

**UNIT-2 : Metal-Ligand Bonding  
in Transition complexes**

Notes by Mr. V. M. DESAI

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**2.1) Isomerism in complexes with CN= 4 & 6**

- a) Introduction- Isomerism
- b) Types of Isomerism
- c) **Stereoisomerism** : i) Geometrical Isomerism & ii) Optical Isomerism
- d) **Structural Isomerism** : i) Ionisation Isomerism
  - ii) Hydrate or Solvate Isomerism
  - iii) Coordination Isomerism
  - iv) Linkage Isomerism
  - v) Coordination Position Isomerism

**2.2) Molecular Orbital Theory (MOT)**

- a) Introduction
- b) MOT of octahedral complexes with sigma bonding such as  
 $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- c) Merits and demerits of MOT

**T. Y. B. Sc. (Part-III)**

**Inorganic Chemistry**

**Academic Year: 2019-20 Sem-V Paper-X**

**"LIFE" AND "TIME" are the world's Best Teachers.**

**Life teaches us to make good use of time and**

**Time teaches us the value of life.**

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

### University Questions:

The Roots of Education are Bitter,  
But the Fruit is Very Sweet...

#### Isomerism:

- Q.1) Enlist different types of isomerism possible in coordination complexes. Give one example of each type.
- Q.2) Enlist different types of structural isomerism possible in coordination complexes. Give one example of each type.
- Q.3) What is geometrical isomerism? Explain it with coordination number 4 & 6.
- Q.4) What is geometrical isomerism? Explain cis-trans isomerism in CN=4 (4M) Oct-2014
- Q.5) Define optical isomerism. Give examples of optical isomerism in CN=4 & 6 (10M) Oct-2015
- Q.6) How many isomers are possible for each of the following complexes?  
i)  $[\text{CoCl}_3(\text{NH}_3)_3]$  ii)  $[\text{CoCl}_2(\text{NH}_3)_4]^+$  iii)  $[\text{PtNH}_3\text{PyClBr}]$  iv)  $[\text{CoCl}_2(\text{NH}_3)_2(\text{Py})_2]$

#### MOT:

- Q.1) Draw MO diagram for an octahedral complex. Explain the formation of bonding, non-bonding and antibonding MOs and  $\Delta_0$  from the diagram.
- Q.2) Draw MO diagrams of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Comment on magnetic properties. (10M) April-2013
- Q.3) Draw MO diagrams of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  complex ion and comment on its magnetic properties. (4M) Nov.2013
- Q.4) Draw MO diagrams of  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Comment on magnetic properties. (10M) Oct-14 Dec.16
- Q.5) Write short note on 'Merits and demerits of MOT' (4M) Oct-2015

### Multiple Choice Questions (MCQ):

- 1) Stereoisomers have same structure but different relative arrangement of \_\_\_\_\_ in space. **IMP**  
a) ions                      b) cations                      c) anions                      **d) atoms of ligands**
- 2) Which of the following is subtype of stereoisomer?  
a) ionization                      b) hydrate                      c) linkage                      **d) optical**
- 3) Which of the following isomers have the different positions of ions are within or outside the coordination sphere?  
a) hydrate                      b) coordination                      c) linkage                      **d) ionization**
- 4) In coordination isomers, \_\_\_\_\_ are interchanged between cationic and anionic parts of the complex.  
a) Metal atom or ion                      b) ligands                      c) negative ions                      **d) both a & b**
- 5) In solvate (hydrate) isomers, \_\_\_\_\_ are replaced by water molecules.  
a) Metal atom or ion                      **b) ligands**                      c) negative ions                      d) both a & b
- 6) Linkage isomers contain \_\_\_\_\_ ligands. **IMP**  
a) unidentate                      b) bidentate                      c) polydentate                      **d) ambidentate**

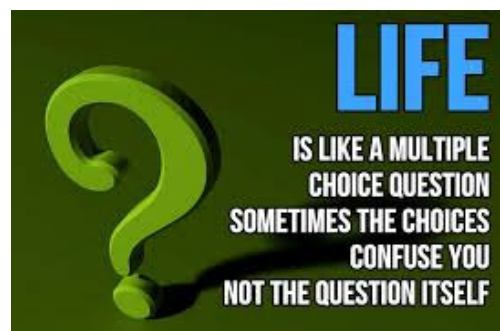
## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

- 7) Coordination position isomers are related to \_\_\_\_\_ complexes. **IMP**  
a) cationic      b) anionic      c) neutral      **d) bridged**
- 8) According to MOT,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion is \_\_\_\_\_. **IMP April-15**  
a) paramagnetic      b) coloured      c) colourless      **d) both a & b**
- 9) According to MOT,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  contains \_\_\_\_ unpaired electrons. **IMP Nov.13**  
a) 1      **b) 2**      c) 3      d) 4
- 10) According to MOT,  $[\text{CoF}_6]^{3-}$  contains \_\_\_\_\_ unpaired electrons. **IMP April-15**  
a) 1      b) 2      c) 3      **d) 4**
- 11) According to MOT,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex is \_\_\_\_\_ **IMP**  
a) paramagnetic      **b) diamagnetic**      c) ferromagnetic      d) none of these
- 12)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion has \_\_\_\_\_ colour. **IMP**  
a) Blue      b) Yellow      c) Orange      **d) Purple (reddish violet)**
- 13) Which of the following complex ion is orange yellow?  
a)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$       b)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$       c)  $[\text{CoF}_6]^{3-}$       **d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$**
- 14) Which of the following complex ion is blue coloured?  
a)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$       b)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$       **c)  $[\text{CoF}_6]^{3-}$**       d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- 15) Which of the following complex has four unpaired electrons?  
a)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$       b)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$       **c)  $[\text{CoF}_6]^{3-}$**       d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- 16) In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  complex, there are \_\_\_\_, \_\_\_\_, \_\_\_\_ bonding, non-bonding and antibonding MOs respectively.  
a) 6,3,6      **b) 6,6,3**      c) 3,6,6      d) 3,3,6
- 17) As \_\_\_\_\_ MOs are available for electronic transition, charge transfer spectra is possible.  
a) bonding      b) non-bonding      **c) antibonding**      d) All of these
- 18) According to MOT, \_\_\_\_ orbitals are remaining non-bonding in sigma bonding case with octahedral geometry. a)  $a_{1g}$       b)  $t_{2g}$       c)  $t_{1u}$       d)  $e_g$  April-13
- 19) According to MOT, overlapping orbitals must have \_\_\_\_\_  
a) Comparable energy      b) same symmetry  
c) appreciable overlap      **d) All of these**
- 20) MOT explains satisfactorily \_\_\_\_\_ of the complexes.  
a) Charge transfer spectra      b) Nephelauxetic effect  
c) Colour & magnetic properties      **d) All of these**

“Success and Excuses do not talk together.

If you want Excuses, forget about Success.

If you want Success, do not give Excuses..!”

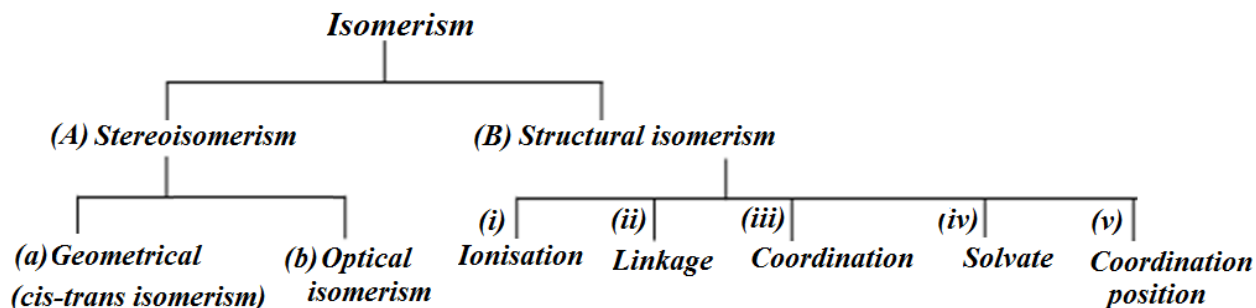


## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

### Isomerism in Coordination Compounds:

Isomers are two or more compounds that have the **same chemical formula** but a **different arrangement of ligands** (or atoms or groups) around central metal atom or ion **due to which they differ in one or more physical or chemical properties**. The phenomena of isomers are known as Isomerism.

#### Classification of Isomerism :



#### A) Structural Isomerism:

- i) Ionization isomerism
- ii) Linkage isomerism
- iii) Coordination isomerism
- iv) Hydrate Or Solvate isomerism
- v) Coordination position isomerism

**i) Ionization isomerism:** The isomerism, in which isomers have the same chemical formula but **produces different ions in the solution**, is known as 'Ionization Isomerism' and isomers thus obtained are known as ionization isomers. It is also known as '**ion-ion exchange isomerism**'.

#### Examples:

	Compounds	Colour	Ions present in the solution
a)	$[\text{Co}(\text{NH}_3)_5\text{SO}_4] \text{Br}$	Red violet	$[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+ + \text{Br}^-$
b)	$[\text{Co}(\text{NH}_3)_5 \text{Br}] \text{SO}_4$	Red	$[\text{Co}(\text{NH}_3)_5 \text{Br}]^{2+} + \text{SO}_4^{2-}$

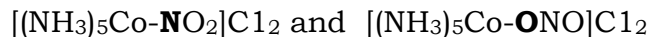
**Explanation:** In the two isomers (a) and (b), there is an **exchange of ions** namely  $\text{Br}^-$  and  $\text{SO}_4^{2-}$  inside and outside the coordination sphere. The aqueous solution of (a) gives the precipitate of  $\text{AgBr}$  on treatment with  $\text{AgNO}_3$  since it contains  $\text{Br}^-$ , while that of (b) gives precipitate of  $\text{BaSO}_4$  on treatment with  $\text{BaCl}_2$ , since it contains  $\text{SO}_4^{2-}$ .

**Other examples:** A few more examples of ionization isomerism are

- i)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{SO})_4$  and  $[\text{Co}(\text{NH}_3)_5(\text{SO})_4] \text{NO}_2$
- ii)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

ii) **Linkage isomerism:** The isomerism in which isomers have the same chemical formula but **differ in the linkage of the ligand to central metal atom or ion**, is known as 'Linkage Isomerism' and isomers thus obtained are known as linkage isomers. Example:



**Explanation:** Here,  $-\text{NO}_2$  ligand can bind to the central metal through **nitrogen** or **oxygen** to give two different isomers.

**Other examples:** A few more examples of ionization isomerism are



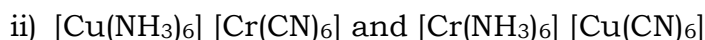
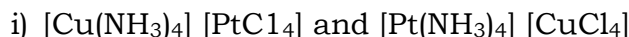
**Note:** A few more **ambidentate ligands** are cyano ( $\text{CN}^-$ ) and thiocyanate ( $\text{SCN}^-$ ) show **Linkage isomerism**

iii) **Coordination isomerism:** The isomerism in which isomers have the same chemical formula but **differ in the interchange of ligands between cationic and anionic entities in the complexes**, is known as 'Coordination Isomerism' and isomers thus obtained are known as Coordination isomers.

**Example:**  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

**Explanation:** In  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  complex,  $\text{NH}_3$  ligands are bound to cobalt ( $\text{Co}^{3+}$ ) and  $\text{CN}^-$  ligands to  $\text{Cr}^{3+}$ . In its coordination isomer  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ , the  $\text{NH}_3$  ligands are bound to  $\text{Cr}^{3+}$  and  $\text{CN}^-$  ligands to  $\text{Co}^{3+}$ .

