

COORDINATION COMPOUNDS

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JEE(Advanced) Syllabus

Nomenclature of mononuclear coordination compounds, cis-trans and ionisation isomerisms, hybridization and geometries of mononuclear coordination compounds (linear, tetrahedral, square planar and octahedral).

JEE(Main) Syllabus

Introduction to co-ordination compounds, Werner's theory; ligands, co-ordination number, denticity, chelation; IUPAC nomenclature of mononuclear co-ordination compounds, isomerism; Bonding-Valence bond approach and basic ideas of Crystal field theory, colour and magnetic properties; Importance of co-ordination compounds (in qualitative analysis, extraction of metals and in biological systems).

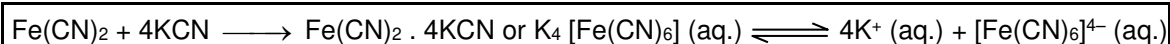


Coordination Compounds

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

Coordination Compounds :

Those addition compounds which retain their identity (i.e. doesn't lose their identity) in solution are called **coordination compounds**. For example, when KCN solution is added to $\text{Fe}(\text{CN})_2$ solution, the species formed when dissolved in water no longer gives tests of Fe^{2+} and CN^- .



Other examples are, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 (\text{aq.}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+} (\text{aq.}) + \text{SO}_4^{2-} (\text{aq.})$
 $\text{K}_2[\text{Zn}(\text{CN})_4] (\text{aq.}) \rightleftharpoons 2\text{K}^+ (\text{aq.}) + [\text{Zn}(\text{CN})_4]^{2-} (\text{aq.})$

Coordination compounds are also acid-base adducts and are frequently called complexes or, if charged then complex ions.

D1 Coordination compound is defined as a species in which metal atom or ion is attached to group of neutral molecules / ions by coordinate covalent bonds.

Coordination Entity/Coordination Sphere :

A coordination entity constitutes a central atom/ion, usually of a metal, to which are attached a fixed number of other atoms or groups each of which is called a ligand. Ligand may be neutral or charged. Examples being: $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{PtCl}_4]^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{NiCl}_2(\text{OH}_2)_4]$.

D2 The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively called as **coordination sphere**.

Note : The remaining ions apart from complex ions i.e. outside the coordination sphere are called counter ions, free ions or ionisable ions. For example, in $\text{K}_4[\text{Fe}(\text{CN})_6]$, the potassium is counter ion of coordination entity $[\text{Fe}(\text{CN})_6]^{4-}$.

D3 Central Atom/ion :

In a coordination entity—the atom/ion around which a fixed number of ligands are bound in a definite geometrical arrangement, is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[\text{NiCl}_2(\text{OH}_2)_4]$, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ are Ni^{2+} , Co^{3+} and Fe^{3+} , respectively. These central atoms / ions are also referred to as Lewis acids since they accept lone pairs from the ligands.

D4 Ligands :

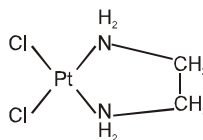
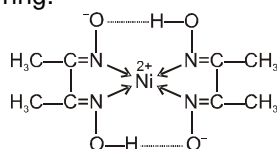
The neutral molecules, anions or cations which are directly linked with central metal atom or ion in the coordination entity are called ligands.

These may be simple ions such as Br^- , small molecules such as H_2O or NH_3 , larger molecules such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or even macromolecules such as proteins.

When a ligand is attached to a metal ion through a single donor atom, as with Cl^- , H_2O or NH_3 , the ligand is said to be unidentate. Similarly when a ligand is bound through two donor atoms (in a single ligand), as in $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethane-1, 2-diamine) or $\text{C}_2\text{O}_4^{2-}$ (oxalate), the ligand is said to be bidentate and when several donor atoms are present in a single ligand as in $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or ethylenediaminetetraacetic acid (EDTA), the ligand is said to be polydentate.

D5 Chelate ligand :

Chelate ligand is a di or polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring.

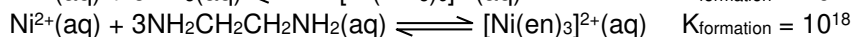
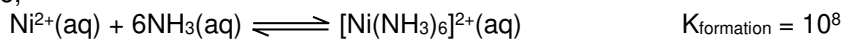




D6 Chelation : The complex formed is referred to as a chelate complex and the process of chelate formation is called chelation.

The number of such ligating groups is called the denticity of the ligand. Chelate rings may have any number of atoms; the most common contain five or six atoms, including the metal ion. Smaller rings have smaller angles and distances that lead to strain; larger rings frequently result in crowding both within the ring and between adjoining ligands. Some ligands can form more than one ring; ethylene diaminetetracetate (EDTA) can form five by using the four carboxylate groups and the two amine nitrogens as given in the structures.

The chelate complexes are more stable than similar complexes containing unidentate ligands. The greater stability of the chelate complex in comparison to normal complex is called chelate effect. For example,



The five and six membered rings are more stable.

Denticity and Chelation :

Tab1 Common Monodentate Ligands

Common Name	IUPAC Name	Formula
methyl isocyanide	methyylisocyanide	CH_3NC
triphenyl phosphine	triphenyl phosphine/triphenyl phosphane	PPh_3
pyridine	pyridine	$\text{C}_5\text{H}_5\text{N}$ (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
fluoro	fluoro or fluoro*	F^-
chloro	chloro or chlorido*	Cl^-
bromo	bromo or bromido*	Br^-
iodo	iodo or iodido*	I^-
cyano	cyanido or cyanido-C* (C-bonded)	CN^-
isocyano	isocyanido or cyanido-N* (N-bonded)	NC^-
thiocyano	thiocyanato-S(S-bonded)	SCN^-
isothiocyano	thiocyanato-N(N-bonded)	NCS^-
cyanato (cyanate)	cyanato-O (O-bonded)	OCN^-
isocyanato (isocyanate)	cyanato-N (N-bonded)	NCO^-
hydroxo	hydroxo or hydroxido*	OH^-
nitro	nitrito-N (N-bonded)	NO_2^-
nitrito	nitrito-O (O-bonded)	ONO^-
nitrate	nitrate	NO_3^-
amido	amido	NH_2^-
imido	imido	NH^{2-}
nitride	nitrido	N^{3-}
azido	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	$(NOS)^-$
nitrosylium	nitrosylium or nitrosonium	NO^+
nitronium	nitronium	NO_2^+

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

Tab2 Common Chelating Amines

Chelating Points	Common Name	IUPAC Name	Abbreviation	Formula
bidentate	ethylenediamine	1,2-ethanediamine/ ethane-1,2-diamine	en	$NH_2CH_2CH_2NH_2$
bidentate	propanediamine	1,2-propanediamine	pn	$ \begin{array}{c} NH_2-CH-CH_2-NH_2 \\ \\ CH_3 \end{array} $
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 ⁻	$NH_2-CH_2-\overset{\overset{O}{\parallel}}{C}-O^-$
hexadentate	ethylenediaminetetraacetate	1,2-ethanediyl (dinitrilo) tetraacetato or ethylenediaminetetraacetato	EDTA	



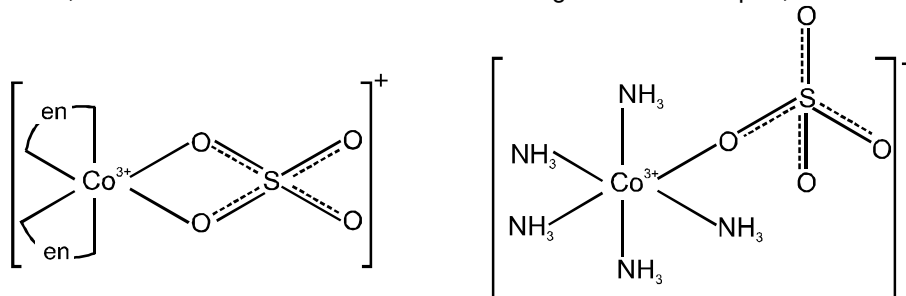
Flexidentate Ligand :

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 $[\text{Cr(III)(OH)(EDTA)}]^{2-}$ and $[\text{Co(III)Br(EDTA)}]^{2-}$ as pentadentate and in $[\text{Pd(II)H}_2(\text{EDTA})]^0$ as a tetradentate ligand.
e.g. NO_3^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$

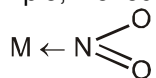
Sulphate ion, SO_4^{2-} can also be **mono** or **bi** dentate ligand. For example ;



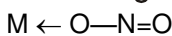
D7 Ambidentate Ligand :

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.

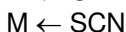
For example; Monodentate and ambidentate :



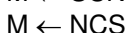
nitrito-N



nitrito-O

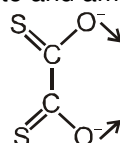


thiocyanato or thiocyanato-S

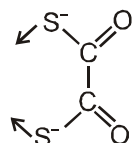


isothiocyanato or thiocyanato-N

Bidentate and ambidentate :



or



dithioxalate

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

D8 Coordination Number :

The coordination number of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ion i.e. the number of ligand donor atoms to which the metal is directly attached. Pi-bonds, if any, between the ligating atom and the central atom/ion are not considered for the determination of **coordination number**. The sigma bonding electrons may be indicated by a pair of dots, preceding the donor atom in the ligand formula as in $[\text{Co}(:\text{NH}_3)_6]^{3+}$, $[\text{Fe}(:\text{CN})_6]^{3-}$, $[\text{Ni}(:\text{CO})_4]$, $[\text{Co}(:\text{Cl}_4)]^{2-}$.

Coordination number of 6 (most common), 4 (after 6) and 2 (after 4) are the most common coordination numbers and odd coordination numbers are generally not found (rare).



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⁺	6
Au ⁺	2, 4	Fe ³⁺	6
Cu ²⁺	4, 6	Co ²⁺	4, 6
Pt ²⁺	4	Co ³⁺	6
Pd ²⁺	4	Al ³⁺	6
Mg ²⁺	6	Pt ⁴⁺	6
		Pd ⁴⁺	6

D9 Oxidation number of Central Atom :

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. Metal oxidation number is represented by a Roman numeral in parentheses following the name of the coordination entity. For example oxidation number of iron in $[\text{Fe}(\text{CN})_6]^{3-}$ is +3 and it is written as Fe(III).

D10 Homoleptic and heteroleptic complexes :

Complexes in which a metal is bound to only one type of donor groups, e.g., $[\text{Cr}(\text{NH}_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one type of donor groups, e.g., $[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+$, are known as heteroleptic.

Section (B) : Nomenclature of coordination compounds

Writing the formulas of Mononuclear Coordination Entities :

The following rules are followed while writing the formulas :

- The central atom is placed first.
- The ligands are then placed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
- Polydentate ligands are also placed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulae is enclosed in parentheses. The abbreviations of the ligands are also enclosed in parentheses.
- There should be no space between the ligands and the metal within a coordination sphere.
- When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$ etc.
- The charge of the cation(s) is balanced by the charge of the anion(s).

Writing the name of Mononuclear Coordination Compounds :

The following rules are followed when naming coordination compounds :

- Like simple salts the cation is named first in both positively and negatively charged coordination entities.

Examples :

$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, diamminesilver(I) chloride. $\text{K}_3[\text{Fe}(\text{CN})_6]$, potassium hexacyanidoferrate(III).

- The ligands are named in an alphabetical order (according to the name of ligand, not the prefix) before the name of the central atom/ion.

Examples :

$[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{CH}_3\text{NH}_2)]$, amminebromidochloridomethylamineplatinum(II).

$[\text{Co}(\text{H}_2\text{O})_2(\text{ox})_2]^-$, diaquabis(oxalato)cobaltate(III).

- Names of the anionic ligands end in -o and those of neutral ligands are the same except aqua for H_2O , ammine for NH_3 , carbonyl for CO, thiocarbonyl for CS and nitrosyl for NO. But names of cationic ligands end in -ium.



Some more important examples of neutral and cationic ligands are :

tetraphosphorus	—	P_4
dioxygen	—	O_2
octasulphur	—	S_8
urea	—	$\text{CO}(\text{NH}_2)_2$
hydrazinium	—	N_2H_5^+

- (iv) Ambidentate ligands are named as follows :
- (i) $\leftarrow : \text{CN}^-$: cyanido or cyanido – C
 $\leftarrow : \text{NC}^-$: isocyanido or cyanido – N
 - (ii) $\leftarrow : \text{NO}_2^-$: nitro or nitrito – N
 $\leftarrow : \text{ONO}^-$: nitrito or nitrito – O
- (v) Prefixes mono, di, tri, etc., are used to indicate the number of the one kind of ligands in the coordination entity. When the names of the ligands include a numerical prefix or are complicated or whenever the use of normal prefixes creates some confusion, it is set off in parentheses and the second set of prefixes is used.

2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	heptakis

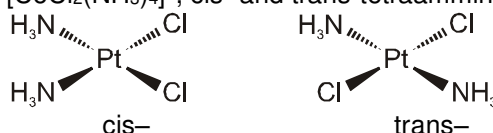
Examples : $[\text{CoCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]^+$, dichloridobis(ethane-1,2-diamine)cobalt(III).
 $[\text{NiCl}_2(\text{PPh}_3)_2]$, dichloridobis(triphenylphosphine)nickel(II).

- (vi) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in the parentheses after the name of metal.
- (vii) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix-ate. For example, Co in a complex anion, $[\text{Co}(\text{SCN})_4]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions.

iron (Fe)	ferrate	lead (Pb)	plumbate
silver (Ag)	argentate	tin (Sn)	stannate
gold (Au)	aurate		

Examples ; $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, tetraamminechloridocobalt(III).
 $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$, ammonium tetrathiocyanato-S-cobaltate(II).

- (viii) The neutral complex molecule is named similar to that of the complex cation.
Example ; $[\text{CrCl}_3(\text{py})_3]$, trichloridotris(pyridine)chromium(III).
- (ix) The prefixes cis- and trans- designate adjacent and opposite geometric locations.
For examples, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, cis- and trans-diamminedichloridoplatinum(II),
 $[\text{CoCl}_2(\text{NH}_3)_4]^+$, cis- and trans-tetraamminedichloridocobalt(III).



- (x) If there is any water of crystallization, it is to be included in the name. For example, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$: tetraaquadichlorido chromium(III) chloride-2-water or tetraaquadichlorido chromium(III) chloride dihydrate.

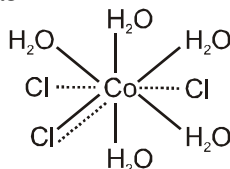
Section (C) : Werner's Theory

Several theories were proposed but none of them could satisfactorily explain the observed properties of Co(III) amines and of other similar compounds like Pt(IV) amines which had been prepared by them. It was only in 1893, that Werner presented a theory known as Werner's coordination theory which could explain all the observed properties of complex compounds. According to him most elements exhibit two types of valencies: (a) Primary valency and (b) Secondary valency.



- (a) **Primary valency** : This corresponds to the oxidation state of the metal ion. This is also called as the principle, ionisable or ionic valency. It is satisfied by the negative ions and its attachment with the central metal ion is shown by dotted lines.
- (b) **Secondary or auxiliary valency** : It is also termed as the coordination number (usually abbreviated as CN) of the central metal ion. It is non-ionic or non-ionisable (i.e. coordinate covalent bond type). This is satisfied by either negative ions or neutral molecules having lone pair of electrons (e.g., H_2O , NH_3 etc.) or even sometimes by some positive groups. The ligands which satisfy the coordination number are directly attached to the metal atom or ion and shown by thick lines.

Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour, i.e. it may satisfy both primary and secondary valencies since in every case the fulfillment of coordination number of the central metal ion appears essential. This dual behaviour is represented by both thick and dotted lines. For example, $[\text{CoCl}(\text{H}_2\text{O})_5]\text{Cl}_2$ is represented as



Every metal has a fixed number of secondary valencies, e.g., cobalt(III) and platinum(IV) have six secondary valencies and copper(II) four. The coordination number of a metal in a particular oxidation state is generally fixed but certain oxidation states of certain metals have found to possess more than one coordination number.

The ions/groups bound by the secondary valencies have characteristic spatial arrangements corresponding to different coordination number. In the modern terminology, such spatial arrangements are called coordination polyhedra and various possibilities are

C.N. = 2	linear	C.N. = 3	Triangular
C.N. = 4	tetrahedral or square planar	C.N. = 6	octahedral.

To distinguish between the two types of valencies, Werner introduced the square brackets [] to enclose those atoms making up the coordination complex and which are, therefore, not ionized.

On the basis of the above postulates Werner formulated the coordination compounds, $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$ as : $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ respectively; the species within the square brackets being the coordination entities (complexes) and the ions outside the square brackets the counter ions. He further postulated that octahedral, square, planar and tetrahedral geometrical shapes are more common in coordination compounds of transition metals. Thus, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, $[\text{CoCl}_2(\text{NH}_3)_4]^+$ are octahedral entities, while $[\text{Ni}(\text{CO})_4]$ and $[\text{PtCl}_4]^{2-}$ are tetrahedral and square-planar respectively.

Tab4

S. No.	Werner complex	Modern notation	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
1	$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$	six (NH_3)	three (Cl^-)
2	$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with dual nature
3	$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with dual nature
4	$\text{CoCl}_3 \cdot 3\text{NH}_3$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	three (NH_3) and three (Cl^-)	three (Cl^-) all with dual nature

From the above table it is clear that (i) the solution conductivities of complexes 1, 2 and 3 correspond to 1 : 3, 1 : 2 and 1 : 1 electrolyte respectively and thus the increasing order of the conductivity can be represented as $\text{CoCl}_3 \cdot 3\text{NH}_3 < \text{CoCl}_3 \cdot 4\text{NH}_3 < \text{CoCl}_3 \cdot 5\text{NH}_3 < \text{CoCl}_3 \cdot 6\text{NH}_3$ and (ii) the complexes 1, 2 and 3 will react with silver nitrate and give 3, 2 and 1 mole of the white precipitate of silver chloride respectively.

**F1 Effective Atomic Number Rule given by Sidgwick :**

Effective Atomic Number (EAN) = No. of electron present on the metal atom/ion + No. of electrons donated by ligands to it.

OR

Effective Atomic Number (EAN) = Atomic no. of central metal – Oxidation state of central metal + No. of electrons donated by ligands.

The complexes in which the EAN of the central atom equals the atomic number of the next noble gas, are found to be extra stable.

e.g. Cr(24) complex : $[\text{Cr}(\text{CO})_6]$ O.S. of Cr^0 EAN = $24 - 0 + 2 \times 6 = 36$

Fe(26) complex : $[\text{Fe}(\text{CN})_6]^{4-}$ O.S. of Fe^{+2} EAN = $26 - 2 + 2 \times 6 = 36$

Note : The EAN rule is generally found to be not valid in case of most of the complexes but in case of metal carbonyls this rule is found to be valid in all cases except one or two exceptions.

Section (D) & (E) : Valence Bond Theory + Crystal Field Theory (Part-I & II)**Bonding in coordination compounds :**

Alfred-Werner described the bonding characteristic in coordination compounds. But this theory failed to explain certain basic questions like :

- (a) Why only certain elements possess the remarkable property of forming compounds ?
- (b) Why the bonds in coordination compounds have directional properties ?
- (c) Why coordination compounds have the characteristic magnetic and optical properties ?

Many theories/approaches have been put forward to explain the nature of bonding in coordination compounds; these are valence bond theory (VBT), crystal field theory (CFT), ligand field theory (LFT) and molecular orbital theory (MOT).

Valence bond theory :

The valence bond theory, VBT, was extended to coordination compounds by Linus Pauling in 1931. The formation of a complex involves reaction between a lewis base (ligand) and a lewis acid (metal or metal ion) with the formation of a coordinate-covalent (or dative) bonds between them. The model utilizes hybridisation of $(n - 1)$ d, ns, np or ns, np, nd orbitals of metal atom or ion to yield a set of equivalent orbitals of definite geometry to account for the observed structures such as octahedral, square planar and tetrahedral, and magnetic properties of complexes. The number of unpaired electrons, measured by the magnetic moment of the compounds determines which d-orbitals are used. These hybrid orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

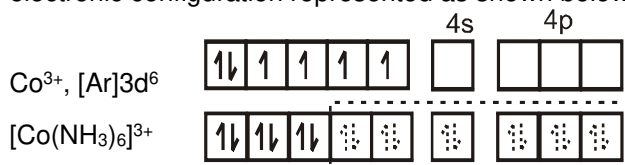
Tab5 Following table provides the types of hybridisation with different coordination number.

Coordination number of metal	Type of hybridisation	Shape of complex	Types of d-orbitals
2	sp	Linear	—
4	sp^3	Tetrahedral	—
4	dsp^2	Square planar	$d_{x^2-y^2}$
4	d^3s	Tetrahedral	d_{xy}, d_{yz}, d_{xz}
5	sp^3d	Trigonal bipyramidal	d_{z^2}
5	dsp^3	Square pyramidal	$d_{x^2-y^2}$
6	sp^3d^2	Octahedral	$d_{x^2-y^2}$ d_{z^2}
6	d^2sp^3	Octahedral	$d_{x^2-y^2}$ d_{z^2}

It is to be noted that the type of hybridisation of metal and shape of complex involved can be predicted conveniently, if some characteristic of the complex like magnetic nature, geometry or whether exhibits isomerism or not, etc., be known.

**Coordination Number Six.**

In the diamagnetic octahedral complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.



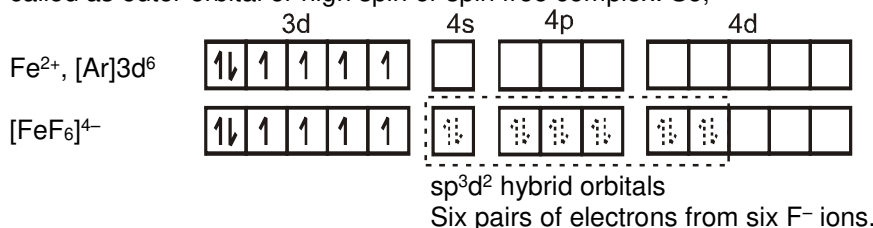
(inner orbital or low spin complex)

d^2sp^3 hybrid orbital

Six pairs of electrons from six NH_3 molecules.

Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. Since in the formation of complex the inner d-orbital (3d) is used in hybridisation, the complex is called an inner orbital or low spin or spin paired complex.

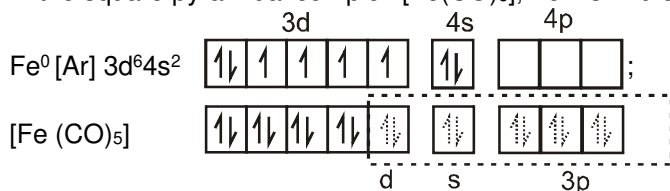
The complex $[\text{FeF}_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridisation (sp^3d^2); it is thus called as outer orbital or high spin or spin free complex. So,



Six pairs of electrons from six F^- ions.

Coordination Number Five :

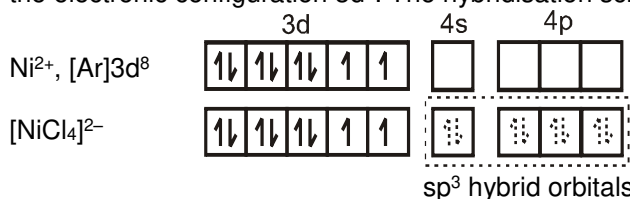
In the square pyramidal complex $[\text{Fe}(\text{CO})_5]$, Iron is in 0 oxidation state



The compound is diamagnetic as it contains 0 unpaired electrons

Coordination Number Four :

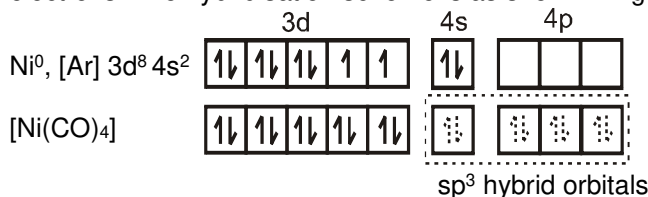
In the paramagnetic and tetrahedral complex $[\text{NiCl}_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in figure.



Four pairs of electrons from four Cl^- ions.

The compound is paramagnetic since it contains two unpaired electrons.

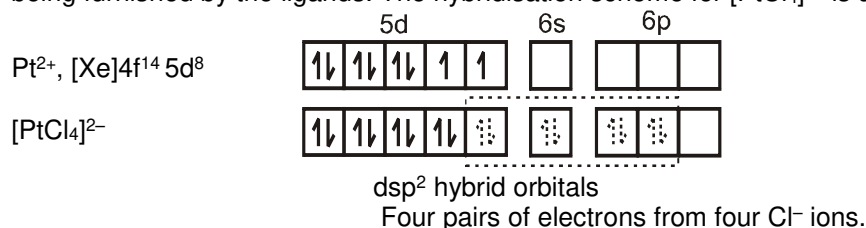
Similarly complex $[\text{Ni}(\text{CO})_4]$ has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridisation scheme is as shown in figure.



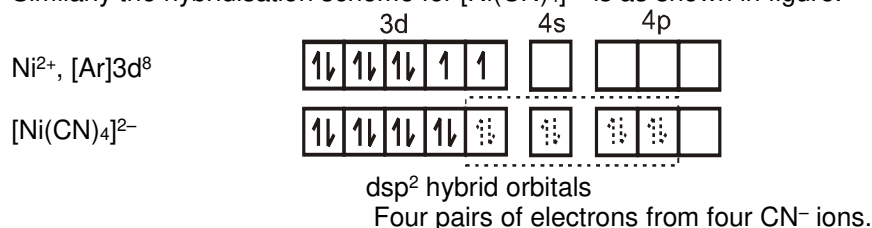
Four pairs of electrons from four CO molecules.



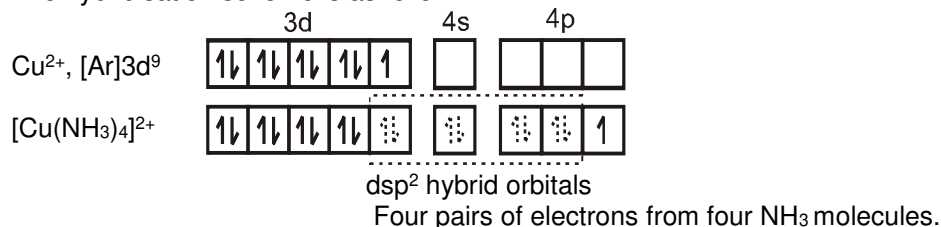
Complexes of Pd(II) and Pt(II) are usually four-coordinate, square planar, and diamagnetic and this arrangement is often found for Ni(II) complexes as well, e.g., in $[\text{Ni}(\text{CN})_4]^{2-}$ (here nickel is in +2 oxidation state and has electronic configuration $3d^8$). In as much as the free ion is in the ground state each case is paramagnetic, the bonding picture has to include pairing of electrons as well as ligand-metal-ligand bond angles of 90° and this occurs via hybridisation of one $(n-1) d$, one ns and two np orbitals to form four equivalent dsp^2 hybrid orbitals directed toward the corners of a square. These orbitals then participate in covalent coordinate σ bonds with the ligands, the bonding electron pairs being furnished by the ligands. The hybridisation scheme for $[\text{PtCl}_4]^{2-}$ is as shown in figure.



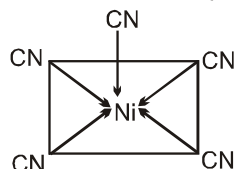
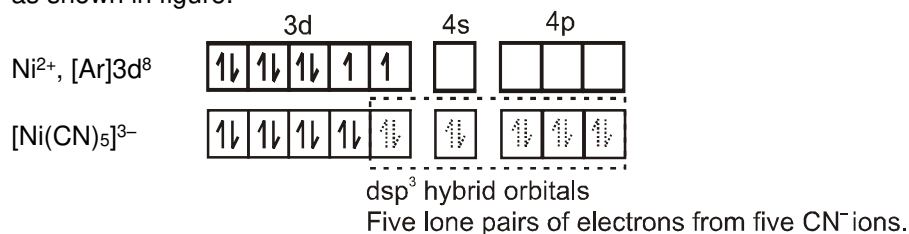
Similarly the hybridisation scheme for $[\text{Ni}(\text{CN})_4]^{2-}$ is as shown in figure.



It is found that $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is square planar and paramagnetic with one unpaired electron in 4p-orbital. The hybridisation scheme is as follow.



Note. $[\text{Ni}(\text{CN})_5]^{3-}$ is found to be diamagnetic with 2 types of Ni – C bond lengths, out of which four bond lengths are found to be equal and the fifth one is different. The hybridisation scheme for $[\text{Ni}(\text{CN})_5]^{3-}$ is as shown in figure.



Square pyramidal.

While the valence bond theory, to a large extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following **shortcomings** :

1. A number of assumptions are involved.
2. There is no quantitative interpretation of magnetic data.
3. It has nothing to say about the spectral (colour) properties of coordination compounds.
4. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.



5. It does not make exact predictions regarding the tetrahedral and square-planar structures of 4-coordinate complexes.
6. It does not distinguish between strong and weak ligands.

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 of 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 crystal 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 $(2/5)\Delta_0$.

