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Coordination Compounds

Definition and Structure

A coordination compound consists of a central metal atom or ion bonded to a set of surrounding molecules or ions called ligands. These ligands are attached through coordinate bonds, where both electrons in the bond are donated by the ligand.

Coordinate Bond

A coordinate bond, also known as a dative covalent bond, is a type of covalent bond in which both electrons come from the same atom, typically the ligand donating a lone pair to the metal ion.

Double Salts

Double salts are stable solid compounds formed by the combination of two or more salts. They dissociate into simple ions in aqueous solution and do not contain coordinate bonds. An example is Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

Central Metal Atom or Ion

The central metal atom or ion is the core of the coordination compound to which ligands are attached. For example, in $K_4[Fe(CN)_6]$, Fe^{2+} is the central metal ion.

Ligands

Ligands are ions or neutral molecules that donate a pair of electrons to the central metal atom or ion, acting as Lewis bases. Examples include Cl^-, OH^-, CN^-, CO, NH_3, and H_2O.

Types of Ligands

Based on Number of Donor Sites

- **Unidentate ligands:** Ligands with one donor atom, e.g., NH_3, H_2O.
- **Bidentate ligands:** Ligands with two donor atoms, e.g., ethylenediamine (en).
- **Polydentate ligands:** Ligands with multiple donor atoms, e.g., EDTA.

Based on Charge

- **Cationic ligands:** Positively charged, e.g., NO_2^+, $N_2H_5^+$.
- **Anionic ligands:** Negatively charged, e.g., Cl^-, CN^-.
- **Neutral ligands:** No charge, e.g., NH_3, H_2O.

Based on Nature

- **Chelate ligands:** Bidentate or polydentate ligands that form ring structures with the metal ion.
- **Ambidentate ligands:** Ligands that can coordinate through two different atoms but only one at a time, e.g., NO_2^-.

Coordination Number and Geometry

The coordination number is the number of ligand donor atoms bonded to the central metal ion. Common coordination numbers are 4 and 6, corresponding to geometries such as tetrahedral, square planar, and octahedral.

Coordination Sphere and Counter Ions

The coordination sphere includes the central metal ion and the ligands directly bonded to it, enclosed in square brackets. Ions outside this sphere are called counter ions.

Nomenclature

Coordination compounds are named by first naming the cation, then the anion. Ligands are named alphabetically with prefixes indicating their number. Anionic ligands end with '-o', neutral ligands retain their names, and cationic ligands end with '-ium'. The oxidation state of the metal is given in Roman numerals.

Isomerism

Coordination compounds exhibit isomerism, where compounds have the same formula but different arrangements of ligands. Types include structural isomerism (ionisation, coordination, solvate, linkage) and stereoisomerism (geometrical and optical).

Solved Examples

Example 1

Identify the type of isomerism in $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$.

Solution: These compounds differ in the number of water molecules inside the coordination sphere and the presence of water outside it. This is an example of solvate isomerism.

Example 2

Assign secondary valency to metals in compounds based on moles of AgCl precipitated when reacted with $AgNO_3$.

Solution: The number of moles of AgCl corresponds to the number of chloride ions outside the coordination sphere, indicating the primary valency. The remaining chloride

ions are inside the coordination sphere, indicating secondary valency.

Example 3

Write formulas for the following coordination compounds:

- Tetraammineaquachloridocobalt(III) chloride
- Potassium tetrahydroxidozincate(II)
- Potassium trioxalatoaluminate(III)
- Dichloridobis(ethane-1,2-diamine)cobalt(III)
- Tetracarbonylnickel(0)

Answer:

- $[Co(NH_3)_4(H_2O)Cl]Cl_2$
- $K_2[Zn(OH)_4]$
- $K_3[Al(C_2O_4)_3]$
- $[CoCl_2(en)_2]^+$
- $[Ni(CO)_4]$

Example 4

Describe the hybridisation of $[Fe(H_2O)_6]^{2+}$.

Solution: Fe^{2+} has electronic configuration $3d^6\ 4s^0\ 4p^0\ 4d^0$. Water is a weak ligand, so no pairing occurs. The six lone pairs from water occupy one 4s, three 4p, and two 4d orbitals, resulting in sp^3d^2 hybridisation.

Example 5

Predict the geometry of $[MnBr_4]^{2-}$ given its spin-only magnetic moment is 5.9 BM.

Solution: Coordination number is 4, so geometry can be tetrahedral or square planar. The magnetic moment indicates five unpaired electrons, consistent with tetrahedral geometry (sp^3 hybridisation).

Practice Set

Conceptual Questions

- **Level 1:** Define a coordination compound and explain the role of ligands.
- **Level 2:** Differentiate between unidentate, bidentate, and polydentate ligands with examples.

