Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry (Part I)

12th Chemistry — Syllabus 2026-27 (New NCERT)

Chapter 5: Coordination Compounds

Why this chapter matters

Coordination compounds form the backbone of bio-inorganic chemistry (haemoglobin, chlorophyll, vitamin B_{12}), industrial catalysis (Wilkinson's catalyst, Ziegler-Natta), metallurgical extraction (cyanide leaching of Au, Ag), and analytical chemistry (EDTA titration). For JEE/NEET, this chapter typically yields 2–3 direct questions on **IUPAC nomenclature**, **isomerism counts**, **VBT/CFT geometry-magnetism prediction**, and **colour explanation**. Expect short multi-step numericals on oxidation state, hybridisation, and unpaired-electron count.

Contents

1 Werner's Theory of Coordination Compounds

Modern coordination chemistry was founded by the Swiss chemist Alfred Werner (1866–1919), who in 1893 explained the puzzling behaviour of cobalt-ammonia complexes that no contemporary valence theory could rationalise. His experimental tool was deceptively simple — precipitating chloride ions as AgCl with excess $AgNO_3$ — yet it revealed that not every chloride in a formula behaved the same way.

1.1 The Cobalt-Ammonia Puzzle

When $CoCl_3$ was crystallised with varying amounts of NH_3, a family of differently coloured compounds emerged. Treatment with $AgNO_3$ in cold solution precipitated only *some* of the chlorides:

Compound	Colour	mol AgCl per mol	Modern formula
$CoCl_3 \cdot 6NH_3$	Yellow	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5NH_3$	Purple	2	$[CoCl(NH_3)_5]Cl_2$
$CoCl_3 \cdot 4NH_3$	Green	1	$[CoCl_2(NH_3)_4]Cl$
$CoCl_3 \cdot 4NH_3$	Violet	1	$[CoCl_2(NH_3)_4]Cl$

The last two compounds have identical empirical formulae but distinct colours — our first glimpse of **isomerism** in coordination compounds (here, geometric: cis-violet and trans-green).

1.2 Postulates of Werner's Theory

Werner's four postulates

1. Metals exhibit **two kinds of valences**: *primary* (now: oxidation number, ionisable) and *secondary* (now: coordination number, non-ionisable).

2. Primary valences are satisfied by negative ions and are ionisable in solution.

3. Secondary valences are non-ionisable and are satisfied by neutral molecules or anions. The secondary valence is fixed for a given metal in a given oxidation state (it is the coordination number).

4. The groups attached by secondary valences occupy fixed **spatial positions** around the metal — the coordination polyhedron (octahedral, tetrahedral, square planar, etc.).

In modern language: primary valences become ionic bonds outside the square bracket; secondary valences become coordinate covalent (dative) bonds inside the square bracket.

Primary vs Secondary — the bracket rule

Inside the [ ], Secondary stays — coordinate bonds, non-ionisable, count = CN.
Outside the [ ], Primary precipitates — ionic bonds, free in solution, give AgCl with $AgNO_3$.

1.3 Double Salt vs Complex Salt

Both are formed by combining two simple salts in a fixed stoichiometry, but their behaviour in aqueous solution is opposite.

Feature	Double salt	Complex (coordination) compound
Example	Mohr's salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$K_4[Fe(CN)_6]$
Behaviour in water	Dissociates into *all* constituent ions (Fe^{2+}, NH_4^+, SO_4^{2-})	Gives K^+ and $[Fe(CN)_6]^{4-}$ only — Fe^{2+} and CN^- are not free
Tests for individual ions	Positive (each ion is free)	Negative (metal is masked inside complex)
Existence	Only in solid state	Exists in solid and in solution

Quick Tip

A test of complex versus double salt is qualitative analysis: pass H_2S into $K_4[Fe(CN)_6]$ — no FeS precipitates because Fe^{2+} is locked inside the coordination sphere. Pass H_2S into Mohr's salt solution — FeS precipitates immediately because Fe^{2+} is free.

2 Definitions of Some Important Terms

Master these eight terms cold: they are the vocabulary of every subsequent topic in the chapter and the source of multiple direct definition-style questions in board exams.

2.1 Coordination Entity, Central Atom and Ligands

Core vocabulary

Coordination entity — a central metal atom/ion bonded to a fixed number of ions or molecules (e.g. $[Ni(CO)_4]$, $[Co(NH_3)_6]^{3+}$).

Central atom/ion — the metal atom/ion to which ligands are bound. It is a **Lewis acid** (electron-pair acceptor).

Ligand — the ion or molecule donating an electron pair to the central atom. It is a **Lewis base** (electron-pair donor).

2.2 Classification of Ligands by Denticity

The *denticity* of a ligand is the number of donor atoms it uses to bind a single metal ion. Ligands range from monodentate to hexadentate.

Type	Donor atoms	Examples
Unidentate (monodentate)	1	Cl^-, H_2O, NH_3, CN^-, CO
Didentate (bidentate)	2	en (ethane-1,2-diamine), ox ($C_2O_4^{2-}$)
Tridentate	3	dien (diethylenetriamine)
Tetradentate	4	porphyrin (in haem)
Pentadentate	5	$EDTA^{3-}$ (rarely)
Hexadentate	6	$EDTA^{4-}$ (2 N + 4 O donor atoms)

Chelate ligand: a di- or polydentate ligand that uses two or more donor atoms simultaneously to bind *one* metal ion, forming a ring. Such complexes are unusually stable — this is the **chelate effect**.

Ambidentate ligand: a unidentate ligand with two *potential* donor atoms, only one of which actually binds in any given complex. The two classic examples:

- **NO_2^-** (nitrite): binds through N (nitrito-N, also called nitro) *or* through O (nitrito-O, also called nitrito).
- **SCN^-** (thiocyanate): binds through S (thiocyanato-S) *or* through N (thiocyanato-N or isothiocyanato).

This dual personality gives rise to *linkage isomerism* (Section 4).

Denticity counter

Count the lone-pair donors that actually touch the metal — not the number of atoms in the ligand. en has two N's, both bonded → didentate. $EDTA^{4-}$

has 6 donors (2N + 4O), all bonded → hexadentate. NO_2^- has two possible donor atoms but uses only one at a time → unidentate (ambidentate).

2.3 Coordination Number, Sphere and Polyhedron

Three geometry words

Coordination number (CN) — the number of *ligand donor atoms* (sigma-bonded) directly attached to the central metal. Pi-bonds are *not* counted.

Coordination sphere — everything inside the square brackets (central atom + ligands). The ions outside the brackets are **counter ions**.

Coordination polyhedron — the 3-D shape traced by the donor atoms (octahedral, tetrahedral, square planar, trigonal bipyramidal, square pyramidal).

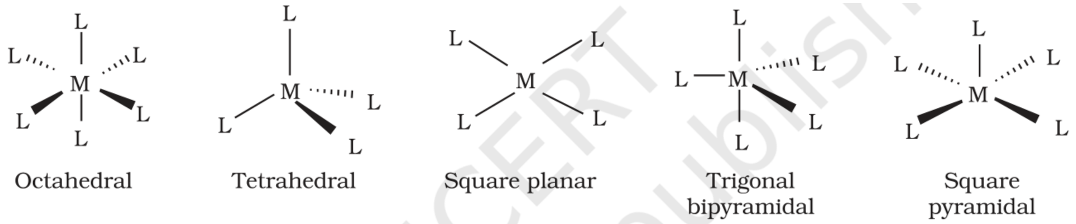


Fig. 5.1: *Shapes of different coordination polyhedra. M represents the central atom/ion and L, a unidentate ligand.*

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.1: Shapes of different coordination polyhedra. M is the central atom/ion; L is a unidentate ligand.

