SOLUTIONS OF COORDINATION COMPOUNDS

EXERCISE # 1

PART - I

C-1.

(a)	$PtCl_4.2NH_3 \overset{aq.}{\rightleftharpoons} [Pt(NH_3)_2Cl_4]$ (aq)	
(b)	$PtCl_4.NH_3.KCl \overset{aq.}{\rightleftharpoons} K^+$ (aq) + $[Pt(NH_3)Cl_5]^-$ (aq)	1 : 1 electrolyte.
(c)	$CrCl_3.5NH_3 \overset{aq.}{\rightleftharpoons} [Cr(NH_3)_5Cl]^{2+}$ (aq) + $2Cl^-$ (aq)	1 : 2 electrolyte
(d)	$PtCl_4.2KCl \overset{aq.}{\rightleftharpoons} 2K^+ + [PtCl_6]^{2-}$	2 : 1 electrolyte.
(e)	$PtCl_4.6NH_3 \overset{aq.}{\rightleftharpoons} [Cr(NH_3)_6]^{3+} + 3Cl^-$	1 : 3 electrolyte.
(f)	$PtCl_4.6NH_3 \overset{aq.}{\rightleftharpoons} [Pt(NH_3)_6]^{4+} + 4Cl^-$	1 : 4 electrolyte.
(g)	$CoBr_3.5NH_3 \overset{aq.}{\rightleftharpoons} [Co(NH_3)_5Br]^{2+} + 2Br^-$	1 : 2 electrolyte.
(h)	$PtCl_4.3NH_3 \overset{aq.}{\rightleftharpoons} [Pt(NH_3)_3Cl_3]^+ + Cl^-$	1 : 1 electrolyte

C-2. 1 mole of complex will give two moles of Cl^- ion, i.e. 2 mole HCl

$[Cr(H_2O)_5\,Cl]Cl_2\,.\,H_2O \rightleftharpoons [Cr(H_2O)_5Cl]^{+2} + 2Cl^-$

1 g

mole of HCl = $\frac{2 \times 1}{266.5}$ (for HCl, V.f. = 1 $\therefore$ N = M)

$\therefore$ N = $\frac{2/266.5}{1}$ = 0.0075.

C-3.

(a) Cr(Z = 24) ; EAN = 24 + 12 = 36.
(b) Fe(Z = 26) ; EAN = 26 – 2 + 12 = 36.
(c) Fe(Z = 26) ; EAN = 26 + 10 = 36.
(d) Co(Z = 27) ; EAN = 27 – 3 + 12 = 36.
(e) Ni(Z = 28) ; EAN = 28 + 8 = 36.
(f) Cu (Z = 29) ; EAN = 29 – 1 + 8 = 36.
(g) Pd(Z = 46) ; EAN = 46 – 4 + 12 = 54.
(h) Pt(Z = 78) ; EAN = 78 – 4 + 12 = 86.

C-4. (i) $K[Co(NH_3)_2(NO_2)_4] \overset{aq.}{\rightleftharpoons} K^+(aq) + [Co(NH_3)_2(NO_2)_4]^-(aq)$; no. of ions = 2.

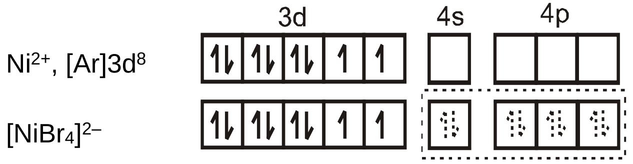
(ii) $[Cr(NH_3)_3(NO_2)_3] \overset{aq.}{\rightleftharpoons} [Cr(NH_3)_3(NO_2)_3]$ (aq) ; no. of ions = 0.

(iii) $[Cr(NH_3)_5(NO_2)]_3[Co(NO_2)_6]_2 \overset{aq.}{\rightleftharpoons} 3[Cr(NH_3)_5(NO_2)]^{2+} + 2[Co(NO_2)_6]^{3-}$; no. of ions = 5.

(iv) $[Cr(NH_3)_6]Cl_3 \overset{aq.}{\rightleftharpoons} [Cr(NH_3)_6]^{3+}$ (aq) + $3Cl^-$; no. of ions = 4.

Conductivity depends on the number of ions produced in solution as well as on the charges developed on the ions. So, the correct order of the increasing molar conductivity is ii < i < iv < iii.

D-2. **(a)** In the paramagnetic and tetrahedral complex $[NiBr_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown below.



sp^3 hybrid orbitals & tetrahedral.

(b) In $[AuCl_4]^-$ the gold is in +3 oxidation state and $5d^8$ configuration has higher CFSE. It is square planar and diamagnetic.

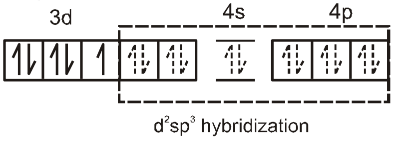
(c) In $[Pt(NH_3)_4]^{2+}$ the platinum is in +2 oxidation state and $5d^8$ configuration has higher CFSE. It is square planar and diamagnetic.

E-1. It contains magnetic moment equal to 1.73 B.M. So number of unpaired electron(s) in the complex is;

$\mu = \sqrt{n\ (n+2)}$ or 1.73 B.M = $\sqrt{n\ (n+2)}$ or n = 1.

The chromium is in +1 oxidation state with $3d^5$ configuration. CN^- and NH_3 are strong field ligands. So,

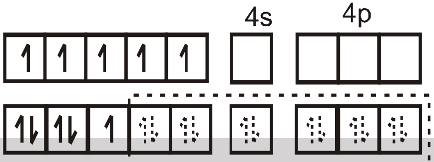
$K_2(\overset{I}{Cr}\ (NO^+)(NH_3)(CN)_4]^{2-}$



E-2. **(a)** In the paramagnetic octahedral complex, $[Fe(CN)_6]^{3-}$, the iron ion is in +3 oxidation state and has the electronic configuration represented as shown below.

Fe^{3+}, $[Ar]3d^5$

$[Fe(CN)_6]^{3-}$

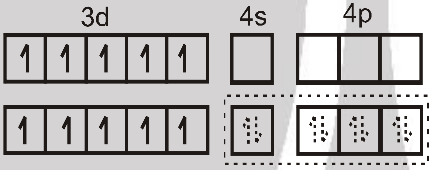


d^2sp^3 hybrid orbital & octahedral.

(b) In the paramagnetic and tetrahedral complex $[MnBr_4]^{2-}$, the manganese is in +2 oxidation state and the ion has the electronic configuration $3d^5$. The hybridisation scheme is as shown below.

Mn^{2+}, $[Ar]3d^5$

$[MnBr_4]^{2-}$

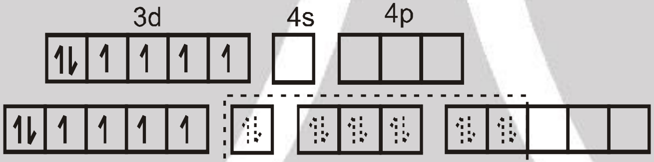


sp^3 hybrid orbitals & tetrahedral.

(c) In the paramagnetic octahedral complex, $[Fe(H_2O)_6]^{2+}$, the iron ion is in +2 oxidation state and has the electronic configuration represented as shown below.

Fe^{2+},$[Ar]3d^6$

$[Fe(H_2O)_6]^{2+}$

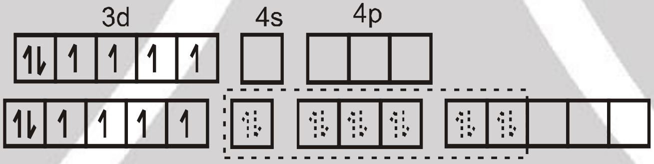


sp^3d^2 hybrid orbitals & octahedral

(d) The hybridisation scheme for $[Co(SCN)_4]^{2-}$ is as shown below.

Co^{2+}, $[Ar]3d^7$

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



sp^3 hybrid orbitals & tetrahedral.

E-4. (a) has 1, (ii) has 3 (iii) has 4 and (iv) has 2 number of ions in solutions respectively. So order of molar conductivity i < iv < ii < iii.

(b) It is factual

(c) According to spectrochemical series (values of Δ have been experimentally determined).

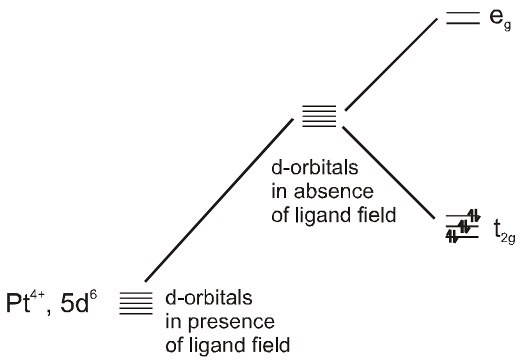
F-2. $240000\ (J) = \frac{hc}{\lambda} = \frac{6\times10^{-34}\times3\times10^{8}\times6\times10^{23}}{\lambda_{(nm)}\times10^{-9}}$

$\therefore\ \lambda_{(nm)} = 450$ $\therefore$ **yellow colour**

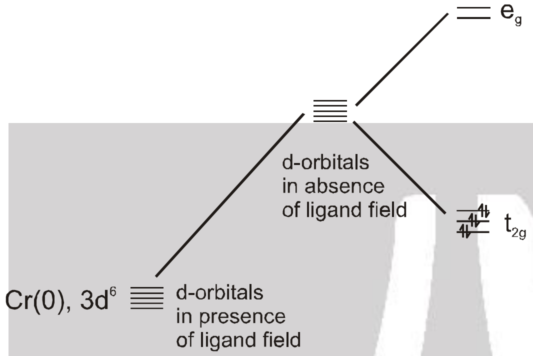
F-3. (a) Any ligand stronger than H_2O will absorb light of lower wavelength than 5000Å and any weaker ligand than H_2O will absorb light of higher wavlength than 5000Å.

(b) $\mu = \sqrt{n\ (n+2)}$

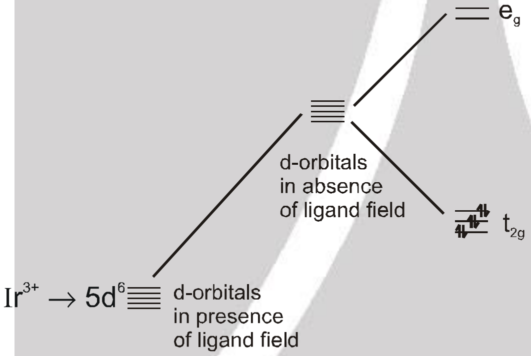
(i)



(ii)



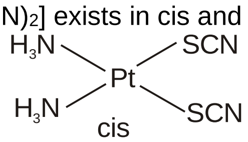
(iii)



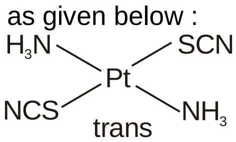
(iv) $Pd^{2+} \rightarrow 4d^8$ configuration has higher CFSE. So complex is square planar and diamagnetic.

G-1. (i) SCN^- can be bonded through sulphur (–SCN) thiocyanate or through nitrogen (–NCS) isothiocyanate as it is an ambidentate ligand.
(ii) Coordination compounds made up of cationic and anionic coordination entities show this type of isomerism due to the interchange of ligands between the cation and anion entities.
(iii) This type of 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) Hydrate isomers differ by whether or not a solvents molecule (i.e. water) is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.

G-3. **(a)** $[Pt(NH_3)_2(SCN)_2]$ exists in cis and trans forms as given below :



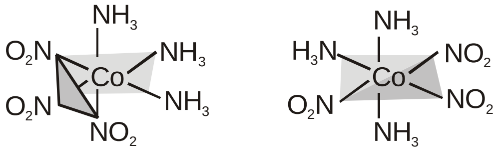
cis



trans

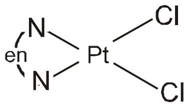
(b) $[CoCl_2Br_2]^{2-}$ (tetrahedral) : In tetrahedral all positions are adjacent to one another. So it does not exhibit geometrical isomerism.

