DAY TWENTY FOUR

Coordination Compounds

Learning & Revision for the Day

- Werner's Theory
- IUPAC Nomenclature of Coordination Compounds
- Isomerism in Coordination Compounds
- Bonding in Coordination Compounds
- Importance and Applications of Coordination Compounds
- Organometallic compounds

Coordination compounds are those molecular compounds which retain their identity in solid as well as in aqueous solution.

In these compounds metal atoms are bound to a number of anions or neutral molecules by coordinate bonds. A part of these compounds is not dissociated in solution and its behaviour is different than its constituents.

e.g. $$\underset{\substack{\text{Ionisable}\\ \text{species}}}{K_4}\;\underset{\substack{\text{Non-ionisable}\\ \text{coordination}\\ \text{sphere}}}{[Fe(CN)_6]} + H_2O \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

Werner's Theory

Alfred Werner a swiss chemist was the first to study the bonding in coordination compounds in 1982.

The main postulates of this theory are:

(i) In complex compounds, metal atom exhibit two types of valencies—primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by anions or neutral molecules (ligands). Primary valency depends upon oxidation number of central metal atom while secondary valency represents the coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non-ionisable and directional. Therefore, geometry of complex is decided by secondary valencies. e.g. $[Cr(H_2O)_6]Cl_3$ has primary valency = 3 (OS of Cr) and secondary valency = 6 (CN of Cr)

Definitions of some important terms pertaining to coordination compounds are as follows :

1. Complex Ion

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or molecules. There are three types of complex ions.

(i) **Anionic Complex** It is the complex ion which carries negative charge.

$$K_3[Fe(C_2O_4)_3] \longrightarrow 3K^+ + \underset{\text{Anionic complex}}{[Fe(C_2O_4)_3]^{3-}}$$

(ii) **Cationic Complex** It is the complex ion which carries positive charge.

$$[CoCl_2(en)_2]Cl \longrightarrow \underset{\text{Cationic complex}}{[CoCl_2(en)_2]^+} + Cl^-$$

(iii) **Neutral Complex** It is the complex ion which does not carry any charge.

$$\underset{\text{Neutral complex}}{[Ni(CO)_4]}$$

2. Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

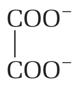
The number of donor groups in a single ligand that bind to a central atom in a coordination complex is known as **denticity**.

There are different types of ligands which are discussed below :

(i) **Unidentate Ligand** It is bound to a metal ion through a single donor atom. e.g. $H_2O, NH_3, CO, Cl^-, NH_2^-$ etc.

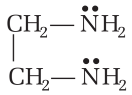
(ii) **Didentate Ligand** It is bound to a metal ion through two donor atoms.

e.g.



$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$$

Oxalate ion



$$\begin{matrix} CH_2 - \ddot{N}H_2 \\ | \\ CH_2 - \ddot{N}H_2 \end{matrix}$$

Ethylene diamine

(iii) **Polydentate ligand** It is bound to a metal ion through several donor atoms. e.g. ethylenediamine tetraacetate ion $[EDTA]^{4-}$.

(iv) **Ambidentate Ligand** These are unidentate ligands which can ligate through more than one coordinating atoms.

e.g. $—NO_2, —ONO, —SCN$ etc.

(v) **Chelate Ligands** It may be di or polydentate ligands which form closed ring with central metal ion. Closed ring is known as chelate ring and this process is called chelation. Chelate complexes tend to be more stable than similar complexes containing unidentate ligands.

3. Coordination Number

The number of ligand donor atoms to which the metal is directly bonded is called the coordination number of that metal ion in a complex.

- In case of monodentate ligand, it is equal to the number of ligands while in bidentate ligand it is twice the number of ligands present in the complex.
- For example in the complex ion $[Ag(CN)_2]^-$ and $[Fe(C_2O_4)_3]^{2-}$, the coordination numbers of Ag and Fe are 2 and 6 respectively.

4. Coordination Sphere

The central ion and the ligands which are directly attached to it are enclosed in square bracket is collectively known as coordination sphere. The ionisable group written outside the bracket is known as **counter ions**.

For example in coordination complex, $[Cu(NH_3)_4]SO_4$ the complex ion $[Cu(NH_3)_4]^{2+}$ forms coordination sphere and SO_4^{2-} ions are the counter ions.

5. Coordination Polyhedron

The spatial arrangement of the ligands which are directly attached to the central atom or ion, is called **coordination polyhedron around the central atom or ion.**

6. Oxidation Number of Cental Atom

The oxidation number of a central atom is defined as the charge that it carries as calculated by assigning appropriate charges to the ligands and equating the sum of the charges on the central atom and ligands equal to the charge on the coordination sphere.

7. Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups, e.g. $[Co(NH_3)_6]^{3+}$ are known as homoleptic complexes.

Complexes in which a metal is bound to more than one kind of donor groups, e.g. $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic complexes.

IUPAC Nomenclature of Coordination Compounds

The following rules are used while naming coordination compounds.

- The cation is named first in both positively and negatively charged coordination entities.
- The ligands are named in an alphabetical order before the name of the central atom.
- Names of the anionic ligands end in —O, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO.

- Prefixes mono, di, tri etc, are used to indicate the number of the individual ligands in the coordination entity. When the name of the ligands include a numerical prefix, then the terms *bis, tris, tetrakis* are used.
- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numerical in parenthesis.
- If the complex ion is cation, the metal is named same as the element. If the complex ion is an anion, the name of the metal ends with suffix-ate.
- The neutral complex molecule is named similar to that of the complex cation.

Isomerism in Coordination Compounds

It is a phenomenon, in which compounds have the same molecular formula but different physical and chemical properties on account of different structures. These compounds are called isomers. There are mainly two types of isomerism shown by coordination compounds which are discussed below :

1. Stereoisomerism

Stereoisomerism occurs due to different arrangement of ligands around central metal atom. It is of two types, geometrical isomerism and optical isomerism.

(i) **Geometrical isomerism** It arises in heteroleptic complexes due to different possible geometric arrangement of the ligands. Important examples of this behaviour are found in square planar and octahedral complexes (discussed below), but tetrahedral complexes do not show geometrical isomerism.

(a) **Square planar complex of the type** $[MX_2L_2]$ (X and L are unidentate), the two X ligands may be arranged adjacent to each other in a *cis*-isomer or opposite to each other in a *trans*-isomer, e.g. $[Pt(NH_3)_2Cl_2]$.

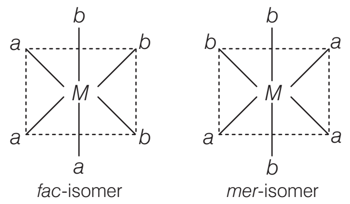
(b) **Square planar complex of the type** $[MABXL]$ (where, A, B, X, L are unidentate) shows three isomers, two *cis* and one *trans*. Such isomerism is not possible for tetrahedral geometry, e.g. $[Pt(NH_3)(Br)(Cl)(Py)]$.

(c) **Square planar complex of the type** $M(XL)_2$, here, XL is unsymmetrical didentate ligand, shows two geometrical isomers, i.e. *cis* and *trans* form, e.g. $[Pt(gly)_2]$.

(d) **Octahedral complexes of formula** $[MX_2L_4]$ in which the two ligands X may be oriented *cis* or *trans* to each other, e.g. $[Co(NH_3)_4Cl_2]^+$.

(e) **Octahedral complexes of formula** $[MX_2A_2]$ (where, X are unidentate ligands and A are didentate ligands) form *cis* and *trans*-isomers, e.g. $[CoCl_2(en)_2]$.

(f) **Octahedral coordination entities of the type** $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$ exist in two geometrical isomers. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the ***facial*** (*fac*) **isomer**. When the positions are around the meridian of the octahedron, we get the ***meridional*** (*mer*) **isomer**.



fac-isomer *mer*-isomer

***fac*- and *mer* isomers of Ma_3b_3**

Octahedral complexes of type $[M(AA)_3]$, $[MA_6]$ and $[MA_5B]$ do not show geometrical isomerism.