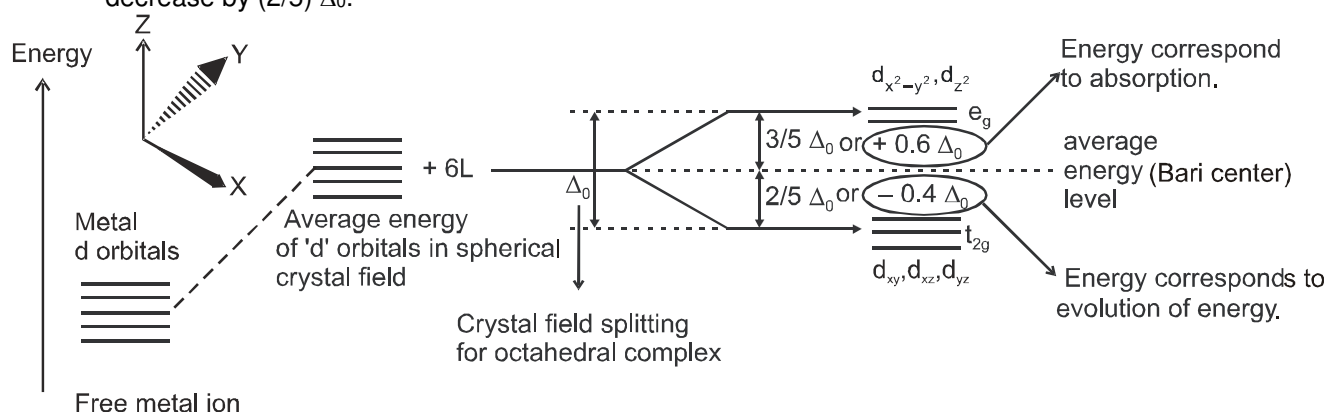


Figure showing crystal field splitting in octahedral complex.

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 :

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_3^- < \text{N}_3^- < \text{F}^- < \text{OH}^- < \text{EtOH} < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{EDTA} < \text{NH}_3 < \text{en} < \text{bipy}$
 $(2, 2'\text{-bipyridine}) < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$



* **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 possibilities are :

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

(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)

F2 Formula : $CFSE = [-0.4 (n) t_{2g} + 0.6 (n') e_g] \Delta_0 + *nP$.

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 complexes :

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 be attributed 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 splitting is also the two thirds the size and (ii) the direction of the orbitals does not coincide with the

direction of the ligands. This reduces the crystal field splitting by roughly further two third. So $\Delta_t = \frac{2}{3} \times$

$$\frac{2}{3} = \frac{4}{9} \Delta_0.$$

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

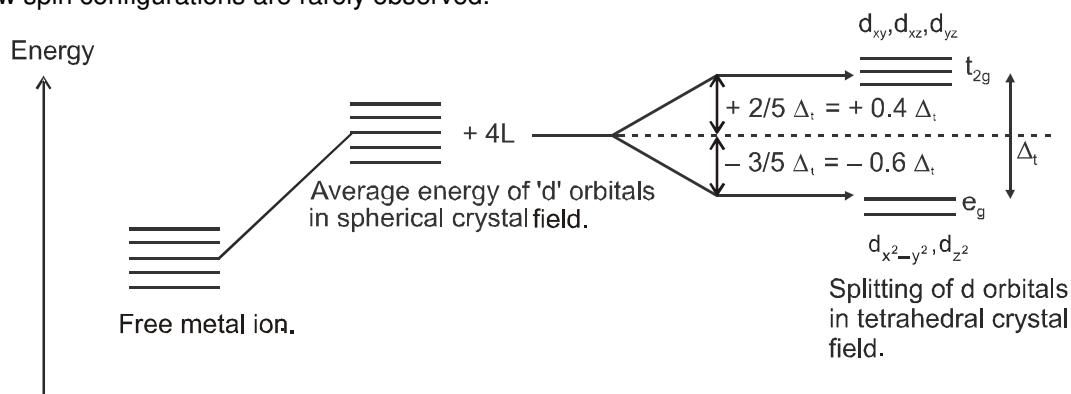


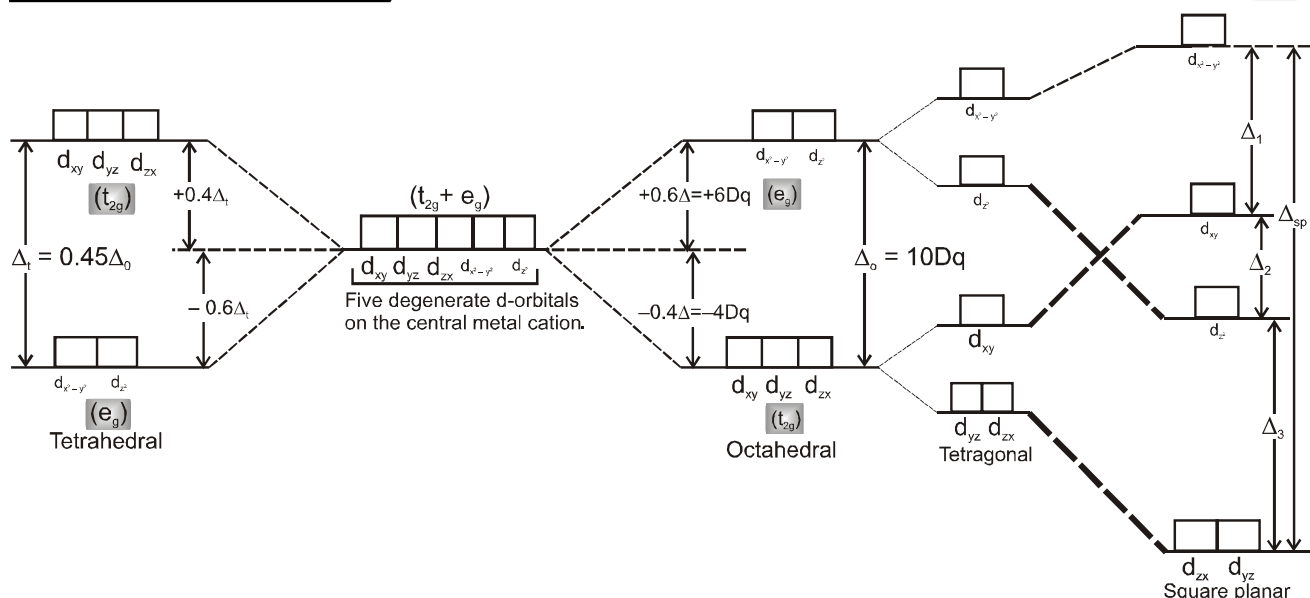
Figure showing crystal field splitting in tetrahedral complex.

Since $\Delta_t < \Delta_0$ crystal field splitting favours the formation of octahedral complexes.

(c) Crystal field splitting in square planar complexes :

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,

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

Section (F) : Applications of crystal field theory

(Magnetic moment of complex, Colour of complex, Limitation, Stability of complex)

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 ;

F3 Magnetic Moment = $\sqrt{n(n+2)}$ Bohr Magnetron ; 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 :

- 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.
- $[\text{Mn}(\text{CN})_6]^{3-}$ has a magnetic moment equal to two unpaired electrons while $[\text{MnCl}_6]^{3-}$ has a magnetic moment equal to four unpaired electrons.
- Similarly $[\text{Fe}(\text{CN})_6]^{3-}$ has magnetic moment of a single unpaired electron while $[\text{FeF}_6]^{3-}$ has a magnetic moment of five unpaired electrons.
- $[\text{CoF}_6]^{3-}$ is paramagnetic with four unpaired electrons while $[\text{Co}(\text{C}_2\text{O}_4)]^{3-}$ is diamagnetic.



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

(vi) $[\text{Mn}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{C}_2\text{O}_4)_2]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two are paramagnetic and the latter diamagnetic. $[\text{MnCl}_6]^{3-}$, $[\text{FeF}_6]^{3-}$ and $[\text{CoF}_6]^{3-}$ 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 $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. 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_{zx} 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.

Tab6 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
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	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 $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ on heating makes it colourless, (ii) similarly anhydrous copper sulphate (CuSO_4) is white, but hydrated copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 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 $[\text{Ni}(\text{H}_2\text{O})_6]$, the colour change is observed when ethylenediamine is progressively added to it.

Tab7

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 :**

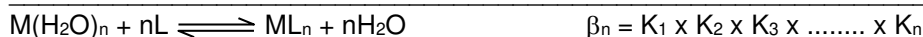
(i) The stability of a coordination compound $[ML_n]$ is measured in terms of the stability constant (equilibrium constant) given by the expression,

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

For the overall reaction :



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, $K_1, K_2, K_3, \dots, K_n$ for each step as represented below :



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. $K_1, K_2, K_3, \dots, K_n$ 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.

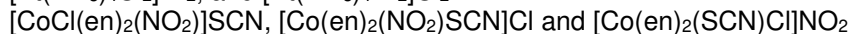
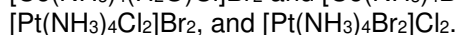
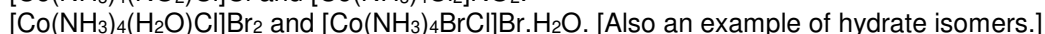
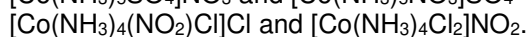
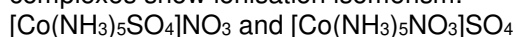
(b) If a multidentate ligand happens to be cyclic and there are no unfavourable steric effects, a further increase in stability occurs. This is termed the **macrocyclic effect**.

Section (G) : Isomerism in Coordination compounds

(Structural Isomerism, Stereoisomerism, Geometrical Isomerism, Optical Isomerism)

ISOMERISM :**(1) STRUCTURAL ISOMERISM :****D11 (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.

**D12 (B) Solvate / hydrate isomerism:**

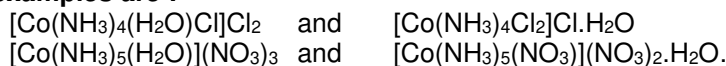
It occurs when water forms a part of the coordination entity or is outside it. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. For example, $CrCl_3 \cdot 6H_2O$ exists in three distinct isomeric forms : $[Cr(H_2O)_6]Cl_3$, violet; $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$, blue green : $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$, dark green. These three cationic isomers can be separated by cation ion exchange from commercial $CrCl_3 \cdot 6H_2O$. 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 ₂ SO ₄ (dehydrating agent)
[Cr(H ₂ O) ₆]Cl ₃	in the molar ratio of 3 : 1	No water molecule is lost or no reaction
[CrCl(H ₂ O) ₅]Cl ₂ .H ₂ O	in the molar ratio of 2 : 1	one mole of water is lost per mole of complex
[CrCl ₂ (H ₂ O) ₄]Cl.2H ₂ O	in the molar ratio of 1 : 1	two mole of water are lost per mole of complex

Other examples are :



D13 (C) Linkage isomerism :

In some ligands, like ambidentate ligands, there are two possible coordination sites. In such cases, linkage isomerism exist. e.g., NO₂ group can be bonded to metal ions through nitrogen (–NO₂) or through oxygen (–ONO). SCN too can be bonded through sulphur (–SCN) thiocyanate or through nitrogen (–NCS) isothiocyanate.

For example : [Co(ONO)(NH₃)₅]Cl₂ & [Co(NO₂)(NH₃)₅]Cl₂.

D14 (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(NH₃)₆][Cr(CN)₆] and [Cr(NH₃)₆][Co(CN)₆]
- (ii) [Cu(NH₃)₄][PtCl₄] and [Pt(NH₃)₄][CuCl₄]
- (iii) [Co(NH₃)₆][Cr(SCN)₆] and [Cr(NH₃)₄(SCN)₂][Co(NH₃)₂(SCN)₄]
- (iv) [Pt(NH₃)₄][PtCl₆] and [Pt(NH₃)₄Cl₂][PtCl₄]

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

D15 (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 (CH₃C₆H₄NH₂).

D16 (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(NH₃)₄(NO₂)₂][Co(NH₃)₂(NO₂)₄], [Co(NH₃)₆][Co(NO₂)₆], [Co(NH₃)₅(NO₂)]₂[Co(NH₃)₂(NO₂)₄]₂, [Co(NH₃)₆][Co(NH₃)₂(NO₂)₄]₃, [Co(NH₃)₄(NO₂)₂]₃[Co(NO₂)₆] and [Co(NH₃)₅(NO₂)₂]₃[Co(NO₂)₆]₂.

These all have the empirical formula Co(NH₃)₃(NO₂)₃, but they have formula weights that are 2,2,3,4,4 and 5 times this, respectively.

(2) Stereoisomerism :

D17 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 :

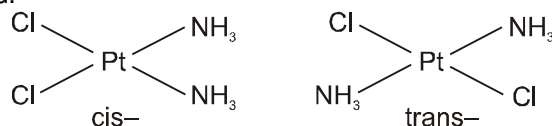
D18 This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Geometrical isomerism is common among coordination compounds with coordination numbers 4 and 6.

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.

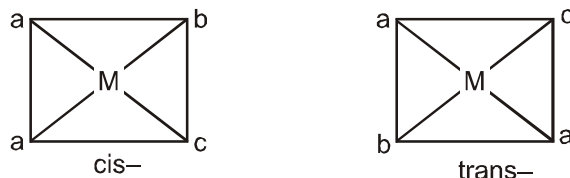


Square Planar Complex : In a square planar complex of formula $[Ma_2b_2]$ [a and b are unidentate], the two ligands 'a' may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer as depicted.

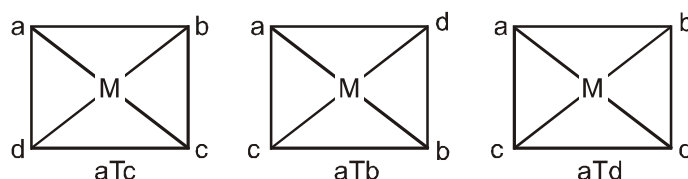


Geometrical isomers (cis and trans) of $Pt(NH_3)_2Cl_2$.

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

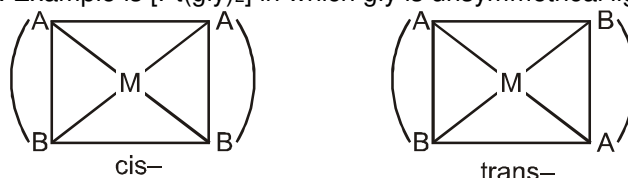


Square planar complex of the type $Mabcd$ (where a,b,c,d are unidentates) shows three geometrical isomers.



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.

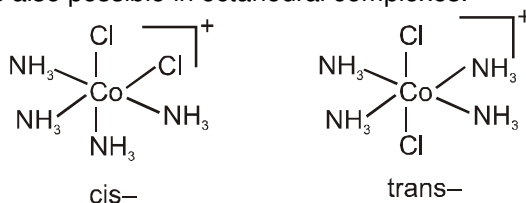


Similarly, $M(AB)(CD)$ also shows two geometrical isomers.

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 $[Co(NH_3)_4Cl_2]^+$

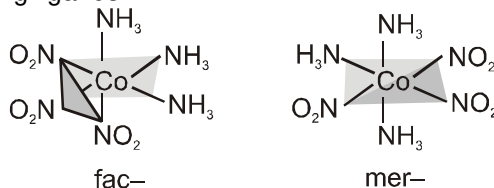
Number of possible isomers and the spatial arrangements of the ligands around the central metal ion for the specific complexes are given below.

(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.



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

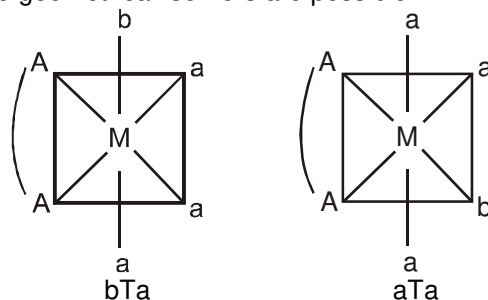
Unsymmetrical bidentate ligands also show fac-mer isomerism.

(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	

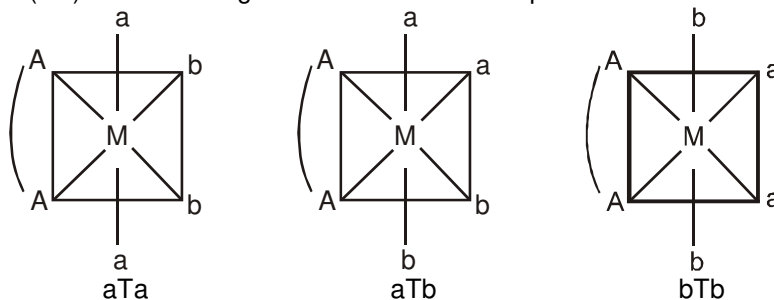
Note : Ma_6 and Ma_5b have only one form.

(II) Compounds containing bidentate ligand and unidentate ligands.

(i) $M(AA)_3b$ – Two geometrical isomers are possible.



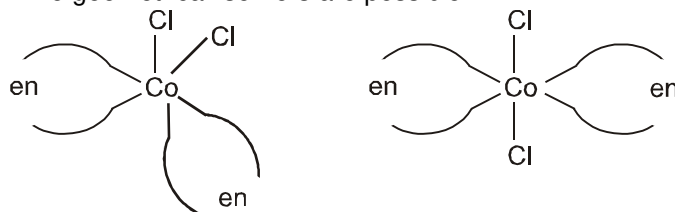
(ii) $M(AA)_2b_2$ – Three geometrical isomers are possible.



Note : With $[M(AA)_4]$, only one form is possible. $M(AA)abcd$ have six geometrical isomers.



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



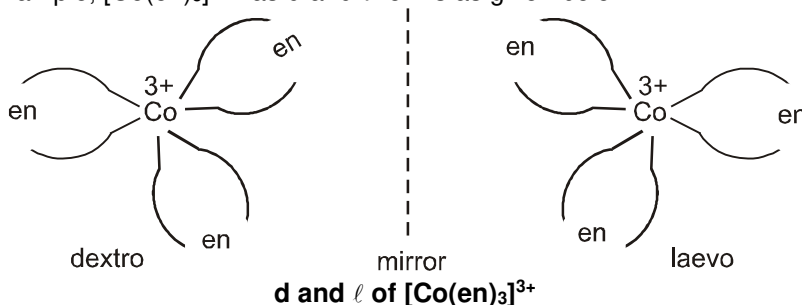
Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

Optical Isomerism:

D19

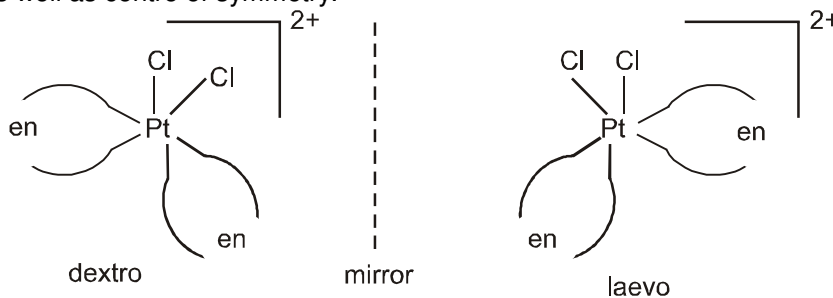
A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their ability to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical 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.



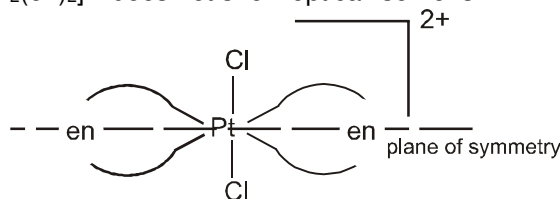
d and ℓ of $[Co(en)_3]^{3+}$

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.



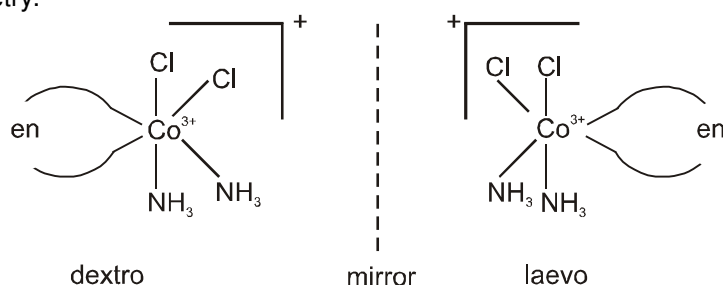
d and ℓ of cis- $[PtCl_2(en)_2]^{2+}$

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



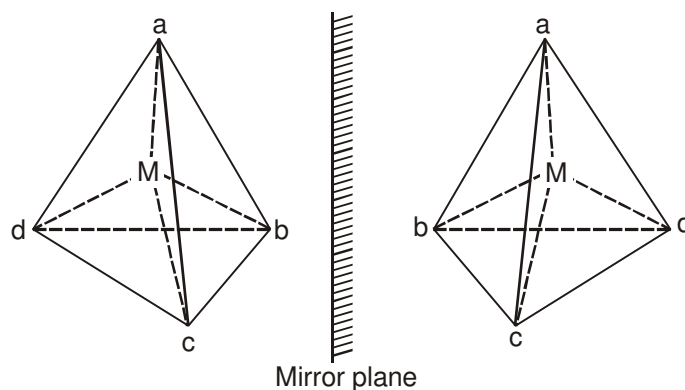


$\text{cis-}[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$ can show optical isomerism due to the absence of plane of symmetry as well as centre of symmetry.

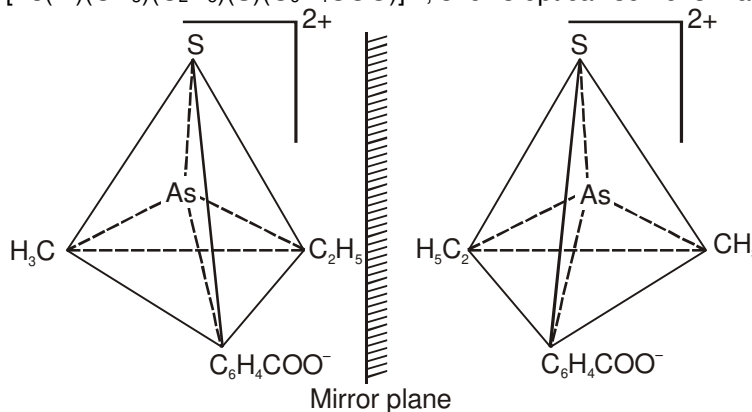


Tetrahedral complex :

Optical isomerism is expected in tetrahedral complexes of the type $[\text{Mabcd}]$ analogous to tetrahedral carbon atom.

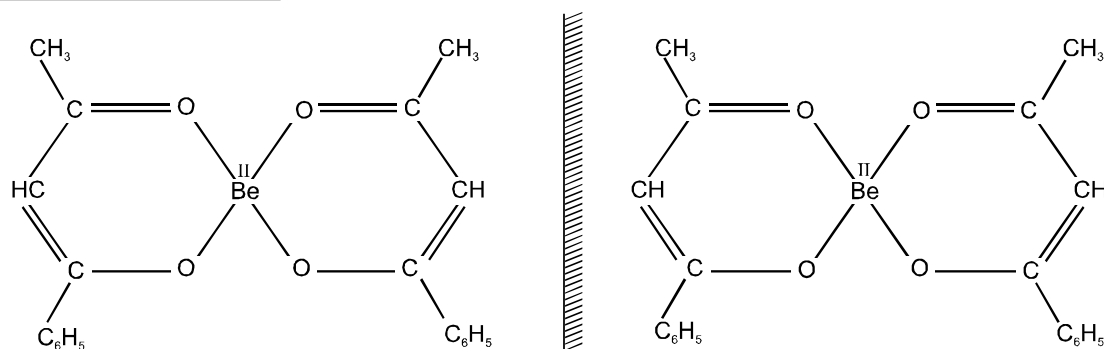


(i) For example $[\text{As}(\text{III})(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{S})(\text{C}_6\text{H}_4\text{COO})]^{2+}$, shows optical isomerism as given below.



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, $[(\text{C}_6\text{H}_5\text{COCHCOCH}_3)_2\text{Be}]^0$ 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), $[\text{Pt}(\text{II})(\text{NH}_2\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CH}(\text{C}_6\text{H}_5\text{NH}_2)\cdot(\text{NH}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{NH}_2)]^{2+}$ which has square planar shape has been resolved into two forms by Mills and Quibell in 1935.

Determination of Stereoisomers in octahedral Coordination compounds

Table -1

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
Ma_6	1	0	0
Ma_5b	1	0	0
Ma_4b_2	2	0	2
Ma_4bc	2	0	2
Ma_3b_3	2	0	2
$\text{Ma}_3\text{b}_2\text{c}$	3	0	3
Ma_3bcd	5	1	4
$\text{Ma}_2\text{b}_2\text{c}_2$	6	1	5
$\text{Ma}_2\text{b}_2\text{cd}$	8	2	6
Ma_5bcde	15	6	9
Mabcdef	30	15	15

Table -2

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[\text{M}(\text{AA})_3]$	2	2	0
$[\text{M}(\text{AA})_2\text{a}_2]$	3	1	2
$[\text{M}(\text{AA})_2\text{ab}]$	3	1	2
$[\text{M}(\text{AA})\text{a}_4]$	1	0	1
$[\text{M}(\text{AA})\text{a}_3\text{b}]$	2	0	2
$[\text{M}(\text{AA})\text{a}_2\text{b}_2]$	4	1	3
$[\text{M}(\text{AA})\text{a}_2\text{bc}]$	6	2	4
$[\text{M}(\text{AA})\text{abcd}]$	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.

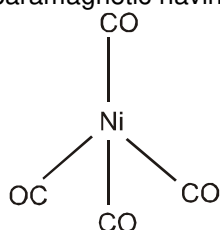
Section (H) : Organometallic Compounds

Organometallic compounds

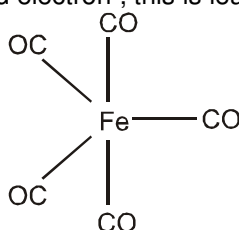
D20 Metal Carbonyls :

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

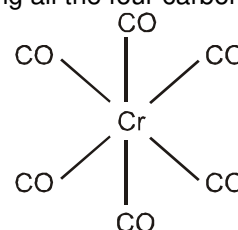
D21 (a) Monomeric: Those metal carbonyls which contain only one metal atom per molecule are called monomeric carbonyls. For examples: $[Ni(CO)_4]$ (sp^3 , tetrahedral); $[Fe(CO)_5]$ (dsp^3 , trigonal bipyramidal); $[Cr(CO)_6]$ (d^2sp^3 , octahedral); $[V(CO)_6]$ (d^2sp^3 , octahedral, only carbonyl which is paramagnetic having one unpaired electron ; this is least stable among all the four carbonyls)



$Ni(CO)_4$
Tetrahedral

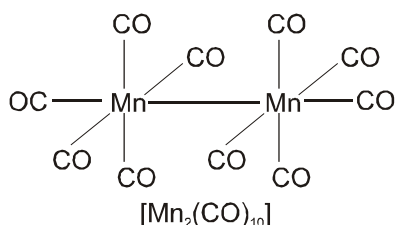


$Fe(CO)_5$
Trigonal bipyramidal

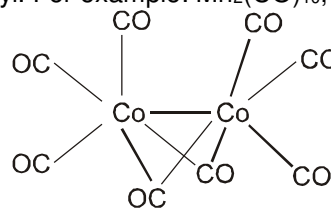


$Cr(CO)_6$
Octahedral

D22 (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: $Mn_2(CO)_{10}$, $Co_2(CO)_8$, etc.



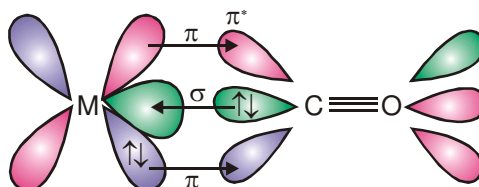
$[Mn_2(CO)_{10}]$



$[Co_2(CO)_8]$

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 $M-C \sigma$ 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 $M-C \pi$ 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.

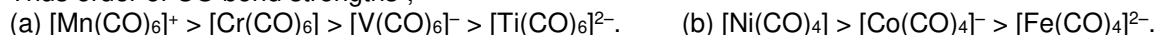


Synergic bonding

(i) As $M-C\pi$ bonding increases, the $C-O$ bond becomes weaker. 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.

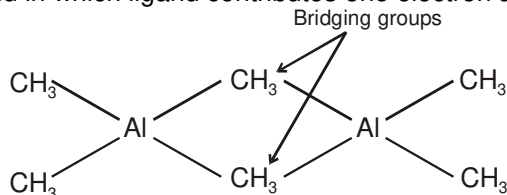
(ii) In contrast, in the anionic complex (i.e. carbonylate anion) the metal has a greater electron density to be dispersed, with the result that $M-C\pi$ bonding is enhanced and the $C-O$ bond is diminished in strength. For example; in isoelectronic complexes the strength of metal-ligand bond increases 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 ;



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.

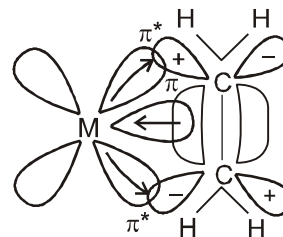
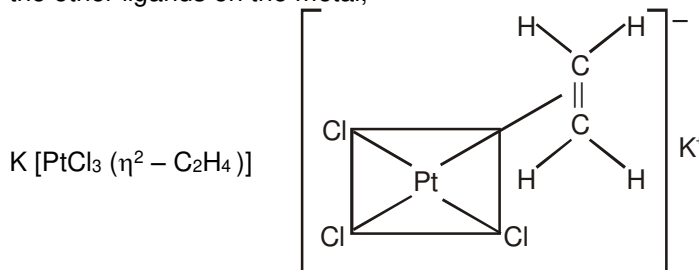
(b) $(CH_3)_4Sn$, $(C_2H_5)_4Pb$, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$ etc.

