CO-ORDINATION COMPOUNDS

CHAPTER

09

SIMPLE SALTS

These are produced as a result of neutralization of an acid by a base. For example,

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

When dissolved in water, they produce ions in the solution.

MIXED SALTS

These salts contain more than one acidic or basic radicals. For example, $NaKSO_4$

MOLECULAR OR ADDITION COMPOUNDS

When solutions containing two or more simple stable salts in stoichiometric proportions are allowed to evaporate, addition compounds are formed. For example,

$$KCl + MgCl_2 + 6H_2O \longrightarrow \underset{\text{(Carnalite)}}{KCl.MgCl_2.6H_2O}$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow \underset{\text{(Potash Alum)}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

$$CuSO_4 + 4NH_3 + H_2O \longrightarrow \underset{\text{(Complex)}}{[Cu(NH_3)_4]SO_4.H_2O}$$

$$4KCN + Fe(CN)_2 \longrightarrow \underset{\text{(Potassium ferrocyanide)}}{K_4[Fe(CN)_6]}$$

Addition compounds are of two types:

(a) Double salts (Lattice compounds):

Addition compounds, which exist as such in crystalline state only and lose their identity in solution are called double salts. For example,

$$FeSO_4.(NH_4)_2SO_4.6H_2O \longrightarrow Fe^{2+}(aq) + 2NH_4^+(aq) + 2SO_4^{2-}(aq) + 6H_2O$$

(b) Complex compounds:

The addition compounds that results from the combination of two or more simple stable salts and retain their identity in the solid as well as in dissolved state are called complex compounds. e.g.

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

A complex compound contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and a complex anion or a neutral molecule. Examples are $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $Ni(CO)_4$ respectively. Thus, a complex ion is defined as “an electrically charged radical, which consists of a central metal atom or ion surrounded by a group of ionic or neutral species.

CO-ORDINATION SPHERE

The central metal ion and the ligands that are directly attached to it, are enclosed in a square bracket, called co–ordination sphere or first sphere of attraction.

CENTRAL ATOM

In co-ordination sphere central atom is usually A d-block element, because of availability of vacant d-orbital.

Some metal ions form their most stable complexes with ligands in which the donor atoms are N, O or F. Such metal ions include group 1 and 2 elements, the first half of the transition elements, the lanthanides and actinides and the p–block elements except for their heavier members. These metals are called “***class–a acceptors***” and correspond to ***‘hard’ acids***.

In contrast the metals Rh, Ir, Pd, Pt, Ag, Au and Hg form their most stable complexes with the heavier elements of groups 15, 16 and 17. These metals are called “***class–b acceptors***” and correspond to ***‘soft’ acids***. The rest of the transition metals and the heaviest elements in the p–block, form complexes with both types of donors and are thus ‘intermediate’ in nature.

Classification of elements on the basis of type of acceptors

Li **(a)**	**Be** **(a)**											**B** **(a)**	**C** **(a)**	**N** **(a)**	**O** **–**
Na **(a)**	**Mg** **(a)**											**Al** **(a)**	**Si** **(a)**	**P** **(a)**	**S** **(a)**
K **(a)**	**Ca** **(a)**	**Sc** **(a)**	**Ti** **(a)**	**V** **(a)**	**Cr** **(a)**	**Mn** **(a)**	**Fe** **(a/b)**	**Co** **(a/b)**	**Ni** **(a/b)**	**Cu** **(a/b)**	**Zn** **(a)**	**Ga** **(a)**	**Ge** **(a)**	**As** **(a)**	**Se** **(a)**
Rb **(a)**	**Sr** **(a)**	**Y** **(a)**	**Zr** **(a)**	**Nb** **(a)**	**Mo** **(a)**	**Tc** **(a/b)**	**Ru** **(a/b)**	**Rh** **(b)**	**Pd** **(b)**	**Ag** **(b)**	**Cd** **(a/b)**	**In** **(a)**	**Sn** **(a)**	**Sb** **(a)**	**Te** **(a)**
Cs **(a)**	**Ba** **(a)**	**La** **(a)**	**Hf** **(a)**	**Ta** **(a)**	**W** **(a)**	**Re** **(a/b)**	**Os** **(a/b)**	**Ir** **(b)**	**Pt** **(b)**	**Au** **(b)**	**Hg** **(b)**	**Tl** **(a/b)**	**Pb** **(a/b)**	**Bi** **(a/b)**	**Po** **(a/b**
Fr **(a)**	**Ra** **(a)**	**Ac** **(a)**													

Ce **(a)**	**Pr** **(a)**	**Nd** **(a)**	**Pm** **(a)**	**Sm** **(a)**	**Eu** **(a)**	**Gd** **(a)**	**Tb** **(a)**	**Dy** **(a)**	**Ho** **(a)**	**Er** **(a)**	**Tm** **(a)**	**Yb** **(a)**
Th **(a)**	**Pa** **(a)**	**U** **(a)**	**Np** **(a)**	**Pu** **(a)**	**Am** **(a)**	**Cm** **(a)**	**Bk** **(a)**	**Cf** **(a)**	**Es** **(a)**	**Fm** **(a)**	**Md** **(a)**	**Mo** **(a)**

LIGANDS

The neutral molecules or ions (usually anions) which are linked directly with the central metal atom/ion are called ligands. In most of the complexes, ligands act as donor of one or more lone pairs to the central metal atom/ion. It should be noted that in metallic carbonyls, the ligand, CO, acts as both donor and acceptor $(M \rightleftarrows CO)$.

CO-ORDINATION NUMBER (OR LIGANCY)

The total number of atoms of ligands that can coordinate to the central metal atom/ion is called co–ordination number. For example, in $[Fe(CN)_6]^{4-}$, the co–ordination number of Fe^{2+} ion is 6.

EFFECTIVE ATOMIC NUMBER (EAN)

Sidgwick extended the Lewis theory to account for the bonding in the co–ordination compounds. He introduced the term co–ordinate bond for a shared electron pair if it initially belonged to one atom (donor atom) only. In this case, the donor atom acts as a Lewis base and the metal ion acts as a Lewis acid. The metal ion accepts the electron pairs till it achieves the next inert gas configuration. This is called the effective number rule.

The total number of electrons, which the central metal atom appears to possess in the complex, including those gained by it in bonding, is called effective atomic number of central metal ion. When the EAN was 36 (Kr), 54 (Xe) or 86 (Rn), the EAN rule was said to be followed.

For example, in $[Co(NH_3)_6]^{3+}$ cobalt has an atomic number 27. In Co^{3+} number of electrons is 24. Each ammonia molecule donates a pair of electrons. So, EAN becomes $24 + (2 \times 6) = 36$.

In many cases it was found EAN in a complex should be equal to number of electrons present in next noble gas.

There are exceptions as well. For example,

EAN of $[Ni(NH_3)_6]^{+2}$ is 38 and $[Cr(NH_3)_6]^{3+}$ is 33.

The EAN of metals in some metal complexes

Metal complex	**Atomic number of metal**	**Electrons on metal ion**	**Electrons donated by the ligands**	**EAN**
$[Co(NO_2)_6]^{3-}$	Co (27)	24	$6 \times 2 = 12$	$24 + 12 = 36$
$[Cd(NH_3)_4]^{2+}$	Cd (48)	46	$4 \times 2 = 8$	$46 + 8 = 54$
$[PtCl_6]^{2-}$	Pt (78)	74	$6 \times 2 = 12$	$74 + 12 = 86$
$[Cr(CO)_6]$	Cr (24)	24	$6 \times 2 = 12$	$24 + 12 = 36$
$[Ni(CO)_4]$	Ni (28)	28	$4 \times 2 = 8$	$28 + 8 = 36$
$[Ag(NH_3)_2]Cl$	Ag (47)	46	$2 \times 2 = 4$	$46 + 4 = 50$
$K_4[Fe(CN)_6]$	Fe (26)	24	$6 \times 2 = 12$	$24 + 12 = 36$

$[Cu(NH_3)_4]SO_4$	Cu (29)	27	$4 \times 2 = 8$	$27 + 8 = 35$
$K_2[Ni(CN)_4]$	Ni (28)	26	$4 \times 2 = 8$	$26 + 8 = 34$
$K_2[PtCl_6]$	Pt (78)	74	$6 \times 2 = 12$	$74 + 12 = 86$
$K_3[Cr(C_2O_4)_3]$	Cr (24)	21	$6 \times 2 = 12$	$21 + 12 = 33$
$K_2[HgI_4]$	Hg (80)	78	$4 \times 2 = 8$	$78 + 8 = 86$

As a theory, EAN rule is of no importance as it merely emphasizes the importance of the inert gas shell stability in compounds. Even though metal carbonyls and related compounds seem to obey this rule, many exceptions exist that invalidate the rule.

CLASSIFICATION OF LIGANDS:-

There are two ways ligands can be classified:

(I) Classification based on the number of donor atoms present in the ligands:

Such ligands are of following types:

(i) Monodentate or unidentate ligands

The ligands that can co–ordinate to the central metal ion at one site only are called monodentate ligands. Such ligands may be neutral molecules, negatively or positively charged ions. For example,

F^-, Cl^-, CN^-, OCN^-, H_2O, NH_3, $\overset{-}{N}O_2$, NO^+, $NH_2NH_3^+$ etc.

A monodentate ligand having more than one lone pair of electrons may simultaneously co–ordinate with two or more atoms and thus acts as a bridge between the metal ions. In such a case, it is called a bridging ligand and the complex thus formed is known as bridged complex. For example,

OH^-, F^-, NH_2^-, CO, O^{2-}, SO_4^{2-} etc.

(ii) Bidentate ligand

Ligands, which have two donor atoms and have the ability to co–ordinate with the central atom/ion at two different sites are called bidentate ligands. For example,

$H_2\ddot{N}-(CH_2)_2-\ddot{N}H_2$ (ethylenediamine)

(iii) Tridentate ligands

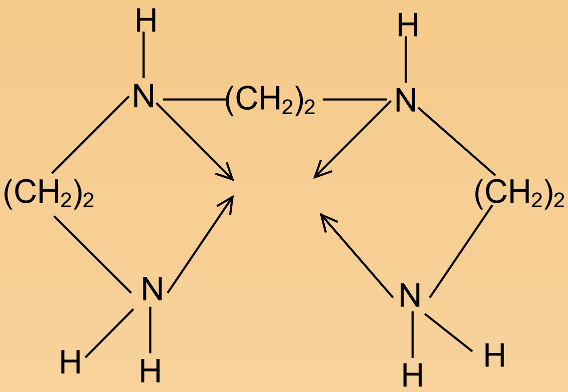
The ligands having three coordination sites are called tridentate ligands. For example,

e.g., $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H-CH_2-CH_2-\ddot{N}H_2$

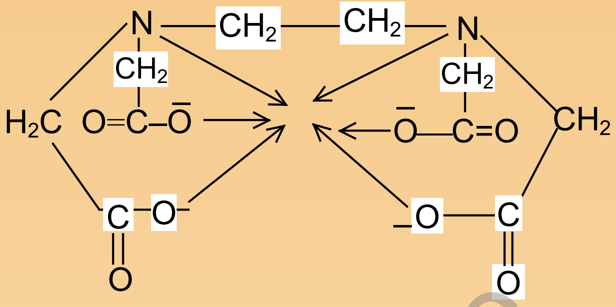
Diethylenetriamine

(iv) Polydentate ligands

The ligands having four or more co-ordination sites are called polydentate ligands. For example,



Triethylenetetramine
(trine)



Ethylenediamine
tetraacetate ion (EDTA)

(v) Ambidentate ligands

They have two or more donor atoms but, while forming complexes only one donor atom is attached to the metal ion. The examples of such ligands are CN^-, NO_2^-, NCS^-, NCO^- etc.

