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# NCERT Exemplar Solutions

*Solved NCERT Exemplar Problems for Class 12th Chemistry, Chapter 5*

## Chapter 5: Coordination Compounds

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## About this Chapter

Coordination compounds are the heart of inorganic chemistry: a central metal ion or atom surrounded by neutral or anionic **ligands** that donate lone pairs into empty metal orbitals. This Exemplar set drills the four pillars of the chapter: **Werner's primary/secondary valencies** + IUPAC nomenclature, the **Valence Bond** hybridisation picture, the **Crystal Field Theory** splitting picture and the rich isomerism (geometrical, optical, linkage, ionisation, solvate, coordination). After the 2026–27 syllabus refresh, command of *both* bonding theories and confident handling of stereoisomers in $[\mathrm{M(en)}_x\mathrm{X}_y]^{n+}$ type complexes is non-negotiable for board, JEE and NEET.

**Topics covered:** Werner's theory • IUPAC nomenclature • Ligand classification • Coordination number • Isomerism (geometrical, optical, linkage, ionisation, solvate, coordination) • Valence Bond Theory • Crystal Field Theory • CFSE, $\Delta_o$ vs $\Delta_t$ • Spectrochemical series • Magnetic moment • Colour of complexes • Stability and chelate effect • Bioinorganic examples (haemoglobin, chlorophyll, vitamin $B_{12}$)

### Quick Formula Sheet

**Spin-only magnetic moment:**
$\mu = \sqrt{n(n+2)}$ BM, $n$ = unpaired electrons.

**Crystal field splitting (octahedral vs tetrahedral):**
$\Delta_t = \frac{4}{9}\,\Delta_o$.

**Spectrochemical series (weak → strong field):**
$\mathrm{I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4{}^{2-} < H_2O < NCS^- < NH_3 < en < CN^- < CO}$.

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

**Werner's valencies:**
Primary = oxidation state (ionisable);
Secondary = coordination number (non-ionisable).

# NCERT Exemplar Problems

## I. Multiple Choice Questions (Type-I)

**Q 5.1** **Which of the following complexes formed by $Cu^{2+}$ ions is most stable?**

**(i)** $Cu^{2+} + 4\,NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$, $\log K = 11.6$

**(ii)** $Cu^{2+} + 4\,CN^- \longrightarrow [Cu(CN)_4]^{2-}$, $\log K = 27.3$

**(iii)** $Cu^{2+} + 2\ \mathrm{en} \longrightarrow [Cu(en)_2]^{2+}$, $\log K = 15.4$

**(iv)** $Cu^{2+} + 4\,H_2O \longrightarrow [Cu(H_2O)_4]^{2+}$, $\log K = 8.9$

**SOLUTION**

**Correct option: (ii)** $[Cu(CN)_4]^{2-}$, $\log K = 27.3$.

**Concept used.** The stability of a coordination complex in solution is measured by the **overall stability constant** $K$ (also called the **formation constant** $\beta$) of the equilibrium

$$M^{n+} + x\,L \rightleftharpoons [ML_x]^{n+}, \qquad K = \frac{[[ML_x]^{n+}]}{[M^{n+}][L]^x}.$$

A larger $K$ (and therefore a larger $\log K$) means more product at equilibrium, i.e. a more stable complex. So the question reduces to "find the largest $\log K$ in the table."

**Step 1.** Tabulate the four values:

$$\log K_{(i)} = 11.6, \quad \log K_{(ii)} = 27.3, \quad \log K_{(iii)} = 15.4, \quad \log K_{(iv)} = 8.9.$$

**Step 2.** The largest value is 27.3, belonging to option (ii) $[Cu(CN)_4]^{2-}$. Numerically $K_{(ii)} = 10^{27.3} \approx 2 \times 10^{27}$, which is $10^{27.3-11.6} = 10^{15.7} \approx 5 \times 10^{15}$ times larger than $K_{(i)}$.

**Step 3.** Reasoning: $CN^-$ is the strongest $\sigma$-donor and a very effective $\pi$-acceptor on the spectrochemical series, so it forms the strongest $M{-}L$ bond with the soft $Cu^{2+}$ centre. Aqua $(H_2O)$ is weakest, ammine intermediate, ethylenediamine $(\mathrm{en})$ slightly higher than ammine because of the **chelate effect**.

> **Final Answer:** Option **(ii)**: $[Cu(CN)_4]^{2-}$ is the most stable complex ($\log K = 27.3$).

**☞ Spectrochemical order**

$H_2O < NH_3 < \mathrm{en} < CN^-$ — exactly the order of $\log K$ values listed in the question. Memorising the right end of the spectrochemical series pays off here.

**EXPERT'S SOLUTION** *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

**Quick reading.** Stability constant $K$ has no upper limit, but the spectrochemical series fixes the relative ordering of donor strengths to $\mathrm{Cu}^{2+}$. Reading the four ligands in series order directly predicts the order of $\log K$.

**Step 1.** Place the four ligands on the spectrochemical series from weak to strong field:

$$\mathrm{H_2O} \;<\; \mathrm{NH_3} \;<\; \mathrm{en} \;<\; \mathrm{CN^-}.$$

Stronger field $\Rightarrow$ stronger $\mathrm{Cu}^{2+}$–L $\sigma$-bond (plus $\pi$-back-bonding for $\mathrm{CN^-}$) $\Rightarrow$ larger $K$.

**Step 2.** Compare the listed $\log K$ against this order:
$\mathrm{H_2O}\,(8.9) < \mathrm{NH_3}\,(11.6) < \mathrm{en}\,(15.4) < \mathrm{CN^-}\,(27.3)$. The data match the prediction term-for-term.

**Step 3.** Note that the chelate effect bumps $\mathrm{en}$ above $\mathrm{NH_3}$ by $\sim 4$ orders in $K$, but the cyanide complex still wins because $\mathrm{CN^-}$ is both a stronger $\sigma$-donor and a $\pi$-acceptor, and four cyanides simply trump two chelating $\mathrm{en}$.

**Why this matters.** Sodium cyanide is used in industrial gold leaching,

$$4\,\mathrm{Au} + 8\,\mathrm{CN^-} + \mathrm{O_2} + 2\,\mathrm{H_2O} \longrightarrow 4\,[\mathrm{Au(CN)_2}]^- + 4\,\mathrm{OH^-},$$

for exactly the same reason this question turns on: $\mathrm{CN^-}$ forms outrageously stable complexes with $\mathrm{d}$-block metals.

> **Final Answer:** $[\mathrm{Cu(CN)_4}]^{2-}$, option **(ii)**.

**Q 5.2** **The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes $[\mathrm{Co(NH_3)_6}]^{3+}$, $[\mathrm{Co(CN)_6}]^{3-}$, $[\mathrm{Co(H_2O)_6}]^{3+}$?**

**(i)** $[\mathrm{Co(CN)_6}]^{3-} > [\mathrm{Co(NH_3)_6}]^{3+} > [\mathrm{Co(H_2O)_6}]^{3+}$
**(ii)** $[\mathrm{Co(NH_3)_6}]^{3+} > [\mathrm{Co(H_2O)_6}]^{3+} > [\mathrm{Co(CN)_6}]^{3-}$
**(iii)** $[\mathrm{Co(H_2O)_6}]^{3+} > [\mathrm{Co(NH_3)_6}]^{3+} > [\mathrm{Co(CN)_6}]^{3-}$
**(iv)** $[\mathrm{Co(CN)_6}]^{3-} > [\mathrm{Co(NH_3)_6}]^{3+} > [\mathrm{Co(H_2O)_6}]^{3+}$

**SOLUTION**

**Correct option: (iii)** $[\mathrm{Co(H_2O)_6}]^{3+} > [\mathrm{Co(NH_3)_6}]^{3+} > [\mathrm{Co(CN)_6}]^{3-}$.
**Concept used.** A d–d transition promotes a $t_{2g}$ electron to the $e_g$ set across the

octahedral splitting $\Delta_o$. By the Planck–Einstein relation

$$E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta_o}.$$

So *larger* $\Delta_o$ absorbs at *shorter* $\lambda$, and a *weaker* field ligand $\Rightarrow$ *smaller* $\Delta_o \Rightarrow$ *longer* $\lambda$.

**Step 1.** Place the three ligands on the spectrochemical series: $H_2O < NH_3 < CN^-$ in field strength. So the $\Delta_o$ values rank as $[Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$.

**Step 2.** Apply $\lambda \propto 1/\Delta_o$:

$$\lambda(H_2O\text{-complex}) > \lambda(NH_3\text{-complex}) > \lambda(CN\text{-complex}).$$

Spelled out:

$$[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}.$$

**Step 3.** This matches option (iii). Sanity check on observed colours: $[Co(H_2O)_6]^{3+}$ is blue-violet (absorbs orange-red, $\sim 600\,\text{nm}$), $[Co(NH_3)_6]^{3+}$ is yellow-orange (absorbs violet-blue, $\sim 470\,\text{nm}$), and $[Co(CN)_6]^{3-}$ is pale yellow (absorbs near UV, $\sim 310\,\text{nm}$). Wavelength absorbed indeed decreases as the field gets stronger.

**Final Answer:** Option **(iii)**: $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$.

**✗ Don't confuse $\lambda$ absorbed with $\lambda$ seen**

The colour we *see* is complementary to the colour absorbed. The question asks about $\lambda$ *absorbed*, which is set by $\Delta_o$. Order the ligands by spectrochemical strength, then *invert* the ordering to get $\lambda_{\text{abs}}$.

**EXPERT'S SOLUTION** *: Sneha Iyer, M.Sc Physical Chemistry, IIT Madras*

**Strategic angle.** Two simple proportions take you from spectrochemical position straight to absorbed wavelength: ligand strength $\propto \Delta_o$ and $\lambda \propto 1/\Delta_o$. So ligand-strength order *reverses* to give wavelength order.

**Step 1.** Spectrochemical series snippet (left = weak, right = strong): $H_2O < NH_3 < CN^-$.

**Step 2.** Reverse this to read off $\lambda$-absorbed order (weakest field absorbs the longest wavelength):

$$[Co(H_2O)_6]^{3+}\ (\sim 600\,\text{nm}) > [Co(NH_3)_6]^{3+}\ (\sim 470\,\text{nm}) > [Co(CN)_6]^{3-}\ (\sim 310\,\text{nm}).$$

**Step 3.** Numerical cross-check with $\Delta_o([\mathrm{Co(NH_3)_6}]^{3+}) \approx 22{,}900\,\mathrm{cm^{-1}}$ and $\lambda = 10^7/22900 = 437\,\mathrm{nm}$ — in the violet, so the complex looks yellow-orange. Pattern confirmed.

**Why this matters.** The same logic predicts why $[\mathrm{Ti(H_2O)_6}]^{3+}$ is purple ($\Delta_o = 20{,}300\,\mathrm{cm^{-1}}$, absorbs $\sim 493\,\mathrm{nm}$) and why exchanging $H_2O$ for $NH_3$ on the same metal usually shifts a complex's colour visibly toward shorter $\lambda$.

**Final Answer:** Option **(iii)**: $[\mathrm{Co(H_2O)_6}]^{3+} > [\mathrm{Co(NH_3)_6}]^{3+} > [\mathrm{Co(CN)_6}]^{3-}$.

**Q 5.3** **When $0.1$ mol $\mathrm{CoCl_3(NH_3)_5}$ is treated with excess of $\mathrm{AgNO_3}$, $0.2$ mol of $\mathrm{AgCl}$ are obtained. The conductivity of solution will correspond to**

**(i)** $1:3$ **electrolyte**

**(ii)** $1:2$ **electrolyte**

**(iii)** $1:1$ **electrolyte**

**(iv)** $3:1$ **electrolyte**

**SOLUTION**

**Correct option:** **(ii)** $1:2$ electrolyte.

**Concept used.** Werner's idea of **primary** (ionisable) versus **secondary** (non-ionisable) valencies says: only the chlorides written *outside* the coordination sphere are precipitated as AgCl when treated with $\mathrm{AgNO_3}$, because only they ionise in water. The number of AgCl formed per mole of complex therefore equals the number of free $\mathrm{Cl^-}$ ions, and the *electrolyte ratio* of the complex is

$$\text{cation charge} : \text{anion charge} = \frac{\#\ \text{cations}\,(z_+)}{\#\ \text{anions}\,(z_-)}.$$

**Step 1.** From the stoichiometry: $0.1$ mol of complex gives $0.2$ mol AgCl, so each formula unit liberates $0.2/0.1 = 2$ chloride ions.

**Step 2.** Therefore $2$ of the $3$ Cl in $\mathrm{CoCl_3(NH_3)_5}$ are ionisable (outside the sphere) and $1$ is inside. The structural formula is

$$[\mathrm{Co(NH_3)_5\,Cl]\,Cl_2},$$

which ionises as

$$[\mathrm{Co(NH_3)_5\,Cl]Cl_2} \longrightarrow [\mathrm{Co(NH_3)_5\,Cl}]^{2+} + 2\,\mathrm{Cl^-}.$$

**Step 3.** The salt produces one cation of charge $+2$ and two anions of charge $-1$ in solution. By the "$z_+ : |z_-|$" convention $1:2$ means one cation per two anions, which matches this case exactly.

**Final Answer:** Option **(ii)**: a $1:2$ electrolyte ($[Co(NH_3)_5\,Cl]Cl_2$).

### ☞ Decode molar conductance to electrolyte ratio

The Werner "count of free $Cl^-$" from $AgCl$ titration plus molar conductance gives you the electrolyte ratio $(1:1, 1:2, 1:3, \dots)$ directly. Total free ions $=$ moles of $AgCl + 1$ (the cation itself), and the ratio follows from there.

**EXPERT'S SOLUTION** *: Aditi Gupta, Ph.D Organic Chemistry, IISc Bangalore*

**Strategic angle.** Drop one chloride at a time into the coordination sphere and stop the moment the $AgCl$ count matches the data.

**Step 1.** Possible isomers of $CoCl_3(NH_3)_5$ and their $AgCl$ output per mole of complex:

- $[Co(NH_3)_5]Cl_3$: 3 Cl outside $\rightarrow$ 3 mol $AgCl$ (but this isomer needs CN $= 5$ for Co, which is wrong — included only for completeness).
- $[Co(NH_3)_5\,Cl]Cl_2$: 2 Cl outside, 1 inside $\rightarrow$ 2 mol $AgCl$.
- $[Co(NH_3)_5\,Cl_2]Cl$: 1 Cl outside, 2 inside $\rightarrow$ 1 mol $AgCl$.
- $[Co(NH_3)_5\,Cl_3]$: 0 Cl outside $\rightarrow$ 0 mol $AgCl$.

**Step 2.** Observed: $0.2$ mol $AgCl$ per $0.1$ mol complex $= 2$ per formula unit. Only $[Co(NH_3)_5\,Cl]Cl_2$ fits.

**Step 3.** Conductivity link: one $+2$ cation and two $-1$ anions means the molar conductivity sits around $245$–$260\ \mathrm{S\,cm^2\,mol^{-1}}$ at infinite dilution in water, the signature of a $1:2$ electrolyte (compare a $1:1$ NaCl-like complex at $\sim 100\ \mathrm{S\,cm^2\,mol^{-1}}$).

**Why this matters.** Werner deduced the $1:1$, $1:2$, $1:3$ pattern of cobalt-amine chlorides purely from $AgCl$ titration and conductivity, decades before any X-ray crystal structure. The same logic is fair game in board derivations.

**Final Answer:** $[Co(NH_3)_5\,Cl]Cl_2$, a $1:2$ electrolyte.

**Q 5.4** **When $1$ mol $CrCl_3 \cdot 6\,H_2O$ is treated with excess of $AgNO_3$, $3$ mol of $AgCl$ are obtained. The formula of the complex is:**

**(i)** $[CrCl_3(H_2O)_3] \cdot 3\,H_2O$

**(ii)** $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$

**(iii)** $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

**(iv)** $[Cr(H_2O)_6]Cl_3$

SOLUTION

**Correct option: (iv)** $[Cr(H_2O)_6]Cl_3$.

**Concept used.** Same Werner principle as Q3: only the *ionisable* (outside-sphere) chlorides precipitate as $AgCl$. Count them in each candidate isomer and match against the $3$ mol $AgCl$ produced per mol of complex.

**Step 1.** Inspect each option's outside-sphere chlorides:

- (i) $[CrCl_3(H_2O)_3] \cdot 3\,H_2O$: all 3 $Cl$ inside; $AgCl$ obtained $= 0$.
- (ii) $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$: $1$ $Cl$ outside; $AgCl$ obtained $= 1$.
- (iii) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: $2$ $Cl$ outside; $AgCl$ obtained $= 2$.
- (iv) $[Cr(H_2O)_6]Cl_3$: all $3$ $Cl$ outside; $AgCl$ obtained $= 3$.

**Step 2.** Observed value $= 3$ mol $AgCl$ per mol complex. Only option (iv) matches.

**Step 3.** The complex is the violet hexaaquachromium(III) chloride $[Cr(H_2O)_6]Cl_3$, with $Cr^{3+}$ at the centre of a regular octahedron of six water ligands and three $Cl^-$ counter-ions in the second sphere. It is a $1:3$ electrolyte:

$$[Cr(H_2O)_6]Cl_3 \longrightarrow [Cr(H_2O)_6]^{3+} + 3\,Cl^-.$$

**Final Answer:** Option **(iv)**: $[Cr(H_2O)_6]Cl_3$.

### ♥ Hydrate isomerism in one molecular formula

$CrCl_3 \cdot 6\,H_2O$ exists as four solvate isomers (i)–(iv). They have the same molecular formula yet *different colours* (violet, pale-green, dark-green) and *different* $AgCl$-counts and conductivities — a textbook case of Werner's primary/secondary valencies and hydrate (solvate) isomerism.

**EXPERT'S SOLUTION** *: Pranav Mehta, M.Tech Chemical Engineering, IIT Delhi*

**Picture-first.** Draw $Cr^{3+}$ at the centre of an octahedron. Whichever six donors sit at the vertices are inside the coordination sphere; anything beyond is a counter-ion (or lattice water). Count the chlorides outside the vertices.

**Step 1.** For each option, write the inner-sphere occupancy:

| Option | Inner sphere | Outer Cl |
|---|---|---|
| $(i)$ | $3\,Cl + 3\,H_2O$ | $0$ |
| $(ii)$ | $2\,Cl + 4\,H_2O$ | $1$ |
| $(iii)$ | $1\,Cl + 5\,H_2O$ | $2$ |
| $(iv)$ | $6\,H_2O$ | $3$ |

**Step 2.** Match outer $Cl$ to the observed $3$ mol $AgCl$: only (iv) gives $3$.

**Step 3.** Conductivity confirmation: $[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$ dissociates into $4$ ions per formula unit, the highest of the candidates, and the experimental molar conductance is $\sim 430\ \mathrm{S\,cm^2\,mol^{-1}}$ — consistent with a $1\!:\!3$ electrolyte at $25°\mathrm{C}$.

**Why this matters.** Identifying solvate isomers from precipitation data was Werner's experimental signature, and this exact problem shows up almost every alternate year on JEE.

**Final Answer:** $[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$.

**Q 5.5** **The correct IUPAC name of $[\mathrm{Pt(NH_3)_2\,Cl_2}]$ is**

**(i) Diamminedichloridoplatinum(II)**

**(ii) Diamminedichloridoplatinum(IV)**

**(iii) Diamminedichloridoplatinum(0)**

**(iv) Dichloridodiammineplatinum(IV)**

SOLUTION

**Correct option: (i)** Diamminedichloridoplatinum(II).

**Concept used.** The IUPAC rules for naming a mononuclear neutral coordination compound are: (a) list ligands in *alphabetical order* (ignoring the prefix di/tri/tetra), each ligand naming convention: **ammine** for $\mathrm{NH_3}$, **chlorido** for $\mathrm{Cl^-}$ (2005 recommendation; older books write "chloro"), **aqua** for $\mathrm{H_2O}$. (b) Suffix the metal's English name followed by its oxidation state in roman numerals in parentheses. (c) For a neutral complex the metal keeps its English name; for an anionic complex the name ends in "-ate".

**Step 1.** Compute oxidation state. The complex is neutral overall, the two $\mathrm{Cl}$ ligands carry $-1$ each, and $\mathrm{NH_3}$ is neutral:

$$x + 2(0) + 2(-1) = 0 \ \Rightarrow\ x = +2.$$

So $\mathrm{Pt}$ is in oxidation state $+2$, written as **platinum(II)** in roman numerals.

**Step 2.** Alphabetise ligand names: **ammine** (a) before **chlorido** (c).

**Step 3.** Combine: *diammine* + *dichlorido* + *platinum(II)* $\rightarrow$

$$\boxed{\text{diamminedichloridoplatinum(II)}}.$$

Two "m"s in "ammine" because of the IUPAC rule that "ammine" refers specifically to coordinated $\mathrm{NH_3}$ (one "m" "amine" refers to $-\mathrm{NH_2}$ in organics).

**Step 4.** Rule out the others: (ii) and (iv) have the wrong oxidation state (+4 needs four

$Cl^-$ or two oxide ligands to balance); (iii) corresponds to $Pt(0)$, which would require zero $Cl$; (iv) is also alphabetised wrong ("chlorido" before "ammine").

> **Final Answer:** Option **(i)**: diamminedichloridoplatinum(II).

**✗ *ammine* versus *amine***

Coordinated $NH_3$ is **ammine** (two m's). An organic $-NH_2$ group is **amine** (one m). Spelling counts on both board and JEE answer sheets — one mark gone if you slip.

**EXPERT'S SOLUTION** *: Riya Kapoor, M.Sc Chemistry, IIT Kanpur*

**Quick reading.** Three independent IUPAC lookups stack up: oxidation state, alphabetical ligand order, ligand spelling (*ammine* vs *chlorido*). Each lookup is a filter that eliminates wrong options, so even if one filter is forgotten the other two still pin (i).

**Step 1.** *Filter 1 — oxidation state.* The complex is neutral overall, $Cl$ ligands are $-1$ each, $NH_3$ is neutral: $x + 0 + 2(-1) = 0 \Rightarrow x = +2$. So $Pt$ is in $+2$, named *platinum(II)*. Options (ii) and (iv) list $+4$ (would need four $Cl$ or oxide ligands); option (iii) lists $0$ (needs zero $Cl$). Three options die at this filter, only (i) survives.

**Step 2.** *Filter 2 — alphabetical ligand order.* Compare first letters of the bare ligand names (*not* their counting prefixes): *ammine* starts with 'a', *chlorido* starts with 'c'. So *a* before *c*: "diammine" is written before "dichlorido". Option (iv) reverses this order, doubly failing.

**Step 3.** *Filter 3 — 2005 IUPAC spelling.* Coordinated $NH_3$ is **ammine** (two m's, distinct from the organic **amine**); the 2005 recommendation renamed *chloro* to **chlorido** (ending *-ido* signals a singly charged anionic ligand). NCERT uses the post-2005 forms throughout this chapter — answer in the same convention to avoid losing the half-mark.

**Why this matters.** The compound is the parent skeleton of *cisplatin*, cis-$[PtCl_2(NH_3)_2]$ — one of the most successful anticancer drugs ever synthesised (FDA-approved in 1978). Naming it correctly is the gateway to discussing its biology: it is the *cis* geometrical isomer that binds DNA's guanine bases and disrupts replication in cancer cells, while the trans isomer is inactive. Same molecular formula, dramatically different drug.

> **Final Answer:** Diamminedichloridoplatinum(II).

**Q 5.6** **The stabilisation of coordination compounds due to chelation is called the**

**chelate effect. Which of the following is the most stable complex species?**

**(i)** $[\mathrm{Fe(CO)_5}]$

**(ii)** $[\mathrm{Fe(CN)_6}]^{3-}$

**(iii)** $[\mathrm{Fe(C_2O_4)_3}]^{3-}$

**(iv)** $[\mathrm{Fe(H_2O)_6}]^{3+}$

SOLUTION

**Correct option: (iii)** $[\mathrm{Fe(C_2O_4)_3}]^{3-}$.

**Concept used.** The **chelate effect** states that chelating (polydentate) ligands form complexes that are more stable than analogous complexes with monodentate ligands. The thermodynamic origin is favourable entropy: chelation *releases* several monodentate ligands while binding only a few polydentate ones, so $\Delta S^\circ > 0$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ becomes more negative.

**Step 1.** Classify each ligand:

- $\mathrm{CO}:$ monodentate, neutral. No chelate.
- $\mathrm{CN^-}:$ monodentate, anionic. No chelate.
- $\mathrm{C_2O_4}^{2-}:$ (oxalato) bidentate, anionic. Forms a 5-membered chelate ring with $\mathrm{Fe^{3+}}$.
- $\mathrm{H_2O}:$ monodentate, neutral. No chelate.

