Coordination Compounds

NCERT Intext Questions

Q. 1. Write the formulas for the following coordination compounds:

(*i*) tetraamminediaquacobalt(III) chloride

(*ii*) Potassium tetracyanidonickelate(II)

(*iii*) tris (ethane-1, 2-diamine) chromium(III) chloride

(*iv*) amminebromidochloridonitrito-N-platinate(II)

(*v*) dichloridobis(ethane-1, 2-diamine)platinum(IV) nitrate

(*vi*) Iron(III)hexacyanidoferrate(II)

Ans. (*i*) $[Co(NH_3)_4(H_2O)_2]Cl_3$ (*ii*) $K_2[Ni(CN)_4]$

(*iii*) $[Cr(en)_3]Cl_3$ (*iv*) $[Pt(NH_3)BrCl(NO_2)]^-$

(*v*) $[PtCl_2(en)_2](NO_3)_2$ (*vi*) $Fe_4[Fe(CN)_6]_3$

Q. 2. Write IUPAC names of the following coordination compounds:

(*i*) $[Co(NH_3)_6]Cl_3$ **(*ii*) $[Co(NH_3)_5Cl]Cl_2$**

(*iii*) $K_3[Fe(CN)_6]$ **(*iv*) $K_3[Fe(C_2O_4)_3]$**

(*v*) $K_2[PdCl_4]$ **(*vi*) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$**

Ans. (*i*) hexaamminecobalt(III) chloride (*ii*) pentaamminechloridocobalt(III) chloride

(*iii*) Potassium hexacyanoferrate(III) (*iv*) Potassium trioxalatoferrate(III)

(*v*) Potassium tetrachloridopalladate(II)

(*vi*) diamminechlorido(methylamine)platinum (II) chloride

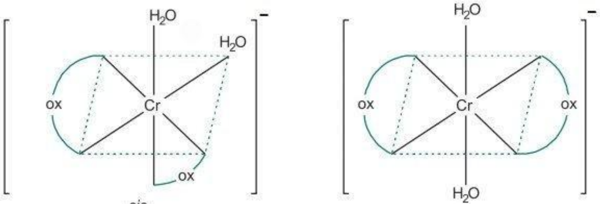
Q. 3. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(*i*) $K[Cr(H_2O)_2(C_2O_4)_2]$ **(*ii*) $[Co(en)_3]Cl_3$**

(*iii*) $[Co(NH_3)_5(NO_2)](NO_3)_2$ **(*iv*) $[Pt(NH_3)(H_2O)Cl_2]$**

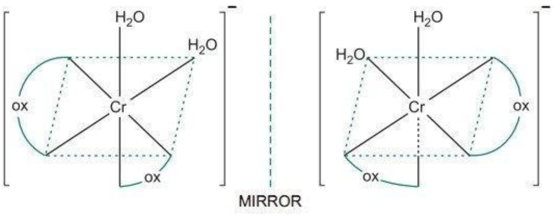
Ans. (*i*) Both geometrical (*cis–trans*) and optical isomers for *cis* can exist.

(*a*) Geometrical isomers of $K[Cr(H_2O)_2(C_2O_4)_2]$:

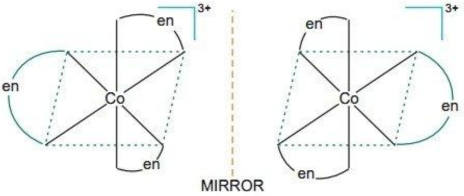


cis *trans*

(*b*) Optical isomers (*d*- and *l*-) of *cis*-$K[Cr(H_2O)_2(C_2O_4)_2]$:



(*ii*) Two optical isomers can exist.



(*iii*) Ionisation isomers:

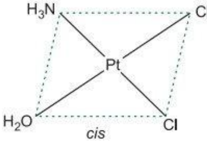
$[Co(NH_3)_5(NO_2)](NO_3)_2]$, $[Co(NH_3)_5(NO_3)](NO_2)(NO_3)]$

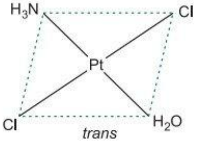
Linkage isomers:

$[Co(NH_3)_5(NO_2)](NO_3)_2]$, $[Co(NH_3)_5(ONO)](NO_3)_2]$

MA_5X type complexes do not show geometrical and optical isomerism.

(*iv*) Geometrical isomers can exist.





Q. 4. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.

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Ans. The ionisation isomers dissolve in water to yield different ions and thus react differently with various reagents:

$$[Co(NH_3)_5Cl]SO_4 + Ba^{2+} \longrightarrow \underset{\text{Ppt}}{BaSO_4(s)\downarrow}$$

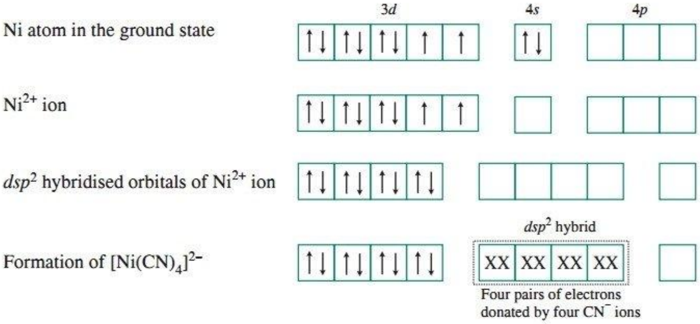
$$[Co(NH_3)_5SO_4]Cl + Ba^{2+} \longrightarrow \text{No reaction}$$

$$[Co(NH_3)_5Cl]SO_4 + Ag^{+} \longrightarrow \text{No reaction}$$

$$[Co(NH_3)_5SO_4]Cl + Ag^{+} \longrightarrow \underset{\text{Ppt}}{AgCl(s)\downarrow}$$

Q. 5. Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Ans. Nickel in $[Ni(CN)_4]^{2-}$ is in the +2 oxidation state. The formation of $[Ni(CN)_4]^{2-}$ may be explained through hybridisation as follows:



Since no unpaired electrons is present, the square planar complex is diamagnetic.

In $[NiCl_4]^{2-}$, Cl^- is a weak field ligand. It is, therefore, unable to pair up the unpaired electrons of the 3*d* orbital. Hence, the hybridisation involved is *sp*^{3} and the shape is tetrahedral. Since two electrons are unpaired, it is paramagnetic.

Q. 6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

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Ans. In $[Ni(CO)_4]$, Ni is in zero oxidation state whereas in $[NiCl_4]^{2-}$ it is in +2 oxidation state. In the presence of strong ligand, CO, the unpaired *d*-electrons of Ni pair up but Cl^- being a weak ligand is unable to pair up the unpaired electrons.

Q. 7. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

Ans. In presence of CN^- (a strong ligand), the $3d^5$ electrons pair up leaving only one unpaired electron. The hybridisation is d^2sp^3 forming an inner orbital complex. In the presence of H_2O (a weak ligand), 3*d* electrons do not pair up. The hybridisation is sp^3d^2 forming an outer orbital complex containing five unpaired electrons. Hence, it is strongly paramagnetic.

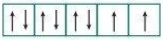
Q. 8. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Ans. In $[Co(NH_3)_6]^{3+}$, Co is in +3 oxidation state and has d^6 electrons. In the presence of NH_3, the 3*d* electrons pair up leaving two *d*-orbitals empty to be involved in d^2sp^3 hybridisation forming inner orbital complex.

In $[Ni(NH_3)_6]^{2+}$, Ni is in +2 oxidation state and has d^8 configuration. The hybridisation involved is sp^3d^2, forming the outer orbital complex.

Q. 9. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

Ans. In $[Pt(CN)_4]^{2-}$ ion, Pt is in +2 oxidation state, its electronic configuration is $5d^8$. It forms a square planar structure, it means the hybridisation is dsp^2.



$5d^8$

CN^- is a strong field ligand so pairing of unpaired electrons takes place. So, the number of unpaired electrons is 0.

Q. 10. The hexaaquamanganese(II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electron. Explain using crystal field theory.

Ans. Mn in the +2 state has the configuration $3d^5$. In the presence of H_2O a weak ligand, the distribution of these five electrons is $t_{2g}^3\,e_g^2$, *i.e.*, all the electrons remain unpaired. In the presence of CN^- a strong ligand, the distribution is $t_{2g}^5\,e_g^0$, *i.e.*, two t_{2g} orbitals contain paired electrons while the third t_{2g} orbital contains one unpaired electron.

NCERT Exercises

Q. 1. Explain the bonding in coordination compounds in terms of Werner's postulates.

Ans. Refer to Points to remember 15.

Q. 2. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

Ans. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio forms double salt $FeSO_4 . (NH_4)_2\,SO_4.6H_2O$ which ionises in the solution to give Fe^{2+} ions. Hence, it gives the test of Fe^{2+} ions.

$CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio forms a complex, with the formula $[Cu(NH_3)_4]SO_4$. The complex ion, $[Cu(NH_3)_4]^{2+}$ does not ionise to give Cu^{2+} ions. Hence, it does not give the test of Cu^{2+} ion.

Q. 3. Explain with two examples for each of the following:

Coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Ans. **Coordination Entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of molecules or ions (ligands), *e.g.*, $[Co(NH_3)_3Cl_3]$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, etc.

Ligands: Ligands are the atoms, molecules or ions which donate a pair of electrons to central metal atom or ion and form a coordinate bond with it.

Example: $\ddot{N}H_3$, $H_2\ddot{N}CH_2—CH_2\ddot{N}H_2$

Coordination Number (CN): The coordination number of a metal ion in a complex may be defined as the total number of ligand donor atoms to which the metal ion is directly bonded. For example, in the complex ions, $[Co(NH_3)_6]^{3+}$ and $[Fe(C_2O_4)_3]^{3-}$ the coordination numbers of both Co and Fe is 6.

Coordination Polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion is known as the coordination polyhedron around the central atom/ion. Tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal are common shapes of coordination polyhedra.

Homoleptic Complex: The complex in which metal atom is bound to only one kind of donor groups, *e.g.*, $[Cu(CN)_4]^{3-}$.

Heteroleptic Complex: The complex in which metal atom is bound to more than one kind of donor groups, *e.g.*, $[Co(NH_3)_4Cl_2]^+$.

Q. 4. What is meant by unidentate, bidentate and ambidentate ligands? Give two examples for each.

Ans. A molecule or an ion which has only one donor atom to form one coordinate bond with the central metal atom is called unidentate ligand, *e.g.*, Cl^- and NH_3.

A molecule or an ion which contains two donor atoms and hence forms two coordinate bonds with the central metal atom is called a bidentate ligand, *e.g.*, $NH_2—CH_2—CH_2—NH_2$ and $^-OOC—COO^-$.

A molecule or an ion which contains two donor atoms but only one of them forms a coordinate bond at a time with the central metal atom is called ambidentate ligand, *e.g.*, CN^- or NC^- and $:NO_2^-$ or $:ONO^-$.

