

Maharashtra State Board 12th Chemistry Important Questions Chapter 9 Coordination Compounds

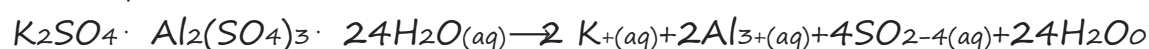
Question 1.

What are double salts?

Answer:

Double salts are crystalline molecular or addition compounds containing more than one salt in simple molecular proportions soluble in water and in solution they ionise and exhibit all the properties of the constituent ions.

For example, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$



Question 2.

Define coordination compound.

Answer:

Coordination compound : It consists of a central metal ion or atom surrounded by atoms, molecules or anions called ligands by coordinate bonds, e.g. cisplatin $Pt(NH_3)_2Cl_2$, $[Cu(NH_3)_4]SO_4$.

Question 3.

Define Lewis bases and Lewis acids with respect to a coordination compound.

Answer:

- Lewis bases : In a coordination compound the ligands being electron pair donors they are Lewis bases.
- Lewis acids : The central metal atom or ion being electron acceptor behaves as a Lewis acid.
- For example, in the coordination compound, $[Cu(NH_3)_4]^{2+}$, NH_3 is a Lewis base and Cu^{2+} is a Lewis acid.

Question 4.

Define coordination sphere. Give example.

Answer:

Coordination sphere : A coordination entity consisting of a central metal atom or ion and the coordinating groups like neutral molecules or anions (ligands) written inside a square bracket is together called coordination sphere. This is a discrete structural unit. The ionisable groups (generally ions) called counter ions are written outside the bracket.

For example, in the coordination compound $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ while K^+ represents counter ion.

Question 5.

Define and explain charge number of a complex ion.

Answer:

Charge number of a complex ion : The net charge carried by a complex ion or a coordination entity is called its charge number.

Explanation :

(i) Charge number is equal to the algebraic sum of the charges carried by central metal atom or ion and all the ligands attached to it.

(ii) E.g. consider anionic complex, $[Fe(CN)_6]^{4-}$.

Charge number of $[Fe(CN)_6]^{4-}$ = Charge on Fe^{2+} ions + 6 x charge on CN^- = $(+2) + 6(-1) = -4$ Hence charge number of $[Fe(CN)_6]^{4-}$ is -4 .

Question 6.

Explain the oxidation state of a metal in a complex.

Answer:

- The oxidation state of a metal atom or ion in the complex is the apparent charge carried by it in the complex.
- It depends upon the atomic number and electronic configuration of the metal atom or ion.
- The coordination number, the formula and geometry of a complex depend upon the oxidation state of the metal atom or ion.

Question 7.

What is the charge on a monodentate ligand X in the complex, $[NiX_4]^{2-}$?

Answer:

The charge number of the complex ion is -2 . Nickel being divalent, its oxidation state is $+2$. If the charge on monodentate ligand X is y, then

Charge number = charge on Ni^{2+} + charge on $4X = +2 + 4y$

$\therefore y = -1$

Hence the charge on ligand X is -1 .

Question 8.

Calculate the oxidation state of a metal in the following complexes :

(a) $[Fe(NH_3)_6](NO_3)_3$

(b) $Ni(CO)_5$.

Answer:

(a) $[Fe(NH_3)_6](NO_3)_3 \rightleftharpoons [Fe(NH_3)_6]^{3+} + 3NO_3^-$

NH_3 is a neutral ligand, and the charge number of complex ion is $+3$.

If the oxidation state of Fe is x then,

$$+ 3 = x + 6(0)$$

$$\therefore x = + 3$$

\therefore The oxidation state of Fe is +3.

(b) $\text{Ni}(\text{CO})_5$ is a neutral complex and CO is a neutral ligand. If the oxidation state of Ni is x, then $0 = x + 5 \times (\text{zero})$

$$\therefore x = \text{zero.}$$

The oxidation state of Ni is zero.

Question 9.

Define and explain the term coordination number (C.N.) of a metal in the complex.

Answer:

Coordination number or legancy (C.N.) : The number of (monodentate) ligands which are directly bonded by coordinate bonds to central metal atom or ion in a coordination compound is called coordination number (C.N.) of the metal atom or ion.

Explanation :

- The coordination number (C.N.) is a characteristic property of the metal and its electronic configuration.
- C.N. takes the values from 2 to 10, of which 4 and 6 are very common.
- The light transition metals show C.N. 4 and 6 while the heavier transition metals show C.N. 8.
- The geometry and shape of a complex compound depends upon C.N. of the metal.

Question 10.

Mention primary valence, secondary valence and coordination number in the following complexes :

(a) $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$

(b) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

(c) $\text{K}_4[\text{Fe}(\text{CN})_6]$

(d) $[\text{CoF}_6]^{3-}$

(e) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

(f) $[\text{Pt}(\text{NH}_3)_2(\text{Py})_2\text{Cl}_2]$

(g) $\text{Cr}(\text{CO})_6$

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

Answer:

Complex	Primary valence/ Valency of metal	Secondary valence	Coordination number
(a) $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$	2	4	4
(b) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	3	6	6
(c) $\text{K}_4[\text{Fe}(\text{CN})_6]$	2	6	6
(d) $[\text{CoF}_6]^{3-}$	3	6	6
(e) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	2	4	4
(f) $[\text{Pt}(\text{NH}_3)_2(\text{Py})_2\text{Cl}_2]$	2	6	6
(g) $\text{Cr}(\text{CO})_6$	0	6	6
(h) $[\text{Ni}(\text{CN})_4]^{2-}$	2	4	4

Question 11.

Classify the following complexes as homoleptic and heteroleptic complex :

(a) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$;

(b) $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$

(c) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$

(d) Tetraaminezinc(II) nitrate.

Question 12.

Summarise the rules of IUPAC nomenclature of coordination compounds.

Answer:

Following rules are followed for naming coordination compounds recommended by IUPAC :

1. In case of a complex ion or a neutral molecule, name the ligand first and then the metal.
2. The names of anionic ligands are obtained by changing the ending -ide to -o and -ate to -ato.
3. The name of a complex is one single word. There must not be any space between different ligand names as well as between ligand name and the name of the metal.
4. After the name of the metal, write its oxidation state in Roman number which appears in parentheses without any space between metal name and parentheses.
5. If complex has more than one ligand of the same type, the number is indicated with prefixes, di-, tri-, tetra-, penta-, hexa- and so on.
6. For the complex having more than one type of ligands, they are written in an alphabetical order. Suppose two ligands with prefixes are tetraaqua and dichloro. While naming in alphabetical order, tetraaqua is written first and then dichloro.

7. If the ligand itself contains numerical prefix in its name, then display number by prefixes bis for 2, tris for 3, tetrakis for 4 and so forth. Put the ligand name in parentheses. For example, (ethylenediamine)₃ or (en)₃ would appear as tris (ethylenediamine) or tris(ethane-1, 2-diamine).
8. The metal in cationic or neutral complex is specified by its usual name while in the anionic complex the name of metal ends with 'ate'.

Question 13.

State effective atomic number (EAN).

OR

State and explain effective atomic number (EAN). How is it calculated?

Answer:

Effective atomic number (EAN) : It is the total number of electrons present around the central metal atom or ion and calculated as the sum of electrons of metal atom or ion and the number of electrons donated by ligands.

It is calculated by the formula : $EAN = Z - X + Y$ where.

Z = Atomic number of metal atom

X = Number of electrons lost by a metal atom forming a metal ion

Y = Total number of electrons donated by all ligands in the complex.

Generally the value of EAN is equal to the atomic number of the nearest inert element.

Explanation : Consider a complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$

Oxidation state of cobalt is + 3 hence $X = 3$.

There are six ligands, hence $Y = 2 \times 6 = 12$

Atomic number of cobalt. $Z = 27$

$\therefore EAN = Z - X + Y = 27 - 3 + 12 = 36$.

Question 14.

Find effective atomic number (EAN) in the following complexes :

- (1) $[\text{Ni}(\text{CO})_4]$
- (2) $[\text{Fe}(\text{CN})_6]^{4-}$
- (3) $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (4) $[\text{Zn}(\text{NH}_3)_4]^{2+}$
- (5) $[\text{Pt}(\text{NH}_3)_6]^{4+}$

Answer:

Ans. Complex	Metal	Atomic number of metal Z	Number of electrons lost by metal X	Number of electrons from ligands Y	EAN = Z - X + Y
(1) $[\text{Ni}(\text{CO})_4]$	Ni	28	0	$4 \times 2 = 8$	$28 - 0 + 8 = 36$ (K_r)
(2) $[\text{Fe}(\text{CN})_6]^{4-}$	Fe	26	2	$6 \times 2 = 12$	$26 - 2 + 12 = 36$ (K_r)
(3) $[\text{Co}(\text{NH}_3)_6]^{3+}$	Co	27	3	$6 \times 2 = 12$	$27 - 3 + 12 = 36$ (K_r)
(4) $[\text{Zn}(\text{NH}_3)_4]^{2+}$	Zn	30	2	$4 \times 2 = 8$	$30 - 2 + 8 = 36$ (K_r)
(5) $[\text{Pt}(\text{NH}_3)_6]^{4+}$	Pt	78	4	$6 \times 2 = 12$	$78 - 4 + 12 = 86$ (R_n)

Question 15.

What is effective atomic number (EAN) in the following complexes ?

- (1) $[\text{Fe}(\text{CN})_6]^{3-}$
- (2) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
- (3) $[\text{Pt}(\text{NH}_3)_4]^{2+}$

Answer:

Ans. Complex	Metal	Atomic number of metal Z	Number of electrons lost by metal X	Number of electrons from ligands Y	EAN = Z - X + Y
(1) $[\text{Fe}(\text{CN})_6]^{3-}$	Fe	26	3	$6 \times 2 = 12$	$26 - 3 + 12 = 35$
(2) $[\text{Cu}(\text{NH}_3)_4]^{2+}$	Cu	29	2	$4 \times 2 = 8$	$29 - 2 + 8 = 35$
(3) $[\text{Pt}(\text{NH}_3)_4]^{2+}$	Pt	78	2	$4 \times 2 = 8$	$78 - 2 + 8 = 84$

Question 16.

Calculate EAN in the following complexes :

(1) $[\text{Cr}(\text{H}_2\text{O})_2(\text{NH}_3)_2(\text{en})]\text{Cl}_3$;(2) $[\text{Ni}(\text{en})_2]\text{SO}_4$;(3) $\text{Na}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$.

Answer:

Ans.	Complex	Metal	Atomic number of metal Z	Number of electrons lost by metal X	Number of electrons from ligands Y	EAN = Z - X + Y
(1)	$[\text{Cr}(\text{H}_2\text{O})_2(\text{NH}_3)_2(\text{en})]\text{Cl}_3$	Cr	24	3	$\left. \begin{array}{l} 2\text{H}_2\text{O} = 4 \\ 2\text{NH}_3 = 4 \\ \text{en} = 4 \end{array} \right\} 12$	$24 - 3 + 12 = 33$
(2)	$[\text{Ni}(\text{en})_2]\text{SO}_4$	Ni	28	2	$2\text{en} = 8$	$28 - 2 + 8 = 34$
(3)	$\text{Na}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$	Cr	24	3	$3\text{C}_2\text{O}_4^{2-} = 12$	$24 - 3 + 12 = 33$

Question 17.

Define in coordination compounds :

(1) Isomerism

(2) Isomers.

Answer:

1. Isomerism : It is the phenomenon in coordination compounds having same molecular formula but different physical and chemical properties due to different arrangements of the ligands around the central metal atom or ion in the space.
2. Isomers : The isomers are the coordination compounds having same molecular formula but different physical and chemical properties due to the difference in arrangements of the ligands in the space.

Question 18.

Mention the types of isomerisms in coordination compounds.

