Warner give co-ordination theory to explain the properties and structure of the complex compound. The important postulate of this theory is —

- i) The metal atom exhibit two type of valency.
- a) Primary valency or principle or ionisable valency.
- b) Secondary or non-ionisable valency.
- ii) Each metal has a fixed number of secondary valency i.e. it has a fixed co-ordination number.
- iii) The primary valency are satisfied by negative ion where as secondary valency

are satisfied by negative or neutral ligand.

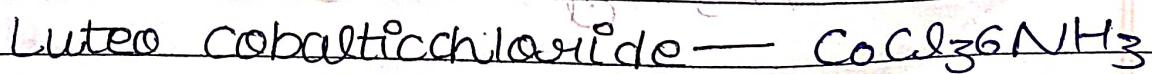
vi Primary valencies of metal are represented by solid line and secondary valencies are represented by dotted line.

iv The secondary valencies are directed towards fixed position in space around the central metal atom.

v The net charge on the complex is the algebraic sum of charge borne by the central metal ion and the ligand.

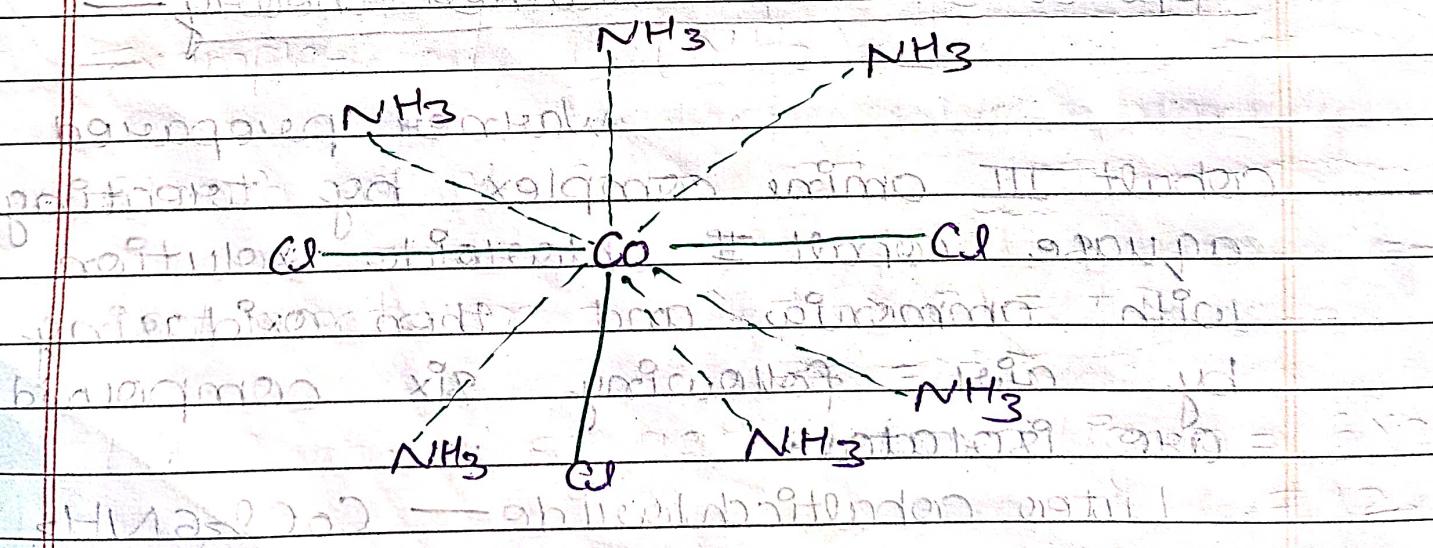
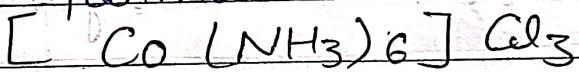
### Application of Werner theory —

Werner prepared cobalt III amine complex by treating aqueous cobalt II chloride solution with ammonia and then oxidising by air, following six compound are isolated.



