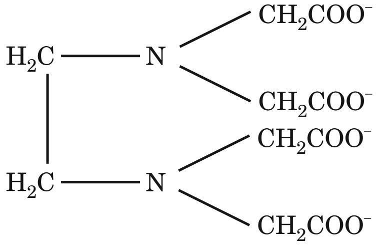
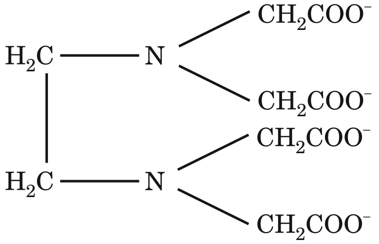
CHAPTER 9

Coordination Compounds

- Coordination compounds are formed when metal atoms bound with anions or neutral molecules to form a compound. For example: $\left[Co(NH_3)_6\right]^{3+}, \left[Ni(CO)_4\right], \left[CoCl_2(NH_3)_4\right]^{+}$, etc.
- **Double Salt:** It differs from coordination compound in such a way that they dissociate into constituent ions when dissolved in water while coordination compounds will not break into its respective ions. Some examples of double salt are Mohr's salt ($FeSO_4.\ (NH_4)_2SO_4.6H_2O$), Potash alum $KAl\ (SO_4)_2.12H_2O$, etc.
- **Coordination entity:** A central metal ion or atom bonded to a fixed number of ions or molecules forms a coordination entity. For example: $[Co(NH_3)_6]^{3+}$ is a coordination entity where a cobalt ion is surrounded by six ammonia molecules.
  - ➢ Here cobalt ion is the central ion.
  - ➢ The ammonia molecules arranged in a pattern around the central ion are called ligands.
  - ➢ When ligand is bound to metal atom/ ion by single donor atom then it is unidentate ligand as in this example ammonia is unidentate.
  - ➢ When a ligand is bound to two donor atoms, it is didentate ligand. For example: $C_2O_4^{2-}$ or $H_2NCH_2CH_2NH_2$
  - ➢ When several donor atoms are present in a single ligand, it is a polydentate ligand. For example: Ethylenediaminetetraacetate ion which contains several donor atoms.



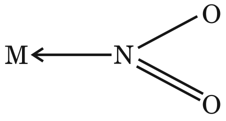
  - ➢ **Denticity** is the number of ligating groups in a ligand.
  - ➢ When two or more donor atoms are used by ligands to bind a metal ion, it is called a **chelate ligand**. For example:



  - ➢ Ligands which can ligate through two different atoms are called **ambidentate ligands**. Some examples are: SCN^- which can coordinate through sulphur or nitrogen atom. NO_2^- can coordinate through nitrogen or oxygen.

$M \longleftarrow SCN \qquad M \longleftarrow NCS$

thiocyanato   isothiocyanato



$M \longleftarrow O - N = O$

  - ➢ Ligands can also be classified on the basis of charge. It is of three types:

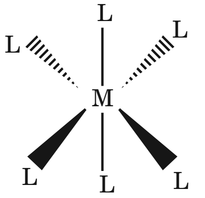
Cationic ligands: The ligands which carry positive charge are cationic ligands. For example:

$N_2H_5^+, NO_2^+$.

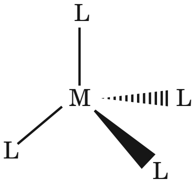
Anionic ligands: The ligands which carry negative charge are anionic ligands. For example: OH^-, CN^-, etc.

Neutral ligands: Ligands which do not carry any charge are neutral ligands. For example: NH_3, N_2, NO, etc.

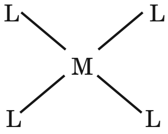
- **Coordination sphere:** It is a collective term for central atom/ ion and ligands written together in square brackets. For example: $[Co\ (NH_3)_6]^{3+}$, $K_4[Fe\ (CN)_6]$ (here $[Fe\ (CN)_6]^{4-}$ is a coordination sphere while K^+ is a counter ion).
- **Coordination number:** Metal atom/ ion is bonded to some ligand donor atoms. The number of donor atoms linked to the metal gives the coordination number. For example, in the compound $[Co\ (NH_3)_6]^{3+}$, coordination number of Co is 6 and in the compound $[Co\ (en)_3]^{3+}$, coordination number is 6 because *en* (ethane-1, 2-diamine) is a didentate ligand.
- **Coordination Polyhedron:** The ligand atoms are arranged around the central atom in a definite pattern which forms a coordination polyhedron. Some of the common examples are: square planar, octahedral, tetrahedral, etc.



