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 $K_2SO_4 \cdot Al_2(SO)_4$, $\cdot 24H_2O$ when dissolved in water breaks down into K^+ , SO_4^{2-} , Al_4^{+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.

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.
$$K_2[Cd(CN)_4] \longrightarrow 2K^+ + [Cd(CN)_4]^{2-}$$



 $Cd^{2+} + 4CN^{-}$ (appreciably dissociated)

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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
Hg_{2}^{2+} Cu^{2+} Ag^{2+} Pt^{2+}	4	A1 ³⁺	6
l .	4	Sc ³⁺	6
Pd ²⁺ Mg 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

Based on charge

(i) Neutral ligands: H₂O, NO, CO, C₆H₆ etc.

(ii) Positive ligands : NO⁺, N₂H₅⁺ (iii) Negative ligands : Cl⁻, NO₂⁻, CN⁻, OH⁻

Based on denticity (B)

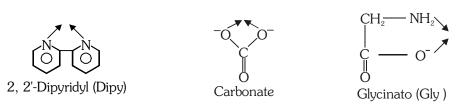
The number of electron pairs donated to central metal by a particular ligand is known as DENTICITY. Depending on number of electron pairs donated, these are classified in following categories.

(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.

Bidentate ligands (b)

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



(c) **Tridentate ligands**

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

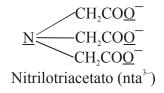
Example.



(**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)



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(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)

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)

$$\begin{array}{c} CH_2CO\underline{O}^-\\ CH_2\underline{-N} \\ CH_2CO\underline{O}^-\\ CH_2\underline{-N} \\ CH_2CO\underline{O}^-\\ CH_2\underline{-N} \end{array}$$

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:

$$\begin{bmatrix} CH_{\overline{2}}-H_{2}N & NH_{\overline{2}}-CH_{2} \\ CH_{\overline{2}}-H_{2}N & NH_{\overline{2}}-CH_{2} \end{bmatrix}^{2+}$$

(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.

$$\begin{bmatrix} \text{CN}^{-} & \begin{bmatrix} \text{NO}_{2}^{-} & \begin{bmatrix} \text{SCN}^{-} & \begin{bmatrix} \text{CNO}^{-} & \begin{bmatrix} \text{S}_{2}\text{O}_{3}^{2-} & \begin{bmatrix} \text{SeCN}^{-} \\ \text{NCO}^{-} & \end{bmatrix} \end{bmatrix} \\ \text{ONO}^{-} & \begin{bmatrix} \text{NCS}^{-} & \begin{bmatrix} \text{NCO}^{-} & \begin{bmatrix} \text{S}_{2}\text{O}_{3}^{2-} & \end{bmatrix} \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \begin{bmatrix} \text{SeCN}^{-} & \end{bmatrix} \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS}^{-2} & \begin{bmatrix} \text{NCS}^{-2} & \end{bmatrix} \\ \text{NCS$$

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.

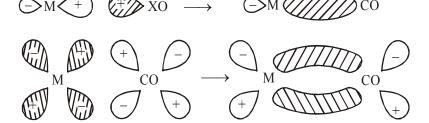
Ex.
$$SO_4^{2-}$$
, CO_3^{2-} etc.

- (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.

(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.

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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.

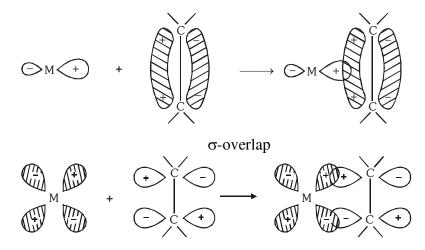
- (a) The metal-carbon bond in metal carbonyls may be represented as the donation of an electron pair from carbon to vacant orbital of metal & form σ bond (M \leftarrow CO).
- (b) A second bond is formed by back bonding sometimes called dative π -bonding. This is arises from side ways overlap of a full orbital on the metal with the empty antibonding $\pi^* p_y / \pi^* p_z$ (if x-axis is molecular axis) molecular orbital of the carbon monooxide, thus forming a π M $\xrightarrow{d\pi-p\pi}$ CO. bond ($d\pi-p\pi$ 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, NO.

Note:- π -acid ligands like PF₃, PPh₃ AsCl₃ 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 Cl₃(π -C₂H₄)]

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 :



□ 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(NH₃)₆]Cl₃ 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 \mathbf{Ex} . C_5H_5N pyridine, $(C_6H_5)_3P$ Triphenyl phosphine.

H₂N — CH₂—CH₂—NH₂ ethylene diamine.

The neutral ligands which are not named as the molecule are CO carbonyl, NO nitrosyl, H₂O Aqua, NH₃ 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	$\mathrm{O_2H}^-$	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 ₃ COO ⁻	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' NH₂—NH₃⁺ 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)₂Cl₂]Cl₂ : Dichlorobis(ethylenediamine)platinum(IV) chloride.

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- (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:** (NH₄)₂[CuCl₄]: 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)	Hexamminecobalt(III) chloride
	so metal is without any suffix	
(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)	Triamminetrichloridocobalt(III)
	So no suffix is used with metal ion	
(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) ₅ Cl] ⁺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.

$$\begin{bmatrix} OH \\ (H_2O)_4Fe & Fe(H_2O)_4 \\ NH_2 \end{bmatrix} (SO_4)_2$$

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 CoCl₃, CuSO₄ 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 referred 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 CoCl₃·5NH₃ only two of the three chlorine atoms are ionic and 5 NH₃ and one Cl form co-ordinate bonds to Co³⁺ ion.

Formula of some cobalt complexes.

Example:

	Old	New	No. of Cl ⁻ lons precipitated	Total No. of ions
(i)	CoCl ₃ · 6 NH ₃	$[Co(NH_3)_6]Cl_3$	3	4
(ii)	CoCl ₅ · 5 NH ₃	[Co(NH ₃) ₅ Cl]Cl ₂	2	3
(iii)	CoCl ₃ · 4 NH ₃	[Co(NH ₃) ₄ Cl ₂]Cl	1	2

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Complex	Modern formula	No. of Cl lons	Total number of ions
		precipitated	
PtCl ₄ . 6NH ₃	$[Pt(NH_3)_6]Cl_4$	4	5
PtCl ₄ . 5NH ₃	$[Pt(NH_3)_5 Cl]Cl_3$	3	4
PtCl ₄ . 4NH ₃	$[\mathrm{Pt}(\mathrm{NH_3}]_4\mathrm{Cl_2}]\mathrm{Cl_2}$	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) ₆ Cl ₃	H ₃ N Cl NH ₃ Fe Cl NH ₃ Cl	[Fe(NH ₃) ₆]Cl ₃ Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.
(ii)	Fe(NH ₃) ₅ Cl ₃	Cl H ₃ N NH ₃ H ₃ N Fe NH ₃ Cl	[Fe(NH ₃) ₅ Cl]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) ₄ Cl ₃	Cl H ₃ N NH ₃ H ₃ N Cl H ₃ N Cl	[Fe(NH ₃) ₄ Cl 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 transferred 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) Bohr magneton = $\frac{\text{eh}}{4\pi\text{mc}}$
- (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.

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.

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

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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	L	[HgI ₃] ⁻
4	sp ³	L 109°28' L L	$[CuCl_4]^{-2}$ $[ZnCl_4]^{-2}$ $[FeCl_4]^{-}$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{+2}$
4	$dsp^2 (d = d_{x2-y2})$	L 90° M 90° L Square planar	$[PdCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{+2}$ $[Cu(NH_3)_4]^{+2}$ $[PtCl_4]^{2-}$
5	$sp^{3}d (d = d_{z2})$ or $dsp^{3} (d = d_{z2})$	L L 200° L L L Trigonal bipyramidal	[Fe(CO) ₅] [CuCl ₅] ³⁻
5	$sp^{3}d (d = d_{x2-y2})$ or $dsp^{3} (d = d_{x2-y2})$	L L L L 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 $d_{z^2} \& d_{x^2-y^2}$.	Doctahedral	$[Cr(NH_3)_6]^{+3}$ $[Ti(H_2O)_6]^{+3}$ $[Fe(CN)_6]^{-3}$ $[Co(NH_3)_6]^{+3}$ $[PtCl_6]^{-2}, [CoF_6]^{-3}$

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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 NH₃ and H₂O) 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 $(2/5)\Delta_0$.

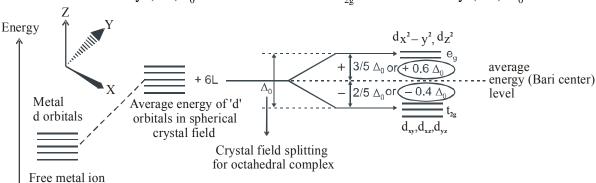


Figure showing crystal field splitting in octahedral complex.

