DAY TWENTY EIGHT

Coordination Compounds

Learning & Revision for the Day

- Coordination Compounds
- Werner's Theory
- Nomenclature of Coordination Compounds
- Isomerism in Coordination Compounds
- Valence Bond Theory (VBT)
- Crystal Field Theory (CFT)
- Importance of Coordination compounds

Coordination Compounds

Complex or 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.
$$\underset{\text{Ionisable species}}{K_4}\ \underset{\text{Non-ionisable coordination sphere}}{[Fe(CN)_6]} + H_2O \longrightarrow 4K^+ + \underset{\text{Central metal atom ligands}}{[Fe(CN)_6]^{4-}}$$

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

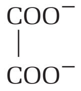
- **Complex Ion** It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or molecules. Based on complex ions, complexes can be of three types
  - (i) **Anionic complex** carries negative charge. e.g.
$$K_3[Fe(C_2O_4)_3] \longrightarrow 3K^+ + \underset{\text{Anionic complex}}{[Fe(C_2O_4)_3]^{3-}}$$
  - (ii) **Cationic complex** carries positive charge. e.g.
$$[CoCl_2(en)_2]Cl \longrightarrow \underset{\text{Cationic complex}}{[CoCl_2(en)_2]^+} + Cl^-$$
  - (iii) **Neutral complex** does not carry any charge. e.g. $\underset{\text{(Neutral complex)}}{[Ni(CO)_4]}$

NOTE
- **Homoleptic complexes** are the complexes in which a metal is bound to only one kind of donor groups, e.g. $[Co(NH_3)_6]^{3+}$.
- **Heteroleptic complexes** are the complexes in which a metal is bound to more than one kind of donor groups, e.g. $[Co(NH_3)_4Cl_2]^+$.

- **Ligands** The ions or molecules bound to the central atom/ion in the coordination entity. It can be of five types:
  - (i) **Unidentate ligand** is bound to a metal ion through a single donor atom.

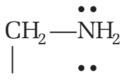
    e.g. $H_2O, NH_3, CO, Cl^-, NH_2^-$ etc.
  - (ii) **Didentate or bidentate ligand** is bound to a metal ion through two donor atoms.

    e.g.



$$\begin{array}{c} COO^- \\ | \\ COO^- \end{array}$$

Oxalate ion (ox)



$$\begin{array}{l} CH_2—\ddot{N}H_2 \\ | \\ CH_2—\ddot{N}H_2 \end{array}$$

Ethylene diamine (en)

  - (iii) **Polydentate** is bound to a metal ion through several donor atoms, e.g. ethylene diamine tetraacetate ion $[EDTA]^{4-}$.
  - (iv) **Ambidentate ligand** can ligate through two different atoms, e.g. $—NO_2$, —ONO, —SCN, —NCS, etc.
  - (v) **Chelate ligand** may be di or polydentate ligands which forms closed ring with central metal ion. Closed ring is known as chelate ring and this process is called **chelation**.
- **Coordination Number** The number of chemical bonds formed by the ligands with central metal atom or ion.
- **Coordination Sphere** The central ion and the ligands attached to it and is written in a square bracket, while writing the chemical formula. The ionisable group written outside the bracket is known as counter ions.
- **Coordination Polyhedron** The spatial arrangement of the ligands which are directly attached to the central atom or ion. e.g. $[Co(NH_3)_6]^{3+}$ is octahedral $[Ni(CO)_4]$ is tetrahedral
- **Oxidation Number of Central Atom** The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom, is called oxidation number of central atom. e.g. oxidation number of copper in $[Cu(Cl)_4]^{3-}$ is + 1 and it is written as Cu(I).
- **Magnetic Properties** It complex is determined by the number of unpaired electron. The given complex compound is paramagnetic, if one or more unpaired electrons are present in the *d*-subshell. If the complex does not contain any unpaired electron, is diamagnetic.

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

Werner's Theory

According to this theory,

- In complex compounds, metal atom exhibit two types of valencies—primary valency and secondary valency.
- Primary valencies are satisfied by anions only, while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents the coordination number of central metal atom.
- 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 (O S of Cr) and secondary valency = 6 (CN of Cr)

Nomenclature of Coordination Compounds

The following rules are used when 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. 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. $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$,
$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

2. Stereoisomerism

Stereo isomerism occurs due to different arrangements 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 arrangements of the ligands. Important examples of this behaviour are found in square planar and octahedral complexes, 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. $[Pt(NH_3)_2Cl_2]$.

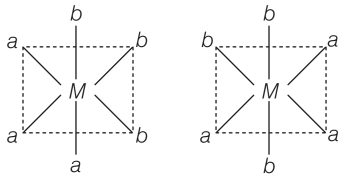
(b) **Square planar complex of the type** $[MABXL]$ (where, A, B, X, L are unidentate) shows three isomers, two *cis* and one *trans*. Such isomerism is not possible for tetrahedral geometry,
e.g. $[Pt(NH_3)(Br)(Cl)(Py)]$.

(c) **Square planar complex of 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

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.

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 (VBT)

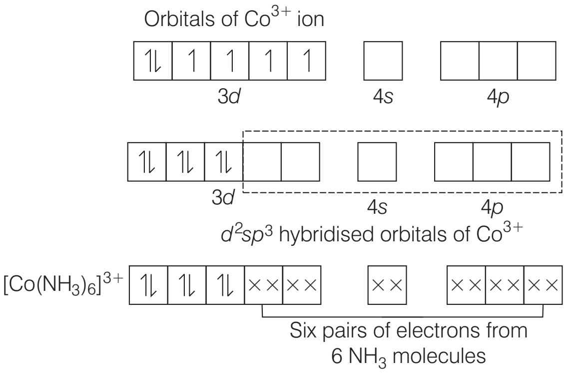
- According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These are hybridised orbitals which are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.
- Octahedral, square planar and tetrahedral complexes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

Hybridisation	Shape of coordination compound	Examples
sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]$
sp^2	Trigonal planar	$[HgI_3]^-$
sp^3	Tetrahedral	$[CuCl_4]^{2-}$, $[ZnCl_4]^{2-}$, $[Ni(CO)_4]$
dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(H_2O)_4]^{2+}$
sp^3d	Trigonal bipyramidal	$[CuCl_5]^{3-}$
dsp^3	Trigonal bipyramidal	$[Ni(CN)_5]^{3-}$ $[Fe(CO)_5]$

- 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.

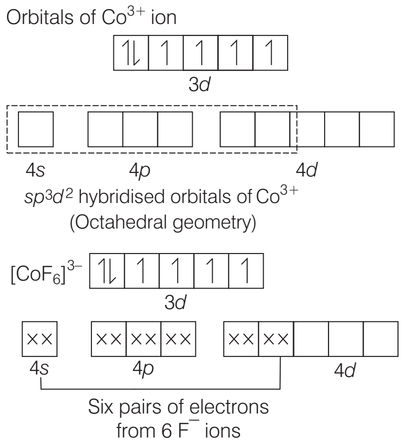
Such complexes are of the following two types:

(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.

