

**CLASS-XII**

*for*

# BRUSH UP NEET/JEE 2021

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Unit  
4

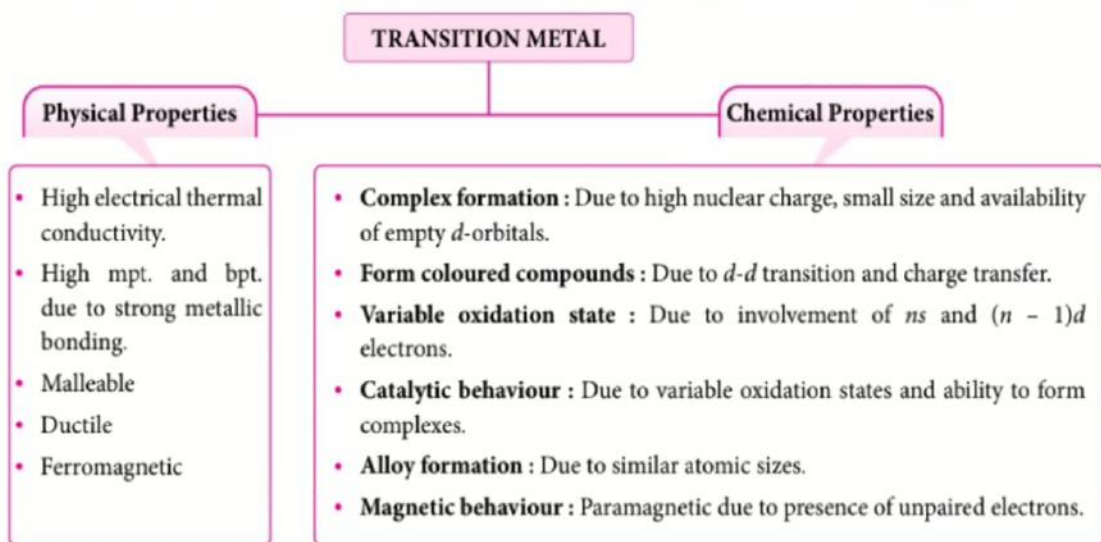
## d- and f-Block Elements | Coordination Compounds

### d - and f-Block Elements

#### TRANSITION ELEMENTS

- ↳ Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shell are known as *transition elements*.
- ↳ General electronic configuration :  $(n - 1)d^{1-10}ns^{0-2}$
- ↳ The presence of unpaired and empty *d*-orbitals favours *covalent bonding*.

#### GENERAL CHARACTERISTICS



Atomic Properties	Ionisation Energy	Atomic size	Electronegativity	Density
	Increases slowly due to ineffective shielding of nuclear charge by <i>d</i> electrons which tend to attract the outer electron cloud with greater force.	Decreases slowly in the series upto the middle due to ineffective shielding of <i>d</i> -electrons and increased nuclear charge but at the end of the series there is a slight increase in atomic radii due to increased electron-electron repulsion between added electrons.	Increases slowly	Increases along a series because atomic size decreases whereas atomic mass increases.

### SOME IMPORTANT COMPOUNDS

Compounds	Preparation	Properties	Uses
Potassium dichromate (K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> )	From sodium dichromate (obtained from chromite ore) $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$	Orange red, crystalline solid, oxidising agent having melting point 398°C. <b>Oxidising agent in acidic medium :</b> $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ <b>Oxidises :</b> I <sup>-</sup> to I <sub>2</sub> , H <sub>2</sub> S to S, Sn <sup>2+</sup> to Sn <sup>4+</sup> , Fe <sup>2+</sup> to Fe <sup>3+</sup>	In dyeing, photography and leather industry.
Potassium permanganate (KMnO <sub>4</sub> )	From potassium manganate (obtained from pyrolusite) $2\text{K}_2\text{MnO}_4 + \text{Cl}_2 \rightarrow 2\text{KMnO}_4 + 2\text{KCl}$	Deep purple, crystalline solid, oxidising agent, having melting point 240°C. <b>Oxidising agent in acidic medium :</b> $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ <b>Oxidises :</b> I <sup>-</sup> to I <sub>2</sub> , Fe <sup>2+</sup> to Fe <sup>3+</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> to CO <sub>2</sub> , S <sup>2-</sup> to S, SO <sub>3</sub> <sup>2-</sup> to SO <sub>4</sub> <sup>2-</sup> , NO <sub>2</sub> <sup>-</sup> to NO <sub>3</sub> <sup>-</sup> <b>Oxidising agent in alkaline or neutral medium :</b> $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$ <b>Oxidises :</b> I <sup>-</sup> to IO <sub>3</sub> <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> to SO <sub>4</sub> <sup>2-</sup> , Mn <sup>2+</sup> to MnO <sub>2</sub>	As a disinfectant, germicide, and Baeyer's reagent (alkaline KMnO <sub>4</sub> ).

