

Chapter 5 · Coordination Compounds

CBSE Class 12 Chemistry (043) · Inorganic · Unit 5 = 7 marks · Ultimate Revision Sheet

60-SECOND RECALL

Coordination number	Number of bonds from ligands to the central metal
Naming order	Ligands alphabetically, then metal ; anion complex → metal ends in -ate
CFT splitting	Octahedral: t_{2g} low, e_g high · Tetrahedral: reversed, $\Delta_t = 4/9 \Delta_o$
Strong field ligand	Large Δ_o → pairing → low spin , inner orbital (d^2sp^3)
Weak field ligand	Small Δ_o → no pairing → high spin , outer orbital (sp^3d^2)
Spectrochemical series	$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^- < CO$
Magnetic moment	$\mu = \sqrt{n(n+2)}$ BM

1. Werner's Theory and Basic Terms

WERNER'S POSTULATES Metals show **two kinds of valency**: **primary (ionisable)**, satisfied by anions and written outside the square bracket, and **secondary (non-ionisable)**, satisfied by ligands and equal to the **coordination number**.

The secondary valencies have **fixed spatial arrangement**, which is what gives the geometry.

THE TERMS **Ligand**: an ion or molecule that donates a **lone pair** to the metal. **Monodentate** (NH_3 , Cl^- , CN^-) · **bidentate** (en , $C_2O_4^{2-}$) · **hexadentate** ($EDTA^{4-}$).

Ambidentate ligand: can attach through **either of two atoms** — NO_2^- (N or O), SCN^- (S or N).

Chelate: a ring formed by a polydentate ligand; chelates are **extra stable** (the chelate effect).

2. Nomenclature

- THE RULES IN ORDER**
1. Name the **cation first**, then the anion.
 2. Within the complex, name **ligands alphabetically**, then the metal.
 3. Anionic ligands end in **-o**: chlorido, cyanido, hydroxido, oxalato. Neutral ones keep their name, except **aqua** (H_2O), **ammine** (NH_3), **carbonyl** (CO), **nitrosyl** (NO).
 4. Use di, tri, tetra — but **bis, tris, tetrakis** for ligands that already contain a prefix (bis(ethylenediamine)).
 5. Oxidation state of the metal in **Roman numerals** in brackets.
 6. If the complex is an **anion**, the metal name ends in **-ate** (ferrate, cuprate, cobaltate, argentate, plumbate).

WORKED NAMES $[Co(NH_3)_6]Cl_3 \rightarrow$ hexaamminecobalt(III) chloride

$K_4[Fe(CN)_6] \rightarrow$ potassium hexacyanidoferrate(II)

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] \rightarrow \text{diamminedichloridoplatinum(II)}$

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \rightarrow \text{tetraaquadichloridochromium(III) chloride}$

3. Isomerism

STRUCTURAL ISOMERISM — four types

Type	Difference	Example
Ionisation	Exchange between inside and outside the sphere $\rightarrow$ different ions in solution	$[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
Hydrate	Water inside vs outside the sphere	$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
Linkage	Ambidentate ligand bonded through a different atom	$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$
Coordination	Ligands swapped between two complex ions	$[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

STEREISOMERISM Geometrical (*cis-trans*): shown by square planar MA_2B_2 and octahedral MA_4B_2 / MA_3B_3 .

Tetrahedral complexes do NOT show geometrical isomerism — all four positions are adjacent.

Optical: shown by octahedral complexes with *bidentate* ligands, e.g. $[\text{Co}(\text{en})_3]^{3+}$ and *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. The *trans* form has a plane of symmetry and is optically inactive.

4. Bonding — VBT and Crystal Field Theory

VALENCE BOND THEORY

Hybridisation	Geometry	Type
d^2sp^3	Octahedral	Inner orbital, low spin (strong field)
sp^3d^2	Octahedral	Outer orbital, high spin (weak field)
dsp^2	Square planar	Usually d^8 , e.g. $[\text{Ni}(\text{CN})_4]^{2-}$
sp^3	Tetrahedral	e.g. $[\text{NiCl}_4]^{2-}$

The classic pair: $[\text{Ni}(\text{CN})_4]^{2-}$ is dsp^2 , square planar, **diamagnetic**; $[\text{NiCl}_4]^{2-}$ is sp^3 , tetrahedral, **paramagnetic** — because CN^- is a strong field ligand and Cl^- is weak.

CRYSTAL FIELD THEORY Ligands are treated as *point charges* that split the five degenerate *d* orbitals.

Octahedral: t_{2g} (3 orbitals) lowered by $0.4\Delta_o$, e_g (2 orbitals) raised by $0.6\Delta_o$.

