HINTS & SOLUTIONS

TOPIC : COORDINATION COMPOUNDS EXERCISE # 1

SECTION (A)

- **1.** $[KAI(SO_4)_2.12H_2O]$ is an example of double salt.
- **2.** $4\text{KCN}.\text{Fe}(\text{CN})_2$ (aq) $\longrightarrow \text{K}_4 [\text{Fe}(\text{CN})_6]$
- 3. $NH_2 CH_2 CH_2 NH_2$. It contains two donor atoms i.e. nitrogen. So it is a bidentate ligand.
- **4.** NO_2^{-} , monodentate monoanion.
- 5. Coordination number is 6 & O.N. x 2 = +1; x = +3
- 6. x + 1 = +2 ; x = +1
- 7. $2x + 4 \times (-2) = -2$ 2x = 6x = +3

,

8. All ligands are lewis bases as they donate lone pair of electrons to the metal ion to form coordinate covalent bonds.

9. (1)
$$\underset{l}{\overset{H_3C}{\underset{l}{\sim}}}_{H_1} \overset{CH_3}{\underset{l}{\sim}}_{U_1}$$
 (2) $\underset{O=C-O^-}{\overset{O=C-O^-}{\underset{l}{\sim}}}_{O=C-O^-}$ (3) $NH_2CH_2CH_2NH_2$

10.
$$\mathbb{NO}_2^- \rightarrow \mathbb{N}$$
-nitro, $-\mathbb{ONO}^- \rightarrow \mathbb{O}$ -nitro.

11.
$$\begin{pmatrix} 0 \\ \parallel \\ -OOC - NH - CH_2 - CH_2 - N \\ \parallel \\ 0 \end{pmatrix}$$

12. NO_2^{-} ion can coordinate through either the nitrogen or the oxygen atoms to a central metal ion.

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13.
$$[Co(NH_3)Cl(gly)_2]^{+x}$$

+3 -1 -2 = x
x = 0
So No charge is there.

14. Tactual

SECTION (B)

1. $[Cr(III)(en)_2(OX)]^+$

2. The charge of the cation is balanced by the charge of the anion.

3. (1) Coordination number of platinum is generally six when its oxidaton state is (IV). So it is incorrect name.

(2) With type of ligand and +4 oxidation state of platinum, the complex should be cationic not anionic. So it is also incorrect name.

not anion but IUPAC name is given as anion.

(3) For coordination number six, the oxidation state of Pt is +IV. So the probable formulae of the complex may be $[Pt(NH_3)_2(en)(SCN)_2]^{2+}$. So its correct IUPAC name is Diammineethylenediaminedithiocyanato-S-platinum (IV).

(4) With two \dot{NH}_3 , two en and two SCN- ligands, the coordination number of Pt becomes eight, which is incorrect according to the question.

- 4. $[Ba^{2+} BrF_4]^{-1}$ oxidation No. of Br = +3 So (2) is correct option.
- 5. The charge of the cation is balanced by the charge of the anion.
- 6. From text.
- 7. (1) If [Cr(Cl)₅N]²⁻, complex is anion so name of the element should be chromate (VI).
 (3) If [Cr(Cl)₅N₃]⁰, complex is neutral so name of the element should be chromium (VI). Therefore, (2) option is correct according to the IUPAC rule.
- 8. $[Fe(II)N_3(O_2) (SCN)_4]^{4-}$; so correct name is azidosuperoxidotetrathiocyanato-S-ferrate(II) according to IUPAC rules.
- **9.** $(Rh(III)(en)_2(ONO)(SCN)]^+(NO_3^-)$
- **10.** According to IUPAC nomenclature.

SECTION (C)

- 1. From text
- 2. From text
- **3.** Complexes formed will be as follows. (1) $[Cr(III)(NH_3)_6]^{3+3}CI^-$ (2) $[Cr(III)(NH_3)_5CI]^{2+2}CI^-(3) [Cr(III)(NH_3)_4CI]^+CI^-$
- 4. $[Co(NH_3)_6]Cl_3 \stackrel{aq.}{\longleftarrow} [Co(NH_3)_6]^{3+} + 3Cl^- No. of total ions = 4$
- **5.** EAN of Ni 28 2 + 8 = 34EAN of Cu = 29 - 2 + 8 = 35EAN of Pt = 78 - 4 + 12 = 86
- **6.** EAN = 26 + 1 + 8 = 35.
- **7.** (1) 24 + 12 = 36 and 26 + 10 = 36(2) 29 1 + 8 = 36 and 28 + 8 = 36(3) 27 2 + 12 = 37 and 28 2 + 12 = 38(4) 23 + 1 + 12 = 36 and 27 3 + 12 = 36
- 8. $[Mn(H_2O)_6]^{2+}$, $[Ar]^{18} 3d^5 4s^0$; rest all have $3d^6$ configuration.
- **9.** CN^{-} is strong field ligand, so $\Delta_0 > P$. Hence $K_3[Fe(CN)_6]$ has d^2sp^3 hybridisation and is diamagnetic. $K_4[Fe(CN)_6]$ has d^2sp^3 hybridisation and is paramagnetic with one unpaired electron.
- **10.** In both complexes the oxidation state of cobalt is +3 with 3d⁶ configuration. Except [CoF₆]^{3–}, all other complexes of cobalt with weak field and strong field ligands are inner orbital complexes and diamagnetic because of higher CFSE.



