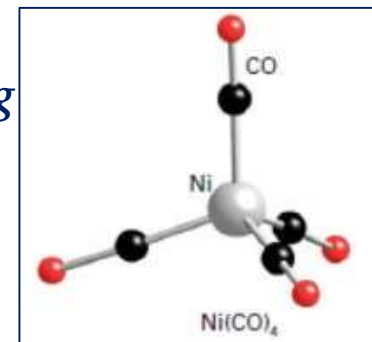


Coordination Chemistry

A co-ordinate bond is a type of covalent bond with a shared pair of e^- s where both e^- s come from the same atom. Coordination compounds are molecules that possess a metal centre bound to ligands (atoms, ions, or molecules that donate electrons to the metal). It may be a neutral complex or an ionic compound in which at least one of the ions is a complex. E.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$. The geometry, bond distances and angles of coordination compounds are determined by X-ray diffraction, vibrational and electronic spectroscopy and nuclear magnetic resonance.

A complex is a combination of one Lewis acid (the central metal atom) with a one or more Lewis bases [ligand(s)]. Complexes may be:

1. Inner-sphere complex: the ligands attach directly to the central metal ion forming the primary coordination sphere of the complex and their number is called the coordination number (CN) of the central metal atom. E.g. $\text{Ni}(\text{CO})_4$



2. Outer-sphere complex: when cation and anion associate electrostatically in solution without displacement of the ligands already present. E.g. $\{[\text{Mn}(\text{OH}_2)_6]_2\text{SO}_4^{-2}\}$

This happens when the the equilibrium concentration of the outer-sphere complex $\{[\text{Mn}(\text{OH}_2)_6]_2\text{SO}_4^{-2}\}$, exceeds that of the inner-sphere complex $[\text{Mn}(\text{OH}_2)_5\text{SO}_4^{-2}]$ in which the ligand SO_4^{-2} is directly attached to the metal ion.

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Double salts :

These are addition compounds in which individual constituents retain their identity.

Example : Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)

Mohr's Salt ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$)

Complex salts:

These are addition compounds in which individual constituents lose their identity in solid as well as liquid state.

Example: $\text{K}_4[\text{Fe}(\text{CN})_6]$

Double Salts	Complex Compound
➤ They usually contain two simple salts in equimolar proportions.	➤ The simple salts from which they are formed may or may not be in equimolar proportions.
➤ They exist only in the solid state. In aqueous solution, they dissociate completely into ions.	➤ They exist in the solid state as well as in aqueous solutions. This is because even in the solution, the complex ion does not dissociate into ions.
➤ They are ionic compounds and do not contain any coordinate bond.	➤ They may or may not be ionic but the complex part is always contains coordinate bonds.
➤ The properties of the double salt are the same as those of its constituent compounds.	➤ The properties of the coordination compound are the different from its constituents.
➤ In the double salts, the metal ions show their normal valency.	➤ In a coordination compound, the metal ions satisfy its 2 types of valencies called primary and secondary valencies.
➤ A double salt loses its identity in the solution.	➤ A coordination compound retains its identity in its solution.

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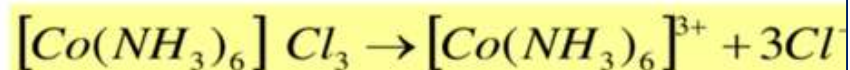
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Werner in 1898 propounded his theory of coordination compounds. The main postulates are :

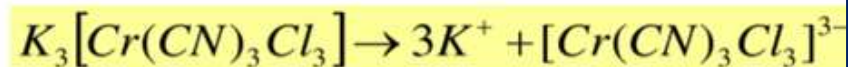
- In coordination compounds metals shows two types of linkages (valences) – primary and secondary.
- The primary valences are normally ionisable and are satisfied by negative ions.
- The secondary valences are non – ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
- The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

Coordination compounds are complex or contain complex ions, for example:

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



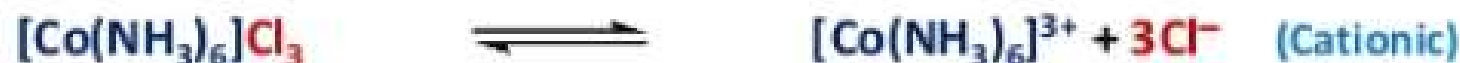
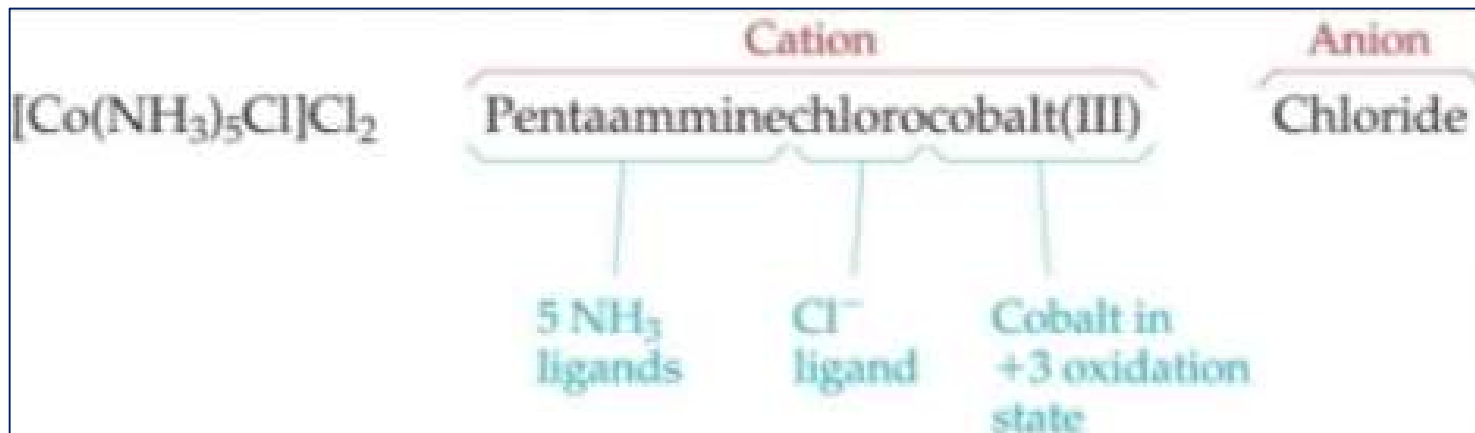
• **Complex Anion:** $[\text{CoCl}_4(\text{NH}_3)_2]^{-1}$



• **Neutral Complex:** $[\text{CoCl}_3(\text{NH}_3)_3]^0$

• **Coordination Compound:** $\text{K}_4[\text{Fe}(\text{CN})_6]$

Nomenclature of Coordination Compounds



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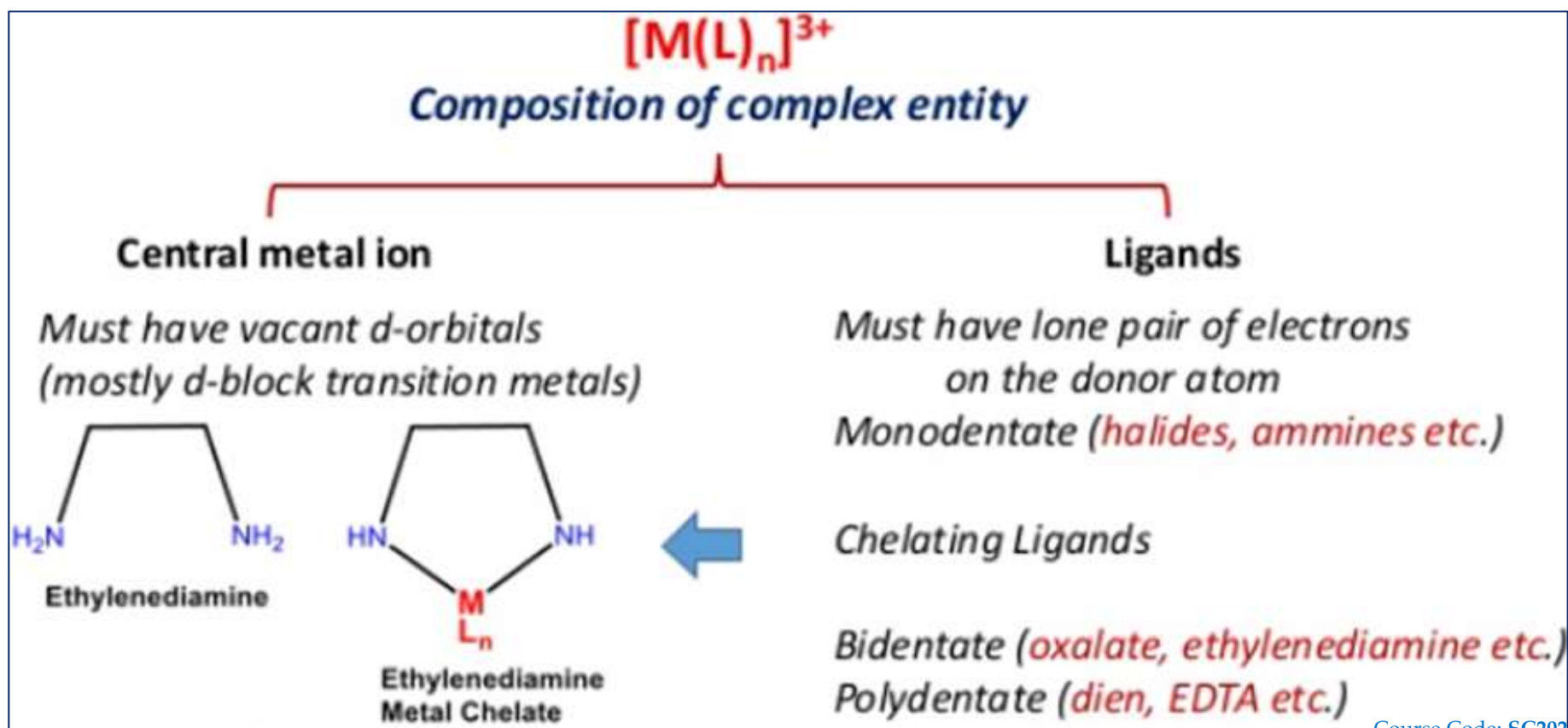
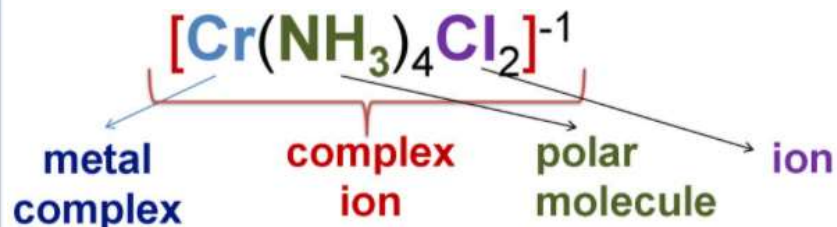
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A central metal atom bonded to a group of polar molecules or ions is a **metal complex**.

If the complex bears a charge, it is a **complex ion**.

Compounds containing complexes are **coordination compounds**.



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A ligand is an ion or molecule that can exist independently. E.g. NH_3 in $[\text{Co}(\text{NH}_3)_6]^{+3}$. Ligands are classified as monodentate (single point of attachment to the metal), bidentate (two points of attachment), tridentate, polydentate etc. Ambidentate ligands have more than one different potential donor atom. E.g. (NCS), which can attach to a metal atom either by the N atom, to give thiocyanato- κN complexes, or by the S atom, to give thiocyanato- κS complexes.

The prefixes used for naming ligands are

Mono-	1	Hepta	7
Di, bis	2	Octa	8
Tri, tris-	3	Nona	9
Tetra, tetrakis	4	Deca	10
Penta	5	Undeca	11
Hexa	6	Dodeca	12

Formula and Names of Some Ligands

H_2O	aqua	NH_3	ammine
CO	carbonyl	NO	nitrosyl
OH^-	hydroxo	O^{2-}	oxo
F^-	fluoro	Cl^-	chloro
Br^-	bromo	I^-	iodo
$-\text{CN}^-$	cyano	$-\text{NC}^-$	isocyano
$-\text{NCS}^-$	isothiocyanato	$-\text{SCN}^-$	thiocyanato
SO_4^{2-}	sulfato	NO_3^-	nitrate
$-\text{NO}_2^-$	nitro	$-\text{ONO}^-$	nitrito
CO_3^{2-}	carbonato		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	ethylenediamine		

The ligand names are followed by the name of the metal with either its oxidation number or overall charge in parentheses, as in hexaamminecobalt(III) for $[\text{Co}(\text{NH}_3)_6]^{3+}$, tris(ethylenediamine)cobalt(II) as in $[\text{Co}(\text{en})_3]^{2+}$, etc.




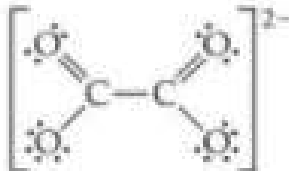
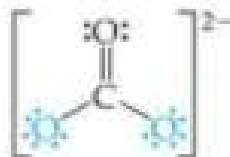

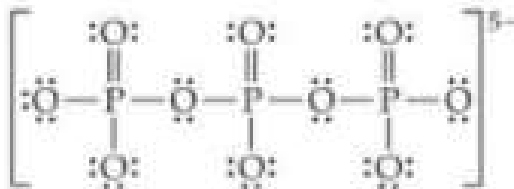
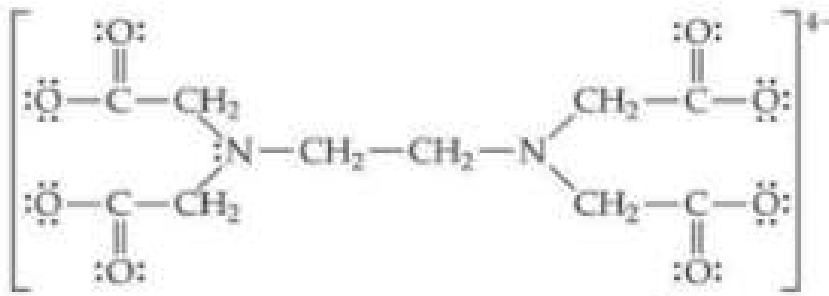
Homoleptic complexes are the complexes in which central metal ion or atom is bound to only one type of donor groups. e.g: $\text{K}_4[\text{Fe}(\text{CN})_6]$

Heteroleptic complexes are the complexes in which central metal ion or atom is bound to more than one type of donor groups. e.g: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

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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	 Ethylenediamine (en)	 Bipyridine (bipy)	 Ortho-phenanthroline (o-phen)	 Oxalate ion	 Carbonate ion
Polydentate	 Diethylenetriamine	 Triphosphate ion			
	 Ethylenediaminetetraacetate ion (EDTA^{4-})				

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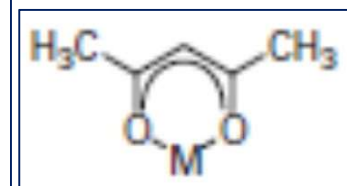
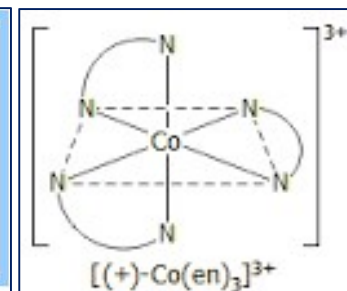
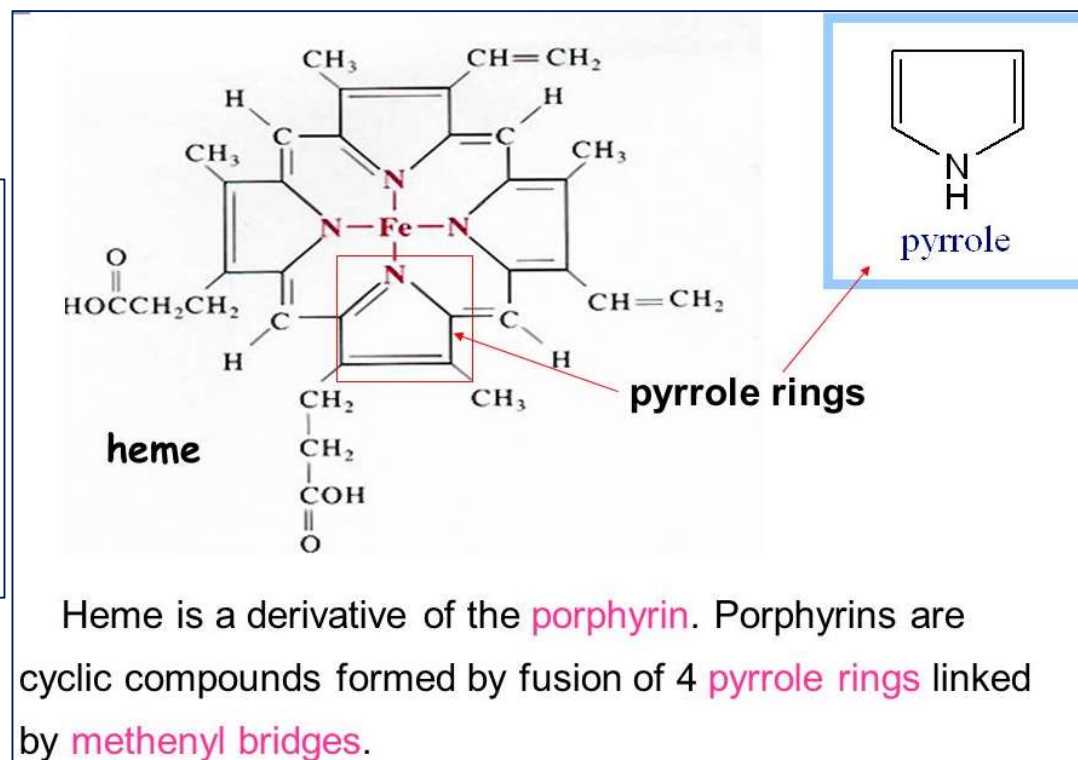
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A chelate is a complex in which a polydentate ligand forms a ring including the metal atom. Chelate effect is additional stability of complexes of chelating ligands over those of non-chelating ligands. The bite angle/ (L-M-L angle) in the chelate ring dictates the degree of strain in a chelating ligand.



A chelate formed from a saturated organic ligand, like ethylenediamine $[H_2N-CH_2-CH_2-NH_2](en)$, a five membered ring can fold into a conformation preserving the tetrahedral angles within the ligand and yet achieving an L-M-L angle of 90° , as in octahedral complexes. Six-membered rings are sterically favored by electron delocalization through their π orbitals. The bidentate β -diketones, coordinate as the anions of their enols in six-membered ring structures.

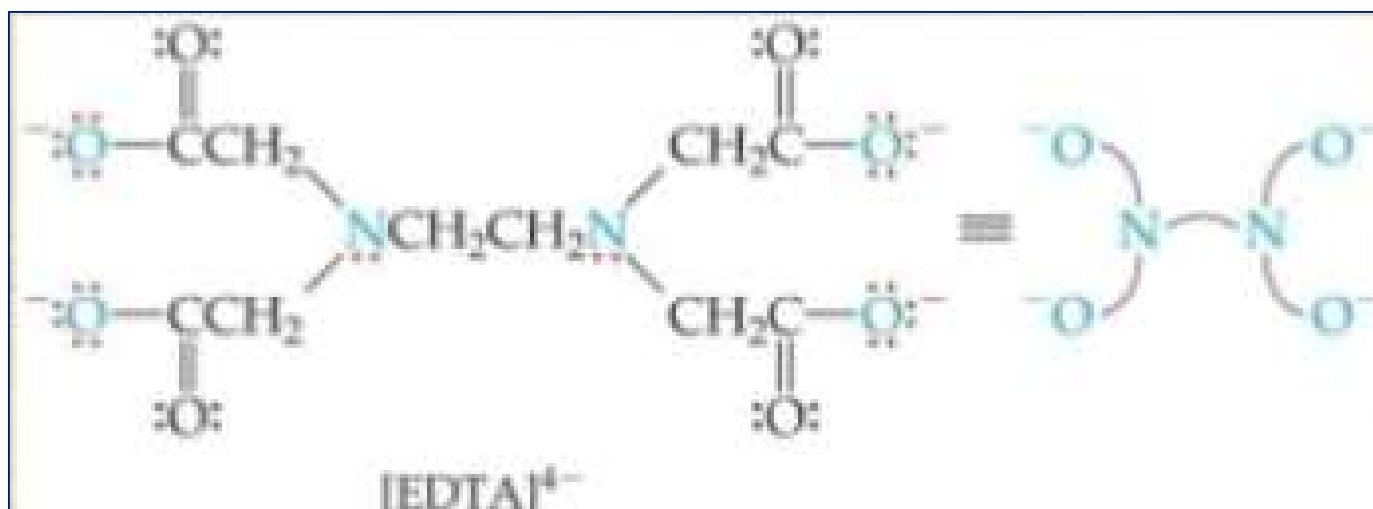
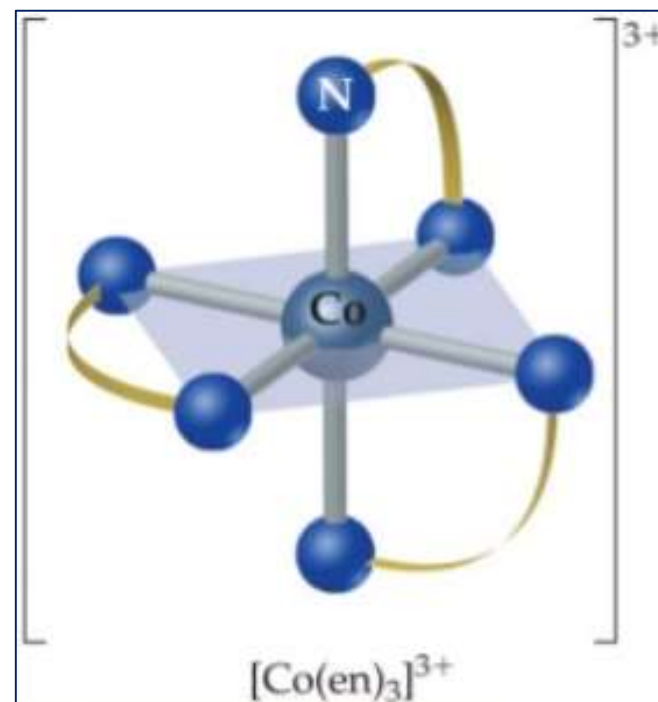
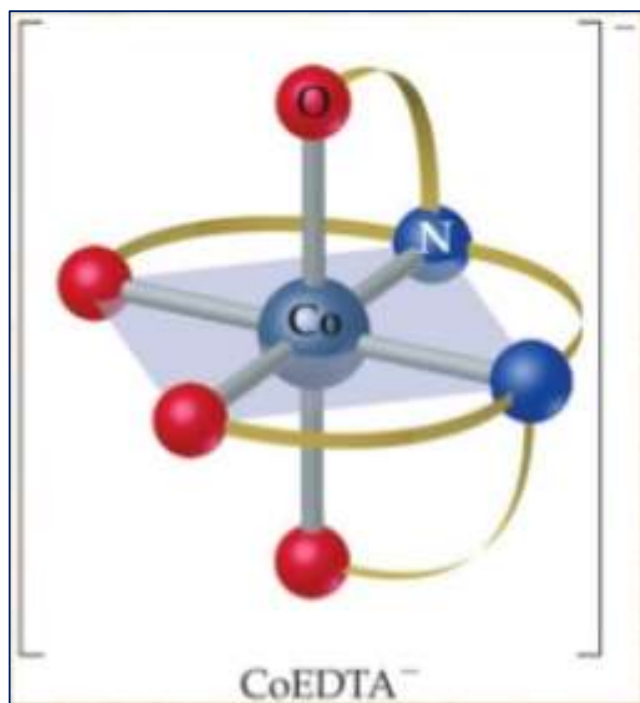
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In a complex, cations are named first and ligands are named in alphabetical order, as in hexaamminecobalt (III) or hexaamminecobalt (+3) for $[\text{Co}(\text{NH}_3)_6]^{+3}$. The number of a ligand in a complex is denoted by the prefixes mono-, di-, tri-, and tetra-. Ligands that bridge two metal centres are assigned a prefix μ (mu) before the name of the ligand, like μ -oxido-bis(pentamminecobalt(III)) ($[(\text{H}_3\text{N})_5\text{CoOCo}(\text{NH}_3)_5]^{4+}$, and if the number of bridging centres is more than two, a subscript is used: μ_3 -H indicates a hydride ligand bridging three metal atoms.

