NCERT Solutions for Class-XII Chemistry

CHAPTER -5

NCERT Chemistry Class 12

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

1. Werner's postulates explain the bonding in coordination compounds as follows:

(i) A metal exhibits two types of valencies namely, primary and secondary valencies. Primary valencies are satisfied by negative ions while secondary valencies are satisfied by both negative and neutral ions. (In modern terminology, the primary valency corresponds to the oxidation number of the metal ion, whereas the secondary valency refers to the coordination number of the metal ion.

(ii) A metal ion ha0s a definite number of secondary valencies around the central atom. Also, these valencies project in a specific direction in the space assigned to the definite geometry of the coordination compound.

(iii) Primary valencies are usually ionizable, while secondary valencies are non-ionizable.

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?

2. The reaction is given below:

$FeSO_4+(NH_4)_2SO_4+6H_2O \rightarrow FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr Salt)

$FeSO_4$, when reacted with $(NH_4)SO_4$, does not form any complex whereas they form a double salt, $FeSO_4.(NH_4)2SO_4.6H_2O$ - (Mohr salt) which dissociates into ions in the solution. So, it gives the test of Fe^{2+} ions.

$CuSO_4 +4NH_3 +5H_2O \rightarrow [Cu(NH_3)_4SO_4].5H_2O$

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

3. Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heterolytic.

3. (i) Coordination entity:

A coordination entity is an electrically charged radical or species carrying a positive or negative charge. In a coordination entity, the central atom or ion is surrounded by a suitable number of neutral molecules or negative ions (called ligands). For example:

$\left[Ni(NH_3)_6\right]^{2+}, \left[Fe(CN)_6\right]^{4+}$ = cationic complex

$[PtCl_4]^{2-}, \left[Ag(CN)_2\right]^{-}$ = anionic complex

$\left[Ni(Co)_4\right], \left[Co(NH_3)_4Cl_2\right]$ = neutral complex

(ii) Ligands

The neutral molecules or negatively charged ions that surround the metal atom in a coordination entity or a coordinal complex are known as ligands. For example, $\ddot{N}H_3, H_2\ddot{O}$, Cl^-, ^-OH. Ligands are usually polar in nature and possess at least one unshared pair of valence electrons.

(iii) Coordination number:

The total number of ligands (either neutral molecules or negative ions) that get attached to the central metal atom in the coordination sphere is called the coordination number of the central metal atom. It is also referred to as its ligancy.

For example:

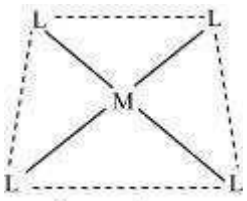
(a) In the complex, $K_2[PtCl_6]$, there as six chloride ions attached to Pt in the coordinate sphere. Therefore, the coordination number of Pt is 6.

(b) Similarly, in the complex $[Ni(NH_3)_4]Cl_2$, the coordination number of the central atom (Ni) is 4.

(vi) Coordination polyhedron:

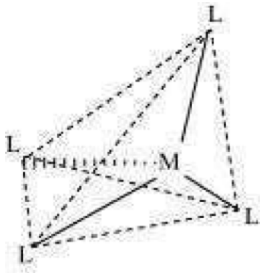
Coordination polyhedrons about the central atom can be defined as the spatial arrangement of the ligands that are directly attached to the central metal ion in the coordination sphere. For example:

(a)



Square planar

(b)



Tetrahedral

(v) Homoleptic complexes:

These are those complexes in which the metal ion is bound to only one kind of a donor group. For eg: $\left[Co(NH_3)_6\right]^{3+}, [PtCl_4]^{2-}$

(vi) Heteroleptic complexes:

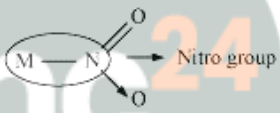
Heteroleptic complexes are those complexes where the central metal ion is bound to more than one type of a donor group.

For e.g.: $\left[Co(NH_3)_4Cl_2\right]^+$, $\left[Co(NH_3)_5CL\right]^{2+}$

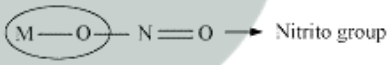
4. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

4. Ligands are the neutral or negatively charged entities surrounding the central metal atom of the coordination complex which possesses at least one unshared pair of electrons.
Based on the number of donor sites of these ligands, Ligands are classified as:
Unidentate ligands: These Ligands which have only one donor site are called unidentate ligands.
Example: F^-,Cl^- etc
Didentate ligands: These Ligands which have only two donor site are called didentate ligands.
Example: Ethane-1,2-diamine, Oxalate ion etc
Ambidentate ligands: These ligands which can attach them with the central metal atom by two different atoms are called as ambidentate ligands.
Example:

(a)

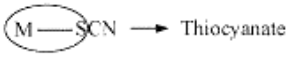


(The donor atom is N)

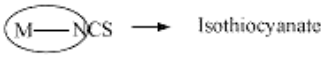


(The donor atom is oxygen)

(b)



(The donor atom is S)



(The donor atom is N)

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) $[Cr(NH_3)_3Cl_3]$

5. (i) $\left[Co(H_2O)(CN)(en)_2\right]^{2+}$
Let the oxidation number of Co be x.
The charge on the complex is +2.

$[CO \quad (H_2O) \quad (CN) \quad (en)_2]^{2+}$

$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$

$x + 0 + (-1) + 2(0) = +2$

$x - 1 = +2$

$x = +3$

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

Let the oxidation number of Pt be x.

The charge on the complex is −2.

