Collegedunia NCERT Formula Sheet

The Ultimate Formula Reference for Class 12 (12th) Chemistry — NCERT 2026-27

Chapter 5: Coordination Compounds

Werner's Theory · Ligands · IUPAC Nomenclature · Isomerism · VBT · CFT · CFSE · Magnetism & Colour · Metal Carbonyls

Key Data & Symbols for this Chapter

Quantity / Symbol	Value / Form	Meaning / Note
Coordination number (CN)	2, 4, 6 (most common)	Number of donor atoms bonded to the central metal
CFSE (octahedral)	$[-0.4\,n_{t_{2g}} + 0.6\,n_{e_g}]\,\Delta_o$	Net stabilisation from d-orbital splitting
Crystal-field splitting	$\Delta_t \approx \frac{4}{9}\,\Delta_o$	Tetrahedral splitting always smaller
Spin-only moment	$\mu = \sqrt{n(n+2)}$ BM	n = unpaired electrons; 1 BM $= 9.274 \times 10^{-24}$ J T^{-1}
Spectrochemical series	weak $\rightarrow$ strong field	$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< CN^- <$ CO
Pairing-energy rule	Strong field ($\Delta_o > P$): **LS**; Weak field ($\Delta_o < P$): **HS**	Decides d^4–d^7 octahedral spin state
EAN rule (Sidgwick)	EAN $= Z -$ O.S. $+ 2 \times$ CN	Stable carbonyls usually obey EAN $=$ noble-gas number

1 Werner's Theory & Basic Definitions (NCERT 5.1–5.2)

Werner (1898) explained the structure of cobalt-ammine complexes by proposing that a metal exhibits **two kinds of valence**—a primary (ionisable) valence and a secondary (non-ionisable) valence. The secondary valence is fixed for a metal and equals the modern **coordination number**.

Primary vs. secondary valence (Werner)

Primary valence = oxidation number; satisfied by negative counter-ions *outside* the bracket; ionisable.

Secondary valence = coordination number; satisfied by ligands directly bonded to the metal *inside* the bracket; non-ionisable, fixed for a metal.

Example: in $[Co(NH_3)_6]Cl_3$, primary valence $= \mathbf{3}$ (three Cl^- outside), secondary valence $= \mathbf{6}$ (six NH_3 inside). All three Cl^- are precipitated by $AgNO_3$.

Cobalt(III)–ammine series (NCERT Table 5.1)

$[Co(NH_3)_6]Cl_3$ (yellow): 1:3 electrolyte, gives **3 mol AgCl**
$[CoCl(NH_3)_5]Cl_2$ (purple): 1:2 electrolyte, gives **2 mol AgCl**
$[CoCl_2(NH_3)_4]Cl$ (green/violet): 1:1 electrolyte, gives **1 mol AgCl**
Conductivity $\propto$ number of ions per formula unit; only ions *outside* the coordination sphere are free in solution. Green and violet isomers are **cis/trans** geometrical isomers.

Key terminology (NCERT 5.2)

Coordination entity: the bracketed unit, e.g. $[Fe(CN)_6]^{4-}$. **Central atom/ion**: the metal at the centre. **Ligand**: the donor species bonded to the metal. **Coordination number (CN)**: number of σ-donor atoms bonded to the metal (only σ counted; π-bonds ignored). **Coordination sphere**: bracketed metal + ligands (a single, non-dissociable unit). **Counter ion**: the ion(s) outside the bracket. **Coordination polyhedron**: the 3-D geometry traced by donor atoms (octahedron, tetrahedron, square plane, etc.). **Oxidation number** of the metal: charge it would carry if all ligands were removed as closed-shell species. **Homoleptic**: only one kind of ligand (e.g. $[Co(NH_3)_6]^{3+}$). **Heteroleptic**: more than one kind of ligand (e.g. $[CoCl_2(NH_3)_4]^+$).

Oxidation number of central metal

For $[M(L_1)_a(L_2)_b]^q$: $\text{O.S.(M)} = q - (a\,c_1 + b\,c_2)$
where c_i = charge on ligand L_i and q = overall charge on the complex.
Example: $[Fe(CN)_6]^{4-} \Rightarrow x + 6(-1) = -4 \Rightarrow x = +2$ (Fe is in $+2$). Neutral ligands (H_2O, NH_3, CO) contribute zero.

