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Step-by-step solutions, alternate methods & exam tips for Class 12 Chemistry

Chapter 5: Coordination Compounds

About this Chapter

This chapter studies **coordination compounds**: molecules in which a central metal atom or ion is surrounded by **ligands** bonded through coordinate (dative) bonds. We learn Werner's theory, IUPAC nomenclature, isomerism (geometrical, optical, linkage, ionisation, coordination, solvate), the three bonding theories (**Valence Bond Theory**, **Crystal Field Theory** and a glimpse of MOT), the spectrochemical series, magnetic behaviour and colour. We close with metal carbonyls and the role of these compounds in biology, medicine, analysis and metallurgy.

Topics covered: Werner's theory • Ligands & denticity • IUPAC nomenclature • Isomerism • VBT • CFT & Δ_o • Spectrochemical series • Colour & magnetism • Metal carbonyls • Stability & applications

Quick Formula Sheet

Oxidation state balance: $x + \sum(\text{ligand charges}) = \text{overall charge}$

EAN (Sidgwick): $\text{EAN} = Z - \text{ox. state} + 2(\text{C.N.})$

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

Magnetic moment (spin only): $\mu = \sqrt{n(n+2)}$ BM

Crystal-field splitting: $\Delta_t \approx \frac{4}{9}\,\Delta_o$

Spectrochemical (rising Δ_o): $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- < \text{CO}$

Pairing rule: if $\Delta_o > P$, low-spin; if $\Delta_o < P$, high-spin.

Chapter 5 Exercises

Q 5.1 **Explain the bonding in coordination compounds in terms of Werner's postulates.**

SOLUTION

Concept used. **Werner's theory** (1893) was the first successful description of bonding in coordination compounds. It introduces two distinct kinds of **valencies** that a metal can exercise: **primary** (ionisable, satisfied by negative ions, non-directional) and **secondary** (non-ionisable, satisfied by neutral or negative ligands, fixed in number and directed in space). The secondary valency is what we now call the **coordination number**; the primary valency is what we now call the oxidation state.

> ☞ **Coordination sphere vs counter ion**
>
> The metal and its directly bonded ligands form the *coordination sphere*, written inside square brackets. Anything outside the brackets is a counter ion that dissociates in water.

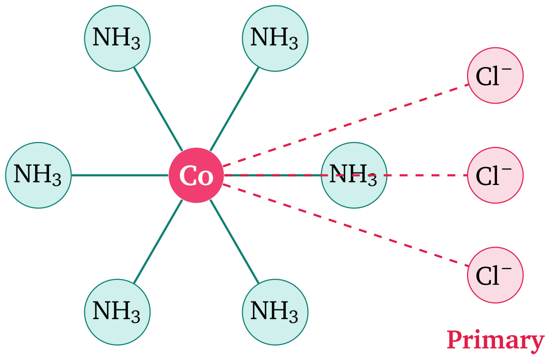
Step 1. **Postulate 1: Two valencies.** A metal exhibits two kinds of linkages: primary (ionisable) and secondary (non-ionisable). In $CoCl_3 \cdot 6\,NH_3$, three Cl^- ions satisfy the primary valency (oxidation state $+3$) and six NH_3 molecules satisfy the secondary valency (coordination number 6).

Step 2. **Postulate 2: Fixed secondary valency.** The number of secondary valencies (coordination number) is fixed for a given metal in a given oxidation state. Typical values are 4 and 6. For Co^{3+} it is 6; for Pt^{2+} it is 4.

Step 3. **Postulate 3: Directional secondary valencies.** Secondary valencies point in fixed directions, giving a definite **coordination polyhedron**: octahedral for C.N. 6, tetrahedral or square planar for C.N. 4. The primary valencies, in contrast, are non-directional.

Step 4. **Postulate 4: Satisfying secondary valencies.** Secondary valencies are satisfied by neutral molecules (NH_3, H_2O) or anions (Cl^-, CN^-). When an anion such as Cl^- is also bonded inside the coordination sphere, it satisfies a secondary valency in addition to (or instead of) a primary one. This explains why $CoCl_3 \cdot 5\,NH_3$ gives only two Cl^- ions on ionisation: one chloride is locked inside the sphere.

$[Co(NH_3)_6]Cl_3$



Secondary (directional, inside sphere)

Final Answer: Werner: primary (ionisable, non-directional) + secondary (non-ionisable, directional, fixed in number) valencies. Secondary valency is today's coordination number; primary valency is today's oxidation state.

♥ Why Werner's idea was revolutionary

Before 1893 no one could explain why $CoCl_3 \cdot 6\,NH_3$ precipitated three Cl^- ions with $AgNO_3$, but $CoCl_3 \cdot 5\,NH_3$ gave only two. Werner proposed a second sphere of bonding for chemists who had only thought in terms of one valency. Almost everything in modern inorganic chemistry sits on top of that single idea.

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

Strategic angle. Frame Werner's theory as the answer to one experimental fact: the conductivity / silver-nitrate test for the four cobalt-ammine chlorides. Once we explain the $1:3$, $1:2$, $1:1$ and 0 ion ratios, the whole theory follows. The four postulates are not arbitrary axioms; they are the simplest set of rules that reproduces every laboratory observation.

- $CoCl_3 \cdot 6\,NH_3$ gives 3 Cl^-, 1 cation: 4 ions total (luteo, yellow).
- $CoCl_3 \cdot 5\,NH_3$ gives 2 Cl^-, 1 cation: 3 ions (purpureo, purple).
- $CoCl_3 \cdot 4\,NH_3$ gives 1 Cl^-, 1 cation: 2 ions (praseo green / violeo violet).
- $CoCl_3 \cdot 3\,NH_3$ gives a non-electrolyte: 0 ions.

Step 1. Werner asked: how can three Cl^- disappear in stages while the cobalt stays Co^{3+}? Answer: chlorides can enter a second, non-ionising sphere around the metal. The question itself is a clue: conductivity in water drops in unit steps as ammonia is replaced by chloride one-for-one.

Step 2. He proposed two valencies. The primary (ionising) valency is 3 in every case (Co^{3+}). The secondary (directional) valency is always 6 for Co^{3+}. The two numbers are independent and can be satisfied by different species, the single deepest insight in the theory.

Step 3. In $[Co(NH_3)_6]Cl_3$ all six secondary valencies are taken by ammonia; the three chlorides sit outside as primary valencies and ionise. Molar conductivity $\Lambda_m \approx 430\ \mathrm{S\,cm^2\,mol^{-1}}$ (a 1:3 electrolyte).

Step 4. In $[Co(NH_3)_5Cl]Cl_2$ one chloride sneaks inside the sphere, satisfying one secondary valency *and* one primary valency; only two chlorides remain outside. $\Lambda_m \approx 260$, a 1:2 electrolyte.

Step 5. Continuing this logic gives $[Co(NH_3)_4Cl_2]Cl$ ($\Lambda_m \approx 100$, 1:1) and the non-electrolyte $[Co(NH_3)_3Cl_3]$ ($\Lambda_m \approx 0$). The model matches experiment exactly.

Step 6. **Alternative approach (geometric).** The fixed secondary valency of 6 on Co^{3+} predicts an octahedron. From an octahedron with two Cl^- ligands we get exactly two arrangements (cis, trans); both $[Co(NH_3)_4Cl_2]Cl$ isomers (violet and green) were isolated, again confirming Werner's geometric prediction.

Why this matters. The same primary/secondary split is the seed of the modern **coordination number**, **oxidation state** and **coordination sphere** vocabulary used in every remaining question of this chapter. Werner won the 1913 Nobel Prize for what is essentially a counting argument applied to a handful of cobalt-ammine salts.
Concept linkage. Modern bonding theories (VBT, CFT, MOT, Q 5.15–5.18) all start from Werner's coordination sphere. Without the sphere idea, the very ligand-field calculations we use to predict Δ_o, magnetic moment and colour have nothing to "split". The chelate effect (Q 5.26) is an entropy argument that runs entirely inside Werner's secondary sphere.

> **Final Answer:** Werner's postulates: two valency types (primary = ionisable, secondary = directional and fixed); the secondary defines the geometry and is today's coordination number.

☞ **Alternative: count ions from $AgNO_3$**

A faster route to Werner's classification is to add excess $AgNO_3$ and count the moles of $AgCl$ precipitated per mole of complex. $3, 2, 1, 0$ moles of $AgCl$ correspond directly to the four salts above. The conductivity method and the silver-nitrate method give the same answer for the same reason: only chlorides outside the sphere are free.

Q 5.2 $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

SOLUTION

Concept used. A **double salt** dissociates completely into all its constituent ions when dissolved in water, so each component ion gives its usual analytical tests. A **coordination compound (complex)** retains the metal-ligand bonds in solution; the metal stays locked inside the complex ion and does *not* give the usual free-ion tests. The difference is therefore one of ion stability in solution.

Step 1. **Mohr's salt is a double salt.** Equimolar $FeSO_4$ and $(NH_4)_2SO_4$ crystallise together as $FeSO_4 \cdot (NH_4)_2SO_4 \cdot {}_6H_2O$ (Mohr's salt). In water it dissociates fully:

$$FeSO_4 \cdot (NH_4)_2SO_4 \cdot {}_6H_2O \longrightarrow Fe^{2+} + 2\,NH_4{}^{+} + 2\,SO_4{}^{2-} + 6\,H_2O.$$

Free Fe^{2+} is present, so the test with $K_3[Fe(CN)_6]$ (a blue precipitate of Turnbull's blue) is positive.

Step 2. Tetraamminecopper(II) is a coordination compound. $CuSO_4$ with four moles of NH_3 produces the deep blue complex

$$CuSO_4 + 4\,NH_3 \longrightarrow [Cu(NH_3)_4]SO_4.$$

In water this dissociates to give the complex cation, not free Cu^{2+}:

$$[Cu(NH_3)_4]SO_4 \longrightarrow [Cu(NH_3)_4]^{2+} + SO_4{}^{2-}.$$

Step 3. Why no Cu^{2+} test. The complex $[Cu(NH_3)_4]^{2+}$ has a very high stability constant ($\beta_4 \approx 10^{12}$), so the concentration of free Cu^{2+} in equilibrium is far below the detection threshold of ordinary tests (no blue precipitate with $NaOH$, no black precipitate with H_2S in ammoniacal medium).

Step 4. General rule. Double salts retain their ions in solution; coordination compounds do not. The presence of a complex ion is detected through its own properties (colour, magnetic moment) rather than through the free-metal-ion tests.

Double salt: $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$

Full ionisation in water
$\longrightarrow Fe^{2+} + 2\,NH_4{}^{+} + 2\,SO_4{}^{2-}$
Free Fe^{2+}: **test positive**

Complex: $[Cu(NH_3)_4]SO_4$

Only partial dissociation
$\longrightarrow [Cu(NH_3)_4]^{2+} + SO_4{}^{2-}$
Free Cu^{2+} negligible: **test negative**

Final Answer: Mohr's salt is a *double salt* (full dissociation, free Fe^{2+} available). $[Cu(NH_3)_4]SO_4$ is a *coordination compound* (the metal is locked inside the stable complex ion), so free Cu^{2+} is not present and its tests fail.

★ Stability constant

The bigger the stability constant β_n, the smaller the equilibrium concentration of free metal ion. For $[Cu(NH_3)_4]^{2+}$, $\log \beta_4 \approx 12$, so almost no free Cu^{2+} survives in solution.

EXPERT'S SOLUTION : *Sneha Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. Two salts; one falls apart, the other does not. The first is a mixture of crystals (a double salt); the second hides the copper inside a complex ion with four NH_3 ligands. The acid test is whether the metal-ligand bond survives dissolution.

Step 1. For Mohr's salt, write the dissolution as four free ion types: Fe^{2+}, ${NH_4}^+$, ${SO_4}^{2-}$ and water. Free Fe^{2+} reacts with potassium ferricyanide $K_3[Fe(CN)_6]$ to give the deep blue Turnbull's precipitate. Equivalently, with KSCN a pale colour is seen (Fe^{2+} gives no red, Fe^{3+} does).

Step 2. For the copper-ammonia mixture, ammonia is a moderately strong field ligand. Four ligands push into the four coordination sites of Cu^{2+} to give a square-planar complex $[Cu(NH_3)_4]^{2+}$ with $\log \beta_4 \approx 12$. Visually: the dirty-blue precipitate of $Cu(OH)_2$ that forms with a few drops of ammonia redissolves as more ammonia is added, giving the famous deep blue **Schweizer's reagent**.

Step 3. Because β_4 is so large, $[Cu^{2+}]_{\text{free}} \approx [Cu(NH_3){_4}^{2+}]/\beta_4 \cdot [NH_3]^{-4}$ is negligible at any practical NH_3 concentration. None of the usual tests for Cu^{2+} work.

Step 4. Sanity check: passing H_2S through the deep blue solution gives no black CuS precipitate, confirming absence of free Cu^{2+}. Compare with $K_{sp}(CuS) \approx 10^{-36}$: an enormous solubility product, yet not crossed because $[Cu^{2+}]_{\text{free}}$ is well below 10^{-14} M inside the complex.

Step 5. **Numerical cross-check.** Take 0.1 M $[Cu(NH_3)_4]^{2+}$ with $[NH_3]_{\text{free}} \approx 0.1$ M. Then

$$[Cu^{2+}]_{\text{free}} = \frac{0.1}{10^{12} \cdot (0.1)^4} \approx 10^{-9}\ \text{M}.$$

Below the precipitation threshold for CuS ($\sim 10^{-18}$ M in saturated H_2S at neutral pH). Hence no CuS.

Why this matters. The contrast between double salts and complexes is the cleanest entry point into coordination chemistry. The whole rest of the chapter (Werner spheres, isomerism, CFT, the chelate effect) is the elaboration of one idea: a metal ion that is not free behaves differently from one that is.

Concept linkage. The stability-constant comparison ($\beta_4 \approx 10^{12}$) is the prototype of the **chelate effect** discussion of Q 5.26 — except there a polydentate ligand adds further entropic stabilisation. The same logic explains Q 5.14 ($[Cu(CN)_4]^{3-}$ even more stable) and Q 5.30 (oxalato beats monodentate).

Final Answer: Mohr's salt: double salt, free ions, Fe^{2+} test positive. $[Cu(NH_3)_4]SO_4$: complex, copper hidden inside the cation, Cu^{2+} test negative.

☞ **K_{sp} vs β in plain words**

A precipitate forms when the *ionic product* of free ions exceeds K_{sp}. If the metal is sequestered by a strongly binding ligand (large β), free-ion concentration is suppressed and the ionic product never reaches K_{sp}. This is the entire basis of **masking** in qualitative analysis.

☞ **One-line board answer**

"Mohr's salt is a double salt; it dissociates fully to give free Fe^{2+}, which gives the test. $[Cu(NH_3)_4]SO_4$ is a coordination compound; the Cu^{2+} stays inside the very stable complex ion and no free-Cu^{2+} test is positive." That single sentence is worth full marks.

Q 5.3 **Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.**

SOLUTION

Concept used. Modern IUPAC vocabulary for coordination chemistry. Each term names a structural feature of a complex; we define it, then give two examples.

Step 1. **Coordination entity.** A **coordination entity** is the central metal atom or ion together with the ligands directly bonded to it, written inside square brackets. It can be a cation, anion or neutral molecule.
Examples: $[Co(NH_3)_6]^{3+}$ (cationic); $[Fe(CN)_6]^{4-}$ (anionic); $[Ni(CO)_4]$ (neutral).

Step 2. **Ligand.** A **ligand** is an ion or neutral molecule that donates a lone pair (or sometimes a π cloud) to the central metal, forming a coordinate bond. The donor atom carries the lone pair.
Examples: ammonia (NH_3, neutral, N-donor); chloride (Cl^-, anionic, Cl-donor); ethane-1,2-diamine (en, neutral, didentate); oxalate ($C_2O_4{}^{2-}$, anionic, didentate).

Step 3. **Coordination number (C.N.).** The **coordination number** of the central atom is the number of *ligating atoms* bonded to it. For monodentate ligands C.N. equals the count of ligands; for a didentate ligand each instance contributes 2.
Examples: in $[PtCl_6]^{2-}$, C.N. $= 6$; in $[Ni(en)_3]^{2+}$, C.N. $= 3 \times 2 = 6$.

Step 4. **Coordination polyhedron.** The geometrical figure whose vertices are the ligating atoms is the **coordination polyhedron**. C.N. 6 usually gives an octahedron; C.N. 4 gives a tetrahedron or a square plane; C.N. 2 gives a linear shape.
Examples: $[Co(NH_3)_6]^{3+}$ is octahedral; $[Ni(CO)_4]$ is tetrahedral; $[PtCl_4]^{2-}$ is square planar; $[Ag(NH_3)_2]^+$ is linear.

Step 5. **Homoleptic complex.** A complex in which the metal is bonded to only *one type* of donor (one kind of ligand).

Examples: $[\mathrm{Co(NH_3)_6}]^{3+}$ (only NH$_3$); $[\mathrm{Fe(CN)_6}]^{4-}$ (only CN$^-$); $[\mathrm{Ni(CO)_4}]$ (only CO).

Step 6. **Heteroleptic complex.** A complex in which the metal is bonded to *more than one* type of donor.
Examples: $[\mathrm{Co(NH_3)_4Cl_2}]^{+}$ (NH$_3$ and Cl$^-$); $[\mathrm{Pt(NH_3)_2Cl_2}]$ (cisplatin, NH$_3$ and Cl$^-$).

Homoleptic	Heteroleptic
$[\mathrm{Co(NH_3)_6}]^{3+}$ one ligand type	$[\mathrm{Co(NH_3)_4Cl_2}]^{+}$ two types
$[\mathrm{Ni(CO)_4}]$ one ligand type	$[\mathrm{Pt(NH_3)_2Cl_2}]$ two types

Final Answer: Six terms, each illustrated by two examples (see Steps 1–6).

EXPERT'S SOLUTION *: Pranav Mehta, M.Sc Physical Chemistry, IIT Madras*

Structural observation. Each term either names a piece of the complex (entity, ligand) or describes its geometry (C.N., polyhedron) or the diversity of its donor set (homo- vs heteroleptic). The six terms are not isolated trivia — they are the orthogonal axes along which any complex can be classified.

Step 1. **Entity vs ligand.** The entity is the whole thing inside the brackets ($[\mathrm{M(L)}_n]^q$). The ligands are the satellites donating lone pairs to the metal. Together they carry the overall charge of the entity. Counter-ions sit outside the brackets and dissociate in solution (Werner's primary valencies, Q 5.1).

Step 2. **Coordination number.** Count the donor atoms (not the ligands) attached to the metal: a didentate ligand counts twice. So $[\mathrm{Co(en)_3}]^{3+}$ has C.N. 6 even though there are only three **en** ligands. Another fooler: $[\mathrm{Pt(en)Cl_2}]$ has C.N. 4 (en counts 2 plus two chlorides), although there are only three "ligands".

Step 3. **Polyhedron.** The shape is determined by C.N. and by the metal's d-electron count. C.N. 6 is almost always octahedral; C.N. 4 splits into tetrahedral ($\mathrm{Ni(CO)_4}$, $[\mathrm{NiCl_4}]^{2-}$) and square planar ($[\mathrm{PtCl_4}]^{2-}$, $[\mathrm{Ni(CN)_4}]^{2-}$). C.N. 5 is rare but real: $\mathrm{Fe(CO)_5}$ trigonal bipyramidal. C.N. 2: linear, $[\mathrm{Ag(NH_3)_2}]^{+}$. Roughly, d^0, d^{10} and d^5 high-spin metals prefer tetrahedral; d^8 strong-field prefers square planar.

Step 4. **Homo- vs heteroleptic.** Identify the donor atom (or the ligand name, since each ligand has one donor type unless ambidentate). One name in the formula

⇒ homoleptic; more than one ⇒ heteroleptic. The distinction matters because heteroleptic complexes routinely show geometrical isomerism (cis/trans, fac/mer), homoleptic ones with symmetric ligands do not.

Step 5. **Alternative classification.** Some texts split further: **cationic** ($[Co(NH_3)_6]^{3+}$), **anionic** ($[Fe(CN)_6]^{4-}$), **neutral** ($[Ni(CO)_4]$) entities. The same complex can be cationic with one counter-ion set and anionic with another (in salts: cation first, anion last).

Why this matters. These six words are used in every question that follows; absorbing them now makes the rest of the chapter a single coherent picture. Q 5.5 (oxidation state) and Q 5.6/5.7 (IUPAC names) lean directly on entity and ligand vocabulary. Q 5.9–5.12 (isomerism) lean on the homo/heteroleptic distinction. Q 5.15–5.16 (VBT, CFT) lean on coordination number and polyhedron.

> **Final Answer:** Definitions and examples as in Steps 1–5.

☞ Two-second test for board MCQs

Coordination number: count donor atoms, not ligands. **Homo vs hetero**: count distinct ligand-name types in the formula. **Polyhedron**: see C.N. → shape (6→oct, 4→tet/sq.pl, 2→lin). These three mental rules cover $\sim 90\%$ of objective-type questions on this topic.

♥ Why “coordination entity” replaced “complex”

IUPAC chose the broader phrase *coordination entity* because the bonded unit is sometimes neutral ($Ni(CO)_4$) and sometimes ionic. “Complex” is fine in conversation but the IUPAC entity is the unambiguous, charge-agnostic name. In all formal nomenclature (Q 5.6, 5.7) the entity sits inside square brackets.

Q 5.4 What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

SOLUTION

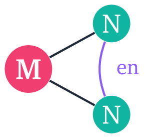
Concept used. The **denticity** of a ligand is the number of donor atoms it uses to bond to a single metal centre. An **ambidentate** ligand has *two different* donor atoms available, but only one bonds at a time (depending on conditions).

Step 1. **Unidentate (monodentate) ligand: denticity** 1**.** Only one donor atom; one metal-ligand bond per ligand molecule.
Examples: NH_3 (donates through N); H_2O (donates through O); Cl^- (donates through Cl).

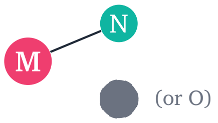
Step 2. **Didentate (bidentate) ligand: denticity** 2. Two donor atoms in the same molecule that bond to the same metal, forming a five- or six-membered chelate ring.
Examples: ethane-1,2-diamine $\mathrm{en} = H_2N{-}CH_2{-}CH_2{-}NH_2$ (two N donors); oxalate ion $C_2O_4{}^{2-}$ (two O donors).

Step 3. **Ambidentate ligand.** A unidentate ligand that has *two different* donor atoms available, but uses only one at a time. Which atom binds depends on the metal and reaction conditions.
Examples: nitrite $NO_2{}^-$ binds either through N (**nitro**, $-NO_2$) or O (**nitrito**, $-ONO$); thiocyanate SCN^- binds through S (**thiocyanato**) or N (**isothiocyanato**).

Unidentate (1 bond)



Didentate (chelate ring)



Ambidentate ($NO_2{}^-$)

> **Final Answer:** Unidentate: 1 donor (NH_3, Cl^-). Didentate: 2 donors (*en*, oxalate). Ambidentate: 1 donor at a time, choice of 2 donor atoms ($NO_2{}^-$, SCN^-).

★ Chelate effect preview

A didentate (or higher) ligand wraps around the metal, forming a ring. This makes the complex thermodynamically more stable than the analogous one with two monodentate ligands. Q 5.26 returns to this.

EXPERT'S SOLUTION : *Riya Banerjee, M.Tech Chemical Engineering, IIT Delhi*

Picture-first. Visualise each ligand as a hand: a unidentate ligand has one finger touching the metal, a didentate ligand grips with two fingers in the same molecule, and an ambidentate ligand has two different fingers but uses only one at a time. The denticity is the count of *fingers actually touching*.

Step 1. Count lone pairs that actually bond. Ammonia has only one lone pair on N; chloride has lone pairs but only one binds at a time: both are unidentate. Carbon monoxide has a lone pair on C; despite having multiple lone pairs in total, only one binds, so CO is unidentate.

Step 2. In **en**, both nitrogens donate to the same metal, and the $-CH_2{-}CH_2{-}$ backbone is the right length to produce a strain-free 5-membered chelate ring (M-N-C-C-N). In oxalate, the two terminal oxygens both donate, again producing a 5-membered ring (M-O-C-C-O). Each ligand brings two donor atoms: didentate.

