CO-ORDINATION CHEMISTRY

INTRODUCTION :

(a) The concept of co-ordination compounds arises from the complex formation tendency of transition elements.

(b) These compounds play a vital role in our lives, as chlorophyll of plants, vitamin B_{12} and haemoglobin of animal blood are the co-ordination compounds of Mg, Co and Fe respectively.

(c) The co-ordination compounds play important role in analytical chemistry , polymerisation reactions, metallurgy and refining of metals, photography, water purification etc.

(d) Co-ordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

ADDITION COMPOUNDS :

When solutions containing two or more salts in simple molecular proportion are evaporated, crystals of new compound separate out.

These compounds are called molecular or addition compounds.

Ex. $K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

$CuSO_4 + 4NH_3 + H_2O \longrightarrow [Cu(NH_3)_4]SO_4 \cdot H_2O$

These addition compounds can be divided into two classes :

(A) DOUBLE SALTS :

Those which lose their identity in solution

In solutions these compounds break down into simpler ions. Such addition compounds which lose their identity in solutions are called **double salts** .

Example :

Potash alum $K_2SO_4 \cdot Al_2(SO)_4)_3 \cdot 24H_2O$ when dissolved in water breaks down into K^+, SO_4^{2-}, Al^{+3} ions and therefore is an example of **double salt**.

(B) COORDINATION COMPOUNDS :

Those which retain their identity in solution.

In aqueous solution, these addition compounds do not furnish all simple ions but instead give more complex ions having complicated structure .

Example :

Potassium ferrocyanide $K_4[Fe(CN)_6]$ does not furnish simple K^+, Fe^{2+} and CN^- ions but gives K^+ ions and complex ferrocyanide ions, $[Fe(CN)_6]^{4-}$. These types of compounds are called **complex compounds or co-ordination compounds**.

On the basis of stability of complex ion, complex ions are further divided as follows –

(i) **Perfect complexes :** The compounds in which complex ion is fairly stable and further dissociation or feebly dissociation is not possible in solution state.

Ex.
$$\begin{tikzcd} K_4[Fe(CN)_6] \arrow[r] & 4K^+ + [Fe(CN)_6]^{4-} \arrow[d] \\ & Fe^{2+} + 6CN^- \text{ (Feebly dissociated)} \end{tikzcd}$$

The ferrocyanide ion $[Fe(CN)_6]^{4-}$ is so insignificantly dissociated that it can be considered as practically undissociated and does not give the qualitative test of Fe^{2+} or CN^- ions..

(ii) **Imperfect complexes :** Those complexes in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus respond to their usual qualitative test.

Ex.
$$\begin{tikzcd} K_2[Cd(CN)_4] \arrow[r] & 2K^+ + [Cd(CN)_4]^{2-} \arrow[d, shift right, harpoon] \\ & Cd^{2+} + 4CN^- \text{ (appreciably dissociated)} \arrow[u, shift right, harpoon] \end{tikzcd}$$

DEFINITIONS OF TERMS USED IN CO-ORDINATION COMPOUNDS

(a) **Co-ordination or complex compound :** Co-ordination compounds are those molecular compounds which retain their identity even when dissolved in water or any other solvent and their properties are completely different from those of the constituent ions.

(b) **Central ion :** The cation to which one or more neutral molecules or ions are attached is called the atom / ion. Since, the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atoms of neutral molecules or ions, it must have empty orbitals of appropriate energy.

(c) **Complex ion :** A complex ion may be defined as an electrically charged radical which is formed by the combination of a simple cation with one/more neutral molecules or one/more simple.

(d) **Co-ordination number :** The total number of co-ordinate covalent bond formed by central metal in complex is called the co-ordination number of the central metal ion .

Some common co-ordination number of important metals are as given below.

Metal	Coordination Number	Metal	Coordination Number
Cu^+	2, 4	Ni^{2+}	4, 6
Ag^+	2	Fe^{2+}	4, 6
Au^+	2, 4	Fe^{3+}	6
Hg_2^{2+}	2	Co^{2+}	4, 6
Cu^{2+}	4, 6	Co^{3+}	6
Ag^{2+}	4	Al^{3+}	6
Pt^{2+}	4	Sc^{3+}	6
Pd^{2+}	4	Pt^{4+}	6
Mg^{2+}	6	Pd^{4+}	6

Example. Coordination number of the central metal ions in

(i) $[Cu(NH_3)_4]^{2+}$ is four (ii) $[Fe(EDTA)]^-$ is six

(e) **Co-ordination sphere :** The part of the complex enclosed in square bracket is known as co-ordination sphere. It is actually combination of central metal and ligands.

(f) **Ligands :**

(a) The ions or neutral molecules which combine with central metal ion to form complex are called ligands.

(b) They act as electron pair donor (i.e. Lewis bases) though certain ligands also accept electron from central metal and such ligands are known as π - acid ligands.

❖ CLASSIFICATION OF LIGANDS

(A) Based on charge

(i) Neutral ligands : H_2O, NO, CO, C_6H_6 etc.

(ii) Positive ligands : NO^+, $N_2H_5^+$

(iii) Negative ligands : Cl^-, NO_2^-, CN^-, OH^-

(B) Based on denticity

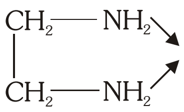
The number of electron pairs donated to central metal by a particular ligand is known as DENTICITY. Depending on number of electron pairs donated, these are classified in following categories.

(a) Unidentate/monodentate ligands

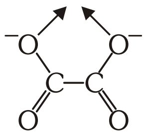
Ligands which donate one pair of electron to the central metal are called unidentate ligands. X^-, CN^-, NO_2^-, NH_3, Pyridine, OH^-, NO_3^-, H_2O, SO_3^{-2}, CO, NO, OH^-, O^{-2}, $(C_6H_5)_3P$ etc.

(b) Bidentate ligands

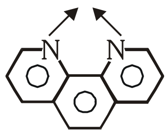
Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.



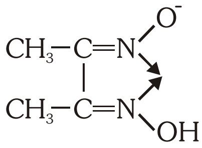
Ethylenediamine (en)



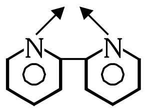
Oxalate (ox)



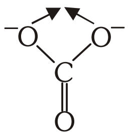
1, 10-Phenanthroline (O-phen)



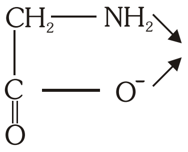
Dimethyl glyoxim ion (DMG)



2, 2'-Dipyridyl (Dipy)



Carbonate

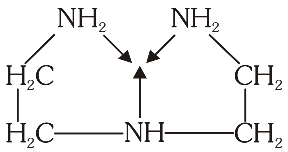


Glycinato (Gly)

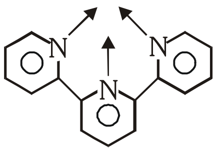
(c) Tridentate ligands

The ligands which donate three pairs of electrons to the central metal are called tridentate ligands

Example.



Diethylene triamine (Dien)

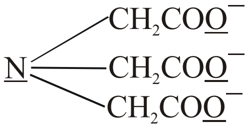


2, 2', 2''-Terpyridine (Terpy)

(d) Tetradentate ligands

Those ligands which can donate four electron pairs to the central metal are known as tetradentate ligands,

Example : (Underline atoms are donating atom)

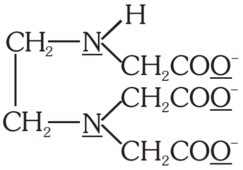


$$\underline{N}(CH_2CO\underline{O}^-)_3$$

Nitrilotriacetato (nta^{3-})

(e) **Pentadentate ligands** : Those ligands which can five electron pairs to the central metal are known as pentadentate ligands.

Example : Ethylenediamine triacetate ion. (Underline atoms are donating atom)

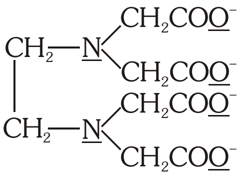


$(EDTA)^{-3}$

Ethylenediaminetriacetate ion

(f) **Hexadentate ligands** : Those ligands which can donate six electron pairs to the central metal are known as hexadentate ligands.

Example : (Underline atoms are donating atom)

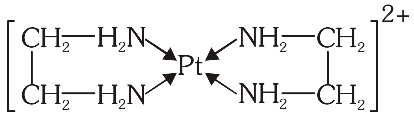


Ethylenediaminetetraacetate ion $(EDTA)^{-4}$

(g) **Chelating ligands**

Polydentate ligands whose structures permit the attachment of two or more donor site to metal ion simultaneously, thus resulting in cyclic structure are called chelating ligands and compound formed is known as **chelate compound**.

Example :



(h) **Ambidentate ligands**

Ligands which can ligate through two different atoms present in it are called ambidentate ligands. At a time only one atom can donate.

$\left[\begin{matrix} CN^- \\ NC^- \end{matrix}\right. \quad \left[\begin{matrix} NO_2^- \\ ONO^- \end{matrix}\right. \quad \left[\begin{matrix} SCN^- \\ NCS^- \end{matrix}\right. \quad \left[\begin{matrix} CNO^- \\ NCO^- \end{matrix}\right. \quad \left[\begin{matrix} S_2O_3^{2-} \\ OSO_2S^{-2} \end{matrix}\right. \quad \left[\begin{matrix} SeCN^- \\ NCSe^- \end{matrix}\right.$

Example :

CN^- can coordinate through either the nitrogen or the carbon atom to central metal ion.

(i) **Flexidentate ligands**

Ligands which sometimes do not use all the donor sites to get coordinated with central metal ion are known as flexidentate ligands.

Ex. SO_4^{2-} , CO_3^{2-} etc.

(C) Based upon bonding interaction between the ligand and the central atom.

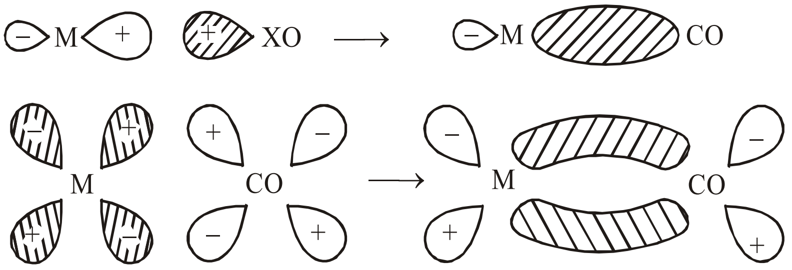
(i) Classical or simple ligand : These ligand only donate the lone pair of electrons to the central atom.

eg. : O^{2-}, OH^-, F^- etc.

(ii) Non classical or π-acid or π-acceptor ligand : These ligand not only donate the lone pair of electrons to central metal but also accept the electron cloud from central atom

eg. : CO, CN^-, NO^+, PF_3, PR_3 etc.

BONDING IN METAL CARBONYL : **Ex.** [Fe(CO)$_5$; [Ni(CO)$_4$] ; [Cr(CO)$_6$]



σ bond

dative π-bond is formed by fullyfilled d orbital on M to empty antibonding molecular orbital on CO

Schematic diagram of orbital overlaps in metal carbonyls.

(a) The metal-carbon bond in metal carbonyls may be represented as the donation of an electron pair from carbon to vacant orbital of metal & form σ bond (M ⟵ CO).

(b) A second bond is formed by back bonding sometimes called dative π-bonding. This is arises from side ways overlap of a full orbital on the metal with the empty antibonding π^*p_y/π^*p_z (if x-axis is molecular axis) molecular orbital of the carbon monooxide, thus forming a π $M \xrightarrow{d\pi-p\pi}$ CO. bond (dπ-pπ back bond).

(c) The filling or partial filling, of the antibonding orbital on CO reduces the bond order of C–O bond from the triple bond in CO towards a double bond. This shown by the increase in C–O bond length from 1.128Å in CO to about 1.15 Å in many carbonyls.

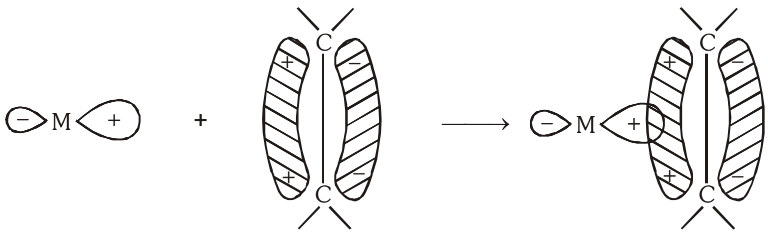
(d) Since CO accept the back donated electrons from the metal atom in to its vacant π* orbital, CO is called π-acid or π-acceptor ligand or π-bonding ligand. Other such π-acid ligands are– CN^-, RCN, $\overset{+}{N}O$.

Note:- π-acid ligands like PF_3, PPh_3 $AsCl_3$ etc. accept the back donated electrons from the metal atom in to its vacant d-orbital of central atom.

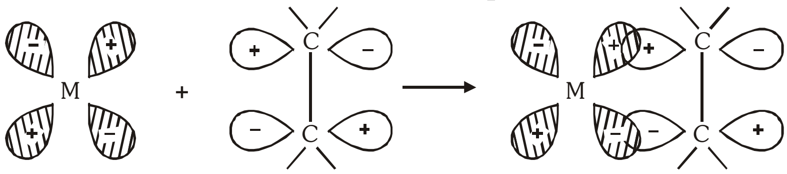
Bonding in π-bonded organo metallic compound. Like zeises salt K [Pt $Cl_3(\pi\text{-}C_2H_4)$]

The bonding of alkenes to a transition metal to form complexes has two components. First, the π-electron density of the alkene overlaps with a σ-type vacant orbital or the metal atom.

Second is the π back bond formed by the flow of electron density from a filled d-orbital on the metal into the vacant π^*-antibonding molecular orbital on the alkene molecule as shown below :



σ-overlap



IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The main rules of naming of complexes are –

(a) Like simple salts, the positive part of the coordination compound is named first.

Ex. $K_4[Fe(CN)_6]$ the naming of this complex starts with potassium.

$[Cr(NH_3)_6]Cl_3$ the naming of this complex starts with name of complex ion.

(b) Naming of coordination sphere :- The names of ligands along with their numerical prefixes (to represent their no) are written first, followed by the name of central metal.

(c) The ligands can be neutral, anionic or cationic.

(i) The neutral ligands are named as the molecule **Ex.** C_5H_5N pyridine, $(C_6H_5)_3P$ Triphenyl phosphine.

$H_2N — CH_2—CH_2—NH_2$ ethylene diamine.

The neutral ligands which are not named as the molecule are CO carbonyl, NO nitrosyl, H_2O Aqua, NH_3 ammine.

(ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chloro/Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo/Peroxido
CN^-	Cyano/Cyanido	O_2H^-	Perhydroxo/Perhydroxido
O^{2-}	Oxo/Oxido	S^{2-}	Sulphido
OH^-	Hydroxo/Hydroxido	NH^{2-}	Imido
H^-	Hydrido/Hydrido	NH_2^-	Amido

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing the ending 'e' with 'o' as follows.

Symbol	Name as ligand	Symbol	Name as ligand
CO_3^{2-}	Carbonato	SO_3^{2-}	Sulphito
$C_2O_4^{2-}$	Oxalato	CH_3COO^-	Acetato
SO_4^{2-}	Sulphato	ONO^-	(bonded through oxygen) nitrito
NO_3^-	Nitrato	NO_2^-	(bonded through nitrogen) nitro
$S_2O_3^{-2}$	Thiosulphato		

(iii) Positive ligands naming ends in 'ium' $NH_2—NH_3^+$ Hydrazinium, NO^+ nitrosonium/nitrosylium.

(d) If ligands are present more than once, then their number is indicated by prefixes like di, tri, tetra etc.

(e) If words like di, tri, tetra are already used in the naming of ligand, or if it is polydented ligand or organic ligand, the prefixes bis–, tris– tetrakis–, pentakis– etc. are used to specify their number.

Example : $[Pt(en)_2Cl_2]Cl_2$: Dichlorobis(ethylenediamine)platinum(IV) chloride.

(f) When more than one type of ligands are present in the complex, then the ligands are named in the alphabetical order.

(g) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is.

If the complex provides anionic complex ion then the name of central metal ion ends with 'ate'

Example : $(NH_4)_2[CuCl_4]$: Ammonium tetrachloridocuprate(II)

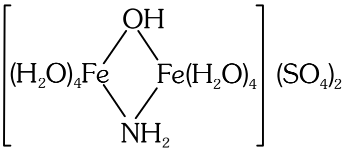
(h) After the naming of central metal ion, anion which is in the outer sphere is to be named.

