28

Co-ordination Compounds

QUICK LOOK

Molecular or addition compounds are formed when stoichiometric amounts of two or more stable compounds join together. These fall into two categories:

- Those which lose their identity in solution.
- Those which retain their identity in solution.

An aqueous solution of carnallite shows the properties of K^+, Mg^{2+} and Cl^- ions. Potassium alum solutions similarly show the properties of K^+, Al^{3+} and SO_4^{2-} ions. They are called double salts and exist only in the crystalline state. The other two examples of addition compounds behave in a very different way from the double salts. When dissolved they do not form Cu^{2-}, or Fe^{2+} and CN^- ions, but instead give more complicated structures-the cuproammonium ion $[Cu(H_2O)_2\ (NH_3)_4]^{2+}$ and the ferrocyanide ion $[Fe(CN)_6]^{4-}$. These are complex ions and exist are a single entity. Complex ions are indicated by square brackets. Molecular compounds of this type are called coordination compounds. Co-ordination compounds are the compounds in which the central metal atom is linked to ions or neutral molecules by co-ordinate bonds, e.g. $\left[Cr\left(H_2O\right)_5 Cl\right]^{2+}$. If the species thus formed as given above carries positive charge, it is called a complex ion.

- **Double salts:** Those addition compounds which lose their identity in solution are called double salts. For example, when K_2SO_4 solution is added to $Al_2(SO_4)_3$ solution, species formed gives tests of K^+, Al^{3+} and SO_4^{2-} ions.

  $$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$$

  $$\xrightleftharpoons{(aq.)} (aq.) + 2Al^{+3}(aq). + 4SO_4^{2-}(aq.)$$

  Other Examples

  Ferric alum: $K_2SO_4.Fe_2(SO_4)_3.24H_2O$

  Chrome alum: $K_2SO_4.Cr_2(SO_4)_3.24H_2O$

  Carnallite: $KCl.MgCl_2.6H_2O$

  Mohr's salt: $(NH_4)_2SO_4.FeSO_4 6H_2O$

  Tutton salt: $M_2SO_4, CuSO_4.6H_2O\ [M = Na, K]$

- **Coordination compounds:** Those addition compounds which retain their identity (*i.e.,* doesn't lose their identity) in solution are called coordination compounds. For example, when KCN solution is added to $Fe(CN)_2$ solution, the species formed, no longer gives tests of Fe^{2+} and CN^-.

  $$Fe(CN_2) + 4KCN \longrightarrow Fe(CN).4KCN \text{ or}$$

  $$K_4[Fe(CN)_6(aq.) \rightleftharpoons 4K^+(aq.) + \underset{4:1\ \text{complex}}{[Fe(CN_6)(aq)]}$$

  Other examples are, $[Cu(NH_3)_4]SO_4(aq.) \rightleftharpoons$

  $$\underset{1:1\ \text{complex}}{[Cu(NH_3)_4]^{2+}(aq.) + SO_4^{2-}(aq.)}\ K_2[Zn(CN_4)](aq.)$$

  $$\rightleftharpoons \underset{2:1\ \text{complex}}{2K^+(aq.) + [Zn(CN)_4]^{2-}(aq.)}$$

  Also, coordination compound is defined as species in which metal atom or ion is attached to group of neutral molecules/ions by coordinate covalent bonds.

- **Ligand:** It is an ion or molecule capable of donating a pair of electrons to the central atom via a donor atom. The neutral molecules, anions or cations which are directly lined with central metal atom or ion in the coordination entity are called ligands. Ligands may be simple ions such as Br^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules such as proteins.

  When a ligand is attached to a metal ion through a single donor atom. As with Cl^-, H_2O or NH_3, the ligand is said to be unidenate. Similarly when a ligand is bond through two dononr atoms, as in $H_2NCH_2CH_2NH_2$ (ethane-1, 2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be didentate and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$ or ethylene-diaminetetraacetic acid (EDTA), the ligand is said to be polydentate.

Classification of Ligands: There are several ways to classify ligands and these are discussed as follow:

- **Based upon charges**

  Neutral ligands: H_2O, NO, CO, C_6H_6, etc.

  Positive ligands: $\overset{+}{N}O$ and $NH_2 - \overset{+}{N}H_3$

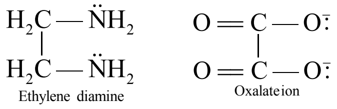
  Negative ligands: Cl^-, NO_2^-, CN^-, OH^-

- **Based upon denticity of the ligand:** The number of donations accepted by a central atoms from a particular ligand is known as the denticity of the ligand. Ligands may be classified as follows based on their denticity: Monodentate: Only one donation is accepted from the ligand.

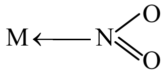
  Example: $H_2O, NO, CO, NH_3, CO_3^{2-}, Cl^-$, etc.

  Bidentate: Ligands with two donor atoms, e.g. ethylenediamine, $C_2O_4^{2-}$ (oxalate ion) etc. Two donations are accepted from the ligand.
- **Chelating:** Multidentate ligand simultaneously co-ordinating to a metal ion through more than one sit, a ligand that can form a ring structure with the central atom is called a chelating ligand. All polydenate ligands are the example of chelating ligands. Chelated complexes are more stable than similar complexes with monodentatc ligands as dissociation of the complex involves breaking two bonds rather than one. However, it must be noted that NH_2NH_2 and $N(CH_2-CH_2)_3N$ cannot act as chelating ligands due to the formation of three membered ring and locked structure, respectively.

  Example:



- **Ambidentate ligand:** A ligand that may have more than one kind of donor sites but at a time only one kind of donor site is utilized for donation is called as ambidenate ligand. Ligands which can ligate through two different atoms present in it. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate through either the nitrogen or the oxygen atoms to a central metals atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds. For example,



nitrito-N

$M \longleftarrow O - N = O$ nitrito-O

$M \longleftarrow SCN$ thiocyanato or thiocyanato-S

$M \longleftarrow NCS$ isothiocyanato or thiocyanato-N

- **Based upon bonding interaction between the ligand and the central atoms**

  Classical or simple donor ligand: These ligands only donate the lone pair of electrons to the central atom. For example, $O^{2-}, OH^-, F^-, NH_2^-, NH_3, N^{3-}$, etc.

  Non-classical or π-acid or π-acceptor ligand: These ligands not only donate the lone pair of electrons to the central atom but also accept the electron cloud from the central atom in their low-lying vacant orbitals. This kind of back donation is known as 'synergic effect' or 'synergic bonding'.

  Example: $Co, \bar{C}N, \bar{N}O, PF_3, PR_3$ $(R = H, Et, Ph...)$, C_2H_4, C_2H_4, CO_2, etc.
- In case of CO, the back donation to the π* orbital of central atom may be depicted as:

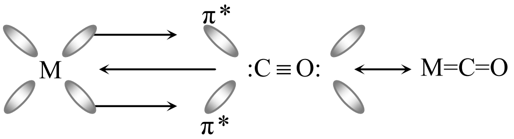


Figure: 28.1

By valence bond or molecular orbital theory, it is well understood that the bond order of C—O bond decreases but the C—O bond length must increase due to synergic effect.

Similarly, as $\bar{C}N$ and $\overset{+}{N}O$ are isoelectronic with CO, so back donation takes place in these species also in the π^* orbitals and the same conclusion can be drawn for the bond order and bond lengths.

- In case of PR_3,the back donation may be depicted as:

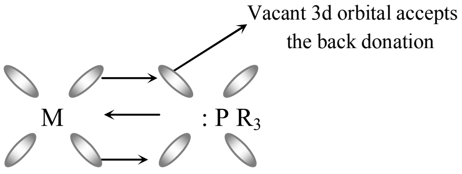


Figure: 28.2

- In case of C_2H_4, the back donation may be depicted using the example of Zeise's salt.

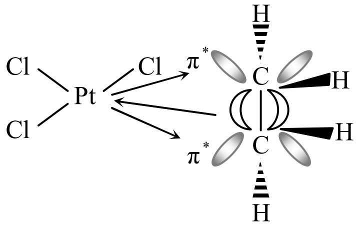


Figure: 28.3

Here the back donation is accepted in the π* orbitals of C—C bond. Hence, the bond order of C—C bond decreases and the bond length increases as compared to free C_2H_4 molecule. Due to back bonding C_2H_4 molecule loses its planarity. Similarly, C_2H_2 molecules loses its linearity not the planarity.