Step 3. In $NO_2{}^-$, N has one lone pair, O has two. Either can donate, but never both to the same metal. This is the defining trait of ambidentate ligands. Hard metals (oxophilic, e.g. Co^{3+}, Cr^{3+}) bind O preferentially $\to$ nitrito-O; soft metals (e.g. Co^{3+} with strong-field set) often switch to nitro-N (Q 5.6).

Step 4. Linkage isomers (Q 5.7 (x) and Q 5.6 (v)) come directly out of this dual binding mode. Two different colours, two different absorption maxima, same formula.

Step 5. **Alternative classification (denticity scale).** Hexadentate ligands like **EDTA** bind through six donors (two N, four O), wrapping the metal in a cage. Such ligands give the most stable chelates and saturate a 6-C.N. site with a single molecule (preview of Q 5.26).

Step 6. **Numerical bookkeeping.** If denticity of a ligand is k and it appears m times in a complex of C.N. 6, then $k\,m = 6$. Examples: $k = 1, m = 6$ for $[Co(NH_3)_6]^{3+}$; $k = 2, m = 3$ for $[Co(en)_3]^{3+}$; $k = 6, m = 1$ for $[Co(EDTA)]^-$.

Why this matters. Denticity directly fixes the C.N. of the metal: pick three **en** ligands and you have C.N. 6 without needing six separate molecules. It also fixes the entropy of complex formation (more donor atoms in one ligand $\Rightarrow$ fewer displaced waters $\Rightarrow$ larger chelate effect, Q 5.26).

Concept linkage. The ambidentate concept connects directly to Q 5.6 (formulas for nitrito-O vs nitrito-N) and Q 5.8 (linkage isomerism). The didentate concept underlies almost every chiral coordination complex (Q 5.10, 5.11).

> **Final Answer:** Unidentate, didentate, ambidentate distinguished by donor-atom count and binding mode; examples in Steps 1–3.

✗ Counting denticity wrong

A frequent slip: calling $NO_2{}^-$ “didentate” because it has two donor-atom *options*. It is not — only one atom binds at a time. The right label is **ambidentate**. Similarly, SCN^- binds either through S (thiocyanato-S) or N (thiocyanato-N, “isothiocyanato”), never through both at once to the same metal.

Q 5.5 **Specify the oxidation numbers of the metals in the following coordination entities:**

(i) $[Co(H_2O)(CN)(en)_2]^{2+}$ **(ii)** $[CoBr_2(en)_2]^+$ **(iii)** $[PtCl_4]^{2-}$
(iv) $K_3[Fe(CN)_6]$ **(v)** $[Cr(NH_3)_3Cl_3]$

SOLUTION

Concept used. The oxidation state of the metal in a coordination entity is found from the charge-balance equation:

$$x + \sum_i (\text{charge on ligand}_i) = (\text{overall charge of entity}).$$

Ligand charges: H_2O, NH_3, en, CO are neutral (0). CN^-, Cl^-, Br^-, F^-, OH^- carry -1. Oxalate $C_2O_4{}^{2-}$ carries -2. For a salt $K_n[M(L)_m]$, K^+ are spectator ions; subtract their charges to get the charge on the complex anion.

Step 1. **(i)** $[Co(H_2O)(CN)(en)_2]^{2+}$. Ligands: H_2O (0), CN^- (-1), 2 en (0 each). Charge balance:

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

Solving: $x = +3$.

Step 2. **(ii)** $[CoBr_2(en)_2]^+$. Ligands: 2 Br^- (-1 each), 2 en (0).

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

Solving: $x - 2 = +1 \Rightarrow x = +3$.

Step 3. **(iii)** $[PtCl_4]^{2-}$. Ligands: 4 Cl^-.

$$x + 4(-1) = -2.$$

Solving: $x - 4 = -2 \Rightarrow x = +2$.

Step 4. **(iv)** $K_3[Fe(CN)_6]$. Three K^+ contribute $+3$ total; the complex anion is therefore $3-$. Inside: ligands are 6 CN^-.

$$x + 6(-1) = -3.$$

Solving: $x - 6 = -3 \Rightarrow x = +3$.

Step 5. **(v)** $[Cr(NH_3)_3Cl_3]$. Neutral entity. Ligands: 3 NH_3 (0), 3 Cl^- (-1).

$$x + 3(0) + 3(-1) = 0.$$

Solving: $x - 3 = 0 \Rightarrow x = +3$.

> **Final Answer:** (i) Co(+3); (ii) Co(+3); (iii) Pt(+2); (iv) Fe(+3); (v) Cr(+3).

☞ **Quick mental rule**

Compute sum of negative ligand charges + overall charge; flip the sign and you have the oxidation state. For $[PtCl_4]^{2-}$: $(-4) + (-2) = -6$; flip sign $\rightarrow +6$; but the *ligand* contribution is -4, so x = overall − (ligand sum) $= -2-(-4) = +2$.

EXPERT'S SOLUTION *: Aanya Verma, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Write every charge balance as one line and solve. Don't memorise individual answers: the method is a single linear equation. The structure of every step is the same: "metal + sum of ligand charges = overall entity charge".

Step 1. Bring all known charges to one side, the unknown x to the other. The unknown is always the metal oxidation state. Ligand-charge cheat-sheet to keep handy: neutral NH_3, H_2O, en, py, CO; -1 for halides, CN^-, OH^-, SCN^-, ${NO_2}^-$; -2 for oxalate ${C_2O_4}^{2-}$, O^{2-}, peroxide.

Step 2. Apply to each case in turn:
(i) ammine and en are neutral, one CN^- (-1); aqua neutral. Sum of ligand charges $= -1$. So $x-1=+2 \Rightarrow x=+3$. (d^6.)
(ii) en neutral, two Br^- (-2). $x-2=+1 \Rightarrow x=+3$. (d^6.)
(iii) four Cl^- (-4). $x-4=-2 \Rightarrow x=+2$. (d^8.)
(iv) charge on complex anion $= -(+3) = -3$ (from three K^+); six CN^- (-6). $x-6=-3 \Rightarrow x=+3$. (d^5.)
(v) neutral entity; three Cl^- (-3): $x-3=0 \Rightarrow x=+3$. (d^3.)

Step 3. Confirm with periodic trends: Co^{3+}, Pt^{2+}, Fe^{3+}, Cr^{3+} are all common, stable oxidation states. Co^{2+} also exists, but the ligand-set of (i) and (ii) (CN^-, en, Br^-) stabilises $+3$ by ligand-field arguments.

Step 4. **Alternative approach (group number).** For first-row metals: d^n = (group number) $- x$. Co in group 9 with $x=+3$ gives d^6 — consistent. Pt is a $5d^8$ metal; Pt^{2+} is $5d^8$ (square planar, diamagnetic). Fe in group 8, Fe^{3+} is $3d^5$ (half-filled, very stable).

Step 5. **Numerical cross-check via μ (peek ahead to Q 5.19).** The d^n count predicts the spin-only $\mu = \sqrt{n(n+2)}$. If a published μ is available it immediately confirms whether your oxidation-state choice is right.

Why this matters. Every magnetic-moment, CFSE and colour calculation in this chapter starts with the metal oxidation state. Get this step wrong and everything downstream is wrong. The same formula handles JEE numerical questions ("find μ for $[Mn(CN)_6]^{3-}$" etc.) which always begin with oxidation-state determination.
Concept linkage. Q 5.6 / 5.7 (IUPAC names ↔ formulas) need exactly the same charge-balance arithmetic. Q 5.15 (VBT bonding) takes x and d^n as inputs.

Final Answer: (i) Co(III); (ii) Co(III); (iii) Pt(II); (iv) Fe(III); (v) Cr(III).

☞ Ligand-charge cheat sheet

Neutral (0): $NH_3, H_2O, \text{en}, \text{py}, CO, CH_3NH_2, NO$ (formally, in linear M-NO).
-1: halides (F^-, Cl^-, Br^-, I^-), CN^-, OH^-, $NO_2{}^-$, NCS^-, SCN^-, $NH_2{}^-$ (amido), H^- (hydrido).
-2: $C_2O_4{}^{2-}$ (oxalato), O^{2-} (oxo), $O_2{}^{2-}$ (peroxo), S^{2-}.
-3: N^{3-} (nitrido), P^{3-} (phosphido).
-4: $EDTA^{4-}$ (hexadentate).

✗ Sign error: outer ion charge vs complex charge

A classic slip is to read the charge from the entity inside the brackets when the salt has counter ions. For $K_3[Fe(CN)_6]$, the complex anion charge is -3 (*not* 0, and *not* $+3$). Always count outer ions first to fix the complex charge; only then balance inside. Sign on x flips every time outer counter-ions are anions: it is one of the most common board errors.

Q 5.6 **Using IUPAC norms write the formulas for the following:**

(i) Tetrahydroxidozincate(II)
(ii) Potassium tetrachloridopalladate(II)
(iii) Diamminedichloridoplatinum(II)
(iv) Potassium tetracyanidonickelate(II)
(v) Pentaamminenitrito-O-cobalt(III)
(vi) Hexaamminecobalt(III) sulphate
(vii) Potassium tri(oxalato)chromate(III)
(viii) Hexaammineplatinum(IV)
(ix) Tetrabromidocuprate(II)
(x) Pentaamminenitrito-N-cobalt(III).

SOLUTION

Concept used. **IUPAC name → formula** rules:

- The name of the cation comes first, the anion second (same order as in salt formulas).
- Inside the coordination sphere (square brackets), write the metal symbol first, then the ligands in alphabetical order of *ligand name* (ignoring the multiplying prefixes di/tri/tetra).
- Ligand-name endings: anionic ligands end in $-o$ (chlorido, bromido, hydroxido, oxalato, cyanido); neutral ligands keep their normal name (ammine for NH_3, aqua for H_2O).
- The oxidation state of the central metal (Roman numeral) is used to balance the overall charge of the complex.
- Linkage isomers of $NO_2{}^-$: **nitrito-N** ($-NO_2$, binding through N) and **nitrito-O** ($-ONO$, binding through O).

Step 1. **(i) Tetrahydroxidozincate(II).** Zn(II): $+2$; 4 OH^-: -4. Complex charge: $+2-4=-2$. Formula: $[Zn(OH)_4]^{2-}$.

Step 2. **(ii) Potassium tetrachloridopalladate(II).** Pd(II): $+2$; 4 Cl^-: -4. Complex charge: -2. Two K^+ balance it. Formula: $K_2[PdCl_4]$.

Step 3. **(iii) Diamminedichloridoplatinum(II).** Pt(II): $+2$; 2 NH_3: 0; 2 Cl^-: -2. Total: 0. Neutral. Formula: $[Pt(NH_3)_2Cl_2]$ (cisplatin).

Step 4. **(iv) Potassium tetracyanidonickelate(II).** Ni(II): $+2$; 4 CN^-: -4. Complex charge: -2. Two potassium ions. Formula: $K_2[Ni(CN)_4]$.

Step 5. **(v) Pentaamminenitrito-*O*-cobalt(III).** Co(III): $+3$; 5 NH_3: 0; ONO^-: -1. Complex charge: $+3-1=+2$. Formula: $[Co(ONO)(NH_3)_5]^{2+}$ (cation only, as no counter ion is specified).

Step 6. **(vi) Hexaamminecobalt(III) sulphate.** Co(III): $+3$; 6 NH_3: 0. Complex charge: $+3$. Two complex cations balance three $SO_4{}^{2-}$ (-6). Formula: $[Co(NH_3)_6]_2(SO_4)_3$.

Step 7. **(vii) Potassium tri(oxalato)chromate(III).** Cr(III): $+3$; 3 $C_2O_4{}^{2-}$: -6. Complex charge: $+3-6=-3$. Three K^+. Formula: $K_3[Cr(C_2O_4)_3]$.

Step 8. **(viii) Hexaammineplatinum(IV).** Pt(IV): $+4$; 6 NH_3: 0. Charge: $+4$. Formula: $[Pt(NH_3)_6]^{4+}$.

Step 9. **(ix) Tetrabromidocuprate(II).** Cu(II): $+2$; 4 Br^-: -4. Complex charge: -2. Formula: $[CuBr_4]^{2-}$.

Step 10. **(x) Pentaamminenitrito-*N*-cobalt(III).** Same charge balance as (v); difference is the donor atom. Formula: $[Co(NO_2)(NH_3)_5]^{2+}$.

> **Final Answer:** See Steps 1–10 for the ten formulas, e.g. (i) $[Zn(OH)_4]^{2-}$, (iii) $[Pt(NH_3)_2Cl_2]$, (vi) $[Co(NH_3)_6]_2(SO_4)_3$.

☞ Alphabetical order: ligand-name based

Order ligands by the first letter of the *name*, not the symbol. “Ammine” beats “chlorido” (a $<$ c), so $[Co(NH_3)_4Cl_2]$ is written with ammines listed first in the name; “nitrito” vs “ammine” gives ammine first too.

EXPERT’S SOLUTION *: Karan Reddy, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The trick is to compute the charge on the complex ion first; then everything else (counter ions, formula brackets) falls into place. Treat each name as a charge-balance exercise rather than a vocabulary test. Four checks per name: oxidation state, ligands and their charges, overall complex charge, counter ion ratio.

Step 1. For neutral complexes (e.g. (iii) cisplatin and the carbonyl-class), the sum of metal + ligand charges must equal 0. No counter ion required outside the brackets.

Step 2. For ionic complexes with K as cation, the number of potassium ions is fixed by the negative charge on the complex. Examples: (ii) $\mathrm{K_2[PdCl_4]}$ (-2 complex, 2 K's); (iv) $\mathrm{K_2[Ni(CN)_4]}$; (vii) $\mathrm{K_3[Cr(C_2O_4)_3]}$.

Step 3. For ionic complexes with $\mathrm{SO_4}^{2-}$ as anion, you may need a ratio: two cations per three sulphates in (vi), because the cation charge is $+3$ and the anion charge is -2; LCM gives $\mathrm{[Co(NH_3)_6]_2(SO_4)_3}$.

Step 4. Linkage isomers (v) vs (x): write ONO for O-donor nitrito and $\mathrm{NO_2}$ for N-donor nitrito. Same formula otherwise. The same Co, same five ammines, same overall $+2$ charge — only the donor atom (and the IR N-O stretching frequency) tells them apart.

Step 5. **Alternative bracket convention.** Some recent IUPAC recommendations always parenthesise the ambidentate donor atom inside the ligand name (*nitrito-κN*, *nitrito-κO*). The Class 12 NCERT uses *nitrito-N* and *nitrito-O*; both are acceptable in the board answer.

Step 6. **Special case for (i): zincate(II).** Zn(II) is the prototypical case where the metal sits inside an anion because the ligand-set is anionic ($\mathrm{OH^-}$). The naming suffix *-ate* on *zinc* signals that the entity is anionic; without the suffix the same formula could mislead.

Why this matters. The reverse mapping (formula → name) in Q 5.7 uses exactly the same rules read backwards. The charge-balance arithmetic is identical to what powers d^n determination (Q 5.5) and downstream all of VBT, CFT, magnetic moment.

Concept linkage. Linkage isomers (v) vs (x) are the prototypical pair used in Q 5.8 to illustrate linkage isomerism quantitatively. Cisplatin in (iii) is the medicinally relevant example revisited in Q 5.27.

> **Final Answer:** Formulas: (i) $\mathrm{[Zn(OH)_4]^{2-}}$; (ii) $\mathrm{K_2[PdCl_4]}$; (iii) $\mathrm{[Pt(NH_3)_2Cl_2]}$; (iv) $\mathrm{K_2[Ni(CN)_4]}$; (v) $\mathrm{[Co(ONO)(NH_3)_5]^{2+}}$; (vi) $\mathrm{[Co(NH_3)_6]_2(SO_4)_3}$; (vii) $\mathrm{K_3[Cr(C_2O_4)_3]}$; (viii) $\mathrm{[Pt(NH_3)_6]^{4+}}$; (ix) $\mathrm{[CuBr_4]^{2-}}$; (x) $\mathrm{[Co(NO_2)(NH_3)_5]^{2+}}$.

✗ Wrong sign on the oxidation state

A common slip in (vi) is to forget that the complex cation is $+3$ but its formula must be written with subscript 2 outside the bracket (*two* cations for three sulphates). Writing $\mathrm{[Co(NH_3)_6]SO_4}$ gives a complex with $+2$ charge — incompatible with Co(III) and six neutral ammines. Always cross- check that the inner-sphere charge times the cation-count equals the outer-sphere anion-count times its charge.

Q 5.7 **Using IUPAC norms write the systematic names of the following:**
(i) $[Co(NH_3)_6]Cl_3$ **(ii)** $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
(iii) $[Ti(H_2O)_6]^{3+}$ **(iv)** $[Co(NH_3)_4Cl(NO_2)]Cl$
(v) $[Mn(H_2O)_6]^{2+}$ **(vi)** $[NiCl_4]^{2-}$ **(vii)** $[Ni(NH_3)_6]Cl_2$
(viii) $[Co(en)_3]^{3+}$ **(ix)** $[Ni(CO)_4]$.

SOLUTION

Concept used. **Formula → IUPAC name** rules:

- Cation first, then anion (same as for any salt).
- Inside the complex: name ligands first (alphabetical by ligand name), then the metal.
- Anionic ligands end in $-o$ (chlorido, cyanido, etc.); neutral keep their name (ammine, aqua, carbonyl).
- Prefixes: di/tri/tetra/penta/hexa for simple ligands; bis/tris/tetrakis when the ligand name itself contains a prefix (e.g. ethane-1,2-diamine, oxalato).
- Metal suffix: $-ate$ if the complex is anionic; otherwise no change.
- Oxidation state of the metal in Roman numerals in parentheses.

Step 1. **(i)** $[Co(NH_3)_6]Cl_3$. Co: $x + 0 = +3$ (three outer Cl^-), so Co(III). Six ammines.
Name: *hexaamminecobalt(III) chloride*.

Step 2. **(ii)** $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$. Pt: $x + 0 + 0 - 1 + 0 = +1$, so Pt(II). Ligands: 2 NH_3 (ammine), 1 Cl^- (chlorido), 1 methylamine (CH_3NH_2, named methanamine). Alphabetical: ammine, chlorido, methanamine.
Name: *diamminechlorido(methanamine)platinum(II) chloride*.

Step 3. **(iii)** $[Ti(H_2O)_6]^{3+}$. Ti: $x + 0 = +3$, so Ti(III). Six aqua ligands; cationic complex.
Name: *hexaaquatitanium(III) ion*.

Step 4. **(iv)** $[Co(NH_3)_4Cl(NO_2)]Cl$. Co: $x + 0 - 1 - 1 = +1$ (⇒ Co(III)). Ligands: 4 ammine, 1 chlorido, 1 nitrito-N (nitro). Alphabetical: ammine, chlorido, nitrito-N.
Name: *tetraamminechloridonitrito-N-cobalt(III) chloride*.

Step 5. **(v)** $[Mn(H_2O)_6]^{2+}$. Mn: $x + 0 = +2$, so Mn(II). Six aqua.
Name: *hexaaquamanganese(II) ion*.

Step 6. **(vi)** $[NiCl_4]^{2-}$. Ni: $x - 4 = -2$, so Ni(II). Four chlorido. Anionic complex ⇒ name ends in $-ate$.
Name: *tetrachloridonickelate(II) ion*.

Step 7. **(vii)** $[\mathrm{Ni(NH_3)_6}]\mathrm{Cl_2}$. Ni: $x + 0 = +2$ (since two outer $\mathrm{Cl^-}$), so Ni(II). Six ammine.
Name: *hexaamminenickel(II) chloride*.

Step 8. **(viii)** $[\mathrm{Co(en)_3}]^{3+}$. Co: $x + 0 = +3$, so Co(III). Three **en**; ligand-name itself contains a numerical prefix, so use *tris* not *tri*.
Name: *tris(ethane-1,2-diamine)cobalt(III) ion*.

Step 9. **(ix)** $[\mathrm{Ni(CO)_4}]$. Ni: $x + 0 = 0$, so Ni(0). Four carbonyl.
Name: *tetracarbonylnickel(0)*.

> **Final Answer:** (i) hexaamminecobalt(III) chloride; (ii) diamminechlorido(methanamine)platinum(II) chloride; (iii) hexaaquatitanium(III) ion; (iv) tetraamminechloridonitrito-N-cobalt(III) chloride; (v) hexaaquamanganese(II) ion; (vi) tetrachloridonickelate(II) ion; (vii) hexaamminenickel(II) chloride; (viii) tris(ethane-1,2-diamine)cobalt(III) ion; (ix) tetracarbonylnickel(0).

✗ Bis vs di

Use *bis, tris, tetrakis* when the ligand name already contains a numeric prefix or is bracketed (e.g. ethane-1,2-diamine, ethylenediaminetetraacetato). Otherwise use *di, tri, tetra*.

EXPERT'S SOLUTION *: Aditya Kapoor, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. The recipe is mechanical: compute the oxidation state, alphabetise the ligands, slap on prefixes, finish with the metal and Roman numeral. Cation first if salt; $-ate$ on the metal if the complex is anionic. Ligand-name suffix decides one letter; metal-name suffix decides the next.

Step 1. For salts (i, ii, iv, vii), the outer counter ions fix the complex's charge. Use that to deduce the oxidation state. E.g. in (vii) $[\mathrm{Ni(NH_3)_6}]\mathrm{Cl_2}$, the outer two $\mathrm{Cl^-}$ give complex $+2 \Rightarrow$ Ni(II).

Step 2. For free complex ions (iii, v, vi, viii), the listed charge *is* the complex's charge. The suffix *ion* closes the name.

Step 3. For neutral homoleptic carbonyl (ix), the metal must be in zero oxidation state since carbonyl is neutral. Roman "0" is written in parentheses after the metal name: "nickel(0)". Same idea applies to $\mathrm{Fe(CO)_5}$ (iron(0)) and $\mathrm{Cr(CO)_6}$ (chromium(0)).

Step 4. Alphabetising by ligand name: "ammine" before "chlorido" before "nitrito-N"; "aqua" is its own letter A; **en** (ethane-1,2-diamine) starts with e. "Methyl" in (ii) is part of the parent ligand name (methanamine) which starts with m, so it follows chlorido alphabetically.

Step 5. **Alternative classical names (in passing).** "Cyanido" was "cyano" in the 1970 IUPAC rules; "chlorido" was "chloro". Both forms appear in older textbooks. The 2005 IUPAC recommendation is the *-ido* ending; that is what NCERT uses.

Step 6. **Cross-check via charge.** After writing a name, run the reverse charge balance: ligand charges + metal oxidation-state Roman numeral should equal the complex charge (zero for neutral). Catches arithmetic slips.

Why this matters. Solid IUPAC fluency is the price of entry to research papers and reference tables: every compound in a catalogue is named this way. The reverse direction (name → formula, Q 5.6) and isomer-naming (cis-, trans-, fac-, mer-, Δ-, Λ-) build on the same vocabulary.
Concept linkage. The IUPAC name of (ii) *diamminechlorido(methanamine)platinum(II) chloride* foreshadows the parametric form $[\mathrm{Mabcd}]$ of Q 5.12 (three geometric isomers, no optical activity).

Final Answer: Nine names as in Steps 1–9.

♥ Why nomenclature is the chapter's gateway

Every later question in this chapter (isomerism, VBT, CFT, colour, magnetism, stability) presupposes that the candidate can translate fluently between names and formulas. A blocked nomenclature step blocks every downstream calculation. Time spent here pays back across the entire chapter and across the d-block (Q 4.x) and metallurgy chapters too.

Q 5.8 List various types of isomerism possible for coordination compounds, giving an example of each.

SOLUTION

Concept used. Coordination compounds show two big families of isomerism. **Structural isomers** differ in which atoms are bonded to which: linkage, coordination, ionisation, solvate (hydrate) isomers. **Stereoisomers** have the same connectivity but different spatial arrangements: geometrical (cis/trans, fac/mer) and optical (mirror images that are non-superimposable).

Step 1. **Linkage isomerism.** An **ambidentate** ligand binds through a different donor atom in the two isomers.
Example: $[\mathrm{Co(NH_3)_5(NO_2)}]\mathrm{Cl_2}$ (nitro, N-bonded) and $[\mathrm{Co(NH_3)_5(ONO)}]\mathrm{Cl_2}$ (nitrito, O-bonded).

