FREE NOTES · NCERT + JEE/NEET LEVEL

Coordination Compounds

Werner's theory, key terms, ligands and denticity, IUPAC naming and formulas, isomerism, valence bond theory, crystal field theory, colour and magnetism, metal carbonyls and uses.

01 Werner's theory
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01 Werner's theory

- A metal shows two kinds of valency: **primary** (ionisable, = oxidation state, satisfied by negative ions) and **secondary** (non-ionisable, = coordination number, satisfied by ligands).
- Secondary valencies are directed in space ⇒ definite geometry (6 ⇒ octahedral, 4 ⇒ tetrahedral or square planar).
- Written as $[Co(NH_3)_6]Cl_3$: inside the bracket = coordination sphere; outside = counter ions (ionisable).

Compound	Formula	AgCl precipitated per mol
$CoCl_3 \cdot 6NH_3$ (yellow)	$[Co(NH_3)_6]Cl_3$	3
$CoCl_3 \cdot 5NH_3$ (purple)	$[CoCl(NH_3)_5]Cl_2$	2
$CoCl_3 \cdot 4NH_3$ (green/violet)	$[CoCl_2(NH_3)_4]Cl$	1

Double salt (Mohr's salt, potash alum) fully breaks into simple ions in water; a **complex** keeps its complex ion.

02 Key terms & ligands

- **Central atom/ion:** Lewis acid that accepts electron pairs (Ni in $[NiCl_2(H_2O)_4]$).
- **Ligand:** Lewis base donating electron pairs. **Donor atom** = atom actually bonded.
- **Coordination number** = number of σ bonds from ligands to the metal.
- **Homoleptic** (one type of ligand, $[Co(NH_3)_6]^{3+}$) vs **heteroleptic** ($[Co(NH_3)_4Cl_2]^{+}$).

Type	Examples
Unidentate	Cl^-, H_2O, NH_3, CN^-, CO
Bidentate	en ($H_2NCH_2CH_2NH_2$), oxalate $C_2O_4^{2-}$ (ox)
Hexadentate	$EDTA^{4-}$ (2 N + 4 O)
Ambidentate (two possible donor atoms)	NO_2^- (nitro N / nitrito O), SCN^- (thiocyanato S / isothiocyanato N), CN^-

CHELATE

A polydentate ligand forms a ring with the metal ⇒ **chelate**, more stable than similar complexes with unidentate ligands (chelate effect). EDTA is used to remove Pb poisoning and to estimate hardness of water (Ca^{2+}, Mg^{2+}).

03 IUPAC naming & formulas

1. Cation first, then anion.
2. Inside the sphere: ligands in **alphabetical order** first, then metal.
3. Anionic ligands end in -o (chlorido, cyanido, hydroxido, oxalato); neutral keep names except **aqua** (H_2O), **ammine** (NH_3), **carbonyl** (CO), nitrosyl (NO).
4. Prefixes di, tri, tetra (bis, tris for complex ligand names like en); prefixes are ignored in alphabetical order.
5. Oxidation state of the metal in Roman numerals in brackets.
6. Anionic complex: metal name ends in **-ate** (cobaltate, ferrate, cuprate, argentate, plumbate).

Formula	Name
$[Cr(NH_3)_3(H_2O)_3]Cl_3$	triamminetriaquachromium(III) chloride
$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethane-1,2-diamine)cobalt(III) sulphate
$K_3[Fe(CN)_6]$	potassium hexacyanidoferrate(III)
$[Ag(NH_3)_2][Ag(CN)_2]$	diamminesilver(I) dicyanidoargentate(I)
$[Pt(NH_3)_2Cl(NO_2)]$	diamminechloridonitrito-N-platinum(II)