E

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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:

$$\Gamma < Br^{-} < SCN^{-} < C\Gamma < F^{-} < OH^{-} < C_{2}O_{4}^{2-} < H_{2}O < NCS^{-} < edta^{4-} < NH_{3} < en < CN^{-} < CO$$

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 $t_{2g}^3 e_g^{-1}$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.

Crystal Field stabilising energy in Octahedral field:

Formula : CFSE =
$$[-0.4 \ n_{t_{2_{\sigma}}} + 0.6 \ n_{e_{\sigma}}] \ \Delta_0 + xP$$
.

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 $\Delta_r = (4/9)\Delta_0$. 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.

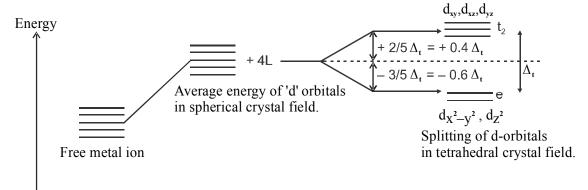


Figure showing crystal field splitting in tetrahedral complex.

Since $\Delta_{t} < \Delta_{0}$ crystal field spliting favours the formation of octahedral complexes.

Crystal Field stabilising energy in Tetrahedral field:

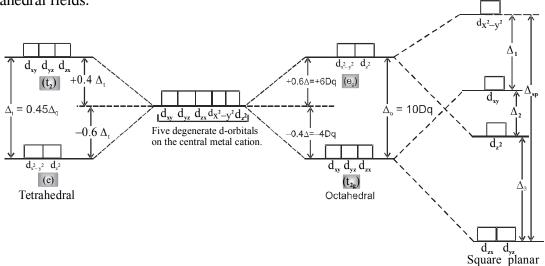
Formula : CFSE = $[-0.6 \text{ n}_e + 0.4 \text{ n}_{t_*}] \Delta_t + xP$.

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.

$$\Delta_{\rm sp} = (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_{\rm o}$$
 and $\Delta_{\rm sp} = 1.3 \Delta_{\rm o}$.

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(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:

$$\begin{split} M(H_{2}O)_{n} + L & \Longrightarrow ML(H_{2}O)_{n-1} + H_{2}O \\ K_{1} &= [ML(H_{2}O)_{n-1}] / \{[M(H_{2}O)_{n}][L]\} \\ ML_{n-1} (H_{2}O) + L & \Longrightarrow ML_{n} + H_{2}O \\ K_{n} &= [ML_{n}] / \{[ML_{n-1} (H_{2}O)] [L]\} \end{split}$$

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

 $\beta_n = K_1 \times K_2 \times K_3 \times \dots \times K_n$

 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.

K₁, K₂, K₃ 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 :

$$\Delta_{\rm t} = \frac{4}{9} \Delta_0$$

5. Presence of cheleting ligand increases CFSE:

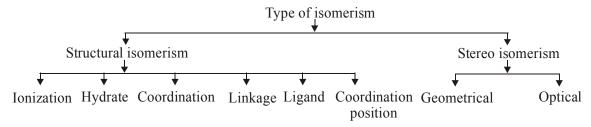
$$[Fe(Ox)_3]^{3-} > [Fe(SCN)_6]^{3-}$$

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□ 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) $Co(NH_3)_4 Br_2 SO_4$ can be represented as $[Co(NH_3)_4 Br_2] SO_4$ (red violet) and $[Co(NH_3)_4 SO_4] Br_2$ (red) These complexes give sulphate ion and bromide ion respectively

- (ii) $[Pt(NH_3)_4 Cl_2]Br_2$ 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

 $[\text{Co(NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2 \text{and} \quad [\text{Co(NH}_3)_4\text{Cl}_2]\text{Cl.H}_2\text{O}$

- (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. • $[Co(NH_3)_5NO_2]Cl_1$ and $[Co(NH_3)_5ONO]Cl_2$

- In NO₂⁻ ligand, The coordinating sites are nitrogen (i.e., NO₂⁻ 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

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

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

$$Pd$$
 Pd
 Cl
 Pd
 Pd
 Pd
 PDh_3

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.





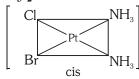
Example. [Pt (NH₃)₂Cl₂]

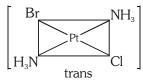
$$\begin{bmatrix} Cl & NH_3 \\ H_3N & Cl \end{bmatrix}$$
 trans

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



Example. [Pt(NH₃),ClBr]





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



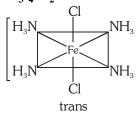


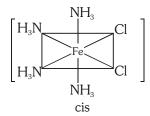


Geometrical isomers with Co-ordination number = 6

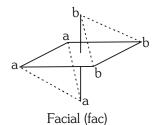
(i) Complexes with general formula $\mathbf{Ma_4b_2}$ can have cis - and trans-isomers.

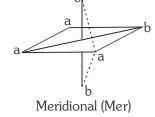
Example. [Fe(NH₃)₄Cl₂]





 $\label{eq:control} \textbf{(iii)} \quad \textbf{Facial and Meridional isomerism } (\textbf{Ma}_3\textbf{b}_3)$





Other 6-Coordinated geometrical isomers are

Note:	General formula	Total No. of geometrical isomers
	Mabcdef	15
	Ma ₂ bcde	9
	Ma_2b_2cd	6
	$Ma_2b_2c_2$	5
	Ma ₃ bcd	4
	Ma_3b_2c	3
	Ma_3b_3	2
	Ma ₄ bc	2
	Ma_4b_2	2
	Ma ₅ b	Not possible
	Ma_6	Not possible

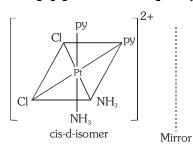
Here M = central atom a, b, c, d, e, f = Monodentate ligands

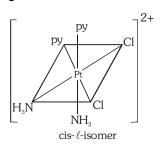
(b) **Optical isomers**

- (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.** '\ell' 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.

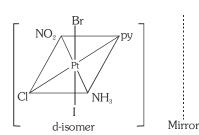
Optical isomers with Co-ordination number = 6

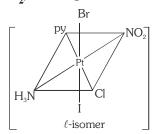
(i) $[Ma_2b_2c_2]^{n+} \rightarrow [Pt(py)_2(NH_3)_2Cl_2]^{2+}$



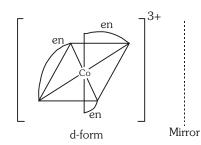


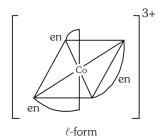
(ii) [Mabcedf] \rightarrow [Pt(py) (NH₃) (NO₂) ClBrI]





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





Formula	Number of stereoisomers	Pairs of Enantiomers
$M_{a_4b_2}$	2	0
$M_{a_3b_3}$	2	0
M_{a_4bc}	2	0
${ m M}_{ m a_3bcd}$	5	1
M _{a2bcde}	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: 0-1

SINGLE OPTION CORRECT:

Double salt and complex compound

- Some salts although containing two different metallic elements give test for one of them in solution. 1. Such salts are
 - (A) complex salt
- (B) double salt
- (C) normal salt
- (D) none of these **CC0001**
- Aqueous solution of FeSO₄ gives tests for both Fe²⁺ and SO ²⁻₄ but after addition of excess of KCN, 2. solution ceases to give test for Fe²⁺. This is due to the formation of
 - (A) the double salt FeSO₄.2KCN.6H₂O
- (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

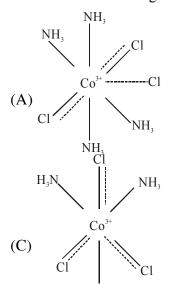
(D) a and b are correct

CC0003

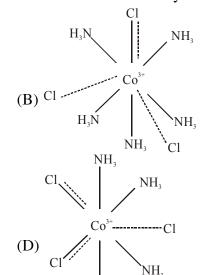
- 4. A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is:
 - (A) $[Pt(NH_3)_4]Cl_4$
- (B) $[Pt(NH_3)_2Cl_4]$
- (C) $[Pt(NH_3)_5Cl]Cl_3$ (D) $[Pt(NH_3)_4Cl_2]Cl_2$