- **IUPAC Nomenclature of complex compounds:** In order to name complex compounds certain rules have been framed by IUPAC. These are as follows:
- The positive part of a coordination compound is named first and is followed by the name of negative part.
- The ligands are named first followed by the central metal. The prefixes di-, tri-, tetra-, etc., are used to indicate the number of each kind of ligand present. The prefixes bis (two ligands), tris (three ligands), etc., are used when the ligands includes a number e.g., dipyridyl, bis (ehylenediamine).
- In polynuclear complexes, the bridging group is indicated in the formula of the complex by separating it from the rest of the complex by hyphens. In polynuclear complexes (a complex with two or more metal atoms), bridging ligand (which links two metal atoms) is denoted by the prefix μ before its name.

- **Naming of ligands**: The different types of ligands i.e. neutral, negative or positive are named differently in a complex compound. When a complex species has negative charge, the name of the central metal ends in – ate. For some elements, the ion name is based on the Latin name of the metal (for example, argentate for silver). Some such latin names used (with the suffix – ate) are given below:

Fe	Ferrate	Cu	Cuperate
Ag	Argentate	Au	Aurate
Sn	Stannate	Pb	Plumbate

- **Point of attachment in case unidentate ligands with more than co-ordinating atoms (ambidentate ligands) :** The point of attachment in case of unidentate ligands with more than one co-ordinating atoms is either indicated by using different names for the ligands (e.g, thiocyanato and isothiocyanato) or by placing the symbol of the donor atom attached, the name of the ligand separated by a hypen.

$(NH_4)_3[Cr(SCN)_6]$
Ammonium hexathioxyanato -S-chromate (III)
or
Ammonium hexathiocyanatochromate (III)

$(NH_4)_2[Pt(NCS)_6]$
Ammonium hexathiocyanato -N-platinate (IV)
or
Ammonium hexaisothiocyanatoplatinate (IV)

- **Name of the bridging groups:** If a complex contains two or more central metal atoms or ions, it is termed as polynuclear. In certain polynuclear complexes. ligands may link the two metal atoms or ions. Such ligands which link the two metal atoms or ions in polynuclear complexes are termed as bridge ligands. These bridge ligands are separated from the rest of the complex by hyphens and denoted by the prefix μ. If there are two or more bridging groups of the same kind, this is indicated by di- $\mu-$, tri $-\mu-$, etc.

$[(NH_3)]_5Co-NH_2-Co(NH_3)_5](NO_3)_5$
μ-amidobis [pentaamminecobalt (III)] nitrate

$[(NH_3)_5Co-OH-Co(NH_3)_5]Cl_5$
μ- hydroxobis [pentaamminecobalt (III)] chloride

$[(CO)_3Fe(CO)_3Fe(CO)_3]$
tri- μ carbonylbis [tricarbonyliron (0)]

$[Be_4O(CH_3COO)_6]$
hexa -μ-acetato(O,O')-$\mu_4$oxotetraberyllium(II)

- If any lattice component such as water or solvent of crystallisation are present, these follow the name and are preceded by the number of these groups (molecules of solvent of crystallisation) in Arabic numerals.

$[Cu(H_2O)_4]SO_4.H_2O$
Tetraaquacopper(II)sulphate1−water

$[Cr(H_2O)_4Cl_2]Cl.2H_2O$
tetraaquadichlorochromium (III(chloride 2-water

- Following punctuation rules should also be followed while writing the name of the complex compounds. The name of the complete compound should not start a capital letter, e.g.,

$[Cu(NH_3)_4]SO_4$
Tetraamminecopper (II) sulphate (Correct)
Tetraamminecopper (II) sulphate (Incorrect)

The full name of the complex ion should be written as one word without any gap. There should be a gap between the cation and anion in case of ionic complexes. The full name of non-ionic complexes should be written as one word without any gap.

- **Drawbacks of valence bond theory**
  - The Classification of complexes as ionic or outer orbital and covalent or inner orbital is arbitrary. It could not explain why some complexes of metal ion use inner orbitals (d^2sp^3, low spin complexes) whereas some other make high spin complexes (sp^3d^2).
  - The expalination offered in the VBT for many complexes of Cu(II) involving promotion of a 3d electron to a 4p orbital was unsatisfactory, as explained earlier. It can't predict effectively whether a four coordinated complex is tetragonal or square planar e.g., $[Cu(NH_3)_4]^{2+}$ is suggested to have sp^3 configuration by Valence Bond. Theory but X-rays study shows its geometry as square planar, *i.e.,* dsp^2.
  - It doesn't explain the variation of magnetic properties of complex with temperature.
  - It doesn't explain or predicted any distortion in symmetrical complexes. A number of assumptions are involved.

  - There is no quantitative interpretation of magnetic data.
  - It has nothing to say about the spectral properties of coordination compounds.
  - It does not given a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
  - It does not distinguish between strong and weak ligand.

- **Crystal field theory:** The crystal field theory, first prposed by Hand Bethe in 1929 to explain the colour and magnetic properties of some solid crystalline salts of metals. It was also applied to interpret the electronic spectra of transition metal complexes. The principal qualitative aspects of the crystal field theory (CFT) may be summarized as follows.
  - It is a hypothetical modal in which the ligands are imagined to be point negative charges (either from the net negative charge on the ligand or from the negative end of the ligand dipole arising from the lone pair of electrons on its donor atom). the ionic ligands (eg F^-,Cl^- etc.) are regarded as negative point charges, while neutral ligands (eg H_2O,NH_3 etc) are regarded as dipoles.
  - The bonding between the central metal cation and ligands is purely electrostatic or coulombic in nature. The theory now considers only the electrostatics interaction between a metal and the ligands. This may be considered in two steps: (i) electrostatics attraction between the positive nucleus of the metal and the negatively charged electrons of the ligands (imagined as point charges): (ii) electrostatic repulsion force between the electrons in the valence shell of the metal and the ligand electrons.
  - The arrangement of the ligands around the central metal ion is such that the repulsion between these negative points is minimum.
  - Splitting of d-orbital energies: The five d-orbitals in an isolated gaseous metal atom/ion are degenerate i.e., they have equal energy. If a spherically symmetric field of negative charges is placed around the metal, the orbitals will remain degenerate, but all of them will be raised in energy as a result of repulsion between the negative field and the negative electrons in the orbitals. If the field results from the influence of real ligands (either anions or the negative ends of dipolar ligands, such as NH_3 or H_2O), the symmetry of the field will be less than spherical and the degeneracy of the d-orbitals will be removed. It is this splitting of d orbital energies and its effects that form the basis of crystal field theory.

- **Geometrical relationship of the d-orbitals:** There is no unique way of representing the five d-orbitals, but the most convenient representations are shown in figure. In fact, there are six wave functions but can be written for orbitals having the typical four-lobed form (d_{xy} and $d_{x^2-y^2}$, for example), but there can be only five d-orbitals having any physical reality, therefore, one of them the "d_{z^2}" orbital is conventionally regarded as a linear combinations of two others, the $d_{z^2-y^2}$ and $d_{z^2-x^2}$.

Thus these latter two orbitals have no independent existence, but the d_{z^2} can be thought of as having the average properties of the two shown in figure. Therefore, since both have high electron density along the z-axis, the d_{z^2} orbital has a large fraction of its electron density concentrated along the same axis. Also, since one of the component wave function ($d_{z^2-x^2}$) has lobes the x-axis and the other ($d_{z^2-y^2}$) along the y-axis, the resultant d_{z^2} orbital has a tours of electron density in the xy plane, which is often referred to as “doughnut or collar”. It will be better to divide the set of d orbitals in two groups:

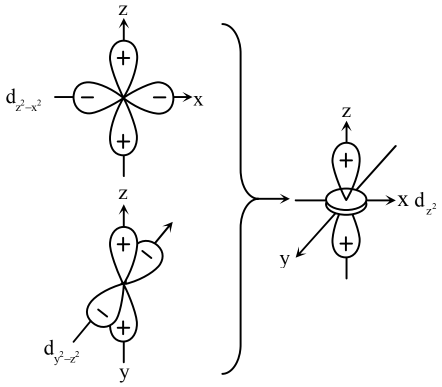


Figure: 28.4

  - The orbitals in which lobes lie along the axes ($d_{x^2-y^2}$, d_{z^2}): reffered to as "e_g" orbitals in Octahedral symmetry and “e” orbitals in Tetrahedral symmetry. (Also called as doubly degenerate orbitals).
  - The orbitals in which lobes lies in between the axes (d_{xy}, d_{yz}, d_{zx}): reffered to as "t_{2g}" orbitals in Octahedral symmetry and "t_2" orbitals in Tetrahedral symmetry. (Also called triply degenerate orbitals.)