$[Pt \quad (Cl)_4]^{2-}$

$\downarrow \quad \downarrow$

$x + 4(-1) = -2 \quad x = +2$

(iii) $[CO \quad (Br)_2 \quad (en)_2]^{2+}$

$\downarrow \quad \downarrow \quad \downarrow$

$x = 2(-1) + 2(0) = +1$

$x - 2 = +1$

$x = +3$

(iv) $K_3[De(CN)_6]$

i.e., $[Fe \quad (CN)_6]^{3-}$

$\downarrow \quad \downarrow$

$x + 6(-1) = -3$

$x = +3$

(v) $[Cr \quad (NH_3)_3 \quad Cl_3]$

$\downarrow \quad \downarrow \quad \downarrow$

$x + 3(0) + 3(-1) = 0$

$x - 3 = 0$

$x = +3$

6. Using IUPAC norms write the formulas for the following:

(i) Tetrahydroxidozincate (II)

(ii) Potassium tetrachloridopalladate(II)

(iii) Diamminedichloridoplatinum(II)

(iv) Potassium tetracyanidonickelate(II)

(v) Pentaamminenitrito-O-cobalt(III)

(vi) Hexaamminecobalt(III) sulphate

(vii) Potassium tri(oxalato)chromate(III)
(viii) Hexaammineplatinum(IV)
(ix) Tetrabromidocuprate(II)
(x) Pentaamminenitrito-N-cobalt(III)

6. (i) $[Zn(OH]^{2-}$
(ii) $K_2[PdCl_4]$
(iii) $[Pt(NH_3)_2Cl_2]$
(iv) $K_2[Ni(CN)_4]$
(v) $[Co(ONO)\ (NH_3)_5]^{2+}$
(vi) $[Co(NH_3)_6]_2\ (SO_4)^3$
(vii) $K_3[Cr(C_2O_4)_3]$
(viii) $[Pt(NH_3)_6]^{4+}$
(ix) $[Cu(Br)_4]^{2-}$
(x) $[Co[NO_2)(NH_3)_5]^{2+}$

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

7. (i) Starting with cation , the complex ion contains six ammonia molecules with cobalt in +3 oxidation state. The name of compound: $[Co(NH_3)_6]Cl_3$ is hexaamminecobalt(III) chloride.

(ii) The complex ion is cation, so there are 2 ammonia molecules, one chloride ion and methyammine molecule qith platinum in +2 state. Going in alphabetical order, the name of compound: $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ is diamminechloridomethylammineplatinum(II) chloride.

(iii) It is a complex cation with six water molecules and titanium atom in +3 state. The name of the compound: $[Ti(H_2O)_6]^{3+}$ is hexaaquatitanium(III) ion

(iv) The complex ion is cation with cobalt in +3 state and with four ammonia molecules i.e tetraammine , one chloride ion and nitrate ion. The name of the compound: $[Co(NH_3)_4Cl(NO_2)]Cl$ is tetraamminechloridonitritocobalt(III) chloride.

(v) The complex ion is cation with manganese in +2 state and six water molecules. The name of compound: $[Mn(H_2O)_6]^{2+}$ is hexaaquamanganese(II) ion.

(vi) The complex is anion with nickel in +2 state and with four chloride ions. The name of the compound: $[NiCl_4]^{2-}$ is tetrachloridonickeltate(II) ion.

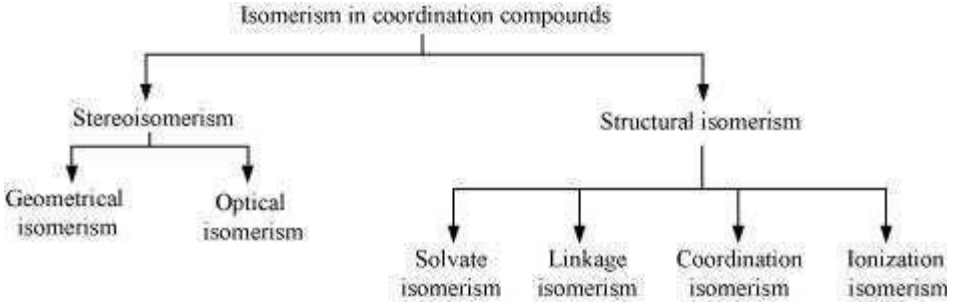
(vii) The complex is cation with nickel in+2 state and six ammonia molecules. The name of compound: $[Ni(NH_3)_6]Cl_2$ is hexaamminenickel(II) chloride.

(viii) The complex is cation withcobalt in +3 stateand there is a bidentate ligand called as ethylenediamine. The name of compound : $[Co(en)_3]^{3+}$ is tris(ethylenediamine)cobalt(III) ion.

(ix) It is neutral complex with four carbonyl molecules and cobalt in 0 state. The name of compound: $[Ni(CO)_4]$ is tetracarbonylcobalt(0).

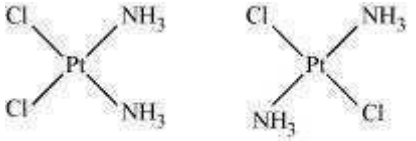
8. List various types of isomerism possible for coordination compounds, giving an example of each.

8.



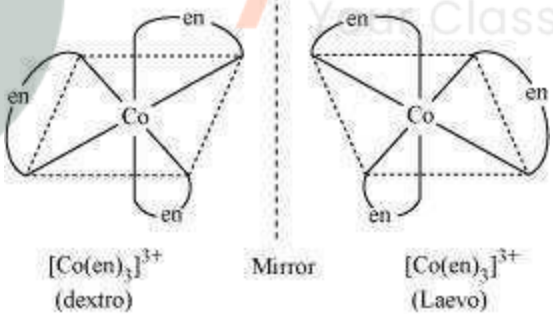
(a) Geometric isomerism:

This type of isomerism is common in heteroleptic complexes. It arises due to the different possible geometric arrangements of the ligands. For example:



(b) Optical isomerism:

This type of isomerism arises in chiral molecules. Isomers are mirror images of each other and are non-superimposable.



