KSQUARE CAREER INSTITUTE

COORDINATION COMPOUNDS

Class 12 Chemistry • Introduction, Terms & Ligands • NEET / JEE Notes

Scan to get all notes

Topics Covered

1. Introduction — salts, addition compounds: double salts vs complex salts
2. Examples — alums, Mohr's salt, carnallite; $[Cu(NH_3)_4]SO_4$, $K_4[Fe(CN)_6]$
3. Representation of coordination compounds; coordination & ionisation sphere
4. Important terms — coordination entity, CMI, homoleptic/heteroleptic, coordination polyhedron
5. Ligands — denticity, classification, ambidentate, chelating, flexidentate; names of important ligands
6. Added: coordination number, oxidation state, IUPAC naming, Werner's theory, isomerism, VBT & CFT overview, practice MCQs

NEET Point / PYQ Alert

"Even the most stable elements need the right partners to unlock their true potential — just like us."

Revise the **Chemical Bonding** chapter before this one — ligands donate lone pairs through **coordinate bonds**.

INTRODUCTION

- **Salt** — formed by an acid and a base; gives identification tests of its ions on dissolving in water (NaOH + HCl → NaCl + H_2O).
- **Addition compound** — made of two or more stable salts in a **fixed stoichiometric ratio**, obtained by **crystallisation**: salt A + salt B + H_2O —Δ→ crystals of addition compound.
- Addition compounds are of two types: **double salts** and **complex salts (coordination compounds)**.

Double Salt vs Complex Salt

Double salt	Complex salt (coordination compound)
Definite identity in solid, but **lose their identity in water**	Retain their identity in the **solid as well as in aqueous solution**
Completely dissociate into constituent ions	Do **not** completely ionise
Aqueous solution gives **positive tests for all ions**	Do **not** give positive tests for all ions
Individual ions **retain** their identity	Individual ions **lose** their identity

Examples of Double Salts

Double salt	Formula
Alums (general formula)	$X_2SO_4 \cdot M_2(SO_4)_3 \cdot 24H_2O$ (X = monovalent cation X^+, M = trivalent cation M^{3+})
Potash alum (X = K, M = Al)	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Chrome alum (X = K, M = Cr)	$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
Ferric alum (X = NH_4^+, M = Fe^{3+})	$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$
Mohr's salt (ferrous ammonium sulphate, FAS)	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$

Class demonstration

Potash alum (aq) contains K^+, SO_4^{2-} and Al^{3+}: + $BaCl_2$ → **white ppt of $BaSO_4$** (test for SO_4^{2-}); + NaOH dropwise → **white gelatinous $Al(OH)_3$** (test for Al^{3+}); + $HClO_4$ → $KClO_4$ (test for K^+) — all ions are detected.

$CuSO_4$ (aq, blue) + excess NH_3 → dark blue $[Cu(NH_3)_4]SO_4$: + $BaCl_2$ → white ppt (SO_4^{2-} is free), but the **test for Cu^{2+} is negative** — Cu^{2+} is locked in the complex.

Examples of Complex Salts

- $[Cu(NH_3)_4]SO_4$ (or $CuSO_4 \cdot 4NH_3$); $K_4[Fe(CN)_6]$ — learn all NCERT examples.

REPRESENTATION OF A COORDINATION COMPOUND

Type	Description	Example
$[ML_n]^o$	**Neutral complex** — no counter ion (generally water-insoluble)	$[Ni(CO)_4]$, $[Fe(CO)_5]$
$X^+[ML_n]^-$	Counter **cation** + complex **anion**	$K_4[Fe(CN)_6]$
$[ML_n]^+X^-$	Complex **cation** + counter **anion**	$[Cu(NH_3)_4]SO_4$
$[ML_n]^+[ML_n]^-$	Complex cation + complex anion	$[Ag(NH_3)_2][Ag(CN)_2]$

Part of $K_4[Fe(CN)_6]$	Name / role
Fe^{2+}	**Central metal ion (CMI)** — electron-pair **acceptor** (**Lewis acid**)
CN^-	**Ligands** — electron-pair **donors** (**Lewis bases**)
$[Fe(CN)_6]^{4-}$	**Coordination sphere** (inside the square bracket)
K^+	**Ionisation sphere** (counter ions outside the bracket)

- Ligand donates a lone pair into a **vacant orbital** of the metal ⇒ **σ coordinate bond** (M ← :L).

IMPORTANT TERMS

Term	Definition	Example
Coordination entity	CMI/CMA bonded to a fixed number of ions or molecules (ligands), enclosed in a square bracket = coordination sphere	$[CoCl_3(NH_3)_3]$, $[Ni(CO)_4]$
Central atom / ion	Lone-pair acceptor — Lewis acid	Fe^{2+} in $[Fe(CN)_6]^{4-}$
Homoleptic complex	CMI bound to **only one kind** of ligand	$K_4[Fe(CN)_6]$, $[Ni(CO)_4]$
Heteroleptic complex	CMI bound to **more than one kind** of ligand	$[Pt(NH_3)_4Cl_2]Cl_2$, $[Fe(H_2O)_5NO]SO_4$
Coordination polyhedron	Spatial arrangement of the ligand atoms around the CMI ("dabbe ki geometry") — linear, trigonal planar, tetrahedral, square planar, trigonal bipyramidal, **octahedral**	$[ML_n]$ with 6 ligands → octahedral

LIGANDS

Ligand & denticity

Ligands — molecules/ions capable of **donating electron pairs** to the CMI (M ← :L).