(vi) Chelating ligands

When a bidentate or a polydentate ligand is attached through two or more donor atoms to the same metal ion forming a ring structure, the ligand is called chelating ligand.
The chelating ligands form more stable complexes than ordinary unidentate ligands.

(II) Classification based on donor and acceptor properties of the ligands

(i) Ligands having one or more lone pair(s) of electrons are further classified as

(a) Ligands containing vacant π–type orbitals can receive back donated π–electrons from the metal ion in low oxidation state. Examples of such ligands are CO, NO, CN^- and unsaturated organic molecules. Such ligands have filled donor orbitals in addition to vacant π– acceptor orbitals. Thus, in the complexes formed by such ligands, both metal and the ligand act as donors and acceptors ($M \underset{\sigma}{\overset{\pi}{\rightleftharpoons}} L$).

(b) Ligands, which have no vacant orbitals to get back donated electrons from the metal. e.g. H_2O, NH_3, F^- etc.

(ii) Ligands having no lone pair of electrons but π–bonding electrons. e.g. C_2H_4, C_6H_6 $C_5\overset{\ominus}{\ddot{H_9}}$ etc.

IUPAC NOMENCLATURE OF COMPLEXES

The following rules are used for naming all types of complexes.

(1) In case of ionic complexes, cation is named first followed by the anion, irrespective of the fact, whether cation or anion or both are complex. Simple cation and anion are named just like naming a simple salt.

(2) Number of cations and anions are not mentioned while writing its name.

(3) Within a complex ion, the ligands are named first in the alphabetical order followed by name of the metal ion, which is followed by the oxidation state of metal ion in Roman numeral in parentheses.

(4) Name of all negative ligands ends with 'o' while the name of all positively charged ligands ends with 'ium'. Neutral ligands have no special ending.

Name of negative ligands

Ligand	Name	Ligand	Name
H^-	hydrido	HS^-	mercapto
O^{2-}	oxo	NH_2^-	amido
O_2^{2-}	peroxo	NH^{2-}	imido
O_2H^-	perhydroxo	NO_3^-	nitrato
OH^-	hydroxo	ONO^-	nitrito
F^-	fluoro	NO_2^-	nitro
Cl^-	chloro	N^{3-}	nitrido
Br^-	bromo	P^{3-}	phosphido
I^-	iodo	N_3^-	azido
CO_3^{2-}	carbonato	CNO^-	cyanato
$C_2O_4^{2-}$	oxalato	NCO^-	isocyanato
$CH_3CO_2^-$	acetato	SCN^-	thiocyanato–S
CN^-	cyano	NCS^-	thiocyanato–N
SO_4^{2-}	sulphato	HCO_3^-	hydrogencarbonato
SO_3^{2-}	sulphito	$S_4O_6^{2-}$	tetrathionato
S^{2-}	sulphido	EDTA	ethylenediaminetetraacetato
HSO_3^-	hydrogensulphito	$NH_2CH_2CO_2^-$	glycinato
$S_2O_3^{2-}$	thiosulphato	$C_5H_5^-$	cyclopentadienyl

Ligands whose names end in –"ite" or –"ate" become –"ito" or –"ato", i.e., by replacing the ending –e with –o.

Name of Neutral ligands

Ligand	Name	Abbreviation	Ligand	Name	Abbreviation
H_2O	aqua/aquo	–	$NH_2(CH_2)_2NH_2$	ethylenediamine	(en)
NH_3	ammine	–	CH_3NH_2	methylamine	–
CO	carbonyl	–	C_6H_6	benzene	–
NO	nitrosyl	–	N_2	dinitrogen	–
CS	thiocarbonyl	–	O_2	dioxygen	–
NS	thionitrosyl	–	Ph_3P	triphenylphosphine	–
C_5H_5N	pyridine	(py)	CH_3COCH_3	acetone	–

Name of Positive ligands

Ligand	Name
NO^+	nitrosonium
NO_2^+	nitronium
$NH_2NH_3^+$	hydrazinium

(5) If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek numbers such as di, tri, tetra, penta, hexa, etc for number of ligands being 2, 3, 4, 5 and 6 respectively.

However, when the name of the ligand includes a number, for example, dipyridyl, ethylenediamine, then bis, tris, tetrakis etc. are used in place of di, tri, tetra etc. The ligands for which such prefixes are used, their names are placed in parenthesis.

(6) For deciding the alphabetical order of ligands, the first letter of the ligand's name is to be considered and prefixes di, tri, tetra, bis, tris, tetrakis etc. are not considered.

(7) Neutral and positive ion complexes have no special ending but complex negative ion ends with the suffix 'ate' attached to names of the metal.

Element	**Metal as named in anionic complex**
Cobalt	Cobaltate
Nickel	Nickelate
Chromium	Chromate
Iron	Ferrate
Copper	Cuprate
Silver	Argentate
Lead	Plumbate

(8) For those complexes containing solvent of crystallization, it is indicated as: first write the cation's name, followed by anion's name followed by a gap and then write the number of solvent molecules in Arabic numeral followed by a hyphen which is followed by solvent's name.

Coordination compounds containing complex cationic ion

$[Pt(NH_3)_6]Cl_4$	Hexaammineplatinum (IV) chloride
$[Co(NH_3)_4(H_2O)Cl]Cl$	Tetraammineaquochlorocobalt(II) chloride
$[Cu(en)_2]SO_4$	*Bis*(ethylenediamine)copper (II) sulphate
$[Cr(H_2O)_4Cl_2]^+$	Tetraaquodichlorochromium (III) ion
$[Fe(H_2O)_4(C_2O_4)]_2SO_4$	Tetraaquooxalatoiron (III) sulphate
$[Cr(NH_3)_4(ONO)Cl]NO_3$	Tetraamminechloronitritochromium (III) nitrate
$[Ag(NH_3)_2]Cl$	Diamminesilver (I) chloride
$[Co(NH_3)_5(NCS)]Cl_2$	Pentaammineisothiocyanatocobalt (III) chloride
$[\{(C_6H_5)_3P\}_3Rh]Cl$	Tris(triphenylphosphine)rhodium (I) chloride

Coordination compounds containing complex anionic ion

$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II)
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate (III)
$K_3[Cr(C_2O_4)_3]$	Potassium trioxalatochromate (III)
$K_3[Co(C_2O_4)_2Cl_2]$	Potassium dichlorodioxalatocobaltate (III)
K_2HgI_4	Potassium tetraiodomercurate(II)
$K_2[PtCl_6]$	Potassium hexachloroplatinate (IV)
$Na[Ag(CN)_2]$	Sodium dicyanoargentate (I)
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate (II) ion
$Na_3[Co(NO_2)_6]$	Sodium hexanitrocobaltate (III)
$K_3[Fe(CN)_5NO]$	Potassium pentacyanonitrosylferrate (II)

Coordination compounds containing complex cationic and anionic ions:

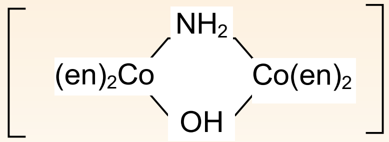
$[Cr(NH_3)_6]\,[Co(CN)_6]$	Hexaamminechromium(III) hexacyanocobaltate(III)
$[Pt(NH_3)_4]\,[CuCl_4]$	Tetraammineplatinum(II) tetrachlorocuprate(II)
$[Cr(NH_3)_6][Co(C_2O_4)_3]$	Hexaamminechromium(III) trioxalatocobaltate(III)
$[Pt(py)_4]\,[PtCl_4]$	Tetrapyridineplatinum(II) tetrachloroplatinate(II)

Non-ionic coordination compounds

$Fe(CO)_5$	Pentacarbonyliron(0)
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt(III)
$Cu(Gly)_2$	Diglycinatocopper(II)
$Ni(DMG)_2$	Bis(dimethylglyoximato) nickel(II)

(9) Naming of the bridging ligands of the bridged polynuclear complexes:

Complexes having two or more metal atoms are called polynuclear complexes. In these complexes, the bridging group is indicated by separating it from the rest of the complex by hyphen and adding the prefix μ–before the name of each different bridging group. Two or more bridging groups of the same type are indicated by di–μ–, tri–μ–etc. When a bridging ligand is attached to more than two metal atoms or ions, this is indicated by a subscript to μ.

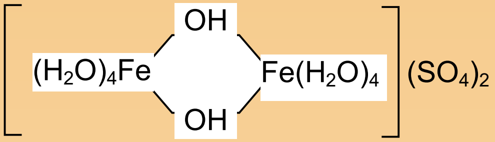


$(SO_4)_2$ is named as

Bis(ethylenediamine)cobalt(III)–μ–amido–μ–hydroxo–bis(ethylenediamine)cobalt(III)sulphate

Bis(ethylenediamine)cobalt(III)–μ–amido–μ–hydroxo–bis(ethylenediamine)cobalt(III)sulphate

The complex



is named as: Tetraaquoiron(III)–di–μ–hydroxo–tetraaquoiron(III) sulphate

The stable oxidation states of some of the transition metals of the three series are given below. These would be helpful to find the oxidation states of the metal ions while naming complexes having cation and anion both as complex species.

(i) First transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2, +3, +4	+2, +3, +4, +5	+2, +3, +6	+2, +3, +4, +7	+2, +3	+2, +3	+2, +3	+1, +2	+2

(ii) Second transition series

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	+4	+3, +5	+6	+4, +6, +7	+3	+3	+2, +4	+1	+2

(iii)Third transition series

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	+4	+5	+6	+4, +6, +7	+3, +4, +6	+1, +3, +4	+2, +4	+1, +3	+1, +2

VALENCE BOND THEORY

The valence bond theory deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes. This theory takes into account the hybridisation of vacant orbitals of central metal ion and was proposed by Linus Pauling, using hybridised orbitals. The main points of the valence bond theory are as follows.

1. The central metal loses requisite number of electrons and forms the cation. The number of electrons lost corresponds to the valency of the resulting cation.
2. The central metal ion makes available a number of empty s, p and d atomic orbitals equal to its coordination number.
3. These vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridising together. These hybrid orbitals are vacant, equivalent in energy and have a definite geometry.

4. The nonbonding metal electrons occupies the inner orbitals and they do not take part in the hybridisation. The electrons are grouped in accordance with the Hund's rule of maximum multiplicity. However, under the influence of a strong ligand, they may be forced to pair up against the Hund's rule.
5. The d–orbitals involved in the hybridisation may be either inner (n–1) d–orbitals or outer nd–orbitals.
6. Each ligand (donor group) must contain a lone pair of electrons.
7. Vacant hybrid orbitals of the metal atom or ion overlap with the filled (for example, containing lone–pair of electrons) σ–orbitals of the ligands to form a covalent σ–bond represented as $M \xleftarrow{\sigma} L$.
8. If the complex contains unpaired electrons, the complex is paramagnetic in nature, whereas, if it does not contain any unpaired electron, the complex is diamagnetic in nature.

C.N.	**Hybridisation**	**Geometry**	**Examples**
2	sp (4s, $4p_x$)	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2 (6s, $6p_x$, $6p_y$)	Trigonal planar	$[HgI_3]^-$
4	sp^3 (4s, $4p_x$, $4p_y$, $4p_z$)	Tetrahedral	$[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $[Ni(CO)_4]$, $[Zn(NH_3)_4]^{2+}$
4	dsp^2 ($3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$)	Square planar	$[Ni(CN)_4]^{2-}$
5	dsp^3 ($3d_{z^2}$, 4s, $4p_x$, $4p_y$, $4p_z$)	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
5	dsp^3 ($3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$, $4p_z$)	Square pyramidal	$[Ni(CN)_5]^{3-}$
6	d^2sp^3($3d_{x^2-y^2}$, $3d_{z^2}$, 4s, $4p_x$, $4p_y$, $4p_z$)	Inner orbital octahedral	$[Ti(H_2O)_6]^{2+}$, $[CrF_6]^{3-}$ uses (n–1) d–orbitals.
6	sp^3d^2(4s, $4p_x$, $4p_y$, $4p_z$, $4d_{x^2-y^2}$, $4d_{z^2}$)	Outer–orbital octahedral	$[Co(H_2O)_6]^{3+}$, $[Zn(NH_3)_6]^{2+}$, $[CoF_6]^{3-}$ uses nd–orbitals.