CC0004

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



NH,



NH,

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 invo			
	(A) ferrocene (B) di	benzene chromium	(C) Zeise's salt	(D) Grignard reagent
				CC0007
8.		ng is not considered as	_	•
	(A) Ferrocene	(B) Cis-platin	(C) Ziese's salt	(D) Grignard reagent
0	Diathylana triamina	:		CC0008
9.	Diethylene triamine (A) Chelating agent	18.	(B) Polydentate ligar	ad.
	(C) Tridentate ligand	ı	(D) All of these	CC0009
10.	, ,	ng species is not expec		CC0007
10.			C	
	(A) NO ⁺	(B) NH_4^+	$(C) NH_2 - NH_3^+$	(D) CO CC0010
11.	The disodium salt of ion(s) in the aqueous	•	raacetic acid can be us	sed to estimate the following
	(A) Mg^{2+} ion	(B) Ca ²⁺ ion	(C) Na ⁺ ion	(D) both Mg^{2+} and Ca^{2+}
				CC0011
12.	Which of the follow	ing ligand does not a	et as bidentate ligand	
	(A) dipy	(B) dien	(C) gly -	(D) dmg ⁻ CC0012
		Synergic	bonding	
13.	Which of the follow	ing order is correct for	or the IR vibrational f	requency of CO.
	(A) $[Fe(CO)_4]^{2-} < [CO]_4$	$Co(CO)_4^- < [Ni(CO)_4^-]$	(B) $[Fe(CO)_4]^{2-} > [C$	$o(CO)_4^- > [Ni(CO)_4^-]$
	(C) $[Fe(CO)_4]^{2-} > [C$	$\text{Co(CO)}_4]^- < [\text{Ni(CO)}_4]$	(D) $[Fe(CO)_4]^{2-} < [CO]_4$	$\text{Co(CO)}_4]^- > [\text{Ni(CO)}_4]$
				CC0013
14.	In the isoelectronic se order.	eries of metal carbonyl,	the C–O bond strength	n is expected to increase in the
	$(A) \left[Mn(CO)_6 \right]^+ < \left[0$	$\operatorname{Cr(CO)}_{6}] < [\operatorname{V(CO)}_{6}]^{-}$	$(B) [V(CO)_6]^- < [Cr($	$(CO)_6] \leq [Mn(CO)_6]^+$
	$(C) [V(CO)_6]^- < [Mnc$	$(\mathrm{CO})_6]^+ < [\mathrm{Cr}(\mathrm{CO})_6]$	(D) $[Cr(CO)_6] < [M]$	$[\mathrm{N}(\mathrm{CO})_6]^+ < [\mathrm{V}(\mathrm{CO})_6]^-$
				CC0014
15.		ing has higher stretch		
	(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) $[Co(CO)_4]^-$	(B) $[Co(CO)_4]^-$					
	(C) $[Fe(CO)_4]^{2-}$						
	(D) (B) and (C) bot	th 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 n	umber and E.A.N.				
18.	8. 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	ng statement is correct	regarding the compour	$nd " [(CO)_3 Fe(CO)_3 I$	$Fe(CO)_3$]".		
	(A) The d_{C-O} (bridge	ging) is greater than d	l _{C-O} (terminal)				
	(B) The bond order	of bridging C – O bo	ond is greater than tha	t of terminal C – C	bond		
	(C) The E.A.N. val	ue 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				by		
	(A) Oxidation of Co (B) Reduction of Co						
	(C) Dimerization		(D) Both (B) & (C)				
22.	In the complex Fe(C	$(CO)_x$, 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 a	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 con	nplex compound				
25.	The IUPAC name for the coordination compound $Ba[BrF_4]_2$ is						
	(A) Barium tetrafluo	orobromate (V)	(B) Barium tetrafluorobromate (III)				
	(C) Barium bis (tetr	rafluorobromate) (III)	(D) none of these CC0025				
26.	The number of ions water will be	formed, when bis (eth	ane-1,2-diamine) copp	er (II) sulphate is di	ssolved in		
	(A) 1	(B) 2	(C) 3	(D) 4	CC0026		

- 27. The IUPAC name of the Wilkinson's catalyst [Rh Cl (P Ph₃)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(NH₃)₄] [PtCl₄]
 - (A) It is the polymerisation isomer of [Pt(NH₃)₃Cl₃]
 - (B) E.A.N. of cationic part is equal to that of anionic part
 - (C) It is the co-ordination isomer of [Pt(NH₃)₃Cl] [Pt(NH₃)Cl₃]
 - (D) Synergic bonding is not involved in the complex

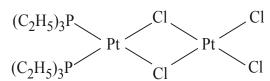
CC0029

- **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:

$$Cl$$
 Pt
 Cl
 Pt
 Cl
 $P(C_2H_5)_3$
 Pt
 Cl
 $P(C_2H_5)_3$



(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(NH₃)₆]Cl₃

(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 CrCl₃.6H₂O, 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) $[Ni(dmg)_{\gamma}]^{o}$

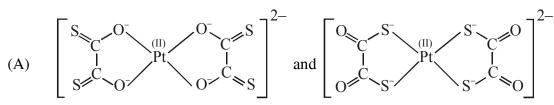
CC0034

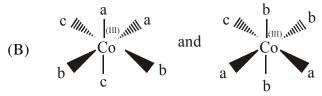
- 35. How many coordination isomers of [Pt(NH₃)₄][PtCl₄] show geometrical isomerism.
 - (A) All

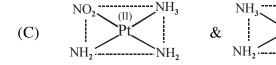
- (B) One
- (C) Two
- (D) None

CC0035

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







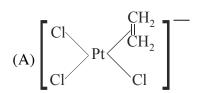
CC0036

- (D) All of the above
- 37. Find complex which have maximum number of stereoisomers -
 - $(A) [Ma_2b_2]$
- (B) $[Ma_3b_3c]$
- (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, [NiCl₂Br₂]²⁻
 - (D) $[Co(NO_3)_3 (NH_3)_3]$, cis- $[Pt(en)_2Cl_2]$

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



(B)
$$\begin{bmatrix} Cl & Cl \\ Cl & Cl \end{bmatrix}^{2-}$$

(C)
$$H_3N$$
 Pt Cl H_3N Cl

(D)
$$\begin{bmatrix} H_3N & Cl \\ Cl & NH_3 \end{bmatrix}$$

CC0039

Which of the following can exhibit geometrical isomerism? **40.**

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

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

 $\text{(C)} \; [\text{PtCl}_2(\text{P(C}_2\text{H}_5)_3)_2]$

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

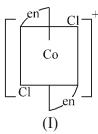
CC0040

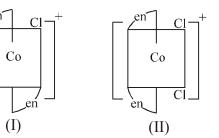
The oxidation state of Mo in its oxo-complex species $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$ is: 41.

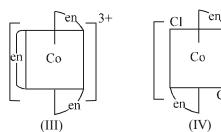
- (A) + 2
- (B) +3
- (C) +4

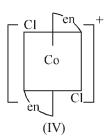
CC0041

42. Which of the following ions are optically active?





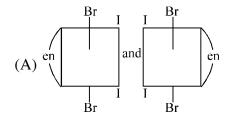


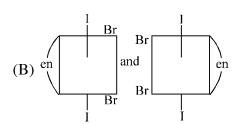


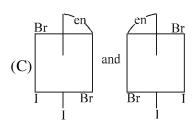
- (A) I only
- (B) II only
- (C) II and III
- (D) IV only

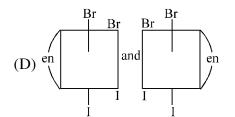
CC0042

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









CC0043

node06\B0B0-BA\Kota\LEE(Advanced)\Lecder\Che\Sheen\Co-ordination Chemistry\Eng\Theory+Ex.p6

