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CH 01

Coordination Chemistry — CFSE & Crystal Field Theory

01

Octahedral, tetrahedral and square planar splitting, the spectrochemical series, high and low spin, CFSE calculations, colour and magnetism — with an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Draw the octahedral, tetrahedral and square planar splitting diagrams and label the orbital sets
- Use the spectrochemical series and Δ versus P to decide high spin or low spin
- Calculate CFSE for any d^n configuration in octahedral and tetrahedral fields
- Predict the number of unpaired electrons and the spin-only magnetic moment of a complex
- Explain colour from d–d transitions and calculate Δ from the absorbed wavelength

INSIDE

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H Colour

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

One splitting diagram, three answers.

IN ONE LINE

Ligands push the five d orbitals apart in energy; how far apart (Δ) compared with the pairing energy (P) decides where the electrons go, and that decides colour, magnetism and CFSE.

- **Crystal field theory (CFT)** treats ligands as point negative charges (or dipoles) and the metal–ligand bond as purely electrostatic.
- In a free ion the five d orbitals have the same energy (degenerate). Ligands approaching along particular directions repel some d orbitals more than others, and the set splits.
- The size of the split, Δ, depends on the ligand, the metal and its oxidation state, and the geometry.

THINK OF IT LIKE THIS

Picture five friends sitting in a room. Six people walk in and stand along the x, y and z axes. The two friends sitting on those axes (dz^2 and dx^2-y^2) are crowded and uncomfortable — higher energy. The three sitting between the axes (dxy, dyz, dxz) are left in peace — lower energy.

SECTION B

Octahedral splitting

B

Six ligands along ±x, ±y, ±z.

Set	Orbitals	Points	Energy relative to the average
eg	dz^2, dx^2-y^2	Directly at the ligands	+0.6 Δo (raised)
t_2g	dxy, dyz, dxz	Between the ligands	−0.4 Δo (lowered)

KEY IDEA

The barycentre rule: the average energy is unchanged, so 2 × (+0.6) + 3 × (−0.4) = 0. Each electron in t_2g stabilises by 0.4 Δo; each in eg destabilises by 0.6 Δo.

SECTION C

Spectrochemical series

C

Ligands ranked by how hard they split the d orbitals.

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

Weak field (small Δ) on the left → strong field (large Δ) on the right

- **Halides are weak field**; CN^- and CO are the strongest (they also accept electron density back from the metal).
- **Oxidation state:** a higher charge on the metal pulls ligands closer → larger Δ. Δo for M^{3+} is roughly 1.5–2 times that for M^{2+}.
- **Down a group:** Δ increases about 30–50% from 3d to 4d to 5d. Complexes of 4d and 5d metals are almost always low spin.
- SCN^- binding through S is weak field; NCS^- binding through N is stronger.

MEMORY HOOK

"**I Bring Some Cold Sandwiches For Our Christmas Holiday, Nobody Eats Nuts Except Cranky Cooks**" — I^-, Br^-, SCN^-, Cl^-, S^{2-}, F^-, OH^-, $C_2O_4^{2-}$, H_2O, NCS^-, edta, NH_3, en, CN^-, CO.

SECTION D

High spin and low spin

D

Pair up, or move upstairs?

For d^1, d^2, d^3 the electrons simply go into t_{2g}. For **d^4 to d^7** there is a choice for the next electron: pay the pairing energy P and stay in t_{2g}, or pay Δo and move up to eg.

Condition	Ligands	Result	Name
Δo < P	Weak field	Electrons spread out into eg before pairing	High spin (maximum unpaired)
Δo > P	Strong field	Electrons pair in t_{2g} before entering eg	Low spin (minimum unpaired)

d^n	High spin (weak field)	Unpaired	Low spin (strong field)	Unpaired
d^4	$t_{2g}^3\ eg^1$	4	t_{2g}^4	2
d^5	$t_{2g}^3\ eg^2$	5	t_{2g}^5	1
d^6	$t_{2g}^4\ eg^2$	4	t_{2g}^6	0
d^7	$t_{2g}^5\ eg^2$	3	$t_{2g}^6\ eg^1$	1

KEY IDEA

Only d^4–d^7 octahedral complexes have a high-spin/low-spin choice. d^1–d^3 and d^8–d^{10} have one arrangement whatever the ligand.