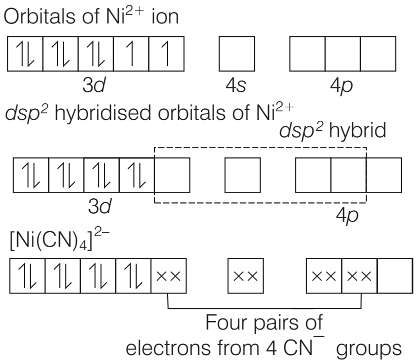
- If the metal has coordination number four and has dsp^2 or sp^3 hybridisation, then the geometry of the complex will be square planar or tetrahedral respectively.
- Square planar complexes form inner orbital and tetrahedral complexes form outer orbital complexes, characteristics of which are shown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

Metal having coordination number four

Inner orbital complexes	Outer orbital complexes
1. Strong field or low spin ligands.	Weak field ligands or high spin ligands.
2. 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 $4p$).
3. Square planar shape.	Tetrahedral shape.

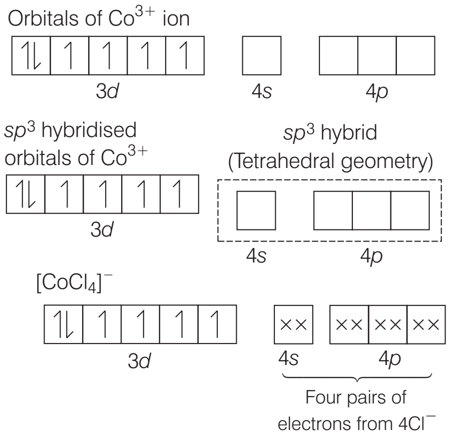
- Generally, halide (F^-, Cl^-, Br^-, I^-) ligands, $[Ni(CO)_4]$, $[Co(CO)_4]$, $[Zn(NH_3)_4]^{2+}$ complexes form outer orbital complexes and other form inner orbital complexes. e.g.

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



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

(b) **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**.

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

Limitations of VBT

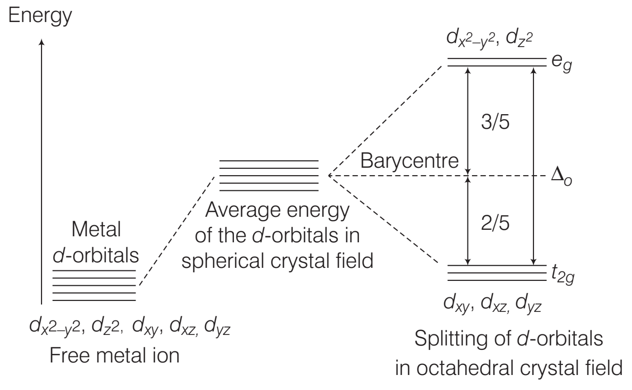
- It involves a number of assumptions.
- It describes bonding in coordination compounds only qualitatively. It does not offer any explanation for the optical absorption spectra of complexes.
- It does not describe the detailed magnetic properties of coordination compounds.
- It does not give a quantitative 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 spliting 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.



- 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 are 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 $\left(\frac{\text{ionic charge}}{\text{ionic radius}}\right)$ 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 of Coordination Compounds in Qualitative Analysis Biological Systems

(i) Hardness of water is estimated by simple titration with Na_2 EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.

(ii) Some important extraction processes of metals, like those of silver and gold make use of complex formation.

(iii) 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).**

(iv) Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, **Wilkinson catalyst**, is used for the hydrogenation of alkenes.

(v) 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**.

(vi) The platinum complex *cis*-$[Pt(NH_3)_2Cl_2]$ (cis-platin is used in the treatment of cancer.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Which of the following species is not expected to be a ligand?

(a) NO (b) NH_4^+ (c) $NH_2CH_2CH_2NH_2$ (d) CO

2 According to Lewis concept, the ligands are

(a) acidic in nature (b) basic in nature
(c) neither acidic nor basic
(d) some are acidic and others are basic

3 Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is

(a) 3 (b) 4 (c) 5 (d) 6

4 EDTA has coordination number

(a) 3 (b) 4
(c) 5 (d) 6

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

6 When 1 mole of $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 moles of AgCl are obtained. The formula of the complex is

(a) $[CrCl_3(H_2O)_3] \cdot 3H_2O$
(b) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
(c) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$
(d) $[Cr(H_2O)_6]Cl_3$

7 Iron carbonyl, $Fe(CO)_5$ is **→ NEET 2018**

(a) trinuclear (b) mononuclear
(c) tetranuclear (d) dinuclear

8 The effective atomic number of Cr ($Z = 24$) in $[Cr(NH_3)_6]Cl_3$ is

(a) 35 (b) 27
(c) 33 (d) 36

9 Which does not give a precipitate with $AgNO_3$ solution?

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

10 An aqueous solution of $CoCl_2$ on addition of excess of concentrated HCl turns blue due to formation of

(a) $[Co(H_2O)_4Cl_2]$ (b) $[Co(H_2O)_2Cl_4]^{2-}$
(c) $[CoCl_4]^{2-}$ (d) $[Co(H_2O)_2Cl_2]$

11 Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at 25°C? **→ CBSE-AIPMT 2015**

(a) $CoCl_3 \cdot 3NH_3$
(b) $CoCl_3 \cdot 4NH_3$
(c) $CoCl_3 \cdot 5NH_3$
(d) $CoCl_3 \cdot 6NH_3$

12 IUPAC name of $Na_3[Co(NO_2)_6]$ is

(a) sodiumcobaltnitrite
(b) sodiumhexanitrito cobaltate (III)
(c) sodiumhexanitrocobalt (III)
(d) sodiumhexanitrocobaltate (III)

13 The IUPAC name of $K_2[Ni(CN)_4]$ is

(a) potassium tetracyanonickelate (II)
(b) potassium tetracyanato nickelate (III)
(c) potassium tetracyanatonickel (II)
(d) potassium tetracyanonickel (III)

14 According to IUPAC nomenclature, sodium nitroprusside is named as

(a) sodium pentacyanonitrosyl ferrate (II)
(b) sodium pentacyanonitrosyl ferrate (III)
(c) Sodium nitroferricyanide
(d) sodium nitroferrocyanide

15 The type of isomerism shown by the complex $[COCl_2(en)_2]$ is **→ NEET 2018**

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

16 Which one of the following complex ions has geometrical isomers?

(a) $[Co(en)_3]^{3+}$
(b) $[Ni(NH_3)_5Br]^+$
(c) $[Co(NH_3)_2(en)_2]^{3+}$
(d) $[Cr(NH_3)_4(en)]^{3+}$

17 Indicate the complex ion which shows geometrical isomerism.

(a) $[Cr(H_2O)_4Cl_2]^+$
(b) $[Pt(NH_3)_3Cl]$
(c) $[Co(NH_3)_6]^{3+}$
(d) $[Co(CN)_5(NC)]^{3-}$