- **Crystal field splitting of d-orbitals in octahedral complexes:** Assume six ligands symmetrically positioned along the Cartesian axes, with metal atom at origin as shown the figure

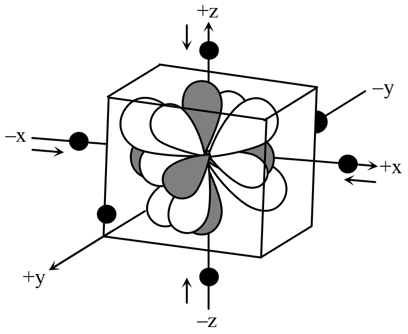


Figure: 28.5

Now there will be repulsion between the electrons of ligands and that present in the d orbitals and consequently the energy of the d orbitals will be raised. However this raise in energy will not be same for every d orbital and it can be clearly seen that the "e_g" orbtials will be raised more in energy due to stronger repulsions than the "t_{2g}" orbitals. To understand this splitting more clearly we can assume it to be a two step process as shown in figure.

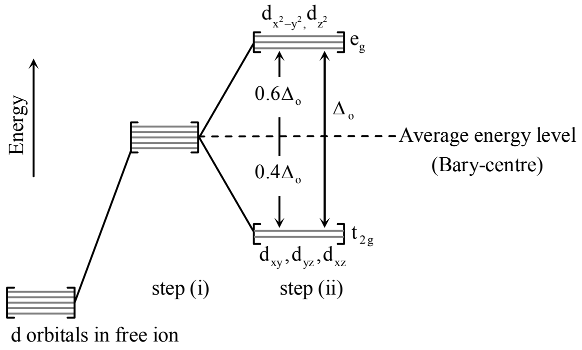


Figure: 28.6

- **Step (i):** Average energy of the d-orbitals of metal atom/ion in a hypothetical spherical crystal field.
- **Step (ii):** Splitting of d-orbitals of metal atom/ion in octahedral crystal field. In the first step, the ligands approach the central metal, producing a hypothetical spherical field which repels all of the d-orbitals to the same extent. In the second, the ligands exert an octahedral field, which splits the orbital degeneracy. In going from the first to the second step, average energy (the bary centre, or "center of gravity") of the orbitals must remains constant and it is necessary for the two e_g orbitals to be the further repelled by 0.6 Δ_0 while the three t_{2g} orbitals are stabilized to an extent of 0.4 Δ_0 as shown in figure. This constancy of the bary centre of the d-orbitals holds for all complexes, regardless of geometry. So

$$\boxed{\text{C.F.S.E.} = [-0.4(n)t_{2g} + 0.6(n')e_g]\Delta_o + np}$$

Where n & n' are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_o crystal field splitting energy for octahedral complex. n represents the number of extra electron pairs formed because of the ligands in comparison to normal degenerate configuration.

- **Isomerism among Coordination Compounds:** When the same empirical formula applies to two or more complexes having different structures, either in atom connectivity or in the orientation of atoms in space, the compounds are referred to as isomers. Isomerism in complex compounds may arise in many ways. The number of isomers depend on the coordination number of the metal and the geometry adopted by it and also on the nature of the ligand. In one respect such isomerism differs from the isomerism observed in carbon compounds. Actually, the stereochemistry of coordination compounds is more varied since metals involves much larger number of orbitals (s, p and d) whose energy and spatial distribution are widely different. The main types within each category may be further classified as follows:

Isomerism

Constitutional Isomerism
1. Ionization
2. Hydrate
3. Coordinate
4. Linkage
5. Polymerization
6. Ligand

Stereoisomerism
1. Geometrical
2. Optical

Names of Ligands

- Names of anionic ligands (both organic and inorganic) end in –o. The anion names are usually changed accordingly:
  $\text{—ide} \longrightarrow \text{ido; —ite} \longrightarrow \text{ito; —ate} \longrightarrow \text{1to.}$
  Exceptions are halides (halo), hydroxides (hydroxo), peroxides (peroxo) etc.
- Names of neutral and cationic ligands are used without modification and placed within enclosing mark except for aqua, ammine carbonyl and nitrosyl.

MULTIPLE CHOICE QUESTIONS

Basic Terms

1. In K_4 Fe $(CN)_6$?

a. (CN) are linked with primary valency
b. (CN) are linked with secondary valency
c. K are linked with secondary valency
d. K are linked with non-ionic valency

2. Which of the following acts as a bidentate ligand in complex formation?

a. Acetate
b. Oxalate
c. Thiocyanate
d. EDTA

3. What is the co-ordination number of the metal in $[Co\ (en)_2\ Cl_2]+$?

a. 4
b. 5
c. 6
d. 3

4. The coordination number of a metal in coordination compounds is:

a. Same as primary valency
b. Sum of primary and secondary valencies
c. Same as secondary valency
d. None of these

5. The number of ions formed when cuprammonium sulphate is dissolved in water is:

a. 1
b. 2
c. 4
d. Zero

6. The coordination number of a central metal atom in a complex is determined by:

a. The number of ligands around a metal ion bonded by sigma and pi-bonds both.
b. The number around a metal ion bonded by pi-bonds
c. The number of ligands around a metal ion bonded by sigma bonds
d. The number of only anionic ligands bonded to the metal ion

7. EDTA has coordination number:

a. 3
b. 4
c. 5
d. 6

8. Coordination number of Zn in ZnS (zinc blende) is:

a. 6
b. 4
c. 8
d. 12

9. The number of neutral molecules or negative groups attached to the central metal atom in a complex ion is called:

a. Atomic number
b. Effective atomic number
c. Coordination number
d. Primary valency

10. The formula of alum is:

a. $K_2SO_4.Al_2(SO_4)_3.24H_2O$
b. $K_4[Fe(CN)_6]$
c. $K_2SO_4.Al_2(SO_4)_3.6H_2O$
d. $Na_2CO_3.10H_2O$

Nomenclature, Oxidation State and EAN number

11. How many ions are produced in aqueous solution of $[Co(H_2O)_6]Cl_2$?

a. 2
b. 3
c. 4
d. 6

12. In K_4 [Fe $(CN)_6$],the E.A.N. of Fe is:

a. 33
b. 35
c. 36
d. 26

13. The oxidation state of cobalt in the complex compound $[Co\ (NH_3)_6]Cl_3$ is:

a. + 3
b. + 6
c. + 5
d. + 2

14. The oxidation number of Pt in $[Pt(C_2H_4)Cl_3]^-$ is:

a. + 1
b. + 2
c. + 3
d. + 4

15. The effective atomic number of cobalt in the complex $[Co(NH_3)_6]^{3+}$ is:

a. 36
b. 33
c. 24
d. 30

16. The EAN of iron in potassium ferricyanide is:

a. 18
b. 54
c. 35
d. 23

17. Oxidation state of Fe in $K_3[Fe(CN)_6]$?

a. 2
b. 3
c. 0
d. None of these

18. IUPAC name of $[Co(NH_3)_5NO_2]Cl_2$?

a. Pentamminenitrocobalt (III) chloride
b. Pentamminenitrosocobalt (III) chloride
c. Pentamminenitrocobalt (II) chloride
d. None of these

19. The IUPAC name of $[Cr(NH_3)_6]^{3+}$ is:

a. Hexamminechromium (VI) ion
b. Hexamminechromium (III) ion
c. Hexamminechromium (II) ion
d. Hexamminechloride

20. The value of x which appears in the complex $[Ni(CN)_4]^x$ is:

a. + 2
b. – 2
c. 0
d. 4

Isomerism and Magnetic properties

21. Which one of the following octahedral complexes will not show geometric isomerism? (A and B are monodentate ligands)

a. $[MA_5B]$

b. $[MA_2B_4]$

c. $[MA_3B_3]$

d. $[MA_4B_2]$

22. $\left[Co(NH_3)_5Br\right]SO_4$ and $\left[Co(NH_3)_5SO_4\right]Br$ are examples of which type of isomerism:

a. Linkage

b. Geometrical

c. Ionization

d. Optical

23. Which would exhibit ionisation isomerism?

a. $[Cr\left(NH_3\right)_6]Cl_3$

b. $[Co\left(NH_3\right)_5Br]SO_4$

c. $[Cr(en)_2Cl_2]$

d. $[Cr(en)_3Cl_3]$

24. Which one of the following will not show geometrical isomerism?

a. $[Cr(NH_3)_4Cl_2]Cl$

b. $[Co(en)_2Cl_2]Cl$

c. $[Co(NH_3)_5NO_2]Cl_2$

d. $[Pt(NH_3)_2Cl_2]$

25. $[Co\left(NH_3\right)_4Cl_2]^+$ exhibits:

a. Geometrical isomerism

b. Optical isomerism

c. Bonding isomerism

d. Ionisation isomerism

26. The number of geometrical isomers for $[Pt(NH_3)_2Cl_2]$ is:

a. Two

b. One

c. Three

d. Four

27. The total number of possible isomers for the complex compound $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ are:

