Exercise-1

Marked Questions may have for Revision Questions.

OBJECTIVE QUESTIONS

Section (A) : General introduction of complex salts and definitions to be used :

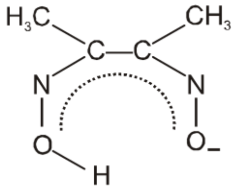
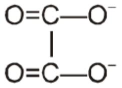
A-1. **Sol.** $\ddot{N}H_2-CH_2-CH_2-\ddot{N}H_2$. It contains two donor atoms i.e. nitrogen. So it is a bidentate ligand.

A-2. **Sol.** NO_2^-, monodentate monoanion.

A-3. **Sol.** Coordination number is 6 & O.N. $x - 2 = +1$; $x = +3$

A-4. **Sol.** $x + 1 = +2$; $x = +1$

A-5. **Sol.** All ligands are lewis bases as they donate lone pair of electrons to the metal ion to form coordinate covalent bonds.

A-6. **Sol.** (1)  (2)  (3) $NH_2CH_2CH_2NH_2$

A-7. **Sol.** $NO_2^- \rightarrow$ N-nitro, $-ONO^- \rightarrow$ O-nitro.

A-8. **Sol.** NO_2^- ion can coordinate through either the nitrogen or the oxygen atoms to a central metal ion.

A-9. **Sol.** $[Co(NH_3)Cl(gly)_2]^{+x}$
$+3 -1 -2 = x$
$x = 0$
So No charge is there.

A-10. **Sol.** Factual

Section (B) : Nomenclature of coordination compounds

B-1. **Sol.** $[Cr(III)(\overset{0}{en})_2(\overset{2-}{ox})]^+$

B-2. **Sol.** The charge of the cation is balanced by the charge of the anion.

B-3. **Sol.** $[Ba^{2+}BrF_4]^{-1}$ oxidation No. of Br = +3
So (2) is correct option.

B-4. **Sol.** From text.

B-5. **Sol.** $[Rh(III)(en)_2(ONO)(SCN)]^+ (NO_3^-)$

B-6. **Sol.** According to IUPAC nomenclature.

Section (C) : Bonding in coordination compounds : (Initial bonding theories and EAN rule, Valence bond theory)

C-1. **Sol.** From text

C-2. **Sol.** From text

C-3. **Sol.** EAN of Ni - 28 - 2 + 8 = 34
EAN of Cu = 29 - 2 + 8 = 35

EAN of Pt = 78 - 4 + 12 = 86

C-4. **Sol.** (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

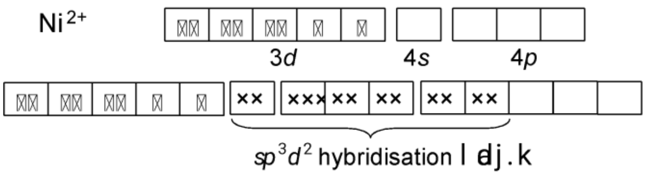
C-5. **Sol.** $[Mn(H_2O)_6]^{2+}$, $[Ar]^{18}$ $3d^5$ $4s^0$; rest all have $3d^6$ configuration.

C-6. **Sol.** $[Co(NH_3)_5(NO_3)]Br_2 \overset{aq.}{\rightleftharpoons} [Co(NH_3)_5(NO_3)]^{2+} + 2Br^-$
It has two ionisable bromide ion. They will react with $AgNO_3$ solution to give two mol of yellow precipitate.

C-7._ **Sol.** (1) In complex $K_4[Fe(CN)_6]$ the Fe obey EAN rule strictly.

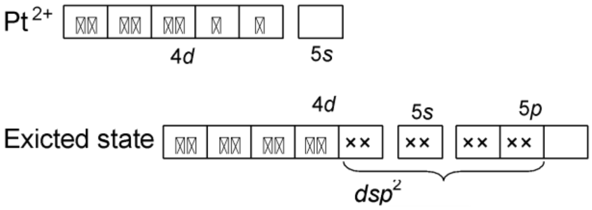
C-8._ **Sol.** (1) Complex with sp^3d-hybridisation show square pyramidal geometry.

C-9._ **Sol.** (2) sp^3d^2



C-10._ **Sol.** (2) Due to formation of inner orbital complex.

C-11._ **Sol.** (1) Since hybridisation is dsp^2 so it is square planar,



C-12._ **Sol.** (1) The most probable complex which gives three moles ions in aqueous solution may be $[Co(NH_3)_5(NO_2)]Cl_2$ because it gives two chlorine atoms on ionisation.

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

Section (D) : Crystal field theory & applications of crystal field theory : (Theory Magnetic moment of complex,Color of complex, Stability of complex)

D-1. **Sol.** According to CFT theroy.

D-2. **Sol.** Order of strength of ligands is $CN^- > NH_3 > H_2O > Cl^-$

D-3. **Sol.** The electron configuration of $_{21}Sc^{+3}$ is $[Ar]^{18}$ $3d^0$ $4s^0$. 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.

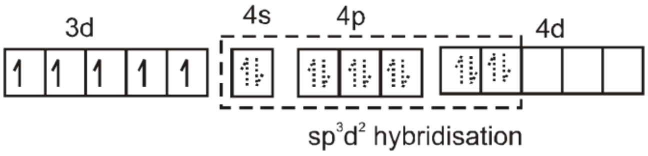
D-4. **Sol.** $[NiCl_4]^{2-}$ ($3d^8$) is tetrahedral with two unpaired electrons, $\mu_{BM} = 2.83$.
$[PdCl_4]^{2-}$ ($4d^8$) is square planar and diamagnetic, $\mu_{BM} = 0$.

D-5. **Sol.** All statements are correct with respect to CFT.

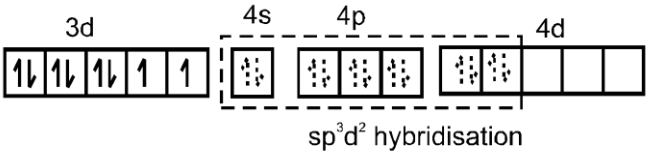
D-6. **Sol.** On the basis of number of electrons the correct order is P > Q > R > S.

D-7. **Sol.** In $[Fe(CN)_6]^{4-}$; Fe(II) is t_{2g}^6, eg^0 due to strong ligands.

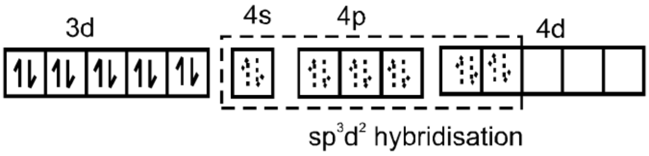
D-8. **Sol.** CN^- is strong field ligand, so $\Delta_0 > P$. Hence $K_3[Fe(CN)_6]$ has d^2sp^3 hybridisation and is diamagnetic. $K_4[Fe(CN)_6]$ has d^2sp^3 hybridisation and is paramagnetic with one unpaired electron.



D-9. **Sol.** $[FeF_6]^{3-}$ unpaired electrons = 5.



D-10. **Sol.** $[\overset{II}{Ni}(NH_3)_6]^{2+}$

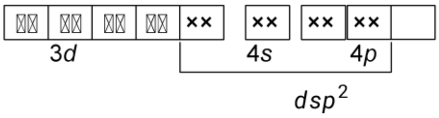


$[\overset{II}{Zn}(NH_3)_6]^{2+}$

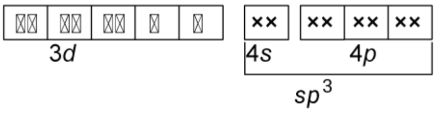
D-11._ **Sol.** (4) The number of unpaired electrons in the Complex ion $[CoF_6]^{3-}$ is 4.

D-12._ **Sol.** (3) The electronic configuration of *Ni* in $[Ni(CN)_4]^{2-}$, $[NiCl_4]^{2-}$ and $Ni(CO)_4$ are as following

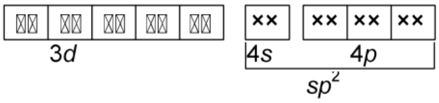
Ni^+ in $[Ni(CN)_4]^{2-}$ –



Ni^{2+} in $[Ni(Cl_4)]^{2-}$ –



Ni in $[Ni(CO)_4]$ –



CO and CN^- are strong ligands so they induces pairing of electrons so their complexes are diamagnetic while CN^- is a weak ligand so it does not induce the pairing of electrons so its complex is paramagnetic.

D-13._ **Sol.** (2) In $[Ag(NH_3)_2]Cl$, Ag^+ contains d^{10} configuration. All others contain unpaired electrons.

Section (E) : Isomerism in coordination compounds : (Structural Isomerism, Stereoisomerism, Geometrical Isomerism, Optical Isomerism)

E-1. **Sol.** Ionization isomerism arises due to the exchange of ligand(s) between ionization sphere and ionic sphere.

E-2. **Sol.** $[Cr(H_2O)_6]Cl_3$ 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.

E-3. **Sol.** 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.