(c) Linkage isomerism:

This type of isomerism is found in complexes that contain ambidentate ligands. For example: $[Co(NH_3)_5 (NO_2)]Cl_2$ and $[Co(NH_3)_5 (ONO)Cl_2$

Yellow form Red form (d)

(d) Coordination isomerism: This type of isomerism arises when the ligands are interchanged between cationic and anionic entities of differnet metal ions present in the complex. $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$ (e)

(e) Ionization isomerism:

This type of isomerism arises when a counter ion replaces a ligand within the coordination sphere. Thus, complexes that have the same composition, but furnish

different ions when dissolved in water are called ionization isomers. For e.g., $Co(NH_3)_5SO_4)Br$ and $Co(NH_3)_5Br]SO_4$

(f) **Solvate isomerism:** Solvate isomers differ by whether or not the solvent molecule is directly bonded to the metal ion or merely present as a free solvent molecule in the crystal lattice. $[Cr[H_2O)_6]Cl_3$ $[Cr(H_2O)_5Cl]Cl_2$ H_2O $[Cr(H_2O)_5Cl_2]Cl_2H_2O$ Violet Blue-green Dark green

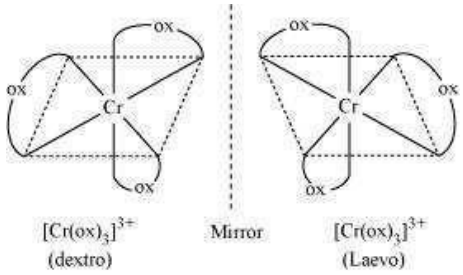
9. How many geometrical isomers are possible in the following coordination entities?
(i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$

9. (i) No geometrical isomer is possible for $[Cr(C2O_4)_3]^{3-}$ because the ligand $C_2O_4^{2-}$ is bidentate ligand(which have two sites of attachment to the central atom) and also in the coordination sphere it is the only ligand bond to it.

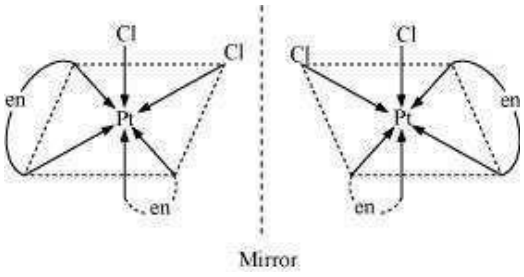
(ii) In the coordination sphere of $[Co(NH_3)_3Cl_3]$ there are two types of ligands present i.e NH_3 and Cl^- Coordination number is 6. There are 2 isomers possible for the complex:
Facial: In this isomer one type of ligand say NH_3 forms the face of the square bipyramidal (triangular) structure. Meridional: In this isomer one type of ligand are along the central axis of the pyramidal structure.

10. Draw the structures of optical isomers of:
(i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[PtCl_2(en)_2]^{2+}$
(iii) $[Cr(NH_3)2Cl_2(en)]^+$

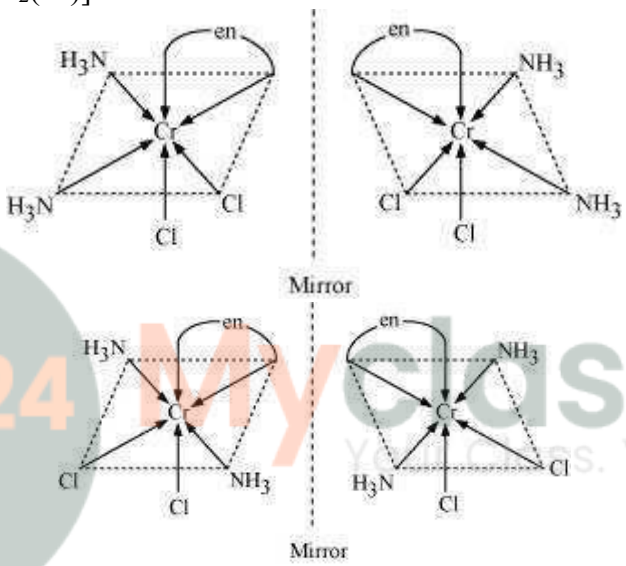
10. (i) $[Cr(C_2O_4)_3]^{3-}$



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



(iii) $[Cr(NH_3)_2Cl_2(en)]^+$



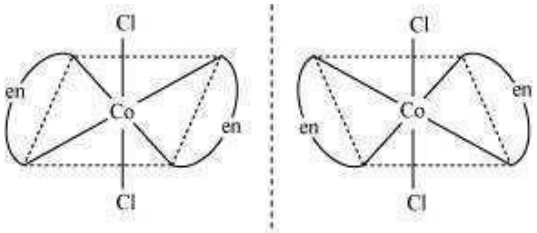
11. Draw all the isomers (geometrical and optical) of:

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

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

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

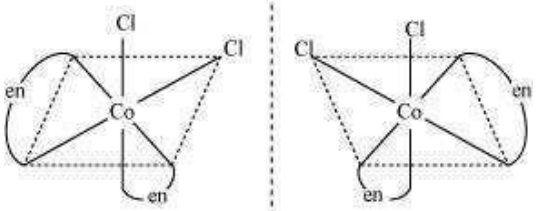
11. (i) $[CoCl_2(en)_2]^+$



Mirror

Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive

(Superimposable mirror images)



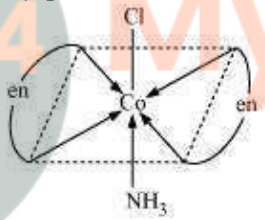
Mirror

Cis $[CoCl_2(en)_2]^+$ isomer-optically active

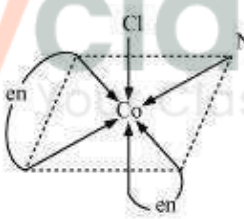
(Non-superimposable mirror images)

In total, three isomers are possible.