18 Octahedral $Co(NH_3)_4Br_2Cl_2$ shows isomerism

I. ionisation
II. geometrical
III. optical
IV. coordination

Choose the correct option

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

19 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) $[Cu(NH_3)_4]^{2+}$

20 Which of the following complex will show geometrical as well as optical isomerism? (en = ethylene diamine)

(a) $[Pt(NH_3)_2Cl_2]$
(b) $[Pt(NH_3)Cl_4]$
(c) $[Pt(en)_2Cl_2]$
(d) $[Pt(en)_3]^{4+}$

21 Which of the following compounds exhibits linkage isomerism?

(a) $[Co(en)_3]Cl_3$
(b) $[Co(NH_3)_6][Cr(en)_3]$
(c) $[Co(en)_2NO_2Cl]Br$
(d) $[Co(NH_3)_5Cl]Br_2$

22 The complexes $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are the examples of which type of isomerism? **→ CBSE-AIPMT 2011**

(a) Ionisation isomerism
(b) Coordination isomerism
(c) Geometrical isomerism
(d) Linkage isomerism

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

(a) 3
(b) 6
(c) 5
(d) 4

24 Which one of the following complex is an outer orbital complex?
(Atomic number : $Mn = 25, Fe = 24, Co = 27, Ni = 28$)

(a) $[Fe(CN)_6]^{4-}$
(b) $[Mn(CN)_6]^{4-}$
(c) $[Co(NH_3)_6]^{3+}$
(d) $[Ni(NH_3)_6]^{2+}$

25 The number of unpaired electrons in the complex ion $[CoF_6]^{3-}$ is (atomic number of $Co = 27$)

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

26 The number of *d*-electrons in $[Cr(H_2O)_6]^{3+}$ (atomic number of $Cr = 24$) is

(a) 2
(b) 3
(c) 4
(d) 5

27 Which one of the following ions exhibits *d*-*d* transition and paramagnetism as well? **→ NEET 2018**

(a) MnO_4^-
(b) $Cr_2O_7^{2-}$
(c) CrO_4^{2-}
(d) MnO_4^{2-}

28 Which of the following pairs of *d*-orbitals will have electron density along the axis? **→ NEET 2016, Phase II**

(a) d_{z^2}, d_{xz}
(b) d_{xz}, d_{yz}
(c) $d_{z^2}, d_{x^2-y^2}$
(d) $d_{xy}, d_{x^2-y^2}$

29 The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are **→ NEET 2018**

(a) square planar geometry and paramagnetic
(b) tetrahedral geometry and diamagnetic
(c) square planar geometry and diamagnetic
(d) tetrahedral geometry and paramagnetic

30 Why do compounds having similar geometry have different magnetic moment?

(a) Due to different reactivity
(b) Due to their labile nature
(c) Due to the presence of weak and strong field ligands
(d) None of the above

31 Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour? **→ CBSE-AIPMT 2012**

(a) $[Ni(NH_3)_6]^{2+}$
(b) $[Zn(NH_3)_6]^{2+}$
(c) $[Cr(NH_3)_6]^{3+}$
(d) $[Co(NH_3)_6]^{3+}$

32 Which of these statements about $[Co(CN)_6]^{3-}$ is true? → **CBSE-AIPMT 2015**

(a) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration
(b) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration
(c) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a high-spin configuration
(d) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a high-spin configuration

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

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

(a) Assertion is true, Reason is true; Reason is a correct explanation for Assertion
(b) Assertion is true, Reason is true; Reason is not a correct explanation for Assertion
(c) Assertion is true, Reason is false
(d) Assertion is false, Reason is true

34 Crystal field stabilisation energy for high spin d^4 octahedral complex is → **CBSE-AIPMT 2010**

(a) $-1.8\Delta_o$ (b) $-1.6\Delta_o + p$
(c) $-1.2\Delta_o$ (d) $-0.6\Delta_o$

35 Among the following complexes the one which shows zero crystal field stabilisation energy (CFSE) is → **CBSE-AIPMT 2014**

(a) $[Mn(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{3+}$
(c) $[Co(H_2O)_6]^{2+}$ (d) $[Co(H_2O)_6]^{3+}$

36 In which of the following octahedral complexes of Co (atomic number = 27), will have highest magnitude of Δ_o ?

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

37 Among the ligands NH_3, en, CN^- and CO, the correct order of their increasing field strength, is

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

38 Which of the following compounds is not coloured?

(a) $Na_2[CuCl_4]$
(b) $K_4[Fe(CN)_6]$
(c) $K_3[Fe(CN)_6]$
(d) $Na_2[CdCl_4]$

39 Correct increasing order for the wavelengths of absorption in the visible region for the complexes of CO^{3+} is → **NEET 2017**

(a) $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(H_2O)_6]^{3+}$
(b) $[Co(H_2O)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$
(c) $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$
(d) $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(H_2O)_6]^{3+}$

40 Which is not π-bonded complex?

(a) Zeise's salt (b) Ferrocene
(c) Dibenzene chromium (d) Tetraethyl lead

41 Which of the following complexes is used to be as an anticancer agent? → **CBSE-AIPMT 2014**

(a) *mer*-$[Co(NH_3)_3Cl_3]$ (b) *cis*-$[PtCl_2(NH_3)_2]$
(c) *cis*-$K_2[PtCl_2Br_2]$ (d) Na_2CoCl_4

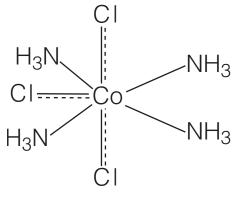
DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?

(a) Thiosulphato (b) Oxalato
(c) Glycinato (d) Ethan-1, 2-diamine

2 The complex



(a) is the molecular complex
(b) has four ions in the aqueous solution
(c) primary valency of cobalt is six
(d) All of the above are correct

3 A complex compound of Co^{3+} with molecular formula $CoCl_x \cdot yNH_3$ gives a total of 3 ions when dissolved in water. How many Cl^- ions satisfy both primary and secondary valencies in this complex?

(a) 3 (b) 1 (c) 4 (d) 0

4 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 4.78g of AgCl (molar mass = 14.5 g mol^{-1}). The formula of the complex is (Atomic mass of Ag = 108 u)

(a) $[Co(NH_3)_6]Cl_3$ (b) $[CoCl_2(NH)_3]_4Cl$
(c) $[CoCl_3(NH_3)_3]$ (d) $[CoCl(NH_3)_5]Cl_2$

5 In the complex $[Pt(O_2)(en)_2(Br)]^{2+}$, coordination number and oxidation number of platinum are

(a) 4, 3 (b) 4, 5 (c) 4, 6 (d) 6, 4

6 A coordination complex compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three moles ion in an aqueous solution; on reacting this solution with excess of $AgNO_3$, AgCl precipitates. The ionic formula for this complex would be

(a) $[Co(NH_3)_5(NO_2)]Cl_2$
(b) $[Co(NH_3)_5Cl]\ [Cl(NO_2)]$
(c) $[Co(NH_3)_4(NO_2)Cl]\ [(NH_3)Cl]$
(d) $[Co(NH_3)_5]\ [(NO_2)_2Cl_2]$

7 Both Co^{3+} and Pt^{4+} have a coordination number of six. Which of the following pairs of complexes will show approximately the same electrical conductance for their 0.001 M aqueous solutions?