### INNER TRANSITION ELEMENTS

- ↳ **Lanthanoids :** The elements with atomic numbers 58 to 71 *i.e.*, cerium to lutetium (which come immediately after lanthanum, Z = 57) are called *lanthanoids*.
- ↳ **Actinoids :** The elements with atomic number 90

to 103 *i.e.*, thorium to lawrencium (which come immediately after actinium, Z = 89) are called *actinoids*.

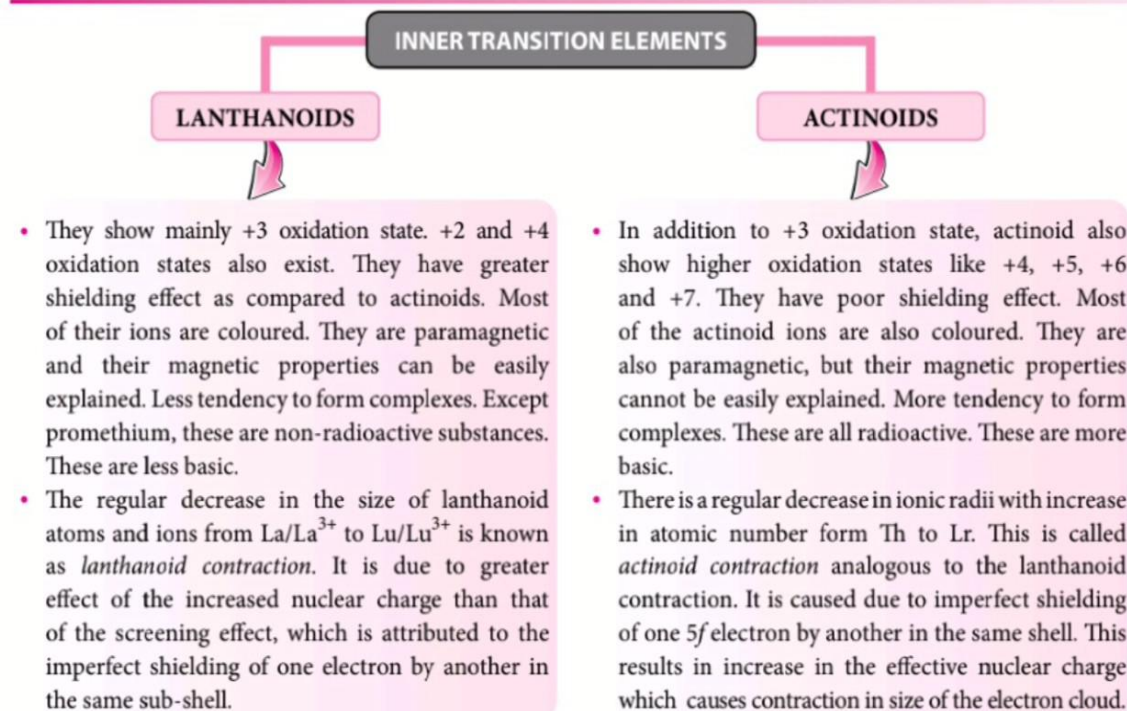
- ↳ They are called *f*-block elements because last electron enters into *f*-orbital.
- ↳ General electronic configuration :  $(n - 2)f^{1-14}(n - 1)d^{0-1}ns^2$



#### Therapeutic and Diagnostic Applications of Lanthanides !

The biological properties of the lanthanoids, primarily based on their similarity to calcium, have been the basis for research into potential therapeutic applications of lanthanoids. Up to date, cerium nitrate has been used as a topical cream with silver sulfadiazene for the treatment of burn wounds. A lanthanoid texaphyrin complex (Motexafin gadolinium) has been evaluated through phase III clinical trials for the treatment of brain metastases in non-small cell lung cancer. Lanthanum carbonate (Fosrenol) as a phosphate binder has been approved for the treatment of hyperphosphatemia in renal dialysis patients in both the USA and Europe.