Answer:

There are two principal types of isomerisms in coordination compounds as follows :

(A) Stereoisomerism

(B) Structural isomerism (OR Constitutional isomerism)

(A) Stereoisomerism is further classified as :

- Geometrical isomerism
- Optical isomerism

(B) Structural isomerism is further classified as :

- Ionisation isomerism
- Linkage isomerism
- Coordination isomerism
- Solvate (or hydrate) isomerism

Question 19.

Why does stereoisomerism arise in the coordination compounds?

Answer:

In the coordination compounds (complexes) the ligands are linked to the central metal atom or ion by coordinate bonds which are directional in nature and hence give rise to the phenomenon of stereoisomerism.

In this isomerism, the different stereoisomers have different arrangements of ligands (atoms, molecules or ions) in space around the central metal atom or ion. Hence they have different physical and chemical properties and give rise to the phenomenon of stereoisomerism.

Question 20.

Define, in coordination compounds : (1) Stereoisomerism (2) Stereoisomers.

Answer:

(1) Stereoisomerism The phenomenon of isomerism in the coordination compounds arising due to different spatial positions of the ligands in the space around the central metal atom or ion is called stereoisomerism.

(2) Stereoisomers : The coordination compounds having same molecular formula but different stereoisomerism due to different spatial arrangements of the ligand groups in the space around the central metal atom or ion are called stereoisomers.

Question 21.

Define :

(1) Geometrical isomerism and

(2) Geometrical isomers.

Answer:

(1) Geometrical isomerism : The phenomenon of isomerism in the heteroleptic coordination compounds with the same molecular formula but different spatial arrangement of the ligands in the space around the central metal atom or ion is called geometrical isomerism.

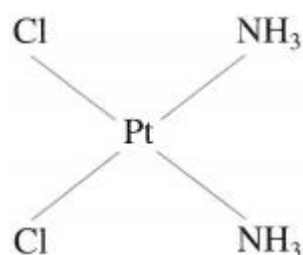
(2) Geometrical isomers : The heteroleptic coordination compounds having same molecular formula but different geometrical isomerism due to different spatial arrangements of the ligands in the space around the central metal atom or ion are called geometrical isomers.

Question 22.

Define cis and trans isomers in the coordination compounds.

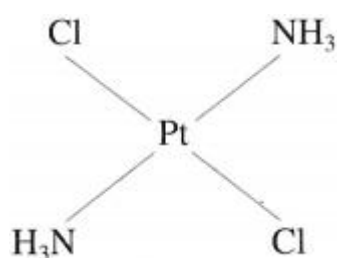
Answer:

(1) Cis-isomer : A heteroleptic coordination compound in which two similar ligands are arranged adjacent to each other is called cis-isomer. For example,



Cis-Diamminedichloroplatinum(II)

(2) Trans-isomer : A heteroleptic coordination compound in which two similar ligands are arranged diagonally opposite to each other is called trans-isomer. For example,

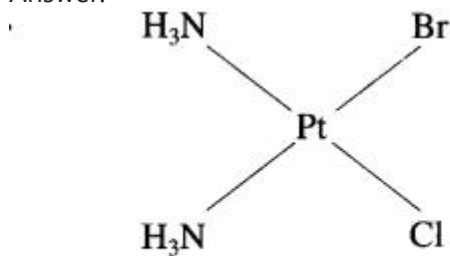


Trans-Diamminedichloroplatinum(II)

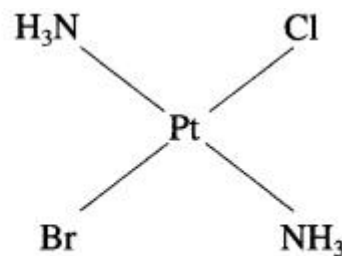
Question 23.

Write structures for geometrical isomers of Diamminebromochloroplatinum(II).

Answer:



Cis-Diamminebromochloroplatinum(II)



Trans-Diamminebromochloroplatinum(II)

Question 24.

Explain the geometrical isomerism of the octahedral complex of the type [MA₄B₂] with a suitable example.

Answer:

- Consider an octahedral complex of a metal M with coordination number six and monodentate ligands a and b having formula [MA₄B₂],
- CA-isomer is obtained when both the B ligands occupy adjacent (1,2) positions.
- Trans-isomer is obtained when the ligands B occupy the opposite (1,6) positions.

- For example, consider a complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. The structures of cis and trans isomers are

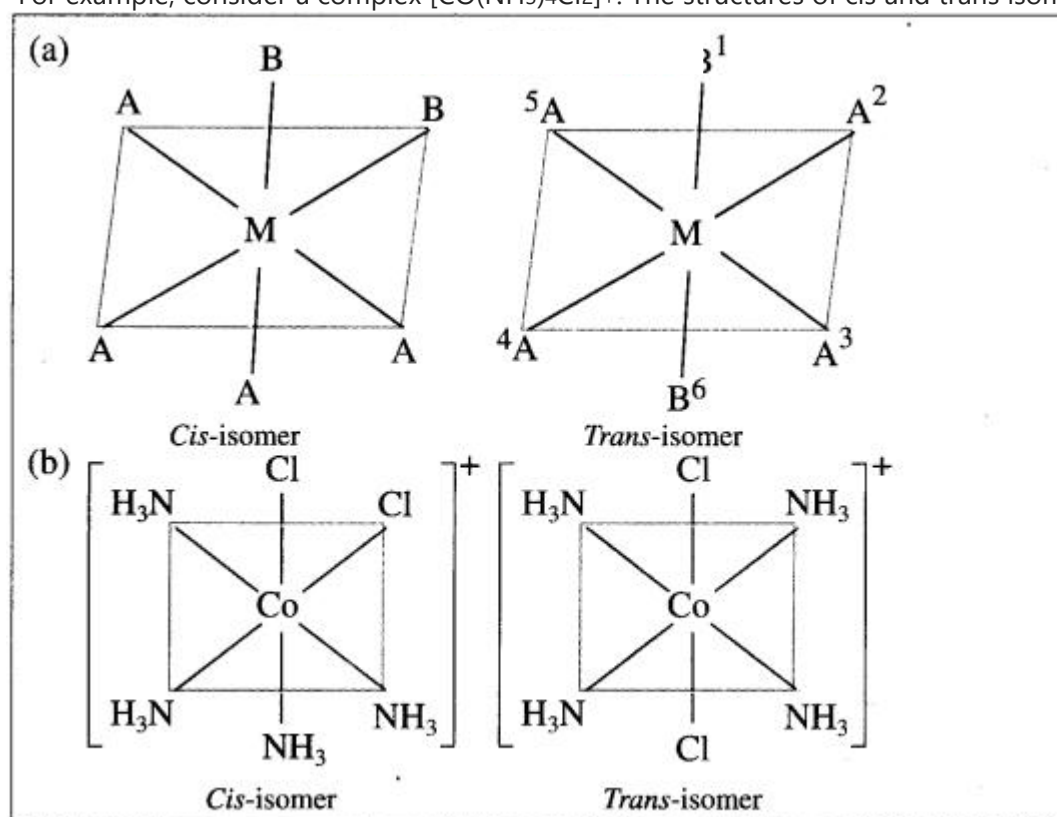


Fig. 9.1 (a) and (b) : Cis and trans-isomers of $[\text{CoCl}_2(\text{NH}_3)_4]^+$

Question 25.

Explain the geometrical isomerism of the octahedral complex of the type $[\text{M}(\text{AA})_2\text{B}_2]_{n\pm}$ with a suitable example.

Answer:

- Consider an octahedral complex of metal M with coordination number six and a bidentate ligand AA and monodentate ligand B having molecular formula $[\text{M}(\text{AA})_2\text{B}_2]_{n\pm}$.
- Bidentate ligand AA has two identical coordinating atoms.
- Cis- isomer is obtained when two bidentate AA ligands as well as two 'B' ligands are at adjacent positions.
- Trans-isomer is obtained when two AA ligands and two B ligands are at opposite positions.
- For example, consider a complex $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.

