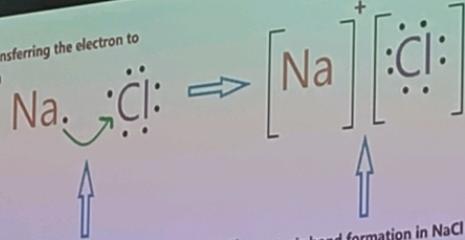
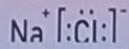
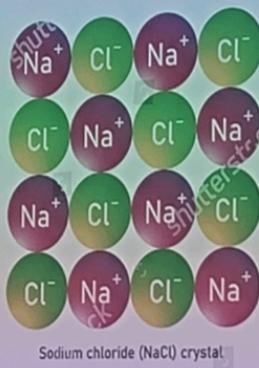
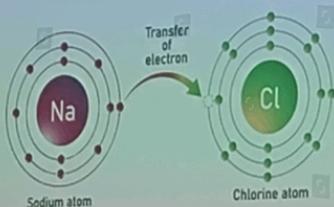


Sodium metal transferring the electron to the chlorine atom

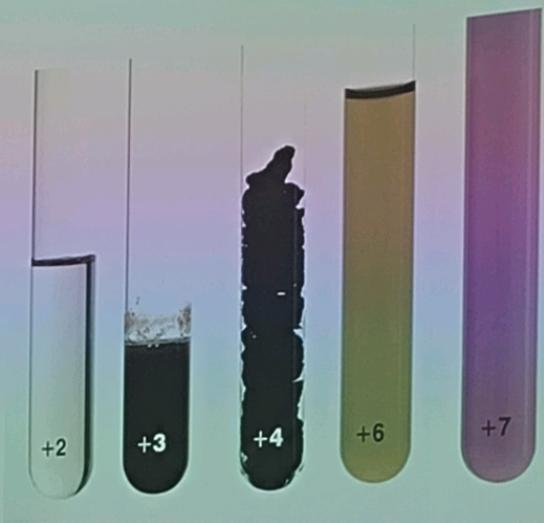


There is no sharing of electrons exist in NaCl compound.

Ionic bond formation in NaCl due to complete transfer of electrons from sodium to chlorine atom.



Compounds of
Mn in +2 to +7
oxidation states



Theories of bonding in transition metal complexes

Valence bond theory

- Based on the concept of hybridization sp^3 , dsp^2 , dsp^3 , d^2sp^3 & sp^3d^2 : Predicts shapes of complexes very efficiently
- Can determine magnetic moment if hybridization is known and vice versa
- Does not explain color of complexes, distortion of shape of complexes
- Does not predict strength of ligands or temperature dependence of magnetic moments



Linus Pauling



Hans Bethe



Mulliken & Hückel

Crystal Field theory

- Basic assumptions: Ligands and metal are point charges and the attraction between them is purely electrostatic in nature
- Considers how the energies of the five metal d orbitals change in the presence of a ligand field (removing /lifting of the degeneracy).
- Provides explanation to color, arranges ligands according to their strength, explains distortion of complexes and anomalies in their physical properties
- VBT and CFT should not be MIXED: A common mistake done by many students

Molecular Orbital Theory

- A larger picture where both metal orbitals and ligand group orbitals are made to form bonding, non bonding and antibonding orbitals.
- CFT splitting is included in this picture; also orbital overlap: π bonding
- Explains color, magnetism and energetics (does not predict shape)



Theories of Bonding in transition metal complexes
 Theories of bonding were proposed and used to explain the observed properties of transition metal complexes such as color, magnetism, shape of complexes

Valence bond theory

Orbitals of Co^{+2} ion

3d	4s	4p
↑↑↑↑↑		

d^5sp^2 hybridized orbitals of Co^{+2}

↑↑↑↑↑		
↓↓↓↓↓		

$[\text{Co}(\text{NH}_3)_6]^{+2}$ (inner orbital or low spin complex)

↑↑↑↑↑↑		
↓↓↓↓↓↓		

d^5sp^2 hybrid

↑↑↑↑↑↑		
↓↓↓↓↓↓		

Six pairs of electrons from six NH_3 molecules

Crystal Field theory

Energy level diagram showing the splitting of d -orbitals in an octahedral field. The energy gap is labeled ΔE .

Molecular Orbital Theory

A π -orbital formation from two p-orbitals

π^* antibonding molecular orbital

π bonding molecular orbital

Linus Pauling
 Nobel 1954, 1962

Hans Bethe
 Nobel 1967

Mulliken (Nobel 1966) & Hund

Legend: Lone pairs

9.5.3 Limitations of Valence Bond Theory

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

- (i) It involves a number of assumptions.
- (ii) It does not give quantitative interpretation of magnetic data.
- (iii) It does not explain the colour exhibited by coordination compounds.
- (iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- (v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- (vi) It does not distinguish between weak and strong ligands.

9.5.4 Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us explain this splitting in different crystal fields.

(a) Crystal field splitting in octahedral coordination entities

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in

Crystal Filed Theory (CFT)

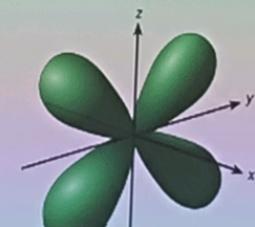
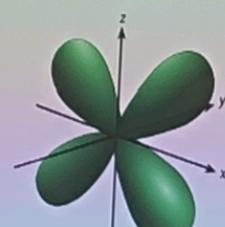
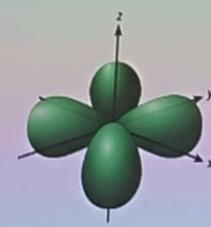
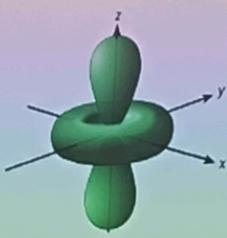
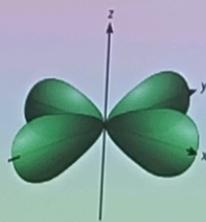


