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B) LnN_2
D) LnN_3

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4. (D)
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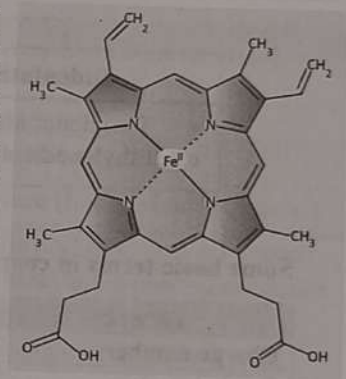
Textbook Chapter No.

09 Coordination Compounds

Subtopics

Haemoglobin

Haemoglobin is the iron-containing oxygen-transport metalloprotein in the red blood cells of vertebrates as well as the tissues of some invertebrates. Haemoglobin in the blood carries oxygen from the respiratory organs (lungs or gills) to the rest of the body (i.e. the tissues). A heme group consists of an iron (Fe) ion (charged atom) held in a heterocyclic ring, known as a porphyrin which consists of four pyrrole molecules cyclically linked together (by methine bridges) with the iron ion bound in the center. The iron ion, which is the site of oxygen binding, coordinates with the four nitrogens in the center of the ring, which all lie in one plane. The iron ion may be either in the Fe^{2+} or in the Fe^{3+} state, but ferrihaemoglobin (Fe^{3+}) cannot bind oxygen. In binding, oxygen temporarily and reversibly oxidizes Fe^{2+} to Fe^{3+} while oxygen temporarily turns into superoxide, thus iron must exist in the +2 oxidation state to bind oxygen.



Quick Review

Components of coordination compounds:

Coordination compound
e.g. $K_4[Fe(CN)_6]$

Central metal atom/ion	Ligand	Coordination sphere	Complex ion	Counter ion
e.g. Fe^{2+} in $K_4[Fe(CN)_6]$	e.g. CN^- in $K_4[Fe(CN)_6]$	e.g. $[Fe(CN)_6]^{4-}$ in $K_4[Fe(CN)_6]$	e.g. $[Fe(CN)_6]^{4-}$ in $K_4[Fe(CN)_6]$	e.g. K^+ in $K_4[Fe(CN)_6]$

➢ **Types of Ligands:**

Ligands
- The species surrounding the central metal atom/ion

Monodentate
- Single donor atom

e.g. Cl^-, OH^-, CN^-

Polydentate
- Two or more donor atoms

Bidentate
- Two donor atoms

e.g. Ethylenediamine, $C_2O_4^{2-}$

Hexadentate
- Six donor atoms

e.g. $(EDTA)^{4-}$

Ambidentate
- Use any one of two donor atoms to form coordinate bond

e.g. $M \leftarrow SCN^-$ or $M \leftarrow NCS^-$

➢ **Some basic terms in coordination chemistry:**

Term	Description
Charge number	The net charge residing on the complex. **e.g.** $[Fe(CN)_6]^{3-}$ has charge number –3.
Oxidation state	The charge carried by metal ion is its oxidation state. E.g. In $[Fe(CN)_6]^{4-}$ Fe has oxidation state +2.
Coordination number	The number of ligand donar atoms directly attached to central metal ion or number of electron pairs involved in the coordinate bond is called coordination number. E.g. $[Co(NH_3)_4Cl_2]^+$ has coordination number 6.

Combination of two or more stable compounds in stoichiometric ratio

Double salts

A double salt dissociates in water completely into simple ions.

e.g. Mohr's salt; $[FeSO_4.(NH_4)_2SO_4.6H_2O]$

Carnalite; $(KCl.\ MgCl_2.\ 6H_2O)$

Coordination compounds

A coordination complex dissociates in water with atleast one complex ion.

e.g. Potassium ferrocyanide $K_4[Fe(CN)_6]$

➢ **Types of coordination complexs:**

On the basis of donar atoms

Homoleptic complexes

Metal atom or ion is attached to one kind of donor atoms or groups.