**Other examples:** A few more examples of coordination isomerism are

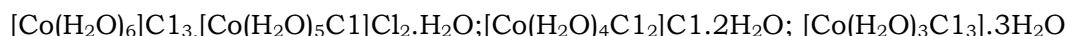


iv) **Hydrate isomerism (Solvate isomerism) :** The isomerism in which isomers have the same chemical formula but differ in the number of molecules of  $\text{H}_2\text{O}$  inside and outside the coordination sphere, is known as '**Hydrate or Solvate Isomerism**' and isomers thus obtained are known as **Hydrate or Solvate isomers**.

Example:  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  exists in three hydrate isomers as given below;

Compound	Colour	Number of $\text{H}_2\text{O}$ Molecules	
		Inside Coordination sphere	Outside coordination sphere
(A) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Violet	6	0
(B) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot 1\text{H}_2\text{O}$	Blue green	5	1
(C) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$	Green	4	2

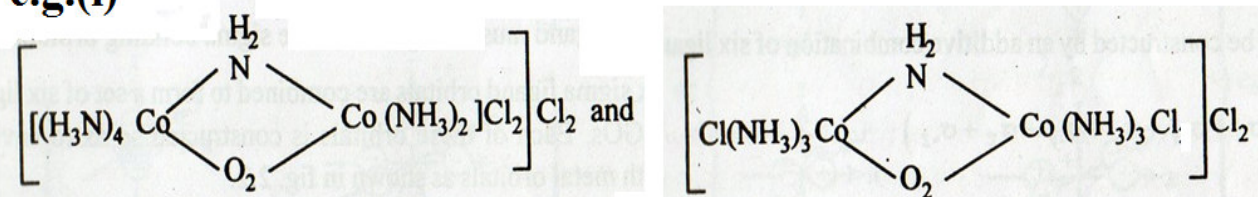
**Other examples:** A few more examples of hydrate or solvate isomerism are



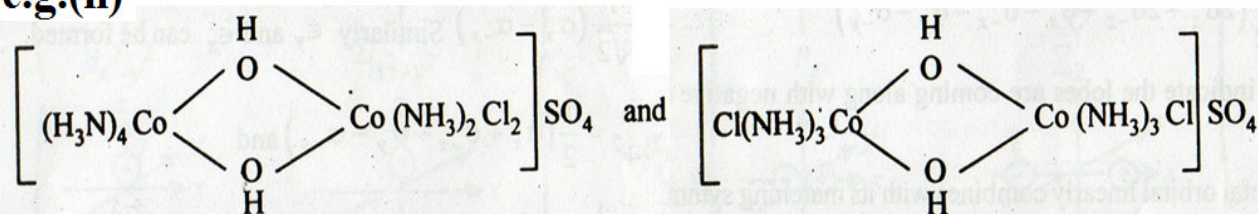
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**v) Coordination Position Isomerism:** The isomerism in which isomers have the same chemical formula but **differ in the arrangement of the ligands relative to the metal ions in the bridged complexes**, is known as 'Coordination position Isomerism' and isomers thus obtained are known as Coordination position isomers.

e.g.(i)



e.g.(ii)



**B) Stereoisomerism:** The isomerism, in which different ligands (or atoms or groups) occupy different spacial positions around the central metal atom or ion, is known as 'Stereoisomerism' and isomer thus obtained are known as 'Stereoisomer'.

### Types of Stereoisomerism:

a) **Geometrical Or Cis-trans Isomerism:** The stereoisomerism which have same chemical formula but different arrangement of ligands or atoms or groups in space around central metal atom or ion, is known as 'Geometrical isomerism'. When ligands (or atoms or groups) occupy **adjacent position**, the corresponding isomer is known as **cis-isomer** whereas if ligands (or atoms or groups) occupy position **opposite to each other** is known as **trans-isomer**. Thus, geometrical isomerism is also known as **cis-trans isomerism**.

Geometrical isomerism is observed with

a) Coordination number = 4    and    b) Coordination number = 6

#### a) Coordination Number 4 :

For CN=4, possible structure will be **tetrahedral or square planar**

a) Tetrahedral geometry does **not show geometrical i.e. cis-trans isomerism**.

**“Only I Can Change My Life. No One Can Do It for Me.”**

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b) **Square Planar geometry show geometrical i.e. cis-trans isomerism** with formula

i)  $[Ma_2b_2]$ , where a and b are unidentate ligands

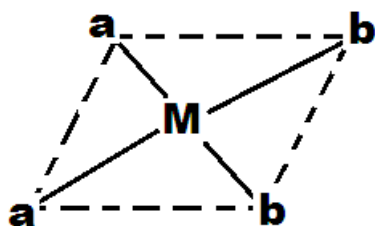
ii)  $[Ma_2bc]$ ,

iii)  $[Mabcd]$ ,

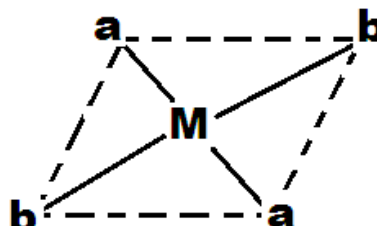
iv)  $[M(A-B)_2]$ ,

i)  $[Ma_2b_2]$  **type:** In Cis isomer, the two similar ligands are arranged adjacent to each other whereas in **Trans isomer**, the two similar ligands are arranged **opposite** to each other as shown in fig.

**Possibilities:**



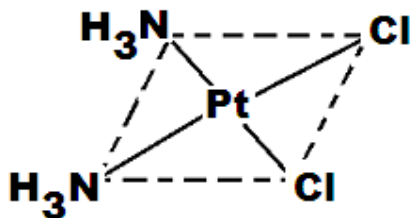
Cis- isomer



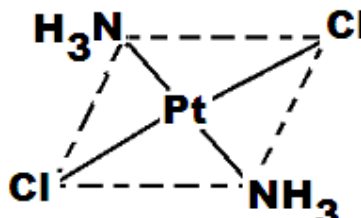
Trans-isomer

(Similar atoms- adjacent to each other) (Similar atoms- Opposite to each other)

**Example:** Geometrical isomers of  $[Pt(NH_3)_2Cl_2]$



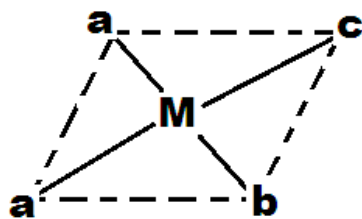
Cis- isomer



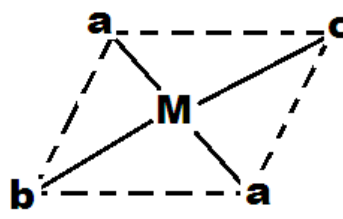
Trans-isomer

ii)  $[Ma_2bc]$  **type:** In Cis isomer, the two similar ligands are arranged adjacent to each other whereas in **Trans isomer**, the two similar ligands are arranged **opposite** to each other as shown in fig.

**Possibilities:**



Cis- isomer



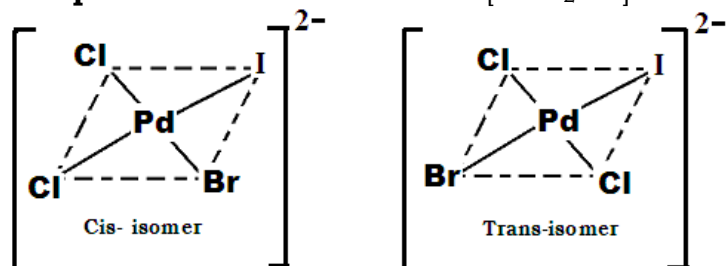
Trans-isomer

(Similar atoms- adjacent to each other)

(Similar atoms- Opposite to each other)

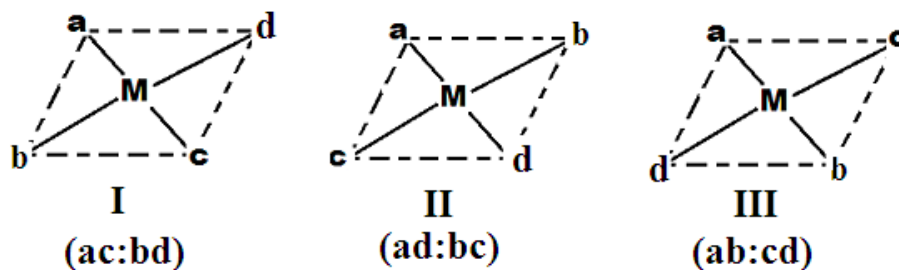
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**Example:** Geometrical isomers of  $[\text{PdCl}_2\text{BrI}]^{2-}$

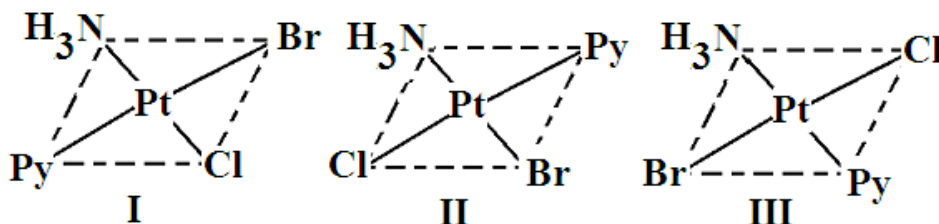


iii) **[Mabcd] type:** Complex of the type **[Mabcd]** when all the four ligands are different, **three** geometrical isomers are possible in square planar complexes.

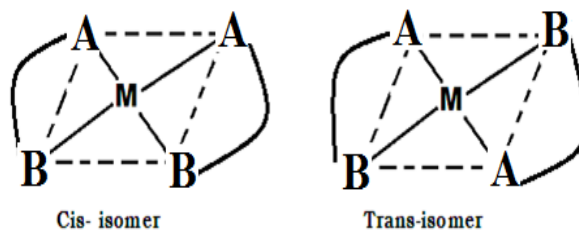
**Possibilities:**



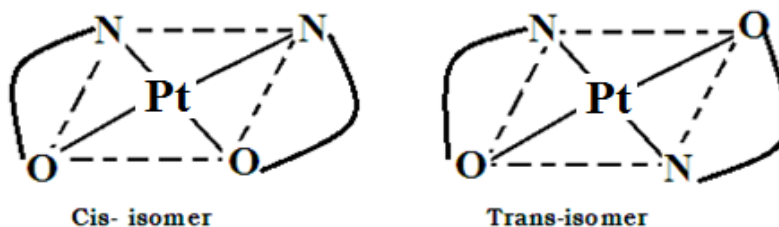
**Example:** Geometrical isomers of  $[\text{PtNH}_3\text{PyClBr}]$



iv) **[M(A-B)<sub>2</sub>] type:** In this complex  $[\text{M}(\text{A-B})_2]$  type, 'M' is the central atom, and 'A-B' is an unsymmetrical bidentate ligand. The cis and trans forms of this complex are shown in Fig.



An example of this type of complex is  $[\text{Pt}(\text{gly})_2]$ , where gly stands for glycino,  $(\text{NH}_2\text{CH}_2\text{COO})$ - ligand.