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,

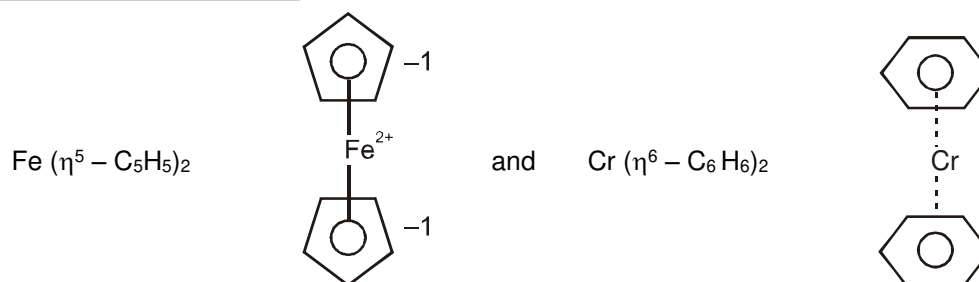


Ferrocene and bis(benzene)chromium :

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.





- * 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) $\pi\text{-C}_5\text{H}_5^-$: η^5 – cyclopentadienyl or pentahaptocyclopentadienyl
 - (ii) $\pi\text{-C}_3\text{H}_5^-$: 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 B₁₂, cyanocobalamin, 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 : ethylenediaminetetraacetic acid (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 $[\text{Au}(\text{CN})_2]^-$ 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 $[\text{Ni}(\text{CO})_4]$, 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- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$) 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), $[\text{RhCl}(\text{PPh}_3)_3]$ 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 $CrCl_3 \cdot 6H_2O$ 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) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ (B) $[Cr(H_2O)_6]Cl_3$
 (C) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ (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

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

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

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

 $\therefore n = 3$
 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) $PtCl_4 \cdot 2NH_3$ (iii) $PtCl_4 \cdot 3NH_3$ (iv) $PtCl_4 \cdot 5NH_3$
 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) $K_2[PtCl_6] \xrightleftharpoons{aq} 2K^+(aq) + [PtCl_6]^{2-}(aq)$ (ii) $[Pt(NH_3)_2Cl_4] \xrightleftharpoons{aq} [Pt(NH_3)_2Cl_4](aq)$
 (iii) $[Pt(NH_3)_3Cl_3]Cl \xrightleftharpoons{aq} [Pt(NH_3)_3Cl_3]^+(aq) + Cl^-(aq)$ (iv) $[Pt(NH_3)_5Cl]Cl_3 \xrightleftharpoons{aq} [Pt(NH_3)_5Cl]^{3+} + 3Cl^-$



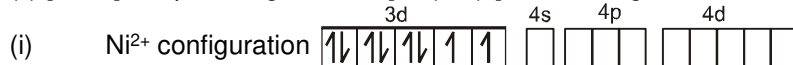
	Complex	Number of ions	Expected electrical conductance
(i)	$K_2[PtCl_6]$	3	256
(ii)	$[Pt(NH_3)_2Cl_4]$	0	0
(iii)	$[Pt(NH_3)_3Cl_3]Cl$	2	97
(iv)	$[Pt(NH_3)_5Cl]Cl_3$	4	404

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.

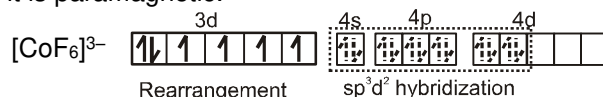
Sol.



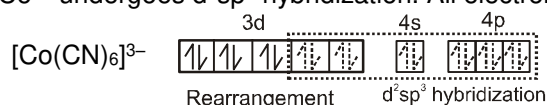
During rearrangement only one 3d-orbital may be made available for pairing of the electrons.

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

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



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



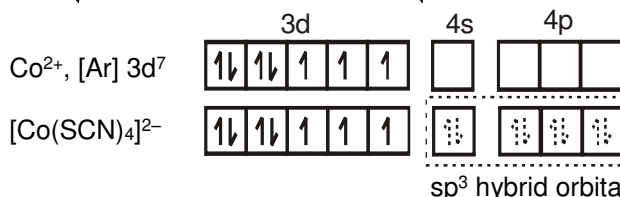
8. You are given the following two complexes X and Y which are isomers of each other; X is $Hg[Co(SCN)_4]$. It is further given that 'spin only' magnetic moment of X is found to be 3.78 B.M. and that of Y is 1.73 B.M. Then which of the following is correct ?

- (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.

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

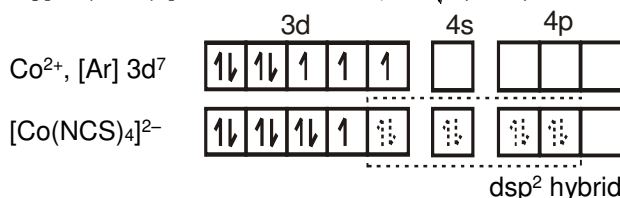
$$\mu = \sqrt{n(n+2)} ; \text{ So, } 3.78 \text{ B.M.} = \sqrt{n(n+2)} \text{ or } n = 3.$$



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,

$$Hg[Co(NCS)_4] \text{ is } 1.73 \text{ B.M. So, } \mu = \sqrt{n(n+2)} ; \text{ So, } 1.73 \text{ B.M.} = \sqrt{n(n+2)} \text{ or } n = 1.$$



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'.

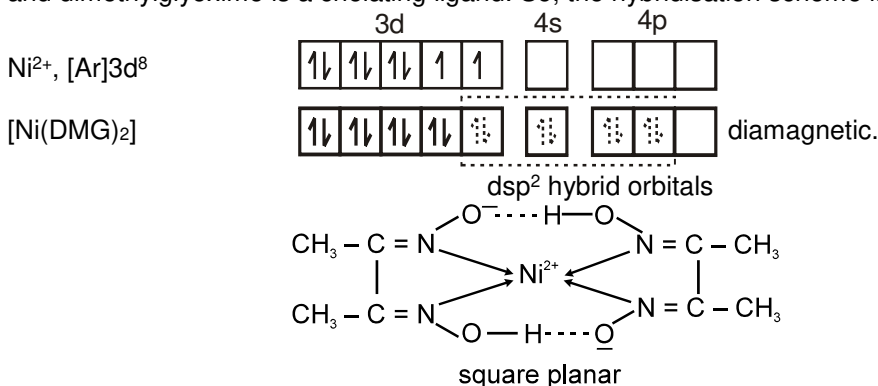
11. It is an experimental fact that : $DMG + Ni(II)\text{salt} + NH_4OH \longrightarrow \text{Red precipitate}$

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.



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** : $[\text{Co}^{\text{II}}(\text{NH}_3)_6]^{2+}$ is not readily oxidized to $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$ when air is bubbled through it.
Statement-2 : Crystal field stabilization energy of $\text{Co}(+\text{III})$ with a d^6 configuration is higher than for $\text{Co}(+\text{II})$ 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.

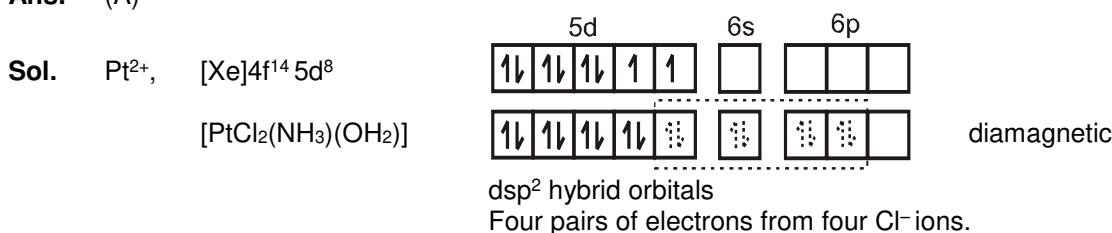
Ans. (D)

Sol. Statement 1 is false statement. $[\text{Co}^{\text{II}}(\text{NH}_3)_6]^{2+}$ is readily oxidised in $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$ in presence of air due to the higher CFSE value ($-2.4\Delta_o$) of d^6 configuration than d^7 configuration ($-0.8\Delta_o$).

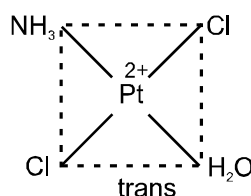
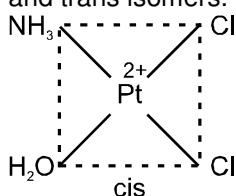
15. Which of the following is true about the complex $[\text{PtCl}_2(\text{NH}_3)(\text{OH}_2)]$? [Atomic number of Pt = 78]

- (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)



Ma_2bc have cis- and trans isomers.

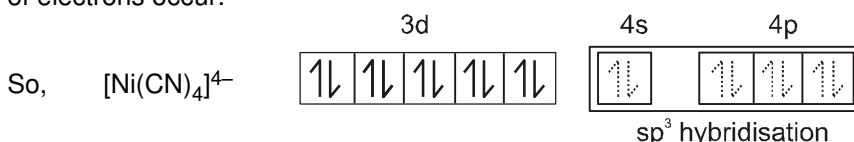


16. Among $[\text{Ni}(\text{CN})_4]^{4-}$, $[\text{Ni}(\text{PPh}_3)_3\text{Br}]$ and $[\text{Ni}(\text{dmg})_2]$ species, the hybridisation states of the Ni-atoms are respectively :

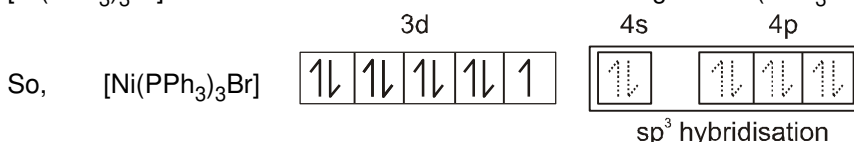
- (A) dsp², dsp², sp³ (B) sp³, sp³, dsp² (C) sp³, dsp², dsp² (D) dsp², sp³, dsp²

Ans. (B)

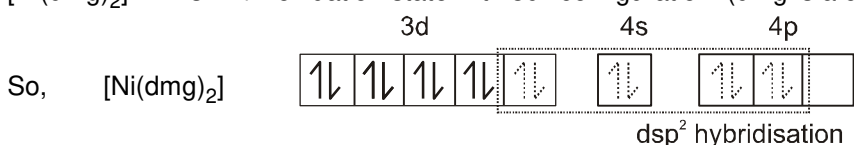
Sol. $[\text{Ni}(\text{CN})_4]^{4-}$ - Ni is in zero oxidation state. The CN⁻ is strong field ligand and, therefore, rearrangement of electrons occur.



$[\text{Ni}(\text{PPh}_3)_3\text{Br}]$ - Ni is in +1 oxidation state with 3d⁹ configuration (PPh₃ is a strong field ligand).



$[\text{Ni}(\text{dmg})_2]$ - Ni is in +2 oxidation state with 3d⁸ configuration. (dmg is a chelating ligand).

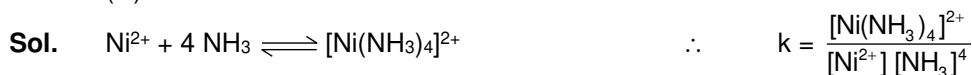




17. For the reaction $\text{Ni}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_4]^{2+}$; at equilibrium, if the solution contains $1.6 \times 10^{-4}\%$ of nickel in the free state, and the concentration of NH_3 at equilibrium is 0.5 M. Then the instability constant of the complex will 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)



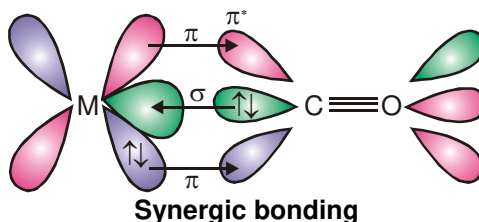
But $\frac{[\text{Ni}^{2+}]}{[\text{Ni}^{2+}] + [\text{Ni}(\text{NH}_3)_4]^{2+}} = 1.6 \times 10^{-6}$

or $\frac{[\text{Ni}^{2+}]}{[\text{Ni}(\text{NH}_3)_4]^{2+}} \approx 1.6 \times 10^{-6} \quad \therefore k = \frac{10^6}{1.6 \times (0.5)^4} = 10^7$

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.



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 $[\text{Rh}(\text{I})\text{Cl}(\text{PPh}_3)_3]$. So it contains rhodium.



Exercise-1

Marked questions are recommended for Revision.

PART - I : SUBJECTIVE 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^-
- 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) Determine the denticity of the ligands in complexes $[Fe(C_2O_4)_3]^{3-}$ and $[Pt(en)_2]^{2+}$. 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 $100^\circ C$.
(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^{+1} ions.



(q) 2	$[\text{Cu}(\text{CN})_4]^{3-}$	Colourless stable soluble complex obtained in detection of Cu^{2+} on adding excess of KCN solution.
(r)	$(\text{NH}_4)_2[\text{PtCl}_6]$	Only few compounds of ammonium ions are precipitate this is one of these, a yellow precipitate.

B-2. Name the following compounds.

- | | |
|--|--|
| (a) $[\text{CoBr}(\text{en})_2(\text{ONO})]^+$ | (b) 2 $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{ONO})_6]$ |
| (c) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$ | (d) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$ |
| (e) 2 $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ | (f) $[(\text{NH}_3)_5\text{Co}-\text{NH}_2-\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})]\text{Cl}_5$ |
| (g) $[\text{Cr}(\text{CO})_5(\text{PPh}_3)]$ | (h) $[(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_5]$ |
| (i) 2 $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$ | (j) $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2][\text{BF}_4]_3$ |
| (k) $\text{Ba}[\text{Zr}(\text{OH})_2(\text{ONO})_2(\text{ox})]$ | (l) 2 $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$ |

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) 2	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 hexafluoroaluminate(III)	Called cryolite, used in the electrolytic refining of aluminium
(f) 2	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)	$\text{PtCl}_4.2\text{NH}_3$	6.99	(i) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
(b)	$\text{PtCl}_4.\text{NH}_3.\text{KCl}$	106.8	(ii) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$
(c)	$\text{CrCl}_3.5\text{NH}_3$	260.2	(iii) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$
(d)	$\text{PtCl}_4.2\text{KCl}$	256.8	(iv) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$
(e)	$\text{CrCl}_3.6\text{NH}_3$	441.7	(v) $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$
(f)	$\text{PtCl}_4.6\text{NH}_3$	522.9	(vi) $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$
(g)	$\text{CoBr}_3.5\text{NH}_3$	257.6	(vii) $\text{K}_2[\text{PtCl}_6]$
(h)	$\text{PtCl}_4.3\text{NH}_3$	96.8	(viii) $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$



- C-2.** 1 g of complex $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ 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) $[\text{Cr}(\text{CO})_6]$ (b) $[\text{Fe}(\text{CN})_6]^{4-}$ (c) $[\text{Fe}(\text{CO})_5]$ (d) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (e) $[\text{Ni}(\text{CO})_4]$ (f) $[\text{Cu}(\text{CN})_4]^{3-}$ (g) $[\text{Pd}(\text{NH}_3)_6]^{4+}$ (h) $[\text{PtCl}_6]^{2-}$
- C-4.** Arrange the following compounds in order of increasing molar conductivity.
 (i) $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ (ii) $[\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3]$
 (iii) $[\text{Cr}(\text{NH}_3)_5(\text{NO}_2)_3][\text{Co}(\text{NO}_2)_6]_2$ (iv) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$

Section (D) : Valence Bond Theory + Crystal Field Theory (Part-I)

- D-1.** A metal complex having composition $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$ 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) State hybridisation of chromium in each.
 (iii) Calculate their magnetic moments for each (spin-only value).
 (iv) Calculate the EAN for both.
 (v) Will they conduct electricity or not.
 (vi) Write the formula of the complexes formed when the precipitates dissolve in aqueous ammonia & the concentrated ammonia respectively.
- D-2.** Predict the hybridisation and geometry of the following complexes.
 (a) $[\text{NiBr}_4]^{2-}$ (b) $[\text{AuCl}_4]^-$ (c) $[\text{Pt}(\text{NH}_3)_4]^{2+}$

Section (E) : Valence Bond Theory + Crystal Field Theory (Part-II)

- E-1.** For the complex $\text{K}_2[\text{Cr}(\text{NO})(\text{NH}_3)(\text{CN})_4]$; $\mu = 1.73 \text{ BM}$.
 (i) Write IUPAC name.
 (ii) What will be structure?
 (iii) How many unpaired electrons are present in the central metal ion?
 (iv) Is it paramagnetic or diamagnetic?
 (v) Calculate the EAN of the complex.
 (vi) What will be the hybridisation of the complex?
- E-2.** Predict the hybridisation and geometry of the following complexes.
 (a) $[\text{Fe}(\text{CN})_6]^{3-}$ (b) $[\text{MnBr}_4]^{2-}$ (c) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (d) $[\text{Co}(\text{SCN})_4]^{2-}$
- E-3.** $[\text{Co}(\text{NH}_3)_6]^{3+}$ & $[\text{CoF}_6]^{3-}$ both are complexes of Co(III) , but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic while $[\text{CoF}_6]^{3-}$ is paramagnetic with $\mu = 4.90 \text{ B.M.}$ Explain.
- E-4.** Arrange the following in increasing order as directed.
 (a) (i) $[\text{CoCl}_3(\text{NH}_3)_3]$, (ii) $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$, (iii) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, (iv) $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ - 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-5.** 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) $[\text{CrF}_6]^{3-}$ (b) $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (c) $[\text{Fe}(\text{CN})_6]^{3-}$
 (d) $[\text{Cu}(\text{en})_3]^{2+}$ (e) $[\text{FeF}_6]^{3-}$

Section (F) : Applications of crystal field theory

(Magnetic moment of complex, Colour of complex, Limitation, Stability of complex)

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



- F-2.** The value of Δ_0 for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is found to be 240 kJ mol^{-1} then predict the colour of the complex using the following table. ($h = 6 \times 10^{-34} \text{ J-sec}$, $N_A = 6 \times 10^{23}$, $c = 3 \times 10^8 \text{ m/sec}$)

Absorbed light	$\lambda \text{ (nm)}$ (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

- F-3.** (a) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs light of wavelength 5000 \AA . Name one ligand which would form a titanium(III) complex absorbing light of lower wavelength than 5000 \AA and one ligand which would form a complex absorbing light of wavelength higher than 5000 \AA .
 (b) Calculate the magnetic moments (spin only) of the following complexes
 (i) $[\text{PtCl}_6]^{2-}$ (ii) $[\text{Cr}(\text{CO})_6]$ (iii) $[\text{Ir}(\text{NH}_3)_6]^{3+}$ (iv) $[\text{Pd}(\text{en})_2]^{2+}$

Section (G) : Isomerism in Coordination compounds

(Structural Isomerism, Stereoisomerism, Geometrical Isomerism, Optical Isomerism)

- G-1.** What type of isomers are the following :

- (i) $[\text{Mn}(\text{CO})_5\text{SCN}]$ and $[\text{Mn}(\text{CO})_5\text{NCS}]$
 (ii) $[\text{Co}(\text{en})_3] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{en})_3] [\text{Co}(\text{CN})_6]$
 (iii) $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$
 (iv) $[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_2(\text{py})_2]\text{Cl}$ and $[\text{Co}(\text{H}_2\text{O})\text{Cl}_3(\text{py})_2]\text{H}_2\text{O}$

- G-2.** (a) Draw all possible constitutional isomers of the compound $\text{Ru}(\text{NH}_3)_5(\text{NO}_2)\text{Cl}$. 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 NH_3 and two SCN^- ligands. Sketch the structures of all six, and label them according to the classification.

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

- (a) $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$ (b) $[\text{CoCl}_2\text{Br}_2]^{2-}$ (tetrahedral)
 (c) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ (d) $[\text{Pt}(\text{en})\text{Cl}_2]$
 (e) $[\text{CrBr}_2(\text{en})_2]^+$ (f) $[\text{Rh}(\text{en})_3]^{3+}$

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

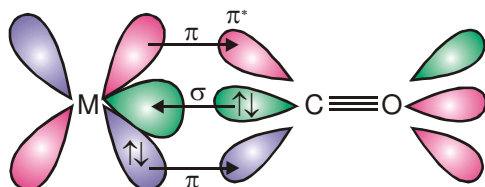
- (a) $\text{cis-}[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+$ (b) $\text{cis-}[\text{Cr}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$ (c) $[\text{Cr}(\text{gly})_3]$
 (d) $[\text{Cr}(\text{en})_3]^{3+}$ (e) $\text{cis-}[\text{Co}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+}$ (f) $\text{trans-}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{2+}$

Section (H) : Organometallic Compounds

- H-1.** Draw the structures of the following metal carbonyls

- (a) $[\text{V}(\text{CO})_6]$ (b) $[\text{Cr}(\text{CO})_6]$ (c) $[\text{Mn}_2(\text{CO})_{10}]$
 (d) $[\text{Fe}(\text{CO})_5]$ (e) $[\text{Ni}(\text{CO})_4]$

- H-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 : ONLY ONE OPTION CORRECT TYPE

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 $(\text{EDTA})^{4-}$ 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 $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O})_2]^{2-}$ is
 (A) +2 (B) +3 (C) +4 (D) +5
- A-6.** Co-ordination number of platinum in $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$ ion is:
 (A) 4 (B) 2 (C) 8 (D) 6
- A-7.** Which of the following is copper(I) compound ?
 (A) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ (B) $[\text{Cu}(\text{CN})_4]^{3-}$ (C) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (D) All of these
- A-8.** In the complex $[\text{CoCl}_2(\text{en})_2]\text{Br}$, 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 $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ 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-platinum (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) $[\text{Co}(\text{en})_2\text{SO}_4]$ (B) $[\text{Co}(\text{en})_3\text{SO}_4]$ (C) $[\text{Co}(\text{en})_3]_2\text{SO}_4$ (D) $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$
- B-4.** The correct IUPAC name for the compound $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{ONO})]\text{Cl}$ 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) $[\text{CoCl}(\text{NH}_3)_3(\text{H}_2\text{O})_2]$ (B) $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_3]$
 (C) $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}_2$ (D) $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$



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) $Co(NO_2)_3 \cdot 2KNO_2$ (B) $Co(NO_2)_3 \cdot 3KNO_2$ (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 dehydrated to relatively minimum extent by conc. H_2SO_4 under identical condition.
(A) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (B) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
(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 + Crystal Field Theory (Part-I)

- 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
- D-3.** The magnitude of crystal field stabilisation energy (CFSE of Δ_t) 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 field is only 2/3 in tetrahedral 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
- D-4.** 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
- D-5.** The crystal field splitting energy for octahedral complex (Δ_o) and that for tetrahedral complex (Δ_t) are related as:
(A) $\Delta_t = \frac{4}{9} \Delta_o$ (B) $\Delta_t = 0.5 \Delta_o$ (C) $\Delta_t = 0.33 \Delta_o$ (D) $\Delta_t = \frac{9}{4} \Delta_o$



- D-6.** All the metal ions contains $t_{2g}^6 e_g^0$ configurations. Which of the following complex will be paramagnetic?
 (A) $[\text{FeCl}(\text{CN})_4(\text{O}_2)]^{4-}$ (B) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (C) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (D) $[\text{Fe}(\text{CN})_5(\text{O}_2)]^{-5}$

Section (E) : Valence Bond Theory + Crystal Field Theory (Part-II)

- 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.** Which of the following molecules is not tetrahedral ?
 (A) $[\text{Pt}(\text{en})_2]^{2+}$ (B) $[\text{Ni}(\text{CO})_4]$ (C) $[\text{Zn}(\text{NH}_3)_4]^{2+}$ (D) $[\text{NiCl}_4]^{2-}$
- E-3.** The complex $[\text{Pt}(\text{NH}_3)_4]^{2+}$ has structure :
 (A) square planar (B) tetrahedral (C) pyramidal (D) pentagonal
- E-4.** Match Column-I with Column-II and select the correct answer with respect to hybridisation using the codes given below :

	Column - I		Column - II
	(Complex)		(Hybridisation)
(I)	$[\text{Au F}_4]^-$	(p)	dsp^2 hybridisation
(II)	$[\text{Cu}(\text{CN})_4]^{3-}$	(q)	sp^3 hybridisation
(III)	$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	(r)	sp^3d^2 hybridisation
(IV)	$[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$	(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

- E-5.** The hybridisation and unpaired electrons in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion are :
 (A) sp^3d^2 ; 4 (B) d^2sp^3 ; 3 (C) d^2sp^3 ; 4 (D) $sp^3 d^2$; 2
- E-6.** The number of unpaired electrons in d^6 , low spin, octahedral complex is :
 (A) 4 (B) 2 (C) 1 (D) 0
- E-7.** Which of the following is a high spin complex ?
 (A) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (B) $[\text{Fe}(\text{CN})_6]^{4-}$ (C) $[\text{Ni}(\text{CN})_4]^{2-}$ (D) $[\text{FeF}_6]^{3-}$
- E-8.** Which has maximum paramagnetic nature ?
 (A) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ (B) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (C) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (D) $[\text{Fe}(\text{CN})_6]^{4-}$
- E-9.** The number of unpaired electrons present in complex ion $[\text{FeF}_6]^{3-}$ is :
 (A) 5 (B) 4 (C) 6 (D) 0
- E-10.** Which of the following complexes has a geometry different from others ?
 (A) $[\text{Ni Cl}_4]^{2-}$ (B) $\text{Ni}(\text{CO})_4$ (C) $[\text{Ni}(\text{CN})_4]^{2-}$ (D) $[\text{Zn}(\text{NH}_3)_4]^{2+}$
- E-11.** Select the correct statement.
 (A) Complex ion $[\text{MoCl}_6]^{3-}$ is paramagnetic. (B) Complex ion $[\text{Co}(\text{en})_3]^{3+}$ is diamagnetic.
 (C) Both (A) and (B) are correct. (D) None of correct.
- E-12.** Amongst $\text{Ni}(\text{CO})_4$, $[\text{Ni}(\text{CN})_4]^{2-}$ and NiCl_4^{2-} :
 (A) $\text{Ni}(\text{CO})_4$ and NiCl_4^{2-} are diamagnetic and $[\text{Ni}(\text{CN})_4]^{2-}$ is paramagnetic.
 (B) NiCl_4^{2-} and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $\text{Ni}(\text{CO})_4$ is paramagnetic.
 (C) $\text{Ni}(\text{CO})_4$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and NiCl_4^{2-} is paramagnetic.
 (D) $\text{Ni}(\text{CO})_4$ is diamagnetic and NiCl_4^{2-} and $[\text{Ni}(\text{CN})_4]^{2-}$ are paramagnetic.