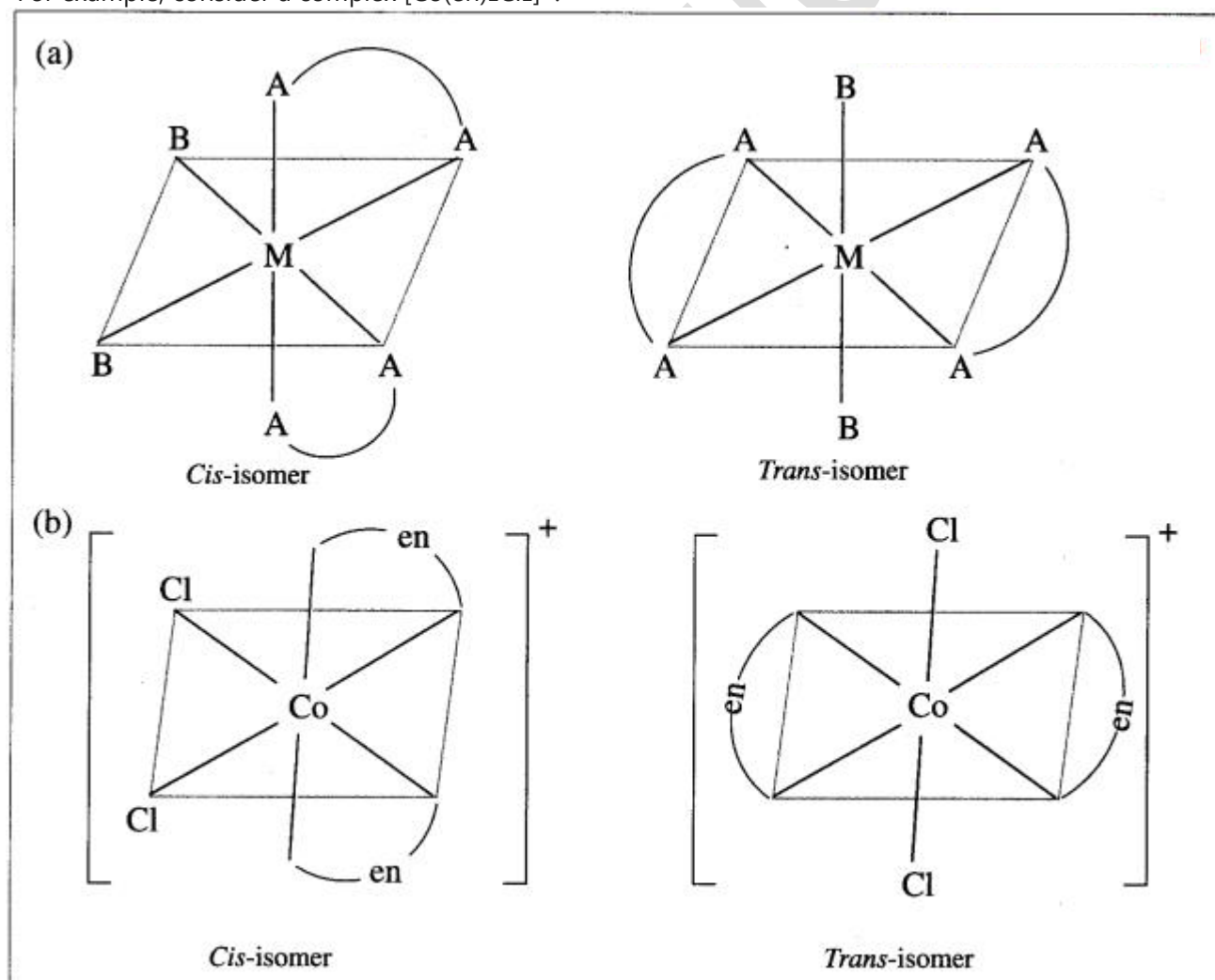


Fig. 9.2 (a) and (b) : cis and trans-isomers of $[\text{CoCl}_2(\text{en})_2]^+$

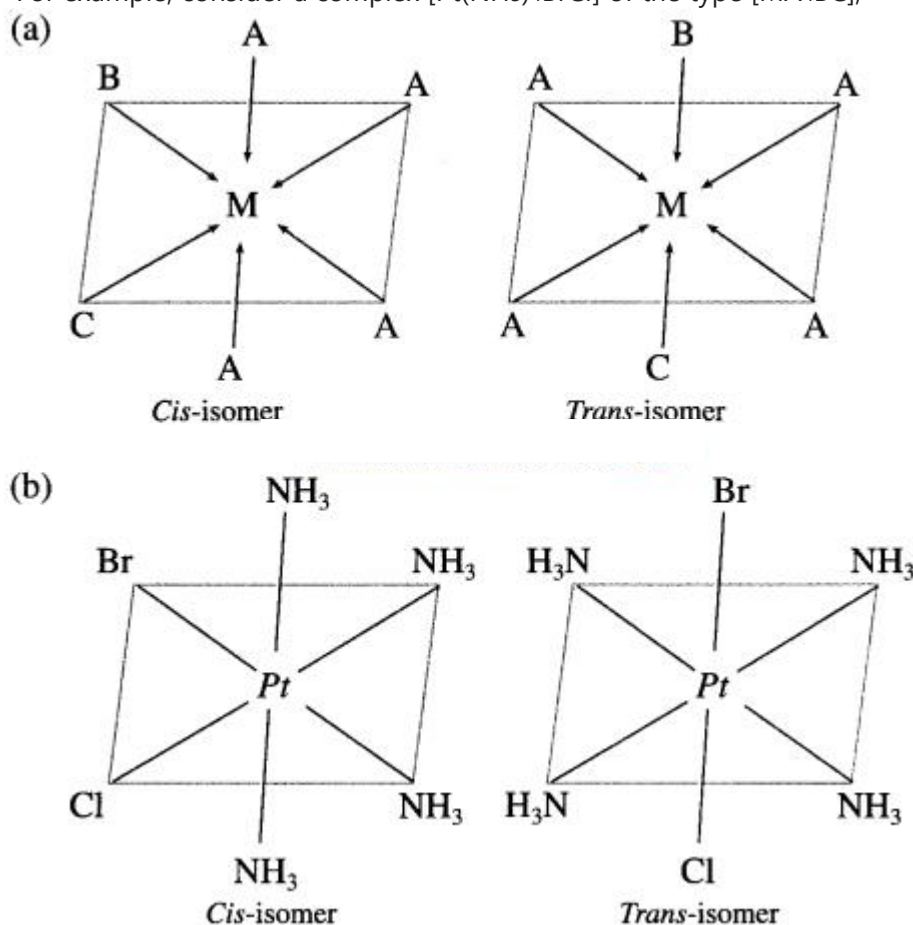
Question 26.

Explain the geometrical isomerism of the octahedral complex of the type $[\text{MA}_4\text{BC}]$ with suitable example.

Answer:

- Consider an octahedral complex of metal M with coordination number six and monodentate ligands A, B and C.
- Cis-isomer is obtained when both the ligands B and C occupy adjacent (1,2) positions.
- Trans-isomer is obtained when the ligands B and C occupy opposite positions.

- For example, consider a complex $[\text{Pt}(\text{NH}_3)_4\text{BrCl}]$ of the type $[\text{MA}_4\text{BC}]$,



Question 27.

Define : (1) Optical isomerism (2) Optical isomers.

Answer:

(1) Optical isomerism : The phenomenon of isomerism in which different coordination compounds having same molecular formula have different optical activity is called optical isomerism.

(2) Optical isomers : Different coordination compounds having same molecular formula but different optical activity are called optical isomers.

Question 28.

Explain : (1) Plane polarised light (2) Optical activity.

Answer:

(1) Plane polarised light : A monochromatic light having vibrations only in one plane is called a plane polarised light. This light is obtained by passing monochromatic light through NICOL prism.

(2) Optical activity : A phenomenon of rotating a plane of a plane polarised light by an optically active substance is called optical activity. This substance is said to be optically active.

Question 29.

Explain : (1) Dextrorotatory substance (2) Laevorotatory substance. (1 mark each)

Answer:

- Dextrorotatory substance : An optically active substance which rotates the plane of a plane polarised light to right hand side is called dextrorotatory or d isomer denoted by d.
- Laevorotatory substance : An optically, active substance which rotates the plane of a plane polarised light to the left hand side is called laevorotatory or l isomer and denoted by l.

Question 30.

What are the conditions for the optical isomerism in coordination compounds?

Answer:

- Optical isomerism is exhibited by those coordination compounds which possess chirality.
- There should not be the presence of element of symmetry which makes the complex optically inactive.
- The mirror images of the complex molecule or ion must be non-superimposable with the molecule or ion.

Question 31.

What are enantiomers?

Answer:

Enantiomers : The two forms of the optical active complex molecule which are mirror images of each other are called enantiomers.

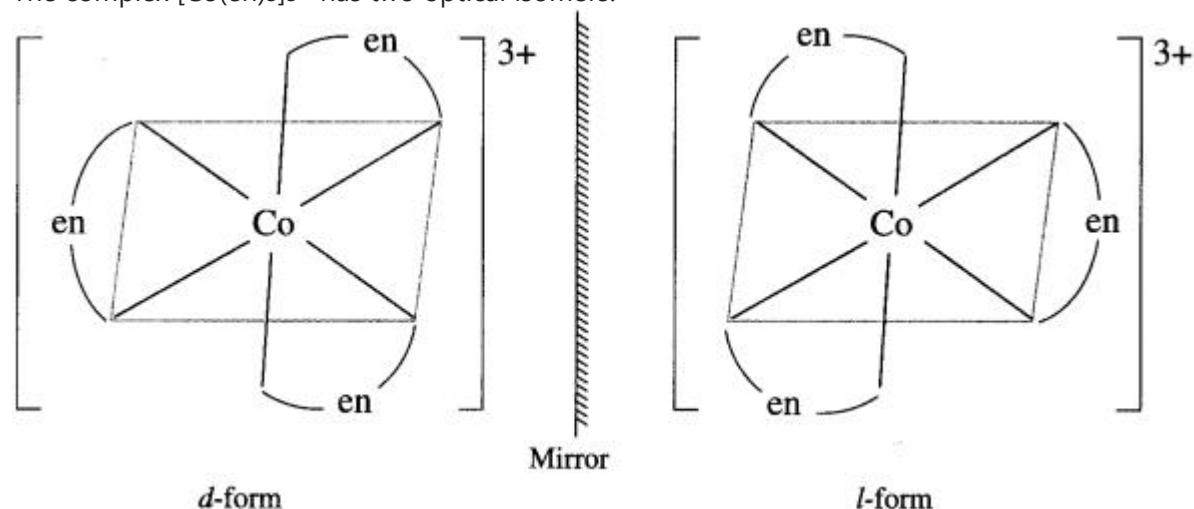
There are two forms of enantiomers, d form and l form.

Question 32.

Draw diagrams for the optical isomers of a complex, $[\text{Co}(\text{en})_3]^{3+}$.

Answer:

The complex $[\text{Co}(\text{en})_3]^{3+}$ has two optical isomers.



Question 33.

Explain the optical isomerism in the octahedral complex with two symmetrical bidentate chelating ligands.

Answer:

The octahedral complexes of the type $[\text{M}(\text{AA})_2(\text{Q})_2]^\pm$, in which two symmetrical bidentate chelating ligands like AA and two monodentate ligands like Q are coordinated to the central metal atom or ion exhibit optical isomerism and two optical isomers d and l can be resolved. For example, $[\text{PtCl}_2(\text{en})_2]^{2+}$.

The cis-form is unsymmetrical and optically active while the trans-form is symmetrical and hence optically inactive. The optical isomers of cis-form (d and l) of this complex along with trans-form are shown below,

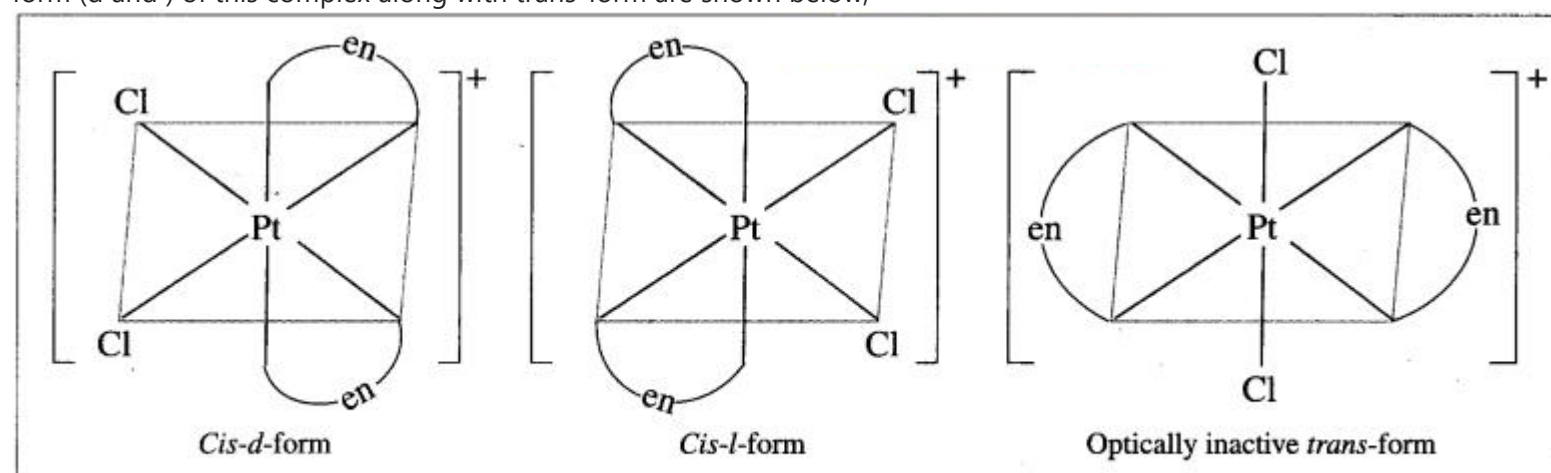


Fig 9.4 : Optically active (cis) and optically inactive (trans) forms of the complex $[\text{PtCl}_2(\text{en})_2]^+$

Question 34.

When are optical isomers called chiral?

Answer:

When the mirror images of optical isomers of the complex are nonsuperimposable they are said to be chiral. For example, $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$.

Question 35.

Define and explain ionisation isomerism.

Answer:

Ionisation isomerism : The phenomenon of isomerism in the metal complexes in which there is an exchange of ions between coordination (or inner) sphere and outer sphere is known as ionisation isomerism.

Explanation :

- Ionisation isomers have same molecular formula but different arrangement of ions in the inner sphere and outer sphere in the complex,
- Hence on ionisation, these ionisation isomers produce different ions in the solution. This ionisation isomerism is also called ion-ion exchange isomerism.

Examples:

(A) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ and (B) $[\text{Co}(\text{NH}_3)_4\text{ClBr}]\text{Cl}$

Ionisation :

(A) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br} \rightleftharpoons [\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Br}^-$

(B) $[\text{Co}(\text{NH}_3)_4\text{ClBr}]\text{Cl} \rightleftharpoons [\text{Co}(\text{NH}_3)_4\text{ClBr}]^+ + \text{Cl}^-$

In the isomers (A) and (B), there is an exchange of ions namely Br^- and Cl^- .

Question 36.

Define : (1) Linkage isomerism (2) Linkage isomers.

OR

What is linkage isomerism ? Explain with an example.

Answer:

(1) Linkage isomerism : The phenomenon of isomerism in which the coordination compounds have same metal atom or ion and same ligand but bonded through different donor atoms or linkages is known as linkage isomerism.

(2) Linkage isomers : The coordination compounds having same metal atom or ion and ligand but bonded through different donor atoms or linkages are called linkage isomers.

For example : Nitro complex $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ = (Yellow) and nitrito complex $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ (Red)

Question 37.

Explain linkage isomers with NO_2^- group as a ligand.