This is orange-yellow crystalline compound. Its important properties are—

- i) With  $\text{AgNO}_3$  solution all the chlorine are precipitated  $\text{AgCl}$  from the solution of this complex, indicating that the bonding between  $\text{Co}$  and  $\text{Cl}$  are purely ionic.
- ii) With  $\text{HCl}$  ammonia is not removed even at  $100^\circ\text{C}$  showing that all the  $6 \text{ NH}_3$  molecule are unremovable from the above consideration it follows that  $\text{NH}_3$  molecule are secondary valency and  $\text{Cl}$  molecules are primary valency. Thus, Werner formula are written as—



## Sidgwick Electronic Interpretation of Co-ordination

Sidgwick suggested that the ligands have

- i - Warner's primary valency are similar to electrovalency and his secondary valency was similar to co-ordination valency.
- ii - The ligand attached with the central metal ion have atoms with at least one lone pair of electron in their balance shell.
- iii - The lone pair of electron is donated to the central metal ion by each ligand. The atoms who called which donate the electron pair are called donor and central metal ion which accept the electron pair is called acceptor. The bonds of this type are called co-ordinate or dative or semi-polar bond. These bonds are represented as  $L \rightarrow M$



## Valence bond theory

Pauling suggested a theory to explain the nature of metal ligand bonding to complex. This theory known as VBT or pauling theory.

This theory is based on the following assumptions—

- i- Central metal atom provides a number of empty s, p-d- atomic orbital equal to its co-ordination number for the formation of co-ordinate bond with ligand orbital.
- ii- The empty orbital of metal ion hybridised together to form hybrid orbital which are equal in number as the atomic orbital taking part in hybridisation. These are valent equivalent in energy and have definite geometry.

Co-ordination No.	Hybridisation	Geometry	Example
2	$sp$	Linear or diagonal	$[Ag(NH_3)_2]$
3	$sp^2$	Trigonal planar	$[HgI_3]^-$
4	$sp^3$	Tetrahedral	$[Ni(CO)_4]^0$
4	$dsp^2$	Square planar	$[Ni(CN)_4]^-$
5	$dsp^3$	Trigonal bipyramidal	$[Fe(CO)_5]$
5	$sp^3d$	Square pyramidal	$[SbF_5]$
6	$d^2sp^3$	Octahedral	$[Fe(CN)_6]^-$
6	$sp^3d^2$	Octahedral	$[Fe(F_6)]^-$

iii) Each ligand has at least one orbital containing a lone pair of electrons

iv) Empty hybrid orbital of the metal ion overlap with the filled lone pair of  $e^-$  of the ligand to form ligand  $\rightarrow$  metal  $\sigma$  bond.

V - Inner orbital i.e.  $(n-1)d$  known as low spin complex and outer orbital  $n d$  complex are known as high spin complex.

Vii - If the complex has paired electron it is called diamagnetic while the complex containing one or more unpaired electron called paramagnetic.

Viii - In complex formation Hund rule of maximum multiplicity is strictly followed.

### Limitation of VBT

This theory fails to explain the following fact -

i) Octahedral, tetrahedral and square planar of  $d^1$ ,  $d^2$ ,  $d^3$  and  $d^9$  ion have the same number of unpaired electrons and hence cannot be distinguished from each other.

ii) Complex formation of certain metal ion is not totally unsatisfactory for example in  $dsp^2$ -hybridisation  $Ti^{+4}$  ion obtained by promoting one p

3d-electron to form d-orbital hence, Cu<sup>+</sup> ion should gradually oxidised to Cu<sup>++</sup> ion which occurs very rarely.

- iii) This theory fails to explain that why a particular structure is preferred i.e. d<sup>8</sup> ion form square planar complex  $d^{sp^2}$ -hybridisation after maximum pairing. These ion may also form tetrahedral complex ( $sp^3$ -hybridisation)
- iv) This theory does not predict magnetic behaviour quantitatively except the number of unpaired electron in the complex.
- v) This theory does not explain rate of reaction and mechanism of reaction.
- vi) It does not explain thermodynamic property of other complex.
- vii) It does not explain spectra of complex.
- viii) This theory fails to explain the temperature dependent paramagnetism of complex.
- ix) It does not consider the splitting of d-block energy level.

