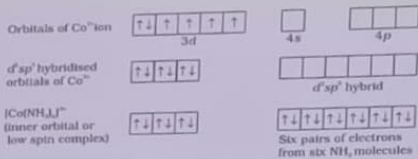


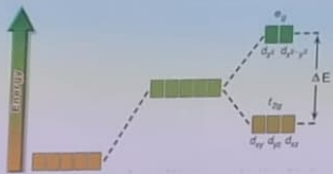
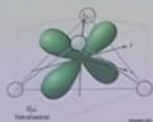
# Theories of Bonding in transition metal complexes

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

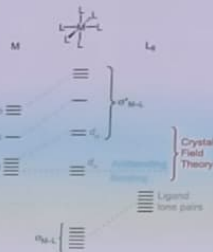
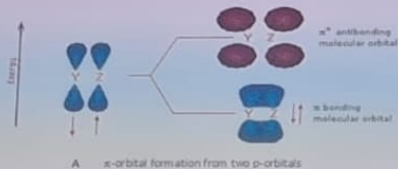
## Valence bond theory



## Crystal Field theory



## Molecular Orbital Theory



Linus Pauling  
Nobel 1954, 1962



Hans Bethe  
Nobel 1967



Mulliken (Nobel 1966) & Hund

# 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

## 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



Hans Bethe

## 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:  $\pi$  bonding
- Explains color, magnetism and energetics (does not predict shape)



Mulliken & Hund

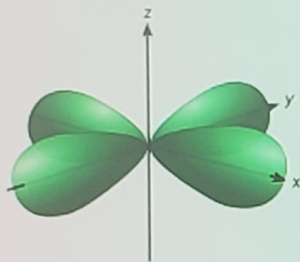
## Crystal Field Theory (CFT)



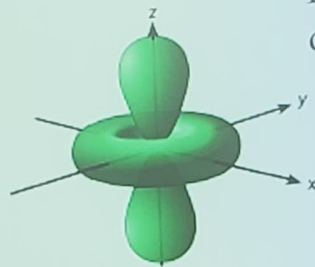
- A purely *ionic* model for transition metal complexes.
- Basic assumptions: Ligands and metal are point charges and the attraction between them is purely electrostatic in nature (Ligands are considered as point charge).
- Splitting of d-orbitals: Considers how the energies of the five metal d orbitals 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

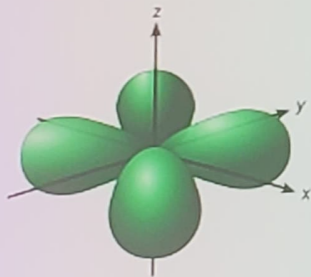
Linear combination of  $d_z^2 - d_x^2$  and  $d_z^2 - d_y^2$   $d_{2z^2 - x^2 - y^2}$