SOLVED EXAMPLE 01 — Fe^{2+} WITH TWO LIGANDS

Compare $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$: configuration and unpaired electrons.

SOLUTION

1. Fe^{2+} is d^6 in both.
2. H_2O is weak field → high spin: $t_{2g}^4\ e_g^2$, four unpaired.
3. CN^- is strong field → low spin: t_{2g}^6, all paired.

ANSWER $[Fe(H_2O)_6]^{2+}$: 4 unpaired, paramagnetic. $[Fe(CN)_6]^{4-}$: 0 unpaired, diamagnetic.

SECTION E

Calculating CFSE

E

Count the electrons in each set, multiply, add.

$$\text{CFSE (octahedral)} = (-0.4\,x + 0.6\,y)\,\Delta o + (\text{extra pairs})\,P$$

x = electrons in t_{2g}; y = electrons in e_g

KEY IDEA

Convention on P: here P is added only for each pair the strong field forces beyond the high-spin arrangement. Some books add P for every pair in the complex. Both give the same Δo part — check which convention your exam uses before writing the P term.

d^n	High spin CFSE	Low spin CFSE
d^1	−0.4 Δo	—
d^2	−0.8 Δo	—
d^3	−1.2 Δo	—
d^4	−0.6 Δo	−1.6 Δo + P
d^5	0	−2.0 Δo + 2P
d^6	−0.4 Δo	−2.4 Δo + 2P
d^7	−0.8 Δo	−1.8 Δo + P
d^8	−1.2 Δo	—

d^n	High spin CFSE	Low spin CFSE
d^9	−0.6 Δo	—
d^{10}	0	—

SOLVED EXAMPLE 02 — CFSE OF A D^6 LOW-SPIN COMPLEX

Find the CFSE of $[Co(NH_3)_6]^{3+}$.

SOLUTION

1. Co^{3+} is d^6; NH_3 with a 3+ ion is strong enough → low spin: $t_2g^6\ eg^0$.
2. Δo part: 6 × (−0.4) = −2.4 Δo.
3. High-spin d^6 has 1 pair; low-spin has 3 → 2 extra pairs.

ANSWER CFSE = −2.4 Δo + 2P; diamagnetic.

SOLVED EXAMPLE 03 — CFSE OF A D^5 HIGH-SPIN COMPLEX

Find the CFSE of $[Mn(H_2O)_6]^{2+}$.

SOLUTION

1. Mn^{2+} is d^5; H_2O is weak field → high spin: $t_2g^3\ eg^2$.
2. 3 × (−0.4) + 2 × (+0.6) = −1.2 + 1.2.

ANSWER CFSE = 0 — five unpaired electrons, no field stabilisation.

CHECK YOURSELF

C1 How many unpaired electrons are in $[CoF_6]^{3-}$?

C2 Write the CFSE of a d^8 octahedral complex.

Answers at the end of the chapter.

SECTION F

Tetrahedral and square planar

F

Different shapes, different splitting.

	Octahedral	Tetrahedral	Square planar
Lower set	t_2g (3 orbitals)	e (dz^2, dx^2-y^2)	dxz, dyz lowest; then dz^2, dxy
Upper set	eg (2 orbitals)	t_2 (dxy, dyz, dxz)	dx^2-y^2 far above all others
Splitting	Δo	Δt = (4/9) Δo	Largest overall
Spin	Depends on ligand	Almost always high spin	Usually low spin (d^8)

$$\text{CFSE (tetrahedral)} = (-0.6\,x + 0.4\,y)\,\Delta t$$

x = electrons in e (lower); y = electrons in t_2 (upper)

- The tetrahedral pattern is **inverted** compared with octahedral, and there is no g label (no centre of symmetry).
- Δt is small (four ligands, none pointing straight at an orbital), so it is almost always smaller than P → **high spin**.
- **Square planar** is typical of d^8 ions with strong-field ligands — Ni^{2+}, Pd^{2+}, Pt^{2+}: $[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$, cisplatin. The eight electrons fill the four lower orbitals and leave dx^2-y^2 empty → diamagnetic.