Q. 5. Specify the oxidation numbers of the metals in the following coordination entities:

(*i*) $[Co(H_2O)(CN)(en)_2]^{2+}$

(*ii*) $[CoBr_2(en)_2]^+$

(*iii*) $[PtCl_4]^{2-}$

(*iv*) $K_3[Fe(CN)_6]$

(*v*) $[Cr(NH_3)_3Cl_3]$

Ans. (*i*) $x + (0) + (-1) + (0) = +2$ or $x = +3$

(*ii*) $x + 2(-1) + 0 = +1$ or $x = +3$

(*iii*) $x - 4 = -2$ or $x = +2$

(*iv*) $3(1) + x + 6(-1) = 0$ or $x = +3$

(*v*) $x + 0 + 3(-1) = 0$ or $x = +3$

Q. 6. Using IUPAC norms, write the formulae of the following:

(*i*) tetrahydroxozincate(II)

(*ii*) Potassium tetrachloridopalladate(II)

(*iii*) diamminedichloridoplatinum(II)

(*iv*) Potassium tetracyanidonickelate(II)

(*v*) pentaamminenitrito-O-cobalt(III)

(*vi*) hexaamminecobalt(III) sulphate

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(*vii*) Potassium tri(oxalato)chromate(III)

(*viii*) hexaammineplatinum(IV)

(*ix*) tetrabromidocuprate(II)

(*x*) pentaamminenitrito-N-cobalt(III)

Ans. (*i*) $[Zn(OH)_4]^{2-}$

(*ii*) $K_2[PdCl_4]$

(*iii*) $[Pt(NH_3)_2Cl_2]$

(*iv*) $K_2[Ni(CN)_4]$

(*v*) $[Co(NH_3)_5(ONO)]^{2+}$

(*vi*) $[Co(NH_3)_6]_2(SO_4)_3$

(*vii*) $K_3[Cr(C_2O_4)_3]$

(*viii*) $[Pt(NH_3)_6]^{4+}$

(*ix*) $[CuBr_4]^{2-}$

(*x*) $[Co(NH_3)_5(NO_2)]^{2+}$

Q. 7. Using IUPAC norms, write the systematic names of the following:

(*i*) $[Co(NH_3)_6]Cl_3$ **(*ii*) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$**
(*iii*) $[Ti(H_2O)_6]^{3+}$ **(*iv*) $[Co(NH_3)_4Cl(NO_2)]Cl$**
(*v*) $[Mn(H_2O)_6]^{2+}$ **(*vi*) $[NiCl_4]^{2-}$**
(*vii*) $[Ni(NH_3)_6]Cl_2$ **(*viii*) $[Co(en)_3]^{3+}$**
(*ix*) $[Ni(CO)_4]$

Ans. (*i*) hexaamminecobalt(III) chloride (*ii*) diamminechlorido(methylamine)platinum (II) chloride
(*iii*) hexaaquatitanium(III) ion (*iv*) tetraamminechloridonitrito-N-cobalt(III) chloride
(*v*) hexaaquamanganese(II) ion (*vi*) tetrachloridonickelate(II)
(*vii*) hexaamminenickel(II) chloride (*viii*) *tris* (ethane-1, 2-diamine) cobalt(III) ion
(*ix*) tetracarbonylnickel (0)

Q. 8. List various types of isomerism possible for coordination compounds, giving an example of each.

Ans. Refer to Points to remember 14.

Q. 9. How many geometrical isomers are possible in the following coordination entities?

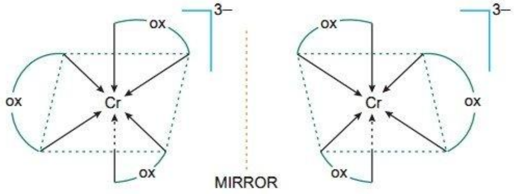
(*i*) $[Cr(C_2O_4)_3]^{3-}$ **(*ii*) $[Co(NH_3)_3Cl_3]$**

Ans. (*i*) Nil (*ii*) Two (*cis* and *trans*)

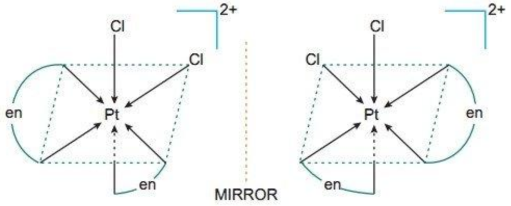
Q. 10. Draw the structures of optical isomers of

(*i*) $[Cr(C_2O_4)_3]^{3-}$ **(*ii*) $[PtCl_2(en)_2]^{2+}$**
(*iii*) $[Cr(NH_3)_2Cl_2(en)]^{+}$

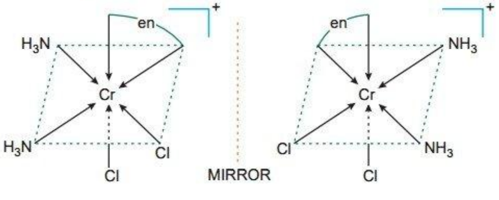
Ans. (*i*) $[Cr(C_2O_4)_3]^{3-}$



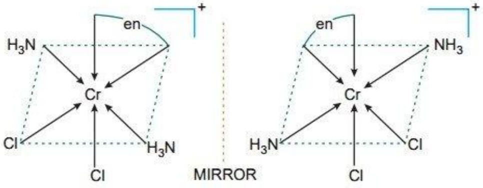
(*ii*) *cis*-$[PtCl_2(en)_2]^{2+}$:



(*iii*) (*a*) *cis*-$[Cr(NH_3)_2Cl_2(en)]^{+}$



(*b*) *trans*-[$Cr(NH_3)_2Cl_2(en)$]$^+$



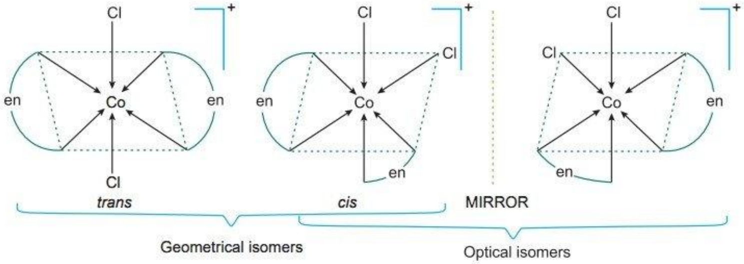
Q. 11. Draw all the isomers (geometrical and optical) of:

(*i*) [$CoCl_2(en)_2$]$^+$

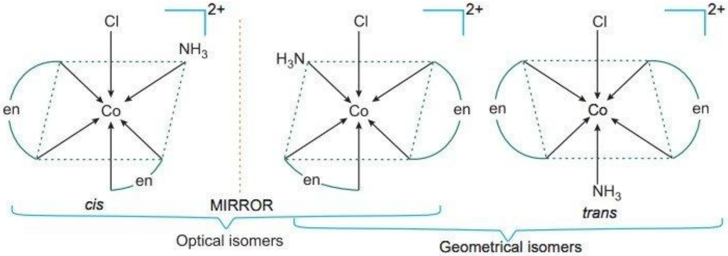
(*ii*) [$Co(NH_3)Cl(en)_2$]$^{2+}$

(*iii*) [$Co(NH_3)_2Cl_2(en)$]$^+$

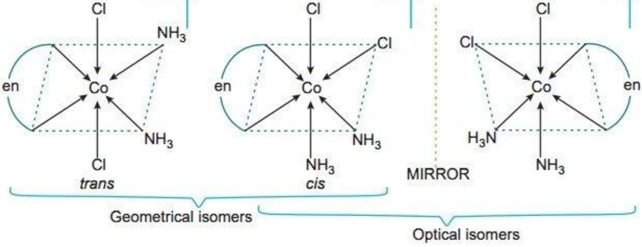
Ans. (*i*)



(*ii*)

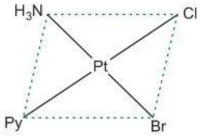


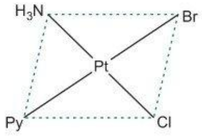
(*iii*)

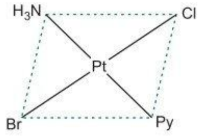


Q. 12. Write all the geometrical isomers of [Pt(NH_3)(Br)(Cl)(py)] and how many of these will exhibit optical isomerism?

Ans. Three isomers are possible as follows:







Isomers of this type do not show any optical isomerism. Optical isomerism rarely occurs in square planar or tetrahedral complexes and that too when they contain unsymmetrical chelating ligand.

Q. 13. Aqueous copper sulphate solution (blue in colour) gives (*i*) a green precipitate with aqueous potassium fluoride, and (*ii*) a bright green solution with aqueous potassium chloride. Explain these experimental results.

Ans. Aqueous copper sulphate exists as $[Cu(H_2O)_4]SO_4$. It is a labile complex. The blue colour of the solution is due to $[Cu(H_2O)_4]^{2+}$ ions.

(*i*) When KF is added, the weak H_2O ligands are replaced by F^- ligands forming $[CuF_4]^{2-}$ ions, which is a green precipitate.

$$[Cu(H_2O)_4]^{2+} + 4F^- \longrightarrow \underset{\substack{\text{tetrafluorocuprate (II)} \\ \text{(Green ppt.)}}}{[CuF_4]^{2-}} + 4H_2O$$

(*ii*) When KCl is added, Cl^- ligands replace the weak H_2O ligands forming $[CuCl_4]^{2-}$ ion, which has bright green colour.

$$[Cu(H_2O)_4]^{2+} + 4Cl^- \longrightarrow \underset{\substack{\text{tetrachlorocuprate (II)} \\ \text{(Green solution)}}}{[CuCl_4]^{2-}} + 4H_2O$$

Q. 14. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

Ans. $K_2[Cu(CN)_4]$ is formed when excess of aqueous KCN is added to an aqueous solution of $CuSO_4$.

$$\underset{\text{Copper sulphate}}{CuSO_4(aq)} + \underset{\text{Potassium cyanide}}{4KCN(aq)} \longrightarrow \underset{\substack{\text{Potassium} \\ \text{tetracyanocuprate (II)} \\ \text{(soluble)}}}{K_2[Cu(CN)_4]} + K_2SO_4(aq)$$

As CN^- ions are strong ligands the complex is very stable. It is not replaced by S^{2-} ions when H_2S gas is passed through the solution and thus no precipitate of CuS is obtained.

Q. 15. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(*i*) $[Fe(CN)_6]^{4-}$ **(*ii*) $[FeF_6]^{3-}$**

(*iii*) $[Co(C_2O_4)_3]^{3-}$ **(*iv*) $[CoF_6]^{3-}$** ***[CBSE 2020 (56/2/1)]***

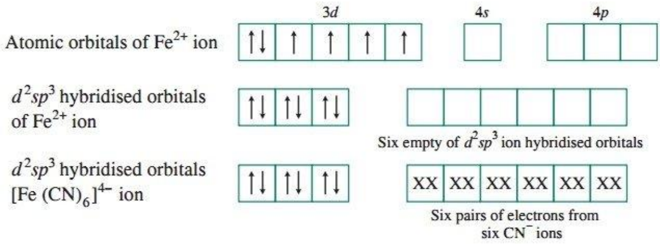
Ans. (*i*) **$[Fe(CN)_6]^{4-}$:** d^2sp^3, octahedral, diamagnetic.

In this complex ion, the oxidation state of iron is +2.