04 Isomerism

Type	What changes	Example
Geometrical (cis/trans)	Position of ligands	$[Pt(NH_3)_2Cl_2]$ square planar; $[Co(NH_3)_4Cl_2]^+$ octahedral; fac/mer in $[Co(NH_3)_3(NO_2)_3]$
Optical	Non-superimposable mirror images	$[Co(en)_3]^{3+}$; cis-$[PtCl_2(en)_2]^{2+}$ (trans is not optically active)
Linkage	Ambidentate ligand's donor atom	$[Co(NH_3)_5(NO_2)]Cl_2$ vs $[Co(NH_3)_5(ONO)]Cl_2$
Coordination	Ligands swap between cation and anion complex	$[Co(NH_3)_6][Cr(CN)_6]$ vs $[Cr(NH_3)_6][Co(CN)_6]$
Ionisation	Counter ion and ligand swap	$[Co(NH_3)_5(SO_4)]Br$ vs $[Co(NH_3)_5Br]SO_4$
Solvate (hydrate)	Water inside vs outside	$[Cr(H_2O)_6]Cl_3$ (violet) vs $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ (green)

Tetrahedral complexes don't show geometrical isomerism.

05 Valence bond theory (VBT)

CN	Hybridisation	Shape	Example
4	sp^3	Tetrahedral	$[NiCl_4]^{2-}$ (paramagnetic, 2 unpaired), $[Ni(CO)_4]$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$ (diamagnetic)
6	d^2sp^3 (inner orbital, low spin)	Octahedral	$[Co(NH_3)_6]^{3+}$ diamagnetic, $[Fe(CN)_6]^{3-}$
6	sp^3d^2 (outer orbital, high spin)	Octahedral	$[CoF_6]^{3-}$ paramagnetic (4 unpaired)

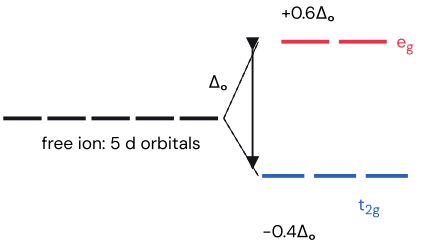
LIMITS OF VBT

Can't explain colour, can't say why some ligands are strong or weak, doesn't explain thermodynamic/kinetic stability quantitatively.

06 Crystal field theory (CFT)

Ligands are point charges. In an octahedral field the five d orbitals split: **e_g** ($d_{x^2-y^2}$, d_{z^2}, point at ligands, higher) and **t_{2g}** (d_{xy}, d_{yz}, d_{xz}, lower). The gap is Δ_o.

- Δ_o > P (pairing energy) ⇒ strong field ⇒ electrons pair in t_{2g} ⇒ **low spin**.
- Δ_o < P ⇒ weak field ⇒ **high spin**.
- Tetrahedral: $\Delta_t = (4/9)\Delta_o$, always high spin; order reversed (e lower, t_2 higher).



Splitting of d orbitals in an octahedral field

SPECTROCHEMICAL SERIES (WEAK → STRONG)

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$$

CFSE (octahedral) = $(-0.4\, n_{t2g} + 0.6\, n_{eg})\, \Delta_o$ + pairing energies.

07 Colour, metal carbonyls & uses

Colour: an electron jumps $t_{2g} \rightarrow e_g$ absorbing light of energy Δ; we see the complementary colour. $[Ti(H_2O)_6]^{3+}$ absorbs green-yellow ⇒ looks violet. Anhydrous $CuSO_4$ is white (no ligand field from water); without ligands there is no splitting.

Metal carbonyls: CO forms a σ bond (C → M) and a **π back bond** (filled metal d → empty π* of CO). This synergic bonding strengthens M–C and weakens C≡O. $[Ni(CO)_4]$ tetrahedral, $[Fe(CO)_5]$ trigonal bipyramidal, $[Cr(CO)_6]$ octahedral.