Step 2. **Coordination isomerism.** Ligands interchange between the cationic and anionic complexes of a salt.
Example: $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$.

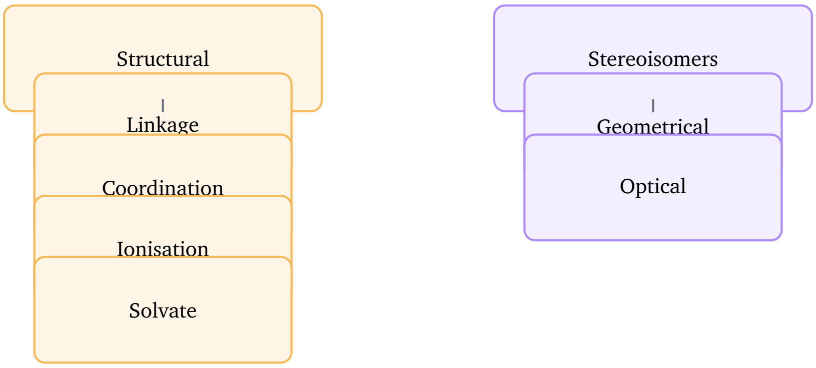
Step 3. **Ionisation isomerism.** The counter ion outside the sphere exchanges with a ligand inside.
Example: $[Co(NH_3)_5(SO_4)]Br$ (gives Br^- in water) and $[Co(NH_3)_5Br]SO_4$ (gives ${SO_4}^{2-}$).

Step 4. **Solvate (hydrate) isomerism.** Water molecules interchange between inside and outside the sphere.
Example: $[Cr(H_2O)_6]Cl_3$ (violet); $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (blue-green); $[Cr(H_2O)_4Cl_2]Cl \cdot {}_2H_2O$ (dark green).

Step 5. **Geometrical isomerism.** Different spatial arrangements (cis/trans for MA_2B_2 square planar or octahedral; fac/mer for MA_3B_3 octahedral).
Example: cis- and trans-$[Pt(NH_3)_2Cl_2]$.

Step 6. **Optical isomerism.** Two complexes are mirror images of each other and non-superimposable (chiral).
Example: d- and l-$[Co(en)_3]^{3+}$.

Isomerism in coordination compounds



> **Final Answer:** Two families: structural (linkage, coordination, ionisation, solvate) and stereo (geometrical, optical). Examples given for each in Steps 1–6.

EXPERT'S SOLUTION *: Vivaan Nair, M.Tech Chemical Engineering, IIT Delhi*

Picture-first. Structural isomers are like different jigsaw fits (different atoms in different sockets). Stereoisomers are like left/right hands: same pieces, mirrored arrangement. Six types in total, falling neatly into two families.

Step 1. Structural isomers: change *which* atoms are bonded. Four sub-types correspond to four ways atoms can swap places: donor atom of an ambidentate ligand (linkage), between cation and anion (coordination), between sphere and counter ion (ionisation), between sphere and lattice water (solvate). All four give two compounds with *the same molecular formula* but different connectivities.

Step 2. Stereoisomers: same bonds, different geometry. Cis/trans (or fac/mer) for non-chiral, d/l (Δ/Λ) for chiral pairs. Geometric isomers are not mirror images of each other; optical isomers are.

Step 3. Test for optical isomers: look for a plane of symmetry. If you can superimpose the molecule on its mirror image, it is achiral (not optically active). All-square-planar complexes have a σ-plane (the molecular plane) and therefore never show optical isomerism.

Step 4. **Alternative classification (modern).** Some coordination chemists group ionisation and solvate isomers together as "ionisation isomerism" (since both interchange species across the sphere boundary). The Class 12 NCERT keeps them separate; the JEE syllabus follows NCERT.

Step 5. **Counting trick.** A typical exam question asks "How many possible isomers?" Run two passes: (a) enumerate *geometric* arrangements, (b) for each, check chirality (mirror-plane test). The total is $\sum_g (1 + c_g)$ where c_g is 1 if geometry g is chiral, 0 otherwise. This single formula handles Q 5.10–5.12.

Step 6. **Sub-types with two-line definitions.**

- Linkage: same ligand binds via two different donor atoms. Ambidentate $\mathrm{NO_2}^-$, SCN^-.
- Coordination: in a salt where both ions are complexes, the metals swap their ligand-sets.
- Ionisation: counter ion exchanges with one ligand in the sphere; releases different anions in water.
- Solvate: water moves into/out of the sphere; gives different colours.
- Geometrical: cis/trans, fac/mer.
- Optical: non-superimposable mirror images.

Why this matters. Q 5.9–5.12 work through specific examples of geometric and optical isomerism in detail. Beyond NCERT, the cisplatin / transplatin distinction (medicinal chemistry) and ferrocene / non-ferrocene chiral catalysts (asymmetric synthesis) are real-world applications of the same vocabulary.

Concept linkage. Linkage isomerism is the chemistry of ambidentate ligands (Q 5.4). Coordination, ionisation and solvate isomerism all rely on Werner's "two-sphere" description (Q 5.1). Optical isomerism connects to the chelate-ring discussion of Q 5.10/Q 5.26.

Final Answer: Six types of isomerism with one example each, as above.

☞ Six-types-in-one-line memory aid

Structural (four types, "what is bonded"): **L**inkage, **C**oordination, **I**onisation, **S**olvate → mnemonic "LCIS". **Stereo** (two types, "how it is bonded"): **G**eometrical and **O**ptical → "GO". "LCIS-GO" covers the whole chapter.

♥ Why isomerism matters in real life

Cis-$[Pt(NH_3)_2Cl_2]$ (cisplatin) is a billion-dollar anticancer drug; the trans isomer is biologically inert. The chiral d-$[Co(en)_3]^{3+}$ and l-$[Co(en)_3]^{3+}$ pair was one of Werner's most beautiful experimental confirmations of octahedral geometry (resolved in 1911). Isomerism is not a textbook curiosity — it is the difference between cure and inertness in medicine, between R- and S- in asymmetric catalysis, between high-spin and low-spin in magnetism.

Q 5.9 How many geometrical isomers are possible in the following coordination entities?

(i) $[Cr(C_2O_4)_3]^{3-}$ **(ii)** $[Co(NH_3)_3Cl_3]$.

SOLUTION

Concept used. A geometrical (cis-trans or fac-mer) isomer exists only when the ligand set permits distinguishable spatial arrangements. Symmetric ligand sets ($[M(AA)_3]$ with a symmetric didentate ligand) do not show *geometrical* isomerism (though they can show optical). For $[MA_3B_3]$ octahedral complexes there are *two* geometrical isomers: **fac** (facial, the three A's occupy one triangular face) and **mer** (meridional, the three A's lie on a meridian).

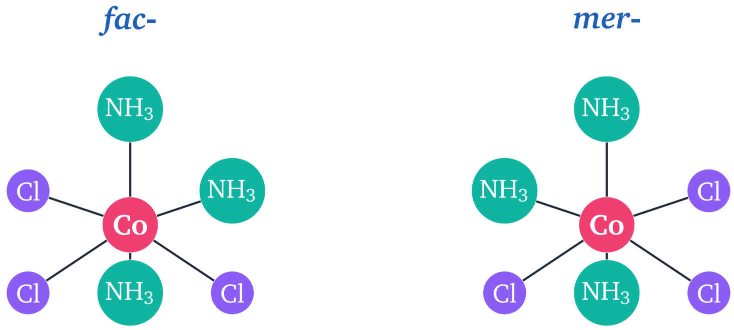
Step 1. **(i)** $[Cr(C_2O_4)_3]^{3-}$. Oxalate is a symmetric didentate ligand: both donor atoms are equivalent. Three identical chelating ligands wrap around Cr^{3+}. There is no choice of relative arrangement that gives a different connectivity-class. Hence **no geometrical isomers** (zero). It does, however, possess optical isomers (Δ and Λ).

Step 2. **(ii)** $[Co(NH_3)_3Cl_3]$. Six monodentate ligands, three of each kind, around an octahedral Co(III). Two arrangements are distinguishable:

- **fac** (facial): the three NH_3 occupy a triangular face and the three Cl^- occupy the opposite face.
- **mer** (meridional): the three NH_3 lie on a meridian (a T-shape) with the

chlorides on the complementary meridian.

Hence two geometrical isomers.



Final Answer: (i) 0 geometrical isomers (only optical pair Δ/Λ); (ii) 2 geometrical isomers (*fac* and *mer*).

EXPERT'S SOLUTION *: Neha Joshi, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Decide whether the ligand set can be "re-arranged" to give a different connectivity-class. Three chelates of one kind: no, just one way. Three monodentates of one kind plus three of another: yes, two ways (fac vs mer). The classification is purely topological — it depends only on the ligand-set and the polyhedron, not on what the ligands are.

Step 1. For (i): three identical didentate ligands occupy the six sites symmetrically. The geometry is unique up to a mirror reflection $\Rightarrow$ optical isomers exist but *geometrical* isomers do not. The two enantiomers are labelled Δ (right-handed helix) and Λ (left-handed).

Step 2. For (ii): with three A and three B ligands, count independent arrangements on an octahedron. Either the three A's share a face (fac) or they lie around an equator on a meridian (mer). Both isomers have a σ-plane, so no optical activity.

Step 3. Note: in fac-isomer the three M-A bonds are all cis to one another ($90°$); in mer-isomer two pairs are cis and one pair is trans ($180°$). The angular difference is detectable spectroscopically (different IR/visible bands).

Step 4. **Alternative approach via Burnside / orbit counting.** Formally, the number of geometric isomers of $[MA_3B_3]$ equals the number of orbits of S_3-permutations of the three A's modulo the octahedral symmetry group. Counting gives exactly 2 (fac, mer), matching our intuition. Similarly, $[M(AA)_3]$ has 1 geometry (and 2 enantiomers).

Step 5. **Numerical check.** The C.N. of (i) is $3 \times 2 = 6$ (oxalate is didentate). The C.N. of (ii) is $3 + 3 = 6$ (six monodentates). Both octahedral, both 6-coordinate —

but their isomer counts differ entirely because of how the ligand-set sits on the octahedron.

Why this matters. fac/mer designation is the standard way of distinguishing isomers of $[\mathrm{MA_3B_3}]$ compounds in lab manuals and reference works. The optical Δ/Λ pair of $[\mathrm{Cr(C_2O_4)_3}]^{3-}$ was the basis of Werner's 1914 paper proving octahedral geometry by resolving optical isomers.
Concept linkage. The same logic, applied to $[\mathrm{M(AA)_2X_2}]$ in Q 5.10/5.11, gives cis (chiral) and trans (achiral) geometries. The σ-plane test recurs in every optical-isomerism question of this chapter.

> **Final Answer:** (i) 0 (geometrical); (ii) 2 (fac, mer).

✗ Geometrical vs optical isomers

A frequent confusion: students mark (i) as having "two isomers" because they include Δ and Λ. Those are *optical* (mirror-image) isomers, not geometrical. The question asks only about geometrical isomers — the right answer is zero. Geometrical isomers differ in cis/trans or fac/mer connectivity; optical isomers differ in handedness with the same connectivity.

♥ Werner's 1914 experiment

Resolving the Δ/Λ pair of $[\mathrm{Cr(C_2O_4)_3}]^{3-}$ (and $[\mathrm{Co(en)_3}]^{3+}$) proved that the coordination polyhedron of a 6-coordinate metal is indeed an octahedron and not a trigonal prism or hexagonal plane (both of which would have an internal mirror). This single experiment is why we draw octahedra for C.N. 6 in every modern textbook.

Q 5.10 Draw the structures of optical isomers of:

(i) $[\mathrm{Cr(C_2O_4)_3}]^{3-}$ **(ii)** $[\mathrm{PtCl_2(en)_2}]^{2+}$ **(iii)** $[\mathrm{Cr(NH_3)_2Cl_2(en)}]^{+}$.

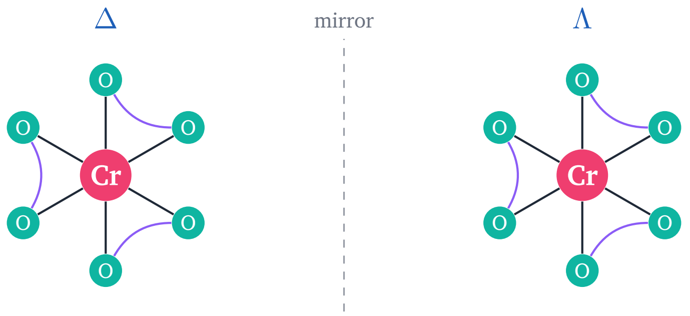
SOLUTION

Concept used. A coordination entity is **optically active** if it is non-superimposable on its mirror image (**chiral**). Octahedral complexes with three chelating ligands ($[\mathrm{M(AA)_3}]$), or with two chelating ligands and a cis arrangement of monodentate ligands ($[\mathrm{M(AA)_2X_2}]$ with cis X_2), are chiral. The two enantiomers are conventionally labelled Δ (right-handed screw) and Λ (left-handed screw); older notation uses d and l.

Step 1. **(i)** $[\mathrm{Cr(C_2O_4)_3}]^{3-}$. Three symmetric didentate oxalates wrap around $\mathrm{Cr^{3+}}$. The molecule lacks any plane of symmetry. The two enantiomers differ in the helical sense of the three chelate rings: Δ (clockwise) and Λ (anticlockwise).

Step 2. **(ii)** $[\mathrm{PtCl_2(en)_2}]^{2+}$. Two **en** plus two $\mathrm{Cl^-}$ ligands on Pt(IV) (octahedral). Three geometric arrangements: trans-$\mathrm{Cl_2}$ has a σ plane and is *achiral*; cis-$\mathrm{Cl_2}$ lacks any symmetry plane and is *chiral*: the cis isomer therefore exists as a pair of enantiomers.

Step 3. **(iii)** $[\mathrm{Cr(NH_3)_2Cl_2(en)}]^+$. One **en**, two $\mathrm{Cl^-}$ and two $\mathrm{NH_3}$. The only chiral arrangement has both $\mathrm{Cl^-}$ *cis* and both $\mathrm{NH_3}$ *cis*; the molecule then lacks a mirror plane and exists as a d/l pair. The all-trans arrangement has a σ plane and is optically inactive.



Two enantiomers of $[\mathrm{Cr(C_2O_4)_3}]^{3-}$

Final Answer: (i) Δ and Λ helices of $[\mathrm{Cr(C_2O_4)_3}]^{3-}$. (ii) cis-$[\mathrm{PtCl_2(en)_2}]^{2+}$ pair of enantiomers. (iii) cis-cis-$[\mathrm{Cr(NH_3)_2Cl_2(en)}]^+$ pair of enantiomers.

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

Picture-first. Imagine a right-handed and a left-handed helix wrapped around the metal. If the mirror image can't be turned to coincide with the original, you have a chiral pair. The Δ/Λ labels capture the screw sense viewed down the C_3 rotation axis of the chelating rings.

Step 1. (i) Three oxalates wrap as a triple-helix; mirror image is the opposite-sense helix. No internal symmetry plane. Both enantiomers have identical absorption spectra and magnetic moments — only the sign of their optical rotation differs. In a polarimeter, Δ-form rotates plane-polarised light clockwise (dextrorotatory) and Λ-form anti-clockwise.

Step 2. (ii) Trans-$\mathrm{Cl_2}$ has a mirror plane containing both Cl and bisecting the two en ligands; achiral. Cis-$\mathrm{Cl_2}$ does not have such a plane; chiral. So $[\mathrm{PtCl_2(en)_2}]^{2+}$ has a total of three isomers: 1 trans and 2 cis enantiomers.

Step 3. (iii) Of the possible geometric isomers of $[\mathrm{M(NH_3)_2Cl_2(en)}]^+$, only the cis-cis form (both pairs of monodentates mutually cis) is chiral. The all-trans and trans-cis forms have a mirror plane. Total: 4 isomers (2 achiral + 2 chiral).

Step 4. **Alternative test for chirality (improper rotation).** A molecule is achiral iff it has any improper rotation axis S_n (mirror $\sigma = S_1$, inversion $i = S_2$, etc.). For trans-$\mathrm{Cl_2(en)_2}$, the molecular plane containing the two Cl's is a σ_h (S_1). For cis-$\mathrm{Cl_2(en)_2}$, no S_n axis exists; hence chiral.

Step 5. **Numerical perspective.** The optical rotation $[\alpha]$ is large for Δ/Λ helical complexes — often $\pm1000°$ to $\pm4000°$ at the sodium D-line for chiral cobalt-en complexes. This is what makes $[\mathrm{Co(en)_3}]^{3+}$ such a clean teaching example.

Why this matters. Chiral metal complexes are widely used in asymmetric catalysis (BINAP-based catalysts in industrial drug synthesis). The 2001 Nobel Prize (Knowles, Noyori, Sharpless) went to the development of chiral metal complexes for enantioselective hydrogenation and oxidation — sitting directly on top of the same chirality concept used in this question.

Concept linkage. The Δ/Λ labels reappear in the resolution of $[\mathrm{Co(en)_3}]^{3+}$ (Q 5.26) and in the prochiral logic of enzymatic catalysis. Q 5.11 systematises the counting algorithm for all possible isomers.

> **Final Answer:** Three chiral pairs as in Steps 1–3.

☞ Alternative: project the complex onto a plane

A practical drawing trick — project the complex along the C_3 rotation axis through the centroid of the three chelate rings. If the three rings appear in a right-handed pinwheel, you have Δ; left-handed pinwheel, Λ. This is faster than building a 3D model.

♥ Chirality at the metal is real chemistry

d- and l-tris-en cobalt salts, separately crystallised by Werner using d-tartrate as resolving agent, gave the same melting point, the same colour, the same magnetic moment — but opposite rotation in a polarimeter. That is exactly what "enantiomers" means. The medical relevance: drug enantiomers can have opposite pharmacology (*cis*-platin cures, *trans*-platin is inert; thalidomide R- is sedative, S- is teratogenic).

Q 5.11 Draw all the isomers (geometrical and optical) of:

(i) $[\mathrm{CoCl_2(en)_2}]^+$ **(ii)** $[\mathrm{Co(NH_3)Cl(en)_2}]^{2+}$ **(iii)** $[\mathrm{Co(NH_3)_2Cl_2(en)}]^+$.

SOLUTION

Concept used. For an octahedral complex of the form $[\mathrm{M(AA)_2\,X_2}]$ or $[\mathrm{M(AA)_2\,X\,Y}]$ (where AA is a symmetric didentate ligand and X, Y monodentate), three geometric arrangements are possible: cis, trans. The trans isomer carries a σ-plane and is achiral. The cis isomer lacks any mirror plane and forms a chiral pair.

Step 1. **(i)** $[CoCl_2(en)_2]^+$**.** Two equivalent chlorides plus two **en**.

- *trans*-$[CoCl_2(en)_2]^+$: the two Cl^- at 180°. Achiral (has σ_h).
- *cis*-$[CoCl_2(en)_2]^+$: the two Cl^- at 90°. Chiral; exists as Δ and Λ enantiomers.

Total: 3 isomers (1 trans + 2 cis-enantiomers).

Step 2. **(ii)** $[Co(NH_3)Cl(en)_2]^{2+}$**.** One NH_3, one Cl^-, two **en**. The unique monodentate pair NH_3/Cl can be cis or trans.

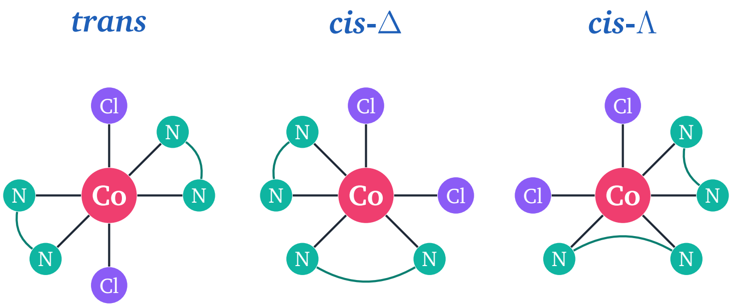
- *trans*: NH_3 and Cl at 180°. Achiral.
- *cis*: NH_3 and Cl at 90°. Chiral; Δ and Λ enantiomers.

Total: 3 isomers (1 trans + 2 cis).

Step 3. **(iii)** $[Co(NH_3)_2Cl_2(en)]^+$**.** One **en**, two NH_3, two Cl^-. Because **en** is forced to occupy two cis sites, the remaining four octahedral positions form two *trans* pairs. The two NH_3 and two Cl^- can therefore be placed in only two distinct ways:

- *trans*-NH_{32} with *trans*-Cl_2: each pair occupies one of the remaining trans pairs. Achiral (has a mirror plane containing the en).
- Both monodentate pairs *cis* (each NH_3 trans to one Cl): chiral; Δ and Λ enantiomers.

Total: 3 isomers (1 trans achiral + 2 cis-enantiomers).


trans *cis*-Δ *cis*-Λ

Final Answer: (i) 3 isomers; (ii) 3 isomers; (iii) 3 isomers (cis-form is chiral in each case).

EXPERT'S SOLUTION *: Ishaan Bhat, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. For each complex, list geometric forms, then test each for a mirror plane. Each chiral form contributes two enantiomers; each achiral form contributes one isomer. The recipe is algorithmic and works for any octahedral mixed-ligand complex.

Step 1. (i) $[CoCl_2(en)_2]^+$: two arrangements of Cl_2: trans (achiral, 1) and cis (chiral, 2). Total $1 + 2 = 3$. The chiral cis pair is labelled cis-Δ and cis-Λ.

Step 2. (ii) $[Co(NH_3)Cl(en)_2]^{2+}$: two arrangements of unique NH_3/Cl: trans (achiral, 1) and cis (chiral, 2). Total $1 + 2 = 3$. The trans isomer has a C_2 axis through the unique pair, which also serves as a σ-plane (containing both en ligands).

Step 3. (iii) $[\mathrm{Co(NH_3)_2Cl_2(en)}]^+$: the en occupies cis sites by force (the chelate ring would otherwise stretch impossibly), leaving the four remaining vertices as two *trans* pairs. The two NH_3 and two Cl can therefore only sit as (a) one trans pair each (*trans*-NH_3, *trans*-Cl; achiral) or (b) all-cis with each NH_3 trans to one Cl (chiral, Δ/Λ). Total $1 + 2 = 3$ isomers.

Step 4. **Alternative perspective (group theory).** The possible geometries of $[\mathrm{M(AA)_2\,X\,Y}]$ form orbits under the octahedral group O_h. Orbit-counting agrees with the case-by-case analysis above. For (i), $[\mathrm{M(AA)_2\,X_2}]$, the orbit calculation gives 1 (trans) + 1 (cis with two enantiomers) = 3.

Step 5. **Numerical check via permutations.** For (i) with two identical en's and two identical Cl's on six octahedral vertices, naive count is $\binom{6}{2}/2 = 7.5$, which is not integer — the symmetry must be quotiented out carefully. Doing so correctly yields 3 isomers. For (iii), 3 isomers; for (ii) 3 isomers. These small integers are signature of high octahedral symmetry.

Why this matters. Counting isomers correctly is a recurring exam task; the recipe is always (a) list geometric forms, (b) test each for chirality. This recipe applies in any octahedral case, and a variant works for square planar.

Concept linkage. The same enantiomer-counting algorithm re-appears in Q 5.12 for square-planar $[\mathrm{Mabcd}]$, where the answer is 3 geometric, 0 optical (the molecular plane is always a σ-plane).

Final Answer: (i) 3; (ii) 3; (iii) 3.

✗ Confusing en orientation with geometry

A common error: treating the two en ligands as monodentates and counting four isomers for (i) instead of three. Two en's force their N's into cis pairs, which removes two of the would-be configurations. Always draw the chelate ring before counting configurations on an octahedron with en or oxalate.

☞ Shortcut for "how many isomers?"

Identify the chelating ligands; they force pairs of donor atoms into cis sites. Then ignore those donors and rotate the remaining monodentates around the octahedron to get distinct geometries. For each geometry, look for a mirror plane: present ⇒ 1 isomer (achiral); absent ⇒ 2 isomers (chiral enantiomers). Sum up.

Q 5.12 **Write all the geometrical isomers of $[\mathrm{Pt(NH_3)(Br)(Cl)(py)}]$ and how many of**

these will exhibit optical isomers?