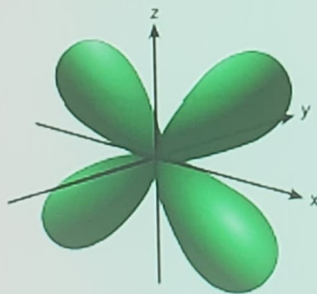
$d_{x^2-y^2}$



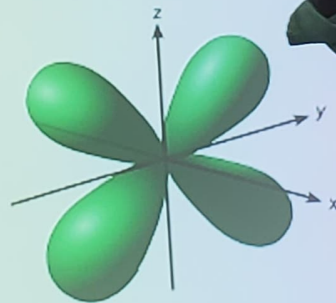
$d_{z^2}$



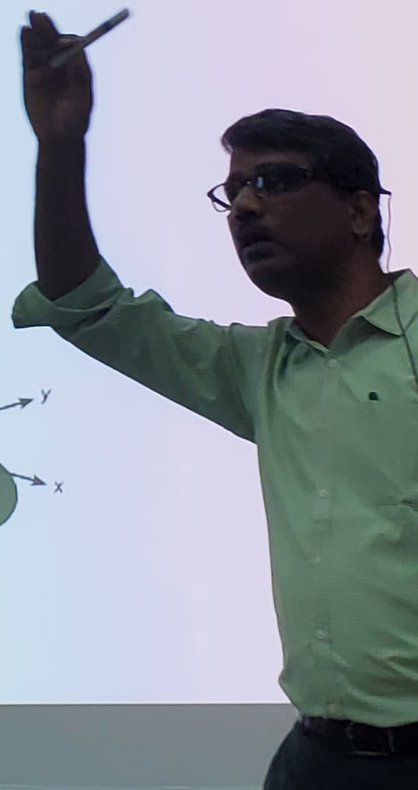
$d_{xy}$



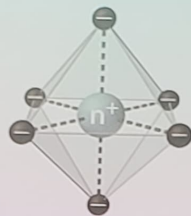
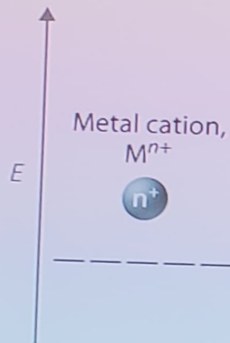
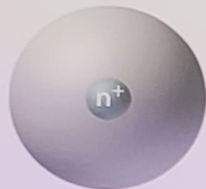
$d_{xz}$



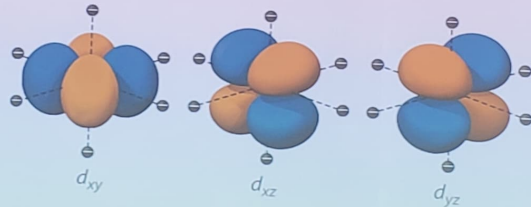
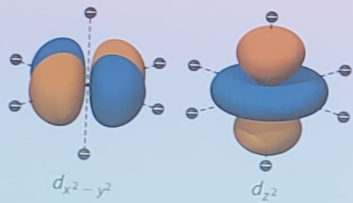
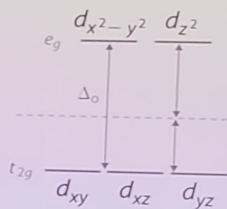
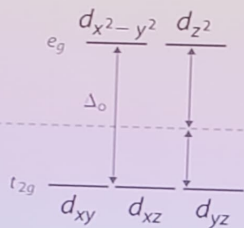
$d_{yz}$



Negative charges distributed uniformly over surface of a sphere

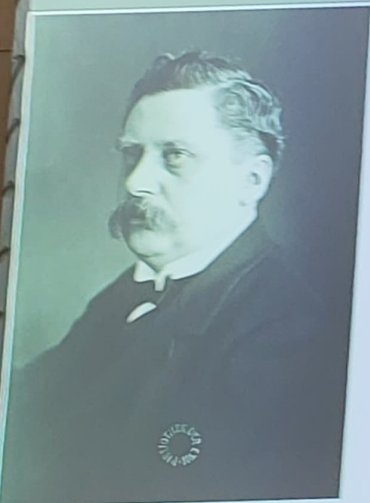


Negative charges located at vertices of an octahedron





## Coordination Chemistry

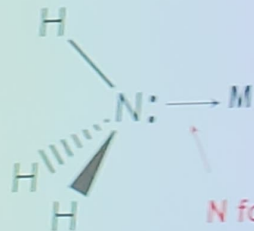
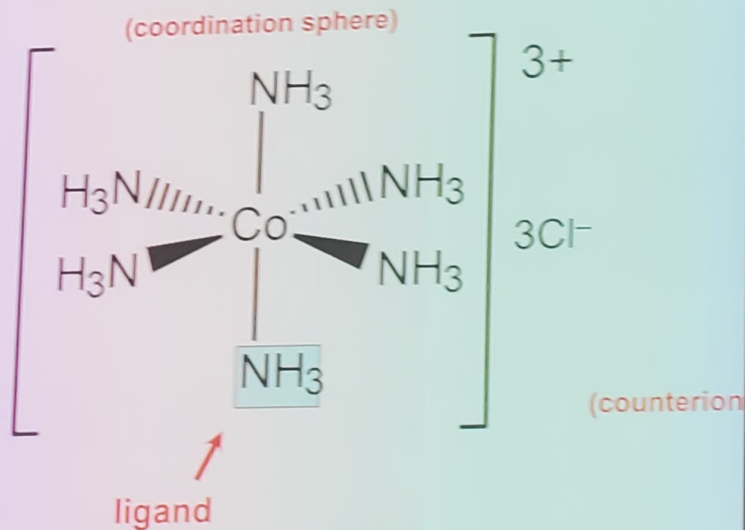