a. 3

b. 4

c. 5

d. 6

28. Which of the following compounds is colourless?

a. $Cu_2(CH_3COO)_4.2H_2O$

b. Cu_2Cl_2

c. $CuSO_4.5H_2O$

d. $[Cu(NH_3)_4]SO_4.4H_2O$

29. Which of the following complex will give white precipitate with $BaCl_2$ (aq.)?

a. $[Co(NH_3)_4SO_4]NO_2$

b. $[Cr\left(NH_3\right)_5SO_4]Cl$

c. $[Cr(NH_3)_5Cl]SO_4$

d. Both b and c

30. In coordination compound $[Co(en)_2Cl_2]Cl$ which is false:

a. Show geometrical Isomerism

b. Show optical Isomerism

c. Show ionic Isomerism

d. A octahedral complex

Hybridisation and Geometry

31. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl(s). The structure of the complex is:

a. $[Co(NH_3)_5Cl]Cl_2$

b. $[Co(NH_3)_3Cl_3].2NH_3$

c. $[Co(NH_3)_4Cl_2]Cl.NH_3$

d. $[Co(NH_3)_4Cl]Cl_2.NH_3$

32. The shape of $[Fe(CN)_6]^{4-}$ ion is:

a. Hexagonal

b. Pyrimidal

c. Octahedral

d. Octagonal

33. The geometry of $Ni(CO)_4$ and $Ni(PPh3)_2Cl_2$ are:

a. Both square planar

b. Tetrahedral and square planar respectively

c. Both tetrahedral

d. Square planar and tetrahedral respectively

34. Which of the following shall form an octahedral complex?

a. d^4 (low spin)

b. d^8 (high spin)

c. d^6 (low spin)

d. None of these

35. CN^- is a strong field ligand. This is due to the fact that:

a. It can accept electron from metal species

b. It forms high spin complexes with metal species

c. It carries negative charge.

d. It is a pseudohalide

Complexes and Complex Stability

36. Which of the following complexes has the highest stability constant at 298 K?

a. $[CdCl_4]^{2-}$

b. $[CdBr_4]^{2-}$

c. $[CdI_4]^{2-}$

d. $[Cd(CN)_4]^{2-}$

37. A co-ordination complex compound of cobalt has the molecular formulae containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution on reacting with excess of $AgNO_3$, AgCl precipitate. The ionic formula for this complex would be:

a. $[Co\ (NH_3)_5\ (NO_2)]\ Cl_2$
b. $[Co(NH_3)_5\ Cl]\ [Cl(NO_2)]$
c. $[Co(NH_3)_4(No_2)Cl][(NH_3)Cl]$
d. $[Co(NH_3)_5][(NO_2)_2Cl_2]$

38. Prussian blue is formed when:

a. Ferrous sulphate reacts with $FeCl_3$
b. Ferric sulphate reacts with $K_4\ [Fe\ (CN)_6]$
c. Ferrous ammonium sulphate reacts with $FeCl_3$
d. Ammonium sulphate reacts with $FeCl_3$

39. Silver sulphide dissolved in a solution of sodium cynamide to form the complex:

a. $Na\ [Ag\ (CN)_2]$
b. $Na_3\ [Ag\ (CN)_4]$
c. $Na_5\ [Ag\ (CN)_6]$
d. $Na_2\ [Ag\ (CN)_2]$

40. The cation that does not form an amine complex with excess of ammonia is:

a. Cd^{2+}
b. Al^{3+}
c. Cu^{2+}
d. Ag^{+}

Application of Organometallics

41. Ziegler-Natta catalyst is an organometallic compound of which metal:

a. Iron
b. Zirconium
c. Rhodium
d. Titanium

42. Which of the following is formed when *n*-butyl lithium reacts with tin (II) chloride:

a. LiBr
b. $Et_4\ Pb$
c. $(C_4H_9)_4\ Sn$
d. $(C_2H_5)_4\ Pb$

43. Which one is not an organometallic compound?

a. RMgX
b. C_2H_5ONa
c. $(CH_3)_4\ Sn$
d. KC_4H_9

44. Among the following, which is not the π-bonded organometallic compound:

a. $(CH_3)_4\ Sn$
b. $K[PtCl_3\ (\eta^2 - C_2H_4)]$
c. $Fe\ (\eta^5 - C_5H_5)_2$
d. $Cr\ (\eta^6 - C_6H_6)_2$

45. Wilkinson's catalyst is used in

a. Polymerization
b. Condensation
c. Halogenation
d. Hydrogenation

46. Which of the following is an organo-metallic compound?

a. Lithium ethoxide
b. Ethyl lithium
c. Lithium acetate
d. Lithium carbide

47. Which of the following is not an organometallic compound?

a. Ethyl magnesium bromide
b. Tetraethyl lead
c. Sodium ethoxide
d. Trimethyl aluminium

48. Which of the following does not have a metal carbon bond?

a. $K\ [Pt\ (C_2\ H_4)\ Cl_3]$
b. $Ni\ (CO)_4$
c. $Al(OC_2H_5)_3$
d. C_2H_5MgBr

49. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect:

a. Cyanocobalamin is B_{12} and contains cobalt.
b. Haemoglobin is the red pigment of blood and contains iron.
c. Chlorophylls are green pigments in plants and contains calcium.
d. Carboxypepticase-A is an enzyme and contains zinc.

50. The π – bonded organo metallic compound which has ethene as one of its component is:

a. Zeise's salt
b. Ferrocene
c. Dibenzene chromium
d. Tetraethyl tin.

NCERT EXEMPLAR PROBLEMS

More than One Answer

51. Which of the following statements is correct for the complex $[Fe(H_2O)_5NO]SO_4$?

a. The EAN value of Fe in this complex depends on the charge of NO ligand
b. The EAN value of Fe in this complex does not depends on the charge of NO ligand
c. The hybridization of the central atom is d^2sp^3.
d. It is paramagnetic with $\mu = 1.73$ B.M.

52. The EAN value of $[\mathrm{Ti}(\sigma-C_5H_5)_2(\pi-C_5H_5)_2]^0$ is:

a. 32 **b.** 33

c. 34 **d.** 35

53. Which of the following ligands can show linkage isomerism?

a. NO **b.** NH_3

c. NO_3^- **d.** None of these

54. In [isothiocyanatothiocyanato (1-diphenylphosphino-3-dimethylaminopropane) palladium (II)], the Pd–NCS combination is linear while the Pd–SCN combination is bent with the $\angle \mathrm{Pd-S-C}$ of 107.3°. Predict the structure adopted for SCN^- group in this complex:

a. $\overline{S}-C\equiv N:$ **b.** $S=C=\overline{N}$

c. Hybrid of (A) and (B) **d.** Cannot be predicted

55. Choose the correct order for Δ_0 for the following complexes:

A. $[Co(H_2O)_6]^{3+}$ **B.** $[Co(H_2O)_6]^{3-}$

C. $[Fe(H_2O)_6]^{3+}$ **D.** $[Fe(CN)_6]^{3-}$

a. A < B < C < D **b.** A < C < B < D

c. A < B = C < D **d.** A < B < D < C

56. $[Fe(H_2O)_4(CN)_2]$ is the empirical formula of a compound which has magnetic moment corresponding to 2^{2}_{3} unpaired electrons per iron. The best possible formula of the compound is:

a. $[Fe(H_2O)_4(CN)_2]_2[Fe(H_2O)_4(CN)_2]$

b. $[Fe(H_2O)_6][Fe(H_2O)_2(CN)_4]$

c. $[Fe(H_2O)_6]_2[Fe(CN)_6]$

d. None of these

57. Which of the following statements is true for the compounds $[CoF_6]^{3-}$ (I) and $[NiF_6]^{2-}$ (II)?

a. Both I and II are paramagnetic

b. Both I and III are diamagnetic

c. I is paramagnetic while II is diamagnetic

d. I is paramagnetic while II is paramagnetic

58. The correct order of C–C bond length in the following compounds is:

A. C_2F_4

B. C_2H_4

C. $[PtCl_3(C_2H_4]^-$

a. A > B > C **b.** A < B < C

c. A > C > B **d.** A > B = C

59. Which of the following statements is incorrect?

a. CN^- is a weaker acceptor than CO

b. The Fe–C bond length is more in $[Fe(CN)_6]^{4-}$ as compared to that in $[Fe(CN)_6]^{3-}$

c. The Fe–C bond length is less in $[Fe(CN)_6]^{4-}$ as compared to that in $[Fe(CN)_6]^{3-}$

d. The d_{Fe-O} {in $[Fe(H_2O)_6]^{3+}$} < d_{Fe-O} {in $[Fe(H_2O)_6]^{2+}$}

60. TheV–Cdistances in$V(CO)_6$and$[V(CO)_6]^-$are respectively: (in pm).

a. 200, 200 **b.** 193, 200

c. 200, 193 **d.** 193, 193

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

a. If both assertion and reason are true and the reason is the correct explanation of the assertion.

b. If both assertion and reason are true but reason is not the correct explanation of the assertion.

c. If assertion is true but reason is false.

d. If the assertion and reason both are false.

e. If assertion is false but reason is true.

