Semester II

CHE-RC/HG-2016 :CHEMISTRY2

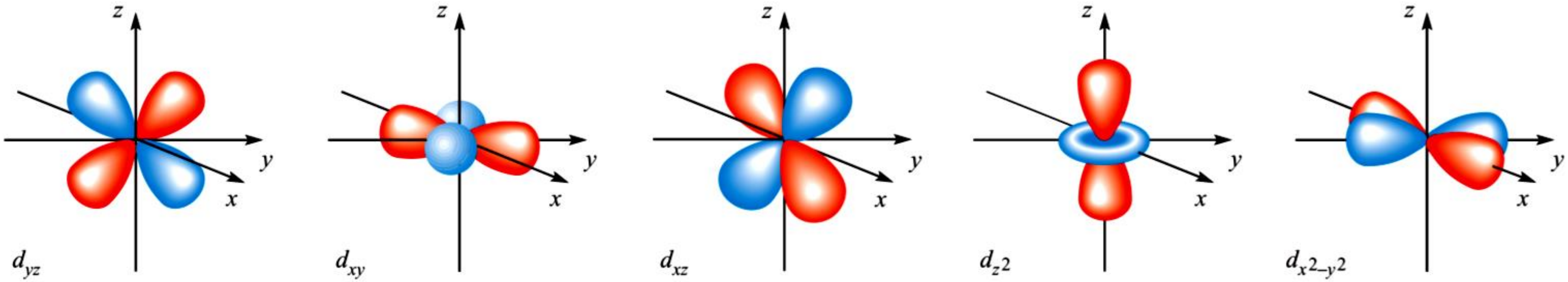
Section A:

Topic: VBT and CFT

Bonding Theories of Coordination Complexes

Valence Bond Theory (VBT)

Shapes of d-orbitals



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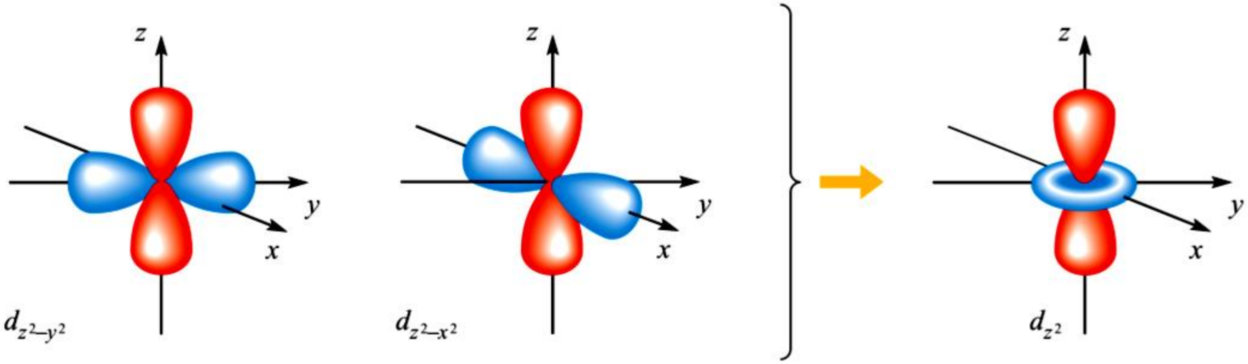


In an octahedral complex, the *d* orbitals that have lobes lying along the axes are the d_{z^2} and the $d_{x^2-y^2}$. The d_{xy}, d_{yz}, and d_{xz} orbitals directed between the axes are considered to be nonbonding.

https://www.chemtube3d.com/orbitals-d/

Valence Bond Theory (VBT)

- In this approach, the empty orbitals on the metal ions are viewed as hybrid orbitals in sufficient number to accommodate the number of electron pairs donated by the ligands.

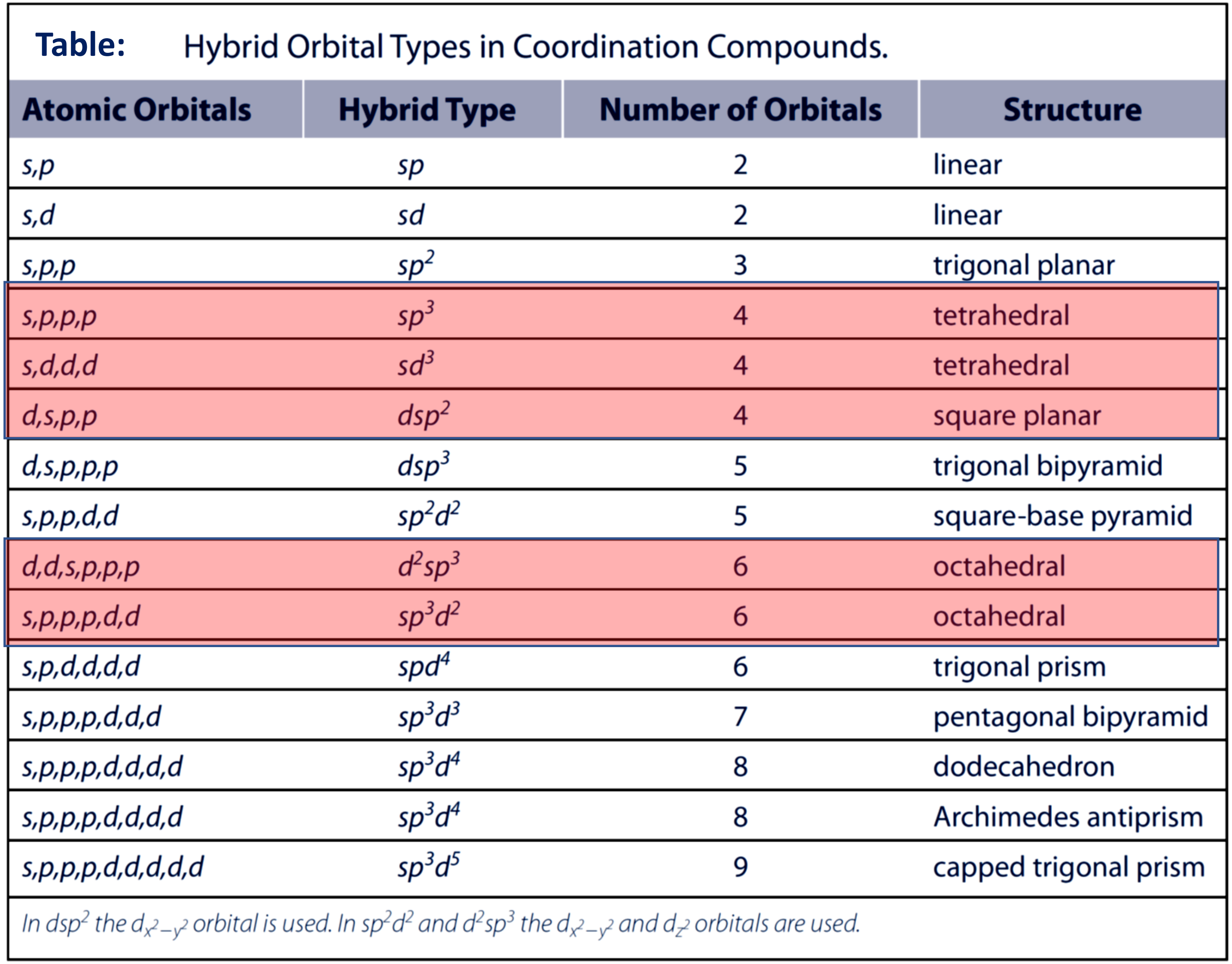


Table: Hybrid Orbital Types in Coordination Compounds.

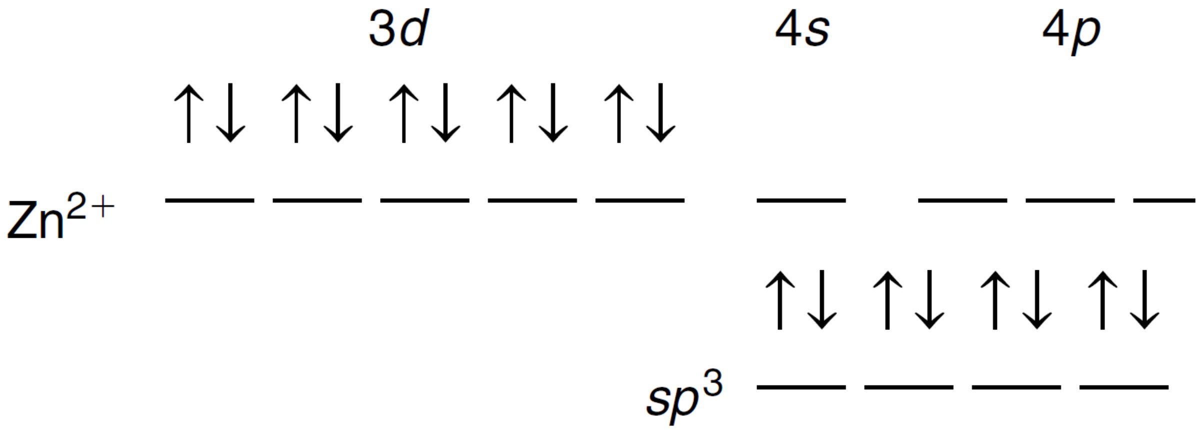
Atomic Orbitals	Hybrid Type	Number of Orbitals	Structure
s,p	sp	2	linear
s,d	sd	2	linear
s,p,p	sp^2	3	trigonal planar
s,p,p,p	sp^3	4	tetrahedral
s,d,d,d	sd^3	4	tetrahedral
d,s,p,p	dsp^2	4	square planar
d,s,p,p,p	dsp^3	5	trigonal bipyramid
s,p,p,d,d	sp^2d^2	5	square-base pyramid
d,d,s,p,p,p	d^2sp^3	6	octahedral
s,p,p,p,d,d	sp^3d^2	6	octahedral
s,p,d,d,d,d	spd^4	6	trigonal prism
s,p,p,p,d,d,d	sp^3d^3	7	pentagonal bipyramid
s,p,p,p,d,d,d,d	sp^3d^4	8	dodecahedron
s,p,p,p,d,d,d,d	sp^3d^4	8	Archimedes antiprism
s,p,p,p,d,d,d,d,d	sp^3d^5	9	capped trigonal prism

In dsp^2 *the* $d_{x^2-y^2}$ *orbital is used. In* sp^2d^2 *and* d^2sp^3 *the* $d_{x^2-y^2}$ *and* d_{z^2} *orbitals are used.*

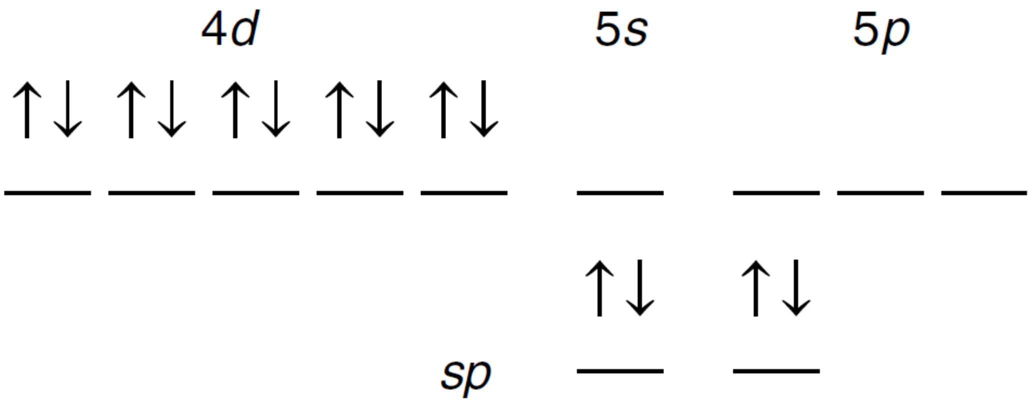
Valence Bond Theory (VBT)

- ❑ It is easy to rationalize the bonding in terms of hybrid orbitals that has a d^{10} configuration with empty 4s and 4p orbitals. For e.g.