Effective Atomic Number (EAN; Sidgwick rule)

$\text{EAN} = Z_\text{M} - \text{O.S.} + 2\,(\text{CN})$
Stable low-O.S. complexes (especially carbonyls) tend to have EAN equal to the atomic number of the **next noble gas** (Kr 36, Xe 54, Rn 86).
Worked: $[Fe(CN)_6]^{4-}$: EAN $= 26 - 2 + 2(6) = 36$ (Kr) ✓. $[Ni(CO)_4]$: $28 - 0 + 8 = 36$ (Kr). $[PtCl_6]^{2-}$: $78 - 4 + 12 = 86$ (Rn). EAN may fail for non-carbonyl complexes but is a quick sanity check.

2 Classification of Ligands (NCERT 5.2)

Ligands are classified by (a) the number of donor atoms they offer to one metal centre (denticity) and (b) the nature of bonding (σ only vs. $\sigma + \pi$).

Denticity classes

Monodentate: one donor atom (e.g. H_2O, NH_3, Cl^-, CN^-, CO).
Bidentate: two donor atoms (e.g. ethane-1,2-diamine **en**, oxalate **ox** $= C_2O_4^{2-}$).
Polydentate: more than two donors; e.g. **EDTA**$^{4-}$ is hexadentate (2 N $+$ 4 O^-).
Ambidentate: one ligand atom *or* another can donate, but not simultaneously: NO_2^- (N → nitrito-N; O → nitrito-O) and SCN^- (S → thiocyanato-S; N → thiocyanato-N).
Chelating: a polydentate ligand that bites the same metal via two or more donors, forming a ring (the *chelate ring*).
Chelate effect: chelating ligands form complexes that are far more stable than those with comparable monodentate ligands, mainly due to a favourable **entropy** change (more particles released into solution).

Common ligand abbreviations (used in IUPAC names)

en $=$ ethane-1,2-diamine, H_2N–CH_2–CH_2–NH_2 (bidentate, neutral).
ox $=$ oxalate, $C_2O_4^{2-}$ (bidentate, $2-$).
acac $=$ acetylacetonate (bidentate, $1-$).
EDTA^{4-} $=$ ethylenediaminetetraacetate (hexadentate, $4-$).
py $=$ pyridine, C_5H_5N (monodentate, neutral).
dien $=$ diethylenetriamine (tridentate, neutral).
bipy (2,2′-bipyridine) and **phen** (1,10-phenanthroline) $=$ bidentate, neutral, strong-field aromatic chelators.
DMG $=$ dimethylglyoximate (bidentate, $1-$) — classic ligand for Ni^{2+} test (rose-red ppt).
CN of metal counts donor *atoms*, not ligand molecules: $[Co(en)_3]^{3+}$ has 3 en but CN $= 6$.

Ambidentate ligand naming convention

A single donor atom is shown with a hyphen and an italic Greek-letter or simple atom label:
NO_2^-: *nitrito-N* (donates via N, written **–NO**$_2$) vs. *nitrito-O* (donates via O, written **–ONO**).
SCN^-: *thiocyanato-S* (donates via S, written **–SCN**) vs. *thiocyanato-N* or *isothiocyanato* (via N, written **–NCS**).
CN^-: *cyanido-C* (via C, normal) vs. *cyanido-N* or *isocyanido* (rare).
These linkage isomers usually differ in colour and IR (ν_{NO} shifts ~ 100 cm^{-1}); cause Δ_o differences along the spectrochemical series.

π-acceptor (back-bonding) ligands

CO, CN^-, NO and isocyanides are **strong-field, π-acceptor** ligands: they donate σ from a lone pair *and* accept electron density from a filled metal d_π orbital into their empty π^* orbital. This **synergic bonding** shortens M–C and lengthens C–O, and explains the high stability of metal carbonyls.

3 IUPAC Nomenclature of Mononuclear Complexes (NCERT 5.3)

The IUPAC name is built in a fixed order: **cation first, anion second** (like any salt); inside the coordination sphere: **ligands first (alphabetical), then metal, then oxidation state in Roman numerals in parentheses**.