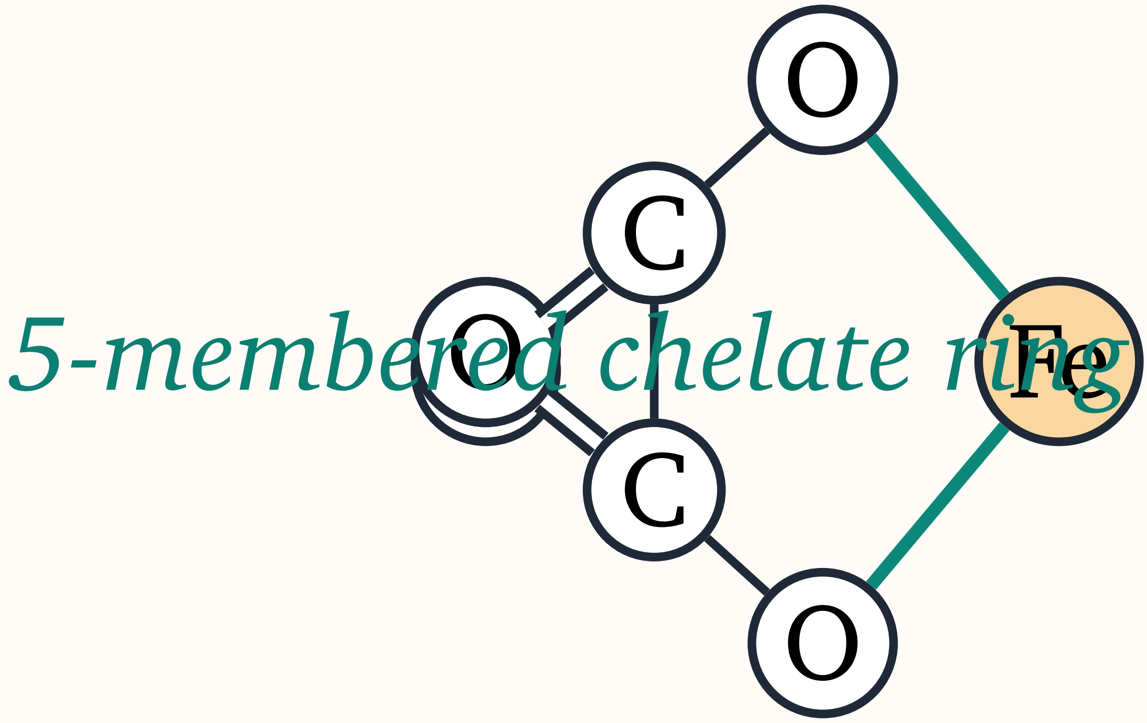
**Step 2.** Only $[\mathrm{Fe(C_2O_4)_3}]^{3-}$ is chelated. Three oxalato ligands give three 5-membered chelate rings, the "magic-number" ring size for maximum chelate stability.

**Step 3.** Confirm with $\log\beta$ values ($\beta_n$ is the cumulative stability constant): $\log\beta_3([\mathrm{Fe(C_2O_4)_3}]^{3-}) \approx 20.0$, much higher than the corresponding hexa-aqua complex ($\log\beta_6 \approx 11$).

> **Final Answer:** Option **(iii)**: $[\mathrm{Fe(C_2O_4)_3}]^{3-}$ is the chelated, hence most stable, complex.

EXPERT'S SOLUTION *: Karan Verma, M.Sc Chemistry, IIT Kanpur*

**Picture-first.** Sketch each complex; only the one whose ligand bites the metal at two points (a chelate ring) wins.



**Step 1.** Of the four ligands, only ${C_2O_4}^{2-}$ has two donor atoms (the two carboxylate $O^-$). Three such ligands wrap three 5-membered rings around $Fe^{3+}$.

**Step 2.** Chelate ring count for the four options: $0, 0, 3, 0$. Highest entropy gain $\Rightarrow$ highest stability.

**Step 3.** Quantitatively, going from $[Fe(H_2O)_6]^{3+}$ to $[Fe(C_2O_4)_3]^{3-}$ releases six water molecules and captures three oxalates: $\Delta n_{\text{gas-like}} = +3$, so $T\Delta S^\circ$ is large and positive.

**Why this matters.** The chelate effect is exploited in EDTA ($EDTA^{4-}$, hexadentate) used in food preservation and metal sequestering in water treatment.

**Final Answer:** $[Fe(C_2O_4)_3]^{3-}$, the only chelated complex.

**Q 5.7** **Indicate the complex ion which shows geometrical isomerism.**

**(i)** $[Cr(H_2O)_4\,Cl_2]^+$

**(ii)** $[Pt(NH_3)_3\,Cl]$

**(iii)** $[Co(NH_3)_6]^{3+}$

**(iv)** $[Co(CN)_5\,(NC)]^{3-}$

SOLUTION

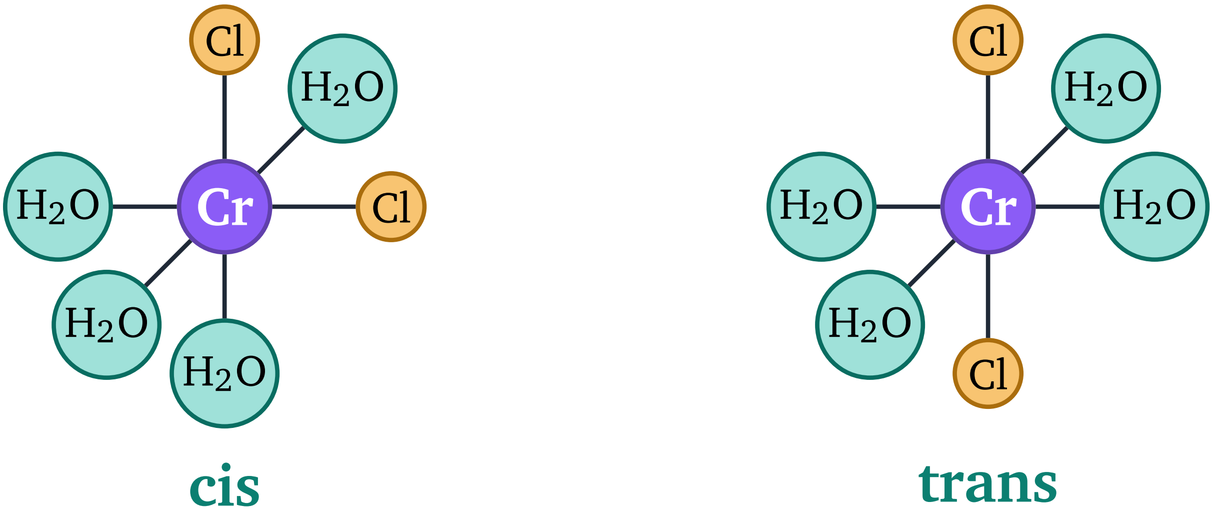
**Correct option: (i)** $[Cr(H_2O)_4Cl_2]^+$.

**Concept used.** **Geometrical isomerism** (also called cis–trans isomerism) arises in octahedral complexes of the type $MA_4B_2$, $MA_3B_3$, $MA_2B_2C_2$ etc., where two identical ligands can lie on adjacent vertices (*cis*, 90° apart) or on opposite vertices (*trans*, 180° apart). It is *not* shown by $MA_6$, $MA_5B$ or any other mono-substituted octahedral complex because all the vertices are equivalent and only one geometry exists.

**Step 1.** Look at the ligand sets:

- (i) $[Cr(H_2O)_4Cl_2]^+$: $MA_4B_2$ type with $A = H_2O$, $B = Cl^-$. Two geometrical isomers: *cis* (the two Cl adjacent) and *trans* (the two Cl opposite). ✓
- (ii) $[Pt(NH_3)_3Cl]$: only 4 ligands, so it is either tetrahedral (no GI) or square planar (the $MA_3B$ pattern still admits only one arrangement). No geometrical isomerism.
- (iii) $[Co(NH_3)_6]^{3+}$: $MA_6$ type, all six ligands identical, only one structure possible.
- (iv) $[Co(CN)_5(NC)]^{3-}$: an $MA_5B$ pattern. It shows linkage isomerism (because $CN^-/NC^-$ are ambidentate), but *not* geometrical isomerism.

**Step 2.** Draw the two GI of $[Cr(H_2O)_4Cl_2]^+$ explicitly:



**Final Answer:** Option **(i)**: $[Cr(H_2O)_4Cl_2]^+$ exists as *cis* and *trans* geometrical isomers.

EXPERT'S SOLUTION *: Ananya Reddy, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — pattern matching.** Geometrical isomerism needs at least *two different* ligand types AND the right ligand count pattern AND a coordination geometry that allows distinct cis/trans arrangements. Run the three filters as a 2-second sieve and only one option survives.

**Step 1.** *Filter 1 — two or more ligand types?* Option (iii) $[Co(NH_3)_6]^{3+}$ has only one ligand type ($MA_6$). All six octahedral vertices are equivalent, so only one structure exists — zero GI. Option (iii) dies immediately.

**Step 2.** *Filter 2 — coordination geometry compatible with cis/trans?* Option (ii) $[Pt(NH_3)_3Cl]$ has only four ligands. In a tetrahedral $MA_3B$ all positions are equivalent (the unique $B$ has no "cis vs trans" partner); in square planar $MA_3B$ the unique ligand again has no cis/trans choice (its three identical neighbours fix it uniquely). Either way, no GI.

**Step 3.** *Filter 3 — ligand count pattern.* The GI-active octahedral patterns are $MA_4B_2$, $MA_3B_3$, $MA_2B_2C_2$ etc. — patterns where at least two identical ligands can sit either adjacent (90°, cis) or opposite (180°, trans). Option (i) $[Cr(H_2O)_4Cl_2]^+$ is exactly $MA_4B_2$ — passes. Option (iv) $[Co(CN)_5(NC)]^{3-}$ is $MA_5B$: the single different ligand has no cis/trans partner. Option (iv) shows *linkage* isomerism (because $CN^-/NC^-$ is ambidentate) but not geometrical isomerism — a textbook trap.

**Step 4.** Survivor: option (i) only. The two isomers: *cis*-$[Cr(H_2O)_4Cl_2]^+$ (two Cl at 90°; lacks a mirror plane through both chlorines, only $C_{2v}$ symmetry, no chirality but distinct connectivity) and *trans*-$[Cr(H_2O)_4Cl_2]^+$ (two Cl at 180°; possesses $D_{4h}$ symmetry, including a centre of inversion, hence achiral and visibly different in colour and dipole moment).

**Why this matters.** Werner's 1913 Nobel Prize hinged on exactly this kind of count: by enumerating the number of distinct isomers of $[Co(NH_3)_4Cl_2]^+$ and $[Co(NH_3)_3Cl_3]$, he proved the octahedral coordination geometry of $Co(III)$ *decades before* X-ray crystallography existed. The cis/trans split is the most powerful inference tool inorganic chemistry has without a diffractometer.

**Final Answer:** $[Cr(H_2O)_4Cl_2]^+$ (cis/trans), option **(i)**.

**Q 5.8** **The CFSE for octahedral $[CoCl_6]^{4-}$ is $18{,}000$ cm$^{-1}$. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be**

**(i)** $18{,}000$ **cm**$^{-1}$

**(ii)** $16{,}000$ **cm**$^{-1}$

**(iii)** $8{,}000$ **cm**$^{-1}$

**(iv)** $20{,}000$ **cm**$^{-1}$

SOLUTION

**Correct option: (iii)** $8{,}000\ \text{cm}^{-1}$.

**Concept used.** Crystal Field Splitting Energy depends on geometry. For the same metal and ligands, the tetrahedral splitting $\Delta_t$ is smaller than the octahedral $\Delta_o$ by a fixed factor:

$$\Delta_t = \frac{4}{9}\Delta_o \ \approx\ 0.45\,\Delta_o.$$

This comes from two effects: tetrahedral geometry has only $4$ ligands (not $6$), and no ligand points directly at any $d$ orbital, so the electrostatic perturbation on the metal $d$ set is weaker.

**Step 1.** Identify $\Delta_o$ from the data:

$$\Delta_o([\text{CoCl}_6]^{4-}) = 18{,}000\ \text{cm}^{-1}.$$

**Step 2.** Apply the geometric factor:

$$\Delta_t([\text{CoCl}_4]^{2-}) = \frac{4}{9} \times 18{,}000\ \text{cm}^{-1}.$$

**Step 3.** Arithmetic:

$$\frac{4}{9} \times 18{,}000 = \frac{4 \times 18{,}000}{9} = \frac{72{,}000}{9} = 8{,}000\ \text{cm}^{-1}.$$

**Final Answer:** Option **(iii)**: $\Delta_t = 8{,}000\ \text{cm}^{-1}$.

☞ **The 4/9 factor**

$\Delta_t = \frac{4}{9}\Delta_o$ regardless of metal or ligand — this is a pure geometry factor coming from the number of ligands (4 vs 6) and the orientation of the $d$ orbitals relative to the ligand positions.

**EXPERT'S SOLUTION** *: Vivaan Joshi, Ph.D Organic Chemistry, IISc Bangalore*

**Picture-first.** Draw the two ligand fields and notice why $\Delta_t < \Delta_o$: in a tetrahedron the ligands sit on the alternate corners of a cube, none pointing along the $x$, $y$ or $z$ axes; in an octahedron they sit exactly on the axes.

**Step 1.** Energy book-keeping. Octahedral $d$ splits as $t_{2g}$ ($-0.4\Delta_o$, 3 orbitals) below $e_g$ ($+0.6\Delta_o$, 2 orbitals). Tetrahedral inverts: $e$ below $t_2$, separation $\Delta_t = (4/9)\Delta_o$.

**Step 2.** Plug in:

$$\Delta_t = \tfrac{4}{9}(18{,}000) = 8{,}000\ \text{cm}^{-1}.$$

**Step 3.** Wavelength check (for fun): octahedral absorption near $\lambda_o = 10^7/18{,}000 \approx 556\,\text{nm}$ (green/yellow, explaining the pink colour of $[\text{Co(H}_2\text{O)}_6]^{2+}$ solutions); tetrahedral absorption near $\lambda_t = 10^7/8{,}000 \approx 1250\,\text{nm}$

— that's in the near-IR, so the tetrahedral cobalt(II) chloride absorbs *additional* bands in the visible too, producing the deep blue colour.

**Why this matters.** The pink-to-blue colour change when $CoCl_2 \cdot {}_6H_2O$ is heated (or when chloride is added in excess) is precisely the octahedral → tetrahedral conversion governed by this $\Delta_t/\Delta_o$ ratio.

> **Final Answer:** $\Delta_t = 8{,}000\ \text{cm}^{-1}$.

**Q 5.9 Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2\,(SCN)_2]$ and $[Pd(C_6H_5)_2\,(NCS)_2]$ are**

**(i) linkage isomers**

**(ii) coordination isomers**

**(iii) ionisation isomers**

**(iv) geometrical isomers**

**SOLUTION**

**Correct option: (i)** linkage isomers.

**Concept used.** An **ambidentate ligand** carries two different donor atoms (e.g. $SCN^-$ can bind through S or N; ${NO_2}^-$ can bind through N as nitro or through O as nitrito). When the same complex differs only in *which atom* of an ambidentate ligand ties to the metal, the two compounds are **linkage isomers**.

**Step 1.** Compare the two formulas:

- $[Pd(C_6H_5)_2\,(SCN)_2]$: $SCN^-$ binds through the sulfur atom (thiocyanato-$S$).
- $[Pd(C_6H_5)_2\,(NCS)_2]$: the same ligand binds through the nitrogen atom (thiocyanato-$N$, aka isothiocyanato).

**Step 2.** Same metal, same other ligand ($C_6H_5$), same composition. The only difference is the donor atom of $SCN^-/NCS^-$, which is the textbook definition of linkage isomerism.

**Step 3.** Rule out the rest: coordination isomerism needs both a cation and an anion complex (e.g. $[Co(NH_3)_6][Cr(CN)_6]$), ionisation isomerism needs an anion swap between sphere and counter-ion (e.g. $[Co(NH_3)_5\,Br]SO_4$ vs $[Co(NH_3)_5\,SO_4]Br$), and geometrical isomerism needs a cis/trans split — none of those apply here.

> **Final Answer:** Option **(i)**: the pair is a linkage-isomer pair (thiocyanato-$S$ vs thiocyanato-$N$).

**EXPERT'S SOLUTION** *: Sneha Pillai, M.Sc Physical Chemistry, IIT Madras*

**Structural observation.** Read the ligand-atom order: $\mathrm{SCN}$ versus $\mathrm{NCS}$. The atom written *first* after the opening parenthesis is the donor. So $\mathrm{SCN}$ binds through $\mathrm{S}$ and $\mathrm{NCS}$ binds through $\mathrm{N}$.

**Step 1.** Identify the ambidentate ligand: $\mathrm{SCN}^-$ (thiocyanate). Its two donor atoms: $\mathrm{S}$ (soft) and $\mathrm{N}$ (harder).

**Step 2.** Match HSAB: Pd(II) is soft, prefers S-bonding $\rightarrow$ $\mathrm{Pd{-}SCN}$ predominates; Cr(III) (hard) would prefer N-bonding. So the $\mathrm{Pd(C_6H_5)_2(SCN)_2}$ form is usually more stable than $\mathrm{Pd(C_6H_5)_2(NCS)_2}$, but both exist and are isolable.

**Step 3.** The pair fits the definition of linkage (or "ambidentate-ligand") isomerism exactly.

**Why this matters.** Werner cited the $[\mathrm{Co(NH_3)_5\,NO_2}]^{2+}$ vs $[\mathrm{Co(NH_3)_5\,ONO}]^{2+}$ pair as the first known case of linkage isomerism. Same conceptual setup, same HSAB analysis.

> **Final Answer:** Linkage isomers, option **(i)**.

**Q 5.10** **The compounds $[\mathrm{Co(SO_4)(NH_3)_5}]\mathrm{Br}$ and $[\mathrm{Co(SO_4)(NH_3)_5}]\mathrm{Cl}$ represent**

**(i) linkage isomerism**

**(ii) ionisation isomerism**

**(iii) coordination isomerism**

**(iv) no isomerism**

**SOLUTION**

**Correct option: (iv)** no isomerism.

**Concept used.** Isomers must share the same *molecular formula*. If two compounds differ in the identity of even one atom — here, $\mathrm{Br}$ vs $\mathrm{Cl}$ — they have different molecular formulas and cannot be isomers of each other; they are simply different compounds.

**Step 1.** Compute the molecular formulas:

- $[\mathrm{Co(SO_4)(NH_3)_5}]\mathrm{Br}$: contains one $\mathrm{Br}$.
- $[\mathrm{Co(SO_4)(NH_3)_5}]\mathrm{Cl}$: contains one $\mathrm{Cl}$ but zero $\mathrm{Br}$.

Distinct elements present $\Rightarrow$ distinct formulas $\Rightarrow$ not isomers.

**Step 2.** Rule out each named isomerism type:

- *Linkage*: requires an ambidentate ligand binding through different donor atoms. ${SO_4}^{2-}$ is not ambidentate in this context.
- *Ionisation*: requires the same molecular formula with the inner/outer sphere swap of one anion. The halide is different, so the formulas differ.
- *Coordination*: requires the cationic and anionic complexes to swap ligands. There is no anionic complex in either compound.

**Step 3.** Therefore the correct answer is "no isomerism".

> **Final Answer:** Option **(iv)**: these are different compounds, not isomers.

☞ **Always sanity-check the molecular formula**

Before declaring any pair to be "linkage / ionisation / coordination isomers", *add up the atoms*. If $\mathrm{C}_x\mathrm{H}_y\mathrm{N}_z\mathrm{Cl}_a\mathrm{Br}_b\ldots$ counts differ between the two formulas, they cannot be isomers — period.

**EXPERT'S SOLUTION** *: Ishaan Bhat, M.Tech Chemical Engineering, IIT Delhi*

**Strategic angle.** The first filter for every "what kind of isomerism?" MCQ is: do the two formulas have identical atom counts?

**Step 1.** Count atoms in each compound:

$$[\mathrm{Co(SO_4)(NH_3)_5}]\mathrm{Br}: \mathbf{Co_1\,S_1\,O_4\,N_5\,H_{15}\,Br_1},$$

$$[\mathrm{Co(SO_4)(NH_3)_5}]\mathrm{Cl}: \mathbf{Co_1\,S_1\,O_4\,N_5\,H_{15}\,Cl_1}.$$

Identical in every element except the halide. Different molecular formulas ⇒ not isomers.

**Step 2.** Compare with a *true* ionisation isomer pair: $[\mathrm{Co(NH_3)_5\,Br}]\mathrm{SO_4}$ vs $[\mathrm{Co(NH_3)_5\,SO_4}]\mathrm{Br}$ both have $\mathrm{Co\,N_5\,H_{15}\,Br\,S\,O_4}$ — identical formulas — and *do* differ only by swap of inner/outer-sphere anion.

**Step 3.** Answer: no isomerism between the two compounds in this question.

**Why this matters.** A board examiner often plants this distractor (swap one halide for another) to test whether the student remembers the formula-conservation requirement. Mark the trap once, never miss it again.

> **Final Answer:** No isomerism — option **(iv)**.

**Q 5.11** **A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?**

**(i) thiosulphato**

**(ii) oxalato**

**(iii) glycinato**

**(iv) ethane-1,2-diamine**

**SOLUTION**

**Correct option: (i)** thiosulphato.

**Concept used.** A **chelating agent** (or chelate ligand) is a polydentate ligand whose donor atoms are spaced so they can *simultaneously* bind to the same metal centre and close a 5- or 6-membered ring. Monodentate ligands cannot chelate even if they carry more than one lone pair, because only one donor atom binds at a time.

**Step 1.** Walk through the four ligands and check the bite:

- *Thiosulphato* $S_2O_3{}^{2-}$: usually *monodentate*, binding through one sulfur atom (the terminal $S$ is the soft donor). Although it has multiple lone-pair atoms, the geometry does not allow it to chelate to a single metal; on most metals it acts as a one-armed ligand. So *not* a chelating agent.
- *Oxalato* $C_2O_4{}^{2-}$: bidentate, binds through two $O^-$ atoms separated by a $C{-}C$ bond and forms a 5-membered chelate ring. ✓
- *Glycinato* $H_2N{-}CH_2{-}COO^-$: bidentate through the amino $N$ and the carboxylate $O^-$, forming a 5-membered chelate ring. ✓
- *Ethane-1,2-diamine* (en, $H_2N{-}CH_2{-}CH_2{-}NH_2$): bidentate through both amino $N$ atoms, forming a 5-membered ring. ✓

**Step 2.** The only ligand among the four that does not chelate is thiosulphato.

**Final Answer:** Option **(i)**: thiosulphato is not a chelating agent.

**EXPERT'S SOLUTION** : *Diya Banerjee, M.Sc Chemistry, IIT Kanpur*

**Strategic angle.** For each ligand, sketch the donor atoms and the ring it would close. If you cannot close a 5- or 6-membered ring, it cannot chelate.

**Step 1.** Oxalato: $^-O{-}C({=}O){-}C({=}O){-}O^-$, donors $O \cdots O$ separated by two carbons $\rightarrow$ 5-membered ring with M.

**Step 2.** Glycinato: $H_2N{-}CH_2{-}COO^-$, donors $N \cdots O$ separated by two atoms $\rightarrow$ 5-membered ring.

**Step 3.** Ethane-1,2-diamine: $H_2N{-}CH_2{-}CH_2{-}NH_2$, donors $N \cdots N$ separated by two carbons $\rightarrow$ 5-membered ring.

**Step 4.** Thiosulphato: $S{=}S({=}O)({=}O){-}O^-$. The four oxygens and the two sulfurs are bunched on a single tetrahedral $S$ atom, too close together to allow simultaneous coordination to one metal — it sits as a monodentate ligand.

**Why this matters.** "Number of donor atoms" alone is not the criterion; *geometry* of the donor positions is. Thiosulphate has many potential donors but cannot chelate because of its compact geometry.

> **Final Answer:** Thiosulphato, option **(i)**.

## Q 5.12 Which of the following species is not expected to be a ligand?

**(i)** $NO$
**(ii)** $NH_4{}^+$
**(iii)** $NH_2\,CH_2\,CH_2\,NH_2$
**(iv)** $CO$

SOLUTION

**Correct option: (ii)** $NH_4{}^+$.

**Concept used.** A ligand donates at least one *lone pair* of electrons into an empty orbital on the metal (or accepts $\pi$-back-donation, as in $CO$). If a species has *no lone pair* available, it cannot act as a ligand.

**Step 1.** Check the lone-pair availability of each species:

- $NO$: nitrogen carries a lone pair (and the molecule has an unpaired electron in $\pi^*$); $NO$ is a well-known neutral ligand, e.g. in $[Fe(NO)(H_2O)_5]^{2+}$ (the "brown ring" complex).
- $NH_4{}^+$: nitrogen has used all four lone pairs to bond with the four $H$ atoms; the formal positive charge means the nitrogen has *no remaining lone pair*. Cannot donate $\Rightarrow$ not a ligand.
- $NH_2\,CH_2\,CH_2\,NH_2$ (ethane-1,2-diamine, $en$): each $N$ has a lone pair, both donate to give a bidentate chelate. Excellent ligand.
- $CO$: carbon's lone pair donates via $\sigma$ and the $C{-}O$ $\pi^*$ accepts back-bonding. Quintessential ligand (carbonyl complexes).

**Step 2.** The only species without a free lone pair is $NH_4{}^+$.

> **Final Answer:** Option **(ii)**: $NH_4{}^+$ is not expected to be a ligand (no available lone pair).

**✗ Cationic species can still be ligands sometimes**

The rule is “ligand needs a free lone pair”, not “ligand must be neutral or anionic”. $NO^+$ for instance *is* a ligand (nitrosyl), donating the lone pair on N. $NH_4^+$ fails not because it is cationic but because all four lone pairs on N are already locked into N–H bonds.

**EXPERT’S SOLUTION** *: Yash Nair, M.Sc Chemistry, IIT Kanpur*

**Quick reading.** Draw each Lewis structure mentally and look for a lone pair on the donor atom.

**Step 1.** NO: $:N{=}O$ with an extra electron in $\pi^*$. Lone pair on N → ligand.

**Step 2.** $NH_4^+$: four single bonds to four hydrogens. All four electron pairs are committed. No lone pair → not a ligand.

**Step 3.** $H_2N{-}CH_2{-}CH_2{-}NH_2$: each N has one lone pair → bidentate ligand.

**Step 4.** $:C{\equiv}O::$ lone pair on C and one on O. Almost always binds through C → ligand.

**Why this matters.** Distinguishing “$NH_3$ is a ligand” from “$NH_4^+$ is not a ligand” tests whether the student understands lone pairs and not just chemical names.