1. $[Zn(NH_3)_4]^{2+}$

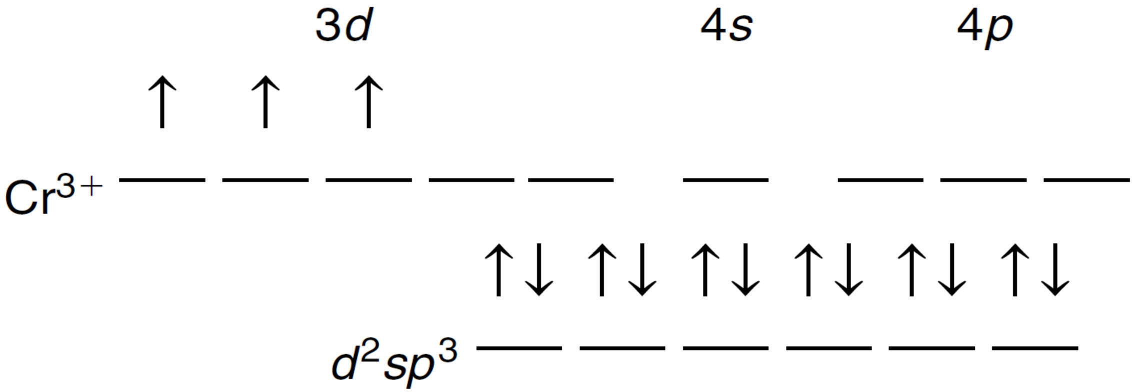


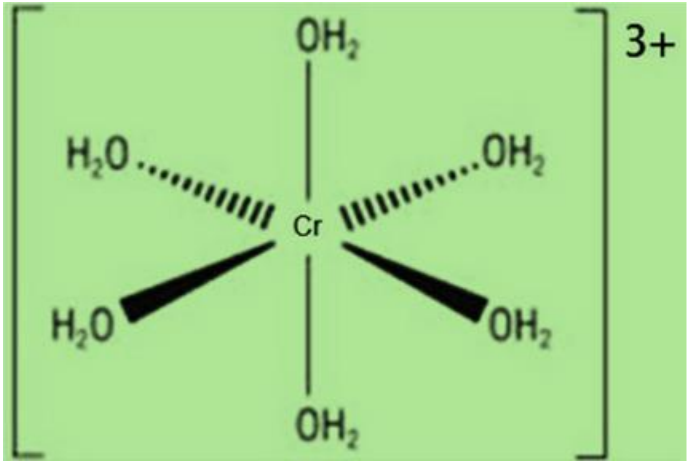
2. $[Ag(NH_3)_2]^+$



Valence Bond Theory (VBT)

- VBT is generally true that first-row transition metals form complexes that in many cases contain six coordinate bonds.
- For metal ions having configurations d^0, d^1, d^2, or d^3, there will always be two of the d orbitals empty to form a set of d^2sp^3 hybrids.
- For example $[Cr(H_2O)_6]^{3+}$

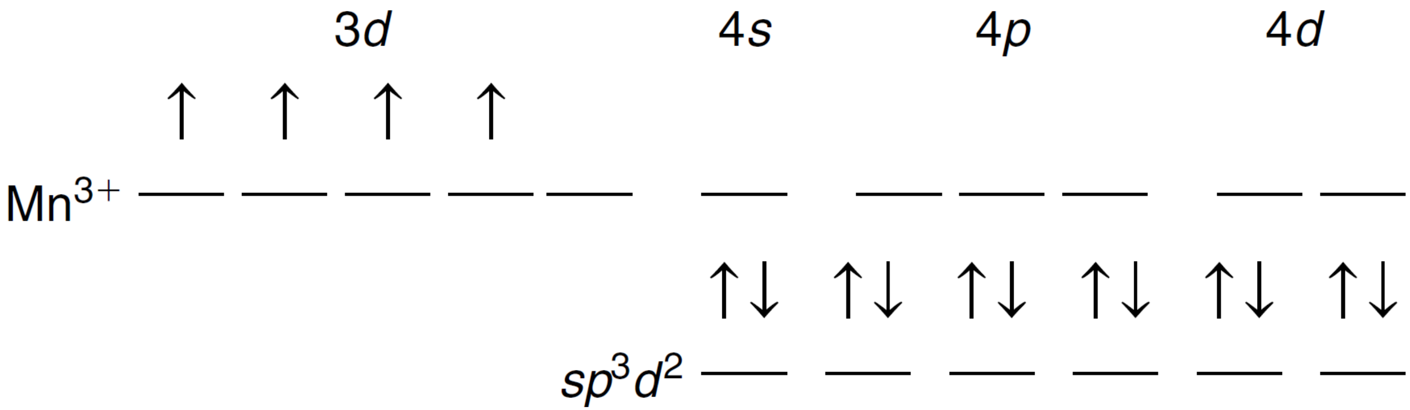




Valence Bond Theory (VBT)

When the number of electrons in the d orbitals is four, as in the case of Mn^{3+} , there exists more than one possible type of hybrid orbital.

Possibility 1. the electrons remain unpaired in the d orbitals. For e.g.: $[Mn(H_2O)_6]^{2+}$

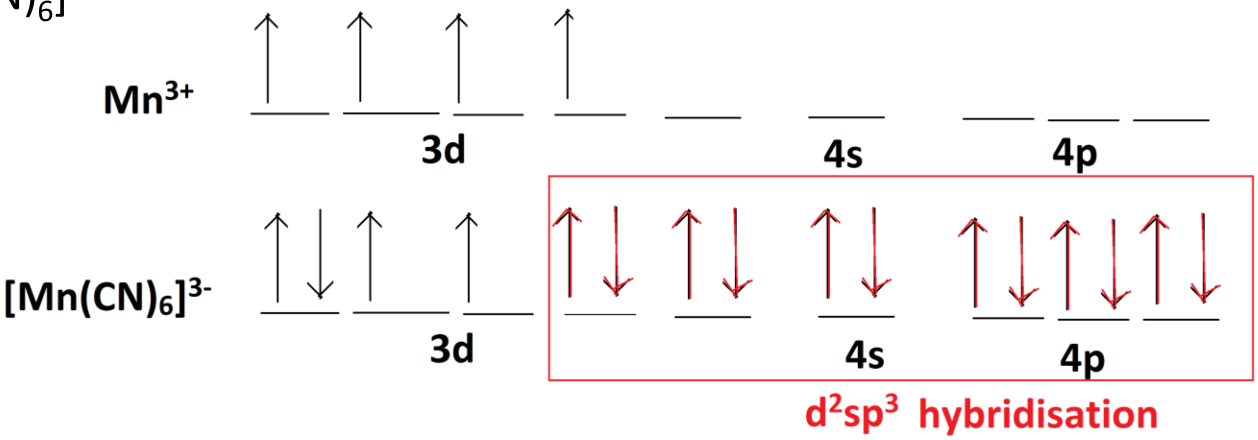


In this case, the 4*d* orbitals used to form hybrids are those outside the usual valence shell that consists of 3*d*, 4*s*, and 4*p* orbitals. Consequently, such a complex is often referred to as an ***outer orbital complex***. To identify the hybrid orbitals, the symbol sp^3d^2 is used. The complex is also referred as ***high-spin complex*** as its magnetic moment is same as that of the ***free ion***.

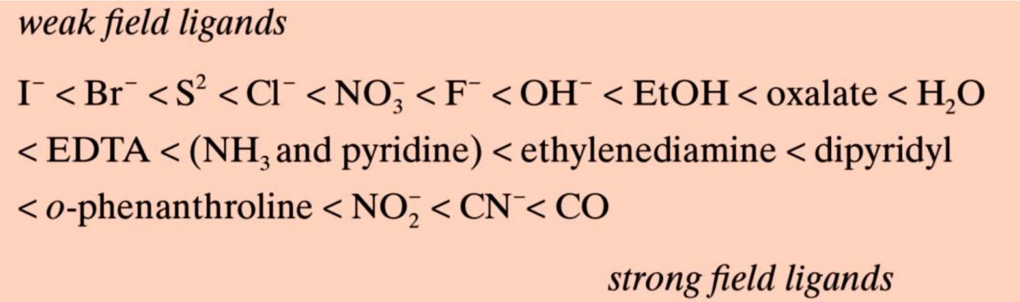
Valence Bond Theory (VBT)

Possibility 2. the electrons gets paired in the d orbitals due to strong field ligands.

For e.g.: $[Mn(CN)_6]^{3-}$



In this case, the *d* orbitals used to form hybrids are those inside the usual valence shell that consists of 3*d*, 4*s*, and 4*p* orbitals. Consequently, such a complex is often referred to as an ***inner orbital complex***. To identify the hybrid orbitals, the symbol d^2sp^3 is used. The complex is also referred as ***low-spin complex*** as its magnetic moment is lowered than that of the ***free ion***.



weak field ligands

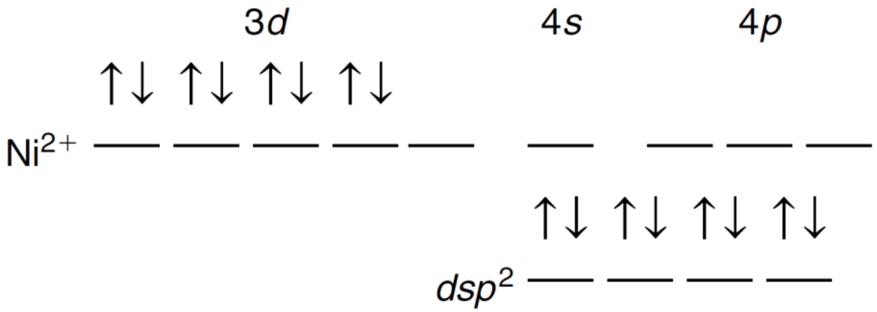
$I^- < Br^- < S^{2} < Cl^- < NO_3^- < F^- < OH^- <$ EtOH < oxalate $< H_2O$
< EDTA < (NH_3 and pyridine) < ethylenediamine < dipyridyl
< *o*-phenanthroline $< NO_2^- < CN^- <$ CO

strong field ligands

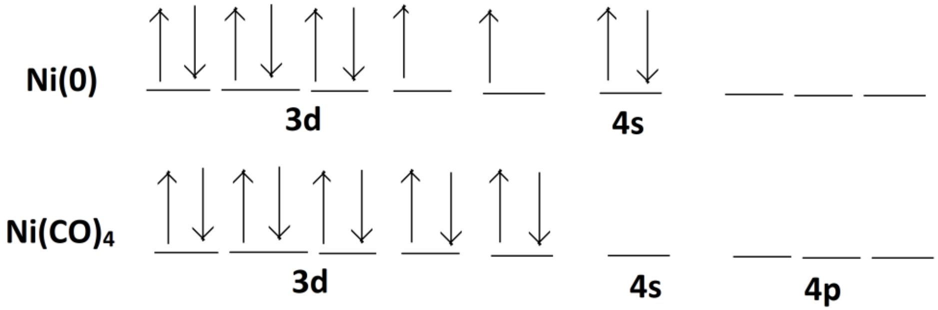
Valence Bond Theory (VBT)

Special examples of Ni^{2+} and Cu^{2+} complex having a coordination number of 4

