

ULTIMATE KCET

CRASH COURSE 2026

Chemistry

Lecture - 02

Coordination compounds

By - Sreeja Ma'am



Recap *of previous lecture*

1 Coordination compound - 1

→ Structural isomerism



Topics *to be covered*



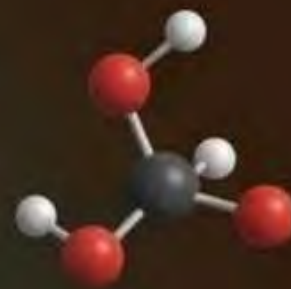
1 Coordination compound - 2






- MCB
- Geometrical / optical isomerism
- VBT / CFT / Spectrochemical Series.
- MCB.





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-  **Chapterwise Most Probable Questions**
-  **Latest 2025 Past Year Paper**
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-  **Comprehensive Coverage of 4 Subjects**

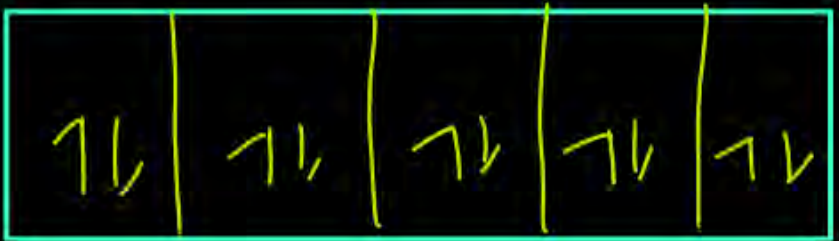
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Valence Bond Theory

$[Ni(CO)_4]$ dsp^3 X
 ↳ strong ligand
 ↳ sp^3

According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals .

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4 } 4 } 5 }	sp^3	Tetrahedral
	dsp^2	Square planar
	dsp^3 / sp^3d → weak	Trigonal bipyramidal
6	sp^3d^2 ✓ weak	Octahedral
6	d^2sp^3 strong	Octahedral



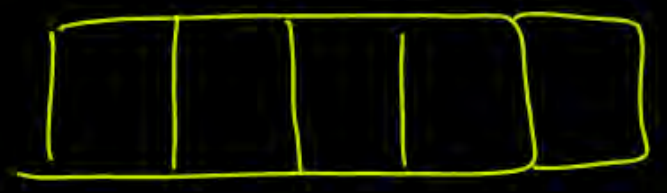
$3d^{10}$



4s



4p



3d

$sp^3 \longrightarrow$ tetrahedral
 \longrightarrow Diamagnetic
 \longrightarrow low spin complex



Geometrical isomerism → GI

Note → tetrahedral complex do not GI → because of ^{only} adjacent positions

→ Square planar complex shows GI (cis/trans)

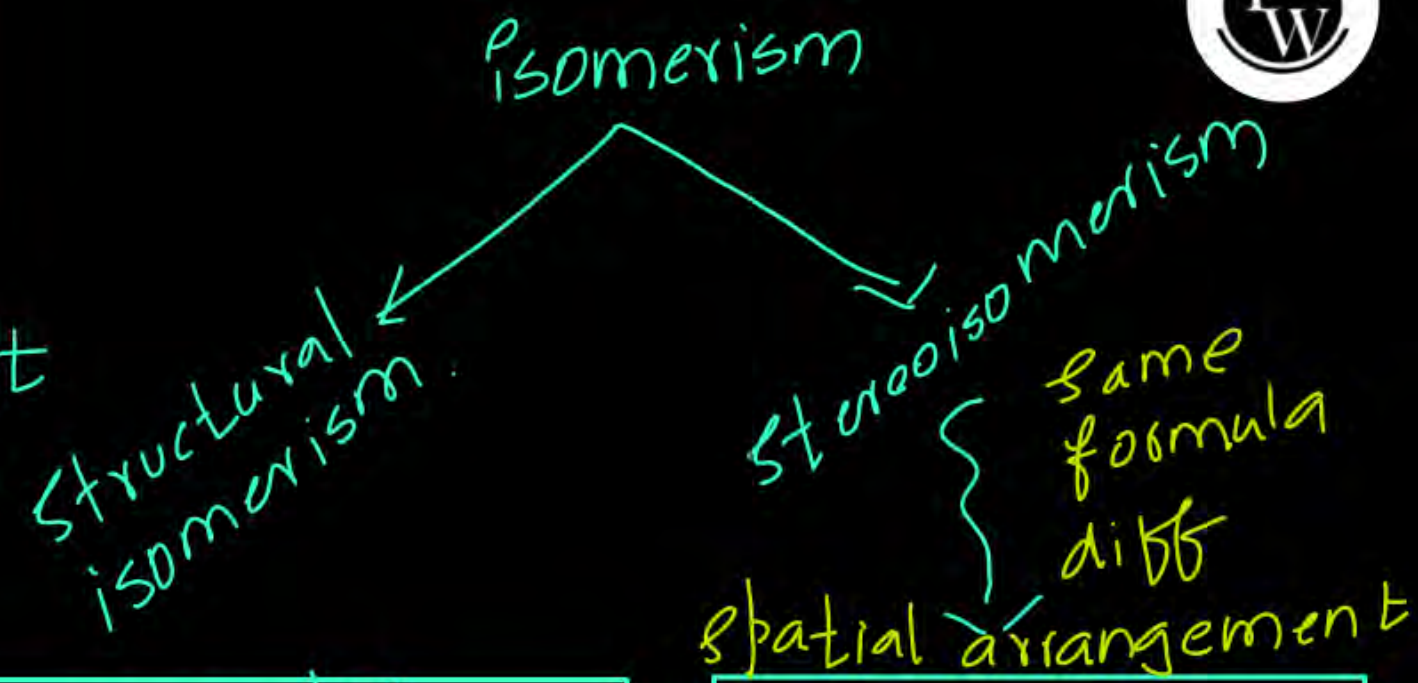
→ Octahedral complex shows GI

cis/trans

Fac/Mer

- solvate
- co-ordination
- linkage
- ionisation

- spatial arrangement
- Geometrical
 - optical





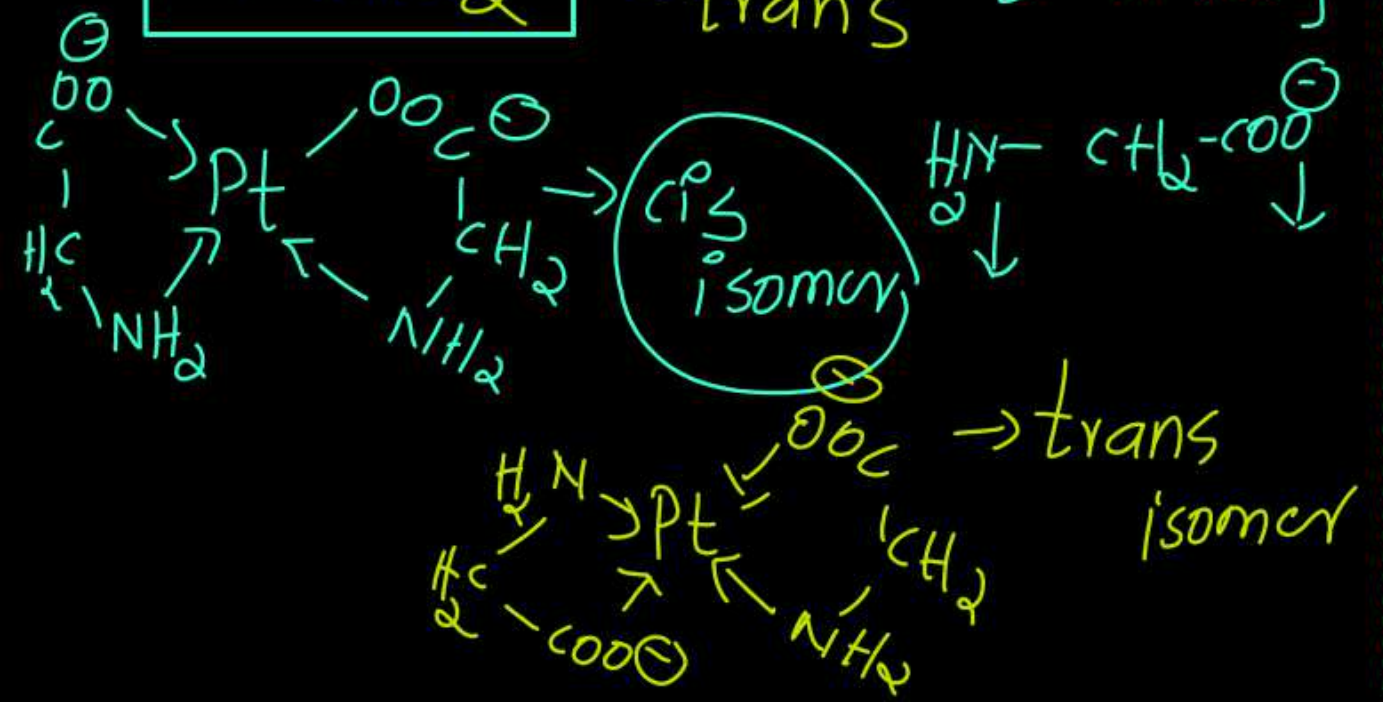
VI or Square planar complex

MA₂BCD → 2 cis isomers
1 trans isomer

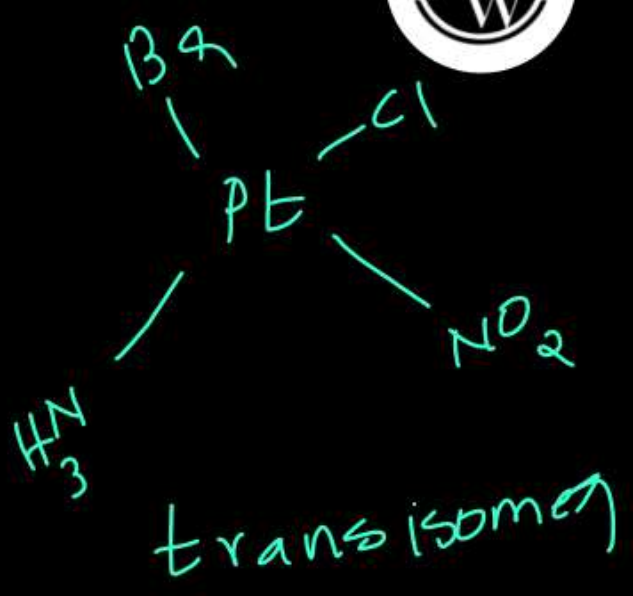
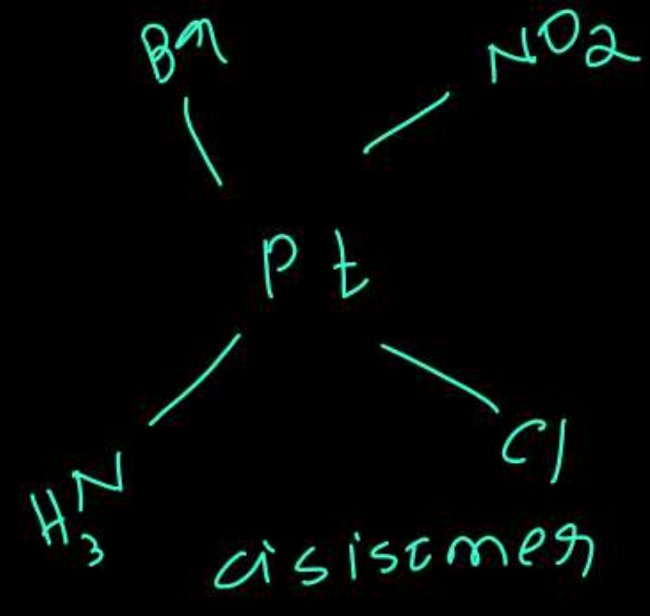
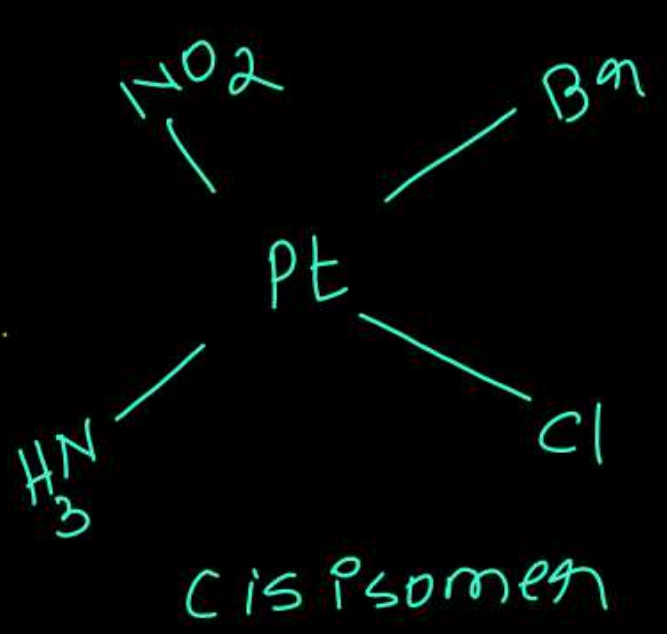
MA₂B₂ → cis
trans