The most frequently encountered polyhedra in board/JEE problems are octahedral (CN = 6, e.g. $[Co(NH_3)_6]^{3+}$), tetrahedral (CN = 4, e.g. $[Ni(CO)_4]$) and square planar (CN = 4, e.g. $[PtCl_4]^{2-}$).

Quick Tip

For a didentate ligand, the coordination number is twice the count of ligand units. $[Co(en)_3]^{3+}$ has three en molecules with two N donors each ⇒ CN = 6 (octahedral). $[Fe(C_2O_4)_3]^{3-}$ has three oxalate ions with two O donors each ⇒ CN = 6.

Common Mistake

Coordination number is *not* the same as the number of ligand molecules. For unidentate ligands they coincide, but for chelating ligands you must multiply by denticity. Also, π-bonds do not add to CN — a metal-arene complex with η^6-benzene contributes only the count of σ-donors elsewhere.

2.4 Oxidation Number; Homoleptic vs Heteroleptic

Oxidation number of the central atom = the hypothetical charge the metal would carry if every ligand were removed along with its bonding electron pair. It is written as a Roman numeral in parentheses after the metal's name: copper(I), iron(III).

Calculation rule: Charge on complex ion $=$ Oxidation state of metal $+$ Sum of charges on ligands.

Worked example: in $[Cu(CN)_4]^{3-}$, four CN^- contribute -4, total charge is -3, so Cu $+ (-4) = -3 \Rightarrow$ oxidation state of Cu $= +1$. The complex is named with Cu(I).

- **Homoleptic complex:** the metal is bound to only one type of donor group. E.g. $[Co(NH_3)_6]^{3+}$, $[Ni(CO)_4]$, $[Fe(CN)_6]^{4-}$.
- **Heteroleptic complex:** the metal is bound to more than one type of donor group. E.g. $[Co(NH_3)_4Cl_2]^+$, $[CoCl(NH_3)_5]^{2+}$.

3 Nomenclature of Coordination Compounds

IUPAC nomenclature is the bread-and-butter of this chapter: every board paper carries at least one direct question, and JEE Main loves multi-step traps where the name encodes oxidation state, ligand identity *and* stereochemistry simultaneously. Master the rules and you bank easy marks.

3.1 Rules for Writing the Formula

Formula rules (IUPAC)

1. The **central atom is written first** inside the square brackets.
2. **Ligands follow alphabetically** (charge is irrelevant for ordering).
3. Polyatomic and abbreviated ligand formulae are enclosed in **parentheses**.
4. The whole coordination entity is enclosed in **square brackets**.
5. No space between metal and ligands.
6. Charge on the complex (if any) is placed outside the bracket as a right superscript: number first, sign second.
7. For neutral compounds, the total cation charge balances the total anion charge.

3.2 Rules for Naming

Naming rules (IUPAC)

1. **Cation first, anion second** (as in ordinary ionic compounds).
2. Within the coordination entity, **ligands are named alphabetically, before the metal** — the opposite order from the formula.
3. Anionic ligand names end in **-o**: chloro → **chlorido**, cyano → **cyanido**, oxalato, hydroxido, nitrito-N, nitrito-O, thiocyanato-S, thiocyanato-N.
4. Neutral ligands keep their molecular name, with four exceptions: H_2O → aqua, NH_3 → ammine (double m!), CO → carbonyl, NO → nitrosyl.
5. Number of identical ligands is indicated by Greek prefixes **di, tri, tetra, penta, hexa**. If the ligand name already contains such a prefix, use **bis, tris, tetrakis** and enclose the ligand in parentheses (e.g. tris(ethane-1,2-diamine)).
6. The oxidation state of the metal is shown in **Roman numerals in parentheses** after the metal's name.
7. If the complex is an **anion**, the metal name ends in **-ate** (with a Latin root for some metals: ferrate, cuprate, argentate, plumbate, stannate, aurate). If it is a cation or neutral entity, the metal's English name is used.

Worked examples:

- $Cr(NH_3)_3(H_2O)_3$ Cl_3 → *triamminetriaquachromium(III) chloride*. (Alphabetise: ammine before aqua. Net charge of complex ion $= +3$, all ligands neutral, so Cr is $+3$.)
- $Co(en)_3$ $_2(SO_4)_3$ → *tris(ethane-1,2-diamine)cobalt(III) sulphate*. (Three sulphates compensate two cations ⇒ each cation is $+3$.)
- $K_3[Fe(CN)_6]$ → *potassium hexacyanidoferrate(III)*.
- $Ag(NH_3)_2$ $[Ag(CN)_2]$ → *diamminesilver(I) dicyanidoargentate(I)* (same metal, different names: argentate for the anionic part).
- $Pt(NH_3)_2Cl(NO_2)$ → *diamminechloridonitrito-N-platinum(II)*.

The 4 neutral-ligand exceptions

AAA-CN: **A**qua (H_2O), **A**mmine (NH_3, double-m), **C**arbonyl (CO), **N**itrosyl (NO). Every other neutral ligand keeps its molecular name (methylamine, pyridine, triphenylphosphine).

Common Mistake

Three common slips: (i) writing "amine" instead of "**ammine**" — amines are amines, ammines are NH_3 ligands. (ii) Using "chloro" instead of the IUPAC 2005 form "**chlorido**". (iii) Forgetting that in the *name* ligands come before the metal alphabetically, but in the *formula* the metal comes first.

3.3 Selected Anionic-Metal Suffixes

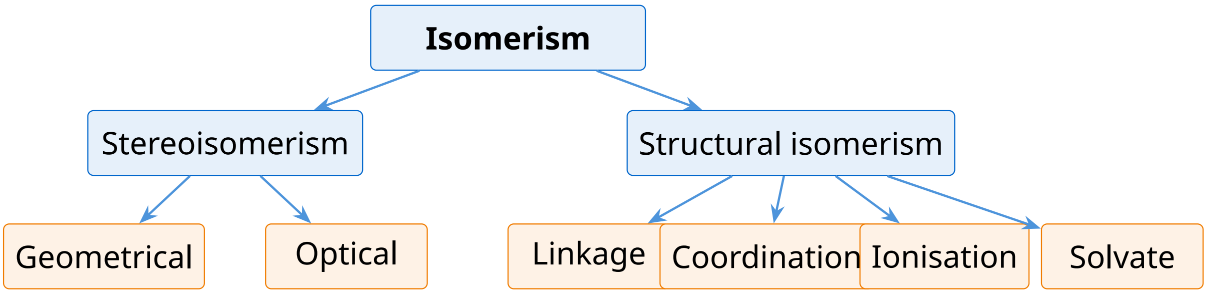
Metal	Anionic suffix
Iron (Fe)	ferrate
Copper (Cu)	cuprate
Silver (Ag)	argentate
Gold (Au)	aurate
Lead (Pb)	plumbate
Tin (Sn)	stannate
Mercury (Hg)	mercurate
Chromium (Cr)	chromate (e.g. trioxalatochromate(III))
Cobalt, Nickel, Platinum, Manganese	cobaltate, nickelate, platinate, manganate

Quick Tip

When you see "-ate" in the name, the complex ion is an *anion*, and a counter cation (K^+, Na^+, NH_4^+) must appear in the formula *outside* the brackets. When you see no "-ate", the complex is either a cation or neutral.