## Chemistry of Lanthanide Elements

### Elements

The elements which have partly filled  $(n-2)f$  orbital are called f-block element.

These elements are also called inner transition element and divided into two series:

**Lanthanide Series** — This series includes fourteen elements from Ce to Lu.

In the elements of this series the additional electron goes to 4f-orbital.

**Actinide series** — This series includes also fourteen elements from Th to Lw.

In the element of this series the additional electron goes to 5f-orbital.

The inner transition of element are those element which possess both d and f orbital respectively.

## Lanthanide shell

## Actinide shell

## Actinides

### Lanthanide shell —

The series include 14 element from Ce to Lu for a group of 14 element in which additional electron goes to  $4f$ - orbital are  $(n-2)$  th main shell are called lanthanide. These are also known as rare earth element because they are found in less abundance.

The name of 14 element of lanthanide series element are given below.

	Symbol	Name
सीनि	58 Ce	Cerium
पर	59 Pr	Praseodymium
नदियाँ	60 Nd	Neodymium
प्रेमकी	61 Pm	Promethium
समरी	62 Sm	Samarium
यूँ	63 Eu	Europium
गदगद	64 Gd	Gadolinium
तब	65 Tb	Terbium
दिल	66 Dy	Dysprosium
हुआ ग्युशा	67 Ho	Holmium
ओर	68 Er	Euribium <u>Taillium</u>

ठुम 69 Tm Thulium

~~इ० ७० ५६~~ Ytterbium  
साप्तवाना ८८ + Lutetium

## General properties of Lanthanide

The general property of lanthanide series is similar to transition metal atom some property of lanthanide is given below—

## Electronic configuration

The electronic configuration of lanthanide series the energy of 5d and 4f orbital is near about similar and thus their filling of so certain perregularities. The electronic configuration of lanthanide in their ground state is given below:-

Trick —

1 2 3 4 5 6 7 8 9 10 11 12 13 14  
Electron 3 4 5 6 7 7 9 10 11 12 13 14 14  
Ln 4 f

Element	Configuration	Oxidation states
58Ce सीटे	[Xe] 4f <sup>1</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+3, +4
59Pr प्रेर	[Xe] 4f <sup>3</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+3, +4
60Nd नंडी	[Xe] 4f <sup>4</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+2, +3, +4
61Pm पीटे	[Xe] 4f <sup>5</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+3
62Sm स्मूनी	[Xe] 4f <sup>6</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+2, +3
63Eu यू	[Xe] 4f <sup>7</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+2, +3
64Gd गुडिया	[Xe] 4f <sup>9</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+3
65Tb टीबी	[Xe] 4f <sup>9</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+3, +4
66Dy देयती	[Xe] 4f <sup>10</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+3, +4
67Ho हो	[Xe] 4f <sup>11</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+3
68Er इरेर	[Xe] 4f <sup>12</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+3
69Tm त्रुम	[Xe] 4f <sup>13</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+2, +3
70Yb यी बी	[Xe] 4f <sup>14</sup> , 5d <sup>0</sup> , 6s <sup>2</sup>	+2, +3
71Lu लू	[Xe] 4f <sup>14</sup> , 5d <sup>1</sup> , 6s <sup>2</sup>	+3

## Oxidation number

Most of the common oxidation number is +3 all lanthanide series but it can show +2, +4 oxidation state when they achieve stable configuration  $f^0$ ,  $f^7$ ,  $f^{14}$ . There are some element which is show +2, +4 oxidation state these are given below—

## Magnetic properties

Most of the lanthanide series element are show paramagnetic property due to presence of unpaired electron and some element of diamagnetic due to presence of paired electron.

Paramagnetic substance are attracted in magnetic field but diamagnetic

In general the magnetic property of these element determined by magnetic movement

The magnetic movement arise from two type motion of electron.