Electronic configuration of Fe = [Ar] $3d^6\,4s^2$

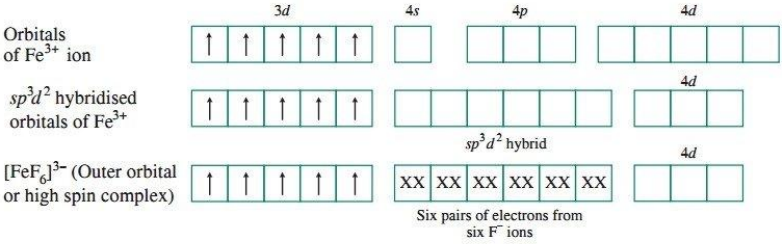
Electronic configuration of Fe^{2+} = [Ar] $3d^6$

To accommodate six pairs of electrons from six cyanide ions, the iron(II) ion must make available six empty orbitals. This can be achieved by the following hybridization scheme wherein electrons in the *d*-subshell have been paired up as CN^- ions are strong field ligands.



Thus, six pairs of electrons from six cyanide ions occupy the six hybridized orbitals of iron (II) ion. At the same time, we find no orbital which contains unpaired electron. Hence, $[Fe(CN)_6]^{4-}$ is octahedral and shows diamagnetism.

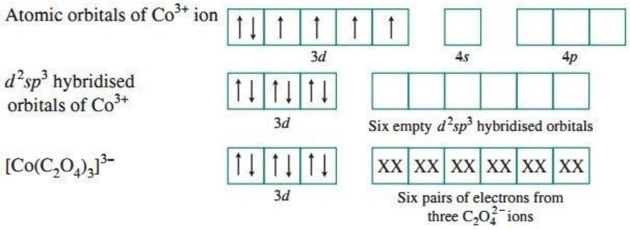
(*ii*) $[FeF_6]^{3-}$



Number of unpaired electrons (n) = 5

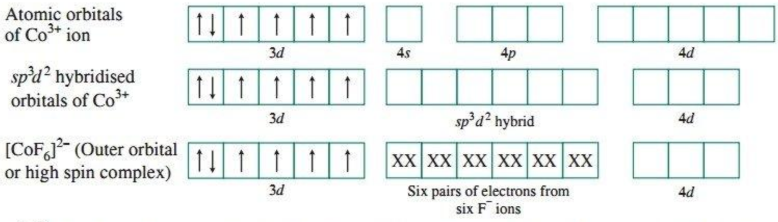
Magnetic moment (μ) = $\sqrt{5(5+2)} = \sqrt{35} = 5.92$ BM

(*iii*) $[Co(C_2O_4)_3]^{3-}$



This complex is inner-orbital complex. It is an octahedral complex with d^2sp^3 hybridisation. As there is no orbital which contains unpaired electron, the complex is diamagnetic.

(*iv*) $[CoF_6]^{3-}$



sp^3d^2 hybridisation leads to octahedral geometry. Paramagnetic, as there are four unpaired electrons.

Q. 16. Draw figure to show the splitting of *d* orbitals in an octahedral crystal field.

Ans. Refer to Points to remember 16 (Fig. 5.2).

Q. 17. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

Ans. The arrangement of ligands in order of their increasing field strengths, *i.e.*, increasing crystal field splitting energy (CFSE) values is called spectrochemical series.

The ligands with a small value of CFSE (Δ_o) are called weak field ligands whereas those with a large value of CFSE are called strong field ligands.

Q. 18. What is crystal field splitting energy? How does the magnitude of Δ_0 decide the actual configuration of *d*-orbitals in a coordination entity?

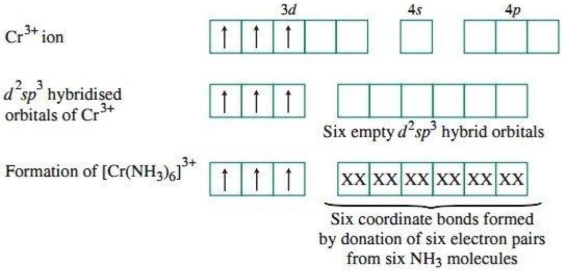
Ans. When ligands approach a transition metal ion, the *d*-orbitals split into two sets, one with lower energy and the other with higher energy. The difference of energy between the two sets of orbitals is called crystal field splitting energy (Δ_o) in case of octahedral field.

If $\Delta_o < P$ (pairing energy), the 4th electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\, e_g^1$, thereby forming high spin complexes. Such ligands for which $\Delta_o < P$ are called weak field ligands.

If $\Delta_o > P$, the 4th electron pairs up in one of the t_{2g} orbitals giving the configuration $t_{2g}^4\, e_g^0$, thus forming low spin complexes. Such ligands for which $\Delta_o > P$ are called strong field ligands.

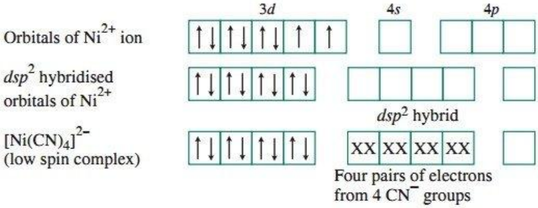
Q. 19. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why.

Ans. (*i*) **Formation of $[Cr(NH_3)_6]^{3+}$:** The oxidation state of chromium in $[Cr(NH_3)_6]^{3+}$ ion is +3. The hybridisation scheme is as shown in figure given below.



Cr^{3+} ion provides six empty orbitals to accommodate six pairs of electrons from six molecules of ammonia. The resulting complex $[Cr(NH_3)_6]^{3+}$ involves d^2sp^3 hybridisation and is hence octahedral. The presence of three unpaired electrons in the complex explains its paramagnetic behaviour.

(*ii*) **Formation of $[Ni(CN)_4]^{2-}$:** In $[Ni(CN)_4]^{2-}$ nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in the diagram given here:



The complex $[Ni(CN)_4]^{2-}$ involves dsp^2 hybridisation and hence square planar.

Each of the dsp^2 hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

Q. 20. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

Ans. In $[Ni(H_2O)_6]^{2+}$, Ni is in +2 state with the configuration $3d^8$, *i.e.*, it has two unpaired electrons which do not pair up in the presence of the weak H_2O ligand. So, it is coloured. The *d–d* transition absorbs red light and the complementary light emitted is green.

In case of $[Ni(CN)_4]^{2-}$, Ni is again in +2 state with the configuration $3d^8$ but in presence of the strong CN^- ligand, the two unpaired electrons in the 3*d*-orbitals pair up. Hence, there is no unpaired electron present. Hence, it is colourless.

Q. 21. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

Ans. In both the complexes, Fe is in +2 oxidation state with d^6 configuration. As the ligands CN^- and H_2O possess different crystal field splitting energy (Δ_o), they absorb different components of visible light for *d-d* transition. Hence, the transmitted colours are different in dilute solutions.

Q. 22. Discuss the nature of bonding in metal carbonyls.

Ans. Refer to Points to remember 18.

Q. 23. Give the oxidation state, *d* orbital occupation and coordination number of the central metal ion in the following complexes:

(*i*) $K_3[Co(C_2O_4)_3]$ **(*ii*) *cis*-$[Cr(en)_2Cl_2]Cl$**

(*iii*) $(NH_4)_2[CoF_4]$ **(*iv*) $[Mn(H_2O)_6]SO_4$**

Ans. Let x be the oxidation state of central metal ion.

S.No.	Complex	Oxidation state	Coordination Number	*d*-orbital occupation
(*i*)	$K_3[Co(C_2O_4)_3]$	$3 \times 1 + x + (-2) \times 3 = +3$	6 (as $C_2O_4^{2-}$ is didentate)	$Co^{3+} = 3d^6 = t_{2g}^6\,e_g^0$
(*ii*)	*cis*-$[Cr(en)_2Cl_2]Cl$	$x + 0 \times 2 + (-2) \times 1 + (-1) \times 1 = +3$	6 (en is didentate)	$Cr^{3+} = 3d^3 = t_{2g}^3$
(*iii*)	$(NH_4)_2[CoF_4]$	$2 \times 1 + x + (-1) \times 4 = +2$	4	$Co^{2+} = 3d^7 = t_{2g}^3\,e_g^4$
(*iv*)	$[Mn(H_2O)_6]SO_4$	$x + 0 \times 6 + (-2) \times 1 = +2$	6	$Mn^{2+} = 3d^5 = t_{2g}^3\,e_g^2$

Q. 24. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(*i*) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ **(*ii*) $[Co(NH_3)_5Cl]Cl_2$**

(*iii*) $[CrCl_3(py)_3]$ **(*iv*) $Cs[FeCl_4]$** **(*v*) $K_4[Mn(CN)_6]$**

Ans. (*i*) Potassium diaquadioxalatochromate(III)trihydrate.

Coordination number = 6 ; Shape = Octahedral

Oxidation state of Cr : $x + 0 + 2(-2) = -1,\ x = +3$

EC of $Cr^{3+} = 3d^3 = t_{2g}^3 e_g^0$; Unpaired electrons ($n$) = 3.

Magnetic moment (μ) = $\sqrt{n(n+2)} = \sqrt{3 \times 5} = \sqrt{15}$ BM = 3.87 BM

(*ii*) pentaamminechloridocobalt (III) chloride

Coordination number of Co = 6; Shape = Octahedral

Oxidation state of Co: $x + 0 - 1 = +2$ or $x = +3$

EC of $Co^{3+} = 3d^6 = t_{2g}^6\ e_g^0$

$n = 0,\ \mu = 0.$

(*iii*) trichloridotripyridinechromium (III)

Coordination number of Cr = 6; Shape = Octahedral

Oxidation state of Cr : $x - 3 + 0 = 0,\ x = +3$

EC of $Cr^{3+} = 3d^3 = t_{2g}^3\ e_g^0$

$n = 3,\ \mu = 3.87$ BM

(*iv*) Caesium tetrachloridoferrate (III)

Coordination number of Fe = 4 ; Shape = Tetrahedral

Oxidation state of Fe: $x - 4 = -1$ or $x = +3$

EC of $Fe^{3+} = 3d^5\, t_{2g}^3 e_g^2$

$n = 5, \mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92$ BM

(*v*) Potassium hexacyanomanganate (II)

Coordination number of Mn = 6; Shape = Octahedral

Oxidation state of Mn : $x - 6 = -4, x = +2$

EC of $Mn^{2+} = 3d^5 = t_{2g}^5\, e_g^0$

$n = 1, \mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM

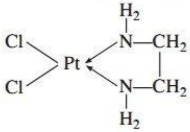
Q. 25. Explain the violet colour of the complex $[Ti(H_2O)_6]^{3+}$ on the basis of crystal field theory.

Ans. In $[Ti(H_2O)_6]^{3+}$, Ti is in +3 oxidation state with d^1 configuration. Therefore, the complex appears violet due to the transition of electron from t_{2g} level to the e_g level, *e.g.*,

$$(t_{2g}^1\, e_g^0 \longrightarrow t_{2g}^0\, e_g^1)$$

Q. 26. What is meant by chelate effect? Give an example. ***[CBSE 2020 (56/2/1)]***

Ans. When a bidentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six-membered ring is formed, the effect is called chelate effect. Example, $[PtCl_2(en)]$.



Q. 27. Discuss briefly giving an example in each case, the role of coordination compounds in:

(*i*) biological systems **(*ii*) medicinal chemistry**

(*iii*) analytical chemistry **(*iv*) extraction/metallurgy of metals**

Ans. Refer to Points to remember 21.

Q. 28. How many ions are produced from the complex, $[Co(NH_3)_6]Cl_2$ in solution?

(*i*) 6 **(*ii*) 4**

(*iii*) 3 **(*iv*) 2**

Ans. The correct option is (*iii*).