Octahedral



Tetrahedral



Square planar

- **Oxidation number of central atom:** The charge on the central atom when all the ligands are removed along with the elctron pairs shared with it gives the oxidation number of central atom. For example: oxidation number of copper in $[Cu\ (CN)_4]^{3+}$ is 1 and it is written in Roman numeral as $Cu\ (I)$.
- **Homoleptic and heteroleptic complexes:** When a complex is bound to more than one donor groups, it is a heteroleptic complex. For example: $[Co\ (NH_3)_6]Cl_3$

  When the metal in a complex is bound to just one type of donor atom, it is a homoleptic complex. For example: $[Cu\ (CN)_4]^{3+}$
- **Nomenclature of Coordination Compounds:** It is based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC). There are some rules for naming coordination compounds which are as follows:
  - ➢ Cation is named first while naming any coordination entity.
  - ➢ Ligands are written before the central atom/ ion in alphabetical order.
  - ➢ Anioinc ligands are written with –o at the end. There are some terms for some specific molecules written in (). aqua is used for H_2O, ammine for NH_3 , nitrosyl for NO and carbonyl for CO.
  - ➢ Number of individual ligands in the coordination entity are represented by some prefixes like mono, di, tri, etc.
  - ➢ Oxidation number of the central atom/ion is written in Roman numerals inside parentheses.
  - ➢ Cations are named same as the element in complex ion while anions end with –ate.

    For example: Co is written as cobalt if it acts as cation and cobaltate if it is present as anion.
- **Isomerism:** The phenomenon of compounds which have same molecular formula but different structural formulae which are isomers is known as isomerism. For example: C_2H_6O can be written as C_2H_6OH and CH_3OCH_3.
- **Types of isomerism:** Isomerism can either be structural or stereo.
  - ➢ **Structural Isomerism:** It can be divided into four types:

    Ionisation isomerism: When isomers have same molecular formula but different ions in solution, it is called ionisation isomerism. For example: $[Co\ (NH_3)_5SO_4]Br$ and $[Co\ (NH_3)_5Br]SO_4$.

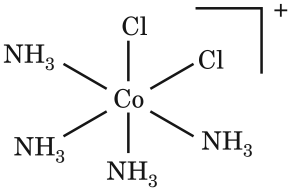
    Linkage isomerism: It arises in compounds which contain ambidentate ligand. For example: $[Co\ (NH_3)_5\ (NO_2)]Cl_2$ where nitrile ligand is bound through oxygen to give red color and nitrile ligand is bound through nitrogen to give yellow color.

    Coordination isomerism: Ligands interchange between cationic and anionic entities of different metal ions in a complex. Such isomerism is a type of coordination isomerism. For example: $[Co\ (NH_3)_6][Cr\ (C_2O_4)_3]$ and $[Cr\ (NH_3)_6][Co\ (C_2O_4)_3]$

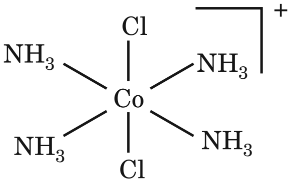
    Hydration isomerism: In this type of isomerism, isomers have same molecular formula but different number of molecules of water. For example: $[Cr\ (H_2O)_5Cl]\ Cl.\ H_2O$ and $[Cr\ (H_2O)_4Cl_2]Cl.\ 2H_2O$

- **Stereo Isomerism:** It can be of two types:

  Geometrical isomerism (cis-trans isomerism): For a tetra co-ordinated square planar complex, trans-isomer has same groups on opposite sides while cis-isomer has same group on same sides. For example: cis and trans isomer of $[Co(NH_3)_4Cl_2]^+$