The naming of some of the complexes is done as follows – (as per IUPAC)

	Complex Compounds	**IUPAC Name**
(i)	$K_4[Fe(CN)_6]$ (anionic complex) so suffix 'ate' is added with metal name	Potassium hexacyanoferrate(II)
(ii)	$K_2[Pt\ Cl_6]$	Potassium hexachloridoplatinate(IV)
(iii)	$[Co\ (NH_3)_6]\ Cl_3$ (Cationic complex) so metal is without any suffix	Hexamminecobalt(III) chloride
(iv)	$[Cr(H_2O)_4Cl_2]\ Cl$	Tetraaquadichloridochromium(III) chloride
(v)	$[Pt(NH_3)_2Cl_4]$	Diamminetetrachloridoplatinum(IV)
(vi)	$[Co(NH_3)_3\ Cl_3]$ (Neutral complex) So no suffix is used with metal ion	Triamminetrichloridocobalt(III)
(vii)	$K_3[Co(NO_2)_6]$	Potassium hexanitrocobaltate(III)
(viii)	$Na_3[Fe(CN)_5\ NO]$	Sodium pentacyanonitrosylferrate(II)
(ix)	$[NiCl_4]^{-2}$	Tetrachloridonickelate(II) ion
(x)	$[Ru(NH_3)_5Cl]^{+2}$	Pentamminechloridoruthenium(III) ion
(xi)	$[Fe(en)_3]Cl_3$	Tris(ethylenediamine)iron(III) chloride
(xii)	$[Ni\ (Gly)_2]$	Bis(glycinato)nickel(II)

(i) If a complex ion has two metal atoms then it is termed polynuclear. The ligand which connects the two metal ions is called as **Bridging ligand or Bridge group**.

A prefix of Greek letter μ, is repeated before the name of each different kind of bridging group.



Tetraaquairon(III)-μ-amido-μ-hydroxotetraaquairon(III) sulphate

FORMATION OF CO-ORDINATION COMPOUNDS

It can be explained by number of theories.

(A) Werner's co-ordination theory

(B) Sidwick theory or Effective Atomic Number Theory (EAN)

(C) Valence bond theory

(D) Crystal field theory

(A) WERNER'S CO-ORDINATION THEORY :

Werner's co-ordination theory was the first attempt to explain the bonding in co-ordination compounds. The main postulates of this theory are :

(a) Metals possesses two types of valencies - Primary valency and secondary valency.

(b) Primary valencies are normally ionisable and are exhibited by a metal in the formation of its simple salts such as $CoCl_3$, $CuSO_4$ and AgCl. In these salts the primary valencies of Co, Cu and Ag are 3, 2, 1 respectively. Primary valencies are referred to as oxidation state of their metal ion.

(c) Secondary valencies are non-ionisable and are exhibited by a metal in the formation of its complex ions such as $[Co(NH_3)_6]^{3+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^+$. In these complex, the secondary valencies of Co^{3+}, Cu^{2+}, Ag^+ are 6, 4 and 2 respectively. These are refered to as co-ordination number (C.N.) of the metal cation.

(d) Primary linkages (valencies) are satisfied by negative ions while secondary valencies are satisfied by neutral molecules, negative ions or in some cases positive ions also.

(e) Every metal atom or ion has a fixed number of secondary valencies. In other words, the co-ordination number of the metal atom is usually fixed.

(f) Every metal has tendency to satisfy both its primary and secondary valencies.

(g) The ligands satisfying secondary valency are always directed towards fixed positions in space about the central metal atom or ion. Thus, the co-ordination compounds have a definite geometry. Werner deduced that in $CoCl_3{\cdot}5NH_3$ only two of the three chlorine atoms are ionic and 5 NH_3 and one Cl form co-ordinate bonds to Co^{3+} ion.

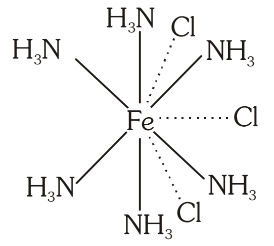
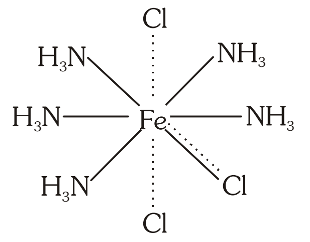
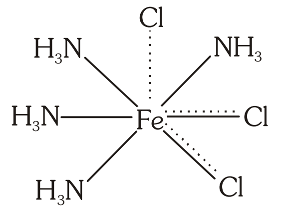
Formula of some cobalt complexes.

Example :

Old	New	No. of Cl^- Ions precipitated	Total No. of ions
(i) $CoCl_3 \cdot 6\,NH_3$	$[Co(NH_3)_6]Cl_3$	3	4
(ii) $CoCl_5 \cdot 5\,NH_3$	$[Co(NH_3)_5Cl]Cl_2$	2	3
(iii) $CoCl_3 \cdot 4\,NH_3$	$[Co(NH_3)_4Cl_2]Cl$	1	2

Complex	Modern formula	No. of Cl^- Ions precipitated	Total number of ions
$PtCl_4 . 6NH_3$	$[Pt(NH_3)_6]Cl_4$	4	5
$PtCl_4 . 5NH_3$	$[Pt(NH_3)_5Cl]Cl_3$	3	4
$PtCl_4 . 4NH_3$	$[Pt(NH_3]_4Cl_2]Cl_2$	2	3
$PtCl_4 . 3NH_3$	$[Pt(NH_3)_3Cl_3]Cl$	1	2
$PtCl_4 2NH_3$	$[Pt(NH_3)_2Cl_4]$	0	0 (non-electrolyte)

❖ WERNER'S REPRESENTATION OF COMPLEXES

(i)	$Fe(NH_3)_6Cl_3$		$[Fe(NH_3)_6]Cl_3$ Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.
(ii)	$Fe(NH_3)_5Cl_3$		$[Fe(NH_3)_5Cl]Cl_2$ In this complex two 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also.
(iii)	$Fe(NH_3)_4Cl_3$		$[Fe(NH_3)_4Cl_2]Cl$ In this complex one 'Cl' group act as primary valency and two of the 'Cl' groups act as secondary valencies also.

(B) SIDWICK THEORY OR EFFECTIVE ATOMIC NUMBER CONCEPT (EAN)

Sidwick proposed effective atomic number theory to explain the stability of the complexes. Total number of electrons on central metal including those tranferred from ligands is known as EAN. The EAN generally coincides with the atomic number of next inert gas except in some cases.

EAN can be calculated by the following relation :

EAN = (atomic number of the metal – oxidation state of central metal with sign) + number of electrons gained from the donor atoms of the ligands.

Example Effective atomic number of the metal atom in the following :

(a) $K_3[Cr(C_2O_4)_3]$ is 33 (b) $K_4[Fe(CN)_6]$ is 36

(C) VALENCE BOND THEORY

The main features of this theory are -

(a) Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond.

(b) During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.

(c) The number of vacant orbitals provided is equal to the coordination number of metal ion.
Example : In the formation of $[Fe(NH_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.
In $[Cu(NH_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

(d) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.

(e) The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.

(f) The number of such overlappings is equal to the coordination number of metal ion.

(g) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and accordingly complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.

(h) In certain complexes pairing of electrons takes place in ligand field, resulting in decrease in spin only magnetic moment, such complexes are known as Low spin complexes

(i) $\text{Bohr magneton} = \dfrac{eh}{4\pi mc}$

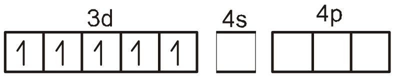
(j) Paramagnetism is represented in the term of spin only magnetic moment.

$\mu = \sqrt{n(n+2)}$ B.M. n = Number of unpaired electron

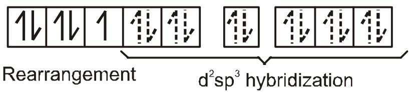
Example $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

Sol. $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridization.

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



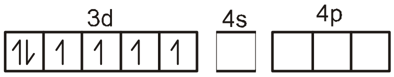
$[Fe(CN)_6]^{3-}$



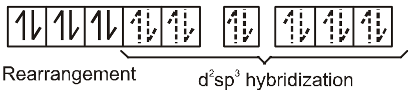
One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[Fe(CN)_6]^{4-}$ also involves d^2sp^3 hybridization but it has Fe^{2+} ion as central ion.

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

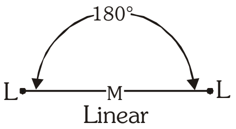
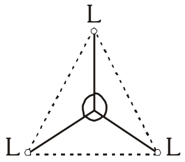
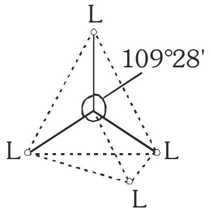
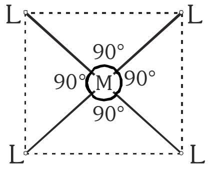
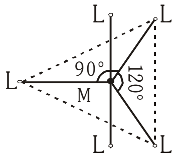
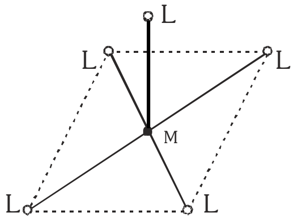
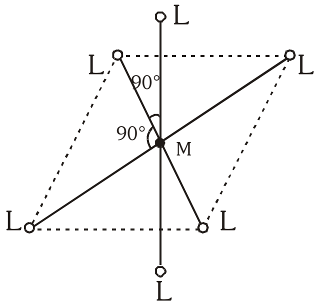


$[Fe(CN)_6]^{4-}$



All electrons are paired, hence it is diamagnetic in nature.

Some Example :

Coordination Number	Hybridised orbitals	Geometrical shape of the Complex	Examples of Complex
2	sp	 Linear	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
3	sp^2		$[HgI_3]^-$
4	sp^3		$[CuCl_4]^{-2}$ $[ZnCl_4]^{-2}$ $[FeCl_4]^-$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{+2}$
4	dsp^2 (d = d_{x2-y2})	 Square planar	$[PdCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{+2}$ $[Cu(NH_3)_4]^{+2}$ $[PtCl_4]^{2-}$
5	sp^3d (d = d_{z2}) or dsp^3 (d = d_{z2})	 Trigonal bipyramidal	$[Fe(CO)_5]$ $[CuCl_5]^{3-}$
5	sp^3d (d = d_{x2-y2}) or dsp^3 (d = d_{x2-y2})	 Square pyramidal	$[Ni(CN)_5]^{-3}$
6	d^2sp^3 (inner orbital complex) or sp^3d^2 (outer orbital complex) in both case d-orbitals are d_{z^2} & $d_{x^2-y^2}$.	 Octahedral	$[Cr(NH_3)_6]^{+3}$ $[Ti(H_2O)_6]^{+3}$ $[Fe(CN)_6]^{-3}$ $[Co(NH_3)_6]^{+3}$ $[PtCl_6]^{-2}$,[CoF]

- **Drawback of valence bond theory :**

(a) It describes bonding in co-ordination compounds only qualitatively but not account for the relative stabilities for different co-ordination complexes.

(b) It does not offer any explanation for optical absorption spectra (coloration) of complexes

(c) It does not describe the detailed magnetic properties of co-ordination compounds.

(D) CRYSTAL FIELD THEORY : The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the Crystal Field Theory.

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of polar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

(a) Crystal field splitting in octahedral coordination entities :

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in d orbitals of metal and the electrons (or negative charges) of the ligands. Such a repulsion is more when the d orbitals of metal are directed towards the ligand than when it is away from the ligand.

Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals (axial orbitals) which point towards the axis along the direction of the ligand will experience more repulsion and will be raised in energy ; and the d_{xy} , d_{yz} and d_{zx} orbitals (non-axial) orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0 (the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by $(3/5)\Delta_0$ and that of the three t_{2g} will decrease by $(2/5)\ \Delta_0$.

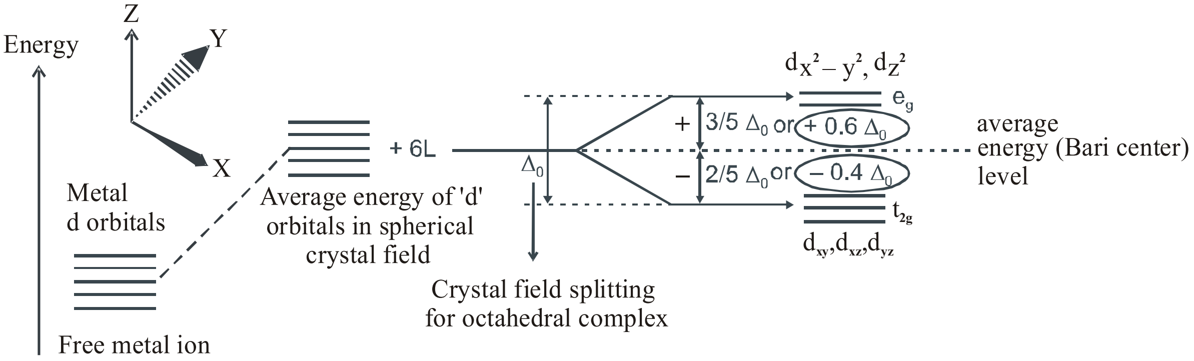


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting, Δ_0, depends upon the fields produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below :

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

Note : In SCN^-, S is donating atom and in NCS^-, N is donating atom.

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. For d^4 configuration, the fourth electron will singly occupy e_g orbital (according to Hund's rule) or will undergo pairing in t_{2g} orbital, which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_0 and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two possibilites are :

(i) If $\Delta_0 < P$, the fourth electron enters in one of the e_g orbitals giving the configuration $t^3_{2g}e_g^1$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.

(ii) If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Crystal Field stabilising energy in Octahedral field :

Formula : CFSE = $[-0.4\, n_{t_{2g}} + 0.6\, n_{e_g}]\, \Delta_0 + xP$.

Where $n_{t_{2g}}$ & n_{e_g} are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

(b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_0$. This may attributes to the following two reasons.

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

Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

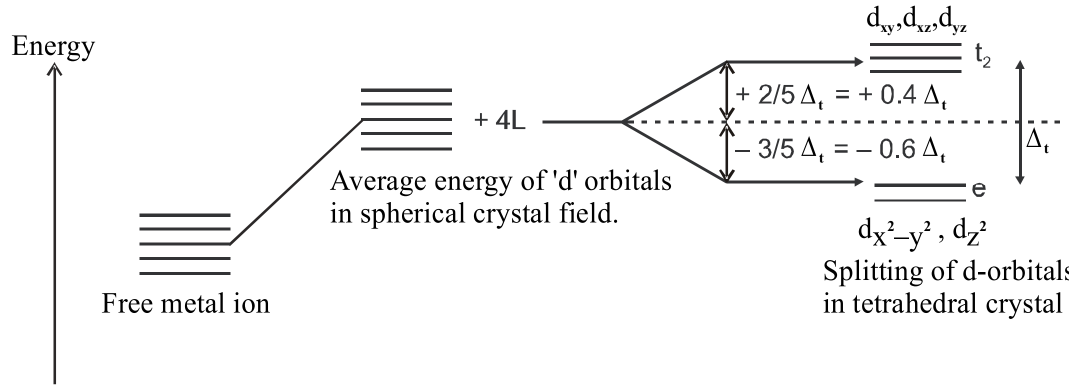


Figure showing crystal field splitting in tetrahedral complex.

Since $\Delta_t < \Delta_o$ crystal field spliting favours the formation of octahedral complexes.