(a) $CoCl_3 \cdot 4NH_3$ and $PtCl_4 \cdot 4NH_3$
(b) $CoCl_3 \cdot 3NH_3$ and $PtCl_4 \cdot 5NH_3$
(c) $CoCl_3 \cdot 6NH_3$ and $PtCl_4 \cdot 5NH_3$
(d) $CoCl_3 \cdot 6NH_3$ and $PtCl_4 \cdot 3NH_3$

8 Among the following complexes (K-P), $K_3[Fe(CN)_6](K)$, $[Co(NH_3)_6]Cl_3(L)$, $Na_3[Co(ox)_3](M)$, $[Ni(H_2O)_6]Cl_2\ (N)$, $K_2[Pt(CN)_4](O)$ and $[Zn(H_2O)_6](NO_3)_2(P)$ the diamagnetic complexes are

(a) K, L, M, N (b) K, M, O, P
(c) L, M, O, P (d) L, M, N, O

9 The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is

(a) d^5 (in strong ligand field)
(b) d^3 (in weak as well as strong ligand fields)
(c) d^4 (in weak ligand field)
(d) d^4 (in strong ligand field)

10 The d-electron configurations of $Cr^{2+}, Mn^{2+}, Fe^{2+}$ and Ni^{2+} are $3d^4$, $3d^5$, $3d^6$ and $3d^8$ respectively. Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour?

(Atomic number Cr = 24, Mn = 25, Fe = 26, Ni = 28)

(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Fe(H_2O)_6]^{2+}$
(c) $[Ni(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$

11 $[Cr(H_2O)_6]Cl_3$(atomic number of Cr = 24) has a magnetic moment of 3.83 BM, the correct distribution of $3d$-electrons in the chromium of the complex is

(a) $3d^1_{x^2-y^2}, 3d^1_{z^2}, 3d^1_{xz}$ (b) $3d^1_{xy}, 3d^1_{x^2-y^2}, 3d^1_{yz}$
(c) $3d^1_{xy}, 3d^1_{zy}, 3d^1_{xz}$ (d) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{z^2}$

12 Among $[Ni(CO)_4]$, $[Ni(CO)_4]^{2-}$, $[NiCl_4]^{2-}$ species, the hybridisation states of the Ni atom are respectively (Atomic number of Ni = 28)

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

13 Nickel (Z = 28) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electron(s) in the nickel and geometry of this complex ion are, respectively

(a) one, tetrahedral (b) two, tetrahedral
(c) one, square planar (d) two, square planar

14 Match Column I and Column II and choose the correct option from the codes given below.

Column I		Column II	
A.	$[Ni(CN)_4]^{2-}$	1.	Ti^{4+}
B.	Chlorophyll	2.	sp^3; paramagnetic
C.	*Ziegler-Natta* catalyst	3.	non-planar
D.	$[NiCl_4]^{2-}$	4.	Mg^{2+}
E.	Deoxyhaemoglobin	5.	Planar
		6.	dsp^2; diamagnetic

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	6	4	1	2	3	(b)	2	4	1	2	3
(c)	2	4	1	6	5	(d)	6	4	1	2	5

15 Which of the following complexes are not correctly matched with hybridisation of their central metal ion?

I. $[Ni(CN)_4]^{2-}$	sp^3
II. $[CoF_6]^{3-}$	d^2sp^3
III. $[Fe(CN)_6]^{3-}$	sp^3d^2
IV. $[Ni(CO)_4]$	sp^3

Choose the correct option.

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

16 The correct order of magnetic moments (spin only value in BM) among the following is
(Atomic number Mn = 25, Fe = 26, Co = 27)

(a) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
(b) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
(c) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
(d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

17 The CFSE for octahedral $[CoCl_6]^{4-}$ is 18000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be

(a) 18000 cm^{-1} (b) 16000 cm^{-1}
(c) 8000 cm^{-1} (d) 20000 cm^{-1}

18 Two isomers X and Y with the formula $Cr(H_2O)_5ClBr_2$ were taken for experiment on depression in freezing point. It was found that one mole of X gave depression corresponding to 2 moles of particles and one mole of Y gave depression due to 3 moles of particles. The structural formula of X and Y respectively, are

(a) $[Cr(H_2O)_5Cl]Br_2; [Cr(H_2O)_4Br_2]Cl \cdot H_2O$
(b) $[Cr(H_2O)_5Cl]Br_2; [Cr(H_2O)_3ClBr_2 \cdot 2H_2O]$
(c) $[Cr(H_2O)_5Br]BrCl; [Cr(H_2O)_4ClBr]Br \cdot H_2O$
(d) $[Cr(H_2O)_4Br_2]ClH_2O;\ [Cr(H_2O)_5Cl]Br_2$

19 A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex?

(a) It has an octahedral geometry
(b) It is a tetrahedral complex
(c) It is a *trans* complex
(d) None of the above

20 Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are

(a) linkage isomers
(b) coordination isomers
(c) ionisation isomers
(d) geometrical isomers

ANSWERS

SESSION 1

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

SESSION 2

1 (a)	**2** (a)	**3** (b)	**4** (a)	**5** (d)	**6** (a)	**7** (c)	**8** (c)	**9** (d)	**10** (c)
11 (c)	**12** (b)	**13** (b)	**14** (a)	**15** (d)	**16** (a)	**17** (c)	**18** (d)	**19** (a)	**20** (a)

Hints and Explanations

SESSION 1

1 Ligand must donate a pair of electron or loosely held electron pair to metal and form a *M*—*L* bond.e.g.

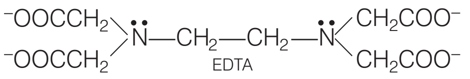
$:\ddot{N}= O,\ \ddot{N}H_2CH_2CH_2\ddot{N}H_2\ ,:CO,$

Among NH_4^+ does not have any pair of electron.
Hence, NH_4^+ is not a ligand.

2 According of Lewis concept, ligands are basic in nature, they donate lone pair of electrons to the central metal atom or ion.

3 $C_2O_4^{2-}$ is a bidentate ligands. As the complex contains 3 bidentate ligand, the central metal ion has a coordination number of 6.

4 EDTA, (ethylene diamine tetraacetate) ion has six donor atoms, i.e. hexadentate ligand. It has four acetate ions and two nitrogen atoms, which tends to the formation of six coordinate bonds.



5 Coordination number is the maximum covalency shown by a metal or metal ion. It is the maximum number of ligands attached to metal by sigma bonds or coordinate bonds.

6 Formation of 3 moles AgCl from 1 mole complex suggests the presence of all the three Cl^- outside the coordination sphere. Thus, the formula of the complex should be $[Cr(H_2O)_6]Cl_3$.