Rules for the coordination entity

1. Ligand order: alphabetical order of ligand name; numerical prefixes do *not* affect alphabetisation.
2. Multiplicity prefixes: use *di, tri, tetra,…* for simple ligands; use *bis, tris, tetrakis,…* (with parentheses) for ligands whose names already contain di/tri/poly or for complicated names (e.g., *bis(ethane-1,2-diamine)* for 2 en).
3. Anionic ligands end in **-o**: F^- fluorido, Cl^- chlorido, Br^- bromido, I^- iodido, CN^- cyanido, OH^- hydroxido, O^{2-} oxido, NO_2^- nitrito-N or nitrito-O, SO_4^{2-} sulfato.
4. Neutral ligands keep their molecular name, with four exceptions:
$H_2O \to$ *aqua*, $NH_3 \to$ *ammine*, CO $\to$ *carbonyl*, NO $\to$ *nitrosyl*.
5. Cationic ligands end in **-ium** (rare in NCERT).
6. Metal name: unchanged in a cationic/neutral complex; takes the **-ate** suffix in an anionic complex (Fe $\to$ ferrate, Cu $\to$ cuprate, Pb $\to$ plumbate, Ag $\to$ argentate, Au $\to$ aurate, Sn $\to$ stannate).
7. Oxidation state of the metal in Roman numerals, in parentheses, immediately after the metal: e.g. cobalt(III).
8. Charge on complex may be shown after the metal name as an Arabic numeral with sign in parentheses (Ewens–Bassett system).
9. Formula writes the metal symbol first, then ligands in alphabetical order of donor-atom sym-

bols/abbreviation; the full coordination entity is enclosed in square brackets.

Worked examples (NCERT 5.3)

$[Cr(NH_3)_3(H_2O)_3]Cl_3$ triamminetriaquachromium(III) chloride
$[Co(en)_3]_2(SO_4)_3$ tris(ethane-1,2-diamine)cobalt(III) sulfate
$[Ag(NH_3)_2][Ag(CN)_2]$ diamminesilver(I) dicyanidoargentate(I)
$K_4[Fe(CN)_6]$ potassium hexacyanidoferrate(II)
$K_2[PdCl_4]$ potassium tetrachloridopalladate(II)
$[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ diamminechlorido(methylamine)platinum(II) chloride
Always identify (i) the metal O.S. from the overall charge, then (ii) alphabetise ligand names, then (iii) attach multiplicity prefixes *after* alphabetising.

Frequent nomenclature traps

• **Alphabetising** uses the ligand name *without* the multiplicity prefix — so *tri*ammine sorts under 'a' (ammine), not 't'. • The metal's O.S. is the *Roman* numeral; the complex *charge* (if shown) is Arabic. • Use *bis/tris* for en, ox, etc., because their names already contain a numerical prefix. • In the *formula*, ligands are listed alphabetically by donor-atom symbol (Cl before NH_3), but in the *name* they are listed alphabetically by ligand name.

4 Isomerism in Coordination Compounds (NCERT 5.4)

Coordination compounds show two large families of isomerism: **stereoisomerism** (same connectivity, different spatial arrangement) and **structural isomerism** (different connectivity).

Stereoisomerism — geometrical (cis/trans, fac/mer)

Square planar $[Ma_2b_2]$: *cis* (like ligands adjacent, $90°$) and *trans* (like ligands opposite, $180°$). Example: cisplatin $=$ *cis*-$[Pt(NH_3)_2Cl_2]$ (anti-cancer; *trans* isomer inactive).
Octahedral $[Ma_4b_2]$: *cis* (the two b at $90°$) and *trans* ($180°$).
Octahedral $[Ma_3b_3]$: *fac* (three a on the same face of the octahedron) and *mer* (three a along the meridian).
Octahedral $[M(AA)_2b_2]$ (AA $=$ symmetric bidentate, e.g. en): *cis* and *trans*; the *cis* is also *chiral*.
Tetrahedral $[Ma_2b_2]$ **does not** show cis/trans (no plane to compare against). Square-planar $[Mabcd]$ shows three isomers.

