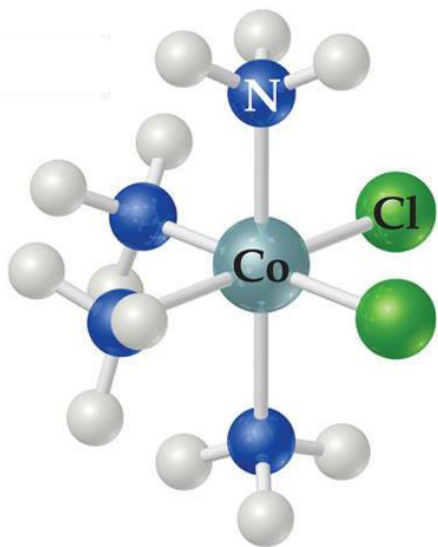


Coordination Compounds



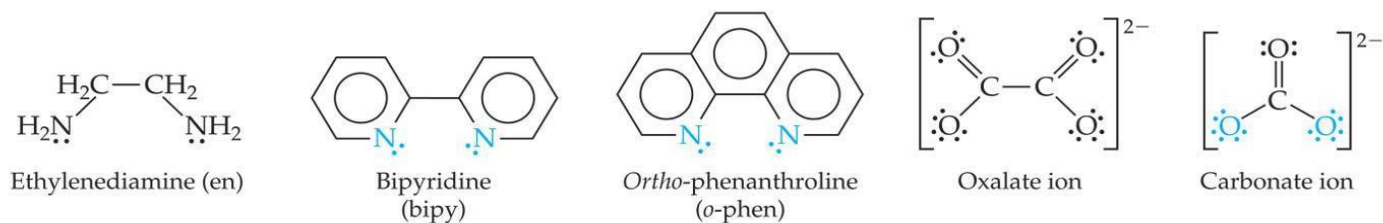
- **Coordination compounds** contain coordinate covalent bonds formed between metal ions with groups of anions or polar molecules.
- A central metal atom bonded to a group of molecules or ions is a **metal complex**.
- The molecules or ions coordinating to the metal are the **ligands**.
 - Metal ion – Lewis acid
 - Bonded groups – Lewis base
- Ligand must have **lone pairs** to interact with metal
- The ligand donates a lone pair of electrons to an empty orbital of the metal ion to form a coordinate covalent bond

Ligands

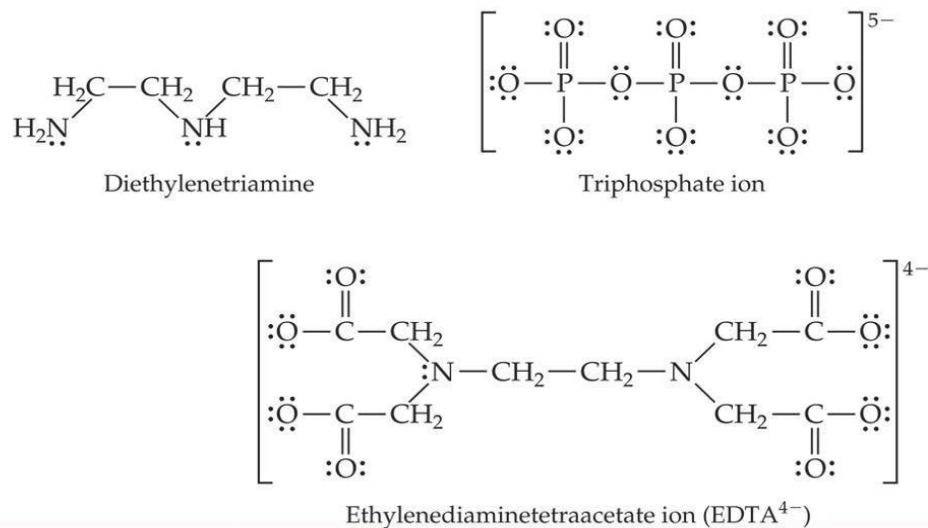
Ligand Type Examples

Monodentate	$\text{H}_2\ddot{\text{O}}:$ Water	$:\ddot{\text{F}}:^-$ Fluoride ion	$[:\text{C}\equiv\text{N}:]^-$ Cyanide ion	$[\ddot{\text{O}}-\text{H}]^-$ Hydroxide ion
	$:\text{NH}_3$ Ammonia	$:\ddot{\text{Cl}}:^-$ Chloride ion	$[\ddot{\text{S}}=\text{C}=\ddot{\text{N}}:]^-$ Thiocyanate ion [or]	$[\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:]^-$ Nitrite ion [or]

