

UNIT 9 Topic: Coordination Compounds

1. State the postulates of Werner's theory of coordination compounds. 3 Marks

Postulates:

1. Central metal ion in a complex shows two types of valences - primary valence and secondary valence.
2. The primary valence is ionisable and satisfied by negative ions.
3. The secondary valence is non ionisable. It is equal to the coordination number of the central metal ion or atom. It is fixed for a metal. Secondary valences are satisfied by negative ions or neutral molecules (ligands).
4. The primary valence is non directional. The secondary valence is directional. Ions or molecules attached to satisfy secondary valences have characteristic spatial arrangements. Secondary valence decides geometry of the complex compound.

2. What are the limitations of Werner's theory of coordination compounds? 3 Marks

This theory fails to explain why,

- a) a few elements have the property to form coordination compounds
- b) the bonds in coordination compounds have directional properties
- c) coordination compounds have characteristic magnetic and optical properties.

3. Write one difference between double salts and complex salts with respect to their ionisation. Give one example for each type of salt. 2 Marks

Double salt	Complex salt
Double salt is stable only in solid state, but dissociate into simple ions completely in solution state.	Complex salt is stable both in solid and solution state and does not dissociate completely in solution state.
E.g: $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	E.g: $\text{K}_4[\text{Fe}(\text{CN})_6]$

4. Define Coordination entity of coordination compounds. 2 Marks

A coordinate entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules (ligands).

e.g: $[\text{Fe}(\text{CN})_6]^{4-}$.

5. What is central metal ion in a coordination compound? Give an example.

2 Marks

The metal atom or ion in a coordination entity to which, a fixed number of ions or molecules (ligands) are bound in a definite geometrical arrangement around it is called central metal ion. It is a Lewis acid.

e.g: In $K_4[Fe(CN)_6]$, central metal ion is Fe^{2+} .

6. What are ligands? Give an example.

2 Marks

The ions or molecules bonded to the central metal atom or ion in a coordination entity are called ligands. Ligands are Lewis bases.

e.g: In $[Ni(CN)_4]^{2-}$, ligand is CN^- ion.

7. Define the term coordination number of a central metal atom or ion in a complex compound.

2 Marks

The coordination number of central metal atom or ion in a complex is the number of ligand donor atoms to which the metal is directly bonded.

In $K_4[Fe(CN)_6]$, coordination number of Fe^{2+} is 6.

8. Define coordination sphere of coordination compounds.

2 Marks

The central metal atom or ion and the ligands of the complex compound are written within square bracket. This is called coordination sphere of coordination compounds.

9. What are homoleptic complexes? Give an example.

2 Marks

Homoleptic complexes are the complexes in which central metal ion or atom is bound to only one type of donor groups.

e.g: $K_4[Fe(CN)_6]$

10. What are heteroleptic complexes? Give an example.

2 Marks

Heteroleptic complexes are the complexes in which central metal ion or atom is bound to more than one type of donor groups.

e.g: $[Co(NH_3)_5Cl]SO_4$

11. Classify the following ligands into unidentate, didentate and polydentate ligands. NH_3 , EDTA, oxalate.

3 Marks

NH₃ Unidentate

EDTA Polydentate

Oxalate Didentate

12. Give the IUPAC name for the following compounds.

- a) $K_4[Fe(CN)_6]$ potassium hexacyanidoferrate(II)
- b) $[Cu(NH_3)_4]SO_4$ tetramminecopper(II) sulphate
- c) $[Co(NH_3)_5Cl]SO_4$ pentamminechloridocobalt(III) sulphate
- d) $K_3[Fe(C_2O_4)_3]$ potassium trioxalatoferrate(III)
- e) $[CoCl_2(en)_2]^+$ dichloridobis(ethane-1,2-diamine)cobalt(III)
- f) $[Co(NH_3)_5(NO_2)]Cl_2$ pentamminenitrito-N-cobalt(III) chloride
- g) $[Co(NH_3)_5(ONO)]Cl_2$ pentamminenitrito-O-cobalt(III) chloride
- h) $[Ni(CO)_4]$ tetracarbonylnickel(0)

13. What are ambidentate ligands? Give one example.

2 Marks

Ligands which have two donor atoms, but can bond to central metal atom or ion through only one donor atom are called ambidentate ligands.