Stereoisomerism — optical (chirality)

A complex is **chiral** (optically active) if its mirror image is non-superimposable on itself. Common chiral complexes:
$[Co(en)_3]^{3+}$ (only Δ/Λ enantiomers — no geometrical isomerism).
cis-$[Co(en)_2Cl_2]^+$ (chiral); *trans*-$[Co(en)_2Cl_2]^+$ (not chiral, has a mirror plane).
cis-$[PtCl_2(en)_2]^{2+}$ (chiral).
Tetrahedral $[Mabcd]$ with four different ligands is also chiral, but such complexes are rare for transition metals; common in main-group and biochemistry (e.g., chiral phosphorus).

Structural isomerism — four NCERT types

1. Linkage isomerism: an ambidentate ligand attaches via different donor atoms. Example: $[Co(NH_3)_5(NO_2)]Cl_2$ (nitrito-N, yellow) vs. $[Co(NH_3)_5(ONO)]Cl_2$ (nitrito-O, red).
2. Coordination isomerism: in salts where *both* cation and anion are complex, the ligands swap between the two metal centres. Example: $[Co(NH_3)_6][Cr(CN)_6]$ vs. $[Cr(NH_3)_6][Co(CN)_6]$.
3. Ionisation isomerism: a ligand and a counter-ion swap places, giving different ions in solution.

Example: $[Co(NH_3)_5(SO_4)]Br$ vs. $[Co(NH_3)_5Br]SO_4$ (one gives Br^-, the other SO_4^{2-} on dissolution).
4. Solvate (hydrate) isomerism: water moves between the coordination sphere and the lattice. Example: $[Cr(H_2O)_6]Cl_3$ (violet), $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (blue-green), $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (dark green). The four can be summarised: linkage = different donor atom; coordination = ligand swap between two complex ions; ionisation = ligand ↔ counter-ion swap; solvate = water in vs. out of the sphere.

Cis/trans counting in $[\mathrm{M}a_4b_2]$

Only **2** geometrical isomers exist (*cis*: b–b at $90°$; *trans*: b–b at $180°$). You can never get a third because the remaining 4 sites for a are fixed once the two b are placed.

5 Valence Bond Theory (VBT) (NCERT 5.5)

VBT (Pauling) treats bonding in a complex as the donation of a ligand lone pair into a set of **empty hybrid orbitals** on the metal. Hybridisation ⇔ geometry; the number of unpaired electrons in the metal d-shell decides magnetism.

Hybridisation ↔ geometry (NCERT Table 5.2)

CN 2: $sp \Rightarrow$ linear; e.g. $[Ag(NH_3)_2]^+$, $[CuCl_2]^-$.
CN 4 tetrahedral: sp^3; e.g. $[NiCl_4]^{2-}$, $[Ni(CO)_4]$.
CN 4 square planar: dsp^2; e.g. $[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_2Cl_2]$.
CN 5 trigonal bipyramidal: dsp^3 or sp^3d; e.g. $[Fe(CO)_5]$.
CN 6 octahedral, inner orbital (d^2sp^3): uses inner $(n-1)d$, so low-spin/strong field; e.g. $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$.
CN 6 octahedral, outer orbital (sp^3d^2): uses outer nd, high-spin/weak field; e.g. $[FeF_6]^{3-}$, $[CoF_6]^{3-}$.
"Inner orbital" $=$ pair-up electrons first to free inner $(n-1)d$ orbitals (strong-field ligand). "Outer orbital" $=$ keep all d-electrons unpaired and use outer nd (weak-field ligand).

Magnetic moment (spin-only)

$\mu_{\text{s.o.}} = \sqrt{n(n+2)}$ BM
where n = number of unpaired electrons; 1 Bohr magneton (BM) $= 9.274 \times 10^{-24}$ J T^{-1}.
Predicted values: $n = 1, 2, 3, 4, 5 \Rightarrow \mu = 1.73, 2.83, 3.87, 4.90, 5.92$ BM. Diamagnetic if $n = 0$. Spin-only formula is accurate for 3d ions; for 4d/5d ions and lanthanoids, orbital contribution becomes significant.