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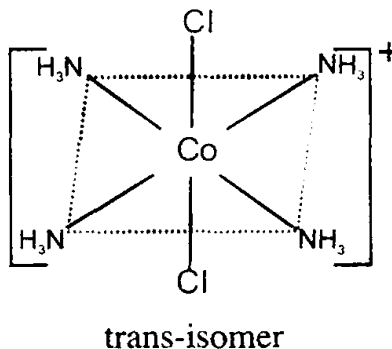
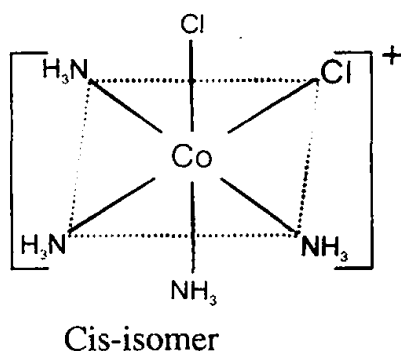
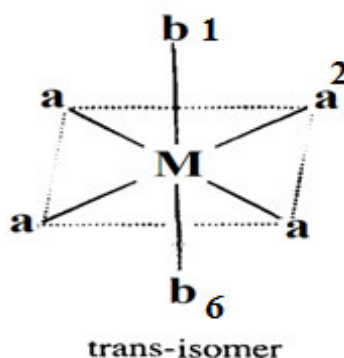
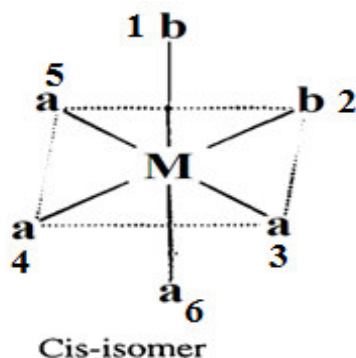
**b) Coordination Number =6:** Complexes with coordination number six are octahedral in shape. Octahedral complexes of the type **Ma<sub>6</sub>** and **Ma<sub>5</sub>b** do not show geometrical isomerism because in these complexes different spatial arrangements of ligands are not possible.

Octahedral geometry **show geometrical i.e. cis-trans isomerism** with formula;

- i) **[Ma<sub>4</sub>b<sub>2</sub>]**, where a and b are unidentate ligands
- ii) **[Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>]**,
- iii) **[Ma<sub>3</sub>b<sub>3</sub>]**,
- iv) **[Mabcdef]**,
- v) **[M(A-A)<sub>2</sub>a<sub>2</sub>]**, where A-A are bidentate symmetrical ligands
- vi) **[M(A-A)a<sub>2</sub>b<sub>2</sub>]**,
- vii) **[M(A-B)<sub>3</sub>]**, where A-B are bidentate unsymmetrical ligands

### i) [Ma<sub>4</sub>b<sub>2</sub>] type:

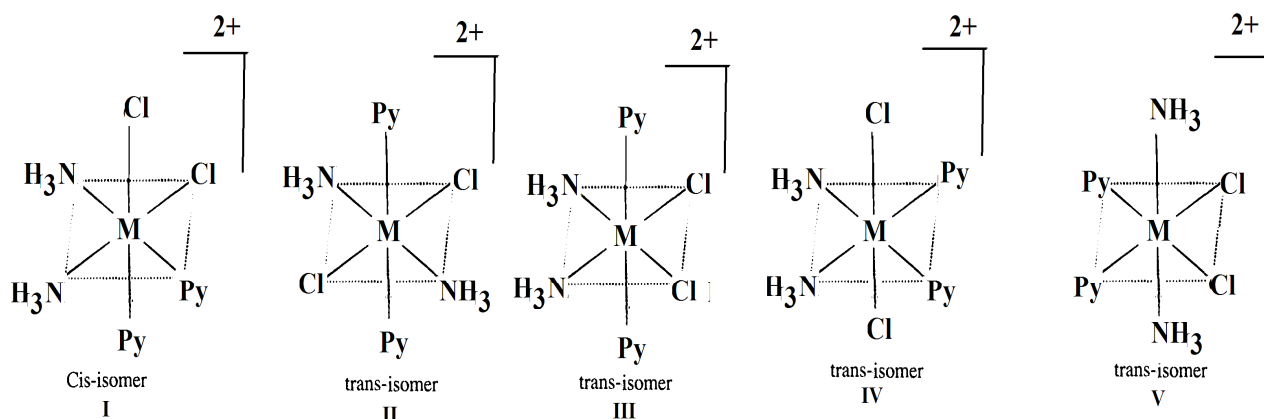
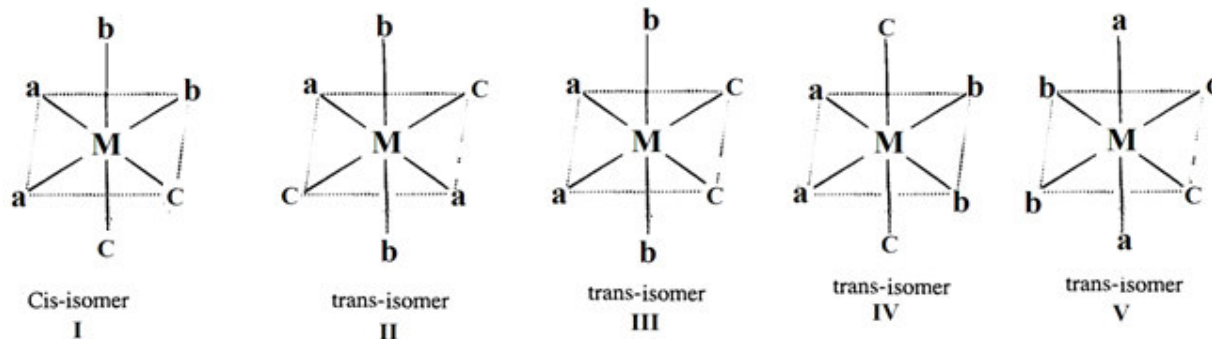
Cis isomer is obtained when ligands 'b' occupy adjacent (**1, 2**) positions, while trans- isomer is obtained when ligands 'b' are opposite to each other, as shown in Fig. where they occupy 1, 6 positions.



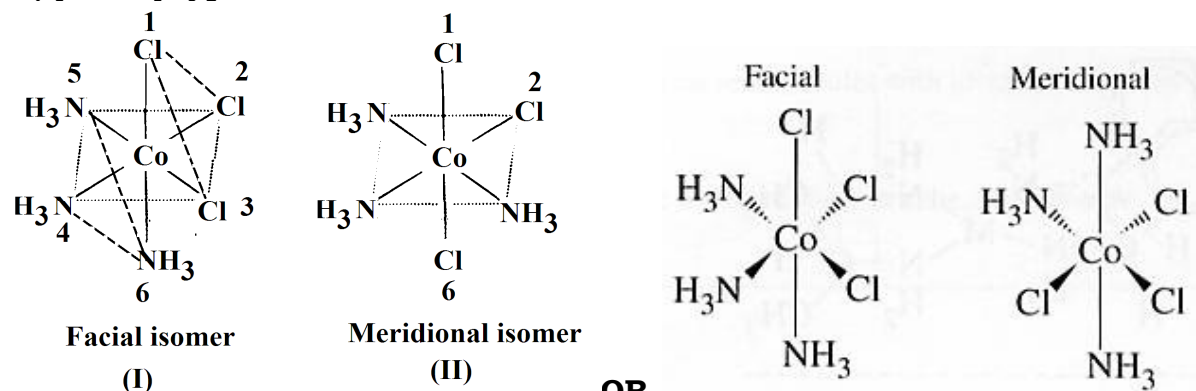
*“When you focus on problem, you will have more problems.  
But when focus on possibility, you will have more opportunity.”*

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### ii) $[Ma_2b_2C_2]$ type:



### iii) $[Ma_3b_3]$ type:



OR

**Cis-isomer or facial or fac**

**Transisomer or meridional or mer**

In this cis-isomer, the three  $Cl^-$  are on one triangular face (positions 1, 2 and 3) and the three  $NH_3$  molecules are placed on the **opposite triangular face** (position 4, 5 and 6). This isomer is designated as **facial (fac) isomer**.

In trans isomer,  $Cl^-$  are placed on the edges of the octahedron (**position 1, 2 and 6**) while  $NH_3$  molecules are present on the opposite edges (**positions 3, 4 and 5**) (**Refer Fig.**). This isomer is termed as meridional (mer) or peripheral isomer.

Another example of this type of complex is  $[Rh(H_2O)_3Cl_3]$ .

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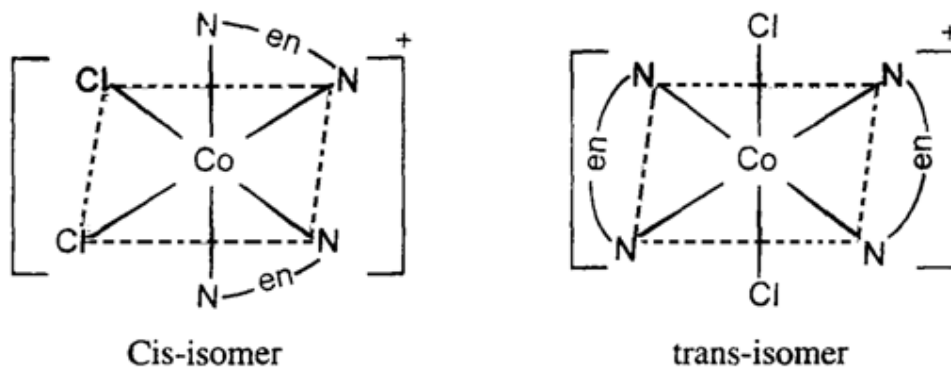
iv) **[Mabcdef] type:** Here, in all **15 isomers are possible**, out of which **only three have been isolated**.

e.g.  $[\text{PtNH}_3\text{PyNO}_2\text{ClBrI}]$

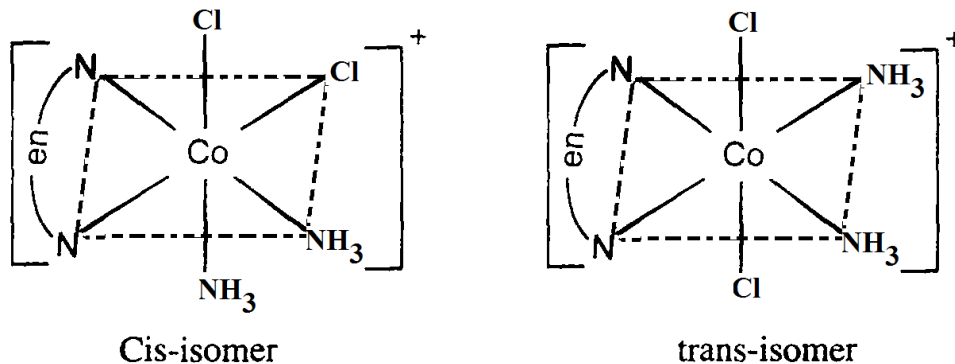
v) **[M(A-A)<sub>2</sub>a<sub>2</sub>] type:** where A-A are bidentate symmetrical ligands

In this type of complexes, central metal atom M is attached to two symmetrical bidentate chelating ligands (A-A) and two monodentate ligands (a). The two letters A and A in A-A indicate the two similar coordinating atoms. These complexes exist in cis and trans forms and exhibit the phenomenon of geometrical isomerism.

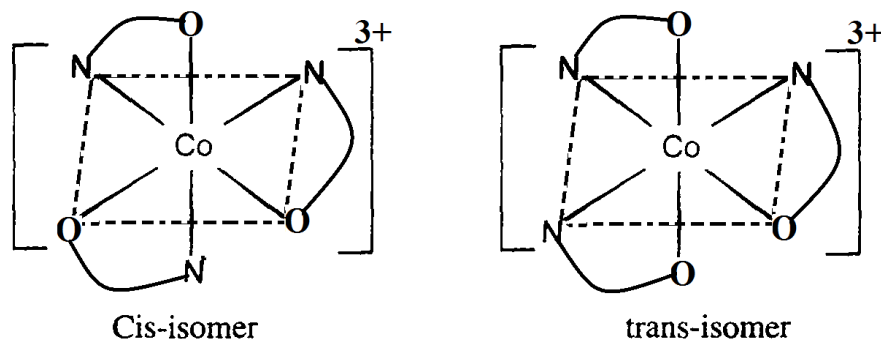
An example of this type of complex is  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ . The cis and trans forms are shown in fig.



vi) **[M(A-A)a<sub>2</sub>b<sub>2</sub>] type:** Example  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$



vii) **[M(A-B)<sub>3</sub>],** where A-B are bidentate unsymmetrical ligands



## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

**2) Optical Isomerism:** The stereoisomerism which have same chemical formula but different arrangement of ligands (or atoms or groups) in space around central metal atom or ion in such a way that **one is the mirror image of the other and cannot be superimposed on each other**, is known as optical isomerism and isomers thus obtained are known as **optical isomers or enantiomers or enantiomorphs**.