(c)

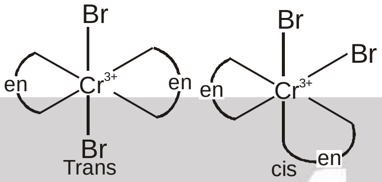


fac– mer–

(d) [Pt(en)Cl$_2$] : It exists in one form.

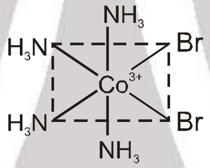


(e) [CrBr$_2$(en)$_2$]$^+$:

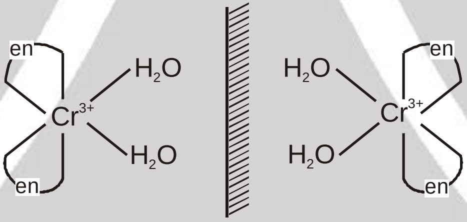


(f) [Rh(en)$_3$]$^{3+}$ does not show geometrical isomerism as all donating atoms are of one type i.e nitrogen atoms.

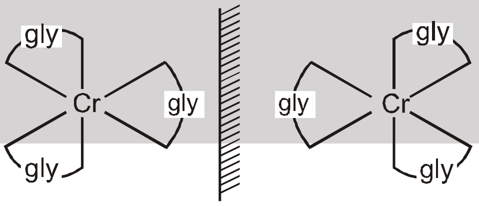
G-4. (a) cis–[Co(NH$_3$)$_4$Br$_2$]$^+$ does not show optical isomerism as there is plane of symmetry and centre of symmetry in the molecule.



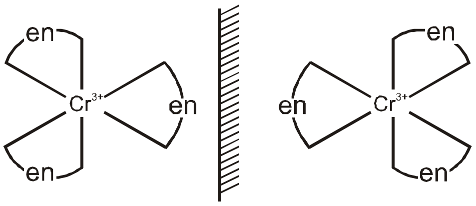
(b) cis–[Cr(H$_2$O)$_2$(en)$_2$]$^{3+}$ show optical isomerism as shown below because of the absence of plane of symmetry as well as centre of symmetry.



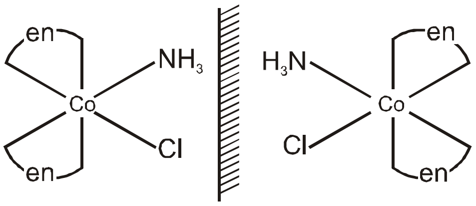
(c) Glycine is NH$_2$CH$_2$COOH in which the donor atoms are nitrogen and oxygen. Hence the ligand is called as unsymmetrical ligand i.e. AB type. The complex, [Cr(gly)$_3$] has two enantiomeric forms as given below.



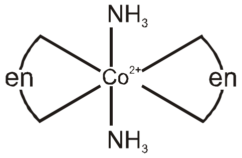
(d) [Cr(en)$_3$]$^{3+}$:



(e) cis–$[Co(NH_3)Cl(en)_2]^{2+}$:



trans–$[Co(NH_3)_2(en)_2]^{2+}$ has plane of symmetry as well as centre of symmetry. So, no optical isomerism is observed.

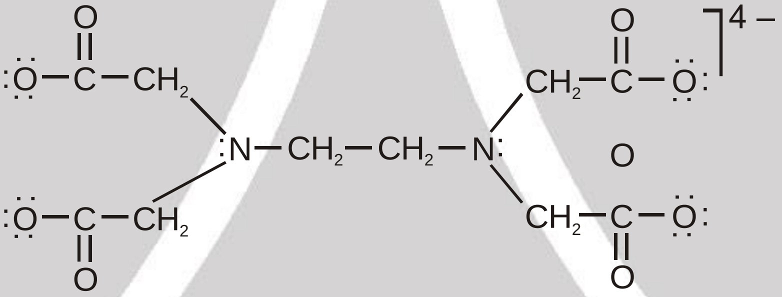


H-2. (i) As delocalisation of π electrons increases the metal-ligand bond strength increases.
(ii) As back donation of d-orbital electrons of metal ion (in same π symmetry) to anti bonding π molecular orbital of CO increase, the C–O bond order decreases.

PART - II

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

A-2. It attaches to the central metal ion through four carboxylate group oxygen atoms and the two amine nitrogens.



$EDTA^{4-}$, Ethylenediaminetetraacetate ion

A-3. $Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2.4\,KCN \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$
It gives test of K^+ but does not give test of Fe^{2+}. These type of salts which do not lose their identity when dissolved in water are called complexes.

A-4. Ligands are Lewis bases as they donate lone pair of electrons to the metal ion to form coordinate covalent bonds.

A-5. (a) Let x be the oxidation state of Mo in $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$. So 2x – 8 = – 2 or x = + 3.

A-6. As there are six σ-bonds between metal atom /ion and ligands, the coordination number of Pt(IV) in this complex is six.

A-7. Let x be the oxidation state of copper in $[Cu(CN)_4]^{3-}$. So, x + 4(–1) = – 3 or x = 1. In (A) and (C) the oxidation state of copper is +2.

A-8. Let x be the oxidation state of cobalt in $[CoCl_2(en)_2]^+$. So, x + 2(–1) + 0 = +1 or x = + 3.
As there are six σ-bonds between cobalt and ligands, it coordination number is 6 (here 'en' is a bidentate ligand).

A-9. H_2O is neutral, chromium oxidation state i.e. charge is +3 and oxalato anion has –2 charge; due to two $C_2O_4^{2-}$ it will be – 4 and net charge on the complex is algebraic sum of the charge on metal ion and ligands present in the coordination sphere. So $3 + 2 \times (-2) = -1$. So the formulae of complex is $[Cr(C_2O_4)(H_2O)]^-$.

B-1. (A) Coordination number of platinum is generally six when its oxidation state is (IV). So it is incorrect name.
(B) With type of ligand and +4 oxidation state of platinum, the complex should be cationic not anionic. So it is also incorrect name.
not anion but IUPAC name is given as anion.
(C) For coordination number six, the oxidation state of Pt is +IV. So the probable formulae of the complex may be $[Pt(NH_3)_2(en)(SCN)_2]^{2+}$. So its correct IUPAC name is Diammineethylenediaminedithiocyanato-S-platinum (IV).
(D) With two NH_3, two en and two SCN^- ligands, the coordination number of Pt becomes eight, which is incorrect according to the question.

B-2. (A) compound $[Cr^{VI}F_4^{-4}O^{-2}]$ (CN = 5) is a neutral molecule so there should not be potassium cation.

B-3. (i) The central atom, Co is placed first.
(ii) The ligands are then placed in alphabetical order.
(iii) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets.

B-4. Cation is named first followed by anion. In coordination sphere the ligands are named alphabetically followed by name of metal ion and then its oxidation state in Roman numeral.
In $[Co(NH_3)_4Cl(ONO)]^+Cl^-$, cobalt is in +3 oxidation state and the complex is cationic. ONO ligand attach to metal ion through O atom; so –O– is used while naming as nitrito before the name of metal ion. So IUPAC name given in option (D) is correct.

B-5. Metal, Co is placed first followed by ligands in alphabetical order as ammine > aqua > chlorido i.e. $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$.

C-1. x is number of lone pairs of electrons donated to central metal ion.

$$\text{So, } 26 + 2x = 36 \qquad \text{or} \qquad x = \frac{10}{2} = 5$$

C-2. $K_2[PtCl_6]$; Platinum is in + 4 oxidation state. Atomic number of Pt = 78..
So EAN Pt(IV) = 78 – 4 + 12 = 86

C-3. $Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6] \overset{aq.}{\rightleftharpoons} 3K^+ + [Co(NO_2)_6]^{3-}$ (total six electric charge)
3 : 1 electrolyte.

C-4. Conductivity α number of ions in the solution.
(A) $K_4[Fe(CN)_6] \overset{aq.}{\rightleftharpoons} 4K^+ (aq) + [Fe(CN)_6]^{4-} (aq)$
4 : 1 electrolyte.
It contains maximum number of ions i.e. 5.
(B) $[Co(NH_3)_6]Cl_3 \overset{aq.}{\rightleftharpoons} [Co(NH_3)_6]^{3+} (aq) + 3Cl^- (aq)$
1 : 3 electrolyte.
(C) $[Cu(NH_3)_4]Cl_2 \overset{aq.}{\rightleftharpoons} [Cu(NH_3)_4]^{2+} (aq) + 2Cl^- (aq)$
1 : 2 electrolyte.
(D) $[Ni(CO)_4] \overset{aq.}{\rightleftharpoons} [Ni(CO)_4] (aq)$ (neutral).

C-5. Molar conductance depends not only on the number of ions in aqueous solution but also on the electrical charges on the ions.

(A) $[Co(NH_3)_6]Cl_3 \overset{aq.}{\rightleftharpoons} [Co(NH_3)_6]^{3+}$ (aq) + $3Cl^-$ (aq). It has 4 ions and six electrical charges.

(B) $[Co(NH_3)_3Cl_3] \overset{aq.}{\rightleftharpoons} [Co(NH_3)_3Cl_3]$ (aq) (neutral)

(C) $[Co(NH_3)_4Cl_2]Cl \overset{aq.}{\rightleftharpoons} [Co(NH_3)_4Cl_2]^+$ (aq) + Cl^- (aq). It has 2 ions and two electrical charges.

(D) $[Co(NH_3)_5Cl]Cl_2 \overset{aq.}{\rightleftharpoons} [Co(NH_3)_5Cl]^{2+}$ (aq) + $2Cl^-$ (aq). It has 3 ions and four electrical charges.

C-6. The counter ion present out side the coordination sphere can give test. Here Cl^- is present in the ionization sphere as counter ion so it will give the test.

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

C-7. Concentrated H_2SO_4 is dehydrating agent. It will not dehydrate the complex in which H_2O molecule is inside the coordination sphere.

C-8. $[Pt(NH_3)_3Cl_3]Cl \overset{aq.}{\rightleftharpoons} [Pt(NH_3)_3Cl_3]^+$ (aq) + Cl^- (aq)

Out of four Cl^- only one Cl^- (i.e. 25%) present in ionization sphere will give preciptate.

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

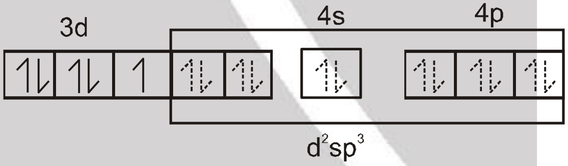
C-9. $[Pt(NH_3)_5Cl]Cl_3 \overset{aq.}{\rightleftharpoons} [Pt(NH_3)_5Cl]^{3+} + 3Cl^-$

D-4. (A) This may attributes to the following two reasons.

(i) There are only four ligands instead of six, so the ligand field is only two thirds the size ; as the ligand field splitting is also the two thirds the size and (ii) the direction of the orbitals does not concide with the direction of the ligands. This reduces the crystal field splitting by roughly further two third. So $\Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9}\Delta_o$.

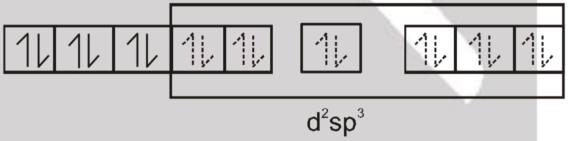
D-5. (A) $[FeCl(CN)_4(O_2)]^{4-}$; O_2 is O_2^{2-} ; CN^- is strong field ligand, so compels for the pairing of electrons.