61. **Assertion:** All the octahedral complexes of Ni^{2+} must be outer orbital complexes.

Reason: Outer orbital octahedral complexes are given by weak ligands.

62. **Assertion:** Potassium ferrocyanide is diamagnetic whereas potassium fericyanide is paramagnetic.

Reason: Crystal field splitting in ferrocyanide ion is greater than that of ferricyanide ion.

63. **Assertion:**$[Fe(CN)_6]^{3-}$is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

Reason: $[Fe(CN)_6]^{3-}$ has +3 oxidation state while $[Fe(CN)_6]^{4-}$ has +2 oxidation state.

64. **Assertion:** H_2N-NH_2 is a chelating ligand.

Reason: A chelating ligand must possess two or more lone pairs at such a distance that it may form suitable strain free rings at the metal ion.

65. **Assertion:** $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Reason: d-d transition is not possible in $[Sc(H_2O)_6]^{3+}$.

66. **Assertion:** Potassium ferrocyanide and potassium ferricyanite both are diamagnetic.

Reason: Both have unpaired electrons.

67 **Assertion:** NF_3 is a weaker ligand than $N(CH_3)_3$

Reason: NF_3 ionizes to give F^- ions in aqueous solution.

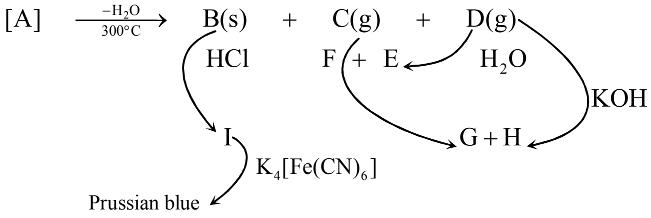
68. **Assertion:** The $[Ni(en)_3]Cl_2$ (en = ethylene diamine) has lower stability than $[Ni(NH_3)_6]Cl_2$

Reason: In $[Ni(en)_3]Cl_2$ the geometry of Ni is trigonal bipyramidal

Comprehension Based

Paragraph –I

A sequence of reaction has been represented in the given chart. A hydrated salt [A] is heated strongly.



A. F is an oxidizing agent which gives colloidal sulphur with H_2S gas and it also gives reddish brown gas with NaCl and H_2SO_4

B. C gives temporary bleaching action with moisture

C. G is a white ppt. and H is a green colour substance

69. The number of hydrated water molecules in [A] is:

a. 7 **b.** 10

c. 5 **d.** 2

70. The nature of compound C is:

a. oxidant **b.** reductant

c. oxidant and reductant **d.** solvent

71. Aqueous solution of [A] does not acts as reducing agent for:

a. $AuCl_3$ **b.** $HgCl_2$

c. $KMnO_4$ **d.** NO

72. Prussian blue compound has molecular formula:

a. $K_2Fe[Fe(CN)_6]$ **b.** $Fe_4[Fe(CN)_6]_3$

c. $K\,Fe[Fe(CN)_6]$ **d**. b and c both

73. Bleaching action of compound C is because of liberation of:

a. nascent H **b.** nascent O

c. nascent Cl **d.** O_3

74. Compound F is:

a. HNO_3 **b.** $K_2Cr_2O_7$

c. $KMnO_4$ **d.** H_2SO_4

75. Aqueous solution of compound [A] is slightly acidic due to:

a. hydrolysis of SO_4^{2-}

b. reducing nature

c. hydrolysis of Fe^{2+} ion

d. oxidizing nature

76. Compound $K_4[Fe(CN)_6]$ is formed when excess KCN reacts with:

a. D **b.** A

c. E **d.** G + H

77. When gas 'C' is heated with K metal, it gives?

a. K_2SO_3

b. K_2CO_3

c. K_2SO_4

d. $K_2SO_4 + K_2S_2O_3$

78. Compound I gives brown ppt. with NH_4OH, which dissolves in:

a. dil. HCl **b.** dil. NaOH

c. Cl_2 gas **d.** CO gas

Paragraph –II

Double salts are the compounds which retain their identity in solid stae but lose their identity in solution state whereas, coordination compounds are the complex salts which retain their identity in solid state as well as in solution state. In a coordination compound the number of ions or molecules (ligend) attached to the central metal atom or ion (central atom) is beyond the number possible, on the basis of electrovalent or covalent bonding. The extra groups or ions linked to the metal by coordination bonds in which the linked group (L) is the donor and the metal (M) is the acceptor i.e., M←L. Coordination compounds are mainly of two types: (i) Neutral compound like $[Fe(CO)_5]$; (ii) Ionic compound, which consists of ions in which atleast one is a complex ion, e.g., cationic complex $[Ag(NH_3)_2]Cl$ or anionic complex $Na[BH_4]$.

Complex ion: A complex ion is an electrically charged radical which consists of a metal atom or ion surrounded by a group of ions or neutral molecules. For example $[Cu(NH_3)_4]^{4+}$, $[Fe(CN)_6]^{3-}$. Ligand: Ligands are defined as molecules or ions having atleast one pair of electrons for donation. Ligands are also known as Lewis bases. There are two main classes of ligands:

A. Classical or simple donor ligands: These are the ligands which act as electron pair donor to acceptor ions or molecules and form complexes with all types of Lewis acids, metal ions or molecules.

B. Non-classified ligands, π-bonding or π-acid ligands: These refer to these ligands which form compound largely with transition metal atoms. This type of interaction is possible due to special properties of both metal and ligand. The metal has d-orbitals that can be used in bonding and the ligand has not only donor capacity but also has acceptor orbitals. Ligand can be negative ions, positive ions or neutral molecules.

Coordination Number: The total number of ligands attached to the central metal atom in coordination sphere is called coordination number. The species outside the coordination number are ionizable species.

79. How many ions are produced by $[Co(NH_3)_6]Cl_3$ ion solution?

a. 6 **b.** 4

c. 3 **d.** 2

80. Which of the following is non-ionizable?

a. $[Co(NH_3)_3Cl_3]$ **b.** $[Co(NH_3)_4Cl_2]Cl$

c. $[Co(NH_3)_5Cl]Cl_2$ **d.** $[Co(NH_3)_6]Cl_2$

81. The complex $CoCl_3 \cdot 3NH_3$ ionizes to give:

a. $2Cl^-$ ions **b.** $1Cl^-$ ion

c. $3Cl^-$ ions **d.** zero Cl^- ion

82. AgCl dissolves in NH_4OH due to the formation of:

a. $[Ag(NH_4)_2Cl]$ **b.** $[Ag(NH_4)_3]Cl$

c. $[Ag(NH_3)_2]Cl$ **d.** $[Ag(NH_3)_2OH]$

83. Which is not π-bonded complex?

a. Zeise's salt **b.** Ferrocence

c. Dibenzene chromium **d.** Tetraethyl lead

84. The correct IUPAC name for $K_3[Fe(C_2O_4)_3]$ is

a. potassium trioxalatoferrate (II)

b. potassium trioxalatoferrate (I)

c. potassium trioxalatoferric (III)

d. potassium trioxalatoferrate (III)

85. The oxidation number, coordination number and effective atomic number respectively of central metal atom in $K_2[HgI_4]$ is:

a. 0, 2, 86 **b.** +2, 4, 86

c. +2, 2, 84 **d.** +2, 2, 86

86. Maximum coordination number of a central atom can be:

a. 2 **b.** 4

c. 6 **d.** > 6

87. The numerical value of 'X' in $H_XCr(CO)_4$ is:

a. 0 **b.** 1

c. 2 **d.** 3

88. Which of the following is ambidentate ligand?

a. NO_2 **b.** $C_2O_4^{2-}$

c. CO **d.** N_2

Paragraph –III

Ni^{2+} ions form the following complexes.

$Ni^{2+} \xrightarrow{KCN}$ Complex I;

$Ni^{2+} \xrightarrow[\text{excess}]{KCl}$ Complex II Both the complex have coordination number 4.