The coordination number of a complex depends on the following factors:

- 1. Size of the central atom or ion.*
- 2. Steric interactions between ligands.*
- 3. Electronic interactions between the central atom/ ion and ligands.*

Sometimes, solvent molecules and potential ligands may fill up spaces within the structure without having any direct bonds to the metal ion. These are called solvent of crystallization.

e.g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \equiv [\text{Co}(\text{Cl})_2(\text{OH}_2)_4] + 2\text{H}_2\text{O}$ (uncoordinated)

Coordination number	Type of hybridisation	Structure
4	sp^3	tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	$sp^3 d^2$ (nd orbitals are involved – outer orbitals complex)	Octahedral
6	d^2sp^3 ((n-1) d orbitals are involved –inner orbital)	octahedral

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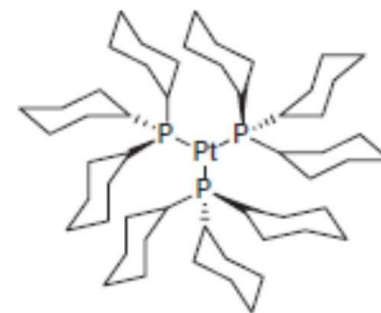
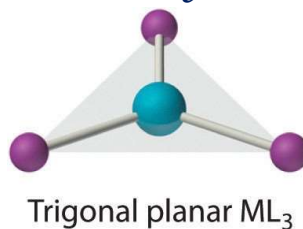
Numbers of coordination:

Two-coordination: Group 11 ions form linear two-coordinate complexes with two identical symmetric ligands.

E.g. complexes of Cu^+ , Ag^+ , Au^+ . Au(I) forms linear complexes of formula LAuX , L: Lewis base like substituted phosphine, R_3P , or thioether, R_2S , X: Halogen; Me-Hg-Me CuCN exists as linear Cu-CN-Cu-CN chains in which the coordination number of copper is 2. Two symmetric ligands have $D_{\infty h}$ symmetry.

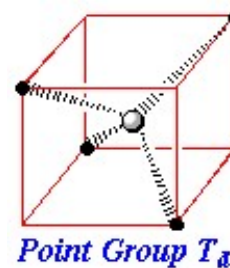
Three-coordination: complexes are rare in metals, but found with bulky ligands such as tricyclohexylphosphine, as in $[\text{Pt}(\text{PCy}_3)_3]$, Cy: cyclohexyl, with trigonal arrangement of the ligand, also $\text{K}[\text{Cu}(\text{CN})_2]$ in the solid state.

Complexes of this type have the formula MX_3 . Three-coordinate complexes with three identical symmetric ligands normally have D_{3h} symmetry.

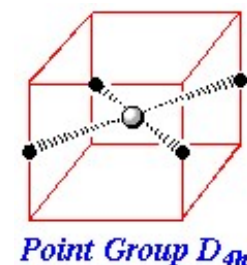
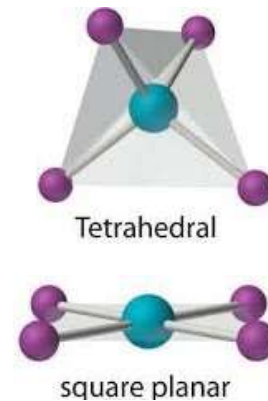


Four-coordination: is very common. Such complexes may be tetrahedral or square-planar. Complexes of this type have the formula MX_2L_2 .

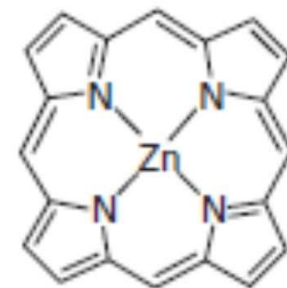
Tetrahedral complexes is favoured over higher coordinate complexes if the central atom is small or the ligands large. (Cl^- , Br^- and I^-), having T_d symmetry.



Metals with d^8 configurations belonging to the 4d- and 5d-series such as Rh, Ir, Pd^{+2} , Pt^{+2} , and Au^{+3} , prefer square-planar complexes., having D_{4h} symmetry.



Square-planar geometry can be achieved by complexation of a central atom with a ligand that contains a rigid ring of four donor atoms, as in a porphyrin complex.



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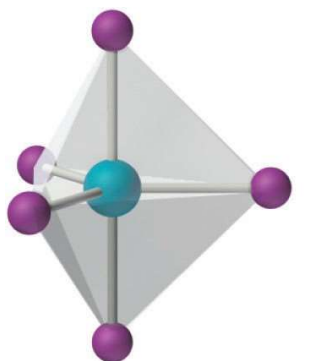
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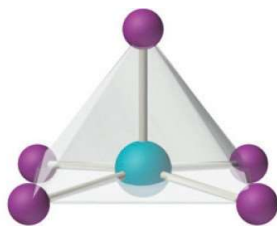
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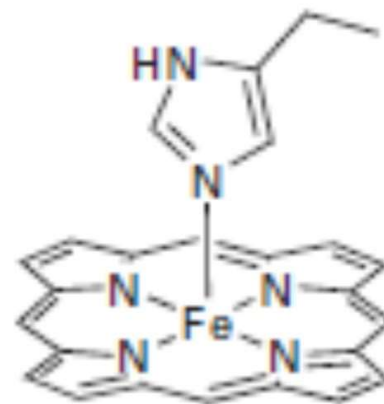
Five-coordinate: complexes are normally either square pyramidal or trigonal bipyramidal. A square-pyramidal complex would have C_{4v} symmetry if all the ligands were identical and the trigonal bipyramidal complex would have D_{3h} symmetry with identical ligands. A trigonal-bipyramidal shape minimizes ligand-ligand repulsions, but steric constraints on ligands that can bond through more than one site to a metal atom can favour a square-pyramidal structure. E.g. the biologically important porphyrins like the active centre of myoglobin below, have square-pyramidal geometry, where the ligand ring enforces a square-planar structure and a fifth ligand attaches above the plane.



Trigonal bipyramidal



square pyramidal



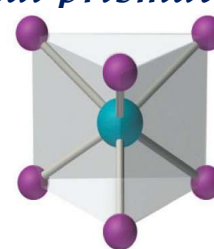
Six-coordination: is the most common arrangement found in s-, p-, d-, and f-metal coordination compounds. Geometry is octahedral or shapes that are small distortions of octahedral.

For the d^9 configuration (Cu^{+2} complexes), a tetragonal distortion may occur due to an inherent effect known as Jahn Teller distortion.

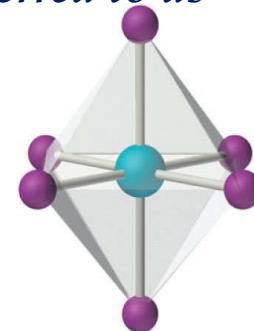
This theorem states that "any non-linear molecular system possessing degenerate electronic states will be unstable and undergo distortion to form a system of lower symmetry and lower energy and thus will remove degeneracy".

Rhombic (D_{2h}) distortions, in which a trans pair of ligands are close in and another trans pair are further out, can occur. Trigonal (D_{3d}) distortions occur when two opposite faces of the octahedron move away & are intermediate between regular octahedral and trigonal prismatic also referred to as rhombohedral.

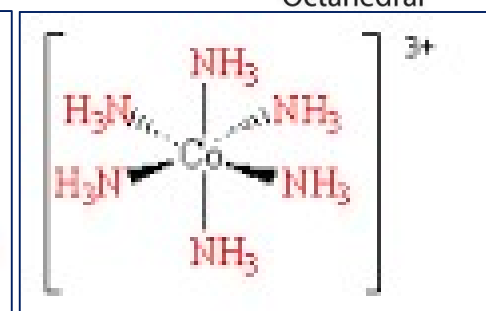
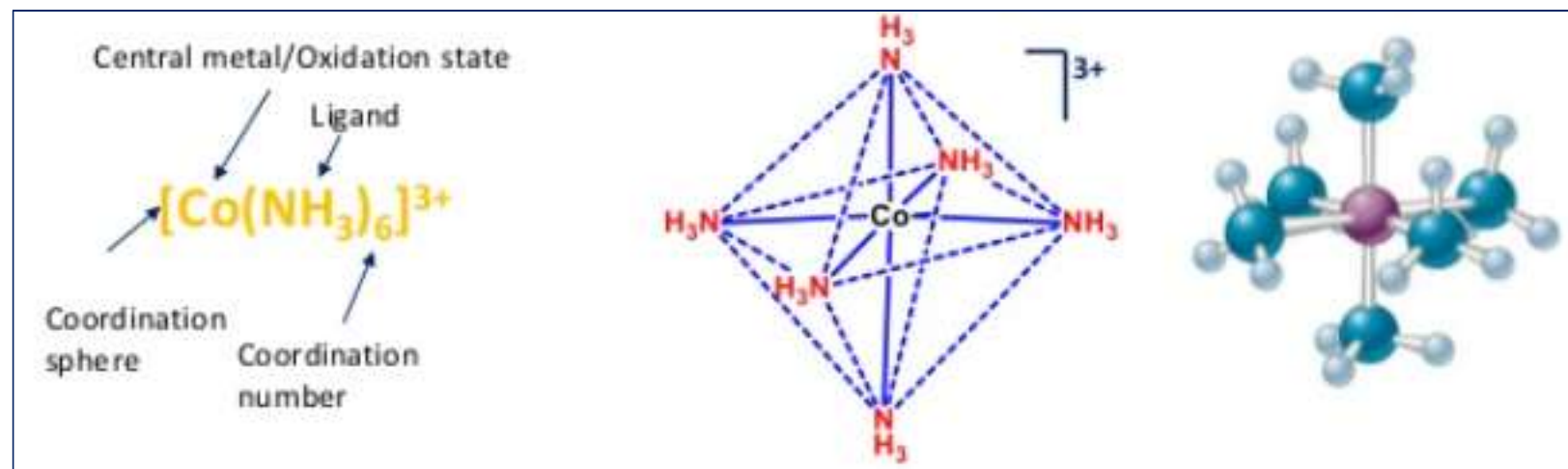
e.g. $\text{Co}(\text{NH}_3)_6$ and trigonal prismatic MoS_2 and WS_2



trigonal prismatic



Octahedral



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Higher coordination numbers:

3d, 4d and 5d complexes, where the larger central atom can accommodate more than six ligands exhibit seven- coordination, where geometries include the pentagonal bipyramid, capped octahedron, and a capped trigonal prism.

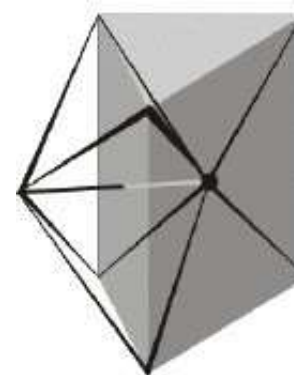
E.g. $[\text{ZrF}_7]^{-3}$, $[\text{ReCl}_6\text{O}]^{-2}$



Pentagonal-bipyramidal complex, D_{5h}



Capped octahedral complex



Capped trigonal prism

Eight-coordination complexes may be square antiprismatic in one crystal but dodecahedral in another.

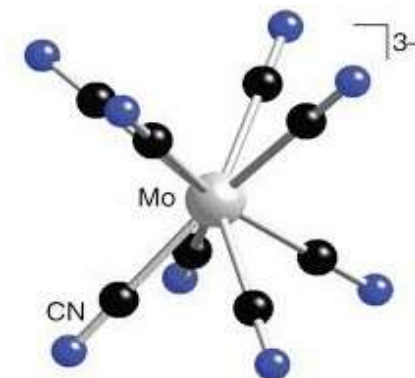
E.g. $[\text{Mo}(\text{CN})_8]^{-3}$ with D_4 symmetry.



Square antiprism



Dodecahedron;
triangulated decahedron



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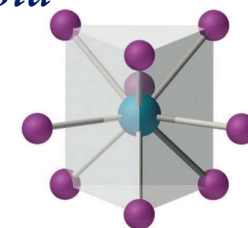
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Nine-coordination is important in the structures of f-block elements e.g. lanthanoid complex $[\text{Nd}(\text{OH}_2)_9]_3^+$. It shows a geometry of tricapped trigonal prism.

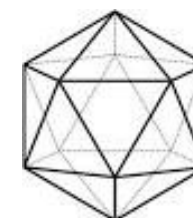
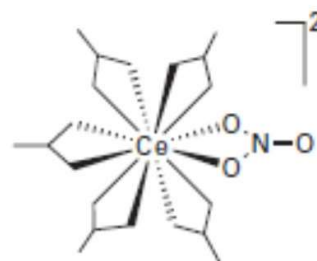


Tricapped trigonal prismatic

Ten- and twelve-coordination are encountered in complexes of the f-block M^{+3} ions. E.g. ten-coordinate complex is $[\text{Th}(\text{ox})_4(\text{OH}_2)_2]^{4-}$, [ox: $^-\text{OOC}-\text{COO}-$]. It shows a geometry of bicapped square antiprism. Example of 12-coordinate complex is f-block metal complex $[\text{Ce}(\text{NO}_3)_6]^{2-}$ (geometry is icosahedron).



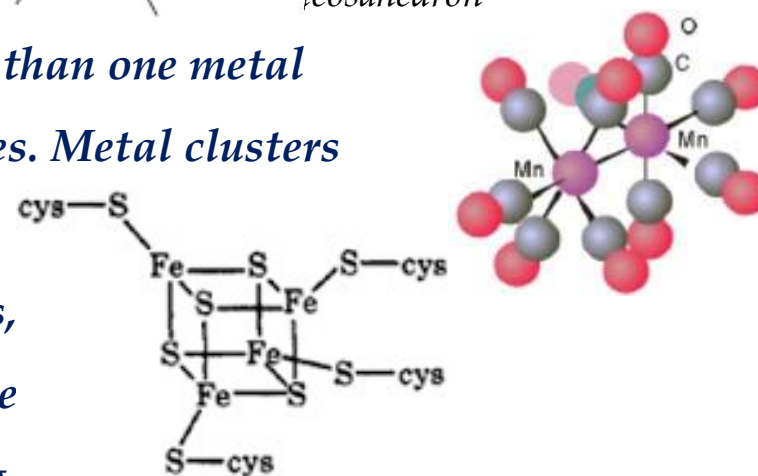
bicapped square antiprism



icosahedron

Polymetallic complexes: are complexes that contain more than one metal atom. They are classified as metal clusters or cage complexes. Metal clusters contain M-M bonds. E.g. $[(\text{CO})_5\text{MnMn}(\text{CO})_5]$

When metal-metal bond is absent in polymetallic complexes, they are referred to as cage complexes or compounds. Cage complexes contain ligand-bridged metal atoms. E.g. $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$



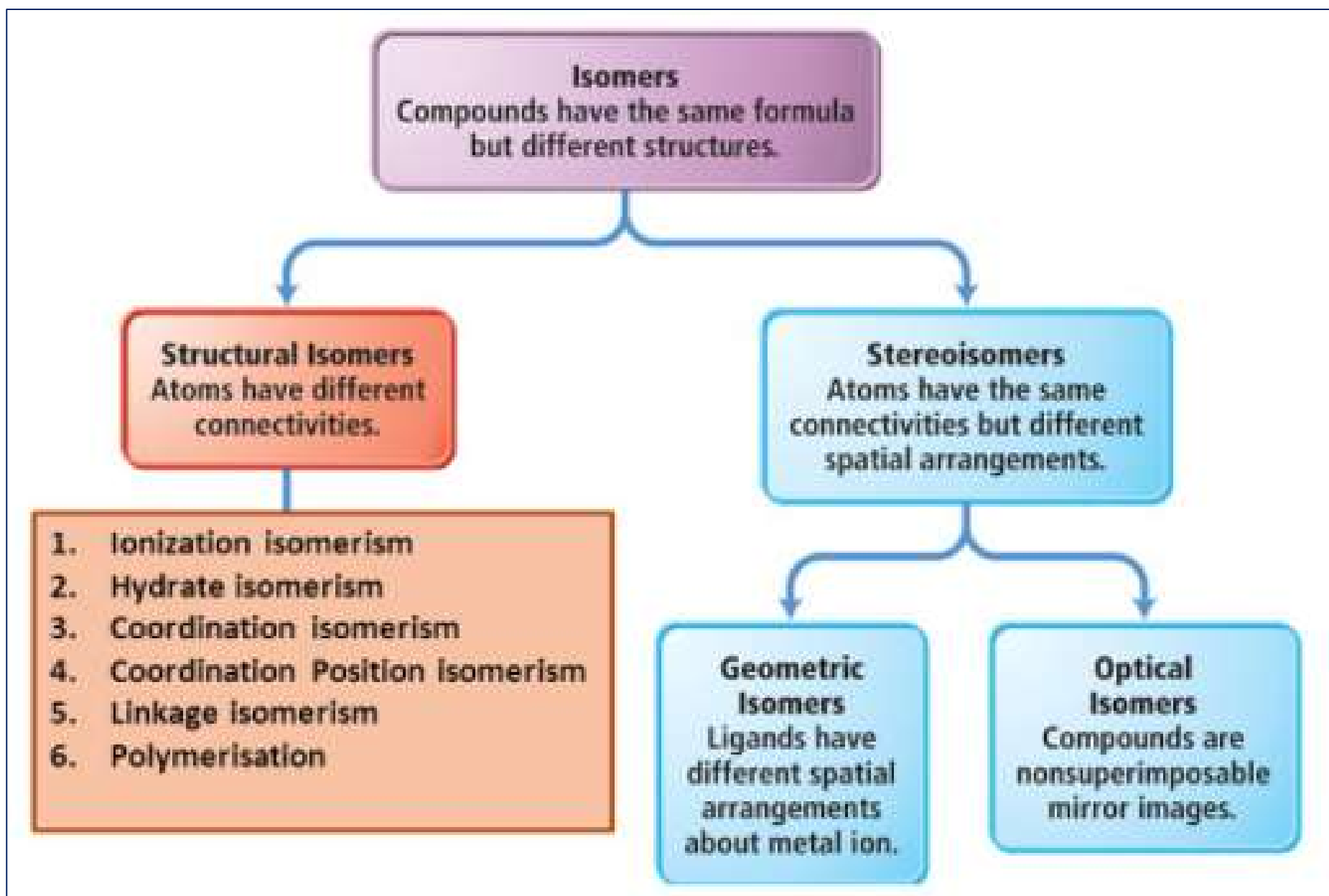
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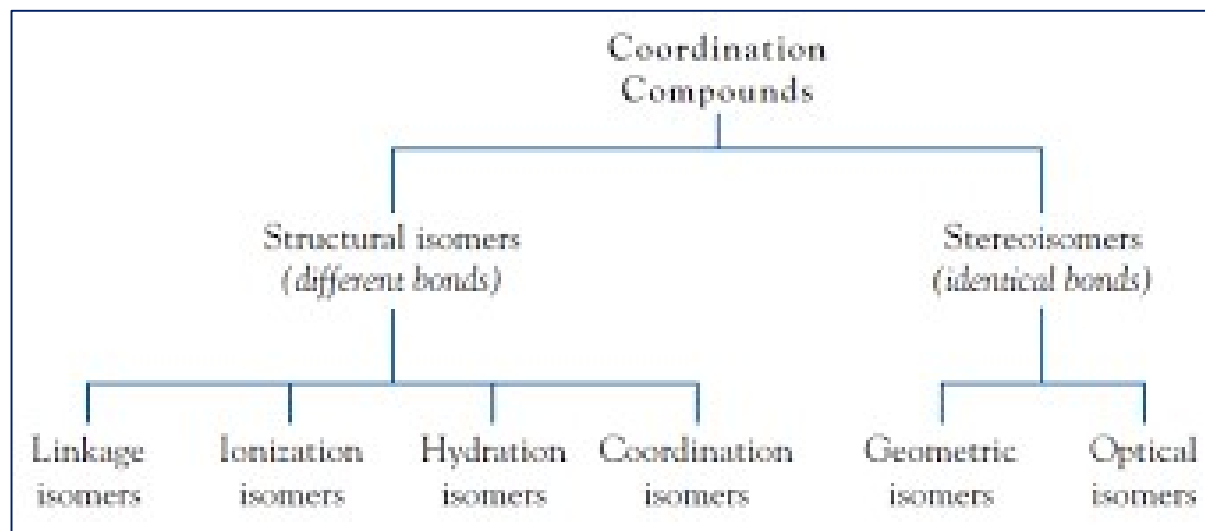
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Isomerism and chirality:



Types of isomerism are:

1.Linkage isomerism: Same ligand links through different atoms as in ambidentate ligands.