Prof. Dr. Alfred Werner (1866-1919)

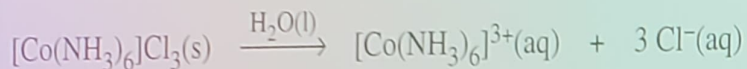
- 1893, age 26: coordination theory
- Nobel prize for Chemistry, 1913
- Addition of 6 mol  $\text{NH}_3$  to  $\text{CoCl}_3(\text{aq})$

Conductivity studies

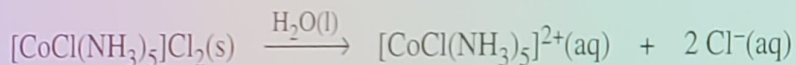
Precipitation with  $\text{AgNO}_3$



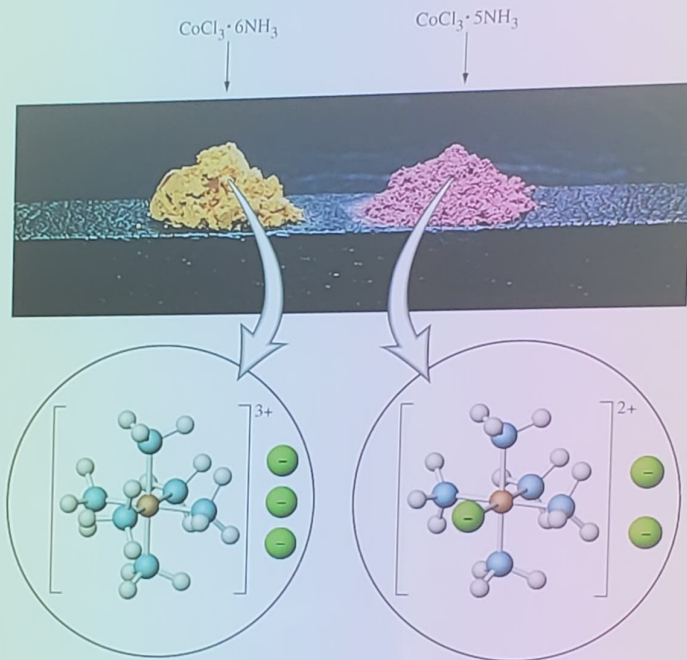
N forms a coordinate covalent bond to the metal



Golden  
orange



Purple

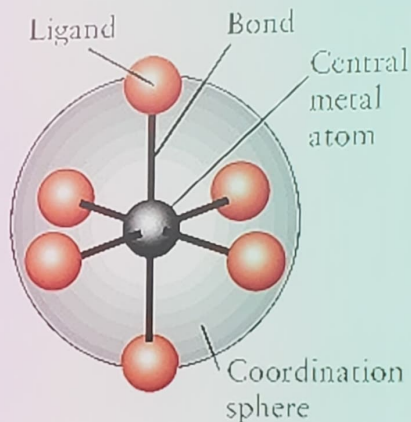
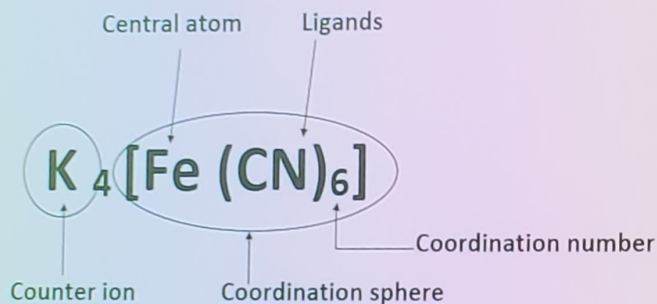


- Metallic elements act as **Lewis acids** form **complexes** with various Lewis bases.