## GENERAL CHARACTERISTICS



### CONSEQUENCES OF LANTHANOID CONTRACTION

- ↻ Separation of lanthanoids is difficult because of small difference in their size. Therefore, lanthanoids are mainly separated by ion exchange method.
- ↻ Basic strength of hydroxides decreases from Ce to Lu. Thus, La(OH)<sub>3</sub> is most basic whereas Lu(OH)<sub>3</sub> is least basic.
- ↻ Radii of elements in same group from 4<sup>th</sup> to 12<sup>th</sup> groups in 4d and 5d series are very close and these elements in each group are called *chemical twins*. e.g., Zr and Hf, Nb and Ta, etc.
- ↻ The properties of complex formation increases from La to Lu because of decrease in size and increase in “charge : size” ratio.
- ↻ There is a very slight increase in electronegativity from La to Lu.

### Coordination Compounds

- ↻ Coordination compounds are those in which a central metal atom or ion is attached with a fixed number of groups or molecules (Ligands) through coordinate bonds.

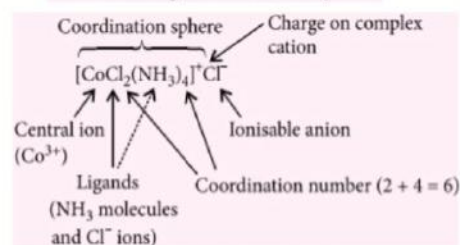
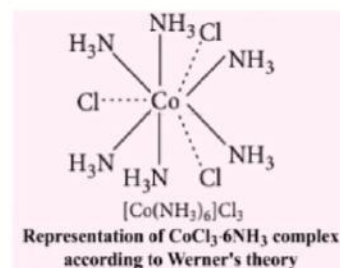
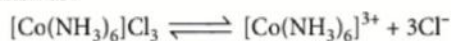
Double Salt	Co-ordination Compound
1. These exist only in solid state and dissociate into constituent species in their solution.	1. They retain their identity in solid as well as in solution state.
2. They lose their identity in dissolved state.	2. They do not lose their identity in dissolved state.
3. Their properties are essentially the same as those of their constituent species.	3. Their properties are different from those of their constituents. For example, K <sub>4</sub> [Fe(CN) <sub>6</sub> ] does not show the test of Fe <sup>2+</sup> and CN <sup>-</sup> ions.
4. In double salts' the metal atom/ion exhibit normal valency.	4. In co-ordination compounds, the number of negative ions or molecules surrounding the central metal atom is different from its normal valency.

## WERNER'S COORDINATION THEORY

It explains the nature of bonding in complexes. Metals show two different kinds of valencies.

- **Primary valency** : Non directional and ionisable. It is equal to the oxidation state of the central metal ion.
- **Secondary valency** : Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged or some times by positively charged ligands.

The ionisation of the coordination compound is written as :



When a polydentate ligand coordinates to a metal ion through more than one electron pairs of donor site simultaneously, is called **chelation**. The resulting complex has ring like structure and such ligand is called chelating ligand.

Chelating ligands form more stable complexes than similar ordinary complexes, in which the ligands act as monodentate.

**Ambidentate Ligand** : A unidentate ligand which can coordinate through two different atoms. *e.g.*,  $\text{NO}_2^-$ ,  $\text{SCN}^-$ , etc.

### Ligands

**Mono or unidentate ligands** : Ligands with one donor site. *e.g.*,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{OH}^-$ ,  $\text{CO}$ , etc.

**Bidentate ligands** : Ligands which have two donor atoms at two positions. *e.g.*, Ethylenediamine, oxalate, glycine, etc.