(ii) **Optical Isomerism** It arises when mirror images cannot be superimposed on one another. These mirror images are called **enantiomers**. The two forms are called *dextro* (d) and *laevo* (l).

Optical isomerism is common in octahedral complexes having atleast one didentate ligand. Complexes of type $[M(AA)_3]$, $[M(AA)_2B_2]$, $M[(AA)_2BC]$, $M[(AA)B_2C_2]$ show optical isomerism. e.g. $[Co(en)_3]^{3+}$, $[PtCl_2(en)_2]^{2+}$ etc.

NOTE Octahedral complexes of type $MA_2X_2Y_2$ shows both optical and geometrical isomerism.

2. Structural Isomerism

In structural isomerism, isomers have different bonding pattern.

Different types of structural isomerism are as follows:

(i) **Linkage isomerism** arises in a coordination compound containing ambidentate ligand.

e.g. $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$

(ii) **Coordination isomerism** arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

e.g. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr[NH_3)_6][Co(CN)_6]$

(iii) **Ionisation isomerism** arises when the ionisable anion exchange with anion ligand.

e.g. $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

(iv) **Solvate isomerism** is also known as "hydrate isomerism". In this case water is involved as a solvent. This is similar to ionisation isomerism.

e.g. $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$,
$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

Bonding in Coordination Compounds

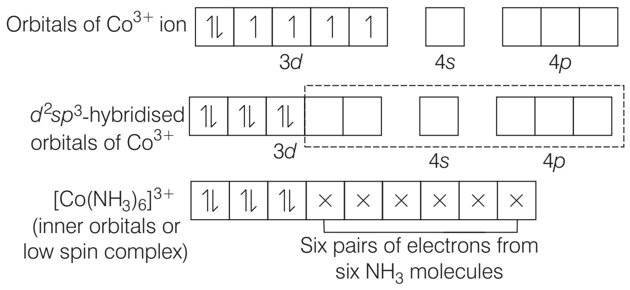
The bond formation in coordination compounds can be explained by using the two approaches which are given below:

Valence Bond Theory

- According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These are hybridised orbitals which are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.
- Octahedral, square planar and tetrahedral complexes are formed as a result of d^2sp^3, dsp^2 and sp^3 hybridisation respectively of the central atom.
- If the metal atom has coordination number six and has d^2sp^3 or sp^3d^2 hybridisation, then the geometry of the complex is octahedral.

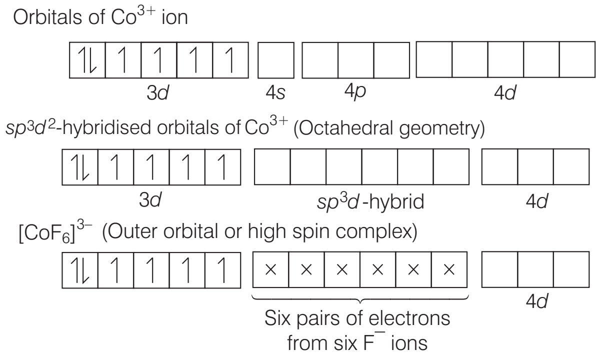
Such complexes are of the following two types:

(i) **Inner orbital complexes** (hyperligated complexes) which are formed due to strong field ligands or low spin ligands, has hybridisation d^2sp^3, i.e. involves inner $(n-1)d$ orbital (where two orbitals are of $3d$, one orbital of $4s$ and three orbitals of $4p$) and shape of complex will be octahedral. e.g. $[Co(NH_3)_6]^{3+}$



All electrons are paired, therefore complex will be diamagnetic in nature.

(ii) **Outer orbital complexes** (hypoligated complexes) which are formed due to weak field ligands or high spin ligands, has hybridisation sp^3d^2, i.e. uses outer nd orbitals (where one orbital is of $4s$, three orbitals of $4p$ and two orbitals of $4d$). Generally halides (F^-, Cl^-, Br^-, I^-), SCN^-, S^{2-} form outer orbital complexes and other ligands form inner orbital complexes. e.g. $[CoF_6]^{3-}$



Complex has unpaired electrons, therefore it will be paramagnetic in nature.

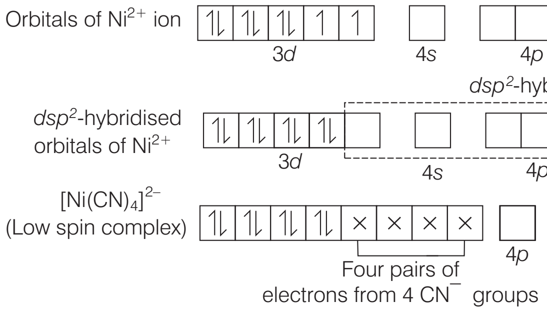
- If the metal has coordination number four and has dsp^2 or sp^3-hybridisation, then the geometry of the complex will be square planar or tetrahedral respectively.
- Square planar complexes form inner orbital complexes and tetrahedral complexes form outer orbital complexes, characteristics of which are shown below:

Difference between inner and orbital complexes
(with coordination number four)

Inner orbital complexes	Outer orbital complexes
- Strong field or low spin ligands.	- Weak field or high spin ligands.
- Hybridisation is dsp^2 (where one orbital is of $3d$, one orbital of $4s$ and two orbitals of $4p$).	- Hybridisation is sp^3 (where one orbital is of $4s$ and three orbitals of $4p$).
- Square planar shape.	- Tetrahedral shape.

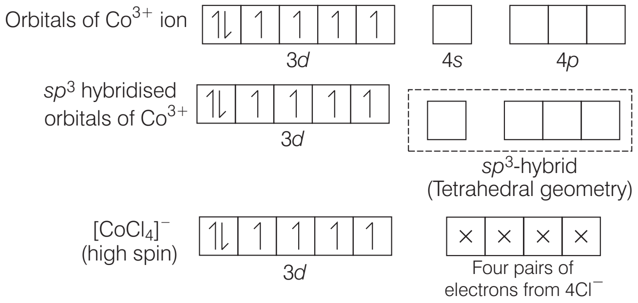
- Generally, halide (F^-, Cl^-, Br^-, I^-) ligands, $[Ni(CO)_4]$, $[Co(CO)_4]$, $[Zn(NH_3)_4]^{2+}$ complexes form outer orbital complexes and other form inner orbital complexes. e.g.

(i) **Inner Orbital Complex** $[Ni(CN)_4]^{2-}$



All electrons are paired, thus complex will be diamagnetic in nature.

(ii) **Outer Orbital Complex** $[CoCl_4]^-$



Complex has unpaired electrons, so it will be paramagnetic in nature.

Magnetic Properties

The complex compound is **paramagnetic** if one or more unpaired electrons are present in the d-subshell. If the complex does not contain any unpaired electrons, it is **diamagnetic**.

Magnetic moment, $\mu = \sqrt{n(n+2)}$ BM

Limitation of VBT

Although this theory described the formation, structure and magnetic behaviour of complexes successfully but it suffers from the following short comings.

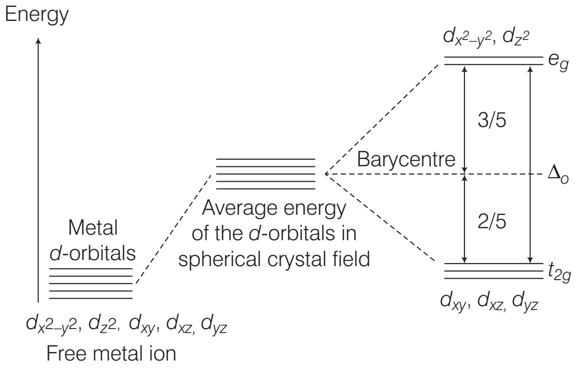
- It involves a number of assumptions.
- It describes bonding in coordination compounds only qualitatively. It does not offer any explanation for the optical absorption spectra of complexes.
- It does not describe the detailed magnetic properties of coordination compounds.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- It does not distinguish between weak and strong ligands.