Denticity — number of electron pairs a ligand can donate to the metal **simultaneously** = number of σ coordinate bonds formed by one unit of the ligand.

Classification of Ligands

Basis	Types
Charge	Anionic (Cl^-, CN^-), neutral (H_2O, NH_3, CO), cationic (NO^+)
Denticity	Monodentate (d = 1), bidentate/didentate (d = 2), polydentate (d > 2: tri-, tetra-, penta-, hexa-)
Electron donation / acceptance	**Classical** — only donate (M ← :L); **non-classical (π-acceptor)** — donate σ and **accept** π back-bonding (e.g. CO)

NEET Point / PYQ Alert

Trick: if a ligand has only **2 or 3 atoms in total, it is always monodentate** (d = 1) — e.g. CN^-, OH^-, NO_2^-, SCN^-.

Chelation needs a stable ring — **5- or 6-membered rings** are stable; a 3- or 4-membered ring is unstable, so such ligands act as monodentate.

▸ Ambidentate, Chelating & Flexidentate Ligands

Type	Meaning	Examples
Ambidentate	More than one donor atom, but **not all functional simultaneously** (binding would give an unstable 3-membered ring, so d = 1)	CN^- (M ← CN cyanido / M ← NC isocyanido), NO_2^-/ONO^-, SCN^-/NCS^-
Chelating	Denticity ≥ 2; forms a **ring** with the CMI (chelate)	Ethylenediamine (en, d = 2, 5-membered ring), oxalate (d = 2), $EDTA^{4-}$ (d = 6)
Flexidentate	Can show **variable denticity**	CO_3^{2-} (d = 1, 2), SO_4^{2-} (d = 1, 2), EDTA (d = 2, 3, 4, 5, 6; common d = 6)

- **Oxalate** ($C_2O_4^{2-}$, from oxalic acid HOOC–COOH by losing $2H^+$): both donor atoms are O ⇒ **symmetrical bidentate**, forms a **5-membered ring**.

▸ Names of Important Ligands

Anionic ligand (suffix 'o')	Name	Anionic ligand	Name
CO_3^{2-}	Carbonato	Cl^-	Chlorido
SO_4^{2-}	Sulphato	Br^-	Bromido
OH^-	Hydroxido	NH_2^-	Amido
O^{2-}	Oxido	NH^{2-}	Imido
O_2^-	Superoxido	S^{2-}	Sulphido
O_2^{2-}	Peroxido	SO_3^{2-}	Sulphito
N_3^-	Azido	$C_2O_4^{2-}$	Oxalato
N^{3-}	Nitrido	F^-	Fluorido

Ambidentate ligand (donor atom)	Name
CN^- (through C)	Cyanido (cyanido-C)
NC^- (through N)	Isocyanido (cyanido-N)
NO_2^- (through N)	Nitro / nitrito-N
ONO^- (through O)	Nitrito-O
SCN^- (through S)	Thiocyanato-S (thiocyanido)
NCS^- (through N)	Thiocyanato-N (isothiocyanato)
OCN^- (through O)	Cyanato-O
NCO^- (through N)	Isocyanato (cyanato-N)

*Note: the PDF table lists CN^- with the alternative name "cyanato-N" and SCN^- as "thiocyanato-N" — the correct names are **cyanido-C** for CN^- (C-bonded) and **thiocyanato-S** for SCN^- (S-bonded).*

Neutral ligand	Name	Neutral / cationic ligand	Name
H_2O	Aqua	CO	Carbonyl
NH_3	Ammine	NO	Nitrosyl
en	Ethane-1,2-diamine	NO^+	Nitrosonium
py	Pyridine	PPh_3	Triphenylphosphine

COORDINATION NUMBER & OXIDATION STATE (ADDITIONAL TOPIC)

- **Coordination number (CN)** = number of ligand donor atoms directly bonded to the CMI = Σ (no. of ligands × denticity). e.g. $[Co(en)_3]^{3+}$: CN = 3 × 2 = **6**; $[Ni(CO)_4]$: CN = 4.
- **Oxidation state** of CMI: charge on entity = x + Σ (ligand charges). e.g. $K_4[Fe(CN)_6]$: x – 6 = –4 ⇒ **Fe = +2**; $[Cu(NH_3)_4]^{2+}$: Cu = +2.

