Chapter 23

Coordination Compounds

Coordination compounds in which the central metal atom is linked to a number of ions or neutral molecules by coordinate bonds, i.e. by donation of ions pairs of e^{-1} s by these ions or neutral molecules to the central metal atom.

DOUBLE SALT AND COMPLEX COMPOUND

The main difference between a double salt (like alums, Mohr's salt, etc.) and a complex (like ferrocyanide) ion is that former dissociates completely into ions in aqueous solution and does not contain any coordinate bond while later does not dissociates completely into ions and always contains coordinate bonds.

WERNER'S THEORY OF COMPLEXES

The main postulates are:

(i) Every metal forming a complex exhibits two types of valencies Primary valency and Secondary valency.

(ii) Primary valency is ionisable in nature whereas secondary valency is non-ionisable.

(iii) Primary valency is also called oxidation state. Secondary valency is also called Coordination number of metal

ex: $\left[Pt\left(NH_3\right)_6\right]Cl_4$, primary valency is 4 (from $4Cl^-$) whereas secondary valency is 6 (from $6NH_3$)

(iv) Primary valencies are satisfied by negative ions whereas secondary valencies are satisfied by negative ion or neutral molecules.

(v) Secondary valencies are directional and determine geometry of the complex. On the other hand, primary valencies are non directional.

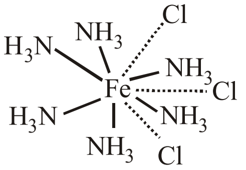
Experimental evidence to Werner's theory of complexes can be provided based on :

(i) Precipitation of primary valencies on the addition of a suitable reagent.

(ii) Electrical conductance of complexes

Representation of Complexes

Werner's representation for $Fe(NH_3)_6Cl_3$



Dotted lines indicate primary valency and solid lines indicate secondary valency of metal ion.

SOME IMPORTANT TERMS USED IN COORDINATION COMPOUNDS

Coordination Entity/ Coordination Sphere

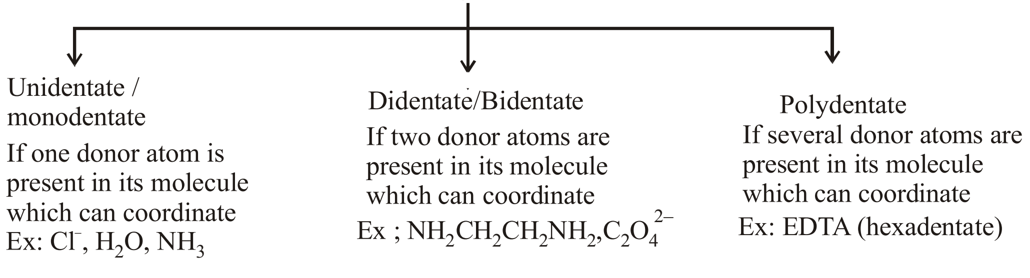
The central metal atom/ ion and the ligands which are directly attached to it are enclosed in square brackets and are collectively called coordination entity. The ionizable groups are written outside the brackets and are called counter ions.

Central Atom / ion:

In a Coordination entity, the atom / ion to which a fixed number of ions / groups are bound in a definite geometrical arrangement around it, is called central atom / ion.
They are also referred to as **Lewis acids**

Ligands

These are ions / molecules which bound to central atom / ion in Coordination entity. Ligands may be ions (ex: Cl^-), small molecules like H_2O or NH_3, larger molecules like $H_2N\ CH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules.
The number of co-ordinating or ligating groups present in a ligand is called its denticity. Based on this, ligands are classified as:



Ligands

Unidentate / monodentate
If one donor atom is present in its molecule which can coordinate
Ex: Cl^-, H_2O, NH_3

Didentate/Bidentate
If two donor atoms are present in its molecule which can coordinate
Ex ; $NH_2CH_2CH_2NH_2, C_2O_4^{2-}$

Polydentate
If several donor atoms are present in its molecule which can coordinate
Ex: EDTA (hexadentate)

Chelating Ligands

If the ligands with two or more electron donor groups (or co-ordinating groups) positioned in such a way that they form five or six membered ring with central metal ion, then the ligands are known as **chelating ligands** and the ring formed is called **chelate ring.** The complex which is thus formed is termed as **metal chelate** or simply **chelate** while this property is called **chelation.**

Chelating ligands form more stable complexes. Complexes formed by ligands with smaller groups are more stable as compared to complexes formed by ligand with larger group.

Chelates are used in softening of hard water, in separation of lanthanoids and actinoids, in qualitative analysis of metals etc.

Ambidentate Ligands

Ligands which can bind through two different sites are called ambidentate ligands. For ex: NO_2^-, SCN^-, etc.

Coordination Number

The number of coordinate bonds formed with the central metal atom/ion by the ligands. For determining Coordination number only sigma bonds are considered not pi-bonds even if formed.

For ex: $[Pt\,Cl_6]^{2-}$, Coordination number of Pt = 6

$[Fe(C_2O_4)_3]^{3-}$, Coordination number of Fe = 6

Coordination Polyhedron

It is the spatial arrangement of ligand atoms which are directly attached to the central atom / ion.

The polyhedron can be octahedral, square planar, square pyramidal, trigonal bipyramidal or tetrahedral.

Oxidation Number of Central Atom

It is the charge which the central atom would carry if all the ligands are removed along with the e^- pairs that are shared with the central atom. For example : Oxidation number of Cu in $[Cu(CN)_4]^{3-}$ is +1 and is written as Cu (I).

Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups are called homoleptic. For ex: $[Cu(NH_3)_6]^{3+}$

Complexes in which a metal is bound to more than one kind of donor groups are heteroleptic : For ex: $[Co(NH_3)_4Cl_2]$

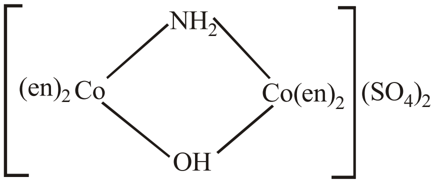
Homonuclear and Polynuclear Complexes :

Complexes in which only one metal atom is present are homonuclear.

Example : $K_3[Fe(C_2O_4)_3]$

Complexes in which more than one metal atoms are present are known as polynuclear.

Example :



NOMENCLATURE OF COORDINATION COMPOUNDS

Formulas of Mononuclear Coordination Compounds

Following rules are applied:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically.

(iv) In case of abbreviated ligands (e.g., en for ethane-1, 2-diamine),the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(v) The formula of the entire coordination entity, whether charged or not, is enclosed in square brackets.

(vi) There should be no space between the ligands and the metal within a co-ordinatiion sphere.

(vii) If the formula is written without the counter ion, the charge is indicated outside the square bracket as a superscript.

(viii) The charge of the cation (s) is balanced by the charge of the anion (s).

Naming of Mononuclear Coordination Compounds

Following rules are used:

(i) The cation is named first in both positively and negatively charged Coordination entities.

(ii) The ligands are named in alphabetical order before the name of the central atom / ion.

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

(a) **Neutral ligands are named as the molecule e.g. C_5H_5N is named as pyridine,**

$(C_6H_5)_3P$ as Triphenyl phosphine,

$H_2N–CH_2–CH_2–NH_2$ as ethylene diamine.

The neutral ligands which are not named as the molecule are

CO	carbonyl
NO	nitrosyl
H_2O	aqua
NH_3	amine

(b) **Negative ligands end in 'O', i.e.,**

Cl^- chloro,	SO_4^{2-} sulphato	NO_2^- Nitro
ONO^- nitrito,	OH^- hydroxo,	NH_2^- amido
NH^{2-} imido	NO_3^- nitrato,	CO_3^{2-} carbonato
CH_3COO^- acetato,	CN^- cyano	

(c) **Positive ligands** end in 'ium' ex : $NH_2-\overset{+}{N}H_3$ Hydrazinium, $\overset{+}{N}O_2$ (nitronium), $\overset{+}{N}O$ (nitrosonium)

(iv) Prefixes mono, di, tri, etc are used to indicate the number of individual ligands in Coordination entity.

(v) Oxidation state of the metal in cation, anion or neutral Coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element.

For example : $[Co(NH_3)_6]Cl_3$

(Cationic complex is present so metal is without any suffix) Hexaaminecobalt (III) chloride.

If the complex ion is an anion, the name of the metal ends with the suffix - ate.

For example : $K_4[Fe(CN)_6]$
(anionic complex is present so suffix ate is added with metal's name) Potassium hexacyanoferrate (II)

(vii) The neutral complex molecule is named similar to that of the complex cation.

(viii) When bidentate ligands are coordinated to the metal ion, their repetition is indicated by prefixes like bis, tris, tetrakis etc. For example :
(a) $[Fe\,(en)_3]\,Cl_3$
Trisethylenediamineiron (III) chloride
(b) $[Ni\,(gly)_2]$
Bisglycinatonickel (II)

ISOMERISM IN COORDINATION COMPOUNDS

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms.Coordination compounds show two main types of isomerism:

Structural Isomerism

(i) Linkage isomerism: It arises in complexes containing ambidentate ligand. For ex: SCN. It can bind through N or S to give M - NCS or M - SCN. For example $[Cr(H_2O)_5(SCN)]^{2+}$ and $[Cr(H_2O)_5(NCS)]^{2+}$ are linkage isomers.

(ii) Coordination isomers : This type of isomerism occurs when both cation and anion of a salt are complex. The isomerism arises by the interchange of ligands between the two complex ions.
For example : $[Co(NH_3)_6]\,[Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

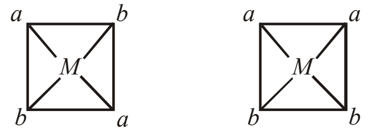
(iii) Ionisation Isomerism: It arises when the counter ion in a complex salt is itself a potential ligand and can displace ligand which can then become the counter ion. This type of isomers yields different types of ions in solution.

For ex: $\left[Co\left(NH_3\right)_5 SO_4\right]Br$ and $\left[Co\left(NH_3\right)_5 Br\right]SO_4$

(iv) Solvate/ Hydrate Isomerism:
The complexes which differ with respect to the number of water molecules attached to the metal ion as ligands are called hydrate isomers.
For e.g. - $Cr(H_2O)_6Cl_3$ has three possible structures
(a) $[Cr(H_2O)_6]Cl_3$ violet
(b) $[Cr(H_2O)_5Cl]\,Cl_2.H_2O$ green
(c) $[Cr(H_2O)_4Cl_2]Cl\,.\,2H_2O$ dark green.

Stereo Isomerism

(I) Geometrical Isomerism
Geometrical isomerism is most important in compounds with coordination numbers 4 and 6. 4-coordinated complexes with tetrahedral geometry do not exhibit *cis-trans* isomerism.
Square planar complexes showing this behaviour are of type:
(i) Ma_2b_2

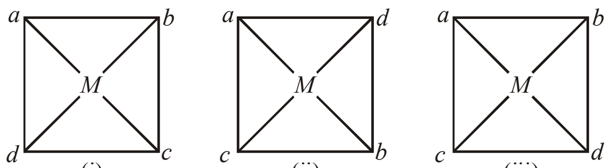


Trans–isomer *Cis*–isomer

$[Ma_2b_2]$

ex: $Pt\,(NH_3)_2\,Cl_2$

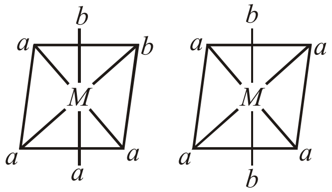
(ii) Mabcd Three isomers are possible



(i) (ii) (iii)

Example : $[Pt(NH_3)(NH_2OH)(NO_2)(py)NO_2$.
Octahedral complexes showing this behaviour are of type:
(i) Ma_4b_2

ex: $\left[Co\left(NH_3\right)_4 Cl_2\right]^+$

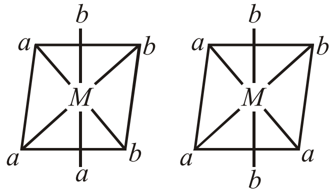


Cis *Trans*

$[Ma_4b_2]$

(ii) $M\,a_2\,(b-b)_2$ i.e. with bidentate ligands b – b (cis and trans forms)
ex: $CoCl_2(en)_2$.

(iii) Ma_3b_3 (facial and meridional isomers).



Cis *Trans*

$[Ma_3b_3]$

Octahedral complexes of general formula, Mabcdef, can have fifteen geometrical isomers.

(II) Optical Isomerism
It is shown by compounds which cannot be superimposed.An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
It has two forms, dextro (d) and laevo (*l*), arise depending upon the direction in which they rotate the plane of polarised light.
This isomerism is common in octahedral complex involving bidentate ligands.

ex: $\left[Co\left(en\right)_3\right]^{3+}$, cis is isomer of $\left[PtCl_2\left(en\right)_2\right]^{2+}$

For complexes with coordination number 4, square planar complexes do not show optical isomerism but tetrahedral complexes having bidentate ligands, ex : $[Ni(gly)_2]$ shows optical isomerism.
Other examples are $[Co(en)_3]^{3+}$, $[CoCl_2(en)_2]^+$ etc.

BONDING IN COORDINATION COMPOUNDS

Valence Bond Theory (VBT)

(i) According to this theory, metal - ligand bonds are formed by the overlap of metal orbitals with those of ligands i.e., by donation of e^--pairs by the ligands to empty hybridized orbitals of metal.

For e.g. -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.

(ii) The metal orbitals undergo hybridisation, to give a set of hybrid orbitals of equal energy.

(iii) The number of vacant orbitals provided is equal to the coordination number of metal ion.

(iv) Octahedral, square planar and tetrahedral complexes are formed as a result of d^2sp^3 (or sp^3d^2), dsp^2 and sp^3 hydridisation respectively of the central metal atom or the ion.

A few examples are:

Complex	Hybridisation	Magnetic behaviour	Nature
(CN = 6)			
$[Cr(NH_3)_6]^{3+}$	d^2sp^3 octahedral	paramagnetic	inner orbital
$[Fe(CN)_0]^{3-}$	d^2sp^3	slightly paramagnetic	inner orbital
$[Fe(CN)_6]^{4-}$	d^2sp^3	diamagnetic	inner orbital
$[CoF_6]^{3-}$	sp^3d^2	paramagnetic	outer orbital
(CN = 4)			
$[Ni(CO_4)]^0$	sp^3 tetrahedral	diamagnetic	—
$[Zn(NH_3)_4]^{2+}$	sp^3	diamagnetic	—
$[Ni(CN)_4]^{2-}$	dsp^2 Square planar	diamagnetic	—
$[Cu(NH_3)_4]^{2+}$	dsp^2	paramagnetic	—
(CN = 5)			
$Fe(CO)_5$	dsp^3 trigonal bipyramidal	diamagnetic	

Note : Number of unpaired electrons present ($\mu = \sqrt{n(n+2)}$ BM) can be calculated by determining magenatic moment value experimentally. Thus type of hybridisation involved in complex can be predicted.

Crystal Field Theory

This theory considers M - L bond to be ionic arising from electrostatic interaction.

Inner and Outer Orbital Complexes

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

In case of inner orbital complex the electrons of the metal are made to pair up, so the complex will be either diamagnetic or less paramagnetic. This type of complex is also known as low spin complex. For outer orbital complex number of unpaired electrons will be large as the configuration of the metal remains unchanged. This type of complex is also known as high spin complex.

The d-orbitals present in metal have the same energy in the free state. This is called degenerate state of d-orbital. But, when a complex is formed the ligands destroy the degeneracy of these orbitals. This effect is known as **Crystal field splitting** of d- orbitals.

Crystal Field Theory for Octahedral Complexes :

When a ligand approaches the metal ion, the 'd' orbitals of the metal ion undergo splitting forming two sets i.e., higher energy set, e_g of $d_{x^2-y^2}$ and d_{z^2} and a lower energy set, t_{2g} of d_{xy}, d_{yz}, and d_{xz}

This is shown diagrammatically as:

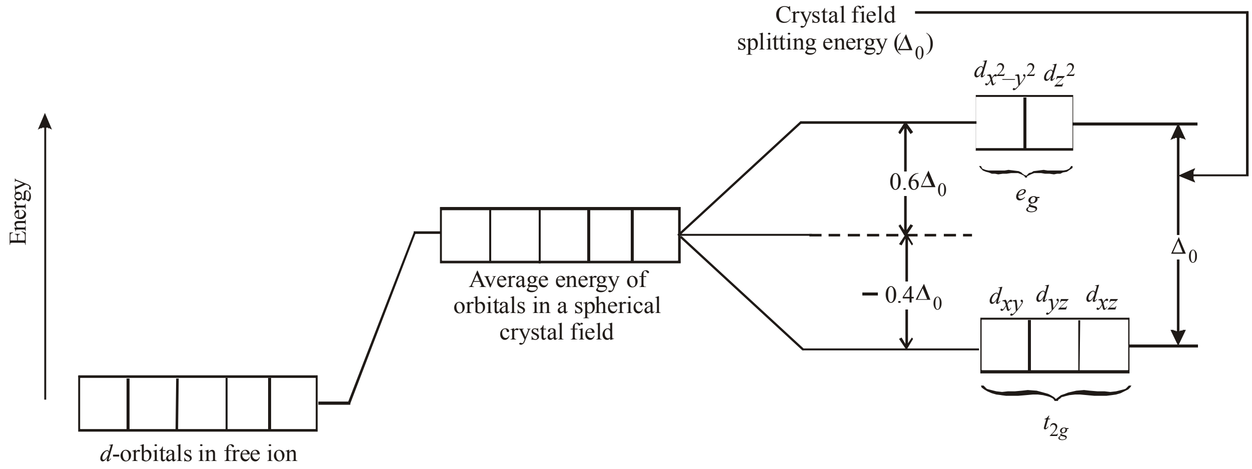


Figure : Splitting of *d*-orbitals in octahedral field

The difference of energy between the two sets of d-orbitals is called crystal field splitting energy or crystal field stabilization energy (CFSE). It is usually represented by the symbol Δ_o.

