Unit II: COORDINATION CHEMISTRY

By

Dr. Ramesh S. Vadavi

References

1. Inorganic Chemistry by C. E. Housecroft and A. G. Sharpe, 3rd / 4th Edition.
2. Inorganic Chemistry by Miessler, Fischer and Tarr, 5th Edition
3. Inorganic Chemistry Principles of Structure and Reactivity by Huheey , Keiter and Keiter, 4th Edition.
4. Advanced Inorganic Chemistry by Cotton and Wilkinson, 3rd Edition
5. Fundamental Concepts of Inorganic Chemistry by A. K. Das and Mahua Das, Vol 4.

Addition Compounds

- These are the compounds formed when stoichiometric amounts of two or more stable compounds join together.

$$KCl + MgCl_2 + 6H_2O \rightarrow KCl \cdot MgCl_2 \cdot 6H_2O$$

(carnallite)

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

(potassium alum)

$$CuSO_4 + 4NH_3 + H_2O \rightarrow CuSO_4 \cdot 4NH_3 \cdot H_2O$$

(tetrammine copper(II) sulphate monhydrate)

$$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2 \cdot 4KCN$$

(potassium ferrocyanide)

- Addition compounds are of two types

1. **Double salts:** The constituent ions **do not lose their parental identity** when dissolved in water.
2. **Complex compounds:** The constituent ions **lose their parental identity** when dissolved in water.

Werner's Theory

Basic Postulates

1. Metal center exhibits two types valence: Primary and secondary
2. Primary valence is the oxidation state of the metal ion and it is satisfied by negatively charged species.
3. Primary valances are ionizable and omnidirectional.
4. The number of Secondary valences is equal to the coordination number of central metal ion and are satisfied usually by negatively charged species or neutral molecules (rarely by +ve ions such as NO^+) .
5. Secondary valences are usually nonionizable and are directed in space and these give definite geometrical shape for the complex compound.

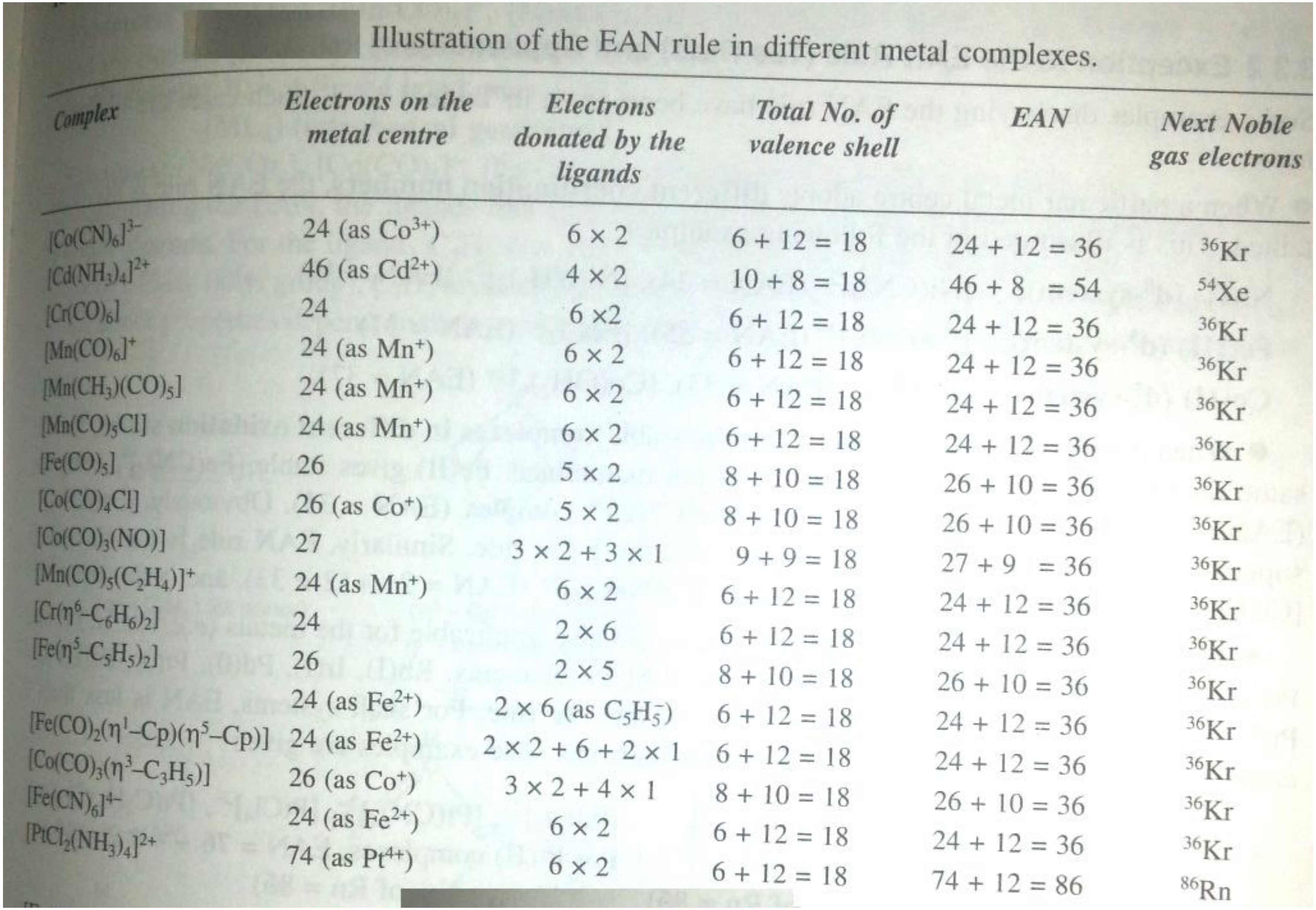
Ex: $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$, $[PtCl_2(NH_3)_4]Cl_2$

Defects of Werner's theory

1. Nature of bonding: It can not explain the nature of bonding, i.e. metal-ligand interaction within the coordination sphere.
2. It can not explain magnetic properties, spectral properties, thermodynamic stabilities, kinetic stabilities of the complexes
3. Werner could not explain the preference among the certain coordination numbers for a particular metal ion. For exmaple $[CoCl_4]^{2-}$, $[Co(H_2O)_6]^{2+}$, $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_6]^{2+}$ etc.

Effective Atomic number Rule: The 18 electron rule.

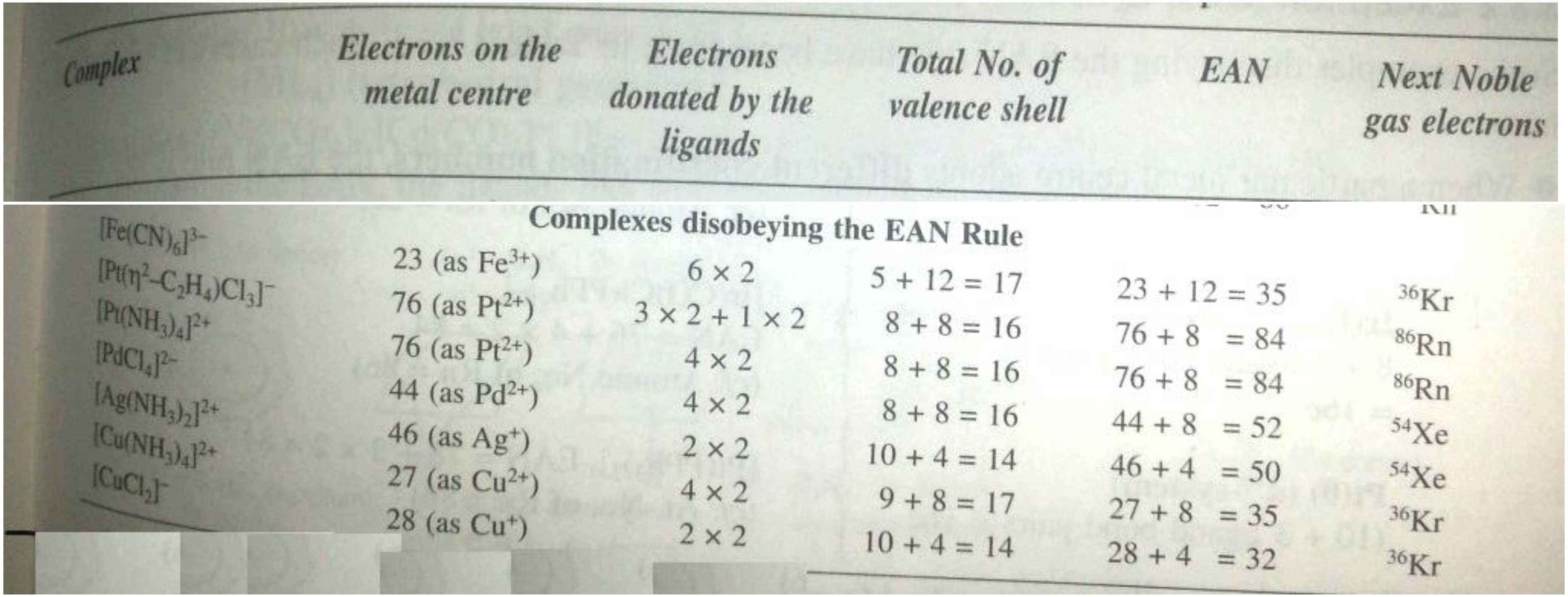
- This rule is proposed by Sidgwick.
- EAN rule states that the ligands donate the electrons to the central metal ion **through the covalent-coordinate bond** and the total number of electrons on the central metal ion including those gained from the ligands is the atomic number of the nearest noble gas.
- For the transition metal complexes, this corresponds to the filling of (n-1)d, ns and np orbitals of the central metal. **These nine valence orbitals can accommodate 18 electrons**. So EAN rule is also referred to as **18-electron rule**.



[redacted] Illustration of the EAN rule in different metal complexes.

Complex	*Electrons on the metal centre*	*Electrons donated by the ligands*	*Total No. of valence shell*	*EAN*	*Next Noble gas electrons*
$[Co(CN)_6]^{3-}$	24 (as Co^{3+})	6 × 2	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Cd(NH_3)_4]^{2+}$	46 (as Cd^{2+})	4 × 2	10 + 8 = 18	46 + 8 = 54	^{54}Xe
$[Cr(CO)_6]$	24	6 ×2	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Mn(CO)_6]^+$	24 (as Mn^+)	6 × 2	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Mn(CH_3)(CO)_5]$	24 (as Mn^+)	6 × 2	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Mn(CO)_5Cl]$	24 (as Mn^+)	6 × 2	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Fe(CO)_5]$	26	5 × 2	8 + 10 = 18	26 + 10 = 36	^{36}Kr
$[Co(CO)_4Cl]$	26 (as Co^+)	5 × 2	8 + 10 = 18	26 + 10 = 36	^{36}Kr
$[Co(CO)_3(NO)]$	27	3 × 2 + 3 × 1	9 + 9 = 18	27 + 9 = 36	^{36}Kr
$[Mn(CO)_5(C_2H_4)]^+$	24 (as Mn^+)	6 × 2	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Cr(\eta^6\text{–}C_6H_6)_2]$	24	2 × 6	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Fe(\eta^5\text{–}C_5H_5)_2]$	26	2 × 5	8 + 10 = 18	26 + 10 = 36	^{36}Kr
	24 (as Fe^{2+})	2 × 6 (as $C_5H_5^-$)	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Fe(CO)_2(\eta^1\text{–}Cp)(\eta^5\text{–}Cp)]$	24 (as Fe^{2+})	2 × 2 + 6 + 2 × 1	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[Co(CO)_3(\eta^3\text{–}C_3H_5)]$	26 (as Co^+)	3 × 2 + 4 × 1	8 + 10 = 18	26 + 10 = 36	^{36}Kr
$[Fe(CN)_6]^{4-}$	24 (as Fe^{2+})	6 × 2	6 + 12 = 18	24 + 12 = 36	^{36}Kr
$[PtCl_2(NH_3)_4]^{2+}$	74 (as Pt^{4+})	6 × 2	6 + 12 = 18	74 + 12 = 86	^{86}Rn

[redacted]



Complex	Electrons on the metal centre	Electrons donated by the ligands	Total No. of valence shell	EAN	Next Noble gas electrons
Complexes disobeying the EAN Rule					
$[Fe(CN)_6]^{3-}$	23 (as Fe^{3+})	6 × 2	5 + 12 = 17	23 + 12 = 35	^{36}Kr
$[Pt(\eta^2\text{-}C_2H_4)Cl_3]^-$	76 (as Pt^{2+})	3 × 2 + 1 × 2	8 + 8 = 16	76 + 8 = 84	^{86}Rn
$[Pt(NH_3)_4]^{2+}$	76 (as Pt^{2+})	4 × 2	8 + 8 = 16	76 + 8 = 84	^{86}Rn
$[PdCl_4]^{2-}$	44 (as Pd^{2+})	4 × 2	8 + 8 = 16	44 + 8 = 52	^{54}Xe
$[Ag(NH_3)_2]^{2+}$	46 (as Ag^+)	2 × 2	10 + 4 = 14	46 + 4 = 50	^{54}Xe
$[Cu(NH_3)_4]^{2+}$	27 (as Cu^{2+})	4 × 2	9 + 8 = 17	27 + 8 = 35	^{36}Kr
$[CuCl_2]^-$	28 (as Cu^+)	2 × 2	10 + 4 = 14	28 + 4 = 32	^{36}Kr

Limitation of the EAN rule

1. When a particular metal center adopts different coordination numbers, the EAN rule is not maintained. Ex: $[Ni(CN)_4]^{2-}$, $[Ni(H_2O)_6]^{2+}$ $[Fe(CN)_6]^{3-}$, $[Co(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$.
2. When a particular metal center forms the stable complexes in different oxidation states for the same coordination number, the EAN rule is not maintained. Ex: $[Fe(CN)_6]^{2-}$ and $[Fe(CN)_6]^{3-}$, $[Cr(CO)_6]$ and $[Cr(NH_3)_6]^{3+}$.

Bonding Theories

- Valence Bond Theory
- Crystal Field Theory
- Molecular Orbital Theory

Valence bond theory

Assumptions

1. The appropriate metal orbitals (s, p, d) of the central metal hybridize to give an equal number of new orbitals of equal energy, called **hybrid orbitals** and these are directed towards the ligand positions according to the geometry of the complex.
2. **The d-orbitals involved in this process may be inner d-orbitals (n-1) or outer d-orbitals (nd).**
3. Each ligand orbital has at least one orbital containing a lone pair of electron.
4. The empty hybrid orbitals of the metal ion overlap with fully filled orbitals of the ligand forming ligand-metal coordinate bond.

Important features of VBT

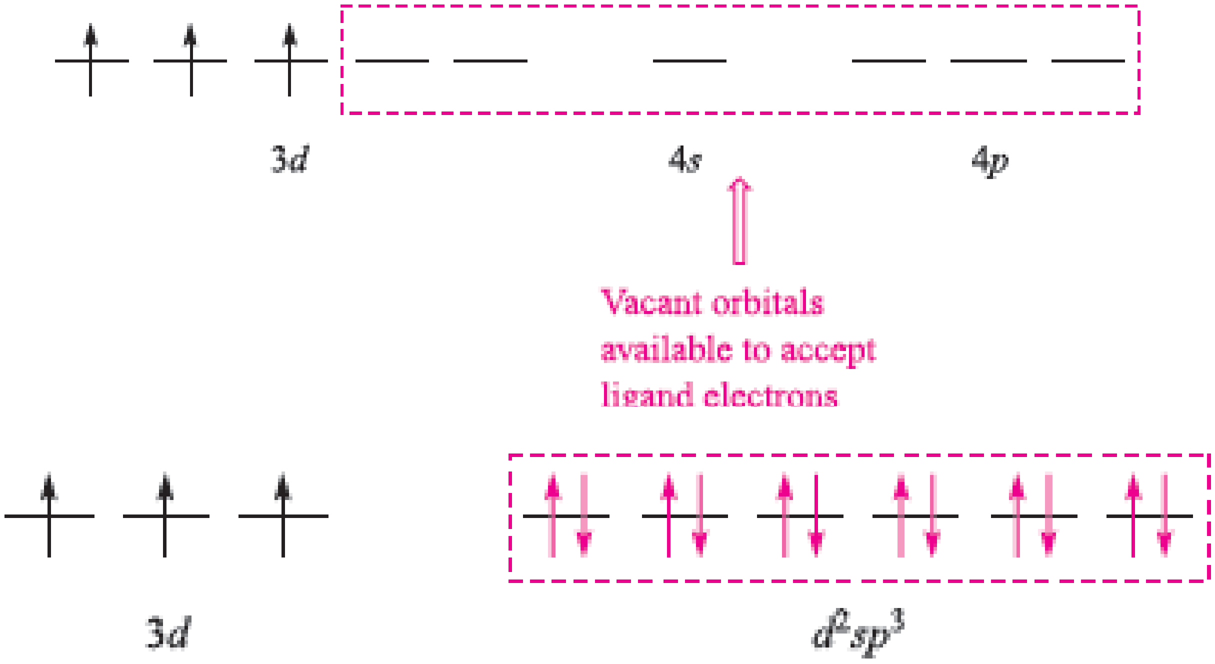
- **Geometry of the complexes:** The mode of hybridization of the central atom determines the geometry of the complexes.

For example:
1. d^2sp^3 or sp^3d^2 hybridization; **octahedral geometry**
2. dsp^2 hybridization : **square planar geometry**
3. sp^3 or sd^3hybridization: **tetrahedral geometry**
4. dsp^3 or sp^3d hybridization : **TBP or Square pyramid**
5. sp hybridization : **linear geometry**
6. sp^2 hybridization: **trigonal planar**

- **Coordination number:** It is given by number of vacant hybrid orbitals available for receiving the electrons from the ligands.
- **Outer and inner orbital complexes**

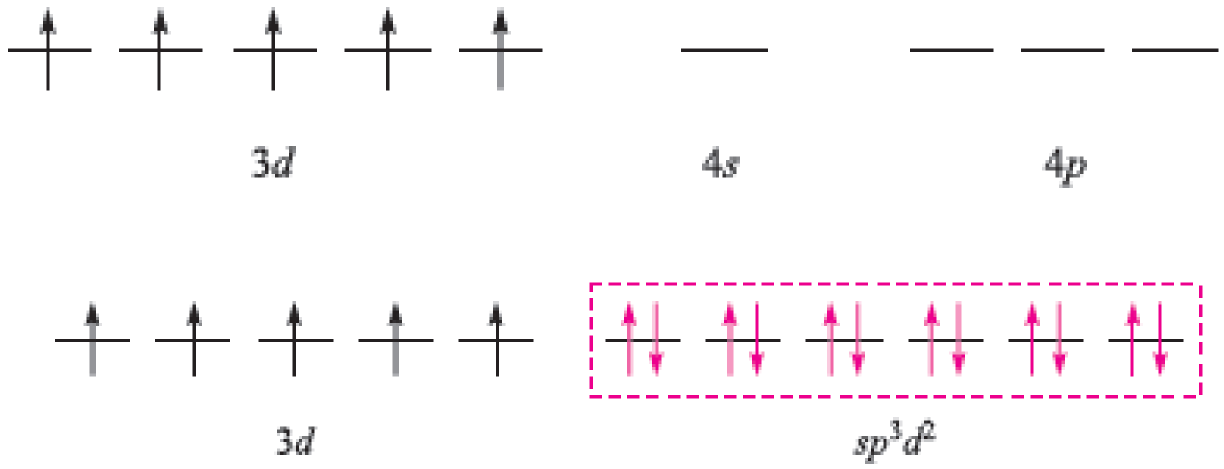
- Examples

1. $[Cr(H_2O)_6]^{3+}$



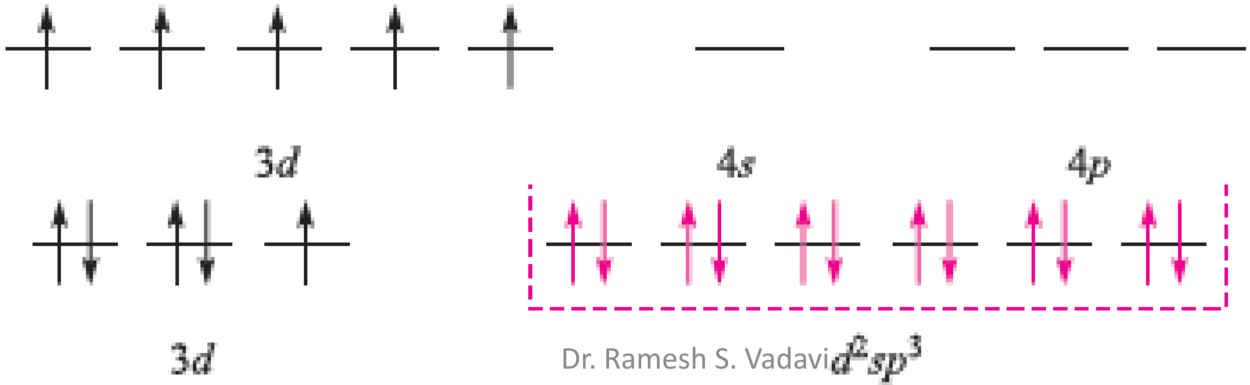
Inner 3d

2. Octahedral Fe(III) complex (H. S.) $[FeF_6]^{3-}$



Outer 4-d

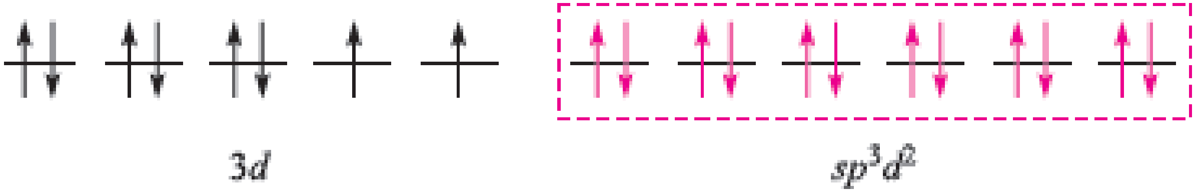
3. Octahedral Fe(III) complex (L. S.) $[Fe(CN)_6]^{3-}$



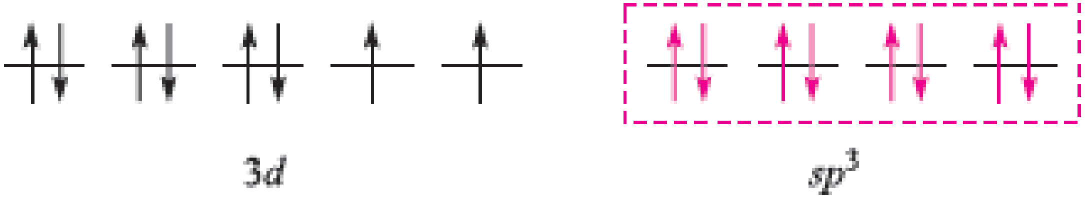
Inner 3-d

4. Ni(II) forms Octahedral, tetrahedral and Square planar complexes

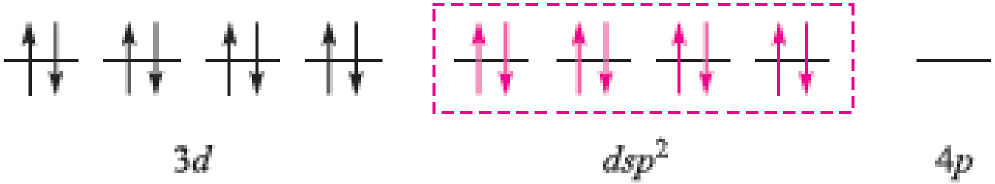
Octahedral:



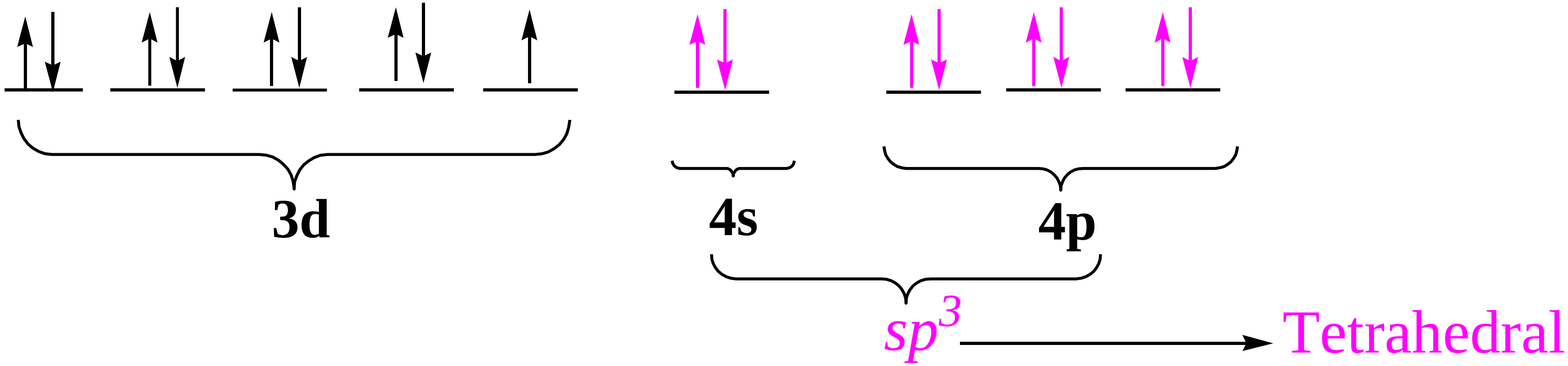
Tetrahedral:



Square planar



5. Cu(II) Complex; Ex: $[Cu(gly)_2]$, where gly = glycinate



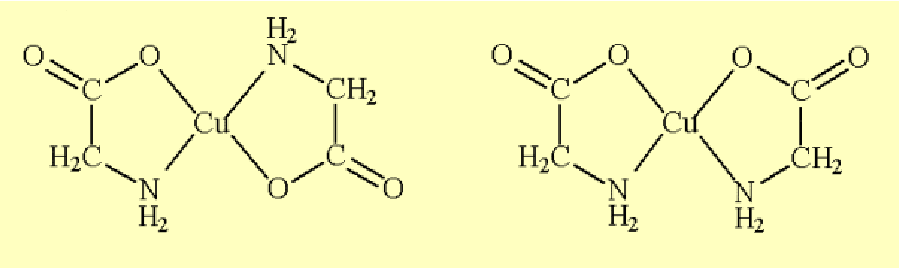
3d

4s

4p

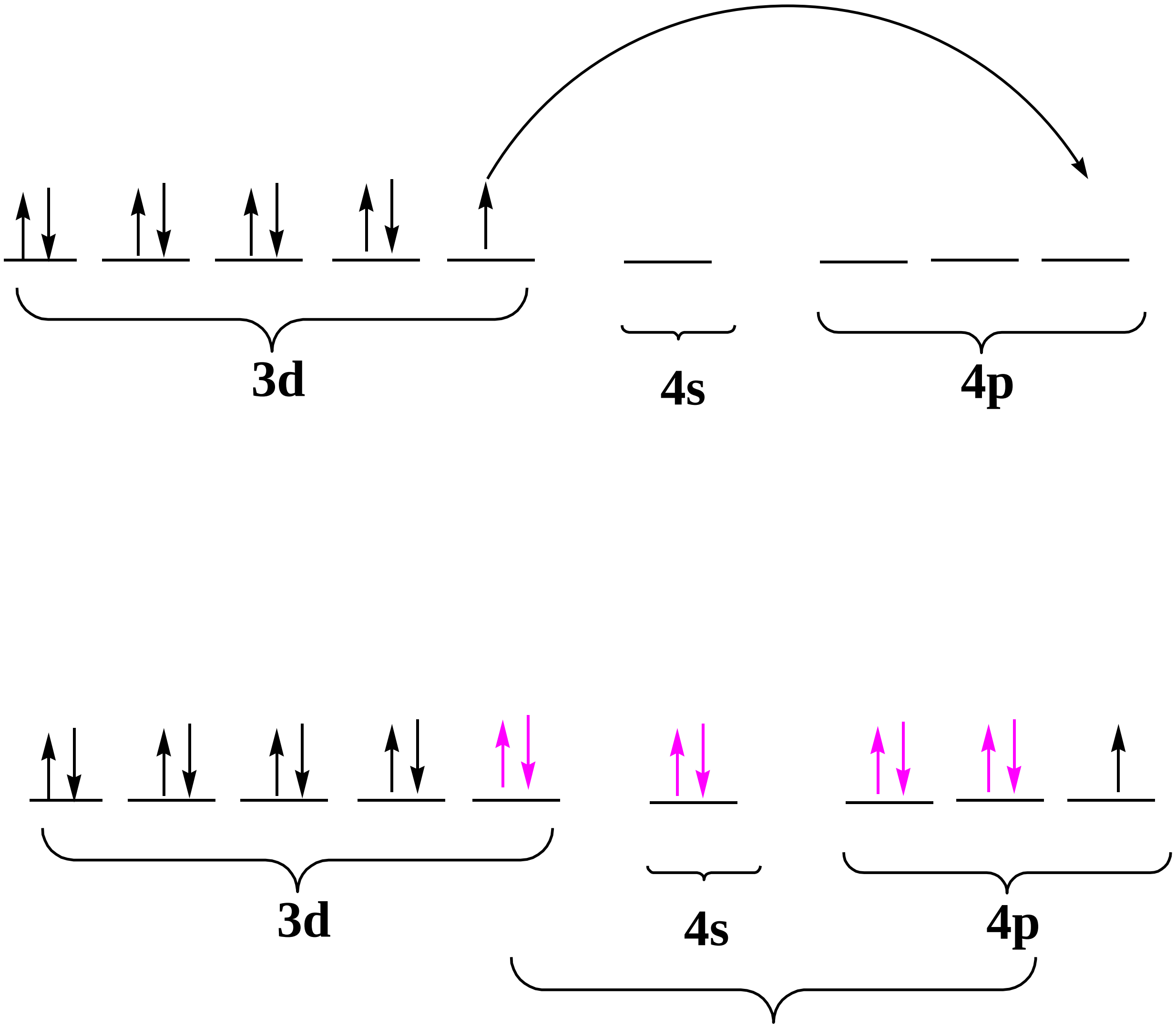
$sp^3 \longrightarrow$ Tetrahedral

What is the Structure of the complex ?



Ans. **Square Planar**

To adopt square Planar geometry, Cu(II) should undergo ***dsp^2*** hybridization.



dsp^2 → Square Planar

Shortcomings of VBT

1. No explanation for the formation of L.S. or H.S. complexes
2. According to VBT, the square planar complexes of Cu(II), utilize dsp^2 hybridized orbitals for bonding with the ligands. For this purpose transfer of an unpaired 3d electron to higher energy 4p orbital is essential. But **ESR spectra reveals that unpaired electron resides in the d orbital**.
3. **Colour of the complexes** could not explained.
4. Magnetic moment as predicted by VBT is due to spin moment of the electron. **So VBT did not consider the magnetic moment due to the orbital motion of the electron.**

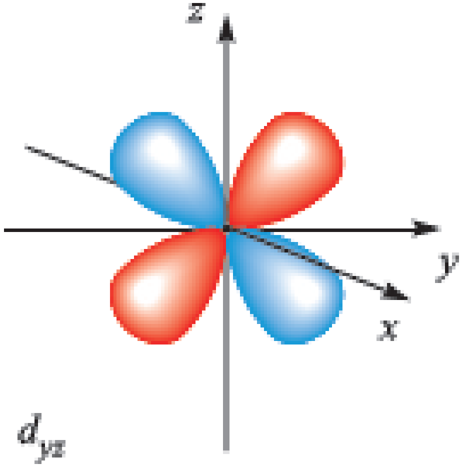
Crystal Field Theory (CFT)

- Crystal field theory is an electrostatic model and was first proposed by Bethe (in 1929) to explain the colour and magnetic properties of crystalline solids of metal salts. It was further modified by van Vleck (in 1935) to account for the magnetic properties of transition metal complexes.