Coordination number of cobalt = 6. It ionises in the solution as:

$[Co(NH_3)_6]Cl_2 \xrightarrow{aq} [Co(NH_3)_6]^{2+} + 2Cl^-$. Hence, three ions are produced.

Q. 29. Amongst the following ions which one has the highest magnetic moment value?

(*i*) $[Cr(H_2O)_6]^{3+}$ **(*ii*) $[Fe(H_2O)_6]^{2+}$**

(*iii*) $[Zn(H_2O)_6]^{2+}$

Ans. The oxidation states are: Cr (III), Fe (II) and Zn (II).

EC of $Cr^{3+} = 3d^3$, unpaired electrons = 3

EC of $Fe^{2+} = 3d^6$, unpaired electrons = 4

EC of $Zn^{2+} = 3d^{10}$, unpaired electrons = 0

As $\mu = \sqrt{n(n+2)}$, therefore, (*ii*) has the highest magnetic moment.

Q. 30. The oxidation number of cobalt in $K[Co(CO)_4]$ is:

(*i*) +1 (*ii*) +3

(*iii*) – 1 (*iv*) – 3

Ans. $K^+[Co(CO)_4]^{-1}$

$\therefore \quad 1 + x + 0 = 0, x = -1$

Therefore, (*iii*) is the correct option.

Q. 31. Amongst the following, the most stable complex is:

(*i*) $[Fe(H_2O)_6]^{3+}$ (*ii*) $[Fe(NH_3)_6]^{3+}$

(*iii*) $[Fe(C_2O_4)_3]^{3-}$ (*iv*) $[FeCl_6]^{3-}$

Ans. In each of the given complex, Fe is in +3 state. As $C_2O_4^{2-}$ is bidentate chelating ligand, it forms chelate rings and therefore, (*iii*) is the most stable complex.

Q. 32. What will be the correct order for the wavelengths of absorption in the visible region for the following: $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$

Ans. As metal ion is fixed, the increasing CFSE values of the ligands from the spectrochemical series are in the order:

$$H_2O < NH_3 < NO_2^-$$

Hence, the energies absorbed for excitation will be in the order:

$$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$$

As $E = \frac{hc}{\lambda}$, therefore, the wavelengths absorbed will be in the opposite order,

$$[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$$

Multiple Choice Questions

Choose and write the correct option(s) in the following questions.

1. **The formula of the complex dichloridobis (ethane –1, 2-diamine) platinum (IV) nitrate is** [*CBSE 2023 (56/2/1)*]

(*a*) $[Pt\,Cl_2(en)_2\,(NO_3)_2]$ (*b*) $[PtCl_2(en)_2]\,(NO_3)_2$

(*c*) $[Pt\,Cl_2(en)_2\,(NO_3)]NO_3$ (*d*) $[Pt\,(en)_2\,(NO_3)_2]Cl_2$

2. **Which of the following has highest molar conductivity?**

(*a*) Potassium hexacyanoferrate (II) (*b*) hexaaquachromium(III)chloride

(*c*) tetraamminedichloridocobalt (III)chloride (*d*) diamminechloridoplatinum (II)

3. **Ambidentate ligands like NO_2^- and SCN^- are:** [*CBSE Sample Paper 2021*]

(*a*) unidentate (*b*) didentate

(*c*) polydentate (*d*) has variable denticity

4. **When 0.1 mol $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to** [*NCERT Exemplar*]

(*a*) 1 : 3 electrolyte (*b*) 1:2 electrolyte

(*c*) 1 : 1 electrolyte (*d*) 3:1 electrolyte

5. **When 1 mol $CrCl_3.6H_2O$ is treated with excess of $AgNO_3$, 3 mol of AgCl are obtained. The formula of the complex is:** [*NCERT Exemplar*]

(*a*) $[CrCl_3(H_2O)_3].3H_2O$ (*b*) $[CrCl_2(H_2O)_4]Cl.2H_2O$

(*c*) $[CrCl(H_2O)_5]Cl_2.H_2O$ (*d*) $[Cr(H_2O)_6]Cl_3$

6. **Which of the following species is not expected to be a ligand?** [*NCERT Exemplar*]

(*a*) NO (*b*) NH_4^+ (*c*) $NH_2CH_2CH_2NH_2$ (*d*) CO

7. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent? ***[NCERT Exemplar]***

(*a*) Thiosulphato (*b*) Oxalato (*c*) Glycinato (*d*) Ethane-1,2-diamine

8. EDTA is a ***[CBSE 2020 (56/3/2)]***

(*a*) monodentate ligand (*b*) bidentate ligand
(*c*) ambidentate ligand (*d*) hexadentate ligand

9. The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(Br)(NH_3)_5]SO_4$ represent : ***[CBSE 2023 (56/1/1)]***

(*a*) optical isomerism (*b*) linkage isomerism
(*c*) ionisation isomerism (*d*) coordination isomerism

10. Total number of unpaired electrons present in Co^{3+} (Atomic number = 27) is ***[CBSE 2020 (56/2/1)]***

(*a*) 2 (*b*) 7 (*c*) 3 (*d*) 4

11. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species? ***[NCERT Exemplar]***

(*a*) $[Fe(CO)_5]$ (*b*) $[Fe(CN)_6]^{3-}$ (*c*) $[Fe(C_2O_4)_3]^{3-}$ (*d*) $[Fe(H_2O)_6]^{3+}$

12. The correct IUPAC name of $[Pt(NH_3)_2Cl_2]$ is ***[NCERT Exemplar]***

(*a*) diamminedichloridoplatinum (II) (*b*) diamminedichloridoplatinum (IV)
(*c*) diamminedichloridoplatinum (0) (*d*) dichloridodiammineplatinum (IV)

13. The formula of the coordination compound tetraammineaquachloridocobalt(III) chloride is

(*a*) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (*b*) $[Co(NH_3)_4(H_2O)Cl]Cl_3$
(*c*) $[Co(NH_3)_2(H_2O)Cl]Cl_2$ (*d*) $[Co(NH_3)_4(H_2O)Cl]Cl$

14. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are ***[NCERT Exemplar]***

(*a*) linkage isomers (*b*) coordination isomers
(*c*) ionisation isomers (*d*) geometrical isomers

15. Indicate the complex ion which shows geometrical isomerism. ***[NCERT Exemplar]***

(*a*) $[Cr(H_2O)_4Cl_2]^+$ (*b*) $[Pt(NH_3)_3Cl]$ (*c*) $[Co(NH_3)_6]^{3+}$ (*d*) $[Co(CN)_5(NC)]^{3-}$

16. The geometry of $Ni(CO)_4$ and $[Ni(PPh_3)_2Cl_2]$ are

(*a*) both square planar (*b*) tetrahedral and square planar, respectively
(*c*) both tetrahedral (*d*) square planar and tetrahedral, respectively

17. Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?

(*a*) $[Co(NH_3)_6]^{3+}$ (*b*) $[Mn(CN)_6]^{3-}$ (*c*) $[Fe(CN)_6]^{4-}$ (*d*) $[Fe(CN)_6]^{2-}$

18. Atomic number of Mn, Fe, Co and Ni are 25, 26 27 and 28 respectively. Which of the following outer orbital octahedral complexes have same number of unpaired electrons?

(*a*) $[MnCl_6]^{2-}$ (*b*) $[FeF_6]^{3-}$ (*c*) $[CoF_6]^{3-}$ (*d*) $[Ni(NH_3)_6]^{2+}$

19. On the basis of crystal field theory, electronic configuration of d^4 complex when $\Delta_o > P$ is ***[CBSE 2020 (56/3/3)]***

(*a*) $t_{2g}^3 e_g^1$ (*b*) $t_{2g}^2 e_g^2$ (*c*) $t_{2g}^1 e_g^3$ (*d*) $t_{2g}^4 e_g^0$

20. Crystal field stabilization energy for high spin d^4 octahedral complex is

(*a*) $-1.6\ \Delta_o + P$ (*b*) $-1.80\ \Delta_o$ (*c*) $-1.2\ \Delta_o$ (*d*) $-0.6\ \Delta_o$

21. The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be ***[NCERT Exemplar]***

(*a*) 18,000 cm^{-1} (*b*) 16,000 cm^{-1} (*c*) 8,000 cm^{-1} (*d*) 20,000 cm^{-1}

22. One mole of $CrCl_3.6H_2O$ compound reacts with excess $AgNO_3$ solution to yield two moles of AgCl(*s*). The structural formula of the compound is ***[CBSE 2020 (56/3/1)]***

(*a*) $[Cr(H_2O)_5Cl]Cl_2 . H_2O$ (*b*) $[Cr(H_2O)_3Cl_3].3H_2O$
(*b*) $[Cr(H_2O)_4Cl_2]Cl . 2H_2O$ (*d*) $[Cr(H_2O)_6]Cl_3$

23. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$ [*NCERT Exemplar*]

(*a*) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

(*b*) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$

(*c*) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

(*d*) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

24. The absorption maxima of several octahedral complex ions are as follows:

S.No	Compound	λ_{max} nm
1.	$[Co(NH_3)_6]^{3+}$	475
2.	$[Co(CN)_6]^{3-}$	310
3.	$[Co(H_2O)_6]^{3+}$	490

The crystal field splitting is maximum for: [*CBSE Sample Paper 2020*]

(*a*) $[Co(H_2O)_6]^{3+}$

(*b*) $[Co(CN)_6]^{3-}$

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

(*d*) All the complex ions have the same splitting, Δ_o.

25. Match the following:

Column–I	Column–II
(*i*) EDTA	A. Unidendate
(*ii*) SCN^-	B. Bidentate
(*iii*) Gly	C. Ambidentate
(*iv*) NH_3	D. Hexadentate

(*a*) (*i*) — D, (*ii*) — B, (*iii*) — C, (*iv*) — A

(*b*) (*i*) — D, (*ii*) — A, (*iii*) — B, (*iv*) — C

(*c*) (*i*) — B, (*ii*) — C, (*iii*) — D, (*iv*) — A

(*d*) (*i*) — D, (*ii*) — C, (*iii*) — B, (*iv*) — A

26. What type of isomerism is shown by the following pair of complex compounds? [*CBSE 2023 (56/4/2)*]

$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(*a*) Linkage isomerism
(*b*) Hydrate isomerism
(*c*) Coordination isomerism
(*d*) Ionization isomerism