For any given metal cation, the magnitude of Δ_o depends upon the nature of the ligands

Spectro chemical series

In general, ligands can be arranged in a series in order of increasing field strength as given below:

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^-$

$< C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^-$

$< CN^- < CO$

This series is called **spectrochemical series**.

Pairing of the two sets of d-orbital depends on the magnitude of Δ_o and P ($\Delta_o \rightarrow$, CFSE and P $\rightarrow$ pairing energy)

If $\Delta_o > P$, EC is $t_{2g}{}^4\ e_g^0$. Upto d^6 pairing will occur in the t_{2g} and e_g. will remain vacant. Ligands which produce this effect are called **strong field ligands** and form **low spin complex**.

If $\Delta_o < P$, EC is $t_{2g}{}^3\ e_g^1$. For d^5 configuration $t_{2g}^3\ e_g^2$ ligands which produce this effect are called **weak field ligands** and form **high spin complexes**.

For **tetrahedral complex,** $\Delta_t = \frac{4}{9}\Delta_0$

Splitting pattern for tetrahedral complexes is just the reverse of the splitting patterns of the octahedral complexes Δ_t is so small that it is unable to force the electrons to pair up.

Here, energy of e_g < energy of t_{2g}.

Colour of the complexes

The coloured nature of solutions of coordination compounds can also be explained on the basis of crystal field theory, because in coordination compounds the energy difference between two sets of *d*-orbitals is usually small (as explained by crystal field splitting) thus, excitation of an electron from lower energy to higher energy is very easy and can be achieved even by the absorption of low energy radiations of visible region. As the result of the absorption of such selected wavelengths of visible light, the complexes appeared coloured.

Different complexes exhibit different colours when either metal is different or ligands are different.

In absence of ligand, crystal field splitting does not occur and hence, the substance is colourless. For ex: $CuSO_4.5H_2O$ is blue but anhydrous $CuSO_4$ is white.

The size of Δ depends on -

(i) **Nature of the ligand :** In Spectrochemical series Δ decreases as shown below

$I^- < Br^- < Cl^- < OH^- < F^- < C_2O_4^{2-} < H_2O < CNS^- <$

weak ligands

$< NH_3 < en < NO_2^- < CN^- < CO$

strong ligands

(ii) **Oxidation state of the metal :** Δ is greater for M^{3+} than for M^{2+}

(iii) **Position of the metal in the periodic table:** For a given ligand and oxidation state of the metal, Δ increases going down in a group eg.

Δ is greater in $[Ru(NH_3)_6]^{3+}$ than in $[Fe(NH_3)_6]^{3+}$

STABILITY OF COORDINATION COMPOUNDS

The stability of a complex in solution can be expressed in terms of equilibrium constant of the dissociation equilibrium

For a general complex dissociating reaction

$$ML_n^{b+} \rightleftharpoons M^{a+} + nL^{x-}$$

$$K_i = \frac{[M^{a+}][L^{x-}]^n}{[ML_n^{b+}]}$$

K_i = instability constant

$$M^{a+} + nL^{x-} \rightleftharpoons ML_n^{b+}$$

$$\beta_n = \frac{[ML_n^{b+}]}{[M^{a+}][L^{x-}]^n}$$

$\beta_n \rightarrow$ stability constant ($\therefore\ \beta = 1/K_i$)

Thus more will be stability constant more will be stability of complex.

For the reaction, $M + 4L \rightleftharpoons ML_4$, overall stability constant is given by $\beta_4 = [ML_4]/[M][L]^4$ whereas the stepwise stability constants are:

(i) $M + L \rightleftharpoons ML$

$K_1 = [ML]/[M][L]$

(ii) $ML + L \rightleftharpoons ML_2$

$K_2 = [ML_2]/[ML][L]$

(iii) $ML_2 + L \rightleftharpoons ML_3$

$K_3 = [ML_3]/[ML_2][L]$

(iv) $ML_3 + L \rightleftharpoons ML_4$

$K_4 = [ML_4]/[ML_3][L]$

and, $\boxed{\beta_4 = K_1 \times K_2 \times K_3 \times K_4}$

or, $\boxed{\beta_n = K_1 \times K_2 \times K_3 ------ K_n}$

Note (i) Greater is the charge on central metal ion, greater will be the stability of the complex

(ii) Greater will be the basic strength of ligand stable will be the complex

(iii) Formation of chelate rings increases the stability of the complex.

IMPORTANCE OF COORDINATION COMPOUNDS

(i) **In qualitative analysis :** In salt analysis, the presence of a number of basic radicals is confirmed by converting them into suitable complexes which have definite colours.

For ex : Fe^{3+} forms a prussian blue complex with potassium ferrocyanide solution :

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Prussian blue)}}{\underset{\text{Ferri-ferrocyanide}}{Fe_4[Fe(CN)_6]_3}} + 12KCl$$

(ii) **In extraction of metals :** The noble metals like silver and gold are extracted from their ores through the formation of cyanide complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$.

(iii) **In biological systems :** A number of biologically important compounds are Coordination compounds, i.e., metal complexes. For ex : chlorophyll is a coordination compound of magnesium; haemoglobin is a complex compound of iron; vitamin B_{12} is a Coordination compound of cobalt, etc.

ORGANOMETALLIC COMPOUNDS

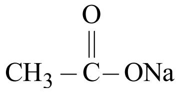
These are compounds containing one or more metal-carbon bonds. The compounds of metalloids (Ge, Sb) and non metals (B, Si, P, As etc.) which are less electronegative than carbon are also categorised under this.

e.g., R - Zn - R Dialkyl zinc (Frankland reagent)

R - Mg - X Alkyl Mg halide (Grignards reagent)

Compounds like

Sodium acetate



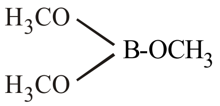
$CH_3-\overset{\overset{O}{\|}}{C}-ONa$

Sodium ethoxide $C_2H_5–O–Na$

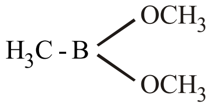
Sodium Mercaptide $H_3C–SNa$

are not organometallic compounds as in these compounds metal is not directly attached with carbon atom.

$B(OCH_3)_3$ is not OMC →



while $CH_3B(OCH_3)_2$ is OMC →



Cyanides, carbides and carbonates are not considered OMC because their properties are very different from those belonging to class of OMC's.

Classification of Organometallic Compounds

OMC can be classified into three main categories

(i) σ - bonded OMC :

These compounds are formed mostly by non transition and metalloid elements.

eg. R - Mg - X, (Grignard reagent)

$(CH_3)_2Zn$ (Dimethyl zinc or Frankland's reagent)

$(R)_2Cd$, (Dialkyl Cadmium)

(ii) π - bonded OMC :

These are usually formed by transition metals.

eg. Ferrocene $[Fe(\eta^5 - C_5H_5)_2]$

where η = No. of carbon atoms combined with metal atom.

Zeise's salt $K[PtCl_3(\eta^2 - C_2H_4)]$

(iii) σ and π - bonded OMC :

Transition metals of gp. 6, 7,8,9 and 10 in their zero oxidation state form such type of OMC.

The carbonyl compounds of these metals have both σ, and π bonds. e.g.

$[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Mn_2(CO)_{10}]$

Metal carbonyls are used as industrial catalysts. They are also used as precursors in synthesis of organic compounds.

Bonding in Metal Carbonyls

Bond is formed between transition metal and C of CO group.

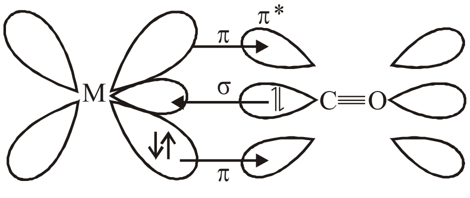
These carbonyls can have tetrahedral, trigonal bipyramidal or octahedral structure.

The M - C bond possesses both s - and p - character.

The M - C σ - bond is formed by donation of lone pair of electrons from a filled bonding π_{2p} orbital on the carbonyl carbon of CO into a vacant d-orbital of metal.

The M - Cπ - bond is formed by donation of a pair of electrons from a filled d - orbital of metal into vacant antibonding π^*_{2p} orbital of CO. Here, donation of electrons from a filled metal d-orbital into a vacant antibonding π* orbital of CO occurs, thus this bonding is called back bonding.

The effect of σ-bond formation strengthens the π bond and vice - versa. This is called **synergic effect** which strengthens the bond between CO and metal.



Synergic bonding

Synthesis of Organometallic Compounds

(i) σ – bonded organometallic compounds

$$R—X + 2M \xrightarrow{(CH_3CH_2)_2O} R—M + MX$$

$$R—X + Mg \xrightarrow{(CH_3CH_2)_2O} R—Mg—X$$

$$SnCl_4 + 4BuLi \longrightarrow \underset{\text{Tetrabutyltin}}{Bu_4Sn} + 4\,LiCl$$

$$PbCl_4 + 4C_2H_5Br \longrightarrow \underset{\text{Tetraethyllead (TEL)}}{(C_2H_5)_4Pb} + 4MgBrCl$$

(ii) $$K_2[PtCl_4] + CH_2 = CH_2 \xrightarrow{\Delta} \underset{\text{Zeise's salt}}{K[PtCl_3(C_2H_4)]} + KCl$$

$$2C_5H_5MgBr + FeCl_2 \longrightarrow \underset{\text{Ferrocene}}{[(C_5H_5)_2Fe]} + 2MgBrCl$$

Applications of Organometallic Compounds

(i) Wilkinsons Catalyst

$[RhCl(Ph_3P)]$ is used for selective hydrogenation of alkenes.

(ii) As heterogenous catalyst

Zeigler – Natta Catalyst is used for low temperature polymerisation of alkenes.

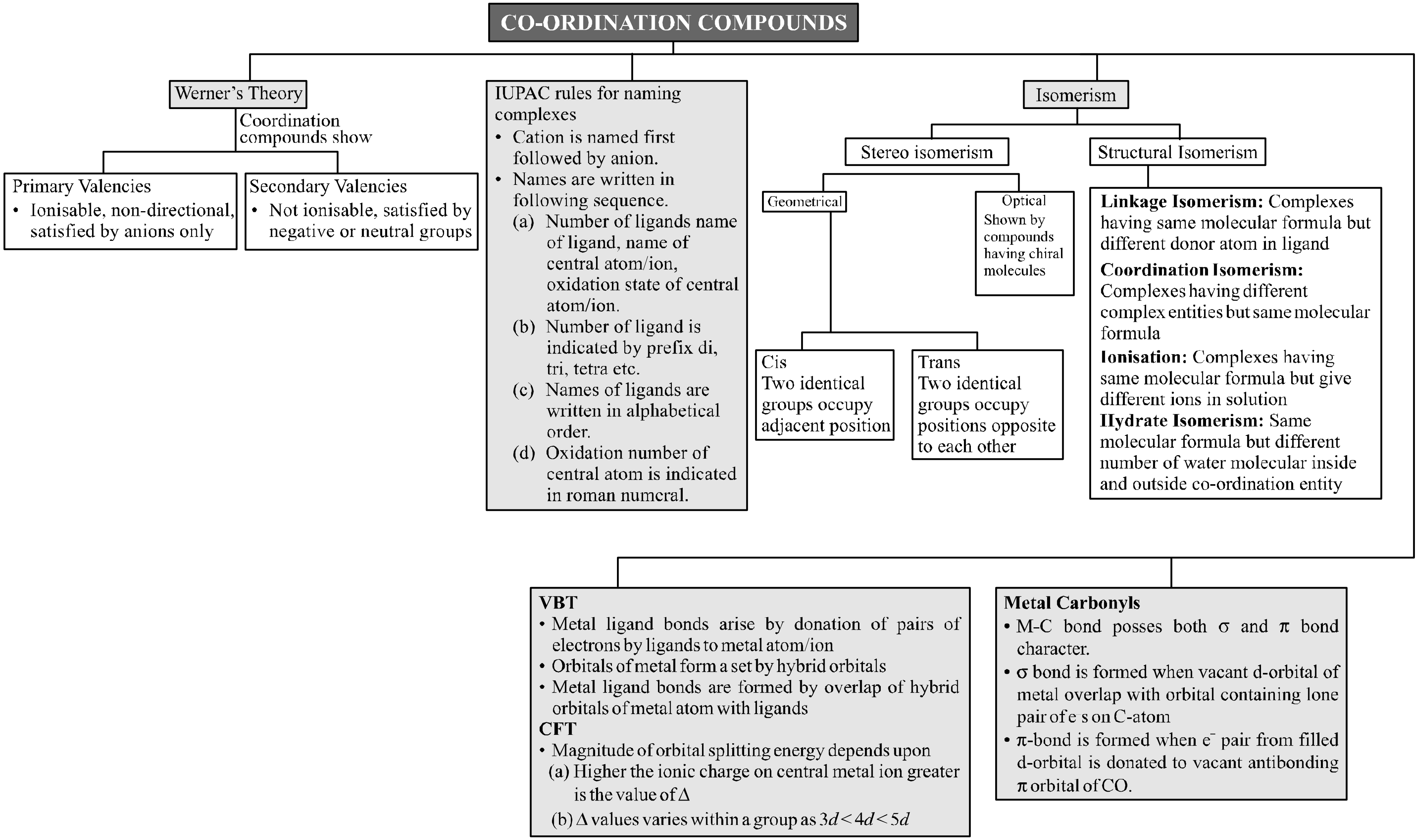
(iii) Organic synthesis - OMC like R - Mg - X, R_2 - Cd, CH_3 - Li etc. are used for preparation of almost all type of organic compounds. .

(iv) As petrol additive - TEL(Tetraethyl lead) is used as an antiknock agent in petrol.

(v) In medicine - Organo arsenic compounds are used as medicine for syphilis disease.

(vi) In agriculture - Seeds are treated with ethyl mercury chloride to protect the plants against infection.

CONCEPT MAP



CO-ORDINATION COMPOUNDS

Werner's Theory

Coordination compounds show

Primary Valencies

- Ionisable, non-directional, satisfied by anions only

Secondary Valencies

- Not ionisable, satisfied by negative or neutral groups

IUPAC rules for naming complexes

- Cation is named first followed by anion.
- Names are written in following sequence.
  - (a) Number of ligands name of ligand, name of central atom/ion, oxidation state of central atom/ion.
  - (b) Number of ligand is indicated by prefix di, tri, tetra etc.
  - (c) Names of ligands are written in alphabetical order.
  - (d) Oxidation number of central atom is indicated in roman numcral.

Isomerism

Stereo isomerism

Geometrical

- Cis
  Two identical groups occupy adjacent position
- Trans
  Two identical groups occupy positions opposite to each other

Optical
Shown by compounds having chiral molecules

Structural Isomerism

Linkage Isomerism: Complexes having same molecular formula but different donor atom in ligand

Coordination Isomerism: Complexes having different complex entities but same molecular formula

Ionisation: Complexes having same molecular formula but give different ions in solution

Hydrate Isomerism: Same molecular formula but different number of water molecular inside and outside co-ordination entity

VBT

- Metal ligand bonds arise by donation of pairs of electrons by ligands to metal atom/ion
- Orbitals of metal form a set by hybrid orbitals
- Metal ligand bonds are formed by overlap of hybrid orbitals of metal atom with ligands

CFT

- Magnitude of orbital splitting energy depends upon
  - (a) Higher the ionic charge on central metal ion greater is the value of Δ
  - (b) Δ values varies within a group as $3d < 4d < 5d$

Metal Carbonyls

- M-C bond posses both σ and π bond character.
- σ bond is formed when vacant d-orbital of metal overlap with orbital containing lone pair of e^-s on C-atom
- π-bond is formed when e^- pair from filled d-orbital is donated to vacant antibonding π orbital of CO.