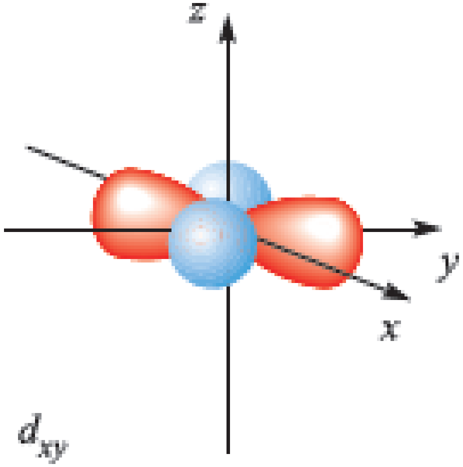
Assumptions

1. Ligands are treated as point negative charges or dipoles which are attracted to the positively charged metal.
2. No covalent interaction between metal and ligand orbitals.
3. The d orbitals on the metal are degenerate in the free atom/ion. However, when ligand approaches the metal, degeneracy will be destroyed. The pattern of splitting of the d orbitals depends on the crystal field and this being determined by the arrangement and type of ligands.
4. The (negatively charged) electrons of the metal and the negative end of ligands repel each other.

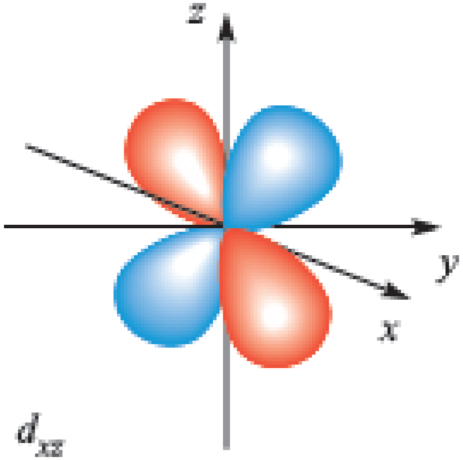
Shapes of d orbitals



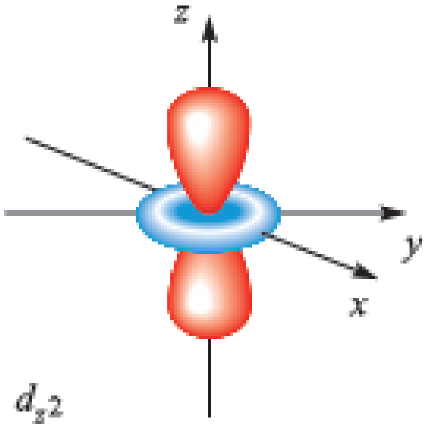
d_{yz}



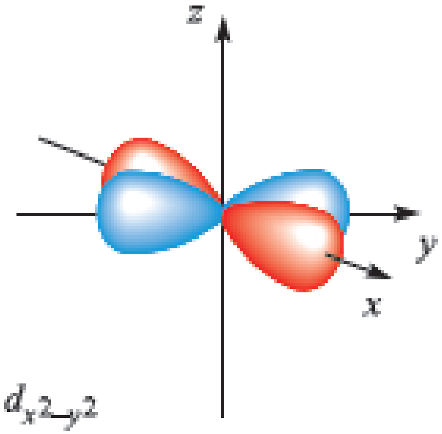
d_{xy}



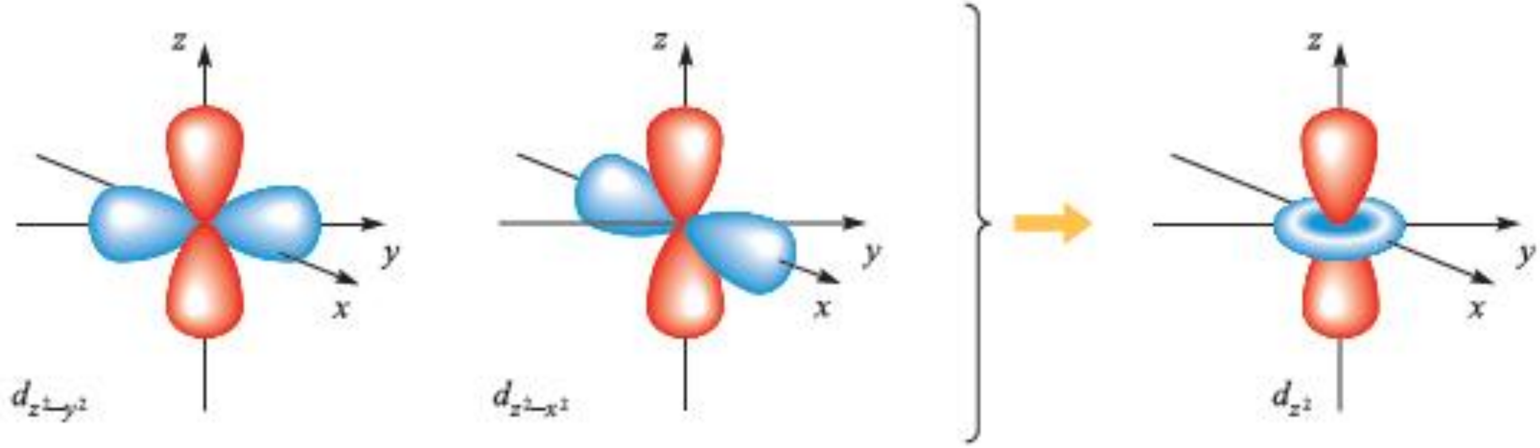
d_{xz}



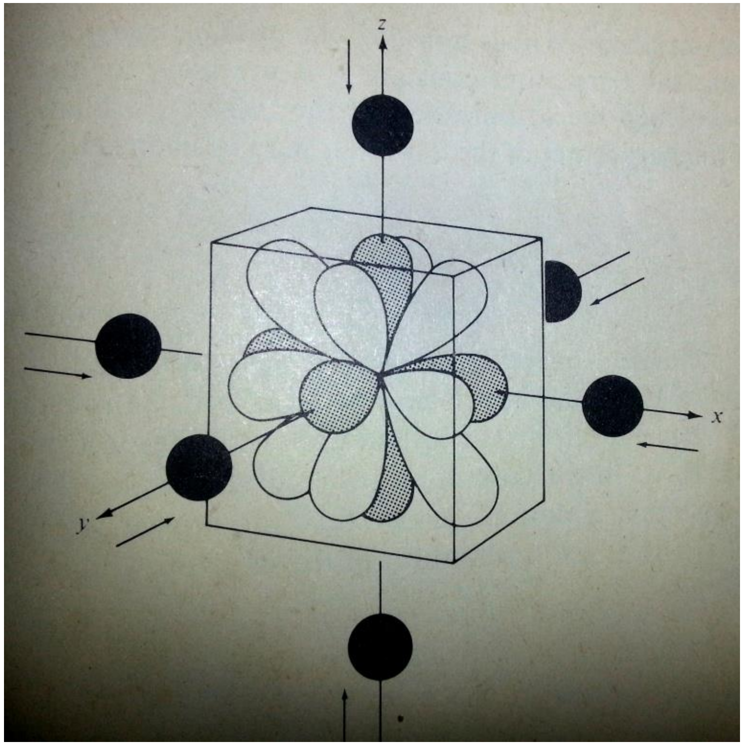
d_{z^2}



$d_{x^2-y^2}$

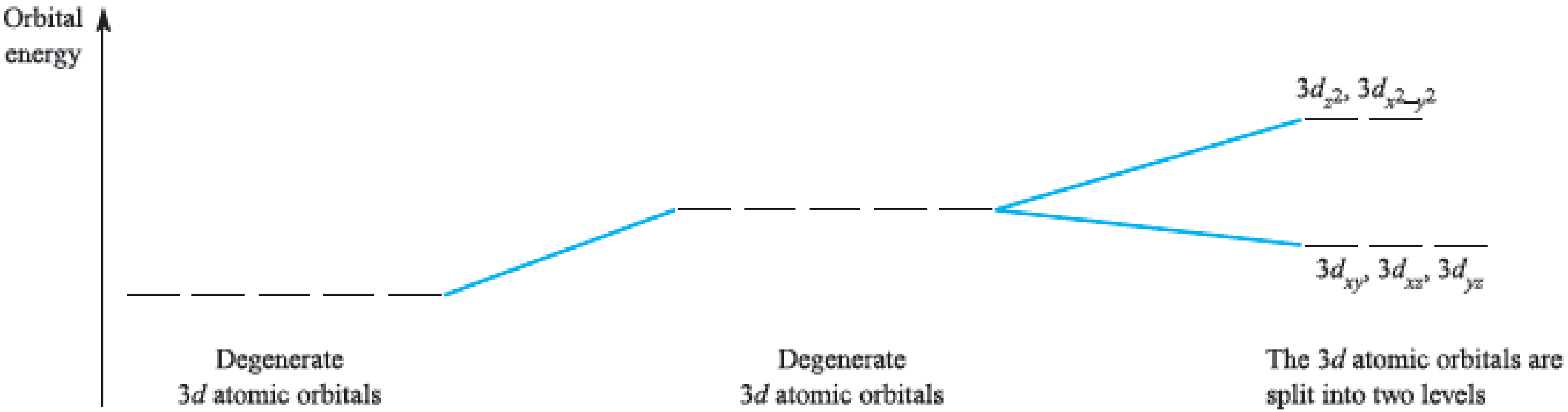


Octahedral crystal field



1. The orbitals lying along the axis are d_{z^2} and $d_{x^2-y^2}$ (shaded).
2. The orbitals lying in between axis are d_{xy}, d_{yz} and d_{zx}

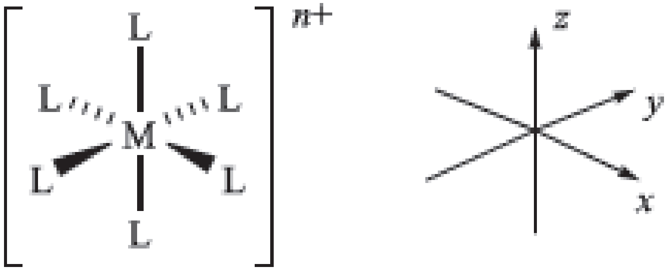
Crystal Field splitting diagram for octahedral complexes



Free metal ion

In the spherically symmetric ligand field

Octahedral ligand field

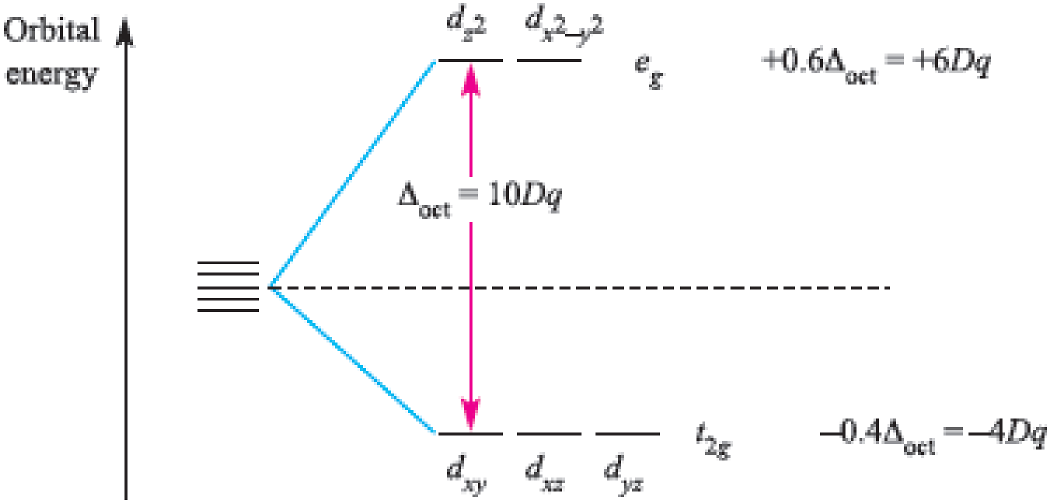


Crystal field splitting

The separation of five d-orbitals of the metal ion into two sets (t_{2g} and e_g) having different energies is called crystal field splitting or ligand field splitting.

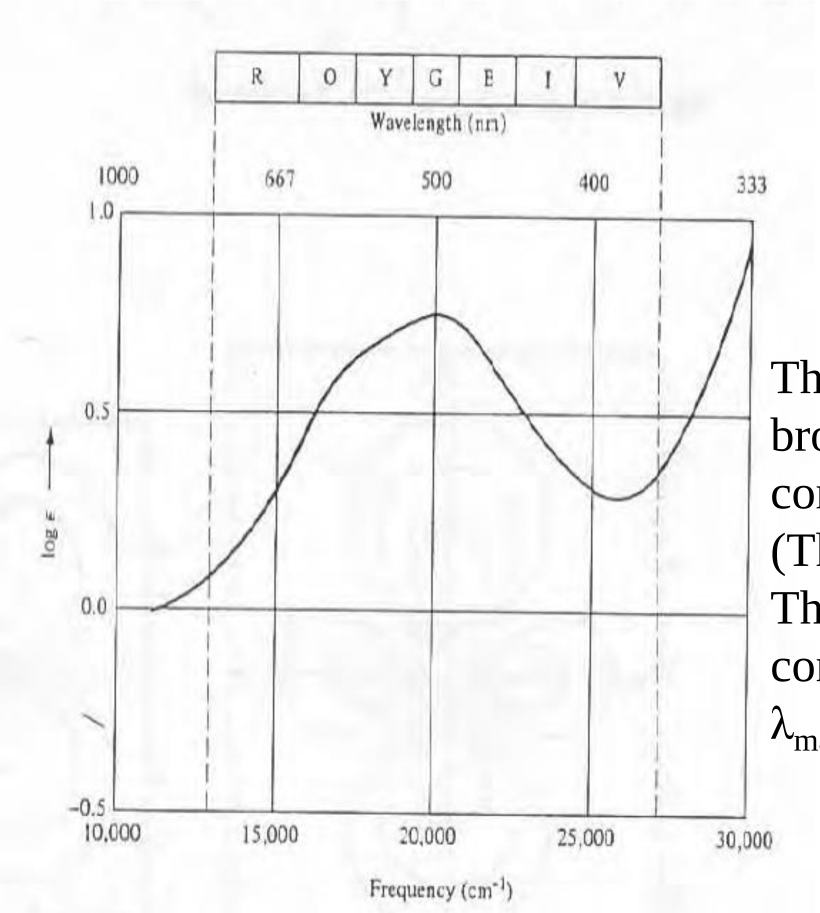
Crystal Field Splitting Parameter (Δ_o or 10 Dq)

The extent to which the e_g and t_{2g} orbitals are separated in octahedral complex is denoted by the quantity 10Dq or Δ_o is called crystal field splitting parameter.

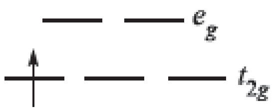


The overall stabilization of the t_{2g} orbitals equals the overall destabilization of the e_g set. Thus, orbitals in the e_g set are raised by 0.6$\boldsymbol{\Delta_o}$ with respect to the barycentre while those in the t_{2g} set are lowered by 0.4$\boldsymbol{\Delta_o}$.

Measurement of Crystal Field Splitting Parameter (Δ_o or 10Dq)



The electronic spectrum of $[Ti(H_2O)_6]^{3+}$in aqueous solution.



The absorption spectrum of the ion exhibits one broad band for which λ_{max}=20300 cm^{-1} corresponding to an energy change of 243 kJ mol^{-1}. (The conversion is 1 cm^{-1} = 11.96 x 10^{-3} kJ mol^{-1}.) The absorption results from a change in electronic configuration from $t_{2g}{}^1e_g{}^0$ to $t_{2g}{}^0e_g{}^1$, and the value of λ_{max} gives a measure of $\boldsymbol{\Delta_o}$.

It is important to remember that Δ_o is an experimental quantity.

For systems with more than one d electron, the evaluation of $\boldsymbol{\Delta_o}$ is more complicated because the energy of a transition depends not only on orbital energies but also on repulsion energies of several electrons present.

Crystal Field Stabilization energy (CFSE)

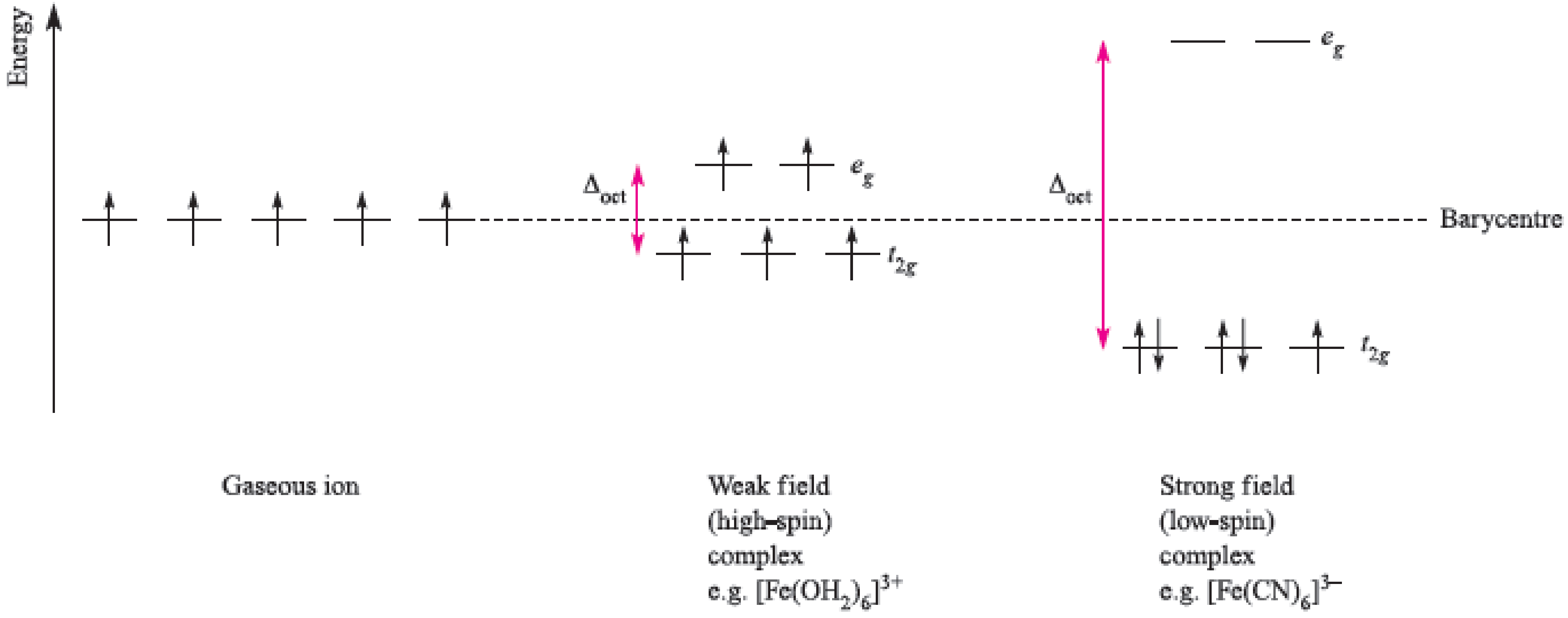
- It is the additional stabilization earned by lowering of energy through the splitting the d-orbitals into t_{2g} and e_g by ligand field.
- Relative to the average energy or barycenter, the energy of the t_{2g} orbitals is stabilized by $-0.4\Delta_o$ or -4 Dq and the energy of the eg orbitals is destabilized by $+0.6\Delta_o$ or +6 Dq
- Destabilization caused by the e_g set = stabilization caused by the t_{2g} set.
- It follows that "the net energy of a $t_{2g}^x e_g^y$ configuration relative to the average energy of the orbitals is called CFSE or LFSE, where x = no. of electrons in t_{2g} orbitals and y = no of electrons in e_g orbitals.

- **CFSE (octahedral) =[-0.4(x) + 0.6(y)] Δ_o**

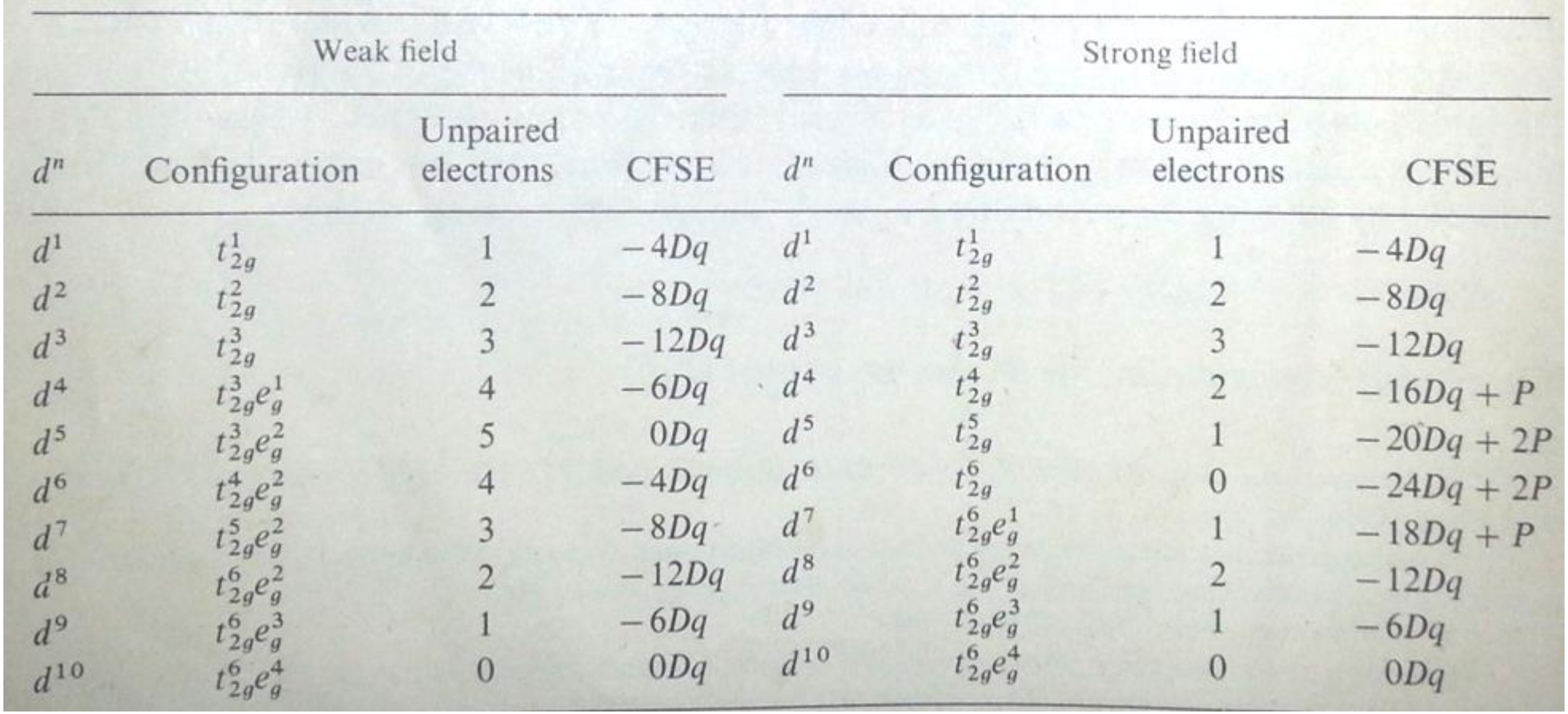
or

CFSE (octahedral) =[-4(x) + 6(y)] Dq

- **Paring Energy:** It is the energy required to overcome electrostatic repulsion to place two electrons in the same orbital.

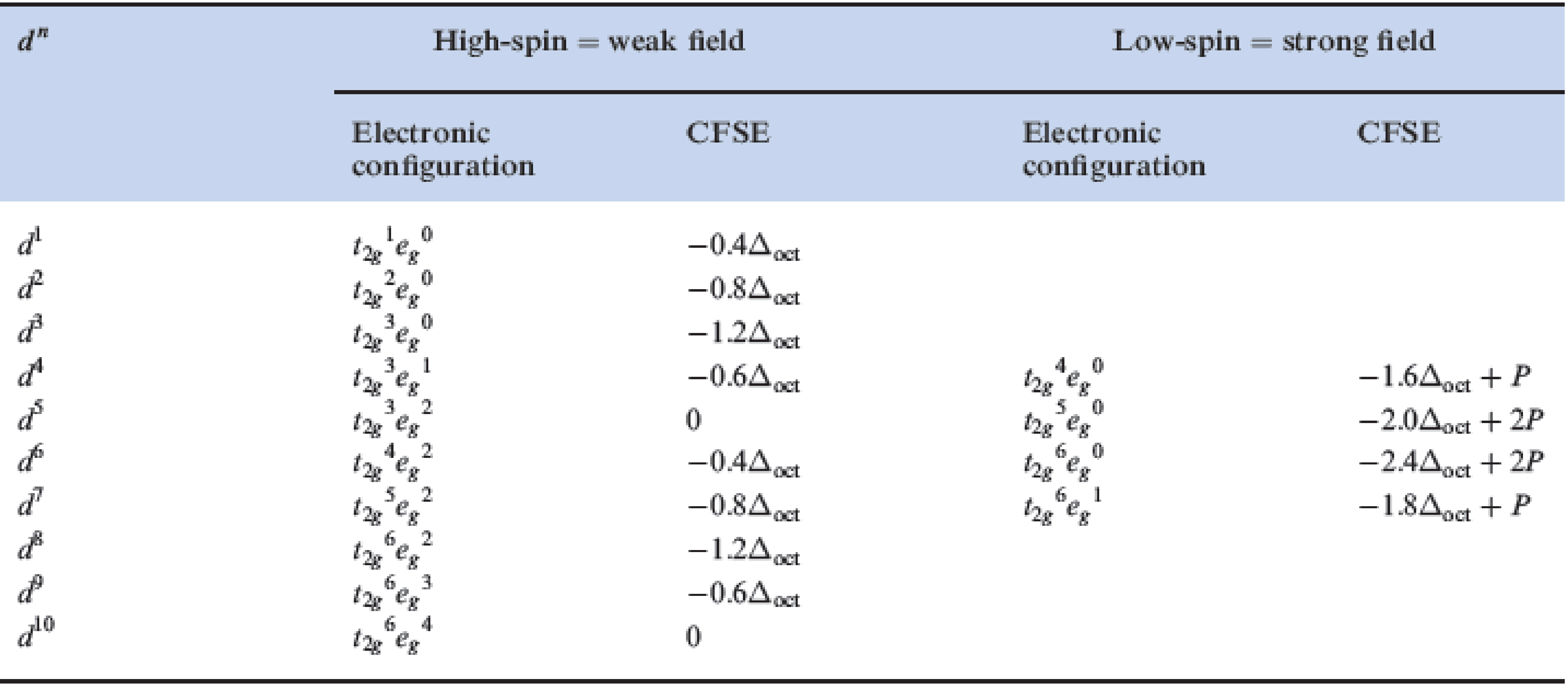

Energy
Δ_{oct}
e_g
t_{2g}
Δ_{oct}
e_g
t_{2g}
Barycentre
Gaseous ion
Weak field (high-spin) complex e.g. $[Fe(OH_2)_6]^{3+}$
Strong field (low-spin) complex e.g. $[Fe(CN)_6]^{3-}$

Crystal field effects for weak and strong octahedral fields in terms of Dq



Weak field				Strong field			
d^n	Configuration	Unpaired electrons	CFSE	d^n	Configuration	Unpaired electrons	CFSE
d^1	t_{2g}^1	1	$-4Dq$	d^1	t_{2g}^1	1	$-4Dq$
d^2	t_{2g}^2	2	$-8Dq$	d^2	t_{2g}^2	2	$-8Dq$
d^3	t_{2g}^3	3	$-12Dq$	d^3	t_{2g}^3	3	$-12Dq$
d^4	$t_{2g}^3e_g^1$	4	$-6Dq$	d^4	t_{2g}^4	2	$-16Dq + P$
d^5	$t_{2g}^3e_g^2$	5	$0Dq$	d^5	t_{2g}^5	1	$-20Dq + 2P$
d^6	$t_{2g}^4e_g^2$	4	$-4Dq$	d^6	t_{2g}^6	0	$-24Dq + 2P$
d^7	$t_{2g}^5e_g^2$	3	$-8Dq$	d^7	$t_{2g}^6e_g^1$	1	$-18Dq + P$
d^8	$t_{2g}^6e_g^2$	2	$-12Dq$	d^8	$t_{2g}^6e_g^2$	2	$-12Dq$
d^9	$t_{2g}^6e_g^3$	1	$-6Dq$	d^9	$t_{2g}^6e_g^3$	1	$-6Dq$
d^{10}	$t_{2g}^6e_g^4$	0	$0Dq$	d^{10}	$t_{2g}^6e_g^4$	0	$0Dq$

Crystal field effects for weak and strong octahedral fields in terms of Δ_o

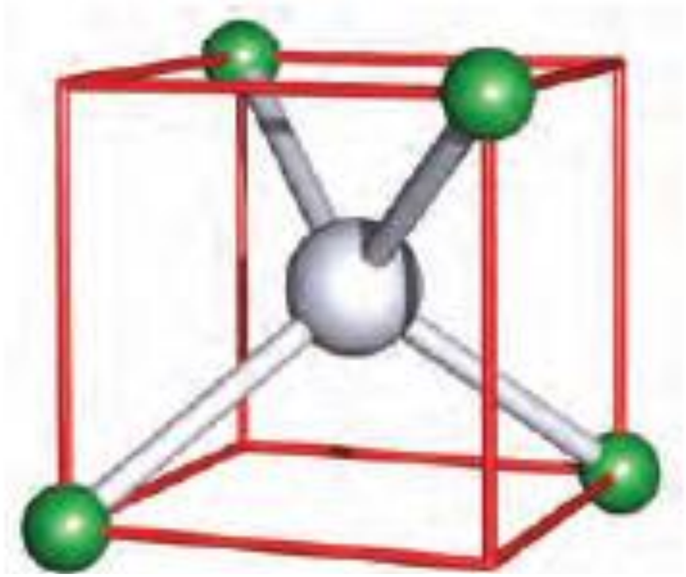


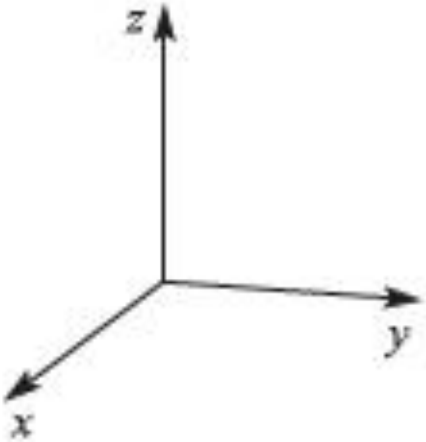
d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}{}^1e_g{}^0$	$-0.4\Delta_{oct}$		
d^2	$t_{2g}{}^2e_g{}^0$	$-0.8\Delta_{oct}$		
d^3	$t_{2g}{}^3e_g{}^0$	$-1.2\Delta_{oct}$		
d^4	$t_{2g}{}^3e_g{}^1$	$-0.6\Delta_{oct}$	$t_{2g}{}^4e_g{}^0$	$-1.6\Delta_{oct} + P$
d^5	$t_{2g}{}^3e_g{}^2$	0	$t_{2g}{}^5e_g{}^0$	$-2.0\Delta_{oct} + 2P$
d^6	$t_{2g}{}^4e_g{}^2$	$-0.4\Delta_{oct}$	$t_{2g}{}^6e_g{}^0$	$-2.4\Delta_{oct} + 2P$
d^7	$t_{2g}{}^5e_g{}^2$	$-0.8\Delta_{oct}$	$t_{2g}{}^6e_g{}^1$	$-1.8\Delta_{oct} + P$
d^8	$t_{2g}{}^6e_g{}^2$	$-1.2\Delta_{oct}$		
d^9	$t_{2g}{}^6e_g{}^3$	$-0.6\Delta_{oct}$		
d^{10}	$t_{2g}{}^6e_g{}^4$	0		

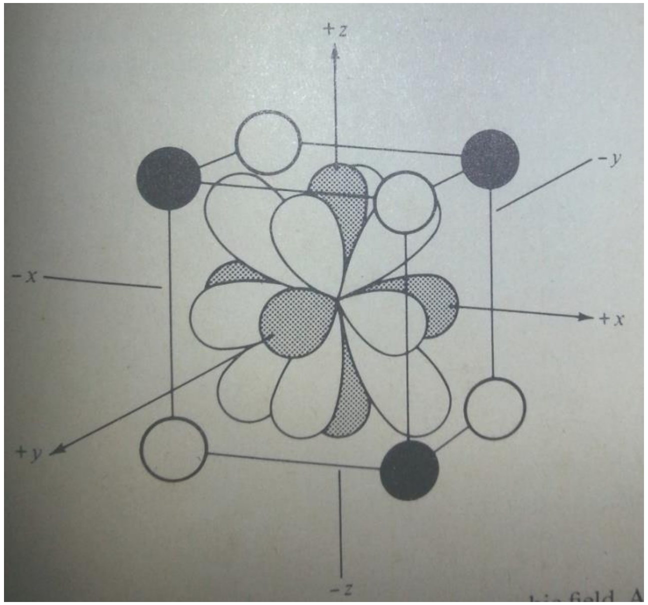
For high spin complexes: $P > 10$ Dq or Δ_o

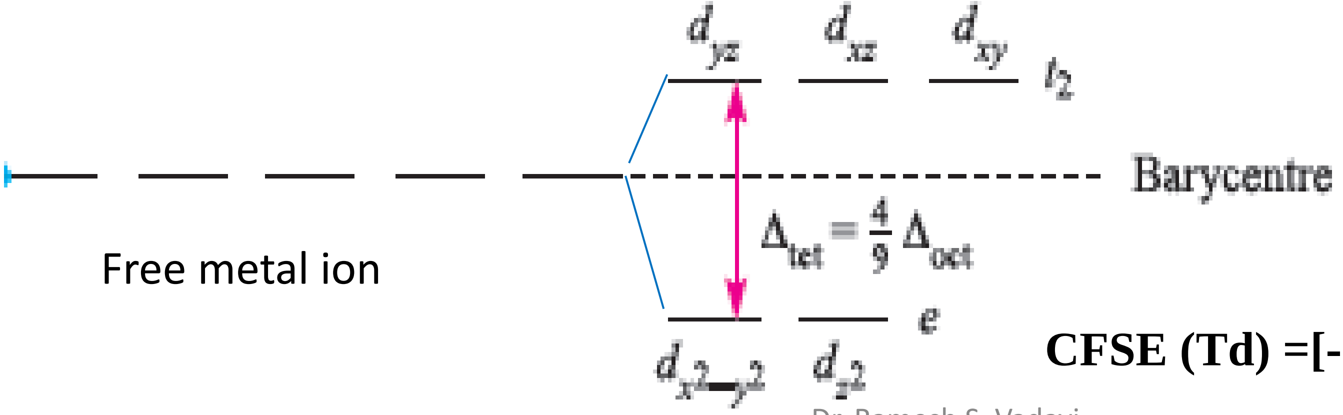
For Low spin complexes : $P < 10$ Dq or Δ_o

Crystal Field Splitting in Tetrahedral Crystal field.