13. $[Pt(NH_3)_5CI]CI_3 \stackrel{aq.}{\Longrightarrow} [Pt(NH_3)_5CI]^{3+} + 3CI^{-}$

14. $[Co(NH_3)_5(NO_3)]Br_2 \stackrel{aq.}{\longleftrightarrow} [Co(NH_3)_5(NO_3)]^{2+} + 2Br^{-}$ It has two ionisable bromide ion. They will react with AgNO₃ solution to give two mol of yellow precipitate.

SECTION (D)

- **1.** According to spectro Chemical series.
- 2. This is in accordance with spectro chemical series.
- **3.** According to CFT theroy.
- 4. Order of strength of ligands is $CN^- > NH_3 > H_2O > CI^-$
- **5.** The electron configuration of ₂₁Sc⁺³ is [Ar]¹⁸ 3d⁰ 4s⁰. All electrons are paired and thus diamagnetic. As there is no unpaired electron in d-orbital, therefore, there is no d-d transition of electron. So according to crystal field theory the compound is colourless.
- **6.** It has one unpaired electron which undergoes d-d transition in presence of ligands.
- 7. Due to thermodynamically stability $[Cd((CN)_4]^{2-}$ is highly stable.

- 8. $[Cu(CN)_4]^{3-}$ is higly stable due to high charge density & thermodynamic stability is also more.
- 9. [NiCl₄]²⁻ (3d⁸) is tetrahedral with two unpaired electrons, $\mu_{BM} = 2.83$. [PdCl₄]²⁻ (4d⁸) is square planar and diamagnetic, $\mu_{BM} = 0$.
- **10.** All statements are correct with respect to CFT.
- **11.** (1) All are diamagnetic and inner orbital complexes because all ligands are strong field ligands.

(2) Fe³⁺ n = 5 ; $\mu = \sqrt{5 (5+2)} \approx 5.92$ with H₂O, so [FeCl₄]⁻ is diamagnetic.

(3) Fe^{_3+} n = 5 ;
$$\mu$$
 = $\sqrt{5 \ (5+2)} \ \approx 5.92$ with $H^{}_2 C$

Fe³⁺ n = 1 ; $\mu = \sqrt{3} = 1.73$ with CN⁻

(4) Mn^{2+} (3d⁵) and Fe³⁺ (3d⁵) have same number of unpaired electrons i.e. 5 with weak field ligands, F⁻

- 12. On the basis of number of electrons the correct order is P > Q > R > S.
- **13.** In $[Fe(CN)_6]^{4-}$; Fe(II) is t_{2g}^{6} , eg^0 due to strong ligands.
- 14. (4) Ti⁴⁺, [Ar]¹⁸ 3d⁰ 4s⁰; as there is no unpaired electron, so no d-d transition occurs. Cu⁺, [Ar]¹⁸ 3d¹⁰ 4s⁰; All electrons paired, so there is no unpaired electron for d-d transition. Hence both complexes are colourless.

SECTION (E)

- **1.** Ionization isomerism arises due to the exchange of ligand(s) between ionization sphere and ionic sphere.
- **2.** $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_4Cl_2]Cl_2H_2O$ are hydrate isomers. This is due to the change in composition with respect to water molecules.
- **3.** H_2O is no ambidentate ligand. CN^- , SCN^- and NO_2^- are ambidentate ligands which can attach to central metal atom through either of the two donor atoms.
- **4.** It exists in cis and trans forms.
- **5.** (1) trans-[Co(NH₃)₄Cl₂]⁺ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.

(2) $[Cr(H_2O)_6]^{3+}$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.



(4) trans- $[Co(NH_3)_2(en)_2]^{3+}$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.

6. cis and trans forms both have an element of symmetry. So does not show optical activity.

(1) No anionic ligand is present in coordination sphere for the exchange with Cl- ions present in ionisation sphere.
 (2) No anionic ligand is present in coordination sphere for the exchange with Cl- ions present in

(2) No anionic ligand is present in coordination sphere for the exchange with Cl- ions present in ionisation sphere.

(3) No anionic ligand is present in coordination sphere for the exchange with Cl- ions present in ionisation sphere.

(4) Br⁻ and SO₄⁻ can exchange their positions between coordination sphere and ionisation sphere. Hence it shows ionization isomerism.

- 8. Co-ordination isomerism occurs when both cation and anion are complex, caused due to interchange of ligands between two complex ions of the same complex.
- **9.** $\mathbb{NO}_{2^{-}}$ is an ambidentate ligand and can link to central metal ion either through N or O. Hence it show linkage isomerism.

There is exchange of NO_2^- and SO_4^{2-} occurs between coordination sphere and ionization sphere. Hence it show ionisation isomerism.

 $\ensuremath{\mathsf{Ma}}_{\ensuremath{\scriptscriptstyle 5}}\ensuremath{\mathsf{b}}$ has only one form, therefore, it does not show geometrical isomerism.