Section (F) : Applications of crystal field theory

(Magnetic moment of complex, Colour of complex, Limitation, Stability of complex)

- F-1. The compound which does not show paramagnetism ?
 (A) $[\text{Cu}(\text{NH}_3)_4\text{Cl}_2]$ (B) $[\text{Ag}(\text{NH}_3)_2\text{Cl}]$ (C) NO (D) NO_2
- F-2. Among the following ions, which one has the highest paramagnetism ?
 (A) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (C) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (D) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

Section (G) : Isomerism in Coordination compounds

(Structural Isomerism, Stereoisomerism, Geometrical Isomerism, Optical Isomerism)

- G-1. The complexes $[\text{Pt}(\text{NH}_3)_4]$, $[\text{PtCl}_6]$ and $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$, $[\text{PtCl}_4]$ are :
 (A) linkage isomers (B) optical isomers
 (C) co-ordination isomers (D) ionisation isomers
- G-2. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ are related to each other as :
 (A) geometrical isomers (B) linkage isomers
 (C) coordination isomers (D) ionisation isomers
- G-3. The number of geometrical isomer of $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$ are :
 (A) 0 (B) 2 (C) 3 (D) 4
- G-4. Geometrical isomerism is found in coordination compounds having coordination number :
 (A) 2 (B) 3 (C) 4 (tetrahedral) (D) 6
- G-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
- G-6. Geometrical isomerism can be shown by :
 (A) $[\text{Ag}(\text{NH}_3)(\text{CN})]$ (B) $\text{Na}_2[\text{Cd}(\text{NO}_2)_4]$ (C) $[\text{PtCl}_4\text{I}_2]$ (D) $[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Au}(\text{CN})_4]$

Section (H) : Organometallic Compounds

- H-1. Which one is not an organometallic compound ?
 (A) RMgX (B) $(\text{C}_2\text{H}_5)_4\text{Pb}$ (C) $(\text{CH}_3)_4\text{Sn}$ (D) $\text{C}_2\text{H}_5\text{ONa}$
- H-2. Formula of ferrocene is:
 (A) $[\text{Fe}(\text{CN})_6]^{4-}$ (B) $[\text{Fe}(\text{CN})_6]^{3+}$ (C) $[\text{Fe}(\text{CO})_5]$ (D) $[\text{Fe}(\text{C}_5\text{H}_5)_2]$

PART - III : MATCH THE COLUMN

1. Match the column :

	Column-I		Column-II
(A)	$[\text{Fe}(\text{en})_3]^{3+}$	(p)	d^2sp^3 hybridisation of central metal
(B)	$[\text{Co}(\text{ox})_3]^{3-}$	(q)	sp^3d^2 hybridisation of central metal
(C)	$[\text{Cr}(\text{CN})_6]^{3-}$	(r)	paramagnetic
(D)	$[\text{NiCl}_6]^{4-}$	(s)	diamagnetic
		(t)	metal ion has +3 oxidation state

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)	$[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}]\text{SO}_4$	(p)	Enantiomer
(B)	$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2](\text{NO}_3)_2$	(q)	Geometrical isomer
(C)	$[\text{Co}(\text{en})(\text{pn})(\text{NO}_2)_2]\text{Cl}$	(r)	Ionization isomer
(D)	$[\text{Co}(\text{gly})_3]$	(s)	Linkage isomer



Exercise-2

Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

- 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
- The EAN of metal atoms in $[\text{Fe}(\text{CO})_2(\text{NO}^+)_2]$ and $\text{Co}_2(\text{CO})_8$ respectively are :
(A) 34, 35 (B) 34, 36 (C) 36, 36 (D) 36, 35
- Which of the following is inner orbital complex as well as diamagnetic in nature ?
(A) $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (C) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (D) $[\text{Co}(\text{NH}_3)_6]^{2+}$
- Which of the following statement is correct ?
(A) The oxidation state of iron in sodium nitro prusside $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ is +3
(B) $[\text{Ag}(\text{NH}_3)_2]^+$ is linear in shape
(C) In $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, Fe is d^2sp^3 hybridized
(D) In $\text{Ni}(\text{CO})_4$, the oxidation state of Ni is 1
- The complex $\text{K}_4[\text{Zn}(\text{CN})_4(\text{O}_2)_2]$ is oxidised into $\text{K}_2[\text{Zn}(\text{CN})_4(\text{O}_2)_2]$, 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
- 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 $\text{Ni}(\text{CO})_4$ II $\text{K}[\text{AgF}_4]$ III $\text{Na}_2[\text{Zn}(\text{CN})_4]$
IV $\text{K}_2[\text{PtCl}_4]$ V $[\text{RhCl}(\text{PPh}_3)_3]$
(A) II, III, V (B) I, II, III (C) I, III, IV (D) none of these
- The complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ 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.
- Which of the following statements is not correct?
(A) TiCl_4 is a colourless compound. (B) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is a coloured compound.
(C) $\text{K}_3[\text{VF}_6]$ is a colourless compound. (D) $[\text{Cu}(\text{NCCH}_3)_4][\text{BF}_4]$ is a colourless compound.
- 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
- The number of geometrical isomers for octahedral $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^-$, square planar $\text{AuCl}_2\text{Br}_2^-$ are :
(A) 4, 2 (B) 2, 2 (C) 3, 2 (D) 2, 3
- Which of the following statements is not true about the complex ion $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$?
(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.
- Both geometrical and optical isomerism are shown by :
(A) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (B) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (C) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (D) $[\text{Cr}(\text{OX})_3]^{3-}$



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

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. Sum of denticity of following ligands are
 Glycinate ion, Oxalate ion, o-phenanthroline, 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 $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
 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 $\text{CrCl}_3 \cdot 5\text{H}_2\text{O}$ as six. The possible volumes of 1 M Ag NO_3 needed to precipitate the chlorine in outersphere in 200 ml of 0.1 M solution of the complex is/are.
 Write your answer as $V_1 + V_2 + V_3 + \dots$
5. Ni^{+2} form a complex ion in water having the formula $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$. 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 $[\text{Ni}(\text{en})_3]^{+2}$ (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
(a)	$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$	+3	t_{2g}^6
(b)	$(\text{NH}_4)_2[\text{CoF}_4]$	+2	$t_{2g}^5 e_g^2$
(c)	Cis - $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	+3	$t_{2g}^3 e_g^0$
(d)	$[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$	+2	$t_{2g}^3 e_g^2$

7. Total number of paramagnetic complexes which are inner orbital complexes :
 (i) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (ii) $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_2$ (iii) $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$
 (iv) $\text{K}_2[\text{PtCl}_6]$ (v) $[\text{V}(\text{H}_2\text{O})_6]\text{SO}_4$ (vi) $[\text{Mn}(\text{NH}_3)_6]\text{SO}_4$
 (vii) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$ (viii) $\text{K}_3[\text{CuCl}_4]$ (ix) $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$
8. The number of coordination isomers possible for $[\text{Fe}(\text{NH}_3)_6]^{3+}$ $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ is _____
9. Find the sum of number of geometrical isomers for following complexes.
 (a) $[\text{CoCl}_2\text{Br}_2]^{2-}$ (b) $[\text{Rh}(\text{en})_3]^{3+}$ (c) $[\text{Cr}(\text{en})_2\text{Br}_2]^+$
 (d) $[\text{Pt en Cl}_2]$ (e) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
10. What is the sum of bond order of Fe–C bond and C–O bond in $\text{Fe}(\text{CO})_5$?
11. How many isomeric forms are possible for the octahedral complex, $[\text{Rh}(\text{en})_2(\text{NO}_2)(\text{SCN})]^+$?

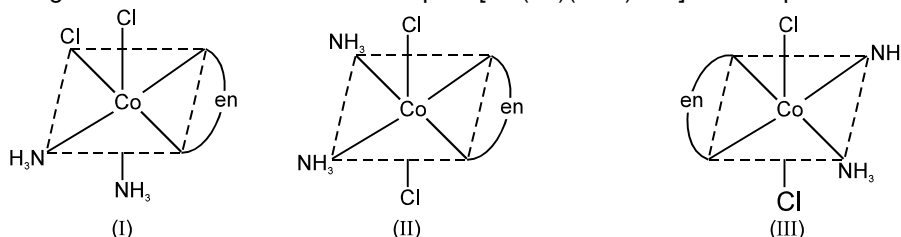


PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

- 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) $[KAl(SO_4)_2 \cdot 12H_2O]$ is a coordination compound.
 (D) All acids are lewis acids and σ donors.
- 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
- 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 $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ can be differentiated by measuring molar conductance
- 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
- 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.
- 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.
- '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 $[Pt(H_2O)_2Br_2]$
- Which complex of the following pairs has the larger value of Δ_o ?
 (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 $[Co(H_2O)_6]^{2+}$ (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) $[Co(NH_3)_6]^{3+} < [CoF_6]^{3-}$
- Which of the following isomerisms is/are shown by the complex $[CoCl_2(OH)_2(NH_3)_2]Br$?
 (A) Ionization (B) Linkage (C) Geometrical (D) optical



10. Three arrangements are shown for the complex $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$. 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 complexes $[\text{V}(\text{CO})_6]^-$, $[\text{Cr}(\text{CO})_6]$ and $[\text{Mn}(\text{CO})_6]^+$. 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, $\text{Co}(\text{CO})_x$ will be :
- (A) $\text{Co}_2(\text{CO})_4$ (B) $\text{Co}_2(\text{CO})_3$ (C) $\text{Co}_2(\text{CO})_8$ (D) $\text{Co}_2(\text{CO})_{10}$

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 $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}_2\text{Br}$, 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) $[\text{CoClBr}(\text{en})_2]\text{H}_2\text{O}$ (B) $[\text{CoCl}(\text{en})_2(\text{H}_2\text{O})]\text{BrCl}$
(C) $[\text{CoBr}(\text{en})_2(\text{H}_2\text{O})]\text{Cl}_2$ (D) $[\text{CoBrCl}(\text{en})_2]\text{Cl} \cdot \text{H}_2\text{O}$
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) will 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 $\text{Pb}(\text{NO}_3)_2$ 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

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

$\text{Ni}^{2+} (\text{aq.}) + \text{Dimethylglyoxime} \xrightarrow{\text{NH}_4\text{OH}} \text{Complex (Y)}.$

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(dimethylglyoximate)nickel (II).
 (C) tetrathiocyanato-S-cobaltate (II) and bis(dimethylglyoximate)nickelate(II).
 (D) tetrathiocyanato-S-cobaltate(III) and bis(dimethylglyoximate)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) $\mu = 2.83$ B.M.	(i) sp^3	(P) 2
(II) $\mu = 5.93$ B.M.	(ii) sp^3d^2	(Q) 3
(III) $\mu = 3.88$ B.M.	(iii) d^2sp^3	(R) 4
(IV) $\mu = 0$ 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

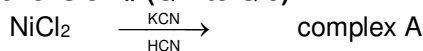
* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. A green complex, $K_2[Cr(NO)(NH_3)(CN)_4]$ is paramagnetic and has $\mu_{eff} = 1.73$ BM. Write the IUPAC name of the complex and draw the structure of anion and find out the hybridisation of metal ion.
[JEE 2003, 4/60]
2. The species having tetrahedral shape is : **[JEE 2004, 3/84]**
 (A) $[PdCl_4]^{2-}$ (B) $[Ni(CN)_4]^{2-}$ (C) $[Pd(CN)_4]^{2-}$ (D) $[NiCl_4]^{2-}$
3. The spin magnetic moment of cobalt in the compound, $Hg[Co(SCN)_4]$ is : **[JEE 2004, 3/84]**
 (A) $\sqrt{3}$ (B) $\sqrt{8}$ (C) $\sqrt{15}$ (D) $\sqrt{24}$



4. When dimethyl glyoxime is added to the aqueous solution of nickel(II) chloride in presence of dilute ammonia solution, a bright red coloured precipitate is obtained. [JEE 2004, 4/60]
 (a) Draw the structure of bright red substance.
 (b) Write the oxidation state of nickel in the substance and hybridisation.
 (c) State whether the substance is paramagnetic or diamagnetic.
5. Which kind of isomerism is exhibited by octahedral $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$? [JEE 2005, 3/84]
 (A) Geometrical and ionization (B) Geometrical and optical
 (C) Optical and ionization (D) Geometrical only
6. The bond length in CO is 1.128 Å. What will be the bond length of CO in $\text{Fe}(\text{CO})_5$? [JEE 2006, 5/184]
 (A) 1.158 Å (B) 1.128 Å (C) 1.178 Å (D) 1.118 Å

Comprehension # (Q.7 to Q.9)


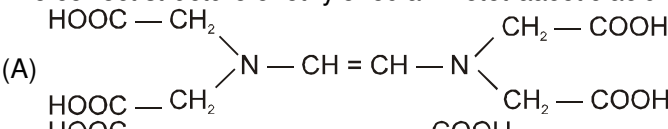
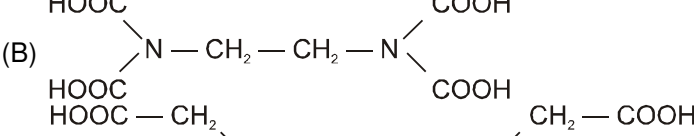
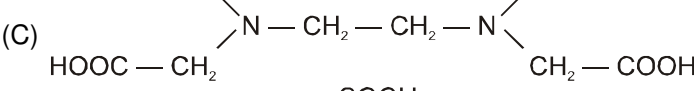
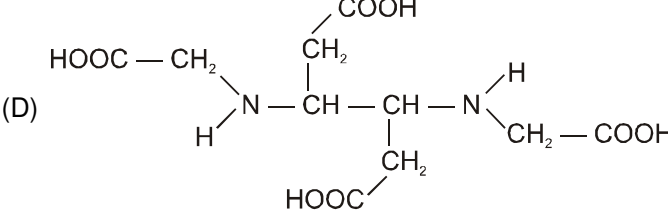
A & B complexes have the co-ordination number 4.

7. The IUPAC name of complexes 'A' & 'B' are respectively : [JEE 2006, 5/184]
 (A) Potassium tetracyanonickelate(II) and Potassium tetrachloronickelate(II)
 (B) Potassium tetracyanonickel(II) and Potassium tetrachloronickel(II)
 (C) Potassium cyanonickelate(II) and Potassium chloronickelate(II)
 (D) Potassium cyanonickel(II) and Potassium chloronickel(II)
8. The hybridisation of both complexes are : [JEE 2006, 5/184]
 (A) dsp^2 (B) sp^2 & dsp^2 (C) dsp^2 & sp^3 (D) both sp^3
9. What are the magnetic nature of 'A' & 'B'? [JEE 2006, 5/184]
 (A) Both diamagnetic.
 (B) 'A' is diamagnetic & 'B' is paramagnetic with one unpaired electrons.
 (C) 'A' is diamagnetic & 'B' is paramagnetic with two unpaired electrons.
 (D) Both are paramagnetic.
10. Among the following metal carbonyls, the C–O bond order is lowest in : [JEE 2007, 3/162]
 (A) $[\text{Mn}(\text{CO})_6]^+$ (B) $[\text{V}(\text{CO})_6]^-$ (C) $[\text{Cr}(\text{CO})_6]$ (D) $[\text{Fe}(\text{CO})_5]$
11. Match the complexes in Column-I with their properties listed in Column-II. [JEE 2007, 6/162]

	Column-I		Column-II
(A)	$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$	(p)	Geometrical isomers
(B)	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	(q)	Paramagnetic
(C)	$[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$	(r)	Diamagnetic
(D)	$[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$	(s)	Metal ion with +2 oxidation state

12. The IUPAC name of $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$ is : [JEE 2008, 3/163]
 (A) Tetrachloronickel(II) tetraamminenickel (II) (B) Tetraamminenickel(II) tetrachloronickel (II)
 (C) Tetraamminenickel(II) tetrachloronickelate (II) (D) Tetraamminenickel(II) tetrachloronickelate (0)
13. Both $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic. The hybridisation of nickel in these complexes, respectively, are : [JEE 2008, 3/163]
 (A) sp^3 , sp^3 (B) sp^3 , dsp^2 (C) dsp^2 , sp^3 (D) dsp^2 , sp^2
14. **Statement-1** : The geometrical isomers of the complex $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ are optically inactive, and **Statement-2** : Both geometrical isomers of the complex $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ possess axis of symmetry. [JEE 2008, 3/163]
 (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.



15. **Statement-1** : $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ is paramagnetic, **and**
Statement-2 : The Fe in $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ has three unpaired electrons. [JEE 2008, 3/163]
 (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.
- 16.* The compound(s) that exhibit(s) geometrical isomerism is(are) : [JEE 2009, 4/160]
 (A) $[\text{Pt}(\text{en})\text{Cl}_2]$ (B) $[\text{Pt}(\text{en})_2]\text{Cl}_2$ (C) $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$ (D) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
17. The spin only magnetic moment value (in Bohr magneton units) of $\text{Cr}(\text{CO})_6$ is : [JEE 2009, 3/160]
 (A) 0 (B) 2.84 (C) 4.90 (D) 5.92
18. The correct structure of ethylenediaminetetraacetic acid (EDTA) is : [JEE 2010, 3/163]
 (A) 
 (B) 
 (C) 
 (D) 
19. The ionization isomer of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ is : [JEE 2010, 3/163]
 (A) $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$ (B) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$
 (C) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$ (D) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)] \cdot \text{H}_2\text{O}$
20. The complex showing a spin-only magnetic moment of 2.82 B.M. is : [JEE 2010, 5/163]
 (A) $\text{Ni}(\text{CO})_4$ (B) $[\text{NiCl}_4]^{2-}$ (C) $\text{Ni}(\text{PPh}_3)_4$ (D) $[\text{Ni}(\text{CN})_4]^{2-}$
21. Total number of geometrical isomers for the complex $[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$ is : [JEE 2010, 3/163]
22. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^- , CN^- and H_2O , respectively, are [JEE 2011, 3/160]
 (A) octahedral, tetrahedral and square planar (B) tetrahedral, square planar and octahedral
 (C) square planar, tetrahedral and octahedral (D) octahedral, square planar and octahedral
23. Among the following complexes (K–P), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (K), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (L), $\text{Na}_3[\text{Co}(\text{oxalate})_3]$ (M), $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (N), $\text{K}_2[\text{Pt}(\text{CN})_4]$ (O) and $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (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
24. 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 $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$, as silver chloride is close to. [JEE 2011, 4/160]
25. As per IUPAC nomenclature, the name of the complex $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$ is : [JEE 2012, 3/143]
 (A) Tetraaquadiaminocobalt (III) chloride (B) Tetraaquadiamminocobalt (III) chloride
 (C) Diaminetetraaquacobalt (III) chloride (D) Diamminetetraaquacobalt (III) chloride



26. $\text{NiCl}_2 \cdot \text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively
[JEE 2012, 3/143]
(A) tetrahedral and tetrahedral (B) square planar and square planar
(C) tetrahedral and square planar (D) square planar and tetrahedral
27. Consider the following complex ions, P, Q and R.
P = $[\text{FeF}_6]^{3-}$, Q = $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ and R = $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.
The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is
(A) $\text{R} < \text{Q} < \text{P}$ (B) $\text{Q} < \text{R} < \text{P}$ (C) $\text{R} < \text{P} < \text{Q}$ (D) $\text{Q} < \text{P} < \text{R}$
[JEE(Advanced) 2013, 2/120]
- 28.* The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) :
[JEE(Advanced) 2013, 4/120]
(A) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (B) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$
(C) $[\text{CoBr}_2\text{Cl}_2]^{2-}$ and $[\text{PtBr}_2\text{Cl}_2]^{2-}$ (D) $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$
29. EDTA^{4-} is ethylenediaminetetraacetate ion. The total number of N-Co-O bond angles in $[\text{Co}(\text{EDTA})]^{1-}$ complex ion is :
[JEE(Advanced) 2013, 4/120]
30. A list of species having the formula XZ_4 is given below.
 XeF_4 , SF_4 , SiF_4 , BF_4^- , BrF_4^- , $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{FeCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$.
Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is
[JEE(Advanced) 2014, 3/120]
31. 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 = $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$; atomic numbers : Ti = 22; Cr = 24; Cp = 27; Pt = 78}
- | | List-I | | List-II |
|----|---|----|--|
| P. | $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ | 1. | Paramagnetic and exhibits ionisation isomerism |
| Q. | $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$ | 2. | Diamagnetic and exhibits <i>cis-trans</i> isomerism |
| R. | $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3$ | 3. | Paramagnetic and exhibits <i>cis-trans</i> isomerism |
| S. | $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$ | 4. | Diamagnetic and exhibits ionisation isomerism |
- Code :
- | | | | | | | | | | |
|-----|---|---|---|---|-----|---|---|---|---|
| | P | Q | R | S | | P | Q | R | S |
| (A) | 4 | 2 | 3 | 1 | (B) | 3 | 1 | 4 | 2 |
| (C) | 2 | 1 | 3 | 4 | (D) | 1 | 3 | 4 | 2 |
32. 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]
33. In the complex acetyl bromododicarbonylbis(triethylphosphine)iron(II), the number of Fe-C bond(s) is
[JEE(Advanced) 2015, 4/168]
34. Among the complex ions, $[\text{Co}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2\text{Cl}_2]^+$, $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$, $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$, $[\text{Co}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is :
[JEE(Advanced) 2015, 4/168]
35. Among $[\text{Ni}(\text{CO})_4]$, $[\text{NiCl}_4]^{2-}$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, $\text{Na}_3[\text{CoF}_6]$, 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
36. The number of geometric isomers possible for the complex $[\text{CoL}_2\text{Cl}_2]^-$ ($\text{L} = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$) is
[JEE(Advanced) 2016, 3/124]
37. 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



- 38.* Addition of excess aqueous ammonia to a pink coloured aqueous solution of $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$ (**X**) and NH_4Cl gives an octahedral complex **Y** in the presence of air. In aqueous solution, complex **Y** behaves as 1 : 3 electrolyte. The reaction of **X** with excess HCl at room temperature results in the formation of a blue coloured complex **Z**. The calculated spin only magnetic moment of **X** and **Z** is 3.87 B.M., whereas it is zero for complex **Y**. [JEE(Advanced) 2017, 4/122]
Among the following options, which statement(s) is (are) correct?
(A) The hybridization of the central metal ion in **Y** is d^2sp^3
(B) Addition of silver nitrate to **Y** gives only two equivalents of silver chloride
(C) When **X** and **Z** are in equilibrium at 0°C , the colour of the solution is pink
(D) **Z** is a tetrahedral complex
- 39.* 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 $\text{Fe}(\text{CO})_5$ or $\text{Ni}(\text{CO})_4$ 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
40. 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 , $(\text{NH}_4)_2[\text{FeCl}_4]$, $(\text{NH}_4)_2[\text{NiCl}_4]$, K_2MnO_4 , K_2CrO_4
41. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 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]
- 42.* The correct option(s) regarding the complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ (en = $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) 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 $[\text{Co}(\text{en})\text{NH}_3)_4]^{3+}$
43. Match each set of hybrid orbitals from LIST-I with complex(es) given in LIST-II. [JEE(Advanced) 2018, 3/120]

LIST-I
(P) dsp^2
(Q) sp^3
(R) sp^3d^2
(S) d^2sp^3

LIST-II
(1) $[\text{FeF}_6]^{4-}$
(2) $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$
(3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
(4) $[\text{FeCl}_4]^{2-}$
(5) $\text{Ni}(\text{CO})_4$
(6) $[\text{Ni}(\text{CN})_4]^{2-}$

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

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. One mole of $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ 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 : [AIEEE 2003, 3/225]
(1) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$
(2) $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2 \cdot \text{NH}_3$
(3) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
(4) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$



2. Ammonia forms the complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ with copper ions in alkaline solution but not in acid solution. The reason for it is : **[AIEEE 2003, 3/225]**
 - (1) in alkaline solution $\text{Cu}(\text{OH})_2$ is precipitated which is soluble in excess of alkali.
 - (2) copper hydroxide is amphoteric.
 - (3) in acidic solution hydration protects Cu^{2+} ions.
 - (4) in acidic solution protons coordinates with ammonia molecule forming NH_4^+ ions and NH_3 molecules are not available.
3. In the coordination compound $\text{K}_4[\text{Ni}(\text{CN})_4]$, the oxidation state of nickel is : **[AIEEE 2003, 3/225]**
 - (1) -1
 - (2) 0
 - (3) +1
 - (4) +2
4. The co-ordination number of a central metal atom in a complex is determined by : **[AIEEE 2004, 3/225]**
 - (1) the number of only anionic ligands bonded to metal ion
 - (2) the number of ligands around a metal ion bonded by pi bonds
 - (3) the number of ligands around a metal ion bonded by sigma and pi bonds
 - (4) the number of ligands around a metal ion bonded by sigma bonds
5. Which one is an outer orbital complex ? **[AIEEE 2004, 3/225]**
 - (1) $[\text{Ni}(\text{NH}_3)_6]^{2+}$
 - (2) $[\text{Mn}(\text{CN})_6]^{4-}$
 - (3) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - (4) $[\text{Fe}(\text{CN})_6]^{4-}$
6. Co-ordination compounds have great importance in biological systems. In this context, which statement is incorrect ? **[AIEEE 2004, 3/225]**
 - (1) Carboxypeptidase-A is an enzyme and contains zinc.
 - (2) Haemoglobin is the red pigment of blood and contains iron.
 - (3) Cyanocobalamin is B_{12} and contains cobalt.
 - (4) Chlorophylls are green pigments in plants and contain calcium.
7. Which one has largest number of isomers ? **[AIEEE 2004, 3/225]**
 - (1) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 - (2) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
 - (3) $[\text{Ir}(\text{PhR}_3)_2\text{H}(\text{CO})]^{2+}$
 - (4) $[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^+$
8. The correct order of magnetic moments (only spin value in BM) among is : **[AIEEE 2004, 3/225]**
 - (1) $\text{Fe}(\text{CN})_6^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$
 - (2) $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$
 - (3) $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$
 - (4) $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$
9. The oxidation state of Cr in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ is : **[AIEEE 2005, 1 1/2/225]**
 - (1) 0
 - (2) +1
 - (3) +2
 - (4) +3
10. The IUPAC name of $\text{K}_3\text{Fe}(\text{CN})_6$ is : **[AIEEE 2005, 3/225]**
 - (1) Potassium hexacyanoferrate(II)
 - (2) Potassium hexacyanoferrate(III)
 - (3) Potassium hexacyanoiron(II)
 - (4) Tripotassium hexacyanoiron(II)
11. Which of the following will show optical isomerism ? **[AIEEE 2005, 3/225]**
 - (1) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 - (2) $[\text{ZnCl}_4]^{2-}$
 - (3) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$
 - (4) $[\text{Co}(\text{CN})_6]^{3-}$
12. Which one of the following complexes would exhibit the lowest value of paramagnetic behaviour ? **[AIEEE 2005, 3/225]**
 - (1) $[\text{Co}(\text{CN})_6]^{3-}$
 - (2) $[\text{Fe}(\text{CN})_6]^{3-}$
 - (3) $[\text{Mn}(\text{CN})_6]^{3-}$
 - (4) $[\text{Cr}(\text{CN})_6]^{3-}$
13. The value of 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is: (Assuming octahedral complex) **[AIEEE 2005, 4 1/2/225]**
 - (1) d^4 (in strong field ligand)
 - (2) d^4 (in weak field ligand)
 - (3) d^3 (in weak as well as strong field ligand)
 - (4) d^5 (in strong field ligand)
14. Nickel ($Z = 28$) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[\text{NiX}_4]^{2-}$. The number of unpaired electron(s) in the nickel and geometry of this complex ion are, respectively : **[AIEEE 2006, 3/165]**
 - (1) one, tetrahedral
 - (2) two, tetrahedral
 - (3) one, square planar
 - (4) two, square planar
15. The IUPAC name for the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ is : **[AIEEE 2006, 3/165]**
 - (1) Nitrito-N-pentaamminecobalt(III) chloride
 - (2) Nitrito-N-pentaamminecobalt(II) chloride
 - (3) Pentaamminenitrito-N-cobalt(II) chloride
 - (4) Pentaamminenitrito-N-cobalt(III) chloride



16. In $\text{Fe}(\text{CO})_5$, the Fe – C bond possesses : [AIEEE 2006, 3/165]
 (1) π -character only (2) both σ and π characters
 (3) ionic character only (4) σ -character only
17. How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with a Ca^{2+} ion ? [AIEEE 2006, 3/165]
 (1) Six (2) Three (3) One (4) Two
18. The 'spin only' magnetic moment (in units of Bohr magneton, μ_B) of Ni^{2+} in aqueous solution would be (atomic number Ni = 28) [AIEEE 2006, 3/165]
 (1) 2.84 (2) 4.80 (3) 0 (4) 1.73
19. Which one of the following has a square planar geometry? [AIEEE 2007, 2/120]
 (1) $[\text{NiCl}_4]^{2-}$ (2) $[\text{PtCl}_4]^{2-}$ (3) $[\text{CoCl}_4]^{2-}$ (4) $[\text{FeCl}_4]^{2-}$
 (At. no. Co = 27, Ni = 28, Fe = 26, Pt = 78)
20. The coordination number and the oxidation state of the element 'E' in the complex $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4)] \text{NO}_2$ (when 'en' is ethylene diamine) are, respectively, [AIEEE 2008, 3/105]
 (1) 4 and 2 (2) 4 and 3 (3) 6 and 3 (4) 6 and 2
21. In which of the following octahedral complexes of Co (at no. 27), will the magnitude of Δ_0 be the highest? [AIEEE 2008, 3/105]
 (1) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ (2) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (3) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (4) $[\text{Co}(\text{CN})_6]^{3-}$
22. Which of the following has an optical isomer ? [AIEEE 2009, 4/144]
 (1) $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$ (2) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$ (3) $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$ (4) $[\text{Co}(\text{NH}_3)_3\text{Cl}]^+$
23. Which of the following pairs represents linkage isomers ? [AIEEE 2009, 4/144]
 (1) $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$ and $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$
 (2) $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{NO}_3$
 (3) $[\text{PtCl}_2(\text{NH}_3)_4\text{Br}_2]$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
 (4) $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
24. A solution containing 2.675 g of $\text{CoCl}_3 \cdot 6\text{NH}_3$ (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) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (2) $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ (3) $[\text{CoCl}_3(\text{NH}_3)_3]$ (4) $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$
25. Which one of the following has an optical isomer ? [AIEEE 2010, 4/144]
 (1) $[\text{Zn}(\text{en})(\text{NH}_3)_2]^{2+}$ (2) $[\text{Co}(\text{en})_3]^{3+}$ (3) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$ (4) $[\text{Zn}(\text{en})_2]^{2+}$
 (en = ethylenediamine)
26. Which of the following facts about the complex $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ 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.
27. The magnetic moment (spin only) of $[\text{NiCl}_4]^{2-}$ is : [AIEEE 2011, 4/144]
 (1) 1.82 BM (2) 5.46 BM (3) 2.82 BM (4) 1.41 BM
28. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide? [AIEEE 2012, 4/144]
 (1) $[\text{Cr}(\text{en})_3]\text{Br}_3$ (2) $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$ (3) $[\text{Cr}(\text{en})\text{Br}_4]^-$ (4) $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$
29. Which of the following complex species is not expected to exhibit optical isomerism ? [JEE(Main) 2013, 4/120]
 (1) $[\text{Co}(\text{en})_3]^{3+}$ (2) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (3) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (4) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$



30. 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) $L_1 < L_2 < L_4 < L_3$
31. 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
32. 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 $[CoCl_4]^{2-}$
33. 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)
34. On treatment of 100 mL of 0.1 M solution of $CoCl_3 \cdot 6H_2O$ with excess $AgNO_3$; 1.2×10^{22} ions are precipitated. The complex is : **[JEE(Main) 2017, 4/120]**
 (1) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$ (2) $[Co(H_2O)_6]Cl_3$
 (3) $[Co(H_2O)_5Cl]Cl_2 \cdot 2H_2O$ (4) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$
35. 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 *trans*-isomer.
 (III) Only one isomer is produced if the reactant complex ion is a *trans*-isomer.
 (IV) Only one isomer is produced if the reactant complex ion is a *cis*-isomer.
 The correct statements are : **[JEE(Main) 2018, 4/120]**
 (1) (III) and (IV) (2) (II) and (IV) (3) (I) and (II) (4) (I) and (III)
36. The oxidation states of Cr in $[Cr(H_2O)_6]Cl_3$, $[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2(O)_2(NH_3)]$ 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