Crystal Field stabilising energy in Tetrahedral field :

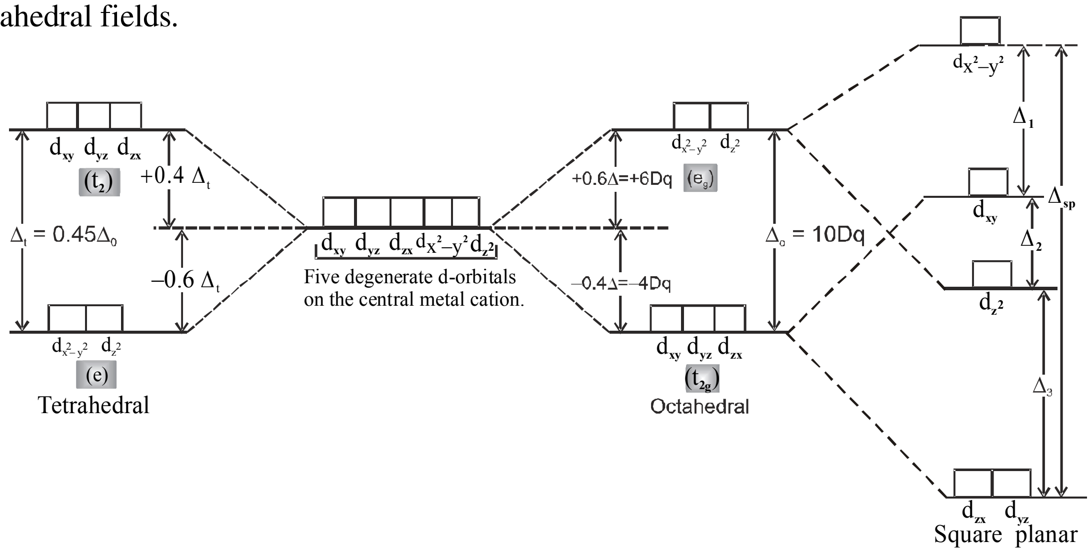
Formula : CFSE = $[-\ 0.6\ n_e + 0.4\ n_{t_2}]\ \Delta_t + xP$.

where n_{t_2} & n_e are number of electron(s) in t_2 & e orbitals respectively and Δ_t crystal field splitting energy for tetrahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

(c) Crystal field splitting in square planar co-ordination entities :

The square planar arrangement of ligands may be considered to be one derived from the octahedral field by removing two trans-ligands located along the Z-axis. In the process, the e_g and t_{2g} sets of orbitals is lifted i.e., these orbitals will no longer be degenerate.

The four ligands in square planar arrangement around the central metal ion are shown in Fig. As the ligands approach through the x and y axis, they would have greatest influence on $d_{x^2-y^2}$ orbital, so the energy of this orbital, will be raised most. The d_{xy} orbital, lying in the same plane, but between the ligands will also have a greater energy though the effect will be less than that on the $d_{x^2-y^2}$ orbitals. On the other hand, due to absence of ligands along Z-axis, the d_{z^2} orbital becomes stable and has energy lower than that of d_{xy} orbital. Similarly d_{yz} and d_{xz} become more stable. The energy level diagram may be represented as shown in figure along with tetrahedral and octahedral fields.



The value of Δ_{sp} has been found larger than Δ_o because of the reason that d_{xz} and d_{yz} orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands. Δ_{sp} has been found equal to $1.3\Delta_o$. Thus.

$$\Delta_{sp} = (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_o \qquad \text{and} \qquad \Delta_{sp} = 1.3\ \Delta_o.$$

(E). STABILITY OF COORDINATION COMPOUNDS :

The stability of a coordination compound [ML_n] is measured in terms of the stability constant (equilibrium constant) given by the expression,

$$\beta_n = [ML_n]/[M(H_2O)_n][L]^n$$

for the overall reaction :

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$$

By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K_1, K_2, K_3, ... K_n for each step as represented below :

$$M(H_2O)_n + L \rightleftharpoons ML(H_2O)_{n-1} + H_2O$$

$$K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$$

$$ML_{n-1} (H_2O) + L \rightleftharpoons ML_n + H_2O$$

$$K_n = [ML_n] / \{[ML_{n-1} (H_2O)] [L]\}$$

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$$

$$\beta_n = K_1 \text{ x } K_2 \text{ x } K_3 \text{ x .... x } K_n$$

β_n, the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing, water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above.

K_1, K_2, K_3 ..... K_n representing the stepwise stability (or formation) constants.

The above is thermodynamic stability criteria, there can be another kind of stability called kinetic stability, which measures the rate of ligand replacement.

(F). FACTORS INFLUENCING THE MAGNITUDE OF C.F.S.E. :

1. **Different charges on the cation of the same metal :** The cation with a higher oxidation state has a larger value of CFSE than that with lower oxidation state e.g.,

$$[Fe(H_2O)_6]^{3+} > [Fe(H_2O)_6]^{2+}$$

2. **Same charges on the cation but the number of d-electrons is different :** The metal cation the magnitude of CFSE with the increase of the number of d-electrons, e.g.,

$$[Co(H_2O)_6]^{2+} < [Ni(H_2O)_6]^{2+}$$

3. **Quantum number (n) of the d-orbitals of the central metal ion :** As 'n' increase CFSE increases.

$$[Co(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+}$$

4. **Types of Hybridisation :**

$$\Delta_t = \frac{4}{9}\Delta_0$$

5. **Presence of cheleting ligand increases CFSE :**

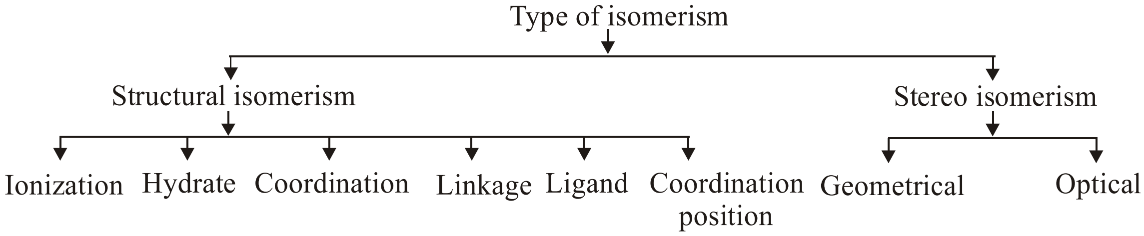
$$[Fe(Ox)_3]^{3-} > [Fe(SCN)_6]^{3-}$$

ISOMERISM IN COMPLEXES

(a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.

(b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

CLASSIFICATION OF ISOMERISM



(A) Structural isomerism

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

(a) **Ionisation isomerism**

The type of isomerism which is due to the exchange of groups or ions between the coordination sphere and the ionisation sphere.

Example. (i) $Co(NH_3)_4Br_2SO_4$ can be represented as

$[Co(NH_3)_4Br_2]SO_4$ (red violet) and $[Co(NH_3)_4SO_4]Br_2$ (red)

These complexes give sulphate ion and bromide ion respectively

(ii) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

(iii) $[Co(NH_3)_4(NO_3)_2]SO_4$ and $[Co(NH_3)_4SO_4](NO_3)_2$

(b) **Hydrate isomerism**

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

Example. $Cr(H_2O)_6Cl_3$ has four possible structures

(i) $[Cr(H_2O)_6]Cl_3$ violet

(ii) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ green

(iii) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ dark green.

(iv) $[Cr(H_2O)_3Cl_3].3H_2O$ dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands. Other hydrate isomers are

$[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H_2O$

(c) **Linkage isomerism**

(i) This type of isomerism arises due to presence of ambidentate ligands like

NO_2^-, CN^- and SCN^-

(ii) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

(iii) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

Example.

- $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$
- In NO_2^- ligand, The coordinating sites are nitrogen (i.e., NO_2^- Nitro ligand) or through oxygen (i.e. ONO Nitrito ligand)
- The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

(d) **Coordination isomerism**

(i) This type of isomerism is exhibited when the complex has two complex ions in it - 'cationic and anionic'.

(ii) This type of isomerism is caused by the interchange of ligands between the two complex ions of the same complex.

Example. $[Co(NH_3)_6]\ [Cr(CN)_6]$ and $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$

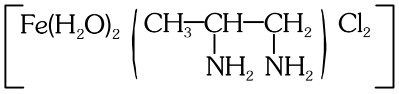
$[\ Cr(NH_3)_6]\ [Co(CN)_6]$ $[Cr(NH_3)_6]\ [Co(C_2O_4)_3]$

(e) **Ligand isomerism**

(i) Ligands with $C_3H_6(NH_2)_2$ have two different structures i.e. 1, 3-diamino propane and 1, 2-diaminopropane(propylene diamine).

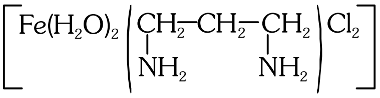
(ii) Those complexes which have same molecular formula, but differ with respect to their ligands are called as **Ligand isomers**.

Example. $[Fe(H_2O)_2\ C_3H_6(NH_2)_2Cl_2]$ has two different structures



$\left[Fe(H_2O)_2\left(CH_3-\underset{NH_2}{\underset{|}{CH}}-\underset{NH_2}{\underset{|}{CH_2}}\right)Cl_2\right]$

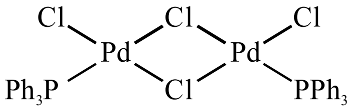
and



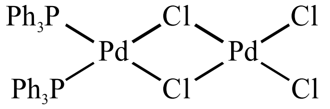
$\left[Fe(H_2O)_2\left(\underset{NH_2}{\underset{|}{CH_2}}-CH_2-\underset{NH_2}{\underset{|}{CH_2}}\right)Cl_2\right]$

(f) **Co-ordination Position Isomerisation :**

It is shown by polynuclear complexs, due interchange of ligands between the different metal nuclei.



Example.



(g) **Polymerization Isomerism :**

This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights.

Example. $[Pt(NH_3)_2Cl_2]$

$[Pt(NH_3)_4]\ [PtCl_4]$

(B) Stereo isomerism

They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion. The two stereo isomers which are possible Geometrical and Optical.

(a) **Geometrical isomerism**

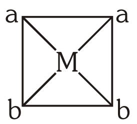
(i) The ligands occupy different positions around the central metal ion.

(ii) When two identical ligands are co-ordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).

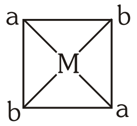
(iii) If the two identical ligands are co-ordinated to the metal ion from opposite side then it is **trans isomer** (in Latin, trans means across).

Geometrical isomers with co-ordination number = 4 (Square planar complexes)

(i) Complexes with general formula, $\mathbf{Ma_2b_2}$ (where both a and b are monodentate) can have cis-and trans isomers.

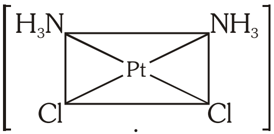


cis-isomer

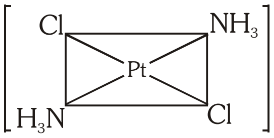


trans-isomer

Example. **$[Pt(NH_3)_2Cl_2]$**

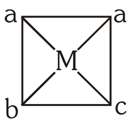


cis
(cis-platin) anti cancer

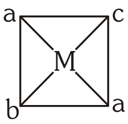


trans

(ii) Complexes with general formula $\mathbf{Ma_2bc}$ can have cis - and trans-isomers.

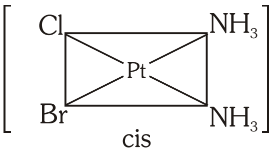


cis

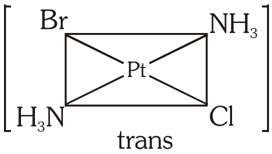


trans

Example. **$[Pt(NH_3)_2ClBr]$**

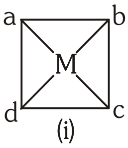


cis

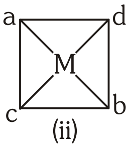


trans

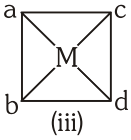
(iii) Complexes with general formula, **Mabcd** can have three isomers.



(i)



(ii)

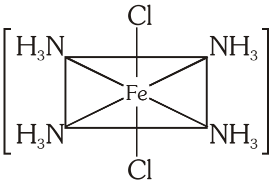


(iii)

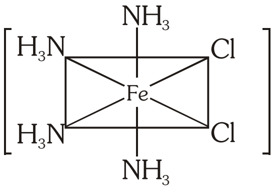
Geometrical isomers with Co-ordination number = 6

(i) Complexes with general formula **Ma_4b_2** can have cis - and trans-isomers.

Example. **$[Fe(NH_3)_4Cl_2]$**

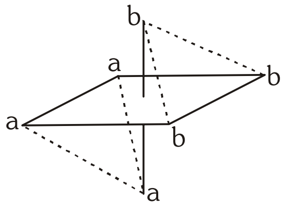


trans

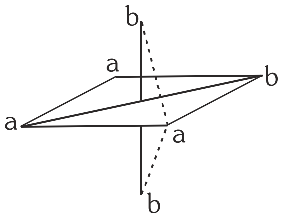


cis

(iii) **Facial and Meridional isomerism (Ma_3b_3)**



Facial (fac)



Meridional (Mer)

Other 6-Coordinated geometrical isomers are

Note :

General formula	**Total No. of geometrical isomers**
Mabcdef	15
Ma_2bcde	9
Ma_2b_2cd	6
$Ma_2b_2c_2$	5
Ma_3bcd	4
Ma_3b_2c	3
Ma_3b_3	2
Ma_4bc	2
Ma_4b_2	2
Ma_5b	Not possible
Ma_6	Not possible

Here M = central atom a, b, c, d, e, f = Monodentate ligands

(b) **Optical isomers**

(i) Optically active complexes are those which are nonsuperimposable over the mirror image structure.

(ii) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.

(iii) The complex which rotates plane polarised light to left hand side is **laevo rotatory i**.e. **'ℓ' or '—'** and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory 'd' or '+'**.

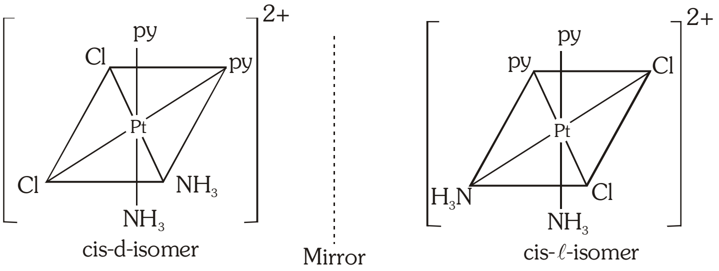
(iv) Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.

(v) The 'd' and 'ℓ' isomers of a compound are called as **Enantiomers or Enantiomorphs**.

(vi) Optical isomerism is expected in tetrahedral complexes of the type Mabcd.

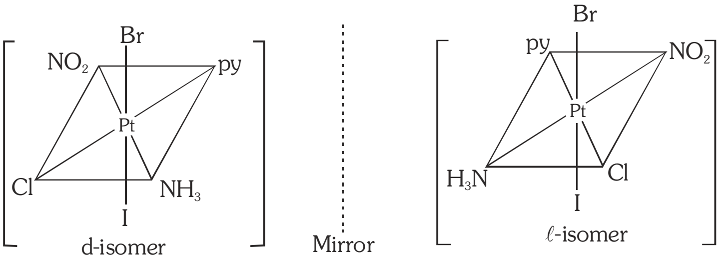
Optical isomers with Co-ordination number = 6

(i) **$[Ma_2b_2c_2]^{n+} \rightarrow [Pt(py)_2(NH_3)_2Cl_2]^{2+}$**



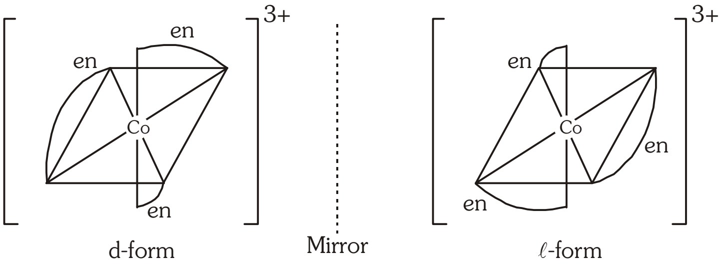
cis-d-isomer Mirror cis-ℓ-isomer

(ii) **$[Mabcedf] \rightarrow [Pt(py)(NH_3)(NO_2)ClBrI]$**



d-isomer Mirror ℓ-isomer

(iii) **$[M(AA)_3]^{n+} \rightarrow [Co(en)_3]^{3+}$**



d-form Mirror ℓ-form

NUMBER OF POSSIBLE ISOMERS FOR SPECIFIC COMPLEXES

Formula	Number of stereoisomers	Pairs of Enantiomers
$M_{a_4b_2}$	2	0
$M_{a_3b_3}$	2	0
M_{a_4bc}	2	0
M_{a_3bcd}	5	1
M_{a_2bcde}	15	6
M_{abcdef}	30	15
$M_{a_2b_2c_2}$	6	1
$M_{a_2b_2cd}$	8	2
$M_{a_3b_2c}$	3	0
M(AA)(BC)de	10	5
M(AB)(AB)cd	11	5
M(AB)(CD)ef	20	10
$M(AB)_3$	4	2

Note : Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.