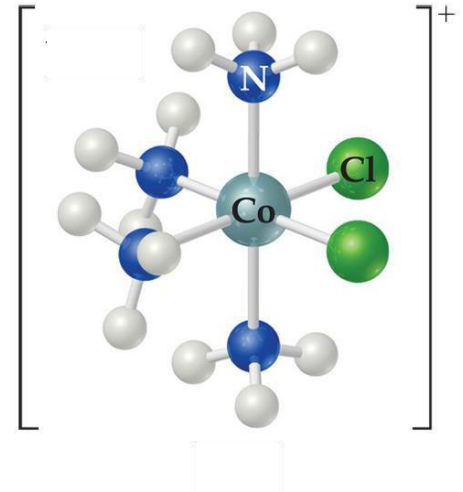
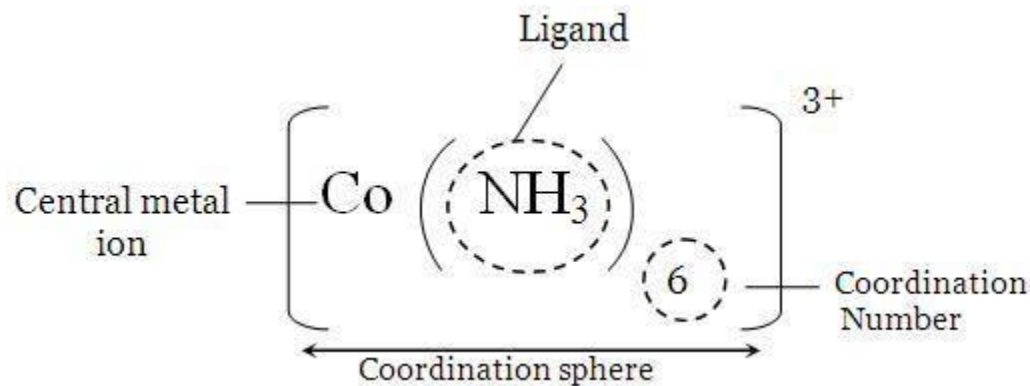
Bidentate



Polydentate



Werner's Theory



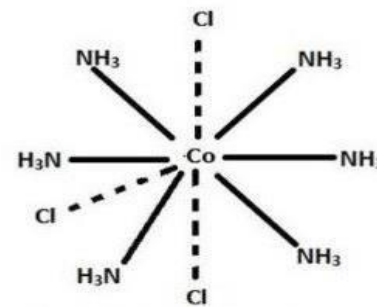
Suggested that metal ions have *primary* and *secondary* valences.

- **Primary valence** equal the metal's **oxidation number**
- **Secondary valence** is the number of atoms directly bonded to the metal (**coordination number**) and placed those molecules and ions within the sphere in brackets
- “free” anions (that dissociate from the complex ion) outside the bracket

Many coordination compounds are having same metal, same ligands

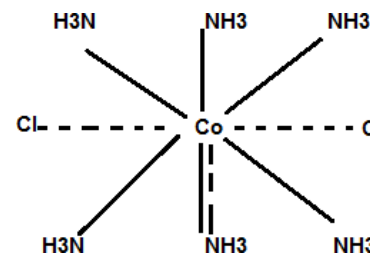
Compound 1: $\text{CoCl}_3 \cdot 6\text{NH}_3 = [\text{Co}(\text{NH}_3)_6](\text{Cl})_3$
 Cl^- is not in coordination sphere
 3 free Cl^- ions, $[\text{Co}(\text{NH}_3)_6]^{3+}$