EXERCISE - 1
Conceptual Questions

1. Which one of the following shows maximum value of paramagnetic behaviour :
(a) $[Sc(CN)_6]^{3-}$ (b) $[Co(CN)_6]^{3-}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(CN)_6]^{3-}$

2. $K_3[Al(C_2O_4)_3]$ is called
(a) Potassium aluminooxalate
(b) Potassium trioxalatoaluminate (III)
(c) Potassium aluminium (III) oxalate
(d) Potassium trioxalatoaluminate (VI)

3. The formula for the complex, dichlorobis (urea) copper (II) is
(a) $[Cu\{O=C(NH_2)_2\}]Cl_2$
(b) $[Cu\{O=C(NH_2)_2\}Cl]Cl$
(c) $[CuCl_2\{O=C(NH_2)_2\}_2]$
(d) $[CuCl_2][\{O=C(NH_2)_2\}]_2$

4. Which of the following is not an organometallic compound?
(a) sodium ethoxide
(b) trimethyl aluminium
(c) tetraethyl lead
(d) ethyl magnesium bromide

5. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are :
(a) both square planar
(b) tetrahedral and square planar respectively
(c) both tetrahedral
(d) square planar and tetrahedral respectively

6. The hypothetical complex chlorodiaquatriamminecobalt (III) chloride can be represented as
(a) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$
(b) $[Co(NH_3)_3(H_2O)Cl_3]$
(c) $[Co(NH_2)_3(H_2O)_2Cl]$
(d) $[Co(NH_3)_3(H_2O)_3]Cl_3$

7. According to IUPAC nomenclature sodium nitroprusside is named as
(a) Sodium pentacyanonitrosylferrate (III)
(b) Sodium nitroferrocyanide
(c) Sodium nitroferricyanide
(d) Sodium pentacyanonitrosylferrate (II)

8. In the coordination compound, $K_4[Ni(CN)_4]$, the oxidation state of nickel is
(a) 0 (b) +1 (c) +2 (d) –1

9. Which does not give a precipitate with $AgNO_3$ solution ?
(a) $[Co(NH_3)_6]Cl_3$ (b) $[Co(NH_3)_5Cl]Cl_2$
(c) $[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_3Cl_3]$

10. The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is
(a) 0 (b) +1 (c) +2 (d) +3

11. The IUPAC name of the coordination compound $K_3[Fe(CN)_6]$ is
(a) Tripotassium hexacyanoiron (II)
(b) Potassium hexacyanoiron (II)
(c) Potassium hexacyanoferrate (III)
(d) Potassium hexacyanoferrate (II)

12. The number of ions formed when triamminetrichloro chromium (III) is dissolved in water :
(a) 2 (b) 3
(c) 1 (d) None of these

13. The IUPAC name for the complex $[Co(ONO)(NH_3)_5]Cl_2$ is
(a) pentaamminenitrito-N-cobalt(II) chloride
(b) pentaamminenitrito-N-cobalt(III) chloride
(c) nitrito-N-pentaamminecobalt(III) chloride
(d) nitrito-N-pentaamminecobalt(II) chloride

14. $K_4[Fe(CN)_6]$ is a :
(a) double salt (b) complex compound
(c) acid (d) base

15. $[EDTA]^{4-}$ is a :
(a) monodentate ligand (b) bidentate ligand
(c) quadridentate ligand (d) hexadentate ligand

16. What is incorrect about homoleptic metal carbonyls ?
(a) M – C σ- bond is formed by donation of lone pair of electrons from CO
(b) M – C π- bond is formed by back donation of electron from filled *d*-orbital of metal to vacant *p*- orbital of carbon
(c) M – CO bonding product synergic effect
(d) Metal carbonyl contain only σ- bonds

17. The compound having the lowest oxidation state of iron is:
(a) $K_4Fe(CN)_6$ (b) K_2FeO_4
(c) Fe_2O_3 (d) $Fe(CO)_5$

18. The IUPAC name of $K_2[PtCl_6]$ is
(a) hexachloroplatinate potassium
(b) potassium hexachloroplatinate (IV)
(c) potassium hexachloroplatinate
(d) potassium hexachloroplatinum (IV)

19. In $K_4[Fe(CN)_6]$, the E.A.N. of Fe is
(a) 33 (b) 35 (c) 36 (d) 26

20. The organometallic compound is :
(a) $Ti(OCOCH_3)_4$ (b) $Ti(C_2H_5)_4$
(c) $Ti(OC_6H_5)_4$ (d) $Ti(OC_2H_5)_4$

21. In $[Ni(NH_3)_4]SO_4$, the E.A.N. of Ni is
(a) 34 (b) 35
(c) 36 (d) 37

22. The effective atomic number of cobalt in the complex $[Co(NH_3)_6]^{3+}$ is
(a) 36 (b) 33 (c) 24 (d) 30

23. The ligand called π acid is :
(a) CO (b) NH_3
(c) $C_2O_4^{2-}$ (d) Ethylenediamine

24. Pick out the complex compound in which the central metal atom obeys EAN rule strictly
(a) $K_4[Fe(CN)_6]$ (b) $K_3[Fe(CN)_6]$
(c) $[Cr(H_2O)_6]Cl_3$ (d) $[Cu(NH_3)_4]SO_4$

25. The number of geometrical isomers for $[Pt(NH_3)_2Cl_2]$ is
(a) 2 (b) 1 (c) 3 (d) 4

26. Which one of the following forms, with an excess of CN^- (cyanide), a complex having co-ordination number two?
(a) Cu^+ (b) Ag^+ (c) Ni^{2+} (d) $Al(OH)_3$

27. Which of the following will give maximum number of isomers?
(a) $[Ni(C_2O_4)(en)_2]^{2-}$ (b) $[Ni(en)(NH_3)_4]^{2+}$
(c) $[Cr(SCN)_2(NH_3)_4]^+$ (d) $[Co(NH_3)_4Cl_2]$

28. Which one of the following octahedral complexes will not show geometric isomerism? (A and B are monodentate ligands)
(a) $[MA_5B]$ (b) $[MA_2B_4]$
(c) $[MA_3B_3]$ (d) $[MA_4B_2]$

29. Which of the following coordination compounds would exhibit optical isomerism?
(a) pentamminenitrocobalt(III) iodide
(b) diamminedichloroplatinum(II)
(c) trans-dicyanobis (ethylenediamine) chromium (III) chloride
(d) tris-(ethylendiamine) cobalt (III) bromide

30. The type of isomerism present in Pentaminenitrochromium (III) chloride is
(a) optical (b) linkage
(c) ionisation (d) polymerisation.

31. The correct order for the wavelength of absorption in the visible region is :

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

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

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

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

32. Which of the following compounds shows optical isomerism?
(a) $[Co(CN)_6]^{3-}$ (b) $[Cr(C_2O_4)_3]^{3-}$
(c) $[ZnCl_4]^{2-}$ (d) $[Cu(NH_3)_4]^{2+}$

33 Which of the following ions can exhibit optical isomerism–
(a) $[Co(NH_3)_4Cl_2]^+$ (b) $[Co(NH_3)_2Cl_4]^-$
(c) Cis-$[Co(en)_2Cl_2]^+$ (d) trans-$[Co(en)_2Cl_2]^+$

34. Which would exhibit co-ordination isomerism
(a) $[Cr(NH_3)_6][Co(CN)_6]$ (b) $[Co(en)_2Cl_2]$
(c) $[Cr(NH_3)_6]Cl_3$ (d) $[Cr(en)_2Cl_2]^+$

35. $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$ are related to each other as
(a) geometrical isomers (b) optical isomers
(c) linkage isomers (d) coordination isomers

36. Coordination isomerism is caused by the interchange of ligands between the
(a) cis and trans structure
(b) complex cation and complex anion
(c) inner sphere and outer sphere
(d) low oxidation and higher oxidation states

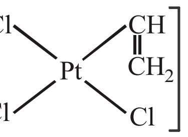
37. The pair in which both species have same magnetic moment (spin only value) is :
(a) $[Cr(H_2O)_6]^{2+}$, $[CoCI_4]^{2-}$
(b) $[Cr(H_2O_6)^{2+}, [Fe(H_2O)_6]^{2+}$
(c) $[Mn(H_2O)_6]^{2+}, [Cr(H_2O)_6]^{2+}$
(d) $[CoCl_4)^{2-}, [Fe(H_2O)_6]^{2+}$

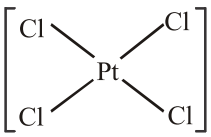
38. The ligands in anti cancer drug *cis*-platin are:
(a) NH_3, CI (b) NH_3, H_2O
(c) Cl, H_2O (d) NO, Cl

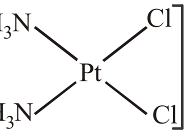
39. The number of precipitable halide ions in the sample $[Pt(NH_3)Cl_2Br]Cl$ will be
(a) 2 (b) 3 (c) 4 (d) 1

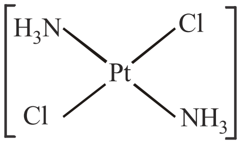
40. Wavelength of red light is absorbed by the complex
(a) $[Cu(CN)_4]^{2-}$ (b) $[Cu(NH_3)_4]^{2+}$
(c) $CuSO_4$ (d) $Cu(CN)_2$

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

(a) 

(b) 

(c) 

(d) 

42. Which one of the following will show paramagnetism corresponding to 2 unpaired electrons?
(Atomic numbers : Ni = 28, Fe = 26)
(a) $[FeF_6]^{3-}$ (b) $[NiCl_4]^{2-}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Ni(CN)_4]^{2-}$

43. $[Fe(NO_2)_3Cl_3]$ and $[Fe(ONO)_3Cl_3]$ shows
(a) linkage isomerism (b) geometrical isomerism
(c) optical isomerism (d) none of the above

44. The number of unpaired electrons in the complex $[Cr(NH_3)_6]Br_3$ is (Atomic number Cr = 24)
(a) 4 (b) 1 (c) 2 (d) 3

45. Atomic number of Cr and Fe are respectively 25 and 26, which of the following is paramagnetic?
(a) $[Cr(CO)_6]$ (b) $[Fe(CO)_5]$
(c) $[Fe(CN)_6]^{-4}$ (d) $[Cr(NH_3)_6]^{+3}$

46. $[Cr(H_2O)_6]Cl_3$ (at. no. of Cr = 24) has a magnetic moment of 3.83 B. M. The correct distribution of 3*d* electrons in the Chromium of the complex is
(a) $3d_{xy^1}, (3d_{x^2-y^2})^1, 3d_{yz^1}$
(b) $3d_{xy^1}, 3d_{yz^1}, 3d_{xz^1}$
(c) $3d_{xy^1}, 3d_{yz^1}, 3d_{z^2}$
(d) $(3d_{x^2-y^2})^1, 3d_{z^2}, 3d_{xz^1}$

47. Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour ?

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

(c) $[Mn(CN)_6]^{3-}$ (d) $[Cr(CN)_6]^{3-}$

(At. Nos : Cr = 24, Mn = 25, Fe = 26, Co = 27)

48. A chemist wants to determine the molecular geometry of the $[CoCl_4]^{2-}$ ion. Which of the following gives the best suggestion for a measurement and for the interpretation of that measurement?

(a) Using absorption spectroscopy, measure λ_{max} then calculate Δ_o for octahedral geometry

(b) Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molecule. If this number is low, the geometry is likely to be square planar; otherwise, it is likely to be tetrahedral

(c) Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molcule.If this number is low, the geometry is likely to be tetrahedral; otherwise, it is likely to be square planar

(d) Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molecule. If this number is low, the geometry is likely to be tetrahedral; otherwise, it is likely to be octahedral

49. The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is

(a) d^5 (in strong ligand field)

(b) d^3 (in weak as well as in strong fields)

(c) d^4 (in weak ligand fields)

(d) d^4 (in strong ligand fields)

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

(a) 6 (b) 1.73 (c) 2.84 (d) 4.90

51. How many pairs of enantiomers are possible for following complex compound, $[M(AB)(CD)ef]^{n\pm}$

(where AB, CD– Unsymmetrical bidentate ligand, e, f– Monodentate ligands)

(a) 20 (b) 5 (c) 10 (d) 8

52. Which has maximum paramagnetic nature ?

(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Cu(NH_3)_4]^{2+}$

(c) $[Fe(CN)_6]^{4-}$ (d) $[Cu(H_2O)_4]^{2+}$

53. The compound which is not coloured is

(a) $K_4[Fe(CN)_6]$ (b) $K_3[Fe(CN)_6]$

(c) $Na_2[CdCl_4]$ (d) $Na_2[CuCl_4]$

54. Which complex of Co^{2+} will have the weakest crystal field splitting –

(a) $[CoCl_6]^{4-}$ (b) $[Co(CN)_6]^{4-}$

(c) $[Co(NH_3)_6]^{2+}$ (d) $[Co(en)_3]^{2+}$

55. A complex $[CoL_6]^{n+}$ where L is neutral ligand has a magnetic moment $\mu = 4.5$ B. M. Hence,

(a) Co must be in +2 oxidation state

(b) L must be a strong ligand

(c) Co must be in +3 oxidation state

(d) None of these

56. Which one of the following complexes is an outer orbital complex ?

(a) $[Co(NH_3)_6]^{3+}$ (b) $[Mn(CN)_6]^{4-}$

(c) $[Fe(CN)_6]^{4-}$ (d) $[Ni(NH_3)_6]^{2+}$

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

57. A square planar complex is formed by hybridisation of which atomic orbitals?

(a) s, p_x, p_y, d_{yz} (b) $s, p_x, p_y, d_{x^2-y^2}$

(c) s, p_x, p_y, d_{z^2} (d) s, p_y, p_z, d_{xy}

58. Which of the following may be considered to be an organometallic compound?

(a) Nickel tetracarbonyl (b) Chlorophyll

(c) $K_3[Fe(C_2O_4)_3]$ (d) $[Co(en)_3]Cl_3$

59. Which of the following organometallic compound is σ and π bonded?

(a) $[Fe(\eta^5-C_5H_5)_2]$ (b) $Fe(CH_3)_3$

(c) $K[PtCl_3(\eta^2-C_2H_4)]$ (d) $[Co(CO)_5NH_3]^{2+}$

60. In $Fe_2(CO)_9$, the two iron atoms are

(a) linked only directly

(b) linked directly along with 3 CO molecules as bridging ligands

(c) linked only through 3 CO molecules as bridging ligands

(d) joined through one CO group as bridging ligands.

61. Among the following, which is **not** the π-bonded organometallic compound?

(a) $(CH_3)_4Sn$ (b) $K[PtCl_3(\eta^2-C_2H_4)]$

(c) $Fe(\eta^5-C_5H_5)_2$ (d) $Cr(\eta^6-C_6H_6)_2$

62. Which one of the following is the correct order of field strength of ligands in spectrochemical series?

(a) $I^- < Cl^- < F^- < H_2O < CN^-$

(b) $F^- < H_2O < I^- < CN^- < Cl^-$

(c) $CN^- < I^- < F^- < Cl^- < H_2O$

(d) $H_2O < F^- < CN^- < Cl^- < I^-$

63. Which of the following does **not** have a metal- carbon bond?

(a) $Al(OC_2H_5)_3$ (b) C_2H_5MgBr

(c) $K[Pt(C_2H_4)Cl_3]$ (d) $Ni(CO)_4$

64. Coordination compounds have great importance in biological systems. In this context which of the following statements is **incorrect** ?

(a) Cyanocobalamin is B_{12} and contains cobalt

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

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

(d) Carboxypeptidase - A is an enzyme and contains zinc.

65. Ammonia will not form complex with

(a) Ag^{2+} (b) Pb^{2+} (c) Cu^{2+} (d) Cd^{2+}

66. In $Fe(CO)_5$, the Fe – C bond possesses

(a) ionic character (b) σ-character only

(c) π-character (d) both σ and π characters

67. Which method can be used to distinguish $[Co(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_6][Co(NO_2)_6]$

(a) by measurement of their conductivity
(b) by titration method
(c) by precipitation method with $AgNO_3$
(d) by electrolysis of their aqueous solutions

68. The organometallic compound is :

(a) $Ti(OCOCH_3)_4$ (b) $Ti(C_2H_4)_4$
(c) $Ti(OC_6H_5)_4$ (d) $Ti(OC_2H_5)_4$

69. Which of the following is an organometallic compound?

(a) Lithium methoxide
(b) Lithium acetate
(c) Lithium dimethylamide
(d) Methyl lithium

70. The formula of ferrocene is

(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(CO)_5]$ (d) $[(C_5H_5)_2Fe]$

71. The π– bonded organometallic compound which has ethene as one of its component is

(a) Zeise's salt (b) Ferrocene
(c) Dibenzene chromium (d) Tetraethyl tin

72. Which of the following will give a pair of enantiomorphs?

(a) $[Cr(NH_3)_6][Co(CN)_6]$
(b) $[Co(en)_2Cl_2]Cl$
(c) $[Pt(NH_3)_4]\,[PtCl_6]$
(d) $[Co(NH_3)_4Cl_2]NO_2$. (en $=NH_2CH_2CH_2NH_2$)

73. The d electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Ni^{2+} are $3d^4$, $3d^5$, $3d^6$ and $3d^8$ respectively. Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour?

(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Ni(H_2O)_6]^{2+}$
(c) $[Cr(H_2O)_6]^{2+}$ (d) $[Mn(H_2O)_6]^{2+}$
(At. No. Cr = 24, Mn = 25, Fe = 26, Ni = 28)

74. Which of the following complexes exhibits the highest paramagnetic behaviour ?

(a) $[V(gly)_2(OH)_2(NH_3)_2]^+$
(b) $[Fe(en)(bpy)(NH_3)_2]^{2+}$
(c) $[Co(ox)_2(OH)_2]^{2-}$
(d) $[Ti(NH_3)_6]^{3+}$

where gly = glycine, en = ethylenediamine and bpy = bipyridyl moities)
(At.nosTi = 22, V = 23, Fe = 26, Co = 27)

75. In which of the following coordination entities the magnitude Δ_0 (CFSE in octahedral field) will be maximum?

(a) $[Co(H_2O)_6]^{3+}$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[Co(CN)_6]^{3-}$ (d) $[Co\,(C_2O_4)_3]^{3-}$
(At. No. Co = 27)

76. Which of the following **does not** show optical isomerism?

(a) $[Co(NH_3)_3Cl_3]^0$ (b) $[Co\,(en)\,Cl_2\,(NH_3)_2]^+$
(c) $[Co\,(en)_3]^{3+}$ (d) $[Co\,(en)_2Cl_2]^+$
(en = ethylenediamine)

77. Which of the following complex ions is expected to absorb visible light?

(a) $[Ti\,(en)_2(NH_3)_2]^{4+}$ (b) $[Cr\,(NH_3)_6]^{3+}$
(c) $[Zn\,(NH_3)_6]^{2+}$ (d) $[Sc\,(H_2O)_3\,(NH_3)_3]^{3+}$
(At. no. Zn = 30, Sc = 21, Ti = 22, Cr = 24)

78. Which of the following complex ion is not expected to absorb visible light ?

(a) $[Ni(CN)_4]^{2-}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Ni(H_2O)_6]^{2+}$

79. Which one of the following complexes is not expected to exhibit isomerism?

(a) $[Ni(en)_3]^{2+}$ (b) $[Ni(NH_3)_4(H_2O)_2]^{2+}$
(c) $[Pt(NH_3)_2\,Cl_2]$ (d) $[Ni(NH_3)_2\,Cl_2]$

80. Of the following complex ions, which is diamagnetic in nature?

(a) $[NiCl_4]^{2-}$ (b) $[Ni(CN)_4]^{2-}$
(c) $[CuCl_4]^{2-}$ (d) $[CoF_6]^{3-}$

81. The complexes $[Co(NH_3)_6]\,[Cr(CN)_6]$ and $[Cr(NH_3)_6]\,[Co(CN)_6]$ are the examples of which type of isomerism?

(a) Linkage isomerism
(b) Ionization isomerism
(c) Coordination isomerism
(d) Geometrical isomerism

82. The complex, $[Pt(py)(NH_3)BrCl]$ will have how many geometrical isomers ?

(a) 3 (b) 4
(c) 0 (d) 2

83. Which of the following complex compounds will exhibit highest paramagnetic behaviour?

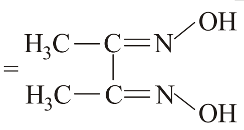
(At. No. : Ti = 22, Cr = 24, Co = 27, Zn = 30)

(a) $[Ti\,(NH_3)_6]^{3+}$ (b) $[Cr\,(NH_3)_6]^{3+}$
(c) $[Co\,(NH_3)_6]^{3+}$ (d) $[Zn\,(NH_3)_6]^{2+}$

84. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal Ni(II). Which of the following statements is not true ?