SOLUTION

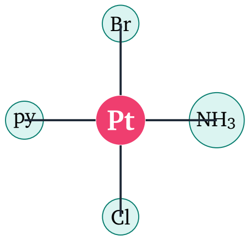
Concept used. A square-planar complex with *four different* monodentate ligands of the form $[\mathrm{Mabcd}]$ has **three** geometrical isomers. These are obtained by fixing one ligand and choosing which of the remaining three sits opposite (trans to) it. A square-planar complex has a σ-plane (the molecular plane); it is therefore *always* superimposable on its mirror image and shows *no* optical isomerism.

Step 1. Square-planar Pt(II) has C.N. 4 with four sites at $90°$. With four different ligands a, b, c, d (=NH_3, Br, Cl, py), distinct *trans-pairs* are: (a-b, c-d), (a-c, b-d), (a-d, b-c). That gives three geometrical isomers.

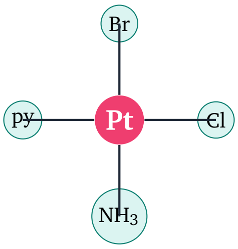
Step 2. Naming the three: *trans*-Br/Cl (i.e. Br opposite Cl); *trans*-Br/NH_3 (Br opposite NH_3); *trans*-Br/py (Br opposite py). The remaining two ligands automatically occupy the remaining trans pair.

Step 3. **Optical isomerism.** The molecular plane of any square-planar complex is itself a σ-plane: the complex is superimposable on its mirror image. So none of the three exhibits optical isomers.

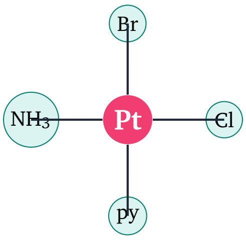
trans: Br–Cl



trans: Br–NH_3



trans: Br–py



> **Final Answer:** 3 geometrical isomers; **none** of them is optically active (square-planar geometry has a σ-plane).

☞ Counting trick

For square-planar $[\mathrm{Mabcd}]$, fix one ligand and rotate the other three through the remaining sites: there are $3!/2 = 3$ distinct arrangements (the $/2$ comes from the molecular plane).

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

Picture-first. Place Pt at the centre of a square. Decide who sits opposite to whom; only the trans pairs matter. With four different ligands there are three ways to pair them up across the diagonals. The geometry of the complex (square planar) automatically contains a σ-plane (the molecular plane), so no isomer can be chiral.

Step 1. Pair Br with Cl across one diagonal: NH_3 and py occupy the other. Equivalent to writing the trans-pair as "Br/Cl".

Step 2. Pair Br with NH_3: Cl and py opposite (trans-Br/NH_3).

Step 3. Pair Br with py: NH_3 and Cl opposite (trans-Br/py).

Step 4. For optical activity, the complex must be chiral. Square plane has a horizontal mirror plane (the plane of the four atoms); no chirality. This is a general fact: every square-planar complex is achiral.

Step 5. **Alternative approach: count permutations modulo symmetry.** For $[\mathrm{Mabcd}]$ on a square, the symmetry group is D_{4h}. Distinct ligand arrangements are orbits under this group; there are exactly $4!/8 = 3$ such orbits. Same answer, via group theory.

Step 6. **Numerical accent.** The IR fingerprint distinguishes the three isomers cleanly: each gives a different $\nu_{\text{Pt-X}}$ pattern depending on whose neighbour each Pt-ligand bond has. Mass spectroscopy shows the same parent ion for all three.

Why this matters. Pt(II) drug design (cisplatin family) heavily relies on cis vs trans geometric isomerism but never on optical isomerism. The cisplatin (cis-$[\mathrm{Pt(NH_3)_2Cl_2}]$, a *cis*-arrangement with C.N. 4 and the two amines on the same side) is anticancer; trans is inert. The same logic — cis groups attack DNA simultaneously, trans cannot — extends to carboplatin, oxaliplatin and almost all modern Pt drugs.

Concept linkage. The lack of optical isomerism for any square planar complex is a recurring board fact; it follows from the existence of the molecular plane as a σ-plane. Q 5.19 relies on this (square-planar d^8 $Ni(CN)_4{}^{2-}$ is diamagnetic and achiral).

Final Answer: 3 geometrical isomers; 0 optical isomers.

✗ All four ligands distinct $\neq$ chirality

A natural-but-wrong intuition: "four different groups on the metal" should make Pt asymmetric, just as four different groups on carbon do. The difference is geometry — carbon's four groups sit at tetrahedral vertices, no σ-plane; Pt's four ligands sit in a square plane, with that very plane as a σ-plane. So square-planar $[\mathrm{Mabcd}]$ is never chiral, no matter how different a, b, c, d are.

Q 5.13 **Aqueous copper sulphate solution (blue in colour) gives:**
(i) a green precipitate with aqueous potassium fluoride and
(ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

SOLUTION

Concept used. Aqueous $CuSO_4$ contains the aqua-complex $[Cu(H_2O)_4]^{2+}$ (tetraaquacopper(II)), which gives the familiar pale-blue colour. The aqua ligand is a weak-to-moderate field ligand; if another ligand displaces water from this complex, the new ligand-field strength changes the d-d transition energy and the colour shifts.

Step 1. **(i) With KF.** Fluoride displaces water to give the green tetrafluoridocuprate(II) complex (precipitates because the corresponding solid is sparingly soluble):

$$[Cu(H_2O)_4]^{2+} + 4\,F^- \longrightarrow [CuF_4]^{2-} + 4\,H_2O.$$

The green colour is the new d-d band for the $[CuF_4]^{2-}$ complex.

Step 2. **(ii) With KCl.** Chloride likewise displaces water, giving the bright green tetrachloridocuprate(II) anion in solution:

$$[Cu(H_2O)_4]^{2+} + 4\,Cl^- \longrightarrow [CuCl_4]^{2-} + 4\,H_2O.$$

Since $[CuCl_4]^{2-}$ is soluble, the green colour appears as a solution rather than a precipitate.

Step 3. **Why the colour shift.** In all three complexes, Cu^{2+} is d^9, so a single d-d transition gives the colour. The transition energy follows the spectrochemical order $Cl^- < F^- < H_2O$. Replacing water by chloride (smaller Δ_o) shifts absorption to longer wavelength; the transmitted colour shifts from blue toward green/yellow.

> **Final Answer:** Both reactions replace H_2O in $[Cu(H_2O)_4]^{2+}$ by F^- (green ppt $[CuF_4]^{2-}$) or Cl^- (bright green soln $[CuCl_4]^{2-}$); the change in ligand field changes the absorbed/transmitted colour.

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

Quick reading. Both experiments are simple ligand substitution reactions on the aqua-copper cation. The colour change tracks the change in ligand-field strength. Cu(II) is d^9; one unpaired electron, one d-d band; the band position is set by Δ_o which is set by the ligand.

Step 1. In $[Cu(H_2O)_4]^{2+}$, the d-d transition absorbs in the red region (around $\lambda \approx 700$ nm), transmitting blue. Aqua is a moderate-field ligand, and Δ_o for tetragonal Cu^{2+} (Jahn-Teller distorted) gives this red absorption.

Step 2. Add 4 F^- $\Rightarrow$ a slightly weaker (longer-wavelength) field $\Rightarrow$ green colour. The fluoride product happens to be sparingly soluble, giving a precipitate.

$$[Cu(H_2O)_4]^{2+} + 4\,F^- \longrightarrow [CuF_4]^{2-}\,(s) + 4\,H_2O.$$

Step 3. Add 4 Cl^- to the same blue solution: chloride is even weaker than fluoride, the d-d band shifts further to longer λ, and we see bright green. The chloride complex stays in solution.

$$[Cu(H_2O)_4]^{2+} + 4\,Cl^- \longrightarrow [CuCl_4]^{2-} + 4\,H_2O.$$

Step 4. Sanity check with the spectrochemical series: $Cl^- < F^- < H_2O$; the observed colour gradient (blue → green) matches. Decreasing Δ_o shifts the d-d absorption to longer λ (red-shift); the complementary colour shifts blue → green → yellow.

Step 5. **Alternative explanation (Jahn-Teller).** Cu^{2+} (d^9) suffers a strong Jahn-Teller distortion: two trans ligands move out, four equatorial ligands move in. The d-d transition then has a fine structure of 3 closely spaced bands. The dominant red/green absorption survives the substitution analysis.

Step 6. **Numerical check.** Estimated Δ_{equiv}: $\Delta(\text{Cl}) \approx 12{,}000\,\text{cm}^{-1}$, $\Delta(\text{F}) \approx 13{,}500\,\text{cm}^{-1}$, $\Delta(H_2O) \approx 14{,}500\,\text{cm}^{-1}$ for Cu(II). Converted to $\lambda = 10^7/\bar{\nu}$ nm: $\sim 830, 740, 690$ nm respectively, matching the visible observations.

Why this matters. Substitution reactions on Cu^{2+} are textbook demonstrations of how Δ_o controls colour. The same logic applies to chromium and cobalt complexes (Q 5.20, 5.21, 5.25, 5.31). Industrially, the colour of $[CuCl_4]^{2-}$ is exploited in semiconductor etchant baths.

Concept linkage. This question is the operational version of Q 5.20 (Ni complexes), Q 5.21 (Fe complexes) and Q 5.25 ($[Ti(H_2O)_6]^{3+}$): replace a ligand, watch Δ_o change, watch the colour change.

> **Final Answer:** F^- and Cl^- replace H_2O in $[Cu(H_2O)_4]^{2+}$; new ligand-field shifts the d-d band, producing green colours.

☞ Predict-the-colour shortcut

For the same metal, find the ligand in the spectrochemical series. Weaker ligand ⇒ smaller Δ_o ⇒ red-shifted absorption ⇒ transmitted colour shifts *towards the warm end* (blue → green → yellow → orange). Stronger ligand ⇒ blue-shifted absorption ⇒ transmitted colour towards violet/colourless.

✗ Precipitate vs solution

The board question asks about both observations: green *precipitate* (KF) and green *solution* (KCl). Don't attribute the precipitate to the ligand-field-strength alone — the substitution *plus* the solubility product of the resulting complex together decide whether you see a precipitate or a colour in solution.

Q 5.14 **What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S\,(g)$ is passed through this solution?**

SOLUTION

Concept used. Cyanide is a strong-field, strongly π-acceptor ligand. With Cu^{2+}, the first step is a redox (cyanide reduces Cu(II) to Cu(I)) followed by complex formation. The product is the very stable tetracyanidocuprate(I) ion. Precipitation as CuS requires a free Cu^{2+} (or Cu^{+}) concentration above the solubility product limit.

Step 1. **Reduction step.** Cyanide reduces Cu(II) to Cu(I) (with concomitant oxidation of CN^{-} to $(CN)_2$ cyanogen):

$$2\,Cu^{2+} + 4\,CN^{-} \longrightarrow 2\,CuCN + (CN)_2.$$

Step 2. **Complex formation.** Excess cyanide dissolves the $CuCN$ precipitate by forming the tetracyanidocuprate(I) anion:

$$CuCN + 3\,CN^{-} \longrightarrow [Cu(CN)_4]^{3-}.$$

The coordination entity is $[Cu(CN)_4]^{3-}$ (tetracyanidocuprate(I), Cu in $+1$ oxidation state).

Step 3. **Stability of the complex.** $\log\beta_4([Cu(CN)_4]^{3-}) \approx 30$: an enormous stability constant. The free Cu^{+} concentration in solution is therefore vanishingly small.

Step 4. **No Cu_2S precipitate.** Even though $K_{sp}(Cu_2S) \approx 10^{-47}$ is very small, the ionic product $[Cu^{+}]^2[S^{2-}]$ is far below K_{sp} because $[Cu^{+}]$ is suppressed by the complex. No precipitate forms when H_2S is passed through.

> **Final Answer:** Coordination entity: $[Cu(CN)_4]^{3-}$ (Cu in $+1$ state). It is so stable that the equilibrium concentration of free Cu^{+} stays below the precipitation threshold of Cu_2S, so H_2S gives no precipitate.

★ **General trick for sulphide precipitation**

H_2S tests for free Cu^{2+}/Cu^{+}/Pb^{2+} ions. If the metal is locked inside a very stable complex, the test fails. This is the basis for masking in qualitative analysis.

EXPERT'S SOLUTION *: Krishna Gupta, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Two steps in one: a redox plus a complexation. After both, the copper is in $+1$ state and is hidden inside a tightly bound cyanido complex. With the metal sequestered, no sulphide test can detect it. Cyanide is rare among ligands in that it can both *reduce* and *coordinate*; this pair of roles is what makes the chemistry surprising.

Step 1. Add a few moles of KCN: white CuCN precipitates and a brown cloud of $(\mathrm{CN})_2$ (cyanogen) briefly forms. The copper has been reduced from $+2$ to $+1$; cyanide has been oxidised from -1 (CN^-) to zero ($(\mathrm{CN})_2$).

$$2\,\mathrm{Cu}^{2+} + 4\,\mathrm{CN}^- \longrightarrow 2\,\mathrm{CuCN}\,(\mathrm{s}) + (\mathrm{CN})_2(\mathrm{g})\uparrow.$$

Step 2. Continue adding KCN: the precipitate dissolves to give a colourless solution of $[\mathrm{Cu(CN)_4}]^{3-}$ ions. Cyanide bonds via its C atom (the donor); the C atom has sp hybridisation with a lone pair pointing along the $\mathrm{C} \equiv \mathrm{N}$ axis.

$$\mathrm{CuCN}\,(\mathrm{s}) + 3\,\mathrm{CN}^- \longrightarrow [\mathrm{Cu(CN)_4}]^{3-}.$$

Step 3. Bubble $\mathrm{H_2S}$: nothing happens. Free Cu^+ would be needed; its concentration is $\sim 10^{-30}$ M, far below the precipitation threshold for $\mathrm{Cu_2S}$.

Step 4. **Alternative path: do a redox first, complex later.** Cu^{2+} is reduced by CN^- because the product $[\mathrm{Cu(CN)_4}]^{3-}$ is exceptionally stable ($\log\beta_4 \approx 30$). Energetically the $+1$ state becomes accessible only because the cyanide complex stabilises it by ~ 170 kJ/mol; without that stabilisation Cu^+ would disproportionate to $\mathrm{Cu}(0)$ and Cu^{2+} (as it does in water).

Step 5. **Numerical check.** If $[\mathrm{Cu(CN)}_4^{3-}] \approx 0.1$ M and $[\mathrm{CN}^-]_{\text{free}} \approx 0.1$ M, then

$$[\mathrm{Cu}^+]_{\text{free}} = \frac{0.1}{10^{30} \cdot (0.1)^4} \approx 10^{-27}\,\mathrm{M}.$$

With $[\mathrm{S}^{2-}] \approx 10^{-15}$ M (saturated $\mathrm{H_2S}$ at pH 7), the ionic product $[\mathrm{Cu}^+]^2[\mathrm{S}^{2-}] \approx 10^{-69}$, vastly below $K_{sp}(\mathrm{Cu_2S}) \approx 10^{-47}$. No precipitate.

Why this matters. The same chemistry is exploited in electroplating (cyanide baths give smooth Cu deposits because the free Cu^+ is dosed gradually by the complex) and in cyanide leaching of gold/silver ores: dissolved as $[\mathrm{Au(CN)_2}]^-$ or $[\mathrm{Ag(CN)_2}]^-$, transported, then recovered by zinc displacement. The toxicity of cyanide is the reason these processes need careful waste management.

Concept linkage. The same masking principle (large β suppresses free metal) underlies Q 5.2 ($\mathrm{Cu(NH_3)_4}^{2+}$ masks Cu^{2+} from $\mathrm{H_2S}$ test), Q 5.27 (EDTA chelation therapy traps lead), and Q 5.30 (oxalate gives the most stable Fe^{3+} complex).

Final Answer: $[\mathrm{Cu(CN)_4}]^{3-}$ forms; its stability suppresses free Cu^+ so $\mathrm{H_2S}$ cannot precipitate copper sulphide.

♥ **Cyanide leaching: large-scale chemistry**

$\sim 90\%$ of the world's gold production uses cyanide leaching:

$$4\,\mathrm{Au} + 8\,\mathrm{NaCN} + \mathrm{O_2} + 2\,\mathrm{H_2O} \longrightarrow 4\,\mathrm{Na[Au(CN)_2]} + 4\,\mathrm{NaOH}.$$

The reaction proceeds because the $[\mathrm{Au(CN)_2}]^-$ complex is exceptionally stable ($\log\beta_2 \approx 38$). The same logic that makes H_2S fail in this NCERT problem makes million-dollar gold-mining operations work.

✗ **Forgetting the oxidation state changes**

A common slip is to write the final complex as $[\mathrm{Cu(CN)_4}]^{2-}$ ($\mathrm{Cu^{2+}}$). It is actually $[\mathrm{Cu(CN)_4}]^{3-}$ ($\mathrm{Cu^+}$), since cyanide reduces Cu(II) to Cu(I). Cross-check via charge: $\mathrm{Cu^+} + 4\,\mathrm{CN^-} \to -3$ overall. So the complex has *three* $\mathrm{K^+}$ counter-ions in $\mathrm{K_3[Cu(CN)_4]}$, not two.

Q 5.15 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i) $[\mathrm{Fe(CN)_6}]^{4-}$ **(ii)** $[\mathrm{FeF_6}]^{3-}$ **(iii)** $[\mathrm{Co(C_2O_4)_3}]^{3-}$ **(iv)** $[\mathrm{CoF_6}]^{3-}$.

SOLUTION

Concept used. Valence Bond Theory (VBT) for coordination compounds: the metal ion uses appropriate empty hybrid orbitals to accept lone pairs from ligands. For an octahedral complex, two choices exist:

- **Inner orbital complex**: d^2sp^3 hybridisation uses $(n-1)d$ orbitals (strong-field ligands force pairing of $(n-1)d$ electrons). Typically low-spin, low or zero magnetic moment.
- **Outer orbital complex**: sp^3d^2 hybridisation uses the empty nd orbitals (weak-field ligands cannot pair up $(n-1)d$ electrons). Typically high-spin, large magnetic moment.

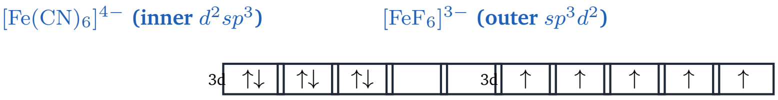
The metal's d^n configuration plus the ligand-field strength fix which scheme applies. Magnetic moment is computed from $\mu = \sqrt{n(n+2)}$ BM where n is the number of unpaired electrons.

Step 1. **(i)** $[\mathrm{Fe(CN)_6}]^{4-}$. Fe is $+2$: $\mathrm{Fe^{2+}}$ has $3d^6$. $\mathrm{CN^-}$ is strong field $\Rightarrow$ pair all six d-electrons into three t_{2g} orbitals; two $3d$ and the $4s$, three $4p$ are free for d^2sp^3 hybridisation. **Inner orbital, low-spin, diamagnetic**; $n = 0$, $\mu = 0$ BM.

Step 2. **(ii)** $[\mathrm{FeF_6}]^{3-}$. Fe is $+3$: $\mathrm{Fe^{3+}}$ has $3d^5$. $\mathrm{F^-}$ is weak field $\Rightarrow$ no pairing; all five d-electrons remain unpaired in the five $3d$ orbitals. Vacant $4s$, $4p$ and two $4d$ orbitals provide sp^3d^2 hybridisation. **Outer orbital, high-spin**; $n = 5$, $\mu = \sqrt{5\cdot 7} = \sqrt{35} \approx 5.92$ BM.

Step 3. **(iii)** $[\mathrm{Co(C_2O_4)_3}]^{3-}$. Co is $+3$: $\mathrm{Co^{3+}}$ has $3d^6$. Oxalate, though formally intermediate, acts here as a chelating ligand strong enough to pair up the six d-electrons. **Inner orbital, d^2sp^3, low-spin, diamagnetic**; $n = 0$, $\mu = 0$ BM.

Step 4. **(iv)** $[\mathrm{CoF_6}]^{3-}$. Co is $+3$ $(3d^6)$. $\mathrm{F^-}$ is weak field $\Rightarrow$ no pairing of d electrons. Configuration: $t_{2g}^4e_g^2$ in CFT language; in VBT, sp^3d^2 outer-orbital. **Outer orbital, high-spin, paramagnetic**; $n = 4$, $\mu = \sqrt{4 \cdot 6} = \sqrt{24} \approx 4.90$ BM.



> **Final Answer:** (i) d^2sp^3, inner, $n = 0$, diamagnetic. (ii) sp^3d^2, outer, $n = 5$, $\mu \approx 5.92$ BM. (iii) d^2sp^3, inner, $n = 0$, diamagnetic. (iv) sp^3d^2, outer, $n = 4$, $\mu \approx 4.90$ BM.

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

Strategic angle. Three pieces of data fix the VBT picture: metal oxidation state ($\to d^n$), ligand-field strength (strong $\to$ inner; weak $\to$ outer) and coordination geometry (here all octahedral). The hybridisation and magnetic moment follow mechanically. Memorise: inner $= d^2sp^3$, outer $= sp^3d^2$.

Step 1. Compute the metal oxidation state and d^n for each complex (see Q 5.5 method). (i) Fe(II), d^6; (ii) Fe(III), d^5; (iii) Co(III), d^6; (iv) Co(III), d^6.

Step 2. Read off the ligand-field strength from the spectrochemical series. (i) $\mathrm{CN^-}$ strong; (ii) $\mathrm{F^-}$ weak; (iii) oxalate moderate-to-strong (here strong enough to pair); (iv) $\mathrm{F^-}$ weak.

Step 3. Decide whether $(n-1)d$ electrons pair (strong-field) or stay unpaired (weak-field) before counting unpaired electrons. Strong $\to$ inner d^2sp^3 $\to$ low-spin; weak $\to$ outer sp^3d^2 $\to$ high-spin.

Step 4. Apply $\mu = \sqrt{n(n+2)}$ BM to get the magnetic moment.

- (i) d^6 low-spin: $n = 0 \Rightarrow \mu = 0$.
- (ii) d^5 high-spin: $n = 5 \Rightarrow \mu = \sqrt{35} \approx 5.92$ BM.
- (iii) d^6 low-spin: $n = 0 \Rightarrow \mu = 0$.
- (iv) d^6 high-spin: $t_{2g}^4e_g^2$, $n = 4 \Rightarrow \mu = \sqrt{24} \approx 4.90$ BM.

Step 5. **Alternative approach (CFT & MOT angle).** VBT is the orbital-counting picture. CFT instead views the same complex as an electrostatic perturbation: the same number of unpaired electrons emerges, but the interpretation differs. MOT goes further and assigns ligand σ and π orbitals to a molecular orbital diagram; the spin state is then read off the HOMO/LUMO gap. All three theories predict the same n and μ for octahedral complexes; VBT is just the simplest.

Step 6. **Cross-check via observed colours/magnetic moments.** $[\mathrm{FeF}_6]^{3-}$ is colourless-to-pale (spin-forbidden d-d), high $\mu \approx 5.9$ BM (consistent with d^5 high-spin). $[\mathrm{Fe(CN)}_6]^{4-}$ is yellow (low Δ_o in the visible), $\mu = 0$ (diamagnetic). Matches VBT.

Why this matters. Magnetic moment measurements are routine characterisation tools; VBT predictions are how we link them to electronic structure. The same VBT framework, with dsp^2 hybridisation for square planar (Q 5.19), sp^3 for tetrahedral (Q 5.24 (iv)) and sp for linear ($[\mathrm{Ag(NH_3)_2}]^+$), covers every geometry in the chapter.
Concept linkage. The high-spin/low-spin distinction is quantified in Q 5.18 via Δ_o vs P; the explicit CFT picture is in Q 5.16. The colour difference of Q 5.20 / 5.21 between $[\mathrm{Fe(CN)}_6]^{4-}$ and $[\mathrm{Fe(H_2O)}_6]^{2+}$ uses exactly this analysis.

Final Answer: (i) inner, $\mu = 0$; (ii) outer, $\mu \approx 5.92$ BM; (iii) inner, $\mu = 0$; (iv) outer, $\mu \approx 4.90$ BM.