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 ³ d	(D) sp^3	CC0045
46.	One unknown comp	lex has the spin only m	nagnetic moment is of	1.73 BM. As per th	e C. F. T.,
	complexe is.				
		h Srong Feild Legand		d, with Srong Feild	_
		Weak Feild Legand			CC0046
47.	-	species which has max	_		
	(A) [CuCl4]2-	(B) $[CoCl_4]^{2-}$	(C) [FeCl ₄] ²⁻	(D) [AlCl ₄] ⁻	CC0047
48.	In the co-ordination	compound Na ₄ [Fe(Cl	N) ₅ NOS] oxidation sta	ate of Fe is -	
	(A) +1	(B) +2	(C) +3	(D) +4	CC0048
49.	Which one of the fo	ollowing complex is	an outer orbital comp	lex -	
	(A) $[Ni(H_2O)_6]^{+2}$		(B) $[Fe(H_2O)_5NO]SO$	O_4	
	(C) $[Fe(NH_3)_6]^{+2}$		(D) All of these		CC0049
50.	Which of the follow	ing is diamagnetic and	sp³ 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				ORRECT
	distribution of 3d electrons in the chromium present in the complex is:				
	(A) $3d_{xy}^1$, $3d_{yz}^1$, $3d_{zz}^1$		(B) $3d_{xy}^1$, $3d_{yz}^1$, $3d_{z}^1$		
	(C) $3d_{(x^2-y^2)}^1$, $3d_{z^2}^1$, 3	d_{xz}^1	(D) $3d_{xy}^1, 3d_{(x^2-y^2)}^1, 3d_{yz}^1$		CC0051
52.	[Fe(H ₂ O) ₆] ⁺² has Crystal Field Splitting Energy value 10,400 cm ⁻¹ and pairing energy value			ergy value	
	17,600 cm ⁻¹ then it is:				
	(A) Low spin complex		(B) Paramagnetic in	/Eng/Theon	
	(C) Diamagnetic in	n nature	(D) None of these		CC0052
53.	In which of the following coordination entities, the magnitude of Δ_0 [CFSE in octahedral field]			edral field]	
	will be maximum?:				
	(A) $[Co(CN)_6]^{3-}$		(B) $[Co(C_2O_4)_3]^{3-}$		Normord)\Lex
	(C) $[Co(H_2O)_6]^{3+}$		(D) $[Co(NH_3)_6]^{3+}$		CC0053
54.		ired electrons calculate		-	CC0052 edral field] CC0053 CC0054 CC0054
	(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	(A) Green, blue and red		(B) Blue, red and green	
	(C) Green, red and b	lue	(D) Red, blue and gr	een	CC0055
56.	Formula of ferrocen	e is:			
	(A) $[Fe(CN)_6]^{4-}$	(B) $[\text{Fe}(\text{CN})_6]^{3+}$	$(C) [Fe(CO)_5]$	(D) $[Fe(C_5H_5)_2]$	
					CC0056
57.	Ni(CO) ₄ and [Ni(NH ₃) ₄] ²⁺ do not differ in				
	(A) magnetic mome	nt	(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 complet the same metal with same oxidation state has zero magnetic moment. The metal ion could			_	
	(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 ion	as 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 aqueous solution				formed in
	$(A) VO_2^+$	(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 satisformula, $[NiCl_2(NH_3)_2]$ are obtained, I can be converted into II by boiling with dilute HCl solution of I reacts with oxalic acid to form $[Ni(C_2O_4)(NH_3)_2]$ wheras II does not react. Pour out the correct statement of the following			te HCl. A	
	(A) I cis, II trans; bo	oth tetrahedral	(B) I cis, II trans; both square planar		
	(C) I trans, II cis; both tetrahedral (D) I trans, II cis; both so		th square planar	CC0061	
62.	Among the followin	g, the compound that i	t is both paramagnetic and coloured is		
	$(A) K_2 Cr_2 O_7$	(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 com $(X = \text{monodentate anionic ligand})$.			olex ion is	
	(A) sp ³ hybridised	(B) spd ² hybridised	(C) dsp ² hybridised	(D) d ² sp hybridise	d

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

- $(A) d^3$
- (B) d^4
- (C) d⁵
- (D) d^{6}

CC0064

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

- (A) d^6 , strong field (B) d^7 , high spin
- (C) d^4 , weak field
- (D) d², strong field

CC0065

66. Select appropriate ligand for given complex

 $[\overset{\text{III}}{\text{Co}}(.....)_{6}]^{\pm x}$; $\mu = 0 \text{ BM}$

- $(A) C_2 O_4^{2-}$
- (B) en
- (C) H₂O
- (D) F

CC0066

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

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

CC0067

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

- (A) 3d
- (B) t_{2g}^1 , e_g^0

(C) t_{2g}^1 , e_g^1

(D) t_{2g}^0 , e_g^1

CC0068

If $\lambda_{absorbed}$ for d-d transition is in order $[\mathrm{Ti}(X)_6]^{3+} > [\mathrm{Ti}(Y)_6]^{3+} > [\mathrm{Ti}(Z)_6]^{3+}$. **69.**

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

EXERCISE: 0-2

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) Ma₂b₂ (Sq. Pl.)
- (B) Ma_4b_2
- (C) Ma₅b
- (D) Ma₆

CC0070

- **2.** Which of the following statement(s) is (are) **CORRECT** ?
 - (A) The oxidation state of iron in sodium nitroprusside Na₂[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?
 - $\mathrm{(A)}\left[\mathrm{Cr}(\mathrm{NO_3})_3\mathrm{(NH_3)_3}\right]$

(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)
- $(C) \qquad [\mathrm{Be}(\mathrm{CH_3}\text{-}\mathrm{CO}\text{-}\mathrm{CH_2}\text{-}\mathrm{CO}\text{-}\mathrm{C}_6\mathrm{H}_5)_2]^\circ$
- 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

8. Which of the following complexes are polymerisation isomers:

(A)
$$\left[(NH_3)_3 \text{ Co} \underbrace{OH}_{OH} \text{Co} (NH_3)_3 \right]^{3+}$$
 and $\left[Co \underbrace{OH}_{OH} \text{Co} (NH_3)_4 \right]_3 \right]^{6+}$

- (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(NH₃)₂]⁺ is linear with sp hybridised Ag⁺ ion
 - (B) NiCl₄²⁻, VO₄³⁻ and MnO₄ 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) $\begin{bmatrix} Ni L_4 \end{bmatrix}$
- (B) [Ni L_6]
- (C) [Fe L₆]
- (D) $[\operatorname{Cr} L_6]$

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

- **14.** Which of the following ion is/are diamagnetic and non planar?
 - (A) $[Ni(CN)_4]^{2-}$
- (B) MnO₄
- (C) $[Cu(NH_3)_4]^{2+}$
- (D) CrO₄²⁻
- CC0083

EXERCISE: S-1

INTEGER TYPE

1. Find number of ligands which is / are stronger ligand as compared to NH₃

$$NO_{2}^{-}$$
, $H_{2}O$, NO_{3}^{-} , F^{-} , $C_{2}O_{4}^{2-}$, en, Cl^{-} , $\overline{C}N$

CC0084

2. If crystal field stablization energy of $[ML_6]^{+n}$ is $-0.8 \Delta_0$.

Find minimum number of electrons in t_{2g} orbitals of metal ion ?

CC0085

3. Find number of Co-N linkage in,

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

CC0086

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 :

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.

2.

EXERCISE: S-2

MATCH THE COLUMN:

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

Column-I

- (A) $[Fe(CO)_4]^{2-}$
- (B) $[Co(NH_3)_5Cl]Cl_2$
- (C) $K_2[Ni(CN)_4]$
- (D) $[Cu(NH_3)_4]^{2+}$
 - Column I
- (A) Na₂ [Fe(CN)₅ NO]
- (B) $[Fe(H_2O)_5 NO] SO_4$
- (C) $[Ag(CN)_2]^-$
- (D) $K_4[Fe(CN)_6]$

Column-II

- (P) 34
- (Q) 35
- (R) 36
- (S) 37

Column -II

- (P) $\mu = 0 \text{ B.M.}$
- (Q) octahedral
- (R) $\mu = \sqrt{15} \, \text{B.M.}$
- (S) NO⁺ ligand

Has a facial isomer

CC0095

CC0094

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

(P)

Column I

- (A) $[CoCl_3(NH_3)_3]$
- (B) $[Cr(ox)_3]^{3-}$
- (C) $[CrCl_2(ox)_2]$
- (D) $[RhCl_3(Py)_3]$

Column II

- (Q) Cis form is optically active
- (R) Trans form is optically inactive
- (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

- (P) $[Co(en)_3]^{3+}$
- (Q) [Ca(EDTA)]2-
- $(R) [Ni(CO)_{4}]$
- (S) $[Ag(NH_3)_2]Cl$

List-II

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

CC0097

Code:

- P
- (A) 2
- (B) 1 1
- (C) 1 (D) 1
- 4

O

1

- 1
- 2 2

3

R

2

- 3 2

 \mathbf{S}

3

3

List-I

- (P) Ferrocene
- $(Q) \operatorname{Mn}_{2}(CO)_{10}$
- (R) Vitamine B₁₂
- (S) Haemoglobin

List-II

- (1) Iron present
- (2) Cobalt
- (3) Metal-Metal bonding
- (4) Sandwich structure

CC0098

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

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

List-I

- (P) EDTA⁴-
- (Q) en
- (R) gly-
- (S) amide

List-II

- (1) N-donor atom
- (2) Chelate ligand with same donor site
- (3) Bidentate with different donor atom
- (4) Hexadentate CC0099

Code:

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

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(NH₃)₄Cl₂]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.