Example 1. $[Ni(CN)_4]^{2-}$

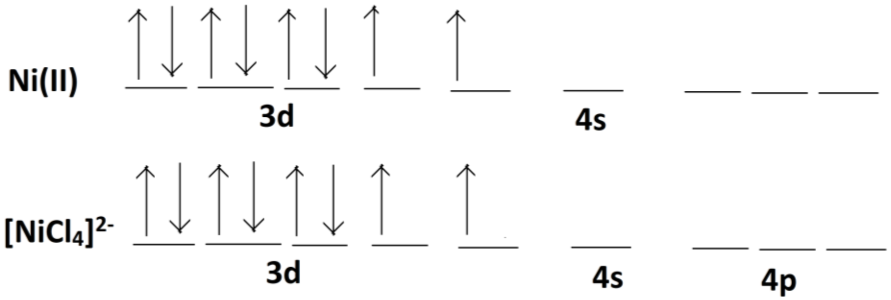


Example 2. $[Ni(CO)_4]$



sp^3 hybridisation

Example 3. $[NiCl_4]^{2-}$

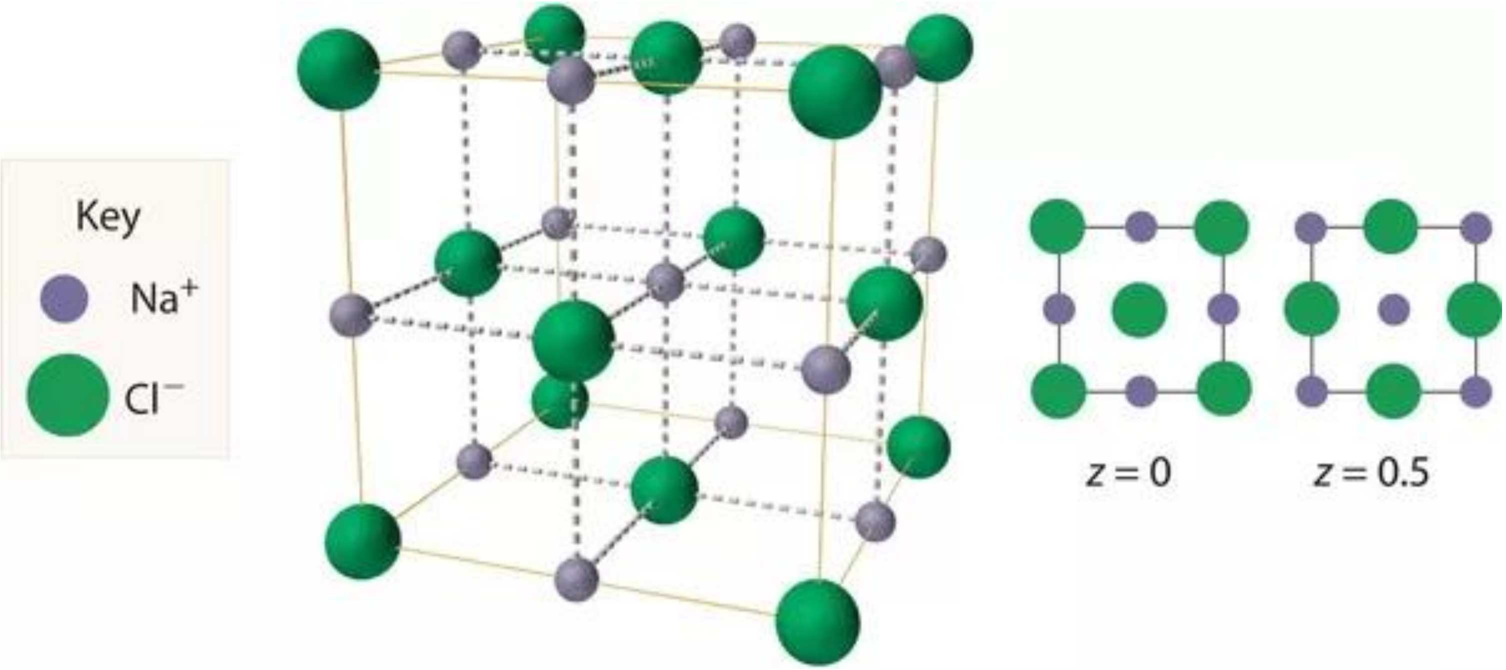


sp^3 hybridisation

Limitations of VBT

- The nature of ligand (weak or strong field) could not be explained.
- The pairing of electrons in the presence of strong field ligands could not be explained.
- It could not explain the temperature dependance of magnetic moment. Also, it could not explain why some complexes show greater magnetic moment than the calculated.
- It could not explain the distorted structures of some octahedral complexes .
- Color and electronic spectra of complexes could not be explained.
- Rection rates and mechanisms of complexes could not be explained.
- It could not explain the square planar geometry of some Cu(II) complexes satisfactorily.

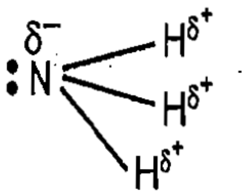
Crystal Field Theory (CFT)



Crystal Field Theory (CFT)

- This theory is based upon the following assumptions:

1. All ligands are considered as point charges or point dipoles. Ionic ligands (OH^-, Cl^-, etc.) are considered as point charges while neutral ligands (NH_3, H_2O, etc.) are considered as point dipoles. The negative end of the dipoles interacts with the metal center.



(Ammonia molecule)

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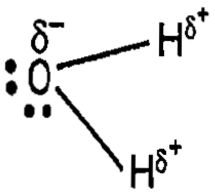


(Water molecule)

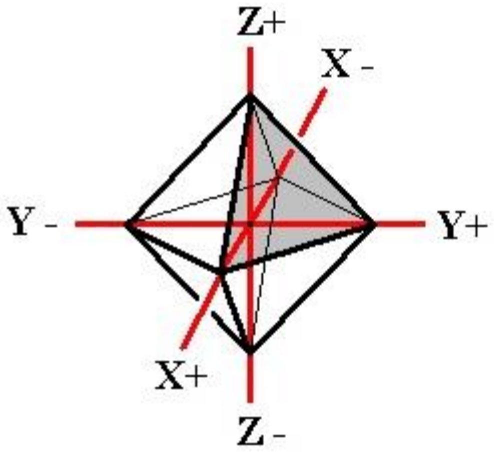
2. The metal-ligand interactions are considered to be purely electrostatic and there is no overlapping of orbitals. The electrostatic interactions are both attractive and repulsive of nature.

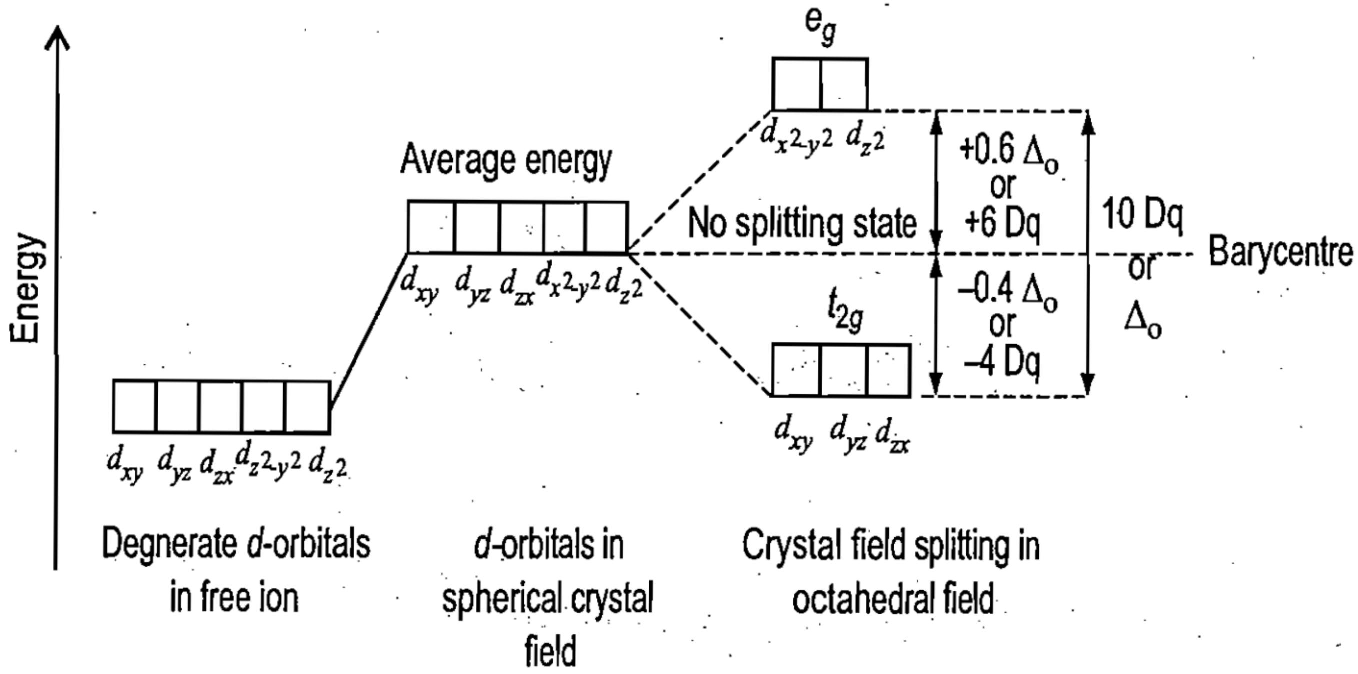
3. Although the d-orbitals are degenerate, in the electrostatic potential created by the ligands (crystal field), this degeneracy gets removed. Now, the orbitals that faces the ligands are raised to higher energies due to electronic repulsion between the metal and ligand electrons.

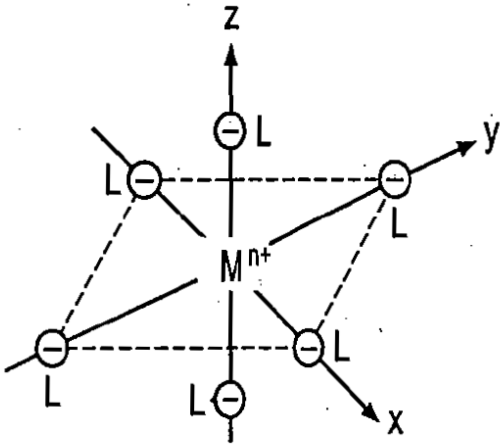
Crystal Field Theory (CFT)

Octahedral Complexes

In an octahedral complex, the *d* orbitals that have lobes lying along the axes are the d_{z^2} and the $d_{x^2-y^2}$. The d_{xy}, d_{yz}, and d_{xz} orbitals directed in between the axes.







Crystal Field Theory (CFT)

Octahedral Complexes

The energy difference between the actual distribution of electrons and that for the hypothetical configuration with all electrons in the uniform (or spherical) field level is called the **crystal field stabilization energy** (**CFSE**) .

For the electronic configuration $t_{2g}^{x}e_{g}^{y}$, the CFSE can be calculated as

$$\boxed{\text{CFSE} = -0.4x + 0.6y}$$

For d^1 complex, electronic configuration is $t_{2g}^{1}\ e_{g}^{0}$.

$$\text{CFSE} = -0.4 \times 1\,\Delta_o = -0.4\,\Delta_o$$

For d^2 complex, electronic configuration is $t_{2g}^{2}\ e_{g}^{0}$.

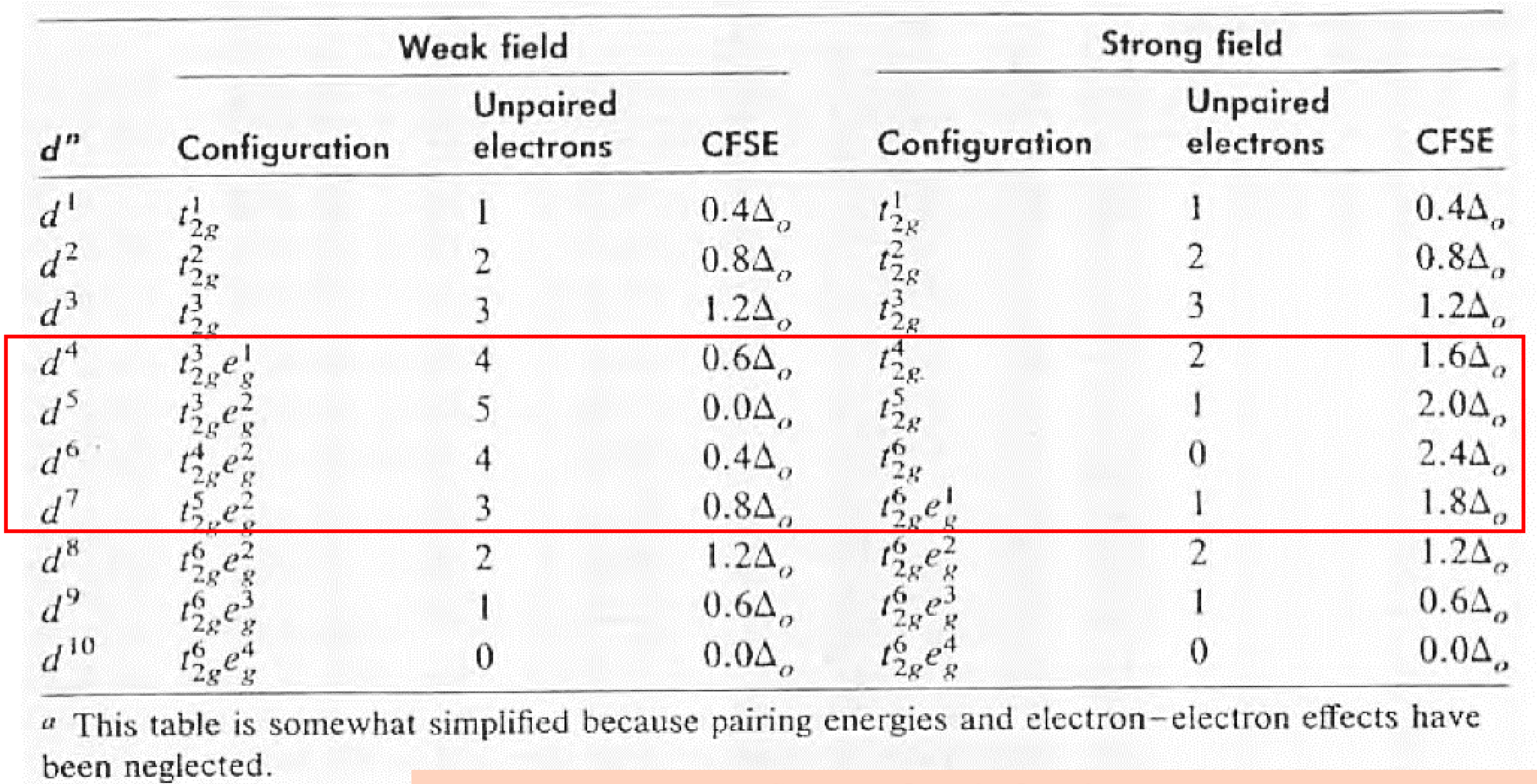
$$\text{CFSE} = -0.4 \times 2\,\Delta_o = -0.8\,\Delta_o$$