E-4. **Sol.** It exists in cis and trans forms.

E-5. **Sol.** cis and trans forms both have an element of symmetry. So does not show optical activity.

E-6. **Sol.** (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 ionisation sphere.

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

(4) Br^- and SO_4^- can exchange their positions between coordination sphere and ionisation sphere. Hence it shows ionization isomerism.

E-7. **Sol.** NO_2^- is an ambidentate ligand and can link to central metal ion either through N or O. Hence it show linkage isomerism.

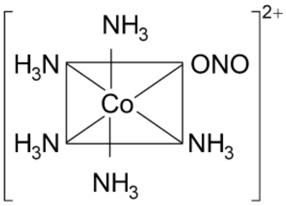
There is exchange of NO_2^- and SO_4^{2-} occurs between coordination sphere and ionization sphere. Hence it show ionisation isomerism.

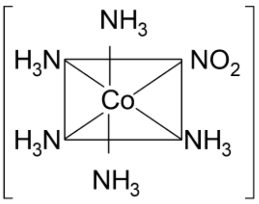
Ma_5b has only one form, therefore, it does not show geometrical isomerism.

Ma_5b has mirror plane , therefore, it does not show optical isomerism.

E-8._ **Sol.** (1) Octahedral complexes of the type $[MA_4B_2]$, $[MA_2B_4]$, $[MA_3B_3]$ exhibit geometrical isomerism.

(1) $[MA_4B_2]$, $[MA_2B_4]$, $[MA_3B_3]$ çdkj ds v"VQydh; ladqy T;kferh leko;ork n'kkZrs gSaaaA





E-10._ **Sol.** (3)

Here more than one atom function as donor, as oxygen in first one and nitrogen in second, so they show linkage isomerism

E-11._ **Sol.** (3) The two given compounds have same composition but in solution both will give different ions. The isomerism is known as ionisation isomerism.

E-12._ **Sol.** (4) Both produce different ions in solution state-

$$[Co(NH_3)_4Cl_2]NO_2 \rightleftharpoons [Co(NH_3)_4Cl_2]^+ NO_2^-$$

$$[Co(NH_3)_4Cl.NO_2]Cl \rightleftharpoons [Co(NH_3)_4Cl.NO_2]^+ + Cl^-$$

E-13._ **Sol.** (2) The compound which has same composition but give different ions in solution, show ionization. So $[Co(NH_3)_5Br]\ SO_4$ is ionization isomer.

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

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

E-15._ **Sol.** (3) $[Co(NH_3)_5NO_2]Cl_2$ will not show geometrical isomerism because this complex showed 4 and 6 co-ordination number.

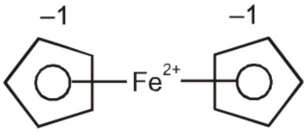
E-17._ **Sol.** (3) Geometrical isomers (cis and trans) and linkage isomers (–SCN and –NCS).

Section : (F) Organometallic Compounds

F-1. **Sol.** (1) Exists as Al^{3+} and C^{4-}
(2) Tetraethyl lead is sigma bonded organometallic compound

F-2. **Sol.** It is true.

F-3. **Sol.**



π – Complex

F-4._ **Sol.** (3) Wilkinson's catalyst is $[Rh(P.Ph_3)_3Cl]$.

Exercise-2

Marked Questions may have for Revision Questions.

OBJECTIVE QUESTIONS

3. **Sol.** Complexes having all identical ligands are called as homoleptic complexes.

5. **Sol.** 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.

6. **Sol.** 1 mole of complex X giving 2 mole of particles will be $[Cr(H_2O)_4Br_2]Cl.H_2O$ i.e $[Cr(H_2O)_4Br_2]^+ + Cl^-$
1 mole of complex Y giving 3 mole of particles will be $[Cr(H_2O)_5Cl]Br_2$ i.e $[Cr(H_2O)_5Cl]^{2+} + 2Br^-$

7. **Sol.** 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 = $(47 - 1) + 2 \times 2 = 50$.

11. **Sol.** $[Co(NH_3)_5NO_2]Cl$ and $[Co(NH_3)_5Cl]NO_2$ are ionisation isomers.
$[Co(NH_3)_5NO_2]Cl$ and $[Co(NH_3)_5(ONO)]Cl$ are linkage isomers.

13. **Sol.** From text.

14. **Sol.** (1) $[CoCl_2(OH_2)_2(NH_3)_2]Br$ and $[CoClBr(OH_2)_2(NH_3)_2]Cl$ are ionisation isomers.
(2) It is $Ma_2b_2c_2$ type.

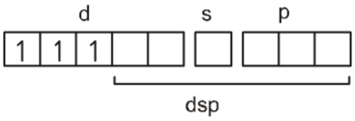
$Ma_2b_2c_2$	–	5	(aa)(bb)(cc)	(optically inactive)
			(aa)(bc)(bc)	(optically inactive)
			(bb)(ac)(ac)	(optically inactive)
			(cc)(ab)(ab)	(optically inactive)

(ab)(ac)(bc) (optically active)

15. **Sol.** In $[Co(CO)_5NH_3]^{2+}$, Co atom is attached with NH_3 by σ-bonds while CO is attached by π-bonds.

16. **Sol.** Atoms, ions or molecules having unpaired electrons are paramagnetic. In $[Cr(NH_3)_6]^{3+}$, Cr is present as Cr (III).

$Cr^{3+} = 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^3$



Number of unpaired electrons = 3, so it is paramagnetic while rest of the species are diamagnetic.

17. **Sol.** Chlorodiaquatriammine cobalt (III) chloride is $[CoCl(NH_3)_3\,(H_2O)_2]Cl_2$.

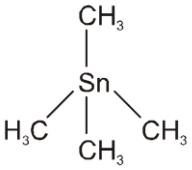
18. **Sol.** Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, is named as sodium pentacyano nitrosyl ferrate(III). In this compound, NO is present as NO^+ and Fe has +2 charge.

19. **Sol.** In complex ion $[CoF_6]^{3-}$, Co is present in + 3 oxidation state.

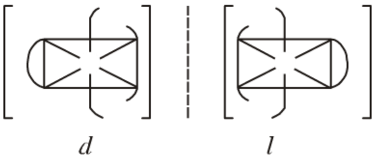
$_{27}Co = 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^7, 4s^2$

$Co^{3+} = 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^6$

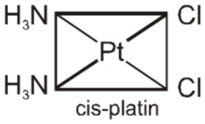
20. **Sol.** In $(CH_3)_4$ Sn (organometallic compounds of tin) single bonds are present in form of sigma bond. pi bonded organometallic compound includes organometllic compounds of alkenes, alkynes and some other carbon containing compounds having pi electrons in their molecular orbitals.



21. **Sol.** Tris-(ethylenediamine) cobalt (III) bromide $[Co(en)_3]Br_3$ exhibits optical isomerism :

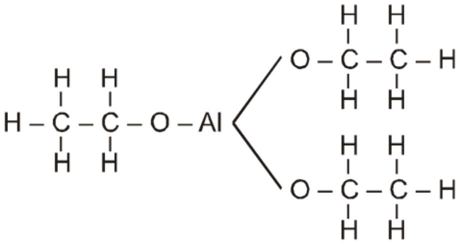


22. **Sol.** Cis-platin is the isomer of $[Pt(NH_3)_2Cl_2]$, which is used as an anticancer drug for treating several types of malignant tumours.

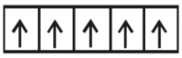


cis-platin

23. **Sol.** $Al(OC_2H_5)_3$ does not have metal-carbon bond (ie, it is not an example of organometallic compound)



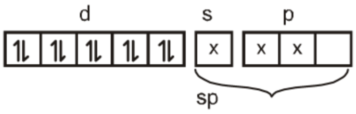
24. **Sol.** CN^- is a strong field ligand because it is an example of pseudohalide. Pseudohalide ions are stronger coordinating ligands and they have the ability to form σ and π bonds.

25. **Sol.** $_{25}Mn = 3d^5 4s^2$, $Mn^{2+} = 3d^5$ = 

In the presence of weak ligand field, there will be no pairing of electrons. It will , therefore, form high spin complex.

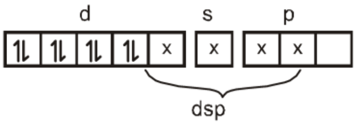
26. **Sol.** In $Ni(CO)_4$, nickel is sp^3-hybridised because in it oxidation state of Ni is zero. So, configuration of

$_{28}Ni = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8, 4s^2$



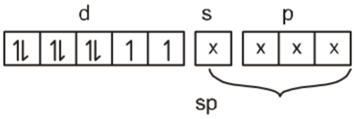
(Co is a strong field ligand, hence does pairing of electrons)

In $[Ni(CN)_4]^{2-}$, nickel is present as Ni^{2+}, so its configuration = $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8$



CN^- is strong field ligand, hece it makes Ni^{2+} electrons to be paired up.