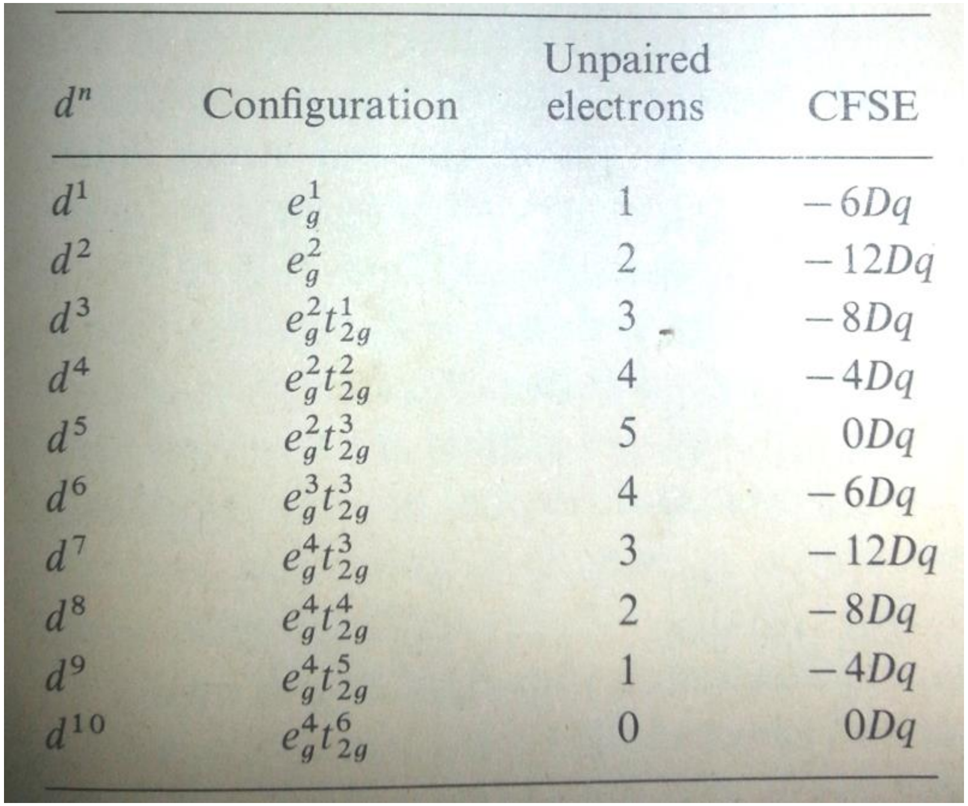


Free metal ion

CFSE (Td) =[-0.6(x) + 0.4(y)] Δ_t

CFSE (Td) =[-6(x) + 4(y)] Dq

Crystal field effects for tetrahedral fields in terms of Dq



d^n	Configuration	Unpaired electrons	CFSE
d^1	e_g^1	1	$-6Dq$
d^2	e_g^2	2	$-12Dq$
d^3	$e_g^2t_{2g}^1$	3	$-8Dq$
d^4	$e_g^2t_{2g}^2$	4	$-4Dq$
d^5	$e_g^2t_{2g}^3$	5	$0Dq$
d^6	$e_g^3t_{2g}^3$	4	$-6Dq$
d^7	$e_g^4t_{2g}^3$	3	$-12Dq$
d^8	$e_g^4t_{2g}^4$	2	$-8Dq$
d^9	$e_g^4t_{2g}^5$	1	$-4Dq$
d^{10}	$e_g^4t_{2g}^6$	0	$0Dq$

Tetrahedral complexes almost invariably high spin complexes

89. Considering the two complexes (A) $[Ni(H_2O)_6]^{2+}$ and (B) $[Ni(NH_3)_6]^{2+}$, the right statement is

1. Complex (A) is diamagnetic and complex (B) is paramagnetic
2. Complex (A) is paramagnetic and complex (B) is diamagnetic
3. Both are paramagnetic
4. Both are diamagnetic

㉑ According to crystal field theory, Ni^{2+} can have two unpaired electrons in

1. octahedral geometry only
2. square-planar geometry only
3. tetrahedral geometry only
4. both octahedral and tetrahedral geometry

22. $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ complex ions are

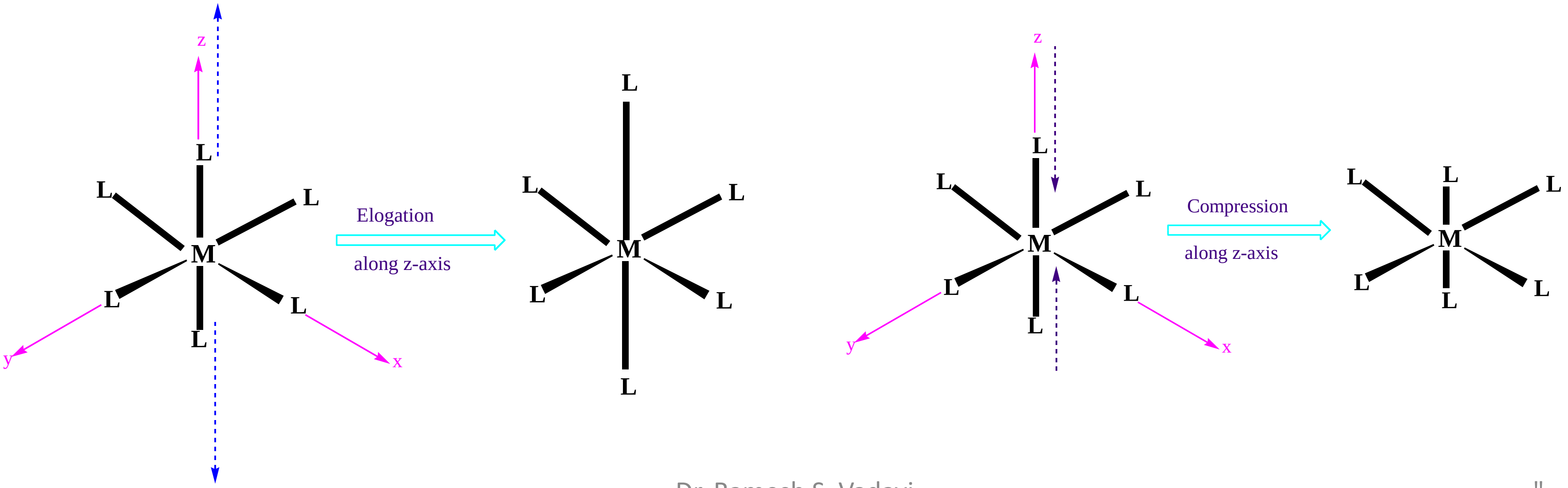
1. both diamagnetic
2. both paramagnetic
3. diamagnetic and paramagnetic respectively
4. antiferromagnetic and diamagnetic respectively

Tetragonally Distorted Octahedral complexes

- In the octahedral system, if the **two trans-ligands lying along the *z*-axis are compressed or elongated compared to other four ligands lying in the *xy*-plane**, then the resulting structures are called as tetragonally distorted octahedrons. These are referred to as tetragonal structures.
- These tetragonal structures are of two types.

1. Tetragonally elongated structures (z-out distortion)

2. Tetragonally compressed structures (z-in distortion)



- **Theoretically, it is not possible to predict, which kind of distortion will occur in octahedral complexes.**
- **The distortion will occur in octahedral complexes, if the d-orbitals are unsymmetrically filled.**

Jahn-Teller Theorem:

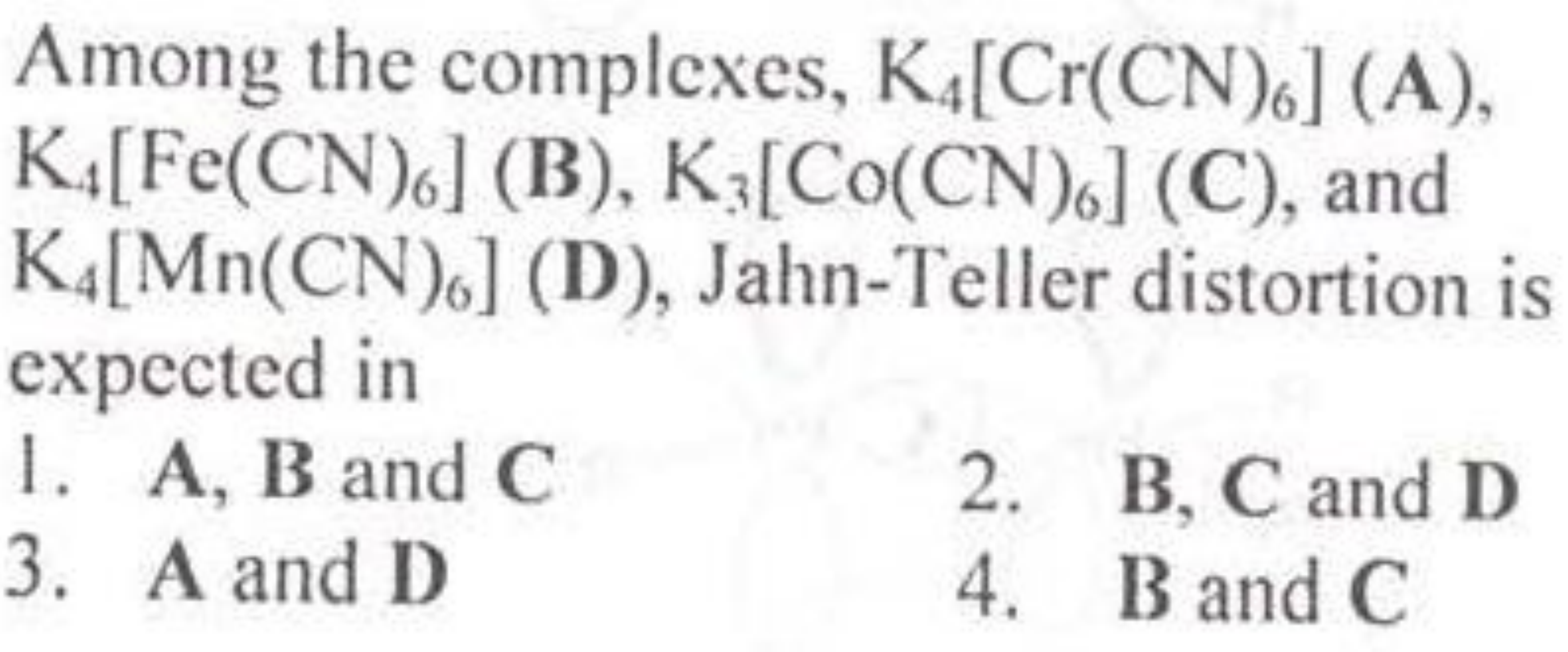
- It states that “any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy”.

The distortion will occur in octahedral complexes, if the d-orbitals are unsymmetrically filled.

d^n	Octahedral			
	High Spin	Yes/ No	Low Spin	Yes/ No
d^1	$t_{2g}^1e_g^0$	Yes		
d^2	$t_{2g}^2e_g^0$	Yes		
d^3	$t_{2g}^3e_g^0$	No		
d^4	$t_{2g}^3e_g^1$	Yes	$t_{2g}^4e_g^0$	Yes
d^5	$t_{2g}^3e_g^2$	No	$t_{2g}^5e_g^0$	Yes
d^6	$t_{2g}^4e_g^2$	Yes	$t_{2g}^6e_g^0$	No
d^7	$t_{2g}^5e_g^2$	Yes	$t_{2g}^6e_g^1$	Yes
d^8	$t_{2g}^6e_g^2$	No		
d^9	$t_{2g}^6e_g^3$	Yes		
d^{10}	$t_{2g}^6e_g^4$	No		

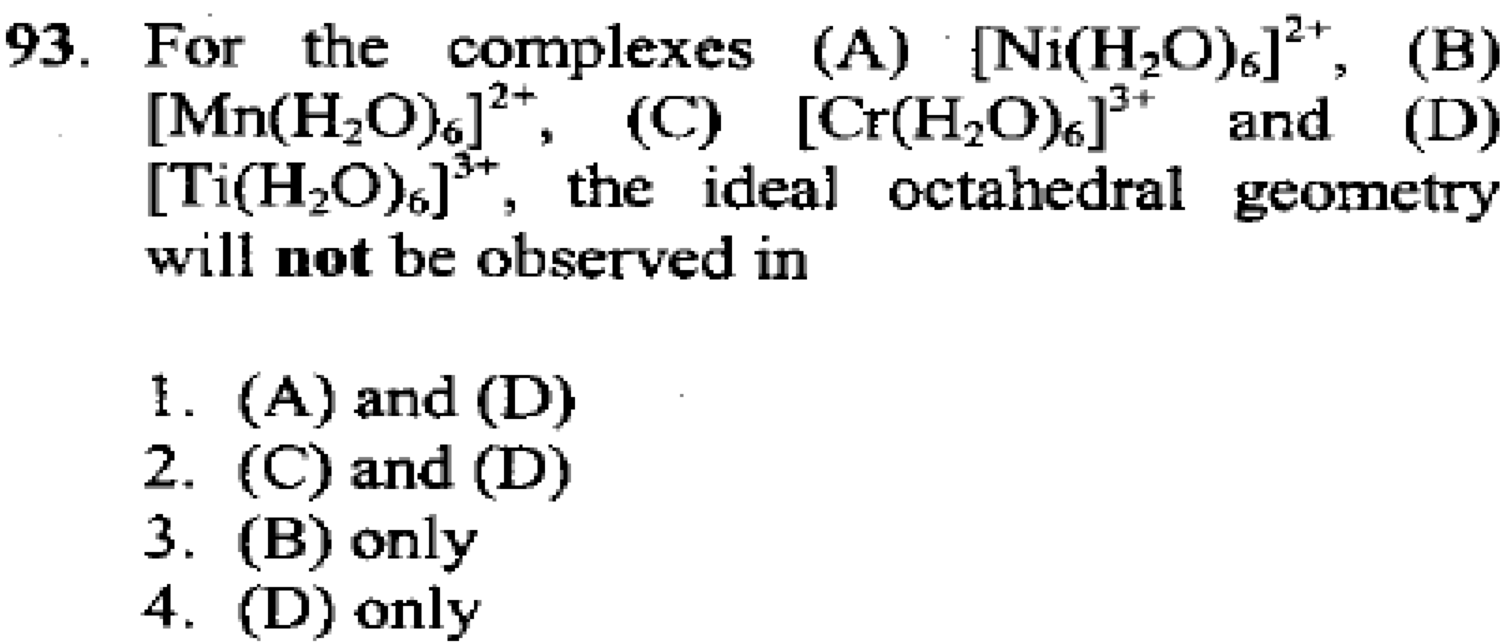
78. Which one of the following pairs of electronic configurations of high-spin transition metal ions (3d) in an octahedral field undergoes a substantial Jahn-Teller distortion:

1. d^3, d^9
2. d^4, d^9
3. d^5, d^9
4. d^6, d^9



Among the complexes, $K_4[Cr(CN)_6]$ (**A**), $K_4[Fe(CN)_6]$ (**B**), $K_3[Co(CN)_6]$ (**C**), and $K_4[Mn(CN)_6]$ (**D**), Jahn-Teller distortion is expected in

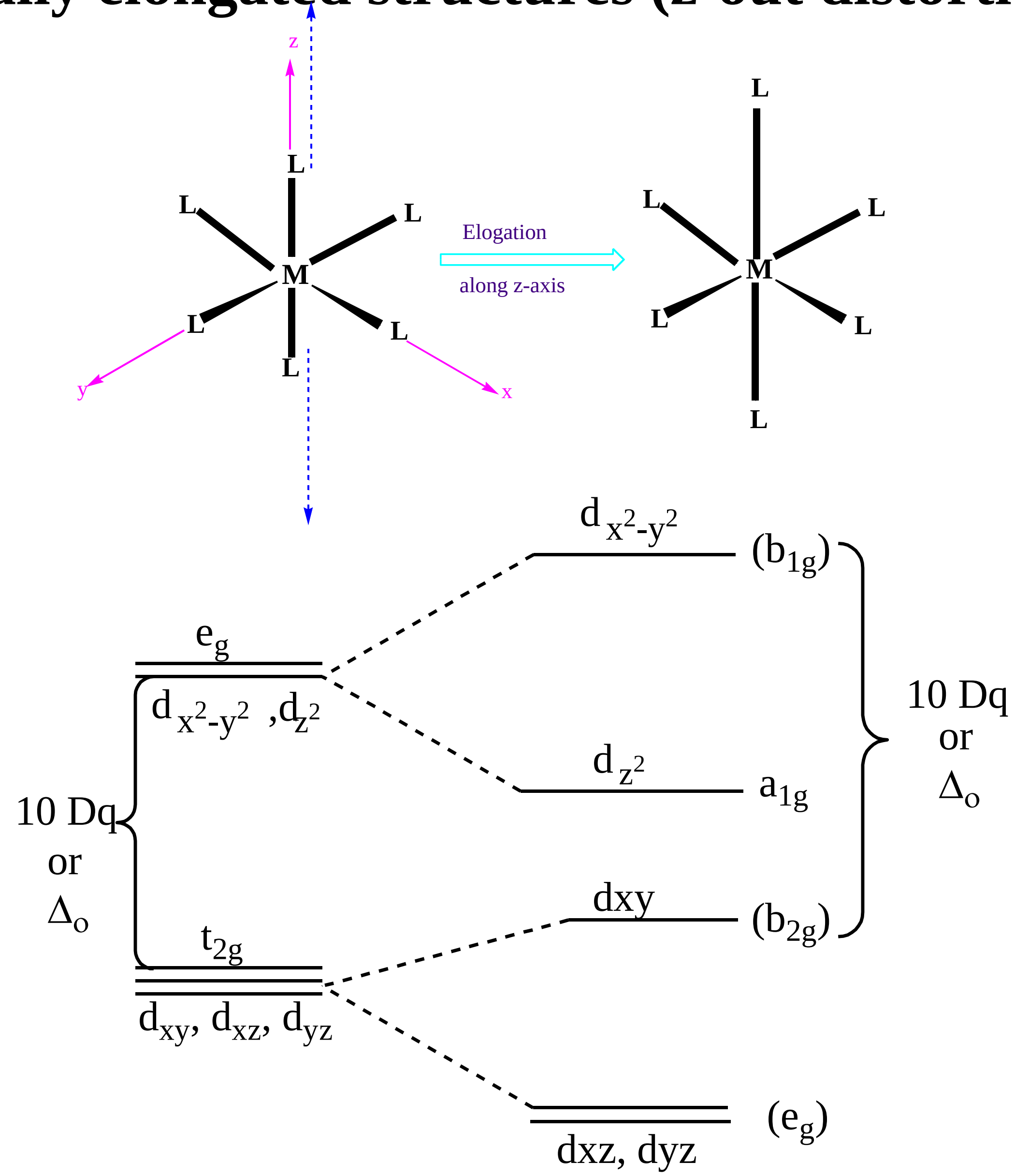
1. **A**, **B** and **C**
2. **B**, **C** and **D**
3. **A** and **D**
4. **B** and **C**



93. For the complexes (A) $[Ni(H_2O)_6]^{2+}$, (B) $[Mn(H_2O)_6]^{2+}$, (C) $[Cr(H_2O)_6]^{3+}$ and (D) $[Ti(H_2O)_6]^{3+}$, the ideal octahedral geometry will **not** be observed in

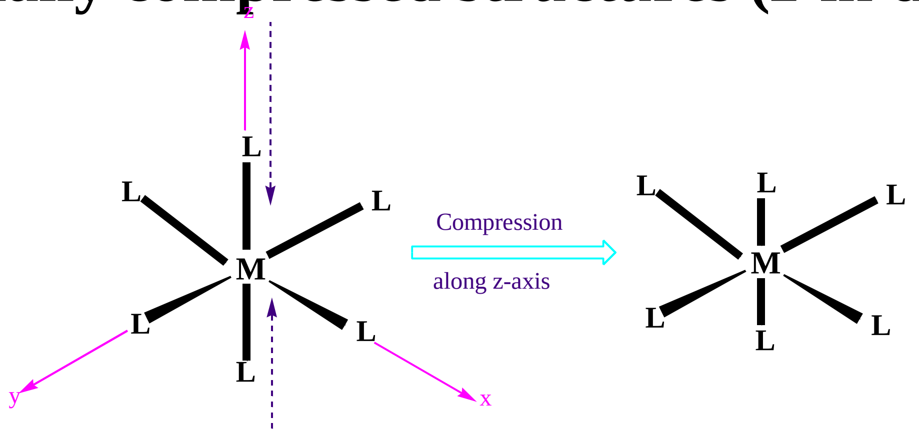
1. (A) and (D)
2. (C) and (D)
3. (B) only
4. (D) only

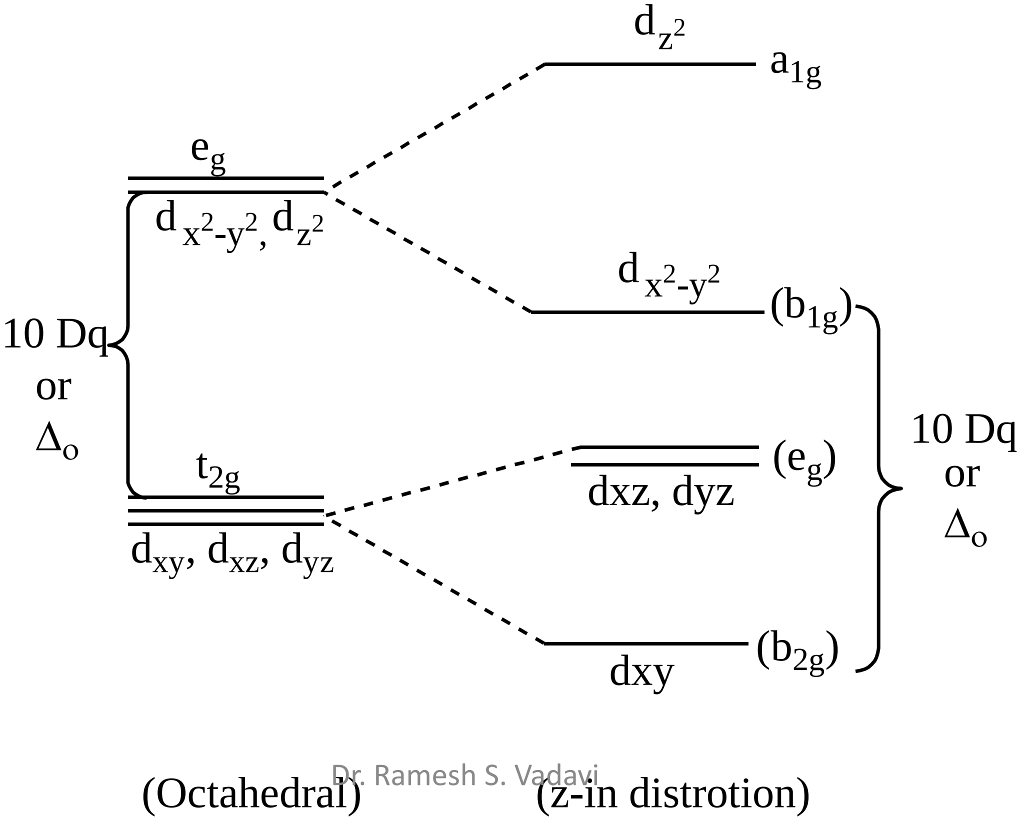
1. Tetragonally elongated structures (z-out distortion)



(Octahedral) (z-out distrotion)

2. Tetragonally compressed structures (z-in distortion)

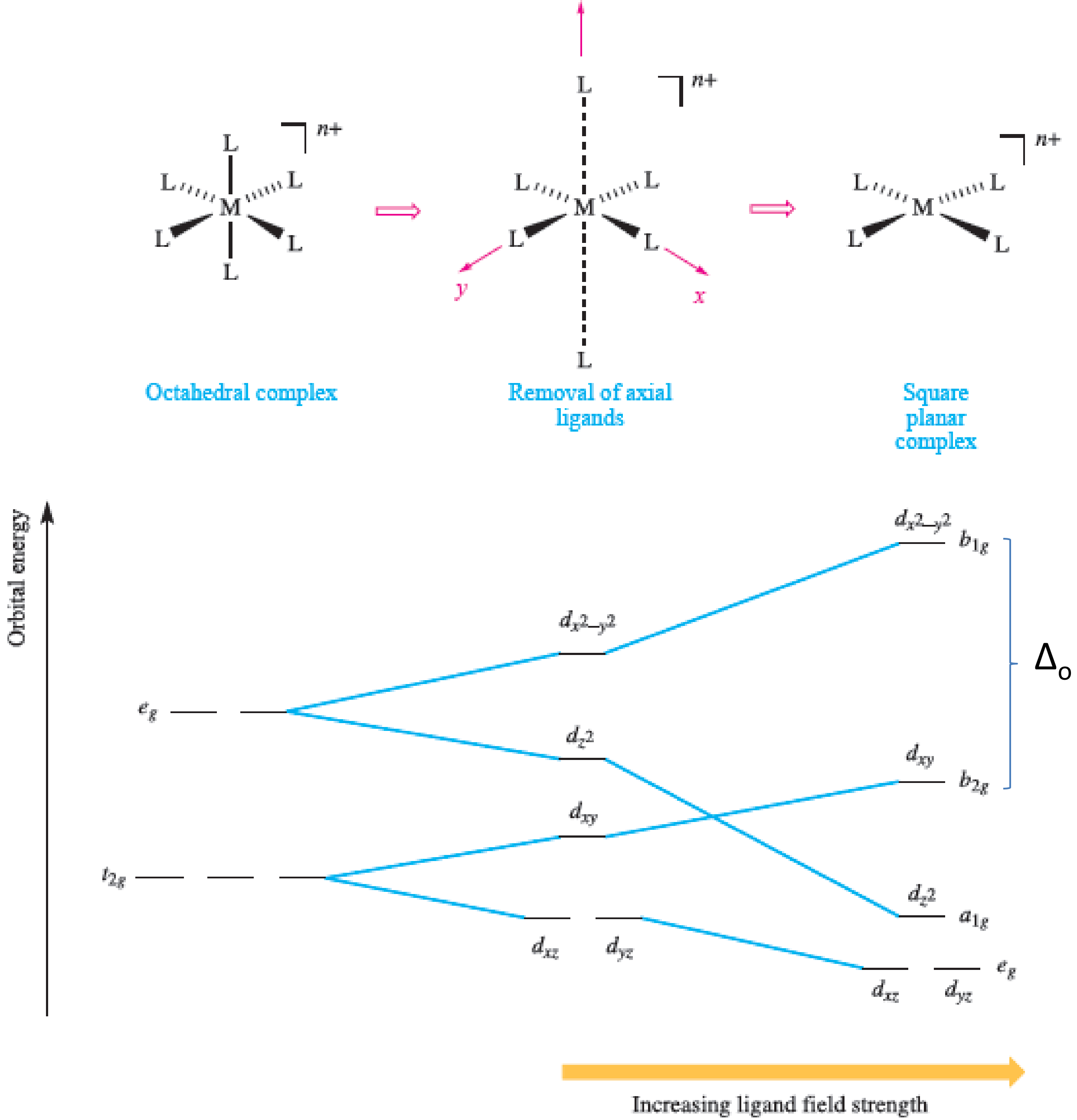




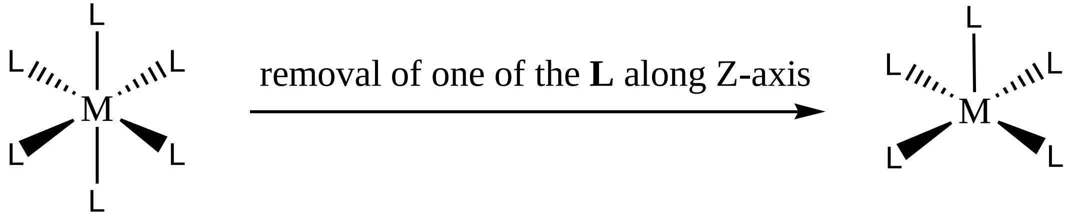
118. Compounds $K_2Ba[Cu(NO_2)_6]$ (A) and $Cs_2Ba[Cu(NO_2)_6]$ (B) exhibit tetragonal elongation and tetragonal compression, respectively. The unpaired electron in A and B are found respectively, in orbitals,

