JEE MAIN · PAPER 1 · CHEMISTRY

12 Coordination Compounds

Formula & concept sheet

Complexes from the ground up: Werner’s theory, ligands and denticity, naming and formulae, isomerism (structural and stereo), bonding by valence bond theory and crystal field theory, colour and magnetism, metal carbonyls and the uses of complexes. Each idea is explained first, then the tables, counting rules and traps.

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READ ALONGSIDE NCERT XII · Coordination Compounds

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

CHAPTER 12

Coordination Compounds

NCERT XII · Coordination Compounds

Covers: Werner's theory · ligands, coordination number, oxidation state, EAN · IUPAC nomenclature · structural and stereoisomerism · valence bond theory (hybridisation, inner and outer orbital) · crystal field theory (Δ_o, Δ_t, CFSE, high and low spin) · colour · metal carbonyls · stability and applications.

1 Werner's theory, ligands and counting

- A **coordination compound** has a central metal atom or ion bonded to a fixed number of **ligands** (ions or molecules that donate an electron pair). The metal and ligands inside the square bracket form the **coordination sphere**; the ions outside are **counter-ions**, which ionise in water.
- **Werner**: a metal has a **primary valency** (the oxidation state, ionisable, satisfied by anions) and a **secondary valency** (the coordination number, non-ionisable, directional, fixes the geometry). $CoCl_3 \cdot 6\,NH_3$ (yellow) gives $3\ AgCl$, $CoCl_3 \cdot 5\,NH_3$ (purple) gives 2, $CoCl_3 \cdot 4\,NH_3$ (green or violet) gives 1: the chloride that precipitates is the one outside the bracket.

LIGAND TYPES

- **Monodentate**: H_2O, NH_3, CO, Cl^-, CN^-, pyridine.
- **Bidentate**: en (ethane-1,2-diamine), oxalate $C_2O_4^{2-}$, glycinate (unsymmetrical), acac, dmg.
- **Polydentate**: $EDTA^{4-}$ is hexadentate.
- **Ambidentate**: NO_2^- (N or O), SCN^- (S or N), CN^-/NC^-.

TERMS

- **Coordination number** = number of donor atoms bonded (a bidentate counts 2).
- **Oxidation state**: charge of complex $= x + \sum$ ligand charges.
- **Chelate**: ring formed by a polydentate ligand; five- and six-membered rings are the most stable (chelate effect).
- **Homoleptic**: one kind of ligand; **heteroleptic**: more than one.

EFFECTIVE ATOMIC NUMBER

$$\text{EAN} = Z - (\text{ox. state}) + 2 \times \text{CN}$$

stable when EAN $= 36$ (Kr): $[Fe(CN)_6]^{4-}$: $26 - 2 + 12 = 36$; $[Co(NH_3)_6]^{3+}$: $27 - 3 + 12 = 36$

COUNTING RULES

- Moles of $AgCl$ from 1 mol complex $=$ number of Cl^- **outside** the bracket; molar conductance rises with the number of ions. $[Cr(H_2O)_4Cl_2]Cl$ gives $1\ AgCl$.
- Oxidation state of Fe in $[Fe(CN)_6]^{3-}$: $x - 6 = -3$, so $+3$; in $[Fe(CO)_5]$: 0.
- 18-electron rule for carbonyls: metal valence electrons $+2$ per CO $(+1$ per $M{-}M$ bond$) = 18$: $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$; $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ need an $M{-}M$ bond.

QUICK CHECK

$[Fe(NH_3)_x(CN)_y]^-$ is an iron(III) complex with no electron in e_g. Find $x + y$.

Answer: Charge: $3 - y = -1$, $y = 4$; octahedral so CN $= 6$, $x = 2$; $x + y = 6$ (low spin, t_{2g}^5).