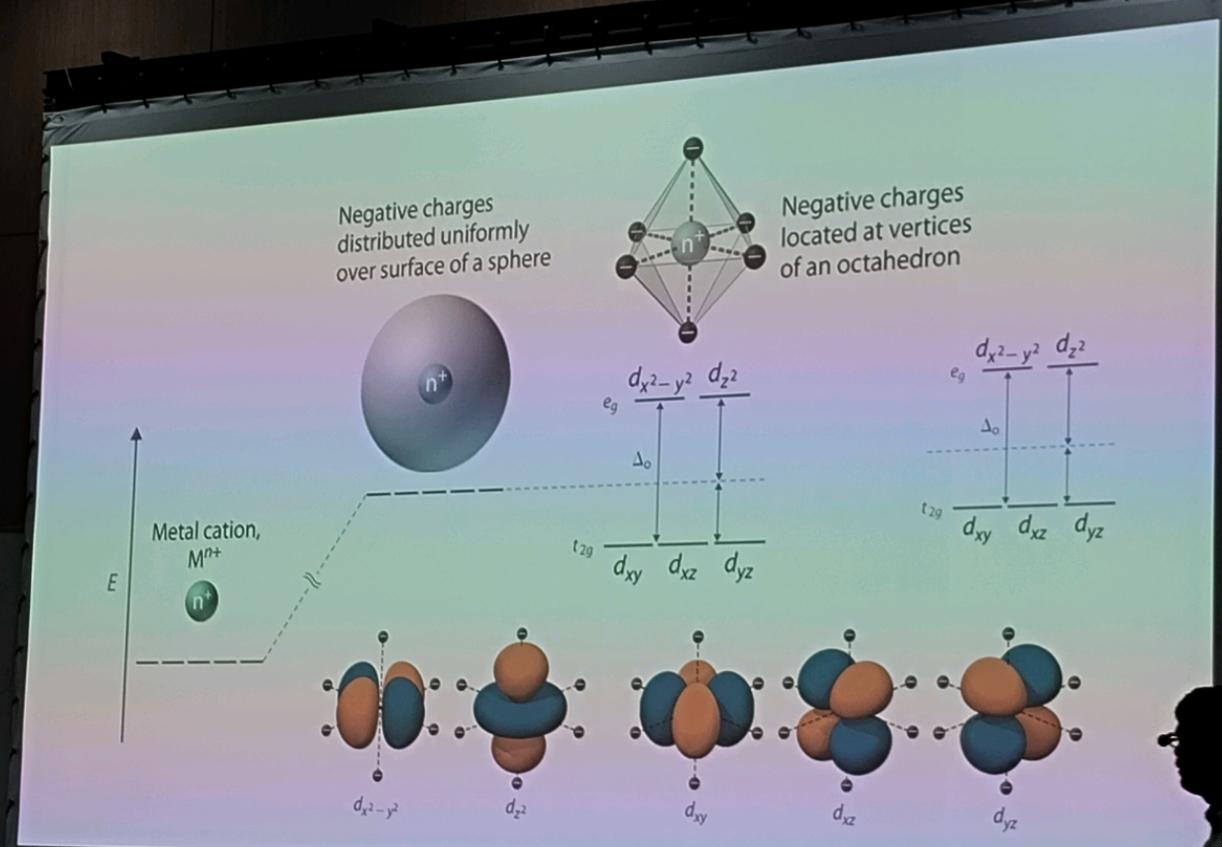
- A purely *ionic* model for transition metal complexes.
- Basic assumptions: Ligands and metal are point charges and the attraction between them is purely electrostatic in nature (Ligands are considered as point charge).
- Splitting of d-orbitals: Considers how the energies of the five metal d orbitals change in the presence of a ligand field (removing /lifting of the degeneracy).
- Provides explanation to color, arranges ligands according to their strength, explains distortion of complexes and anomalies in their physical properties
- Used to rationalize spectroscopic and magnetic properties.

d-orbitals: look attentively along the axis



Linear combination of
 $d_z^2 - d_x^2$ and $d_z^2 - d_y^2$ $d_{2z}^2 - d_x^2 - d_y^2$





Coordination Chemistry

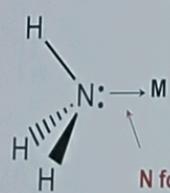
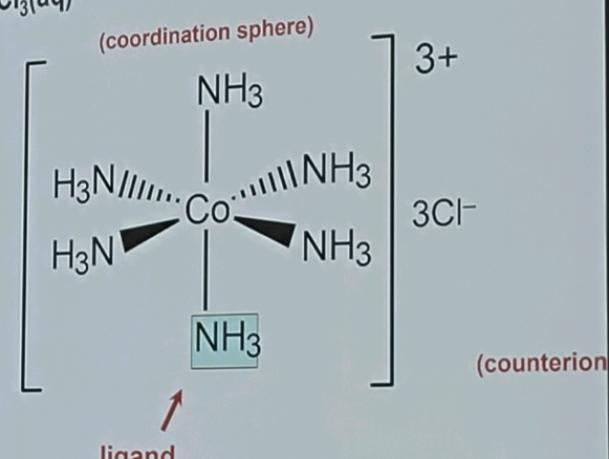


Prof. Dr. Alfred Werner (1866-1919)

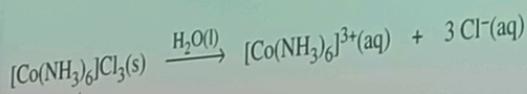
- 1893, age 26: coordination theory
- Nobel prize for Chemistry, 1913
- Addition of 6 mol NH_3 to $\text{CoCl}_3(\text{aq})$

Conductivity studies

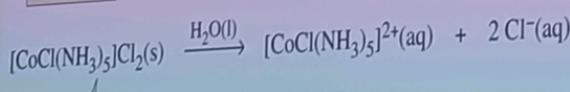
Precipitation with AgNO_3



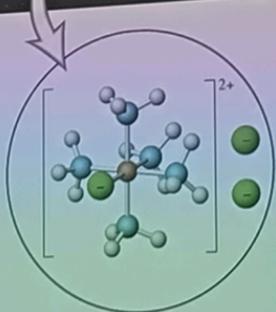
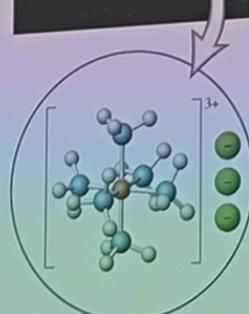
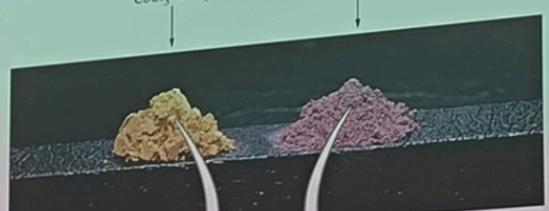
N forms a coordinate covalent bond to the metal