MA₂BC → cis
trans

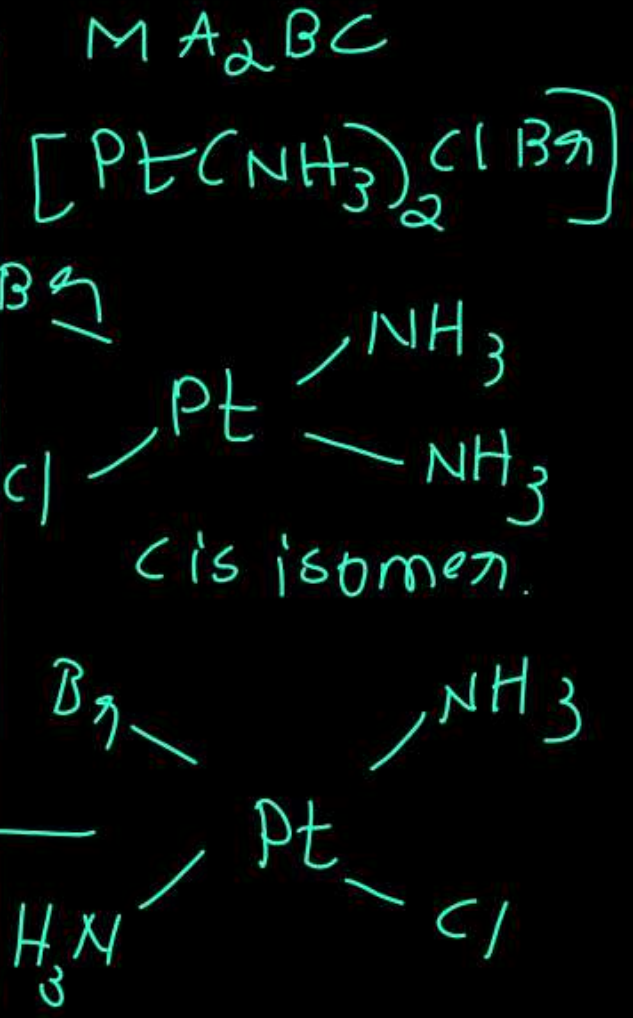
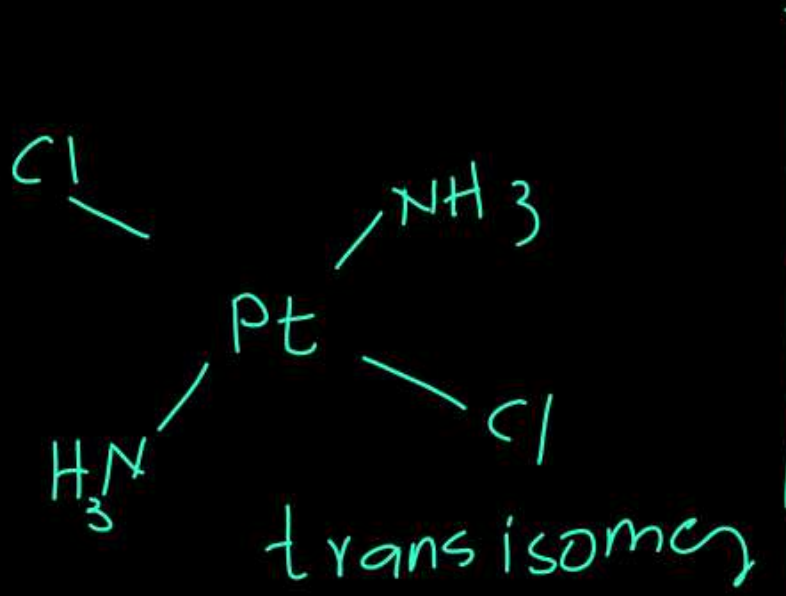
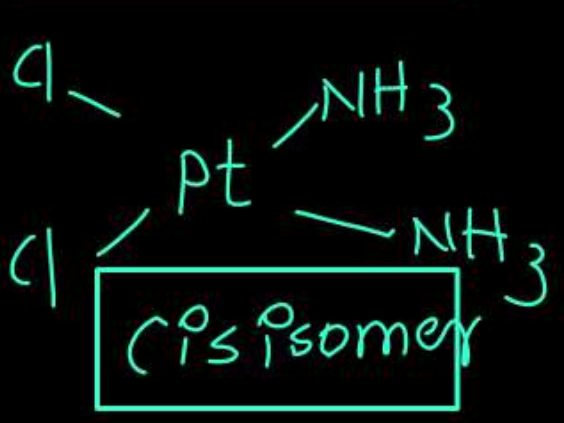
M(AB)₂ → cis
trans



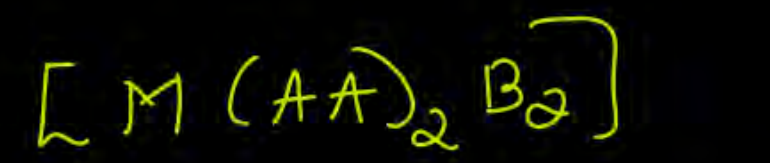
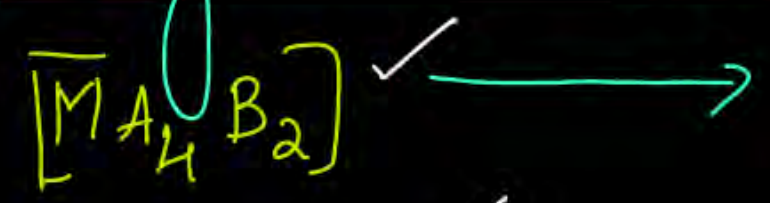
$[Pt(NH_3)ClBrNO_2]$



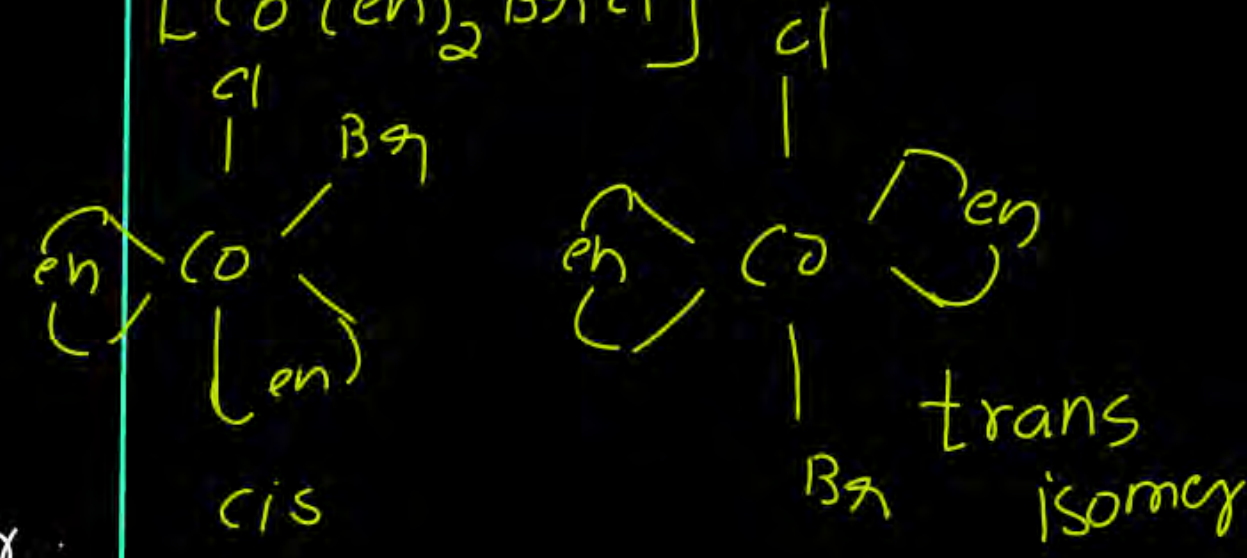
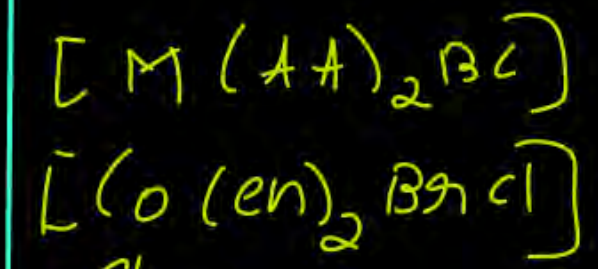
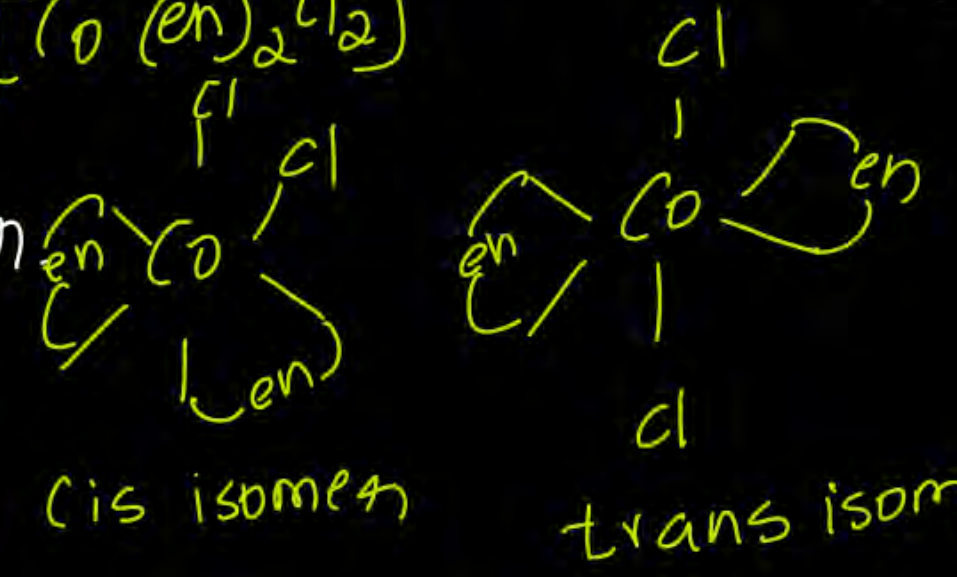
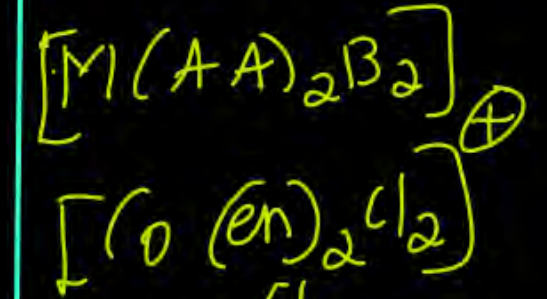
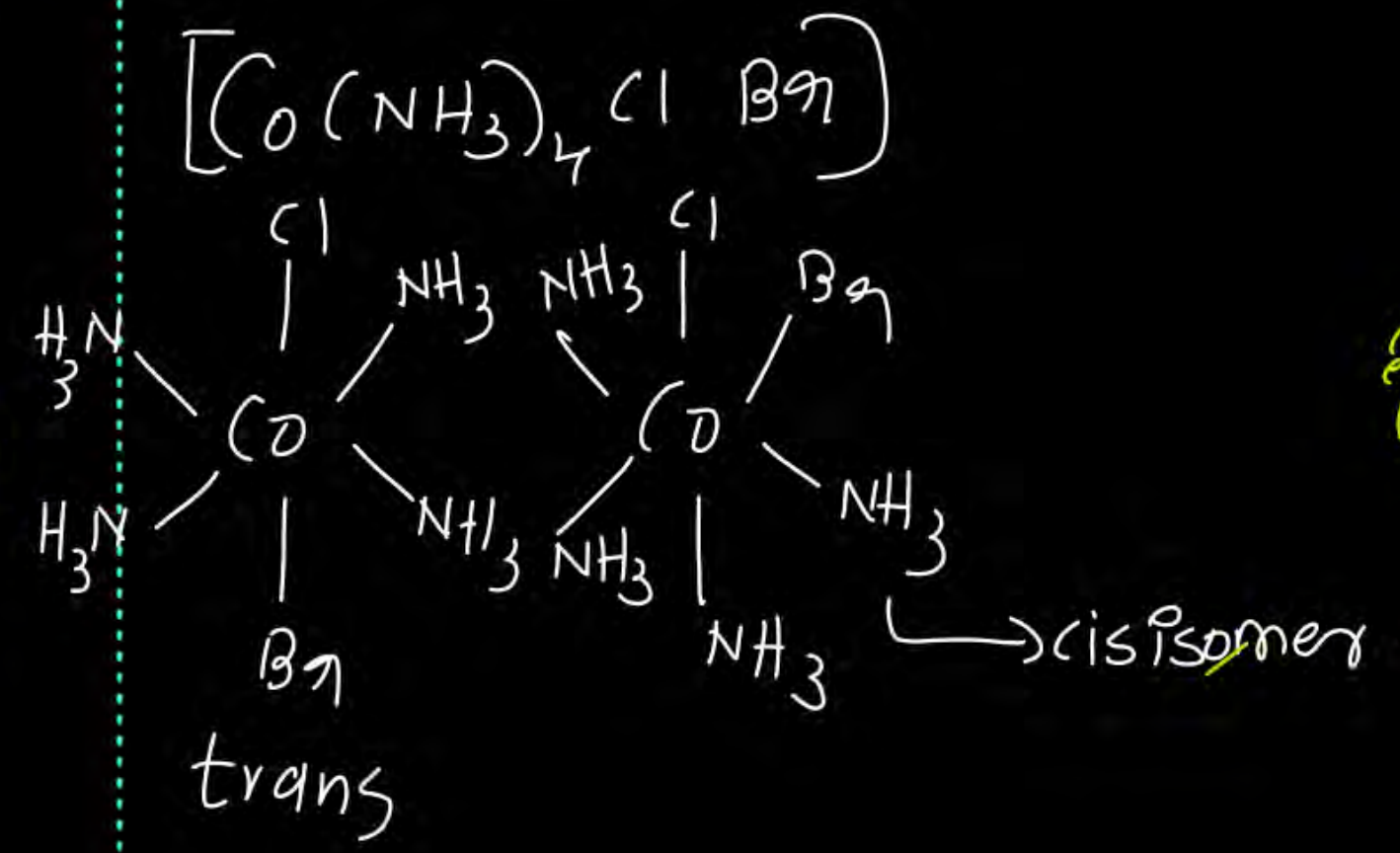
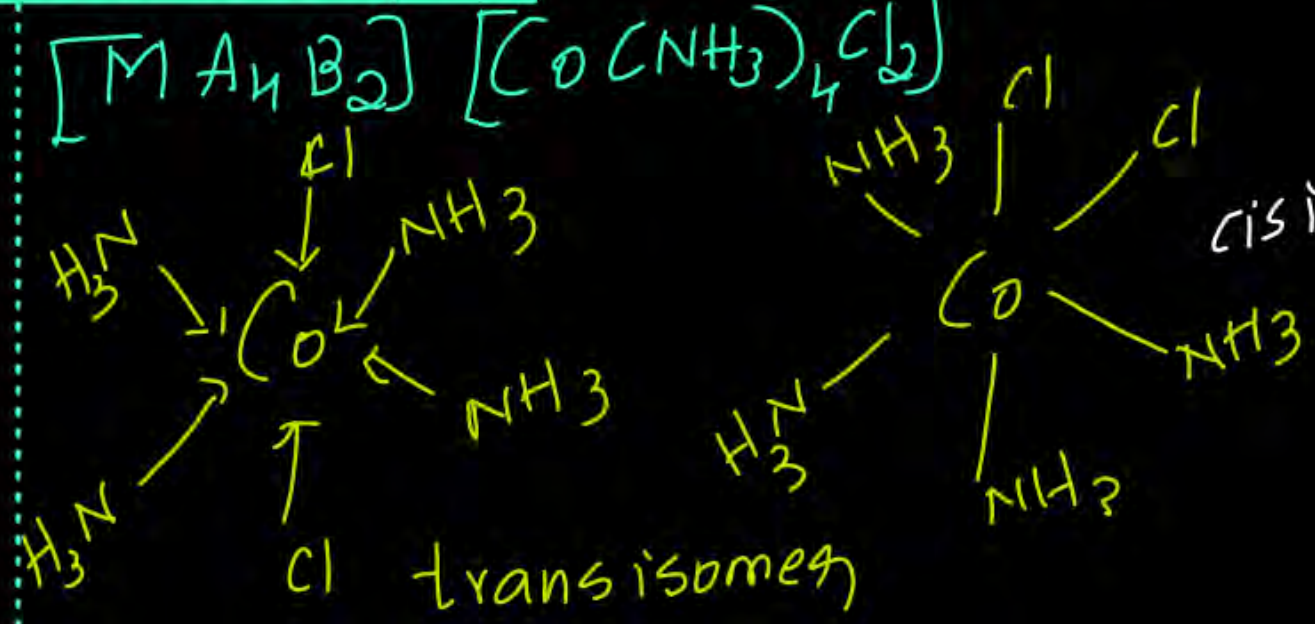
$[Pt(NH_3)_2Cl_2]$