Crystal Field Theory (CFT)

- The splitting of five d-orbitals of a metal ion into lower and higher energy levels due to approach of ligands, is explained by crystal field theory.
- The five d-orbitals in a gaseous metal atom/ion have same energy, i.e. degenerate.
- However, when the negative field due to ligands surrounds the metal atom, the degeneracy of d-orbitals get split depending upon the nature of the crystal field.

Crystal Field Splitting in Octahedral Coordination Entities

- Energy separation of d-orbitals is denoted by Δ_o (the subscript o is for octahedral). This is also known as crystal field splitting energy (CFSE).
- The energy of the two e_g orbitals (higher energy orbitals) will increase by (3/5) Δ_o and that of the three t_{2g} (lower energy orbitals) will decrease by (2/5) Δ_o.



Splitting of d-orbitals in octahedral crystal field

- The value of Δ_o is usually compared with the energy required for electron pairing in a single orbital (pairing energy, p).
- If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.
- If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Crystal Field Splitting in Tetrahedral Coordination Entities

- In tetrahedral coordination entity formation, d-orbital splitting pattern is reverse of splitting pattern in octahedral complexes and $\Delta_t = (4/9)\Delta_o$.
- The orbital splitting energies are not sufficiently large for forcing pairing and therefore, low spin configurations are rarely observed.
- Due to less crystal field stabilisation energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.
- An arrangement of ligands in order of increasing crystal field strength is known as **spectrochemical series**.

$$I^- < Br^- < Cl^- < F^- < C_2O_4^{2-} < H_2O < NH_3 < en < NO_2^- < CN^- < CO$$

Colour in Coordination Compounds

- In complex compounds, d-orbitals split in two sets t_{2g} and e_g. These have different energies. The difference in energies lies in visible region and electron jump from ground state t_{2g} level to higher state e_g level.
- This is known as $d-d$ transition and is responsible for colour of coordination compounds. $d-d$ transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configuration are coloured.
- On the other hand, the ions with d^0 and d^{10} configuration do not show $d-d$ transition.

NOTE Some coordination complexes have colour due to charge transfer.

Stability Constant and Stability of Complex

- **Stability of a complex** can be expressed in terms of stability constant, k. If the complex is ML_n and β_n is the overall formation constant, then

$$M + nL \rightleftharpoons ML_n$$

$$\beta_n = \frac{[ML_n]}{[M]\,[L]^n} = k_1 \times k_2 \times k_3 \ldots k_n$$

- $k_1, k_2, \ldots k_n$ are called stepwise formation constants. Alternatively, $1/k$ is known as instability constant.

The stability of a complex ion depends upon the following factors :

(i) **Higher charge** of the central metal ion, i.e. greater ionic potential $\left(\dfrac{\text{ionic charge}}{\text{ionic radius}}\right)$ and greater is the stability.

(ii) **Greater base strength** of the ligand, greater will be the stability.

(iii) **Ring formation** (chelation) in structure of the complexes is the chief factor, which increases the stability of the complexes in solution.

(iv) If a multidentate ligand happens to be cyclic without any steric effects, a further increase in stability occurs. This is called **macrocyclic effect.**

The stability of complex can be determined by EAN rule

Effective atomic number EAN of a metal in a complex = atomic number of nearest inert gas.

or EAN = atomic number of metal ± valency + 2 × CN
where, CN = coordination number.

Importance and Applications of Coordination Compounds

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.
- Some important extraction processes of metals, like those of silver and gold make use of complex formation.
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds, e.g. impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel (Mond's process).
- Coordination compounds are used as catalysts for many industrial processes. e.g. rhodium complex, $[(Ph_3P)_3RhCl]$, (Wilkinson catalyst) is used for the hydrogenation of alkenes.
- Metals present in toxic proportions in animals and plants are removed by chelate therapy, e.g. Cu and Fe are removed by D-penicillamine and desferrioxime-B.

Organometallic Compounds

- Organometallic compounds contain atleast one metal carbon bond. These are of three types, *viz*, σ-bond (e.g. $(C_2H_5)_2Zn$, $(CH_3)_3Al]$, π-bonded (Zeisse's salt, ferrocene) and mixed or σ-and π-bonded (e.g. $Fe(CO)_5$, $[Ni(CO)_4]$.
- π-acid ligands have lone pair of electrons as well as π or π* molecular orbitals. They form σ coordinate bond through lone pair and also form π bond by accepting an appreciable amount of π electron density from metal atom into empty π or π* orbital. e.g. CO is a good π-acceptor (Lewis acid).
- In Zeise's salt, ethylene acts as ligand but it does not have a lone pair of electrons.
- Oxidation state of Fe in ferrocene is Fe^{2+}. In this compound there are two cyclopentadienyl anion $(C_5H_5^-)$ and iron is sandwiched between two aromatic rings.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 If excess of $AgNO_3$ is added to 100 mL of a 0.024 M solution of dichlorobis (ethylene diamine) cobalt (III) chloride how many moles of AgCl be precipitated?

(a) 0.0012 (b) 0.0016
(c) 0.0024 (d) 0.0048

2 Consider the following complexes,

1. K_2PtCl_6 2. $PtCl_4 \cdot 2NH_3$
3. $PtCl_4 \cdot 3NH_3$ 4. $PtCl_4 \cdot 5NH_3$

Their respective electrical conductances in aqueous solutions are

(a) 256, 0, 97, 404
(b) 404, 0, 97, 256
(c) 256, 97, 0, 404
(d) 404, 97, 256, 0

3 A solution containing 2.675 g of $CoCl_3 \cdot 6NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is (Atomic mass of Ag = 108 u) ➜ AIEEE 2010

(a) $[Co(NH_3)_6]Cl_3$ (b) $[CoCl_2(NH_3)_4]Cl$
(c) $[CoCl_3(NH_3)_3]$ (d) $[CoCl(NH_3)_5]Cl_2$

4 On treatment of 100 mL of 0.1 M solution of $CoCl_3.6H_2O$ with excess of $AgNO_3$; 1.2×10^{22} ions are precipitated. The complex is ➜ JEE Main 2018

(a) $[Co(H_2O)_4Cl_2]$ Cl H_2O (b) $[Co(H_2O)_3Cl_3].3H_2O$
(c) $[Co(H_2O)_6]Cl_3$ (d) $[Co(H_2O)_5Cl]$ $Cl_2.H_2O$

5 The coordination number and the oxidation state of the element E in the complex $[E(en)_2(C_2O_4)]NO_2$ are respectively, [where, en is ethylene diamine]

(a) 6 and 2 (b) 4 and 2 (c) 4 and 3 (d) 6 and 3

6 The oxidation states of Cr, in $[Cr(H_2O)_6]Cl_3$, $[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$ respectively are

➜ JEE Main 2018

(a) +3, +4 and +6 (b) +3, +2 and +4
(c) +3, 0 and +6 (d) +3, 0 and +4

7 IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is

(a) platinum diamminechloronitrite
(b) chloronitrito-N-ammineplatinum (II)
(c) diamminechloridonitrito-N-platinum (II)
(d) diamminechloronitrito-N-platinate (II)

8 Which among the following will be named as dibromidobis-(ethylenediamine) chromium (III) bromide? ➜ AIEEE 2012

(a) $[Cr(en)_3]Br_3$ (b) $[Cr(en)_2Br_2]Br$
(c) $[Cr(en)Br_4]^-$ (d) $[Cr(en)Br_2]Br$

9 The number of geometrical isomers of the complex $[Co(NO_2)_3(NH_3)_3]$ is

(a) 2 (b) 4 (c) 3 (d) 0

10 The complex, $[Pt(py)(NH_3)BrCl]$ will have how many geometrical isomers? ➜ CBSE-AIPMT 2011

(a) 2 (b) 3 (c) 4 (d) 0

11 The number of geometrical isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is (py = pyridine) ➜ JEE Main 2015

(a) 2 (b) 3 (c) 4 (d) 6

12 Consider the following reaction and statements :

$[Co(NH_3)_4Br_2]^+ + Br^- \longrightarrow [Co(NH_3)_3Br_3] + NH_3$

I. Two isomers are produced if the reactant complex ion is a *cis*-isomer.

II. Two isomers are produced if the reactant complex ion is a *trans*-isomer.

III. Only one isomer is produced if the reactant complex ion is a *trans*-isomer.

IV. Only one isomer is produced if the reactant complex ion is a *cis*-isomer. ➜ JEE Main 2018

The correct statements are

(a) (I) and (II) (b) (I) and (III)
(c) (III) and (IV) (d) (II) and (IV)