4 Isomerism in Coordination Compounds

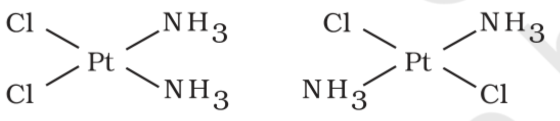
Two coordination compounds with the same molecular formula but different arrangements of atoms (or bonds) are *isomers*. NCERT recognises two broad families, each subdivided:



4.1 Geometrical Isomerism

This arises in *heteroleptic* complexes with the same ligands arranged differently in space. It is most common at CN = 4 (square planar only — not tetrahedral) and CN = 6 (octahedral).

Square planar [MX_2L_2]: the two X ligands can be adjacent (**cis**) or opposite (**trans**). The textbook example is $Pt(NH_3)_2Cl_2$.

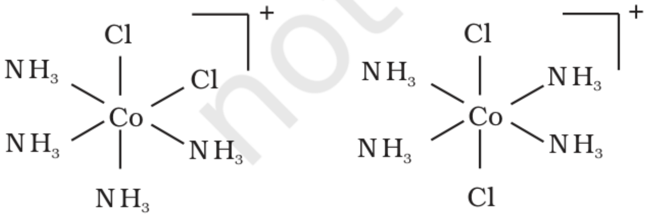


cis *trans*

Fig. 5.2: Geometrical isomers (cis and trans) of Pt [NH$_3$)$_2$Cl$_2$]

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.2: Geometrical isomers (cis and trans) of [Pt(NH$_3$)$_2$Cl$_2$].

Octahedral [MX_2L_4]: cis (two X adjacent, 90° apart) and trans (two X opposite, 180° apart).



cis *trans*

Fig. 5.3: Geometrical isomers (cis and trans) of[Co(NH$_3$)$_4$Cl$_2$]$^+$

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.3: Geometrical isomers (cis and trans) of [Co(NH$_3$)$_4$Cl$_2$]$^+$.

Octahedral [$MX_2(L–L)_2$] with a didentate ligand also shows cis-trans isomerism. The didentate "bite" forces specific orientations:

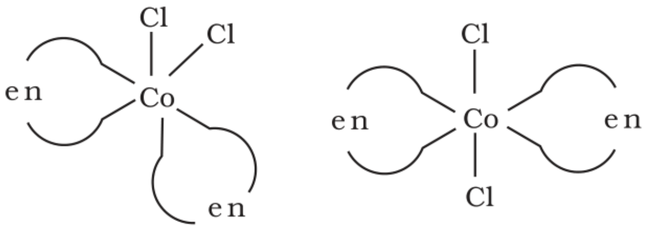
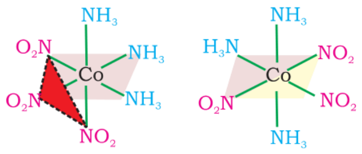


Fig. 5.4: Geometrical isomers (cis and trans) of [CoCl$_2$(en)$_2$]

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.4: Geometrical isomers (cis and trans) of [CoCl$_2$(en)$_2$].

Octahedral [Ma_3b_3] — the **fac** (facial) and **mer** (meridional) isomers. In *fac*, three identical ligands cap one face of the octahedron; in *mer*, they lie along a meridian (three corners of one square face).



fac– *mer–*

Fig. 5.5 *The facial (fac) and meridional (mer) isomers of [Co(NH$_3$)$_3$(NO$_2$)$_3$]*

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.5: Facial (fac) and meridional (mer) isomers of [Co(NH_3)$_3$(NO_2)$_3$].

Why tetrahedral complexes do *not* show geometric isomerism

In a tetrahedron every pair of corners is equivalent — there is no "adjacent" versus "opposite" distinction because all four bond angles are the same 109.5°. So any rearrangement of unidentate ligands yields the same structure (just rotated).

Quick Tip

For octahedral [$MA_2B_2C_2$] count isomers carefully — there are exactly 6 geometric isomers (including chiral pairs). For [MABXL] square planar, there are 3 geometric isomers (two cis + one trans). Knowing the counts speeds up MCQ elimination.

4.2 Optical Isomerism

Optical isomers are non-superimposable mirror images — enantiomers. The molecule is **chiral** (has no plane or centre of symmetry). The pair rotates plane-polarised light: **d** (*dextro*) rotates right; **l** (*laevo*) rotates left.

Optical isomerism is common in octahedral complexes with didentate ligands. The classic example is tris(ethane-1,2-diamine)cobalt(III):

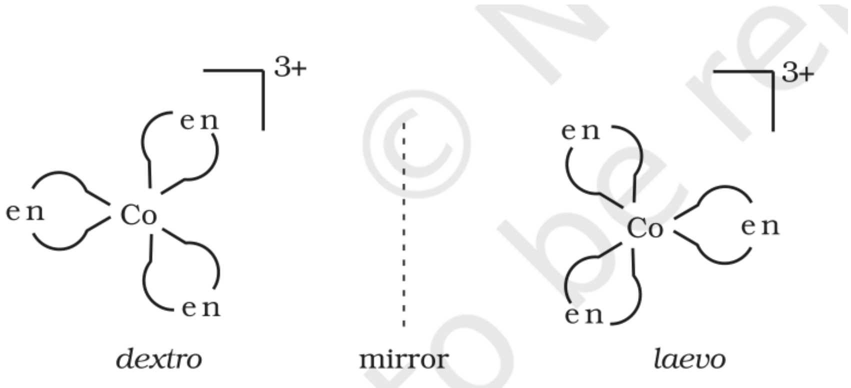
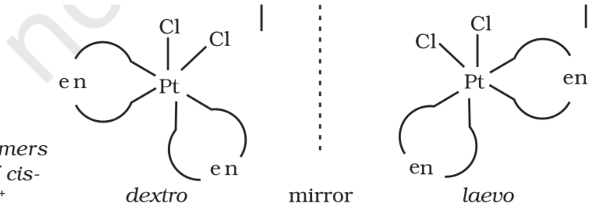


Fig.5.6: Optical isomers (d and l) of $[Co(en)_3]^{3+}$

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.6: Optical isomers (d and l) of $[Co(en)_3]^{3+}$.

For $[PtCl_2(en)_2]^{2+}$, only the cis isomer is chiral — the trans isomer has a plane of symmetry and is therefore optically inactive (achiral):

Fig.5.7 *Optical isomers (d and l) of cis-$[PtCl_2(en)_2]^{2+}$*



Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.7: Optical isomers (d and l) of cis-$[PtCl_2(en)_2]^{2+}$.

Spotting chirality in octahedral complexes

A complex is chiral if it has **no plane of symmetry and no centre of inversion**. Quick checks for the standard NCERT cases:
- $[M(L–L)_3]$ (three chelates) → always chiral (propeller).
- cis-$[MX_2(L–L)_2]$ → chiral.
- trans-$[MX_2(L–L)_2]$ → achiral (has a mirror plane through the X–M–X axis).