The magnetic movement arise from two type -

- ① Spin motion
- ② Orbital motion

The spin motion of electron produces spin magnetic moment while the orbital motion of electron produces orbital magnetic moment.

The magnetic property of the lanthanides are different from those of the transition elements.

For f-block element, the electric field of ligands does not restricted the orbital motion of electron thus, orbital moment which was ignored in d-block but can not ignored in case of f-block element.

The magnetic moment in such case can be calculated by the following formula -

$$\mu = g \sqrt{J(J+1)} B \cdot M$$

where, 'g' is Lande splitting factor

and ' $J$ ' is the total angular momentum.

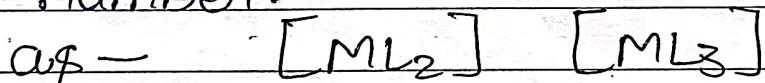
### Formation of complex compound

Most of lanthanide element show +3 oxidation state. Its f- and d- orbital are incomplete.

It is completed by gaining/accepting pair of electron to form complex compound.

In complex compound central metal atom is lanthanide element which surrounded by ligand.

These ligand donate a pair of electron to vacant f- and d- orbital of central metal atom to form co-ordinate bond. The total number of co-ordinate bond in complex compound are known as co-ordination number.



Lanthanide element have less tendency to complex formation due to high charge and large size.

## Colour property

Some trivalent ion of lanthanide series are coloured in solid and liquid state.

Lanthanide	Colourless	Pink	Yellow	Red	Coloured
La <sup>3+</sup>	Colourless				
Ce <sup>3+</sup>	Colourless				
Pr <sup>3+</sup>	Colourless				
Nd <sup>3+</sup>	Colourless				
Pm <sup>3+</sup>	Colourless				
Sr <sup>3+</sup>	Colourless				
Eu <sup>3+</sup>	Colourless				
Gd <sup>3+</sup>	Colourless				
Tb <sup>3+</sup>	Colourless				
Dy <sup>3+</sup>	Colourless				
Ho <sup>3+</sup>	Colourless				
Er <sup>3+</sup>	Colourless				
Tm <sup>3+</sup>	Colourless				
Yb <sup>3+</sup>	Colourless				
Lu <sup>3+</sup>	Colourless				

## Ionic and atomic radii — (lanthanide contraction)

In lanthanide series there is a regular decrease in the atomic size as well as atomic radii of trivalent ion as the

atomic number increase thus decrease in size of atom is known as lanthanide contraction. Atomic radii do show some irregularities but ionic radii are decreases from La to Lu.

Atoms	atomic size	ionic size
Ce	183	103
Pr	182	107
Nd	181	99
Pm	181	98
Sm	186	96
Gd	180	95
Eu	178	94
Tb	178	92
Dy	177	91
Ho	176	89
Er	175	88
Tm	174	87
Hf	173	86
Lu	170	86

On the moving from Ce to Lu decrease in atomic radii from 183 to 170 i.e. the decrease is only 13 pm similarly the decrease in ionic radii 103 - 86 pm i.e. decrease only 17 pm. cause of

## Cause of lanthanide contraction

The size of lanthanide series are decreased with increase atomic number because the number of nuclear charge outer most shell electron increases with increase in atomic number.

## Effect of lanthanide contraction

Some effect of lanthanide contraction are given below-

I Hardness (MP and BP increase) of some element of lanthanide series are higher this is becomes the attraction between the atom as the size decreases.

II Similarities of chemical property -

The change in the ionic radii in lanthanide series is very small. Therefore, chemical property of these element are similar. Thus, it is very difficult to separate these element in pure state.

## Basic strength of hydroxides

The size of lanthanide series is decreases therefore the basic strength of  $\text{OH}^-$  is decreases because  $\text{OH}^-$  group is strongly attached to inner transition metal ion so,  $\text{OH}^-$  ion is not easily remove therefore  $[\text{Ce}(\text{OH})_3]$  is more basic than  $[\text{Lu}(\text{OH})_3]$

Q-  $[\text{La}(\text{OH})_3]$  is more basic than  $[\text{Lu}(\text{OH})_3]$  why?

