

CHEMISTRY -THEORY

(CYI 101)

UNIT – III

(Inorganic Chemistry)

Instructor: Dr. C. Haldar



Department of Chemistry

Time: 3.00 PM-3.50 PM

(Friday)

Evaluation and Study Material

Examination/Class tests/others

- See Academic Calendar
- Will be informed time to time

Course Material

- What the instructor teaches!
- Books: *Inorganic chemistry: Huheey, Keiter and Keiter*
Inorganic Chemistry: Housecroft and Sharpe

What is a Transition Metal?

IUPAC Periodic Table of the Elements

IUPAC Periodic Table of the Elements																	18	
1 H hydrogen 1.008 [1.0078, 1.0082]																	2 He helium 4.0026	
3 Li lithium 6.94 [6.938, 6.997]		4 Be beryllium 9.0122											5 B boron 10.81 [10.806, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990		12 Mg magnesium 24.305 [24.304, 24.307]											13 Al aluminium 26.982	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.948
19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2)	
37 Rb rubidium 85.468	38 Sr strontium 87.62	39 Y yttrium 88.906	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906	42 Mo molybdenum 95.95	43 Tc technetium 98.906	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.91	46 Pd palladium 106.42	47 Ag silver 107.87	48 Cd cadmium 112.41	49 In indium 114.82	50 Sn tin 118.71	51 Sb antimony 121.76	52 Te tellurium 127.60(3)	53 I iodine 126.90	54 Xe xenon 131.29	
55 Cs caesium 132.91	56 Ba barium 137.33	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.95	74 W tungsten 183.84	75 Re rhenium 186.21	76 Os osmium 190.23(3)	77 Ir iridium 192.22	78 Pt platinum 195.08	79 Au gold 196.97	80 Hg mercury 200.59	81 Tl thallium 204.38 [204.38, 204.39]	82 Pb lead 207.2	83 Bi bismuth 208.98	84 Po polonium	85 At astatine	86 Rn radon	
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganeson	

57 La lanthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium 144.91	62 Sm samarium 150.36(2)	63 Eu europium 151.96	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 173.05	71 Lu lutetium 174.97
89 Ac actinium 227.03	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium 237.05	94 Pu plutonium 244.06	95 Am americium 243.06	96 Cm curium 247.07	97 Bk berkelium 247.07	98 Cf californium 251.08	99 Es einsteinium 252.08	100 Fm fermium 257.10	101 Md mendelevium 258.10	102 No nobelium 259.10	103 Lr lawrencium 262.10



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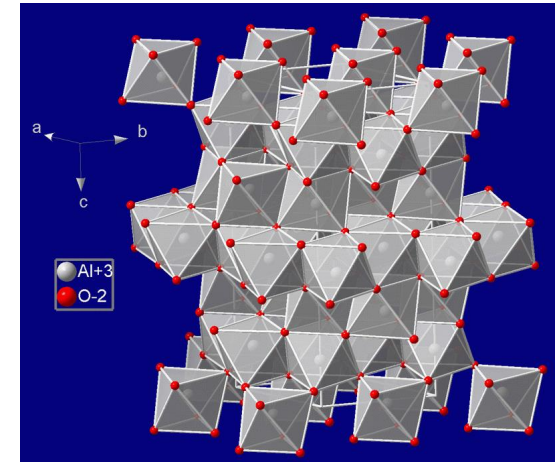
For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.
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Color of transition metal complexes

Sapphire: Al_2O_3 with titanium and iron impurities are present together, and in the correct valence states, the result is a deep-blue color. Fe^{2+} and Ti^{4+} ions are substituted for Al^{3+}

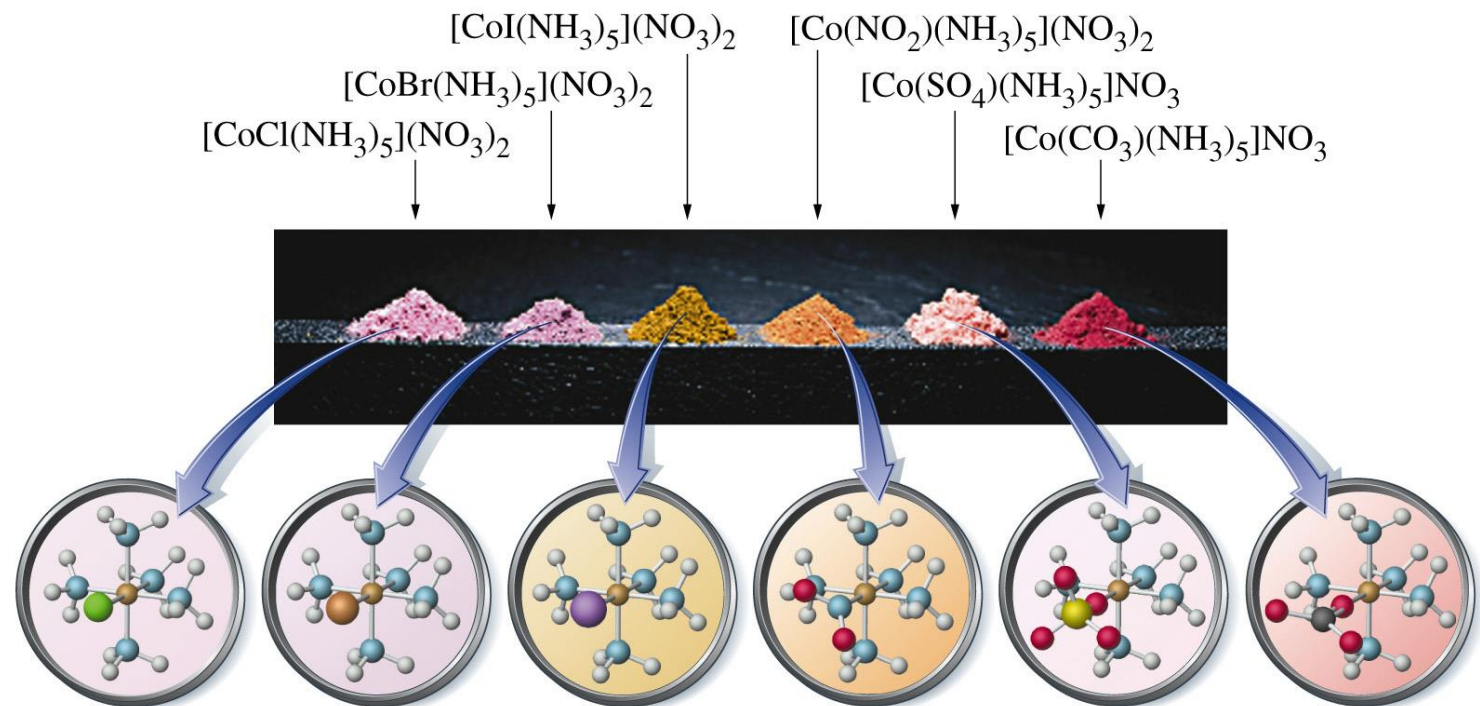


Ruby: Al_2O_3 With Impurity of Chromium

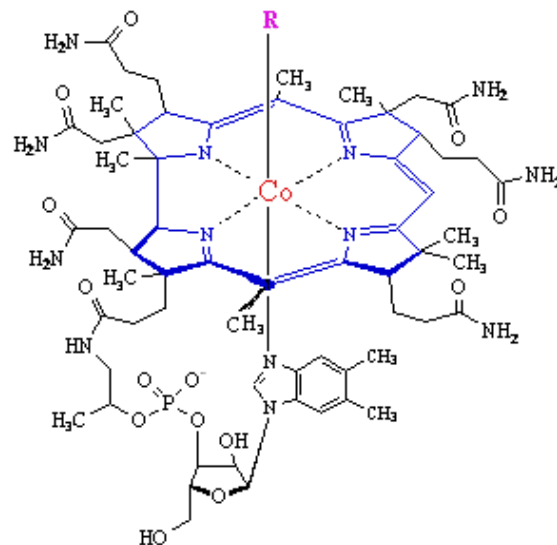
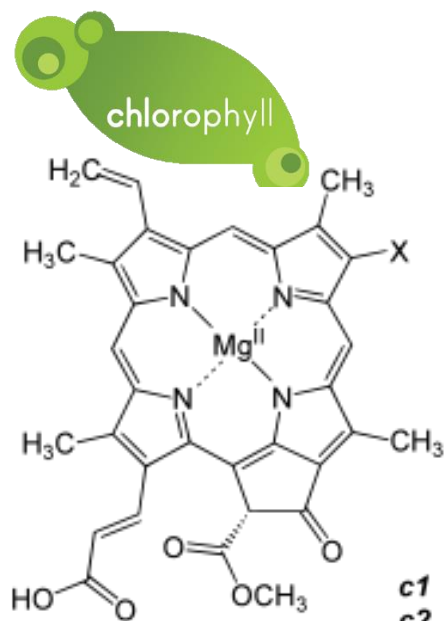
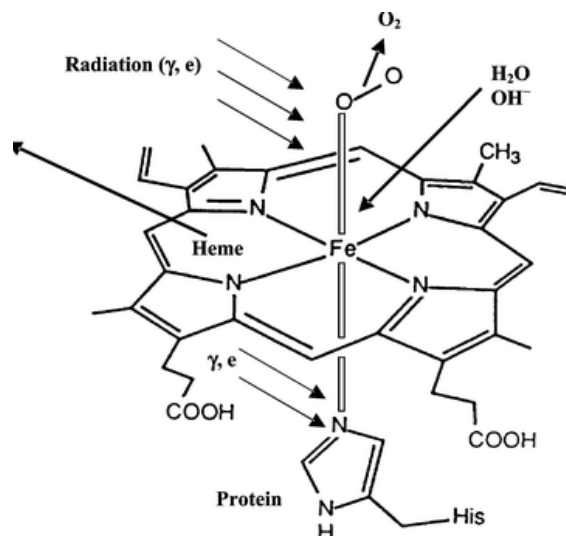
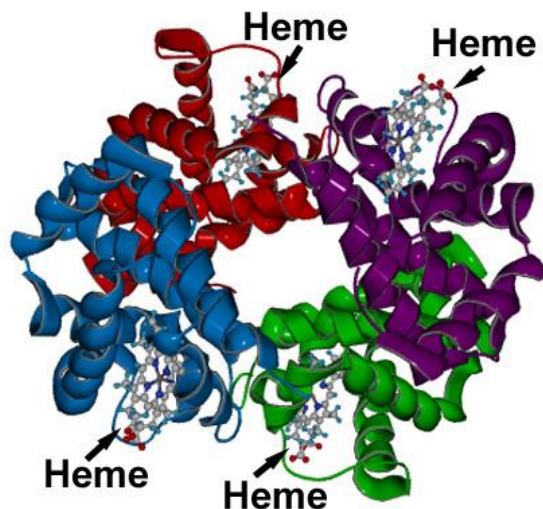


Emerald is a gemstone and a variety of the mineral beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$) colored green by trace amounts of chromium and sometimes vanadium

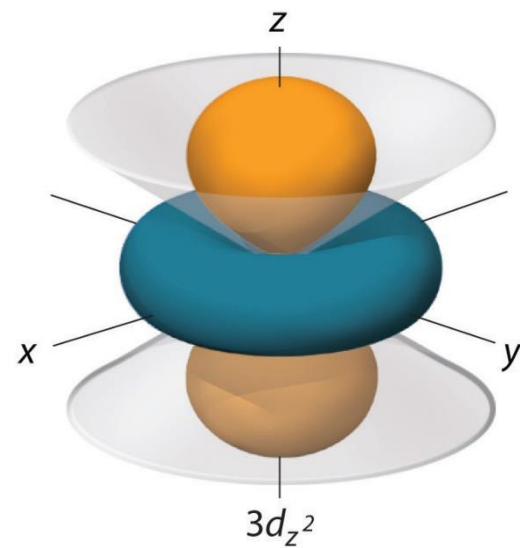
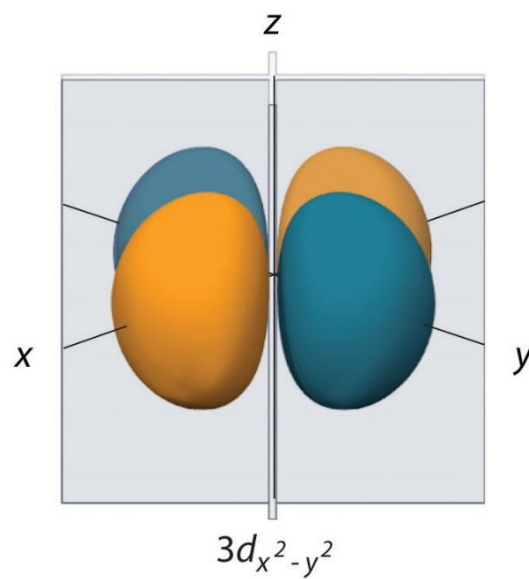
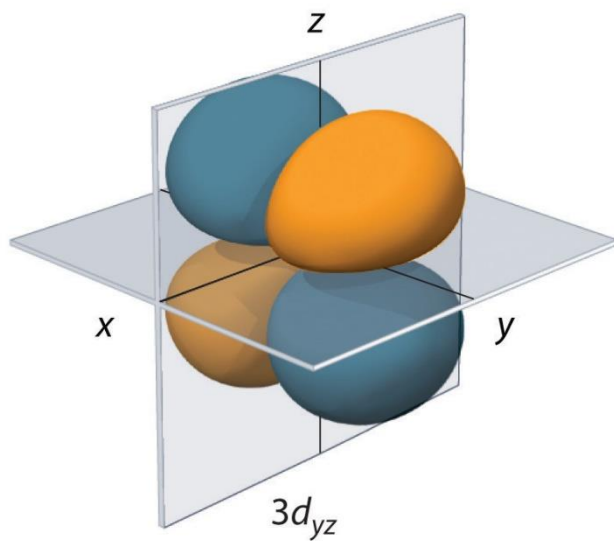
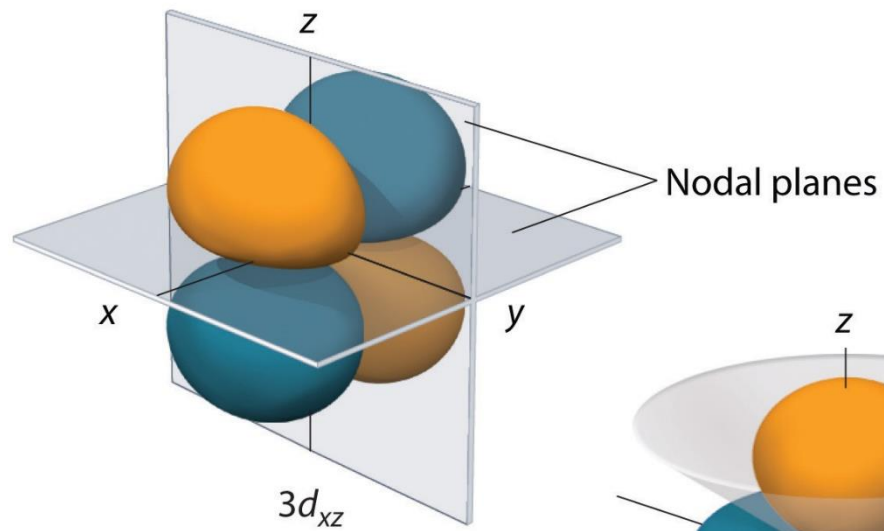
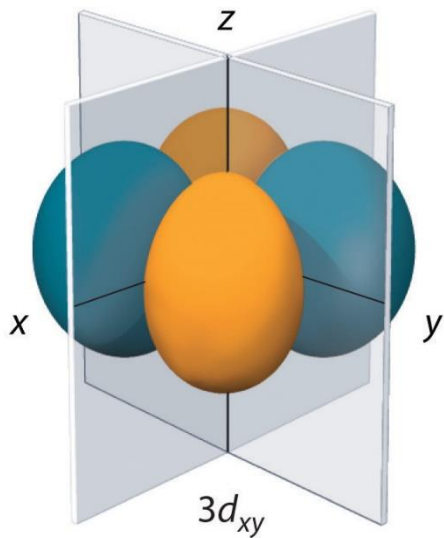
Color of transition metal complexes



Naturally Occurring Coordination Compounds

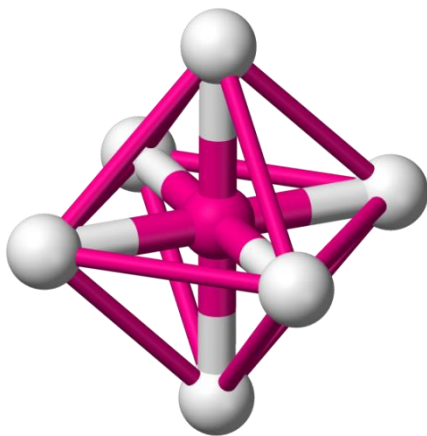


d-orbitals

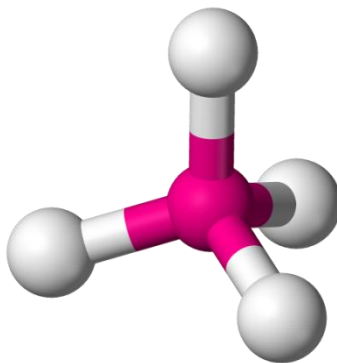


Crystal Field Theory

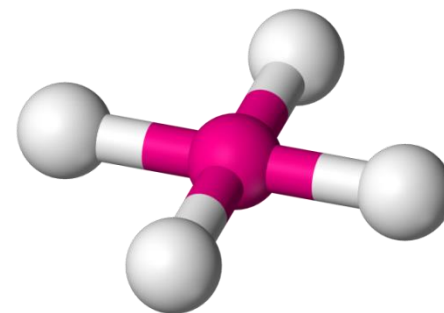
1. This is an electrostatic model for transition metal complexes.
2. Ligands are considered as point charge.
3. The CFT does not provide for electrons to enter the metal orbitals, i.e. it does not consider any orbital overlap.
4. Predicts the pattern of splitting of d-orbitals.
5. Used to rationalize spectroscopic and magnetic properties.