4.3 Structural Isomerism

(a) Linkage isomerism — occurs when an *ambidentate* ligand binds through different donor atoms. Jorgensen's classic example: $[Co(NH_3)_5(NO_2)]Cl_2$ exists as a *red* form (Co–ONO, nitrito-O) and a *yellow* form (Co–NO_2, nitrito-N). Similarly, SCN^- gives M–SCN (thiocyanato-S) and M–NCS (thiocyanato-N) pairs.

(b) Coordination isomerism — both cation and anion are complex ions, and the ligands interchange between the two metals. Example pair:

$$[Co(NH_3)_6][Cr(CN)_6] \quad \text{vs.} \quad [Cr(NH_3)_6][Co(CN)_6].$$

(c) Ionisation isomerism — the counter ion and a ligand swap places between the inside and the outside of the coordination sphere. Example pair:

$$[Co(NH_3)_5SO_4]Br \quad \text{vs.} \quad [Co(NH_3)_5Br]SO_4.$$

The two isomers can be distinguished chemically: the first gives a positive Ag^+/AgBr test but no Ba^{2+}/$BaSO_4$ test; the second is the reverse.

(d) Solvate (hydrate) isomerism — a solvent (usually water) is either bonded directly to the metal or merely present in the crystal lattice. Three isomers of chromium chloride hexahydrate are known:

$$\begin{aligned} Cr(H_2O)_6 \; & Cl_3 \text{ — violet} \\ Cr(H_2O)_5Cl \; & Cl_2 \cdot H_2O \text{ — grey-green} \\ Cr(H_2O)_4Cl_2 \; & Cl \cdot 2H_2O \text{ — dark green} \end{aligned}$$

Quick Tip

A wet-chemistry shortcut to identify ionisation vs solvate isomers: add

AgNO$_3$. Only chlorides outside the brackets precipitate. CrCl$_3\cdot$ 6H$_2$O sold as the violet isomer gives 3 AgCl per formula unit; the dark-green form gives only 1.

5 Bonding in Coordination Compounds

Werner's theory described *what* coordination compounds look like, but not *why* they form or why they have such a rich variety of magnetic and optical properties. Three modern theories have been developed: Valence Bond Theory (VBT), Crystal Field Theory (CFT), and Ligand Field Theory / Molecular Orbital Theory (LFT/MOT). Class 12 NCERT covers VBT and CFT in detail.

5.1 Valence Bond Theory (VBT)

Pauling proposed that the metal atom or ion offers *empty hybrid orbitals* that accept lone pairs from ligands, forming coordinate-covalent bonds. The geometry of the complex is determined by which atomic orbitals are mixed.

VBT hybridisation $\rightarrow$ geometry map

CN	Hybridisation $\rightarrow$ geometry
4	sp^3 $\rightarrow$ tetrahedral
4	dsp^2 $\rightarrow$ square planar (uses inner $(n-1)d$)
5	sp^3d $\rightarrow$ trigonal bipyramidal
6	d^2sp^3 $\rightarrow$ octahedral (*inner* orbital, uses $(n-1)d$; low spin)
6	sp^3d^2 $\rightarrow$ octahedral (*outer* orbital, uses nd; high spin)

Inner vs outer orbital complexes (octahedral, d^4–d^7):

- Strong-field ligand (e.g. CN$^-$, CO, en, NH$_3$) $\rightarrow$ pairs up the $(n-1)d$ electrons, freeing two $(n-1)d$ orbitals for d^2sp^3 hybridisation. Result: **inner orbital complex**, **low spin**.
- Weak-field ligand (e.g. F$^-$, Cl$^-$, Br$^-$, H$_2$O) $\rightarrow$ cannot pair the d electrons, so nd orbitals are used: sp^3d^2. Result: **outer orbital complex**, **high spin**.

Worked example 1 — [Co(NH$_3$)$_6$]$^{3+}$: Co^{3+} is $3d^6$; NH$_3$ is strong-field, so the six $3d$ electrons pair into three orbitals, leaving two $3d$ orbitals free. Hybridisation d^2sp^3 (inner orbital, octahedral). No unpaired electron $\Rightarrow$ **diamagnetic**.

Worked example 2 — [CoF$_6$]$^{3-}$: Co^{3+} is $3d^6$; F$^-$ is weak-field, electrons stay unpaired in $3d$. Hybridisation sp^3d^2 (outer orbital, octahedral). Four unpaired electrons $\Rightarrow$ **paramagnetic**, $\mu_s = \sqrt{4(4+2)} = \sqrt{24} \approx 4.9$ BM.

Worked example 3 — [Ni(CO)$_4$]: Ni is in 0 oxidation state, $3d^84s^2$. CO pairs the electrons, $3d^{10}$ configuration, and sp^3 hybridisation gives tetrahedral. No unpaired electrons ⇒ **diamagnetic**.

Worked example 4 — [NiCl$_4$]$^{2-}$: Ni^{2+} is $3d^8$; Cl$^-$ is weak-field, electrons not paired. sp^3 hybridisation → tetrahedral. Two unpaired ⇒ **paramagnetic**, $\mu_s \approx 2.83$ BM.

Worked example 5 — [Ni(CN)$_4$]$^{2-}$: Ni^{2+} is $3d^8$; CN$^-$ is strong-field, so the two unpaired $3d$ electrons pair, freeing one $3d$ orbital. Hybridisation dsp^2 → square planar. No unpaired ⇒ **diamagnetic**.

5.2 Magnetic Properties and Spin-only Formula

A coordination compound is *paramagnetic* if it has unpaired electrons, *diamagnetic* if all are paired. The magnitude of paramagnetism (in Bohr magnetons, BM) follows the **spin-only formula**:

Spin-only magnetic moment

$$\boxed{\mu_s = \sqrt{n(n+2)} \quad \text{BM}}$$

where n is the number of unpaired electrons.

Quick lookup:

$n = 1 \Rightarrow \mu_s = 1.73$ BM
$n = 2 \Rightarrow \mu_s = 2.83$ BM
$n = 3 \Rightarrow \mu_s = 3.87$ BM
$n = 4 \Rightarrow \mu_s = 4.90$ BM
$n = 5 \Rightarrow \mu_s = 5.92$ BM
$n = 0 \Rightarrow$ diamagnetic.

Quick Tip

The reverse problem (given μ_s, find geometry) is a JEE classic. Example: [MnBr$_4$]$^{2-}$ has $\mu_s = 5.9$ BM ⇒ $n = 5$ unpaired. Mn^{2+} is $3d^5$. Five unpaired means *no* pairing, so the geometry must be sp^3 (tetrahedral), *not* dsp^2 (square planar, which would force pairing).

Common Mistake

The spin-only formula ignores orbital angular-momentum contributions. For first-row transition metals it is usually accurate to ± 0.3 BM; for $4d$ and $5d$ metals it can be off by 1–2 BM. NCERT problems stick to first-row, so use $\mu_s = \sqrt{n(n+2)}$ confidently.

5.3 Limitations of VBT

VBT was a remarkable advance but it has six well-known shortcomings:

1. It rests on many ad-hoc assumptions about hybridisation.
2. It gives no quantitative interpretation of magnetic data (cannot predict the *magnitude* of Δ_0).
3. It does not explain the colour of coordination compounds.