Ans-  $[\text{La}(\text{OH})_3]$  is more basic than  $[\text{Lu}(\text{OH})_3]$  because when we move from La to Lu in lanthanide series then the size of these element generally decrease therefore the size of La is larger than Lu and La is loosely bonded with  $\text{OH}^-$  and easily remove  $\text{OH}^-$  so it is more basic.

Due to smaller size of Lu it is tightly bonded to  $\text{OH}^-$  hence it is not easily remove  $\text{OH}^-$  so it is less basic.

## Chemistry of Actinides

A group of 14 element in which the additional e<sup>-</sup> goes to 5f orbital of (n=2) main shell are called actinide or actinones or 5f-block element. The elements beyond 'U' which does not occurs in nature. The elements having atomic number higher than 'U' are known as trans-uranic element. These element are man-made. The 14 elements of actinide are —

Ac 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk  
एक्सी थार्मियम पार्सी अर्जेन्ट एन्पी एप्युरोम एमीमी बीकी और के लिए नियम सुनित थार्मियम मीडीम एन्पी एप्युरोम एमीमी बीकी और

### Properties of actinides

#### Electronic configuration

The electronic configuration of outermost shell of these element are given below—

Trick-	1	2	3	4	5	6	7	8	9	10	11	12	13	14
e <sup>-</sup> inst-	1	2	3	4	5	7	7	9	10	11	12	13	14	14

88 Ae

Element

E. Configuration

Oxidation No.

g<sub>0</sub> Th - [Rn] 5f<sup>1</sup>, 6d<sup>1</sup>, 7s<sup>2</sup> +3, +4

थार्मस

g<sub>1</sub> Pa - [Rn] 5f<sup>2</sup>, 6d<sup>1</sup>, 7s<sup>2</sup> +3, +4, +5

पाकरी

g<sub>2</sub> U - [Rn] 5f<sup>3</sup>, 6d<sup>1</sup>, 7s<sup>2</sup> +3, +4, +5, +6

चुरोप

g<sub>3</sub> Np - [Rn] 5f<sup>4</sup>, 6d<sup>1</sup>, 7s<sup>2</sup> +3, +4, +5, +6, +7

नाचन

g<sub>4</sub> Pu - [Rn] 5f<sup>5</sup>, 6d<sup>1</sup>, 7s<sup>2</sup> +2, +3, +4, +5, +6

पहुंच

g<sub>5</sub> Am - [Rn] 5f<sup>7</sup>, 6d<sup>0</sup>, 7s<sup>2</sup> +3, +4

अमेरिका

g<sub>6</sub> Cm - [Rn] 5f<sup>7</sup>, 6d<sup>1</sup>, 7s<sup>2</sup> +3, +4

कमिंग

g<sub>7</sub> Bk - [Rn] 5f<sup>9</sup>, 6d<sup>0</sup>, 7s<sup>2</sup> +2, +3

ब्रिक

g<sub>8</sub> Cf - [Rn] 5f<sup>10</sup>, 6d<sup>0</sup>, 7s<sup>2</sup> +2, +3

कैलिफोर्निया

g<sub>9</sub> Es - [Rn] 5f<sup>11</sup>, 6d<sup>0</sup>, 7s<sup>2</sup> +2, +3

रेस्ट

g<sub>10</sub> Fm - [Rn] 5f<sup>12</sup>, 6d<sup>0</sup>, 7s<sup>2</sup> +2, +3

फर्म

g<sub>11</sub> Md - [Rn] 5f<sup>13</sup>, 6d<sup>0</sup>, 7s<sup>2</sup> +2, +3

मीडम

g<sub>12</sub> No - [Rn] 5f<sup>14</sup>, 6d<sup>0</sup>, 7s<sup>2</sup> +2, +3

नोआके

g<sub>13</sub> Lw - [Rn] 5f<sup>14</sup>, 6d<sup>1</sup>, 7s<sup>2</sup> +2, +3

लोक्यु आये

## Oxidation state —

Most of the actinides series element shows +3 oxidation number but some element shows +2 to +7 the different oxidation state. The +4 state is shown by first element and +5 oxidation state shown by five element and +7 oxidation state is shown by Pu and Np. In oxidation variation is because on the element of actinide, the energy of 5f, 6d and 7s are about similar.