Ma_sb has mirror plane, therefore, it does not show optical isomerism.

- **10.** Ma_2b_4 has two geometrical isomers one cis- and one trans. Similarly Ma_2b_2 also has one cis- and transforms.
- **11.** It is Ma_3b_2c type so = 3 i.e.(aa)(ab)(bc)(optically inactive)(aa)(bb)(ac)(optically inactive)(ab)(ab)(ac)(optically inactive)(ab)(ab)(ac)(optically inactive)
- 12. (1) I is trans form which has centre of symmetry as well as plane of symmetry; so optically inactive
 - (2) II is cis form which lacks centre of symmetry as well as plane of symmetry ; so optically active
 - (3) (II) and (III) lack symmetry elements ; so both are optically active.
 - (4) IV is trans form which has centre of symmetry as well as plane of symmetry ; so optically inactive

SECTION : (F)

1. Order of C – O bond strength ;

 $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^2 - and [Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^2 - .$ (1) True statement.

(2) As + ve charge on the central metal atom increases, the less readily the metal can donate electron density into the π^* orbitals of CO ligand to weaken the C – O bond.

(3) In the carbonylate anions, the metal has a greater electron density to be dispersed, with the result that $M - C\pi$ bonding is enhanced and the C – O bond is diminished in strength.

2. Compounds in which metal is directly attached to carbon are called as organometallic compounds.
 (3) carbon is attached to N, it is not organometallic compound.

EXERCISE # 2

2. (1) $\overline{N} = \overline{N} = \overline{N}$ Four membered ring is not stable.

- (2) Both N–N bond lengths are identical and that is 1.15 Å
- (3) N_3^- and CO₂ both have same number of electrons i.e. 22; so isoelectronic.

$$\bar{N} = N_{sp}^{+} = \bar{N}$$
 (linear) $O = C_{sp}^{-} = O$ (linear)

So both are also isostructural

(4) There are two σ and two π bonds. ${}^{2-1}N = N : \longleftrightarrow N = N = N^{2-1} : N = N = N = N$

5. Diethylenetriamine is a tridentate neutral molecules with three donor nitrogen atoms. Polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring is called as chelating ligand.

- 7. $Na_2[Cr (edta)].$
- **8.** (1) If $[Os(CI)_5N]^{2-}$, complex is anion, so name of the element should be osmate (VI). (3) If $[Os(CI)_5N_3]^0$, complex is neutral, so name of the element should be osmium (VI). Therefore, (2) option is correct according to the IUPAC rule.
- **9.** Complexes having all identical ligands are called as homoleptic complexes.
- According to Werner's theory statements (2) and (3) are correct.
 (1) Ligands are connected to the metal ion by coordinate covalent bond (dative bond).
 (2) Secondary valencies i.e. coordination number give rise to stereochemistry of the complexes because of their directional properties.
 (3) Secondary valencies correspond to coordination number i.e. number of σ-bonds between metal ion and lignds.
- **14.** EAN of $Co^{3+} = 24 + 12 = 36$. EAN of Ni²⁺ = 26 + 12 = 38.
- **15.** Tollen's reagent is $[Ag(NH_3)_2]^*$. Oxidation no. of silver = x + 2 (0) = +1 or x = + 1. As there are two σ bonds between silver and ligands its coordination number is 2. EAN = (47 - 1) + 2 × 2 = 50.
- **19.** $[\text{Ni Cl}_2 (\text{PPh}_3)_2]$ is non-ionic and tetrahedral.
- (1) [Fe(en)₃]³⁺ d²sp³ with one unpaired electron. 'en' is a strong field chelating ligand and thus compels for the pairing of electrons to have d²sp³ hybridisation. It is paramagnetic with one unpaired electron (valence shell electron configuration, 3d⁵)

(2) $[FeCl_2 (PPh_3)_2] - sp^3$ with four unpaired electrons. 'PPh₃' is a strong field ligand but is bulkier one ; so it favours tetrahedral geometry. It is paramagnetic with four unpaired electrons (valence shell electron configuration, $3d^6$).

(3) $[Fe(CN)_6]^3$ - d^2sp^3 with one unpaired electron. 'CN^{-'} is a strong field ligand and, therefore, it compels for pairing of electrons to have d^2sp^3 hybridisation. It is paramagnetic with one unpaired electron (valence shell electron configuration, $3d^5$)

(4) $[Fe(CO)_2(NO)_2]$ - sp³ and diamagnetic. Iron is in -II oxidation state (here NO is three electron 3d 4s 4p

donor). So



sp³ hybridisation

It is diamagnetic as all electrons are paired.





sp³ hybridisation

No empty d-orbital is available for dsp² hybridisation and so complex is tetrahedral and diamagnetic.

sp³ hybridisation

No empty d-orbital is available for dsp² hybridisation and so complex is tetrahedral and diamagnetic.

- **22.** In $[Fe(CN)_6]^{4-}$; Fe(II) is t_{2a}^6 , e_a^0 due to strong ligands.
- **23.** (1) $Ti(NO_3)_4$, [Ar]¹⁸ 3d⁰ 4s⁰; there is no unpaired electron and, therefore, there is no d-d transition of electron. So compound is colourless.