VBT–OCTAHEDRAL COMPLEXES

On the basis of VBT, octahedral complexes are of two types:

1. Inner–orbital octahedral complexes, which result from d^2sp^3 hybridisation of the central metal atom/ion.

Difference between inner and outer orbital octahedral complexes

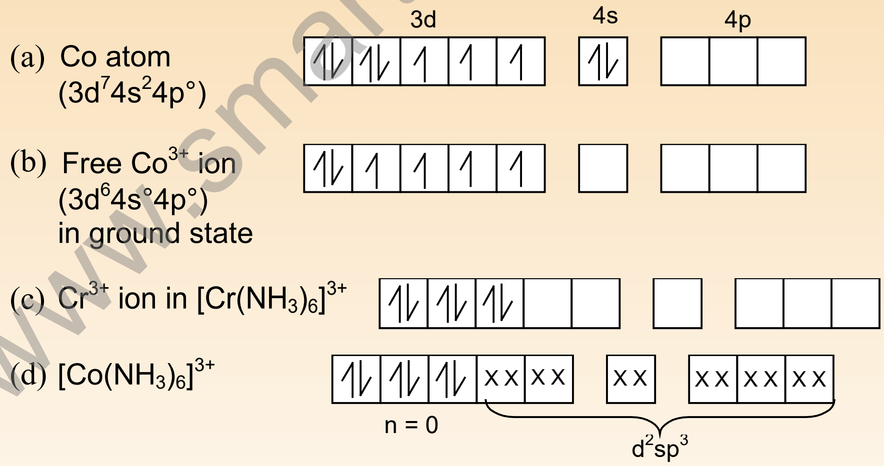
Inner Orbital octahedral complex	Outer orbital octahedral complex
1. d^2sp^3 hybridisation	1. sp^3d^2 hybridisation
2. The inner orbital complexes are formed with covalent metal ligand bonds.	2. The outer orbital complexes are formed with ionic bond.
3. Low spin complexes	3. High spin complexes

2. Outer orbital octahedral complexes, which result from sp^3d^2 hybridisation.

(a) Inner orbital octahedral complexes

The formation of these complexes can be explained on the basis of VBT by considering the complex ion, viz $[Co(NH_3)_6]^{3+}$.

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

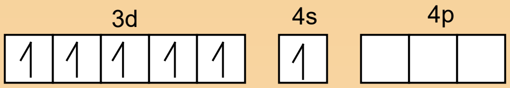


Here n represents the number of unpaired electrons and 'XX' represents an electron pair donated by each of free six NH_3 ligands. The two electrons of the electron pair have opposite spin. The above complex ion is diamagnetic as all the electrons are paired.

In order to make 3d electrons paired, the two unpaired electrons residing in $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals are forced by the six NH_3 ligands to occupy $3d_{yz}$ and $3d_{zx}$ orbitals. By doing so, all the 3d electrons become paired and also at the same time, two 3d orbitals namely $3d_{z^2}$, $3d_{x^2-y^2}$, hybridise together with. 4s, $4p_x$, $4p_y$ and $4p_z$ orbitals to give six d^2sp^3 hybrid orbitals which, being empty accepts the six electron pairs donated by six NH_3 ligand molecules.

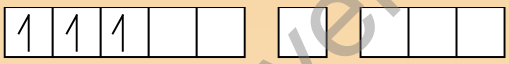
$[Cr(NH_3)_6]^{3+}$

(a) Cr atom ($3d^54s^1$)

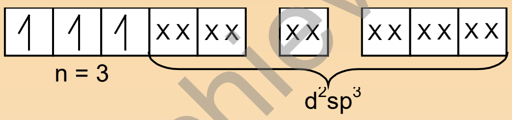


(b) Free Cr^{3+} ion ($3d^34s^\circ4p^\circ$) in ground state

(c) Cr^{3+} ion in $[Cr(NH_3)_6]^{3+}$



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

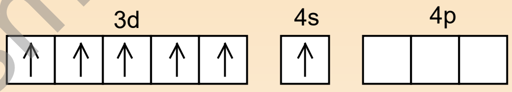


The above complex ion is paramagnetic as there are three unpaired electrons.

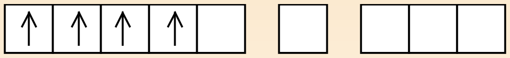
$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15}$ B.M.

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

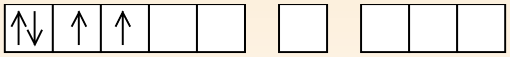
(a) Cr atom ($3d^54s^1$)



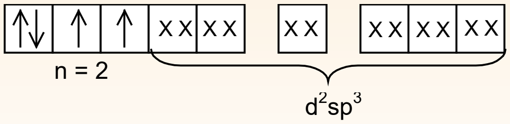
(b) Cr^{2+} ion ($3d^4$) in ground state



(c) Cr^{2+} ion in $[Cr(CN)_6]^{4-}$



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



The above complex ion is paramagnetic since two unpaired electrons are present.

$$\mu = \sqrt{2(2+2)} = \sqrt{8} \text{ B.M.}$$

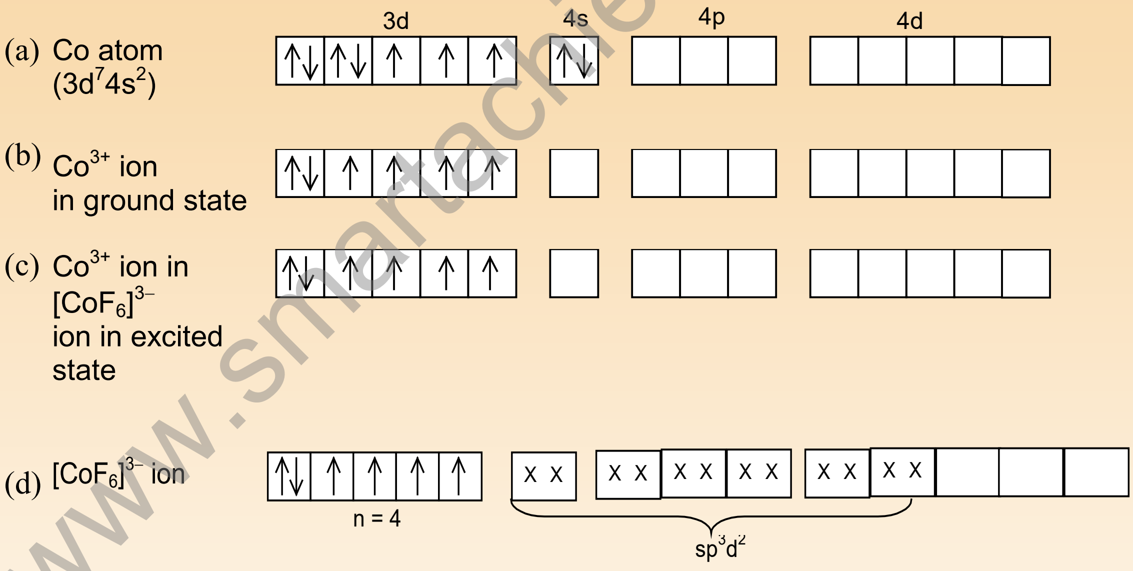
Other examples of inner orbital octahedral paramagnetic complexes are $[Ti(H_2O)_6]^{3+}$ (n=1), $[Mn(CN)_6]^{4-}$ (n = 1), $[Mn(CN)_6]^{3-}$ (n = 2), $[Fe(CN)_6]^{3-}$ (n =1), $[Co(CN)_6]^{4-}$ (n = 1 in 5s orbital) while the examples of inner orbital octahedral diamagnetic complexes are: $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)_6]^{3-}$, $[Pt(NH_3)_6]^{4+}$ etc.

All these complexes result from d^2sp^3 hybridisation of the central metal ion.

(b) Outer orbital octahedral complexes

Octahedral complexes resulted from sp^3d^2 hybridisation, using outer d– and outer s and p orbitals are called outer–orbital octahedral complexes.

$[CoF_6]^{3-}$



In this complex ion, it is $4d_{x^2-y^2}$ and $4d_{z^2}$ orbitals that mix with one 4s and three 4p orbitals to give six sp^3d^2 hybrid orbitals, which being empty, accept the six electron pairs denoted by each of the six F^- ligands. It is paramagnetic as there are four unpaired electrons.

$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} \text{ B.M.}$$

Some other examples of outer orbital octahedral paramagnetic complex are:

$[Cr(H_2O)_6]^{2+}$ (n = 4), $[Mn(H_2O)_6]^{2+}$ (n = 5), $[Fe(H_2O)_6]^{2+}$ (n = 4), $[Fe(NH_3)_6]^{2+}$ (n = 4)

$[Fe(H_2O)_6]^{3+}$ (n = 5), $[Fe(F)_6]^{3-}$ (n = 5), $[CoF_6]^{3-}$ (n = 4),

$[Co(NH_3)_6]^{2+}$ (n = 3)

$[Co(H_2O)_6]^{2+}$ (n = 3), $[Ni(NH_3)_6]^{2+}$ (n = 2),

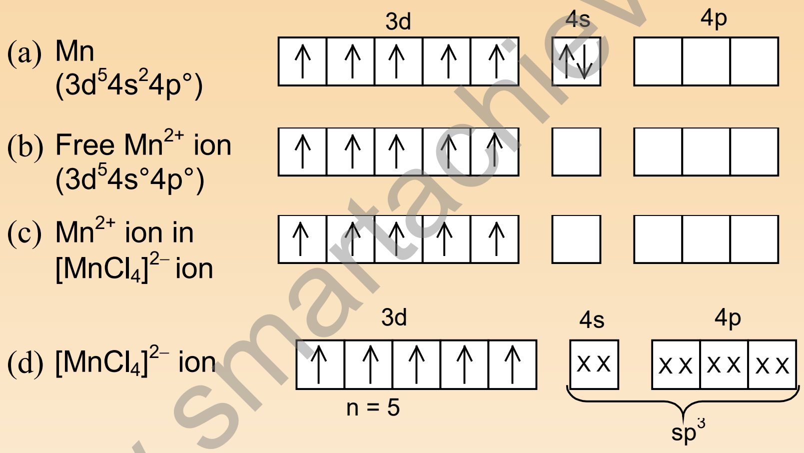
$[Ni(H_2O)_6]^{2+}$ (n = 2), $[Ni(NCS)_6]^{4-}$ (n = 2),

$[Ni(NO_2)_6]^{4-}$ (n = 2), $[CuF_6]^{3-}$ (n = 2).

$[Zn(NH_3)_6]^{2+}$ (n = 0) is an example of outer orbital octahedral diamagnetic complex.

VBT–TETRAHEDRALCOMPLEXES(Co–ordination no. = 4, sp^3 hybridisation)

Tetrahedral complexes result from sp^3 hybridisation. In sp^3 hybridisation the s– and three p–orbitals should belong to the same shell. The formation of tetrahedral complexes by VBT can be explained by considering the complex ion like $[MnCl_4]^{2-}$. This complex ion is paramagnetic corresponding to the presence of five unpaired electrons and hence the configuration of Mn^{2+} ion in the free state and in the complex ion remains the same.