13 Which one of the following complexes shows optical isomerism? ➜ JEE Main 2016

(a) *cis* $[Co(en)_2Cl_2]Cl$ (b) *trans* $[Co(en)_2Cl_2]Cl$
(c) $[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_3Cl_3]$

14 Which of the following complex species is not expected to exhibit optical isomerism? ➜ JEE Main 2013

(a) $[Co(en)_2Cl_2]^+$ (b) $[Co(NH_3)_3Cl_3]$
(c) $[Co(CN)(NH_3)_2Cl_2]^+$ (d) $[Co(en)_3]^{3+}$

15 Which one of the following has an optical isomer? (en= ethylenediamine) ➜ AIEEE 2010

(a) $[Zn(en)(NH_3)_2]^{2+}$ (b) $[Co(en)_3]^{3+}$
(c) $[Co(H_2O)_4(en)]^{3+}$ (d) $[Zn(en)_2]^{2+}$

16 Type of isomerism which exists between $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ is

➜ JEE Main (Online) 2013

(a) linkage isomerism (b) coordination isomerism
(c) ionisation isomerism (d) solvate isomerism

17 Which of the following pairs represents linkage isomers?

➜ JEE Main 2009

(a) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
(b) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$
(c) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$
(d) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

18 Match the following and assign the correct code.

	Column I (Complex species)		**Column II** (Isomerism)
A.	$[Co(NH_3)_4Cl_2]^+$	1.	Optical
B.	*cis* $[Co(en)_2Cl_2]^+$	2.	Ionisation
C.	$[Co(NH_3)_5(NO_2)]Cl_2$	3.	Coordination
D.	$[Co(NH_3)_6][Cr(CN)_6]$	4.	Geometrical
		5.	Linkage

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	5	(b)	4	3	2	1
(c)	4	1	5	3	(d)	4	1	2	3

19 The structure of which of the following chloro species can be explained on the basis of dsp^2 hybridisation?

➜ JEE Main 2013

(a) $PdCl_4^{2-}$ (b) $FeCl_4^{2-}$ (c) $CoCl_4^{2-}$ (d) $NiCl_4^{2-}$

20 Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes are respectively,

(a) sp^3, sp^3 (b) sp^3, dsp^2
(c) dsp^2, sp^3 (d) dsp^2, dsp^2

21 Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong? ➜ AIEEE 2011

(a) The complex involves d^2sp^3 hybridisation and is octahedral in shape
(b) The complex is paramagnetic
(c) The complex is an outer orbital complex
(d) The complex gives white precipitate with silver nitrate solution

22 Which of the following is diamagnetic ?

➜ JEE Main (Online) 2013

(a) $[Fe(CN)_6]^{3-}$ (b) $[Co(ox)_3]^{3-}$
(c) $[FeF_6]^{3-}$ (d) $[CoF_6]^{3-}$

23 $NiCl_2[P(C_2H_5)_2(C_2H_5)_2]$ exhibit temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively

(a) tetrahedral and tetrahedral ➜ AIEEE 2012
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

24 The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is ➜ AIEEE 2011

(a) 1.82 BM (b) 5.46 BM (c) 2.82 BM (d) 1.41 BM

25 The magnetic moment of the complex anion $[Cr(NO)(NH_3)(CN)_4]^{2-}$ is ➜ JEE Main (Online) 2013

(a) 5.91 BM (b) 3.87 BM (c) 1.73 BM (d) 2.82 BM

26 In which of the following complexes the crystal field splitting will be least?

(a) $[Fe(H_2O)_6]^{3-}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Co(C_2O_4)_3]^{3-}$ (d) $Ni(CO)_4$

27 In which of the following octahedral complex species the magnitude of Δ_o will be maximum? ➜ JEE Main (Online) 2013

(a) $[Co(H_2O)_6]^{2+}$ (b) $[Co(CN)_6]^{3-}$
(c) $[Co(C_2O_4)_3]^{3-}$ (d) $[Co(NH_3)_6]^{3+}$

28 Among the ligands NH_3, en, CN^- and CO, the correct order of their increasing field strength, is ➜ AIEEE 2011

(a) $CO < NH_3 < en < CN^-$ (b) $NH_3 < en < CN^- < CO$
(c) $CN^- < NH_3 < CO < en$ (d) $en < CN^- < NH_3 < CO$

29 The colour of the coordination compounds depend on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3+}$
(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$
(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

30 Which of the following compounds is not yellow coloured? ➜ JEE Main 2015

(a) $Zn_2[Fe(CN)_2]$ (b) $K_3[Co(NO_2)_6]$
(c) $(NH_4)_3[As(Mo_3O_{10})_4]$ (d) $BaCrO_4$

31 The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is ➜ JEE Main 2014

(a) $L_4 < L_3, L_2 < L_1$ (b) $L_1 < L_3 < L_2 < L_4$
(c) $L_3 < L_2 < L_4 < L_1$ (d) $L_1 < L_2 < L_4 < L_3$

32 According to EAN rule, how many CO groups should be attached to Fe?

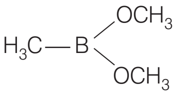
(a) 4 (b) 5 (c) 6 (d) 8

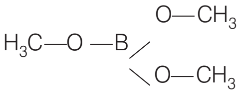
33 Among the following which is not the π-bonded organometallic compound?

(a) $K[PtCl_3(\eta^2 - C_2H_4)]$ (b) $Fe(\eta^5 - C_5H_5)_2$
(c) $(CH_3)_4Sn$ (d) $Cr(\eta^6 - C_6H_6)_2$

34 Which of the following is an organometallic compound ?

(a) $C_2H_5 - Zn - C_2H_5$

(b)


(c)


(d) None of these

35 Ferrocene is an example of

(a) sandwiched complex
(b) pi-bonded complex
(c) a complex in which all the five carbon atoms of cyclopentadiene anion are bonded to the metal
(d) All of the above

36 An aqueous solution of an inorganic salt (X), when added to an aqueous solution of barium chloride, a precipitate insoluble in dil. HCl is obtained. Addition of excess of KI to X gives a brown precipitate which turns white on addition of excess of hypo. With an aqueous solution of potassium ferrocyanide, a chocolate coloured precipitate is formed. X is

(a) $Cu(NH_3)_4SO_4$ (b) $CuSO_4 \cdot 5H_2O$
(c) $ZnSO_4 \cdot 5H_2O$ (d) $AgNO_3$

37 The equation which is balanced and represents the correct product(s) is ➜ JEE Main 2014

(a) $Li_2O + 2KCl \longrightarrow 2LiCl + K_2O$
(b) $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$
(c) $[Mg(H_2O_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{Excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$
(d) $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$

38 Which of the following statements is incorrect ? ➜ JEE Main (Online) 2013

(a) Fe^{3+} ion also gives blood red colour with SCN^- ion
(b) Fe^{3+} ion gives red colour with SCN^- ion
(c) On passing H_2S into Na_2ZnO_2 solution, a white ppt of ZnS is formed
(d) Cupric ion reacts with excess of ammonia solution to give deep blue colour of $[Cu(NH_3)_4]^{2+}$ ion

39 **Assertion** (A) $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature.

Reason (R) Chelate complexes tend to be more stable.

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct incorrect and Reason is incorrect
(d) Both Assertion and Reason are incorrect

Direction (Q. Nos. 40 and 41) *Each of these questions contains two statements : Statement* I *(Assertion) and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true

40 **Statement I** $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.

Statement II The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons.

41 **Statement I** The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.

Statement II Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?