JEE(MAIN) ONLINE PROBLEMS

1. An octahedral complex of Co^{3+} is diamagnetic. The hybridisation involved in the formation of the complex is: **[JEE(Main) 2014 Online (09-04-14), 4/120]**
 (1) sp^3d^2 (2) dsp^2 (3) d^2sp^3 (4) sp^3d
2. The correct statement about the magnetic properties of $[Fe(CN)_6]^{3-}$ and $[FeF_6]^{3-}$ is : (Z = 26) **[JEE(Main) 2014 Online (09-04-14), 4/120]**
 (1) both are paramagnetic
 (2) both are diamagnetic
 (3) $[Fe(CN)_6]^{3-}$ is diamagnetic, $[FeF_6]^{3-}$ is paramagnetic.
 (4) $[Fe(CN)_6]^{3-}$ is paramagnetic, $[FeF_6]^{3-}$ is diamagnetic.
3. Which of the following name formula combinations is not correct ? **[JEE(Main) 2014 Online (11-04-14), 4/120]**
- | | Formula | Name |
|-----|--------------------------|--|
| (1) | $K_2[Pt(CN)_4]$ | Potassium tetracyanoplatinate (II) |
| (2) | $[Mn(CN)_5]^{2-}$ | Pentacyanomagnate (II) ion |
| (3) | $K[Cr(NH_3)_2Cl_4]$ | Potassium diammine tetrachlorochromate (III) |
| (4) | $[Co(NH_3)_4(H_2O)]SO_4$ | Tetraammine aquaiodo cobalt (III) sulphate |
4. Consider the coordination compound, $[Co(NH_3)_6]Cl_3$. In the formation of the complex, the species which acts as the Lewis acid is : **[JEE(Main) 2014 Online (11-04-14), 4/120]**
 (1) $[Co(NH_3)_6]^{3+}$ (2) Cl^- (3) Co^{3+} (4) NH_3



5. Among the following species the one which causes the highest CFSE, Δ_o as a ligand is :
[JEE(Main) 2014 Online (12-04-14), 4/120]
 (1) CN^- (2) NH_3 (3) F^- (4) CO
6. Which one of the following complexes will most likely absorb visible light ?
 (At nos. Sc = 21, Ti = 22, V = 23, Zn = 30)
[JEE(Main) 2014 Online (12-04-14), 4/120]
 (1) $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ (2) $[\text{Ti}(\text{NH}_3)_6]^{4+}$ (3) $[\text{V}(\text{NH}_3)_6]^{3+}$ (4) $[\text{Zn}(\text{NH}_3)_6]^{2+}$
7. An octahedral complex with molecular composition $\text{M.5NH}_3.\text{Cl}.\text{SO}_4$ has two isomers, A and B. The solution of A gives a white precipitate with AgNO_3 solution and the solution of B gives white precipitate with BaCl_2 solution. The type of isomerism exhibited by the complex is:
[JEE(Main) 2014 Online (19-04-14), 4/120]
 (1) Linkage isomerism (2) Ionisation isomerism
 (3) Coordinate isomerism (4) Geometrical isomerism
8. Nickel ($Z = 28$) combines with a uninegative monodentate ligand to form a diamagnetic complex $[\text{NiL}_4]^{2-}$. The hybridisation involved and the number of unpaired electrons present in the complex are respectively:
[JEE(Main) 2014 Online (19-04-14), 4/120]
 (1) sp^3 , two (2) dsp^2 , zero (3) dsp^2 , one (4) sp^3 , zero
9. The correct statement on the isomerism associated with the following complex ions,
[JEE(Main) 2015 Online (10-04-15), 4/120]
 (a) $[\text{Ni}(\text{H}_2\text{O})_5\text{NH}_3]^{2+}$, (b) $[\text{Ni}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$ and (c) $[\text{Ni}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{2+}$ is :
 (1) (a) and (b) show only geometrical isomerism.
 (2) (b) and (c) show geometrical and optical isomerism
 (3) (b) and (c) show only geometrical isomerism
 (4) (a) and (b) show geometrical and optical isomerism
10. Which molecule/ion among the following cannot act as a ligand in complex compounds?
[JEE(Main) 2015 Online (10-04-15), 4/120]
 (1) CH_4 (2) CN^- (3) Br^- (4) CO
11. Which of the following complex ions has electrons that are symmetrically filled in both t_{2g} and e_g orbitals?
[JEE(Main) 2015 Online (11-04-15), 4/120]
 (1) $[\text{FeF}_6]^{3-}$ (2) $[\text{Mn}(\text{CN})_6]^{4-}$ (3) $[\text{CoF}_6]^{3-}$ (4) $[\text{Co}(\text{NH}_3)_6]^{2+}$
12. Identify the correct trend given below: (Atomic No.: Ti = 22, Cr = 24 and Mo = 42)
[JEE(Main) 2016 Online (09-04-16), 4/120]
 (1) Δ_o of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and Δ_o of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (2) Δ_o of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and Δ_o of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (3) Δ_o of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and Δ_o of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (4) Δ_o of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and Δ_o of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
13. Which one of the following complexes will consume more equivalents of aqueous solution of $\text{Ag}(\text{NO}_3)$?
[JEE(Main) 2016 Online (09-04-16), 4/120]
 (1) $\text{Na}_3[\text{CrCl}_6]$ (2) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ (3) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (4) $\text{Na}_2[\text{CrCl}_5(\text{H}_2\text{O})]$
14. Which of the following is an example of homoleptic complex ?
[JEE(Main) 2016 Online (09-04-16), 4/120]
 (1) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$ (2) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (3) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (4) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
15. sp^3d^2 hybridization is **not** displayed by :
[JEE(Main) 2017 Online (08-04-17), 4/120]
 (1) PF_5 (2) SF_6 (3) $[\text{CrF}_6]^{3-}$ (4) BrF_5
16. $[\text{Co}_2(\text{CO})_8]$ displays :
[JEE(Main) 2017 Online (09-04-17), 4/120]
 (1) one 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, four terminal CO and four bridging CO
 (4) no Co–Co bond, six terminal CO and two bridging CO



17. The correct combination is : **[JEE(Main) 2018 Online (15-04-18), 4/120]**
 (1) $[\text{NiCl}_4]^{2-}$ – square-planar; $[\text{Ni}(\text{CN})_4]^{2-}$ – paramagnetic
 (2) $[\text{Ni}(\text{CN})_4]^{2-}$ – tetrahedral; $[\text{Ni}(\text{CO})_4]$ – paramagnetic
 (3) $[\text{NiCl}_4]^{2-}$ – paramagnetic; $[\text{Ni}(\text{CO})_4]$ – tetrahedral
 (4) $[\text{NiCl}_4]^{2-}$ – diamagnetic; $[\text{Ni}(\text{CO})_4]$ – square-planar
18. The correct order of spin-only magnetic moments among the following is :
 (Atomic number : Mn = 25, Co = 27, Ni = 28, Zn = 30) **[JEE(Main) 2018 Online (15-04-18), 4/120]**
 (1) $[\text{ZnCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$ (2) $[\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$
 (3) $[\text{NiCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$ (4) $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$
19. The total number of possible isomers for square-planar $[\text{Pt}(\text{Cl})(\text{NO}_2)(\text{NO}_3)(\text{SCN})]^{2-}$ is : **[JEE(Main) 2018 Online (15-04-18), 4/120]**
 (1) 8 (2) 12 (3) 16 (4) 24
20. In a complexometric titration of metal ion with ligand
 $\text{M (Metal ion)} + \text{L (Ligand)} \rightarrow \text{C (Complex)}$ end point is estimated spectrophotometrically (through light absorption). If 'M' and 'C' do not absorb light and only 'L' absorbs, then the titration plot between absorbed light (A) versus volume of ligand 'L' (V) would look like : **[JEE(Main) 2018 Online (16-04-18), 4/120]**
- (1)

(2)

(3)

(4)
21. In Wilkinson's catalyst, the hybridization of central metal ion and its shape are respectively : **[JEE(Main) 2018 Online (16-04-18), 4/120]**
 (1) sp^3d , trigonal bipyramidal (2) d^2sp^3 , octahedral
 (3) dsp^2 , square planar (4) sp^3 , tetrahedral
22. Which of the following complexes will show geometrical isomerism ? **[JEE(Main) 2018 Online (16-04-18), 4/120]**
 (1) Potassium tris(oxalato)chromate(III)
 (2) Pentaquaachlorochromium(III)chloride
 (3) Aquaachlorobis(ethylenediamine)cobalt(II) chloride
 (4) Potassium amminetrichloroplatinate(II)
23. Two complexes $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (A) and $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (B) 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 (A) is less than that of (B).
 (2) both absorb energies corresponding to their complementary colors.
 (3) Δ_0 values of (A) and (B) are calculated from the energies of violet and yellow light, respectively.
 (4) both are paramagnetic with three unpaired electrons.
24. 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) $\text{L}_1 < \text{L}_2 < \text{L}_3$ (2) $\text{L}_3 < \text{L}_2 < \text{L}_1$ (3) $\text{L}_2 < \text{L}_1 < \text{L}_3$ (4) $\text{L}_3 < \text{L}_1 < \text{L}_2$
25. The complex that has highest crystal field splitting energy (Δ), is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**
 (1) $\text{K}_2[\text{CoCl}_4]$ (2) $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ (3) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (4) $\text{K}_3[\text{Co}(\text{CN})_6]$
26. Wilkinson catalyst is : **[JEE(Main) 2019 Online (10-01-19), 4/120]**
 (1) $[(\text{Et}_3\text{P})_3\text{IrCl}]$ (Et = C_2H_5) (2) $[(\text{Et}_3\text{P})_3\text{RhCl}]$
 (3) $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ (4) $[(\text{Ph}_3\text{P})_3\text{IrCl}]$



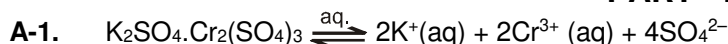
27. The total number of isomers for a square planar complex $[M(F)(Cl)(SCN)(NO_2)]$ is :
[JEE(Main) 2019 Online (10-01-19), 4/120]
 (1) 16 (2) 4 (3) 12 (4) 8
28. The difference in the number of unpaired electrons of a metal ion in its high-spin and low-spin octahedral complexes is two. The metal ion is:
[JEE(Main) 2019 Online (10-01-19), 4/120]
 (1) Co^{2+} (2) Fe^{2+} (3) Mn^{2+} (4) Ni^{2+}
29. A reaction of cobalt(III) chloride and ethylenediamine in a 1 : 2 mole ratio generates two isomeric products A (violet coloured) and B (green coloured). A can show optical activity, but, B is optically inactive. What type of isomers does A and B represent? **[JEE(Main) 2019 Online (10-01-19), 4/120]**
 (1) Ionisation isomers (2) Linkage isomer
 (3) Coordination isomers (4) Geometrical isomers
30. Match the metals (column I) with the coordination compound(s)/ enzyme (s) (column II):
[JEE(Main) 2019 Online (11-01-19), 4/120]
- | (column I)
Metal | (column II)
Coordination compound(s)/enzyme(s) |
|---|---|
| (A) Co | (i) Wilkinson catalyst |
| (B) Zn | (ii) Chlorophyll |
| (C) Rh | (iii) Vitamin B ₁₂ |
| (D) Mg | (iv) Carbonic anhydrase |
| (1) (A)-(i);(B)-(ii);(C)-(iii);(D)-(iv) | (2) (A)-(iv);(B)-(iii);(C)-(i);(D)-(ii) |
| (3) (A)-(iii);(B)-(iv);(C)-(i);(D)-(ii) | (4) (A)-(ii);(B)-(i);(C)-(iv);(D)-(iii) |
31. The coordination number of Th in $K_4[Th(C_2O_4)_4(OH_2)_2]$ is: **[JEE(Main) 2019 Online (11-01-19), 4/120]**
 ($C_2O_4^{2-}$ = Oxalato)
 (1) 14 (2) 10 (3) 6 (4) 8
32. The number of bridging CO ligand(s) and Co-Co bond (s) in $Co_2(CO)_8$, respectively are :
[JEE(Main) 2019 Online (11-01-19), 4/120]
 (1) 4 and 0 (2) 0 and 2 (3) 2 and 1 (4) 2 and 0
33. The metal d-orbitals that are directly facing the ligands in $K_3[Co(CN)_6]$ are :
[JEE(Main) 2019 Online (12-01-19), 4/120]
 (1) d_{xz} , d_{yz} and d_{z^2} (2) d_{xy} and $d_{x^2-y^2}$ (3) d_{xy} , d_{xz} and d_{yz} (4) $d_{x^2-y^2}$ and d_{z^2}
34. $Mn_2(CO)_{10}$ is an organometallic compound due to the presence of :
[JEE(Main) 2019 Online (12-01-19), 4/120]
 (1) Mn – C bond (2) C – O bond (3) Mn – O bond (4) Mn – Mn bond
35. The magnetic moment of an octahedral homoleptic Mn(II) complex is 5.9 BM. The suitable ligand for this complex is:
[JEE(Main) 2019 Online (12-01-19), 4/120]
 (1) Ethylenediamine (2) CN^- (3) NCS^- (4) CO



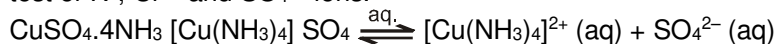
Answers

EXERCISE - 1

PART - I



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.



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.

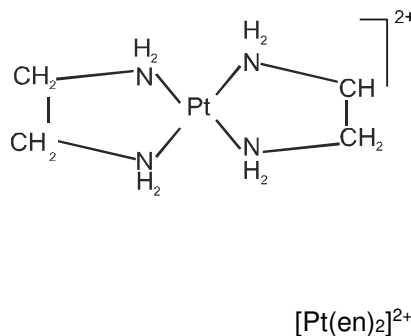
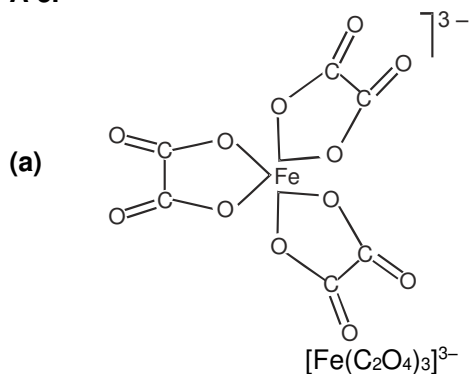
The oxidation number of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.

	Complex	Coordination Number	Oxidation State
(a)	$[\text{AgCl}_2]^-$	2	1
(b)	$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$	6	3
(c)	$[\text{Co}(\text{NCS})_4]^{2-}$	4	2
(d)	$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	6	3
(e)	$[\text{Fe}(\text{EDTA})]^-$	6	3
(f)	$[\text{Cu}(\text{en})_2]\text{SO}_4$	4	2
(g)	$\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$	6	4

- A-3.** (A) methyl isocyanide, monodentate. (B) acetylacetonato, bidentate
 (C) azido, monodentate (D) diethylenetriamine, tridentate
 (E) ethylenediamine tetraacetato, hexadentate (F) ethylenediamine triacetato, pentadentate
 (G) oxalato, bidentate (H) dimethylglyoximate
 (I) isocyanido, monodentate (J) nitrito, monodentate
 (K) oxido, monodentate (L) superoxido, monodentate

- A-4.** (A) $\text{M} \leftarrow \text{N} \begin{array}{l} \text{O} \\ \text{O} \end{array}$ nitrito-N $\text{M} \leftarrow \text{O}-\text{N}=\text{O}$ nitrito-O
 (B) $\text{M} \leftarrow \text{SCN}$ thiocyanato or thiocyanato-S, $\text{M} \leftarrow \text{NCS}$ isothiocyanato or thiocyanato-N
 (C) $\begin{array}{c} \text{S}=\text{C}=\text{O} \\ | \\ \text{C}=\text{O} \\ | \\ \text{S}=\text{C}=\text{O} \end{array}$ or $\begin{array}{c} \text{S}^--\text{C}=\text{O} \\ | \\ \text{C}=\text{O} \\ | \\ \text{S}^--\text{C}=\text{O} \end{array}$ dithioxalate
 (D) $\text{M} \leftarrow \text{OCN}$ cyanato-O or cyanato-N, $\text{M} \leftarrow \text{NCO}$ isothiocyanato or thiocyanato-N
 (E) $\text{M} \leftarrow \text{NOS}$ thionitrito-N or, $\text{M} \leftarrow \text{SON}$ thionitrito-S

A-5.





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) $K_2[Ni(CN)_4] \xrightleftharpoons{aq.} 2K^+(aq) + [Ni(CN)_4]^{2-}(aq)$
 $[Cr(en)_3]Cl_3 \xrightleftharpoons{aq.} [Cr(en)_3]^{3+}(aq) + 3Cl^-(aq)$
 $Fe_4[Fe(CN)_6]_3 \xrightleftharpoons{aq.} 4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq)$
 $[PtCl_2(en)_2](NO_3)_2 \xrightleftharpoons{aq.} [PtCl_2(en)_2]^{2+}(aq) + 2(NO_3)^-(aq)$
 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 hexanitrito-N-cobaltate(III)
(m)	$[Ni(dmgl)_2]$	Bis(dimethylglyoximate)nickel(II)
(n)	$K_2[PtCl_6]$	Potassium hexachloridoplatinate(IV)
(o)	$Na_2[Fe(CN)_5NO^+]$	Sodium pentacyanonitrosoniumferrate(II)
(p)	$[Fe(H_2O)_5(NO^+)]SO_4$	Pentaaquanitrosoniumiron(I) sulphate
(q)	$[Cu(CN)_4]^{3-}$	Tetracyanidocuprate(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)	$[(NH_3)_5Co-NH_2-Co(NH_3)_4(H_2O)]Cl_5$	Pentaamminecobalt(III)-μ-amidotetraammineaquacobalt(III) chloride
(g)	$[Cr(CO)_5(PPh_3)]$	Pentacarbonyltriphenylphosphinechromium(0)
(h)	$[(CO)_5Mn-Mn(CO)_5]$	Decacarbonyldimanganese(0)
(i)	$Cr(\pi-C_6H_6)_2$	Bis(η ⁶ -benzene)chromium(0)
(j)	$[Co(NH_3)_4(OH_2)_2][BF_4]_3$	Tetraamminediaquacobalt(III) tetrafluoroborate(III)



(I)	Ba[Zr(OH) ₂ (ONO) ₂ (ox)]	Barium dihydroxidodinitrito-O-oxalatozirconate(IV)
(I)	[Co(NH ₃) ₆][Co(C ₂ O 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 hexafluoroaluminate(III)	Na ₃ [AlF ₆]
(f)	Diamminesilver(I) ion	[Ag(NH ₃) ₂] ⁺

B-4.

(a)	Diamminetriaquahydroxidochromium(III) nitrate	[Cr(NH ₃) ₂ (H ₂ O) 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) ₅ N 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]

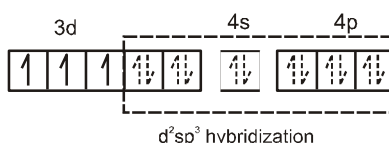
C-1. (a) – iv, (b) – viii, (c) – i, (d) – vii,
(e) – iii, (f) – v, (g) – ii, (h) – vi

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) $[\text{Cr}(\text{NH}_3)_4\text{Cl Br}]\text{Cl} \xrightleftharpoons{\text{aq.}} [\text{Cr}(\text{NH}_3)_4\text{Cl Br}]^+ + \text{Cl}^-$; $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl} \downarrow$ (white); soluble in dilute NH_3 .
 $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br} \xrightleftharpoons{\text{aq.}} [\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Br}^-$; $\text{Ag}^+ + \text{Br}^- \longrightarrow \text{AgBr} \downarrow$ (yellow); soluble in conc. NH_3 .
 So, A = $[\text{Cr}(\text{NH}_3)_4\text{Cl Br}]\text{Cl}$ and B = $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$.
 (ii) In both complexes chromium is in +3 oxidation state. Chromium with 3d³ configuration has 3 unpaired electrons with weak field as well as strong field ligand. So, the hybridisation scheme is as follow :



(iii) $\mu = \sqrt{n(n+2)} = \sqrt{15}$

(iv) EAN = 24 – 3 + 12 = 33

(v) Yes, both have two ions per formula unit.



D-2.

	Complex	Hybridization	Geometry
(a)	[NiBr ₄] ²⁻	sp ³	Tetrahedral
(b)	[AuCl ₄] ⁻	dsp ²	square planar
(c)	[Pt(NH ₃) ₄] ²⁺	dsp ²	square planar

E-1. (i) potassium amminetetracyanonitrosoniumchromate(I)
 (ii) Octahedral
 (iii) One unpaired electron
 (iv) It is paramagnetic with one unpaired electron
 (v) EAN = 24 – 1 + 2 × 6 = 35
 (vi) d²sp³

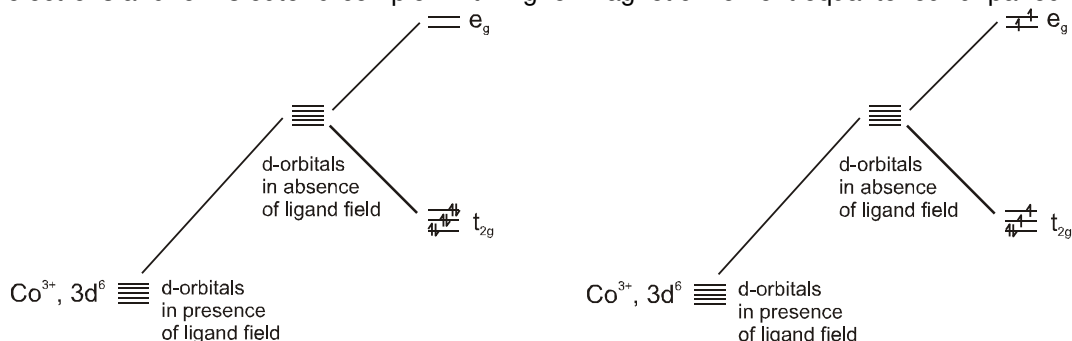


E-2.

	Complex	Hybridization	Geometry
(a)	$[\text{Fe}(\text{CN})_6]^{3-}$	d^2sp^3	octahedral
(b)	$[\text{MnBr}_4]^{2-}$	sp^3	Tetrahedral
(c)	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	sp^3d^2	Octahedral
(d)	$[\text{Co}(\text{SCN})_4]^{2-}$	sp^3	Tetrahedral

E-3.

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-4.

 (a) $i < iv < ii < iii$

 (b) $X < O < N < C$

 (c) $\text{Br}^- < \text{S}^{2-} < \text{NO}_3^- < \text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^- < \text{CN}^- < \text{CO}$

E-5.

(a)	F^- is weak field ligand. Cr^{3+} , $3d^3$	Diagram showing d-orbital splitting for Cr^{3+} ($3d^3$) with F^- as a weak field ligand. The t_{2g} orbitals are partially filled with 3 unpaired electrons.	So number of unpaired electrons = 3
(b)	H_2O is weak field ligand. V^{3+} , $3d^2$	Diagram showing d-orbital splitting for V^{3+} ($3d^2$) with H_2O as a weak field ligand. The t_{2g} orbitals are partially filled with 2 unpaired electrons.	So number of unpaired electrons = 2
(c)	CN^- is strong field ligand. Fe^{3+} , $3d^5$	Diagram showing d-orbital splitting for Fe^{3+} ($3d^5$) with CN^- as a strong field ligand. The t_{2g} orbitals are fully filled with 5 paired electrons.	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.

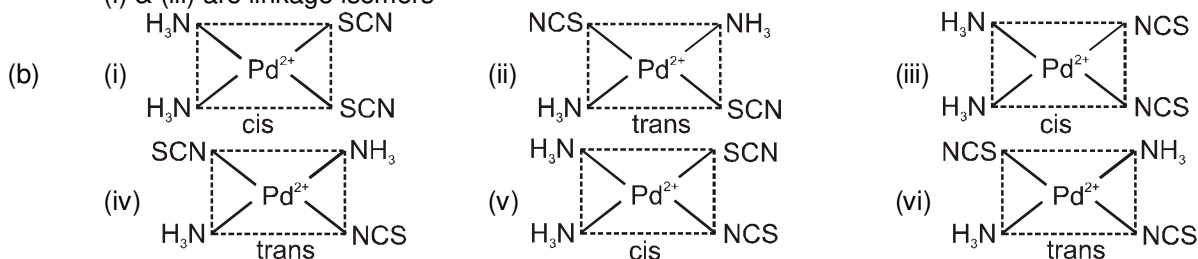
F-1. As $3d^6$ configuration has higher CFSE as compared to $3d^7$ so it gets oxidised in presence of complexing reagent to easily have d^2sp^3 hybridisation.

F-2. Yellow colour

F-3. (a) CN^- , F^-
(b) (i) 0 (ii) 0 (iii) 0 (iv) 0

G-1. (i) Linkage (ii) Coordination (iii) Ionisation (iv) Hydrate

G-2. (a) There are three constitutional isomers
(i) $[\text{Ru}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}$
(ii) $[\text{Ru}(\text{NH}_3)_5\text{Cl}](\text{NO}_2)$ or $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{ONO}$
(iii) $[\text{Ru}(\text{NH}_3)_5\text{ONO}]\text{Cl}$
(i) & (ii) are ionisation isomers
(i) & (iii) are linkage isomers

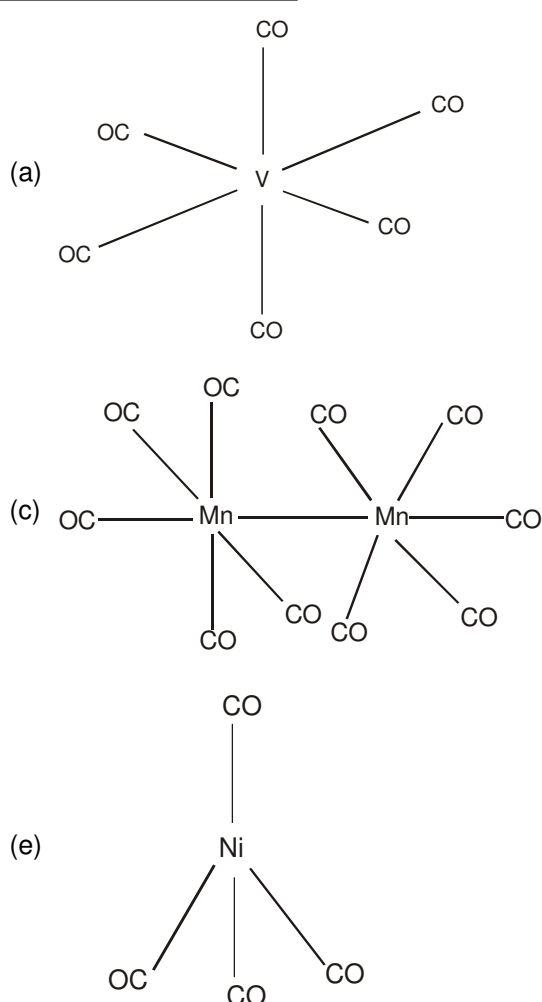


G-3. (a) Two (b) None (c) Two (d) None (e) Two (f) None

G-4. (a) No ; (b) Yes ; (c) Yes ; (d) Yes ; (e) Yes ; (f) No.



H-1.



H-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)

D-3. (C)

D-4. (B)

D-5. (A)

D-6. (A)

E-1. (C)

E-2. (A)

E-3. (A)

E-4. (B)

E-5. (A)

E-6. (D)

E-7. (D)

E-8. (C)

E-9. (A)

E-10. (C)

E-11. (C)

E-12. (C)

F-1. (B)

F-2. (B)

G-1. (C)

G-2. (B)

G-3. (B)

G-4. (D)

G-5. (C)

G-6. (C)

H-1. (D)

H-2. (D)

PART - III

1. (A - p,r,t); (B - p,s,t); (C - p,r,t); (D - q,r)

2. (A - p,q,r); (B - q,r,s); (C - p,q,r,s); (D - p,q)


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EXERCISE - 2

PART - I

- | | | | | |
|---------|---------|---------|--------|---------|
| 1. (B) | 2. (C) | 3. (A) | 4. (B) | 5. (D) |
| 6. (D) | 7. (D) | 8. (C) | 9. (D) | 10. (B) |
| 11. (B) | 12. (A) | 13. (A) | | |

PART - II

- | | | | |
|------------------------------|----------------|--------------|-------------------------|
| 1. 13 | 2. 05 | 3. 26 | 4. (40 + 20) ml = 60 ml |
| 5. 4 (i, iii, iv, vii) | 6. 3 (a, c, d) | 7. 2 (i & v) | 8. 4 |
| 9. 4 (0 + 0 + 2 + 0 + 2 = 4) | 10. 4 | 11. 12 | |

PART - III

- | | | | | |
|-----------|---------|-----------|----------|-----------|
| 1. (BCD) | 2. (BC) | 3. (ABCD) | 4. (B) | 5. (BD) |
| 6. (ABCD) | 7. (BD) | 8. (AB) | 9. (ACD) | 10. (BCD) |
| 11. (BCD) | 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. IUPAC name is :

Potassium amminetetraacyanonitrosoniumchromate(I)

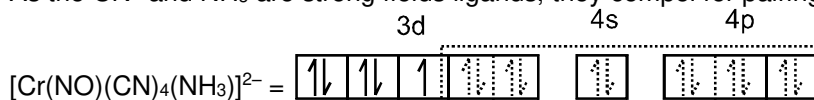
or Potassium amminetetraacyanonitrocylumchromate(I).