2 Nomenclature

IUPAC NAMING

1. Cation first, then anion; inside the bracket: **ligands in alphabetical order** (ignore the multiplying prefix), then the metal, then its oxidation state in Roman numerals.
2. Anionic ligands end in -ido/-ato/-ito: chlorido, cyanido, hydroxido, oxalato, nitrito-N, sulfato. Neutral: aqua (H_2O), ammine (NH_3 with two m), carbonyl, nitrosyl; others keep their name (ethane-1,2-diamine, pyridine).
3. Prefixes di, tri, tetra; bis, tris, tetrakis (with brackets) for ligands whose own names contain a prefix. If the complex is an anion the metal ends in **-ate**, with Latin roots: Fe ferrate, Cu cuprate, Ag argentate, Au aurate, Pb plumbate, Sn stannate; others cobaltate, nickelate, chromate, zincate, platinate.

EXAMPLES

FORMULA	NAME
$[Co(NH_3)_5Cl]Cl_2$	pentaamminechloridocobalt(III) chloride
$K_3[Fe(CN)_6]$	potassium hexacyanidoferrate(III)
$[Cr(H_2O)_4Cl_2]Cl$	tetraaquadichloridochromium(III) chloride
$[PtBr_2(PMe_3)_2]$	dibromidobis(trimethylphosphine)platinum(II)
$[Ni(CO)_4]$	tetracarbonylnickel(0)
$K_4[Fe(CN)_6]$	potassium hexacyanidoferrate(II)
$Na_2[Zn(OH)_4]$	sodium tetrahydroxidozincate(II)

TRAP

"Alphabetical" uses the name without the multiplying prefix: tetraaqua sits under *a*, dichlorido under *c*. **Ammine** (NH_3, two m) is not the organic **amine**. An anionic complex takes the "-ate" form of the metal and the oxidation state follows it.

QUICK CHECK

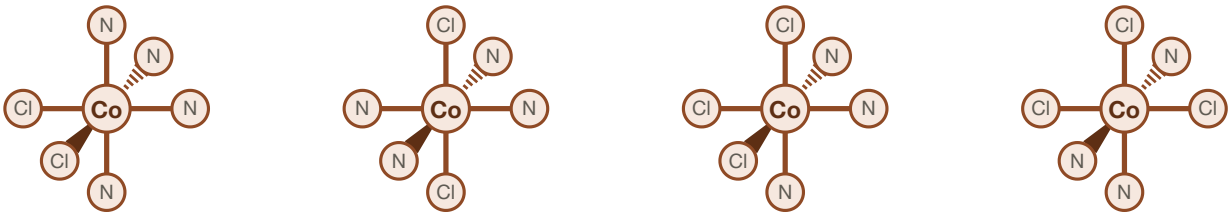
Formula of potassium tetrachloridonickelate(II) and of diamminedichloridoplatinum(II).

Answer: $K_2[NiCl_4]$ (charge $+2-4=-2$ balanced by $2\,K^+$); $[Pt(NH_3)_2Cl_2]$.

3 Isomerism

STRUCTURAL ISOMERISM

TYPE	EXAMPLE
ionisation	$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$ (different ions in solution: Br^- or SO_4^{2-})
linkage	$[Co(NH_3)_5(NO_2)]^{2+}$ (nitrito-N, yellow) and $[Co(NH_3)_5(ONO)]^{2+}$ (nitrito-O, red): needs an ambidentate ligand
coordination	$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$: ligands exchanged between the two metals
hydrate (solvate)	$[Cr(H_2O)_6]Cl_3$ violet, $[Cr(H_2O)_5Cl]Cl_2\cdot H_2O$ grey-green, $[Cr(H_2O)_4Cl_2]Cl\cdot 2\,H_2O$ dark green: water inside or outside



cis-$[Co(NH_3)_4Cl_2]^+$ trans-$[Co(NH_3)_4Cl_2]^+$ fac-$[Co(NH_3)_3Cl_3]$ mer-$[Co(NH_3)_3Cl_3]$

geometrical isomerism in octahedral MA_4B_2 (cis, trans) and MA_3B_3 (fac, mer)

ISOMER COUNTS (OCTAHEDRAL; A, B, C MONODENTATE; AA SYMMETRIC BIDENTATE)