Octahedral complex (O_h)

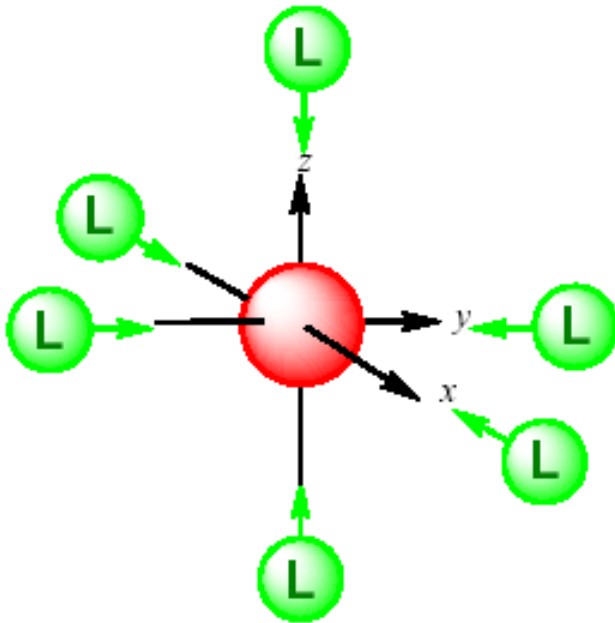


Tetrahedral complex (T_d)



Square planer complex (Sp)

Octahedral Field



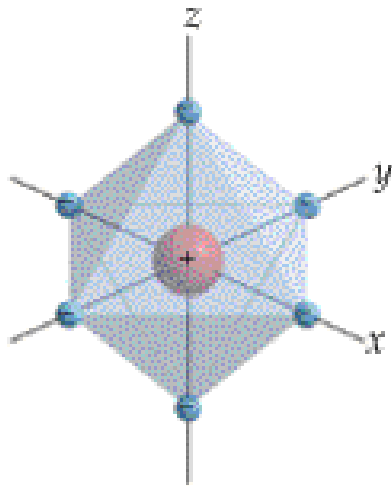
- Six point negative charges (Ligands) representing the ligands are placed in an octahedral array around the central metal ion.
- The ligand and orbitals lie on the same axes.
- These charges interact strongly with the central metal ion.

1. The stability of the complex in large part from this attractive interaction between opposite charges.

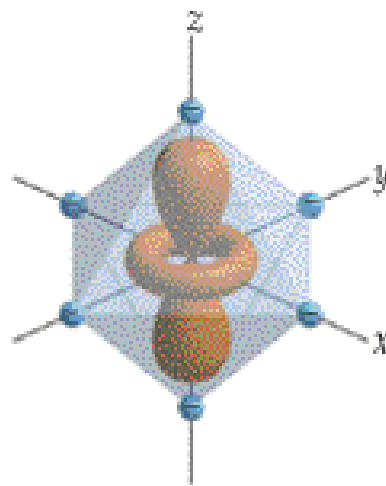
2. There is a much smaller but very important secondary effect arising from the fact that electrons in different d orbitals interact with the ligands to different extents.

❖ Although this differential interaction is little more than about 10 per cent of the overall metal-ligand interaction energy, it has major consequences for the properties of the complex.

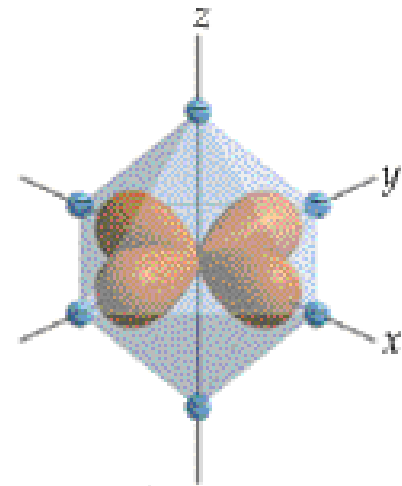
Octahedral Field



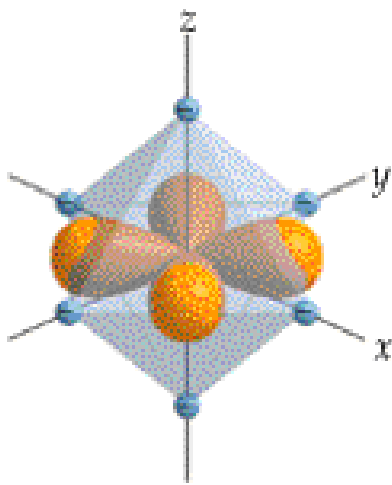
(a)



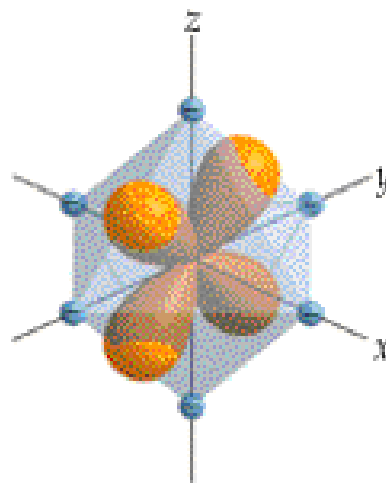
d_{z^2}
(b)



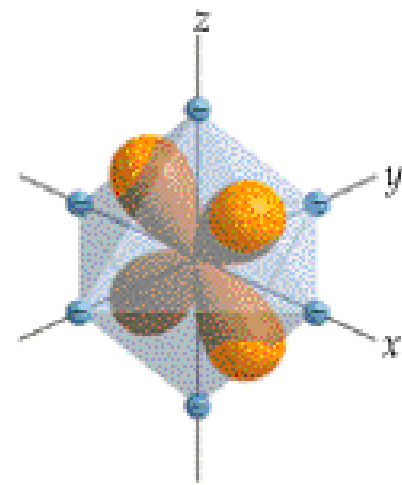
$d_{x^2-y^2}$
(c)



d_{xy}
(d)

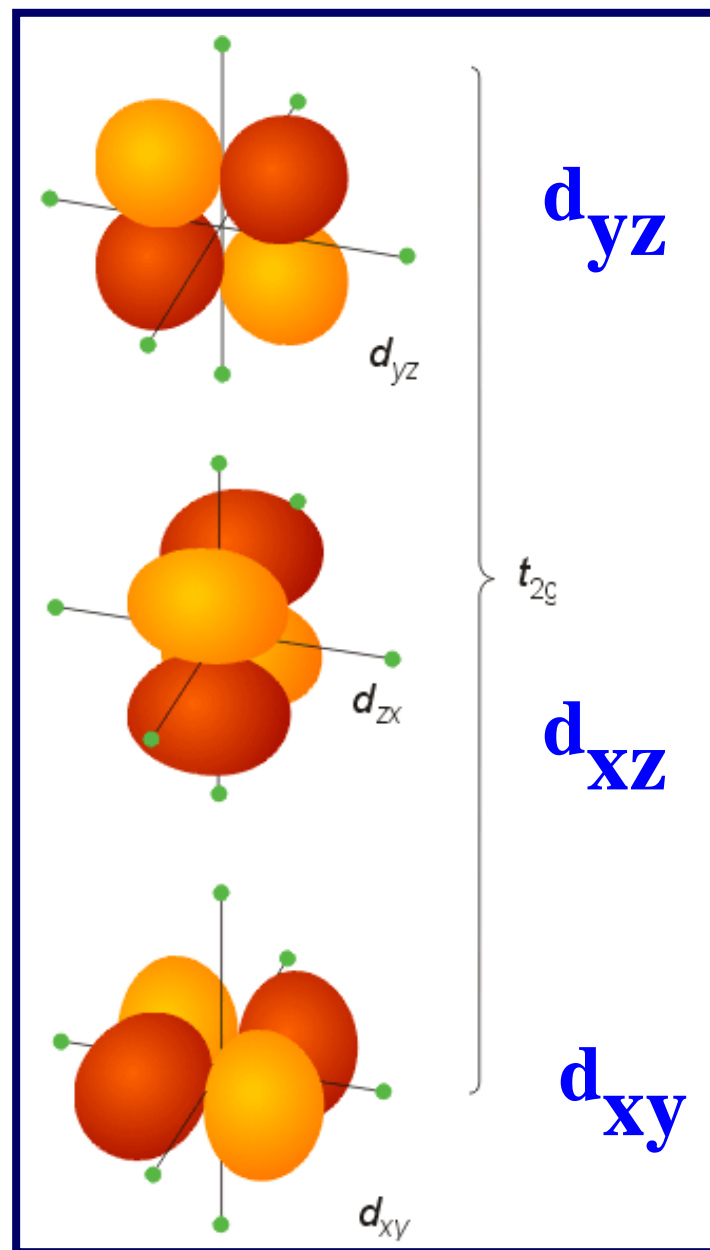
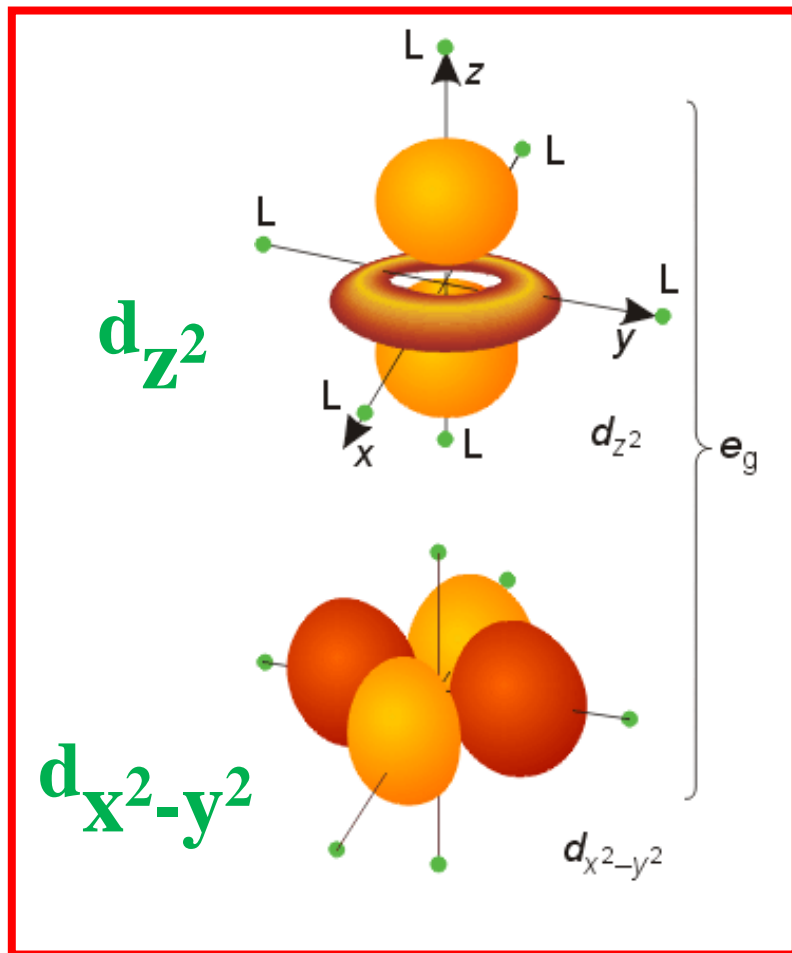


d_{yz}
(e)

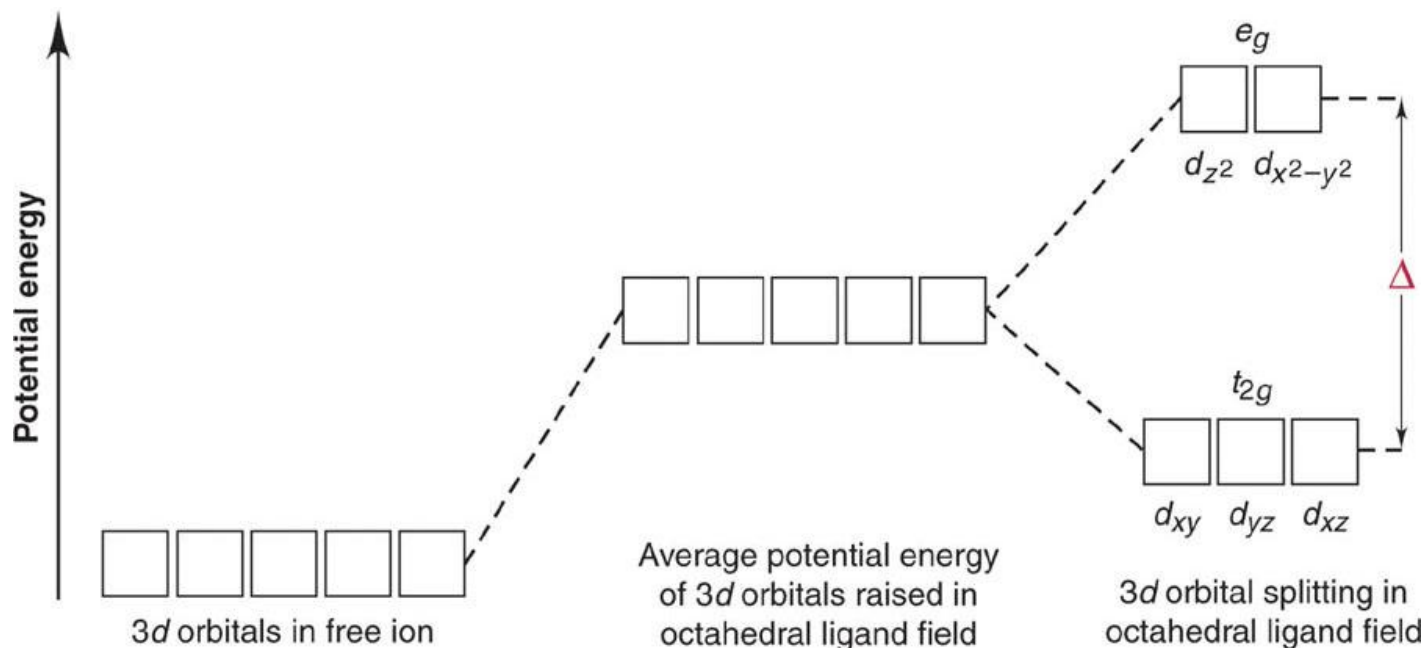


d_{xz}
(f)

Octahedral Field

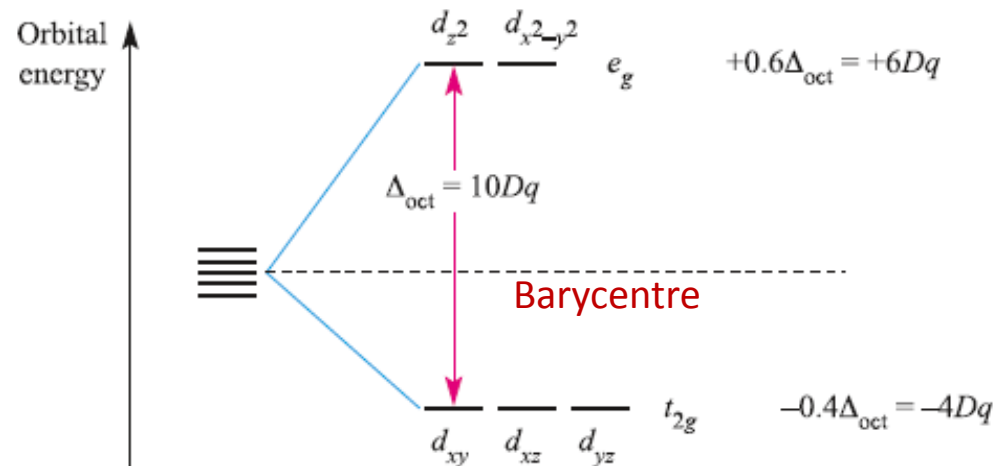
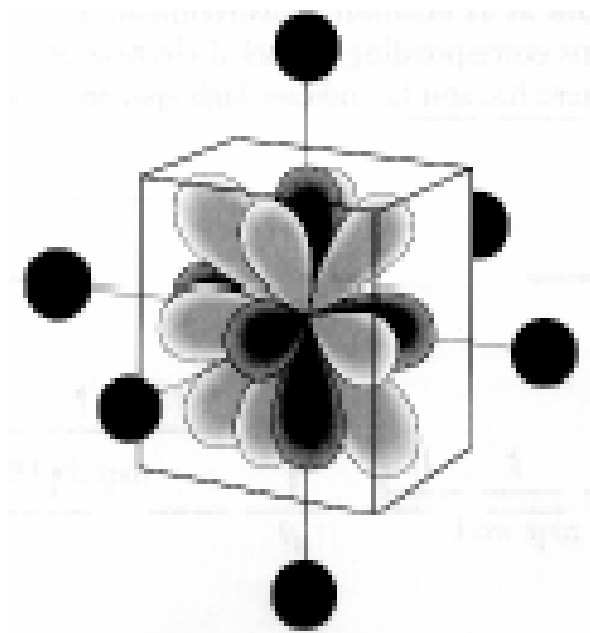


Splitting of d -orbital energies in an octahedral field of ligands.



The d orbitals split into two groups. The difference in energy between these groups is called the **crystal field splitting energy**, symbol Δ_o .