(a) $[Fe(CO)_5]$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$

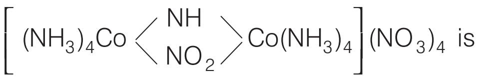
2 The value of CFSE for complex ion $[CoCl_6]^{4-}$ is 18000 cm^{-1}. The CFSE for $[CoCl_4]^{2-}$ complex ion will be

(a) 18000 cm^{-1} (b) 16000 cm^{-1} (c) 8000 cm^{-1} (d) 2000 cm^{-1}

3 For an octahedral complex, which of the following *d*- electron configuration will give maximum CFSE ?

(a) High spin d^6 (b) Low spin d^4
(c) Low spin d^5 (d) High spin d^7

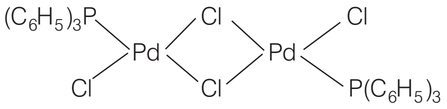
4 The oxidation state of cobalt in



$$\left[(NH_3)_4Co\begin{matrix}NH\\NO_2\end{matrix}Co(NH_3)_4\right](NO_3)_4$$ is

(a) 2 (b) 3
(c) 4 (d) 6

5 IUPAC name for



(a) chlorotriphenylphosphinepalladium (II)- μ-dichloro chlorotriphenylphosphinepalladium (II)
(b) chlorotriphenylphosphine palladium (III)- μ-dichlorochlorotriphenyl phosphine palladium (II)
(c) triphenylphosphinechloro palladium (II)- μ-dichlorido triphenylphosphinechloro palladium (III)
(d) triphenylphosphinechloro palladium (III)- μ-dichlorotriphenylphosphinechloro palladium (III)

6 Among the following metal carbonyls, the C—O bond order is lowest in

(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]^+$
(c) $[Cr(CO)_6]^+$ (d) $[V(CO)_6]^-$

7 Which of the following compounds shows optical isomerism?

(a) $[Co(CN)_6]^{3-}$ (b) $[Cr(C_2O_4)_3]^{3+}$
(c) $[ZnCl_4]^{2-}$ (d) $[Cu(NH_3)_4]^{2+}$

8 Which can exist both as diastereomer and enantiomer?

(a) $[Pt(en)_3]^{4+}$ (b) $[Pt(en)_2ClBr]^{2+}$
(c) $[Ru(NH_3)_4Cl_2]^0$ (d) $[PtCl_2Br_2]^0$

9 The correct order for the wavelength of absorption in the visible region is

(a) $[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$
(b) $[Ni(NO_2)_6]^{4-} < [Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+}$
(c) $[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$
(d) $[Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+} < [Ni(NO_2)_6]^{4-}$

10 A complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio 1 : 4. 0.1 M solution of this complex was found to freeze at $-0.372°$ C. What is the formula of the complex ? $[K_f(\text{water}) = 1.86° \text{ C/m}]$

(a) $[Co(NH_3)_4Cl_2]Cl$ (b) $[Co(NH_3)_5Cl]Cl_2$
(c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(NH_3)_6]Cl_3$

11 Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in the alkaline solutions but not in acidic solutions. What is the reason for it ?

(a) In acidic solutions hydration protects copper ions
(b) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available
(c) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali
(d) Copper hydroxide is an amphoteric substance

12 What is the ratio of uncomplexed to complexed Zn^{2+} ion in a solution that is 10 M in NH_3, if the stability constant of $[Zn(NH_3)_4]^{2+}$ is 3×10^9?

(a) 3.3×10^{-9} (b) 3.3×10^{-11}
(c) 3.3×10^{-14} (d) 3×10^{-13}

13 How many moles of AgCl would be obtained, when 100 mL of 0.1 M $Co(NH_3)_5Cl_3$ is treated with excess of $AgNO_3$?

(a) 0.01 (b) 0.02
(c) 0.03 (d) None of these

14 The complex $[Fe(H_2O)_5NO]^{2+}$ is formed in the brown ring test for nitrates when freshly prepared $FeSO_4$ solution is added to aqueous solution of NO_3^- followed by addition of conc. H_2SO_4. Select the correct statement about this complex.

(a) Colour change is due to charge transfer
(b) It has iron in +1 oxidation state and nitrosyl as NO^+
(c) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe
(d) All the above are correct statements

ANSWERS

SESSION 1	**1** (c)	**2** (a)	**3** (a)	**4** (d)	**5** (d)	**6** (c)	**7** (c)	**8** (b)	**9** (a)	**10** (b)
	11 (b)	**12** (b)	**13** (a)	**14** (b)	**15** (b)	**16** (a)	**17** (b)	**18** (d)	**19** (a)	**20** (b)
	21 (c)	**22** (b)	**23** (c)	**24** (c)	**25** (c)	**26** (a)	**27** (b)	**28** (b)	**29** (c)	**30** (a)
	31 (d)	**32** (b)	**33** (c)	**34** (a)	**35** (d)	**36** (b)	**37** (b)	**38** (a)	**39** (b)	**40** (a)
	41 (a)									
SESSION 2	**1** (c)	**2** (c)	**3** (c)	**4** (b)	**5** (a)	**6** (b)	**7** (b)	**8** (b)	**9** (a)	**10** (a)
	11 (b)	**12** (c)	**13** (b)	**14** (d)						

Hints and Explanations

SESSION 1

1 100 mL of 0.024 M = 0.0024 mole of the complex.
Complex is $[Co(en)_2Cl_2]Cl$ and thus, one Cl^- is formed per mole of the complex which gives 1 mole of AgCl.
Hence, moles of AgCl precipitated are = 0.0024

2 Greater the number of ions produced greater, the conductance.

1. $K_2[PtCl_6] \rightleftharpoons 2K^+ + [PtCl_6]^{2-}$ (3 ions)
2. $PtCl_4 \cdot 2NH_3 \rightleftharpoons [Pt(NH_3)_2Cl_4] \longrightarrow$ no ions (least)
3. $[Pt(NH_3)_3Cl_3]Cl \rightleftharpoons [Pt(NH_3)_3Cl_3]^+ + Cl^-$ (2 ions)
4. $[Pt(NH_3)_5Cl]Cl_3 \rightleftharpoons [Pt(NH_3)_5Cl] + 3Cl^-$ (4 ions maximum)

3 Mole of $CoCl_3 \cdot 6NH_3 = \dfrac{2.675}{267.5} = 0.01$ mol

$$AgNO_3(aq) + Cl^-(aq) \longrightarrow AgCl\downarrow(\text{white}) + NO_3^-(aq)$$

Moles of AgCl $= \dfrac{4.78}{143.5} = 0.03$ mol

0.01 mol $CoCl_3 \cdot 6NH_3$ gives = 0.03 mol AgCl
$\therefore$ 1 mol $CoCl_3 \cdot 6NH_3$ ionises to give = 3 mol Cl^-
Hence, the formula of compound is $[Co(NH_3)_6]Cl_3$.

4 Molarity (M) $= \dfrac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$

$\therefore$ Number of moles of complex

$$= \frac{\text{Molarity} \times \text{volume (in mL)}}{1000} = \frac{0.1 \times 100}{1000} = 0.01 \text{ mol}$$

Number of moles of ions precipitate $= \dfrac{12 \times 10^{22}}{6.02 \times 10^{23}} = 0.02$ mol

$\therefore$ Number of Cl^- present in ionisation sphere

$$= \frac{\text{Number of moles of ions precipitated}}{\text{Number of moles of complex}} = \frac{0.02}{0.01} = 2$$

$\therefore$ $2Cl^-$ are present outside the square brackets, i.e. in ionisation sphere. Thus, the formula of complex is $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$.