TYPE	GEOMETRICAL	TOTAL STEREOISOMERS
MA_6, MA_5B	1	1
MA_4B_2	2 (cis, trans)	2
MA_3B_3	2 (fac, mer)	2
MA_4BC	2	2
$MA_2B_2C_2$	5	6 (all-cis form chiral)
$M(AA)_2B_2$	2 (cis, trans)	3 (cis pair of enantiomers + trans)
$M(AA)_3$	1	2 (Δ, Λ)
square planar MA_2B_2	2 (cis, trans)	2
square planar $MABCD$	3	3
tetrahedral MA_2B_2 / $MABCD$	1	1 / 2

OPTICAL ISOMERISM

- A complex is optically active if it has **no mirror plane** (non-superimposable on its mirror image): $[M(AA)_3]$ ($[Co(en)_3]^{3+}$) and **cis**-$[M(AA)_2X_2]$ are active; the **trans** forms are inactive.
- Of cis-$[Cr(ox)_2Cl_2]^{3-}$, $[Co(en)_3]^{3+}$, cis-$[Pt(en)_2Cl_2]^{2+}$, cis-$[Co(en)_2Cl_2]^{+}$, trans-$[Pt(en)_2Cl_2]^{2+}$, trans-$[Cr(ox)_2Cl_2]^{3-}$ the **first four** are optically active.

TRAP

Tetrahedral complexes show no geometrical isomerism; square planar MA_2B_2 does (cis-platin $cis-[Pt(NH_3)_2Cl_2]$ is the anticancer drug). Linkage isomerism needs an ambidentate ligand; ionisation isomers give different ions in solution.

4 Valence bond theory

The ligand donates an electron pair into an empty orbital of the metal; the metal orbitals hybridise to match the geometry. Strong-field ligands (CN^-, CO, en, NH_3 with M^{3+}) **pair up** the metal d electrons and use the inner $(n-1)d$ orbitals (**inner-orbital**, low spin); weak-field ligands (F^-, Cl^-, H_2O) leave them unpaired and use the outer nd (**outer-orbital**, high spin).

HYBRIDISATION, GEOMETRY AND MAGNETISM

CN	HYBRID	GEOMETRY	EXAMPLES (UNPAIRED ELECTRONS)
4	sp^3	tetrahedral	$[NiCl_4]^{2-}$ (2), $[Ni(CO)_4]$ (0), $[Zn(NH_3)_4]^{2+}$ (0), $[CoCl_4]^{2-}$ (3)
4	dsp^2	square planar	$[Ni(CN)_4]^{2-}$ (0), $[PtCl_4]^{2-}$ (0), $[Pt(NH_3)_2Cl_2]$ (0), $[Cu(NH_3)_4]^{2+}$ (1)
5	dsp^3	trigonal bipyramidal	$Fe(CO)_5$ (0)
6	d^2sp^3 (inner, low spin)	octahedral	$[Co(NH_3)_6]^{3+}$ (0), $[Fe(CN)_6]^{4-}$ (0), $[Fe(CN)_6]^{3-}$ (1), $[Cr(NH_3)_6]^{3+}$ (3)
6	sp^3d^2 (outer, high spin)	octahedral	$[CoF_6]^{3-}$ (4), $[Fe(H_2O)_6]^{2+}$ (4), $[FeF_6]^{3-}$ (5), $[Mn(H_2O)_6]^{2+}$ (5)

RULES THAT DECIDE IT

- Cr^{3+} (d^3) and Ni^{2+} (d^8) octahedral complexes have the same number of unpaired electrons for any ligand (3 and 2); octahedral Ni^{2+} is always sp^3d^2.
- $Pd(II)$, $Pt(II)$, $Au(III)$ (d^8, $4d/5d$) are square planar even with weak ligands.
- NH_3 gives an inner-orbital complex with Co^{3+} but outer-orbital ones with Co^{2+} and Ni^{2+}.

TRAP

$[Ni(CO)_4]$ is tetrahedral sp^3, diamagnetic (Ni(0), $3d^{10}$); $[Ni(CN)_4]^{2-}$ is square planar dsp^2, diamagnetic; $[NiCl_4]^{2-}$ is tetrahedral and paramagnetic. Tetrahedral complexes are never low spin.