### Conditions:

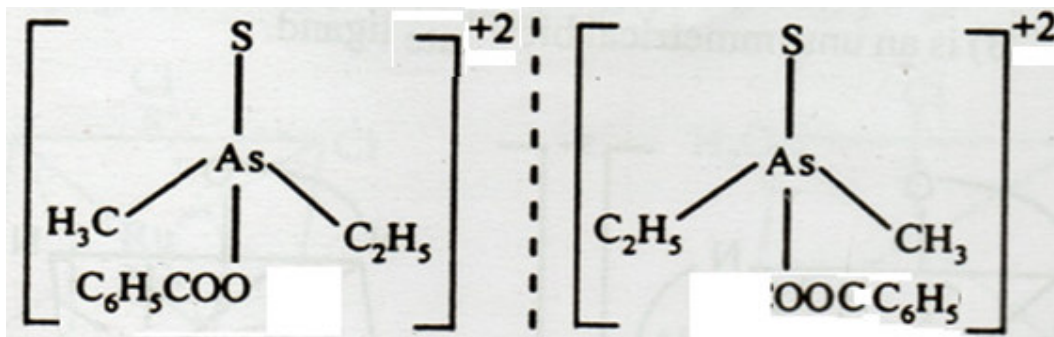
- 1) A complex should be **asymmetric**.
- 2) The different arrangement of ligands in space around central metal atom or ion in such a way that **one is the mirror image of the other and cannot be superimposed on each other**.
- 3) **Optically Activity: Symmetry elements** such as axis of rotating reflection, plane of symmetry, center of symmetry etc. **must be absent in complex**, then compound is **optically active**.
- 4) **d and l form:** If plane polarized light (PPL) is rotated to left, it is called laevo form (or l-form) , while if the plane polarized light is rotated to the right, it is called dextro form (or d-form).
- 5) **Racemic mixture:** When 50% l and 50% d form are present in a solution then it is known as '**Racemic mixture**' *i.e. dl form* . This solution is **optically inactive due to external compensation**.

### a) Optical isomerism with CN=4:

For CN=4, possible structure will be **tetrahedral or square planar**.

**i) Tetrahedral complexes:** Tetrahedral complex of  $[Ma_4]$  and  $[Ma_3b]$  type do not show optical activity but  $[Mabcd]$  type show optical isomers.

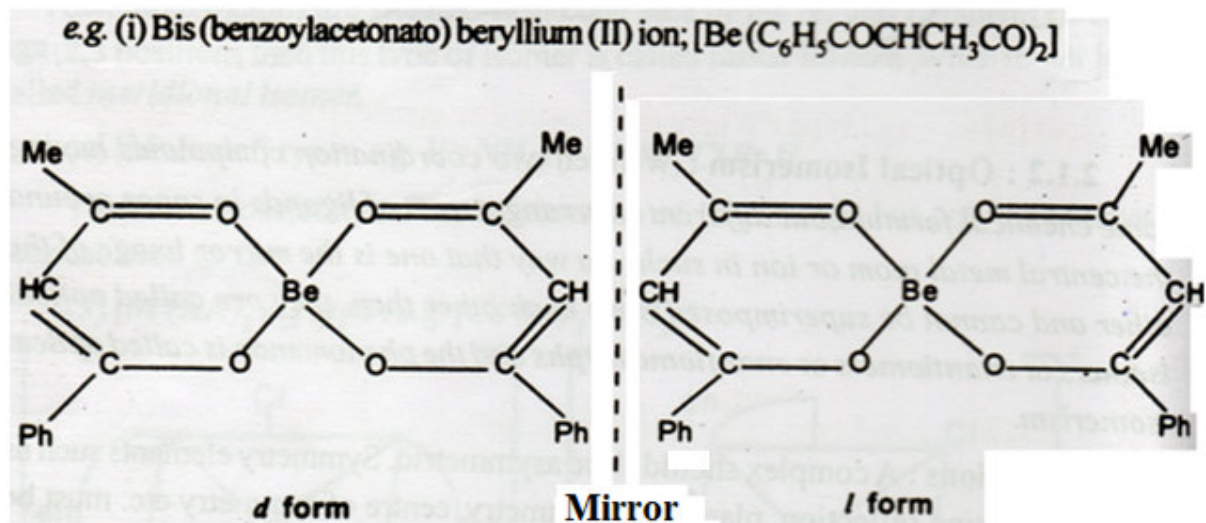
e.g.  $[As(CH_3)(C_2H_5)(S)(C_6H_5COO)]^{+2}$  ion



Tetrahedral complexes of Be(II), Be(III) with unsymmetric bidentate ligands are resolved into optically active forms.

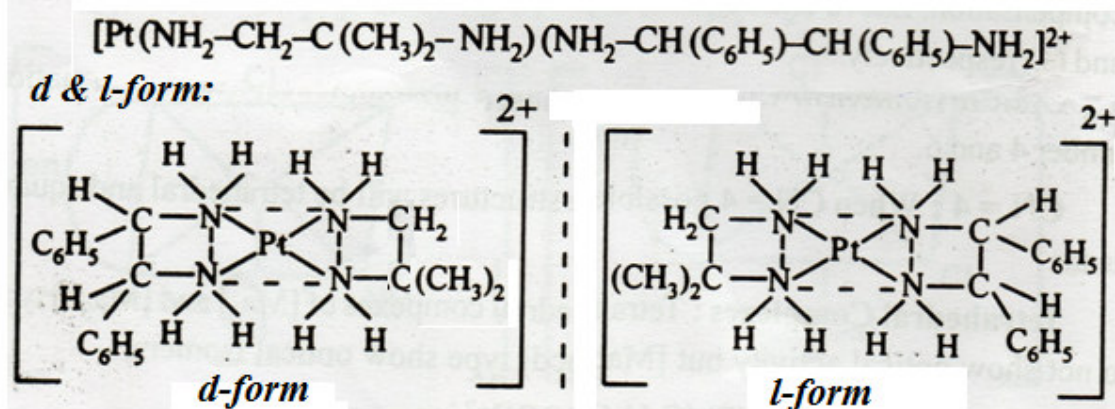
**Don't limit your challenges, Challenge your limits.**

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI



**ii) Square Planar Complexes:** In square planar complexes, all the four ligands and central metal atom **lie in the same plane**. Therefore, they possess a **plane or axis of symmetry** and are generally **not chiral** in nature. Hence, optical isomerism is not common in square planar complexes and is **very rarely observed**.

**Example : Linear structure**



### **b) Optical isomerism with CN=6:**

Optical isomerism is more common in six coordination compounds (i.e. in Octahedral complexes).

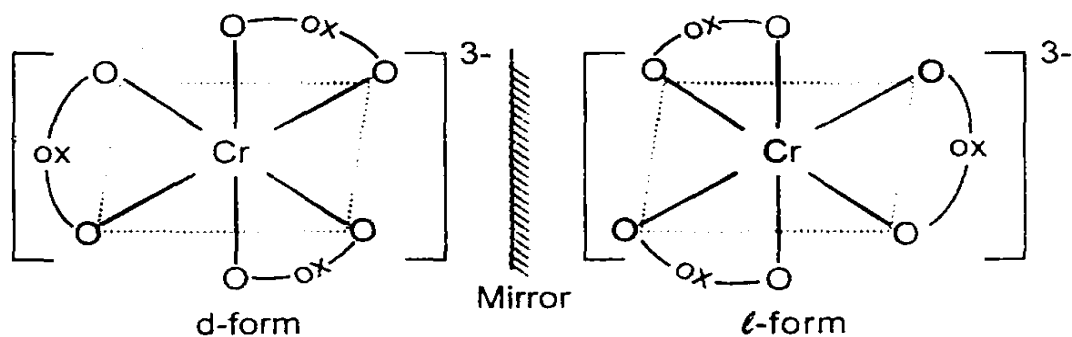
**i) Octahedral complexes containing only monodentate ligands:** The octahedral complex of the type  $[\text{Ma}_4\text{b}_2]$ ,  $[\text{Ma}_3\text{b}_3]$ ,  $[\text{Ma}_2\text{b}_2\text{c}_2]$ ,  $[\text{Ma}_2\text{b}_2\text{cd}]$ ,  $[\text{Ma}_2\text{bcde}]$  and  $[\text{Mabcdef}]$  does not optical isomerism because these types are **optically inactive**.

**ii) Octahedral complexes containing one or more symmetrical bidentate chelating ligands:** If an octahedral complex contains one or more bidentate chelating ligands, it is **optically active**.

**a) Complexes of the type  $[\text{M}(\text{A-A})_3]^{n\pm}$  :** In this type, three symmetrical bidentate chelating ligands (A-A) are coordinated to the central metal atom M.

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

An example of this type of complexes is  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  Or  $[\text{Cr}(\text{OX})_3]^{3-}$



It is optically active and has been resolved into d— and l— forms.

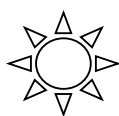
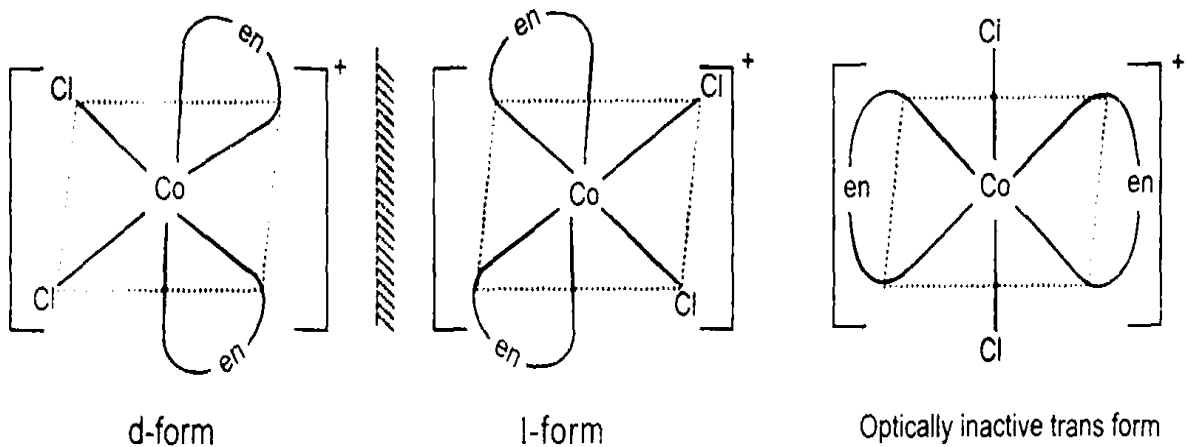
**b) Complexes of the type  $[\text{M}(\text{A-A})_2\text{a}_2]^{n\pm}$  :** The complexes in which two symmetrical bidentate chelating ligands (A-A) and two monodentate ligands (a), are coordinated to central metal atom M, exhibit the phenomenon of optical isomerism.

**Example:**

An example of this type of complexes is  $[\text{CoCl}_2(\text{en})_2]^+$  shows both geometrical as well as optical isomerism. Its cis form is unsymmetrical, while the trans form is symmetrical because it contains a plane of symmetry.