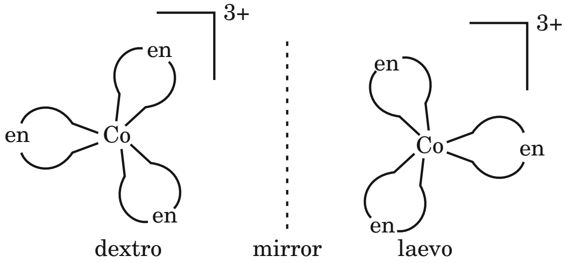


cis



trans

  Optical isomerism: Optical isomers also called enantiomers are mirror images which cannot be superimposed on one another. The molecules or ions involved in this isomerism are called chiral. Depending on the direction of rotation of plane polarised light in a polarimeter, there are two forms dextro (d) and laevo (l).

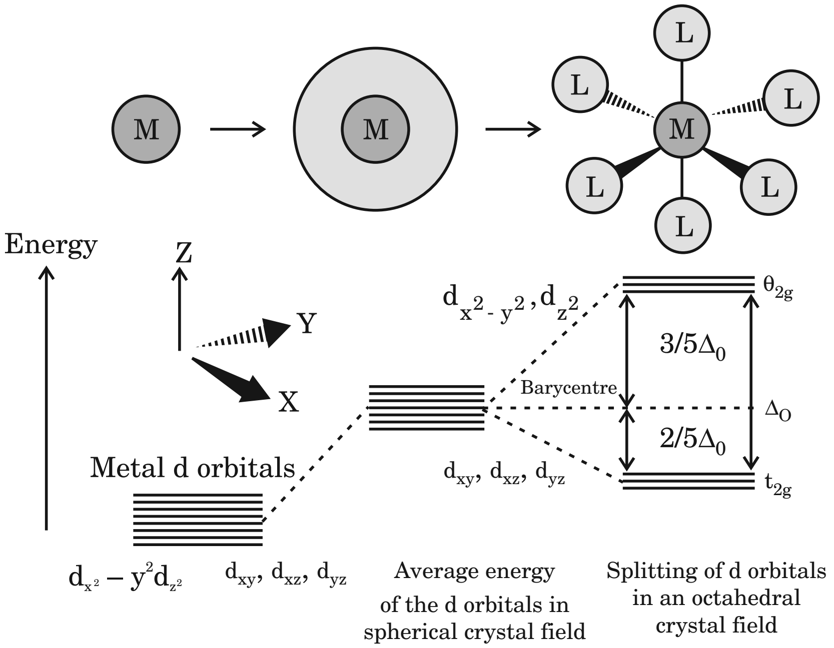


Optical isomers of $[Co(en)_3]^{3+}$

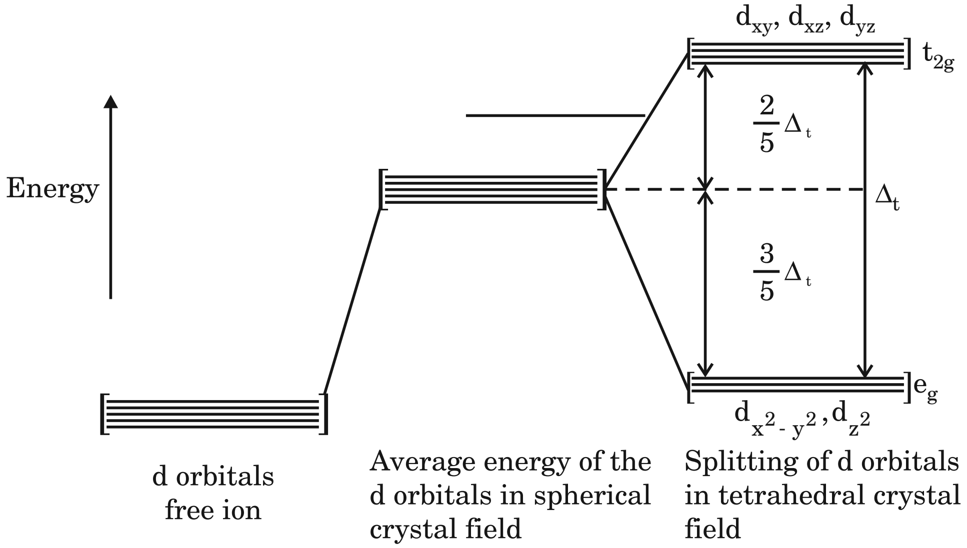
- Bonding in coordination compounds can be explained by different theories like Valence Bond Theory (VBT), Werner's Theory, Crystal Field Theory (CFT), Ligand Field Theory (LFT), and Molecular Orbit Theory (MOT).
- **Werner's Theory of Coordination Compounds:**