4. It does not give quantitative thermodynamic or kinetic stability data.
5. It does not reliably predict tetrahedral vs square planar for 4-coordinate complexes.
6. It does not distinguish weak-field from strong-field ligands; the spectrochemical series is fed in by hand.

These limitations motivated the development of Crystal Field Theory.

5.4 Crystal Field Theory (CFT)

CFT models the metal-ligand interaction as purely *electrostatic*: ligands are point charges (anions) or point dipoles (neutral molecules), and the metal d-orbitals split in energy under their field. The key insight is that the five d-orbitals are no longer degenerate when surrounded by a non-spherical field of ligands.

Octahedral field — d-orbital splitting:

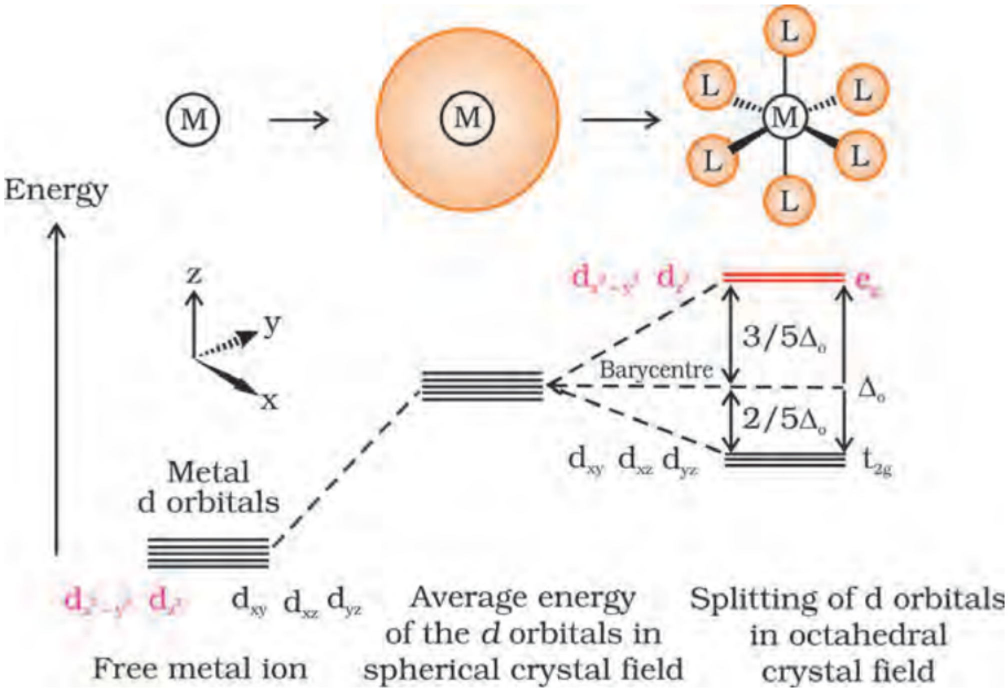


Fig.5.8: *d orbital splitting in an octahedral crystal field*

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.8: d-orbital splitting in an octahedral crystal field.

In an octahedral complex, the $d_{x^2-y^2}$ and d_{z^2} orbitals (collectively e_g) point *at* the ligands; they are destabilised. The d_{xy}, d_{yz}, d_{xz} orbitals (collectively t_{2g}) point *between* the ligands; they are stabilised.

Octahedral crystal field splitting

The energy gap between t_{2g} and e_g is the **crystal field splitting parameter**

Δ_o (subscript o for octahedral).

$$E(e_g) = +\tfrac{3}{5}\Delta_o, \qquad E(t_{2g}) = -\tfrac{2}{5}\Delta_o$$

relative to the barycentre (the spherical-field average). The energy is conserved: the rise of two e_g orbitals equals the fall of three t_{2g} orbitals: $2 \times \frac{3}{5}\Delta_o = 3 \times \frac{2}{5}\Delta_o$.

Spectrochemical series — ligands ranked by the splitting they produce, weakest first:

Spectrochemical series (weak → strong field)

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

Spectrochemical mnemonic

"**I B**rought **S**o **Cl**ean **S**o **F**ine, **OH Ox**ford, **H**ad **N**o **ED**ucational **N**eeds, **en CN CO**llege". Translating the bold letters back: I, Br, SCN, Cl, S^{2-}, F, OH, ox, H_2O, NCS, edta, NH_3, en, CN, CO. Devise your own — the trick is to lock in the four "strong" end-of-list ligands: **NH_3** < **en** < **CN** < **CO**.

Electron filling under Δ_o vs pairing energy P:

For d^4–d^7 in an octahedral field, the fourth d-electron faces a choice:

- If $\Delta_o < P$: enter e_g to avoid pairing (**high-spin**, weak-field configuration $t_{2g}^3 e_g^1$).
- If $\Delta_o > P$: pair up in t_{2g} (**low-spin**, strong-field configuration $t_{2g}^4 e_g^0$).

Quick Tip

A simple high-spin/low-spin rule: **weak-field → high-spin, strong-field → low-spin** — but the choice only matters for d^4 through d^7. For $d^1, d^2, d^3, d^8, d^9, d^{10}$ the filling pattern is forced by Hund's rule and is the same either way.

Tetrahedral field — d-orbital splitting:

In a tetrahedron, the four ligands sit in the alternating corners of a cube. None of the d-orbitals point directly at a ligand, but d_{xy}, d_{yz}, d_{xz} (now labelled t_2) point closer to the ligand directions than $d_{x^2-y^2}, d_{z^2}$ (labelled e). The order is inverted from octahedral.

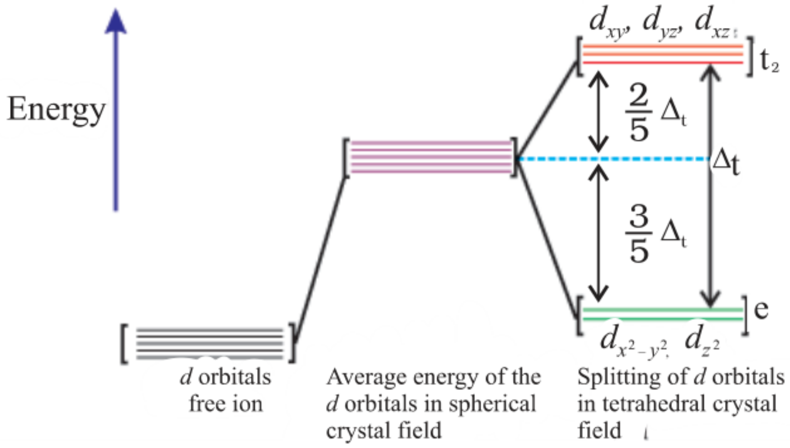


Fig.5.9: d orbital splitting in a tetrahedral crystal field.

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.9: d-orbital splitting in a tetrahedral crystal field.

Tetrahedral splitting

$$\boxed{\Delta_t = \tfrac{4}{9}\Delta_o}$$

The tetrahedral splitting is only about 44% of the octahedral splitting (same metal, same ligands, same M–L distance).

Consequence: Δ_t is almost always less than the pairing energy P, so **tetrahedral complexes are almost always high-spin**.

Why no 'g' subscript for tetrahedral?