## Magnetic property —

Most of the ion of actinide series are paramagnetic i.e. they are attracted in magnetic field. This is due to the presence of unpaired electron  $\text{Ac}^{+3}$ ,  $\text{SrTh}^{4+}$ ,  $\text{Lu}^{3+}$  are diamagnetic which are repelled in magnetic field. The magnetic properties of these element can be explained on the basis of magnetic moment. The magnetic moment of these can be calculated by the following formula —

$$\mu = g \sqrt{J(J+1)} B.M.$$

OR

$$\mu = \sqrt{4S(S+1) + L(L+1)} BM$$

### Actinide contraction

The atomic and ionic radii decreases with increasing of atomic number when we move actinide series from left to right. It has been observed that on going  $Act^{++}$  to  $Cm^{++}$ , Ionic radii decreases from  $99\text{ Å} - 88\text{ Å}$ . This irregular decrease the atomic and ionic radii in actinide element are known as actinide contraction.

The contraction is causes due to increasing the number of nuclear charge the attraction between outer most shell electron and nuclear charge increasing show, the size of atom or ion decreases.

## Similarities of Lanthanide and actinide series

There are some similarities between lanthanide and actinide series -

- i - both the series there is irregular filling of f-orbital in their electronic configuration.
- ii - Both shows common oxidation number +3.
- iii - Both are electropositive and high chemical reactivity.
- iv - There is a decrease in the atomic / ionic sizes in both the series with increase in atomic number.
- v - The elements of both series are neutral paramagnetic.
- vi - Both have tendency to form complex compound.

Difference between Lanthanide and actinide -

## Lanthanide (Lanthanides) & Actinide

- i - The electrons enters in  $4f$ - orbital
- i - The electron enters in  $5f$ - orbital
- ii - Their highest oxidation state is +4.
- ii - They show highest oxidation state +6, +7
- iii - Their paramagnetic property easily explained.
- iii - They are also paramagnetic but it is difficult to explain their magnetic property
- iv -  $4f$ - electron have greater shielding effect
- iv - It have less shielding effect
- v - They have less tendency to form complex compound.
- v - They have greater tendency to form complex compound.
- vi - They are non-radioactive
- vi - They are radioactive

## Oxidation and Reduction

### Oxidation number

Oxidation number of atom is the charge on the atom in compound.

general rule to calculate the oxidation number

The following rule to determine the oxidation number of the element -

i- Oxidation number of an element in the combined or free state is zero

ii- oxidation number of hydrogen in all its compound is +1. but in hydride the oxidation number of hydrogen is -1

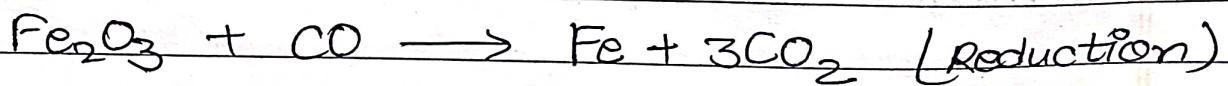
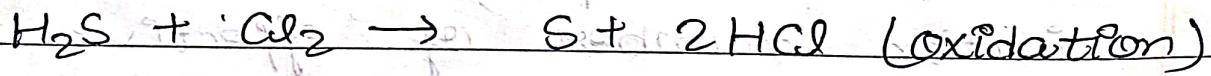
iii- Oxidation number of oxygen in all its compound is -2 but in peroxide in -1 and  $\text{OF}_2$  in +2.

iv- Oxidation number of alkali metal is +1 and alkali earth metal have +2.

- v - The oxidation number of ion or radical is equal to the charge present in it.
- vi - The sum of oxidation number of all the atom in a given molecule is zero. and is determined by the sum of oxidation number of the individual atom each multiplied by number of atom present in molecule.
- vii - The sum of the oxidation number of the atoms in a poly atomic ion is equal to the charge carried by the ion.