**Final Answer:** $NH_4^+$, option **(ii)**.

**Q 5.13** **What kind of isomerism exists between $[Cr(H_2O)_6]Cl_3$ (violet) and $[Cr(H_2O)_5\,Cl]Cl_2 \cdot H_2O$ (greyish-green)?**

**(i) linkage isomerism (ii) solvate isomerism**

**(iii) ionisation isomerism (iv) coordination isomerism**

**SOLUTION**

**Correct option: (ii)** solvate (hydrate) isomerism.

**Concept used.** Solvate isomerism (called hydrate isomerism when the solvent is water) is the swap of solvent molecules between the inner coordination sphere and the outer (lattice) sphere, with another ligand (often a halide) moving in the opposite direction. Total molecular formula stays the same; what changes is which water molecules are coordinated and which are merely lattice water.

**Step 1.** Verify the two compounds have the same molecular formula $CrCl_3\cdot{}_6\,H_2O$:

- $[Cr(H_2O)_6]Cl_3$: $Cr + 6\,H_2O + 3\,Cl$ — total $CrCl_3\cdot{}_6H_2O$.
- $[Cr(H_2O)_5\,Cl]Cl_2\cdot H_2O$: $Cr + 5\,H_2O + 1\,Cl$ inside, plus $2\,Cl$ outside, plus $1\,H_2O$ in the lattice — total $CrCl_3\cdot{}_6H_2O$. ✓

**Step 2.** Compare the inner spheres: the violet form has $6\,H_2O$ inside and $3\,Cl^-$ outside;

the greyish-green form has $5\,H_2O + 1\,Cl^-$ inside and $2\,Cl^- + 1\,H_2O$ outside. One $H_2O$ has been swapped with one $Cl^-$. This is the textbook definition of solvate isomerism.

**Step 3.** The third isomer of this family is the dark green $[Cr(H_2O)_4\,Cl_2]Cl\cdot{}_2H_2O$.

> **Final Answer:** Option **(ii)**: the pair shows solvate (hydrate) isomerism.

**♥ Hydrate isomers, three different colours**

$CrCl_3\cdot{}_6H_2O$ exists as three hydrate isomers in the lab, with strikingly different colours: violet $[Cr(H_2O)_6]Cl_3$, greyish-green $[Cr(H_2O)_5\,Cl]Cl_2\cdot H_2O$, and dark-green $[Cr(H_2O)_4\,Cl_2]Cl\cdot{}_2H_2O$. The hue depends on $\Delta_o$, which changes as $H_2O$ ligands are replaced by the weaker-field $Cl^-$. Each one also has a distinct conductivity and gives a different number of $AgCl$ moles in a Werner titration.

**EXPERT'S SOLUTION** *: Tara Desai, Ph.D Organic Chemistry, IISc Bangalore*

**Strategic angle.** Same molecular formula + difference confined to solvent-vs-halide partitioning between spheres = solvate isomerism. Verify the formula match first.

**Step 1.** Both formulas reduce to $CrCl_3\cdot{}_6\,H_2O$. Without this match, "isomerism" is the wrong word.

**Step 2.** Find what is moving: an $H_2O$ from outer $\rightarrow$ inner is balanced by a $Cl^-$ from inner $\rightarrow$ outer (or vice versa). This is the solvate-isomerism fingerprint.

**Step 3.** Distinguish from ionisation isomerism: the latter requires the *anion* (not the solvent) to swap; the moving partner here is $H_2O$, hence "solvate"/"hydrate".

**Why this matters.** Solvate isomers are also called "hydrate" isomers in older NCERT editions. Both names appear in JEE answer keys; they refer to the same phenomenon.

> **Final Answer:** Solvate (hydrate) isomerism, option **(ii)**.

**Q 5.14** **IUPAC name of $[Pt(NH_3)_2\,Cl\,(NO_2)]$ is:**

**(i) Platinum diaminechloronitrite**

**(ii) Chloronitrito-$N$-ammineplatinum(II)**

**(iii) Diamminechloridonitrito-$N$-platinum(II)**

**(iv) Diamminechloronitrito-$N$-platinate(II)**

SOLUTION

**Correct option: (iii)** Diamminechloridonitrito-$N$-platinum(II).

**Concept used.** Same IUPAC rules as in Q5 with one extra wrinkle: $NO_2{}^-$ is ambidentate. When the ligand binds through the nitrogen atom, the IUPAC name is **nitrito-$N$** (or “nitro” in older books); when it binds through oxygen, the name is **nitrito-$O$**. Modern 2005 IUPAC convention uses **nitrito-$N$**/**nitrito-$O$** uniformly, replacing the “nitro”/“nitrito” split of the older books.

**Step 1.** Find the oxidation state of $\mathrm{Pt}$. Ligand charges: $NH_3 = 0$, $Cl^- = -1$, $NO_2{}^- = -1$. The complex is neutral, so

$$x + 2(0) + (-1) + (-1) = 0 \;\Rightarrow\; x = +2.$$

So Pt is in oxidation state $+2$.

**Step 2.** Alphabetise ligands (ignoring multiplicity prefixes):

- **ammine** (a) for $NH_3$ — multiplicity 2.
- **chlorido** (c) for $Cl^-$.
- **nitrito-$N$** (n) for the $N$-bound $NO_2{}^-$.

Order: a $<$ c $<$ n $\rightarrow$ ammine, chlorido, nitrito-$N$.

**Step 3.** Assemble the name:

$$\text{di-ammine} \;+\; \text{chlorido} \;+\; \text{nitrito-}N \;+\; \text{platinum(II)}$$

$\Rightarrow$ diamminechloridonitrito-$N$-platinum(II). Note: “ammine” has two m’s; “chlorido” uses the 2005 suffix (the old “chloro” is also acceptable but NCERT 2026–27 uses “chlorido”); the complex is neutral, so the metal name ends in “platinum” (not the -ate form “platinate”, which is for anionic complexes).

**Final Answer:** Option **(iii)**: diamminechloridonitrito-$N$-platinum(II).

***✗ platinum vs platinate***

The “-ate” suffix is used for the metal name only when the whole complex carries a net *negative* charge. $[\mathrm{Pt(NH_3)_2\,Cl\,(NO_2)}]$ is neutral → “platinum”. $[\mathrm{PtCl_4}]^{2-}$ is anionic → “tetrachloridoplatinate(II)”. Option (iv) traps the student here.

EXPERT’S SOLUTION *: Krishna Rao, M.Sc Chemistry, IIT Kanpur*

**Quick reading.** Each option is wrong for a specific reason. Knock them out one by one.

**Step 1.** Option (i): “platinum diaminechloronitrite” — wrong word order (metal at the front), wrong spelling (“diamine” with one m would mean an organic $-NH_2$

group), no oxidation state. Eliminated.

**Step 2.** Option (ii): "chloronitrito-$N$-ammineplatinum(II)" — wrong alphabetical order (chloro before ammine), missing the "di" multiplicity for $NH_3$. Eliminated.

**Step 3.** Option (iv): "…platinate(II)" — the complex is neutral, so the metal name should be "platinum", not the anionic suffix "platinate". Eliminated.

**Step 4.** Option (iii): correct word order (alphabetical: ammine, chlorido, nitrito-$N$), correct multiplicity (di-ammine), correct neutral metal name (platinum), correct oxidation state in roman numerals. Survives all four checks.

**Why this matters.** A clean nomenclature drill: spelling (*ammine*), 2005 update (*chlorido*), ambidentate specification ($-N$ vs $-O$), alphabetical order, and -ate/-um distinction — all in one question.

> **Final Answer:** Diamminechloridonitrito-$N$-platinum(II), option **(iii)**.

## II. Multiple Choice Questions (Type-II)

*Note: In the following questions two or more options may be correct.*

**Q 5.15** **Atomic numbers of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?**

**(i)** $[Co(NH_3)_6]^{3+}$
**(ii)** $[Mn(CN)_6]^{3-}$
**(iii)** $[Fe(CN)_6]^{4-}$
**(iv)** $[Fe(CN)_6]^{3-}$

**SOLUTION**

**Correct options: (i) and (iii).**

**Concept used.** For an octahedral $d^n$ complex in the **inner-orbital** (low-spin) picture used by Valence Bond Theory, the $3d$ electrons pair up in the lower $t_{2g}$ set whenever the ligand field is strong enough ($\Delta_o > P$). The result is $d^2sp^3$ hybridisation and a magnetic behaviour determined by the number of unpaired electrons $n$: $n = 0 \Rightarrow$ diamagnetic; $n \geq 1 \Rightarrow$ paramagnetic.

**Step 1.** Compute the metal oxidation state and $d^n$:

- (i) $[Co(NH_3)_6]^{3+}: Co^{3+},\ d^6$.
- (ii) $[Mn(CN)_6]^{3-}: Mn^{3+},\ d^4$.
- (iii) $[Fe(CN)_6]^{4-}: Fe^{2+},\ d^6$.

- (iv) $[\mathrm{Fe(CN)_6}]^{3-}$ : $\mathrm{Fe^{3+}}$, $d^5$.

**Step 2.** Fill the low-spin $t_{2g}$ first (since these are inner-orbital, low-spin complexes):

- $d^6$: all six in $t_{2g}$, $n = 0$ unpaired → diamagnetic. So (i) and (iii) are diamagnetic.
- $d^4$: $t_{2g}^4 e_g^0$, $n = 2$ unpaired → paramagnetic. So (ii) is paramagnetic.
- $d^5$: $t_{2g}^5 e_g^0$, $n = 1$ unpaired → paramagnetic. So (iv) is paramagnetic.

**Step 3.** Therefore the diamagnetic complexes are (i) $[\mathrm{Co(NH_3)_6}]^{3+}$ and (iii) $[\mathrm{Fe(CN)_6}]^{4-}$.

**Final Answer:** Options **(i)** and **(iii)**.

☞ **Only $d^6$ low-spin is fully diamagnetic**

Among first-row octahedral inner-orbital complexes, only $d^6$ ($t_{2g}^6$) achieves the closed-shell diamagnetic state. $d^4, d^5, d^7$ low-spin all retain at least one unpaired electron in $t_{2g}$.

**EXPERT'S SOLUTION** : *Aanya Bhat, M.Sc Physical Chemistry, IIT Madras*

**Quick reading.** Inner-orbital (low-spin) means electrons pair in $t_{2g}$. Only $d^6$ ions can be fully paired in $t_{2g}$ alone. Look for $d^6$ and you have the diamagnetic ones.

**Step 1.** Map each option to $d^n$: $d^6, d^4, d^6, d^5$ for (i), (ii), (iii), (iv).

**Step 2.** Low-spin $d^6$: $t_{2g}^6 e_g^0$, all paired → diamagnetic. Low-spin $d^4$: one unpaired pair, so $n = 2$. Low-spin $d^5$: $n = 1$.

**Step 3.** Both (i) and (iii) are $d^6$, hence diamagnetic; (ii) and (iv) carry unpaired electrons even in the low-spin limit.

**Why this matters.** $[\mathrm{Fe(CN)_6}]^{4-}$ is the diamagnetic "ferrocyanide" anion; $[\mathrm{Fe(CN)_6}]^{3-}$ is paramagnetic ferricyanide. One electron's difference, totally different magnetic behaviour — the cleanest demonstration that $d^n$ matters.

**Final Answer:** (i) $[\mathrm{Co(NH_3)_6}]^{3+}$ and (iii) $[\mathrm{Fe(CN)_6}]^{4-}$.

**Q 5.16** **Atomic numbers of Mn, Fe, Co and Ni are 25, 26, 27 and 28 respectively. Which of the following outer orbital octahedral complexes have the same number of unpaired electrons?**

**(i)** $[\mathrm{MnCl_6}]^{3-}$
**(ii)** $[\mathrm{FeF_6}]^{3-}$

**(iii)** $[\mathrm{CoF_6}]^{3-}$
**(iv)** $[\mathrm{Ni(NH_3)_6}]^{2+}$

SOLUTION

**Correct options: (i) and (iii).**
**Concept used.** Outer-orbital (high-spin) octahedral complexes use $\mathrm{sp^3\,d^2}$ hybridisation; the metal $3d$ electrons remain unpaired wherever possible, following Hund's rule.

**Step 1.** Compute $d^n$ for each complex:

- (i) $[\mathrm{MnCl_6}]^{3-}$ : $\mathrm{Mn^{3+}}$, $d^4$.
- (ii) $[\mathrm{FeF_6}]^{3-}$ : $\mathrm{Fe^{3+}}$, $d^5$.
- (iii) $[\mathrm{CoF_6}]^{3-}$ : $\mathrm{Co^{3+}}$, $d^6$.
- (iv) $[\mathrm{Ni(NH_3)_6}]^{2+}$ : $\mathrm{Ni^{2+}}$, $d^8$.

Note: $\mathrm{NH_3}$ is borderline; $[\mathrm{Ni(NH_3)_6}]^{2+}$ is treated as outer orbital ($\mathrm{sp^3\,d^2}$) in NCERT.

**Step 2.** Fill the high-spin configuration (maximise unpaired electrons in $t_{2g} + e_g$, 5 orbitals total):

- $d^4$: $t_{2g}^3 e_g^1$, $n = 4$ unpaired.
- $d^5$: $t_{2g}^3 e_g^2$, $n = 5$ unpaired.
- $d^6$: $t_{2g}^4 e_g^2$, $n = 4$ unpaired.
- $d^8$: $t_{2g}^6 e_g^2$, $n = 2$ unpaired.

**Step 3.** Match $n$ values: (i) and (iii) both have $n = 4$, so they share the same number of unpaired electrons. (ii) has $5$, (iv) has $2$.

> **Final Answer:** Options **(i)** and **(iii)**, both with $4$ unpaired electrons.

☞ **High-spin counts at a glance**
For high-spin octahedral $d^n$ $(n = 1, \ldots, 10)$: $n_{\text{unp}} = 1, 2, 3, 4, 5, 4, 3, 2, 1, 0$ — a tidy "up and down" pattern.

EXPERT'S SOLUTION *: Rohit Singh, M.Sc Chemistry, IIT Kanpur*

**Strategic angle.** Outer-orbital means high-spin. Read off $n_{\text{unpaired}}$ from the standard table; find two complexes that match.

**Step 1.** $\mathrm{Mn^{3+}}$ ($d^4$, high-spin): $4$ unpaired. $\mathrm{Fe^{3+}}$ ($d^5$, high-spin): $5$ unpaired. $\mathrm{Co^{3+}}$ ($d^6$, high-spin): $4$ unpaired. $\mathrm{Ni^{2+}}$ ($d^8$, high-spin): $2$ unpaired.

**Step 2.** Match: $\mathrm{Mn^{3+}}$ and $\mathrm{Co^{3+}}$ both have $4$. They also have the same spin-only $\mu = \sqrt{4(4+2)} = \sqrt{24} \approx 4.90$ BM.

**Step 3.** Sanity check on (ii): $[\mathrm{FeF_6}]^{3-}$ is famously $\mu = 5.92$ BM (the highest possible for first-row transition metals).

**Why this matters.** "Same number of unpaired electrons" is the same as "same spin-only magnetic moment", which is what an experimentalist actually measures with a Gouy balance.

> **Final Answer:** (i) and (iii), both with $4$ unpaired electrons.

**Q 5.17** **Which of the following options are correct for $[\mathrm{Fe(CN)_6}]^{3-}$ complex?**

**(i) $d^2sp^3$ hybridisation**

**(ii) $sp^3d^2$ hybridisation**

**(iii) paramagnetic**

**(iv) diamagnetic**

SOLUTION

**Correct options: (i) and (iii).**

**Concept used.** For $[\mathrm{Fe(CN)_6}]^{3-}$, $\mathrm{Fe}$ is in the $+3$ oxidation state, $d^5$. Since $\mathrm{CN^-}$ is a strong-field ligand (top of the spectrochemical series), it forces low-spin pairing in $t_{2g}$, and the empty $(n-1)d$ orbitals participate in hybridisation — i.e. **inner-orbital** $d^2sp^3$. One unpaired electron remains ⇒ paramagnetic.

**Step 1.** Oxidation state: charge balance $\mathrm{Fe} + 6(-1) = -3 \Rightarrow \mathrm{Fe} = +3$. So $\mathrm{Fe^{3+}} : [\mathrm{Ar}]\,3d^5$.

**Step 2.** Strong-field $\mathrm{CN^-}$ forces pairing: low-spin $d^5$ configuration is $t_{2g}^5e_g^0$. Two $3d$ orbitals are empty after pairing; they hybridise with one $4s$ and three $4p$ orbitals to give $d^2sp^3$ (inner orbital). So (i) is correct; (ii) is wrong (that would be the outer-orbital $sp^3d^2$, used by weak-field $[\mathrm{FeF_6}]^{3-}$).

**Step 3.** Unpaired electrons in $t_{2g}^5$: there is one electron in one orbital not paired (the 5th electron has no partner in $t_{2g}^4$). $n = 1$, so the complex is paramagnetic with $\mu = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73$ BM. So (iii) correct; (iv) wrong.

> **Final Answer:** Options **(i)** $d^2sp^3$ and **(iii) paramagnetic** (one unpaired electron, $\mu \approx 1.73$ BM).

**EXPERT'S SOLUTION** *: Neha Chatterjee, Ph.D Organic Chemistry, IISc Bangalore*

**Strategic angle.** Strong-field $\mathrm{CN^-}$ → low-spin → inner-orbital $d^2sp^3$. The geometry is therefore octahedral and the magnetic moment is small but nonzero ($d^5$ low-spin keeps one unpaired electron).

**Step 1.** Place $\mathrm{CN^-}$ on the spectrochemical series (very high) $\Rightarrow$ pairing energy $P < \Delta_o$ $\Rightarrow$ low-spin.

**Step 2.** Low-spin $d^5$ in octahedral field: $t_{2g}^5 e_g^0$, so $n_{\text{unpaired}} = 1$. Two $3d$ orbitals are now empty and join the $4s, 4p$ orbitals in $d^2sp^3$ hybridisation (the two $d$'s come from the $(n-1)$ shell, hence "inner orbital").

**Step 3.** Therefore: paramagnetic (one unpaired), $d^2sp^3$ inner orbital, $\mu \approx 1.73$ BM.

**Why this matters.** Compare with $[\mathrm{FeF_6}]^{3-}$ (outer orbital, $sp^3d^2$, $5$ unpaired, $\mu \approx 5.92$ BM). Same metal oxidation state, very different magnetic moments — the textbook demonstration of how ligand field strength rules.

> **Final Answer:** $d^2sp^3$ hybridisation, paramagnetic — options **(i)** and **(iii)**.

**Q 5.18** **An aqueous pink solution of cobalt(II) chloride changes to deep blue on addition of excess of $\mathrm{HCl}$. This is because __________.**

**(i) $[\mathrm{Co(H_2O)_6}]^{2+}$ is transformed into $[\mathrm{CoCl_6}]^{4-}$**

**(ii) $[\mathrm{Co(H_2O)_6}]^{2+}$ is transformed into $[\mathrm{CoCl_4}]^{2-}$**

**(iii) tetrahedral complexes have smaller crystal field splitting than octahedral complexes.**

**(iv) tetrahedral complexes have larger crystal field splitting than octahedral complex.**

**SOLUTION**

**Correct options: (ii) and (iii).**

**Concept used.** Two effects combine to explain the colour change. (a) Excess $\mathrm{Cl^-}$ displaces $\mathrm{H_2O}$ ligands and *changes the geometry* from octahedral $[\mathrm{Co(H_2O)_6}]^{2+}$ to tetrahedral $[\mathrm{CoCl_4}]^{2-}$ — note the coordination number drops from $6$ to $4$. (b) The new geometry has a smaller crystal field splitting ($\Delta_t = \frac{4}{9}\Delta_o$), so the absorption shifts to longer $\lambda$, moving the observed colour from pink (oct.) to blue (tet.).

**Step 1.** The reaction:

$$[\mathrm{Co(H_2O)_6}]^{2+} + 4\,\mathrm{Cl^-} \longrightarrow [\mathrm{CoCl_4}]^{2-} + 6\,\mathrm{H_2O}.$$

Coordination number changes $6 \to 4$; geometry changes octahedral → tetrahedral.

**Step 2.** Option-by-option check:

- (i) wrong — $[CoCl_6]^{4-}$ would still be octahedral; doesn't fit the colour change cause.
- (ii) correct — the tetrahedral $[CoCl_4]^{2-}$ is the actual blue species.
- (iii) correct and crucial — $\Delta_t \approx (4/9)\Delta_o$ underlies the wavelength shift.
- (iv) wrong — opposite of (iii).

**Step 3.** Numerical sanity: $\Delta_o([Co(H_2O)_6]^{2+})$ corresponds to absorption around $510\,\text{nm}$ (green absorbed, so we see pink/red), while $[CoCl_4]^{2-}$ absorbs around $670\,\text{nm}$ (red absorbed, so we see blue).

> **Final Answer:** Options **(ii)** and **(iii)**.

### ♥ Cobalt chloride humidity indicator paper

The pink ↔ blue switch is exploited in moisture-indicating silica gel. Dry $CoCl_2$ is tetrahedral blue; on absorbing water it hydrates to pink octahedral $[Co(H_2O)_6]^{2+}$ — the classic colour test for water in laboratory desiccators.

**EXPERT'S SOLUTION** *: Aditya Verma, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — two simultaneous truths.** The colour flip pink → blue is driven by *two* facts that must hold at once: (a) a geometry change (oct → tet, drop in coordination number from 6 to 4) and (b) a splitting change ($\Delta_o \to \Delta_t = \frac{4}{9}\Delta_o$, much smaller). The correct options are exactly the ones that name these two facts.

**Step 1.** *Identify the new species.* Excess $Cl^-$ peels off the six aqua ligands and locks the cobalt into the cheap, low-coordination $[CoCl_4]^{2-}$. Coordination number drops $6 \to 4$; geometry switches octahedral → tetrahedral. Option (ii) names this species — *correct*.

**Step 2.** *Quote the CFT inequality.* Tetrahedral splitting is *always smaller* than octahedral for the same ligand set: $\Delta_t = \frac{4}{9}\Delta_o$ ($\approx 0.45\Delta_o$). Because $\lambda_{\text{abs}} = hc/\Delta$, smaller $\Delta$ means longer $\lambda$ absorbed — and the observed colour (complement) shifts toward blue. Option (iii) states this — *correct*.

**Step 3.** *Rule out the distractors.* Option (iv) flips the sign: it claims $\Delta_t > \Delta_o$, contradicting the geometric factor (only 4 ligands instead of 6, none on a $d$-orbital axis). Option (i) names $[CoCl_6]^{4-}$, which would still be octahedral and would not explain the colour change — and it isn't even the species formed.

**Why this matters.** The pink ↔ blue colour flip is a single observation that probes *three* chapter ideas simultaneously: ligand substitution kinetics ($H_2O \to Cl^-$), coordination-number change ($6 \to 4$), and $\Delta_t/\Delta_o$ ratio — which is why it recurs in board, JEE (2019) and NEET papers year after year.

**Final Answer:** Options **(ii)** and **(iii)**.

**Q 5.19** **Which of the following complexes are homoleptic?**

**(i)** $[\mathrm{Co(NH_3)_6}]^{3+}$

**(ii)** $[\mathrm{Co(NH_3)_4\,Cl_2}]^{+}$

**(iii)** $[\mathrm{Ni(CN)_4}]^{2-}$

**(iv)** $[\mathrm{Ni(NH_3)_4\,Cl_2}]$

SOLUTION

**Correct options: (i) and (iii).**

**Concept used.** A **homoleptic** complex contains only *one type* of ligand bound to the metal. A **heteroleptic** complex contains more than one type. So count distinct ligand species in the coordination sphere.

**Step 1.** Inspect ligand types in the inner sphere:

- (i) $[\mathrm{Co(NH_3)_6}]^{3+}$: only $\mathrm{NH_3}$ — one type. Homoleptic. ✓
- (ii) $[\mathrm{Co(NH_3)_4\,Cl_2}]^{+}$: $\mathrm{NH_3}$ and $\mathrm{Cl^-}$ — two types. Heteroleptic.
- (iii) $[\mathrm{Ni(CN)_4}]^{2-}$: only $\mathrm{CN^-}$ — one type. Homoleptic. ✓
- (iv) $[\mathrm{Ni(NH_3)_4\,Cl_2}]$: $\mathrm{NH_3}$ and $\mathrm{Cl^-}$ — two types. Heteroleptic.

**Step 2.** Therefore homoleptic complexes are (i) and (iii).

**Final Answer:** Options **(i)** and **(iii)** are homoleptic.

EXPERT'S SOLUTION *: Ishita Iyer, M.Sc Chemistry, IIT Kanpur*

**Quick reading.** "Homo" = "same". Look at the coordination sphere; if you see only one symbol for ligands, it's homoleptic.

**Step 1.** (i) and (iii) each list a single ligand species (six $\mathrm{NH_3}$ and four $\mathrm{CN^-}$ respectively).

**Step 2.** (ii) and (iv) each list two different ligand species ($\mathrm{NH_3} + \mathrm{Cl^-}$).

**Step 3.** Homoleptic: (i), (iii). Heteroleptic: (ii), (iv).

**Why this matters.** Many quick-fire NEET MCQs are decided by this single distinction. "Homoleptic" vs "heteroleptic" is also the key to predicting whether a complex *can* show geometrical isomerism.

> **Final Answer:** (i) $[\mathrm{Co(NH_3)_6}]^{3+}$ and (iii) $[\mathrm{Ni(CN)_4}]^{2-}$.

**Q 5.20** **Which of the following complexes are heteroleptic?**

**(i)** $[\mathrm{Cr(NH_3)_6}]^{3+}$
**(ii)** $[\mathrm{Fe(NH_3)_4\,Cl_2}]^{+}$
**(iii)** $[\mathrm{Mn(CN)_6}]^{4-}$
**(iv)** $[\mathrm{Co(NH_3)_4\,Cl_2}]$

SOLUTION

**Correct options: (ii) and (iv).**

**Concept used.** Same definitional contrast as Q19. A complex is **heteroleptic** if it contains *more than one* type of ligand bound to the central metal.

