COORDINATION COMPOUNDS

CONTENTS

JEE (Advanced) Syllabus

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JEE (MAIN) Syllabus

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Coordination compounds

INTRODUCTION

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

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

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

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

ADDITION COMPOUNDS :

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

These compounds are called molecular or addition compounds.

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

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

These addition compounds can be divided into two classes :

(A) DOUBLE SALTS :

Those which lose their identity in solution

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

Example :

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

(B) COORDINATION COMPOUNDS :

Those which retain their identity in solution.

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

Example :

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

DEFINITIONS OF TERMS USED IN CO-ORDINATION COMPOUNDS

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

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

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

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

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

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

Example. Coordination number of the central metal ions in
(i) $[Cu(NH_3)_4]^{2+}$ is four (ii) $[Fe(EDTA)]^{-}$ is six

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

(f) Ligands :

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

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

CLASSIFICATION OF LIGANDS

(A) Based on charge

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

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

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

(B) Based on denticity

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

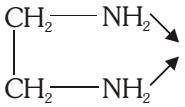
(a) Unidentate/monodentate ligands

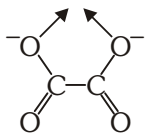
Ligands which donate one pair of electron to the central metal are called unidentate ligands.

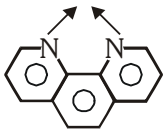
X^{-}, CN^{-}, NO_2^{-}, NH_3, Pyridine, OH^{-}, NO_3^{-}, H_2O, SO_3^{-2}, CO, NO, OH^{-}, O^{-2}, $(C_6H_5)_3P$ etc.

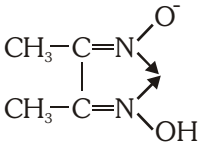
(b) Bidentate ligands

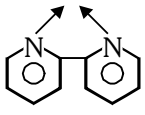
Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.

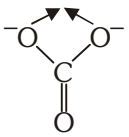

Ethylenediamine (en)

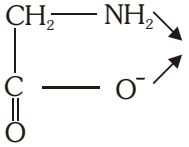

Oxalate (ox)


1, 10-Phenanthroline (O-phen)


Dimethyl glyoxim ion (DMG)


2, 2'-Dipyridyl (Dipy)

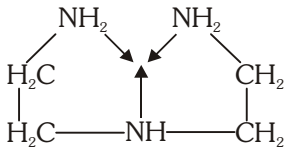

Carbonate


Glycinato (Gly)

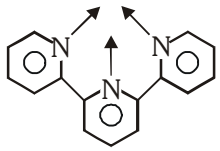
(c) Tridentate ligands

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

Example.



Diethylene triamine (Dien)

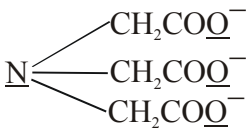


2, 2', 2"-Terpyridine (Terpy)

(d) Tetradentate ligands

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

Example : (Underline atoms are donating atom)

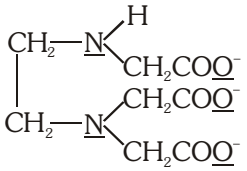


Nitrilotriacetato (nta^{3-})

(e) Pentadentate ligands :

Those ligands which can five electron pairs to the central metal are known as pentadentate ligands.

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

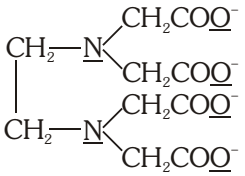


$(EDTA)^{-3}$

Ethylenediaminetriacetate ion

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

Example : (Underline atoms are donating atom)

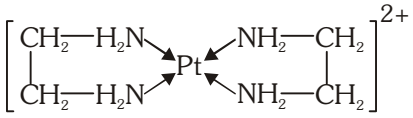


Ethylenediaminetetraacetate ion $(EDTA)^{4}$

(g) Chelating ligands

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

Example :



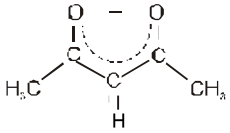
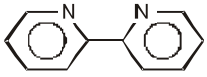
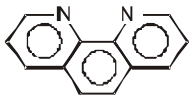
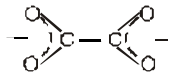
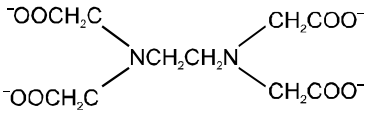
Denticity and Chelation :

Table-1 Common Monodentate Ligands

Common Name	*IUPAC Name*	*Formula*
methyl isocyanide	methylisocyanide	CH_3NC
triphenyl phosphine	triphenyl phosphine/triphenyl phosphane	PPh_3
pyridine	pyridine	C_5H_5N (py)
ammonia	ammine	NH_3
methyl amine	methylamine	$MeNH_2$
water	aqua or aquo	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO
fluoride	fluoro or fluorido*	F^-
chloride	chloro or chlorido*	Cl^-
bromride	bromo or bromido*	Br^-
iodide	iodo or iodido*	I^-
cyanide	cyanido or cyanido-C* (C-bonded)	CN^-
isocyanide	isocyanido or cyanido-N* (N-bonded)	NC^-
thiocyanate	thiocyanato-S(S-bonded)	SCN^-
isothiocyanate	thiocyanato-N(N-bonded)	NCS^-
cyanato (cyanate)	cyanato-O (O-bonded)	OCN^-
isocyanato (isocyanate)	cyanato-N (N-bonded)	NCO^-
hydroxide	hydroxo or hydroxido*	OH^-
nitro	nitrito–N (N–bonded)	NO_2^-
nitrito	nitrito–O (O–bonded)	ONO^-
nitrate	nitrato	NO_3^-
amide	amido	NH_2^-
imide	imido	NH^{2-}
nitride	nitrido	N^{3-}
azide	azido	N_3^-
hydride	hydrido	H^-
oxide	oxido	O^{2-}
peroxide	peroxido	O_2^{2-}
superoxide	superoxido	O_2^-
acetate	acetato	CH_3COO^-
sulphate	sulphato	SO_4^{2-}
thiosulphate	thiosulphato	$S_2O_3^{2-}$
sulphite	sulphito	SO_3^{2-}
hydrogen sulphite	hydrogensulphito	HSO_3^-
sulphide	sulphido or thio	S^{2-}
hydrogen sulphide	hydrogensulphido or mercapto	HS^-
thionitrito	thionitrito	$(NOS)^-$
nitrosonium	nitrosylium or nitrosonium	NO^+
nitronium	nitronium	NO_2^+

* The 2004 IUPAC draft recommends that anionic ligands will end with-ido.

Table-2 Common Chelating Amines

Chelating Points	Common Name	IUPAC Name	Abbreviation	Formula
bidentate	ethylenediamine	1,2-ethanediamine/ ethane-1,2-diamine	en	$NH_2,CH_2CH_2NH_2$
bidentate	propanediamine	1,2-propanediamine	pn	$NH_2–CH(CH_3)–CH_2–NH_2$
bidentate	acetylacetonate	2,4-pentanediono or acetylacetonato	acac	
bidentate	2,2'-bipyridine	2,2'-bipyridyl	bipy	
bidentate	1,10-phenanthroline/ phenanthroline	1,10-diaminophenanthrene	phen,o-phen	
bidentate	oxalate	oxalato	ox	
bidentate	glycinate	glycinato	gly^-	$NH_2–CH_2–C(=O)–O^-$
hexadentate	ethylenediaminetetraacetate	1,2–ethanediyl (dinitrilo) tetraacetato or ethylenediaminetetraacetato	EDTA	

Flexidentate Ligand :

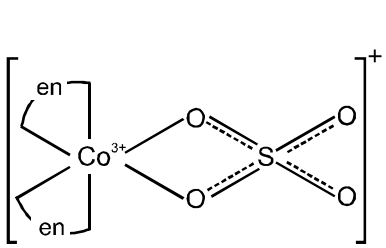
It is not necessary that all the donor items present in the polydentate ligands should form coordinate bonds with the central metal atom or ion i.e. a polydentate ligand which is found to have different denticity in different coordination compounds is called a flexidentate ligand. Note that in a particular complex denticity of a particular ligand is fixed, it can not be flexible in the same compound.

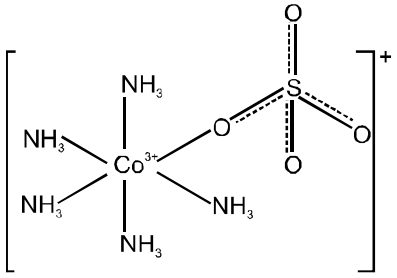
EDTA can act as **hexa, penta** as well as **tetra** dentate ligand. For example ;

EDTA usually acts as hexadentate ligand but in $[Cr(III)(OH)(EDTA)]^{2-}$ and $[Co(III)Br(EDTA)]^{2-}$ as pentadentate and in $[Pd(II)H_2(EDTA)]^0$ as a tetradentate ligand.

e.g. NO_3^- , CO_3^{2-} , SO_4^{2-} , $S_2O_3^{2-}$

Sulphate ion, $\mathbf{SO_4^{2-}}$ can also be **mono** or **bi** dentate ligand. For example ;

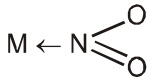




Ambidentate Ligand :

Ligands which can ligate through two different sites present in it are called ambidentate ligands. Examples of such ligands are the CN^-, NO_2^- and SCN^- ions. NO_2^- ion can coordinate through either the nitrogen or the oxygen atoms to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds.

For example; Monodentate and ambidentate :



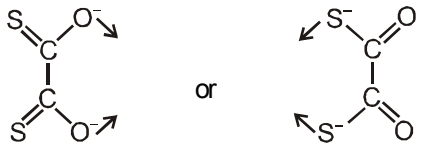
nitrito-N

$M \leftarrow O—N=O$ nitrito-O

$M \leftarrow SCN$ thiocyanato or thiocyanato-S

$M \leftarrow NCS$ isothiocyanato or thiocyanato-N

Bidentate and ambidentate :



dithioxalate

Note : ***Although ambidentate ligands have two or more donor sites but during complex formation*** **different sites** ***can be used by them.***

Homoleptic and heteroleptic complexes :

Complexes in which a metal is bound to only one type of donor groups, e.g., $[Cr(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one type of donor groups, e.g., $[Co(NH_3)_4Br_2]^+$, are known as heteroleptic.

IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The main rules of naming of complexes are –

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

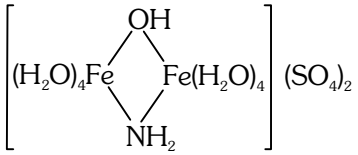
(h) After the naming of central metal ion, anion which is in the outer sphere is to be named.

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

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

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

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



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

FORMATION OF CO-ORDINATION COMPOUNDS

It can be explained by number of theories.

- Werner's co-ordination theory
- Sidwick theory or Effective Atomic Number Theory (EAN)
- Valence bond theory
- Crystal field theory

Werner's co-ordination theory

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

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

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

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

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

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

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

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

Formula of some cobalt complexes.

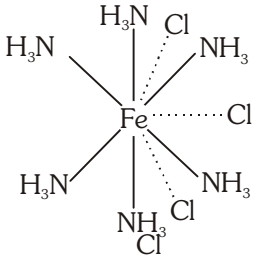
Example :

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

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

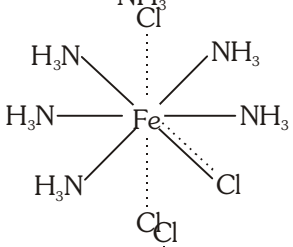
WERNER'S REPRESENTATION OF COMPLEXES

(i) $Fe(NH_3)_6Cl_3$



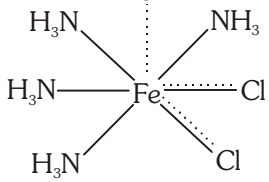
$[Fe(NH_3)_6]Cl_3$
Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.

(ii) $Fe(NH_3)_5Cl_3$



$[Fe(NH_3)_5Cl]Cl_2$
In this complex two 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also.

(iii) $Fe(NH_3)_4Cl_3$



$[Fe(NH_3)_4Cl_2]Cl$
In this complex one 'Cl' group act as primary valency and two of the 'Cl' groups act as secondary valencies also.

Sidwick Theory or Effective Atomic Number Concept (EAN)

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

EAN can be calculated by the following relation :

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

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

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

Valence Bond Theory

The main features of this theory are -

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

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

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

Example : In the formation of $[Fe(NH_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.

In $[Cu(NH_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

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

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

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

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

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

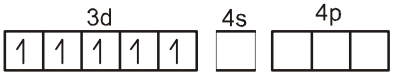
(i) Paramagnetism is represented in the term of spin only magnetic moment.

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

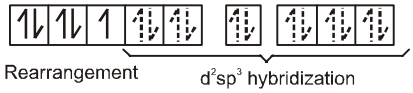
Example $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

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

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



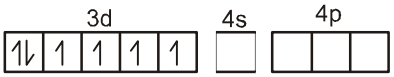
$[Fe(CN)_6]^{3-}$



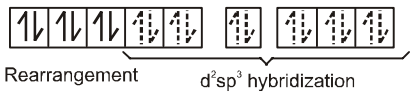
One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

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

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

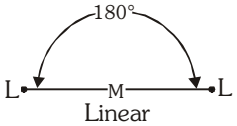
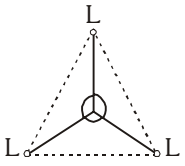


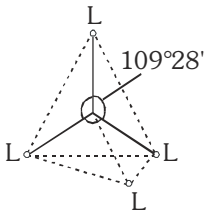
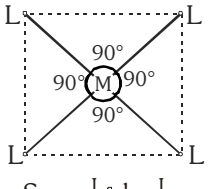
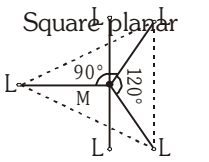
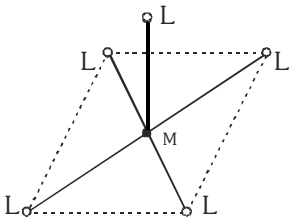
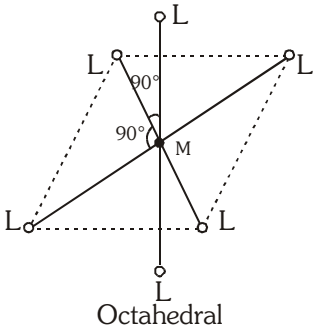
$[Fe(CN)_6]^{4-}$



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

Some Example :

Coordination Number	Hybridised orbitals	Geometrical shape of the Complex	Examples of Complex
2	sp		$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
3	sp^2		$[HgI_3]^-$

4	sp^3		$[CuCl_4]^{-2}$ $[ZnCl_4]^{-2}$ $[FeCl_4]^{-}$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{+2}$
4	dsp^2 ($d = d_{x2-y2}$)	 Square planar	$[PdCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{+2}$ $[Cu(NH_3)_4]^{+2}$ $[PtCl_4]^{2-}$
5	sp^3d ($d = d_{z2}$) or dsp^3 ($d = d_{z2}$)	 Trigonal bipyramidal	$[Fe(CO)_5]$ $[CuCl_5]^{3-}$
5	sp^3d ($d = d_{x2-y2}$) or dsp^3 ($d = d_{x2-y2}$)	 Square pyramidal	$[Ni(CN)_5]^{-3}$
6	d^2sp^3 (inner orbital complex) or sp^3d^2 (outer orbital complex) in both case d-orbitals are d_{z^2} & $d_{x^2-y^2}$.	 Octahedral	$[Cr(NH_3)_6]^{+3}$ $[Ti(H_2O)_6]^{+3}$ $[Fe(CN)_6]^{-3}$ $[Co(NH_3)_6]^{+3}$ $[PtCl_6]^{-2}$,$[CoF_6]^{-3}$

Drawback of valence bond theory :

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

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

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

Crystal Field Theory

The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the Crystal Field Theory.

(i) The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand.

(ii) Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules.

(iii) The five d orbitals is an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal

atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystals field.

(a) Crystal field splitting in octahedral coordination entities :

(i) In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands.

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

(iii) Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.

(iv) This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0 (the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by $(3/5)\Delta_0$ and that of the three t_{2g} will decrease by $(2/5)\ \Delta_0$.

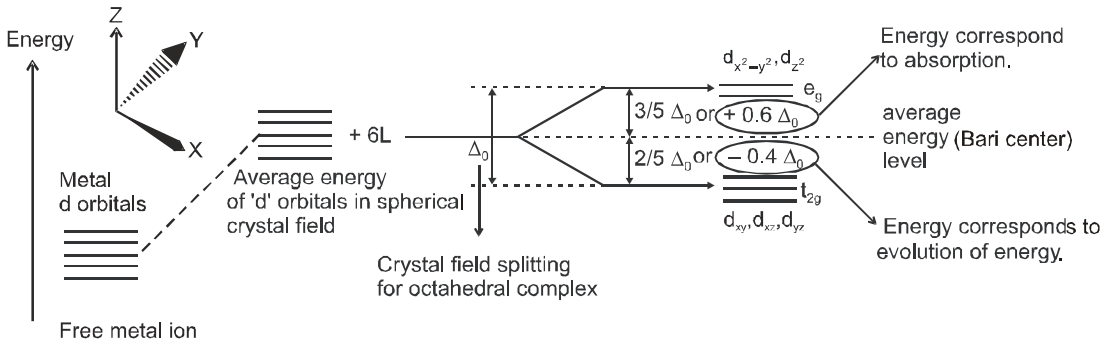


Figure showing crystal field splitting in octahedral complex.

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

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < EtOH < C_2O_4^{2-} < H_2O < NCS^- <$ EDTA $< NH_3 <$ en $<$ bipy (2, 2'-bipyridine) $< NO_2^- < PPh_3 < CN^- <$ CO

***Halide donors < O donors < N donors < C donors**

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

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

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

CALCULATION OF CRYSTAL FIELD STABILISATION ENERGY (CFSE)

Formula : CFSE = [– 0.4 (n) t_{2g} + 0.6 (n′) e_g] Δ_0 + *nP.

where n & n′ are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. *n represents the number of extra electron pairs formed because of the ligands in comparison to normal degenerate configuration.

(b) Crystal field splitting in tetrahedral coordination entities :

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

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

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

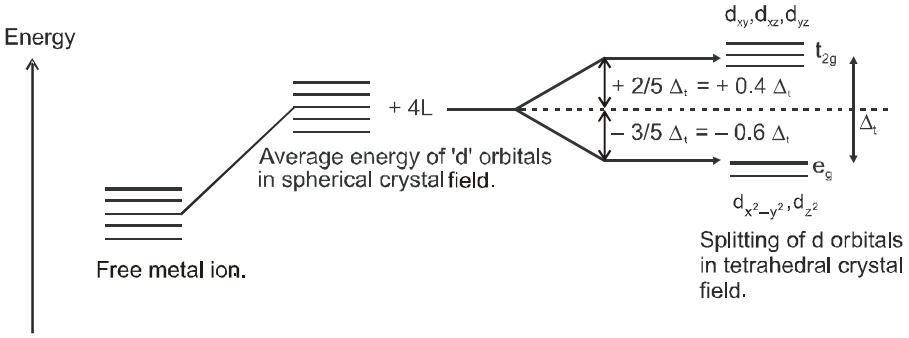


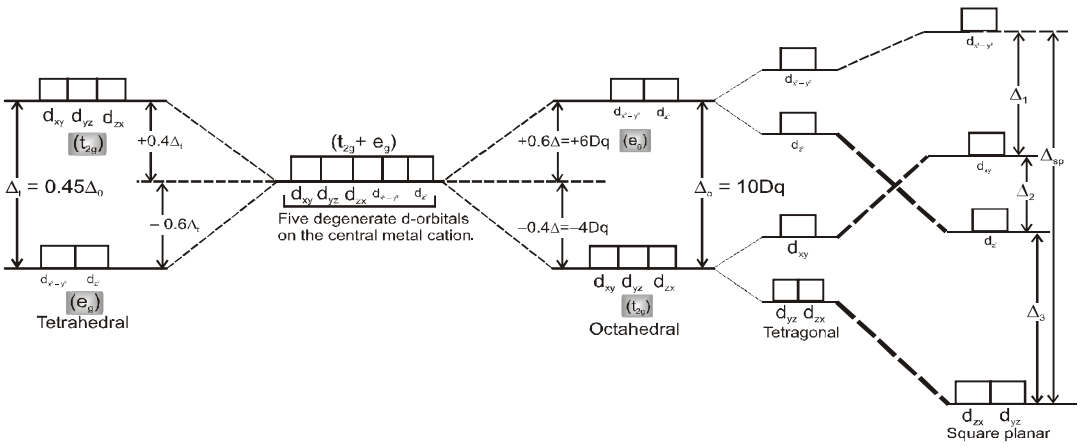
Figure showing crystal field splitting in tetrahedral complex.

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

(c) Crystal field splitting in square planar coordination entities :

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

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



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

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

MAGNETIC PROPERTIES OF COORDINATION COMPOUNDS :

Additional information for understanding the nature of coordination entities is provided by magnetic susceptibility measurements. We have noted that coordination compounds generally have partially filled d orbitals and as such they are expected to show characteristic magnetic properties depending upon the oxidation state, electron configuration, coordination number of the central metal and the nature of the ligand field. It is experimentally possible to determine the magnetic moments of coordination compounds which can be utilized for understanding the structures of these compounds.

The number of unpaired electrons in any complex can be easily calculated from the configuration of the metal ion, its coordination number and the nature of the ligands involved(strong or weak from the spectrochemical series) and after that the magnetic moment of the complexes can be easily calculated using ;

Magnetic Moment = $\sqrt{n(n+2)}$ **Bohr Magneton ; n = number of unpaired electrons**

For metal ions with upto three electrons in the d-orbitals like Ti^{3+}, (d^1) ; V^{3+} (d^2) ; Cr^{3+} (d^3) ; two vacant d-orbitals are easily available for octahedral hybridisation. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3d electrons are present, like in Cr^{2+} and Mn^{3+} (d^4) ; Mn^{2+} and Fe^{3+}(d^5) ; Fe^{2+} and Co^{3+}(d^6) ; the required two vacant orbitals for hybridisation is not directly available (as a consequence of Hund's rules). Thus, for d^4, d^5 and d^6 cases, two vacant d-orbitals are only available for hybridisation as a result of pairing of 3d electrons which leaves two, one and zero unpaired electrons respectively.

Application of magnetic moment :

(i) The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ion. However, there are complications with the coordination compounds / species having d^4 and d^5 ions.

(ii) $[Mn(CN)_6]^{3-}$ has a magnetic moment equal to two unpaired electrons while $[MnCl_6]^{3-}$ has a magnetic moment equal to four unpaired electrons.

(iii) Similarly $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a magnetic moment of five unpaired electrons.

(iv) $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)]^{3-}$ is diamagnetic.

(v) This anomalous behaviour is explained by valence bond theory in terms of formation of inner orbitals and outer orbitals complexes.

(vi) $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_2]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two are paramagnetic and the latter diamagnetic. $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic having four, five and four electrons respectively.

COLOUR IN COORDINATION COMPOUNDS :

Coordination compounds of transition metals have fascinating colours. According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmission or reflection of the rest of the wavelengths. An object that absorbs all visible light appears black. The mechanism of light absorption in coordination compounds is that photons of appropriate energy can excite the coordination entity from its ground state to an excited state. Consider the Ti(III) ion in solution, that is $[Ti(H_2O)_6]^{3+}$. This is a violet colour octahedral complex, where in the ground state of the complex a single electron is present in t_{2g} level. The next higher state available for the transition is the empty e_g level. If the light corresponding to the energy of yellow-green is absorbed by the complex, it would excite the electron from t_{2g} level to e_g level. Consequently the complex appears violet in colour. In case of copper (II) ions in solution, for example, it can be imagined that one of the d-electrons from

the t_{2g} set (d_{xy}, d_{yz}, d_{xz} orbitals) gets excited to the e_g set ($d_{x^2-y^2}$, d_{z^2} orbitals). In this case since high energy light is transmitted it means that low energy light (red region) is absorbed. For copper (II) ions in aqueous solution, the energy gap Δ_t is relatively small. Table below gives the relationship of the wavelength of light absorbed and the colour observed.

Relationship between the wavelength of light absorbed and the colour observed In some coordination entities

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Purple

Note : (a) In absence of ligand, crystal field splitting does not occur and as a consequence the substance appears colourless. For example ; (i) removal of water from violet coloured complex $[Ti(H_2O)_6]Cl_3$ on heating makes it colourless, (ii) similarly anhydrous copper sulphate ($CuSO_4$) is white, but hydrated copper sulphate ($CuSO_4.5H_2O$) is blue coloured.

(b) The nature of the ligand and the molar ratio of metal : ligands also influence the colour of the complex. For example ; in the pale green complex of $[Ni(H_2O)_6]$, the colour change is observed when ethylenediamine is progressively added to it.

Molar ratio of en : Ni	Coloured observed
1 : 1	Pale blue
2 : 1	Blue/Purple
3 : 1	Violet

Limitations of crystal field theory

(1) It considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals (such as s, p_x, p_y and p_z orbitals).

(2) It is unable to account satisfactorily for the relative strengths of ligands. For example it gives no explanation as to why H_2O is a stronger ligand than OH^- in the spectrochemical series.

(3) According to this theory, the bond between the metal and ligands are purely ionic. It gives no account on the partly covalent nature of the metal ligand bonds.

(4) The CFT cannot account for the π-bonding in complexes.

Stability of coordination compounds :

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

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

For the overall reaction :

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

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

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

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

$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$ $\beta_n = K_1 \times K_2 \times K_3 \times ..... \times K_n$

β_n, the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above. K_1, K_2, K_3 ..... K_n representing the stepwise stability (or formation) constants.

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

Some important generalisation regarding stability constants :

(ii) For a given metal and ligand the stability is generally greater when the charge on the metal ion is greater. Thus, stability of coordination entities of ions of charge 3+ is greater than the entities of 2+ ions.

(iii) Further, for the divalent ions of the first row transition elements, irrespective of the ligand involved, the stabilities vary in the Irving-Williams order : $Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$

(iv) This order is according to the size of the ions, smaller the size of the ion or greater the charge density on the metal greater is the stability of the complex.

In F^-, Cl^-, Br^-, I^- ; F^- forms strongest complexes due to small size & hence high charge density.

(v) (a) The stability also depends on the formation of chelate rings. If L is an unidentate ligand and L–L, a didentate ligand and if the donor atoms of L and L–L are the same element, then L–L will replace L. The stabilisation due to chelation is called the chelate effect. It is of great importance in biological systems and analytical chemistry.

(b) If a multidentate ligand happens to be cyclic and there are no unfavourable steric effects, a further increase in stability occurs. This is termed the **macrocyclic effect.**

ISOMERISM :

(1) Structural isomerism :

(A) Ionisation isomerism :

This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand and can displace a ligand which can then become the counter ion. For example, following complexes show ionisation isomerism.

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

$[Co(NH_3)_4(NO_2)Cl]Cl$ and $[Co(NH_3)_4Cl_2]NO_2$.

$[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4BrCl]Br.H_2O$. [Also an example of hydrate isomers.]

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

$[CoCl(en)_2(NO_2)]SCN$, $[Co(en)_2(NO_2)SCN]Cl$ and $[Co(en)_2(SCN)Cl]NO_2$

(B) Solvate / hydrate isomerism :

It occurs when water forms a part of the coordination entity or is outside it. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. For example, $CrCl_3 . 6H_2O$ exists in three distinct isomeric forms : $[Cr(H_2O)_6]Cl_3$, violet ; $[CrCl(H_2O)_5]Cl_2.H_2O$, blue green : $[CrCl_2(H_2O)_4]Cl.2H_2O$, dark green. These three cationic isomers can be separated by cation ion exchange from commercial $CrCl_3.6H_2O$.