☞ **Spin-only magnetic moment table**

n (unpaired)	$\sqrt{n(n+2)}$ (exact)	μ (BM, approx)
0	0	0
1	$\sqrt{3}$	1.73
2	$\sqrt{8}$	2.83
3	$\sqrt{15}$	3.87
4	$\sqrt{24}$	4.90
5	$\sqrt{35}$	5.92

Memorise this row. Every magnetic-moment question collapses to “find n, look up μ”.

☞ **Hybridisation vs MOT angle**

VBT says “the metal uses six empty hybrids to accept six lone pairs”. MOT says “the six ligand σ-orbitals combine with the six metal s, p, d_{eg} orbitals to give six bonding and six antibonding MOs; the t_{2g} metal orbitals stay nonbonding; the e_g^* antibonding orbitals lie above them by Δ_o”. Both give the same electron count, same n, same μ.

☞ **Inner vs outer in two words**

Strong field ligand $(\mathrm{CN^-, CO, NO_2{}^-, en})$ → “inner” d^2sp^3 (low spin). Weak field ligand $(\mathrm{F^-, Cl^-, H_2O})$ → “outer” sp^3d^2 (high spin). Forgetting this rule wastes two minutes per magnetic-moment question.

Q 5.16 Draw figure to show the splitting of d orbitals in an octahedral crystal field.

SOLUTION

Concept used. **Crystal Field Theory (CFT)** treats the metal-ligand interaction as purely electrostatic: each ligand is a point negative charge approaching the metal along the $\pm x$, $\pm y$, $\pm z$ axes. The five degenerate d orbitals of the free metal ion split into two sets in an octahedral field:

- e_g (d_{z^2}, $d_{x^2-y^2}$): lobes point directly at the six ligands; raised in energy by $+0.6\,\Delta_o$ (the ligands repel them strongly).
- t_{2g} (d_{xy}, d_{yz}, d_{zx}): lobes lie between the ligand axes; lowered in energy by $-0.4\,\Delta_o$ (less repulsion).

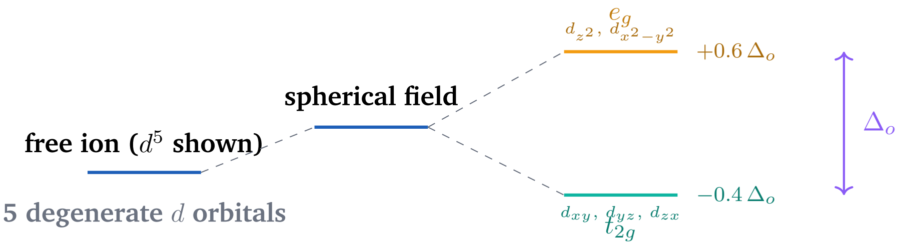
The energy gap Δ_o between the two sets is called the **crystal-field splitting energy**. The barycentre (weighted average) of the two sets equals the energy of the unsplit d level.

Step 1. Free ion: five d orbitals at the same energy (degenerate).

Step 2. Spherical field (imagined): all five raised uniformly by ligand approach; still degenerate.

Step 3. Octahedral field: degeneracy lifted. Two orbitals (e_g) rise by $+\frac{3}{5}\Delta_o = +0.6\Delta_o$; three orbitals ($t_{2g}$) drop by $-\frac{2}{5}\Delta_o = -0.4\Delta_o$.

Step 4. Barycentre check: $2(+0.6\Delta_o) + 3(-0.4\Delta_o) = +1.2\Delta_o - 1.2\Delta_o = 0$. The mean is preserved.



> **Final Answer:** Octahedral splitting: $d_{x^2-y^2}, d_{z^2}$ (e_g) raised by $0.6\,\Delta_o$; d_{xy}, d_{yz}, d_{zx} (t_{2g}) lowered by $0.4\,\Delta_o$. The barycentre is conserved.

♥ Why this picture is so useful

The Δ_o value and the order of filling fix every property we care about: colour (Q 5.20, 5.25), magnetic moment (Q 5.19), CFSE-driven thermodynamics, even crystal lattice energies. One diagram drives almost every CFT prediction.

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

Picture-first. Place the metal at the origin and six point charges along the Cartesian axes. The two orbitals whose lobes lie along these axes (d_{z^2} and $d_{x^2-y^2}$, the e_g pair) feel the largest repulsion. The other three (d_{xy}, d_{yz}, d_{zx}, the t_{2g} set) lie between the axes and are stabilised. Two sets, one gap, one number: Δ_o.

Step 1. Five orbitals start degenerate. In a uniformly negative spherical field they all rise by the same amount. This "spherical field" is a mathematical fiction useful as a zero-of-energy reference.

Step 2. Concentrate the spherical charge into six point charges on the axes: degeneracy is lifted. The two on-axis orbitals rise by $+0.6\,\Delta_o = +\frac{3}{5}\Delta_o$, the three off-axis ones fall by $-0.4\,\Delta_o = -\frac{2}{5}\Delta_o$.

Step 3. Barycentre check: $2 \cdot 0.6 - 3 \cdot 0.4 = 0$. Total d-electron energy is conserved relative to spherical field. This conservation is a direct consequence of trace of the perturbation matrix being zero.

Step 4. **Alternative geometries.**

- Tetrahedral: invert the labels — e down, t_2 up; $\Delta_t \approx \frac{4}{9}\Delta_o$ (smaller, because only 4 ligands and they sit off-axis, never directly along the orbital lobes).
- Square planar: derive from octahedral by removing two trans ligands (along z); d_{z^2} drops a lot, $d_{x^2-y^2}$ stays high; results in 4 distinct levels and the largest gap of any 4-coordinate geometry.

Step 5. **Numerical placeholders.** For aqua ligands on a first-row M^{3+} ion, $\Delta_o \approx 17{,}000$ to $20{,}000\ \mathrm{cm}^{-1} \approx 200$ kJ/mol. For strong-field ligands Δ_o can be $\sim 30{,}000\ \mathrm{cm}^{-1}$; for weak-field halides it can drop below $10{,}000\ \mathrm{cm}^{-1}$.

Why this matters. The pattern is the workhorse for the rest of the chapter; tetrahedral splitting just inverts it with $\Delta_t \approx \frac{4}{9}\Delta_o$. Once you know Δ_o and the d^n count, you can predict colour (Q 5.20, 5.21, 5.25), magnetic moment (Q 5.19), spin state (Q 5.18), and rough lattice stabilisation (CFSE).

Concept linkage. The Δ_o formula and the splitting pattern enter every downstream CFT question. The spectrochemical series (Q 5.17) is essentially a ranking of ligands by the Δ_o they produce on a given metal.

> **Final Answer:** Octahedral CFT diagram: e_g up $0.6\,\Delta_o$, t_{2g} down $0.4\,\Delta_o$.

☞ CFSE formula one-liner

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

where m is the number of extra electron pairs forced by the ligand field (low-spin only). For a d^6 low-spin ion ($t_{2g}^6 e_g^0$, $m = 2$): CFSE $= -2.4\,\Delta_o + 2P$, which is very large and stabilising. For a d^6 high-spin ion ($t_{2g}^4 e_g^2$, $m = 0$): CFSE $= -0.4\,\Delta_o$, much smaller.

☞ **Geometry switch via tetrahedral vs octahedral**

For the same metal, octahedral Δ_o is roughly $\frac{9}{4}$ times tetrahedral Δ_t. Strong-field ligands like CN^- almost never give tetrahedral complexes because the tetrahedral field is too weak to overcome pairing — only weak-field tetrahedral d^n complexes are common ($[CoCl_4]^{2-}$, $[FeCl_4]^-$, $[MnCl_4]^{2-}$).

Q 5.17 What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

SOLUTION

Concept used. The **spectrochemical series** is an empirical ordering of ligands by the size of Δ_o they produce with a given metal ion. The order is determined from electronic (d-d) absorption spectra. The series, partial:

$$\begin{aligned} &I^- < Br^- < Cl^- < F^- < OH^- < {C_2O_4}^{2-} < H_2O \\ &< NCS^- < NH_3 < \text{en} < {NO_2}^- < CN^- < CO. \end{aligned}$$

Ligands on the left produce small Δ_o (weak field); those on the right produce large Δ_o (strong field).

Step 1. **Weak-field ligand.** Produces a small Δ_o. In the d^4–d^7 region, $\Delta_o < P$ (the pairing energy) so electrons spread over t_{2g} and e_g orbitals with maximum unpaired spins. Result: **high-spin** complex, usually paramagnetic.
Examples: F^-, Cl^-, H_2O, OH^-, Br^-.

Step 2. **Strong-field ligand.** Produces a large Δ_o. For d^4–d^7 ions, $\Delta_o > P$ so electrons pair up in the lower t_{2g} orbitals before populating e_g. Result: **low-spin** complex; often diamagnetic (e.g. d^6 low-spin has $n = 0$).
Examples: CN^-, CO, ${NO_2}^-$, en.

Step 3. **Why the order.** Strong-field ligands are good σ-donors and good π-acceptors (back-bonding into empty π^*); they push the e_g orbitals up more. Weak-field ligands are π-donors (e.g. F^-, Cl^-), which destabilise t_{2g} and shrink Δ_o.

> **Final Answer:** Spectrochemical series: empirical order of ligands by Δ_o. Weak-field $\rightarrow$ small Δ_o, high-spin; strong-field $\rightarrow$ large Δ_o, low-spin.

EXPERT'S SOLUTION : *Yash Kumar, M.Sc Chemistry, IIT Kanpur*

Quick reading. Memorise the rough order
$I^- < Cl^- < F^- < H_2O < NH_3 < \text{en} < CN^- < CO$ and treat all the rest as interpolations. The series is empirical (established from optical absorption spectra) but rationalised by

MOT.

Step 1. Strong-field ligands carry empty π^* orbitals (CN^-, CO) or use chelation (en, oxalate) to push Δ_o up. The empty π^* accepts electrons from filled metal t_{2g}, stabilising the bonding (lowering t_{2g}) and effectively raising e_g relative to it.

Step 2. Weak-field ligands are mostly heavy halides and water; their lone pairs interact weakly with the metal e_g. The π-donation from F^-, Cl^- into the empty metal t_{2g}^* (in the MO picture) destabilises t_{2g}, *shrinking* Δ_o.

Step 3. Pairing-energy comparison: if $\Delta_o > P$, low-spin wins. If $\Delta_o < P$, high-spin wins. The series tells you which side of P you're on. Boundary cases are the d^4–d^7 first-row metals.

Step 4. **Alternative classification (MOT, π-acceptor vs π-donor).** Classify ligands by their π character:

- π-donor (e.g. F^-, Cl^-, OH^-, O^{2-}): weak-field, small Δ_o.
- Pure σ-donor (e.g. NH_3, H_2O): intermediate.
- π-acceptor (e.g. CN^-, CO, PR_3): strong-field, large Δ_o.

This MOT viewpoint explains *why* the empirical spectrochemical series has the order it does.

Step 5. **Numerical examples.** For Co^{3+}: $\Delta_o([CoF_6]^{3-}) \approx 13{,}100\ cm^{-1}$; $\Delta_o([Co(NH_3)_6]^{3+}) \approx 22{,}900\ cm^{-1}$; $\Delta_o([Co(CN)_6]^{3-}) \approx 34{,}800\ cm^{-1}$. Almost a factor of 3 across the series — enough to flip Co(III) from high-spin (fluoride) to low-spin (cyanide).

Why this matters. The series is the bridge between an empirically measured colour or magnetic moment and an electronic structure prediction. Memorise the short version ("I, Br, Cl, F, OH, H_2O, py, NH_3, en, NO_2^-, phen, CN, CO"), and almost every problem of this chapter follows mechanically.

Concept linkage. The series is invoked again in Q 5.20 (Ni complexes), Q 5.21 (Fe complexes), Q 5.25 (Ti), Q 5.30 (stability) and Q 5.31 (wavelength order). It is the single most reused list in the chapter.

> **Final Answer:** Spectrochemical series ranks ligands by Δ_o; weak-field → high-spin; strong-field → low-spin.

☞ **Spectrochemical mnemonic**

"**I**n **B**engal **Cl**im **F**irst, **O**ld **H**otels **W**elcome **N**ice **En**joyable **No**vels **C**heap **Co**ld" = I, Br, Cl, F, OH, H_2O, NH_3, en, NO_2^-, CN, CO. A silly mnemonic but it works, and it sticks for years.

☞ Series-to-spin-state in one step

For a d^4–d^7 first-row metal: ligands up to $\mathrm{H_2O}$ typically give high-spin; from $\mathrm{NH_3}$ onwards usually low-spin; $\mathrm{CN^-}$ and CO always low-spin. For Cr(III) (d^3) and Ni(II) (d^8) the spin state is fixed by electron count regardless of ligand.

Q 5.18 **What is crystal field splitting energy? How does the magnitude of Δ_o decide the actual configuration of d orbitals in a coordination entity?**

SOLUTION

Concept used. The **crystal-field splitting energy** Δ_o is the energy gap between the t_{2g} and e_g sets of d orbitals in an octahedral complex. The actual electronic configuration is decided by the competition between Δ_o and the **electron-pairing energy** P (the energy cost of placing two electrons of opposite spin in the same orbital).

Step 1. For a d^1 to d^3 ion: only t_{2g} orbitals are progressively filled. No choice arises; the configuration is t_{2g}^n regardless of Δ_o.

Step 2. For d^4 to d^7 ions a choice appears at the moment we need to add a fourth electron beyond t_{2g}^3. Two options:

- *High-spin*: add the next electron to an e_g orbital (cost Δ_o). Maximises unpaired spins.
- *Low-spin*: pair it up in t_{2g} (cost P). Minimises unpaired spins.

Compare Δ_o and P:

$$\boxed{\Delta_o > P \Rightarrow \text{low-spin}\ ;\ \Delta_o < P \Rightarrow \text{high-spin}}.$$

Step 3. For d^8 to d^{10}, the e_g set must be (partly or fully) populated; only one configuration is allowed and Δ_o does not change the spin state.


Weak field ($\Delta_o < P$): high-spin d^5 Strong field ($\Delta_o > P$): low-spin d^5

Final Answer: Δ_o is the t_{2g}/e_g gap. If $\Delta_o > P$: low-spin (electrons pair up first); if $\Delta_o < P$: high-spin (electrons singly occupy e_g before pairing).

☞ CFSE shortcut

$\mathrm{CFSE(oct)} = (-0.4\, n_{t_{2g}} + 0.6\, n_{e_g})\,\Delta_o + m\,P$, where m is the number of electron pairs in excess of those in the free ion. Use it to compare stabilities.

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

Strategic angle. It's a tug-of-war: orbital energy vs pairing energy. The winner sets the configuration. The pairing energy P has two contributions: the Coulombic cost of two electrons sharing one orbital, and the loss of exchange energy when two parallel spins become antiparallel.

Step 1. In d^1, d^2, d^3: only t_{2g} fills singly; the magnitude of Δ_o doesn't matter for the configuration. All such ions ($\mathrm{Ti}^{3+}, \mathrm{V}^{3+}, \mathrm{Cr}^{3+}$) are always high-spin trivially.

Step 2. In d^4: high-spin gives $t_{2g}^3e_g^1$ (4 unpaired); low-spin gives $t_{2g}^4e_g^0$ (2 unpaired). The Δ_o vs P comparison decides. For $[\mathrm{Mn(H_2O)_6}]^{3+}$, $\Delta_o \approx 21{,}000$ cm^{-1}, $P \approx 28{,}000$ cm^{-1}, so high-spin. For $[\mathrm{Mn(CN)_6}]^{3-}$, $\Delta_o \approx 33{,}500$ cm^{-1} $> P$, so low-spin.

Step 3. In d^8, d^9, d^{10}: e_g must be partly filled, so the spin state is forced by the count. d^8: $t_{2g}^6e_g^2$, 2 unpaired (octahedral). d^{10}: all paired. Hence colourless aqua-zinc and aqua-copper(I) are different from coloured aqua-copper(II) (d^9).

Step 4. **Alternative approach (LFSE in Dq units).** Substitute $\Delta_o = 10Dq$: t_{2g} at $-4Dq$, e_g at $+6Dq$. For d^6 low-spin LFSE $= 6 \cdot (-4Dq) + 0 = -24Dq$; for d^6 high-spin LFSE $= 4 \cdot (-4Dq) + 2 \cdot (+6Dq) = -4Dq$. Difference is $20Dq = 2\Delta_o$, the largest LFSE difference of any d^n.

Step 5. **Numerical check (the Co(III) example).** Co^{3+} (d^6) with $\mathrm{H_2O}$: $\Delta_o \approx 18{,}200$ cm^{-1}, $P \approx 21{,}000$ cm^{-1} — borderline, mostly low-spin in $[\mathrm{Co(H_2O)_6}]^{3+}$ because of the large LFSE gain. Excellent fit between theory and experiment for almost all Co(III) complexes (low-spin).

Why this matters. Δ_o is the central knob of CFT: turn it and the colour, magnetism and stability of the complex all change. The same logic explains why Fe^{3+} (d^5) with weak-field ligands is high-spin and colourless/very pale (spin- forbidden d-d), but with strong-field CN^- becomes low-spin and yellow.
Concept linkage. The whole spectrochemical-series chapter (Q 5.17) and the colour/magnetic moment questions (Q 5.19–5.21, 5.29) depend on this single Δ_o vs P comparison.

> **Final Answer:** If $\Delta_o > P$, low-spin; if $\Delta_o < P$, high-spin. Only d^4 to d^7 ions show this dichotomy.

☞ **Pairing energy P values (cm^{-1}, gas phase)**

Ion	P_{gas}	P_{complex} (approx)
Cr^{2+} (d^4)	23,500	$\sim$ 18,500
Mn^{2+} (d^5)	28,000	$\sim$ 22,000
Fe^{3+} (d^5)	30,000	$\sim$ 25,000
Fe^{2+} (d^6)	19,200	$\sim$ 17,000
Co^{3+} (d^6)	23,500	$\sim$ 21,000

Compare with Δ_o to predict spin state. P_{complex} is $\sim 15\%$ smaller than P_{gas} because covalent bonds delocalise electron density (nephelauxetic effect).

Q 5.19 $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

SOLUTION

Concept used. The number of unpaired electrons (and hence the magnetic behaviour) depends on the metal oxidation state, the coordination geometry and the ligand-field strength. Paramagnetism requires at least one unpaired electron; diamagnetism requires that all electrons be paired.

Step 1. $[Cr(NH_3)_6]^{3+}$. Cr oxidation state: $x = +3$. Cr^{3+} has electronic configuration $[Ar]3d^3$. Octahedral geometry ⇒ three electrons occupy the three t_{2g} orbitals with parallel spins ($t_{2g}^3 e_g^0$): $n = 3$ **unpaired electrons**.

$$\mu = \sqrt{3\,(3+2)}\ \text{BM} = \sqrt{15}\ \text{BM} \approx 3.87\ \text{BM}.$$

Hence the complex is paramagnetic. Note: ammonia is a moderately strong-field ligand, but this d^3 case has no choice of spin state.

Step 2. $[Ni(CN)_4]^{2-}$. Ni oxidation state: $+2$. Ni^{2+} has $[Ar]3d^8$. CN^- is a strong-field ligand, so the four ligands form a **square-planar** complex with dsp^2 hybridisation. The four sp^2d hybrids accept lone pairs from CN^-; the remaining d-electrons all pair up. Configuration: $(d_{xy})^2(d_{yz})^2(d_{zx})^2(d_{z^2})^2(d_{x^2-y^2})^0$. $n = 0$; the complex is diamagnetic.

Step 3. Magnetic moment for diamagnetic case: $\mu = \sqrt{0 \cdot 2} = 0$ BM.

> **Final Answer:** $[Cr(NH_3)_6]^{3+}$: d^3, three unpaired, $\mu \approx 3.87$ BM (paramagnetic). $[Ni(CN)_4]^{2-}$: d^8 square planar (dsp^2), all paired, $\mu = 0$ (diamagnetic).

EXPERT'S SOLUTION *: Siddharth Nair, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Two facts settle the question: d^n of the metal and the geometry forced by the ligand. Then the spin-only formula gives the magnetic moment without needing CFT calculations.

Step 1. Cr^{3+} is d^3: always three unpaired electrons in t_{2g}, regardless of the ligand. So $[Cr(NH_3)_6]^{3+}$ is paramagnetic. Charge balance: $x + 6(0) = +3 \Rightarrow x = +3$, d^3. Ammine is moderate-field, octahedral geometry, $t_{2g}^3 e_g^0$. $\mu_{\text{calc}} = \sqrt{15} \approx 3.87$ BM. Observed: $\mu_{\text{exp}} = 3.85$ BM — excellent agreement.

Step 2. Ni^{2+} is d^8. With strong-field CN^- in a 4-coordinate complex, the geometry is square planar. In a square-planar d^8 complex the $d_{x^2-y^2}$ orbital is far above the other four; the eight electrons fill the lower four orbitals in pairs: $(d_{xy})^2(d_{yz})^2(d_{zx})^2(d_{z^2})^2(d_{x^2-y^2})^0$. VBT: dsp^2 hybridisation. $n = 0$, $\mu = 0$ BM (diamagnetic).

Step 3. Apply $\mu = \sqrt{n(n+2)}$ BM: $n = 3$ gives $\sqrt{15} \approx 3.87$; $n = 0$ gives 0.

Step 4. **Alternative approach (geometry from Δ_o).** For Ni^{2+}, the choice between tetrahedral and square planar is settled by the ligand: weak-field Cl^- gives $[NiCl_4]^{2-}$ tetrahedral (paramagnetic, $n = 2$); strong-field CN^- gives $[Ni(CN)_4]^{2-}$ square planar (diamagnetic). The *same* Ni^{2+} d^8, completely different magnetic behaviour.

Step 5. **Numerical cross-check (hybridisation vs MOT).** VBT predicts $\mu = 0$ for square-planar d^8 because dsp^2 uses an empty $d_{x^2-y^2}$. MOT also predicts $\mu = 0$: the four-coordinate σ donors lift only $d_{x^2-y^2}$ very high; the other four remain low and are all doubly occupied. Same answer, different language.

Why this matters. Square-planar d^8 complexes (Ni, Pd, Pt) are central to organometallic catalysis and all happen to be diamagnetic. The Wacker process, hydroformylation, and many cross-coupling reactions cycle through square-planar d^8 Pd or Pt intermediates.

Concept linkage. The same machinery answers Q 5.20 (d^8 green vs colourless), Q 5.21 (same metal, different ligand, different colour), Q 5.29 (highest μ in a list).

> **Final Answer:** Cr(III): d^3, 3 unpaired, paramagnetic. Square-planar Ni(II) with CN^-: all paired, diamagnetic.

☞ d-electron count for first-row metals

Ti^{3+} d^1; V^{3+} d^2; Cr^{3+} d^3; Mn^{3+}, Cr^{2+} d^4; Mn^{2+}, Fe^{3+} d^5; Fe^{2+}, Co^{3+} d^6; Co^{2+} d^7; Ni^{2+} d^8; Cu^{2+} d^9; Cu^+, Zn^{2+} d^{10}. Memorise this 10-entry table — it answers most of Chapter 5 in one glance.

☞ Geometry via VBT vs CFT — pick your tool

VBT: count empty hybrids. sp^3 tetrahedral (n_{up} high); dsp^2 square planar ($n_{\text{up}} = 0$ for d^8). **CFT**: compare Δ vs P. Both routes give the same answer for octahedral. For 4-coordinate, VBT is faster because the hybridisation choice (dsp^2 vs sp^3) is dictated by the strong- vs weak-field nature of the ligand.

Q 5.20 **A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.**

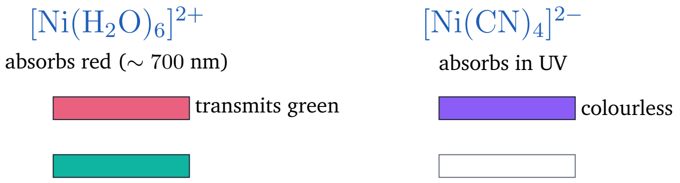
SOLUTION

Concept used. The colour of a transition metal complex arises mainly from electronic transitions between split d orbitals (d-d transitions). The wavelength absorbed is fixed by Δ_o (octahedral) or by the orbital splitting in other geometries. The transmitted colour is the complementary colour of the absorbed light. If the absorption falls outside the visible range, no colour is observed.