For d^3 complex, electronic configuration is $t_{2g}^{3}\ e_{g}^{0}$.

$$\text{CFSE} = -0.4 \times 3\,\Delta_o = -1.2\,\Delta_o$$

Crystal Field Theory (CFT)

Distribution of d-electrons in octahedral CF



	Weak field			Strong field		
d^n	Configuration	Unpaired electrons	CFSE	Configuration	Unpaired electrons	CFSE
d^1	t_{2g}^1	1	$0.4\Delta_o$	t_{2g}^1	1	$0.4\Delta_o$
d^2	t_{2g}^2	2	$0.8\Delta_o$	t_{2g}^2	2	$0.8\Delta_o$
d^3	t_{2g}^3	3	$1.2\Delta_o$	t_{2g}^3	3	$1.2\Delta_o$
d^4	$t_{2g}^3e_g^1$	4	$0.6\Delta_o$	t_{2g}^4	2	$1.6\Delta_o$
d^5	$t_{2g}^3e_g^2$	5	$0.0\Delta_o$	t_{2g}^5	1	$2.0\Delta_o$
d^6	$t_{2g}^4e_g^2$	4	$0.4\Delta_o$	t_{2g}^6	0	$2.4\Delta_o$
d^7	$t_{2g}^5e_g^2$	3	$0.8\Delta_o$	$t_{2g}^6e_g^1$	1	$1.8\Delta_o$
d^8	$t_{2g}^6e_g^2$	2	$1.2\Delta_o$	$t_{2g}^6e_g^2$	2	$1.2\Delta_o$
d^9	$t_{2g}^6e_g^3$	1	$0.6\Delta_o$	$t_{2g}^6e_g^3$	1	$0.6\Delta_o$
d^{10}	$t_{2g}^6e_g^4$	0	$0.0\Delta_o$	$t_{2g}^6e_g^4$	0	$0.0\Delta_o$

[a] This table is somewhat simplified because pairing energies and electron–electron effects have been neglected.

Spectrochemical series

weak field ligands

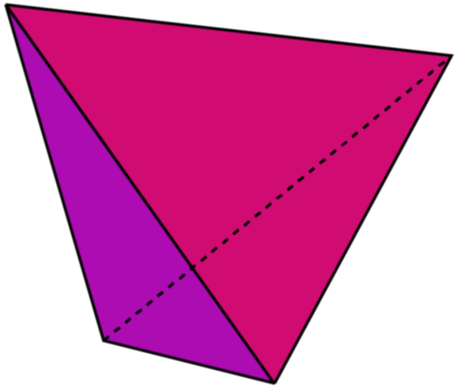
$I^- < Br^- < S^{2} < Cl^- < NO_3^- < F^- < OH^- < EtOH <$ oxalate $< H_2O$
$<$ EDTA $< (NH_3$ and pyridine$) <$ ethylenediamine $<$ dipyridyl
$<$ *o*-phenanthroline $< NO_2^- < CN^- < CO$

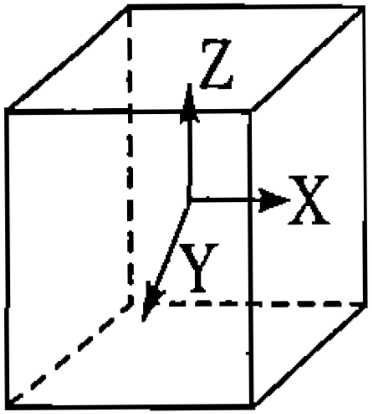
strong field ligands

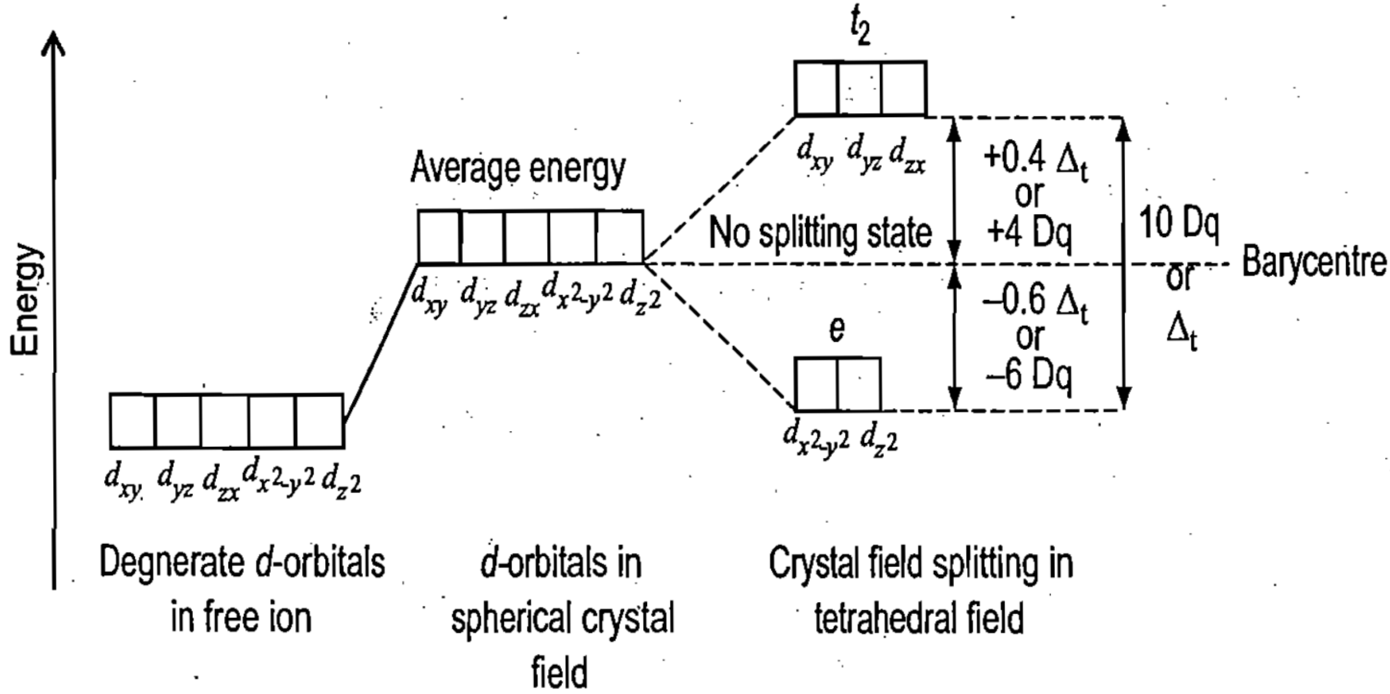
Crystal Field Theory (CFT)

Tetrahedral Complexes

In tetrahedral complex, none of the d orbitals points directly towards the ligands. However, the d_{xy}, d_{yz}, and d_{xz} orbitals are much closer to the ligands and experience relatively larger repulsion than that of the d_{z^2} and the $d_{x^2-y^2}$ orbitals.

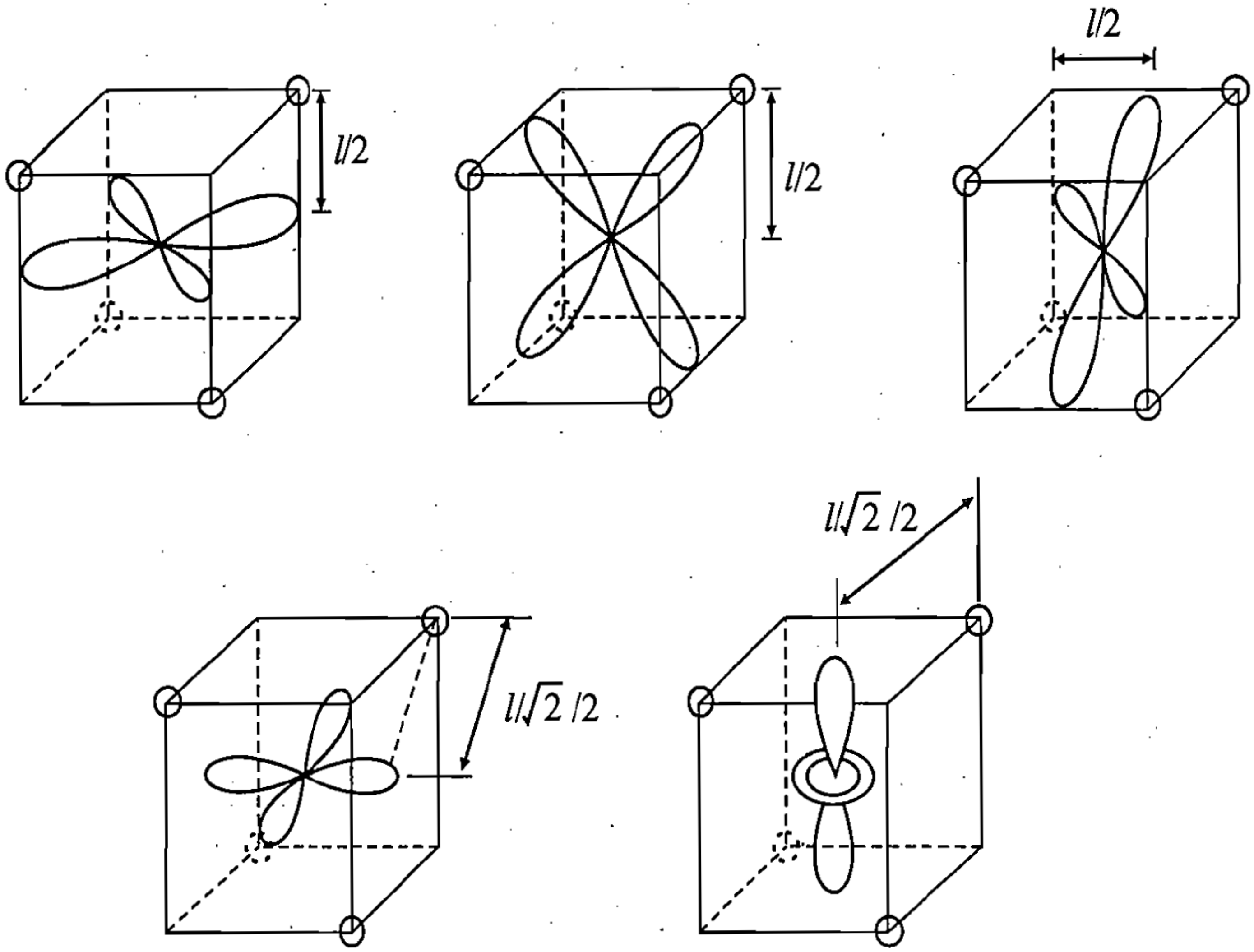






Crystal Field Theory (CFT)

Tetrahedral Complexes



Crystal Field Theory (CFT)

