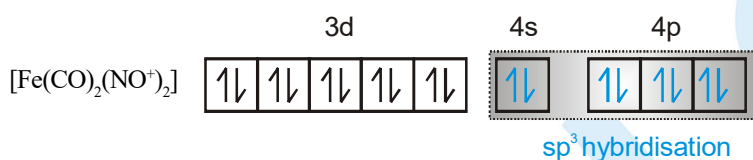


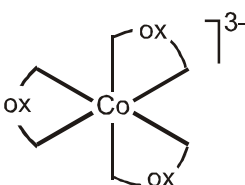
HINTS & SOLUTIONS

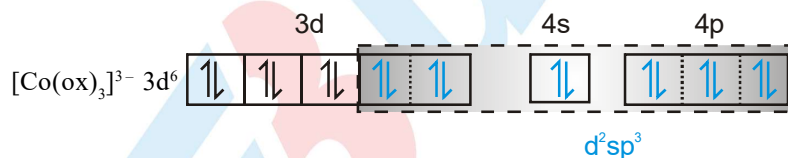
EXERCISE - 1

Single Choice

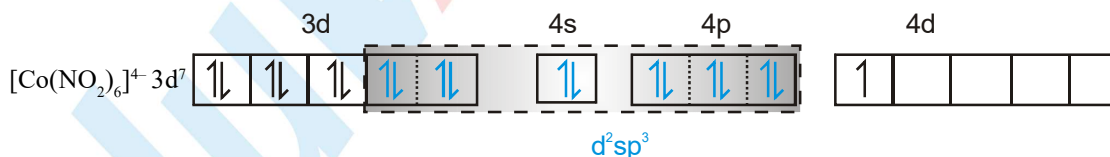
1. (A) $[\text{Fe}(\text{en})_3]^{3+}$ - d^2sp^3 with one unpaired electron. 'en' is a strong field chelating ligand and thus compels for the pairing of electrons to have d^2sp^3 hybridisation. It is paramagnetic with one unpaired electron (valence shell electron configuration, $3d^5$)
- (B) $[\text{FeCl}_4]^{2-}$ - sp^3 with four unpaired electrons. It is paramagnetic with four unpaired electrons (valence shell electron configuration, $3d^6$).
- (C) $[\text{Fe}(\text{CN})_6]^{3-}$ - 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, $3d^5$)
- (D) $[\text{Fe}(\text{CO})_2(\text{NO}^+)_2]$ - sp^3 and diamagnetic. Iron is in $-II$ oxidation state. So,



5. S1 :  chelate complex, diamagnetic and has d^2sp^3 hybridisation.



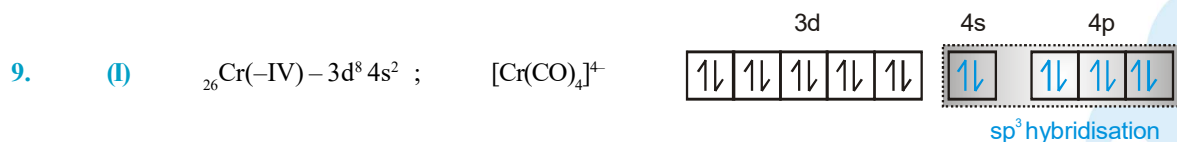
- S2 : NO_2^- is strong field ligand and thus it is inner orbital complex and paramagnetic with one unpaired electron present in higher $4d$ -orbital



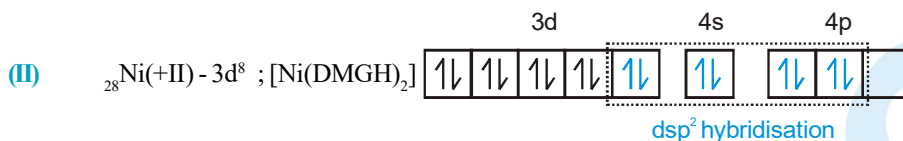
- S3 : $5d^8$ configuration; thus diamagnetic and dsp^2 hybridisation ($5d^8$ has higher CFSE so that $\Delta_o > p$)

7. (I) It is tetrahedral (sp^3) because there is no $(n-1)d$ orbital vacant for dsp^2 hybridisation.
- (II) Ag with +3 oxidation state and $4d^8$ configuration has square planar geometry.
- (III) It is tetrahedral (sp^3) because there is no $(n-1)d$ orbital vacant for dsp^2 hybridisation.
- (IV) Pt with +2 oxidation state and $5d^8$ configuration has square planar geometry.
- (V) Rh with +1 oxidation state and $4d^8$ configuration has square planar geometry.

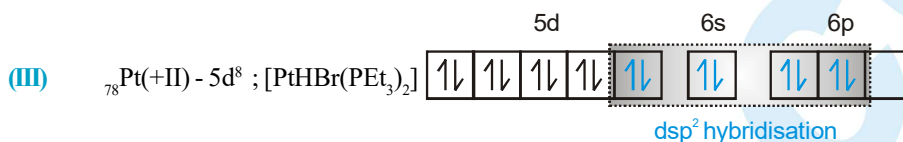
When we place these complexes in a magnetic balance, then there is decrease in their weights. This indicates that the complexes are diamagnetic.



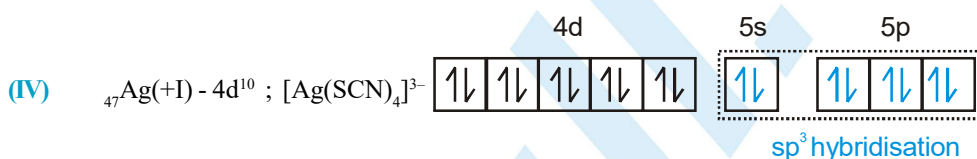
CO is strong field ligand; so complex is diamagnetic and tetrahedral.



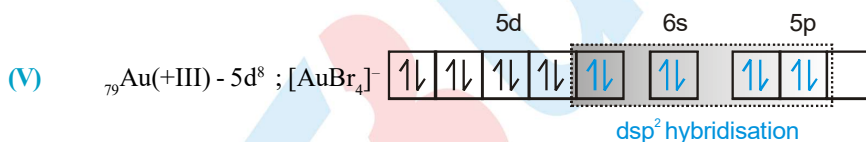
DMGH is a chelating ligand; so complex is diamagnetic and square planar.



5d⁸ configuration has greater CFSE, so complex is diamagnetic and square planar.

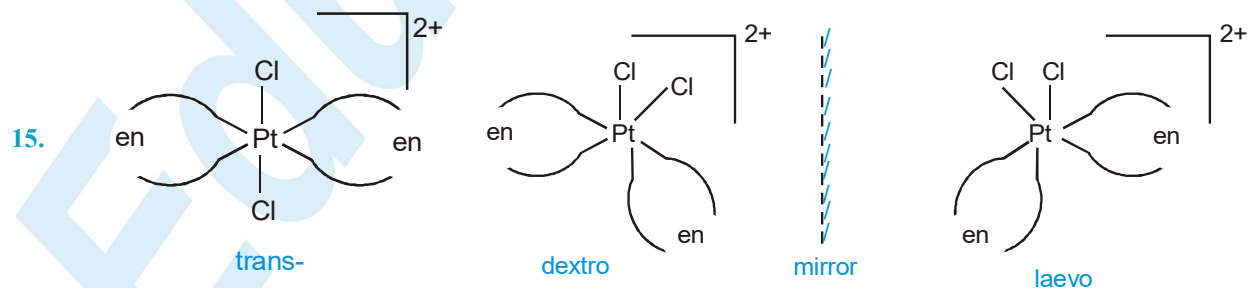


No empty d-orbital is available for dsp² hybridisation and SCN⁻ is weak field ligand, so complex is tetrahedral and diamagnetic.



5d⁸ configuration has greater CFSE, so complex is diamagnetic and square planar.

11. (1) cis - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has plane of symmetry as well as centre of symmetry ; so optically inactive.
 (2) trans - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ has plane of symmetry as well as centre of symmetry ; so optically inactive.
 (3) cis - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ lacks plane of symmetry as well as centre of symmetry ; so optically active.
 (4) $[\text{Co}(\text{en})_3]^{3+}$ lacks axis of internal rotation ; so optically active.

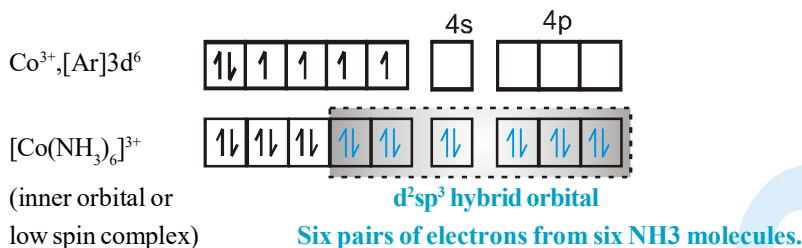


As trans isomer has symmetry elements it does not show optical isomerism.

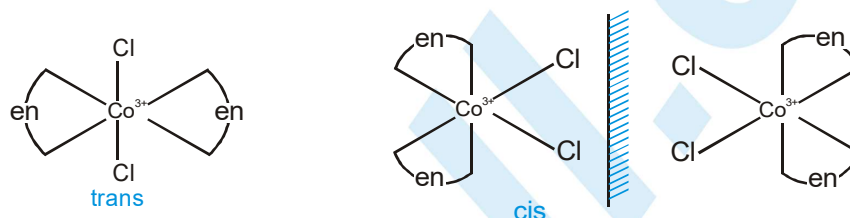
(A), (C) and (D) are correct statements.

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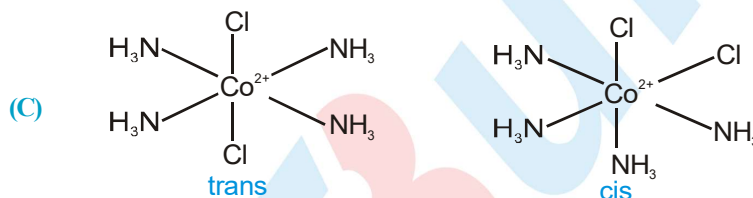
16. (A) Because of $3d^{10}$ configuration no $(n-1)d$ orbital is available for d^2sp^3 hybridisation and thus forms outer orbital complex. The complex is diamagnetic.
- (B) Because of $3d^8$ configuration no $(n-1)d$ orbital is available for d^2sp^3 hybridisation and thus forms outer orbital complex. The complex is paramagnetic with two unpaired electrons.
- (C) The complex is inner orbital complex but $3d^3$ configuration has three unpaired electrons with weak as well as with strong field ligand.
- (D) In the diamagnetic octahedral complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.



17. (A) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ show geometrical isomerism and its only cis-form show optical isomerism.

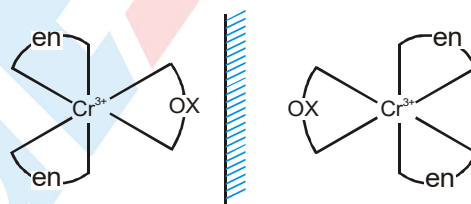


- (B) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ exists only in one form.



It does not show optical isomerism because of the presence of plane of symmetry and centre of symmetry.

- (D) $[\text{Cr}(\text{OX})_3]^{3-}$ shows optical isomerism but does not show geometrical isomerism because of the same type of ligands.



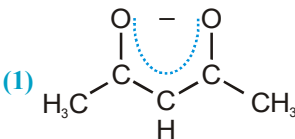
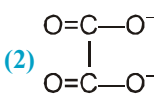
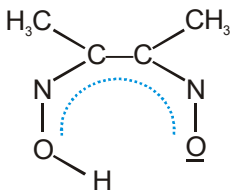
20. As +ve charge on the central metal atom increases, the less readily the metal can donate electron density into the π^* orbitals of CO ligand to weaken the C – O bond.

Hence order of C – O bond strength is : $[\text{Mn}(\text{CO})_6]^+ > [\text{Cr}(\text{CO})_6] > [\text{V}(\text{CO})_6]^- > [\text{Ti}(\text{CO})_6]^{2-}$.

22. (A) If $[\text{Os}(\text{Cl})_5\text{N}]^{2-}$, complex is anion, so name of the element should be osmate (VI).
- (C) If $[\text{Os}(\text{Cl})_5\text{N}_3]^{0}$, complex is neutral, so name of the element should be osmium (VI).
- Therefore, (B) option is correct according to the IUPAC rule.

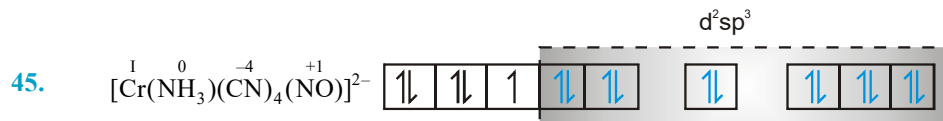
23. $[\text{Fe}(\text{II})\text{N}_3(\text{O}_2)(\text{SCN})_4]^{4-}$; so correct name is azidosuperoxidotetrathiocyanato-S-ferrate(II) according to IUPAC rules.

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

25. (1)  (2)  (3) 
26. 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.
27. $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$; $x + 5(-1) + 1 = -2$ or $x = +2$
 $[\text{Fe}(\text{CN})_5\text{NOS}]^{4-}$; $x + 5(-1) + (-1) = -4$ or $x = +2$
28. 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 ligands.
29. (I) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 + 3\text{Ag}^+ \longrightarrow 3\text{AgCl}\downarrow + [\text{Co}(\text{NH}_3)_6]^{3+}$
 $\text{Co}^{3+} \longrightarrow$ Primary valencies i.e. ionisable valency = 3.
 (II) $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + 3\text{Ag}^+ \longrightarrow 3\text{AgCl}\downarrow + [\text{Pt}(\text{NH}_3)_5\text{Cl}]^{3+}$
 $\text{Pt}^{4+} \longrightarrow$ Primary valencies = 4.
30. Let x be the oxidation state of nickel then,
 (A) $[\text{Ni}(\text{CO})_4]$; $x + 4(0) = 0$ or $x = 0$; (B) $[\text{NiF}_6]^{2-}$; $x + 6(-1) = -2$ or $x = +4$.
 (C) $[\text{Ni}(\text{NH}_3)_6]^{2+}$; $x + 4(0) = +2$ or $x = +2$ (D) $[\text{Ni}(\text{CN})_6]^{4-}$; $x + 6(-1) = -4$ or $x = +2$
31. $\text{K}_6[(\text{CN})_5\text{Co}(\text{III}) - \text{O}^{2-} - \text{Co}(\text{III})(\text{CN})_5]^{6+} \xrightarrow{\text{oxidizes}} \text{K}_5[(\text{CN})_5\text{Co} - \text{O}^{-1} - \text{Co}(\text{CN})_5]^{5+}$.
 $\text{O}_2^{2-} \xrightarrow{\text{oxidized}} \text{O}_2^-$; bond order of $\text{O}_2^{2-} = \frac{10-8}{2} = 1$; bond order of $\text{O}_2^- = \frac{10-7}{2} = 1.5$
 Bond strength \propto bond order; so,
 Bond energy of $\text{O}_2^{2-} <$ Bond energy of O_2^- .
32. (I) Coordination compounds made up of cationic and anionic coordination entities show coordination isomerism due to the interchange of ligands between the cation and anion entities.
 (II) Hydrate isomers differ by whether or not a water molecule is directly bonded to the metal ion or merely present as free water molecules in the crystal lattice.
 (III) 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.
 (IV) $[\text{NiCl}_2(\text{PPh}_3)_2]$ has tetrahedral geometry on account of the bulkier nature of triphenyl phosphine. In tetrahedral geometry all positions are adjacent to each other and therefore, does not show geometrical isomerism.
33. The complex is $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and there are two moles of Cl which can react with Ag^+ to form white precipitate of AgCl .
 $\frac{(100 \times 0.1)}{1000} \times 2 = 0.02$ mole of AgCl
34. $[\text{Ni}(\text{H}_2\text{O})_4]\text{SO}_4 + \text{Pyridine} + \text{NaNO}_2 \longrightarrow [\text{Ni}(\text{Py})_4](\text{NO}_2)_2$
 Stronger ligand, pyridine displaces weaker ligand, H_2O in aqueous solution.
 $[\text{Ni}(\text{py})_4](\text{NO}_2)_2$ is formed as dark blue crystals on crystallisation.
35. Order of crystal field splitting $\text{en} > \text{H}_2\text{O} > \text{Br}^-$ so, more stronger ligand will absorb lower wavelength light and reflect back higher wavelength light.

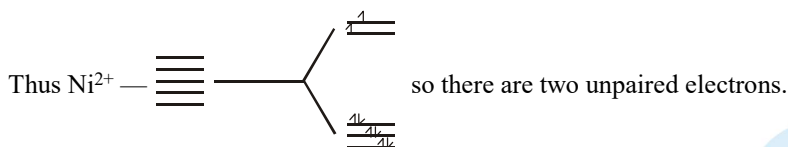
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36. (A) I and III both are identical structures (i.e. trans-isomers).
 (B) II and IV are identical structures (i.e. cis - isomers).
 (C) I and II are cis - and trans - isomers (i.e. they are geometrical isomers).
37. $2X + 1(-2) + 1(-1) = +3$; $x = \frac{6}{2} = +3$.
38. Oxidation state of iron in $[\text{Fe}(\text{CO})_2(\text{NO})_2]^+$ $= x + 2(0) + 2 = 0$; $x = -2$
 So EAN = $28 + 8 = 36$
 Oxidation state of cobalt in $\text{Co}_2(\text{CO})_8 = 2x + 8(-0) = 0$ or $x = 0$
 So EAN = $27 + 1 + 8 = 36$.
39. Oxidation state of cobalt in $\text{Co}_2(\text{CO})_8 = 2x + 8(-0) = 0$ or $x = 0$
 So EAN = $27 + 1 + 8 = 36$.
 As it will be the atomic number of Kr and according to EAN rule, the complex having EAN equal to noble gas is more stable.
40. (A) $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br} \xrightleftharpoons{\text{aq.}} [\text{Co}(\text{NH}_3)_5\text{SO}_4]^+(\text{aq}) + \text{Br}^-(\text{aq})$
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4 \xrightleftharpoons{\text{aq.}} [\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
 Both complexes have same number of ions in solutions but have different number of electrical charges. Hence they can be distinguished by conductance measurement.
 (B) $\text{Br}^-(\text{aq}) + \text{Ag}^+(\text{aq}) \longrightarrow \text{AgBr} \downarrow$ (pale yellow); $\text{SO}_4^{2-}(\text{aq.}) + \text{Ag}^+ \longrightarrow \text{Ag}_2\text{SO}_4 \downarrow$ (white)
 (C) $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{BaSO}_4 \downarrow$ (white); $\text{Ba}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq}) \longrightarrow \text{BaBr}_2(\text{aq})$.
41. mole of complex = $50 \times 0.2 = 0.01$ and mole of $\text{AgCl} = \frac{1.435}{143.5} = 0.01$
 $n\text{Ag}^+ = n\text{Cl}^-$
 \therefore 1 mole complex = 1 mole AgCl
42. (A) $\text{CoCl}_3 \cdot 6\text{NH}_3 \xrightleftharpoons{\text{aq.}} [\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$ (no. of ions = 4 & total electrical charges = 6)
 (B) $\text{CoCl}_3 \cdot 5\text{NH}_3 \xrightleftharpoons{\text{aq.}} [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$ (no. of ions = 3 & total electrical charges = 4)
 (C) $\text{CoCl}_3 \cdot 4\text{NH}_3 \xrightleftharpoons{\text{aq.}} [\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$ (no. of ions = 2 & total electrical charges = 2)
 (D) $\text{CoCl}_3 \cdot 3\text{NH}_3 \xrightleftharpoons{\text{aq.}} [\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (neutral solution). It will not conduct electricity.
43. (A) Dimethylglyoximate is a bidentate ligand so it can attach to central metal ion through two donor atoms, N and O forming a ring.
 (B) Ethylenediamine is a bidentate ligand so it can attach to central metal ion through two donor atoms, N and N forming a ring.
 (C) All ligands act as monodentate ligand and thus do not form ring structure.
 (D) Glycinato is a bidentate ligand so it can attach to central metal ion through two donor atoms, N and O forming a ring.
44. (A) $\text{Sc}^{3+} - [\text{Ar}]^{18} 3d^0 4s^0$; there is no unpaired electron in d-orbitals so no d-d transition takes place and the complex is colourless.
 $\text{Ti}^{3+} - [\text{Ar}]^{18} 3d^1 4s^0$; It has one unpaired electron; so d-d transition of electron from t_{2g} level to empty level takes place and thus the complex is coloured.
 (B) Pd has $4d^8$ configuration which has higher CFSE and thus the complex is square planar and diamagnetic. In some ligands, like ambidentate ligands, there are two possible coordination sites. In such cases, linkage isomerism exist. e.g., NO_2 group can be bonded to metal ions through nitrogen ($-\text{NO}_2$) or through oxygen ($-\text{ONO}$).