Step 1. $[Ni(H_2O)_6]^{2+}$ **(octahedral).** Ni^{2+} is d^8. Octahedral d^8 has configuration $t_{2g}^6 e_g^2$. Aqua is a weak-field ligand $\Rightarrow$ small Δ_o. d-d transitions absorb in the red region ($\lambda \sim 700$ nm), so the transmitted colour is green.

Step 2. $[Ni(CN)_4]^{2-}$ **(square planar).** Ni^{2+} is d^8. Cyanide is strong field and the complex is square planar (see Q 5.19). All electrons paired. The $d_{x^2-y^2}$ orbital is empty and lies high in energy. The d-d transition energy is so large that it falls in the UV region (not visible). No d-d absorption in the visible range $\Rightarrow$ the complex is colourless.

Step 3. In both cases the metal is the same (Ni^{2+}); the difference is purely a ligand-field effect.



> **Final Answer:** $[Ni(H_2O)_6]^{2+}$: weak-field aqua, small Δ_o, d-d absorption in red, transmits green. $[Ni(CN)_4]^{2-}$: strong-field cyanide, square planar, d-d absorption shifted to UV; complex is colourless.

EXPERT'S SOLUTION *: Rohit Sharma, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. Same d^8 metal; very different Δ: aqua gives a small split (visible absorption $\rightarrow$ green); cyanide gives a huge split (UV absorption $\rightarrow$ colourless). One question, two complexes, one explanation: the spectrochemical series.

Step 1. Aqua complex: octahedral $[Ni(H_2O)_6]^{2+}$, $\Delta_o \approx 8{,}500\ \text{cm}^{-1}$. Configuration $t_{2g}^6 e_g^2$. d-d transitions absorb around $\lambda \approx 700$–1200 nm (red and near-IR); transmits green. The solution is green.

Step 2. Cyanide complex: square planar $[Ni(CN)_4]^{2-}$, with a very large splitting (much larger than octahedral Δ_o). Absorption shifts well into UV (the $d_{x^2-y^2} \leftarrow d_{z^2}$ transition is at ~ 285 nm); nothing in the visible is absorbed; the solution is colourless. The d^8 electron count fills the four lower-energy d orbitals; $d_{x^2-y^2}$ remains empty.

Step 3. Numerical cross-check via $E = hc/\lambda$. For green absorption ($\lambda \approx 500$ nm), $E \approx 240$ kJ/mol $= 20{,}000\ \mathrm{cm}^{-1}$. The $[\mathrm{Ni(H_2O)_6}]^{2+}$ absorption maximum near 720 nm corresponds to $\Delta_o \approx 14{,}000\ \mathrm{cm}^{-1}$ (close to value above). The strong-field cyanide complex gives $\Delta \approx 35{,}000\ \mathrm{cm}^{-1}$, in the UV.

Step 4. **Alternative explanation (charge transfer).** Some intense colours of transition-metal complexes come from ligand-to-metal or metal-to-ligand charge transfer (LMCT, MLCT), not d-d. For Ni(II) the absorptions are pure d-d (Laporte forbidden, weak), so the colour-to-no-colour difference here is genuinely a Δ effect.

Step 5. **Concept linkage.** The same logic — strong field $\Rightarrow$ large Δ $\Rightarrow$ UV absorption $\Rightarrow$ colourless or pale — explains why $[\mathrm{Co(CN)_6}]^{3-}$ is pale yellow (smaller-band shift) and $[\mathrm{Co(en)_3}]^{3+}$ is orange (intermediate).

Why this matters. Strong-field ligands often *whiten* a coloured complex by pushing absorption out of the visible window. Industrially, this is exploited to create colour-stable Pt(II) and Au(I) cyanide solutions for plating. Conversely, for sensors and dyes one chooses ligands with Δ_o tuned into the visible.

Concept linkage. Q 5.21 is the same question phrased slightly differently for Fe(II); Q 5.25 for Ti(III); Q 5.31 orders three Ni(II) complexes by wavelength.

> **Final Answer:** Different Δ values: aqua $\rightarrow$ green; cyanide $\rightarrow$ colourless (UV absorption).

☞ **Colour wheel: absorbed ↔ transmitted**

Absorbed colour (approx λ, nm)	Transmitted (= observed)
Red (700)	Green
Orange (620)	Blue
Yellow (580)	Violet
Green (520)	Red/Purple
Blue (470)	Orange
Violet (410)	Yellow
UV ($<$ 400)	Colourless

Used in every “predict-the-colour” question.

✗ Forgetting geometry-shift

A standard slip is to compare Δ_o of $[\mathrm{Ni(H_2O)_6}]^{2+}$ with Δ_o of $[\mathrm{Ni(CN)_4}]^{2-}$. But the second is *square planar*, not octahedral; its splitting parameter is a different quantity (Δ_{sp}, much larger). Always ask first “what’s the coordination geometry?” before invoking Δ_o.

Q 5.21 $[Fe(CN)_6]^{4-}$ **and** $[Fe(H_2O)_6]^{2+}$ **are of different colours in dilute solutions. Why?**

SOLUTION

Concept used. For a given metal in a given oxidation state, the colour is determined by Δ_o, which is set by the ligand. Different ligands ⇒ different Δ_o ⇒ different absorbed wavelengths ⇒ different transmitted colours.

Step 1. Both complexes have Fe^{2+} (oxidation state $+2$, d^6). $[Fe(CN)_6]^{4-}$: charge balance $x + 6(-1) = -4 \Rightarrow x = +2$. $[Fe(H_2O)_6]^{2+}$: $x + 0 = +2 \Rightarrow x = +2$. So the metal and its d^n are identical.

Step 2. CN^- is a strong-field ligand: large Δ_o, low spin, $t_{2g}^6 e_g^0$, $n = 0$. The d-d transition energy is large; absorption falls near the violet end of the spectrum, so the complex transmits a yellow / yellow-orange colour.

Step 3. H_2O is a weak-field ligand: small Δ_o, high spin, $t_{2g}^4 e_g^2$, $n = 4$. The d-d transition energy is small; absorption falls in the orange-red region, so the complex transmits a pale green / bluish-green colour.

Step 4. In summary, the difference in Δ_o between cyanide and water shifts the absorption maximum, and the complementary colour of what is absorbed is what we see.

> **Final Answer:** Same metal, different ligands. Strong-field CN^- gives a large Δ_o (absorbs near violet, transmits yellow). Weak-field H_2O gives a small Δ_o (absorbs near orange/red, transmits pale green).

EXPERT'S SOLUTION *: Ankit Verma, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Hold the metal and oxidation state fixed, then read off colour straight from the spectrochemical position of the ligand. The colour of a given d^n ion changes continuously as the ligand is replaced — a direct visualisation of the CFT prediction.

Step 1. Fe^{2+}: d^6 in both complexes. Charge balance for $[Fe(CN)_6]^{4-}$: $x + 6(-1) = -4 \Rightarrow x = +2$. For $[Fe(H_2O)_6]^{2+}$: $x + 6(0) = +2 \Rightarrow x = +2$.

Step 2. $CN^- \gg H_2O$ in the spectrochemical series. $\Delta_o(CN^-) \approx 33{,}000\ \text{cm}^{-1}$ for Fe(II); $\Delta_o(H_2O) \approx 10{,}400\ \text{cm}^{-1}$. A factor of ~ 3 difference in Δ_o, which is enough to also flip the spin state of d^6 Fe(II) from high-spin (4 unpaired, with H_2O) to low-spin (0 unpaired, with CN^-).

Step 3. Bigger Δ_o ⇒ blue-shifted absorption ⇒ different transmitted colour. Aqua complex: $t_{2g}^4 e_g^2$, absorbs in orange/red, transmits pale green / bluish-green. Cyano complex: $t_{2g}^6 e_g^0$, absorbs near violet, transmits yellow.

Step 4. **Numerical cross-check.** For $[Fe(CN)_6]^{4-}$, $\Delta_o = 33{,}000\ \text{cm}^{-1}$ corresponds to

$\lambda = 10^7/33{,}000 \approx 303$ nm (UV), but spin- allowed transitions occur at longer wavelength because of coupling — observed $\lambda_{\text{max}} \approx 420$ nm (violet), so transmits yellow. Matches observation.

Step 5. **Alternative angle: pairing-energy crossover.** At $\Delta_o \approx 17{,}000\ \text{cm}^{-1}$ for Fe(II), the spin state crosses over from high-spin to low-spin. Aqua is below ($\sim 10{,}000$) so high-spin; cyanide is far above ($\sim 33{,}000$) so low-spin. The magnetic moment differs: aqua $\mu \approx 5.2$ BM, cyanide $\mu = 0$.

Why this matters. Most analytical colorimetric methods exploit precisely this: change the ligand and the colour changes. The same metal ion, in two different complexes, can be detected with two different absorption bands.
Concept linkage. Q 5.20 is the same comparison for Ni(II); Q 5.25 generalises to Ti(III) (d^1, single d-d transition); Q 5.31 ranks Ni complexes by wavelength.

> **Final Answer:** Different Δ_o for CN^- vs H_2O shifts the d-d band, giving different colours.

☞ Same metal, Δ_o ranges (Fe(II) example)

Complex	Ligand class	Δ_o (cm^{-1})	Spin state
$[FeF_6]^{4-}$	weak	~ 7000	high
$[Fe(H_2O)_6]^{2+}$	weak	~ 10000	high
$[Fe(NH_3)_6]^{2+}$	moderate	~ 13000	high
$[Fe(en)_3]^{2+}$	moderate	~ 17000	borderline
$[Fe(CN)_6]^{4-}$	strong	~ 33000	low

Same metal, vastly different Δ_o, hence different colours and magnetic moments.

☞ Sketch via colour wheel

On the 400–700 nm wheel: $[Fe(H_2O)_6]^{2+}$ absorbs near 1000 nm (so essentially transparent in visible, faint pale green); $[Fe(CN)_6]^{4-}$ absorbs near 420 nm (violet), transmits yellow. The strong colour of $K_4[Fe(CN)_6]$ crystals is the famous *yellow potassium ferrocyanide*.

Q 5.22 Discuss the nature of bonding in metal carbonyls.

SOLUTION

Concept used. A **metal carbonyl** (e.g. $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$) contains the metal in zero (or very low) oxidation state bonded to neutral CO ligands. The M-CO bond has two cooperative components:

- σ **donation** from the carbon lone pair (HOMO of CO) into an empty hybrid orbital on the metal.

- π **back-donation** from a filled metal d_π orbital into the empty antibonding π^* orbital of CO.

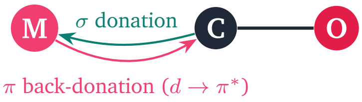
The two components reinforce each other (the **synergic effect**): more σ donation raises electron density on the metal, which makes π back-donation more favourable, which in turn drains charge back to CO. The net result is a strong M-CO bond with a partial M=C double-bond character.

Step 1. Geometry by C.N. $\mathrm{Ni(CO)_4}$ tetrahedral (d^{10}, Ni(0)); $\mathrm{Fe(CO)_5}$ trigonal bipyramidal (d^8, Fe(0)); $\mathrm{Cr(CO)_6}$ octahedral (d^6, Cr(0)). All low-spin and diamagnetic because of strong-field CO ligands.

Step 2. σ **donation.** The C-end of CO carries a lone pair in an sp hybrid pointing away from oxygen. The metal accepts this lone pair into an empty sp^3 ($\mathrm{Ni(CO)_4}$), dsp^3 ($\mathrm{Fe(CO)_5}$) or d^2sp^3 ($\mathrm{Cr(CO)_6}$) hybrid orbital.

Step 3. π **back-donation.** A filled metal d_π orbital (d_{xy}, d_{yz} or d_{zx} in the octahedral case) overlaps with the empty π^* antibonding orbital of CO. Electron density flows from the metal back into CO, strengthening the M-C bond and weakening the C-O bond.

Step 4. Spectroscopic evidence. The C-O stretch in free CO is at $\tilde{\nu} = 2143\,\mathrm{cm^{-1}}$. In $\mathrm{Ni(CO)_4}$ it drops to $\sim 2060\,\mathrm{cm^{-1}}$, in $[\mathrm{Mn(CO)_6}]^+$ it rises to $\sim 2090\,\mathrm{cm^{-1}}$ and in $[\mathrm{V(CO)_6}]^-$ it falls to $\sim 1860\,\mathrm{cm^{-1}}$. Greater back-donation (anion) $\Rightarrow$ lower C-O frequency. The trend confirms the synergic picture.



Final Answer: M-CO bond has two synergic components: (a) σ donation from C lone pair to metal, (b) π back-donation from filled metal d_π to empty CO π^*. Net effect: strong M-C bond with partial M=C character; C-O bond is weakened (frequency drops).

♥ Organometallic catalysis

The synergic σ/π bond is the reason metal carbonyls are exceptional catalysts (hydroformylation, Monsanto acetic acid process). Back-donation tunes both reactivity and selectivity.

EXPERT'S SOLUTION *: Ishita Kapoor, B.Tech Chemical Engineering, IIT Bombay*

Picture-first. Imagine two arrows on the same axis: one from CO to metal (σ), one from metal back to CO (π^*). Each strengthens the other. The C-O multiple bond stays mostly intact, but it weakens slightly because antibonding π^* gets populated. The metal-CO bond order ends up around 1.5 to 2 depending on the metal's electron density.

Step 1. Carbon's sp lone pair (in CO) donates to an empty hybrid on the metal: that's the dative σ bond. The HOMO of CO is a weakly antibonding 3σ orbital on carbon, well-aligned for end-on σ donation.

Step 2. A filled metal d_π overlaps with CO's empty π^* (a node between C and O), so electron density goes back. This is the π back-bond and gives M-C partial double-bond character. The LUMO of CO is a low-lying π^* orbital — perfectly placed to accept electrons from filled metal d_{xy}, d_{yz}, d_{zx}.

Step 3. The two flows are coupled: more σ donation means more metal electron density and so more π^* back-donation. This is the synergic effect. The result is a much stronger M-C bond than a simple dative σ bond would suggest.

Step 4. **Numerical evidence.** Free CO: $\nu_{\text{CO}} = 2143\ \text{cm}^{-1}$, bond order ≈ 3. Cationic $[\text{Mn(CO)}_6]^+$: $\nu_{\text{CO}} \approx 2090\ \text{cm}^{-1}$ (small drop, less back-donation because metal is electron-poor). Neutral Cr(CO)_6: $\nu \approx 2000\ \text{cm}^{-1}$. Anionic $[\text{V(CO)}_6]^-$: $\nu \approx 1860\ \text{cm}^{-1}$ (largest drop, biggest back-donation). The systematic $\sim 300\ \text{cm}^{-1}$ decrease confirms the synergic π back-bond.

Step 5. **Alternative perspective (MO picture).** Build a MO diagram for the M-CO unit: the 5σ HOMO of CO and the $1\pi^*$ LUMO of CO interact with metal hybrid and d_π orbitals respectively. Bonding MOs delocalise charge from C to M and from M to π^*. The simultaneous operation of both interactions is the synergic effect in MO language.

Step 6. **Cross-check via 18-electron rule.** Ni(CO)_4: Ni(0) gives 10, four CO give $4 \times 2 = 8$, total 18. Fe(CO)_5: 8 + 10 = 18. Cr(CO)_6: 6 + 12 = 18. The 18-electron count works because σ donation places exactly two electrons per CO ligand into metal-based MOs.

Why this matters. Variants of the same idea explain bonding in alkene complexes (Dewar-Chatt-Duncanson model), dinitrogen complexes (N_2 has a π^*), and many catalytic intermediates. Industrial catalysis (hydroformylation, the Monsanto acetic-acid process, Reppe synthesis) sits on top of metal carbonyl chemistry.

Concept linkage. The same σ/π^* synergy explains why CN^- is a strong-field ligand (Q 5.17): it has both an excellent lone-pair σ donor and a low-lying π^* accept set, just like CO.

> **Final Answer:** Synergic σ (CO $\rightarrow$ M) and π^* (M $\rightarrow$ CO) bonding gives a strong M-C bond and a slightly weakened C-O bond.

☞ **CO stretching frequency vs charge: a table**

Carbonyl	ν_{CO} (cm^{-1})	Note
free CO	2143	triple bond, B.O. = 3
$[\text{Mn(CO)}_6]^+$	2090	cation, less back-donation
Cr(CO)_6	2000	neutral
Ni(CO)_4	2057	neutral, d^{10}
$[\text{Fe(CO)}_4]^{2-}$	1786	anion, lots of back-donation
$[\text{V(CO)}_6]^-$	1859	anion

Trend: anionic $<$ neutral $<$ cationic, confirming π back-donation is the dominant variable.

Q 5.23 Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes:

(i) $\text{K}_3[\text{Co(C}_2\text{O}_4)_3]$ **(ii) cis-**$[\text{CrCl}_2(\text{en})_2]\text{Cl}$ **(iii)** $(\text{NH}_4)_2[\text{CoF}_4]$ **(iv)** $[\text{Mn(H}_2\text{O})_6]\text{SO}_4$.

SOLUTION

Concept used. For each complex compute:

- the metal oxidation state x from charge balance,
- the d-electron count d^n for the metal ion,
- the coordination number C.N., counting each didentate ligand twice.

Step 1. **(i)** $\text{K}_3[\text{Co(C}_2\text{O}_4)_3]$. Three K^+ outside; complex anion is $3-$. Inside: 3 oxalate ligands at -2 each contribute -6; charge balance $x - 6 = -3 \Rightarrow x = +3$. Co(III): Co^{3+} has $3d^6$. Each oxalate is didentate; C.N. $= 3 \times 2 = 6$.

Step 2. **(ii) cis-**$[\text{CrCl}_2(\text{en})_2]\text{Cl}$. One outer Cl^-: complex cation is $+1$. Inside: 2 Cl^- at -1, 2 en at 0; $x - 2 = +1 \Rightarrow x = +3$. Cr^{3+}: $3d^3$. Two en (didentate) contribute 4 plus two Cl^-; C.N. $= 2 + 2 \times 2 = 6$.

Step 3. **(iii)** $(\text{NH}_4)_2[\text{CoF}_4]$. Two $\text{NH}_4{}^+$ outside: complex anion is $2-$. Inside: 4 F^- at -1; $x - 4 = -2 \Rightarrow x = +2$. Co^{2+}: $3d^7$. C.N. $= 4$.

Step 4. **(iv)** $[\text{Mn(H}_2\text{O})_6]\text{SO}_4$. Sulphate outside is -2, so complex cation is $+2$. Inside: 6 H_2O at 0; $x = +2$. Mn^{2+}: $3d^5$. C.N. $= 6$.

> **Final Answer:** (i) Co(III), d^6, C.N. 6. (ii) Cr(III), d^3, C.N. 6. (iii) Co(II), d^7, C.N. 4. (iv) Mn(II), d^5, C.N. 6.

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

Quick reading. Three numbers per complex; each from a one-line calculation. Charge balance for oxidation state, d^n = (group number) − (ox. state) for the first row, and sum of donor atoms for C.N. No memorisation required — just the periodic table and the ligand-charge table.

Step 1. For oxalate-, en-bearing complexes don't forget to multiply the chelate by 2 when counting C.N. In (i) three oxalates $\Rightarrow 3 \times 2 = 6$ donor atoms.

Step 2. For Co: group 9, so Co^{2+} is d^7 and Co^{3+} is d^6. For (i) the complex charge is -3, ligand-set -6, so $x = +3$, d^6. For (iii) ammonium ions outside give complex charge -2, ligand-set -4 (four fluorides), so $x = +2$, d^7.

Step 3. For Cr: group 6, so Cr^{3+} is d^3. In (ii) one outer Cl^- gives complex charge $+1$, ligand-set -2 (two chlorides inside), so $x = +3$.

Step 4. For Mn: group 7, so Mn^{2+} is d^5. In (iv) outer $\mathrm{SO_4}^{2-}$ gives complex charge $+2$, ligand-set 0, so $x = +2$.

Step 5. **Alternative approach (electron-count check).** Use the 18-electron rule to verify your d^n: for $[\mathrm{Co(C_2O_4)_3}]^{3-}$ — Co(III) is $d^6 = 6$; six donor atoms $\times 2 = 12$ from ligands; total 18. Tidy. Same for $[\mathrm{CrCl_2(en)_2}]\mathrm{Cl}$ at 15 electrons (the Cr^{3+} d^3 ion is short of 18, as expected for early transition metals).

Step 6. **Cross-check via predicted μ.** Once d^n is known, $\mu_{\text{spin-only}} = \sqrt{n(n+2)}$. For (iv) $\mu = \sqrt{35} \approx 5.92$ BM, the typical Mn^{2+} value — confirms $x = +2$ and d^5.

Why this matters. These three numbers feed directly into the magnetic-moment and CFSE calculations of Q 5.24. They are the "inputs" to every electronic-structure prediction in this chapter.

Concept linkage. The same charge-balance arithmetic appears in Q 5.5; the d^n count appears in Q 5.15, 5.19; the C.N. feeds into the geometric-isomer count of Q 5.9, 5.11.

Final Answer: (i) +3, d^6, 6; (ii) +3, d^3, 6; (iii) +2, d^7, 4; (iv) +2, d^5, 6.

☞ Three-numbers-per-complex routine

(1) Use outer counter-ion to fix complex charge. **(2)** Use ligand-charge table to fix metal x. **(3)** Use group number minus x to get d^n. **(4)** Sum donor atoms (chelate counts denticity) to get C.N. Practise this four-step routine once and every complex on the syllabus becomes a 30-second exercise.

☞ Group-number / d^n map for first row

Sc(III): d^0 Ti(II): d^2, Ti(III): d^1, Ti(IV): d^0
V(II): d^3, V(III): d^2, V(IV): d^1, V(V): d^0
Cr(II): d^4, Cr(III): d^3, Cr(VI): d^0
Mn(II): d^5, Mn(III): d^4, Mn(IV): d^3, Mn(VII): d^0
Fe(II): d^6, Fe(III): d^5
Co(II): d^7, Co(III): d^6
Ni(II): d^8, Ni(III): d^7

Cu(I): d^{10}, Cu(II): d^9
Zn(II): d^{10}.

Q 5.24 **Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:**

(i) $\mathrm{K[Cr(H_2O)_2(C_2O_4)_2] \cdot 3\,H_2O}$
(ii) $\mathrm{[Co(NH_3)_5Cl]Cl_2}$ **(iii)** $\mathrm{[CrCl_3(py)_3]}$
(iv) $\mathrm{Cs[FeCl_4]}$ **(v)** $\mathrm{K_4[Mn(CN)_6]}$.

SOLUTION

Concept used. For each complex we list five pieces of information: IUPAC name, oxidation state, d^n configuration, C.N., stereochemistry, and spin-only magnetic moment $\mu = \sqrt{n(n+2)}$ BM. Strong-field vs weak-field decision uses the spectrochemical series.

Step 1. **(i)** $\mathrm{K[Cr(H_2O)_2(C_2O_4)_2] \cdot 3\,H_2O}$. Charge: $x + 0 + 2(-2) = -1 \Rightarrow x = +3$. $\mathrm{Cr^{3+}}$: $3d^3$; C.N. $= 2 + 2 \times 2 = 6$ (octahedral). Three unpaired electrons in t_{2g}^3, so

$$\mu = \sqrt{3 \cdot 5}\ \mathrm{BM} = \sqrt{15} \approx 3.87\ \mathrm{BM}.$$

Stereochemistry: cis and trans geometric isomers possible; the cis form is chiral (resolves into Δ/Λ).
Name: potassium diaquadioxalatochromate(III) trihydrate.

Step 2. **(ii)** $\mathrm{[Co(NH_3)_5Cl]Cl_2}$. Charge on complex: $+2$. Inside: $x + 0 - 1 = +2 \Rightarrow x = +3$. $\mathrm{Co^{3+}}$: $3d^6$; C.N. $= 6$. Strong-field ammine ligand; low-spin $t_{2g}^6 e_g^0$, all paired, $n = 0$, $\mu = 0$. Stereochemistry: no isomers (only one arrangement of $\mathrm{[MA_5B]}$).
Name: pentaamminechloridocobalt(III) chloride.