Octahedral Field



- The overall stabilization of the t_{2g} orbitals equals the overall destabilization of the e_g set.
- Thus, the two orbitals in the e_g set are raised by $0.6 \Delta_o$ with respect to the **Barycentre** while the three in the t_{2g} set are lowered by $0.4 \Delta_o$.
- The magnitude of Δ_o is determined by the strength of the crystal field, the two extremes being called weak field and strong field.

$$\Delta_o (\text{Weak field}) < \Delta_o (\text{Strong field})$$

Crystal Field Splitting Energy

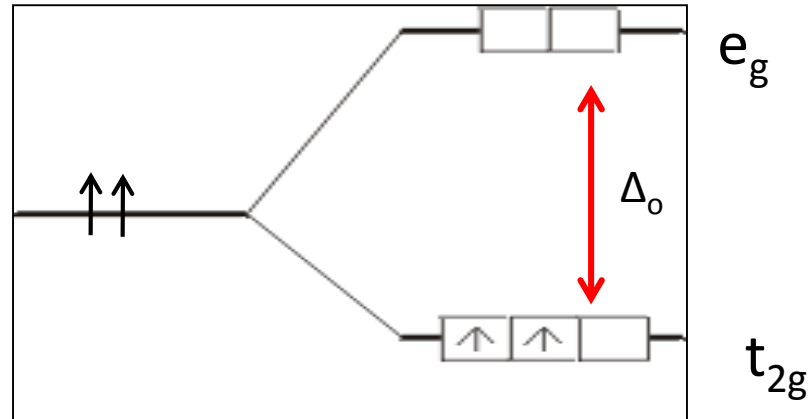
- In Octahedral field, **configuration is: $t_{2g}^x e_g^y$**
- Net energy of the configuration relative to the average energy of the orbitals is:

$$= (-0.4x + 0.6y)\Delta_o$$

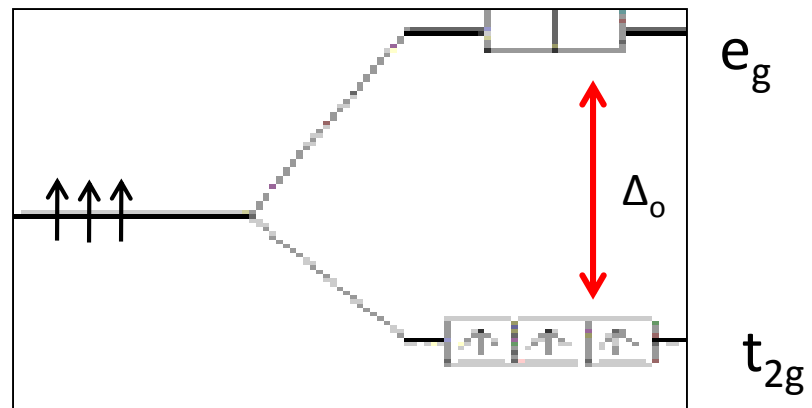
$$\Delta_o = 10 Dq$$



Crystal Field Splitting Energy In O_h Field

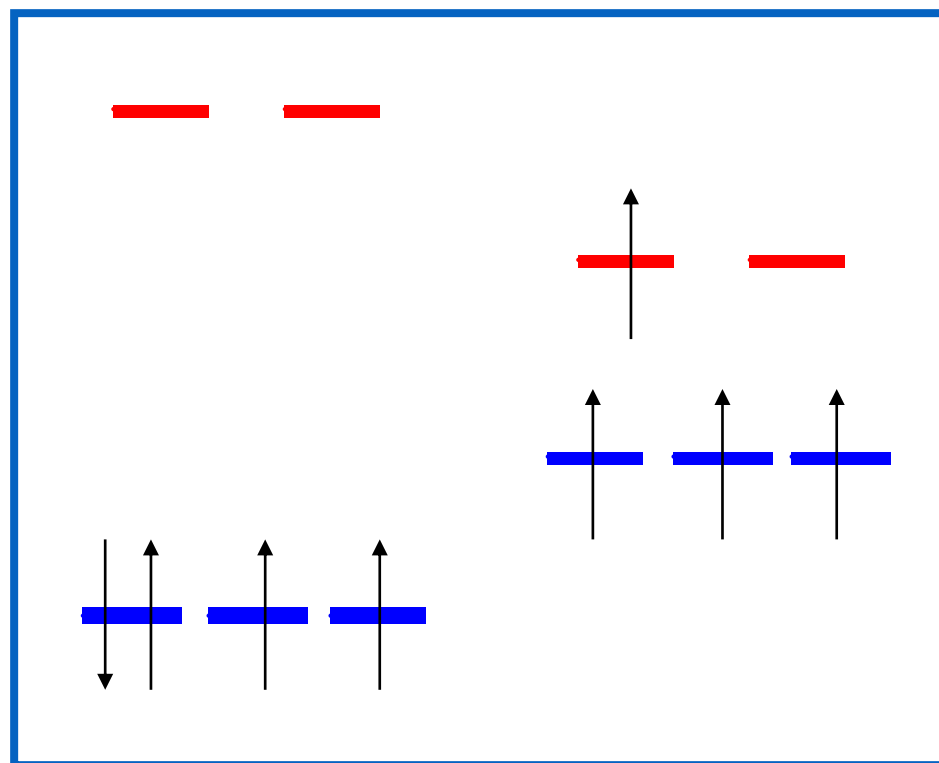


d^2 Ti^{2+} , V^{3+}



d^3 Cr^{3+} , Mn^{4+} , V^{2+}

When the **4th electron** is assigned it will either go into **the higher energy e_g orbital** at an energy cost of Δ_o or be **paired** at an energy cost of **P**, the pairing energy.



Strong field =
Low spin
(2 unpaired)

d⁴

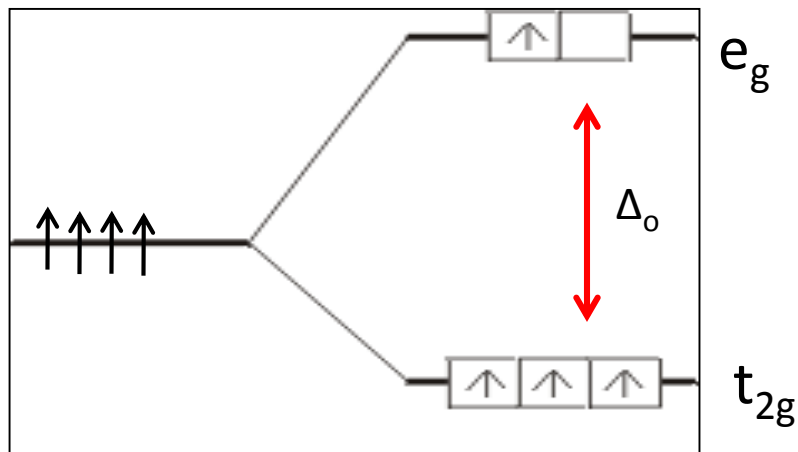
Weak field =
High spin
(4 unpaired)

$$P < \Delta_o$$

$$P > \Delta_o$$

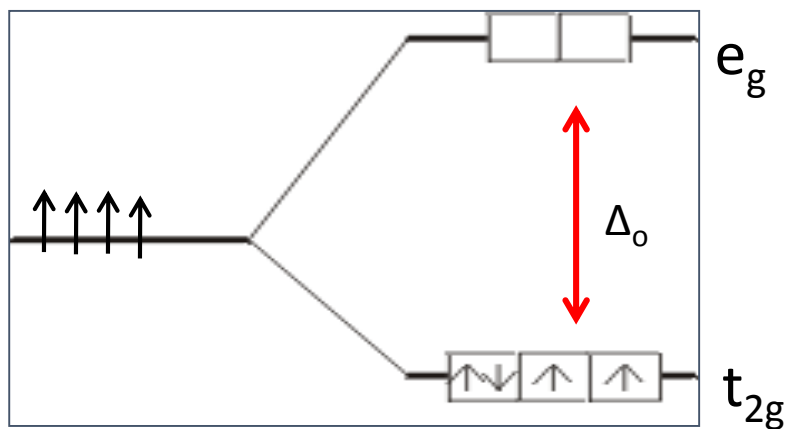
Coulombic repulsion energy and **exchange** energy

Crystal Field Splitting Energy



Weak field d^4

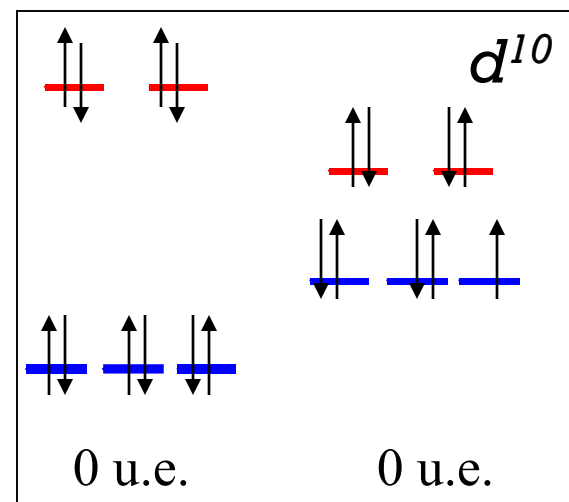
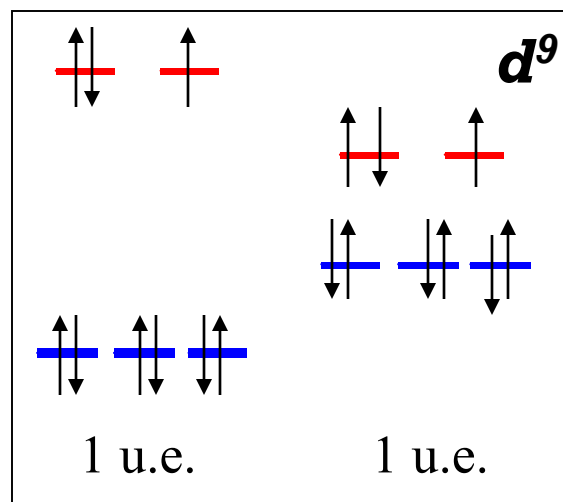
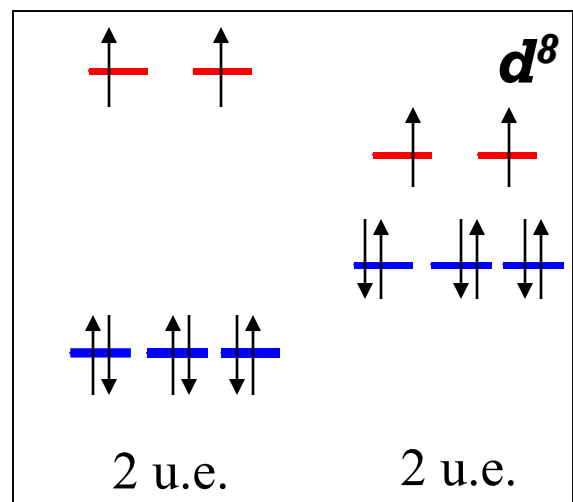
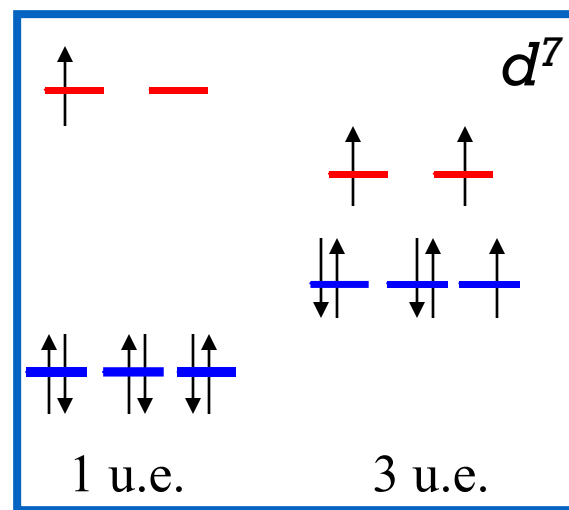
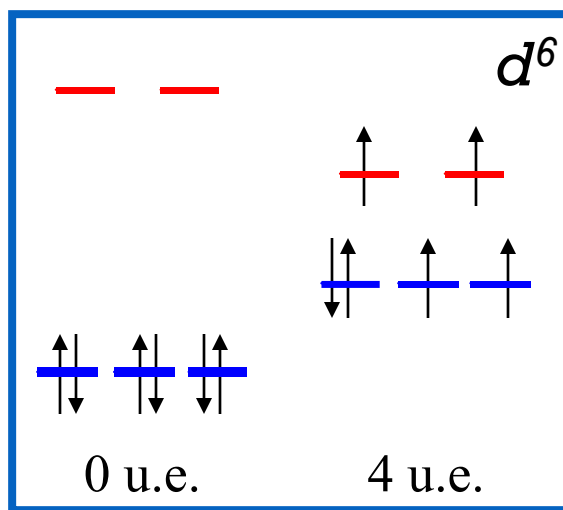
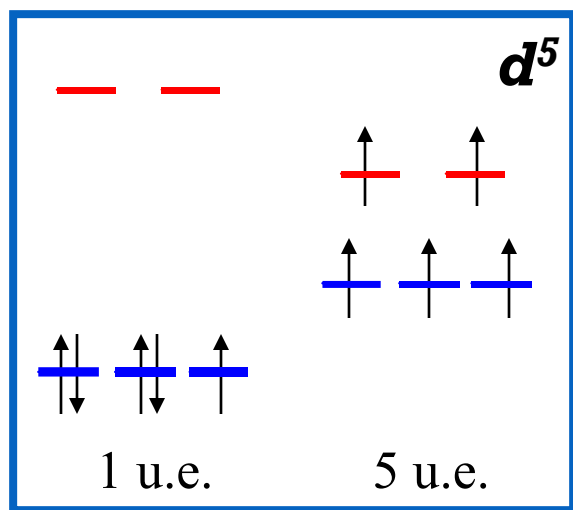
$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$
Weak Field Complex
the total spin (S) is $4 \times \frac{1}{2} = 2$
High Spin Complex



Strong field d^4

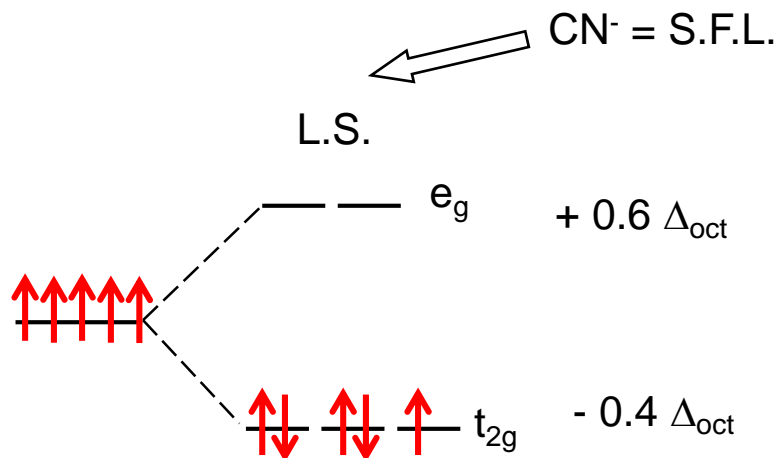
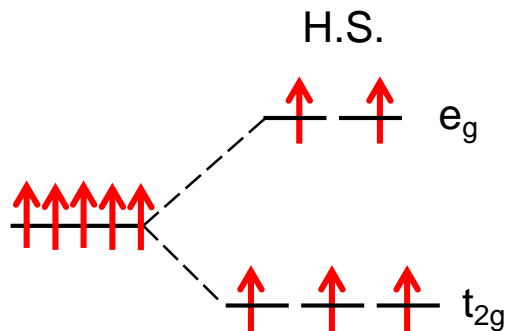
$[\text{Mn}(\text{CN})_6]^{3-}$
Strong field Complex
total spin (S) is $2 \times \frac{1}{2} = 1$
Low Spin Complex

Placing electrons in d orbitals



Q. What is the CFSE of $[\text{Fe}(\text{CN})_6]^{3-}$?

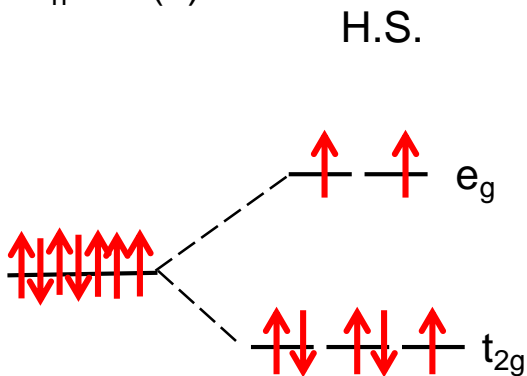
C.N. = 6 \therefore O_h Fe(III) \therefore d^5



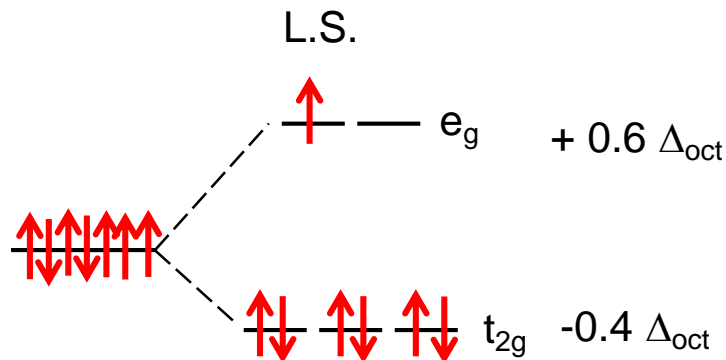
$$\text{CFSE} = 5 \times -0.4 \Delta_{\text{oct}} + 2P = -2.0 \Delta_{\text{oct}} + 2P$$

Q. If the CFSE of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is $-0.8 \Delta_o$, what spin state is it in?

C.N. = 6 \therefore O_h Co(II) \therefore d^7



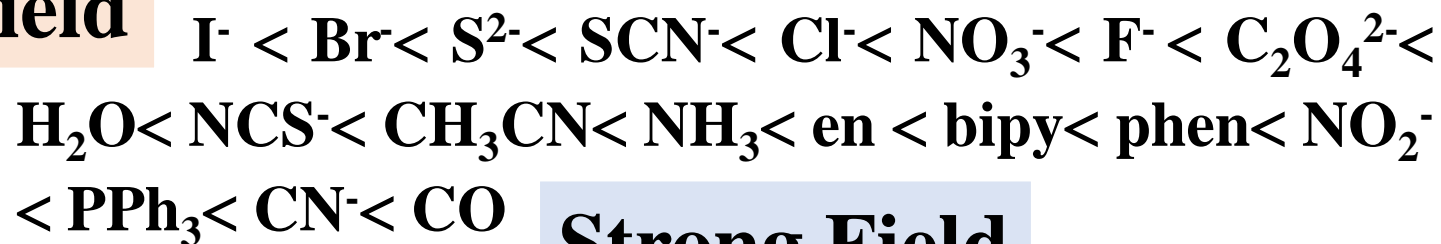
$$\begin{aligned} \text{CFSE} &= (5 \times -0.4 \Delta_{\text{oct}}) + (2 \times 0.6 \Delta_{\text{oct}}) \\ &= -0.8 \Delta_{\text{oct}} \end{aligned}$$



$$\begin{aligned} \text{CFSE} &= (6 \times -0.4 \Delta_{\text{oct}}) + (0.6 \Delta_{\text{oct}}) \\ &= -1.8 \Delta_{\text{oct}} + P \end{aligned}$$

Strong and weak ligands: Spectrochemical Series

Weak Field



Strong Field

Factors influencing the Magnitude of Δ_o for Octahedral complexes

1. The nature of metal cation:

i) Oxidation state of the metal ion

$[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$	28600 cm^{-1}
$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$	19800 cm^{-1}

ii) Different charges on the cation of different metals

$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	12400 cm^{-1}	$3d^3$
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17400 cm^{-1}	$3d^3$

iii) Same charges on the cation but the number of d- electrons is different

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	9300 cm^{-1}	$3d^7$
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	8500 cm^{-1}	$3d^8$

iv) Quantum number (n) of the d- orbitals of the central metal ion.