Answer:

(1) Nitro group ($-\text{NO}_2^-$) is an ambidentate ligand. NO_2^- group may link to central metal atom, through N or O.

(2) The two linkage isomers are, $[\text{Cl}: \rightarrow \text{Ag} \leftarrow : \text{NO}_2]^-$ and $[\text{Cl}: \rightarrow \text{Ag} \leftarrow \text{O}-\text{NO}]^-$

Chloronitroargentate(I) ion and Chloronitritoargentate(I) ion

Question 38.

Write linkage isomers of a complex having constituents Co^{3+} , 5NH_3 and NO_2^- .

Answer:

(i) NO_2^- is an ambidentate ligand which can be linked through N or O.

(ii) The linkage isomers are as follows :

(a) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ Pentaamminenitrocobalt(III) ion

(b) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ Pentaamminenitritocobalt(III) ion

Question 39.

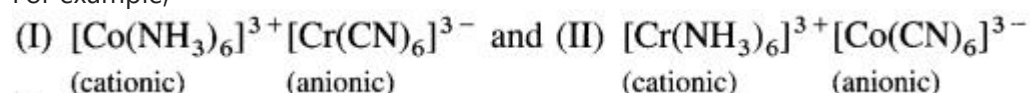
Define: (1) Coordination isomerism (2) Coordination isomers.

Answer:

(1) Coordination isomerism : The phenomenon of isomerism in the ionic coordination compounds having the same molecular formula but different complex ions involving the interchange of ligands between cationic and anionic spheres of different metal. ions is called coordination isomerism.

(2) Coordination isomers : The ionic coordination compounds having same molecular formula but different complexions due to interchange of ligands between cationic and anionic spheres of different metal ions are called coordination isomers.

For example,



Question 40.

Give three examples of coordination isomers. (1 mark each)

Answer:

- $[\text{Cu}(\text{NH}_3)_4] [\text{PtCl}_4]$ and I $[\text{Pt}(\text{NH}_3)_4] [\text{ICuCl}_4]$
- $[\text{Cr}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_4(\text{CN})_2] [\text{Cr}(\text{NH}_3)_2(\text{CN})_4]$
- $[\text{Cr}(\text{NH}_3)_6] [\text{Cr}(\text{SCN})_6]$ and $[\text{Cr}(\text{NH}_3)_4(\text{SCN})_2] [\text{Cr}(\text{SCN})_4(\text{NH}_3)_2]$

Question 41.

Define Solvate or Hydrate isomerism.

Answer:

Solvate ate or Hydrate isomerism : The phenomenon of isomerism in the coordination compounds arising due to the exchange of solvent or H_2O molecules inside the coordination sphere and outer sphere of the complex is known as solvate or hydrate isomerism.

Question 42.

Define solvate or hydrate isomers.

OR

What are hydrate isomers? Explain with examples.

Answer:

Solvate or Hydrate isomers : The coordination compounds having the same molecular formula but differ in the number of solvent or H_2O molecules inside the coordination sphere and outer sphere of the complexes are called solvate or hydrate isomers.

For example : $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$; $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$; and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$.

Question 43.

A coordination compound has the formula $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$. Write the hydrate isomers of the complex.

Answer:

The possible hydrate isomers of the coordination compounds having molecular formula $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$ are as follows :

- (1) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$;
- (2) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- (3) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$
- (4) $[\text{Co}(\text{H}_2\text{O})_3 \text{Cl}_3] \cdot 3\text{H}_2\text{O}$.

Question 44.

Explain the steps involved in describing the bonding in coordination compounds using valence bond theory.

Answer:

- Vacant d-orbitals of metal ion form coordination bonds with ligands.

- s, p orbitals along with vacant d-orbitals of metal ion take part in hybridisation.
- The number of vacant hybrid orbitals formed is equal to number of hybridising orbitals which is equal to the number of ligand donor atoms or coordination number of the metal.
- The metal-ligand coordination bonds are formed by the overlap between the vacant hybrid orbitals of metal and the filled orbitals of the ligands.
- The hybrid orbitals used by the metal ion point in the direction of the ligands.
- When inner (n – 1)d orbitals of metal ion are used in the hybridisation then the complex is called (a) inner orbital complex while when outer nd orbitals are used, complexes are called (b) outer orbital complexes. .

Question 45.

Explain the steps involved in the metal-ligand bonding.

Answer:

- Find the oxidation state of central metal ion in the complex.
- Write the valence shell electronic configuration of metal ion.
- From the formula of the complex determine the number of ligands and find the number of metal ion orbitals required for bonding.
- Find the orbitals of metal ion available for hybridisation and the type of hybridisation involved.
- Represent the electronic configuration of metal ion after hybridisation.
- Exhibit filling of hybrid orbitals after complex formation.
- Determine the number of unpaired electrons and predict magnetic property of the complex.
- Find whether the complex is low spin or high spin (applicable for octahedral complexes with d4 or d8 electronic configuration.)

Question 46.

What are the salient features of valence bond theory (VBT)?

Answer:

The salient features of valence bond theory (VBT) are as follows :

1. According to this theory, a central metal atom or ion present in a complex provides a definite number of vacant orbitals (s, p, d and) to accommodate the electrons from the ligands for the formation coordinate bonds with the metal ion atom.
2. The number of vacant orbitals provided by the central metal atom or ion is the same as the coordination number of the metal. For example : Cu^{2+} provides 4 vacant orbitals in the complex. $[\text{Cu}(\text{NH}_3)_4]^{2+}$.
3. The vacant orbitals of metal atom or ion undergo hybridisation forming the same number of hybridised orbitals, since the bonding with the hybrid orbitals is stronger.
4. Each ligand has one or more orbitals containing one or more lone pairs of electrons.
5. The shape or geometry of the complex depends upon the type of hybridisation of the metal atom.
6. When inner orbitals namely (n – 1) d orbitals in transition metal atom or ion hybridise, the complex is called inner complex and when outer orbitals i.e., nd orbitals hybridise then the complex is called outer complex.
7. When the central metal atom or ion in the complex contains one or more unpaired electrons the complex is paramagnetic while if all the electrons are paired, the complex is diamagnetic.

Question 47.

What is the spin pairing process in the coordination compound?

Answer:

When the ligands approach the metal atom or ion for the formation of a complex, they influence the valence electrons of metal atom or ion. Accordingly the ligands are classified as (A) strong ligands and (B) weak ligands.

(A) Strong ligands :

- They cause the pairing of unpaired electrons present in the metal atom or ion.
- Spin pairing process :
 - The process of pairing of unpaired electrons in metal atom or ion due to the presence of ligands in the complex is called spin pairing process.
 - This spin pairing process decreases the number of unpaired electrons and hence decreases the paramagnetic character of the complex.
 - The strong ligands also promote the outer ns electrons to the vacant inner (n – 1)d orbitals.

(B) Weak ligands : The weak ligands have no effect on the electrons in the valence shell of a metal atom or ion.

Strong ligands : CO, CN, ethylenediamine (en), NH_3 , EDTA, etc.

Weak ligands : Cl^- , I^- , OH^- , etc.

[Note : If a complex has n number of unpaired electrons then the magnetic moment, μ is given by 'spin only' formula $\mu = n(n + 2)$ B.M. where B.M. (Bohr Magneton) is the unit of magnetic moment. Hence from the magnitude of μ , the number of unpaired electrons in the complex and its structure can be evaluated.]

Question 48.

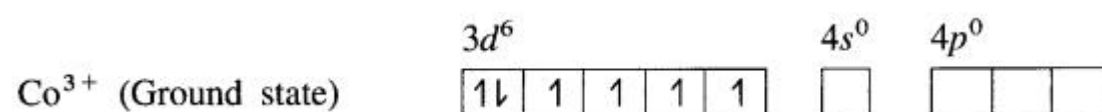
Explain the structure of octahedral complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$ on the basis of valence bond theory.

Answer:

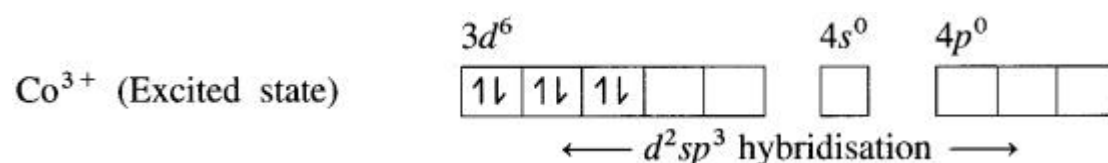
(1) Hexaamminecobalt(III) ion, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is a cationic complex, the oxidation state of cobalt is + 3 and the coordination number is 6.

(2) Electronic configuration : ^{27}Co $[\text{Ar}]_{18} 3d^7 4s^2$

Electronic configuration : Co^{3+} $[\text{Ar}]_{18} 3d^6 4s^0 4p^0$



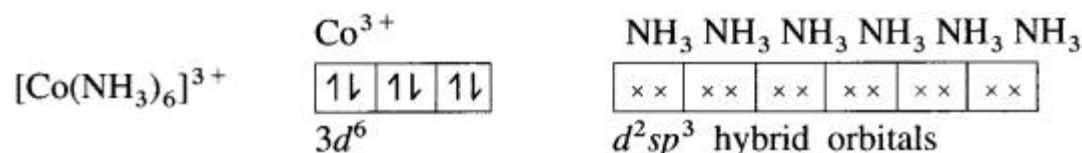
(3) Since NH_3 is a strong ligand, due to spin pairing effect, all the four unpaired electrons in 3d orbital are paired giving two vacant 3d orbitals.



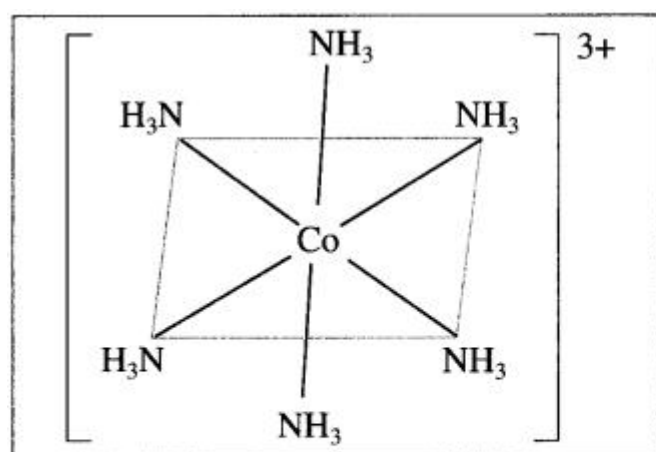
(4) Since the coordination number is 6, Co^{3+} ion gets six vacant orbitals by hybridisation of two 3d vacant orbitals, one 4s and three 4p orbitals forming six d^2sp^3 hybrid orbitals giving octahedral geometry. It is an inner complex.



(5) 6 lone pairs of electrons from 6 NH_3 ligands are accommodated in the six vacant d^2sp^3 hybrid orbitals. Thus six hybrid orbitals of Co^{3+} overlap with filled orbitals of NH_3 forming 6 coordinate bonds giving octahedral geometry to the complex.



Since the complex has all electrons paired, it is diamagnetic.



$[\text{Co}(\text{NH}_3)_6]^{3+}$

Fig. 9.5 : Structure of $[\text{Co}(\text{NH}_3)_6]^{3+}$

Complex	Hybridisation	Geometry	Magnetic property
$[\text{Co}(\text{NH}_3)_6]^{3+}$	d^2sp^3 (inner)	Octahedral	Diamagnetic ($\mu = 0$)

Question 49.

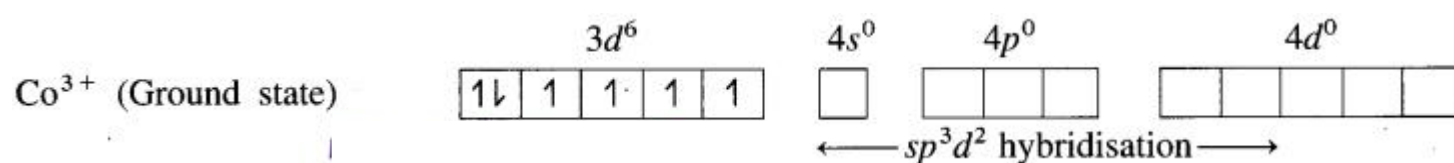
Explain the geometry of $[\text{CoF}_6]^{3-}$ on the basis of valence bond theory.