Golden
orange



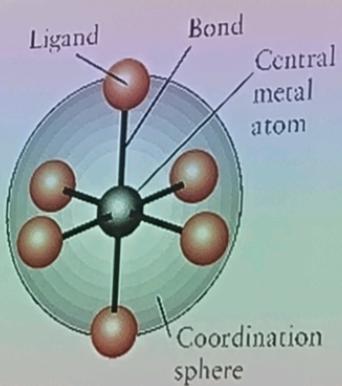
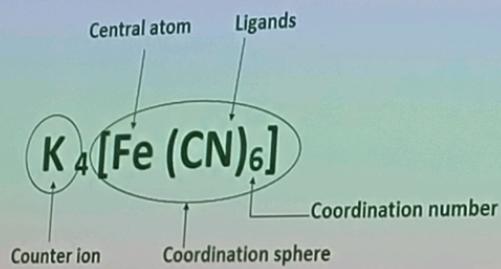
Purple



- Metallic elements act as **Lewis acids** form **complexes** with various Lewis bases.

Werner's Theory

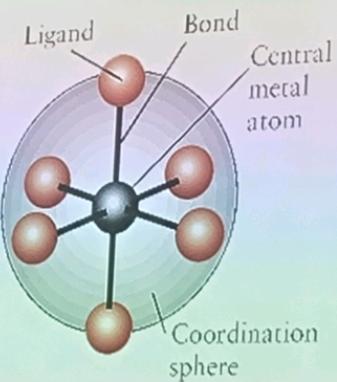
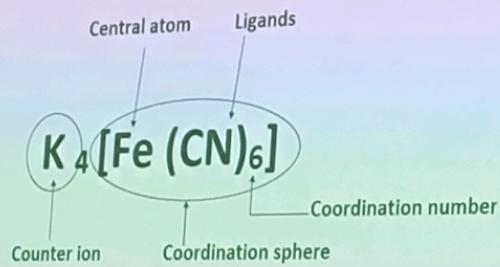
Example of $K_4[Fe(CN)_6]$:



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

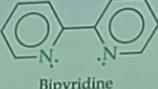
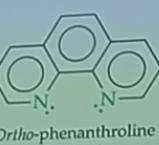
Werner's Theory

Example of $K_4[Fe(CN)_6]$:



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

Ligands

Ligand Type	Examples
Monodentate	$\text{H}_2\ddot{\text{O}}$: Water $:\text{NH}_3$ Ammonia
	$:\ddot{\text{F}}^-$ Fluoride ion $:\ddot{\text{Cl}}^-$ Chloride ion $[\text{:S}=\text{C}=\ddot{\text{N}}:\text{]}^-$ Thiocyanate ion $[\text{:C}\equiv\text{N}:\text{}]^-$ Cyanide ion
Bidentate	$\text{H}_2\text{C}-\text{CH}_2-\text{NH}_2$ Ethylenediamine (en)  Bipyridine (bipy)  Ortho-phenanthroline (o-phen)
Polydentate	$[\text{O}=\text{C}(\text{O})-\text{C}(\text{O})=\text{O}]^{2-}$ Oxalate ion $[\text{O}=\text{C}(\text{O})-\text{C}(\text{O})=\text{O}]^{2-}$ Carbonate ion $\text{H}_2\text{C}-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ Diethylenetriamine $[\text{:O}-\text{P}(\text{O})-\text{O}-\text{P}(\text{O})-\text{O}-\text{P}(\text{O})-\text{O}:]^{5-}$ Triphosphate ion $[\text{:O}-\text{C}(\text{O})-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{C}(\text{O})=\text{O}:]^{4-}$ Ethylenediaminetetraacetate ion (EDTA^{4-})

Effective atomic number (EAN) Rule



In 1927, developed by Sidgwick

d electrons of metal + electrons of ligand = 18 electrons

3	4	5	6	7	8	9	10	11	12
d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}		
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
									Hg



Effective atomic number (EAN) Rule :

" Effective atomic number is the total number of electrons present around central metal ion in a complex."

EAN=[Atomic number of the metal]-[Number of electrons lost in the formation of ion] + [Number of electrons gained from ligands].

Example:



$$\text{EAN} = [29 - 2 + 4(2)] = 35$$



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

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

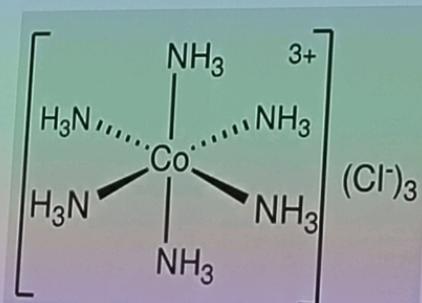
$$\text{Number of electrons donated by six NH}_3\text{ ligands} = 6 \times 2 = 12$$