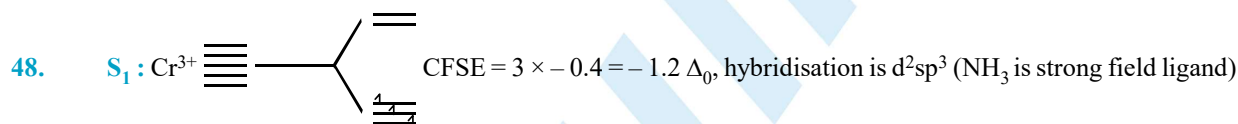


Central metal ion has one unpaired electron and thus d-d transition of electron is possible. This attributes to the colour of the solution. As different types of ligands are attached to central metal ion, the complex is called heteroleptic complex.

46. Bulkier groups favour tetrahedral geometry i.e. sp^3 hybridisation.

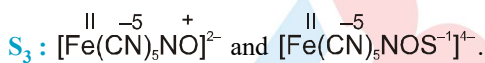


47. (A) Cr^{3+} , 3d^3 ; sp^3d^2 hybridisation with three unpaired electrons (weak field as well as strong field ligand).
 Fe^{+} , 3d^7 ; sp^3d^2 hybridisation with three unpaired electron (one 4s electron jumps to 3d orbital for the pairing)
 (B) Mn^{2+} , 3d^5 ; d^2sp^3 hybridisation with one unpaired 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).
 (C) Ni , $3\text{d}^8 4\text{s}^2$; 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.

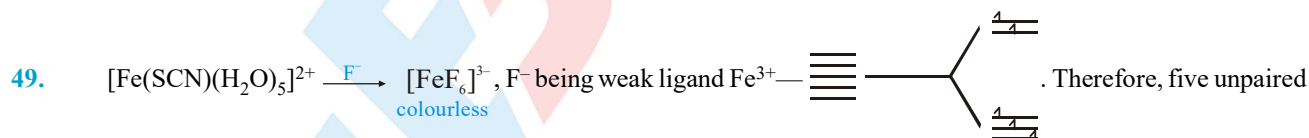


S_2 : Fe^{3+} , 3d^5 - one unpaired electron after pairing (CN^- is stronger field ligand)

$$\therefore \mu = \sqrt{1(1+2)} \approx 1.73 \text{ BM}$$

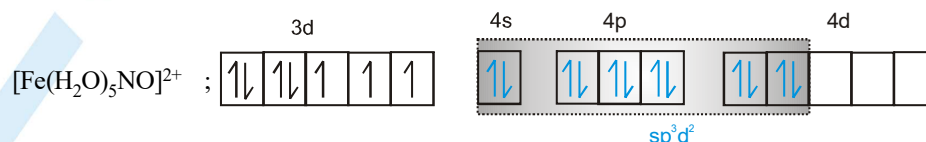


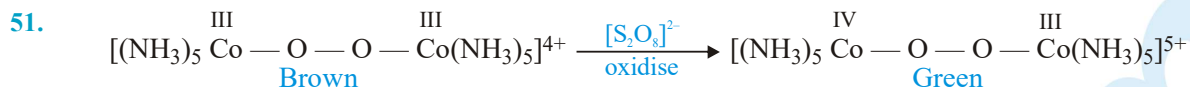
In reactant and product, the iron is in same oxidation state i.e. +2.



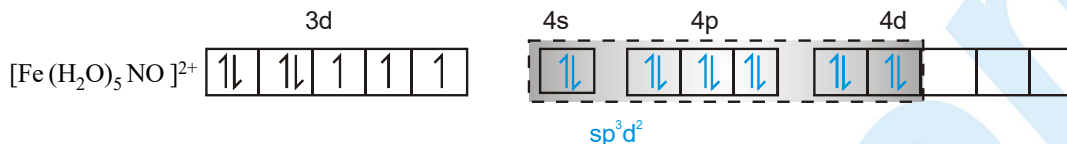
electrons and so $\mu = \sqrt{5(5+2)} \text{ B.M.} \approx 5.92$.

50. (I) Au in +3 oxidation state with 5d^8 configuration has higher CFSE. So complex has dsp^2 hybridisation and is diamagnetic.
 (II) Cu is in +1 oxidation state with 3d^{10} configuration and no $(n-1)\text{d}$ orbital is available for dsp^2 hybridisation, so ns and np orbitals undergo sp^3 hybridisation and complex is diamagnetic.
 (III) Co is in +3 oxidation state and 3d^6 configuration has higher CFSE. So complex is diamagnetic and has d^2sp^3 hybridisation.
 (IV) Fe is in +1 oxidation state and the complex is paramagnetic with three unpaired electrons.





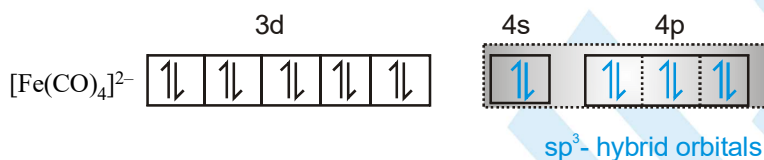
52. The iron is in +1 oxidation state with $3d^7$ electron configuration and NO is NO^+ .



So, $\mu = \sqrt{n(n+2)}$ or $\mu = \sqrt{3(3+2)} = 3.9$

The colour is due to charge transfer not because of d-d transition of electron.

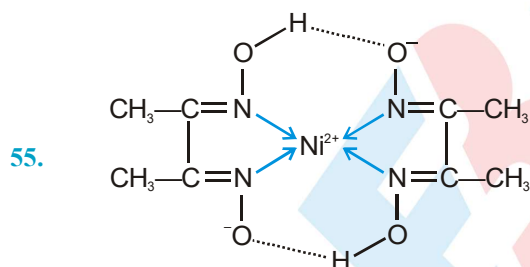
53. (A) Py is strong field ligand and the complex is square planar and paramagnetic.
 (B) Copper (I) has electron configuration $[\text{Ar}]^{18} 3d^{10}$. With CN^- (strong field ligand) there is no empty d-orbital for dsp^2 hybridisation and so the complex is tetrahedral not square planar.
 (C) Iron is in -2 oxidation state and CO is strong field ligand so after rearrangement of electrons, pairing of electrons occurs. So,



54. Order of the strength of ligands magnitude wise in spectrochemical series :



Hence the wave length of the light observed will be in the order

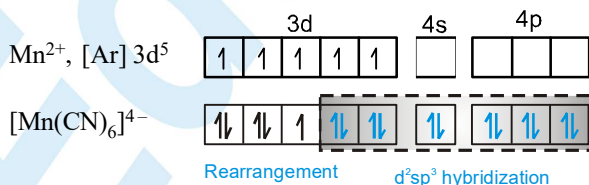


DMG is a bidentate ligand.

56. Statements 1, 3 and 4 are correct but 2 is incorrect.

$3d^6$ configuration of Co^{3+} has greater CFSE and this favours the d^2sp^3 hybridisation. NO_2^- is ambidentate ligand and Cl^- and NO_2^- can exchange as counter ion ; so complex can show ionisation as well as linkage isomerism. The complex also exists in cis and trans isomeric forms.

57. All are low spin complexes but (3) has one unpaired electron so it is diamagnetic .



58. $[\text{Fe}(\text{en})_2(\text{H}_2\text{O})_2]^{2+} + \text{en} \rightarrow [\text{Fe}(\text{en})_3]^{2+} + 2\text{H}_2\text{O}$
 Complex is $[\text{Fe}(\text{en})_3]^{2+}$. 'en' is a strong field ligand and thus it is inner orbital complex (d^2sp^3) and diamagnetic. It is $\text{M}(\text{AA})_3$ type which has only one form.

59. All statements are correct and factual.
60. (1) $[\text{AuCl}_4]^-$ - highly charged species with $5d^8$ has greater CFSE and thus $\Delta_t > P$ and so dsp^2 hybridisation.
 (2) $[\text{Pt}(\text{Cl})_4]^{2-}$ - $5d^8$ has greater CFSE and thus $\Delta_t > P$ and so dsp^2 hybridisation.
 (3) $[\text{Mn}(\text{Br})_4]^{2-}$ - sp^3 hybridisation as Br^- is weak field ligand.
 (4) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ - dsp^2 hybridisation, one d-electron jumped to 4p-orbital leaving behind one empty d-orbital for dsp^2 hybridisation.
61. (C) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is coloured as it has three unpaired electrons while $[\text{Cu}(\text{NCCH}_3)_4][\text{BF}_4]$ is colourless as Cu(I) i.e. $3d^{10}$ electron configuration has all electrons paired, so there is no d-d transition of electron.
62. H_2O is weak field ligand but Co^{3+} with $3d^6$ configuration has greater CFSE and thus $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is inner orbital complex and is diamagnetic.
63. (A) 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.
 (B) 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).

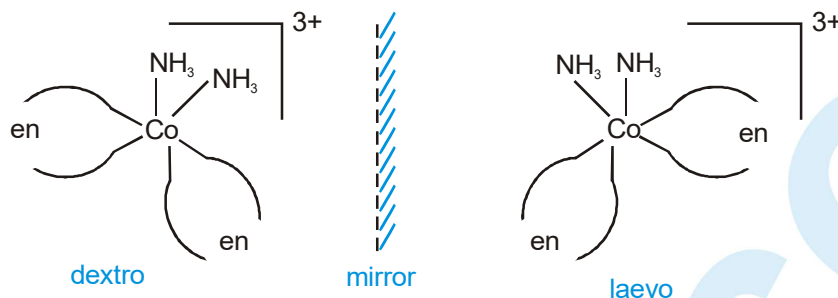


Similarly for d^0 and d^{10} configurations the CFSE is zero in both octahedral and tetrahedral complexes with weak field ligands.

64. (A) $\text{Ti}(\text{NO}_3)_4$, $[\text{Ar}]^{18} 3d^0 4s^0$; there is no unpaired electron and, therefore, there is no d-d transition of electron. So compound is colourless.
 (B) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Ar}]^{18} 3d^3$; there is three unpaired electrons and, therefore, there is d-d transition of electron. So compound is coloured.
 (C) $\text{K}_3[\text{VF}_6]$, $[\text{Ar}]^{18} 3d^1$; there is one unpaired electron and, therefore, there is d-d transition of electron. So compound is coloured.
 (D) $[\text{Cu}(\text{NCCH}_3)_4][\text{BF}_4]$ $[\text{Ar}]^{18} 3d^{10}$; there is no unpaired electron and, therefore, there is no d-d transition of electron. So compound is colourless.
65. It has octahedral geometry with d^2sp^3 hybridisation and is paramagnetic with one unpaired electron. CFSE is greater because of strong field ligand, CN^- . So the $[\text{Fe}(\text{CN})_6]^{3-}$ complex ion should be very stable.
66. EDTA forms soluble complex with Ca^{2+} and Mg^{2+} (present in hard water) and thus they can be estimated by titrating against EDTA using eriochrome black-T as indicator.
67. All statements are correct.
 (I) High CFSE in low spin d^5 configuration. It is reported square planar.
 (II) Δ_o increases with increase in charge on central metal ion.
 (III) $4d^8$ configuration has higher CFSE; so dsp^2 hybridisation and diamagnetic with red-violet colour.
 (IV) SCN^- is weak field ligand; so complex with $3d^7$ configuration is tetrahedral with three unpaired electrons.

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68. (A) $\text{trans}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.
 (B) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.
 (C) $\text{cis}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$ lacks one of the symmetry elements.



- (D) $\text{trans}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.
69. Complex with five coordination number has trigonal bipyramidal geometry or square pyramidal geometry. As it has zero dipole moment, its geometry will be trigonal bipyramidal.

70. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ $n = 4$ and $\mu = 4.91$
 $[\text{Fe}(\text{CN})_6]^{4-}$ $n = 0$ and $\mu = 0$

71. (A) Both are identical structures and each have plane of symmetry ; so they are not optical isomers.
 (B) Both are identical structures and each have plane of symmetry ; so they are not optical isomers.
 (C) Both are identical structures and each have plane of symmetry ; so they are not optical isomers.
 (D) Both are mirror images of each other which are non-superimposable (they lack plane of symmetry)

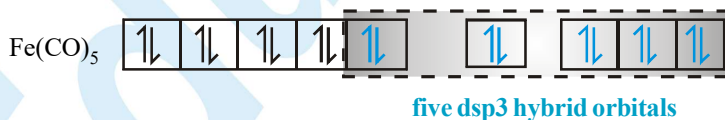
72. $\text{Zn}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Zn}(\text{NH}_3)_4]^{2+}$.

$$K_f = \frac{[\text{Zn}(\text{NH}_3)_4]^{2+}}{[\text{Zn}^{2+}][\text{NH}_3]^4} \Rightarrow \frac{[\text{Zn}(\text{NH}_3)_4]^{2+}}{[\text{Zn}^{2+}]} = K_f[\text{NH}_3]^4$$

$$= 3 \times 10^9 \times 10^4 = 3 \times 10^{13}.$$

$$\Rightarrow \frac{[\text{Zn}^{2+}]}{[\text{Zn}(\text{NH}_3)_4]^{2+}} = \frac{1}{3 \times 10^{13}} = 3.3 \times 10^{-14}.$$

73. In $\text{Fe}(\text{CO})_5$, Fe in zero oxidation state and CO is stronger field ligand. So,

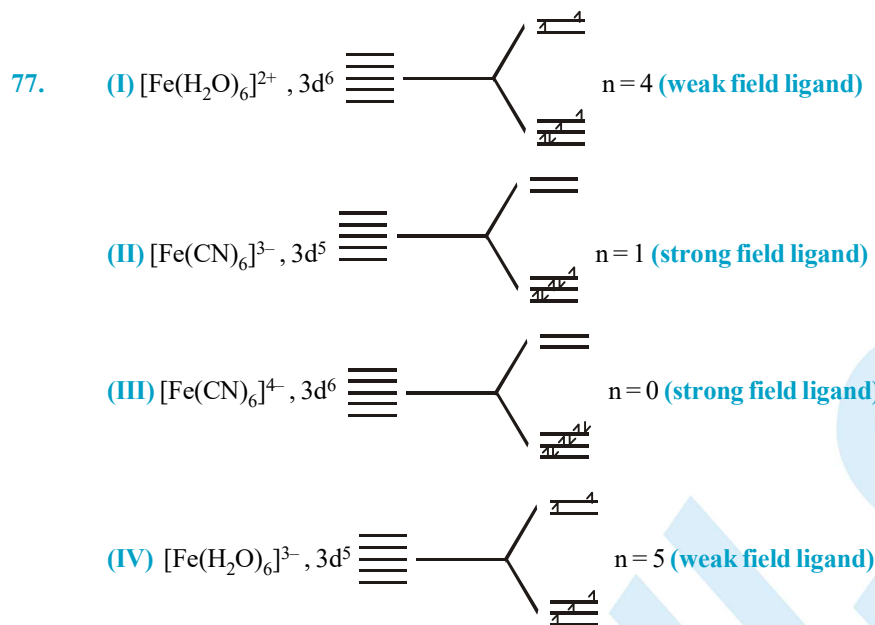


Hence it is diamagnetic and low spin complex.

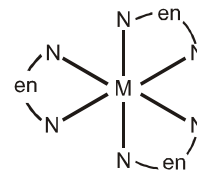
74. (C) $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Ar}]^{18}3d^{10}$; As there is no empty d-orbital for dsp^2 hybridization. So it has sp^3 hybridization and is tetrahedral, and diamagnetic.

75. It can be predicted, by knowing the number of unpaired electrons or paired electrons that how many empty d-orbitals will be available for hybridisation or not available for hybridisation.

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



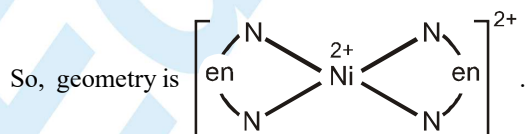
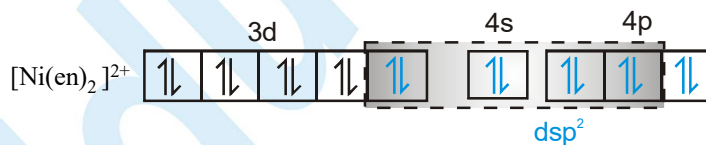
78. (A) There are two geometrical isomers, cis and trans.
 (B) There are two geometrical isomers, facial and meridional.
 (C) 'en' is a symmetrical ligand, and $\text{M}(\text{AA})_3$ has only one form.
 (D) There are two geometrical isomers because glycine is an unsymmetrical ligand.



79. $[\text{CoCl}_2(\text{en})_2]\text{Cl}$, One mole complex contains, one mole of ionisable Cl^- .
 One mole of complex = one mole of Cl^- .

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

80. The oxidation state of nickel is in complex $= x + 4(0) = +2$ or $x = +2$.
 Ethylenediamine is a strong field chelating ligand and so,



81. (D) Chelate complex has higher stability than the similar complexes having monodentate ligands and an higher stability means higher overall formation constant.

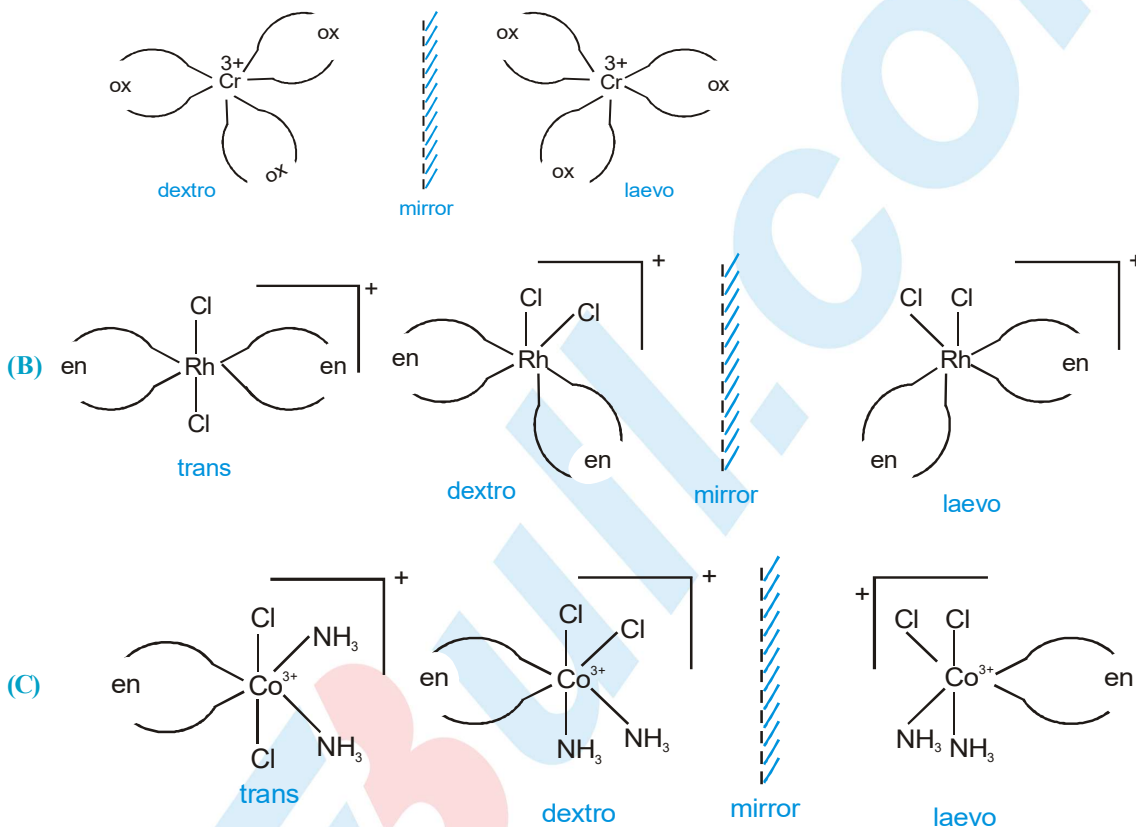
82. NO_2^- is an ambidentate ligand and can link to central metal ion either through N or O. Hence it shows linkage isomerism.

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.

83. (A) With symmetrical bidentate ligands. $[\text{Cr}(\text{ox})_3]^{3-}$ does not show geometrical isomerism but it can show only optical isomerism.



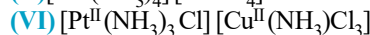
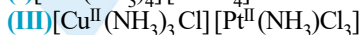
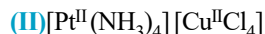
84. Geometrical isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.