27. Which of the following analogy is correct?

(*a*) $K_4[Fe(CN)_6]$: Anionic complex :: $Na[Ag(CN)_2]$: Cationic complex

(*b*) $[Pt(NH_3)_6]^{4+}$: Octahedral :: $[Zn(NH_3)_4]^{2+}$: Tetrahedral

(*c*) $[NiCl_4]^{2-}$: Diamagnetic :: $[Ni(CN)_4]^{2-}$: Paramagnetic

(*d*) $K_3[CoF_6]$: Low spin complex :: $[Ni(CN)_4]^{2-}$: High spin complex

Answers

1. (*b*) **2.** (*a*) **3.** (*a*) **4.** (*b*) **5.** (*d*) **6.** (*b*) **7.** (*a*) **8.** (*d*) **9.** (*c*) **10.** (*d*)
11. (*c*) **12.** (*a*) **13.** (*a*) **14.** (*a*) **15.** (*a*) **16.** (*c*) **17.** (*a*) **18.** (*c*) **19.** (*d*) **20.** (*d*)
21. (*c*) **22.** (*a*) **23.** (*c*) **24.** (*b*) **25.** (*d*) **26.** (*c*) **27.** (*b*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion** (*A*) : EDTA is a hexadentate ligand. [*CBSE 2023 (56/5/2)*]
   Reason (*R*) : EDTA has 2 nitrogen and 4 oxygen donor atoms.
2. **Assertion** (*A*) : Linkage isomerism arises in coordination compounds containing ambidentate ligand.
   Reason (*R*) : Ambidentate ligand like NO_2 has two different donor atoms *i.e.*, N and O. [*CBSE 2020 (56/1/1)*]
3. **Assertion** (*A*) : Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.
   Reason (*R*) : Geometrical isomerism is not shown by complexes of coordination number 6.
4. **Assertion** (*A*) : The complex $[Cr(H_2O)_3Cl_3]$ does not give precipitate with $AgNO_3$ solution.
   Reason (*R*) : The complex $[Cr(H_2O)_3Cl_3]$ is non-ionizable. [*CBSE 2020 (56/3/3)*]
5. **Assertion** (*A*) : $[Ni(CN)_4]^{2-}$ is square planar and diamagnetic.
   Reason (*R*) : It has no unpaired electrons due to presence of strong ligand.
6. **Assertion** (*A*) : $[Ni(CO)_4]$ has square planar geometry while $[Ni(CN)_4]^{2-}$ has tetrahedral geometry.
   Reason (*R*) : Geometry of any complex depends upon the nature of ligands attached.
7. **Assertion** (*A*) : $[FeF_6]^{3-}$ is a low spin complex.
   Reason (*R*) : Low spin complexes have lesser number of unpaired electrons.
8. **Assertion** (*A*) : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
   Reason (*R*) : Because it has d^2sp^3 type hybridisation.
9. **Assertion** (*A*) : $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature.
   Reason (*R*) : Unpaired electrons are present in their *d*-orbitals.
10. **Assertion** (*A*) : F^- ion is a weak ligand and forms outer orbital complex.
    Reason (*R*) : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell.
11. **Assertion** (*A*) : Toxic metal ions are removed by the chelating ligands.
    Reason (*R*) : Chelate complexes tend to be more stable.
12. **Assertion** (*A*) : Low spin tetrahedral complexes are rarely observed.
    Reason (*R*) : Crystal field splitting energy is less than pairing energy for tetrahedral complexes. [*CBSE 2023 (56/1/1)*]

Answers

1. (*a*) **2.** (*a*) **3.** (*b*) **4.** (*a*) **5.** (*a*) **6.** (*d*) **7.** (*d*) **8.** (*d*) **9.** (*b*) **10.** (*a*)
11. (*a*) **12.** (*a*)

Passage-based/Case-based/ Source-based Questions

Read the given passages and answer the questions that follow.

PASSAGE-1

In coordination compounds, metals show two types of linkages, primary and secondary. Primary valencies are ionisable and are satisfied by negatively charged ions. Secondary valencies are non-ionisable and are satisfied by neutral or negative ions having lone pair of electrons. Primary valencies are non-directional while secondary valencies decide the shape, of the complexes. *[CBSE 2023 (56/1/1)]*

1. **If $PtCl_2.2NH_3$ does not react with $AgNO_3$, what will be its formula?**
2. **What is the secondary valency of $[Co(en)_3]^{3+}$?**
3. **(*a*) Write the formula of Iron(III) hexacyanidoferrate(II).**
   (*b*) Write the IUPAC name of $[Co(NH_3)_5Cl]Cl_2$.

OR

Write the hybridization and magnetic behaviour of $[Ni(CN)_4]^{2-}$.
[Atomic number : Ni = 28]

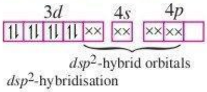
Answers

1. $[Pt(NH_3)_2Cl_2]$
   Diamminedichloridoplatinum(II)
2. Secondary valency = coordination number = 6
3. (*a*) $Fe_4[Fe(CN)_6]_3$ (*b*) Pentaaminechloridocobalt(III) chloride.

OR

In +2 oxidation state ($Ni^{2+} = 3d^84s^0$)

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



×× = Electron pair from Ligand CN^-

Magnetic behaviour: Diamagnetic as there is no unpaired electron present in the complex.

PASSAGE-2

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. Formation of coordination compounds is largely used in analytical chemistry for the qualitative detection and quantitative estimation of metal ions. Coordination compounds also find several important applications in the field of medicine. Several coordination compounds are also used as antidote to poisoning caused by the ingestion of poisonous metals by human beings.

1. **Which complexing material is added to vegetable oils to remove the ill effects of undesired metal ions?**
2. **Which complex is used in the treatment of cancer?**
3. **How would you detect the presence of nickel in a food sample?**

OR

What is chelate therapy?

Answers

1. EDTA **2.** Cisplatin
3. With the help of dimethylglyoxime which forms a red complex with Ni^{2+} ions.

OR

Chelate therapy is used for the removal of excess of metal ions present in toxic amounts in the body.

CONCEPTUAL QUESTIONS

Q. 1. A coordination compound with the molecular formula $CrCl_3.4H_2O$ precipitates AgCl with $AgNO_3$ solution. Its molar conductivity is found to be equivalent to two ions. What is the structural formula and name of the compound? **[*HOTS*]**

Ans. $[Cr(H_2O)_4Cl_2]Cl$; tetraaquadichloridochromium(III) chloride

Q. 2. Arrange the following complexes in the order of increasing electrical conductivity: **[*HOTS*]**

$[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4Cl_2]Cl$

Ans. $[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$

Q. 3. Which of the following is more stable complex and why? $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$? **[*CBSE Delhi 2014*]**

Ans. $[Co(en)_3]^{3+}$ is more stable complex because of chelation.

Q. 4. Why is CO a stronger ligand than Cl^-? **[*CBSE (F) 2011*]**

Ans. CO is a stronger ligand than Cl^- as it is a π-acceptor ligand.

Q. 5. Square planar complexes with coordination number of four exhibit geometrical isomerism whereas tetrahedral complexes do not. Why?

Ans. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the ligands attached to the central metal atom are same with respect to each other.

Q. 6. How many isomers are there for octahedral complex $[CoCl_2(en)(NH_3)_2]^+$? **[*NCERT Exemplar*]**

Ans. There will be three isomers: *cis* and *trans* isomers. *Cis* will also show optical isomerism.

Q. 7. A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex? Give one example of such complex. **[*NCERT Exemplar*] [*HOTS*]**

Ans. An optically active complex of the type $[M(AA)_2X_2]^{n+}$ indicates *cis*-octahedral structure, *e.g.*, *cis*-$[Pt(en)_2Cl_2]^{2+}$ or *cis*-$[Cr(en)_2Cl_2]^+$.

Q. 8. Give IUPAC name of linkage isomer of $[Co(NH_3)_5(NO_2)]^{2+}$. **[*HOTS*]**

Ans. The linkage isomer is $[Co(NH_3)_5(ONO)]^{2+}$. Its IUPAC name is pentaaminenitrito-O-cobalt (III) ion.

Q. 9. What type of isomerism is shown by the following complex: **[*CBSE (F) 2014*]**

$[Co(NH_3)_6]$ $[Cr(CN)_6]$?

Ans. Coordination isomerism

Q. 10. Write IUPAC name of coordination isomer of $[Co(NH_3)_6]$ $[Cr(CN)_6]$. **[*HOTS*]**

Ans. The coordination isomer is $[Cr(NH_3)_6]$ $[Co(CN)_6]$, hexaamminechromium(III) hexacyanidocobaltate(III).

Q. 11. What type of isomerism is exhibited by the following complex: $[Co(NH_3)_5SO_4]Cl$ **[*CBSE (F) 2014*]**

Ans. Ionisation isomerism

Q. 12. What is spectrochemical series?

Ans. The series in which ligands are arranged in the order of increasing field strength is called spectrochemical series. The order is

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

Q. 13. Write the electronic configuration of Fe(III) on the basis of crystal field theory when it forms an octahedral complex in the presence of (*i*) strong field ligand, and (*ii*) weak field ligand.

(Atomic no. of Fe = 26) **[*CBSE 2019 (56/3/2)*]**

Ans. (*i*) $t_{2g}^5 e_g^0$

(*ii*) $t_{2g}^3 e_g^2$

Q. 14. Why are low spin tetrahedral complexes not formed? **[*NCERT Exemplar*]**

Ans. Because for tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy.

Q. 15. Do we call metal carbonyls as organometallics? Why?

Ans. Yes, metal carbonyls are called organometallics because C atom of CO is linked to the metal atom. In fact, the metal–carbon bonds have both σ and π character.

Short Answer Questions–I

Each of the following questions are of 2 marks.

Q. 1. (*a*) Which of the following species cannot act as a ligand? Give reason.

OH^-, NH_4^+, CH_3NH_2, H_2O

(*b*) The complex $[Co(NH_3)_5(NO_2)]Cl_2$ is red in colour. Give IUPAC name of its linkage isomer.

[CBSE 2023 (56/5/2)]

Ans. (*a*) NH_4^+ cannot act as a ligand because NH_4^+ has no lone pair of electrons on nitrogen.

(*b*) $[Co(NH_3)_5(ONO)]Cl_2$.

Pentaamminenitrito-O-cobalt(III) chloride

Q. 2. Using IUPAC norms write the formulae for the following:

(*i*) tris(ethane-1, 2-diamine) chromium (III) chloride

(*ii*) Potassium tetrahydroxozincate(II) ***[CBSE (AI) 2017]***

Ans. (*i*) $[Cr(en)_3]Cl_3$ **1**

(*ii*) $K_2[Zn(OH)_4]$ **1**

[CBSE Marking Scheme (AI) 2017]

Q. 3. When a coordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write

(*i*) structural formula of the complex.

(*ii*) IUPAC name of the complex. ***[CBSE Delhi 2016; 2019 (56/4/3)]***

Ans. (*i*) $[Cr(H_2O)_5Cl]Cl_2.H_2O$

(*ii*) pentaaquachloridochromium(III)chloridemonohydrate

Q. 4. When a coordination compound $PtCl_4.6NH_3$ is mixed with $AgNO_3$, 4 moles of AgCl are precipitated per mole of the compound. Write

(*i*) structural formula of the complex.

(*ii*) IUPAC name of the complex. ***[CBSE East 2016]***

Ans. (*i*) $[Pt(NH_3)_6]Cl_4$

(*ii*) hexaammineplatinum(IV)chloride

Q. 5. A chloride of fourth group cation in qualitative analysis gives a green coloured complex [*A*] in aqueous solution which when treated with ethane-1, 2-diamine (en) gives pale-yellow solution [*B*] which on subsequent addition of ethane-1, 2-diamine turns to blue/purple [*C*] and finally to violet [*D*]. Write the structures of complexes [*A*], [*B*], [*C*] and [*D*]. ***[CBSE Sample Paper 2017]***

Ans. $A = [Ni(H_2O)_6]^{2+}$ $B = [Ni(H_2O)_4(en)]^{2+}$

$C = [Ni(H_2O)_2(en)_2]^{2+}$ $D = [Ni(en)_3]^{2+}$

Q. 6. Using IUPAC norms, write the formulae for the following complexes: ***[CBSE 2019 (56/2/1)]***

(*i*) hexaaquachromium (III) chloride **(*ii*) Sodium trioxalatoferrate (III)**

Ans. (*i*) $[Cr(H_2O)_6]Cl_3$

(*ii*) $Na_3[Fe(C_2O_4)_3]$

Q. 7. Write IUPAC name of the complex $[Co(en)_2(NO_2)Cl]^+$. What type of structural isomerism is shown by this complex? *[CBSE 2019 (56/2/1)]*

Ans. Chloridobis(ethane-1,2-diamine)nitrito-N-cobalt(III) ion **1**

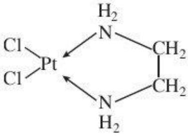
Linkage isomerism **1**

[CBSE Marking Scheme 2019 (56/2/1)]

Q. 8. (*i*) What is a chelate complex? Give one example. *[CBSE 2023 (56/2/1)]*

(*ii*) What are heteroleptic complexes? Give one example.