**Hence, optical isomerism is shown by cis form only.**

The cis form is resolved into d— and l— forms. The d— and l— forms along with the optically inactive trans form are shown in Fig. 9.15.



**You Can't Change Your Future  
But You Can Change Your Habits**

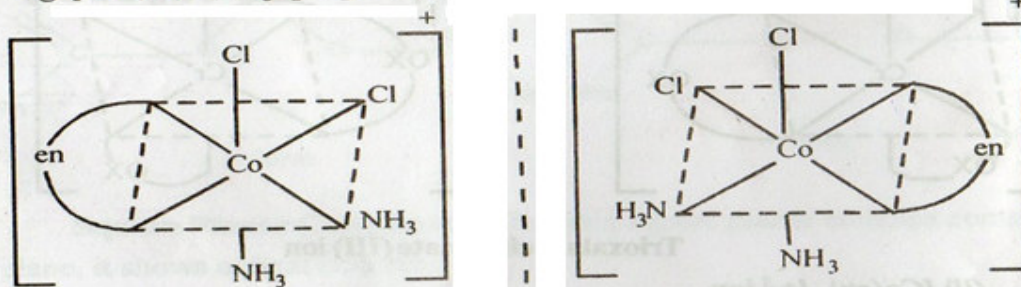


**And Surely Your Habits Will Change Your Future**

**Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI**

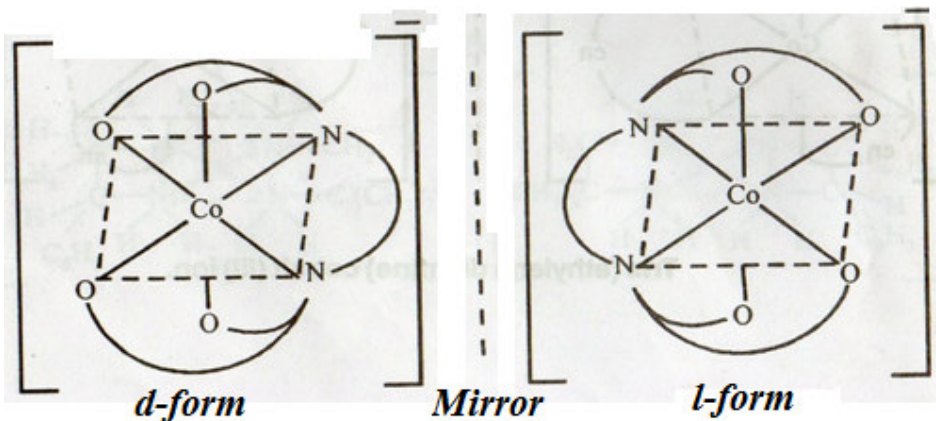
(c)  $[M(A-A)a_2 b_2]$  type:

e.g.  $[Co(en)(NH_3)_2Cl_2]^+$  ion.



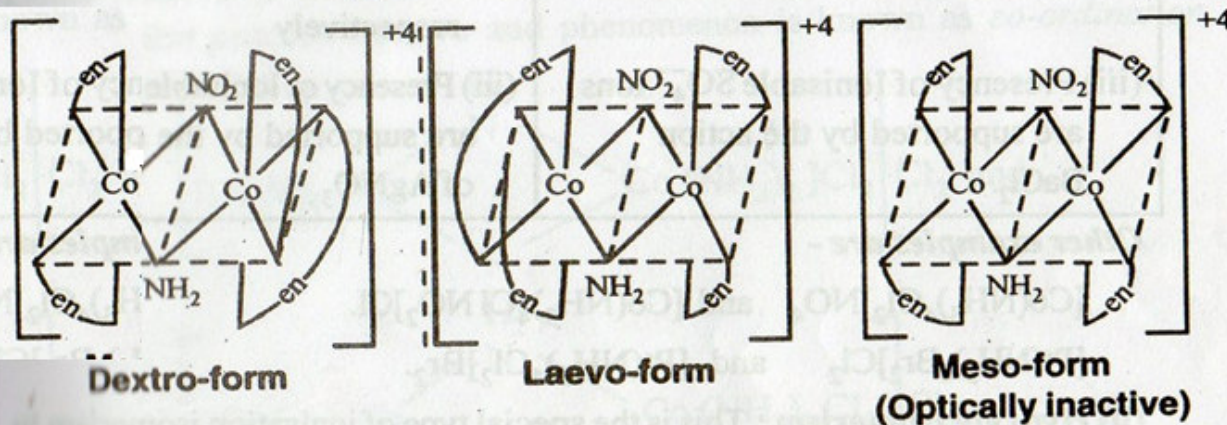
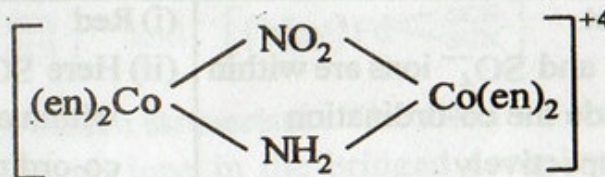
**Cis diammine dichloro (ethylenediamine) cobalt (III) ion.**

(d) **Complexes containing hexadentate ligands** can be resolved into optical isomers. e.g.  $[Co(edta)]^-$  ion



(e) The optical isomerism is also observed in polynuclear complexes.

e.g.



## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

### ➤ Molecular Orbital Theory (MOT) –

MOT was developed by Scientist J. Van Vleck. According to MOT molecular orbitals are formed by linear combination of atomic orbitals. Therefore, MOT is also called as LCAO (Linear Combination of Atomic Orbitals) method.

### ❖ Formation of Octahedral complexes –

During the formation of octahedral complexes MOT uses nine metal orbitals 3d, 4s & 4p orbitals and six ligand orbitals from six ligands.

- **Metal orbitals** : Nine metal orbitals are classified in four groups, on the basis of their symmetry.

**a<sub>1g</sub>** – This group contains one 4s orbital which is spherically symmetrical.

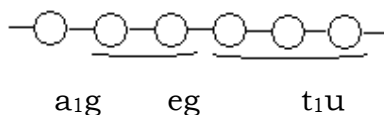
**t<sub>1u</sub>** – This group contains three 4p orbitals having equal energies and differing in spacial orientation only.

**eg** – This group contains two equivalent 3d orbitals  $dx^2-y^2$ ,  $dz^2$

**t<sub>2g</sub>** – This group contains three equivalent 3d orbitals  $dxz$ ,  $dyz$ ,  $dxy$  having equal energies and differing in spacial orientation only.

Out of these nine metal ion orbitals, only a<sub>1g</sub>, t<sub>1u</sub> & eg orbitals are involved in sigma ( $\sigma$ ) bond formation. While t<sub>2g</sub> orbitals are involved in pi ( $\pi$ ) bonding.

- **Ligand orbitals** : Six orbitals from six ligands are combined to form a set of six equal energy orbitals called as ligand group orbitals LGO. These six LGOs fall into three groups: a<sub>1g</sub>, t<sub>1u</sub> & eg.



During octahedral complex formation, the metal orbitals overlap linearly with LGOs having appropriate symmetry, to form bonding molecular orbitals (BMOs) and antibonding molecular orbitals (ABMOs). Thus,

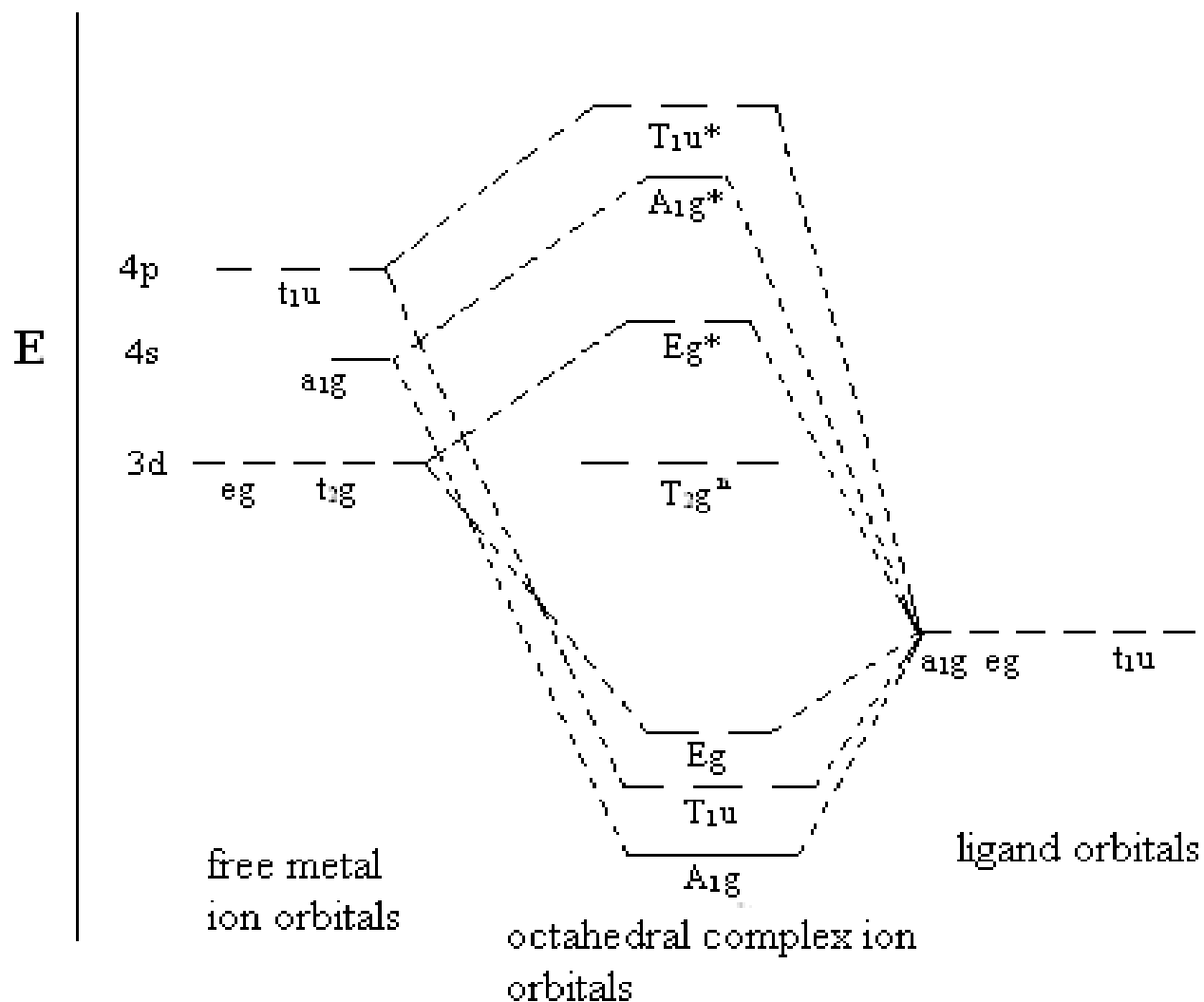
- i) Metal a<sub>1g</sub> orbital combines linearly with a<sub>1g</sub> LGOs to form A<sub>1g</sub> bonding molecular orbitals and A<sub>1g</sub>\* antibonding molecular orbitals.
- ii) Three t<sub>1u</sub> metal orbitals combine linearly with three t<sub>1u</sub> LGOs to form three T<sub>1u</sub> bonding molecular orbitals and three T<sub>1u</sub>\* antibonding molecular orbitals.



## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

- iii) Two  $e_g$  metal orbitals combine linearly with two  $e_g$  LGOs to form two  $E_g$  bonding molecular orbitals and two  $E_g^*$  antibonding molecular orbitals.
- iv) While the  $t_{2g}$  orbitals ( $dxz$ ,  $dyz$  and  $dxy$ ) of the metal ion remain unchanged in the complex ion since they do not overlap with the ligand orbitals. They are nonbonding  $T_{2g}^n$  orbitals.

### ❖ MO energy level diagram for Octahedral complex :



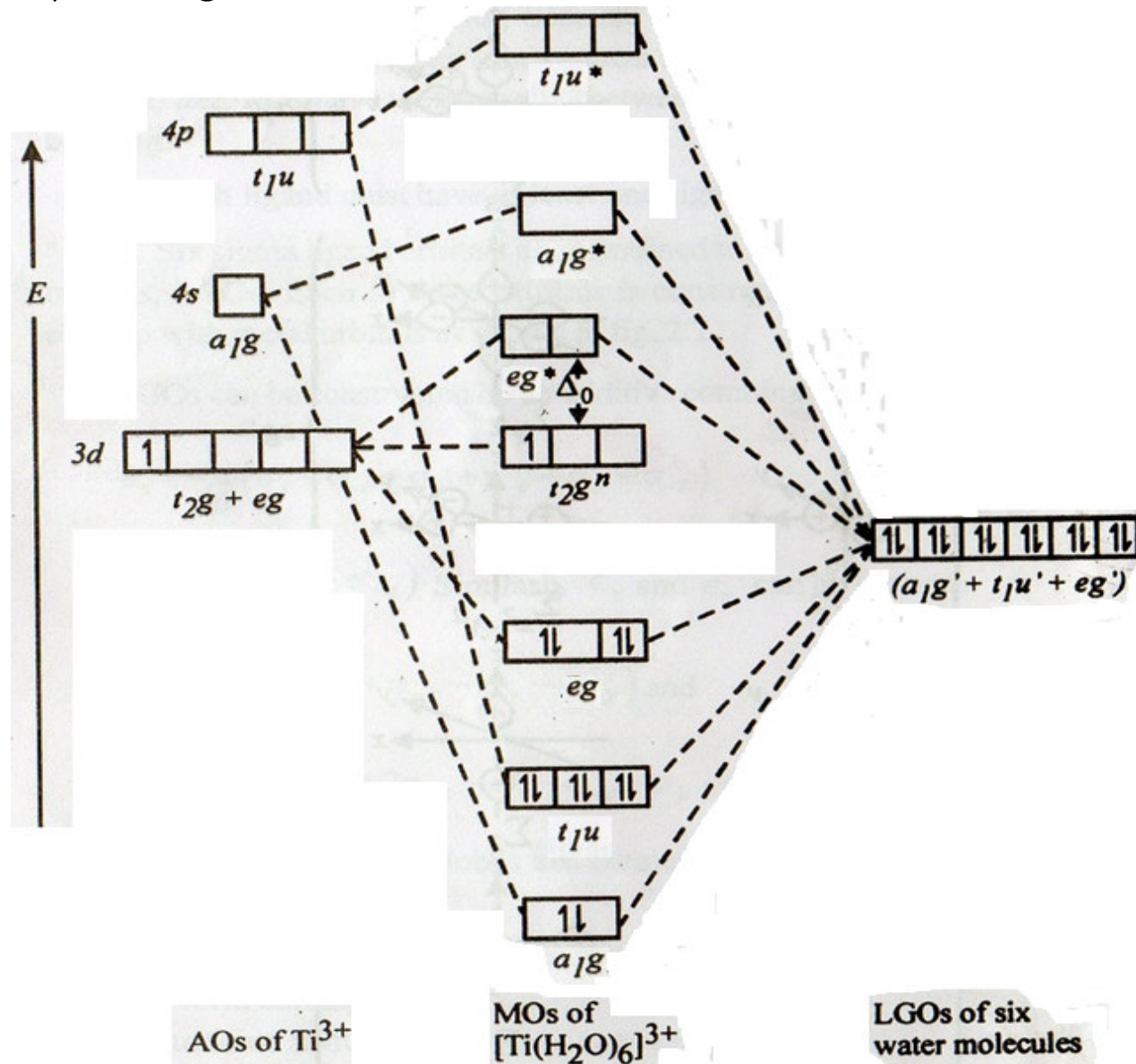
All these orbitals are arranged according to their increasing energies. Six LGOs have same energy and their energy is less than that of metal orbitals. Antibonding molecular orbitals lie above and bonding molecular orbitals lie below the mean value of combining orbitals. After MO formation electrons present in metal orbitals and ligand orbitals are filled in available lower energy molecular orbitals.

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

### 1) Hexaaqua titanium (III) ion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ :

In this complex, central metal ion is  $\text{Ti}^{3+}$  and surrounding neutral ligand is  $\text{H}_2\text{O}$ .

#### 1) M.O. Diagram:



#### 2) Explanation:

During the formation of this complex,  $3d$ ,  $4s$  &  $4p$  orbitals of  $\text{Ti}^{3+}$  ion are available for linear combination with LGOs. Thus,  $a_{1g}$ ,  $t_{1u}$  &  $e_g$  orbitals of  $\text{Ti}^{3+}$  ion combine with  $a_{1g}$ ,  $t_{1u}$  &  $e_g$  LGOs to form **six bonding** molecular orbitals  $a_{1g}$ ,  $t_{1u}$  &  $e_g$  and **six antibonding** molecular orbitals  $a_{1g}^*$ ,  $t_{1u}^*$  &  $e_g^*$ . While  $t_{2g}$  orbitals remain **non-bonding**  $t_{2g}^n$ .

#### 3) Electronic Configuration (EC) of metal ion:

E.C. of  $\text{Ti}$  ( $Z=22$ ) :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$  Or  $[\text{Ar}] 3d^2, 4s^2$

E.C. of  $\text{Ti}^{3+}$  ( $Z=19$ ) :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^0$  Or  $[\text{Ar}] 3d^1, 4s^0$

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

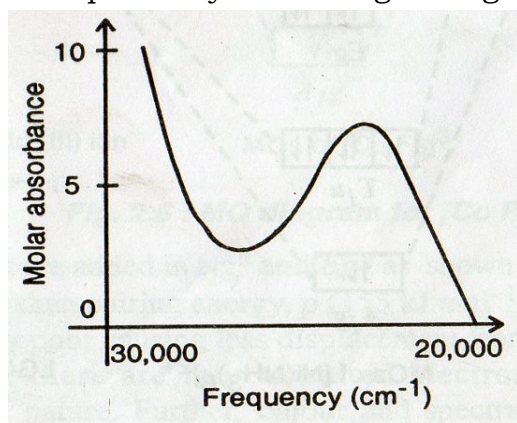
### 4) Filling of electrons:

- In all **13 electrons** are involved in complex formation; one from  $Ti^{+3}$  ion and 12 from six ligands.
- These electrons are then filled in MOs according to Aufbau principle. The electrons are first filled in lower energy bonding molecular orbitals and then higher energy orbitals are occupied.
- Thus, the E.C. of this complex is :  $a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^1$

**5) Magnetic Character:** In this complex, **one unpaired** electron is present in MO. Therefore, this complex is **paramagnetic** in nature.

### 6) Colour and Spectra:

- This can be explained by the transition of electron from  $t_{2g}^n$  to  $e_g^*$  which develops **purple or reddish violet colour** to the complex solution due to absorption of yellow and green light.



- The absorption spectrum of  $[Ti(H_2O)_6]^{3+}$  shows the maxima at **20,300 cm<sup>-1</sup>** which corresponds to the **243 kJ/mol of energy for  $\Delta_0$**  as shown in M.O. diagram.
- Further the **steep portion of the curve 27,000 cm<sup>-1</sup> to 30,000 cm<sup>-1</sup>** is due to **charge transfer as shown in fig.**

**Q.1)** Draw MO diagram for  $[Ti(H_2O)_6]^{3+}$  octahedral complex. Explain the formation of bonding, non-bonding and antibonding MOs and comment on spectra & its magnetic properties. **IMP**

**Q.2)** Draw MO diagrams of  $[Ti(H_2O)_6]^{3+}$  complex ion and comment on its magnetic properties. **Nov.2013**

### 2) Hexamine nickel (II) ion $[Ni(NH_3)_6]^{2+}$ :

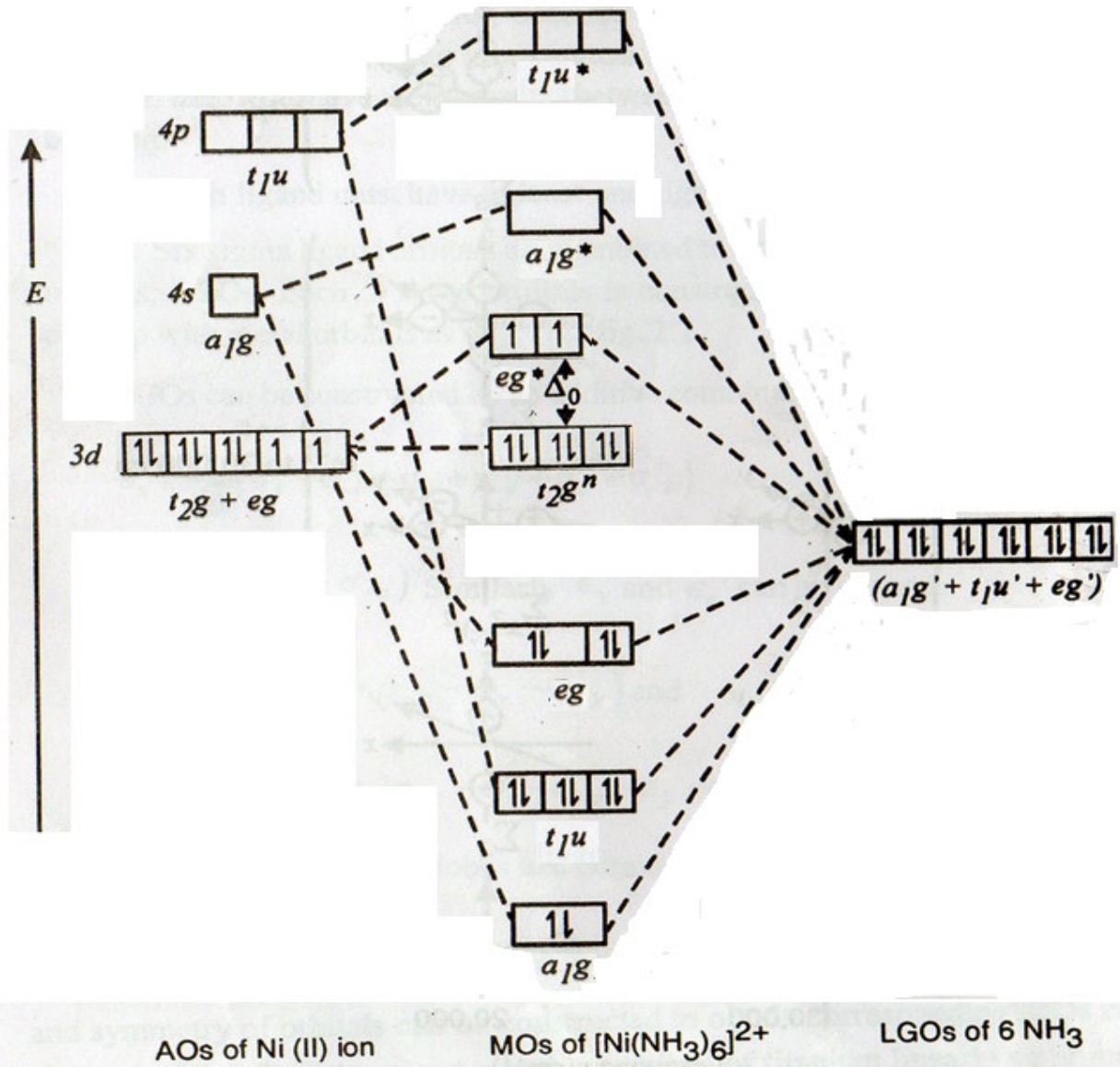
In this complex, central metal ion is  $Ni^{2+}$  and surrounding neutral ligand is  $NH_3$ .