When two $(\text{C}_2\text{H}_5)_3\text{P}$ groups are on same side it is cis - and when those are on opposite side it is trans -

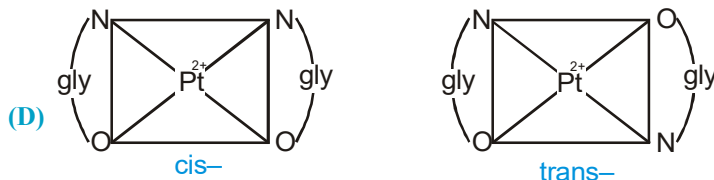
85. (A) I and II are geometrical isomers (i.e. cis - and trans isomers)
 (B) I and III are identical structures (both are trans-isomers having plane of symmetry)
 (C) II and IV are mirror images of each other and are non-superimposable.
 (D) II and III are geometrical isomers (i.e. cis - and trans isomers)
86. (A) I is trans form which has centre of symmetry as well as plane of symmetry ; so optically inactive.
 (B) II is cis form which lacks centre of symmetry as well as plane of symmetry ; so optically active.
 (C) (II) and (III) lack symmetry elements ; so both are optically active.
 (D) IV is trans form which has centre of symmetry as well as plane of symmetry ; so optically inactive.

87. Polymerisation isomers of the compounds are a special case of coordination isomerism, in which the various isomers differ in formula weight from one another. As all have two chromium ions (+3), six ammonia molecules and six NO_2^- ions, they will have same molecular masses.

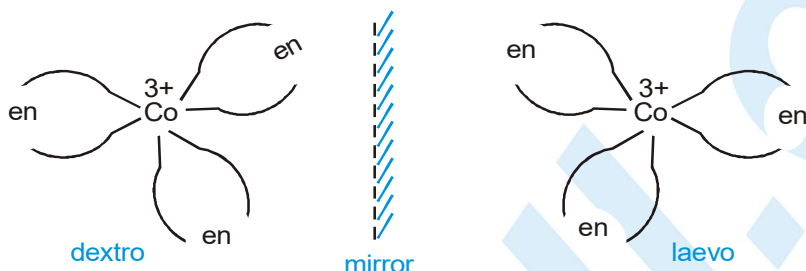
88. (C) There are four possible coordination isomers as given below :



89. (A) The tetrahedral compounds can not show geometrical isomerism as we all know that all four positions are equivalent in tetrahedral geometry.
 (B) In a square planar complex of formula $[Ma_2b_2]$ [a and b are unidentate], the two ligands 'a' may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer.
 (C) Ma_3b and Mab_3 have only one form.



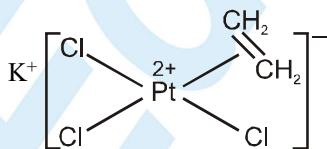
90. $[Co(en)_3]^{3+}$ ion due to absence of one of the symmetry elements it has two d- and •-optically active forms.



91. It is Ma_3b_2c type. So it has three isomer which are as follow :

$(aa)(ab)(bc)$	(optically inactive)
$(aa)(bb)(ac)$	(optically inactive)
$(ab)(ab)(ac)$	(optically inactive)

92. (B) Chelate ligands i.e. oxalato being too small to span the trans-positions and thus prefer to occupy the cis-position. So (I) is cis and (II) is trans. Platinum is in +2 oxidation state with $5d^8$ valence shell electron configuration. This configuration has higher CFSE and thus favours square planar geometry.
93. (A) No anionic ligand is present in coordination sphere for the exchange with Cl^- ions present in ionisation sphere.
 (B) No anionic ligand is present in coordination sphere for the exchange with Cl^- ions present in ionisation sphere.
 (C) No anionic ligand is present in coordination sphere for the exchange with Cl^- ions present in ionisation sphere.
 (D) Br^- and SO_4^{4-} can exchange their positions between coordination sphere and ionisation sphere. Hence it shows ionization isomerism.
94. (A) Primary and secondary valencies.
 (B) $[RhCl(PPh_3)_3]$, Wilkinson catalyst used as homogeneous catalyst for hydrogenation.
 (C) $M \xrightleftharpoons[\sigma]{\pi} CO$ which is called as synergic interaction.
95. In Zeise's salt structure, the ethylene occupies the fourth coordination site of the square planar complex with the C—C axis perpendicular to the platinum ligand plane.



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

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97. (A) $[\text{Cr(en)}_3]^{3+}$ exists in d- and \bullet -forms due to the absence of one of the symmetry element(s). So it will give racemic mixture when d- and \bullet -forms are mixed in 1 : 1 molar ratio.
 (B) $[\text{Ni(DMG)}_2]$ have square planar geometry and thus have mirror plane so optically inactive.
 (C) $\text{cis-}[\text{Cu(Gly)}_2]$ have square planar geometry and thus have mirror plane so optically inactive.

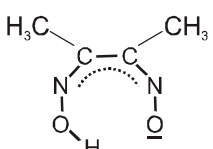
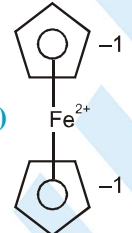
98. (A) No ionisation isomerism because the counter anion is absent.

(B) No hydrate isomerism because the counter anion is absent.

(C) $\text{Ma}_2\text{b}_2\text{c}_2$ — 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)

99. Chiral molecules have a degree of asymmetry that makes their mirror images non-superimposable. So (A) will exhibit chirality.

100. In $\text{K}^+ \left[\text{Pt} \begin{array}{c} \text{Cl} \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{Pt}^{2+} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_2 \end{array} \right]^-$ the bond between the ethylene molecule and the metal ion may be considered as **additive** σ bond to an available orbital on the metal. So there are nine σ bonds.

101. (A)  (B)  It has aromatic ring.

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

103. (A) $[\text{Cr(NH}_3)_6]^{3+}$ and $[\text{Cr(NO}_2)_6]^{3-}$ and $[\text{Cr(NH}_3)_4(\text{NO}_2)_2]^+$ and $[\text{Cr(NH}_3)_2(\text{NO}_2)_4]^-$ have same number of ions, so cryoscopic method can not be used.
 (B) Molar conductance depends on the number of ions as well as on the charge on the complexes. $[\text{Cr(NH}_3)_6]^{3+}$, $[\text{Cr(NO}_2)_6]^{3-}$ and $[\text{Cr(NH}_3)_4(\text{NO}_2)_2]^+$ and $[\text{Cr(NH}_3)_2(\text{NO}_2)_4]^-$ have same number of ions but different electrical charges.
 (C) Both complexes have same number of unpaired electrons, so measuring magnetic moments methods can not be used.
 (D) They have similar colour because of the similar conditions.

104. Order of C – O bond strength :

$[\text{Mn(CO)}_6]^+ > [\text{Cr(CO)}_6] > [\text{V(CO)}_6]^- > [\text{Ti(CO)}_6]^{2-}$ and $[\text{Ni(CO)}_4] > [\text{Co(CO)}_4]^- > [\text{Fe(CO)}_4]^{2-}$.

(A) True statement.

(B) 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.

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

105. $[\text{CrF}_6]^{4-}$ n = 4 (3d⁴)
 $[\text{MnF}_6]^{4-}$ n = 5 (3d⁵)
 $[\text{Cr(CN)}_6]^{4-}$ n = 2 (3d⁴)
 $[\text{Mn(CN)}_6]^{4-}$ n = 1 (3d⁵)

n = number of unpaired electrons and that can be calculated by CFT.

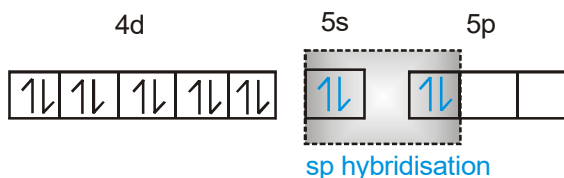
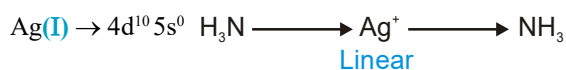


106. (P) $3 \times (-0.4) + 2 \times 0.6 = 0$.
 (Q) $3 \times (-0.4) + 1 \times 0.6 = -0.6\Delta_0$.
 (R) $4 \times (-0.4) + 2 \times 0.6 = -0.4\Delta_0$.
 (S) $3 \times (-0.4) + 0 \times 0.6 = -1.2\Delta_0$.

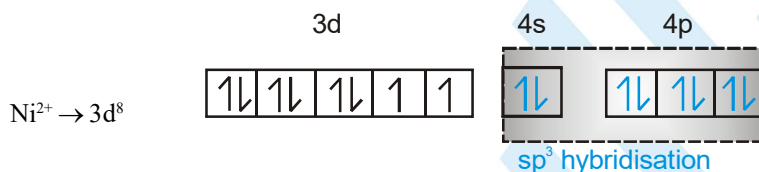
EXERCISE - 2

Part # I : Multiple Choice

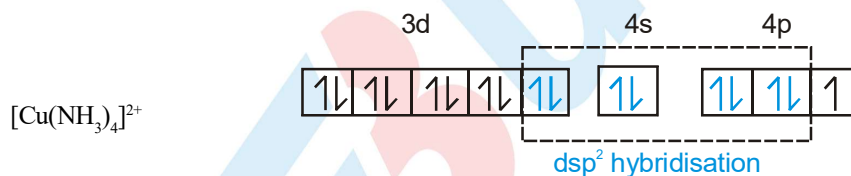
2. (A) $[\text{Ag}(\text{NH}_3)_2]^+$



- (B) NiCl_4^{2-} , VO_4^{3-} and MnO_4^- have tetrahedral geometries.



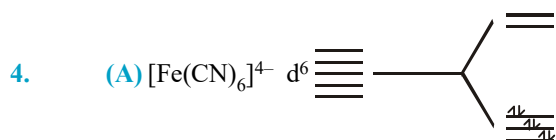
- (C) $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ have square planar geometries.



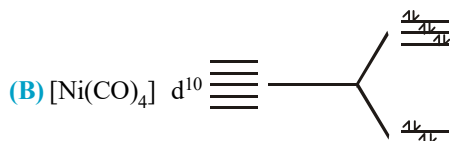
Similarly the hybridisation scheme for $[\text{Ni}(\text{CN})_4]^{2-}$ (CN^- is a strong field ligand) is as shown in figure.



- (D) $[\text{Fe}(\text{CO})_5]$ is diamagnetic and has dsp³ hybridisation. So it has trigonal bipyramidal geometry.

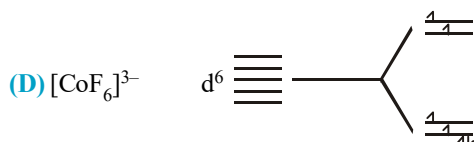


CN⁻ is strong field ligand.

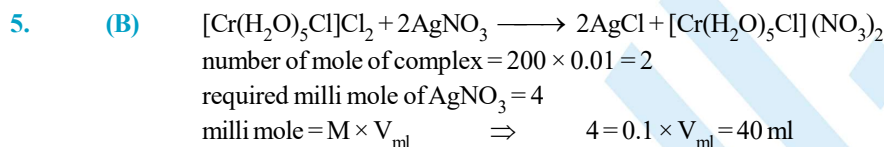


CO is strong field ligand.

(C) $[\text{Ni}(\text{CN})_4]^{2-}$; Ni^{2+} has $3d^8$ configuration and CN^- is strong field ligand. So, complex is square planar and diamagnetic.



F⁻ being weak field ligand does not allow pairing.



8. (A) $[\text{CoCl}_2(\text{OH})_2(\text{NH}_3)_2]\text{Br}$ and $[\text{CoClBr}(\text{OH})_2(\text{NH}_3)_2]\text{Cl}$ are ionisation isomers.

(B) Does not have ambidentate ligand; so does not show linkage isomerism.

(C) It is $\text{Ma}_2\text{b}_2\text{c}_2$ type.

$\text{Ma}_2\text{b}_2\text{c}_2 -$	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)

9. (A) is not correct, as metal can exhibit more than one coordination number, e.g., Cu^{2+} has 4 and 6 coordination number.

(B) The coordination number of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ions i.e. the number of ligand donor atoms to which the metal is directly attached (C) It is incorrect statement (D) Tetrahedral complexes i.e. coordination number 4 are favoured by steric requirements, either simple electrostatic repulsion of charge ligands or vander wall's repulsions of large one.

10. (A) All are diamagnetic and inner orbital complexes because all ligands are strong field ligands.

(B) Fe^{3+} $n = 5$; $\mu = \sqrt{5(5+2)} \approx 5.92$ with H_2O , so $[\text{FeCl}_4]^-$ is diamagnetic.

(C) Fe^{3+} $n = 5$; $\mu = \sqrt{5(5+2)} \approx 5.92$ with H_2O

Fe^{3+} $n = 1$; $\mu = \sqrt{3} = 1.73$ with CN^-

(D) Mn^{2+} ($3d^5$) and Fe^{3+} ($3d^5$) have same number of unpaired electrons i.e. 5 with weak field ligands, F^-

11. All statements are correct with respect to CFT.

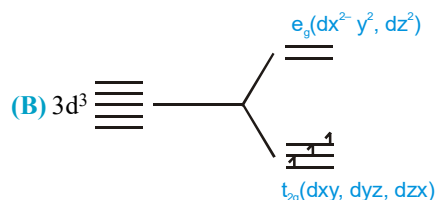
12. $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})(\text{Cl})_2]$ is square planar (dsp^2 hybridisation) and diamagnetic on account of the higher CFSE of $5d^8$ configuration. It does not show optical isomerism due to the presence of mirror plane but exists as cis and trans forms.

13. $K_3[Fe(CN)_6]$; Coordination number (i.e. secondary valencies) of Fe^{3+} is 6 which are satisfied by negatively charged ligands, CN^- and primary valencies (i.e. oxidation state) of iron is 3 which are also satisfied by negatively charged ligands, CN^- .

$K_4[Fe(CN)_6]$; Coordination number (i.e. secondary valencies) of Fe^{2+} is 6 which are satisfied by negatively charged ligands, CN^- and primary valencies (i.e. oxidation state) of iron is 2 which are also satisfied by negatively charged ligands, CN^- .

$[Cu(NH_3)_4]SO_4$; Coordination number (i.e. secondary valencies) of Cu^{2+} is 4 which are satisfied by neutral ligands, NH_3 . The primary valencies of Cu^{2+} are not satisfied by neutral ligands, NH_3 .

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



(C) H_2O being neutral molecule satisfies only secondary valencies.

(D) It shows hydrate isomerism and not ionisation isomerism because anionic ligand is not present in coordination sphere.

15. S_1 : Square planar complexes with symmetrical ligands like (en) do not show geometrical isomerism and they have plane of symmetry, so optically inactive.

S_2 and S_3 are correct statements.

16. Δ_0 depends on (A) strength of ligands ; $CN^- > NH_3^-$
(B) oxidation state of metal ; $Co^{3+} > Co^{2+}$

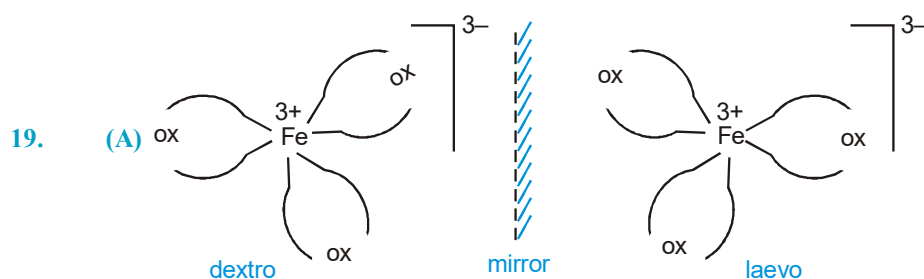
Δ_0 also increases down the group due to increasing effective nuclear charge.

17. Tetrahedral complexes are favoured by steric requirements, either simple electrostatic repulsion of charge ligands or vander wall's repulsions of large one.

Tetrahedral complexes are thus generally favoured by large ligands like Cl^- , Br^- , I^- and PPh_3 and metal ions of three types ;

- (1) those with a noble gas configuration such as Be^{2+} (ns^0) ;
- (2) those with pseudo noble gas configuration $(n-1)d^{10} ns^0 np^0$, such as Zn^{2+} , Cu^+ and Ga^{3+} , and
- (3) those transition metal ions which do not strongly favour other structure by virtue of the CFSE, such as Co^{2+} , d^7 .

18. (A) sp^3 and paramagnetic. (B) sp^3 and diamagnetic. (C) dsp^2 and diamagnetic. (D) sp^3 and diamagnetic.



$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ do not show optical isomerism because of the presence of plane of symmetry as well as centre of symmetry.

(B) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ has three, five membered chelating rings and thus is more stable due to chelation.

(C) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$; EAN = $26 - 2 + 12 = 36$

$[\text{Fe}(\text{CN})_6]^{4-}$; EAN = $26 - 2 + 12 = 36$

$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$; EAN = $26 - 3 + 12 = 35$

(D) $\text{Fe} \xrightleftharpoons[\sigma]{\Delta} \text{CO}$.

20. Exchange of Cl^- and Br^- leads to ionisation isomerism. It shows cis-trans isomerism and its cis-isomer shows optical isomerism due to the absence of one of the symmetry element(s).

21. (A) cis- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$ does not show optical isomerism due to the presence of symmetry element.

(C) For same reason $[\text{Ni}(\text{NH}_3)_3\text{Cl}_3]$ and $[\text{Pt}(\text{en})\text{Cl}_2]$.

22. $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}(\text{NO}_2)$ are ionisation isomers.

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ are linkage isomers.

Cobalt in +3 oxidation state has $3d^6$ configuration which has higher CFSE. So the complex is inner orbital (i.e. d^2sp^3 hybridisation) and diamagnetic.

23. (A) Exists as cis and trans form but neither of the forms can have enantiomeric forms on account of presence of the plane of symmetry as well as centre of symmetry.

(B) Only one form possible

(C) Tetrahedral in which all positions are adjacent to each other.

(D) Exists as cis and trans form but neither of the forms can have enantiomeric forms on account of presence of the plane of symmetry.

24. (A) $[\text{Co}(\text{EDTA})]^-$ shows optical isomerism.

(B) NO_2^- being bidentate ligands can attach to central metal ion through N or O.

(C) It is Mabcdef type and thus has fifteen different geometrical isomers.

(D) Ionisation isomerism involves exchange of different ions between coordination sphere and ionisation sphere. In complex, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, same anionic ligands, i.e., Cl^- are present in coordination sphere and ionisation sphere; so no exchange of ions takes place.

25. Complex must be having the composition $\text{Co}(\text{Cl})_2(\text{en})_2(\text{NO}_2)$ i.e. $[\text{CoCl}_2(\text{en})_2]\text{NO}_2$ or $[\text{CoCl}(\text{en})_2\text{NO}_2]\text{Cl}$

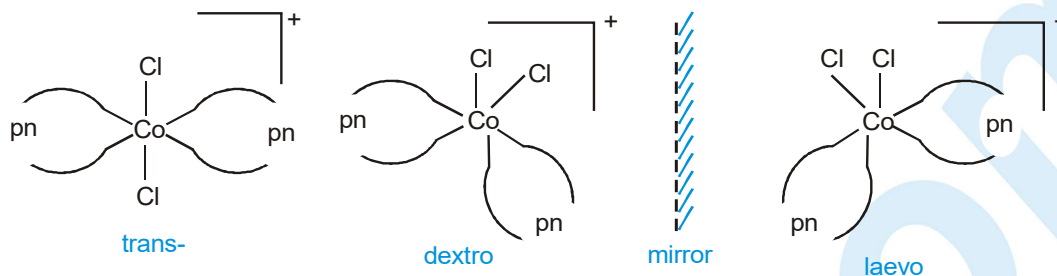
(I) Linkage; NO_2 can link through N as well as through O

(II) Ionisation: $[\text{Co}(\text{en})_2\text{Cl}_2]\text{NO}_2$ and $[\text{Co}(\text{en})_2\text{Cl}(\text{NO}_2)]\text{Cl}$

(III) It may exist as cis and trans isomers.

(IV) Its cis form lacks plane of symmetry as well as centre of symmetry and thus is optically active.

26. Diaminopropane can exist as 1,2,- diaminopropane (pn) and 1,3- diaminopropane (tn.) So exhibits ligand isomerism.

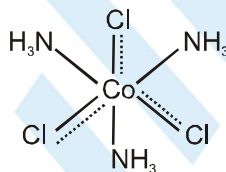


Note : pn can be replaced by tn.