$Fe^{3+} \rightarrow 3d^5$;



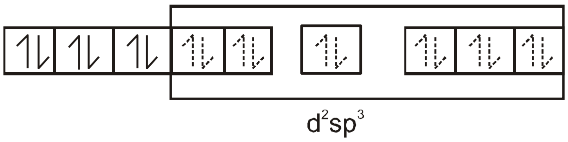
(B) $K_4[Fe(CN)_6]$; CN^- is strong field ligand so compels for the pairing of electrons.

$Fe^{2+} \rightarrow 3d^6$:



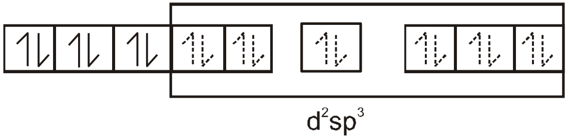
(C) $[Co(NH_3)_6]Cl_3$; NH_3 is strong field ligand and $3d^6$ configuration has higher CFSE compelling for the pairing of electrons.

$Co^{3+} \rightarrow 3d^6$:



(D) $[Fe(CN)_5(O_2)]^{5-}$; O_2 is O_2^{2-} ; CN^- is strong field ligand so compels for the pairing of electrons.

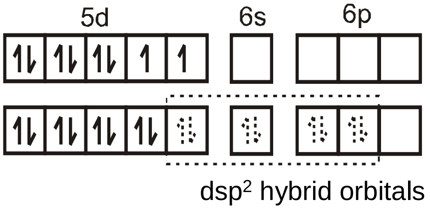
$Fe^{2+} \rightarrow 3d^6$:



E-3. $5d^8$ configuration have higher CFSE and the complex is thus square planar and diamagnetic.

Pt^{2+}, $[Xe]4f^{14}\,5d^8$

$[Pt(NH_3)_4]^{2-}$



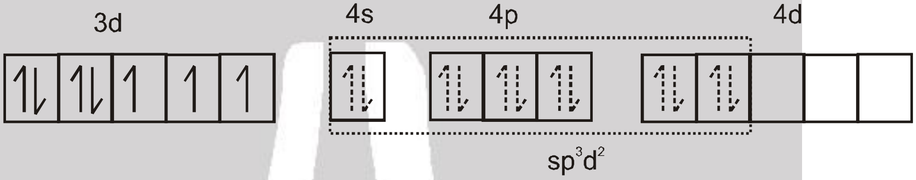
E-4. (I) Au in +3 oxidation state with $5d^8$ configuration has higher CFSE. So complex has dsp^2 hybridisation and is diamagnetic.

(II) Cu is in +1 oxidation state with $3d^{10}$ configuration and no (n –1)d orbital is available for dsp^2 hybridisaiton, 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.

$[Fe(H_2O)_5NO]^{2+}$;

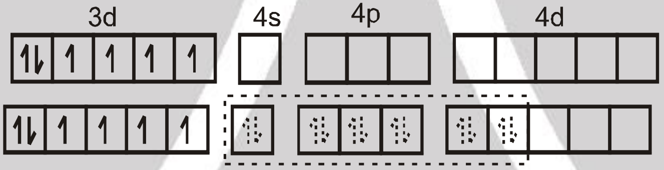


E-6. In d^6, 'low spin' octahedral complex all electron will be paired because of higher CFSE.

E-7. The complex $[FeF_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridisation (sp^3d^2) ; it is thus called as outer orbital or high spin or spin free complex. So :

Fe^{2+}, $[Ar]3d^6$

$[FeF_6]^{4-}$



sp^3d^2 hybrid orbitals

Six pairs of electrons from six F^- ions.

E-8. (C) Mn^{2+}, $3d^5$ configuration has 5 unpaired electrons.

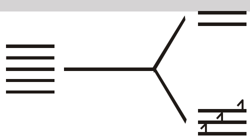
In (D) Fe^{2+} ($3d^6$) has no unpaired electrons because of strong field ligand (CN^-), all electrons are paired.

In (A) and (B) $Cu^{2+}(3d^9)$ has one unpaired electron.

E-9. Fe^{3+}, $3d^5$ configuration has 5 unpaired electrons because F^- is a weak field ligand.

E-10. (A), (B) and (C) all have tetrahedral geometry except (C) which has square planer geometry.

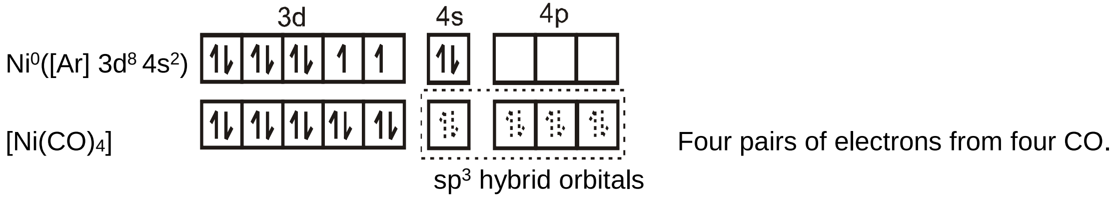
E-11. (A) Mo^{3+}, $4d^3$



$4d^3$ contains three unpaired electrons with strong field as well as with weak field ligand.

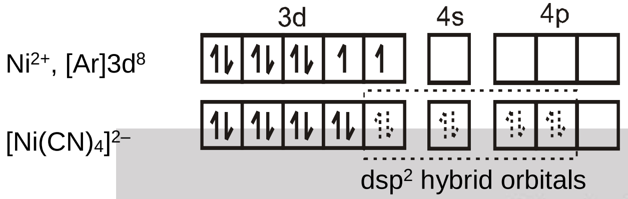
(B) It is inner orbital complex (d^2sp^3) and all six electrons are paired as $3d^6$ configuration has higher CFSE.

E-12. In complex, $[Ni(CO)_4]$ nickel is in zero oxidation state. The CO is strong field ligand and, therefore compels for the pairing of electrons. The hybridisation scheme is as shown in figure.

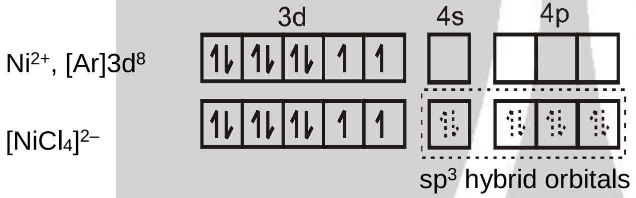


It is tetrahedral and as all electrons are paired so diamagnetic.

In the diamagnetic and square planar complex $[Ni(CN)_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in figure.

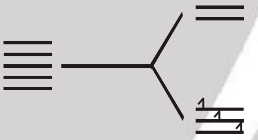


In the paramagnetic and tetrahedral complex $[NiCl_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in figure.



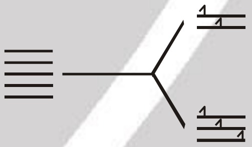
F-1. **(B)** Ag^+ has $4d^{10}$ configuration and thus all electrons are paired in 4d-orbitals.

F-2. (A) Cr^{3+}, $3d^3$



n = 3.

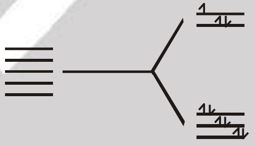
(B) Fe^{2+}, $3d^5$



n = 5.

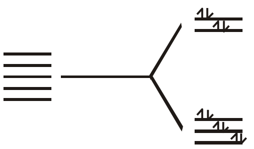
It has maximum number of unpaired electrons.

(C) Cu^{2+}, $3d^9$



n = 0.

(D) Zn^{2+}, $3d^{10}$

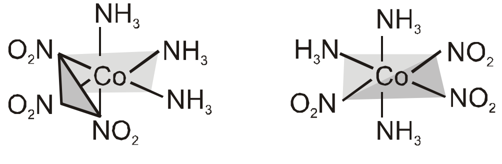


n = 0.

G-1. (C) 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.

G-2. NO_2^- is an ambidentate ligand and thus it can linkage to metal ion through O as well as through N. Hence show linkage isomerism.

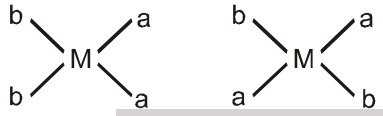
G-3. $[Co(NH_3)_3(NO_3)_3]$ exists in following to isomeric forms.



fac– mer–

G-4. Geometrical isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Geometrical isomerism is common among coordination compounds with coordination numbers 4 having square planar geometry and 6 having octahedral geometry.

G-5.

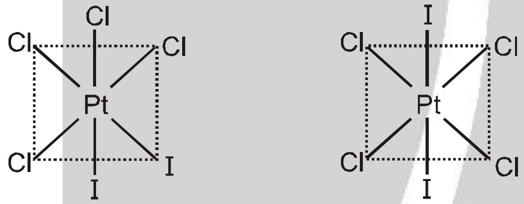


Cis Trans

G-6. (A) Linear geometry

(B) Ma_4b has one form

(C)



cis – trans –

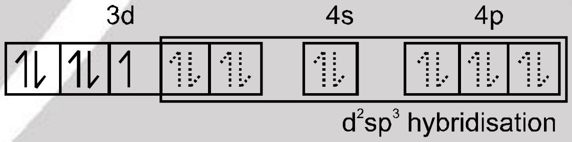
(D) Ma_3b and Ma_4 both have one form each.

H-1. In organometallic compounds, the metal is directly attached to the carbon atom. In C_2H_5ONa, the Na is attached to oxygen atom.

H-2. Ferrocene, Fe $(\eta^5 - C_5H_5)_2$ is bis(cyclopentadienyl)iron(II)

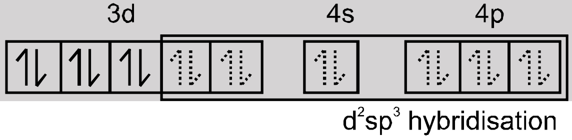
PART - III

1. (A) $\overset{III}{Fe}$ $[(en)_3]^{3+}$ -



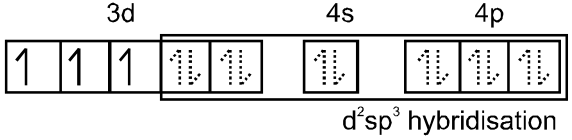
Number of unpaired electrons = 1; so paramagnetic

(B) $\overset{III}{Co}$ $[(ox)_3]^{3-}$ -



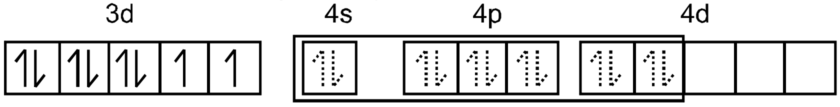
Number of unpaired electrons = 0; so diamagnetic.

(C) $\overset{III}{Cr}$ $[(CN)_6]^{3-}$ -



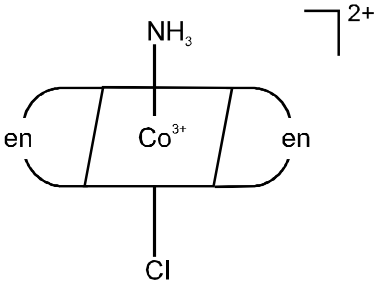
Number of unpaired electrons = 3 ; so paramagnetic.

(D) $\overset{II}{Ni}$ $[Cl_6]^{4-}$ -

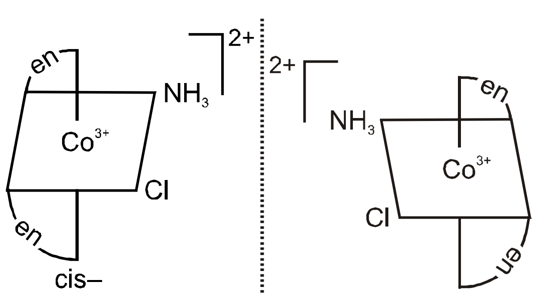


Number of unpaired electrons = 2; so paramagnetic.