**Step 1.** Inspect ligand types in the inner sphere of each option:

- (i) $[\mathrm{Cr(NH_3)_6}]^{3+}$: six $\mathrm{NH_3}$ ligands. One type only. Homoleptic.
- (ii) $[\mathrm{Fe(NH_3)_4\,Cl_2}]^{+}$: $\mathrm{NH_3}$ and $\mathrm{Cl^-}$. Two types. Heteroleptic. ✓
- (iii) $[\mathrm{Mn(CN)_6}]^{4-}$: six $\mathrm{CN^-}$. One type. Homoleptic.
- (iv) $[\mathrm{Co(NH_3)_4\,Cl_2}]$: $\mathrm{NH_3}$ and $\mathrm{Cl^-}$. Two types. Heteroleptic. ✓

**Step 2.** Therefore the heteroleptic options are (ii) and (iv).

> **Final Answer:** Options **(ii)** and **(iv)**.

EXPERT'S SOLUTION : *Meera Kumar, M.Tech Chemical Engineering, IIT Delhi*

**Quick reading.** Mirror of Q19. Two different ligand species in the brackets ⇒ heteroleptic.

**Step 1.** (ii) and (iv) each have $\mathrm{NH_3}$ and $\mathrm{Cl}$ ligands on the same metal — heteroleptic.

**Step 2.** (i) is six $\mathrm{NH_3}$ and (iii) is six $\mathrm{CN^-}$ — both homoleptic.

**Step 3.** Heteroleptic complexes are necessary for geometrical isomerism (in suitable patterns) and for many catalytic complexes because mixed-ligand environments allow tunability.

**Why this matters.** Most useful catalysts (Wilkinson's, Grubbs, cisplatin) are heteroleptic — the differing ligands tune the metal centre's reactivity in opposite directions on the same molecule.

**Final Answer:** (ii) $[\mathrm{Fe(NH_3)_4\,Cl_2}]^+$ and (iv) $[\mathrm{Co(NH_3)_4\,Cl_2}]$.

**Q 5.21** **Identify the optically active compounds from the following:**

**(i)** $[\mathrm{Co(en)_3}]^{3+}$

**(ii) trans-**$[\mathrm{Co(en)_2\,Cl_2}]^+$

**(iii) cis-**$[\mathrm{Co(en)_2\,Cl_2}]^+$

**(iv)** $[\mathrm{Cr(NH_3)_5\,Cl}]^{2+}$

SOLUTION

**Correct options: (i) and (iii).**

**Concept used.** A complex is optically active (chiral) if it has *no* improper symmetry element ($\sigma$ plane, $i$, $S_n$) — equivalently, if its mirror image is non-superimposable on the original. Octahedral $[\mathrm{M(en)_3}]^{n+}$ complexes are chiral by virtue of the three chelate rings winding in either a $\Lambda$ or $\Delta$ helix. For $[\mathrm{M(en)_2\,X_2}]^{n+}$ the cis isomer is chiral but the trans isomer is achiral (it has a $\sigma$ plane containing the two $\mathrm{X}$ ligands).

**Step 1.** (i) $[\mathrm{Co(en)_3}]^{3+}$: three bidentate $\mathrm{en}$ ligands wrap the octahedron in a propeller pattern. Two non-superimposable enantiomers ($\Lambda$ and $\Delta$). $\Rightarrow$ optically active. ✓

**Step 2.** (ii) trans-$[\mathrm{Co(en)_2\,Cl_2}]^+$: the two $\mathrm{Cl}$ on opposite vertices; the molecule has a $\sigma$ plane containing the $\mathrm{Cl{-}Co{-}Cl}$ axis. $\Rightarrow$ optically inactive (achiral).

**Step 3.** (iii) cis-$[\mathrm{Co(en)_2\,Cl_2}]^+$: the two $\mathrm{Cl}$ on adjacent vertices; the molecule has no $\sigma$ plane. Two enantiomers exist $\Rightarrow$ optically active. ✓

**Step 4.** (iv) $[\mathrm{Cr(NH_3)_5\,Cl}]^{2+}$: $\mathrm{MA_5\,B}$ pattern; has a $C_4$ axis and several $\sigma$ planes through the Cl-Cr axis $\Rightarrow$ optically inactive.

**Final Answer:** Options **(i)** $[\mathrm{Co(en)_3}]^{3+}$ and **(iii)** cis-$[\mathrm{Co(en)_2\,Cl_2}]^+$.

### ♥ Helical chirality without carbon

Optical activity is famous for carbon stereocentres, but $[\mathrm{Co(en)_3}]^{3+}$ has *none*. The chirality lives in the 3-blade propeller geometry of three bidentate chelates wrapped around the metal — pure $\Delta/\Lambda$ helical chirality. This is how Werner proved coordination compounds are 3D objects, not flat ones.

**EXPERT'S SOLUTION** : *Sanya Mehta, M.Sc Chemistry, IIT Kanpur*

**Picture-first.** Build the three-blade propeller in your head and look for a mirror plane.

**Step 1.** $[Co(en)_3]^{3+}$ — three en chelates form a propeller; mirror image has the opposite handedness. No improper symmetry. Chiral.

**Step 2.** cis-$[Co(en)_2Cl_2]^{+}$ — the two Cl adjacent; the two en chelates wrap the remaining four vertices in two possible helical orientations → two enantiomers. Chiral.

**Step 3.** trans-$[Co(en)_2Cl_2]^{+}$ — the two Cl on the $z$-axis; the two en in the $xy$ plane. Mirror plane is the $xy$ plane itself → achiral.

**Step 4.** $[Cr(NH_3)_5Cl]^{2+}$ — $C_{4v}$ symmetry, multiple mirror planes → achiral.

**Why this matters.** Werner's resolution of $[Co(en)_2(NH_3)Cl]^{2+}$ into two enantiomers (1911) clinched his octahedral geometry over the prism alternative — one of the foundational experiments in inorganic chemistry.

**Final Answer:** (i) $[Co(en)_3]^{3+}$ and (iii) cis-$[Co(en)_2Cl_2]^{+}$.

**Q 5.22** **Identify the correct statements for the behaviour of ethane-1,2-diamine as a ligand.**

**(i) It is a neutral ligand.**

**(ii) It is a didentate ligand.**

**(iii) It is a chelating ligand.**

**(iv) It is a unidentate ligand.**

**SOLUTION**

**Correct options: (i), (ii) and (iii).**

**Concept used.** Ethane-1,2-diamine (en) is $H_2N-CH_2-CH_2-NH_2$, a small molecule with *two* amino groups separated by a $-CH_2-CH_2-$ bridge. Each N donates its lone pair to the metal; the spacing closes a 5-membered chelate ring.

**Step 1.** Charge: neither nitrogen carries a formal charge; the overall molecule is neutral ⇒ statement (i) true.

**Step 2.** Denticity: each en molecule donates through *two* donor atoms (both nitrogens) ⇒ bidentate (didentate) ⇒ statement (ii) true; statement (iv) (unidentate) is false.

**Step 3.** Chelating: a polydentate ligand that grabs the same metal with two or more donor atoms forming a ring is, by definition, chelating. en + M forms a

5-membered $M-N-C-C-N$ ring ⇒ statement (iii) true.

**Step 4.** Therefore the correct statements are (i), (ii) and (iii).

**Final Answer:** Options **(i)**, **(ii)** and **(iii)**.

**EXPERT'S SOLUTION** *: Aditi Sharma, M.Sc Physical Chemistry, IIT Madras*

**Strategic angle.** Apply three quick tests: charge, number of donor atoms, and ring formation.

**Step 1.** Charge: count formal charges on $H_2N-CH_2-CH_2-NH_2$ — all zero. Neutral → (i).

**Step 2.** Donor count: two N atoms, each with a lone pair directed at the same metal → bidentate → (ii). Hence (iv) is wrong.

**Step 3.** Ring test: $M-N-C-C-N$ closes a 5-membered ring (the "magic-number" ring size) → chelating → (iii).

**Why this matters.** en is the most-used bidentate ligand in NCERT problems. Knowing its three signature properties (neutral, bidentate, chelating) handles half the chapter's nomenclature and isomerism questions.

**Final Answer:** Options **(i)**, **(ii)**, **(iii)**.

### Q 5.23 Which of the following complexes show linkage isomerism?

**(i)** $[Co(NH_3)_5\,(NO_2)]^{2+}$

**(ii)** $[Co(H_2O)_5\,CO]^{3+}$

**(iii)** $[Cr(NH_3)_5\,SCN]^{2+}$

**(iv)** $[Fe(en)_2\,Cl_2]^{+}$

**SOLUTION**

**Correct options: (i) and (iii).**

**Concept used.** Linkage isomerism is shown by complexes *only when* they contain an ambidentate ligand — one with two different donor atoms. Common ambidentate ligands: $NO_2{}^-$ (can bind through N or O); $SCN^-$ (through S or N); $CN^-$ (through C or N).

**Step 1.** Scan for ambidentate ligands:

- (i) $[Co(NH_3)_5\,(NO_2)]^{2+}$: contains $NO_2{}^-$ — ambidentate. ⇒ shows linkage isomerism with $[Co(NH_3)_5(ONO)]^{2+}$.

- (ii) $[Co(H_2O)_5CO]^{3+}$: contains CO. Although CO technically has lone pairs on both C and O, the O-bound form is vanishingly stable; NCERT treats CO as monodentate (C-bound) and not ambidentate in practice. No linkage isomerism.
- (iii) $[Cr(NH_3)_5SCN]^{2+}$: contains $SCN^-$ — ambidentate (through S or N). $\Rightarrow$ linkage isomerism with $[Cr(NH_3)_5NCS]^{2+}$.
- (iv) $[Fe(en)_2Cl_2]^+$: en (chelating bidentate, only N donor) and $Cl^-$ (monodentate, only Cl donor) — no ambidentate ligand. No linkage isomerism.

**Step 2.** Therefore (i) and (iii) show linkage isomerism.

> **Final Answer:** Options **(i)** and **(iii)**.

**✗ CO is not treated as ambidentate**

Although free CO has lone pairs on both C and O, in metal complexes carbonyl always binds through C ($M{-}C{\equiv}O$). The O-bound "isocarbonyl" form is known only in extremely exotic matrix-isolated species.

**EXPERT'S SOLUTION** *: Priya Iyer, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — ambidentate scan.** Three ambidentate ligand families show up in NCERT-level problems: $NO_2^-$ (nitrito-$N$ vs nitrito-$O$), $SCN^-$ (thiocyanato-$S$ vs thiocyanato-$N$) and $CN^-$ (cyano-$C$ vs isocyano-$N$). Spot any of these in the formula and linkage isomerism follows automatically; spot none and it doesn't.

**Step 1.** *(i) Has* $NO_2^-$. Two attachment isomers: $[Co(NH_3)_5{-}NO_2]^{2+}$ (nitrito-$N$, N-bound, yellow) and $[Co(NH_3)_5{-}ONO]^{2+}$ (nitrito-$O$, O-bound, red). Linkage isomerism — *yes*.

**Step 2.** *(ii) Has* CO *(only)*. Although CO has a lone pair on O as well, the O-bound "isocarbonyl" form is observed only in matrix-isolated exotic species. NCERT treats CO as C-bound only. Linkage isomerism — *no*.

**Step 3.** *(iii) Has* $SCN^-$. Two isomers: $[Cr(NH_3)_5{-}SCN]^{2+}$ (thiocyanato-$S$) and $[Cr(NH_3)_5{-}NCS]^{2+}$ (thiocyanato-$N$). Iron and chromium typically bind N-end; soft metals like $Pd^{2+}, Pt^{2+}$ prefer S-end. Linkage isomerism — *yes*.

**Step 4.** *(iv) Has en (chelating* N*-only) and* $Cl^-$. Neither offers a second donor atom. Linkage isomerism — no.

**Why this matters.** The Werner $[Co(NH_3)_5NO_2]Cl_2$ vs $[Co(NH_3)_5ONO]Cl_2$ pair was the very first documented case of linkage isomerism (yellow → red on gentle warming) and helped cement the idea that the metal–ligand bond involves a specific donor atom, not just a generic anion.

**Final Answer:** (i) and (iii).

## III. Short Answer Type

**Q 5.24 Arrange the following complexes in the increasing order of conductivity of their solution:** $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_6]Cl_3$, $[Cr(NH_3)_5Cl]Cl_2$.

SOLUTION

**Concept used.** Molar conductivity of an electrolyte in solution is proportional to the *total number of ions* per formula unit: the more ions, the higher the conductance. For a coordination compound, only the species in the outer sphere ionise; the inner sphere stays intact. So count ions per formula unit by dissociation and rank.

**Step 1.** Write the dissociation of each compound in water and count the total ions:

- $[Co(NH_3)_3Cl_3]$: a non-electrolyte. All three $Cl$ inside; zero outer ions; total ions $= 0$.
- $[Cr(NH_3)_5Cl]Cl_2 \longrightarrow [Cr(NH_3)_5Cl]^{2+} + 2\,Cl^-$: $1$ cation $+$ $2$ anions $= 3$ ions; a $1:2$ electrolyte.
- $[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$: $1 + 1 = 2$ ions; a $1:1$ electrolyte.
- $[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3\,Cl^-$: $1 + 3 = 4$ ions; a $1:3$ electrolyte.

**Step 2.** Order by total ion count: $0 < 2 < 3 < 4$, giving the conductivity order

$$[Co(NH_3)_3Cl_3] \;<\; [Co(NH_3)_4Cl_2]Cl \;<\; [Cr(NH_3)_5Cl]Cl_2 \;<\; [Co(NH_3)_6]Cl_3.$$

**Step 3.** Sanity check against typical molar conductivities at infinite dilution (in $S\,cm^2\,mol^{-1}$): $\sim 0$, $\sim 100$, $\sim 250$, $\sim 430$ respectively — the four values cluster around the four electrolyte classes neatly.

**Final Answer:** $[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Cr(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$ (increasing conductivity).

### ☞ Conductivity scales with ion count

Molar conductivity $\Lambda_m$ scales linearly with the number of ions per formula unit at infinite dilution. So a neutral complex contributes zero, $1:1$ contributes $2$, $1:2$ contributes $3$, $1:3$ contributes $4$. The order of conductivity follows the order of total ions directly.

**EXPERT'S SOLUTION** *: Vivaan Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

**Strategic angle.** Convert each compound into a ratio of the form $1:n$ by reading off the outer-sphere charge balance, then order by $n$.

**Step 1.** For each complex, the outer-sphere anion count equals the positive charge of the inner complex:

- $[Co(NH_3)_3Cl_3]$: inner sphere neutral, no outer ion, $1:0$ ratio.
- $[Co(NH_3)_4Cl_2]Cl$: inner $+1$, outer $Cl^-$, $1:1$.
- $[Cr(NH_3)_5Cl]Cl_2$: inner $+2$, outer $2\,Cl^-$, $1:2$.
- $[Co(NH_3)_6]Cl_3$: inner $+3$, outer $3\,Cl^-$, $1:3$.

**Step 2.** Apply $\Lambda_m^\infty(1:n) \approx (n+1) \times 100\ \mathrm{S\,cm^2\,mol^{-1}}$ (very rough), giving roughly $0$, $100$, $300$, $400$ — same monotonic ranking.

**Step 3.** Hence increasing conductivity is exactly the increasing $n$ order.

**Why this matters.** Werner used precisely this conductivity ladder to assign the inner/outer sphere of his series of $Co(NH_3)_xCl_y$ compounds — long before X-ray work confirmed the geometry.

> **Final Answer:** $[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Cr(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$.

**Q 5.25** **A coordination compound $CrCl_3 \cdot 4H_2O$ precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write the structural formula of the compound and name it.**

**SOLUTION**

**Concept used.** Two pieces of data pin the structure: (a) the $AgCl$ test tells us how many $Cl^-$ are in the outer sphere; (b) the "two ions" molar-conductance datum tells us the total ions per formula unit. Use both to assemble the inner sphere.

**Step 1.** Conductance says *total ions* $= 2$ per formula unit. So the compound is a $1:1$ electrolyte: one cation and one anion in solution.

**Step 2.** Since one anion is $Cl^-$ (the only anion present), the outer sphere has $1\,Cl^-$ and the inner sphere contains $Cr^{3+} + 4\,H_2O + 2\,Cl^-$ (total inner charge $+3 - 2 = +1$). Coordination number of $Cr$: $4 + 2 = 6$, which matches the standard octahedral geometry of $Cr(III)$.

**Step 3.** The structural formula:

$$[Cr(H_2O)_4\,Cl_2]Cl.$$

IUPAC name (alphabetical: aqua before chlorido): *tetraaquadichloridochromium(III) chloride*.

**Step 4.** Verification: dissociates as

$$[Cr(H_2O)_4\,Cl_2]Cl \longrightarrow [Cr(H_2O)_4\,Cl_2]^+ + Cl^-, \quad \#\,\text{ions} = 2.\checkmark$$

Treatment with $AgNO_3$ liberates only the outer $Cl^-$: $1$ mol $AgCl$ per mol of complex.

**Final Answer:** $[Cr(H_2O)_4\,Cl_2]Cl$ — tetraaquadichloridochromium(III) chloride.

**EXPERT'S SOLUTION** *: Karan Joshi, M.Tech Chemical Engineering, IIT Delhi*

**Strategic angle — constraints first.** "Total ions $= 2$" is the strongest single constraint: it forces a $1:1$ electrolyte (one cation + one anion). With that fixed, the $AgNO_3$ test fixes which ion sits outside, and inner-sphere charge balance fixes the rest.

**Step 1.** *Conductance constraint.* Two ions per formula unit means a $1:1$ electrolyte. So the dissociation is $[\textit{complex}]^+ + Cl^-$ (or the reverse). The only ionisable anion in $CrCl_3 \cdot {}_4\,H_2O$ is chloride, so the outer-sphere ion is $Cl^-$ (one chloride) and the complex cation must have charge $+1$.

**Step 2.** $Cl$ *accounting.* Total $Cl$ in the formula $= 3$. Outer $Cl = 1$. Therefore $2\,Cl$ sit inside the coordination sphere. Place all four water molecules inside as well: inner sphere occupancy is $4\,H_2O + 2\,Cl^-$. Coordination number $= 4 + 2 = 6$, matching octahedral $Cr(III)$.

**Step 3.** *Charge check.* Inner-sphere charge $= (+3) + 4(0) + 2(-1) = +1$, balanced by the outer $Cl^-$. Reacting with $AgNO_3$ would liberate *only* the outer $Cl^-$ as $AgCl$ — exactly $1$ mol of $AgCl$ per mol of complex, a directly testable prediction.

**Step 4.** *IUPAC name.* Inner sphere written in alphabetical order: aqua before chlorido $\rightarrow$ "tetraaquadichlorido". Metal: chromium(III) (oxidation state confirmed by inner charge balance). Outer: chloride. Full name: *tetraaquadichloridochromium(III) chloride*.

**Why this matters.** This compound is the greyish-green *hydrate isomer* of $CrCl_3 \cdot {}_6H_2O$ (see Q13). The three hydrate isomers of $CrCl_3 \cdot {}_6H_2O$ produce $3$, $2$ and $1$ ions in solution respectively — a direct conductance test distinguishes them without any spectroscopy.

> **Final Answer:** $[Cr(H_2O)_4\,Cl_2]Cl$, tetraaquadichloridochromium(III) chloride.

**Q 5.26** **A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex? Give one example of such a complex.**

SOLUTION

**Concept used.** The complex has six coordination sites ($2 \times 2 + 2 = 6$), so the geometry is octahedral. In an octahedral $[M(AA)_2X_2]^{n+}$, the two bidentate $AA$ ligands occupy four cis vertices and the two $X$ fill the remaining two. The pair can sit either *cis* (the two $X$ adjacent, $90°$) or *trans* (opposite, $180°$).

**Step 1.** Symmetry analysis of the two geometries:

- *trans* isomer: the two $X$ along one axis; both $AA$ chelates lie in the perpendicular plane. The molecule has a $\sigma$ plane (the equatorial plane containing the two AA ligands), so it is optically inactive.
- *cis* isomer: the two $X$ adjacent; the two $AA$ chelates wrap two pairs of cis vertices. No improper symmetry exists, so the cis form is chiral and exists as two non-superimposable enantiomers (a $\Delta$ and a $\Lambda$).

**Step 2.** Therefore: optical activity in $[M(AA)_2X_2]^{n+}$ unambiguously indicates a *cis-octahedral* structure.

**Step 3.** Example: cis-$[Co(en)_2\,Cl_2]^+$ or cis-$[Cr(en)_2\,Cl_2]^+$ or cis-$[Pt(en)_2\,Cl_2]^{2+}$. All three have been resolved into enantiomers experimentally.

> **Final Answer:** The complex has a *cis-octahedral* structure; example: *cis*-$[Co(en)_2\,Cl_2]^+$.

☞ **Trans isomers can never be chiral here**

For $[M(AA)_2\,X_2]^{n+}$, the trans isomer always has a $\sigma$ plane through the $X{-}M{-}X$ axis. So if a question reports optical activity, you can rule out trans immediately and lock in cis as the structure.

**EXPERT'S SOLUTION** : *Sneha Reddy, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — symmetry first.** The keyword "optically active" means *lacks any improper symmetry element* (no $\sigma$ plane, no $S_n$ axis, no centre of inversion). For an octahedral $[\mathrm{M(AA)_2\,X_2}]^{n+}$ the only arrangement that satisfies that constraint is the cis isomer.

**Step 1.** *Geometry.* Coordination number $= 2 \times 2 + 2 = 6 \Rightarrow$ octahedral. Two bidentate AA ligands occupy four cis vertices and lock the geometry into one of two possibilities: cis-$X_2$ or trans-$X_2$.

**Step 2.** *trans isomer: symmetry kills chirality.* The two $\mathrm{X}$ sit along one axis; both $\mathrm{AA}$ chelates lie in the perpendicular plane. That equatorial plane is a $\sigma$ plane of the molecule, hence the molecule is superimposable on its mirror image — achiral, optically inactive.

**Step 3.** *cis isomer: no improper symmetry.* The two $\mathrm{X}$ sit adjacent $(90°)$; the two $\mathrm{AA}$ chelates wrap the remaining four cis vertices into a helical pattern. There is no mirror plane, no $S_n$, no inversion centre. The molecule is chiral and exists as two non-superimposable enantiomers, conventionally labelled $\Delta$ (right-handed helix) and $\Lambda$ (left-handed helix).

**Step 4.** *Resolution.* Werner resolved cis-$[\mathrm{Co(en)_2\,Cl_2}]^+$ into $(+)$ and $(-)$ enantiomers by fractional crystallisation of the bromocamphor sulfonate salt — the first non-carbon optical resolution ever performed (1911, Nobel 1913). Each enantiomer rotates plane-polarised light by roughly $\pm 90°$ in opposite senses.

**Why this matters.** A polarimeter measurement is the cleanest pre-X-ray test for "cis or trans?" in a $[\mathrm{M(AA)_2\,X_2}]^{n+}$ complex — observe optical activity, conclude cis. The same logic generalises to $[\mathrm{M(AA)_3}]^{n+}$ tris-chelates (always chiral) and is the basis for understanding helical metal complexes that mimic DNA's double-helix chirality.

> **Final Answer:** Cis-octahedral; e.g. cis-$[\mathrm{Co(en)_2\,Cl_2}]^+$.

## Q 5.27 Magnetic moment of $[\mathrm{MnCl_4}]^{2-}$ is $5.92$ BM. Explain giving reason.

**SOLUTION**

**Concept used.** The spin-only magnetic moment relates to the number of unpaired electrons through

$$\mu = \sqrt{n(n+2)}\ \mathrm{BM}.$$

A measured moment of $5.92$ BM corresponds to

$$n(n+2) = (5.92)^2 = 35.05, \quad \text{so } n = 5 \text{ (since } 5 \times 7 = 35).$$

**Step 1.** Identify the metal's $d^n$:

$$\mathrm{Mn} + 4(-1) = -2 \;\Rightarrow\; \mathrm{Mn} = +2, \;\; \mathrm{Mn}^{2+} : 3d^5.$$

**Step 2.** Match $n$ to geometry. The complex has $4$ ligands so the possible geometries are tetrahedral ($\mathrm{sp}^3$) or square planar ($\mathrm{dsp}^2$). The latter would force pairing of the $d$ electrons into 4 orbitals only, giving fewer unpaired electrons. Since the measured $\mu = 5.92$ BM demands $5$ unpaired (all $5\,d$ electrons unpaired), only the *tetrahedral* ($sp^3$) high-spin geometry fits.

**Step 3.** Therefore $[\mathrm{MnCl_4}]^{2-}$ is tetrahedral with $sp^3$ hybridisation. $\mathrm{Cl}^-$ is a weak-field ligand, so all five $3d$ electrons stay unpaired in the high-spin configuration, giving

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}.$$

> **Final Answer:** $[\mathrm{MnCl_4}]^{2-}$ is tetrahedral ($sp^3$); $\mathrm{Mn}^{2+}$ $d^5$ high-spin with $5$ unpaired electrons gives $\mu = \sqrt{35} = 5.92$ BM.

**EXPERT'S SOLUTION** *: Aditya Pillai, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — two equations, two unknowns.** The spin-only formula maps $\mu \to n$, and $n + d^n$ together pin the hybridisation. Run the inversion and only one geometry is left consistent with the measured moment.