(a) d_z^2 and $d_{x^2-y^2}$ (b) $d_{x^2-y^2}$ and d_z^2 (c) d_z^2 and d_z^2 (d) $d_{x^2-y^2}$ and $d_{x^2-y^2}$

Tetragonal elongation and Formation of square planar complex

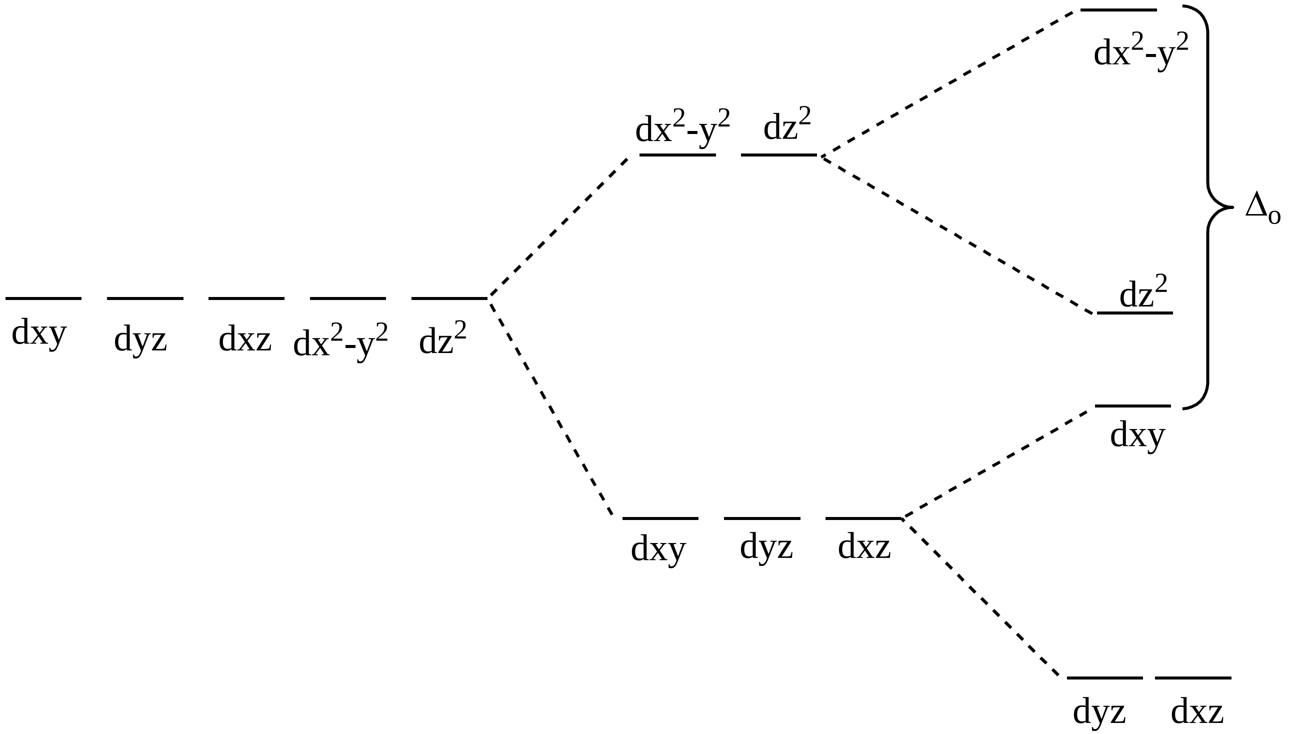


Crystal Field splliting in Square Pyramid geometry



Octahedral

Square Pyramid

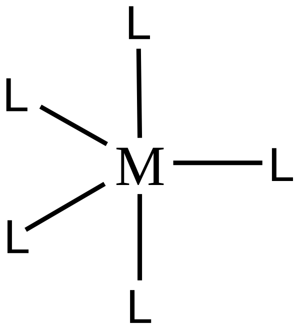


Free M$^+$

Octahedral

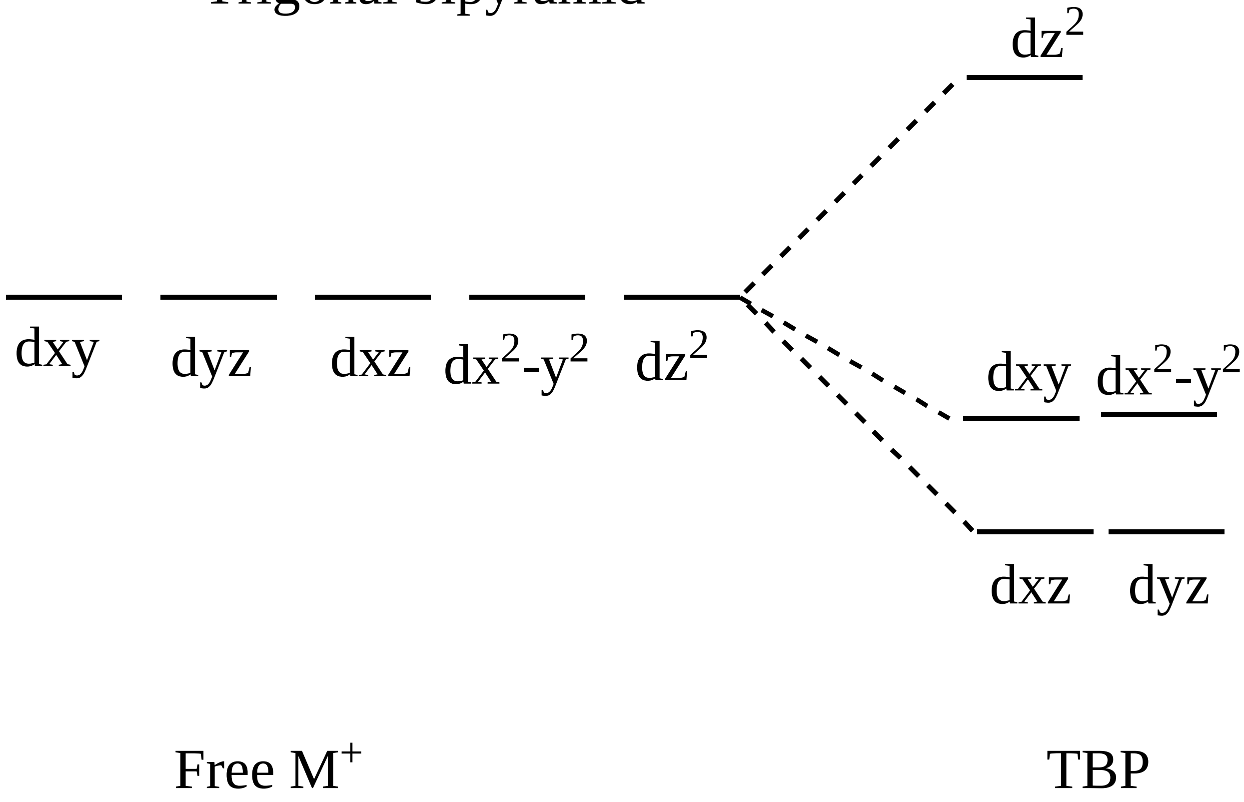
Square Pyramid

Crystal Field splliting in Trigonal bipyramid geometry

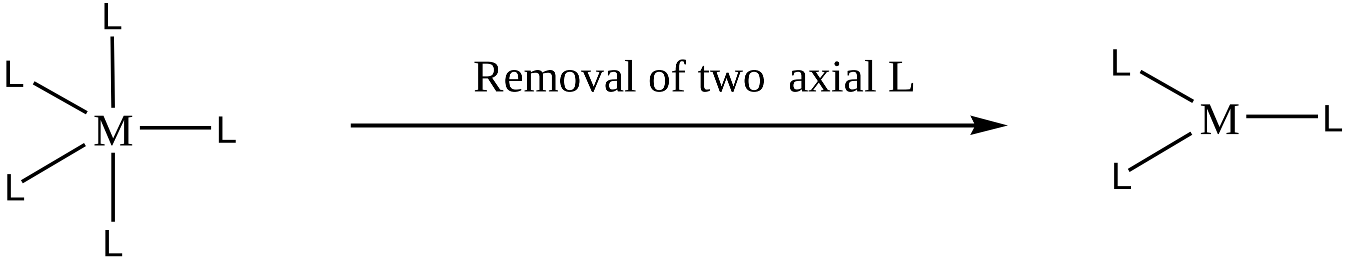


Trigonal bipyramid

Note: Three ligands in the equatorial position lie in *xy* plane, where as two axial ligands lie along z-axis

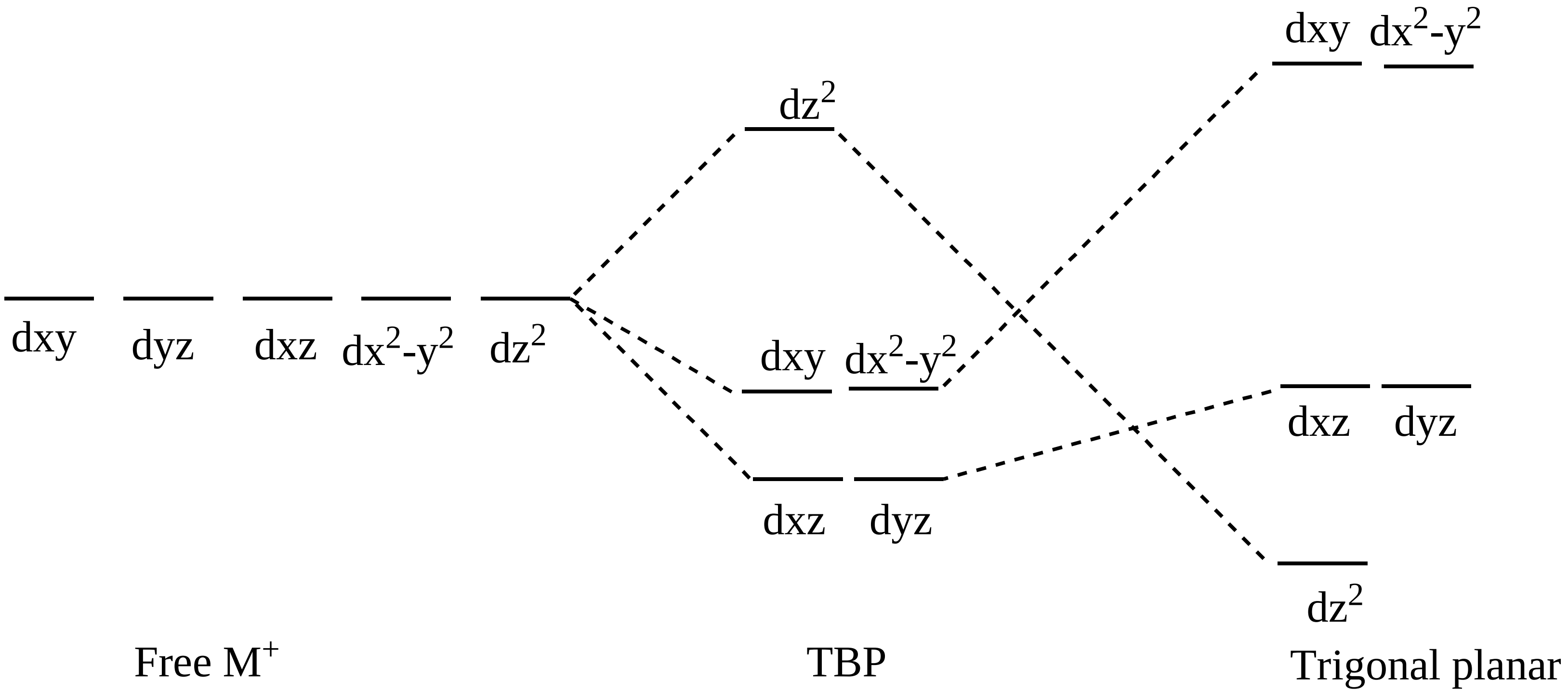


Crystal Field splliting in Trigonal Planar geometry



Trigonal bipyramid

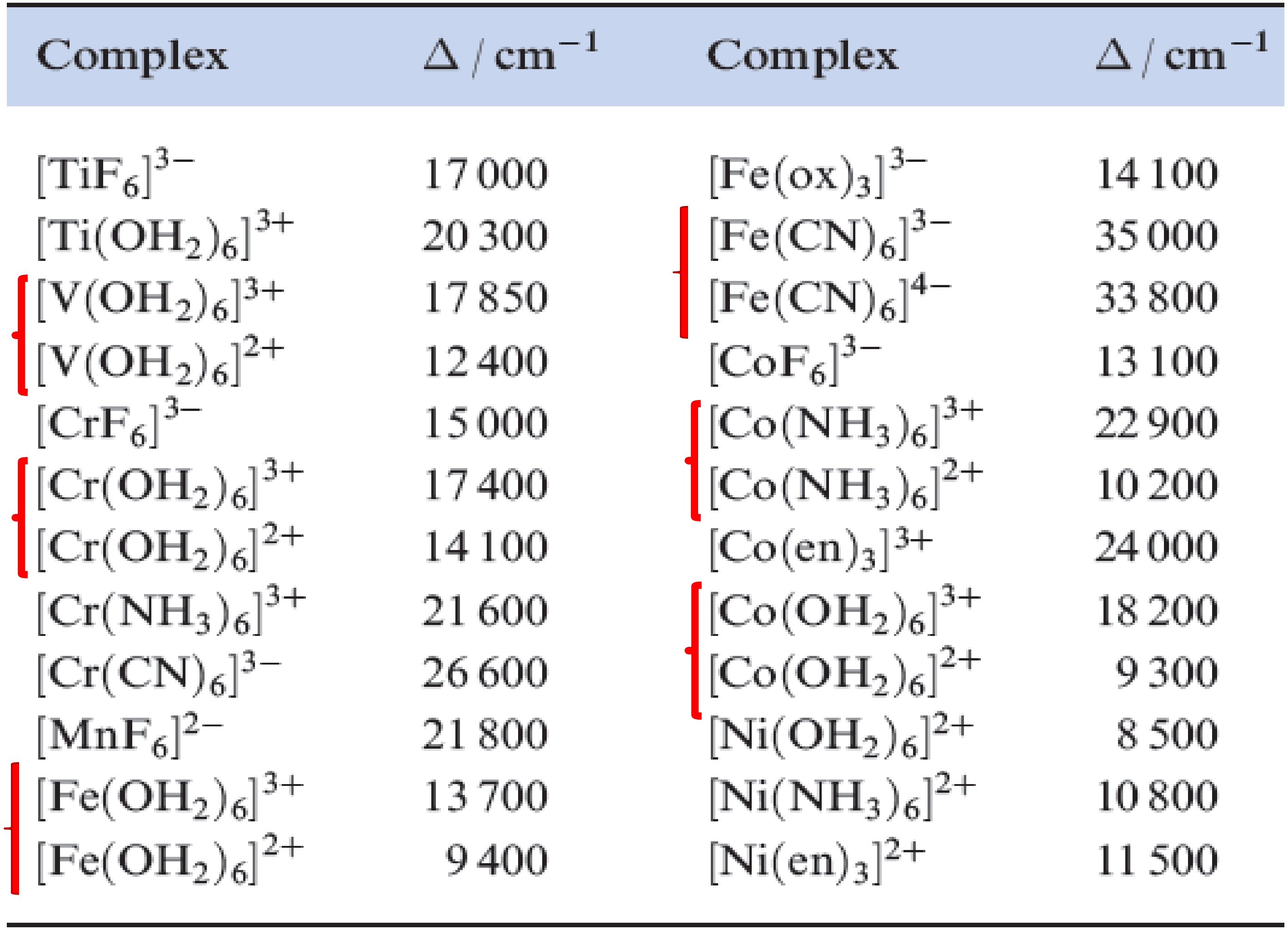
Trigonal planar



Factors affecting Crystal Field Splitting Energy, i.e., 10 Dq or Δ_o

1. Oxidation state of the metal ion
2. Geometry of the complex and number of ligands
3. Strength of the ligand.
4. The position of metal ion in the periodic table

1. Oxidation state of the metal ion : As the oxidation state of central metal increases, crystal field splitting energy increases.



Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[TiF_6]^{3-}$	17 000	$[Fe(ox)_3]^{3-}$	14 100
$[Ti(OH_2)_6]^{3+}$	20 300	$[Fe(CN)_6]^{3-}$	35 000
$[V(OH_2)_6]^{3+}$	17 850	$[Fe(CN)_6]^{4-}$	33 800
$[V(OH_2)_6]^{2+}$	12 400	$[CoF_6]^{3-}$	13 100
$[CrF_6]^{3-}$	15 000	$[Co(NH_3)_6]^{3+}$	22 900
$[Cr(OH_2)_6]^{3+}$	17 400	$[Co(NH_3)_6]^{2+}$	10 200
$[Cr(OH_2)_6]^{2+}$	14 100	$[Co(en)_3]^{3+}$	24 000
$[Cr(NH_3)_6]^{3+}$	21 600	$[Co(OH_2)_6]^{3+}$	18 200
$[Cr(CN)_6]^{3-}$	26 600	$[Co(OH_2)_6]^{2+}$	9 300
$[MnF_6]^{2-}$	21 800	$[Ni(OH_2)_6]^{2+}$	8 500
$[Fe(OH_2)_6]^{3+}$	13 700	$[Ni(NH_3)_6]^{2+}$	10 800
$[Fe(OH_2)_6]^{2+}$	9 400	$[Ni(en)_3]^{2+}$	11 500

$\frac{4}{9}$

2. Geometry of the complex and number of ligands:

For the same metal ion in the same oxidation state with the same ligands but with different coordination number and geometry, Crystal field splitting energy will vary.

For example: The extent of d-orbital splitting will be more in Octahedral geometry with six ligands as compared to tetrahedral geometry with four ligands.

Generally $\Delta_{Td} \approx \frac{4}{9} \Delta_o$

Example: $[VCl_4]$---------- 10 Dq = 7900 cm^{-1} (Tetrahedral)

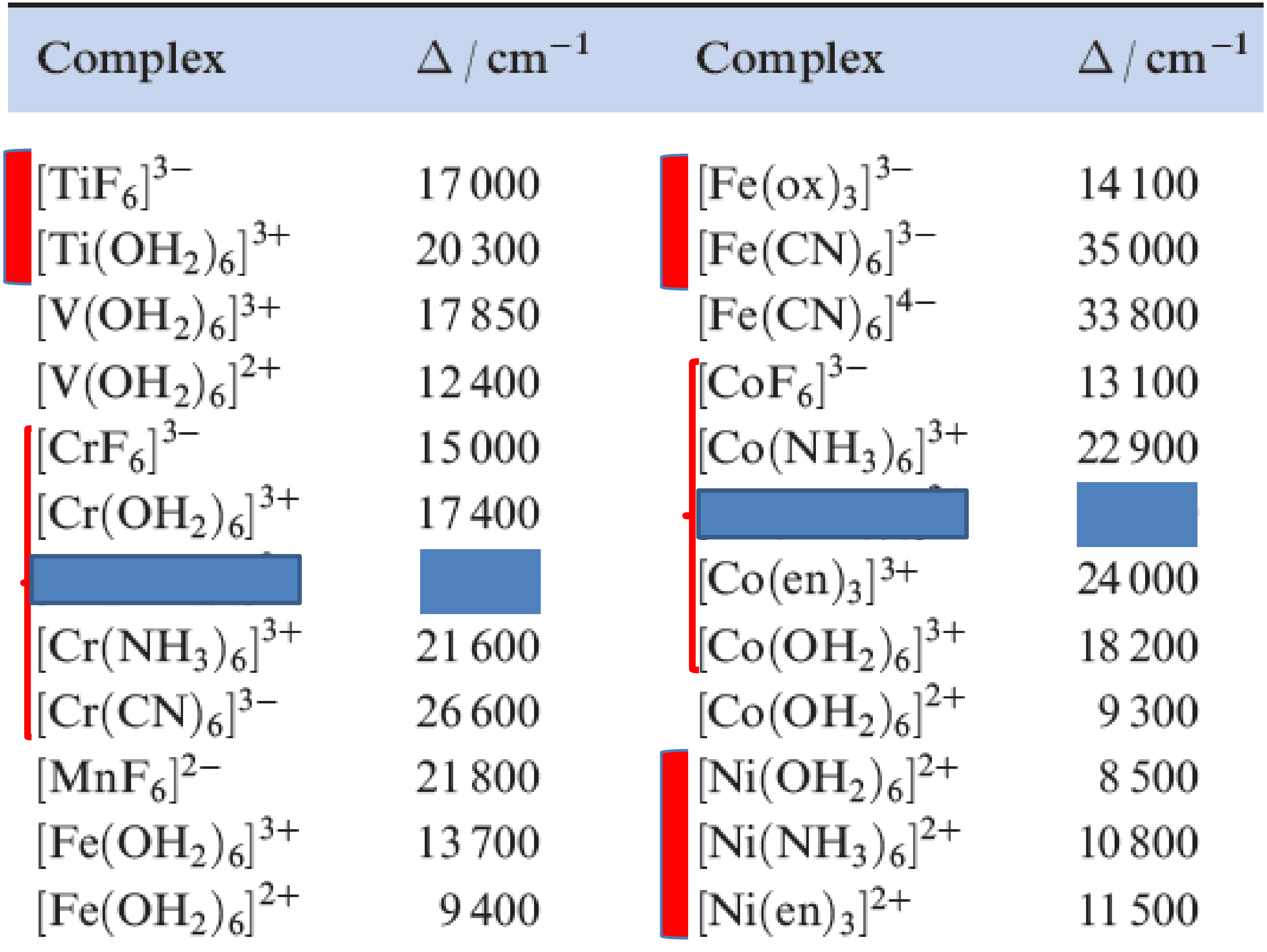
$[VCl_6]^{2-}$ 10 Dq = 18000 cm^{-1} (Octahedral)

$[Co(NH_3)_4]^{2+}$ 10 Dq = 5900 cm^{-1} (Tetrahedral)

$[Co(NH_3)_6]^{2+}$ 10 Dq = 10200 cm^{-1} (Octahedral)

3. Strength of the ligand.

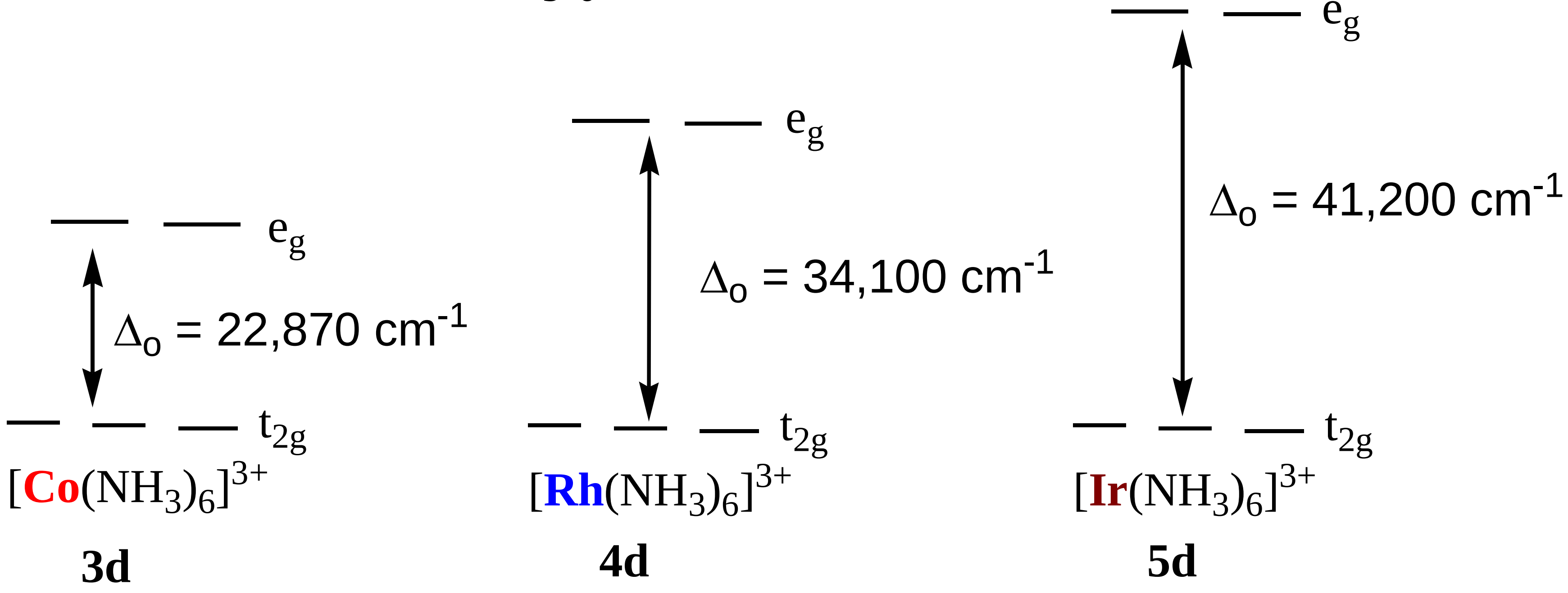
As the strength of the ligand increases, Δ_o value increases.



Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[TiF_6]^{3-}$	17 000	$[Fe(ox)_3]^{3-}$	14 100
$[Ti(OH_2)_6]^{3+}$	20 300	$[Fe(CN)_6]^{3-}$	35 000
$[V(OH_2)_6]^{3+}$	17 850	$[Fe(CN)_6]^{4-}$	33 800
$[V(OH_2)_6]^{2+}$	12 400	$[CoF_6]^{3-}$	13 100
$[CrF_6]^{3-}$	15 000	$[Co(NH_3)_6]^{3+}$	22 900
$[Cr(OH_2)_6]^{3+}$	17 400	[redacted]	[redacted]
[redacted]	[redacted]	$[Co(en)_3]^{3+}$	24 000
$[Cr(NH_3)_6]^{3+}$	21 600	$[Co(OH_2)_6]^{3+}$	18 200
$[Cr(CN)_6]^{3-}$	26 600	$[Co(OH_2)_6]^{2+}$	9 300
$[MnF_6]^{2-}$	21 800	$[Ni(OH_2)_6]^{2+}$	8 500
$[Fe(OH_2)_6]^{3+}$	13 700	$[Ni(NH_3)_6]^{2+}$	10 800
$[Fe(OH_2)_6]^{2+}$	9 400	$[Ni(en)_3]^{2+}$	11 500

4. The position of metal ion in the periodic table: The extent of d-orbital splitting (Δ_o) vary within a group. The Δ varies in the following order within a group, i.e., 3d < 4d < 5d.

For example: $[M(NH_3)_6]^{3+}$ complexes of group 9 metals



Demerits of CFT

1. **It assumes purely ionic bonding** (electrostatic interaction) between metal center and ligand. But this idea is strictly wrong . The metal centre is associated with its electrons in different orbitals and the ligands are also associated with their electrons in different orbitals. Thus, the orbital overlap , i,e., mixing of the metal and ligand orbitals must occur at least to some extent as it is supported by many experimental facts, such as nephelauxetic effect, reduction of interelectronic repulsion, ESR signals etc.
2. **Charge transfer bands:** It fails to explain the origin of the intense charge transfer bands. Ex: intense colour of KMnO4.
3. **Intensities of the of the d-d-transitions** can not be explained by CFT. Ex: Intensity of d-d transitions are weak in octahedral whereas d-d transtions are stronger in tetrahedral complexes.
4. **Antiferromagnetic exchange interaction** in some of the metal complexes has not explained by CFT which requires overlap of metal and ligand orbitals.

5. CFT could not explain the position of the ligands in the spectrochemical series, which requires orbital mixing

$$\mathrm{I^- < Br^- < [NCS]^- < Cl^- < F^- < [OH]^- < [ox]^{2-}}$$

$$\mathrm{\approx H_2O < [NCS]^- < NH_3 < en < bpy < phen < [CN]^- \approx CO}$$

$$\text{weak field ligands} \xrightarrow[\text{ligands increasing } \Delta_{oct}]{} \text{strong field}$$

This may appear reasonable for $[TiF_6]^{3-}$ where it appears reasonable to assign the ligands as being negatively charged and there is a considerable electronegativity difference (Ti 1.5; F 4.0).

- This is far harder to rationalise for complexes with neutral ligands, e.g. $Cr(CO)_6$ (Cr 1.6; C 2.5) or those with small electronegativity differences, e.g. $[PtBr_4]^{2-}$ (Pt 2.2; Br 2.8).
- F^- « CN^- (should be the same by point charge argument).

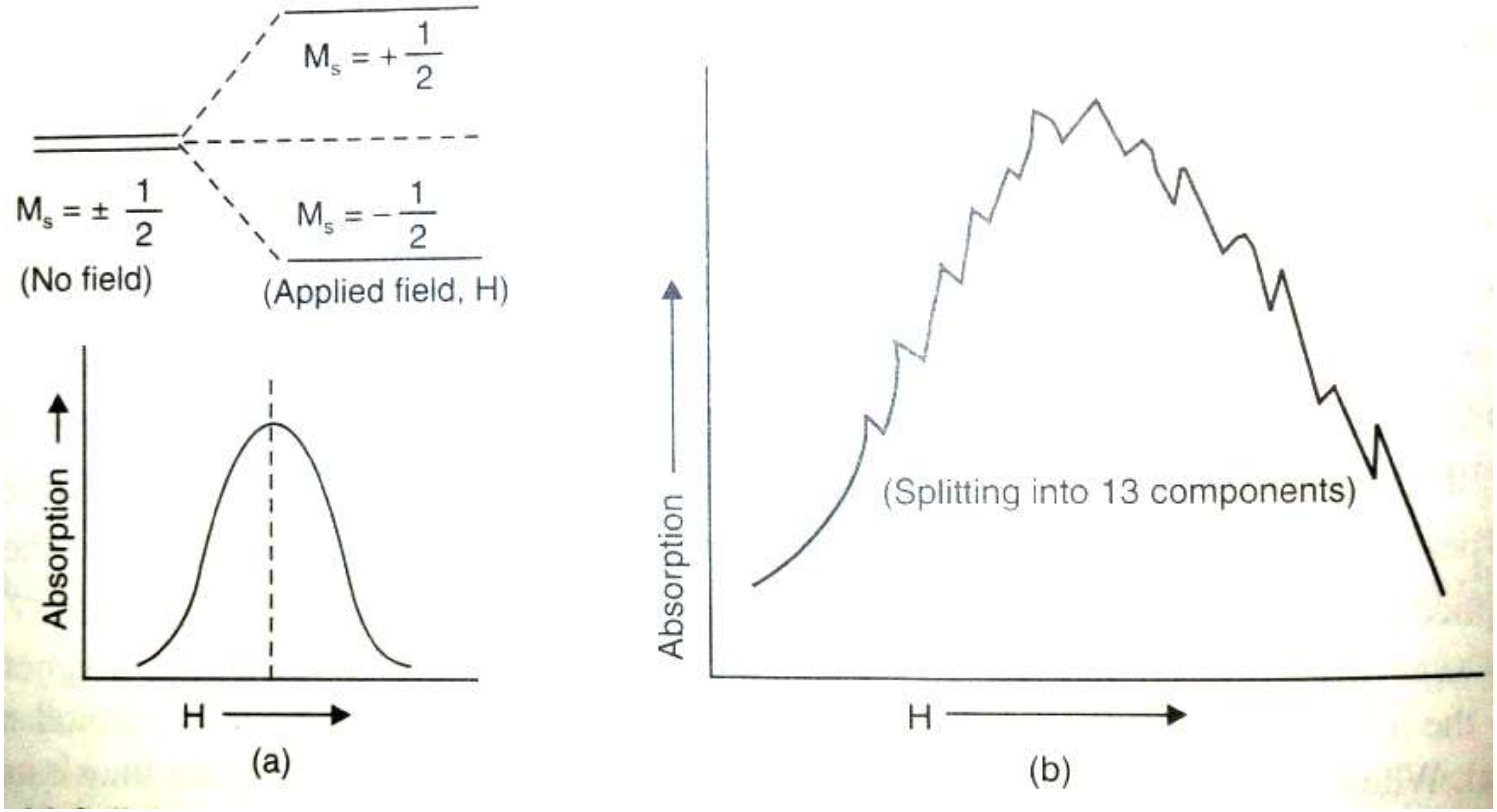
  Even worse, why does (negative) F^- give smaller CFS than (neutral) H_2O

6. Pi(π)-bonding interactions are not explained by the CFT, which is important to explain the ligand field strength (spectrochemical series.)