Ans. (*i*) When a bidentate or a polydentate ligand uses its two or more donor atoms to bind a single metal ion, then a ring like structure is obtained called chelate complex e.g., $[PtCl_2(en)]$.



Dichloridoethane-1, 2-diamineplatinum(II)

(*ii*) Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic complexes e.g., $[Co(NH_3)_4Cl_2]^+$.

Q. 9. Give the formula of each of the following coordination entities:

(*i*) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylene diamine (en) molecules.

(*ii*) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behaviour of each of the above coordination entities.

(At. nos. Co = 27, Ni = 28) *[CBSE Delhi 2012]*

Ans. (*i*) $[Co(NH_3)Cl(en)_2]^{2+}$: amminechloridobis(ethane-1,2-diamine)cobalt(III) ion

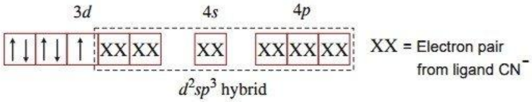
Magnetic behaviour : Diamagnetic

(*ii*) $[Ni(H_2O)_2(ox)_2]^{2-}$: diaquadioxalatonickelate (II)

Magnetic behaviour : Paramagnetic

Q. 10. For the complex $[Fe(CN)_6]^{3-}$, write the hybridisation type, magnetic character and spin nature of the complex. (At. Number : Fe = 26). *[CBSE Delhi 2016]*

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

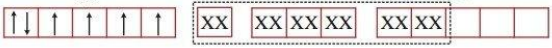


- d^2sp^3 hybridisation
- Paramagnetic in nature and low spin complex.

Q. 11. Write IUPAC name and hybridisation of the complex: $[CoF_6]^{3-}$.

(Atomic number of Co = 27) *[CBSE 2020 (56/4/2)]*

Ans. $[CoF_6]^{3-}$: hexafluoridocobaltate (III); $Co^{3+} = [Ar]3d^6$



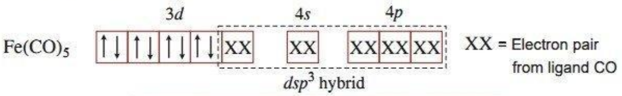
XX = Electron pair from ligand F^-

Hybridisation = sp^3d^2, Shape = Octahedral

Q. 12. For the complex $[Fe(CO)_5]$, write the hybridization, magnetic character and spin of the complex.

(At. number: Fe = 26) *[CBSE (F) 2016]*

Ans. Fe([Ar] $3d^6 4s^2$)



Hybridisation	dsp^3
Magnetic character	Diamagnetic
Spin of the complex	Low spin complex or inner orbital complex

Q. 13. Explain why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM. [*NCERT Exemplar*]

Ans. $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridisation with one unpaired electron and $[Fe(H_2O)_6]^{3+}$ involves sp^3d^2 hybridisation with five unpaired electrons. This difference is due to the presence of strong CN^- and weak ligand H_2O in these complexes.

Q. 14. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when

(*i*) $\Delta_o > P$ (*ii*) $\Delta_o < P$ [*CBSE (AI) 2013*]

Ans. The difference of energy between two sets of degenerate orbitals after crystal field splitting is known as crystal field splitting energy.

(*i*) $t_{2g}^4 e_g^0$ (*ii*) $t_{2g}^3 e_g^1$

Q. 15. The π-complexes are known for transition metals only. Why?

Ans. Transition metals have vacant *d*-orbitals in their atoms or ions into which the electron pairs can be donated by ligands containing π-electrons, *e.g.*, C_6H_6, $CH_2{=\!=}CH_2$, etc. Thus, $d\pi - p\pi$ bonding is possible.

Q. 16. On the basis of crystal field theory explain why Co(III) forms paramagnetic octahedral complex with weak field ligands whereas it forms diamagnetic octahedral complex with strong field ligands. [*NCERT Exemplar*]

Ans. With weak field ligands, $\Delta_o < P$, the electronic configuration of Co(III) will be $t_{2g}^4 e_g^2$ and it has 4 unpaired electrons and is paramagnetic. With strong field ligands, $\Delta_o > P$ the electronic configuration will be $t_{2g}^6 e_g^0$. It has no unpaired electrons and is diamagnetic.

Q. 17. What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex? [*NCERT Exemplar*]

Ans. When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.

Q. 18. Write IUPAC names of the following coordination entities:

(*i*) $[Cr(NH_3)_3(H_2O)_3]Cl_3$ (*ii*) $K_3[Al(C_2O_4)_3]$

Ans. (*i*) Triamminetriaquachromium(III) chloride

(*ii*) Potassium trioxalatoaluminate(III)

Short Answer Questions–II

Each of the following questions are of 3 marks.

Q. 1. Answer any three of the following questions: [*CBSE 2023 (56/4/2)*]

(*i*) Explain the type of hybridization in $[Fe(CN)_6]^{3-}$ on the basis of valence bond theory.

(Given : Atomic number of Fe = 26)

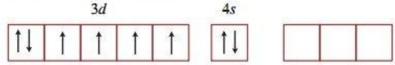
(*ii*) Draw the geometrical isomers of $[PtCl_2(en)_2]^{2+}$ ion.

(*iii*) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

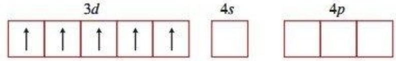
(*iv*) Name the type of isomerism when ambidentate ligands are attached to central metal ion. Give one example of ambidentate ligand.

Ans. (*i*) Electronic configuration of Fe is $[Ar]4s^2 3d^6$

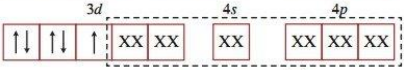
Fe in G.S



Fe^{3+} ion



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

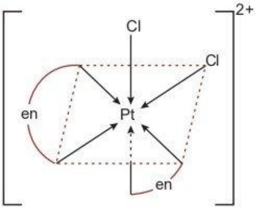


Hybridisation = d^2sp^3

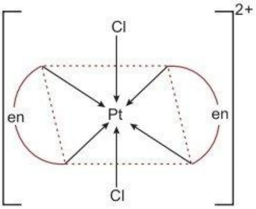
Six pairs of electrons from six CN$^-$ ion

Since CN$^-$ ligands are strong, they form inner-orbital complexes/low-spin complexes. The hybridisation of the complex is, therefore, d^2sp^3

(*ii*)



cis-$[PtCl_2(en)_2]^{2+}$

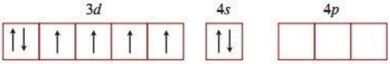


trans-$[PtCl_2(en)_2]^{2+}$

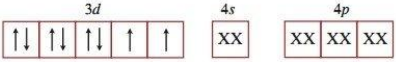
(*iii*) $[NiCl_4]^{2-}$

In this complex Ni is in +2 oxidation state.

Electronic configuration of Ni(GS)



Electronic configuration of Ni^{2+} in the complex

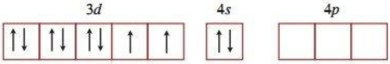


The Cl$^-$ are low weak field ligands so, they do not cause the pairing of unpaired 3*d*-electrons. Due to the presence of these two unpaired electrons, the complex is paramagnetic.

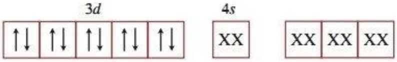
$[Ni(CO)_4]$

In this complex Ni is in 0 oxidation state.

Electronic configuration of Ni



Electronic configuration of Ni in $[Ni(CO)_4]$



The strong field ligand CO causes the pairing of unpaired electrons of 3*d* as well as shifting of 4*s* electrons to the 3*d*-orbital. Therefore, the complex has as sp^3 hybridisation. But due to the presence of no unpaired electrons, the complex is diamagnetic.

(*iv*) Ambidentate ligands show 'Linkage isomerism'.

Example– NCS — the ligand can bind to the central metal ion through either N-donor atom or S-donor atom. (*Any three*)

Q. 2. Write the correct formulae for the following coordination compounds:

- **(i) $CrCl_3.6H_2O$ (violet with 3 chloride ions precipitated as AgCl)**
- **(ii) $CrCl_3.6H_2O$ (light green colour, with 2 chloride ions precipitated as AgCl)**
- **(iii) $CrCl_3.6H_2O$ (dark green colour, with 1 chloride ion precipitated as AgCl)**

[*CBSE Sample Paper 2017*]

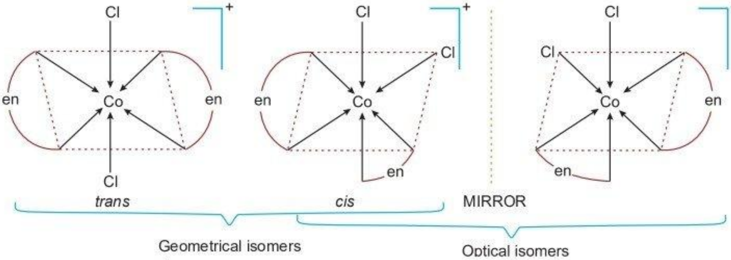
Ans. (i) $[Cr(H_2O)_6]Cl_3$ (ii) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (iii) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Q. 3. (i) Draw the geometrical isomers of $[Co(en)_2Cl_2]^{2+}$. Which geometrical isomer of $[Co(en)_2Cl_2]^{2+}$ is not optically active and why? **[*CBSE 2023 (56/2/1)*]**

(ii) Write the hybridisation and magnetic behaviour of $[CoF_6]^{3-}$.

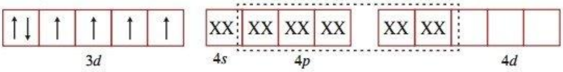
[Given : Atomic number of Co = 27]

Ans. (i)



trans —$[Co(en)_2Cl_2]^{2+}$ is optically inactive because its mirror image is superimposable.

(ii) $[CoF_6]^{3-}$: In +3 oxidation state ($Co^{3+} = 3d^6 4s^0$)



XX = Electron pair from ligand F^-

Hybridisation = sp^3d^2

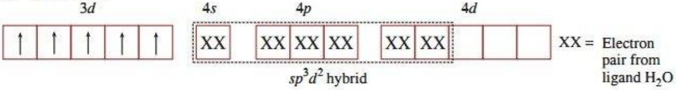
Paramagnetic as there are four unpaired electrons present.

Q. 4. (i) For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridisation, magnetic character and spin of the complex. (At. number: Fe = 26)

(ii) Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive.