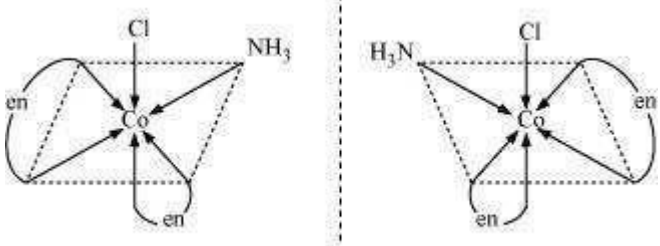
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$



Trans



Cis

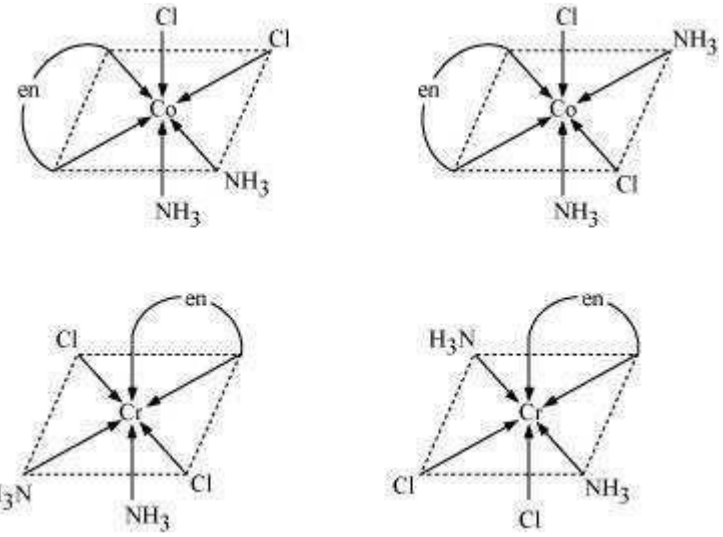


Mirror

Trans-isomers are optically inactive.

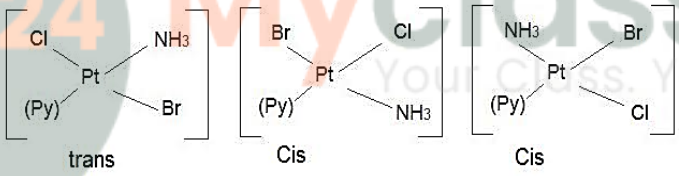
Cis-isomers are optically active.

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



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

12. There are four different types of ligands present in the complex. So, by fixing the position of 2 ligands we get 2 geometrical isomers and by changing the position of fixed isomer we get one more geometrical isomer.



Since it is tetrahedral complex so it should be optically active. But however it has not been possible to resolve optically active d and l forms of such a complex due to its complicated nature.

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.

13. Aqueous $CuSO_4$ exists as $[Cu(H_2O)_4]SO_4$. It is blue in colour due to the presence of $[Cu[H_2O)_4]^{2+}$ ions.

(i) When KF is added:

$$\left[Cu\left(H_2O\right)_4\right]^{2+} + 4F^- \longrightarrow \underset{(green)}{\left[Cu\left(F\right)_4\right]^{2-}} + 4H_2O$$

(ii) When KCl is added:

$$\left[Cu\left(H_2O\right)_4\right]^{2+} + 4Cl^- \longrightarrow \underset{\text{(bright green)}}{\left[CuCl_4\right]^{2-}} + 4H_2O$$

In both these cases, the weak field ligand water is replaced by the F^- and Cl^- ions.

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?

14. $CuSO_4 + KCN \Rightarrow K_2[Cu(CN)_4] + K_2SO_4$

$[Cu(H_2O)_4]^{2+} + 4CN^- \Rightarrow [Cu(CN)_4]^{2-} + 4H_2O$

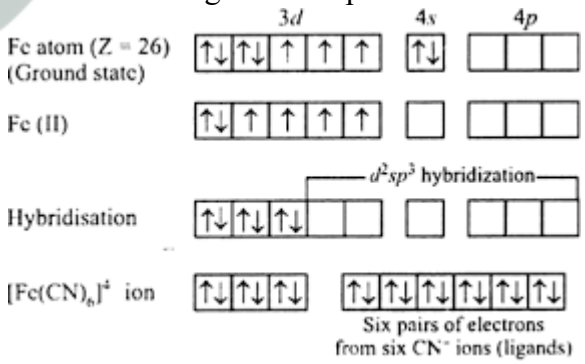
The coordination entity formed is $K_2[Cu(CN)_4]$.

IUPAC name of the coordination entity is potassium tetracyanocuprate

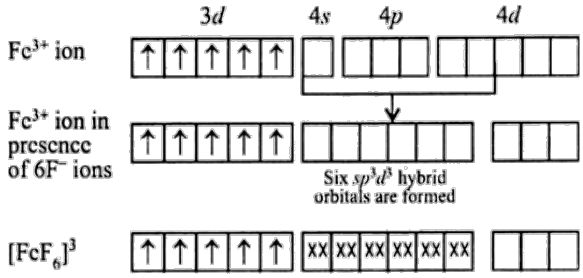
(II). It is a very stable complex. The copper atom present inside the coordination sphere does not separate out to form copper ions and cyanide ions due to strong bond between them. It does not ionize to give Cu^{2+} ions and hence on adding H_2S, since there are no copper ions present so no precipitate of copper sulfide is formed.