2. (A) $[\overset{III}{Co}(en)_2(NH_3)Cl]^{2+}\ SO_4^{2-}$ and $[\overset{III}{Co}(en)_2(NH_3)SO_4]^{+}\ Cl^{-}$ ionisation isomerism.



trans–



cis–

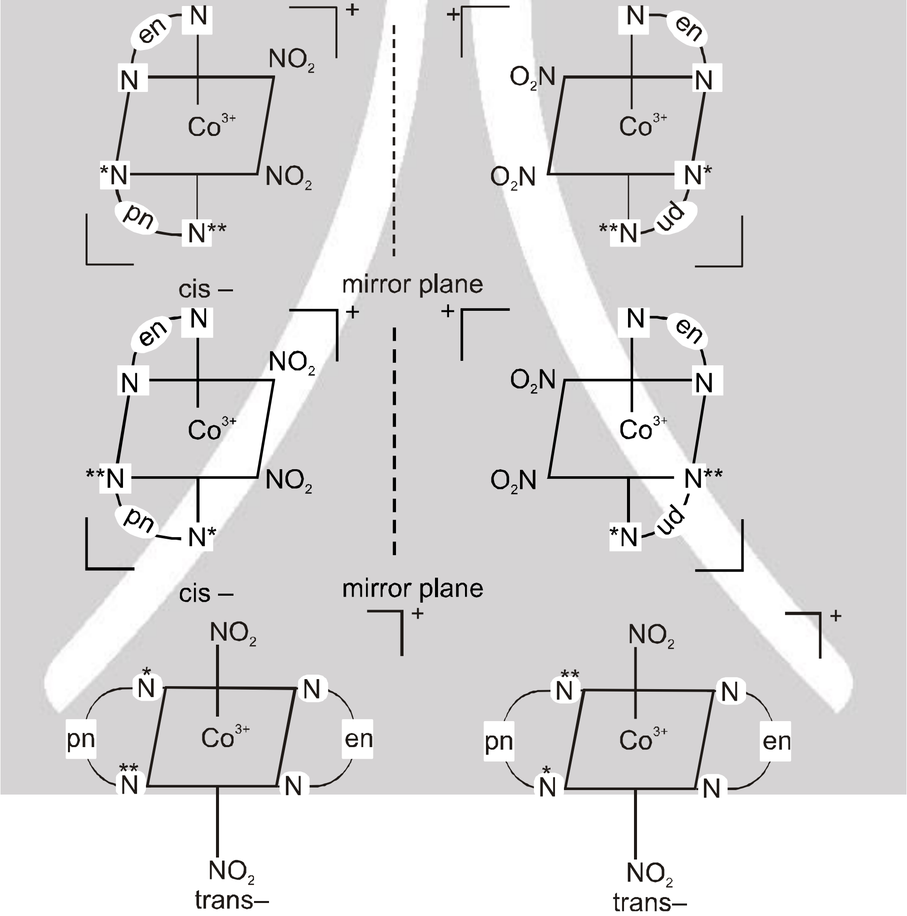
Note: trans-form has a centre of symmetry and several planes of symmetry, but the cis-form has neither.

(B) Has total 12-isomeric forms including linkage (NO_2 - ambidentate ligand), ionisation (exchange of NO_2^- and NO_3^-), geometrical isomers (cis- and trans-).

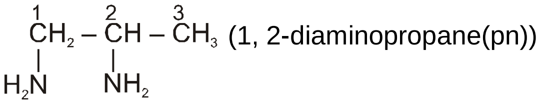
Compound is optically inactive as cis- as well as trans-forms possess at least one plane of symmetry.

(C) Exchange of NO_2^- and Cl^- gives rise to ionisation isomerism.

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

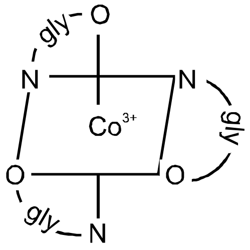


Thus exists in two trans – and two cis-isomers and each of cis-isomers show optical isomerism.

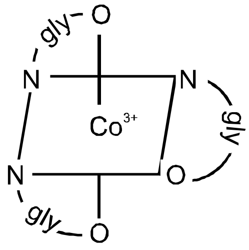


$\underset{H_2N}{\overset{1}{C}H_2} - \underset{NH_2}{\overset{2}{C}H} - \overset{3}{C}H_3$ (1, 2-diaminopropane(pn))

(D)



cis –



trans –

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

EXERCISE # 2

PART - I

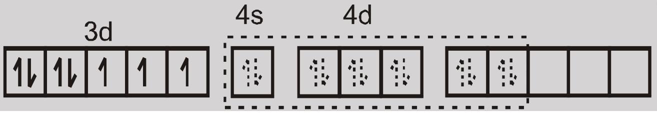
1. (A) If $[Os(Cl)_5N]^{2-}$, complex is anion, so name of the element should be osmate (VI).
(C) If $[Os(Cl)_5N_3]^0$, complex is neutral, so name of the element should be osmium (VI).
Therefore, (B) option is correct according to the IUPAC rule.

2. Oxidation state of iron in $[\overset{-2}{Fe}(\overset{0}{CO})_2(\overset{+}{NO})_2]$ = x + 2(0) + 2 = 0; x = –2
So EAN = 28 + 8 = 36
Oxidation state of cobalt in $CO_2(CO)_8$ = 2x + 8 (–0) = or x = 0
So EAN = 27 + 1 + 8 = 36.

5. $K_4[Zn^{II}(CN)_4(O_2)_2]^{4-} \xrightarrow{\text{oxidised}} K_2[Zn^{II}(CN)_4(O_2)_2]^{2-}$.
O_2^- (has 1unpaired electron in antibonding MO) $\xrightarrow{\text{oxidised}}$ O_2 (has 2 unpaired electrons in antibonding MO).
So, paramagnetic moment increases.

6. (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 dimagnetic.

7. $[Fe(I)\ (H_2O)_5\ NO^+]$



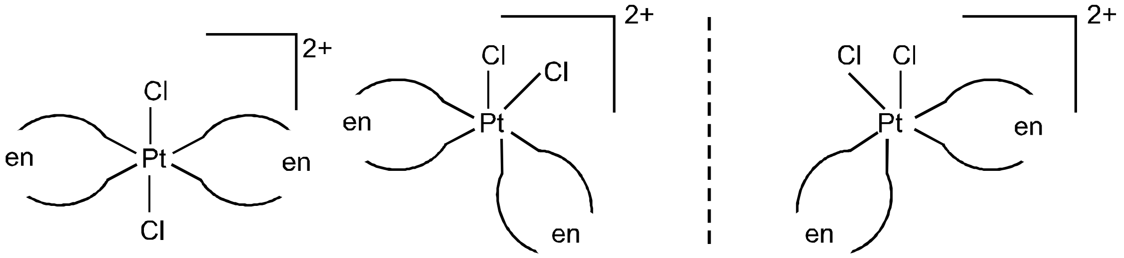
Three unpaired electrons
six – sp^3d^2 hybrid orbital
So μ = 3.87.

8. (A) $TiCl_4$, $[Ar]^{18}3d^04s^0$; there is no unpaired electron and, therefore, there is no d-d transition of electron. So compound is colourless.
(B) $[Cr(NH_3)_6)]Cl_3$, $[Ar]^{18}3d^3$; there is three unpaired electrons and, therefore, there is d-d transition of electron. So compound is coloured.
(C) $K_3[VF_6]$, $[Ar]^{18}\ 3d^1$; there is one unpaired electron and, therefore, there is d-d transition of electron. So compound is coloured.
(D) $[Cu(NCCH_3)_4][BF_4][Ar]^{18}3d^{10}$; there is no unpaired electron and, therefore, there is no d-d transition of electron. So compound is colourless.

9. (D) Ti^{4+}, $[Ar]^{18}$ $3d^0$ $4s^0$; as there is no unpaired electron, so no d-d transition occurs.
Cu^+ , $[Ar]^{18}$ $3d^{10}$ $4s^0$; all electrons are paired, so there is no unpaired electron for d-d transition.
Hence both complexes are colourless.

10. Ma_2b_4 has two geometrical isomers one cis- and one trans. Similarly Ma_2b_2 also has one cis- and one trans-forms.

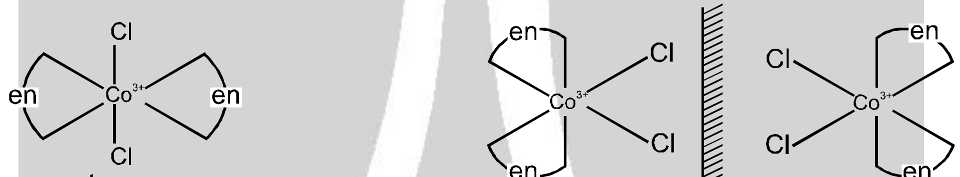
11.



trans- dextro mirror laevo

As trans isomer has symmetry elements it does not show optical isomerism.
(A), (C) and (D) are correct statements.

12. (A) $[Co(en)_2Cl_2]^+$ show geometrical isomerism and its only cis-form show optical isomerism.



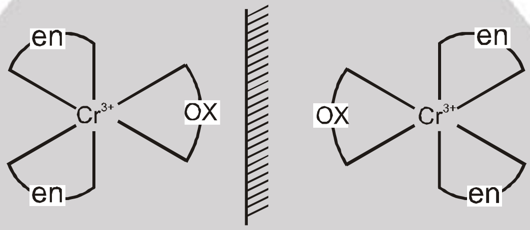
trans cis

(B) $[Co(NH_3)_5Cl]^{2+}$ exists only in one form.

(C)

trans cis

It does not shows optical isomerism because of the presence of plane of symmetry and centre of symmetry.
(D) $[Cr(OX)_3]^{3-}$ shows optical isomerism but does not show geometrical isomerism because of the same type of ligands.



13. 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 : $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$.

PART - II

1. All are bidentate except diethylenetriamine which is tridentate.

2. $Na_2[Cr(edta)]$ - $2Na^+$
$Na_3[Co(NO_2)_6]$ - $3Na^+$

5. True statements : (i), (iii), (iv), (vii).

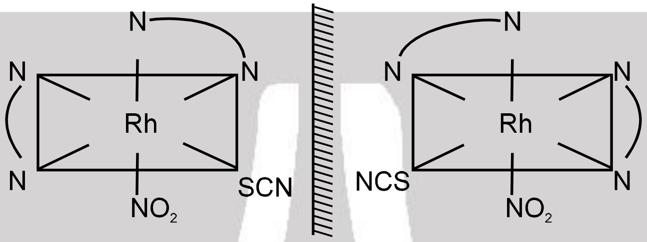
6. Correct options are (a), (c) & (d).

7. Paramagnetic × Inner orbital complexes are $[Cr(NH_3)_6Cl_3$, $[V(H_2O)_6]SO_4$

9. For $CoCl_2Br_2 \rightarrow$ No. of G.I. = 0
For $[Rh(en)_3]^{3+} \rightarrow$ No. of G.I. = 0
For $[Cr(en)_2Br_2]^{+} \rightarrow$ No. of G.I. = 2
For $[Pt (en) Cl_2] \rightarrow$ No. of G.I. = 0
For $[Co(NH_3)_3 (NO_2)_3] \rightarrow$ No. of G.I. = 2
Hence sum of Geometrical isomers = 4.

11. It shows linkage, geometrical and optical isomerism.

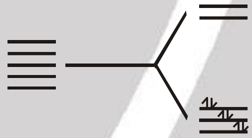
(1) cis-NO_2 / SCN	(5) trans-NO_2 / SCN	(9)	Mirror images of (1), (2), (3), (4)
(2) cis-ONO / SCN	(6) trans-ONO / SCN	(10)	
(3) cis-NO_2 / NCS	(7) trans-NO_2 / NCS	(11)	
(4) cis-ONO / NCS	(8) trans-ONO / NCS	(12)	



PART - III

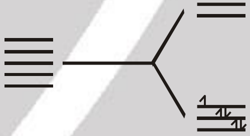
2. As on dimerisation the EAN of each Co metal becomes 36 (Kr configuration); EAN = 27 + 1 + 8 = 36.