2.Ionization isomerism: occurs when a ligand and a counterion in one compound exchange places. An example is $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$. If the compounds are soluble, the two isomers exist as different ionic species in solution.

3.Hydrate isomerism: when one of the ligands is water, there are three differently colored hydration isomers of a compound with molecular formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$: the violet $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$, the pale green $[\text{CrCl}(\text{OH}_2)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$, and the dark green $[\text{CrCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$.

Hydrate isomerism



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4. Coordination isomerism: when there are different complex ions that can form from the same molecular formula, as in $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$.

5. Geometric isomerism: when the permutations of ligand arrangement for each of the common complex geometries, this type of isomerism is known as geometric isomerism. The three-dimensional character of metal complexes can give rise to different arrangements in space.

Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral.

6. Optical isomerism: Different types of ligand arrangements at tetrahedral and octahedral centres give rise to chiral compounds designated as Δ or Λ which rotate the plane of polarized light. Optical isomers are possible for both tetrahedral and octahedral complexes, but not square planar.

Tetrahedral complexes: only optical

Square planar complexes: only geometric

Octahedral complexes: Geometric and optical isomerism

1. Structural Isomerism

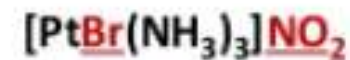
a) Coordination isomerism



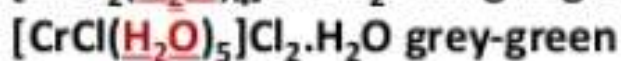
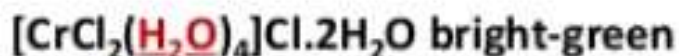
b) Linkage isomerism



c) Ionisation isomerism



d) Hydrate isomerism



2. Stereoisomerism

a) Geometrical isomerism

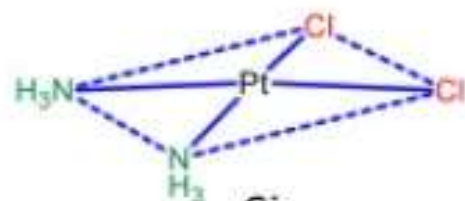
Square Planar ✓

Tetrahedral

Octahedral ✓

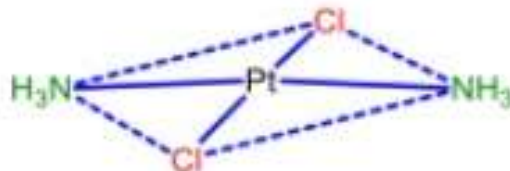
Ma_2b_2 / Ma_2bc / $\text{M}(\text{ab})_2$ / Mab cd

Ma_2b_4 / Ma_4bc / Ma_3b_3 / $\text{M}(\text{aa})_2\text{b}_2$ / $\text{M}(\text{aa})_2\text{bc}$ / Mab cdef

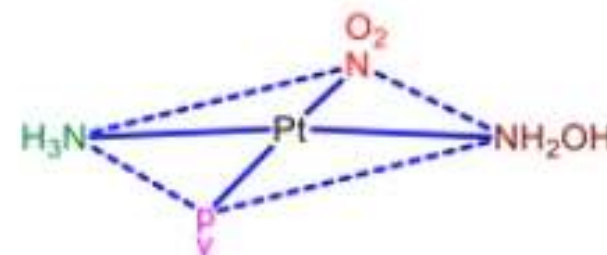


Cis

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ /Square Planar

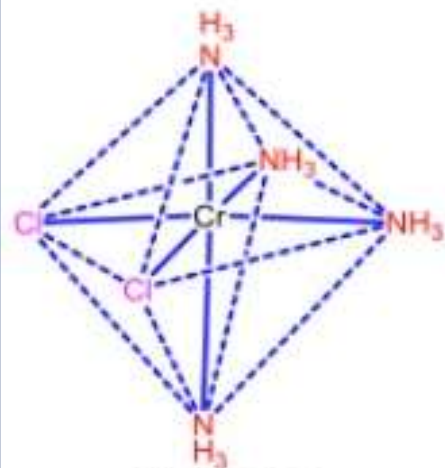


trans



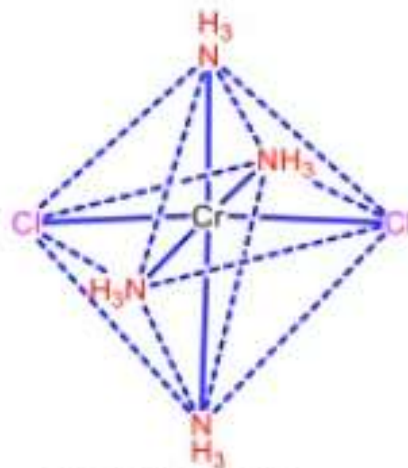
Mab cd / 3 isomers

Ma_2b_4 / Ma_4bc / Ma_3b_3 / $M(aa)_2b_2$ / $M(aa)_2bc$ / $Mabcdef$

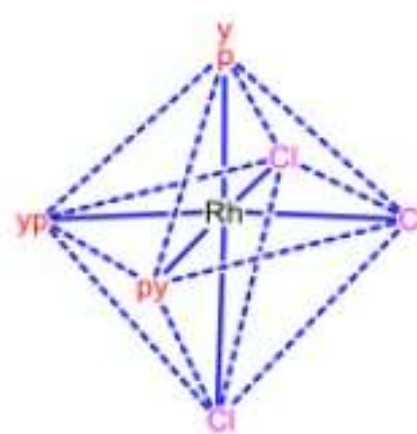


Cis/ violet

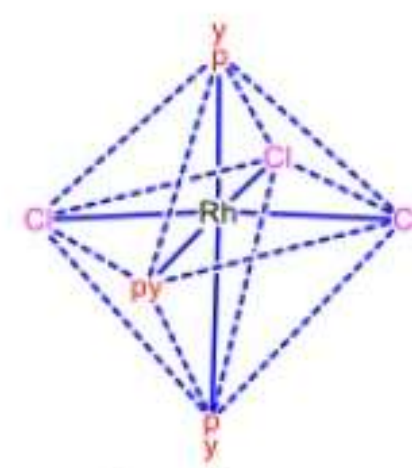
$Ma_2b_4/[CrCl_2(NH_3)_4]^+$



trans/ green

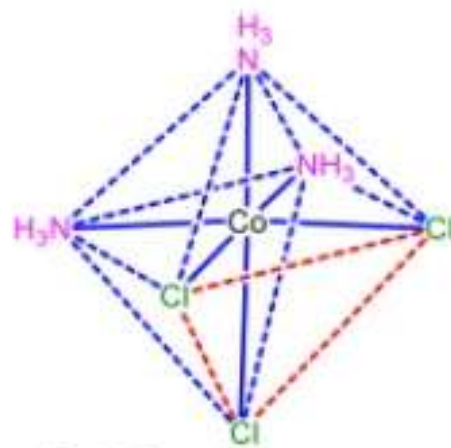


Cis form

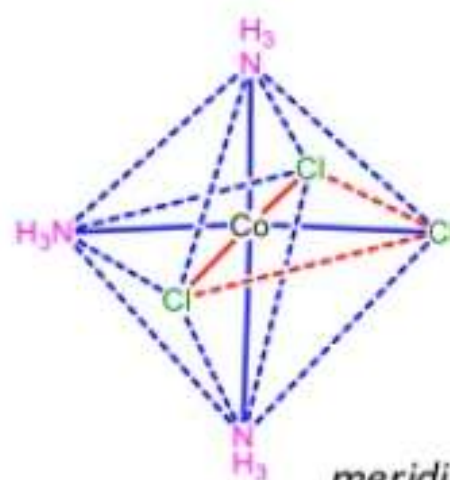


Trans form

$Ma_3b_3/[RhCl_3py_3]$



facial



meridional

$[Co(NH_3)_3(Cl)_3]$ /Octahedral

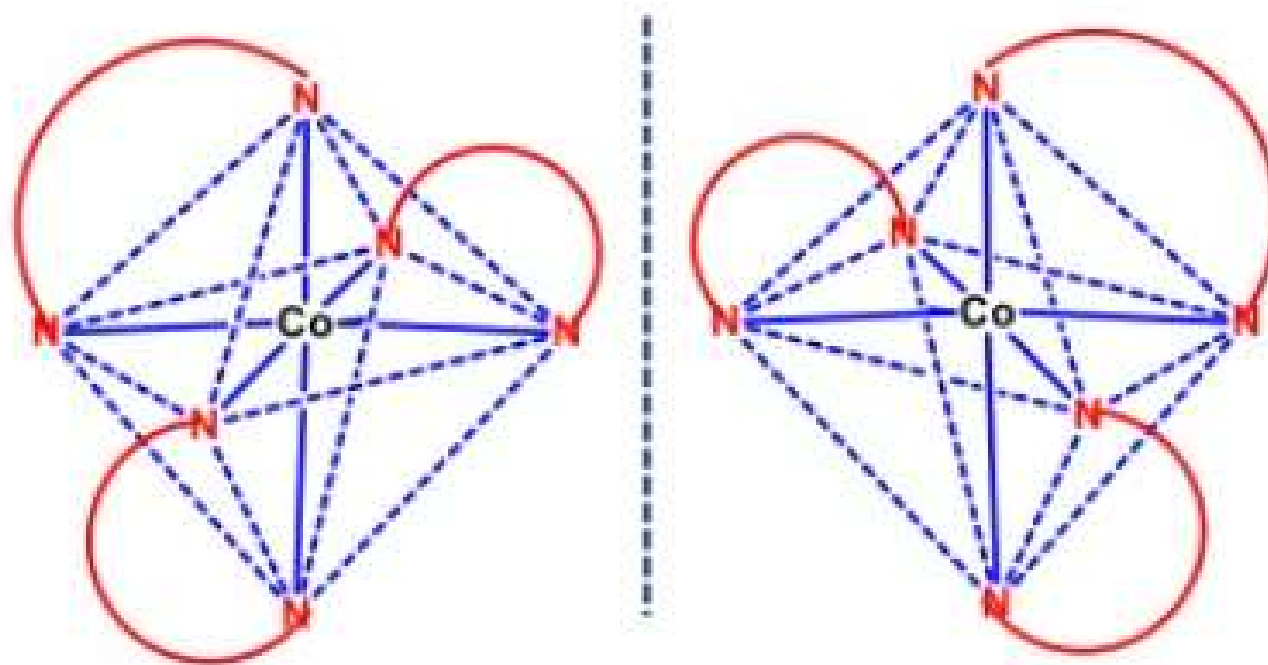
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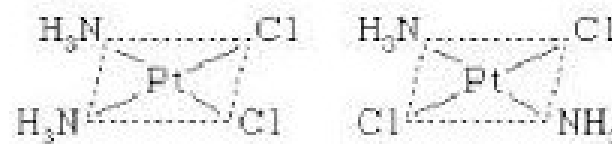
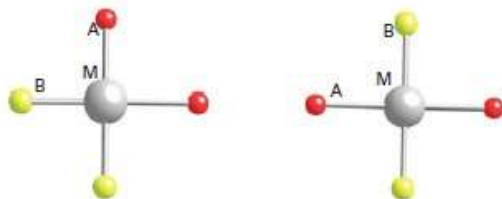
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two optically active isomeric form of the complex $[\text{Co}(\text{en})_3]^{3+}$

Square-planar complexes: isomers of square-planar complexes are cis/trans isomers.

In the simple case of two sets of two different monodentate ligands, as in $[MA_2B_2]$, there is only the case of cis/trans isomerism to consider.

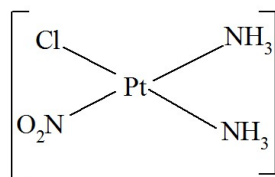
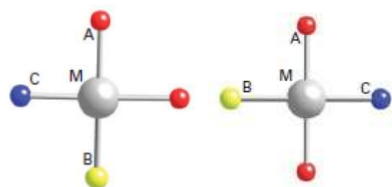


cis

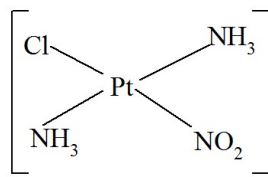
trans

cisplatin

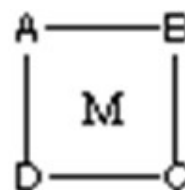
With three different ligands, as in $[MA_2BC]$, the locations of the two A ligands also allow us to distinguish the geometric isomers as cis and trans. When there are four different ligands, as in $[MABCD]$, there are three different isomers and we have to specify the geometry more explicitly.



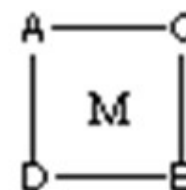
cis-isomer



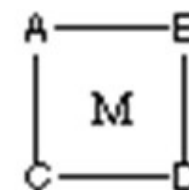
trans-isomer



A trans to C



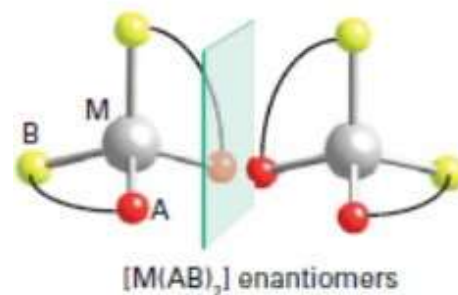
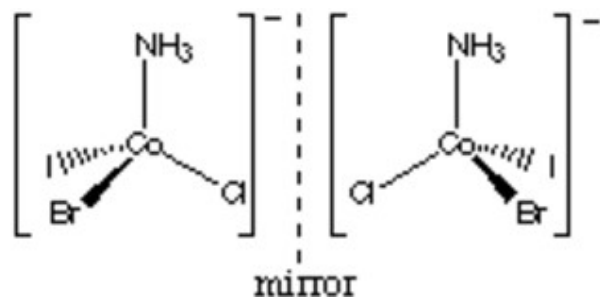
A trans to B



A trans to D

Tetrahedral complexes

Only simple isomers of tetrahedral complexes show optical isomerism, when all four ligands are different or where there are two unsymmetrical bidentate chelating ligands resulting in both molecules chiral, not superimposable on their mirror images. This pair of chiral complexes make up an enantiomeric pair. i.e. one enantiomer rotates the plane of polarized light in one direction and the other rotates it through an equal angle in the opposite direction.

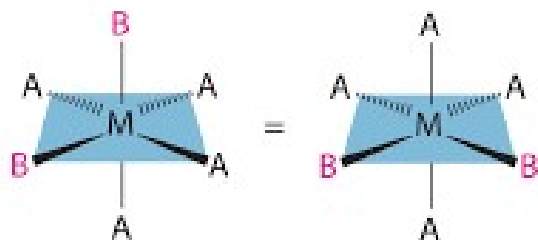


Trigonal-bipyramidal and square-pyramidal complexes

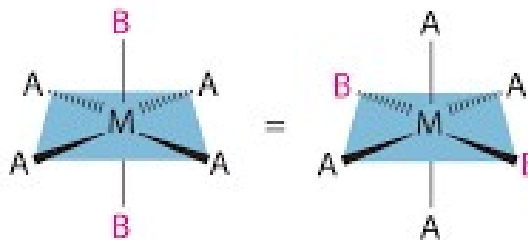
Five-coordinate complexes are not stereochemically rigid; two chemically distinct coordination sites exist within both trigonal-bipyramidal and square-pyramidal complexes, where a ligand that is axial at one moment becomes equatorial at the next moment: the conversion is called a *Berrypseudorotation*.

Octahedral complexes: Geometrical isomerism

Cis and trans isomers exist for octahedral complexes of formula $[MA_4B_2]$ [D_{4h} symmetry]

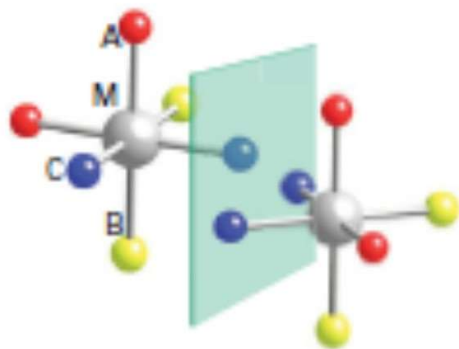


MA_4B_2 octahedral complex, cis isomer

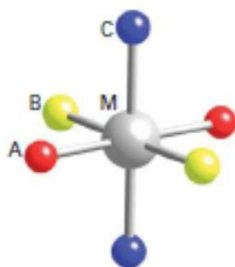


MA_4B_2 octahedral complex, trans isomer

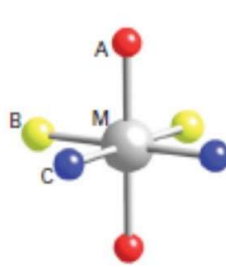
Also chirality can exist for complexes of formula $[MA_2B_2C_2]$: there are 5 different geometrical isomers.



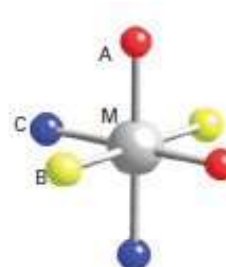
all-cis



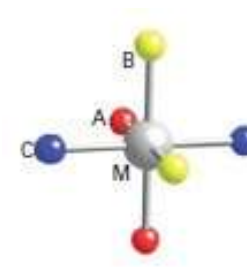
all-trans



trans-cis-cis



trans-cis-cis

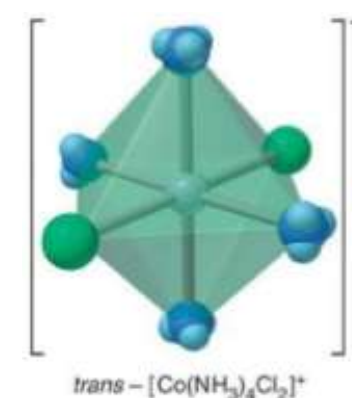
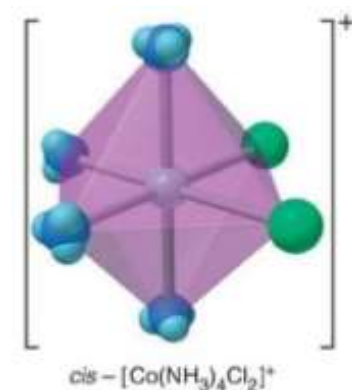
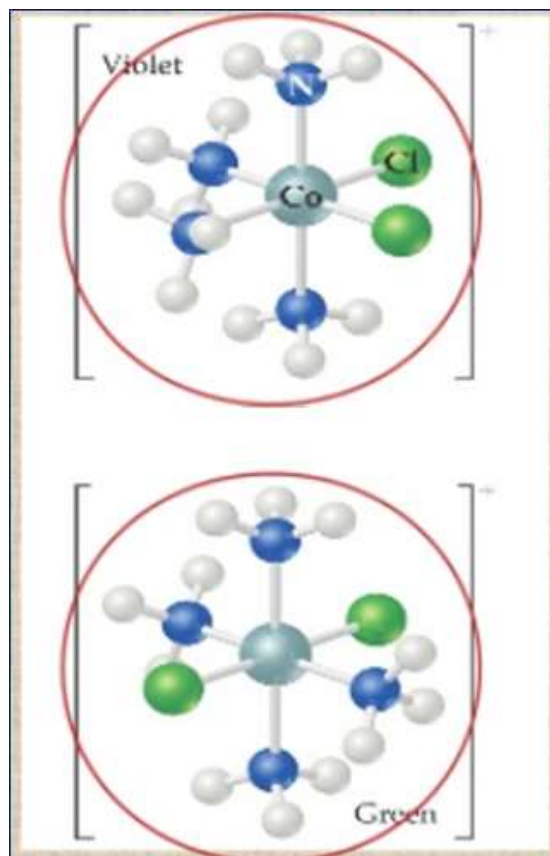
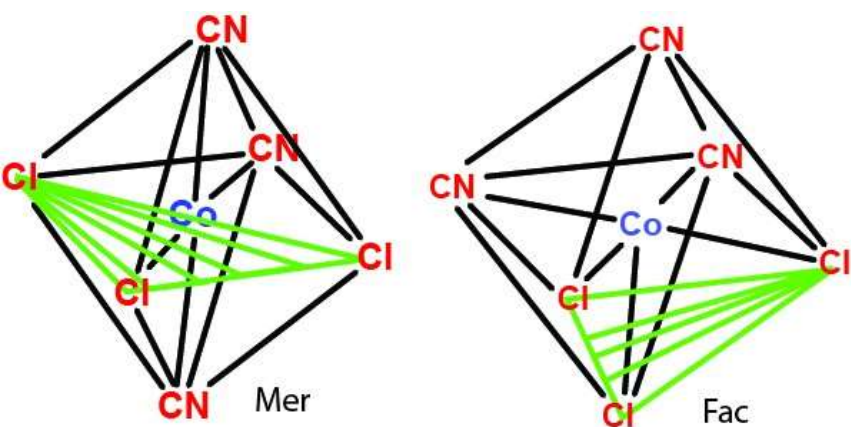


trans-cis-cis

Fac and Mer Stereoisomers

When three identical ligands occupy one face of an octahedron, the isomer is said to be facial, or fac. In a fac isomer, any two identical ligands are adjacent or cis to each other.

