## Coordination Compounds - Part I

Coordination sphere consists of the central atom/ion and the ligands attached to it.


## IUPAC Nomenclature of Coordination

Name the Cation before the anion.

Name Ligands in the alphabetic order

## I

Ligands have a numerical prefix

## Ligands ions or molecules bound he central atom/ion in a <br> Ligands the ions or molecules bound to the central atom/ion in a <br> Ligands the ions or molecules bound to the central atom/ion in a coordination entity.

 After ligands, Centralmetal atom/ion is named

Neutral ligands are given the same name as the uncoordinated molecule $I$
The ligands are named alphabetically, ignoring the prefixes bis, tris, etc...

Anionic ligands are given names that end in the letter " 0 ".

## I

When the coordination entity is an anion, the name of the metal is altered to end in "ate"

## Isomerism



## Coordination Compounds - Part II

## Structural Isomerism

Coordination isomerism observed in the coordination compounds having both cationic and anionic complex ions.

| complex | $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4}\right]\left[\mathrm{CuCl}_{4}\right]$ |
| :---: | :---: |
| ions | Tetraammineplatinum(II) |
| tetrachloridocuprate(II) |  |

and
$\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]\left[\mathrm{PtCl}_{4}\right]$
Tetraamminecopper(II)
tetrachloridoplatinate(II)
Ionization isomerism afford different anions and cations in solution

| $\left[\mathrm{Pt}(\mathrm{OH})_{2}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{SO}_{4}$ |  |
| :---: | :---: |
| and | Tetraamminesulphato- |
| Tetraamminedihydroxo- | ats) $\left.\left(\mathrm{NH}_{3}\right)_{4}\right](\mathrm{OH})_{2}$ |
| platinum(IV)sulphate |  |
| platinum(IV)hydroxide |  |

Hydrate isomerism arises when different number of water molecules are present inside and outside the coordination sphere.
$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{H}_{2} \mathrm{OCl}\right] \mathrm{Br}_{2}$
Tetraammineaquachlorido-
cobalt(III)bromide
$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4}(\mathrm{Br})_{2}\right] \mathrm{Cl} . \mathrm{H}_{2} \mathrm{O}$ Tetraamminedibromidocobalt(III) chloride monohydrate

Linkage Isomerism isomerism occurs in complex compounds which contain ambidentate ligands

| $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{NO}_{2}\right] \mathrm{Cl}_{2}$ |  | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{ONO}\right] \mathrm{Cl}_{2}$ |
| :---: | :---: | :---: |
| Pentaaminenitrito-n-cobalt(III) <br> chloride(yellow) | and | Pentaaminenitrito-o-cobalt(III) <br> chloride(yellow) |

Polymerisation Isomerism it occurs between compounds having the same empirical formula, but different molecular weights.

$$
\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{2}\right] \mathrm{Cl}_{2} ;\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{4}\right] ;\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{2}\left[\mathrm{PtCl}_{4}\right]\right.
$$

Coordination position Isomerism exhibited by polynuclear complexes by changing the position of ligands


Unsymmetrical


Symmetrical

## Coordination Compounds - Part III

## Stereo Isomerism

Geometric Ligands at different locations relative to one another.

trans

cis

fac

mer

Anti-cancer drug

Transplatin
Toxic

Nonsuperimposable mirror images of each other.


## Werner's Theory

## Basically explains the structure of the complex compounds

Postulates

- Metals consist of two types of valencies; Primary and Secondary
- Primary is fulfilled by anions which are non directional.
- Secondary are fulfilled by Ligands which are directional


## Limitations

- Why Complex compounds are formed by few metals?
- Why Coordinate bonds are directional in nature?
- Why these compounds show magnetic and optical properties?


## Valence Bond Theory

Explains Bonding in terms of Hybridisation and explains the magnetic behaviour of the hybridised bonds.

> Postulates

Limitations

- Central atom makes available vacant orbitals equal to its coordination number
- These vacant hybrid orbitals form bonds with ligands which are directional in nature
- Couldn't explain colour and electronic spectra of complexes
- Couldn't explain structure of $[\mathrm{Cu}(\mathrm{NH} 3) 4]^{2+}$ Couldn't explain pairing of electrons in presence of ligands
Hybridisation and Geometry of complex

| Complex Compound or Iron | Magnetic Behaviour | Hybridisation | Shape |
| :---: | :---: | :---: | :---: |
| $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$ | Paramagnetic | $\mathrm{d}^{2} \mathrm{sp}^{3}$ | Octahedral |
| $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$ | Diamagnetic | $\mathrm{d}^{2} \mathrm{sp}^{3}$ | Octahedral |
| $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ | Diamagnetic | dsp ${ }^{2}$ | Square Planar |
| $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{SO}_{4}$ | Paramagnetic | dsp ${ }^{2}$ | Square Planar |
| $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{SO}_{4}$ | Paramagnetic | $\mathrm{sp}^{3}$ | Tetrahedral |
| $\left[\mathrm{Cu}\left(\mathrm{CN}_{4}\right)\right]^{2-}$ | Paramagnetic | dsp ${ }^{2}$ | Square Planar |
| $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ | Paramagnetic | $\mathrm{d}^{2} \mathrm{sp}^{3}$ | Octahedral |
| $\left[\mathrm{Cr}(\mathrm{CN})_{6}\right]^{3-}$ | Paramagnetic | $\mathrm{d}^{2} \mathrm{sp}^{3}$ | Octahedral |
| $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ | Diamagnetic | $\mathrm{d}^{2} \mathrm{sp}^{3}$ | Octahedral |
| $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ | Diamagnetic | $d^{2} s p^{3}$ | Octahedral |

Crystal Field Theory
Ligand field destroys the degeneracy of d orbitals and splits it into two or more energy levels.


Octahedral
In an octahedral complex, there are six ligands attached to the central transition metal. The d-orbital splits into two different levels. The bottom three energy levels are named $d_{x y}, d_{x z}$, and $d_{y z}$ (collectively referred to as $\mathrm{t}_{2 \mathrm{~g}}$ ). The two upper energy levels are named $\mathrm{d}_{x^{2}-y^{\prime}}$, and $\mathrm{d}_{z^{2}}$ (collectively referred to as eg).

Tetrahedral
In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. The top three consist of the $\mathrm{d}_{\mathrm{xy}}, \mathrm{d}_{\mathrm{xz}}$, and $\mathrm{d}_{\mathrm{yz}}$ orbitals. The bottom two consist of the $d_{x^{2}-y^{2}}$ and $d_{z^{2}}$ orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligands are not.