3. (A) $K_4[Fe(CN)_6]$; $3d^6$,



CN^- is strong field ligand and thus compels for the pairing of electrons.

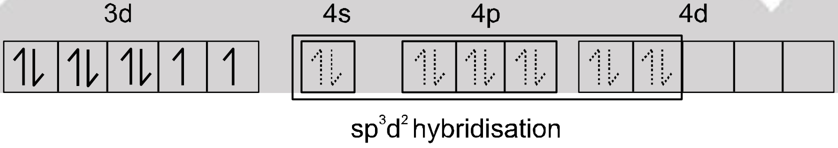
$K_3 [Fe(CN)_6]$; $3d^5$,



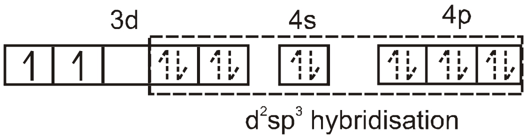
CN^- is strong field ligand and thus compels for the pairing of electrons.
(B) $SO_4^{2-} (aq) + Ba^{2+} (aq) \longrightarrow BaSO_4\downarrow$ (white); $Br^- (aq) + Ba^{2+} (aq) \longrightarrow$ no visible change.
(C) $Cl^- (aq) + Ag^+ (aq) \longrightarrow AgCl\downarrow$ (white); $Br^- (aq) + Ag^+ (aq) \longrightarrow AgBr\downarrow$ (pale yellow)

5. (A) $[Ni(CO)_4]$ diamagnetic in presence of strong field ligand.

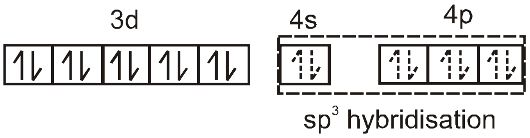
(B) $[Ni(en)_3]^{2+}$



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



(D) $[Mn^{3-} (NO^+)_3 (CO)]$



6. All statements are correct with respect to CFT.

7. Ni (dmg)$_2$ complex is square planar and dimagnetic.
(B) Mn in $[MnO_4]^-$ is in +7 oxidation state having $[Ar]^{18}\ 3d^0$ configuration. Complex ion is tetrahedral and diamagnetic
(D) Pt(II) – $5d^8$ configuration. Complex is square planar and therefore, dimagnetic. So, $\mu = 0$

8. 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.

9. (A) $[CoCl_2(OH_2)_2(NH_3)_2]Br$ and $[CoClBr(OH_2)_2(NH_3)_2]Cl$ are ionisation isomers.
(B) Does not have ambidentate ligand; so does not show linkage isomerism.
(C) It is $Ma_2b_2c_2$ type.

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

10. (A) I and II are geometrical isomers as cis and trans.
(B) II and III have mirror plane; they are not optical isomers.
(C) I and III are not mirror images of each other.
(D) Both are identical structures i.e. trans isomers.

12. Oxidation state of cobalt in $Co_2(CO)_8 = 2x + 8\,(-0) =$ 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.

PART - IV

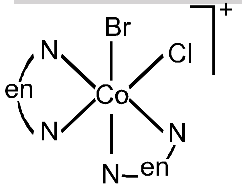
1. (D) Water present in ionisation sphere is absorbed by conc. H_2SO_4 (dehydrating agent). If Cl^- present as counter ion then reacts with, $AgNO_3$ to give white precipitate of AgCl.

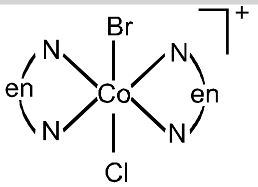
2. With F^- ligand, metal ion has electron configuration, $t_{2g}^{2,\,1,\,1}\ e_g^{1,1}$.
So, $\mu = \sqrt{4\ (4+2)} \approx 4.9$ BM; where n = number of unpaired electrons.

3. With NO_2^- ligand, electron configuration in crystal field splitting for Co^{3+} will be $t_{2g}^{2,2,2}\ e_g^0$ i.e. no unpaired electrons.

4. 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 ½mole of $PbCl_2$.

5. Only two geometrical isomers are possible of $[CoBrCl(en)_2]^+$.

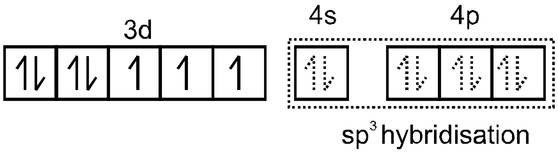




6. (X) = $[Co(SCN)_4]^{2-}$; (Y) = $[Co(dmg)_2]$.

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

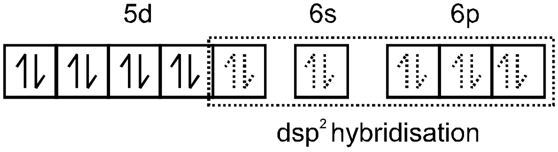
$[Co(SCN)_4]^{2-}$:



(tetrahedral)

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

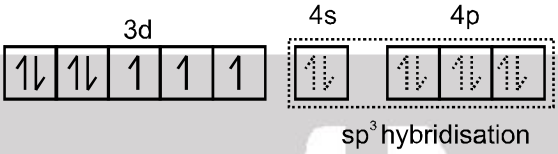
$[Ni(dmg)_2]$:



(square planar)

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

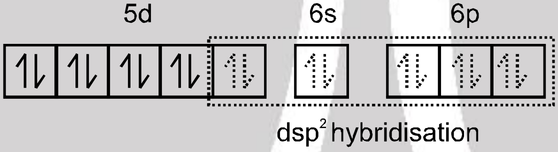
$[Co(SCN)_4]^{2-}$:



(tetrahedral)

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

$[Ni(dmg)_2]$:



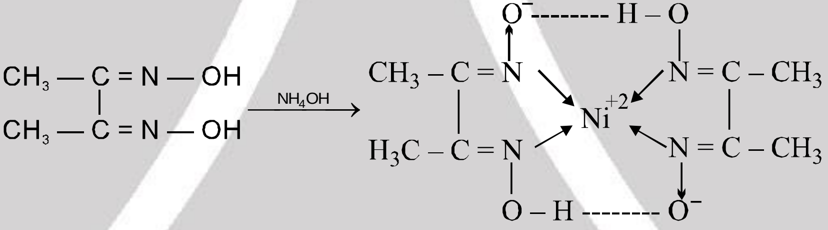
(square planar)

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

Reactions involved :

Co^{2+} (aq) + $4SCN^-$ (aq) $[Co(SCN)_4]^{2-}$ (aq.) blue colour complex.

Ni^{2+} (aq) + 2



red precipitate

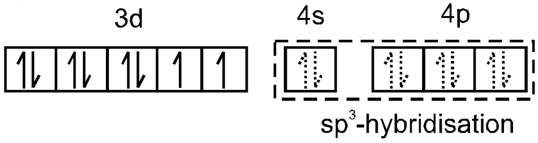
EXERCISE # 3

PART - I

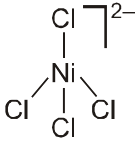
2. In $[NiCl_4]^{2-}$, the Ni is in +2 oxidation state.

Cl^- is a weak field ligand. So,

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



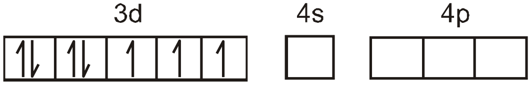
Hence the shape is tetrahedral and complex is paramagnetic with two unpaired electrons.



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

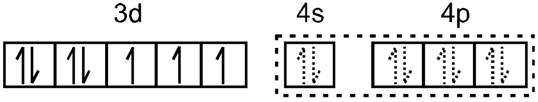
3. In the complex Hg $[Co(SCN)_4]^{2-}$ cobalt is in +2 oxidation state. So

Co^{2+}



SCN^- is weak field ligand so,

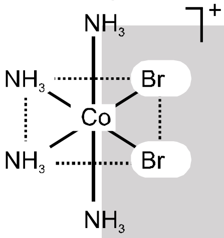
$[Co(SCN)_4]^{2-}$



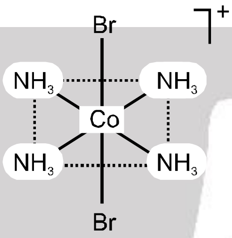
As it contains three unpaired electrons, so $\mu = \sqrt{3(3+2)} = \sqrt{15}$.

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

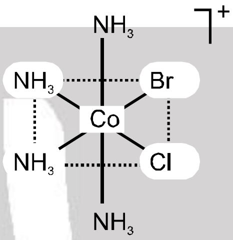
Each complex has one cis- and one trans- isomers.



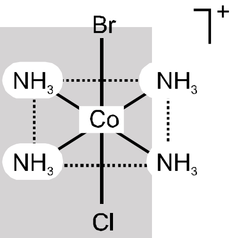
cis-



trans-

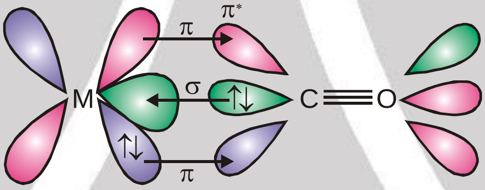


cis-



trans-

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

7. (i) $NiCl_2 + 4KCN\ (excess) \longrightarrow K_2[Ni(CN)_4] + 2KCl$

Potassium tetracyanonickelate(II)
(A)

(ii) $NiCl_2 + 2KCl\ (excess) \longrightarrow K_2[Ni(Cl)_4]$

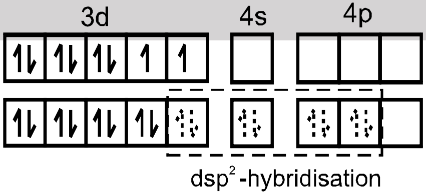
Potassium tetrachloronickelate(II)
(B)

8. Refer above solutions.

9. In cyano complex, $K_2[Ni(CN)_4]$, complex ion is $[Ni(CN)_4]^{2-}$ and Ni is present as Ni^{2+} or Ni (II) and CN^- is strong field ligand. Thus it compels for pairing of electrons. So,

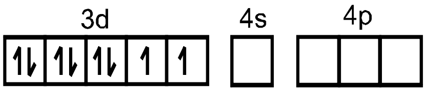
Ni^{2+}

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

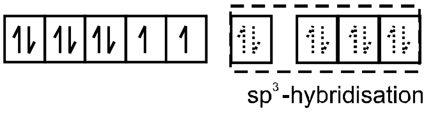


It does not contain unpaired electron. So it is diamagnetic in character and has square planar geometry. In chloro complex, $K_2[Ni(Cl)_4]$, complex ion is $[Ni(Cl)_4]^{2-}$ and Ni is present as Ni^{2+} or Ni (II) and Cl^- is weak field ligand. So,

Ni^{2+}



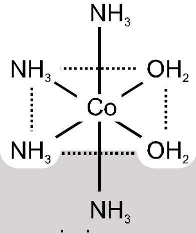
$[Ni(Cl)_4]^{2-}$

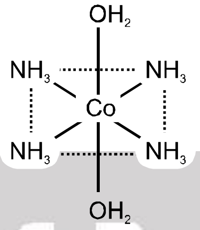


It contains two unpaired electrons. So it is paramagnetic in character and has tetrahedral geometry.

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 $[V(CO)_6]^-$.