Orange colour



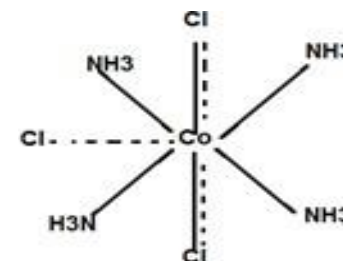
Compound 2: $\text{CoCl}_3 \cdot 5\text{NH}_3 = [\text{Co}(\text{NH}_3)_5\text{Cl}](\text{Cl})_2$
 2 free Cl^- ions, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

Purple colour

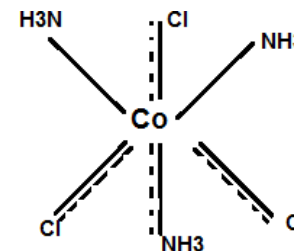


Compound 3: $\text{CoCl}_3 \cdot 4\text{NH}_3 = [\text{Co}(\text{NH}_3)_4\text{Cl}_2](\text{Cl})$
 1 free Cl^- ion, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{1+}$

Green Colour



Compound 4: $\text{CoCl}_3 \cdot 3\text{NH}_3 = [\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
 No free Cl^- ions



Effective atomic number (EAN) Rule :

The sum of the electrons on the central atom (Lewis acid) including those donated from the ligands (Lewis base) should be equal to the number of electrons on a noble gas element found in the same period in which the metal is situated.

Let us take the case $[\text{Co}(\text{NH}_3)_6]^{3+}$

Oxidation state of Co in $[\text{Co}(\text{NH}_3)_6]^{3+} = +3$

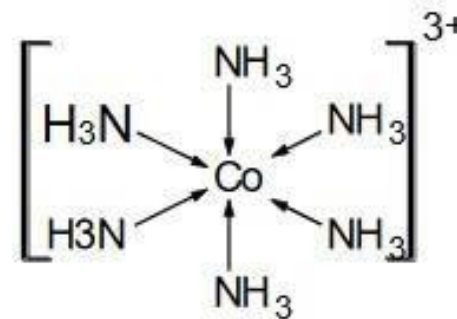
No. of electrons in Cobalt = 27

\therefore No. of electrons in Co(III) of the complex = $27 - 3 = 24$

Number of electrons donated by six NH_3 ligands = $6 \times 2 = 12$

\therefore EAN of Co(III) in $[\text{Co}(\text{NH}_3)_6]^{3+} = 24 + 12 = 36$ Noble gas (Kr),

$\therefore [\text{Co}(\text{NH}_3)_6]^{3+}$ follows the EAN rule

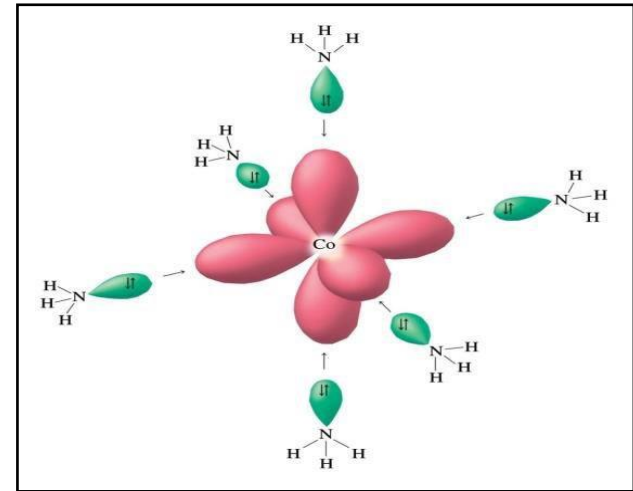
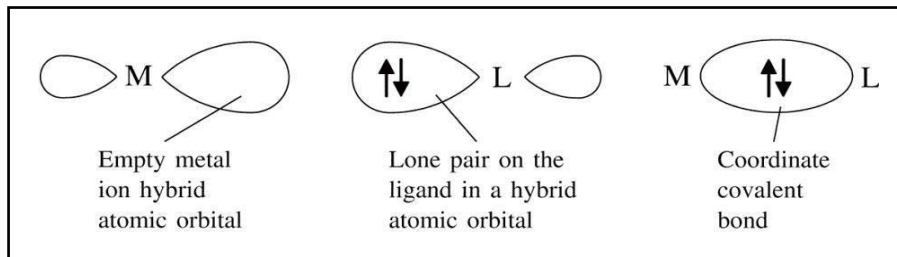