  This theory explained the nature of bonding in complex compounds. Primary and Secondary valency are the different kinds of valencies shown by metals.
  - Primary valency is equal to the oxidation state of the metal which is satisfied by anions.
  - Secondary valencies are similar to coordination number which is satisfied by opposite charged ions, neutral molecules or cations.
- **Limitations of Werner's theory:**
  - It does not explain the reason of only some elements forming complexes.
  - It does not explain the magnetic nature of complexes.
  - It does not explain the directional nature of coordination complexes.
- **Valence Bond Theory:**
  - A suitable number of vacant orbitals must be present for the formation of coordinate bond in the central metal atom/ion.
  - *s, p* or *d*-orbitals are appropriately used for hybridization by central metal ion depending on the number of ligands.
  - The ligands which donate electron pair overlap with the hybridized orbitals.
  - Outer or inner orbital complexes are formed on the basis of outer or inner *d*-orbitals used.
- **Limitations of Valence Bond Theory:**
  - Detailed magnetic properties of complex compounds are not explained.
  - Optical absorption spectra of coordination compounds are not explained by this theory.
  - It does not differentiate between strong and weak ligands.
  - Thermodynamic or kinetic stabilities of coordination compounds is not explained by this theory.
  - Geometry of 4 coordinate complex (square planar or tetrahedral) is not predicted.
- **Crystal Field Theory:**
  - Ligands are point charges according to this theory.
  - *d*-orbitals of metal ion split on approaching ligands.
  - In tetrahedral complexes, t_{2g} orbitals have high energy.
  - Splitting of *d*-orbitals is large when ligands produce strong fields and splitting is small when ligands produce weak fields.
  - Ligands are arranged according to increasing field strength as follows:

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

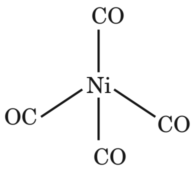


Splitting octahedral crystal field

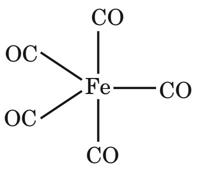


  - There is high energy of e_g orbitals in octahedral and lower energy in tetrahedral complexes.

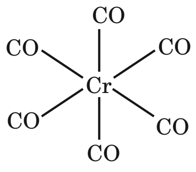
- **Limitations of crystal field theory:**
  - It does not consider the covalent bonding between ligand and central atom.
  - According to this theory anionic ligands exert greatest splitting effect but actually the splitting is small.
- Bonding in metal carbonyls: Homoleptic carbonyls are formed by transition metals. Some examples are pentacarbonyliron (0) is trigonalbipyramidal, tetracarbonylnickel (0) is tetrahedral and hexacarbonyl chromium (0) is octahedral.



$Ni(CO)_4$
Tetrahedral



$Fe(CO)_5$
Trigonal bipyramidal



$Cr(CO)_6$
Octahedral

- Metal-carbon bond possess both *s* and *p* character. There is a synergic effect between the metal and ligand bond which strengthens the bond.
- **Stability of Coordination compounds:** The degree of association between two species gives the stability of complex in solution. Stability is expressed by magnitude of equilibrium constant. Larger the stability constant/ association constant, higher the proportion of the product in solution.