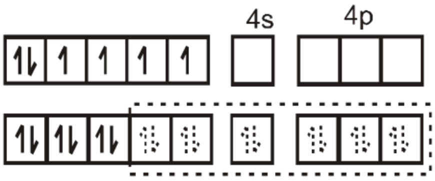
In $[NiCl_4]^{2-}$, nickel is present as Ni^{2+}, so its configuration = $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8$



Cl^- is a weak field ligand, hence in Ni^{2+} electrons are not paired.

27. **Sol.** 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.

Co^{3+},[Ar]$3d^6$



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

(inner orbital or low spin complex)

d^2sp^3 hybrid orbital

Six pairs of electrons from six NH_3 molecules.

28. **Sol.** $[Co(NH_3)_4(NO_2)_2]Cl$ & $[Co(NH_3)_4(Cl)(NO_2)]NO_2$ = ionization isomers

$[Co(NH_3)_4(NO_2)_2]Cl$ & $[Co(NH_3)_4(ONO)_2]Cl$ = linkage isomers

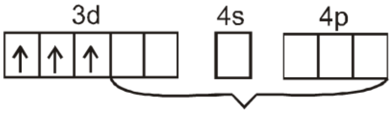
29. **Sol.** KCN first reduces cupric ions to cuprous ions which are precipitated as cuprous cyanide. This reacts with excess of CN^- to form soluble four-coordinated complex $[Cu(CN)_4]^{3-}$ which is tetrahedral in shape.

$$2Cu^{2+} + 4\,CN^- \longrightarrow 2\,Cu^+\,CN^- + \underset{\text{Cyanogen}}{(CN)_2}$$

$$CuCN + 3\,CN^- \longrightarrow [Cu(CN)_4]^{3-}$$

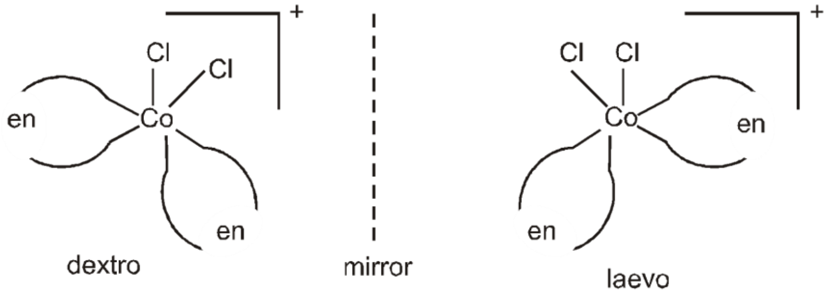
30. **Sol.** Magnetic moment = $\sqrt{n\ (n+2)}$ B.M = 3.83 B.M. (Given).

Hence, n= 3 , i.e. there are three unpaired electrons. Thus, we have



In d^2sp^3 hybridisation, the orbitals taking part are $d_{x^2-y^2}$ and d_{z^2}. Hence, unpaired electrons are present in $3d_{xy}$, $3d_{yz}$, $3d_{xz}$.

31. **Sol.**



d and l of cis-$[CoCl_2(en)_2]^+$

32. **Sol.** 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.

$[x + (0) + (0) + (0) \times 2] = +2$

$x = +2$

$Fe^{2+} = [Ar]\ 4s^0, 3d^6$ ($\because$ no unpaired electron) but, bpy, en and NH_3 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 $[Co (OX)_2 (OH)_2]^-$

$x + (-2) \times 2 + (-1) \times 2 = -1$

$x = +5$

$Co^{5+} = [Ar], 3d^4$ [4 unpaired electrons]

OX and OH are weak field ligands.

The electronic configuration of

$Ti (22) = [Ar]\ 4s^2, 3d^2$

Oxidation state of Ti in $[Ti(NH_3)_6]^{3+}$ is 3.

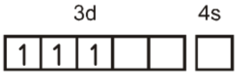
$Ti^{3+} = [Ar], 3d^1$ (one unpaired electron)

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

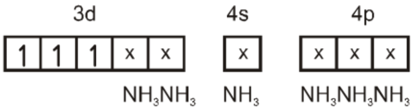
33. **Sol.** As in all the given complex the central metal atom is same and contains same number of d electrons, thus CFSE is decided by ligands. In case of strong field ligand, CFSE is maximum. CN^- is a strong field ligand, Hence, in $[Co(CN)_6]^{3-}$ CFSE is maximum.

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

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

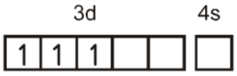


$[Cr(NH_3)_6]^{3+} = [Ar]$

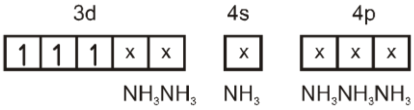


Since, this complex has three unpaired electrons, excitation of electrons is possible and thus, it is expected that this complex will absorb visible light.

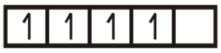
Cr^{3+} = [Ar] $3d^3$, $4s^0$



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



35. **Sol.** Due to two different Geometrical isomers.

36. **Sol.** Cr^{2+} d^4  4

Mn^{2+} d^5  5

Fe^{2+} d^6  4

Co^{2+} d^7  3

Minimum Paramagnetic behaviour = $[Co(H_2O)_6]^{2+}$

37. **Sol.**

$$[Cr(H_2O)_4Cl_2]Cl + AgNO_3 \longrightarrow \underset{\text{ppt}}{AgCl} + [Cr(H_2O)_4Cl_2]NO_3$$

mole = $0.01 \times \frac{10}{1000} = 10^{-3}$

So mole of AgCl = 0.001

38. **Sol.** $[Fe(H_2O)_6]^{3+}$

$Fe^{+2} = 3d^5$ ($t_{2g}^{1,1,1}$ $e_g^{1,1}$)

so C.F.S.E. is = $[-0.4 \times 3 + 0.6 \times 2]\, \Delta_0 = 0$

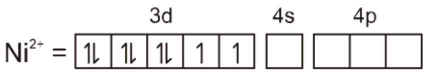
39. **Ans.** **(4)**

Sol. $CoCl_3 \cdot 3NH_3$ is $[Co(NH_3)_3Cl_3]$ so it will not ionize and does not give Cl^- ion test.

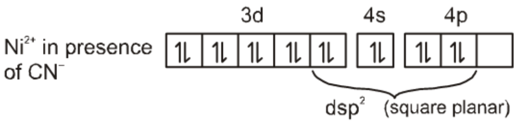
40. **Ans.** **(4)**

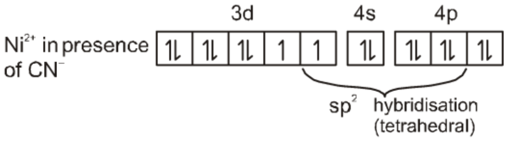
41. **Sol.** The geometry of $[Ni(CN)_4]^{2-}$ is square planar and $[NiCl_4]^{2-}$ is tetrahedral

Ni [Ar]$3d^8$ $4s^2$

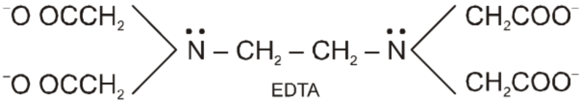


CN^- is a strong ligand (crystal field theory) hence it cause the pairing of electron in Ni^{2+} while Cl^- is a weak ligand so it does not cause pairing of electrons.





42. **Sol.** EDTA^{4-} (Ethylene diamine tetra acetate) ion has six donor atoms i.e., is a hexadentate ligand. It has four acetate ions and two nitrogen atoms which let to the formation of six coordinate bond.



43. **Sol.** In $CuSO_4 . 5H_2O$, only 4 water molecules are bonded by co-ordination bond inside co-ordination sphere i.e, $Cu[(H_2O)_4]\ SO_4 . H_2O$. Co-ordination number of copper is four.

44. **Sol.** Ionisation isomerism occurs when the counter ion in a coordination compound is itself a potential ligand and can displace a ligand which can then become the counter ion. Here exchange of SO_4^{2-} and Br^- ions take place.

45. **Sol.** EAN (effective atomic number) = Atomic number of central metal atom–oxidation number of metal + number of electron gained from ligand.

In $K_4\ [Fe(CN)_6]$ number of ligands = 6 and each ligand donates two electrons to Fe = 26 – 2 + 2 × 6 = 36.

46. **Sol.** The primary valency is ionisable valency. It corresponds to oxidation state of metal. The primary valency is always satisfied by negatively charged ion i.e. anion.

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

(1)

∴ number of primary valency is 3.

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

(2)

∴ number of primary alency is 3.

$[Co(III)(NH_3)_4Cl_2]Cl \rightarrow [Co(III)(NH_3)_4Cl_2]^{+} + Cl^-$

(3)

∴ number of primary valency is 3.

47. **Sol.** Potassium amminedicyanodioxoperoxochromate(VI)

(1) is correct answar.

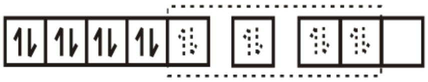
(2) is wrong because name of anionic complex ends in ate.

(3) is wrong because name of co-ordination sphere is one word.