A fourth isomer $[Cr(H_2O)_3Cl_3]$, yellow green also occurs at high concentration of HCl. Apart from their distinctive colours, the three isomers can be identified by the addition of excess of aqueous silver nitrate to their aqueous solutions, which precipitates chloride in the molar ratio of 3 : 2 : 1 respectively.

Complex	Reaction with $AgNO_3$	Reaction with conc. H_2SO_4(dehydrating agent)
$[Cr(H_2O)_6]Cl_3$	in the molar ratio of 3 : 1	No water molecule is lost or no reaction
$[CrCl(H_2O)_5]Cl_2.H_2O$	in the molar ratio of 2 : 1	one mole of water is lost per mole of complex
$[CrCl_2(H_2O)_4]Cl.2H_2O$	in the molar ratio of 1 : 1	two mole of water are lost per mole of complex

Other examples are :

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

$[Co(NH_3)_5(H_2O)](NO_3)_3$ and $[Co(NH_3)_5(NO_3)](NO_3)_2.H_2O$.

(C) Linkage isomerism :

In some ligands, like ambidentate ligands, there are two possible coordination sites. In such cases, linkage isomerism exist. e.g.,NO_2 group can be bonded to metal ions through nitrogen (–NO_2) or through oxygen (–ONO). SCN too can be bonded through sulphur (–SCN) thiocyanate or through nitrogen (–NCS) isothiocyanate.

For example : $[Co(ONO)(NH_3)_5]\ Cl_2$ & $[Co(NO_2)\ (NH_3)_5]\ Cl_2$.

(D) Coordination isomerism :

Coordination compounds made up of cationic and anionic coordination entities show this type of isomerism due to the interchange of ligands between the cation and anion entities. Some of the examples are :

(i) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

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

(iii) $[Co(NH_3)_6][Cr(SCN)_6]$ and $[Cr(NH_3)_4(SCN)_2][Co(NH_3)_2(SCN)_4]$

(iv) $[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2][PtCl_4]$

Such isomers are expected to have significant differences in their physical and chemical properties.

(E) Ligand isomerism :

Since many ligands are organic compounds which have possibilities for isomerism, the resulting complexes can show isomerism from this source.

For example; ligands 1,2-diaminopropane(propylenediamine or **pn)** and 1,3-diaminopropane (trimethylenediamine or **tn**) are such pairs. Similarly ortho-, meta- and para-toluidine ($CH_3C_6H_4NH_2$).

(F) Polymerisation isomerism :

Considered to be a special case of coordination isomerism, in this the various isomers differ in formula weight from one another, so not true isomers in real sense.

For example $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$, $[Co(NH_3)_6][Co(NO_2)_6]$, $[Co(NH_3)_5(NO_2)][Co(NH_3)_2(NO_2)_4]_2$, $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$, $[Co(NH_3)_4(NO_2)_2]_3[Co(NO_2)_6]$ and $[Co(NH_3)_5(NO_2)_2]_3[Co(NO_2)_6]_2$.

These all have the empirical formula $Co(NH_3)_3(NO_2)_3$, but they have formula weights that are 2,2,3,4,4 and 5 times this, respectively.

(2) Stereoisomerism :

The isomers in which atoms are bonded to each other in the same order but that differ in the arrangement of these atoms in the space are called as stereoisomers and the phenomenon as stereoisomerism.

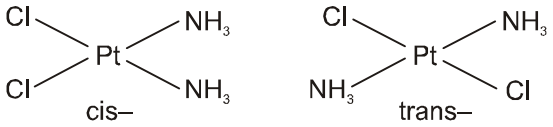
Geometrical Isomerism :

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Geometrical isomerism is common among coordination compounds with coordination numbers 4 and 6.

Coordination Number Four :

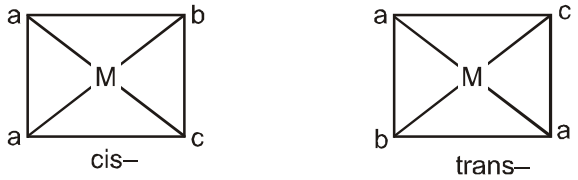
Tetrahedral Complex : The tetrahedral compounds can not show geometrical isomerism as we all know that all four positions are equivalent in tetrahedral geometry.

Square Planar Complex : In a square planar complex of formula $[Ma_2b_2]$ [a and b are unidentate], the two ligands 'a' may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer as depicted.

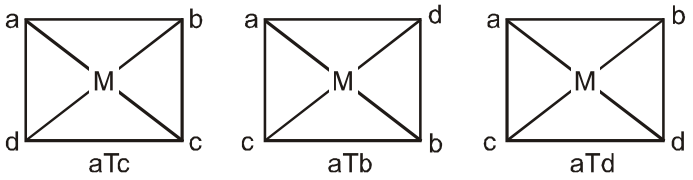


Geometrical isomers (cis and trans) of $Pt(NH_3)_2Cl_2$.

Square planar complex of the type Ma_2bc (where a,b,c are unidentates) shows two geometrical isomers.



Square planar complex of the type Mabcd (where a,b,c,d are unidentates) shows three geometrical isomers.



Example is $[Pt(NH_3)BrCl(py)]$. Three isomers of the complex $[Pt(NH_3)(NH_2OH)(py)(NO_2)]^+$ have been isolated and identified.

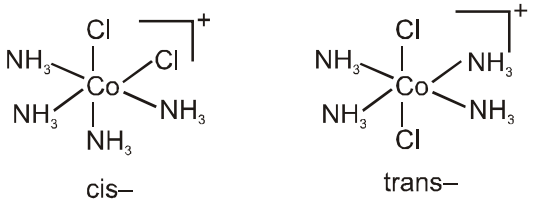
Square planar complex of the type $M(AB)_2$ (where AB are unsymmetrical bidentates) shows two geometrical isomers. Example is $[Pt(gly)_2]$ in which gly is unsymmetrical ligand.

Similarly, M(AB)(CD) also shows two geometrical isomers.

Note : $M(AA)_2$, (where AA are symmetrical bidentates) does not show geometrical isomerism. e.g., $[Cu(en)_2]^{2+}$ $[Pt(ox)_2]^{2-}$, etc.

Coordination Number Six :

Geometrical isomerism is also possible in octahedral complexes.



Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$

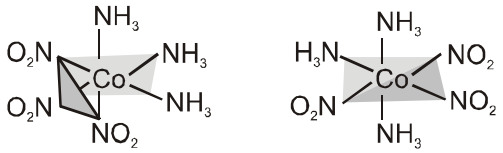
Number of possible isomers and the spatial arrangements of the ligands around the central metal ion for the specific complexes are given below.

(I) Complexes containing only unidentate ligands

(i) **Ma_2b_4**	**–**	**2**	(aa)(bb)(bb) (ab)(ab)(bb)
(ii) **Ma_4bc**	**–**	**2**	(aa)(aa)(bc) (aa)(ab)(ac)

(iii) **Ma_3b_3**

Complexes of the formula Ma_3b_3, where a and b are monodentate ligands, may show two isomeric forms called fac– and mer–. Facial isomers have three identical ligands on one triangular face where as meridional isomers have three identical ligands in a plane bisecting the molecule. Similar isomers are possible with some chelating ligands.



fac– mer–

The facial(fac) and meridional(mer) isomers of $[Co(NH_3)_3(NO_2)_3]$.

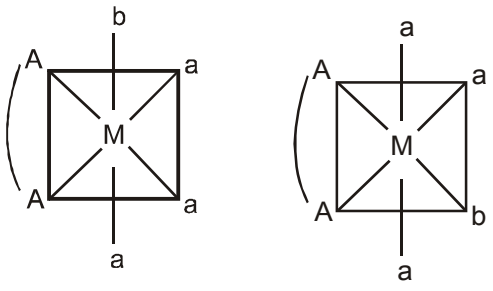
Unsymmetrical bidentate ligands also show fac-mer isomerism.

(iv) Ma_3b_2c	–	3	(aa)(ab)(bc) (aa)(bb)(ac) (ab)(ab)(ac)
(v) Ma_3bcd	–	4	(aa)(ab)(cd) (aa)(ac)(bd) (aa)(ad)(bc) (ab)(ac)(ad)
(vi) $Ma_2b_2c_2$	–	5	(aa)(bb)(cc) (aa)(bc)(bc) (bb)(ac)(ac) (cc)(ab)(ab) (ab)(ac)(bc)
(vii) Ma_2b_2cd	–	6	
(viii) Ma_2bcde	–	9	
(ix) Mabcdef, $[Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)]$	–	15	

Note : Ma_6 and Ma_5b have only one form.

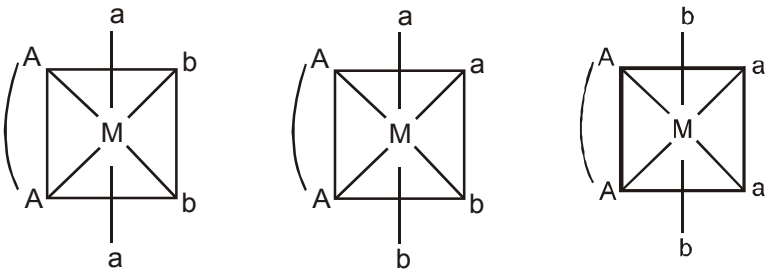
(II) Compounds containing bidentate ligand and unidentate ligands.

(i) $M(AA)a_3b$ – Two geometrical isomers are possible.



bTa aTa

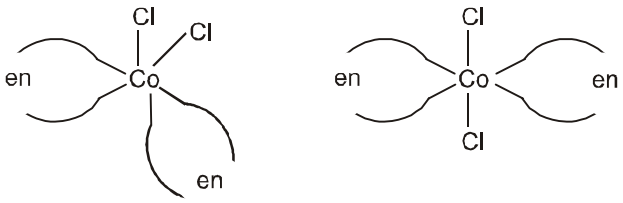
(ii) $M(AA)a_2b_2$ – Three geometrical isomers are possible.



aTa aTb bTb

Note : With $[M(AA)b_4]$, only one form is possible. M(AA)abcd have six geometrical isomers.

(iii) $M(AA)_2a_2$ – Two geometrical isomers are possible.

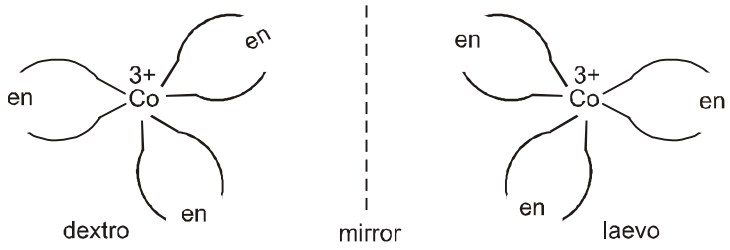


Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

Optical Isomerism :

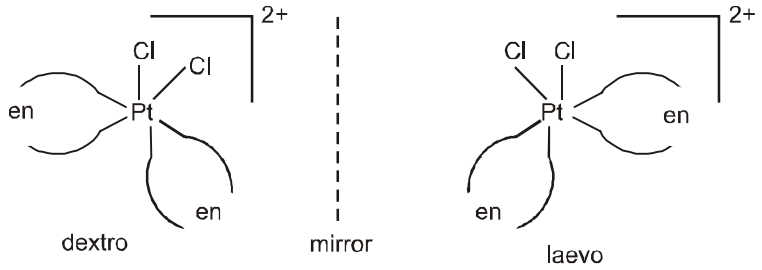
A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their ability to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical isomers. Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. This is due to the absence of elements of symmetry in the complex. The two forms are called dextro(d) and laevo(l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, ℓ to the left).

Octahedral complex : Optical isomerism is common in octahedral complexes involving didentate ligands. For example, $[Co(en)_3]^{3+}$ has d and ℓ forms as given below.



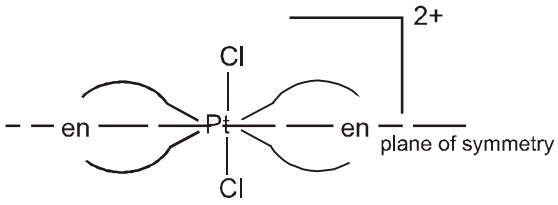
d and ℓ of $[Co(en)_3]^{3+}$

Cis-isomer of $[PtCl_2(en)_2]^{2+}$ show optical isomerism as shown below because of the absence of plane of symmetry as well as centre of symmetry.

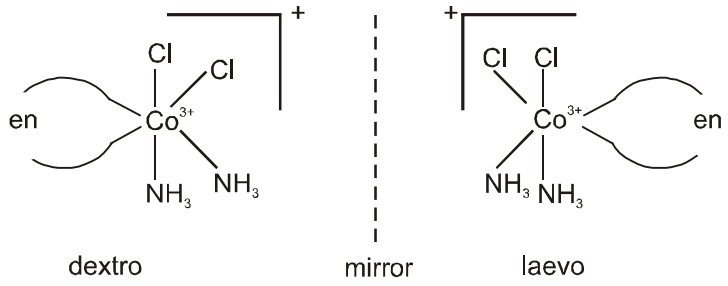


d and ℓ of cis-$[PtCl_2(en)_2]^{2+}$

But trans isomer of $[PtCl_2(en)_2]^{2+}$ does not show optical isomerism.

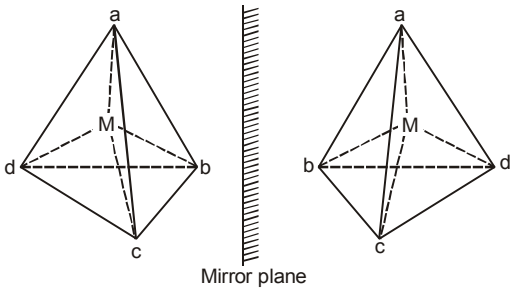


cis-$[Co(NH_3)_2Cl_2(en)]^+$ can show optical isomerism due to the absence of plane of symmetry as well as centre of symmetry.

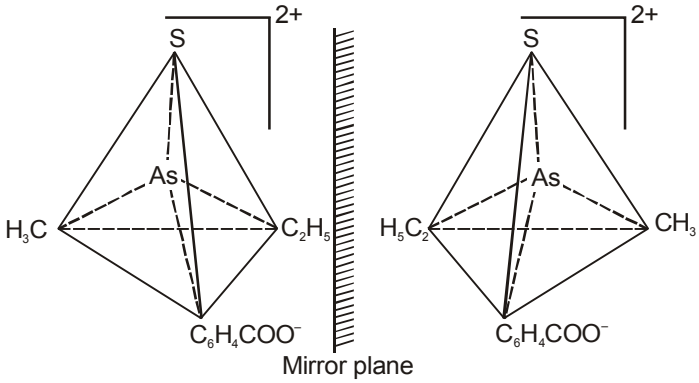


Tetrahedral complex :

Optical isomerism is expected in tetrahedral complexes of the type [Mabcd] analogous to tetrahedral carbon atom.

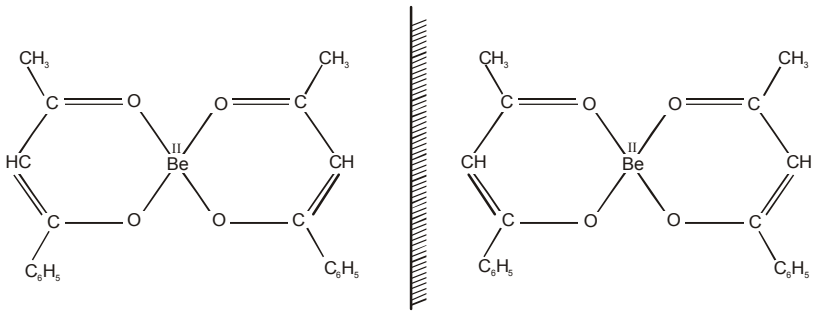


(i) For example $[As(III)(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2+}$, shows optical isomerism as given below.



Here it may be noted that 4 different groups round the central metal ion are not the only requirement to make the complex to show mirror-image isomerism. All that is required is that the molecule should be asymmetric (i.e., unsymmetrical), i.e., it should have no plane of symmetry so that it can exist in two mirror-image forms.

(ii) Tetrahedral complexes of Be, B, Cu(II) and Zn(II) with unsymmetrical bidentate ligands have been resolved into optical isomers. In order for the complex to be chiral, the chelating ligand must be unsymmetrical (not necessarily asymmetric or chiral, itself). An example is bis(benzoylacetonato) Be(II) complex, $[(C_6H_5COCHCOCH_3)_2Be]^0$ whose mirror-image isomers are shown in figure.



Here it may be noted from the figure that the complex has no centre or plane of symmetry and the two forms are not superimposable on each other. This explains the resolution of the complex into d-and ℓ-forms.

Square planar complex :

Square planar complexes are rarely found to show the optical isomerism. The plane formed by the four ligating atoms and the metal ion is considered to be a mirror plane and thus prevents the possibility of chirality. Although, square planar complexes seldom show optical isomerism, yet a four -coordinated complex of Pt(II), $[Pt(II)(NH_2.CH(C_6H_5).CH(C_6H_5NH_2).(NH_2.CH_2.C(CH_3)_2.NH_2)]^{2+}$ which has square-planar shape has been resolved into two forms by Mills and Quibell in 1935.

Determination of stereoisomers in Coordination compounds

Table-1

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
Ma_6	1	0	1
Ma_5b	1	0	1
Ma_4b_2	2	0	2
Ma_4bc	2	0	2
Ma_3b_3	2	0	2
Ma_3b_2c	3	0	3
Ma_3bcd	5	1	4
$Ma_2b_2c_2$	6	1	5
Ma_2b_2cd	8	2	6
Ma_2bcde	15	6	9
Mabcdef	30	15	15

Table-2

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[M(AA)_3]$	2	1	1
$[M(AA)_2a_2]$	3	1	2
$[M(AA)_2ab]$	3	1	2
$[M(AA)a_4]$	1	0	1
$[M(AA)a_3b]$	2	0	2
$[M(AA)a_2b_2]$	4	1	3
$[M(AA)_2bc]$	6	2	4
[M(AA)abcd]	12	6	6

Table-3

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[M(AB)_3]$	4	2	2
$[M(AB)_2a_2]$	8	3	5
$[M(AB)_2ab]$	11	5	6
$[M(AB)a_4]$	1	0	1
$[M(AB)a_3b]$	4	1	3
$[M(AB)a_2b_2]$	6	2	4
$[M(AB)a_2bc]$	12	5	7
[M(AB)abcd]	24	12	12

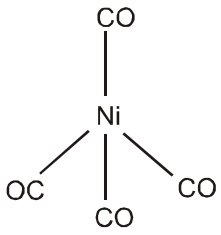
M is the metal ion and a,b,c,d,e and f represent monodentate ligands. AA is a bidentate symmetrical ligand. AB is a bidentate unsymmetrical ligand.

Organometallic compounds

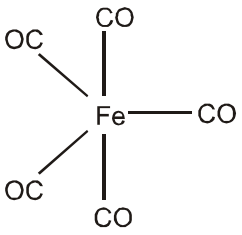
Metal Carbonyls

Compounds of metals with CO as a ligand are called metal carbonyls.
They are of two types.

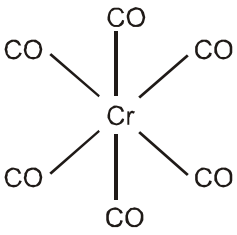
(a) Monomeric : Those metal carbonyls which contain only one metal atom per molecule are called monomeric carbonyls. For examples :[$Ni(CO)_4$] (sp^3, tetrahedral); [$Fe(CO)_5$] (dsp^3, trigonal bipyramidal); [$Cr(CO)_6$] (d^2sp^3, octahedral) ; [$V(CO)_6$] (d^2sp^3, octahedral, only carbonyl which is paramagnetic having one unpaired electron ; this is least stable among all the four carbonyls)



$Ni(CO)_4$
Tetrahedral

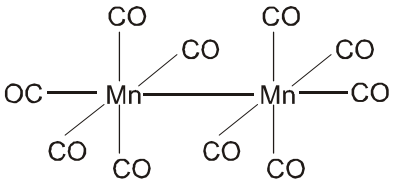


$Fe(CO)_5$
Trigonal bipyramidal

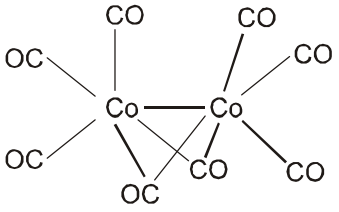


$Cr(CO)_6$
Octahedral

(b) Polymeric : Those metal carbonyls which contain two or more than two metal atoms per molecule and they have metal-metal bonds are called polymeric carbonyl. For example : $Mn_2(CO)_{10}$, $Co_2(CO)_9$, etc.



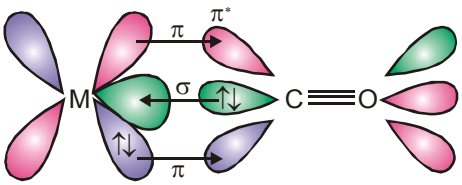
$[Mn_2(CO)_{10}]$



$[Co_2(CO)_8]$

Metal carbonyls are mostly solids at room temperature and atmospheric pressure. The mononuclear carbonyls are volatile and toxic. With the exception of $Fe_2(CO)_9$, carbonyls are soluble in hydrocarbon solvents. Mononuclear carbonyls are either colourless or light-coloured. Polynuclear carbonyls are more deeply coloured. $Fe_3(CO)_{12}$, dodecacarbonyltriiron(o), for example, is a deep grass green solid. Metal carbonyls find use as industrial catalysts and as precursors in organic synthesis.

The metal–carbon bond in metal carbonyls possess both s and p character. The M—C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon (CO is a weak base) into a vacant orbital of the metal. The M—Cπ bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. Thus carbon monoxide acts as σ donor (OC $\rightarrow$ M) and a π acceptor (OC $\leftarrow$ M), with the two interactions creating a synergic effect which strengthens the bond between CO and the metal as shown in figure.



Synergic bonding

(i) As M—Cπ bonding increases, the C—O bond becomes weaken. The greater the positive charge on the central metal atom, the less readily the metal can donate electron density into the π^* orbitals of the carbon monoxide ligands to weaken the C—O bond.

(ii) In contrast, in the anionic complex (i.e. carbonylate anion) the metal has a greater electron density to be dispersed, with the result that M—Cπ bonding is enhanced and the C—O bond is diminished in strength. For example ; in isoelectronic complexes the strength of metal-ligand bond increases and strength of C—O bond in CO decreases (because bond order decreases) as the negative charge on the complexes increases.

Thus order of CO bond strengths ;

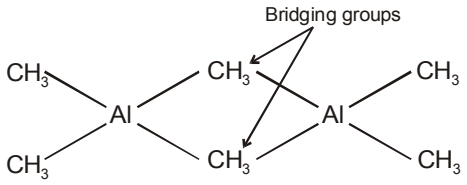
(a) $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$. (b) $[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$.

Sigma (σ) bonded organometallic compounds :

In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond in which ligand contributes one electron and is therefore called one electron donor. For example :

(a) Grignard's Reagent R–Mg–X where R is a alkyl or aryl group and X is halogen.

(b) $(CH_3)_4Sn$, $(C_2H_5)_4Pb$, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$ etc.



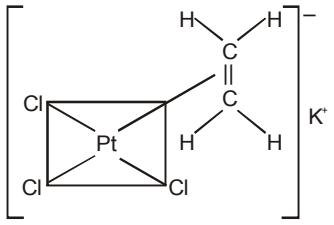
Pie (π)-bonded organometallic compounds :

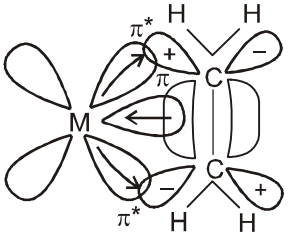
These are the compounds of metal with alkenes, alkynes, benzene and other ring compounds.

Zeise's salt :

In Zeise's salt structure, the ethylene occupies the fourth coordination site of the square planar complex with the C—C axis perpendicular to the platinum ligand plane. Relative to free ethylene the C—C bond is lengthened (from 133.77 pm to 137.5 pm), and the hydrogen are slightly tilted back from a planar arrangement. The bond between the ethylene molecule and the metal ion may be considered as a dative σ bond to an available orbital on the metal. The bonding scheme is analogous to that in carbon monoxide complexes in which there is a ligand metal σ donation and a reciprocal metal to ligand π bonding. The extent of back bonding varies depending on the metal, the substituents on ethylene, and the other ligands on the metal,

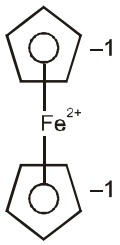
K $[PtCl_3(\eta^2 - C_2H_4)]$

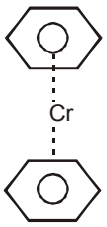




Ferrocene and bis(benzene)chromium **:**

Ferrocene obeys 18-electrons rule. Depending on the electron counting method adopted, the cyclopentadienyl ligand may be viewed as either a five electron donor (neutral atom) or a six electron donor (oxidation state). Similarly, the benzene ligand may be viewed as a six electron donor in neutral atom as well as in the oxidation state. Ferrocene show thermal stability and is not oxidised by air.

Fe $(\eta^5 - C_5H_5)_2$ 

and Cr $(\eta^6 - C_6H_6)_2$ 

* For the π-donors, the prefix like η^x is to be used, where η indicates π-electron donation and x is known as the hapticity of the ligand, i.e. the number of atoms involved in the π-donation. For example:

(i) π-$C_5H_5^-$: η^5 – cyclopentadienyl or pentahaptocyclopentadienyl

(ii) π-$C_3H_5^-$: η^3 – allyl or trihaptoallyl

Applications of coordination and organometallic compounds :

(i) Coordination compounds are of great importance in biological systems. Example being–chlorophyll (the green pigment in plants); haemoglobin (the red pigment of blood, which acts as oxygen carrier) along with myoglobin (which stores oxygen and is a regulator of respiration); Vitamin B_{12}, cyanocobalammine, the anti-pernicious anaemia factor. All of these, respectively, are the coordination compounds of magnesium, iron and cobalt with the macrocyclic porphyrin and corrin ligands.

(ii) There are many examples of the use of coordination compounds in qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially the chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Familiar examples of such reagents are :

ethylenediaminetetraaceticacid (EDTA), dimethylglyoxime, α-nitroso β-naphthol, cupron, etc.

(iii) Some important extraction processes of metals, like those of extraction of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be precipitated from this solution by the addition of Zinc.

(iv) Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

(v) EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumors. Examples are : cis-platin (cis-$[Pt(NH_3)_2Cl_2]$ and related compounds.

(vi) Organometallic compounds are used as catalysts. These catalysts are either of the homogeneous type (soluble in the reaction medium) or of the heterogeneous type (insoluble in the reaction medium). The catalysed polymerisation of alkenes at atmospheric pressure and ambient temperature using Ziegler-Natta catalyst (titanium tetrachloride plus triethylaluminium) is one of the important discoveries of organometallic chemistry. The first effective homogeneous catalyst chloridotris(triphenylphosphine) rhodium(I), $[RhCl(PPh_3)_3]$ for hydrogenation was given by Wilkinson.

(vii) Tetra ethyl lead (TEL) is used as antiknock compound in gasoline.

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

1. Give the order of chelating effect of following ligands.

(i) $C_2O_4^{2-}$ (ii) EDTA (iii) dien

(A) iii > ii > i (B) i > ii > iii (C) ii > iii > i (D) i > iii > ii

Ans. (C)

Sol. As number of donor atoms increases the number of bonds increase. So the chelating effect of ligands increase as oxalato, dien and EDTA has two, three and six donor atoms respectively.