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

15. (i) In the coordination entity iron exists in +2 oxidation state. Overall charge balance:
X+6(-1)=-4 X=+2.
Its electronic configuration is: $3d^6$ CN^- is strong field ligand so it causes pairing of the unpaired electron and undergoes hybridisation to form 6 d^2sp^3 hybrid orbitals to be filled by the six cyanide ions. It's geometry is octahedral with no unpaired electrons and hence is diamagnetic complex.



(ii) In the coordination entity iron exists in +3 oxidation state.
Overall charge balance:
X+6(–1) = –3
X = +3.
Its electronic configuration is: $3d^6$
F^- is weak field ligand so it not causes pairing of the unpaired electron and undergoes hybridisation to form 6 sp^3d^2 hybrid orbitals to be filled by the six fluoride ions. It's geometry is octahedral and is paramagnetic.



(iii) In the coordination entity cobalt exists in +3 oxidation state.

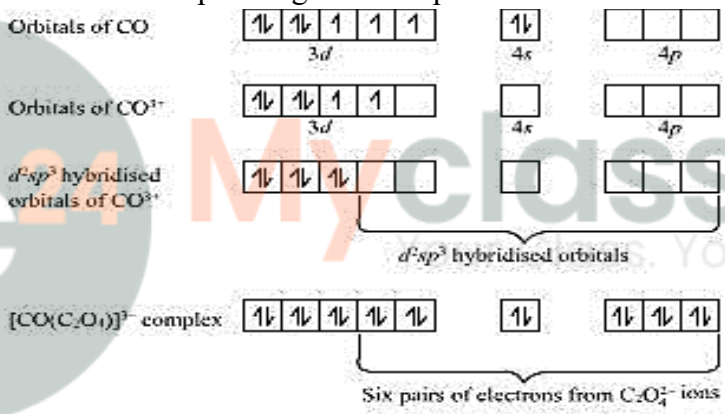
Overall charge balance:

$X + 3(-2) = -3$

$X = +3$.

Its electronic configuration is: $3d^5$

$C_2O_4^-$ is weak-field ligand so it not causes pairing of the unpaired electron and undergoes hybridisation to form 6 sp^3d^2 hybrid orbitals to be filled by the three oxolate ions (it is bidentate ligand). It's geometry is octahedral with unpaired electrons and hence is paramagnetic complex.



(iv) In the coordination entity cobalt exists in +3 oxidation state.

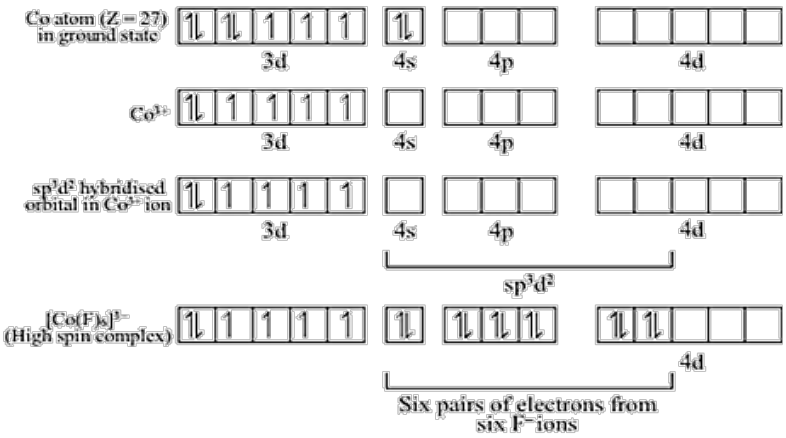
Overall charge balance:

$X + 6(-1) = -3$

$X = +3$.

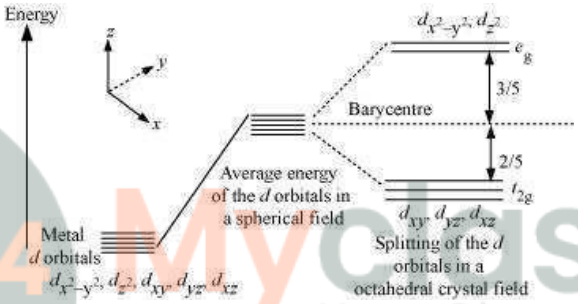
Its electronic configuration is: $3d^5$

Fluoride ion is weak field ligand so it not causes pairing of the unpaired electron and undergoes hybridisation to form 6 sp^3d^2 hybrid orbitals to be filled by the six fluoride ions. It's geometry is octahedral with unpaired electrons and hence is paramagnetic complex.



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

16.



The splitting of the d orbitals in an octahedral field takes palce in such a way that $d_{x^2-y^2}$, d_{x^2} experience a rise in energy and form the e_g level, while d_{xy}, d_{yz} and d_{zx} experience a fall in energy and form the t_{2g} level.

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

17. The strong ligands have higher splitting power of d orbitals of the central metal ion, whereas weak ligand has relatively lower splitting power of d orbitals of the central metal ion. The energy difference between t_{2g} and e_g sets of d orbitals is CFSE. The strength of the ligands depends on the magnitude of Δ. Strong ligands have larger value of CFSE and in case of weak ligands the CFSE values are smaller. The common ligands can be arranged in a series in the order of their decreasing field strength, as follows.

$I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < py < NH_3 < en < bipy < o\text{–}phen < NO_2^- < CN^- < CO$.

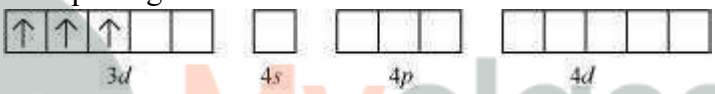
This series depends on the power of splitting the d orbitals and is called spectrochemical series, The order of field strength of the common ligands neither depends on the geometry of the complex the nature of central metal ion.