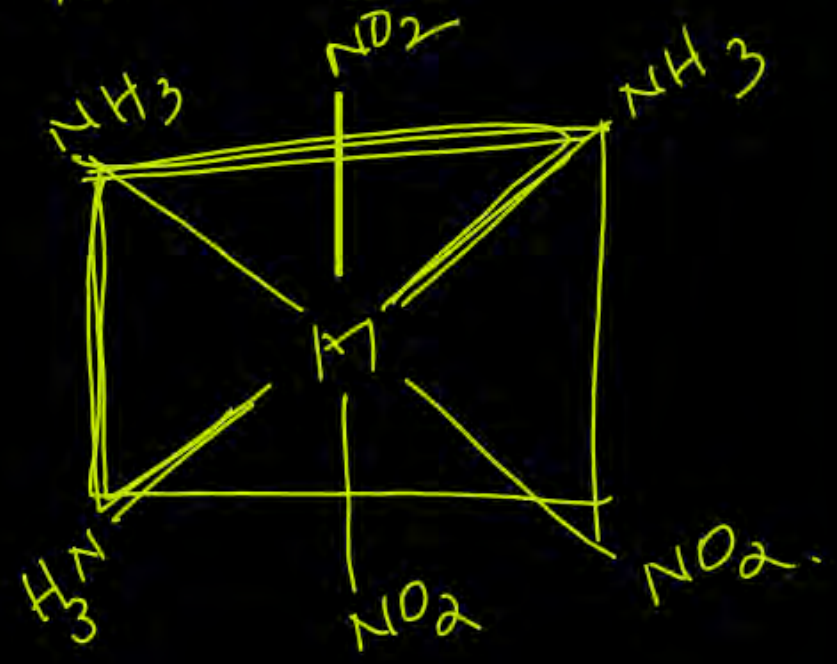
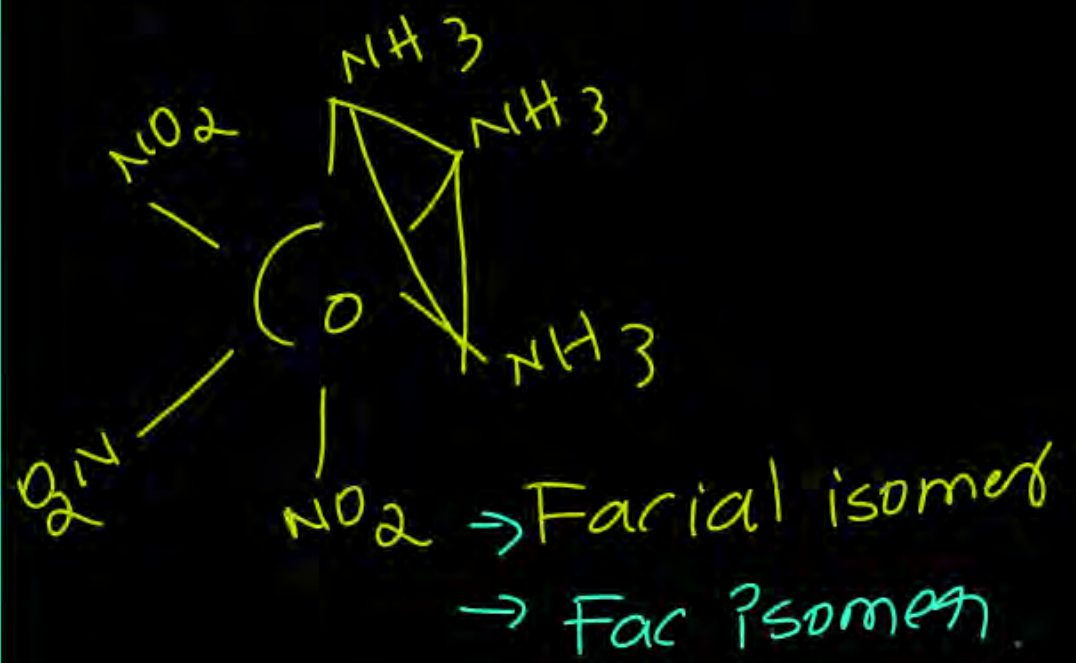
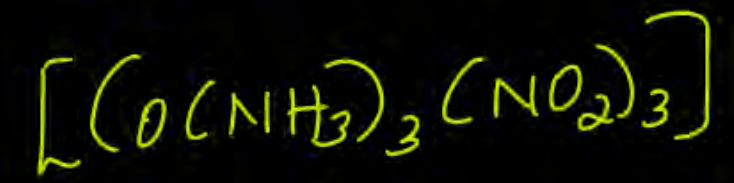
Geometrical isomerism in Octahedral complex



15 isomers
GI



G.I \rightarrow Fac/Mer $\rightarrow [MA_3B_3]$



Meridional

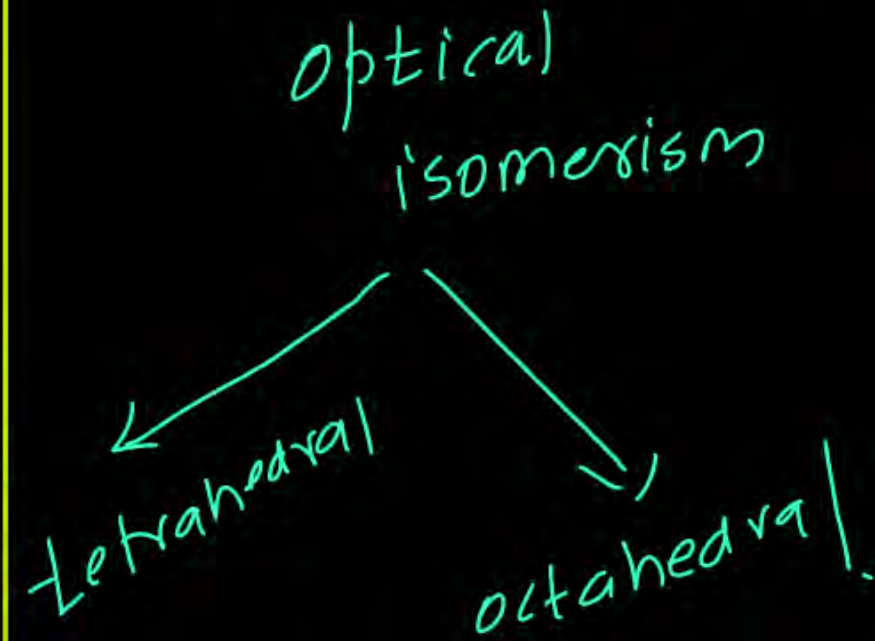


Optical isomerism \rightarrow Co-ordination compounds which rotates plane polarised light

Enantiomers \rightarrow Nonsuperimposable mirror images.

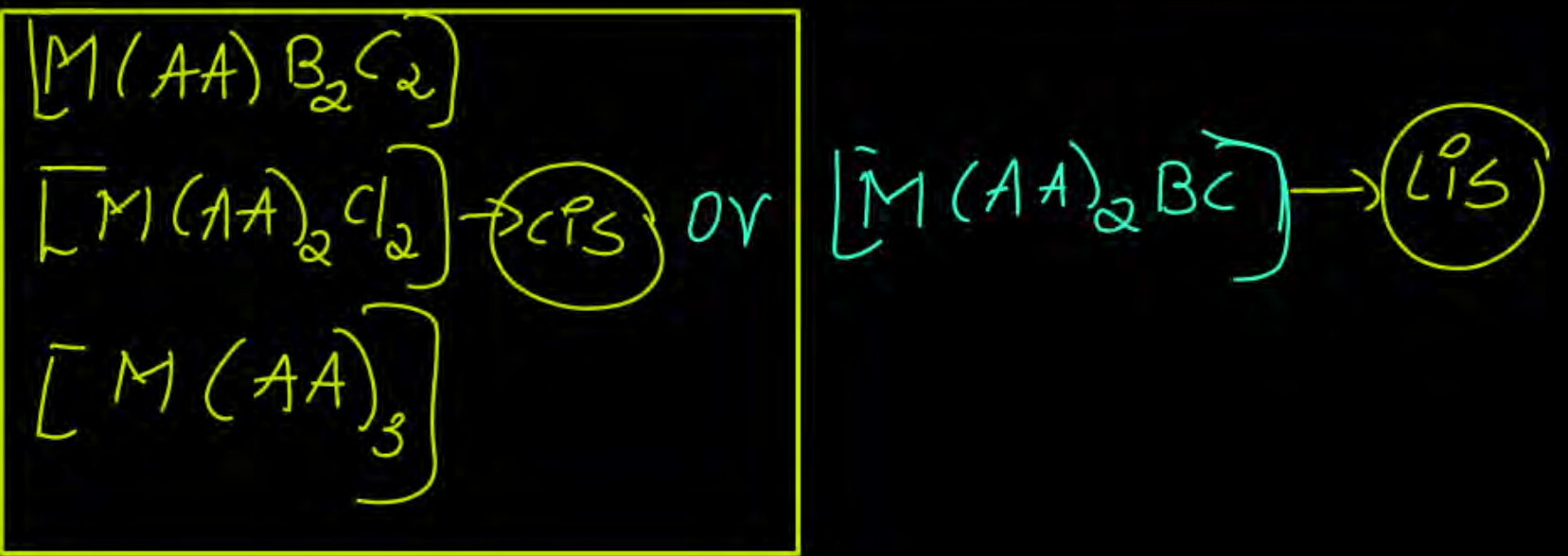
Condition \rightarrow POS

trans-geometrical isomerism \rightarrow optically inactive. plane of symmetry should not be there.

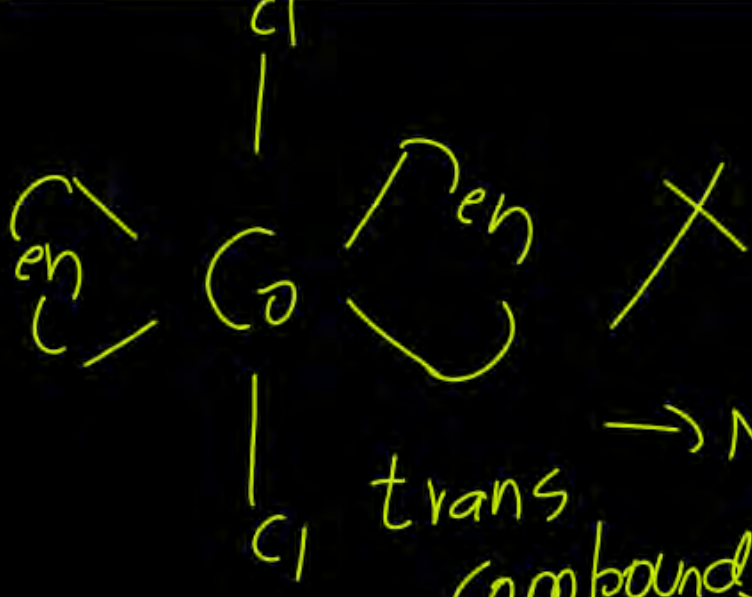
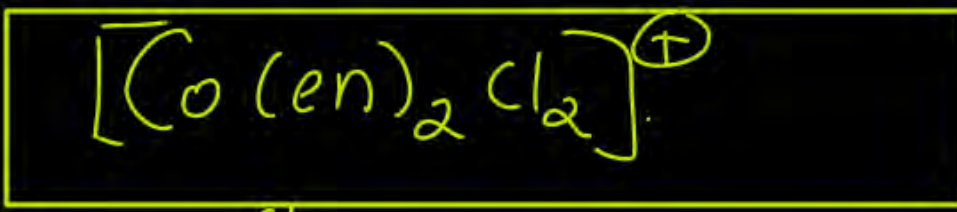
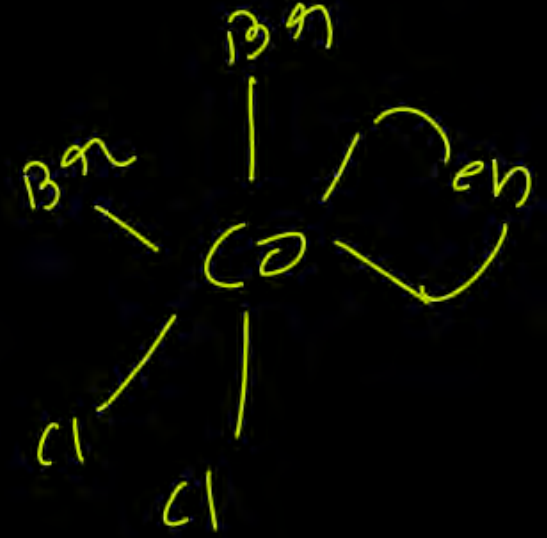
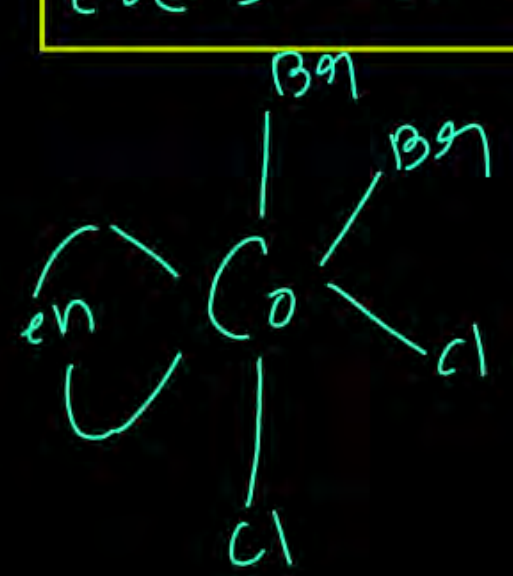
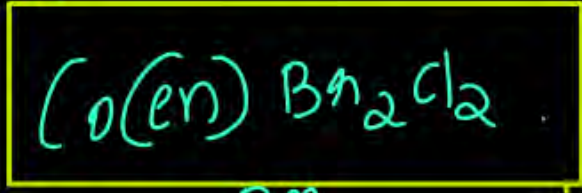


\rightarrow Square planar complex do not show optical isomerism

\rightarrow Optical isomerism in octahedral complex.

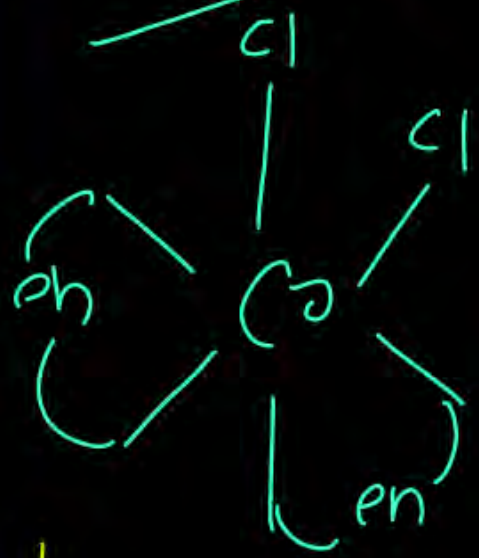


$[M(AA)B_2Cl_2] \rightarrow O.I$

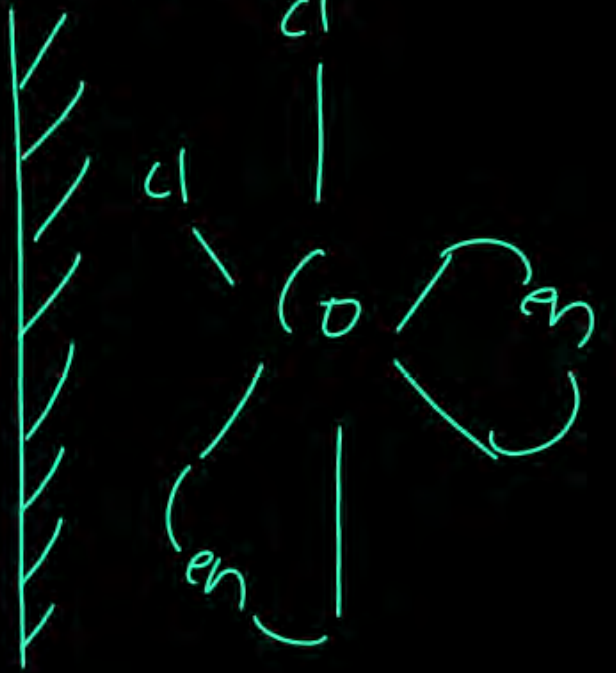


trans compounds \rightarrow No optical isomerism.