Worked VBT examples

$[CoF_6]^{3-}$: Co^{3+} is $3d^6$; F^- weak field $\Rightarrow$ **no pairing**, 4 unpaired, sp^3d^2, **outer-orbital**, paramagnetic, $\mu \approx 4.90$ BM.
$[Co(NH_3)_6]^{3+}$: Co^{3+} is $3d^6$; NH_3 strong field $\Rightarrow$ pair to t_{2g}^6, 0 unpaired, d^2sp^3, **inner-orbital**, diamagnetic.
$[NiCl_4]^{2-}$: Ni^{2+} is $3d^8$; Cl^- weak field $\Rightarrow sp^3$ tetrahedral, 2 unpaired, $\mu \approx 2.83$ BM.
$[Ni(CN)_4]^{2-}$: Ni^{2+} is $3d^8$; CN^- strong field $\Rightarrow$ pairs the two e_g-like electrons, dsp^2 square-planar, diamagnetic.

Limitations of VBT (NCERT 5.5.2)

• Cannot quantitatively explain magnetic data of all complexes. • Does not predict or explain **colour**. • Cannot account for the *kinetic* stability difference between similar complexes. • Does not distinguish weak-field vs. strong-field ligands in advance; one must *know* the magnetic data to assign inner-/outer-orbital. • Gives no insight into the **relative strengths** of metal–ligand bonds.

6 Crystal Field Theory — Octahedral (NCERT 5.6.1)

CFT treats ligands as point negative charges (or dipoles) that electrostatically destabilise the metal d-orbitals. The five degenerate d-orbitals **split** in the ligand field; the splitting pattern is fixed by the geometry, and the size of the gap, Δ, depends on the ligand.

Octahedral splitting: t_{2g} & e_g

d_{xy}, d_{yz}, d_{xz} **between** the x, y, z axes $\rightarrow$ stabilised, labelled $\mathrm{t_{2g}}$.
$d_{x^2-y^2}, d_{z^2}$ **along** the axes (point at ligands) $\rightarrow$ destabilised, labelled $\mathrm{e_g}$.
Energy gap: Δ_o (also called $10\,Dq$).
Relative energies (barycentre-conserving): $E(t_{2g}) = -0.4\,\Delta_o$; $E(e_g) = +0.6\,\Delta_o$.
"t_{2g} down by $-2/5\,\Delta_o$, e_g up by $+3/5\,\Delta_o$" is the standard NCERT diagram. The three t_{2g} and two e_g orbitals keep the same total energy as before splitting.

High-spin vs. low-spin (octahedral d^4–d^7)

Let **P** $=$ pairing energy (electron–electron repulsion cost) and $\Delta_o =$ crystal-field splitting.
$\Delta_o < P$ (weak field): electrons go to e_g first $\Rightarrow$ **high spin (HS)**, maximum unpaired electrons.
$\Delta_o > P$ (strong field): electrons pair within t_{2g} first $\Rightarrow$ **low spin (LS)**, minimum unpaired electrons.
$d^1, d^2, d^3, d^8, d^9, d^{10}$ are **spin-state invariant** in octahedral fields (only one possible filling). HS/LS choice arises only for d^4, d^5, d^6, d^7.

Spectrochemical series (increasing Δ_o)

$\mathrm{I^-} < \mathrm{Br^-} < \mathrm{S^{2-}} < \mathrm{SCN^-} < \mathrm{Cl^-} < \mathrm{NO_3^-} < \mathrm{F^-} < \mathrm{OH^-} < \mathrm{C_2O_4^{2-}} < \mathrm{H_2O}$
$< \mathrm{NCS^-} < \mathrm{EDTA^{4-}} < \mathrm{NH_3} < \mathrm{en} < \mathrm{bipy} < \mathrm{phen} < \mathrm{NO_2^-} < \mathrm{CN^-} < \mathrm{CO}$.
Empirical and metal-independent (approximately). **$\mathrm{CN^-}$ and CO** are the strongest field ligands (extra π-back-bonding); **halides** are the weakest (purely σ donors with low charge density per donor atom).