USES

- Hardness of water: titration with Na_2EDTA.
- Metallurgy: Ag and Au extracted as $[Ag(CN)_2]^-$, $[Au(CN)_2]^-$; Ni purified via $Ni(CO)_4$ (Mond process).
- Biology: chlorophyll (Mg), haemoglobin (Fe), vitamin B_{12} (Co).
- Medicine: cis-platin $[Pt(NH_3)_2Cl_2]$ against cancer; EDTA for lead poisoning.
- Analysis: Ni^{2+} with dimethylglyoxime gives a red ppt; photography uses $[Ag(S_2O_3)_2]^{3-}$.

08 JEE Extra + Tricks

JEE LEVEL

- EAN rule: EAN = Z − (oxidation state) + 2 × (coordination number); 36 (Kr) for $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$.
- Spectrochemical series (weak → strong): $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< CN^- <$ CO. Strong field ⇒ pairing ⇒ low spin (inner orbital d^2sp^3).
- $\Delta_t = (4/9)\Delta_o$, so tetrahedral complexes are almost always high spin.
- Isomer count: $[MA_4B_2]$ 2 geometrical (cis, trans); $[MA_3B_3]$ fac and mer; $[M(AA)_2B_2]$ cis is optically active.
- CFSE (octahedral) = $(-0.4\ n_{t2g} + 0.6\ n_{eg})\Delta_o$ + pairing energy.
- Applications: EDTA (hexadentate) in hardness estimation, cisplatin in cancer, Wilkinson's catalyst in hydrogenation.

09 Solved questions

Q1. Find the oxidation state, CN and number of unpaired electrons in $[Fe(CN)_6]^{4-}$.

x − 6 = −4 ⇒ Fe(+2), d^6. CN = 6. CN^- is strong field ⇒ t_{2g}^6 ⇒ **0 unpaired**, diamagnetic, d^2sp^3.

Q2. $[NiCl_4]^{2-}$ is paramagnetic but $[Ni(CN)_4]^{2-}$ is diamagnetic. Why?

Ni^{2+} is d^8. Cl^- is weak: no pairing, sp^3, 2 unpaired. CN^- is strong: forces pairing, dsp^2, square planar, 0 unpaired.

Q3. Write the formula: tetraamminediaquacobalt(III) chloride.

$[Co(NH_3)_4(H_2O)_2]Cl_3$.

Q4. Number of geometrical isomers of $[Pt(NH_3)_2Cl_2]$?

2 (cis and trans).

10 Common mistakes

- Ordering ligands by charge instead of alphabetically when naming.
- Forgetting "-ate" in anionic complexes ($K_4[Fe(CN)_6]$ is ferrate, not iron).
- Counting en as one bond: it is bidentate, so $[Co(en)_3]^{3+}$ has CN 6.
- Saying tetrahedral complexes show cis-trans isomerism.
- Assuming every Ni(II) complex is tetrahedral.

11 Practice questions

1. Name $[Co(NH_3)_5Cl]Cl_2$.
2. What type of isomerism do $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$ show?
3. Hybridisation of $[CoF_6]^{3-}$?
4. Why is CO a strong field ligand?
5. Denticity of EDTA?

ANSWERS

1) pentaamminechloridocobalt(III) chloride · 2) Linkage · 3) sp^3d^2 (outer orbital, high spin) · 4) π back bonding increases splitting · 5) 6

12 Quick revision: 5 minutes before the exam

WERNER & NAMING

- Primary = OS, secondary = CN.
- Ligands alphabetical, then metal(OS).
- Anionic complex: -ate.

VBT

- sp^3 tetrahedral, dsp^2 square planar.
- d^2sp^3 inner (low spin), sp^3d^2 outer.

CFT

- Octahedral: t_{2g} low, e_g high.
- $\Delta > P \Rightarrow$ low spin.
- $\Delta_t = 4/9\ \Delta_o$.
- I^- weakest … CO strongest.

ISOMERS & USES

- Linkage: NO_2^-/ONO^-, SCN^-.
- Cis-platin: cancer.
- EDTA: hardness, Pb poisoning.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.