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ALLEN

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 M³⁺ 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 NH₃ 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

- 15. In which of the following pairs, both the complexes have the same geometry but different hybridisation
 - (A) [NiCl₄]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 $1 \times 3Q$. (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) $-0.4 \Delta_0$	(i) t_{2g}^{5}, e_{g}^{0}	(P) High spin & Paramagnetic
(II) $-2.0 \Delta_{\rm o}$	(ii) t_{2g}^{4} , e_{g}^{0}	(Q) Low spin & Paramagnetic
(III) $-2.4 \Delta_{\rm o}$	$(iii) t_{2g}^6, e_g^0$	(R) High spin & Diamagnetic
(IV) –1.2 Δ_{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)

EXERCISE: JEE-MAIN

In $[Cr(C_2O_4)_3]^{3-}$, th	e isomerism shown is	-	[,	AIEEE-2002]
(1) Ligand	(2) Optical	(3) Geometrical	(4) Ionizatio	n
				CC0112
In the complexes [F by -	$[Fe(H_2O)_6]^{3+}, [Fe(SCN)_6]$	$^{3-}$, $[Fe(C_2O_4)_3]^{3-}$ and $[Fe(C_2O_4)_3]^{3-}$		oility is shown AIEEE-2002]
(1) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	(2) $[Fe(SCN)_6]^{-3}$	(3) $[Fe(C_2O_4)_3]^{3-}$	(4) [FeCl ₆] ³⁻	CC0113
One male of the co	mpley compound Co(N	H) Cl. gives 3 moles (of ions on dissolu	
				AIEEE-2003]
_	_			
		J	2	CC0114
3 4	2 9	3 3	-	
				CC0115
	• •	` '	` ,	
(1) 4	(2) 5	(3) 6	(4) 3	CC0116
Ammonia forms the	e complex ion [Cu(NH ₂	$(a,b)_4$ ²⁺ with copper ions	in alkaline soluti	ons but not in
		•		AIEEE-2003]
(1) In acidic soluti	ons hydration protects	copper ions		
(2) In acidic solution	ons protons coordinate	with ammonia moleculo	es forming NH ₄	ions and NH,
			.	3
		is precipitated which is	s soluble in exces	s of any alkali
				CC0117
	-		the set of proper	
CN ⁻ ion towards m	netal species is :-		[/	AIEEE-2004]
(1) c, a	(2) b, c	(3) a, b	(4) a, b, c	CC0118
The coordination nu	imber of a central metal	atom in a complex is de	etermined by :- [A	AIEEE-2004]
(1) The number of	ligands around a meta	l ion bonded by sigma	and pi-bonds be	oth
(2) The number of	ligands around a meta	l ion bonded by pi-bor	nds	· -
(3) The number of	ligands around a meta	l ion bonded by sigma	bonds	† *
(4) The number of	only anionic ligands b	onded to the metal ior	1	CC0119
(+) The number of				
	following complexes is	an outer orbital comp	olex :- [A	AIEEE-2004]
Which one of the	Following complexes is (2) $[Mn(CN)_6]^{4-}$	-	_	AIEEE-2004]
Which one of the function $(1) \left[\text{Co(NH}_3)_6 \right]^{3+}$		(3) $[Fe(CN)_6]^{4-}$	_	_ {
	In the complexes [F by - (1) [Fe(H ₂ O) ₆] ³⁺ One mole of the correction of the same and the same and the same and the correction of the same and the same an	In the complexes [Fe(H ₂ O) ₆] ³⁺ , [Fe(SCN) ₆] by - (1) [Fe(H ₂ O) ₆] ³⁺ (2) [Fe(SCN) ₆] ⁻³ One mole of the complex compound Co(N One mole of the same complex reacts with AgCl(s). The structure of the complex is (1) [Co(NH ₃) ₃ Cl ₃].2NH ₃ (3) [Co(NH ₃) ₄ Cl]Cl ₂ .NH ₃ In the coordination compound K ₄ [Ni(CN) (1) 0 (2) +1 The number of 3d-electrons remained in 10 (1) 4 (2) 5 Ammonia forms the complex ion [Cu(NH ₃ acidic solution. What is the reason for it (1) In acidic solutions hydration protects (2) In acidic solutions protons coordinate in 10 (3) In alkaline solutions insoluble Cu(OH) ₂ (4) Copper hydroxide is an amphoteric standard in 10 (3) In alkaline solutions insoluble Cu(OH) ₂ (4) Copper hydroxide is an amphoteric standard in 10 (5) The coordination number of a central metal (6) The number of ligands around a metal (7) The number of ligands around a metal	In the complexes [Fe(H ₂ O) ₆] ³⁺ , [Fe(SCN) ₆] ³⁻ , [Fe(C ₂ O ₄) ₃] ³⁻ and [Fe by - (1) [Fe(H ₂ O) ₆] ³⁺ (2) [Fe(SCN) ₆] ⁻³ (3) [Fe(C ₂ O ₄) ₃] ³⁻ One mole of the complex compound Co(NH ₃) ₅ Cl ₃ , gives 3 moles on the complex of the same complex reacts with two moles of AgNO ₃ AgCl(s). The structure of the complex is - (1) [Co(NH ₃) ₃ Cl ₃].2NH ₃ (2) [Co(NH ₃) ₄ Cl ₂]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₂]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₂]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₂]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₂]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₂]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₃]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₃ Cl ₃]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₃ Cl ₃]C(s) [Co(NH ₃) ₄ Cl ₃ Cl ₃ Cl ₃]C(s) [Co(NH ₃) ₄ Cl ₃	In the complexes $[Fe(H_2O)_6]^{3+}$, $[Fe(SCN)_6]^{3-}$, $[Fe(C_2O_4)_3]^{3-}$ and $[FeCl_6]^{3-}$, more state by - [A (1) $[Fe(H_2O)_6]^{3+}$ (2) $[Fe(SCN)_6]^{-3}$ (3) $[Fe(C_2O_4)_3]^{3-}$ (4) $[FeCl_6]^{3-}$ One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolutions on the same complex reacts with two moles of AgNO3 solution to yield AgCl(s). The structure of the complex is - [A (1) $[Co(NH_3)_3Cl_3].2NH_3$ (2) $[Co(NH_3)_4Cl_3]Cl.NH_3$ (3) $[Co(NH_3)_4Cl]Cl_2.NH_3$ (4) $[Co(NH_3)_5Cl]Cl_2$ In the coordination compound $K_4[Ni(CN)_4]$, the oxidation state of nickel is - [A (1) 0 (2) +1 (3) +2 (4) -1 (4) -1 (4) (2) 5 (3) 6 (4) 3

(3) $[NiCl_4]^{2-}$

(3) 4 and 3

The coordination number and the oxidation state of the element 'E' in the complex

(4) $[PtCl_4]^{2-}$

(4) 6 and 3

CC0129

CC0130

[AIEEE-2008]

19.

(1) [CoCl₄]²⁻

(1) 6 and 2

(2) $[FeCl_4]^{2-}$

(2) 4 and 2

 $[E(en)_2(C_2O_4^{-2})]$ NO₂ (where (en) is ethylene diamine) are, respectively -

bromide?

(1) $[Cr(en)Br_2]Br$

(2) $[Cr(en)_3]Br_3$

20.	. In which of the following octahedral comple	xes 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 link	age isomers ?	[AIEEE-2009]
	(1) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]N$	NO_3	
	(2) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$	J	
	(3) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$	₄]	
	(4) [Pd (PPh ₃) ₂ (NCS) ₂] and [Pd(PPh ₃) ₂ (SC	$N)_2$	CC0132
22.	. Which of the following has an optical isom	er?	[AIEEE-2009]
	(1) $[Co(H_2O)_4(en)]^{3+}$ (2) $[Co(en)_2(NH)^{3+}]$	$[(3)_2]^{3+}$ (3) $[Co(NH_3)_3C]$	$[Co(en)(NH_3)_2]^{2+}$
			CC0133
23.	• Which one of the following has an optical	isomer ?	[AIEEE-2010]
	(1) $[Zn(en)_2]^{2+}$ (2) $[Zn(en)(NH_3)_2]^{2+}$		(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 i	n solution were treated v	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 $Ag = 108 \text{ u}$)		
	(1) $[CoCl(NH_3)_5]Cl_2$ (2) $[Co(NH_3)_6]Cl_3$	(3) [CoCl2(NH3)4]Cl	(4) [CoCl3(NH3)3]
			CC0135
25.	. Which of the following facts about the com	plex $[Cr(NH_3)_6]Cl_3$ is	wrong? [AIEEE-2011]
	(1) The complex is an outer orbital comple	X	
	(2) The complex gives white precipitate wi		
	(3) The complex involves d ² sp ³ hybridisation	on 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 the	neir increasing field strength,
	is:-		[AIEEE-2011]
	(1) $CO < NH_3 < en < CN^-$	(2) $NH_3 < en < CN^-$	
	(3) $CN^- < NH_3 < CO < en$	(4) en $<$ CN $^ <$ NH $_3$	
28.	e i	_	
	(1) $[\text{Co (en)}_3]^{3+}$ (2) $[\text{Ni (NH}_3)_5\text{Br}]^+$	(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 (ethyle	ene diamine) chromium (III)