(4) is wrong because oxidation state of Cr and its name both are wrong.

48. **Sol.** $[CuCl_2\ (CH_3NH_2)_2]$; dichlorobis(methylamine)copper(II)

49. **Sol.** $[Ni(CN)_4]^{2-}$



dsp^2 hybrid orbitals

Four pairs of electrons from four CN$^-$

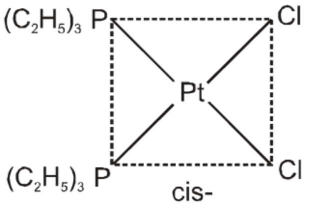
50. **Sol.** CN$^-$ ion is at the extreme right but before CO in the spectrochemical series. So it can cause maximum splitting of d-orbitals.

51. **Sol.** Effective atomic number (EAN) = 28 + 2 × 4 = 28 + 8 = 36.

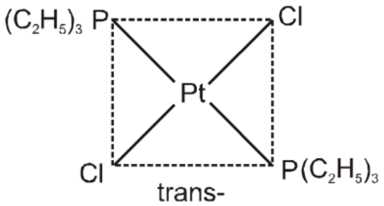
52. **Sol.** According to spectro chemical series.

53. **Sol.** $[PtCl_2\{P(C_2H_5)_3\}_2]$ is a bridged complex and shows geometrical isomerism.

Pt(II) having 5d^8 configuration is square planar and diamagnetic. It has cis-trans isomers.



cis-



trans-

54. **Sol.** On charge balancing, $[Co(III)(NH_3)_5(CO_3)]^+ + Cl^-$.

55. **Sol.** **Assertion :** I^- ion is a stronger reducing agent than Cl^- ion. It reduces Cu^{2+} to Cu^+ ion.
Reason : $[NiCl_2(PPh_3)_2]$ has tetrahedral geometry (triphenyl phosphine is a bulkier group).

Exercise-3

PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

OFFLINE JEE-MAIN

1. **Sol.** The stability of complexes increases with increase in the strength of the ligand field. The strength of ligand field according to spectrochemical series increase as given below
$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

2. **Sol.** $[Cr(NO_2)(NH_3)_5]Cl$ show linkage isomerism.

NO_2^- can bind through $^-O - N = O$ or ^-N  i.e. M—O—N=O or M—N 
$[Cr(NH_3)_5(NO_2)]Cl$ and $[Cr(NH_3)_5Cl](NO_2)$ are ionisation isomers on account of exchange of ions between two complexes.

3. **Sol.** Only primary valencies out side the coordination sphere are ionised and these react with $AgNO_3$ to give white precipitate of AgCl.

$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl] + 2Cl^- \xrightarrow{2AgNO_3} 2AgCl + 2NO_3^-$

4. **Sol.** It is a reason for given fact.

$NH_3 + H^+ \longrightarrow NH_4^+$; NH_4^+ does not act as ligand because it does not have a lone pair of electron to donate to Cu^{2+} ions to form $[Cu(NH_3)_4]^{2+}$.

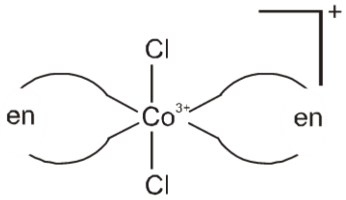
5. **Sol.** $4K^+[Ni(CN)_4]^{4-}$; let the oxidation state of nickel is x, then $x + 4(-1) = -4$
So, $x = 0$

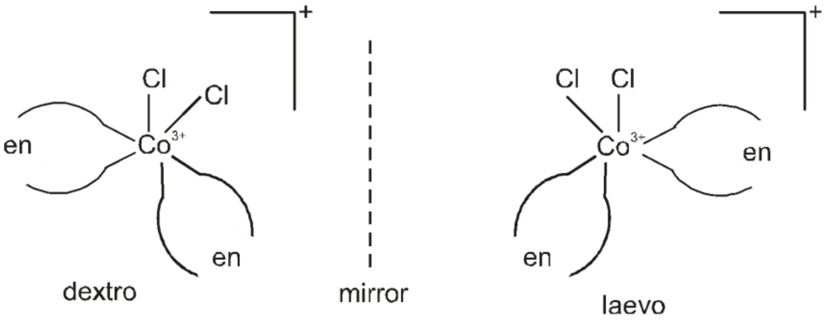
6. **Sol.** Coordination number of a central metal atom in a complex is the number of σ-bonds between metal M and ligand L.

7. **Sol.** $[Ni(NH_3)_6]^{2+}$ has sp^3d^2 hybridisation having octahedral geometry as with d^8 configuration no two empty d-orbitals are available for d^2sp^3 hybridisation. As sp^3d^2 hybridisation involves nd orbital (i.e. outer orbitals), so the complex is called as outer orbital complex.

8. **Sol.** Chlorophyll a green pigment in plants contains Mg.

9. **Sol.** (1) $[Co(en)_2Cl_2]^+$ shows geometrical as well as optical isomerism. (Only cis-form but not trans form as it has one of the symmetry elements).

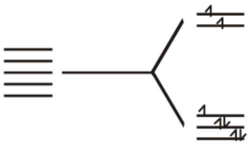




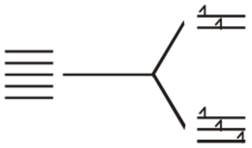
(2) It exists only in one.

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

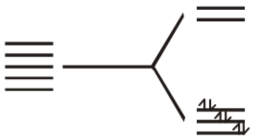
(4) Exist in cis and trans forms only (no optical isomerism because of the presence of the plane of symmetry).



10. **Sol.** (i) Co^{2+}, $3d^7$ Cl^- is weak field ligand.



(ii) Mn^{2+}, $3d^5$ Cl^- is weak field ligand.

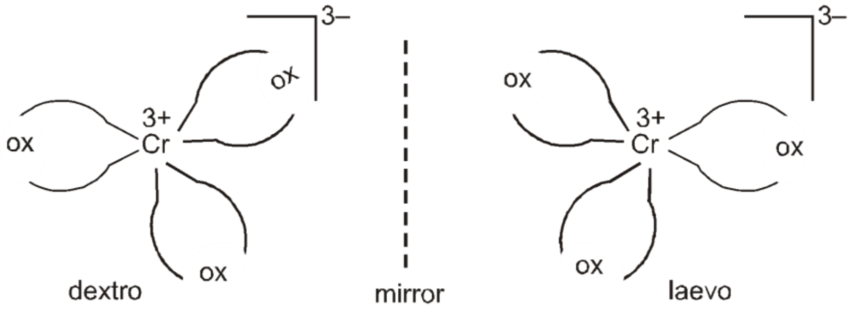


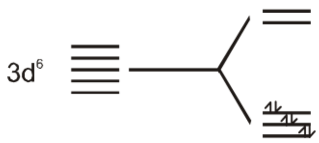
(iii) Fe^{2+}, $3d^6$ CN^- is strong field ligand so compels for pairing of electrons.

11. **Sol.** $[Cr(NH_3)_4Cl_2]^+$; let the oxidation state of Cr is x, then $x + 4(-0) + 2(-1) = +1$
So, $x = 3$

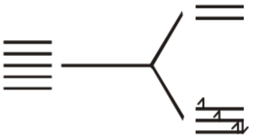
12. **Sol.** $3K^+ + [Fe(III)(CN)_6]^{3-}$ now follow IUPAC nomenclature.

13. **Sol.** (3) Due to the absence of symmetry elements it shows optical isomerism.





14. **Sol.** $[Co(CN)_6]^{3-}$; $n = 0$
CN^- is strong field ligand ; so it compels for pairing of electrons.



15. **Sol.** $3d^4$

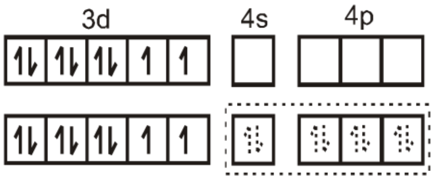
CN^- is strong field ligand ; so it compels for pairing of electrons to have two d-orbital empty.

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

16. **Sol.** If X^- is weak filed then (say Cl^-) $[Ni(Cl)_4]^{2-}$ is tetrahedral (sp^3) with two unpaired electrons. If X^- is strong field ligand then (say CN^-), $[Ni(CN)_4]^{2-}$ is square planar (dsp^2) with no unpaired electrons. Also given $[NiX_4]^{2-}$ is paramagnetic. So,

Ni^{2+}, $[Ar]3d^8$

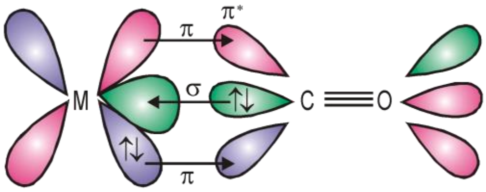
$[NiX_4]^{2-}$



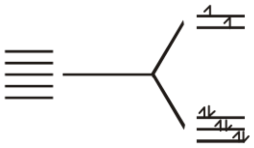
sp^3 hybrid orbitals

17. **Sol.** $[Co(II)(NO_2)(NH_3)_5]^{2+} + 2Cl^-$ and now follow IUPAC rules.