2. Write the structural formula corresponding to each of the following IUPAC names :

(a) potassium tetracyanidozincate (II) (b) tetracarbonyl nickel (0)

(c) potassium tetracyanonickelate (0) (d) potassium tris(oxalato)aluminate (III)

Ans. (a) $K_2[Zn^{II}(CN)_4]$ (b) $[Ni^0(CO)_4]$ (c) $K_4[Ni^0(CN)_4]$ (d) $K_3[Al^{III}(C_2O_4)_3]$

Sol. Refer IUPAC rule.

3. Write IUPAC names of the following :

(a) $[Cr(acac)_3]$ (b) $[V(H_2O)_6]Cl_3$ (c) $(NH_4)_3[Co(C_2O_4)_3]$ (d) $K_2[CrO_4]$

Ans. (a) tris (acetylacetonato) chromium(III)

(b) hexaaquavanadium (III) chloride

(c) ammonium tris(oxalato)cobaltate(III) or ammonium trioxalatocobaltate(III)

(d) potassium tetraoxidochromate(VI)

Sol. Refer IUPAC nomenclature rule.

4. A solution containing 0.319 g of complex $CrCl_3.6H_2O$ was passed through cation exchanger and the solution given out was neutralised by 28.5 ml of 0.125 M NaOH. The correct formula of the complex will be: [molecular weight of complex = 266.5]

(A) $[CrCl(H_2O)_5]Cl_2 . H_2O$ (B) $[Cr(H_2O)_6]Cl_3$

(C) $[CrCl_2(H_2O)_4]Cl. 2H_2O$ (D) All are correct

Ans. (B)

Sol. $Cl^- = HCl = NaOH$

$nCl^- + nH^+ \longrightarrow nHCl$

Thus 1 mol of complex will form n mol of HCl

1 mole of complex = n mol of HCl = n mole of NaOH

mole of complex = $\frac{0.319}{266.5}$ = 0.0012; mole of NaOH used = $\frac{28.5 \times 0.125}{1000}$ = 0.0036

So 0.0012 mole of complex = 0.0036 mole of NaOH = 0.0036 mole of HCl

1 mole of complex = $\frac{0.0036}{0.0012}$ = 3 mole of HCl

$\therefore$ n = 3

So complex is $[Cr(H_2O)_6]Cl_3$.

5. Calculate the effective atomic number of the metal atoms in the following complexes / complex ions.

(a) $[Cr(CO)_6]$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Co(CN)_6]^{4-}$ (d) $[Ni(NH_3)_6]^{2+}$

[Cr = 24 ; Fe = 26; Co = 27 and Ni = 28 as atomic numbers]

Ans. (a) 36 (b) 35 (c) 37 (d) 38

Sol. EAN = Number of electrons in metal atom or ion + Number of electrons donated by ligands to metal.

(a) $[Cr^0(CO)_6]$; EAN = 24 + 12 = 36 ; (b) $[Fe^{III}(CN)_6]^{3-}$; EAN = 23 + 12 = 35

(c) $[Co^{II}(CN)_6]^{4-}$; EAN = 25 + 12 = 37 ; (d) $[Ni^{II}(NH_3)_6]^{2+}$; EAN = 26 + 12 = 38

6. Consider the following complexes :

(i) K_2PtCl_6 (ii) $PtCl_4 . 2NH_3$ (iii) $PtCl_4 . 3NH_3$ (iv) $PtCl_4 . 5NH_3$

their electrical conductance in aqueous solutions are :

(A) 256, 0, 97, 404 (B) 404, 0, 97, 256 (C) 256, 97, 0, 404 (D) 404, 97, 256, 0

Ans. (A)

Sol. The electrical conductance of the complexes depend upon the number of ions given by them in the aqueous solutions.

(i) $K_2[PtCl_6] \overset{aq}{\rightleftharpoons} 2K^+(aq) + [PtCl_6]^{2-}(aq)$ (ii) $[Pt(NH_3)_2Cl_4] \overset{aq}{\rightleftharpoons} [Pt(NH_3)_2Cl_4]\,(aq)$

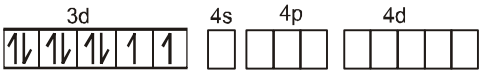
(iii) $[Pt(NH_3)_3Cl_3]Cl \overset{aq}{\rightleftharpoons} [Pt(NH_3)_3Cl_3]^+(aq) + Cl^-(aq)$ (iv) $[Pt(NH_3)_5Cl]Cl_3 \overset{aq}{\rightleftharpoons} [Pt(NH_3)_5Cl]^{3+} + 3Cl^-$

	Complex	**Number of ions**	**Expected electrical conductance**
(i)	$K_2[PtCl_6]$	3	256
(ii)	$[Pt(NH_3)_2Cl_4]$	0	0
(iii)	$[Pt(NH_3)_3Cl_3]Cl$	2	97
(iv)	$[Pt(NH_3)_5Cl]Cl_3$	4	404

7. Explain the following :

(i) All the octahedral complexes of Ni^{2+} must be outer orbital complexes.

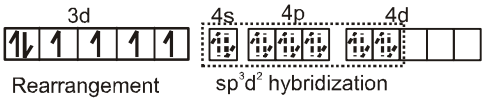
(ii) $[CoF_6]^{3-}$ is paramagnetic but $[Co(CN)_6]^{3-}$ is diamagnetic.

Sol. (i) Ni^{2+} configuration 

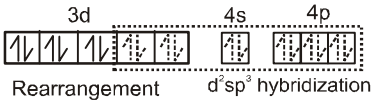
During rearrangement only one 3d-orbital may be made available for pairing of the electrons.

Thus, d^2sp^3 hybridization is not possible. So only sp^3d^2 (outer) hybridization can occur.

(ii) In $[CoF_6]^{3-}$, Co^{3+} undergoes sp^3d^2 hybridization. Four d-orbitals are singly occupied. Hence, it is paramagnetic.

$[CoF_6]^{3-}$ 

In $[Co(CN)_6]^{3-}$, Co^{3+} undergoes d^2sp^3 hybridization. All electrons are paired and thus it is diamagnetic.

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

8. You are given the following two complexes X and Y which are isomers of each other ; X is Hg $[Co(SCN)_4]$. It is further given that 'spin only' magnetic moment of X is found to be 3.78 B.M. and that of Y is 1.73 B.M. Then which of the following is correct ?

(A) Anion of X will be tetrahedral and that of Y will be square planar.

(B) Anion of X will be square planar but that of Y will be tetrahedral

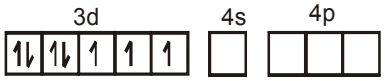
(C) Both the anions will be tetrahedral

(D) Both the anions will be square planar

Ans. (A)

Sol. In Hg $[Co(SCN)_4]$ (X), the cobalt is in +2 oxidation state.

$\mu = \sqrt{n(n+2)}$; So, 3.78 B.M = $\sqrt{n(n+2)}$ or n = 3.

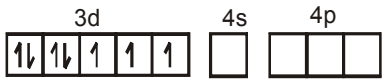
Co^{2+}, [Ar] $3d^7$ 

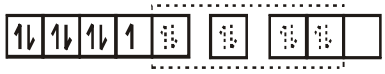
$[Co(SCN)_4]^{2-}$ 

sp^3 hybrid orbitals

Four pairs of electrons from four SCN^- ions.

In Hg $[Co(NCS)_4]$ (Y), the cobalt is in +2 oxidation state. Further 'spin only' magnetic moment of complex, $Hg[Co(NCS)_4]$ is 1.73 B.M. So, $\mu = \sqrt{n(n+2)}$; So, 1.73 B.M = $\sqrt{n(n+2)}$ or n = 1.

Co^{2+}, [Ar] $3d^7$ 

$[Co(NCS)_4]^{2-}$ 

dsp^2 hybrid orbitals

Four pairs of electrons from four NCS^- ions.

So, X is tetrahedral and Y is square planar.

9. All the following complexes show a decreases in their weights when placed in a magnetic balance. Then which of the these has square planar geometry ?

(A) $Ni(CO)_4$ (B) $K[AgF_4]$ (C) $Na_2[Zn(CN)_4]$ (D) None of these

Ans. (B)

Sol. In $K[AgF_4]$, Ag(III) has $4d^8$ configuration. This has higher CFSE which favours pairing of electrons and thus complex is diamagnetic and square planar.

10. It is an experimental fact that $Cs_2[CuCl_4]$ is orange coloured but $(NH_4)_2[CuCl_4]$ is yellow. It is further known that total paramagnetic moment of a unpaired electron is due to spin as well as due to nature of orbital ; 'd' orbital contributing more than 's' or 'p'. Thus the total paramagnetic moment of orange compound is found to be more than that of yellow compound. Then which of the following is correct ?

(A) Anion of orange compound is tetrahedral and that of yellow is square planar

(B) Anion of orange compound is square planar and that of yellow is tetrahedral

(C) Both the anions are tetrahedral

(D) Both the anions are square planar

Ans. (A)

Sol. $Cs_2[CuCl_4]$ (orange) is tetrahedral because in Cu(II) the unpaired electron is in 3d. But $(NH_4)_2[CuCl_4]$ (yellow) is square planar because the unpaired electron is not in 3d rather in some promoted state 's' or 'p'.

11. It is an experimental fact that : DMG + Ni(II)salt + $NH_4OH \longrightarrow$ Red precipitate

Which of the following is wrong about this red precipitate?

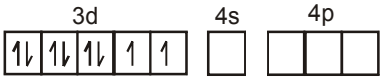
(A) It is a non–ionic complex. (B) It involves intra molecular H–bonding.

(C) Ni(II) is sp^3 hybridised. (D) It is a diamagnetic complex.

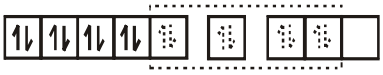
Ans. (C)

Sol. In complex $[Ni(DMG)_2]$, the nickel is in +2 oxidation state ; the ion has the electronic configuration $3d^8$ and dimethylglyoxime is a chelating ligand. So, the hybridisation scheme is as shown in figure.

Ni^{2+}, $[Ar]3d^8$

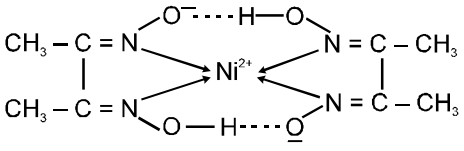


$[Ni(DMG)_2]$



diamagnetic.

dsp^2 hybrid orbitals



square planar

12. The correct order for the CFSE (numerical value) for the following complexes is :

Complex	P	Q	R	S
Formula	$[CoF_6]^{3-}$	$[Co(CN)_6]^{3-}$	$[Co(NH_3)_6]^{3+}$	$[Co(H_2O)_6]^{3+}$

(A) P > Q > R > S (B) Q > R > S > P

(C) S > R > P > Q (D) R > Q > P > S

Ans. (B)

Sol. CFSE depends on the relative magnitude of crystal field splitting, Δ_o and pairing energy, p and in turns Δ_o depends upon the field produced by ligand and charge on the metal ion. So,the order of increasing crystal field strength is $F^- < H_2O < NH_3 < CN^-$. (Co is in +3 oxidation state in all complexes).

Thus the (B) option is correct.

13. Which of the following statements is not correct ?

(a) $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have same value of CFSE

(b) $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have same value of magnetic moment

(A) Only a (B) Only b (C) Both a and b (D) None of these

Ans. (A)

Sol. (a) Ammonia is a stronger field ligand than water. So $[Ni(NH_3)_6]^{2+}$ will have higher CFSE than $[Ni(H_2O)_6]^{2+}$.

(b) Both complexes $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have sp^3d^2 hybridisation with two unpaired electrons. So, they possess same magnetic moment ('spin only')

14. **Statement-1 :** $[Co^{II}(NH_3)_6]^{2+}$ is not readily oxidized to $[Co^{III}(NH_3)_6]^{3+}$ when air is bubbled through it.

Statement-2 : Crystal field stabilization energy of Co(+III) with a d^6 configuration is higher than for Co(+II) with a d^7 arrangement.

(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

Ans. (D)

Sol. Statement 1 is false statement. $[Co^{II}(NH_3)_6]^{2+}$ is readily oxidised in $[Co^{III}(NH_3)_6]^{3+}$ in presence of air due to the higher CFSE value ($-2.4\Delta_o$) of d^6 configuration than d^7 configuration ($-0.8\,\Delta_o$).

15. Which of the following is true about the complex $[PtCl_2(NH_3)(OH_2)]$? [Atomic number of Pt = 78]

(i) It will have two geometrical isomeric forms, cis and trans.

(ii) The hybridisation state of Pt(II) is sp^3.

(iii) It is a square planar complex.

(iv) It is a diamagnetic complex.

(v) It can show hydrate isomerism.

(vi) It is a tetrahedral complex.

(A) (i), (iii),(iv)

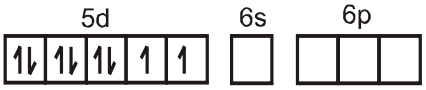
(B) (ii),(iv),(v)

C) (ii),(v),(vi)

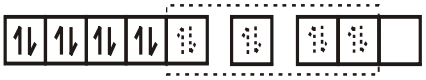
(D) (i),(v),(vi)

Ans. (A)

Sol. Pt^{2+}, $[Xe]4f^{14}5d^8$



$[PtCl_2(NH_3)(OH_2)]$

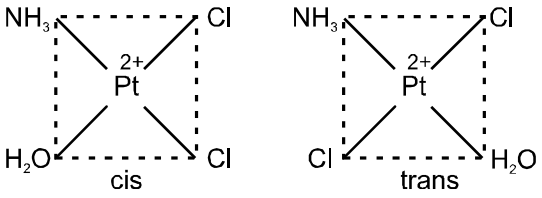


diamagnetic

dsp^2 hybrid orbitals

Four pairs of electrons from four Cl^- ions.

Ma_2bc have cis- and trans isomers.



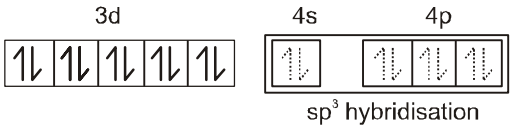
16. Among $[Ni(CN)_4]^{4-}$, $[Ni(PPh_3)_3Br]$ and $[Ni(dmg)_2]$ species, the hybridisation states of the Ni-atoms are respectively :

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

Ans. (B)

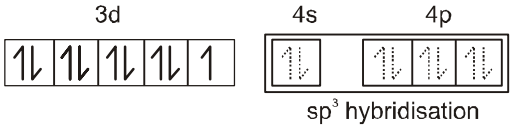
Sol. $[Ni(CN)_4]^{4-}$ - Ni is in zero oxidation state. The CN^- is strong field ligand and, therefore, rearrangement of electrons occur.

So, $[Ni(CN)_4]^{4-}$



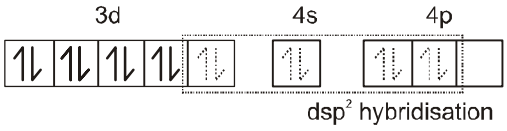
$[Ni(PPh_3)_3Br]$ - Ni is in +1 oxidation state with $3d^9$ configuration (PPh_3 is a strong field ligand).

So, $[Ni(PPh_3)_3Br]$



$[Ni(dmg)_2]$ - Ni is in +2 oxidation state with $3d^8$ configuration. (dmg is a chelating ligand).

So, $[Ni(dmg)_2]$



17. For the reaction $Ni^{2+} + 4NH_3 \rightleftharpoons [Ni(NH_3)_4]^{2+}$; at equilibrium, if the solution contains 1.6×10^{-4}% of nickel in the free state, and the concentration of NH_3 at equilibrium is 0.5 M. Then the instability constant of the complex will be approximately equal to :

(A) 1.0×10^{-5} (B) 1.5×10^{-16} (C) 1.0×10^{-7} (D) 1.5×10^{-17}

Ans. (C)

Sol. $Ni^{2+} + 4\ NH_3 \rightleftharpoons [Ni(NH_3)_4]^{2+}$ $\therefore$ $k = \dfrac{[Ni(NH_3)_4]^{2+}}{[Ni^{2+}][NH_3]^4}$

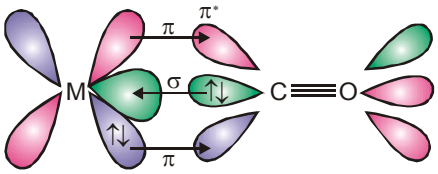
But $\dfrac{[Ni^{2+}]}{[Ni^{2+}]+[Ni(NH_3)_4]^{2+}} = 1.6 \times 10^{-6}$

or $\dfrac{Ni^{2+}}{[Ni(NH_3)_4]^{2+}} \approx 1.6 \times 10^{-6}$ $\therefore$ $k = \dfrac{10^6}{1.6 \times (0.5)^4} = 10^7$

Hence instability constant = 10^{-7}

18. In metal carbonyls the metal carbon bond length is found to be less than the expected bond length. Explain why ?

Sol. It is due to synergic interaction between metal and CO which develops partial double bond character between metal and CO.



Synergic bonding

19. π-bonding is not involved in :

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

Ans. (D)

Sol. RMgX i.e. Grignard's reagent is σ bonded complex.

20. Wilkinson's catalyst contains :

(A) rhodium (B) iron (C) aluminium (D) cobalt

Ans. (A)

Sol. Wilkinson's catalyst is $[Rh(I)Cl(PPh_3)_3]$. So it contains rhodium.

Exercise # 1

PART - I : SUBJECTIVE QUESTIONS

Marked Questions may have for Revision Questions.

Section (A) : General introduction of complex salts and definitions to be used

A-1. K_2SO_4 solution mixed with $Cr_2(SO_4)_3$ solution in 1 : 1 molar ratio gives the test of Cr^{3+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why ?

A-2. What is the coordination number and the oxidation state of the metal in each of the following complexes?
(a) $[AgCl_2]^-$; (b) $[Cr(H_2O)_5Cl]^{2+}$; (c) $[Co(NCS)_4]^{2-}$
(d) $[Co(NH_3)_3(NO_2)_3]$; (e) $[Fe(EDTA)]^-$ (f) $[Cu(en)_2]SO_4$;
(g) $K[Pt(NH_3)Cl_5]$

A-3. Write the name of the following ligands and classify their denticity
(A) CH_3NC (B) $acac^{-1}$ (C) N_3^- (D) dien (E) $edta^{4-}$
(F) $edta^{3-}$ (G) ox^{2-} (H) dmg^{-1} (I) NC^- (J) NO_2^-
(K) O^{2-} (L) O_2^{2-} (M) O_2^-

A-4. Predict the different ligating sites by drawing structures in the following ligands.
(A) $(NO_2)^-$ (B) $(SCN)^-$ (C) $(C_2O_2S_2)^{2-}$ (D) $(OCN)^-$
(E) $(NOS)^-$

A-5.(a) Draw the structure of the complexes $[Fe(C_2O_4)_3]^{3-}$ and $[Pt(en)_2]^{2+}$. Determine the denticity of the ligands and identify any chelate rings. What are the coordination number and the oxidation number of the central metal ion?

(b) Designate the coordination entities and counter ions in the coordination compounds.
$K_2[Ni(CN)_4]$; $[Cr(en)_3]Cl_3$; $Fe_4[Fe(CN)_6]_3$; $[PtCl_2(en)_2](NO_3)_2$.

(c) Identify the Lewis acid and Lewis base components of the following complexes.
(i) $[HgBr_4]^{2-}$ (ii) $[Ni(H_2O)_6]^{2+}$ (iii) $[PdCl_2(NH_3)_2]$
(iv) $[Al(OH)_4]^-$ (v) $[Ag(CN)_2]^-$ (vi) $[Cr(CO)_6]$

Section (B) : Nomenclature of coordination compounds

B-1. Name the following compounds

(a) **$[Co(NH_3)_6]Cl_3$**, Prepared in 1798 by B.M. Tassaert and considered to be first complex salt prepared.
(b) **$[Rh(NH_3)_5I]I_2$**, A yellow colored complex obtained by heating $[Rh(NH_3)_5(H_2O)]I_3$ above 100^0C.
(c) **$[Fe(CO)_5]$**, A highly toxic volatile liquid.
(d) **$[Fe(C_2O_4)_3]^{3-}$**, The ion formed when Fe_2O_3 rust is dissolved in oxalic acid, $H_2C_2O_4$.
(e) **$[Cu(NH_3)_4]SO_4$**, A deep blue compound obtained when $CuSO_4$ is treated with excess of NH_3.
(f) **$Na[Cr(OH)_4]$**, The compound formed when $Cr(OH)_3$ precipitate is dissolved in excess of NaOH.
(g) **$[Co(gly)_3]$**, A complex that contains the anion of amino acid, glycine.
(h) **$[Fe(H_2O)_5(SCN)]^{2+}$**, The red complex ion formed in the qualitative analysis test of Fe^{3+} ion.
(i) **$K_2[HgI_4]$**, Alkaline solution of this complex is called **Nessler's Reagent.**
(j) **$Co[Hg(SCN)_4]$**, Deep blue crystalline precipitate obtained in qualitative detection of Hg^{2+}.
(k) **$Fe_4[Fe(CN)_6]_3$**, **Prussian blue**, deep blue colored complex obtained in detection of Fe^{2+}.
(l) **$K_3[Co(NO_2)_6]$**, **Potassium cobaltinitrite** or **Fischer salt** yellow precipitate obtained in detection of Co^{2+}.
(m) **$[Ni(dmg)_2]$**, Rosy red precipitate obtained in detection of Ni^{2+} ions.
(n) **$K_2[PtCl_6]$**, Yellow precipitate obtained in detection of potassium ions.
(o) **$Na_2[Fe(CN)_5NO^+]$**, **Sodium nitroprusside** used for detection of sulphide ions/sulphur.
(p) **$[Fe(H_2O)_5(NO^+)]SO_4$**, Brown ring complex, obtained in detection of Fe^{2+} ions.
(q) **$[Cu(CN)_4]^{3-}$**, Colourless stable soluble complex obtained in detection of Cu^{2+} on adding excess of KCN solution.
(r) **$(NH_4)_2[PtCl_6]$**, Only few compounds of ammonium ions are precipitate this is one of these, a yellow precipitate.

B-2. Name the following compounds.

(a) $[CoBr(en)_2(ONO)]^+$
(b) $[Co(NH_3)_6][Co(ONO)_6]$
(c) $[Co(NH_3)_5(CO_3)]Cl$
(d) $[Pt(NH_3)_4Cl_2][PtCl_4]$
(e) $[Co(en)_3]_2(SO_4)_3$
(f) $[(NH_3)_5Co\text{-}NH_2\text{-}Co(NH_3)_4(H_2O)]Cl_5$
(g) $[Cr(CO)_5(PPh_3)]$
(h) $[(CO)_5Mn\text{-}Mn(CO)_5]$
(i) $Cr(\eta^6\text{–}C_6H_6)_2$
(j) $[Co(NH_3)_4(OH_2)_2][BF_4]_3$
(k) $Ba[Zr(OH)_2(ONO)_2(ox)]$
(l) $[Co(NH_3)_6][Co(C_2O_4)_3]$

B-3. Write down the formulae of the following compounds

(a)	Tetraamminezinc(II) Nitrate,	The compound formed when zinc nitrate is treated with an excess of ammonia
(b)	Tetracarbonylnickel(0),	The first metal carbonyl(prepared in 1888) and an important compound in the industrial refining of nickel metal
(c)	Potassium amminetrichloridoplatinate(II)	A compound that contains a square planar anion
(d)	Dicyanidoaurate(I) ion	An ion important in the extraction of gold from its ores
(e)	Sodium hexafluoridoaluminate(III)	Called cryolite, used in the electrolytic refining of aluminium
(f)	Diamminesilver(I) ion	Ion formed when AgCl is dissolved in excess of ammonia

B-4. Write down the formulae of the following compounds

(a) diamminetriaquahydroxidochromium (III) nitrate
(b) tetrakis(pyridine)platinum(II) tetraphenylborate(III)
(c) dibromidotetracarbonyliron (II)
(d) ammonium diamminetetrakis(isothiocyanato)chromate(III).
(e) pentaamminedinitrogenruthenium(II) chloride
(f) barium dihydroxidodinitrito-O-oxalatozirconate(IV)
(g) tetrapyridineplatinum(II) tetrachloridonickelate(II)

Section (C) : Werner's Theory

(Initial bonding theories and EAN rule)

C-1. Werner conducted many experiments to establish the formula of complexes, one of these were conductivity measurements. On the basis of the experiments performed he obtained the following values of conductivity for different type of complexes.

Type of complex	**Electrical Conductivity**	
Nonelectrolyte	0 – 10	(due to impurities)
1:1 Electrolyte	90 – 130	
1:2 or 2:1 Electrolyte	230 – 290	
1:3 or 3:1 Electrolyte	390 – 450	
1:4 Electrolyte	500 – 550	

On the basis of above table Match the following two columns.

	COLUMN A		**COLUMN B**
	Formula of compound	**Conductivity**	**Correct Werner's Representation**
(a)	$PtCl_4.2NH_3$	6.99	(i) $[Cr(NH_3)_5Cl]Cl_2$
(b)	$PtCl_4.NH_3.KCl$	106.8	(ii) $[Co(NH_3)_5Br]Br_2$
(c)	$CrCl_3.5NH_3$	260.2	(iii) $[Cr(NH_3)_6]Cl_3$
(d)	$PtCl_4.2KCl$	256.8	(iv) $[Pt(NH_3)_2Cl_4]$
(e)	$CrCl_3.6NH_3$	441.7	(v) $[Pt(NH_3)_6]Cl_4$
(f)	$PtCl_4.6NH_3$	522.9	(vi) $[Pt(NH_3)_3Cl_3]Cl$
(g)	$CoBr_3.5NH_3$	257.6	(vii) $K_2[PtCl_6]$
(h)	$PtCl_4.3NH_3$	96.8	(viii) $K[Pt(NH_3)Cl_5]$

C-2. 1 g of complex $[Cr(H_2O)_5Cl]Cl_2.H_2O$ was passed through a cation exchanger to produce HCl. The acid liberated was diluted to 1 litre. What will be the molarity of acid solution [Molecular weight of complex = 266.5] ?

C-3. Calculate the EAN of central atom in the following complexes

(a) $[Cr(CO)_6]$ (b) $[Fe(CN)_6]^{4-}$ (c) $[Fe(CO)_5]$ (d) $[Co(NH_3)_6]^{3+}$

(e) $[Ni(CO)_4]$ (f) $[Cu(CN)_4]^{3-}$ (g) $[Pd(NH_3)_6]^{4+}$ (h) $[PtCl_6]^{2-}$

C-4. Arrange the following compounds in order of increasing molar conductivity.

(i) $K[Co(NH_3)_2(NO_2)_4]$ (ii) $[Cr(NH_3)_3(NO_2)_3]$ (iii) $[Cr(NH_3)_5(NO_2)]_3[Co(NO_2)_6]_2$ (iv) $[Cr(NH_3)_6]Cl_3$

Section (D) : Valence Bond Theory

D-1. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A and B. The form A reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas B gives a yellow precipitate soluble in concentrated ammonia.

(i) Write the formulae of A and B.

(ii) Calculate the EAN for both.

(iii) Will they conduct electricity or not.

(iv) Write the formula of the complexes formed when the precipitates dissolve in aqueous ammonia & the concentrated ammonia respectively.

D-2. Complete the following table (using concepts of VBT).