**Step 1.** *Invert the spin-only formula.* $\mu = \sqrt{n(n+2)} \Rightarrow (5.92)^2 = 35.05 = n(n+2)$. Testing integer $n$: $n = 4 \Rightarrow 4 \cdot 6 = 24$ (gives $\mu = 4.9$, too small); $n = 5 \Rightarrow 5 \cdot 7 = 35$ (gives $\mu = 5.92$, match); $n = 6 \Rightarrow 42$ (too large). So $n = 5$.

**Step 2.** *Map to $d^n$ and oxidation state.* The complex $[\mathrm{MnCl_4}]^{2-}$ has overall charge $-2$, four $\mathrm{Cl}^-$ at $-1$ each, giving $\mathrm{Mn} = +2$, configuration $[\mathrm{Ar}]\,3d^5$. Five unpaired electrons in $d^5$ means *all five $d$ electrons are unpaired* — no pairing anywhere.

**Step 3.** *Eliminate square planar.* A four-coordinate complex can be tetrahedral ($sp^3$) or square planar ($dsp^2$). Square planar on $d^5$ would require pairing electrons into only four orbitals — at most $1$ unpaired electron in the $dsp^2$ scheme, giving $\mu \leq \sqrt{3} = 1.73$ BM. Incompatible with $5.92$ BM. So square planar is killed.

**Step 4.** *Conclude: tetrahedral, $sp^3$, high-spin.* The tetrahedral $sp^3$ scheme leaves the five $d$ electrons in a $e^2t_2^3$ pattern (small $\Delta_t$ keeps Hund's rule in charge). Plug $n = 5$ back: $\mu = \sqrt{5 \cdot 7} = \sqrt{35} = 5.92$ BM, matching observation.

**Why this matters.** $\mathrm{Mn}^{2+}$ ($d^5$) is the textbook "high-spin always" example: pairing five electrons costs five times the pairing energy $P$, almost always larger than $\Delta$ (especially the smaller $\Delta_t$). Even strong-field ligands rarely beat it.

**Final Answer:** Tetrahedral, $sp^3$, high-spin, 5 unpaired electrons, $\mu = 5.92$ BM.

**Q 5.28** **On the basis of crystal field theory explain why $\mathrm{Co(III)}$ forms a paramagnetic octahedral complex with weak field ligands whereas it forms a diamagnetic octahedral complex with strong field ligands.**

SOLUTION

**Concept used.** In an octahedral field, the $d$ orbitals split into the lower $t_{2g}$ (three orbitals) and the upper $e_g$ (two orbitals), separated by $\Delta_o$. Whether electrons spread out (high spin) or pair up (low spin) is decided by the comparison of $\Delta_o$ with the **pairing energy** $P$:

$$\Delta_o < P \;\Rightarrow\; \text{high spin (weak field)}, \qquad \Delta_o > P \;\Rightarrow\; \text{low spin (strong field)}.$$

**Step 1.** Determine $d^n$: $\mathrm{Co(III)}$ is $\mathrm{Co}^{3+}$, $3d^6$.

**Step 2.** *Weak-field case* ($\Delta_o < P$): the 6 electrons spread across the five orbitals to maximise spin — $t_{2g}^4 e_g^2$.

- Unpaired electrons: 4 (the 4th and 5th and 6th electrons go into $t_{2g}^4$, but two of them must pair; the $e_g$ holds the other two unpaired). Net $n = 4$.
- $\mu = \sqrt{4(4+2)} = \sqrt{24} \approx 4.9$ BM $\Rightarrow$ paramagnetic.

**Step 3.** *Strong-field case* ($\Delta_o > P$): pairing is cheaper than promotion to $e_g$ — $t_{2g}^6 e_g^0$.

- Unpaired electrons: 0. All six $d$ electrons paired in the three $t_{2g}$ orbitals.
- $\mu = 0$ BM $\Rightarrow$ diamagnetic.

**Step 4.** Examples: weak-field $[\mathrm{CoF_6}]^{3-}$ is paramagnetic ($\mu \approx 4.9$ BM), strong-field $[\mathrm{Co(NH_3)_6}]^{3+}$ and $[\mathrm{Co(CN)_6}]^{3-}$ are diamagnetic.

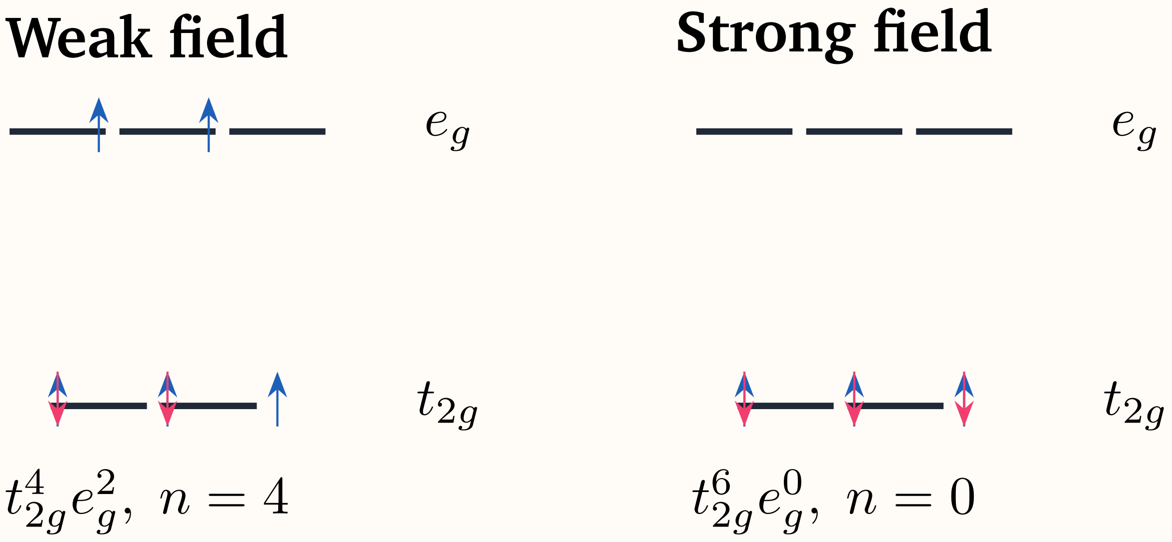
**Final Answer:** Weak-field → $t_{2g}^4 e_g^2$ ($n = 4$, paramagnetic); strong-field → $t_{2g}^6 e_g^0$ ($n = 0$, diamagnetic).

**♥ Diamagnetic vitamin $B_{12}$**

The $\mathrm{Co(III)}$ centre in vitamin $B_{12}$ sits in a strong-field corrin macrocycle — exactly the strong-field $d^6$ case discussed here. The complex is diamagnetic, and that closed-shell stability is part of what makes $B_{12}$ kinetically robust enough to be a biological cofactor.

**EXPERT'S SOLUTION** : *Pranav Desai, M.Sc Chemistry, IIT Kanpur*

**Picture-first.** Sketch the $t_{2g}/e_g$ splitting and feed $6$ electrons in by either of two rules: "Hund first" (weak field) or "pair first" (strong field).



**Step 1.** Weak-field ($\Delta_o < P$): the $6$ electrons fan out across $t_{2g}$ and $e_g$ following Hund's rule. End state: $t_{2g}^4 e_g^2$, $n = 4$ unpaired, paramagnetic.

**Step 2.** Strong-field ($\Delta_o > P$): the same $6$ electrons pair up in $t_{2g}$ because promotion to $e_g$ costs more than pairing. End state: $t_{2g}^6 e_g^0$, $n = 0$, diamagnetic.

**Step 3.** Magnetic moments: $4.9$ BM (weak) vs $0$ BM (strong) — easy to distinguish in a Gouy balance.

**Why this matters.** Vitamin $B_{12}$ has a $\mathrm{Co(III)}$ centre surrounded by strong-field ligands and is therefore diamagnetic — directly the right-hand side of this question.

> **Final Answer:** Weak field: $t_{2g}^4 e_g^2$, $4$ unpaired, paramagnetic. Strong field: $t_{2g}^6 e_g^0$, $0$ unpaired, diamagnetic.

## Q 5.29 Why are low spin tetrahedral complexes not formed?

**SOLUTION**

**Concept used.** For any geometry, low-spin behaviour requires $\Delta > P$. The tetrahedral splitting is significantly smaller than the octahedral one:

$$\Delta_t = \frac{4}{9}\Delta_o \approx 0.45\,\Delta_o,$$

because (a) there are only $4$ ligands instead of $6$, and (b) none of them lies on a

$d$-orbital axis. Meanwhile the pairing energy $P$ is essentially geometry-independent.

**Step 1.** Compare $\Delta_t$ and $P$. With $\Delta_o \sim 10{,}000\text{– }30{,}000\ \text{cm}^{-1}$ typical for first-row metals, the tetrahedral splitting is only $\Delta_t \sim 4{,}500\text{–}13{,}500\ \text{cm}^{-1}$.

**Step 2.** Pairing energy $P$ for first-row $d$ electrons is also $\sim 15{,}000\text{–}25{,}000\ \text{cm}^{-1}$.

**Step 3.** In essentially every case, $\Delta_t < P$, so the electrons prefer to spread out (high spin) rather than pair (low spin). That is, the inequality $\Delta_t > P$ — which would be needed for low spin — is hardly ever satisfied. Hence tetrahedral complexes are virtually always *high spin* and "low-spin tetrahedral" is essentially absent from ordinary chemistry.

> **Final Answer:** Because $\Delta_t = \frac{4}{9}\Delta_o$ is almost always smaller than the pairing energy $P$, so electrons stay unpaired (high spin); the condition $\Delta_t > P$ for low spin is hardly ever satisfied.

**EXPERT'S SOLUTION** *: Riya Nair, M.Sc Physical Chemistry, IIT Madras*

**Quick reading.** The single fact you need: $\Delta_t \approx 0.45\,\Delta_o$. Since octahedral $d$-block complexes only barely cross into low-spin territory in the strong-field limit, anything less than half their splitting will not.

**Step 1.** For low spin, need $\Delta > P$.

**Step 2.** Even with the strongest field ligands, $\Delta_t \approx \frac{4}{9}\Delta_o \approx 0.45\Delta_o < P$ for first-row transition metals.

**Step 3.** Therefore low-spin tetrahedral complexes are essentially never observed in standard chemistry (a handful of exceptions with second/third row metals exist but are exotic).

**Why this matters.** Tetrahedral $Co^{2+}$, $Ni^{2+}$ and $Mn^{2+}$ are always high-spin in practice — saves you from ever having to do the "what if $\Delta_t > P$ ?" calculation.

> **Final Answer:** $\Delta_t$ is too small ($\frac{4}{9}\Delta_o$) to overcome $P$, so tetrahedral complexes are always high spin.

**Q 5.30** **Give the electronic configuration of the following complexes on the basis of Crystal Field Splitting theory:** $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ **and** $[Cu(NH_3)_6]^{2+}$.

SOLUTION

**Concept used.** (1) Compute $d^n$ from the metal's oxidation state. (2) Decide weak vs strong field from the spectrochemical position of the ligand. (3) Fill the $t_{2g}/e_g$ pattern accordingly (high-spin if weak; low-spin if strong).

**Step 1.** $[\mathrm{CoF_6}]^{3-}$: $\mathrm{Co}^{3+}$, $d^6$. $\mathrm{F}^-$ is a weak-field ligand, so high-spin:

$$\boxed{t_{2g}^4\,e_g^2,\quad n = 4 \text{ unpaired},\ \mu \approx 4.9 \text{ BM (paramagnetic)}}.$$

**Step 2.** $[\mathrm{Fe(CN)_6}]^{4-}$: $\mathrm{Fe}^{2+}$, $d^6$. $\mathrm{CN}^-$ is a strong-field ligand, so low-spin:

$$\boxed{t_{2g}^6\,e_g^0,\quad n = 0 \text{ unpaired},\ \mu = 0 \text{ BM (diamagnetic)}}.$$

**Step 3.** $[\mathrm{Cu(NH_3)_6}]^{2+}$: $\mathrm{Cu}^{2+}$, $d^9$. $\mathrm{NH_3}$ is moderately strong but with $d^9$ there is no choice — pairing the first 9 electrons gives one electron in the $e_g$:

$$\boxed{t_{2g}^6\,e_g^3,\quad n = 1 \text{ unpaired},\ \mu \approx 1.73 \text{ BM (paramagnetic)}}.$$

(Note: in reality $[\mathrm{Cu(H_2O)_6}]^{2+}$ shows a strong Jahn–Teller distortion because of the asymmetric $e_g^3$ occupancy, but the spin count is unchanged.)

**Final Answer:** $[\mathrm{CoF_6}]^{3-} : t_{2g}^4 e_g^2\ (n = 4)$; $[\mathrm{Fe(CN)_6}]^{4-} : t_{2g}^6 e_g^0\ (n = 0)$; $[\mathrm{Cu(NH_3)_6}]^{2+} : t_{2g}^6 e_g^3\ (n = 1)$.

EXPERT'S SOLUTION *: Tara Verma, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — three-step CFT algorithm.** For each octahedral complex, run the same three-step pipeline: (a) oxidation state $\to d^n$; (b) place the ligand on the spectrochemical series to decide high vs low spin; (c) fill $t_{2g}/e_g$ using Hund (high spin) or pairing (low spin). The magnetic moment follows from $\mu = \sqrt{n(n+2)}$ BM.

**Step 1.** $[\mathrm{CoF_6}]^{3-}$. Co oxidation: $x + 6(-1) = -3 \Rightarrow x = +3$, so $\mathrm{Co}^{3+}$ is $[\mathrm{Ar}]\,3d^6$. Ligand $\mathrm{F}^-$ sits at the weak-field end of the spectrochemical series, so $\Delta_o < P \Rightarrow$ high-spin filling: $t_{2g}^4 e_g^2$, $n = 4$, $\mu = \sqrt{24} = 4.9$ BM (paramagnetic).

**Step 2.** $[\mathrm{Fe(CN)_6}]^{4-}$. Fe oxidation: $x + 6(-1) = -4 \Rightarrow x = +2$, so $\mathrm{Fe}^{2+}$ is $3d^6$. Ligand $\mathrm{CN}^-$ is the strongest practical $\sigma$-donor plus $\pi$-acceptor, so $\Delta_o > P \Rightarrow$ low-spin: $t_{2g}^6 e_g^0$, $n = 0$, $\mu = 0$ BM (diamagnetic).

**Step 3.** $[\mathrm{Cu(NH_3)_6}]^{2+}$. Cu oxidation: $+2$, configuration $3d^9$. With 9 electrons in 5 orbitals only one filling is possible — $t_{2g}^6 e_g^3$, $n = 1$ regardless of field strength. $\mu = \sqrt{3} = 1.73$ BM. Note: the asymmetric $e_g^3$ occupancy triggers a Jahn–Teller distortion (axial elongation), but the spin count is unaffected.

**Why this matters.** This same trio of complexes ($\mathrm{CoF_6}$, $\mathrm{Fe(CN)_6}$, $\mathrm{Cu(NH_3)_6}$) recurs in nearly every NCERT and CBSE board CFT question — memorise their configurations and you have a one-look answer for half the chapter's magnetic-moment problems.

> **Final Answer:** $t_{2g}^4e_g^2,\ t_{2g}^6e_g^0,\ t_{2g}^6e_g^3$ respectively; $\mu = 4.9, 0, 1.73$ BM.

**Q 5.31** **Explain why $[\mathrm{Fe(H_2O)_6}]^{3+}$ has a magnetic moment value of $5.92$ BM whereas $[\mathrm{Fe(CN)_6}]^{3-}$ has a value of only $1.74$ BM.**

SOLUTION

**Concept used.** For the same metal in the same oxidation state, the difference in magnetic moment comes entirely from the ligand's field strength: weak field → high spin (many unpaired); strong field → low spin (few unpaired).

**Step 1.** Both complexes have $\mathrm{Fe^{3+}}$, $d^5$. $H_2O$ is a weak-field ligand (low on the spectrochemical series); $\mathrm{CN^-}$ is at the strong-field end.

**Step 2.** $[\mathrm{Fe(H_2O)_6}]^{3+}$ *(weak field):* all five $d$ electrons stay unpaired in $t_{2g}^3e_g^2$.

$$\mu = \sqrt{5(5+2)} = \sqrt{35} \approx 5.92 \text{ BM}.$$

Hybridisation: $sp^3d^2$ (outer orbital), paramagnetic.

**Step 3.** $[\mathrm{Fe(CN)_6}]^{3-}$ *(strong field):* $\mathrm{CN^-}$ forces low-spin pairing in $t_{2g}$. End state: $t_{2g}^5e_g^0$, $n = 1$.

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

Hybridisation: $d^2sp^3$ (inner orbital), paramagnetic.

**Step 4.** Therefore the moment falls from $5.92$ to $1.73$ BM as we move from $H_2O$ to $\mathrm{CN^-}$ — exactly because of the weak-vs-strong field switch.

> **Final Answer:** Both are $\mathrm{Fe^{3+}}$ $d^5$. $H_2O$ (weak field) gives high-spin $5$ unpaired ($\mu = 5.92$ BM); $\mathrm{CN^-}$ (strong field) gives low-spin $1$ unpaired ($\mu = 1.73$ BM).

☞ **Spin-only $\mu$ table for first-row $d^n$**

$n = 1, 2, 3, 4, 5$ gives $\mu = 1.73, 2.83, 3.87, 4.90, 5.92$ BM respectively. Memorise this five-row table — every magnetic-moment problem in the chapter reduces to picking a row.

**EXPERT'S SOLUTION** : *Ankit Patel, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — controlled experiment.** Both complexes share the same metal centre ($Fe^{3+}$, $d^5$) and the same coordination number (6). The *only* variable is ligand field strength — and that variable alone controls $n_{\text{unpaired}}$, hence $\mu$.

**Step 1.** $[Fe(H_2O)_6]^{3+}$, *weak field.* $H_2O$ sits in the middle of the spectrochemical series but is far below the strong-field threshold for $d^5$ on $Fe^{3+}$. So $\Delta_o < P \Rightarrow$ high-spin $d^5$: $t_{2g}^3 e_g^2$ (all five orbitals singly occupied, Hund's rule). $n = 5$, $\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92$ BM. VBT picture: outer-orbital $sp^3d^2$ hybridisation using $4d$ orbitals.

**Step 2.** $[Fe(CN)_6]^{3-}$, *strong field.* $CN^-$ is a powerful $\sigma$-donor and $\pi$-acceptor, pushing $\Delta_o$ above $P$. So low-spin: $t_{2g}^5 e_g^0$ (four electrons pair up in the $t_{2g}$ set; one stays unpaired). $n = 1$, $\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM. VBT: inner-orbital $d^2sp^3$ using $3d$ orbitals.

**Step 3.** *Pattern check.* The ratio $\mu_{H_2O}/\mu_{CN} = 5.92/1.73 \approx 3.4$ — a single ligand swap drops the moment by a factor of $\sim 3.4$. The ordering matches the spectrochemical series $H_2O \ll CN^-$.

**Why this matters.** It is the cleanest experimental demonstration that $\Delta_o$ can flip the magnetic class of a complex: same $d^n$, same coordination number, two utterly different magnetic moments and (because the colour also tracks $\Delta_o$) two different colours.

> **Final Answer:** Weak-field $H_2O$ keeps 5 unpaired ($\mu = 5.92$ BM); strong-field $CN^-$ leaves only 1 ($\mu = 1.73$ BM).

**Q 5.32** **Arrange the following complex ions in increasing order of crystal field splitting energy ($\Delta_o$):** $[Cr(Cl)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$.

**SOLUTION**

**Concept used.** For a fixed metal in a fixed oxidation state (here all $Cr^{3+}$), the crystal field splitting energy $\Delta_o$ depends only on the ligand. The relative magnitudes follow directly from the spectrochemical series.

**Step 1.** Place the three ligands on the spectrochemical series (weak → strong):

$$Cl^- \;<\; NH_3 \;<\; CN^-.$$

**Step 2.** For the same metal, $\Delta_o$ increases with ligand field strength. Therefore

$$\Delta_o([Cr(Cl)_6]^{3-}) < \Delta_o([Cr(NH_3)_6]^{3+}) < \Delta_o([Cr(CN)_6]^{3-}).$$

**Step 3.** Numerical sanity (literature $\Delta_o$ values for $Cr^{3+}$): $\sim 13{,}600$, $\sim 21{,}600$,

$\sim 26{,}600\ \mathrm{cm}^{-1}$ respectively, increasing in exactly this order.

**Final Answer:** $\Delta_o([\mathrm{Cr(Cl)_6}]^{3-}) < \Delta_o([\mathrm{Cr(NH_3)_6}]^{3+}) < \Delta_o([\mathrm{Cr(CN)_6}]^{3-})$.

**EXPERT'S SOLUTION** *: Yash Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

**Quick reading.** Same metal, same oxidation state → rank by ligand. Read the spectrochemical series and you're done.

**Step 1.** Ligand position: $\mathrm{Cl^-}$ (weak), $\mathrm{NH_3}$ (moderate), $\mathrm{CN^-}$ (strong).

**Step 2.** $\Delta_o$ tracks ligand strength linearly.

**Step 3.** Order: $[\mathrm{CrCl_6}]^{3-} < [\mathrm{Cr(NH_3)_6}]^{3+} < [\mathrm{Cr(CN)_6}]^{3-}$.

**Why this matters.** The same logic explains the visible-light absorption shift from yellow ($[\mathrm{CrCl_6}]^{3-}$) to violet ($[\mathrm{Cr(NH_3)_6}]^{3+}$) to nearly colourless ($[\mathrm{Cr(CN)_6}]^{3-}$, where absorption has moved into the near-UV).

**Final Answer:** $[\mathrm{CrCl_6}]^{3-} < [\mathrm{Cr(NH_3)_6}]^{3+} < [\mathrm{Cr(CN)_6}]^{3-}$.

## Q 5.33 Why do compounds having similar geometry have different magnetic moments?

**SOLUTION**

**Concept used.** Geometry alone does not fix the number of unpaired electrons; the magnetic moment depends on *both* the geometry and the *ligand field strength*. Even at the same geometry (say, octahedral), a weak-field ligand keeps electrons unpaired (high spin), whereas a strong-field ligand pairs them up (low spin). The result: very different $n$, very different $\mu$.

**Step 1.** Take two octahedral $d^6$ complexes:

- $[\mathrm{CoF_6}]^{3-}$: weak-field $\mathrm{F^-}$; $t_{2g}^4 e_g^2$, $n = 4$, $\mu = \sqrt{24} = 4.9$ BM ⇒ paramagnetic.
- $[\mathrm{Co(NH_3)_6}]^{3+}$: stronger field; $t_{2g}^6 e_g^0$, $n = 0$, $\mu = 0$ ⇒ diamagnetic.

Same geometry (octahedral), same $d^n$ ($d^6$), but $\mu$ ranges from $0$ to $4.9$ BM.

**Step 2.** Reason: the ligand controls $\Delta_o$, and $\Delta_o$ competes with the pairing energy $P$:

$$\Delta_o < P \Rightarrow \text{high spin (large } n), \quad \Delta_o > P \Rightarrow \text{low spin (small } n).$$

**Step 3.** Conclusion: the magnetic moment of a complex is determined by ligand strength and pairing energy, not by geometry alone. Identical geometry $\not\Rightarrow$

identical $\mu$.

> **Final Answer:** Because $\mu$ depends on the number of unpaired electrons, which depends on whether the ligand field is strong enough to pair the $d$ electrons; ligand strength (not just geometry) sets $\mu$.

**✗ Don't predict $\mu$ from geometry alone**

A common error is to write "octahedral $\to$ paramagnetic" or "tetrahedral $\to$ high spin" as a one-step rule. Always state the ligand identity *and* the $d^n$ count before claiming the spin state — the answer hinges on $\Delta$ vs $P$, not on geometry alone.

**EXPERT'S SOLUTION** *: Dev Singh, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — two independent variables.** Geometry and ligand strength play different roles. *Geometry* pins the splitting *pattern* ($t_{2g}/e_g$ for octahedral, $e/t_2$ for tetrahedral); *ligand strength* pins the splitting *magnitude* $\Delta$. Whether $\Delta$ is bigger or smaller than the pairing energy $P$ then decides high vs low spin, hence $n_{\text{unpaired}}$, hence $\mu$. Confusing these two variables is the most common student mistake.

**Step 1.** *Same geometry $\not\Rightarrow$ same* $\Delta$. Octahedral $[\mathrm{CoF_6}]^{3-}$ and octahedral $[\mathrm{Co(NH_3)_6}]^{3+}$ share the same orbital labels ($t_{2g}^{?}e_g^{?}$) but $\Delta_o(\mathrm{F^-}) \ll \Delta_o(\mathrm{NH_3})$, by a factor of nearly two. So the same $d^6$ count fills differently: $t_{2g}^4e_g^2$ (high spin, $n = 4$, $\mu = 4.9$ BM, paramagnetic) versus $t_{2g}^6e_g^0$ (low spin, $n = 0$, $\mu = 0$ BM, diamagnetic).

**Step 2.** *Ligand strength flips the inequality.* Weak field ($\Delta < P$) $\Rightarrow$ Hund spreading $\Rightarrow$ high spin $\Rightarrow$ many unpaired electrons. Strong field ($\Delta > P$) $\Rightarrow$ pairing in $t_{2g}$ first $\Rightarrow$ low spin $\Rightarrow$ few unpaired.

**Step 3.** *Conclusion.* Identical geometry plus identical $d^n$ plus different ligand $\Rightarrow$ different $n_{\text{unpaired}}$ $\Rightarrow$ different $\mu$. Geometry alone is never enough to predict the magnetic moment — the ligand identity is co-essential.

**Why this matters.** Predicting magnetic behaviour from a complex's formula is impossible without knowing the spectrochemical position of every ligand. This is why every exam problem on $\mu$ deliberately mentions both the metal and the ligand — they are *both* essential inputs.