Answer:

(1) Hexafluorocobaltate(III) ion, $[\text{CoF}_6]^{3-}$ is an anionic complex, the oxidation state of cobalt is +3 and the coordination number is 6.

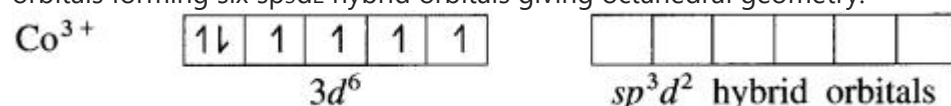
(2) Electronic configuration : $27\text{Co} [\text{Ar}] 3d^7 4s^2 4p^0 4d^0$

Electronic configuration : $\text{Co}^{3+} [\text{Ar}] 3d^6 4s^0 4p^0 4d^0$

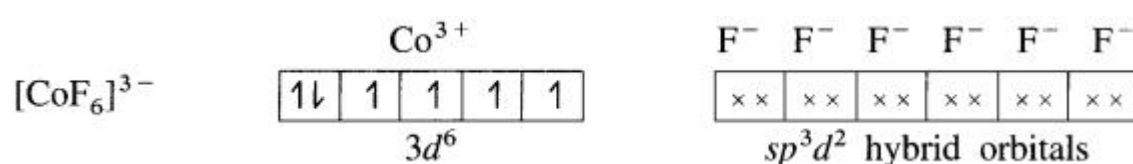


(3) Since F is a weak ligand, there is no spin pairing effect and Co^{3+} possesses 4 unpaired electrons.

(4) Since the coordination number is 6, the Co^{3+} ion gets six vacant orbitals by hybridisation of one 4s orbital, three 4p orbitals and two 4d orbitals forming six sp^3d^2 hybrid orbitals giving octahedral geometry.



(5) 6 lone pairs of electrons from 6 F^- ligands are accommodated in the six vacant sp^3d^2 hybrid orbitals. Thus six hybrid orbitals of Co^{3+} overlap with filled orbitals of F^- forming 6 coordinate bonds giving octahedral geometry to the complex. It is an outer complex.



As the complex has 4 unpaired electrons it is paramagnetic.

Magnetic moment μ is, $\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.9 \text{ B.M.}$

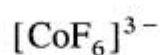
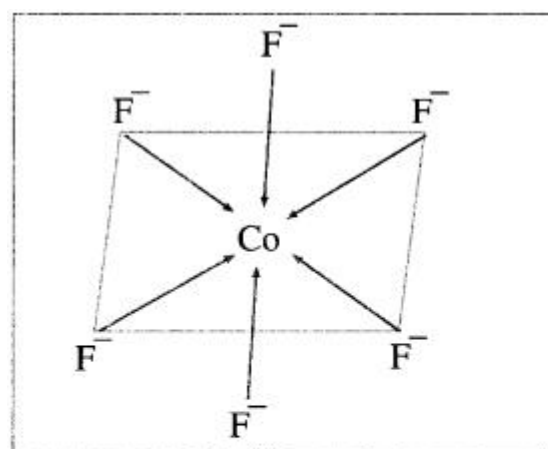


Fig. 9.6 : Structure of $[\text{CoF}_6]^{3-}$

Complex	Hybridisation	Geometry	Magnetic property
$[\text{CoF}_6]^{3-}$	sp^3d^2 (outer)	Octahedral	Paramagnetic ($\mu = 4.9$ B.M.)

Question 50.

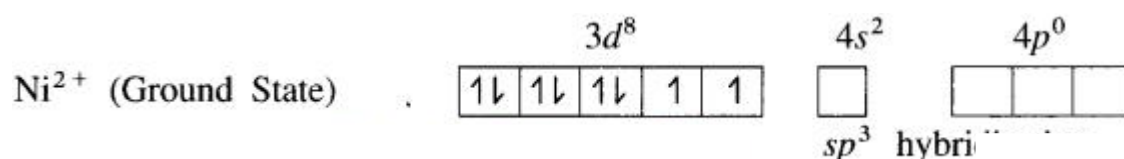
Explain the structure of tetrachloronickelate(II) $[\text{NiCl}_4]^{2-}$ on the basis of valence bond theory.

Answer:

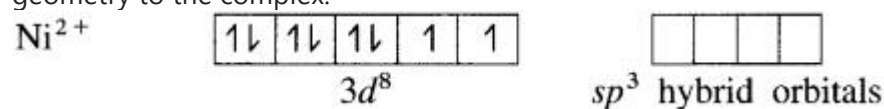
(1) Tetrachloronickelate(II) ion is an anionic complex, oxidation state of Ni is +2 and the coordination number is 4.

(2) Electronic configuration : $28\text{Ni} [\text{Ar}]18 3d^8 4s^2 4p^0$

Electronic configuration : $\text{Ni}^{2+} [\text{Ar}]18 3d^8 4s^0 4p^0$



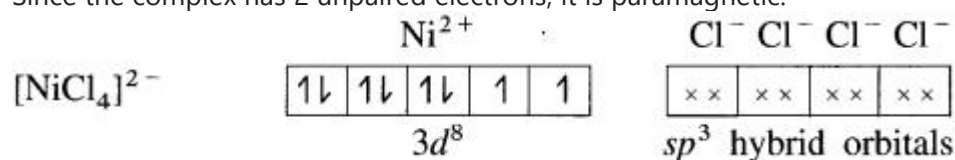
(3) Since the coordination number is 4, it gets 4 vacant hybrid orbitals by sp^3 -hybridisation of one 4s and three 4p orbitals giving tetrahedral geometry to the complex.



(4) As Cl is a weak ligand, 2 unpaired electrons in Ni^{2+} remain undisturbed.

(5) 4 lone pairs of electrons from 40 ligands are accommodated in the vacant four sp^3 hybrid orbitals. Thus four sp^3 hybrid orbitals of Ni^{2+} overlap with filled orbitals of Cl^- forming 4 coordination bonds, giving tetrahedral geometry to the complex.

Since the complex has 2 unpaired electrons, it is paramagnetic.



Magnetic moment μ is, $\mu = n(n+2) \dots \dots \dots \sqrt{2(2+2)} \dots \dots \dots \sqrt{2.83}$ B.M.

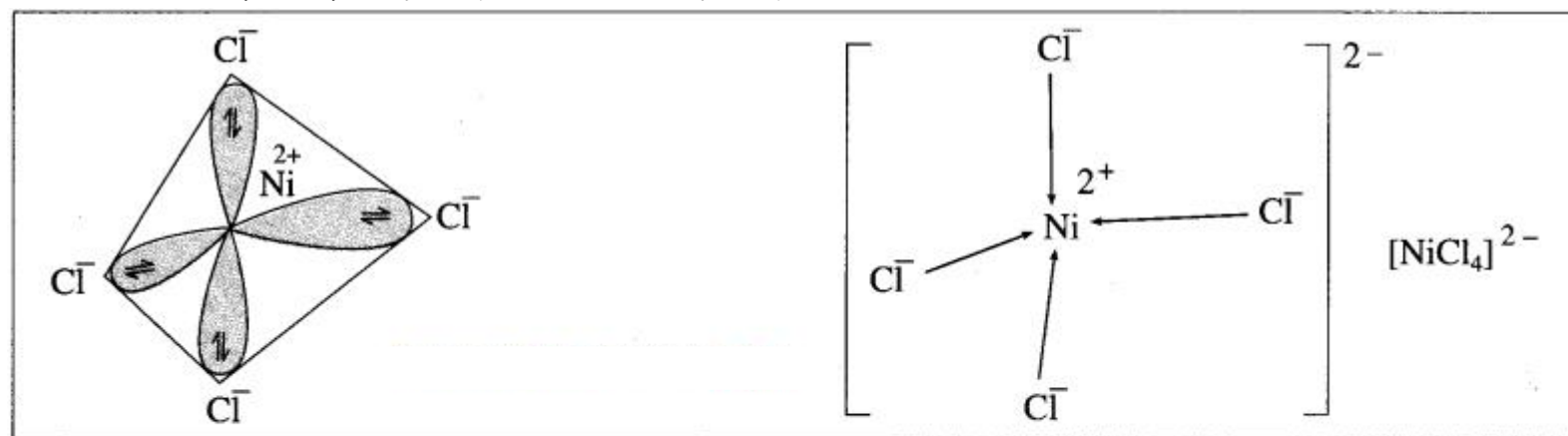


Fig. 9.7 : Structure of $[\text{NiCl}_4]^{2-}$

Hybridisation	Geometry	Magnetic property
sp^3	Tetrahedral	Paramagnetic ($\mu = 2.83$ B.M.)

Question 51.

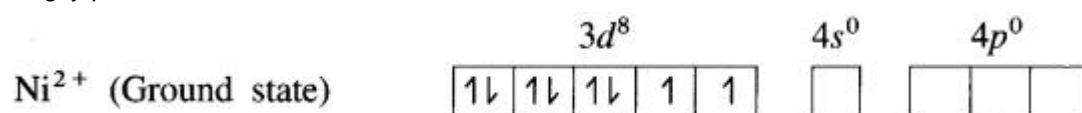
Explain the structure of $[\text{Ni}(\text{CN})_4]^{2-}$ on the basis of valence bond theory.

Answer:

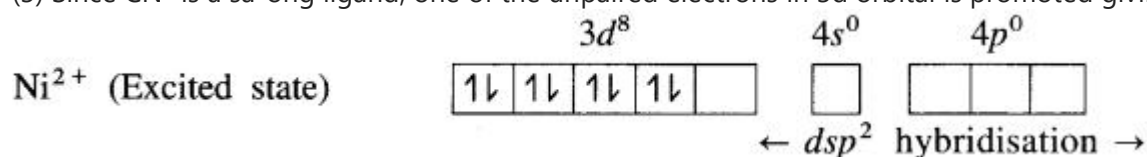
(1) Tetracyanonickelate (II) ion, $[\text{Ni}(\text{CN})_4]^{2-}$ is an anionic complex, oxidation state of Ni is + 2 and the coordination number is 4.

(2) Electronic configuration : $28\text{Ni} [\text{Ar}]18 3d^8 4s^2 4p^0$

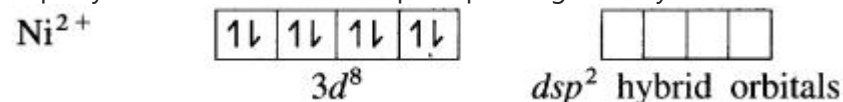
Electronic configuration: $\text{Ni}^{2+} [\text{Ar}]18 3d^8 4s^0 4p^0$



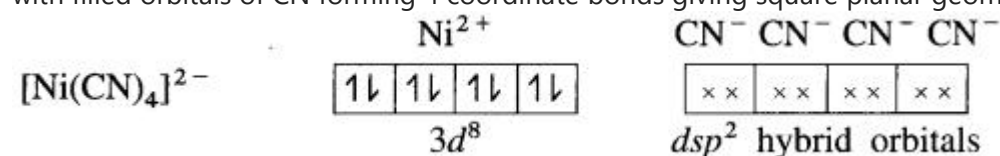
(3) Since CN^- is a strong ligand, one of the unpaired electrons in 3d orbital is promoted giving two paired electrons and one vacant 3d orbital.



(4) Since the coordination number is 4, Ni^{2+} gets 4 vacant hybrid orbitals by hybridisation of one 3d, one 4s and two 4p orbitals forming four dsp^2 hybrid orbitals. This has square planar geometry.



