

COORDINATION COMPOUNDS

SOME IMPORTANT TERMS AND DEFINITIONS:

Coordination compound: A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ion or neutral molecules.

e.g.: $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$ etc.

Double salts: These are the addition compounds which are stable only in solid state but lose their identity in solution form.

e.g.: $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (Potash alum), $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (mohr's salt) etc.

Central metal atom or ion: The metal ion surrounded by number of ions or molecules is called central metal atom or ion.

Ligands: An atom or group of atoms that can donate a pair of electrons to the central metal atom or ion. It may be neutral, positively charged or negatively charged. e.g.: H_2O , NH_3 , CO , CN^- etc.

Chelating ligands: Multidentate ligands are chelating ligands if they can be attached to a particular atom simultaneously through two or more than two sides.

Coordination number: The total number of ligands or donor sites attached to the central metal atom in the coordination sphere is called coordination number.

Isomers: Compounds having same molecular formula but different structures are called isomers.

Types of isomers: (i) Structural isomerism

(ii) Stereoisomerism

(iii) Geometrical or cis-trans Isomerism

Ambidentate ligands: Any ligand which has two or more donor atoms but only one donor atom is attached to the metal ion (M) at a time, during complex formation, is known as ambidentate ligand. E.g.: SCN^- , CN^- , NO_2^- etc.

GUESS QUESTIONS

Q1. Write the IUPAC name of the linkage isomer of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$.

Ans. $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$. - Pentaaminenitrito-O- cobalt (III) chloride.

Q2. Write the IUPAC name of ionisation isomer of $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$.

Ans. The ionisation isomer is $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and its IUPAC name is Pentaamminebromido (III) sulphate.

Q3. What is the coordination number of central metal ion in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$?

Ans. The coordination number of central metal ion (Fe^{3+}) is six.

Q4. Give an example of hexadentate ligand. Write its one use.

Ans. EDTA^{4-} (Ethane 1, 2-diamminetetraacetate ion). It is used in the treatment of lead poisoning.

Q5. What happens when aqueous solution of KCl is added to copper solution?

Ans. A bright green coloured soluble complex, Potassiumtetrachloridocuprate (II) is formed.



Q6. If the value of Δ_0 is less than P in the crystal field, write the arrangement of d4 configuration entity in the crystal field split.

Ans. If $\Delta_0 < P$, no pairing will occur in t_{2g} orbitals. Hence, the configuration of d^4 entity will be $t_{2g}^3 e_g^1$.

Q7. How is ammonia molecule a good ligand?

Ans. Nitrogen in ammonia has a lone pair of electrons. Because of small size of nitrogen, the tendency of donating the lone pair of electron is very high and hence it is a good ligand.

Q8. CO is a stronger complexing agent than ammonia. Why?

Ans. CO ligand produces the large crystal field splitting Δ_0 than ammonia ligand, therefore it is considered to be the stronger ligand.

Q9. Why does a tetrahedral complex of the type $[Ma_2b_2]$ not show geometrical isomerism?

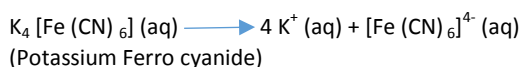
Ans. Because the relative position of ligand A and B are same with respect to each other in the tetrahedral complex $[Ma_2b_2]$, so it does not show geometrical isomerism.

Q10. What do you mean by the double salts and coordination compounds?

Ans. An addition or molecular compound which dissociates into its constituents ions when dissolved in water, is known as double salt. For example,



Any addition or molecular compound which does not lose its identity in aqueous solution i.e. does not dissociates into its constituent ions. Is known as a coordination compound. For example,

**Q11. Write the postulates of Werner's theory of coordination compounds.**

1. The central metal atom possess two types of valencies: (i) Primary valencies and (ii) Secondary valencies.
2. Primary valencies denote oxidation state of the metal ion in the complex and are always satisfied by the negative ions.
3. Secondary valencies correspond to the coordination number of the metal ion in the complex.
4. The geometry of the complex depends upon the arrangements of the secondary valencies in the space.

Q12. Write the formulas for the following coordination compounds:

(i) Tetraammineaquachloridocobalt (III) chloride

(ii) Potassium tetrahydroxozincate (II)

(iii) Potassium trioxalatoaluminate (III)

(iv) Dichloridobis (ethane-1, 2-diamine) cobalt (III) ion.

(v) Tetracarbonylnickel (0)

Ans. (i) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (ii) $K_2[Zn(OH)_4]$ (iii) $K_3[Al(C_2O_4)_3]$ (iv) $[CoCl_2(en)_2]^+$ (v) $[Ni(CO)_4]$

Q13. Write the IUPAC names of the following coordination compounds:

(i). $[Pt(NH_3)_2Cl(NO_2)]$ (ii) $K_3[Cr(C_2O_4)_3]$ (iii) $[CoCl_2(en)_2]Cl$ (iv) $[Co(NH_3)_5(CO_3)]Cl$ (v) $Hg[Co(SCN)_4]$

Ans. (i) Diamminechloridonitrito-N-platinum (II)

(ii) Potassium trioxalatochromate (III)

(iii) Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride.