27. All statements are correct.

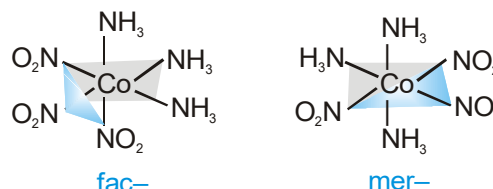
Part # II : Assertion & Reason

1. **Statement-1 :** Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour, i.e. it may satisfy both primary and secondary valencies since in every case the fulfillment of coordination number of the central metal ion appears essential. This dual behaviour is represented by both thick and dotted lines.



Statement-2 :

Complex $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ may show two isomeric forms called fac- and mer-. Facial isomers have three identical ligands on one triangular face whereas meridional isomers have three identical ligands in a plane bisecting the molecule.



It does not show optical isomerism because of the presence of plane of symmetry.

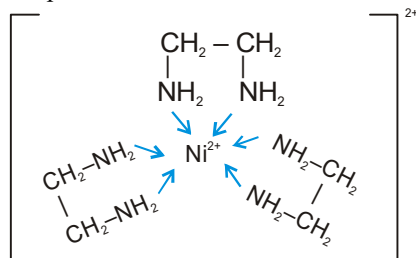
3. Ni^{2+} , $[\text{Ar}]3d^8$ 3d 4s 4p
- | | | | | | | | |
|----|----|----|---|---|--|--|--|
| ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ | | | |
|----|----|----|---|---|--|--|--|
- $[\text{Ni}(\text{CN})_4]^{2-}$
- | | | | | | | | |
|----|----|----|----|----|----|--|--|
| ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | | |
|----|----|----|----|----|----|--|--|
- dsp² hybrid orbitals (spin paired complex)

As all ligands are same, it is homoleptic complex.

5. In $\text{H}_2\ddot{\text{N}}-\text{H}_2\text{C}-\text{CH}_2-\ddot{\text{N}}\text{H}_2$ two ammine nitrogen atoms act as donor atoms. So, it acts as a bidentate ligand.

Hence, there are six σ -bonds between metal and ligands, thereby given coordination number six.

7. **Statement-1** : The chelate complexes are more stable than similar complexes containing unidentate ligands.



Statement-2 : Ni^{2+} with coordination number six forms octahedral complexes.

EXERCISE - 3

Part # I : Matrix Match Type

- (A) Ni has zero oxidation state and CO is stronger field ligands ; so pairing of electrons takes place so as to have sp^3 hybridisation and diamagnetic.

(B) Ag has + 3 oxidation state and 4d^8 configuration ; so dsp^2 hybridisation and diamagnetic.

(C) Zn has + 2 oxidation state and d^{10} configuration ; so all electrons are paired and hybridisation is sp^3 .

(D) Rh has + 1 oxidation state and 4d^8 configuration ; so dsp^2 and diamagnetic.

Note : In all complexes, the ligands are unidentate.
- (A) $[\text{NiCl}_2(\text{PPh}_3)_2]$ has two unpaired electrons i.e. $\text{e}_g^{2,2} \text{t}_{2g}^{2,1,1}$ electron configuration.

(B) $[\text{V}(\text{CO})_5]$ has one unpaired electron i.e. $\text{t}_{2g}^{2,2,1} \text{e}_g^{0,0}$ electron configuration.

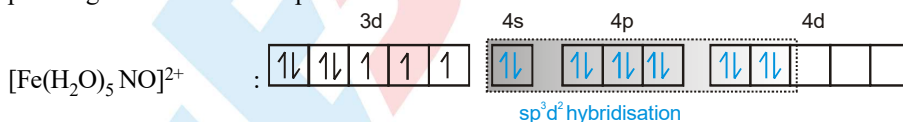
(C) $[\text{Cr}(\text{CN})_6]^{4-}$ has two unpaired electrons i.e. $\text{t}_{2g}^{2,1,1} \text{e}_g^0$ electron configuration.

(D) $[\text{Ni}(\text{CO})_4]$ all electrons are paired i.e. $\text{e}_g^{2,2} \text{t}_{2g}^{2,2,2}$ electron configuration.
- (A) $[\text{AuF}_4]^-$; Au is in +3 oxidation state with 5d^8 configuration ; so complex is diamagnetic with dsp^2 hybridisation.

(B) $[\text{Cu}(\text{CN})_4]^{3-}$; Cu is in +1 oxidation state with 3d^{10} configuration ; so complex is diamagnetic with sp^3 hybridisation.

(C) $[\text{Co}(\text{NH}_3)_6]^{3+}$; Co^{3+} has d^6 configuration which has higher CFSE ; so hybridisation is d^2sp^3 and complex is diamagnetic.

(D) $[\text{Fe}(\text{H}_2\text{O})_5 \text{NO}]^{2+}$; Fe is in +1 oxidation state having 3d^7 configuration ; so hybridisation of complex is sp^3d^2 and paramagnetic with three unpaired electrons.



- (A) Ni^{2+} ions in both complexes have same primary valencies, i.e. + 2 Same number of ions i.e.3 and so have same conductance. Both have same EAN i.e. 34. Cl^- ions in both complexes are in coordination sphere so no precipitate is obtained with AgNO_3 .

(B) $[\text{Co}(\text{NH}_3)_6]^{3+} \text{Cl}_3$ and $[\text{Pt}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_3$ have different primary valencies but same number of ions. So same electrical conductance. Do not have same effective atomic number as in both complexes metals have different atomic number. As there are three Cl^- ions out side the coordination sphere both will gives 3 moles of the precipitate of AgCl (white).

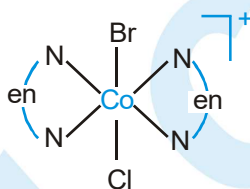
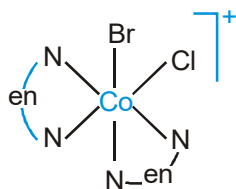
(C) $[\text{Pt}(\text{NH}_3)_2 \text{Cl}_2]$ and $(\text{NH}_4)_2[\text{PtCl}_4]$. Pt is in +2 oxidation state so same primary valencies and same effective atomic number (84) and does not have same electrical conductance (former is neutral complex where as later one has 3 ions in aqueous solutions). No precipitate with AgNO_3 as Cl^- ions in both complexes are in coordination sphere.

(D) Both have Fe in +2 oxidation state so same primary valencies but have different number of ions, so different electrical conductance (former has 3 ions where as later one has 5 ions in aqueous solutions).Both complexes have same effective atomic number (i.e. 36).

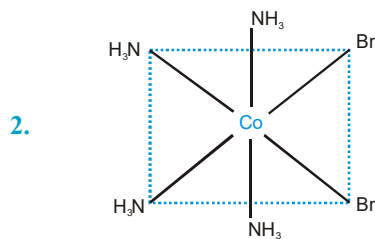
5. (A) CO is strong field ligand and thus compels for pairing of electrons. Hence hybridisation is sp^3 and complex is diamagnetic. Ligand is two electron donor.
 (B) When NO molecule co-ordinates with metal atom to form metallic nitrosyls, the single electron present in π^* antibonding molecular orbital is transferred to metal atom M so that NO molecule is converted into NO^+ . Since NO^+ is isoelectronic with CO molecule, this ion coordinates with M^+ ion as a two electron donor in metal nitrosyls in the same way as CO coordinates to M atom in metal carbonyls. Note that NO molecule is a three electron donor. Now the empty π^* antibonding molecular orbital can overlap with the filled d-orbital of metal to form $M^+ \rightarrow NO^+ \pi$ bond.
 (C) $[Ni(PF_3)_4]$ has bonding like that of $[Ni(CO)_4]$
 (D) Complex, $[PtCl_3(C_2H_4)]^-$ has $5d^8$ electron configuration. It is diamagnetic and square planar. There is π back donation between metal ion and ethylene.
6. (A), (B) $3d^6$ configuration, d^2sp^3 hybridisation and complex is diamagnetic.
 This arrangement has a very large CFSE. Most of the ligands are strong enough to cause spin pairing. Such complexes are diamagnetic. The one exception is $[CoF_6]^{3-}$ which is a high spin complex and is paramagnetic.
 (C) Diamagnetic with d^2sp^3 hybridisation as NO_2^- is strong field ligand.
 (D) The complex has d^2sp^3 hybridisation and is diamagnetic.
7. (A) $[MnCl_6]^{2-}$; d^3 configuration has $t_{2g}^{1,1,1}$ electron configuration with weak and strong ligand; Cl^- weak field ligand but Mn^{4+} is highly charged which favours high CFSE; so $\Delta_o > P$ and therefore, hybridisation is d^2sp^3 .
 (B) $[Fe(CN)_6]^{3-}$; $t_{2g}^{2,2,1}$; CN^- is strong field ligand and thus compels for pairing of electrons and thus the hybridisation is d^2sp^3 .
 (C) $[CoF_6]^{3-}$; $t_{2g}^{2,1,1}$ $e_g^{1,1}$; F^- weak field ligand and, therefore does not compel for the pairing of electrons and thus the hybridisation is sp^3d^2 .
 (D) $[Fe(H_2O)_6]^{2+}$; $t_{2g}^{2,1,1}$ $e_g^{1,1}$; H_2O weak field ligand and thus does not compel for the pairing of electrons and thus the hybridisation is sp^3d^2 .
8. (A) $[Ni(CN)_4]^{2-}$; $Ni(II) = 3d^8$ and all electrons are paired because CN^- is a strong field anionic ligand. EAN = $26 + 8 = 34$.
 $[Co(C_2O_4)_3]^{3-}$; $Co(III) = 3d^6$ and all electrons are paired because $C_2O_4^{2-}$ is chelating anionic ligand. EAN = $24 + 12 = 36$.
 (B) $[Mn(CN)_6]^{3-}$; $Mn(III) = 3d^4$ and it contains two unpaired electrons because CN^- is strong field anionic ligand. EAN = $22 + 12 = 34$.
 $[Cr(NH_3)_6]^{3+}$; $Cr(III) = 3d^3$ and it contains three unpaired electrons because NH_3 is strong field neutral ligand. EAN = $21 + 12 = 33$.
 (C) $[Cu(CN)_4]^{3-}$; $Cu(I) = 3d^{10}$ and all electrons are paired. CN^- is strong field anionic ligand but there is no empty d-orbital available for dsp^2 hybridisation, therefore, the hybridisation must be sp^3 . EAN = $28 + 8 = 36$.
 $[Fe(CO)_4]^{2-}$; $Fe(-II) = 3d^{10}$ and all electrons are paired because CO is strong field neutral ligand but there is no empty d-orbital available for dsp^2 hybridisation after rearrangement of 3d and 4s-electrons. Therefore, the hybridisation must be sp^3 . EAN = $26 + 2 + 8 = 36$.
 (D) $[PtCl_4]^{2-}$; $Pt(II) = 5d^8$ and all electrons are paired because of higher CFSE of $5d^8$ configuration; the hybridisation must be dsp^2 . Cl^- is weak field anionic ligand. EAN = $76 + 8 = 84$.
 $[FeF_4]^{2-}$; $Fe(II) = 3d^6$ and there are four unpaired electrons because F^- is a weak field anionic ligand. EAN = $24 + 8 = 32$.

Comprehension # 1 :

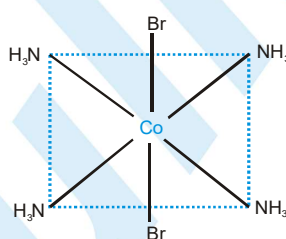
- With F^- ligand, metal ion has electron configuration, $t_{2g}^{2,1,1} e_g^{1,1}$.
So, $\mu = \sqrt{4(4+2)} \approx 4.9 \text{ BM}$; where n = number of unpaired electrons.
- Complex contains one Cl^- as counter ion.
One mole of complex = one mole of Cl^-
As two mole of Cl^- gives one mole of $PbCl_2$.
 \therefore One mole of Cl^- will give $\frac{1}{2}$ mole of $PbCl_2$.
- Only two geometrical isomers are possible of $[CoBrCl(en)_2]^+$.



Comprehension # 2 :



cis -

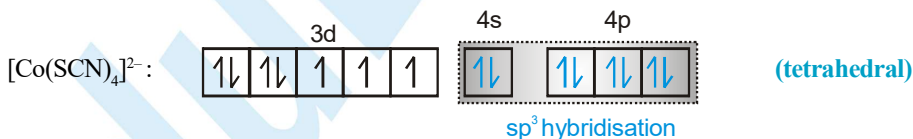


trans -

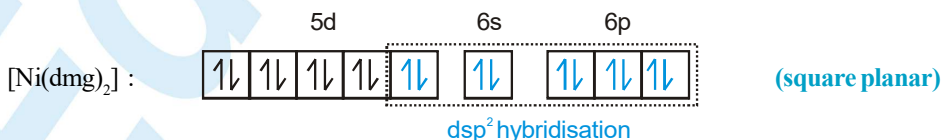
It shows geometrical isomerism but not optical isomerism due to the presence of at least one plane of symmetry. $[Co(NH_3)_4Br_2]NO_2$ and $[Co(NH_3)_4BrNO_2]Br$ are ionisation isomers and later complex reacts with $AgNO_3$ solution to give pale yellow precipitate. $[Co(NH_3)_4BrNO_2]Br$ and $[Co(NH_3)_4BrONO]Br$ are linkage isomers.

Comprehension # 3 :

- $X = [Co(SCN)_4]^{2-}$, cobalt is in +2 oxidation state and SCN^- is weak field ligand. So ,



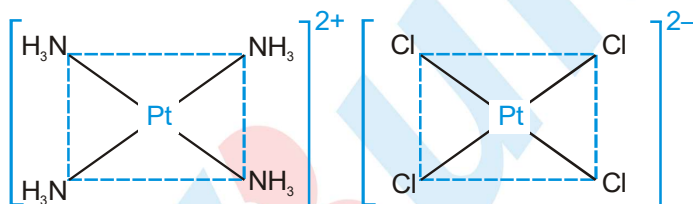
$Y = [Ni(dmg)_2]$: Nickel is in +2 oxidation state and dmg is chelating ligand. So,



$[Ni(dmg)_2]$ shows intra molecular H-bonding as shown below.

- (i) $K[PtCl_3(C_2H_4)]$ Potassium trichlorido(η²-ethylene)platinate(II)
 (j) $Cr(\pi-C_6H_6)_2$ Bis(η⁶-benzene)chromium(0)
 (k) $[Co(NH_3)_4(OH_2)_2][BF_4]_3$ Tetraamminediaquacobalt(III) tetrafluoroborate(III)
 (l) $K[(NH_3)_5Co-CN-Co(CN)_5]$ Potassium pentaamminecobaltate(II)-μ-cyanidopentacyanidocobaltate(III)
 OR
 Potassium pentaamminecobaltate(III)-μ-cyanidopentacyanidocobaltate(II)
 (m) $Na_4[Cu_6(S_2O_3)_5]$ Sodium pentakis(thiosulphato)hexacuprate(I)
 (n) $Ba[Zr(OH)_2(ONO)_2(ox)]$ Barium dihydroxidodinitrito-O-oxalatozirconate(IV)
 (o) $[Co(NH_3)_6][Co(C_2O_4)_3]$ Hexaamminecobalt(III) trioxalatocobaltate(III)

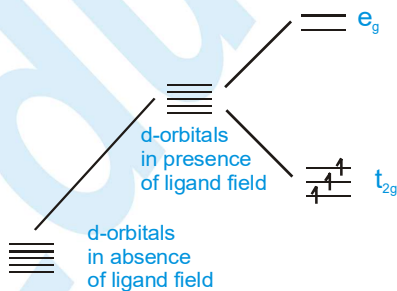
5. (a) Tetraamminezinc(II) Nitrate, $[Zn(NH_3)_4](NO_3)_2$
 (b) Tetracarbonylnickel(0), $[Ni(CO)_4]$
 (c) Potassium amminetrichloridoplatinate(II), $K[Pt(NH_3)Cl_3]$
 (d) Dicyanidoaurate(I) ion, $[Au(CN)_2]^-$
 (e) Sodium hexafluoroaluminate(III), $Na_3[AlF_6]$
 (f) Diamminesilver(I) ion, $[Ag(NH_3)_2]^+$
6. $ii < i < iv < iii$.
7. $AgNO_3 + 2PtCl_2 \cdot 2NH_3 \longrightarrow [Pt(NH_3)_4](NO_3)_2 + Ag_2[PtCl_4]$.
 It reveals that the compound may be $[Pt(NH_3)_4]^{2+} [PtCl_4]^{2-}$.



In both cationic as well as anionic complexes the hybridisation of Pt(II) ion is dsp^2 ($5d^8$ configuration has greater CFSE).

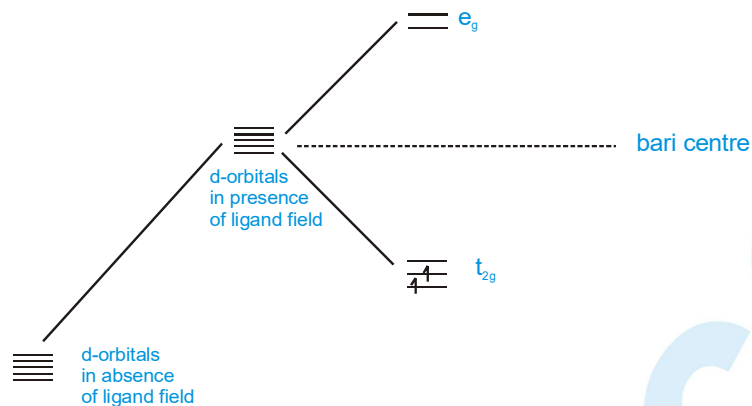
IUPAC Name : tetraammineplatinum(II) tetrachloridoplatinate(II).

8. (A) F^- is weak field ligand. Cr^{3+} , $3d^3$



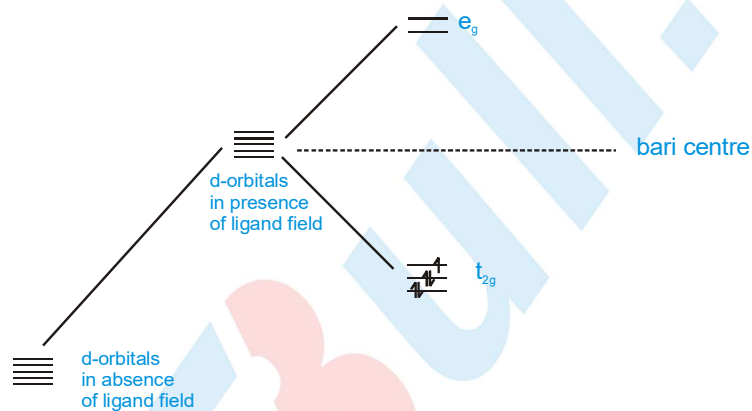
So number of unpaired electrons = 3

(B) H_2O is weak field ligand. V^{3+} , $3d^2$



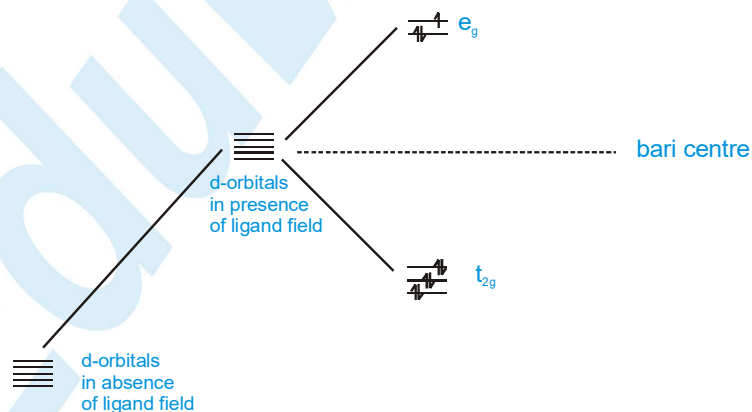
So number of unpaired electrons = **2**

(C) CN^- is strong field ligand. Fe^{3+} , $3d^5$



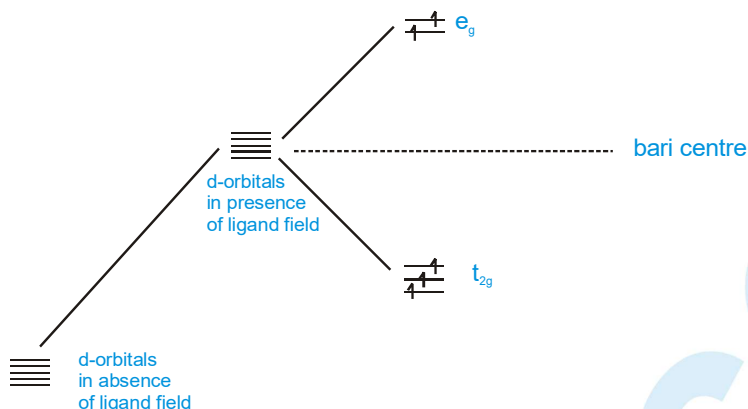
So number of unpaired electron = **1**.