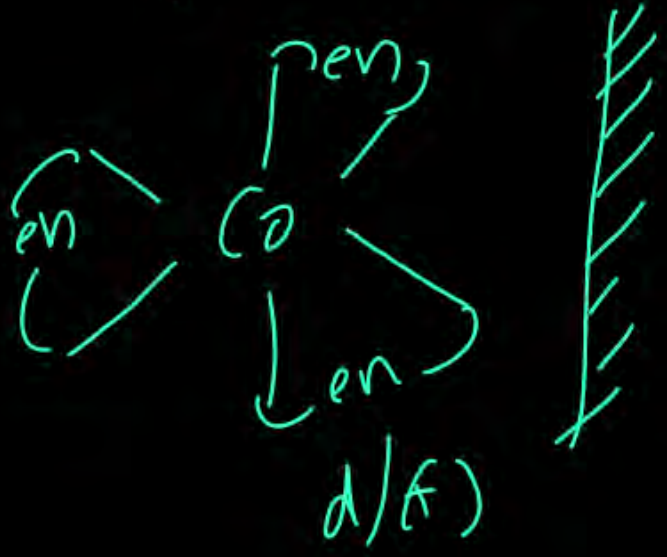
CPS isomer

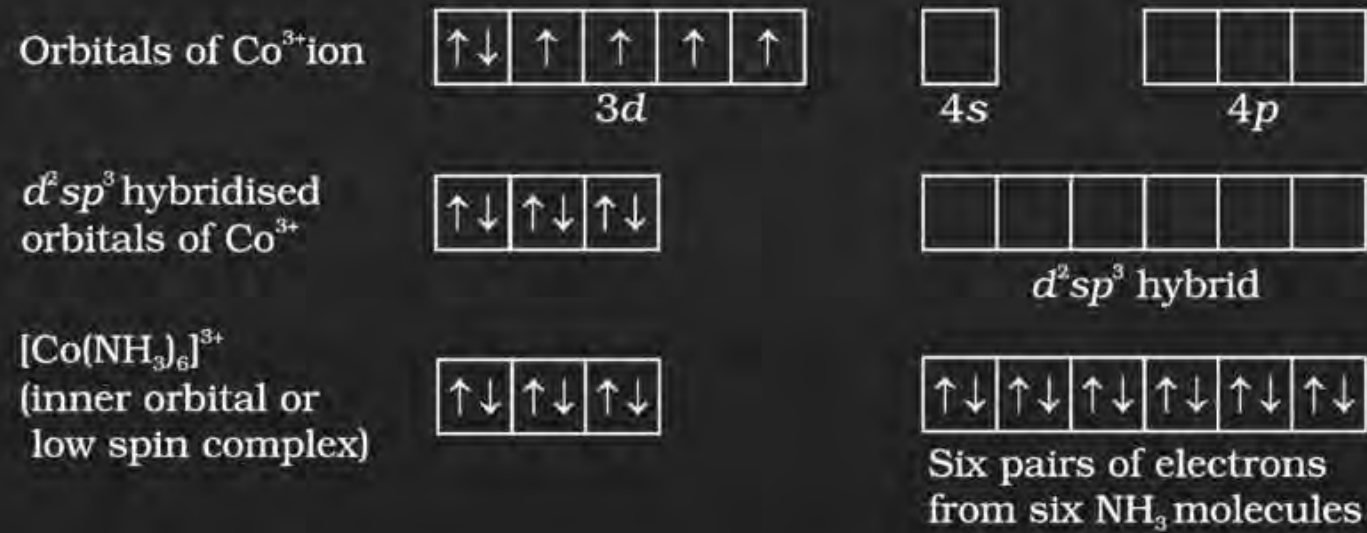


cis isomer



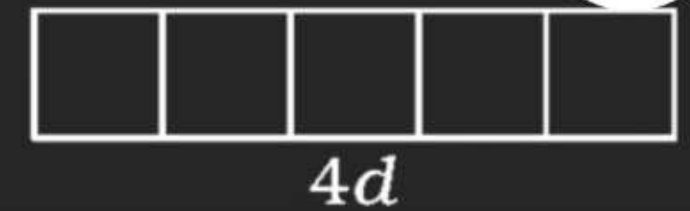
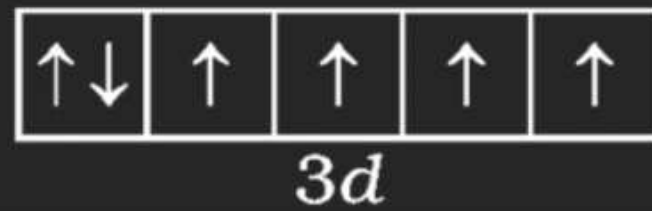
$[Co(en)_3]^{3+}$



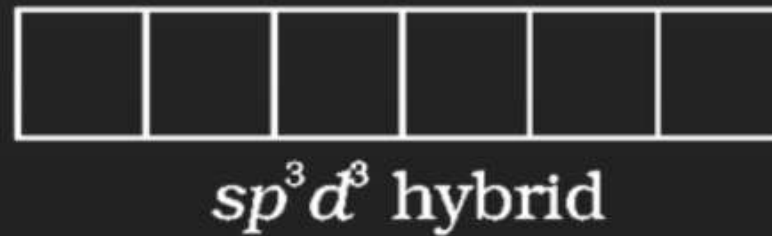


- Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals.
- Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron.
- In the formation of this complex, since the inner d orbital ($3d$) is used in hybridisation, the complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is called an **inner orbital or low spin or spin paired complex**.

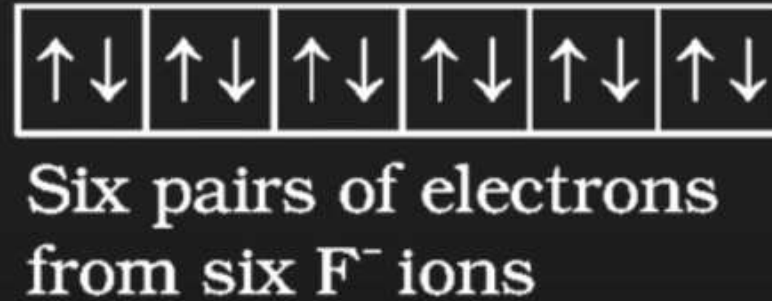
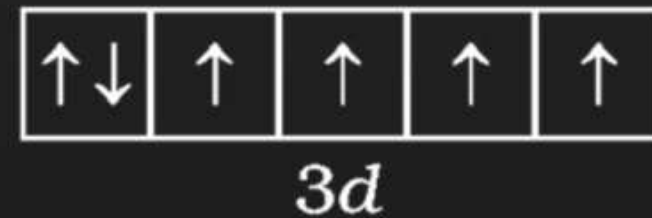
Orbitals of Co^{3+} ion



sp^3d^2 hybridised orbitals of Co^{3+}



$[\text{CoF}_6]^{3-}$
(outer orbital or high spin complex)

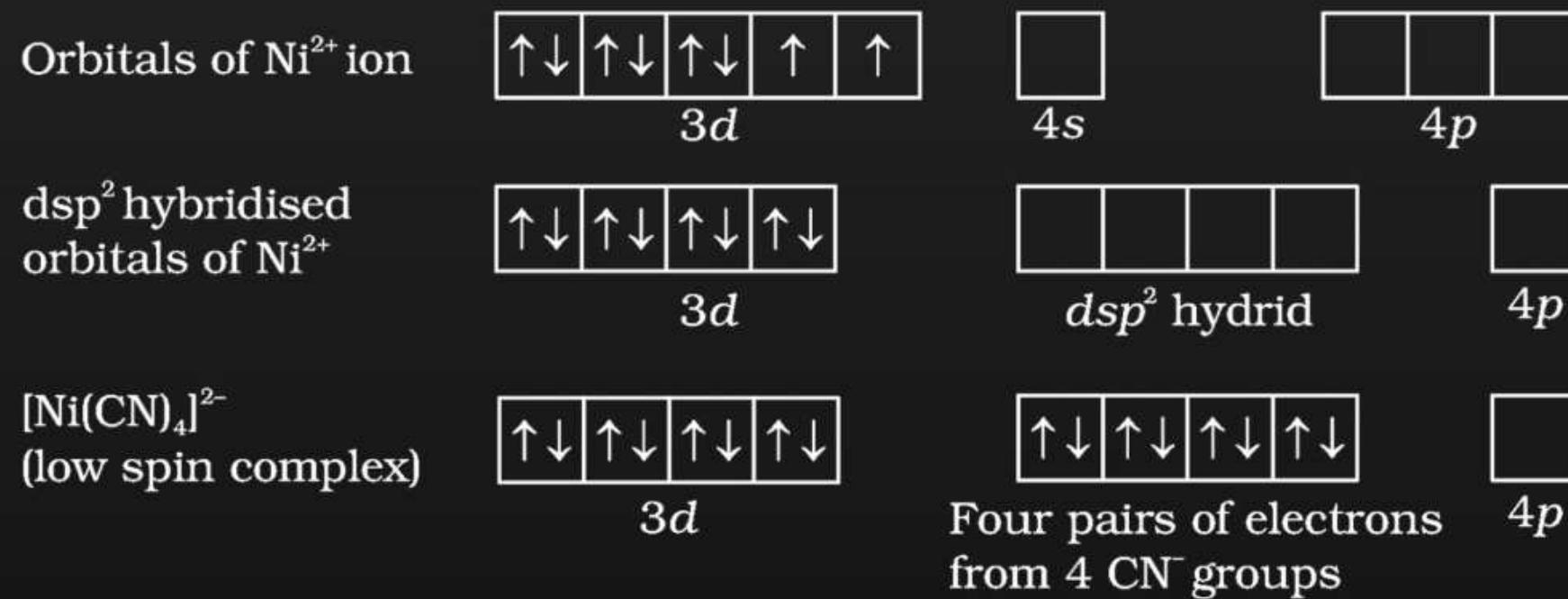


- The paramagnetic octahedral complex, $[\text{CoF}_6]^{3-}$ uses outer orbital ($4d$) in hybridisation (sp^3d^2).
- It is thus called outer orbital or high spin or spin free complex.

In the square planar complexes, the hybridisation involved is dsp^2 .

An example is $[\text{Ni}(\text{CN})_4]^{2-}$.

Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$.



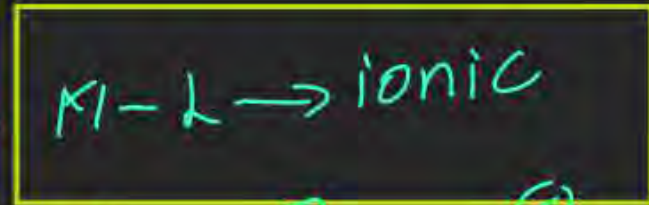
Valence Bond Theory

- $[\text{Mn}(\text{CN})_6]^{3-}$ has magnetic moment of two unpaired electrons while $[\text{MnCl}_6]^{3-}$ has a paramagnetic moment of four unpaired electrons.
- $[\text{Fe}(\text{CN})_6]^{3-}$ has magnetic moment of a single unpaired electron while $[\text{FeF}_6]^{3-}$ has a paramagnetic moment of five unpaired electrons.
- $[\text{CoF}_6]^{3-}$ is paramagnetic with four unpaired electrons while $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ is diamagnetic.

Limitations of Valence Bond Theory

- (i) It involves a number of assumptions. ✓
- (ii) It does not give quantitative interpretation of magnetic data. ✓
- (iii) It does not explain the colour exhibited by coordination compounds. ✓
- (iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds. ✓
- (v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes. ✓✓
- (vi) It does not distinguish between weak and strong ligands. ✓✓

Crystal Field Theory



point charge

Cl^-
 Br^- OH^-

$NH_3 \rightarrow$ point dipoles
 $H_2O \rightarrow$ point dipoles

- The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand.
- Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules.
- The five d orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate.
- This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion.
- However, when this negative field of a ligands becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals.
- The pattern of splitting depends upon the nature of the crystal field.

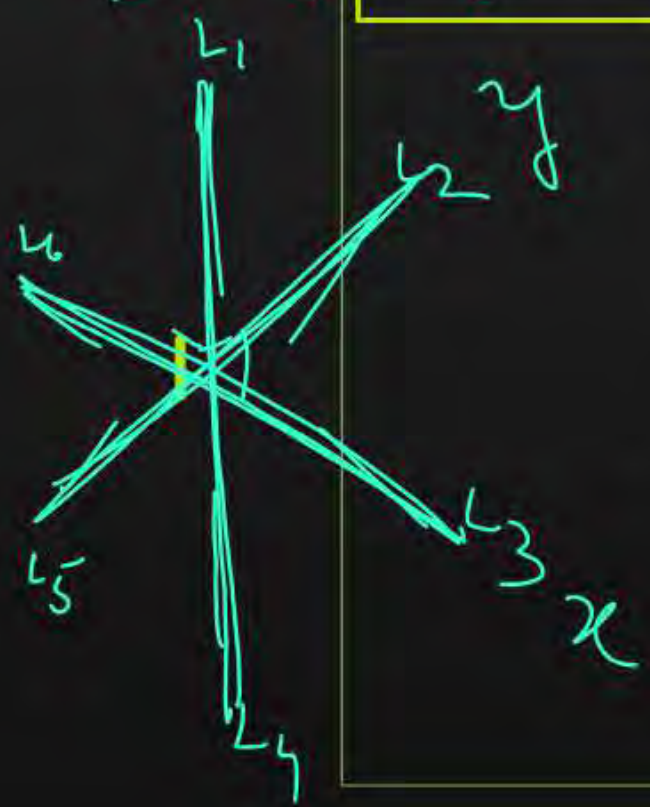
d orbital splitting in an octahedral crystal field