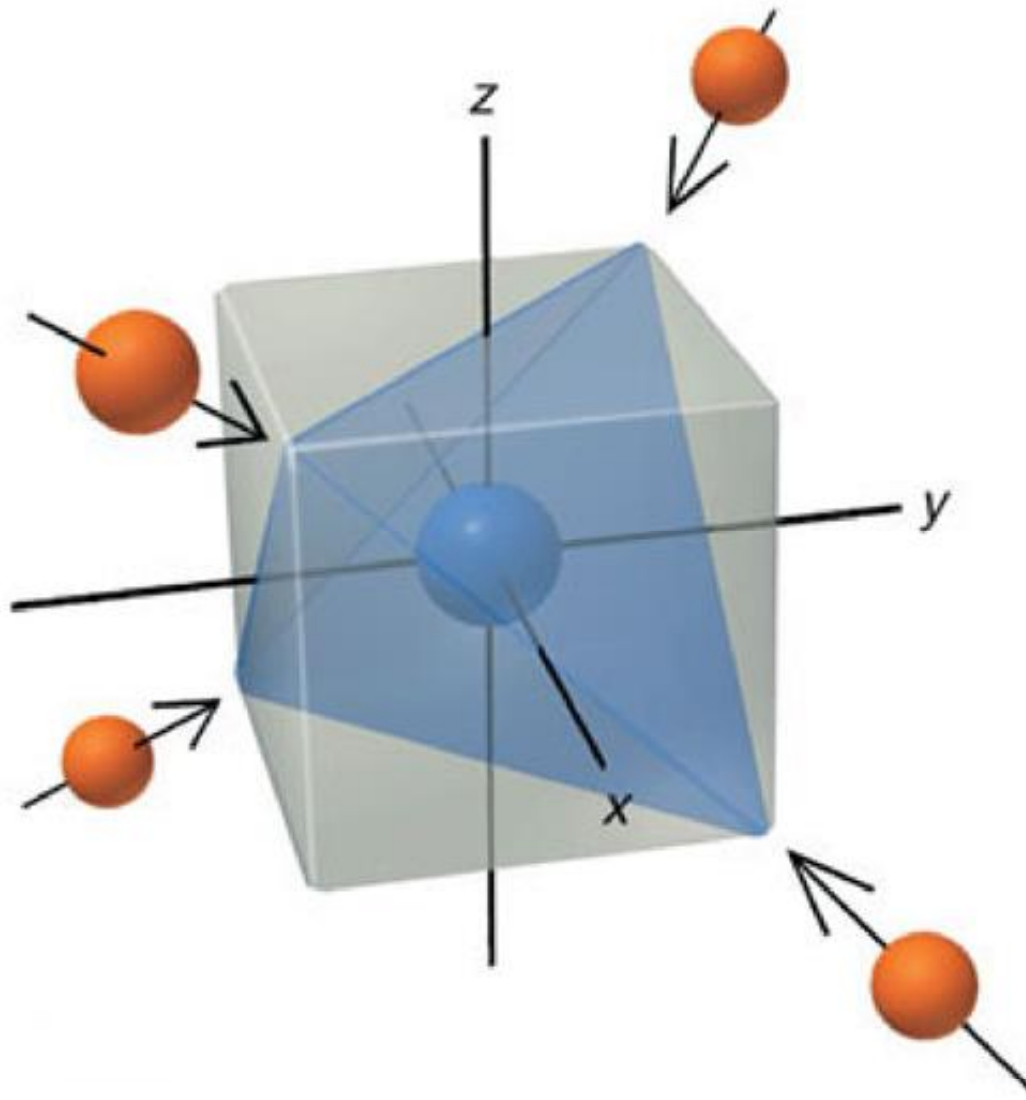
$[\text{Co}(\text{NH}_3)_6]^{3+}$	23000 cm^{-1}	$3d^6$
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34000 cm^{-1}	$4d^6$
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41000 cm^{-1}	$5d^6$

Δ_o increases about 30% to 50% from $3d^n$ to $4d^n$. And by about same amount again from $4d^n$ to $5d^n$.

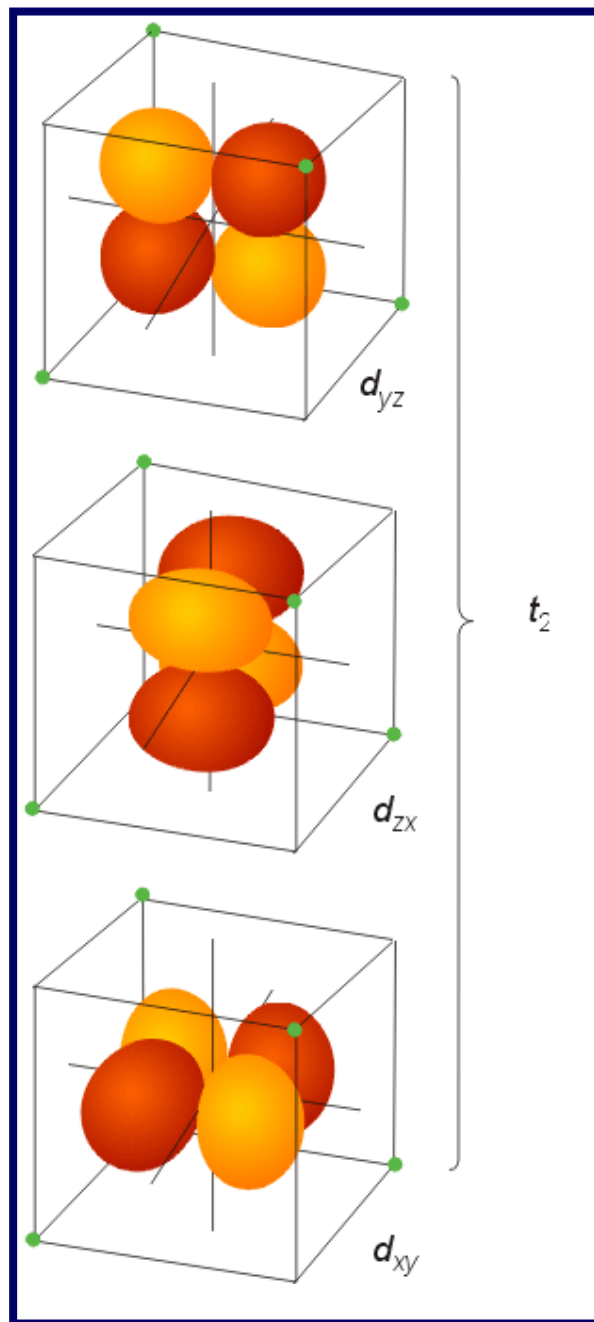
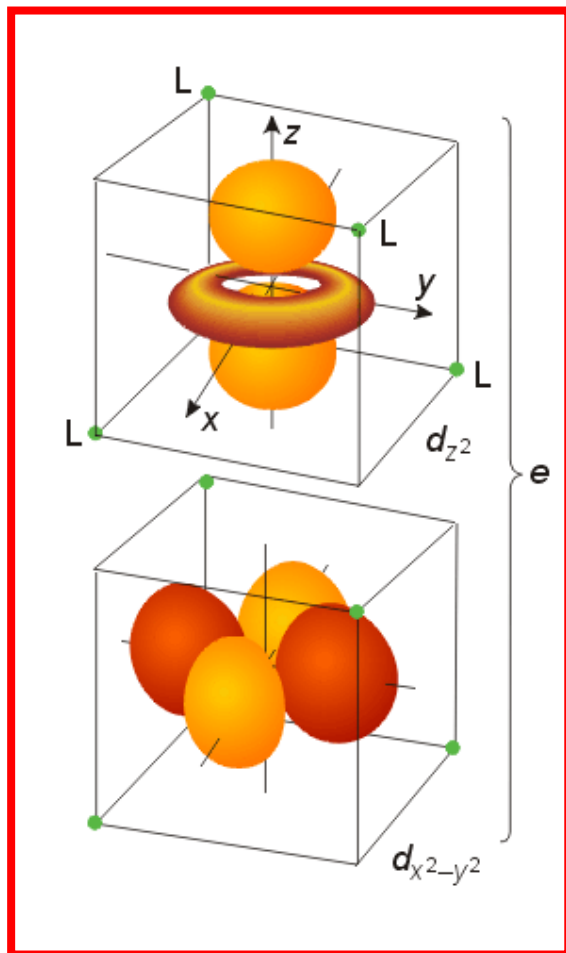
Crystal Field Splitting Energy (CFSE)

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

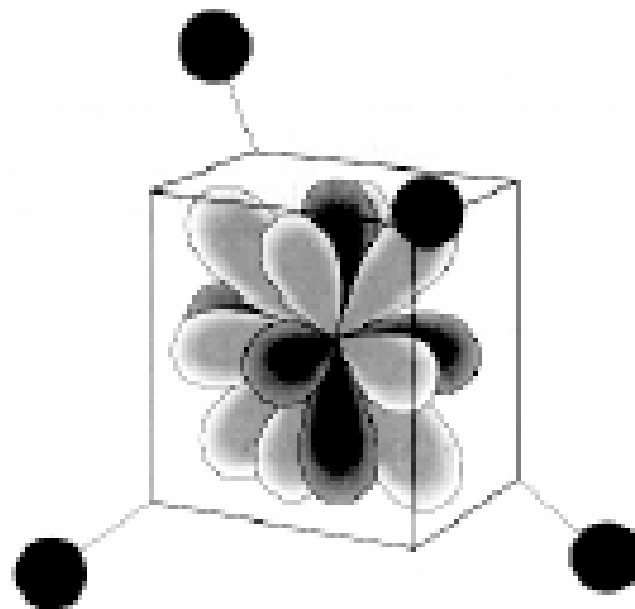
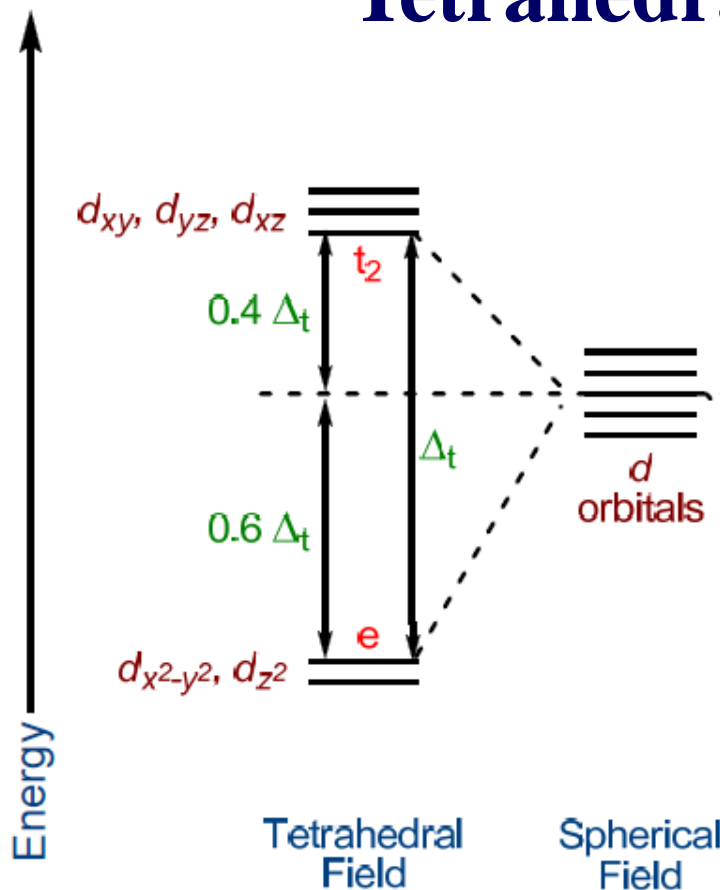
Tetrahedral Field