QUICK CHECK

Hybridisation and magnetic moment of $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$.

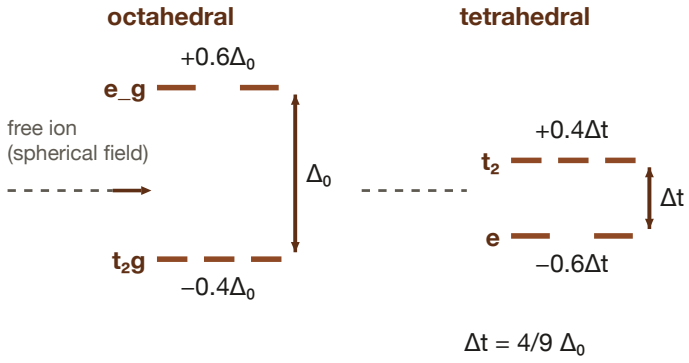
Answer: Both Co^{3+} (d^6). F^- weak: sp^3d^2, 4 unpaired, 4.90 BM. NH_3 strong: d^2sp^3, 0 unpaired, diamagnetic.

QUICK CHECK

Match $K_2[Ni(CN)_4]$, $[Ni(CO)_4]$, $[Co(NH_3)_6]Cl_3$, $Na_3[CoF_6]$ with sp^3, sp^3d^2, dsp^2, d^2sp^3.

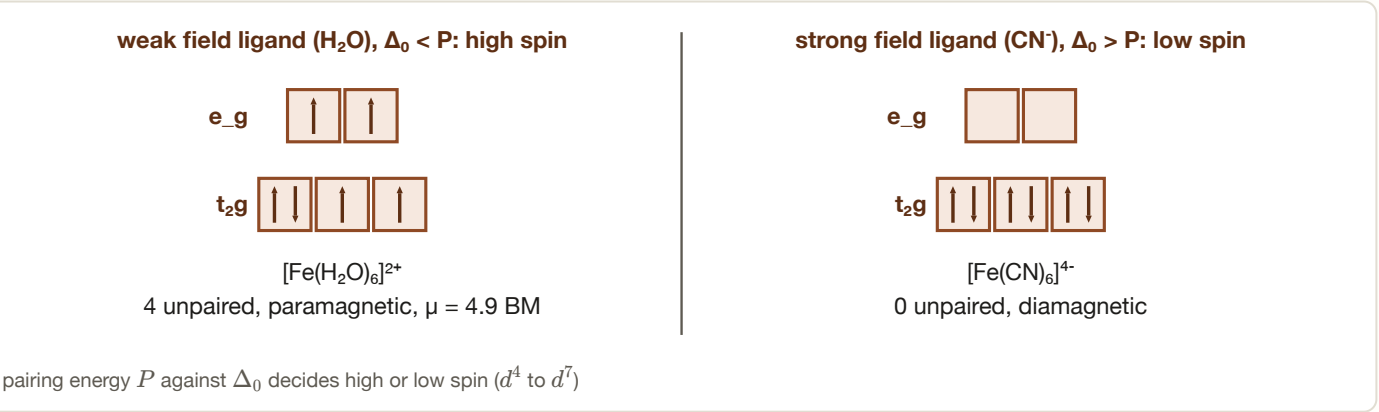
Answer: dsp^2; sp^3; d^2sp^3; sp^3d^2.

5 Crystal field theory



d orbitals split in a ligand field; octahedral t_{2g} lower, e_g higher; tetrahedral is inverted and smaller

- Ligands are treated as point charges. In a **spherical** field the five d orbitals stay degenerate; in an **octahedral** field the e_g orbitals ($d_{x^2-y^2}$, d_{z^2}) point at the ligands and rise ($+0.6\Delta_o$), while t_{2g} (d_{xy}, d_{yz}, d_{xz}) lie between them and fall ($-0.4\Delta_o$).
- In a **tetrahedral** field the pattern is inverted (e below, t_2 above) and smaller: $\Delta_t = \frac{4}{9}\Delta_o$, so tetrahedral complexes are always high spin.