(D) en is strong field ligand. Cu^{2+} , $3d^9$



So number of unpaired electron = **1**.

(E) F^- is weak field ligand. Fe^{3+} , $3d^5$



So number of unpaired electrons = 5.

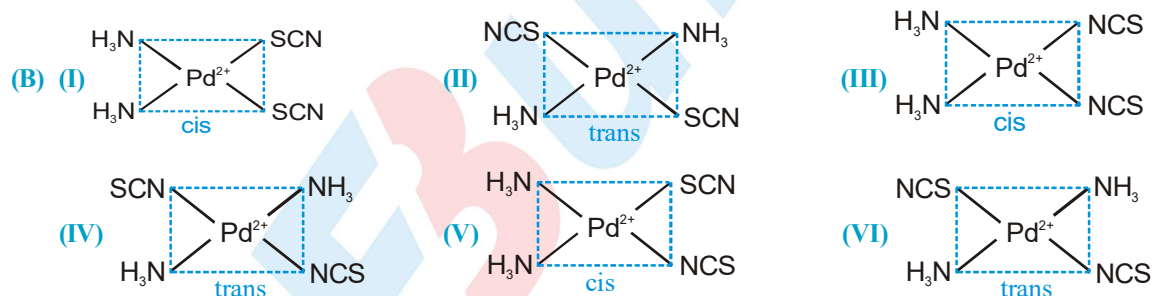
9. In the complex $[Fe(CN)_6]^{3-}$ the iron is in +3 oxidation state having d^5 configuration, so even after pairing due to strong field cyanide ligands one electron will remain unpaired and hence it is weakly paramagnetic. While in the complex $[Fe(CN)_6]^{4-}$ iron is in +2 oxidation state and having d^6 configuration, so after pairing due to strong field cyanide ligand no unpaired electron remains, so is diamagnetic.

10. (A) There are three constitutional isomers

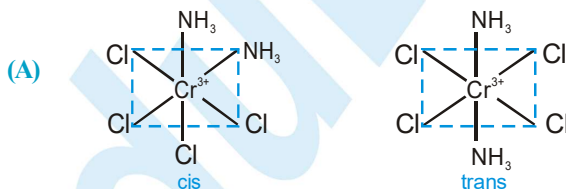
(I) $[Ru(NH_3)_5(NO_2)]Cl$ (II) $[Ru(NH_3)_5Cl](NO_2)$ or $[Ru(NH_3)_5Cl]ONO$ (III) $[Ru(NH_3)_5ONO]Cl$

(I) & (II) are ionisation isomers

(I) & (III) are linkage isomers

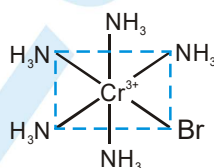


11. Diastereoisomers are stereoisomers which are not enantiomers.



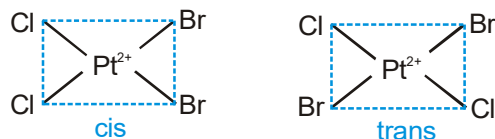
Both cis and trans isomers do not show optical activity because of the presence of plane and centre of symmetries.

(B) It will not exhibit geometrical isomerism as it exists only in one form as given below.

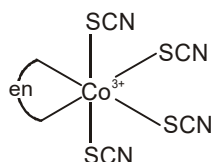


(C) In tetrahedral geometry all positions are adjacent to each other so it will not exhibit geometrical isomerism.

(D) In square planar geometry there is plane of symmetry. So it does not show optical isomerism.

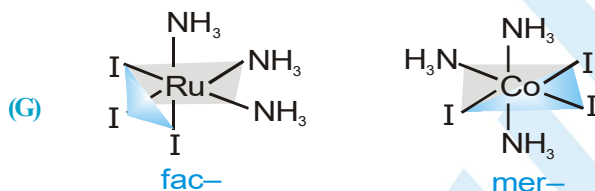


(E) It will not exhibit geometrical isomerism as it exists only in one form as given below.



(F) $\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$ is of $\text{Ma}_2\text{b}_2\text{c}_2$ type which has following isomeric forms.

(aa)(bb)(cc)
 (aa)(bc)(bc)
 (bb)(ac)(ac)
 (cc)(ab)(ab)
 (ab)(ac)(bc)



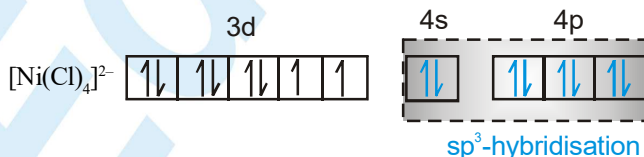
12. (I) Increases (II) Decreases

13. Octahedral complexes require d^2sp^3 hybridisation for being inner d-orbital complexes, which will not be available in d^8 configuration of Ni^{2+} , hence all complexes are outer d-orbital complexes.

14. As $3d^6$ configuration has higher CFSE as compared to $3d^7$ so it gets oxidised in presence of complexing reagent to easily have d^2sp^3 hybridisation.

15. In $[\text{Ni}(\text{CO})_4]$, Ni is in 0 oxidation state so it has $3d^84s^2$ configuration which after pairing due to strong field CO ligands will become $3d^{10}$, and hence no d orbitals are empty, it can only undergo sp^3 hybridisation leading to tetrahedral geometry. While in other given complexes Ni is in 2+ oxidation state and after pairing one vacant 3d-orbital is available for dsp^2 hybridisation because of stronger ligand CN^- . Similarly $5d^8$ configuration due to higher CFSE in Pt(II) favours pairing and thus one empty d-orbital is available.

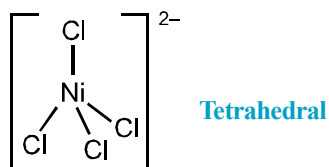
16. In $[\text{NiCl}_4]^{2-}$ nickel is in +2 oxidation state and Cl^- is weak field ligand. So,



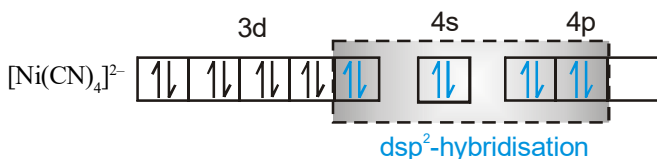
$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.82 \text{ B.M.} \quad ; \quad n = \text{No. of unpaired electrons.}$$

CHEMISTRY FOR JEE MAIN & ADVANCED

Hence with coordination number four, the structure is

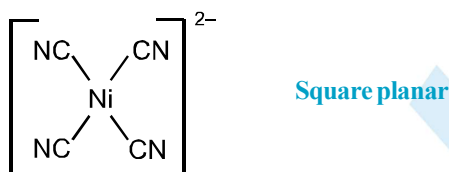


In $[\text{Ni}(\text{CN})_4]^{2-}$ nickel is in +2 oxidation state and CN^- is strong field ligand, So it compels for pairing of electrons. Then,



As all electrons are paired so diamagnetic.

Hence with coordination number four, the structure is



18. (I) $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$

A should be $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ because it is not reacting with H_2SO_4 if there would have some moles of water outer the coordination sphere then it will be reacting with H_2SO_4

(B) weight of $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr} = 266.5$

$$266.5 \times \frac{6.73}{100} = 17.96 \approx 18 \text{ (H}_2\text{O weight)}$$

It means one mole of H_2O in B complex outer the coordination sphere



(C) $266.5 \times \frac{13.5}{100} \approx 36 \text{ (2H}_2\text{O weight)}$

It means $\text{C} = [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

(II) $\text{A} = [\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$; $\text{B} = [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$; $\text{C} = [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

(III) $\text{EAN} = 33$

(IV) $\text{C} - 1 \text{ mole AgCl ppt}$; $\text{B} - 2 \text{ mole AgCl ppt}$; $\text{A} - 3 \text{ mole AgCl ppt}$

19.

(I) octahedral

(II) 3 isomers (hydrate isomers)

(III) $\mu = 3.87 \text{ PM}$

(IV) coloured

(V) $\text{EAN} = 33$

(VI) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

(VII) (A) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

Hexaaquachromium(III) chloride

(B) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$

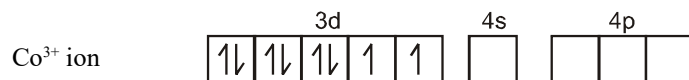
Pentaaquachloridochromium(III) chloride monohydrate

(C) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

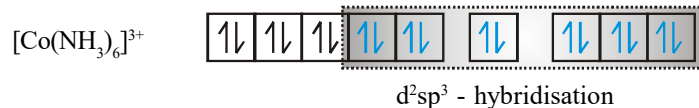
Tetraaquadichloridochromium(III) chloride dihydrate (2 - G.I.)



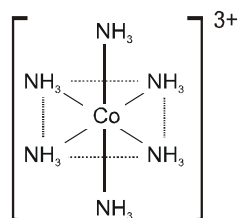
20. In $[\text{Co}(\text{NH}_3)_6]^{3+}$, the oxidation state of cobalt is +3 and coordination number is 6. So



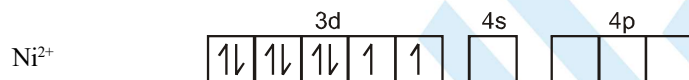
NH_3 is stronger field ligand. So it compels for the pairing of electrons. Then



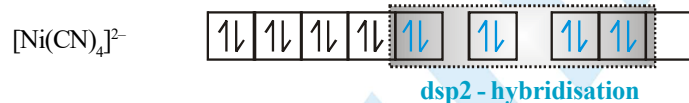
Thus with 6 coordination number, the complex $[\text{Co}(\text{NH}_3)_6]$ is octahedral as given below.



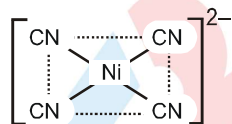
In $[\text{Ni}(\text{CN})_4]^{2-}$, the oxidation state of nickel is +2 and coordination number is 4. So



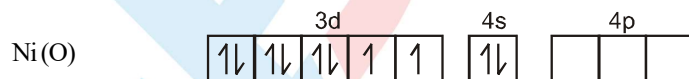
CN^- is stronger field ligand. So it compels for the pairing of electrons. Then



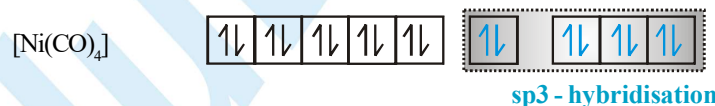
Thus with 4 coordination number four, the complex is square planar as given below



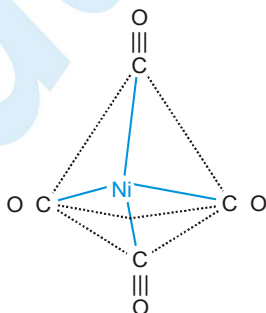
In $[\text{Ni}(\text{CO})_4]$, the oxidation state of nickel is zero and the coordination number is four. So



CO is strong field ligand. So it compels for the pairing of electrons; so nickel under goes rearrangement. Then



Thus with 4 coordination number, the complex is tetrahedral as given below.



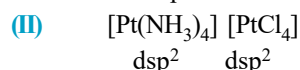
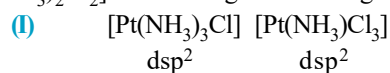
21. $[\text{Co}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3$; Cobalt is in +3 oxidation state with $3d^6$ configuration which has higher CFSE, so hybridisation is d^2sp^3 and as all d-electrons are paired, therefore, diamagnetic. Excess of F^- ions form $[\text{CoF}_6]^{3-}$. As F^- is a weak ligand, so hybridisation is sp^3d^2 and thus it has 4 unpaired electrons.

22. (A) dxy^2, dyz^2, dzx^2
 (B) $dxy^1, dyz^1, dzx^1, (dx^2 - y^2)^1, (dz^2)^1$
 (C) dxy^1, dyz^1, dzx^1

23. Blue light is absorbed and colour of the entity is yellow orange.

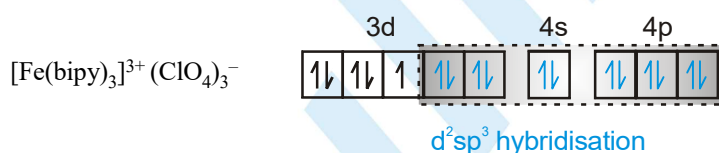
24. $\Delta_o (= 13,900 \text{ cm}^{-1}) < P (= 23,500 \text{ cm}^{-1})$, the high spin configuration would be more stable.

25. (A) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ - $5d^8$ configuration has greater CFSE ; so hybridisation is dsp^2 and geometry square planar.



(B) $1.7 = \sqrt{n(n+2)} \quad \text{or} \quad n = 1$

So there is one unpaired electron. The ligand 2, 2' bipyridyl is bidentate neutral ligand. The oxidation state of iron in the complex is +3. So,

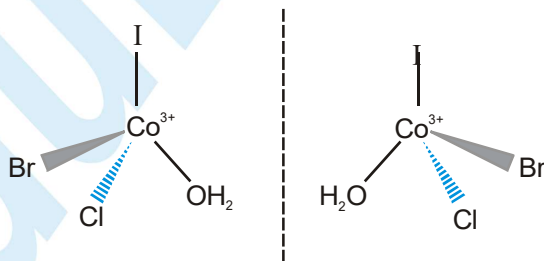


Hence the complex is inner orbital complex as it involves $(n-1)d$ orbitals in hybridisation.

26. Although the lanthanide ions have a high charge (+3) yet the size of their ions is very large (yielding small charge to size ratio). As a consequence, they have poor tendency to form complexes. They form complexes mainly with chelating agents such as β -diketones, EDTA etc.

27. (I) There are only four ligands instead of six, so the ligand field is only two thirds size; hence the ligand field splitting is also two thirds the size.
 (II) The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further two thirds.
 Hence $\Delta_t = 2/3 \times 2/3 = 4/9 \Delta_o$

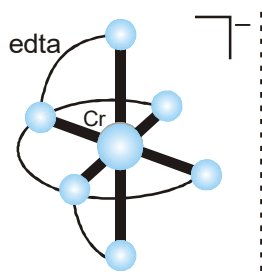
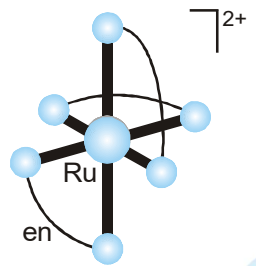
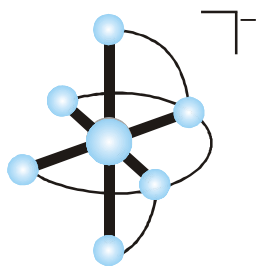
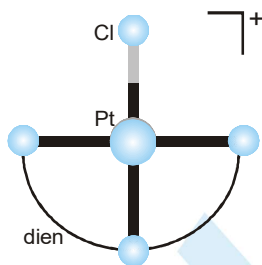
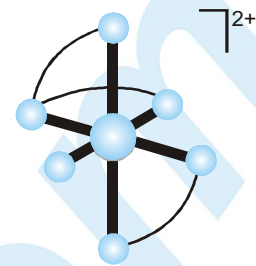
28. No isomers with $[\text{CoCl}_2\text{Br}_2]^-$ or $[\text{CoCl}_2\text{Br}(\text{OH}_2)]$ but two optical isomers for $[\text{CoClBrI}(\text{OH}_2)]$ possible.



29. Hydrate isomers : $[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_2)] \text{NO}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_6](\text{NO}_2)_2$
 Linkage isomer : $[\text{Cr}(\text{H}_2\text{O})_5(\text{ONO})] \text{NO}_2 \cdot \text{H}_2\text{O}$.

30.

(A)

 $[\text{Cr}(\text{edta})]^-$ enantiomers $[\text{Ru}(\text{en})_3]^{2+}$ enantiomers $[\text{Pt}(\text{dien})]^+$

diethylenetriamine

dien

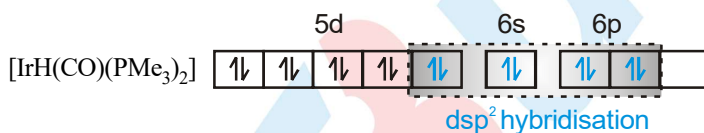
 $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$

tridentate

Neither $[\text{Cr}(\text{edta})]^-$ nor $[\text{Ru}(\text{en})_3]^{2+}$ has a mirror plane or a centre of inversion; so both are chiral (they also have no higher S_n axis); $[\text{Pt}(\text{dien})\text{Cl}]^+$ has a plane of symmetry and hence is achiral.

(B) Carbonylhydridobis(trimethylphosphine)irridium(I).

Ir is in +1 oxidation state; $5d^8$ configuration has higher CFSE and thus the complex is square planar.



Geometry = Square planar

Magnetic moment = 0 (all electrons are paired).

31.

Complex is $\text{Co}(\text{en})_2\text{Cl}_2\text{NO}_2$ and will show ionisation isomerism, linkage isomerism, geometrical isomerism and optical isomerism.

Linkage : Point of attachment is through either O or N

Ionisation : $[\text{CoCl}_2(\text{en})_2]\text{NO}_2$

$[\text{CoCl}(\text{en})_2\text{NO}_2]\text{Cl}$

Geometrical : (A) $[\text{CoCl}_2(\text{en})_2]\text{NO}_2$ cis and trans

(B) $[\text{CoCl}(\text{en})_2\text{NO}_2]\text{Cl}$ cis and trans

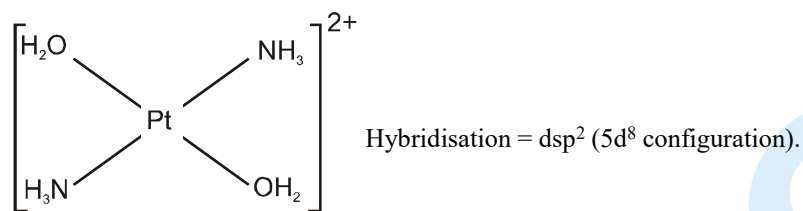
(C) $[\text{CoCl}(\text{en})_2\text{ONO}]\text{Cl}$ cis and trans

Optical : (A) Cis form will show optical isomerism

(B) Cis-trans both will show optical isomerisms

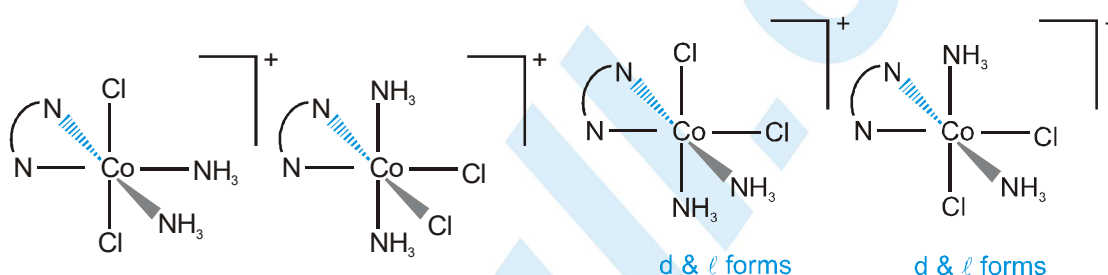
(C) Cis-trans both will show optical isomerisms

32. As complex $[\text{Pt}(\text{NH}_3)_2(\text{OH}_2)_2]^{2+}$ does not react with ethylenediamine to give a chelated complex, it should be its trans isomer having the structure as given below. A reasonable explanation for this is that 'en' molecule cannot reach across the square plane to bridge two trans positions.



IUPAC Name : trans-diamminediaquaplatinum(II).

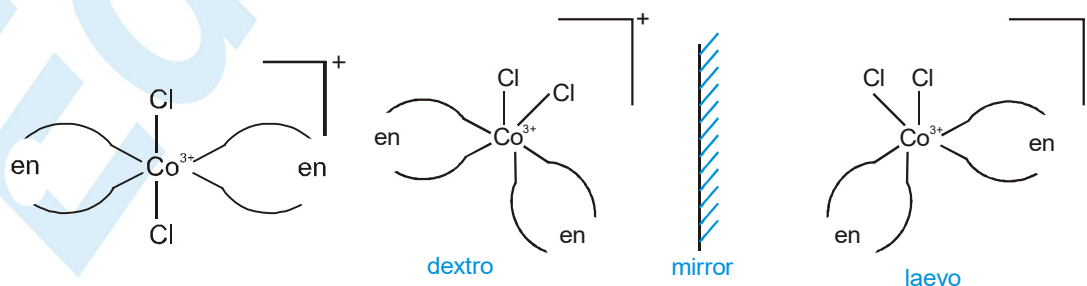
33. cis, trans and optical isomers are possible.