Octahedral vs Tetrahedral CF

- Tetrahedral complexes do not have inversion symmetry, so the *g* and *u* subscripts are not used.
- The CFSE of tetrahedral complexes are smaller compared to octahedral complexes. ***For the same metal, ligand and metal-ligand distances***

$$\boxed{\Delta_t = \frac{4}{9}\Delta_o}$$

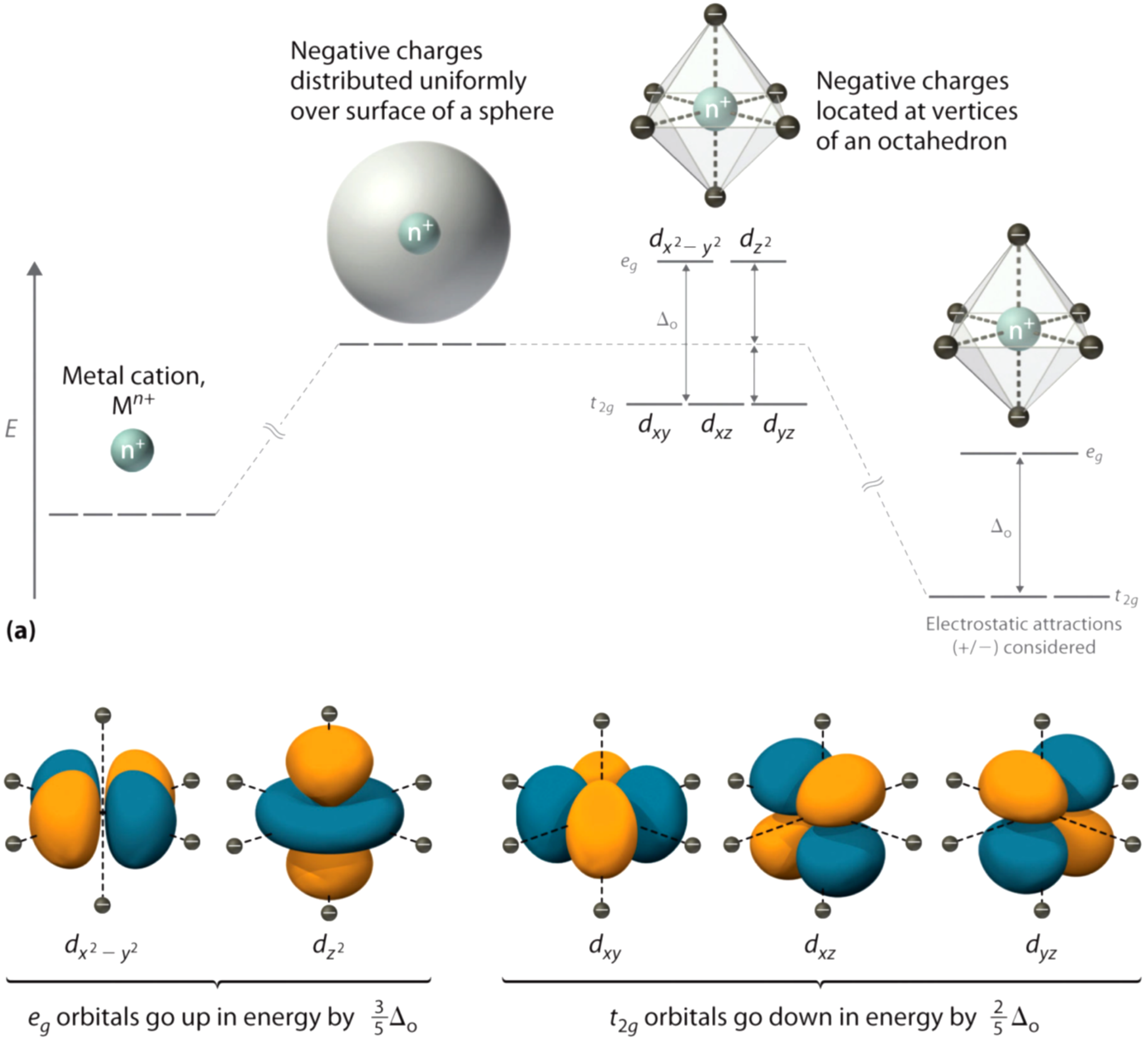
(In both, d_{xy}, d_{yz}, and d_{xz} orbitals lie at 45 degrees so repel equally. In octahedral CF, the d_{z^2} and the $d_{x^2-y^2}$ orbitals points directly while in tetrahedral CF it is equal to 0.71*l (ca. 2/3)*

- Since, CFSE of tetrahedral complexes is smaller than the octahedral complexes, they always forms high spin complexes.

Octahedral Complexes

Crystal Field Theory (CFT)

Summary



Crystal Field Theory (CFT)

Factors affecting the magnitude of Δ

1. *Oxidation state of the metal ion*: Magnitude of Δ increases with increasing the charge on the metal ion. For e.g.:

$$\Delta_o \text{ for } [\mathrm{Co(H_2O)_6}]^{2+} = 9200\ \mathrm{cm^{-1}}$$

$$\Delta_o \text{ for } [\mathrm{Co(H_2O)_6}]^{3+} = 20760\ \mathrm{cm^{-1}}$$

(*Higher the oxidation state of the metal ion, larger will be the metal ligand interaction and therefore, higher splitting of the d orbitals***)**

2. *Nature of the metal ion:* Δ for analogous c*complexes in a group increases as 3d<4d<5d. For e.g. the value of* Δo increases by 50% in the 4d series while it increase to 25% in the 5d series.

$$\text{For } [\mathrm{Co(NH_3)_6}]^{3+}, \quad \Delta_o = 23000\ \mathrm{cm^{-1}}$$

$$\text{For } [\mathrm{Rh(NH_3)_6}]^{3+}, \quad \Delta_o = 34100\ \mathrm{cm^{-1}}$$

$$\text{For } [\mathrm{Ir(NH_3)_6}]^{3+}, \quad \Delta_o = 41200\ \mathrm{cm^{-1}}$$

(*The 4d and 5d orbitals are diffused in nature so the ligands can experience these orbitals closely, therefore it increase with increasing the group number***)**

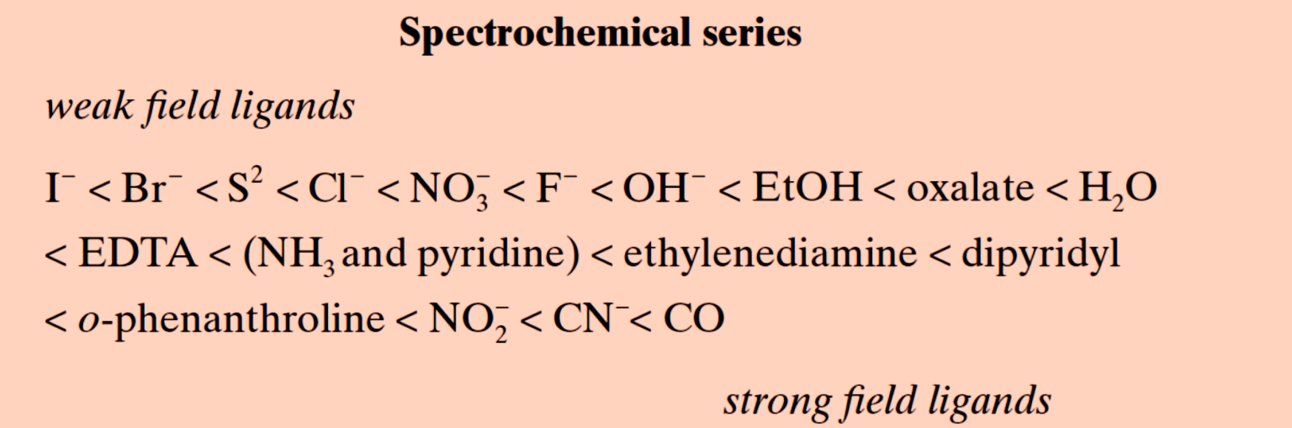
Crystal Field Theory (CFT)

Factors affecting the magnitude of Δ

3. *Number and geometry of ligands*: The magnitude of Δ increases with increasing the no. of ligands. For e.g.: the point charge model predicts 50% higher CFSE for the octahedral complexes compared to the tetrahedral complexes i.e. $\Delta_o > \Delta_t$

(**Note: although square planar complexes has a smaller number of ligands compared to octahedral complexes, the CFSE of square planar CF is higher than that of octahedral CF. The relationship is $\Delta_{sp} = 1.3\ \Delta_o$**)

4. *Nature of the ligands:* Ligands that causes large CF splitting are called **strong field ligands** while the ligand that causes small CF splitting are called **weak field ligands**. It is given by the **spectrochemical series**.



Spectrochemical series

weak field ligands

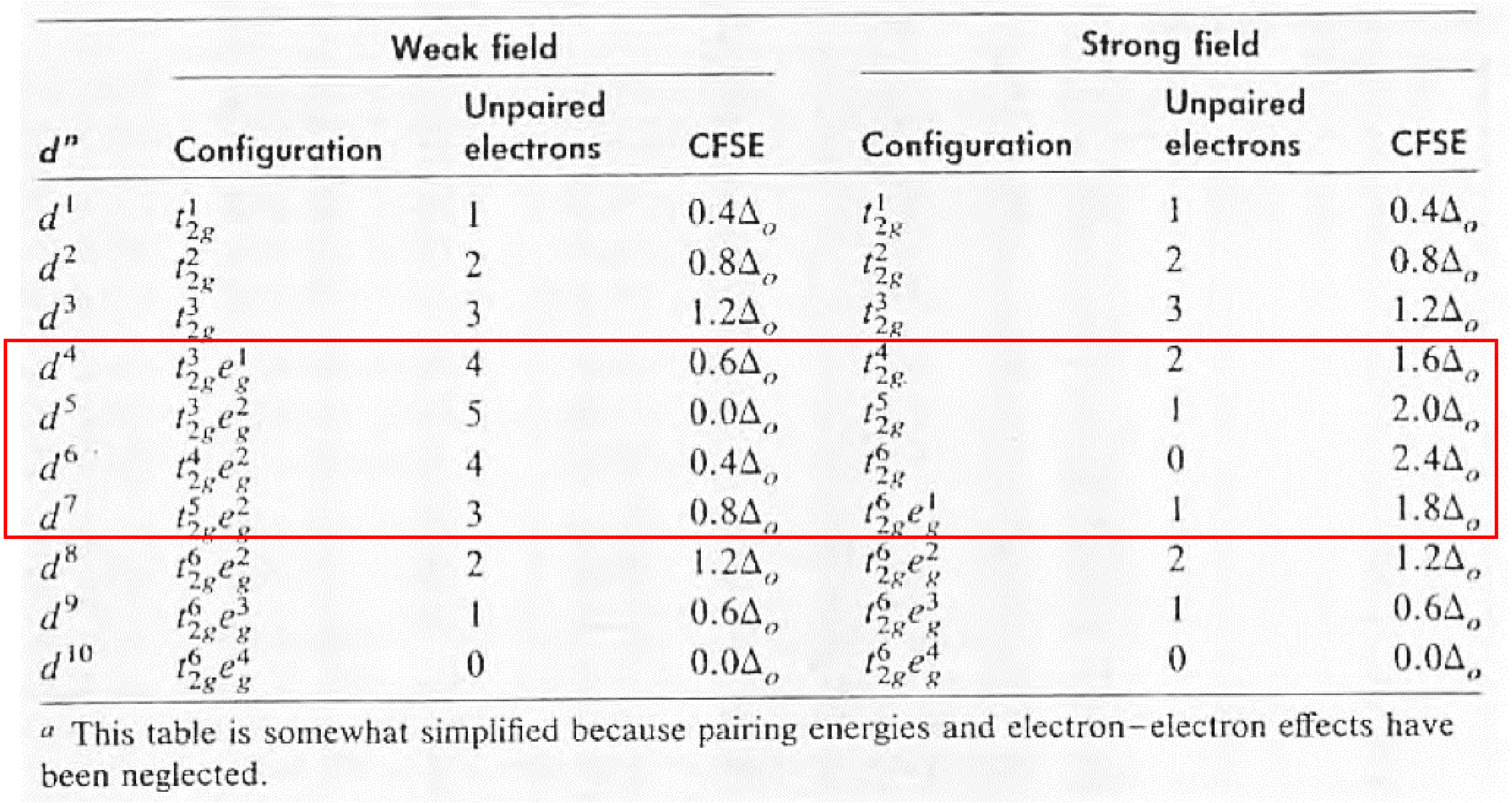
$I^- < Br^- < S^2 < Cl^- < NO_3^- < F^- < OH^- < EtOH < oxalate < H_2O$
$< EDTA < (NH_3 \text{ and pyridine}) < ethylenediamine < dipyridyl$
$< \textit{o}\text{-phenanthroline} < NO_2^- < CN^- < CO$

strong field ligands

halide donors < O donors < N donors < C donors

Crystal Field Theory (CFT)