CFSE (octahedral)

$\mathrm{CFSE} = \left[\,-0.4\,n_{t_{2g}} + 0.6\,n_{e_g}\,\right]\Delta_o + p\,P$
where $n_{t_{2g}}, n_{e_g}$ are the electron counts in each set and p is the number of *extra* paired electrons beyond the free-ion ground state. The pP correction is often dropped at NCERT level.
Useful comparison: d^3 HS $\Rightarrow$ CFSE $= -1.2\,\Delta_o$; d^6 LS $\Rightarrow$ $-2.4\,\Delta_o$; d^5 HS $\Rightarrow$ 0 (no net stabilisation, which is why high-spin $\mathrm{Mn^{2+}}$ and $\mathrm{Fe^{3+}}$ complexes are colourless or only faintly coloured).

CFSE table (octahedral, all d^n)

d^n	HS config	HS CFSE	LS config	LS CFSE
d^1	t_{2g}^1	$-0.4\Delta_o$	—	—
d^2	t_{2g}^2	$-0.8\Delta_o$	—	—
d^3	t_{2g}^3	$-1.2\Delta_o$	—	—
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_o$	t_{2g}^4	$-1.6\Delta_o + P$
d^5	$t_{2g}^3 e_g^2$	0	t_{2g}^5	$-2.0\Delta_o + 2P$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_o$	t_{2g}^6	$-2.4\Delta_o + 2P$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_o$	$t_{2g}^6 e_g^1$	$-1.8\Delta_o + P$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_o$	—	—
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_o$	—	—
d^{10}	$t_{2g}^6 e_g^4$	0	—	—

Maximum CFSE in HS occurs at d^3 and d^8 ($-1.2\Delta_o$); maximum LS at d^6 ($-2.4\Delta_o$) — which is why Co^{3+} (LS d^6) and Cr^{3+} (d^3) form unusually stable, slow-substituting (inert) complexes.

Worked CFT examples

$[Fe(CN)_6]^{4-}$: Fe^{2+}, d^6; CN^- strong field $\Rightarrow t_{2g}^6 e_g^0$, low-spin, $n = 0$, diamagnetic, CFSE $= -2.4\,\Delta_o$.
$[Fe(H_2O)_6]^{2+}$: Fe^{2+}, d^6; H_2O weak field $\Rightarrow t_{2g}^4 e_g^2$, high-spin, $n = 4$, $\mu \approx 4.90$ BM, CFSE $= -0.4\,\Delta_o$.
$[Co(NH_3)_6]^{3+}$: Co^{3+}, d^6; NH_3 strong field $\Rightarrow t_{2g}^6$, LS, diamagnetic, CFSE $= -2.4\,\Delta_o$.
$[Mn(H_2O)_6]^{2+}$: Mn^{2+}, d^5; H_2O weak field $\Rightarrow t_{2g}^3 e_g^2$, HS, $n = 5$, $\mu \approx 5.92$ BM, CFSE $= 0$.

7 CFT — Tetrahedral & Square-Planar (NCERT 5.6.2)

Tetrahedral splitting: e & t_2

In a tetrahedral field the orbital labelling *inverts*:
$d_{x^2-y^2}, d_{z^2}$ point *between* ligand bonds $\rightarrow$ stabilised, labelled e.
d_{xy}, d_{yz}, d_{xz} point *closer to* ligand bonds $\rightarrow$ destabilised, labelled $\mathrm{t_2}$.
Energy gap: $\Delta_t \approx \frac{4}{9}\,\Delta_o$ (for the same metal and same ligands).
Because Δ_t is small, $\Delta_t < P$ *always*: **tetrahedral complexes are practically always high-spin.** No tetrahedral LS examples appear in NCERT.

Square-planar splitting (limiting case)

Order (ascending): $d_{xz}, d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$.
The huge gap between d_{xy} and $d_{x^2-y^2}$ is essentially Δ_o (and is large).
Square-planar geometry is favoured for d^8 ions with strong-field ligands (Ni^{2+}, Pd^{2+}, Pt^{2+}, Au^{3+}) because pairing into the lower four d-levels and leaving $d_{x^2-y^2}$ empty gives maximum CFSE.