If these three ligands and the metal ion are in one plane, the isomer is said to be meridional, or mer. A mer isomer can be considered as a combination of a trans and a cis, since it contains both trans and cis pairs of identical ligands. E. g. $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{NO}_2)_2]^{-1}$

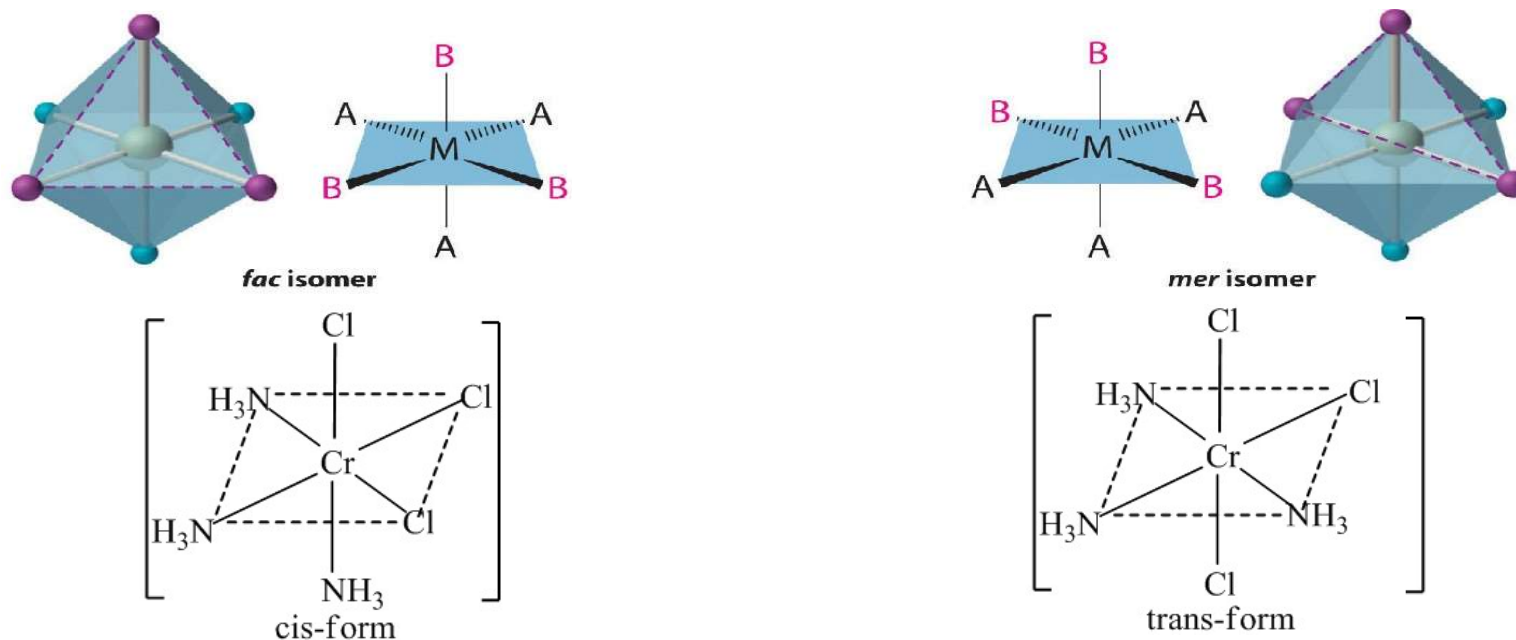


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Chirality also exists for complexes of formula $[MA_3B_3]$: they exist as fac and mer isomers.

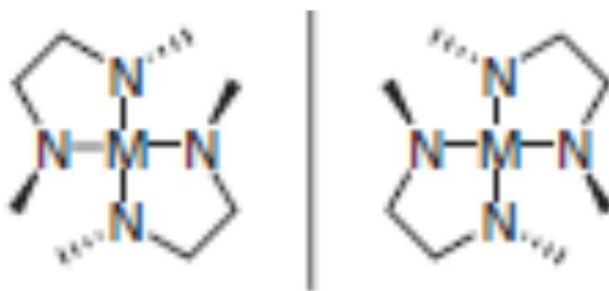


Complexes with coordination numbers more than six may have many isomers, both geometrical and optical.

Ligand Chirality:

Sometimes, achiral ligands become chiral on coordination to a metal, leading to a complex that is chiral.

E.g. ligand $\text{MeNHCH}_2\text{CH}_2\text{NHMe}$: two N-atoms become chiral centres by coordinating to a metal atom.

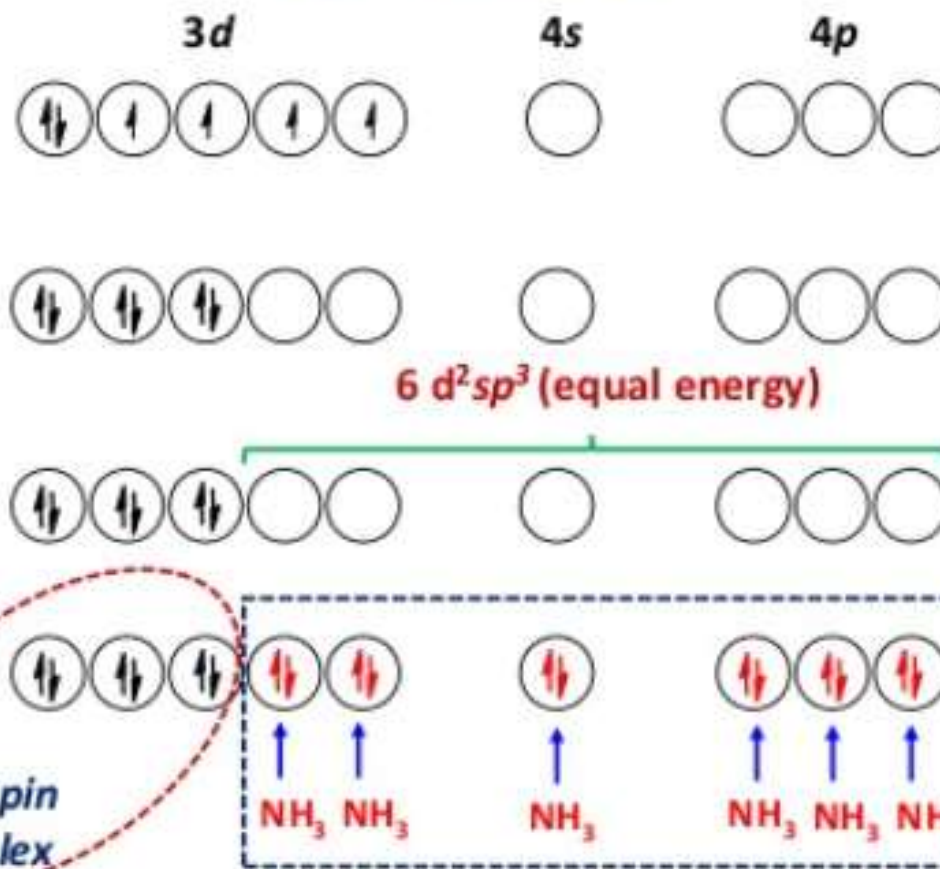
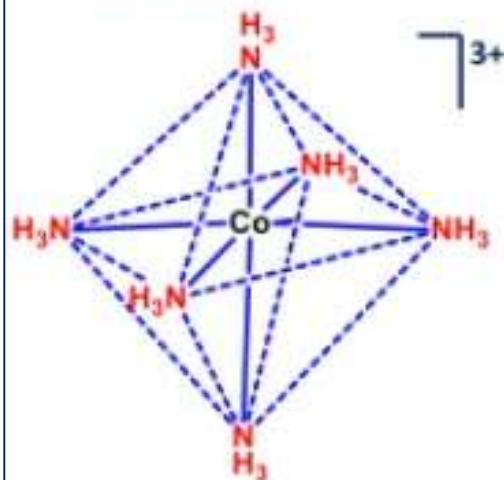


Bonding in Coordination Complexes: Valence Bond Theory



Co(III) ion

6 empty orbitals
for coordination
number 6



Low Spin
Complex

$[\text{Co}(\text{NH}_3)_6]^{3+}$ is called an **inner orbital complex**
 Co^{3+} uses inner d orbital for hybridization

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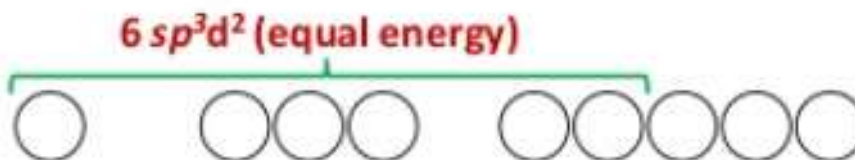
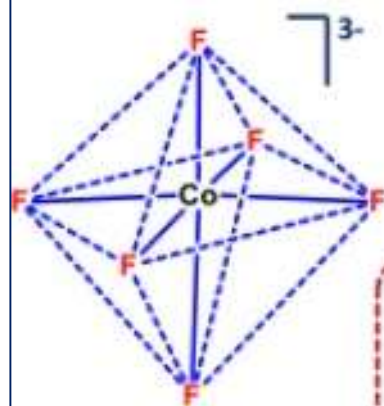
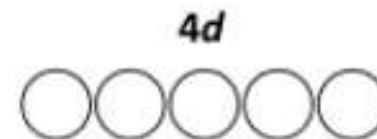
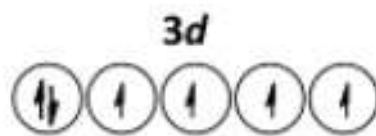
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$[\text{CoF}_6]^{3-}$ C.N. = 6; O.S. = +3 (Paramagnetic)

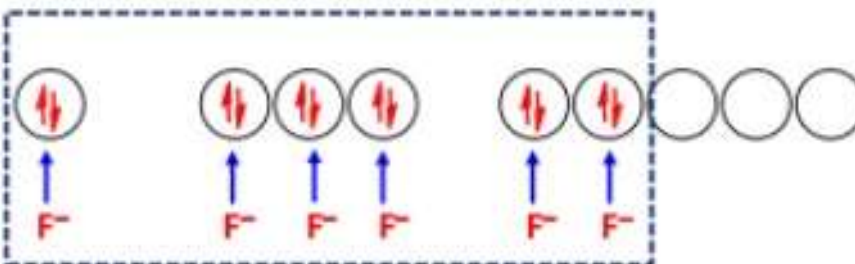
$^{27}\text{Co} = [\text{Ar}] 3d^7 4s^2$

$\text{Co}^{3+} = [\text{Ar}] 3d^6 4s^0$

Co(III) ion



High Spin Complex



$[\text{CoF}_6]^{3-}$ is called an outer orbital complex
 Co^{3+} uses outer d orbital (4d) for hybridization

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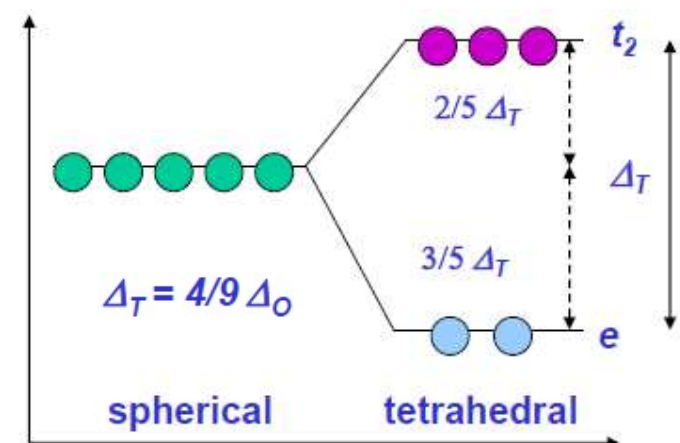
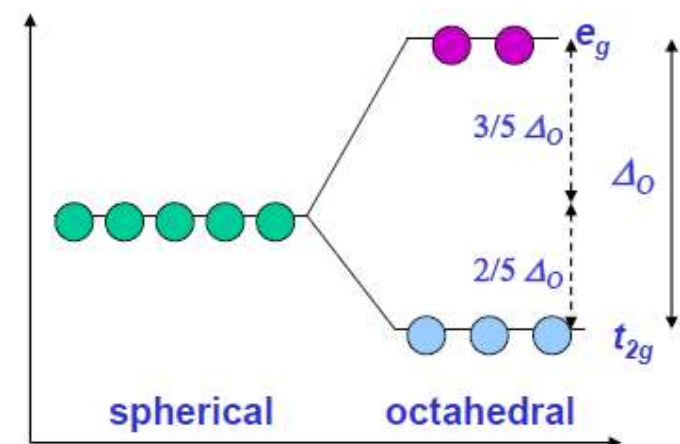
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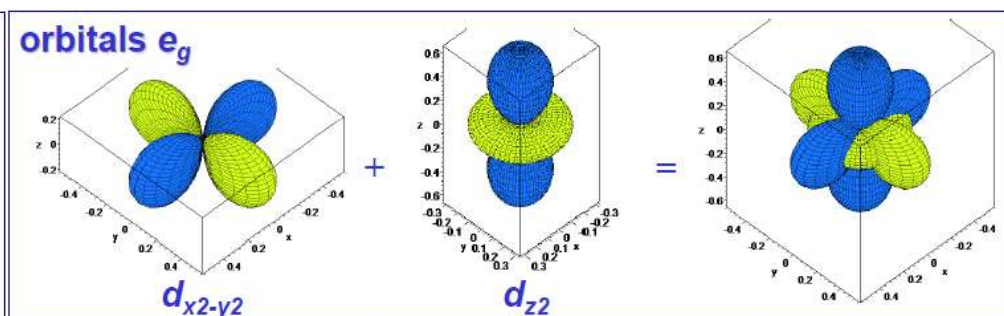
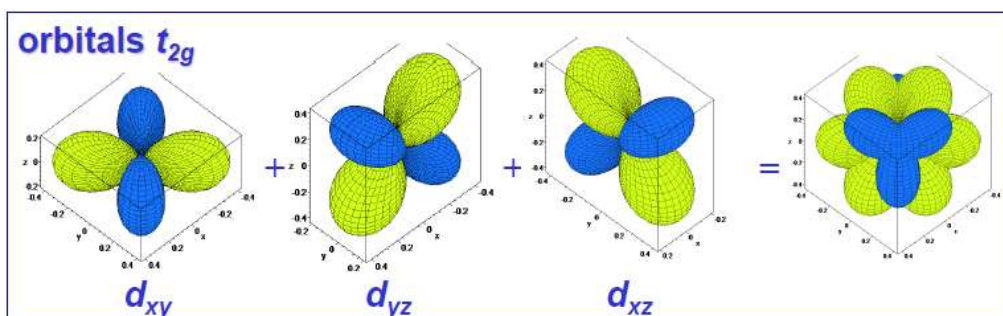
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Crystal Field Theory (CFT)

Crystal field theory is developed by H. Bethe and V. Vleck. In the case of an isolated gaseous metal ion, all the five d-orbitals are in **degenerate state**. That means all d orbitals are having same energy. Crystal field theory explains the breaking of this degeneracy of transition metal complexes. When the ligands approach the central metal ion, an electric field will produce by the ligands and this will result in breaking of the degeneracy of orbitals. The electrons in the d orbitals of the metal ion and those in the ligands repel each other. The d electrons closer to the ligands will undergo more repulsion and having higher energy. This is known as **crystal field splitting**. Crystal field splitting will be different for different geometries like octahedral, tetrahedral etc as in different geometries the ligands approach central metal ion in different manner. Crystal field stabilization energy is the energy by which a particular d electron configuration stabilized by the splitting of the d orbitals. The energy gap between t_{2g} and e_g set is denoted by Δ_o or $10Dq$ (D means deci and q means quanta the energy) for octahedral field. This energy gap is formed due to the difference in electrostatic field exerted by the ligands on t_{2g} and e_g set of orbitals of the central metal ion.



$$CFSE = n_{t_{2g}}(-4Dq) + n_{e_g}(6Dq); \text{ where } n = \text{no. of electrons}$$



There is a second kind of overlap of ligand orbitals with d-orbitals (in O_h , only for d_{xy} , d_{xz} , $d_{yz} \equiv d_{\pi}$).

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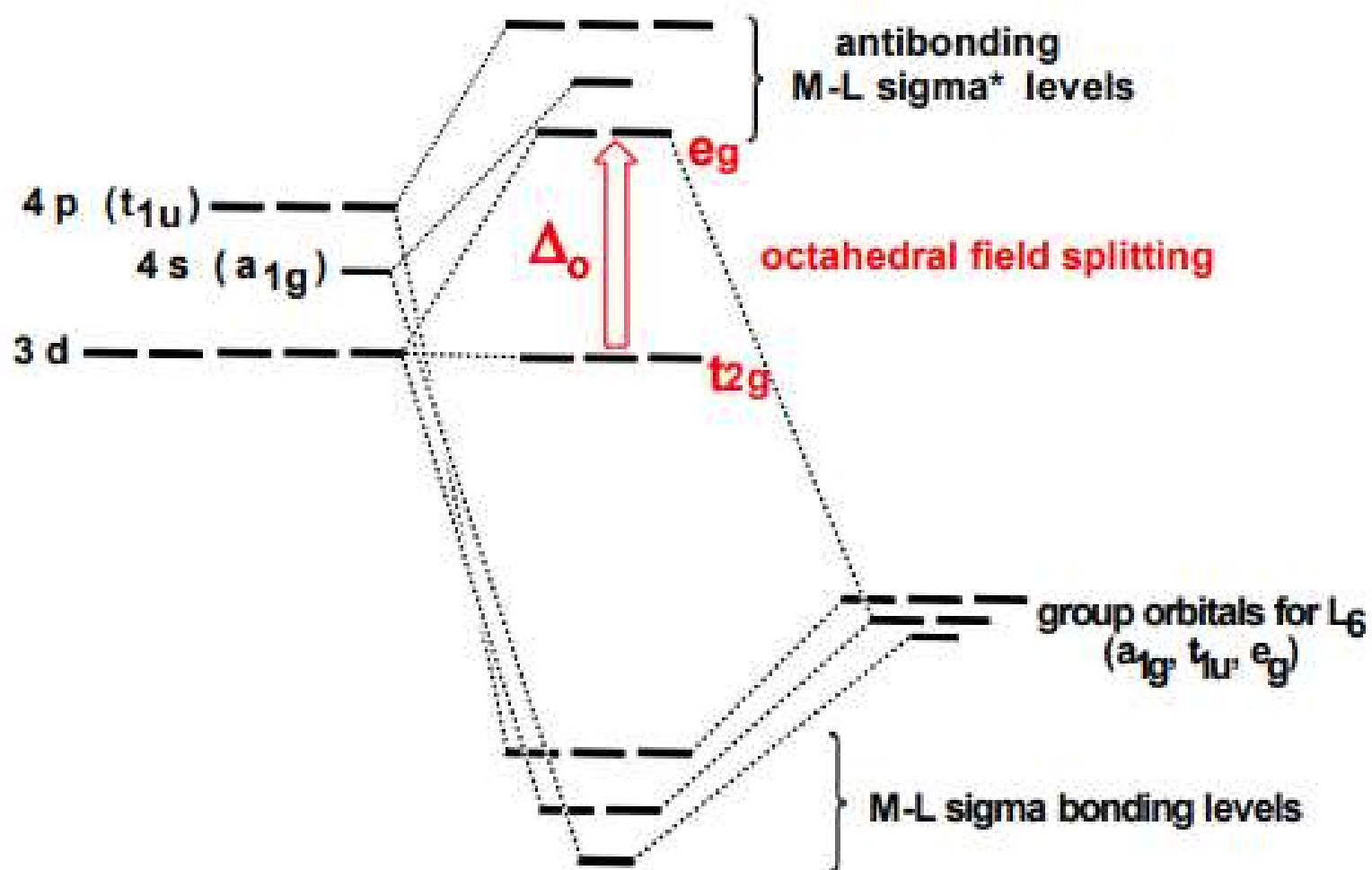
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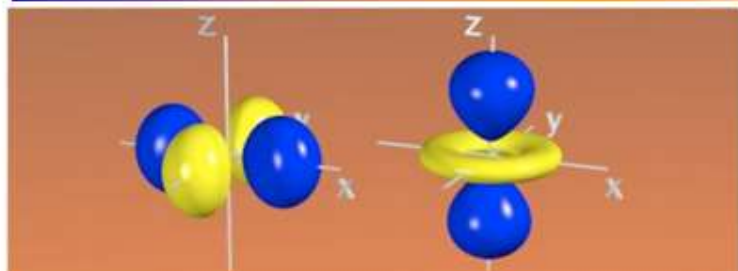
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The Octahedral *Ligand* Field M.O.s



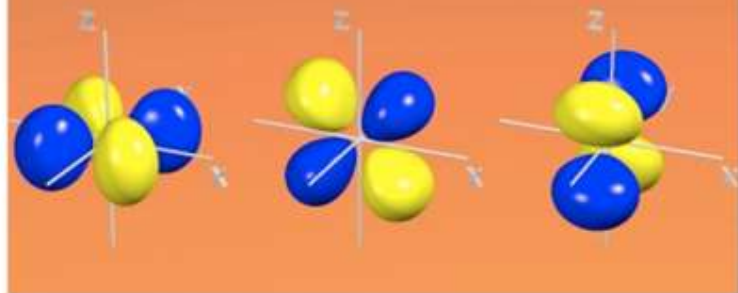
Two Kinds of d Orbitals in Octahedral Field

e_g



Pointed
at
Ligands.

t_{2g}



Pointed
between
Ligands.

d Orbitals in a Octahedral Ligand Field

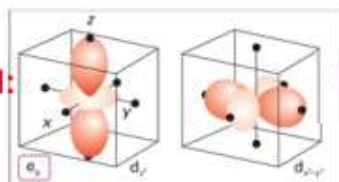
consider d-orbitals in an octahedral complex:
i.e., an octahedral "Ligand Field".