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

Hetroleptic complexes

Metal atom or ion is attached to more than one kind of donor atoms or groups.

e.g. $[Co(NH_3)_4Cl_2]^+$

On the basis of charge on complex ion

Cationic complexes
A coordination compound having a positively charged coordination sphere
e.g. $[Zn(NH_3)_4]^{2+}$

Neutral complexes
A coordination compound having negatively charged coordination sphere
e.g. $[Fe(CN)_6]^{3-}$

Anionic complexes
A coordination complex which does not possess cationic or anionic sphere
e.g. $[Ni(CO)_4]$

Names of common ligands in coordination compounds:

Anionic ligand	IUPAC name	Anionic ligand	IUPAC name
Br^-, Bromide	Bromo	CO_3^{2-}, Carbonate	Carbonato
Cl^-, Chloride	Chloro	OH^-, Hydroxide	Hydroxo
F^-, Fluoride	Fluoro	$C_2O_4^{2-}$, Oxalate	Oxalato
I^-, Iodide	Iodo	NO_2^-, Nitrite	Nitro (For N - bonded ligand)
CN^-, Cyanide	Cyano	ONO^-, Nitrite	Nitrito(For O-bonded ligand)
SO_4^{2-}, Sulphate	Sulphato	SCN^-, Thiocyanate	Thiocyanato (For ligand donor atom S)
NO_3^-, Nitro	Nitrato	NCS^-, Thiocyanate	Isothiocyanato (For ligand donor atom N)
Neutral ligand	IUPAC name	Neutral ligand	IUPAC name
NH_3, Ammonia	Ammine	H_2O, water	Aqua
CO, Carbon monoxide	Carbonyl	en, Ethylene diamine	Ethylenediamine

IUPAC names of metals in anionic complexes:

Metal	IUPAC name	Metal	IUPAC name
Aluminium, Al	Aluminate	Chromium, Cr	Chromate
Cobalt, Co	Cobaltate	Copper, Cu	Cuprate
Gold, Au	Aurate	Iron, Fe	Ferrate
Manganese, Mn	Manganate	Nickel, Ni	Nickelate
Platinum, Pt	Platinate	Zinc, Zn	Zincate

IUPAC names of some complexes:

Complex	IUPAC name
i. Anionic complexes:	
a. $[Ni(CN)_4]^{2-}$	Tetracyanonickelate(II) ion
b. $[Co(C_2O_4)_3]^{3-}$	Trioxalatocobaltate(III) ion
c. $[Fe(CN)_6]^{4-}$	Hexacyanoferrate(II) ion
ii. Compounds containing complex anions and metal cations:	
a. $Na_3[Co(NO_2)_6]$	Sodium hexanitrocobaltate(III)
b. $K_3[Al(C_2O_4)_3]$	Potasium trioxalatoaluminate(III)
c. $Na_3[AlF_6]$	Sodium hexafluoroaluminate(III)
iii. Cationic complexes:	
a. $Cu(NH_3)_4^{2+}$	Tetraamminecopper(II) ion
b. $[Fe(H_2O)_5(NCS)]^{2+}$	Pentaaquaisothiocyanatoiron(III) ion
c. $[Pt(en)_2(SCN)_2]^{2+}$	Bis(ethylenediamine)dithiocyanatoplatinum(IV)

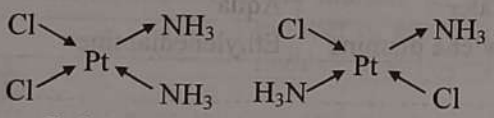
iv. Compounds containing complex cations and anion:	
a. $[PtBr_2(NH_3)_4]Br_2$	Tetraamminedibromoplatinum(IV) bromide
b. $[Co(NH_3)_5CO_3]Cl$	Pentaamminecarbonatocobalt(III) chloride
c. $[Co(H_2O)(NH_3)_5]I_3$	Pentaammineaquacobalt(III) iodide
v. Neutral complexes:	
a. $[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt(III)
b. $Fe(CO)_5$	Pentacarbonyliron(0)
c. $[Rh(NH_3)_3(SCN)_3]$	Triamminetrithiocyanatorhodium(III)

➢ **Isomerism in coordination compounds:**

Isomerism
(Same molecular formula but different physical or chemical properties)

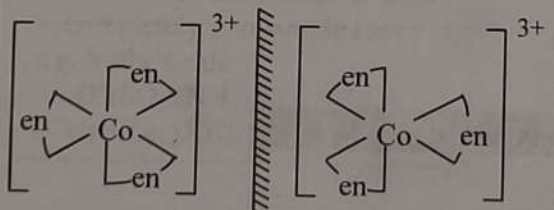
Stereoisomerism
- Difference in the spatial arrangement of atoms or groups of atoms around the central metal atom/ion.