5 $\begin{array}{l} CH_2—NH_2 \\ | \\ CH_2—NH_2 \end{array}$ is a bidentate ligand. $C_2O_4^{2-}$ is also a bidentate ligand. Hence, coordination number = 6
Complex can be ionised as

$$[E(en)_2(C_2O_4)]NO_2 \longrightarrow [E(en)_2(C_2O_4)]^+ + NO_2^-$$

Oxidation number $= x + 0 + (-2) = 1$
$\therefore \quad x = 3$

6 Let the oxidation state of Cr in all cases is 'x'.

(i) Oxidation state of Cr in $[Cr(H_2O)_6]Cl_3$
$x + (0 \times 6) + (-1 \times 3) = 0$
or $x + 0 - 3 = 0$ or $x = +3$

(ii) Oxidation state of Cr in $[Cr(C_6H_6)_2]$
$x + (2 \times 0) = 0$ or $x = 0$

(iii) Oxidation state of Cr in
$K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$
$1 \times 2 + x + (-1 \times 2) + (-2 \times 2) + (-2) + 0 = 0$
or $2 + x - 2 - 4 - 2 = 0$ or $x - 6 = 0$
Hence, $x = +6$
Thus, +3, 0 and +6 is the answer.

7 Diamminechloridonitrito-N-platinum (II).

8 Two Br, two (en) and one Cr are parts of complex. Charge on the complex is

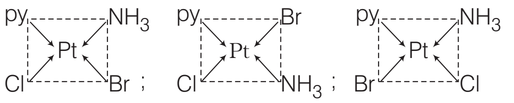
$$\left.\begin{aligned}2\,(\text{Br}) &= -2\\ 2\,(\text{en}) &= 0\\ 1\,(\text{Cr}) &= +3\end{aligned}\right\} = +1$$

Thus, complex ion is $[Cr(en)_2Br_2]^+$.

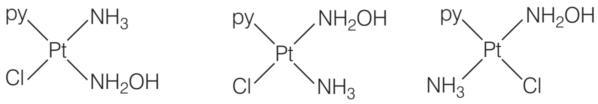
Since, anion is bromide thus, complex is $[Cr(en)_2Br_2]$ Br.

9 Complex $[Co(NO_2)_3(NH_3)_3]$ is of type MA_3B_3 which have 2 geometrical isomers that is *fac* and *mer* isomers.

10 *M*(*ABCD*) type complex have three geometrical isomers as:

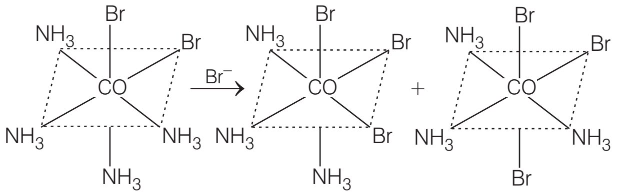


11 $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is square planar complex. The structures are formed by fixing a group and then arranging all the groups.



Hence, this complex has 3 geometrical isomers.

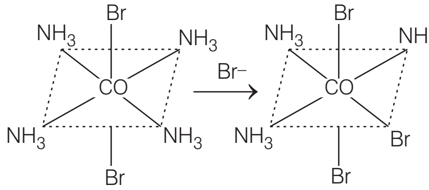
12 If the reactant is *cis* isomer than following reaction takes place.



cis-isomer *Facial* *Meridonial*

i.e. two isomers are produced.

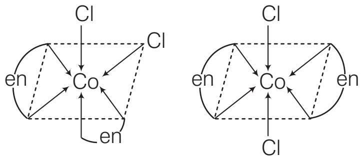
If the reactant is *trans* isomer than following reaction takes place.



trans *Meridonial*

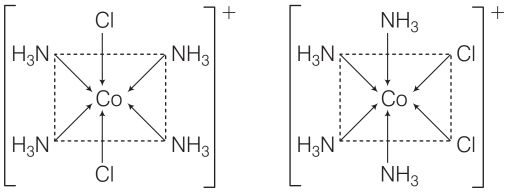
i.e. only 1 isomer is produced. Thus, statement (I) and (III) are correct resulting to option (b) as the correct answer.

13 $[Co(en)_2Cl_2]Cl$ is of type $M(AA)_2B_2$, where only *cis* isomer shows optical isomerism.



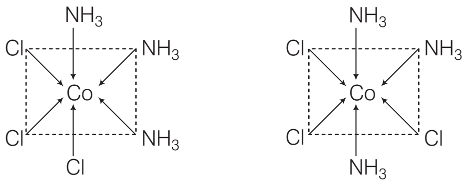
cis-$[Co(en)_2Cl_2]Cl$ (optically active) *trans*-$[Co(en)_2Cl_2]Cl$ (optically inactive due to plane of symmetry)

$[Co(NH_3)_4Cl_2]Cl$ can exist in both *cis* and *trans* forms that are shown below:



trans-$[Co(NH_3)_4Cl_2]Cl$ (optically inactive) *cis*-$[Co(NH_3)_4Cl_2]Cl$ (optically inactive)

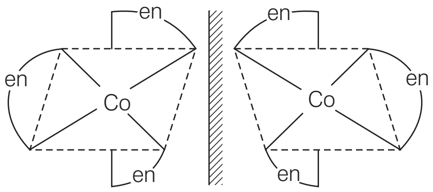
$[Co(NH_3)_3Cl_3]$ exists in *fac* and *mer*-isomeric forms and both are optically inactive.



fac-isomer (optically inactive) *mer*-isomer (optically inactive)

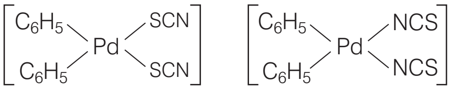
14 Optical isomerism is exhibited by only those complexes which lacks elements of symmetry. $[Co(NH_3)_3Cl_3]$ is of type MA_3B_3 which shows *facial* as well as *meridional* isomerism. But both the forms contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

15 Complex $[Co(en)_3]^{3+}$ is of type MA_3 has no plane of symmetry and centre of symmetry that's why it is optically active.



Mirror images (Non-superimposable)

16 Given compound shows linkage isomerism because SCN is ambidentate ligand.

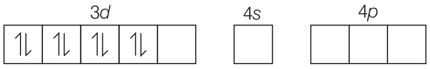


17 Linkage isomers are formed due to the presence of ambidentate ligands. $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$ are linkage isomers due to SCN, ambidentate ligand.

18 A → 4, B → 1, C → 2, D → 3.

19 In $[PdCl_4]^{2-}$, the oxidation state of Pd is +2.

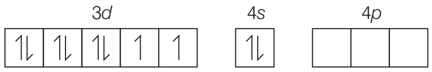
$Pd = [kr]4d^8 5s^0 =$



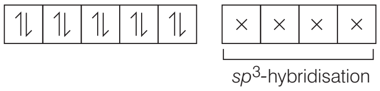
Although Cl^- is a weak field ligand but in case of $[PdCl_4]^{2-}$, the electrons of Pd are paired up because of its large size and results in dsp^2-hybridisation. In all other cases pairing is not possible because of weak ligand Cl^-, so hybridisation is sp^3 with tetrahedral structure.

20 In $[Ni(CO)_4]$, the oxidation state of Ni is zero.

$NI(28) = [Ar]3d^8, 4s^2$

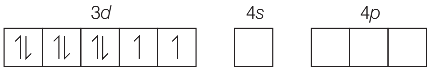


CO is strong field ligand, causes pairing, thus

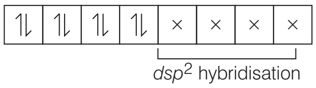


In $[Ni(CN)_4]^{2-}$, the oxidation state of Ni is $+2$.

$NI^{2+} = [Ar]3d^8, 4s^0$



CN^- is strong field ligand causes pairing, thus

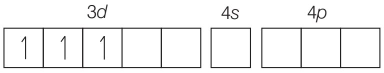


21 $\underbrace{[Cr(NH_3)_6]}_{\text{Coordinate sphere}} \cdot \underbrace{Cl_3}_{\text{Ionisable}}$

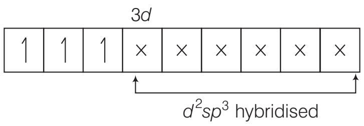
$[Cr(NH_3)_6]^{3+} + 3Cl^- \xrightarrow{AgNO_3} AgCl\downarrow$
White precipitate

$Cr^{3+} = [Ar]3d^3\ 4s^0$

$Cr^{3+} = [Ar]$



$[Cr(NH_3)_6]^{3+} = [Ar]$



Indicates that lone pair of NH_3 are donated to Cr.