The 6 ligands are put on the x, y, z axes (black dots below)

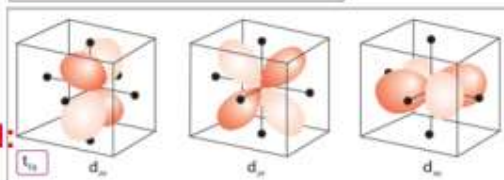
Two d-orbitals are pointing right at the ligands (anti-bonding).

Three d-orbitals are pointing in-between ligands (nonbonding).

Antibonding d:



Nonbonding d:



The Negatively Charged Ligands Produce an Electric Field+Potential



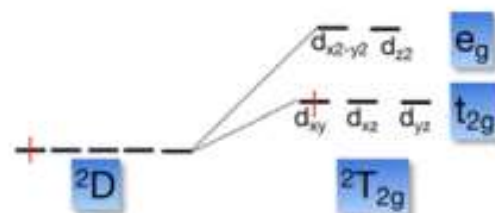
The Field Interacts with the d-Electrons on the Metal (Repulsion)



The Interaction is NOT Equal for All Five d-Orbitals



1. The Spherical Symmetry of the Free Ions is Lifted
2. The d-Orbitals Split in Energy
3. The Splitting Pattern Depends on the Arrangement of the Ligands



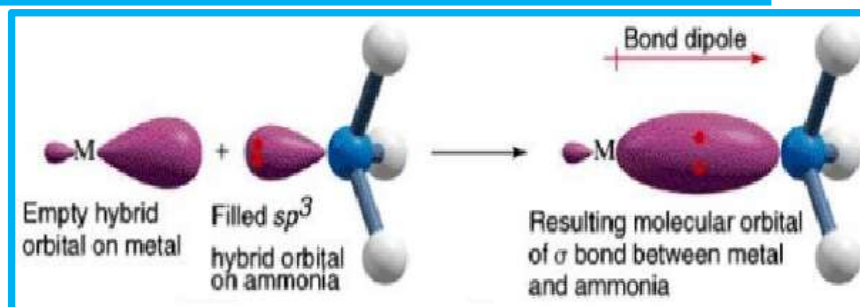
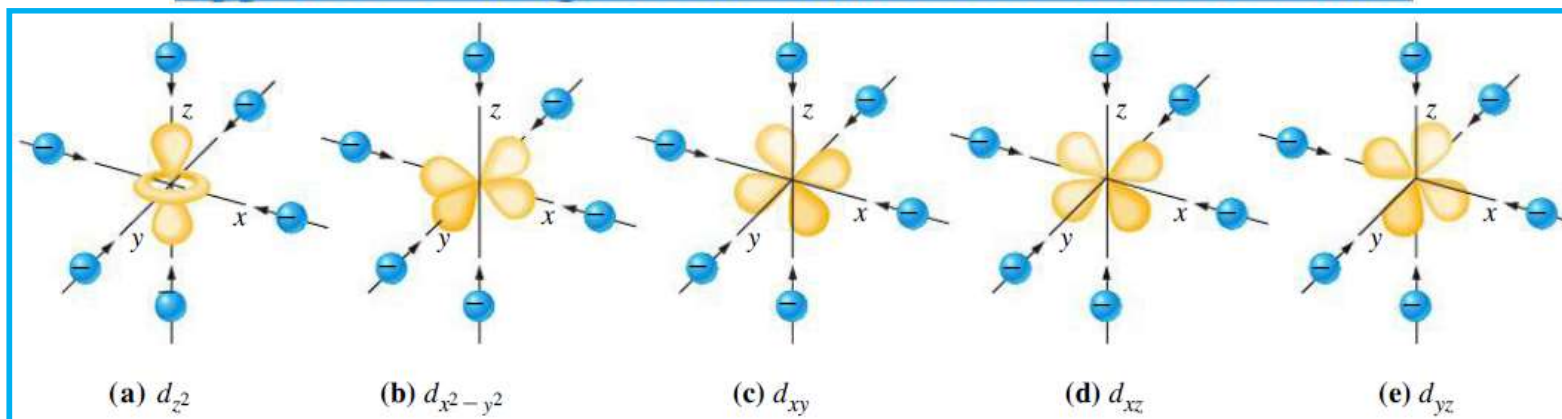
No π interactions
possible

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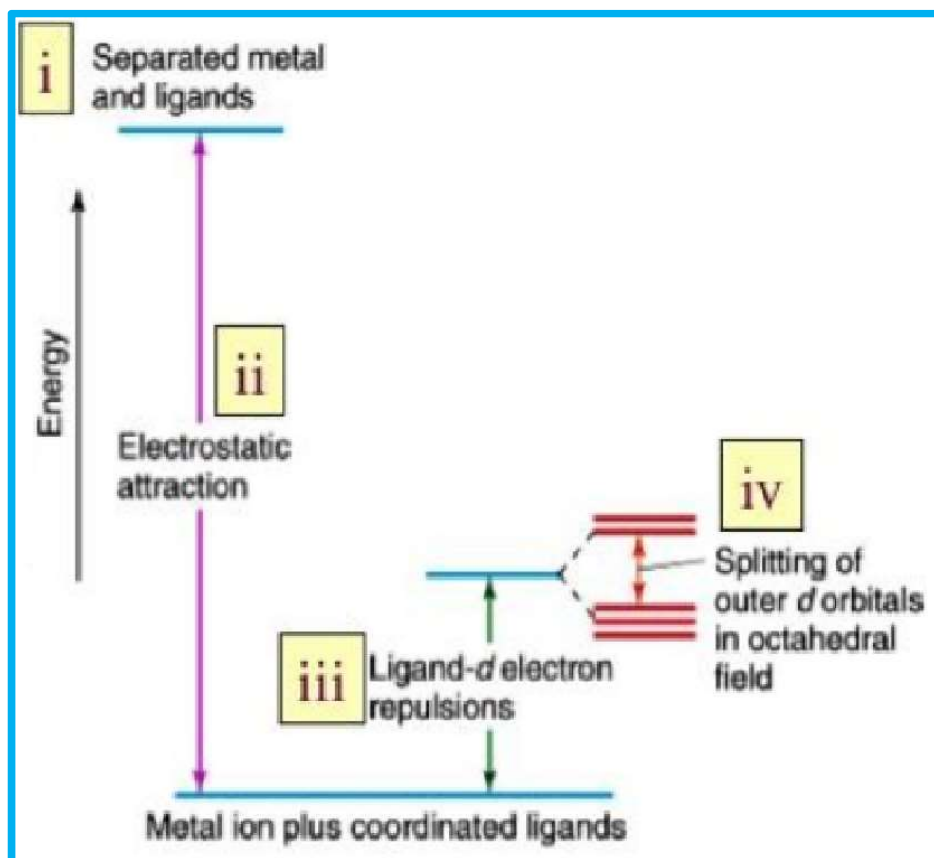
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Approach of six ligands to a metal ion in Octahedral Field



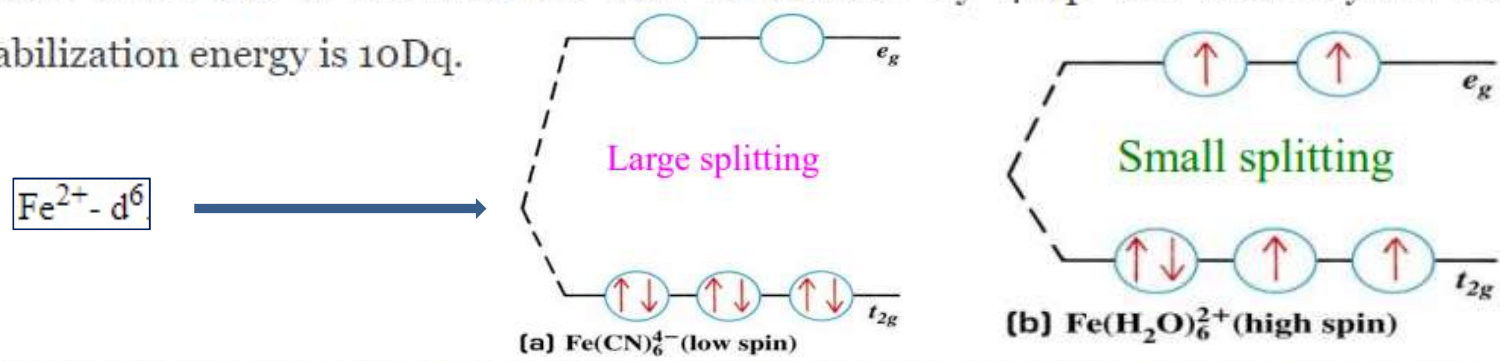
- 1) Metals and ligands orbitals initially have high energy when they are separated.
- 2) Metal –ligand orbitals get stabilized due to electrostatic interaction
- 3) Next destabilization happens due to ligand-d electron repulsion
- 4) Finally results splitting of metal 5, d-orbitals.
- 5) Depending upon the number (4 or 6) of attached ligand metal ion gives different geometry and consequently d-orbitals are not affected equally by the ligand field.



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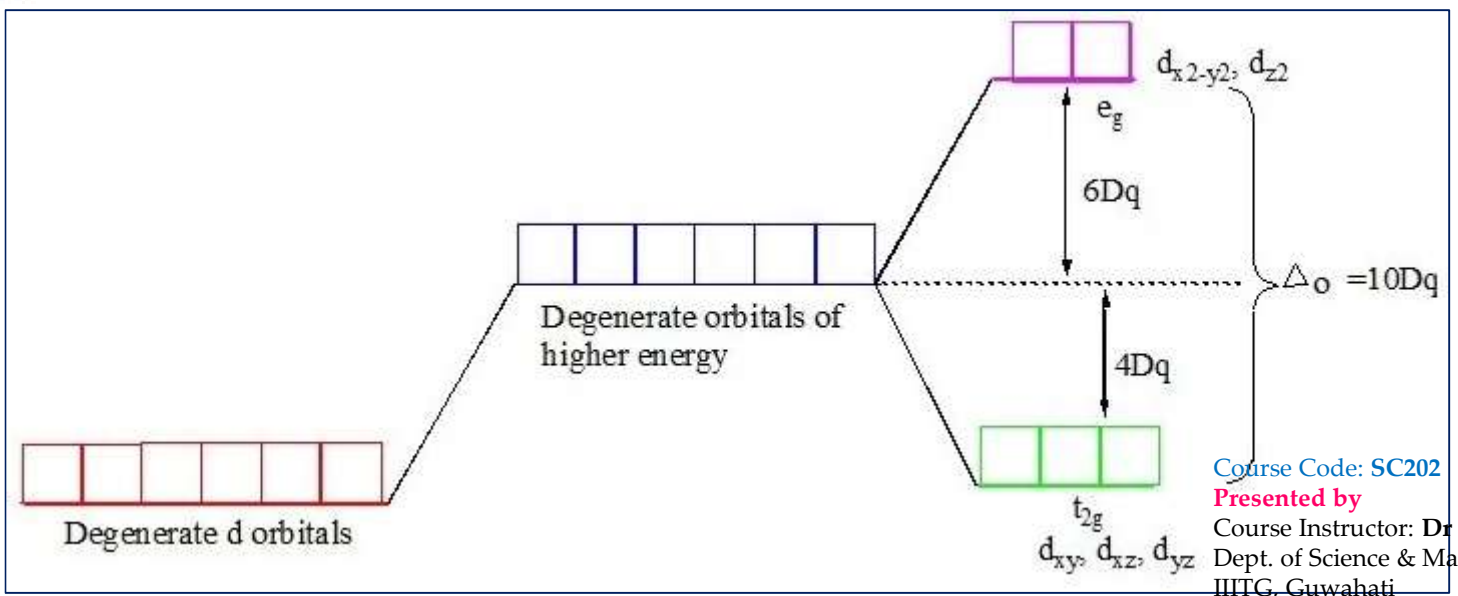
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From the diagram we can observe in the absence of ligands all the five d orbitals are in the degenerate state. Then these degenerate orbitals will go to higher energy when ligands are approaching towards the central metal ion. When ligands approach more closer through the axes to the central metal ion, $d_{x^2-y^2}$ and d_{z^2} undergo more repulsion and its energy raised by $6Dq$. While the energy of other three orbitals d_{xy} , d_{xz} and d_{yz} whose lobes are in between the axes is lowered by $4Dq$. The total crystal field stabilization energy is $10Dq$.

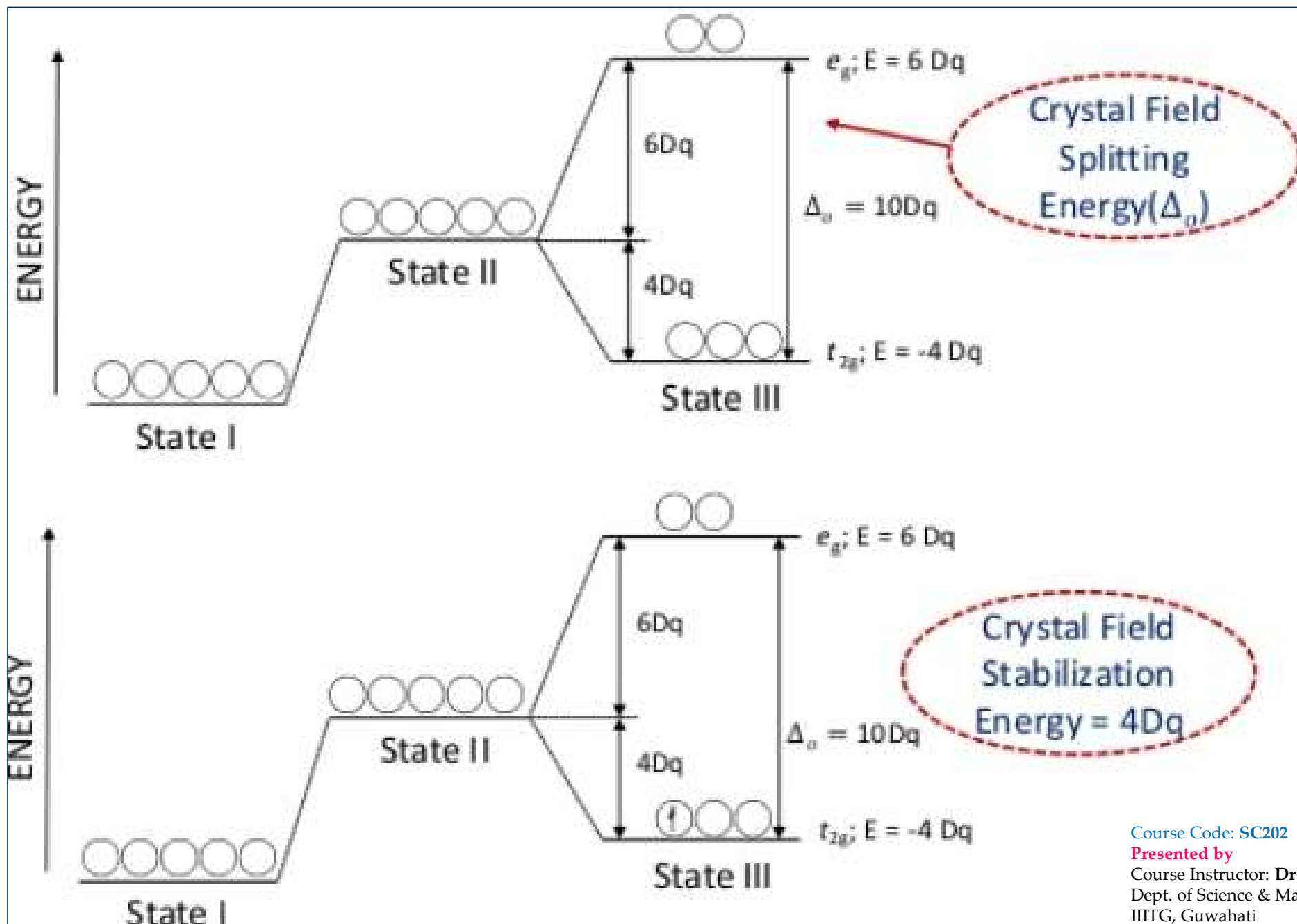


In an octahedral complex, six ligands surround the central metal ion. $d_{x^2-y^2}$ and d_{z^2} orbitals (called e_g set) are directed along the direction of ligands and experience more repulsion. They have more energy. d_{xy} , d_{yz} and d_{zx} orbitals (called t_{2g} set) are directed between the axes of attacking ligands and experience lesser repulsion by the ligands. They have lesser energy. The energy separation between two split sets is denoted as Δ_o . The energy of e_g orbitals increase by $3/5 \Delta_o$ and that of t_{2g} set decrease by $2/5 \Delta_o$.

When metal ions that have between 4 and 7 electrons in the d orbitals form octahedral compounds, two possible electron distributions can occur. These are referred to as either weak field - strong field or high spin - low spin configurations.



Crystal Field Splitting in octahedral complexes



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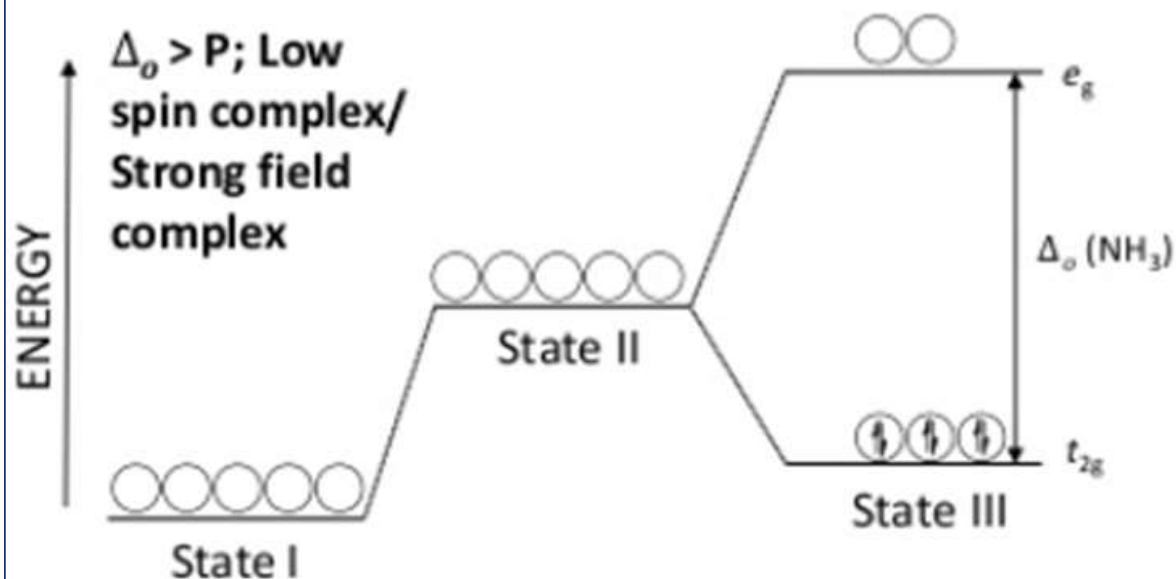
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$[\text{Co}(\text{NH}_3)_6]^{3+}$ C.N. = 6; O.S. = +3 (Diamagnetic)

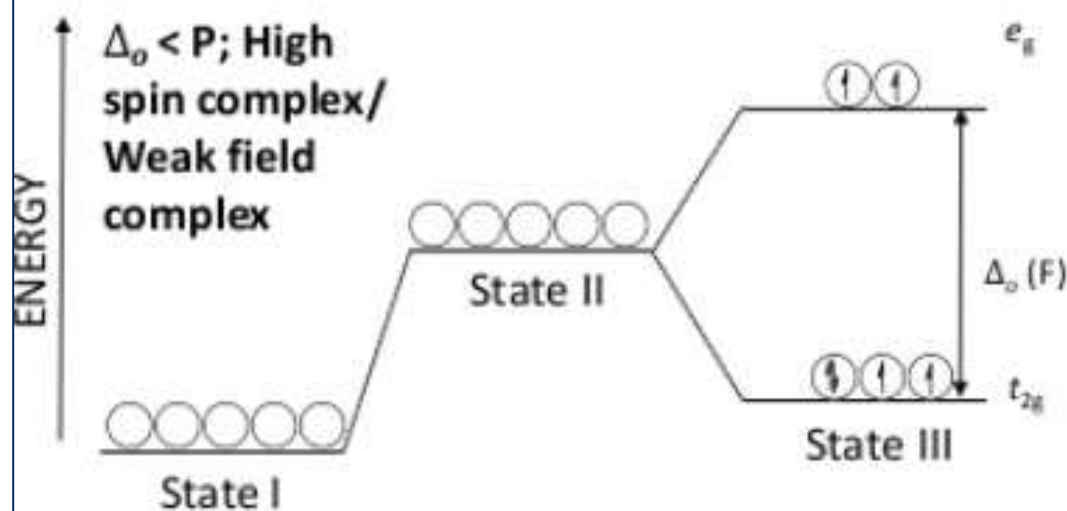


diamagnetic, $\mu=0$ Bohr Magneton (B.M.)