Let n is the number of unpaired electron in the chromium ion.

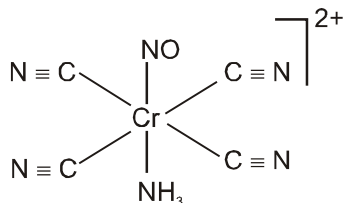
Since $\mu = \sqrt{n(n+2)}$ or $1.73 = \sqrt{n(n+2)}$ B.M. or $1.73 \times 1.73 = n^2 + 2n$.

Hence $n = 1$.

As the CN^- and NH_3 are strong fields ligands, they compel for pairing of electrons. So,



Hence, the oxidation state of chromium is +1 (having $3d^5$ configuration). So according to charge on the complex NO should be NO^+ and the structure of this complex is octahedral with d^2sp^3 hybridisation as given below

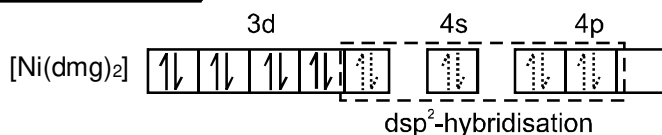


2. (D) 3. (C)

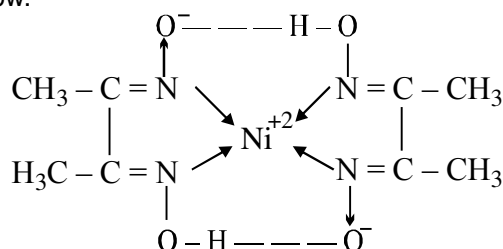
4. $\text{Ni}^{2+} + 2\text{dmg} \xrightarrow{\text{NH}_4\text{OH}} [\text{Ni}(\text{dmg})_2] \downarrow$ (bright red).

It acquires stability through chelation and intra molecular H-bonding.

In $[\text{Ni}(\text{dmg})_2]$ the nickel is in +2 oxidation state and to have square planar geometry because of chelation the pairing of electrons takes place. So



As all electrons are paired, so complex is diamagnetic. Nickel with coordination number four will have the structure as given below.



rosy red ppt

5. (A)	6. (A)	7. (A)	8. (C)	9. (C)
10. (B)	11. (A - p,q,s); (B - p,r,s); (C - q,s); (D - q,s)	12. (C)	13. (B)	
14. (B)	15. (A)	16.* (CD)	17. (A)	18. (C)
19. (B)	20. (B)	21. 3	22. (B)	23. (C)
24. 6	25. (D)	26. (C)	27. (B)	28.* (BD)
29. 8	30. 4	31. (B)	32. 4	33. 3
34. 6	35. (B)	36. 5	37. (A)	38. (ACD)
39.* (BC)	40. 1	41. 2992	42.* (ABD)	43. (C)

PART - II

JEE(MAIN) OFFLINE PROBLEMS

1. (3)	2. (4)	3. (2)	4. (4)	5. (1)
6. (4)	7. (1)	8. (4)	9. (4)	10. (2)
11. (3)	12. (1)	13. (1)	14. (2)	15. (4)
16. (2)	17. (3)	18. (1)	19. (2)	20. (3)
21. (4)	22. (3)	23. (1)	24. (1)	25. (2)
26. (3)	27. (3)	28. (2)	29. (3)	30. (2)
31. (2)	32. (1)	33. (1)	34. (4)	35. (4)
36. (1)				

JEE(MAIN) ONLINE PROBLEMS

1. (3)	2. (1)	3. (2)	4. (3)	5. (4)
6. (3)	7. (2)	8. (2)	9. (3)	10. (1)
11. (1)	12. (4)	13. (3)	14. (2)	15. (1)
16. (2)	17. (3)	18. (4)	19. (2)	20. (1)
21. (3)	22. (3)	23. (3)	24. (4)	25. (4)
26. (3)	27. (3)	28. (1)	29. (4)	30. (3)
31. (2)	32. (3)	33. (4)	34. (1)	35. (3)



Additional Problems For Self Practice (APSP)

✎ Marked questions are recommended for Revision.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

Important Instructions

- The test is of **1 hour** duration.
- The Test Booklet consists of **30** questions. The maximum marks are **120**.
- Each question is allotted **4 (four)** marks for correct response.
- Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. **¼ (one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

- In which of the following complexes the nickel metal is in highest oxidation state ?
(1) $\text{Ni}(\text{CO})_4$ (2) K_2NiF_6 (3) $[\text{Ni}(\text{NH}_3)_6](\text{BF}_4)_2$ (4) $\text{K}_4[\text{Ni}(\text{CN})_6]$
- The EAN of platinum in potassium hexachloroplatinate (IV) is :
(1) 46 (2) 86 (3) 36 (4) 84
- ✎ The IUPAC name of $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O})_2(\text{NH}_3)]$ is :
(1) Potassium amminedicyanodioxoperoxochromate(VI)
(2) Potassium amminecyanoperoxodioxochromium(VI)
(3) Potassium amminedicyanoperoxooxochromium(VI)
(4) Potassium amminecyanodiperoxodioxochromate(VI)
- Which one of the following high-spin complexes has the largest CFSE (Crystal field stabilization energy)?
(1) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (3) $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ (4) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- ✎ Which of the following complex will show optical activity ?
(1) $\text{trans-}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
(3) $\text{cis-}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$ (4) $\text{trans-}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$
- Which kind of isomerism is shown by the complex $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{SO}_4$?
1. Ionisation isomerism 2. Linkage isomerism
3. Geometrical isomerism 4. Optical isomerism
(1) 1, 2, 3 and 4 are correct (2) 1, 3 and 4 are correct only
(3) 1 and 2 are correct only (4) 2, 3 and 4 are correct only
- Which of the following statements is correct for complex $[\text{Cr}(\text{NH}_3)(\text{CN})_4(\text{NO})]^{2-}$ (given that $n = 1$)?
(1) It is d^2sp^3 hybridised .
(2) The chromium is in +1 oxidation state
(3) It is heteroleptic complex and its aqueous solution is coloured
(4) All of these.
- Consider the following statements
S₁ : $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex with crystal field stabilization energy equal to $-1.2 \Delta_o$
S₂ : The complex formed by joining the CN^- ligands to Fe^{3+} ion has theoretical value of 'spin only' magnetic moment equal to 1.73 B.M.
S₃ : $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$, In reactant and product the oxidation states of iron are same.
and arrange in the order of true/false.
(1) F T F (2) T T F (3) T T T (4) F F F



9. Which of the following statements is false ?
 (1) Complex of Pt(+II) and Au(+III) are square planar - including those with weak field ligands such as halide ions.
 (2) In tetrahedral complex, the t_{2g} orbitals are nearer to the direction of the ligands.
 (3) For d^0 , d^5 and d^{10} arrangements the CFSE is zero in both octahedral and tetrahedral complexes with weak field ligands.
 (4) None.
10. 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 ?
 (1) 0.0012 (2) 0.0016 (3) 0.0024 (4) 0.0048
11. A complex of certain metal has the magnetic moment of 4.91 BM whereas another complex of the same metal with same oxidation state has zero magnetic moment. The metal ion could be :
 (1) Co^{2+} (2) Mn^{2+} (3) Fe^{2+} (4) Fe^{3+}
12. Oxidation number of Fe in violet coloured complex $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$ is :
 (1) 0 (2) 2 (3) 3 (4) 4
13. Aqueous solution of nickel sulphate on treating with pyridine and then adding a solution of sodium nitrite gives dark blue crystals of :
 (1) $[\text{Ni}(\text{py})_4]\text{SO}_4$ (2) $[\text{Ni}(\text{py})_2(\text{NO}_2)_2]$ (3) $[\text{Ni}(\text{py})_4](\text{NO}_2)_2$ (4) $[\text{Ni}(\text{py})_3(\text{NO}_2)_2]\text{SO}_4$
14. The IUPAC name of $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$ is :
 (1) Hexaamminecobalt(III) tris(oxalato)chromate(III)
 (2) Hexaamminecobalt(III) tris(oxalato)chromium(III)
 (3) Hexaamminecobalt(II) tris(oxalato)chromium(III)
 (4) Hexaamminecobalt(III) trioxalatechromium(III)
15. In the compound lithiumtetrahydroaluminate, the ligand is :
 (1) H^+ (2) H (3) H^- (4) None of these
16. The oxidation number of Co in the complex ion $[(\text{en})_2\text{Co} \begin{smallmatrix} \text{NH} \\ \text{OH} \end{smallmatrix} \text{Co}(\text{en})_2]^{3+}$ is :
 (1) +2 (2) +3 (3) +4 (4) +6
17. The magnitude of crystal field stabilisation energy (CFSE of Δ_t) in tetrahedral complexes is considerably less than that in the octahedral field. Because
 (1) There are only four ligands instead of six so the ligand field is only 2/3 in tetrahedral complex
 (2) 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
 (3) Both points (1) and (2) are correct
 (4) Both points (1) and (2) are wrong
18. Other than the X-ray diffractions, how could be the following pairs of isomers be distinguished from one another by ;
 $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$ and $[\text{Cr}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Cr}(\text{NH}_3)_2(\text{NO}_2)_4]$
 (1) cryoscopic method (2) measurement of molar conductance
 (3) measuring magnetic moments (4) observing their colours
19. $[\text{Fe}(\text{en})_2(\text{H}_2\text{O})_2]^{2+} + \text{en} \longrightarrow \text{complex(X)}$. The correct statement about the complex (X) is :
 (1) it is a low spin complex. (2) it is diamagnetic.
 (3) it shows geometrical isomerism. (4) (1) and (2) both.
20. Which of the following pairs will show the same magnetic moment ('spin only')?
 (1) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ (2) $[\text{Mn}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$
 (3) $[\text{Ni}(\text{CO})_4]$ and $[\text{Zn}(\text{NH}_3)_4]^{2+}$ (4) All of these.
21. What will be the theoretical value of 'spin only' magnetic moment when $\text{Fe}(\text{SCN})_3$ reacts with a solution containing F^- ions to yield a colourless complex ?
 (1) 2.83 B.M. (2) 3.87 B.M. (3) 5.92 B.M. (4) 1.73 B.M.



22. Which of the following statements about $\text{Fe}(\text{CO})_5$ is correct?
 (1) It is paramagnetic and high spin complex (2) It is diamagnetic and high spin complex
 (3) It is diamagnetic and low spin complex (4) It is paramagnetic and low spin complex
23. The crystal field-splitting for Cr^{3+} ion in octahedral field changes for ligands I^- , H_2O , NH_3 , CN^- and the increasing order is :
 (1) $\text{I}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$ (2) $\text{CN}^- < \text{I}^- < \text{H}_2\text{O} < \text{NH}_3$
 (3) $\text{CN}^- < \text{NH}_3 < \text{H}_2\text{O} < \text{I}^-$ (4) $\text{NH}_3 < \text{H}_2\text{O} < \text{I}^- < \text{CN}^-$
24. Which of the following complex ion is not expected to absorb visible light ?
 (1) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Zn}(\text{NH}_3)_4]^{2+}$ (3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (4) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
25. Of the following complex ions, the one that probably has the largest overall formation constant, K_f , is :
 (1) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (2) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (3) $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{3+}$ (4) $[\text{Co}(\text{en})_3]^{3+}$
26. The correct structure of $\text{Fe}(\text{CO})_5$ is :
 (1) octahedral (2) tetrahedral (3) square pyramidal (4) trigonal bipyramidal
27. Arrange the following in order of decreasing number of unpaired electrons :
 I : $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ II : $[\text{Fe}(\text{CN})_6]^{3-}$ III : $[\text{Fe}(\text{CN})_6]^{4-}$ IV : $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 (1) IV, I, II, III (2) I, II, III, IV (3) III, II, I, IV (4) II, III, I, IV
28. Match List-I (Complexes) with List-II (Hybridization) of central atom and select the correct answer using the codes given below the lists :

	List-I		List-II
A	$\text{Ni}(\text{CO})_4$	1.	sp^3
B	$[\text{Ni}(\text{CN})_4]^{2-}$	2.	dsp^2
C	$[\text{Fe}(\text{CN})_6]^{4-}$	3.	sp^3d^2
D	$[\text{MnF}_6]^{4-}$	4.	d^2sp^3

Code :

	A	B	C	D		A	B	C	D
(1)	1	3	2	4	(2)	5	2	4	3
(3)	5	3	2	4	(4)	1	2	4	3

29. Which of the following complexes shows ionization isomerism ?
 (1) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (2) $[\text{Cr}(\text{en})_2]\text{Cl}_2$ (3) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ (4) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
30. Coordination number of Ni in $[\text{Ni}(\text{C}_2\text{O}_4)_3]^{4-}$ is :
 (1) 3 (2) 6 (3) 4 (4) 2

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

PART-II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. The angle between the bonding orbitals of a molecule AX_3 with zero dipole moment is [NSEC-2000]
 (A) 120° (B) 109° (C) 104° (D) 180°



2. In which of the following compounds, the oxidation number of the stated transition metal is zero. **[NSEC-2000]**
 (A) $[\text{Ni}(\text{CO})_4]$ (B) $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ (C) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ (D) $[\text{Fe}(\text{H}_2\text{O})_3](\text{OH})_2$
3. Ligands contain : **[NSEC-2001]**
 (A) lone pair of electron (B) incomplete octet
 (C) unpaired electron (D) shared pair of electron
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. 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.
6. A $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ complex typically absorbs at around 600 nm. It is allowed to react with ammonia to form a new complex $[\text{M}(\text{NH}_3)_6]^{2+}$ that should have absorption at **[NSEC-2003]**
 (A) 800nm (B) 580nm (C) 620nm (D) 320nm.
7. The least stable metal carbonyl as per the bonding considerations should be **[NSEC-2003]**
 (A) $\text{Cr}(\text{CO})_6$ (B) $\text{Mn}(\text{CO})_6$ (C) $\text{Fe}(\text{CO})_5$ (D) $\text{Ni}(\text{CO})_4$.
8. 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) 0 and 2 (B) 2 and 1 (C) 1 and 3 (D) 3 and 2
9. The compound in which nickel has the lowest oxidation number is **[NSEC-2004]**
 (A) $\text{Ni}(\text{CO})_4$ (B) $(\text{CH}_3\text{COO})_2\text{Ni}$ (C) NiO (D) $\text{NiCl}_2(\text{PPh}_3)_2$.
10. IUPAC name for $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ is **[NSEC-2004]**
 (A) potassium trioxalatoaluminate (III) (B) potassium aluminiumoxalate
 (C) potassium trioxalatealuminium (II) (D) potassium trioxalatealuminium (III)
11. Geometrical isomerism would be expected for which of the following compounds **[NSEC-2005]**
 (A) $[\text{Zn}(\text{NH}_3)_4]^{2+}$ (B) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (C) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ (D) $\text{K}_2[\text{CuCl}_4]$.
12. Co-ordination compounds $[\text{Pt}(\text{NH}_3)_3(\text{SCN})]$ and $[\text{Pt}(\text{NH}_3)_3(\text{NCS})]$ are examples of **[NSEC-2005]**
 (A) co-ordination isomerism (B) linkage isomerism
 (C) optical isomerism (D) hydrate isomerism.
13. The highest molar conductivity will be exhibited by the complex **[NSEC-2005]**
 (A) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (B) $[\text{Cr}(\text{NH}_3)_6\text{Cl}]\text{Cl}_2$ (C) $[\text{Cr}(\text{NH}_3)_6\text{Cl}_2]\text{Cl}$ (D) $[\text{Cr}(\text{NH}_3)_6\text{Cl}_3]$.
14. How many isomers are possible for the complex $[\text{Co}(\text{en})_2\text{Cl}_2]$ (en = ethylene diamine) **[NSEC-2006]**
 (A) 4 (B) 2 (C) 6 (D) 3
15. Which of the following complex ions does satisfy the effective atomic number (EAN) rule ? **[NSEC-2006]**
 (A) $[\text{Pt}(\text{NH}_3)_4]^{2+}$ (B) $[\text{PtCl}_4]^{2-}$ (C) $[\text{PtCl}_6]^{2-}$ (D) $[\text{Fe}(\text{CN})_6]^{3-}$.
16. In which of the following compounds is the oxidation number of the transition metal zero? **[NSEC-2007]**
 (A) $[\text{Ni}(\text{CO})_4]$ (B) $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ (C) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ (D) $[\text{Fe}(\text{H}_2\text{O})_3](\text{OH})_2$
17. $[\text{NiCl}_4]^{2-}$ is paramagnetic and therefore its geometry is : **[NSEC-2007]**
 (A) pyramidal (B) bi-pyramidal (C) tetrahedral (D) square planar
18. dsp^2 hybridization represents **[NSEC-2007]**
 (A) octahedral geometry (B) square-planar geometry
 (C) trigonal-bipyramidal geometry (D) square-pyramidal geometry
19. Which isomerism is exhibited by $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$? **[NSEC-2007]**
 (A) Ionization (B) Linkage (C) Coordination (D) Polymerization
20. The complex pentaaminecarbonatocobalt (III) chlorides is: **[NSEC-2007]**
 (A) $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$ (B) $[\text{Co}(\text{NH}_2)_5\text{CO}_3]\text{Cl}$ (C) $[\text{Co}(\text{NH}_2)_5\text{CO}_2]\text{Cl}$ (D) $[\text{Co}(\text{NH}_3)_5\text{CO}_2]\text{Cl}$



21. 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.
22. The orbitals of iron involved in the hybridization in $\text{Fe}(\text{CO})_5$ 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, p_x , p_y , p_z and d_{z^2} (D) s, p_x , p_z , d_{xy} and $d_{x^2-y^2}$
23. The crystal field stabilization energy (CFSE) in $[\text{Co}(\text{SCN})_6]^{3-}$ is : [NSEC-2007]
 (A) $24 \Delta q$ (B) $18 \Delta q$ (C) $4 \Delta q$ (D) $0 \Delta q$
24. How many isomers are possible for a compound with formula, $[\text{Rh}(\text{en})_2\text{Cl}(\text{NO}_2)]$? [NSEC-2007]
 (A) 2 (B) 4 (C) 6 (D) 8
25. 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 σ -bonding ligand. (D) carbonyl is a strongly π -acidic ligand.
26. Among the following, the chiral complex is : [NSEC-2009]
 (A) $[\text{Cr}(\text{OX})_3]^{3-}$ (B) $\text{cis}[\text{PtCl}_2(\text{en})]$ (C) $\text{cis}[\text{RhCl}_2(\text{NH}_3)_4]^+$ (D) $\text{trans}[\text{PtCl}_2(\text{en})]$
27. The species having tetrahedral shape is : [NSEC-2009]
 (A) $[\text{PdCl}_4]^{2-}$ (B) $[\text{Ni}(\text{CN})_4]^{2-}$ (C) $[\text{Pd}(\text{CN})_4]^{2-}$ (D) $[\text{Ni}(\text{Cl})_4]^{2-}$
28. The types of isomerism shown by $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$ are : [NSEC-2009]
 (A) Geometrical and ionization (B) Optical and ionization
 (C) Geometrical and optical (D) Geometrical only
29. The formula of tetraammineaquachlorocobalt(III) chloride is : [NSEC-2010]
 (A) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ (B) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}$
 (C) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ (D) $[\text{Co}(\text{NH}_3)_4(\text{OH})\text{Cl}_2]\text{Cl}$
30. The oxidation number and co-ordination number of chromium in complex ion $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$ are [NSEC-2010]
 (A) 3,6 (B) 2,6 (C) 2,8 (D) 3,8
31. The complex that exhibits Co-ordination isomerism is [NSEC-2010]
 (A) $[\text{Cr}(\text{NCS})(\text{H}_2\text{O})_5]^{2+}$ (B) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$
 (C) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ (D) $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$
32. The strong field ligand is : [NSEC-2010]
 (A) SCN^- (B) NO_2^- (C) I^- (D) S^{2-}
33. The correct formula for hexaamminecobalt (III) nitrate is [NSEC-2011]
 (A) $[\text{Co}_3(\text{NH}_3)](\text{NO}_3)_3$ (B) $[\text{Co}_3(\text{NH}_3)_6](\text{NO}_3)_3$ (C) $[\text{Co}(\text{NO}_3)_3] \cdot 6\text{NH}_3$ (D) $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$
34. The IUPAC name of complex $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ is [NSEC-2011]
 (A) ethylene diamine Cu(II) dihydrate (B) diaquobis(ethylenediamine) Cu(II) ion
 (C) diaquobisdithylamine Cu(II) ion (D) diaquobis(ethylenediamine) cuprate(II)
35. The electronic spectrum of $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ shows a band at 8500 cm^{-1} due to d-d transition. $[\text{Ph}_4\text{As}]_2[\text{NiCl}_4]$ will have such a transition in cm^{-1} at [NSEC-2011]
 (A) 3778 (B) 8500 (C) 4250 (D) 850



36. In the coordination compound, $\text{Na}_2[\text{Pt}(\text{CN})_4]$ the Lewis acid is [NSEC-2011]
 (A) $[\text{Pt}(\text{CN})_4]^{2-}$ (B) Na^+ (C) Pt^{2+} (D) CN^-
37. The 'd' orbitals will be split under square planar geometry into [NSEC-2011]
 (A) two levels (B) three levels (C) four levels (D) five levels
38. 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
39. The formula of the isothiocyanate ion is [NSEC-2011]
 (A) OCN^- (B) SCN^- (C) ONC^- (D) NCS^-
40. The bond order for a species with the configuration $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma p_x^1$ will be [NSEC-2012]
 (A) 1 (B) $1/2$ (C) Zero (D) $3/2$
41. Which of the following compounds has the least tendency to form hydrogen bonds between molecules? [NSEC-2012]
 (A) NH_3 (B) H_2NOH (C) HF (D) CH_3F
42. The species in which the central atom uses sp^2 hybrid orbitals is [NSEC-2012]
 (A) PH_3 (B) NH_3 (C) CH_3^+ (D) SbH_3
43. In which of the following ion/molecule, the 'S' atom does not assume sp^3 hybridization? [NSEC-2012]
 (A) SO_4^{2-} (B) SF_4 (C) SF_2 (D) S_8
44. Which of the following contain maximum number of electrons in the antibonding molecular orbitals [NSEC-2012]
 (A) O_2^{2-} (B) O_2 (C) O_2^{-1} (D) O_2^+
45. Lattice energy for an ionic compound is calculated by using [NSEC-2012]
 (A) Kirchoff's equation (B) Markownikoff's rule
 (C) Born Haber cycle (D) Carnot cycle
46. The IUPAC name of $[\text{Co}(\text{ONO})(\text{NH}_3)_5\text{Cl}_2]$ is : [NSEC-2012]
 (A) pentamminenitrocobalt(II)chloride (B) pentamminenitrosocobalt(III)chloride
 (C) pentamminenitritocobalt(III)chloride (D) pentammineoxo-nitrocobalt(III)chloride
47. The metal carbonyl which is paramagnetic is [NSEC-2013]
 (A) $\text{Ni}(\text{CO})_4$ (B) $\text{V}(\text{CO})_6$ (C) $\text{Cr}(\text{CO})_6$ (D) $\text{Fe}(\text{CO})_5$
48. 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
49. The complex having zero crystal field stabilization energy is [NSEC-2014]
 (A) $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (C) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (D) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
50. 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 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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 chromium (III) chloride
 (C) pentaquamonochloro chromium (III) chloride monohydrate
 (D) tetraaquadichloro chromium (III) chloride dihydrate
51. 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



52. Four statements for the following reaction are given below [NSEC-2015]
 $[\text{CoCl}_2(\text{NH}_3)_4]^+ + \text{Cl}^- \rightarrow [\text{CoCl}_3(\text{NH}_3)_3] + \text{NH}_3$
 (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
53. The complex that shows optical activity is [NSEC-2015]
 (A) *trans*- $[\text{CoCl}_2(\text{en})_2]^+$ (B) *cis*- $[\text{CoCl}_2(\text{en})_2]^+$
 (C) *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$ (D) $[\text{CoCl}_2(\text{NH}_3)_2(\text{en})]^+$
54. For $[\text{FeF}_6]^{3-}$ and $[\text{CoF}_6]^{3-}$, the statement that is correct is : [NSEC-2015]
 (A) both are colored (B) both are colorless
 (C) $[\text{FeF}_6]^{3-}$ is colored and $[\text{CoF}_6]^{3-}$ is colorless (D) $[\text{FeF}_6]^{3-}$ is colorless and $[\text{CoF}_6]^{3-}$ is colored
55. Which of the following statements about ammonium cerium (IV) nitrate, $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ 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.
56. Which one of the following reactions is correct ? [NSEC-2016]
 (A) $[\text{Fe}(\text{CO})_5] + 2\text{NO} \rightarrow [\text{Fe}(\text{CO})_2(\text{NO})_2] + 3\text{CO}$ (B) $[\text{Fe}(\text{CO})_5] + 2\text{NO} \rightarrow [\text{Fe}(\text{CO})_3(\text{NO})_2] + 2\text{CO}$
 (C) $[\text{Fe}(\text{CO})_5] + 3\text{NO} \rightarrow [\text{Fe}(\text{CO})_2(\text{NO})_3] + 3\text{CO}$ (D) $[\text{Fe}(\text{CO})_5] + 3\text{NO} \rightarrow [\text{Fe}(\text{CO})_3(\text{NO})_3] + 2\text{CO}$
57. How many isomers are possible for complex $[\text{Co}(\text{ox})_2\text{Cl}_2]^+$? [NSEC-2016]
 (A) 1 (B) 3 (C) 2 (D) 4
58. In which of the following complexes the metal ion has the lowest ionic radius ? [NSEC-2016]
 (A) $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ (B) $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ (C) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (D) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
59. Which of the complex has the magnetic moment of 3.87 B.M.? [NSEC-2016]
 (A) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (B) $[\text{CoF}_6]^{3-}$
 (C) $[\text{CoCl}_4]^{2-}$
 (D) $[\text{Co}(\text{dmg})_2]$ square planar complex (dmg = dimethyl glyoxime)
60. IUPAC name of complex ion $[\text{CrCl}_2(\text{ox})_2]^{3-}$ is [NSEC-2017]
 (A) dichlorodioxalatochromium (III) (B) dioxalatodichlorochromate(III)
 (C) dichlorodioxalatochromate(III) (D) bisoxalatoedichlorochromate(III)
61. The type of isomerism that $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$ can exhibit is/are [NSEC-2017]
 (A) geometric and ionisation (B) ionisation
 (C) Optical and ionisation (D) Optical, ionisation and geometric
62. Metal 'M' forms a carbonyl compound in which it is present in its lower valance state. Which of the following bonding is possible in this metal carbonyl ? [NSEC-2017]
- (A)

(C)

(B)

(D)
63. An appropriate reagent for the conversion of 1-propanol to 1-propanal is [NSEC-2017]
 (A) acidified potassium dichromate (B) alkaline potassium permanganate
 (C) pyridinium chlorochromate (D) acidified CrO_3



64. The complex ion that does not have d electrons in the metal atom is [NSEC-2017]
 (A) $[\text{MnO}_4]^-$ (B) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (C) $[\text{Fe}(\text{CN})_6]^{3-}$ (D) $\text{Cr}(\text{H}_2\text{O})_6^{3+}$
65. The complex $[\text{M}(\text{en})\text{Br}_2(\text{Cl})_2]$ has two optical isomers. Their configurations can be represented as [NSEC-2018]
- (A)

(B)
- (C)

(D)
66. The IUPAC name of the complex $[\text{Pt}(\text{en})(\text{NH}_3)(\text{Cl})_2(\text{ONO})][\text{Ag}(\text{CN})_2]$ is [NSEC-2018]
 (A) monoamminedichlorido(ethane-1,2-diammine)nitritoplatinum(IV) dicyanoargentate(I)
 (B) monoaminebischlorido(ethane-1,2-diammine)nitroplatinate(IV) dicyanosilver(I)
 (C) monoaminebischlorido(ethane-1,2-diammine)nitritoplatinate(IV) dicyanoargentate(I)
 (D) monoamminedichlorido(ethane-1,2-diammine)nitritoplatinum(IV) dicyanoargentate(I)
67. The C–O bond length is the shortest in : [NSEC-2018]
 (A) $[\text{Cr}(\text{CO})_6]$ (B) $[\text{Mo}(\text{CO})_6]$ (C) $[\text{Mn}(\text{CO})_6]^+$ (D) $[\text{V}(\text{CO})_6]^-$
68. The spin-only magnetic moments of $[\text{Fe}(\text{NH}_3)_6]^{3+}$ and $[\text{FeF}_6]^{3-}$ (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

PART - III : HIGH LEVEL PROBLEMS (HLP)

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 B₁₂ 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

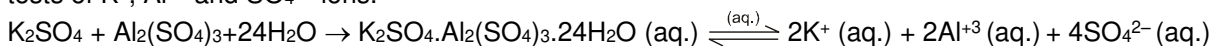
|
Double salts

|
Coordination compounds
(Complexes)



Double salts:

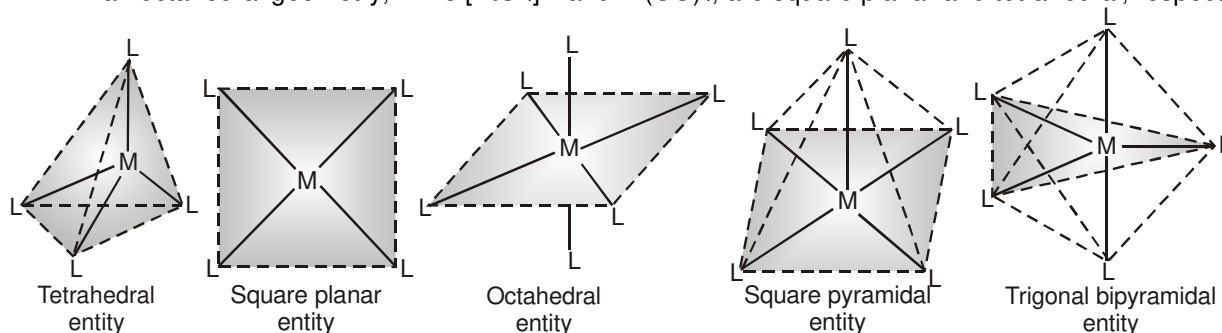
Those addition compounds which lose their identity in solutions are called **double salts**. For example, when K_2SO_4 solution is added to $Al_2(SO_4)_3$ solution, the species formed when dissolved in water gives tests of K^+ , Al^{3+} and SO_4^{2-} ions.