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

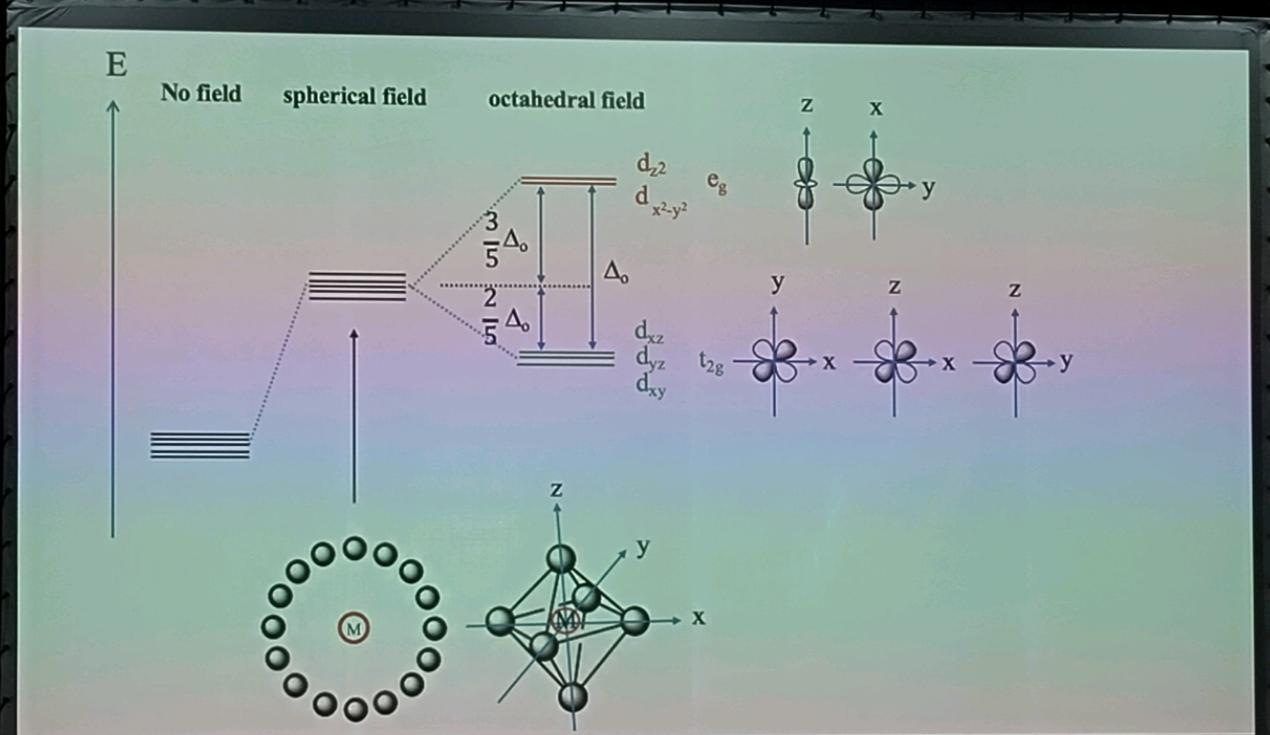
$\therefore [\text{Co}(\text{NH}_3)_6]^{3+}$ follows the EAN rule

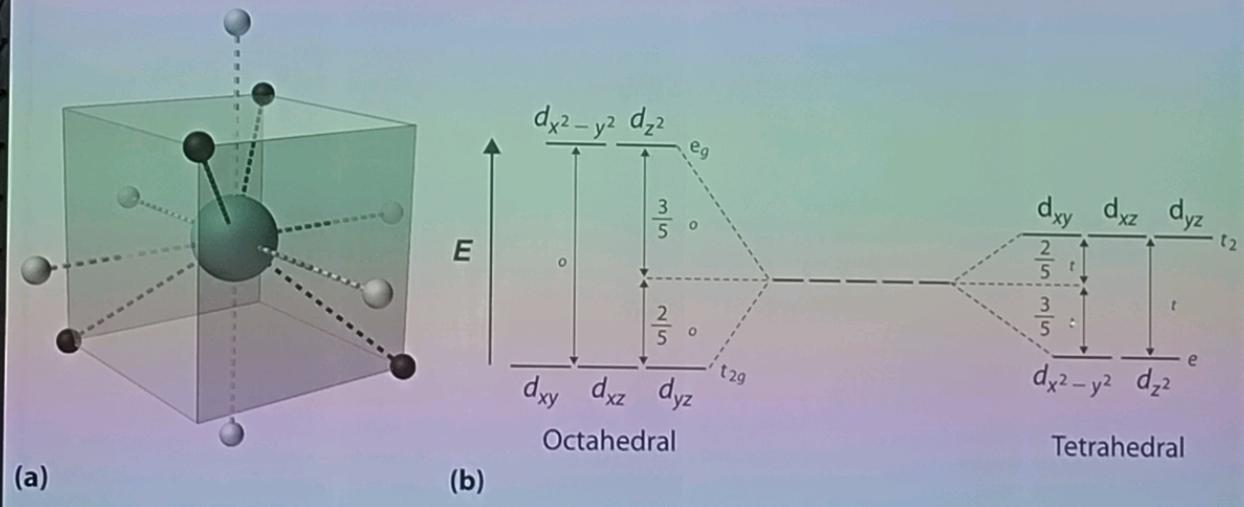
Drawbacks:

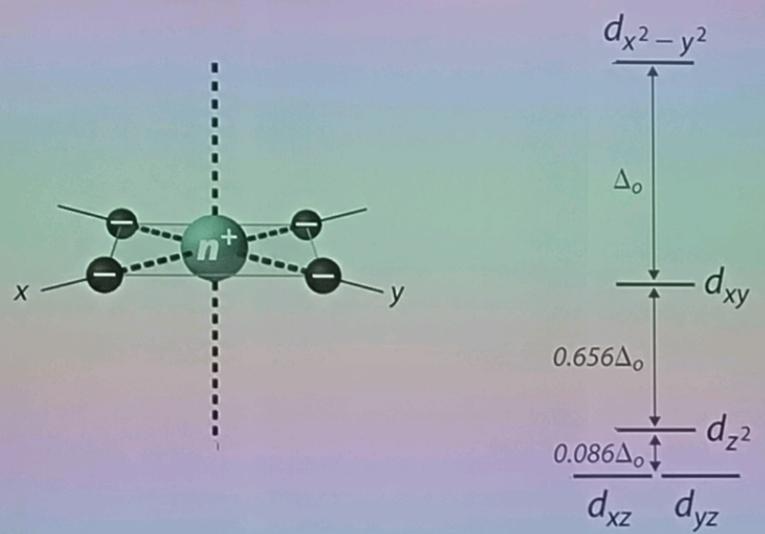
1. The donation of electron pairs to central metal ion produce an improper accumulation of negative charge on this ion. Such condition is not fair.
2. Complexes of Ni(II), Co(II), Ag(I) etc. generally do not follow this rule, even then they are stable
3. Metals are electro positive in nature, then how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