	Complex	Geometry	Hybridisation	Number of unpaired electrons(n)	Mag. moment
	CN =2				
(a)	$[Ag(NH_3)_2]^+$	----------	----------	0	----------
(b)	$[Cu(CN)_2]^-$	Linear	----------	----------	----------
(c)	$[AuCl_2]^-$	----------	----------	----------	0
	CN = 4				
(d)	$[PtCl_2(NH_3)_2]$	----------	----------	0	----------
(e)	$[Zn(CN)_4]^{2-}$	----------	----------	0	----------
(f)	$[Cu(CN)_4]^{3-}$	----------	----------	0	----------
(g)	$[MnBr_4]^{2-}$	----------	----------	5	----------
(h)	$[Cu(NH_3)_4]^{2+}$	Square Planar	----------	----------	----------
(i)	$[CoI_4]^{2-}$	----------	----------	3	----------
	CN = 6				
(j)	$[Mn(CN)_6]^{3-}$	----------	----------	2	----------
(k)	$[Cr(NH_3)_6]^{3+}$	----------	----------	3	----------
(l)	$[Fe(CN)_6]^{3-}$	----------	----------	1	----------
(m)	$[Ir(NH_3)_6]^{3+}$	----------	----------	0	----------
(n)	$[V(CO)_6]$	----------	----------	1	----------
(o)	$[Fe(H_2O)_6]^{2+}$	----------	----------	4	----------
(p)	$[MnCl_6]^{3-}$	----------	----------	4	----------

Section (E) : Crystal Field Theory (CN=6)

E-1. $[Co(NH_3)_6]^{3+}$ & $[CoF_6]^{3-}$ both are complexes of Co(III), but $[Co(NH_3)_6]^{3+}$ is diamagnetic while $[CoF_6]^{3-}$ is paramagnetic with μ = 4.90 B.M. Explain.

E-2. Arrange the following in increasing order as directed.
(a) (i) $[CoCl_3(NH_3)_3]$, (ii) $[CoCl(NH_3)_5]Cl_2$, (iii) $[Co(NH_3)_6]Cl_3$, (iv) $[CoCl_2(NH_3)_4]Cl$ – Molar conductance
(b) C, N, O, F (halogen) - tendency of σ donation.
(c) Br^-, S^{2-}, NO_2^-, CO, H_2O, CN^-, NH_3, NO_3^- - strength of ligands.

E-3. For each of the following complexes, draw a crystal field energy-level diagram, assign the electrons to orbitals, and predict the number of unpaired electrons:
(a) $[CrF_6]^{3-}$ (b) $[V(H_2O)_6]^{3+}$ (c) $[Fe(CN)_6]^{3-}$
(d) $[Cu(en)_3]^{2+}$ (e) $[FeF_6]^{3-}$

Section (F) : Crystal Field Theory (CN = 4)

F-1. Predict the hybridisation and geometry of the following complexes.
(a) $[NiBr_4]^{2-}$ (d) $[AuCl_4]^-$ (f) $[Pt(NH_3)_4]^{2+}$

F-2. Predict the hybridisation and geometry of the following complexes.
(a) $[Fe(CN)_6]^{3-}$ (b) $[MnBr_4]^{2-}$ (c) $[Fe(H_2O)_6]^{2+}$ (d) $[Co(SCN)_4]^{2-}$

Section (G) : Applications of crystal field theory (Colour of complex, Magnetic moment of complex, Stability of complex)

G-1. Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents(strong field ligands) it is readily oxidised. why ?

G-2. Find number of ligands which is / are stronger ligand as compared to NH_3

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

G-3. The value of Δ_0 for $[Ti(H_2O)_6]^{3+}$ is found to be 240 kJ mol^{-1} then predict the colour of the complex using the following table. ($h = 6 \times 10^{-34}$ J-sec, $N_A = 6 \times 10^{23}$, $c = 3 \times 10^8$ m/sec)

Absorbed light	λ (nm) (absorbed)	Colour exhibited
Blue	435 – 480	Yellow
green-blue	480 – 490	orange
blue – green	490 – 500	red
green	500 – 560	purple
yellow – green	560 – 580	violet
Yellow	580 – 595	blue
Red	605 – 700	blue green

G-4.(a) $[Ti(H_2O)_6]^{3+}$ absorbs light of wavelength 5000 Å. Name one ligand which would form a titanium(III) complex absorbing light of lower wavelength than 5000 Å and one ligand which would form a complex absorbing light of wavelength higher than 5000 Å.
(b) Calculate the magnetic moments (spin only) of the following complexes
(i) $[PtCl_6]^{2-}$ (ii) $[Cr(CO)_6]$ (iii) $[Ir(NH_3)_6]^{3+}$ (iv) $[Pd(en)_2]^{2+}$

G-5. If crystal field stablization energy of $[ML_6]^{+n}$ is $-0.8\ \Delta_O$.

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

Section (H) : Isomerism in Coordination compounds (Structural Isomerism, Stereoisomerism, Geometrical Isomerism, Optical Isomerism)

H-1. What type of isomers are the following :

(i) $[Mn(CO)_5SCN]$ and $[Mn(CO)_5NCS]$

(ii) $[Co(en)_3][Cr(CN)_6]$ and $[Cr(en)_3][Co(CN)_6]$

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

(iv) $[Co(H_2O)_2Cl_2(py)_2]Cl$ and $[Co(H_2O)Cl_3(py)_2]H_2O$

H-2. (a) Draw all possible constitutional isomers of the compound $Ru(NH_3)_5(NO_2)Cl$. Label the isomers as linkage isomers or ionization isomers.

(b) There are six possible isomers for a square planar palladium(II) complex that contains two Cl^- and two SCN^- ligands. Sketch the structures of all six, and label them according to the classification.

H-3. How many geometrical isomers are possible for each of the following complexes?

(a) $[Pt(NH_3)_2(SCN)_2]$ (b) $[CoCl_2Br_2]^{2-}$ (tetrahedral)

(c) $[Co(NH_3)_3(NO_2)_3]$ (d) $[Pt(en)Cl_2]$

(e) $[Cr\ Br_2(en)_2]^+$ (f) $[Rh(en)_3]^{3+}$

H-4. Which of the following complexes can exist as enantiomers? Draw their structures

(a) cis-$[Co(NH_3)_4Br_2]^+$ (b) cis-$[Cr(H_2O)_2(en)_2]^{3+}$ (c) $[Cr(gly)_3]$

(d) $[Cr(en)_3]^{3+}$ (e) cis-$[Co(NH_3)Cl(en)_2]^{2+}$ (f) trans-$[Co(NH_3)_2(en)_2]^{2+}$

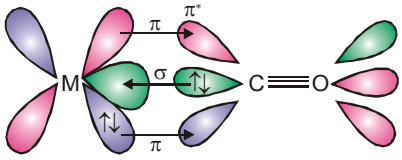
Section (I) : Organometallic Compounds

I-1. Draw the structures of the following metal carbonyls

(a) $[V(CO)_6]$ (b) $[Cr(CO)_6]$ (c) $[Mn_2(CO)_{10}]$

(d) $[Fe(CO)_5]$ (e) $[Ni(CO)_4]$

I-2.



The figure represents the synergic bonding interaction in metal carbonyl complex. On the basis of this explain the following :

(i) Strength of Metal-ligand bond

(ii) Bond order of CO in carbonyl complex as compared to bond order in carbon monoxide.

PART-II : OBJECTIVE QUESTIONS

Section (A) : General introduction of complex salts and definitions to be used

A-1. Ethylene diamine is an example of a ..... ligand :

(A) monodentate (B) bidentate (C) tridentate (D) hexadentate

A-2. The donor sites of $(EDTA)^{4-}$ are ?
(A) O atoms only (B) N atoms only
(C) Two N atoms and four O atoms (D) Three N atoms and three O atoms

A-3. Some salts although containing two different metallic elements give test for one of them in solution. Such salts are :
(A) complex salt (B) double salt (C) normal salt (D) none

A-4. Ligands are :
(A) Lewis acids (B) Lewis bases (C) neutral (D) none

A-5. The oxidation state of Mo in its oxido-complex species $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$ is
(A) +2 (B) +3 (C) +4 (D) +5

A-6. Co-ordination number of platinum in $[Pt(NH_3)_4Cl_2]^{2+}$ ion is:
(A) 4 (B) 2 (C) 8 (D) 6

A-7. Which of the following is copper(I) compound ?
(A) $[Cu(H_2O)_4]^{2+}$ (B) $[Cu(CN)_4]^{3-}$ (C) $[Cu(NH_3)_4]^{2+}$ (D) All of these

A-8. In the complex $[CoCl_2(en)_2]Br$, the co-ordination number and oxidation state of cobalt are :
(A) 6 and +3 (B) 3 and +3 (C) 4 and +2 (D) 6 and +1

A-9. What is the charge on the complex $[Cr(C_2O_4)_2(H_2O)_2]$ formed by Cr(III) ?
(A) +3 (B) +1 (C) +2 (D) –1

Section (B) : Nomenclature of coordination compounds

B-1. 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) ion
(B) Diammineethylenediaminedithiocyanato-S-platinate (IV) ion
(C) Diammineethylenediaminedithiocyanato-S-platinum (IV) ion
(D) Diamminebis (ethylenediamine) dithiocyanate-S- platinum (IV) ion

B-2. Which of the following names is impossible ?
(A) Potassium tetrafluoridooxidochromate (VI) (B) Barium tetrafluoridobromate (III)
(C) Dichlorobis(urea)copper (II) (D) All are impossible.

B-3. The formula of the complex tris(ethylenediamine)cobalt(III) sulphate is :
(A) $[Co(en)_2SO_4]$ (B) $[Co(en)_3SO_4]$ (C) $[Co(en)_3]_2SO_4$ (D) $[Co(en)_3]_2(SO_4)_3$

B-4. The correct IUPAC name for the compound $[Co(NH_3)_4Cl(ONO)]Cl$ is :
(A) Tetraamminechloridonitrito–N–cobalt(III) chloride
(B) Chloridonitrito–O–tetraamminecobalt(II) chloride
(C) Dichloridonitrito–O–tetraamminecobalt(III)
(D) Tetraamminechloridonitrito–O–cobalt(III) chloride

B-5. The hypothetical complex triamminediaquachloridocobalt(III) chloride can be represented as :
(A) $[CoCl(NH_3)_3(H_2O)_2]$ (B) $[Co(NH_3)_3(H_2O)Cl_3]$
(C) $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ (D) $[Co(NH_3)_3(H_2O)_3]Cl_3]$

Section (C) : Werner's Theory (Initial bonding theories and EAN rule)

C-1. EAN of a metal carbonyl $M(CO)_x$ is 36. If atomic number of metal M is 26, what is the value of x ?
(A) 4 (B) 8 (C) 5 (D) 6

C-2. The EAN of platinum in potassium hexachloridoplatinate(IV) is (Atomic number of Pt = 78) :
(A) 90 (B) 86 (C) 76 (D) 88

C-3. A compound is made by mixing cobalt (III) nitrite and potassium nitrite solutions in the ratio of 1 : 3. The aqueous solution of the compound showed 4 particles per molecule whereas molar conductivity reveals the presence of six electrical charges. The formula of the compound is :
(A) $Co(NO_2)_3 . 2KNO_2$ (B) $Co(NO_2)_3 . 3KNO_2$ (C) $K_3[Co(NO_2)_6]$ (D) $K[Co(NO_2)_4]$

C-4. Which of the following will exhibit maximum ionic conductivity?
(A) $K_4[Fe(CN_6]$ (B) $[Co(NH_3)_6]Cl_3$ (C) $[Cu(NH_3)_4]Cl_2$ (D) $[Ni(CO)_4]$

C-5. Which of the following shows maximum molar conductance ?
(A) $[Co(NH_3)_6]Cl_3$ (B) $[Co(NH_3)_3Cl_3]$ (C) $[Co(NH_3)_4Cl_2]Cl$ (D) $[Co(NH_3)_5Cl]Cl_2$

C-6. The complex $[Cr(H_2O)_4Br_2]Cl$ gives the test for :
(A) Br^- (B) Cl^- (C) Cr^{3+} (D) Br^- and Cl^- both

C-7. Which of the following complexes will be dehydraded to relatively minimum extent by conc. H_2SO_4 under identical condition.
(A) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (B) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$
(C) $[Cr(H_2O)_6]Cl_3$ (D) all of these.

C-8. On adding $AgNO_3$ solution to a solution of $[Pt(NH_3)_3Cl_3]Cl$, the percentage of total chloride ion precipitated is:
(A) 100 (B) 75 (C) 50 (D) 25

C-9. A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is:
(A) $[Pt(NH_3)_4]Cl_4$ (B) $[Pt(NH_3)_2Cl_4]$ (C) $[Pt(NH_3)_5Cl]Cl_3$ (D) $[Pt(NH_3)_4Cl_2]Cl_2$

Section (D) : Valence Bond Theory

D-1. The complex ion which has no 'd' electrons in the central metal atom is :
(A) $[MnO_4]^-$ (B) $[Co(NH_3)_6]^{3+}$ (C) $[Fe(CN)_6]^{3-}$ (D) $[Cr(H_2O)_6]^{3+}$

D-2. For the correct assignment of electronic configuration of a complex, the valence bond theory often requires the measurement of
(A) molar conductance (B) optical activity (C) magnetic moment (D) dipole moment

Section (E) : Crystal Field Theory (CN = 6)

E-1. Chromium hexacarbonyl is an octahedral compound involving :
(A) sp^3d^2 (B) dsp^2 (C) d^2sp^3 (D) dsp^3

E-2. The hybridisation and unpaired electrons in $[Fe(H_2O)_6]^{2+}$ ion are :
(A) sp^3d^2 ; 4 (B) d^2sp^3 ; 3 (C) d^2sp^3 ; 4 (D) $sp^3 d^2$; 2

E-3. The number of unpaired electrons in d^6, low spin, octahedral complex is :
(A) 4 (B) 2 (C) 1 (D) 0

E-4. The number of unpaired electrons present in complex ion $[FeF_6]^{3-}$ is :
(A) 5 (B) 4 (C) 6 (D) 0

E-5. Select the correct statement.
(A) Complex ion $[MoCl_6]^{3-}$ is paramagnetic. (B) Complex ion $[Co(en)_3]^{3+}$ is diamagnetic.
(C) Both (A) and (B) are correct. (D) None of correct.

Section (F) : Crystal Field Theory (CN = 4)

F-1._ $Ni(CO)_4$ and $[Ni(NH_3)_4]^{2+}$ do not differ in
(A) magnetic moment (B) oxidation number of Ni
(C) geometry (D) EAN

F-2._ The tetrahedral $[CoI_4]^{2-}$ and square planar $[PdBr_4]^{2-}$ complex ions are respectively
(A) low spin, high spin (B) high spin, low spin
(C) both low spin (D) both high spin

F-3. Which of the following is a high spin complex ?
(A) $[Co(NH_3)_6]^{3+}$ (B) $[Fe(CN)_6]^{4-}$ (C) $[Ni(CN)_4]^{2-}$ (D) $[FeF_6]^{3-}$

F-4. The magnitude of crystal field stabilisation energy (CFSE of Δ_1) in tetrahedral complexes is considerably less than that in the octahedral field. Because
(A) There are only four ligands instead of six so the ligand fild is only 2/3 in tetradedral complex
(B) The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field stabilization energy (Δ) by further 2/3
(C) Both points (A) and (B) are correct
(D) Both points (A) and (B) are wrong

F-5. The crystal field splitting energy for octahedral complex (Δ_o) and that for tetrahedral complex (Δ_t) are related as:
(A) $\Delta_t = \frac{4}{9}\Delta_0$ (B) $\Delta_t = 0.5\,\Delta_o$ (C) $\Delta_t = 0.33\,\Delta_o$ (D) $\Delta_t = \frac{9}{4}\Delta_0$

F-6. Which of the following complexes has a geometry different from others ?
(A) $[Ni\,Cl_4]^{2-}$ (B) $Ni\,(CO)_4$ (C) $[Ni(CN)_4]^{2-}$ (D) $[Zn(NH_3)_4]^{2+}$

F-7. Which of the following molecules is not tetrahedral ?
(A) $[Pt(en)_2]^{2+}$ (B) $[Ni(CO)_4]$ (C) $[Zn(NH_3)_4]^{2+}$ (D) $[NiCl_4]^{2-}$

F-8. The complex $[Pt(NH_3)_4]^{2+}$ has ..... structure :
(A) square planar (B) tetrahedral (C) pyramidal (D) pentagonal

F-9. Match Column-I with Column-II and select the correct answer with respect to hybridisation using the codes given below :

	Column - I (Complex)		**Column - II (Hybridisation)**
(I)	$[Au F_4]^-$	(p)	dsp^2 hybridisation
(II)	$[Cu(CN)_4]^{3-}$	(q)	sp^3 hybridisation
(III)	$[Co(C_2O_4)_3]^{3-}$	(r)	sp^3d^2 hybridisation
(IV)	$[Fe(H_2O)_5NO]^{2+}$	(s)	d^2sp^3 hybridisation

Codes :

	(I)	(II)	(III)	(IV)		(I)	(II)	(III)	(IV)
(A)	q	p	r	s	(B)	p	q	s	r
(C)	p	q	r	s	(D)	q	p	s	r

F-10. Which has maximum paramagnetic nature ?
(A) $[Cu(H_2O)_4]^{2+}$ (B) $[Cu(NH_3)_4]^{2+}$ (C) $[Mn(H_2O)_6]^{2+}$ (D) $[Fe(CN)_6]^{4-}$

F-11. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$:
(A) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic.
(B) $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic.
(C) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $NiCl_4^{2-}$ is paramagnetic.
(D) $Ni(CO)_4$ is diamagnetic and $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic.

F-12. Identify tetrahedral species which has maximum magnetic moment value :
(A) $[CuCl_4]^{2-}$ (B) $[CoCl_4]^{2-}$ (C) $[FeCl_4]^{2-}$ (D) $[AlCl_4]^-$

Section (G) : Applications of crystal field theory (Colour of complex, Magnetic moment of complex, Stability of complex)

G-1. The compound which does not show paramagnetism ?
(A) $[Cu(NH_3)_4Cl_2]$ (B) $[Ag(NH_3)_2]Cl$ (C) NO (D) NO_2

G-2. Among the following ions, which one has the highest paramagnetism ?
(A) $[Cr(H_2O)_6]^{3+}$ (B) $[Fe(H_2O)_6]^{2+}$ (C) $[Cu(H_2O)_6]^{2+}$ (D) $[Zn(H_2O)_6]^{2+}$

G-3. Which of the following complex is coloured and diamagnetic -
(A) MnO_4^{2-} (B) $[Ni(H_2O)_6]^{2+}$ (C) $[CrCl_6]^{3-}$ (D) CrO_4^{2-}

G-4. One unknown complex has the spin only magnetic moment is of 1.73 BM. As per the C. F. T., complexe is.
(A) d^7, Oh-field, with Srong Feild Legand (B) d^9, sq.planar-field, with Srong Feild Legand
(C) d^9, Td,field with Weak Feild Legand (D) All of these

G-5. $[Fe(H_2O)_6]^{+2}$ has Crystal Field Splitting Energy value 10,400 cm^{-1} and pairing energy value 17,600 cm^{-1} then it is :
(A) Low spin complex (B) Paramagnetic in nature
(C) Diamagnetic in nature (D) None of these

G-6. Among the following, the compound that is both paramagnetic and coloured is
(A) $K_2Cr_2O_7$ (B) $(NH_4)_2[TiCl_6]$ (C) $VOSO_4$ (D) $K_3[Cu(CN)_4]$

G-7._ If $\lambda_{absorbed}$ for d-d transition is in order $[Ti(X)_6]^{3+} > [Ti(Y)_6]^{3+} > [Ti(Z)_6]^{3+}$.
Select correct order of strength of ligands (X, Y, Z are monodentate ligand)-
(A) Z > Y > X (B) X > Y > Z
(C) Z > X > Y (D) Not predictable

G-8. Which of the following factors tends to increase the stability of metal ion complexes ?
(A) Higher ionic radius of the metal ion (B) Higher charge/size ratio of the metal ion
(C) Lower ionisation potential of the metal ion (D) Lower basicity of the ligand

Section (H) : Isomerism in Coordination compounds
(Structural Isomerism, Stereoisomerism, Geometrical Isomerism, Optical Isomerism)

H-1. The complexes $[Pt(NH_3)_4]$ $[PtCl_6]$ and $[Pt(NH_3)_4Cl_2]$ $[PtCl_4]$ are :
(A) linkage isomers (B) optical isomers
(C) co-ordination isomers (D) ionisation isomers

H-2. $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$ are related to each other as :
(A) geometrical isomers (B) linkage isomers
(C) coordination isomers (D) ionisation isomers

H-3. The number of geometrical isomer of $[Co(NH_3)_3(NO_3)_3]$ are :
(A) 0 (B) 2 (C) 3 (D) 4

H-4. Geometrical isomerism is found in coordination compounds having coordination number :
(A) 2 (B) 3 (C) 4 (tetrahedral) (D) 6

H-5. Cis-trans isomerism is found in square planar complexes of molecular formula ('a' and 'b' are monodentate ligands) :
(A) Ma_4 (B) Ma_3b (C) Ma_2b_2 (D) Mab_3

H-6. Geometrical isomerism can be shown by :
(A) $[Ag(NH_3)(CN)]$ (B) $Na_2[Cd(NO_2)_4]$ (C) $[PtCl_4I_2]$ (D) $[Pt(NH_3)_3Cl][Au(CN)_4]$

H-7._ Find the name of the hydrate isomer of $CrCl_3.6H_2O$, which is having lowest electrical conductivity excluding zero value of conductivity.
(A) Hexaaquachromium(III) chloride
(B) Tetraaquadichloridochromium(III) chloride dihydrate
(C) Pentaaquachloridochromium(III) chloride monohydrate
(D) Triaquatrichloridochromium(III) chloride trihydrate

H-8._ Which of the following complex shows optical isomerism -
(A) $[Cd(CN)_4]^{2-}$ (B) $[Cr(H_2O)_3Cl_3].3H_2O$
(C) $[Zn(gly)_2]$ (D) $[Ni(dmg)_2]$

H-9._ Find complex which have maximum number of stereoisomers -
(A) $[Ma_3b_3]$ (B) $[Ma_3b_2c]$ (C) $[Ma_2b_2c_2]$ (D) $[M(AA)a_2b_2]$

H-10._ Which of the following can exhibit geometrical isomerism ?

(A) $[MnBr_4]^{2-}$ (B) $[Pt(NH_3)_3Cl]^+$

(C) $[PtCl_2(P(C_2H_5)_3)_2]$ (D) $[Fe(H_2O)_5NOS]^{2+}$

Section (I) : Organometallic Compounds

I-1. Which one is not an organometallic compound ?

(A) RMgX (B) $(C_2H_5)_4Pb$ (C) $(CH_3)_4Sn$ (D) C_2H_5ONa

I-2. Formula of ferrocene is:

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

I-3._ In the isoelectronic series of metal carbonyl, the C–O bond strength is expected to increase in the order.

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

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

I-4._ Which of the following has higher multiple bond character in M–C bond -

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

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

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

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

I-5._ The V–C distance in $V(CO)_6$ and $[V(CO)_6]^-$ are respectively (in pm)-

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

PART-III : MATCH THE COLUMN

1. Match the complexes listed in column-I with characteristic(s) / type of hybridisation listed in column-II.

Column – I	**Column – II**
(A) $[Co\ (en)_3]^{3+}$	(p) sp^3d^2 hybridisaion
(B) $[Co\ (ox)_3]^{3-}$	(q) Diamagnetic
(C) $[Co\ (H_2O)_6]^{2+}$	(r) d^2sp^3 hybridisation
(D) $[Co\ (NO_2)_6]^{3-}$	(s) Paramagnetic
	(t) Chelate ligand

2. There are some coordination compounds given in column-I which may exist in different isomeric forms as given in column-II. Select the correct option(s) for the coordination compounds and their respective isomeric forms.

Column-I	**Column-II**
(A) $[Co(en)_2NH_3Cl]SO_4$	(p) Enantiomer
(B) $[Co(NH_3)_4(NO_2)_2](NO_3)_2$	(q) Geometrical isomer
(C) $[Co(en)(pn)(NO_2)_2]Cl$	(r) Ionization isomer
(D) $[Co(gly)_3]$	(s) Linkage isomer

Exercise # 2

PART - I : OBJECTIVE QUESTIONS

Marked Questions may have for Revision Questions.

1._ Which of the following are bidentate monoanion ligands ?
(a) Dimethylglyoximato
(b) Oxalato ion
(c) Bis(ethane-1,2-diamine)
Select the correct answer using the codes given below :
(A) a only (B) a and c only (C) c only (D) b and c only

2._ Diethylenetriamine is:
(A) chelating agent (B) tridentate neutral molecule
(C) tridentatemonoanion (D) (A) and (B) both

3. A complex anion is formed by Osmium (in some oxidation state) with ligands (in proper number so that coordination number of osmium becomes six). Which of the following can be its correct IUPAC name?
(A) pentachloridonitridoosmium(VI) (B) pentachloridonitridoosmate(VI)
(C) azidopentachloridoosmate(VI) (D) None of these

4. The EAN of metal atoms in $[Fe(CO)_2(NO^+)_2]$ and $Co_2(CO)_8$ respectively are :
(A) 34, 35 (B) 34, 36 (C) 36, 36 (D) 36, 35

5. Which of the following is inner orbital complex as well as diamagnetic in nature ?
(A) $[Ir(H_2O)_6]^{3+}$ (B) $[Ni(NH_3)_6]^{2+}$ (C) $[Cr(NH_3)_6]^{3+}$ (D) $[Co(NH_3)_6]^{2+}$

6. Which of the following statement is correct ?
(A) The oxidation state of iron in sodium nitro prusside $Na_2[Fe(CN)_5(NO)]$ is +3
(B) $[Ag(NH_3)_2]^+$ is linear in shape
(C) In $[Fe(H_2O)_6]^{3+}$, Fe is d^2sp^3 hybridized
(D) In $Ni(CO)_4$, the oxidation state of Ni is 1

7. The complex $K_4[Zn(CN)_4(O_2)_2]$ is oxidised into $K_2[Zn(CN)_4(O_2)_2]$, then which of the following is correct ?
(A) Zn (II) is oxidised into Zn (IV) (B) Paramagnetic moment decreases
(C) O – O bond length increases (D) Paramagnetic moment increases

8. All the following complexes show decrease in their weights when placed in a magnetic balance then the group of complexes having tetrahedral geometry is :
I $Ni(CO)_4$ II $K[AgF_4]$ III $Na_2[Zn(CN)_4]$
IV $K_2[PtCl_4]$ V $[RhCl(PPh_3)_3]$
(A) II , III , V (B) I , II , III (C) I , III , IV (D) none of these

9. The complex $[Fe(H_2O)_5NO]^{2+}$ is formed in the brown ring test for nitrates when freshly prepared $FeSO_4$ solution is added to aqueous solution of NO_3^- ions followed by addition of conc. H_2SO_4. Select correct statement about this complex.
(A) Hybridisation of iron is sp^3d^2.
(B) Iron has +1 oxidation state.
(C) It has magnetic moment of 3.87 B. M. confirming three unpaired electrons in Fe.
(D) All the above are correct statements.

10. All the metal ions contains $t_{2g}^6 e_g^0$ configurations. Which of the following complex will be paramagnetic?
(A) $[FeCl(CN)_4(O_2)]^{4-}$ (B) $K_4[Fe(CN)_6]$ (C) $[Co(NH_3)_6]Cl_3$ (D) $[Fe(CN)_5(O_2)]^{-5}$

11. Which of the following statements is not correct?
(A) $TiCl_4$ is a colourless compound. (B) $[Cr(NH_3)_6)]Cl_3$ is a coloured compound.
(C) $K_3[VF_6]$ is a colourless compound. (D) $[Cu(NCCH_3)_4][BF_4]$ is a colourless compound.