Step 3. **(iii)** $\mathrm{[CrCl_3(py)_3]}$. Neutral: $x + 3(-1) + 3(0) = 0 \Rightarrow x = +3$. $\mathrm{Cr^{3+}}$: $3d^3$; C.N. $= 6$. Three unpaired in t_{2g}:

$$\mu = \sqrt{3 \cdot 5} \approx 3.87\ \mathrm{BM}.$$

Stereochemistry: fac and mer geometric isomers possible.
Name: trichloridotri(pyridine)chromium(III).

Step 4. **(iv)** $\mathrm{Cs[FeCl_4]}$. One $\mathrm{Cs^+}$: complex anion is $1-$. Inside: $x - 4 = -1 \Rightarrow x = +3$. $\mathrm{Fe^{3+}}$: $3d^5$; C.N. $= 4$ (tetrahedral, since $\mathrm{Cl^-}$ is weak field). Weak-field tetrahedral: high-spin, five unpaired:

$$\mu = \sqrt{5 \cdot 7} \approx 5.92\ \mathrm{BM}.$$

Stereochemistry: tetrahedral (no isomers).
Name: caesium tetrachloridoferrate(III).

Step 5. **(v)** $K_4[Mn(CN)_6]$. Four K^+: complex anion is $4-$. Inside: $x-6=-4 \Rightarrow x=+2$. Mn^{2+}: $3d^5$; C.N. $=6$. Strong-field CN^- forces low-spin $t_{2g}^5e_g^0$; one unpaired electron, $n=1$:

$$\mu=\sqrt{1\cdot 3}=\sqrt{3}\approx 1.73 \text{ BM}.$$

Stereochemistry: octahedral; only one isomer.
Name: potassium hexacyanidomanganate(II).

> **Final Answer:** (i) K diaquadioxalatochromate(III) trihydrate; Cr(III); d^3; C.N. 6; cis/trans; $\mu\approx 3.87$ BM. (ii) Pentaamminechloridocobalt(III) chloride; Co(III); d^6 low-spin; C.N. 6; $\mu=0$. (iii) Trichloridotri(pyridine)chromium(III); Cr(III); d^3; C.N. 6; fac/mer; $\mu\approx 3.87$ BM. (iv) Cs tetrachloridoferrate(III); Fe(III); d^5 high-spin; tetrahedral C.N. 4; $\mu\approx 5.92$ BM. (v) K hexacyanidomanganate(II); Mn(II); d^5 low-spin; C.N. 6; $\mu\approx 1.73$ BM.

EXPERT'S SOLUTION *: Aanya Bhat, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Same recipe applied five times: charge balance $\to x$; group number $\to d^n$; ligand-field strength $\to$ spin state; n unpaired $\to \mu$. After two or three complexes the routine becomes automatic.

Step 1. For (i) $K[Cr(H_2O)_2(C_2O_4)_2]\cdot 3\,H_2O$: two anionic oxalates contribute -4, two waters contribute 0; the complex anion must be -1 (one K^+ outside). So $x=+3$. Cr(III) is d^3, C.N. $=6$ (oxalate is didentate, so $2+2\times 2=6$). Three unpaired in t_{2g}, $\mu\approx 3.87$ BM. Stereochemistry: cis (chiral) / trans (achiral) of two oxalates and two waters.

Step 2. For (ii) $[Co(NH_3)_5Cl]Cl_2$, the ammine ligand on Co^{3+} is strong enough to give a low-spin d^6 closed shell (diamagnetic). Charge balance: $x+5(0)-1=+2 \Rightarrow x=+3$. $\mu=0$. Only one geometry ([MA$_5$B], no isomers).

Step 3. For (iii) $[CrCl_3(py)_3]$, pyridine is comparable to NH_3, weakly strong-field. The d^3 count of Cr^{3+} doesn't permit a choice of spin: three unpaired regardless. $\mu\approx 3.87$ BM. fac and mer isomers possible (Q 5.9 logic).

Step 4. For (iv) $Cs[FeCl_4]$, tetrahedral fields are inherently small ($\Delta_t\approx\frac{4}{9}\Delta_o$), so almost all tetrahedral complexes are high-spin. Fe(III) is d^5 high-spin, $n=5$, $\mu=\sqrt{35}\approx 5.92$ BM. No isomers (single tetrahedral arrangement).

Step 5. For (v) $K_4[Mn(CN)_6]$, CN^- is the strongest common ligand and forces low-spin even on Mn^{2+} (d^5). Configuration $t_{2g}^5e_g^0$, $n=1$, $\mu=\sqrt{3}\approx 1.73$ BM. Octahedral, no isomers.

Step 6. **Alternative approach (CFSE comparison).** CFSE gives a cross-check for the spin assignment. For (ii) d^6 low-spin: CFSE $= -2.4\Delta_o + 2P$, a substantial stabilisation that explains why Co(III) is almost always low-spin. For (v) d^5 low-spin: CFSE $= -2.0\Delta_o + 2P$, also substantial, hence cyanide does force low-spin.

Step 7. **Numerical cross-check.** Experimental μ values: $[Co(NH_3)_5Cl]^{2+}$ shows $\mu_{exp} = 0$ (diamagnetic, confirming d^6 low-spin); $[Cr(NH_3)_6]^{3+}$ shows $\mu_{exp} = 3.85$ BM (d^3); $[FeCl_4]^-$ shows $\mu_{exp} = 5.9$ BM (d^5 high-spin). All consistent with the table above.

Why this matters. A practising inorganic chemist runs this recipe almost unconsciously every time a new complex appears. For board-paper style synthesis: 5 complexes, 5 sets of (name, x, d^n, C.N., stereochemistry, μ) is a 12-marker that rewards systematic application of the same formula.

Concept linkage. Builds on Q 5.5 (oxidation state), Q 5.7 (IUPAC name), Q 5.9–5.12 (isomerism), Q 5.15 (VBT), Q 5.17 (spectrochemical series), Q 5.19 (magnetic moment). It is the chapter's integrative question.

Final Answer: Five complexes, five sets of (name, x, d^n, C.N., stereochemistry, μ) as above.

☞ **All five complexes at a glance**

	x	d^n	C.N.	μ (BM)
(i) $K[Cr(H_2O)_2(ox)_2]$	+3	d^3	6	3.87
(ii) $[Co(NH_3)_5Cl]Cl_2$	+3	d^6 ls	6	0
(iii) $[CrCl_3(py)_3]$	+3	d^3	6	3.87
(iv) $Cs[FeCl_4]$	+3	d^5 hs	4 (tet)	5.92
(v) $K_4[Mn(CN)_6]$	+2	d^5 ls	6	1.73

(ls = low-spin, hs = high-spin)

✗ Tetrahedral d^5 vs octahedral d^5

A frequent slip is to mark $Cs[FeCl_4]$ as having $\mu = 5.92$ BM "because it is octahedral d^5". It is tetrahedral, not octahedral, but the magnetic moment is still 5.92 BM because tetrahedral fields are too small to pair d^5 — the same answer arises but for a different reason. Always identify the geometry before quoting μ.

♥ Why one chapter integrates so many threads

This question is essentially a complete review of Chapter 5: it weaves IUPAC nomenclature (Q 5.7), oxidation state (Q 5.5), electron count (Q 5.23), isomerism (Q 5.9–5.12), VBT (Q 5.15) and magnetism (Q 5.19) into one problem. Mastery here is mastery of the entire chapter.

Q 5.25 **Explain the violet colour of the complex $[\mathrm{Ti(H_2O)_6}]^{3+}$ on the basis of crystal field theory.**

SOLUTION

Concept used. Ti^{3+} has the electronic configuration $[\mathrm{Ar}]3d^1$: a single d-electron. In the octahedral $[\mathrm{Ti(H_2O)_6}]^{3+}$ cation, that electron sits in a t_{2g} orbital. Absorbing one photon of energy Δ_o promotes the electron to the e_g set, producing a single d-d absorption band. The observed colour is the complementary of the absorbed colour.

Step 1. Find the metal oxidation state: Ti^{3+} from charge balance $x + 0 = +3$ $(x = +3)$. d^1 configuration.

Step 2. Configuration in the octahedral field: $t_{2g}^1 e_g^0$. Only one d-d transition is possible: $t_{2g} \to e_g$, energy $= \Delta_o$.

Step 3. For aqua ligands, the absorption maximum is near $\lambda \approx 500$ nm (green-yellow region). Using $E = hc/\lambda$:

$$E = \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{500 \times 10^{-9}}\ \mathrm{J} = 3.98 \times 10^{-19}\ \mathrm{J}.$$

Per mole: $E_{\mathrm{mol}} = 3.98 \times 10^{-19} \times 6.022 \times 10^{23} \approx 2.4 \times 10^{5}\ \mathrm{J/mol} = 240\,\mathrm{kJ/mol}$. That is the magnitude of Δ_o.

Step 4. The complex absorbs in the green-yellow region. The complementary colour is violet, so the transmitted (and observed) colour of the solution is violet.

> **Final Answer:** Ti^{3+} is d^1; one $t_{2g} \to e_g$ transition with $\Delta_o \approx 240\ \mathrm{kJ/mol}$ absorbs green-yellow light, so the complex transmits its complementary colour: violet.

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

Picture-first. One d electron, one $t_{2g} \to e_g$ transition, one absorbed wavelength. The transmitted light is the complementary colour: violet. $[\mathrm{Ti(H_2O)_6}]^{3+}$ is the textbook prototype of a d^1 ion because its absorption spectrum is the simplest possible — a single broad band centred near 500 nm.

Step 1. Find d^n: Ti^{3+} is d^1. Charge balance: $x + 6(0) = +3 \Rightarrow x = +3$. Then $d^n = 4 - 3 = d^1$ (Ti is group 4).

Step 2. Place the electron in t_{2g}. Promotion to e_g needs Δ_o of energy. There is only one possible d-d transition for a d^1 ion in an octahedral field.

Step 3. For aqua at C.N. 6, this Δ_o corresponds to absorption at ~ 500 nm (green-yellow). Numerically, $\Delta_o = hc/\lambda$:

$$\Delta_o = \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{500 \times 10^{-9}}\ \mathrm{J} = 3.98 \times 10^{-19}\ \mathrm{J}.$$

Per mole: $E_{\mathrm{mol}} = 3.98 \times 10^{-19} \times 6.022 \times 10^{23} \approx 240\,\mathrm{kJ/mol}$, equivalent to $\sim 20{,}000\ \mathrm{cm}^{-1}$. The observed Δ_o for $[\mathrm{Ti(H_2O)_6}]^{3+}$ is $20{,}300\ \mathrm{cm}^{-1}$ — excellent match.

Step 4. Colour wheel: green-yellow absorbed $\Rightarrow$ violet transmitted. The observed solution colour is a pale, attractive violet.

Step 5. **Alternative approach (Jahn-Teller asymmetry).** The absorption band of $[\mathrm{Ti(H_2O)_6}]^{3+}$ shows a slight shoulder, betraying a Jahn-Teller distortion (the t_{2g}^1 state is JT-active for an octahedral d^1 ion). The asymmetry of the band is one of the smallest clean experimental measurements of JT effects.

Step 6. **Why broad and not sharp?** d-d transitions are Laporte forbidden in centrosymmetric (octahedral) complexes — the transition gains intensity through vibronic coupling with antisymmetric stretches. The absorption is therefore always broad ($\sim 100\ \mathrm{nm}$ wide) and weak ($\varepsilon < 100$).

Why this matters. The same logic explains the colour of every transition-metal aqua-ion: Cu^{2+} blue, Ni^{2+} green, Fe^{3+} pale violet, Cr^{3+} violet. A single d electron, the simplest possible case, fixes the whole Δ_o scale for aqua complexes.

Concept linkage. Ti^{3+} is the calibration point for the spectrochemical series for aqua ligands. Q 5.20, 5.21, 5.31 all extend this single-band analysis to multi-electron d^n cases.

Final Answer: d^1 Ti(III), single d-d transition $t_{2g} \rightarrow e_g$, absorbs green-yellow, complex appears violet.

☞ **Photon energy ↔ wavelength conversion**

E (J/photon) $= hc/\lambda$, where $h = 6.626 \times 10^{-34}$ J s and $c = 3 \times 10^{8}$ m/s. Practical shortcut: E (kJ/mol) $= 1.196 \times 10^{5}/\lambda$ (nm). Example: $\lambda = 500$ nm $\Rightarrow E = 239$ kJ/mol $= \Delta_o$ for $[\mathrm{Ti(H_2O)_6}]^{3+}$.

☞ **Alternative: Δ_o in cm^{-1}**

Spectroscopists report Δ_o as a wavenumber: $\bar{\nu} = 1/\lambda$ in cm^{-1}. Convert: $\bar{\nu}$ (cm^{-1}) $= 10^7/\lambda$ (nm). For $\lambda = 500$ nm, $\bar{\nu} = 20{,}000\ \mathrm{cm}^{-1}$. Most data tables use cm^{-1}; convert before applying $E = hc\bar{\nu}$ to find energy in J.

Q 5.26 What is meant by the chelate effect? Give an example.

SOLUTION

Concept used. The **chelate effect** is the observation that a complex containing chelating (polydentate) ligands is thermodynamically more stable than a comparable complex with the same donor atoms supplied by monodentate ligands. The effect has both an enthalpic component (similar bond strengths) and a much larger entropic component (one polydentate ligand releases several solvent water molecules per binding event).

Step 1. Compare $[\mathrm{Ni(en)_3}]^{2+}$ with $[\mathrm{Ni(NH_3)_6}]^{2+}$: each has six N-donor atoms bonded to Ni^{2+}. Experimental stability constants: $\log\beta_3(\mathrm{Ni(en)_3}^{2+}) \approx 18.3$, $\log\beta_6(\mathrm{Ni(NH_3)_6}^{2+}) \approx 8.6$. The chelate complex is roughly 10^{10} times more stable.

Step 2. **Enthalpy.** Both complexes have six Ni-N bonds of comparable strength, so ΔH is similar (slightly more favourable for en because the chelate ring is geometrically strain-free).

Step 3. **Entropy.** When 3 en displace 6 $\mathrm{H_2O}$:

$$[\mathrm{Ni(H_2O)_6}]^{2+} + 3\,\mathrm{en} \longrightarrow [\mathrm{Ni(en)_3}]^{2+} + 6\,\mathrm{H_2O}.$$

Particle count goes from $1+3=4$ to $1+6=7$: $\Delta n = +3$. This positive entropy change drives the equilibrium far to the right. When 6 $\mathrm{NH_3}$ displace 6 $\mathrm{H_2O}$, $\Delta n = 0$; no entropic advantage.

Step 4. **Example.** The replacement of six aqua by three en ligands in $[\mathrm{Ni(H_2O)_6}]^{2+}$ to form $[\mathrm{Ni(en)_3}]^{2+}$, with the large $\log\beta$ gap quoted above.

> **Final Answer:** Chelate effect: complexes with polydentate ligands are far more stable than monodentate analogues, mainly because the chelate substitution releases more particles into solution (positive ΔS). Example: $[\mathrm{Ni(en)_3}]^{2+}$ is $\sim 10^{10}$ more stable than $[\mathrm{Ni(NH_3)_6}]^{2+}$.

EXPERT'S SOLUTION *: Kavya Banerjee, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. It is entropy, not enthalpy. Six water molecules leave; three ethylenediamines arrive. Particle count rises, $\Delta S > 0$, ΔG becomes very negative. The enthalpic contributions from M-N bond formation are very similar in $[\mathrm{Ni(en)_3}]^{2+}$ and $[\mathrm{Ni(NH_3)_6}]^{2+}$, so the entropy term carries almost all of the stability difference.

Step 1. Write the substitution: $[\mathrm{M(H_2O)_6}]^{n+} + 3\,\mathrm{en} \longrightarrow [\mathrm{M(en)_3}]^{n+} + 6\,\mathrm{H_2O}$; $\Delta n = +3$ on the right. Particles in $= 4$, particles out $= 7$. The entropy gain of the system is positive.

Step 2. Compute $\Delta S^\circ \approx R\ln(\text{ratio})$; for $\Delta n = +3$, this is $\sim +25\,\mathrm{J/(K\,mol)}$ when considering translational entropy alone. Including rotational and configurational contributions can push it to $+40$ to $+50$ J/(K mol).

Step 3. At $T = 298$ K, $T\Delta S \sim 7.5$ to $15\,$kJ/mol, which translates to a large factor in K_{eq}, on top of any enthalpic advantage. Numerically: $\Delta(\log\beta) = -\Delta\Delta G^\circ/(2.303RT) \approx -1.3$ per kJ/mol at room temp, so 7–15 kJ/mol explains $\Delta(\log\beta) \sim 9$–20, fitting the experimental gap.

Step 4. Larger ring sizes (5- or 6-membered) give the strongest chelate effect; very small or very large rings strain and weaken the effect. Three-membered rings (no chelation possible). Four-membered rings (rare; M-N-C-N geometry is unfavourable). Five-membered (en, oxalate): widely observed. Six-membered (acac, glycinato): also common. Seven-membered: rare.

Step 5. **Alternative perspective (energy-decomposition).** Modern DFT analysis decomposes the chelate effect into electrostatic, exchange-repulsion, polarisation, charge- transfer and dispersion contributions. The entropy term dominates, but the slight extra enthalpic gain (geometric rigidity of the 5-membered ring) accounts for the residual few kJ/mol stabilisation.

Step 6. **Numerical example: EDTA chelates.** EDTA (Y^{4-}) is hexadentate: it replaces 6 waters with one ligand. $\Delta n = +5$ (1 + 1 in to 1 + 6 out). $\log\beta([\mathrm{CaY}]^{2-}) \approx 10.7$; $\log\beta([\mathrm{FeY}]^{-}) \approx 25.1$. Used for water hardness titrations.

Why this matters. EDTA and the $[\mathrm{Ca(EDTA)}]^{2-}$ complex are stabilised by exactly the same entropy argument scaled up to a hexadentate ligand. In pharmacology, chelation therapy ($\mathrm{Na_2[Ca(EDTA)]}$ swallowed by a lead-poisoned patient) works because $\mathrm{Pb^{2+}}$ displaces $\mathrm{Ca^{2+}}$ from EDTA and is excreted as the soluble Pb-EDTA chelate (no chelate effect $\Rightarrow$ no medicine).
Concept linkage. The same idea explains the stability of porphyrin-based chelates (haemoglobin, chlorophyll, vitamin B_{12}) in Q 5.27. The cyanide complex of Q 5.14 also benefits from a related effect (very high β_4).

Final Answer: Chelate effect: extra stability of chelate complexes due to favourable entropy. Example: $\log\beta(\mathrm{Ni(en)_3}^{2+}) - \log\beta(\mathrm{Ni(NH_3)_6}^{2+}) \approx 10$.

♥ Why chelation is everywhere in biology

Every metal-containing biomolecule uses a chelating ligand to lock the metal in place: haemoglobin's porphyrin (Fe), chlorophyll's porphyrin (Mg), vitamin B_{12}'s corrin (Co), carbonic anhydrase's three-histidine pocket (Zn). The chelate effect is not a textbook curiosity — it is the structural basis of metalloenzymes, drug design, and water-hardness chemistry.

✗ Counting ring size wrong

A 5-membered chelate ring includes the metal: M-N-C-C-N (5 atoms). Some students count only the four ligand atoms; that's wrong. The metal is the fifth ring atom. Similarly, oxalate gives a 5-membered ring M-O-C-C-O. EDTA gives multiple 5-membered rings fused at the metal centre.

Q 5.27 Discuss briefly giving an example in each case the role of coordination compounds in:
(i) biological systems (ii) medicinal chemistry (iii) analytical chemistry (iv) extraction/metallurgy of metals.

SOLUTION

Concept used. Coordination compounds are central to life, medicine, analysis and industrial chemistry. A polydentate ligand wrapping around a metal ion provides controlled reactivity, transport and binding selectivity.

Step 1. **(i) Biological systems.**

- **Haemoglobin**: an iron(II) porphyrin complex in red blood cells; reversibly binds O_2 at the iron and transports it from lungs to tissues.
- **Chlorophyll**: a magnesium(II) porphyrin in green plants; absorbs sunlight and drives photosynthesis.
- **Vitamin B_{12} (cobalamin)**: a cobalt(III) corrinoid complex essential for DNA synthesis.
- **Carboxypeptidase A**: a zinc(II) metalloenzyme that hydrolyses peptide bonds.

Step 2. **(ii) Medicinal chemistry.**

- **Cisplatin**, cis-$[Pt(NH_3)_2Cl_2]$, treats several cancers (testicular, ovarian, lung) by cross-linking DNA via Pt-N coordination.
- EDTA chelation: $Na_2[Ca(EDTA)]$ is used as an antidote for heavy-metal (lead, mercury) poisoning; Pb^{2+} displaces Ca^{2+} from EDTA and is excreted.

Step 3. **(iii) Analytical chemistry.**

- **EDTA titrations** of Ca^{2+} and Mg^{2+} for water hardness.
- Detection of Ni^{2+} with dimethylglyoxime (DMG): a rose-red insoluble $[Ni(dmgH)_2]$ chelate forms.
- Detection of Fe^{3+} with SCN^-: deep blood-red $[Fe(SCN)]^{2+}$.

Step 4. **(iv) Extraction/metallurgy.**

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

$4\,\mathrm{Au} + 8\,\mathrm{CN}^- + \mathrm{O}_2 + 2\,\mathrm{H}_2\mathrm{O} \longrightarrow 4\,[\mathrm{Au(CN)}_2]^- + 4\,\mathrm{OH}^-$; gold is later recovered by zinc.

- Purification of nickel by the **Mond process**: $\mathrm{Ni} + 4\,\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)}_4$ at $\approx 330\,\mathrm{K}$, then thermal decomposition at higher temperature releases pure Ni.
- Aluminium refining: bauxite is processed via $[\mathrm{Al(OH)}_4]^-$ in the Bayer process.

Final Answer: Biology: haemoglobin, chlorophyll, vitamin B_{12}. Medicine: cisplatin, EDTA. Analysis: EDTA, DMG, SCN^-. Metallurgy: cyanide leaching of Au, Mond process for Ni.

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

Strategic angle. Each application exploits one of three features: (a) selective metal binding, (b) reversible ligand-exchange, (c) thermodynamic stability of a chelate. Often two or three of these features work together — a single coordination compound can be both selective *and* reversible *and* thermodynamically stable.

Step 1. Biology: porphyrin and corrin ligands tune the metal's reactivity. Iron in haemoglobin binds O_2 reversibly; same iron in cytochromes does electron transfer. Magnesium in chlorophyll converts photons to electrochemical potential. Cobalt in B_{12} catalyses rearrangements via a Co-C bond that is unusually weak. Zinc in carbonic anhydrase activates a water molecule for nucleophilic attack on CO_2. Each example combines a metal with a polydentate ligand that fine-tunes its reactivity.

Step 2. Medicine: cisplatin's two cis-Cl^- ligands are replaced inside the cell by N7 of guanine, locking onto DNA. The trans-isomer doesn't work (geometry mismatch). The IC_{50} of cisplatin for testicular cancer cells is $\sim 1\ \mu\mathrm{M}$; transplatin is essentially inert. EDTA chelation therapy: $\mathrm{Na}_2[\mathrm{Ca(EDTA)}]$ swaps Ca for Pb/Hg/As, mobilising the toxic metal for renal excretion.

Step 3. Analysis: chelates have intense, narrow absorption bands, useful for colorimetric / titrimetric detection. EDTA titrations measure Ca^{2+} and Mg^{2+} (water hardness). DMG gives a rose-red precipitate with Ni^{2+} at ~ 1 ppm sensitivity. SCN gives a blood-red colour with Fe^{3+} at ~ 0.1 ppm. Each test relies on the chelate effect to ensure that the analyte ion is fully captured by the indicating ligand.

Step 4. Metallurgy: form a soluble metal complex, separate, then thermally decompose. Mond and cyanide leaching are textbook examples. **Mond process**: $\mathrm{Ni} + 4\,\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)}_4$ at ≈ 330 K; the volatile carbonyl distils away from impurities; decomposition at ~ 470 K gives 99.99% pure Ni. **Cyanide leaching**:

gold dissolves as $[\mathrm{Au(CN)_2}]^-$; recovered by Zn cementation. **Bayer process**: bauxite dissolved as $[\mathrm{Al(OH)_4}]^-$; gibbsite separated, then converted to $\mathrm{Al_2O_3}$ for Hall-Heroult.