# 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 sphere in brackets
- “free” anions (that dissociate from the complex ion) outside the bracket



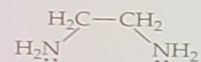
# Ligands



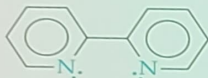
## Ligand Type Examples

Monodentate	$\text{H}_2\ddot{\text{O}}:$ Water	$\ddot{\text{F}}:^-$ Fluoride ion	$[:\text{C}\equiv\text{N}:]^-$ Cyanide ion	$[:\ddot{\text{O}}-\text{H}]^-$ Hydroxide ion
	$:\text{NH}_3$ Ammonia	$\ddot{\text{Cl}}:^-$ Chloride ion	$[\ddot{\text{S}}=\text{C}=\ddot{\text{N}}:]^-$ Thiocyanate ion [or]	$[\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:]^-$ Nitrite ion [or]

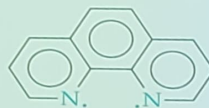
## Bidentate



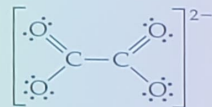
Ethylenediamine (en)



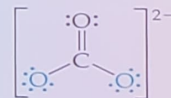
Bipyridine (bipy)



Ortho-phenanthroline (o-phen)

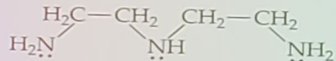


Oxalate ion

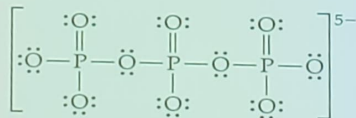


Carbonate ion

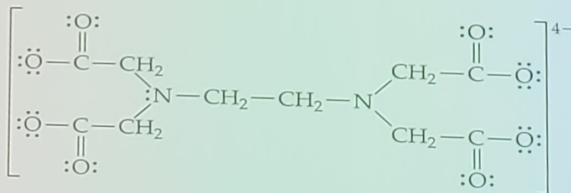
## Polydentate



Diethylenetriamine



Triphosphate ion



Ethylenediaminetetraacetate ion ( $\text{EDTA}^{4-}$ )

## 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 <sup>3</sup>	d <sup>4</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	d <sup>9</sup>	d <sup>10</sup>		
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
		Ta	W	Re	Os	Ir	Pt	Au	Hg

# Effective atomic number (EAN) Rule :

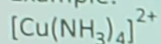


"Effective atomic number is the total number of electrons present around central metal ion in a complex."

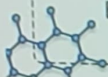


$EAN = [\text{Atomic number of the metal}] - [\text{Number of electrons lost in the formation of ion}] + [\text{Number of electrons gained from ligands}]$ .

Example:



$$EAN = [29 - 2 + 4(2)] = 35$$



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

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

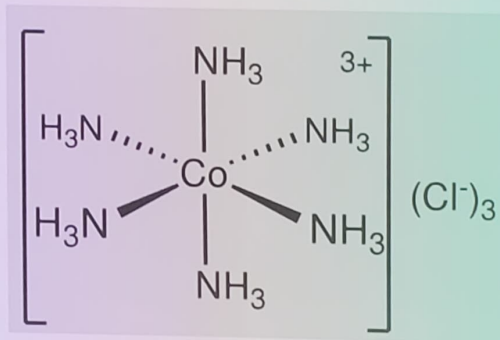
Number of electrons donated by six  $\text{NH}_3$  ligands  $= 6 \times 2 = 12$

$\therefore$  EAN of Co(III) in  $[\text{Co}(\text{NH}_3)_6]^{3+}$   $= 24 + 12 = 36$  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 <sup>-</sup> lost in ion formation	e <sup>-</sup> given by ligands	EAN / noble gas
Fe	26	$K_4[Fe(CN)_6]$	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	8	$28-0+8=36$ Kr
Cu	29	$[Cu(NH_3)_4]^+$	1+	1	8	$29-1+8=36$ Kr
Zn	30	$[Zn(H_2O)_6]^{2+}$	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	$[PtCl_6]^{2-}$	4+	4	12	$78-4+12=86$ Rn
Cr	24	$[Cr(NH_3)_6]^{3+}$	3+	3	12	$24-3+12=33$
Fe	26	$K_3[Fe(CN)_6]$	3+	3	12	$26-3+12=35$
Ni	28	$[Ni(NH_3)_6]^{2+}$	2+	2	12	$28-2+12=38$