12. Among TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$ the colourless species are:
(A) CoF_6^{3-} and $NiCl_4^{2-}$ (B) TiF_6^{2-} and CoF_6^{3-} (C) $NiCl_4^{2-}$ and Cu_2Cl_2 (D) TiF_6^{2-} and Cu_2Cl_2

13. The number of geometrical isomers for octahedral $[Co(NH_3)_2Cl_4]^-$, square planar $AuCl_2Br_2^-$ are :
(A) 4, 2 (B) 2, 2 (C) 3, 2 (D) 2, 3

14. Which of the following statements is not true about the complex ion $[Pt(en)_2Cl_2]^{2+}$?
(A) It has two geometrical isomers – cis and trans.
(B) Both the cis and trans isomers display optical activity.
(C) Only the cis isomer displays optical activity.
(D) Only the cis isomer has non–superimposable mirror image.

15. Both geometrical and optical isomerism are shown by :
(A) $[Co(en)_2Cl_2]^+$ (B) $[Co(NH_3)_5Cl]^{2+}$ (C) $[Co(NH_3)_4Cl_2]^+$ (D) $[Cr(OX)_3]^{3-}$

16. Among the following, metal carbonyls, the C—O bond is strongest :
(A) $[Mn(CO)_6]^+$ (B) $[Cr(CO)_6]$ (C) $[V(CO)_6]^-$ (D) $[Ti(CO)_6]^{2-}$

PART - II : NUMERICAL TYPE QUESTIONS

1. Sum of denticity of following ligands are
Glycinate ion, Oxalate ion, o-phenathroline, 2,2-bipyridyl, diethylenetriamine, ethylenediamine

2. How many total sodium ions are present in one formula unit of sodium ethane-1,2-diaminetetraacetatochromate (II) and sodium hexanitrito cobaltate (III) ?

3. A blue colour complex is obtained in the analysis of Fe^{+3} having formula $Fe_4[Fe(CN)_6]_3$
Let a = oxidation number of Iron in the coordination sphere
b = no. of secondary valencies of central iron ion.
c = Effective atomic number of Iron in the coordination sphere.
Then find the value of (c + a – 2b)

4. Coordination number of Cr in $CrCl_3.5H_2O$ as six. The possible volumes of 1 M Ag NO_3 needed to precipitate the chlorine inoutersphere in 200 ml of 0.1 M solution of the complex is/are.
Write your answer as $V_1 + V_2 + V_3 + ...$

5. Ni^{+2} form a complex ion in water having the formula $[Ni(H_2O)_6]^{+2}$. How many of the following statements are true for the complex ion ?
(i) The complex is octahedral in shape. (ii) The complex is diamagnetic in nature.
(iii) Ni^{+2} has incompletely filled 3d subshell. (iv) Secondary valency of Ni^{+2} is 6.
(v) All the bonds (metal-ligand) are perpendicular to each other.
(vi) All the 3d orbitals of Ni^{+2} are degenerate
(vii) Total spin of the complex is 1. (viii) The hybridisation of Ni^{+2} is d^2sp^3
(ix) The complex is more stable than $[Ni(en)_3]^{+2}$ (x) Effective atomic number of Ni^{+2} is 36.

6. How many of the following is correctly matched complex ?

Complex	Oxidation no. on central metal	Electronic configuration
(1) $K_3[Co(C_2O_4)_3]$	+3	$t_{2g}^6\ e_g^0$
(2) $(NH_4)_2[CoF_4]$	+2	$t_{2g}^5\ e_g^2$
(3) Cis - $[Cr(en)_2Cl_2]Cl$	+3	$t_{2g}^3\ e_g^0$
(4) $[Mn(H_2O)_6]SO_4$	+2	$t_{2g}^3\ e_g^2$

7. Total number of paramagnetic complexes which are inner orbital complexes :
$[Cr(NH_3)_6]Cl_3$, $[Co(NH_3)_6](NO_3)_2$, $[Ni(NH_3)_6]SO_4$, $K_2[PtCl_6]$,
$[V(H_2O)_6]SO_4$, $[Mn(NH_3)_6]SO_4$, $[Fe(H_2O)_5(NO)]SO_4$, $K_3[CuCl_4]$, $Na_4[Fe(CN)_5(NOS)]$

8. The number of coordination isomers possible for $[Fe(NH_3)_6]^{3+}[Cr(C_2O_4)_3]^{3-}$ is _____

9. Find the sum of number of geometrical isomers for following complexes.
(a) $[CoCl_2Br_2]^{2-}$ (b) $[Rh(en)_3]^{3+}$ (c) $[Cr(en)_2Br_2]^+$
(d) [Pt en Cl_2] (e) $[Co(NH_3)_3(NO_2)_3]$

10. How many isomeric forms are possible for the octahedral complex, $[Rh(en)_2(NO_2)(SCN)]^+$?

11. What is the sum of bond order of Fe–C bond and C–O bond in $Fe(CO)_5$?

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which of the following statement(s) are incorrect ?
(A) Those additional compounds which lose their identity in solution are called double salts.
(B) In $K_3[Fe(CN)_6]$ Fe^{2+} and CN^- ion can give quantitative identification test.
(C) $[KAl(SO_4)_2.12H_2O]$ is a coordination compound.
(D) All acids are lewis acids and σ donors.

2. The effective atomic number of $Co(CO)_4$ is 35 and hence is less stable. It attains stability by
(A) oxidation of Co (B) reduction of Co (C) dimerization (D) none

3. Select the correct statements ;
(A) Potassium ferrocyanide and potassium ferricyanide can be differentiated by measuring the solid state magnetic moment.
(B) The complex $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ can be differentiated by adding aqueous solution of barium chloride
(C) The complex $[Co(NH_3)_5Cl]Br$ and $[Co(NH_3)_5Br]Cl$ can be differentiated by adding aqueous solution of silver nitrate.
(D) the complex $[Co(NH_3)_6Cl_3]$ and $[Co(NH_3)_5Cl]Cl_2$ can be differentiated by measuring molar conductance

4. Consider the following statements :
S_1 : $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are paramagnetic having four, five and four unpaired electrons respectively.
S_2 : Low value of formation constant of a complex indicates its high thermodynamic stability.
S_3 : The crystal field splitting Δ_o, depends upon the field produced by the ligand and charge on the metal ion.
and arrange in the order of true/ false.
(A) T T T (B) T F T (C) F T F (D) T F F

5. Which of the following is/are correctly matched ?
(A) $[Ni(CO)_4]$ - dsp^2 and diamagnetic.
(B) $[Ni(en)_3](NO_2)_2$ - sp^3d^2 and two unpaired electrons.
(C) $[V(NH_3)_6]Cl_3$- sp^3d^2 and two unpaired electrons.
(D) $[Mn(NO^+)_3(CO)]$ - sp^3 and diamagnetic.

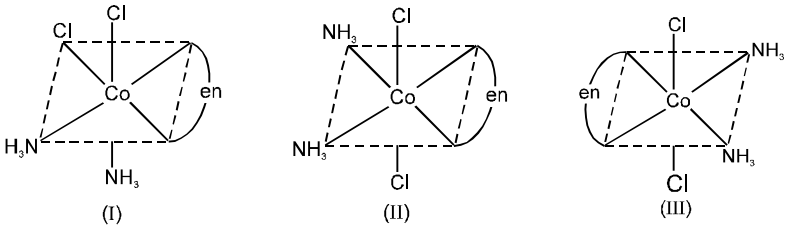
6. Which of the following statement(s) is/are correct with respect to the crystal field theory ?
(A) It considers only the metal ion d–orbitals and gives no consideration at all to other metal orbitals.
(B) It cannot account for the π bonding in complexes.
(C) The ligands are point charges which are either ions or neutral molecules
(D) The magnetic properties can be explained in terms of splitting of d- orbitals in different crystal field.

7. 'Spin only' magnetic moment of Ni in $[Ni(dmg)_2]$ is same as that found in :
(A) Ni in $[NiCl_2(PPh_3)_2]$ (B) Mn in $[MnO_4]^-$
(C) Co in $[CoBr_4]^{2-}$ (D) Pt in $[Pt(H_2O)_2Br_2]$

8. Which complex of the following pairs has the larger value of Δ_0 ?
(i) $[Co(CN)_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ (ii) $[Co(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$
(iii) $[Co(H_2O)_6]^{3+}$ and $[Co(H_2O)_3]^{3+}$ (iv) $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$
Select the correct one
(A) $[Co(CN)_6]^{3-} > [Co(H_2O)_6]^{3+}$ (B) $[Co(H_2O)_6]^{2+} < [Co(H_2O)_6]^{3+}$
(C) $[Co(H_2O)_6]^{3+} > [Rh(H_2O)_6]^{3+}$ (D) $[Co(NH_3)_6]^{3+} < [CoF_6]^{3-}$

9. Which of the following isomerisms is/are shown by the complex $[CoCl_2(OH_2)_2(NH_3)_2]Br$?
(A) Ionization (B) Linkage (C) Geometrical (D) optical

10. Three arrangements are shown for the complex $[Co(en)(NH_3)_2Cl_2]^+$. Pick up the wrong statement.



(A) I and II are geometrical isomers (B) II and III are optical isomers
(C) I and III are optical isomers (D) II and III are geometrical isomers

11. Consider the following complexies $[V(CO)_6]^-$, $[Cr(CO)_6]$ and $[Mn(CO)_6]^+$. Then incorrect statement (s) about metal carbonyls is /are.
(A) 'C –O' bond is strongest in the cation and weakest in the anion
(B) 'C –O' bond order is less in the cation than in anion.
(C) 'C –O' bond longer in the cation than in anion or neutral carbonyl.
(D) 'M–C' bond order is higher in the cation than in anionic or neutral carbonyl.

12. Following Sidwick's rule of EAN, $Co(CO)_x$ will be :
(A) $Co_2(CO)_4$ (B) $Co_2(CO)_3$ (C) $Co_2(CO)_8$ (D) $Co_2(CO)_{10}$

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

In coordination chemistry there are a variety of methods applied to find out the structure of complexes. One method involves treating the complex with known reagents and from the nature of reaction, the formula of the complex can be predicted. An isomer of the complex $Co(en)_2(H_2O)Cl_2Br$, on reaction with concentrated H_2SO_4 (dehydrating agent) it suffers loss in weight and on reaction with $AgNO_3$ solution it gives a white precipitate which is soluble in NH_3 (aq).

1. The **correct** formula of the complex is :
(A) $[CoClBr(en)_2]\,H_2O$ (B) $[CoCl(en)_2\,(H_2O)]\,BrCl$
(C) $[CoBr(en)_2(H_2O)]Cl_2$ (D) $[CoBrCl(en)_2]Cl\,.\,H_2O$

2. If all the ligands in the coordination sphere of the above complex be replaced by F^-, then the magnetic moment of the complex ion (due to spin only) wll be :
(A) 2.8 BM (B) 5.9 BM (C) 4.9 BM (D) 1.73 BM

3. Similarly if all the ligands in the coordination sphere be replaced by NO_2^-, then the magnetic moment of the complex ion (due to spin only) will be :
(A) 1.73 BM (B) 0.0 BM (C) 4.9 BM (D) 5.9 BM

4. If one mole of original complex is treated with excess $Pb(NO_3)_2$ solution, then the number of moles of white precipitate (of $PbCl_2$) formed will be :
(A) 0.5 (B) 1.0 (C) 0.0 (D) 3.0

5. The number of geometrical isomers of the formula of the above original complex are (including the complex):
(A) 2 (B) 3 (C) 4 (D) 1

Comprehension # 2

Co^{2+} (aq.) + SCN^- (aq.) $\longrightarrow$ Complex (X).

Ni^{2+} (aq.) + Dimethylglyoxime $\xrightarrow{NH_4OH}$ Complex (Y).

The coordination number of cobalt and nickel in complexes X and Y are four.

6. The IUPAC names of the complexes (X) and (Y) are respectively :
(A) tetrathiocyanato-S-cobalt(II) and bis(dimethylglyoximate) nickel(II).
(B) tetrathiocyanato-S-cobaltate (II) and bis(dimethylglyoximato)nickel (II).
(C) tetrathiocyanato-S-cobaltate (II) and bis(dimethylglyoximato)nickelate(II).
(D) tetrathiocyanato-S-cobaltate(III) and bis(dimethylglyoximato)nickel(II).

7. The geometry of complexes (X) and (Y) are respectively :
(A) tetrahedral and square planar. (B) both tetrahedral.
(C) square planar and tetrahedral (D) both square planar.

8. Select the correct statement for the complexes (X) and (Y).
(A) (X) is paramagnetic with two unpaired electrons.
(B) (Y) is diamagnetic and shows intermolecular H-bonding.
(C) (X) is paramagnetic with three unpaired electrons and (Y) is diamagnetic.
(D) (X) and (Y) both are diamagnetic.

Comprehension # 3

Q.9, Q.10 and Q.11 by appropriately matching the information given in the three columns of the following table.

Let us consider following columns		
Column 1	**Column 2**	**Column 3**
μ (in B.M.)	Hybridisation state	No. of geometrical isomers
(I) μ = 2.83 B.M.	(i) sp^3	(P) 2
(II) μ = 5.93 B.M	(ii) sp^3d^2	(Q) 3
(III) μ = 3.88 B.M.	(iii) d^2sp^3	(R) 4
(IV) μ = 0 B.M.	(iv) dsp^2	(S) 5

[**Note** : Atomic Number of Cr = 24, V = 23, Pt = 78]

9. About $[CrCl_3(NH_3)_3]$ which of following combination is correct ?
(A) (III), (iii), P (B) (II), (iv), Q (C) (IV), (i), R (D) (I), (ii), S

10. Correct combination for $[VCl_2(NO_2)_2(NH_3)_2]^-$.
(A) (II), (i), P (B) (I), (iii), S (C) (III), (ii), R (D) (IV), (iv), Q

11. Correct combination for $[PtCl_2(NH_3)_2]$ is :
(A) (II), (iii), Q (B) (I), (iv), S (C) (IV), (iv), P (D) (III), (ii), R

Exercise # 3

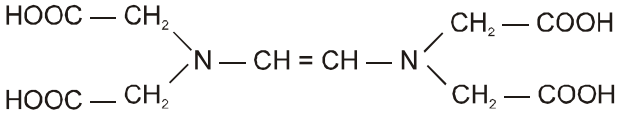
PART- I : JEE ADVANCE PROBLEMS (PREVIOUS YEARS)

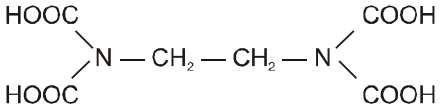
*** Marked Questions may have more than one correct option.**

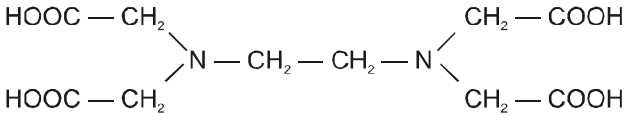
1.* The compound(s) that exhibit(s) geometrical isomerism is(are) : **[JEE 2009, 4/160]**
(A) $[Pt(en)Cl_2]$ (B) $[Pt(en)_2]Cl_2$ (C) $[Pt(en)_2Cl_2]Cl_2$ (D) $[Pt(NH_3)_2Cl_2]$

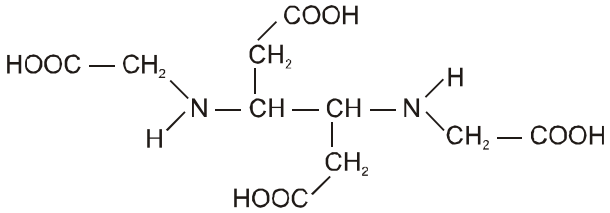
2. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is : **[JEE 2009, 3/160]**
(A) 0 (B) 2.84 (C) 4.90 (D) 5.92

3. The correct structure of ethylenediaminetetraacetic acid (EDTA) is : **[JEE 2010, 3/163]**

(A)


(B)


(C)


(D)


4. The ionization isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is : **[JEE 2010, 3/163]**
(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) $[Cr(H_2O)_4Cl_2(NO_2)].H_2O$

5. The complex showing a spin-only magnetic moment of 2.82 B.M. is : **[JEE 2010, 5/163]**
(A) $Ni(CO)_4$ (B) $[NiCl_4]^{2-}$ (C) $Ni(PPh_3)_4$ (D) $[Ni(CN)_4]^{2-}$

6. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is : **[JEE 2010, 3/163]**

7. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O, respectively, are
(A) octahedral, tetrahedral and square planar (B) tetrahedral, square planar and octahedral
(C) square planar, tetrahedral and octahedral (D) octahedral, square planar and octahedral

8. 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 : **[JEE 2011, 3/160]**
(A) K, L, M, N (B) K, M, O, P (C) L, M, O, P (D) L, M, N, O

9. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to. **[JEE 2011, 4/160]**

10. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is : **[JEE 2012, 3/143]**

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

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

11. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ 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 **[JEE 2012, 3/143]**

(B) square planar and square planar

(C) tetrahedral and square planar

(D) square planar and tetrahedral

12. Consider the following complex ions, P, Q and R. **[JEE(Advanced) 2013, 2/120]**

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

The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is

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

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

13.* The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) : **[JEE(Advanced) 2013, 4/120]**

(A) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$ (B) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$

(C) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$ (D) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$

14. *$EDTA^{4-}$* is ethylenediaminetetraacetate ion. The total number of *N–Co–O* bond angles in *$[Co(EDTA)]^{1-}$* complex ion is : **[JEE(Advanced) 2013, 4/120]**

15. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists. **[JEE(Advanced) 2014, 3/120]**

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

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

Code :

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

16. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is : [Atomic number of Fe = 26] **[JEE(Advanced) 2015, 4/168]**

17. In the complex acetylbromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe–C bond(s) is **[JEE(Advanced) 2015, 4/168]**

18. Among the complex ions, $[Co(NH_2–CH_2–CH_2–NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_2–CH_2–CH_2–NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is : **[JEE(Advanced) 2015, 4/168]**

19. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is : **[JEE(Advanced) 2016, 3/124]**

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

20. The number of geometric isomers possible for the complex $[CoL_2Cl_2]^-$ ($L = H_2NCH_2CH_2O^-$) is **[JEE(Advanced) 2016, 3/124]**

21. The geometries of the ammonia complexes of Ni^{2+}, Pt^{2+} and Zn^{2+}, respectively, are **[JEE(Advanced) 2016, 3/124]**

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

22.* The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers: Fe = 26, Ni = 28) **[JEE(Advanced) 2018, 4/128]**

(A) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16
(B) These are predominantly low spin in nature
(C) Metal–carbon bond strengthens when the oxidation state of the metal is lowered
(D) The carbonyl C-O bond weakens when the oxidation state of the metal is increased

23. Among the species given below, the total number of diamagnetic species is ___. **[JEE(Advanced) 2018, 3/120]**

H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapour phase,
Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$, K_2MnO_4, K_2CrO_4

24. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $NiCl_2.6H_2O$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $NiCl_2.6H_2O$ are used in the preparation, the combined weight (in grams) of gypsum and the nickel-ammonia coordination compound thus produced is ____. (Atomic weights in g mol^{-1}: H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59) **[JEE(Advanced) 2018, 3/120]**

25.* The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$ ($en = H_2NCH_2CH_2NH_2$) is (are) **[JEE(Advanced) 2018, 4/120]**

(A) It has two geometrical isomers
(B) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands
(C) It is paramagnetic
(D) It absorbs light at longer wavelength as compared to $[Co(en)NH_3)_4]^{3+}$

26. Match each set of hybrid orbitals from LIST-I with complex(es) given in LIST-II. **[JEE(Advanced) 2018, 3/120]**

LIST-I	LIST-II
(P) dsp^2	(1) $[FeF_6]^{4-}$
(Q) sp^3	(2) $[Ti(H_2O)_3Cl_3]$
(R) sp^3d^2	(3) $[Cr(NH_3)_6]^{3+}$
(S) d^2sp^3	(4) $[FeCl_4]^{2-}$
	(5) $Ni(CO)_4$
	(6) $[Ni(CN)_4]^{2-}$

The correct option is

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

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

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

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

27. Total number of cis N–Mn–Cl bond angles (that is, Mn–N and Mn–Cl bonds in cis position) present in a molecule of cis-$[Mn(en)_2Cl_2]$ complex is_____ (en = $NH_2CH_2CH_2NH_2$) **[JEE(Advanced) 2019, 3/124]**

PART - II : JEE MAIN PROBLEMS (PREVIOUS YEARS)

1. Which of the following has an optical isomer ? **[AIEEE 2009, 4/144]**

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

2. Which of the following pairs represents linkage isomers ? **[AIEEE 2009, 4/144]**

(1) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$ (2) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5(SO_4)]NO_3$

(3) $[PtCl_2(NH_3)_4Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$ (4) $[Cu(NH_3)_4]$ $[PtCl_4]$ and $[Pt(NH_3)_4]$ $[CuCl_4]$

3. 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) **[AIEEE 2010, 8/144]**

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

4. Which one of the following has an optical isomer ? **[AIEEE 2010, 4/144]**

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

(en = ethylenediamine)

5. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is **wrong** ? **[AIEEE 2011, 4/144]**

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

(2) The complex is paramagnetic.

(3) The complex is an outer orbital complex.

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

6. The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is : **[AIEEE 2011, 4/144]**

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

7. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide? **[AIEEE 2012, 4/144]**

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

8. Which of the following complex species is not expected to exhibit optical isomerism ? **[JEE(Main) 2013, 4/120]**

(1) $[Co(en)_3]^{3+}$ (2) $[Co(en)_2 Cl_2]^+$ (3) $[Co(NH_3)_3 Cl_3]$ (4) $[Co(en)(NH_3)_2 Cl_2]^+$

9. Type of isomerism which exists between $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ is : **[JEE(Main) 2013, Online]**

(1) Solvate isomerism (2) Ionisation isomerism

(3) Linkage isomerism (4) Coordination isomerism

10. Which of the following is diamagnetic ? **[JEE(Main) 2013, Online]**

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

11. The magnetic moment of the complex anion $[Cr^{I}(NO)(NH_3)(CN)_4]^{2-}$ is : **[JEE(Main) 2013, Online]**

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

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

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

(2) both are diamagnetic.

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

(4) both are paramagnetic

13. Which of the following name formula combinations is **NOT CORRECT**? **[JEE(Main) 2014, Online]**

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

14. Consider the coordination compound, $[Co(NH_3)_6]Cl_3$. In the formation of this complex, the species which acts as the Lewis acid is : **[JEE(Main) 2014, Online]**

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

15. Among the following species the one which causes the highest CFSE, Δ_0 as a ligand is :- **[JEE(Main) 2014, Online]**

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

16. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is : **[JEE(Main) 2014, 4/120]**

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

17. The number of geometric isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is (py = pyridine) : **[JEE(Main) 2015, 4/120]**

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

18. Which of the following complex ions has electrons that are symmetrically filled in both t_{2g} and e_g orbitals ? **[JEE(Main) 2015, Online]**

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

19. When concentrated HCl is added to an aqueous solution of $CoCl_2$, its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction ?:-
(1) $[Co(H_2O)_6]^{2+}$ (2) $[CoCl_6]^{3-}$ **[JEE(Main) 2015, Online]**
(3) $[CoCl_4]^{2-}$ (4) $[CoCl_6]^{4-}$

20. The **CORRECT** statement on the isomerism associated with the following complex ions,
(1) $[Ni(H_2O)_5NH_3]^{2+}$ **[JEE(Main) 2015, Online]**
(2) $[Ni(H_2O)_4(NH_3)_2]^{2+}$ and
(3) $[Ni(H_2O)_3(NH_3)_3]^{2+}$ is :
(1) (1) and (2) show geometrical and optical isomerism
(2) (2) and (3) show geometrical and optical isomerism
(3) (1) and (2) show only geometrical Isomerism
(4) (2) and (3) show only geometrical Isomerism

21. The pair having the same magnetic moment is : [At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]
[JEE(Main) 2016, 4/120]
(1) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ (2) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$
(3) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$ (4) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

22. Which one of the following complexes shows optical isomerism ? **[JEE(Main) 2016, 4/120]**
(1) cis$[Co(en)_2Cl_2]Cl$ (2) trans$[Co(en)_2Cl_2]Cl$
(3) $[Co(NH_3)_4Cl_2]Cl$ (4) $[Co(NH_3)_3Cl_3]$
(en = ethylenediamine)

23. Which one of the following complexes will consume more equivalents of aqueous solution of $Ag(NO_3)$?
[JEE(Main) 2016, Online]
(1) $[Cr(H_2O)_6]Cl_3$ (2) $Na_2[CrCl_5(H_2O)]$
(3) $Na_3[CrCl_6]$ (4) $[Cr(H_2O)_5Cl]Cl_2$

24. Identify the **CORRECT** trend given below : **[JEE(Main) 2016, Online]**
(Atomic No.= Ti : 22, Cr : 24 and Mo : 42)
(1) Δ_0 of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$
(2) Δ_0 of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$
(3) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$
(4) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$

25. On treatment of 100 mL of 0.1 M solution of $CoCl_3.6H_2O$ with excess $AgNO_3$; 1.2×10^{22} ions are precipitated. The complex is : **[JEE(Main) 2017, 4/120]**
(1) $[Co(H_2O)_3Cl_3].3H_2O$ (2) $[Co(H_2O)_6]Cl_3$
(3) $[Co(H_2O)_5Cl]Cl_2.H_2O$ (4) $[Co(H_2O)_4Cl_2]Cl.2H_2O$

26. $[Co_2(CO)_8]$ displays:- **[JEE(Main) 2017, Online]**
(1) no Co-Co bond, four terminal CO and four bridging CO
(2) one Co-Co bond, six terminal CO and two bridging CO
(3) no Co–Co bond, six terminal CO and two bridging CO
(4) one Co-Co bond, four terminal CO and four bridging CO

27. The pair of compounds having metal in their highest oxidation state is : **[JEE(Main) 2017, Online]**

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

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

28. Consider the following reaction and statements :

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

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

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

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

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

The correct statements are : **[JEE(Main) 2018, 4/120]**

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

29.^ The oxidation states of Cr in $[Cr(H_2O)_6]Cl_3$, $[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$ respectively are : **[JEE(Main) 2018, 4/120]**

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

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

30. The total number of possible isomers for square-planar $[Pt(Cl)(NO_2)(NO_3)(SCN)]^{2-}$ is :- **[JEE(Main) 2018, Online]**

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

31. The correct order of spin-only magnetic moments among the following is : **[JEE(Main) 2018, Online]**

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

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

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

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

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

32. The correct combination is **[JEE(Main) 2018, Online]**

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

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

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

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

33. Two complexes $[Cr(H_2O)_6]Cl_3$ (1) and $[Cr(NH_3)_6]Cl_3$ (2) are violet and yellow coloured respectively. The incorrect statement regarding them is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

(1) Δ_0 value for (1) is less than that of (2).

(2) both absorb energies corresponding to their complementary colors.

(3) Δ_0 values of (1) and (2) are calculated from the energies of violet and yellow light, respectively.

(4) both are paramagnetic with three unpaired electrons.