(large Δ , t_{2g}^6).

$$\Delta_o(\text{NH}_3) > \Delta_o(\text{F})$$

$[\text{CoF}_6]^{3-}$ C.N. = 6; O.S. = +3 (Paramagnetic)



(small Δ , $t_{2g}^4 e_g^2$)

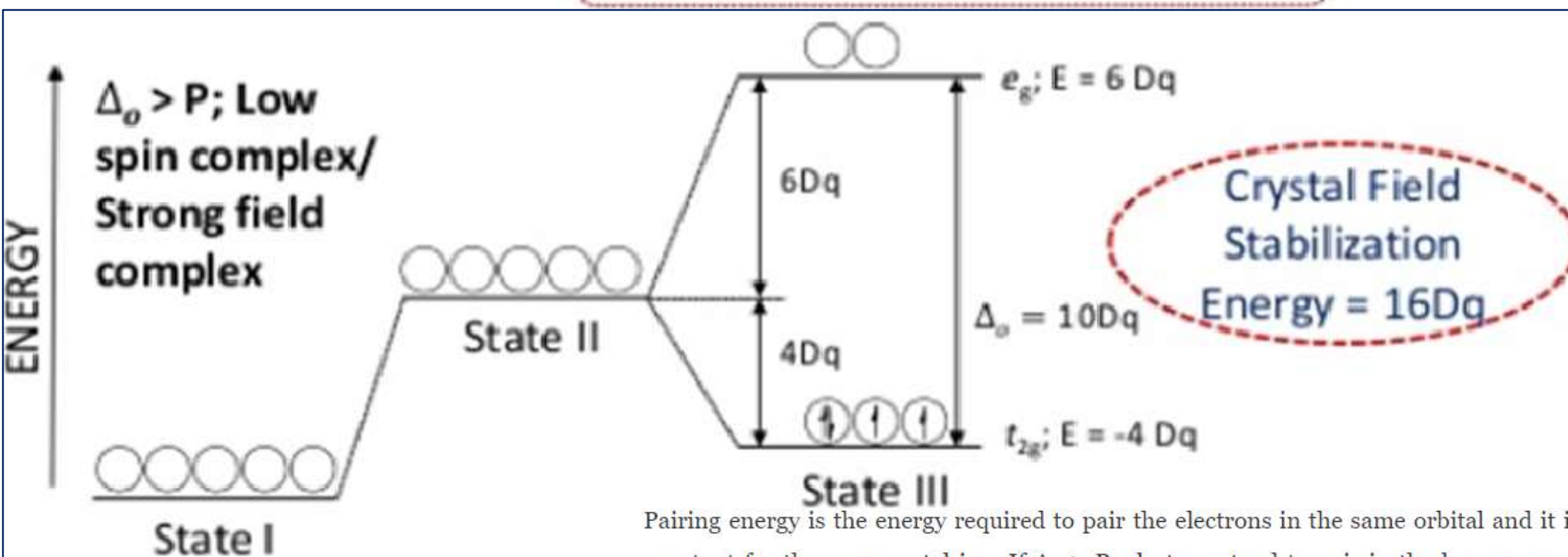
Crystal Field
Splitting
energy

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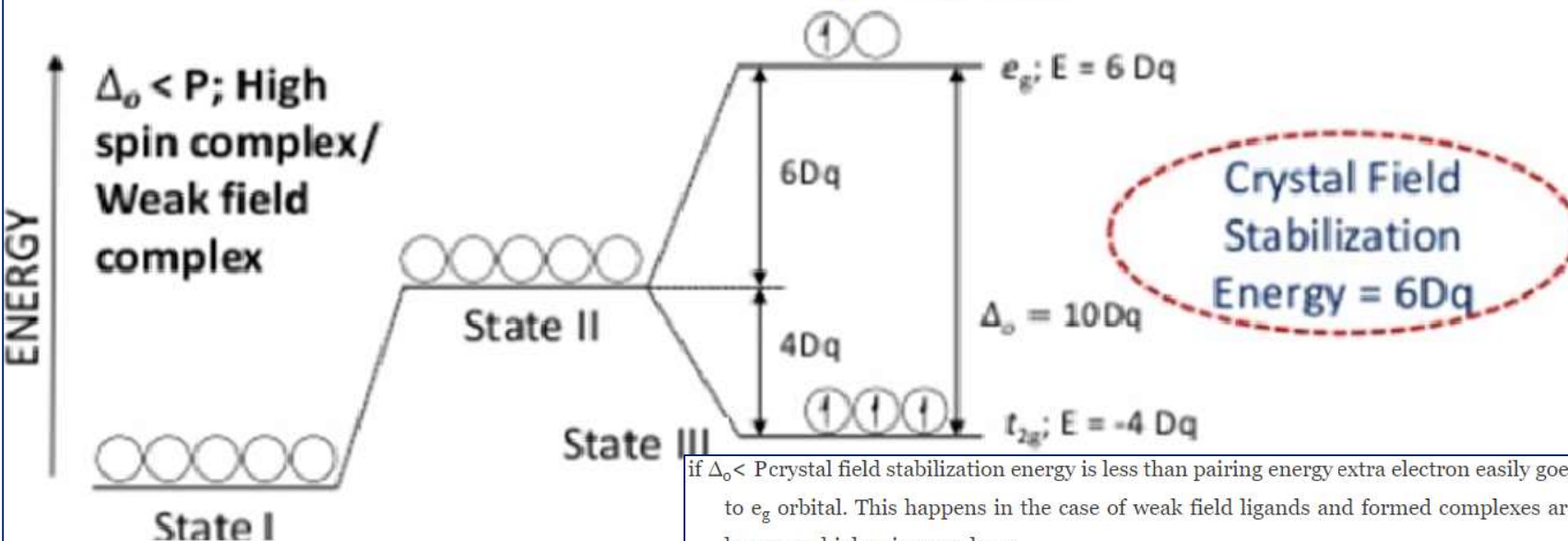
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Concept of pairing energy $\Delta_o > P$ OR $\Delta_o < P$



Pairing energy is the energy required to pair the electrons in the same orbital and it is constant for the same metal ion. If $\Delta_o > P$, electrons tend to pair in the lower energy orbital thus spin paired or low spin complexes are formed.

This happens in the case of strong field ligands like CO, CN etc which we can get from the [spectrochemical series](#).



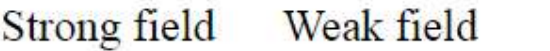
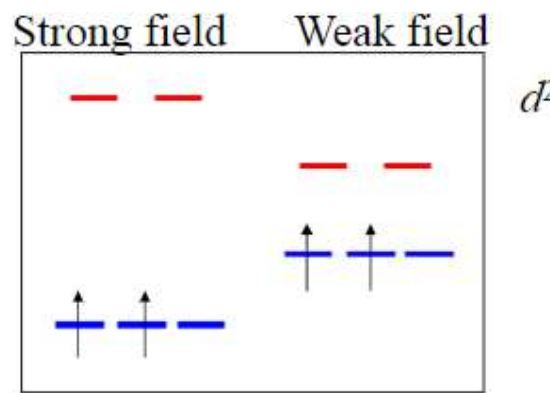
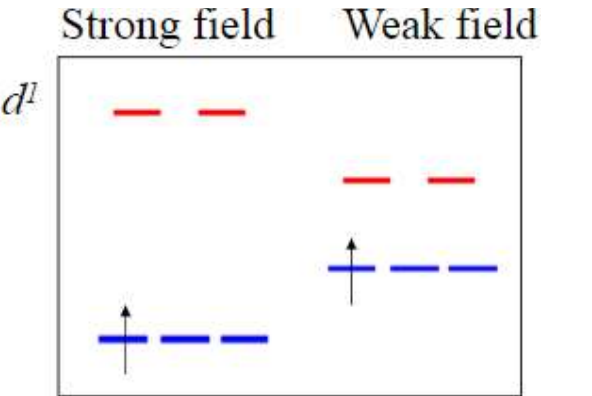
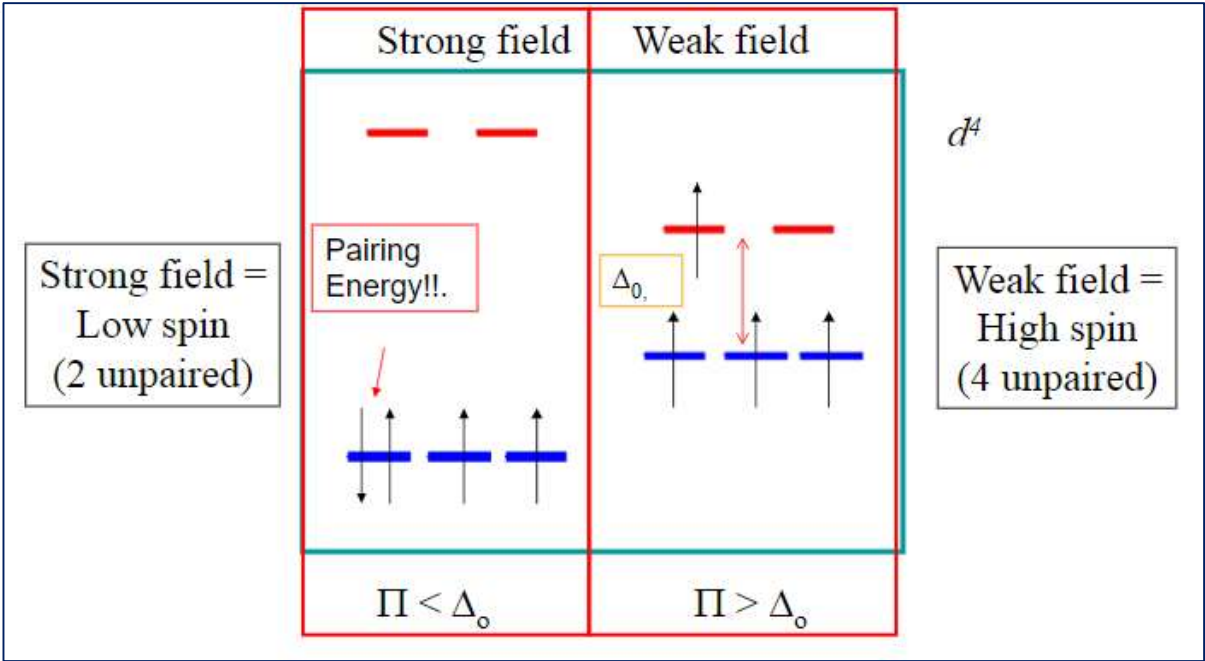
if $\Delta_o < P$ crystal field stabilization energy is less than pairing energy extra electron easily goes to e_g orbital. This happens in the case of weak field ligands and formed complexes are known as high spin complexes.

D1 system (Ti3+): In this system there is only one electron and obviously it will go to more stable t_{2g} orbital and $CFSE = 1(-4Dq) = -4Dq$ [- denotes energy is lowered by 4 Dq]

D2 system (V3+): Here two electrons are present and goes to more stable t_{2g} orbital, $CFSE = 2(-4Dq) = -8Dq$

D3 system (Cr3+): Here three electrons are present and goes to more stable t_{2g} orbital, $CFSE = 3(-4Dq) = -12Dq$

D4 system (Mn3+): In this case 4 electrons are present and two possibilities are there for electron filling. (a) All the four electrons may occupy t_{2g} orbitals with one electron getting paired. ie, t_{2g}^4 $CFSE = 4(-4Dq) = -16Dq$ and other possibility is (b) 3 electrons occupy t_{2g} and 4th electron goes to e_g orbitals. ie, $t_{2g}^3 e_g^1$ $CFSE = 3(-4Dq) + 1(6Dq) = -6Dq$ Which configuration is more stable? This depends on the CFSE and pairing energy (P).

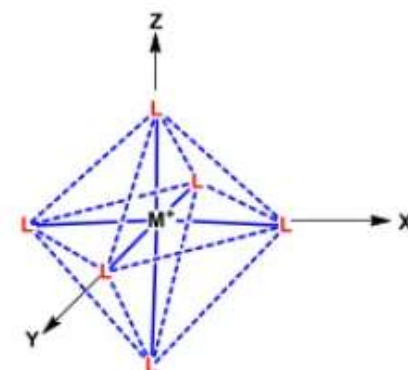


Bonding in Coordination Complexes: Crystal Field Theory

Bonding between a central metal ion and its ligand arises from purely electrostatic interactions

$$B.E. = -\frac{q_1 q_2}{r}$$

Metal orbital	Symmetry label	Degeneracy
s	a_{1g}	1
p_x, p_y, p_z	t_{1u}	3
$d_{x^2-y^2}, d_{z^2}$	e_g	2
d_{xy}, d_{yz}, d_{zx}	t_{2g}	3



A simple crystal field theory approach to the bonding in these ions assumes that when they form octahedral complexes, the d orbitals are no longer degenerate but are split such that two orbitals, the $d_{x^2-y^2}$ and the d_{z^2} (e_g subset) are at higher energy than the d_{xy} , d_{xz} , d_{yz} orbitals (the t_{2g} subset).

In tetrahedral complexes, the energy levels of the orbitals are again split, such that two orbitals, the $d_{x^2-y^2}$ and the d_{z^2} (e subset) are now at lower energy (more favoured) than the remaining three d_{xy} , d_{xz} , d_{yz} (the t_2 subset) which are destabilised.

P is the **spin pairing energy** and represents the energy required to pair up electrons within the same orbital

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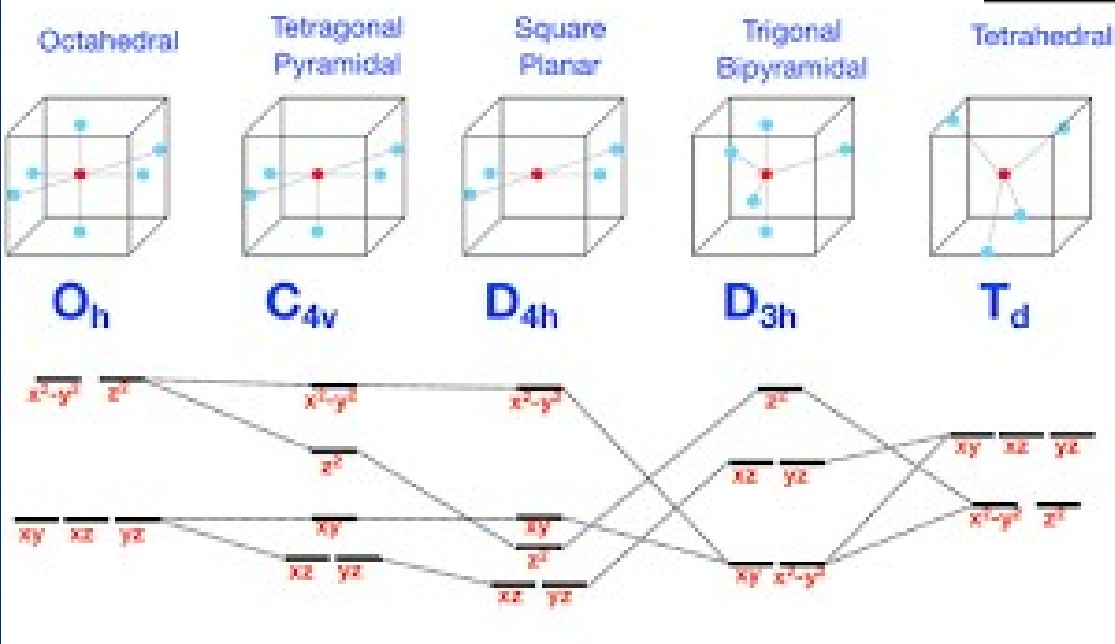
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d Orbital Splittings vs. Ligand Field Symmetry

O_h (octahedral)	D_{4h} (tetragon. elong.)	C_{4v} (sq. pyram.)
e_g z^2, x^2-y^2 t_{2g} xy, xz, yz	b_{1g} x^2-y^2 a_{1g} z^2 b_{2g} xy e_g xz, yz	b_1 x^2-y^2 a_1 z^2 b_2 xy e xz, yz
T_d (tetrahedral)	D_{4h} (sq. planar)	D_{3h} (trig. bipyram.)
t_2 xy, xz, yz e z^2, x^2-y^2	b_{1g} x^2-y^2 b_{2g} xy a_{1g} z^2 e_g xz, yz <small>$xy, z^2, (xz, yz)$ energies can switch</small>	a'_1 z^2 e' x^2-y^2, xy e'' xz, yz



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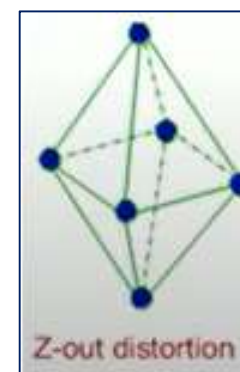
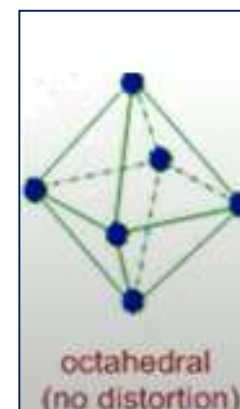
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Tetragonal distortion of Octahedral Complexes (Jahn Teller Distortion)

The removal of degeneracy of the d-orbitals in a crystal field offers greater stability through crystal field stabilization energy. Sometimes further removal of degeneracy of the d-orbitals can also provide additional stability. Certain electron configurations with asymmetrical filling of degenerate d-orbitals of a metal ion results in unequal repulsion with incoming ligands. This facilitates such distortion in perfectly symmetric geometries. Practically, distortion in the regular octahedral geometry is observed when e_g orbitals which point directly at ligands, are asymmetrally filled. The t_{2g} orbitals do not point directly at ligands, asymmetrical filling of electrons in them does not give any observable distortion. Thus high spin $d^4(t_{2g}^3 e_g^1)$, low spin $d^7(t_{2g}^6 e_g^1)$ and $d^9(t_{2g}^6 e_g^3)$ configurations result in Jahn Teller distortion as e_g orbitals are asymmetrally filled. Among e_g orbitals, the electron in d_{z^2} experiences repulsion from two ligands but that in $d_{x^2-y^2}$ experiences repulsion from four ligands. Therefore, the electron tends to be present in d_{z^2} . Since the electron lies in d_{z^2} orbital the ligand approaching towards it, will be more repelled as compared to vacant $d_{x^2-y^2}$ orbital. Consequently, two of the bond lengths along Z-axis will be longer than the rest four. This is known as **tetragonal elongation or Z-out distortion**. On the other hand, if the electron is placed in $d_{x^2-y^2}$ orbital, reverse would occur and bond lengths along z axis are shorter than the rest four. This would result in **tetragonal compression or Z-in type of distortion**.

Jahn-Teller Theorem:

Any system which has a partially-filled degenerate set of orbitals will undergo a distortion to split that degeneracy and lower the **electronic** energy of the system.



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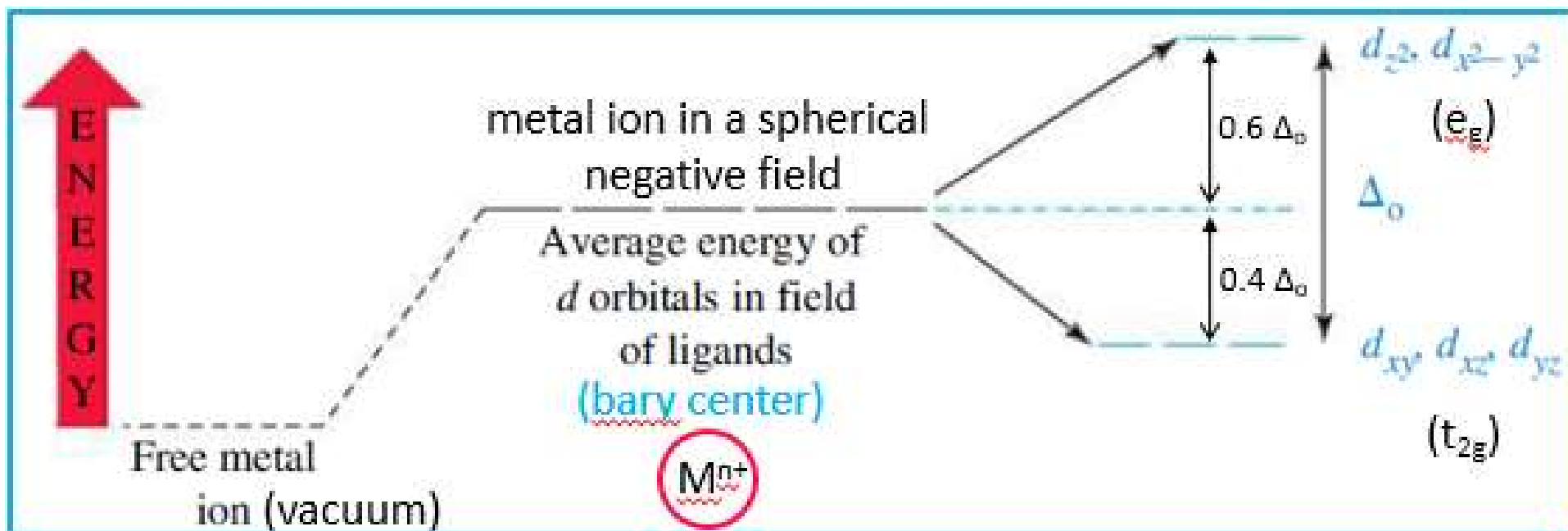
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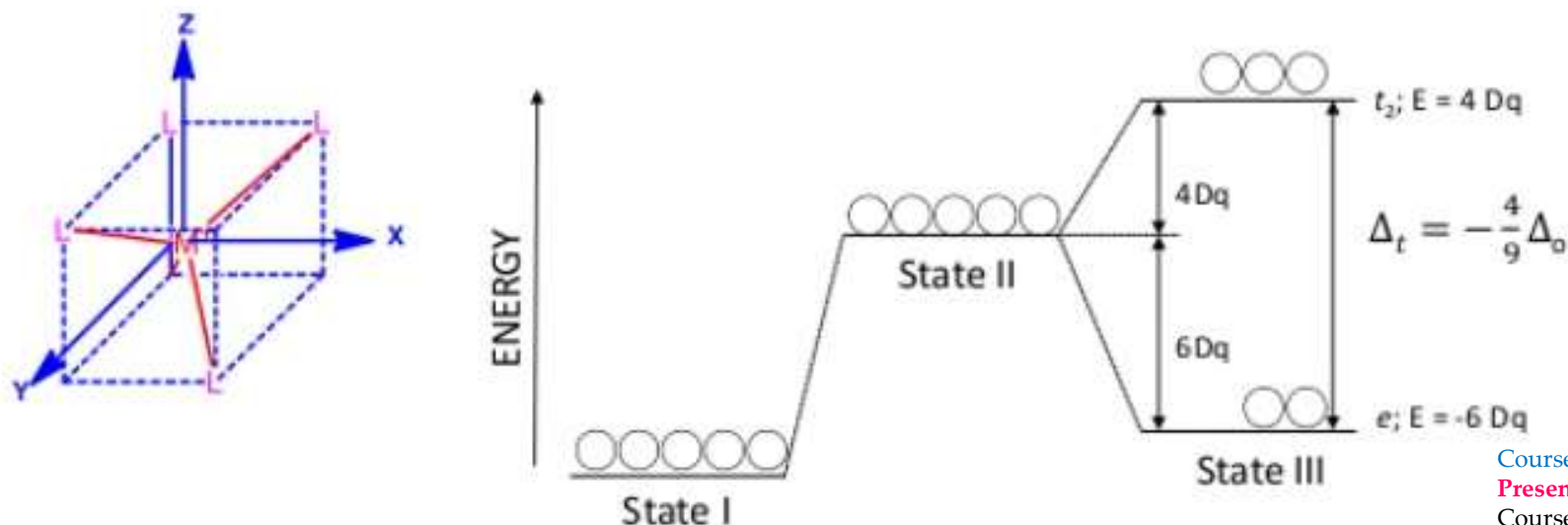
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Splitting of d energy levels in the formation of an octahedral complex ion