### Older concept of oxidation and Reduction

According to this concept  
The addition of oxygen or removed of hydrogen is called oxidation and addition of hydrogen or removed of oxygen is called reduction.

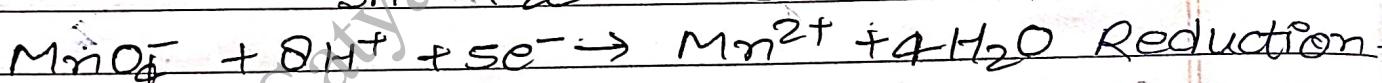
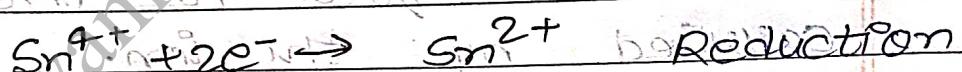
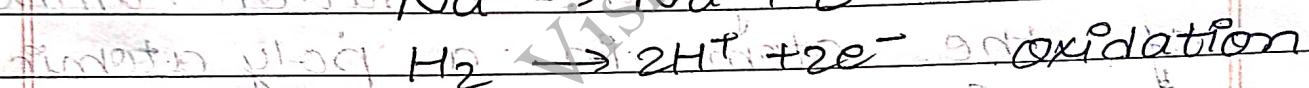


Differentiation based on the electron transfer  
 (Electronical concept) →

According to

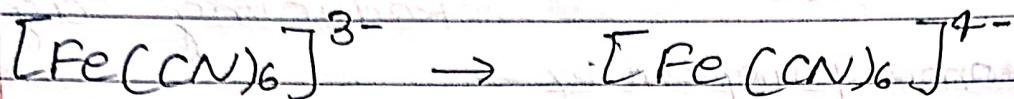
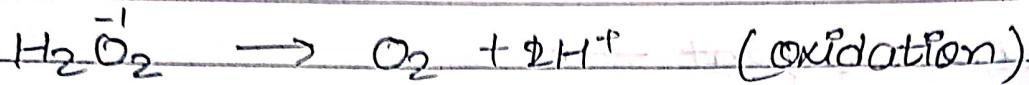
this concept oxidation is a process in which ion, atom or molecule loses one or more electron. On the other hand, reduction is a process in which ion, atom or molecule accept one or more electron.

Example -



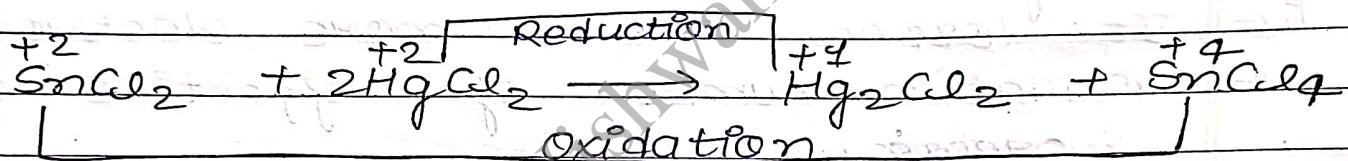
Differentiation based on oxidation number

According to this concept oxidation can be defined as a process in which oxidation number of effective element increases and reduction is a process in which oxidation number of effective element decreases.



### Redox reaction —

A reaction in which oxidation and reduction takes place simultaneously is called Redox or oxidation- Reduction reaction.



### Oxidising agent —

An oxidising agent have some properties —

- i - It oxidized some other substance and itself it reduced.
- ii - It losses oxygen or any electro-negative element.
- iii - It accept Hydrogen or any electro-positive element.
- iv - It gains one or more electron.
- v - oxidation number of effective element decreases.

## Reducing agent

Reducing agent have some properties -

- i- It reduced some other substance and itself it oxidised.
- ii- It losses Hydrogen or any electro positive element.
- iii- It accept oxygen or any electro negative element.
- iv- It losses one or more electron.
- v- Oxidation number of effective element increases.



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