18. **Sol.** Metal-carbon bond in metal carbonyls has σ as well as π characters.



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



20. **Sol.** $3d^8$

H_2O is weak field ligand ; so it does not compel for pairing of electrons. So,

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

21. **Sol.** In 4-coordinate complex of platinum (Pt^{II}), the four ligands are arranged about the central platinum ion(II) in a square planar geometry (dsp^2) because of higher CFSE of $5d^8$ configuration.

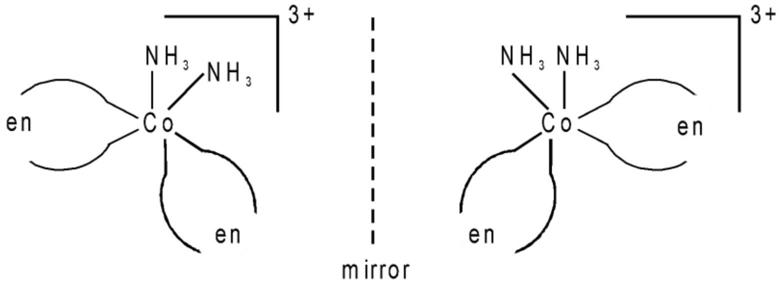
22. **Sol.** Let oxidation state of E is x so $x + (-2) + 0 = +1$ or $x = +3$

Coordination 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.

23. **Sol.** 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.

24. **Sol.** cis-form of $[Co(en)_2(NH_3)_2]^{3+}$ has optical isomers.



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

M ← SCN thiocyanato or thiocyanato-S
M ← NCS isothiocyanato or thiocyanato-N

26. **Sol.** Mole of $CoCl_3 . 6NH_3 = \frac{2.675}{267.5} = 0.01$

$AgNO_3 (aq) + Cl^- (aq) \xrightarrow{} AgCl \downarrow$ (white)

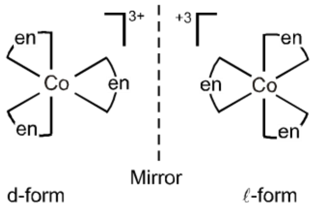
Mole of $AgCl = \frac{4.78}{143.5} = 0.03$

0.01 mole of $CoCl_3.6NH_3$ gives 0.03 mole of AgCl

∴ 1 mole of $CoCl_3 . 6NH_3$ ionises to give 3 moles of Cl^-.

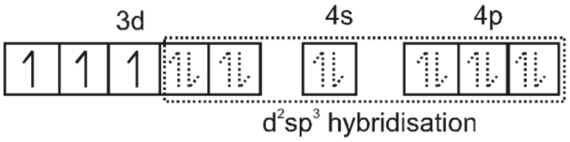
Hence the formula of compound is $[Co(NH_3)_6] Cl_3$.

27. **Sol.** Complex $[Co(en)_3]^{3+}$ lacks plane of symmertry and thus is optically active having following to enantiomeric forms.



28. **Sol.** In case of d^3 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 :

$[Cr(NH_3)_3]^{3+}$ =



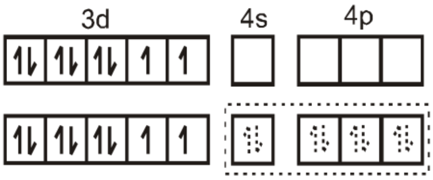
Hence the complex is inner orbital complex as it involves (n – 1) d orbitals for hybridisation,

$3.93 = \sqrt{n\ (n+2)}$; so n = 3 (here n is number of unpaired electron(s)).

29. **Sol.** In the paramagnetic and tetrahedral complex $[NiCl_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in figure.

Ni^{2+}, $[Ar]3d^8$

$[NiCl_4]^{2-}$



sp^3 hybrid orbitals

$\mu_{B.M.} = \sqrt{n\ (n+2)} = \sqrt{2\ (2+2)} = \sqrt{8} = 2.82$ BM

30. **Sol.** $[Cr(en)_2Br_2]Br$

dibromidobis(ethylenediamine)chromium(III) Bromide.

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

32. **Sol.**

	L_1	L_2	L_3	L_4
λ absorbed	red	green	yellow	blue

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

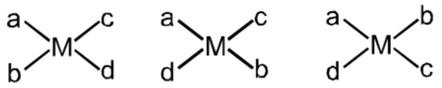
Energy : Blue (L_4) > green (L_2) > yellow (L_3) > red (L_1)

∴ $L_4 > L_2 > L_3 > L_1$ in field strength of ligands.

33. **Sol.** The complex is of the type [Mabcd]

M = metal

a, b, c, d = Monodentate ligands.



3 geometrical isomers

34. **Sol.** Each $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ contain 4 unpaired electron.

35. **Sol.** With coordination number six, if two bidentate ligands in *cis*-position are present, then it is optically active.

36. **Sol.** 10 millimoles of

Complex or 0.01 mol

1.2 ×10^{22} ions $= \dfrac{1.2\times10^{22}}{6\times10^{23}}$ mol or 0.02 mol

$$\left[Co\left(H_2O\right)_5 Cl\right]Cl_2.H_2O \xrightarrow{+AgNO_3\,(excess)} 2\ AgCl\downarrow$$

0.01 mol 0.02 mol

ONLINE JEE-MAIN

9. **Sol.** (a) does not show G.I.(b) and (c) show G.I.but all isomers are optically inactive.

10. **Sol.** CH_4 does not have lone pair.

11. **Sol.** (1) Fe^{3+} (d^5) → t_{2g}^3, e_g^2 (symmetrically filled) (2) Mn^{2+}(d^5) → t_{2g}^5, e_g^0 (t_{2g} unsymmetrically filled)

(3) Co^{3+}(d^6) → t_{2g}^4, e_g^2 (non-unsymmetrical) (4) Co^{2+}(d^7) → t_{2g}^6, e_g^1 (non-symmetrical)

12. **Sol.** $\Delta_o \propto$ CFSE (Crystal field stabilization energy)

Δ_o of $[Cr(H_2O)_6]^{2+} < \Delta_o$ of $[Mo(H_2O)_6]^{2+}$

Because here Δ_o depends on Z_{eff} & Z_{eff} of 4d series is more than 3d series.

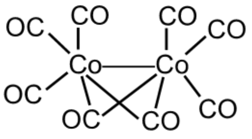
But Δ_o of $[Ti(H_2O)_6]^{3+} > \Delta_o$ of $[Ti(H_2O)_6]^{2+}$

13. **Sol.** Complex $[Cr(H_2O)_6]Cl_3$ will consume more equivalents of aqueous solution of $Ag(NO_3)$.

14. **Sol.** Complex having only 1 type of ligands are examples of homoleptic complex.

15. **Sol.** In PF_5 hybridisation is sp^3d.

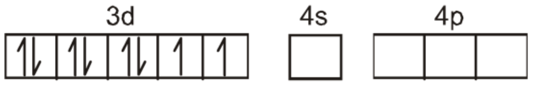
16. **Sol.**



PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

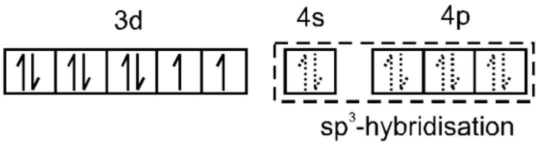
1. **Sol.** In $[NiCl_4]^{2-}$, the Ni is in +2 oxidation state.

Ni^{2+}

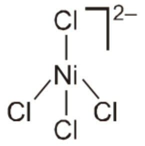


Cl^- is a weak field ligand. So,

$[Ni(Cl)_4]^{2-}$



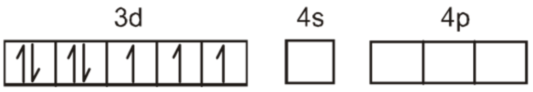
Hence the shape is tetrahedral and complex is paramagnetic with two unpaired electrons.



$[PdCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$ are square planar.

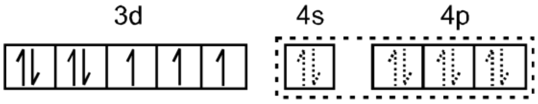
2. **Sol.** In the complex Hg $[Co(SCN)_4]^{2-}$ cobalt is in +2 oxidation state. So

Co^{2+}



SCN^- is weak field ligand so,

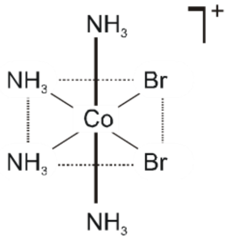
$[Co(SCN)_4]^{2-}$



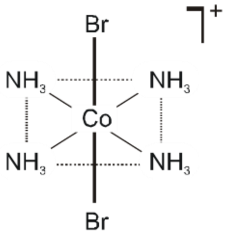
As it contains three unpaired electrons, so μ = = .