Tetrahedral Field



Tetrahedral Field



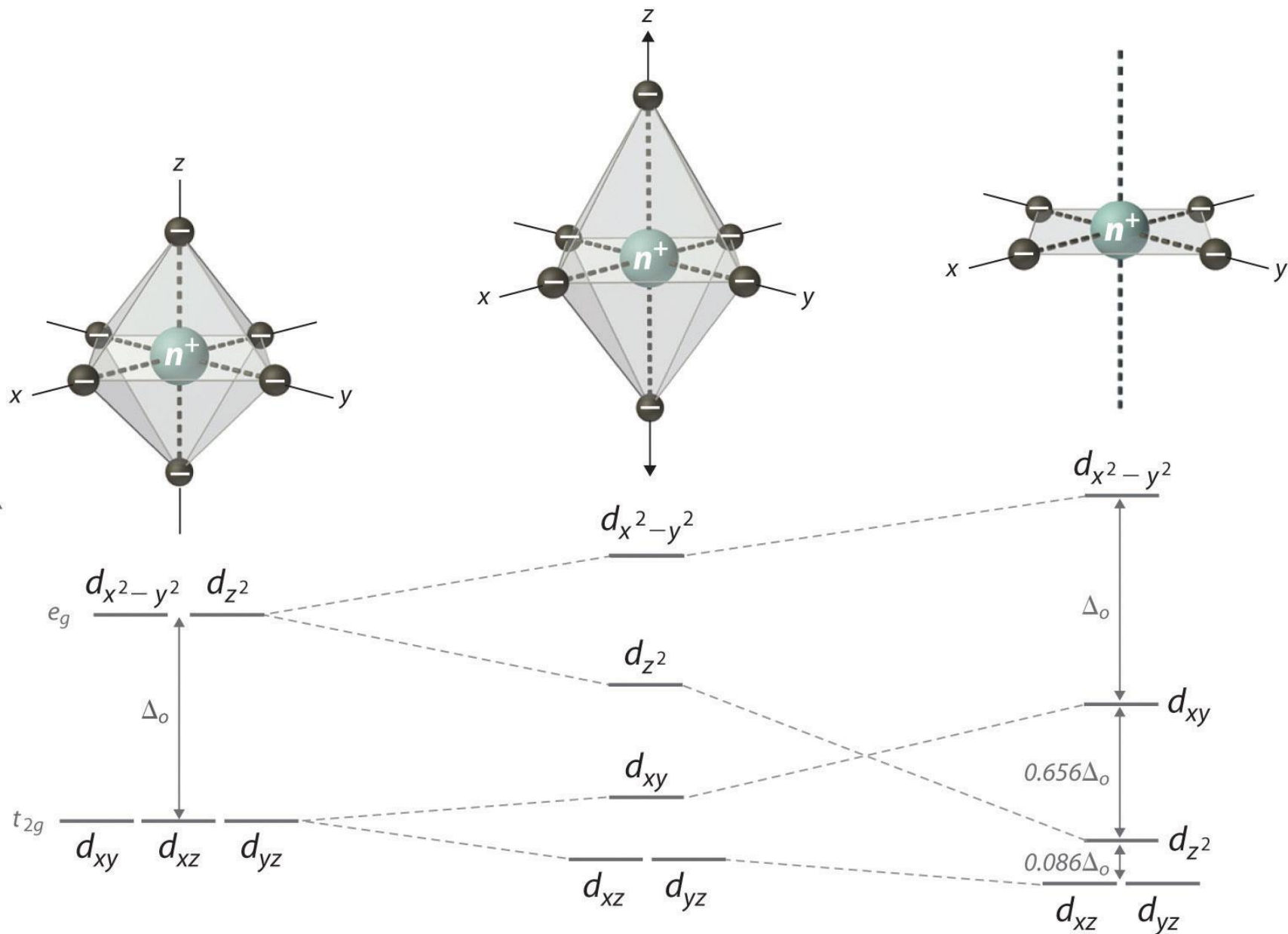
$$\Delta_t < \Delta_o$$

$$\Delta_t = 0.45 \Delta_o$$

For the same metal and ligands and the same internuclear distances

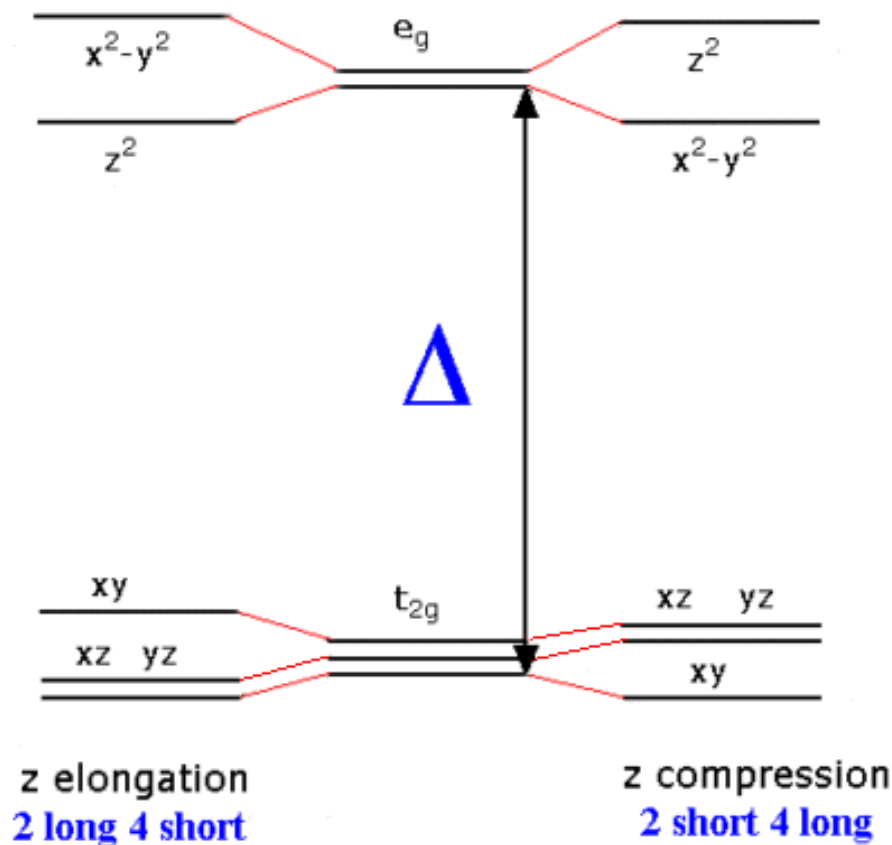
Crystal field splitting favors the formation of octahedral complexes

Distortions of Octahedral Complexes

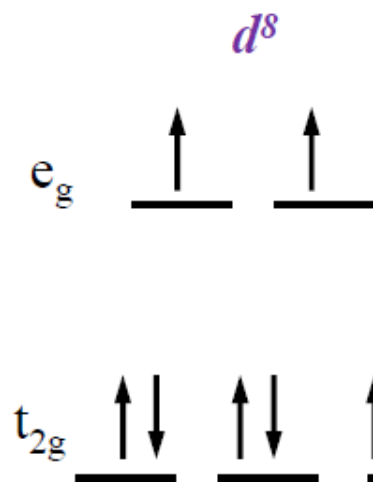


Distortions of Octahedral Complexes: Jahn-Teller effect

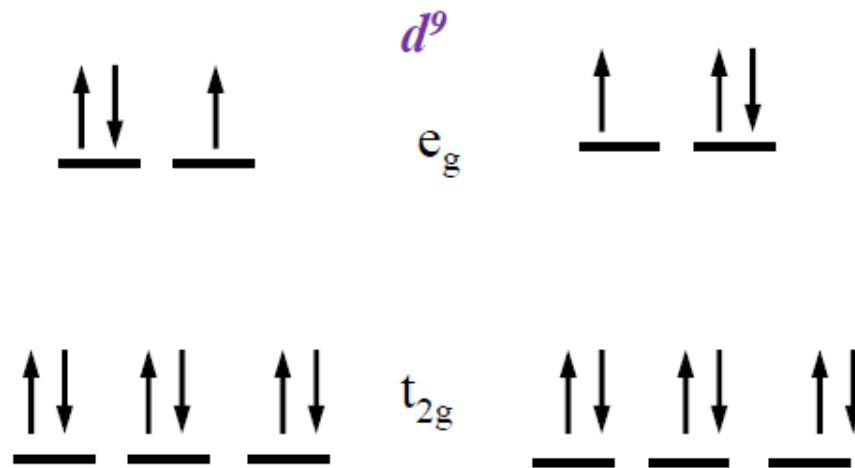
‘Any non-linear molecule having an orbitally degenerate electronic configuration is unstable, and the system undergo distortion to remove the degeneracy.’



Distortions of Octahedral Complexes

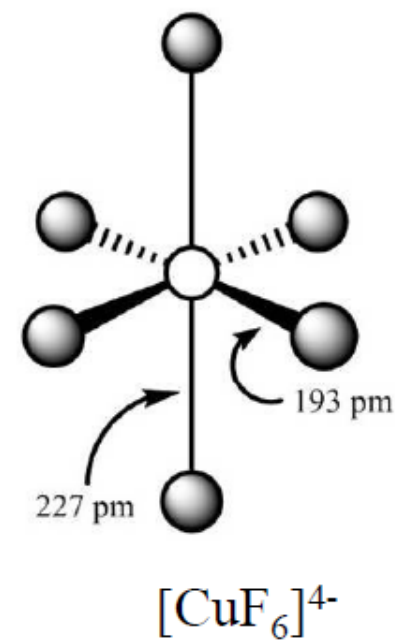
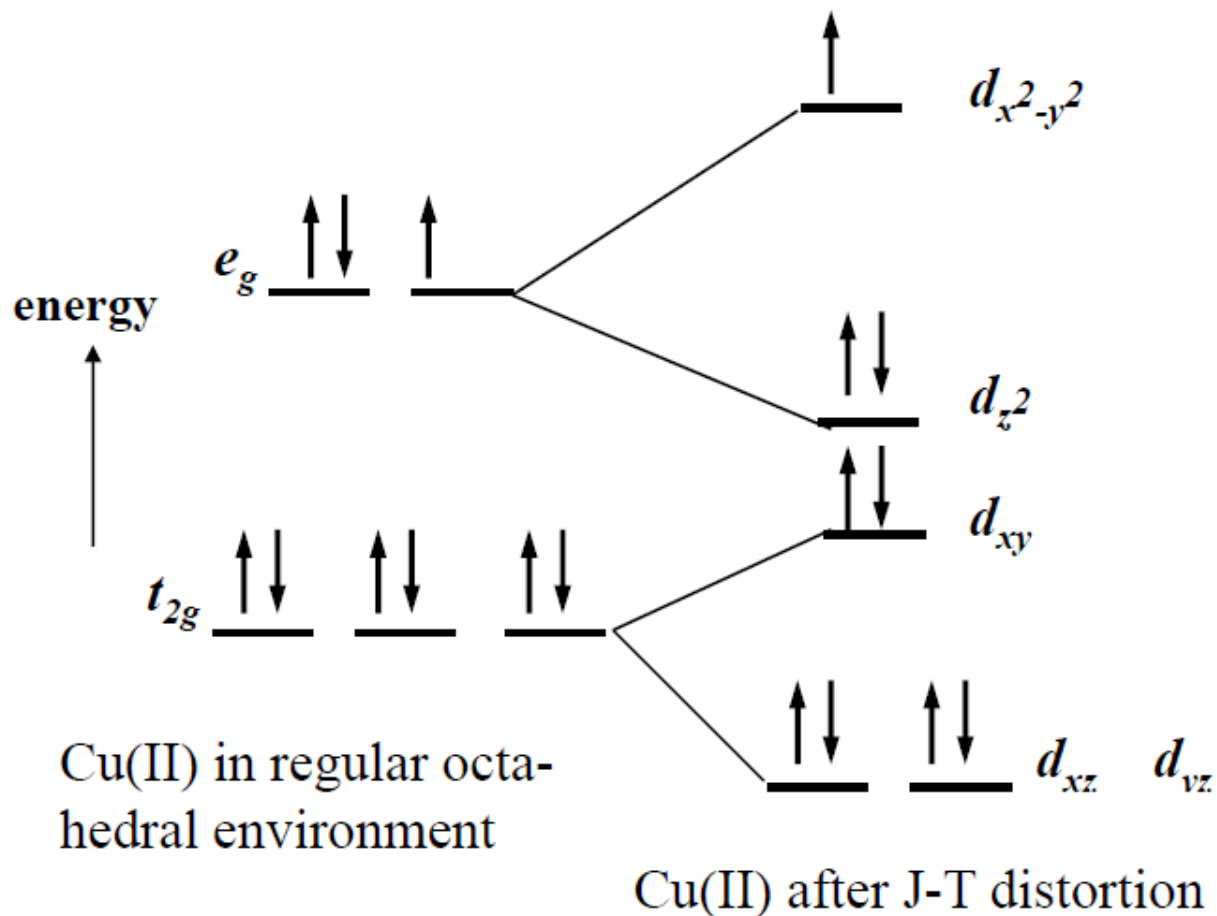


Ni^{2+} : Only one way of filling the orbitals; not degenerate and no Jahn-Teller Distortion

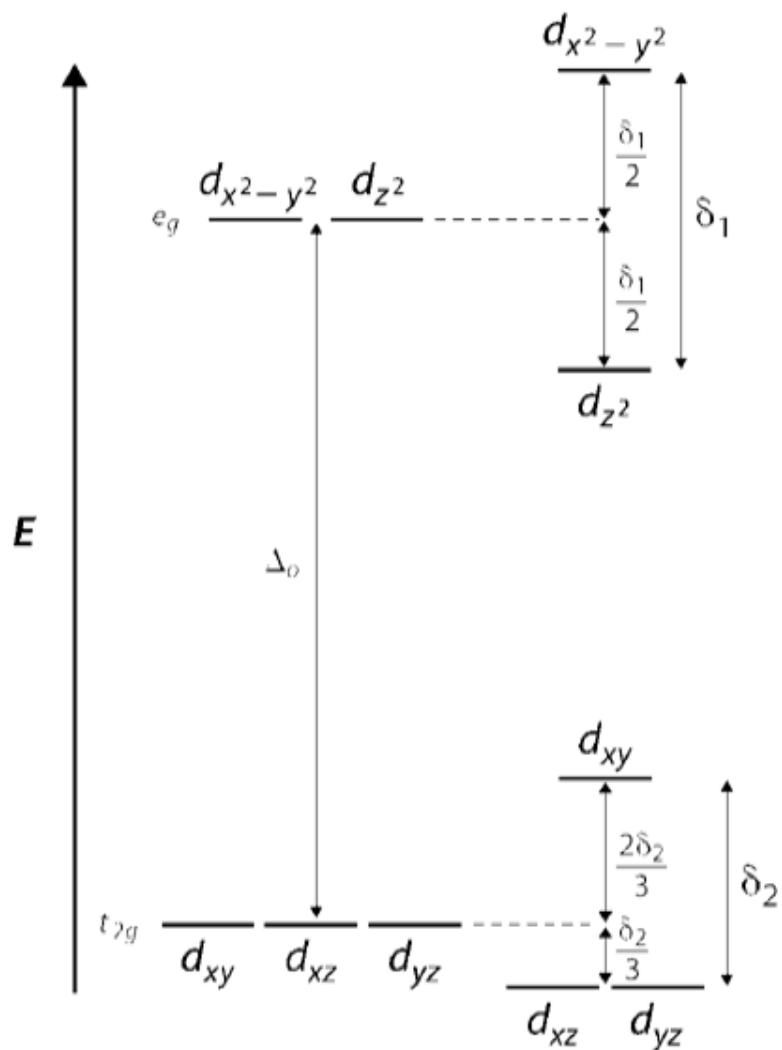


Cu^{2+} : Two ways of filling the e_g orbitals; there is degeneracy and Jahn-Teller Distortion is observed

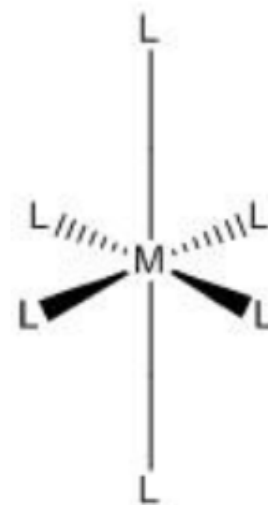
Distortions of Octahedral Complexes



Jahn-Teller Distortion in d^9 Complexes

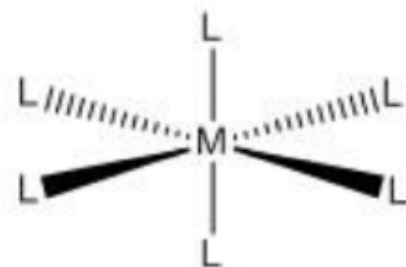
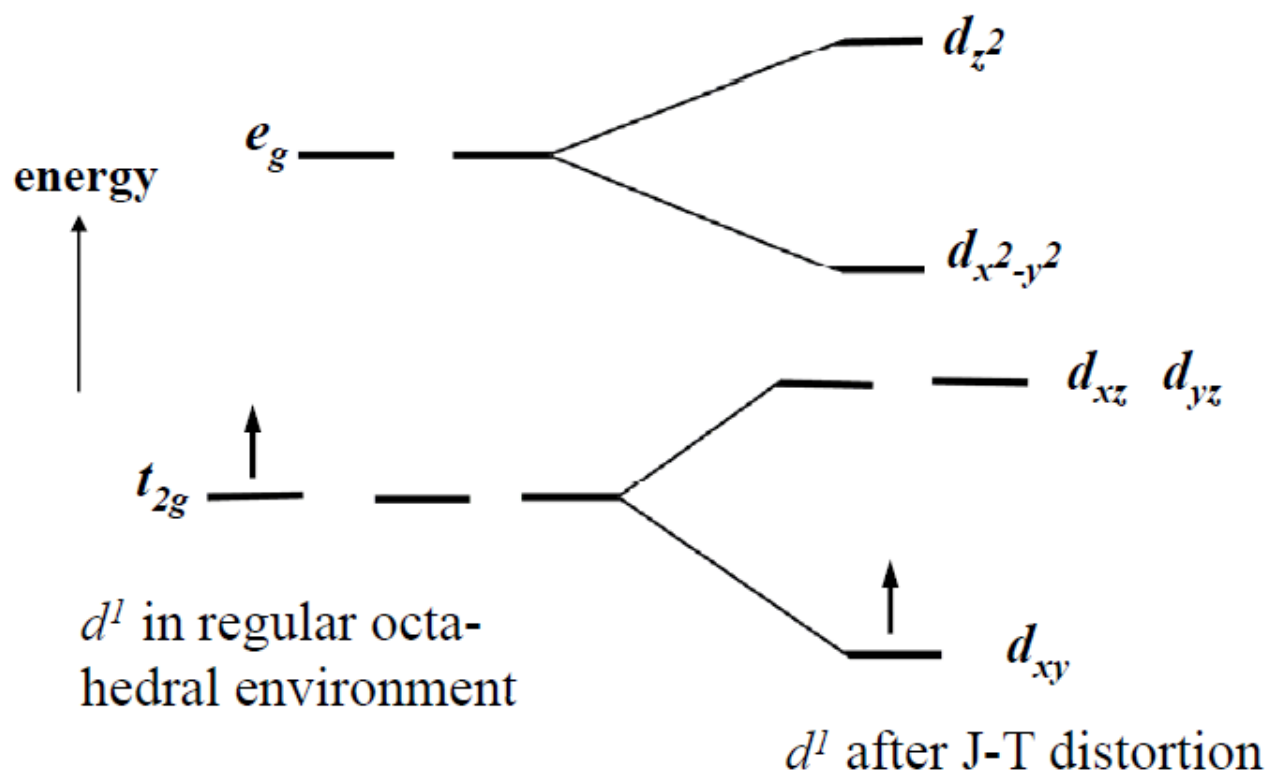