EXERCISE : O-1

SINGLE OPTION CORRECT :

Double salt and complex compound

1. Some salts although containing two different metallic elements give test for one of them in solution. Such salts are

(A) complex salt (B) double salt

(C) normal salt (D) none of these

CC0001

2. Aqueous solution of $FeSO_4$ gives tests for both Fe^{2+} and SO_4^{2-} but after addition of excess of KCN, solution ceases to give test for Fe^{2+}. This is due to the formation of

(A) the double salt $FeSO_4.2KCN.6H_2O$

(B) $Fe(CN)_3$

(C) the complex ion $[Fe(CN)_6]^{4-}$

(D) the complex ion $[Fe(CN)_6]^{3-}$

CC0002

Werner theory

3. Consider the following statements:

According the Werner's theory.

(a) Ligands are connected to the metal ions by covalent bonds.

(b) Secondary valencies have directional properties

(c) Secondary valencies are non-ionisable

Of these statements:

(A) a, b and c are correct (B) b and c are correct

(C) a and c are correct (D) a and b are correct

CC0003

4. A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is:

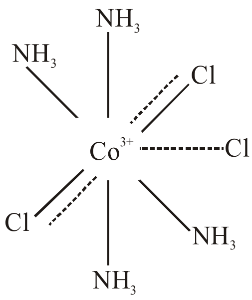
(A) $[Pt(NH_3)_4]Cl_4$ (B) $[Pt(NH_3)_2Cl_4]$

(C) $[Pt(NH_3)_5Cl]Cl_3$ (D) $[Pt(NH_3)_4Cl_2]Cl_2$

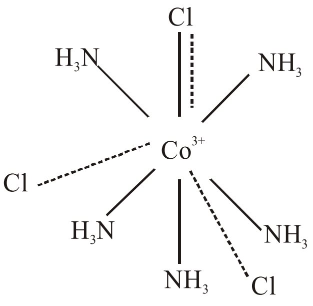
CC0004

5. Which of the following Werner's complex has least electrical conductivity ?

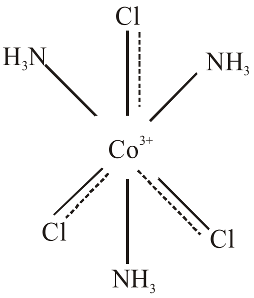
(A)



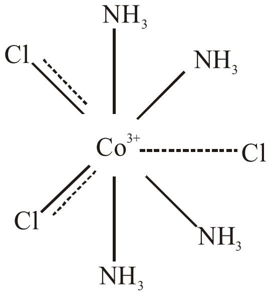
(B)



(C)



(D)



CC0005

Classification of ligand

6. How many $EDTA^{-4}$ molecules are required to make an octahedral complex with a Ca^{2+} ion ?

(A) Six (B) Three (C) One (D) Two

CC0006

7. π-bonding is not involved in :

(A) ferrocene (B) dibenzene chromium (C) Zeise's salt (D) Grignard reagent

CC0007

8. Which of the following is not considered as an organometallic compound ?

(A) Ferrocene (B) Cis-platin (C) Ziese's salt (D) Grignard reagent

CC0008

9. Diethylene triamine is:

(A) Chelating agent (B) Polydentate ligand

(C) Tridentate ligand (D) All of these

CC0009

10. Which of the following species is not expected to be a ligand

(A) NO^+ (B) NH_4^+ (C) $NH_2-NH_3^+$ (D) CO

CC0010

11. The disodium salt of ethylene diamine tetraacetic acid can be used to estimate the following ion(s) in the aqueous solution

(A) Mg^{2+} ion (B) Ca^{2+} ion (C) Na^+ ion (D) both Mg^{2+} and Ca^{2+}

CC0011

12. Which of the following ligand does not act as bidentate ligand

(A) dipy (B) dien (C) gly^- (D) dmg^-

CC0012

Synergic bonding

13. Which of the following order is correct for the IR vibrational frequency of CO.

(A) $[Fe(CO)_4]^{2-} < [Co(CO)_4]^- < [Ni(CO)_4]$ (B) $[Fe(CO)_4]^{2-} > [Co(CO)_4]^- > [Ni(CO)_4]$

(C) $[Fe(CO)_4]^{2-} > [Co(CO)_4]^- < [Ni(CO)_4]$ (D) $[Fe(CO)_4]^{2-} < [Co(CO)_4]^- > [Ni(CO)_4]$

CC0013

14. In the isoelectronic series of metal carbonyl, the C–O bond strength is expected to increase in the order.

(A) $[Mn(CO)_6]^+ < [Cr(CO)_6] < [V(CO)_6]^-$ (B) $[V(CO)_6]^- < [Cr(CO)_6] < [Mn(CO)_6]^+$

(C) $[V(CO)_6]^- < [Mn(CO)_6]^+ < [Cr(CO)_6]$ (D) $[Cr(CO)_6] < [Mn(CO)_6]^+ < [V(CO)_6]^-$

CC0014

15. Which of the following has higher stretching frequency for C–O bond -

(A) $[Ni(CO)_3PF_3]$ (B) $[Ni(CO)_3(PMe_3)]$

(C) both have equal stretching frequency (D) None of these

CC0015

16. Which of the following has higher multiple bond character in M–C bond -

(A) $[Ni(CO)_4]$

(B) $[Co(CO)_4]^-$

(C) $[Fe(CO)_4]^{2-}$

(D) (B) and (C) both have equal multiple bond character in M–C bond

CC0016

17. The V–C distance in $V(CO)_6$ and $[V(CO)_6]^-$ are respectively (in pm)-

(A) 200, 200 (B) 193, 200 (C) 200, 193 (D) 193, 193

CC0017

Co-ordination number and E.A.N.

18. Among the following complexes which can act as oxidising agent.

(A) $[Mn(CO)_6]$ (B) $[Mn(CO)_6]^+$ (C) $[Mn(CO)_5]^-$ (D) $[V(CO)_6]$

CC0018

19. Which of the following statement is correct regarding the compound " $[(CO)_3Fe(CO)_3Fe(CO)_3]$".

(A) The d_{C-O} (bridging) is greater than d_{C-O} (terminal)

(B) The bond order of bridging C – O bond is greater than that of terminal C – O bond

(C) The E.A.N. value of each Fe-atom is 35

(D) The oxidation state of Fe in this complex is (–I)

CC0019

20. How many π electrons are donated by $C_5H_5^-$ ligand -

(A) 2 (B) 4 (C) 5 (D) 6

CC0020

21. Effective atomic number of $Co(CO)_4$ is 35, hence it is less stable. It attains stability by

(A) Oxidation of Co (B) Reduction of Co

(C) Dimerization (D) Both (B) & (C)

CC0021

22. In the complex $Fe(CO)_x$, the value of x is:

(A) 3 (B) 4 (C) 5 (D) 6

CC0022

23. The EAN of platinum in potassium hexachloroplatinate (IV) is:

(A) 46 (B) 86 (C) 36 (D) 84

CC0023

24. The EAN of metal atoms in $Fe(CO)_2(NO)_2$ and $Co_2(CO)_8$ respectively are

(A) 34, 35 (B) 34, 36 (C) 36, 36 (D) 36, 35

CC0024

Naming of complex compound

25. The IUPAC name for the coordination compound $Ba[BrF_4]_2$ is

(A) Barium tetrafluorobromate (V) (B) Barium tetrafluorobromate (III)

(C) Barium bis (tetrafluorobromate) (III) (D) none of these

CC0025

26. The number of ions formed, when bis (ethane-1,2-diamine) copper (II) sulphate is dissolved in water will be

(A) 1 (B) 2 (C) 3 (D) 4

CC0026

27. The IUPAC name of the Wilkinson's catalyst $[Rh\,Cl\,(P\,Ph_3)_3]$ is

(A) Chloridotris(triphenylphosphine)rhodium(I)

(B) Chloridotris(triphenylphosphine)rhodium(IV)

(C) Chloridotris(triphenylphosphine)rhodium(0)

(D) Chloridotris(triphenylphosphine)rhodium(VI)

CC0027

28. The formula for the compound tris (ethane-1, 2-diamine)cobalt (III) sulphate is

(A) $[Co(en)_3]SO_4$ (B) $[Co(SO)_4(en)_3]$

(C) $[Co(en)_3](SO_4)_2$ (D) $[Co(en)_3]_2(SO_4)_3$

CC0028

Structural isomerism

29. Which of the following statement is **INCORRECT** regarding the following compound

$[Pt(NH_3)_4]\ [PtCl_4]$

(A) It is the polymerisation isomer of $[Pt(NH_3)_3Cl_3]$

(B) E.A.N. of cationic part is equal to that of anionic part

(C) It is the co-ordination isomer of $[Pt(NH_3)_3Cl]\ [Pt(NH_3)Cl_3]$

(D) Synergic bonding is not involved in the complex

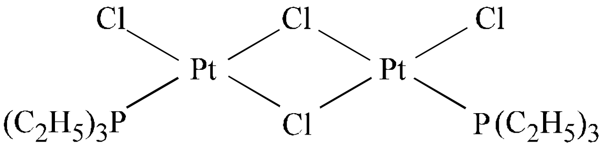
CC0029

30. The type of isomerism present in pentaamminenitrochromium (III) chloride is :

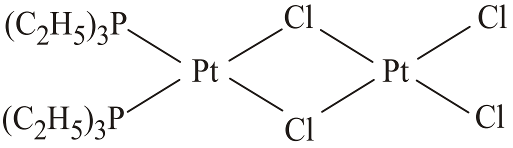
(A) optical (B) linkage (C) hydrate (D) polymerisation

CC0030

31. The complexes given below show:



and



(A) Optical isomerism (B) Co-ordination isomerism

(C) Geometrical isomerism (D) Co-ordination position isomerism

CC0031

32. Which of the following complex shows ionization isomerism

(A) $[Cr(NH_3)_6]Cl_3$ (B) $[Cr(en)_2]Cl_2$

(C) $[Cr(en)_3]Cl_3$ (D) $[CoBr(NH_3)_5]SO_4$

CC0032

33. Find the name of the hydrate isomer of $CrCl_3.6H_2O$, which is having lowest electrical conductivity excluding zero value of conductivity.

(A) Hexaaquachromium(III) chloride

(B) Tetraaquadichloridochromium(III) chloride dihydrate

(C) Pentaaquachloridochromium(III) chloride monohydrate

(D) Triaquatrichloridochromium(III) chloride trihydrate

CC0033

Stereoisomerism

34. Which of the following complex shows optical isomerism -

(A) $[Cd(CN)_4]^{2-}$ (B) $[Cr(H_2O)_3Cl_3].3H_2O$

(C) $[Zn(gly)_2]^o$ (D) $[Ni(dmg)_2]^o$

CC0034

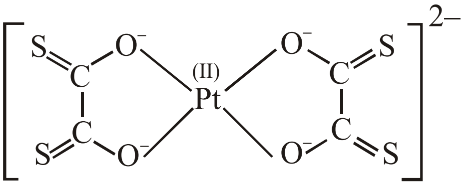
35. How many coordination isomers of $[Pt(NH_3)_4][PtCl_4]$ show geometrical isomerism.

(A) All (B) One (C) Two (D) None

CC0035

36. Identify the pair of complex which are stereoisomer of each other -

(A)



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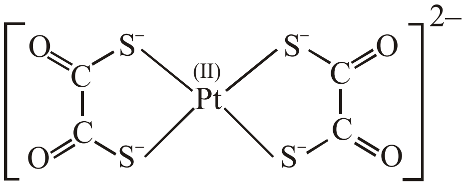
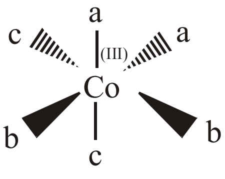


(B)



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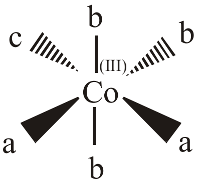
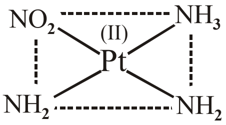


(C)



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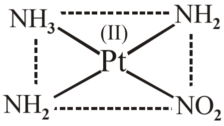


(D) All of the above

CC0036

37. Find complex which have maximum number of stereoisomers -

(A) $[Ma_3b_3]$ (B) $[Ma_3b_2c]$ (C) $[Ma_2b_2c_2]$ (D) $[M(AA)a_2b_2]$

CC0037

38. In which of the following pairs both the complexes show optical isomerism ?

(A) cis-$[Cr(C_2O_4)_2Cl_2]^{3-}$, trans-$[Co(NH_3)_4Cl_2]$

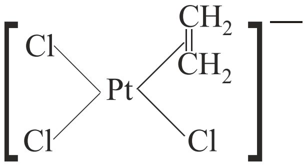
(B) $[Co(en)_3]Cl_3$, cis-$[Co(en)_2Cl_2]Cl$

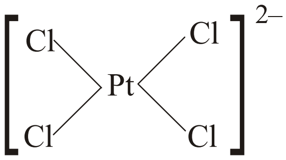
(C) $[PtCl\,(dien)]Cl$, $[NiCl_2Br_2]^{2-}$

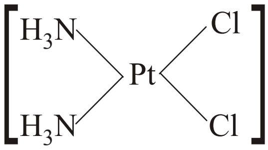
(D) $[Co(NO_3)_3\,(NH_3)_3]$, cis-$[Pt(en)_2Cl_2]$

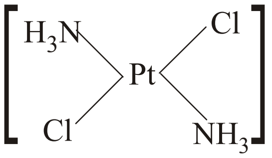
CC0038

39. Which of the following is considered to be an anticancer species ?

(A) 

(B) 

(C) 

(D) 

CC0039

40. Which of the following can exhibit geometrical isomerism ?

(A) $[MnBr_4]^{2-}$

(B) $[Pt(NH_3)_3Cl]^+$

(C) $[PtCl_2(P(C_2H_5)_3)_2]$

(D) $[Fe(H_2O)_5NOS]^{2+}$

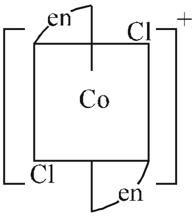
CC0040

41. The oxidation state of Mo in its oxo-complex species $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$ is:

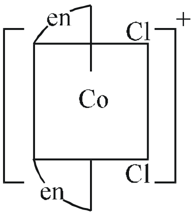
(A) +2 (B) +3 (C) +4 (D) +5

CC0041

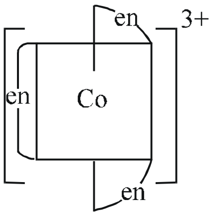
42. Which of the following ions are optically active?