Crystal Field Splitting in Tetrahedral complexes



Tetrahedral complexes are always high spin since the splitting is appreciably smaller than P

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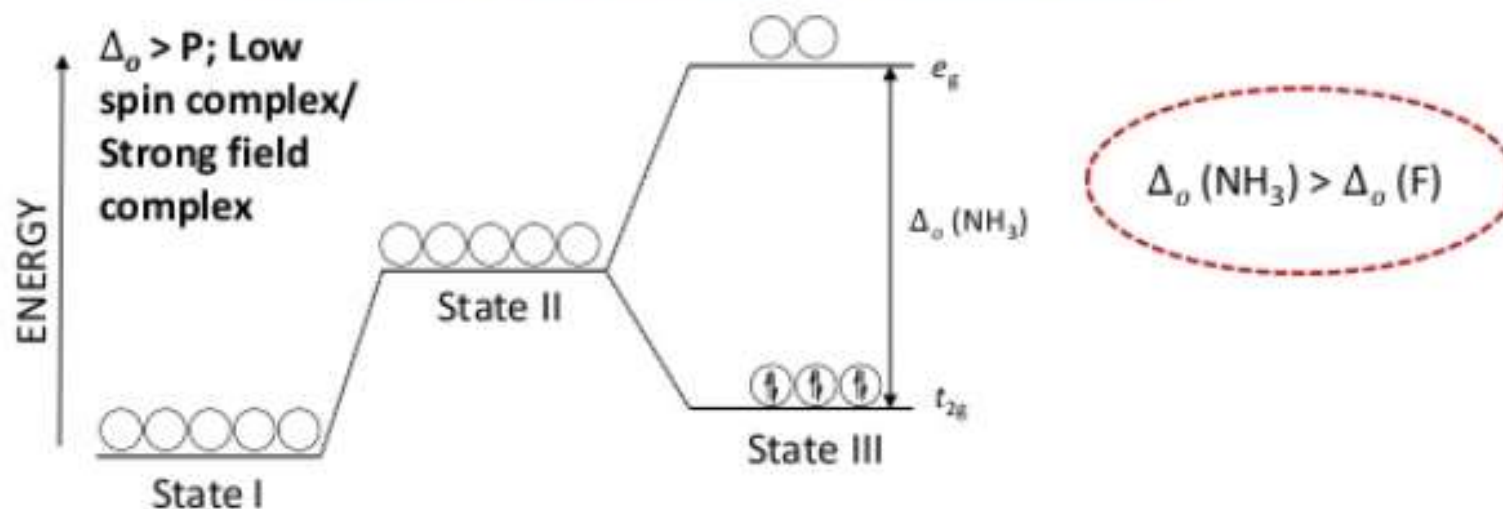
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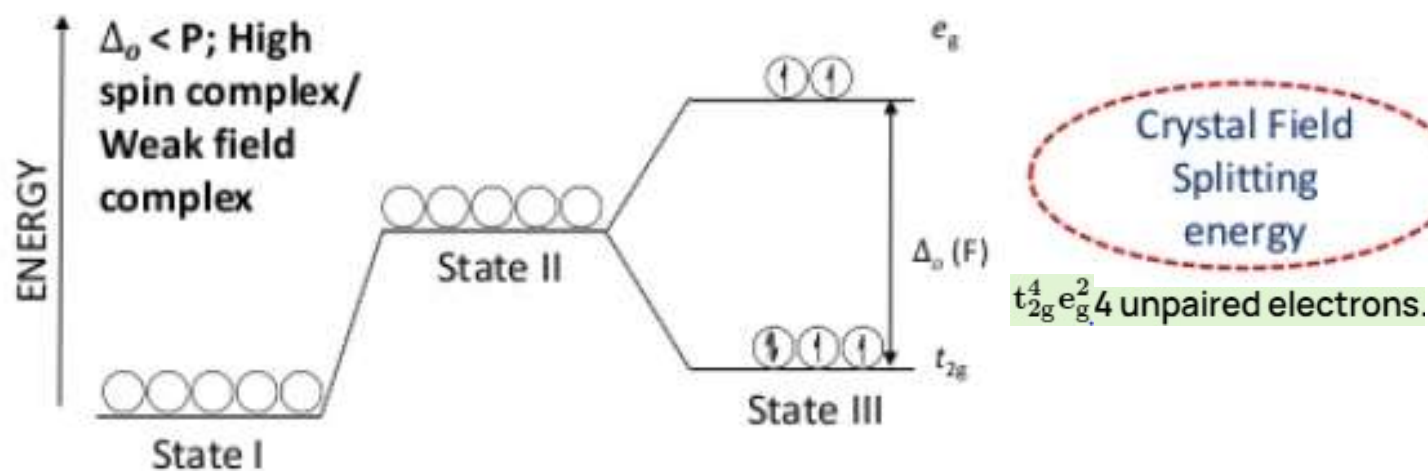
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Crystal Field Theory

$[\text{Co}(\text{NH}_3)_6]^{3+}$ C.N. = 6; O.S. = +3 (Diamagnetic)



$[\text{CoF}_6]^{3-}$ C.N. = 6; O.S. = +3 (Paramagnetic)



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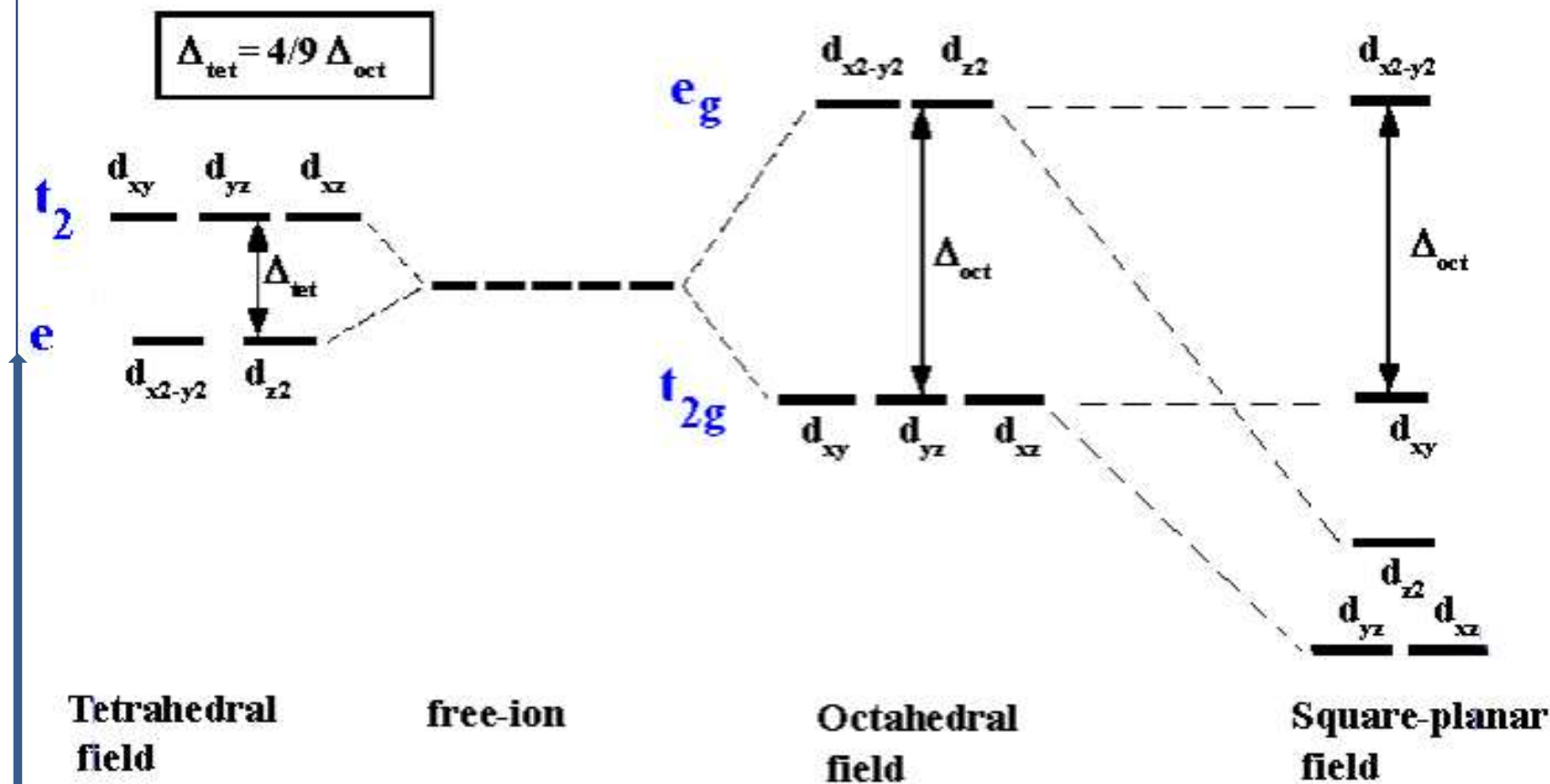
O_h

$$CFSE = n_{t_{2g}} \times (-0.4 \Delta_o) + n_{e_g} \times 0.6 \Delta_o$$

 T_d

$$CFSE = n_e \times (-0.6 \Delta_o) + n_{t_2} \times 0.4 \Delta_o$$

Energy levels of the d-orbitals in common stereochemistries

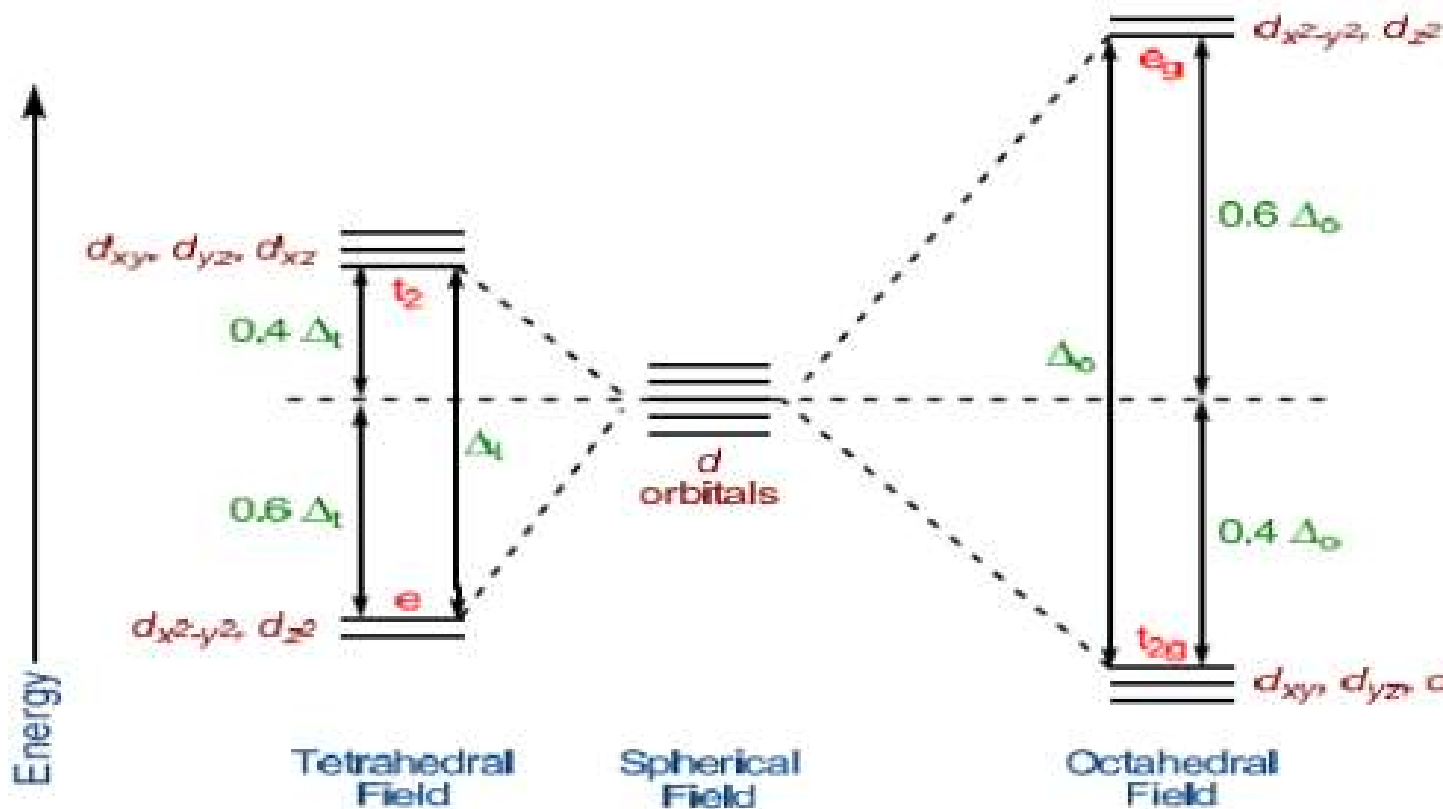
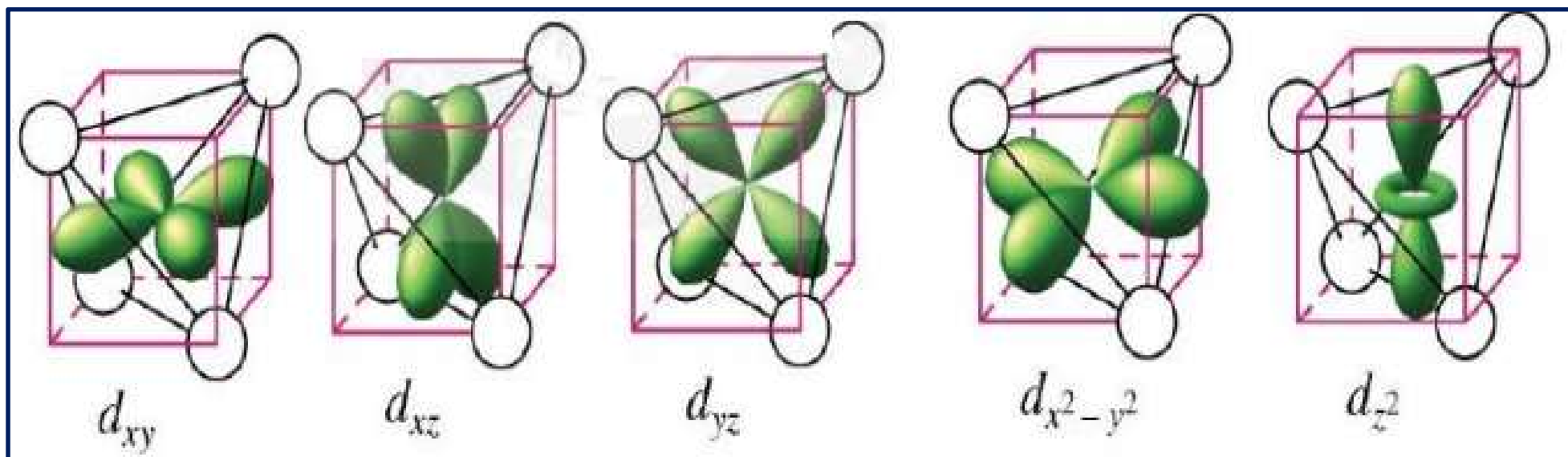


(Note that the orbitals are labelled t_2 and e , not t_{2g} and e_g ; g refers to a geometry, such as octahedral, that has a center of symmetry. The tetrahedral geometry has no center of symmetry)

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Tetrahedral (T_d) lacks a center of inversion



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Electron configurations in the weak and strong crystal field

d^n	octahedral				tetrahedral			
n	weak		strong		weak		strong	
	t_{2g}	e_g	t_{2g}	e_g	e	t_2	e	t_2
1	1	0	1	0	1	0	1	0
2	2	0	2	0	2	0	2	0
3	3	0	3	0	2	1	3	0
4	3	1	4	0	2	2	4	0
5	3	2	5	0	2	3	4	1
6	4	2	6	0	3	3	4	2
7	5	2	6	1	4	3	4	3
8	6	2	6	2	4	4	4	4
9	6	3	6	3	4	5	4	5
10	6	4	6	4	4	6	4	6

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Distribution of Electrons in an Octahedral Complex

	High-spin	CFSE	Low-spin	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4 \Delta_o$	$t_{2g}^1 e_g^0$	$-0.4 \Delta_o$
d^2	$t_{2g}^2 e_g^0$	$-0.8 \Delta_o$	$t_{2g}^2 e_g^0$	$-0.8 \Delta_o$
d^3	$t_{2g}^3 e_g^0$	$-1.2 \Delta_o$	$t_{2g}^3 e_g^0$	$-1.2 \Delta_o$
d^4	$t_{2g}^3 e_g^1$	$-0.6 \Delta_o$	$t_{2g}^4 e_g^0$	$-1.6 \Delta_o$
d^5	$t_{2g}^3 e_g^2$	$0.0 \Delta_o$	$t_{2g}^5 e_g^0$	$-2.0 \Delta_o$
d^6	$t_{2g}^4 e_g^2$	$-0.4 \Delta_o$	$t_{2g}^6 e_g^0$	$-2.4 \Delta_o$
d^7	$t_{2g}^5 e_g^2$	$-0.8 \Delta_o$	$t_{2g}^6 e_g^1$	$-1.8 \Delta_o$
d^8	$t_{2g}^6 e_g^2$	$-1.2 \Delta_o$	$t_{2g}^6 e_g^2$	$-1.2 \Delta_o$
d^9	$t_{2g}^6 e_g^3$	$-0.6 \Delta_o$	$t_{2g}^6 e_g^3$	$-0.6 \Delta_o$
d^{10}	$t_{2g}^6 e_g^4$	$-0.0 \Delta_o$	$t_{2g}^6 e_g^4$	$0.0 \Delta_o$

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Comparison of calculated spin-only magnetic moments with experimental data for some octahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Ti(III)	d1 ($t_{2g}1$)	$\sqrt{3} = 1.73$	1.6-1.7
V(III)	d2 ($t_{2g}2$)	$\sqrt{8} = 2.83$	2.7-2.9
Cr(III)	d3 ($t_{2g}3$)	$\sqrt{15} = 3.88$	3.7-3.9
Cr(II)	d4 high spin ($t_{2g}3 e_g 1$)	$\sqrt{24} = 4.90$	4.7-4.9
Cr(II)	d4 low spin ($t_{2g}4$)	$\sqrt{8} = 2.83$	3.2-3.3
Mn(II)/ Fe(III)	d5 high spin ($t_{2g}3 e_g 2$)	$\sqrt{35} = 5.92$	5.6-6.1
Mn(II)/ Fe(III)	d5 low spin ($t_{2g}5$)	$\sqrt{3} = 1.73$	1.8-2.1
Fe(II)	d6 high spin ($t_{2g}4 e_g 2$)	$\sqrt{24} = 4.90$	5.1-5.7
Co(III)	d6 low spin ($t_{2g}6$)	0	0
Co(II)	d7 high spin ($t_{2g}5 e_g 2$)	$\sqrt{15} = 3.88$	4.3-5.2
Co(II)	d7 low spin ($t_{2g}6 e_g 1$)	$\sqrt{3} = 1.73$	1.8
Ni(II)	d8 ($t_{2g}6 e_g 2$)	$\sqrt{8} = 2.83$	2.9-3.3
Cu(II)	d9 ($t_{2g}6 e_g 3$)	$\sqrt{3} = 1.73$	1.7-2.2

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Electronic configuration of some $n^+ d^n$ metal cations in octahedral complexes

Complex	Valence electrons	Unpaired electrons	Electron configuration	Spin configuration
$\text{Ti}(\text{H}_2\text{O})_6^{3+}$	$3d^1$	1	$(t_{2g})^1$	$(\uparrow)^1$
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	$3d^3$	3	$(t_{2g})^3$	$(\uparrow\uparrow\uparrow)^3$
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	$3d^5$	5	$(t_{2g})^3(e_g)^2$	$(\uparrow\uparrow\uparrow)\square\square\uparrow\uparrow\square$
$\text{Fe}(\text{CN})_6^{3-}$	$3d^5$	1	$(t_{2g})^5$	$(\uparrow\downarrow\uparrow\downarrow\uparrow)^5$
$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	$3d^6$	4	$(t_{2g})^4(e_g)^2$	$(\uparrow\downarrow\uparrow\uparrow)^4(\uparrow\uparrow)^2$
$\text{Fe}(\text{CN})_6^{2-}$	$3d^6$	0	$(t_{2g})^6$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6$
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	$3d^8$	2	$(t_{2g})^6(e_g)^2$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\uparrow)^2$
$\text{Cu}(\text{H}_2\text{O})_6^{2+}$	$3d^9$	1	$(t_{2g})^6(e_g)^3$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\downarrow\uparrow)^3$
$\text{Zn}(\text{H}_2\text{O})_6^{2+}$	$3d^{10}$	0	$(t_{2g})^6(e_g)^4$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\downarrow\uparrow\downarrow)^4$

Different ligands have different ability to split the d levels

- depends mainly on the degree of covalent interaction with the central atom

- increase of the ligand strength due to the π -backbonding (σ donors + π acceptors)

spectrochemical series – ordering of ligands according their strength

I^- , Br^- , Cl^- , SCN^- , F^- , $S_2O_3^{2-}$, CO_3^{2-} , OH^- , NO_3^- , SO_4^{2-} , H_2O , $C_2O_4^{2-}$, NO_2^- , NH_3 , C_5H_5N , en , NH_2OH^- , H^- , CH_3^- , $C_5H_5^-$, CO , CN^-

central atom $\Delta(3d) : \Delta(4d) : \Delta(5d) = 1 : 1.45 : 1.7$
 $\Delta(M^{2+}) : \Delta(M^{3+}) : \Delta(M^{4+}) = 1 : 1.6 : 1.9$

$$\Delta_o = f_{\text{ligand}} \times g_{\text{ion}}$$

I^-	0.72	NCS^-	1.02
Br^-	0.72	C_5H_5N	1.23
SCN^-	0.73	NH_3	1.25
Cl^-	0.78	en	1.28
NO_3^-	0.82	$dien$	1.30
F^-	0.90	NO_2^-	1.40
OH^-	0.94	CN^-	~1.7
$C_2O_4^{2-}$	0.98	CO	~1.7
H_2O	1.00		

Selection rule (Brief description of Laporte and Spin Selection rule)

Laporte or Orbital selection rule:

$\Delta l = \pm 1$: Only allowed transitions are those with change of parity: gerade (g) to ungerade (u) or vice versa or allowed but not $g \rightarrow g$ or $u \rightarrow u$. Since all the d orbitals have gerade symmetry in centrosymmetric molecules, this means that all $d-d$ transitions in octahedral complexes are formally forbidden. In Td complexes, there is no center of symmetry and thus orbitals have no g or u designation.