(2) $[Cr(NH_3)_6)]Cl_3$, $[Ar]^{18} 3d^3$; there is three unpaired electron and, therefore, there is d-d transition of electron. So compound is coloured.

(3*) $K_3[VF_6]$, [Ar]¹⁸ 3d¹; there is one unpaired electron and, therefore, there is d-d transition of electron. So compound is coloured.

(4) $[Cu(NCCH_3)_4][BF_4] [Ar]^{18} 3d^{10}$; there is no unpaired electron and, therefore, there is no d-d transition of electron. So compound is colourless.

- 24. $Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$ $K_f = \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}] [NH_3]^4} \Rightarrow \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}]} = K_f[NH_3]^4$ $= 3 \times 10^9 \times 10^4 = 3 \times 10^{13} \Rightarrow \frac{[Zn^{2+}]}{[Zn(NH_3)_4]^{2+}} = \frac{1}{3 \times 10^{13}} = 3.3 \times 10^{-14}$.
- **26.** $[Co(NH_3)_5NO_2]CI$ and $[Co(NH_3)_5CI]NO_2$ are ionisation isomers. $[Co(NH_3)_5NO_2]CI$ and $[Co(NH_3)_5(ONO)]CI$ are linkage isomers.
- (1) I and III both are same i.e. trans-isomers
 (2) II and IV are identical structures (i.e. cis form)
 (3) I and II are cis and trans isomers (i.e. they are geometrical isomers)
- (1) cis [Co(NH₃)₄ Cl₂]⁺ has plane of symmetry as well as centre of symmetry ; so optically inactive.
 (2) trans [Co(en)₂Cl₂]⁺ has plane of symmetry as well as centre of symmetry ; so optically inactive.
 (3) cis [Co(en)₂Cl₂]⁺ lacks plane of symmetry as well as centre of symmetry ; so optically active.
 (4) [Co(en)₃]³⁺ lacks axis of internal rotation ; so optically active.
- **32.** Solution $(C O) = (C O)^{-1} + [Cr(CO)_6]^{-1} + [Cr(CO)_6]^{-1} + [Cr(CO)_6]^{-1} + [Cr(CO)_6]^{-1} + Cr(CO)_6]^{-1}$. As + ve charge on the central metal atom increases, the less readily the metal can donate electron density into the π^* orbitals of CO ligand to weaken the C – O bond.
- **33.** CH₃O Li is not an organo metallic compound because metal is not directly attached with carbon.
- 34. From text.

EXERCISE # 3 PART - I

1. In $[Co(CO)_5 NH_3]^{2+}$, Co atom is attached with NH_3 by σ -bonds while CO is attached by π -bonds.

- **2.** $[Cr(SCN)_2 (NH_3)_4]^+$ shows linkage, geometrical and optical isomerism.
- **3.** Chlorodiaquatriammine cobalt (III) chloride is $[CoCl(NH_3)_3 (H_2O)_2]Cl_2$.
- **5.** Tris-(ethylenediamine) cobalt (III) bromide [Co(en)₃]Br₃ exhibits optical isomerism :



- 7. In Ni(CO)₄, nickel is sp³-hybridised because in it oxidation state of Ni is zero. So, configuration of $_{26}$ Ni = 1s², 2s²2p⁶, 3s²3p⁶3d⁸, 4s²



(Co is a strong field ligand, hence does pairing of electrons)

In [Ni(CN)₄]²⁻, nickel is present as Ni²⁺, so its configuration = 1s², 2s²2p⁶, 3s²3p⁶3d⁸



CN⁻ is strong field ligand, hece it makes Ni²⁺ electrons to be paired up.

In [NiCl₄]²⁻, nickel is present as Ni²⁺, so its configuration = 1s², 2s²2p⁶, 3s²3p⁶3d⁸



 $CI^{\scriptscriptstyle -}$ is a weak field ligand, hence in $Ni^{_{2+}}$ electrons are not paired.

8. In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.

Co³⁺,[Ar]3d⁶

[Co(NH₃)₆]³⁺ (inner orbital or low spin complex)

 $\begin{array}{c|c} 4s & 4p \\ \hline 1 \downarrow 1 & 1 & 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \downarrow 1 \downarrow 1 \downarrow 1 \\ \hline 1 \\$

Six pairs of electrons from six NH_3 molecules.

9. cis-[Co(en)₂Cl₂]⁺ is able to show the phenomenon of optical isomerism because it can form a superimposable mirror image.



but trans-form is optically inactive.