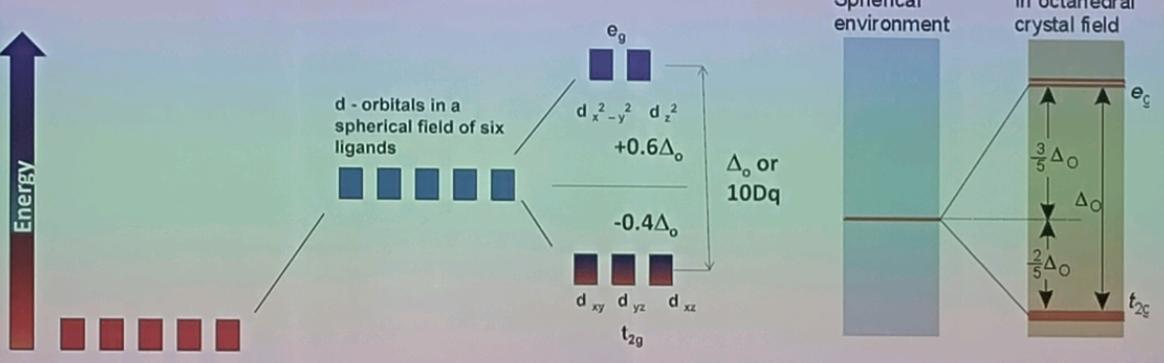
Metal atom	at. no	complex	O.S. of the metal ion	e ⁻ lost in ion formation	e ⁻ given by ligands	EAN / noble gas
Fe	26	K ₄ [Fe(CN) ₆] ⁴⁻	2+	2	12	26-2+12=36 Kr
Co	27	[Co(NH ₃) ₆] ³⁺	3+	3	12	27-3+12=36 Kr
Ni	28	[Ni(CO) ₄] ⁰	0	0	8	28-0+8=36 Kr
Cu	29	[Cu(NH ₃) ₄] ¹⁺	1+	1	8	29-1+8=36 Kr
Zn	30	[Zn(H ₂ O) ₄] ²⁺	2+	2	8	30-2+8=36 Kr
Pd	46	[Pd(NH ₃) ₆] ⁴⁺	4+	4	12	46-4+12=54 Xe
Pt	78	[Pt(Cl) ₆] ²⁻	4+	4	12	78-4+12=86 Rn
Cr	24	[Cr(NH ₃) ₆] ³⁺	3+	3	12	24-3+12=35
Fe	26	K ₃ [Fe(CN) ₆] ³⁻	3+	3	12	26-3+12=35
Ni	28	[Ni(NH ₃) ₆] ²⁺	2+	2	12	28-2+12=38







Splitting of the d-orbitals in an octahedral field



d - orbitals stabilized by metal-ligand electrostatic attraction

t_{2g} : triply degenerate set of orbitals :
 e_g doubly degenerate set of orbitals
 g = gerade: symmetric with respect to the centre of inversion
 u = ungerade : antisymmetric w. r. t the centre of inversion
 Barycenter: A point between objects where they balance each other

Crystal Field Splitting Energy (CFSE)

- 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: $= (-0.4x + 0.6y)\Delta_O$
 $\Delta_O = 10 Dq$

Beyond d^3

- In weak field: $\Delta_O < P, \Rightarrow t_{2g}^3 e_g^1$
- In strong field $\Delta_O > P, \Rightarrow t_{2g}^4$
- P - paring energy

Crystal Field Stabilization Energy (CFSE)



- The Crystal Field Stabilization Energy is defined as the energy of the electron configuration in the ligand field minus the energy of the electronic configuration in the isotropic field.

$$\text{CFSE} = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}}$$

The CSFE will depend on multiple factors including:

1. Geometry (which changes the d-orbital splitting patterns)
2. Number of d-electrons
3. Spin Pairing Energy
4. Ligand field strength (via Spectrochemical Series)

For an octahedral complex, an electron in the more stable t_{2g} subset is treated as contributing $-2/5\Delta_o$ whereas an electron in the higher energy e_g subset contributes to a destabilization of $+3/5\Delta_o$. The final answer is then expressed as a multiple of the crystal field splitting parameter Δ_o . If any electrons are paired within a single orbital, then the term P is used to represent the spin pairing energy.

Pairing Energy (P)



The pairing energy is not an experimentally obtained value like Δ_o and is same for a metal ion irrespective of the ligands. It is made up of two terms.

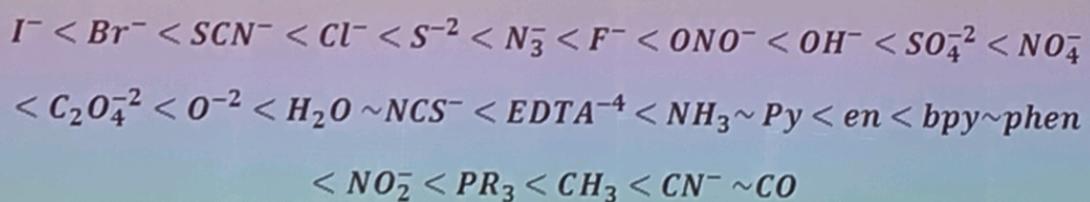
- 1) The inherent coulombic repulsion that must be overcome when two electrons are forced to occupy the same orbital. (*Destabilizing energy contribution of P_c for each doubly occupied orbital*).
- 2) Loss of exchange energy (based on Hunds rule) that occurs as two electrons with parallel spin ($\uparrow\uparrow$) are forced to become antiparallel ($\uparrow\downarrow$) in an orbital. (*contribution of P_e for each pair having same spin and same energy*)

$$P = \text{sum of all } P_c \text{ and } P_e \text{ interactions}$$

Spectrochemical series



- In 1938, the Spectrochemical series was established, which is a list of ligands organized by strength or a list of metal ions organized by oxidation number, group, and identity.
- Weak field ligands and strong field ligands are the two types of ligands.
- Strong field ligands, on the other hand, are those that cause a big crystal field splitting and so have a low spin value, whereas weak field ligands have a low crystal field splitting and hence have a high value.
- A series that arrange the ligands from large splitting value to small splitting value is known as spectrochemical



From I^- To H_2O are weak field ligands

From NCS^- To CO are strong field ligands

Strong field Vs. Weak Field ligands

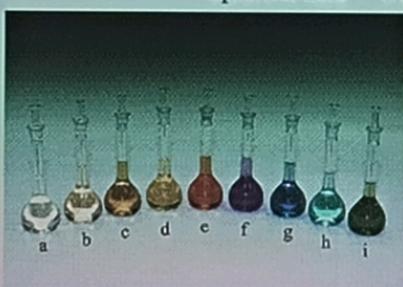
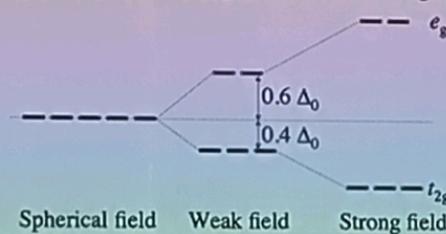
Strong field ligands	Weak field ligands
These are the ligands used in octahedral complexes in which the crystal field stabilization energy Δ_0 is greater than pairing energy (p).	These are the ligands used in octahedral complexes in which the crystal field stabilization energy Δ_0 is less than pairing energy (p) in a single orbital.
Contains C, N and P as donor sites.	Contains X, O and S as donor atoms
Complexes formed by these ligands are also known as low spin complexes.	Complexes formed by these ligands are also known as high spin complexes.
The complexes formed are mostly diamagnetic or comparatively less paramagnetic in nature.	The complexes formed are generally paramagnetic in nature.