pairing energy P against Δ_0 decides high or low spin (d^4 to d^7)

CFSE (OCTAHEDRAL)

$\mathrm{CFSE} = (-0.4\,n_{t_{2g}} + 0.6\,n_{e_g})\Delta_o$

plus mP for the extra electron pairs formed; negative means stabilisation

SPIN RULE

$\Delta_o < P$: high spin; $\Delta_o > P$: low spin

only for d^4 to d^7 octahedral complexes; P is the pairing energy

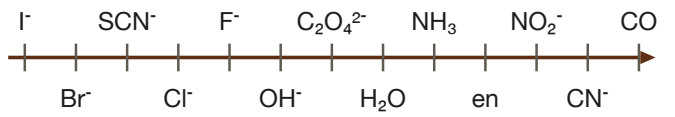
TETRAHEDRAL

$\mathrm{CFSE} = (-0.6\,n_e + 0.4\,n_{t_2})\Delta_t$

$\Delta_t = \frac{4}{9}\Delta_o$; always high spin

OCTAHEDRAL CFSE AND UNPAIRED ELECTRONS (IN UNITS OF Δ_o, PAIRING ENERGY OMITTED)

d^n	HIGH SPIN	UNPAIRED	LOW SPIN	UNPAIRED
d^1, d^2, d^3	$-0.4, -0.8, -1.2$	1, 2, 3	same	same
d^4	-0.6 $(t_{2g}^3 e_g^1)$	4	-1.6 (t_{2g}^4)	2
d^5	0 $(t_{2g}^3 e_g^2)$	5	-2.0 (t_{2g}^5)	1
d^6	-0.4 $(t_{2g}^4 e_g^2)$	4	-2.4 (t_{2g}^6)	0
d^7	-0.8 $(t_{2g}^5 e_g^2)$	3	-1.8 $(t_{2g}^6 e_g^1)$	1
d^8, d^9, d^{10}	$-1.2, -0.6, 0$	2, 1, 0	same	same



the order of Δ_0 for common ligands, an experimental series

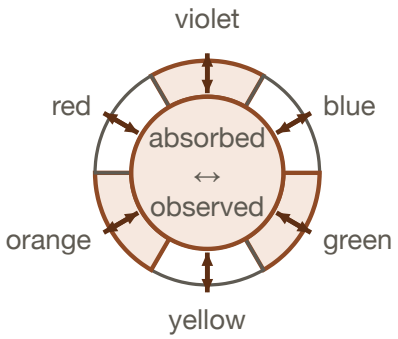
WHAT INCREASES Δ_O

- ✓ The ligand: the spectrochemical series (strong field to the right).
- ✓ The metal oxidation state: $\mathrm{M}^{3+} > \mathrm{M}^{2+}$ for the same ligand.
- ✓ Down a group: $3d < 4d < 5d$, so $4d$ and $5d$ complexes are nearly always low spin.

WHY IT WORKS

A stronger ligand repels the e_g electrons more, so the gap Δ_o grows; once $\Delta_o > P$ it is cheaper to pair electrons in t_{2g} than to place them in e_g. Aqua complexes of $3d$ M^{2+} are high spin; Co^{3+} complexes with $\mathrm{NH_3}$, $\mathrm{CN^-}$, en are low spin.