7 Complexes following EAN rule have EAN of central metal/ion equal to nearest inert gas configuration and hence, are stable.

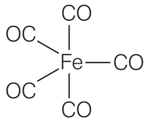
Effective atomic number (EAN) of the metal in a complex is given by

EAN = Atomic number (*Z*) – Oxidation number (ON) + 2(Coordination number)

$= 26 - 0 + 2\,(5) = 36$

Thus, $Fe(CO)_5$ is a stable complex/ion. Since, there is only one central metal atom present in iron carbonyl, $Fe(CO)_5$, thus it is mononuclear.

The structure of $Fe(CO)_5$ is shown below:



The examples of dinuclear, trinuclear complexes are $Co_2(CO)_{18}$, $Fe_3(CO)_{12}$ respectively.

8 Effective atomic number = electrons on Cr^{3+} + electrons from $6NH_3 = 21 + 6\times 2 = 21 + 12 = 33$

9 $[Co(NH_3)_3Cl_3]$ does not give a precipitate with $AgNO_3$ as all Cl atoms are attached by secondary valency.

10 $CoCl_2$ reacts with chloride ion to produce salt containing the tetrahedral $[CoCl_4]^{2-}$ ion which is blue in colour. The oxidation state of Co is + 2.

11 $[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$

$[Co(NH_3)_3Cl_3] \longrightarrow [Co(NH_3)_3Cl_3]$

$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$

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

So, $[Co(NH_3)_3Cl_3]$ does not ionise, so does not give test for chloride ions.

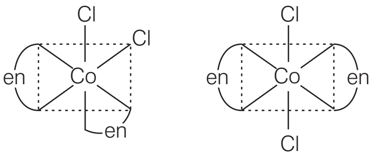
12 IUPAC name of $Na_3[Co(NO_2)_6]$ is sodiumhexanitrocobaltate (III).

13 The IUPAC name of $K_2[Ni(CN)_4]$ is potassium tetracyanonickelate (II).

14 IUPAC name of sodium nitroprusside $Na_2[Fe(CN)_5NO]$ is sodium pentacyanonitrosylferrate (III) because in it NO is neutral ligand and oxidation number of Fe is $+3$.

15 Isomers in which the atoms or ligands occupy different positions around central metal/ion are called geometrical isomers. Complexes having coordination number of central atom/ion 6 with formula $M(AA)_2B_2$ exhibit geometrical isomerism [where, AA is a bidentate ligand].

In $[CoCl_2(en)_2]$, coordination number of Co is 6 with octahedral geometry.



cis-isomer (Optically active) *trans*-isomer (Optically inactive)

Thus, $[CoCl_2(en)_2]$ show geometrical isomerism.

16

	Complex	Isomerism shown
(a)	$[Co(en)_3]^{3+}$	Optical only
(b)	$[Ni(NH_3)_5Br]^+$	No geometrical isomerism
(c)	$[Co(NH_3)_2(en)_2]^{3+}$	*cis* and *trans* (geometrical)
(d)	$[Cr(NH_3)_4(en)]^{3+}$	No geometrical isomerism

17 $[Cr(H_2O)_4Cl_2]^+$ shows geometrical isomerism because this complex follows MA_4B_2 type.

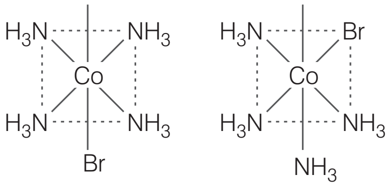
18 Octahedral $Co(NH_3)_4Br_2Cl_2$ shows both ionisation and geometrical isomerism.

In ionisation isomerism ligands shows different coordination sphere and the anions present outside the coordination sphere. These are exchanged with each other as follows:

$$\underset{\text{I}}{[Co(NH_3)_4Br_2]Cl} \rightleftharpoons [Co(NH_3)_4Br_2]^+ + Cl^-$$

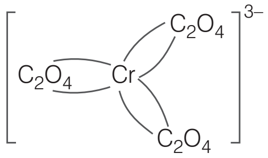
$$\underset{\text{II}}{[Co(NH_3)_4BrCl]Br} \rightleftharpoons [Co(NH_3)_4BrCl]^+ + Br^-$$

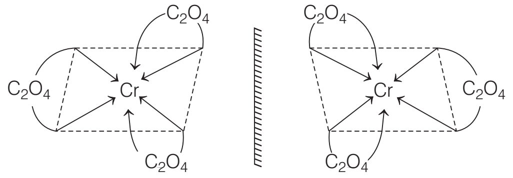
In geometrical isomerism, coordination number of central atom (cobalt) is six and shape is octahedral, so it shows following geometrical isomers.



trans-isomer *cis*-isomer

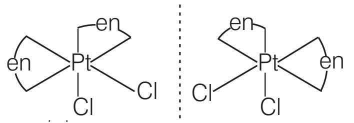
19



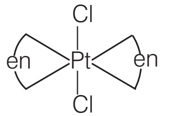


There mirror image is not superimposable, hence, optical isomerism is possible.

20 $[Pt(en)_2Cl_2]$ show geometrical as well as optical isomerism.



cis-isomers (two optical isomers)



trans-isomer

21 $—NO_2$ group shows linkage isomerism.

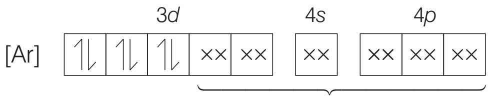
22 The complexes $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are the examples of coordination isomerism. This isomerism occurs only in those complexes in which both cation and anion are complex. It occurs due to exchange of ligands between cation and anion.

23 (*a*) $[\overset{\text{II}}{Pt}(NH_3)_4]\ [\overset{\text{II}}{Cu}Cl_4]$; $[\overset{\text{II}}{Pt}(NH_3)_3Cl]\ [\overset{\text{II}}{Cu}(NH_3)Cl_3]$

$[\overset{\text{II}}{Cu}(NH_3)_3Cl]\ [\overset{\text{II}}{Pt}(NH_3)Cl_3]$

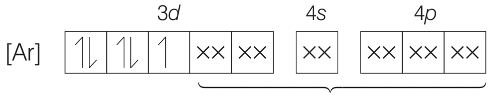
24 The complex in which *nd*-orbitals are used in hybridisation are called outer orbital complex.

(a) $[Fe(CN)_6]^{4-}$ =



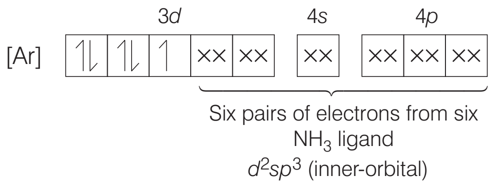
six pairs of electrons from six CN^- ions d^2sp^3 (inner-orbital)

(b) $[Mn(CN)_6]^{4-}$ =

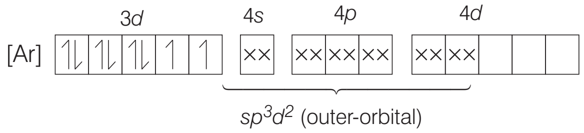


Six pairs of electrons from six CN^- ions d^2sp^3 (inner-orbital)

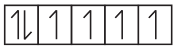
(c) $[Co(NH_3)_6]^{3+}$ =



(d) $[Ni(NH_3)_6]^{2+}$ =



25 In $[CoF_6]^{3-}$, Co is in + 3 state, unpaired electrons = 4 ($_{27}Co^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$)



26 The number of *d*-electrons in $[Cr(H_2O)_6]^{3+}$ is 3. $_{24}Cr^{3+}$ = [Ar] $3d^3$

27 (i) **In MnO_4^-,** The electronic configuration of Mn^{7+} is $[Ar]3d^0$.