Tetrahedral: the reverse order, and $\Delta_t = (4/9)\Delta_o$ — always too small to force pairing, so tetrahedral complexes are **always high spin**.

If $\Delta_o > P$ (pairing energy) $\rightarrow$ electrons pair up $\rightarrow$ low spin. If $\Delta_o < P \rightarrow$ high spin.

Colour arises when an electron absorbs light to jump from t_{2g} to e_g ; the colour seen is the complement of the light absorbed.

TRAP $[\text{Ni}(\text{CO})_4]$ is tetrahedral and diamagnetic even though Ni normally is not — CO is so

strong a ligand that it pairs the $3d^8$ electrons, giving sp^3 with all electrons paired.

In metal carbonyls the M–C bond has both a σ bond ($\text{C} \rightarrow \text{M}$) and a π back bond ($\text{M} \rightarrow \text{C}$); this synergic effect strengthens M–C and weakens C–O.

WORKED EXAMPLE Predict the hybridisation, geometry and magnetic behaviour of $[\text{Fe}(\text{CN})_6]^{3-}$.

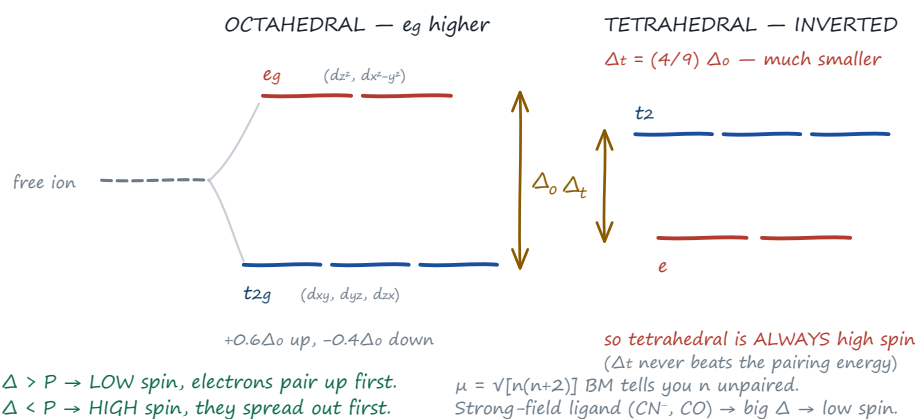
Charge on Fe: $x + 6(-1) = -3 \Rightarrow x = +3 \rightarrow \text{Fe}^{3+}$ is $3d^5$

CN^- is a strong field ligand $\rightarrow$ electrons pair up $\rightarrow t_{2g}^5 e_g^0$, leaving 1 unpaired electron

Hybridisation d^2sp^3 , geometry octahedral, low spin

$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM} \rightarrow$ paramagnetic

Crystal field splitting — octahedral vs tetrahedral



Spectrochemical order: $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- < \text{CO}$. Learn the two ends and you can place the rest.

5. Question Triggers what the wording wants

If the question says...	The answer is...
" CN^- , CO or NO_2^- as ligand"	Strong field $\rightarrow$ low spin, inner orbital
" Cl^- , F^- , H_2O as ligand"	Weak field $\rightarrow$ high spin, outer orbital
"tetrahedral complex, is it low spin?"	Never — Δ_t is too small
"shows optical isomerism"	Octahedral with bidentate ligands, cis form
"same formula, different ions in solution"	Ionisation isomerism
" NO_2^- bonded through N or O"	Linkage isomerism (ambidentate)
"why is $[\text{Ni}(\text{CO})_4]$ diamagnetic"	CO pairs all electrons; sp^3
"why are complexes coloured"	d-d transition across Δ_o

MOST-ASKED BOARD QUESTIONS

1. [3M] For a given complex, state the **oxidation state**, **hybridisation**, **geometry** and **magnetic moment**.
2. [3M] Explain **crystal field splitting** in octahedral and tetrahedral complexes, with diagrams.
3. [3M] Write IUPAC names / formulas for given coordination compounds.
4. [2M] Draw all the **isomers** of a given complex and identify the optically active one.
5. [2M] Explain why $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic but $[\text{NiCl}_4]^{2-}$ is paramagnetic.
6. [2M] What is the **synergic effect** in metal carbonyls?
7. [1M] Give an example of an **ambidentate** ligand. $\rightarrow \text{NO}_2^-$ or SCN^-

THE HABIT THAT SCORES — Work every bonding question in the same four steps: **oxidation state** $\rightarrow$ **d-electron count** $\rightarrow$ **strong or weak field** $\rightarrow$ **pair or don't pair**. Hybridisation, geometry and magnetic moment all follow automatically, and you never have to memorise individual complexes.