Other examples are carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), Mohr's salt [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$], potash alum [$KAl(SO_4)_2 \cdot 12H_2O$] or $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$ etc.

Coordination Polyhedron:

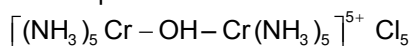
The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion gives a coordination polyhedron about the central atom. Figure below shows the shapes of tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal coordination polyhedra. $[Co(NH_3)_6]^{3+}$ 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:

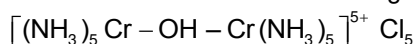
- (i) **Ist case:** The name of a bridge complex is prefixed by μ -.

If the situation on both sides of the bridge is symmetrical then we can write the name of remaining complex at one place like



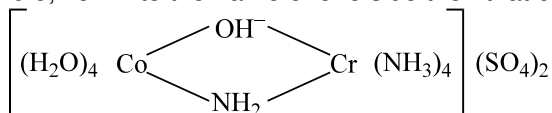
μ -Hydroxidobis(pentaamminechromium(III)) chloride

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



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 -hydroxidotetraamminechromium(III) sulphate

SUBJECTIVE QUESTIONS

- What is the coordination number and the oxidation state of the metal in each of the following complexes?
(a) $[ZrF_8]^{4-}$; (b) $K_3[Cr(C_2O_4)_2Cl_2]$
- Write the name of the following ligands and classify their denticity
(a) o-phen (b) NOS^-
- Name the $K[PtCl_3(\eta^2-C_2H_4)]$ compound.
- 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) $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ (b) $[\text{Fe}(\text{C}_5\text{H}_5)_2]$

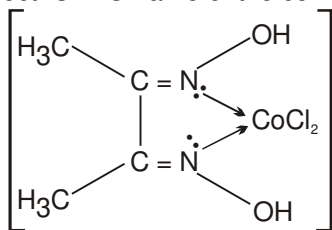
6. Complete the following table (using concepts of VBT).

	Complex	Geometry	Hybridisation	Number of unpaired electrons(n)	Mag. moment
	CN = 2				
(a)	$[\text{Ag}(\text{NH}_3)_2]^+$			0	
(b)	$[\text{Cu}(\text{CN})_2]^-$	Linear			
(c)	$[\text{AuCl}_2]^-$				0
	CN = 4				
(d)	$[\text{PtCl}_2(\text{NH}_3)_2]$			0	
(e)	$[\text{Zn}(\text{CN})_4]^{2-}$			0	
(f)	$[\text{Cu}(\text{CN})_4]^{3-}$			0	
(g)	$[\text{MnBr}_4]^{2-}$			5	
(h)	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	Square Planar			
(i)	$[\text{CoI}_4]^{2-}$			3	
	CN = 6				
(j)	$[\text{Mn}(\text{CN})_6]^{3-}$			2	
(k)	$[\text{Cr}(\text{NH}_3)_6]^{3+}$			3	
(l)	$[\text{Fe}(\text{CN})_6]^{3-}$			1	
(m)	$[\text{Ir}(\text{NH}_3)_6]^{3+}$			0	
(n)	$[\text{V}(\text{CO})_6]$			1	
(o)	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$			4	
(p)	$[\text{MnCl}_6]^{3-}$			4	

7. Draw the structures of the following metal carbonyls
 (a) $[\text{Co}_2(\text{CO})_8]$ (b) $[\text{Fe}_2(\text{CO})_9]$

ONLY ONE OPTION CORRECT TYPE

8. The correct IUPAC name of the complex is :



- (A) Dichloridodimethylglyoximecobalt(II) (B) Bis(dimethylglyoxime)dichloridocobalt(II)
 (C) Dimethylglyoximecobalt(II) chloride (D) Dichlorido(dimethylglyoximate)cobalt(II)
9. A co-ordination complex has the formula $\text{PtCl}_4 \cdot 2\text{KCl}$. 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
10. Which of the following complexes produces three moles of silver chloride when its one mole is treated with excess of silver nitrate ?
 (A) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$ (B) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ (C) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ (D) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
11. The number of chloride ions which would be precipitated when one mole of the complex $\text{PtCl}_4 \cdot 4\text{NH}_3$ is treated with silver nitrate is: (here coordination number of platinum is 6).
 (A) four (B) one (C) three (D) two



12. 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) $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}][(\text{NH}_3)\text{Cl}]$ (B) $[\text{Co}(\text{NH}_3)_5\text{Cl}][\text{ClNO}_2]$
 (C) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ (D) $[\text{Co}(\text{NH}_3)_5][(\text{NO}_2)_2\text{Cl}_2]$
13. From the stability constant (hypothetical values), given below, predict which is the most stable complex?
 (A) $\text{Cu}^{2+} + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$, $K = 4.5 \times 10^{11}$
 (B) $\text{Cu}^{2+} + 4\text{CN}^- \longrightarrow [\text{Cu}(\text{CN})_4]^{3-}$, $K = 2.0 \times 10^{27}$
 (C) $\text{Cu}^{2+} + 2\text{en} \longrightarrow [\text{Cu}(\text{en})_2]^{2+}$, $K = 3.0 \times 10^{15}$
 (D) $\text{Cu}^{2+} + 4\text{H}_2\text{O} \longrightarrow [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, $K = 9.5 \times 10^8$
14. In Zeise's salt $\text{C} = \text{C}$ bond length is:
 Note : $\left\{ \begin{array}{l} \text{C} - \text{C} \text{ bond length in ethane is } 1.54 \text{ \AA} \\ \text{C} = \text{C} \text{ bond length in ethene is } 1.34 \text{ \AA} \\ \text{C} \equiv \text{C} \text{ bond length in ethyne is } 1.20 \text{ \AA} \end{array} \right\}$
 (A) 1.37 Å (B) 1.19 Å (C) 1.87 Å (D) 1.34 Å
15. Which is not a π -bonded complex?
 (A) Zeise's salt (B) Ferrocene (C) bis(benzene) chromium (D) Tetraethyl lead
16. What is wrong about the compound $\text{K}[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_3]$?
 (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.
17. Which of the following are bidentate monoanion ligands ?
 (a) Dimethylglyoximate (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
18. Diethylenetriamine is:
 (A) chelating agent (B) tridentate neutral molecule
 (C) tridentate monoanion (D) (A) and (B) both
19. In $\text{K}_4[\text{Fe}(\text{CN})_6]$, Fe is in the form of
 (A) An atom (B) Neutral complex (C) Cationic complex (D) Anionic complex
20. Complex ion $[\text{FeN}_3(\text{O}_2)(\text{SCN})_4]^{4-}$ is named as: (coordination number of central metal ion in complex is six)
 (A) azidosuperoxidotetrathiocyanato-S-ferrate(II)
 (B) azidodioxigentetrathiocyanatoferrate(III)
 (C) azidoperoxidotetrathiocyanato-S-ferrate(II)
 (D) azidodioxidotetrathiocyanato-S-ferrate(III)
21. The IUPAC name of $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O})_2(\text{NH}_3)]$ is :
 (A) potassium amminecyanoperoxodioxochromate(VI).
 (B) potassium amminedicyanoperoxodioxochromium(VI).
 (C) potassium amminecyanoperoxodioxochromium(VI).
 (D) potassium amminedicyanodioxoperoxochromate(VI).
22. Consider the following statements:
 According to 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



23. Which of the following is correct for both the following coordination compounds ?
 (I) $\text{CoCl}_3 \cdot 6\text{NH}_3$ and (II) $\text{PtCl}_4 \cdot 5\text{NH}_3$
 (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
24. In the complex $[\text{SbF}_5]^{2-}$, sp^3d hybridisation is present. Geometry of the complex is :
 (A) Square pyramidal (B) Square bipyramidal (C) Tetrahedral (D) Square planar
25. 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) $-1.2 \Delta_0$
26. $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{+4} \xrightarrow[\text{oxidise}]{[\text{S}_2\text{O}_8]^{2-}} [(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{+5}$
 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 & IV III (B) III II & III III
 brown green brown green
 (C) III III & III II (D) III IV & III III
 brown green brown green
27. Which one of the following will be able to show cis-trans isomerism ?
 (A) Ma_3b (B) $\text{M}(\text{AA})_2$ (C) $\text{M}(\text{AB})(\text{CD})$ (D) Ma_4
28. Which of the following compounds show optical isomerism ?
 1. cis - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ 2. trans - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 3. cis - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ 4. $[\text{Co}(\text{en})_3]^{3+}$
 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

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

	Column – I		Column – II
(A)	$[\text{Co}(\text{en})_3]^{3+}$	(p)	sp^3d^2 hybridisation
(B)	$[\text{Co}(\text{ox})_3]^{3-}$	(q)	Diamagnetic
(C)	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	(r)	d^2sp^3 hybridisation
(D)	$[\text{Co}(\text{NO}_2)_6]^{3-}$	(s)	Paramagnetic
		(t)	Chelate ligand

SINGLE AND DOUBLE VALUE INTEGER TYPE

30. What is the coordination number of metal in $[\text{M}(\text{trien})(\text{dipy})]^{+n}$?
31. Out of the following. How many have correct IUPAC naming :
 (1) $[\text{Ni}(\text{CN})_4]^{2-}$ - Tetracyanonickel (II) ion
 (2) $[\text{Pt}(\text{Py})_4][\text{PtCl}_4]$ - Tetrapyridine platinum (II) tetrachloride platinate (II)
 (3) $[\text{Ni}(\text{dmg})_2]$ - Bis(dimethylglyoximate) nickel (II)
 (4) $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$ - Potassium pentacyanonitrosylferrate (II)
 (5) $[\text{Fe}(\text{CO})_5]$ - Pentacyanocarbonyl Ferrate (O)
 (6) $\text{K}_2[\text{HgI}_4]$ - Potassium tetraiodidomercurate (II)
 (7) $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$ - Tetraammineplatinum (IV) tetrachlorido cuprate (II)
 (8) $[\text{Cu}(\text{gly})_2]$ - Diglycinate copper (II)
 (9) $\text{K}_4[\text{Fe}(\text{CN})_6]$ - Potassium hexacyanidoferrate (II)
 (10) $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ - Hexaammine platinum (IV) chloride.



32. How many of the given complexes follow E.A.N. rule ?
 (a) $[\text{Fe}(\text{CO})_5]$ (b) $[\text{Co}_2(\text{CO})_8]$ (c) $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ (d) $\text{K}_3[\text{Fe}(\text{CN})_6]$
 (e) $[\text{Fe}(\text{NO})_2(\text{CO})_2]$ (f) $[\text{CoF}_6]^{4-}$
33. A name of neutral complex is :
 Bis(acetyl acetanato) methylcyanidoethiocyanato-s-iron (Y)
 The 'Y' is O.N. of metal then calculate sum of primary and secondary valency ?
34. $\text{Na}_2[\text{Cr}(\text{NO})(\text{NH}_3)(\text{C}_2\text{O}_4)_2]$, $\mu = \sqrt{3}$ B.M., Then total no. of electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals of metal :
35. 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
36. For the $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ 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 $\left(\frac{y-x}{100}\right)$.
37. The possible number of stereoisomers for the formula $[\text{Ma}_2\text{b}_2\text{cd}]^{\pm n}$.
38. A complex is prepared by mixing CoCl_3 & NH_3 0.1 M solution of the complex was found to freeze at -0.372°C . Total geometrical isomers of complex are x. (Molar depression constant of water = 1.86°C/m) Report your answer by multiplying x with 6.
39. Calculate total number of geometrical, optical and structural isomers in the compound.
 $[\text{Rh}(\text{en})_2(\text{NO}_2)_2]\text{NO}_3$
40. What is the EAN value of $\text{W}(\text{CO})_6$ carbonyl compounds ?

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

41. Which of the following pairs of name and formula of complexes, is correct ?
 (A) Tetramminecopper(II) sulphate..... $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 (B) Diamminesilver(I) chloride $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
 (C) Potassium hexacyanidoferrate (III) $\text{K}_4[\text{Fe}(\text{CN})_6]$
 (D) Potassium amminepentachloridoplatinate (IV) $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$
42. In which of the following pairs of complexes the central metals/ions do have same effective atomic number ?
 (A) $[\text{Cr}(\text{CO})_6]$ and $[\text{Fe}(\text{CO})_5]$ (B) $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$
 (C) $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Ni}(\text{CO})_4]$ (D) $[\text{V}(\text{CO})_6]^-$ and $[\text{Co}(\text{NO}_2)_6]^{3-}$
43. Which of the following statements is/are correct ?
 (A) $\text{Ni}(\text{CO})_4$ — Tetrahedral, paramagnetic (B) $[\text{Ni}(\text{CN})_4]^{2-}$ — Square planar, diamagnetic
 (C) $\text{Ni}(\text{dmg})_2$ — Square planar, diamagnetic (D) $[\text{NiCl}_4]^{2-}$ — Tetrahedral, paramagnetic
44. Which of the following statement(s) is/are correct ?
 (A) $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{NO}_2)_6]^{3-}$ are diamagnetic involving d^2sp^3 hybridisation.
 (B) $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{FeCl}_4]^-$ and $[\text{Ni}(\text{CO})_4]$ are diamagnetic involving sp^3 hybridisation.
 (C) The magnetic moment of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is 5.92 B.M and that of $[\text{Fe}(\text{CN})_6]^{3-}$ is 1.73.
 (D) The magnetic moment of $\text{K}_4[\text{MnF}_6]$ and $\text{K}_3[\text{FeF}_6]$ are same.
45. Consider the following statements :
S₁ : Generally square planar complexes show geometrical isomerism but do not exhibit optical isomerism because they do not possess plane of symmetry.
S₂ : $\Delta_t = \frac{4}{9} \Delta_o$
S₃ : 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) **S₁** and **S₃** are correct (B) **S₂** and **S₃** are correct
 (C) **S₁** is incorrect (D) **S₂** and **S₃** are incorrect



46. Select the correct statement(s).
 (A) $[\text{Co}(\text{EDTA})]^-$ has two optical isomers.
 (B) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ show linkage isomerism.
 (C) For $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{NO}_2)\text{py}]$, theoretically fifteen different geometrical isomers are possible.
 (D) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ is an example of hydrate as well as ionisation isomerism.
47. 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.

48. 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 $[\text{Ni}(\text{CO})_4]$ and $[\text{Fe}(\text{CN})_6]^{4-}$ is same.
 (D) Chloridotris (triphenylphosphine) rhodium(I) is effective heterogeneous catalyst for hydrogenation of alkenes.
49. Which of the following statements is true for the complex, $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{NO}_2$?
 (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.
50. Choose the correct option for the complex $[\text{PtCl}_2(\text{en})_2]^{2+}$.
 (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

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format :

- Each part consists of five sections.
- Section 1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section 2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section 3 contains 5 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

**C. Marking Scheme :**

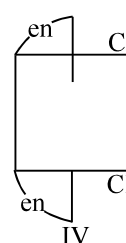
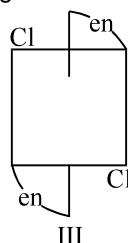
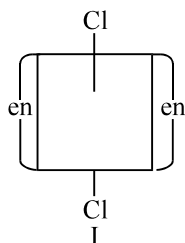
9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.
10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1. Given that the energy of the photons of different colours decreases in the order of **V I B G Y O R** (Violet > Indigo > Blue > Green > Yellow > Orange > Red) and that if complex absorbs a photon of low energy then it shows colour of high energy photon. If an ion, M^{2+} , forms the complexes $[M(H_2O)_6]^{2+}$, $[MBr_6]^{4-}$, and $[M(en)_3]^{2+}$. The colours of the complexes, though not necessarily in order, are green, red, and blue. Match the complexes with the appropriate colour. **(Do not use the table of complementary colours for this question)**
- (A) $[MBr_6]^{4-}$ blue, $[M(H_2O)_6]^{2+}$ green, $[M(en)_3]^{2+}$ red
 (B) $[MBr_6]^{4-}$ green, $[M(H_2O)_6]^{2+}$ blue, $[M(en)_3]^{2+}$ red
 (C) $[MBr_6]^{4-}$ green, $[M(H_2O)_6]^{2+}$ red, $[M(en)_3]^{2+}$ blue
 (D) $[MBr_6]^{4-}$ red, $[M(H_2O)_6]^{2+}$ green, $[M(en)_3]^{2+}$ blue

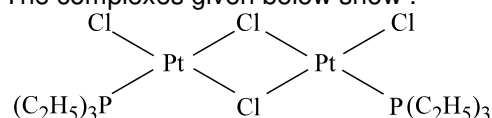
2. Which of the following pairs of structures shows geometrical isomerism ?



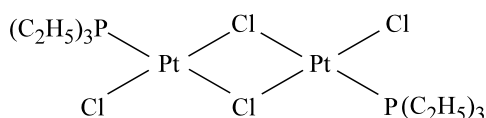
- (A) I with III (B) II with IV (C) I with II (D) none of these
3. 50 ml of 0.2 M solution of a compound with empirical formula $CoCl_3 \cdot 4NH_3$ on treatment with excess of $AgNO_3(aq)$ yields 1.435 g of $AgCl$. Ammonia is not removed by treatment with concentrated H_2SO_4 . The formula of the compound is:
 (A) $[Co(NH_3)_4Cl]Cl_2$ (B) $[Co(NH_3)_4Cl_2]Cl$ (C) $[Co(NH_3)_4]Cl_3$ (D) $[CoCl_3(NH_3)_3]NH_3$
4. Which of the following statements is incorrect ?
 (A) Potassium amminetetracyanonitrosoumchromate(I) having $\mu = 1.73$ B.M has d^2sp^3 hybridisation.
 (B) $K_3[AlF_6] + BF_3 \longrightarrow AlF_3 + 3K[BF_4]$
 (C) $[Cr(NH_3)_6]Cl_3$ and $[Cu(NCCH_3)_4][BF_4]$ both are coloured .
 (D) $[Cr(NH_3)_4Cl_2]Br$ can show ionisation isomerism with $[Cr(NH_3)_4ClBr]Cl$
5. Which of the following statements is not true?
 (A) $MnCl_4^-$ ion has tetrahedral geometry and is paramagnetic.
 (B) $[Mn(CN)_6]^{2-}$ ion has octahedral geometry and is paramagnetic.
 (C) $[Cu(CN)_4]^{3-}$ has square planar geometry and is diamagnetic.
 (D) $[Ni(Ph_3P)_2Br_3]$ has trigonal bipyramidal geometry and is paramagnetic.



6. The complexes given below show :



and



- (A) optical isomerism
(B) co-ordination isomerism
(C) geometrical isomerism
(D) bridged isomerism
7. Which of the following statements is correct with respect to the metal carbonyls of 1st transition series?
(A) As M–C π bonding increases, the C–O bond length increases.
(B) As positive charge on the central metal atom increases, the C–O bond length increases.
(C) As electron density on the central metal atom increases, the C–O bond length increases.
(D) (A) and (C) both.

Section-2 : (One or More than one options correct Type)

This section contains 5 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

8. Which of the following statement(s) is/are correct ?
(A) cis-[Pt(NH₃)₂Cl₂] 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 AgNO₃.
(D) CN⁻ ions show the reducing as well as complexing properties towards metal species.
9. Which of the following is true for the complex Co(NO₂)(Cl)₂.5NH₃ (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.
10. Which of the following complexes can exist as diastereoisomers ?
(A) [Cr(NH₃)₂Cl₄]⁻ (B) [Co(NH₃)₅Br]²⁺ (C) [FeCl₂(NCS)₂]²⁻ (D) [PtCl₂Br₂]²⁻
11. 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 d⁰ d⁵ or d¹⁰ (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) d¹⁰ns⁰np⁰.
12. Which of the following statements is/are incorrect for the complex [Cr(H₂O)₆]Cl₃ ?
(A) It has a magnetic moment of 3.83 BM.
(B) The distribution of 3d electrons is 3dxy¹, 3dyz¹, 3dzx¹
(C) The ligand has satisfied both primary and secondary valencies of chromium.
(D) It shows ionization as well as hydrate isomerism.

Section-3 : (One Integer Value Correct Type.)

This section contains 5 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

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 [NiF₆]²⁻ is
16. The sum of stereoisomers of complex-A, complex-B and complex-C in following reaction is

$$[\text{PtCl}_4]^{2-} \xrightarrow[-2\text{Cl}^-]{+2 \text{ (pyridine)}} [\text{Complex-A}] \xrightarrow[-\text{Cl}^-]{+\text{NH}_3} [\text{Complex-B}] \xrightarrow[-(\text{Pyridine})]{+\text{Br}^-} [\text{Complex-C}]$$
17. The number of d-electrons in [Cr(H₂O)₆]³⁺ [atomic number of Cr = 24] is :

**SECTION-4 : Comprehension Type (Only One options correct)**

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 18 to 20

The magnetic moment for two complexes of empirical formula $\text{Ni}(\text{NH}_3)_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is zero and 2.84 BM respectively. The second complex is not a neutral complex.

18. The number of water molecules of crystallization are respectively.
(A) zero, two (B) zero, zero (C) two, zero (D) two, two
19. The correct formula and geometry of the first complex is :
(A) $[\text{Ni}(\text{H}_2\text{O})_2(\text{NO}_3)_2] \cdot 4\text{NH}_3$; tetrahedral. (B) $[\text{Ni}(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; tetrahedral.
(C) $[\text{Ni}(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; square planar (D) $[\text{Ni}(\text{NH}_3)_4](\text{H}_2\text{O})_2(\text{NO}_3)_2$; octahedral
20. Which of the following statements are true for the second complex?
(A) It has the EAN value of 36.
(B) It can show optical isomerism.
(C) It cannot show geometrical isomerism
(D) It produces three-fold freezing point depression.

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

21. **Column-I** and **Column-II** contains four entries each. Entries of **Column-I** are to be matched with some entries of **Column-II**. One or more than one entries of **Column-I** may have the matching with the same entries of **Column-II**.

	Column-I		Column-II
	(Coordination compounds)		(Type of isomerism)
P.	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$	1.	Optical isomerism
Q.	$\text{cis-}[\text{Co}(\text{en})_3]\text{Cl}_2$	2.	Ionization isomerism
R.	$[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{SCN}$	3.	Coordination isomerism
S.	$[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$	4.	Geometrical isomerism

Code :

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

Practice Test-2 (IIT-JEE (ADVANCED Pattern))**OBJECTIVE RESPONSE SHEET (ORS)**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21									
Ans.										



APSP Answers

PART - I

1.	(2)	2.	(2)	3.	(1)	4.	(4)	5.	(3)
6.	(3)	7.	(4)	8.	(3)	9.	(4)	10.	(3)
11.	(3)	12.	(2)	13.	(3)	14.	(1)	15.	(3)
16.	(2)	17.	(3)	18.	(2)	19.	(4)	20.	(4)
21.	(3)	22.	(3)	23.	(1)	24.	(2)	25.	(4)
26.	(4)	27.	(1)	28.	(4)	29.	(4)	30.	(2)

PART - II

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

PART - III

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.

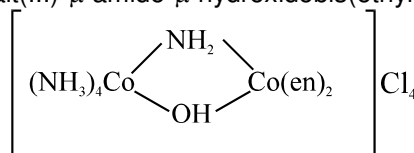
The oxidation number of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.

	Complex	Coordination Number	Oxidation State
(a)	$[\text{ZrF}_8]^{4-}$	8	4
(b)	$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_2\text{Cl}_2]$	6	3

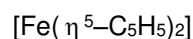
2. (a) 1, 10-diaminophenanthrene, bidentate (b) thionitrito, monodentate
3. $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ Potassium trichlorido(η^2 -ethylene)platinate(II)



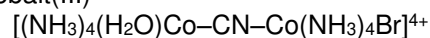
4. (a) Tetraamminecobalt(III)-μ-amido-μ-hydroxidobis(ethylenediamine or ethane-1,2-diamine)cobalt(III) chloride



(b) Bis(η⁵-cyclopentadienyl)iron(II)



(c) Tetraammineaquacobalt(III)-μ-cyanidotetraamminebromidocobalt(III)



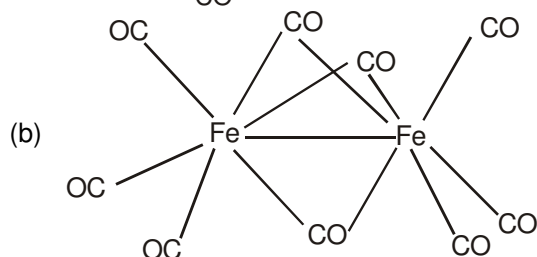
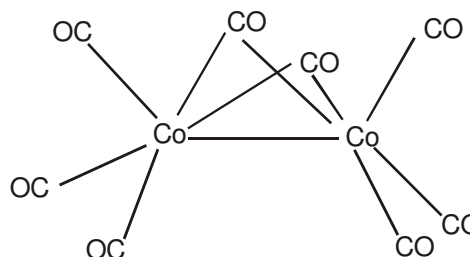
5. (a) 36 (b) 36

6.

	Complex	Geometry	Hybridisation	Number of unpaired electrons(n)	Mag. moment
	CN = 2				
(a)	$[\text{Ag}(\text{NH}_3)_2]^+$	Linear	sp	0	0
(b)	$[\text{Cu}(\text{CN})_2]^-$	Linear	sp	0	0
(c)	$[\text{AuCl}_2]^-$	Linear	sp	0	0
	CN = 4				
(d)	$[\text{PtCl}_2(\text{NH}_3)_2]$	Square Planar	dsp ²	0	0
(e)	$[\text{Zn}(\text{CN})_4]^{2-}$	Tetrahedral	sp ³	0	0
(f)	$[\text{Cu}(\text{CN})_4]^{3-}$	Tetrahedral	sp ³	0	0
(g)	$[\text{MnBr}_4]^{2-}$	Tetrahedral	sp ³	5	5.92 BM
(h)	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	Square Planar	dsp ²	1	1.73 BM
(i)	$[\text{CoI}_4]^{2-}$	Tetrahedral	sp ³	3	3.87 BM
	CN = 6				
(j)	$[\text{Mn}(\text{CN})_6]^{3-}$	Octahedral	d ² sp ³	2	2.83 BM
(k)	$[\text{Cr}(\text{NH}_3)_6]^{3+}$	Octahedral	d ² sp ³	3	3.87 BM
(l)	$[\text{Fe}(\text{CN})_6]^{3-}$	Octahedral	d ² sp ³	1	1.73 BM
(m)	$[\text{Ir}(\text{NH}_3)_6]^{3+}$	Octahedral	d ² sp ³	0	0
(n)	$[\text{V}(\text{CO})_6]$	Octahedral	d ² sp ³	1	1.73 BM
(o)	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	Octahedral	sp ³ d ²	4	4.90 BM
(p)	$[\text{MnCl}_6]^{3-}$	Octahedral	sp ³ d ²	4	4.90 BM

7. (a)

OR



8. (A) 9. (B) 10. (D) 11. (D) 12. (C)
 13. (B) 14. (A) 15. (D) 16. (C) 17. (A)
 18. (D) 19. (D) 20. (A) 21. (D) 22. (B)
 23. (C) 24. (A) 25. (A) 26. (A) 27. (C)



28. (C)	29. (A - q, r, t) ; (B - q, r, t) ; (C - p, s) ; (D - q, r).	30. 6
31. 5 (3,4,6,9,10)	32. 4 (a,b,c,e)	33. 09
36. 96	37. 8	34. Zero
41. (ABD)	42. (ACD)	35. 82
46. (ABC)	47. (AD)	38. 12
		39. 15
		40. 86
		41. (BC)
		42. (BC)
		43. (BCD)
		44. (ACD)
		45. (BC)
		46. (D)
		47. (B)
		48. (C)
		49. (B)
		50. (C)

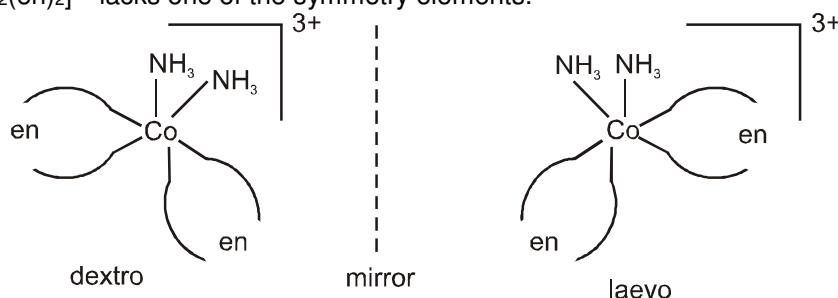
PART - IV

1. (A)	2. (C)	3. (B)	4. (C)	5. (C)
6. (C)	7. (D)	8. (ABCD)	9. (ABCD)	10. (AD)
11. (ACD)	12. (CD)	13. 5	14. 4	15. 0
16. 7	17. 3	18. (C)	19. (C)	20. (D)
21. (D)				

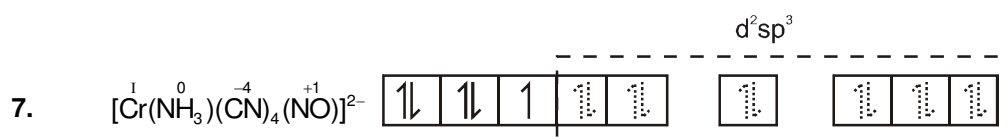
APSP Solutions

PART - I

- Let x be the oxidation state of nickel then,
 (1) $\text{Ni}(\text{CO})_4$; $x + 4(0) = 0$ or $x = 0$;
 (2) $[\text{NiF}_6]^{2-}$; $x + 6(-1) = -2$ or $x = +4$;
 (3) $[\text{Ni}(\text{NH}_3)_6]^{2+}$; $x + 4(0) = +2$ or $x = +2$;
 (4) $[\text{Ni}(\text{CN})_6]^{4-}$; $x + 6(-1) = -4$ or $x = +2$.
- $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} = 3 \times (-0.4) + 2 \times (0.6) = 0$; $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} = 3 \times (-0.4) + 1 \times (0.6) = 0.6 \Delta_0$
 $[\text{Mn}(\text{H}_2\text{O})_6]^{3+} = 3 \times (-0.4) + 1 \times (0.6) = 0.6 \Delta_0$; $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} = 3 \times (-0.4) + 0 \times (0.6) = 1.2 \Delta_0$
- (1) $\text{trans}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.
 (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.
 (3) $\text{cis}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$ lacks one of the symmetry elements.