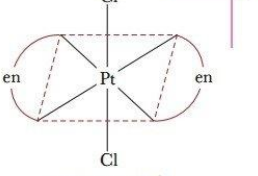
[*CBSE Central 2016*]

Ans. (i) $Fe^{3+}([Ar]3d^5)$



Hybridisation	sp^3d^2
Magnetic character	Paramagnetic
Spin of the complex	High spin complex

(ii)



trans-$[Pt(en)_2Cl_2]^{2+}$

Q. 5. Write the name, the structure and the magnetic behaviour of each one of the following complexes:

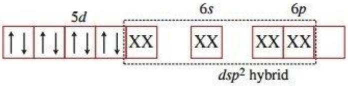
(*i*) $[Pt(NH_3)_2Cl(NO_2)]$

(*ii*) $[Co(NH_3)_4Cl_2]Cl$

(*iii*) $[Ni(CO)_4]$

(At. nos. Co = 27, Ni = 28, Pt = 78) **[*CBSE Delhi 2012, 2020 (56/2/1)*]**

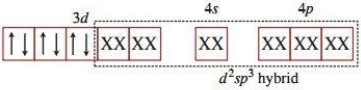
Ans. (*i*) $[Pt(NH_3)_2ClNO_2]$: diamminechloridonitrito-N-platinum (II); $Pt^{2+} = 5d^8$



XX = Electron pair from ligands NH_3, Cl^- and NO_2

Structure = Square planar; **Magnetic behaviour** : Diamagnetic

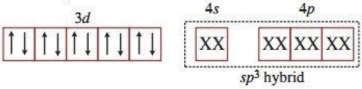
(*ii*) $[Co(NH_3)_4Cl_2]Cl$: tetraamminedichloridocobalt (III) chloride; $Co^{3+} = 3d^6$



XX = Electron pair from ligands NH_3, Cl^- and NO_2

Structure = Octahedral; **Magnetic behaviour** : Diamagnetic

(*iii*) $[Ni(CO)_4]$: tetracarbonyl nickel(0); $Ni = 3d^8\ 4s^2$



XX = Electron pair from ligand CO

Structure = Tetrahedral; **Magnetic behaviour** : Diamagnetic

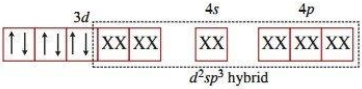
Q. 6. Name the following coordination entities and describe their structures:

(*i*) $[Fe(CN)_6]^{4-}$ **(*ii*) $[Cr(NH_3)_4Cl_2]^+$**

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

(Atomic Numbers: Fe = 26, Cr = 24, Ni = 28) **[*CBSE (AI) 2012*]**

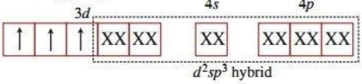
Ans. (*i*) $[Fe(CN)_6]^{4-}$ = hexacyanoferrate (II) ion; $Fe^{2+}(3d^6)$



XX = Electron pair from the CN^- ion

d^2sp^3 hybridisation in $[Fe(CN)_6]^{4-}$ leads to octahedral structure.

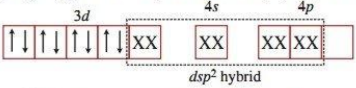
(*ii*) $[Cr(NH_3)_4Cl_2]^+$ = tetraamminedichloridochromium (III) ion; $Cr^{3+}(3d^3)$



XX = Electron pair from NH_3 molecule and Cl^- ion

d^2sp^3 hybridisation in $[Cr(NH_3)_4Cl_2]^+$ leads to octahedral structure.

(*iii*) $[Ni(CN)_4]^{2-}$ = tetracyanonickelate(II)ion; $Ni^{2+}\ (3d^8)$



XX = Electron pair from CN^- ion

dsp^2 hybridisation in $[Ni(CN)_4]^{2-}$ leads to square planar structure.

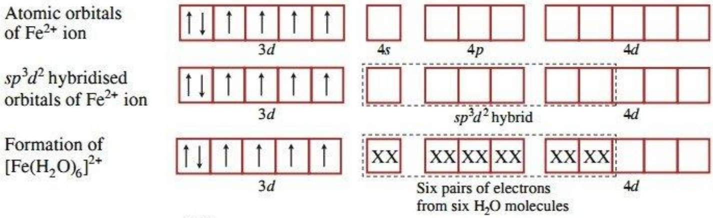
Q. 7. Describe for any two of the following complex ions, the type of hybridisation, shape and magnetic property:

(*i*) $[Fe(H_2O)_6]^{2+}$ **(*ii*) $[Co\ (NH_3)_6]^{3+}$**

(*iii*) $[NiCl_4]^{2-}$

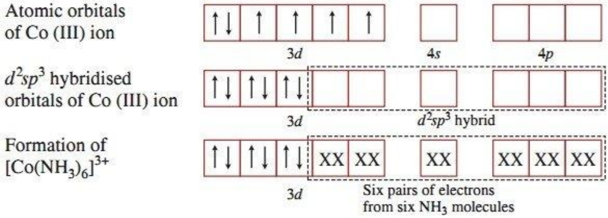
(At. Nos. Fe = 26, Co = 27, Ni = 28)

Ans. (*i*)



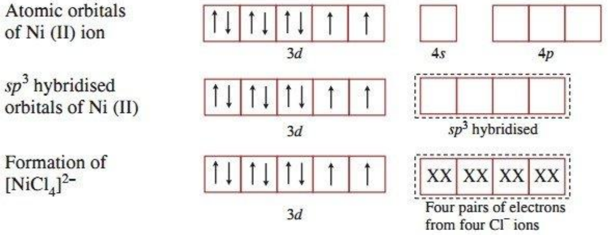
Octahedral because of sp^3d^2 hybridisation. Paramagnetic, as there are four unpaired electrons present in the complex ion.

(*ii*)



d^2sp^3 hybridisation leads to octahedral geometry. Diamagnetic, as there is no unpaired electron present in the complex.

(*iii*)



sp^3 hybridisation leads to tetrahedral geometry. Paramagnetic, as there are two unpaired electrons.

(*any two*)

Q. 8. Answer the following questions:

(*i*) $[Ni(H_2O)_6]^{2+}(aq)$ is green in colour whereas $[Ni(H_2O)_4(en)]^{2+}(aq)$ is blue in colour, give reason in support of your answer.

(*ii*) Write the formula and hybridization of the following compound:

***tris*(ethane-1, 2–diamine)cobalt(III) sulphate** **[*CBSE Sample Paper 2022*]**

Ans. (*i*) The colour of coordination compound depends upon the type of ligand and *d*–*d* transition taking place.

H_2O is weak field ligand , which causes small splitting , leading to the *d-d* transition corresponding green colour, however due to the presence of (*en*) which is a strong field ligand, the splitting is increased. Due to the change in $t_{2g} - e_g$ splitting the colouration of the compound changes from green to blue.

(*ii*) Formula of the compound is $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$.

The hybridisation of the compound is: d^2sp^3

Q. 9. Write the name, stereochemistry and magnetic behaviour of the following:

(At. nos. Mn = 25, Co = 27, Ni = 28)

(*i*) $K_4[Mn(CN)_6]$ **(*ii*) $[Co(NH_3)_5Cl]Cl_2$**

(*iii*) $K_2[Ni(CN)_4]$ **[*CBSE Delhi 2011*]**

Ans.

S. No.	Name of the complex	Hybridisation of metal ion involved	Geometry of complex	Magnetic behaviour
(*i*)	potassiumhexacyanomanganate (II)	d^2sp^3	Octahedral	Paramagnetic
(*ii*)	pentaamminechloridocobalt (III) chloride	d^2sp^3	Octahedral	Diamagnetic
(*iii*)	potassiumtetracyanonickelate (II)	dsp^2	Square planar	Diamagnetic

Q. 10. In a coordination entity, the electronic configuration of the central metal ion is $t_{2g}{}^3\ e_g{}^1$.

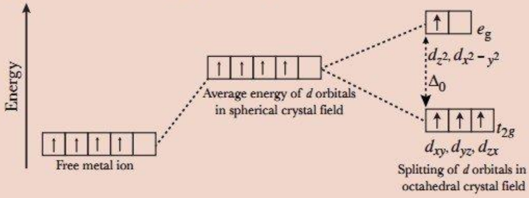
[*CBSE Sample Paper 2022*]

(*i*) Is the coordination compound a high spin or low spin complex?

(*ii*) Draw the crystal field splitting diagram for the above complex.

Ans. (*i*) As the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\ e_g{}^1$, which indicates $\Delta_0 < P$ hence forms high spin complex. **1**

(*ii*)



1 + 1

[*CBSE Marking Scheme 2022*]

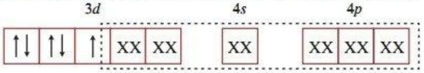
Q. 11. (*i*) On the basis of crystal field theory write the electronic configuration for d^5 ion with a weak ligand for which $\Delta_0 < P$.

(*ii*) Explain $[Fe(CN)_6]^{3-}$ is an inner orbital complex whereas $[FeF_6]^{3-}$ is an outer orbital complex. [Atomic number : Fe = 26] **[*CBSE 2023 (56/5/2)*]**

Ans. (*i*) If $\Delta_0 < P$, electronic configuration becomes $t_2g^3eg^2$.

(*ii*) In the presence of CN^- (a strong ligand), the $3d^5$ electrons pair up, the hybridisation is d^2sp^3 forming an inner orbital complex $[Fe(CN)_6]^{3-}$. In the presence of F^- (a weak ligand)$3d^5$ electrons do not pair up, the hybridisation is sp^3d^2 forming an outer orbital complex $[FeF_6]^{3-}$.

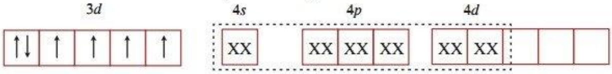
$[Fe(CN)_6]^{3-}$



d^2sp^3 hybridisation

XX = Electron pair from ligand CN^-

$[FeF_6]^{3-}$



sp^3d^2 hybridisation

XX = Electron pair from ligand F^-

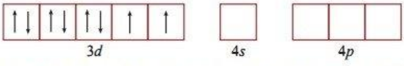
Q. 12. Explain the following: **[*HOTS*]**

(*i*) Low spin octahedral complexes of nickel are not known.

(*ii*) Co^{2+} is easily oxidised to Co^{3+} in the presence of a strong ligand.

(*iii*) CO is a stronger complexing reagent than NH_3.

Ans. (*i*) Orbitals of Ni^{2+}



For the formation of low spin complex, electrons present in 3*d* electrons of Ni^{2+} should pair up. This will produce only one empty *d* orbital. Hence, d^2sp^3 hybridisation in nickel is not possible to form low spin octahedral complex.

(*ii*) With the electronic configuration $3d^74s^0$, Co^{2+} has three unpaired electrons. H_2O being a weak ligand, the unpaired electrons present in 3*d* orbitals of Co (II) do not pair up. In the presence of strong ligands, two unpaired electrons in 3*d* orbitals pair up and the third unpaired electron shifts to higher energy orbital from where it can be easily lost and hence shows an oxidation state of III.

(*iii*) CO has empty π-orbitals which overlap with filled *d*-orbitals (t_{2g} orbitals) of transition metals and form π-bonds by back bonding. These π-interactions increase the value of crystal field stabilisation energy (Δ_o).

As NH_3 cannot form π bonds by back bonding, therefore, CO is stronger ligand than NH_3.

Q. 13. Give the electronic configuration of the [*HOTS*]

(*i*) *d*-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field.

(*ii*) Why is this complex coloured? Explain on the basis of distribution of electrons in the *d*-orbitals.