$$\Delta_o \gg \delta_1 > \delta_2.$$



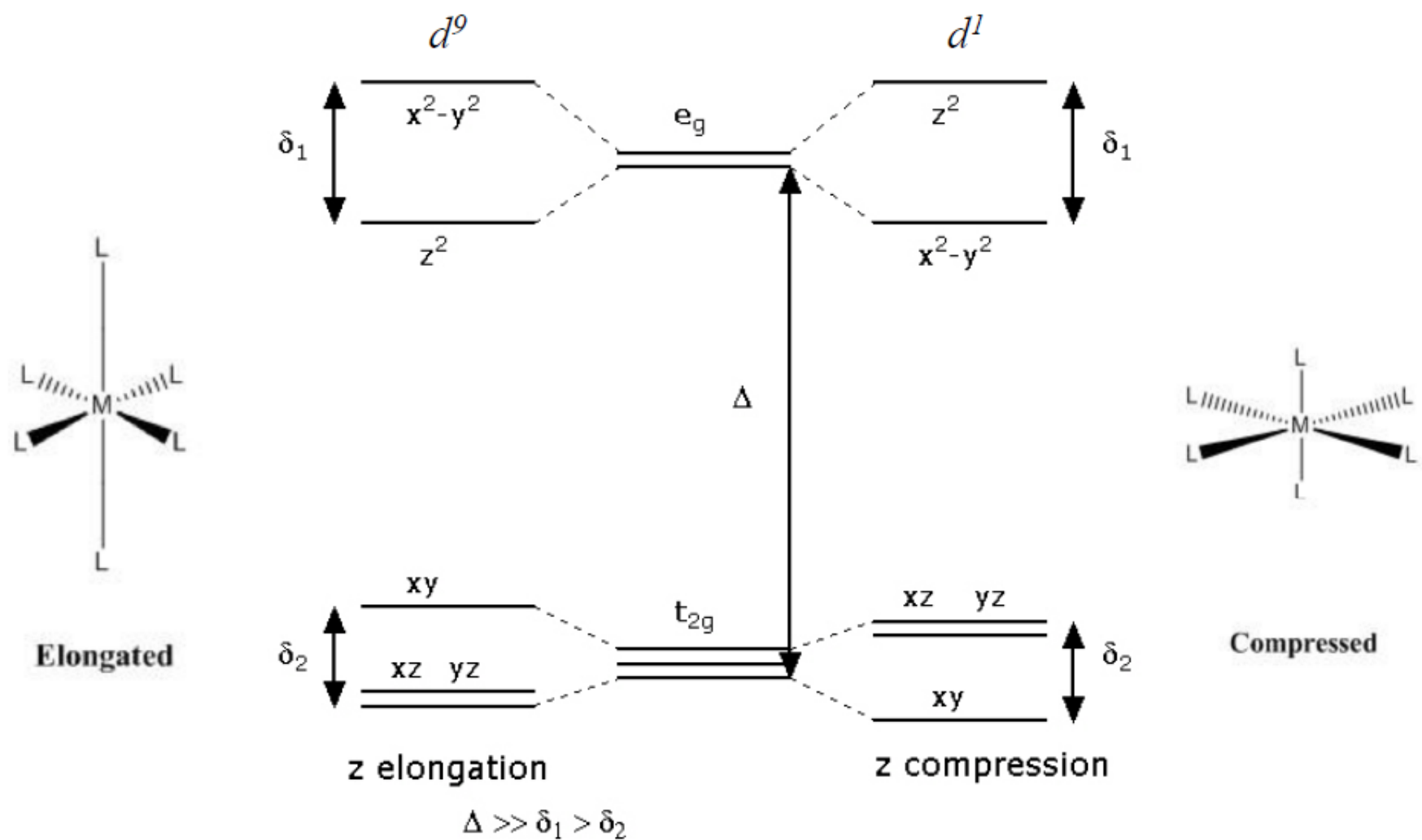
Elongated

Jahn-Teller Distortion in d^1 Complexes



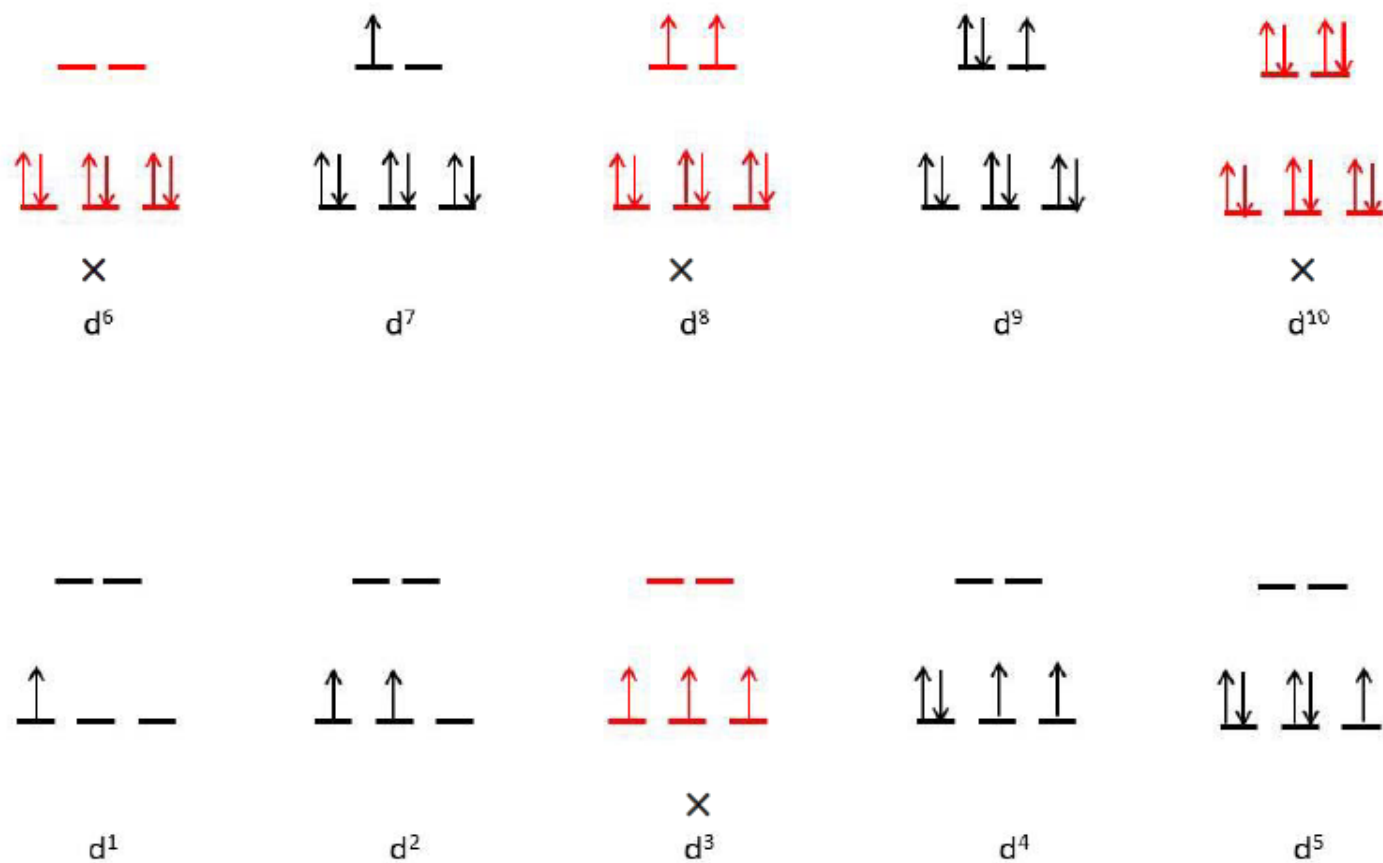
Compressed

$d^1 \text{ Vs } d^9$

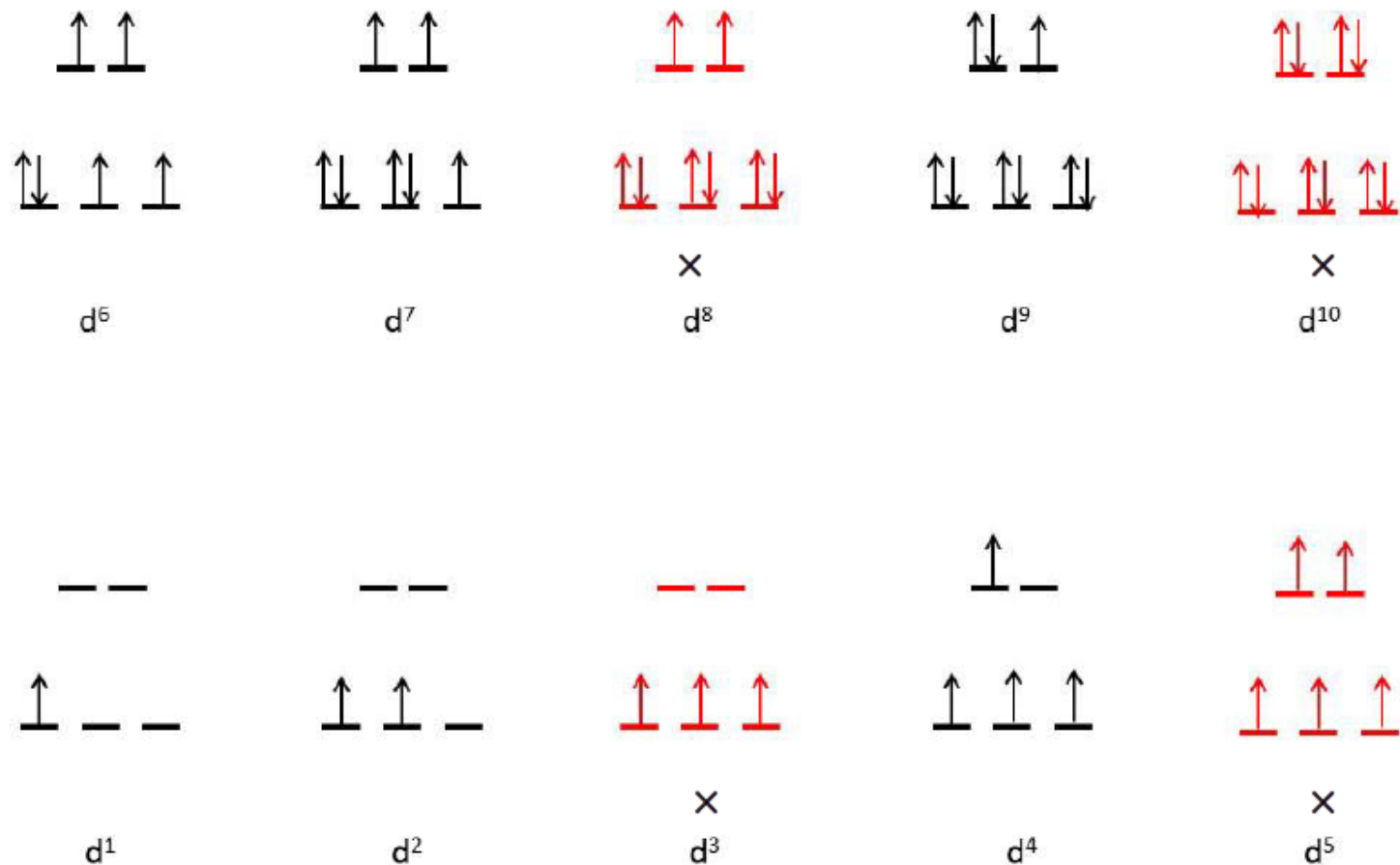


Distortions are more pronounced if the degeneracy occurs in an e_g orbital

Distortions in Low-Spin Complexes



Distortions in High-Spin Complexes

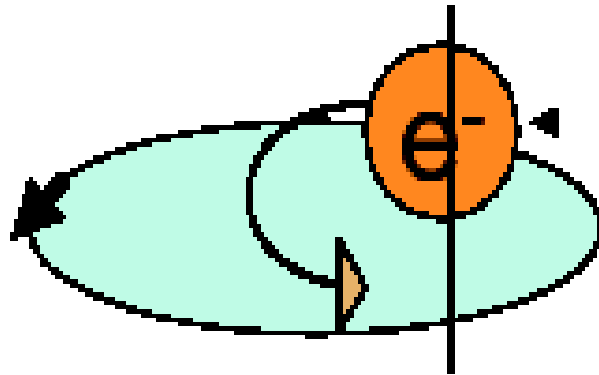


Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum

orbital angular momentum



**Orbital motion of e generates
current and magnetic field**

**Spin motion of e about its own
Axis also generates a magnetic field**

- The magnetic moment μ of a complex with total spin quantum number S is:
- $\mu = 2\{S(S+1)\}^{1/2} \mu_B$ (μ_B is the Bohr magneton)
- $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$
- Since each unpaired electron has a **spin** $1/2$,
- $S = (1/2)n$, where n = no. of unpaired electrons
- $\mu = \{n(n+2)\}^{1/2} \mu_B$
- In **d^4 , d^5 , d^6 , and d^7 octahedral complexes**, magnetic measurements can very easily predict **weak** versus **strong field**.
- **Tetrahedral complexes** - only **high spin** complexes result, for $\Delta_t \ll \Delta_o$.

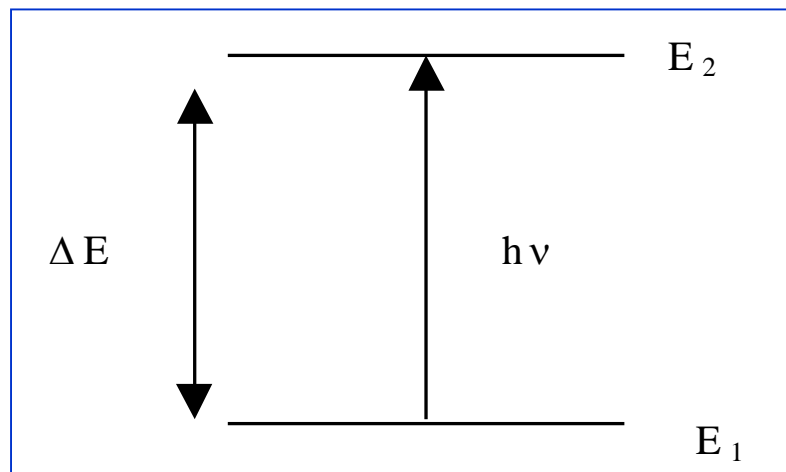
n = no. of unpaired electrons

$$\mu = \{n(n+2)\}^{1/2} \mu_B$$

Ion	n	S	μ/μ_B Calculated	Experimental
Ti³⁺	1	1/2	1.73	1.7 – 1.8
V³⁺	2	1	2.83	2.7 – 2.9
Cr³⁺	3	3/2	3.87	3.8
Mn³⁺	4	2	4.90	4.8 – 4.9
Mn²⁺	5	5/2	5.92	5.9 - 6.3

**Similar Calculation can be done
for Low-spin Complex**

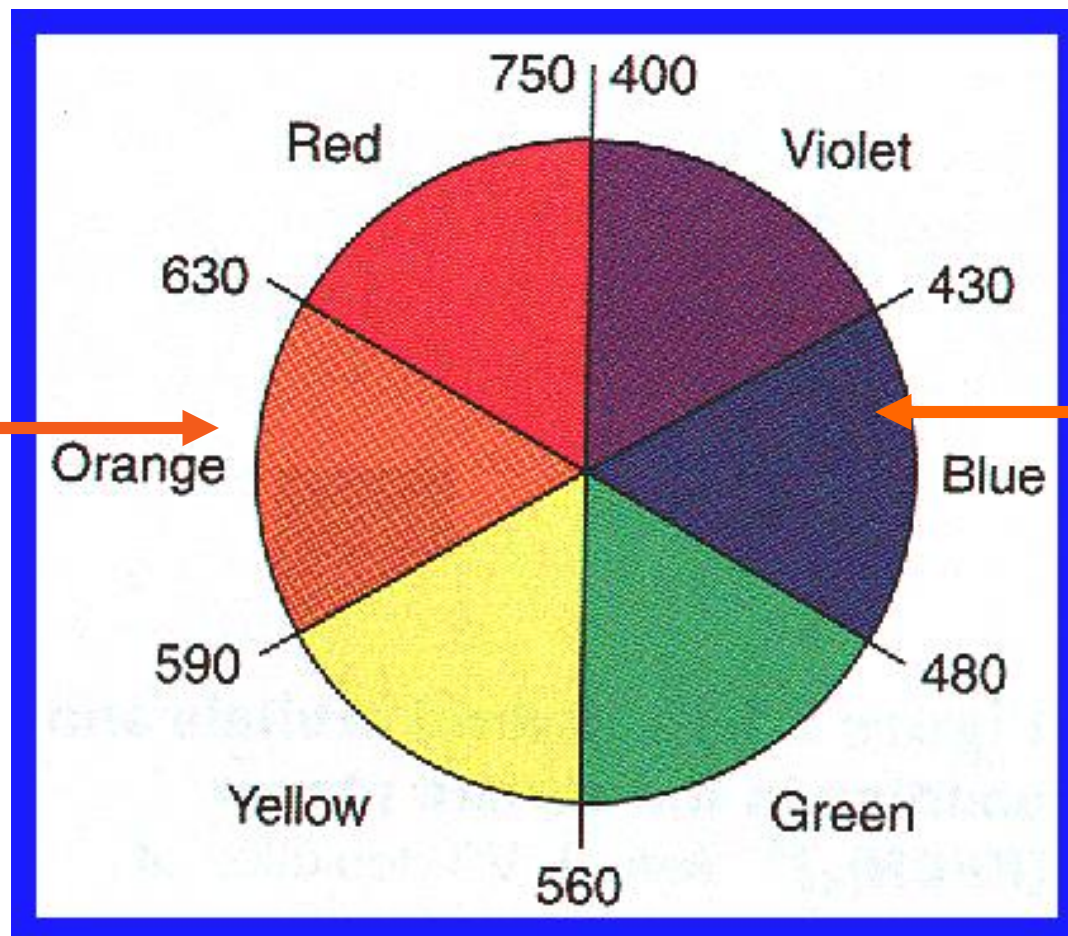
The origin of the color of the transition metal compounds