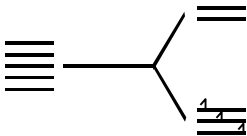


- (4) $\text{trans}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$ has plane of symmetry as well as centre of symmetry. Hence it does not show optical isomerism.
- NO_2^- is an ambidentate ligand and can link to central metal ion either through N or O. Hence it shows linkage isomerism.
 There is exchange of NO_2^- and SO_4^{2-} occurs between coordination sphere and ionization sphere. Hence it shows ionisation isomerism.
 Ma_5b has only one form, therefore, it does not show geometrical isomerism.
 Ma_5b has mirror plane, therefore, it does not show optical isomerism.



Central metal ion has one unpaired electron and thus d-d transition of electron is possible. This attributes to the colour of the solution. As different types of ligands are attached to central metal ion, the complex is called heteroleptic complex.



8. $S_1 : Cr^{3+}$  $CFSE = 3 \times -0.4 = -1.2 \Delta_0$, hybridisation is d^2sp^3 (NH_3 is strong field ligand)

ligand)

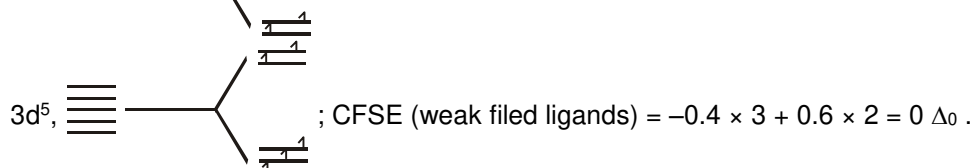
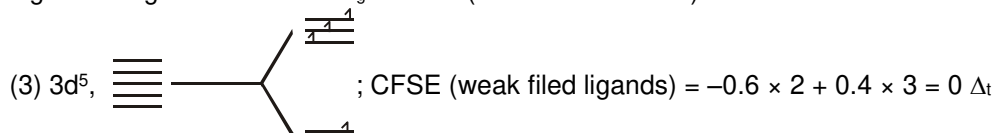
$S_2 : Fe^{3+}, 3d^5$ - one unpaired electron after pairing (CN^- is stronger field ligand)

$$\therefore \mu = \sqrt{1(1+2)} \approx 1.73 \text{ BM}$$

$S_3 : [Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_5NOS]^{4-}$.

In reactant and product, the iron is in same oxidation state i.e. +2.

9. (1) $Pt(+II)$ and $Au(+III)$ with $5d^8$ configuration have greater CFSE and thus favours square planar geometry (i.e. dsp^2 hybridisation) with weak as well as strong field ligands.
(2) In tetrahedral complex, the t_{2g} orbitals are nearer to the direction of the ligands. Hence they have higher energies than that of e_g orbitals (for detail refer text).



Similarly for d^0 and d^{10} configurations the CFSE is zero in both octahedral and tetrahedral complexes with weak field ligands.

10. $[CoCl_2(en)_2]Cl$, One mole complex contains, one mole of ionisable Cl^- .

One mole of complex = one mole of Cl^- .

$$\therefore \text{One mole of } AgCl = \text{One mole of complex} = \frac{100 \times 0.024}{1000} = 0.0024.$$

11. $[Fe(H_2O)_6]^{2+}$ $n = 4$ and $\mu = 4.91$
 $[Fe(CN)_6]^{4-}$ $n = 0$ and $\mu = 0$

12. Let the oxidation state of Fe is x

$$4 + x - 5 - 1 = 0$$

$$\text{so } x = 2$$

13. $[Ni(H_2O)_4]SO_4 + \text{Pyridine} + NaNO_2 \longrightarrow [Ni(Py)_4](NO_2)_2$

Stronger ligand, pyridine displaces weaker ligand, H_2O in aqueous solution.

$[Ni(py)_4](NO_2)_2$ is formed as dark blue crystals on crystallisation.

16. $2X + 1(-2) + 1(-1) = +3$; $x = \frac{6}{2} = +3$.

18. (1) $[Cr(NH_3)_6]^{3+}$, $[Cr(NO_2)_6]^{3-}$ and $[Cr(NH_3)_4(NO_2)_2]^+$, $[Cr(NH_3)_2(NO_2)_4]^-$ have same number of ions, so cryoscopic method can not be used.

(2) Molar conductance depends on the number of ions as well as on the charge on the complexes. $[Cr(NH_3)_6]^{3+}$, $[Cr(NO_2)_6]^{3-}$ and $[Cr(NH_3)_4(NO_2)_2]^+$, $[Cr(NH_3)_2(NO_2)_4]^-$ have same number of ions but different electrical charges.

(3) Both complexes have same number of unpaired electrons, so measuring magnetic moments methods can not be used.

(4) They have similar colour because of the similar conditions.

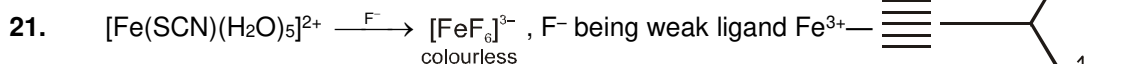
19. $[Fe(en)_2(H_2O)_2]^{2+} + en \longrightarrow [Fe(en)_3]^{2+} + 2H_2O$

Complex is $[Fe(en)_3]^{2+}$. 'en' is a strong field ligand and thus it is inner orbital complex ($d^2 sp^3$) and diamagnetic.

It is $M(AA)_3$ type which has only one form.

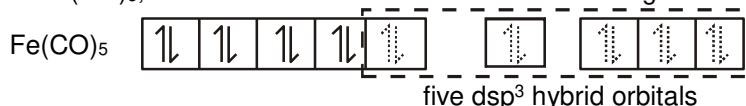


20. (1) Cr^{3+} , $3d^3$; sp^3d^2 hybridisation with three unpaired electrons (weak field as well as strong field ligand).
 Fe^{3+} , $3d^5$; sp^3d^2 hybridisation with three unpaired electron (one 4s electron jumps to 3d orbital for the pairing)
 (2) Mn^{2+} , $3d^5$; d^2sp^3 hybridisation with one unpaired electron after pairing (CN^- is strong field ligand).
 Fe^{3+} , $3d^5$; d^2sp^3 hybridisation with one unpaired electron after pairing (CN^- is strong field ligand).
 (3) Ni , $3d^8 4s^2$; sp^3 hybridisation and all electrons are paired because CO is strong field ligand (4s-electrons jumps to 3d-orbitals for the pairing)
 Zn^{2+} , $3d^{10}$; sp^3 hybridisation and all electrons are paired.



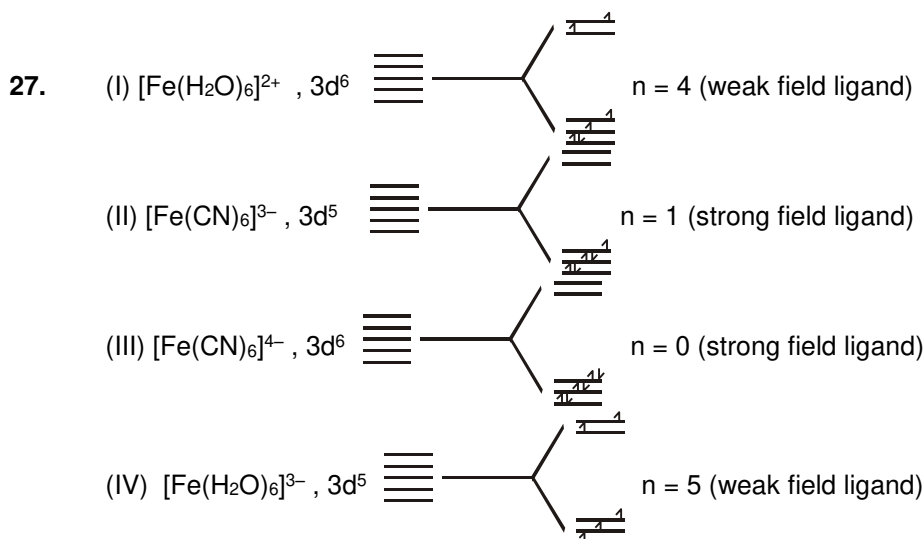
Therefore, five unpaired electrons and so $\mu = \sqrt{5(5+2)}$ B.M. ≈ 5.92 .

22. In $\text{Fe}(\text{CO})_5$, Fe in zero oxidation state and CO is stronger field ligand. So,



Hence it is diamagnetic and low spin complex.

23. (1) The crystal field-splitting for Cr^{3+} ion in octahedral field increases with increasing strength of ligands. This order given in (1) is according to spectrochemical series.
 25. (4) Chelate complex has higher stability than the similar complexes having monodentate ligands and an higher stability means higher overall formation constant.
 26. In $\text{Fe}(\text{CO})_5$, Fe is dsp^3 hybridised. Hence, its structure is trigonal bipyramidal.

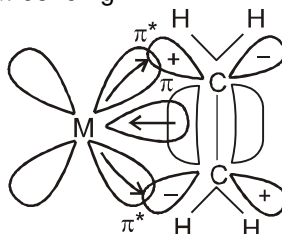


28. $[\text{Ni}(\text{CO})_4] = sp^3$; $[\text{Ni}(\text{CN})_4]^{2-} = dsp^2$; $[\text{Fe}(\text{CN})_6]^{4-} = d^2sp^3$; $[\text{MnF}_6]^{4-} = sp^3d^2$.
 29. (1) No anionic ligand is present in coordination sphere for the exchange with Cl^- ions present in ionisation sphere.
 (2) No anionic ligand is present in coordination sphere for the exchange with Cl^- ions present in ionisation sphere.
 (3) No anionic ligand is present in coordination sphere for the exchange with Cl^- ions present in ionisation sphere.
 (4) Br^- and SO_4^{2-} can exchange their positions between coordination sphere and ionisation sphere. Hence it shows ionization isomerism.
 30. Coordination number of nickel in $[\text{Ni}(\text{C}_2\text{O}_4)_3]^{4-}$ is 6 because $\text{C}_2\text{O}_4^{2-}$ is a bidentate ligand.



PART - III

5. (a) $\text{Fe}(Z = 26)$; $\text{EAN} = 26 + 2 + 8 = 36$. (b) $\text{Fe}(Z = 26)$; $\text{EAN} = 26 + 10 = 36$.
8. Correct name is dichloridodimethylglyoximatecobalt (II)
9. $\text{PtCl}_4 \cdot 2\text{KCl} \equiv \text{K}_2[\text{PtCl}_6] \xrightleftharpoons{\text{aq.}} 2\text{K}^+ + [\text{PtCl}_6]^{2-}$.
So, it has three ions per formula unit. The Cl^- is present in coordination sphere so it will not give white precipitate with silver nitrate solution. So in the compound the coordination number of platinum is 6.
10. (D) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 \xrightleftharpoons{\text{aq.}} [\text{Cr}(\text{H}_2\text{O})_6]^{3+} (\text{aq}) + 3\text{Cl}^- (\text{aq})$.
 Cl^- present in ionisation sphere will give precipitate with AgNO_3 .
 $3\text{Cl}^- + 3\text{Ag}^+ \longrightarrow 3\text{AgCl}$
So, one mole of complex will give three moles of AgCl precipitate.
11. $\text{PtCl}_4 \cdot 4\text{NH}_3 \equiv [\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2 \xrightleftharpoons{\text{aq.}} [\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+} (\text{aq}) + 2\text{Cl}^- (\text{aq})$.
 $2\text{Ag}^+ + 2\text{Cl}^- \longrightarrow 2\text{AgCl} \downarrow (\text{white})$
Concentrated H_2SO_4 will not dehydrate the following complex.
12. (C) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2 \xrightleftharpoons{\text{aq.}} [\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+} (\text{aq}) + 2\text{Cl}^- (\text{aq})$ (no. of ions = 3)
 $2\text{Ag}^+ + 2\text{Cl}^- \longrightarrow 2\text{AgCl} \downarrow (\text{white})$.
13. $K \propto \text{stability}$.
14. Relative to free ethylene the C—C bond is lengthened (from 133.77 pm to 137.5 pm). 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.



15. $(\text{C}_2\text{H}_5)_4\text{Pb}$ is a σ -bonded complex.
16. $X + 3(-1) = 1 \therefore X = +2$.
17. (1) (2) (3) $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

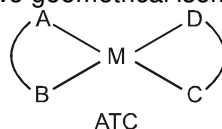
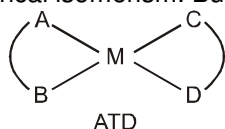
18. Diethylenetriamine is a tridentate neutral molecules with three donor nitrogen atoms. Polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring is called as chelating ligand.
20. $[\text{Fe}(\text{II})\text{N}_3(\text{O}_2)^{-1}(\text{SCN})_4]^{4-}$; so correct name is azidosuperoxidotetrathiocyanato-S-ferrate(II) according to IUPAC rules.
21. $2\text{K}^+[\text{Cr}(\text{CN})_2\text{O}_2(\text{O})_2(\text{NH}_3)]^{2-}$
Oxidation state of chromium = $x + 2(-1) + (-2) + 2(-2) + (0) = -2$.
 $\therefore x = +6$.
As per IUPAC name.
Complex is anionic, so metal ion will be named as chromate with +6 oxidation state. So, potassium amminedicyanodioxoperoxochromate(VI).



22. According to Werner's theory statements (2) and (3) are correct.
 (1) Ligands are connected to the metal ion by coordinate covalent bond (dative bond).
 (2) Secondary valencies i.e. coordination number give rise to stereochemistry of the complexes because of their directional properties.
 (3) Secondary valencies correspond to coordination number i.e. number of σ -bonds between metal ion and ligands.

23. (I) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 + 3\text{Ag}^+ \longrightarrow 3\text{AgCl}\downarrow + [\text{Co}(\text{NH}_3)_6]^{3+}$
 $\text{Co}^{3+} \longrightarrow$ Primary valencies i.e. ionisable valency = 3.
 (II) $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3 + 3\text{Ag}^+ \longrightarrow 3\text{AgCl}\downarrow + [\text{Pt}(\text{NH}_3)_5\text{Cl}]^{3+}$
 $\text{Pt}^{4+} \longrightarrow$ Primary valencies = 4.

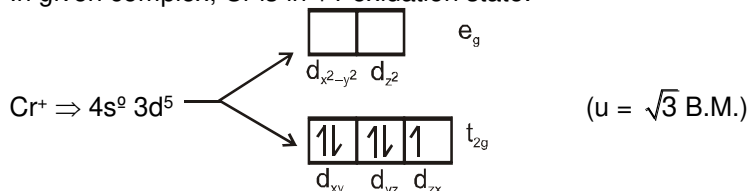
27. Ma_3b , Ma_4 and $\text{M}(\text{AA})_2$ (symmetrical bidentate ligand) have only one form; they does not show geometrical isomerism. But $\text{M}(\text{AB})(\text{CD})$ shows two geometrical isomerism.



28. (1) $\text{cis-}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has plane of symmetry as well as centre of symmetry; so optically inactive.
 (2) $\text{trans-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ has plane of symmetry as well as centre of symmetry; so optically inactive.
 (3) $\text{cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ lacks plane of symmetry as well as centre of symmetry; so optically active.
 (4) $[\text{Co}(\text{en})_3]^{3+}$ lacks axis of internal rotation; so optically active.
29. (A) $[\text{Co}(\text{en})_3]^{3+}$; Co^{3+} has d^6 configuration which has higher CFSE; so hybridisation is d^2sp^3 and complex is diamagnetic. 'en' is a bidentate chelate ligand.
 (B) $[\text{Co}(\text{ox})_3]^{3-}$; Co^{3+} has d^6 configuration which has higher CFSE; so hybridisation is d^2sp^3 and complex is diamagnetic. 'ox' is a bidentate chelate ligand.
 (C) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$; Co^{2+} has d^7 configuration; H_2O is a weak field monodentate ligand, so it is paramagnetic with three unpaired electrons having sp^3d^2 hybridisation.
 (D) $[\text{Co}(\text{NO}_2)_6]^{3-}$; Co^{3+} has d^6 configuration which has higher CFSE; so hybridisation is d^2sp^3 and complex is diamagnetic. ' NO_2^- ' is a monodentate ligand.
30. Trien (triethylene teramine) is a tetradentate Ligand while dipy (2, 2'-dipyridyl) is a Bidentate Ligand.
31. Naming of (1), (2), (5), (7) and (8) are wrong.
32. (d) $\text{K}_3[\text{Fe}(\text{CN})_6] = 26 - 3 + 2 \times 6 = 35$ does not follow E.A.N. rule.
 (f) $[\text{CoF}_6]^{4-} = 27 - 2 + 2 \times 6 = 37$ does not follow E.A.N. rule.

33. Complex $[\text{Fe}(\text{acac})_2(\text{NCCH}_3)(\text{SCN})]$
 $\text{Y} - 2 + 0 - 1 = 0 \Rightarrow \text{Y} = +3$
 sec. valency = 6
 sum = $3 + 6 = 9$

34. In given complex, Cr is in +1 oxidation state.



36. For a d^4 ion in a high spin state.
 $\text{CFSE} = -0.6 \Delta_o = -0.6 \times (13,900 \text{ cm}^{-1}) = -8340 \text{ cm}^{-1}$
 For a d^4 ion in a low spin state, the net CFSE is,
 $= -1.6 \Delta_o + P = -1.6 \times (13,900 \text{ cm}^{-1}) + 23500 \text{ cm}^{-1} = +1,260 \text{ cm}^{-1}$
 Since $\Delta_o (= 13,900 \text{ cm}^{-1}) < P (= 23,500 \text{ cm}^{-1})$, the high spin configuration would be more stable.
38. $\Delta T_f = imK_f$
 $0.372 = 1.86 \times 0.1 \times i$
 $i = 2$
 Complex is $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ octahedral with two geometrical isomers.



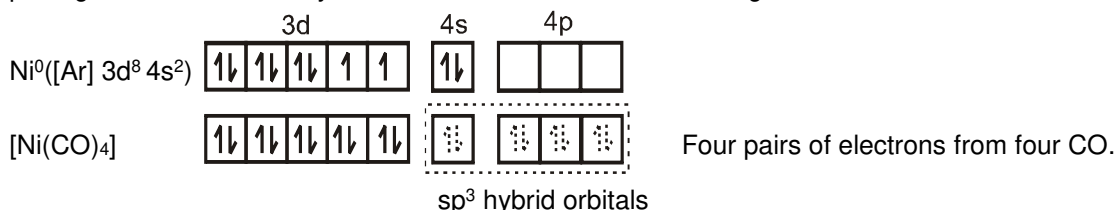
39.	$[\text{Rh}(\text{en})_2(\text{NO}_2)_2]\text{NO}_3$	Linkage	Geo.	Optical
		$\text{NO}_2 \quad \text{NO}_2$	Cis + trans	Cis
		$\text{NO}_2 \quad \text{ONO}$	Cis + trans	Cis
		$\text{ONO} \quad \text{ONO}$	Cis + trans	Cis
	$[\text{Rh}(\text{en})_2(\text{NO}_2)\text{NO}_3]\text{NO}_2$	$\text{NO}_2 \quad \text{NO}_3$	Cis + trans	Cis
		$\text{ONO} \quad \text{NO}_3$	Cis + trans	Cis

$5 \times 3 = 15$ isomers.

41. (C) It is not correct formula because the Fe is in +3 oxidation state and as such formula should be $[\text{Fe}^{3+}(\text{CN})_6]^{3-}$ or $\text{K}_3[\text{Fe}(\text{CN})_6]$.

42. (A) EAN of Cr = $24 + 12 = 36$ and EAN of Fe = $26 + 10 = 36$.
 (B) EAN of $\text{Co}^{3+} = 25 + 12 = 37$ and EAN of $\text{Ni}^{2+} = 26 + 12 = 38$.
 (C) EAN of $\text{Cu}^+ = 28 + 12 = 36$ and EAN of Ni = $28 + 8 = 36$.
 (D) EAN of $\text{V}^- = 24 + 12 = 36$ and EAN of $\text{Co}^{3+} = 24 + 12 = 36$.

43. In complex nickel is in zero oxidation state. The CO is strong field ligand and therefore compels for the pairing of electrons. The hybridisation scheme is as shown in figure.

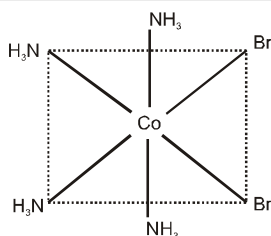


It is tetrahedral and as all electrons are paired so diamagnetic.

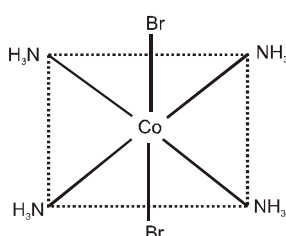
44. (A) All are diamagnetic and inner orbital complexes because all ligands are strong field ligands.
 (B) $\text{Fe}^{3+} n = 5$; $\mu = \sqrt{5(5+2)} \approx 5.92$ with H_2O , so $[\text{FeCl}_4]^-$ is diamagnetic.
 (C) $\text{Fe}^{3+} n = 5$; $\mu = \sqrt{5(5+2)} \approx 5.92$ with H_2O .
 $\text{Fe}^{3+} n = 1$; $\mu = \sqrt{3} = 1.73$ with CN^- .
 (D) $\text{Mn}^{2+} (3d^5)$ and $\text{Fe}^{3+} (3d^5)$ have same number of unpaired electrons i.e. 5 with weak field ligands, F^- .
45. S_1 : Square planar complexes with symmetrical ligands like (en) do not show geometrical isomerism and they have plane of symmetry, so optically inactive.
 S_2 and S_3 are correct statements.
46. (A) $[\text{Co}(\text{EDTA})]^- \leftrightarrow$ shows optical isomerism.
 (B) NO_2^- being bidentate ligands can attach to central metal ion through N or O.
 (C) It is Mabcdef type and thus have fifteen different geometrical isomers.
 (D) Ionisation isomerism involves exchange of different ions between coordination sphere and ionisation sphere. In complex, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, same anionic ligands, i.e., Cl^- are present in coordination sphere and ionisation sphere; so no exchange of ions takes place.
47. (A) and (D) are π -bonded organometallic compounds as they involve the formation of π -bonds between metal and carbon.
 (B) and (C) are σ -bonded organometallic compounds as they only form σ bond by sharing of electrons between metal and carbon.
48. It is homogeneous catalyst for hydrogenation of alkenes.



49.



cis -

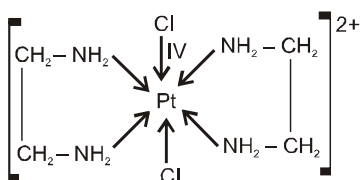


trans -

It shows geometrical isomerism but not optical isomerism due to the presence of at least one plane of symmetry.

$[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{NO}_2$ and $[\text{Co}(\text{NH}_3)_4\text{BrNO}_2]\text{Br}$ are ionisation isomers and later complex reacts with AgNO_3 solution to give pale yellow precipitate. $[\text{Co}(\text{NH}_3)_4\text{BrNO}_2]\text{Br}$ and $[\text{Co}(\text{NH}_3)_4\text{BrONO}]\text{Br}$ are linkage isomers.

50.



trans-form is optically inactive because it is achiral.

PART - IV

- Order of crystal field splitting $e_n > \text{H}_2\text{O} > \text{Br}^-$ so, more stronger ligand will absorb lower wavelength light and reflect back higher wavelength light.
- (A) I and III both are identical structures (i.e. trans-isomers).
(B) II and IV are identical structures (i.e. cis - isomers).
(C) I and II are cis- and trans-isomers (i.e. they are geometrical isomers).
- Mole of complex = $50 \times 0.2 = 0.01$ and mole of $\text{AgCl} = \frac{1.435}{143.5} = 0.01$
 $n\text{Ag}^+ = n\text{Cl}^-$
 $\therefore 1 \text{ mole complex} = 1 \text{ mole AgCl}$
- (C) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is coloured as it has three unpaired electrons while $[\text{Cu}(\text{NCCH}_3)_4][\text{BF}_4]$ is colourless as Cu(I) i.e. $3d^{10}$ electron configuration has all electrons paired, so there is no d-d transition of electron.
- (C) $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Ar}]^{18}3d^{10}$; As there is no empty d-orbital for dsp^2 hybridization. So it has sp^3 hybridization and is tetrahedral, and diamagnetic.
- Geometrical isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.
When two $(\text{C}_2\text{H}_5)_3\text{P}$ groups are on same side it is cis - and when those are on opposite side it is trans-
- Order of C–O bond strength :
 $[\text{Mn}(\text{CO})_6]^+ > [\text{Cr}(\text{CO})_6] > [\text{V}(\text{CO})_6]^- > [\text{Ti}(\text{CO})_6]^{2-}$ and $[\text{Ni}(\text{CO})_4] > [\text{Co}(\text{CO})_4]^- > [\text{Fe}(\text{CO})_4]^{2-}$.
(A) True statement.
(B) As + ve charge on the central metal atom increases, the less readily the metal can donate electron density into the π^* orbitals of CO ligand to weaken the C–O bond.
(C) In the carbonylate anions, the metal has a greater electron density to be dispersed, with the result that M–C π bonding is enhanced and the C–O bond is diminished in strength.



8. All statements are correct.
9. $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}(\text{NO}_2)$ are ionisation isomers.
 $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ are linkage isomers.
 Cobalt in +3 oxidation state has $3d^6$ configuration which has higher CFSE. So the complex is inner orbital (i.e. d^2sp^3 hybridisation) and diamagnetic.
10. (A) Exists as cis and trans form but neither of the forms can have enantiomeric forms on account of presence of the plane of symmetry as well as centre of symmetry.
 (B) Only one form possible.
 (C) Tetrahedral in which all positions are adjacent to each other.
 (D) Exists as cis and trans form but neither of the forms can have enantiomeric forms on account of presence of the plane of symmetry.
11. Tetrahedral complexes are favoured by steric requirements, either simple electrostatic repulsion of charge ligands or vander wall's repulsions of large one.
 Tetrahedral complexes are thus generally favoured by large ligands like Cl^- , Br^- , I^- and PPh_3 and metal ions of three types ;
 (1) those with a noble gas configuration such as Be^{2+} (ns^0) ;
 (2) those with pseudo noble gas configuration $(n-1)d^{10} ns^0 np^0$, such as Zn^{2+} , Cu^+ and Ga^{3+} , and
 (3) those transition metal ions which do not strongly favour other structure by virtue of the CFSE, such as Co^{2+} , d^7 .
12. (A) The $3d^3$ electron configuration always have three unpaired electrons with weak field as well as strong field ligands.
- (B) $3d^3$

$e_g(dx^2-y^2, dz^2)$

$t_{2g}(dxy, dyz, dzx)$
- (C) H_2O being neutral molecule satisfies only secondary valencies.
 (D) It shows hydrate isomerism and not ionisation isomerism because anionic ligand is not present in coordination sphere.
13. According to EAN rule
 $26 - 0 + 2x = 36$
 $x = 5$
14. Ni^{+2} , Cu^{+2} only high spin complex.
15. $[\text{NiF}_6]^{2-}$ oxidation number = +4
 $t_{2g}^{2,2,2} eg^{0,0}$ (pairing occur due to high oxidation number of Ni).
16. A $[\text{Pt}(\text{Py})_2\text{Cl}_2] \equiv \text{Ma}_2\text{b}_2$ (2 G.I.)
 B $[\text{Pt}(\text{Py})_2(\text{NH}_3)\text{Cl}] \equiv \text{Ma}_2\text{bc}$ (2 G.I.)
 C $[\text{Pt}(\text{Py})_2(\text{NH}_3)(\text{Br})\text{Cl}] \equiv \text{Mabcd}$ (3 G.I.)
17. $3d^3 = t_{2g}^{1,1,1} eg^{0,0}$