The 'g' (*gerade*) subscript indicates a centre of symmetry. Octahedral and square-planar geometries have such a centre; **tetrahedral does not**. Hence we write e_g, t_{2g} for octahedral but e, t_2 (no g) for tetrahedral.

5.5 Colour in Coordination Compounds

CFT's most spectacular success is explaining the colour of transition-metal complexes. A complex absorbs visible light at the wavelength corresponding to Δ_o and *transmits* the complementary colour. The absorption promotes an electron from the lower d-set to the upper d-set — a d-d **transition**.

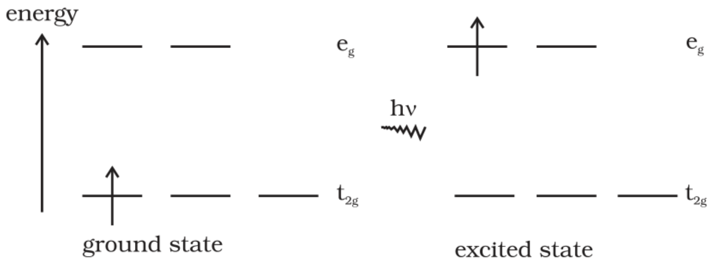


Fig.5.10: Transition of an electron in

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.10: d-d transition of an electron in [Ti(H_2O)$_6$]$^{3+}$ from the t_{2g} to the e_g level.

Worked example — [Ti(H_2O)$_6$]$^{3+}$: Ti^{3+} is $3d^1$. The lone electron sits in t_{2g} in the ground state. Light of wavelength ∼498 nm (blue-green) is absorbed, promoting the electron to e_g. The transmitted light is the *complement* of blue-green, namely *violet* — which is the observed colour of [Ti(H_2O)$_6$]$^{3+}$ solution.

Complex	λ_{abs} (nm)	Colour absorbed	Colour observed
[CoCl(NH_3)$_5$]$^{2+}$	535	Yellow	Violet
[Co(NH_3)$_5$(H_2O)]$^{3+}$	500	Blue-green	Red
[Co(NH_3)$_6$]$^{3+}$	475	Blue	Yellow-orange
[Co(CN)$_6$]$^{3-}$	310	Ultraviolet	Pale yellow
[Cu(H_2O)$_4$]$^{2+}$	600	Red	Blue
[Ti(H_2O)$_6$]$^{3+}$	498	Blue-green	Violet

Effect of the ligand on colour:

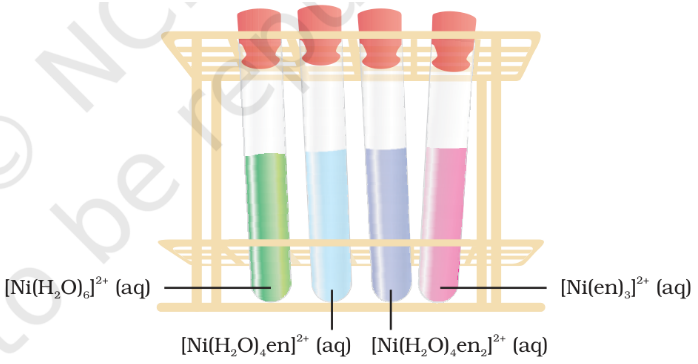


Fig.5.11
Aqueous solutions of complexes of nickel(II) with an increasing number of ethane-1, 2-diamine ligands.

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.11: Aqueous solutions of Ni(II) complexes with increasing number of en ligands. Green → pale-blue → blue/purple → violet.

As stronger-field ligands replace water, Δ_o rises, the absorbed wavelength shifts to shorter wavelengths, and the observed (complementary) colour shifts to longer wavelengths — exactly what the photograph shows.

No ligand → no splitting → no colour. Anhydrous $CuSO_4$ is white; $CuSO_4 \cdot 5H_2O$ is blue. Anhydrous [Ti(H_2O)$_6$]Cl_3 on heating loses water and becomes colourless.

Gemstone colours

Ruby is Al_2O_3 doped with 0.5–1% Cr^{3+} (d^3) ions at octahedral sites in the alumina lattice; d-d transitions absorb green/yellow light, giving the red colour. Emerald is Cr^{3+} in beryl ($Be_3Al_2Si_6O_{18}$); a slightly different crystal field shifts the absorption to yellow-red and blue, transmitting green. Same impurity, different host crystal, dramatically different colour — a textbook demonstration of ligand-field effects.

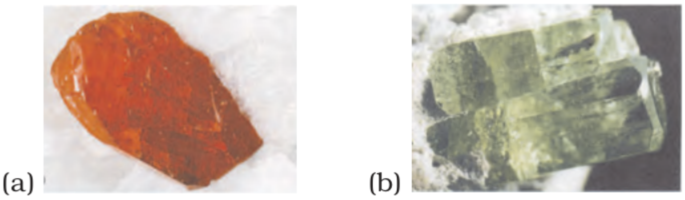


Fig.5.12: *(a) Ruby: this gemstone was found in marble from Mogok, Myanmar; (b) Emerald: this gemstone was found in Muzo, Columbia.*

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.12: (a) Ruby and (b) emerald — both coloured by Cr^{3+} in different crystal fields.

Common Mistake

Don't say "$[Sc(H_2O)_6]^{3+}$ is coloured because of d-d transition." Sc^{3+} is d^0 — no d-electron to promote, no d-d transition. It is colourless. Similarly Zn^{2+} is d^{10} — e_g is already full, so no d-d transition either. Both are colourless. **Coloured complexes require a partly-filled d-subshell.**

5.6 Limitations of CFT

CFT explains formation, geometry, magnetism and colour, but has weaknesses:

1. It treats ligands as point charges/dipoles, ignoring the partly *covalent* character of M–L bonds.
2. It predicts that anionic ligands should produce the largest splitting (highest charge), but the spectrochemical series places anions at the *low* end — a serious failure.
3. It cannot explain the bonding in metal carbonyls and other π-acceptor complexes.

These flaws led to **Ligand Field Theory** (LFT) and **Molecular Orbital Theory** (MOT), which incorporate covalency and orbital overlap. They are beyond the scope of Class 12 NCERT.

6 Bonding in Metal Carbonyls

Metal carbonyls are coordination compounds of transition metals with CO as the only (or principal) ligand — the simplest **homoleptic** examples are tetrahedral $[Ni(CO)_4]$, trigonal-bipyramidal $[Fe(CO)_5]$, and octahedral $[Cr(CO)_6]$. Polynuclear carbonyls (with M–M bonds, sometimes bridging COs) include $[Mn_2(CO)_{10}]$ and $[Co_2(CO)_8]$.

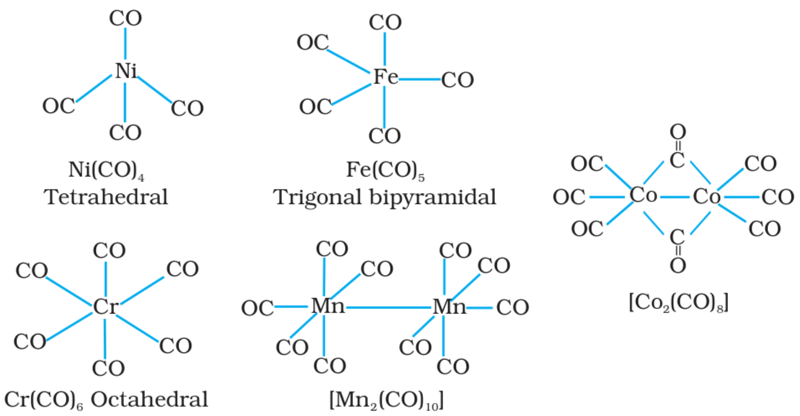


Fig. 5.13 Structures of some representative homoleptic metal carbonyls.