$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} \text{ B.M.}$$

Examples of some paramagnetic tetrahedral complexes are

$[NiCl_4]^{2-}$ (n = 2), $[Ni(NH_3)_4]^{2+}$ (n = 2)

$[MnBr_4]^{2-}$ (n = 5), $[FeCl_4]^{2-}$ (n = 4),

$[CoCl_4]^{2-}$ (n =3), $[CuCl_4]^{2-}$ (n = 1) etc.

While the examples of some diamagnetic tetrahedral complexes are:

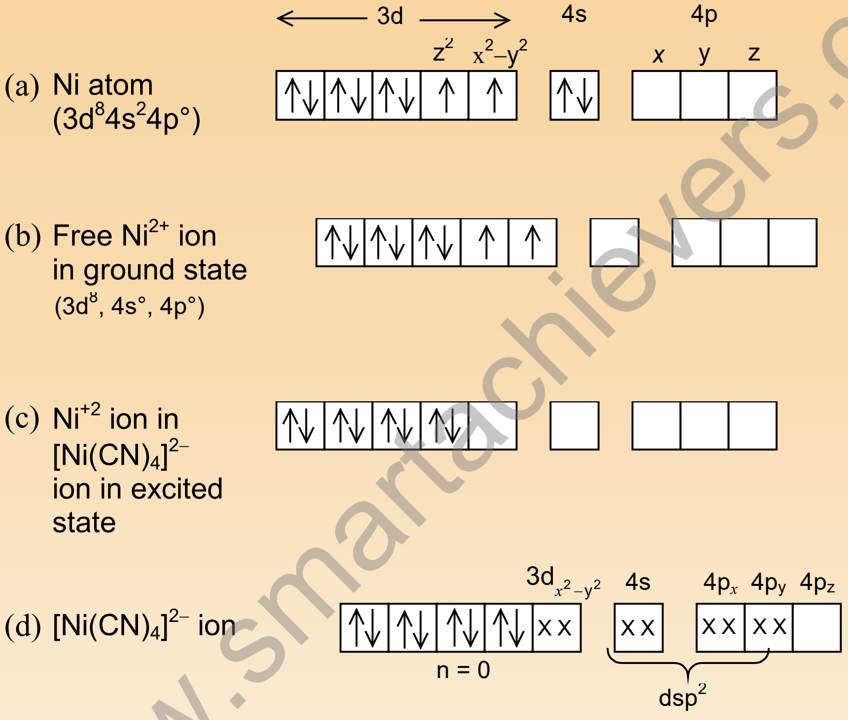
$[Ni(CO)_4]$ (n = 0), $[Cu(CN)_4]^{3-}$ (n = 0), $[Zn(NH_3)_4]^{2+}$ (n = 0), $[ZnCl_4]^{2-}$ (n = 0), $[Cd(CN)_4]^{2-}$ (n = 0), etc. All these complexes result from sp^3 hybridisation of the central metal atom/ion.

VBT–SQUARE PLANAR COMPLEXES

(Coordination no. = 4, dsp^2 hybridisation)

Square planar complexes result from dsp^2 hybridisation. In dsp^2 hybridisation, d–orbital should be $d_{x^2-y^2}$ orbital (belonging to the lower shell) while s and p orbitals should be from the higher shell. The two p–orbitals should be p_x and p_y orbitals. The selection of $d_{x^2-y^2}$,

p_x and p_y orbitals is based on the fact that all these orbitals lie in the same plane. The formation of square planar complexes by VBT can be explained by considering the complex ion like $[Ni(CN)_4]^{2-}$. The measurement of magnetic moment value for $[Ni(CN)_4]^{2-}$ ion has shown that $\mu = 0$ i.e. the complex ion has no unpaired electron and hence it is diamagnetic.



In order to make all the 3d–electrons paired, one unpaired electron residing in $3d_{x^2-y^2}$ orbital is forced by the four CN^- ligand to occupy $3d_{z^2}$ orbital. Now $3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$ orbitals mix together to form four dsp^2 hybrid orbitals which, being empty, accept the four electron pairs donated by the four CN^- ligand ions.

Examples of paramagnetic square planar complexes are:

$[Cu(CN)_4]^{2-}$ (n = 1), $[Cu(NH_3)_4]^{2+}$ (n = 1), $[CuCl_4]^{2-}$ derived from $(NH_4)_2[CuCl_4]$ (n = 1) etc. While the examples of diamagnetic square planar complexes are: $[Ni(CN)_4]^{2-}$ (n = 0), $[PtCl_4]^{2-}$ (n = 0), $[Pt(NH_3)_4]^{2+}$ (n = 0) etc.

LIMITATIONS OF VBT

1. Although valence bond theory provides a satisfactory representation of the complex compound based upon the concept of orbital hybridisation, it cannot account for the relative stabilities for different shapes and coordination numbers in metal complexes.
2. The valence bond theory does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.
3. Sometimes the theory requires the transfer of electron from lower energy to the higher energy level, which is very much unrealistic in absence of any energy supplier (For exatmple, this happens in the case of $[CuX_4]^{-2}$).
4. The changes in the properties of the metal ion along with the ligands and the simple metal ions can not be explained. For example, the colour changes associated with electronic transition within d orbitals are affected on formation of complex, but the valence bond theory does not offer any explanation.
5. Sometimes the same metal acquires different geometry when formation of complex takes place with different ligands. The theory does not explain as to why at one time the electrons must be rearranged against the Hund's rule while, at other times the electronic configuration is not disturbed.
6. The VBT does not explain why certain complexes are more labile than the others.
7. It does not give quantitative interpretation of thermodynamic or kinetic stabilities of coordination compounds.

CRYSTAL FIELD THEORY (CFT)

In crystal field theory, we assume the ligands to be the point charges and there is interaction between the electrons of the ligands and the electrons of the central metal atom or ion. The five d–orbitals in an isolated gaseous metal atom or ion are degenerate. This degeneracy is maintained if an spherically symmetrical negative field surrounds the metal atom/ion. However, when ligands approach the central metal atom/ion, the field created is not exactly spherically symmetrical and the degeneracy of the d–orbitals is lifted. It results in the splitting of d–orbitals and the pattern of splitting depends upon the nature of the crystal field. This splitting of d–orbitals energies and its effects, form the basis of the crystal field treatment of the coordination compounds.

Ligands that cause large degree of crystal filed splitting are termed as ***strong field* ligands.** Ligands that cause only a small degree of crystal filed splitting are termed as ***weak field ligands***. The common ligands can be arranged in ascending order of crystal field splitting energy. The order remains practically constant for different metals and this series is called the ***spectrochemical series***.

$I^- < Br^- < S^{2-} < Cl^- \sim SCN^- \sim N_3^- < NO_3^- < F^- < OH^- < CH_3CO_2^- < ox^{2-} < H_2O \,||\, < NCS^- < EDTA^{4-} < NH_3 \sim Py < en < NO_2^- < H^- \sim CH_3^- < CO \sim CN^-$

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effect of σ and π–bonding. The halides are in the order expected from electrostatic effects. In other cases, we must consider covalent bonding to explain the order. A pattern of increasing σ–donation is as follows:

Halides donors < O donors < N donors < C donors

The crystal field stabilization produced by the strong CN^- is almost double that of halide ions. This is attributing π–bonding in which the metal donates electrons from a filled t_{2g} orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as π–acceptors.

FACTORS AFFECTING THE STABILITY OF COMPLEXES

1. A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. The overall stability constant is given by

$$M + nL \rightleftharpoons MLn;\ K_f = \frac{[MLn]}{[M][L]^n}$$

$\frac{1}{K_f}$ is called instability constant. Higher the value of K_f, more stable is the complex.

2. Higher is the charge density on the central metal ion, greater is the stability of the complexes. For example, $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)_6]^{4-}$

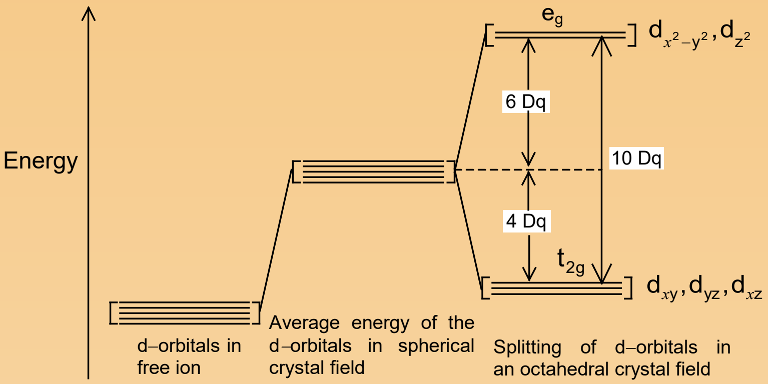
3. More is the basic character of ligand, more stable is the complex.

For example, the cyano and amino complexes are far more stable than the halo complexes.

4. Chelating ligands form more stable complexes than the monodentate ligands.

Crystal field effects in octahedral coordination entities

Let us assume that the six ligands are positioned symmetrically along the Cartesian axis with the metal atom or ion at the origin. As the ligands approach the central metal atom or ion, the energy of the d–orbitals of the central metal atom or ion increases. If the field created by the ligands is spherical, then the increase in the energies of all the d-orbitals is the same. However, under the influence of octahedral field, the energies of the d–orbitals lying along the axis (i.e. d_{z^2} and $d_{x^2-y^2}$) increases more than the d–orbitals lying between the axis (i.e. d_{xy}, d_{yz} and d_{xz}). Thus, the degenerate d–orbitals (with no field effect or spherical field effect) splits up into two sets of orbitals (i) the lower energy set, t_{2g} (d_{xy}, d_{yz} and d_{xz}) and (ii) the higher energy set, e_g ($d_{x^2-y^2}$ and d_{z^2}). The energy separation is denoted by Δ_o or 10 Dq. (where $_o$ stands for octahedral field), as shown below:



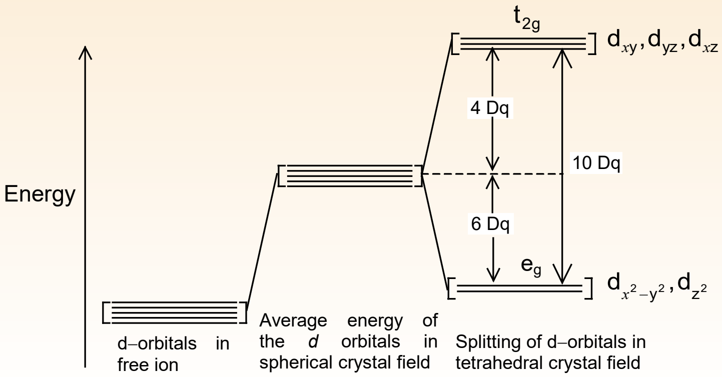
Significance of Δ_o

A strong field ligand approaches the central metal atom/ion strongly and thus the magnitude of Δ_o is high. Hence, in the case of strong field ligand, the magnitude of Δ_o is greater than the pairing energy (the energy required to pair up two negatively charged electrons having opposite spin in an orbital). However, under the influence of weak field ligand, $\Delta_o < P$ (where P represents the pairing energy).

Now, let us consider the d^4 configuration of the central metal atom/ion. The first three electrons will go into t_{2g} orbitals using Hund's rule of maximum multiplicity. The fourth electron will go in the e_g orbital when the ligands are weak as, $\Delta_o < P$ giving the configuration $t_{2g}^3 e_g^1$. But if the ligands are strong then the fourth electron will pair up with any of the singly occupied t_{2g} orbitals (as $\Delta_o > P$) to give the configuration $t_{2g}^4 e_g^0$.