Spectrochemical series

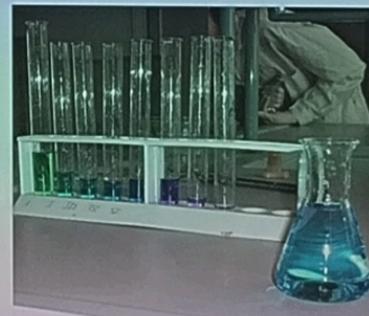
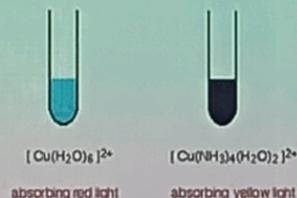


$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < Ox < ONO^- < H_2O$ Weak field
 $< NCS^- < edta^{4-} < NH_3 \sim Py < en < bipy < Phen < NO_2^- < PPh_3 < CN^- \sim CO$ Strong field

Halides ; sulfur donors < Oxygen donors < Nitrogen donors < CN-, CO



COBALT(III) Complexes of
(a) CN^- , (b) NO_2^- , (c) phen, (d) en, (e) NH_3 , (f) gly, (g) H_2O , (h) ox^{2-} , (i) CO_3^{2-}



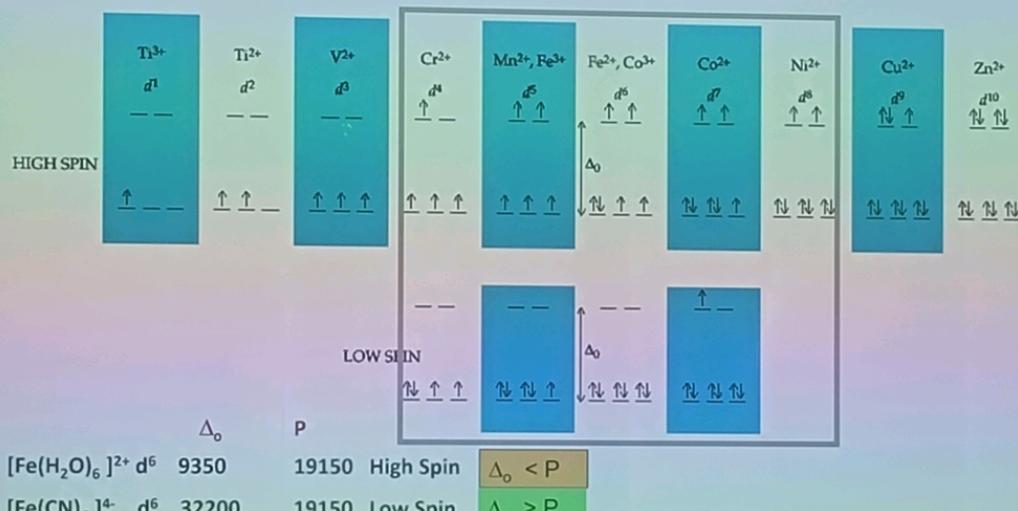
Stepwise addition of 'en' to $[Ni(H_2O)_6]^{2+}$

High Spin Vs. Low Spin (d^1 to d^{10})

- How complexes prefer to adopt High Spin/ low spin arrangement of electrons?

Ans: $\Delta_o <$ Pairing energy : High Spin

$\Delta_o >$ Pairing Energy : Low Spin



Crystal Field Splitting Energy (CFSE) in Oh

Total d-electrons	Octahedral configuration	CFSE	Tetrahedral configuration	CFSE	OSPE
d ⁰	t _{2g} ⁰	0 Δo	e ⁰	0 Δt	0 Δo
d ¹	t _{2g} ¹	-2/5 Δo	e ¹	-3/5 Δt	-6/45 Δo
d ²	t _{2g} ²	-4/5 Δo	e ²	-6/5 Δt	-12/45 Δo
d ³	t _{2g} ³	-6/5 Δo	e ² t ₂ ¹	-4/5 Δt	-38/45 Δo
d ⁴	t _{2g} ³ e _g ¹	-3/5 Δo	e ² t ₂ ²	-2/5 Δt	-19/45 Δo
d ⁵	t _{2g} ³ e _g ²	0 Δo	e ² t ₂ ³	0 Δt	0 Δo
d ⁶	t _{2g} ⁴ e _g ²	-2/5 Δo + P	e ³ t ₂ ³	-3/5 Δt + P	-6/45 Δo
d ⁷	t _{2g} ⁵ e _g ²	-4/5 Δo + 2P	e ⁴ t ₂ ³	-6/5 Δt + 2P	-12/45 Δo
d ⁸	t _{2g} ⁶ e _g ²	-6/5 Δo + 3P	e ⁴ t ₂ ⁴	-4/5 Δt + 3P	-38/45 Δo
d ⁹	t _{2g} ⁶ e _g ³	-3/5 Δo + 4P	e ⁴ t ₂ ⁵	-2/5 Δt + 4P	-19/45 Δo
d ¹⁰	t _{2g} ⁶ e _g ⁴	0 Δo	e ⁴ t ₂ ⁶	0 Δt	0 Δo

T_d Vs O_h Splitting



- The Crystal Field Stabilization Energy (CFSE) is the additional stabilization gained by the splitting of the orbitals according to the CFT against the energy of the original five degenerate d orbitals.

Example: in a d^1 situation such as $[Ti(OH_2)_6]^{3+}$, putting the electron into one of the orbitals of the t_{2g} level gains $-0.4 \Delta_o$ of CFSE. The Octahedral complexes will be favored over tetrahedral ones because

1. It is more (energetically) favorable to form six bonds rather than four
2. The CFSE is usually greater for octahedral than tetrahedral complexes (Δ_o is bigger than Δ_{tet} (in fact, Δ_{tet} is approximately $4/9 \Delta_o$).