$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_o , therefore the colour

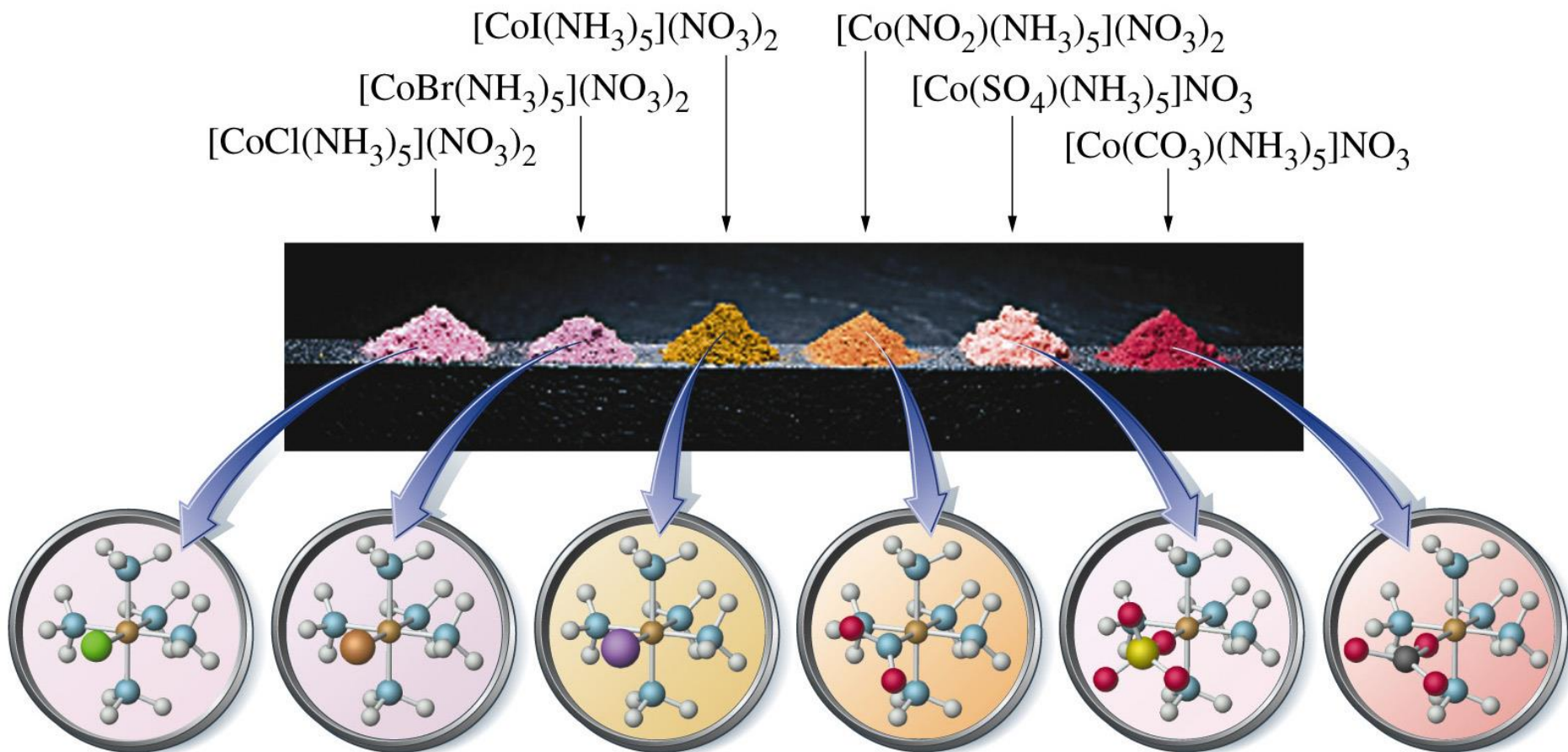
**absorbed
color**

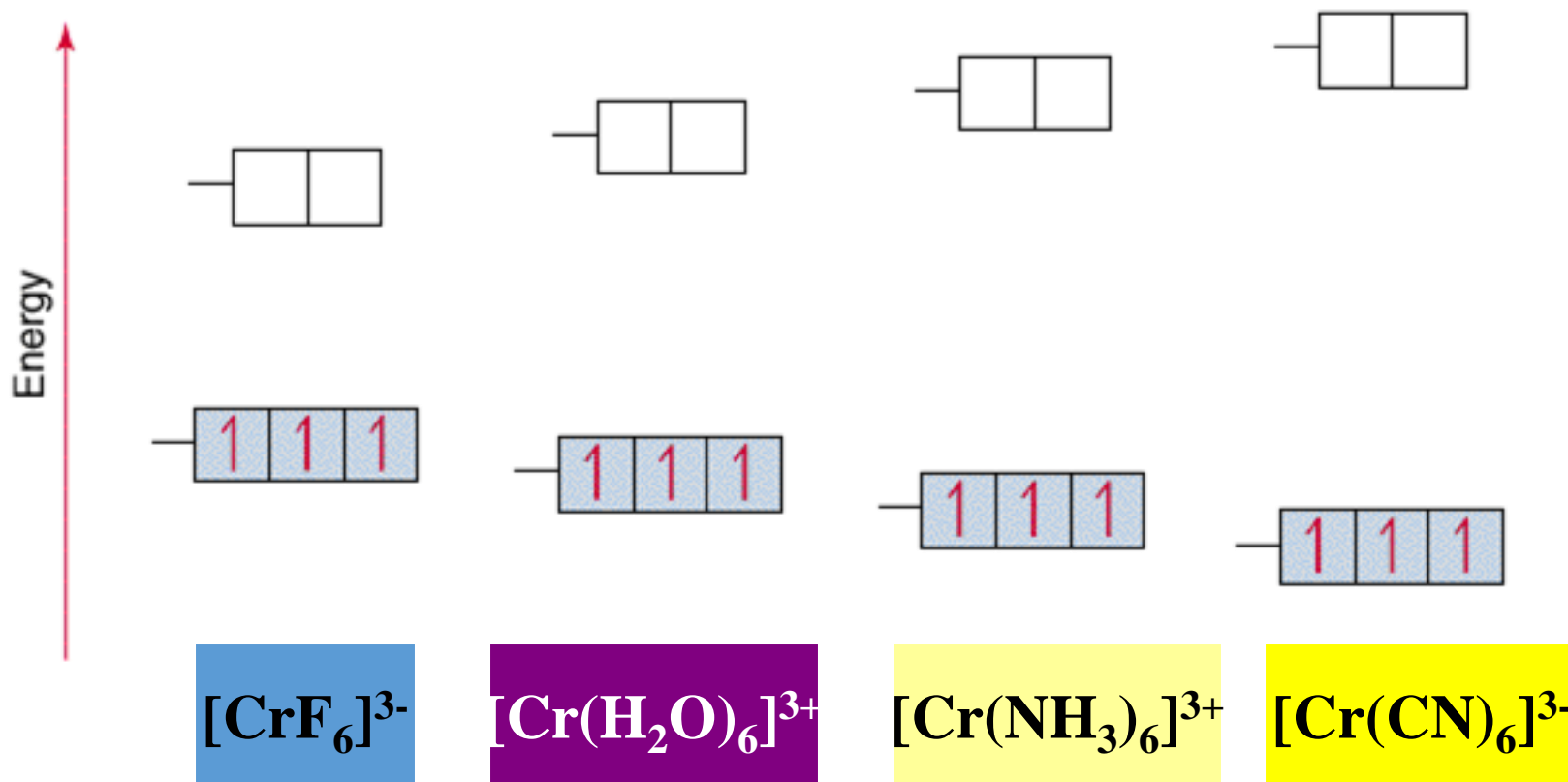


**observed
color**

The colour can change depending on a number of factors
e.g.

1. Metal charge
2. Ligand strength





As Cr^{3+} goes from being attached to a **weak field** ligand to a **strong field** ligand, Δ **increases** and the **color** of the complex changes from **green** to **yellow**.

Limitations of CFT

Considers Ligand as Point charge/dipole only

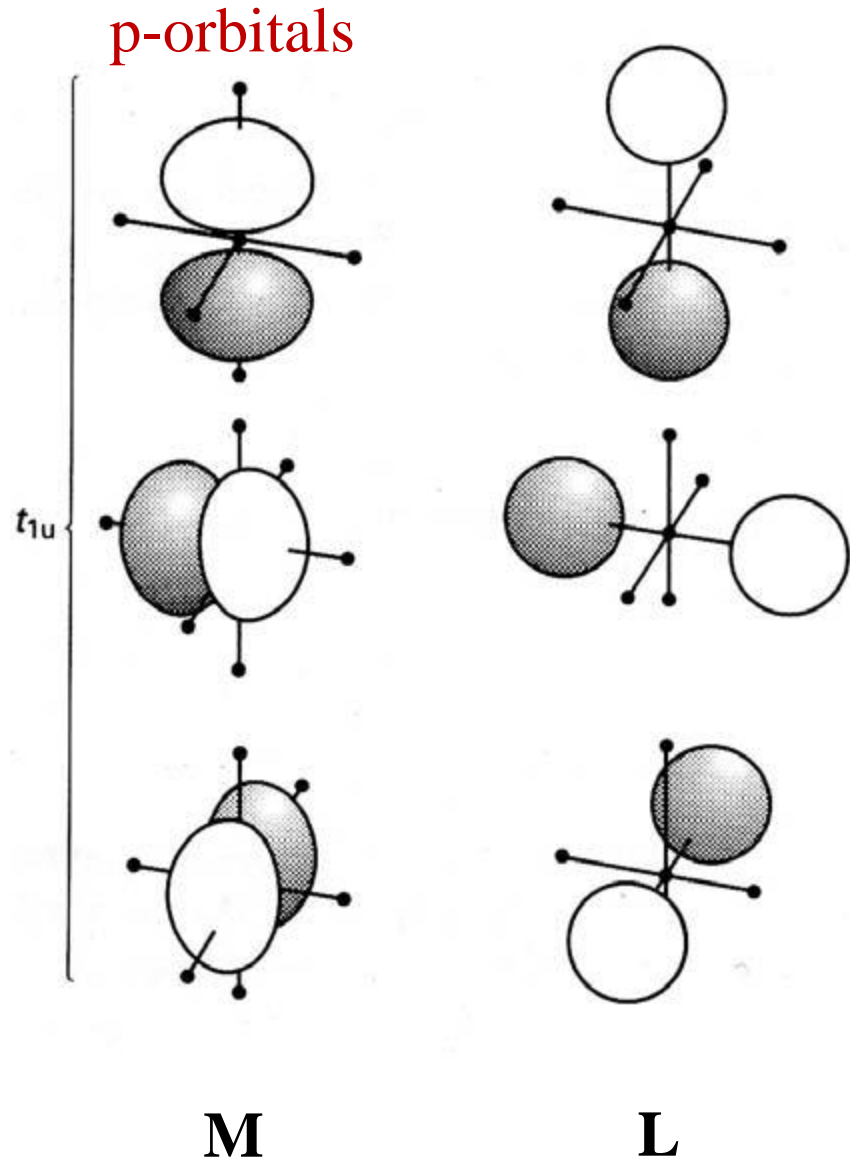
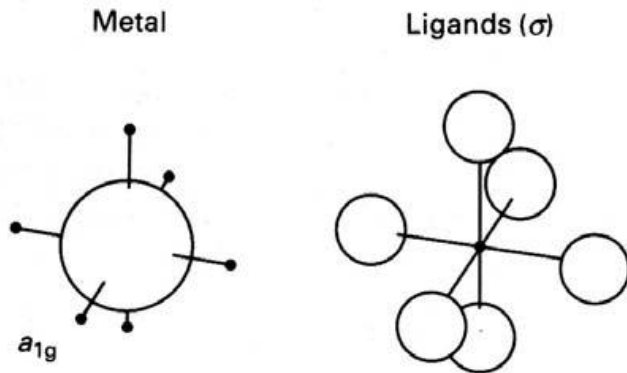
Does not take into account of the overlap of ligand and metal orbitals

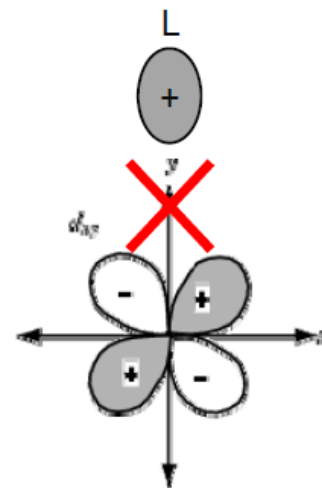
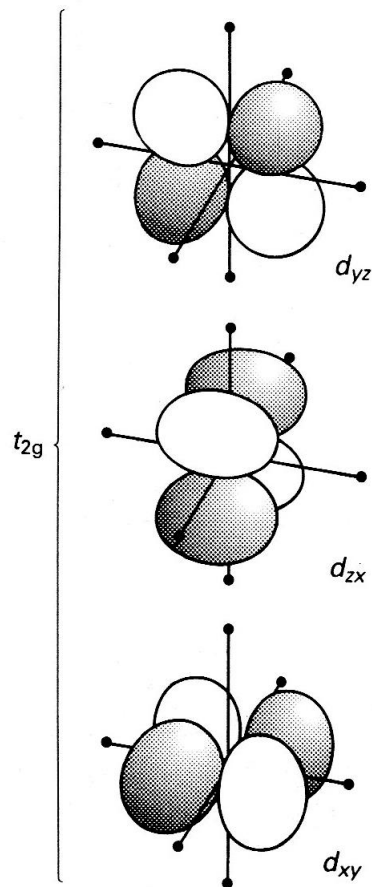
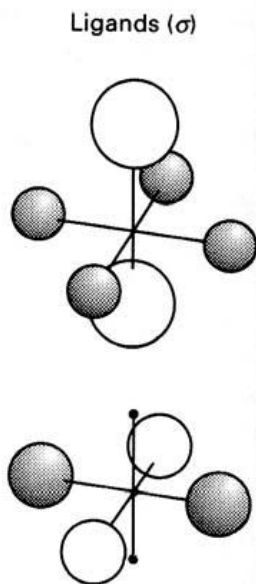
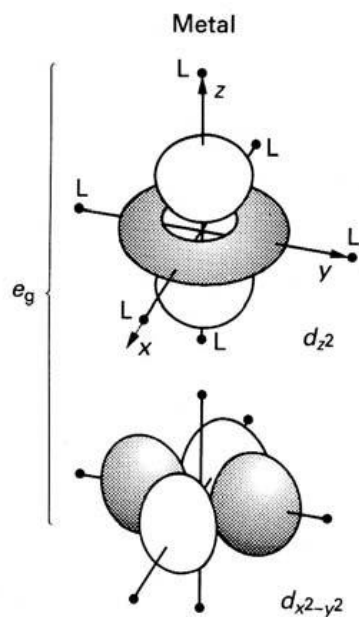
Consequence

e.g. Fails to explain why CO is stronger ligand than CN^- in complexes having metal in low oxidation state

Ligand Field Theory: Concepts

- Ligand Orbitals(LGO)are obtained by Linear Combination of Atomic Orbitals (LCAO)
- LGOs overlap with symmetry related Metal Orbitals





T_{2g} orbitals cannot form sigma bonds with the L_6 set.

$S = 0$.