Molecular Orbital Theory

Evidences for metal orbitals – ligand orbitals overlap

1. **EPR spectrum of $[IrCl_6]^{2-}$:**

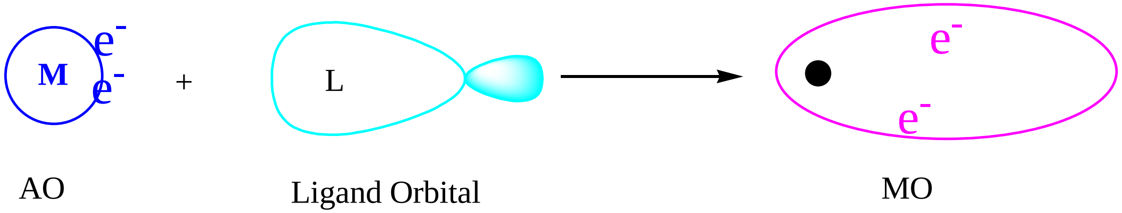


2. **NMR studies:** NMR studies clearly reveal that the spin of an unpaired electron of a metal ion interacts with nuclear spins of ^{19}F in the fluoro complex $[MnF_6]^{2-}$ of a paramagnetic metal ion.

3. **Nephelauxetic effect:** It is the effect of the ligands to expand the d-electron cloud to reduce the interelectron repulsion .

- Through the nephelauxetic effect, it is found that electron-electron repulsion in complexes is somewhat less than that in the free ion.
- The extent of inter-electron repulsion is measured by the parameter called **Racah parameter (B).**
- The Racah parameters are found to be much smaller in the complexes compared to those in their free ions.
- The extent of delocalization is expressed in terms of the **nephelauxetic parameter β**

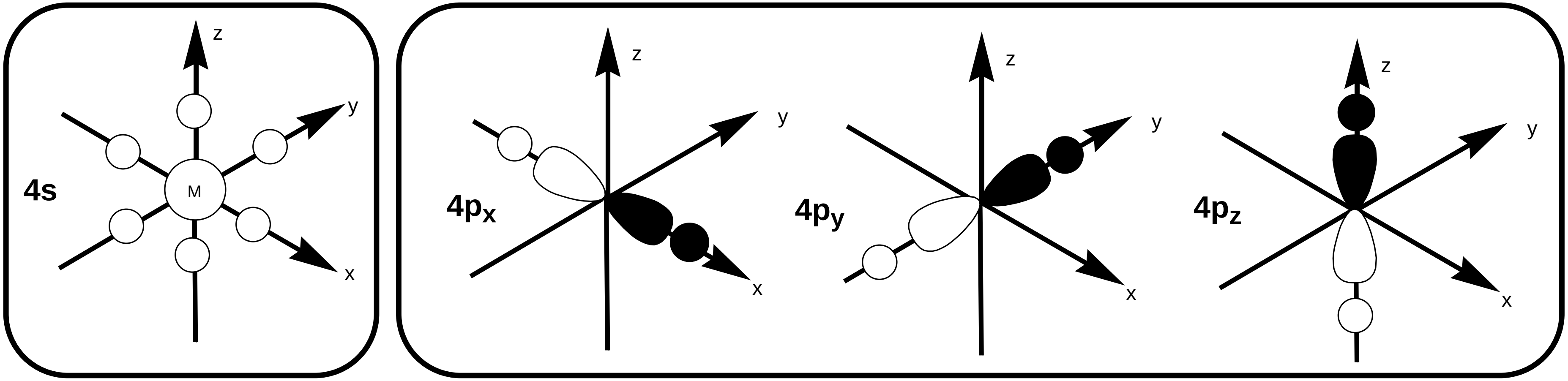
$$\beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}}$$



MOT for octahedral complexes

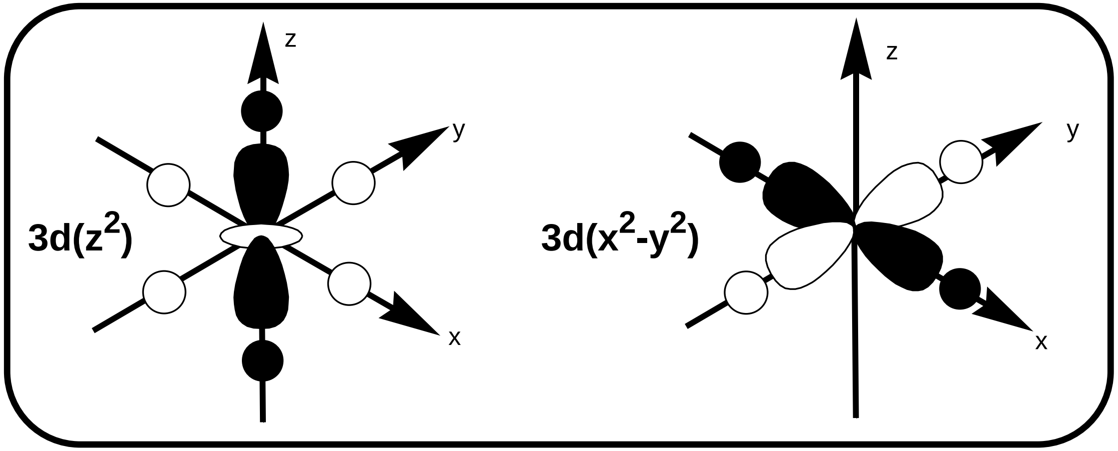
- Metal and ligand orbitals will overlap as long as they are of the correct symmetry to do so.
- The appropriate AOs of the metal are combined with atomic or molecular orbitals of the ligands by **Linear Combination of Atomic Orbitals**
- Overlap of metal and ligand orbitals of widely differing energy can be neglected, so only valence orbitals need be considered.

- 6 of the metal orbitals are directed along the axes and are capable of forming σ bonds with the ligands
- Metal s and p orbitals are clearly of the correct symmetry to overlap with the ligands.



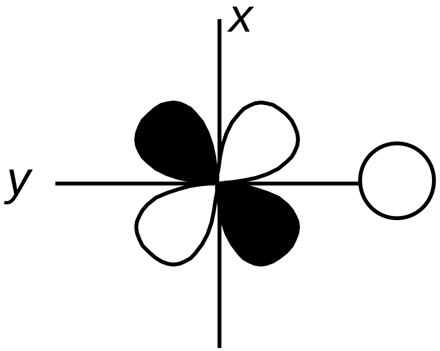
BONDING

- Of the metal d orbitals, two are correctly aligned to form σ-bonds; the remaining three orbitals will be non-bonding



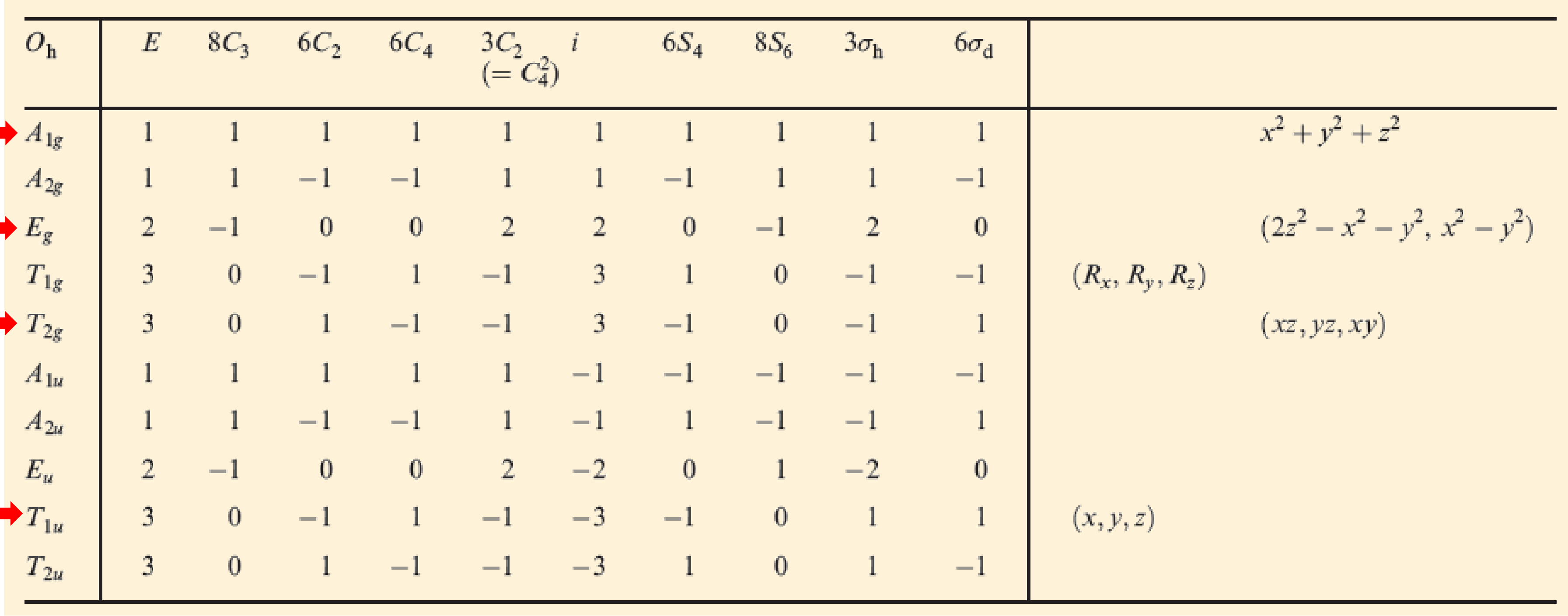
BONDING

Using d_{xy} orbital as an example



Overlap integral is zero
i.e. **NON BONDING**

Symmetry labels of the metal orbitals derived from O_h point group character table for ML_6 complex



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
→ A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
→ E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
→ T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
→ T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

Symmetry properties of the metal atomic orbitals in octahedral ML_6 system

Consider the 1st transition series.
The nine valence orbitals of metal have been classified into **four types** by using concept of group theory

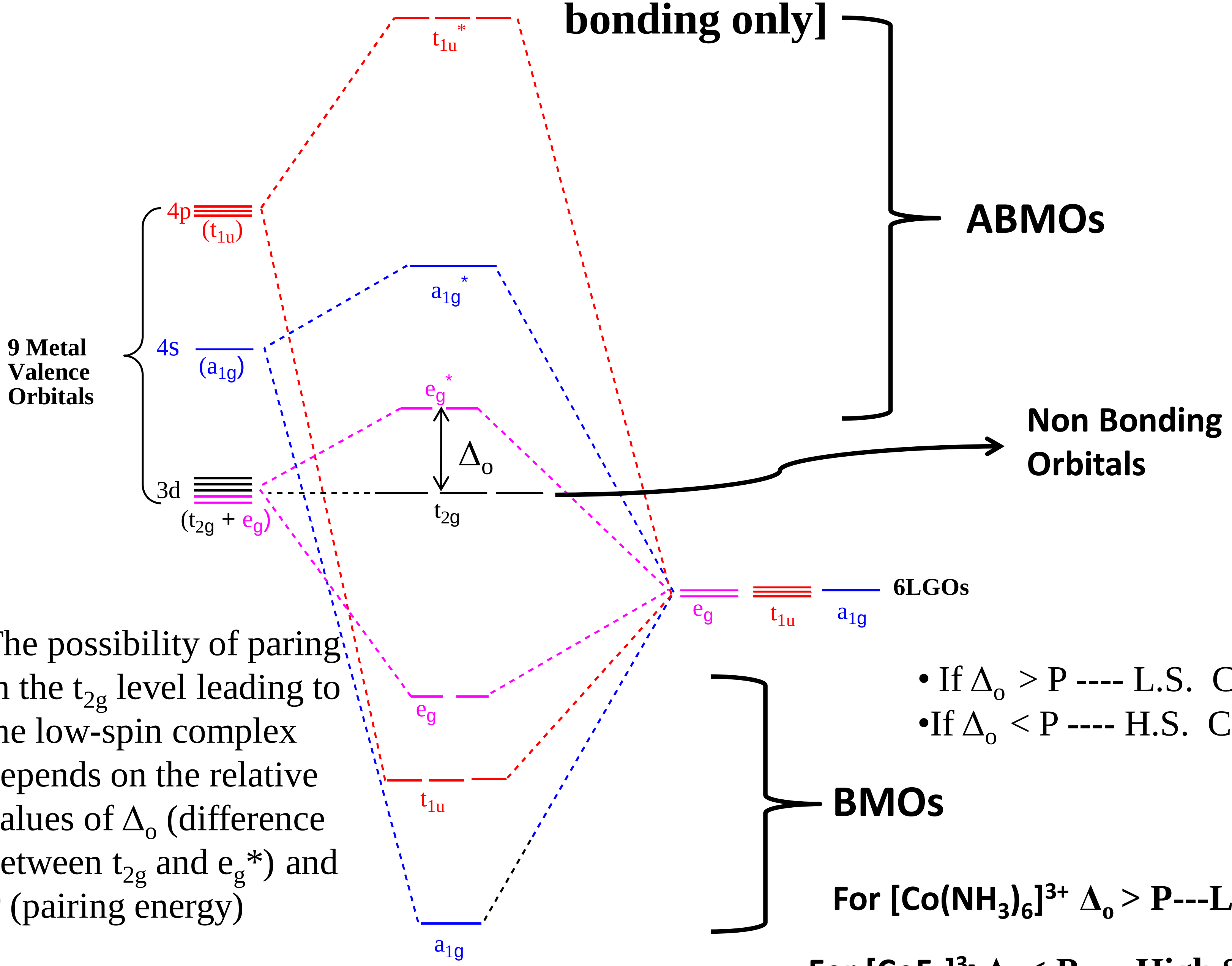
1. 4s orbital: $\mathbf{a_{1g}}$ (spherically symmetrical)
2. $4p_x$, $4p_y$ and $4p_z$: $\mathbf{t_{1u}}$ (a set of three equivalent orbitals lying along the axis)
3. $3d_{x^2-y^2}$ and $3d_{z^2}$: $\mathbf{e_g}$ (a pair of equivalent orbitals lying along the axis)
4. $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$: $\mathbf{t_{2g}}$ (a set of three equivalent orbitals lying in between the axis)

Formation of **σ-Ligand Group Orbitals (LGOs)** with proper symmetries.

1. Consider the **σ-bonding orbitals** of the ligands. For most of the ligands, these are composed of s and p-atomic orbitals (Eg: sp^3 for H_2O, NH_3: *p* for halides etc.)
2. These orbitals approaching the metal from directions +x. –x, +y, -y, +z and –z and are described as $\boldsymbol{\sigma_x}$, $\boldsymbol{\sigma_{-x}}$, $\boldsymbol{\sigma_y}$, $\boldsymbol{\sigma_{-y}}$, $\boldsymbol{\sigma_z}$ **and** $\boldsymbol{\sigma_{-z}}$ respectively.
3. From these ligand orbitals through the linear combinations, different LGOs can be constructed to match the metal orbitals.
4. These LGOs are grouped into 3 types

I. $\mathbf{a_{1g}}$
II. $\mathbf{t_{1u}}$
III.$\mathbf{e_g}$

Molecular orbital Energy Level diagram for ML_6 (octahedral) [sigma bonding only]



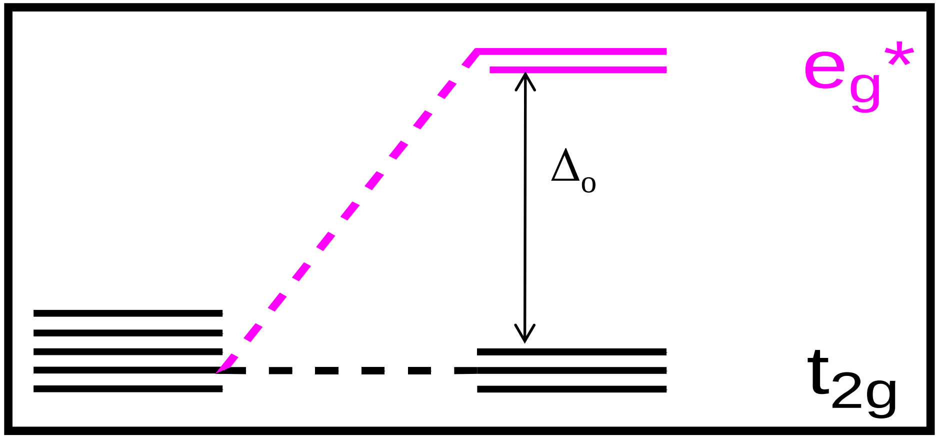
The possibility of paring in the t_{2g} level leading to the low-spin complex depends on the relative values of Δ_o (difference between t_{2g} and e_g*) and P (pairing energy)

- If Δ_o > P ---- L.S. Complex.
- If Δ_o < P ---- H.S. Complex

For $[Co(NH_3)_6]^{3+}$ Δ_o > P---Low Spin

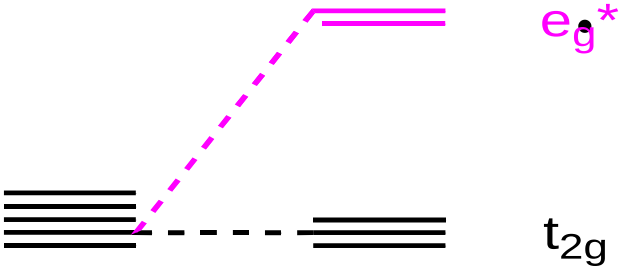
For $[CoF_6]^{3-}$ Δ_o < P---- High Spin

σ- Bonding



- Any extra electrons from metal d orbitals go into t_{2g}/e_g* levels
  - Thus, metal d-electrons *do not participate* in forming M–L σ-bonds, but remain in the frontier orbitals
- e_g* levels {$d_{x^2-y^2}$ and d_{z^2} according to CFT} are actually *weakly antibonding molecular orbitals*, **not** pure metal d-orbitals
- t_{2g} orbitals in contrast are pure d-orbitals **(by σ bonding only model)**

σ- Bonding



- Separation of t_{2g} and e_g* (ie Δ_o) depends on extent of interaction of metal and ligand orbitals
  - stronger bonding will lower e_g and raise e_g*, giving bigger $\Delta_{o.}$

Consequences of the σ- bonding model

- ❖Any electron in e_g* is antibonding and will weaken and lengthen bonds in the complex.
- ❖This will result in faster substitution reactions for complexes with occupied e_g* orbitals.
- ❖Occupation of all bonding and non-bonding orbitals requires 18 electrons, 12 from ligands and six from metal.

Molecular orbital Energy Level diagram for ML_4 (tetrahedral) [sigma bonding only)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

1. In Tetrahedral complex, the metal orbitals available are as follows

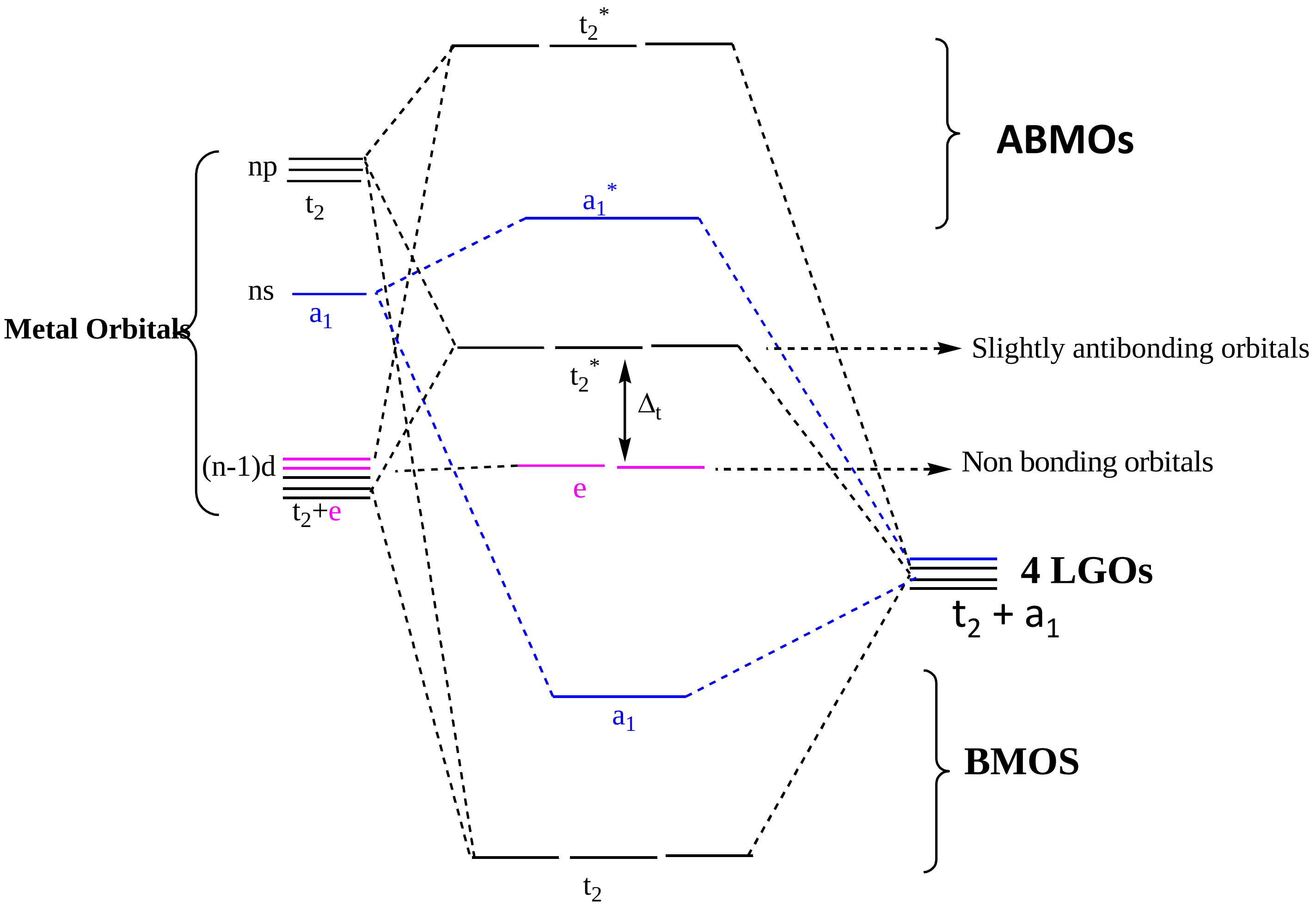
Atomic orbitals	Symmetry
s	a_1
p (p_x, p_y, p_z)	t_2
d_{z2}, d_{x2-y2}	e
d_{xy}, d_{yz}, d_{zx}	t_2

2. The ligand orbitals produce the **4 LGOs** and are as follows

3 LGOs------t_2
1 LGOs------a_1

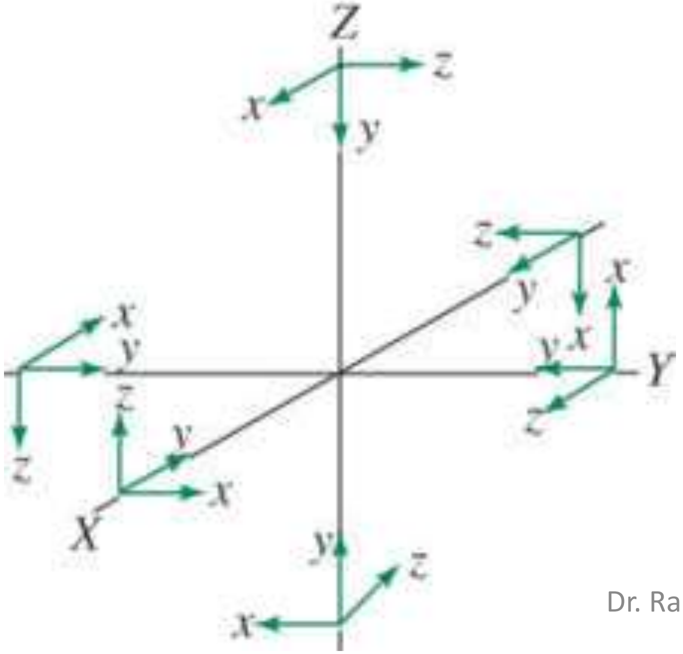
3. There is no LGO **of e-symmetry.**

Molecular orbital Energy Level diagram for ML_4 (tetrahedral) [sigma bonding only) Ex: $[CoCl_4]^{2-}$, $[NiCl_4]^{2-}$, etc.



Application of MOT to Octahedral complexes involving both σ and π-Bonding

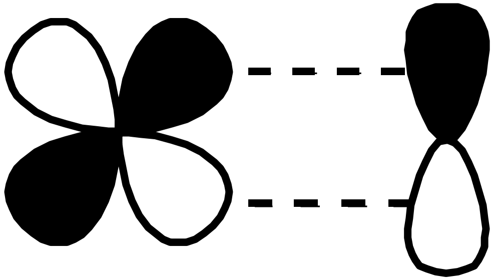
- The metal t_{2g} orbitals cannot participate in the formation of **σ-**bonds but are of the correct symmetry to overlap with ***pi*-orbitals** of ligands (if there are any).
- In contrast, the e_g and e_g* orbitals cannot participate in pi-bonding with ligands
- Four types of **pi- interactions** are commonly encountered.



Metal d-orbital

d(π)–p(π) interaction

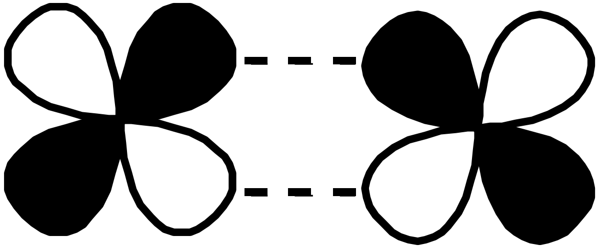
Donation of electrons from filled p orbitals of ligand to empty d orbitals of metal



Ligand p-orbital
(e.g. halide ligand)

d(π)–d(π) interaction

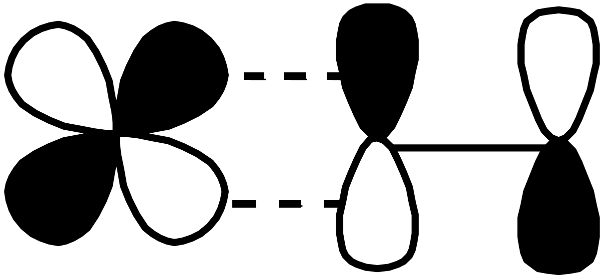
Donation of electrons from filled d-orbitals of metal to empty d-orbitals of ligand



Ligand d-orbital
(e.g. P, S, ligand)

d(π)–p(π*) interaction

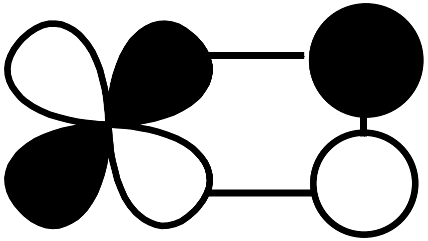
Donation of electrons from filled d-orbitals of metal to empty π-antibonding orbitals of ligand



Ligand π* orbital
(e.g. CN^-, pyridine, CO...)