Geometrical isomerism
(cis-trans isomerism)
e.g. $[Pt(NH_3)_2Cl_2]$



Cis isomer Trans isomer

Optical isomerism
(non-superimposable mirror images)
(enantiomers)
e.g. $[Co(en)_3]^{3+}$



d-form mirror *l*-form

Structural isomerism
- Same molecular formula, but different structural arrangement of ligands around central metal atom/ion.

Ionisation isomerism
- exchange of ions inside and outside the coordination sphere.

e.g. $Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

Linkage isomerism
- ambidentate ligands attached through different donor atoms.

e.g. $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5 ONO]Cl_2$

Coordination isomerism
- different complex ions with same molecular formula and interchange of ligands between cations and anions.

e.g. $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Co(CN)_6][Cr(NH_3)_6]$

Solvate isomerism
- exchange of solvent molecules inside and outside the coordination sphere. If solvent is H_2O, isomers are called hydrate isomers.

e.g. $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and

➢ **Irving William order of stability:**

For same ligands, the stability of complexes formed by M^{2+} ions follows the order:
$Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Cd^{2+}$

Structure of complexes based on valence bond theory:

Complex	Oxidation state of metal	Outer electronic configuration of metal	Hybridisation	Geometry	No. of unpaired electrons	Magnetic property
$[Ni(CN)_4]^{2-}$	+2	$3d^8$	dsp^2	Square planar	0	Diamagnetic
$[Co(NH_3)_6]^{3+}$	+3	$3d^6$	d^2sp^3	Octahedral	0	Diamagnetic
$[NiCl_4]^{2-}$	+2	$3d^8$	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{2-}$	+2	$3d^8$	dsp^2	Square planar	0	Diamagnetic
$[CoF_6]^{3-}$	+3	$3d^6$	sp^3d^2	Octahedral	4	Paramagnetic
$[ZnCl_4]^{2-}$	+2	$3d^{10}$	sp^3	Tetrahedral	0	Diamagnetic
$[Co(H_2O)_6]^{2+}$	+2	$3d^7$	sp^3d^2	Octahedral	3	Paramagnetic
$[Pt(CN)_4]^{2-}$	+2	$3d^8$	dsp^2	Square planner	0	Diamagnetic
$[CoCl_4]^{2-}$	+2	$3d^7$	sp^3	Tetrahedral	3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$	+3	$3d^3$	d^2sp^3	Octahedral	3	Paramagnetic
$[Ni(NH_3)_6]^{3+}$	+3	$3d^7$	sp^3d^2	Octahedral	1	Paramagnetic
$[VCl_4]^-$	+3	$3d^2$	sp^3	Tetrahedral	2	Paramagnetic

Spectrochemical series: Increasing order of ligand field:

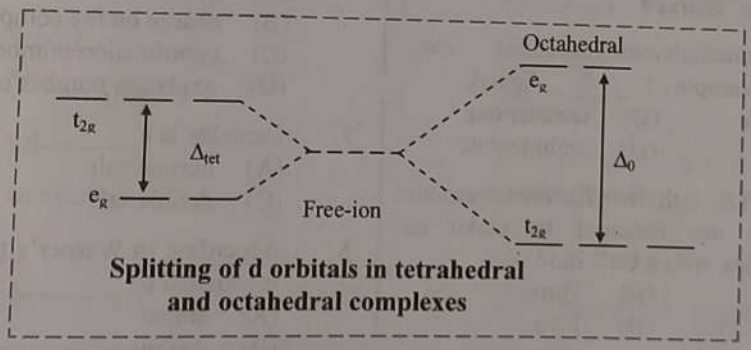
$I^- < Br^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA < NH_3 < en < CN^- < CO$

Types of coordination complexes

High spin complexes
Crystal field energy greater than pairing energy ($\Delta_0 > P$).

Low spin complexes
Crystal field energy is less than pairing energy ($\Delta_0 < P$).

Crystal field splitting in tetrahedral and octahedral complexes:



Splitting of d orbitals in tetrahedral and octahedral complexes

Formulae

1. **Effective atomic number (EAN):**

$EAN = Z - X + Y$

where,

Z = Atomic number of metal

X = Number of electrons lost by metal to form the ion

Y = Number of electrons donated by ligands