Step 5. **Alternative classification.** One can group applications by which property is exploited: (a) reactivity (catalysis, organic synthesis); (b) colour (analysis, dyes); (c) magnetism (single-molecule magnets); (d) solubility (extraction, hydrometallurgy).

Step 6. **Numerical examples.** Average adult haemoglobin carries $\sim 4 \times 10^{19}$ Fe(II) ions; chlorophyll in a typical maple leaf has $\sim 10^{18}$ Mg(II) ions per cm^2. Cisplatin's annual market is ~ 100 tonnes worldwide. Mond process delivers $\sim 100{,}000$ tonnes of pure nickel per year.

Why this matters. Coordination chemistry is one of the broadest unifying ideas in chemistry: same principles in a hospital, a forensic lab and a copper smelter. The four examples in this question span biology, medicine, analytics and industrial chemistry — together they illustrate why the coordination compound is among the most useful molecular architectures known.

Concept linkage. The chelate effect (Q 5.26) underlies every biological example. The spectrochemical-series colour arguments (Q 5.13, 5.20, 5.25) explain why analytical reagents work. VBT/CFT (Q 5.15, 5.16) explains why Mond-process $\mathrm{Ni(CO)_4}$ is tetrahedral and stable.

> **Final Answer:** Four domains, four key examples (haemoglobin, cisplatin, EDTA, Mond / cyanide leaching).

☞ The four-domain summary table

Biology: haemoglobin (Fe), chlorophyll (Mg), $\mathrm{B_{12}}$ (Co), carbonic anhydrase (Zn). **Medicine**: cisplatin, EDTA, gadolinium MRI contrast. **Analysis**: EDTA titration, DMG test, SCN test. **Metallurgy**: Mond (Ni), cyanide leaching (Au/Ag), Bayer (Al). Memorise this 4×3 grid for board revision.

♥ Coordination chemistry pays the bills

Almost every Nobel Prize in catalysis has gone to coordination chemistry: Ziegler-Natta (1963, polymerisation), Heck-Negishi-Suzuki (2010, cross-coupling), Noyori-Knowles-Sharpless (2001, asymmetric catalysis). The chemistry of one metal ion plus a few well-chosen ligands has reshaped pharmaceuticals, plastics, displays and agriculture. The principles in this chapter — geometry, Δ_o, π-back-bonding, the chelate effect — are the working vocabulary of one of the most consequential scientific industries.

Q 5.28 **How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution? (i) 6 (ii) 4 (iii) 3 (iv) 2.**

SOLUTION

Concept used. The number of ions a complex produces in water is the number of separate species (cations + anions) that result from full dissociation of the salt. Only the species outside the coordination sphere dissociate; the metal and its ligands inside the brackets stay together as one ion.

Step 1. Identify the coordination sphere. The compound formula $Co(NH_3)_6Cl_2$ corresponds to the complex $[Co(NH_3)_6]Cl_2$: six NH_3 inside the sphere, two Cl^- outside as counter ions.

Step 2. Charge balance inside the sphere: $x + 6(0) = +2 \Rightarrow x = +2$. So the cation is $[Co(NH_3)_6]^{2+}$.

Step 3. Dissolution:

$$[Co(NH_3)_6]Cl_2 \longrightarrow [Co(NH_3)_6]^{2+} + 2\,Cl^-.$$

Three species in solution: one $[Co(NH_3)_6]^{2+}$ and two Cl^-.

Step 4. Total number of ions: $1 + 2 = 3$.

> **Final Answer:** The complex $[Co(NH_3)_6]Cl_2$ produces **3 ions** in solution: one $[Co(NH_3)_6]^{2+}$ and two Cl^-. Correct option: (iii).

☞ Counting ions in complex salts

Strip everything outside the square brackets, divide it into its ions; what remains inside counts as one. Add up.

EXPERT'S SOLUTION *: Aditi Gupta, M.Sc Chemistry, IIT Kanpur*

Quick reading. The cobalt + ammines travel together as a single 2+ cation; the two chlorides break off as Cl^- ions. Two species + one cation = three ions.

Step 1. Identify the bracket: $Co(NH_3)_6Cl_2$ is the same as $[Co(NH_3)_6]Cl_2$. The six ammines are inside the coordination sphere; the two chlorides are outside as counter ions.

Step 2. Charge balance: $x + 6(0) = +2 \Rightarrow x = +2$. So Co(II), and the cation is $[Co(NH_3)_6]^{2+}$.

Step 3. Write the dissociation $[Co(NH_3)_6]Cl_2 \longrightarrow [Co(NH_3)_6]^{2+} + 2\,Cl^-$.

Step 4. Count: one complex cation, two chloride anions: $1 + 2 = 3$.

Step 5. **Alternative check via Werner's model.** Co(II) prefers C.N. 6 (octahedral) and primary valency 2 (since the cation is Co^{2+}). All six secondary valencies are taken by ammonia; the two chlorides sit outside as primary valencies and ionise. The number of chlorides outside equals the cation charge, equals the number of Cl^- ions released $= 2$.

Step 6. **Numerical conductivity check.** Molar conductivity of $[Co(NH_3)_6]Cl_2$ in dilute aqueous solution is $\sim 260\ S\ cm^2\ mol^{-1}$, characteristic of a $1:2$ electrolyte. Compare with the $1:3$ electrolyte $[Co(NH_3)_6]Cl_3$ ($\Lambda_m \approx 430$) — the higher value corresponds to the higher ion count.

Why this matters. Werner's original conductivity measurements (Q 5.1) relied on exactly this counting argument. Modern day quality-control assays for inorganic drug formulations still measure conductivity to confirm complex stoichiometry.

Concept linkage. Same counting recipe as Q 5.1 (Werner). Bonus: contrasts well with $[Co(NH_3)_5Cl]Cl$ which gives *two* ions (one complex cation + one Cl^-), illustrating how a chloride inside the sphere lowers the ion count.

Final Answer: 3 ions. Option (iii).

✗ Counting ammines as ions

A common slip is to count the six ammonia molecules as separate ions in the dissolution equation. Ammonia is inside the sphere (neutral) and stays bonded to cobalt in solution. It is not released as NH_3 molecules in any measurable concentration on the conductivity timescale. Only species outside the brackets ionise.

Q 5.29 Amongst the following ions which one has the highest magnetic moment value?

(i) $[Cr(H_2O)_6]^{3+}$ **(ii)** $[Fe(H_2O)_6]^{2+}$ **(iii)** $[Zn(H_2O)_6]^{2+}$.

SOLUTION

Concept used. The spin-only magnetic moment is

$$\mu = \sqrt{n(n+2)}\ \text{BM},$$

where n is the number of unpaired electrons. For weak-field aqua ligands all three octahedral complexes follow the high-spin filling rule.

Step 1. **(i)** $[Cr(H_2O)_6]^{3+}$. Cr^{3+} is $3d^3$: three unpaired in t_{2g}^3. So $n = 3$ and

$$\mu = \sqrt{3 \cdot 5}\ \text{BM} = \sqrt{15}\ \text{BM} \approx 3.87\ \text{BM}.$$

Step 2. **(ii)** $[\mathrm{Fe(H_2O)_6}]^{2+}$. Fe^{2+} is $3d^6$; aqua is weak-field ⇒ high-spin $t_{2g}^4 e_g^2$: $n = 4$, and

$$\mu = \sqrt{4 \cdot 6}\ \mathrm{BM} = \sqrt{24}\ \mathrm{BM} \approx 4.90\ \mathrm{BM}.$$

Step 3. **(iii)** $[\mathrm{Zn(H_2O)_6}]^{2+}$. Zn^{2+} is $3d^{10}$: completely filled, all paired. $n = 0$; $\mu = 0$ BM.

Step 4. Compare: $3.87 < 4.90$; option (iii) is zero. So option (ii) has the highest magnetic moment.

> **Final Answer:** $[\mathrm{Fe(H_2O)_6}]^{2+}$ has the highest magnetic moment ($\mu \approx 4.90$ BM); option (ii).

EXPERT'S SOLUTION : *Sanya Pillai, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. Count n. The one with the most unpaired electrons wins. Aqua is weak field, so all three are high-spin octahedral cases.

Step 1. Cr^{3+} (group 6, $x = +3$): $d^3 \Rightarrow t_{2g}^3 e_g^0 \Rightarrow n = 3$. $\mu = \sqrt{15} \approx 3.87$ BM.

Step 2. Fe^{2+} (group 8, $x = +2$): d^6, weak-field high-spin $\Rightarrow t_{2g}^4 e_g^2 \Rightarrow n = 4$. $\mu = \sqrt{24} \approx 4.90$ BM.

Step 3. Zn^{2+} (group 12, $x = +2$): d^{10}, all paired $\Rightarrow n = 0$. $\mu = 0$.

Step 4. Largest n is 4 (Fe^{2+}); $\mu \approx 4.90$ BM. Option (ii).

Step 5. **Alternative cross-check.** For high-spin first-row octahedral ions, $n_{\max}$ peaks at d^5 ($n = 5$, $\mu = 5.92$ BM) and decreases symmetrically on both sides: $d^4 \Leftrightarrow d^6$ both give $n = 4$; $d^3 \Leftrightarrow d^7$ both give $n = 3$. Fe(II) is at d^6 = near the peak; Cr(III) at d^3 = further away.

Step 6. **Numerical experimental data.** $\mu_{\text{exp}}([\mathrm{Cr(H_2O)_6}]^{3+}) = 3.84$ BM (vs spin-only 3.87, excellent agreement); $\mu_{\text{exp}}([\mathrm{Fe(H_2O)_6}]^{2+}) = 5.20$ BM (slightly higher than spin-only 4.90 because of orbital contribution to T-state ground term — the *orbital contribution* that NCERT mentions in passing); $\mu_{\text{exp}}([\mathrm{Zn(H_2O)_6}]^{2+}) = 0$ (diamagnetic).

Why this matters. Magnetic susceptibility is the simplest experimental window into d-electron count and spin state. For a board-paper MCQ, the recipe "count n from d^n and compute μ" is the fastest route.

Concept linkage. The spin-only formula $\mu = \sqrt{n(n+2)}$ is the most-used formula in the chapter; recurs in Q 5.15, 5.19, 5.24, here and in the d-block chapter (Q 4.x). Always know it cold.

> **Final Answer:** Option (ii): $[\mathrm{Fe(H_2O)_6}]^{2+}$, $\mu \approx 4.90$ BM.

☞ **μ for first-row d^n aqua ions (high-spin)**

Ion	d^n	n_{unpaired}	μ_{calc} (BM)
Ti^{3+}	d^1	1	1.73
V^{3+}	d^2	2	2.83
Cr^{3+}	d^3	3	3.87
Mn^{3+}	d^4	4	4.90
Mn^{2+}, Fe^{3+}	d^5	5	5.92
Fe^{2+}	d^6	4	4.90
Co^{2+}	d^7	3	3.87
Ni^{2+}	d^8	2	2.83
Cu^{2+}	d^9	1	1.73
Zn^{2+}	d^{10}	0	0

Peak at d^5 ($\mu = 5.92$ BM); zero at d^{10}.

☞ **Alternative with CFT/MOT angle**

For octahedral high-spin: $n = d^n$ for $d^{1,2,3}$; $n = 10 - d^n$ for $d^{8,9,10}$; $n = d^n$ minus appropriate pair count otherwise. Equivalent to filling t_{2g} and e_g with single electrons first (Hund), then doubling up. For low-spin d^4, d^5, d^6, d^7: n shrinks dramatically.

Q 5.30 **Amongst the following, the most stable complex is**

(i) $[Fe(H_2O)_6]^{3+}$ **(ii)** $[Fe(NH_3)_6]^{3+}$ **(iii)** $[Fe(C_2O_4)_3]^{3-}$ **(iv)** $[FeCl_6]^{3-}$.

SOLUTION

Concept used. Two factors govern complex stability: ligand-field strength (place in the spectrochemical series) and the chelate effect (chelating ligands give much more stable complexes than monodentate ones with the same donor atom). All four complexes have the same metal (Fe^{3+}, d^5).

Step 1. Place the ligands in the spectrochemical series:

$$Cl^- < H_2O < NH_3 < {C_2O_4}^{2-}.$$

(Note: although oxalate's Δ_o is not the largest of these, its didentate (chelating) character pushes its complexes ahead.)

Step 2. Comment on chelation: oxalate is the only didentate ligand in the list. Three oxalates per Fe give a 5-membered chelate ring each, so $[Fe(C_2O_4)_3]^{3-}$ enjoys a **chelate-effect bonus** that the three monodentate complexes cannot match.

Step 3. Numerical comparison of stability constants for Fe^{3+}: $\log\beta_3([Fe(C_2O_4)_3]^{3-}) \approx 20$; $\log\beta_6([FeCl_6]^{3-}) \approx 2$; $\log\beta_6([Fe(H_2O)_6]^{3+}) \approx 0$ (water is the reference state); $\log\beta_6([Fe(NH_3)_6]^{3+}) \approx 5$. The oxalato complex is by far the most stable.

Step 4. Conclusion: option (iii) $[Fe(C_2O_4)_3]^{3-}$ is the most stable complex.

Final Answer: $[Fe(C_2O_4)_3]^{3-}$ is the most stable; the chelate effect plus moderately strong-field oxalate together outpace the other three monodentate ligands. Option (iii).

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

Structural observation. Chelation gives a thermodynamic advantage of $\sim 10^{10}$ over monodentate equivalents. Oxalate is the only chelate ligand in the list. Combine that with its moderately strong-field character and the answer is clear.

Step 1. Compare ligand-field strength: oxalate is intermediate but beats Cl^-, H_2O and NH_3 for Fe^{3+}. Position in series: $Cl^- < H_2O < NH_3 < {C_2O_4}^{2-}$ (for hard, oxophilic Fe^{3+}).

Step 2. Add the chelate bonus: a 5-membered ring is the most favourable size. Three oxalates per iron give three 5-membered rings $\Rightarrow$ very high entropy gain on ligand substitution.

Step 3. Compare stability constants numerically:

- $\log \beta_3([Fe(C_2O_4)_3]^{3-}) \approx 20$.
- $\log \beta_6([Fe(NH_3)_6]^{3+}) \approx 5$ (unstable because NH_3 is a poor donor for hard Fe^{3+} — actually decomposes in water).
- $\log \beta_6([Fe(H_2O)_6]^{3+}) \approx 0$ (water is the reference for aqueous Fe^{3+}).
- $\log \beta_6([FeCl_6]^{3-}) \approx 2$.

Oxalato wins by $\sim 10^{15}$ over the chloride and by $\sim 10^{20}$ over the aqua reference.

Step 4. Add up: by both metrics, $[Fe(C_2O_4)_3]^{3-}$ wins. Option (iii).

Step 5. **Alternative perspective (HSAB).** Fe^{3+} is a hard Lewis acid (small, highly charged). It prefers hard Lewis bases: $F^-, O^{2-}, OH^-, {C_2O_4}^{2-}$ (O-donor). Soft NH_3 and Cl^- are less compatible. HSAB plus chelate effect together explain the clear win for oxalate.

Step 6. **Numerical cross-check via free energy.** $\Delta G^\circ = -2.303RT \log K$. For oxalato: $\log K \approx 20 \Rightarrow \Delta G^\circ \approx -114$ kJ/mol. For ammonia: $\log K \approx 5 \Rightarrow \Delta G^\circ \approx -29$ kJ/mol. The 85 kJ/mol gap is almost entirely entropic — the chelate effect in thermodynamic units.

Why this matters. The same reasoning explains why EDTA ($\log \beta \approx 25$ with Fe^{3+}) sequesters Fe^{3+} even more effectively than oxalate. EDTA is hexadentate; the entropic advantage scales with denticity. In rust-removal and food-preservation, EDTA is the active sequestering agent for free Fe^{3+}.

Concept linkage. Q 5.26 (chelate effect) is the theoretical justification; Q 5.27 (applications) is the practical use. The HSAB principle hinted at here was developed by

Pearson in 1963 and is the rationale for ligand selection in catalysis, medicine and environmental chemistry.

Final Answer: Option (iii): $[Fe(C_2O_4)_3]^{3-}$.

✗ Picking by ligand-field strength alone

A common slip is to mark $[Fe(NH_3)_6]^{3+}$ as "more stable than $[Fe(H_2O)_6]^{3+}$ because NH_3 is higher in the spectrochemical series". Actually $[Fe(NH_3)_6]^{3+}$ does not exist in aqueous solution — NH_3 deprotonates around Fe^{3+} to form $Fe(OH)_3$ instead. The spectrochemical order is a guide to Δ_o, not to overall stability in water; chemistry of the metal-ligand-solvent system can override it.

♥ Why ferric oxalate wins outside the textbook

$Fe(C_2O_4)_3{}^{3-}$ is the active species in "ferric oxalate" (*ammonium ferric oxalate*), a vintage photographic emulsion. The same species drives iron mobilisation in plant roots ("rhizosphere acidification"). The chelate effect that makes this complex stable in the lab also makes it useful in agriculture and photography.

Q 5.31 What will be the correct order for the wavelengths of absorption in the visible region for the following: $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

SOLUTION

Concept used. The d-d absorption maximum λ of a complex is related to its crystal-field splitting energy by $E = hc/\lambda$, so larger Δ_o corresponds to shorter λ. To compare wavelengths between complexes with the same metal and same coordination, compare Δ_o values; the bigger the Δ_o, the smaller the λ.

Step 1. All three complexes have the same Ni^{2+} (d^8) and octahedral coordination; only the ligand differs.

Step 2. Spectrochemical-series order for these ligands:

$$H_2O < NH_3 < NO_2{}^{-}.$$

So $\Delta_o([Ni(H_2O)_6]^{2+}) < \Delta_o([Ni(NH_3)_6]^{2+}) < \Delta_o([Ni(NO_2)_6]^{4-})$.

Step 3. Convert to wavelengths using $\lambda = hc/E$: bigger $\Delta_o \Rightarrow$ smaller λ. Hence

$$\lambda([Ni(H_2O)_6]^{2+}) > \lambda([Ni(NH_3)_6]^{2+}) > \lambda([Ni(NO_2)_6]^{4-}).$$

Step 4. Sanity check with observed colours: $[Ni(H_2O)_6]^{2+}$ is green (absorbs red, large

λ); $[Ni(NH_3)_6]^{2+}$ is blue/violet (absorbs orange-yellow); $[Ni(NO_2)_6]^{4-}$ is yellow/orange (absorbs blue-violet, smallest λ). The trend matches.

> **Final Answer:** λ: $[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$ (because Δ_o goes in the opposite order).

☞ Δ_o and λ are inverse

For the same metal, going from a weaker to a stronger ligand shrinks λ (blue-shift). Memorise the spectrochemical positions and the rest is bookkeeping.

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

Quick reading. Larger $\Delta_o \Rightarrow$ higher absorption energy $\Rightarrow$ smaller λ. Order the ligands on the spectrochemical scale and flip. Same metal (Ni^{2+}, d^8), same geometry (octahedral); only the ligand differs.

Step 1. Order Δ_o: $H_2O < NH_3 < NO_2{}^-$. Aqua at $\sim 8{,}500\ cm^{-1}$ for Ni(II); ammonia at $\sim 11{,}000\ cm^{-1}$; nitrite at $\sim 22{,}000\ cm^{-1}$. A factor of ~ 3 from end to end.

Step 2. Invert to get λ: aqua complex has the largest λ (~ 1200 nm and red region), nitrite complex the smallest (~ 450 nm, violet).

Step 3. **Observed colours.** $[Ni(H_2O)_6]^{2+}$ green (transmits green because it absorbs red); $[Ni(NH_3)_6]^{2+}$ blue/violet; $[Ni(NO_2)_6]^{4-}$ yellow/orange (because it absorbs violet-blue).

Step 4. **Numerical sanity check.** Using $E = hc/\lambda$, $\bar{\nu} = 1/\lambda$: $[Ni(NO_2)_6]^{4-}$ at $22{,}000\ cm^{-1} \Rightarrow \lambda \approx 455$ nm (violet absorption, yellow transmission). $[Ni(H_2O)_6]^{2+}$ at $8500\ cm^{-1} \Rightarrow \lambda \approx 1176$ nm (near-IR, but tail extends into visible red — hence green solution).

Step 5. **Alternative angle: π-donor vs π-acceptor.** H_2O is a weak σ-donor (and weak π-donor). NH_3 is a stronger σ-donor only (no π capability). $NO_2{}^-$ is both a strong σ-donor and a π-acceptor, so it has the largest Δ_o. The order in the spectrochemical series follows directly from this MOT analysis.

Step 6. **Cross-check via colour wheel.** Aqua green; NH_3 blue; nitrite yellow. The visible colour sequence (green → blue/violet → yellow) is exactly what one expects from the absorption sequence moving from red to violet (in the complementary direction).

Why this matters. This is the standard exam template for “predict the colour” style questions on coordination compounds. Variants of this question appear in every JEE and NEET paper on coordination chemistry. Mastering the recipe “spectrochemical order →

Δ_o order → λ inverse order → transmitted-colour order" is essential.
Concept linkage. Q 5.13 (Cu colour change), Q 5.20 (Ni complexes by colour), Q 5.21 (Fe complexes by colour), Q 5.25 (Ti(III) violet) all use the same logic.

> **Final Answer:** λ: $[\mathrm{Ni(H_2O)_6}]^{2+} > [\mathrm{Ni(NH_3)_6}]^{2+} > [\mathrm{Ni(NO_2)_6}]^{4-}$.

☞ Δ_o scaling factors for $\mathrm{Ni^{2+}}$

For the same metal in octahedral C.N. 6:

$$\Delta_o(\mathrm{Ni^{2+}}, L) \approx 8.5\,(L = \mathrm{H_2O}),\;\; 11\,(L = \mathrm{NH_3}),\;\; 12.5\,(L = \mathrm{en}),\;\; 22\,(L = \mathrm{NO_2}^-)\;\; (\text{in } 10^3\ \mathrm{cm^{-1}}).$$

This is the same metal sampled across the spectrochemical series — a factor-of-three swing in Δ_o.

☞ Alternative: predict the absorbed colour first

Step 1: locate the ligand on the series. Step 2: rough Δ_o estimate (10^4 cm^{-1} for weak field, 3×10^4 for strong field). Step 3: convert Δ_o to wavelength ($\lambda = 10^7/\bar{\nu}$ in nm). Step 4: find the *complementary* colour on the wheel — that's the transmitted colour. Four mechanical steps; works every time.

Key Takeaways

- **Werner's theory** introduced primary (ionisable) and secondary (directional, non-ionisable) valencies. Modern terms: oxidation state and coordination number.
- Distinguish a **double salt** (fully dissociates) from a **coordination compound** (metal hidden inside a complex ion).
- Compute oxidation state from charge balance: $x + \sum(\text{ligand charges}) = \text{overall charge}$.
- Naming rules: cation first, then anion; inside the sphere, ligands alphabetical, prefixes di/tri/tetra (or bis/tris/tetrakis for complex names), metal last; Roman numeral oxidation state; $-ate$ suffix on the metal in anionic complexes.
- Isomerism: structural (linkage, coordination, ionisation, solvate) and stereo (geometrical, optical). Square-planar complexes never show optical isomerism.
- **VBT**: d^2sp^3 inner-orbital (strong field, often low-spin), sp^3d^2 outer-orbital (weak field, high-spin). **CFT**: e_g up $0.6\,\Delta_o$, t_{2g} down $0.4\,\Delta_o$; high- vs low-spin decided by Δ_o vs P.
- Spectrochemical series: $\mathrm{I^-} < \mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{F^-} < \mathrm{OH^-} < \mathrm{H_2O} < \mathrm{NH_3} < \mathrm{en} < \mathrm{NO_2}^- < \mathrm{CN^-} < \mathrm{CO}$.
- Spin-only magnetic moment: $\mu = \sqrt{n(n+2)}$ BM, where n is the number of unpaired electrons.
- Colour arises from d-d transitions: larger Δ_o shifts absorption to shorter λ; transmitted colour is complementary.
- Metal carbonyls: M(0) state, synergic σ donation from CO plus π back-donation from

> metal to CO π^*.
>
> - Applications: haemoglobin and chlorophyll (biology), cisplatin and EDTA (medicine), DMG and SCN tests (analysis), cyanide leaching and Mond process (metallurgy).

End of Chapter 5 Exercises