(5) 4 lone pairs from 4 CN^- ligands are accommodated in the vacant four dsp^2 hybrid orbitals. Thus four dsp^2 hybrid orbitals of Ni^{2+} overlap with filled orbitals of CN^- forming 4 coordinate bonds giving square planar geometry to the complex. It is an inner complex.



Since the complex ion has all electrons paired, it is diamagnetic.

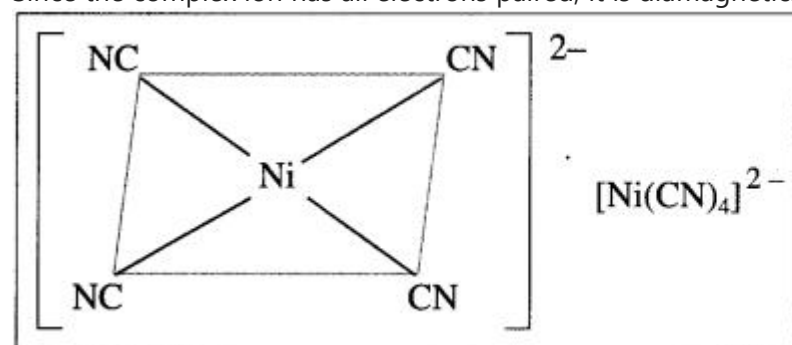


Fig. 9.8 : Structure of $[\text{Ni}(\text{CN})_4]^{2-}$

Complex	Hybridisation	Geometry	Magnetic property
$[\text{Ni}(\text{CN})_4]^{2-}$	dsp^2 (inner)	Square planar	Diamagnetic ($\mu = 0$)

Question 52.

What are the limitations of valence bond theory?

Answer:

In case of the coordination compounds, the valence bond theory has the following limitations :

- (1) It cannot explain the spectral properties (colours) of the complex compounds.
- (2) Even if the magnetic moments can be calculated from the number of unpaired electrons, it cannot explain the magnetic moment arising due to orbital motion of electrons.
- (3) It cannot explain why the metal ions with the same oxidation state give inner complexes and outer complexes with different ligands.
- (4) In every complex, it cannot explain magnetic properties based on geometry of the complex.
- (5) Quantitative interpretations of thermodynamic and kinetic stabilities of the coordination compounds cannot be accounted.
- (6) The complexes with weak field ligands and strong field ligands cannot be distinguished.
- (7) It cannot predict the tetrahedral and square planar geometry of complexes with coordination number 4.
- (8) The order of reactivity of inner complexes of d_3 , d_4 , d_5 and d_6 metal ions cannot be explained.
- (9) It cannot explain the rates and mechanisms of reactions of the coordination compounds.

Question 53.

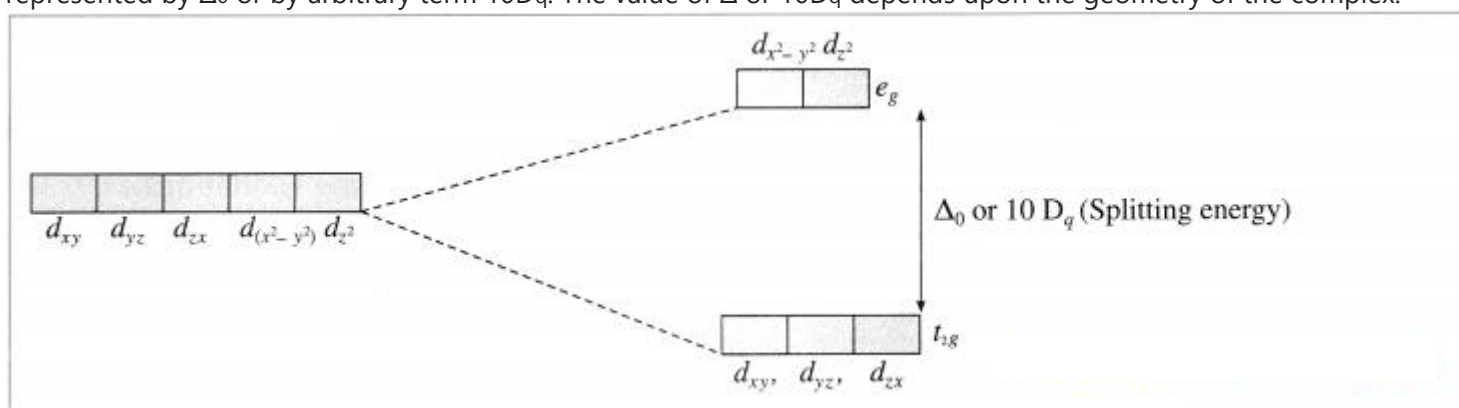
What are the assumptions of Crystal Field Theory (CFT)?

Answer:

Bethe and van Vleck developed Crystal Field Theory (CFT) to explain various properties of coordination compounds. The salient features of CFT are as follows :

1. In a complex, the central metal atom or ion is surrounded by various ligands which are either negatively charged ions (F^- , Cl^- , CN^- , etc.) or neutral molecules (H_2O , NH_3 , en, etc.) and the most electronegative atom in them points towards central metal ion.
2. The ligands are treated as point charges involving purely electrostatic attraction between them and metal ion.
 - The central metal ion has five, $(n-1)d$ degenerate orbitals namely d_{xy} , d_{yz} , d_{zx} , $d_{(x^2-y^2)}$ and d_{z^2} .
 - When the ligands approach the metal ion, due to repulsive forces, the degeneracy of d -orbitals is destroyed and they split into two groups of different energy, t_{2g} and e_g orbitals. This effect is called crystal field splitting which depends upon the geometry of the complex.
 - The T -orbitals lying in the direction of ligands are affected to a greater extent while those lying in between the ligands are affected to a less extent.
 - Due to repulsion, the orbitals along the axes of ligands acquire higher energy while those lying in between the ligands acquire less energy.
 - Hence repulsion by ligands give two sets of split up orbitals of metal ion with different energies.

- The energy difference between two sets of d-orbitals after splitting by ligands is called crystal field splitting energy (CFSE) and represented by Δ_0 or by arbitrary term $10Dq$. The value of Δ or $10Dq$ depends upon the geometry of the complex.



- The electrons of metal ion occupy the split d-orbitals according to Hund's rule, aufbau principle and those orbitals with minimum repulsion and the farthest away from the ligands.
- CFI' does not account for overlapping of orbitals of central metal ion and ligands, hence does not consider covalent nature of the complex.
- From the crystal field stability energy, the stability of the complexes can be known.

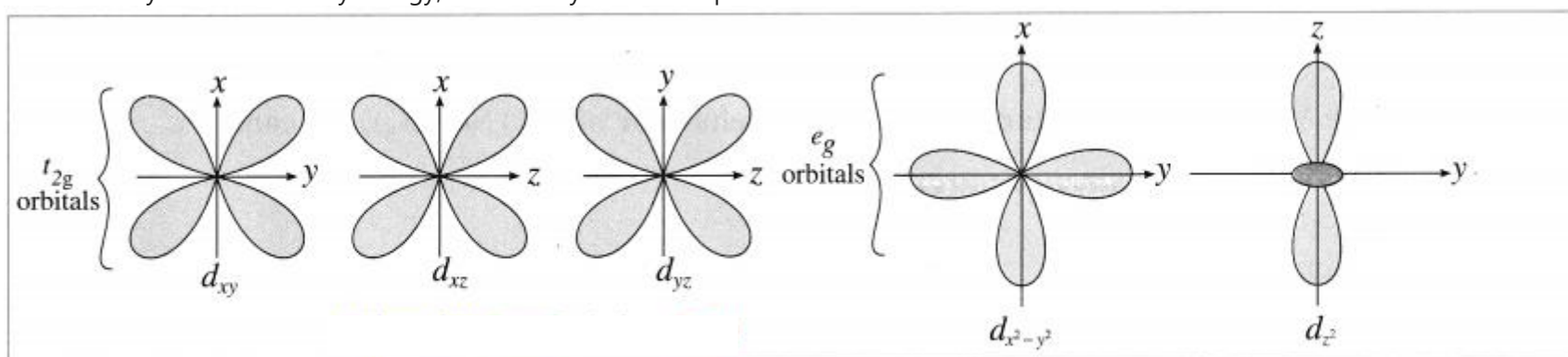


Fig. 9.9 : Shapes of d-orbitals

Question 54.

What is crystal field splitting?

Answer:

The splitting of five degenerate d-orbitals of the transition metal ion into different sets of orbitals (t_{2g} and e_g) having different energies in the presence of ligands in the complex is called crystal field splitting.

Question 55.

What is crystal field stabilisation energy?

Answer:

Crystal field stabilisation energy (CFSE) It is the change in energy achieved by preferential filling up of the orbitals by electrons in the complex of metal atom or ion.

CFSE is expressed as a negative quantity i.e., $CFSE \leq 0$. Higher the negative value more is the stability of the complex.

Question 56.

Explain the factors affecting Crystal Field Splitting parameter (Δ_0).

Answer:

Crystal Field Splitting parameter (Δ_0) depends on. (a) Strength of the ligands and (b) Oxidation state of the metal.

(a) Strength of the ligands : Since strong field ligands like CN^- , en, etc. approach closer to the central metal ion, it results in a large crystal field splitting and hence Δ_0 has higher values.

(b) Oxidation state of the metal A metal ion with the higher positive charge draws the ligands closer to it which results in large separation of t_{2g} and e_g set of orbitals. The complexes involving metal ions with low oxidation state have low values of Δ_0 . For example $[Fe(NH_3)_6]^{3+}$ has higher Δ_0 than $[Fe(NH_3)_6]^{2+}$.

Question 57.

Explain the octahedral geometry of complexes using crystal field theory.

Answer:

(1) In an octahedral complex $[MX_6]^{n\pm}$, the metal atom or ion is placed at the centre of regular octahedron while six ligands occupy the positions at six vertices of the octahedron.

(2) Among five degenerate d-orbitals, two orbitals namely $d_{x^2-y^2}$ and d_{z^2} are axial and have maximum electron density along the axes, while remaining three e-orbitals namely d_{xy} , d_{yz} and d_{zx} are planar and have maximum electron density in the planes and in-between the axes.

(3) Hence, when the ligands approach a metal ion, the orbitals $d_{x^2-y^2}$ and d_{z^2} experience greater repulsion and the orbitals d_{xy} , d_{yz} and d_{zx} experience less repulsion.

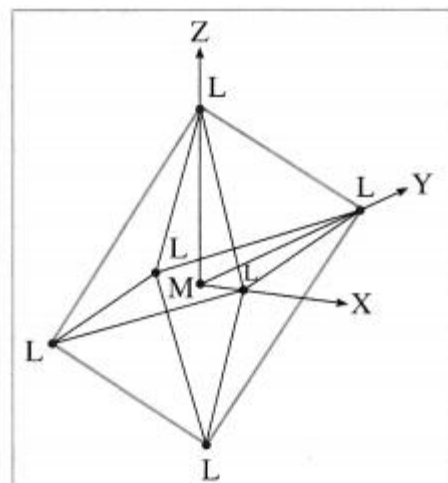


Fig. 9.10 : Octahedral geometry having central metal (M) at the centre and six ligands (L) at the vertices of the octahedron.

(4) Therefore the energy of $d_{x^2-y^2}$ and d_{z^2} increases while the energy of d_{xy} , d_{yz} and d_{zx} decreases and five d-orbitals lose degeneracy and split into two point groups. The orbitals d_{xy} , d_{yz} and d_{zx} form t_{2g} group of lower energy while $d_{x^2-y^2}$ and d_{z^2} form e_g group of higher energy.

Thus t_{2g} has three degenerate orbitals while e_g has two degenerate orbitals.

(5) Experimental calculations show that the energy of t_{2g} orbitals is lowered by $0.4\Delta_0$ or $4Dq$ and energy of e_g orbital is increased by $0.6\Delta_0$ or $6Dq$. Thus energy difference between t_{2g} and e_g orbitals is Δ_0 or $10Dq$ which is crystal field splitting energy.