Spin selection rule

A second selection rule states that any transition for which $\Delta S \neq 0$ is forbidden and $\Delta S = 0$ is allowed.

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Selection Rules

Selection rules determine the intensity of electronic transitions
(intensity ~ allowedness)

Spin Selection Rule

$$\Delta S = 0$$

There must be no change in spin multiplicity during an electronic transition
(for light elements where S is a “good” QN).

Symmetry (a.k.a. Laporte) Selection Rule (essentially dipole change requirement)

$$\Delta l = \pm 1$$

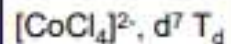
For centrosymmetric systems
there must be a change in parity during an electronic transition: i.e.,



Basically, d-d transitions are forbidden for octahedral complexes.
There must be a change in dipole moment during an electronic transition.

Relaxation of the Laporte Selection Rule Tetrahedral vs. Octahedral Complexes

No inversion center in T_d , therefore no ungerade vs. gerade



Spin-allowed;
Laporte-allowed



Spin-allowed;
Laporte-forbidden

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Selection rules for Charge-Transfer (CT) Bands

CT transitions are spin-allowed and symmetry-allowed

Transitions occur from a singlet G.S. to a singlet E.S.:
 $\Delta S = 0$

Transitions occur between metal based orbitals with d -character and ligand based orbitals with p -character:
 $\Delta l = \pm 1$

allowed CT transitions can therefore be much more intense than $d-d$ transitions.

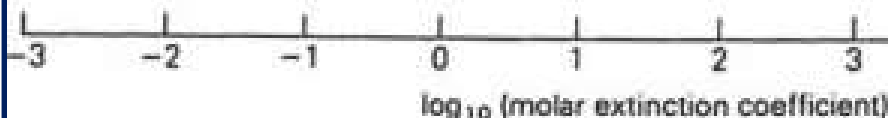
Selection Rules

spin forbidden
Laporte forbidden
 d^5 ions, e.g. $[\text{Mn}(\text{OH}_2)_6]^{2+}$

spin allowed
Laporte forbidden
e.g. $[\text{Ni}(\text{OH}_2)_6]^{2+}$

spin allowed; Laporte forbidden
tetrahedral complexes
e.g. NiCl_4^{2-}

charge transfer
spin allowed; Laporte allowed
e.g. MnO_4^-

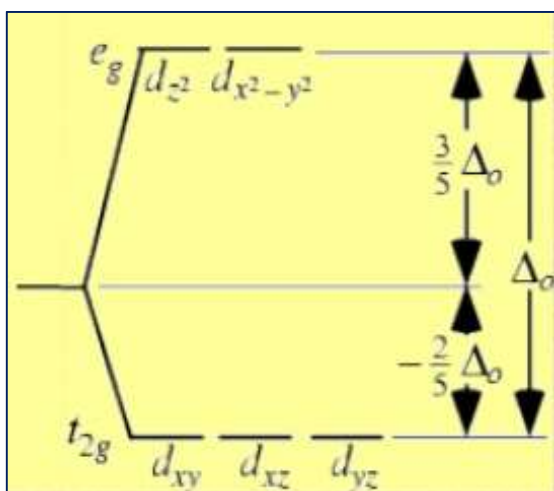


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	$K_3[Fe(oxalate)_3] \cdot 3H_2O$	$K_2[CuCl_4]$
metal ion	Fe^{3+}	Cu^{2+}
number of d electrons	$5 - t_{2g}^3 e_g^2$	$9 - e^4 t_2^5$
stereochemistry	octahedral	tetrahedral
High Spin/Low Spin	High Spin	Not relevant (all High spin)
# of unpaired electrons	5	1
magnetic moment	$\sqrt{35}$ B.M	$\sqrt{3}$ B.M

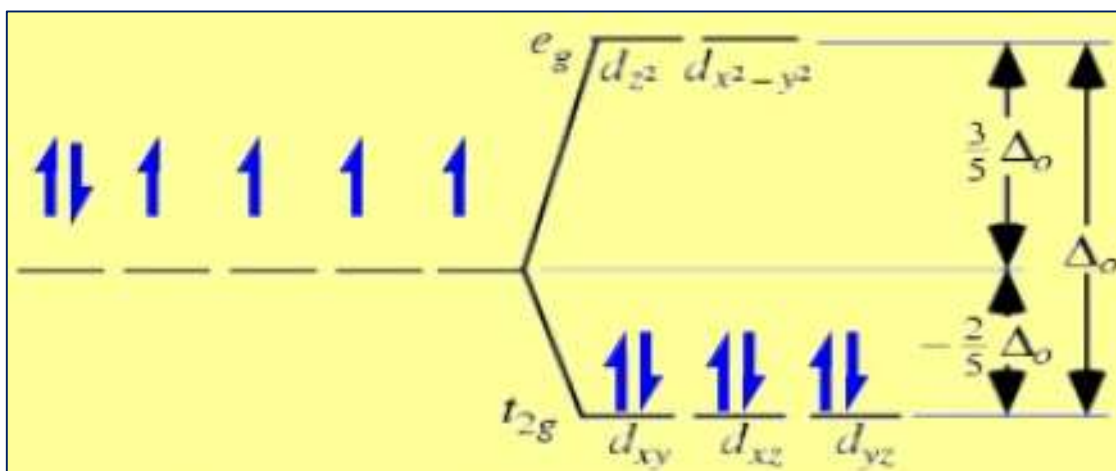


$$\mu = \sqrt{4S(S+1)} \quad \text{Bohr Magnetons (BM)}$$

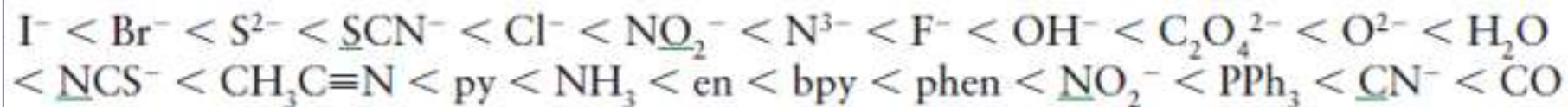
where S is the spin quantum number (1/2 for each unpaired electron)

$$\mu = \sqrt{4S(S+1)} \quad \text{Bohr Magnetons (BM)}$$

where S is the spin quantum number (1/2 for each unpaired electron).



Spectrochemical Series



weak field ligands
→
 increasing Δ_o
←
 strong field ligands

- Ligands with the same donor atoms are close together in the series.
- Ligands up to H_2O are weak-field ligands and tend to result in high-spin complexes.
- Ligands beyond H_2O are strong-field ligands and tend to result in low-spin complexes.

Factors affecting the magnitude of crystal field splitting

Nature of Ligands: large negative charge, small size, good sigma donor and pi acceptors

Oxidation state of the metal: higher for higher oxidation state

Size of d orbitals: $5d > 4d > 3d$

Geometry of the complex: Crystal field splitting energy in octahedral

Complexes will always be more than the tetrahedral complexes



increasing Δ

- This trend is independent of ligand

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Octahedral splitting = Δ_o is larger for

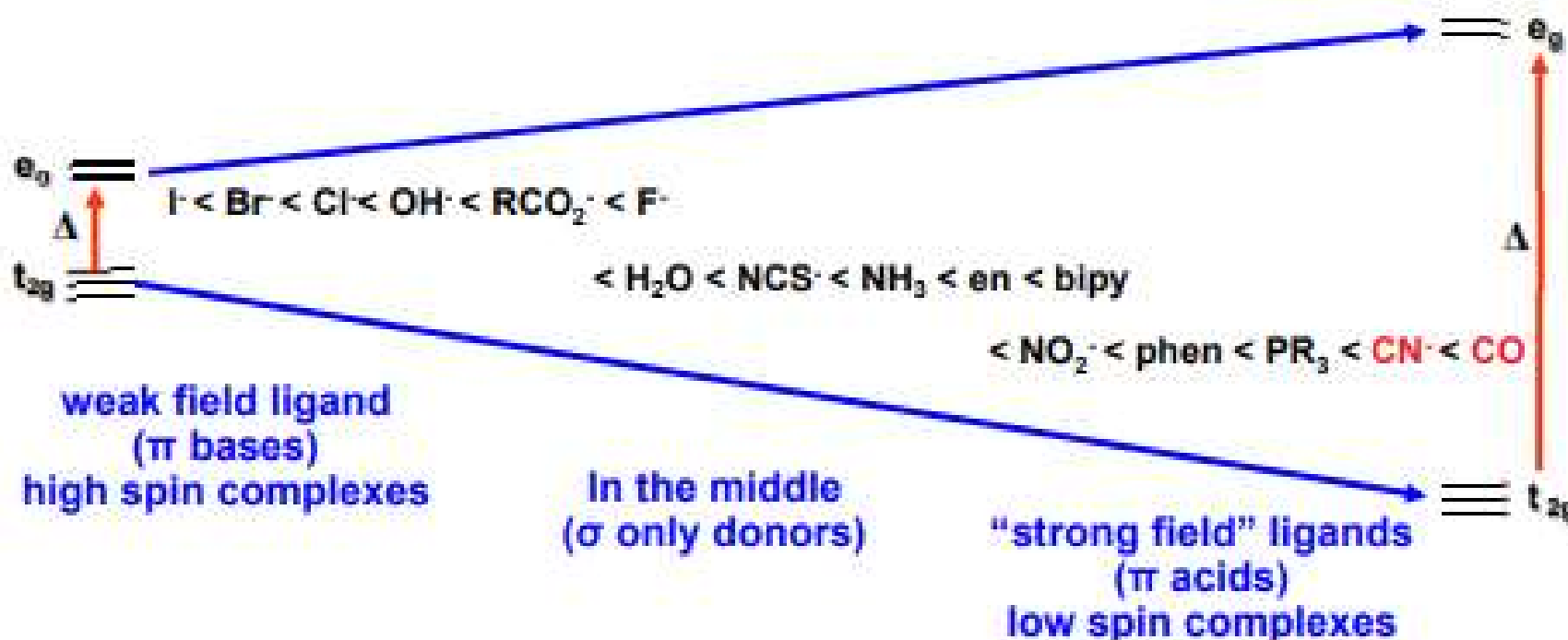
- High metal ion charge
- Ligands with strong σ donation
- Ligands with weak π donation
- Ligands with strong π acceptance
- 2nd & 3rd Row T.M.

Three kinds of Ligands:

1. Non- π σ -donors (i.e., σ bases)
2. π -donors (i.e., π -bases)
3. π -acceptors (i.e., π -acids)

π interaction < σ interaction
 π interaction = 0 for non- π bonding ligands (e.g. NH_3)

BOTH are ALSO σ -donors



CN^- leads to large splitting (big Δ):
 Highly basic: raises energy of e_g levels.
 π -bonding: lowers energy of t_{2g} orbitals, π -back bonding.

In contrast, consider CO:

little σ basicity (not protonated) – mostly π -back bonding effect (i.e., lowers t_{2g} orbitals a lot)

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Crystal Field Stabilization Energy: High & Low Spin Octahedral Complexes

▪ **Electron-pairing energy (P):** Energy required to change two electrons with parallel spin in different degenerate orbitals into spin-paired electrons in the same orbital.

▪ **Two terms** contribute to pairing energy:

a) **loss in the exchange energy** which occurs upon pairing the electrons.

b) **Coulombic repulsion** between the spin-paired electrons.

▪ **CFSE for $(t_{2g})^x(e_g)^y$ configuration = $(0.4x - 0.6y)\Delta_o - pP$** (considering pairing energy)

p = total number of electron pairs compared to corresponding high-spin configuration; P = mean pairing energy

Free Ion	CFSE	
	High Spin	Low Spin
d^4	$0.6\Delta_o$	$1.6\Delta_o - P$
d^5	$0\Delta_o$	$2.0\Delta_o - 2P$
d^6	$0.4\Delta_o$	$2.4\Delta_o - 2P$
d^7	$0.8\Delta_o$	$1.8\Delta_o - P$

▪ CFT can not explain why certain anionic ligands lies lower in the series than neutral ligands, although reverse should be expected based on electrostatic interactions.

▪ It also can not explain why OH^- lies lower in the series than H_2O and NH_3 , although reverse should be expected, since dipole moment of OH^- is greater than H_2O and NH_3 .

d Orbitals in a Tetrahedral Ligand Field

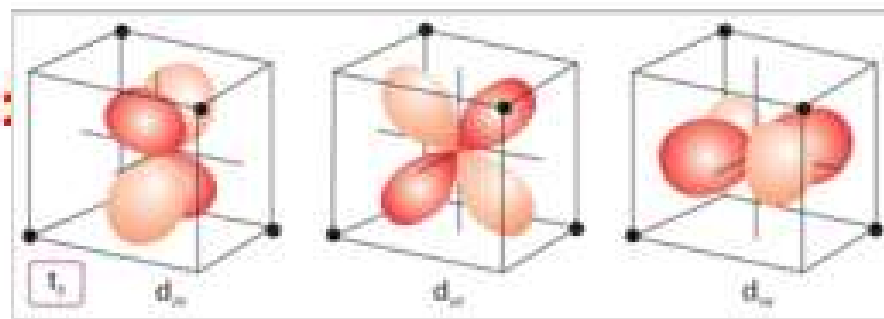
consider d-orbitals in a tetrahedral complex:
i.e., an tetrahedral “Ligand Field”.

The 4 ligands are put on corners of cube (black dots below)

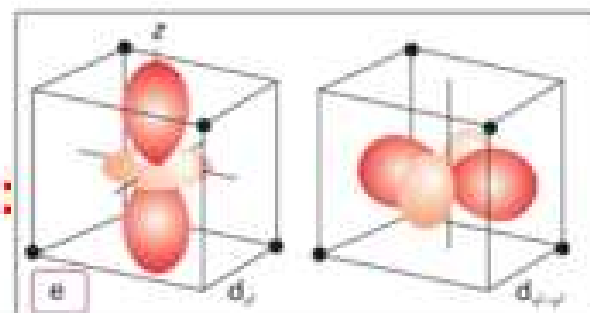
Three d-orbitals are pointing right at the ligands (anti-bonding).

Two d-orbitals are pointing in-between ligands (nonbonding).

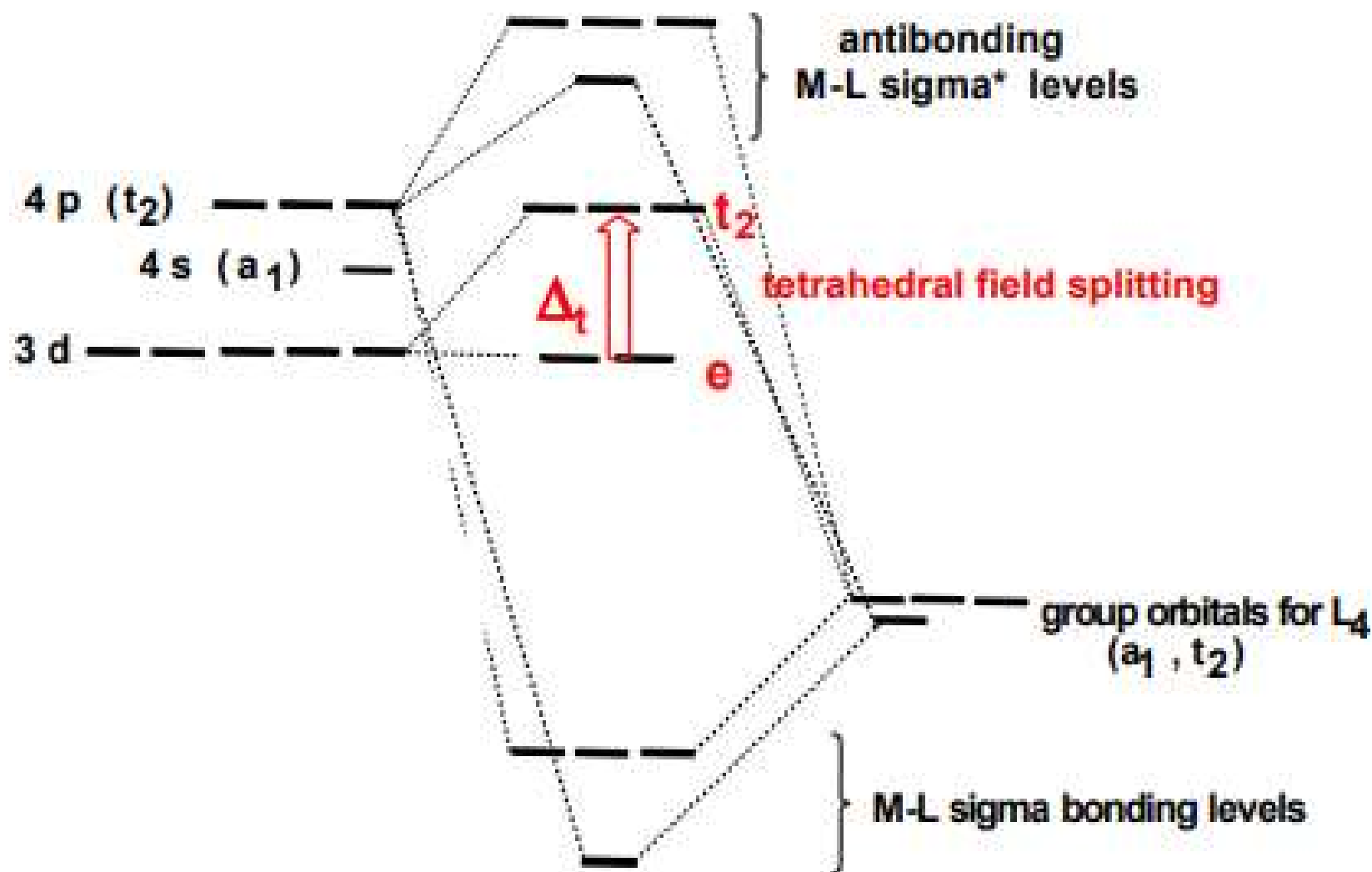
Antibonding d:



Nonbonding d:



The Tetrahedral *Ligand* Field M.O.s



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Types of Electronic Transitions in TM Complexes

d-d: usually in the visible region
relatively weak, $\epsilon \sim 1 - 100$ if spin allowed
 < 0.1 if spin forbidden
energy varies with Δ_o (or Δ_t)

LMCT: Ligand to Metal Charge Transfer
 $\sigma_L \text{ or } \pi_L \xrightarrow{h\nu} d^*$
very intense, generally in UV or near UV

MLCT: Metal to Ligand Charge Transfer
 $d^* \xrightarrow{h\nu} \pi_L$
very intense ($\epsilon \sim 100 - 10,000$)
needs π -acceptor Ligand (CO, CN^- , ...)

LL: Ligand to Ligand
 $\pi_L \xrightarrow{h\nu} \pi_L^*$
very intense ($\epsilon \sim 100 - 10,000$)

Rydberg: localized MO $\xrightarrow{h\nu}$ high energy,
highly delocalized, deep UV

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Tetrahedral Complexes



Why almost all tetrahedral complexes are high spin:

- There are only 4 ligands in the tetrahedral complex and hence the ligand field is roughly $2/3$ of the octahedral field.
- The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of $2/3$. Therefore Δ_t is roughly $2/3 \times 2/3 = 4/9$ of Δ_o .
- As a result, all tetrahedral complexes are **high-spin** since the Δ_t is normally smaller than the pairing energy. Hence, low spin configurations are rarely observed. Usually, if a very strong field ligand is present, **square planar** geometry will be favored.

When to expect tetrahedral geometry:

- Small metal ions and large ligands (Cl^- , Br^- and I^-) because then ligand-ligand repulsions cancel the energy advantage of forming more metal-ligand bonds.
- Metal ions with zero CFSE (d^0 , d^5 , d^{10}) or small CFSE (d^2 and d^7).
- **Examples:** MnO_4^- (d^0), FeCl_4^- (d^5 , h.s.), CoCl_4^{2-} (d^7 , h.s.), ZnCl_4^{2-} (d^{10})

Charge Transfer Transitions

d^0 and d^{10} ions have no d-d transitions, BUT often still colored.

Zn^{2+}	d^{10} ion	colorless
TiF_4	d^0 ion	white
$TiCl_4$	d^0 ion	white
$TiBr_4$	d^0 ion	orange
TiI_4	d^0 ion	dark brown
$[MnO_4]^-$	Mn(VII) d^0 ion	intensely purple
$[Cr_2O_7]^-$	Cr(VI) d^0 ion	bright orange
$[Cu(MeCN)_4]^+$	Cu(I) d^{10} ion	colorless
$[Cu(phen)_2]^+$	Cu(I) d^{10} ion	dark orange

These colors come from excitation of electrons from M-centered orbitals to Ligand-centered orbitals (or the reverse). MLCT and LMCT.

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