3. **Sol.** **(A)** Br^- and Cl^- can be exchanged between coordination and ionization spheres, thus show ionisation isomerism. Show geometrical isomerism (as it is Ma_4b_2 type) but not optical isomerism due to the presence of one of the symmetry of elements.

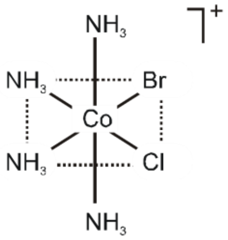
Each complex has one cis- and one trans- isomers.



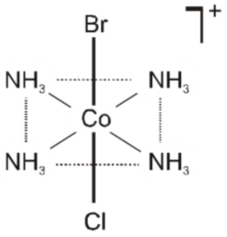
cis-



trans-

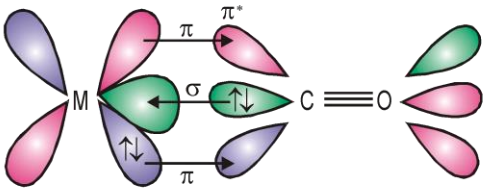


cis-



trans-

4. **Sol.** On account of synergic interaction between metal and CO bond order of CO reduces to approximately two and half from three in carbonmonoxide. Thus bond length increases to 1.158 Å.

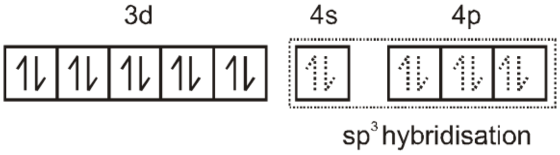


5. **Sol.** As formal negative charge increases on the complex the tendency of π back bonding between metal ion and CO increases and thus the bond order of CO decreases. Hence the CO bond order is lowest in $[V(CO)_6]^-$.

6. **Sol.** The IUPAC name of $[Ni(NH_3)_4]^{2+}$ $[NiCl_4]^{2-}$ is Tetraamminenickel(II) tetrachloronickelate (II).

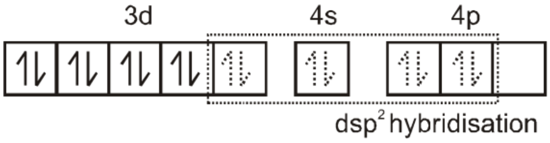
7. **Sol.** Ni (28) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8, 4s^2$

In $[Ni(CO)_4]$, Ni is in zero oxidation state and CO being strong field ligand compels for paring of electrons.



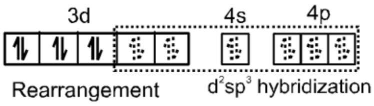
So, $[Ni(CO)_4]$

In $[Ni(CN)_4]^{2-}$, Ni is in +2 oxidation state and CN^- being strong field ligand compels for paring of electrons.



So, $[Ni(CN_4]^{2-}$

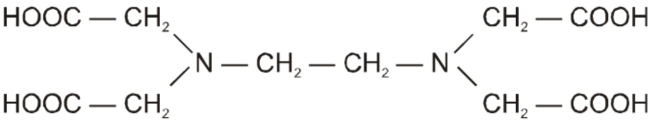
8. **Sol.** The chromium is in zero oxidation state having configuration $[Ar]^{18}\ 3d^5\ 4s^1$. The CO is a strong field ligand so compels for the pairing of electrons. Thus the complex has d^2sp^3 hybridisation and is diamagnetic.



$[Cr(CO)_6]$

$\mu_{BM} = \sqrt{n(n+2)}$ = 0 as there is no unpaired electrons.

9. **Sol.** Structure of EDTA is :



10. **Sol.** The ionisation isomer for the given compound will be obtained by exchanging ligand with counter ion as

$[Co(H_2O)_4Cl_2](NO_2)$.

11. **Sol.** Ni : $3d^8\ 4s^2$

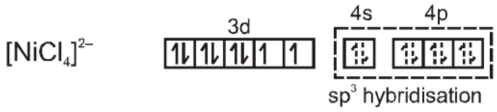
Ni^{2+}, $3d^8$

since Cl is a weak field ligand, so it will not cause a paring of electron.

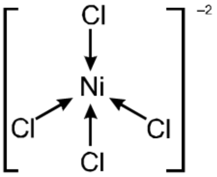
N = 2 = $\sqrt{N(N+2)}$ = $\sqrt{2(2+2)}$ B.M. = $\sqrt{8}$ B.M. = 2.82 B.M.

12. **Sol.** $Ni^{2+}(aq) + 4Cl^{-}(aq) \longrightarrow [NiCl_4]^{2-}(aq)$

$[NiCl_4]^{2-}$; $3d^8$ electron configuration with nickel in + 2 oxidation state. Cl^- being weak field ligand does not compel for pairing of electrons. So,

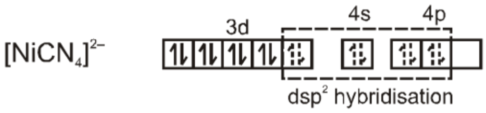


Hence, complex has tetrahedral geometry.

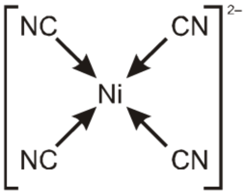


Ni^{2+} (aq) + $4CN^-$ (aq) $\longrightarrow$ $[Ni(CN)_4]^{2-}$ (aq)

$[Ni(CN)_4]^{2-}$; $3d^8$ electron configuration with nickel in + 2 oxidation state. CN^- being strong field ligand compels for pairing of electrons. So,

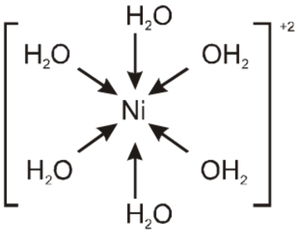


Hence, complex has square planar geometry.



Ni^{2+} (aq) + $6H_2O$ (ℓ) $\longrightarrow$ $[Ni(H_2O)_6]^{2+}$ (aq)

$[Ni(H_2O)_6]^{2+}$; $3d^8$ configuration with nickel in + 2 oxidation state. As with $3d^8$ configuration, two d-orbitals are not available for d^2sp^3 hybridisation. So, hybridisation of Ni (II) is sp^3d^2 and Ni (II) with six co-ordination number will have octahedral geometry.



Note : With water as ligand Ni (II) forms octahedral complex.

13. **Sol.** K–$[Fe(CN)_6]^{3-}$: $3d^5$ electron configuration after pairing of electrons for d^2sp^3 hybridisation it contains one unapaired electrons.

L–$[Co(NH_3)_6]^{3+}$: $3d^6$ electron configuration, d^2sp^3, diamagnetic.

M–$[Co(ox)_3]^{3-}$: $3d^6$ electron configuration, d^2sp^3, diamagnetic.

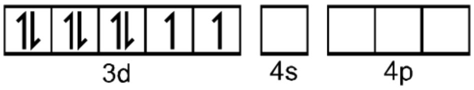
N–$[Ni(H_2O)_6]^{2+}$: $3d^8$ electron configuration, sp^3d^2, with two unpaired electrons paramagnetic.

O–$[Pt(CN)_4]^{2-}$: $5d^8$ electron configuration, dsp^2, diamagnetic.

P–$[Zn(H_2O)_6]^{2+}$: $3d^{10}$ electron configuration, sp^3d^2, diamagnetic.

14. **Sol.** $[Co(H_2O)_4(NH_3)_2]Cl_3$ = diamminetetraaquacobalt (III) chloride

15. **Sol.** $[NiCl_2 \{PEt_2Ph\}]$ contains Ni^{2+} with electronic configuration



Ni^{2+} = [Ar] $3d^84s^0$

In high spin state, it is paramagnetic, sp^3 hybridised, tetrahedral.

In low spin state, it is diamagnetic, dsp^2, square planar.

16. **Sol.** **P = $[FeF_6]^{3-}$** ox. no. of Fe = +3 , configuration : - $3d^5\ 4s^0$

As F^- is weak ligand, pairing does not take place.

so it has 5 unpaired electron

Q = $[V(H_2O)_6]^{2+}$ ox. no. of V = + 2, configuration $3d^3\ 4s^0$

It has 3 unpaired electrons.

R = $[Fe(H_2O)_6]^{2+}$, ox. no. of Fe = +2, configuration $3d^6$, $4s^0$

As H_2O is weak ligand, pairing does not take place, so it has 4 unpaired electron

$\Rightarrow$ order of spin only magnetic moment $\Rightarrow$ $Q < R < P$

so, answer is (B).

17.

Sol. (P) $[Cr(NH_3)_4Cl_2]Cl$ → Cr^{+3} is d^3. It is paramagnetic and it shows cis-trans isomerism.

(Q) $[Ti(H_2O)_5Cl](NO_3)_2$ → Ti^{+3} is d^1. It is paramagnetic and it show ionisation isomerism.

(R) $[Pt(en)(NH_3)Cl]NO_3$ → Pt^{+2} is d^8. But this complex is square planar and all electron are paired. So it is diamagnatic. It exhibit ionisation isomerism.