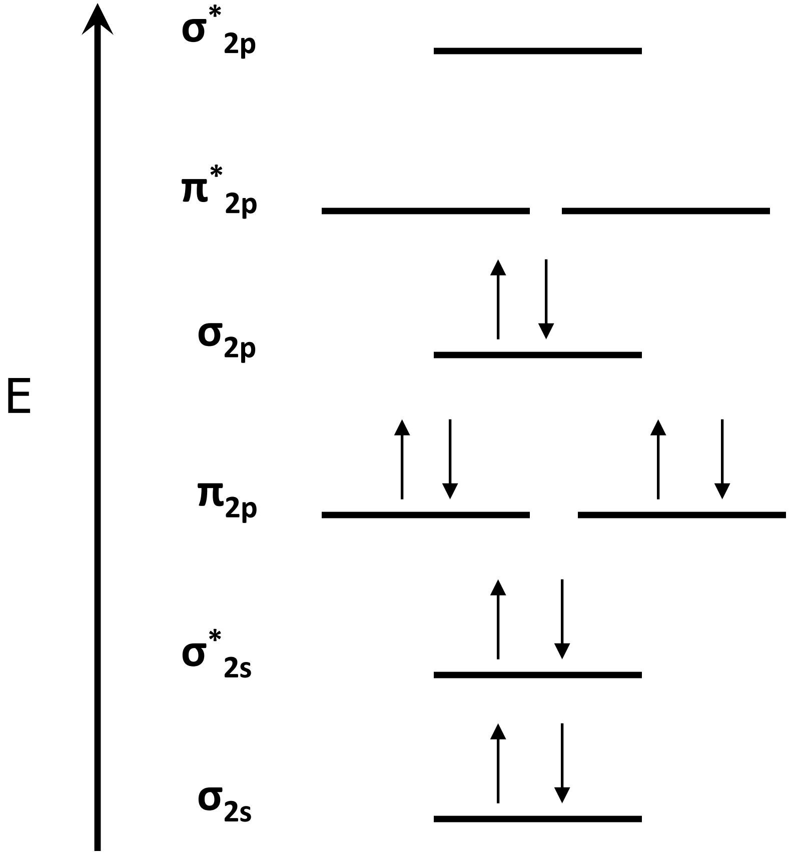
d(π)–σ* interaction

Donation of electrons from filled d-orbitals of metal to empty σ*-antibonding orbitals of ligand



Ligand σ* orbital
(e.g. H_2, Alkanes)

MO Energy level diagram for CO



E

σ^*_{2p}

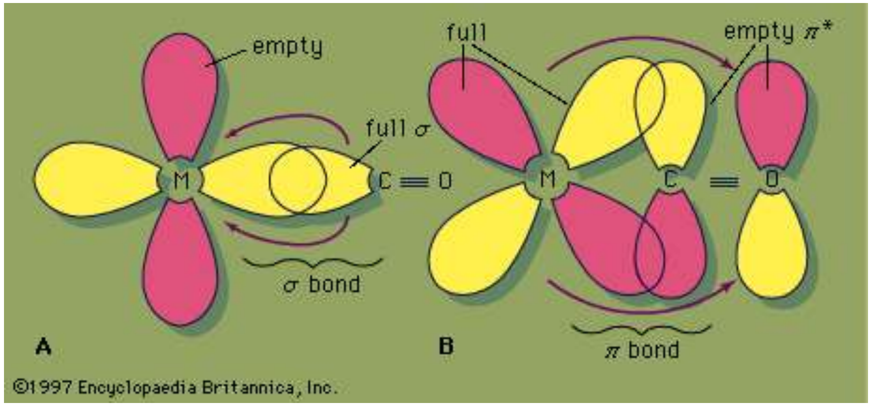
π^*_{2p}

σ_{2p}

π_{2p}

σ^*_{2s}

σ_{2s}

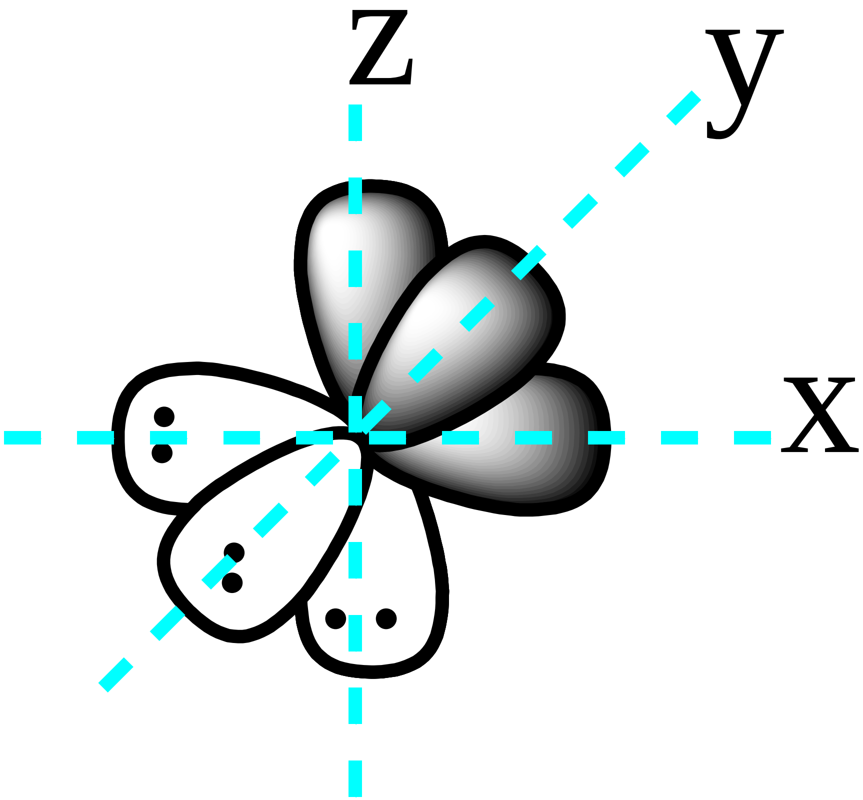


©1997 Encyclopaedia Britannica, Inc.

π effects are subdivided into two extreme cases

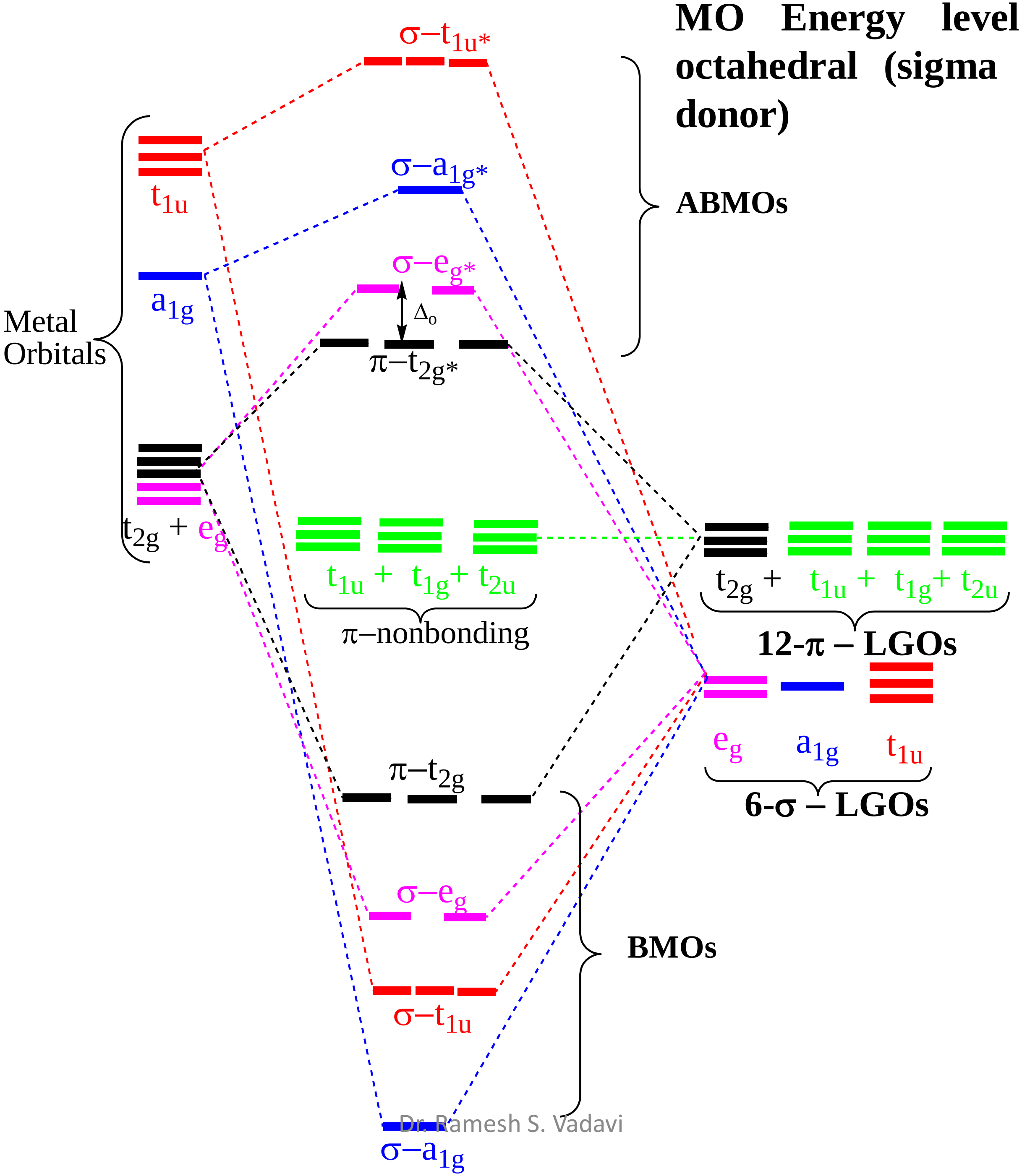
1. π–donor ligands having filled orbitals
2. π–acceptor ligands having empty orbitals

1. π–donor ligands having filled orbitals. For example halides

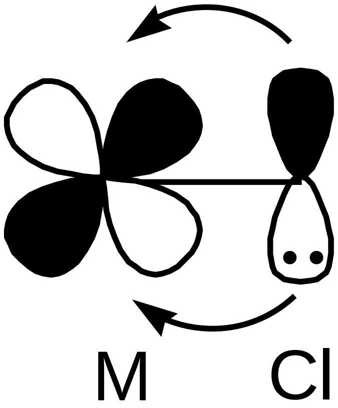


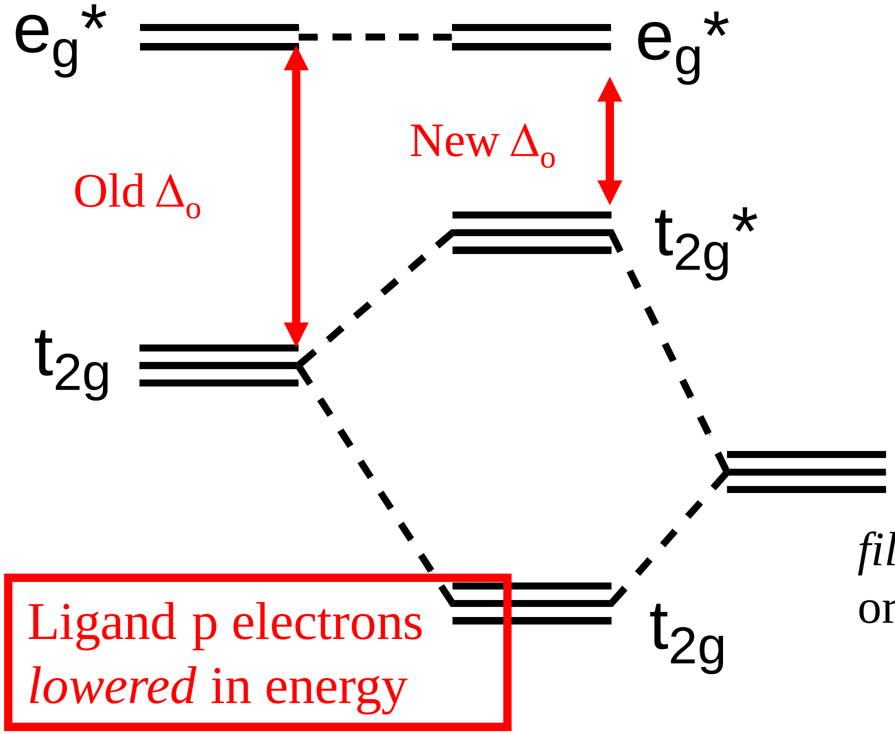
1. If p_x orbital is involved in sigma bonding, then p_y and p_z filled orbitals are available for pi-bonding.
2. From each ligand, two orbitals are available for pi-bonding. So from all six ligands in octahedral complex, the available filled orbitals for pi-bonding is equal to 12.
3. These 12 orbitals have been grouped in to 4 sets of LGOS (12 LGOs) and are $t_{2g}+t_{1g}+t_{1u}+t_{2u}$

MO Energy level diagram for octahedral (sigma donor and pi-donor)



- pi-donor ligands
  - e.g. Halide anions possess lone pairs in p orbitals



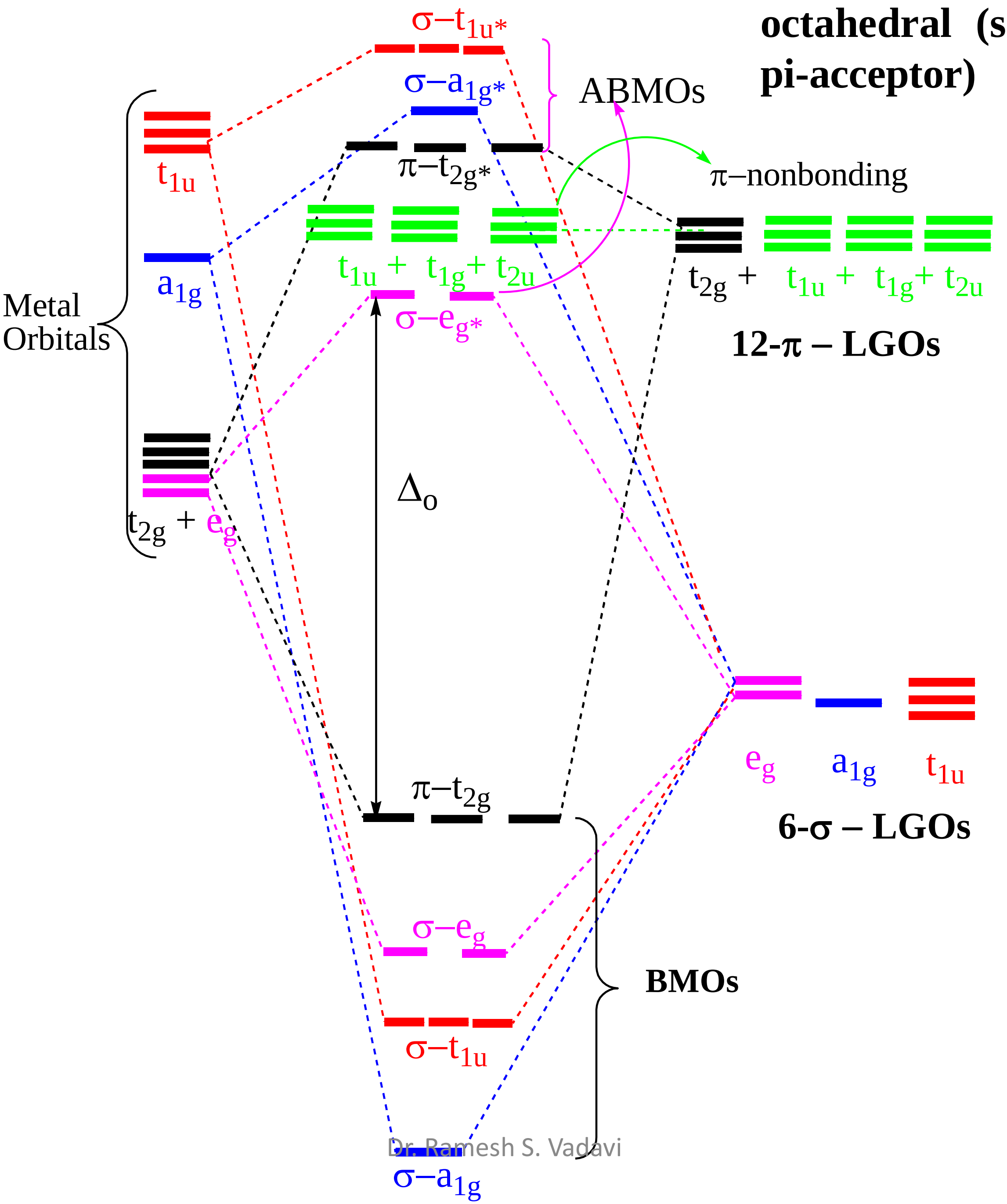


Ligand p electrons *lowered* in energy

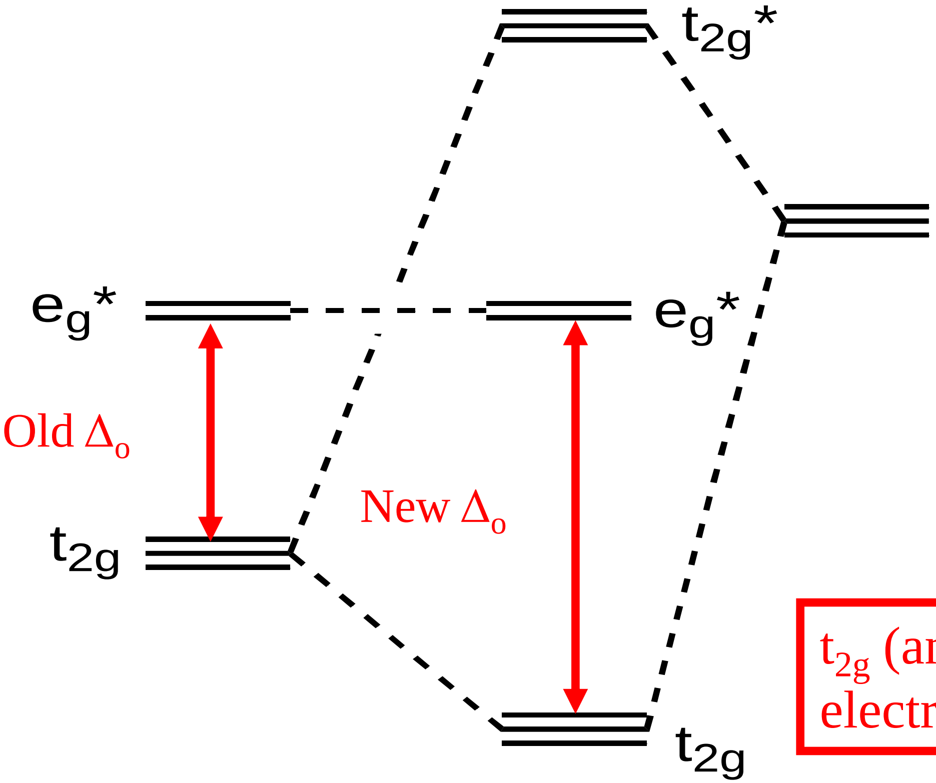
t_{2g}* (and hence the metal electrons) are raised in energy – the orbital is now antibonding

filled, low energy ligand p orbitals of t_{2g} symmetry

MO Energy level diagram for octahedral (sigma donor and pi-acceptor)



- pi- acceptor ligands
  - e.g. CN^-, CO (using π^* orbitals)
  - e.g. PPh_3 {using d orbitals (or more correctly σ^* orbitals but the symmetry is the same whichever)}

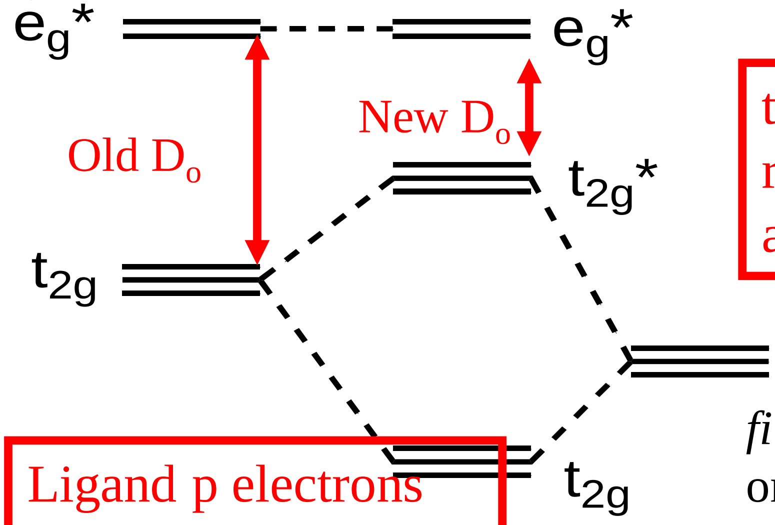


empty, *high energy* ligand pi-orbitals

t_{2g} (and hence the metal electrons) *lowered* in energy

What is Δ_o or 10 Dq ??

- **Ligands having only sigma-donor properties: (e. g. NH_3).**
  In the absence of π-bonding, the energy difference between the σ-e_g* and nonbonding t_{2g} orbital (NBMO) of the metal is known as 10 Dq or Δ_o.
- **Ligands with the pi-donor and sigma-donor properties (e. g. halides, OH^-):**
  When, the π-LGO (t_{2g}) is of lower energy than the metal t_{2g} orbitals, then the π-t_{2g}* (ABMO) becomes more enriched with the metal t_{2g} character and π-t_{2g} (BMO) becomes more enriched with the ligand character. In such cases the energy difference between σ-e_g* and π-t_{2g}* is known as 10 Dq or Δ_o. It reduces the 10 Dq or Δ_o value when compared to the sigma only bonding. It happens so when the ligand uses the filled orbitals for π-donation.



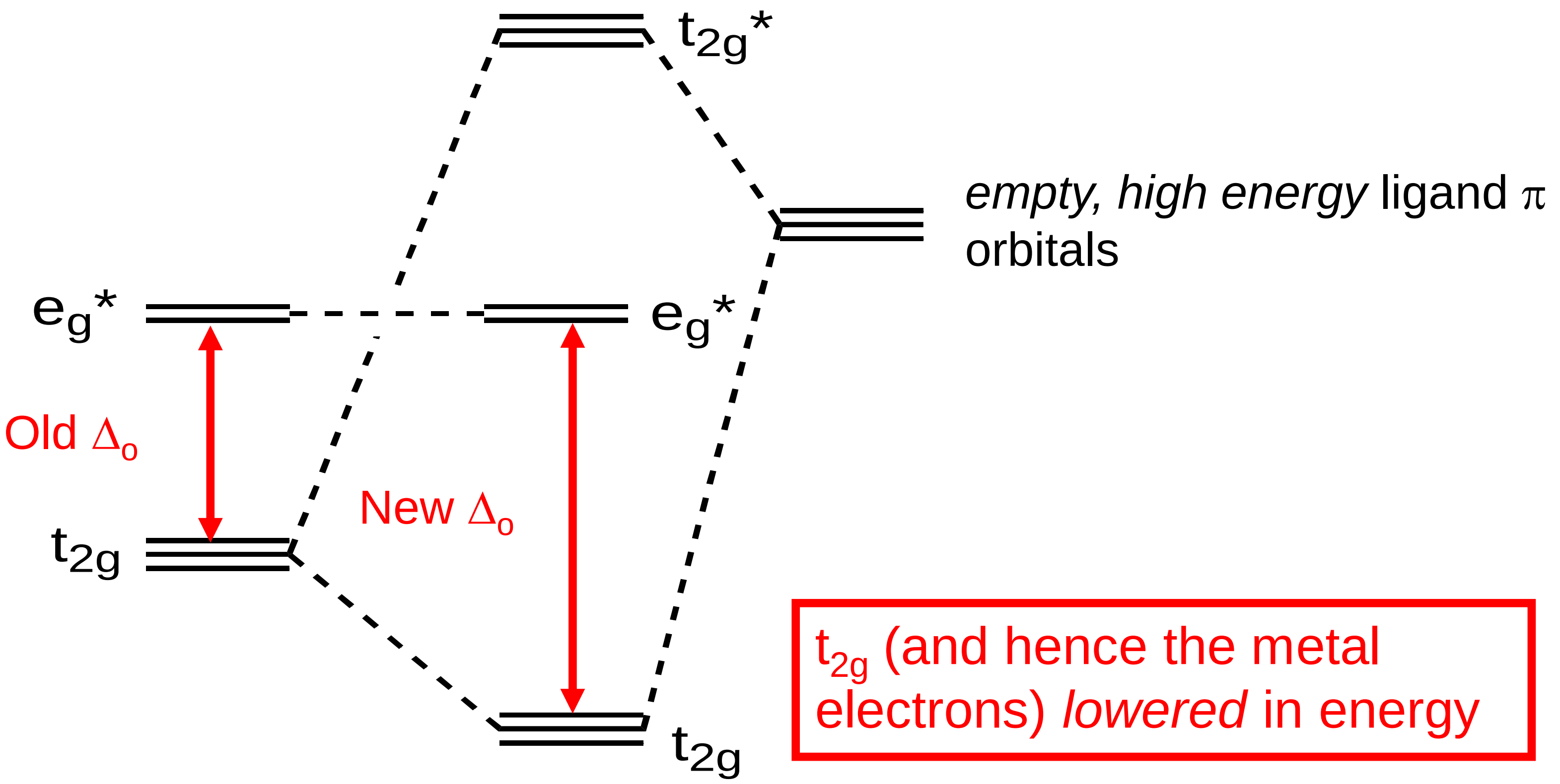
t_{2g}* (and hence the metal electrons) are raised in energy – the orbital is now antibonding

filled, *low energy* ligand p orbitals of t_{2g} symmetry

Ligand p electrons *lowered* in energy

- **Ligands with the π-acceptor and σ-donor properties: (e. g. CO):**

When, **the π-LGO (t2g) is of higher energy than the metal t2g orbitals,** then the π-t_{2g} (BMO) becomes more enriched with the character of the metal t_{2g} orbital. In such cases the energy difference between σ-e_g* and π-t_{2g} is known as 10 Dq or Δ_o. It enhances the 10 Dq or Δ_o value when compared to the sigma only bonding. It happens so when the ligand uses the empty orbitals for π-acceptance (π-acid ligands).



t_{2g} (and hence the metal electrons) *lowered* in energy

- Overall: π donor ligands decrease Δ_o

  π acceptor ligands increase Δ_o
- Similarly: good σ donors increase Δ_o

  poor σ donors decrease Δ_o
- We can now explain the spectrochemical series:

Spectrochemical series: The nature of the ligand affects the degree of splitting of d-orbitals of the metal.

- The ligands with **filled pi-orbitals act as both sigma and pi-donor and split the d-orbitals to the lesser extent resulting in small Δo** and are considered as **weak field ligands.**
- The ligands which acts as **good sigma donor and poor pi-donor** split the d-orbitals moderately and hence are considered as **intermediate in field strength**.
- The ligands with **high energy empty orbitals of pi-symmetry act as both sigma donor and pi-acceptor** and split the d-orbitals to the larger extent resulting in **larger Δo.** These are considered as **strong field ligands.**
- Thus the order of arrangement of the ligands in the increasing order of their field strength is known as spectrochemical series and it has been derived from the electronic spectral studies.

Weak Field (small Δ_o)

$$I^- < Br^- < {}^-\underline{\mathbf{S}}CN < Cl^- < NO_3^- < F^- < (O^{2-} \approx {}^-OH \approx H_2O)$$

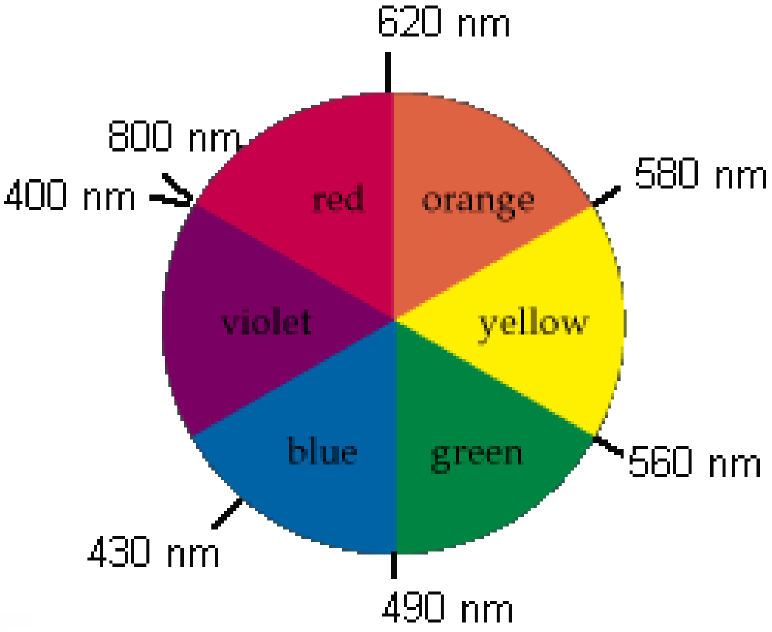
$$< {}^-\underline{\mathbf{N}}CS < NH_3 < \text{bipy} < {}^-CN < PR_3 < CO$$

Strong Field (large Δ_o)

In order to explain the Relative position of ligands in the spectrochemical series, ***both σ and π effects must be considered.***

Electronic Spectroscopy of Transition Metal Complexes

$[CoCl_4]^{2-}$ $[Co(H_2O)_6]^2$



$[Mn(H_2O)_6]^{2+}$

$KMnO_4$

K_2CrO_4

The ferroin-ferriin indicator

Fe^{2+}(o-phen)$_3$

Purple-red predominant if system is in its reducing state.

Fe^{3+}(o-phen)$_3$

Blue predominant if system is in its oxidising state.

Color Chemistry

1. Variety of colors among transition metal complexes is the most striking aspect.

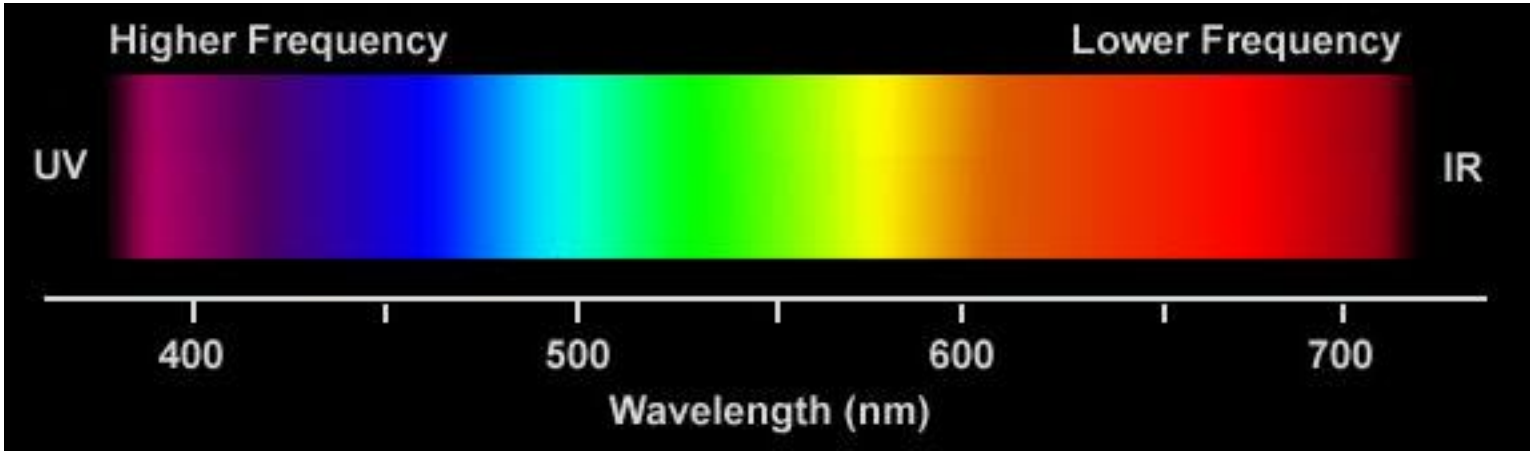
   For example: Aqueous solution of octahedral $[Co(H_2O)_6]^{2+}$ is pink

   Aqueous solution of Tetrahedral $[CoCl_4]^{2-}$ is blue

   Aqueous solution of $[Ni(H_2O)_6]^{2+}$ is green
2. Prussian blue – used as a pigment in blue prints, which is a complicated coordination compound involving Fe(II) and Fe(III)
3. Many Precious gems
4. Blood

Why so many coordination compounds are colored in contrast to most organic compounds?

The Color of the coordination compounds arise from electronic transitions between levels whose spacing correspond to the wavelength available in the visible region and these transitions are known as d-d transitions as they involve the molecular orbitals that are mainly metal d in character.



Electronic spectroscopy provides valuable information related to **bonding and structure.**

Four Quantum numbers

1. **Principal Quantum number (n**): It represents the main energy level in which electron revolves around the nucleus.
2. **Azimuthal quantum number (l):** It represents shape of the orbit or subshell.
3. **Magnetic quantum number (m_l):** It describes the orientaion of electron in space
4. **Spin quantum number (m_s)**: It describes the spin orientation of electron.

Electronic configuration:

$2p^2$ configuration indicates n = 2, l = 1 but it doesn't provide the information about m_l and m_s.

Electronic configuration is an **incomplete description** of the arrangement of electrons in an atom.

1. In the configuration $2p^2$, the two electrons might occupy orbitals with different values of m_l from among the possibilities, +1, 0, -1 that are available when l = 1.
2. Similarly the designation $2p^2$ tells us nothing about the spin orientation of two electrons, i.e., $m_s = +1/2$ or $-1/2$
3. The different ways in which the electrons can occupy the orbitals specified in the configuration are called **microstates of the configuration.**

One microstate of a $2p^2$ configuration indicates is $[1^+, 1^-]$.
This notation signifies that both electrons occupy an orbital with $m_l = +1$, the superscript + indicating $m_s = +1/2$ and – indicating $m_s = -1/2$.