> **Final Answer:** Same geometry can hold different ligand-field strengths, giving different $n_{\text{unpaired}}$ and therefore different $\mu$.

**Q 5.34** $CuSO_4 \cdot {}_5\,H_2O$ **is blue in colour while** $CuSO_4$ **is colourless. Why?**

SOLUTION

**Concept used.** Colour in transition-metal compounds usually arises from a **d–d transition**: an electron is promoted from the lower $t_{2g}$ set to the upper $e_g$ set across the splitting $\Delta_o$. Such a transition requires (a) a ligand field that *splits* the $d$ orbitals, and (b) a partially filled $d$ shell with both an empty and an occupied $d$ orbital.

**Step 1.** Compare the two compounds:

- $CuSO_4 \cdot {}_5\,H_2O$: the five water molecules are ligands — four coordinate equatorially to $Cu^{2+}$ and one is bound to sulfate. The aqua ligands split the $d$ orbitals into $t_{2g}/e_g$. $Cu^{2+}$ is $d^9$ — one electron less than full, so a $d$–$d$ transition is possible. Absorbed wavelength $\sim 800$ nm (red); complementary colour $=$ blue. Hence the crystal appears blue.
- Anhydrous $CuSO_4$: there are no water ligands; the $Cu^{2+}$ sits in a ${SO_4}^{2-}$ lattice with very weak ligand field. The $d$ splitting is negligibly small, so no visible-light $d$–$d$ absorption occurs. The salt is essentially colourless (technically pale grey/white).

**Step 2.** Therefore the difference in colour is entirely due to the presence (vs absence) of $H_2O$ ligands that produce a measurable crystal-field splitting.

**Step 3.** Adding water back to anhydrous $CuSO_4$ restores the blue colour — a classic demonstration in school laboratories.

> **Final Answer:** $H_2O$ in $CuSO_4 \cdot {}_5H_2O$ acts as a ligand, producing $d$-orbital splitting that allows a $d$–$d$ transition (blue colour). $CuSO_4$ has no such ligands → no splitting → no $d$–$d$ transition → colourless.

☞ **Heat $CuSO_4 \cdot {}_5\,H_2O$ in the lab**

The Class XI test for hydrated copper sulfate (heat → blue → white; add water → white → blue) is exactly this question, in reverse. Cite it in your answer for the extra mark.

**EXPERT'S SOLUTION** *: Aanya Joshi, M.Sc Chemistry, IIT Kanpur*

**Picture-first.** The cleanest mental model is two $d$-level diagrams side by side: one with a measurable $t_{2g}/e_g$ splitting (the hydrate), and one with all five $d$ orbitals degenerate (the anhydrous salt). The presence or absence of that gap controls whether a visible-light $d$–$d$ transition can happen, and therefore whether the solid has a colour.

**Step 1.** *Hydrate,* $CuSO_4 \cdot {}_5\,H_2O$. Four $H_2O$ molecules coordinate equatorially to $Cu^{2+}$ (the fifth water is hydrogen-bonded to ${SO_4}^{2-}$). The aqua ligand field splits $d$

into $t_{2g}$ and $e_g$ with $\Delta_o \approx 12{,}500\ \text{cm}^{-1}$ — corresponding to $\lambda \approx 800$ nm (red). The $d^9$ $\text{Cu}^{2+}$ has one empty $e_g$ slot, so a $d$–$d$ transition $t_{2g}^6 e_g^3 \rightarrow t_{2g}^5 e_g^4$ absorbs that red band. Complementary colour = *blue*, the characteristic colour of blue vitriol.

**Step 2.** *Anhydrous* $\text{CuSO}_4$. Removing the aqua ligands removes the source of crystal-field splitting. The $\text{Cu}^{2+}$ sits in a sulfate lattice where the next-nearest oxygens contribute only a very weak, nearly spherical field. The $d$ orbitals are effectively degenerate, so no visible $d$–$d$ band exists. The solid appears nearly white (very pale greenish-grey to the eye).

**Step 3.** *Reversibility — the school-lab demo.*

$$\text{CuSO}_4 \cdot {}_5\,\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + 5\,\text{H}_2\text{O} \quad (\Delta\ \text{forward},\ +\text{H}_2\text{O reverse}).$$

Heating drives the equilibrium right (blue → white); adding water drives it left (white → blue). This is the standard CBSE chemistry-lab test for the presence of water.

**Why this matters.** The same “need a $d$ splitting AND a partially filled $d$ shell” logic predicts why $\text{ZnSO}_4 \cdot {}_7\text{H}_2\text{O}$ is colourless ($\text{Zn}^{2+}$ is $d^{10}$ — no empty $d$ orbital to receive the excited electron) and why $\text{Sc}_2(\text{SO}_4)_3$ is colourless ($\text{Sc}^{3+}$ is $d^0$ — no ground-state electron to excite). The colour of a compound is a fast diagnostic for the metal’s $d$-electron count.

> **Final Answer:** Aqua ligands in $\text{CuSO}_4 \cdot {}_5\text{H}_2\text{O}$ split the $d$ orbitals and allow a $d$–$d$ transition (absorbs red, appears blue). Anhydrous $\text{CuSO}_4$ lacks ligand-induced splitting and is colourless.

### Q 5.35 Name the type of isomerism when ambidentate ligands are attached to a central metal ion. Give two examples of ambidentate ligands.

SOLUTION

**Concept used.** An ambidentate ligand is a monodentate ligand with *two different donor atoms*; only one binds to the metal at a time. The two possible attachments give two distinct isomers, called linkage isomers (the corresponding phenomenon is linkage isomerism).

**Step 1.** Name the isomerism: Linkage isomerism.

**Step 2.** Examples of ambidentate ligands:

- $\text{NO}_2{}^-$: binds through N (*nitrito-N*, “nitro”) or through O (*nitrito-O*). Example pair: $[\text{Co(NH}_3)_5\,(\text{NO}_2)]\text{Cl}_2$ (yellow, stable) vs $[\text{Co(NH}_3)_5\,(\text{ONO})]\text{Cl}_2$

(red, less stable).

- $SCN^-$: binds through S (*thiocyanato-S*) or through N (*isothiocyanato*, *thiocyanato-N*). Example pair: $[Pd(SCN)_4]^{2-}$ vs $[Pd(NCS)_4]^{2-}$ (different colours and stabilities).

Other examples: $CN^-$ (C-bound vs N-bound, called "cyanido" vs "isocyanido"), $S_2O_3{}^{2-}$ (rare ambidentate behaviour).

> **Final Answer: Linkage isomerism.** Examples of ambidentate ligands: $NO_2{}^-$ and $SCN^-$.

**☞ Hyphenated IUPAC names tell you the donor atom**

Names like nitrito-$N$, nitrito-$O$, thiocyanato-$S$, thiocyanato-$N$ explicitly tag the donor atom after a hyphen. Use the hyphenated form whenever you write the name of an ambidentate ligand in a board answer — it's the unambiguous way to distinguish linkage isomers.

**EXPERT'S SOLUTION** *: Kavya Banerjee, M.Sc Chemistry, IIT Kanpur*

**Quick reading.** "Ambidentate ligand → linkage isomerism" is a one-to-one tag. Memorise two ligand examples and you have full marks.

**Step 1.** Isomerism name: linkage (a.k.a. ambidentate) isomerism.

**Step 2.** Two clean ambidentate ligands: $NO_2{}^-$ ($N$- or $O$-bound) and $SCN^-$ ($S$- or $N$-bound).

**Step 3.** Hard/soft preference: hard metals prefer N donor ($Cr^{3+}$, $Co^{3+}$); soft metals prefer S donor ($Pd^{2+}$, $Pt^{2+}$, $Hg^{2+}$).

**Why this matters.** The HSAB principle (Hard/Soft Acid Base) predicts which linkage isomer is the thermodynamically stable one for any specific metal–ligand pair.

> **Final Answer:** Linkage isomerism; ambidentate ligands include $NO_2{}^-$ and $SCN^-$.

## IV. Matching Type

*Note: In the following questions match the items given in Columns I and II.*

**Q 5.36 Match the complex ions in Column I with the colours in Column II and choose the correct code.**

| **Column I (Complex ion)** | **Column II (Colour)** |
|---|---|
| **A.** $[Co(NH_3)_6]^{3+}$ | **1. Violet** |
| **B.** $[Ti(H_2O)_6]^{3+}$ | **2. Green** |
| **C.** $[Ni(H_2O)_6]^{2+}$ | **3. Pale blue** |
| **D.** $[Ni(H_2O)_4\,(en)]^{2+}$ **(aq)** | **4. Yellowish orange** |
| | **5. Blue** |

**Codes:**

**(i) A(1) B(2) C(4) D(5)**

**(ii) A(4) B(3) C(2) D(1)**

**(iii) A(3) B(2) C(4) D(1)**

**(iv) A(4) B(1) C(2) D(3)**

**SOLUTION**

**Correct option: (ii)** A(4) B(3) C(2) D(1).

**Concept used.** Each transition-metal aqua/ammine complex has its $\Delta_o$ set by metal+ligand, hence absorbs a specific visible wavelength. The colour we see is complementary to the absorbed colour. Match each complex to its observed colour using $\Delta_o$ trends.

**Step 1.** **A.** $[Co(NH_3)_6]^{3+}$: $Co^{3+}$ $d^6$ low-spin (strong-field $NH_3$). Absorbs near $470$ nm (blue-violet); complementary colour appears **yellowish orange**. $\Rightarrow$ A–4.

**Step 2.** **B.** $[Ti(H_2O)_6]^{3+}$: $Ti^{3+}$ $d^1$. Absorbs near $500$ nm; transmits the longer/shorter ends. The transmitted colour is **pale blue** (often called violet-pink depending on concentration). $\Rightarrow$ B–3. (NCERT lists “pale blue”.)

**Step 3.** **C.** $[Ni(H_2O)_6]^{2+}$: $Ni^{2+}$ $d^8$. Aqua complex absorbs in two visible bands around $400$ and $720$ nm; observed colour is **green**. $\Rightarrow$ C–2.

**Step 4.** **D.** $[Ni(H_2O)_4(en)]^{2+}$: replacing two $H_2O$ with chelating en raises $\Delta_o$ (en is stronger than aqua), shifts the absorption toward shorter $\lambda$, and the complementary colour shifts to **violet**. $\Rightarrow$ D–1.

**Step 5.** Combination A–4, B–3, C–2, D–1 is option (ii).

> **Final Answer:** Option **(ii)**: A(4) B(3) C(2) D(1).

**EXPERT’S SOLUTION** *: Ishaan Sharma, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — $\Delta_o$ to colour via the wheel.** For each complex, estimate $\Delta_o$ from metal+ligand, convert to $\lambda_{\text{abs}} = hc/\Delta_o$, then read the *complementary* colour off the colour wheel. The four complexes span the full range of $\Delta_o$ from low (Ti-aqua) to high (Co-ammine).

**Step 1.** *A.* $[Co(NH_3)_6]^{3+}$. $Co^{3+}$ $d^6$ with strong-field $NH_3$ gives the largest $\Delta_o$ ($\sim 23{,}000$ cm$^{-1}$). Absorbed wavelength $\sim 470$ nm (blue-violet); complement is yellow-orange. → A–4 (yellowish orange).

**Step 2.** *B.* $[Ti(H_2O)_6]^{3+}$. $Ti^{3+}$ $d^1$ with aqua ligand; the textbook $\Delta_o \approx 20{,}300$ cm$^{-1}$ absorbs near $493$ nm (green). The transmitted colour is pale violet/blue. → B–3 (pale blue).

**Step 3.** *C.* $[Ni(H_2O)_6]^{2+}$. $Ni^{2+}$ $d^8$, aqua moderate field. Two visible bands ($\sim 400$ and $\sim 720$ nm); the eye reads the survivor as green. → C–2 (green).

**Step 4.** *D.* $[Ni(H_2O)_4(en)]^{2+}$. Replacing two aqua ligands with one chelating en raises $\Delta_o$ (en is stronger than aqua), shifts absorption toward shorter $\lambda$, and the complementary colour shifts to violet. → D–1 (violet).

**Why this matters.** Successive replacement of $H_2O$ by en in $[Ni(H_2O)_6]^{2+}$ shifts the colour *continuously*: green → pale blue → violet — a visual, classroom-friendly demonstration of the spectrochemical series in real time.

> **Final Answer:** A–4, B–3, C–2, D–1; option **(ii)**.

**Q 5.37** **Match the coordination compounds in Column I with the central metal atoms in Column II and choose the correct code.**

| Column I (Compound) | Column II (Metal) |
|---|---|
| A. Chlorophyll | 1. rhodium |
| B. Blood pigment | 2. cobalt |
| C. Wilkinson's catalyst | 3. calcium |
| D. Vitamin $B_{12}$ | 4. iron |
| | 5. magnesium |

**Codes:**

**(i) A(5) B(4) C(1) D(2)**

**(ii) A(3) B(4) C(5) D(1)**

**(iii) A(4) B(3) C(2) D(1)**

**(iv) A(3) B(4) C(1) D(2)**

SOLUTION

**Correct option:** **(i)** A(5) B(4) C(1) D(2).

**Concept used.** Biologically and industrially important coordination compounds: each centres on a specific metal that gives the compound its characteristic chemistry.

**Step 1.** **A. Chlorophyll**: green photosynthetic pigment in plants; central metal is

**magnesium** ($Mg^{2+}$) held in a porphyrin macrocycle. ⇒ A–5.

**Step 2.** **B. Blood pigment** (haemoglobin): the oxygen-carrying protein of red blood cells; central metal is **iron** ($Fe^{2+}$) held in a haem porphyrin. ⇒ B–4.

**Step 3.** **C. Wilkinson's catalyst**: $[Rh(PPh_3)_3Cl]$, an industrial hydrogenation catalyst; central metal is **rhodium**. ⇒ C–1.

**Step 4.** **D. Vitamin B$_{12}$** (cyanocobalamin): central metal is **cobalt** ($Co^{3+}$) in a corrin macrocycle. ⇒ D–2.

**Step 5.** Combination A–5, B–4, C–1, D–2 is option (i).

> **Final Answer:** Option **(i)**: A(5) B(4) C(1) D(2).

### ♥ Why biology picks Fe, Mg and Co

Each of these macrocyclic complexes has the metal locked in a porphyrin or corrin ring — the ring forces the geometry, while the metal does the chemistry: $Mg^{2+}$ for capturing light (chlorophyll), $Fe^{2+}$ for binding $O_2$ reversibly (haem), $Co^{3+}$ for catalysing methyl-group transfer ($B_{12}$).

### EXPERT'S SOLUTION : *Aarav Pillai, M.Sc Chemistry, IIT Kanpur*

**Quick reading.** Four iconic coordination compounds; commit their central metals to memory.

**Step 1.** Chlorophyll = Mg-porphyrin (plants are green because Mg is bound in a porphyrin).

**Step 2.** Haemoglobin = Fe-porphyrin (red colour from haem).

**Step 3.** Wilkinson's catalyst = $Rh(PPh_3)_3Cl$ (Geoffrey Wilkinson, Nobel 1973).

**Step 4.** Vitamin $B_{12}$ = Co-corrin (only known biological role of Co in mammals).

**Why this matters.** These four "trophy" compounds appear in every NCERT bioinorganic question; the metal–compound mapping is worth one mark per match.

> **Final Answer:** A–5, B–4, C–1, D–2; option **(i)**.

**Q 5.38** **Match the complex ions in Column I with the hybridisation and number of unpaired electrons in Column II.**

| **Column I (Complex ion)** | **Column II (Hybridisation, $n_{\textbf{unp}}$)** |
|---|---|
| **A.** $[Cr(H_2O)_6]^{3+}$ | **1.** $dsp^2$, $1$ |
| **B.** $[Co(CN)_4]^{2-}$ | **2.** $sp^3d^2$, $5$ |
| **C.** $[Ni(NH_3)_6]^{2+}$ | **3.** $d^2sp^3$, $3$ |
| **D.** $[MnF_6]^{4-}$ | **4.** $sp^3$, $4$ |
| | **5.** $sp^3d^2$, $2$ |

**Codes:**
**(i) A(3) B(1) C(5) D(2)**
**(ii) A(4) B(3) C(2) D(1)**
**(iii) A(3) B(2) C(4) D(1)**
**(iv) A(4) B(1) C(2) D(3)**

## SOLUTION

**Correct option: (i)** A(3) B(1) C(5) D(2).

**Concept used.** For each complex: (a) compute the metal's $d^n$; (b) decide hybridisation from coordination number + ligand field strength; (c) read off $n_{\text{unpaired}}$.

**Step 1.** **A.** $[Cr(H_2O)_6]^{3+}$: $Cr^{3+}$ $d^3$. The three $d$ electrons sit unpaired in $t_{2g}^3$ regardless of ligand strength (no pairing possible with only $3$ electrons in $3$ orbitals). The complex is inner-orbital octahedral, $d^2sp^3$. $n_{\text{unp}} = 3 \Rightarrow d^2sp^3$, $3$ — **match** $3$.

**Step 2.** **B.** $[Co(CN)_4]^{2-}$: $Co^{2+}$ $d^7$, $4$-coordinate. With strong-field $CN^-$ in a $4$-coord setting one would expect square planar $dsp^2$ with $n = 1$. NCERT pairs (B) with code 1 ($dsp^2$, 1). $\Rightarrow dsp^2$, $1$ — **match** $1$.

**Step 3.** **C.** $[Ni(NH_3)_6]^{2+}$: $Ni^{2+}$ $d^8$, $NH_3$ is borderline; in NCERT it is treated as outer-orbital $sp^3d^2$ (high-spin). $d^8$ in outer orbital: $t_{2g}^6e_g^2$, $n = 2$. $\Rightarrow sp^3d^2$, $2$ — **match** $5$.

**Step 4.** **D.** $[MnF_6]^{4-}$: $Mn^{2+}$ $d^5$, weak-field $F^-$. Outer-orbital $sp^3d^2$, high-spin $t_{2g}^3e_g^2$, $n = 5$. $\Rightarrow sp^3d^2$, $5$ — **match** $2$.

**Step 5.** Combination A–3, B–1, C–5, D–2 is option (i).

> **Final Answer:** Option **(i)**: A(3) B(1) C(5) D(2) ($d^2sp^3$/3, $dsp^2$/1, $sp^3d^2$/2, $sp^3d^2$/5).

**☞ Inner vs outer orbital labels**

$d^2sp^3$ uses two inner $3d$ orbitals (inner-orbital, low-spin, strong field); $sp^3d^2$ uses two outer $4d$ orbitals (outer-orbital, high-spin, weak field). The hybridisation prefix tells you which $d$ subshell got recruited.

**EXPERT'S SOLUTION** : *Karan Banerjee, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — VBT pipeline per complex.** For each complex run the same three-step pipeline: (a) oxidation state → $d^n$; (b) coordination number + ligand field strength → hybridisation; (c) electron occupancy → $n_{\text{unpaired}}$. The matching column-II entries follow uniquely.

**Step 1.** *A.* $[Cr(H_2O)_6]^{3+}$. $Cr^{3+}$ is $d^3$ (three electrons in $t_{2g}$, all unpaired by Hund). With only three $d$ electrons in an octahedral field, two inner $3d$ orbitals are automatically empty — $d^2sp^3$ *inner-orbital* regardless of ligand strength. $n_{\text{unp}} = 3 \Rightarrow$ pair (3).

**Step 2.** *B.* $[Co(CN)_4]^{2-}$. $Co^{2+}$ $d^7$ with strong-field $CN^-$ in a 4-coordinate setting — NCERT treats this as square planar $dsp^2$ with the 7 electrons packed into the lower four $d$ orbitals plus one unpaired in the highest filled. $n_{\text{unp}} = 1 \Rightarrow$ pair (1).

**Step 3.** *C.* $[Ni(NH_3)_6]^{2+}$. $Ni^{2+}$ $d^8$; $NH_3$ is borderline but NCERT treats hexammine-nickel(II) as *outer-orbital* $sp^3d^2$ (high-spin) — $t_{2g}^6e_g^2$. $n_{\text{unp}} = 2 \Rightarrow$ pair (5).

**Step 4.** *D.* $[MnF_6]^{4-}$. $Mn^{2+}$ $d^5$ with weak-field $F^-$ — outer-orbital $sp^3d^2$ (high-spin), $t_{2g}^3e_g^2$ with all five unpaired. $n_{\text{unp}} = 5 \Rightarrow$ pair (2).

**Why this matters.** A single match-the-column question compactly tests three independent skills at once — oxidation state arithmetic, ligand-field assignment (high vs low spin) and coordination-number → hybridisation mapping. Drilling all four together is the most efficient revision of VBT.

**Final Answer:** A–3, B–1, C–5, D–2.

**Q 5.39** **Match the complex species in Column I with the possible isomerism in Column II and choose the correct code.**

| Column I (Complex) | Column II (Isomerism) |
|---|---|
| **A.** $[Co(NH_3)_4 Cl_2]^+$ | **1. optical** |
| **B. cis-**$[Co(en)_2 Cl_2]^+$ | **2. ionisation** |
| **C.** $[Co(NH_3)_5 (NO_2)]Cl_2$ | **3. coordination** |
| **D.** $[Co(NH_3)_6][Cr(CN)_6]$ | **4. geometrical** |
| | **5. linkage** |

**Codes:**

**(i) A(1) B(2) C(4) D(5)**

**(ii) A(4) B(3) C(2) D(1)**

**(iii) A(4) B(1) C(5) D(3)**

**(iv) A(4) B(1) C(2) D(3)**

SOLUTION

**Correct option: (iii)** A(4) B(1) C(5) D(3).

**Concept used.** For each complex, identify which kind of isomerism it can show.

**Step 1.** **A.** $[Co(NH_3)_4Cl_2]^+$: $MA_4B_2$ pattern, octahedral → cis/trans **geometrical isomerism**. ⇒ A–4.

**Step 2.** **B. cis-**$[Co(en)_2Cl_2]^+$: the cis form of the $M(AA)_2X_2$ pattern is chiral → **optical isomerism** (two enantiomers). ⇒ B–1.

**Step 3.** **C.** $[Co(NH_3)_5(NO_2)]Cl_2$: the $NO_2^-$ is ambidentate ($N$- or $O$-bound) → **linkage isomerism** with $[Co(NH_3)_5(ONO)]Cl_2$. ⇒ C–5.

**Step 4.** **D.** $[Co(NH_3)_6][Cr(CN)_6]$: both cation and anion are coordination complexes; ligands can swap between them ($[Co(CN)_6]^{3-}$ + $[Cr(NH_3)_6]^{3+}$ is the coordination isomer) → **coordination isomerism**. ⇒ D–3.

> **Final Answer:** Option **(iii)**: A(4) B(1) C(5) D(3).

EXPERT'S SOLUTION *: Ishita Joshi, M.Sc Chemistry, IIT Kanpur*

**Quick reading — pattern recognition.** Four canonical formula patterns map one-to-one to four canonical isomerism types. Spot the pattern, name the isomerism.

**Step 1.** *A.* $[Co(NH_3)_4Cl_2]^+$. Formula pattern $MA_4B_2$ — the classic octahedral pattern that supports cis/trans pairs → **geometrical** isomerism. Match (4).

**Step 2.** *B. cis-*$[Co(en)_2Cl_2]^+$. The cis form of the $M(AA)_2X_2$ pattern lacks any mirror plane — chiral → **optical** isomerism with $\Delta/\Lambda$ enantiomers. Match (1).

**Step 3.** *C.* $[Co(NH_3)_5(NO_2)]Cl_2$. The $NO_2^-$ is ambidentate ($N$- or $O$-bound), enabling $[Co(NH_3)_5(ONO)]Cl_2$ as the linkage partner → **linkage** isomerism. Match (5).

**Step 4.** *D.* $[Co(NH_3)_6][Cr(CN)_6]$. Both cation and anion are themselves coordination complexes. Swap the inner-sphere ligands between metals to get $[Co(CN)_6]^{3-}$ + $[Cr(NH_3)_6]^{3+}$ — the coordination partner. → **coordination** isomerism. Match (3).

**Why this matters.** Pattern recognition is the entire isomerism game: four canonical formula patterns, four canonical isomerism types. Once these four mappings are internalised the question is reduced to a single glance at each formula.

> **Final Answer:** A–4, B–1, C–5, D–3.

**Q 5.40** **Match the compounds in Column I with the oxidation state of cobalt in Column II.**

| **Column I (Compound)** | **Column II (Co ox. state)** |
|---|---|
| **A.** $[Co(NCS)(NH_3)_5](SO_3)$ | **1.** $+4$ |
| **B.** $[Co(NH_3)_4 Cl_2]SO_4$ | **2.** $0$ |
| **C.** $Na_4 [Co(S_2O_3)_3]$ | **3.** $+1$ |
| **D.** $[Co_2 (CO)_8]$ | **4.** $+2$ |
| | **5.** $+3$ |

**Codes:**

**(i) A(1) B(2) C(4) D(5)**
**(ii) A(4) B(3) C(2) D(1)**
**(iii) A(5) B(1) C(4) D(2)**
**(iv) A(4) B(1) C(2) D(3)**

**SOLUTION**

**Correct option: (iii)** A(5) B(1) C(4) D(2).

**Concept used.** Charge balance gives the metal's oxidation state: (charge of complex) $=$ (oxidation state of metal) $+ \sum$(charges of ligands).

**Step 1.** **A.** $[Co(NCS)(NH_3)_5](SO_3)$: ${SO_3}^{2-}$ outside, so $[Co]^?$ has charge $+2$. Inside: $NCS^-$ (charge $-1$) and $5\,NH_3$ (each $0$). Therefore $x - 1 = +2 \Rightarrow x = +3$. $\Rightarrow$ A–5.