(S) $[Co(NH_3)_4(NO_3)_2]NO_3$ → Co^{+3} is d^6. Since ligands are strong, so electron are paired. it is diamagnetic. It exhibit cis-trans isomerism.

Ans. is (B).

18.

Sol.

$[Ni(CO)_4]$	$3d^{10}$, sp^3	0 unpaired electron
$[NiCl_4]^{2-}$	$3d^8$, sp^3	2
$[Co(NH_3)_4Cl_2]Cl$	$3d^6$, d^2sp^3	0
$Na_3[CoF_6]$	$3d^6$, sp^3d^2	4
Na_2O_2	O_2^{2-}	0
CsO_2	O_2^{-1}	1

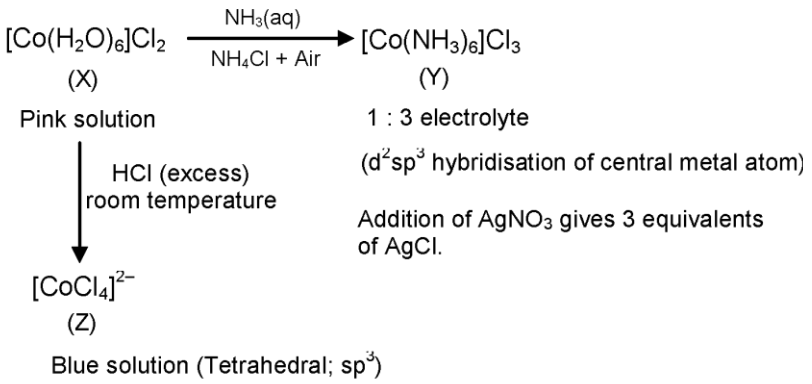
19. **Sol.** Ni^{2+} with NH_3 shows CN=6 forming $[Ni(NH_3)_6]^{2+}$ (Octahedral)

Pt^{2+} with NH_3 shows CN = 4 forming $[Pt(NH_3)_4]^{2+}$ (5d series CMA, square planner)

Zn^{2+} with NH_3 shows CN = 4 forming $[Zn(NH_3)_4]^{2+}$ ($3d^{10}$ configuration, tetrahedral)

20. **Ans.** **(ACD)**

Sol.



X & Z in equilibrium at 0°C ⇒ Then equilibrium is shifted towards X, making colour of solution pink

APSP Solutions

PART - I

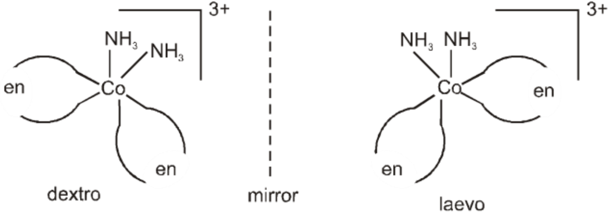
1. Let x be the oxidation state of nickel then,
(1) $Ni(CO)_4$; x + 4 (0) = 0 or x = 0; (2) $[NiF_6]^{2-}$; x + 6 (–1) = – 2 or x = +4;
(3) $[Ni(NH_3)_6]^{2+}$; x + 4 (0) = +2 or x = +2; (4) $[Ni(CN)_6]^{4-}$; x + 6 (–1) = –4 or x = + 2.

3. $2K^+[Cr(\overset{-2}{CN})_2\overset{-2}{O_2}(\overset{-4}{O})_2(\overset{0}{NH_3})]^{2-}$

Oxidation state of chromium = x + 2(– 1) + (– 2) + 2(– 2) + (0) = – 2.
∴ x = + 6.
As per IUPAC name.
Complex is anionic, so metal ion will be named as chromate with +6 oxidation state. So, potassium amminedicyanodioxoperoxochromate(VI).

4. $[Mn(H_2O)_6]^{2+} = 3 \times (-0.4) + 2 \times (0.6) = 0$
$[Cr(H_2O)_6]^{2+} = 3 \times (-0.4) + 1 \times (0.6) = 0.6\ \Delta_0$
$[Mn(H_2O)_6]^{3+} = 3 \times (-0.4) + 1 \times (0.6) = 0.6\ \Delta_0$
$[Cr(H_2O)_6]^{3+} = 3 \times (-0.4) + 0 \times (0.6) = 1.2\ \Delta_0$

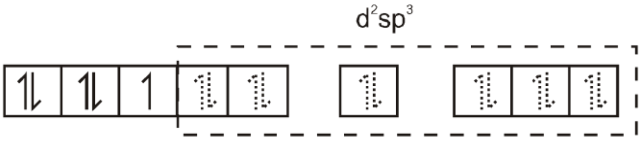
5. (1) trans$[Co(NH_3)_4Cl_2]^+$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.
(2) $[Cr(H_2O)_6]^{3+}$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.
(3) (3) cis$[Co(NH_3)_2(en)_2]^{3+}$ lacks one of the symmetry elements.



(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.

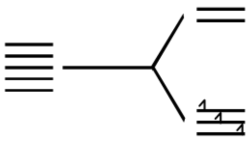
6. NO_2^- is an ambidentate ligand and can link to central metal ion either through N or O. Hence it show linkage isomerism.
There is exchange of NO_2^- and SO_4^{2-} occurs between coordination sphere and ionization sphere. Hence it shows ionisation isomerism.
Ma_5b has only one form, therefore, it does not show geometrical isomerism.
Ma_5b has mirror plane, therefore, it does not show optical isomerism.

7. $[\overset{I}{Cr}(\overset{0}{NH_3})(\overset{-4}{CN})_4(\overset{+1}{NO})]^{2-}$



Central metal ion has one unpaired electron and thus d-d transition of electron is possible. This attributes to the colour of the solution. As different types of ligands are attached to central metal ion, the complex is called heteroleptic complex.

8. S_1 : Cr^{3+}



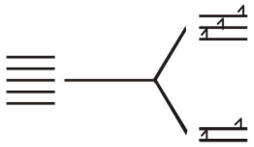
CFSE = 3 × – 0.4 = – 1.2 Δ_0, hybridisation is d^2sp^3 (NH_3 is strong field ligand)
S_2 : Fe^{3+}, $3d^5$ - one unpaired electron after pairing (CN^- is stronger field ligand)
∴ $\mu = \sqrt{1\ \ (1+2)} \approx 1.73$ BM

S_3 : $[\overset{II}{Fe}(\overset{-5}{CN})_5\overset{+}{NO}]^{2-}$ and $[\overset{II}{Fe}(\overset{-5}{CN})_5NOS^{-1}]^{4-}$.

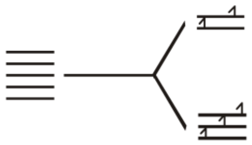
In reactant and product, the iron is in same oxidation state i.e. +2.

9. (1) Pt(+II) and Au(+III) with $5d^8$ configuration have greater CFSE and thus favours square planar geometry (i.e. dsp^2 hybridisation) with weak as well as strong field ligands.

(2) In tetrahedral complex, the t_{2g} orbitals are nearer to the direction of the ligands. Hence they have higher energies than that of e_g orbitals (for detail refer text).



(3) $3d^5$, ; CFSE (weak filed ligands) = $-0.6 \times 2 + 0.4 \times 3 = 0\ \Delta_t$



$3d^5$, ; CFSE (weak filed ligands) = $-0.4 \times 3 + 0.6 \times 2 = 0\ \Delta_0$.

Similarly for d^0 and d^{10} configurations the CFSE is zero in both octahedral and tetrahedral complexes with weak field ligands.

10. $[CoCl_2(en)_2]Cl$, One mole complex contains, one mole of ionisable Cl^-.

One mole of complex = one mole of Cl^-.

$\therefore$ One mole of AgCl = One mole of complex = $\frac{100 \times 0.024}{1000}$ = 0.0024.

11. $[\overset{II}{Fe}(H_2O)_6]^{2+}$ n = 4 and $\mu = 4.91$

$[\overset{II}{Fe}(CN)_6]^{4-}$ n = 0 and $\mu = 0$

13. $[Ni(H_2O)_4]SO_4 + \text{Pyridine} + NaNO_2 \longrightarrow [Ni(Py)_4](NO_2)_2$

Stronger ligand, pyridine displaces weaker ligand, H_2O in aqueous solution.

$[Ni(py)_4](NO_2)_2$ is formed as dark blue crystals on crystallisation.

16. $2X + 1(-2) + 1(-1) = +3$; $x = \frac{6}{2} = +3$.

18. (1) $[Cr(NH_3)_6]^{3+}\ [Cr(NO_2)_6]^{3-}$ and $[Cr(NH_3)_4(NO_2)_2]^+\ [Cr(NH_3)_2(NO_2)_4]^-$ have same number of ions, so cryoscopic method can not be used.

(2) Molar conductance depends on the number of ions as well as on the charge on the complexes. $[Cr(NH_3)_6]^{3+}\ [Cr(NO_2)_6]^{3-}$ and $[Cr(NH_3)_4(NO_2)_2]^+\ [Cr(NH_3)_2(NO_2)_4]^-$ have same number of ions but different electrical charges.