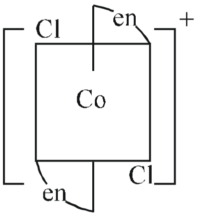
(I)



(II)



(III)

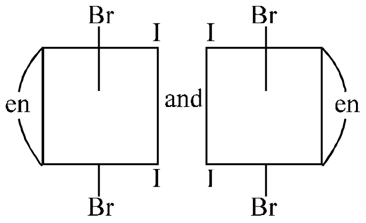


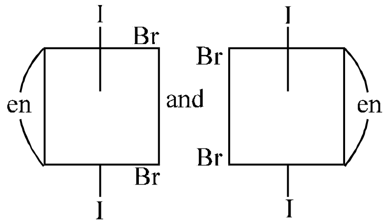
(IV)

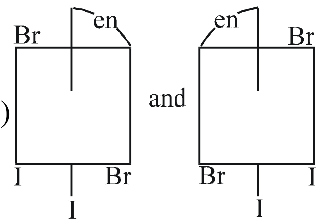
(A) I only (B) II only (C) II and III (D) IV only

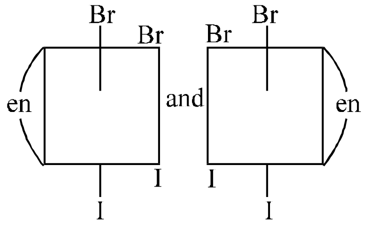
CC0042

43. The complex ion has two optical isomers. Their **CORRECT** configurations are:

(A) 

(B) 

(C) 

(D) 

CC0043

V.B.T/CFT

44. Which of the following complex is coloured and diamagnetic -

(A) MnO_4^{2-} (B) $[Ni(H_2O)_6]^{2+}$ (C) $[CrCl_6]^{3-}$ (D) CrO_4^{2-}

CC0044

45. What is the hybridisation of Fe in $[Fe(CO)_4]^{-2}$

(A) d^2sp^3 (B) sp^3d^2 (C) sp^3d (D) sp^3

CC0045

46. One unknown complex has the spin only magnetic moment is of 1.73 BM. As per the C. F. T., complexe is.

(A) d^7, Oh-field, with Srong Feild Legand (B) d^9, sq.planar-field, with Srong Feild Legand

(C) d^9, Td,field with Weak Feild Legand (D) All of these

CC0046

47. Identify tetrahedral species which has maximum magnetic moment value :

(A) $[CuCl_4]^{2-}$ (B) $[CoCl_4]^{2-}$ (C) $[FeCl_4]^{2-}$ (D) $[AlCl_4]^-$

CC0047

48. In the co-ordination compound $Na_4[Fe(CN)_5NOS]$ oxidation state of Fe is -

(A) +1 (B) +2 (C) +3 (D) +4

CC0048

49. Which one of the following complex is an outer orbital complex -

(A) $[Ni(H_2O)_6]^{+2}$ (B) $[Fe(H_2O)_5NO]SO_4$

(C) $[Fe(NH_3)_6]^{+2}$ (D) All of these

CC0049

50. Which of the following is diamagnetic and sp^3 hybridised -

(A) $[NiCl_4]^{2-}$ (B) $[Ni(CN)_4]^{4-}$ (C) $[Ni(CN)_4]^{2-}$ (D) $[NiCl_2(PPh_3)_2]$

CC0050

51. $[Cr(H_2O)_6]Cl_3$ (atomic number of Cr = 24) has a magnetic moment of 3.83 B.M. The **CORRECT** distribution of 3d electrons in the chromium present in the complex is:

(A) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}$ (B) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{z^2}$

(C) $3d^1_{(x^2-y^2)}, 3d^1_{z^2}, 3d^1_{xz}$ (D) $3d^1_{xy}, 3d^1_{(x^2-y^2)}, 3d^1_{yz}$

CC0051

52. $[Fe(H_2O)_6]^{+2}$ has Crystal Field Splitting Energy value 10,400 cm^{-1} and pairing energy value 17,600 cm^{-1} then it is :

(A) Low spin complex (B) Paramagnetic in nature

(C) Diamagnetic in nature (D) None of these

CC0052

53. In which of the following coordination entities, the magnitude of Δ_0 [CFSE in octahedral field] will be maximum? :

(A) $[Co(CN)_6]^{3-}$
(B) $[Co(C_2O_4)_3]^{3-}$
(C) $[Co(H_2O)_6]^{3+}$
(D) $[Co(NH_3)_6]^{3+}$

CC0053

54. The number of unpaired electrons calculated in $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ are :

(A) 4 and 4
(B) 0 and 2
(C) 2 and 4
(D) 0 and 4

CC0054

55. An ion M^{2+}, forms the complexes $[M(H_2O)_6]^{2+}$, $[M(en)_3]^{2+}$ and $[MBr_6]^{4-}$, match the complex with the appropriate colour.

(A) Green, blue and red
(B) Blue, red and green
(C) Green, red and blue
(D) Red, blue and green

CC0055

56. Formula of ferrocene is:

(A) $[Fe(CN)_6]^{4-}$
(B) $[Fe(CN)_6]^{3+}$
(C) $[Fe(CO)_5]$
(D) $[Fe(C_5H_5)_2]$

CC0056

57. $Ni(CO)_4$ and $[Ni(NH_3)_4]^{2+}$ do not differ in

(A) magnetic moment
(B) oxidation number of Ni
(C) geometry
(D) EAN

CC0057

58. A complex of certain metal has the magnetic moment of 4.91 BM whereas another complex of the same metal with same oxidation state has zero magnetic moment. The metal ion could be

(A) Co^{2+}
(B) Mn^{2+}
(C) Fe^{2+}
(D) Fe^{3+}

CC0058

59. The tetrahedral $[CoI_4]^{2-}$ and square planar $[PdBr_4]^{2-}$ complex ions are respectively

(A) low spin, high spin
(B) high spin, low spin
(C) both low spin
(D) both high spin

CC0059

60. Which one of the following species does not represent cationic species of vanadium formed in aqueous solution

(A) VO_2^{+}
(B) VO^{2+}
(C) $[V(H_2O)_6]^{3+}$
(D) VO_2^{2+}

CC0060

61. On treatment of $[Ni(NH_3)_4]^{2+}$ with concentrated HCl, two compounds I and II having the same formula, $[NiCl_2(NH_3)_2]$ are obtained, I can be converted into II by boiling with dilute HCl. A solution of I reacts with oxalic acid to form $[Ni(C_2O_4)(NH_3)_2]$ wheras II does not react. Point out the correct statement of the following

(A) I cis, II trans; both tetrahedral (B) I cis, II trans; both square planar
(C) I trans, II cis; both tetrahedral (D) I trans, II cis; both square planar

CC0061

62. Among the following, the compound that is both paramagnetic and coloured is

(A) $K_2Cr_2O_7$ (B) $(NH_4)_2[TiCl_6]$ (C) $VOSO_4$ (D) $K_3[Cu(CN)_4]$

CC0062

63. The magnetic moment of $[NiX_4]^{2-}$ ion is found to be zero. Then the metal of the complex ion is (X = monodentate anionic ligand).

(A) sp^3 hybridised (B) spd^2 hybridised (C) dsp^2 hybridised (D) d^2sp hybridised

CC0063

64. For which of the following types of d^n configuration, the number of unpaired electrons in octahedral complexes remains same irrespective of the ligand field strength.

(A) d^3 (B) d^4 (C) d^5 (D) d^6

CC0064

65. Which of the follwoing electronic arrangement gives the highest value of the magnetic moment?

(A) d^6, strong field (B) d^7, high spin (C) d^4, weak field (D) d^2, strong field

CC0065

66. Select appropriate ligand for given complex

$[\overset{III}{Co}(.....)_6]^{\pm x}$; $\mu = 0$ BM

(A) $C_2O_4^{2-}$ (B) en (C) H_2O (D) F^-

CC0066

67. According to C.F.T. , ligands are treated as -

(A) Point charges (B) Lewis acids (C) Proton donor (D) All of the above

CC0067

68. Which of the following is correct electronic configuration of 3d orbital in excited state of central metal ion, when $[Ti(H_2O)_6]^{3+}$ absorbed yellow-green light.

(A) 3d $\boxed{}\boxed{}\boxed{}\boxed{1}\boxed{}$ (B) t_{2g}^1, e_g^0
(C) t_{2g}^1, e_g^1 (D) t_{2g}^0, e_g^1

CC0068

69. If $\lambda_{absorbed}$ for d-d transition is in order $[Ti(X)_6]^{3+} > [Ti(Y)_6]^{3+} > [Ti(Z)_6]^{3+}$.
Select correct order of strength of ligands (X, Y, Z are monodentate ligand)-

(A) Z > Y > X (B) X > Y > Z
(C) Z > X > Y (D) Not predictable

CC0069

EXERCISE : O-2

MORE THAN ONE MAY BE CORRECT

1. Which of the following exhibit geometrical isomerism (M stands for a metal, and a and b are achiral ligands)?

(A) Ma_2b_2 (Sq. Pl.) (B) Ma_4b_2 (C) Ma_5b (D) Ma_6

CC0070

2. Which of the following statement(s) is (are) **CORRECT** ?

(A) The oxidation state of iron in sodium nitroprusside $Na_2[Fe(CN)_5(NO)]$ is +II.

(B) $[Ag(CN)_2]^-$ is linear in shape.

(C) In $[Fe(H_2O)_6]^{3+}$, Fe is d^2sp^3 hybridized.

(D) In $Ni(CO)_4$, the oxidation state of Ni is zero.

CC0071

3. Which of the following compound(s) show(s) optical isomerism.

(A) $[Pt(bn)_2]^{2+}$ (B) $[CrCl_2(en)_2]^+$ (C) $[Co(en)_3]\,[CoF_6]$ (D) $[Zn(gly)_2]$

CC0072

4. Select **INCORRECT** statement(s) for $[Cu(CN)_4]^{3-}$, $[Cd(CN)_4]^{2-}$ and $[Cu(NH_3)_4]^{2+}$ complex ion.

(A) Both $[Cd(CN)_4]^{2-}$ and $[Cu(NH_3)_4]^{2+}$ have square planar geometry

(B) $[Cu(CN)_4]^{3-}$ and $[Cu(NH_3)_4]^{2+}$ have equal no. of unpaired electron

(C) $[Cu(CN)_4]^{3-}$ and $[Cd(CN)_4]^{2-}$ can be separated from the mixture on passing H_2S gas.

(D) All the three complexes have magnetic moment equal to zero.

CC0073

5. Which of the following will have two stereoisomeric forms?

(A) $[Cr(NO_3)_3(NH_3)_3]$ (B) $K_3[Fe(C_2O_4)_3]$

(C) $[CoCl_2(en)_2]^+$ (D) $[CoBrCl(Ox)_2]^{3-}$

CC0074

6. Which is / are **NOT** correctly matched.

	Complex compounds	**IUPAC name**
(A)	$K[CrF_4O]$	Potassium tetrafluoridooxidochromate(V)
(B)	$Na[BH(OCH_3)_3]$	Sodium hydridotrimethoxyborate(III)
(C)	$[Be(CH_3–CO–CH_2–CO–C_6H_5)_2]^\circ$	Bis(benzoylacetonato)beryllium(III)
(D)	$H[AuCl_4]$	Hydrogen tetrachloroaurate(III)

CC0075

7. Which of the following statement(s) is/are **INCORRECT**

(A) In $[CoBrCl(en)_2]^+$ geometrical isomerism exists, while optical isomerism does not exist

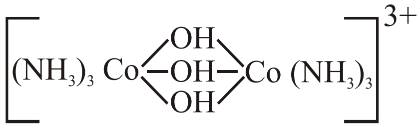
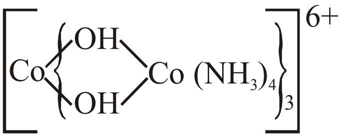
(B) Potassium aquadicyanidosuperoxidoperoxidochromate(III) is IUPAC name for $K_2[Cr(CN)_2O_2(O_2)(H_2O)]$

(C) There are 3 geometrical isomers and 15 stereoisomers possible for $[Pt(NO_2)(NH_3)(NH_2OH)(py)]^+$ and $[PtBr\,Cl\,I\,(NO_2)(NH_3)(py)]$ respectively

(D) cis and trans forms are not diastereomers of each other

CC0076

8. Which of the following complexes are polymerisation isomers :

(A)  and 

(B) $[Pt(NH_3)_4]\,[PtCl_4]$ and $[Pt(NH_3)_4]\,[Pt(NH_3)Cl_3]_2$

(C) $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_3Cl]_2\,[PtCl_4]$

(D) $[Pt(NH_3)_2Cl_4]$ and $[Pt(NH_3)_2Cl_2]$

CC0077

9. Which of the following is **CORRECT** about

Tetraamminedithiocyanato-Scobalt(III) tris(oxalato)cobaltate(III)

(A) formula of the complex is $[Co(SCN)_2(NH_3)_4][Co(ox)_3]$

(B) It is a chelating complex and show linkage isomerism.

(C) It shows optical isomerism.

(D) It shows geometrical isomerism.

CC0078

10. Which is **CORRECT** statement(s)?

(A) $[Ag(NH_3)_2]^+$ is linear with sp hybridised Ag^+ ion

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

(C) $[Cu(NH_3)_4]^{2+}$, $[Pt(NH_3)_4]^{2+}$ & $[Ni(CN)_4]^{2-}$ have dsp^2 hybridisation of the metal ion

(D) $Fe(CO)_5$ has trigonal bipyramidal structure with $d_{z^2}sp^3$ hybridised iron.

CC0079

11. In which of the following complex(s) spin only magnetic moment is independent , from the nature of ligand. (L = monodented ligand) -

(A) $[\overset{II}{Ni}L_4]$ (B) $[\overset{II}{Ni}L_6]$ (C) $[\overset{III}{Fe}L_6]$ (D) $[\overset{III}{Cr}L_6]$

CC0080

12. Which of the following compound(s) can show optical isomerism ?

(A) $[PtCl_4]^{2-}$ (B) $[PtCl_2(NH_3)_2]$ (C) $[Fe(EDTA)]^-$ (D) $[Fe(en)_3]^{3+}$

CC0081

13. Which of the following compounds are resolvable into d or ℓ-forms?

(A) $[ZnCl_2(en)]$ (B) $[Be(acac)_2]$ (C) $[Co(gly)_3]$ (D) $[Cr(C_2O_4)_3]^{3-}$

CC0082

14. Which of the following ion is/are diamagnetic and non planar ?

(A) $[Ni(CN)_4]^{2-}$ (B) MnO_4^- (C) $[Cu(NH_3)_4]^{2+}$ (D) CrO_4^{2-}

CC0083

EXERCISE : S-1

INTEGER TYPE

1. Find number of ligands which is / are stronger ligand as compared to NH_3

NO_2^-, H_2O, NO_3^-, F^-, $C_2O_4^{2-}$, en, Cl^-, $\overline{C}N$

CC0084

2. If crystal field stablization energy of $[ML_6]^{+n}$ is $-0.8\ \Delta_O$.
Find minimum number of electrons in t_{2g} orbitals of metal ion ?

CC0085

3. Find number of Co–N linkage in,

CC0086

Pentaamminecobalt(III)–μ–amidodiamminetriaquacobalt(III) chloride.

4. Find the EAN value of central atom of $[Fe(\pi-C_4H_4)(CO)_3]$

CC0087

5. Find the maximum number of atoms lying in one plane for $[Cr(CN)_6]^{3-}$

CC0088

6. Select complex in which metal–carbon linkage(s) is / are present :

$\left[\overset{III}{Fe}(EDTA)\right]^-$, $K[PtCl_3(\pi-C_2H_4)]$, $[Cr(acac)_3]^\circ$, $[Fe(CO)_5]$, $[Co(C_2H_5O)_6]^{3-}$, $[Ni(dmg)_2]$

CC0089

7. Find out the total number of geometrical isomers of $[Co(H_2O)_3Cl_3]$.

CC0090

8. Find the value of E.A.N of $[Pd(CO)_4]^{+2}$ (atomic number = 46) :

CC0091

9. A co-ordination compound have magnetic moment 5.92 B.M. Find out the number of unpaired electron(s) in the compound.

CC0092

10. Find the number of optically active isomers for $[Pd(en)_2(NH_3)(H_2O)]^{4+}$ cation.

CC0093

EXERCISE : S-2

MATCH THE COLUMN :

1. Match the complexes in column-I with the EAN of central atom in column-II:

	Column-I		**Column-II**
(A)	$[Fe(CO)_4]^{2-}$	(P)	34
(B)	$[Co(NH_3)_5Cl]Cl_2$	(Q)	35
(C)	$K_2[Ni(CN)_4]$	(R)	36
(D)	$[Cu(NH_3)_4]^{2+}$	(S)	37

CC0094

2.

	Column - I		**Column -II**
(A)	$Na_2\ [Fe(CN)_5\ NO]$	(P)	$\mu = 0$ B.M.
(B)	$[Fe(H_2O)_5\ NO]\ SO_4$	(Q)	octahedral
(C)	$[Ag(CN)_2]^-$	(R)	$\mu = \sqrt{15}$ B.M.
(D)	$K_4[Fe(CN)_6]$	(S)	NO^+ ligand

CC0095

3. Match the complexes in column I with their stereoproperties is column II

	Column I		**Column II**
(A)	$[CoCl_3(NH_3)_3]$	(P)	Has a facial isomer
(B)	$[Cr\ (ox)_3]^{3-}$	(Q)	Cis form is optically active
(C)	$[CrCl_2(ox)_2]$	(R)	Trans form is optically inactive
(D)	$[RhCl_3(Py)_3]$	(S)	Has a meridional form
		(T)	Two optically active isomer

CC0096

4. Match each coordination compound in List-I with co-ordination number of central metal/ion from List-II and select the correct answer using the code given below the lists.