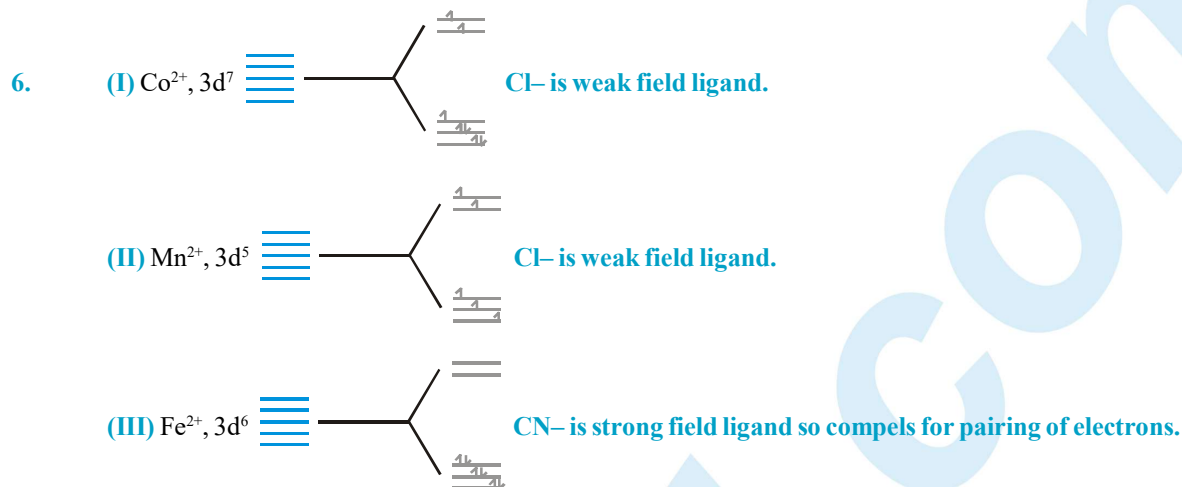
EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

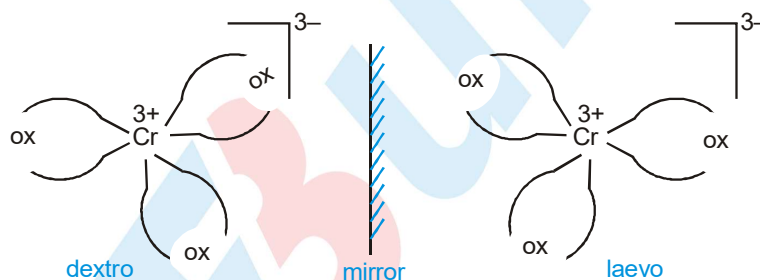
- $4\text{K}^+[\text{Ni}(\text{CN})_4]^{4-}$; let the oxidation state of nickel is x , then $x + 4(-1) = -4$
So, $x = 0$
- Coordination number of a central metal atom in a complex is the number of σ -bonds between metal M and ligand L .
- $[\text{Ni}(\text{NH}_3)_6]^{2+}$ has sp^3d^2 hybridisation having 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.
- Chlorophyll a green pigment in plants contains Mg .
- (1) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ 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).

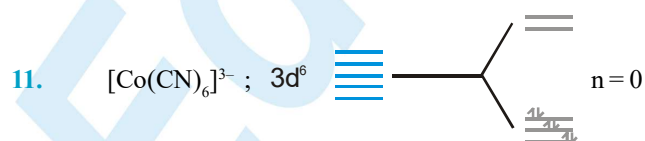


7. $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$; let the oxidation state of Cr is x, then $x + 4(-0) + 2(-1) = +1$
 So, $x = 3$
8. $3\text{K}^+ + [\text{Fe}(\text{III})(\text{CN})_6]^{3-}$ now follow IUPAC nomenclature.
9. (3) Due to the absence of symmetry elements it shows optical isomerism.



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

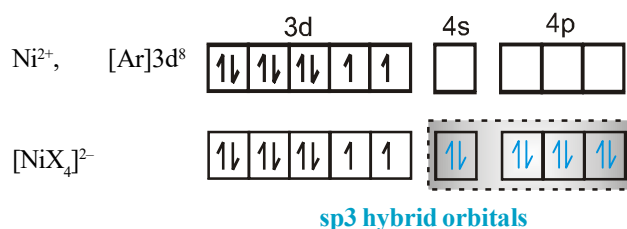
$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.84 \text{ B.M}$$



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

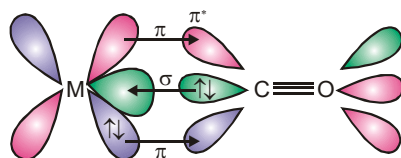
12. If X^- is weak field then (say Cl^-) $[\text{Ni}(\text{Cl})_4]^{2-}$ is tetrahedral (sp^3) with two unpaired electrons. If X^- is strong field ligand then (say CN^-), $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar (dsp^2) with no unpaired electrons. Also given $[\text{NiX}_4]^{2-}$ is paramagnetic.

So,



13. $[\text{Co}(\text{III})(\text{NO}_2)(\text{NH}_3)_5]^{2+} + 2\text{Cl}^-$ and now follow IUPAC rules.

14. Metal-carbon bond in metal carbonyls has σ as well as π characters.



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



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

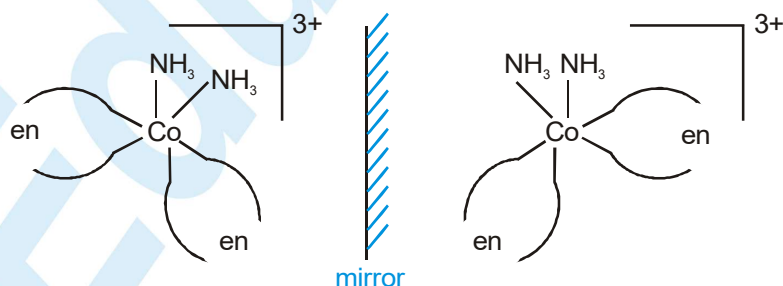
$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.84 \text{ B.M}$$

17. 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.

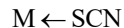
18. Let oxidation state of E is x so $x + (-2) + 0 = +1$ or $x = +3$
 Coordination number is number of σ -bonds between metal ion and ligands. 'en' and 'ox' are bidentate ligands Thus ;
 coordination number of E = $4 + 2 = 6$.

19. 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 $\text{C}_2\text{O}_4^{3-} < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$.
 Thus the (4) option is correct.

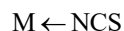
20. cis-form of $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$ has optical isomers.



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

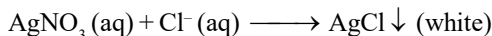


thiocyanato or thiocyanato-S



isothiocyanato or thiocyanato-N

22. Mole of $\text{CoCl}_3 \cdot 6\text{NH}_3 = \frac{2.675}{267.5} = 0.01$



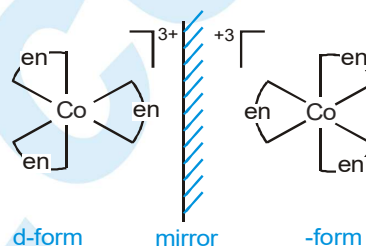
$$\text{Mole of AgCl} = \frac{4.78}{143.5} = 0.03$$

0.01 mole of $\text{CoCl}_3 \cdot 6\text{NH}_3$ gives 0.03 mole of AgCl

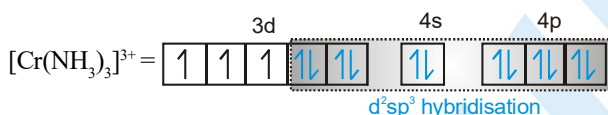
\therefore 1 mole of $\text{CoCl}_3 \cdot 6\text{NH}_3$ ionises to give 3 moles of Cl^- .

Hence the formula of compound is $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$.

23. Complex $[\text{Co}(\text{en})_3]^{3+}$ lacks plane of symmetry and thus is optically active having following to enantiomeric forms.



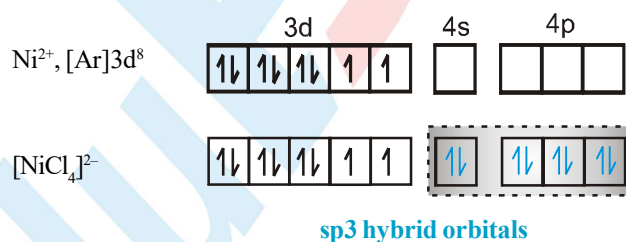
24. In case of d^3 configuration, the number of unpaired electrons remains 3 whether the ligand is strong field or weak field. The hybridisation scheme can be shown as follow :



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

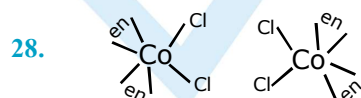
$$3.93 = \sqrt{n(n+2)} ; \text{ so } n = 3 \text{ (here } n \text{ is number of unpaired electron(s)).}$$

25. In the paramagnetic and tetrahedral complex $[\text{NiCl}_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in figure.



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

26. $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$
dibromidobis(ethylenediamine)chromium(III) Bromide.
27. $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ show facial as well as meridional isomerism. But both contain plane of symmetry.
So, the answer is (3).



29. $\text{Cr} = 3d^5 4s^1$
 $\text{Cr}^{+2} = 3d^4 4s^0$
 $\text{Fe}^{+2} = 3d^6 4s^0$
Hence both have same number of unpaired electron.

30. Moles of complex = $\frac{\text{Molarity} \times \text{volume (ml)}}{1000}$

$$= \frac{100 \times 0.1}{1000} = 0.01 \text{ mole}$$

$$\text{Moles of ions precipitated with excess of } \text{AgNO}_3 = \frac{1.2 \times 10^{22}}{6.02 \times 10^{23}} = 0.02$$

$$\text{Number of } \text{Cl}^- \text{ present in ionization sphere} = \frac{\text{Mole of ion precipitated with excess } \text{AgNO}_3}{\text{mole of complex}} = \frac{0.02}{0.01} = 2$$

It means 2Cl^- ions present in ionization sphere

\therefore complex is $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$

31. (i) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$: Hexaaquachromium (III) chloride

$$x + 6 \times 0 + (-1) \times 3 = 0 \Rightarrow x = +3$$

(ii) $[\text{Cr}(\text{C}_6\text{H}_6)_2]$: bis(η^6 -benzene) chromium (0)

$$y + 2 \times 0 = 0 \Rightarrow y = 0$$

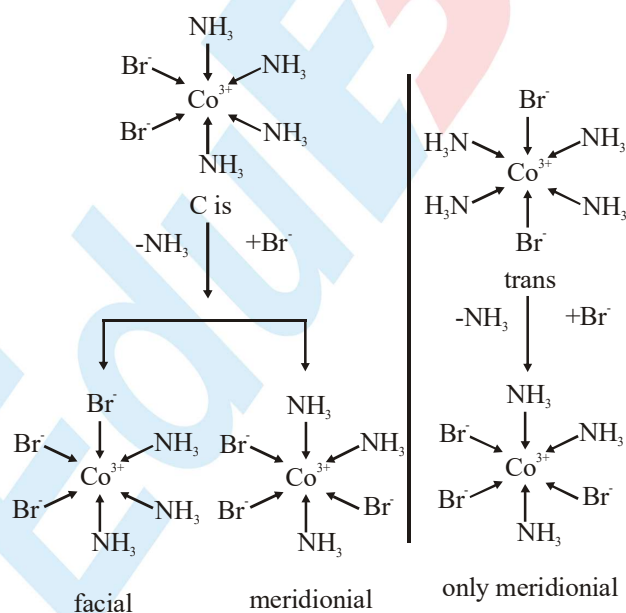
(iii) $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O})_2(\text{O}_2)(\text{NH}_3)]$:

Potassium amminedicyanidodioxidoperoxidochromate (VI)

$$2 \times 1 + z + 2 \times (-1) + 2 \times (-2) + (-2) + 0 = 0 \Rightarrow z = +6$$

The oxidation states of Cr in $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ and $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O})_2(\text{O}_2)(\text{NH}_3)]$ respectively are +3, 0 and +6.

32.

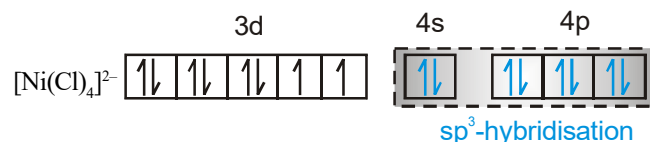


Part # II : IIT-JEE ADVANCED

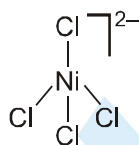
1. In $[\text{NiCl}_4]^{2-}$, the Ni is in +2 oxidation state.



Cl^- is a weak field ligand. So,



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

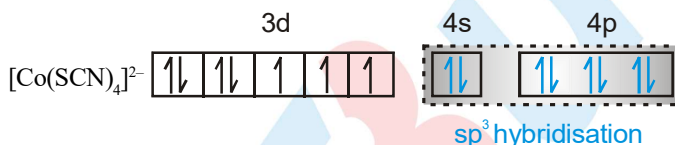


$[\text{PdCl}_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Pd}(\text{CN})_4]^{2-}$ are square planar.

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

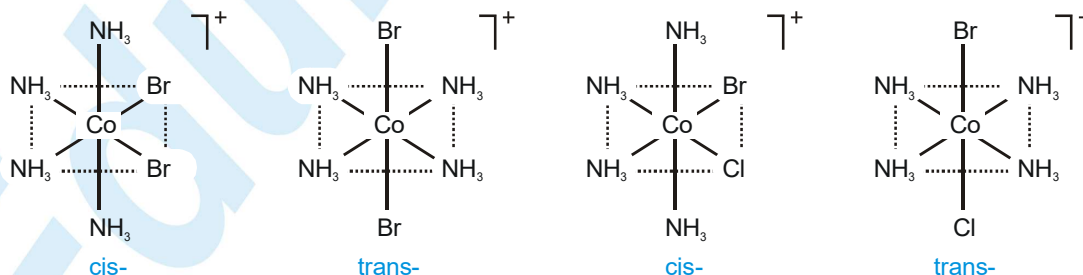


SCN^- is weak field ligand so,

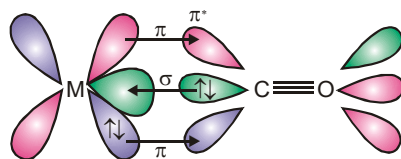


As it contains three unpaired electrons, so $\mu = \sqrt{3(3+2)} = \sqrt{15}$.

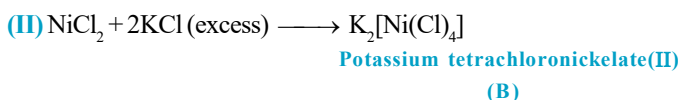
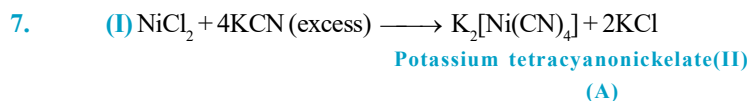
4. (A) Br^- and Cl^- can be exchanged between coordination and ionization spheres, thus show ionisation isomerism. Show geometrical isomerism (as it is Ma_4b_2 type) but not optical isomerism due to the presence of one of the symmetry of elements. Each complex has one cis- and one trans- isomers.



6. 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.

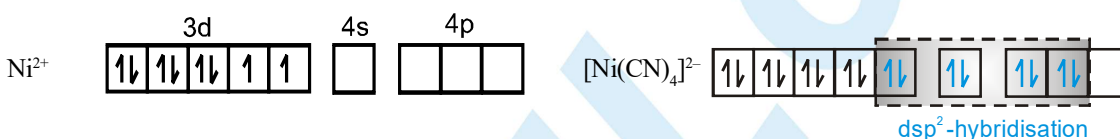


Synergic bonding



8. Refer above solutions.

9. (C) In cyano complex, $\text{K}_2[\text{Ni(CN)}_4]$, complex ion is $[\text{Ni(CN)}_4]^{2-}$ and Ni is present as Ni^{2+} or Ni (II) and CN^- is strong field ligand. Thus it compels for pairing of electrons. So,



It does not contain unpaired electron. So it is diamagnetic in character and has square planar geometry.

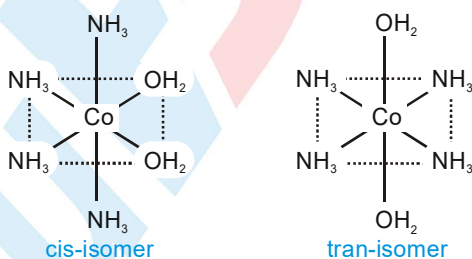
In chloro complex, $\text{K}_2[\text{Ni(Cl)}_4]$, complex ion is $[\text{Ni(Cl)}_4]^{2-}$ and Ni is present as Ni^{2+} or Ni (II) and Cl^- is weak field ligand. So,



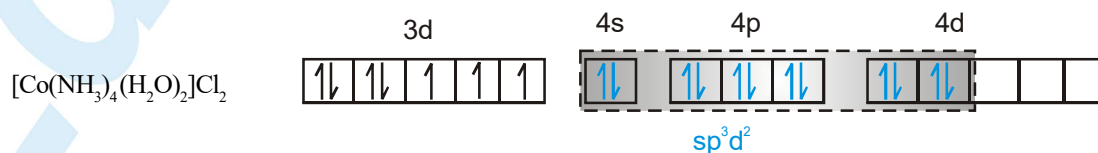
It contains two unpaired electrons. So it is paramagnetic in character and has tetrahedral geometry.

10. 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 $[\text{V(CO)}_6]^-$.

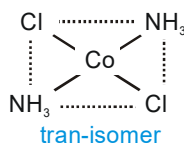
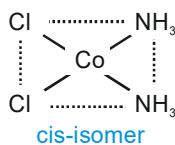
11. (A) $[\text{Co(NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}_2]$, it shows geometrical isomerism



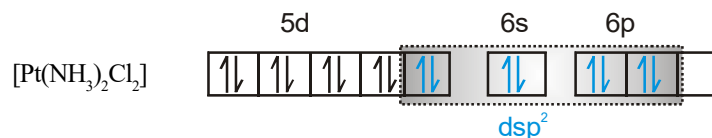
Co is in +2 oxidation state with $[\text{Ar}]^{18} 3d^7 4s^0$ electron configuration ; so complex is paramagnetic .
So,



(B) $[\text{Pt(NH}_3)_2\text{Cl}_2]$, it show geometrical isomers.

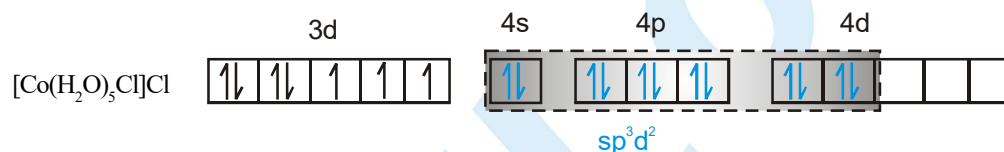


Pt is in +2 oxidation state and because of $5d^8$ configuration, it has higher CFSE. So $\Delta_0 > P$ and thus,



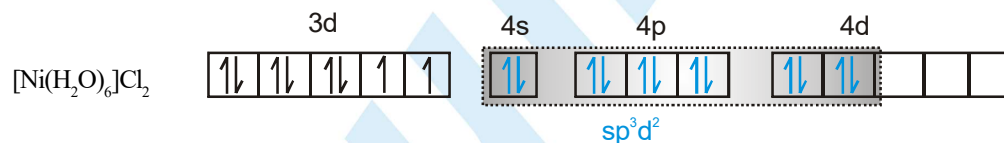
As all electrons are paired so it is diamagnetic.

- (C) [Co(H₂O)₅Cl]Cl, it does not show geometrical isomerism. Co is in +2 oxidation state and because H₂O is weak field ligand. So,



As it contains 3 unpaired electrons so it is paramagnetic.

- (D) [Ni(H₂O)₆]Cl₂, it does not show geometrical isomerism. Ni is in +2 oxidation state and because H₂O is weak field ligand. So,

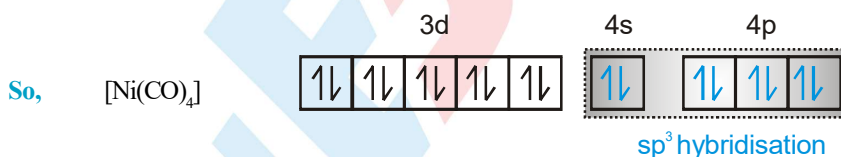


As it contains two unpaired electrons ; so it is paramagnetic.