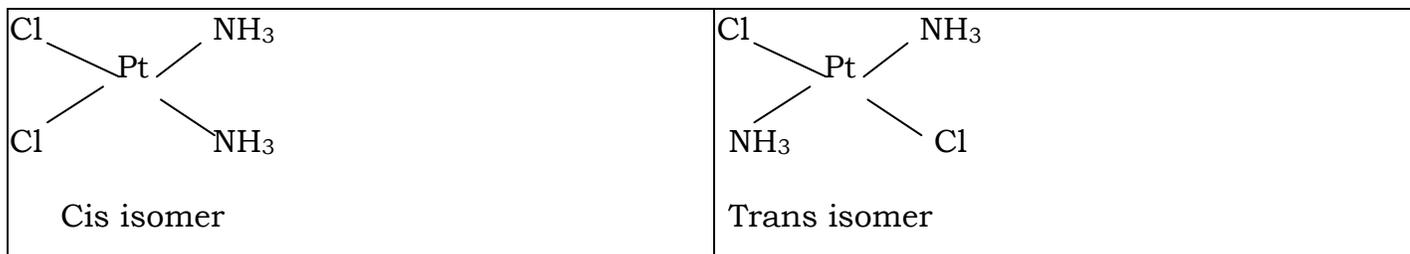
e.g: NO_2^- , SCN^- etc.,

14. What is geometrical isomerism in complexes? Give an example.

2 Marks

It is a phenomenon in which two complex compounds have the same molecular formula and same chemical bonds, but different geometrical arrangement of the ligands. The two forms are called cis and trans forms.

e.g: $[Pt(NH_3)_2Cl_2]$

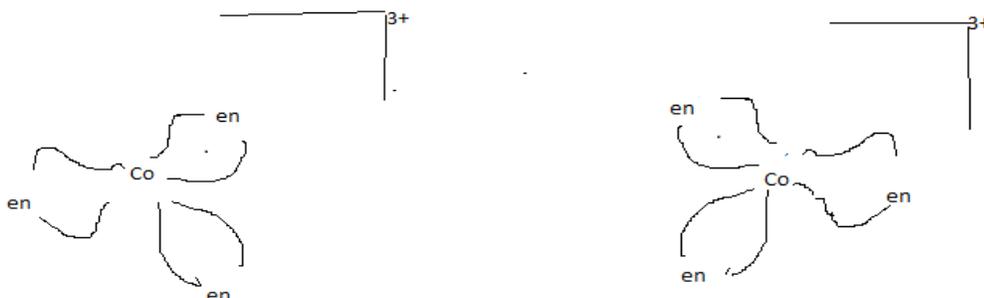


15. Explain optical isomerism in complexes with an example.

2 Marks

It is a phenomenon in which two complex compounds have the same molecular formula and same chemical bonds but cannot be superposed on one another. They differ in the rotation of plane of plane polarised light. These isomers are called enantiomers. The two forms are called dextro (d) and laevo (l).

e.g:



16. What is linkage isomerism? Give an example.

2 Marks

Linkage isomerism is type of isomerism in which two complex compounds differ in the donor atoms for ligands (different ligating atoms). It is shown by complex compounds containing ambidentate ligands.

e.g: $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$

17. Indicate the type of isomerism in the following set of complex compounds.

a) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$

b) $[\text{Co}(\text{NH}_3)_5(\text{SCN})]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$

2 Marks

a) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$

Ionisation isomerism

b) $[\text{Co}(\text{NH}_3)_5(\text{SCN})]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$

Linkage isomerism

18. Explain coordination isomerism in complexes. Give one example.

Coordination isomerism is type of isomerism due to interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

e.g: $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$

19. Explain ionization isomerism in complexes. Give an example.

Ionisation isomerism is type of isomerism in which two complex compounds produce different ions in solution form.

e.g: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$

20. What is solvate isomerism? Explain with an example.

Solvate isomerism is a type of isomerism in which complex compounds differ in the number of water molecules acting as ligands and water of hydration.