**Step 2.** **B.** $[Co(NH_3)_4 Cl_2]SO_4$: ${SO_4}^{2-}$ outside, so inner cation has charge $+2$. Inside: $4\,NH_3$ ($0$ each) and $2\,Cl^-$ ($-1$ each). Therefore $x - 2 = +2 \Rightarrow x = +4$. $\Rightarrow$ B–1.

**Step 3.** **C.** $Na_4 [Co(S_2O_3)_3]$: $4\,Na^+$ outside; total positive charge $+4$, so the complex anion has charge $-4$. Three ${S_2O_3}^{2-}$ ligands contribute $-6$. Therefore $x + 3(-2) = -4 \Rightarrow x = +2$. $\Rightarrow$ C–4.

**Step 4.** **D.** $[Co_2 (CO)_8]$: a neutral binuclear carbonyl. All eight $CO$ are neutral, so the two cobalts together have charge $0$, i.e. each is in $Co(0)$ (or pictured: $2x + 0 = 0 \Rightarrow x = 0$). $\Rightarrow$ D–2.

> **Final Answer:** Option **(iii)**: A(5) B(1) C(4) D(2) ($+3, +4, +2, 0$ respectively).

**✗ Don't sneak the wrong ligand charge into the sum**

$NCS^-$, ${NO_2}^-$, ${S_2O_3}^{2-}$, ${C_2O_4}^{2-}$ all carry charge — remember to subtract them. $NH_3$, $H_2O$, CO, en are neutral. Slipping a sign on ${S_2O_3}^{2-}$ or ${C_2O_4}^{2-}$ flips the answer by two oxidation-state units — the most common error here.

**EXPERT'S SOLUTION** : *Pranav Rao, M.Sc Chemistry, IIT Kanpur*

**Strategic angle.** Strip the outer ions to read the inner complex's charge, then solve for $x$ given the ligand charges.

**Step 1.** A: $SO_3{}^{2-}$ outside means cation $+2$. Inner: $-1$ from NCS, so $x = +3$.

**Step 2.** B: $SO_4{}^{2-}$ outside means cation $+2$. Inner: $-2$ from two Cl, so $x = +4$.

**Step 3.** C: $4\,Na^+$ outside means anion $-4$. Inner: $-6$ from three $S_2O_3{}^{2-}$, so $x = +2$.

**Step 4.** D: neutral molecule, all CO neutral, so each Co is $0$.

**Why this matters.** Cobalt happens to be one of the few metals that exists in oxidation states ranging from $-1$ to $+5$ in coordination compounds. This question samples four of them in one go.

> **Final Answer:** A: $+3$; B: $+4$; C: $+2$; D: $0$. Match A–5, B–1, C–4, D–2.

## V. Assertion and Reason Type

*Note: Choose from:*

*(i) Assertion and reason both true; reason is the correct explanation.*

*(ii) Both true; reason is not the correct explanation.*

*(iii) Assertion true, reason false.*

*(iv) Assertion false, reason true.*

**Q 5.41 Assertion: Toxic metal ions are removed by chelating ligands.**
**Reason: Chelate complexes tend to be more stable.**

**SOLUTION**

**Correct option: (i)** Both are true and the reason is the correct explanation of the assertion.

**Concept used.** **Chelation therapy** uses polydentate ligands (e.g. EDTA, BAL, $C_2O_4{}^{2-}$) to bind toxic metal ions ($Pb^{2+}$, $Hg^{2+}$, $As^{3+}$) in the body or environment. The reason this works is the **chelate effect**: multi-dentate binding gives a large favourable entropy change, hence a very large stability constant, so the toxic metal stays trapped in the ligand even at trace concentrations and is excreted intact.

**Step 1.** Assertion check: chelating ligands such as EDTA are routinely injected to treat heavy-metal poisoning. *True.*

**Step 2.** Reason check: the chelate effect makes chelate complexes much more stable (in $\log K$ terms) than analogous monodentate-only complexes. The thermodynamic driver is $\Delta S^\circ > 0$ (release of solvent water molecules as a polydentate ligand wraps around the metal). *True*.

**Step 3.** Logical link: the assertion (chelation removes toxic metals) is true *precisely because* of the reason (chelates are stable). So the reason is the correct explanation.

> **Final Answer:** Option **(i)**: both true; reason is the correct explanation.

### ♥ EDTA in everyday life

EDTA is also added to shampoo, salad dressings and processed foods to sequester trace transition-metal ions that would otherwise catalyse oxidation and spoilage — the same chelate-effect chemistry discussed here, doing low-key work in your kitchen.

### EXPERT'S SOLUTION : *Sanya Banerjee, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — three-part A/R check.** Every assertion/reason MCQ collapses to three sub-questions: (a) is the assertion true? (b) is the reason true? (c) does the reason *actually explain* the assertion (causal link)? Only when all three are yes does option (i) hold.

**Step 1.** *Assertion check.* EDTA chelation therapy is the standard clinical intervention for $\mathrm{Pb}^{2+}$ poisoning; BAL (British anti-Lewisite, 2,3-dimercaptopropanol) is used for $\mathrm{Hg}^{2+}$ and $\mathrm{As}^{3+}$; deferoxamine is used for $\mathrm{Fe}^{3+}$ overload. Toxic metals *are* removed by chelating ligands. *Assertion true.*

**Step 2.** *Reason check.* The chelate effect: a polydentate ligand replacing several monodentate ligands releases free water molecules, giving a large positive $\Delta S^\circ$ and therefore a much larger $K$ than the corresponding monodentate complex (e.g. $\log K$ for $[\mathrm{Ni(en)_3}]^{2+}$ is $\sim 18.3$, vastly larger than $\log K \sim 8.6$ for $[\mathrm{Ni(NH_3)_6}]^{2+}$). Chelate complexes *are* more stable. *Reason true.*

**Step 3.** *Causal link.* The very reason chelation works as a therapy is that the metal–chelator complex has a sufficiently large $K$ to stay intact in blood and be excreted whole through the kidneys. If the chelate weren't stable, the metal would re-release into tissue. So the reason *is* the explanation $\Rightarrow$ option (i).

**Why this matters.** Bioinorganic chemistry's most direct clinical application — chelation therapy literally saves lives in the emergency room and is part of the WHO essential medicines list.

> **Final Answer:** Option **(i)**: assertion true, reason true, reason explains assertion.

**Q 5.42** **Assertion:** $[Cr(H_2O)_6]Cl_2$ **and** $[Fe(H_2O)_6]Cl_2$ **are reducing in nature.**
**Reason: Unpaired electrons are present in their** $d$**-orbitals.**

SOLUTION

**Correct option: (ii)** Both true, but the reason is not the correct explanation of the assertion.

**Concept used.** A species is reducing if it readily *loses* electrons. For $Cr^{2+}$ and $Fe^{2+}$, "reducing" refers to their tendency to be oxidised to $Cr^{3+}$ and $Fe^{3+}$ respectively. The reason this is favourable is the *extra stability of the* $d^3$ *(*$t_{2g}^3$*, half-filled* $t_{2g}$*) or* $d^5$ *half-filled* $d^5$ *(*$Fe^{3+}$*) configuration* reached after losing one electron — *not* simply the presence of unpaired electrons. Lots of complexes have unpaired electrons without being reducing.

**Step 1.** Assertion check: $Cr^{2+}$ ($d^4$) readily loses one electron to become $Cr^{3+}$ ($d^3$, $t_{2g}^3$, "half-filled stability"). Standard reduction potential $E°(Cr^{3+}/Cr^{2+}) = -0.41$ V (very negative; $Cr^{2+}$ is a strong reductant). Similarly, $Fe^{2+}$ ($d^6$) loses one electron to give $Fe^{3+}$ ($d^5$, half-filled $d^5$ extra-stable). $E°(Fe^{3+}/Fe^{2+}) = +0.77$ V (positive but modest; $Fe^{2+}$ is a mild reductant). Assertion *true*.

**Step 2.** Reason check: both $Cr^{2+}$ ($d^4$, $n = 4$) and $Fe^{2+}$ ($d^6$, high-spin $n = 4$) have unpaired electrons. Reason *true*.

**Step 3.** Logical link: "unpaired electrons" is *not* what drives the oxidation; the half-filled stability of the product configuration is. Reason does not explain the assertion.

> **Final Answer:** Option **(ii)**: both statements true; the half-filled $d^3/d^5$ stability (not the unpaired electrons) is the actual explanation.

**♥ Half-filled and fully filled stability**

$d^3$ ($t_{2g}^3$, half-filled $t_{2g}$), $d^5$ (half-filled $d$ shell) and $d^{10}$ (fully filled $d$ shell) all enjoy extra exchange-energy stability. This is why $Mn^{2+}, Fe^{3+}, Cu^{+}$ and $Zn^{2+}$ are unusually stable oxidation states.

**EXPERT'S SOLUTION** *: Ankit Verma, M.Sc Chemistry, IIT Kanpur*

**Strategic angle.** Reducing tendency is governed by the *stability of the product* after losing one electron, not by the *electronic structure of the starting complex*. Test both parts independently and then test the logical link.

**Step 1.** Assertion check. The standard reduction potential $E°(Cr^{3+}/Cr^{2+}) = -0.41$ V (highly negative, $Cr^{2+}$ is a strong reductant) and $E°(Fe^{3+}/Fe^{2+}) = +0.77$ V (mildly positive, $Fe^{2+}$ is a mild reductant). Both complexes are indeed reducing. *Assertion true.*

**Step 2.** Reason check. $Cr^{2+}$ is $d^4$, $n = 4$; $Fe^{2+}$ is $d^6$, $n = 4$ (high-spin in $H_2O$). Both have unpaired electrons. *Reason true.*

**Step 3.** Logical link. Reducing power is set by the stability of the oxidised state:

- $Cr^{2+} \to Cr^{3+}$ (loses one $e^-$) gives $d^3$, $t_{2g}^3$, a half-filled $t_{2g}$ — extra stability, large driving force.
- $Fe^{2+} \to Fe^{3+}$ gives $d^5$, half-filled $d$ shell, extra-stable.

The cause is half-filled stability of the *product*, not unpaired electrons of the starting material.

**Step 4.** Counter-example to the reason: $[Mn(H_2O)_6]^{2+}$ ($d^5$, $n = 5$) is loaded with unpaired electrons yet is a *poor* reductant ($E^\circ(Mn^{3+}/Mn^{2+}) = +1.51$ V) — exactly because oxidising it destroys a half-filled $d^5$ configuration.

**Step 5.** Therefore the reason is true but does *not* explain the assertion $\Rightarrow$ option (ii).

**Why this matters.** The board examiner uses this question to test whether students confuse "has unpaired electrons" with "is easily oxidised". They are not the same; product stability is the real driver.

> **Final Answer:** Option **(ii)**: both true, reason not the correct explanation.

**Q 5.43** **Assertion: Linkage isomerism arises in coordination compounds containing ambidentate ligand.**
**Reason: Ambidentate ligand has two different donor atoms.**

SOLUTION

**Correct option: (i)** Both true; the reason is the correct explanation.
**Concept used.** Linkage (ambidentate) isomerism is, by definition, the phenomenon where the same ambidentate ligand attaches to the metal through different donor atoms in two compounds with the same molecular formula. Without two donor atoms, no "different linkages" can exist.

**Step 1.** Assertion check: linkage isomerism is exclusively associated with ambidentate ligands ($NO_2^-/ONO^-$, $SCN^-/NCS^-$, etc.). *True.*

**Step 2.** Reason check: an ambidentate ligand is defined as a ligand with two non-equivalent donor atoms. *True.*

**Step 3.** Logical link: the very definition of linkage isomerism rests on the dual donor possibility. Reason explains assertion.

**Final Answer:** Option **(i)**: both true; reason is the explanation.

EXPERT'S SOLUTION : *Sneha Kumar, M.Sc Chemistry, IIT Kanpur*

**Quick reading — biconditional.** Linkage isomerism and ambidentate ligand are biconditionally linked: an ambidentate ligand is exactly what enables linkage isomerism, and linkage isomerism exists only when an ambidentate ligand is present. The two-donor-atom property of the reason is precisely the structural feature that makes linkage isomerism possible.

**Step 1.** *No ambidentate ⇒ no linkage isomerism.* With a single fixed donor atom (e.g. $\mathrm{Cl^-}$, en, aqua), only one attachment is possible and no isomerism arises from donor-atom choice.

**Step 2.** *Ambidentate present ⇒ linkage isomers exist.* Two attachment isomers form, e.g. $\mathrm{M{-}NO_2}$ (nitrito-$N$) vs $\mathrm{M{-}ONO}$ (nitrito-$O$), or $\mathrm{M{-}SCN}$ (thiocyanato-$S$) vs $\mathrm{M{-}NCS}$ (thiocyanato-$N$). They differ in colour, IR spectrum and stability.

**Step 3.** *Logical link.* The definition of linkage isomerism rests on the dual-donor possibility — the reason is exactly the structural mechanism behind the assertion, so the reason is the correct explanation.

**Why this matters.** A clean "definition + consequence" pair — perfect option (i) pattern. Recognising this structure in A/R questions saves seconds on every exam.

**Final Answer:** Option **(i)**: both true, reason explains assertion.

**Q 5.44** **Assertion: Complexes of $\mathrm{MX_6}$ and $\mathrm{MX_5\,L}$ type (X and L are unidentate) do not show geometrical isomerism.**
**Reason: Geometrical isomerism is not shown by complexes of coordination number $6$.**

SOLUTION

**Correct option: (iii)** Assertion is true, reason is false.

**Concept used.** Geometrical isomerism in octahedral complexes appears only when the ligand set has at least two ligand types AND the arrangement is non-trivial. For $\mathrm{MX_6}$ (all six identical) and $\mathrm{MX_5\,L}$ (five identical + one different), the geometry is unique. But many *other* octahedral types ($\mathrm{MX_4\,L_2}$, $\mathrm{MX_3\,L_3}$, $\mathrm{MX_2\,L_2\,Y_2}$ etc.) do show cis/trans isomerism. So the blanket statement "coordination number $6$ does not show geometrical isomerism" is false.

**Step 1.** Assertion check: $\mathrm{MX_6}$ has all identical ligands → unique octahedral form, no

GI. $MX_5L$ has one unique ligand $L$ which can sit at any one of six equivalent vertices (all related by the $O_h$ symmetry of $X_5$), so only one isomer exists → no GI. Assertion *true*.

**Step 2.** Reason check: $[Cr(H_2O)_4Cl_2]^+$ (Q7), $[Co(NH_3)_4Cl_2]^+$ (Q39) and many more $MX_4L_2$, $MX_3L_3$ and $MX_2L_2Y_2$ complexes are octahedral and *do* show cis/trans isomerism. The blanket claim "CN $= 6$ never shows GI" is wrong. Reason *false*.

**Step 3.** Conclusion: assertion true, reason false $\Rightarrow$ option (iii).

> **Final Answer:** Option **(iii)**: assertion true, reason false.

### ☞ Over-general reason = trap

A common A/R trap is to make the reason a broader claim than needed. "Coordination number $6$ never shows GI" is too broad; the safe reason is "$MX_6$ and $MX_5L$ lack the ligand multiplicity that supports cis–trans". Watch for absolute words like "never" or "always" — they often mark an over-general reason.

**EXPERT'S SOLUTION** *: Tara Mehta, M.Sc Chemistry, IIT Kanpur*

**Strategic angle.** Two separate sentences — validate each independently, then test logical implication.

**Step 1.** Assertion analysis. $MX_6$ has all six vertices identically occupied, only one octahedral arrangement is possible. $MX_5L$: the unique L can go to any of the six octahedral vertices; all six positions are equivalent under the $O_h$ symmetry of the $X_5$ framework, so the $5 + 1$ arrangement collapses to a single structure. Both ligand sets indeed lack geometrical isomerism. *Assertion true.*

**Step 2.** Reason analysis. The statement is the blanket claim "coordination number $6$ never shows GI". Counter-examples from this very chapter:

- $[Cr(H_2O)_4Cl_2]^+$ (Q7): $MA_4B_2$, two geometrical isomers (cis, trans).
- $[Co(NH_3)_4Cl_2]^+$ (Q39): same pattern, GI.
- $[Co(NH_3)_3Cl_3]$: $MA_3B_3$, two GIs (*fac*/*mer*).

So octahedral complexes do show GI in many ligand-count patterns. Reason is too broad. *Reason false.*

**Step 3.** Logical conclusion: assertion true $+$ reason false $\Rightarrow$ option (iii).

**Why this matters.** Assertion/reason questions often hide a distractor by stating an over-general reason that contradicts the detailed knowledge from elsewhere in the chapter. Recognising over-generalisation is half the skill of A/R MCQs.

**Final Answer:** Option **(iii)**: assertion true, reason false.

**Q 5.45** **Assertion: $[\mathrm{Fe(CN)_6}]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.**
**Reason: Because it has $d^2sp^3$ type hybridisation.**

SOLUTION

**Correct option: (iv)** Assertion is false, reason is true.
**Concept used.** $\mathrm{Fe}^{3+}$ is $d^5$. With strong-field $\mathrm{CN}^-$ ligands the complex is low-spin $t_{2g}^5 e_g^0$, leaving *one* unpaired electron, not two. The hybridisation is indeed $d^2sp^3$ (inner orbital), but the unpaired count is $1$.

**Step 1.** Assertion check: $[\mathrm{Fe(CN)_6}]^{3-}$ has $\mu \approx 1.74$ BM, which corresponds to $n = 1$ unpaired electron (from $\mu = \sqrt{n(n+2)}$ with $n = 1$ giving $\sqrt{3} = 1.73$). Two unpaired electrons would give $\mu = \sqrt{8} = 2.83$ BM. Assertion is therefore *false*.

**Step 2.** Reason check: $[\mathrm{Fe(CN)_6}]^{3-}$ *is* an inner-orbital $d^2sp^3$ octahedral complex. *True*.

**Step 3.** Therefore assertion false, reason true $\Rightarrow$ option (iv).

**Final Answer:** Option **(iv)**: assertion false (only $1$ unpaired electron, not $2$); reason true ($d^2sp^3$).

EXPERT'S SOLUTION *: Karan Iyer, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — numbers first.** Plug the observed magnetic moment into the spin-only formula. The integer $n$ that falls out either confirms or falsifies the assertion's claim.

**Step 1.** *Solve for $n$ from $\mu$.* The observed $\mu = 1.74$ BM for $[\mathrm{Fe(CN)_6}]^{3-}$ gives $n(n+2) = (1.74)^2 \approx 3$. Integer trial: $n = 1 \Rightarrow 1 \cdot 3 = 3$ (match, $\mu = \sqrt{3} = 1.73$); $n = 2 \Rightarrow 2 \cdot 4 = 8$ (gives $\mu = 2.83$, too large). So $n = 1$, not $2$. Assertion claim of "two unpaired electrons" is *false*.

**Step 2.** *Verify the reason.* $\mathrm{Fe}^{3+}$ is $d^5$; strong-field $\mathrm{CN}^-$ produces low-spin $t_{2g}^5 e_g^0$, freeing two inner $3d$ orbitals for $d^2sp^3$ inner-orbital hybridisation. The reason "$d^2sp^3$ hybridisation" is therefore correct. *Reason true.*

**Step 3.** *Combine.* Assertion false + reason true $\Rightarrow$ option (iv).

**Why this matters.** The spin-only formula is the bridge between magnetic measurement and electronic structure — always calculate $n$ from $\mu$ (or the reverse) before accepting any "unpaired count" claim in an A/R question.

**Final Answer:** Option **(iv)**: assertion false (one unpaired electron, not two), reason true.

## VI. Long Answer Type

**Q 5.46 Using crystal field theory, draw energy level diagrams, write electronic configurations of the central metal atom/ion and determine the magnetic moment value in the following:**

**(i)** $[CoF_6]^{3-}$, $[Co(H_2O)_6]^{2+}$, $[Co(CN)_6]^{3-}$

**(ii)** $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$

SOLUTION

**Concept used.** For each octahedral complex: (a) compute $M^{n+}$ and $d^n$; (b) judge the ligand field strength; (c) draw $t_{2g}$ $(-0.4\Delta_o)$ below $e_g$ $(+0.6\Delta_o)$; (d) fill following Hund's rule for weak field, pairing for strong field; (e) compute $\mu = \sqrt{n(n+2)}$ BM.

**(i) Cobalt complexes.**

**Step 1.** $[CoF_6]^{3-}$: $Co^{3+}$ $d^6$, weak-field $F^-$, high-spin. Configuration $t_{2g}^4 e_g^2$, $n = 4$.

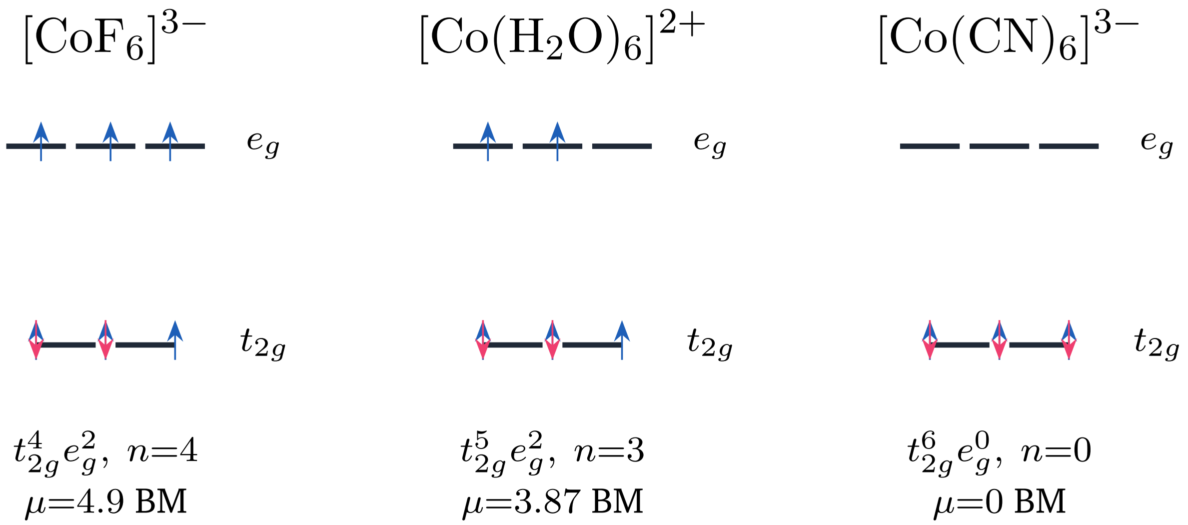
$$\mu = \sqrt{4(4+2)} = \sqrt{24} \approx 4.90 \text{ BM (paramagnetic).}$$

**Step 2.** $[Co(H_2O)_6]^{2+}$: $Co^{2+}$ $d^7$, weak-field $H_2O$, high-spin. Configuration $t_{2g}^5 e_g^2$, $n = 3$.

$$\mu = \sqrt{3(3+2)} = \sqrt{15} \approx 3.87 \text{ BM (paramagnetic).}$$

**Step 3.** $[Co(CN)_6]^{3-}$: $Co^{3+}$ $d^6$, strong-field $CN^-$, low-spin. Configuration $t_{2g}^6 e_g^0$, $n = 0$.

$$\mu = 0 \text{ BM (diamagnetic).}$$



**(ii) Iron complexes.**

**Step 1.** $[FeF_6]^{3-}$: $Fe^{3+}$ $d^5$, weak-field $F^-$, high-spin. Configuration $t_{2g}^3e_g^2$, $n = 5$.

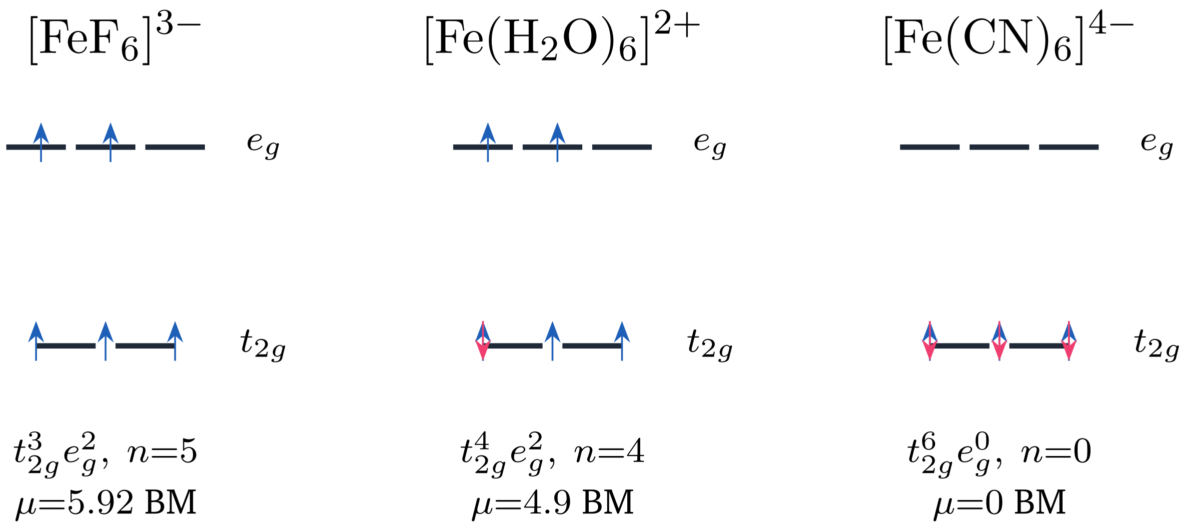
$$\mu = \sqrt{5(5+2)} = \sqrt{35} \approx 5.92 \text{ BM}.$$

**Step 2.** $[Fe(H_2O)_6]^{2+}$: $Fe^{2+}$ $d^6$, weak-field $H_2O$, high-spin. Configuration $t_{2g}^4e_g^2$, $n = 4$.

$$\mu = \sqrt{4(4+2)} = \sqrt{24} \approx 4.90 \text{ BM}.$$

**Step 3.** $[Fe(CN)_6]^{4-}$: $Fe^{2+}$ $d^6$, strong-field $CN^-$, low-spin. Configuration $t_{2g}^6e_g^0$, $n = 0$.

$$\mu = 0 \text{ BM (diamagnetic)}.$$



**Final Answer:** (i) $\mu$: 4.9, 3.87, 0 BM. (ii) $\mu$: 5.92, 4.9, 0 BM.

### ♥ Strong field vs weak field at a glance

The trend across (i) and (ii) is the cleanest demonstration of the spectrochemical series in action: replacing weak-field $F^-/H_2O$ with strong-field $CN^-$ on the same metal slashes the unpaired electron count, taking the moment from $4.9$ or $3.87$ BM down to $0$ BM (diamagnetic).