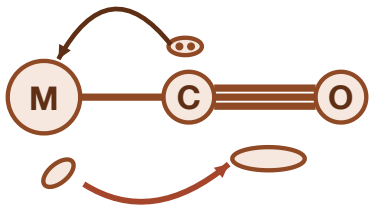
6 Colour, carbonyls and applications



a complex appears as the complement of the colour it absorbs

- The colour of a complex arises from d-d transitions ($t_{2g} \rightarrow e_g$): it absorbs light of energy $\Delta_o = hc/\lambda$ and shows the **complement**. $[\mathrm{Ti(H_2O)_6}]^{3+}$ absorbs near 498 nm (blue-green) and looks violet; $\Delta_o = \dfrac{N_A hc}{\lambda} = \dfrac{1.196 \times 10^5}{498} = 240$ kJ mol^{-1}.
- A stronger ligand gives a larger Δ_o and a **shorter** wavelength absorbed. With no ligand there is no splitting: anhydrous $\mathrm{CuSO_4}$ is white, $\mathrm{CuSO_4 \cdot 5\,H_2O}$ is blue. Colourless when d^0 or d^{10} (no d-d transition).
- Stepwise addition of en to $[\mathrm{Ni(H_2O)_6}]^{2+}$ (green): pale blue, blue-purple, violet $[\mathrm{Ni(en)_3}]^{2+}$. $[\mathrm{Co(H_2O)_6}]^{2+}$ is pink; $[\mathrm{CoCl_4}]^{2-}$ blue.

σ: C → M donation



π back-donation:
M(d) → CO(π*)

back-donation strengthens M–C and weakens C–O

METAL CARBONYLS AND SYNERGIC BONDING CO donates a lone pair from C to the metal (a σ bond) and the metal donates d electrons back into the empty π^* orbital of CO (π back-donation). Each strengthens the other, so the M−C bond order rises and the C−O bond order falls (the C−O stretch is below that of free CO, $2143\ \text{cm}^{-1}$).

SHAPES

- ✓ Ni(CO)_4 tetrahedral; Fe(CO)_5 trigonal bipyramidal; Cr(CO)_6 octahedral.
- ✓ $\text{Mn}_2\text{(CO)}_{10}$: two square pyramids joined by an $\text{Mn}-\text{Mn}$ bond, no bridging CO. $\text{Co}_2\text{(CO)}_8$ ($\text{Co}-\text{Co}$ + 2 bridging CO, solid) and $\text{Fe}_2\text{(CO)}_9$ (3 bridging CO) have bridging carbonyls.

STABILITY AND USES

TOPIC	FACT OR REACTION
stability constant	$\beta_n = K_1K_2\cdots K_n$, $\log\beta_n = \sum \log K_i$; the larger β the more stable; chelates have large β
gold, silver extraction	$4\,\text{Au} + 8\,\text{CN}^- + 2\,\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\,[\text{Au(CN)}_2]^- + 4\,\text{OH}^-$; $2\,[\text{Au(CN)}_2]^- + \text{Zn} \longrightarrow [\text{Zn(CN)}_4]^{2-} + 2\,\text{Au}$
Mond process	$\text{Ni} + 4\,\text{CO} \longrightarrow \text{Ni(CO)}_4$ (330 to 350 K), decomposed at 450 to 470 K to pure Ni
photography (fixing)	$\text{AgBr} + 2\,\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3[\text{Ag(S}_2\text{O}_3)_2] + \text{NaBr}$
qualitative tests	Ni^{2+} + dmg: red $[\text{Ni(dmg)}_2]$; Cu^{2+} + excess NH_3: deep blue $[\text{Cu(NH}_3)_4]^{2+}$; Fe^{3+} + $[\text{Fe(CN)}_6]^{4-}$: Prussian blue; Fe^{3+} + SCN^-: blood red
biology and medicine	chlorophyll (Mg), haemoglobin (Fe), vitamin B_{12} (Co); cisplatin $\text{cis}-[\text{Pt(NH}_3)_2\text{Cl}_2]$ against tumours; EDTA for lead poisoning, desferrioxamine for iron; EDTA titration for water hardness
catalysis	Wilkinson's catalyst $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ hydrogenates alkenes

KEY IDEA

Everything in this chapter follows from the metal's d^n count, the ligand field strength and the geometry: first the ligand strength decides high or low spin, then the spin gives the unpaired count (magnetic moment) and the hybridisation (VBT), and Δ_o gives the colour.

QUICK CHECK

Spin-only moments of $[\text{Fe(H}_2\text{O)}_6]^{2+}$, $[\text{Fe(CN)}_6]^{4-}$, $[\text{Cu(H}_2\text{O)}_6]^{2+}$, $[\text{Mn(H}_2\text{O)}_6]^{2+}$.

Answer: 4.90 (d^6 HS), 0 (d^6 LS), 1.73 (d^9), 5.92 (d^5 HS).