	List-I		**List-II**
(P)	$[Co(en)_3]^{3+}$	(1)	6
(Q)	$[Ca(EDTA)]^{2-}$	(2)	4
(R)	$[Ni(CO)_4]$	(3)	2
(S)	$[Ag(NH_3)_2]Cl$	(4)	5

Code :

	P	**Q**	**R**	**S**
(A)	2	1	2	3
(B)	1	1	2	3
(C)	1	4	2	3
(D)	1	1	3	2

CC0097

5. Match the List-I with List-II :

List-I	List-II
(P) Ferrocene	(1) Iron present
(Q) $Mn_2(CO)_{10}$	(2) Cobalt
(R) Vitamine B_{12}	(3) Metal-Metal bonding
(S) Haemoglobin	(4) Sandwich structure

Code :

	P	Q	R	S
(A)	4	3	1	2
(B)	1	3	1	2
(C)	1,4	3	2	1
(D)	1	3	4	2

CC0098

6. Match the List-I with List-II :

List-I	List-II
(P) $EDTA^{4-}$	(1) N-donor atom
(Q) en	(2) Chelate ligand with same donor site
(R) gly^{-}	(3) Bidentate with different donor atom
(S) amide	(4) Hexadentate

Code :

	P	Q	R	S
(A)	4	2	1	3
(B)	2	1	3	4
(C)	4	1	2	3
(D)	4	2	3	1

CC0099

Assertion Reason :

7. **Statement-1**: Complexes containing three bidentate groups such as $[Cr(ox)_3]^{3-}$ and $[Co(en)_3]^{3+}$ do not show optical activity.

Statement-2: Octahedral complex, $[Co(NH_3)_4Cl_2]Cl$ shows geometrical isomerism.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CC0100

8. **Statement-1**: After splitting of d-orbitals during complex formation, the orbitals form two sets of orbitals t_{2g} and e_g in an octahedral field.

Statement-2: Splitting of d-orbitals occur only in the case of strong field ligands such as CN^-.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CC0101

9. **Statement-1**: $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Statement-2: d–d transition is not possible in $[Sc(H_2O)_6]^{3+}$ because no d-electron is present while possible for Ti^{3+} having d^1 system.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CC0102

Comprehension (10 to 12)

Ligands are neutral or ionic species capable of donating at least one electron pair to central metal. Hence ligands can be of different denticities.

10. For a given metal M^{3+} coordination number is six, then for which set of ligands, complex will be most stable-

(A) $6H_2O$ (B) $6F^-$ (C) $EDTA^{4-}$ (D) $2H_2O$ and $2C_2O_4^{2-}$

CC0103

11. $[Mn(CO)_5]$ can attain more stability by :

(A) Oxidation of itself (B) Reduction of itself

(C) Dimerization (D) Both (B) and (C)

CC0104

12. The metal cation that has least tendency to accept electron pair from NH_3 is

(A) Fe^{3+} (B) Rh^{3+} (C) Zn^{2+} (D) Ba^{++}

CC0105

Comprehension (13 to 15)

Complex compounds are molecular compounds which retain their identities even when dissolved in water. They do not give all the simple ions in solution but instead furnish complex ions with complicated structures. The complex compounds are often called coordination compounds because certain groups called ligands are attached to the central metal ion by coordinate or dative bonds. Coordination compounds exhibit isomerism, both structural and stereoisomerism. The structure, magnetic property, colour and electrical properties of complexes are explained by various theories.

13. Arrange the following compounds in order of their Molar conductance:

(I) $K[Co(NO_2)_4(NH_3)_2]$ (II) $[Cr(ONO)_3(NH_3)_3]$

(III) $[Cr(NO_2)(NH_3)_5]_3[Co(NO_2)_6]_2$ (IV) $Mg[Cr(NO_2)_5(NH_3)]$

(A) II < I < IV < III (B) I < II < III < IV

(C) II < I < III < IV (D) IV < III < II < I

CC0106

14. The oxidation number and coordination number of chromium in the following complex is $[Cr(C_2O_4)_2(NH_3)_2]^{1-}$

(A) O.N. = + 4, C.N. = 4 (B) O.N. = +3, C.N. = 4

(C) O.N. = – 1, C.N. = 4 (D) O.N. = + 3, C.N. = 6

CC0107

15. In which of the following pairs, both the complexes have the same geometry but different hybridisation

(A) $[NiCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$ (B) $[CoF_6]^{3-}$, $[Co(NH_3)_6]^{3+}$

(C) $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ (D) $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)_6]^{2+}$

CC0108

Matching list type 1 × 3Q. (Three list type Question)

The following column I, II, III represent the different type of observations based on CFT in complex compounds.

Answer the questions that follow

Column-I - Crystal field stablization energy (CFSE) (neglecting PE in all cases)

Column-II - Electronic configuration

Column-III - Type of complex

Column - I CFSE (neglecting PE in all cases	**Column - II** Electronic Configuration	**Column - III** Type of Complex
(I) $-0.4\ \Delta_O$	(i) t_{2g}^5, e_g^0	(P) High spin & Paramagnetic
(II) $-2.0\ \Delta_O$	(ii) t_{2g}^4, e_g^0	(Q) Low spin & Paramagnetic
(III) $-2.4\ \Delta_O$	(iii) t_{2g}^6, e_g^0	(R) High spin & Diamagnetic
(IV) $-1.2\ \Delta_O$	(iv) t_{2g}^4, e_g^2	(S) Low spin & Diamagnetic

16. For sodium nitroprusside complex the only **CORRECT** combination is

(A) (III), (iv), (Q) (B) (III), (iii), (S) (C) (III), (iii), (R) (D) (II), (iii), (Q)

CC0109

17. For $[Co(H_2O)_3F_3]$ complex the only **CORRECT** combination is.

(A) (I), (iv), (Q) (B) (II), (iv), (S) (C) (III), (ii), (R) (D) (I), (iv), (P)

CC0110

18. For $[Mn(CN)_6]^{4-}$ complex the only **CORRECT** combination is.

(A) (IV), (i), (S) (B) (II), (i), (R) (C) (I), (i), (S) (D) (II), (i), (Q)

CC0111

EXERCISE : JEE-MAIN

1. In $[Cr(C_2O_4)_3]^{3-}$, the isomerism shown is - **[AIEEE-2002]**

(1) Ligand (2) Optical (3) Geometrical (4) Ionization

CC0112

2. In the complexes $[Fe(H_2O)_6]^{3+}$, $[Fe(SCN)_6]^{3-}$, $[Fe(C_2O_4)_3]^{3-}$ and $[FeCl_6]^{3-}$, more stability is shown by - **[AIEEE-2002]**

(1) $[Fe(H_2O)_6]^{3+}$ (2) $[Fe(SCN)_6]^{-3}$ (3) $[Fe(C_2O_4)_3]^{3-}$ (4) $[FeCl_6]^{3-}$

CC0113

3. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl(s). The structure of the complex is - **[AIEEE-2003]**

(1) $[Co(NH_3)_3Cl_3].2NH_3$ (2) $[Co(NH_3)_4Cl_2]Cl.NH_3$

(3) $[Co(NH_3)_4Cl]Cl_2.NH_3$ (4) $[Co(NH_3)_5Cl]Cl_2$

CC0114

4. In the coordination compound $K_4[Ni(CN)_4]$, the oxidation state of nickel is – **[AIEEE-2003]**

(1) 0 (2) +1 (3) +2 (4) –1

CC0115

5. The number of 3d-electrons remained in Fe^{2+} (At.no. of Fe = 26) ion is – **[AIEEE-2003]**

(1) 4 (2) 5 (3) 6 (4) 3

CC0116

6. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solution. What is the reason for it :- **[AIEEE-2003]**

(1) In acidic solutions hydration protects copper ions

(2) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available

(3) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali

(4) Copper hydroxide is an amphoteric substance

CC0117

7. Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN^- ion towards metal species is :- **[AIEEE-2004]**

(1) c, a (2) b, c (3) a, b (4) a, b, c

CC0118

8. The coordination number of a central metal atom in a complex is determined by :- **[AIEEE–2004]**

(1) The number of ligands around a metal ion bonded by sigma and pi-bonds both

(2) The number of ligands around a metal ion bonded by pi-bonds

(3) The number of ligands around a metal ion bonded by sigma bonds

(4) The number of only anionic ligands bonded to the metal ion

CC0119

9. Which one of the following complexes is an outer orbital complex :- **[AIEEE–2004]**

(1) $[Co(NH_3)_6]^{3+}$ (2) $[Mn(CN)_6]^{4-}$ (3) $[Fe(CN)_6]^{4-}$ (4) $[Ni(NH_3)_6]^{2+}$

(Atomic nos.:Mn=25 ; Fe=26 ; Co=27 ; Ni = 28)

CC0120

10. Coordination compounds have great importance in biological systems. In this contect which of the following statements is **INCORRECT** ? **[AIEEE–2004]**

(1) Cyanocobalamin is vitamin B_{12} and contains cobalt

(2) Haemoglobin is the red pigment of blood and contains iron

(3) Chlorophylls are green pigments in plants and contain calcium

(4) Carboxypeptidase - A is an enzyme and contains zinc

CC0121

11. The **CORRECT** order of magnetic moments (spin only values in B.M.) among is :- **[AIEEE–2004]**

(1) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$ (2) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$

(3) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$ (4) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

(Atomic nos. : Mn = 25, Fe = 26, Co = 27)

CC0122

12. For octahedral complex, the value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The **CORRECT** one is
[AIEEE–2005]

(1) d^4 (in strong ligand field) (2) d^4 (in weak ligand field)

(3) d^3 (in weak as well as in strong field) (4) d^5 (in strong ligand field)

CC0123

13. The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]Cl_2$ is - **[AIEEE–2006]**

(1) pentaammine nitrito-N- cobalt (II) chloride

(2) pentaammine nitrito-N- cobalt (III) chloride

(3) nitrito-N- pentaamminecobalt (III) chloride

(4) nitrito-N- pentaamminecobalt (II) chloride

CC0124

14. Nickel (Z=28) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electrons in the nickel and geometry of this complex ion are, respectively. **[AIEEE–2006]**

(1) one, square planar (2) two, square planar (3) one, tetrahedral (4) two, tetrahedral

CC0125

15. In $Fe(CO)_5$, the Fe–C bond possesses **[AIEEE–2006]**

(1) ionic character (2) σ – character only (3) π –character only (4) both σ and π character

CC0126

16. How many EDTA (ethylenediaminetetraacetate) molecules are required to make an octahedral complex with a Ca^{2+} ion ? **[AIEEE–2006]**

(1) One (2) Two (3) Six (4) Three

CC0127

17. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. Ni= 28)- **[AIEEE–2006]**

(1) 0 (2) 1.73 (3) 2.84 (4) 4.90

CC0128

18. Which one of the following has a square planar geometry :-
(Co = 27, Ni = 28, Fe=26, Pt = 78) **[AIEEE–2007]**

(1) $[CoCl_4]^{2-}$ (2) $[FeCl_4]^{2-}$ (3) $[NiCl_4]^{2-}$ (4) $[PtCl_4]^{2-}$

CC0129

19. The coordination number and the oxidation state of the element 'E' in the complex $[E(en)_2(C_2O_4^{-2})]\ NO_2^{\ominus}$ (where (en) is ethylene diamine) are, respectively - **[AIEEE–2008]**

(1) 6 and 2 (2) 4 and 2 (3) 4 and 3 (4) 6 and 3

CC0130

20. In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of Δ_0 be the highest ? **[AIEEE–2008]**

(1) $[Co(CN)_6]^{3-}$ (2) $[Co(C_2O_4)_3]^{3-}$ (3) $[Co(H_2O)_6]^{3+}$ (4) $[Co(NH_3)_6]^{3+}$

CC0131

21. Which of the following pairs represent linkage isomers ? **[AIEEE–2009]**

(1) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$
(2) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$
(3) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
(4) $[Pd\ (PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2\ (SCN)_2]$

CC0132

22. Which of the following has an optical isomer? **[AIEEE–2009]**

(1) $[Co(H_2O)_4(en)]^{3+}$ (2) $[Co(en)_2(NH_3)_2]^{3+}$
(3) $[Co(NH_3)_3Cl]^{+}$ (4) $[Co(en)(NH_3)_2]^{2+}$

CC0133

23. Which one of the following has an optical isomer ? **[AIEEE–2010]**

(1) $[Zn(en)_2]^{2+}$ (2) $[Zn(en)(NH_3)_2]^{2+}$
(3) $[Co(en)_3]^{3+}$ (4) $[Co(H_2O)_4(en)]^{3+}$
(en = ethylenediamine)

CC0134

24. A solution containing 2.675 g of $CoCl_3.6NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is :- **[AIEEE–2010]**
(At. mass of Ag = 108 u)

(1) $[CoCl(NH_3)_5]Cl_2$ (2) $[Co(NH_3)_6]Cl_3$
(3) $[CoCl_2(NH_3)_4]Cl$ (4) $[CoCl_3(NH_3)_3]$

CC0135

25. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is **wrong** ? **[AIEEE–2011]**

(1) The complex is an outer orbital complex

(2) The complex gives white precipitate with silver nitrate solution

(3) The complex involves d^2sp^3 hybridisation and is octahedral in shape

(4) The complex is paramagnetic

CC0136

26. The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is :- **[AIEEE–2011]**

(1) 2.82 BM (2) 1.41 BM (3) 1.82 BM (4) 5.46 BM

CC0137

27. Among the ligands NH_3,en, CN^- and CO the **CORRECT** order of their increasing field strength, is :- **[AIEEE–2011]**

(1) $CO < NH_3 < en < CN^-$ (2) $NH_3 < en < CN^- < CO$

(3) $CN^- < NH_3 < CO < en$ (4) $en < CN^- < NH_3 < CO$

CC0138

28. Which one of the following complex ions has geometrical isomers ? **[AIEEE–2011]**

(1) $[Co\ (en)_3]^{3+}$ (2) $[Ni\ (NH_3)_5Br]^+$ (3) $[Co\ (NH_3)_2\ (en)_2]^{3+}$(4) $[Cr\ (NH_3)_4(en)]^{3+}$

CC0139

29. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide ? **[AIEEE–2012]**

(1) $[Cr(en)Br_2]Br$ (2) $[Cr(en)_3]Br_3$ (3) $[Cr(en)_2Br_2]Br$ (4) $[Cr(en)Br_4]^-$

CC0140

30. The complex ion

$[Pt(NO_2)\ (Py)\ (NH_3)\ (NH_2OH)]^+$ will give :- **[J-MAIN–2012, Online]**

(1) 4 isomers (Geometrical) (2) 2 isomers (Geometrical)

(3) 3 isomers (Geometrical) (4) 6 isomers (Geometrical)

CC0141

31. Which of the following complex ions will exhibit optical isomerism? **[J-MAIN–2012, Online]**

(en = 1, 2-diamine ethane)

(1) $[Co(en)_2Cl_2]^+$ (2) $[Zn(en)_2]^{2+}$ (3) $[Co(NH_3)_4Cl_2]^+$ (4) $[Cr(NH_3)_2Cl_2]^+$

CC0142

32. Which of the following complex species is **NOT** expected to exhibit optical isomerism ?

(1) $[Co(en)_3]^{3+}$ (2) $[Co(en)_2\ Cl_2]^+$ **[J-MAIN–2013]**

(3) $[Co(NH_3)_3\ Cl_3]$ (4) $[Co(en)\ (NH_3)_2Cl_2]^+$

CC0143

33. Type of isomerism which exists between $[Pd(C_6H_5)_2(SCN)_2]$ and **[J-MAIN–2013, Online]** $[Pd(C_6H_5)_2\ (NCS)_2]$ is :

(1) Solvate isomerism (2) Ionisation isomerism

(3) Linkage isomerism (4) Coordination isomerism

CC0144

34. Which of the following is diamagnetic ? **[J-MAIN–2013, Online]**

(1) $[CoF_6]^{3-}$ (2) $[FeF_6]^{3-}$ (3) $[Fe(CN)_6]^{3-}$ (4) $[Co(Ox)_3]^{3-}$

CC0145

35. The magnetic moment of the complex anion $[\overset{I}{Cr}(NO)\,(NH_3)\,(CN)_4]^{2-}$ is :**[J-MAIN–2013, Online]**

(1) 2.82 BM (2) 5.91 BM (3) 1.73 BM (4) 3.87 BM

CC0146

36. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelength in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is: **[J-MAIN–2014]**

(1) $L_3 < L_2 < L_4 < L_1$ (2) $L_1 < L_2 < L_4 < L_3$ (3) $L_4 < L_3 < L_2 < L_1$ (4) $L_1 < L_3 < L_2 < L_4$

CC0147

37. The equation which is balanced and represents the **CORRECT** product (s) is : **[J-MAIN–2014]**

(1) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$

(2) $CuSO_4 + 4KCN \rightarrow K_2[Cu(CN)_4] + K_2SO_4$

(3) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$

(4) $[CoCl\,(NH_3)_5]^{+} + 5H^{+} \rightarrow Co^{2+} + 5NH_4^{+} + Cl^{-}$

CC0148

38. The **CORRECT** statement about the magnetic properties of $[Fe(CN)_6]^{3-}$ and $[FeF_6]^{3-}$ is : (Z = 26).

(1) $[Fe(CN)_6]^{3-}$ is paramagnetic, $[FeF_6]^{3-}$ is diamagnetic. **[J-MAIN–2014, Online]**

(2) both are diamagnetic.