 $(3) [Cr(en)_2Br_2]Br$

 $(4) [Cr(en)Br_4]^-$

30.	The complex ion			
	[Pt(NO ₂) (Py) (NH ₃) (NH ₂ OH)]+ will giv	e:-	[J-MAIN-2012, Online]
	(1) 4 isomers (Geor	metrical)	(2) 2 isomers (Geon	netrical)
	(3) 3 isomers (Geor	metrical)	(4) 6 isomers (Geon	netrical) CC0141
31.	Which of the follow	ring complex ions will	l exhibit optical isomerisi	m? [J-MAIN-2012, Online]
	(en = 1, 2-diamine	ethane)		
	(1) [Co(en)2Cl2]+	(2) $[Zn(en)_2]^{2+}$	(3) $[Co(NH_3)_4Cl_2]^+$	(4) $[Cr(NH_3)_2Cl_2]^+$
				CC0142
32.	Which of the follow	ving complex species	is NOT expected to exh	ibit 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) $(NH_3)_2C$	l ₂]+ CC0143
33.	Type of isomerism	which exists between	$[Pd(C_6H_5)_2(SCN)_2]$ and	[J-MAIN-2013, Online]
	$[Pd(C_6H_5), (NCS)_2]$	is:	0 3 2 2	
	(1) Solvate isomeris		(2) Ionisation isome	rism
	(3) Linkage isomeri	ism	(4) Coordination iso	merism CC0144
34.	Which of the follow	ving is diamagnetic?		[J-MAIN-2013, Online]
	(1) $[CoF_6]^{3-}$	(2) $[FeF_6]^{3-}$	(3) $[\text{Fe}(\text{CN})_6]^{3-}$	(4) $[Co(Ox)_3]^{3-}$
	Ů	Ţ	v	CC0145
35.	The magnetic mome	nt of the complex anio	$n [C_r^I(NO) (NH_3) (CN)_4]^{2-1}$	is:[J-MAIN-2013, Online]
	(1) 2.82 BM	(2) 5.91 BM	3 1	(4) 3.87 BM CC0146
36.	The octahedral comp	olex of a metal ion M ³⁺	with four monodentate lig	ands L_1 , L_2 , L_3 and L_4 absorb
	wavelength in the re	egion of red, green, y	ellow and blue, respectiv	ely. The increasing order of
	ligand strength of the	he four ligands is:		[J-MAIN-2014]
	$(1) L_3 < L_2 < L_4 < 1$	$L_1 (2) L_1 < L_2 < L_4 <$	$L_3 (3) L_4 < L_3 < L_2 < I$	L_1 (4) $L_1 < L_3 < L_2 < L_4$
				CC0147
37.	The equation which	is balanced and represe	ents the CORRECT prod	uct (s) is: [J-MAIN-2014]
	(1) $[Mg(H_2O)_6]^{2+}$ +	(EDTA)4- excess NaOH	$\rightarrow [Mg(EDTA)]^{2+} + 6H_2$	O
	- •	$\rightarrow K_2[Cu(CN)_4] + K_2$	_	
	(3) $\text{Li}_2\text{O} + 2\text{KCl} \rightarrow$		· •	
	-	_		CC0140
20	3.3	$-5H^+ \rightarrow Co^{2+} + 5NH_4^+$		CC0148
38.			,	$_{5}]^{3-}$ and $[FeF_{6}]^{3-}$ is : $(Z = 26)$.
	· ·	paramagnetic, [FeF ₆] ³ -	is diamagnetic.	[J-MAIN-2014, Online]
	(2) both are diamag			
	· ·	diamagnetic, [FeF ₆] ^{3–}	is paramagnetic.	000440
20	(4) both are parama	~		CC0149
39.	=	olex of Co ³⁺ is diamag	gnetic. The hybridisation	involved in the formation of
	the complex is:			[J-MAIN-2014]

(3) dsp²

(4) sp^3d^2

CC0150

 $(2) dsp^3d$

 $(1) d^2sp^3$

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40.	Which of the following Formula	g name formula combina	ations is NOT CORREC ' Name	Τ? [J-MAIN–2014, Online]
	(1) $K[Cr(NH_3)_2Cl_4]$			Tetrachlorochromate (III)
	(2) $[Co(NH_3)_4(H_2O)]$	SO		do cobalt (III) sulphate
	(3) $[Mn(CN)_5]^{2-}$	\mathcal{O}_4	Pentacyanomagnate (, , <u>*</u>
	(4) $K_2[Pt(CN)_4]$		Potassium tetracyano	· · · ·
41.	- · · · · · · · · · · · · · · · · ·	tion compound [Co(NI	=	n of this complex, the species
71.	which acts as the Le		113)61C13. III tile 101111atio	[J-MAIN-2014, Online]
	(1) $[Co(NH_3)_6]^{3+}$		(3) Co ³⁺	(4) Cl ⁻ CC0152
42.	2 0	2		est CFSE, Δ_0 as a ligand
	is:-	ing species the one v	which causes the high	[J-MAIN–2014, Online]
	(1) CN ⁻	(2) NH ₃	(3) CO	(4) F^{-} CC0153
43.		3	• •	t? [J-MAIN-2014, Online]
		= 22, V = 23, Zn = 30		[6 :::::::]
	(1) [Ti (NH ₂) ₂] ⁴⁺	(2) $[V(NH_a)_c]^{3+}$	(3) $[\text{Zn (NH}_3)_6]^{2+}$	(4) [Sc $(H_2O)_c$] ³⁺
	(-) [(3/61	(=) [((3)6]	(=) [=== (= ===3/6]	CC0154
44.	Nickel(Z = 28) comb	ines with a uninegative	monodentate ligand to	form a diamagnetic complex
		_	_	etrons present in the complex
	are respectively:		•	[J-MAIN-2014, Online]
	$(1) \text{ sp}^3, \text{ zero}$	(2) sp ³ . two	(3) dsp ² one	(4) dsp ² , zero CC0155
45.	The number of geome	_	_	t (Cl) (py) (NH ₃) (NH ₂ OH)]+
	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) $L \rightarrow M$ charge to	ransfer transition	(2) $\sigma - \sigma^*$ transition	ı
	(3) $M \rightarrow L$ charge to	ransfer transition	(4) d – d transition	CC0157
47.	Which of the following	ng complex ions has ele	ectrons that are symmetric	cally 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.				colour changes from reddish
	•	hich complex ion give	es blue colour in this re	
	(1) $[Co(H_2O)_6]^{2+}$		(2) $[CoCl_6]^{3-}$	[J-MAIN-2015, Online]
	(3) $[CoCl_4]^{2-}$		(4) [CoCl ₆] ⁴⁻	CC0159
49.		tement on the isomeris	sm associated with the f	following complex ions,
	(a) $[Ni(H_2O)_5NH_3]^{2+}$	2.		[J-MAIN-2015, Online]
	(b) [Ni(H ₂ O) ₄ (NH ₃) ₂]			
	(c) $[Ni(H_2O)_3(NH_3)_3]$		1	
		geometrical and optic		
		geometrical and optic		
		only geometrical Ison		CC0160
5 0		only geometrical Ison		CC0160
50.		nowing complexes sno	ows optical isomerism:	- [J-MAIN-2016]
	(1) $[Co(NH_3)_4Cl_2]Cl$	1	(2) $[Co(NH_3)_3Cl_3]$	Cl
	(3) $\operatorname{cis}[\operatorname{Co}(\operatorname{en})_2\operatorname{Cl}_2]\operatorname{C}$		(4) trans[$Co(en)_2Cl_2$]	
	(en = ethylenediamir	1C)		CC0161

Ε

51.	The pair having the same magnetic momen		[J-MAIN-2016]
	[At. No.: $Cr = 24$, $Mn = 25$, $Fe = 26$, $Co = (1)$		ra al 12
	. 2 0	(2) $[Cr(H_2O)_6]^{2+}$ and	•
52.	(3) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ Which one of the following complexes will		- 0
J 4.	Ag(NO_3)?	consume more equivar	[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 ₂ O) ₅ Cl]Cl ₂
	3. 2 . 3	, , J- U-	CC0163
53.	Identify the CORRECT trend given below	:	[J-MAIN-2016, Online]
	(Atomic No.= Ti : 22, Cr : 24 and Mo : 42	<i>'</i>	
	(1) Δ_0 of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$		
	(2) Δ_0 of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$		
	(3) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$		_ ~
	(4) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$	and Δ_0 of [11(H ₂ O) ₆] ³	$^{+} < [11(H_{2}O)_{6}]^{2+}$ CC0164
54.	[Co ₂ (CO) ₈] displays:-		[J-MAIN-2017, Online]
J-1.	(1) no Co-Co bond, four terminal CO and t	four bridging CO	
	(2) one Co-Co bond, six terminal CO and t		
	(3) no Co–Co bond, six terminal CO and ty		
	(4) one Co-Co bond, four terminal CO and	0 0	CC0165
55.			
33.	On treatment of 100 mL of 0.1 M solution of are precipitated. The complex is:-	1 COCI ₃ . OII ₂ O with ext	[J-MAIN-2017, Offline]
	(1) $[Co(H_2O)_4 Cl_2]Cl.2H_2O$	(2) $[Co(H_2O)_3Cl_3].3H$	
	(3) [Co(H ₂ O) ₆]Cl ₃	(4) $[Co(H_2O)_5Cl]Cl_2$.	_
56.	The pair of compounds having metal in their		2
	(1) $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$	(2) $[Fe(CN)_6]^{3-}$ and [
	(3) $[FeCl_4]^-$ and Co_2O_3	(4) MnO ₂ and CrO ₂ C	•
57.	The oxidation states of Cr in $[Cr(H_2O)_6]$. , , , , , , , , , , , , , , , , , , ,	2
	respectively are:	213,[21(26216)2], and 11	[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 statem	ents:	[J-MAIN-2018, Offine]
	$[\text{Co(NH}_3)_4\text{Br}_2]^+ + \text{Br}^- \rightarrow [\text{Co(NH}_3)_3\text{Br}_3] + \text{N}_3$	NH ₃	
	(I) Two isomers are produced if the reactar		-isomer.
	(II) Two isomers are produced if the reacta	•	
	(III) Only one isomer is produced if the rea	-	
	(IV) Only one isomer is produced if the rea	-	
	The correct statements are:	1	
	(1) (I) and (III) (2) (III) and (IV)	(3) (II) and (IV)	(4) (I) and (II)
	() () () () () () () () () ()	(-) () (1)	() (-)

- **59.** For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point?

 [J-MAIN-2018, Offine]
 - $(1) [\mathrm{Co(H_2O)}_5\mathrm{Cl}]\mathrm{Cl}_2.\mathrm{H_2O}$

(2) [Co(H₂O)₄Cl₂]Cl.2H₂O

(3) $[Co(H_2O)_3Cl_3].3H_2O$

 $(4) \left[\text{Co(H}_2\text{O)}_6 \right] \text{Cl}_3$

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) $[ZnCl_4]^{2-} > [NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$
 - $(2) \ [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$
 - $(3) \ [\mathrm{MnCl_4}]^{2-} > [\mathrm{CoCl_4}]^{2-} > [\mathrm{NiCl_4}]^{2-} > [\mathrm{ZnCl_4}]^{2-}$
 - (4) $[NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-} > [ZnCl_4]^{2-}$

CC0172

62. The correct combination is

[J-MAIN-2018, Onine]

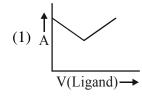
- (1) $[Ni(CN)_4]^{2-}$ tetrahedral; $[Ni(CO)_4]$ - paramagnetic
- (2) $[NiCl_4]^{2-}$ paramagnetic; $[Ni(CO)_4]$ tetrahedral
- (3) $[NiCl_4]^{2-}$ diamagnetic; $[Ni(CO)_4]$ square-planar
- (4) $[NiCl_4]^{2-}$ square-planar; $[Ni(CN)_4]^{2-}$ paramagnetic

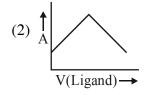
CC0173

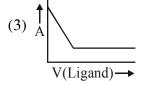
- 63. Which of the following complexes will show geometrical isomerism ? [J-MAIN-2018, Onine]
 - (1) Potassium amminetrichloroplatinate(II)
 - (2) Aquachlorobis (ethylenediamine) cobalt(II) chloride
 - (3) Potassium tris(oxalato) chromate(III)
 - (4) Pentaaquachlorochromium(III) chloride

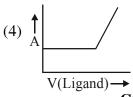
CC0174

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]









CC0175

- 65. In Wilkinson's catalyst, the hybridization of central metal ion and its shape are respectively
 - (1) dsp², square planar

[J-MAIN-2018, Onine]

- (2) sp³d, trigonal bipyramidal
 (3) sp³, tetrahedral
- (4) d²sp³, octahedral

1.	The complex ion wh	ich has no 'd' electrons	in the central metal ator	n is:	[JEE 2001]
	[At No. Cr = 24, M	In = 25, Fe= 26, Co =	27]		
	$(A) [MnO_4]^-$	(B) $[\text{Co } (\text{NH}_3)_6]^{3+}$	(C) $[Fe(CN)_6]^{3-}$	(D) [Cr(H ₂ O)	$[6]^{3+}$
					CC0177
2.	The CORRECT ord	er of hybridisation of t	he central atom in the f	following specie	s.[JEE 2001]
	NH ₃ , [PtCl ₄] ²⁻ , PCl ₅	and BCl ₃ is [At No. P	t = 78		
	(A) dsp^2 , sp^3d , sp^2 and	1 sp^3	(B) sp^3, dsp^2, sp^3d, sp) ²	
	(C) dsp^2 , sp^2 , sp^3 and	sp ³ d	(D) dsp^2 , sp^3 , sp^2 and	sp ³ d	CC0178
3.	The species having t	tetrahedral shape is:			[JEE 2004]
	(A) [PdCl4]2-	(B) $[Ni(CN)_4]^{2-}$	(C) $[Pd(CN)_4]^{2-}$	(D) [NiCl ₄] ²⁻	CC0179
4.	The pair of compound	nds having metals in the	heir highest oxidation s	state is	[JEE 2004]
	(A) MnO ₂ , FeCl ₃		(B) $[MnO_4]^-$, CrO_2C		
	(C) $[\text{Fe(CN)}_6]^{3-}$, $[\text{Co}_6]^{3-}$	$(CN)_3$	(D)[NiCl ₄] ²⁻ , [CoCl	₄]	CC0180
5.	Spin only magnetic	moment of the compou	and Hg $[Co(SCN)_4]$ is		[JEE 2004]
	(A) $\sqrt{3}$	(B) $\sqrt{15}$	$(C)\sqrt{24}$	(D) $\sqrt{8}$	CC0181
6.	Which of the follow	ing pair is expected to	exhibit same colour ir	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 isome	erism is shown by Co(NH_3 ₄ Br_2 Cl?		[JEE 2005]
	(A) Geometrical and	Ionisation	(B) Optical and Ioni	sation	
	(C) Geometrical and	Optical	(D) Geometrical only		
	Question No. 8 to 10	0 (3 questions)			[JEE 2006]
	The coordination nur	nber of Ni^{2+} is 4.			
	NiCl ₂ + KCN (exces	$s) \rightarrow A$ (cyano complex)	x)		
	NiCl ₂ + KCl (excess	$A \rightarrow B$ (chloro comple	x)		CC0183
8.	The IUPAC name of	A and B are			
	(A) Potassium tetracy	anidonickelate (II), pota	ssium tetrachloridonick	elate (II)	
	(B) Tetracyanidopota	ssiumnickelate (II), teter	rachloridopotassiumnick	elate (II)	
	(C) Tetracyanidornicl	kel (II), tetrachloridonic	kel (II)		
	(D) Potassium tetrac	yanidonickel (II), pota	ssium tetrachloridonic	cel (II)	CC0184
9.	Predict the magnetic	nature of A and B.			
	(A) Both are diamag	gnetic.			
	(B) A is diamagnetic	c and B is paramagnet	ic with one unpaired el	ectron.	
	(C) A is diamagnetic	c and B is paramagneti	ic with two unpaired el	ectrons.	
	(D) Both are parama	ignetic.			CC0185
	-				

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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 mor	noxide is 1.128Å, then v	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 low	rest in [JEE 2007]
	$(A) [Mn(CO)_6]^+$	(B) $[Fe(CO)_5]$	$(C) [Cr(CO)_6]$	(D) $[V(CO)_6]^-$
				CC0188
13.	-			umn II. Indicate your answer
	by darkening the app	ropriate bubbles of the	$e 4 \times 4$ matrix given in	the ORS.
	Column I		Column II	[JEE 2007]
	(A) $[Co(NH_3)_4(H_2O)_2]$]Cl ₂	(P) Geometrical ison	ners
	(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 compou	and 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) Tetrachloronicke	l (II)-tetraamminenick	el (II)	
	(B) Tetraamminenick	tel (II)-tetrachloronick	el (II)	
	(C) Tetraamminenick	tel (II)-tetrachloronick	elate (II)	
	(D) Tetrachloronicke	l (II)-tetraamminenick	elate (0)	CC0191
16.	Both [Ni(CO) ₄] and [N	Ni(CN) ₄] ^{2–} are diamagn	etic. 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 g	eometrical isomers of	the complex $[M(NH_3)_4]$	[Cl ₂] are optically inactive.
	Statement-2 : Both ge	ometrical isomers of th	e complex [M(NH ₃) ₄ Cl	₂] possess axis of symmetry.
	(A) Statement-1 is Tru	ie, Statement-2 is True	; Statement-2 is a correc	t explanation for Statement-1
	(B) Statement-1 is True	e, Statement-2 is True; S	tatement-2 is NOT a corre	ect explanation for Statement-1
	(C) Statement-1 is Tr	rue, Statement-2 is Fa	lse	