(a) d^2sp^3 hybridisation, octahedral. Thus, statement is correct.

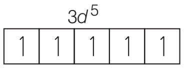
(b) There are three unpaired electrons, hence paramagnetic. Thus, statement is correct.

(c) d^2sp^3 inner orbital complex. thus statement is incorrect.

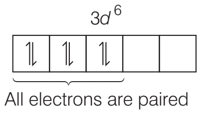
(d) Due to ionisable Cl^- ions, white precipitate with $AgNO_3$ thus, statement is correct.

22 Fe^{3+} and Co^{3+} both the ions have unpaired electrons in their ground state, but strong field ligands, like CN^-, ox if present, pair up the unpaired electrons resulting in diamagnetism.

In $[Fe(CN^-)_6]^{3-}, Fe^{3+} = 3d^5 4s^0$



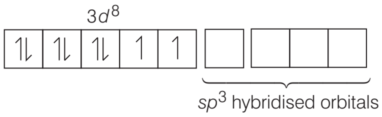
In $[Co(ox)_3]^{3-}, Co^{3+} = 3d^6 4s^0$



Also after pairing there is one unpaired electron in $[Fe(CN)_6]^{3-}$. Thus, $[Co(ox)_3]^{3-}$ is a diamagnetic species as all the electrons are paired in it.

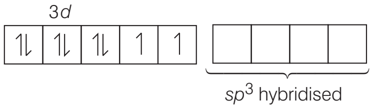
23 In the given complex, $NiCl_2\ \{P(C_2H_5)_2(C_2H_5)_2\}$, Ni is in $+2$ oxidation state.

$Ni^{2+} =$



For the given four-coordinated complex to be paramagnetic, it must possess unpaired electrons in the valence shell. The geometry of paramagnetic complex must be tetrahedral. On the other hand, for complex to be diamagnetic, there should not be any unpaired electrons in the valence shell. This condition can be fullfilled by pairing electrons of 3*d*- orbitals. The geometry of diamagnetic complex is square planar.

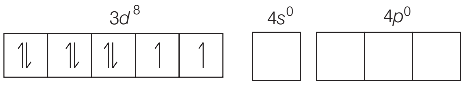
$Ni^{2+} =$



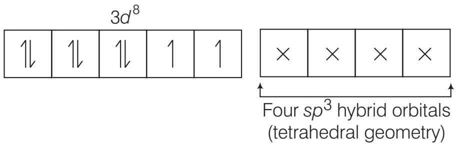
24 $[NiCl_4]^{2-}$; oxidation number of Ni, $x - 4 = -2 \quad \therefore \quad x = +2$

$Ni_{(28)} = [Ar]\ 3d^8, 4s^2$

$Ni^{2+} = [Ar]$



$[NiCl_4]^{2-}$



Cl^- is a weak field ligand and thus, unpaired electrons are not paired. Lone pairs from $4Cl^-$ are accommodated in four sp^3 hybrid orbitals and thus $[NiCl_4]^{2-}$ has 2 unpaired electrons.

Magnetic moment (spin only)

$= \sqrt{n(n+2)}$ BM, $n =$ unpaired electrons $= 2$,

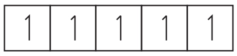
$= \sqrt{2(2+2)}$

$= 2.828$ BM ≈ 2.82 BM

25 In $[Cr(NO)(NH_3)(CN)_4]^{2-}$, let the oxidation state of Cr be x.

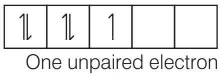
$\therefore x + (+1) + (0) + (-1)4 = -2, \ x - 3 = -2 \ \text{ or } \ x = 1$

$Cr^+ = [Ar]3d^5 4s^0 =$



But CN^- and NO being strong field ligands pair up the unpaired electrons of Cr^+.

$[Cr(NO)(NH_3)(CN)_4]^{2-} =$



$\therefore \qquad n = 1$

Magnetic moment, $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM

26 Δ_o depends on the strength of negative field ligand. Spectrochemically, it has been found that the strength of splitting is as follows :

$CO > \underline{CN^-} > \underline{NO_2^-} > en > \underline{NH_3} > py > NCS^- > \underline{H_2O} > \underline{O^{2-}} >$

$\underline{ox^{2-}} > OH^- > F^- > Cl^- > SCN^- > S^{2-} > Br^- > I^-$

As H_2O is a weak field ligand among the other given ligands, so it will have Δ_o value least.

27 Δ_o magnitude depends upon the charge of central metal atom and strength of ligand. Among the given, CN^- is the strongest field ligand. So, complex $[Co(CN)_6]^{3-}$ will exhibit the maximum value of Δ_o.

28 Based on spectrochemical series, ligands arranged in increasing order of crystal field strength are as follows:

$$NH_3 < en < CN^- < CO$$

29 The CFSE of the ligands in the order $H_2O < NH_3 < CN^-$.

$$\text{As CFSE} \propto \frac{1}{\lambda}$$

Therefore, wavelengths absorbed will be in the opposite order as $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co\,(CN)_6]^{3-}$.

30 $Zn_2\,[Fe\,(CN)_6]$, $K_3\,[Co\,(NO_2)_6]$ and $[(NH_4)_3\text{ As }(Mo_3O_{10})_4]$ show colour due to d-d transition while $BaCrO_4$ is coloured due to charge transfer phenomenon.
Further, according to spectro-chemical series the strong ligand possessing complex has higher energy and hence lower wavelength. Therefore, complexes containing NO_2, NH_4^+, O^{2-} etc., ligands show yellow colour while CN^- forces the complex to impart white colour.

31 Ligand field strength ∝ Energy of light absorbed

$$\propto \frac{1}{\text{Wavelength of light absorbed}}$$

λ Absorbed light	L_1 Red	L_2 Green	L_3 Yellow	L_4 Blue

$\longrightarrow$

Wavelength of absorbed light decreases.

∴ Lesser is the wavelength of light absorbed, greater the extent of crystal-field splitting, hence higher is the field strength of the ligand.

The increasing order of wavelength is blue < yellow < green < red. There increasing order of ligand strength $L_1 < L_2 < L_3 < L_4$.

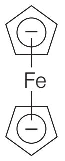
32 Atomic number of Fe = 26

Atomic number of next noble gas = 36
∴ Number of electrons to be provided by ligands = 36 – 26 = 10
∵ Each CO group provide 2 electrons,
∴ Number of CO groups attached to Fe = 5

33 The organometallic compounds having π-bond between carbon and metal are known as π-bonded organometallic compound. $(CH_3)_4Sn$ is not a π-bonded organometallic compound.

34 An organometallic compound is one, which contains atleast one metal-carbon bond. In $B(OCH_3)_3$ and $CH_3B(OCH_3)_2$ there is no carbon atom that linked directly to a metal. Thus, $C_2H_5 — Zn — C_2H_5$ is an organometallic compound.

35 Ferrocene is a sandwich complex compound in which all the five carbon atoms of ferropentadiene anions are linked directly to the metal Fe (π-bonds).



Ferrocene, Fe (η^5–C_5H_5)

36 $\underset{(X)}{CuSO_4 \cdot 5H_2O} + BaCl_2 \longrightarrow \underset{\text{Insoluble in HCl}}{BaSO_4} + CuCl_2$

$$2CuSO_4 + KI\,(\text{excess}) \longrightarrow \underset{\text{Brown ppt}}{Cu_2I_2} + 2K_2SO_4 + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$$2CuSO_4 + K_4\,[Fe(CN)_6] \longrightarrow \underset{\text{Chocolate ppt.}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

37 (a) $\underset{\text{Weak base}}{Li_2O} + 2KCl \longrightarrow 2LiCl + \underset{\text{Strong base}}{K_2O}$

This is wrong equation, since a stronger base K_2O cannot be generated by a weaker base Li_2O.