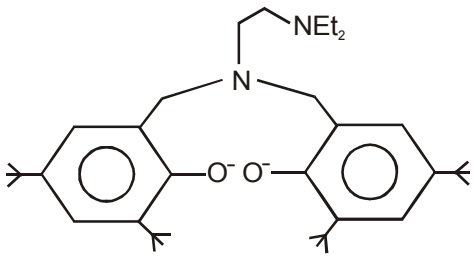
34. Homoleptic octahedral complexes of a metal ion 'M^{3+}' with three monodentate ligands L_1, L_2 and L_3 absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligand strength is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

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

35. The complex that has highest crystal field splitting energy (Δ), is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

(1) $K_2[CoCl_4]$ (2) $[Co(NH_3)_5(H_2O)]Cl_3$ (3) $[Co(NH_3)_5Cl]Cl_2$ (4) $K_3[Co(CN)_6]$

36. The following ligand is : **[JEE(Main) 2019 Online (08-04-19)S1, 4/120]**



(1) bidentate (2) hexadentate (3) tridentate (4) tetradentate

37. The correct order of the spin-only magnetic moment of metal ions in the following low-spin complexes, $[V(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$, $[Ru(NH_3)_6]^{3+}$, and $[Cr(NH_3)_6]^{2+}$ is : **[JEE(Main) 2019 Online (08-04-19)S1, 4/120]**

(1) $V^{2+} > Cr^{2+} > Ru^{3+} > Fe^{2+}$ (2) $Cr^{2+} > Ru^{3+} > V^{2+} > Fe^{2+}$

(3) $V^{2+} > Ru^{3+} > Cr^{2+} > Fe^{2+}$ (4) $Cr^{2+} > V^{2+} > Ru^{3+} > Fe^{2+}$

38. The compound that inhibits the growth of tumors is : **[JEE(Main) 2019 Online (08-04-19), 4/120]**

(1) cis-$[Pd(Cl)_2(NH_3)_2]$ (2) cis-$[Pt(Cl)_2(NH_3)_2]$

(3) trans-$[Pt(Cl)_2(NH_3)_2]$ (4) trans-$[Pd(Cl)_2(NH_3)_2]$

39. The calculated spin-only magnetic moments (BM) of the anionic and cationic species of $[Fe(H_2O)_6]_2$ and $[Fe(CN)_6]$, **[JEE(Main) 2019 Online (08-04-19)S2, 4/120]**

(1) 0 and 5.92 (2) 4.9 and 0 (3) 0 and 4.9 (4) 2.84 and 5.92

40. The theory that can completely/properly explain the nature of bonding in $[Ni(CO)_4]$ is : **[JEE(Main) 2020 Online (Jan)]**

(1) Werner's theory (2) Crystal field theory

(3) Valence bond theory (4) Molecular orbital theory

41. The IUPAC name of the complex **[JEE(Main) 2020 Online (Jan)]**
$[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ is :

(1) Diammine (methanamine) chlorido platinum (II) chloride

(2) Bisammine (methanamine) chlorido platinum (II) chloride

(3) Diamminechlorido (aminomethane) platinum(II) chloride

(4) Diamminechlorido (methanamine) platinum (II) chloride

42. Among the statements(1)-(4), the incorrect ones are- **[JEE(Main) 2020 Online (Jan)]**

(1) Octahedral Co(III) complexes with strong field ligands have very high magnetic moments

(2) When $\Delta_0 < P$, the d-electron configuration of Co(III) in an octahedral complex is $t_{eg}^4 e_g^2$

(3) Wavelength of light absorbed by $[Co(en)_3]^{3+}$ is lower than that of $[CoF_6]^{3-}$

(4) If the Δ_0 for an octahedral complex of Co(III) is 18,000 cm^{-1}, the Δ_t for its tetrahedral complex with the same ligand will be 16,000 cm^{-1}

(1) (1) and (2) only (2) (3) and (4) only

(3) (2) and (3) only (4) (1) and (4) only

43. The number of possible optical isomers for the complexes MA_2B_2 with sp^3 and dsp^2 hybridised metal atom, respectively, is : **[JEE(Main) 2020 Online (Jan)]**

Note : A and B are unidentate neutral and unidentate monoanionic ligands, respectively

(1) 0 and 0 (2) 0 and 2

(3) 0 and 1 (4) 2 and 2

ANSWER KEY

EXERCISE # 1

PART - I

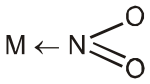
A-1. $K_2SO_4.Cr_2(SO_4)_3 \xrightleftharpoons{aq.} 2K^+(aq) + 2Cr^{3+}(aq) + 4SO_4^{2-}$
So chrome alum is a double salt. It when dissolved in water gives its constituent ions. Hence it gives the test of K^+, Cr^{3+} and SO_4^{2-} ions.

$CuSO_4.4NH_3 \rightleftharpoons [Cu(NH_3)_4]SO_4 \xrightleftharpoons{aq.} [Cu(NH_3)_4]^{2+}(aq) + SO_4^{2-}(aq)$
As copper (II) is present in coordination sphere it will not give the test of Cu^{2+} ion.

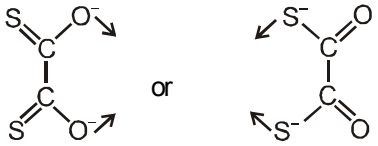
A-2. The coordination number of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ions i.e. the number of ligand donor atoms to which the metal is directly attached.The oxidation number of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.

	Complex	Coordination Number	Oxidation State
(a)	$[AgCl_2]^-$	2	1
(b)	$[Cr(H_2O)_5Cl]^{2+}$	6	3
(c)	$[Co(NCS)_4]^{2-}$	4	2
(d)	$[Co(NH_3)_3(NO_2)_3]$	6	3
(e)	$[Fe(EDTA)]^-$	6	3
(f)	$[Cu(en)_2]SO_4$	4	2
(g)	$K[Pt(NH_3)Cl_5]$	6	4

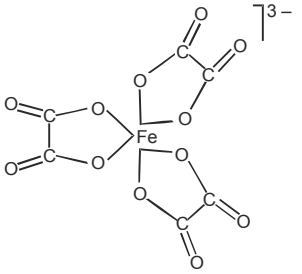
A-3.
(A) Methyl isocyanide, monodentate.
(B) acetylacetonate, bidentate
(C) azide, monodentate
(D) diethylenetriamine, tridentate
(E) ethylenediamine tetraacetate, hexadentate
(F) ethylenediamine triacentate, pentadentate
(G) oxalato, bidentate
(H) dimethylglyoximato
(I) isocyanido, monodentate
(J) nitrito, monodentate
(K) Oxido, monodentate
(L) peroxido, bidentate
(M) superoxido, monodentate

A-4. (A) M ←  nitrito-N M ← O—N=O nitrito-O

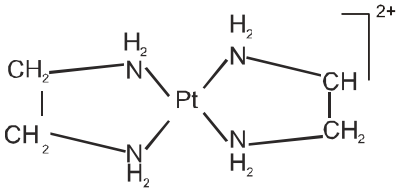
(B) M ← SCN thiocyanato or thiocyanato-S, M ← NCS isothiocyanato or thiocyanato-N

(C)  or dithioxalate

(D) M ← OCN cyanato-O or cyanato-N, M ← NCO isothiocyanato or thiocyanato-N
(E) M ← NOS thionitrito-N or , M ← SON thionitrito-S

A-5.(a) 

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



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

The ligands, oxalate and ethylenediamine are bidentate as each ligand has two donor atoms. So in 1st case the number of chelate rings (five membered) are three where as in 2nd case the number of chelate rings (five membered) are two. The coordination number and oxidation state of iron are six and +3 respectively and the coordination number and oxidation state of platinum are four and +2 respectively.

(b) $K_2[Ni(CN)_4] \overset{aq.}{\rightleftharpoons} 2K^+(aq) + [Ni(CN)_4]^{2-}(aq)$

$[Cr(en)_3]Cl_3 \overset{aq.}{\rightleftharpoons} [Cr(en)_3]^{3+}(aq) + 3Cl^-(aq)$

$Fe_4[Fe(CN)_6]_3 \overset{aq.}{\rightleftharpoons} 4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq)$

$[PtCl_2(en)_2](NO_3)_2 \overset{aq.}{\rightleftharpoons} [PtCl_2(en)_2]^{2+}(aq) + 2(NO_3)^-(aq)$

So, $[Ni(CN)_4]^{2-}$, $[Cr(en)_3]^{3+}$, $3[Fe(CN)_6]^{4-}$ and $[PtCl_2(en)_2]^{2+}$ are coordination entities and K^+, Cl^-, Fe^{3+} and NO_3^- are counter ions.

(c) Coordination compounds are acid-base adduct. Cations are electron deficient, therefore, are called Lewis acids where as ligands are electrons donors, therefore, are called as Lewis base.

		LEWIS ACID	LEWIS BASE
(i)	$[HgBr_4]^{2-}$	Hg^{2+}	$4Br^-$
(ii)	$[Ni(H_2O)_6]^{2+}$	Ni^{2+}	$6H_2O$
(iii)	$[PdCl_2(NH_3)_2]$	Pd^{2+}	$2Cl^-$ & $2NH_3$
(iv)	$[Al(OH)_4]^-$	Al^{3+}	$4OH^-$
(v)	$[Ag(CN)_2]^-$	Ag^+	$2CN^-$
(vi)	$[Cr(CO)_6]$	Cr^0	$6CO$

B-1.(a) **$[Co(NH_3)_6]Cl_3$**, Hexaamminecobalt(III) chloride

(b) **$[Rh(NH_3)_5I]I_2$**, Pentaammineiodidorhodium(III) iodide

(c) **$[Fe(CO)_5]$**, Pentacarbonyliron(0)

(d) **$[Fe(C_2O_4)_3]^{3-}$**, Trioxalatoferrate(III) ion OR Tris(oxalato)ferrate(III) ion

(e) **$[Cu(NH_3)_4]SO_4$**, Tetraamminecopper(II) sulphate

(f) **$Na[Cr(OH)_4]$**, Sodium tetrahydroxidochromate(III)

(g) **$[Co(gly)_3]$**, Triglycinatocobalt(III) OR Tris(glycinato)cobalt(III)

(h) **$[Fe(H_2O)_5(SCN)]^{2+}$**, Pentaaquathiocyanato–S–iron(III) ion

(i) **$K_2[HgI_4]$**, Potassium tetraiodidomercurate(II)

(j) **$Co[Hg(SCN)_4]$**, Cobalt(II) tetrathiocyanato–S–mercurate(II)

(k) **$Fe_4[Fe(CN)_6]_3$**, Iron(III) hexacyanidoferrate(II)

(l) **$K_3[Co(NO_2)_6]$**, Potassium hexanitro–N–cobaltate(III)

(m) **$[Ni(dmg)_2]$**, Bis(dimethylglyoximato)nickel(II)

(n) **$K_2[PtCl_6]$**, Potassium hexachloridoplatinate(IV)

(o) **$Na_2[Fe(CN)_5NO^+]$**, Sodium pentacyanidonitrosoniumferrate(II)

(p) **$[Fe(H_2O)_5(NO^+)]SO_4$**, Pentaaquanitrosoniumiron(I) sulphate

(q) **$[Cu(CN)_4]^{3-}$**, Tetracyanidocuperate(I) ion

(r) **$(NH_4)_2[PtCl_6]$**, Ammonium hexachloridoplatinate(IV)

B-2.(a) $[CoBr(en)_2(ONO)]^{+1}$ Bromidobis(ethylenediamine)nitrito–O–cobalt(III)

(b) $[Co(NH_3)_6][Co(ONO)_6]$ Hexaamminecobalt(III) hexanitrito–O–cobaltate(III)

(c) $[Co(NH_3)_5(CO_3)]Cl$ Pentaamminecarbonatocobalt(III) chloride

(d) $[Pt(NH_3)_4Cl_2][PtCl_4]$ Tetraamminedichloridoplatinum(IV) tetrachloridoplatinate(II)

(e) $[Co(en)_3]_2(SO_4)_3$ Tris(ethylenediamine)cobalt(III) sulphate or Tris(ethane -1, 2-diamine)cobalt(III) sulphate.

(f) $[(NH_3)_5Co\text{-}NH_2\text{-}Co(NH_3)_4(H_2O)]Cl_5$ Pentaamminecobalt(III)–μ–amidotetraammineaquacobalt(III) chloride

(g) $[Cr(CO)_5(PPh_3)]$ Pentacarbonyltriphenylphosphinechromium(0)

(h) $[(CO)_5Mn\text{-}Mn(CO)_5]$ Decacarbonyldimanganese(0)

(i) $Cr(\pi\text{-}C_6H_6)_2$ Bis(η^6–benzene)chromium(0)

(j) $[Co(NH_3)_4(OH_2)_2][BF_4]_3$ Tetraamminediaquacobalt(III) tetrafluoridoborate(III)

(l) $Ba[Zr(OH)_2(ONO)_2(ox)]$ Barium dihydroxidodinitrito–O–oxalatozirconate(IV)

(l) $[Co(NH_3)_6][Co(C_2O_4)_3]$ Hexaamminecobalt(III) trioxalatocobaltate(III)

B-3.(a) Tetraamminezinc(II) Nitrate, $[Zn(NH_3)_4](NO_3)_2$

(b) Tetracarbonylnickel(0), $[Ni(CO)_4]$

(c) Potassium amminetrichloridoplatinate(II), $K[Pt(NH_3)Cl_3]$

(d) Dicyanidoaurate(I) ion, $[Au(CN)_2]^-$

(e) Sodium hexafluoridoaluminate(III), $Na_3[AlF_6]$

(f) Diamminesilver(I) ion, $[Ag(NH_3)_2]^+$

B-4.(a) Diamminetriaquahydroxidochromium(III) nitrate $[Cr(NH_3)_2(H_2O)_3(OH)](NO_3)_2$

(b) Tetrakis(pyridine)platinum(II) tetraphenylborate(III) $[Pt(Py)_4][B(ph)_4]_2$

(c) Dibromidotetracarbonyliron(II) $[Fe(Br)_2(CO)_4]$

(d) Ammonium diamminetetrakis(isothiocyanato)chromate(III). $(NH_4)[Cr(NH_3)_2(NCS)_4]$

(e) Pentaamminedinitrogenruthenium(II) chloride $[Ru(NH_3)_5N_2]Cl_2$

(f) Barium dihydroxidodinitrito-O-oxalatozirconate(IV) $Ba[Zr(OH)_2(ONO)_2(ox)]$

(g) Tetrapyridineplatinum(II) tetrachloridoplatinate(II) $[Pt(py)_4][PtCl_4]$

C-1. (a) – iv, (b) – viii, (c) – i, (d) – vii,
(e) – iii, (f) – v, (g) – ii, (h) – vi

C-2. 0.0075.

C-3.

(a)	36	(b)	36	(c)	36	(d)	36
(e)	36	(f)	36	(g)	54	(h)	86

C-4. ii < i < iv < iii.

D-1. (i) $[Cr(NH_3)_4Cl\,Br]Cl \overset{aq.}{\rightleftharpoons} [Cr(NH_3)_4Cl\,Br]^+ + Cl^-$; $Ag^+ + Cl^- \longrightarrow AgCl\downarrow$ (white) ; soluble in dilute NH_3.

$[Cr(NH_3)_4Cl_2]Br \overset{aq.}{\rightleftharpoons} [Cr(NH_3)_4Cl_2]^+ + Br^-$; $Ag^+ + Br^- \longrightarrow AgBr\downarrow$ (yellow) ; soluble in conc. NH_3.

So, A = $[Cr(NH_3)_4Cl\,Br]Cl$ and B = $[Cr(NH_3)_4Cl_2]Br$.

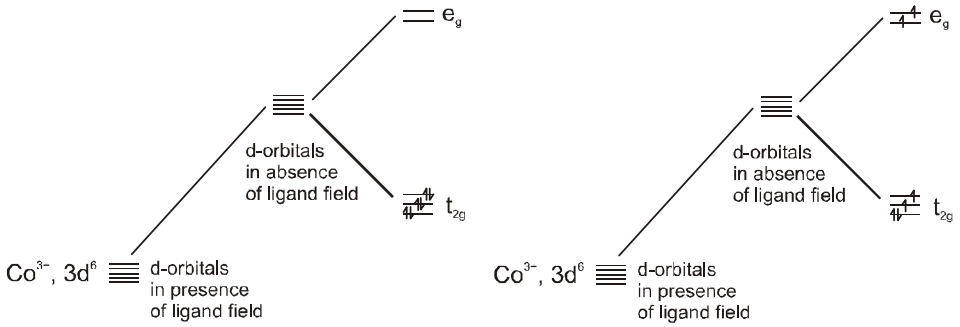
(ii) EAN = 24 – 3 + 12 = 33

(iii) Yes, both have two ions per formula unit.

(iv) $AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]Cl$; $AgBr + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]Br$

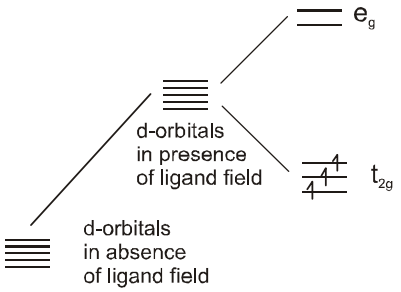
D-2.	Complex	Geometry	Hybridisation	Number of unpaired electrons(n)	Mag. moment
	CN =2				
(a)	$[Ag(NH_3)_2]^+$	Linear	sp	0	0
(b)	$[Cu(CN)_2]^-$	Linear	sp	0	0
(c)	$[AuCl_2]^-$	Linear	sp	0	0
	CN = 4				
(d)	$[PtCl_2(NH_3)_2]$	Square Planar	dsp^2	0	0
(e)	$[Zn(CN)_4]^{2-}$	Tetrahedral	sp^3	0	0
(f)	$[Cu(CN)_4]^{3-}$	Tetrahedral	sp^3	0	0
(g)	$[MnBr_4]^{2-}$	Tetrahedral	sp^3	5	5.92 BM
(h)	$[Cu(NH_3)_4]^{2+}$	Square Planar	dsp^2	1	1.73 BM
(i)	$[CoI_4]^{2-}$	Tetrahedral	sp^3	3	3.87 BM
	CN = 6				
(j)	$[Mn(CN)_6]^{3-}$	Octahedral	d^2sp^3	2	2.83 BM
(k)	$[Cr(NH_3)_6]^{3+}$	Octahedral	d^2sp^3	3	3.87 BM
(l)	$[Fe(CN)_6]^{3-}$	Octahedral	d^2sp^3	1	1.73 BM
(m)	$[Ir(NH_3)_6]^{3+}$	Octahedral	d^2sp^3	0	0
(n)	$[V(CO)_6]$	Octahedral	d^2sp^3	1	1.73 BM
(o)	$[Fe(H_2O)_6]^{2+}$	Octahedral	sp^3d^2	4	4.90 BM
(p)	$[MnCl_6]^{3-}$	Octahedral	sp^3d^2	4	4.90 BM

E-1. Since ammonia is a strong field ligand so can pair up the electrons of Co(III), so will form an inner d-orbital complex having zero magnetic moment while fluoride being a weak field ligand can not pair up electrons and forms outer d-complex with higher magnetic moment equal to four unpaired electrons.



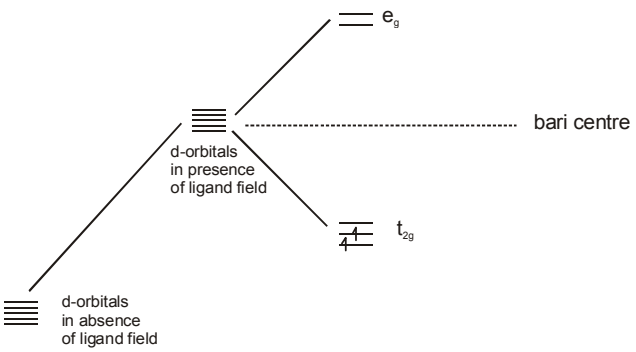
E-2. (a) i < iv < ii < iii (b) X < O < N < C (c) $Br^- < S^{2-} < NO_3^- < H_2O < NH_3 < NO_2^- < CN^- < CO$

E-3. **(a)** F^- is weak field ligand. Cr^{3+}, $3d^3$



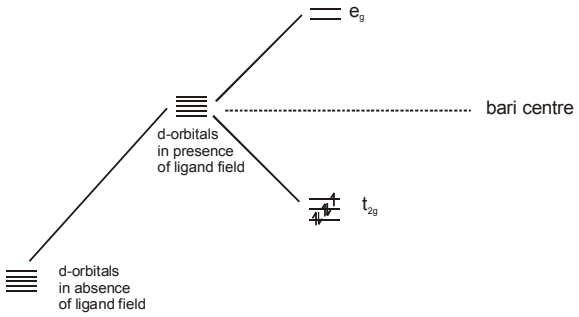
So number of unpaired electrons = 3

(b) H_2O is weak field ligand. V^{3+}, $3d^2$



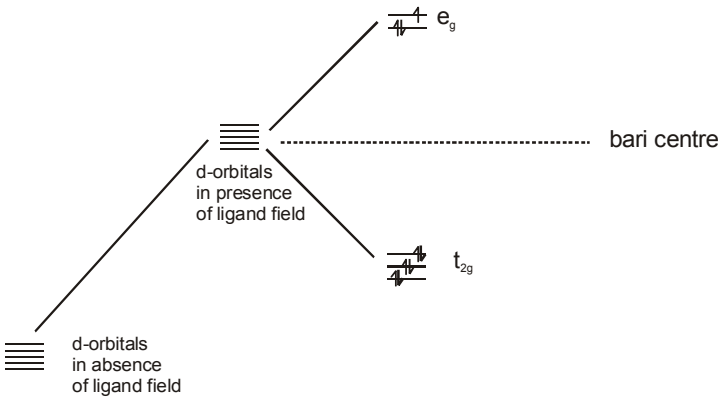
So number of unpaired electrons = 2

(c) CN^- is strong field ligand. Fe^{3+}, $3d^5$



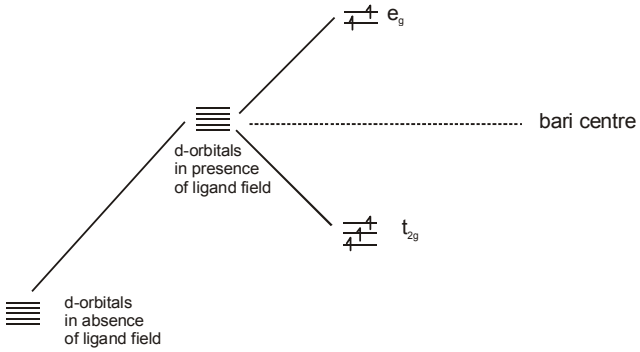
So number of unpaired electron = 1.

(d) en is strong field ligand. Cu^{2+}, $3d^9$



So number of unpaired electron = 1.

(e) F^- is weak field ligand. Fe^{3+}, $3d^5$



So number of unpaired electrons = 5.

F-1. (a) $[NiBr_4]^{2-}$ sp^3, tetrahedral
(d) $[AuCl_4]^-$ dsp^2, square planar
(f) $[Pt(NH_3)_4]^{2+}$ dsp^2, square planar

F-2. (a) $[Fe(CN)_6]^{3-}$ d^2sp^3, octahedral
(b) $[MnBr_4]^{2-}$ sp^3, tetrahedral
(c) $[Fe(H_2O)_6]^{2+}$ sp^3d^2, octahedral
(d) $[Co(SCN)_4]^{2-}$ sp^3, tetrahedral

G-1. As $3d^6$ configuration has higher CFSE as compared to $3d^7$ so it gets oxidised in presence of complexing reagent to easily have d^2sp^3 hybridisation.

G-2. 3

G-3. yellow colour

$$240000\ (J) = \frac{hc}{\lambda} = \frac{6\times10^{-34}\times3\times10^{8}\times6\times10^{23}}{\lambda_{(nm)}\times10^{-9}}$$

$\therefore$ $\lambda_{(nm)} = 450$ $\therefore$ **yellow colour**

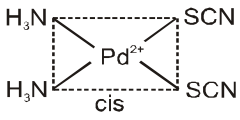
G-4. (a) CN^-, F^-
(b) (i) 0 (ii) 0 (iii) 0 (iv) 0

G-5. 2

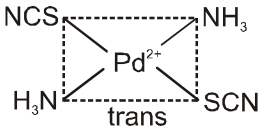
H-1. (i) Linkage (ii) Coordination (iii) Ionisation (iv) Hydrate

H-2.(a) There are three constitutional isomers
(i) $[Ru(NH_3)_5(NO_2)]Cl$
(ii) $[Ru(NH_3)_5Cl](NO_2)$ or $[Ru(NH_3)_5Cl]ONO$
(iii) $[Ru(NH_3)_5\ ONO]Cl$
(i) & (ii) are ionisation isomers
(i) & (iii) are linkage isomers

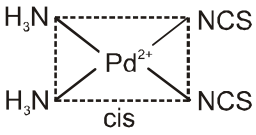
(b) (i)



(ii)



(iii)



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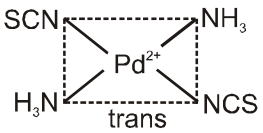

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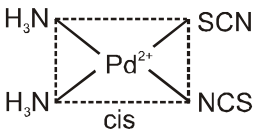
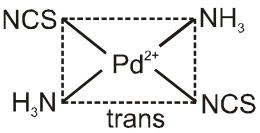


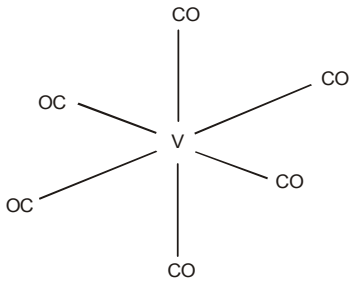
(vi)



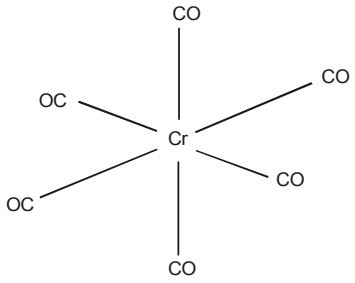
H-3. (a) Two (b) None (c) Two (d) None (e) Two (f) None

H-4. (a) No ; (b) Yes ; (c) Yes ; (d) Yes ; (e) Yes ; (f) No.