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

18. The degenerate d-orbitals (in a spherical field environment) split into two levels i.e., e_g and t_{2g} in the presence of ligands. The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting while the energy difference between the two levels (e_g and t_{2g}) is called the crystal-field splitting energy. It is denoted by Δ_0. After the orbitals have split, the filling of the electrons takes place. After 1 electron (each) has been filled in the three t_{2g} orbitals, the filling of the fourth electron takes place in two ways. It can enter the eg orbital (giving rise to t_{2g} 3 eg 1 like electronic configuration) or the pairing of the electrons can take place in the t_{2g} orbitals (giving rise to t_{2g} 4 eg 0 like electronic configuration). If the Δ_0 value of a ligand is less than the pairing energy (P), then the electrons enter the e_g orbital. On the other hand, if the Δ_0 value of a ligand is more than the pairing energy (P), then the electrons enter the t_{2g} orbital.

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

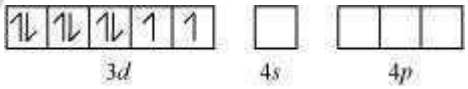
19. Cr is in the +3 oxidation state i.e., d^3 configuration. Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital. Cr^{3+}



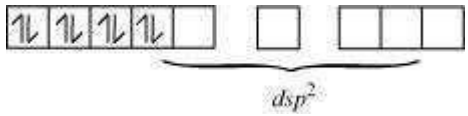
Therefore, it undergoes d_2sp_3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.

In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d8 configuration.

Ni^{2+}:



CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then, Ni^{2+} undergoes dsp^2 hybridization.



As there are no unpaired electrons, it is diamagnetic.

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

20. In case of $[Ni(H_2O)_6]^{2+}$ H_2O is a weak field ligand , so it does not cause the pairing of the unpaired electron of Ni^{2+} ion. Thus there is possibility of the intra d-d transition from the d orbital of lower energy to that of higher energy. Thus the light is absorbed from the visible region and complimentary colour is observed. But in case of $[Ni(CN)_4]^{2-}$ CN^- is strong field ligand.

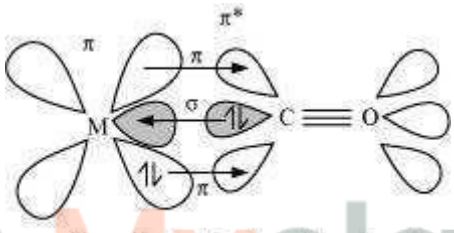
Therefore it will cause pairing of the unpaired electrons of Ni^{2+} ion. There are no unpaired electrons present, so there is no d-d transition and hence it is colourless.

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

21. The colour of a particular coordination compound depends on the magnitude of the crystalfield splitting energy, Δ. This CFSE in turn depends on the nature of the ligand. In case of $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$, the colour differs because there is a difference in the CFSE. Now, CN^- is a strong field ligand having a higher CFSE value as compared to the CFSE value of water. This means that the absorption of energy for the intra *d-d* transition also differs. Hence, the transmitted colour also differs.

22. Discuss the nature of bonding in metal carbonyls.

22. The metal-carbon bonds in metal carbonyls have both σ and π characters. A σ bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal. A π bond is formed by the donation of a pair of electrons from the filled metal d orbital into the vacant anti-bonding π* orbital (also known as back bonding of the carbonyl group). The σ bond strengthens the π bond and vice-versa. Thus, a synergic effect is created due to this metal-ligand bonding. This synergic effect strengthens the bond between CO and the metal.



Synergic bonding in metal carbonyls

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) $[Mn(H_2O)_6]SO_4$

23. (i) Overall charge balance:

$X + 3(-2) = -3$

$X = +3$

Oxidation state of Co is +3. As there are 3 oxolate ion and being bidentate , coordination no. Of complex is 6. So it is octahedral complex. d orbital occupation: $t_{2g}^6 eg^0$(oxolate ion is weak field ligand , does not cause pairing of electron as the energy required for pairing of electron is more than CFSE).

(ii) Overall charge balance:

X + balance $4(-1) = -2$

$X = +2$

Oxidation state of Co is +2.

As there are 4 fluoride ion, coordination no. Of complex is 4 i.e. Tetrahedral complex. d orbital occupation: $eg^4 t_{2g}^3$(fluoride ion is weak field ligand , does not

cause pairing of electron as the energy required for pairing of electron is more than CFSE).

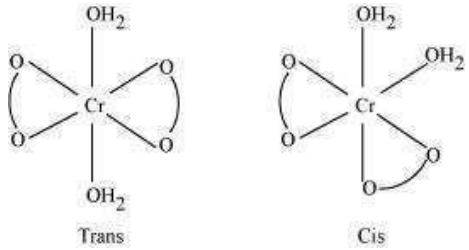
(iii) Overall charge balance:
X + 2(–1) + 2(0) = +1
X = +3
Oxidation state of Cr is +3
Coordination no. Of complex is 6. (-en is a bidentate ligand). Octahedral complex.
d orbital complex: t_{2g}^3

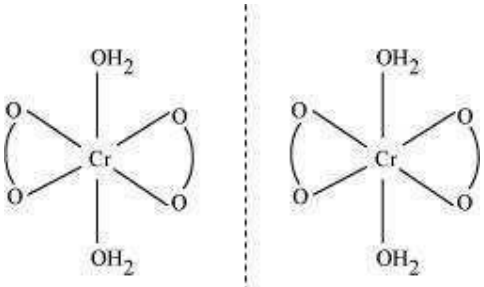
(iv) Ovearll charge balance:
X + 6(0) = +2
X=+2
Oxidation state of Mn is +2.
Coordination no. Of complex is 6. Octahedral complex. d orbital occupation: $t_{2g}^3e_g^2$(water is weak field ligand, does not cause pairing of the electron).