89. The IUPAC name of the complex respectively are:

a. potassium tetracyanonickel(II) and potassium tetrachloronickelate (II)

b. potassium tetracyanonickelate(II) and potassium tetrachloronickel(II)

c. potassium tetracynonickel (II) and potassium tetrachloronickel(II)

d. potassium tetrcyanonickelate(II) and potassium tetrachloronickelate (II)

90. Which of the following statement is correct?

a. The cyano complex is diamagnetic and the chloro complex is paramagnetic

b. The cyano complex is paramagnetic and the chloro complex is diamagnetic

c. Both the complexes are diamagnetic

d. Both the complexes are paramagnetic

91. Nickel ion involves:

a. dsp^2- hybridization in both complexes

b. sp^3 -hybridization in both complexes

c. dsp^2 -hybridization in cyano complex and sp^3 -hybridization in chloro complex

d. sp^3 -hybridization in cyano complex and dsp^2 -hybridization in chloro complex

Match The Column

92. Match the metal complex type with the properties:

Column I	**Column II**
(A) $[M(AA)abcd]^{n\pm}$	**1.** All geometrical isomers are optica -lly active.
(B) $[M(AB)a_2b_2]^{n\pm}$	**2.** The number of stereoisomers is four.
(C) $[M(AB)_3]^{n\pm}$	**3.** The number of geometrical isomers is four
(D) $[Ma_2b_2cd]^{n\pm}$	**4.** The number of optically active isomers is four.

a. A→1; B→3,4, C→1,2,4; D→4

b. A→2; B→4; C→3; D→1

c. A→1; B→3; C→2; D→4

d. A→4; B→1; C→3; D→2

93. Match the complex compounds with their properties:

Column I	**Column II**
(A) $[CoFe_3(H_2O)_3]^0$	**1.** Diamagnetic and low spin complex.
(B) $[Cr(C_2O_4)_3]^{3-}$	**2.** Paramagnetic and outer orbital complex.
(C) $[AuCl_4]^-$	**3.** Paramagnetic but inner orbital complex.
(D) $[Fe(CN)_6]^{3-}$	**4.** Diamagnetic and high spin complex.
	5. Paramagnetic and low spin complex.

a. A→2, B→3, C→1, D→5

b. A→2, B→5, C→3, D→1

c. A→1, B→3, C→5, D→4

d. A→4, B→5, C→3, D→2

94. Match the processes carried out with the changes observed:

Column I	**Column II**
(A) $[M(AB)a_3b]^{n\pm} \xrightarrow{-a/+b} [M(AB)a_2b_2]^{n\pm}$	**1.** The number of pairs of enantiomers is increased by one.
(B) $[M(AB)a_3bc]^{n\pm} \xrightarrow{-c/+b} [M(AB)a_3b_2]^{n\pm}$	**2.** The number of geometrical isomers in the final product in four.
(C) $[Ma_3b_2c]^{n\pm} \xrightarrow{-b/+d} [Ma_3bcd]^{n\pm}$	**3.** The number of stereoisomers is increased to double of the original or decreased to half of the original
(D) $[M(AA)a_3b]^{n\pm} \xrightarrow{-a/+d} [M(AA)a_2b_2]^{n\pm}$	

a. A→1,2; B→2,3; C→1,2; D→1,3

b. A→2; B→4; C→3; D→1

c. A→1; B→3; C→2; D→4

d. A→4; B→1; C→3; D→2

95. Match the complex compounds with the properties not depicted by them:

Column I	**Column II**
(A) $[Fe(CO_4)]^{2-}$	**1.** Hybridization is dsp^2.
(B) $[Pt(NH_3)_2Cl_2]$	**2.** Hybridization is sp^3.
(C) $[Pt(bn)_2]^{2+}$	**3.** Exhibits geometrical isomerism.
(D) $[Zn(gly)_2]^0$	**4.** Low spin complex.
	5. Exhibits optical isomerism.

a. A→1,3,4,5; B→2,5; C→2; D→1,3,4

b. A→2; B→4; C→3, D→1

c. A→1; B→3; C→2; D→4

d. A→4; B→1; C→3; D→2

Integer

96. The co-ordination number of copper in cuprammonium sulphate is :

97. The co-ordination number of cobalt in the complex $[Co(en)_2Br_2]Cl_2$ is:

98. The primary valence of the metal ion in the co-ordination compound $K_2[Ni(CN)_4]$ is:

99. What is the EAN of nickel in $Ni(CO)_4$?

100. The oxidation number of Cr in $[Cr(NH_3)_6]Cl_3$ is:

ANSWER

1.	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**10.**
b	b	c	c	b	c	d	b	c	a
11.	**12.**	**13.**	**14.**	**15.**	**16.**	**17.**	**18.**	**19.**	**20.**
b	c	a	b	a	c	b	a	b	b
21.	**22.**	**23.**	**24.**	**25.**	**26.**	**27.**	**28.**	**29.**	**30.**
b	a	c	c	a	a	a	a	c	c
31.	**32.**	**33.**	**34.**	**35.**	**36.**	**37.**	**38.**	**39.**	**40.**
a	c	d	d	d	d	a	b	a	b
41.	**42.**	**43.**	**44.**	**45.**	**46.**	**47.**	**48.**	**49.**	**50.**
d	c	b	a	d	b	c	c	c	a
51.	**52.**	**53.**	**54.**	**55.**	**56.**	**57.**	**58.**	**59.**	**60.**
b	c	a	a	b	c	c	b	b	c
61.	**62.**	**63.**	**64.**	**65.**	**66.**	**67.**	**68.**	**69.**	**70.**
b	c	b	e	a	d	c	d	a	c
71.	**72.**	**73.**	**74.**	**75.**	**76.**	**77.**	**78.**	**79.**	**80.**
d	b	a	b	c	b	d	a	b	a
81.	**82.**	**83.**	**84.**	**85.**	**86.**	**87.**	**88.**	**89.**	**90.**
d	c	d	d	b	d	b	a	d	a
91.	**92.**	**93.**	**94.**	**95.**	**96.**	**97.**	**98.**	**99.**	**100.**
c	a	a	a	a	4	6	2	36	3

SOLUTION

Multiple Choice Questions

1. **(b)** (CN) are linked with secondary valency.

2. **(b)** As it makes use of its two atoms to form two co-ordinate covalent bonds with the central metal ion.

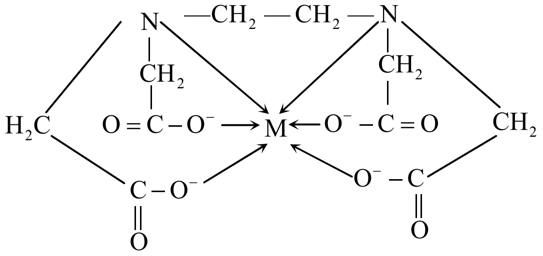
3. **(c)** In $[Co(en)_2Cl_2]^+$
No. of monodentate ligand = 2
No. of bidentate ligand = 2
Co-ordination no. of the metal = 2 + 2(2) = 6.

4. **(c)** According to modern view primary valency of complex compound is its oxidation number while

5. **(b)** Cuprammonium salt-$[Cu(NH_3)_4]SO_4$
$[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$
So, it will give two ions in water.

6. **(c)** The number of atoms of the ligand that are directly bounded to the central metal atom or ion by coordinate bond is known as the coordination number of the metal atom or ion coordination number of metal = number of σ bonds formed by metal with ligand .

7. **(d)** The number of atom of the ligand that are directly bound to the central metal atom or ion by coordinate bonds is known as the coordinate number of the metal or ion. It is actually the number of chemical bonds which the ligand form with the central metal atom or ion.



8. **(b)** ZnS structure shows the coordination number of Zn is 4.

9. **(c)** When a ligand attaches to the central metal atom through two or more atoms to form a ring like structure is known as chelats and the ligand is called chelating ligand.

10. **(a)** General formula for alum is $M_2SO_4.R_2(SO_4)_3.24H_2O$
$M =$ mono valent cation $(K^+, Na^+....)$
$R =$ Trivalent cation (Al^{+3}, Fe^{+3})
Hence, $K_2SO_4Al_2(SO_4)_2.24H_2O$ represent an alum.

11. **(b)** $[Co(H_2O)_6]Cl_2 \rightleftharpoons [Co(H_2O)_6]^+ + 2Cl^-$.

12. **(c)** EAN =Atomic number – Oxidation state + 2 × number of Ligands = 26 – 2 + 2 (6) = 36.

13. **(a)** $[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$
$x + 6(0) = +3$
$\Rightarrow$ $x = +3$.

14. **(b)** $[\underset{x}{Pt}(\underset{0}{C_2H_4})\underset{-1}{Cl_3}]^-$
$x + 0 + 3x(-1) = -1$, $x - 3 = -1$, $x = +2$.

15. **(a)** EAN = at. no. of central atom - oxidation state + $2 \times$ (no. of ligands)
$= 27 - 3 + 2 \times 6 = 36.$

16. **(c)** EAN of a central metal ion=(atomic no. of central atom) – oxidation state + no. of ligands × 2
$= 26 - 3 + (6 \times 2) = 23 + 12 = 35$

17. **(b)** $3 \times (+1) + x + 6 \times (-1) = 0$
or $x = 6 - 3 = +3$
Oxidation state of $Fe = +3$.