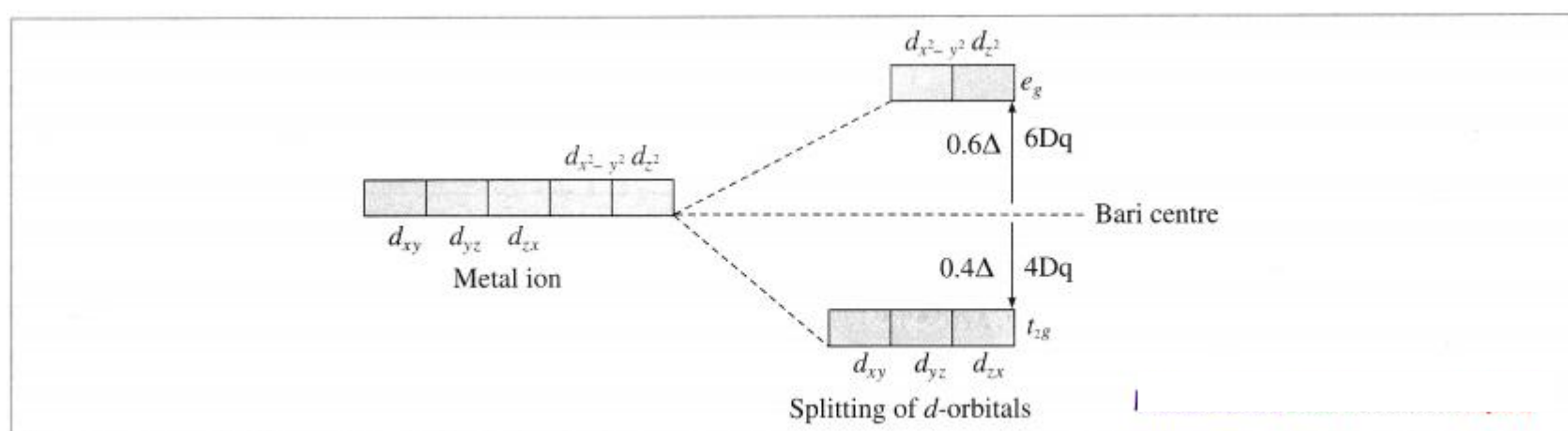


Fig. 9.11 : Crystal field splitting in octahedral complex

(6) CFSF increases with the increasing strength of ligands and oxidation state of central metal ion.

Question 58.

Explain the tetrahedral geometry of complexes using crystal field theory.

Answer:

(1) In the tetrahedral complex, $[MX_4]^{n\pm}$, the metal atom or ion is placed at the centre of the regular tetrahedron and the four ligands are placed at four corners of the tetrahedron.

(2) The ligands approach the central metal atom or ion in-between the three coordinates x , y and z . The orbitals d_{xy} , d_{yz} and d_{zx} are pointed towards ligands and experience greater repulsion while the axial orbitals $d_{x^2-y^2}$ and d_{z^2} lie in-between metal-ligand bond axes and experience comparatively less repulsion.

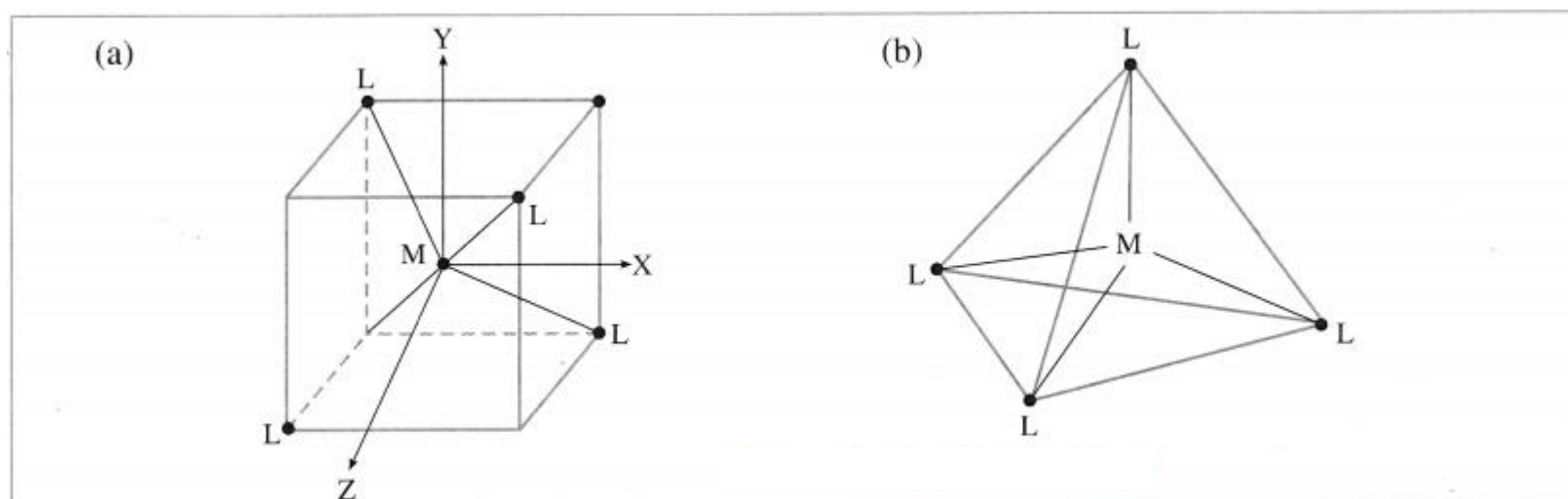


Fig. 9.12 (a) and (b) : Tetrahedral geometry having central metal atom (M) at the centre and four ligands (L) at the four corners

(3) Therefore energy of d_{xy} , d_{yz} and d_{zx} orbitals is increased while that of $d_{x^2-y^2}$ and d_{z^2} is lowered. Hence 5d-orbitals lose their degeneracy and split into two point groups, namely t_{2g} of higher energy (d_{xy} , d_{yz} and d_{zx}) and e_g of lower energy ($d_{x^2-y^2}$ and d_{z^2}).

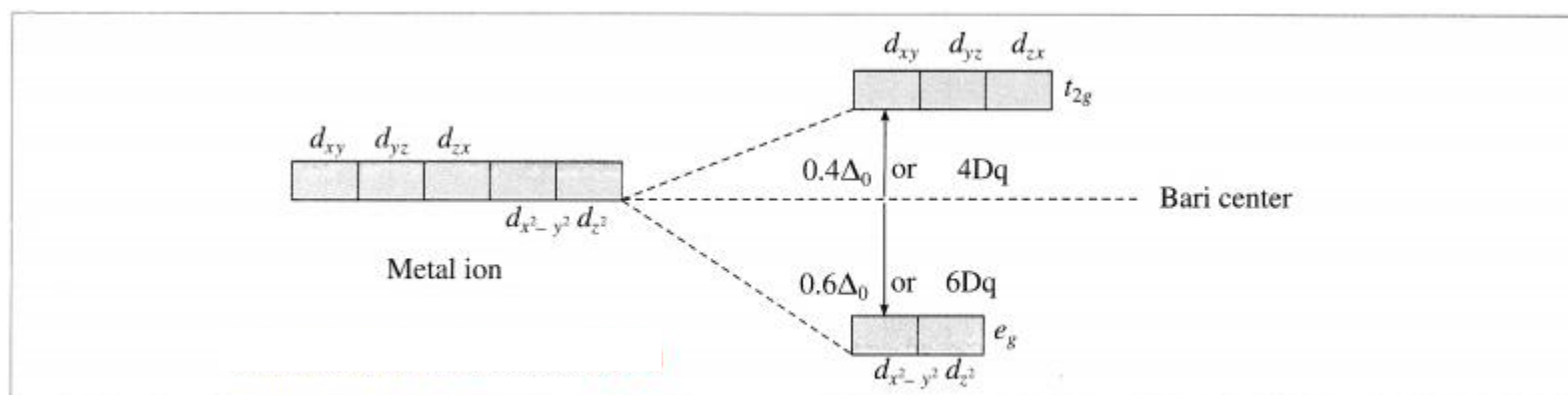


Fig. 9.13 : Crystal field splitting in tetrahedral complex

(4) The experimental calculations show that the energy of t_{2g} orbitals is increased by $0.4 \Delta_0$ or $4Dq$ and energy of e_g is lowered by $0.6 \Delta_0$ or $6Dq$. Thus energy difference between t_{2g} and e_g orbitals is Δ_0 or $10Dq$ which is crystal field splitting energy (CFSE).

(5) This explains that the entry of each electron in e_g orbitals, stabilises the complex by $0.6 \Delta_0$ or $6Dq$ While the entry of each electron in t_{2g} orbitals destabilises the tetrahedral complex by $0.4 \Delta_0$ or $4Dq$.

(6) In case of strong field ligands, the electrons prefer to pair up in e_g orbitals giving low spin (LS) complexes while in case of weak field ligands, the electrons prefer to enter higher energy t_{2g} orbitals giving more unpaired electrons and hence form high spin (HS) complexes.

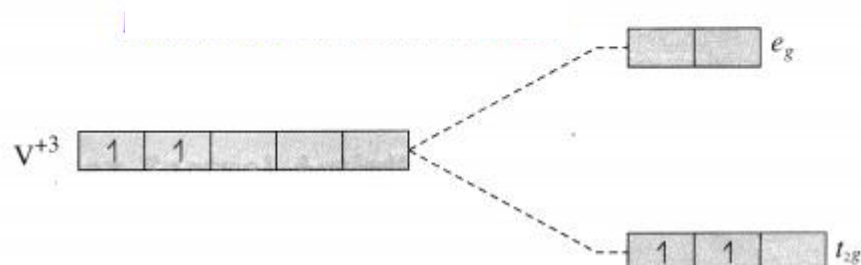
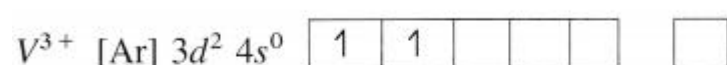
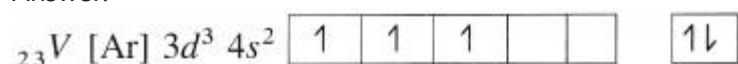
Table 9.4 : Properties of complexes

Complex	Hybridisation	Geometry	Magnetic property
(1) $[\text{NiCl}_4]^{2-}$	sp^3	Tetrahedral	Paramagnetic
(2) $[\text{Ni}(\text{CO})_4]$	sp^3	Tetrahedral	Diamagnetic
(3) $[\text{Ni}(\text{CN})_4]^{2+}$	dsp^2	Square planar	Diamagnetic
(4) $[\text{CuCl}_4]^{2-}$	sp^3	Tetrahedral	Paramagnetic
(5) $[\text{Cu}(\text{NH}_3)_4]^{2+}$	dsp^2 (inner)	Square planar	Paramagnetic
(6) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	sp^3d^2 (outer)	Octahedral	Paramagnetic
(7) $[\text{Fe}(\text{CN})_6]^{3-}$	d^2sp^3 (inner)	Octahedral	Paramagnetic
(8) $[\text{Fe}(\text{CO})_5]$	dsp^3 (inner)	Trigonal bipyramidal	Diamagnetic
(9) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	sp^3d^2 (outer)	Octahedral	Paramagnetic
(10) $[\text{Co}(\text{NH}_3)_6]^{3+}$	d^2sp^3 (inner)	Octahedral	Diamagnetic

Question 59.

Give valence bond description for the bonding in the complex $[\text{VCl}_4]^-$. Draw box diagrams for free metal ion. Which hybrid orbitals are used by the metal? State the number of unpaired electrons.

Answer:



Since Cl^- is a weak ligand, there is no pairing of electrons.

Number of unpaired electrons = 2

Type of hybridisation = sp^3

Geometry of complex ion = Tetrahedral

The complex ion is paramagnetic.

Write a note on colour in coordination compounds.