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.13: Structures of some representative homoleptic metal carbonyls.

6.1 The Synergic M–CO Bond

The metal-carbon bond in metal carbonyls is unusually strong because it has *two* simultaneous components — a σ-donation and a π-back-donation that reinforce each other. This mutual reinforcement is called **synergic bonding** or the **synergic effect**.

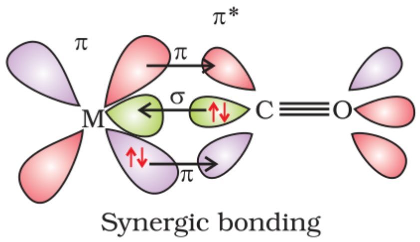


Fig. 5.14: Example of synergic bonding interactions in a carbonyl complex.

Source: NCERT Class 12 Chemistry Part I, Chapter 5 — Fig. 5.14: Example of synergic bonding interactions in a carbonyl complex — σ donation from C to M and π back-bonding from M to CO.

The two components of the M–CO bond

σ **bond (C → M):** the carbon lone pair on CO donates into a vacant metal orbital. CO is a Lewis base here.

π **bond (M → C):** a filled metal d-orbital donates back into the empty π^* antibonding orbital of CO. The metal is a Lewis base here.

Synergic effect: the σ-donation removes electron density from C; the π-back-donation puts electron density back. The two transfers *strengthen each other*, making M–CO bonds among the strongest known M–L bonds.

Quick Tip

Synergic bonding is why CO can stabilise metals in unusual *low* oxidation states — including zero. In $[Ni(CO)_4]$ and $[Cr(CO)_6]$, the metal is in 0 oxidation state. The back-donation drains excess electron density from the electron-rich metal, making the bonding favourable.

Common Mistake

Don't confuse synergic bonding with simple Lewis acid-base donation. In NH_3 or H_2O complexes, only σ-donation occurs (those ligands have no low-lying π^*). CO is special because it has *both* a lone pair (for σ) and an empty π^* (for back-bonding). Other classic π-acceptors: CN^-, NO, PR_3.

7 Importance and Applications

Coordination compounds are not laboratory curiosities — they underpin biology, industry and medicine. NCERT highlights six major application areas; expect 2-mark and 3-mark direct questions on these.

7.1 Analytical and Quantitative Chemistry

- **Qualitative analysis:** characteristic colour reactions of metal ions with chelating ligands form the basis for detection. Examples:
  - Ni^{2+} + DMG (dimethylglyoxime) in basic medium → rose-red precipitate of $[Ni(DMG)_2]$.
  - Fe^{3+} + SCN^- → blood-red $[Fe(SCN)]^{2+}$.
  - Cu^{2+} + NH_3 (excess) → deep blue $[Cu(NH_3)_4]^{2+}$.
- **Quantitative analysis:** EDTA titration determines water hardness. Ca^{2+} and Mg^{2+} form stable 1:1 chelates with Na_2EDTA; the difference in their stability constants allows selective estimation.

7.2 Metallurgical Extraction and Purification

- **Cyanide leaching of gold and silver:**

  $$4\,\text{Au} + 8\,\text{CN}^- + \text{O}_2 + 2\,\text{H}_2\text{O} \rightarrow 4\,[\text{Au(CN)}_2]^- + 4\,\text{OH}^-$$

  Gold is then displaced by zinc: $2\,[\text{Au(CN)}_2]^- + \text{Zn} \rightarrow [\text{Zn(CN)}_4]^{2-} + 2\,\text{Au}$.
- **Mond's process for nickel purification:** impure Ni reacts with CO at ∼50°C to give volatile $[\text{Ni(CO)}_4]$, which is then decomposed thermally at ∼230°C to deposit pure Ni.

7.3 Biological Systems

Three life-critical coordination compounds

Chlorophyll — a Mg^{2+} porphyrin complex. Absorbs red and blue light, transmits green; drives photosynthesis.

Haemoglobin — an Fe^{2+} porphyrin (haem). The Fe binds O_2 reversibly for transport through the bloodstream. CO and CN^- are toxic because they bind more strongly than O_2 to the same Fe^{2+} site.

Vitamin B$_{12}$ (cyanocobalamine) — a Co^{3+} corrin complex. The anti-pernicious-anaemia factor; essential for red-blood-cell formation.

Other biologically important coordination metals: Zn^{2+} in carboxypeptidase A and carbonic anhydrase enzymes; Mn^{2+} in the oxygen-evolving complex of photosystem II; Cu^{2+} in tyrosinase and haemocyanin.

7.4 Industrial Catalysis

- **Wilkinson's catalyst** $[(\text{PPh}_3)_3\text{RhCl}]$: homogeneous hydrogenation of alkenes at room temperature and 1 atm H_2.
- **Ziegler-Natta catalysts** (TiCl_4 with $\text{Al(C}_2\text{H}_5)_3$): stereospecific polymerisation of ethene and propene.
- **Hydroformylation** (oxo process): cobalt carbonyl $[\text{HCo(CO)}_4]$ catalyses the addition of CO + H_2 across an alkene to give aldehydes.

7.5 Electroplating, Photography and Dyeing

- **Electroplating:** silver and gold deposit more uniformly from $[\text{Ag(CN)}_2]^-$ or $[\text{Au(CN)}_2]^-$ baths than from free Ag^+ or Au^+ solutions — the complex acts as a slow-release reservoir.
- **Photography:** undeveloped AgBr is fixed by washing with hypo ($\text{Na}_2\text{S}_2\text{O}_3$); soluble $[\text{Ag(S}_2\text{O}_3)_2]^{3-}$ forms and rinses away, leaving only the developed image.

7.6 Medicinal Chemistry — Chelation Therapy

- **D-penicillamine** and **desferrioxime B** sequester excess Cu and Fe respectively in Wilson's disease and iron overload.
- **$Na_2Ca(EDTA)$** removes toxic lead from the body (Pb^{2+} displaces Ca^{2+} inside the chelate).
- **cis-platin**, cis-$[PtCl_2(NH_3)_2]$, is a front-line chemotherapy drug for testicular and ovarian cancers — and a textbook reminder that *geometric isomerism matters*: trans-platin is biologically inactive.

Cis-platin — isomerism that saves lives

The cis isomer of $[PtCl_2(NH_3)_2]$ binds the N7 atoms of adjacent guanine bases on DNA, kinking the helix and triggering cell death. The trans isomer cannot bridge adjacent guanines because the Cl's point opposite ways — a clinical demonstration that the geometric isomers you draw in your textbook have life-or-death consequences in oncology.

8 JEE / NEET Extensions Beyond NCERT

The five most-tested topics in this chapter that go beyond plain NCERT statements:

8.1 Crystal Field Stabilisation Energy (CFSE)

CFSE for octahedral d^n

$$\boxed{\text{CFSE} = [\,-0.4\,n(t_{2g}) + 0.6\,n(e_g)\,]\,\Delta_o + mP}$$

where $n(t_{2g})$ and $n(e_g)$ are the electron counts in each set, and m is the *extra* pairings caused by the field (compared with the free ion). P is the pairing energy.