(a) Red complex has a square planar geometry.
(b) Complex has symmetrical H-bonding
(c) Red complex has a tetrahedral geometry.
(d) Dimethylglyoxime functions as bidentate ligand.

dimethylglyoxime =



85. Low spin complex of d^6-cation in an octahedral field will have the following energy :

(a) $\frac{-12}{5}\Delta_0 + P$ (b) $\frac{-12}{5}\Delta_0 + 3P$

(c) $\frac{-2}{5}\Delta_0 + 2P$ (d) $\frac{-2}{5}\Delta_0 + P$

(Δ_0= Crystal Field Splitting Energy in an octahedral field, P = Electron pairing energy)

86. Which of the following has a square planar geometry?

(a) $[PtCl_4]^{2-}$ (b) $[CoCl_4]^{2-}$

(c) $[FeCl_4]^{2-}$ (d) $[NiCl_4]^{2-}$

(At. nos.: Fe = 26, Co = 27, Ni = 28, Pt = 78)

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

$[E(en)_2(C_2O_4)]NO_2$ (where (en) is ethylene diamine) are, respectively,

(a) 6 and 2 (b) 4 and 2

(c) 4 and 3 (d) 6 and 3

88. Which of the following pairs represent linkage isomers?

(a) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$

(b) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

(c) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

(d) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

89. A solution containing 2.675 g of $CoCl_3.6NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is

(At. mass of Ag = 108 u)

(a) $[Co(NH_3)_6]Cl_3$ (b) $[CoCl_2(NH_3)_4]Cl$

(c) $[CoCl_3(NH_3)_3]$ (d) $[CoCl(NH_3)_5]Cl_2$

90. Which one of the following has an optical isomer?

(a) $[Zn(en)(NH_3)_2]^{2+}$ (b) $[Co(en)_3]^{3+}$

(c) $[Co(H_2O)_4(en)]^{3+}$ (d) $[Zn(en)_2]^{2+}$

(en = ethylenediamine)

91. Which one of the following complex ions has geometrical isomers ?

(a) $[Ni(NH_3)_5Br]^+$ (b) $[Co(NH_3)_2(en)_2]^{3+}$

(c) $[Cr(NH_3)_4(en)_2]^{3+}$ (d) $[Co(en)_3]^{3+}$

(en = ethylenediamine)

92. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong?

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

(b) The complex is paramagnetic.

(c) The complex is an outer orbital complex

(d) The complex gives white precipitate with silver nitrate solution.

93. Among the ligands NH_3, en, CN^- and CO the correct order of their increasing field strength, is :

(a) $NH_3 < en < CN^- < CO$

(b) $CN^- < NH_3 < CO < en$

(c) $en < CN^- < NH_3 < CO$

(d) $CO < NH_3 < en < CN^-$

94. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide?

(a) $[Cr(en)_3]Br_3$ (b) $[Cr(en)_2Br_2]Br$

(c) $[Cr(en)Br_4]^-$ (d) $[Cr(en)Br_2]Br$

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

(a) Tetraaquadiaminecobalt (III) chloride

(b) Tetraaquadiamminecobalt (III) chloride

(c) Diaminetetraaquacoblat (II) chloride

(d) Diamminetetraaquacobalt (III) chloride

96. The charge on the central metal ion in the complex $[Ni(CO)_4]$ is

(a) +2 (b) +4

(c) 0 (d) +3

97. The ligand $N(CH_2CH_2NH_2)_3$ is

(a) tridentate (b) pentadentate

(c) tetradentate (d) bidentate

98. The IUPAC name of the complex $[Co(NH_3)_4(H_2O)Cl]Cl_2$ is

(a) aquatetramminechloridocobalt (III) chloride

(b) chloridoaquatetramminechloridocobalt (III) chloride

(c) chloridoaquatetramminechloridocobalt (III) chloride

(d) tetrammineaquachloridocobalt (III) chloride

99. The magnetic moment of $[NiCl_4]^{-2}$ is expected to be

(a) 2.88 BM (b) 1.44 BM

(c) 5.25 BM (d) 4.91 BM

100. Ammonia will not form complex with

(a) Ag^{2+} (b) Pb^{2+}

(c) Cu^{2+} (d) Cd^{2+}

EXERCISE - 2

Applied Questions

1. The crystal field splitting energy for octahedral (Δ_0) and tetrahedral (Δ_t) complexes is related as

(a) $\Delta_t = -\frac{1}{2}\Delta_0$ (b) $\Delta_t = -\frac{4}{9}\Delta_0$

(c) $\Delta_t = -\frac{3}{5}\Delta_0$ (d) $\Delta_t = -\frac{2}{5}\Delta_0$

2. Among the following complexes, optical activity is possible in

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

(b) $[Co(H_2O)_2(NH_3)_2Cl_2]^+$

(c) $[Cr(H_2O)_2Cl_2]^+$

(d) $[Co(CN)_5NC]$

3. Facial and meridional isomerism will be exhibited by

(a) $[Co(NH_3)_3Cl_3]$ (b) $[Co(NH_3)_4Cl_2]Cl$

(c) $[Co(en)_3]Cl_3$ (d) $[Co(NH_3)_5Cl]Cl_2$

4. A co-ordination complex compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of $AgNO_3$ solution, we get two moles of AgCl precipitate. The ionic formula for this complex would be

(a) $[Co(NH_3)_4(NO_2)Cl][(NH_3)Cl]$

(b) $[Co(NH_3)_5Cl][Cl(NO_2)]$

(c) $[Co(NH_3)_5(NO_2)]Cl_2$

(d) $[Co(NH_3)_5][(NO_2)_2Cl_2]$

5. Which of the following complexes exists as pair of enantiomers?

(a) trans-$[Co(en)_2Cl_2]^+$

(b) $[Co(NH_3)_4Cl_2]^+$

(c) $[Co\{P(C_2H_5)_3\}_2ClBr]$

(d) $[Cr(en)_3]^{+3}$

6. Which one of the following is an inner orbital complex as well as diamagnetic in behaviour? (Atomic number: Zn = 30, Cr = 24, Co = 27, Ni = 28)

(a) $[Zn(NH_3)_6]^{2+}$ (b) $[Cr(NH_3)_6]^{3+}$

(c) $[Co(NH_3)_6]^{3+}$ (d) $[Ni(NH_3)_6]^{2+}$

7. $[Co(NH_3)_4(NO_2)_2]Cl$ exhibits

(a) linkage isomerism, ionization isomerism and geometrical isomerism

(b) ionization isomerism, geometrical isomerism and optical isomerism

(c) linkage isomerism, geometrical isomerism and optical isomerism

(d) linkage isomerism, ionization isomerism and optical isomerism

8. Which one of the following has the highest molar conductivity?

(a) Diamminedichloroplatinum (II)

(b) Tetraamminedichlorocobalt (III) chloride

(c) Potassium hexacyanoferrate (II)

(d) Hexaaquochromium (III) chloride

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

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

(c) $[Co(NH_3)_4Cl]Cl_2.NH_3$ (d) $[Co(NH_3)_5Cl]Cl_2$

10. The ligand $N(CH_2CH_2NH_2)_3$ is

(a) tridentate (b) pentadentate

(c) tetradentate (d) bidentate

11. Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN^- ion towards metal species is

(a) c, a (b) b, c (c) a, b (d) a, b, c

12. Which one of the following has largest number of isomers ?

(a) $[Ir(PR_3)_2H(CO)]^{2+}$

(b) $[Co(NH_3)_5Cl]^{2+}$

(c) $[Ru(NH_3)_4Cl_2]^+$

(d) $[Co(en)_2Cl_2]^+$ (R = alkyl group, en = ethylenediamine)

13. Which among the following statements are true for the complex $[Co(NH_3)_6][Cr(CN)_6]$?

1. It is a non-electrolyte
2. The magnitude of the charge on each complex ion is 3
3. The complex will not conduct current
4. The complex will exhibit coordination isomerism
5. The magnitude of the charge on each complex ion is 1

(a) 1 and 4 (b) 1 and 2

(c) 1 and 3 (d) 2 and 4

14. The correct order of magnetic moments (spin only values in B.M.) among is

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

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

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

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

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

15. Among the following coordination compounds/ions

(i) $\left[Fe(CN)_6\right]^{3-}$ (ii) $\left[Pt(NH_3)_2Cl_2\right]$

(iii) $\left[Co(NH_3)_6\right]^{3+}$ (iv) $\left[Cr(H_2O)_6\right]Cl_3$

Which species exhibit geometrical isomerism?

(a) (ii) only (b) (i) and (ii)

(c) (ii) and (iv) (d) (i) and (iii)

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

(a) one, square planar (b) two, square planar
(c) one, tetrahedral (d) two, tetrahedral

17. A complex cation is formed by Pt (in some oxidation state) with ligands (in proper number so that coordination number of Pt becomes six). Which of the following can be its correct IUPAC name ?

(a) Diammineethylenediaminedithiocyanato-S-platinum (II)
(b) Diammineethylenediaminedithiocyanato-S-platinate (IV) ion
(c) Diammineethylenediaminedithiocyanato-S-platinum (IV) ion
(d) Diamminebis (ethylenediamine) dithiocyanato-S-platinum (IV) ion

18. $[Fe(en)_2(H_2O)_2]^{2+}$ + en → complex (X). The correct statement about the complex (X) is –

(a) it is a low spin complex
(b) it is diamagnetic
(c) it shows geometrical isomerism
(d) (a) and (b) both

19. Among the following, the species that is both paramagnetic and coloured is –

(a) $[MnO_4]^{2-}$ (b) $[TiCl_6]^{2-}$
(c) $[VO_4]^{3-}$ (d) CrO_2Cl_2

20. 0.02 mole of $[Co(NH_3)_5Br]Cl_2$ and 0.02 mole of $[Co(NH_3)_5Cl]SO_4$ are present in 200 cc of a solution X. The number of moles of the precipitates Y and Z that are formed when the solution X is treated with excess silver nitrate and excess barium chloride are respectively

(a) 0.02, 0.02 (b) 0.01, 0.02
(c) 0.02, 0.04 (d) 0.04, 0.02

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

(a) $-1.8\ \Delta_0$ (b) $-1.6\,\Delta_0 + P$
(c) $-1.2\ \Delta_0$ (d) $-0.6\ \Delta_0$

22. The existence of two different coloured complexes with the composition of $[Co(NH_3)_4Cl_2]^+$ is due to :

(a) linkage isomerism (b) geometrical isomerism
(c) coordination isomerism (d) ionization isomerism

23. The *d*-electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and d^7, respectively. Which one of the following will exhibit minimum paramagnetic behaviour?

(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Fe(H_2O)_6]^{2+}$
(c) $[Co(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$
(At, nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)

24. Which of the following carbonyls will have the strongest C – O bond ?

(a) $[Mn(CO)_6]^+$ (b) $[Cr(CO)_6]$
(c) $[V(CO)_6]^-$ (d) $[Fe(CO)_5]$

25. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour ?

(a) $[Ni(NH_3)_6]^{2+}$ (b) $[Zn(NH_3)_6)]^{2+}$
(c) $[Cr(NH_3)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

26. In which of the following complexes of the Co (at. no. 27), will the magnitude of Δ_o be the hightest?

(a) $[Co(CN)_6]^{3-}$ (b) $[Co(C_2O_4)_3]^{3-}$
(c) $[Co(H_2O)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

27. Which of the following has an optical isomer

(a) $[Co(en)(NH_3)_2]^{2+}$ (b) $[Co(H_2O)_4(en)]^{3+}$
(c) $[Co(en)_2(NH_3)_2]^{3+}$ (d) $[Co(NH_3)_3Cl]^+$

28. Among the following metal carbonyls, the C–O bond order is lowest in

(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$
(c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$

29. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is

(a) Tetrachloronickel (II) - tetraamminenickel (II)
(b) Tetraamminenickel (II) - tetrachloronickel (II)
(c) Tetraamminenickel (II) - tetrachloronickelate (II)
(d) Tetrachloronickel (II) - tetrachloronickelate (0)

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

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

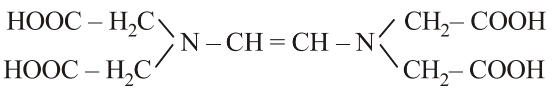
31. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is

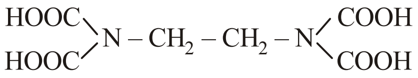
(a) 0 (b) 2.84 (c) 4.90 (d) 5.92

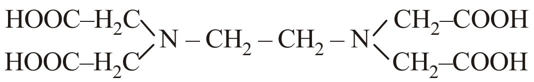
32. The ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is

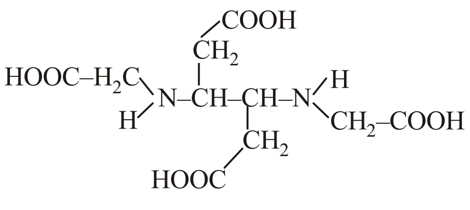
(a) $[Cr(H_2O)_4(O_2N)]Cl_2$
(b) $[Cr(H_2O)_4Cl_2](NO_2)$
(c) $[Cr(H_2O)_4Cl(ONO)]Cl$
(d) $[Cr(H_2O)_4Cl_2(NO_2)].H_2O$

33. The correct structure of ethylenediaminetetraacetic acid (EDTA) is

(a)


(b)


(c)


(d)


34. The complex showing a spin-only magnetic moment of 2.82 B.M. is :

(a) $Ni(CO)_4$ (b) $[NiCl_4]^{2-}$

(c) $Ni(PPh_3)_4$ (d) $[Ni(CN)_4]^{2-}$

35. Among the following complexes (K–P)

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

(a) K, L, M, N (b) K, M, O, P

(c) L, M, O, P (d) L, M, N, O

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

(a) tetrahedral and tetrahedral

(b) square planar and square planar

(c) tetrahedral and square planar

(d) square planar and tetrahedral

37. Which of the following complex species is not expected to exhibit optical isomerism ?

(a) $[Co(en)_3]^{3+}$ (b) $[Co(en)_2Cl_2]^{+}$

(c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(en)(NH_3)_2Cl_2]^{+}$

38. Which one of the following is the correct order of field strength of ligands in spectrochemical series?

(a) $I^- < Cl^- < F^- < H_2O < CN^-$

(b) $F^- < H_2O < I^- < CN^- < Cl^-$

(c) $CN^- < I^- < F^- < Cl^- < H_2O$

(d) $H_2O < F^- < CN^- < Cl^- < I^-$

39. Which of the following organometallic compound is σ and π bonded?

(a) $[Fe(\eta^5-C_5H_5)_2]$ (b) $Fe(CH_3)_3$

(c) $K[PtCl_3(\eta^2-C_2H_4)]$ (d) $[Co(CO)_5NH_3]^{2+}$

40. Which one of the following coordination compounds is used to inhibit the growth of tumours?

(a) Trans-platin (b) EDTA complex of calcium

(c) $[(Ph_3P)_3RhCl]$ (d) Cis-platin

41. Which of the following complexes exists as pair of enantiomers?

(a) trans-$[Co(en)_2Cl_2]^+$ (b) $[Co(NH_3)_4Cl_2]^+$

(c) $[Co\{P(C_2H_5)_3\}_2ClBr]$ (d) $[Cr(en)_3]^{+3}$

42. Which of the following complex ions is diamagnetic?

(a) $[FeF_6]^{3-}$ (b) $[CoF_6]^{3-}$

(c) $[Co(C_2O_4)_3]^{3-}$ (d) $[Fe(CN)_6]^{3-}$

43. Which one of the following has the highest molar conductivity?

(a) Diamminedichloroplatinum (II)

(b) Tetraamminedichlorocobalt (III) chloride

(c) Potassium hexacyanoferrate (II)

(d) Hexaaquochromium (III) chloride

44. Among the following coordination compounds/ions

(i) $[Fe(CN)_6]^{3-}$ (ii) $[Pt(NH_3)_2Cl_2]$

(iii) $[Co(NH_3)_6]^{3+}$ (iv) $[Cr(H_2O)_6]Cl_3$

Which species exhibit geometrical isomerism?

(a) (ii) only (b) (i) and (ii)

(c) (ii) and (iv) (d) (i) and (iii)

45. The crystal field splitting energy for octahedral (Δ_0) and tetrahedral (Δ_t) complexes is related as

(a) $\Delta_t = -\frac{1}{2}\Delta_0$ (b) $\Delta_t = -\frac{4}{9}\Delta_0$

(c) $\Delta_t = -\frac{3}{5}\Delta_0$ (d) $\Delta_t = -\frac{2}{5}\Delta_0$

46. Facial and meridional isomerism will be exhibited by

(a) $[Co(NH_3)_3Cl_3]$ (b) $[Co(NH_3)_4Cl_2]Cl$

(c) $[Co(en)_3]Cl_3$ (d) $[Co(NH_3)_5Cl]Cl_2$

DIRECTIONS for Qs. 47 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

(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

47. **Statement-1 :** $[FeF_6]^{3-}$ is a low spin complex.

Statement-2 : Low spin complexes have lesser number of unpaired electrons.

48. **Statement-1 :** NF_3 is a weaker ligand than $N(CH_3)_3$.

Statement-2 : NF_3 ionizes to give F^- ions in aqueous solution.

49. **Statement-1 :** $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

Statement-2 : $[Fe(CN)_6]^{3-}$ has +3 oxidation state while $[Fe(CN)_6]^{4-}$ has +2 oxidation state.