Limitations of CFT (NCERT 5.6.4)

- Treats ligands as point charges/dipoles — ignores the *covalent character* of M–L bonding.
- Cannot explain the position of ligands in the spectrochemical series; in particular cannot account for the strong-field nature of neutral π-acceptors (CO, CN^-).
- Does not address π-bonding contributions.
- Predicts anions should be stronger-field than neutral ligands; observation contradicts this for CO, NH_3. The **Ligand Field Theory** (extended MO version) repairs these gaps.

8 Colour & Magnetism (NCERT 5.6.3)

d–d transition ⇒ colour

$\Delta E = \Delta_o = h\nu = \dfrac{hc}{\lambda}$

An electron is promoted from t_{2g} to e_g by absorbing a photon of energy equal to Δ_o. The complex appears in the **complementary** colour of the absorbed wavelength.

Example: $[Ti(H_2O)_6]^{3+}$ absorbs at ~ 498 nm (green–yellow) ⇒ transmitted colour is purple/violet.

Stronger-field ligand ⇒ larger Δ_o ⇒ absorption shifts to shorter λ (blue end) ⇒ transmitted colour shifts towards orange/red.

Why d^0 and d^{10} ions are colourless

With no d-electron to promote (d^0, e.g. Sc^{3+}, Ti^{4+}) or no empty d-orbital to receive a promoted electron (d^{10}, e.g. Zn^{2+}, Cu^{+}, Cd^{2+}, Hg^{2+}), **d–d transitions cannot occur** ⇒ the ion is colourless. Charge-transfer transitions can still give intense colour ($KMnO_4$, $K_2Cr_2O_7$), but those are not d–d.

Magnetic-behaviour summary

Paramagnetic: at least one unpaired d-electron; magnitude follows $\mu = \sqrt{n(n+2)}$ BM.
Diamagnetic: all d-electrons paired; weakly repelled by a magnetic field.
Spin state from ligand (octahedral, d^4–d^7):
weak-field ligand (H_2O, F^-, Cl^-) ⇒ HS ⇒ maximum n.
strong-field ligand (CN^-, CO, NH_3 for Co^{3+}) ⇒ LS ⇒ minimum n.
Worked: $[Co(NH_3)_6]^{3+}$ (d^6, LS) ⇒ $n = 0$, diamagnetic, $\mu = 0$. $[CoF_6]^{3-}$ (d^6, HS) ⇒ $n = 4$, $\mu \approx 4.90$ BM.

9 Bonding in Metal Carbonyls (NCERT 5.7)

Metal carbonyls $[M_x(CO)_y]^q$ are homoleptic complexes of CO with metals in low (often zero) oxidation states. CO is a textbook **σ-donor / π-acceptor** ligand.

Common neutral metal carbonyls

Mononuclear (NCERT Fig. 5.10):
$[Ni(CO)_4]$: tetrahedral, sp^3, diamagnetic, EAN $= 36$ (Kr).
$[Fe(CO)_5]$: trigonal bipyramidal, dsp^3, diamagnetic, EAN $= 36$ (Kr).
$[Cr(CO)_6]$: octahedral, d^2sp^3, diamagnetic, EAN $= 36$ (Kr).
Binuclear: $[Mn_2(CO)_{10}]$, $[Co_2(CO)_8]$, $[Fe_2(CO)_9]$ — contain M–M bonds and/or bridging CO.
EAN $= Z_{\mathrm{M}} - \text{O.S.} + 2(\text{CN})$. All three mononuclear NCERT carbonyls satisfy the 18-electron / noble-gas rule.

Synergic σ/π bonding in M–CO

σ donation: lone pair on C of CO → empty metal hybrid orbital (M–CO σ bond).
π^* back-donation: filled metal d_π orbital → empty π^* orbital on CO.
Net: **shortens M–C** (extra π character) and **lengthens C–O** (population of antibonding π^*).
IR signature: free CO stretches at ~ 2143 cm^{-1}; coordinated CO (terminal) stretches at 1850–2125 cm^{-1} — lowered by back-bonding. Bridging CO stretches even lower (~ 1750–1850 cm^{-1}).