18. **(a)** In the compounds $[Co(NH_3)_5NO_2]Cl_2$, the oxidation state of cobalt is +3 and here 5 NH_3 ligand, a NO_2 ligand are attached to the central atom. therefore its name is pentaamminecobalt (III) chloride.

19. **(b)** In the given ion $[\mathrm{Cr(NH_3)_6}]^{3+}$, the oxidation state of chromium is +3 and here $6\mathrm{NH_3}$ ligand are attached to the central metal atom. Therefore its IUPAC name is hexamminechromium (III) ion.

20. **(b)** $[\mathrm{Ni(CN)_4}]^x$, $(\mathrm{Ni} = +2)$ $(\mathrm{CN} = -1)$; $x = 2 + 4(-1)$

$\Rightarrow$ $x = -2$.

21. **(a)** Octahedral complexes of the type $[\mathrm{MA_4B_2}]$, $[\mathrm{MA_2B_4}]$, $[\mathrm{MA_3B_3}]$, exhibit geometrical isomerism.

22. **(c)** The two given compounds have same composition but in solution both will give different ions. The isomerism is known as ionisation isomerism.

23. **(c)** The compound which has same composition but give different ions in solution, show ionization.

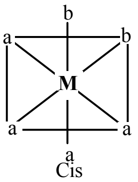
So, $[\mathrm{Co\ (NH_3)_5Br]\ SO_4}$ is ionization isomer.

$$[\mathrm{Co(NH_3)_5Br]SO_4} \rightleftharpoons [\mathrm{Co(NH_3)_5Br}]^{2+} + \mathrm{SO_4^{2-}}$$

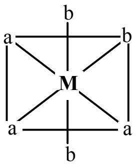
$$[\mathrm{Co(NH_3)_5SO_4]Br} \rightleftharpoons [\mathrm{Co(NH_3)SO_4}]^{+} + \mathrm{Br}^{-}.$$

24. **(c)** $[\mathrm{Co(NH_3)_5NO_2]Cl_2}$ will not show geometrical isomerism because this complex showed 4 and 6 co-ordination number.

25. **(a)** $[\mathrm{Co\ (NH_3)_4\ Cl_2}]^+$ is the $\mathrm{Ma_4b_2}$ and $\mathrm{Ma_2b_3}$ type complex.

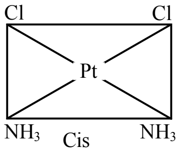


Cis

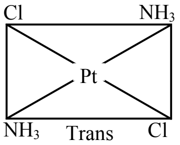


trans

26. **(a)** $\mathrm{Pt(NH_3)_2Cl_2}]$.



Cis



Trans

27. **(a)** $[\mathrm{Cu(NH_3)_4}].[\mathrm{PtCl_4}]$

$[\mathrm{Cu(NH_3)_3Cl}].[\mathrm{PtCl_3(NH_3)}]$

$[\mathrm{Cu(NH_3)_2Cl_2}].[\mathrm{PtCl_2(NH_3)_2}]\mathrm{cis}$

$[\mathrm{Cu(NH_3)_2Cl_2}].[\mathrm{PtCl_2(NH_3)_2}]\mathrm{Trans}$

$[\mathrm{Cu(NH_3)Cl_3}].[\mathrm{Pt(Cl)(NH_3)_3}]$

$[\mathrm{Pt(NH_3)_4Cl}].[\mathrm{CuCl_4}]$

28. **(a)** $\mathrm{Mn^{2+}}\ \underset{3d^7}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{4s^0}{\boxed{}}$

In presence of $\mathrm{H_2O}$ which is a weak ligand no pairing occurs which results in unpaired electrons left in the compound, due to which it shows paramagnetism.

29. **(c)** $[\mathrm{Cr(NH_3)_5Cl]SO_4} \longrightarrow [\mathrm{Cr(NH_3)_5Cl}]^{2+} + \mathrm{SO_4^{2-}}$

$(\mathrm{Cr(NH_3)_5Cl}]^{2+} + \mathrm{SO_4^{2-}} + \mathrm{BaCl_2} \longrightarrow$

$[\mathrm{Cr(NH_3)_5Cl]Cl_2} + \mathrm{BaSO_4} + \mathrm{HCl}$.

30. **(c)** When coordinate compounds gives different ions in solution then it produces ionic isomerism while this situation is not present in $[\mathrm{Co(en)_2Cl_2]Cl}$.

31. **(a)** $2\mathrm{Cl}^-$ ions are ionizable

$$\therefore \quad [\mathrm{Co(NH_3)_5Cl]Cl_2} \rightleftharpoons \underbrace{[\mathrm{Co(NH_3)_5Cl}]^{2+} + 2\mathrm{Cl}^-}_{\text{3 ions}}$$

$$2\mathrm{Cl}^- + 2\mathrm{AgNO_3} \longrightarrow 2\mathrm{AgCl} + 2\mathrm{NO_3^-}.$$

32. **(c)** $[\mathrm{Fe(CN)_6}]^{4-}$

$\mathrm{Fe^{2+}} - \underset{3d}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{4s}{\boxed{}}\quad \underset{4p}{\boxed{}\boxed{}\boxed{}}$

In presence of CN^-

$$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\underbrace{\boxed{\times\times}\boxed{\times\times}\quad\boxed{\times\times}\quad\boxed{\times\times}\boxed{\times\times}\boxed{\times\times}}_{d^2sp^3\ \text{hybridisation}}$$

Hence, Octahedral geometry.

33. **(d)** $\mathrm{Ni(CO)_4}$ and $\mathrm{Ni(PPh_3)_2Cl_2}$ have $\mathrm{sp_3}$ and $\mathrm{dsp^2}$-hybridisation respectively.

34. **(c)** The compounds which show d^6 – configuration are octahedral complexes.

35. **(d)** Cyanide ion is strong field ligand because it is a pseudohalide ion pseudohalide ions are stronger coordinating ligand & they have the ability to form σ bond (from the pseudohalide to the metal) and π bond (from the metal to pseudohalide).

36. **(d)** The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that $\mathrm{NH_3}$ and CN^- are strong lewis bases.

37. **(a)** The most probable complex which gives three moles ions in aqueous solution may be $[\mathrm{Co(NH_3)_5NO_2]Cl_2}$ because it gives two chlorine atoms on ionisation.

$$[\mathrm{Co(NH_3)_5NO_2]Cl_2} \longrightarrow [\mathrm{Co(NH_3)_5NO_2}]^{2+} + 2\mathrm{Cl}^-$$

38. **(b)** $\mathrm{Fe_2(SO_4)_3} \longrightarrow 2\mathrm{Fe^{3+}} + 3\mathrm{SO_4^{2-}}$

$$\mathrm{K_4[Fe(CN)_6]} + 2\mathrm{Fe^{3+}} \longrightarrow \underset{\text{Prussion blue}}{\mathrm{Fe_4[Fe(CN)_6]_3}}.$$

39. **(a)** $\mathrm{Ag_2S} + \mathrm{NaCN} \rightleftharpoons \mathrm{Na\,[Ag(CN)_2]} + \mathrm{Na_2S}$.

40. **(b)** Aluminum is a p-block element and does not form complex compounds.

41. **(d)** $\mathrm{(CH_3CH_2)_3Al} + \mathrm{TiCl_4}$ is the Ziegler-Natta catalyst.

42. **(c)** $4CH_3CH_2CH_2CH_2-Li+SnCl_2 \rightarrow (C_4H_9)_4Sn$.

43. **(b)** As there is no direct bonding between the metal atom and the carbon atom.

44. **(a)** $(CH_3)_4$ Sn is a σ –bonded organometallic compound.

45. **(d)** Wilkinson's catalyst is used as homogeneous catalyst in the hydrogenation of alkenes as –

$$H-H+ \rangle C=C\langle \longrightarrow H-C-C-H.$$

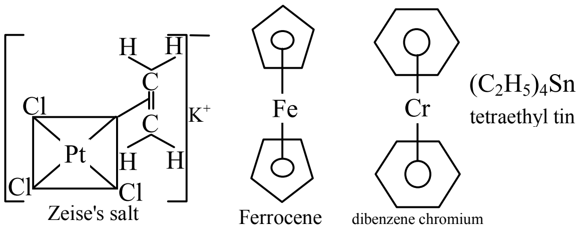
46. **(b)** C_2H_5 Li is an organo-metallic compound.

47. **(c)** Organometallic compounds are those compounds in which carbon atom is directly linked to metal. But in sodium ethoxide as oxygen is attached to sodium metal so it is not a organometallic compound.

48. **(c)** $Al(OC_2H_5)_3$ contains bonding through O and thus it does not have metal-carbon bond.