Crystal field effects in tetrahedral coordination entities

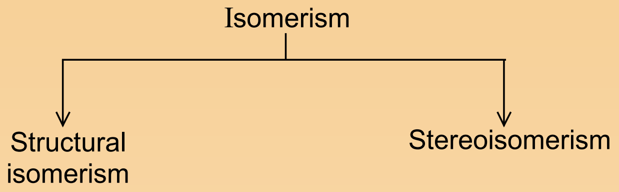
Under the influence of tetrahedral field, the d-orbital splitting is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = -\frac{4}{9}\Delta_o$. Consequently the orbital splitting energies are not sufficiently large for forcing pairing and therefore low spin or spin paired configurations are rarely observed.



ISOMERISM

The compounds having same chemical formula but different structural arrangement of their atoms and hence different physical and chemical properties are called isomers and the phenomenon is called isomerism. Isomerism in complexes are of two types:

(i) Structural Isomerism (ii) Stereoisomerism



(i) Ionisation Isomerism
(ii) Hydrate isomerism
(iii) Ligand isomerism
(iv) Coordination isomerism
(v) Linkage isomerism
(vi) Coordination position isomerism
(vii) Polymerisation isomerism

(i) Geometrical or cis-trans isomerism
(ii) Optical isomerism

STRUCTURAL ISOMERISM

This isomerism arises due to the difference in structures of coordination compounds and are of the following types.

(a) Ionisation isomerism

Complexes that have the same empirical formula and are produced by the interchange of the position of the ligands inside the complex zone and outside the complex zone are called ionisation isomers. They give different ions e.g.

(i) $[Co(NH_3)_4Cl_2]NO_2 \rightleftharpoons [Co(NH_3)_4Cl_2]^+ + NO_2^-$

$[Co(NH_3)_4Cl(NO_2)]Cl \rightleftharpoons [Co(NH_3)_4Cl(NO_2)]^+ + Cl^-$

(ii) $[Co(NH_3)_5SO_4]Br \rightleftharpoons [Co(NH_3)_5SO_4]^+ + Br^-$

$[Co(NH_3)_5\,Br]SO_4 \rightleftharpoons [Co(NH_3)_5\,Br]^{++} + SO_4^{2-}$

The number of ions in a solution can be determined by conductivity measurement. More the number of ions in a solution more is the conductivity. Greater the charge on ions, greater is the conductivity of solution.

(b) Hydrate isomerism

This type of isomerism arises due to the different position of water molecules inside and outside the coordination sphere. For example,

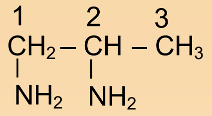
(i) $[Cr(H_2O)_6]Cl_3$ (violet), does not lose water over H_2SO_4 and all Cl^- ions are immediately precipitated by (Ag^+) ions.

(ii) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (green), loses H_2O over H_2SO_4 and two Cl^- ions are precipitated by (Ag+) ions.

(iii) $[Cr(H_2O)_4 Cl_2] Cl \cdot 2H_2O$ (green), loses two water molecules over H_2SO_4 and only one Cl^- ion is precipitated by Ag^+ ions.

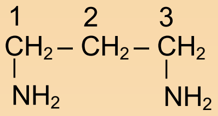
(c) Ligand isomerism

Some ligands themselves are of capable of existing as isomers, for example diamino propane can exist both as 1, 2–diaminopropane (pn) and 1,3–diaminopropane, also called trimethylenediamine (tn)



$$\overset{1}{C}H_2(NH_2)-\overset{2}{C}H(NH_2)-\overset{3}{C}H_3$$

1,2–diamino propane (pn)



$$\overset{1}{C}H_2(NH_2)-\overset{2}{C}H_2-\overset{3}{C}H_2(NH_2)$$

1,3–diamino propane (tn)

When these ligands (for example, pn and tn) are associated to form complexes, the complexes are isomers of each other. e.g. $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$ ions.

(d) Coordination isomerism

If both cation and anion of a complex compound are complex, there may be an exchange of ligands between the two coordination spheres, giving rise to isomers known as coordination isomers. e.g.

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

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

(e) Linkage isomerism

Those complexes in which the ligands can coordinate with the central metal ion through either of the two atoms, give rise to the linkage isomerism.

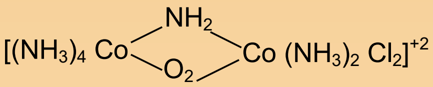
The best known ligands of this type are NO_2^-, SCN^- and $S_2O_3^{2-}$ ions. In complexes containing NO_2^- ion as ligand, NO_2^- ion may attach with the central ion either through O-atom or through N-atom.

(i) $[Co(NH_3)_5(NO_2)]Cl_2 \longrightarrow$ Pentaamminenititto-N cobalt(III) chloride.

$[Co(NH_3)_5(ONO)]Cl_2 \longrightarrow$ Pentaamminenitrito-O cobalt(III) chloride.

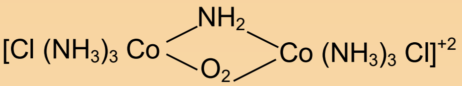
(f) Coordination position isomerism

In some poly-nuclear complexes, interchange of the ligands between the metal atoms which are present as a part of the complex is possible. This type of interchange of ligands between the metal atoms gives rise to coordination position isomerism for example,



(unsymmetrical form)

and



(symmetrical form)

are coordination position isomers.

(g) Polymerisation isomerism

This is not the true isomerism because it occurs between compound having the same empirical formula, but different molecular weights. For example, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4]^{2+}$ $[Pt(Cl_4)]^{2-}$ have the same empirical formula.

STEREOISOMERISM OR SPACE ISOMERISM

When two compounds contain the same ligands coordinated to the same central ion, but the arrangement of ligands in the space is different, the two compounds are said to be stereoisomers and the type of isomerism is called stereoisomerism.

Stereoisomerism is of two types:

(i) Geometrical or cis-trans isomerism

(ii) Optical or mirror image isomerism.

Geometrical isomerism

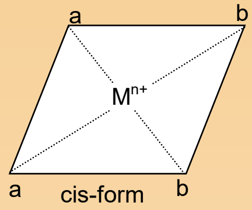
Geometrical isomerism is due to ligands occupying different positions around the central metal ion. The ligands occupy positions either adjacent to one another or opposite to one another. These are referred to as cis-form and trans-form respectively. This type of isomerism is, therefore, also referred to as cis-trans isomerism.

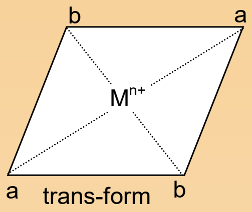
(a) Geometrical isomerism in 4–coordinate complex

Complexes having central metal atom with co–ordination number = 4 may be either tetrahedral or square planar. Geometrical isomerism cannot arise in tetrahedral complexes because this geometry contains all the ligands in the cis (i.e., adjacent) position with respect to each other, i.e., each ligand is equidistant from the other three ligands and all the bond angles are the same (109.5°). Hence geometrical isomerism cannot be expected in tetrahedral complexes.

Square planar complexes of [Ma_4], [Ma_3b] and [Mab_3] type (a and b are monodentate ligands) do not show geometrical isomerism, since every conceivable spatial arrangement of the ligands a round the metal ion is exactly equivalent.

(1) [Ma_2b_2] type complexes



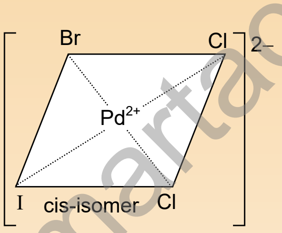


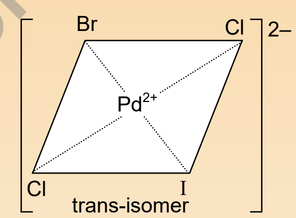
e.g. [Pt^{+2} $(NH_3)_2$ Cl_2], [$Pt^{2+}(NH_3)_2$ Br_2] and

[Pd^{2+} $(NH_3)_2(NO_2)_2$].

(2) [Ma_2bc] type complexes

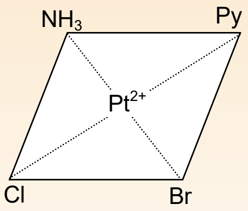
Square planar complexes of this type also show cis-trans isomerism. For example, [$Pd^{2+}Cl_2BrI$]$^{2-}$ exists in the following cis–trans

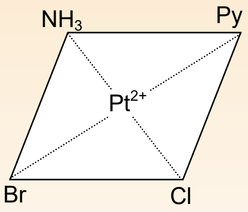


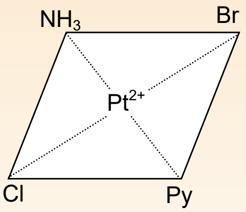


(3) [Mabcd] type complexes

Square planar complexes of this type exist in three isomeric forms for example, [Pt^{2+} (NH_3) (Py) (Cl) (Br)] exist in the following structures.



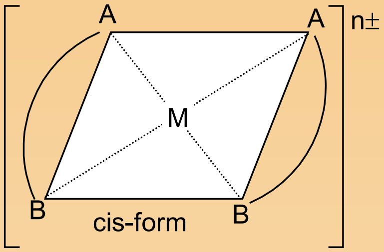


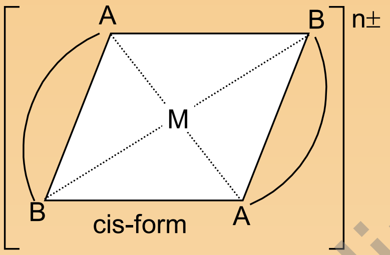


[$Pt^{2+}(NO_2)$(Py) (NH_3) (NH_2OH)]$^+$ and [$Pt^{2+}(C_2H_4)$ (NH_3) (Cl) (Br)] are other examples

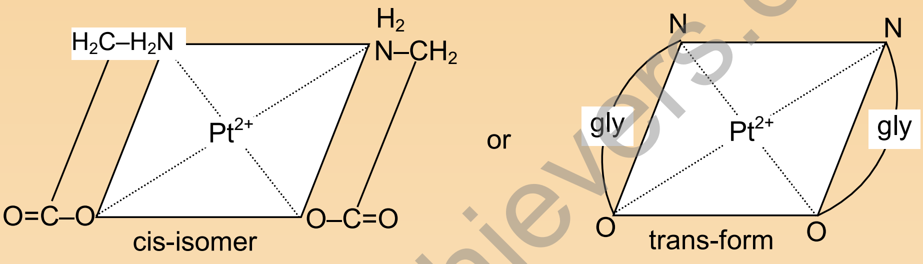
(4) $[M(AB)_2]^{n\pm}$ type complexes

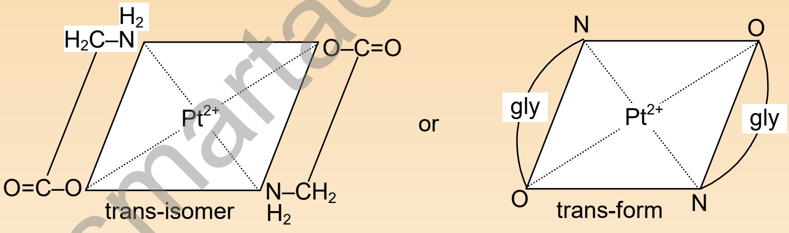
Here *M* is the central metal ion and (AB) represents an unsymmetrical bidentate ligand. (A) and (B) are the two ends (i.e., coordinating atoms) of the bidentate ligand. Such type of complexes also show cis and trans isomerism.





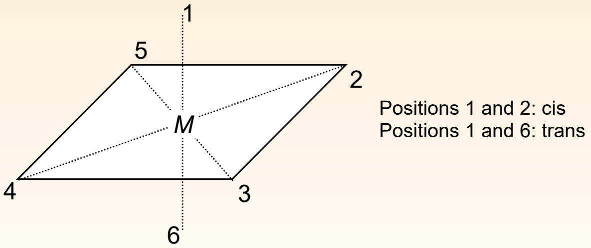
For example, $[Pt^{2+}(gly)_2]$; Here gly represents the glycinato ligand, $NH_2CH_2COO^-$ which has N and O atoms as its donor atoms.