Strong ligand

$$\Delta_o > P$$

Weak ligand

$$\Delta_o < P$$

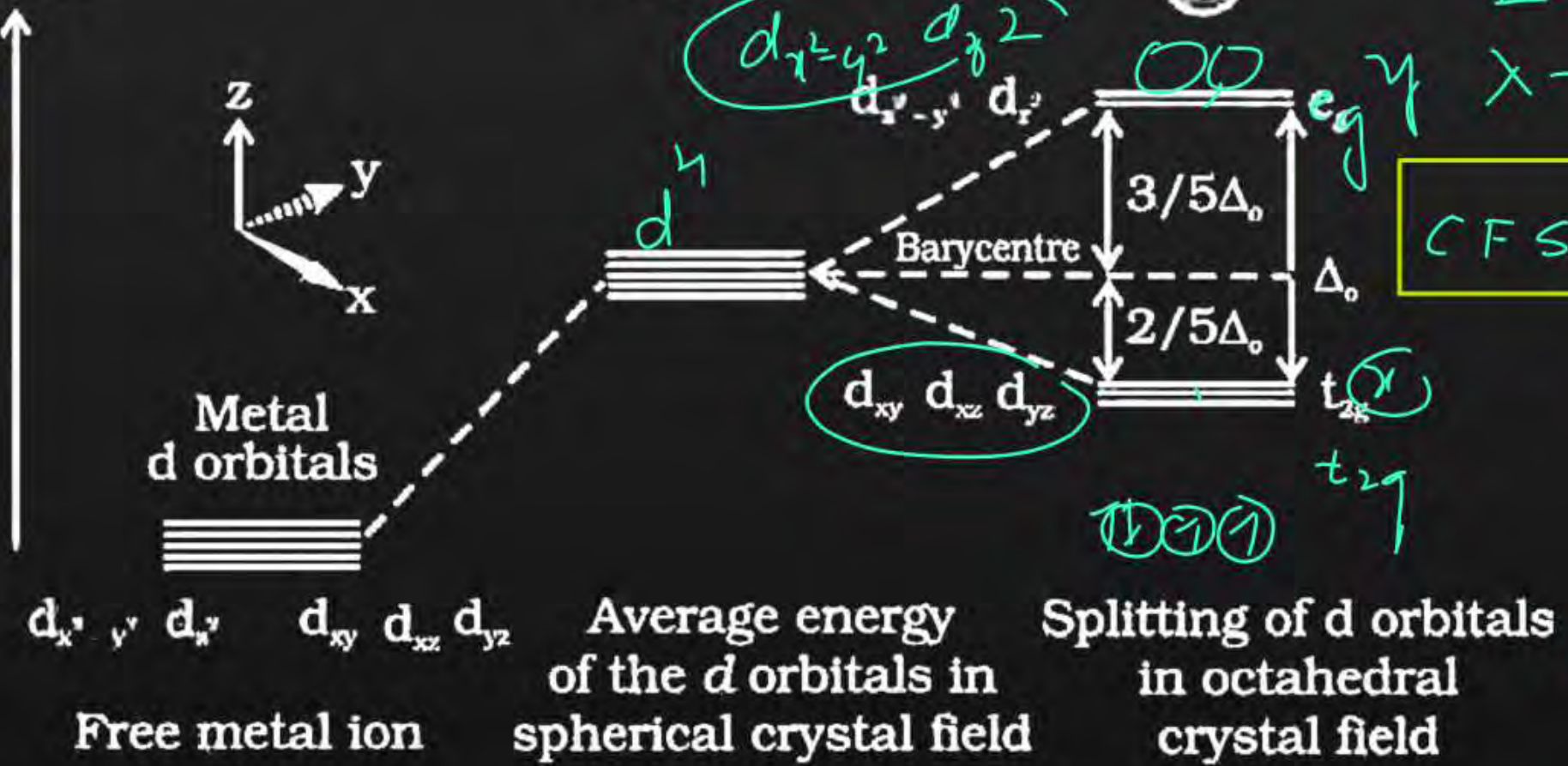


$$E = h\nu$$

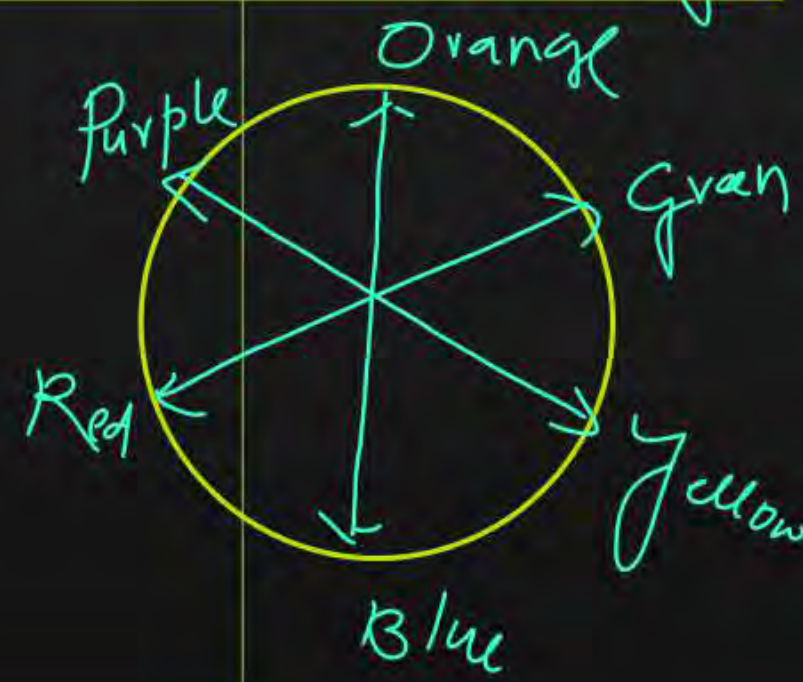
$$E = h \frac{c}{\lambda}$$

$E_{max} \rightarrow$ strong ligands
 $\lambda \rightarrow$ minimum.

Energy



$$CFSE = -0.4x + 0.6y$$



d orbital splitting in an octahedral crystal field

the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the d_{xy} , d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.

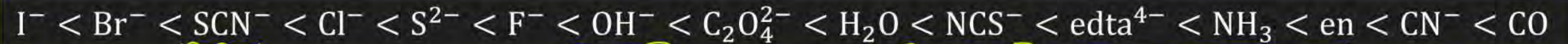
This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_o (the subscript o is for octahedral)

Thus, the energy of the two e_g orbitals will increase by $(3/5) \Delta_o$ and that of the three t_{2g} will decrease by $(2/5)\Delta_o$.

The crystal field splitting, Δ_o , depends upon the field produced by the ligand and charge on the metal ion.

Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals.

In general, ligands can be arranged in a series in the order of increasing field strength as given below:

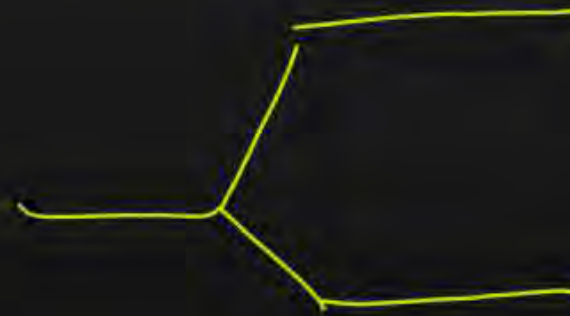


weak ligand

oxygen based

nitrogen base

carbon based



- (i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or
- (ii) it could avoid paying the price of the pairing energy by occupying the e_g level.

The two options are:

- (i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.
- (ii) If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

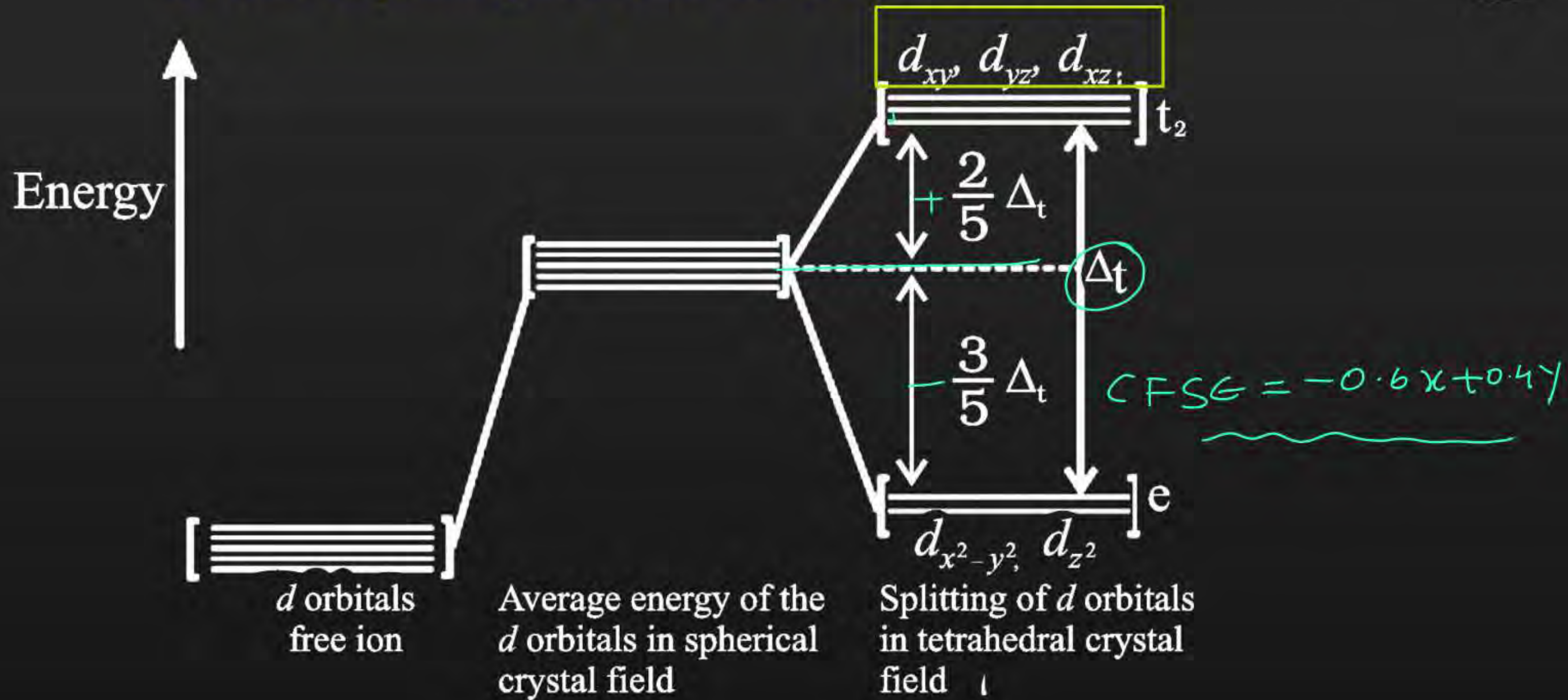
Crystal field splitting in tetrahedral coordination entities

$$\Delta_t = (4/9) \Delta_0$$

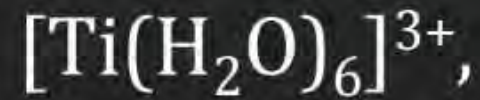
The 'g' subscript is used for the octahedral and square planar complexes which have centre of symmetry. Since tetrahedral complexes lack symmetry, 'g' subscript is not used with energy levels.



d orbital splitting in a tetrahedral crystal field.



Colour in Coordination Compounds



the electron excite from t_{2g} level to the e_g level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$)

Consequently, the complex appears violet in colour

The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron.

The colour of the complex is complementary to that which is absorbed.

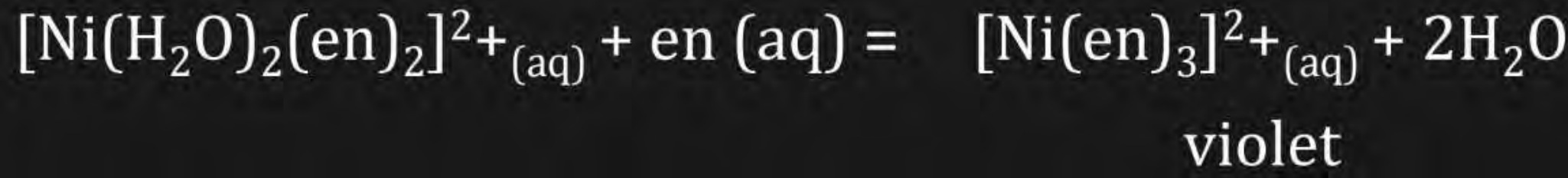
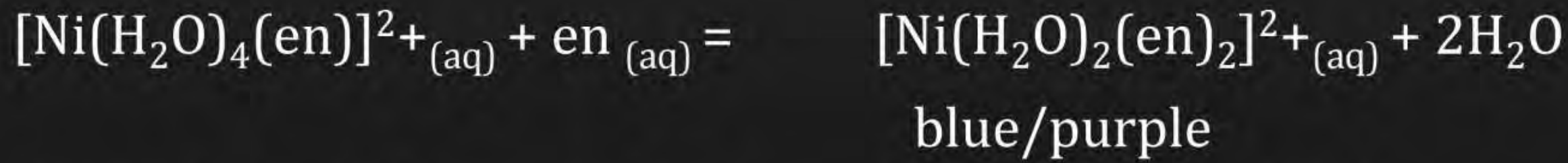
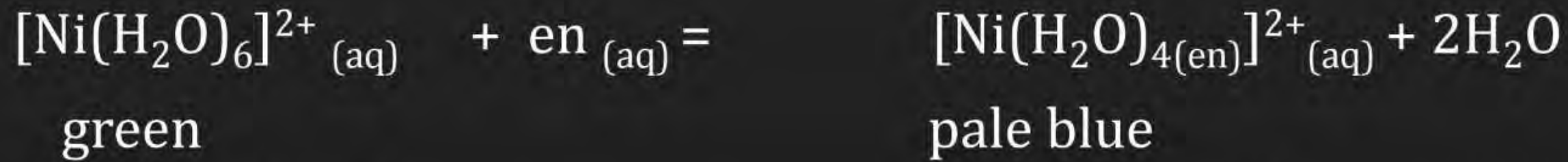
The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red.

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless.

Removal of water from $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ on heating renders it colourless.

Anhydrous CuSO_4 is white, but $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue in colour.

The influence of the ligand on the colour of a complex may be illustrated by considering the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex, which forms when nickel(II) chloride is dissolved in water.



Limitations of Crystal Field Theory

From the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series.

Further, it does not take into account the covalent character of bonding between the ligand and the central atom.

Bonding in Metal Carbonyls

Metals — C

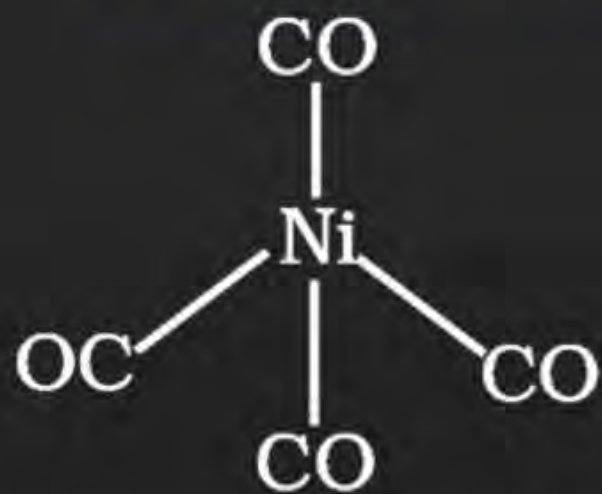
Tetracarbonylnickel(0) is tetrahedral,
 pentacarbonyliron(0) is trigonalbipyramidal
 hexacarbonyl chromium(0) is octahedral.