Another microstate of the same configuration is $[-1^+, 0^+]$.
One electron occupies $m_l = -1$ and another occupies $m_l = 0$, but electron occupies $m_s = +1/2$.
How many microstates are possible for a particular configuration?

$$\text{Number of microstates} = \frac{n!}{r!\,(n - r)!}$$

Where **n** is twice the number of orbitals and **r** is the number of electrons.

For p^2 configuration

$$\text{Number of microstates} = \frac{6!}{2!\,(6 - 2)!}$$

$$= 15$$

Spectroscopic Terms

- The microstates of a given configuration have the same energy only if interelectronic repulsions are negligible. However atoms and most molecules are compact, interelectronic repulsions are strong and can not be ignored.
- Microstates that corresponds to different relative spatial distributions of electrons have different energies.
- The microstates can be sorted out in the order of energy according to two new quantum numbers.

1. **Total Spin Quantum numbers S =** Summation of all the spins (m_s)

For a given Value of **S, there will be 2S+1 spin states characterized by** M_S

i.e., $M_S = S, S-1, S-2, \ldots\ldots, -S$

2. **Total Orbital Quantum number L** = summation of all (m_l) values

For a given Value of **L, there will be 2L+1 number of** M_L ***values.***

i.e., $M_L = L, L-1, L-2, \ldots\ldots, -L$

A systematic approach to Spectroscopic Terms

Example: p^2 configuration.

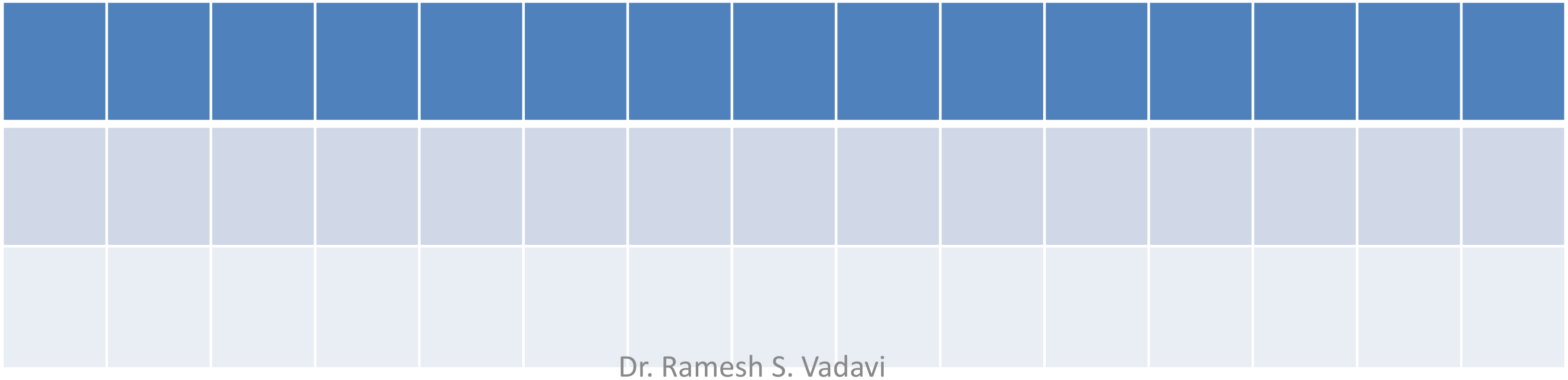
1. Draw the vertical columns, which are equal to the number of microstates.

For p^2 ; 15 columns

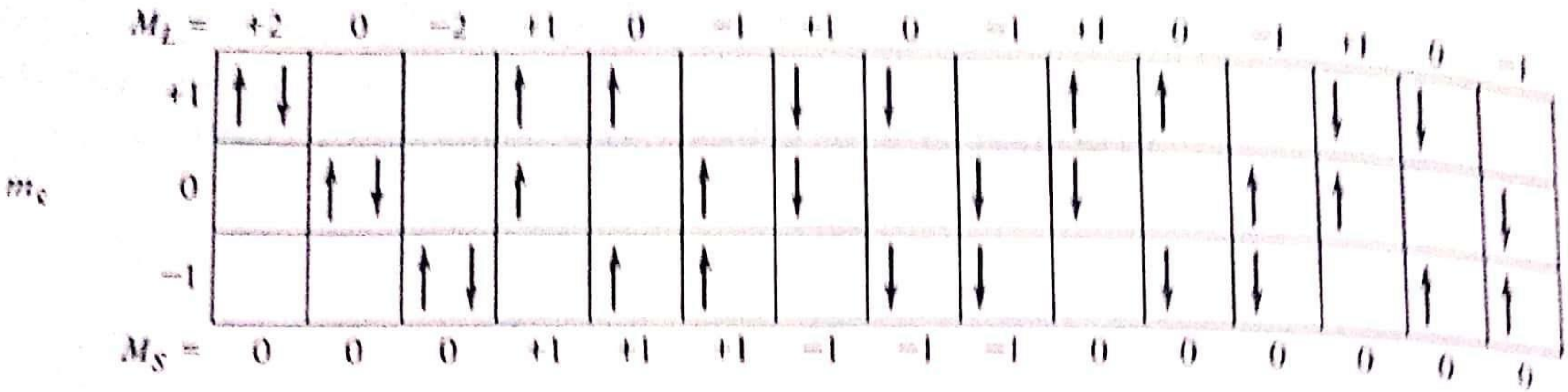
2. Determine the electron configurations that are allowed by the Pauli principle.

This can be done by drawing a number of sets of *p*-orbitals (m_l values) as horizontal rows.

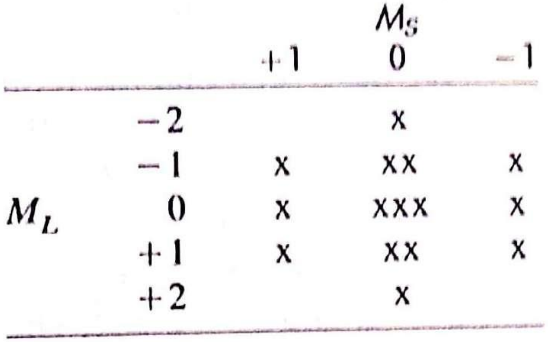
i.e., 3 horizontal rows for p^2 configuration.



3. Place the electrons by following Pauli’s principle and for every arrangement of electrons calculate the M_L and M_S value as shown below

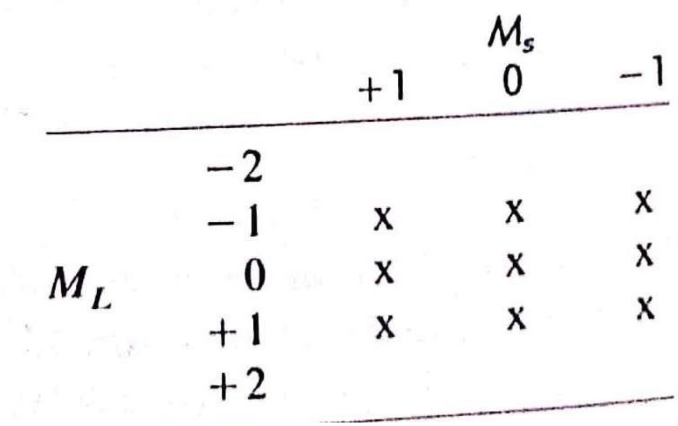


3. Set up a chart of microstates as shown below.



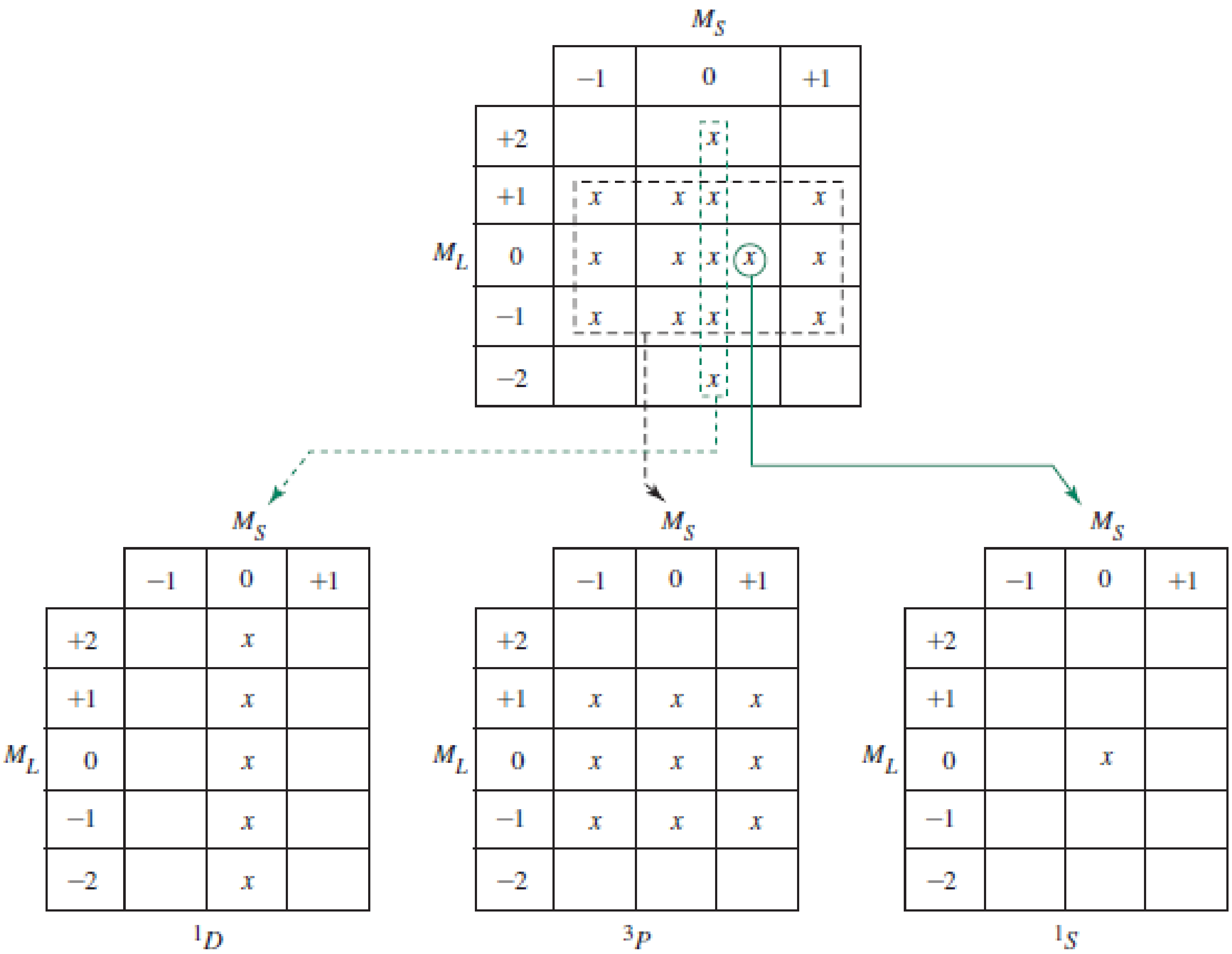
M_L \ M_S	+1	0	−1
−2		x	
−1	x	xx	x
0	x	xxx	x
+1	x	xx	x
+2		x	

4. Resolve the chart of microstates into appropriate atomic states



			M_s	
		+1	0	−1
	−2			
	−1	x	x	x
M_L	0	x	x	x
	+1	x	x	x
	+2			

TABLE 11.4 The Microstate Table for p^2 and Its Reduction to Free-Ion Terms



M_L \ M_S	-1	0	$+1$
$+2$		x	
$+1$	x	x x	x
0	x	x x x	x
-1	x	x x	x
-2		x	

M_L \ M_S	-1	0	$+1$
$+2$		x	
$+1$		x	
0		x	
-1		x	
-2		x	

^1D

M_L \ M_S	-1	0	$+1$
$+2$			
$+1$	x	x	x
0	x	x	x
-1	x	x	x
-2			

^3P

M_L \ M_S	-1	0	$+1$
$+2$			
$+1$			
0		x	
-1			
-2			

^1S

NOTE: The ^1S and ^1D terms have higher energy than the ^3P term. The relative energies of higher energy terms like these cannot be determined by simple rules.

Spectroscopic Terms: The grouping of microstates together that have same energy, when electron repulsions are taken into account, results in spectroscopically distinguishable energy levels called Terms.

The microstates can be sorted out in the order of energy according to two new quantum numbers.

1. Total Spin Quantum numbers **S =** Summation of all the spins (m_s)
2. Total Orbital Quantum number **L** = summation of all l (m_l) values

Coupling Schemes: Two types

1. **R – S coupling or L- S Coupling or Spin-Orbit Coupling:** Applies to lighter elements
2. **j – j coupling:** Applies to heavier atoms

R-S Coupling: It involves three types couplings

1. Spin-Spin coupling: Spin angular momenta of two electrons are coupled = S
2. Orbit-orbit coupling: Orbital angluar momenta of two electrons are coupled = L
3. Spin-Orbit Coupling: Spin anngular momenta and Orbital angular momenta of same electrons are coupled. L+S = J

The possible number of J values is = 2S+1, when $L \geq S$

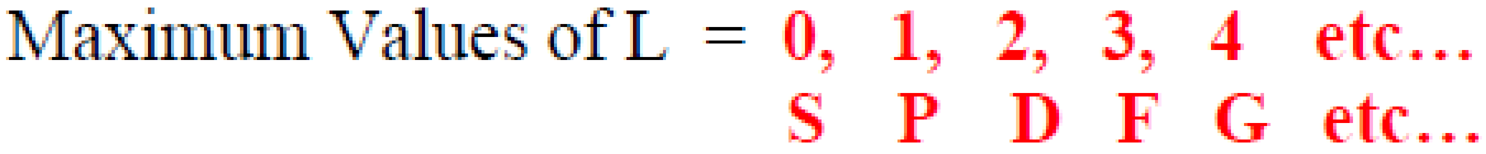
The possible number of J values is = 2L+1, when $L \leq S$

J = L+S, L+S-1, L+S-2……0…..L-S.

J is never negative.

Spin-spin coupling > orbit-orbit coupling > Spin-Orbit coupling for elements with atomic number less than 30

Different values of L define the state of an atom or ion as a whole.



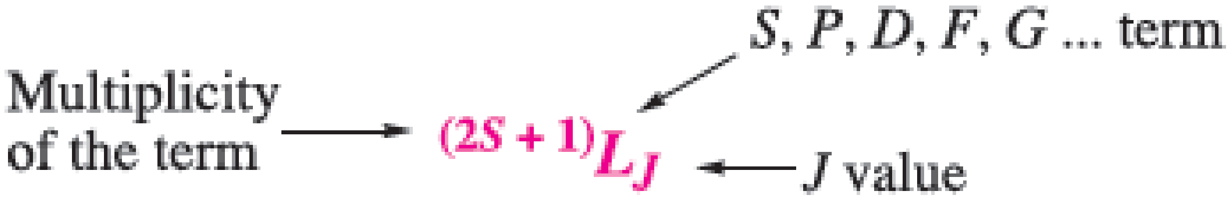
Maximum Values of L = 0, 1, 2, 3, 4 etc…

S P D F G etc…

Term Symbols

- These are symbolic representation of atomic states characterized by total spin quantum number **S** **,** total angular momentum quantum number **L** and total resultant quantum number **J**

- Term symbol of an atom or ion is represented as



Hund's rules for determination of Spectroscopic ground state

1. Ground state is characterized by the ***highest spin multiplicity***.
2. After having highest spin multiplicity, the ground state will be characterized by the highest possible orbital multiplicity, i.e., ***highest value of L***
3. For *half-filled shell or less than half filled shell,* the ground state is characterized by ***lowest J value***, while for a *more than half filled shell* the ground state is characterized by ***highest J value***.

Derivation of Spectroscopic Ground state term symbol

Ex: Carbon

1. The Value of **L** is obtained by adding the **m_l** values for all the electrons in incomplete shell. In Carbon incomplete shell is having two electrons i.e.p^2 According to Hund's rule of maximum multiplicity and Pauli's exclusion principle,

   1st Electron will occupy the orbital with $m_l = +1$, and

   2nd electron will occupy the orbital with $m_l = 0$.

   $L = +1+0 = 1$.

2. The value for S is sum of spin quantum numbers for each unpaired elctron.

   So for Carbon $S = +1/2 +1/2 = 1$

3. Complete subshells contribute nothing to L and S.

   For Carbon **L = 1** indicates **P** state

   S = 1

   2S + 1 =3

4. Here $L = S$, So J can have maximum of $2S+1$ or $2L+1$ values, i.e. three values are possible.

$J = L+S, L+S-1, L+S-2$

$= 2, 1, 0$

5. Since carbon has **less than half filled** configuration, the value $J = 0$ is lowest in energy.

6. The Spectroscopic ground term symbol for Carbon is $\mathbf{{}^{3}P_{0}}$.

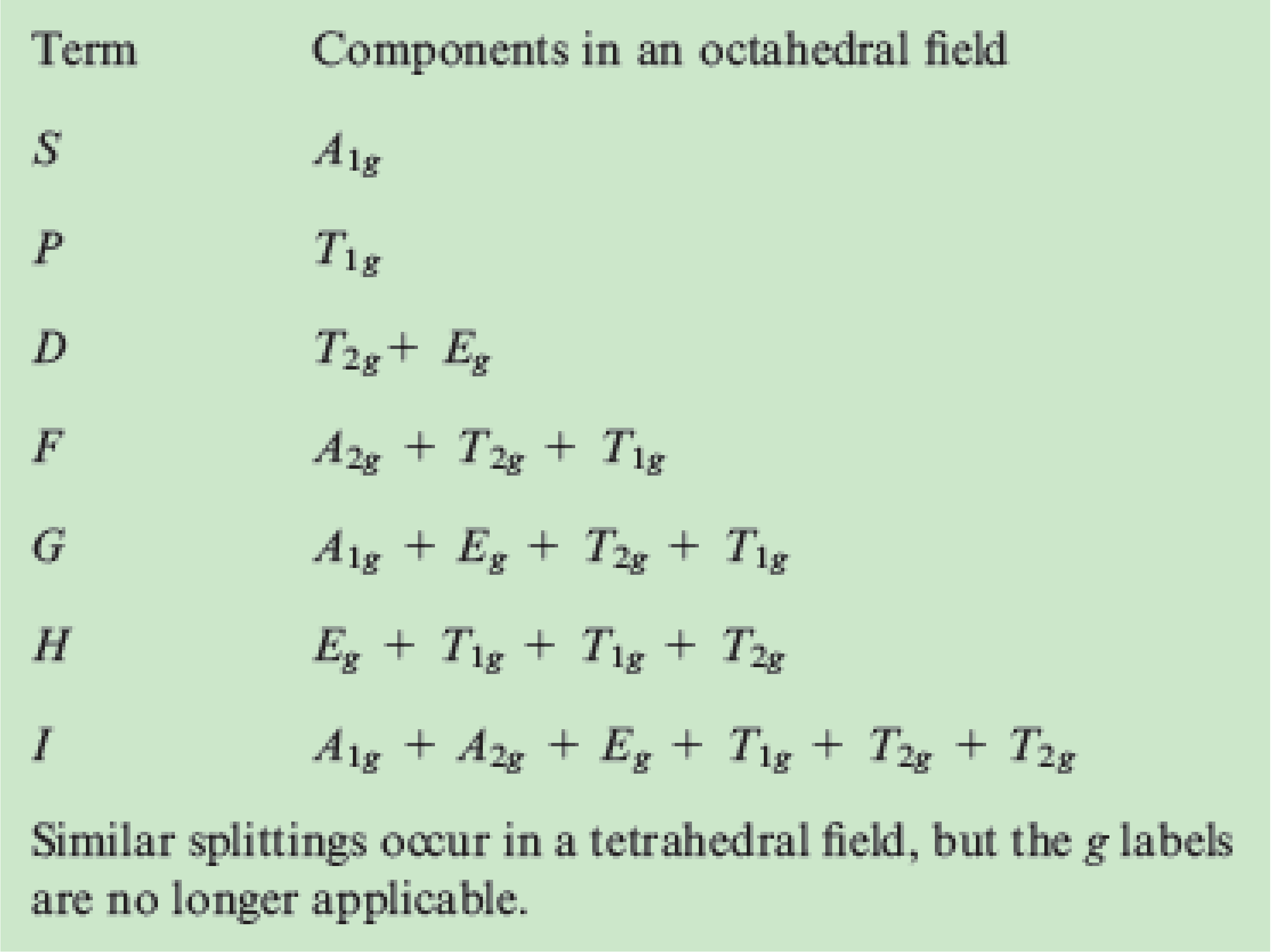
Spectroscopic ground terms for d^n configurations.

d^n	m_l values					L	S	2S+1	J	Ground Term
	+2	+1	0	-1	-2					
d^1	↑					2 = **D**	½	2	5/2, **3/2**	$^{2}\mathbf{D}_{3/2}$
d^2	↑	↑				3 = **F**	1	3	4, 3, **2**	$^{3}\mathbf{F}_{2}$
d^3	↑	↑	↑			3 = **F**	3/2	4	9/2, 7/2, 5/2**, 3/2**	$^{4}\mathbf{F}_{3/2}$
d^4	↑	↑	↑	↑		2 = **D**	2	5	4,3,2,1,**0**	$^{5}\mathbf{D}_{0}$
d^5	↑	↑	↑	↑	↑	0 = **S**	5/2	6	**5/2**	$^{6}\mathbf{S}_{5/2}$
d^6	↑↓	↑	↑	↑	↑	2 = **D**	2	5	**4**,3,2,1,0	$^{5}\mathbf{D}_{4}$
d^7	↑↓	↑↓	↑	↑	↑	3 = **F**	3/2	4	**9/2**, 7/2, 5/2, 3/2	$^{4}\mathbf{F}_{9/2}$
d^8	↑↓	↑↓	↑↓	↑	↑	3 = **F**	1	3	**4**, 3, 2,	$^{3}\mathbf{F}_{4}$
d^9	↑↓	↑↓	↑↓	↑↓	↑	2 = **D**	½	2	**5/2**, 3/2	$^{2}\mathbf{D}_{5/2}$
d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	0 = **S**	0	0	**0**	$^{1}\mathbf{S}_{0}$

Derive the ground state term symbol for following.

1. Ti^{3+}
2. V^{2+}
3. V^{3+}
4. Cr^{2+}
5. Cr^{3+}
6. Mn^{2+}
7. Mn^{3+}
8. Fe^{2+}
9. Fe^{3+}
10. Co^{2+}
11. Co^{3+}
12. Ni^{2+}
13. Cu^{2+}
14. Cu^{+}
15. Zn^{2+}

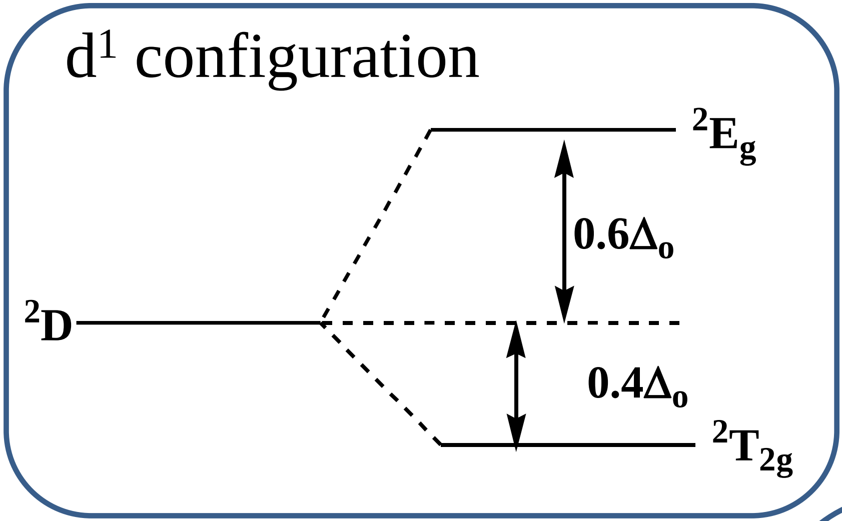
Splitting of Spectroscopic Terms



Term	Components in an octahedral field
S	A_{1g}
P	T_{1g}
D	$T_{2g} + E_g$
F	$A_{2g} + T_{2g} + T_{1g}$
G	$A_{1g} + E_g + T_{2g} + T_{1g}$
H	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Similar splittings occur in a tetrahedral field, but the *g* labels are no longer applicable.

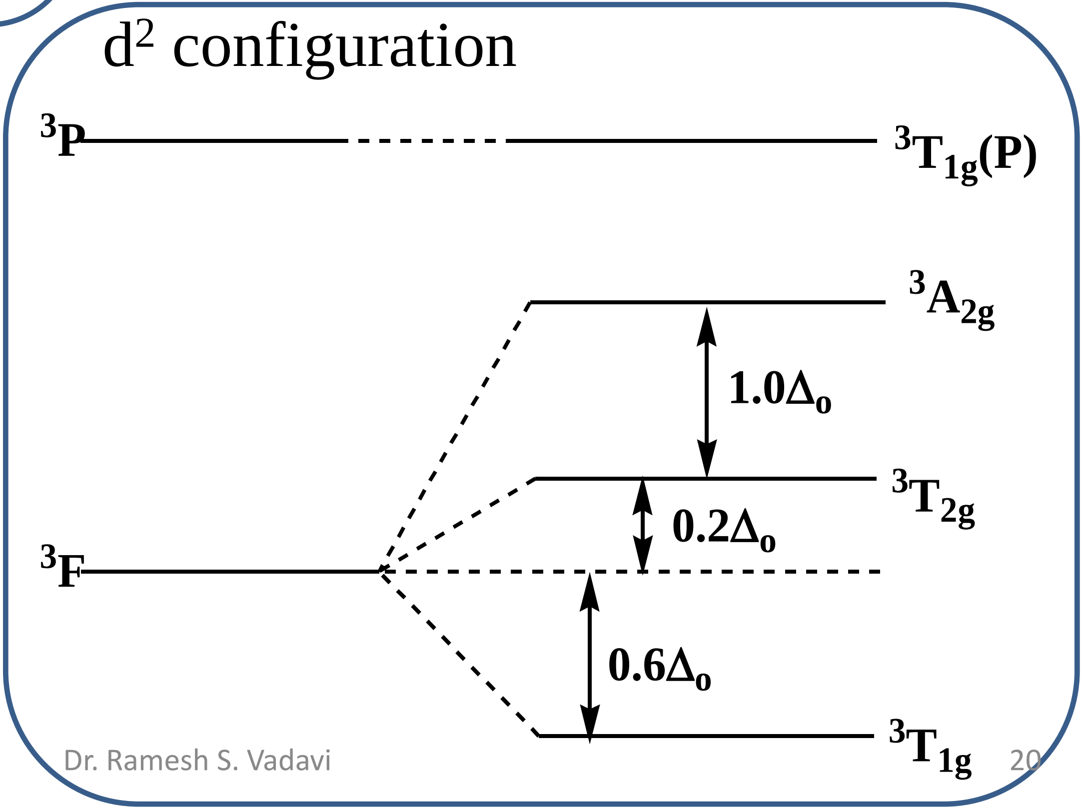
Splitting of the Ground Terms in Octahedral Field



d^1 configuration

Fig. 1

Fig. 2



d^2 configuration

Splitting of the terms for **d^n** configuration in weak octahedral field

Configuration of free ion	Ground state of free ion	Configuration of complexed ion	Energy level diagram
d^1	^2D	t^1_{2g}	Fig. 1
d^2	^3F	t^2_{2g}	Fig. 2
d^3	^4F	t^3_{2g}	Inverted Fig. 2
d^4	^5D	$t^3_{2g}e^1_g$	Inverted Fig. 1
d^5	^6S	$t^3_{2g}\ e^2_g$	No splitting
d^6	^5D	$t^4_{2g}e^2_g$	Same as Fig. 1
d^7	^4F	$t^5_{2g}e^2_g$	Same as Fig. 2
d^8	^3F	$t^6_{2g}e^2_g$	Inverted Fig. 2
d^9	^2D	$t^6_{2g}e^3_g$	Inverted Fig. 1
d^{10}	^1S	$t^6_{2g}\ e^4_g$	No splitting

NB: Inversion applies only to F state and that the F state is always lower in energy than P state

Splitting of the terms for **d^n** configuration in tetrahedral field

Configuration of free ion	Ground state of free ion	Configuration of complexed ion	Energy level diagram
d^1	^2D	e^1	Inverted Fig. 1
d^2	^3F	e^2	Inverted Fig. 2
d^3	^4F	$e^2t^1_2$	Same as Fig. 2
d^4	^5D	$e^2t^2_2$	Same as Fig 1
d^5	^6S	$e^2t^3_2$	No splitting
d^6	^5D	$e^3t^3_2$	Inverted Fig. 1
d^7	^4F	$e^4t^3_2$	Inverted Fig. 2
d^8	^3F	$e^4t^4_2$	Same as Fig. 2
d^9	^2D	$e^4t^5_2$	Same as Fig. 1
d^{10}	^1S	$e^4t^6_2$	No splitting

NB: Since Td geometry lacks center of inversion, there is no subscript for terms.

Types of electronic transitions

1. Ligand field transitions or d-d transitions: mainly involves metal d orbitals.

2. Charge transfer Transitions: mainly 3 types

   a. MLCT: Involves the transitions from metal based Molecular orbital to ligand based Molecular orbitals.
   $[Fe(H_2O)_5(SCN)]^{2+}$, $[Fe(Phen)_3]^{2+}$

   b. LMCT: Involves the transitions from **Ligand based Molecular orbital to Metal** based Molecular orbitals.
   Examples: $[MnO_4]^-$

   c. ILCT: involves Ligand based molecular orbitals.

   d. Intervalence charge transfer transitions.

$[CoCl_4]^{2-}$ $[Co(H2O)_6]^{2+}$

$MnCl_2$

$[Mn(H_2O)_6]^{2+}$

Concentrated $[Mn(H2O)_6]^{2+}$


The ferroin-ferriin indicator

$Fe^{2+}(o\text{-}phen)_3$

Purple-red predominant if system is in its reducing state.

$Fe^{3+}(o\text{-}phen)_3$

Blue predominant if system is in its oxidising state.

$KMnO_4$

K_2CrO_4

The relative intensities of absorption bands are governed by two selection rules

1. **Laporte selection rule**: Transition between states of same parity are forbidden but between different parity are allowed

   i.e. Allowed transitions : g ↔ u

   Forbidden transitions: g ↔ g, u ↔ u

   It leads to $\Delta l = \pm 1$

   So the allowed transitions are : s → p, p → d, d → f, and forbidden transitions are : s → s, d → d, p → p, f → f

   For ex: Transition between d-orbitals are forbidden

2. **Spin selection rule**: Transition between states of different spin multiplicities are forbidden forbidden but between same spin multiplicities are allowed.

   i.e. Allowed transitions : Triplet → Triplet, Singlet → singlet

   Forbidden transitions: Singlet ↔ Triplet, u ↔ u

   It leads to $\Delta S = 0$

These rules seem to rule out most of electronic transitions for transition metal complexes, but in reality, many of the complexes are vividly colored.

Relaxation of Selection rules

1. Vibronic coupling mechanism relaxes Laporte rule

   The bonds in transition metal complexes are not rigid but undergo vibrations that may temporarily change the symmetry

   For example: Octahedral complexes vibrate in ways in which the center of symmetry is temporarily lost. This phenomenon is called vibronic coupling.