  Consider a reaction: $A + 4B \rightleftharpoons AB_4$

  Here A is surrounded by solvent molecules, B and the reaction goes in the following order using stability constants:

  $$A + B \rightleftharpoons AB \qquad K_1 = \frac{[AB]}{[A][B]}$$

  $$AB + B \rightleftharpoons AB_2 \qquad K_2 = \frac{[AB_2]}{[AB][B]}$$

  $$AB_2 + B \rightleftharpoons AB_3 \qquad K_3 = \frac{[AB_3]}{[AB_2][B]}$$

  $$AB_3 + B \rightleftharpoons AB_4 \qquad K_4 = \frac{[AB_4]}{[AB_3][B]}$$

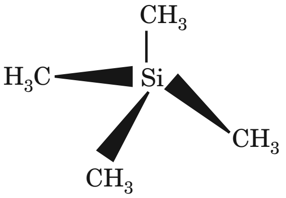
  Here K_1, K_2,...... are stepwise stability constants.

  $\beta_4 = \frac{[AB_4]}{[A][B]^4}$, β_4 is overall stability constant

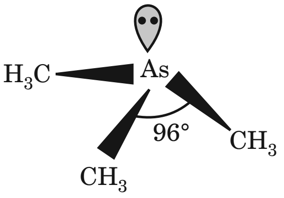
  $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$

  Dissociation constant or instability constant is the reciprocal of association/ stability constant.

- **Classification of organometallic compounds:** These are divided into two groups as main group organometallics and *d*- and *f*- block organometallics.
  - **Main Group organometallics:** These are *s*- and *p*- block organometallics. Here are some examples with diagram: Tetramethyl silane, trimethyl arsene, etc.



$Si(CH_3)_4$



$As(CH_3)_3$

  - *d*- and *f*- block organometallics: The elements of *d*- and *f*- block form these kind of organometallics. Some examples are: Pentamethyl cyclopentadienyl ligand (C_5Me_5) forms *f*- block compounds, $[PtCl_3\ (C_2H_4)^-]$, $(C5H_5)_2Fe$, etc.
- **Applications of complex compounds:**
  - These compounds are used in qualitative and quantitative analysis.
  - Stability constants of calcium and magnesium complexes are different which can be used for selective estimation of calcium and magnesium ions.
  - Purification of metals is carried out by formation and decomposition of coordination compounds.
  - Extraction processes are carried out using complex formation.
  - These compounds are used as catalysts. For example, Wilkinson catalyst (rhodium complex) is used for hydrogenation of alkenes.
  - Medicinal chemistry make use of chelate therapy.

EXERCISE

1. The Coordination number of copper in cuprammonium sulphate is

(*a*) 2 (*b*) 6
(*c*) 4 (*d*) –4

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

(*a*) Acetate (*b*) Oxalate
(*c*) Thiocyanate (*d*) EDTA

3. The coordination number of cobalt in the complex $[Co(en)_2Br_2]Cl_2$ is

(*a*) 2 (*b*) 6
(*c*) 5 (*d*) 4

4. Which of the following ligands forms a chelate

(*a*) Acetate (*b*) Oxalate
(*c*) Cyanide (*d*) Ammonia

5. $[Pt(NH_3)_6]Cl_4$ complex gives.

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

6. The coordination number of a metal in coordination compounds is

(*a*) Same as primary valency
(*b*) Sum of primary and secondary valencies
(*c*) Same as secondary valency
(*d*) None of these

7. Which of the following complexes show six coordination number

(*a*) $[Zn(CN)_4]^{2-}$ (*b*) $[Cr(H_2O)_6]^{3+}$
(*c*) $[Cu(CN)_4]^{2-}$ (*d*) $[Ni(NH_3)_4]^{2+}$