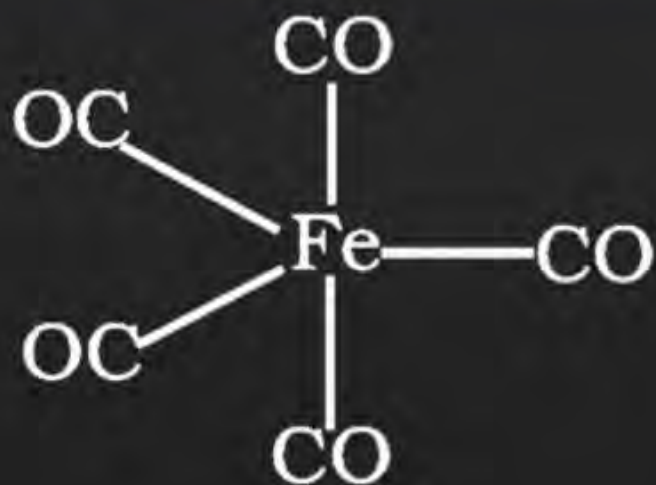
Decacarbonyldimanganese(0) is made up of two square pyramidal $\text{Mn}(\text{CO})_5$ units joined by a Mn — Mn bond.

Octacarbonyldicobalt(0) has a Co — Co bond bridged by two CO groups

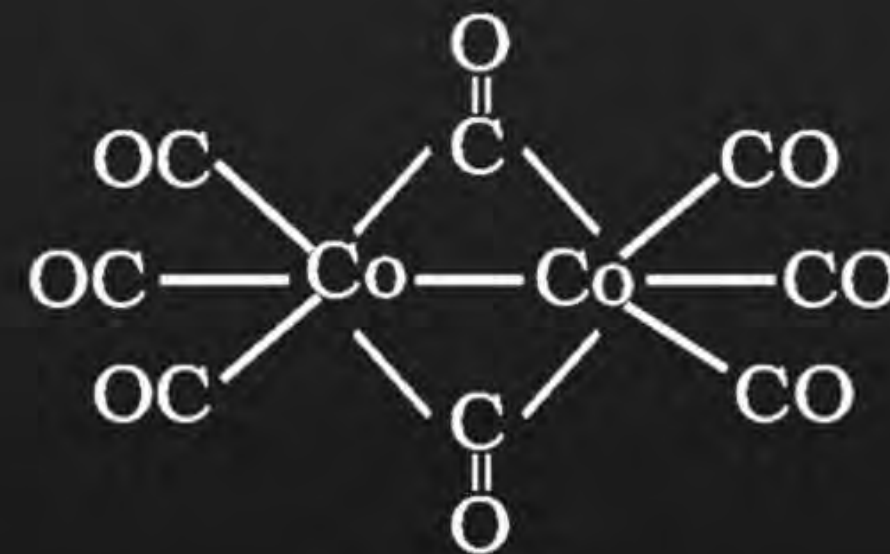
Structures of some representative homoleptic metal carbonyls.



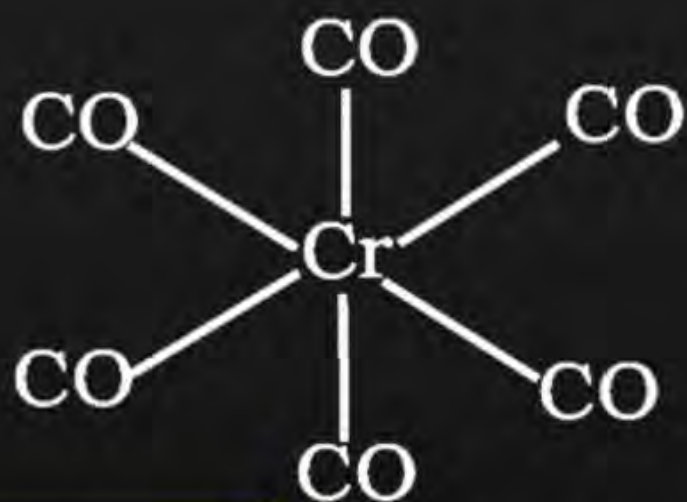
$\text{Ni}(\text{CO})_4$
Tetrahedral



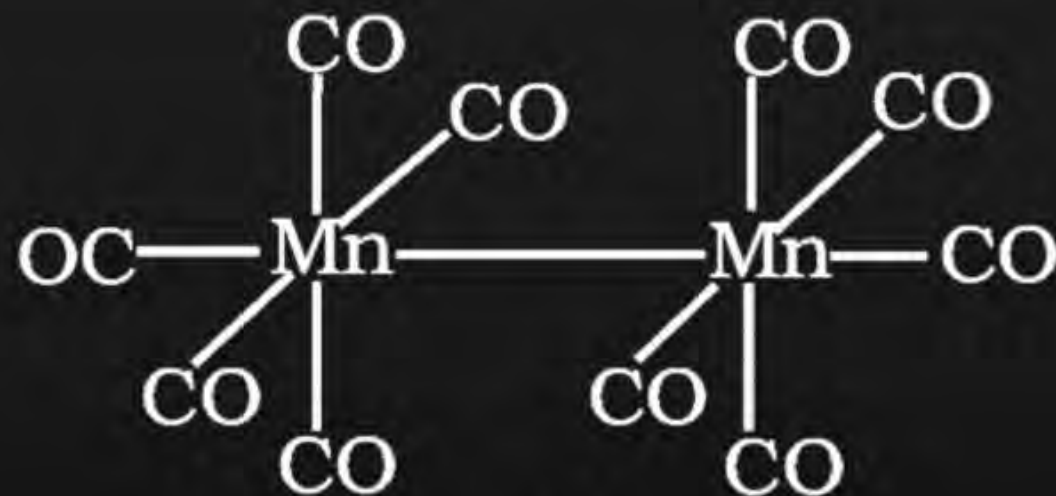
$\text{Fe}(\text{CO})_5$
Trigonal bipyramidal



$[\text{Co}_2(\text{CO})_8]$



$\text{Cr}(\text{CO})_6$ Octahedral



$[\text{Mn}_2(\text{CO})_{10}]$

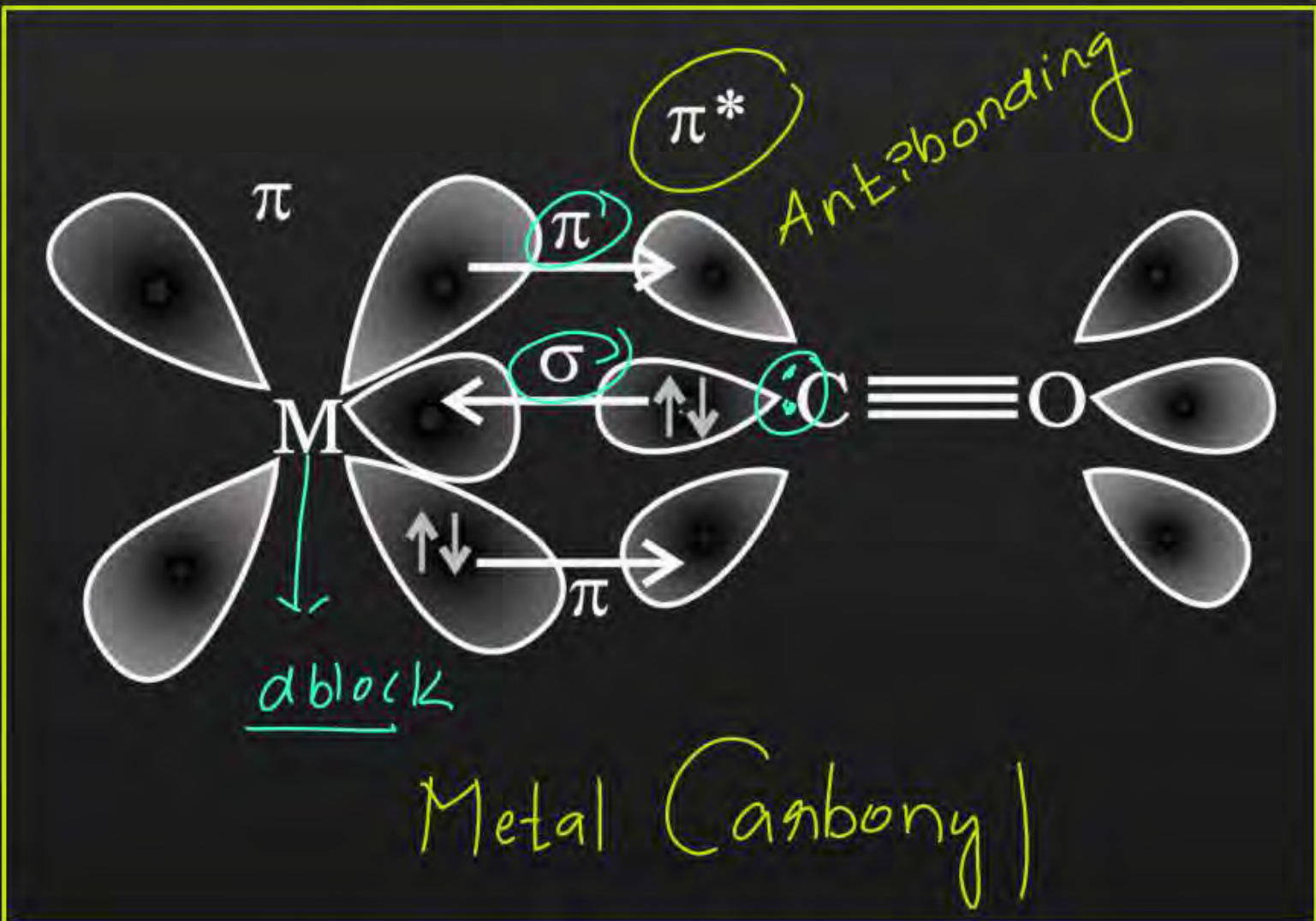
Example of synergic bonding interactions in a carbonyl complex.

The metal-carbon bond in metal carbonyls possess both σ and π character.

The M-C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal.

The M-C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide.

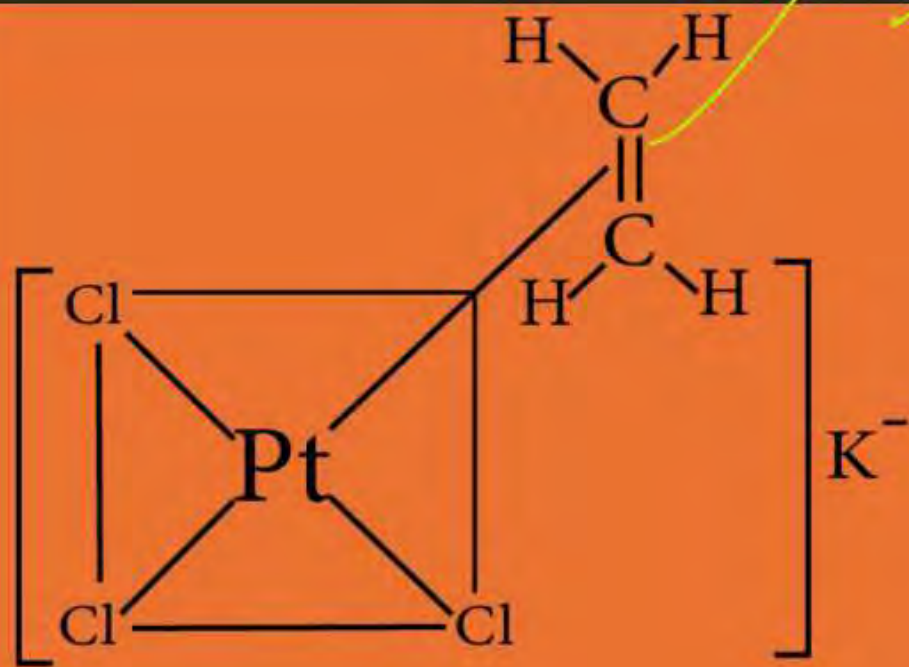
The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal).



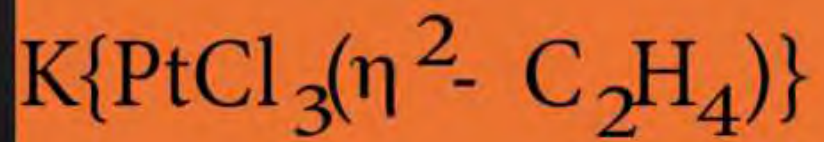
$$\psi_{AB} = \psi_A + \psi_B \rightarrow \text{BMO}$$

$$\psi_A - \psi_B \rightarrow \text{ABMO}$$

- As reagents include EDTA, DMG (dimethylglyoxime), α -nitroso- β -naphthol, etc
- Hardness of water is estimated by simple titration with Na_2EDTA . The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Gold can be separated in metallic form from this solution by the addition of zinc .
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[\text{Ni}(\text{CO})_4]$, which is decomposed to yield pure nickel.