Drawbacks:

1. The donation of electron pairs to central metal ion produce an improper accumulation of negative charge on this ion. Such condition is not fair.
2. Some complexes i.e., Ni(II), Co(II) are not follow the EAN rule, even then they are stable
3. Metals are electro positive in nature, then how they many accept electrons from ligands-not explained?

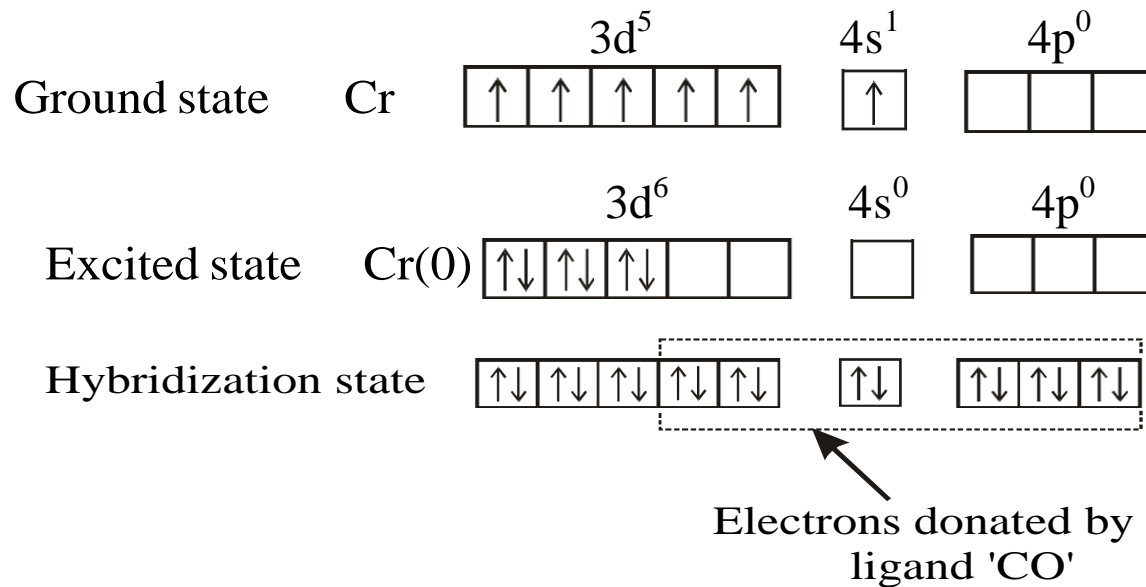
Valence Bond Theory

1. **Valence Bond Theory** predicts Atomic orbitals undergo hybridization and form new hybrid orbitals
2. Then, hybrid orbitals (filled ligand orbitals) overlap with vacant orbitals of metal and form chemical bond



Hybridization & geometry of the Complex

CN	Geometry	Hybridorbitals	Example
2	Linear	sp	$[\text{Ag}(\text{NH}_3)_2]^+$
4	Tetrahedral	sp^3	$[\text{CoCl}_4]^{2-}$
4	Squareplaner	dsp^3	$[\text{Ni}(\text{CN})_4]^{2-}$
6	Octahedral	d^2sp^3 or sp^3d^2	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$



d^2sp^3 hybridization = octahedral geometry

Drawbacks-VBT

1. Why in some complexes the electrons must be rearranged against Hund's Rule?-not explained
2. Existence of inner and outer orbitals-not explained
3. In some complexes, transfer of electron from lower energy level to higher energy level taken place, even in absence of energy supplier
ex: $[\text{Cu}(\text{NH}_3)_4]^{2+}$