(3) Both complexes have same number of unpaired electrons, so measuring magnetic moments methods can not be used.

(4) They have similar colour because of the similar conditions.

19. $[Fe(en)_2(H_2O)_2]^{2+} + en \rightarrow [Fe(en)_3]^{2+} + 2H_2O$

Complex is $[Fe(en)_3]^{2+}$. 'en' is a strong field ligand and thus it is inner orbital complex ($d^2\,sp^3$) and diamagnetic.

It is $M(AA)_3$ type which has only one form.

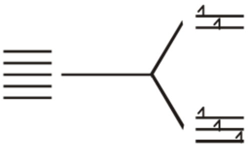
20. (1) Cr^{3+}, $3d^3$; sp^3d^2 hybridisation with three unpaired electrons (weak field as well as strong field ligand). Fe^+ , $3d^7$; sp^3d^2 hybridisation with three unpaired electron (one 4s electron jumps to 3d orbital for the pairing)

(2) Mn^{2+}, $3d^5$; d^2sp^3 hybridisation with one unpaired electron after pairing (CN^- is strong field ligand).

Fe^{3+}, $3d^5$; d^2sp^3 hybridisation with one unpaired electron after pairing (CN^- is strong field ligand).

(3) Ni, $3d^8$ $4s^2$; sp^3 hybridisation and all electrons are paired because CO is strong field ligand (4s-electrons jumps to 3d-orbitals for the pairing)
Zn^{2+}, $3d^{10}$; sp^3 hybridisation and all electrons are paired.

21. $[Fe(SCN)(H_2O)_5]^{2+} \xrightarrow{F^-} \underset{\text{colourless}}{[FeF_6]^{3-}}$, F^- being weak ligand Fe^{3+}— .



Therefore, five unpaired electrons and so $\mu = \sqrt{5\ \ (5+2)}$ B.M. ≈ 5.92.

22. In $Fe(CO)_5$, Fe in zero oxidation state and CO is stronger field ligand. So,

$Fe(CO)_5$

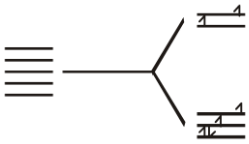
Hence it is diamagnetic and low spin complex.

23. The crystal field-splitting for Cr^{3+} ion in octahedral field increases with increasing strength of ligands. This order given in (1) is according to spectrochemical series.

25. Chelate complex has higher stability than the similar complexes having monodentate ligands and an higher stability means higher overall formation constant.

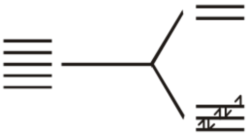
26. In $Fe(CO)_5$, Fe is dsp^3 hybridised. Hence, its structure is trigonal bipyramidal.

27. (I) $[Fe(H_2O)_6]^{2+}$, $3d^6$



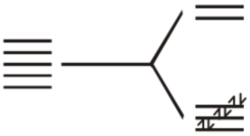
n = 4 (weak field ligand)

(II) $[Fe(CN)_6]^{3-}$, $3d^5$



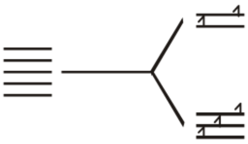
n = 1 (strong field ligand)

(III) $[Fe(CN)_6]^{4-}$, $3d^6$



n = 0 (strong field ligand)

(IV) $[Fe(H_2O)_6]^{3-}$, $3d^5$



n = 5 (weak field ligand)

28. $[Ni(CO)_4] = sp^3$; $[Ni(CN)_4]^{2-} = dsp^2$; $[Fe(CN)_6]^{4-} = d^2sp^3$; $[MnF_6]^{4-} = sp^3d^2$.

29. (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 ionisation sphere.
(3) No anionic ligand is present in coordination sphere for the exchange with Cl^- ions present in ionisation sphere.
(4) Br^- and SO_4^- can exchange their positions between coordination sphere and ionisation sphere. Hence it shows ionization isomerism.

30. Coordination number of nickel in $[Ni(C_2O_4)_3]^{4-}$ is 6 because $C_2O^{2-}{}_4$ is a bidentate ligand.

PART - II

1. $PtCl_4.2KCl \equiv K_2[PtCl_6] \xrightleftharpoons{aq.} 2K^+ + [PtCl_6]^{2-}$.

So, it has three ions per formula unit. The Cl^- is present in coordination sphere so it will not give white precipitate with silver nitrate solution. So in the compound the coordination number of platinum is 6.

2. $[Cr(H_2O)_6]Cl_3 \xrightleftharpoons{aq.} [Cr(H_2O)_6]^{3+}$ (aq) + $3Cl^-$ (aq).

Cl^- present in ionisation sphere will give precipitate with $AgNO_3$.

$$3Cl^- + 3Ag^+ \longrightarrow 3AgCl$$

So, one mole of complex will give three moles of AgCl precipitate.

3. $PtCl_4.4NH_3 \equiv [Pt(NH_3)_4Cl_2]Cl_2 \xrightleftharpoons{aq.} [Pt(NH_3)_4Cl_2]^{2+}$ (aq) + $2Cl^-$ (aq).

$2Ag^+ + 2Cl^- \longrightarrow 2AgCl \downarrow$ (white)

Concentrated H_2SO_4 will not dehydrate the following complex.

4. $K \propto$ stability.

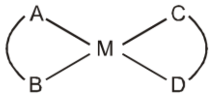
5. $X + 3(-1) = 1 \therefore X = +2$.

6. 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.

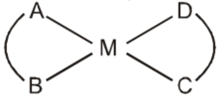
8. More spliting energy ($\Delta_0\uparrow$) requires $\lambda\downarrow$ and appeared colour will have $\lambda\uparrow$.

9. According to Werner's theory statements (b) and (c) are correct.
(a) Ligands are connected to the metal ion by coordinate covalent bond (dative bond).
(b) Secondary valencies i.e. coordination number give rise to stereochemistry of the complexes because of their directional properties.
(c) Secondary valencies correspond to coordination number i.e. number of σ-bonds between metal ion and lignds.

11. Ma_3b, Ma_4 and $M(AA)_2$ (symmetrical bidentate ligand) have only one form; they does not show geometrical isomerism. But M(AB)(CD) shows two geometrical isomerism.



ATD

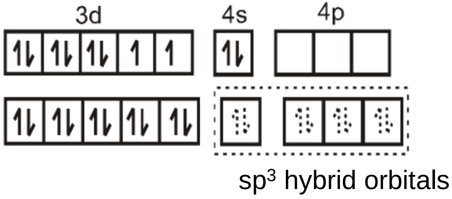


ATC

12. (a) cis-$[Co(NH_3)_4Cl_2]^+$ has plane of symmetry as well as centre of symmetry; so optically inactive.
(b) trans-$[Co(en)_2Cl_2]^+$ has plane of symmetry as well as centre of symmetry; so optically inactive.
(c) cis-$[Co(en)_2Cl_2]^+$ lacks plane of symmetry as well as centre of symmetry; so optically active.
(d) $[Co(en)_3]^{3+}$ lacks axis of internal rotation; so optically active.

13. It is not correct formula because the Fe is in +3 oxidation state and as such formula should be $[Fe^{3+}(CN)_6]^{3-}$ or $K_3[Fe(CN)_6]$.

14. In complex nickel is in zero oxidation state. The CO is strong field ligand and therefore compels for the pairing of electrons. The hybridisation scheme is as shown in figure.



$Ni^0([Ar]\ 3d^8\ 4s^2)$

$[Ni(CO)_4]$

Four pairs of electrons from four CO.

It is tetrahedral and as all electrons are paired so diamagnetic.

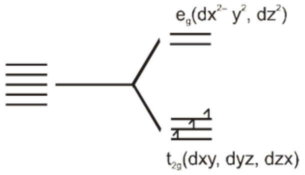
15. (1) is π-bonded organometallic compounds as this involve the formation of π-bonds between metal and carbon.
(2) and (3) are σ-bonded organometallic compounds as they only form σ bond by sharing of electrons between metal and carbon.

16. mole of complex = 50 × 0.2 = 0.01 and mole of AgCl = $\frac{1.435}{143.5}$ = 0.01 ; n Ag^+ = n Cl^-
∴ 1 mole complex = 1 mole AgCl

17. $[Cu(CN)_4]^{3-}$, $[Ar]^{18}3d^{10}$; As there is no empty d-orbital for dsp^2 hybridization. So it has sp^3 hybridization and is tetrahedral, and diamagnetic.

18. 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–Cπ bonding is enhanced and the C–O bond is diminished in strength.

19. (1) The $3d^3$ electron configuration always have three unpaired electrons with weak field as well as strong field ligands.



(2) $3d^3$
(3) H_2O being neutral molecule satisfies only secondary valencies.

20. $[NiF_6]^{2-}$ oxidation number = +4
$t_{2g}^{2,2,2}\ eg^{0,0}$ (pairing occur due to high oxidation number of Ni).