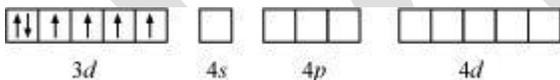
e.g: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$

21. Explain the formation of $[\text{CoF}_6]^{3-}$. Is this complex paramagnetic?

3 Marks

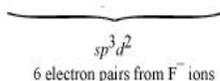
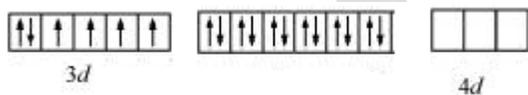
Co, $Z=27$ $[\text{Ar}]3d^7 4s^2 4p^0 4d^0$

Co^{3+} $[\text{Ar}] 3d^6 4s^0 4p^0 4d^0$



It undergoes sp^3d^2 hybridisation.

When F⁻ ligand attacks the central metal ion, Co^{3+}

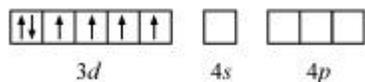


This complex uses outer d orbital (4d) for hybridisation. It is an outer orbital complex. It has unpaired electrons. $[\text{CoF}_6]^{3-}$ is paramagnetic. This complex is called high spin or spin free complex.

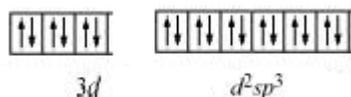
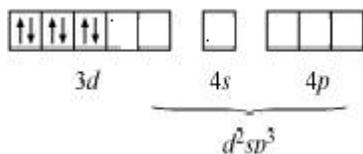
22. Give the geometry, hybridization and magnetic property of $[\text{Co}(\text{NH}_3)_6]^{3+}$ based on VBT. **3 Marks**

Co, $Z=27$ $[\text{Ar}]3d^7 4s^2 4p^0$

Co^{3+} $[\text{Ar}] 3d^6 4s^0 4p^0$



When NH_3 ligand attacks the central metal ion Co^{3+} , pairing of electrons in 3d orbital occurs against Hund's rule. Co^{3+} can undergo d^2sp^3 hybridization.

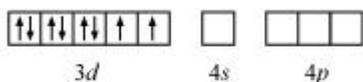


This complex uses inner d orbital (3d) for hybridisation. It is an inner orbital complex. It has no unpaired electrons. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic. This complex is called low spin or spin paired complex.

It has octahedral geometry.

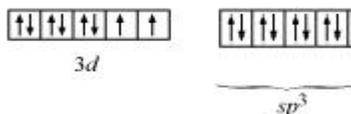
23. Using VBT, explain the type of hybridization, geometry and magnetic property of $[\text{NiCl}_4]^{2-}$. **3 Marks**

Ni, $Z =28$ $[\text{Ar}] 3d^8 4s^2 4p^0$



Ni^{2+} , $[\text{Ar}] 3d^8 4s^0 4p^0$

It undergoes sp^3 hybridisation.



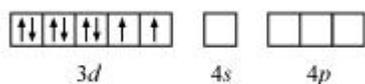
Four pair of electrons from 4 Cl⁻ ions

This complex has unpaired electrons. It is paramagnetic.

$[\text{NiCl}_4]^{2-}$ has tetrahedral structure.

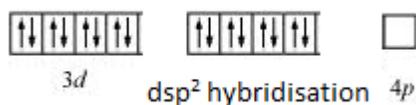
24. Explain the hybridization, geometry and magnetic property in the complex compound $[\text{Ni}(\text{CN})_4]^{2-}$. 3 Marks

Ni, $Z = 28$ $[\text{Ar}] 3d^8 4s^2 4p^0$



Ni^{2+} , $[\text{Ar}] 3d^8 4s^0 4p^0$

When CN^- ligand attacks the central metal ion Ni^{2+} , unpaired electrons in 3d orbital are paired up against Hund's rule. It undergoes dsp^2 hybridisation.



Four pair of electrons from 4 CN^- ligands.

This complex has no unpaired electrons. It is diamagnetic.

$[\text{Ni}(\text{CN})_4]^{2-}$ has square planar structure.