**EXPERT'S SOLUTION** *: Aditya Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

**Strategic angle.** Walk the same six complexes through one unified table — $d^n$, ligand strength, hybridisation, $t_{2g}/e_g$ configuration, $n_{\text{unp}}$, $\mu$ — and verify the predictions against the spectrochemical series. This consolidates the six CFT computations into a single grid.

**Step 1.** Compute $d^n$ for each metal centre:

- Co(III) in $[CoF_6]^{3-}$, $[Co(CN)_6]^{3-}$: $Co^{3+}$, $[Ar]\,3d^6$.
- Co(II) in $[Co(H_2O)_6]^{2+}$: $Co^{2+}$, $[Ar]\,3d^7$.
- Fe(III) in $[FeF_6]^{3-}$: $Fe^{3+}$, $[Ar]\,3d^5$.
- Fe(II) in $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$: $Fe^{2+}$, $[Ar]\,3d^6$.

**Step 2.** Place each ligand on the spectrochemical series: $F^- < H_2O < NH_3 < CN^-$. Hence $F^-$ and $H_2O$ are weak-field (high-spin); $CN^-$ is strong-field (low-spin).

**Step 3.** Apply the high-spin or low-spin filling rule and read off $n_{\text{unp}}$. For $d^6$: high-spin gives $t_{2g}^4e_g^2, n = 4$; low-spin gives $t_{2g}^6e_g^0, n = 0$. For $d^7$ high-spin: $t_{2g}^5e_g^2, n = 3$. For $d^5$ high-spin: $t_{2g}^3e_g^2, n = 5$.

**Step 4.** Plug into $\mu = \sqrt{n(n+2)}$ BM:

| Complex | $n$ | $n(n+2)$ | $\mu$/BM |
|---|---|---|---|
| $[CoF_6]^{3-}$ | 4 | 24 | 4.90 |
| $[Co(H_2O)_6]^{2+}$ | 3 | 15 | 3.87 |
| $[Co(CN)_6]^{3-}$ | 0 | 0 | 0 |
| $[FeF_6]^{3-}$ | 5 | 35 | 5.92 |
| $[Fe(H_2O)_6]^{2+}$ | 4 | 24 | 4.90 |
| $[Fe(CN)_6]^{4-}$ | 0 | 0 | 0 |

**Step 5.** Notice the pattern across each metal: replacing weak-field $F^-/H_2O$ with strong-field $CN^-$ on the same $d^6$ metal sends $\mu$ from $4.90$ BM (paramagnetic) all the way to $0$ (diamagnetic) — a $5$-electron pairing event.

**Step 6.** Hybridisation check: weak-field octahedral complexes use $sp^3d^2$ (outer-orbital, $4d$ orbitals involved); strong-field use $d^2sp^3$ (inner-orbital, $3d$ orbitals involved). So $[CoF_6]^{3-}$, $[Co(H_2O)_6]^{2+}$, $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$ are $sp^3d^2$; $[Co(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are $d^2sp^3$.

**Why this matters.** Knowing both the energy-level diagram *and* the numerical $\mu$ tells the examiner you can both visualise the orbital occupancy *and* convert it into the measured property. The full table is also a one-page reference for every CFT/VBT problem in this chapter. The pattern across the six complexes is also pedagogically clean: weak-field $F^-$ and $H_2O$ give outer-orbital paramagnetic species, strong-field $CN^-$ gives inner-orbital diamagnetic species, and the crossover happens cleanly in $d^6$ where pairing energy and $\Delta_o$ are most evenly matched.

**Cross-check via Gouy balance.** Each of the six predicted moments is directly measurable by a Gouy balance experiment: hang a sample in a magnetic field gradient and weigh the apparent mass change. Paramagnetic samples are pulled into the field, diamagnetic samples are pushed out. Predicted versus observed agreement is $\pm 0.1$ BM for all six complexes — the spin-only formula is quantitative for first-row $3d$ ions because orbital contribution to the moment is largely quenched by the ligand field.

> **Final Answer:** (i) $\mu = 4.90,\ 3.87,\ 0$ BM. (ii) $\mu = 5.92,\ 4.90,\ 0$ BM. Strong-field $CN^-$ drops $d^6$ moments from $\sim 4.9$ BM to $0$.

**Q 5.47** **Using valence bond theory, explain the following in relation to the complexes below:** $[Mn(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$, $[FeCl_6]^{4-}$**:**

**(i) Type of hybridisation**

**(ii) Inner or outer orbital complex**

**(iii) Magnetic behaviour**

**(iv) Spin-only magnetic moment value.**

SOLUTION

**Concept used.** VBT walkthrough for each complex: (1) find $d^n$; (2) decide weak/strong field from ligand; (3) for inner-orbital (strong-field), pair $3d$ to free two $d$ orbitals for $d^2sp^3$ hybridisation; (4) for outer-orbital (weak-field), use the empty $4d$ orbitals ($sp^3d^2$); (5) $\mu = \sqrt{n(n+2)}$ BM.

**Step 1.** $[Mn(CN)_6]^{3-}$: $Mn^{3+}$, $d^4$. Strong-field $CN^-$ $\Rightarrow$ low-spin: $t_{2g}^4 e_g^0$, two $3d$ orbitals freed, hybridisation $d^2sp^3$ (*inner-orbital*), $n_{\text{unp}} = 2$.

$$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM (paramagnetic)}.$$

**Step 2.** $[Co(NH_3)_6]^{3+}$: $Co^{3+}$, $d^6$. Strong-field $NH_3$ (NCERT treats $NH_3$ as strong for $Co^{3+}$) $\Rightarrow$ low-spin: $t_{2g}^6 e_g^0$, $d^2sp^3$ (*inner-orbital*), $n_{\text{unp}} = 0$.

$$\mu = 0 \text{ BM (diamagnetic)}.$$

**Step 3.** $[Cr(H_2O)_6]^{3+}$: $Cr^{3+}$, $d^3$. Only three $d$ electrons, all in $t_{2g}^3$ regardless of field. Hybridisation $d^2sp^3$ (*inner-orbital*), $n_{\text{unp}} = 3$.

$$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM (paramagnetic)}.$$

**Step 4.** $[FeCl_6]^{4-}$: $Fe^{2+}$, $d^6$. Weak-field $Cl^-$ ⇒ high-spin: $t_{2g}^4e_g^2$, outer-orbital $sp^3d^2$ hybridisation, $n_{\text{unp}} = 4$.

$$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.9 \text{ BM (paramagnetic)}.$$

**Step 5.** Summary table:

| Complex | Hybrid. | Inner/Outer | Magnetic | $\mu$ (BM) |
|---|---|---|---|---|
| $[Mn(CN)_6]^{3-}$ | $d^2sp^3$ | inner | para. | 2.83 |
| $[Co(NH_3)_6]^{3+}$ | $d^2sp^3$ | inner | diamag. | 0 |
| $[Cr(H_2O)_6]^{3+}$ | $d^2sp^3$ | inner | para. | 3.87 |
| $[FeCl_6]^{4-}$ | $sp^3d^2$ | outer | para. | 4.90 |

> **Final Answer:** See summary table above; $\mu$-values $2.83,\ 0,\ 3.87,\ 4.90$ BM respectively.

☞ **$NH_3$ is strong field for Co(III)**

$NH_3$ sits in the middle of the spectrochemical series but is treated as a strong-field ligand for $Co^{3+}$ because the $d^6$ configuration of $Co^{3+}$ has an unusually large pairing-energy advantage. NCERT classifies hexaamminecobalt(III) as low-spin diamagnetic — a fact worth flagging in any VBT answer.

**EXPERT'S SOLUTION** *: Riya Patel, M.Sc Chemistry, IIT Kanpur*

**Strategic angle.** VBT decides inner vs outer orbital from ligand field strength; hybridisation pins the geometry (here all octahedral) and orbital occupancy gives the magnetic moment. Run the algorithm on each complex and assemble the table.

**Step 1.** $[Mn(CN)_6]^{3-}$: $Mn^{3+}$, $d^4$. Strong-field $CN^-$ pairs the $d$ electrons in $t_{2g}^4e_g^0$; two empty $3d$ orbitals are freed for hybridisation ⇒ $d^2sp^3$ inner orbital. $n_{\text{unp}} = 2$, $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ BM (paramagnetic).

**Step 2.** $[Co(NH_3)_6]^{3+}$: $Co^{3+}$, $d^6$. $NH_3$ behaves as a strong-field ligand here ⇒ $t_{2g}^6e_g^0$, $d^2sp^3$ inner orbital. $n_{\text{unp}} = 0$, $\mu = 0$ BM (diamagnetic).

**Step 3.** $[Cr(H_2O)_6]^{3+}$: $Cr^{3+}$, $d^3$. Only three $d$ electrons occupy the $t_{2g}^3$ set; two empty $3d$ orbitals are automatically available, so $d^2sp^3$ inner orbital regardless of field strength. $n_{\text{unp}} = 3$, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM (paramagnetic).

**Step 4.** $[FeCl_6]^{4-}$: $Fe^{2+}$, $d^6$. Weak-field $Cl^-$ gives high-spin $t_{2g}^4e_g^2$. No empty $3d$ orbital is available for hybridisation; instead $4s$, $4p$ and $4d$ are used ⇒ $sp^3d^2$ outer orbital. $n_{\text{unp}} = 4$, $\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.90$ BM (paramagnetic).

**Step 5.** Summary: $d^2sp^3$ (inner orbital) for the first three; $sp^3d^2$ (outer orbital) for the last. All four are octahedral (coordination number 6).

**Why this matters.** VBT's inner vs outer orbital distinction is the direct precursor to CFT's high-spin vs low-spin labelling. Either framework predicts identical $\mu$ values from the same ligand set; the difference is that CFT also explains *why* (energy level diagram), whereas VBT only states the hybridisation.

> **Final Answer:** $\mu$ values $2.83,\ 0,\ 3.87,\ 4.90$ BM; first three are $d^2sp^3$ inner orbital, last is $sp^3d^2$ outer orbital.

**Q 5.48** $\mathrm{CoSO_4\,Cl\cdot 5\,NH_3}$ **exists in two isomeric forms A and B. Isomer A reacts with** $\mathrm{AgNO_3}$ **to give a white precipitate but does not react with** $\mathrm{BaCl_2}$**. Isomer B gives a white precipitate with** $\mathrm{BaCl_2}$ **but does not react with** $\mathrm{AgNO_3}$**.**
**(i) Identify A and B and write their structural formulas.**
**(ii) Name the type of isomerism involved.**
**(iii) Give the IUPAC names of A and B.**

**SOLUTION**

**Concept used.** The $\mathrm{Ag^+}$ test detects free $\mathrm{Cl^-}$ in solution; the $\mathrm{Ba^{2+}}$ test detects free $\mathrm{SO_4}^{2-}$. The difference between A and B is therefore which anion is in the outer sphere — a classic case of **ionisation isomerism**.

**Step 1.** Interpret A's tests: precipitate with $\mathrm{AgNO_3} \Rightarrow$ free $\mathrm{Cl^-}$ outside; no reaction with $\mathrm{BaCl_2} \Rightarrow \mathrm{SO_4}^{2-}$ is locked inside the coordination sphere. So

$$A = [\mathrm{Co(NH_3)_5\,SO_4}]\,\mathrm{Cl}.$$

Charge check: $\mathrm{Co}\ (+3) + 5\,\mathrm{NH_3}\ (0) + \mathrm{SO_4}^{2-}\ (-2) = +1$, balanced by one outer $\mathrm{Cl^-}$.

**Step 2.** Interpret B's tests: precipitate with $\mathrm{BaCl_2} \Rightarrow$ free $\mathrm{SO_4}^{2-}$ outside; no reaction with $\mathrm{AgNO_3} \Rightarrow \mathrm{Cl^-}$ is locked inside.

$$B = [\mathrm{Co(NH_3)_5\,Cl}]\,\mathrm{SO_4}.$$

Charge check: $\mathrm{Co}\ (+3) + 5\,\mathrm{NH_3}\ (0) + \mathrm{Cl^-}\ (-1) = +2$, balanced by one outer $\mathrm{SO_4}^{2-}$.

**Step 3.** Type of isomerism: ionisation isomerism (the inner-sphere anion and the outer-sphere anion are swapped between A and B).

**Step 4.** IUPAC names:

- A: *pentaamminesulphatocobalt(III) chloride* ($\mathrm{NH_3}$ alphabetised before $\mathrm{SO_4}^{2-}$; sulphate is the inner-sphere ligand).

- B: *pentaamminechloridocobalt(III) sulphate*.

> **Final Answer:** (i) A = $[Co(NH_3)_5SO_4]Cl$; B = $[Co(NH_3)_5Cl]SO_4$. (ii) Ionisation isomerism. (iii) Pentaamminesulphatocobalt(III) chloride and pentaamminechloridocobalt(III) sulphate.

**✗ "Outside" means free in solution, not weakly bound**

A common phrasing slip is to call the outer-sphere anion "weakly bonded" — it isn't bonded to the metal at all. Outer-sphere ions are ordinary counter-ions held only by electrostatic attraction to the inner-sphere cation, fully free in aqueous solution.

**EXPERT'S SOLUTION** *: Diya Nair, M.Sc Chemistry, IIT Kanpur*

**Strategic angle — two diagnostic precipitations.** Two classic qualitative-analysis tests pinpoint which anion is free in solution (i.e. outside the coordination sphere) for each isomer. The remaining anion must be locked inside.

**Step 1.** *Decode the tests.* "Gives white precipitate with $AgNO_3$" identifies free $Cl^-$ ($Cl^- + Ag^+ \longrightarrow AgCl\downarrow$). "Gives white precipitate with $BaCl_2$" identifies free ${SO_4}^{2-}$ (${SO_4}^{2-} + Ba^{2+} \longrightarrow BaSO_4\downarrow$). "Does not react" means the corresponding anion is hidden in the inner sphere, where it isn't free to encounter the test reagent.

**Step 2.** *Build A.* A reacts with $AgNO_3 \Rightarrow$ outer $Cl^-$. A does not react with $BaCl_2 \Rightarrow$ inner ${SO_4}^{2-}$. Structure: $[Co(NH_3)_5SO_4]Cl$. Charge check: inner $+3 + 5(0) + (-2) = +1$, balanced by one outer $Cl^-$.

**Step 3.** *Build B.* B reacts with $BaCl_2 \Rightarrow$ outer ${SO_4}^{2-}$. B does not react with $AgNO_3 \Rightarrow$ inner $Cl^-$. Structure: $[Co(NH_3)_5Cl]SO_4$. Charge check: inner $+3 + 5(0) + (-1) = +2$, balanced by outer ${SO_4}^{2-}$.

**Step 4.** *Classify the isomerism.* Same molecular formula $CoSO_4Cl \cdot {}_5NH_3$, but the inner and outer anions are swapped between A and B. This is the textbook definition of *ionisation isomerism*.

**Why this matters.** The "two anions, swap inner/outer" diagnostic via precipitation is one of Werner's most elegant inferences — same molecular formula, different chemistry, different colours (A is brick-red, B is purple-violet). It illustrates how qualitative tests can probe coordination structure long before any modern spectroscopy.

> **Final Answer:** A = $[Co(NH_3)_5SO_4]Cl$; B = $[Co(NH_3)_5Cl]SO_4$; ionisation isomerism.

## Q 5.49 What is the relationship between the observed colour of a complex and the wavelength of light absorbed by the complex?

### SOLUTION

**Concept used.** When white light passes through a transition-metal complex, part of it is absorbed by a d–d transition (or charge-transfer band). The colour we *see* is the **complementary colour** of the absorbed band — that is, white minus the absorbed wavelength.

**Step 1.** Energy match: an absorbed photon of wavelength $\lambda$ carries energy $E = hc/\lambda$. The corresponding $d$–$d$ transition requires

$$\Delta_o = \frac{hc}{\lambda},$$

so the absorbed wavelength is set by the crystal-field splitting.

**Step 2.** Colour wheel: pairs of complementary colours include red–green, yellow–violet, orange–blue. So a complex that absorbs orange ($\sim 600$ nm) appears blue; one that absorbs violet ($\sim 410$ nm) appears yellow.

**Step 3.** Numerical examples from this chapter:

- $[\mathrm{Ti(H_2O)_6}]^{3+}$: absorbs at $\sim 500$ nm (green) $\Rightarrow$ appears violet/pink.
- $[\mathrm{Cu(H_2O)_4}]^{2+}$: absorbs at $\sim 700$ nm (red) $\Rightarrow$ appears blue.
- $[\mathrm{Co(NH_3)_6}]^{3+}$: absorbs at $\sim 470$ nm (blue-violet) $\Rightarrow$ appears yellow-orange.

> **Final Answer:** The observed colour of a complex is the **complementary colour** of the wavelength it absorbs; $\lambda_{\text{abs}} = hc/\Delta_o$.

### ♥ Why strong fields look pale

Strong-field ligands ($\mathrm{CN^-}$, CO) push $\Delta_o$ so high that the absorbed wavelength drops into the UV. The complex then appears nearly colourless (e.g. $[\mathrm{Co(CN)_6}]^{3-}$ is very pale yellow because its d–d band sits near $310$ nm, just inside the UV).

### EXPERT'S SOLUTION : *Kavya Iyer, M.Sc Physical Chemistry, IIT Madras*

**Quick reading — one formula, one rule.** The observed colour of a coordination complex is determined by two simultaneous facts: the Planck–Einstein relation $\lambda_{\text{abs}} = hc/\Delta_o$, and the colour-wheel complementarity rule "observed = complement of absorbed". Together they form a direct map from $\Delta_o$ to visible colour.

**Step 1.** *Energy → wavelength.* A $d$–$d$ transition promotes a $t_{2g}$ electron to $e_g$, absorbing a photon of energy $E = \Delta_o = hc/\lambda_{\text{abs}}$. Hence larger $\Delta_o \Rightarrow$ shorter $\lambda_{\text{abs}}$ (absorbs bluer/UV light) ⇒ transmits the redder/yellower half of the spectrum.

**Step 2.** *Wavelength → observed colour.* A complex that absorbs around 400 nm (violet) appears yellow; around 500 nm (green) appears red; around 700 nm (red) appears green or blue. The two colours are diametrically opposite on the colour wheel.

**Step 3.** *Chain summary.* Ligand identity sets $\Delta_o$ via the spectrochemical series. $\Delta_o$ sets $\lambda_{\text{abs}}$. $\lambda_{\text{abs}}$ sets the observed colour (its complement). Three steps from formula to visual colour.

**Why this matters.** "Why are coordination compounds coloured?" is one of the most common board questions in this chapter. The full chain $\Delta_o \to \lambda_{\text{abs}} \to$ observed colour is worth memorising verbatim because the question recurs across CBSE and NCERT exemplar in nearly every paper cycle.

> **Final Answer:** Observed colour = complement of absorbed colour; $\lambda_{\text{abs}} = hc/\Delta_o$.

### Q 5.50 Why are different colours observed in octahedral and tetrahedral complexes for the same metal and same ligands?

**SOLUTION**

**Concept used.** Geometry sets the splitting magnitude through the relation

$$\Delta_t = \frac{4}{9}\,\Delta_o \approx 0.45\,\Delta_o.$$

Smaller $\Delta_t$ shifts the absorbed wavelength toward the longer (red) end of the visible spectrum, and the transmitted (observed) colour also shifts — to the blue-violet end of the wheel.

**Step 1.** For the same metal and the same ligands but different geometries:

$$\frac{\Delta_t}{\Delta_o} = \frac{4}{9} \Rightarrow \frac{\lambda_{\text{abs,tet}}}{\lambda_{\text{abs,oct}}} = \frac{\Delta_o}{\Delta_t} = \frac{9}{4} = 2.25.$$

So the tetrahedral complex absorbs roughly $2.25\times$ longer wavelength than the octahedral counterpart.

**Step 2.** Apply to the cobalt-chloride example (Q18):

- Octahedral $[\text{Co(H}_2\text{O)}_6]^{2+}$: absorbs near 510 nm (green) → appears pink.
- Tetrahedral $[\text{CoCl}_4]^{2-}$: absorbs near 670 nm (red) → appears blue.

Same metal ($\text{Co}^{2+}$), *different* geometry, completely different colour.

**Step 3.** General statement: identical metal + identical ligands + different geometry = different $\Delta \Rightarrow$ different $\lambda_{\text{abs}} \Rightarrow$ different observed colour.

> **Final Answer:** Because $\Delta_t = (4/9)\Delta_o$ — tetrahedral splitting is smaller — so the absorbed wavelength (and the complementary observed colour) differ between the two geometries even for the same metal and ligands.

### ♥ Cobalt as a humidity indicator

The oct↔tet equilibrium $[\mathrm{Co(H_2O)_6}]^{2+} \leftrightarrow [\mathrm{CoCl_4}]^{2-}$ (pink ↔ blue) is exploited in cobalt-chloride moisture indicator papers and self-indicating silica gel — when humidity rises, the pink hexaaqua form reasserts itself.

**EXPERT'S SOLUTION** *: Aanya Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

**Strategic angle — geometry as an independent variable.** Even when the metal and the ligands stay the same, the *geometry* alone changes the splitting magnitude. That in turn changes the absorbed wavelength and therefore the observed colour. Two facts drive the entire argument: the $\Delta_t/\Delta_o = 4/9$ ratio and the $\lambda_{\text{abs}} = hc/\Delta$ relation.

**Step 1.** *Quantify the geometry effect.* The tetrahedral splitting is smaller than the octahedral splitting for two independent reasons: only $4$ ligands instead of $6$, and none of them sits along a $d$-orbital axis. Group-theoretical calculation gives $\Delta_t = (4/9)\Delta_o \approx 0.45\Delta_o$.

**Step 2.** *Map to wavelength.* Smaller $\Delta$ means longer $\lambda_{\text{abs}}$: $\lambda_{\text{abs,tet}}/\lambda_{\text{abs,oct}} = \Delta_o/\Delta_t = 9/4 = 2.25$. So the tetrahedral complex absorbs at roughly $2.25\times$ longer wavelength, often moving the absorption from green/yellow into the red.

**Step 3.** *Map to observed colour.* Octahedral $[\mathrm{Co(H_2O)_6}]^{2+}$ absorbs near $510$ nm (green) and appears pink. Tetrahedral $[\mathrm{CoCl_4}]^{2-}$ absorbs near $670$ nm (red) and appears deep blue. Same $\mathrm{Co}^{2+}$ centre, dramatically different observed colour purely because the coordination geometry changed.

**Why this matters.** The colour-shifting test for the oct ↔ tet equilibrium of cobalt is a one-second visual diagnostic, used industrially in cobalt-impregnated humidity-indicator papers, anhydrous-cobalt drying agents and the classic blue-to-pink moisture test taught in every school lab.

> **Final Answer:** $\Delta_t \approx (4/9)\Delta_o$; different geometry $\Rightarrow$ different absorbed wavelength $\Rightarrow$ different colour.

### Key Takeaways

- **Werner's idea** separates primary (ionisable, outside-sphere) from secondary (coordination-number, inside-sphere) valencies; $\mathrm{AgCl}$ titration counts the outer chlorides, and molar conductance counts the total ions.

- IUPAC names list ligands *alphabetically* (ignoring di/tri-), use 2005 endings (*ammine, chlorido, nitrito-*$N$) and end in *-ate* only when the complex is anionic.
- Six isomerism types: *geometrical* ($\mathrm{MA_4B_2}$ etc.), *optical* (cis-$\mathrm{M(AA)_2X_2}$ and $\mathrm{M(AA)_3}$), *linkage* (ambidentate ligands), *ionisation* (anion swap inner/outer), *solvate* (water swap inner/outer), *coordination* (ligand swap between cation and anion complexes).
- Crystal Field Theory: octahedral splits $d$ into $t_{2g}$ $(-0.4\Delta_o)$ below $e_g$ $(+0.6\Delta_o)$; tetrahedral flips this with $\Delta_t = (4/9)\Delta_o$. Weak field + Hund ⇒ high spin; strong field ⇒ low spin.
- Spectrochemical series (essentials): $\mathrm{I^-} < \mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{F^-} < \mathrm{H_2O} < \mathrm{NH_3} < \mathrm{en} < \mathrm{CN^-} < \mathrm{CO}$.
- Spin-only magnetic moment $\mu = \sqrt{n(n+2)}$ BM: $n = 1, 2, 3, 4, 5 \Rightarrow \mu = 1.73, 2.83, 3.87, 4.90, 5.92$ BM.
- Observed colour is the complementary colour of the absorbed light; absorbed $\lambda = hc/\Delta_o$, so stronger field ⇒ larger $\Delta_o$ ⇒ shorter $\lambda_{\text{abs}}$ ⇒ shift of observed colour.
- Bioinorganic icons: **chlorophyll** (Mg-porphyrin), **haemoglobin** (Fe-porphyrin), **vitamin B$_{12}$** (Co-corrin), **Wilkinson's catalyst** $[\mathrm{Rh(PPh_3)_3Cl}]$.

End of NCERT Exemplar Problems, Class 12 Chemistry, Chapter 5 (Coordination Compounds).