- If we assume, $\Delta_{tet} = 4/9 \Delta_o$, we can calculate the difference in stabilization energy between octahedral and tetrahedral geometries by referencing everything in terms of Δ_o .
- Which is the preferred configuration for a d^3 metal: tetrahedral or octahedral?

To answer this, the Crystal Field Stabilization Energy has to be calculated for a (d^3) metal in both configurations. The geometry with the greater stabilization will be the preferred geometry)

T_d Vs O_h Splitting



- $d^3 O_h$ configuration, the Crystal Field Stabilization Energy is
 $CFSE = 3 \times -0.4\Delta_o = -1.2\Delta_o$
- $d^3 Td$ configuration
 $CFSE = 0.8\Delta_{tet}$
- Because Δ_{tet} is less than half the size of Δ_o , tetrahedral complexes are often high spin. We can now put this in terms of Δ_o (we can make this comparison because we're considering the same metal ion and the same ligand: all that's changing is the geometry)

So for tetrahedral d_3 , the Crystal Field Stabilization Energy is:
 $CFSE = -0.8 \times 4/9 \Delta_o = -0.355 \Delta_o$.

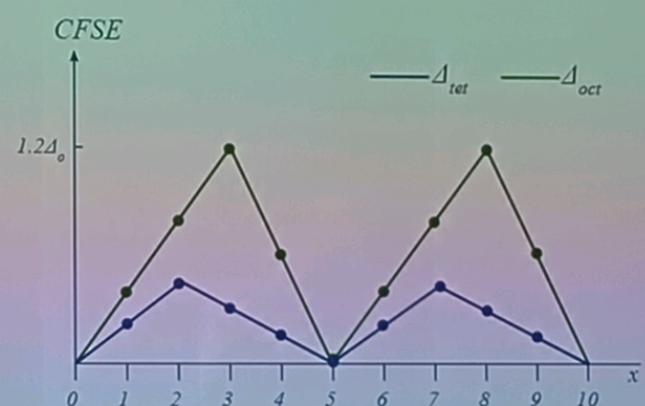
- The difference in Crystal Field Stabilization Energy between the two geometries will be:

$$1.2 - 0.355 = 0.845 \Delta_o.$$

T_d Vs O_h Splitting

This table compares the values of the CFSE for octahedral and tetrahedral geometries, assuming high spin configurations. The units are Δ_o , and we're assuming that $\Delta_{\text{tet}} = 4/9 \Delta_o$.

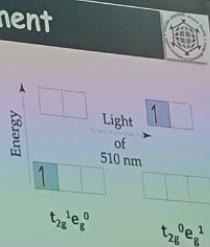
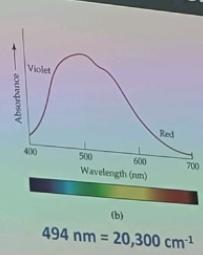
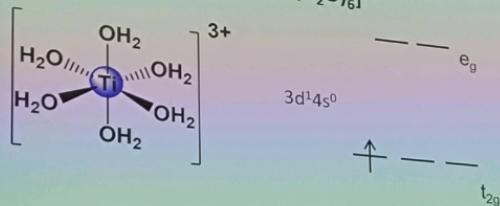
	O _h	T _d	Difference
d ⁰ , d ⁵ , d ¹⁰	0	0	0
d ¹ , d ⁶	0.4	0.27	0.13
d ² , d ⁷	0.8	0.53	0.27
d ³ , d ⁸	1.2	0.36	0.84
d ⁴ , d ⁹	0.6	0.18	0.42



The ordering of favorability of octahedral over tetrahedral is: d³, d⁸ > d⁴, d⁹ > d², d⁷ > d¹, d⁶ > d⁰, d⁵, d¹⁰

Significance of Δ_o and its physical measurement

Electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



$$1 \text{ kJ} = 83.7 \text{ cm}^{-1}$$

$$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} \quad \Delta_o = 20,300 \text{ cm}^{-1} = 243 \text{ kJ/mol}$$

Since an electron in the t_{2g} set is stabilized by $-0.4 \Delta_o$ $243 \times -0.4 = -97 \text{ kJ/mol}$

The complex is stabilized to the extent of 97 kJ/mol compared to a hypothetical spherical field due to the splitting of the d orbitals; This extra stabilization of the complex is called crystal field stabilization energy (CFSE)



Factors affecting the magnitude of crystal field splitting, Δ

1. Nature of metal ion (row to which it belongs)
Going from the first row to second row there is an increase in Δ_0 : Larger the metal \rightarrow larger is the Δ
2. Oxidation state of the metal ion (higher the oxidation state more is the Δ_0)
3. Number of ligands and shape of complex
(Octahedral, tetrahedral, square planar....)
4. Relative strength of the ligand (Spectrochemical Series)

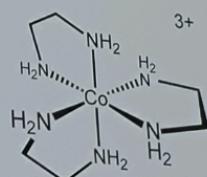
Factors affecting the magnitude of crystal field splitting, Δ_0

1. Size of the metal ion / Row to which the metal ion belong: Larger the size (row to which it belongs) larger the Δ value

$[\text{Co}(\text{en})_3]^{3+}$	23,200 cm^{-1}
$[\text{Rh}(\text{en})_3]^{3+}$	34,600 cm^{-1}
$[\text{Ir}(\text{en})_3]^{3+}$	41,000 cm^{-1}

~ 50% increase
~ 25% increase

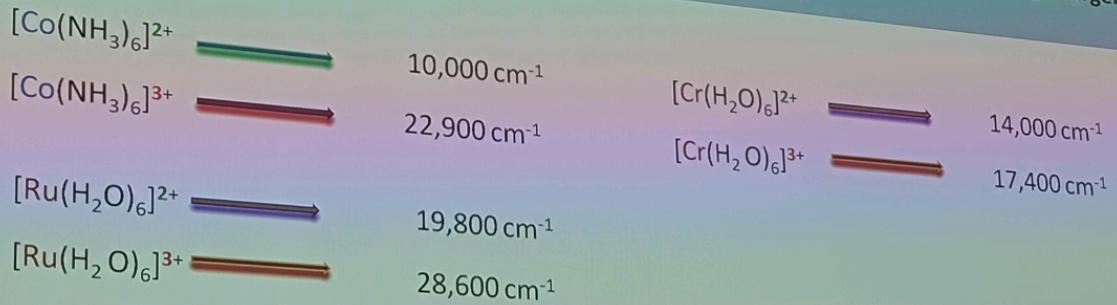
$$\Delta_0 \text{ (cm}^{-1}\text{)} = 3d < 4d < 5d$$