Zeise's salt



ethene

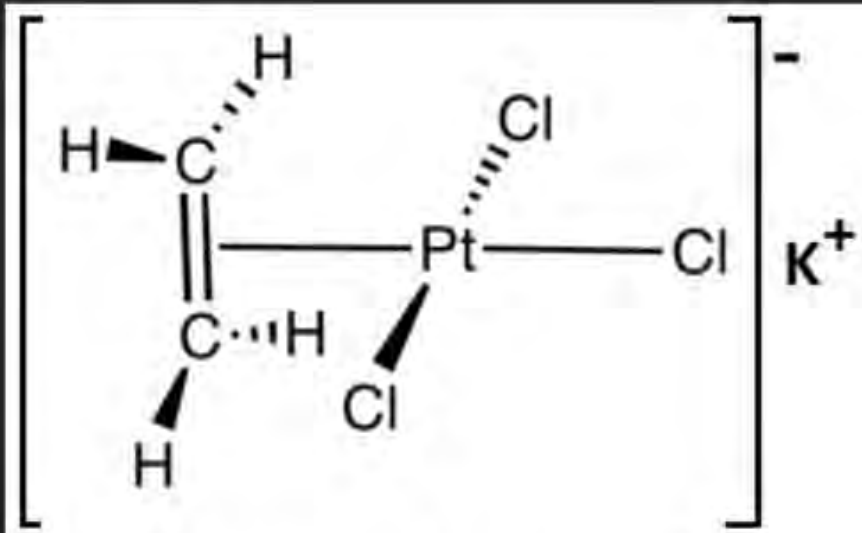


Ferrocene

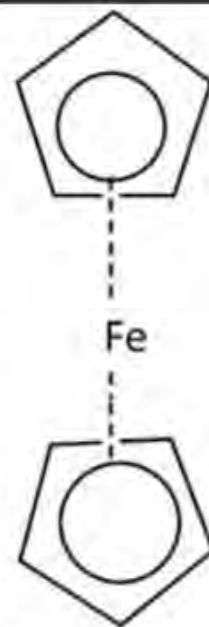


Dibenzene Chromium

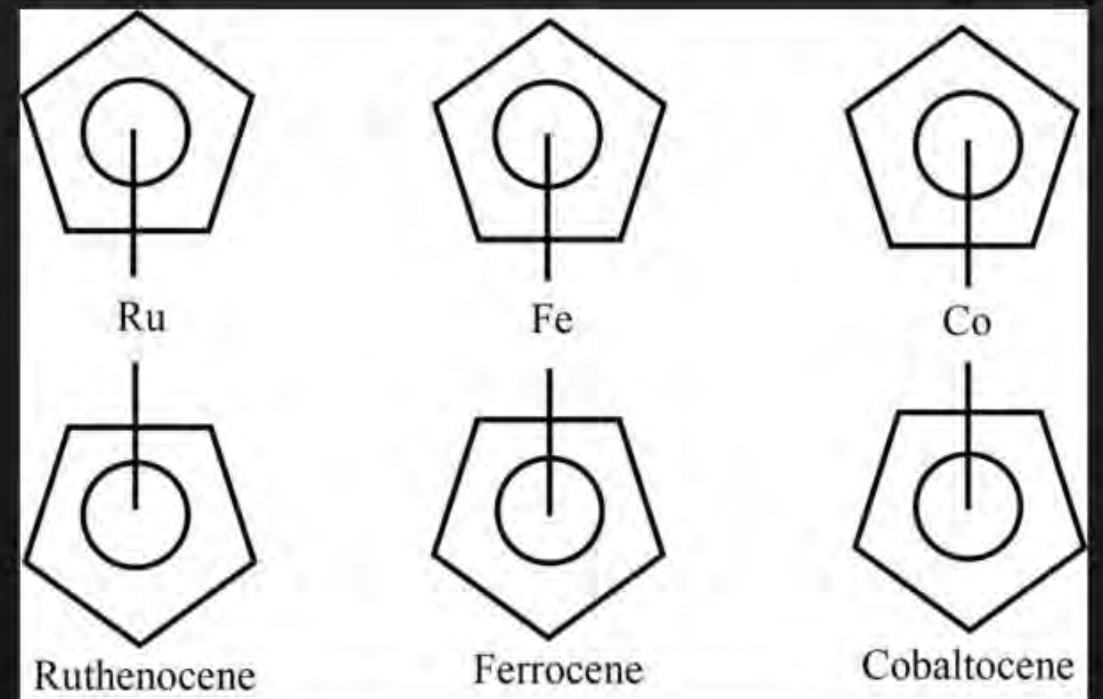




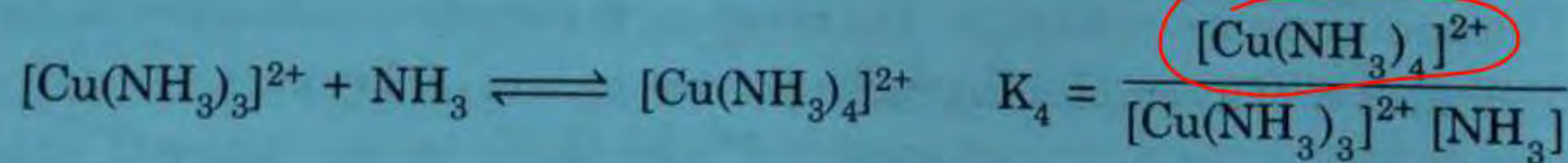
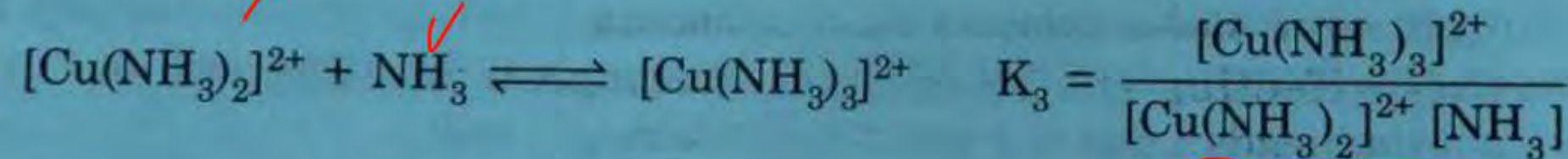
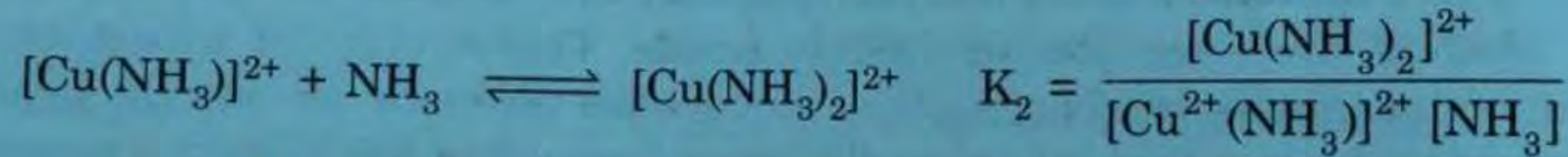
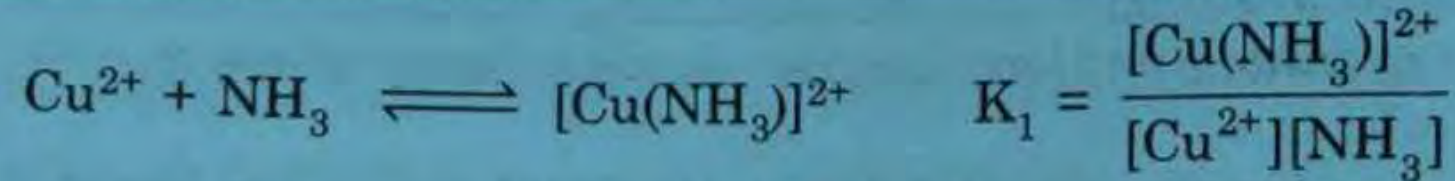
[Zeise's salt]



[Ferrocene]



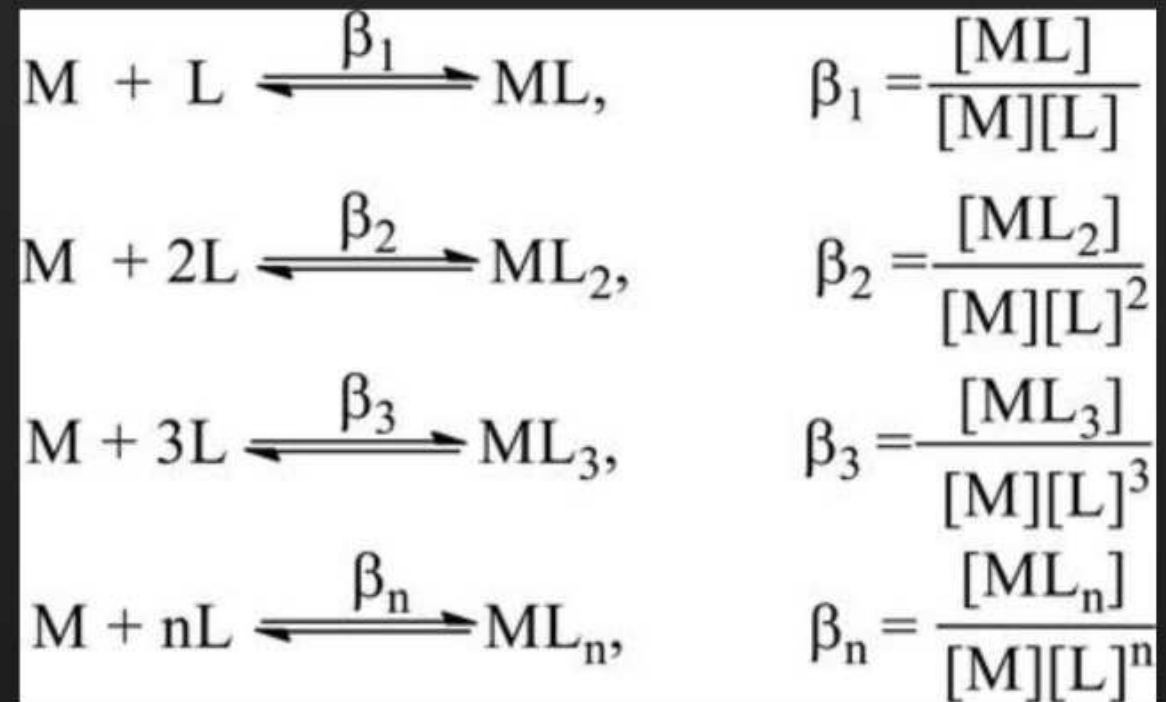
Stability of the complex

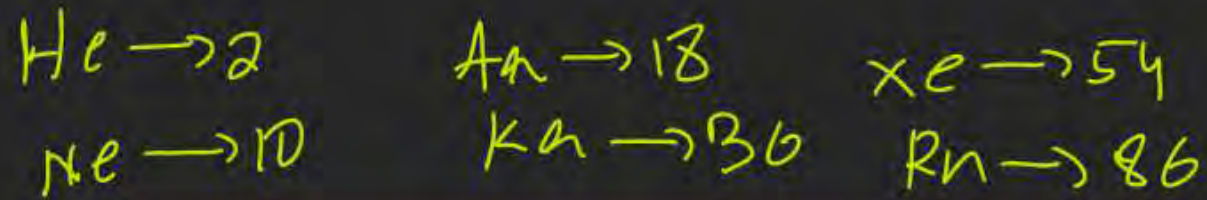


$\beta = K_1 \times K_2 \times K_3 \times K_4$



$$\beta = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} \quad \text{-----(1)}$$





Effective atomic number (EAN)

• $EAN = Z - X + Y$

Where,

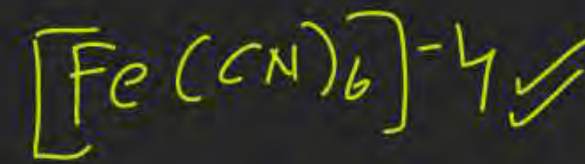
Z = atomic no. of the metal.

X = no. of electron lost during the formation of the metal ion from its atom.

Y = no. of electrons donated by the ligands.

Eg. $[Fe(CN)_6]^{-4}$, Fe oxidation = +2 & Z = 26

$$[Fe(CN)_6]^{-4} = 26 - 2 + 6(2) = 36$$



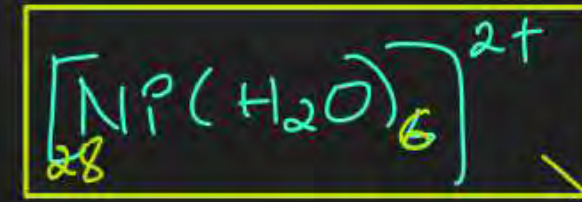
$2 - x + y$

$EAN = 26 - 2 + 12$

$EAN = 24 + 12 = 36$



$x \rightarrow 0.5$



$x + (-1 \times 6) = -4$

$EAN = 2 - x + y$

1e4 stable

$x = +2$

$= 28 - 2 + 12$

1 ligand $\rightarrow 2e^-$

$= 26 + 12 = 38$

6 $\rightarrow 12e^-$

$x(+0) = +2$



9.7 Importance and Applications of Coordination Compounds

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α -nitroso- β -naphthol, cupron, etc.
- Hardness of water is estimated by simple titration with Na_2EDTA . The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[\text{Au}(\text{CN})_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc (Unit 6).
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

$P(Ph)_3 \rightarrow$ triphenyl phosphine

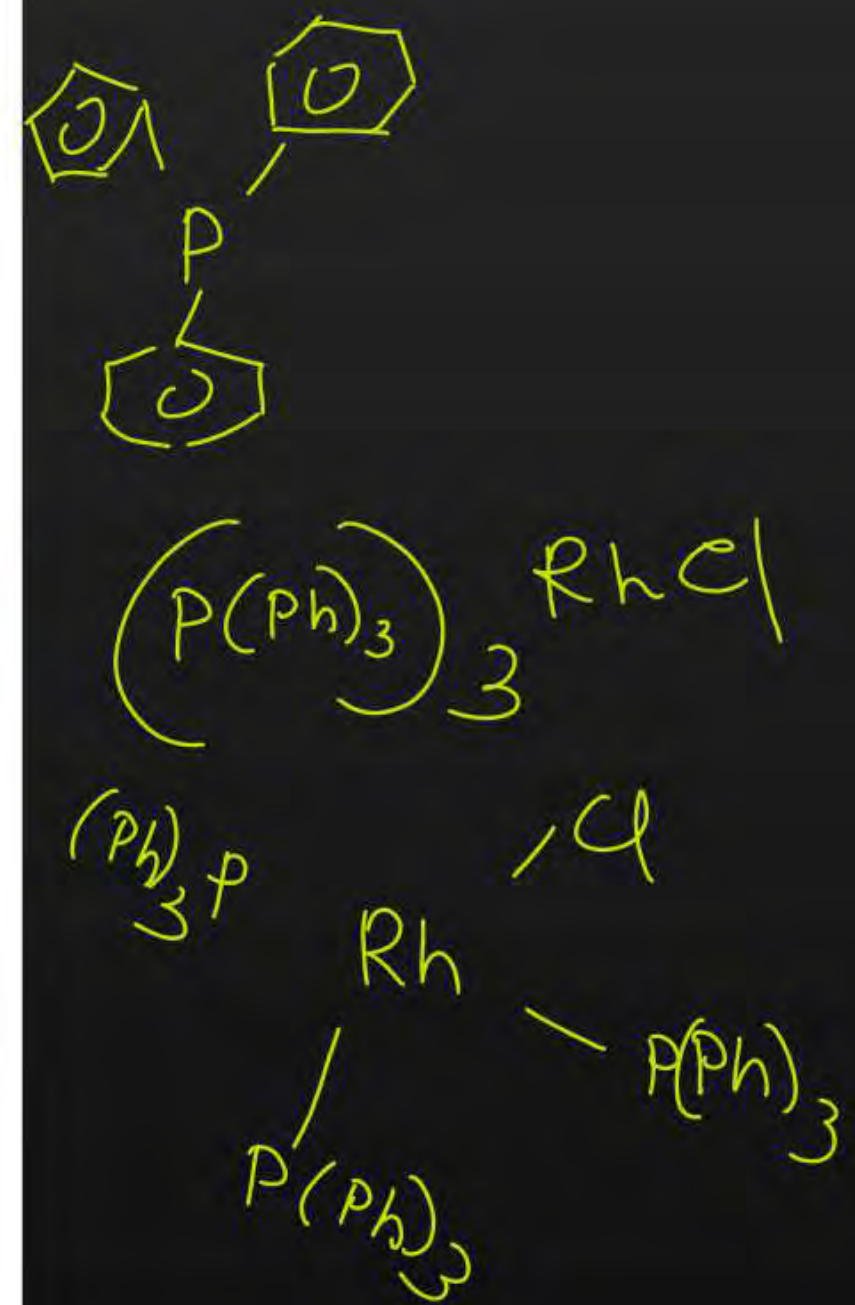


For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B₁₂, cyanocobalamin, the anti-pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes. $C=C + H_2 \rightarrow C-C + H_2$
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: cis-platin and related compounds.