T_{2g} are non-bonding

MO diagram of an Octahedral complex

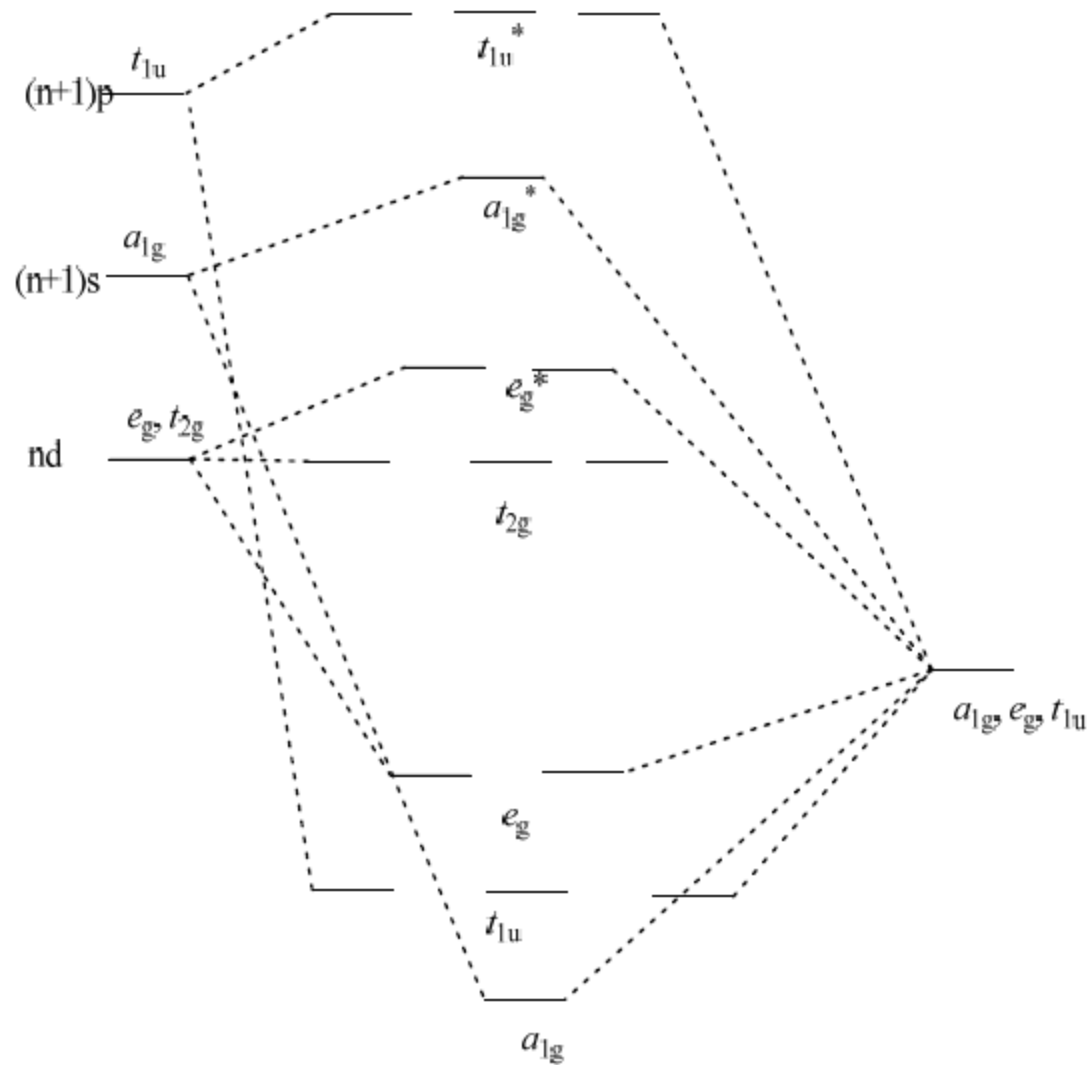


Fig 1.4.1 M.O. Diagram of σ -only octahedral complex

M

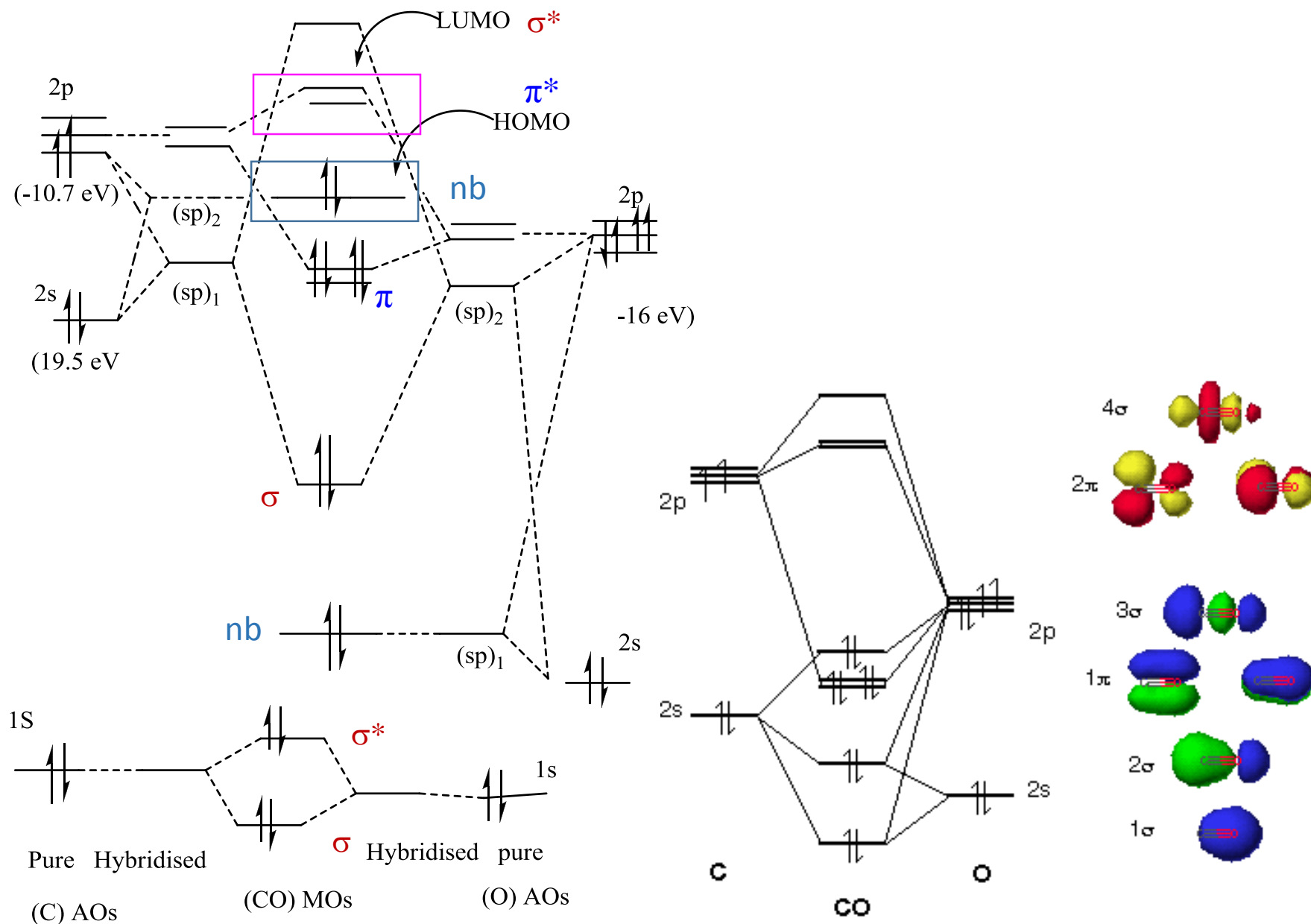
ML₆

6LGOs

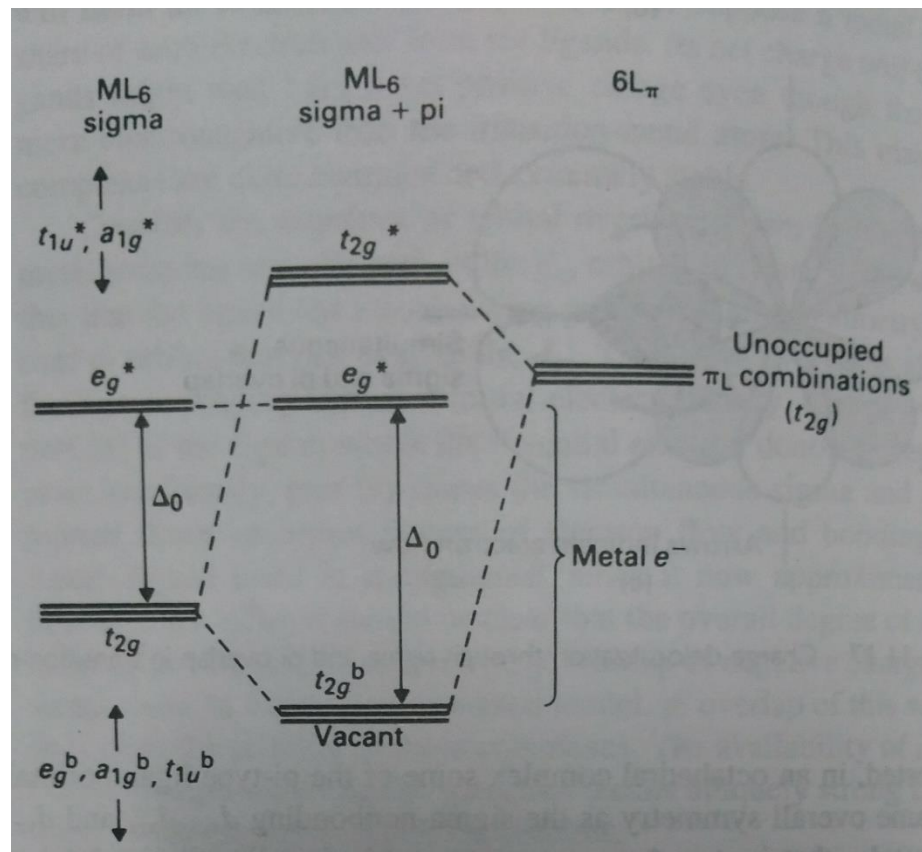
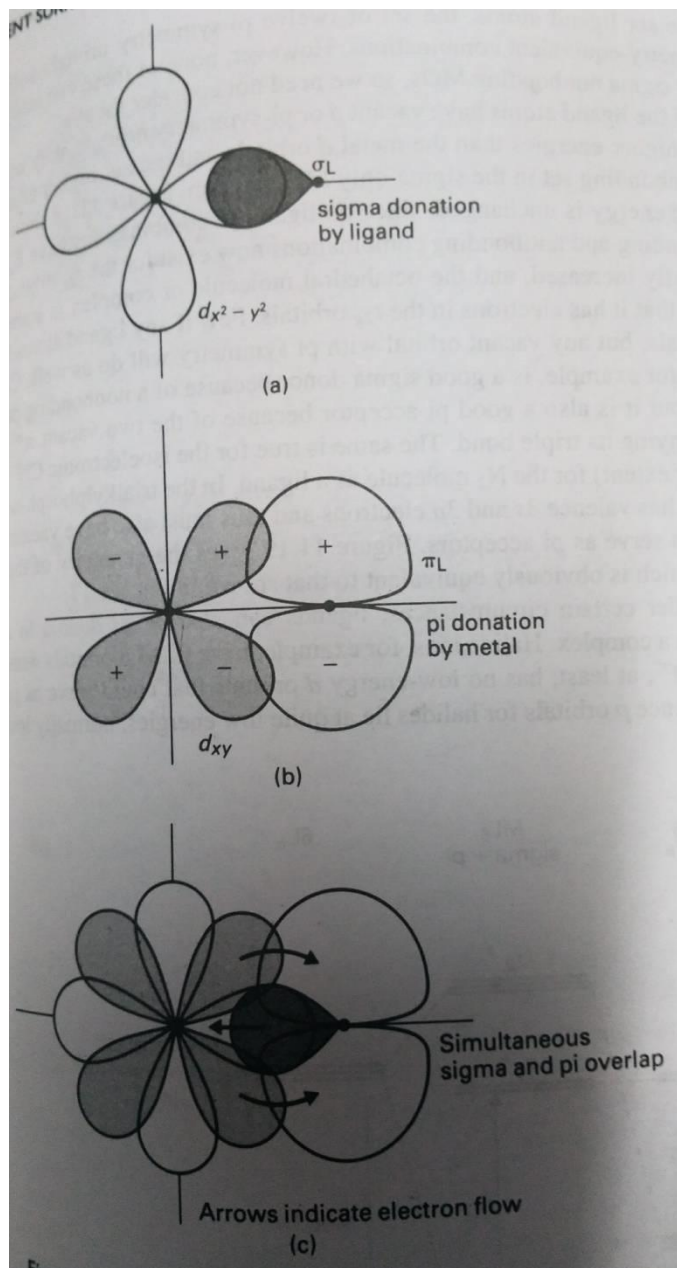
Metals in Low Oxidation States

- In low oxidation states, the electron density on the metal ion is very high.
- To stabilize low oxidation states, we require ligands, which can simultaneously bind the metal center and also withdraw electron density from it.

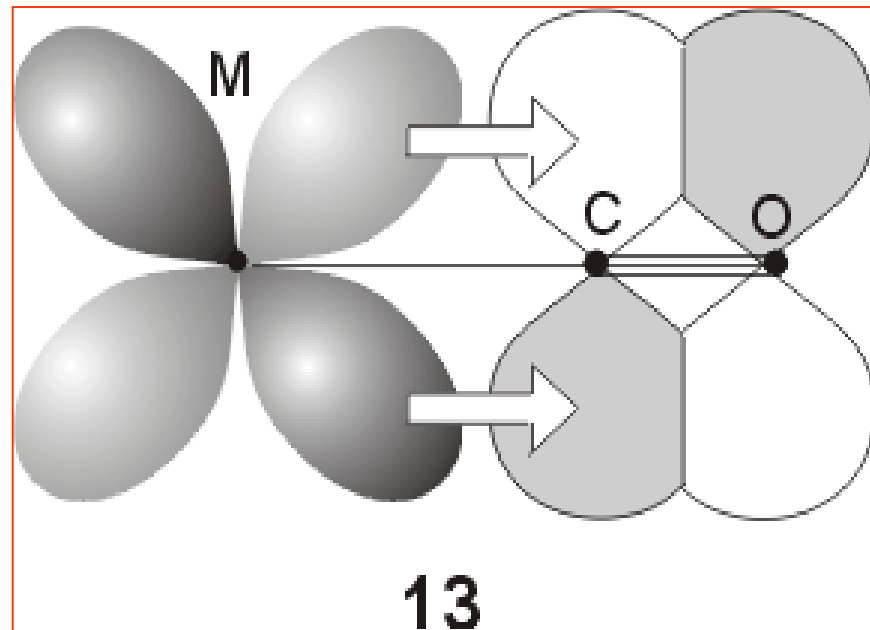
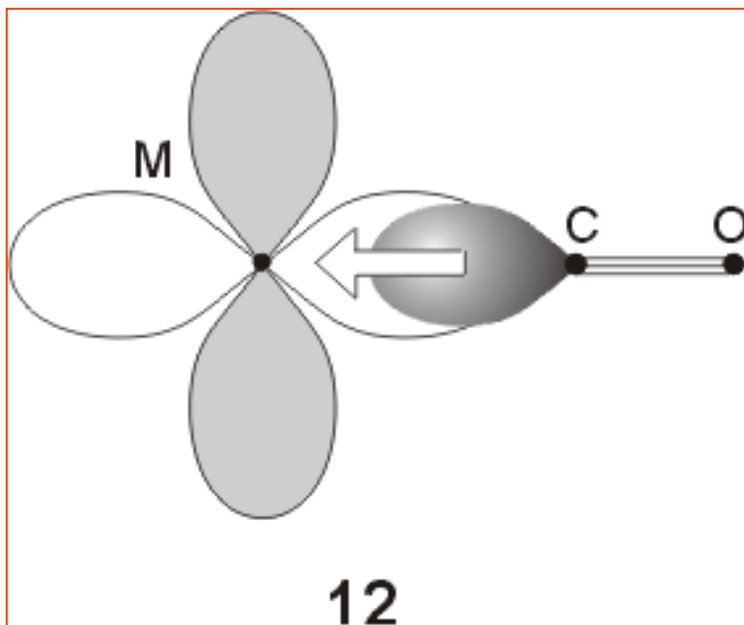
Stabilizing Low Oxidation State: CO Can Do the Job



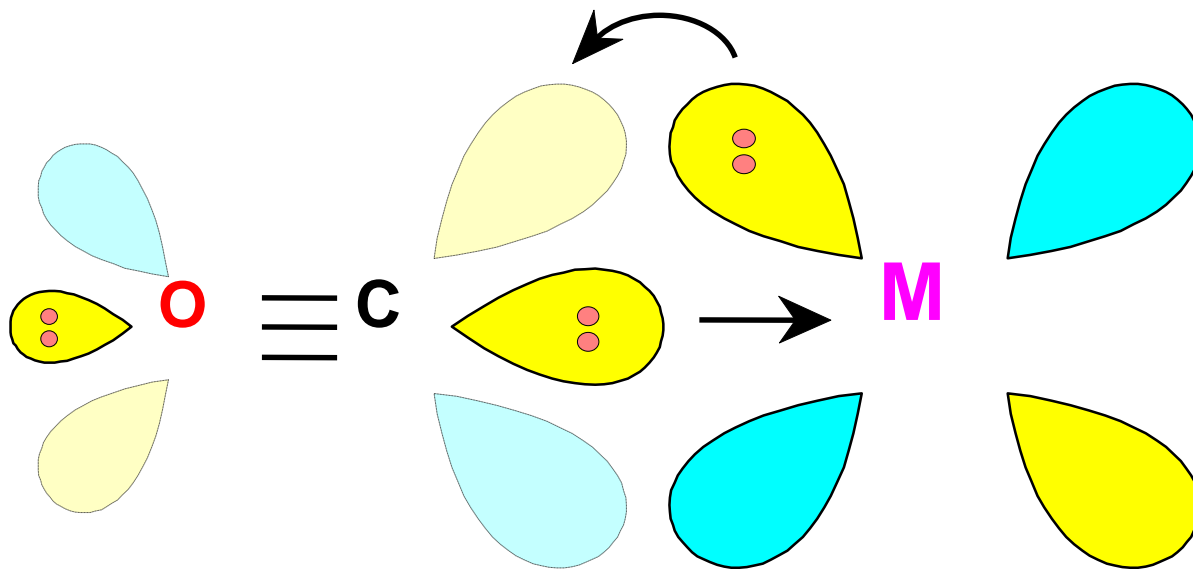
MO of π -complex



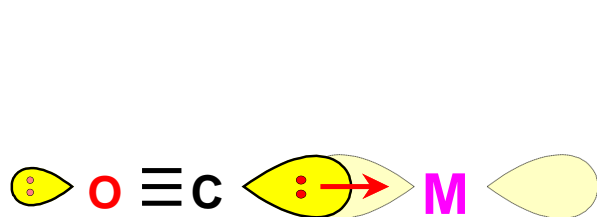
Stabilizing Low Oxidation State: CO Can Do the Job



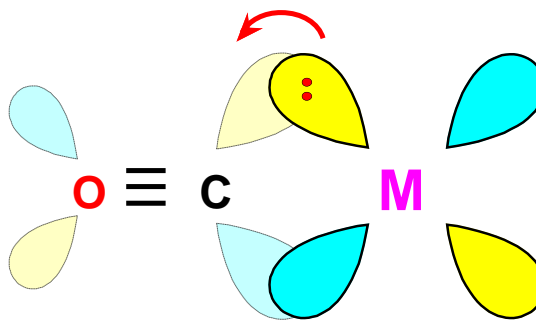
**$\text{Ni}(\text{CO})_4$, $[\text{Fe}(\text{CO})_5]$, $[\text{Cr}(\text{CO})_6]$, $[\text{Mn}_2(\text{CO})_{10}]$,
 $[\text{Co}_2(\text{CO})_8]$, $\text{Na}_2[\text{Fe}(\text{CO})_4]$, $\text{Na}[\text{Mn}(\text{CO})_5]$**



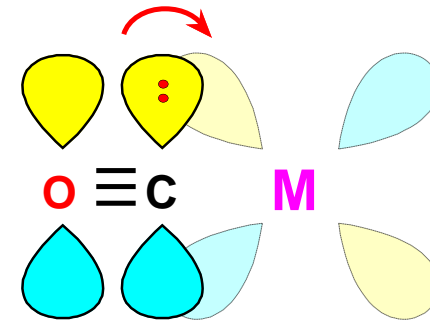
σ orbital serves as a very weak donor to a metal atom



CO-M sigma bond



M to CO pi backbonding



CO to M pi bonding
(rare)