(b) Geometrical isomerism in 6–coordinate complexes

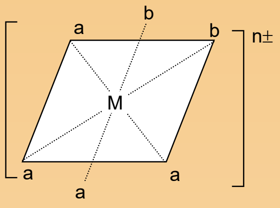
A complex compound having the central metal ion with coordination number equal to 6 has octahedral shape. The system used for numbering different positions of the ligands in an octahedral geometry has been shown below.



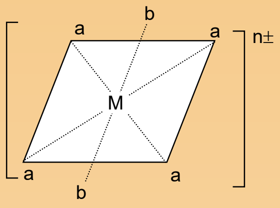
The octahedral complexes of the types $[Ma_6]$, $[M(AA)_3]$ and $[Ma_5b]$ do not show geometrical isomerism.

The following octahedral complexes give two or more geometrical isomers

(1) $[Ma_4b_2]^{n\pm}$ type complexes:



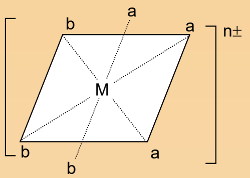
cis–form



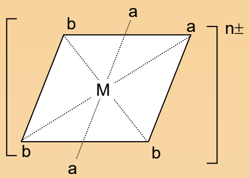
trans–form

Examples of such complexes are $[Co^{3+}(NH_3)_4Cl_2]^+$, $[Co^{3+}(NH_3)_4(NO_2)_2]^+$ etc.

(2) $[Ma_3b_3]^{n\pm}$ type complexes:



Facial (fac)



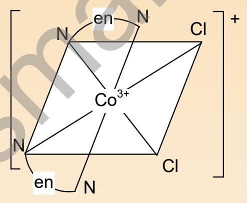
Meridional (mer)

(When each trio of donor atoms (viz the ligands a, a and a) occupy adjacent positions at the corners of an octahedral face, we have facial (fac) isomer. When the positions are around the meridian of the octahedron, we get Meridional (mer) isomer.

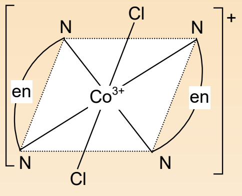
Complexes like $[Co^{3+}(NH_3)_3Cl_3]$, $[Cr^{3+}(H_2O)_3F_3]$, $[Pt^{3+}(Py)_3Cl_3]$, $[Cr^{3+}(NH_3)_3Cl_3]$, $[Ru^{3+}(H_2O)_3Cl_3]$, $[Pt^{4+}(NH_3)_3Br_3]^+$ etc exhibit such type of isomerism.

(3) $[M(AA)_2a_2]$ type complexes: Here (AA) represents a symmetrical bidentate ligand in which *A* and *A* are two identical co-ordinating atoms.

Examples of such complexes are $[Co^{3+}(en)_2Cl_2]^+$, $[Co^{3+}(en)_2(NH_3)_2]^{3+}$, $[Co^{3+}(en)_2(NO_3)_2]^+$, $[Cr^{3+}(en)_2Cl_2]^+$, $[Cr^{3+}(C_2O_4)_2 (H_2O)_2]^-$ (where en = ethylenediamine).



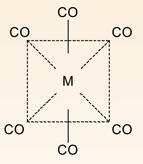
cis–isomer



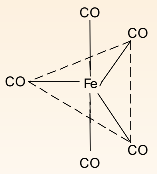
trans–isomer

Metal Carbonyls:

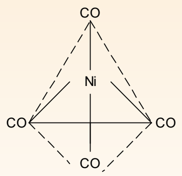
These are the complexes where carbon of carbon monoxide donates a pair of electrons to the metal. Nickel carbonyl and iron carbonyl are the common examples.



$[M(CO)_6]$
(M = Cr, Mo, W)

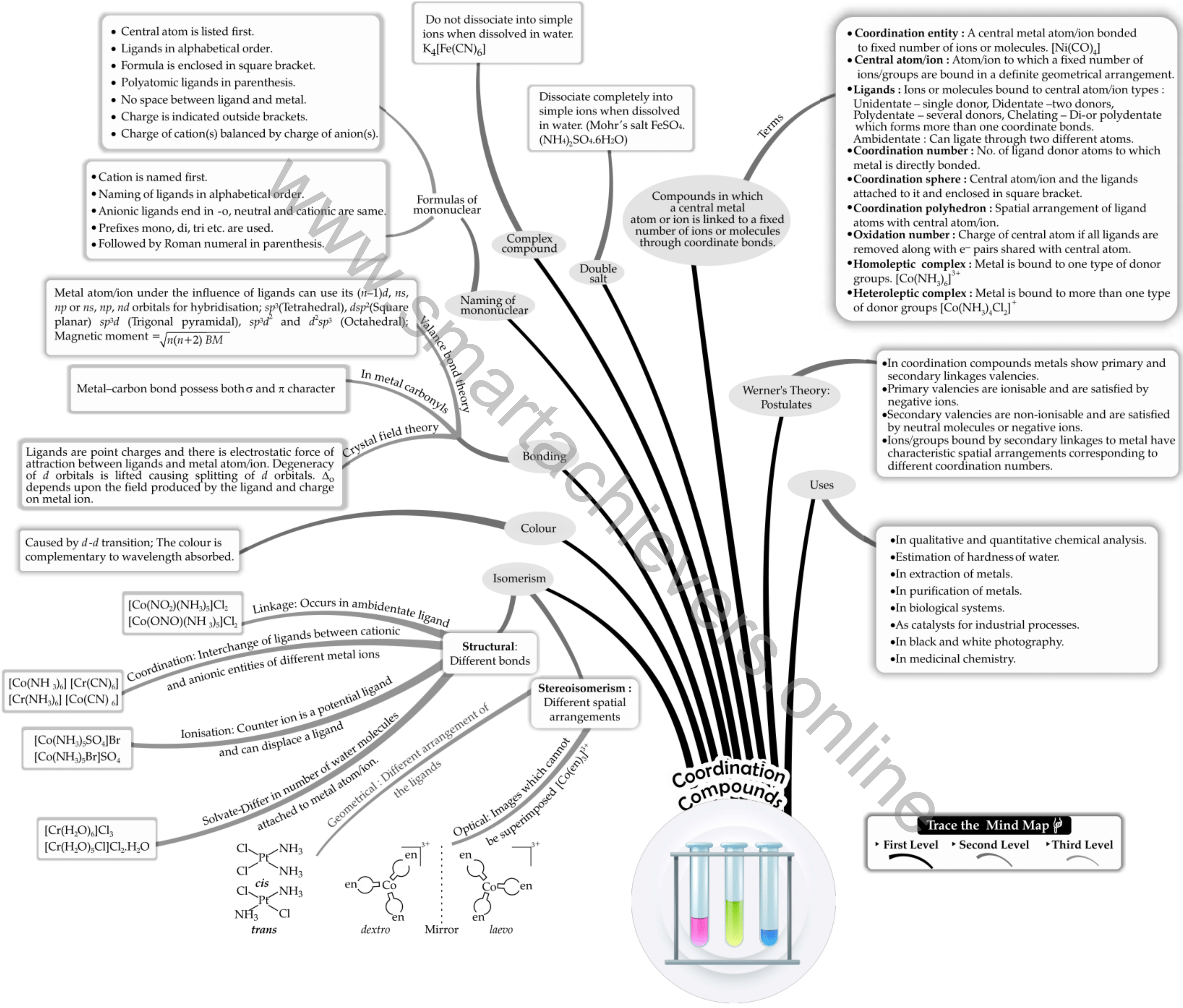


$[Fe(CO)_5]$



$[Ni(CO)_4]$

In metal carbonyl the oxidation state of the metal is zero. These metal carbonyls may be monomeric bridged or polynuclear.



Coordination Compounds

Trace the Mind Map
- First Level
- Second Level
- Third Level

Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

Terms
- **Coordination entity :** A central metal atom/ion bonded to fixed number of ions or molecules. $[Ni(CO)_4]$
- **Central atom/ion :** Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
- **Ligands :** Ions or molecules bound to central atom/ion types : Unidentate – single donor, Didentate –two donors, Polydentate – several donors, Chelating – Di-or polydentate which forms more than one coordinate bonds. Ambidentate : Can ligate through two different atoms.
- **Coordination number :** No. of ligand donor atoms to which metal is directly bonded.
- **Coordination sphere :** Central atom/ion and the ligands attached to it and enclosed in square bracket.
- **Coordination polyhedron :** Spatial arrangement of ligand atoms with central atom/ion.
- **Oxidation number :** Charge of central atom if all ligands are removed along with e^- pairs shared with central atom.
- **Homoleptic complex :** Metal is bound to one type of donor groups. $[Co(NH_3)_6]^{3+}$
- **Heteroleptic complex :** Metal is bound to more than one type of donor groups $[Co(NH_3)_4Cl_2]^+$

Werner's Theory: Postulates
- In coordination compounds metals show primary and secondary linkages valencies.
- Primary valencies are ionisable and are satisfied by negative ions.
- Secondary valencies are non-ionisable and are satisfied by neutral molecules or negative ions.
- Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.

Uses
- In qualitative and quantitative chemical analysis.
- Estimation of hardness of water.
- In extraction of metals.
- In purification of metals.
- In biological systems.
- As catalysts for industrial processes.
- In black and white photography.
- In medicinal chemistry.

Double salt

Dissociate completely into simple ions when dissolved in water. (Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$)

Complex compound

Do not dissociate into simple ions when dissolved in water. $K_4[Fe(CN)_6]$

Naming of mononuclear

Formulas of mononuclear
- Central atom is listed first.
- Ligands in alphabetical order.
- Formula is enclosed in square bracket.
- Polyatomic ligands in parenthesis.
- No space between ligand and metal.
- Charge is indicated outside brackets.
- Charge of cation(s) balanced by charge of anion(s).

- Cation is named first.
- Naming of ligands in alphabetical order.
- Anionic ligands end in -o, neutral and cationic are same.
- Prefixes mono, di, tri etc. are used.
- Followed by Roman numeral in parenthesis.

Bonding

Valance bond theory

Metal atom/ion under the influence of ligands can use its $(n-1)d$, ns, np or ns, np, nd orbitals for hybridisation; sp^3(Tetrahedral), dsp^2(Square planar) sp^3d (Trigonal pyramidal), sp^3d^2 and d^2sp^3 (Octahedral); Magnetic moment $= \sqrt{n(n+2)}\ BM$

In metal carbonyls

Metal–carbon bond possess both σ and π character

Crystal field theory

Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lifted causing splitting of d orbitals. Δ_o depends upon the field produced by the ligand and charge on metal ion.

Colour

Caused by d-d transition; The colour is complementary to wavelength absorbed.

Isomerism

Structural: Different bonds

Linkage: Occurs in ambidentate ligand

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

Coordination: Interchange of ligands between cationic and anionic entities of different metal ions

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

Ionisation: Counter ion is a potential ligand and can displace a ligand

$[Co(NH_3)_5SO_4]Br$
$[Co(NH_3)_5Br]SO_4$

Solvate-Differ in number of water molecules attached to metal atom/ion.