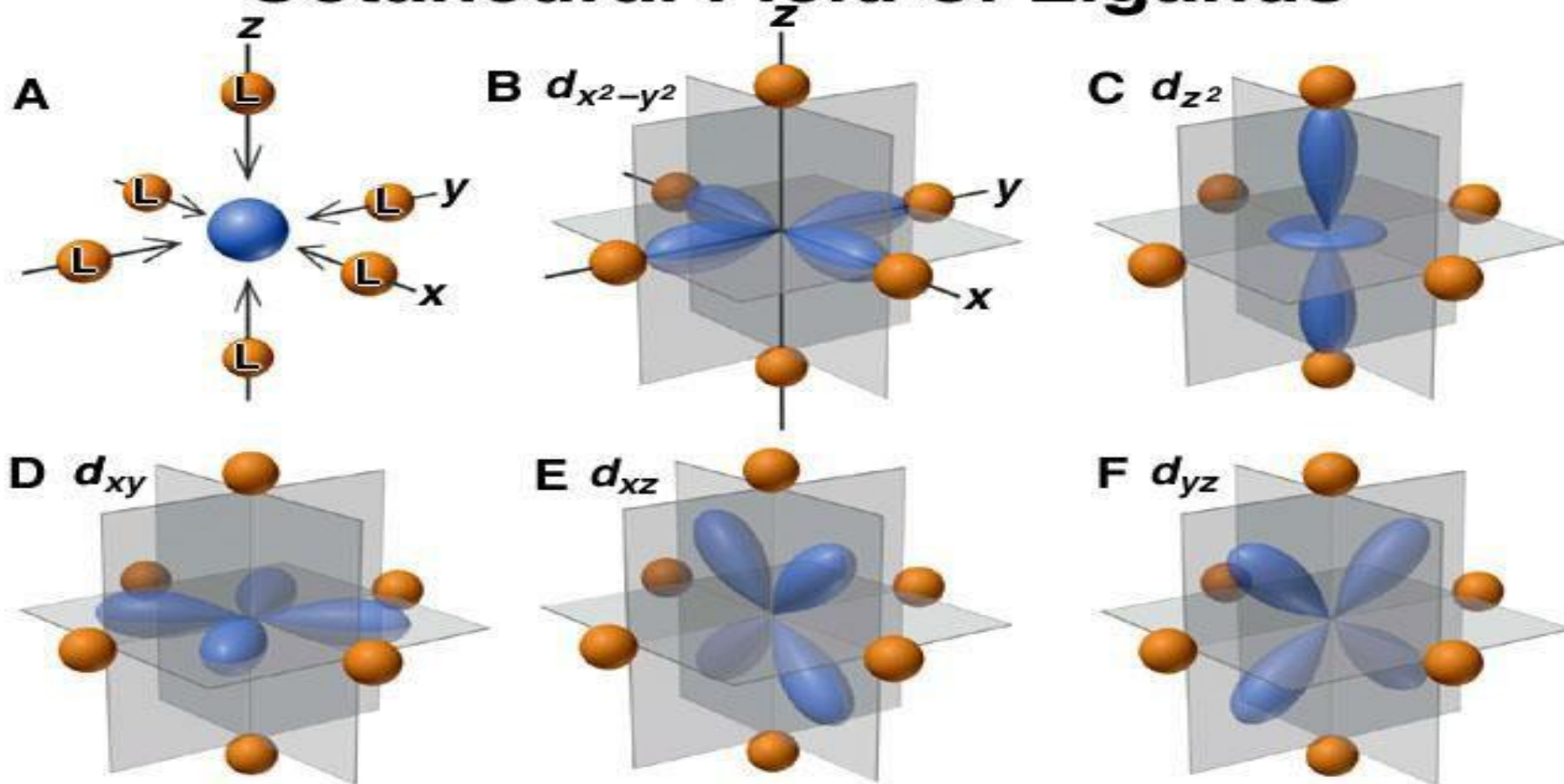
Crystal Field Theory

- Focuses on the effect of ligands on the energies of the d orbitals of metals.
- Assumptions
 1. Ligands are negative point charges.
 2. Metal–ligand bonding is 100% ionic:
 - strong-field (low–spin): large splitting of d orbitals
 - weak-field (high–spin): small splitting of d orbitals
 3. Crystal field theory explains the bonding in complex ions purely in terms of electrostatic forces.
 4. Attraction between the metal ion (atom) and the ligands
 5. Repulsion between the lone pairs on the ligands and the electrons in the d orbitals of the metal
 6. In the absence of ligands, the d orbitals are degenerate
 7. In the presence of ligands, electrons in d orbitals experience different levels of repulsion for the ligand lone pairs