(iv) Pentaamminecarbonatocobalt (III) chloride

(v) Mercury tetrathiocyanatocobaltate (III)

Q14. Write the IUPAC name of the following coordination compounds:

(i). $[Co(NH_3)_6]Cl_3$ (ii) $[Co(NH_3)_5Cl]Cl_2$ (iii) $K_3[Fe(CN)_6]$ (iv) $K_3[Fe(C_2O_4)_3]$ (v) $[Co(en)_3]Cl_3$

Ans. (i) Hexaamminecobalt (III) chloride

(ii) Pentaamminechloridocobalt (III) chloride

(iii) Potassium hexacyanoferrate (III)

(iv) Potassium trioxalatoferrate (III)

(v) Tris-(ethane-1, 2-diamine) cobalt (III) chloride

Q15. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with central metal ion?

Ans. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

Q16. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.

Ans. $[Co(NH_3)_5Cl]SO_4$ gives white precipitate with $BaCl_2$ solution while $[Co(NH_3)_5SO_4]Cl$ does not respond to this test. On contrary to this, $[Co(NH_3)_5SO_4]Cl$ gives white precipitate with silver nitrate solution while $[Co(NH_3)_5Cl]SO_4$ does not respond to this test. These observations confirm that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.

Q17. What do you mean by spectrochemical series?

Ans. The arrangement of ligands in order of increasing field strength is called a spectrochemical series.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$ from the complex

Q18. How many ions are produced from the complex $[Co(NH_3)_6]Cl_2$ in solution?

Ans. Three (03) ions are produced in the solutions.



Q19. How would you account for the following?

- (a) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
 (b) $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic while $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic.
 (c) $[\text{Ni}(\text{CO})_4]$ possess tetrahedral geometry while $[\text{Ni}(\text{CN})_4]^{2-}$ is square planer.

Ans. (a) In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, metal ion has d^1 configuration. Because of this unpaired electron, d-d transition is possible and hence, it appears coloured. In $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$, no unpaired electron is present in the d-subshell of metal ion hence, d-d transition is not possible, therefore, it would be colourless.

(b) In $[\text{Fe}(\text{CN})_6]^{3-}$, Fe is in +3 oxidation state and has 5 unpaired electrons in its d-orbitals. This complex is formed due to d^2sp^3 hybridisation, after the pairing of d- electrons (because of strong ligand field of CN^- ions). These six hybridised orbitals receive six electron pairs from six molecules of CN^- but one electron in d-subshell remains unpaired, hence it is weakly paramagnetic. But in $[\text{Fe}(\text{CN})_6]^{4-}$, the oxidation state of iron is +2 and has d^6 configuration. These six electrons get paired under the influence of ligand molecules and no electron remains unpaired in d-orbitals, therefore, it is diamagnetic.

(c) In $[\text{Ni}(\text{CO})_4]$, Ni is in zero oxidation state and is sp^3 oxidised. As a result, it possess tetrahedral geometry. While in $[\text{Ni}(\text{CN})_4]^{2-}$, Ni is in +2 oxidation state and is dsp^2 hybridised. As a result, it is square planer.

Q20. Draw figures to show splitting of degenerate d-orbitals in an octahedral and a tetrahedral crystal field.

(i) **In octahedral complex.**

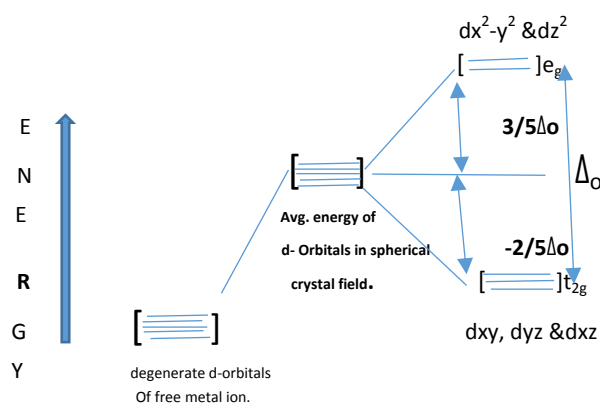


Fig: Splitting of five d-orbitals in octahedral crystal field.

(ii) **In tetrahedral crystal field.**

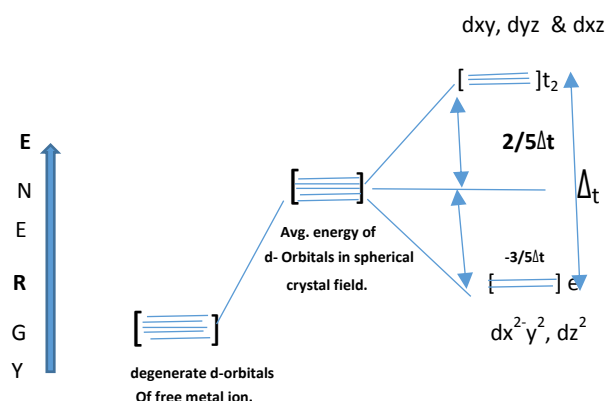


Fig: Splitting of five d-orbitals in tetrahedral crystal field.