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:

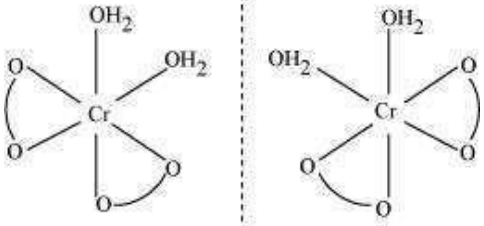
(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$
(ii) $[Co(NH_3)_5Cl]Cl_2$
(iii) $CrCl_3(py)_3$
(iv) $Cs[FeCl_4]$
(v) $K_4[Mn(CN)_6]$

24. (i) Potassium diaquadioxalatochromate (III) trihydrate.
Oxidation state of chromium = 3
Electronic configuration: $3d^3$: $t_{2g}3$
Coordination number = 6
Shape: octahedral Stereochemistry:





Trans is optically inactive



Cis is optically active

Magnetic moment, $\mu = \sqrt{n(n+2)}$

$= \sqrt{3(3+2)}$

$= \sqrt{15}$

4BM

(ii) $[Co(NH_3)_5Cl]Cl_2$

IUPAC name: Pentaamminechloridocobalt(III) chloride

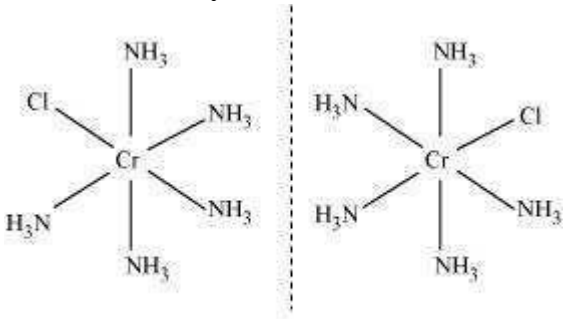
Oxidation state of Co = +3

Coordination number = 6 Shape:

octahedral.

Electronic configuration: d^6: $t_{2g}6$.

Stereochemistry:



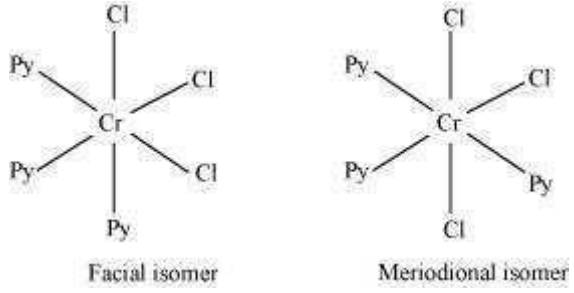
2 isomers

Magnetic Moment = 0

(iii) $CrCl_3(py)_3$

IUPAC name: Trichloridotripyridinechromium (III)
Oxidation state of chromium = +3
Electronic configuration for $d^3 = t_{2g}3$
Coordination number = 6 Shape:
octahedral.

Stereochemistry:



Both isomers are optically active. Therefore, a total of 4 isomers exist.

Magnetic moment, $\mu = \sqrt{n(n+2)}$

$= \sqrt{3(3+2)}$

$= \sqrt{15}$

4BM

(iv) $Cs[FeCl_4]$

IUPAC name: Caesium tetrachloroferrate (III)
Oxidation state of Fe = +3
Electronic configuration of $d^6 = e_g^2 t_{2g}^3$
Coordination number = 4
Shape: tetrahedral
Stereochemistry: optically inactive Magnetic moment:

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

$= \sqrt{5(5+2)}$

$= \sqrt{35} \sim 6BM$

(v) $K_4[Mn(CN)_6]$

Potassium hexacyanomanganate(II)
Oxidation state of manganese = +2
Electronic configuration: $d_5+: t_2g_5$
Coordination number = 6 Shape:
octahedral.
Streochemistry: optically inactive
Magnetic moment, $\mu\sqrt{n(n+2)}$

$= \sqrt{1(1+2)}$

$= \sqrt{3}$

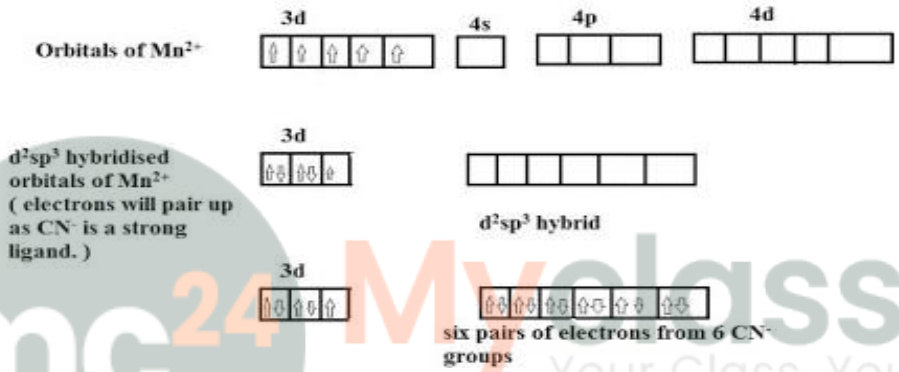
= 1.732 BM

25. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

25. Stability of coordination compounds in a solution refers to the association of the two species i.e coordination sphere and counter ions involved in a state of equilibrium. Stability of complex is expressed in terms of formation constant as:

Stability constant= $[ML_3]/[M][L]^3$

The more will be the value of stability constant, the more will be the amount of $[ML_3]$ in the solution.