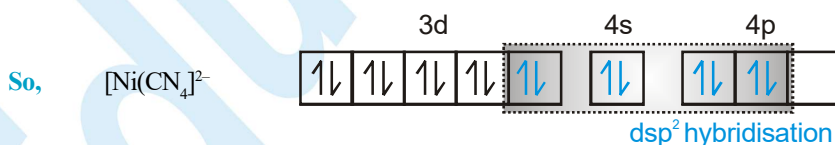
12. The IUPAC name of [Ni(NH₃)₄]²⁺ [NiCl₄]²⁻ is Tetraamminenickel(II) tetrachloronickelate (II).

13. Ni (28) → 1s², 2s²2p⁶, 3s²3p⁶3d⁸, 4s²

In [Ni(CO)₄], Ni is in zero oxidation state and CO being strong field ligand compels for pairing of electrons.



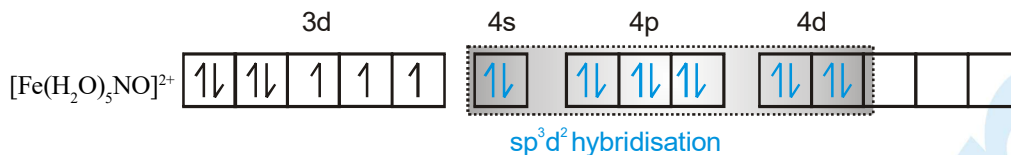
In [Ni(CN)₄]²⁻, Ni is in +2 oxidation state and CN⁻ being strong field ligand compels for pairing of electrons.



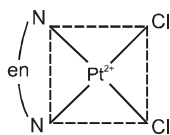
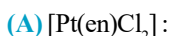
14. Both Cis- and trans forms of complex [M(NH₃)₄Cl₂] are optically inactive because of the presence of plane of symmetry and centre of symmetry in them.

Both geometrical isomers of the complex [M(NH₃)₄Cl₂] have alternate axis of symmetry.

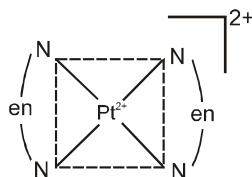
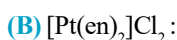
15. In [Fe(H₂O)₅NO]⁺SO₄⁻, Fe is in +1 oxidation state and water is weak field ligand. So,



As it contains three unpaired electrons, the complex is paramagnetic.

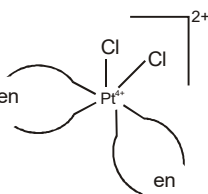
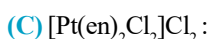


exists only in one form.

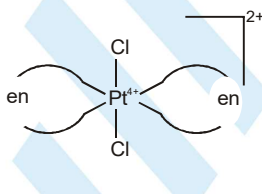


exists only in one form

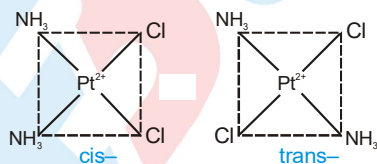
('en' is symmetrical ligand).



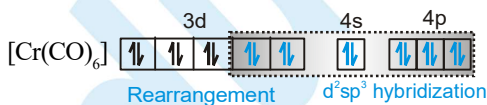
cis-



trans-



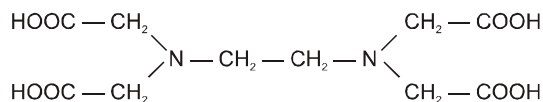
The chromium is in zero oxidation state having configuration $[\text{Ar}]^{18} 3d^5 4s^1$. The CO is a strong field ligand so compels for the pairing of electrons. Thus the complex has $d^2 sp^3$ hybridisation and is diamagnetic.



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



Structure of EDTA is :



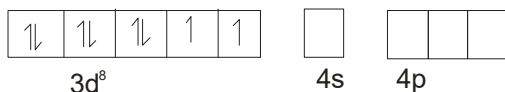
The ionisation isomer for the given compound will be obtained by exchanging ligand with counter ion as :



20. Ni : $3d^8 4s^2$

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

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

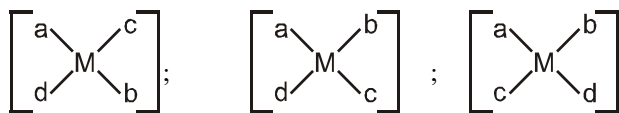


$N = 2$

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

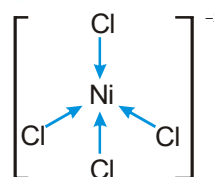
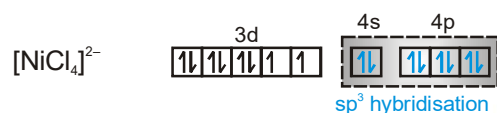
21. $[M(abcd)]$ complex is square planar, so will have 3 geometrical isomers.

(I) (a T b) (c T d) ; (II) (a T c) (b T d) ; (III) (a T d) (b T c)



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

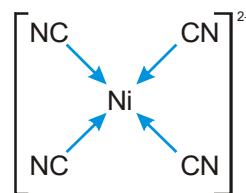
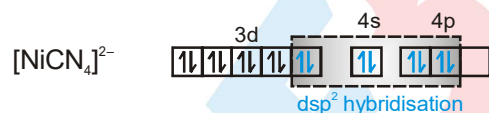
$[NiCl_4]^{2-}$; $3d^8$ electron configuration with nickel in +2 oxidation state. Cl^- being weak field ligand does not compel for pairing of electrons. So,



Hence, complex has tetrahedral geometry.

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

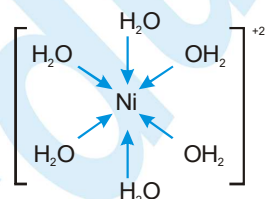
$[Ni(CN)_4]^{2-}$; $3d^8$ electron configuration with nickel in +2 oxidation state. CN^- being strong field ligand compels for pairing of electrons. So,



Hence, complex has square planar geometry.

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

$[Ni(H_2O)_6]^{2+}$; $3d^8$ 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.

23. $K-[Fe(CN)_6]^{3-}$; $3d^5$ electron configuration after pairing of electrons for d^2sp^3 hybridisation it contains one unpaired electrons.

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

M-[Co(ox)₃]³⁻ : 3d⁶ electron configuration, d²sp³, diamagnetic.

N-[Ni(H₂O)₆]²⁺ : 3d⁸ electron configuration, sp³d², with two unpaired electrons paramagnetic.

O-[Pt(CN)₄]²⁻ : 5d⁸ electron configuration, dsp², diamagnetic.

P-[Zn(H₂O)₆]²⁺ : 3d¹⁰ electron configuration, sp³d², diamagnetic.

24. m moles of [Cr(H₂O)₅Cl]Cl₂ = 0.01 × 30 = 0.3.

$$\Rightarrow \text{mmole of Cl}^- = 0.3 \times 2 = 0.6$$

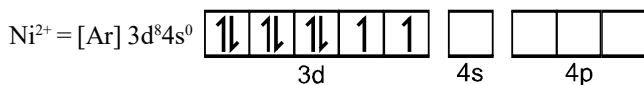
$$\Rightarrow \text{mmole of Ag}^+ = \text{mmoles of Cl}^-$$

$$\Rightarrow 0.1 \times V = 0.6$$

$$\Rightarrow V = 6 \text{ mL.}$$

25. [Co(H₂O)₄(NH₃)₂]Cl₃ = diamminetetraaquacobalt (III) chloride

26. [NiCl₂ {PEt₂Ph}] contains Ni²⁺ with electronic configuration



In high spin state, it is paramagnetic, sp³ hybridised, tetrahedral.

In low spin state, it is diamagnetic, dsp², square planar.

27. P=[FeF₆]³⁻ ox. no. of Fe = +3, configuration : - 3d⁵ 4s⁰

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

so it has 5 unpaired electron

Q=[V(H₂O)₆]²⁺ ox. no. of V = +2, configuration 3d³ 4s⁰

It has 3 unpaired electrons.

R=[Fe(H₂O)₆]²⁺, ox. no. of Fe = +2, configuration 3d⁶, 4s⁰

As H₂O is weak ligand, pairing does not take place, so it has 4 unpaired electron

⇒ order of spin only magnetic moment

$$\Rightarrow Q < R < P$$

so, answer is (B).

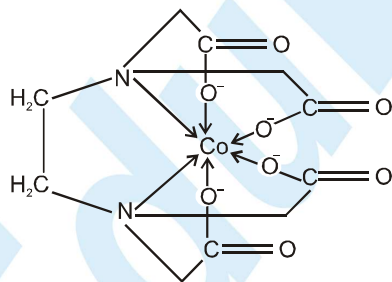
28. (A) [Cr(NH₃)₅Cl]Cl₂ and [Cr(NH₃)₄Cl₂]Cl, both compounds will not show either structural or stereoisomerism.

(B) [Co(NH₃)₄Cl₂]⁺ and [Pt(NH₃)₂(H₂O)Cl]⁺, Ma₄b₂ type (octahedral), Ma₂bc type (square planar) and both will show geometrical isomerism.

(C) [CoBr₂Cl₂]²⁻ and [PtBr₂Cl₂]²⁻, Ma₂b₂ type (tetrahedral), Ma₂b₂ (square planar).

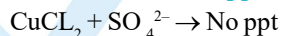
(D) [Pt(NH₃)₃(NO₃)]Cl and [Pt(NH₃)₃Cl]Br both will show ionisation isomerism.

29.



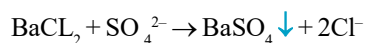
30. (A) CuCl₂ + S²⁻ → CuS ↓ + 2Cl⁻

Black ppt.

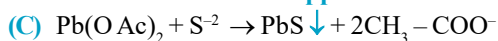


(B) BaCl₂ + S²⁻ → BaS + 2Cl⁻

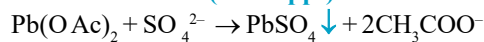
No ppt.



white ppt.



(Black ppt)

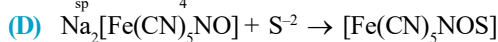


(White ppt)

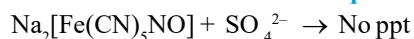
PbS can be selective ppt out first as K_{sp} is much less than K_{sp} of PbSO_4 .

$$K_{sp} \text{ of } \text{PbS} = 3 \times 10^{-28}$$

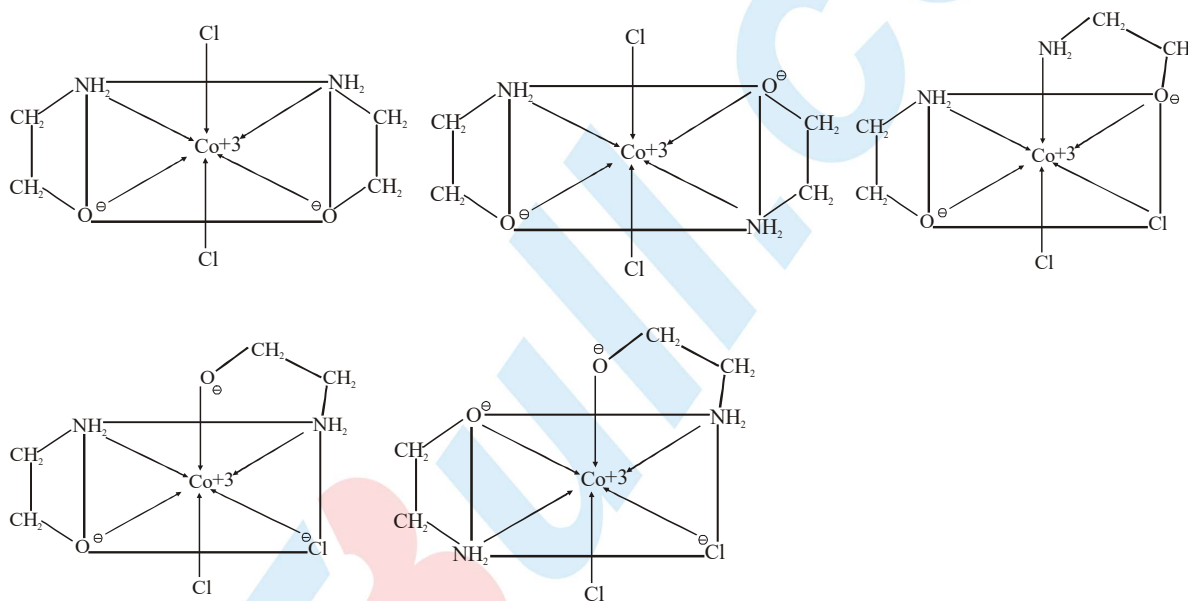
$$K_{sp} \text{ of } \text{PbSO}_4 = 25 \times 10^{-8}$$



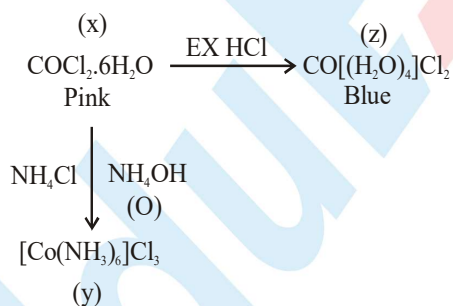
Purple colour



31.



32. Cobalt salts are pink in anhydrous & blue in hydrated form.



33. $\Rightarrow \text{Fe}(\text{CO})_5$: Total number of valence electrons is 18

: low spin complex

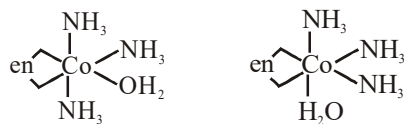
$\Rightarrow \text{Ni}(\text{CO})_4$: Total number of valence electrons is 18

: low spin complex

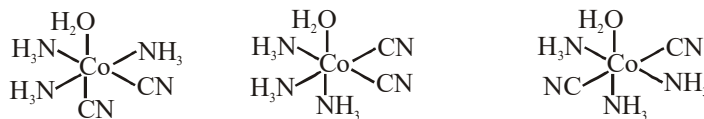
\Rightarrow Metal - carbonyl bond strengthens when the oxidation state of metal is lowered.

\Rightarrow The carbonyl C-O bond is stronger in case of increased oxidation state of metal.

34. (A) $[\text{Co(en)}(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ has 2 geometrical isomers



- (B) Compound $[\text{Co}(\text{CN})_2(\text{NH}_3)_3(\text{H}_2\text{O})]^+$ will have three geometrical isomers.



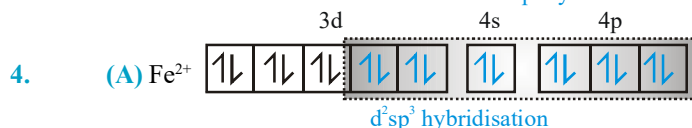
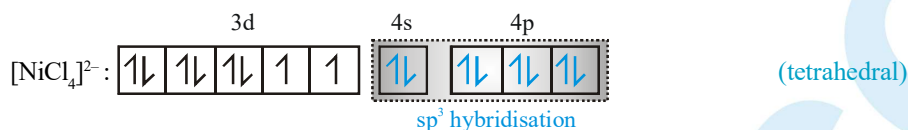
- (C) $[\text{Co(en)}(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ is diamagnetic

- (D) $[\text{Co(en)}(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ absorbs light at longer wavelength as compared to $[\text{Co(en)}(\text{NH}_3)_4]^{3+}$ as H_2O is weaker ligand than NH_3 .

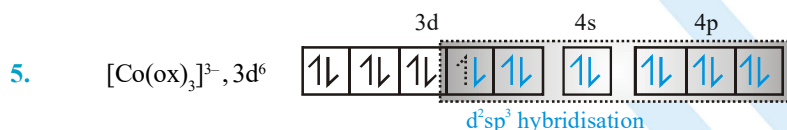
35. 1. FeF_6^{4-} , $3d^6$ & weak field ligand
 \therefore Hybridization is sp^3d^2
2. $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$, $3d^1$ & weak field ligand
 \therefore Hybridization is d^2sp^3
3. $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $3d^3$ & strong field ligand
 \therefore Hybridization is d^2sp^3
4. $[\text{FeCl}_4]^{2-}$, $3d^6$ & weak field ligand
 \therefore Hybridization is sp^3
5. $\text{Ni}(\text{CO})_4$, $3d^{10}$
 \therefore Hybridization is sp^3
6. $[\text{Ni}(\text{CN})_4]^{2-}$, $3d^8$
 \therefore dsp^2 hybridization

MOCK TEST

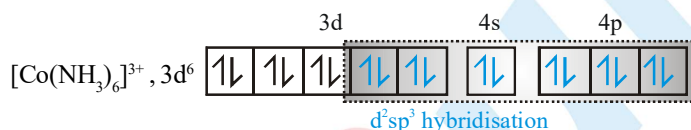
- (P) $\rightarrow \text{Fe}^{3+}$, $n = 5$; (Q) Co^{3+} , $n = 4$
 (Q) $\rightarrow \text{V}^{3+}$, $n = 2$; (S) Ti^{3+} , $n = 1$
 $n = \text{no. of unpaired electrons}$
- (A) ${}_{22}\text{Ti}^{4+}$ E.C. = $3d^0 4s^0$ colourless (B) ${}_{29}\text{Cu}^+$ E.C. = $3d^{10} 4s^0$ colourless
 (C) ${}_{24}\text{Cr}^{3+}$ E.C. = $3d^3 4s^0$ coloured (most likely) (D) ${}_{23}\text{V}^{3+}$ E.C. = $3d^2 4s^0$ coloured (most likely)
- (A), (B) and (C) dsp^2 hybridisation while (D) is sp^3 , Cl^- is weak field ligand, so



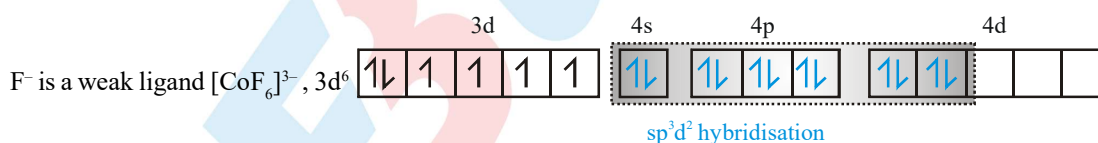
All electrons are paired, so diamagnetic.



All electrons are paired, so diamagnetic.



All electrons are paired, so diamagnetic.

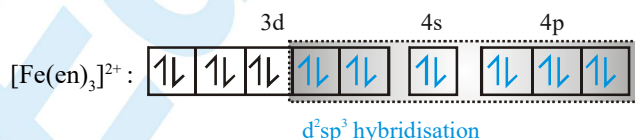


It contains four unpaired electrons, so it is paramagnetic.

- $\text{Ni}(\text{CO})_4 - sp^3$ (CO strong field ligand) ; $[\text{AgF}_4]^- - dsp^2$ ($4d^8$ electron configuration) ;
 $[\text{Zn}(\text{CN})_4]^{2-} - sp^3$ ($3d^{10}$ electron configuration) ; $[\text{PtCl}_4]^{2-} - dsp^2$ ($5d^8$ electron configuration) ;
 $[\text{RhCl}(\text{PPh}_3)_3] - dsp^2$ ($4d^8$ electron configuration)

all complexes are diamagnetic in nature which show decrease in their weights in magnetic field.

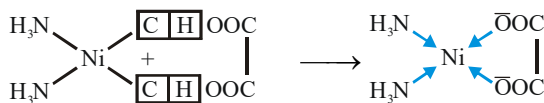
- Complex is $[\text{Fe}(\text{en})_3]^{2+}$; as 'en' is a strong field ligand pairing of electrons will take place.



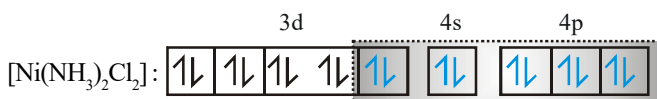
Hence, hybridisation is d^2sp^3 and complex is diamagnetic. As it has 3 bidentate symmetrical 'en' ligands so it will not show geometrical isomerism.

CHEMISTRY FOR JEE MAIN & ADVANCED

8. Oxalato being bidentate ligand cannot attach to nickel in trans-position. Thus the cis-form of compound will react with oxalic acid as given in the following reaction.