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

[JEE 2008]

18. Statement-1 : [Fe(H₂O)₅NO]SO₄ is paramagnetic

[JEE 2008]

Statement-2: The Fe in [Fe(H₂O)₅NO]SO₄ 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)Cl₂]
- (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 CuSO₄. 5H₂O 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)(PPh₃)(NH₃)] is.[JEE 2010]

CC0199

24. The correct structure of ethylenediaminetetraacetic acid (EDTA) is –

[JEE 2010]

(A)
$$HOOC-CH_2$$
 N-CH=CH-N CH_2 -COOH CH_2 -COOH

(B)
$$\frac{\text{HOOC}}{\text{HOOC}}$$
 N-CH₂-CH₂-N $\frac{\text{COOH}}{\text{COOH}}$

(C)
$$\frac{\text{HOOC-CH}_2}{\text{HOOC-CH}_2}$$
 N -CH $_2$ -CH $_2$ -COOH $\frac{\text{CH}_2$ -COOH

CC0200

- 25. Geometrical shapes of the complexes formed by the reaction of Ni²⁺ with Cl⁻, CN⁻ and H₂O 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), (**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

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- As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is : [JEE 2012] 28.
 - (A) Tetraaquadiaminecobalt(III) chloride
- (B) Tetraaquadiamminecobalt(III) chloride
- (C) Diaminetetraaquacobalt(III) chloride
- (D) Diamminetetraaquacobalt(III) chloride

CC0204

- The colour of light absorbed by an aqueous solution of CuSO_4 is -**29.** [JEE 2012]
 - (A) orange-red
- (B) blue-green
- (C) yellow
- (D) violet

CC0205

- $NiCl_2{P(C_2H_5)_2(C_6H_5)}_2$ exhibits temperature dependent magnetic behavior (paramagnetic/ **30.** diamagnetic). The coordination geometries of Ni²⁺ in the paramagnetic and diamagnetic states [JEE 2012] are respectively:
 - (A) tetrahedral and tetrahedral
- (B) square planar and square planar
- (C) tetrahedral and square planar
- (D) square planar and tetrahedral

CC0206

Consider the following complex ions P, Q and R,

$$\mathbf{P} = [\text{FeF}_6]^{3-}, \ \mathbf{Q} = [\text{V(H}_2\text{O)}_6]^{2+} \text{ and } \mathbf{R} = [\text{Fe(H}_2\text{O)}_6]^{2+}$$

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 < RCC0207
- EDTA⁴⁻ 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(NH₃)₅Cl]Cl₂ and [Cr(NH₃)₄Cl₂]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(NH₃)₃(NO₃)] Cl and [Pt(NH₃)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]

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

List-I

List-II

- (P) $[Cr(NH_3)_4Cl_2]Cl$
- (Q) [Ti(H₂O)₅Cl](NO₃),
- (R) [Pt(en)(NH₃)Cl]NO₃
- (S) $[Co(NH_3)_4(NO_3)_2]NO_3$

- (4) Dimagnetic and exhibits ionisation isomerism

Code:

- P R S 0
- 1
- 3 (C) 2 4

- (1) Paramagnetic and exhibits ionisation isomerism
- (2) Dimagnetic and exhibits *cis-trans* isomerism
- (3) Paramagnetic and exhibits *cis-trans* isomerism
- - P S Q R
- (B) 2
- 2 (D) 1 3

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

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(NH₃)₄ Cl₂Br has been isolated in two forms A and B. The form A reacts with AgNO₃ 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.** NiCl₂ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH₄OH, 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 Fe³⁺ 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

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43. Among the complex ions, $[\text{Co(NH}_2\text{-CH}_2\text{-NH}_2)_2\text{Cl}_2]^+$, $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$, $[\text{Fe(H}_2\text{O})_4(\text{OH})_2]^+$, $[\text{Fe(NH}_3)_2(\text{CN})_4]^-$, $[\text{Co(NH}_2\text{-CH}_2\text{-NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$ and $[\text{Co(NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is -

CC0219

44. Among [Ni(CO)₄], [NiCl₄]²⁻, [Co(NH₃)₄Cl₂]Cl, Na₃[CoF₆], Na₂O₂ and CsO₂, 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 MCl₂. 6H₂O (X) and NH₄Cl 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 = H₂NCH₂CH₂NH₂) 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

-8A/Kota/VEE[Advanced]/Leader/Che/Sheet/Co-ordination Chemistry/Eng/Theory+Ex.p65

50. Match each set of hybrid orbitals from LIST-I with complex (es) given in LIST-II.

LIST-I

P. dsp²

 $Q. sp^3$

R. sp^3d^2

S. d^2sp^3

LIST-II

[JEE Ad. 2018]

1. $[FeF_6]^{4-}$

2. [Ti(H₂O)₃Cl₃]

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

4. [FeCl₄]²⁻

5. Ni(CO)₄

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

The correct option is

(A) $P \rightarrow 5$; $Q \rightarrow 4,6$; $R \rightarrow 2,3$; $S \rightarrow 1$ (B) $P \rightarrow 5,6$; $Q \rightarrow 4$; $R \rightarrow 3$; $S \rightarrow 1,2$

(C) P \rightarrow 6; Q \rightarrow 4,5; R \rightarrow 1; S \rightarrow 2,3 (D) P \rightarrow 4,6; Q \rightarrow 5,6; R \rightarrow 1,2; S \rightarrow 3

CC0226

Among the species given below, the total number of diamagnetic species is____. **51.** H atom, NO₂ monomer, O₂ (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

Total number of cis N-Mn-Cl bond angles (that is, Mn-N and Mn-Cl bonds in cis positions) **52.** present in a molecule of cis-[Mn(en)₂Cl₂] complex is ____ (en = NH₂CH₂CH₂NH₂)

[JEE Ad. 2019]

ANSWERS KEY

EXERCISE: 0-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	С	В	С	С	С	D	В	D	В
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	В	A	В	A	С	С	D	A	D
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	D	С	В	С	В	В	A	D	A	В
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	D	В	С	D	С	С	В	С	С
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	В	С	D	D	D	D	С	В	D	В
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	A	В	A	D	В	D	A	С	В	D
Que.	61	62	63	64	65	66	67	68	69	
Ans.	В	С	C	A	С	С	A	D	A	

EXERCISE: 0-2

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)**

- **(2)** 6.
- 7. **(2)**
- **(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				

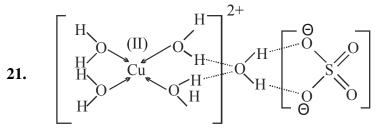
Que.	4	5	6	7	8	9	10	11	12	13
Ans.	В	С	D	D	С	A	С	D	D	A
Que.	14	15	16	17	18					
Ans.	D	В	В	D	D					

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	В	D	В	В	В	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	С	В	В
Que.	18	19	20			•			-	
Ans.	A	A	C, D	*						



Que.	22	23	24	25	26	27	28	29	30	31
Ans.	В	3	C	В	C	6	D	A	С	В
Que.	32	33	34	35		-	•	•	•	
Ans.	8	B, D	В	4						

36. d^2sp^3 , dsp^2 and sp^3

37. $A \rightarrow [Cr(NH_3)_4ClBr]Cl$

 $\mathrm{B} \to [\mathrm{Cr}(\mathrm{NH_3})_4\mathrm{Cl_2}]\mathrm{Br}$

In both Cr is d^2 sp³ 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) \rightarrow d²sp³, octahedral

40.
$$H_3C-C$$
 Ni $C-CH_3$ $H_3C-C=N$ $N=C-CH_3$ $N=C-$

dsp², Ni²⁺, diamagnetic

- 41. Ans. (4)
- 42. Ans. (3)
- 43. Ans. (6)
- 44. Ans. (B)

- 45. Ans. (5)
- 46. Ans. (A)
- 47. Ans. (A,B,D)

$$\begin{array}{c}
\text{II} \\
[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2 \xrightarrow{\text{Excess NH}_4\text{OH} / \text{NH}_4\text{Cl}} & \text{III} \\
\text{Air } / \text{O}_2 & \text{IV}
\end{array}$$
Pink (X)

(Y)

$$[Co(H2O)6]2+ + 4C\Gamma \longrightarrow [CoCI4]2-$$
(X) (excess) (Z) blue colour

- (A) Hybridisation of (Y) is d²sp³ as NH₃ is strong field ligand
- (B) [CoCl₄]²⁻ have sp³ hybridisation as Cl⁻ is weak field ligand

(C)
$$[Co(NH_3)_6]Cl_3 + 3AgNO_3(aq.) \rightarrow 3AgCl$$
(Y)

(D)
$$[CoCl_4]^{2-} + 6H_2O \Longrightarrow [Co(H_2O)_6]^{2+} + 4Cl^- \Delta H = (-)ve$$
 (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)