49. **(c)** Chlorophyll are green pigment in plant & contain magnesium instead of calcium.

50. **(a)**



Zeise's salt Ferrocene dibenzene chromium

NCERT Exemplar Problems

More than One Answer

51. **(b)** The EAN value of Fe in this complex does not depends on the charge of NO ligand

52. **(c)** 34

53. **(a)** NO

54. **(a)** $\overline{S}-C\equiv N:$

55. **(b)** $A<C<B<D$

56. **(c)** $[Fe(H_2O)_6]_2[Fe(CN)_6]$

57. **(c)** I is paramagnetic while II is diamagnetic

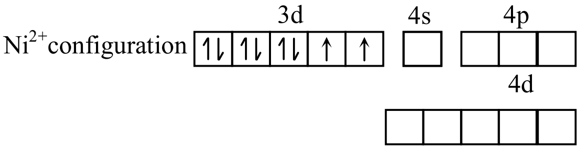
58. **(b)** $A<B<C$

59. **(b)**The Fe–C bond length is more in $[Fe(CN)_6]^{4-}$ as compared to that in $[Fe(CN)_6]^{3-}$

60. **(c)** 200, 193

Assertion and Reason

61. **(b)** Both assertion and reason are true but reason is not the correct explanation of assertion.



During rearrangement only one 3d - orbital may be made available by pairing the electrons. Thus, inner d^2sp^3 hybridization is not possible, so, only sp^3d^2 (outer) hybridization can occur.

62. **(c)** K_4 $[Fe\ (CN)_6]$ and K_3 $[Fe(CN)_6]$ both are low spin complex due to strong ligand field. That is why it is false that crystal field splitting in ferrocyanide ion is greater than ferricyanide ion.

63. **(b)** Both assertion and reason are true but reason is not the correct explanation of assertion. $[Fe(CN)_6]^{3-}$ has EAN equal to 35 and thus possesses unpaired electron to show paramagnetic nature while $[Fe(CN)_6]^{4-}$ possesses no unpaired electron and thus shows diamagnetic nature.

64. **(e)** Assertion is false but reason is true. H_2N-NH_2 does not act as chelating ligand. The coordination by hydrazine leads to a three member highly unstable strained ring and thus it does not act as chelating agent.

65. **(a)** Both assertion and reason are true and reason is the correct explanation of assertion. $[Sc(H_2O)_6]^{3+}$ has no unpaired electron in its d subshell and thus d–d transition is not possible whereas $[Ti\ (H_2O)_6]^{3+}$ has one unpaired electron in its d subshell which gives rise to d–d transition to impart colour.

66. **(d)** Potassium ferrocyanide and potassium ferricyanide both are not diamagnetic because both do not have paired electrons. Assertion and reason both are false.

67. **(c)** It is correct statement that NF_3 is a weaker ligand than $N(CH_3)_3$, the reason is that fluorine is highly electronegative therefore, it with draw electrons from nitrogen atom. Hence, the lone pair of nitrogen atom cannot be ligated. While $N(CH_3)_3$ is a strong ligand because CH_3 has electron releasing group.

68. **(d)** Both assertion and reason are false. $[Ni\ (en)_3]Cl_2$ is a chelating compound and chelated complexes are more stable than similar complexes involves breaking of two bonds rather than one. In $[Ni(en)_3]Cl_2$, Ni with d^8 configuration shows octahedral geometry. Six electrons will occupy the t_{2g} orbitals and two electrons will occupy the e_g orbitals.

Comprehension Based

For 69 to 78

The reaction sequence is:

$$\underset{[A]}{2FeSO_4 \cdot 5H_2O} \xrightarrow{-5H_2O} \underset{[B]}{Fe_2O_3(s)} + \underset{[C]}{SO_2(g)} + \underset{[D]}{SO_3(g)}$$

$$\underset{[B]}{Fe_2O_3} + 6HCl \longrightarrow \underset{[I]}{2FeCl_3} + 3H_2O$$

$$\underset{[I]}{4FeCl_3} + 3K_4Fe(CN)_6 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12\,KCl$$

$$\underset{C}{3SO_2} + \underset{[F]\text{Oxidant}}{K_2Cr_2O_7} + \underset{E}{H_2SO_4} \longrightarrow \underset{[G]\text{White}}{K_2SO_4} + \underset{[H]\text{Green}}{Cr_2(SO_4)_3} + H_2O$$

$$\underset{[D]}{SO_3} + H_2O \longrightarrow \underset{[E]}{H_1SO_4} \quad \underset{[C]}{3SO_2} + 4K \longrightarrow K_2SO_3 + K_2S_2O_3;$$

$$\underset{[D]}{SO_3} + 2KOH \longrightarrow \underset{[G]}{K_2SO_4} + H_2O$$

69. **(a)** The compound is $FeSO_4 \cdot 7H_2O$

70. **(c)** SO_2 acts as oxidant and reductant both ax ox number of S is + 4 (between) +6 (max) and –2 (min).

71. **(d)** Fe^{2+} reduces Au^{3+} to Au,

Hg^{2+} to Hg_g^{2+}, Mn^{7+} to Mn^{2+}.

It absorbs NO to form $FeSO_4.NO$

72. **(b)** Prussian blue is $F_4[Fe(CN)_6]_3$.

73. **(a)** $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$

74. **(b)** Follow sequence of reaction.

75. **(c)** $Fe^{2+} + 2H_2O \longrightarrow Fe(OH)_2 + \underset{\text{Strong acid}}{4H^+}$

76. **(b)** $FeSO_4 + \underset{\text{Excess}}{6KCN} \longrightarrow K_4Fe(CN)_6 + K_2SO_4$

77. **(d)** Follow sequence of reaction.

78. **(a)** $\underset{[I]}{FeCl_3} + NH_4OH \longrightarrow \underset{\text{Brown ppt}}{Fe(OH)_3} \xrightarrow{HCl}$ Soluble

79. **(b)** $[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$

80. **(a)** All ligands (NH_3 and Cl) are in side coordination sphere.

81. **(d)** Co^{2+} has six coordination number thus it is $[Co(NH_3)_3Cl_3]$

82. **(c)** $AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$

83. **(d)** Tetraethyl lead $[(C_2H_5)_4\,Pb]$ has no π -bonding in it.

84. **(d)** Follow IUPAC rule.

85. **(b)** $K_2[HgI_4] \rightleftharpoons 2K^+ + [HgI_4]^{2-}$

∴ Oxidation number of Hg^{2+} = + 2, number of ligands = 4.

EAN = At. Number of Hg – electrons lost in the formation of Hg^{2+} + 4 × number of electrons in coordination

$= 80 - 2 + 4 \times 2 = 86$.

86. **(d)** It is a fact.

87. **(b)** In carbonyls, the effective at. Number = At. number of next noble gas EAN or Cr = 36 [EAN of Cr]

∴ In Hx Cr $(CO)_4$; X + 27 + 4 × 2 = 36

∴ X=1

88. **(a)** An ambidentate ligand possesses two donor atoms, but in forming complex only one atom is involved.

← NO_2 or ← ONO

89. **(d)** The complexes are $K_2[Ni(CN)_4]$ and $K_2[Ni(Cl)_4]$. Hecne, their names are potassium tetracyanonickelate(II) and potassium tetrachloronickelate(II)

90. **(a)** ${}_{28}Ni^{2+}$ $(3d^8)$

Ni^{2+} in cyano complex

Ni^{2+} in chloro complex

91. **(c)** dsp^2 -hybridization in cyano complex and sp^3 -hybridization in chloro complex

Match the Column

92. **(a)** A→1; B→3,4, C→1,2,4; D→4

93. **(a)** A→2, B→3, C→1, D→5

94. **(a)** A→1,2; B→2,3; C→1,2; D→1,3

95. **(a)** A→1,3,4,5; B→2,5; C→2; D→1,3,4

Integer

96. **(4)** In Cuprammonium sulphate $[Cu(NH_3)_4]SO_4$ co-ordination no. of Cu is 4.

97. **(6)** $[Co(en)_2Br_2]Cl_2$

C.N.of Co = 2 × number of bidentate ligand

+ 1 5 number of monodentate ligand

= 2 × 2 + 1 × 2 = 6.

98. **(2)** Primary valencies are also known as oxidation state.

$K_2[Ni(CN)_4],\ 2 + x - 4 = 0 \Rightarrow x = +2$

99. **(36)** EAN = (At. number $-0.S + 2 \times C.N.$)

Hence, EAN of Ni in $Ni(CO)_4$ is

$= 28 - 0 + 2 \times 4 = 36$

100. **(3)** $x + 6 \times (0) + 3 \times (-1) = 0 \quad x - 3 = 0,\ x = +3,$

Oxidation number of Cr is = + 3.

* * *