Number of unpaired electrons = 0

Therefore, it will be diamagnetic and will not show *d-d* transition.

(ii) **In $Cr_2O_7^{2-}$**, The electronic configuration of Cr^{6+} is $[Ar]3d^0$.

Number of unpaired electrons = 0

So, it will be diamagnetic and will not show *d-d* transition.

(iii) **In CrO_4^{2-}**, The electronic configuration of Cr^{6+} is $[Ar]3d^0$.

Number of unpaired electrons = 0

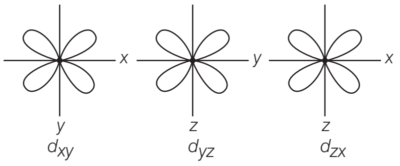
Therefore, it is also diamagnetic and will not show *d-d* transition.

(iv) **In MnO_4^{2-}**, The electronic configuration of Mn^{6+} is $[Ar]3d^1$.

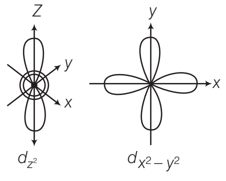
Number of unpaired electrons = 1

Since, it contains one unpaired electron, so it will exhibit both *d-d* transition and paramagnetism.

28

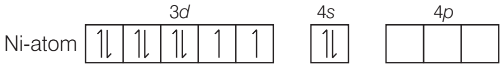


Thus, d_{xy}, d_{yz} and d_{zx} orbitals have maximum electron density between the axis.

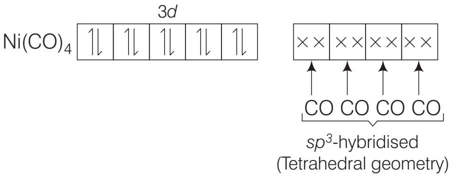


d_{z^2} and $d_{x^2-y^2}$ orbitals have maximum electron density along the axis.

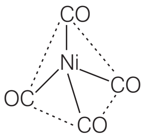
29 The complexes having sp^3-hybridisation are tetrahedral, while having dsp^2-hybridisation are square planar. The magnetic behaviour of complexes can be paramagnetic and diamagnetic based on the presence and absence of unpaired electrons, respectively. Electronic configuration of Ni(Z = 28) is $[Ar]_{18}$ $3d^8 4s^2$. Due to presence of CO (neutral ligand), oxidation state of Ni in $[Ni(CO)_4]$ is 0.



Since, CO is a strong field ligand, it pair up the unpaired electrons of Ni.



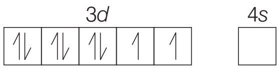
There is no unpaired electron, hence, $Ni(CO)_4$ is diamagnetic with tetrahedral geometry.



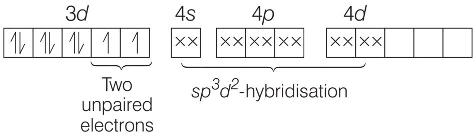
30 It is due to the presence of weak and strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and *vice-versa*, e.g. $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic, and the latter is diamagnetic because F^- is a weak field ligand and NH_3 is a strong field ligand.

31 Outer orbital complex utilises *nd*-orbitals for bonding and exhibit paramagnetic behaviour, only if there present unpaired electrons.

(a) In $[Ni(NH_3)_6]^{2+}$; Ni^{2+} = [Ar] $3d^8 4s^0$

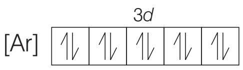


$[Ni(NH_3)_6]^{2+}$ =

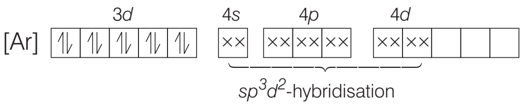


So, this is an outer orbital complex having paramagnetic character.

(b) In $[Zn(NH_3)_6]^{2+}$; Zn^{2+} = [Ar] $3d^{10}$

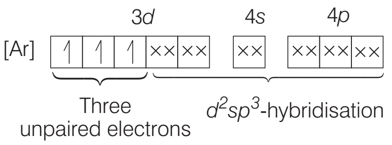


$[Zn(NH_3)_6]^{2+}$ =



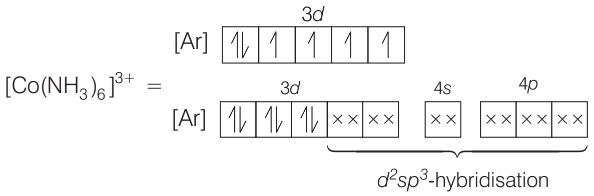
Thus, it is also an outer orbital complex but it is diamagnetic as all the electrons are paired.

(c) In $[Cr(NH_3)_6]^{3+}$, $Cr^{3+} = [Ar]\,3d^3$ $[Cr(NH_3)_6]^{3+}$ =



Because of the involvement of $(n-1)d$, i.e. $3d$ orbital in hybridisation, it is an inner orbital complex. Its nature is paramagnetic because of the presence of three unpaired electrons.

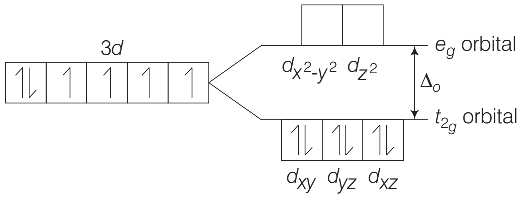
(d) In $[Co(NH_3)_6]^{3+}$; $Co^{3+} = [Ar]\,3d^6$



Due to the involvement of $(n-1)d$, i.e. $3d$-orbitals in hybridisation, it is an inner orbital complex. As all the electrons are paired, it is a diamagnetic complex.

32 $[Co(CN)_6]^{3-}$ $Co^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

CN^- is a strong field ligand and as it approaches the metal ion, the electrons must pair up.



The splitting of the d-orbitals into two sets of orbitals in an octahedral $[Co(CN)_6]^{3-}$ may be represented as :

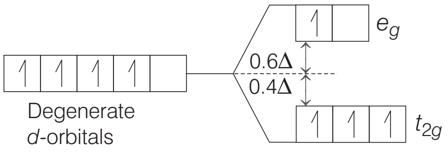
Here, for d^6 ions, three electrons first enter orbitals with parallel spin put the remaining may pair up in t_{2g} orbital giving rise to low spin complex (strong ligand field).