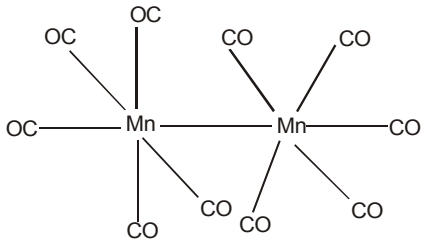
I-1. (a)



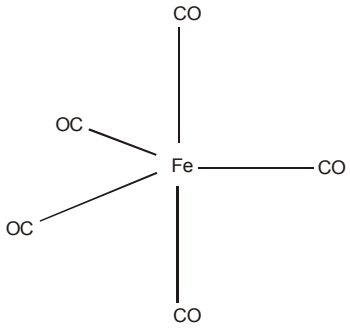
(b)



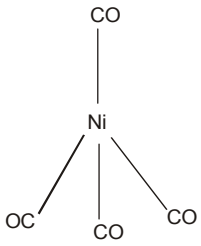
(c)



(d)



(e)



I-2. (i) Increases (ii) Decreases

PART-II

A-1.	(B)	**A-2.**	(C)	**A-3.**	(A)	**A-4.**	(B)	**A-5.**	(B)	**A-6.**	(D)	**A-7.**	(B)
A-8.	(A)	**A-9.**	(D)	**B-1.**	(C)	**B-2.**	(A)	**B-3.**	(D)	**B-4.**	(D)	**B-5.**	(C)
C-1.	(C)	**C-2.**	(B)	**C-3.**	(C)	**C-4.**	(A)	**C-5.**	(A)	**C-6.**	(B)	**C-7.**	(C)
C-8.	(D)	**C-9.**	(C)	**D-1.**	(A)	**D-2.**	(C)	**E-1.**	(C)	**E-2.**	(A)	**E-3.**	(D)
E-4.	(A)	**E-5.**	(C)	**F-1.**	(A)	**F-2.**	(B)	**F-3.**	(D)	**F-4.**	(C)	**F-5.**	(A)
F-6.	(C)	**F-7.**	(A)	**F-8.**	(A)	**F-9.**	(B)	**F-10.**	(C)	**F-11.**	(C)	**F-12.**	(C)
G-1.	(B)	**G-2.**	(B)	**G-3.**	(D)	**G-4.**	(D)	**G-5.**	(B)	**G-6.**	(C)	**G-7.**	(A)
G-8.	(B)	**H-1.**	(C)	**H-2.**	(B)	**H-3.**	(B)	**H-4.**	(D)	**H-5.**	(C)	**H-6.**	(C)
H-7.	(B)	**H-8.**	(C)	**H-9.**	(C)	**H-10.**	(C)	**I-1.**	(D)	**I-2.**	(D)	**I-3.**	(B)
I-4.	(C)	**I-5.**	(C)										

PART-III

1. (A - q, r, t) ; (B - q, r, t) ; (C - p, s) ; (D - q, r). **2.** (A - p,q,r); (B - q,r,s) ; (C - p,q,r,s) ; (D - p,q)

EXERCISE # 2

PART - I

1.	(A)	**2.**	(D)	**3.**	(B)	**4.**	(C)	**5.**	(A)	**6.**	(B)	**7.**	(D)
8.	(D)	**9.**	(D)	**10.**	(A)	**11.**	(C)	**12.**	(D)	**13.**	(B)	**14.**	(B)
15.	(A)	**16.**	(A)										

PART - II

1.	13	**2.**	05	**3.**	26	**4.**	(40 + 20) ml = 60 ml			**5.**	4	**6.**	3
7.	3	**8.**	4	**9.**	4	**10.**	**12**	**11.**	4				

PART - III

1.	(B,C,D)	**2.**	(B,C)	**3.**	(A,B,C,D)	**4.**	(B)	**5.**	(B)	**6.**	(A,B,C,D)	**7.**	(B,D)
8.	(A,B)	**9.**	(A,C,D)	**10.**	(B,C,D)	**11.**	(B,C,D)	**12.**	(C)				

PART - IV

1.	(D)	**2.**	(C)	**3.**	(B)	**4.**	(A)	**5.**	(A)	**6.**	(B)	**7.**	(A)
8.	(C)	**9.**	(A)	**10.**	(B)	**11.**	(C)						

EXERCISE # 3

PART- I

1.*	(C)	**2.**	(A)	**3.**	(C)	**4.**	(B)	**5.**	(B)	**6.**	3	**7.**	(B)
8.	(C)	**9.**	6	**10.**	(D)	**11.**	(C)	**12.**	(B)	**13.***	(B,D)	**14.**	8
15.	(B)	**16.**	4	**17.**	3	**18.**	6	**19.**	(B)	**20.**	5	**21.**	(A)
22.*	(B,C)	**23.**	1	**24.**	2992	**25.***	(A,B,D)	**26.**	(C)	**27.**	6.00		

PART - II

1.	(3)	**2.**	(1)	**3.**	(1)	**4.**	(2)	**5.**	(3)	**6.**	(3)	**7.**	(2)
8.	(3)	**9.**	(3)	**10.**	(4)	**11.**	(3)	**12.**	(4)	**13.**	(3)	**14.**	(3)
15.	(3)	**16.**	(2)	**17.**	(2)	**18.**	(3)	**19.**	(3)	**20.**	(4)	**21.**	(1)
22.	(1)	**23.**	(1)	**24.**	(2)	**25.**	(4)	**26.**	(2)	**27.**	(2)	**28.**	(4)
29.	(1)	**30.**	(4)	**31.**	(3)	**32.**	(2)	**33.**	(3)	**34.**	(4)	**35.**	(4)
36.	(4)	**37.**	(1)	**38.**	(2)	**39.**	(Bonus)	**40.**	(4)	**41.**	(4)	**42.**	(4)
43.	(1)												

✍ **Marked Questions may have for Revision Questions.**

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1. One mole of $Co(NH_3)_5Cl_3$ gives 3 moles of ions on dissolution in water. One mole of this reacts with two moles of $AgNO_3$ to give two moles of AgCl. The complex is :
(A) $[Co(NH_3)_4Cl_2]Cl.NH_3$ (B) $[Co(NH_3)_4Cl]Cl_2.NH_3$ (C) $[Co(NH_3)_5Cl]Cl_2$ (D) $[Co(NH_3)_3Cl_3].2NH_3$

2. Ammonia forms the complex $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solution but not in acid solution. The reason for it is :
(A) in alkaline solution $Cu(OH)_2$ is precipitated which is soluble in excess of alkali.
(B) copper hydroxide is amphoteric.
(C) in acidic solution hydration protects Cu^{2+} ions.
(D) in acidic solution protons coordinates with ammonia molecule forming NH_4^+ ions and NH_3 molecules are not available.

3. In the coordination compound $K_4[Ni(CN)_4]$, the oxidation state of nickel is :
(A) – 1 (B) 0 (C) + 1 (D) + 2

4. The co-ordination number of a central metal atom in a complex is determined by :
(A) the number of only anionic ligands bonded to metal ion
(B) the number of ligands around a metal ion bonded by pi bonds
(C) the number of ligands around a metal ion bonded by sigma and pi bonds
(D) the number of ligands around a metal ion bonded by sigma bonds

5. Which one is an outer orbital complex ?
(A) $[Ni(NH_3)_6]^{2+}$ (B) $[Mn(CN)_6]^{4-}$ (C) $[Co(NH_3)_6]^{3+}$ (D) $[Fe(CN)_6]^{4-}$

6. Co-ordination compounds have great importance in biological systems. In this context, which statement is incorrect ?
(A) Carboxypeptidase–A is an enzyme and contains zinc.
(B) Haemoglobin is the red pigment of blood and contains iron.
(C) Cyanocobalmin is B_{12} and contains cobalt.
(D) Chlorophylls are green pigments in plants and contain calcium.

7. Which one has largest number of isomers ?
(A) $[Co(en)_2Cl_2]^+$ (B) $[Co(NH_3)_5Cl]^{2+}$ (C) $[Ir(PhR_3)_2H(CO)]^{2+}$ (D) $[Ru(NH_3)_4Cl_2]^+$

8. The correct order of magnetic moments (only spin value in BM) among is :
(A) $Fe(CN)_6^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$ (B) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
(C) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$ (D) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$

9. The IUPAC name of $K_3Fe(CN)_6$ is :
(A) Potassium hexacyanoferrate(II) (B) Potassium hexacyanoferrate(III)
(C) Potassium hexacyanoiron(II) (D) Tripotassium hexacyanoiron(II)

10. Which of the following will show optical isomerism ?
(A) $[Cu(NH_3)_4]^{2+}$ (B) $[ZnCl_4]^{2-}$ (C) $[Cr(C_2O_4)_3]^{3-}$ (D) $[Co(CN)_6]^{3-}$

11. Which one of the following 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) $[Cr(CN)_6]^{3-}$

12. The value of 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is: (Assuming octahedral complex)
(A) d^4 (in strong field ligand) (B) d^4 (in weak field ligand)
(C) d^3 (in weak as well as strong field ligand) (D) d^5 (in strong field ligand)

13. 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, tetrahedral (B) two, tetrahedral
(C) one, square planar (D) two, square planar

14. The IUPAC name for the complex $[Co(NH_3)_5(NO_2)]Cl_2$ is :
(A) Nitrito-N-pentaamminecobalt(III) chloride (B) Nitrito-N-pentaamminecobalt(II) chloride
(C) Pentaamminenitrito-N-cobalt(II) chloride (D) Pentaamminenitrito-N-cobalt(III) chloride

15. In $Fe(CO)_5$, the Fe – C bond possesses :
(A) π-character only (B) both σ and π characters
(C) ionic character only (D) σ-character only

16. How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with a Ca^{2+} ion ?
(A) Six (B) Three (C) One (D) Two

17. Which one of the following has a square planar geometry?
(A) $[NiCl_4]^{2-}$ (B) $[PtCl_4]^{2-}$ (C) $[CoCl_4]^{2-}$ (D) $[FeCl_4]^{2-}$
(At. no. Co = 27, Ni = 28, Fe = 26, Pt = 78)

18. The coordination number and the oxidation state of the element 'E' in the complex $[E(en)_2(C_2O_4)]NO_2$ (when 'en' is ethylene diamine) are, respectively,
(A) 4 and 2 (B) 4 and 3 (C) 6 and 3 (D) 6 and 2

19. In which of the following octahedral complexes of Co (at no. 27), will the magnitude of Δ_0 be the highest?
(A) $[Co(C_2O_4)_3]^{3-}$ (B) $[Co(H_2O)_6]^{3+}$ (C) $[Co(NH_3)_6]^{3+}$ (D) $[Co(CN)_6]^{3-}$

20. The IUPAC name of $K_2[Cr(CN)_2O_2(O)_2(NH_3)]$ is :
(A) Potassium amminedicyanodioxoperoxochromate(VI)
(B) Potassium amminecyanoperoxodioxochromium(VI)
(C) Potassium amminedicyanoperoxooxochromium(VI)
(D) Potassium amminecyanodiperoxodioxochromate(VI)

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

21. The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is :

22. The 'spin only' magnetic moment (in units of Bohr magneton, μ_B) of Ni^{2+} in aqueous solution would be (atomic number Ni = 28)

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

24. If excess of $AgNO_3$ solution is added to 100 mL of a 0.024 M solution of dichlorobis(ethylenediamine)cobalt (III) chloride. How many moles of AgCl be precipitated ?

25. What will be the theoretical value of 'spin only' magnetic moment when $Fe(SCN)_3$ reacts with a solution containing F^- ions to yield a colourless complex ?

PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks	:	+3	If only the bubble corresponding to the correct option is darkened.
Zero Marks	:	0	If none of the bubbles is darkened.
Negative Marks	:	–1	In all other cases

1. The species having tetrahedral shape is :
(A) $[PdCl_4]^{2-}$ (B) $[Ni(CN)_4]^{2-}$ (C) $[Pd(CN)_4]^{2-}$ (D) $[NiCl_4]^{2-}$

2. The spin magnetic moment of cobalt in the compound, $Hg[Co(SCN)_4]$ is :

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

3. Which kind of isomerism is exhibited by octahedral $[Co(NH_3)_4Br_2]Cl$?

(A) Geometrical and ionization (B) Geometrical and optical

(C) Optical and ionization (D) Geometrical only

4. The bond length in CO is 1.128 Å. What will be the bond length of CO in $Fe(CO)_5$?

(A) 1.158 Å (B) 1.128 Å (C) 1.178 Å (D) 1.118 Å

SECTION-II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	:	+4	If only (all) the correct option(s) is (are) chosen.
Partial Marks	:	+3	If all the four options are correct but ONLY three options are chosen.
Partial Marks	:	+2	If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks	:	+1	If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks	:	0	If none of the options is chosen (i.e. the question is unanswered).
Negative Marks	:	–1	In all other cases.

- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

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5. Which of the following statement(s) is/are correct ?

(A) cis-$[Pt(NH_3)_2Cl_2]$ is used as an anticancer species.

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

(C) In the silver electroplating of copper, $K[Ag(CN)_2]$ is used in place of $AgNO_3$.

(D) CN^- ions show the reducing as well as complexing properties towards metal species.

6. Which of the following is true for the complex $Co(NO_2)(Cl)_2.5NH_3$ (Co is in + III oxidation state) ?

(A) It shows linkage isomerism. (B) It show ionisation isomerism.

(C) It is inner orbital complex. (D) It is diamagnetic.

7. Which of the following complexes can exist as diastereoisomers ?

(A) $[Cr(NH_3)_2Cl_4]^-$ (B) $[Co(NH_3)_5Br]^{2+}$ (C) $[FeCl_2(NCS)_2]^{2-}$ (D) $[PtCl_2Br_2]^{2-}$

8. Tetrahedral complexes are generally favoured :

(A) where the ligands are bulky

(B) when the ligands are stronger

(C) where the electronic configuration of the central metal is d^0 d^5 or d^{10} (with weak field ligands) as there is no CFSE.

(D) when the central metal ion has pseudo noble gas electron configuration, i.e. (n-1) $d^{10}ns^0np^0$.

9. Which of the following statements is/are incorrect for the complex $[Cr(H_2O)_6]Cl_3$?
(A) It has a magnetic moment of 3.83 BM.
(B) The distribution of 3d electrons is $3dxy^1$, $3dyz^1$, $3dzx^1$
(C) The ligand has satisfied both primary and secondary valencies of chromium.
(D) It shows ionization as well as hydrate isomerism.

10. Which of the following pairs of name and formula of complexes, is correct ?
(A) Tetramminecopper(II) sulphate..... $[Cu(NH_3)_4]SO_4$
(B) Diamminesilver(I) chloride ..... $[Ag(NH_3)_2]Cl$
(C) Potassium hexacyanidoferrate (III) ..... $K_4[Fe(CN)_6]$
(D) Potassium amminepentachloridoplatinate (IV) ..... $K[Pt(NH_3)Cl_5]$

11. In which of the following pairs of complexes the central metals/ions do have same effective atomic number ?
(A) $[Cr(CO)_6]$ and $[Fe(CO)_5]$ (B) $[Co(NH_3)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$
(C) $[Cu(CN)_4]^{3-}$ and $[Ni(CO)_4]$ (D) $[V(CO)_6]^-$ and $[Co(NO_2)_6]^{3-}$

12. Which of the following statements is/are correct ?
(A) $Ni(CO)_4$ —— Tetrahedral, paramagnetic (B) $Ni(CN)_4]^{2-}$ —— Square planar, diamagnetic
(C) $Ni(dmg)_2$ —— Square planar, diamagnetic (D) $[NiCl_4]^{2-}$ —— Tetrahedral, paramagnetic

SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.
  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +3 If ONLY the correct numerical value is entered as answer.
  Zero Marks : 0 In all other cases.

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

14. Count the no. of ions which can form both low spin & high spin complexes when co-ordination no. 6
Co^{+3}, Ni^{+2} , Cr^{+3} , Fe^{+2}, Fe^{+3} , Cu^{+2} , Ti^{+3}, Co^{+2}

15. The number of unpaired electrons present in $[NiF_6]^{2-}$ is ..... .

16. The sum of stereoisomers of complex-A, complex-B and complex-C in following reaction is .....

$$[PtCl_4]^{2-} \xrightarrow[-2Cl^-]{+2\,(pyridine)} [Complex\text{-}A] \xrightarrow[-Cl^-]{+NH_3} [Complex\text{-}B] \xrightarrow[-(Pyridine)]{+Br^-} [Complex\text{-}C]$$

17. The number of d-electrons in $[Cr(H_2O)_6]^{3+}$ [atomic number of Cr = 24] is :

18. The possible number of stereoisomers for the formula $[Ma_2b_2cd]^{\pm n}$.

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

STAGE - I (NATION STANDARD EXAMINATION IN CHEMISTRY (NSEC))

1. In which of the following compounds, the oxidation number of the stated transition metal is zero. **[NSEC-2000]**

(A) $[Ni(CO)_4]$ (B) $[Pt(C_2H_4)Cl_3]$ (C) $[Co(NH_3)_6]Cl_2$ (D) $[Fe(H_2O)_3](OH)_2$

2. Ligands contain : **[NSEC-2001]**

(A) lone pair of electron (B) incomplete octet (C) unpaired electron (D) shared pair of electron

3. Valency bond theory was proposed by : **[NSEC-2001]**

(A) Heitler and London (B) Slater and Mullican (C) Pauling (D) Rutherford

4. e_g orbitals include **[NSEC-2002]**

(A) d_{xy} and d_{yz} (B) d_{yz} and d_{xz} (C) d_{yz} and d_{xz} (D) $d_{x^2-y^2}$ and d_{z^2}

5. The theory which utilises pure electrostatic bonding between metal and ligand is : **[NSEC-2002]**

(A) valency bond theory (B) molecular orbital theory

(C) crystal field theory (D) ligand field theory

6. Dimethyl glyoxime forms a square planar complex with Ni^{2+}. This complex should be **[NSEC-2003]**

(A) diamagnetic (B) paramagnetic having 1 unpaired electron

(C) paramagnetic having 2 unpaired electrons (D) ferromagnetic.

7. A $[M(H_2O)_6]^{2+}$ complex typically absorbs at around 600 nm. It is allowed to react with ammonia to form a new complex $[M(NH_3)_6]^{2+}$ that should have absorption at **[NSEC-2003]**

(A) 800nm (B) 580nm (C) 620nm (D) 320nm.

8. The least stable metal carbonyl as per the bonding considerations should be **[NSEC-2003]**

(A) $Cr(CO)_6$ (B) $Mn(CO)_6$ (C) $Fe(CO)_5$ (D) $Ni(CO)_4$.

9. A coordination complex of type MX_2Y_2 [M = metal ion; X,Y = monodentate ligands], can have either a tetrahedral or a square planar geometry. The maximum number of possible isomers in these two cases are respectively **[NSEC-2003]**

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

10. The blue pigment prussian blue is an iron complex with formula **[NSEC-2003]**

(A) $K_4[Fe(CN)_6]$ (B) $K_2[Fe(CN)_4(NH_3)_2]$ (C) $Fe_4[Fe(CN)_6]_3$ (D) $Na_2[Fe(CN)_5NO]$.

11. When H_2S is passed through a solution containing Cu^{2+} , Cd^{2+} and an excess of cyanide ions, cadmium sulphide precipitates while copper ions remain in solution. This is because **[NSEC-2003]**

(A) Cu^{2+} forms a stable complex with cyanide while Cd^{2+} does not

(B) Cu^{2+} forms a more stable complex with cyanide than Cd^{2+}

(C) Cu^{2+} does not form a sulphide

(D) both CdS and CuS are formed, but CuS is soluble.

12. IUPAC name for $K_3[A\ell(C_2O_4)_3]$ is **[NSEC-2004]**

(A) potassium trioxalatoaluminate (III) (B) potassium aluminiumoxalate

(C) potassium trioxalatealuminium (II) (D) potassium trioxalatealuminium (III)

13. Geometrical isomerism would be expected for which of the following compounds **[NSEC-2005]**
(A) $[Zn(NH_3)_4]^{2+}$ (B) $[Pt(NH_3)_2C1_2]$ (C) $[Pt(NH_3)_3Cl]^+$ (D) $K_2[CuCl_4]$.

14. Co-ordination compounds $[Pt(NH_3)_3(SCN)]$ and $[Pt(NH_3)_3(NCS)]$ are examples of **[NSEC-2005]**
(A) co-ordination isomerism (B) linkage isomerism
(C) optical isomerism (D) hydrate isomerism.

15. The highest molar conductivity will be exhibited by the complex **[NSEC-2005]**
(A) $[Cr(NH_3)_6]Cl_3$ (B) $[Cr(NH_3)_6Cl]Cl_2$ (C) $[Cr(NH_3)_6Cl_2]Cl$ (D) $[Cr(NH_3)_6Cl_3]$.

16. The number of unpaired electrons in the scandium atom is **[NSEC-2006]**
(A) 1 (B) 2 (C) 0 (D) 3.

17. How many isomers are possible for the complex $[Co(en)_2Cl_2]$ (en = ethylene diamine) **[NSEC-2006]**
(A) 4 (B) 2 (C) 6 (D) 3

18. In which of the following compounds is the oxidation number of the transition metal zero? **[NSEC-2007]**
(A) $[Ni(CO)_4]$ (B) $[Pt(C_2H_4)Cl_3$ (C) $[Co(NH_3)_6]Cl_2$ (D) $[Fe(H_2O)_3](OH)_2$

19. $[NiCl_4]^{2-}$ is paramagnetic and therefore its geometry is : **[NSEC-2007]**
(A) pyramidal (B) bi-pyramidal (C) tetrahedral (D) square planar

20. dsp^2 hybridization represents **[NSEC-2007]**
(A) octahedral geometry (B) square-planar geometry
(C) trigonal-bipyramidal geometry (D) square-pyramidal geometry

21. Which isomerism is exhibited by$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$? **[NSEC-2007]**
(A) Ionization (B) Linkage (C) Coordination (D) Polymerization

22. The complex pentaaminecarbonatocobalt (III) chlorides is: **[NSEC-2007]**
(A) $[Co(NH_3)_5CO_3]$ Cl (B) $[Co(NH_2)_5CO_3]Cl$ (C) $[Co(NH_2)_5CO_2]Cl$ (D) $[Co(NH_3)_5CO_2]Cl$

23. According to the Crystal Field Theory, the energy of d_{xy} orbital is lower than $d_{x^2-y^2}$ in an octahedral complex because **[NSEC-2007]**
(A) the d_{xy} orbital near the ligands.
(B) the repulsion between the d_{xy} electrons and ligand electrons is less than that between $d_{x^2-y^2}$ and ligand electrons.
(C) the repulsion between the d_{xy} electrons and ligand electrons is more than that between $d_{x^2-y^2}$ and ligand electrons.
(D) the $d_{x^2-y^2}$ orbital is away the ligands.

24. The orbitals of iron involved in the hybrdization in $Fe(CO)_5$ are **[NSEC-2007]**
(A) s, p_x, p_y, p_z and $d_{x^2-y^2}$ (B) s, p_x, p_y, d_{z^2} and $d_{x^2-y^2}$
(C) s, px, py, pz and d_{z^2} (D) s, p_x, p_z, d_{xy} and $d_{x^2-y^2}$

25. The crystal field stabilization energy (CFSE) in $[Co(SCN)_6]^{3-}$ is : **[NSEC-2007]**
(A) 24 Dq (B) 18 Dq (C) 4 Dq (D) 0 Dq

26. Metal carbonyls have the metal ions in zero or unusually lower oxidation states. This is because : **[NSEC-2007]**
(A) carbonyl ligand is reducing in nature. (B) carbonyl is a highly electron rich ligand.
(C) carbonyl is a strongly o –bonding ligand. (D) carbonyl is a strongly p -acidic ligand.

27. In which of the following transition metal ion complexes, the colour in not due to d-d transition ? **[NSEC-2008]**
(A) $[Ti(H_2O)_6]^{3+}$ and $[CoF_6]^3$ (B) $[Ti(H_2O)_6]^{3+}$ and $[MnO_4]$
(C) (C) $[CoF_6]^3$ and $[CrO_4]^2$ (D) $[MnO_4]$ and $[CrO_4]^2$

28. Among the following, the chiral complex is – **[NSEC-2009]**
(A) $[Cr(OX)_3]^{3-}$ (B) cis-$[PtCl_2(en)]$ (C) cis-$[RhCl_2(NH_3)_4]^+$ (D) trans-$[PtCl_2(en)]$

29. The species having tetrahedral shape is : **[NSEC-2009]**
(A) $[PdCl_4]^{2-}$ (B) $[Ni(CN)_4]^{2-}$ (C) $[Pd(CN)_4]^{2-}$ (D) $[Ni(Cl)_4]^{2-}$

30. The types of isomerism shown by $Co(NH_3)_4Br_2Cl$ are – **[NSEC-2009]**
(A) Geometrical and ionization (B) Optical and ionization
(C) Geometrical and optical (D) Geometrical only

31. The complex that exhibits Co-ordination isomerism is **[NSEC-2010]**
(A) $[Cr(NCS)(H_2O)_5]^{2+}$ (B) $[Cr(NH_3)_6]Cl_3$
(C) $[Cr(NH_3)_6][Co(CN)_6]$ (D) $[CoCl_2(NH_3)_4]Cl.H_2O$

32. The strong field ligand is : **[NSEC-2010]**
(A) SCN^- (B) NO_2 (C) I^- (D) S^{2-}

33. The IUPAC name of complex $[Cu(en)_2(H_2O)_2]^+$ is **[NSEC-2011]**
(A) ethylene diamine Cu(II) dihydrate (B) diaquobis (ethylenediamine) Cu(II) ion
(C) diaquobisdiethylamine Cu(II) ion (D) diaquobis(ethylenediamine) cuprate(II)

34. The electronic spectrum of $[Ni(H_2O)_6]^{++}$ shows a band at 8500 cm^{-1} due to d-d transition. $[Ph_4As]_2[NiCl_4]$ will have such a transition in cm^{-1} at **[NSEC-2011]**
(A) 3778 (B) 8500 (C) 4250 (D) 850

35. Dimethyl glyoxime forms a square planar complex with Ni^{2+}. This complex should be : **[NSEC-2011]**
(A) diamagnetic (B) paramagnetic having 1 unpaired electron
(C) paramagnetic having 2 unpaired electrons (D) ferromagnetic

36. The IUPAC name of $[Co(ONO)(NH_3)_5Cl_2]$ is : **[NSEC-2012]**
(A) pentamminenitrocobalt(II)chloride (B) pentamminenitrosocobalt(III)chloride
(C) pentamminenitritocobalt(III)chloride (D) pentammineoxo-nitrocobalt(III)chloride

37. In which of the following compounds is the oxidation number of the transition metal, zero ? **[NSEC-2013]**
(A) $[Fe(H_2O)_3](OH_2)$ (B) $[Co(NH_3)_6]Cl_2$ (C) $[Ni(CO_4)]$ (D) $[Pt(C_2H_4)Cl_3]$

38. The metal carbonyl which is paramagnetic is **[NSEC-2013]**
(A) $Ni(CO)_4$ (B) $V(CO)_6$ (C) $Cr(CO)_6$ (D) $Fe(CO)_5$

39. High spin complexes having coordination number ' 6 ' are usually formed through **[NSEC-2013]**
(A) sp^3d^2 hybridisation (B) d^2sp^3 hybridisation (C) sp^3 hybridisation (D) sp^3d hybridisation

40. The complex having zero crystal field stabilization energy is **[NSEC-2014]**
(A) $[Mn(H_2O)_6]^{3+}$ (B) $[Fe(H_2O)_6]^{3+}$ (C) $[Co(H_2O)_6]^{2+}$ (D) $[Co(H_2O)_6]^{3+}$

41. When any solution passes through a cation exchange resin that is in acidic form, H ion of the resin is replaced by cations of the solution. A solution containing 0.319 g of an isomer with molecular formula $CrCl_3.6H_2O$ is passed through a cation exchange resin in acidic form. The eluted solution requires 19 cm^3 of 0.125 N NaOH. The isomer is **[NSEC-2015]**
(A) triaquatrichloro chromium (III) chloride trihydrate
(B) hexaaqua chrominum (III) chloride
(C) pentaaquamonochloro chromium (III) chloride monohydrate
(D) tetraaquadichloro chromium (III) chloride dihydrate

42. A person having osteoporosis is suffering from lead poisoning. Ethylene diamine tetra acetic acid (EDTA) is administered for this condition. The best form of EDTA to be used for such administration is - **[NSEC-2015]**
(A) EDTA (B) tetrasodium salt
(C) disodium salt (D) calcium dihydrogen salt

43. Four statements for the following reaction are given below **[NSEC-2015]**
$[CoCl_2(NH_3)_4]^+ + Cl^- \rightarrow [CoCl_3(NH_3)_3] + NH_3$
(i) only one isomer is produced if the reactant complex ion is a trans isomer
(ii) three isomers are produced if the reactant complex ion is a cis isomer
(iii) two isomers are produced if the reactant complex ion is a trans isomer
(iv) two isomers are produced if the reactant complex ion is cis isomer The correct statements are
(A) I and II (B) III and IV (C) I and IV (D) II and III

44. The complex that shows optical activity is **[NSEC-2015]**
(A) trans-$[CoCl_2(en)_2]^+$ (B) cis-$[CoCl_2(en)_2]^+$
(C) trans-$[PtCl_2(NH_3)_2]$ (D) $[CoCl_2(NH_3)_2(en)]^+$

45. For $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$, the statement that is correct is : **[NSEC-2015]**
(A) both are colored
(B) both are colorless
(C) $[FeF_6]^{3-}$ is colored and $[CoF_6]^{3-}$ is colorless
(D) $[FeF_6]^{3-}$ is colorless and $[CoF_6]^{3-}$ is colored

46. Which of the following statements about ammonium cerium (IV) nitrate, $(NH_4)_2[Ce(NO_3)_6]$ is false? **[NSEC-2016]**
(A) NO_3^- acts as a monodentate ligand.
(B) The Ce atom has a coordination number of 12.
(C) The shape of the complex ion is icosahedron
(D) The solution is used as oxidizing agent.