 8. As a result (Depending on the geometry) some d orbitals attain higher energy and others lower energy

Octahedral Complexes

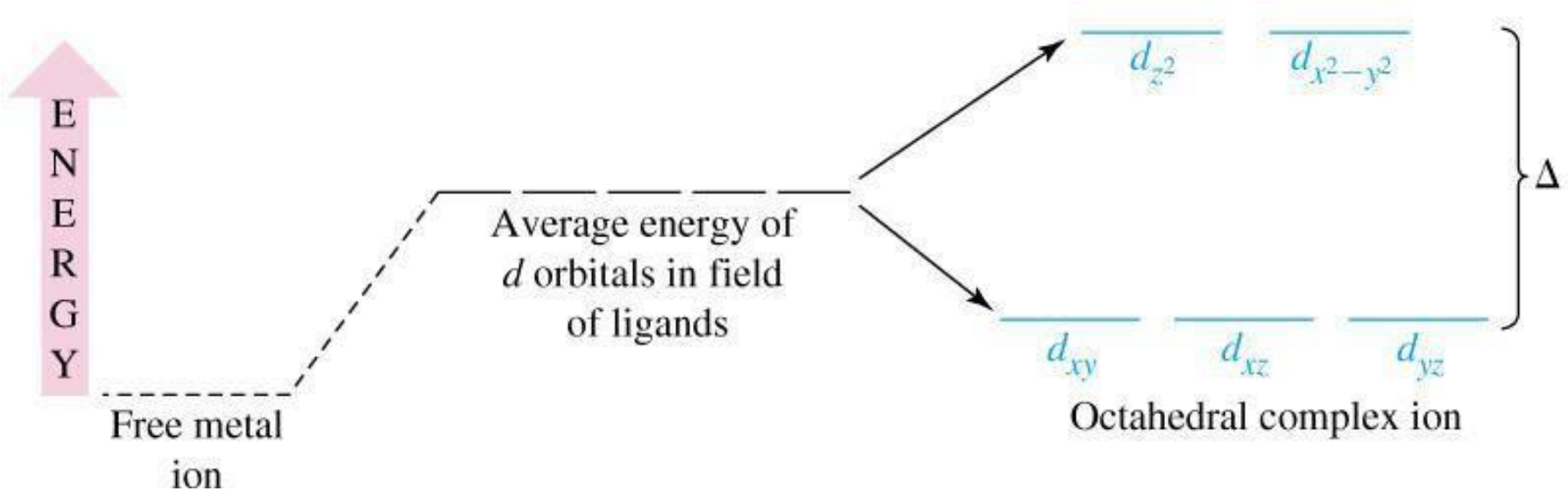
- d_{z^2} and $d_{x^2-y^2}$ orbitals have maximum electron density along the axis and point-charge ligands also approaching central metal ion in same direction –
- Hence, these d-orbitals experience stronger repulsions and increase in energy
- d_{xz} , d_{yz} , and d_{xy} orbitals lobes are in between the axes and point charge ligands are approaching central metal ion in same direction along the axis- These orbitals experience less repulsions and decrease in energy
- The orbitals d_{xz} , d_{yz} , and d_{xy} are at a lower energy in the octahedral complex than are the d_{z^2} and $d_{x^2-y^2}$ orbitals