10. KCN first reduces cupric ions to cuprous ions which are precipitated as cuprous cyanide. This reacts with excess of CN^- to form soluble four-coordinated complex $[Cu(CN)_4]^{3-}$ which is tetrahedral in shape. $2Cu^{2+} + 4CN^- \longrightarrow 2Cu^+ CN^- + (CN)_2$

| | Cyanogen $CuCN + 3 CN^{-} \longrightarrow [Cu(CN)_4]^{3-}$ |
|-----|---|
| 11. | Magnetic moment = $\sqrt{n (n+2)}$ B.M = 3.83 B.M. (Given). Hence, n= 3, i.e. there are three unpaired electrons. Thus, we have 3d $4s$ $4p$ $4p$ |
| | In d ² sp ³ hybridisation, the orbitals taking part are $d_{x^2-y^2}$ and d_{z^2} . Hence, unpaired electrons are present in $3d_{xy}$, $3d_{yz}$, $3d_{xz}$. |
| 12. | en Co en + |
| 13. | $Cr^{2+}, 3d^4 \qquad \blacksquare \qquad \checkmark \qquad \qquad$ |
| | $Fe^{2_+}, 3d^6 = \qquad \qquad$ |
| | en Cl Cl Cl en + dextro mirror |
| 14. | d and I of cis-[CoCl₂(en)₂]* |
| 15. | The electron configuration of V (23) = [Ar], 4s ² , 3d ³ Let in [V(gly) ₂ (OH) ₂ (NH ₃) ₂]* oxidation state of V is x. $x + (-1) \times 2 (-1)2 + (0 \times 2) = + 1$ V ⁵⁺ = [Ar], 4s ⁰ , 3d ⁰ (no unpaired electrons) The electronic configuration of Fe(26) = [Ar] 4s ² , 3d ⁶ Let the oxidation state of Fe in [Fe(en)(ppy)(NH ₃) ₂] ²⁺ is x. [x + (0) + (0) + (0) $\times 2$] = + 2 x = + 2 Fe ²⁺ = [Ar] 4s ⁰ 3d ⁶ (:: no unpaired electron) but boy en and NH all are strong field ligands so pairing |
| | occurs and thus, Fe ²⁺ contains no unpaired electron. The electronic configuration of |

 $Co(27) = [Ar] 4s^2, 3d^7$ Oxidation state of Co in $[Co (OX)_2 (OH)_2]^-$

 $x + (-2) \times 2 + (-1) \times 2 = -1$ x = +5Co⁵⁺ = [Ar], 3d⁴ [4 unpaired electrons] OX and OH are weak field ligands. The electronic configuration of Ti (22) = [Ar] 4s², 3d² Oxidation state of Ti in [Ti(NH₃)₆]³⁺ is 3.

 $Ti^{3+} = [Ar]$. $3d^1$ (one unpaired electron)

Hence, complex $[Co(OX)_2(OH)_2]^-$ has maximum number of unpaired electrons, thus show maximum paramagnetic.

- 16. As in all the given complex the central metal atom is same and contains same number of d electrons, thus CFSE is decided by ligands. In case of strong field ligand, CFSE is maximum. CN⁻ is a strong field ligand, Hence, in [Co(CN)₆]³⁻ CFSE is maximum.
- **17.** Optical isomerism is exhibited by only those complexes in which elements of symmetry are absent. Octahedral complexes of the types $[M(aa)_3, [M(aa)x_2,y_2]$ and $[M(aa)_2x_2]$ have absence of elements of symmetry, thus exhibit optical isomerism. Here, aa represents bidentate ligand, x or y represents monodentate ligand and M represent central metal ion.

Hence, [Co (NH₃)₃Cl₃]^o due to presence of symmetrry elements does not exhibit optical isomerism.

18. In $[Cr(NH_3)_6]^{3+}$, Cr is present as Cr^{3+} .



Since, this complex has three unpaired electrons, excitation of electrons is possible and thus, it is expected that this complex will absorb visible light.

19. In TiF²⁻₆, Ti is present as Ti⁴⁺.

Ti⁴⁺ = [Ar]3d⁰4s⁰ Hence, TiF²⁻, is colourless.

In Cu₂Cl₂, Cu is present as Cu⁺.

| | | | 3d1 | 0 | | 4s |
|------------|----|-----|-----|----|----|----|
| Cu⁺ = [Ar] | 11 | 11. | 11 | 11 | 11 | |

Due to absence of unpaired electrons, Cu₂Cl₂ is colourless.

- **20.** There is no unpaired electrons in $[Ni(CN)_{4}]^{2-}$ due to strong field ligand.
- **21.** CFSE = $(-3 \times 0.4 + 1 \times 0.6) \Delta_0 = -0.6 \Delta_0$
- 22. Due to two different Geometrical isomers.
- **23.** $[Co(NH_3)_6] [Cr(CN)_6]$ and $[Cr(NH_3)_6] [Co(CN)_6]$
- **24.** $[Pt (Py)(NH_3)(Br)(Cl)]$
 - \Rightarrow [M(abcd)] (ab) (cd)
 - \Rightarrow [M(abcd)] (ac) (bd)
 - \Rightarrow [M(abcd)] (ad) (bc)

There are 3 Geometrical isomerism.