(3) $[\,Fe(CN)_6]^{3-}$ is diamagnetic, $[FeF_6]^{3-}$ is paramagnetic.

(4) both are paramagnetic

CC0149

39. An octahedral complex of Co^{3+} is diamagnetic. The hybridisation involved in the formation of the complex is : **[J-MAIN–2014]**

(1) d^2sp^3 (2) dsp^3d (3) dsp^2 (4) sp^3d^2

CC0150

40. Which of the following name formula combinations is **NOT CORRECT**?

[J-MAIN–2014, Online]

Formula	**Name**
(1) $K[Cr(NH_3)_2Cl_4]$	Potassium diammine Tetrachlorochromate (III)
(2) $[Co(NH_3)_4(H_2O)I]SO_4$	Tetraammine aquaiodo cobalt (III) sulphate
(3) $[Mn(CN)_5]^{2-}$	Pentacyanomagnate (II) ion
(4) $K_2[Pt(CN)_4]$	Potassium tetracyanoplatinate(II)

CC0151

41. Consider the coordination compound, $[Co(NH_3)_6]Cl_3$. In the formation of this complex, the species which acts as the Lewis acid is : **[J-MAIN–2014, Online]**

(1) $[Co(NH_3)_6]^{3+}$ (2) NH_3 (3) Co^{3+} (4) $C\ell^-$

CC0152

42. Among the following species the one which causes the highest CFSE, Δ_0 as a ligand is :- **[J-MAIN–2014, Online]**

(1) CN^- (2) NH_3 (3) CO (4) F^-

CC0153

43. Which one of the following complexes will most likely absorb visible light ? **[J-MAIN–2014, Online]**

(At nos. Sc = 21, Ti = 22, V = 23, Zn = 30) :-

(1) $[Ti\ (NH_3)_6]^{4+}$ (2) $[V(NH_3)_6]^{3+}$ (3) $[Zn\ (NH_3)_6]^{2+}$ (4) $[Sc\ (H_2O)_6]^{3+}$

CC0154

44. Nickel(Z = 28) combines with a uninegative monodentate ligand to form a diamagnetic complex $[NiL_4]^{2-}$. The hybridisation involved and the number of unpaired electrons present in the complex are respectively : **[J-MAIN–2014, Online]**

(1) sp^3, zero (2) sp^3. two (3) dsp^2 one (4) dsp^2, zero

CC0155

45. The number of geometrical isomers that can exist for square planar $[Pt\ (Cl)\ (py)\ (NH_3)\ (NH_2OH)]^+$ is (py = pyridine) : **[J-MAIN–2015]**

(1) 4 (2) 6 (3) 2 (4) 3

CC0156

46. The color of $KMnO_4$ is due to : **[J-MAIN–2015]**

(1) L → M charge transfer transition (2) $\sigma - \sigma^*$ transition

(3) M → L charge transfer transition (4) d – d transition

CC0157

47. Which of the following complex ions has electrons that are symmetrically filled in both t_{2g} and e_g orbitals ? **[J-MAIN–2015, Online]**

(1) $[CoF_6]^{3-}$ (2) $[Mn(CN)_6]^{4-}$ (3) $[FeF_6]^{3-}$ (4) $[Co(NH_3)_6]^{2+}$

CC0158

48. When concentrated HCl is added to an aqueous solution of $CoCl_2$, its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction ?:-

(1) $[Co(H_2O)_6]^{2+}$ (2) $[CoCl_6]^{3-}$ **[J-MAIN–2015, Online]**

(3) $[CoCl_4]^{2-}$ (4) $[CoCl_6]^{4-}$

CC0159

49. The **CORRECT** statement on the isomerism associated with the following complex ions, **[J-MAIN–2015, Online]**

(a) $[Ni(H_2O)_5NH_3]^{2+}$

(b) $[Ni(H_2O)_4(NH_3)_2]^{2+}$ and

(c) $[Ni(H_2O)_3(NH_3)_3]^{2+}$ is :

(1) (a) and (b) show geometrical and optical isomerism

(2) (b) and (c) show geometrical and optical isomerism

(3) (a) and (b) show only geometrical Isomerism

(4) (b) and (c) show only geometrical Isomerism

CC0160

50. Which one of the following complexes shows optical isomerism :- **[J-MAIN–2016]**

(1) $[Co(NH_3)_4Cl_2]Cl$ (2) $[Co(NH_3)_3Cl_3]$

(3) cis$[Co(en)_2Cl_2]Cl$ (4) trans$[Co(en)_2Cl_2]Cl$

(en = ethylenediamine)

CC0161

51. The pair having the same magnetic moment is:- **[J-MAIN–2016]**

[At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]

(1) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$ (2) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

(3) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ (4) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$

CC0162

52. Which one of the following complexes will consume more equivalents of aqueous solution of $Ag(NO_3)$? **[J-MAIN–2016, Online]**

(1) $[Cr(H_2O)_6]Cl_3$ (2) $Na_2[CrCl_5(H_2O)]$ (3) $Na_3[CrCl_6]$ (4) $[Cr(H_2O)_5Cl]Cl_2$

CC0163

53. Identify the **CORRECT** trend given below : **[J-MAIN–2016, Online]**

(Atomic No.= Ti : 22, Cr : 24 and Mo : 42)

(1) Δ_0 of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$

(2) Δ_0 of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$

(3) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$

(4) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$

CC0164

54. $[Co_2(CO)_8]$ displays:- **[J-MAIN–2017, Online]**

(1) no Co-Co bond, four terminal CO and four bridging CO

(2) one Co-Co bond, six terminal CO and two bridging CO

(3) no Co–Co bond, six terminal CO and two bridging CO

(4) one Co-Co bond, four terminal CO and four bridging CO

CC0165

55. On treatment of 100 mL of 0.1 M solution of $CoCl_3 . 6H_2O$ with excess $AgNO_3$; 1.2×10^{22} ions are precipitated. The complex is :- **[J-MAIN–2017, Offline]**

(1) $[Co(H_2O)_4 Cl_2]Cl.2H_2O$ (2) $[Co(H_2O)_3Cl_3].3H_2O$

(3) $[Co(H_2O)_6]Cl_3$ (4) $[Co(H_2O)_5Cl]Cl_2.H_2O$

CC0166

56. The pair of compounds having metal in their highest oxidation state is : **[J-MAIN–2017, Online]**

(1) $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$ (2) $[Fe(CN)_6]^{3-}$ and $[Cu(CN)_4]^{2-}$

(3) $[FeCl_4]^-$ and Co_2O_3 (4) MnO_2 and CrO_2Cl_2

CC0167

57. The oxidation states of Cr in $[Cr(H_2O)_6]Cl_3$,$[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2 (O)_2(O_2)(NH_3)]$ respectively are : **[J-MAIN–2018, Offine]**

(1) +3, +2, and +4 (2) +3, 0, and +6

(3) +3, 0, and +4 (4) +3, +4, and +6

CC0168

58. Consider the following reaction and statements : **[J-MAIN–2018, Offine]**

$[Co(NH_3)_4Br_2]^+ + Br^- \rightarrow [Co(NH_3)_3Br_3] + NH_3$

(I) Two isomers are produced if the reactant complex ion is a *cis*-isomer.

(II) Two isomers are produced if the reactant complex ion is a *trans*-isomer.

(III) Only one isomer is produced if the reactant complex ion is a *trans*-isomer.

(IV) Only one isomer is produced if the reactant complex ion is a *cis*-isomer.

The correct statements are :

(1) (I) and (III) (2) (III) and (IV) (3) (II) and (IV) (4) (I) and (II)

CC0169

59. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? **[J-MAIN–2018, Offine]**

(1) $[Co(H_2O)_5Cl]Cl_2.H_2O$ (2) $[Co(H_2O)_4Cl_2]Cl.2H_2O$

(3) $[Co(H_2O)_3Cl_3].3H_2O$ (4) $[Co(H_2O)_6]Cl_3$

CC0170

60. The total number of possible isomers for square-planar $[Pt(Cl)(NO_2)(NO_3)(SCN)]^{2-}$ is :- **[J-MAIN–2018, Onine]**

(1) 16 (2) 8 (3) 24 (4) 12

CC0171

61. The correct order of spin-only magnetic moments among the following is : **[J-MAIN–2018, Onine]**

(Atomic number : Mn = 25, Co = 27, Ni= 28, Zn = 30)

(1) $[ZnCl_4]^{2-} > [NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

(2) $[CoCl_4]^{2-} > [MnCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$

(3) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$

(4) $[NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-} > [ZnCl_4]^{2-}$

CC0172

62. The correct combination is **[J-MAIN–2018, Onine]**

(1) $[Ni(CN)_4]^{2-}$ – tetrahedral;
$[Ni(CO)_4]$ – paramagnetic

(2) $[NiCl_4]^{2-}$ – paramagnetic;
$[Ni(CO)_4]$ – tetrahedral

(3) $[NiCl_4]^{2-}$ – diamagnetic;
$[Ni(CO)_4]$ – square-planar

(4) $[NiCl_4]^{2-}$ – square-planar;
$[Ni(CN)_4]^{2-}$ – paramagnetic

CC0173

63. Which of the following complexes will show geometrical isomerism ? **[J-MAIN–2018, Onine]**

(1) Potassium amminetrichloroplatinate(II)

(2) Aquachlorobis (ethylenediamine) cobalt(II) chloride

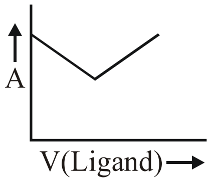
(3) Potassium tris(oxalato) chromate(III)

(4) Pentaaquachlorochromium(III) chloride

CC0174

64. In a complexometric titration of metal ion with ligand M(Metal ion) + L(Ligand) → C(Complex) end point is estimated spectrophotometrically (through light absorption). If 'M' and 'C' do not absorb light and only 'L' absorbs, then the titration plot between absorbed light (A) versus volume of ligand 'L' (v)would look like :- **[J-MAIN–2018, Onine]**

(1)



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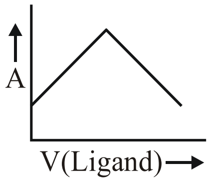

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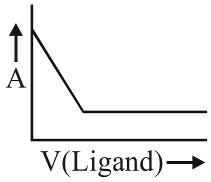

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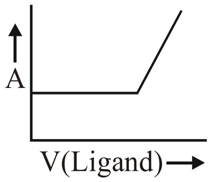


CC0175

65. In Wilkinson's catalyst, the hybridization of central metal ion and its shape are respectively

(1) dsp^2, square planar **[J-MAIN–2018, Onine]**

(2) sp^3d, trigonal bipyramidal

(3) sp^3, tetrahedral

(4) d^2sp^3, octahedral

CC0176

EXERCISE : JEE-ADVANCED

1. The complex ion which has no 'd' electrons in the central metal atom is : **[JEE 2001]**

[At No. Cr = 24, Mn = 25, Fe= 26, Co = 27]

(A) $[MnO_4]^-$ (B) $[Co(NH_3)_6]^{3+}$ (C) $[Fe(CN)_6]^{3-}$ (D) $[Cr(H_2O)_6]^{3+}$

CC0177

2. The **CORRECT** order of hybridisation of the central atom in the following species. **[JEE 2001]**

NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is [At No. Pt = 78]

(A) dsp^2, sp^3d, sp^2 and sp^3 (B) sp^3, dsp^2, sp^3d, sp^2

(C) dsp^2, sp^2, sp^3 and sp^3d (D) dsp^2, sp^3, sp^2 and sp^3d

CC0178

3. The species having tetrahedral shape is : **[JEE 2004]**

(A) $[PdCl_4]^{2-}$ (B) $[Ni(CN)_4]^{2-}$ (C) $[Pd(CN)_4]^{2-}$ (D) $[NiCl_4]^{2-}$

CC0179

4. The pair of compounds having metals in their highest oxidation state is **[JEE 2004]**

(A) MnO_2, $FeCl_3$ (B) $[MnO_4]^-$, CrO_2Cl_2

(C) $[Fe(CN)_6]^{3-}$, $[Co(CN)_3]$ (D) $[NiCl_4]^{2-}$, $[CoCl_4]^-$

CC0180

5. Spin only magnetic moment of the compound Hg $[Co(SCN)_4]$ is **[JEE 2004]**

(A) $\sqrt{3}$ (B) $\sqrt{15}$ (C) $\sqrt{24}$ (D) $\sqrt{8}$

CC0181

6. Which of the following pair is expected to exhibit same colour in solution? **[JEE 2005]**

(A) $VOCl_2$; $FeCl_2$ (B) $CuCl_2$; $VOCl_2$ (C) $MnCl_2$; $FeCl_2$ (D) $FeCl_2$; $CuCl_2$

CC0182

7. Which type of isomerism is shown by $Co(NH_3)_4Br_2Cl$? **[JEE 2005]**

(A) Geometrical and Ionisation (B) Optical and Ionisation

(C) Geometrical and Optical (D) Geometrical only

CC0183

Question No. 8 to 10 (3 questions) **[JEE 2006]**

The coordination number of Ni^{2+} is 4.

$NiCl_2 + KCN \text{ (excess)} \rightarrow A$ (cyano complex)

$NiCl_2 + KCl \text{ (excess)} \rightarrow B$ (chloro complex)

8. The IUPAC name of A and B are

(A) Potassium tetracyanidonickelate (II), potassium tetrachloridonickelate (II)

(B) Tetracyanidopotassiumnickelate (II), teterachloridopotassiumnickelate (II)

(C) Tetracyanidornickel (II), tetrachloridonickel (II)

(D) Potassium tetracyanidonickel (II), potassium tetrachloridonickel (II)

CC0184

9. Predict the magnetic nature of A and B.

(A) Both are diamagnetic.

(B) A is diamagnetic and B is paramagnetic with one unpaired electron.

(C) A is diamagnetic and B is paramagnetic with two unpaired electrons.

(D) Both are paramagnetic.

