

### Werner's Theory: Postulates

- In coordination compounds metals show primary and secondary linkages (valences)
- Primary valences are ionisable and are satisfied by negative ions.
- Secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions.
- Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.

### Crystal field theory

Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lifted causing splitting of d orbitals.  $\Delta_0$  depends upon the field produced by the ligand and charge on metal ion.

### Colour

Caused by d-d transition; the colour is complementary to wavelength absorbed

### In metal carbonyls

Metal-carbon bond possess both  $\sigma$  and  $\pi$  character

### Bonding

### Valence bond theory

Metal atom/ion under the influence of ligands can use its  $(n-1)d$ ,  $ns$ ,  $np$  or  $ns$ ,  $np$ ,  $nd$  orbitals for hybridisation;  $sp^3$ (Tetrahedral),  $dsp^2$ (square planar),  $sp^3d$  (Trigonal pyramidal),  $sp^3d^2$  and  $d^2sp^3$  (Octahedral);  
 Magnetic moment  $= \sqrt{n(n+2)} \text{ BM}$

## Coordination Compounds

### Isomerism

### Uses

- In qualitative and quantitative chemical analysis.
- Estimation of hardness of water.
- In extraction of metals.
- In purification of metals.
- In biological systems.
- As catalysts for industrial processes.
- In black and white photography.
- In medicinal chemistry.

Ionisation counter ion is a potential ligand and can displace a ligand  
 $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$

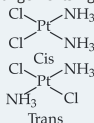
Coordination interchange of ligands between cationic and anionic entities of different metal ions  
 $[\text{Co}(\text{NH}_3)_6]^{3+} [\text{Cr}(\text{CN})_6]^{3-}$   
 $[\text{Cr}(\text{NH}_3)_6]^{3+} [\text{Co}(\text{CN})_6]^{3-}$

Solvate differ in number of water molecules attached to metal atom/ion  
 $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$   
 $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$

Linkage occurs in ambidentate ligand  
 $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}$   
 $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}$

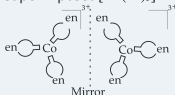
### Stereoisomerism: different spatial arrangements

Geometrical: different arrangements Ligand



### Structural: different bonds

Optical: images which cannot be superimposed  $[\text{Co}(\text{en})_3]^{3+}$



### Formulas of mononuclear

- Central atom is listed first
- Ligands in alphabetical order.
- Formula is enclosed in square bracket.
- Polyatomic ligands in parenthesis.
- No space between ligand and metal.
- Charge is indicated outside brackets.
- Charge of cation(s) balanced by charge of anion(s)

### Naming of mononuclear

- Cation is named first.
- Naming of ligands in alphabetical order.
- Anionic ligands end in-o, neutral and cationic are same
- Prefixes mono, di, tri etc. are used.
- Followed by roman numeral in parentheses.

Complex compound: do not dissociate into simple ions when dissolved in water ( $K_4[Fe(CN)_6]$ )

Stability: expressed by equilibrium constant  
 $Br = K_1 \times K_2 \times K_3 \dots K_n$

Double salt: Dissociate completely into simple ions when dissolved in water.  
(Mohr's salt  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ )

## Coordination Compounds

Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

### Terms

- Coordination entity : A central metal atom/ion bonded to fixed number of ions or molecules.  $[Ni(CO)_4]$
- Central atom/ion : Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
- Ligands : Ions or molecules bound to central atom/ion types :
  - Unidentate – single donor, Didentate –two donors
  - Polydentate – several donors,
  - Chelating – Di- or polydentate which forms more than one coordinate bonds.
  - Ambidentate : Can ligate through two different atoms.
- Coordination number : No. of ligand donor atoms to which metal is directly bonded
- Coordination sphere : Central atom/ion and the ligands attached to it and enclosed in square bracket.
- Oxidation number : Charge of central atom if all ligands are removed along with  $e^-$  pairs shared with central atom.
- Homoleptic complex : Metal is bound to one type of donor groups.  $[Co(NH_3)_6]^{3+}$
- Heteroleptic complex: Metal is bound to more than one type of donor groups