Why CO stabilises low oxidation states

A low-O.S. metal has many filled d-orbitals available for back-donation; this back-donation lowers the metal's electron density (delocalising it onto CO π^*) and stabilises what would otherwise be an electron-rich centre. That is why M(0) carbonyls exist but M(+3) carbonyls do not.

10 Stability of Complexes & Applications (NCERT 5.8–5.9)

Stepwise & overall stability constants

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML}: \quad K_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}$$

$$\mathrm{ML}_{n-1} + \mathrm{L} \rightleftharpoons \mathrm{ML}_n: \quad K_n = \frac{[\mathrm{ML}_n]}{[\mathrm{ML}_{n-1}][\mathrm{L}]}$$

Overall (cumulative): $\beta_n = K_1 K_2 \cdots K_n = \dfrac{[\mathrm{ML}_n]}{[\mathrm{M}][\mathrm{L}]^n}$

Generally $K_1 > K_2 > \cdots > K_n$ (statistical and electrostatic reasons). Large $\beta_n \Rightarrow$ thermodynamically stable complex; e.g. β_4 for $[\mathrm{Cu(NH_3)_4}]^{2+} \approx 4.5 \times 10^{11}$.

Factors affecting stability

- **Charge & size of M**: high charge density (small, highly-charged ion) ⇒ greater stability (e.g. $\mathrm{Fe^{3+}} > \mathrm{Fe^{2+}}$ with the same ligand).
- **Nature of ligand**: π-acceptors and chelators give the most stable complexes.
- **Chelate effect**: bidentate / polydentate $\gg$ comparable monodentate (entropy-driven).
- **Macrocyclic effect**: macrocyclic ligands (porphyrins, crown ethers) are even more stabilising than open-chain chelators.

Important applications (NCERT 5.9)

Biological: chlorophyll ($\mathrm{Mg^{2+}}$ in a porphyrin), haemoglobin ($\mathrm{Fe^{2+}}$ in a porphyrin), vitamin $\mathrm{B_{12}}$ ($\mathrm{Co^{3+}}$ in corrin).

Metallurgy: Ag/Au extraction via $[\mathrm{Ag(CN)_2}]^-$ and $[\mathrm{Au(CN)_2}]^-$ (Mac-Arthur–Forrest); Ni purification via $[\mathrm{Ni(CO)_4}]$ (Mond process).

Analytical: EDTA titration for hardness of water; DMG for $\mathrm{Ni^{2+}}$ detection (rose-red ppt); $[\mathrm{Fe(SCN)}]^{2+}$ blood-red for $\mathrm{Fe^{3+}}$.

Medicinal: cis-platin, *cis*-$[\mathrm{PtCl_2(NH_3)_2}]$ — anti-cancer; EDTA chelation therapy for lead/mercury poisoning.

Industrial: catalysts (Wilkinson's $[\mathrm{RhCl(PPh_3)_3}]$ for hydrogenation); electroplating from $[\mathrm{Ag(CN)_2}]^-$, $[\mathrm{Au(CN)_2}]^-$.

Photography: fixing of film uses $\mathrm{Na_3[Ag(S_2O_3)_2]}$ (sodium thiosulfato-argentate).

JEE / NEET Extension — 18-electron rule

For low-oxidation-state organometallics, total valence-electron count at the metal $= n(d) + 2 \times (\mathrm{CN}) = 18$ for the most stable species. Use it to predict CN of an unknown carbonyl: e.g. $\mathrm{V(CO)}_x$ neutral ⇒ V ($\mathrm{d^5}$) contributes 5 ⇒ need 13 more ⇒ $x = 13/2 = 6.5$, non-integer ⇒ the stable species is the dimer or the anion $[\mathrm{V(CO)_6}]^-$.

Spectrochemical-series mnemonic

"**I** **Br**ought **Cl**ay **F**or **O**ur **H**ouse, **N**ow **En**joy **C**old **N**ights **C**osily" for: $\mathrm{I^-} < \mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{F^-} < \mathrm{OH^-} < \mathrm{H_2O} < \mathrm{NH_3} < \mathrm{en} < \mathrm{NO_2^-} < \mathrm{CN^-} < \mathrm{CO}$. Left half = HS (weak field); right half = LS (strong field).