Common CFSE values (in Δ_o units):

d^n	High-spin CFSE	Unpaired (HS)	Low-spin CFSE	Unpaired (LS)
d^1	-0.4	1	—	—
d^2	-0.8	2	—	—
d^3	-1.2	3	—	—
d^4	-0.6	4	$-1.6 + P$	2
d^5	0	5	$-2.0 + 2P$	1
d^6	-0.4	4	$-2.4 + 2P$	0
d^7	-0.8	3	$-1.8 + P$	1
d^8	-1.2	2	—	—
d^9	-0.6	1	—	—

Quick Tip

CFSE is the gain in stability relative to the spherical (barycentre) field. The more negative the CFSE (in Δ_o units), the more stable the complex — which is why d^6 low-spin (e.g. $[Co(NH_3)_6]^{3+}$) and d^3 (e.g. $[Cr(H_2O)_6]^{3+}$) complexes are unusually stable and inert.

8.2 Chelate Effect and Stability Constants

The **chelate effect** is the enhanced stability of complexes formed by polydentate (chelating) ligands compared with otherwise-similar complexes of unidentate ligands. Quantitatively, the stability constants differ by 4–10 orders of magnitude.

Example: log β for $[Ni(NH_3)_6]^{2+}$ is about 8.6, but log β for $[Ni(en)_3]^{2+}$ is about 18.3 — ten orders of magnitude larger, even though en is just two NH_3-like donors tethered together.

Origin of the chelate effect

Replacing n unidentate ligands with one n-dentate chelate releases $n-1$ free ligand molecules into solution. The *entropy increase* ($\Delta S > 0$) drives $\Delta G = \Delta H - T\Delta S$ more negative ⇒ larger K. Five- and six-membered chelate rings are most stable (minimum ring strain).

8.3 Number of Geometric and Optical Isomers — Counting Formulae

For octahedral complexes the standard counts are:

- $[Ma_2b_4]$ or $[Ma_4b_2]$ $\rightarrow$ 2 (cis, trans)
- $[Ma_3b_3]$ $\rightarrow$ 2 (fac, mer)
- $[Ma_2b_2c_2]$ $\rightarrow$ 6 (5 distinct + 1 chiral pair)
- $[Mabcdef]$ (all different) $\rightarrow$ 15 pairs of enantiomers = 30 isomers (rarely asked)
- $[M(AA)_3]$ (three didentate, like $Co(en)_3$) $\rightarrow$ 2 (d and l, both chiral)
- $[M(AA)_2b_2]$ $\rightarrow$ 3 (cis-d, cis-l, trans)

For square-planar [MABCD] (four *different* unidentate ligands), there are **3 geometric isomers**, none of which is optically active (square planar with a mirror plane through the metal).

8.4 Jahn-Teller Distortion (Brief)

If a degenerate electronic state would be the ground state, a non-linear molecule distorts to lift the degeneracy and lower its energy. This is the **Jahn-Teller theorem**, and its imprint on coordination chemistry is widespread.

- Strong distortion occurs for d^9 (Cu^{2+}), low-spin d^7, and high-spin d^4 — the e_g orbitals are unevenly occupied.
- Weak distortion for unequally filled t_{2g} sets (d^1, d^2, low-spin d^4, d^5).
- Net effect: octahedral [Cu(H$_2$O)$_6$]$^{2+}$ is tetragonally distorted — two axial M–O bonds are longer than four equatorial ones. This shows up in the absorption spectrum as a broad asymmetric band.

8.5 18-Electron Rule for Organometallics

A useful electron-counting trick for low-oxidation-state complexes: count metal d electrons + lone pairs donated by ligands. The stable complex usually has 18 valence electrons (filled $nd, (n+1)s, (n+1)p$).

Verify for [Ni(CO)$_4$]: Ni(0) contributes 10 ($3d^{10}$); four CO donate 2 each = 8. Total = 18. ✓
Verify for [Cr(CO)$_6$]: Cr(0) contributes 6 ($3d^5 4s^1 = 6$); six CO donate 12. Total = 18. ✓
Verify for [Fe(CO)$_5$]: Fe(0) contributes 8; five CO donate 10. Total = 18. ✓

9 Quick Reference Summary

9.1 Key formulae and constants

Master sheet

1. **Oxidation number balance:** Charge on complex $=$ Ox. state of metal $+ \sum$ ligand charges.
2. **Spin-only magnetic moment:** $\mu_s = \sqrt{n(n+2)}$ BM.
3. **Octahedral splitting:** $E(e_g) = +\frac{3}{5}\Delta_o$; $E(t_{2g}) = -\frac{2}{5}\Delta_o$.
4. **Tetrahedral splitting:** $\Delta_t = \frac{4}{9}\Delta_o$.
5. **Strong-field condition (low-spin):** $\Delta_o > P$.
6. **Weak-field condition (high-spin):** $\Delta_o < P$.
7. **CFSE (oct):** $[-0.4\,n_{t_{2g}} + 0.6\,n_{e_g}]\Delta_o + mP$.

9.2 Hybridisation → geometry summary

CN	Hybridisation	Geometry	Example
2	sp	Linear	$[Ag(NH_3)_2]^+$
4	sp^3	Tetrahedral	$[NiCl_4]^{2-}$, $[Ni(CO)_4]$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
5	sp^3d	Trigonal bipyramidal	$[Fe(CO)_5]$
6	d^2sp^3	Octahedral (inner / low-spin)	$[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$
6	sp^3d^2	Octahedral (outer / high-spin)	$[CoF_6]^{3-}$, $[FeF_6]^{3-}$

9.3 Spectrochemical series (memorise)

Field strength, weak → strong

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

9.4 Magnetic-moment lookup

Unpaired e⁻ (n)	μ_s (BM)	Behaviour
0	0	Diamagnetic
1	1.73	Paramagnetic
2	2.83	Paramagnetic
3	3.87	Paramagnetic
4	4.90	Strongly paramagnetic
5	5.92	Very strongly paramagnetic

9.5 Common ambidentate ligands and their two names

Ligand	Bound through	IUPAC name
NO_2^-	N	nitrito-N (older: nitro)
NO_2^-	O	nitrito-O (older: nitrito)
SCN^-	S	thiocyanato-S (older: thiocyanato)
SCN^-	N	thiocyanato-N (older: isothiocyanato)
CN^-	C (usually)	cyanido-C
CN^-	N (rare)	cyanido-N (isocyanido)

Final exam-day reminders

- Always identify the *oxidation state of the metal* first — everything else (electronic configuration, d^n, geometry, magnetism, colour) follows from it.
- For magnetism questions, decide **weak-field or strong-field** first → then high-spin/low-spin → then count unpaired electrons → then μ_s.
- For colour, remember d^0 and d^{10} are colourless — there is no electron to promote or no empty e_g slot.
- For isomer-counting questions, draw the structures: don't guess. Six possible answers for [$Ma_2b_2c_2$] is too many to memorise as a formula.
- IUPAC names: alphabetise ligands ignoring di/tri/tetra prefixes (so "*di*amminechlorido" alphabetises under A, not D).