**Polydentate ligands** : The ligands having several donor atoms are called polydentate ligands. *e.g.*, Diethylenetriamine having 3 donor atoms is tridentate, EDTA with 6 donor atoms is hexadentate.

## IUPAC NOMENCLATURE

Naming and writing formulas of coordination compounds -

- The cation comes first, then the anion(s)
  - diammine silver(I) chloride  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
  - potassium hexacyanoferrate(III)  $\text{K}_3[\text{Fe}(\text{CN})_6]$
- Complex ion is enclosed in brackets
  - Ligands are named first in alphabetical order followed by metal atom.
    - **Anionic ligands** : End in -o *e.g.*,  $\text{Cl}^-$  : Chlorido
    - **Neutral ligands** : Retain their names with a few exceptions *e.g.*,  $\text{NH}_3$  : Ammine
    - **Cationic ligands** : End in -ium, *e.g.*,  $\text{NO}_2^+$  : Nitronium
    - **Ambidentate ligands** : Named by using

different names of ligands or by placing the symbol of donor atom. *e.g.*,  $-\text{SCN}^-$  (Thiocyanato-S or Thiocyanato),  $-\text{ONO}^-$  (Nitrito-O or Nitrito),  $-\text{NO}_2^-$  (Nitrito-N or Nitro),  $-\text{NCS}^-$  (Thiocyanato-N or Isothiocyanato).

- Metal is written first in the formula
- Naming is started with a small letter and complex part is written as one word.
- Metal oxidation state in roman numerals in parentheses after the metal ion.
- A space only between cation and anion.
- When coordination sphere is anionic, name of central metal ends in -ate. For *e.g.*,
  - tetraamminecopper(II) sulphate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
  - hexaamminecobalt(III) chloride  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Prefixes denote the number of each ligand type. Special prefixes and parentheses are used if the ligand already contains a prefix.

2	di	bis	4	tetra	tetrakis
3	tri	tris	5	penta	pentakis

6	hexa	hexakis	8	octa	octakis
7	hepta	heptakis	9	nona	nonakis
			10	deca	decakis

#### Some examples -

Sodium bis(thiosulphato) argentate (I) :  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$   
 tris(ethylene diamine) cobalt (III) ion :  $[\text{Co}(\text{en})_3]^{3+}$

## ISOMERISM

### ISOMERISM

#### Structural isomerism

It is displayed by compounds that have different ligands within their coordination sphere.

**Ionisation isomerism** : Isomers that give different ions in solution. e.g.,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}$ ;  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}$ .

**Hydrate isomerism** : Isomers having different number of  $\text{H}_2\text{O}$  as a ligand and as water of hydration. e.g.,  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ;  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ;  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ .

**Coordination isomerism** : The ligands are interchanged in both the cationic and anionic ions. e.g.,  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ ;  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

**Linkage isomerism** : This type of isomerism exists when ambidentate ligand is coordinated with its different donor atoms. e.g.,  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ ;  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ .

#### Stereoisomerism

Shown by compounds having same structural formula but differ only in the spatial arrangement of ligands around the central atom.

#### Geometrical isomerism

Arises due to different possible geometric arrangement of ligands.

#### In octahedral complex $[\text{Ma}_3\text{b}_3]$

**Facial (fac)** : 3 donor atoms of same ligands occupy adjacent positions at the corners.

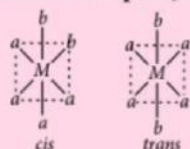


**Meridional (mer)** :

When the positions are around the meridian.

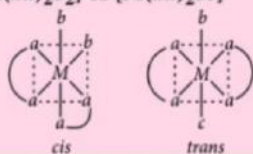


#### In octahedral complex $[\text{Ma}_4\text{b}_2]$



#### In octahedral complex

$[\text{M}(\text{aa})_2\text{b}_2]$  or  $[\text{M}(\text{aa})_2\text{bc}]$



#### In square planar complex $[\text{Ma}_2\text{b}_2]$

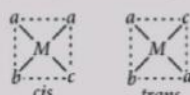
**cis** : 2 same ligands are arranged adjacent to each other.