- M.O. Diagram:** (Draw diagram here)
- Explanation :** During the formation of this complex, 3d, 4s & 4p orbitals of  $Ni^{2+}$  ion are available for linear combination with LGOs. Thus,  $a_{1g}, t_{1u}$  &  $e_g$  orbitals of  $Ni^{2+}$  ion combine with  $a_{1g}, t_{1u}$  &  $e_g$  LGOs to form **six bonding** molecular orbitals  $a_{1g}, t_{1u}$  &  $e_g$  and **six antibonding** molecular orbitals  $a_{1g}^*, t_{1u}^*$  &  $e_g^*$ . While  $t_{2g}$  orbitals remain **non-bonding  $t_{2g}^n$** .

**3) Electronic Configuration (EC) of metal ion:**

E.C. of Ni (Z= 28) :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$  Or [Ar]  $3d^8, 4s^2$

E.C. of Ni<sup>2+</sup> (Z= 26) :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^0$  Or [Ar]  $3d^8, 4s^0$



**4) Filling of electrons:**

- In all **20 electrons** are involved in complex formation; eight from Ni<sup>2+</sup> ion and 12 from six NH<sub>3</sub> ligands.
- These electrons are then filled in MOs according to Aufbau principle & **Hund's rule**. The electrons are first filled in **lower energy** bonding molecular orbitals and then **higher energy orbitals** are occupied.
- Due to strong field ligand, t<sub>2g</sub> orbitals are first filled completely and then electrons enter in eg\* orbitals.
- Thus, the E.C. of this complex is :  $a_{1g}^2, t_{1u}^6, eg^4, t_{2g}^6, eg^{*2}$

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

5) **Magnetic Character:** In this complex, **two unpaired electrons** are present in MO. Therefore, this complex is **paramagnetic in nature**.

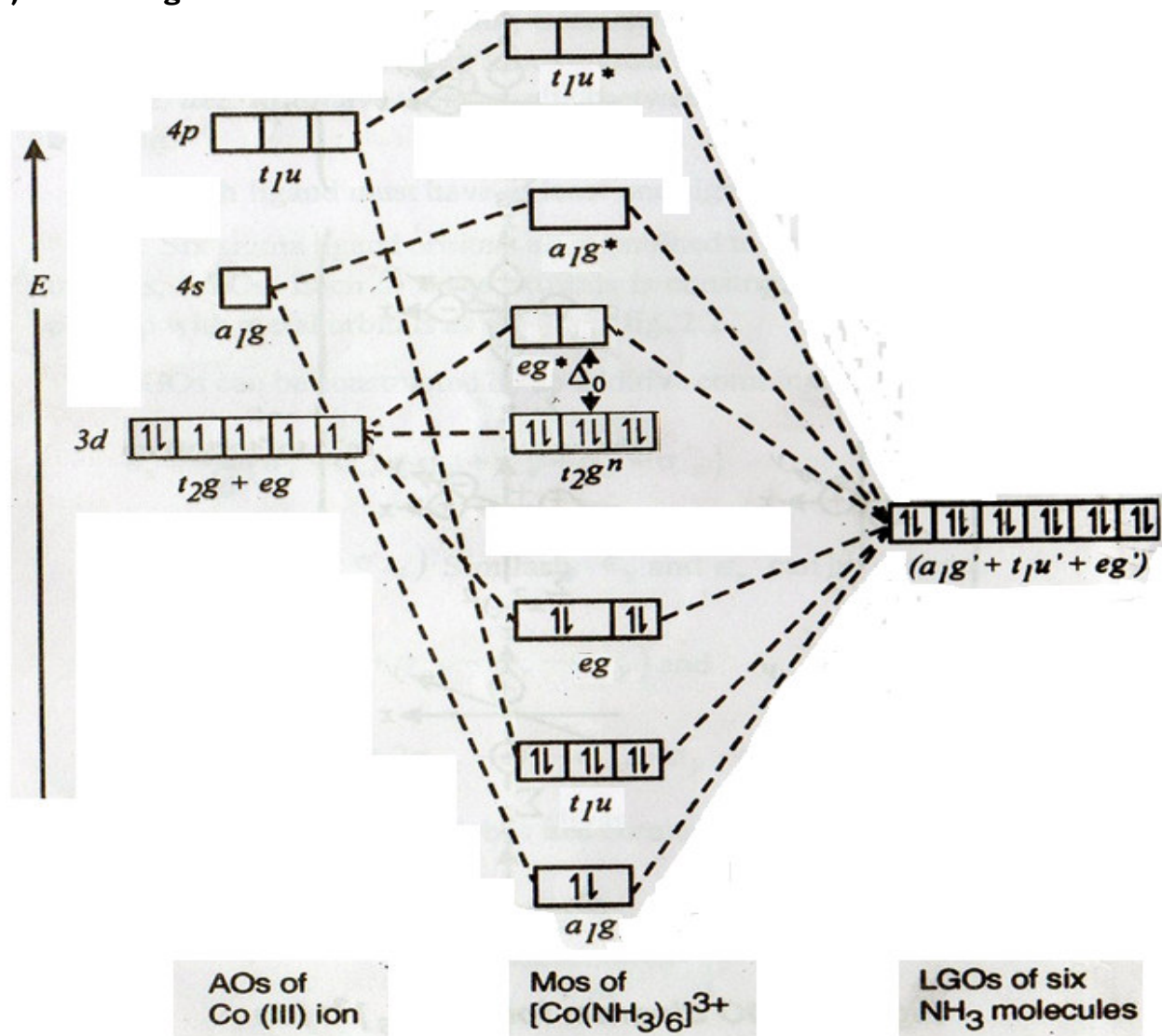
6) **Colour and Spectra:**

- This can be explained by the transition of electron from  $t_{2g}^n$  to  $eg^*$  which develops **violet blue colour** to the complex solution due to absorption of light.
- $\Delta_0$  of this complex is **129.28kJ/mol** which is comparatively small.
- The energy gap ( $\Delta_0$ ) in between  $t_{2g}$  &  $eg^*$  is **small**, because  $\text{NH}_3$  is a strong field ligand. So,  $t_{2g}$  orbitals are first filled completely and then electrons enter in  $eg^*$  orbitals.

3)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  :

In this complex, central metal ion is  $\text{Co}^{3+}$  and surrounding ligand is  $\text{NH}_3$ .

1) **M.O. Diagram:**



## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

2) **Explanation:** During the formation of this complex, 3d, 4s & 4p orbitals of  $\text{Co}^{3+}$  ion are available for linear combination with LGOs. Thus,  $a_{1g}$ ,  $t_{1u}$  &  $eg$  orbitals of  $\text{Co}^{3+}$  ion combine with  $a_{1g}$ ,  $t_{1u}$  &  $eg$  LGOs to form **six bonding** molecular orbitals  $a_{1g}$ ,  $t_{1u}$  &  $eg$  and **six antibonding** molecular orbitals  $a_{1g}^*$ ,  $t_{1u}^*$  &  $eg^*$ . While  $t_{2g}$  orbitals remain **non-bonding**  $t_{2g}^n$ .

### 3) Electronic Configuration (EC) of metal ion:

E.C. of Co ( $Z=27$ ):  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$  Or [Ar]  $3d^7, 4s^2$

E.C. of  $\text{Co}^{3+}$  ( $Z=24$ ):  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^0$  Or [Ar]  $3d^6, 4s^0$

### 4) Filling of electrons:

- In all **18 electrons** are involved in complex formation; eight from  $\text{Co}^{3+}$  ion and 12 from six  $\text{NH}_3$  ligands.
- These electrons are then filled in MOs according to Aufbau principle & **Hund's rule**. The electrons are first filled in **lower energy** bonding molecular orbitals and then **higher energy orbitals** are occupied.
- Due to strong field  $\text{NH}_3$  ligand,  $t_{2g}$  orbitals are filled completely and  $eg^*$  orbital remains vacant.
- Thus, the E.C. of this complex is :  $a_{1g}^2, t_{1u}^6, eg^4, t_{2g}^6$

5) **Magnetic Character:** In this complex, **all electrons present** in MOs are paired, therefore this complex is **diamagnetic in nature**.

### 6) Colour and Spectra:

- This can be explained by the transition of electron from  $t_{2g}^n$  to  $eg^*$  which develops **orange yellow colour** to the complex solution due to absorption of light.
- $\Delta_0$  of this complex is **296kJ/mol** which is comparatively large.
- The energy gap ( $\Delta_0$ ) in between  $t_{2g}$  &  $eg^*$  **is large**, because  $\text{NH}_3$  is a strong field ligand. So,  $t_{2g}$  orbitals are filled completely and  $eg^*$  orbitals remain vacant.

**The best preparation of tomorrow is doing your best today.**

4) **Hexafluoro cobalt (III) ion  $[\text{CoF}_6]^{3-}$**  : In this complex, central metal ion is  $\text{Co}^{3+}$  and surrounding six weak field ligand is  $\text{F}^-$ .

1) **M.O. Diagram:** (Draw diagram here)

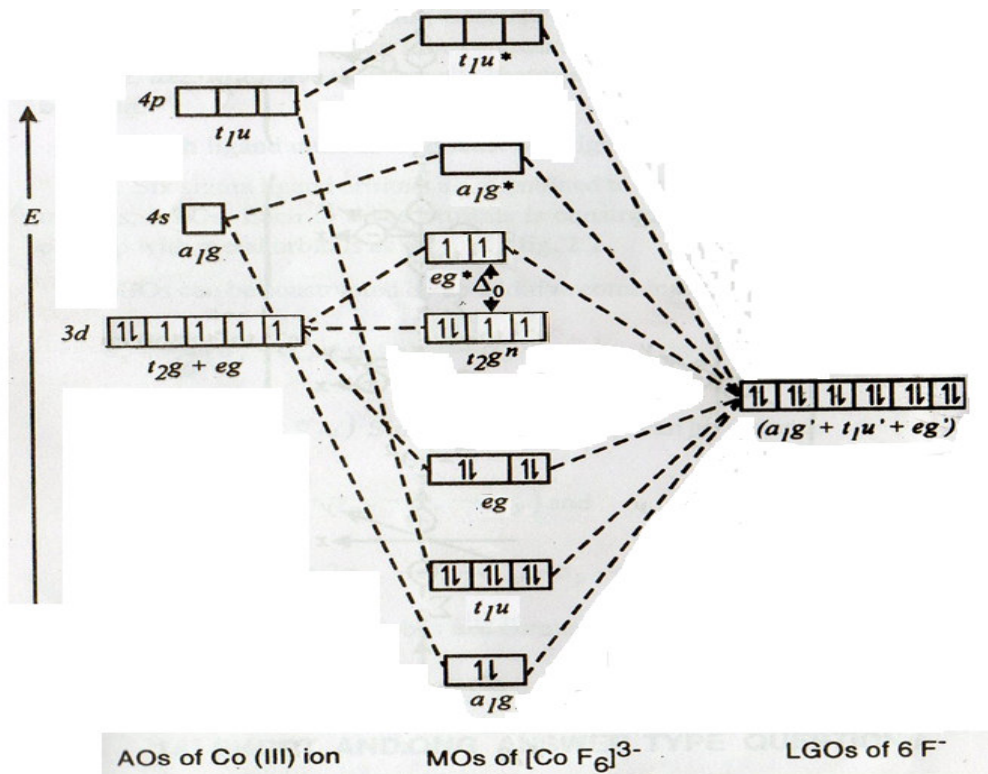
2) **Explanation :** During the formation of this complex, 3d, 4s & 4p orbitals of  $\text{Co}^{3+}$  ion are available for linear combination with LGOs. Thus,  $a_{1g}$ ,  $t_{1u}$  &  $eg$  orbitals of  $\text{Co}^{3+}$  ion combine with  $a_{1g}$ ,  $t_{1u}$  &  $eg$  LGOs to form **six bonding** molecular orbitals  $a_{1g}$ ,  $t_{1u}$  &  $eg$  and **six antibonding** molecular orbitals  $a_{1g}^*$ ,  $t_{1u}^*$  &  $eg^*$ . While  $t_{2g}$  orbitals remain **non-bonding**  $t_{2g}^n$ .