| 25. | Cr ²⁺ d ⁴ | 4 |
|-----|---------------------------------|---|
| | Mn²+ d⁵ | 5 |
| | Fe ²⁺ d ⁶ | 4 |

| | $\begin{array}{c c} Co^{2+} d^7 & 1 & 1 & 1 & 1 \\ \hline Minimum \ Paramagnetic \ behaviour = [Co \ (H_2O)_6]^{2+} \end{array} 3$ |
|-----|---|
| 26. | $[Ni(NH_3)_6]^{2+}$ Ni ²⁺ = 3d ⁸ , according to CFT = $t_2g ^{222}e_g^{11}$, therefore, hybridisation is sp ³ d ² & complex is paramagnetic. |
| 27. | d ⁶ - $t_{2g}^{2,2,2} = 0.0_{eg}^{0,0}$ (in low spin) C.F.S.E. = $-0.4 \times 6 \Delta_0 + 3P = \frac{12}{5} - \Delta_0 + 3P$ |
| 28. | [Cu(NH ₃) ₄] ²⁺ hybridisation dsp ² Cu ⁺² − 3d ⁹ has one unpaired e ⁻ So magnetic moment $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ |
| 29. | $[Cr(H_2O)_4Cl_2]Cl + AgNO_3 \longrightarrow AgCl + [Cr(H_2O)_4Cl_2]NO_3$ ppt $mole = 0.01 \times \frac{10}{1000} = 10^{-3}$ |

30. [Fe(H₂O)₆]³⁺ $Fe^{+2} = 3d^5 (t_{2a}^{1,1,1} e_a^{1,1})$ so C.F.S.E. is = $[-0.4 \times 3 + 0.6 \times 2] \Delta_0 = 0$

So mole of AgCl = 0.001

- 31. Cis - [Pt Cl₂(NH₂)₂] known as cis platin is used as an anticancer agent.
- 32. CoCl₃·3NH₃ is [Co(NH₃)₃Cl₃] so it will not ionize and does not give Cl⁻ ion test.
- 34. Ca+2 are important in blood clotting and are also important in maintaining the regular beating of the heart.
- 35.

Due to back bonding between metal-carbon bond length of C-O increase (B.O of M-C ? B.O of C-C ? B.L. of C-O ?) Higher is negative charge on metal, higher is back bonding (synergic effect) so bond length is higher so answer is $[Fe(CO)_{4}]^{2-}$

Fe=C===O

Jahn teller effect : This is geometric distortion occur in unsymmetrical octahedral complexes for 36. example high spin complexes of (high spin)

| d4 1 | d ⁷ 1 1 | d ⁸ 1 1 | d ⁹ 1 1 |
|---------------|--------------------|--------------------|--------------------|
| 1 1 1 | 11 11 1 | 11 11 11 | 1 1 1 |
| unsymmetrical | unsymmetrical | Symmetrical | unsymmetrical |

unsymmetrical unsymmetrical

- 37. RMgX₂ is a organometallic compound and it has only sigma bonds.
- 38. 1 mole of [Co(NH₃)₆]Cl₃ gives 3 moles of AgCl with excess of AgNO₃ 1 mole of [Co(NH₃)₅Cl]Cl₂, gives 2 moles of AgCl with excess of AgNO₃ 1 mole of [Co(NH₃)₄Cl₂]Cl gives 1 moles of AgCl with excess of AgNO₃
- Strength of ligands attached with Co³⁺ ion is in the order of en> NH₃ > H₂O. So order of spliting (value 39. \therefore Wave length absorbing light $\alpha \frac{1}{\Delta_0}$ of Δ_0) will be in the same order.
- Oxidation number of Mn in the complex $[Mn(CN)_6]^{3-}$ is +3. 40. $Mn^{3+} = 3d^4 (t2g^4, eg^0)$ in presence of strong field lingand so complex is d^2sp^3 hybridised

- 41. Fe(CO)5 is mononuclear
- 42. [Ni(CO)₄] $Ni = 3d^8 4s^2 = 3d^{10} 4s^0$: C.N. = 4
- 43. It shows Geometrical isomerism and Optical isomerism.
- K₄[Fe(CN)₆] 44.

4(+1) + x + 6(-1) = 0x = +2



t_{2g} $Fe^{2+} = [Ar]3d^{6}4s^{0}$

CN- is a strong ligand due to this pairing of e occur



CFSE for
$$[C_0Cl_4]^{-2}$$
 is $\Delta_t = \frac{4}{9} \times 18000 = 8000 \text{ cm}^{-1}$

PART - II

CI



45.

46.



As all are octahedral complexes of the same metal(Ni), absorption will depend only on the nature of the 2. ligand. From spectrochemical series, the CFSE of the given ligands are in the order : H₂O < NH₃ < NO₂⁻ Hence, excitation energies absorbed to show particular colour will be in the order :

 $[Ni(H_2O)_{6}]^{2+} < [Ni(NH_3)_{6}]^{2+} < [Ni(NO_2)_{6}]^{4-}$

The wavelength absorbed will be in the opposite order.

 $K_4[Fe(CN)_6]$ 3.



Thus, the assertion that $K_4[Fe(CN)_6]$ is diamagnetic and $K_3[Fe(CN)_6]$ is paramagnetic is true. But the reason is false as crystal field splitting in ferrocyanide is less than ferricyanide ion because higher the oxidation state of the metal, greater the crystal field splitting.