Q21. $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why?

Ans. In $[\text{NiCl}_4]^{2-}$, Ni is in +2 oxidation state with the configuration $3d^8 4s^0$. Cl^- ion being weak ligand, it cannot pair up the electrons in 3d-orbitals. Hence, it is paramagnetic. In $[\text{Ni}(\text{CO})_4]$, Ni is in zero oxidation with the configuration $3d^8 4s^2$. In the presence of CO ligand, the 4s electrons shift to 3d to pair up 3d electrons. Thus, there is no unpaired electron present. Hence, it is diamagnetic.

Q22. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital octahedral complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital octahedral complex. Explain

Ans. In $[\text{Co}(\text{NH}_3)_6]^{3+}$, Co is in +3 oxidation state with the configuration $3d^6$. In the presence of NH_3 a strong ligand, the 3d electrons pair up leaving two d-orbitals empty. Hence, the hybridization is d^2sp^3 forming an inner orbital octahedral complex.

In $[\text{Ni}(\text{NH}_3)_6]^{2+}$, Ni is in +2 oxidation state with the configuration $3d^8$. In presence of NH_3 , the 3d electrons do not pair up. The hybridization involved is sp^3d^2 forming an outer orbital octahedral complex.

Q. Predict the shapes and magnetic properties of the following compounds:

$[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoF}_6]^{3-}$, $[\text{NiCl}_4]^{2-}$, $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{FeF}_6]^{3-}$, $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

Ans.

Compounds	O.S of M^{n+}	Configuration	Nature of ligand	Type of hybridization	Shape of the compound	No. of unpaired electrons.	Magnetic Properties.
$[\text{Co}(\text{NH}_3)_6]^{3+}$	+3	$3d^6 4s^0$	Strong	$d^2 sp^3$	Octahedral	0	diamagnetic
$[\text{CoF}_6]^{3-}$	+3	$3d^6 4s^0$	Weak	$sp^3 d^2$	Octahedral	4	paramagnetic
$[\text{NiCl}_4]^{2-}$	+2	$3d^8 4s^0$	Weak	sp^3	Tetrahedral	2	paramagnetic
$[\text{Ni}(\text{CO})_4]$	0	$3d^8 4s^2$	Strong	sp^3	Tetrahedral	0	diamagnetic
$[\text{Ni}(\text{CN})_4]^{2-}$	+2	$3d^8 4s^0$	Strong	dsp^2	Square planer	0	diamagnetic
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	+2	$3d^8 4s^0$	Strong	$sp^3 d^2$	Octahedral	2	paramagnetic
$[\text{Fe}(\text{CN})_6]^{4-}$	+2	$3d^6 4s^0$	Strong	$d^2 sp^3$	octahedral	0	diamagnetic
$[\text{Fe}(\text{CN})_6]^{3-}$	+3	$3d^5 4s^0$	Strong	$d^2 sp^3$	Octahedral	1	paramagnetic
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	+3	$3d^5 4s^0$	Weak	$sp^3 d^2$	Octahedral	5	paramagnetic
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	+3	$3d^3 4s^0$	Strong	$d^2 sp^3$	Octahedral	3	paramagnetic
$[\text{FeF}_6]^{3-}$	+3	$3d^5 4s^0$	Weak	$sp^3 d^2$	Octahedral	5	paramagnetic
$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	+3	$3d^6 4s^0$	Strong	$d^2 sp^3$	Octahedral	0	diamagnetic
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	+2	$3d^8 4s^0$	weak	$sp^3 d^2$	octahedral	2	paramagnetic

Q. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic. Explain

Ans. In both the complexes, Fe is in +3 oxidation state with the configuration $3d^5$. CN^- is strong ligand. In its presence, 3d electrons pair up leaving only one electron unpaired. The hybridization is $d^2 sp^3$ and forms inner orbital octahedral complex. In contrary to this, H_2O is a weak ligand and in its presence 3d electrons do not pair up. The hybridization is $sp^3 d^2$ and forms an outer orbital octahedral complex containing 5 unpaired electrons. Hence it is strongly paramagnetic.

Q23. Distinguish between inner orbital octahedral and outer orbital octahedral complex.

Ans.

Inner orbital octahedral complex	Outer orbital octahedral complex
<ol style="list-style-type: none"> It involves (n-1) d, ns and np orbitals for $d^2 sp^3$ hybridization. It is also known as low spin complex. It is generally diamagnetic in nature due to all paired electrons. Ligands present in these complexes are strong field. Ex. $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ etc. 	<ol style="list-style-type: none"> It involves n d, n s and n p orbitals for $sp^3 d^2$ hybrid orbitals. It is known as high spin complex. It is generally paramagnetic in nature due to presence of unpaired electron. Ligands present in these complexes are weak field. Ex. $[\text{FeF}_6]^{3-}$, $[\text{CoF}_6]^{3-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ etc.

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