$[Cr(H_2O)_6]Cl_3$
$[Cr(H_2O)_5Cl]Cl_2.H_2O$

Stereoisomerism : Different spatial arrangements

Geometrical : Different arrangement of the ligands

Optical: Images which cannot be superimposed $[Co(en)_3]^{3+}$

PRACTICE QUESTIONS

01. The IUPAC name for $[Pt(NH_3)_3(Br)(NO_2)(Cl)]Cl$ is

(a) triamminechlorobromonitroplatinum(IV) chloride
(b) triamminebromochloronitroplatinum(IV) chloride
(c) triaminenitrochlorobromoplatinum(IV) chloride
(d) triamminechloronitrobromoplatinum(IV) chloride

02. The IUPAC name of the complex $Ni[C_4H_7O_2N_2)_2]$, formed by the reaction between Ni^{2+} and dimethylglyoxime, is
(a) bis(methylglyoxal)nickel(II)
(b) bis(dimethylyoxime)nickel
(c) bis(2,3–butanediol dioximato)nickel(II)
(d) bis(2,3–butanedione dioximato)nickel(II)

03. Which of the following complex ions obeys Sidgwick's effective atomic number (EAN) rule?
(a) $[Fe(CN)_6]^{3-}$
(b) $[Fe(CN)_6]^{4-}$
(c) $[Cr(NH_3)_6]^{3+}$
(d) $[Ni(en)_3]^{2+}$

04. Which one of the following coordination compounds exhibits ionization isomerism?
(a) $[Cr(NH_3)_6]Cl_3$
(b) $[Cr(en)_3Cl_3]$
(c) $[Cr(en)_3]Cl_3$
(d) $[Co(NH_3)_5Br]SO_4$

05. The pair $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$ will exhibit
(a) hydrate isomerism
(b) linkage isomerism
(c) ionization isomerism
(d) coordinate isomerism

06. Which of the following will have three stereoisomeric forms?
(i) $[Cr(NO_3)_3(NH_3)_3]$ (ii) $K_3[Co(C_2O_4)_3]$
(iii) $K_3[Co(C_2O_4)_2Cl_2]$ (iv) $[Co(en)_2ClBr]$
(where en = ethylene diamine)
(a) (iv) and (iii)
(b) (iv) and (i)
(c) (iii) and (ii)
(d) (i) and (ii)

07. A coordination compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three moles of ions in an aqueous solution. The aqueous solution on treatment with an excess of $AgNO_3$ gives two moles of AgCl as a precipitate. The formula of this complex would be
(a) $[Co(NH_3)_4NO_2Cl]\ [NH_3Cl]$
(b) $[Co(NH_3)Cl][ClNO_2]$
(c) $[Co(NH_3)_5NO_2]Cl_2$
(d) $[Co(NH_3)_5][(NO_2)_2Cl_2]$

08. The hydridization states of the central atom in the complex ions $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{3+}$ and $[Ni(NH_3)_6]^{2+}$ are

(a) sp^3d^2, dsp^2 and d^4s^2 respectively
(b) all $3d^24s4p^3$
(c) all $4s4p^34d^2$
(c) sp^3d^2, dsp^3 and p^4d^2 respectively

09. Among TiF_6^{2-}, CoF_6^{3-}, $CuCl_2$ and $NiCl_4^{2-}$ (atomic numbers of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are

(a) CoF_6^{3-} and $NiCl_4^{2-}$
(b) TiF_6^{2-} and CoF_6^{3-}
(c) Cu_2Cl_2 and $NiCl_4^{2-}$
(d) TiF_6^{3-} and Cu_2Cl_2

10. Among $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$

(a) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic.
(b) $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[Ni(CO)_4]$ is paramagnetic.
(c) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2-}$ is paramagnetic.
(d) $[Ni(CO)_4]$ is diamagnetic and $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic.

11. Zeise salt, an organometallic compound, has the formula

(a) $(C_6H_6)_2Cr^+\ AlCl_4^-$
(b) $(CH_3)_2AlF$
(c) $Ni(CO)_4$
(d) $K^+[PtC_2H_4Cl_3]^-\ H_2O$

12. Which of the following mixtures is known as Zeigler–Natta catalyst?

(a) $Al(OCH_3)_3 + TiCl_4$
(b) $(C_2H_5)_3Al + TiCl_4$
(c) $[(CH_3)_2CHO]_3Al + TiCl_4$
(d) $LiCH_3 + TiCl_4$

13. Which of the following is not an organometallic compound?

(a) Ferrocene
(b) Ruthenocene
(c) Beryllium acetylacetonate
(d) bis(benzene)chromium

14. Which is not a π–bonded complex?

(a) Zeise salt
(b) Ferrocene
(c) bis(benzene) chromium
(d) Tetraethyl lead

15. Which of the following is an organometallic compound?

(a) Lithium methoxide
(b) Lithium acetate
(c) Lithium dimethylamide
(d) Methyllithium

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

(a) $[Co(NH_3)_4Cl]Cl_2.NH_3$
(b) $[Co(NH_3)_5Cl]Cl_2$
(c) $[Co(NH_3)_3Cl_3].2NH_3$
(d) $[Co(NH_3)_4Cl_2]Cl.NH_3$

17. Which of the following aquated metal ions has the highest paramagnetism?

(a) $[Cr(H_2O)_6]^{3+}$
(b) $[Fe(H_2O)_6]^{2+}$
(c) $[Cu(H_2O)_6]^{3+}$
(d) $[Zn(H_2O)_2]^{2+}$

18. Which of the following species is expected to be colourless?

(a) $[Ti(H_2O)_6]^{3+}$
(b) $[Ti(NO_3)_4]$
(c) $[Cr(NH_3)_2]^{+}$
(d) $[Fe(CN)_6]^{4-}$

19. Tollen's reagent contains

(a) $AgNO_3$
(b) AgOH
(c) $[Ag(NH_3)_2]^{+}$
(d) $[Ag(NO_3)_2]^{+}$

20. The ferric ion is detected by the formation of a Prussian blue precipitate on addition of potassium ferrocyanide solution. The formula of the prussian blue precipitate is

(a) $Fe_4^{III}[Fe^{II}(CN)_6]_3$
(b) $Fe_3^{II}[Fe^{III}(CN)_6]_4$
(c) $KFe^{III}[Fe^{II}(CN)_6]$
(d) $KFe^{II}[Fe^{III}(CN)_6]$

21. When a solution of potassium ferricyanide is added to an aqueous solution of ferrous sulphate, a deep blue colour, known as Turnbull's blue, is produced. The formula of the compound responsible for this deep blue colour is

(a) $KFe^{III}[Fe^{II}(CN)_6]$
(b) $Fe_4^{III}[Fe^{II}(CN)_6]_3$
(c) $KFe^{II}[Fe^{III}(CN)_6]$
(d) $Fe_3^{III}[Fe^{III}(CN)_6]_3$

22. The coordination number of Ag in $[Ag(NH_3)_2]Cl$ is

(a) one
(b) two
(c) three
(d) zero

23. The formation of the complex ion $[Co(NH_3)_6]^{3+}$ involves sp^3d^2 hybridization of Co^{3+}. Hence, the complex ion should possess

(a) octahedral geometry
(b) tetrahedral geometry
(c) square planar geometry
(d) tetragonal geometry

24. The compounds $[Cr(H_2O)_6Cl_3]$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ exhibit
(a) linkage isomerism
(b) geometrical isomerism
(c) ionization isomerism
(d) hydrate isomerism

25. Which of the following complex compounds exhibits cis–trans isomerism?
(a) $[PtCl_2(NH_3)_2]$
(b) $[PdCl_2BrI]$
(c) $[Pt(NH_3)(py)(Cl)(Br)]$
(d) All of these

26. $(EDTA)^{4-}$ is a ……. Ligand.
(a) Bidentate
(b) Pentadentate
(c) Tridentate
(d) Hexadentate

27. The total number of possible isomers of the compound
$[Cu^{II}(NH_3)4][Pt^{II}Cl_4]$ is
(a) 3
(b) 6
(c) 5
(d) 4

28. 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) $[Ni(CO)_4]$

29. Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is
(a) 3
(b) 6
(c) 4
(d) 5

30. Which among the following is not a π bonded organometallic compound?
(a) $K[PtCl_3(\eta^2-C_2H_4)]$
(b) $Fe(\eta^5-C_5H_5)_2$
(c) $Cr(\eta^6-C_6H_6)_2$
(d) $(CH_3)_4Sn$

31. A positive carbylamine test is given by:
a) *N*, *N*-dimethylaniline
b) 2,4-dimethylaniline
c) *N*-methyl-*o*-methylaniline
d) *p*-methyl benzylamine

32. CN^- is strong field ligand. This is due to the fact that
a) It carries negative charge
b) It is a pseudohalide
c) It can accept electrons from metal species
d) It forms high spin complexes with metal species.

33. Which of the following is not true for ligand metal complex?
    a) Highly charged ligand forms strong bond
    b) Greater the ionization potential of central metal, the stronger is the bond
    c) Larger the permanent dipole moment of ligand, the more stable is the bond
    d) Larger the ligand, the more stable is the metal-ligand bond

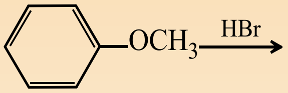
34. The nitration of nitrobenzene with fuming HNO_3 will give:
    a) TNB b) 1,3-dinitrobenzene c) Picric acid d) 1,4-dinitrobenzene

35. A ligand can also be regarded as
    a) Lewis acid b) Bronsted base c) Lewis base d) Bronsted acid

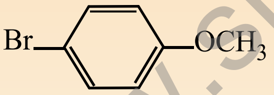
36. The correct statement with respect to the complexes $Ni(CO)_4$ and $[Ni\ (CN)_4]^{2-}$ is
    a) Nickel is in the same oxidation state in both
    b) Both have terahedral geometry
    c) Both have square planar geometry
    d) Have tetrahedral and square planar geometry respectively

37. Which one of the following has lowest value of paramagnetic behaviour?
    a) $[Cr(CN_6)_4]^{3-}$ b) $[Mn(CN)_6]^{3-}$ c) $[Fe(CN)_6]^{3-}$ d) $[Co(CN)_6]^{3-}$

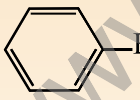
38. In the reaction;

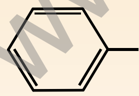


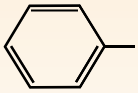
the products are:

a) 

and H_2

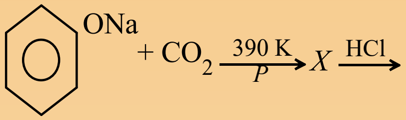
b) 
Br and CH_3Br

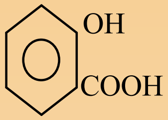
c) 
Br and CH_3OH

d) 
OH and CH_3Br

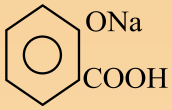
39. An octahedral complex is formed when central metal atom undergoes hybridization amongst the….orbitals.

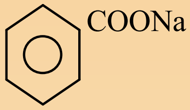
a) sp^3 b) dsp^2 c) sp^3d d) sp^3d^2

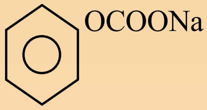
40. 