***d* Orbitals in an Octahedral Field of Ligands**



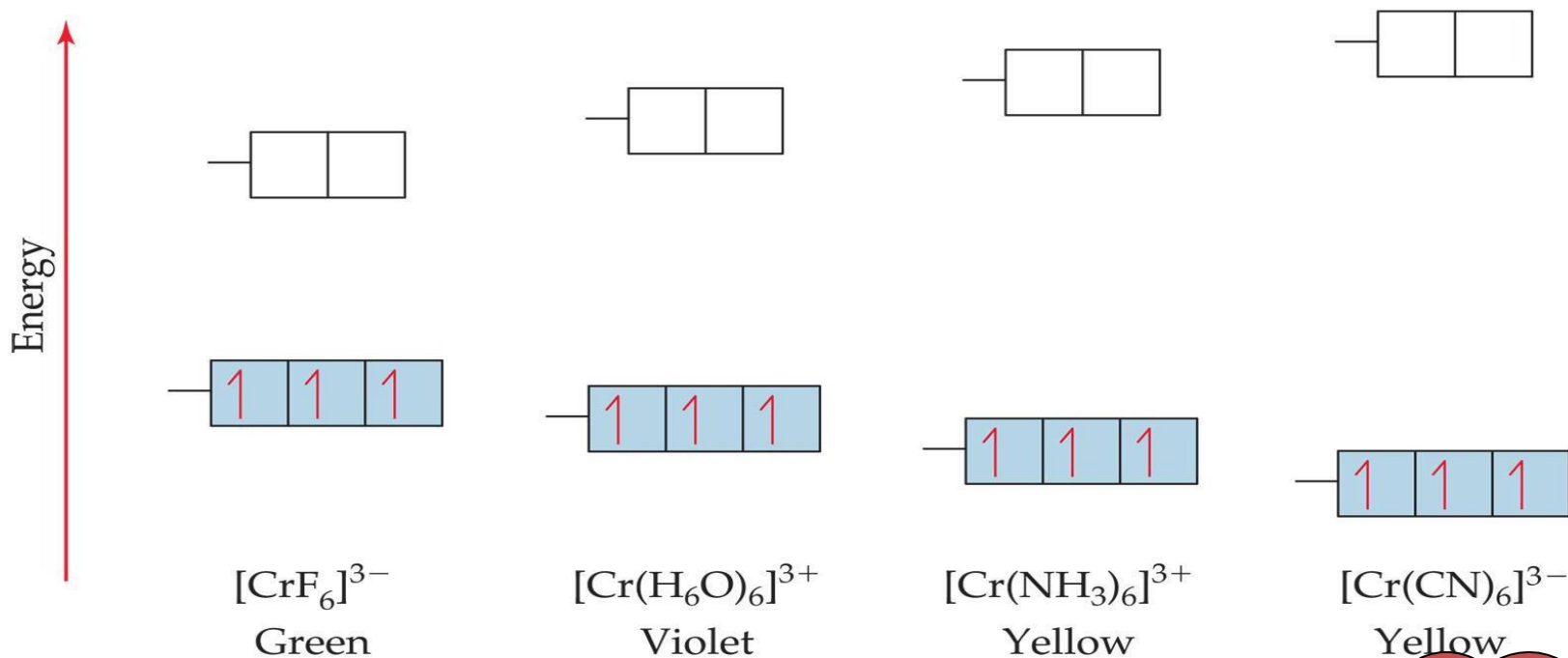
The ligands are between the lobes of d_{xy} , d_{yz} and d_{zx} orbitals. Hence, they interact less strongly

Now, think of point charges being attracted to metal nucleus Positive charge. What about electrons in d orbitals?



- ✓ Energy difference between the two sets is equal to Δ_o .
- ✓ The t_{2g} set is lowered by $0.4 \Delta_o$ and the e_g set is raised by $0.6 \Delta_o$.