50. **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 $[Sc(H_2O)_6]^{3+}$.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Which of the following complexes formed by Cu^{2+} ions is most stable?
(a) $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$, log K = 11.6
(b) $Cu^{2+} + 4CN^{-} \rightarrow [Cu(CN)_4]^{2-}$, log K = 27.3
(c) $Cu^{2+} + 2en \rightarrow [Cu(en)_2]^{2+}$, lok K = 15.4
(d) $Cu^{2+} + 4H_2O \rightarrow [Cu(H_2O)_4]^{2+}$, log K = 8.9

2. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$.
(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$
(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$
(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} < [Co(H_2O)_6]^{3+}$

3. When 0.1 mol $CoCl_3$ $(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to
(a) 1 : 3 electrolyte
(b) 1 : 2 electrolyte
(c) 1 : 1 electrolyte
(d) 3 : 1 electrolyte

4. When 1 mole of $CrCl_3 . 6H_2O$ is treated with excess of $AgNO_3$, 3 moles of AgCl are obtained. The formula of the complex is
(a) $[CrCl_3(H_2O)_3] . 3H_2O$
(b) $[CrCl_2(H_2O)_4]Cl . 2H_2O$
(c) $[CrCl(H_2O)_5]Cl_2 . H_2O$
(d) $[Cr(H_2O)_6]Cl_3$

5. The correct IUPAC name of $[Pt (NH_3)_2Cl_2]$ is
(a) Diamminedichloridoplatinum (II)
(b) Diamminedichloridoplatinum (IV)
(c) Diamminedichloridoplatinum (0)
(d) Dichloridodiammineplatinum (IV)

6. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?
(a) $[Fe(CO)_5]$
(b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(C_2O_4)_3]^{3-}$
(d) $[Fe(H_2O)_6]^{3+}$

7. Indicate the complex ion which shows geometrical isomerism.
(a) $[Cr(H_2O)_4Cl_2]^{+}$
(b) $[Pt(NH_3)_3Cl]^{3-}$
(c) $[Co(NH_3)_6]^{3-}$
(d) $[Co(CN)_5(NC)]^{3-}$

8. The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be
(a) 18,000 cm^{-1}
(b) 16,000 cm^{-1}
(c0 8,000 cm^{-1}
(d) 20,000 cm^{-1}

9. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2 (SCN)_2]$ and $[Pd(C_6H_5)_2 (NCS)_2]$ are
(a) linkage isomers
(b) coordination isomers
(c) ionisation isomers
(d) geometrical isomers

10. The compounds $[Co(SO_4) (NH_3)_5]$ Br and $[Co(SO_4) (NH_3)_5]$ Cl represent
(a) linkage isomerism
(b) ionisation isomerism
(c) coordination isomerism
(d) no isomerism

11. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?
(a) Thiosulphato
(b) Oxalato
(c) Glycinato
(d) Ethane-1, 2-diamine

12. Which of the following species is not expected to be a ligand?
(a) NO
(b) NH_4^+
(c) $NH_2CH_2CH_2NH_2$
(d) CO

13. What kind of isomerism exists between $[Cr(H_2O)_6]$ Cl_3 (violet) and $[Cr (H_2O)_5Cl]$ $Cl_2 . H_2O$ (greyish-green)?
(a) Linkage isomerism
(b) Solvate isomerism
(c) Ionisation isomerism
(d) Coordination isomerism

14. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is
(a) Platinum diamminechloronitrite
(b) Chloronitrito-N-ammineplatinum (II)
(c) Diamminechloridonitrito-N-platinum (II)
(d) Diamminechloronitrito-N-plantinate (II)

NEET/AIPMT (2013-2017) Questions

15. A magnetic moment of 1.73 BM will be shown by one among the following : ***[2013]***
(a) $[Ni(CN)_4]^{2-}$
(b) $TiCl_4$
(c) $[CoCl_6]^{4-}$
(d) $[Cu(NH_3)_4]^{2+}$

16. An excess of $AgNO_3$ is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium (III) chloride. The number of moles of AgCl precipitated would be : ***[2013]***
(a) 0.002
(b) 0.003
(c) 0.01
(d) 0.001

17. The correct IUPAC name for $[CrF_2(en)_2]Cl$ is: ***[NEET Kar. 2013]***
(a) Chlorodifluoridobis (ethylene diamine) chromium (III)
(b) Chlorodifluoridoethylenediaminech-romium (III) chloride
(c) Difluoridobis (ethylene diamine) chromium (III) chloride
(d) Difluorobis-(ethylene diamine) chromium (III) chloride

18. Crystal field splitting energy for high spin d^4 octahedral complex is: ***[NEET Kar. 2013]***
(a) $-1.6\,\Delta_0$
(b) $-1.2\,\Delta_0$
(c) $-0.6\,\Delta_0$
(d) $-0.8\,\Delta_0$

19. Which is diamagnetic? ***[NEET Kar. 2013]***
(a) $[Fe(CN)_6]^{3-}$
(b) $[Co(F_6)]^{3-}$
(c) $[Ni(CN)_4]^{2-}$
(d) $[NiCl_4]^{2-}$

20. In a particular isomer of $[Co(NH_3)_4Cl_2]^0$, the Cl-Co-Cl angle is 90°, the isomer is known as ***[NEET Kar. 2013]***
(a) Linkage isomer
(b) Optical isomer
(c) *cis*-isomer
(d) Position isomer

21. The anion of acetylacetone (acac) forms $Co(acac)_3$ chelate with Co^{3+}. The rings of the chelate are ***[NEET Kar. 2013]***

(a) three membered
(b) five membered
(c) four membered
(d) six membered

22. Which among the following is a paramagnetic complex? ***[NEET Kar. 2013]***

(a) $Mo(CO)_6$
(b) $[Co(NH_3)_6]^{3+}$
(c) $[Pt(en)Cl_2]$
(d) $[CoBr_4]^{2-}$

(At. No. of Mo = 42, Pt = 78)

23. Among the following complexes the one which shows zero crystal field stabilization energy (CFSE): ***[2014]***

(a) $[Mn(H_2O)_6]^{3+}$
(b) $[Fe(H_2O)_6]^{3+}$
(c) $[Co(H_2O)_6]^{2+}$
(d) $[Co(H_2O)_6]^{3+}$

24. Which of the following complexes is used as an anti-cancer agent: ***[2014]***

(a) *mer*-$[Co(NH_3)_3Cl_3]$
(b) *cis*-$[PtCl_2(NH_3)_2]$
(c) *cis*-$K_2[PtCl_2Br_2]$
(d) Na_2CoCl_4

25. Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test of chloride ions with silver nitrate at 25ºC ? ***[2015]***

(a) $CoCl_3 \cdot 4NH_3$
(b) $CoCl_3 \cdot 5NH_3$
(c) $CoCl_3 \cdot 6NH_3$
(d) $CoCl_3 \cdot 3NH_3$

26. Which of these statements about $[Co(CN)_6]^{3-}$ is true ? ***[2015]***

(a) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration.
(b) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a high spin configuration.
(c) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a high-spin configurtion.
(d) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration.

27. The sum of coordination number and oxidation number of the metal M in the complex $[M(en)_2(C_2O_4)]Cl$ (where *en* is ethylenediamine) is: ***[2015 RS]***

(a) 9
(b) 6
(c) 7
(d) 8

28. The name of complex ion, $[Fe(CN)_6]^{3-}$ is : ***[2015 RS]***

(a) Hexacyanoiron (III) ion
(b) Hexacyanitoferrate (III) ion
(c) Tricyanoferrate (III) ion
(d) Hexacyanidoferrate (III) ion

29. Number of possible isomers for the complex $[Co(en)_2Cl_2]Cl$ will be (en = ethylenediamine) ***[2015 RS]***

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

30. Which of the following has longest C–O bond length? (Free C–O bond length in CO is 1.128Å) ***[2016]***

(a) $Ni(CO)_4$
(b) $[Co(CO)_4]^-$
(c) $[Fe(CO)_4]^{2-}$
(d) $[Mn(CO)_6]^+$

31. An example of a sigma bonded organometallic compound is : ***[2017]***

(a) Grignard's reagent
(b) Ferrocene
(c) Cobaltocene
(d) Ruthenocene

32. $HgCl_2$ and I_2 both when dissolved in water containing I ions the pair of species formed is : ***[2017]***

(a) HgI_2, I^-
(b) HgI_4^{2-}, I_3^-
(c) Hg_2I_2, I^-
(d) HgI_2, I_3^-

33. The correct order of the stoichiometries of AgCl formed when $AgNO_3$ in excess is treated with the complexes : $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$ respectively is :- ***[2017]***

(a) 3 AgCl, 1 AgCl, 2 AgCl
(b) 3 AgCl, 2 AgCl, 1 AgCl
(c) 2 AgCl, 3 AgCl, 1 AgCl
(d) 1 AgCl, 3 AgCl, 2 AgCl

34. Correct increasing order for the wavelengths of absorption in the visible region the complexes of Co^{3+} is :- ***[2017]***

(a) $[Co(H_2O)_6]^{3+}, [Co(en)_3]^{3+}, [Co(NH_3)_6]^{3+}$
(b) $[Co(H_2O)_6]^{3+}, [Co(NH_3)_6]^{3+}, [Co(en)_3]^{3+}$
(c) $[Co(NH_3)_6]^{3+}, [Co(en)_3]^{3+}, [Co(H_2O)_6]^{3+}$
(d) $[Co(en)_3]^{3+}, [Co(NH_3)_6]^{3+}, [Co(H_2O)_6]^{3+}$

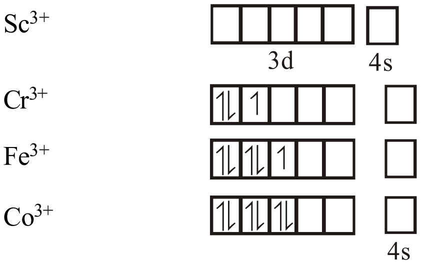
35. Pick out the correct statement with respect to $[Mn(CN)_6]^{3-}$ ***[2017]***

(a) It is sp^3d^2 hybridised and tetrahedral
(b) It is d^2sp^3 hybridised and octahedral
(c) It is dsp^2 hybridised and square planar
(d) It is sp^3d^2 hybridised and octahedral

Hints & Solutions

EXERCISE - 1

1. (c) CN^- is a strong ligand so it forces the electrons to pair up.



In Sc^{3+}, no electron is there in d orbital, in Cr^{3+} one electron is unpaired. In Fe^{3+} also one electron is unpaired, Co^{3+} has no unpaired electrons. As both Cr^{3+} and Fe^{3+} contain one electron in unpaired state so both may be paramagnetic. But as we know Fe has more magnetic properly. Fe^{3+} will be more paramagnetic. So option (c) is correct.

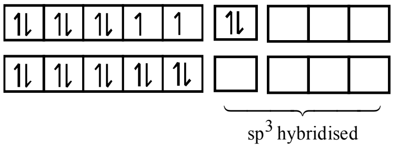
2. (b) IUPAC name is Potassium trioxalatoaluminate (III).

3. (c) $[CuCl_2\{(O=C(NH_2)_2\}_2]$

4. (a) Sodium ethoxide is not an organometallic compound as in this compound carbon is not directly attached with metal.

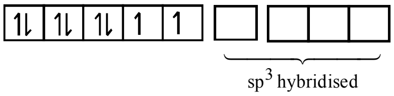
5. (b) Both are tetrahedral. CO is a strong ligand and $P(Ph_3)$ is a weak ligend. So, CO pair up electrons while $P(PH_3)$ do not pair up. Oxidation state of Ni is zero in carboxyl compound which in other Ni has + 2 oxidation state.

Ni(28)



Shape is tetrahedral.

Ni^{2+}



Shape is tetrahedral.

6. (a) Chlorodiaquatriamminecobalt (III) chloride is $[CoCl(NH_3)_3(H_2O)_2]Cl_2$.

7. (a) IUPAC name of sodium nitroprusside $Na_2[Fe(CN)_5NO]$ is sodium pentacyanonitrosylferrate (III) because in it NO is neutral ligand. Hence

2×O.N. of Na + O.N. of Fe + 5×O.N. of CN

1×O.N. of NO = 0

2×(+1) + O.N. of Fe + 5 ×(–1) +1×0 = 0

O.N. of Fe = 5 – 2 = +3, Hence ferrate (III)

8. (a) Let the O. No. of Ni in $K_4[Ni(CN)_4]$ be $= x$ then

$4(+1) + x + (-1) \times 4 = 0 \Rightarrow 4 + x - 4 = 0$

$x = 0$

9. (d) In $[Co(NH_3)_3Cl_3]$, all chlorine atoms are inside the co-ordination sphere so they will not ionise and this compound will not give precipitate with $AgNO_3$.

10. (d) Oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$.

Let it be x, $1 \times x + 4 \times 0 + 2 \times (-1) = 1$ Therefore $x = 3$.

11. (c) $K_3[Fe(CN)_6]$ is Potassium hexacyanoferrate (III).

12. (d) The given complex is $[Cr(NH_3)_3Cl_3]^{3+}$. When it is dissolved in water it forms none other ion.

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

pentaamminenitrito-N-cobalt (III) chloride

14. (b) Complex compounds do not dissociate into constituent ions.

$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN_6)]^{4-}$

∴ It is a complex because no CN^- is formed on dissociation.

15. (d) $[EDTA]^{4-}$ is a hexadentate ligand, because it has six donor atoms and donate 6 pairs of electrons to central metal atom in the complex.

16. (c) It is incorrect statement.

All other statements i.e. (a), (b) and (d) are correct.

17. (d) In $Fe(CO)_5$, Fe is in minimum oxidation state (zero).

18. (b) $K_2[PtCl_6]$

Potassium hexachloroplatinate (IV)

Oxidation state of Pt is + 4 in the complex and anion is present in form of complex.

19. (c) EAN = Atomic number – Oxidation state + 2 × number of Ligands = 26 – 2 + 2 (6) = 36.

20. (b) Organo-metallic compound is (b) as it contains metal-carbon bonds. In others, direct link of carbon with metal is not present.

21. (a) EAN = (atomic no) – (oxidation state) + (2 × number of Ligands) = 28 – 2 + 2 × 4 = 34

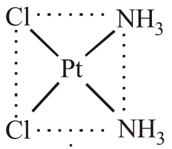
22. (a) EAN = at. no. of central atom – oxidation state + 2 × (no. of ligands) = 27 – 3 + 2 × 6 = 36.

23. (a) Due to back bonding present between metal and carbonyl ligand in metal carbonyl, CO is termed as π-acid ligand.

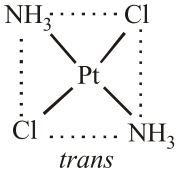
24. (a) In complex $K_4[Fe(CN)_6]$ the Fe obey EAN rule strictly. As in this complex EAN of Fe is 36, which corresponds to the atomic number of krypton

Hence, according to sidwick the complex will be stable

25. (a) Pt $(NH_3)_2$ Cl_2 is a disubstituted complex and shows only *cis*-& *trans*-isomers



cis



trans

26. (b) Among the given metal ions only Ag^+ forms complex with CN^- having co-ordination number 2.

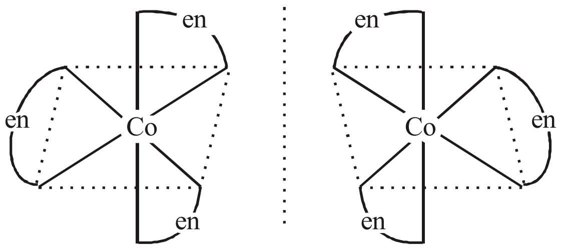
$Ag + 2CN^- \to [Ag(CN)_2]^-$

Coordination number of metals is defined as the number of σ bonds by which ligands are attached to the metal atom.

27. (c) $[Cr(SCN)_2(NH_3)_4]^+$ shows linkage, geometrical and optical isomerism. Hence produces maximum no. of isomers.

28. (a) MA_3B_3 – 2 geometrical isomers
MA_2B_4 – 2 geometrical isomers
MA_4B_2 – 2 geometrical isomers
The complexes of general formula MA_6 and MA_5B having octahedral geometry do not show geometrical isomerism.

29. (d) The optical isomers are pair of molecules which are non superimposable mirror images of each other.



$[Co(en)_3]^{3+}$ (*dextro*) Mirror $[Co(en)_3]^{3+}$ (*laevo*)

The two optically active isomers are collectivity called enantiomers.

30. (b) The chemical formula of Pentaminenitrochromium (III) chloride is

$$\left[Cr\left(NH_3\right)_5 NO_2\right]Cl_2$$

It can exist in following two structures

$$\left[Cr\left(NH_3\right)_5 NO_2\right]Cl_2 \text{ and}$$

$$\left[Cr\left(NH_3\right)_5 ONO\right]Cl_2$$

Therefore the type of isomerism found in this compound is linkage isomerism as nitro group is linked through N as $-NO_2$ or through O as $-ONO$.

31. (a) For any metal cation, the magnitude of Δ_0 depends upon the nature of ligand. Higher the value of Δ_0, lower will be the wave length absorbed. Δ_0 is crystal field stabilisation energy.
The value of Δ_0 for ligands varies as follows

$$H_2O < NH_3 < NO_2^-$$

So, the wavelength absorbed will vary in reverse order

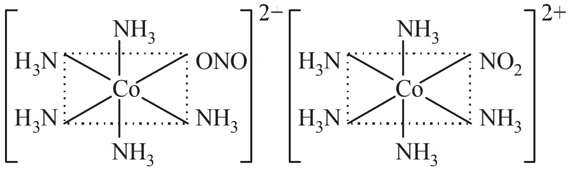
or $NO_2^- < NH_3 < H_2O$

32. (b)

33. (c) *cis*-$[Co(en)_2Cl_2]^+$: *cis*-$[M(aa)_2b_2]$ can show optical isomerism.