∴ $[Co(CN)_6]^{3-}$ has no unpaired electron and will be in a low spin configuration.

33 $[Sc(H_2O)_6]^{3+}$ has no unpaired electrons 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.

34 In case of high spin complex, Δ_o is small. Thus, the energy required to pair up the fourth electron with the electrons of lower energy d-orbitals would be higher than that required to place the electrons in the higher d-orbital. Thus, pairing does not occur.

For high spin, d^4 octahedral complex,

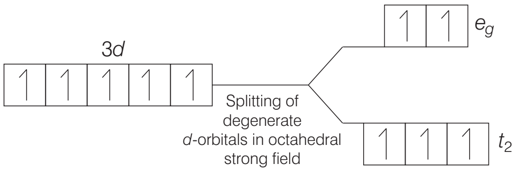


∴ Crystal field stabilisation energy

$= (-3 \times 0.4 + 1 \times 0.6)\Delta_o$

$= (-1.2 + 0.6)\Delta_o = -0.6\Delta_o$

35 $[Fe(H_2O)_6]^{3+}$ $Fe^{3+} = [Ar]\ 3d^5$



$$\text{CFSE} = -(0.4 \times t_{2g}e^-) + 0.6 \times e_g e^- = -(0.4 \times 3) + 0.6 \times 2$$

$$= -1.2 + 1.2$$

$$\text{CFSE} = 0$$

36 CFSE (Crystal Field Splitting Energy) for octahedral complex, Δ_O depends on the strength of negative ligand. Spectrochemically, it has been found that the strength of splitting is as follows :

$$CO > CN^- > NO_2^- > en > NH_3 > py > NCS^- > H_2O > O^{2-} > ox^{2-} > OH^- > F^- > Cl^- > SCN^- > S^{2-} > Br^- > I^-$$

Therefore, magnitude of Δ_o will be highest in case of $[Co(CN)_6]^{3-}$

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

$NH_3 < en < CN^- < CO$

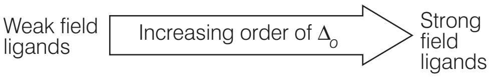
38 $Na_2[CdCl_4]$ is not coloured due to completely filled $4d^{10}$-orbitals.

39 Wavelength (λ) of absorption is inversely proportional to CFSE (Δ_O value) of ligands attached with the central metal ion

i.e. $\lambda \propto \dfrac{1}{\Delta_O}$

According to spectrochemical series,

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NSS^- < NH_3 < en < NO_2^- < CN^-$$



The CFSE of ligands attached with Co^{3+} ion is in the order

$en > NH_3 > H_2O$ (From spectrochemical series)

∵ Wavelength of absorbed light $(\lambda) \propto \dfrac{1}{\Delta_o}$

∴ For ligand the order of wavelength of absorption in the visible region will be : $en < NH_3 < H_2O$

or, $[Co(en)_3]^{3+} < [Co(NH_3)_6]^{3+} < [Co(H_2O)_6]^{3+}$

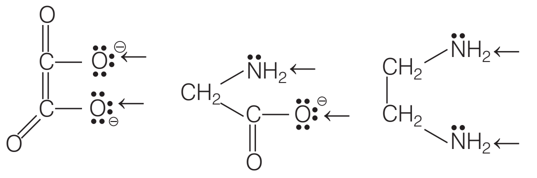
40 All the given compounds except tetraethyl lead are π-bonded complex.

41 The platinum complex *cis* - $[Pt(NH_3)_2Cl_2]$ (*cis*-platin) is used in the treatment of cancer.

SESSION 2

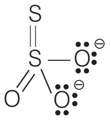
1 A chelating ligand has two or more binding donor atoms to a single metal ion.

e.g.



Oxalato　　Glycinato　　Ethan-1, 2-diamine

Here, (⟵) denotes binding site.



thiosulphato ($S_2O_3^{2-}$) is not a chelating ligand because geometrically it is not favourable for $S_2O_3^{2-}$ to chelate a metal ion.

2 $[Co(NH_3)_3Cl_3]$ is molecular complex no ionisation.

Primary valency is three thus (a) only.

========= Indicates primary and secondary valencies
——————— Indicates secondary valencies
- - - - - - - - Indicates primary valencies

3 As cobalt is present as Co^{3+} and coordination number of cobalt is 6, the molecular formula of compound should be $CoCl_3 \cdot yNH_3$. Now, as it gives a total of three ions when dissolved in water, its structural formula must be $[CoCl(NH_3)_5]Cl_2$, $[CoCl(NH_3)_5]Cl_2 \rightleftharpoons [CoCl(NH_3)_5]^{2+} + 2Cl^-$

Thus, only one Cl^- ion is satisfying both primary and secondary valency of Co^{3+} in this compound.

4 Mole of $CoCl_3 \cdot 6NH_3 = \frac{2.675}{267.5} = 0.01$

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

$$\text{Moles of AgCl} = \frac{4.78}{143.5} = 0.03$$

0.01 mole $CoCl_3 \cdot 6NH_3$ gives = 0.03 mole AgCl

$\therefore$ 1 mole $CoCl_3 \cdot 6NH_3$ ionises to give = 3 moles Cl^-

Hence, the formula of compound is $[Co(NH_3)_6]Cl_3$.

5 O_2^- (superoxide) — Monodentate
en — Bidentate
Br — Monodentate

Thus, CN of Pt is = 6

$$\begin{array}{cccc} [Pt(O_2) & (en)_2 & (Br)]^{2+} \\ \downarrow\ \downarrow & \downarrow & \downarrow \\ x-1 & +0 & -1 & =2 \end{array}$$

$\therefore$ $x = +4$

Thus, ON of Pt = + 4 .

6 $[Co(NH_3)_5NO_2]Cl_2 \rightleftharpoons [Co(NH_3)_5NO_2]^{2+} + 2Cl^-$

7 For Co^{3+} and Pt^{4+}, coordination number = 6

$$[Co(NH_3)_6]Cl_3 \xrightarrow{\text{In solution}} [Co(NH_3)_6]^{3+} + 3Cl^-$$

$$[PtCl(NH_3)_5]Cl_3 \xrightarrow{\text{In solution}} [PtCl(NH_3)_5]^{3+} + 3Cl^-$$

Number of ionic species are same in the solution of both complexes, therefore their equimolar solutions will show same conductance.

8 For a diamagnetic complex, there should not be any unpaired electron in the valence shell of the central metal.

In (*K*) $K_3[Fe(CN)_6]$, Fe(III) has d^5-configuration (odd electrons), hence it is paramagnetic.

In (*L*) $[Co(NH_3)_6]Cl_3$, Co(III) has d^6-configuration in a strong ligand field, hence all the electrons are paired and the complex is diamagnetic.

In (*M*) $Na_3[Co(ox)_3]$, Co(III) has d^6-configuration and oxalate being a chelating ligand, very strong ligand and all the six electrons remains paired in lower t_{2g} level, so it is diamagnetic.