- Second and third row transition metals will have greater tendency to form low spin complexes
- Around a large metal ion, a given set of ligands experience less steric crowding and therefore can approach closer to the metal ion. More closer- larger will be the splitting

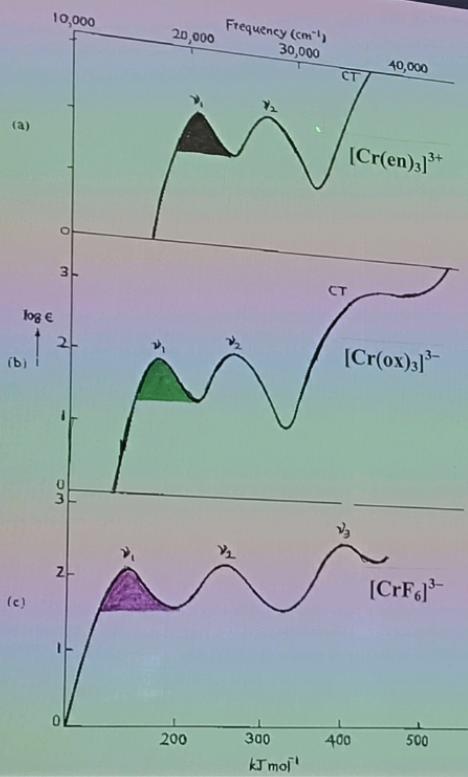
Factors affecting the magnitude of crystal field splitting, Δ

2. Charge on the metal ion / Oxidation state of the metal ion: Greater the charge larger the Δ value



- Higher the charge on the metal, the ligands are pulled in towards the metal more and therefore the ligands split the energies of the metal d orbitals to a greater extent

Factors affecting the magnitude of crystal field splitting, Δ



The effect of different ligands on the degree of Δ splitting is understood from the UV-Vis absorption spectra of complexes of the same metal-ion with different ligands

There is an increase in the frequency of the ν_1 (Δ_0) absorption band as the ligands on Cr^{3+} is changed from F \rightarrow O based \rightarrow N based ligands

1. For Mn^{2+} ion, $P = 28,000 \text{ cm}^{-1}$. Δ_o value for $[Mn(CN)_6]^{3+}$ ion is $38,500 \text{ cm}^{-1}$. Does this complex has high spin or low spin configuration? Also write the configuration.
2. Calculate CFSE values in terms of Δ_o and P for HS and LS octahedral complexes of $Fe(II)$ and $Co(II)$? Predict whether the complexes are paramagnetic or diamagnetic.
3. Determine CFSE of a d^6 octahedral complex having $\Delta_o = 25000 \text{ cm}^{-1}$ and $P = 15000 \text{ cm}^{-1}$.
4. The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single d electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_{Oct} and occurs at 499 nm. Calculate the value of Δ_{Oct} in Joules and predict what color the solution will appear.
5. Which ligand generates a stronger magnetic complex ion when bound to Fe^{2+} : EDTA or CN^- ?
6. ZnI_4 have eight valence electrons. If it is found to be diamagnetic, then does it occupy a tetrahedral or square plan geometry?

Application of CFT

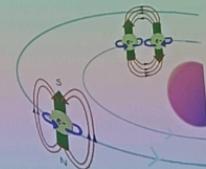


1. Spectral Properties (colors and their origin)
 - d-d, LMCT and MLCT Transitions
2. Magnetic Properties
 - Due to the presence of unpaired electrons in the $(n-1)d$ -orbitals, most of the transition metals ions and their compounds are paramagnetic i.e. they are attracted by the magnetic field.
 - As the number of unpaired electrons increases from 1 to 5, the magnetic moment and hence paramagnetic character also increase.
 - Those transition elements which have paired electrons are diamagnetic i.e. they are repelled by the magnetic field.
 - Metals like Co and Ni possess high paramagnetism where they obtain permanent magnetic moment and are referred as ferromagnetic.

Magnetic properties of metal complexes



- Magnetism is caused by moving charged electrical particles (Faraday, 1830s). These particles can be the current of electrons through an electric wire, or the movement of charged particles (protons and electrons) within an atom. These charged particles move much like planets in a solar system:
 - ✓ **nucleus spin** around its own axis, causing a **very weak** magnetic field.
 - ✓ electrons **orbit** around the nucleus, causing a **weak** magnetic field.
 - ✓ electrons **spin** around their own axis, causing a **significant** magnetic field.
- Spinning electrons generate the bulk of the magnetism in an atom.



Within each orbit, electrons with opposite spins pair together, resulting in no net magnetic field. Therefore, only **unpaired electrons** lead to magnetic moment

The **spin-only** formula (μ_s)

$$\mu_s = \sqrt{n(n+2)}$$

Magnetic properties: Spin only and effective

- The spin-only formula (μ_s) applies reasonably well to metal ions from the first row of transition metals: (units = μ_B , Bohr-magneton)

Metal ion	d^n configuration	μ_s (calculated)	μ_{eff} (observed)
$\text{Ca}^{2+}, \text{Sc}^{3+}$	d^0	0	0
Ti^{3+}	d^1	1.73	1.7-1.8
V^{3+}	d^2	2.83	2.8-3.1
$\text{V}^{2+}, \text{Cr}^{3+}$	d^3	3.87	3.7-3.9
$\text{Cr}^{2+}, \text{Mn}^{3+}$	d^4	4.90	4.8-4.9
$\text{Mn}^{2+}, \text{Fe}^{3+}$	d^5	5.92	5.7-6.0
$\text{Fe}^{2+}, \text{Co}^{3+}$	d^6	4.90	5.0-5.6
Co^{2+}	d^7	3.87	4.3-5.2
Ni^{2+}	d^8	2.83	2.9-3.9
Cu^{2+}	d^9	1.73	1.9-2.1
$\text{Zn}^{2+}, \text{Ga}^{3+}$	d^{10}	0	0