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

### 3) Electronic Configuration (EC) of metal ion:

E.C. of Co ( $Z=27$ ):  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$  Or [Ar]  $3d^7, 4s^2$

E.C. of  $\text{Co}^{3+}$  ( $Z=24$ ):  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^0$  Or [Ar]  $3d^6, 4s^0$



### 4) Filling of electrons:

- In all **18 electrons** are involved in complex formation; eight from  $\text{Co}^{3+}$  ion and 12 from six  $\text{F}^-$  ligands.
- These electrons are then filled in MOs according to **Hund's rule**. The electrons are first filled in **lower energy** bonding molecular orbitals and then **higher energy orbitals** are occupied.
- The energy gap  $\Delta_0$  in between  $t_{2g}$  &  $eg^*$  is small, as  $\text{F}^-$  is a weak field ligand. Thus, first 12 electrons are filled in lower energy bonding molecular orbitals  $a_{1g}$ ,  $t_{1u}$ ,  $eg$  MOs, while remaining 6 electrons are added in  $t_{2g}$  and  $eg^*$  orbitals singly and then pairing starts in  $t_{2g}$  orbitals.
- Thus, the E.C. of this complex is :  $a_{1g}^2, t_{1u}^6, eg^4, t_{2g}^4, eg^{*2}$

**5) Magnetic Character:** In this complex, **four unpaired electrons** are present in MO. Therefore, this complex is **paramagnetic in nature**.

### 6) Colour and Spectra:

- This can be explained by the transition of electron from  $t_{2g}^n$  to  $eg^*$  which develops **blue colour** to the complex solution due to absorption of light.
- $\Delta_0$  of this complex is **very small** and less than pairing energy.
- The energy gap ( $\Delta_0$ ) in between  $t_{2g}$  &  $eg^*$  is **small**, because  $\text{F}^-$  is a weak field ligand. So,  $t_{2g}$  orbitals are filled completely and  $eg^*$  orbitals remain vacant.

## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

Q.1) Draw molecular orbital diagram for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  &  $[\text{CoF}_6]^{3-}$  ion. Explain the magnetic properties of these ions. Dec.2016 10Marks

Q.2) Why  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion is diamagnetic while &  $[\text{CoF}_6]^{3-}$  ion is paramagnetic in nature? 5Marks OR

Q.2) What are high spin & low spin complexes of Co(III)? Dec.2016 5Marks

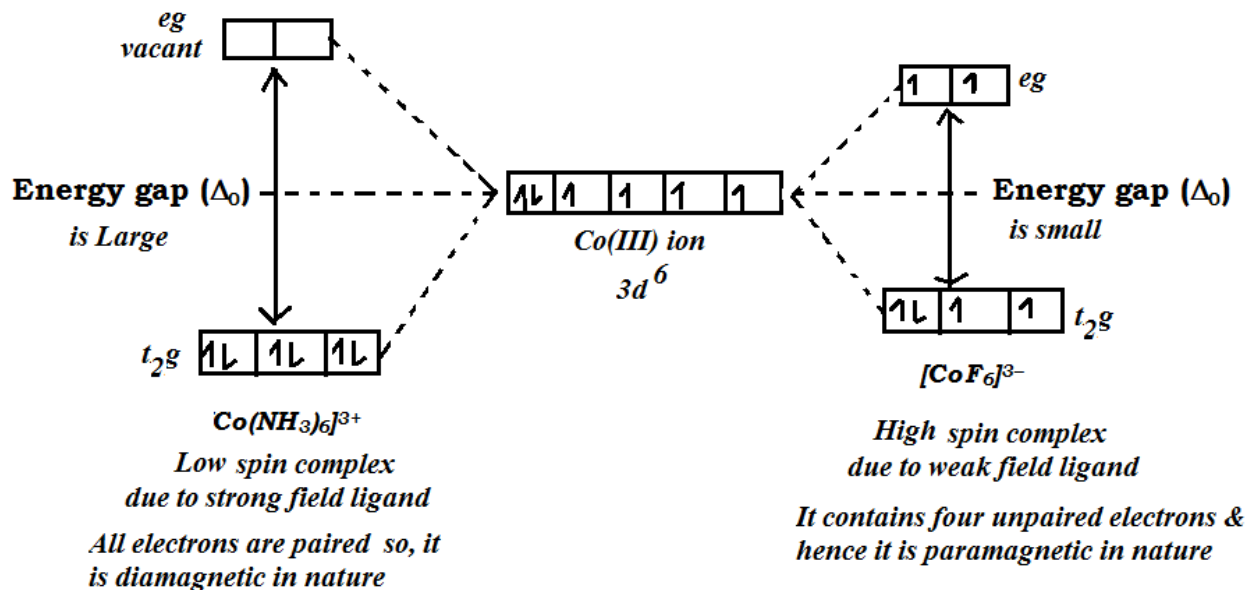
Ans. **Electronic Configuration (EC) of Co(III) ion:**

E.C. of Co (Z= 27) :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$  Or  $[\text{Ar}] 3d^7, 4s^2$

E.C. of  $\text{Co}^{3+}$  (Z= 24) :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^0$  Or  $[\text{Ar}] 3d^6, 4s^0$

a) **Low spin complex:** Due to **strong field  $\text{NH}_3$**  ligand in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex, the distribution of  $3d^6$  electrons in  $t_{2g}$  &  $e_g$  orbitals takes place in such a way that **all electrons get paired**. Thus, it is **diamagnetic** in nature due to **absence of unpaired electrons** & hence this complex is known as **low spin complex**.

b) **High spin complex:** Due to **weak field  $\text{F}^-$**  ligand in  $[\text{CoF}_6]^{3-}$  complex, the distribution of  $3d^6$  electrons in  $t_{2g}$  &  $e_g$  orbitals takes place in such a way that we get **maximum number of unpaired electrons**. Thus, it is **paramagnetic** in nature due to **presence of unpaired electrons** & hence this complex is known as **high spin complex**.





## Unit-2) Metal-Ligand Bonding (Isomerism & MOT) By V.M. DESAI

### ❖ Merits of MOT –

1. MOT considers all possible **interaction between metal orbitals & ligand orbitals**.
2. This is a **complete theory** because it gives satisfactory information for stability, geometry and relative energies of different structures of metal complexes unlike VBT or CFT.
3. It gives satisfactory information **for high spin and low spin complexes**, their different magnetic moments and variation in CFSE ( $\Delta_0$  values).
4. It gives satisfactory information **for stability of complexes w.r.t. weak and strong field ligands**.
5. MOT explains  **$\pi$ -bonding**.
6. MOT also explains **charge transfer spectra**.
7. Magnetic properties are also explained by this theory.
8. Nephelauxetic effect (cloud expansion effect), shifts in NMR spectra etc. could be explained by MOT.

### ❖ Demerits of MOT –

1. MOT is a complicated theory.
2. The complex ion containing many atoms cannot be explained easily by MOT i.e. **multiatom complex ion system** cannot be explained easily.
3. For simple molecular orbital calculations, computer is necessary.

**Use Chemistry Blog** (Click on Following Link)

<https://vmdesaichemistry.blogspot.com/>

#### **For downloading**

- ✓ *Study Materials (Notes, PPT, Videos, Animations etc.),*
- ✓ *Syllabus & Lecture Plan*
- ✓ *Old University Question Papers,*
- ✓ *M.Sc. Entrance Question Papers*
- ✓ *Online Chemistry Resource Materials Links*
- ✓ *Virtual Chemistry Lab Links*
- ✓ *Digital Chemistry Magazine*
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- ✓ *SET/NET/GATE Study Materials & Question Papers*
- ✓ *Other Technical Supporting Links*

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**B.Sc. (Part - III) (Semester - V) (Revised) Examination, December - 2016**  
**CHEMISTRY**  
**Inorganic Chemistry (Paper - X)**  
**Sub. Code : 65824**

**Day and Date : Thursday, 8 - 12 - 2016**

**Total Marks : 40**

**Time : 12.00 noon to 02.00 p.m.**

- Instructions :**
- 1) All questions are compulsory.
  - 2) Figures to the right indicate full marks.
  - 3) Draw neat labeled diagrams and write balanced equations wherever necessary.

**Q1)** Select the most correct alternative among those given below and rewrite the sentences. **[8]**

- a) Soft acid and soft base interaction is generally \_\_\_\_\_ in nature.
- i) interstitial
  - ii) covalent
  - iii) metallic
  - iv) ionic
- b) During the formation of octahedral complex ligands approach with the metal \_\_\_\_\_.
- i) along the axes
  - ii) either along the axes or between the axes
  - iii) between the axes
  - iv) neither along the axes nor between the axes
- c) Increase in CFSE \_\_\_\_\_ the stability of complexes.
- i) increases
  - ii) decreases
  - iii) first increases then decreases
  - iv) remains the same

- d) The backbones in fluorocarbons consists of structural units of \_\_\_\_\_
- i)  $-C-C-$
  - ii)  $F - F$
  - iii)  $C - H$
  - iv)  $-C - F$
- e) When Germanium is doped with pentavalent impurity then the resulting substance is \_\_\_\_\_.
- i) superconductor
  - ii) p - type semiconductor
  - iii) n - type semiconductor
  - iv) insulator
- f) If there is no gap between valence band and conduction band then the substance becomes \_\_\_\_\_
- i) bad conductor
  - ii) insulator
  - iii) good conductor
  - iv) neutral
- g) In  $[Ti(H_2O)_6]^{3+}$  ion there are \_\_\_\_\_ bonding \_\_\_\_\_ antibonding and \_\_\_\_\_ non bonding MOS.
- i) 3, 6, 3
  - ii) 6, 6, 3
  - iii) 6, 3, 6
  - iv) 3, 3, 6
- h) In dimethyl beryllium  $Be - C - Be$  bridges are formed by \_\_\_\_\_ bonds.
- i)  $(2C - 2e)$
  - ii)  $(3C - 3e)$
  - iii)  $(1C - 2e)$
  - iv)  $(3C - 2e)$

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**Q2) Attempt any TWO of the following :** [20]

- Draw molecular orbital diagram for  $[\text{Co}(\text{NH}_3)_6]^{+3}$  ion and  $[\text{CoF}_6]^{3-}$  ion. Explain the magnetic properties of these ions.
- What are semiconductors? Discuss intrinsic and extrinsic conductors.
- Discuss the structures of alkyl and aryl compounds of Be and Al.

**Q3) Attempt any Three of the following :** [12]

- Discuss in brief acid - base strength, hardness and softness.
- What are high spin and low spin complexes of Co (III)?
- Give the points of difference between organic and inorganic polymers.
- What are phosphonitrilic compounds? Discuss the structure of  $(\text{PNCl}_2)_3$ .
- Discuss the structure and bonding in  $\text{Ni}(\text{CO})_4$ .