CC0185

10. The hybridization of A and B are

(A) dsp^2, sp^3 (B) sp^3, sp^3 (C) dsp^2, dsp^2 (D) sp^3d^2, d^2sp^3

CC0186

11. If the bond length of CO bond in carbon monoxide is 1.128Å, then what is the value of CO bond length in $Fe(CO)_5$? **[JEE 2006]**

(A) 1.15Å (B) 1.128Å (C) 1.72Å (D) 1.118Å

CC0187

12. Among the following metal carbonyls, the C–O bond order is lowest in **[JEE 2007]**

(A) $[Mn(CO)_6]^+$ (B) $[Fe(CO)_5]$ (C) $[Cr(CO)_6]$ (D) $[V(CO)_6]^-$

CC0188

13. Match the complexes in Column I with their properties listed in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS. **[JEE 2007]**

Column I	**Column II**
(A) $[Co(NH_3)_4(H_2O)_2]Cl_2$	(P) Geometrical isomers
(B) $[Pt(NH_3)_2Cl_2]$	(Q) Paramagnetic
(C) $[Co(H_2O)_5Cl]Cl$	(R) Diamagnetic
(D) $[Ni(H_2O)_6]Cl_2$	(S) Metal ion with 2+ oxidation state

CC0189

14. Among the following, the coloured compound is **[JEE 2008]**

(A) CuCl (B) $K_3[Cu(CN)_4]$ (C) CuF_2 (D) $[Cu(CH_3CN)_4]BF_4$

CC0190

15. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is **[JEE 2008]**

(A) Tetrachloronickel (II)-tetraamminenickel (II)

(B) Tetraamminenickel (II)-tetrachloronickel (II)

(C) Tetraamminenickel (II)-tetrachloronickelate (II)

(D) Tetrachloronickel (II)-tetraamminenickelate (0)

CC0191

16. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are **[JEE 2008]**

(A) sp^3, sp^3 (B) sp^3, dsp^2 (C) dsp^2, sp^3 (D) dsp^2, dsp^2

CC0192

17. Statement-1 : The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.

Statement-2 : Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True **[JEE 2008]**

CC0193

18. Statement-1 : $[Fe(H_2O)_5NO]SO_4$ is paramagnetic **[JEE 2008]**

Statement-2 : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

CC0194

19. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is **[JEE 2009]**

(A) 0 (B) 2.84 (C) 4.90 (D) 5.92

CC0195

20. The compound(s) that exhibit(s) geometrical isomerism is (are) : **[JEE 2009]**

(A) $[Pt(en)Cl_2]$ (B) $[Pt(en)_2]Cl_2$ (C) $[Pt(en)_2Cl_2]Cl_2$ (D) $[Pt(NH_3)_2Cl_2]$

CC0196

21. The number of water molecule(s) directly bonded to the metal centre in $CuSO_4 . 5H_2O$ is. **[JEE 2009]**

CC0197

22. The ionization isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is – **[JEE 2010]**

(A) $[Cr(H_2O)_4(O_2N)]Cl_2$ (B) $[Cr(H_2O)_4Cl_2](NO_2)$

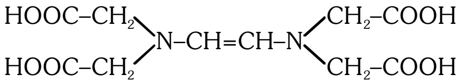
(C) $[Cr(H_2O)_4Cl(ONO)]Cl$ (D) $[Cr(H_2O)_4Cl_2(NO_2)].H_2O$

CC0198

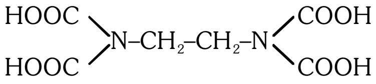
23. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is. **[JEE 2010]**

CC0199

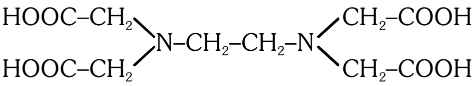
24. The correct structure of ethylenediaminetetraacetic acid (EDTA) is – **[JEE 2010]**

(A) 

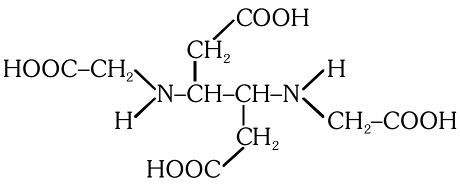
$(HOOC-CH_2)_2N-CH=CH-N(CH_2-COOH)_2$

(B) 

$(HOOC)_2N-CH_2-CH_2-N(COOH)_2$

(C) 

$(HOOC-CH_2)_2N-CH_2-CH_2-N(CH_2-COOH)_2$

(D) 

$(HOOC-CH_2)(H)N-CH(CH_2COOH)-CH(CH_2COOH)-N(H)(CH_2-COOH)$

CC0200

25. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O respectively, are - **[JEE 2011]**

(A) octahedral, tetrahedral and square planar (B) tetrahedral, square planar and octahedral

(C) square planar, tetrahedral and octahedral (D) octahedral, square planar and octahedral

CC0201

26. Among the following complexes (**K–P**) **[JEE 2011]**

$K_3[Fe(CN)_6]$ **(K)**, $[Co(NH_3)_6]Cl_3$ **(L)**, $Na_3[Co(oxalate)_3]$ **(M)**, $[Ni(H_2O)_6]Cl_2$ **(N),** $K_2[Pt(CN)_4]$ **(O)** and $[Zn(H_2O)_6](NO_3)_2$ **(P)**

The diamagnetic complex are -

(A) K, L, M, N (B) K, M, O, P (C) L, M, O, P (D) L, M, N, O

CC0202

27. The volume (in mL) of 0.1M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to. **[JEE 2011]**

CC0203

28. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is : **[JEE 2012]**

(A) Tetraaquadiaminecobalt(III) chloride (B) Tetraaquadiamminecobalt(III) chloride

(C) Diaminetetraaquacobalt(III) chloride (D) Diamminetetraaquacobalt(III) chloride

CC0204

29. The colour of light absorbed by an aqueous solution of $CuSO_4$ is - **[JEE 2012]**

(A) orange-red (B) blue-green (C) yellow (D) violet

CC0205

30. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behavior (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively : **[JEE 2012]**

(A) tetrahedral and tetrahedral (B) square planar and square planar

(C) tetrahedral and square planar (D) square planar and tetrahedral

CC0206

31. Consider the following complex ions P, Q and R ,

P = $[FeF_6]^{3-}$, **Q** = $[V(H_2O)_6]^{2+}$ and **R** = $[Fe(H_2O)_6]^{2+}$

The **CORRECT** order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is - **[JEE 2013]**

(A) R < Q < P (B) Q < R < P (C) R < P < Q (D) Q < P < R

CC0207

32. $EDTA^{4-}$ is ethylenediaminetetraacetate ion. The total number of N–Co–O bond angles in $[Co(EDTA)]^{-1}$ complex ion is **[JEE 2013]**

CC0208

33. The pair(s) of coordination complex/ion exhibiting the same kind of isomerism is(are) - **[JEE 2013]**

(A) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$

(B) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$

(C) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$

(D) $[Pt(NH_3)_3(NO_3)]$ Cl and $[Pt(NH_3)_3Cl]$ Br

CC0209

34. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists. **[JEE Adv. 2014]**

{en = $H_2NCH_2CH_2NH_2$ ' atomic numbers ; Ti = 22 ; Cr = 24 ; Co = 27 ; Pt = 78}

List-I	**List-II**
(P) $[Cr(NH_3)_4Cl_2]Cl$	(1) Paramagnetic and exhibits ionisation isomerism
(Q) $[Ti(H_2O)_5Cl](NO_3)_2$	(2) Dimagnetic and exhibits *cis-trans* isomerism
(R) $[Pt(en)(NH_3)Cl]NO_3$	(3) Paramagnetic and exhibits *cis-trans* isomerism
(S) $[Co(NH_3)_4(NO_3)_2]NO_3$	(4) Dimagnetic and exhibits ionisation isomerism

Code :

	P	**Q**	**R**	**S**		**P**	**Q**	**R**	**S**
(A)	4	2	3	1	(B)	3	1	4	2
(C)	2	1	3	4	(D)	1	3	4	2

CC0210

35. A list of species having the formula XZ_4 is given below : **[JEE Adv. 2014]**

XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$.

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

CC0211

Subjective

36. Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. **[JEE 2000]**

CC0212

37. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A and B. The form A reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas B gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of A and B and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). **[JEE 2001]**

CC0213

38. Deduce the structures of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. **[JEE 2002]**

CC0214

39. Write the IUPAC name of the compound $K_2[Cr(NO)(CN)_4(NH_3)]$. Spin magnetic moment of the complex $\mu = 1.73$ BM. Give the structure of anion. **[JEE 2003]**

CC0215

40. $NiCl_2$ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH_4OH, giving a bright red colour. **[JEE 2004]**

(a) Draw its structure and show H-bonding

(b) Give oxidation state of Ni and its hybridisation

(c) Predict whether it is paramagnetic or diamagnetic

CC0216

41. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is : [Atomic number of Fe = 26] **[JEE Ad. 2015]**

CC0217

42. In the complex acetylbromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe–C bond(s) is- **[JEE Ad. 2015]**

CC0218

43. Among the complex ions, $[Co(NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is - **[JEE Ad. 2015]**

CC0219

44. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is - **[JEE Ad. 2016]**

(A) 2 (B) 3 (C) 4 (D) 5

CC0220

45. The number of geometric isomers possible for the complex $[CoL_2Cl_2]^-$ ($L = H_2NCH_2CH_2O^-$) is

[JEE Ad. 2016]

CC0221

46. The geometries of the ammonia complexes of Ni^{2+}, Pt^{2+} and Zn^{2+}, respectively, are :

(A) octahedral, square planar and tetrahederal **[JEE Ad. 2016]**

(B) square planar, octahederal and tetrahederal

(C) tetrahederal, square planar and octahederal

(D) octahederal , tetrahederal and square planar

CC0222

47. Addition of excess aqueous ammonia to a pink coloured aqueous solution of $MCl_2 . 6H_2O$ (X) and NH_4Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. **[JEE Ad. 2017]**

Among the following options, which statements is(are) **CORRECT** ?

(A) The hybridization of the central metal ion in Y is d^2sp^3

(B) Z is tetrahedral complex

(C) Addition of silver nitrate to Y gives only two equivalents of silver chloride

(D) When X and Z are in equilibrium at 0°C, the colour of the solution is pink

CC0223

48. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are)

(Atomic numbers : Fe = 26, Ni = 28) **[JEE Ad. 2018]**

(A) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16

(B) These are predominantly low spin in nature

(C) Metal - carbon bond strengthens when the oxidation state of the metal is lowered

(D) The carbonyl C–O bond weakens when the oxidation state of the metal is increased

CC0224

49. The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$:- **[JEE Ad. 2018]**

(en = $H_2NCH_2CH_2NH_2$) is (are)

(A) It has two geometrical isomers

(B) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands

(C) It is paramagnetic

(D) It absorbs light at longer wavelength as compared to $[Co(en)(NH_3)_4]^{3+}$

CC0225

50. Match each set of hybrid orbitals from LIST-I with complex (es) given in LIST-II.

[JEE Ad. 2018]

LIST-I	**LIST-II**
P. dsp^2	1. $[FeF_6]^{4-}$
Q. sp^3	2. $[Ti(H_2O)_3Cl_3]$
R. sp^3d^2	3. $[Cr(NH_3)_6]^{3+}$
S. d^2sp^3	4. $[FeCl_4]^{2-}$
	5. $Ni(CO)_4$
	6. $[Ni(CN)_4]^{2-}$

The correct option is

(A) P → 5; Q → 4,6; R → 2,3; S → 1

(B) P → 5,6; Q → 4; R → 3; S → 1,2

(C) P → 6; Q → 4,5; R → 1; S → 2,3

(D) P → 4,6; Q → 5,6; R → 1,2; S → 3

CC0226

51. Among the species given below, the total number of diamagnetic species is____.

H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapour phase, **[JEE Ad. 2018]**

Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$, K_2MnO_4, K_2CrO_4

CC0227

52. Total number of *cis* N–Mn–Cl bond angles (that is, Mn–N and Mn–Cl bonds in *cis* positions) present in a molecule of *cis*-$[Mn(en)_2Cl_2]$ complex is ____ (*en* = $NH_2CH_2CH_2NH_2$) **[JEE Ad. 2019]**

CC0228

ANSWERS KEY

EXERCISE : O-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	C	B	C	C	C	D	B	D	B
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	B	A	B	A	C	C	D	A	D
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	D	C	B	C	B	B	A	D	A	B
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	D	B	C	D	C	C	B	C	C
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	B	C	D	D	D	D	C	B	D	B
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	A	B	A	D	B	D	A	C	B	D
Que.	61	62	63	64	65	66	67	68	69	
Ans.	B	C	C	A	C	C	A	D	A	

EXERCISE : O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,B	A,B,D	A,B,C,D	A,B,D	A,B	B,C,D	A,B,C,D	A,B,C	B,C,D	A,B,C,D
Que.	11	12	13	14						
Ans.	B,D	C,D	C,D	B,D						

EXERCISE : S-1

1. (3) 2. (2) 3. (9) 4. (36)

5. (9) 6. (2) 7. (2) 8. (52)

9. (5) 10. (2)

EXERCISE : S-2

Que.	1				2			
Ans.	(A)-R,	(B)-R	(C)-P	(D)-Q	(A)-P,Q,S	(B)-Q,R,S	(C)-P	(D)-P,Q
Que.	3							
Ans.	(A)-P,S	(B)-T	(C)-Q,R,T	(D)-P,S				

Que.	4	5	6	7	8	9	10	11	12	13
Ans.	B	C	D	D	C	A	C	D	D	A
Que.	14	15	16	17	18					
Ans.	D	B	B	D	D					

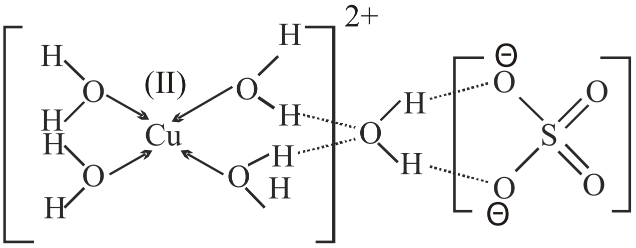
EXERCISE : J-MAIN

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.	2	3	4	1	3	2	1	3	4	3
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
	3	1	2	4	4	1	3	4	4	1
Que.	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
Ans.	4	2	3	2	1	1	2	3	3	3
Que.	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
Ans.	1	3	3	4	3	4	4	4	1	3
Que.	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**
Ans.	3	3	2	4	4	1	3	3	4	3
Que.	**51**	**52**	**53**	**54**	**55**	**56**	**57**	**58**	**59**	**60**
Ans.	3	1	2	2	1	2	2	1	3	4
Que.	**61**	**62**	**63**	**64**	**65**					
Ans.	3	2	2	4	1					

EXERCISE : J-ADVANCED

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.	A	B	D	B	B	B	A	A	C	A
Que.	**11**	**12**	**13**				**14**	**15**	**16**	**17**
Ans.	A	D	(A)-P,Q,S ; (B)-PR,S ; (C)-Q,S ; (D)-Q,S				C	C	B	B
Que.	**18**	**19**	**20**							
Ans.	A	A	C, D							

21.



Que.	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**
Ans.	B	3	C	B	C	6	D	A	C	B
Que.	**32**	**33**	**34**	**35**						
Ans.	8	B, D	B	4						

36. d^2sp^3 , dsp^2 and sp^3

37. A → $[Cr(NH_3)_4ClBr]Cl$

B → $[Cr(NH_3)_4Cl_2]Br$

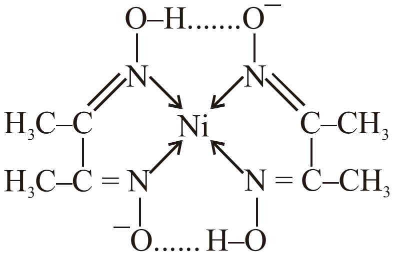
In both Cr is $d^2\ sp^3$ hybridised and magnetic moment is $\sqrt{15}$ BM

38. $[NiCl_4]^{2-} \rightarrow sp^3$, $\sqrt{8}$ BM

$[Ni(CN)_4]^{2-} \rightarrow dsp^2$, 0

39. Potassium amminetetracyanidonitrosoniumchromate(I) → d^2sp^3 , octahedral

40.



dsp^2 , Ni^{2+} , diamagnetic

41. Ans. (4) **42. Ans. (3)** **43. Ans. (6)** **44. Ans. (B)**

45. Ans. (5) **46. Ans. (A)**

47. Ans. (A,B,D)

$$\underset{\text{Pink }\mathbf{(X)}}{[\overset{\text{II}}{Co}(H_2O)_6]Cl_2} \xrightarrow[\text{Air / }O_2]{\text{Excess }NH_4OH\text{ / }NH_4Cl} \underset{\mathbf{(Y)}}{[\overset{\text{III}}{Co}(NH_3)_6]Cl_3}$$

$$\underset{\mathbf{(X)}}{[Co(H_2O)_6]^{2+}} + \underset{\text{(excess)}}{4Cl^-} \longrightarrow \underset{\mathbf{(Z)}\text{ blue colour}}{[CoCl_4]^{2-}}$$

(A) Hybridisation of (Y) is d^2sp^3 as NH_3 is strong field ligand

(B) $[CoCl_4]^{2-}$ have sp^3 hybridisation as Cl^- is weak field ligand

(C) $\underset{\mathbf{(Y)}}{[\overset{\text{III}}{Co}(NH_3)_6]Cl_3} + 3AgNO_3(aq.) \rightarrow 3AgCl$

(D) $\underset{\text{(Blue)}}{[CoCl_4]^{2-}} + 6H_2O \rightleftharpoons \underset{\text{(Pink)}}{[Co(H_2O)_6]^{2+}} + 4Cl^-$ ΔH = (–)ve (exothermic)

When ice is added to the solution the equilibrium shifts right hence pink colour will remain predominant

So, correct answer is (A,B& D)

48. Ans. (B,C) **49. Ans. (A,B,D)** **50. Ans. (C)** **51. Ans.(1)**

52. Ans.(6.00)