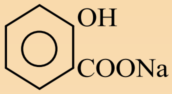


;the product X in the reaction is:

a) 

b) 

c) 

d) 

41. Biological oxidation of C_6H_6 taking place in body of dog, gives:

a) Benzoic acid b) Toluic acid c) Maleic acid d) Muconic acid

41. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in the alkaline solutions
not in acidic solutions .What is the reason for it?

a) In acidic solutions hydration protects copper ions

b) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and N
molecules are not available

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

d) Copper hydroxide is an amphoteric substance

42. Which of the following has the highest molar conductivity in solution?

a) $[Pt(NH_3)_6]Cl_4$ b) $[Pt(NH_3)_5Cl]Cl_3$ c) $[Pt(NH_3)_4Cl_2]Cl_2$ d) $[Pt(NH_3)_3Cl_3]Cl$

43. Which of the following is not *meta* directing group?

a) $—SO_3H$ b) $—NO_2$ c) $—CN$ d) $—NH_2$

44. Which of the following is an organometallic compound?

a) Lithium methoxide b) Lithium acetate
c) Lithium dimethylamine d) Methyl lithium

45. Which among the following is very strong *o*-, *p*-directing group?
a) —Cl b) —O*R* c) —NH_2 d) —NH*R*

46. The type of hybridisation in tetrahedral complexes of metal atom is
a) dsp^2 b) d^2sp c) sp^3 d) sp^2

47. The coordination number of Fe in $[Fe(CN)_6]^{4-}$ $[Fe(CN)_6]^{3-}$ and $[FeCl_4]^-$ are respectively.
a) 2, 3, 3 b) 6, 6, 4 c) 6, 3, 3 d) 6, 4, 6

48. Consider the following statements
I. Chain and position isomerism are not possible together between two isomers
II. Tautomerism is a chemical phenomenon which is catalysed by acid as well as base
III. Tautomers are always metamers
IV. Tautomers are always functional isomers
Select the correct answer by using the codes given below
a) Only III is correct b) III and IV are correct
c) I, II and III are correct d) I, II and IV are correct

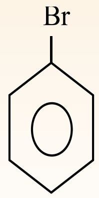
49. What is the EAN of nickel in $[Ni(CN)_4]^{2-}$?
a) 32 b) 35 c) 34 d) 36

50. Which of the following alcohols is dehydrated most readily with conc. H_2SO_4?
a) *p*-$O_2NC_6H_4CH(OH)CH_3$
b) *p*-$ClC_6H_4CH(OH)CH_3$
c) *p*-$CH_3OC_6H_4CH(OH)CH_3$
d) $C_6H_5CH(OH)CH_3$

51. The compound having tetrahedral geometry is
a) $[Ni(CN)_4]^{2-}$ b) $[Pd(CN_4)]^{2-}$ c) $[PdCl_4]^{2-}$ d) $[NiCl_4]^{2-}$

52. Identify '*Z*' in the change;

$$C_6H_5NH_2 \xrightarrow[280\text{ K}]{NaNO_2/HCl} X \xrightarrow{CuBr/HBr} Z:$$

a)


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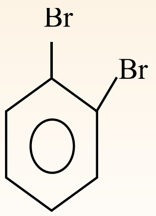

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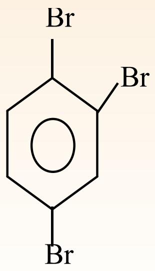

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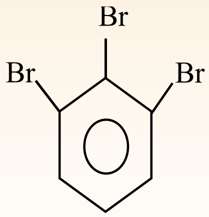


HINTS ANS SOLUTIONS

01. (a) triamminechlorobromonitroplatinum (IV) chloride

Explanation: In the IUPAC name, the ligands are listed alphabetically followed by their position and then the metal name.

02. (b) bis(dimethyl oxime)nickel

Explanation: The ligand dimethylglyoxime forms a bidentate complex with nickel.

03. (c) [Cr(NH3)6]3+

Explanation: EAN rule states that the sum of metal's valence electrons and electrons donated by ligands should be equal to the atomic number of the next noble gas. [Cr(NH3)6]3+ fits this rule.

04. (a) $[Cr(NH_3)_6]Cl_3$

Explanation: Ionization isomerism involves the interchange of ligands between the coordination sphere and the outside of it. In this case, the chloride ions can interchange with the ammonia ligands.

05. (d) coordinate isomerism

Explanation: Coordinate isomerism occurs when a ligand can bond through different atoms. In this case, NO3- can bind through N or O, resulting in coordinate isomerism.

06. (b) (iv) and (i)

Explanation: Geometrical isomers are possible for (iv) [Co(en)2ClBr], and optical isomers are possible for (i) [Cr(NO3)3(NH3)3].

07. (c) [Co(NH3)5NO2]Cl2

Explanation: The given information about the composition and the behavior with AgNO3 indicates that two moles of Cl- ions are present for each mole of the complex cation.

08. (a) sp3d2, dsp2 and d4s2 respectively

Explanation: Different central atoms can have different hybridization states depending on their surroundings and coordination number.

09. (a) Cu2Cl2 and

Explanation: Copper(II) chloride (CuCl2) is blue-green in color, while the copper(I) compound Cu2Cl2 is white.

10. (c) [Ni(CO)4] and [Ni(CN)4]2- are diamagnetic and [NiCl4]2- is paramagnetic.

Explanation: The magnetic behavior is determined by the presence of unpaired electrons. Diamagnetic compounds have all paired electrons, while paramagnetic compounds have unpaired electrons.

11. (d) K+[PtC2H4Cl3]− H2O

Explanation: Zeise's salt has a metal-carbon double bond and forms an interesting linkage isomer.

12. (b) (C2H5)3Al + TiCl4

Explanation: Zeigler-Natta catalysts are used in polymerization processes, particularly for the production of polyethylene and polypropylene.

13. (d) bis(benzene)chromium

Explanation: Organometallic compounds contain metal-carbon bonds. Bis(benzene)chromium is not an organometallic compound.

14. (d) Tetraethyl lead

Explanation: π-bonded complexes involve the interaction of metal d-orbitals with ligand π-bonds. Tetraethyl lead is not a complex.

15. (d) Methyllithium

Explanation: Organometallic compounds contain metal-carbon bonds. Methyllithium is a well-known organometallic compound.

16. (b) [Co(NH3)5Cl]Cl2

Explanation: The information about the number of ions produced and the behavior with AgNO3 points to this structure.

17. (a) [Cr(H2O)6]3+

Explanation: Higher unpaired electrons generally lead to higher paramagnetism.

18. (a) [Ti(H2O)6]3+

Explanation: The color of a complex often arises due to transitions involving d-orbitals. Ti(III) complexes are often colorless.

19. (c) [Ag(NH3)2]+

Explanation: Tollen's reagent is used to test for aldehydes. It contains diamminesilver(I) complex ion.

20. (a) [Fe4[Fe(CN)6]3]

Explanation: Prussian blue has a complex composition involving iron ions and cyanide ligands.

21. (c) [Fe(Fe(CN)6)]3

Explanation: Turnbull's blue involves the reaction between ferricyanide and ferrous ions.

22. (b) two

Explanation: Ag is bonded to two NH3 ligands.

23. (a) octahedral geometry

Explanation: Hybridization and geometry are related in coordination complexes.

24. (d) hydrate isomerism

Explanation: Hydrate isomerism involves different numbers of water molecules in the complex.

25. (a) [PtCl2(NH3)2]

Explanation: Cis-trans isomerism is possible when two ligands are the same and two are different.

26. (c) Tridentate

Explanation: A tridentate ligand forms three bonds to the metal atom.

27. (a) 3

Explanation: Isomers can be structural or stereoisomers.

28. (b)

Explanation: Ionic conductivity depends on the mobility of ions.

29. (c) 4

Explanation: Coordination number is the number of ligands bonded to the central metal atom.

30. (d)

Explanation: The listed compounds do not represent π-bonded organometallic compounds.

31 **(d)**
It is a test for primary amines. No doubt 2,4-dimethylaniline is also primary amine but it does not give test due to steric hindrance.

32 **(b)**
CN^- is strong field ligand because it is an example of pseudohalide. Pseudohalide ions are stronger coordinating ligands and they have the ability to form σ bond and π-bond.

33 **(b)**
Higher the charge and smaller the size of ligand, more stable is the complex formed

34 **(a)**
Trinitrobenzene is an explosive compound formed during nitration of C_6H_6 with fuming HNO_3.

35 **(c)**

A ligand is a species that is capable of donating an electron pair(s) to the central metal ion. The substances which are capable of donating an electron pair are called Lewis base, so a ligand is also a Lewis base.

36 **(d)**

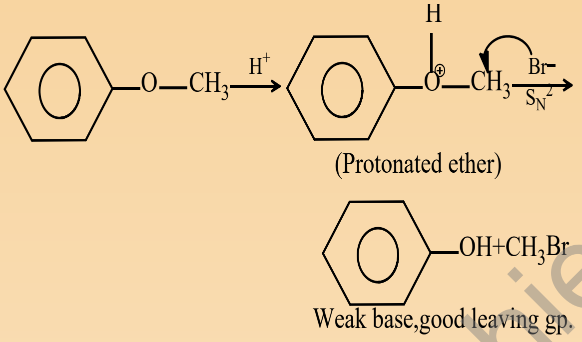
In $Ni(CO)_4$, Ni is in zero oxidation state. It has tetrahedral geometry but is diamagnetic. In $[Ni(CN)_4]^{2-}$, Ni is in +2 oxidation state. It is dsp^2 hybridised and have square planar shape. The compound is diamagnetic.

37 **(d)**

$[Co(CN)_6]^{3-}$ has d^2sp^3-hybridisation and six d-electrons are paired due to strong field ligand. Thus no unpaired electron.

38 **(d)**

HBr⟶ H++B r−

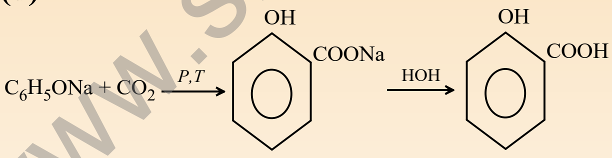


Ether reacts with acid to give protonated ether. The next step involves nucleophilic attack by halide ion with the displacement of weakly basic alcohol molecule.

39 **(d)**

Octahedral complex should have six hybridized orbitals.

40 **(d)**



Kolbe-Schmidt's reaction.

41 **(b)**

The pair of electron present with nitrogen will not be available to be donated as H^+ will consume that one.

42 **(a)**

It provides maximum number of ions (five) on ionization.

43 **(d)**

Follow Vorlander's rule.

44 **(d)**

Organometallic compounds are those in which metal is linked directly with carbon. CH_3Li, methyl lithium due to the presence of metal-carbon bond, is an organometallic

45 **(d)**

The directive influence order is:

$\mathrm{O}^- > \mathrm{N}R_2 > \mathrm{NH}R > \mathrm{NH}_2 > \mathrm{OH} > \mathrm{OCH}_3 \approx \mathrm{NHCOCH}_3 > \mathrm{CH}_3 > X$

46 **(c)**

Hybridisation	Shape
dsp^2	Square planar
sp^3	Tetrahedral
sp^2	Trigonal planar

Hence, in tetrahedral complexes metal atom is sp^3 hybridised.

47 **(b)**

The number of ligands attached to the central metal ion is called the coordination number.

So, coordination numbers of Fe in

$[\mathrm{Fe\,(CN)_6}]^{4-}$, $[\mathrm{Fe(CN)_6}]^{3-}$ and $[\mathrm{FeCl_4}]^-$ are 6, 6 and 4 respectively.

48 **(d)**

Tautomers may or may not be metamers

49 **(c)**

EAN=(Atomic number $-\mathrm{O.S} + 2 \times \mathrm{C.N.}$)

Hence, EAN of Ni in $[\mathrm{Ni(CN)_4}]^{2-} = (28 - 2 + 2 \times 4) = 34$

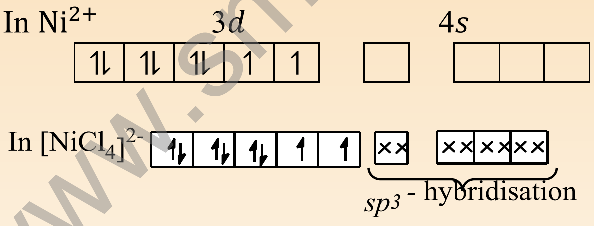
50 **(c)**

Electron repelling nature of methoxy gp. facilitate the protonation of alcohol.

51 **(d)**

$[\mathrm{Ni(Cl)_4}]^{2-}$ oxidation state of Ni is +2

So, configuration of $Ni^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8$



Thus, due to sp^3-hybridisation of Ni^{2+} in $[\mathrm{NiCl_4}]^{2-}$, the shape of $[\mathrm{NiCl_4}]^{2-}$is tetrahedra

52 **(a)**

This is Sandmeyer's reaction.