Distribution of d-electrons in octahedral CF



	Weak field			Strong field		
d^n	Configuration	Unpaired electrons	CFSE	Configuration	Unpaired electrons	CFSE
d^1	t_{2g}^1	1	$0.4\Delta_o$	t_{2g}^1	1	$0.4\Delta_o$
d^2	t_{2g}^2	2	$0.8\Delta_o$	t_{2g}^2	2	$0.8\Delta_o$
d^3	t_{2g}^3	3	$1.2\Delta_o$	t_{2g}^3	3	$1.2\Delta_o$
d^4	$t_{2g}^3e_g^1$	4	$0.6\Delta_o$	t_{2g}^4	2	$1.6\Delta_o$
d^5	$t_{2g}^3e_g^2$	5	$0.0\Delta_o$	t_{2g}^5	1	$2.0\Delta_o$
d^6	$t_{2g}^4e_g^2$	4	$0.4\Delta_o$	t_{2g}^6	0	$2.4\Delta_o$
d^7	$t_{2g}^5e_g^2$	3	$0.8\Delta_o$	$t_{2g}^6e_g^1$	1	$1.8\Delta_o$
d^8	$t_{2g}^6e_g^2$	2	$1.2\Delta_o$	$t_{2g}^6e_g^2$	2	$1.2\Delta_o$
d^9	$t_{2g}^6e_g^3$	1	$0.6\Delta_o$	$t_{2g}^6e_g^3$	1	$0.6\Delta_o$
d^{10}	$t_{2g}^6e_g^4$	0	$0.0\Delta_o$	$t_{2g}^6e_g^4$	0	$0.0\Delta_o$

[a] This table is somewhat simplified because pairing energies and electron–electron effects have been neglected.

Crystal Field Theory (CFT)

Magnetic properties

When there are unpaired electrons, a compound behaves as paramagnets and attracted by a magnetic field. The measure of this magnetism is **magnetic susceptibility** (χ) which is related to the **magnetic moment** (μ) as

$$\boxed{\mu = 2.828(\chi T)^{\frac{1}{2}}}$$

where χ = magnetic susceptibility ($\mathrm{cm^3/mol}$)
T = temperature (Kelvin)
The unit of magnetic moment is the Bohr magneton, μ_B
$1\ \mu_B = 9.27 \times 10^{-24}\ \mathrm{J\,T^{-1}}$ (joules/tesla)

For most complexes of the first transition series, the spin only moment is sufficient as the orbital contribution is negligible. The spin only magnetic moment (μ_S) is given by-

$$\mu_S = g\sqrt{S(S+1)} \quad \textbf{or} \quad \mu_S = \sqrt{n(n+2)}$$

Question: Show that both the above stated equations are equivalent. Consider S = n/2 and the gyromagnetic ration (g) = 2, where n is the no. of unpaired electron.

Crystal Field Theory (CFT)

High-spin and Low-spin Complexes

1. *High-spin (spin free) complexes*: In **weak field** octahedral complexes of 3d metal ions, the magnitude of **Δo is small**. Thus, these complexes have maximum no. of unpaired electrons and are called **high-spin** complexes. High-spin 3d-metal complexes have the same no. of unpaired electron as in the 3d orbital of free metal ion.

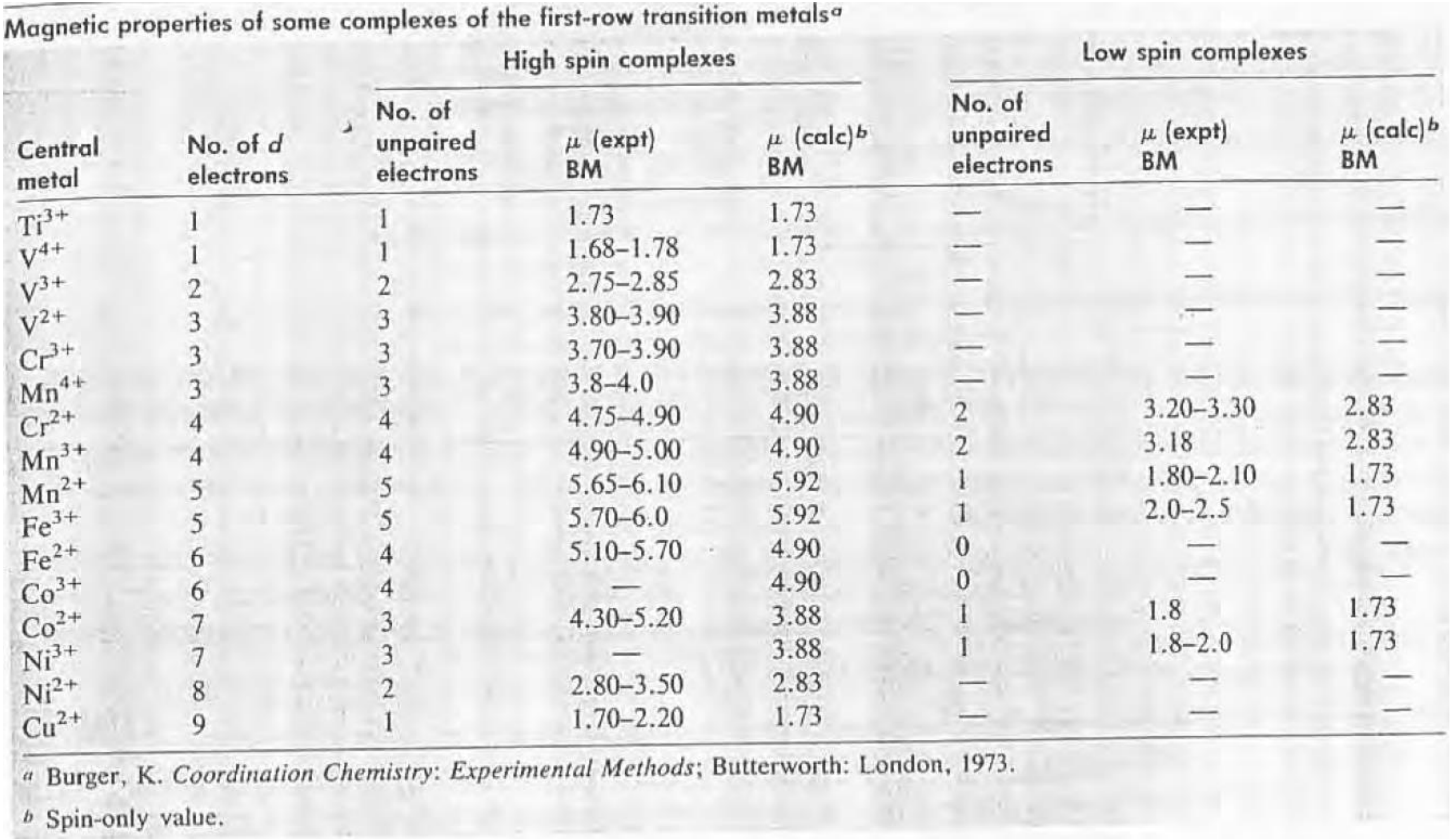
2. Low-spin (spin paired) complexes: In **strong field** octahedral complexes of 3d metal ions, the magnitude of **Δo is large**. Thus, electrons will be paired in the t_{2g} orbital first before occupying the higher energy e_g orbitals. Thus, these complexes have minimum no. of unpaired electrons and are called **low-spin** complexes.

Note:

1. 3d metals with oxidation state ≥ 4, 4d and 5d complexes even in the presence of weak field ligands tend to form low-spin complexes. E.g.: $[NiF_6]^{2-}$
2. Co^{3+} forms low spin complexes with H_2O and O^{2-} ligands although they are weak field ligands.

Crystal Field Theory (CFT)

High-spin and Low-spin Complexes



Magnetic properties of some complexes of the first-row transition metals[a]

		High spin complexes			Low spin complexes		
Central metal	No. of *d* electrons	No. of unpaired electrons	μ (expt) BM	μ (calc)[b] BM	No. of unpaired electrons	μ (expt) BM	μ (calc)[b] BM
Ti^{3+}	1	1	1.73	1.73	—	—	—
V^{4+}	1	1	1.68–1.78	1.73	—	—	—
V^{3+}	2	2	2.75–2.85	2.83	—	—	—
V^{2+}	3	3	3.80–3.90	3.88	—	—	—
Cr^{3+}	3	3	3.70–3.90	3.88	—	—	—
Mn^{4+}	3	3	3.8–4.0	3.88	—	—	—
Cr^{2+}	4	4	4.75–4.90	4.90	2	3.20–3.30	2.83
Mn^{3+}	4	4	4.90–5.00	4.90	2	3.18	2.83
Mn^{2+}	5	5	5.65–6.10	5.92	1	1.80–2.10	1.73
Fe^{3+}	5	5	5.70–6.0	5.92	1	2.0–2.5	1.73
Fe^{2+}	6	4	5.10–5.70	4.90	0	—	—
Co^{3+}	6	4	—	4.90	0	—	—
Co^{2+}	7	3	4.30–5.20	3.88	1	1.8	1.73
Ni^{3+}	7	3	—	3.88	1	1.8–2.0	1.73
Ni^{2+}	8	2	2.80–3.50	2.83	—	—	—
Cu^{2+}	9	1	1.70–2.20	1.73	—	—	—

[a] Burger, K. *Coordination Chemistry: Experimental Methods*; Butterworth: London, 1973.

[b] Spin-only value.

Crystal Field Theory (CFT)

Pairing Energy

- The energy required to force two unpaired electrons to pair in an orbital is called the pairing energy (P).

If $\Delta_o > P$, it favours the low spin complexes,
If $\Delta_o < P$, it favours the high spin complexes,
If $\Delta_o = P$, high spin and low spin complexes equally exist.
In general, for 4*d*- and 5*d*- series transition metal complexes, magnitude of Δ_o is greater than that of P.

- For tetrahedral complexes, Δ_t < P therefore, tetrahedral complexes are always high-spin irrespective of the strength of ligand field.
- Occupation of electrons in the tetrahedral crystal field follows the Hund's rule.

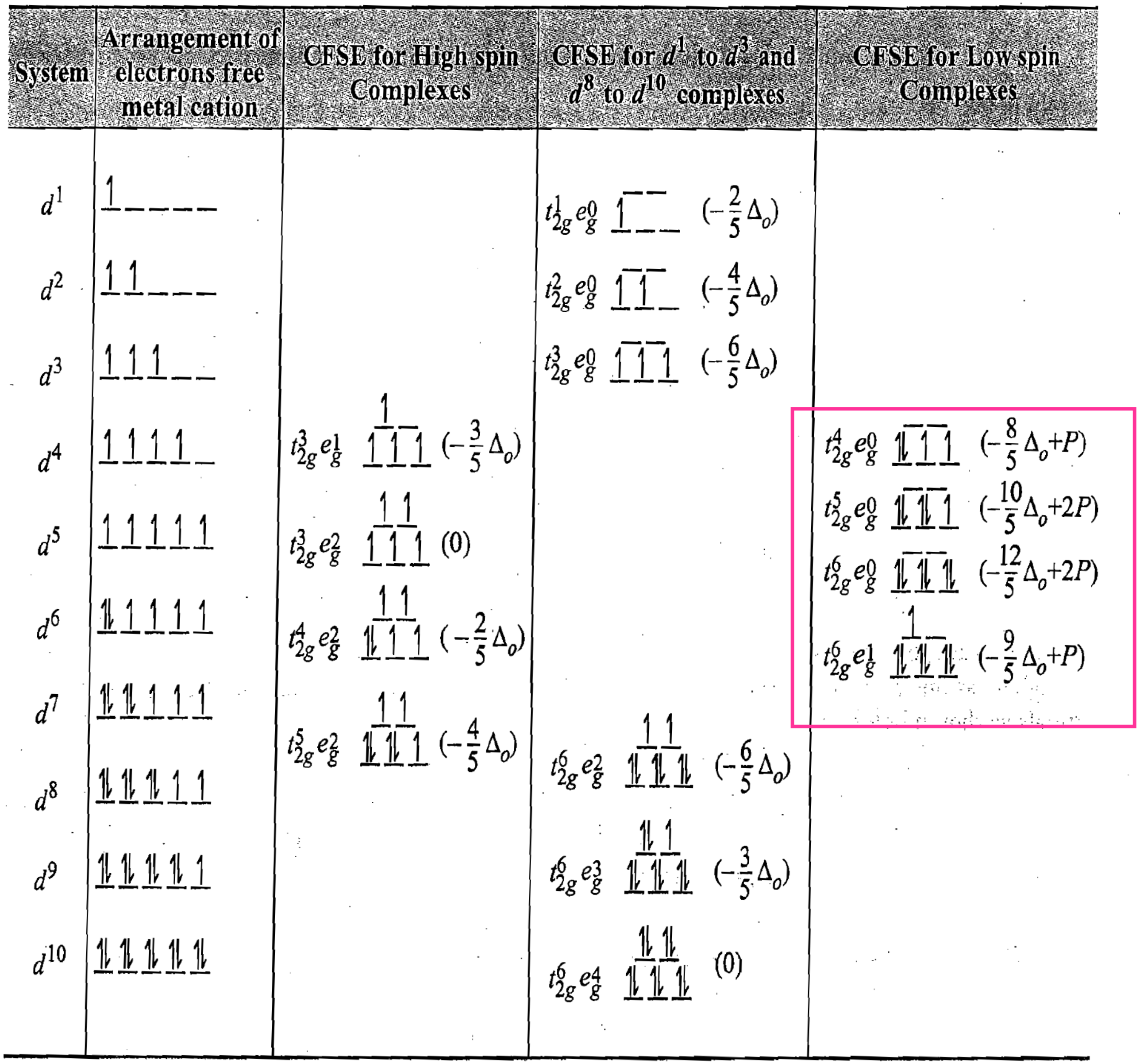
For d^n low spin octahedral complexes with electronic configuration $t_{2g}^p \; e_g^q$