NH_3 is stronger ligand. So,



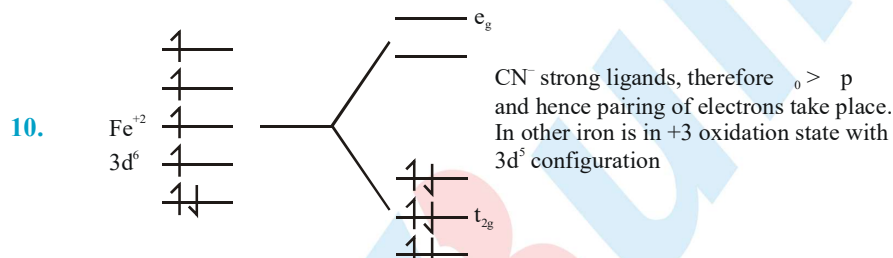
dsp^2 hybridisation

Hence the complex will have square planar geometry and will show geometrical isomerism, cis and trans. cis $\neq \mu = 0$, polar and trans $\mu = 0$, non-polar.

9. It shows geometrical, ionisation and linkage isomers.

$\text{NO}_2 - \text{NO}_2$	cis-trans.
$\text{NO}_2 - \text{ONO}$	cis-trans.
$\text{ONO} - \text{ONO}$	cis-trans.
$\text{NO}_2 - \text{NO}_3$	cis-trans.
$\text{ONO} - \text{NO}_3$	cis-trans.

Total number of isomers = 10.



11. (A) $\Delta_0 \propto$ strength of ligand. CN^- is stronger field than H_2O . So Δ_0 of $[\text{Co}(\text{CN})_6]^{3-} > [\text{Co}(\text{H}_2\text{O})_6]^{3+}$.

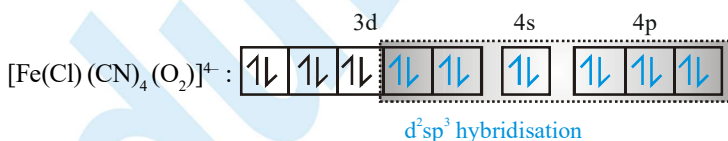
(B) $\Delta_0 \propto$ oxidation state of central metal ion. So Δ_0 of $[\text{Co}(\text{H}_2\text{O})_6]^{2+} < [\text{Co}(\text{H}_2\text{O})_6]^{3+}$

Note: $\Delta_0 \propto$ principal quantum number of central metal atom/ion i.e. n.

12. $[\text{Rh}^{\text{I}}\text{Cl}(\text{PPh}_3)_3] + \text{H}_2 \longrightarrow [\text{Rh}^{\text{III}}\text{ClH}_2(\text{PPh}_3)_3]$

$[\text{Rh}^{\text{III}}\text{ClH}_2(\text{PPh}_3)_3]$ gives electronic configuration of $t_{2g}^{2,2,2}, e_g^{0,0}$, inner orbital complex and thus to have two d-orbital empty, electrons will pair up and give d^2sp^3 hybridisation. Rh^{I} with C. N = 4 has dsp^2 hybridisation (4d series element)

13. CN^- is strong field ligand so complex for pairing of electrons. So,



d^2sp^3 hybridisation

(A) No unpaired electrons in Fe^{2+} but O_2^- , has unpaired electron

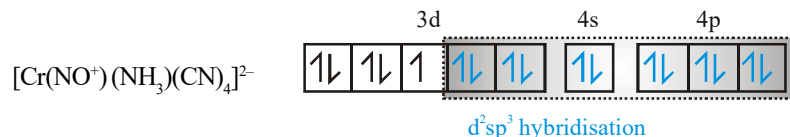
(B) (O_2^-) is O_2^- i.e. superoxide ion which has B.O (1.5) less than O_2 molecule (2.0) and thus this statement is correct.

(C) Total negative charge of negative ligands in coordination sphere is -6 . So oxidation state of Fe is (II) and thus its IUPAC name is correct.

(D) It has a plane of symmetry, thus does not show optical isomerism.

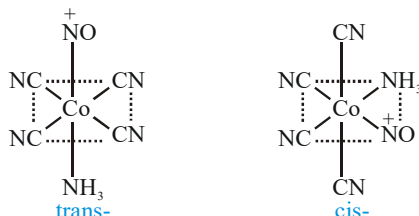
14. Option (A) is correct according to IUPAC nomenclature.

Ni is in +1 oxidation state and CN^- is strong field ligand. So,

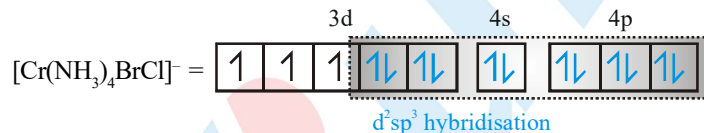


One electron is unpaired in 3d subshell, so magnetic moment = $\sqrt{1(1+2)} = \sqrt{3}$ B.M.

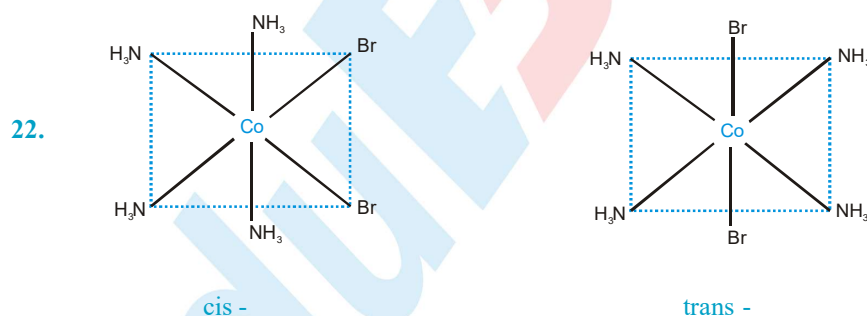
It can exist in two geometrical isomers as given below.



15. S_1 and S_3 are correct statements. S_2 V.B.T. does not give any interpretation about the relative thermodynamic stabilities of various complexes. This is one of the limitation of V.B.T.
16. **S1** : Has plane of symmetry, therefore, does not show optical isomerism.
S2 and S_3 are correct statements.
17. **S1** : $[\text{CoF}_6]^{3-}$ is paramagnetic with 5 unpaired electrons but $[\text{Co}(\text{ox})_3]^{3-}$ is diamagnetic as all electrons are paired.
S2 : It exists as $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
S3 : It is correct statement.
S4 : $[\text{Fe}(\text{+I})(\text{H}_2\text{O})_5\text{NO}^+]\text{SO}_4^{2-}$
20. Cr^{3+} having $3d^3$ configuration always have 3 unpaired electrons with strong field as well as weak field ligands.

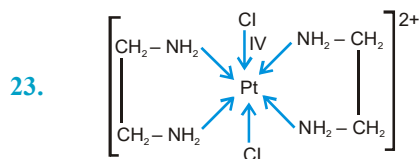


21. It is homogeneous catalyst for hydrogenation of alkenes.

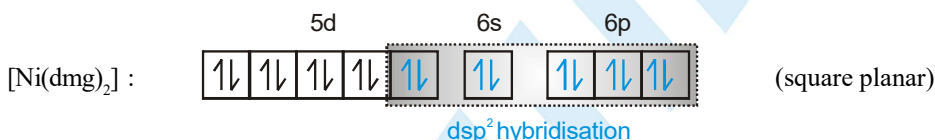
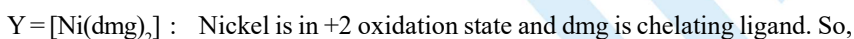
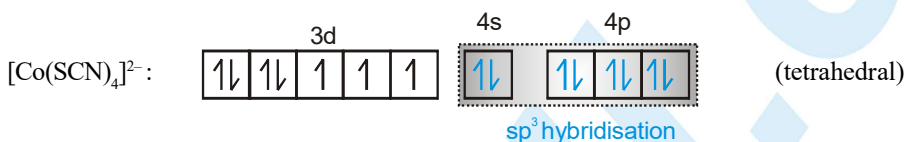
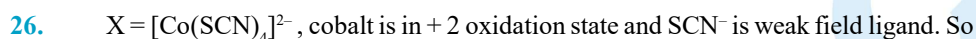
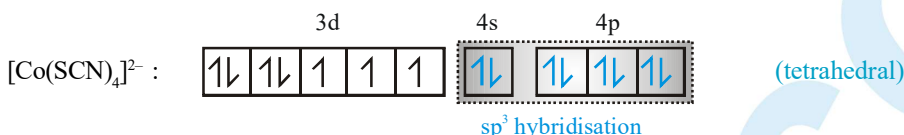
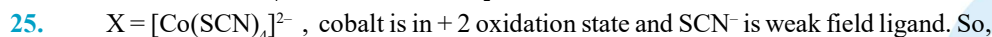
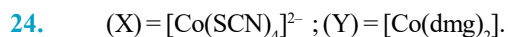


It shows geometrical isomerism but not optical isomerism due to the presence of at least one plane of symmetry.

$[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{NO}_2$ and $[\text{Co}(\text{NH}_3)_4\text{BrNO}_2]\text{Br}$ are ionisation isomers and later complex reacts with AgNO_3 solution to give pale yellow precipitate $[\text{Co}(\text{NH}_3)_4\text{BrNO}_2]\text{Br}$ and $[\text{Co}(\text{NH}_3)_4\text{BrONO}]\text{Br}$ are linkage isomers.

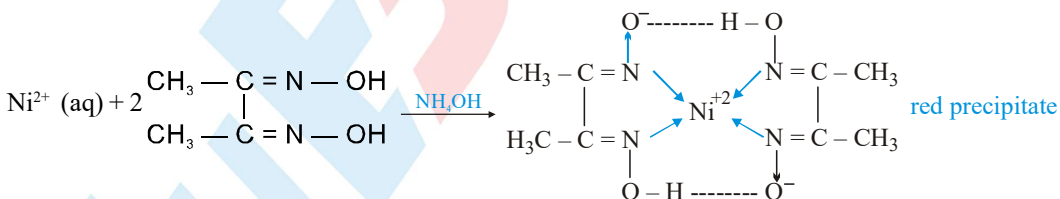
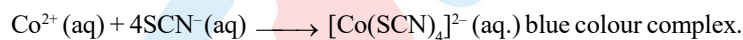


Trans-form is optically inactive as it is achiral.



$[Ni(dmg)_2]$ shows intra molecular H-bonding as shown below.

Reactions involved :



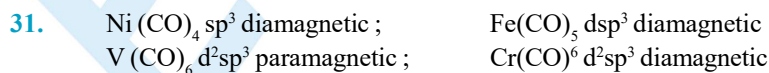
27. All form square planar complexes.

28. $4d^8$, configuration as Rh is in +1 oxidation state. $4d^8$ because of greater CFSE favours square planar geometry.

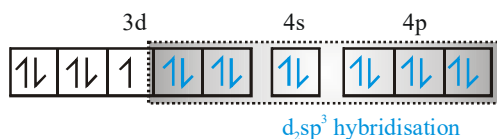
29. (A) Will not show geometrical isomers because 'en' is a symmetrical ligand and hence all forms will be identical.

30. Donation of electrons from a filled d-orbital of metal into the vacant antibonding π^* bonding orbital of CO decreases the bond order three to two and half or slightly more thus increasing the bond length between C – O.

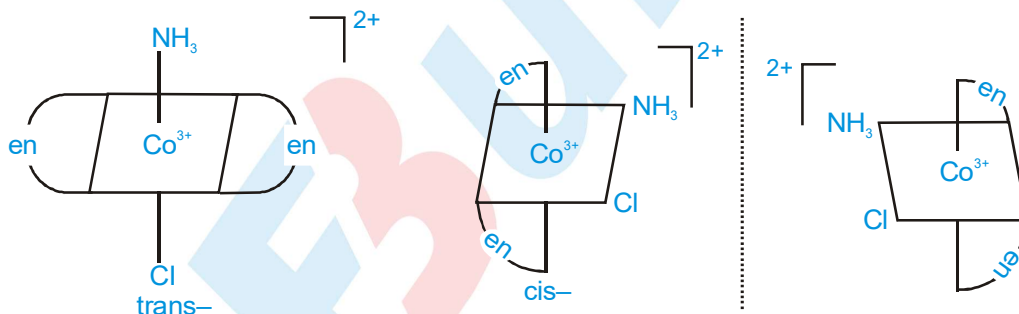
$$\text{Bond order} \propto \frac{1}{\text{Bond length}}$$



32. V = 23

[V(CO)₆]

33. (A) CO stronger field ligand complexes for pairing of electrons and so sp³ hybridisation and diamagnetic. Ligand is two electron donor.
- (B) When NO molecule co-ordinates with metal atom to form metallic nitrosyls, the single electron present in π* antibonding molecular orbital is transferred to metal atom M so that NO molecule is converted into NO⁺. Since NO⁺ is isoelectronic with CO molecule, this ion coordinates with M⁺ ion as a two electron donor in metal nitrosyls in the same way as CO coordinates to M atom in metal carbonyls. Note that NO molecule is a three electron donor. Now the empty π* antibonding molecular orbital can overlap with the filled d-orbital of metal to form M⁺ → NO⁺ π bond.
- (C) [Ni(PF₃)₄] has bonding like that of [Ni(CO)₄]
34. (A) d⁶ – configuration, CO³⁺ → d²sp³, diamagnetic en multidentate ligand – chelation possible.
- (B) d⁶ – configuration, Co³⁺ and diamagnetic → d²sp³.
Stabilisation through chelation – ox multidentate ligand.
- (C) d⁷ – configuration, Co²⁺ and paramagnetic with three unpaired electrons – sp³d² (H₂O weak field ligand).
- (D) d⁷ – configuration, Co²⁺ and paramagnetic, one electron jumps to 5s – orbital, d²sp³.
35. (A) ^{III}[Co(en)₂(NH₃)Cl]²⁺ ^{III}SO₄²⁻ and ^{III}[Co(en)₂(NH₃)SO₄]⁺ Cl⁻ ionisation isomerism.



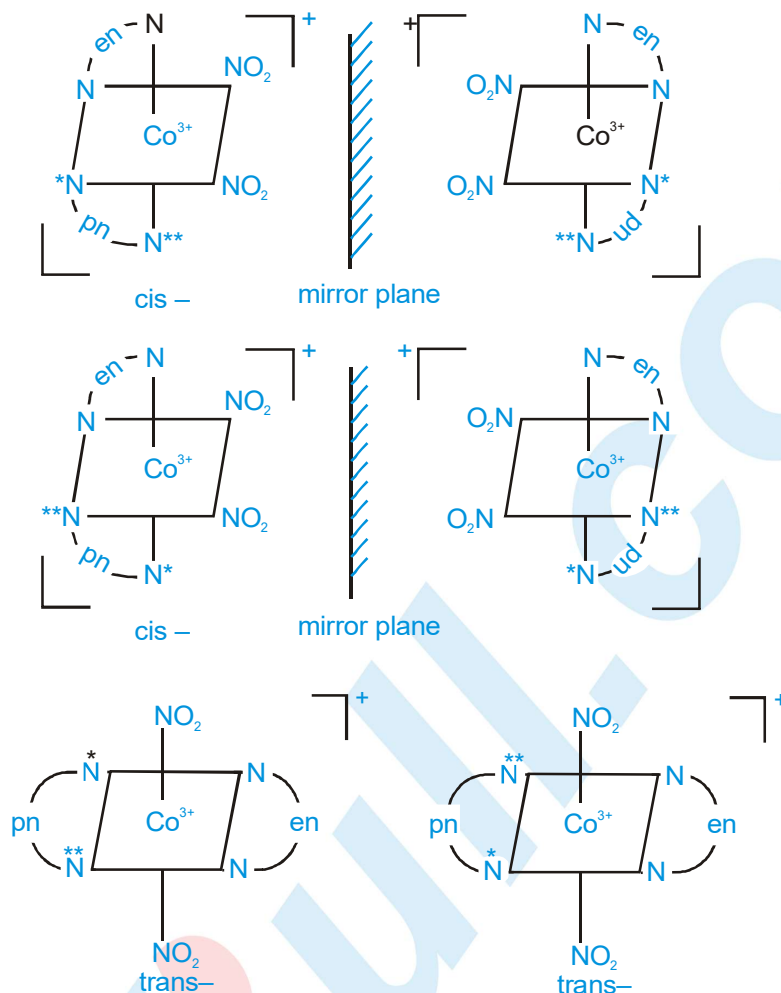
Note : trans-form has a centre of symmetry and several planes of symmetry, but the cis-form has neither.

(B) Has total 10-isomeric forms including linkage (NO₂ – ambidentate ligand), ionisation (exchange of NO₂⁻ and NO₃⁻), geometrical isomers (cis- and trans-).

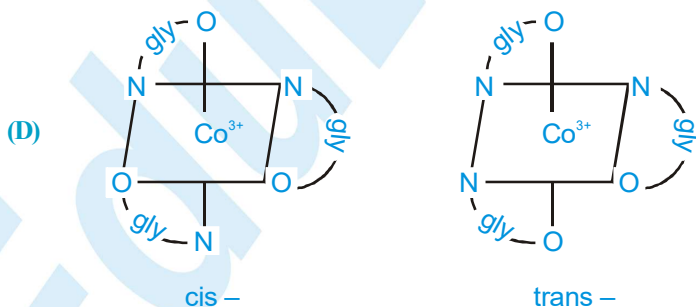
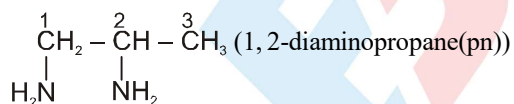
Compound is optically inactive as cis- as well as trans-forms possess at least one plane of symmetry.

(C) Exchange of NO₂⁻ and Cl⁻ gives rise to ionisation isomerism.

Linkage through either O – and N – gives rise to linkage isomerism.



Thus exists in two trans – and two cis-isomers and each of cis-isomers show optical isomerism.



Both cis – and trans – isomers have each a pair of optical isomers because the absence of any one of symmetry elements.

36. Net stabilization energy of Fe^{2+} with CN^-

$$\text{ligands } t_{2g}^{2,2,2} e_g^{0,0} = -2.4 \Delta_0 + 2P = (-2.4 \times 25000 + 2 \times 15000) \text{ cm}^{-1} = -30000 \text{ cm}^{-1}$$

$$\text{Net stabilisation energy of } \text{Fe}^{2+} \text{ ions with } \text{H}_2\text{O} \text{ ligands } t_{2g}^{2,1,1} e_g^{1,1} = -0.4 \Delta_0 = 4000 \text{ cm}^{-1}$$

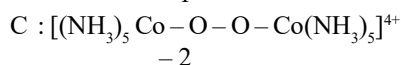
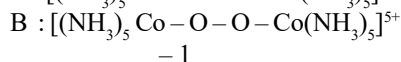
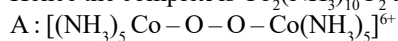
$$\begin{aligned} \text{So required difference} &= 26000 \text{ cm}^{-1} = 26 \times 10^5 \text{ m}^{-1} \\ &= 6 \times 10^{-34} \times 3 \times 10^8 \times 26 \times 10^5 \times 6 \times 10^{23} \times 10^{-3} \text{ kJ/mole} \\ &= 2808 \times 10^{-1} \text{ kJ/mole} \\ &= 281 \text{ kJ/mole} = 280.8 \text{ kJ/mole} \end{aligned}$$

37. $\text{Co} = \frac{36.875}{59} = 0.625$; $\frac{0.625}{0.625} = 1$

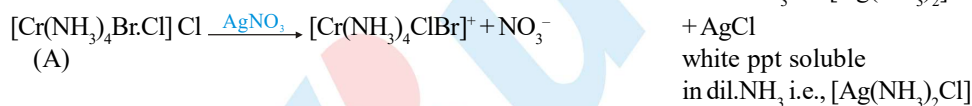
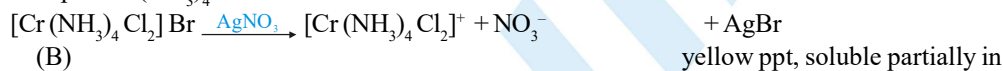
$$\text{NH}_3 = \frac{53.125}{17} = 3.125$$
 ; $\frac{3.125}{0.625} = 5$

$$\text{O} = \frac{10}{16} = 0.625$$
 ; $\frac{0.625}{0.625} = 1$

Hence the complex is $\text{Co}_2(\text{NH}_3)_{10}\text{O}_2$ and the cations are



38. Complex $\text{Cr}(\text{NH}_3)_4 \text{ClBr}$ has two isomers. Since co-ordination number of Cr is six and thus two forms may be



NH_3 is strong field ligand so,



Hybridisation of Cr in (A) and (B) is $d^2 sp^3$ having 3 unpaired electrons ($3d^3$)

For d^3 configuration, the magnetic moment is always 3.87 with weak field or strong field ligand.

$$\text{Magnetic moment} = \sqrt{n(n+2)} \text{ B.M.} = \sqrt{3(3+2)} = 3.87 \text{ B.M.}$$