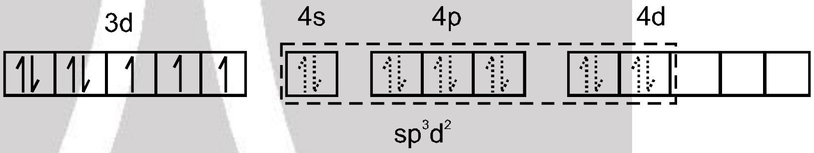
11. **(A)** $[Co(NH_3)_4(H_2O)Cl_2]$, it shows geometrical isomerism


cis-isomer

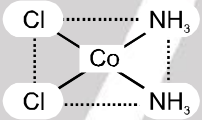

tran-isomer

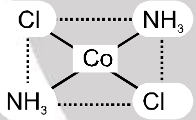
Co is in +2 oxidation state with $[Ar]^{18}$ $3d^7$ $4s^0$ electron configuration ; so complex is paramagnetic.
So,

$[Co(NH_3)_4(H_2O)_2]Cl_2$



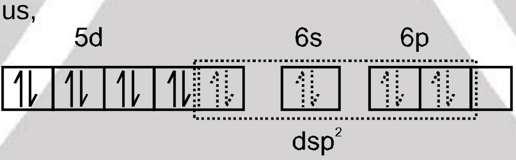
(B) $[Pt(NH_3)_2Cl_2]$, it show geometrical isomers.


cis-isomer


tran-isomer

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

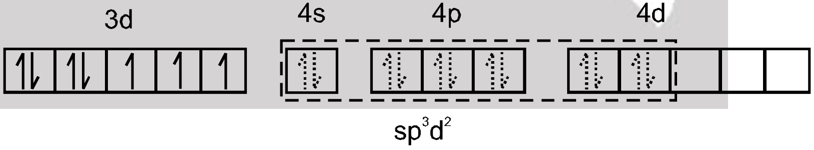
$[Pt(NH_3)_2Cl_2]$



As all electrons are paired so it is diamagnetic.

(C) $[Co(H_2O)_5Cl]Cl$, it does not show geometrical isomerism.
Co is in +2 oxidation state and because H_2O is weak field ligand. So,

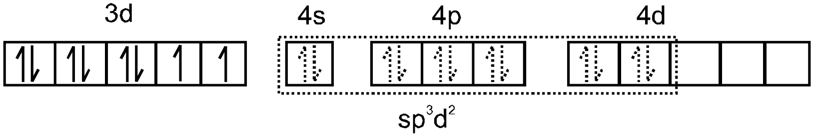
$[Co(H_2O)_5Cl]Cl$



As it contains 3 unpaired electrons so it is paramagnetic.

(D) $[Ni(H_2O)_6]Cl_2$, it does not show geometrical isomerism.
Ni is in + 2 oxidation state and because H_2O is weak field ligand. So,

$[Ni(H_2O)_6]Cl_2$



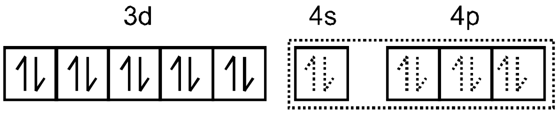
As it contains two unpaired electrons ; so it is paramagnetic.

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

13. Ni (28) → $1s^2, 2s^22p^6, 3s^23p^63d^8, 4s^2$

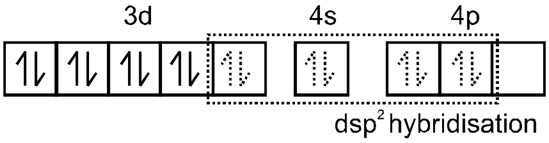
In $[Ni(CO)_4]$, Ni is in zero oxidation state and CO being strong field ligand compels for paring of electrons.

So, $[Ni(CO)_4]$



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

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

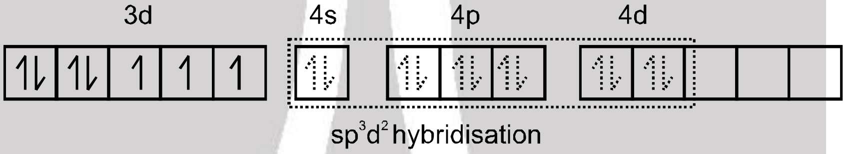


14. Both Cis– and trans forms of complex $[M(NH_3)_4Cl_2]$ are optically inactive because of the presence of plane of symmetry and centre of symmetry in them.

Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ have alternate axis of symmetry.

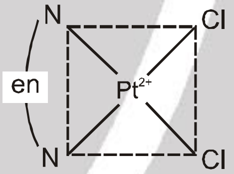
15. In $\overset{+1}{Fe}[(H_2O)_5]\ \overset{+1}{NO}SO_4$, Fe is in +1 oxidation state and water is weak field ligand. So,

$[Fe(H_2O)_5NO]^{2+}$



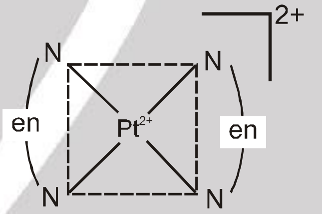
As it contains three unpaired electrons, the complex is paramagnetic.

16. (A) $[Pt(en)Cl_2]$:



exists only in one form.

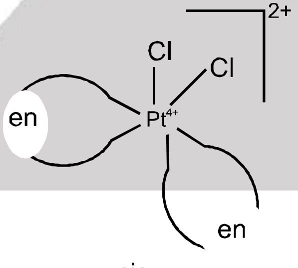
(B) $[Pt(en)_2]Cl_2$:



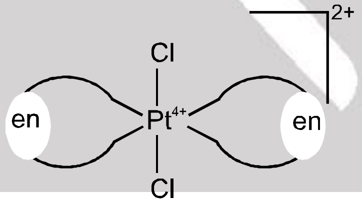
exists only in one form

('en' is symmetrical lignad).

(C) $[Pt(en)_2Cl_2]Cl_2$:

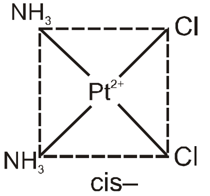


cis–

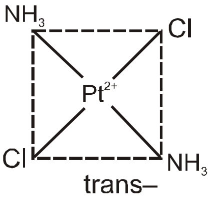


trans–

(D) $[Pt(NH_3)_2Cl_2]$: Pt is in +2 oxidation state having $5d^8$ configuration. Hence the hybridisation of complex is dsp^2 and geometry is square planar.



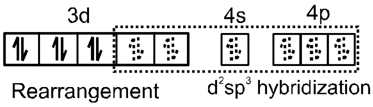
cis–



trans–

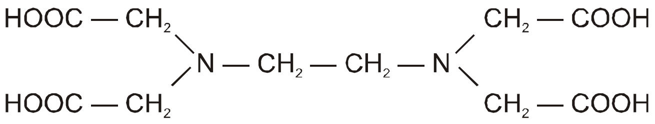
17. The chromium is in zero oxidation state having configuration $[Ar]^{18}$ $3d^5$ $4s^1$. The CO is a strong field ligand so compels for the pairing of electrons. Thus the complex has d^2 sp^3 hybridisation and is diamagnetic.

$[Cr(CO)_6]$



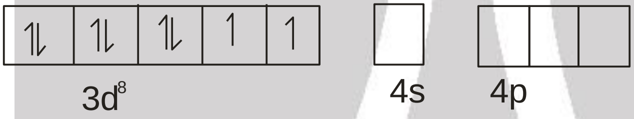
$\mu_{BM} = \sqrt{n(n+2)}$ = 0 as there is no unpaired electrons.

18. Structure of EDTA is :



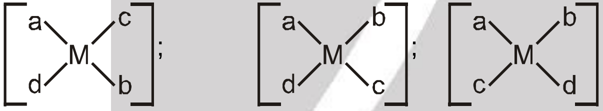
19. The ionisation isomer for the given compound will be obtained by exchanging ligand with counter ion as:
$[Co(H_2O)_4Cl_2](NO_2)$.

20. Ni : $3d^8$ $4s^2$
Ni^{2+}, $3d^8$
since Cl is a weak field ligand, so it will not cause a paring of electron.



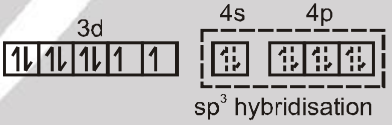
N = 2
$\mu = \sqrt{N(N+2)} = \sqrt{2(2+2)}$ B.M. $= \sqrt{8}$ B.M. = 2.82 B.M.

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)

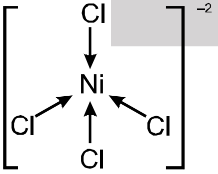


22. $Ni^{2+}(aq) + 4Cl^-(aq) \longrightarrow [NiCl_4]^{2-}(aq)$
$[NiCl_4]^{2-}$; $3d^8$ electron configuration with nickel in + 2 oxidation state. Cl^- being weak field ligand does not compel for pairing of electrons. So,

$[NiCl_4]^{2-}$

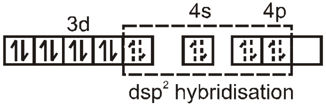


Hence, complex has tetrahedral geometry.

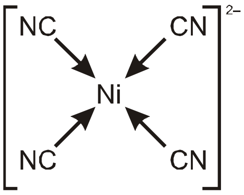


$Ni^{2+}(aq) + 4CN^-(aq) \longrightarrow [Ni(CN)_4]^{2-}(aq)$
$[Ni(CN)_4]^{2-}$; $3d^8$ electron configuration with nickel in + 2 oxidation state. CN^- being strong field ligand compels for pairing of electrons. So,

$[NiCN_4]^{2-}$

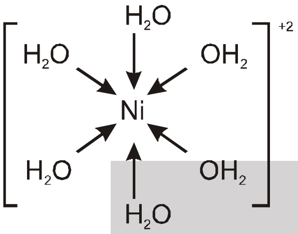


Hence, complex has square planar geometry.



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

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



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

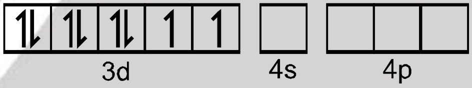
23. K–$[Fe(CN)_6]^{3-}$: $3d^5$ electron configuration after pairing of electrons for d^2sp^3 hybridisation it contains one unapaired electrons.
L–$[Co(NH_3)_6]^{3+}$: $3d^6$ electron configuration, d^2sp^3, diamagnetic.
M–$[Co(ox)_3]^{3-}$: $3d^6$ electron configuration, d^2sp^3, diamagnetic.
N–$[Ni(H_2O)_6]^{2+}$: $3d^8$ electron configuration, sp^3d^2, with two unpaired electrons paramagnetic.
O–$[Pt(CN)_4]^{2-}$: $5d^8$ electron configuration, dsp^2, diamagnetic.
P–$[Zn(H_2O)_6]^{2+}$: $3d^{10}$ electron configuration, sp^3d^2, diamagnetic.

24. m moles of $[Cr(H_2O)_5Cl]Cl_2 = 0.01 \times 30 = 0.3$.
$\Rightarrow$ mmole of $Cl^- = 0.3 \times 2 = 0.6$
$\Rightarrow$ mmole of Ag^+ = mmoles of Cl^-
$\Rightarrow$ $0.1 \times V = 0.6$
$\Rightarrow$ V = 6 mL.

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

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

$Ni^{2+} = [Ar]\ 3d^8 4s^0$

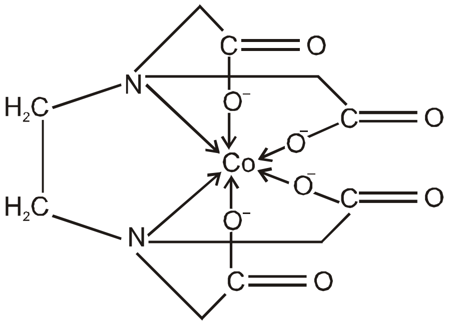


In high spin state, it is paramagnetic, sp^3 hybridised, tetrahedral.
In low spin state, it is diamagnetic, dsp^2, square planar.