$$\boxed{\text{CFSE} = [-0.4\,p + 0.6\,q]\,\Delta_o + mp}$$

Where p and q are the number of electrons in t_{2g} and e_g orbitals respectively.
m = Number of pairs of electrons caused by the ligands.

Crystal Field Theory (CFT)

CFSE with Pairing Energy

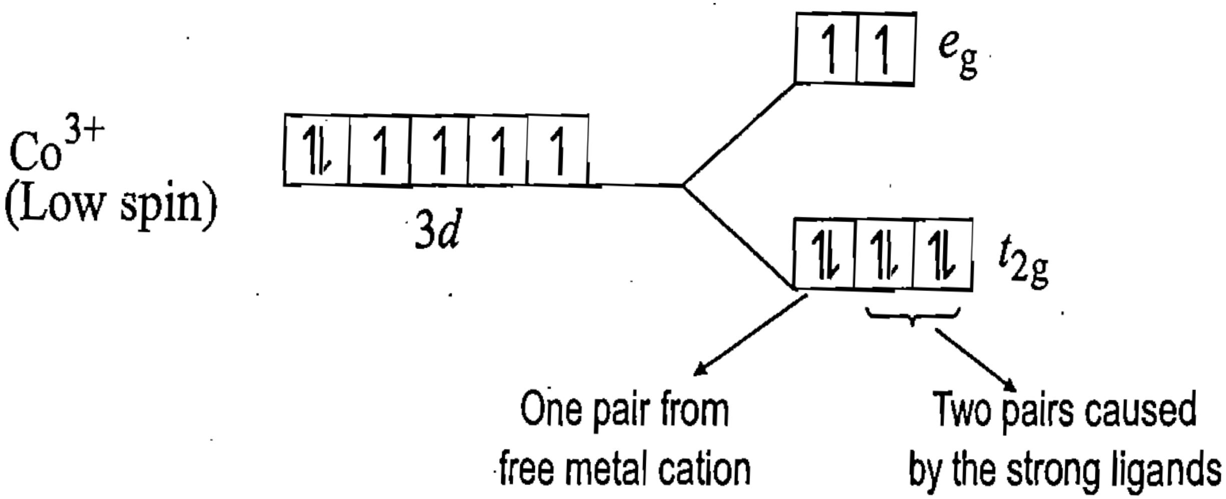


System	Arrangement of electrons free metal cation	CFSE for High spin Complexes	CFSE for d^1 to d^3 and d^8 to d^{10} complexes	CFSE for Low spin Complexes
d^1	↑ _ _ _ _		$t_{2g}^{1}e_{g}^{0}$ _ _ / ↑ _ _ $(-\frac{2}{5}\Delta_o)$	
d^2	↑ ↑ _ _ _		$t_{2g}^{2}e_{g}^{0}$ _ _ / ↑ ↑ _ $(-\frac{4}{5}\Delta_o)$	
d^3	↑ ↑ ↑ _ _		$t_{2g}^{3}e_{g}^{0}$ _ _ / ↑ ↑ ↑ $(-\frac{6}{5}\Delta_o)$	
d^4	↑ ↑ ↑ ↑ _	$t_{2g}^{3}e_{g}^{1}$ ↑ _ / ↑ ↑ ↑ $(-\frac{3}{5}\Delta_o)$		$t_{2g}^{4}e_{g}^{0}$ _ _ / ↑↓ ↑ ↑ $(-\frac{8}{5}\Delta_o+P)$
d^5	↑ ↑ ↑ ↑ ↑	$t_{2g}^{3}e_{g}^{2}$ ↑ ↑ / ↑ ↑ ↑ (0)		$t_{2g}^{5}e_{g}^{0}$ _ _ / ↑↓ ↑↓ ↑ $(-\frac{10}{5}\Delta_o+2P)$
d^6	↑↓ ↑ ↑ ↑ ↑	$t_{2g}^{4}e_{g}^{2}$ ↑ ↑ / ↑↓ ↑ ↑ $(-\frac{2}{5}\Delta_o)$		$t_{2g}^{6}e_{g}^{0}$ _ _ / ↑↓ ↑↓ ↑↓ $(-\frac{12}{5}\Delta_o+2P)$
d^7	↑↓ ↑↓ ↑ ↑ ↑	$t_{2g}^{5}e_{g}^{2}$ ↑ ↑ / ↑↓ ↑↓ ↑ $(-\frac{4}{5}\Delta_o)$		$t_{2g}^{6}e_{g}^{1}$ ↑ _ / ↑↓ ↑↓ ↑↓ $(-\frac{9}{5}\Delta_o+P)$
d^8	↑↓ ↑↓ ↑↓ ↑ ↑		$t_{2g}^{6}e_{g}^{2}$ ↑ ↑ / ↑↓ ↑↓ ↑↓ $(-\frac{6}{5}\Delta_o)$	
d^9	↑↓ ↑↓ ↑↓ ↑↓ ↑		$t_{2g}^{6}e_{g}^{3}$ ↑↓ ↑ / ↑↓ ↑↓ ↑↓ $(-\frac{3}{5}\Delta_o)$	
d^{10}	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		$t_{2g}^{6}e_{g}^{4}$ ↑↓ ↑↓ / ↑↓ ↑↓ ↑↓ (0)	

Crystal Field Theory (CFT)

Example

Let us consider the example of a d^6-low spin complex in octahedral CF. The d-electronic configuration is $t_{2g}^6 e_g^0$



$$\mathrm{CFSE} = [-0.4 \times 6 + 0.6 \times 0]\,\Delta_o + 2P$$
$$= -2.4\,\Delta_o + 2P$$

Limitations of CFT

- CFT considers the contribution of ***d***-orbitals only, the ***s***- and ***p***-orbitals are completely ignored.
- The theory do not consider covalent character in M-L bonding.
- CFT considers only σ-bonding characteristics of ligands, the π-bonding is completely ignored.
- CFT could not explain the relative strength of ligands given in the spectrochemical series.
- The CFT is based on purely electrostatic interactions, however, there are numerous stable coordination compounds with metal in the zero-oxidation state and neutral ligands. For e.g.: metal carbonyls.

Jahn-Teller Theorem

- ☐ The theorem states that for a non-linear molecule in electronically degenerate state which are unsymmetrically filled undergoes distortion to lower the symmetry, remove the degeneracy and lower the energy.
- ☐ In octahedral complexes, distortion occurred in such a way that two trans ligands (say along the z-axis) are moved either towards the metal (***z-in***) or away from the metal center (***z-out***).
- ☐ The resulting complex is thus said to be ***tetragonally distorted***.