(*iii*) How does the colour change on heating $[Ti(H_2O)_6]^{3+}$ ion?

Ans. (*i*) In $[Ti(H_2O)_6]^{3+}$ ion, Ti is in +3 oxidation state. There is one electron in *d*-orbital and the electronic configuration is $t^1_{2g}\,e^0_g$.

(*ii*) Due to *d*-*d* transition, the electron present in t_{2g} absorbs green and yellow radiation of white light for excitation to e_g and the configuration becomes e^1_g. The complementary colour is purple.

(*iii*) On heating, H_2O is lost. In the absence of ligand, crystal field splitting does not occur hence the substance becomes colourless.

Long Answer Questions

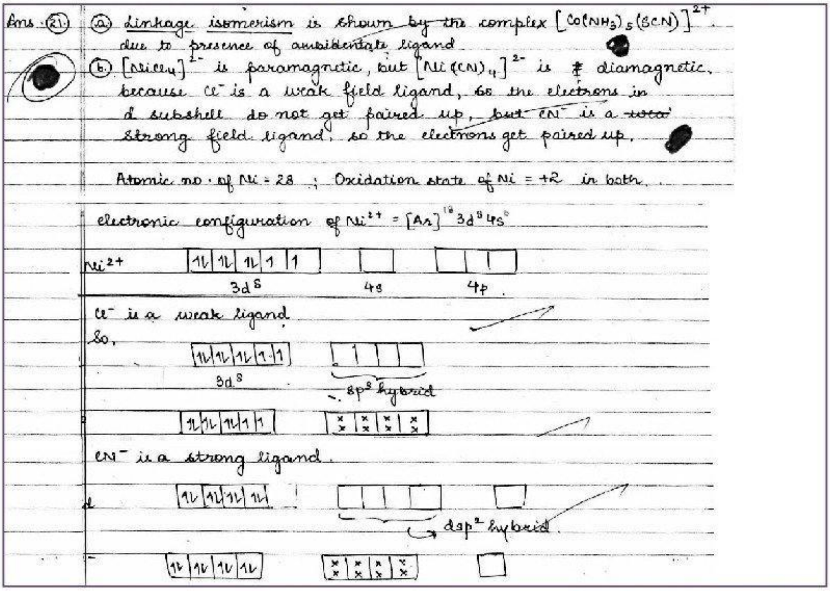
Each of the following questions are of 5 marks.

Q. 1. (*i*) What type of isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$?

(*ii*) Why is $[NiCl_4]^{2-}$ paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic? (Atomic number of Ni = 28)

(*iii*) Why are low spin tetrahedral complexes rarely observed? [*CBSE (AI) 2017*]

Ans.



Ans. (21.) (a) Linkage isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$. due to presence of ambidentate ligand.

(b.) $[NiCl_4]^{2-}$ is paramagnetic, but $[Ni(CN)_4]^{2-}$ is diamagnetic. because Cl^- is a weak field ligand, so the electrons in d subshell do not get paired up, but CN^- is a ~~wea~~ strong field ligand, so the electrons get paired up.

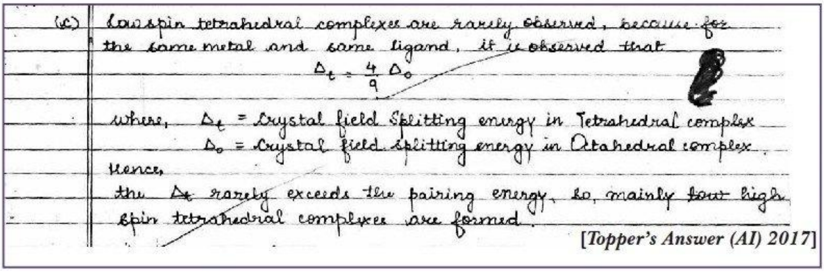
Atomic no. of Ni = 28 ; Oxidation state of Ni = +2 in both.

electronic configuration of $Ni^{2+} = [Ar]^{18} 3d^8 4s^0$

Cl^- is a weak ligand

So,

CN^- is a strong ligand.



(c) Low spin tetrahedral complexes are rarely observed, because for the same metal and same ligand, it is observed that

$$\Delta_t = \frac{4}{9}\Delta_o$$

where, Δ_t = Crystal field Splitting energy in Tetrahedral complex

Δ_o = Crystal field splitting energy in Octahedral complex.

Hence,

the Δ_t rarely exceeds the pairing energy, so, mainly ~~four~~ high spin tetrahedral complexes are formed.

[*Topper's Answer (AI) 2017*]

Q. 2. A metal ion M^{n+} having d^4 valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming $\Delta_o > P$: [*HOTS*]

(*i*) Explain orbital splitting during this complex formation.

(*ii*) Write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g.

(*iii*) What type of hybridisation will M^{n+} ion have?

(*iv*) Name the type of isomerism exhibited by this complex.

Ans. (*i*) As $\Delta_o > P$ pairing will occur in the t_{2g} orbitals and e_g orbitals will remain vacant.

(*ii*) $t_{2g}^4\, e_g^0$

(*iii*) As there are three bidentate ligands to combine therefore hybridisation will be d^2sp^3.

(*iv*) Optical isomerism

Questions for Practice

Choose and write the correct answer for each of the following.

1. Predict the number of ions produced per formula unit in an aqueous solution of $[Co(en)_3]Cl_3$. [*CBSE Sample Paper 2020*]

(*a*) 4 (*b*) 3
(*c*) 6 (*d*) 2

2. **Which of the following compounds can show optical isomerism?**

(*a*) *trans*-$[Co(en)_2Cl_2]Br$ (*b*) $[Co(en)_3]Cl_3$
(*c*) *trans*-$[Co(NH_3)_4Cl_2]Cl$ (*d*) $[(NH_3)_5Cl]Cl_2$

3. **Which of the following is π-acid ligand?**

(*a*) NH_3 (*b*) CO
(*c*) F^- (*d*) ethylenediammine

4. **Ethylene diammine is a**

(*a*) monodentate ligand (*b*) bidentate ligand
(*c*) hexadentate ligand (*d*) tridentate ligand

5. **Complete the following analogy.**

$K_2[PtCl_6]$: A :: Tetrachloronickelate : B

(*a*) A = Potassium hexachloroplatinate; B = $[NiCl_4]^{2-}$
(*b*) A = Potassium hexachloroplatinate (I); B = $[NiCl_4]^{3-}$
(*c*) A = Potassium hexachloroplatinate (IV); B = $[NiCl_4]^{2-}$
(*d*) A = Potassium hexachloroplatinate (V); B = $[NiCl_4]^-$

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- *(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- *(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- *(c) Assertion (A) is correct, but Reason (R) is incorrect statement.*
- *(d) Assertion (A) is incorrect, but Reason (R) is correct statement.*

6. **Assertion (*A*) :** Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ is not a coordination compound.
   Reason (*R*) : The aqueous solution of this salt gives the test of Fe^{2+}, NH_4^+ and SO_4^{2-} ions.
7. **Assertion (A) :** The tetrahedral complexes can show geometrical isomerism.
   Reason (*R*) : This is because all the four ligands lie at the same distance from central metal atom in a tetrahedral geometry.
8. **Assertion (*A*) :** The complex $[Fe(H_2O)_6]^{2+}$ is paramagnetic in nature.
   Reason (*R*) : It consists of two unpaired electrons.
9. **Assertion (*A*) :** Oxalate ion is a bidentate ligand.
   Reason (*R*) : Oxalate ion has two donor atoms.
10. **Assertion (*A*) :** Low spin tetrahedral complexes are rarely observed.
    Reason (*R*) : The orbital splitting energies are not sufficiently large to force pairing.
    [*CBSE 2020 (56/2/1)*]

Answer the following questions:

11. (*i*) Write the IUPAC name of the isomer of the following complex:
    $[Pt(NH_3)_2Cl_2]$
    (*ii*) Write the formula for the following:
    tetraammineaquachloridocobalt (III) nitrate **[*CBSE (F) 2017*]**
12. Why do compounds having similar geometry have different magnetic moment? **[*NCERT Exemplar*]**
13. Write the IUPAC names of the following:
    (*i*) $[Co(NH_3)_5(ONO)]^{2+}$ (*ii*) $K_2[NiCl_4]$
14. An octahedral complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio 1 : 4, 0.1 m solution of this complex was found to freeze at 0.372°C. What is the formula of the complex? Given that molal depression constant (K_f) for water = 1.86°C/m.
15. (*i*) What is meant by denticity of a ligand?
    (*ii*) Which compound is used to estimate the hardness of water volumetrically?
16. Using valence bond theory explain the $[Co(NH_3)_6]^{3+}$ in relation to the terms given below:
    (*i*) Type of hybridisation
    (*ii*) Inner or outer orbital complex
    (*iii*) Magnetic behaviour
    (*iv*) Spin only magnetic moment value
17. $CuSO_4.5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why?
18. Give the name, the stereochemistry and the magnetic behaviour of the following complexes:
    (*i*) $[Co(NH_3)_5Cl]Cl_2$
    (*ii*) $K_2[Ni(CN)_4]$

19. (*i*) What is the coordination number of central metal ion in $[Fe(C_2O_4)_3]^{3-}$?

(*ii*) Write the formula of pentamminechloridoplatinum (IV).

(*iii*) Arrange following complex ions in increasing order of crystal field splitting energy (Δ_0):
$[Cr(Cl)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$

20. (*i*) What type of isomerism is shown by the complex $[Cr(H_2O)_6]Cl_3$?

(*ii*) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o > P$.

(*iii*) Write the hybridisation and shape of $[CoF_6]^{3-}$.
(Atomic number of Co = 27) ***[CBSE Allahabad 2015]***

21. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following:
$[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$

22. (*i*) Write the electronic configuration of d^4 on the basis of crystal field splitting theory, if $\Delta_0 < P$.

(*ii*) $[Ni(CN)_4]^{2-}$ with square-planar structure is diamagnetic and $[NiCl_4]^{2-}$ with tetrahedral geometry is paramagnetic. Give reason to support the statement.
[Atomic number : Ni = 28]

(*iii*) Write the number of ions produced in the solution from the following complex:
$[PtCl_2(NH_3)_4]Cl_2$

23. $Fe^{3+} \xrightarrow[\text{excess}]{SCN^-} A \xrightarrow[\text{excess}]{F^-} B$

What are A and B? Give IUPAC names of A and B. Find spin only magnetic moment of B.

24. (*i*) Calculate the spin only magnetic moment of the complex $[FeF_6]^{3-}$.
(Atomic number of Fe = 26)

(*ii*) Write the IUPAC name of the given complex:
$[Co(NH_3)_5Cl]Cl_2$

(*iii*) Why is the complex $[Co(en)_3]^{3+}$ more stable than $[CoF_6]^{3-}$?

25. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the $[Fe(H_2O)_6]^{2+}$.
[NCERT Exemplar]

26. $CoSO_4Cl.5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$. Answer the following questions:

(*i*) Identify 'A' and 'B' and write their structural formulae.

(*ii*) Name the type of isomerism involved.

(*iii*) Give the IUPAC name of 'A' and 'B'.

Answers

1. (*a*) **2.** (*b*) **3.** (*b*) **4.** (*b*) **5.** (*c*) **6.** (*b*) **7.** (*d*) **8.** (*c*) **9.** (*a*) **10.** (*a*)
23. 5.916 BM **25.** 419 BM