IUPAC NOMENCLATURE — RULES (ADDITIONAL TOPIC)

1. Name the **cation first**, then the anion (as in simple salts).
2. Inside the coordination entity, **ligands are named first in alphabetical order**, then the metal.
3. Prefixes di-, tri-, tetra- for simple ligands; bis-, tris-, tetrakis- for complex ligand names (e.g. bis(ethane-1,2-diamine)); prefixes are ignored in alphabetisation.
4. Oxidation state of metal in **Roman numerals** in parentheses.
5. If the complex is an **anion**, the metal name ends in **'-ate'** (ferrate, cuprate, argentate, plumbate, stannate, aurate).
6. Neutral complex is named as one word.

Compound	IUPAC name
$K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate(II)
$[Cu(NH_3)_4]SO_4$	Tetraamminecopper(II) sulphate
$[Co(NH_3)_5Cl]Cl_2$	Pentaamminechloridocobalt(III) chloride
$[Ni(CO)_4]$	Tetracarbonylnickel(0)
$[Pt(NH_3)_2Cl_2]$	Diamminedichloridoplatinum(II)
$K_3[Al(C_2O_4)_3]$	Potassium trioxalatoaluminate(III)

WERNER'S THEORY, ISOMERISM & BONDING — OVERVIEW (ADDITIONAL TOPIC)

Topic	Key points
Werner's theory	**Primary valency** = oxidation state (ionisable, satisfied by anions); **secondary valency** = coordination number (non-ionisable, directional — fixes geometry). E.g. $CoCl_3 \cdot 6NH_3$ gives 3 AgCl; $CoCl_3 \cdot 4NH_3$ gives 1 AgCl

Topic	Key points
Structural isomerism	Ionisation, hydrate (solvate), linkage (ambidentate ligands: $–NO_2$ / –ONO), coordination isomerism
Stereoisomerism	Geometrical (cis/trans in square planar MA_2B_2 & octahedral MA_4B_2; fac/mer in MA_3B_3) and optical (e.g. $[Co(en)_3]^{3+}$)
VBT	Hybridisation: sp^3 (tetrahedral), dsp^2 (square planar), d^2sp^3 inner orbital / sp^3d^2 outer orbital (octahedral)
CFT	Ligands split d-orbitals (octahedral: t_{2g} lower, e_g higher, gap Δ_o); spectrochemical series: $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< CN^- <$ CO (weak → strong field)

PRACTICE MCQS

Q1. Which of the following is a double salt?

(a) $K_4[Fe(CN)_6]$
(b) $FeSO_4·(NH_4)_2SO_4·6H_2O$
(c) $[Cu(NH_3)_4]SO_4$
(d) $[Ni(CO)_4]$

Answer: (b) — Mohr's salt.

Q2. An aqueous solution of $[Cu(NH_3)_4]SO_4$ gives a positive test for

(a) Cu^{2+} only
(b) SO_4^{2-} only
(c) both Cu^{2+} and SO_4^{2-}
(d) NH_3

Answer: (b)

Q3. In $K_4[Fe(CN)_6]$, the ionisation sphere contains

(a) Fe^{2+}
(b) CN^-
(c) K^+
(d) $[Fe(CN)_6]^{4-}$

Answer: (c)

Q4. Which of the following is a heteroleptic complex?

(a) $[Ni(CO)_4]$
(b) $K_4[Fe(CN)_6]$
(c) $[Pt(NH_3)_4Cl_2]Cl_2$
(d) $[Co(NH_3)_6]^{3+}$

Answer: (c)

Q5. Which ligand is ambidentate?

(a) NH_3
(b) H_2O
(c) SCN^-
(d) en

Answer: (c)

Q6. The denticity of $EDTA^{4-}$ (commonly) is

(a) 2
(b) 4
(c) 6
(d) 5

Answer: (c) — It is flexidentate (2 to 6).

Q7. Ethylenediamine forms a chelate ring of size

(a) 3
(b) 4
(c) 5
(d) 6

Answer: (c)

Q8. The oxidation state and coordination number of Fe in $K_4[Fe(CN)_6]$ are

(a) +3, 6
(b) +2, 6
(c) +2, 4
(d) +4, 6

Answer: (b)

Q9. The central metal ion in a coordination compound acts as a

(a) Lewis base
(b) Lewis acid
(c) Brønsted acid
(d) Reducing agent

Answer: (b)

QUICK REVISION

- Double salt: loses identity in water, all ion tests positive (alums, Mohr's salt, carnallite). Complex salt: retains identity, not all ion tests positive.
- Alum: $X_2SO_4 \cdot M_2(SO_4)_3 \cdot 24H_2O$; Mohr's salt: $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$; carnallite: $KCl \cdot MgCl_2 \cdot 6H_2O$.
- CMI = Lewis acid (acceptor); ligand = Lewis base (donor); [ ] = coordination sphere; outside = ionisation sphere.
- Homoleptic — one kind of ligand; heteroleptic — more than one kind; coordination polyhedron = geometry.
- Denticity: mono (1), bi (2), poly (> 2); ambidentate (CN^-, NO_2^-, SCN^-); chelating (en, ox, EDTA); flexidentate (CO_3^{2-}, SO_4^{2-}, EDTA).
- Trick: ligand with only 2–3 atoms is always monodentate; 5/6-membered chelate rings are stable.

Notes revise 2 times — revise Chemical Bonding too!