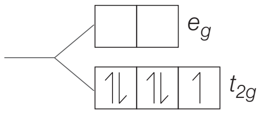
In (*N*) $[Ni(H_2O)_6]Cl_2$Ni(II) has $3d^8$-configuration and H_2O is a weak ligand therefore, unpaired electrons are not paired. Hence, it has 2 electrons unpaired in *d*-orbital.

In (*O*) $K_2[Pt(CN)_4]$, Pt (II) has d^8-configuration and CN^- is a strong ligand, hence all the eight electrons are spin-paired. Therefore, complex is diamagnetic.

In (*P*) $[Zn(H_2O)_6](NO_3)_2$, Zn (II) has $3d^{10}$-configuration with all the ten electrons spin paired, hence it is diamagnetic.

9 (a) d^5 in strong field

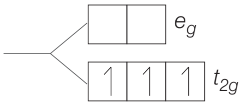
n = unpaired electron = 1



$n = 1$

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

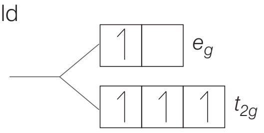
(b) d^3 in strong/weak field



$n = 3$

$$\text{Magnetic moment} = \sqrt{15} = 3.87\ \text{BM}$$

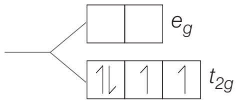
(c) d^4 in weak field



$n = 4$

$$\text{Magnetic moment} = \sqrt{24} = 4.90\ \text{BM}$$

(d) d^4 in strong field



$n = 2$

$$\text{Magnetic moment} = \sqrt{8} = 2.83\ \text{BM}$$

10 As the number of unpaired electron increases, the magnetic moment increases and hence the paramagnetic behaviour increases.

$$Cr^{2+}(22e^-) = 3d^4$$

⇒ 4 unpaired electrons.

$$Mn^{2+}(23e^-) = 3d^5$$

⇒5 unpaired electrons.

$$Fe^{2+}(24e^-) = 3d^6$$

⇒4 unpaired electrons.

$$Ni^{2+}(26e^-) = 3d^8$$

⇒2 unpaired electrons.

So, $[Ni(H_2O)_6]^{2+}$ exhibit minimum paramagnetic behaviour.

11 Magnetic moment, $\mu = \sqrt{n(n+2)}$ BM, $3.83 = \sqrt{n(n+2)}$

$$3.83 \times 3.83 = n(n+2)$$
$$14.6689 = n^2 + 2n$$

On solving , $n = 3$ (number of unpaired electron in d-subshell)

In $[Cr(H_2O)_6]Cl_2$, oxidation state ofCr is + 3.

Hence, in $3d^3$ the distribution of electrons

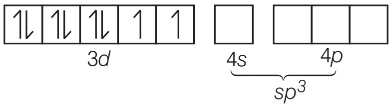
$$3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1, 3d_{x^2-y^2}^0, 3d_{z^2}^0$$

12 In $Ni(CO)_4$, Ni is sp^3-hybridised. Its oxidation state is zero. CO is strong field ligand so it causes pairing. It is diamagnetic.

In $[Ni(CN)_4]^{2-}$, nickel is in Ni^{2+} stable CN^- also causes pairing of electrons hence, it is dsp^2-hybridised and diamagnetic.

In $[NiCl_4]^{2-}$, Ni is in +2 oxidation state. Cl^- is weak field ligand. It does not cause pairing, hence it is sp^3-hybridised and paramagnetic.

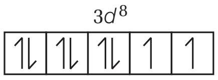
13 $_{28}Ni = [Ar]\ 4s^2, 3d^8 \qquad Ni^{2+} = [Ar]\ 3d^8$



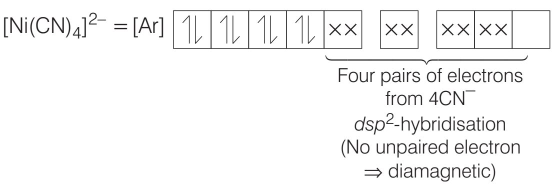
Nickel has two unpaired electrons and geometry is tetrahedral due to sp^3-hybridisation.

14 (a) $[Ni(CN)_4]^{2-}$

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



Since, CN^- is a strong field ligand, it causes pairing of electrons.

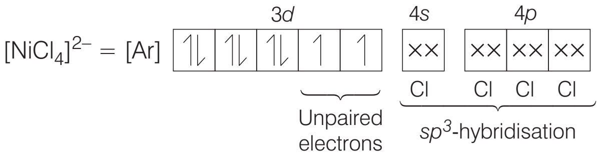


(b) Chlorophyll contains Mg^{2+} ion.

(c) *Ziegler-Natta* catalyst is $Ti^{4+} + (C_2H_5)_3Al$

(d) $[NiCl_4]^{2-}$

In this case, Cl^- is a weak field ligand, so does not cause pairing. Hence,



Due to the presence of unpaired electrons, it is paramagnetic.

(e) Deoxyhaemoglobin is non-planar, while oxyhaemoglobin is planar.

15

Complex	Hybridisation
$[Fe(CN)_6]^{3-}$	d^2sp^3
$[Ni(CN)_4]^{2-}$	dsp^2
$[CoF_6]^{3-}$	sp^3d^2
$[Ni(CO)_4]$	sp^3

16 Number of unpaired electrons in $[Fe(CN)_6]^{4-}$ is zero.

Thus, magnetic moment $= \sqrt{n(n+2)} = 0$ BM

(n = unpaired electrons)

n in $[MnCl_4]^{2-} = 5, \sqrt{35}$ BM $\qquad$ n in $[CoCl_4]^{2-} = 3, \sqrt{15}$ BM

Hence, correct increasing order of magnetic moments

$$[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$$

17 CFSE for octahedral and tetrahedral complexes are closely related to each other by formula $\Delta_t = -\frac{4}{9}\Delta_o$.

where, Δ_o = CFSE for octahedral complex,

Δ_t = CFSE for tetrahedral complex ($\Delta E = h\nu$, $\Delta E \propto \nu$)

According to question,

$$\Delta_o = 18000\ \text{cm}^{-1}$$

$$\therefore \Delta_t = \frac{4}{9}\Delta_o = \frac{4}{9} \times 18000\ \text{cm}^{-1} = 4 \times 2000\ \text{cm}^{-1} = 8000\ \text{cm}^{-1}$$

18 One mole of X gave depression corresponding to 2 moles of particles, i.e. on ionisation X gives 2 moles of ions, thus it contains only 1 ion outside the coordination sphere and its structural formula is $[Cr(H_2O)_4Br_2]Cl \cdot H_2O$, while Y gives 3 moles of ions, thus it contains two ions outside the coordination sphere and its structural formula is $[Cr(H_2O)_5Cl]Br_2$.

19 An optically active complex of the type $[M(AA)_2X_2]^{n+}$ indicates *cis*-octahedral structure,

e.g. *cis*-$[Pt(en)_2Cl_2]^{2+}$ or *cis*-$[Cr(en)_2Cl_2]^+$.

20 Complexes having ambidentate ligands like SCN exhibit linkage isomerism.