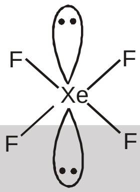
27. **P = $[FeF_6]^{3-}$** ox. no. of Fe = +3 , configuration : - $3d^5\ 4s^0$
As F^- is weak ligand, pairing does not take place.
so it has 5 unpaired electron
Q = $[V(H_2O)_6]^{2+}$ ox. no. of V = + 2, configuration $3d^3\ 4s^0$
It has 3 unpaired electrons.
R = $[Fe(H_2O)_6]^{2+}$, ox. no. of Fe = +2, configuration $3d^6$, $4s^0$
As H_2O is weak ligand, pairing does not take place, so it has 4 unpaired electron
$\Rightarrow$ order of spin only magnetic moment $\Rightarrow$ $Q < R < P$
so, answer is (B).

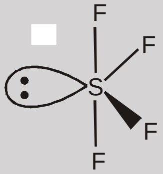
28. (A) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2)Cl$, both compounds will not show either structural or stereoisomerism.
(B) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$, Ma_4b_2 type (octahedral), Ma_2bc type (square planar) and both will show geometrical isomerism.
(C) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$, Ma_2b_2 type (tetrahedral), Ma_2b_2 (square planar).
(D) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$ both will show ionisation isomerism.

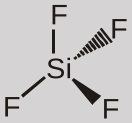
29.

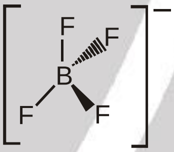


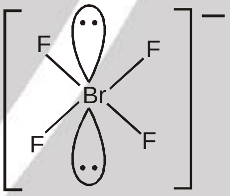
30.

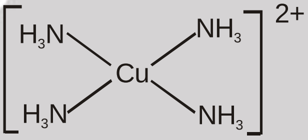
XeF$_4$ =  Square planar (sp^{3}d^2)

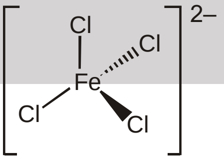
SF$_4$ =  See-saw (sp^{3}d)

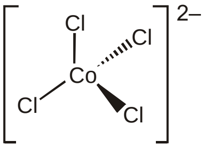
SiF$_4$ =  Tetrahedral (sp^3)

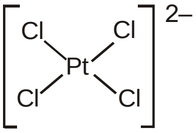
BF$_4^-$ =  Tetrahedral (sp^3)

BrF$_4^-$ =  Square planar (sp^{3}d^2)

[Cu(NH$_3$)$_4$]$^{2+}$ =  Square planar (dsp^2)

[FeCl$_4$]$^{2-}$ =  Tetrahedral (sp^3)

[CoCl$_4$]$^{2-}$ =  Tetrahedral (sp^3)

[Pt Cl$_4$]$^{2-}$ =  Square planar (dsp^2)

31.

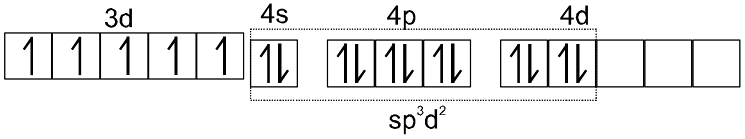
(P)	$[Cr(NH_3)_4Cl_2]Cl$	Cr^{+3} is d^3. It is paramagnetic and it shows cis-trans isomerism.
(Q)	$[Ti(H_2O)_5Cl](NO_3)_2$	Ti^{+3} is d^1. It is paramagnetic and it show ionisation isomerism.
(R)	$[Pt(en)(NH_3)Cl]NO_3$	Pt^{+2} is d^8. But this complex is square planar and all electron are paired. So it is diamagnatic. It exhibit ionisation isomerism.
(S)	$[Co(NH_3)_4(NO_3)_2]NO_3$	Co^{+3} is d^6. Since ligands are strong, so electron are paired. It is diamagnetic. It exhibit cis-trans isomerism.

Ans. is (B).

32. SCN^- is weak field effect (WFE) ligand whereas CN^- is strong field effect (SFE) ligand.

$_{26}Fe^{+3}$ in

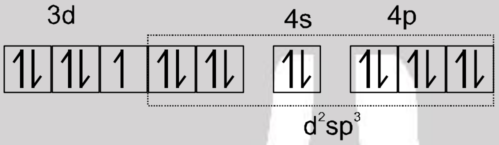
$[Fe(SCN)_6]^{3-}$ = [Ar]



Spin only magnetic moment = $\sqrt{5(5+2)}$ = $\sqrt{35}$ BM

$_{26}Fe^{+3}$ in

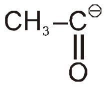
$[Fe(CN)_6]^{3-}$ = [Ar]



Spin only magnetic moment = $\sqrt{1(1+2)}$ = $\sqrt{3}$ BM

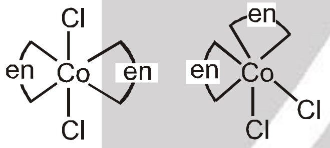
Difference = $\sqrt{35}$ – $\sqrt{3}$ = 4

33. $[Fe(CH_3CO)Br(CO)_2\{P(C_2H_5)_3\}_2]$

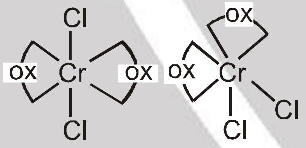

$CH_3-\underset{\underset{O}{\|}}{C}^{\ominus}$ Ligand $\longrightarrow$ One Fe–C bond

34. All the complexes given show cis-trans isomerism

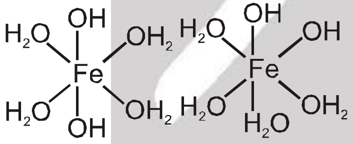
$[Co(NH_2–CH_2–CH_2–NH_2)Cl_2]^+$



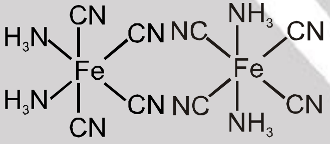
$[(CrCl_2(C_2O_4)_2]^{3-}$



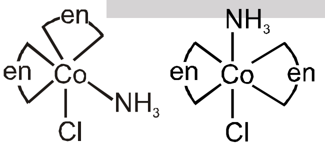
$[Fe(H_2O)_4(OH)_2]^+$



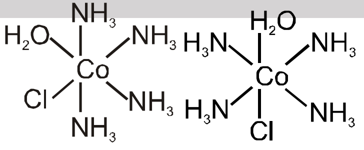
$[Fe(NH_3)_2(CN)_4]^-$



$[Co(NH_2–CH_2–CH_2–NH_2)_2(NH_3)Cl]^{2+}$



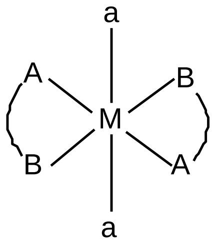
$(CO(NH_3)_4(H_2O)Cl]^{2+}$

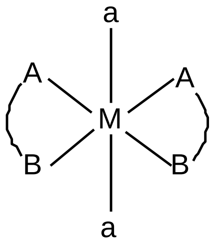


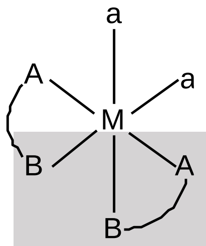
35.

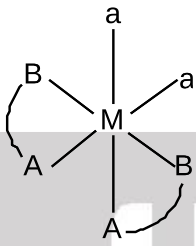
$[Ni(CO)_4]$	$3d^{10}$, sp^3	0 unpaired electron
$[NiCl_4]^{2-}$	$3d^8$, sp^3	2
$[Co(NH_3)_4Cl_2]Cl$	$3d^6$, d^2sp^3	0
$Na_3[CoF_6]$	$3d^6$, sp^3d^2	4
Na_2O_2	O_2^{2-}	0
CsO_2	O_2^{-1}	1

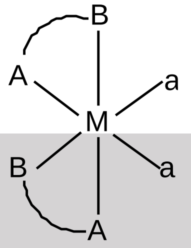
36. $[CoL_2Cl_2]^-$ ($L = H_2NCH_2CH_2O^-$)
L is unsymmetrical didentate ligand.
So it is equivalent to $[M(AB)_2a_2]$ Possible G.I. are











37. Ni^{2+} with NH_3 shows CN = 6 forming $[Ni(NH_3)_6]^{2+}$ (Octahedral)
Pt^{2+} with NH_3 shows CN = 4 forming $[Pt(NH_3)_4]^{2+}$ (5d series CMA, square planner)
Zn^{2+} with NH_3 shows CN = 4 forming $[Zn(NH_3)_4]^{2+}$ ($3d^{10}$ configuration, tetrahedral)

38. $\Rightarrow$ $Fe(CO)_5$: Total number of valence electrons is 18
: low spin complex.
$\Rightarrow$ $Ni(CO)_4$: 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.

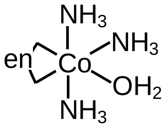
39. Paramagnetic : Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$, K_2MnO_4
Diamagnetic : K_2CrO_4

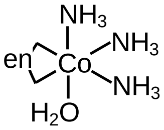
40.

$$\begin{tikzcd} Ca(OH)_2 + \underset{1584\ g}{(NH_4)_2SO_4} \arrow[r] & 2NH_3 + CaSO_4.2H_2O \arrow[d, "{[Ni(H_2O)_6]Cl_2}"] \\ & \text{Complex Compound} \end{tikzcd}$$

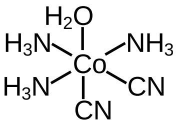
Number of Moles of $(NH_4)_2SO_4 = \frac{1584}{132} = 12$ moles
Moles of NH_3 released = 24 moles
Moles of $NiCl_2.6H_2O = \frac{952}{238} = 4$ moles
Number of moles of Gypsum ($CaSO_4.2H_2O$) formed = 12 moles
Mass of Gypsum formed = 12 × 172 = 2064
Number of moles of complex formed $[Ni(NH_3)_6]Cl_2 = \frac{24}{6} = 4$ moles
Mass of complex formed = 4 × 232 = 928 g
Total Mass = 2064 + 928 = 2992 g

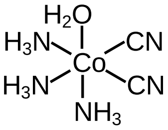
41. **(A)** $[Co(en)(NH_3)_3(H_2O)]^{3+}$ has 2 geometrical isomers

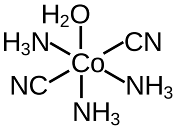




(B) Compound $[Co(CN)_2(NH_3)_3(H_2O)]^+$ will have three geometrical isomers.







(C) $[Co(en)(NH_3)_3(H_2O)]^{3+}$ is diamagnetic

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

42. 1. FeF_6^{4-} $3d^6$ & weak field ligand
$\therefore$ Hybridization is sp^3d^2

2. $[Ti(H_2O)_3Cl_3]$ $3d^1$ & weak field ligand
$\therefore$ Hybridization is d^2sp^3

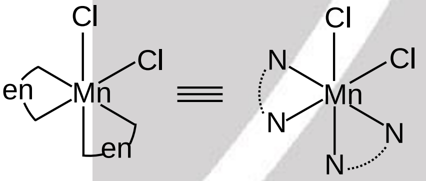
3. $[Cr(NH_3)_6]^{3+}$, $3d^3$ & strong field ligand.
$\therefore$ Hybridization is d^2sp^3

4. $[FeCl_4]^{2-}$ $3d^6$ & weak field ligand.
$\therefore$ Hybridization is sp^3

5. $Ni(CO)_4$, $3d^{10}$
$\therefore$ Hybridization is sp^3

6. $[Ni(CN)_4]^{2-}$, $3d^8$
$\therefore$ dsp^2 hybridization

43.