(b) $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+}\,(aq) + 5\,NH_4^+ + Cl^-$

This is correct. All amine complexes can be destroyed by adding $H^{\oplus}$. Hence, on adding acid to $[CoCl\,(NH_3)_5]$. It gets converted to $Co^{2+}\,(aq)$, NH_4^+ and Cl^-.

(c) $[Mg(H_2O)_6]^{2+} + EDTA^{4-} \xrightarrow[\text{excess}]{OH^-} [Mg\,(EDTA)]^{2+} + 6\,H_2O$

This is wrong equation, since the formula of complex must be $[Mg\,(EDTA)]^{2-}$.

(d) The 4th reaction is incorrect. It can be correctly represented as:

$$2CuSO_4 + 10KCN \longrightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2\uparrow$$

38 $Fe^{3+} + SCN^- \longrightarrow \underset{\substack{\text{Red colour, not}\\ \text{blood red colour}}}{[Fe\,(SCN)]^{2+}}$

All other given statements are correct.

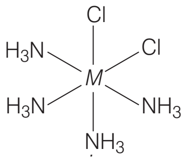
39 **Correct Explanation** Cr in the given complex $[Cr(H_2O)_6]Cl_2$ is present as Cr^{2+} which undergo oxidation to Cr^{3+} and Fe in the complex $[Fe(H_2O)_6]Cl_2$ is present as Fe^{2+} which can undergo oxidation to Fe^{3+} (H_2O is a weak ligand in both).

40 In $[Fe(H_2O)_5NO]SO_4$; Let oxidation state of Fe be x.

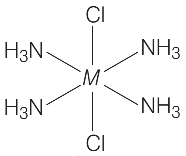
$$x + 5 \times (0) + 1 + (-2) = 0,\quad x = +1,\ Fe^+ = [Ar]\,3d^6\,4s^1$$

As NO^+ is a strong ligand causes pairing of 4s electron. Thus, the configuration is $3d^7$ and number of unpaired electrons = 3.

41 Both *cis* and *trans* forms of complexes $[M(NH_3)_4Cl_2]$ are optically inactive. There are plane of symmetry in addition to that there is alternate axis of symmetry which makes them opticaly inactive.



cis



trans

SESSION 2

1 $C_2O_4^{2-}$ is bidentate ligand that forms the chelate and hence $[Fe(C_2O_4)_3]^{3-}$ is the most stable complex.

2 Δ_o value of $[CoCl_6]^{4-} = 18000\text{ cm}^{-1}$

$$\Delta_t = \frac{4}{9} \times \Delta_o = \frac{4}{9} \times 18000 = 8000\text{ cm}^{-1}$$

3 $\Delta_o = -0.4 \times n_{t_{2g}} + 0.6 \times n_{e_g}$ [where, n = number of electrons]

(a) For high spin d^6, Δ_o (CFSE) $= -0.4 \times 4 + 0.6 \times 2 = -0.4$

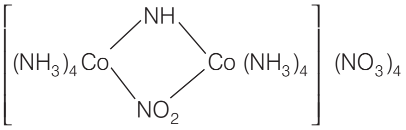
(b) For low spin d^4, Δ_o (CFSE) $= -0.4 \times 4 + 0.6 \times 0 = -1.6$

(c) For low spin d^5, Δ_o (CFSE) $= -0.4 \times 5 + 0.6 \times 0 = -2.0$

(d) For high spin d^7, Δ_o (CFSE) $= -0.4 \times 5 + 0.6 \times 2 = -0.8$

The calculations reveal that maximum CFSE is for low spin d^5 configuration.

4



$\because$ $(4 \times 0) + x + (1 \times -1) + (1 \times -1) \times x + (4 \times 0) + (4 \times -1) = 0$

$\therefore$ $x = +3$

5 The IUPAC name of the compound is

chlorotriphenylphosphine palladium (II)-μ- dichloro chlorotriphenylphosphinepalladium (II).

6 If the metal in the metal carbonyl has more number of electrons then back donation will be more, more will the bond order of M—C bond and less is the bond order of C—O bond.

The electrons present in the metals are as follows:

In $[Mn(CO)_6]^+$, $Mn^+ = 3d^5 4s^1$

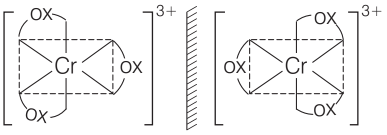
In $[Fe(CO)_5]^+$, $Fe^+ = 3d^6 4s^1$

In $[Cr(CO)_6]^+$, $Cr = 3d^5 4s^0$

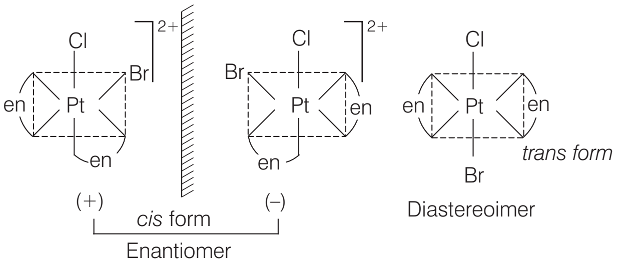
In $[V(CO)_6]^-$, $V^- = 3d^4 4s^0$

As Fe in $[Fe(CO)_5]^+$ has maximum d -electrons therefore bond order of C—O will be least.

7 $[Cr(C_2O_4)_3]^{3+}$ complex is of type $[M(AA)_3]$ shows optical isomerism because its mirror image is not superimposable and do not possess plane of symmetry.



8 $[Pt(en)_2Cl\,Br]^{2+}$ will exist both as diastereoimer and enantiomer.



9 The absorption of light in a complex depends upon the charge of the metal ion and on the nature of the ligands. As the complexes given in the options have same charge on the metal ion (Ni^{2+}), therefore absorption is only dependent on the nature of ligand. Stronger field ligand absorbs maximum light, i.e. of minimum wavelength as $\Delta E \propto \frac{1}{\lambda}$.

Since, the Increasing order of nature of ligand given in the options is $H_2O < NH_3 < NO_2^-$.

Therefore, the correct order of wavelength of absorption will be $[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$.

10 $\Delta T_f = K_f \times m = 1.86 \times 0.1 = 0.186\,°C$

Observed value of $\Delta T_f = 0.372\,°C$

As observed value of ΔT_f is double the theoretical value, this shows that each molecule of the complex dissociates to form two ions. Hence, formula is $[Co(NH_3)_4Cl_2]Cl$.

11 Ammonia forms complex ion $[Cu(NH_3)_4]^{2+}$ with Cu^{2+} ions only in the alkaline medium as in acidic medium H^+ coordinates with ammonia molecule forming NH_4^+ ions and the electron pair present on NH_4^+ will not be available for donation.

12 $Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$,

$$K_f = \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}]\,[NH_3]^4} = 3 \times 10^9$$

$$\therefore \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}]} = [NH_3]^4 \times 3 \times 10^9 = [10]^4 \times 3 \times 10^9 = 3 \times 10^{13}$$

$$\therefore \frac{[Zn^{2+}]}{[Zn(NH_3)_4]^{2+}} = 3.3 \times 10^{-14}$$

13 $Co(NH_3)_5Cl_3$ is an octahedral complex ionising in aqueous solution as :

$$[Co\,(NH_3)_5Cl]\,Cl_2 \longrightarrow [Co\,(NH_3)_5Cl]^{2+} + 2Cl^-$$

Moles of $[Co\,(NH_3)_5Cl]\,Cl_2 = \frac{0.1}{1000} \times 100 = 0.01$ mol

Moles of AgCl formed $= 2 \times$ moles of Cl^- in complex

$= 0.01 \times 2 = 0.02$ mol

14 $Fe^{2+} = \overset{3d^6}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$

$$\left.\begin{array}{l} \underset{\text{Electron transfer from NO.}}{NO} \longrightarrow NO^+ + e^- \\ Fe^{2+} + e^- \longrightarrow Fe^+ \end{array}\right] \text{Charge transfer}$$

$Fe^+ = \overset{\substack{(c)\\ 3d^7}}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$

$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.87$ BM

$\therefore$ Thus, all the given options are correct.