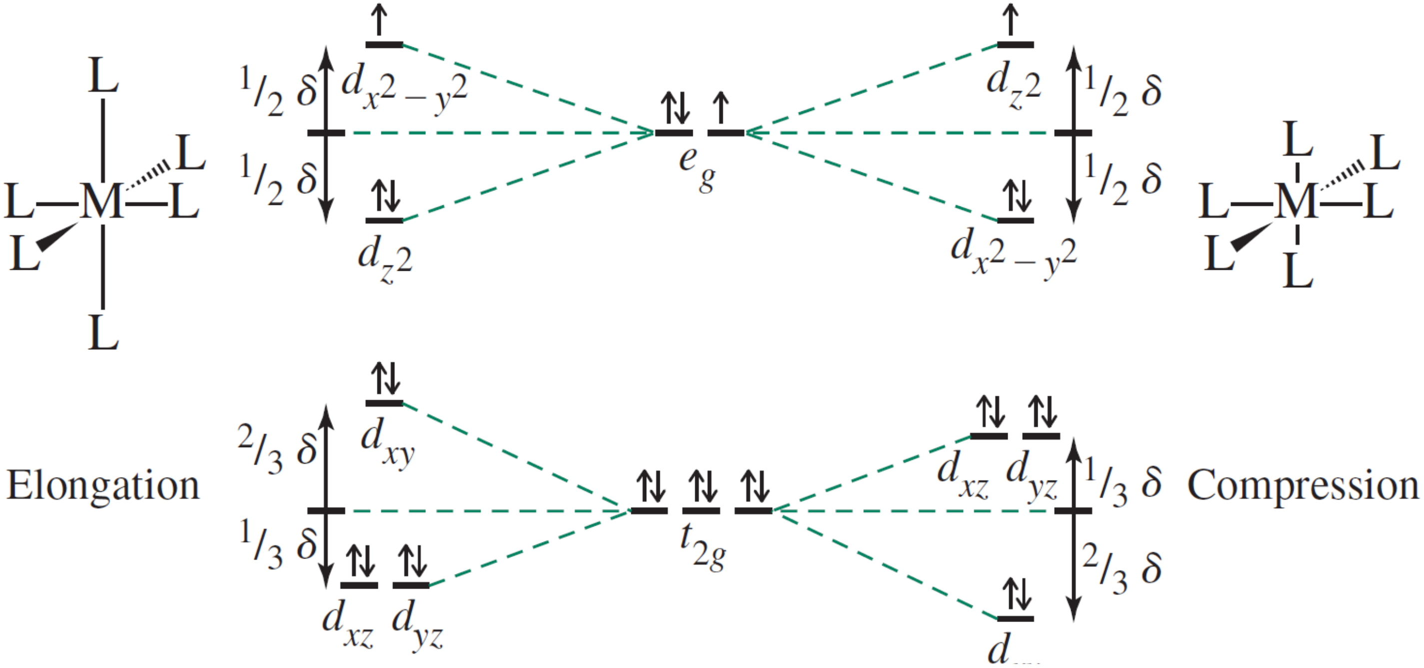


Fig: JT effect in an octahedral Cu(II) complex

Jahn-Teller Theorem

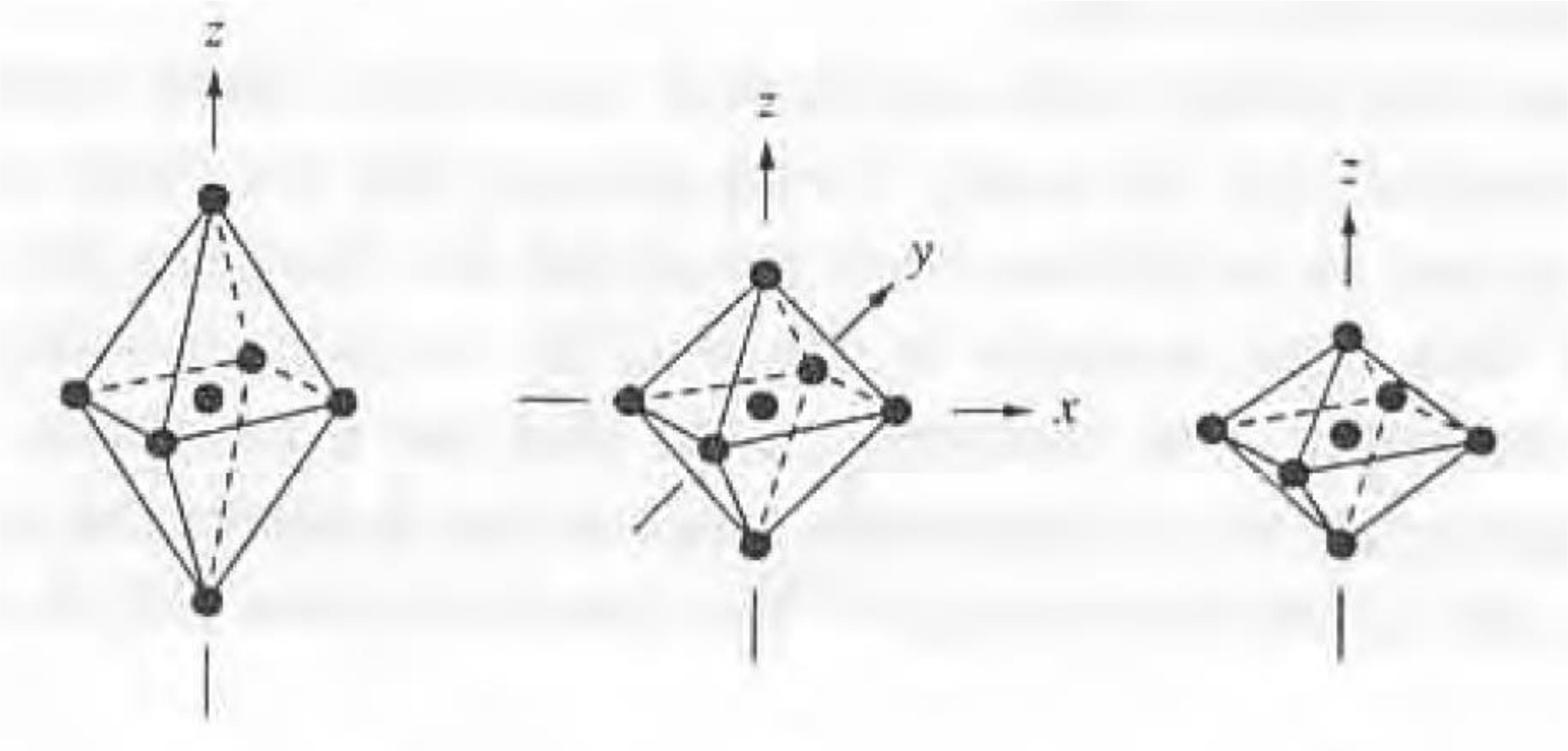
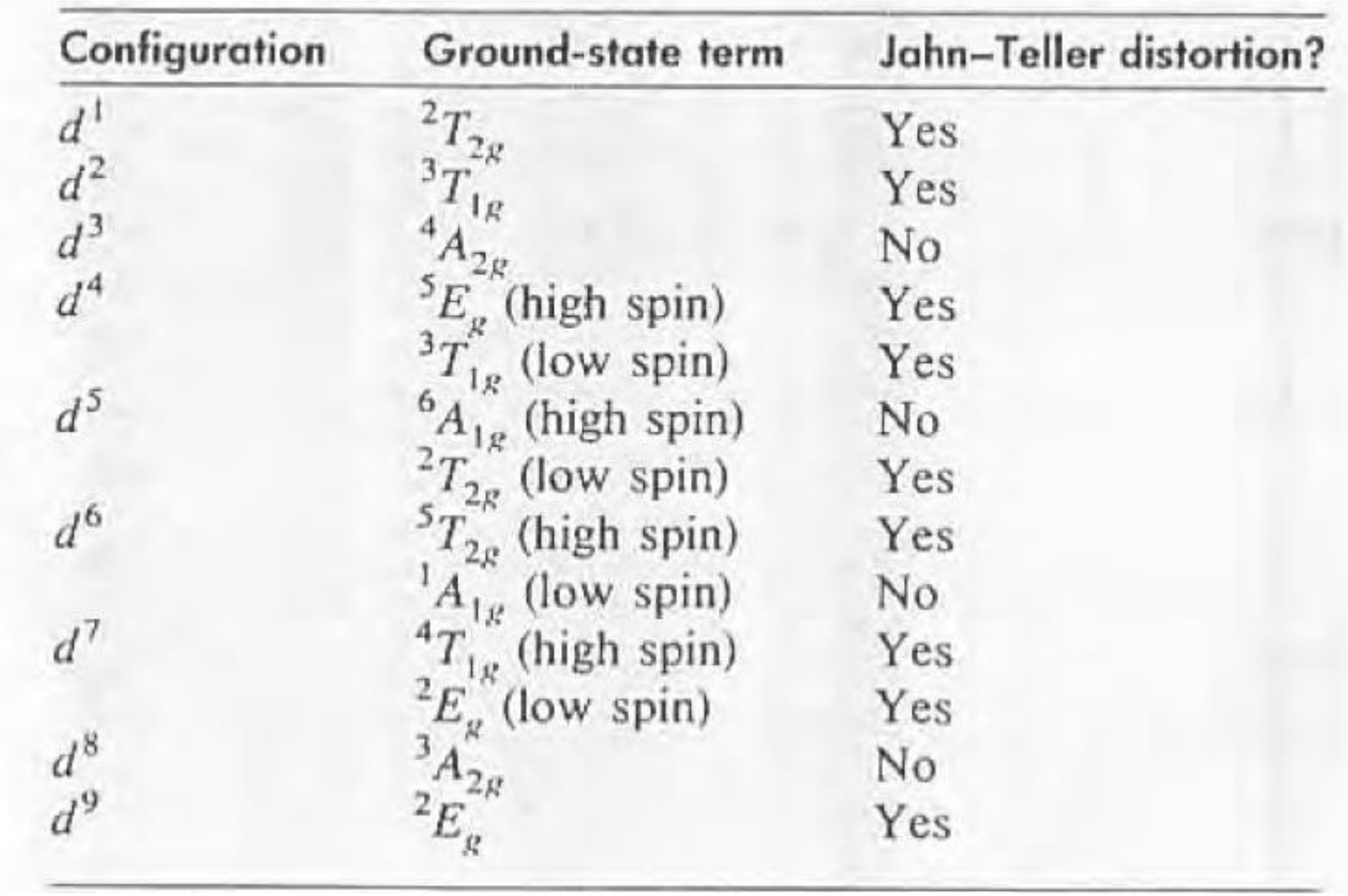
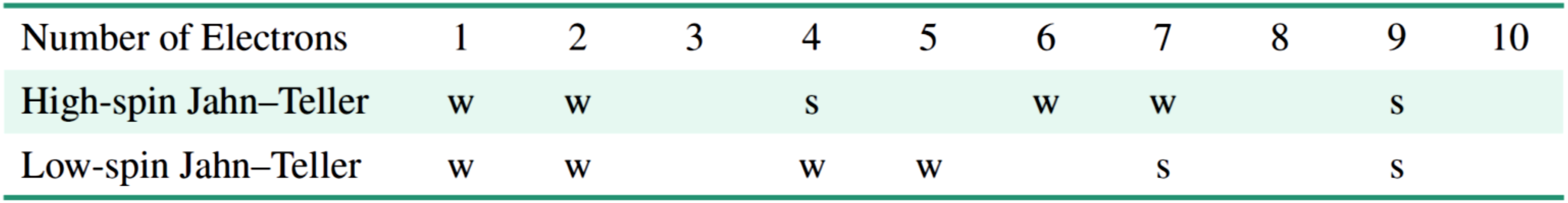


Figure: Tetragonal distortion from octahedral geometry

Configurations for which Jahn-Teller distortion are expected in octahedral ML_6 complexes



Configuration	Ground-state term	Jahn–Teller distortion?
d^1	$^2T_{2g}$	Yes
d^2	$^3T_{1g}$	Yes
d^3	$^4A_{2g}$	No
d^4	^5E_g (high spin)	Yes
	$^3T_{1g}$ (low spin)	Yes
d^5	$^6A_{1g}$ (high spin)	No
	$^2T_{2g}$ (low spin)	Yes
d^6	$^5T_{2g}$ (high spin)	Yes
	$^1A_{1g}$ (low spin)	No
d^7	$^4T_{1g}$ (high spin)	Yes
	^2E_g (low spin)	Yes
d^8	$^3A_{2g}$	No
d^9	^2E_g	Yes



Number of Electrons	1	2	3	4	5	6	7	8	9	10
High-spin Jahn–Teller	w	w		s		w	w		s	
Low-spin Jahn–Teller	w	w		w	w		s		s	

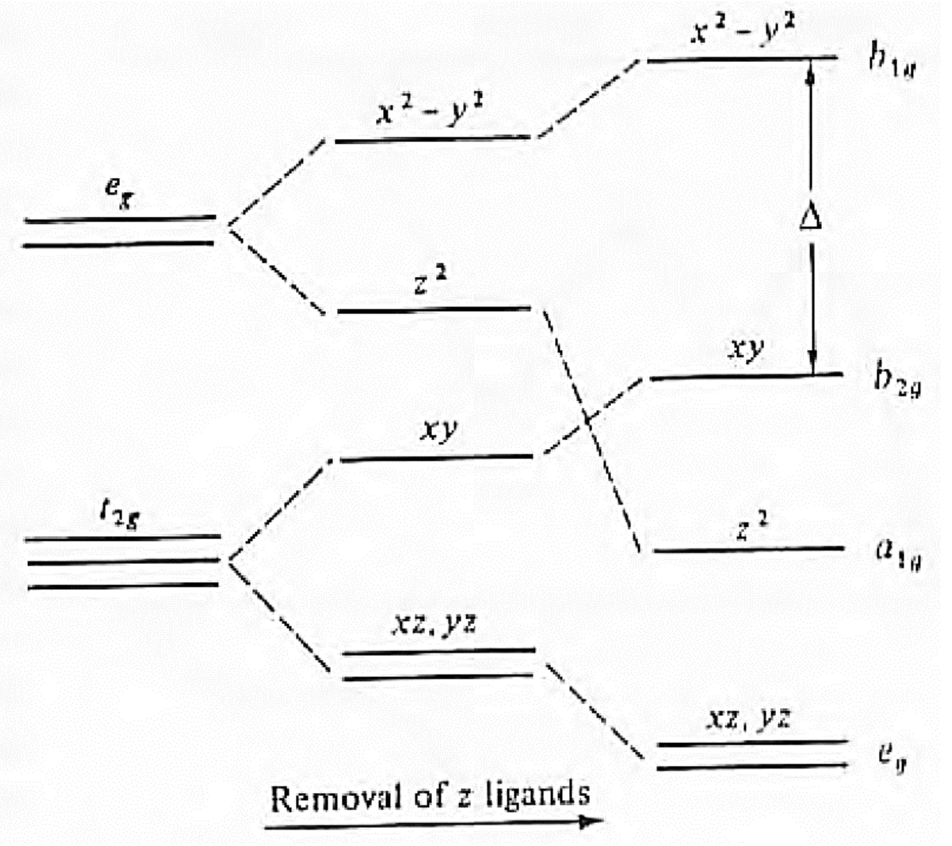
✓ *More significant Jahn–Teller distortions occur when e_g* orbitals would be unequally occupied within an octahedral geometry.*

Square Planar Crystal Field

Square planar complexes

- If we consider the **z-out distortion**, it is to be noted that complete removal of the trans ligands in the z-direction results in square planar crystal field.
- Metal cations with d^8 configuration form square planar complex with strong ligands such as CN^-. E.g. $[Ni(CN)_4]^{2-}$
- Heavier 4d and 5d transition (d^8) metals such as Pd(II), Pt(II), and Au(III) forms low-spin square planar complexes irrespective of the nature of ligands. E.g., $[PtCl_4]^{2-}$, $[AuCl_4]^-$, etc.
- Spectroscopic studies revealed

$$\Delta_{sp} = 1.3\,\Delta_o \quad (i.e., \Delta_{sp} > \Delta_o)$$



Octahedral

Tetragonal distortion

Square planar