2. Mixing of the orbitals in tetrahedral complexes leads to relax Laporte rule (d-p mixing).

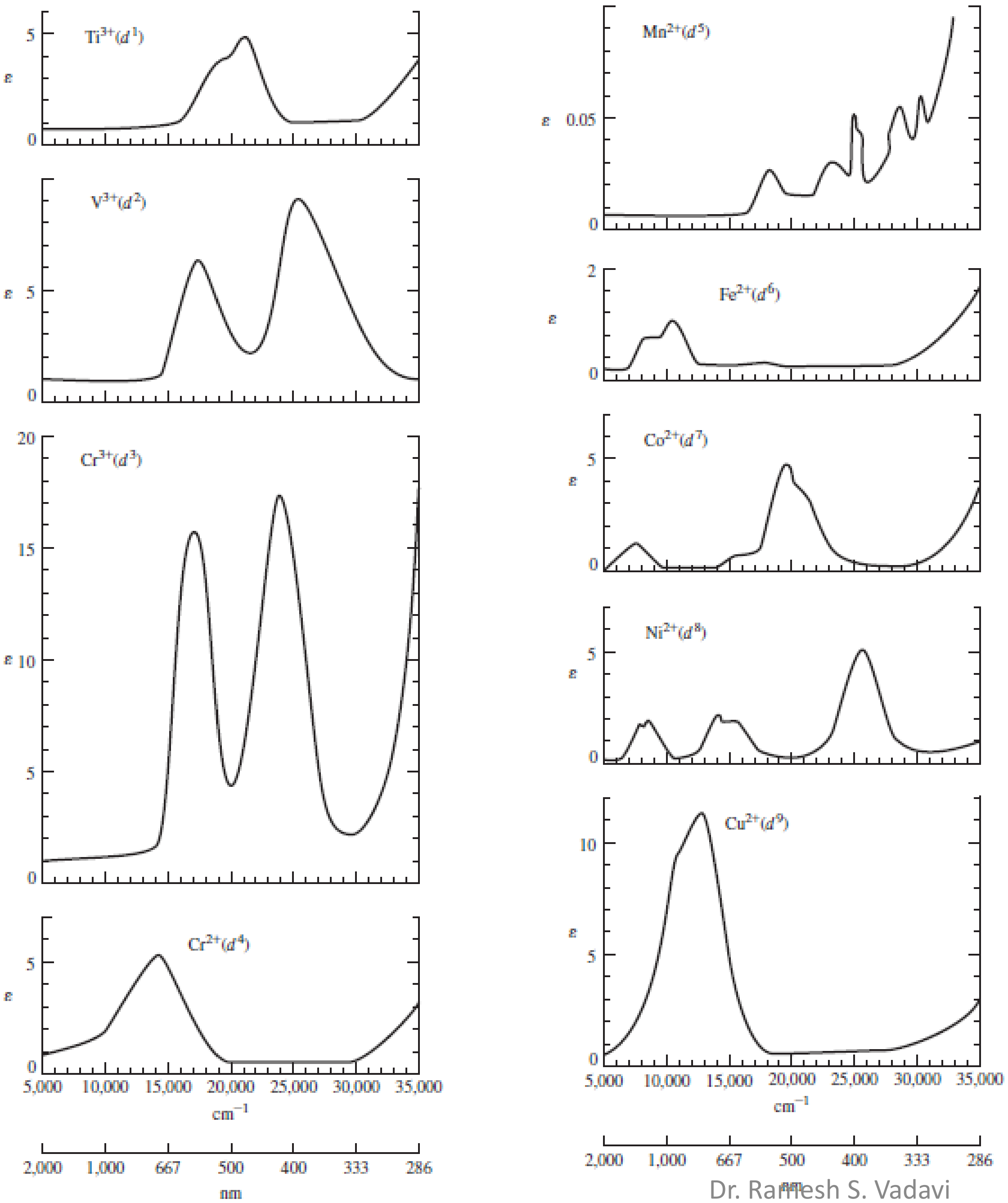
3. Spin-orbit coupling phenomenon relaxes the spin selection rule:

   Ex: very pale pink color of $[Mn(H_2O)_6]^{2+}$

Number of Transitions possible for d^1 to d^{10} configurations

1. Octahedral complexes having d^1, d^4 (weak ligand field), d^6 (weak ligand field) and d^9 configuration show only one spin allowed transition corresponding to Δ_o.
2. Octahedral complexes having d^2, d^3, d^7 (weak ligand field) and d^8 configuration show three spin allowed transitions. The energy difference between adjacent A_{2g} and T_{2g} terms corresponds to Δ_o.
3. Tetrahedral complexes having d^1, d^4, d^6 and d^9 configuration also show only one spin and Laporte allowed transition corresponding to Δ_o.
4. Tetrahedral complexes having d^2, d^3, d^7 and d^8 configuration exhibit three spin and Laporte allowed transitions. The energy difference between adjacent A_2 and T_2 terms corresponds to Δ_o.

NB: The metal ions with D ground state term exhibit only one transition, whereas the metal ions with F ground state term show three transitions



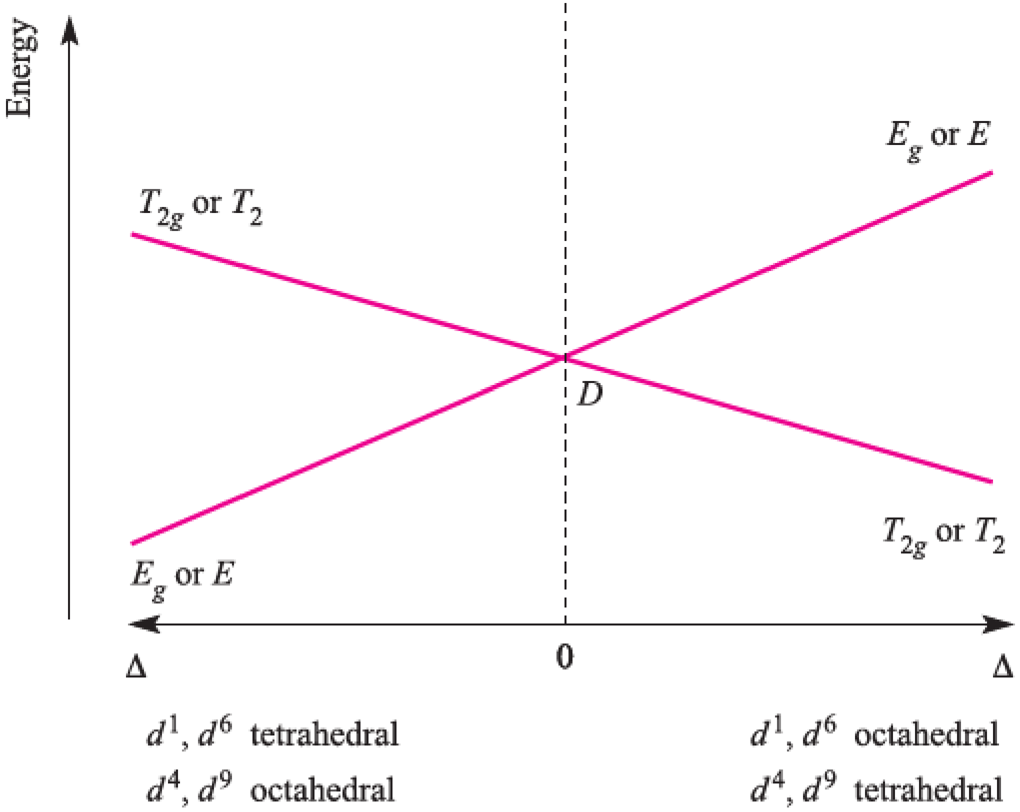
Electronic spectrum of First row transition metal complexes of formula $[M(H_2O)_6]^{n+}$

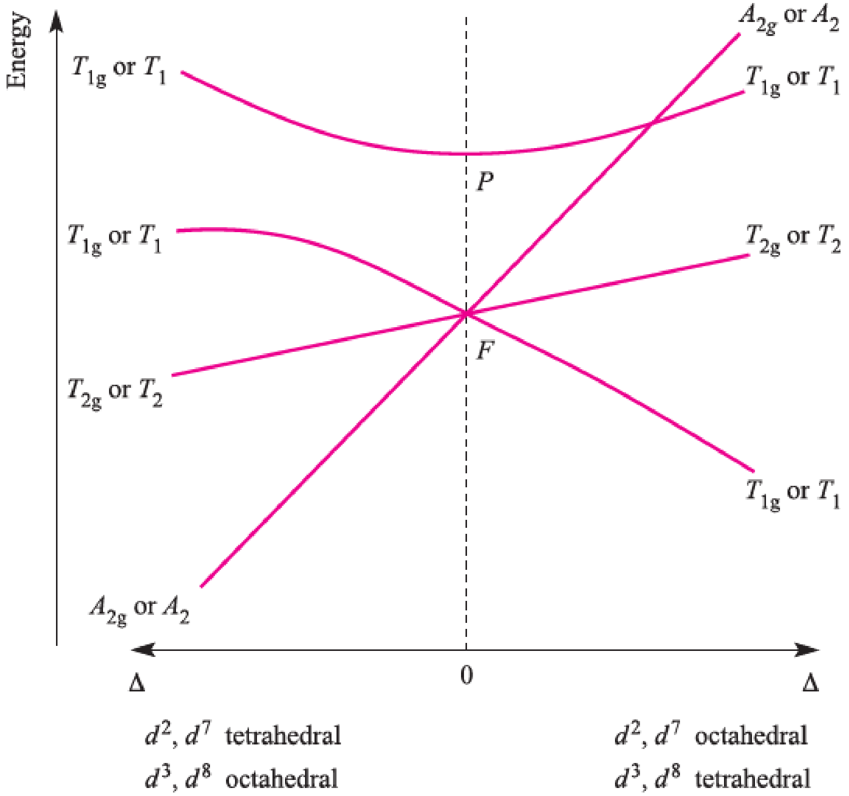
Molar absorptivities (ε) for various types of electronic transitions observed in complexes

Type of Transition	ε ($Lmol^{-1}cm^{-1}$)	Typical complexes
Spin forbidden and Laporte forbidden	$10^{-3} – 1$	Many Oh complexes of d^5 and d^{10} ions. Eg: $[Mn(H_2O)_6]^{2+}$, $[Zn(H_2O)_6]^{2+}$
Spin allowed and Laporte forbidden	$1 – 10$	Many Octahedral complexes with Oh symmetry; ex: $[Ni(H_2O)_6]^{2+}$
	$10 – 10^2$	Some Square Planar complexes: eg: $[PdCl_4]^{2-}$
	$10^2 - 10^3$	Six coordinate complexes of low symmetry and non-centrosymmetric complexes such as Tetrahedral complexes (ex: $[CoCl_4]^{2-}$)
Spin allowed and Laporte allowed	$10^2 – 10^3$	Some MLCT band in molecules with unsaturated ligands.
	$10^3 – 10^6$	Many charge transfer bands [LMCT]; transition in organic species.

Orgel Diagrams

These are the pictorial representations describing the electronic transitions in high spin transition metal complexes in a qualitative way using the spectroscopic terms and are proposed by Orgel





- There are two T_{1g} state, one from P state and other from F state,
- The two T_{1g} states are slightly curved lines, because they have the same symmetry and they interact with one another.
- The interelectronic repulsion lowers the energy of the lower state and increases the energy of the higher state.
- If the lines had been straight, they would cross each other indicating , at cross-over point that two electrons in one atom may have the same symmetry and the same energy. But it **violates non-crossing rule** which **states that Electronic states of same symmetry cannot cross each other**

Limitations of Orgel diagrams

1. They treat only high spin cases
2. These are useful for only spin allowed transition as the high energy terms of other spin multiplicities and the terms arsing from them are not included.

Coordination numbers and their geometries

- Because of the directionality in nature of ligands, complex ion should have particular shape and hence particular geometry.
- In coordination chemistry, a structure is first described by its coordination number. i.e., the number of donor atoms attached to metal.
- Coordination numbers from 1 to 12 are known. Among these some are rare (not frequently occurring).

Factors favoring low coordination numbers

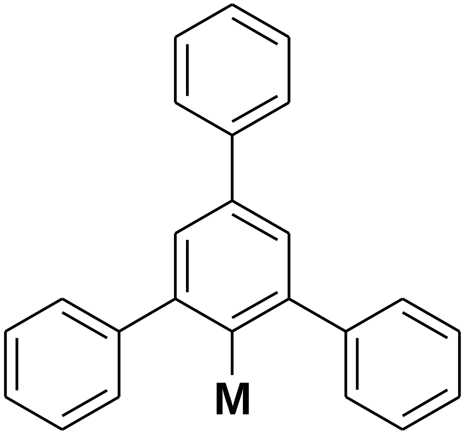
1. **Soft ligands and metals in low oxidation state**: Ex: Organometallic compounds with pi-acid ligands
2. **Large and bulky ligands:** Steric hindrance prevents additional ligands from coordinating to the metal.
3. **Counterions of low basicity:** For example: Nitrate, perchlorate, PF_6^-, BF_4^-, triflate

Factors favoring High coordination numbers

1. **Hard ligands and metals in high oxidation state:** Ex: Highly electronegative donor atoms will bind the metals of high oxidation state.
2. **Small steric requirements of the ligand: $[NiCl_4]^{2-}$ Vs $[NiF_6]^{4-}$.**
3. **Small and nonacidic cations:** Large cationic counter ions are needed when large number of negative ions make the anionic complexes. For example: $K_3[Cr(ox)_3]$, $KMnO_4$, $[CoF_6]^{3-}$ etc.

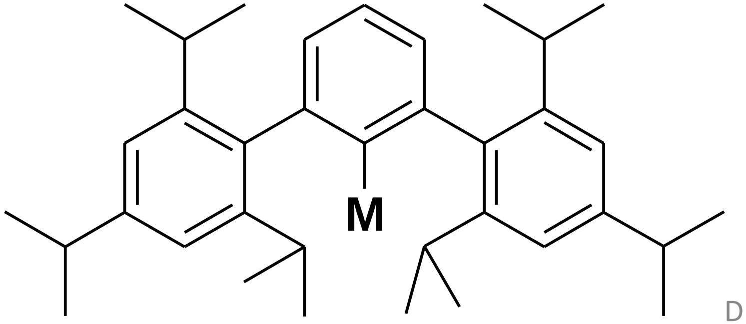
Coordination number 1

- It is rare CN.
- 1,3,5-tripheylbenzene, which is more sterically hindered forms one-one organometallic ompound with Cu(I) and Ag(I).



Geometry : Linear

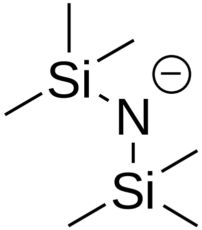
- Tl(I) and In(I) orgnaometallic complexes of 2,6-(2,4,6-triisopropylphenyl)benzene



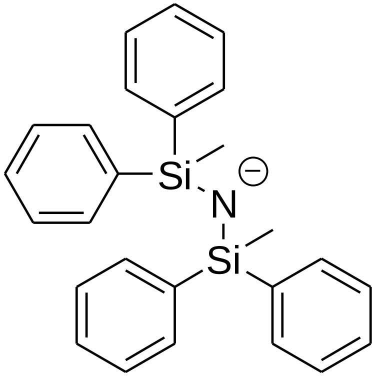
Geometry : Linear

Coordination number 2

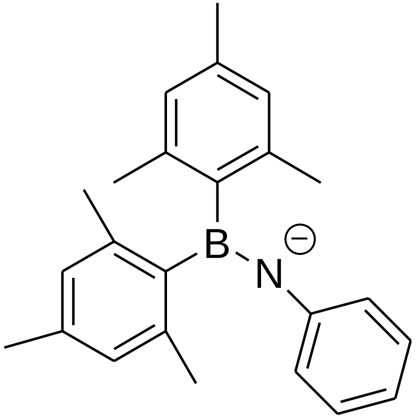
- Few complexes are known with CN 2.
- It is generally restricted to the metal ions of group 11 in +1 oxidation state and Hg(II) species.
- Examples: $[Cu(NH_3)_2]^+$, $[Ag(NH_3)_2]^+$, $[CuCl_2]^-$, $[AgCl_2]^-$, $[AuCl_2]^-$, $[Au(CN)_2]$- etc. These may react with additional ligands to form higher coordinate complexes.
- If the ligands are sterically hindered sufficiently, two coordinate complexes also be formed by ions such as Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}.
- For example



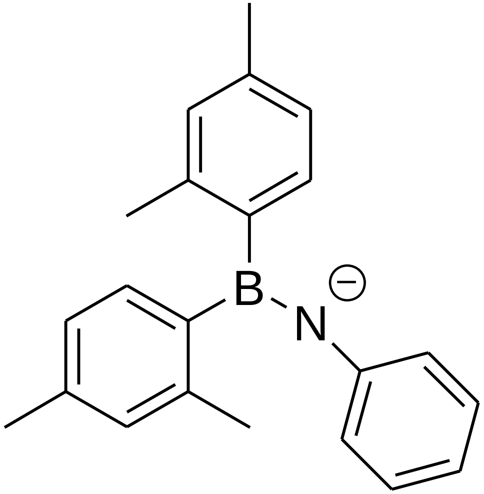
$[N(SiMe_3)_2]^-$



$[N(SiMePh_2)_2]^-$

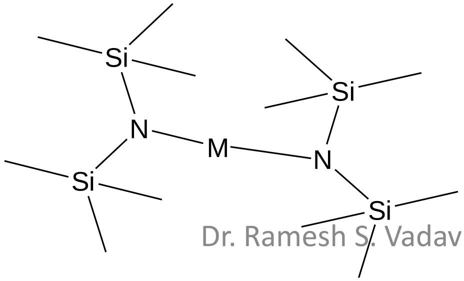


$[NPhBMes_2]^-$



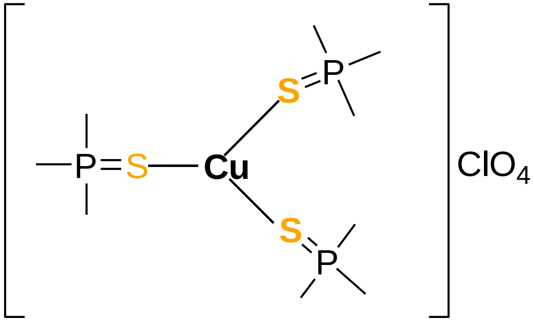
$[NPhBXyl_2]^-$

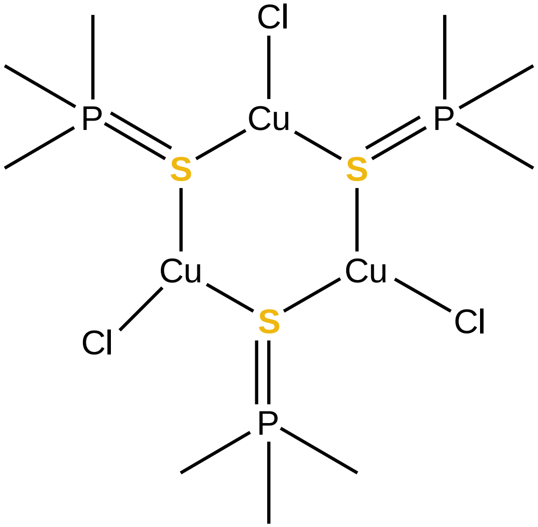
Geometry : Linear



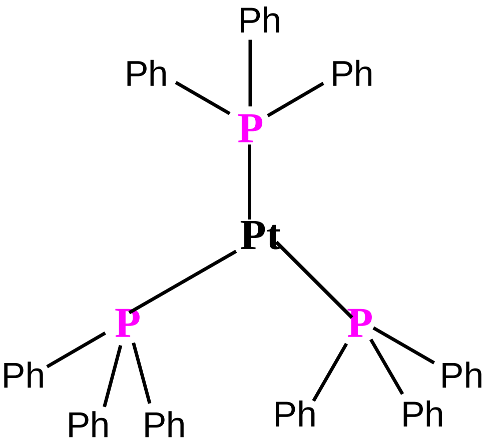
Coordination number 3

- This is a rare coordination number
- Examples: 1. Tris(trimethylphosphine sulfide)copper(I) perchlorate
- Example 2. Cyclo-tris(chloro-μ-trimethylphosphine sulfide)copper(I)
- Example 3. Tris(triphenylphosphine)platinum(0)





Geometry: Trigonal planar



Coordination number 4

It is very common coordination number. Two types of geometry are possible for this coordination number.

1. Tetrahedral
2. Square planar

1. Tetrahedral complexes : These are favored by large ligands like Cl^-, Br^- and I^- and small metal ions of three types

a. Those with noble gas configuration such as Be^{2+}

b. Those with a pseudonoble gas coniguration such as Zn^{2+}, Ga^{3+}

Examples: $[BeCl_4]^{2-}$, $[ZnCl_4]^{2-}$, $[AlCl_4]^-$, $[CoCl_4]^{2-}$, $[FeCl_4]^{2-}$, $[MnO_4]^-$, $[CuCl_4]^-$, $[Ni(CO)_4]$, $[Cu(CN)_4]^{3-}$, etc.

2. Square Planar complexes: These are favored by small ligands and the metal ions with d^8 system (Ni^{2+}, Pt^{2+}, Pd^{2+}, Au^{3+}, Ir^+).

Uncommon: Cu^{2+}, Co^{2+}, Cr^{2+}, Co^{3+}.

Condition to favor Square Planar geometry: **Presence of non-bulky strong field pi-acid ligands.**

Exceptional: [**Cd**$(OAr)_2(thf)_2$]---- Square Planar, [**Zn**$(OAr)_2(thf)_2$]---- distorted Td.

$[Ni\{R_2P(O)NR'\}_2]$– **Square planar and paramagnetic**

[R= tert-Bu, R' = iso-Propyl]

Coordination number 5

Two types of geometry are possible for this coordination number and are interconvertible.

1. Trigonal bipyramid
2. Square pyramid

Usually the geometry of the five coordinate complexes lies in between these two geometry (distorted structures).

Examples for TBP: $[CuCl_5]^{3-}$, $[CdCl_5]^{3-}$, $[HgCl_5]^{3-}$

Examples for SP: $[Ni(CN)_5]^{3-}$

Coordination number 6

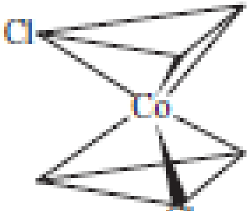
This is the commonest and most important coordination number for transition metal complexes. Three types geometry are possible.

1. Octahedral
2. Trigonal prism
3. Trigonal antiprism.

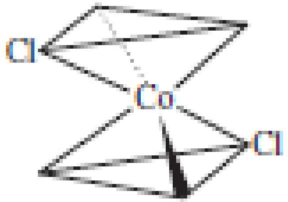
1. Octahedral: Ex: $[Co(NH_3)_6]^{3+}$, $[FeF_6]^{3-}$, $[TiF_6]^{2-}$, $[Zn(H_2O)_6]^{3+}$, $[Co(en)_3]^{3+}$etc.

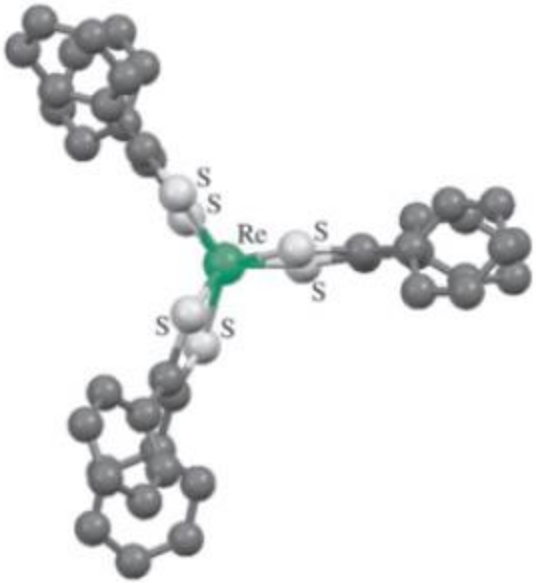
Tetragonally elongated and tetragonally compressed structures: Due to J-T distortion

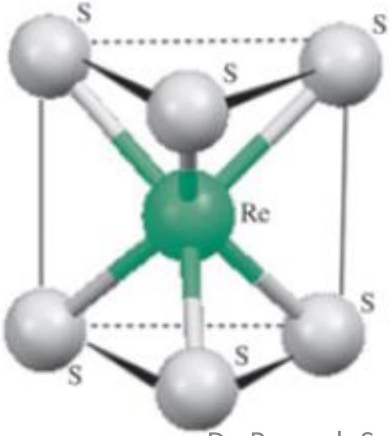
2**. Trigonal Prism**

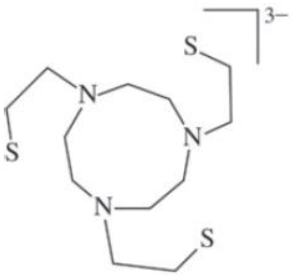


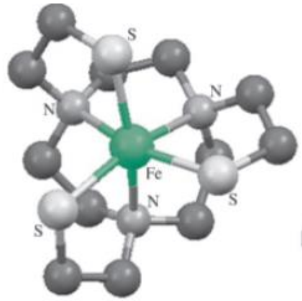
3. Trigonal Antiprism

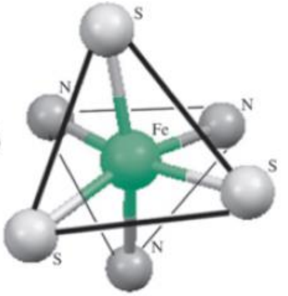








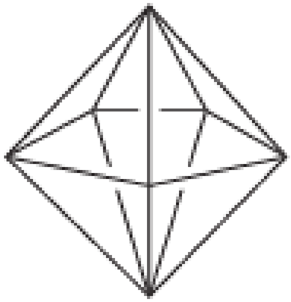


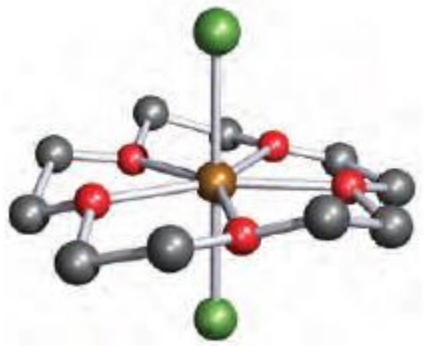


Coordination number 7

Three geometries are known.

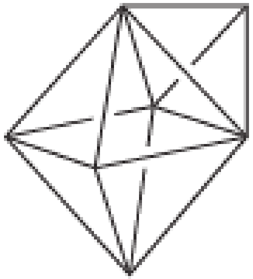
1. Pentagonal bipyramid: Example: $[UF_7]^{3-}$, $[UO_2F_5]^{3-}$

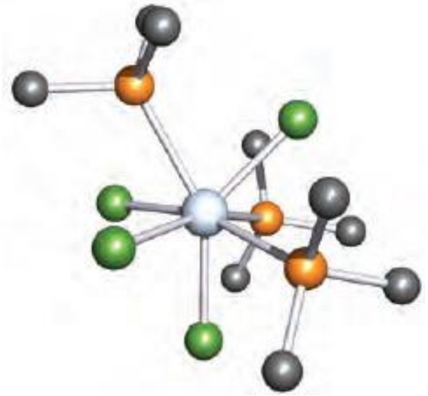




$[ScCl_2(15\text{-crown-}5)]_2[CuCl_4]$

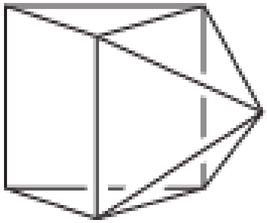
2. Capped octahedron : Examples: $[NbOF_6]^{3-}$,

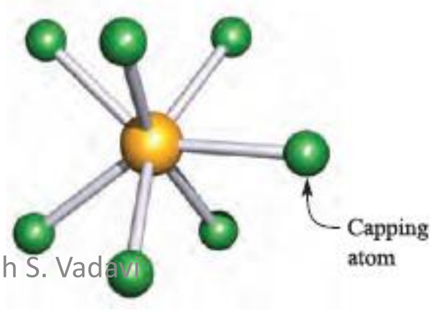


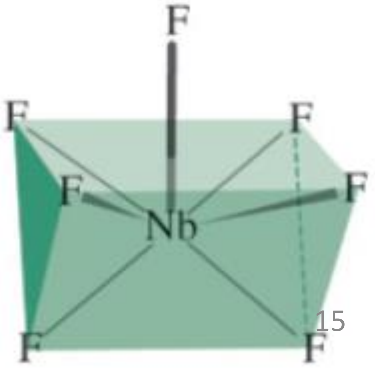


$[TaCl_4(PMe_3)_3]$

3. Capped Trigonal prism: Examples: $[TaF_7]^{2-}$, $[NbF_7]^{2-}$







Coordination number 8

Eight coordinate complexes are rare for 3d-transition metals because of their small size.

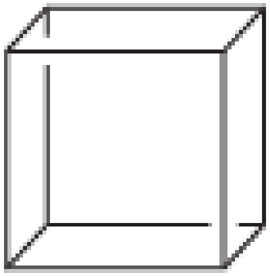
Factors favoring eight coordination

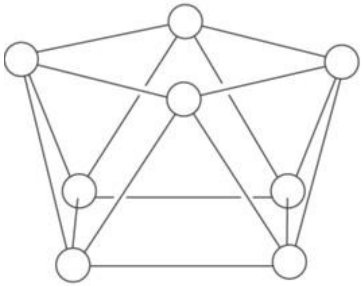
1. **Size of the metal ion ad size of the ligand:** Metal ion should be large to accommodate eight coordination and ligand should be relatively small and electronegative.
   Examples: Metal ions: Lathanides and Actindies, Zr, Hf, Nb, Ta, Mo, W etc
   Ligating atoms: Carbon, nitrogen, oxygen and Fluorine.

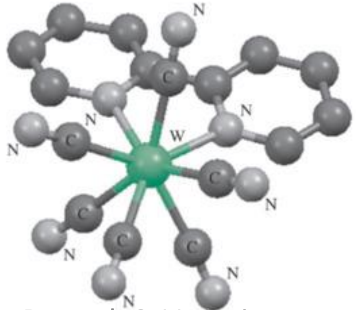
2. **Oxidation state of the metal ions:** High oxidation state favors eight coordination. So common oxidation states are +3 or greater.

Three important geometries are known.

1. The Cube: It is rare; $[UF_8]^{3-}$
2. The square antiprism: It is common;$[ReF_8]^-$, $[Zr(acac)_4]$, $[TaF_8]^-$, $[W(bipy)(CN)_6]^-$
3. Dodecahedron: It is also common $[Mo(CN)_8]^{4-}$, $[Zr(ox)_4]^4$

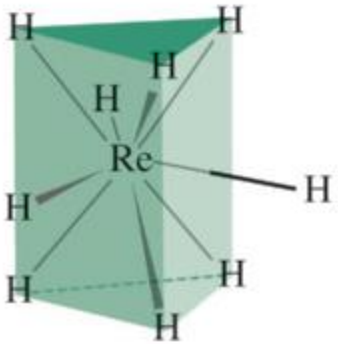






Higher coordination numbers

Nine coordinate complexes: $[Ln(H_2O)_9]^{3+}$, $[TcH_9]^{2-}$, $[ReH_9]^{2-}$; These structures are formed by adding a ligand to each of the rectangular faces of a trigonal prism.



Coordination numbers 10 to 12: These will exist for largest metal ions, but these do not refer to any regular geometry.

For Coordination number 10: bicapped square antiprism is sometimes found.
Ex: $K_4[Th(ox)_4(H_2O)_2]. 2H_2O$

For Coordination number 12: Distorted icosahedral

$[Ce(NO_3)_6]^{2-}$, $[Pr(naph)_6]^{3+}$,