**trans** : 2 same ligands are arranged opposite to each other.



#### In square planar complex $[\text{Ma}_2\text{bc}]$



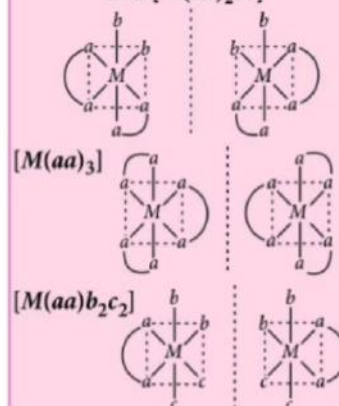
#### In square planar complex $[\text{Mabcd}]$

These isomers are obtained by selecting 1 ligand, (a) and then placing the remaining 3 ligands (b, c and d), one by one, trans to ligand (a). These type of complex shows three isomers – two cis and one trans. **Geometrical isomerism** is not possible in tetrahedral complexes.

#### Optical isomerism

Shown by molecule which do not have plane of symmetry.

#### Optical isomerism in $[\text{M}(\text{aa})_2\text{b}_2]$ and $[\text{M}(\text{aa})_2\text{bc}]$



**Optical isomerism** in tetrahedral complex of type  $\text{M}(\text{AB})_2$  where AB is unsymmetrical bidentate ligand. **Square planar complexes** do not show optical isomerism because of plane of symmetry.

## BONDING IN COORDINATION COMPOUNDS

☞ **Valence Bond Theory** : According to this theory, the metal atom/ion makes available empty orbitals equal to its coordination number.

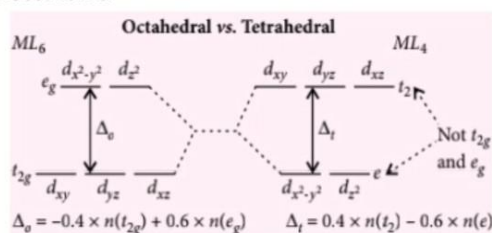
- The orbitals may be inner orbitals (Low spin) *i.e.*,  $(n-1)d$ ,  $ns$  and  $np$  or outer orbitals (High spin) *i.e.*,  $nd$ ,  $ns$  and  $np$  depending upon the strength of ligand.
- The vacant orbitals undergo hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral and square planar.
- These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

C. No.	Type of hybridisation	Geometry	Examples
2	$sp$	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]^-$
3	$sp^2$	Trigonal planar	$[\text{HgI}_3]^-$
4	$sp^3$	Tetrahedral	$\text{Ni}(\text{CO})_4$ , $[\text{NiX}_4]^{2-}$ , $[\text{ZnCl}_4]^{2-}$ , $[\text{CuX}_4]^{2-}$ where $X = \text{Cl}^-, \text{Br}^-, \text{I}^-$
	$dsp^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , $[\text{Ni}(\text{NH}_3)_4]^{2+}$
5	$dsp^3$	Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$ , $[\text{CuCl}_5]^{3-}$
	$sp^3d$	Square pyramidal	$[\text{SbF}_5]^{2-}$
6	$d^2sp^3$	Octahedral (Inner orbital)	$[\text{Cr}(\text{NH}_3)_6]^{3+}$ , $[\text{Fe}(\text{CN})_6]^{3-}$
	$sp^3d^2$	Octahedral (Outer orbital)	$[\text{FeF}_6]^{3-}$ , $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , $[\text{Ni}(\text{NH}_3)_6]^{2+}$

➤ **Magnetic properties :**

- Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.
- Paramagnetism  $\propto$  No. of unpaired electrons
- Magnetic moment =  $\sqrt{n(n+2)}$  B.M. where  $n$  = number of unpaired electrons.

☞ **Crystal Field Theory** : This theory is based on the assumption that the metal ion and the ligands act as a point charges and the interaction between them is purely electrostatic, *i.e.*, metal-ligand bonds are 100% ionic.



- $\Delta_o > P$  (low spin complex)
- $\Delta_o < P$  (high spin complex)
- $\Delta_t = \frac{4}{9} \Delta_o$
- **Spectrochemical series** : Arrangement of ligands in the order of increasing field strength.  $\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{ox}^{2-} < \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py} = \text{NH}_3 < \text{en} < \text{dipy} < \text{O} - \text{phen} < \text{NO}_2^- < \text{CN}^- < \text{CO}$ .