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

(*a*) 1 (*b*) 2
(*c*) 4 (*d*) Zero

9. The coordination number of Cu in complex $[Cu(H_2O)_4]^{++}$ is

(*a*) 4 (*b*) 3
(*c*) 2 (*d*) 1

10. The primary valency of metal ion in the coordination compound $K_2[Ni(CN)_4]$ is

(*a*) Four (*b*) Zero
(*c*) Two (*d*) Six

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

(*a*) 33 (*b*) 35
(*c*) 36 (*d*) 26

12. The oxidation number of chromium in sodium tetrafluora oxochromate complex is

(*a*) II (*b*) IV
(*c*) VI (*d*) III

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

(*a*) 8 (*b*) 6
(*c*) 4 (*d*) 3

14. In $[Ni(NH_3)_4]SO_4$, the E.A.N. of Ni is

(*a*) 34 (*b*) 35
(*c*) 36 (*d*) 37

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

(*a*) +3 (*b*) +6
(*c*) +5 (*d*) +2

16. The EAN of iron in potassium ferricyanide is

(*a*) 18 (*b*) 54
(*c*) 35 (*d*) 23

17. In the coordination compound, $K_4[Ni(CN)_4]$ oxidation state of nickel is

(*a*) –1 (*b*) 0
(*c*) +1 (*d*) +2

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

(*a*) $[MA_5B]$ (*b*) $[MA_2B_4]$
(*c*) $[MA_3B_3]$ (*d*) $[MA_4B_2]$

19. The number of unpaired electrons in the complex ion $[CoF_6]^{3-}$ is (Atomic no. of Co = 27)

(*a*) Zero (*b*) 2
(*c*) 3 (*d*) 4

20. Coordination isomerism is caused by the interchange of ligands between the

(*a*) Cis and Trans structure
(*b*) Complex cation and complex anion
(*c*) Inner sphere and outer sphere
(*d*) Low oxidation and higher oxidation states.

Answer Keys

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

Solutions

1. In Cuprammonium sulphate $[Cu(NH_3)]_4SO_4$
Coordination number of Cu is 4.

2. As it makes use of its two atoms to form coordinate covalent bonds with the central metal ion.

3. $[CO(en)_2\ Br_2]Cl_2$
C.N. of Co = 2 × number of bidentate ligand + 1 × number of monodentate ligand
$= 2 \times 2 + 1 \times 2 = 4 + 2 = 6$

4. **Chelating ligand:** When a multidentate ligand simultaneously coordinates to a metal ion by more than one donor site. Then a ring like structure is formed. it is called chelation and in this question only oxalate is bidentate all others are unidentate.

5. $[Pt\,(NH_3)_6]Cl_4$ complex gives 5 ions in the solution

$$\left[Pt\left(NH_3\right)_6\right]Cl_4 \rightleftharpoons \left[Pt\left(NH_3\right)_6\right]^{4+} + 4Cl^-$$

6. According to modern view primary valency of complex compound is its oxidation number while secondary valency is the coordination number.

7. Coordination number is equal to total number of ligands in a complex.

8. Cuprammonium salt $[Cu(NH_3)_4]SO_4$

$$\left[Cu\left(NH_3\right)_4\right]SO_4 \rightleftharpoons \left[Cu\left(NH_3\right)_4\right]^{2+} + SO_4^{\ 2-}$$

So, it will give two ions in water.

9. The coordination no. = no. of ligands attached.

10. Primary valencies are also known as oxidation state.
$K_2[Ni(CN)_4]$, $2 + x - 4 = 0$
$\Rightarrow x = +2$

11. EAN = Atomic number-Oxidationstate + 2 × no. of Ligands
$= 26 - 2 + 2 \times 6 = 24 + 12 = 36$

12. $Na_2\,[CrF_4O]$
$\Rightarrow x + 4 \times (-1) + (-2) = -2$
$\Rightarrow x - 6 = -2 \Rightarrow x = -2 + 6 = +4$

13. $x + 6 \times 0 + 3 \times -1 = 0$
$x - 3 = 0 \Rightarrow x = +3$
Hence, Oxidation number of Cr is +3.

14. EAN = (atomic no) – (oxidation state) + 2 × no. of Ligands
$= 28 - 2 + 2 \times 4 = 26 + 8 = 34$

15. $[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$
$x + 6(0) = +3 \Rightarrow x = +3$

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

17. $+1 \times 4 + x - 1 \times 4 = 0$
$4 + x - 4 = 0 \Rightarrow x = 0$ for Ni

18. Octahedral complexes of the type
$[MA_4B_2]$, $[MA_2B_4]$, $[MA_3B_3]$ exhibit geometrical isomerism.

19. The number of unpaired electrons in the complex ion $[CoF_6]^{3-}$ is 4.

20. Coordination isomerism is caused by the interchanged of ligands between cation and anion complexes.