Application-based Question

- **Level 3:** Explain the difference between cis and trans isomers in square planar complexes and their significance in medicinal chemistry.

Numerical Question

- **Level 2:** Calculate the coordination number and oxidation state of the metal in $[Co(NH_3)_4Cl_2]^+$.

Answer Key

Conceptual Questions

- **Level 1:** A coordination compound consists of a central metal atom or ion bonded to ligands via coordinate bonds. Ligands donate electron pairs to the metal, stabilizing the complex.

- **Level 2:** Unidentate ligands have one donor atom (e.g., NH_3), bidentate have two (e.g., en), and polydentate have multiple donor atoms (e.g., EDTA).

Application-based Question

- **Level 3:** Cis isomers have similar ligands adjacent, trans have them opposite. Cis-platin (cis isomer) is used in cancer treatment due to its ability to bind DNA, while trans isomer is inactive.

Numerical Question

- **Level 2:** Coordination number is 6 (4 NH_3 + 2 Cl ligands). Oxidation state of Co is +3 (charge of complex +1, ligands neutral NH_3 and Cl^- anions).

Werner’s Theory and Bonding

Werner's Theory

Werner proposed that metal ions have two types of valencies: primary (ionisable) and secondary (non-ionisable or coordination number). Primary valencies are satisfied by anions, and secondary valencies by ligands. Secondary valencies are spatially directed.

Limitations of Werner's Theory

- Does not explain why complex formation is limited to certain elements.
- Cannot explain directional nature of bonds.
- Fails to account for magnetic properties and isomerism.

Valence Bond Theory (VBT)

VBT explains bonding in coordination compounds by hybridisation of metal orbitals (s, p, d) to form hybrid orbitals that overlap with ligand orbitals donating electron pairs.

Limitations of VBT

- Cannot explain magnetic properties in detail.
- Fails to explain optical absorption spectra.
- Cannot predict geometry of four-coordinate complexes accurately.
- Does not distinguish strong and weak field ligands.
- Does not explain thermodynamic or kinetic stability.

Crystal Field Theory (CFT)

CFT treats ligands as point charges or dipoles that create an electrostatic field, causing splitting of metal d-orbitals into groups with different energies, explaining color and magnetic properties.

Splitting in Octahedral and Tetrahedral Fields

In octahedral complexes, d-orbitals split into higher energy e_g and lower energy t_{2g} orbitals. In tetrahedral complexes, the splitting pattern is reversed and smaller.

Spectrochemical Series

Ligands are arranged by field strength: $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$.

Metal Carbonyls

Metal carbonyls are homoleptic complexes with CO ligands, exhibiting both σ and π bonding. They are important in catalysis and organic synthesis.

Factors Affecting Stability

- Charge density of central ion.
- Basicity of ligands.
- Chelate effect increasing entropy and stability.

Applications

- Photography, electroplating, metal extraction.
- Medical uses such as cis-platin in cancer treatment.
- Hard water treatment and metal ion estimation.

Solved Examples

Example 4

Determine hybridisation of $[Fe(H_2O)_6]^{2+}$.

Solution: Fe^{2+} has $3d^6$ configuration. Water is a weak ligand, so no pairing occurs. Hybridisation is sp^3d^2.

Example 5

Predict geometry of $[MnBr_4]^{2-}$ with magnetic moment 5.9 BM.

Solution: Coordination number 4; magnetic moment indicates five unpaired electrons, consistent with tetrahedral geometry.

Practice Set

Conceptual Questions

- **Level 1:** State the postulates of Werner's theory.
- **Level 2:** Explain the difference between high spin and low spin complexes.

Application-based Question

- **Level 3:** Discuss the role of crystal field splitting in determining the color of coordination compounds.

Numerical Question

- **Level 2:** Calculate the number of unpaired electrons in $[Fe(CN)_6]^{4-}$.

Answer Key

Conceptual Questions

- **Level 1:** Werner's theory postulates primary and secondary valencies; primary valencies are ionisable, secondary are coordination number; secondary valencies are satisfied by ligands.
- **Level 2:** High spin complexes have maximum unpaired electrons due to weak field ligands; low spin complexes have paired electrons due to strong field ligands.

Application-based Question

- **Level 3:** Crystal field splitting causes d-orbitals to have different energies; electronic transitions between these levels absorb specific wavelengths, giving color.

Numerical Question

- **Level 2:** $[Fe(CN)_6]^{4-}$ is low spin d^6 complex; all electrons paired; number of unpaired electrons = 0.

Quick Reference Table

Common Mistakes and Misconceptions

Glossary