7 Worked examples

SILVER CHLORIDE

100 mL of 0.05 M $[\text{Cr(H}_2\text{O)}_4\text{Cl}_2]\text{Cl}$ is treated with excess AgNO_3. Moles of AgCl?

only the outer Cl^- precipitates: $0.1 \times 0.05 \times 1 = 5 \times 10^{-3}$ mol

OXIDATION STATE

Oxidation state and d^n of the metal in $[\text{Co(NH}_3)_4\text{Cl}_2]^+$ and $\text{K}_3[\text{Fe(CN)}_6]$.

$x + 0 - 2 = +1$: Co $+3$, d^6; $x - 6 = -3$: Fe $+3$, d^5

CFSE

CFSE (units Δ_o, ignore P) of $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$.

d^6: HS $t_{2g}^4 e_g^2$: $-1.6 + 1.2 = -0.4$; LS t_{2g}^6: -2.4

COLOUR

Which absorbs the shorter wavelength: $[Co(NH_3)_6]^{3+}$ or $[CoF_6]^{3-}$?

NH_3 is the stronger ligand, larger Δ_o, higher energy, shorter λ: $[Co(NH_3)_6]^{3+}$

ISOMER COUNT

Total stereoisomers of $[Co(en)_2Cl_2]^+$ and of $[Co(NH_3)_3Cl_3]$.

$[Co(en)_2Cl_2]^+$: $M(AA)_2B_2$: cis (2 enantiomers) + trans $= 3$; MA_3B_3: fac + mer $= 2$

HYBRIDISATION

Hybridisation and magnetism of $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$.

Ni^{2+} d^8: CN^- strong, pairs up: dsp^2, square planar, diamagnetic; Cl^- weak: sp^3, tetrahedral, 2 unpaired (2.83 BM)

MAGNETIC MOMENT

Spin-only μ of $[Co(H_2O)_6]^{2+}$ and of $[Cr(H_2O)_6]^{2+}$.

Co^{2+} d^7 (HS): 3 unpaired, 3.87 BM; Cr^{2+} d^4 (HS): 4, 4.90 BM

NAME THE COMPLEX

Name $[Co(NH_3)_5(NO_2)]Cl_2$ and $K_2[PtCl_4]$.

pentaamminenitrito-N-cobalt(III) chloride (charge: $x + 0 - 1 = +2$, $x = 3$); potassium tetrachloridoplatinate(II)

8 Last-minute checklist

BEFORE YOU ANSWER

Find the oxidation state and d^n first. Strong or weak field ligand? Which geometry (CN 4 or 6)? Does the question want hybridisation, spin-only moment, CFSE, colour or isomer count?

- Primary valency = oxidation state (ionisable), secondary = CN; $AgCl$ moles = Cl^- outside the bracket; EAN $= Z - ox + 2\,CN$; naming: ligands alphabetical, metal -ate if anionic, Roman numeral.
- Isomers: ionisation, linkage (ambidentate), coordination, hydrate; MA_4B_2 cis/trans; MA_3B_3 fac/mer; $M(AA)_3$ and cis-$M(AA)_2X_2$ optically active; tetrahedral: none geometrical.
- VBT: sp^3 tetrahedral, dsp^2 square planar, d^2sp^3 inner (low spin), sp^3d^2 outer (high spin); $[Ni(CO)_4]$ sp^3, $[Ni(CN)_4]^{2-}$ dsp^2, $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$ diamagnetic.
- CFT: t_{2g} at $-0.4\Delta_o$, e_g at $+0.6\Delta_o$; $\Delta_t = \frac{4}{9}\Delta_o$; $\Delta_o > P$ low spin; $\mu = \sqrt{n(n+2)}$; spectrochemical: $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < en < CN^- < CO$.
- Colour is the complement of the absorbed light; stronger ligand gives shorter λ absorbed; CO bonds by σ donation and π back-donation; bridging CO in $Co_2(CO)_8$ and $Fe_2(CO)_9$, not in $Mn_2(CO)_{10}$.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**