34. (a)

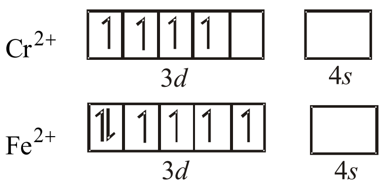
35. (c)



Here more than one atom function as donor, as oxygen in first one and nitrogen in second, so they show linkage isomerism.

36. (b) Co-ordination isomerism is caused by the interchange of ligands between cation and anion complexes.

37. (b) $[Cr(H_2O)_6]^{2+}$. Here Cr is in Cr^{2+} form



In $[Fe(H_2O)]^{2+}$, Fe is in Fe^{2+} form. Both will have 4 unpaired electrons.

38. (a) The ligands in *cis*-platin $[PtCl_2(NH_3)_2]$ are Cl and NH_3.

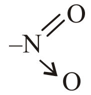
39. (d) $[Pt(NH_3)Cl_2Br]Cl \rightleftharpoons [Pt(NH_3)Cl_2Br]^+ + Cl^-$

Cl^- ion is precipitable.

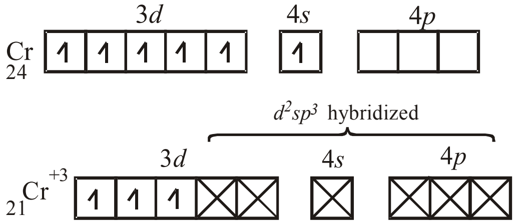
40. (b) The compound which appears blue green, absorb red light as blue-green is complementary to red colour.
Here $[Cu(NH_3)_4]^{2+}$ appears blue-green, so it absorbs red colour.

41. (c) Diaminodichloroplatinum (II) commonly known as *cis*-platin is found to have anticancer property.

42. (b) As in $[NiCl_4]^{-2}$ Chloride ion being a weak ligand is not able to pair the electrons in d orbital.

43. (a) The given compound contains $-NO_2$ group which can donate electrons either from O– or from N– . Thus, it shows linkage isomerism. Thus the two given compounds are linkage isomers, one is nitrite $-O-N=O$ form and the other is nitro,  form.

44. (d) In $[Cr(NH_3)_6]Br_3$, Cr is in +3 oxidation state



Its ion is octahedral in nature. Due to the presence of three unpaired electrons it is paramagnetic.

45. (d) Cr^{3+} has $4s^o\ 3d^3$ electronic configuration with 3 unpaired electrons, hence paramagnetic. In other cases pairing of d-electrons take place in presence of strong field ligands such as CO or CN^-.
In $Cr(CO)_6$ molecule 12 electrons are contributed by CO group and it contain no odd electron

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

$$3.83 = \sqrt{n(n+2)}$$

on solving $n = 3$
as per magnetic moment, it has three unpaired electron.
Cr^{3+} will have configuration as
Cr $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$
Cr^{3+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

$$\underset{d_{xy}}{\boxed{\uparrow}}\underset{d_{yz}}{\boxed{\uparrow}}\underset{d_{zx}}{\boxed{\uparrow}}\boxed{}\boxed{}$$

So, $3d_{xy^1}, 3d_{yz^1}, 3d_{xz^1}$

47. (a) Co^{3+} : $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

$[Co(CN)_6]^{3-}$: $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{}\boxed{}$

CN^- is a strong field ligand and it causes pairing of electrons as a result number of unpaired electrons in Co^{3+} becomes zero and hence it has lowest value of paramagnetic behaviour.

48. (b) In the complexes of C.N. 4, square planar geometry gives rise to low spin (spin paired) configurations whereas tetrahedral complexes display high spin configurations.

49. (d) d^5 —— strong ligand field

$$\underset{t_{2g}}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}}\quad\underset{e_g}{\boxed{}\boxed{}}$$

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

d^3— in weak as well as in strong field

$$\underset{t_{2g}}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad\underset{e_g}{\boxed{}\boxed{}}$$

$\mu = \sqrt{3(5)} = \sqrt{15} = 3.87$ B.M.

d^4– in weak ligand field

$$\underset{t_{2g}}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad\underset{e_g}{\boxed{\uparrow}\boxed{}}$$

$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89$

d^4– in strong ligand field

$$\underset{t_{2g}}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}}\quad\underset{e_g}{\boxed{}\boxed{}}$$

$\mu = \sqrt{2(4)} = \sqrt{8} = 2.82.$

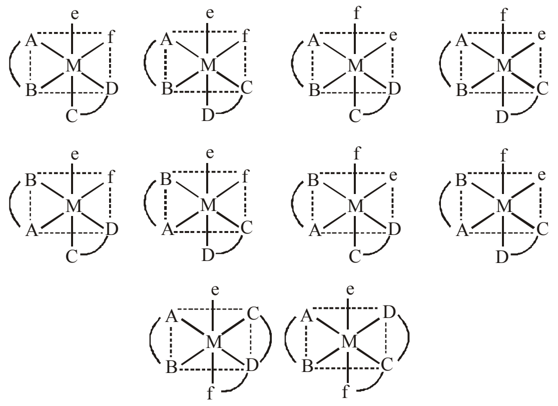
50. (c) The number of unpaired electrons in $Ni^{2+}(aq) = 2$

Water is weak ligand hence no pairing will take place

spin magnetic moment $= \sqrt{n(n+2)} = \sqrt{2(2+2)}$

$= \sqrt{8} = 2.83$

51. (c)



52. (a) Paramagnetic species has unpaired electron. More the no. of unpaired electrons, more will be paramagnetic character.

Complex	O. S. of metal
$[Mn(H_2O)_6]^{2+}$	Mn^{2+}
$[Cu(NH_3)_4]^{2+}$	Cu^{2+}
$[Fe(CN)_6]^{4-}$	Fe^{2+}
$[Cu(H_2O)_4]^{2+}$	Cu^{2+}

Electronic configuration of the ion present in complex

$$Mn^{2+}\ \underset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad\underset{4s}{\boxed{}}\quad\underset{4p}{\boxed{}\boxed{}\boxed{}}$$

No. of unpaired electron = 5

$$Cu^{2+}\ \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\quad\boxed{}\quad\boxed{}\boxed{}\boxed{}$$

No. of unpaired electron = 1

$$Fe^{2+}\ \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\quad\boxed{}\quad\boxed{}\boxed{}\boxed{}$$

However, CN^- is a strong ligand, so pairing of electrons will occur in the complex having CN^- ions.

$\therefore$ Fe^{2+} in presence of CN^-

$$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{}\boxed{}\quad\boxed{}\quad\boxed{}\boxed{}\boxed{}$$

$\therefore$ No. of unpaired electron = 0

Thus $[Mn(H_2O)_6]^{2+}$ having maximum no. of unpaired electrons has maximum paramagnetic nature.

53. (c) In $Na_2[CdCl_4]$, Cd has oxidation state +2.

So, its electronic configuration is $4d^{10}5s^0$

or all the 4*d* orbitals are fully filled.

Hence, there will be no *d*-*d* transition. So, it is colourless.

54. (a) Cl^- is a weak field ligand.

55. (c) Co must be in +3 oxidation state and the ligand L should be a weak ligand.

$Co^{3+} = [Ar]3d^6$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

$n = 4, \mu = 4.5$ BM.

56. (d) Hybridisation

$$\underset{d^2sp^3}{[Fe(CN)_6]^{4-}}, \underset{d^2sp^3}{[Mn(CN)_6]^{4-}},$$

$$\underset{d^2sp^3}{[Co(NH_3)]^{3+}}, \underset{sp^3d^2}{[Ni(NH_3)_6]^{2+}}$$

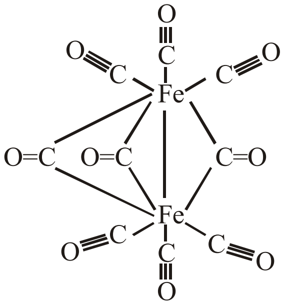
Hence $[Ni(NH_3)_6]^{2+}$ is outer orbital complex.

57. (b) A square planar complex is formed by hybridisation of s, p_x, p_y and $d_{x^2-y^2}$ atomic orbitals.

58. (b) Organometallic compounds are those compounds in which a metal is bonded directly to a carbon atom of a molecule. In chlorophyll there is bond involving metal Mg

59. (d) $[Co(CO)_5 NH_3]^{2+}$. In this complex Co-atom attached with NH_3 through σ bonding and with CO with dative π-bond.

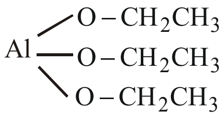
60. (b)



61. (a) The number of carbon atom found in π bonded organometallic compounds is indicated by the greek letter 'η' with a number. The prefixes η^2, η^5 and η^6 indicate that 2, 5 and 6 carbon atom are bound to the metal in the compound.$(CH_3)_4Sn$ does not involve any pi (π) bond formation. This is a σ bonded organometallic compound.

62. (a)

63. (a) Triethoxyaluminium has no Al – C linkage



64. (c) The chlorophyll molecule plays an important role in photosynthesis, contain porphyrin ring and the metal Mg not Ca.

65. (b) The complex formation is a characteristic of d-block elements. Lead is a *p*-block element hence does not forms complex compounds.

66. (d) Due to some backbonding by sidewise overlapping between *d*-orbitals of metal and *p*-orbital of carbon, the Fe–C bond in $Fe(CO)_5$ has both σ and π character.

67. (d) In one case, on electrolysis of aqueous solution, the complex ion of cobalt [i.e., $\{Co(NH_3)_6\}^{3+}$] of the complex $[Co(NH_3)_6][Cr(NO_2)_6]$ moves towards cathode (i.e., negative electrode) and on this electrode finally cobalt would be deposited.

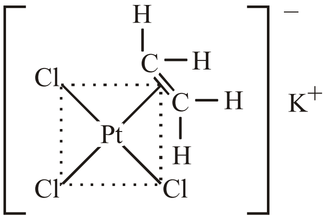
In another case, on electrolysis of aqueous solution, the complex ion of chromium [i.e., $\{Cr(NH_3)_6\}^{3+}$] of the complex $[Cr(NH_3)_6][Co(NO_2)_6]$ moves towards cathode (i.e., negative electrode) and on this electrode chromium would finally be deposited.

68. (b) Organometallic compound is (b) as it contains metal-carbon bonds. In others, direct link of carbon with metal is not present.

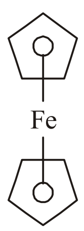
69. (d) Compounds that contain atleast one carbon metal bond are called organometallic compound. Hence, based on above definition methyl lithium is an organometallic compound. In other chemical compounds carbon is not linked with metal.

70. (d)

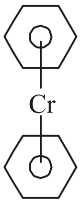
71. (a)



Zeise's salt



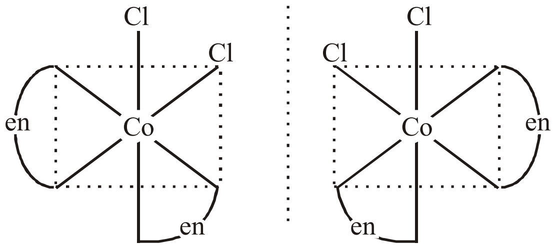
Ferrocene



dibenzene chromium

$(C_2H_5)_4Sn$
tetraethyl tin

72. (b) Non superimposable mirror images are called optical isomers and may be described as "chiral'. They are also called enantiomers and rotate plane polarised light in opposite directions.



73. (b) Lesser is the number of unpaired electrons smaller will be the paramagnetic behaviour. As Cr^{++}, Mn^{++}, Fe^{++} and Ni^{++} contains.

$Cr^{++}(3d^4)$ = | ↑ | ↑ | ↑ | ↑ | |
= 4 unpaired e^-.

$Mn^{++}(3d^5)$ = | ↑ | ↑ | ↑ | ↑ | ↑ |
= 5 unpaired e^-.

$Fe^{++}(3d^6)$ = | ⇅ | ↑ | ↑ | ↑ | ↑ |
= 4 unpaired e^-.

$Ni^{++}(3d^8)$ = | ⇅ | ⇅ | ⇅ | ↑ | ↑ |
= 2 unpaired e^-.

As Ni^{++} has minimum no. of unpaired e^- thus this is least paramagnetic.

74. (c)

75. (c) In octahedral field the crystal field splitting of d- orbitals of a metal ion depends upon the field produced by the ligands. In general ligands can be arranged in a series in the order of increasing fields and splittings which they produce around a central metal ion. A portion of the series is given below.

cyanide > ethylene - diamine > ammonia > pyridine > thiocyanate > water > oxalate > hydroxide > fluoride > chloride > bromide > iodide.

Out of the given ligands water, ammonia, cyanide and oxalate, we can find from the above series of ligands that the maximum splitting will occur in case of cyanide (CN^-) i.e. the magnitude of Δ_0 will be maximum in case of $[Co(CN)_6]^{3+}$.

76. (a) The octahedral coordination compounds of the type MA_3B_3 exhibit fac-mer isomerism.

77. (b) Since Cr^{3+} in the complex has unpaired electrons in the d orbital, hence it will absorb visible light and will be coloured

$Ti = [Ar]3d^2\,4s^2$; $Ti^{4+} = 3d^0$

$Cr = [Ar]\,3d^5\,4s^1$; $Cr^{3+} = 3d^3$

$Zn = [Ar]\,3d^{10}\,4s^2$; $Zn^{2+} = 3d^{10}$

$Sc = [Ar]\,3d^1\,4s^2$; $Sc^{3+} = 3d^0$

78. (a) $[Ni(CN)_4]^{2-}$: Number of unpaired electrons = 0

$[Cr(NH_3)_6]^{3+}$: Number of unpaired electrons = 3

$[Fe(H_2O)_6]^{2+}$: Number of unpaired electrons = 4

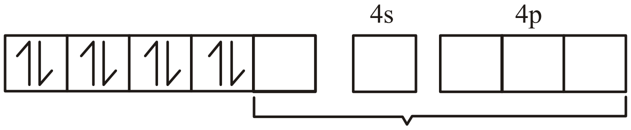
$[Ni(H_2O)_6]^{2+}$: Number of unpaired electrons = 2

79. (d) In $[Ni(NH_3)_2Cl_2]$, Ni^{2+} is in sp^3 hybridisation, thus tetrahedral in shape. Hence the four ligands are not different to exhibit optical isomerism. In tetrahedral geometry all the positions are adjacent to one another $\therefore$ geometrical isomerism is not possible.

80. (b) $Ni^{++} = 3d^8\,4s^0$

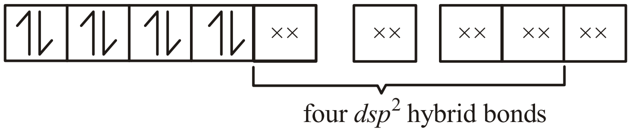
Since, the coordination number of Ni in this complex is 4, the configuration of Ni^{++} at first sight shows that the complex is paramagnetic with two unpaired electron. However, experiments show that the complex is diamagnetic. This is possible when the 3d electrons rearrange against the Hund's rule as shown below. This is in accordance with the fact that the ligand involved here is strong i.e., CN^- ion.

Ni^{++} (after rearrangement)



Hence, now dsp^2 hybridization involving one 3*d*, one 4*s* and two 4*p* orbitals, takes place leading to four dsp^2 hybrid orbitals, each of which accepts four electron pairs from CN^- ion forming $[Ni(CN)_4]^{2-}$ ion.

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

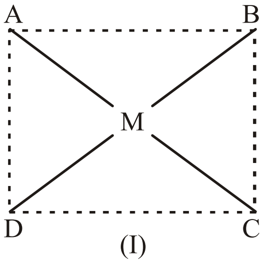


Thus, the complex is diamagnetic as it has no unpaired electron.

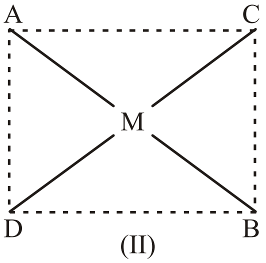
81. (c) Coordination isomerism occurs when cationic and anionic complexes of different metal ions are present in a salt. The two isomers differ in the distribution of ligands in cation and anion e.g.,

$[Co(NH_3)_6][Cr(CN)_6]$ is an isomer of $[Co(CN)_6][Cr(NH_3)_6]$

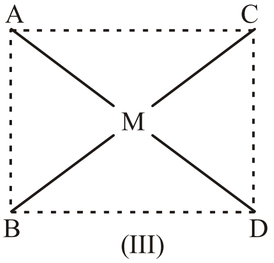
82. (a) Complexes of the type M_{ABCD} may exist in three isomeric forms.



(I)



(II)



(III)

Similarly, $[Pt(py)(NH_3)BrCl]$ may exist in three isomeric form in which

M = Pt, A = Py, B = NH_3, C = Br, D = Cl.

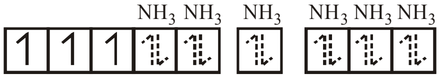
83. (b)

(a) $[Ti(NH_3)_6]^{3+}$: $3d^1$ configuration and thus has one unpaired electron.

(b) $[Cr(NH_3)_6]^{3+}$: In this complex Cr is in +3 oxidation state.

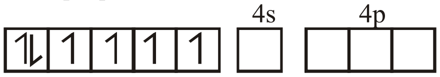
Cr^{3+} : $3d^3\,4s^0$

It has 3 unpaired electrons thus complex is paramagnetic

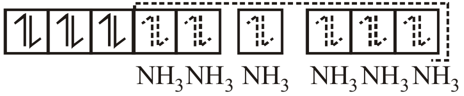


(c) $[Co(NH_3)_6]^{3+}$: In this complex cobalt ion is in + 3 oxidation state with $3d^6$ configuration.