- A large number of coordination compounds show wide range of colours due to d – d transition of electron and this can be explained by crystal field theory (CFT).
- The complex absorbs the light in one visible region (400 nm to 700 nm) and transmits the light in different visible region giving complementary colour.
- Consider an octahedral purple coloured complex of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ which absorbs green light and transmits purple colour. Similarly $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ absorbs the light in the red region of radiation spectrum and transmits in the blue region, hence the complex appears blue.
- The absorption of light arises due to d-d transition of electron from lower energy level (t_{2g}) to higher energy level (e_g) in octahedral complex.
- The energy required for transition depends upon crystal field splitting energy Δ_0 . If $\Delta_0 = \Delta E$, then the energy of an absorbed photon ($h\nu$) is $\Delta E = h\nu = hc/\lambda$ where λ , ν and c are wavelength, frequency and velocity of the absorbed light.
- Higher the magnitude of Δ_0 or ΔE , higher is the frequency or lower is the wavelength of the absorbed radiation.
- Since Δ_0 depends upon nature of metal atom or ion, its oxidation state, nature of ligands and the geometry of the complex, different coordination compounds have different colours.

Explain the purple colour of the complex, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ with the help of crystal field theory.

(1) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is an octahedral complex, oxidation state of titanium is +3 (Ti^{3+}) and the coordination number is 6.

Electronic configuration = $\text{Ti}^{3+} + [\text{Ar}]18\ 3d^1$

1				
---	--	--	--	--

Ground state

Excited state in the presence of ligands

Excited state

Ground state

$\Delta_0 = \Delta E = 3.99 \times 10^{-19} \text{ J/ion}$

(4) The crystal field splitting energy (CFSE), Δ_0 is found to be 3.99×10^{-19} J/ion from the spectrochemical studies.

$t^1_{2g} e_g^0 \longrightarrow t^0_{2g} e_g^1$

Lower energy configuration Higher energy configuration

Photon energy $h\nu$

(a) Absorption of a photon (b) Excitation of an electron

Adsorption

400 500 600 700

(c) Wavelength (nm)

(6) The wavelength of the absorbed radiation will be.

(7) Hence the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs the green radiation of wavelength 498 nm in the visible region and transmits the complementary purple light. Therefore the complex is purple coloured.

An octahedral complex absorbs the radiation of wavelength 620 nm. Find the crystal field splitting energy.

Answer:

Crystal field splitting energy Δ_0 is given by,

$$\Delta_0 = \Delta E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{620 \times 10^{-9} \text{ m}} = 3.2 \times 10^{-19} \text{ J}$$

Question 63.

What are the applications of coordination compounds ?

Answer:

(1) In biology : Several biologically important natural compounds are metal complexes which play an important role in number of processes occurring in plants and animals.

For example, chlorophyll in plants is a complex of Mg^{2+} ions, haemoglobin in blood is a complex of iron, vitamin B₁₂ is a complex of cobalt.

(2) In medicine : The complexes are used on a large scale in medicine. Many medicines in the complex form are more stable, more effective and can be assimilated easily.

For example, platinum complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ known as cisplatin is effectively used in cancer treatment. EDTA is used to treat poisoning by heavy metals like lead.

(3) To estimate hardness of water :

- The hardness of water is due to the presence Mg^{2+} and Ca^{2+} ion in water.
- The strong field ligand EDTA forms stable complexes with Mg^{2+} and Ca^{2+} . Hence these ions can be removed by adding EDTA to hard water.

Similarly these ions can be selectively estimated due to the difference in their stability constants.

(4) Electroplating : This involves deposition of a metal on the other metal. For smooth plating, it is necessary to supply continuously the metal ions in small amounts.

For this purpose, a solution of a coordination compound is used which dissociates to a very less extent. For example, for uniform and thin plating of silver and gold, the complexes $\text{K}[\text{Ag}(\text{CN})_2]$ and $\text{K}[\text{Au}(\text{CN})_2]$ are used.

Multiple Choice Questions

Select and write the most appropriate answer from the given alternatives for each subquestion :

Question 1.

The coordination number of cobalt in the complex $[\text{Co}(\text{en})_2\text{Br}_2]\text{Cl}_2$ is

- 4
- 5
- 6
- 7

Answer:

- 6

Question 2.

EDTA combines with cations to form

- chelates
- polymers
- clathrates
- non-stoichiometric compounds

Answer:

- chelates

Question 3.

Which one of the following compounds can exhibit coordination isomerism?

- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Br}$
- $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$
- $[\text{Co}(\text{en})_3]\text{Cl}_3$
- $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$

Answer:

- $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$

Question 4.

Which of the following compounds can exhibit linkage isomerism?

- $[\text{Co}(\text{en})_3]\text{Cl}_3$

Allguidesite -

- Arjun

- Digvijay

(b) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$

(c) $[\text{Co}(\text{en})_2\text{NO}_2\text{Br}]\text{Cl}$

(d) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2$

Answer:

(c) $[\text{Co}(\text{en})_2\text{NO}_2\text{Br}]\text{Cl}$

Question 5.

Oxidation number of cobalt in $\text{K}[\text{CoCl}_4]$ is

(a) +1

(b) -1

(c) +3

(d) -3

Answer:

(b) -1

Question 6.

The correct structure of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is

(a) octahedral

(b) tetrahedral

(c) square pyramidal

(d) trigonal bipyramidal

Answer:

(b) tetrahedral

Question 7.

Amongst the following ions which one has the highest paramagnetism?

(a) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

(b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

(c) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

(d) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

Answer:

(b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

Question 8.

The geometry of $[\text{Ni}(\text{CN})_4]^{3-}$ and $[\text{NiCl}_4]^{2-}$ are

(a) both tetrahedral

(b) both square planar

(c) tetrahedral and square planar respectively

(d) square planar and tetrahedral respectively

Answer:

(d) square planar and tetrahedral respectively

Question 9.

The complex $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is used in treatment of cancer under the name.

(a) Aspirin

(b) Eqanil

(c) cisplatin

(d) transplatin

Answer:

(c) cisplatin

Question 10.

$[\text{Co}(\text{NH}_3)_6]^{3+}$ is an orbital complex and is in nature.

(a) inner, paramagnetic

(b) inner, dimagnetic

(c) outer, paramagnetic

(d) outer, dimagnetic

Answer:

(b) inner, dimagnetic

Question 11.

The IUPAC name of $[\text{Ni}(\text{Co})_4]$ is

(a) tetra carbonyl nickel (O)

(b) tetra carbonyl nickel (II)

(c) tetra carbonyl nickelate (O)

(d) tetra carbonyl nickelate (II)

Answer:

(a) tetra carbonyl nickel (O)

Question 12.

The number of ions produced by the complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is

Allguidesite -

- Arjun

- Digvijay

(a) 1

(b) 2

(c) 3

(d) 4

Answer:

(b) 2

Question 13.

The dimagnetic species is

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

(b) $[\text{NiCl}_4]^{2-}$

(c) $[\text{CoCl}_4]^{2-}$

(d) $[\text{CoF}_6]^{2-}$

Answer:

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

Question 14.

Which one of the following is an inner orbital complex as well as diamagnetic in behaviour (Atomic no. Zn = 30, Cr = 24, Co = 27, Ni = 28)

(a) $[\text{Zn}(\text{NH}_3)_6]^{2+}$

(b) $[\text{Cr}(\text{NH}_3)_6]^{3+}$

(c) $[\text{Co}(\text{NH}_3)_6]^{3+}$

(d) $[\text{Ni}(\text{NH}_3)_6]^{2+}$

Answer:

(c) $[\text{Co}(\text{NH}_3)_6]^{3+}$

Question 15.

Among $[\text{Ni}(\text{Co})\text{J}]$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{NiCl}_2]^{2-}$ Species, the hybridisation states at the Nickel atom are respectively

(a) sp^3 , dsp^2 , sp^3

(b) sp^3 , dsp^2 , dsp^2

(c) dsp^2 , sp^3 , sp^3

(d) sp^3 , sp^3 , dsp^2

Answer:

(a) sp^3 , dsp^2 , sp^3

Question 16.

The strongest ligand in the following is

(a) CN^-

(b) Br^-

(c) HO^-

(d) F^-

Answer:

(a) CN^-

Question 17.

Magnetic moment of $(\text{NH}_4)_2(\text{MnBr}_4)$ is BM

(a) 5.91

(b) 4.91

(c) 3.91

(d) 2.91

Answer:

(a) 5.91

Question 18.

The complex which violates EAN rule is

(a) $\text{Fe}(\text{CO})_5$

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

(c) $\text{Ni}(\text{CO})_4$

(d) $[\text{Zn}(\text{NH}_3)_4]\text{Cl}_2$

Answer:

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

Question 19.

EDTA is a ligand of the type

(a) bidentate

(b) tridentate

(c) tetradentate

(d) hexadentate

Answer:

(d) hexadentate

Question 20.

The cationic complex among the following is

- (a) $K_3[Fe(CN)_6]$
- (b) $Ni(CO)_4$
- (c) K_2HgI_4
- (d) $[Co(NH_3)_6]Cl_2$

Answer:

- (d) $[Co(NH_3)_6]Cl_2$

Question 21.

If Z is the atomic number of a metal, X is number of electrons lost forming metal ion and Y is the number of electrons from the ligands then EAN is

- (a) $Z + X + Y$
- (b) $X - Z + Y$
- (c) $Z - X + Y$
- (d) $X + Z - Y$

Answer:

- (c) $Z - X + Y$

Question 22.

Octahedral complex has hybridisation,

- (a) dsp^2
- (b) d^3sp^3
- (c) dsp^3
- (d) d^2sp^3

Answer:

- (d) d^2sp^3

Question 23.

Inner complex has hybridisation,

- (a) d^2sp^3
- (b) sp^3d^2
- (c) sp^3d
- (d) sp^3d^3

Answer:

- (a) d^2sp^3

Question 24.

The number of unpaired electrons in $[Co(NH_3)_6]^{3+}$ is

- (a) 0
- (b) 1
- (c) 2
- (d) 4

Answer:

- (a) 0

Question 25.

The number of unpaired electrons in $[NiCl_2]^-$ and $[Ni(CN)_4]^{2-}$ are respectively,

- (a) 2, 2
- (b) 2, 0
- (c) 0, 0
- (d) 1, 2

Answer:

- (b) 2, 0

Question 26.

Among the following complexes, the highest magnitude of crystal field stabilisation energy will be for $[Co(H_2O)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$

- (a) $[Co(H_2O)_6]^{3+}$
- (b) $[Co(CN)_6]^{3-}$
- (c) $[Co(NH_3)_6]^{3+}$
- (d) $[CoF_6]^{3-}$

Answer:

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

Question 27.

The number of unpaired electrons in a low spin octahedral complex ion of d^1 is

- (a) 0
- (b) 1
- (c) 2
- (d) 3

Answer:

(b) 1

Question 28.

The number of unpaired electrons in a high spin octahedral complex ion of d^7 is

(a) 0

(b) 1

(c) 2

(d) 3

Answer:

(d) 3

Question 29.

Ligand used in the estimation of hardness of water is

(a) EDTA

(b) DBG

(c) chloride

(d) bromo

Answer:

(a) EDTA

Question 30.

Which of the following complexes will give a white precipitate on treatment with a solution of barium nitrate?

(a) $[\text{Cr}(\text{NH}_3)_4\text{SO}_4] \text{Cl}$

(b) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{NO}_2$

(c) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2] \text{SO}_4$

(d) $[\text{CrCl}_3(\text{H}_2\text{O})_4] \text{Cl}$

Answer:

(c) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2] \text{SO}_4$

Question 31.

What is effective atomic number of Fe ($z = 26$) in $[\text{Fe}(\text{CN})_6]^{4-}$?

(a) 12

(b) 30

(c) 26

(d) 36

Answer:

(d) 36

Question 32.

Cisplatin compound is used in the treatment of

(a) malaria

(b) cancer

(c) AIDS

(d) yellow fever

Answer:

(b) cancer