PART - II

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

10. CH_4 does not have lone pair.

11. (1) Fe^{3+} $(d^5) \rightarrow t_{2g}^3, e_g^2$ (symmetrically filled) (2) $Mn^{2+}(d^5) \rightarrow t_{2g}^5, e_g^0$ (t_{2g} unsymmetrically filled)

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

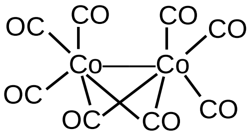
12. $\Delta_o \propto$ CFSE (Crystal field stabilization energy)
Δ_o of $[Cr(H_2O)_6]^{2+} < \Delta_o$ of $[Mo(H_2O)_6]^{2+}$
Because here Δ_o depends on Z_{eff} & Z_{eff} of 4d series is more than 3d series.
But Δ_o of $[Ti(H_2O)_6]^{3+} > \Delta_o$ of $[Ti(H_2O)_6]^{2+}$

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

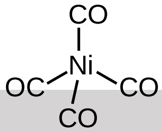
14. Complex having only 1 type of ligands are examples of homoleptic complex.

15. In PF_5 hybridisation is sp^3d.

16.

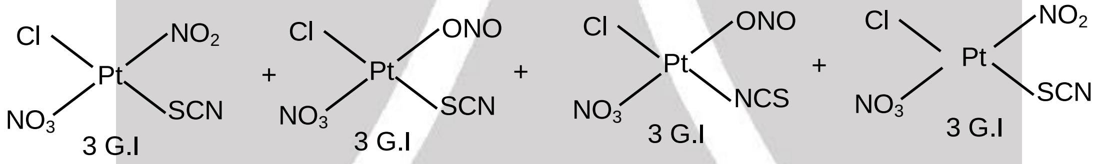


17.

$[NiCl_4]^{2-}$	$[Ni(CO)_4]$
sp^3	sp^3
Paramagnetic (2 unpaired electron)	
$Ni^{2+} \rightarrow [Ar]3d^8, 4s^0, 4p^0$	$Ni(O) \rightarrow [Ar]3d^8, 4s^2, 4p^0$
Cl^- (W.F.L.) (No pairing)	CO is S.F.L. $[Ar]\ \ 3d^{10}\underbrace{4s^0, 4p^0}_{sp^3}$ (Tetrahedral)

18. $[MnCl_4]^{2-}$ unpaired electrons = 5 ; $[CoCl_4]^{2-}$ unpaired electrons = 3
$[NiCl_4]^{2-}$ unpaired electrons = 2 ; $[ZnCl_4]^{2-}$ unpaired electrons = 0

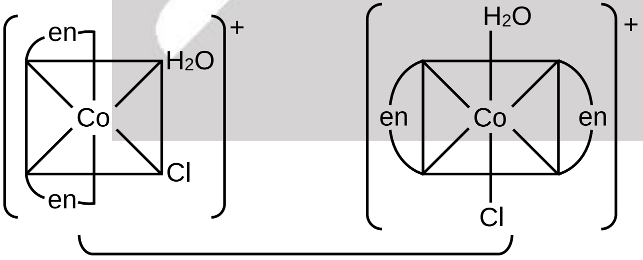
19. Total 12 isomers are possible including geometrical and linkage isomers.



20. Initially ligand consumed by metal due to formation of complex. So absorbed light (A) remain constant, after complex formation is completed, extra volume of ligand solution increases ligand concentration and also increases absorbed light.

21. Wilkinson catalyst
$[RhCl(PPh_3)_3]$

22. $[Co(H_2O)Cl(en)_2]Cl$



(Geometrical Isomer)

23. The crystal field splitting parameter can't be measured by wavelength of yellow and violet colours for (A) and (B) respectively

24. λ Blue < Green < Red
$\lambda\ L_2 < L_1 < L_3$
$\Delta_{\text{Absorption}}\ L_2 > L_1 > L_3$
$\therefore$ Ligand strength = $L_2 > L_1 > L_3$

25. CN^- is strong ligand, So $[Co(CN)_6]^{-3}$ have maximum CFSE

26. Refer Notes

27.

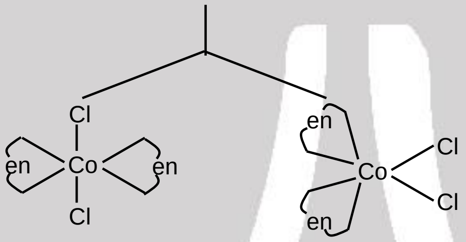
	No. of Isomers
$[M(F)(Cl)(SCN)(NO_2)] \rightarrow$	3
$[M(F)(Cl)(NCS)(NO_2)] \rightarrow$	3
$[M(F)(Cl)(SCN)(ONO)] \rightarrow$	3
$[M(F)(Cl)(NCS)(ONO)] \rightarrow$	3
	Total = 12

28.

$$d^7 \begin{cases} t_{2g}^{2,\,2,\,2}\, eg^{1,\,0} & \text{Low spin} \\ t_{2g}^{2,\,2,\,1}\, eg^{1,\,1} & \text{High spin} \end{cases}$$

29. $CoCl_3$ + en → $[Co(en)_2Cl_2]Cl$

1 mole 2 mole



Geometrical Isomers

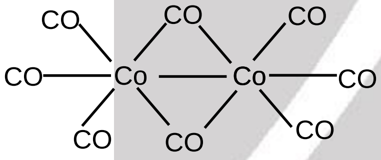
30. Based on Fact

31. C.No. = 4 × 2 + 2× 1 = 10

$C_2O_4^{-2}$ bidentate

OH^- monodentate

32.



No of Co–Co bond = 1

no of briding carbonyl = 2

33. $K_3[Co(CN)_6]$ is octahedral geometry. Ligands are approaching there co-ordinate metal along the there coordinate axes. Hence $d_{x^2-y^2}, d_{z^2}$ (axial orbitals) orbitals are directly infront of the ligands.

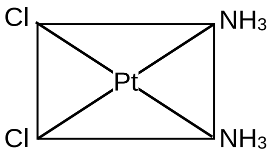
34. Organometallic compound have bond between "Metal or Metalloid" and carbon.

36. The given ligand is tetradentate

37.

Complex ion	**Electronic configuration of metal ion in the complex ion**	**Magnetic moment in B.M.**
$[V(CN)_6]^{4-}$	$t_{2g}^{1,1,1}$, $e_g^{0,0}$	$\sqrt{15}$
$[Fe(CN)_6]^{4-}$	$t_{2g}^{2,2,2}$, $e_g^{0,0}$	0
$[Ru(NH_3)_6]^{3+}$	$t_{2g}^{2,2,1}$, $e_g^{0,0}$	$\sqrt{3}$
$[Cr(NH_3)_6]^{2+}$	$t_{2g}^{2,1,1}$, $e_g^{0,0}$	$\sqrt{8}$

38.



39. $[Fe(CN)_6]^{-4}$
$Fe^{+2} \longrightarrow 3d^6$
$CN^- \longrightarrow$ S.F.L.
$t_{2g}^{2,2,2}\ eg^{0,0}$
No. of unpaired e^- = 0
B.M. = 0
$[Fe(H_2O)_6]^{+2}$
$Fe^{+2} \longrightarrow 3d^6$
$H_2O \longrightarrow$ W.F.L.
$t_{2g}^{2,1,1}\ eg^{1,1}$
No. of unpaired e^- = 4
$\mu = \sqrt{4\times6} = \sqrt{24}$ B.M. = 4.9BM

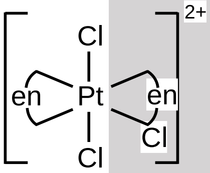
40. $\left[Cr(H_2O)_6\right]^{3+}$ has d^2sp^3 hybridisation. dxy, dyz, dxz orbitals are degenerate

41. $[M(AA)\ a_2b_2]$ shows optical activity in cis-arrangement.

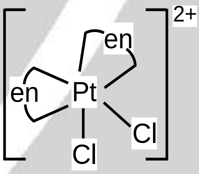
42. VBT does not explain the colour exhibited by co-ordination compounds.
VBT does not explains and gives quantitative interpretation of magnetic data.
VBT does not distinguish between weak field ligand and strong field ligand.

43. λ absorbed depends on strength of ligand. For stronger ligand, Δ_0 will be higher, λ will be lesser.
$NH_3 > H_2O > Cl^-$ decreasing order of strength of ligand.

44. $[Pt(en)_2Cl_2]^{2+}$



trans



cis

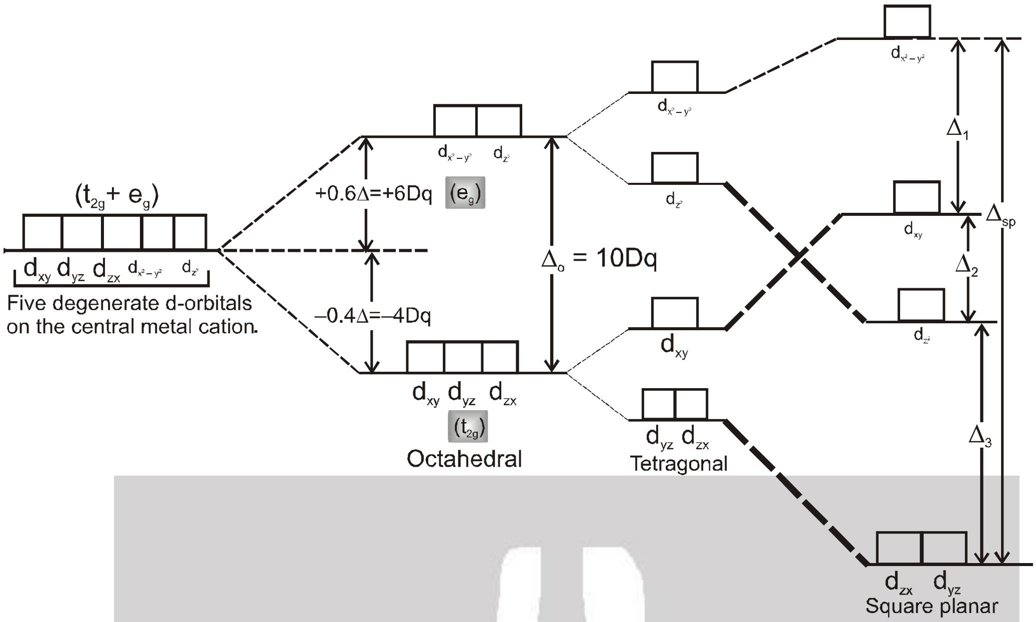
all other do not show geometrical isomerism.

45. The gemstone, emerald, has Cr^{3+} ions occupying the octahedral sites of beryl.

46. $[Fe(H_2O)_6]^{2+}$
$Fe^{+2} \longrightarrow [Ar]3d^6$
$H_2O \longrightarrow$ weak field ligand, so pairing do not take place.
$t_{2g}^{2,1,1}\quad eg^{1,1}$
CFSE = $-\,0.4 \times 4\ \Delta_0 + 0.6 \times 2\ \Delta_0 = -\,0.4\ \Delta_0$
$[NiCl_4]^{2-}$
$Ni^{+2} \longrightarrow [Ar]3d^8$
$Cl^- \longrightarrow$ weak field ligand, so pairing do not take place and have tetrahedral geometry
$eg^{2,2}\ ,\ t_{2g}^{2,1,1}$
CFSE = $-\,0.6 \times 4\ \Delta_t + 0.4 \times 4\ \Delta_t = -\,2.4\ \Delta_t + 1.6\ \Delta_t = -\,0.8\ \Delta_t$

47. $[Fe(phen)_3]^{2+}$ will lose its crystal field stabilization energy upon oxidation of its metal to +3 state.

48.



49. In $[Co(en)_2Cl]Cl$, co-ordination no = 2 × 2 + 1= 5
In $Na_3[Al(C_2O_4)_3]$, co-ordination no = 3 × 2 = 6

50. EDTA is used in the treatment of lead poisoning.