## STABILITY OF COORDINATION COMPOUNDS

Stability depends on

**Charge on the central metal ion (oxidation state) :** Greater the charge on central metal ion, more is the stability.

**Basic nature of ligand :** More the basic strength of ligand, more is the stability of complex.

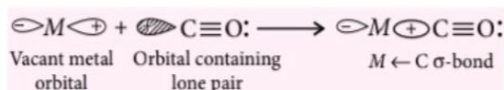
**Presence of chelate rings :** Formation of chelate ring increases the stability of complex.

**Size of the metal ion :** Smaller the size of metal ion, more is the stability.

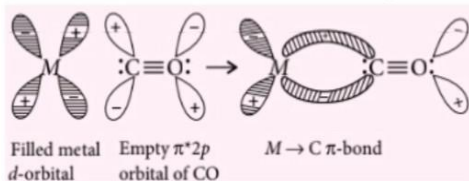
**Electronegativity and polarising power of the central metal ion :** More is the electronegativity and polarising power of the metal ion, more stable is the complex.

## BONDING IN METAL CARBONYLS

There is an overlap of filled  $\pi 2p$  orbital of CO with suitable empty orbital of metal resulting in the formation of sigma bond.



Then there is a  $\pi$ -overlap involving filled metal  $d$ -orbital and empty antibonding  $\pi^* 2p$  orbital of same CO. This results in formation of  $M \rightarrow C$   $\pi$ -bond. This is also called *back bonding*.



## ORGANOMETALLIC COMPOUNDS

Compounds having one or more metal carbon bonds.

**Types of organometallic compounds :**

Based on nature of metal - carbon bond, they are classified into :

- **$\sigma$ -bonded organometallic compounds :**  
*e.g.*;  $R-Mg-X$ ,  $(C_2H_5)_2Zn$ , etc.
- **$\pi$ -bonded organometallic compounds ( $\pi$  complexes) :** *e.g.*; Zeise's salt,  $K[PtCl_3(\eta^2-C_2H_4)]$ ; ferrocene,  $[Fe(\eta^5-C_5H_5)_2]$ , etc.
- **$\sigma$ - and  $\pi$ -bonded organometallic compounds (Metal carbonyls) :** *e.g.*,  $[Fe(CO)_5]$ ,  $[Ni(CO)_4]$ .



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## APPLICATIONS OF COORDINATION COMPOUNDS

Complex  $cis-[PtCl_2(NH_3)_2]$  known as *cis-platin* is used in cancer treatment.

Coordination compounds are also used in electroplating, photography, dyes, etc.

Hardness of water can be estimated by complex formation using EDTA.

Coordination compounds are used as catalyst, *e.g.*, Wilkinson's catalyst,  $(Ph_3P)_3RhCl$  Ziegler-Natta catalyst,  $[TiCl_4 + (C_2H_5)_3Al]$

EDTA is often used for treatment of lead poisoning.

Coordination compounds are of great importance in biological system, *e.g.*, chlorophyll, haemoglobin, myoglobin, etc. are coordinate compounds of Mg, Fe and Co respectively.

## INFOSHOTS

### A Balancing Act : Stability versus Reactivity of Mn(O) Complexes !

A large class of heme and non-heme metalloenzymes utilize  $O_2$  or its derivatives (*e.g.*,  $H_2O_2$ ) to generate high-valent metal-oxo intermediates for performing challenging and selective oxidations. Due to their reactive nature, these intermediates are often short-lived and very difficult to characterize. Synthetic chemists have sought to prepare analogous metal-oxo complexes with ligands that impart enough stability to allow for their characterization and an examination of their inherent reactivity. The challenge in designing these molecules is to achieve a balance between their stability, which should allow for their in situ characterization or isolation, and their reactivity, in which they can still participate in interesting chemical transformations. This account focuses on our recent efforts to generate and stabilize high-valent manganese-oxo porphyrinoid complexes and tune their reactivity in the oxidation of organic substrates.