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



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

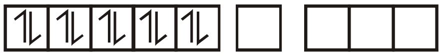


(inner orbital or d^2sp^3 hybrid orbital, low spin complex)

$\therefore$ diamagnetic

(d) In this complex Zn exists as Zn^{++} ion

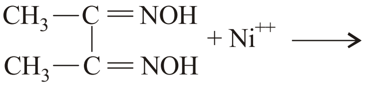
Zn^{++} ion : $3d^{10}\,4s^0$



Zn^{++} ion in $[Zn(NH_3)_4]^{2+}$

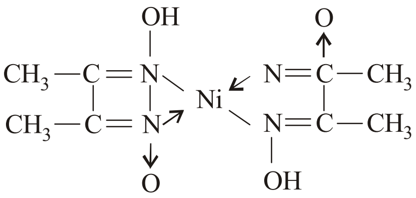
Due to presence of paired electrons complex is diamagnetic in nature.

84. (c) Nickel ions are frequently detected by the formation of red precipitate of the complex of nickel dimethylglyoxime, when heated with dimethylglyoxime.



$$\begin{matrix} CH_3-C=NOH \\ | \\ CH_3-C=NOH \end{matrix} + Ni^{++} \longrightarrow$$

Dimethylglyoxime



Nickel dimethylglyoxime

85. (b) $d^6 - t_{2g}^{\;2,2,2}\; e_g^{\;0,0}$ (in low spin)

$$C.F.S.E = -0.4 \times 6\Delta_0 + 3P = -\frac{12}{5}\Delta_0 + 3P$$

86. (a) Complexes with dsp^2 hybridisation are square planar. So, $[PtCl_4]^{2-}$ is square planar in shape.

87. (d) In the given complex we have two bidentate ligands (i.e en and C_2O_4), so coordination number of E is 6
$(2 \times 2 + 1 \times 2 = 6)$
Let the oxidation state of E in complex be x, then
$[x + (-2) = 1]$ or $x - 2 = 1$
or $x = +3$, so its oxidation state is + 3
Thus option (d) is correct.

88. (a) The SCN^- ion can coordinate through S or N atom giving rise to linkage isomerism
$M \leftarrow SCN$ thiocyanato
$M \leftarrow NCS$ isothiocyanato.

89. (a) $\underset{2.675g}{CoCl_3.6NH_3} \longrightarrow xCl^-$

$xCl^- + AgNO_3 \longrightarrow \underset{4.78g}{xAgCl\downarrow}$

Number of moles of the complex

$$= \frac{2.675}{267.5} = 0.01 \text{ moles}$$

Number of moles of AgCl obtained

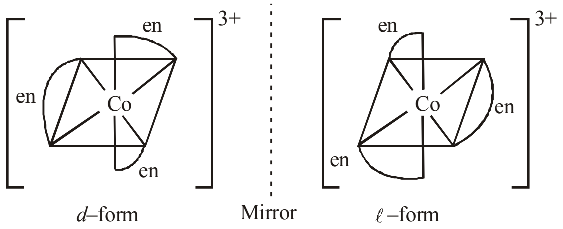
$$= \frac{4.78}{143.5} = 0.03 \text{ moles}$$

$\therefore$ No. of moles of AgCl obtained
$= 3 \times$ No. of moles of complex

$$\therefore n = \frac{0.03}{0.01} = 3$$

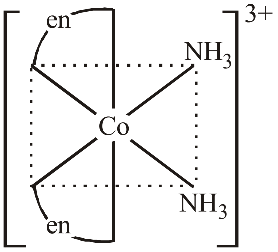
$\therefore$ $3Cl^-$ ions are precipitable
Hence the formula of the complex is $[Co(NH_3)_6]Cl_3$

90. (b) Option (b) shows optical isomerism $[Co(en)_3]^{3+}$

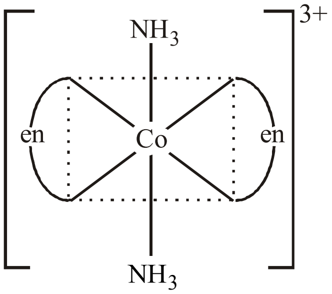


Complexes of Zn^{++} cannot show optical isomerism as they are tetrahedral complexes with plane of symmetry.
$[Co(H_2O)_4(en)]^{3+}$ have two planes of symmetry hence it is also optically inactive.
$[Zn(en)_2]^{2+}$ cannot show optical isomerism

91. (b)



cis



trans-

92. (c) $[Cr(NH_3)_6]Cl_3$ is an inner orbital complex, because in this complex inner d-orbital is used for hybridisation (d^2sp^3)

93. (a) Ligands can be arranged in a series in the orders of increasing field strength as given below :
Weak field ligands :

$$I^- < Br^- < S^{2-} < SCN < Cl^- < N_3^-, F^- < \text{Urea}, OH^- < \text{oxalate}$$

Strong field ligands

$$O^{--} < H_2O < NCS^- < EDTA < Py, NH_3 < en = SO_3^- < \text{bipy, Phen} < NO_2^- < CH_3^- < C_6H_5^- < CN^- < CO$$

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.

94. (b) $[Cr(en)_2Br_2]Br$
dibromidobis (ethylenediamine) chromium (III) bromide.

95. (d) $[Co(H_2O)_4(NH_3)_2]Cl_3$
= Diamminetetraaquacobalt (III) chloride.

96. (c) In case of $[Ni(CO)]_4$, the ligand CO, is neutral thus the charge on Ni is zero.

97. (c) Number of donor atoms (N) in $N(CH_2CH_2NH_2)_3$ are four. So, $N(CH_2CH_2NH_2)_3$ is a tetradentate ligand.

98. (d)

99. (a) In $[NiCl_4]^{-2}$, Ni is in +2 oxidation state

$Ni^{2+} = 3d^8$ i.e. 2 unpaired e^-

Magnetic moment $(\mu) = \sqrt{n(n+2)} = \sqrt{8} = 2.82$ B.M.

100. (b) The complex formation is a characteristic of d-block elements.

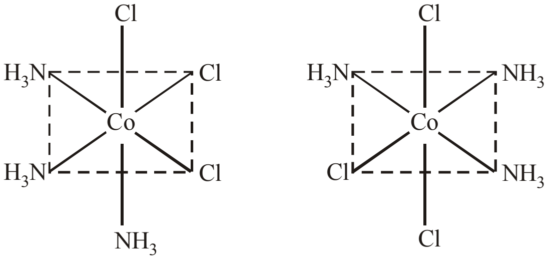
Lead is a *p*-block element hence does not forms complex compounds.

EXERCISE - 2

1. (b) The crystal field splitting in tetrahedral complexes is lower than that in octahedral complexes, and $\Delta_t = -\frac{4}{9}\Delta_0$.

2. (b) It is optically active.

3. (a) Octahedral complexes of the type $[MA_3B_3]$ like $[Co(NH_3)_3Cl_3]$ exhibit *fac-mer* isomerism.



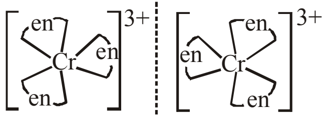
fac-isomer mer-isomer

4. (c) As it forms two moles of silver chloride thus it has two moles of ionisable Cl.

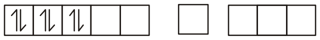
$$[Co(NH_3)_5NO_2]Cl_2 \rightarrow [Co(NH_3)_5NO_2]^{++} + 2Cl^-$$

$$2Cl^- + 2AgNO_3 \rightarrow 2AgCl + 2NO_3^-$$

5. (d) Optical isomerism is generally shown by octahedral complexes of the formula, $[Ma_2b_2c_2]^{n\pm}$, $[Mabcdef]^{th}$ $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$, $[M(AA)_2ab]^{n\pm}$ and $[M(AB)_3]^{th}$. Thus, among the given compounds, only $[Cr(en)_3]^{3+}$ exhibits optical isomerism and exists as a pair of enantiomers.

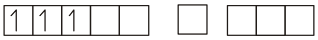


6. (c) $[Co(NH_3)_6]^{3+}$, $Co^{3+}(27-3=24)$



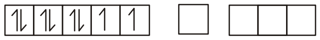
$d^2sp^3 \rightarrow$ (inner octahedral complex & diamagnetic)

$[Cr(NH_3)_6]^{3+}$, $Cr^{3+}(24-3=21)$



$d^2sp^3 \rightarrow$(inner octahedral complex & paramagnetic)

$[Ni(NH_3)_6]^{2+}$, $Ni^{2+}(28-2=26)$



$sp^3d^2 \rightarrow$(outer octahedral complex & paramagnetic)

$[Zn(NH_3)_6]^{2+}$, $Zn^{2+}(30-2=28)$

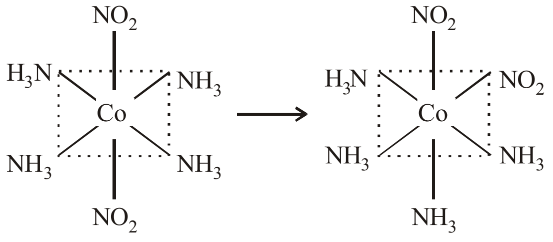
$sp^3d^2 \rightarrow$ (outer octahedral complex &diamagnetic)

7. (a) The given compound may have linkage isomerism due to presence of NO_2 group which may be in the form $-NO_2$ or $-ONO$.

It may have ionisation isomerism due to presence of two ionisable group $-NO_2$ & $-Cl$. It may have geometrical isomerism in the form of *cis-trans* form as follows :

$[Co(NH_3)_4Cl(NO_2)]NO_2$ & $[Co(NH_3)(NO_2)_2]Cl$ —— ionisation isomers.

$[Co(NH_3)_5(NO_2)_2]Cl$ & $[Co(NH_3)_5(ONO)_2]Cl$ —— Linkage isomers



Trans-form *cis-form*

Geometrical isomers

8. (c) $K_4[Fe(CN)_6]$ produces maximum number of ions (5) in the solution.

$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{-4}$

9. (d) $Co(NH_3)_5Cl_3 \rightleftharpoons [Co(NH_3)_5Cl]^{+2} + 2Cl^-$

$\therefore$ Structure is $[Co(NH_3)_5Cl]Cl_2$.

Now $[Co(NH_3)_5Cl]Cl_2 + 2AgNO_3$

$$\rightarrow [Co(NH_3)_5Cl](NO_3)_2 + 2AgCl$$

10. (c) Number of donor atoms (N) in $N(CH_2CH_2NH_2)_3$ are four. So, $N(CH_2CH_2NH_2)_3$ is a tetradentate ligand.

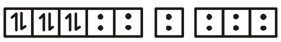
11. (a) CN^- ion acts good complexing as well as reducing agent.

12. (d) Isomers

$[Ru(NH_3)_4Cl_2]^+$, $[Co(NH_3)_5Cl]^{2+}$,
cis and trans none

$[Ir(PR_3)_2H(CO)]^{2+}$, $[Co(en)_2Cl_2]^+$
cis and trans cis and trans and optical isomers

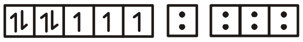
13. (d) $[Co(NH_3)_6][Cr(CN)_6]$ is an ionic compound. Both cation and anion carry 3 unit charges. It exhibits co-ordination isomerism.

14. (c) $[Fe(CN)_6]^{4-} \rightarrow$ 

– no. of unpaired electrons = 0

$[MnCl_4]^{2-} \rightarrow$ 

– no. of unpaired electrons = 5

$[CoCl_4]^{2-} \rightarrow$ 

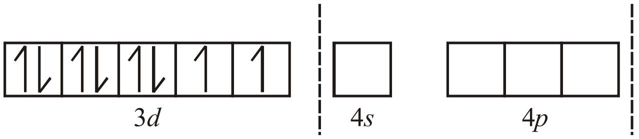
– no. of unpaired electrons = 3

The greater the number of unpaired electrons, greater the magnitude of magnetic moment. Hence the correct order will be

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

15. (a) Geometrical isomerism is possible only in square planar complexes of the type MA_2B_2 and MA_2BC and for octahedral complexes of the type MA_4B_2 and MA_4BC. Hence only (ii) will show geometrical isomerism.

16. (d) $[Ni\ X_4]^{2-}$, the electronic configuration of Ni^{2+} is

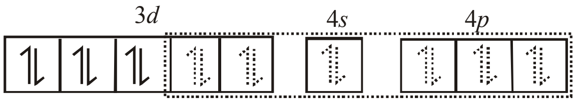


It contains two unpaired electrons and the hybridisation is sp^3 (tetrahedral).

17. (c) (1) $[Pt(en)(SCN)_2(NH_3)_2]^0$; it is not ion
 (2) $[Pt(en)(SCN)_2(NH_3)_2]^{2+}$; it should not be platinate
 (3) $[Pt(en)(SCN)_2(NH_3)_2]^{2+}$: correct name
 (4) $[Pt(en)_2(SCN)_2(NH_3)_2]^{2+}$; its coordination number is 8

18. (d) Complex X is $[Fe(en)_3]^{2+}$; as 'en' is a strong field ligand pairing of electrons will take place.

$[Fe(en)_3]^{2+}$:



d^2sp^3 hybridisation

Hence, hybridisation is d^2sp^3 and complex is diamagnetic. As it has 3 bidentate symmetrical 'en' ligands so it will not show geometrical isomerism.

19. (a) $[MnO_4]^{2-}$; Mn is in +6 oxidation state. Electronic configuration is $[Ar]^{18}3d^14s^0$. As it contains one unpaired electron it is paramagnetic and green coloured $[TiCl_6]^{2-}$, $[VO_4]^{3-}$ and CrO_2Cl_2 are diamagnetic as all electrons are paired.

20. (d) When excess of $AgNO_3$ and $BaCl_2$ are added to solution X.

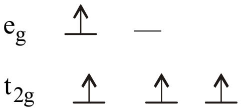
$$\underset{\substack{1\,mole \\ 0.02\,mole}}{[Co(NH_3)_5Br]Cl_2} + \underset{2\,moles}{2AgNO_3} \rightarrow$$

$$\underset{1\,mole}{[Co(NH_3)_5Br](NO_3)_2} + \underset{\substack{2\,moles \\ 0.02\times2=0.04\,mole}}{2AgCl(ppt.)(Y)}$$

$$\underset{\substack{1\,mole \\ 0.02\,mole}}{[Co(NH_3)_5Cl]SO_4} + BaCl_2 \rightarrow$$

$$[Co(NH_3)_5Cl]Cl_2 + \underset{\substack{1\,mole \\ 0.02\,mole}}{BaSO_4\,(ppt.)\,(Z)}$$

21. (d) d^4 in high spin octahedral complex

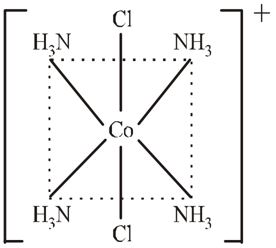


$CFSE = (-0.4x + 0.6y)\Delta_0$

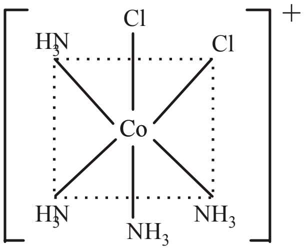
Where, $x \rightarrow$ electrons in t_{2g} orbital
 $y \rightarrow$ electrons in e_g orbital

$CFSE = [0.6 \times 1] + [-0.4 \times 3] = -0.6\ \Delta_0$

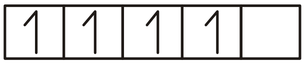
22. (b)

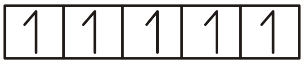


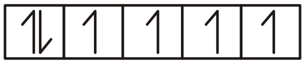
trans (green)

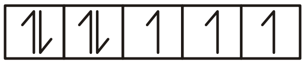


cis (violet)

23. (c) Cr^{2+} d^4  4

Mn^{2+} d^5  5

Fe^{2+} d^6  4

Co^{2+} d^7  3

Minimum paramagnetic behaviour = $[Co(H_2O)_6]^{2+}$

24. (a) As positive charge on the central metal atom increases, the less readily the metal can donate electron density into the π* orbitals of CO ligand (donation of electron density into π* orbitals of CO result in weakening of C – O bond). Hence, the C – O bond would be strongest in $[Mn(CO)_6]^+$.

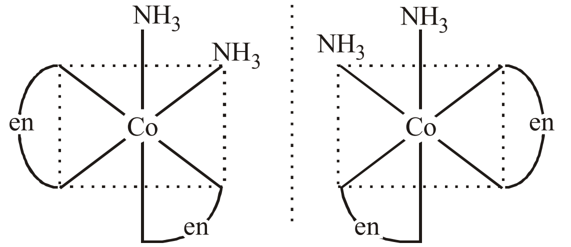
25. (a) $[Ni(NH_3)_6]^{2+}$

$Ni^{2+} = 3d^8$, according to CFT $= t_{2g}^6\, e_g^2$ therefore, hybridisation is sp^3d^2 and complex is paramagnetic.

26. (a) In octahedral complex the magnitude of Δ_o will be highest in a complex having strongest ligand. Out of

the given ligands CN^- is strongest. So, Δ_o will be highest for $[Co(CN)_6]^{3-}$. Thus option (a) is correct.

27. (c)



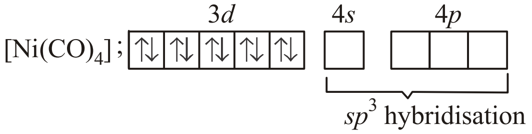
Enantiomers of *cis*-$\left[Co(en)_2(NH_3)_2\right]^{3+}$

28. (d) An anionic carbonyl complex can delocalise more electron density to antibonding pi-orbital of CO and hence, lowers the bond order.

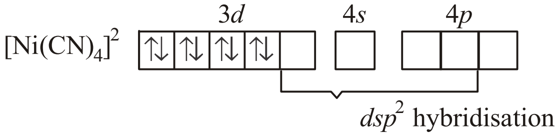
29. (c) The correct IUPAC name of the given compound is tetramminenickel (II) - tetrachloronickelate (II) thus (c) is the correct answer.

30. (b) In carbonyls O.S. of metal is zero

In $[Ni(CO)_4]$, the oxidation state of nickel is zero. Its configuration in $Ni(CO)_4$ is



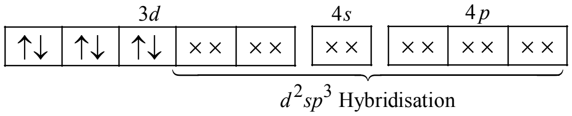
In $[Ni(CN)_4]^{2-}$ the oxidation state of Ni is 2+ and its configuration is



Thus the hybridisations of nickel in these compounds are sp^3 and dsp^2 respectively.