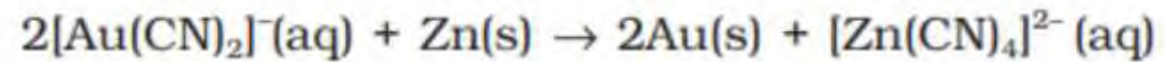
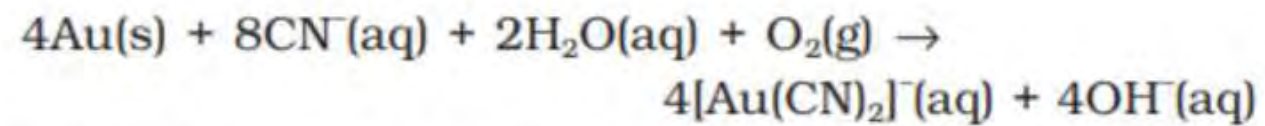
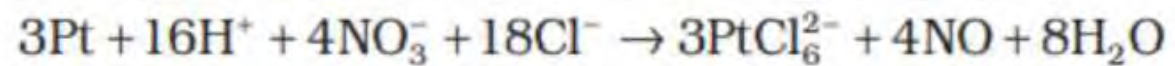
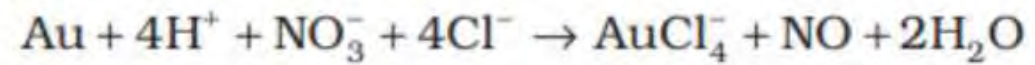
2-
S₂O₃

Cisplatin





When three parts of concentrated HCl and one part of concentrated HNO₃ are mixed, **aqua regia** is formed which is used for dissolving noble metals, e.g., gold, platinum.



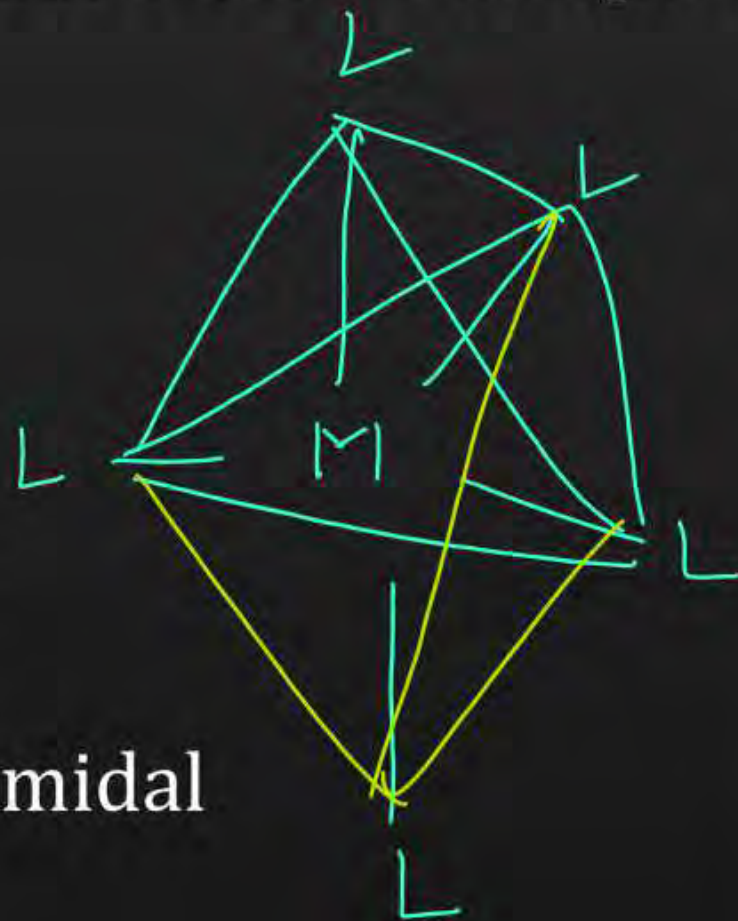
In this reaction zinc acts as a reducing agent.

QUESTION



A metal ion in the coordination compound has dsp^3 hybridisation. Hence, its geometry is

- A** tetrahedral
- B** square planar
- C** trigonal bipyramidal
- D** pentagonal bipyramidal.



5 ligands \rightarrow strong/weak $\rightarrow sp^3d$

dsp^3

\rightarrow trigonal bipyramidal

$d, s, p, p, p \rightarrow 5$ ligands

VBT \rightarrow Theory \rightarrow $M-L$ \rightarrow covalent

\rightarrow orbitals overlap \rightarrow ligand & d block central metal atom's

$(n-1)d, ns, np, nd$

$3d, 4s, 4p, 4d$

4 ligands \rightarrow strong $\rightarrow dsp^2$
 \rightarrow weak $\rightarrow sp^3$

6 ligands \rightarrow strong $\rightarrow 3d^2 4s 4p \rightarrow dsp^3$
 \rightarrow weak $\rightarrow 4s, 4p, 4d \rightarrow sp^3d^2$

QUESTION



The complexes of nickel (II) can be

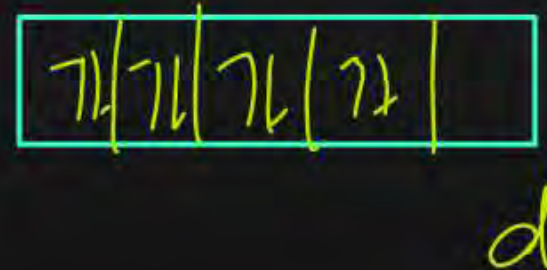
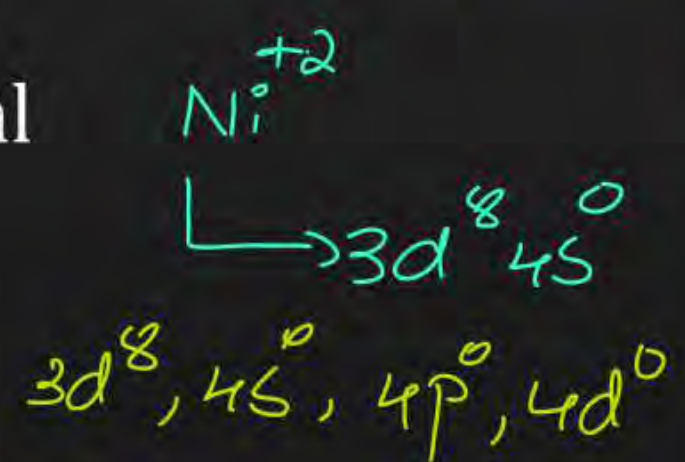
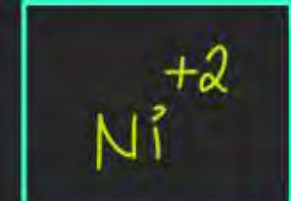
A square planar, tetrahedral and octahedral

B square planar and tetrahedral

C tetrahedral and octahedral

D square planar only.

6 ← sp^3d^2
 d^2sp^3



QUESTION



Using valence bond theory, the complex $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ can be described as

- A** sp^3d^2 , outer orbital complex, paramagnetic
- B** d^2sp^2 , inner orbital complex, diamagnetic
- C** d^2sp^3 , inner orbital complex, paramagnetic
- D** d^2sp^3 , outer orbital complex, diamagnetic.

QUESTION



$K_3[CoF_6]$ is high spin complex. What is the hybrid state of Co atom in this complex?

A $\underline{d^2sp^3}$ ✗

B $\underline{dsp^2}$ ✗

C $\underline{sp^3d}$ 3 ligands

D $\underline{sp^3d^2}$ ✓✓
→ 6 ligands

weak ligand.

VBT Theory → covalent bond.

2 ligands → sp

3 ligands → sp^2

4 ligands → sp^3 → weak ligands → high spin
→ outer orbital

→ dsp^2 → strong ligands → inner orbital low spin.

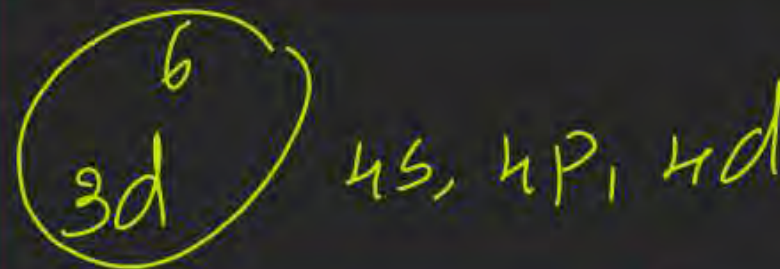
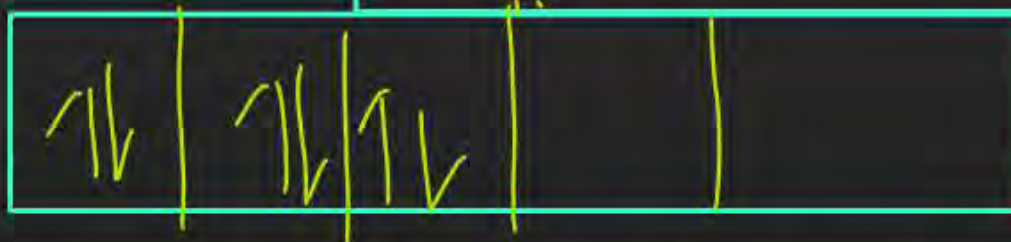
5 ligands → dsp^3 → strong ligands

6 ligands → sp^3d → weak ligands
→ d^2sp^3 → strong ligand
→ sp^3d^2 → weak ligand.

QUESTION



Mark the incorrect statement.



A Inner orbital (low spin) complexes involve d^2sp^3 hybridisation. ✓

B Outer orbital (high spin) complexes involve sp^3d^2 hybridisation. ✓

C Tetrahedral complexes generally involve dsp^2 hybridisation. ✗

D Stereoisomerism involves geometrical and optical isomerism. ✓

✓
Square planar


QUESTION



Match the examples given in column I with the shapes of the compounds given in column II and mark the appropriate choice.

	Column I		Column II
(A)	$[\text{Ag}(\text{NH}_3)_2]^+$ <i>sp</i>	(i)	d^2sp^3 , octahedral
(B)	$[\text{Ni}(\text{CN})_4]^{2-}$ <i>d^2sp^3</i>	(ii)	dsp^2 , square planar
(C)	$[\text{Ni}(\text{CO})_4]$ <i>sp^3</i>	(iii)	<i>sp</i> , linear
(D)	$[\text{Fe}(\text{CN})_6]^{3-}$ <i>d^2sp^3</i>	(iv)	sp^3 , tetrahedral

A (A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iii), (D) \rightarrow (iv)

~~**B** (A) \rightarrow (iii), (B) \rightarrow (ii), (C) \rightarrow (iv), (D) \rightarrow (i)~~

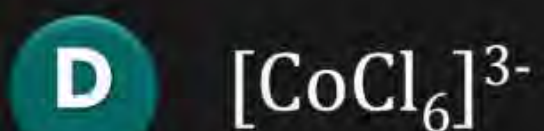
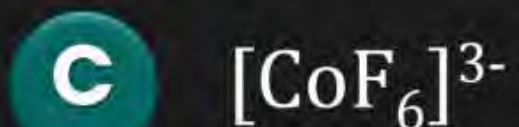
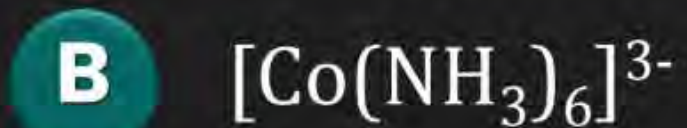
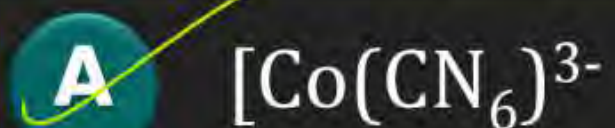
C (A) \rightarrow (iv), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (i)

D (A) \rightarrow (ii), (B) \rightarrow (i), (C) \rightarrow (ii), (D) \rightarrow (iv)

QUESTION



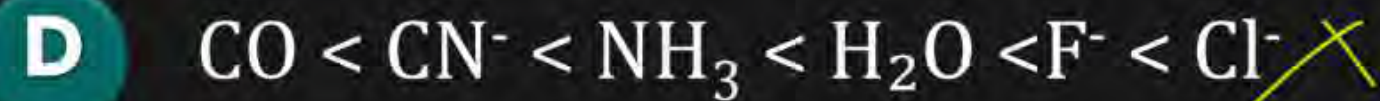
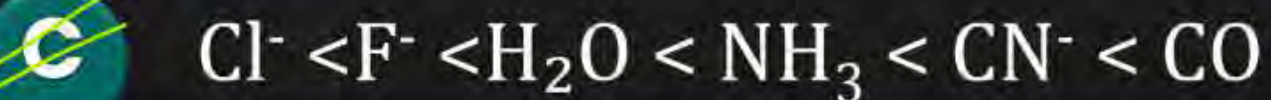
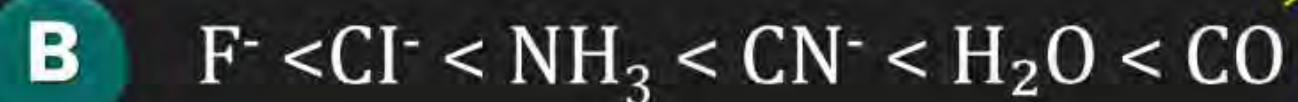
Which of the following complex has large value of Δ_0 ?



QUESTION



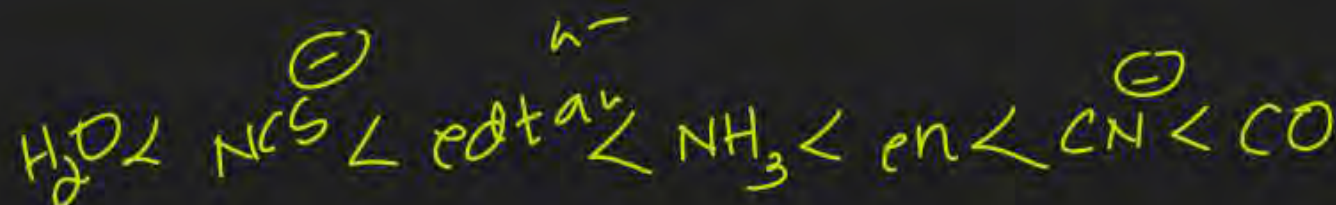
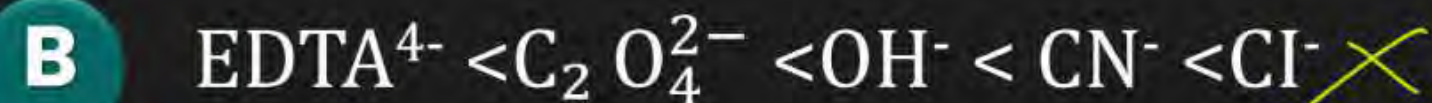
The increasing order of crystal field splitting strength of the given ligands is



QUESTION



Which of the following is the correct increasing order of strength in spectrochemical series of ligands?



QUESTION



λ of absorption



Arrange following complex ions in increasing order of crystal field splitting energy (Δ_0) $[\text{CrCl}_6]^{3-}$, $[\text{Cr}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$

- A** $[\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{CrCl}_6]^{3-} < [\text{Cr}(\text{CN})_6]^{3-}$
- B** $[\text{CrCl}_6]^{3-} < [\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{CN})_6]^{3-}$
 $[\text{CrCl}_6]^{3-} > [\text{Cr}(\text{NH}_3)_6]^{3+} > [\text{Cr}(\text{CN})_6]^{3-}$
strong ligand $\rightarrow \Delta_0 / E_{\text{max}}$
 λ order $E \downarrow \lambda \uparrow$
- C** $[\text{CrCl}_6]^{3-} < [\text{Cr}(\text{CN})_6]^{3-} < [\text{Cr}(\text{NH}_2)_6]^{+3}$
- D** $[\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{CN})_6]^{3-} < [\text{CrCl}_6]^{3-}$

Thank

You