- 4. $XeF_4 = square planar (sp^3d^2)$ $SF_4 = distorted trigonal bipyramidal (sp^3d)$ $[NiCl_4]^{2-} = tetrahedral (sp^3)$ $[PtCl_4]^{2-} = tetrahedral (dsp^2)$
- **5.** $\mu = \sqrt{n (n+2)}$

No. of unpaired electrons are : $Cr^{2+}(3d^4)$, n = 4 $Co^{2+}(3d^7)$, n = 3 $Fe^{2+}(3d^6)$, n = 4 $Mn^{2+}(3d^5)$, n = 5 Thus, Cr^{2+} and Fe^{2+} have same number of unpaired electrons. Hence, in pair(2),both species will have same magnetic moment.



- 7. In anticancer drug cis-platin NH_3 and CI ligands are present.
- 8. The coordination entity, for which crystal field splitting is smaller, absorbs light of lowest frequency. Weaker the ligand field strength, smaller will be the crystal field splitting. The order of field strength of various ligands is as

 $CN > en > NH_3 > CI$

Hence, [CrCl₆]³⁻ due to the presence of Cl⁻ ligand absorbs light of lowest frequency.

- **9.** FeSO₄ when reacts with NO, a brown colour complex called ferrous nitroso sulphate is formed.
- **10.** The ligands having vacant π -type orbitals have a tendency to receive back donated π -electrons, thus these are called π -acid ligands or π -acceptor ligands.
- **11.** $Ni^{2+} \rightarrow 3d^8$ So there are two unpaired electrons.

12. (ab) (cd)

- (ac) (bd)
- (ad) (bc)

aTb aTc aTd

So 3 geometrical isomers

- **13.** Since the precipitate of AgCI shows two ionisable chloride ion the complex must have the structure. $[Co(NH_3)_5CI]CI_2 + 2AgNO_3 \rightarrow [Co(NH_3)_5CI](NO_3)_2 + 2AgCI$ Hence two chlorine atoms satisfy the primary valency and one, secondary valency.
- **14.** The complex chlorodiaquatriammine cobalt (III) chloride can have the structure $[CoCl(NH_3)_3(H_2O)_2]Cl_2$.
- 17. $[Co(NH_3)_5SO_4] Br + AgNO_3 \longrightarrow [Co(NH_3)_5SO_4] + AgBr \quad 0.02 \text{ mole } (Y) \\ [Co(NH_3)_5Br] SO_4 + BaCl_2 \longrightarrow [Co(NH_3)_5Br] Cl_2 + BaSO_4 \quad \frac{0.02}{2} \text{mol} L^{-1}(Z) \ 0.01 \text{ mol} L^{-1}$

- **18.** Both assertion and reason are true and reason is the correct explanation of assertion.
- **19.** Assertion is true reason is false There will be repulsion between electrons in d-orbit of metal atom and lone pair of electrons of ligands this repulsion will be greater when these d-orbitals of metal are directed towards the ligands than when there d-orbital are away from the ligand the $d_{x^2-y^2}$ and d_{z^2} orbitals of metal atom will experience maximum repulsion. While d_{xy} , d_{yx} and d_{xz} orbitals suffers minimum repulsion. This causes splitting of the d-orbitals
- 23. Diamagnetic complex is are $[Co(Ox)_3]^{3-}$ and $[Fe(CN)_6]^{3-}$
- **24.** $V(CO)_6$ easily reduces to $\left[V(CO)_6\right]^-$

25.
$$[Cr(H_2O)_6]^{+3} + 6NH_3 \text{ s} \longrightarrow [Cr(NH_3)_6]^{+3} = + 6H_2O$$

Cr⁺³ show six C.N. with NH₃

PART - III

1. (1) [Co(en)₂Cl₂]⁺ shows geometrical as well as optical isomerism. (Only cis-form but not trans form as it has one of the symmetry elements).



⁽²⁾ It exists only in one.

(3) Exist in cis and trans forms only (no optical isomerism because of the presence of the plane of symmetry).

(4) Exist in cis and trans forms only (no optical isomerism because of the presence of the plane of symmetry).



- 3. [Cr(NH₃)₄Cl₂]⁺; let the oxidation state of Cr is x, then x + 4 (-0) + 2 (-1) = +1 So, x = 3
- 4. (3) Due to the absence of symmetry elements it shows optical isomerism.



CN⁻ is strong field ligand ; so it compels for pairing of electrons to have two d-orbital empty. $\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.84$ B.M

6.
$$[Co(CN)_6]^{3-}$$
; $3d^6 = n = 0$

CN- is strong field ligand ; so it compels for pairing of electrons.

- $[Co(II)(NO_2) (NH_3)_5]^{2+} + 2CI^{-}$ and now follow IUPAC rules.
- 8. Metal-carbon bond in metal carbonyls has σ as well as π characters.



9. EDTA has four carboxylate oxygens and two ammine nitrogens as donor atoms. So it is a hexadentate ligand.

7.