Hence (b) is the correct answer.

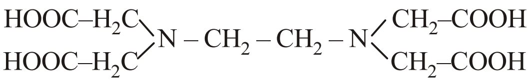
31. (a) Chromium in $Cr(CO)_6$ is in zero oxidation state and has $[Ar]^{18}\ 3d^5 4s^1$ as the electronic configuration. However, CO is a strong ligand, hence pairing up of electrons takes place leading to following configuration in $Cr(CO)_6$.



Since the complex has no unpaired electron, its magnetic moment is zero.

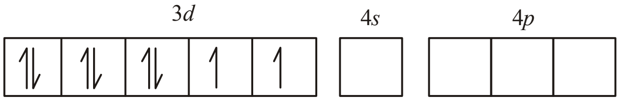
32. (b) Ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is $[Cr(H_2O)_4Cl_2]NO_2$.

33. (c) The correct structure of EDTA is

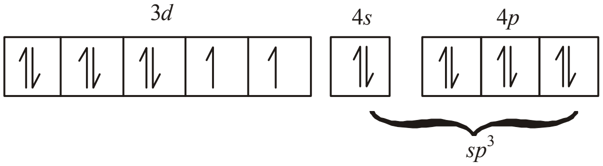


34. (b) $[NiCl_4]^{2-}$, O.S. of Ni = +2

$Ni(28) = 3d^8\ 4s^2$



Cl^- being weak ligand it cannot pair up the two electrons present in $3d$ orbital



No. of unpaired electrons = 2

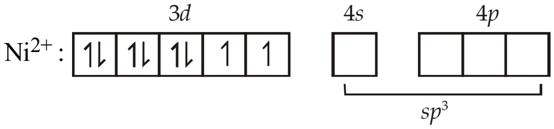
Magnetic moment, μ = 2.82 BM.

35. (c)

Complex	**No. of electrons in outer *d* orbital**	**No. of unpaired electron (s)**
$[Fe(CN)_6]^{3-}$	$3d^5$	1 (CN^- causes pairing of electrons)
$[Co(NH_3)_6]^{3+}$	$3d^6$	0
$[Co(oxal.)_3]^{3-}$	$3d^6$	0
$[Ni(H_2O)_6]^{2+}$	$3d^8$	2
$[Pt(CN)_4]^{2-}$	$5d^8$	0 (CN^- causes pairing of electrons)
$[Zn(H_2O)_6]^{2+}$	$3d^{10}$	0

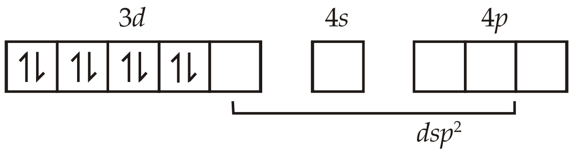
Thus L, M, O and P are diamagnetic.

36. (c) In both states (paramagnetic and diamagnetic) of the given complex, Ni exists as Ni^{2+} whose electronic configuration is $[Ar]\ 3d^8 4s^0$.



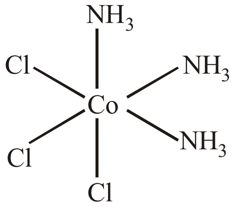
In the above paramagnetic state the geometry of the complex is sp^3 giving tetrahedral geometry.

The diamagnetic state is achieved by pairing of electrons in $3d$ orbital.

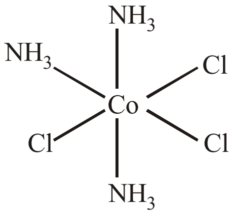


Thus the geometry of the complex will be dsp^2 giving square planar geometry.

37. (c) Octahedral coordination entities of the type Ma_3b_3 exhibit geometrical isomerism. The compound exists both as facial and meridional isomers, both contain plane of symmetry



fac-



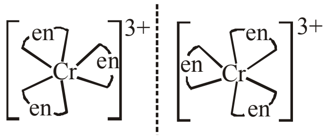
mer

38. (a)

39. (d) $[Co(CO)_5NH_3]^{2+}$. In this complex. Co-atom attached with NH_3 through σ bonding while with CO it is attached with dative π-bond.

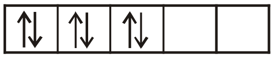
40. (d)

41. (d) Optical isomerism is generally shown by octahedral complexes of the formula, $[Ma_2b_2c_2]^{n\pm}$, $[Mabcdef]^{th}$ $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$, $[M(AA)_2ab]^{n\pm}$ and $[M(AB)_3]^{th}$. Thus, among the given compounds, only $[Cr(en)_3]^{3+}$ exhibits optical isomerism and exists as a pair of enantiomers.



42. (c) $[Co(C_2O_4)_3]^{3-}$ has Co^{3+} (d^6 system) due to presence of stronger $C_2O_4^{2-}$ chelating ligand pairing of electrons occurs in this case.

Co^{3+}:



; Diamagnetic.

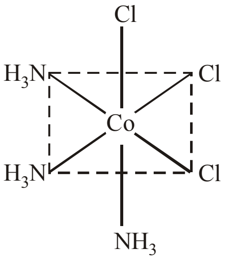
43. (c) $K_4[Fe(CN)_6]$ produces maximum number of ions (5) in the solution.

$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{-4}$

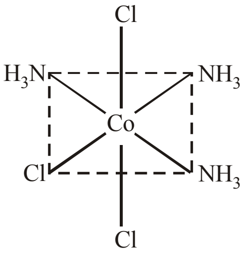
44. (a) Geometrical isomerism is possible only in square planar complexes of the type MA_2B_2 and MA_2BC and for octahedral complexes of the type MA_4B_2 and MA_4BC. Hence only (ii) will show geometrical isomerism.

45. (b) The crystal field splitting in tetrahedral complexes is lower than that in octahedral complexes, and $\Delta_t = -\frac{4}{9}\Delta_0$.

46. (a) Octahedral complexes of the type $[MA_3B_3]$ like $[Co(NH_3)_3Cl_3]$ exhibit *fac-mer* isomerism.



fac-isomer



mer-isomer

47. (d) $[FeF_6]^{3-}$ is a high spin complex since F^- is a weak ligand.

48. (c) It is correct statement that NF_3 is a weaker ligand than $N(CH_3)_3$, the reason is that fluorine is highly electronegative therefore, it with draw electrons from nitrogen atom. Hence, the lone pair of nitrogen atom cannot be ligated. While $N(CH_3)_3$ is a strong ligand because CH_3 is electron releasing group.

49. (b) Both statement-1 and statement-2 are true but statement-2 is not the correct explanation of statement-1. $[Fe(CN)_6]^{3-}$ is weakly paramagnetic as it has unpaired electrons while $[Fe(CN)_6]^{2-}$ has no unpaired electron.

∴ It is diamagnetic.

50. (a) Both statement-1 and statement-2 are true and statement-2 is the correct explanation of statement-1. $[Sc(H_2O_6]^{3+}$ has no unpaired electron in its *d* subshell and thus *d–d* transition is not possible whereas $[Ti(H_2O)_6]^{3+}$ has one unpaired electron in its d subshell which gives rise to *d–d* transition to impart colour.

EXERCISE - 3

Exemplar Questions

1. (b) Higher the value of log K, higher will be stability of complex compound formed.

2. (c) Strength of ligand increases as crystal field splitting energy increases.

Ligand strength order : $CN^- > NH_3 > H_2O$

As energy separation increases, wavelength decreases. Thus, the correct order is :

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

3. (b) In above reaction, when 0.1 mol $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained thus, there must be two free chloride ions in the solution of electrolyte as one mole of $AgNO_3$ precipitates one mole of chloride. So, molecular formula of complex will be $[Co(NH_3)_5Cl]Cl_2$ and electrolytic solution must contain $[Co(NH_3)_5Cl]^{2+}$ and two Cl^- as constituent ions. Thus, it is 1 : 2 electrolyte.

$$\left[Co(NH_3)_5Cl\right]Cl_2 \rightarrow \left[Co(NH_3)_5Cl\right]^{2\oplus}(aq) + 2Cl^-(aq)$$

4. (d) 1 mole of $AgNO_3$ precipitates one free chloride ion (Cl^-). Here, 3 moles of AgCl are precipitated by excess of $AgNO_3$. Hence, there must be three free Cl^- ions. So, the formula of the complex can be $[Cr(H_2O)_6]Cl_3$

5. (a) Ligands present in the compound are

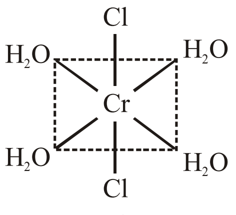
(i) NH_3

(ii) Cl (chlorido; di prefixed to represent two ligands.)

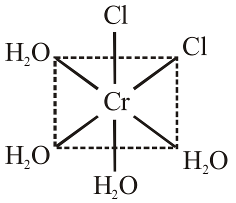
The oxidation number of platinum in the compound is 2. Hence, correct IUPAC name is Diamminedichloridoplantinum (II)

6. (c) Ligand which chelates the metal ion are known as chelating ligand. Here, only oxalate ion is a chelating ligand. Hence, it stabilises coordination compound by chelating Fe^{3+} ion.

7. (a) $[Cr(H_2O)_4Cl_2]^+$ shows geometrical isomerism. The possible geometrical isomers are



trans-isomer



cis-isomer

8. (c) Relation between CFSE of octahedral and tetrahedral complexes is $\Delta_t = \frac{4}{9}\Delta_o$

According to question, $\Delta_o = 18{,}000\text{cm}^{-1}$

$\therefore \quad \Delta_t = \frac{4}{9}\Delta_o = \frac{4}{9} \times 18{,}000\text{cm}^{-1}$

$= 4 \times 2{,}000\ \text{cm}^{-1} = 8{,}000\ \text{cm}^{-1}$

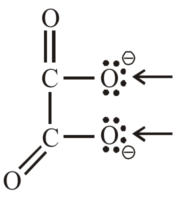
9. (a) NCS (thiocyanate) can bind to the metal ion in two ways :

$M \leftarrow NCS$ or $M \rightarrow SNC$

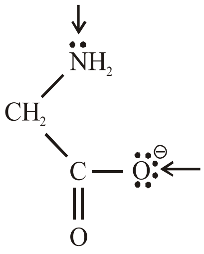
Thus, coordination compounds $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NSC)_2]$ are linkage isomers.

10. (d) Isomers are the compounds having same molecular formula but different structural formula. $[Co(SO_4)_2(NH_3)_5]$ Br and $[Co(SO_4)(NH_3)_5]Cl$ do not have same molecular formula. Hence, they are not isomers.

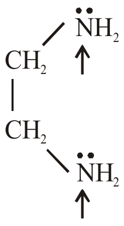
11. (a) Chelating ligand has two or more donor atoms to a single metal ion e.g.,



Oxalato

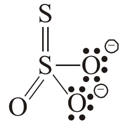


Glycinato



Ethane-1, 2 diamine

Here (←) denotes binding site.



Thiosulphato $\left(S_2O_3^{2-}\right)$ is not a chelating ligand because geometrically it is not favourable for $S_2O_3^{2-}$ to chelate a metal ion.

12. (b) Ligand should have a pair of electron which is loosely held and form a M – L bond.

e.g., $:\ddot{N}=O, \ddot{N}H_2CH_2CH_2\ddot{N}H_2, :CO,$

Amongst the species given $\overset{+}{N}H_4$ does not have any pair of electron.

So, it is not expected to be a ligand.

13. (b) The compounds having same molecular formula but differ in ligands inside & outside the coordination sphere are solvate (hydration) isomers.

Coordination compound $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]\ H_2O \cdot Cl_2$ are solvate isomers, because water is exchanged by chloride ion. This is why both of them show different colour on exposure to sunlight.

14. (c) Ligands (based on priority) present are :

(i) NH_3

(ii) $Cl^{\ominus}$

(iii) $NO_2^{\ominus}$

So, IUPAC name will be Diamminechloridonitrito-N-platinum (II).

NEET/AIPMT (2013-2017) Questions

15. (d) $[Cu(NH_3)_4]^{2+}$ hybridisation dsp^2

$Cu^{+2} - 3d^9$ has one unpaired e^-

$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

So magnetic moment

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

$= \sqrt{3} = 1.73$

16. (d) $[Cr(H_2O)_4Cl_2]Cl + AgNO_3 \longrightarrow AgCl + [Cr(H_2O)_4Cl_2]NO_3$

$$\text{Molarity} = \frac{\text{wt}}{\text{mol. mass}} \times \frac{1000}{\text{vol.}}$$

$$\frac{\text{wt}}{\text{mol. mass}} = \text{molarity} \times \frac{\text{vol.}}{1000} = \frac{0.01 \times 100}{1000}$$

$= 0.001$

17. (c) IUPAC name of $[CrF_2(en)_2]Cl$ is

Difluoridobis(ethylenediamine) chromium (III) chloride.

18. (c) CFSE = $(-0.4x + 0.6y)\Delta_o$

where

$x \rightarrow e^-$s in t_{2g} orbital

$y \rightarrow e^-$s in e_g orbital

For high spin 4*d* complex, x = 3 & y = 1

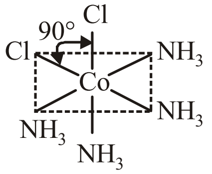
$\therefore \ -0.4 \times 3 + 0.6 \times 1 = -0.6\ \Delta_0$

19. (c) $Ni^{+2} \rightarrow 3d^8 = \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

CN^- is a strong ligand and causes pairing of 3*d* electrons of Ni^{2+}.

$\therefore$ It is diamagnetic.

20. (c)



cis-isomer

21. (d) Acetylacetone forms six membered stable ring complexes.

22. (d) $Co^{2+} \Rightarrow [Ar]3d^7 4s^0$, here, Br^- is a weak field ligand so will not cause pairing of d-electrons in Co^{2+}.

$\therefore\ [CoBr_4]^{2-}$ will exhibit paramagnetic behaviour due to unpaired electrons.

23. (b) Due to d^5 configuration CFSE is zero.

24. (b)

25. (d) $CoCl_3 . 3NH_3$ will not give test for chloride ions with silver nitrate due to absence of ionisable chloride atoms.

$CoCl_3 . 3NH_3 \Rightarrow [Co(NH_3)_3 Cl_3]$

$[Co(NH_3)_3 Cl_3] \xrightarrow{AgNO_3}$ no ppt

26. (d) In $[Co(CN)_6]^{-3}$, O.N. of Co is +3

$\therefore$ $Co^{+3} = 3d^6 4s^0$

CN^- is a strong field ligand

$\therefore$ Pairing of electrons occurs so in this complex no unpaired electron is present and it is low spin complex.

27. (a) $[M (en)_2 (C_2O_4)] Cl$

C_2O_4 = bidentate ligand, carry – 2 charge

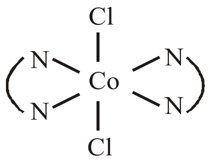
en = bidentate ligand, carry 0 charge

$\therefore$ M carry + 3 charge; coordination number = 6

$\therefore$ Sum = $+3 + 6 = 9$

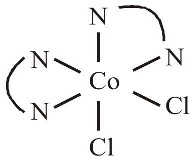
28. (d) Hexacyanidoterrate (III) ion.

29. (c) $[Co (en)_2 Cl_2] Cl$



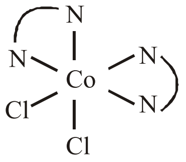
trans
(I)

and



cis
(II)

Mirror image of (II)



30. (c) $[Fe(CO)_4]^{2-}$

Since metal atom is carrying maximum –ve charge therefore it would show maximum synergic bonding as a resultant C—O bond length would be maximum.

31. (a) Grignard's reagent (RMgX) is a σ-bonded organometallic compound.

32. (b) In a solution containing $HgCl_2$, I_2 and I^-, both $HgCl_2$ and I_2 compete for I^-.

Since formation constant of $[HgI_4]^{2-}$ is very large (1.9×10^{30}) as compared with I_3 ($K_f = 700$)

$\therefore$ I^- will preferentially combine with $HgCl_2$.

$$HgCl_2 + 2I^- \rightarrow \underset{\text{Red ppt}}{HgI_2} \downarrow + 2Cl^-$$

$$\underset{}{HgI_2} + 2I^- \rightarrow \underset{\text{soluble}}{[HgI_4]^{2-}}$$

33. (b) $[Co(NH_3)_6]Cl_3 \xrightarrow{AgNO_3} 3\text{mol of AgCl}$

$[Co(NH_3)_5 Cl]Cl_2 \xrightarrow{AgNO_3} 2\text{mol of AgCl}$

$[Co(NH_3)_4 Cl_2]Cl \xrightarrow{AgNO_3} 1\text{mol of AgCl}$

Complexes are respectively $[Co(NH_3)_6Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$

34. (d) The order of the ligand in the spectrochemical series is :

$H_2O < NH_3 < en$

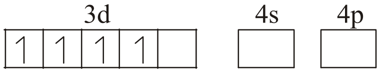
Hence, the wavelength of the light observed will be in the order

$[Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(en)_3]^{3+}$

Thus, wavelength absorbed will be in the opposite order i.e., $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(H_2O)_6]^{3+}$

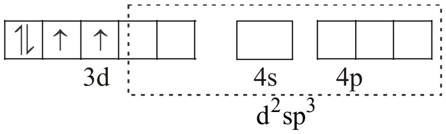
35. (b) In the complex $[Mn(CN)_6]^{3-}$, O.S. of Mn is + 3

E.C. of $Mn^{+3} \rightarrow 3d^4$



The presence of a strong field ligand CN^- causes pairing of electrons.

$\Rightarrow$



As, coordination number of Mn = 6, so it will form an octahedral complex.

$\therefore$ $[Mn(CN)_6]^{3-} =$