Splitting of d orbitals in an octahedral ligand field



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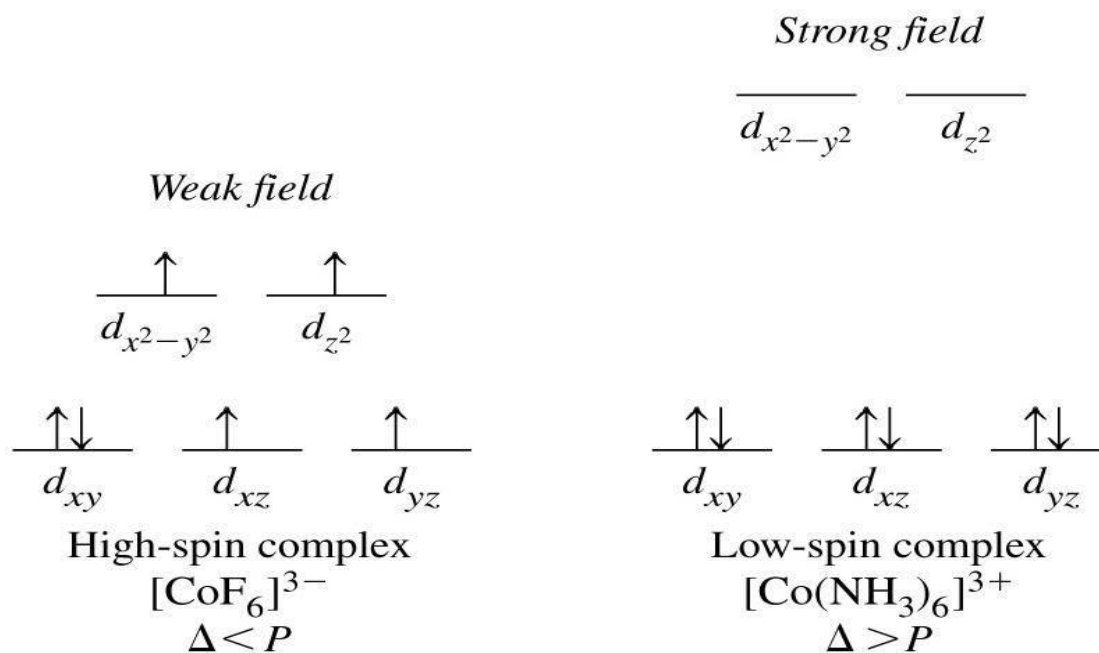
*Large Δ
Strong field
ligands*

Spectrochemical Series



Weak and Strong Field Ligands

d⁶ - Complexes



Limitations of CFT

- As ligands are assumed to be point charges, it is expected that the ionic ligand should have a greater splitting effect. However, they are actually found to be at the lower end of the spectrochemical series.
- According to CFT, metal–ligand bonding is purely electrostatic. Which is not so true.
- CFT takes only d-orbitals of the central atom into account. The s and p orbitals are not considered for study.
- Though OH^- in the spectrochemical series lies below H_2O and NH_3 , yet it produces a greater splitting effect.
- CFT gave no information about π bond formation in ligands.

Essay Questions:

1. . Explain the Geometry and Magnetic Properties of the following Complex compounds based on valence Bond theory
a) $[\text{Co}(\text{NH}_3)_6]^{+3}$ b) $[\text{Fe}(\text{CN})_6]^{+3}$ c) $[\text{Fe}(\text{CN})_6]^{3-}$ d) $[\text{Cr}(\text{NH}_3)_6]^{+3}$ e) $[\text{Fe}(\text{CN})_6]^{4-}$
f) $[\text{Zn}(\text{NH}_3)_6]^{+2}$ g) $[\text{Ni}(\text{CO})_4]$ h) $[\text{Cu}(\text{NH}_3)_4]^{+2}$ i) $[\text{Ni}(\text{CN})_4]^{2-}$ j) $[\text{CoF}_6]^{3-}$
2. Discuss the salient features of crystal field theory. Explain the Crystal field splitting of d- orbitals in Octahedral, Tetrahedral and Square planar complexes.
3. Describe the geometrical isomerism in compounds with coordination number 4 & 6
4. Explain the different types of Structural isomerism exhibited by complexes with examples.

Short Answer Questions:

5. Explain Werner theory of complex compounds.
6. Effective atomic number (EAN)
7. Explain High spin and Low spin complexes with examples.
8. What is a chelating? Give two examples.
9. What is meant by crystal field stabilization energy.
10. Explain the electronic absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion