COORDINATION COMPOUNDS AND ORGANOMETALLICS - II

Objectives

- Valence bond theory
- Crystal Field Theory
- Colour
- Magnetic properties
- Stability of coordination compound
- Uses of coordination compounds
- Organometallic compounds

Bonding in co-ordination compounds

Effective atomic number (EAN) rule : based on the octet theory of Lewis this is the first attempt to account for the bonding in complexes

The formation of a complex was described as an acid - base reaction according to Lewis

The sum of the electrons on the central atom (Lewis acid) including those donated from the ligands (Lewis base) should be equal to the number of elctrons on a noble gas

Valence bond theory

Valence Bond Theory predicts metal complex bonding arises from overlap of filled ligand orbitals and vacant metal orbitals.

Resulting bond is a *coordinate covalent bond*.



Complex geometry can be linked to five main orbital hybridization processes.

Coordinati on number	Geometry	Hybrid orbitals	Example
2	Linear	sp	[Ag(NH ₃) ₂]+
4	Tetrahedral	sp ³	[CoCl ₄] ²⁻
4	Square planer	dsp ³	[Ni(CN) ₄] ²⁻
6	Octahedral	d ² sp ³ or sp ³ d ²	$[Cr(H_2O)_6]^{3+}, [Co(H_2O)_6]^{2+}$



it paramagnetic and attracted by magnets.

Square Planar Geometry



Gives [Ni(CN)₄]^{2–} all paired electrons, which makes it diamagnetic and weakly repelled by magnets.

Octahedral *sp*³*d*² **Geometry**

Gives [CoF₆]^{3–} four unpaired electrons, which makes it paramagnetic and is called a *high-spin complex*.

$$Co^{3+}: [Ar] \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{4s} - \frac{1}{4p} - - \frac{1}{4d} - -$$

$$[CoF_6]^{3-}: [Ar] \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \frac{1}{4s} - \frac{1}{4p} \stackrel{\uparrow}{\longrightarrow} \frac{1}{4p} \stackrel{\uparrow}{\longrightarrow} \frac{1}{4d} - -$$

$$Six sp^3d^2 \text{ bonds to the ligands}$$



- The difference between sp³d² and d²sp³ hybrids lies in the principal quantum number of the d orbital.
- In sp³d² hybrids, the s, p, and d orbitals have the same principal quantum number—High Spin.
- In *d²sp³* hybrids, the principal quantum number of the *d* orbitals is one less than *s* and *p* orbitals—Low Spin.
- A complex's magnetic properties determine which hybrid is being used.



Where n is the number of unpaired electrons





Solution contd.

Geometry of [NiCl₄]²⁻



sp³ hybrid = tetrahedral.

Illustrative Example

$[Co(NH_3)_6]^{3+}$ is diamagnetic and $[CoF_6]^{3-}$ is paramagnetic. Explain with the help of valence bond theory.





Crystal Field Theory

Consider bonding in a complex to be an electrostatic attraction between a positively charged nucleus and the electrons of the ligands.

-Electrons on metal atom repel electrons on ligands.

-Focus particularly on the *d*-electrons on the metal ion.

Octahedral Complex and *d***-Orbital Energies**



Electron Configuration in *d***-Orbitals**





Weak and Strong Field Ligands

Two d⁶ complexes:



Energy Effects in a *d*¹⁰ System

 d_{z^2} 0.6 Δ $d_{x^2-y^2}$ 0.4Δ d_{xz} d_{xy} d_{yz}

Tetrahedral Crystal Field



Square Planar Crystal Field



Color and the Colors of Complexes





Effect of ligands on the colors of coordination compounds



Illustrative Example

Write the order of paramagnetism of following complex ions.

 $[Fe(H_2O)_6]^{2+}, [Cr(H_2O)_6]^{3+}, [Cu(H_2O)_6]^{2+}, [Zn(H_2O)_6]^{2+}$

Solution H_2O is a weak field ligand. $[Fe(H_2O)_6]^{2+}$ has four unpaired electrons, $[Cr(H_2O)_6]^{3+}$, $[Cu(H_2O)_6]^{2+}$ and $[Zn(H_2O)_6]^{2+}$

have 3, 1, 0 unpaired electrons respectively. So the order of paramagnetism is

 $[Fe(H_2O)_6]^{2+} > [Cr(H_2O)_6]^{3+} > [Cu(H_2O)_6]^{2+} > [Zn(H_2O)_6]^{2+}$

Stability of coordination compounds

Stability is measured in terms of the stability constant(equilibrium constant), given by the expression

$$\beta_n = \frac{[ML_n]}{[M(H_2O)_n][L]^n}$$

For the overall reaction:

 $M(H_2O)_n + nL f ML_n + nH_2O$

Important generalizations for stability

For a given metal and ligand, the stability is greater for greater charge on central metal ion.

For divalent ions of first row transition elements, irrespective the ligand involved, the stabilities very in the Irving-Williams Order: Mn(II)<Fe(II)<Co(II)<Ni(II)<Cu(II)<Zn(II).

Class 'a' acceptors like metals of group 1 and 2, the inner transition elements and the early members of the transition series (group 3 to 6) form their most stable coordination entities with ligands containing N, O and F donor atoms.

Class 'b' acceptors like the transition elements- Rh, Pd, Ag, Ir, Au and Hg having relatively full d orbitals form their most stable complexes with ligands whose donor atoms are the heavier members of the N, O and F groups.

Ring formation provide the greater stability to the complex.

Illustrative Example

The stability constant of some reactions are given below. Predict which of the ligands is strongest?

$$Cu^{2+} + 4NH_3 f \left[Cu(NH_3)_4\right]^{2+}; K = 4.5 \times 10^{12}$$

$$Cu^{2+} + 4CN^{-} f \left[Cu(CN)_{4}\right]^{2-}; K = 2.0 \times 10^{27}$$

$$Cu^{2+} + 2en f \left[Cu(en)_2\right]^{2+}$$
; K = 3.0 × 10¹⁵

$$Cu^{2+} + 4H_2O f \left[Cu(H_2O)_4\right]^{2+}$$
; K = 9.5 × 10⁸
olution:

Higher the stability constant, more stronger will be the ligand. Therefore CN⁻ is the strongest ligand.

Illustrative Example

- Out of K₄[Fe(CN)₆] and K₃[Fe(CN)₆] which is more stable and why? Solution
 - $K_3[Fe(CN)_6]$ is more stable than $K_4[Fe(CN)_6]$ as in $K_3[Fe(CN)_6]$, Fe is in +III oxidation state while in $K_4[Fe(CN)_6]$ Fe is in +II oxidation state and this can be oxidised to +III state.

Application of coordination compound

- i. In the animal world
- ii. In the plant world
- iii. In medicine(Cis-platin)
- iv. extraction of metals
- v. analytical chemistry

Organmetallic Compounds Classification σ -bonded compounds R-Mg-X **Grignard reagent** $(CH_3)_3AI$ **Trimethyl aluminium** $(CH_3CH_2)_2Zn$ **Diethylzinc Dimethyl cadmium** $(CH_3)_2Cd$

Organmetallic Compounds

 π – bonded compounds

Zeise's salt K $\left[PtCl_3 \left(n^2 - C_2 H_4 \right) \right]$ $\left[Fe \left(n^5 - C_5 H_5 \right)_2 \right]$: Ferrocene $\left[Cr \left(n^6 - C_6 H_6 \right)_2 \right]$: Dibenzene chromium

Organmetallic Compounds

 $\sigma \& \pi$ – bonded compounds





 $Fe(CO)_{5}$

Synthesis

Direct reaction of metals

 $R - X + Mg \xrightarrow{dry ether} R - Mg X$

 $R - X + 2M \longrightarrow R - M + MX$

By use of alkylating reagents

 $CdCl_{2} + 2C_{2}H_{5}MgCl \xrightarrow{\text{ether}} (C_{2}H_{5})_{2}Cd + 2MgCl_{2}$ $PbCl_{4} + 4C_{2}H_{5}MgBr \longrightarrow (C_{2}H_{5})_{4}Pb + 4MgBrCl$

Synthesis

Preparation of π -complexes

 $H_2C = CH_2 + K_2PtCI_4 \longrightarrow \left[PtCI_3(C_2H_4)\right] K^+ + KCI$

 $2C_5H_5$ Mg Br + Fe Cl₂ $\longrightarrow [(C_5H_5)_2$ Fe] + 2Mg Br Cl

Preparation of metal carbonyls

 $Ni + 4CO \longrightarrow Ni(CO)_4$

Bonding in carbonyls

Donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal.



donation of a pair of electrons from a filled d-orbital of metal into vacant antibonding (π^*) orbital of CO.



Bonding in alkenes

p-electron density of the alkene overlaps with a s-type vacant orbital on the metal atom

 σ - overlap

flow of electron density from a filled d-orbital on the metal into the vacant π^* antibonding molecular orbital on the carbon atoms

Back-bonding

Application of organometallics

- i. Wilkinson's catalyst, (Ph₃P)₃RhCl, used in hydrogenation of alkenes.
- ii. Ziegler Natta catalyst, [(C₂H₅)₃AlTiCl₄], for the polymerization of alkenes.

iii. Organoarsenic compounds are used for treatment of syphilis Seeds are treated with ethyl mercury chloride to protect the plants against infection.

Illustrative Example

Write the formula of Zeise's salt.

Solution:

The formula of Zeise's salt is $K^+[PtCl_3(C_2H_4)]^-$