H₂O is weak field ligand ; so it does not compel for pairing of electrons. So,

$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.84$$
 B.M

- **11.** In 4-coordinate complex of platinum (Pt^{II}), the four ligands are arranged about the central platinum ion(II) in a square planar geometry (dsp²) because of higher CFSE of 5d⁸ configuration.
- **12.** Let oxidation state of E is x so x + (-2) + 0 = +1 or x = +3Coordination number is number of σ -bonds between metal ion and ligands. 'en' and 'ox' are bidentate ligands Thus ; coordination number of E = 4 + 2 = 6.
- **13.** CFSE depends on the relative magnitude of crystal field splitting, Δ_o and pairing energy and in turns Δ_o depends upon the field produced by ligand and charge on the metal ion. The order of increasing crystal field strength is $C_2O_4^{3-} < H_2O < NH_3 < CN^-$. Thus the (4) option is correct.
- **14.** cis-form of $[Co(en)_2(NH_3)_2]^{3+}$ has optical isomers.



15. SCN⁻ ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds.

 $M \leftarrow SCN$ thiocyanato or thiocyanato-S

 $M \leftarrow NCS$ isothiocyanato or thiocyanato-N

16. Complex [Co(en)₃]³⁺ lacks plane of symmetrry and thus is optically active having following to enantiomeric forms.



17. In case of d³ configuration, the number of unpaired electrons remains 3 whether the ligand is strong field or weak field. The hybridisation scheme can be shown as follow :

| | | | 3d | , | | 4s | | | 4p | | |
|-----------------------|---|---|----|-------|----------------------|-------------------|-------|-------|----|---|--|
| $[Cr(NH_3)_3]^{3+} =$ | 1 | 1 | 1 | | | | | | | 4 | |
| | | | | ····· | d ² s | o ^³ hy | bridi | satic | n | | |

Hence the complex is inner orbital complex as it involves (n - 1) d orbitals for hybridisation, 3.93 = $\sqrt{n (n+2)}$; so n = 3 (here n is number of unpaired electron(s)).

18. In the paramagnetic and tetrahedral complex [NiCl₄]²⁻, the nickel is in +2 oxidation state and the ion has the electronic configuration 3d⁸. The hybridisation scheme is as shown in figure.



19. [Cr(en)₂Br₂]Br

dibromidobis(ethylenediamine)chromium(III) Bromide.

20. $[Co(NH_3)_3Cl_3]$ show facial as well as meridional isomerism. But both contain plane of symmetry. So, the answer is (3)

| | L ₁ | L_2 | L ₃ | L_4 |
|---------------|----------------|-------|----------------|-------|
| λ absorbed | red | green | yellow | blue |

21.

 \therefore Increasing order of energy of wavelengths absorbed reflect greater extent of crystal-field splitting, hence higher field strength of the ligand.

Energy : Blue (L_4) > green (L_2) > yellow (L_3) > red (L_1) \therefore L_4 > L_2 > L_3 > L_1 in field strength of ligands.

22. The complex is of the type [Mabcd]

M = metal a, b, c, d = Monodentate ligands.



3 geometrical isomers

- **23.** Each $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ contain 4 unpaired electron.
- 24. With coordination number six, if two bidentate ligands in *cis*-position are present, then it is optically active.
- 25. 10 millimoles of Complex or 0.01 mol

 $1.2 \times 10^{22} \text{ ions} = \frac{1.2 \times 10^{22}}{6 \times 10^{23}} \text{ mol or } 0.02 \text{ mol}$ $\left[\text{Co}(\text{H}_2\text{O})_5 \text{ Cl} \right] \text{Cl}_2.\text{H}_2\text{O} \xrightarrow{+\text{AgNO}_3(\text{excess})}{0.02 \text{ mol}} 2 \text{ AgCl} \downarrow$



- λ Blue < Green < Red λ L₂ < L₁ < L₃ $Δ_{Absorption}$ L₂ > L₁ > L₃ ∴ Ligand strength = L₂ > L₁ > L₃
- **29.** CN^{-} is strong ligand, So $[Co(CN)_6]^{-3}$ have maximum CFSE
- **30.** The crystal field splitting parameter can't be measured by wavelength of yellow and violet colours for (A) and (B) respectively

31. $d^7 < t_{2g^{2, 2, 2}} eg^{1, 0}$ Low spin $t_{2g^{2, 2, 1}} eg^{1, 1}$ High spin

- 32. CoCl_3 + en \rightarrow [$\operatorname{Co}(en)_2 \operatorname{Cl}_2$] Cl 1 mole 2 mole
 - Geometrical Isomers

- 33.
- $\begin{array}{c} \text{No. of Isomers} \\ [M(F) (CI) (SCN) (NO_2)] \rightarrow & 3 \\ [M(F) (CI) (NCS) (NO_2)] \rightarrow & 3 \\ [M(F) (CI) (SCN) (ONO)] \rightarrow & 3 \\ [M(F) (CI) (NCS) (ONO)] \rightarrow & 3 \\ \text{Total} = 12 \end{array}$
- **34.** C.No. = $4 \times 2 + 2 \times 1 = 10$ C₂O₄⁻² bidentate OH⁻ monodentate



No of Co–Co bond = 1no of briding carbonyl = 2

36. Based on Fact

35.

- **38.** Organometallic compound have bond between "Metal or Metalloid" and carbon.
- **39.** $K_3[Co(CN)_6]$ is octahedral geometry. Ligands are approaching there co-ordinate metal along the there coordinate axes. Hence $d_{x^2-v^2}$, d_{z^2} (axial orbitals) orbitals are directly infront of the ligands.