25. What are the limitations of Valence Bond Theory? 2 Marks

This theory,

- has a number of assumptions
- does not give quantitative interpretation of magnetic data
- does not explain colour shown by complexes.
- could not predict tetrahedral or square planar shape for the coordination number 4
- could not distinguish between strong and weak ligands.

26. Why $[\text{CoF}_6]^{3-}$ is called an outer orbital complex? 1 Mark

In this complex, Co^{3+} uses outer d orbital (4d) for hybridization. Therefore it is called an outer orbital complex.

27. What are inner orbital complexes? Give an example.

2 Marks

Inner orbital complex is one where the central metal ion uses inner d orbital $\{(n-1)d$ orbital $\}$ for hybridisation.

e.g: $[\text{Co}(\text{NH}_3)_6]^{3+}$

28. Explain the salient features of crystal field theory.

2 Marks

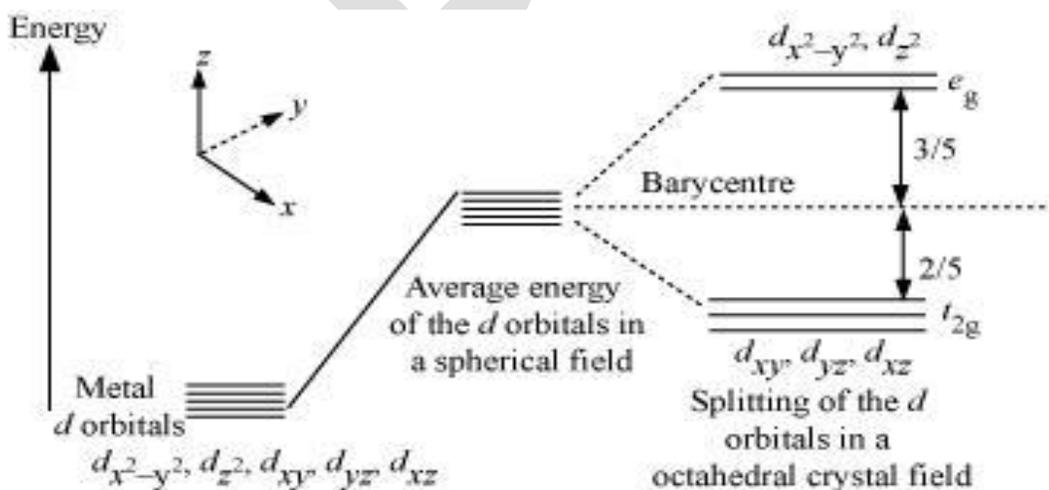
This theory considers ligands as point charges in case of anionic ligands and dipoles in case of neutral molecules. The bond formed between central metal ion and the ligands is purely ionic.

29. What is crystal field splitting? Explain crystal field splitting in octahedral entities using energy level diagram.

3 Marks

In an isolated gaseous central metal atom or ion, all the five d orbitals are having same energy. i.e they are degenerated. In the presence of attacking ligands, it becomes asymmetric and the d orbitals lose degeneracy, resulting in splitting of d orbitals. This is called crystal field splitting.

In an octahedral complex, six ligands surround the central metal ion. $d_{x^2-y^2}$ and d_{z^2} orbitals (called e_g set) are directed along the direction of ligands and experience more repulsion. They have more energy. d_{xy} , d_{yz} and d_{zx} orbitals (called t_{2g} set) are directed between the axes of attacking ligands and experience lesser repulsion by the ligands. They have lesser energy. The energy separation between two split sets is denoted as Δ_o . The energy of e_g orbitals increase by $3/5 \Delta_o$ and that of t_{2g} set decrease by $2/5 \Delta_o$.



30. What is spectrochemical series? Arrange the following ligands in the increasing order of their field strength.

Br⁻, I⁻, H₂O, CO, F⁻

2 Marks

Spectrochemical series is the arrangement of ligands in the order of increasing field strength.

Correct order for the given set is,

I⁻ < Br⁻ < F⁻ < H₂O < CO

31. Draw a figure to show the splitting of d orbitals in a tetrahedral crystal field.

2 Marks