47. Which one of the following reactions is correct ? **[NSEC-2016]**
(A) $[Fe(CO)_5] + 2NO \rightarrow [Fe(CO)_2(NO)_2] + 3CO$ (B) $[Fe(CO)_5] + 2NO \rightarrow [Fe(CO)_3(NO)_2] + 2CO$
(C) $[Fe(CO)_5] + 3NO \rightarrow [Fe(CO)_2(NO)_3] + 3CO$ (D) $[Fe(CO)_5] + 3NO \rightarrow [Fe(CO)_3(NO)_3] + 2CO$

48. How many isomers are possible for complex $[Co(ox)_2Cl_2]^+$? **[NSEC-2016]**
(A) 1 (B) 3 (C) 2 (D) 4

49. In which of the following complexes the metal ion has the lowest ionic radius ? **[NSEC-2016]**
(A) $[Ti(H_2O)_6]^{2+}$ (B) $[V(H_2O)_6]^{2+}$
(C) $[Cr(H_2O)_6]^{2+}$ (D) $[Mn(H_2O)_6]^{2+}$

50. IUPAC name of complex ion $[CrCl_2(ox)_2]^{3-}$ is **[NSEC-2017]**
(A) dichlorodioxalatochromium (III)
(B) dioxalatodichlorochromate(III)
(C) dichlorodioxalatochromate(III)
(D) bisoxalaeodichlorochromate(III)

51. The complex ion that does not have d electrons in the metal atom is **[NSEC-2017]**
(A) $[MnO_4]^-$ (B) $[Co(NH_3)_6]^{3+}$ (C) $[Fe(CN)_6]^{3-}$ (D) $[Cr(H_2O)_6]^{3+}$

52. The C–O bond length is the shortest in : **[NSEC-2018]**
(A) $[Cr(CO)_6]$ (B) $[Mo(CO)_6]$ (C) $[Mn(CO)_6]^+$ (D) $[V(CO)_6]^-$

53. The spin-only magnetic moments of $[Fe(NH_3)_6]^{3+}$ and $[FeF_6]^{3-}$ (in units of BM) respectively are **[NSEC-2018]**
(A) 1.73 and 1.73 (B) 5.92 and 1.73 (C) 1.73 and 5.92 (D) 5.92 and 5.92

54. The alkene ligand ($\pi - C_2R_4$) is both a 'σ' donoar and a 'π' acceptor, similar to the CO ligand in metal carbonyls, and exhibits synergic bonding with metals. Correct order of C–C bond length in $K[PtCl_3(\pi - C_2R_4)]$ complexes in which R = H, F or CN is **[NSEC-2019]**
(A) H > F > CN (B) H > CN > F (C) CN > F > H (D) F > H > CN

55. The correct order of CFSE among $[Zn(NH_3)_4]^{2+}$ and $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ is **[NSEC-2019]**
(A) $[Co(NH_3)_6]^{3+} > [Co(NH_3)_6]^{2+} > [Zn(NH_3)_4]^{2+}$
(B) $[Zn(NH_3)_4]^{2+} > [Co(NH_3)_6]^{2+} > [Co(NH_3)_6]^{3+}$
(C) $[Co(NH_3)_6]^{3+} > [Zn(NH_3)_4]^{2+} > [Co(NH_3)_6]^{2+}$
(D) $[Co(NH_3)_6]^{2+} > [Co(NH_3)_6]^{3+} > [Zn(NH_3)_4]^{2+}$

56. The number of stereoisomers is maximum for **[NSEC-2019]**
(A) $[Co(en)_3]^{3+}$ (B) $[Co(en)_2ClBr]^+$ (C) $[Co(NH_3)_4Cl_2]^+$ (D) $[Co(NH_3)_4ClBr]^+$

57. $MnCl_2.4H_2O$ (molar mass = 198 g mol^{-1}) when dissolved in water forms a complex of Mn^{2+}. An aqueous solution containing 0.400 g of $MnCl_2.4H_2O$ was passed through a column of a cation exchange resin and the acid solution coming out was neutralized with 10 mL of 0.20 M NaOH. The formula of the complex formed is **[NSEC-2019]**
(A) $[Mn(H_2O)_4Cl_2]$ (B) $[Mn(H_2O)_6]Cl_2$
(C) $[Mn(H_2O)_5Cl]Cl$ (D) $Na[Mn(H_2O)_3Cl_3]$

58. The correct IUPAC name of the compound, $[Pt(py)_4][Pt(Br)_4]$ is **[NSEC-2019]**
(A) tetrapyridineplatinum(II) tetrabromidoplatinate(II)
(B) tetrabromidoplatinum(IV) tetrapyridineplatinate(II)
(C) tetrabromidoplatinate(II) tetrapyridineplatinum(II)
(D) tetrapyridineplatinum(IV) tetrabromidoplatinate(IV)

59. Among the following, the complex ion/s that will have a magnetic moment of 2.82 B.M. is/are **[NSEC-2019]**
I.$[Ni(CO)_4]$ II. $[NiCl_4]^{2-}$ III. $[Ni(H_2O)_6]^{2+}$ IV. $[Ni(CN)_4]^{2-}$
(A) I and IV (B) II only (C) II and III (D) II, III and IV

PART - 4 : ADDITIONAL PROBLEMS

THEORY

Introduction :

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

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

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

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

Addition Compounds :

They are formed by the combination of two or more stable compounds in stoichiometric ratio.

Addition Compounds

Double salts | **Coordination compounds (Complexes)**

Double salts

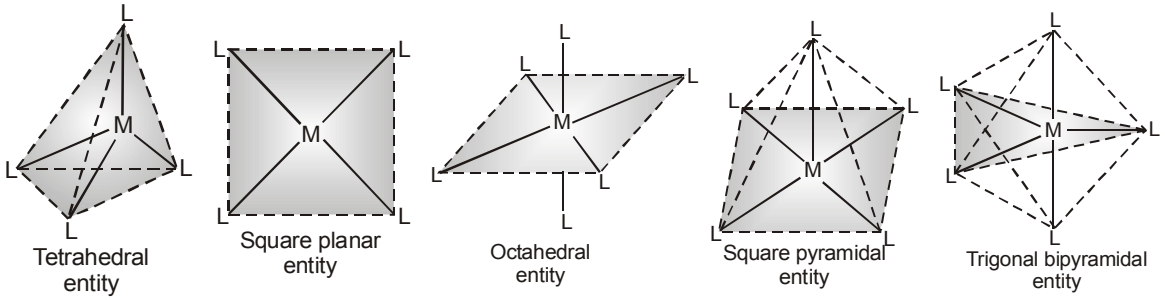
Those addition compounds which lose their identity in solutions are called **double salts**. For example, when K_2SO_4 solution is added to $Al_2(SO_4)_3$ solution, the species formed when dissolved in water gives tests of K^+, Al^{3+} and SO_4^{2-} ions.

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O\ (aq.) \rightleftharpoons 2K^+\ (aq.) + 2Al^{+3}\ (aq.) + 4SO_4^{2-}\ (aq.)$$

Other examples are carnallite ($KCl.\ MgCl_2 \cdot 6H_2O$), Mohr's salt [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$], potash alum [$KAl(SO_4)_2.12H_2O$] or [$K_2SO_4.Al_2(SO_4)_3.24H_2O$] etc.

Coordination Polyhedron

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion gives a coordination polyhedron about the central atom. Figure below shows the shapes of tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal coordination polyhedra. $[Co(NH_3)_6]^{3+}$ has an octahedral geometry, while $[PtCl_4]^{2-}$ and $Ni(CO)_4$, are square planar and tetrahedral, respectively.



Writing the name of Polynuclear Coordination Compounds :

(i) **Ist case :** The name of a bridge complex is prefixed by μ–.
If the situation on both sides of the bridge is symmetrical then we can write the name of remaining complex at one place like

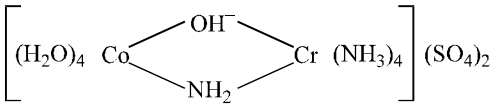
$$\left[(NH_3)_5\,Cr-OH-Cr\,(NH_3)_5\right]^{5+}\;Cl_5$$

μ–hydroxidobis(pentaamminechromium(III)) chloride
OR we could also have written the name of one side of the bridge ligand and then the name of bridge ligand and then the other side of the bridge, like

$$\left[(NH_3)_5\,Cr-OH-Cr\,(NH_3)_5\right]^{5+}\;Cl_5$$

pentaamminechromium(III)–μ–hydroxidopentaamminechromium(III) chloride

(ii) **IInd case :**
If the compound is unsymmetrical on both sides of the bridge then we have to follow the second rule, i.e. write the name of one side then that of the bridge and then that of the second side, like



tetraaquacobalt(III)–μ–amido–μ–hydroxidotetramminechromium(III) sulphate

SUBJECTIVE QUESTIONS

1. What is the coordination number and the oxidation state of the metal in each of the following complexes?
(a) $[ZrF_8]^{4-}$ (b) $K_3[Cr(C_2O_4)_2Cl_2]$

2. Write the name of the following ligands and classify their denticity
(a) o-phen (b) NOS^-

3. Name the $K[PtCl_3(\eta^2\text{–}C_2H_4)]$ compound.

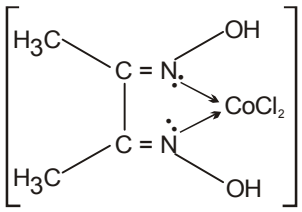
4. Write down the formulae of the following compounds
(a) tetraamminecobalt(III)-μ-amido-μ-hydroxidobis(ethylenediamine)cobalt(III) chloride
(b) bis(η^5-cyclopentadienyl)iron(II)
(c) tetraammineaquacobalt(III)-μ-cyanidotetraamminebromidocobalt(III)

5. Calculate the EAN of central atom in the following complexes
(a) $[Fe(CO)_2(NO)_2]$ (b) $[Fe(C_5H_5)_2]$

6. Draw the structures of the following metal carbonyls
(a) $[Co_2(CO)_8]$ (b) $[Fe_2(CO)_9]$

ONLY ONE OPTION CORRECT TYPE

7. The correct IUPAC name of the complex is :



(A) Dichloridodimethylglyoximecobalt(II)
(B) Bis(dimethyglyoxime)dichloridocobalt(II)
(C) Dimethylglyoximecobalt(II) chloride
(D) Dichlorido(dimethylglyoximato)cobalt(II)

8. A co-ordination complex has the formula $PtCl_4.2KCl$. Electrical conductance measurements indicate the presence of three ion in one formula unit. Treatment with $AgNO_3$ produces no precipitate of AgCl. What is the co-ordination number of Pt in this complex ?
(A) 5 (B) 6 (C) 4 (D) 3

9. Which of the following complexes produces three moles of silver chloride when its one mole is treated with excess of silver nitrate ?
(A) $[Cr(H_2O)_3Cl_3]$ (B) $[Cr(H_2O)_4Cl_2]Cl$ (C) $[Cr(H_2O)_5Cl]Cl_2$ (D) $[Cr(H_2O)_6]Cl_3$

10. The number of chloride ions which would be precipitated when one mole of the complex $PtCl_4.4NH_3$ is treated with silver nitrate is:(here coordination number of platinum is 6).
(A) four (B) one (C) three (D) two

11. A coordination 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 moles of ions in an aqueous solution. The aqueous solution on treatment with an excess of $AgNO_3$ gives two moles of AgCl as a precipitate. The formula of 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) $[Co\,(NH_3)_5]\,[(NO_2)_2Cl_2]$

12. From the stability constant (hypothetical values), given below, predict which is the most stable complex ?
(A) $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$, $K = 4.5 \times 10^{11}$
(B) $Cu^{2+}\ 4CN^- \longrightarrow [Cu(CN)_4]^{3-}$, $K = 2.0 \times 10^{27}$
(C) $Cu^{2+} + 2en \longrightarrow [Cu(en)_2]^{2+}$, $K = 3.0 \times 10^{15}$
(D) $Cu^{2+} + 4H_2O \longrightarrow [Cu(H_2O)_4]^{2+}$, $K = 9.5 \times 10^{8}$

13. In Ziesses salt C = C bond length is :

Note : $\left\{\begin{matrix} C-C \text{ bond length in ethane is } 1.54\text{Å} \\ C=C \text{ bond length in ethene is } 1.34\text{Å} \\ C\equiv C \text{ bond length in ethyne is } 1.20\text{Å} \end{matrix}\right\}$

(A) 1.37Å (B) 1.19Å (C) 1.87Å (D) 1.34 Å

14. Which is not a π-bonded complex ?
(A) Zeise's salt (B) Ferrocene
(C) bis(benzene) chromium (D) Tetraethyl lead

15. What is wrong about the compound $K\,[Pt\,(\eta^2 - C_2H_4)\,Cl_3]$?
(A) It is called Zeise's salt. (B) It is π bonded complex.
(C) Oxidation number of Pt is +4. (D) Four ligands surround the platinum atom.

16. In $K_4[Fe(CN)_6]$, Fe is in the form of
(A) An atom (B) Neutral complex (C) Cationic complex (D) Anionic complex

17. Complex ion $[\,FeN_3(O_2)(SCN)_4]^{4-}$ is named as : (coordination number of central metal ion in complex is six)
(A) azidosuperoxidotetrathiocyanato-S-ferrate(II) (B) azidodioxygentetrathiocyanatoferrate(III)
(C) azidoperoxidotetrathiocyanato-S-ferrate(II) (D) azidodioxidotetrathiocyanato-S-ferrate(III)

18. The IUPAC name of $K_2[Cr(CN)_2O_2(O)_2(NH_3)]$ is :
(A) potassium amminecyanoperoxodioxochromatic(VI).
(B) potassium amminedicyanoperoxodioxochromium(VI).
(C) potassium amminecyanoperoxodioxochromium(VI).
(D) potassium amminedicyanodioxoperoxochromate(VI).

19. Consider the following statements:
According the Werner's theory.
(1) Ligands are connected to the metal ions by ionic bonds.
(2) Secondary valencies have directional properties
(3) Secondary valencies are non-ionisable
Of these statements:
(A) 1, 2 and 3 are correct (B) 2 and 3 are correct
(C) 1 and 3 are correct (D) 1 and 2 are correct

20. Which of the following is correct for both the following coordination compounds ?
(I) $CoCl_3.6NH_3$ and (II) $PtCl_4.5NH_3$
(A) They give white precipitate with $AgNO_3$ solution.
(B) They have different primary valencies for the central metal ions.
(C) Both (A) and (B)
(D) None of these

21. In the complex $[SbF_5]^{2-}$, sp^3d hybridisation is present. Geometry of the complex is :
(A) Square pyramidal (B) Square bipyramidal (C) Tetrahedral (D) Square planar

22. Crystal field stabilization energy for high spin d^4 octahedral complex is :
(A) $-0.6\,\Delta_0$ (B) $-1.8\,\Delta_0$ (C) $-1.6\,\Delta_0 + P$ (D) $-1.2\,\Delta_0$

23. $[(NH_3)_5Co–O–O–Co(NH_3)_5]^{+4} \xrightarrow[\text{oxidise}]{[S_2O_8]^{2-}} [(NH_3)_5Co–O–O–Co(NH_3)_5]^{+5}$
Brown Green

The magnetic moment of green complex is 1.7 BM & for brown complexes magnetic moment is zero. (O–O) is same in all respect in both the complexes.
The O.S. of Co in brown complex & green complex respectively are-

(A)	III III brown	&	IV III green	(B)	III II brown	&	III III green
(C)	III III brown	&	III II green	(D)	III IV brown	&	III III green

24. Which one of the following will be able to show cis-trans isomerism ?
(A) Ma_3b (B) $M(AA)_2$ (C) M(AB)(CD) (D) Ma_4

25. Which of the following compounds show optical isomerism ?
1. cis - $[Co(NH_3)_4Cl_2]^+$ 2. trans - $[Co(en)_2Cl_2]^+$
3. cis - $[Co(en)_2Cl_2]^+$ 4. $[Co(en)_3]^{3+}$
Select the correct answer using the codes given below :
(A) 1 and 2 (B) 2 and 3 (C) 3 and 4 (D) 1, 3 and 4

MATCH THE COLUMN

26.

Column - I	Column - II
(A) $[Fe(en)_3]^{3+}$	(p) d^2sp^3 hybridisation of central metal
(B) $[Co(ox)_3]^{3-}$	(q) sp^3d^2 hybridisation of central metal
(C) $[Cr(CN)_6]^{3-}$	(r) paramagnetic
(D) $[NiCl_6]^{4-}$	(s) diamagnetic
	(t) metal ion has +3 oxidation state

SINGLE AND DOUBLE VALUE INTEGER TYPE

27. What is the coordination number of metal in $[M(trien)(dipy)]^{\pm n}$?

28. Out of the following. How many have correct IUPAC naming :
(1) $[Ni(CN)_4]^{2-}$ - Tetracyanonickel (II) ion
(2) $[Pt(Py)_4][PtCl_4]$ - Tetrapyridine platinum (II) tetrachloride platinate (II)
(3) $[Ni(dmg)_2]$ - Bis(dimethylglyoximato) nickel (II)
(4) $K_3[Fe(CN)_5NO]$ - Potassium pentacyanonitrosylferrate (II)
(5) $[Fe(CO)_5]$ - Pentacyanocarbonyl Ferrate (O)
(6) $K_2[HgI_4]$ - Potassium tetraiodidomercurate (II)
(7) $[Pt(NH_3)_4][CuCl_4]$ - Tetraammineplatinum (IV) tetrachlorido cuprate (II)
(8) $[Cu(gly)_2]$ - Diglycinate copper (II)
(9) $K_4[Fe(CN)_6]$ - Potassium hexacyanidoferrate (II)
(10) $[Pt(NH_3)_6]Cl_4$ - Hexaammine platinum (IV) chloride.

29. How many of the given complexes follow E.A.N. rule ?
(a) $Fe(CO)_5$ (b) $Co_2(CO)_8$ (c) $Fe(C_5H_5)_2$ (d) $[K_3Fe(CN)_6]$
(e) $Fe(NO)_2(CO)_2$ (f) $[CoF_6]^{4-}$

30. A name of neutral complex is :
Bis(acetyl acetanato) methylcyanidethiocyanato-s-iron (Y)
The 'Y' is O.N. of metal then calculate sum of primary and secondary valency ?

31. $Na_2[Cr(NO)(NH_3)(C_2O_4)_2]$, u = $\sqrt{3}$ B.M., Then total no. of electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals of metal :

32. If CFSE increases by 30% and 40% respectively for Co^{3+} to Rh^{3+} to Ir^{3+} , then the total increase in CFSE for Ir^{3+} with respect to Co^{3+} is .....

33. For the $[Cr(H_2O)_6]^{2+}$ ion, the mean pairing energy P is found to be 23500 cm^{-1}. The magnitude of Δ_0 is 13900 cm^{-1}. Calculate the C.F.S.E (cm^{-1})for this complex ion corresponding to high spin state (x) and low spin state (y).

Write your answer as $\left(\frac{y-x}{100}\right)$

34. A complex is prepared by mixing $CoCl_3$ & NH_3 0.1 M solution of the complex was found to freeze at –0.372ºC. Total geometrical isomers of complex are x. (Molar depression constant of water = 1.86ºC/m)
Report your answer by multiplying x with 6.

35. Calculate total number of geometrical, optical and structural isomers in the compound.
$[Rh(en)_2(NO_2)_2]NO_3$

36. What is the EAN value of $W(CO)_6$ carbonyl compounds ?

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

37. Which of the following statement(s) is /are correct ?
(A) $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$ and $[Co(NO_2)_6]^{3-}$ are diamagnetic involving d^2sp^3 hybridisation.
(B) $[Zn(NH_3)_4]^{2+}$, $[FeCl_4]^-$ and $[Ni(CO)_4]$ are diamagnetic involving sp^3 hybridisation.
(C) The magnetic moment of $[Fe(H_2O)_6]^{3+}$ is 5.92 B.M and that of $[Fe(CN)_6]^{3-}$ is 1.73.
(D) The magnetic moment of $K_4[MnF_6]$ and $K_3[FeF_6]$ are same.

38. Consider the following statements :
S_1 : Generally square planar complexes show geometrical isomerism but do not exhibit optical isomerism because they do not possess plane of symmetry.
S_2 : $\Delta_t = \frac{4}{9}\Delta_o$
S_3 : In octahedral complexes each electron entering the t_{2g} orbitals stabilizes the complex ion by $0.4\ \Delta_o$ and each electron entering the e_g orbital destabilizes the complex by an amount of $0.6\ \Delta_o$.
Select the correct statement from the codes given below.
(A) S_1 and S_3 are correct (B) S_2 and S_3 are correct
(C) S_1 is incorrect (D) S_2 and S_3 are incorrect

39. Select the correct statement (s) .
(A) $[Co(EDTA)]^-$ has two optical isomers.
(B) $[Co(NH_3)_5(NO_2)]^{2+}$ show linkage isomerism.
(C) For [Pt (NH_3)BrClI(NO_2)py], theoretically fifteen different geometrical isomers are possible.
(D) $[Cr(H_2O)_4Cl_2]Cl_2.2H_2O$ is an example of hydrate as well as ionisation isomerism.

40. Which of the following are π-bonded organometallic compounds ?
(A) Ferrocene (B) Diethyl zinc
(C) Ethylmagnesium iodide (D) Bis(benzene) chromium(0)

COMPREHENSION

Comprehension

Double salts are addition compounds which lose their identity in aqueous solution whereas complexes which are also addition compounds do not lose their identity in aqueous solution. The coordination compounds show isomerism and find applications in photography, qualitative analysis, metallurgy, water purification and in the treatment of various diseases.

41. Which of the following statements is incorrect ?
(A) Alum is a double salt.
(B) EDTA salt of calcium is used in the treatment of lead poisoning.
(C) Effective atomic number of the metals in complexes $[Ni(CO)_4]$ and $[Fe(CN)_6]^{4-}$ is same.
(D) Chloridotris (triphenylphosphine) rhodium(I) is effective heterogeneous catalyst for hydrogenation of alkenes.

42. Which of the following statements is true for the complex, $[Co(NH_3)_4Br_2]NO_2$?
(A) It shows ionisation, linkage and geometrical isomerism.
(B) It does not show optical isomerism because its cis and trans forms each have at least one plane of symmetry.
(C) Its ionisation isomers cannot be differentiated by silver nitrate solution.
(D) (A) and (B) both.

43. Choose the correct option for the complex $[PtCl_2(en)_2]^{2+}$.
(A) Platinum is in +2 oxidation state
(B) Racemic mixture is obtained on mixing mirror images of its trans form in 1 : 1 molar ratio.
(C) It has two five membered chelating rings
(D) (B) and (C) both

RRP ANSWER KEY

PART- 1

1.	(C)	**2.**	(D)	**3.**	(B)	**4.**	(D)	**5.**	(A)	**6.**	(D)	**7.**	(A)
8.	(D)	**9.**	(B)	**10.**	(C)	**11.**	(A)	**12.**	(A)	**13.**	(B)	**14.**	(D)
15.	(B)	**16.**	(C)	**17.**	(B)	**18.**	(C)	**19.**	(D)	**20.**	(A)	**21.**	3
22.	02.84	**23.**	86	**24.**	0.0024	**25.**	05.92						

PART 2

1.	(D)	**2.**	(C)	**3.**	(A)	**4.**	(A)	**5.**	(ABCD)	**6.**	(A,B,C,D)	**7.**	(A,D)
8.	(A,C)	**9.**	(C,D)	**10.**	(A,B,D)	**11.**	(A,C,D)	**12.**	(B,C,D)	**13.**	5	**14.**	4
15.	0	**16.**	7	**17.**	3	**18.**	8						

PART - 3

1.	(A)	**2.**	(A)	**3.**	(A)	**4.**	(D)	**5.**	(C)	**6.**	(A)	**7.**	(D)
8.	(B)	**9.**	(A)	**10.**	(C)	**11.**	(B)	**12.**	(A)	**13.**	(B)	**14.**	(B)
15.	(A)	**16.**	(A)	**17.**	(D)	**18.**	(A)	**19.**	(C)	**20.**	(B)	**21.**	(C)
22.	(A)	**23.**	(B)	**24.**	(C)	**25.**	(A)	**26.**	(D)	**27.**	(D)	**28.**	(A)
29.	(D)	**30.**	(A)	**31.**	(C)	**32.**	(B)	**33.**	(B)	**34.**	(A)	**35.**	(A)
36.	**(Bonus)**	**37.**	(C)	**38.**	(B)	**39.**	(A)	**40.**	(B)	**41.**	(C)	**42.**	(D)
43.	(C)	**44.**	(B)	**45.**	(D)	**46.**	(A)	**47.**	(A)	**48.**	(B)	**49.**	(B)
50.	(C)	**51.**	(A)	**52.**	(C)	**53.**	(C)	**54.**	(C)	**55.**	(A)	**56.**	(B)
57.	(C)	**58.**	(A)	**59.**	(C)								

PART - 4

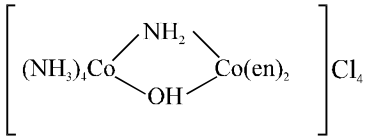
1. The coordination number of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ions i.e. the number of ligand donor atoms to which the metal is directly attached.The oxidation number of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.

	Complex	**Coordination Number**	**Oxidation State**
(a)	$[ZrF_8]^{4-}$	8	4
(b)	$K_3[Cr(C_2O_4)_2Cl_2]$	6	3

2. (a) 1, 10-diaminophenanthrene, bidentate (b) thionitrito, monodentate

3. $K[PtCl_3(C_2H_4)]$ Potassium trichlorido(η^2–ethylene)platinate(II)

4. (a) Tetraamminecobalt(III)-μ-amido-μ-hydroxidobis(ethylenediamine or ethane-1,2-diamine)cobalt(III) chloride

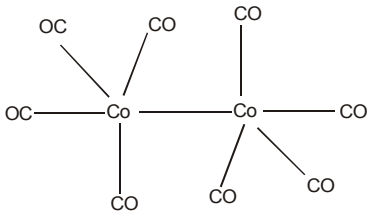


(b) Bis(η^5-cyclopentadienyl)iron(II) $[Fe(\eta^5\text{–}C_5H_5)_2]$

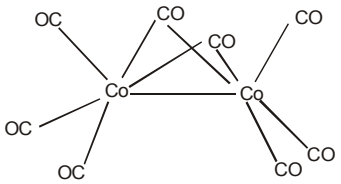
(c) Tetraammineaquacobalt(III)-μ-cyanidotetraamminebromidocobalt(III) $[(NH_3)_4(H_2O)Co\text{–}CN\text{–}Co(NH_3)_4Br]^{4+}$

5. (a) 36 (j) 36

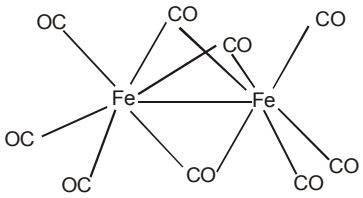
6. (a)



OR



(b)



7.	(A)	**8.**	(B)	**9.**	(D)	**10.**	(D)	**11.**	(C)	**12.**	(B)	**13.**	(A)
14.	(D)	**15.**	(C)	**16.**	(D)	**17.**	(A)	**18.**	(D)	**19.**	(B)	**20.**	(C)
21.	(A)	**22.**	(A)	**23.**	(A)	**24.**	(C)	**25.**	(C)				
26.	(A - p,r,t); (B - p,s,t); (C - p,r,t); (D - q,r)												
27.	6	**28.**	5	**29.**	4	**30.**	09	**31.**	Zero	**32.**	82	**33.**	96
34.	12	**35.**	15	**36.**	86	**37.**	(A,C,D)	**38.**	(B,C)	**39.**	(A,B,C)	**40.**	(A,D)
41.	(D)	**42.**	(B)	**43.**	(C)								