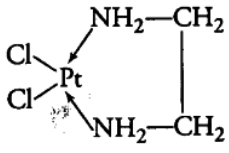
Stability can be of 2 types:

Thermodynamics stability (the extent to which complex is formed or will be transformed to other species at point of equilibrium) Kinetic stability (speed at which the complex is formed) Stability of complex depends on factors:

(i) Charge on central atom:. More will be the charge on central atom more will be the strong bond between atom and ligand and more will be the stability of the complex.

(ii) Basic nature of ligand: More will be the basic character of ligand, more it will try to donate the electrons to the metal atom, hence greater stability.

(iii) Presence of chelate ring: The presence of chelate ring give more stability to the complex. (Stronger interaction)



26. What is meant by the chelate effect? Give an example.

26. When a ligand attaches to the metal ion in a manner that forms a ring, then the metalligand association is found to be more stable. In other words, we can say that complexes

containing chelate rings are more stable than complexes without rings. This is known as the chelate effect.

For example:

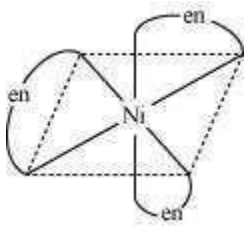
$$Ni^{2+}_{(aq)} + 6NH_{3(aq)} \longleftrightarrow \left[Ni(NH_3)_6\right]^{2+}_{(aq)}$$

$\log\beta = 7.99$

$$Ni^{2+}_{(aq)} + 3en_{(aq)} \longleftrightarrow \left[Ni(en)_3\right]^{2+}_{(aq)}$$

$\log\beta = 18.1$

(more stable)



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

27. (i) Role of coordination compounds in biological system:

We know that in the process of photosynthesis, sunlight is absorbed by the plants through a green pigment called as chlorophyll. This chlorophyll is a co-ordination compound of magnesium. In our human biological body, coordination compounds play a major role. In our blood the oxygen carrier i.e hemoglobin is a co-ordination compound of iron.

(ii) In medicinal chemistry:

A co-ordination compound of platinum called as cis-platin is used in the treatment of stopping the growth of the tumour in our body.

(iii) In analytical chemistry: In the analysis of salt, when different reagents containing ligands are added to different basic radicals, they form coordination compounds. These coordination compounds exhibit different colours associated with each of the basic radicals. Thus it can be used in detection of various radicals.

(iv) In extraction or metallurgy of metals:

In the extraction of the metals from their ores the ability of the metals to form complexes or coordination comppunds are used. For eg. In aqueous solution, gold combines with the cyanide ions to form a complex. Later gold can be extracted from this complex by treating it with zinc metal.

28. How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?

(i) 6 (ii) 4

(iii) 3 (iv)2

28. (iii) The given complex can be written as $[Co(NH_3)_6]Cl_2$.

Thus, $[Co(NH_3)_6]^+$ along with two Cl^- ions are produced.

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

29. (i) Overall charge balance :
$X + 6(0) = +3$
$X = +3$.
Cr is in +3 oxidation state.
Electronic configuration:$3d^3$
As water is a weak field ligand, it does not call pairing up of the electrons.Number of unpaired electron is equal to 3.
Spin only magnetic moment is given by:
$\mu=[n(n+2)]^{1/2}$
$\mu=[3\times5]^{1/2}$
$\mu=4BM$

(ii) In $[Fe(H_2O)_6]^{3+}$
Electronic configuration of Fe is: $[Ar]3d^64s^2$
$[Ar]=1s^22s^22p^63s^23p^6$
Electronic configuration of $Fe^{+3}=[Ar]3d^5$
Outer electronic configuration of $Fe^{+3}=3d^5$
Overall charge balance:
$X + 6(0) = 3$
$X = +3$
H_2O is weak field ligand so it does not pair the unpaired electron. Total no. of unpaired electron, n=5.
Spin only magnetic moment is given by: $\mu=[n(n+2)]^{1/2}$
$\mu=[5\times7]^{1/2}$
$\mu=5.916BM$

(iii) Overall charge balance:
$X + 6(0) = +2$
$X = +2$
Electronic configuration:$3d^{10}$
It has completely filled d orbital, so no. Of unpaired electrons is 0.
$\mu = 0$.
Thus, $[Fe(H_2O)_6]^{3+}$ has highest magnetic moment value.

30. The oxidation number of cobalt in $K[Co(CO)_4]$ is
(i) +1 (ii) +3
(iii) −1 (iv)−3

30. We know that CO is a neutral ligand and K carries a charge of +1.

Therefore, the complex can be written as $K^+[Co(CO)_4]^-$. Therefore, the oxidation number of Co in the given complex is −1. Hence, option (iii) is correct.

31. Amongst the following, the most stable complex is

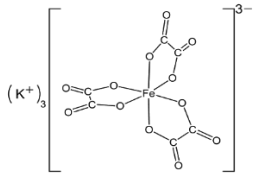
(i) $[Fe(H_2O)_6]^{3+}$

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

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

(iv) $[FeCl_6]^3$

Among all the complex given $[Fe(C_2O_4)_3]^{3-}$ have a bidentate ligand whereas all the other three have unidentated ligand. Now we know that in chelate effect, the bidentate ligand forms a ring like structure and complex so formed is very stable with strong bond between them. So, $[Fe(C_2O_4)_3]^{3-}$ is the most stable complex.



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

32. In all the complex the central metal atom/ion is nickel, Ni. Hence the absorption of wavelength from visible region depends on the ligands attached. The order in which the CFSE energy values of ligands increase according to the spectrochemical series is as follows:

$H_2O<NH_3<NO_2^{2-}$.

So the order of crystal field splitting of d orbitals will also be in the same order because more will be the CFSE energy more will be the energy gap between orbitals. Hence order of wavelength absorption

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