SOLVED EXAMPLE 04 — TWO NI^{2+} COMPLEXES

$[NiCl_4]^{2-}$ is paramagnetic but $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain.

SOLUTION

1. Ni^{2+} is d^8.
2. Cl^- is weak field → tetrahedral: $e^4\,t_2^4$ → two unpaired electrons.
3. CN^- is strong field → square planar: all eight paired below the empty dx^2-y^2.

ANSWER Tetrahedral $[NiCl_4]^{2-}$ has 2 unpaired; square planar $[Ni(CN)_4]^{2-}$ has none.

SECTION G

Magnetism

G

Unpaired electrons, counted from the splitting diagram.

$$\mu\ (\text{spin-only}) = \sqrt{n(n+2)}\ \text{BM}$$

n = unpaired electrons: 1 → 1.73, 2 → 2.83, 3 → 3.87, 4 → 4.90, 5 → 5.92 BM

Complex	Metal ion	Field	Arrangement	Unpaired	μ / BM
$[Fe(H_2O)_6]^{3+}$	Fe^{3+} d^5	Weak	$t_2g^3\,eg^2$	5	5.92
$[Fe(CN)_6]^{3-}$	Fe^{3+} d^5	Strong	t_2g^5	1	1.73
$[CoF_6]^{3-}$	Co^{3+} d^6	Weak	$t_2g^4\,eg^2$	4	4.90
$[Co(NH_3)_6]^{3+}$	Co^{3+} d^6	Strong	t_2g^6	0	0
$[Cr(H_2O)_6]^{3+}$	Cr^{3+} d^3	Either	t_2g^3	3	3.87
$[Cu(NH_3)_4]^{2+}$	Cu^{2+} d^9	—	one unpaired	1	1.73

KEY IDEA

Working back from μ: if a question gives μ, find n first (4.90 BM → 4 unpaired), then decide whether the complex must be high or low spin. This is the fastest way to identify the field strength in assertion–reason questions.

SECTION H

Colour

H

What we see is what is not absorbed.

An electron absorbs a photon of energy Δo and jumps from t_2g to eg — a **d–d transition**. The complex shows the **complementary colour** of the light absorbed.

$$\Delta o = hc / \lambda \text{ (per ion); multiply by } N_a \text{ for per mole}$$

A larger Δo absorbs shorter wavelengths

- **No d–d transition, no colour:** d^0 (Sc^{3+}, Ti^{4+}) and d^{10} (Zn^{2+}, Cu^{+}) complexes are colourless.
- Changing the ligand changes Δo and so the colour: $[Ni(H_2O)_6]^{2+}$ is green; $[Ni(en)_3]^{2+}$ is violet (stronger field, larger Δo, absorbs shorter wavelength).
- Anhydrous $CuSO_4$ is white; with water ligands it becomes blue — no ligand field, no splitting, no colour.

SOLVED EXAMPLE 05 — ΔO FROM ABSORPTION

$[Ti(H_2O)_6]^{3+}$ absorbs most strongly at 498 nm. Find Δo in kJ mol^{-1}. (h = 6.626×10^{-34} J s, c = 3.0×10^8 m s^{-1}, $N_a = 6.022 \times 10^{23}$)

SOLUTION

1. Per ion: $E = hc/\lambda = (6.626 \times 10^{-34} \times 3.0 \times 10^8) / (498 \times 10^{-9}) = 3.99 \times 10^{-19}$ J.
2. Per mole: $3.99 \times 10^{-19} \times 6.022 \times 10^{23} = 2.40 \times 10^5$ J.

ANSWER Δo ≈ 240 kJ mol^{-1}. It absorbs blue-green light and looks purple.

CHECK YOURSELF

C3 Why is $[Sc(H_2O)_6]^{3+}$ colourless?

C4 Which absorbs at a shorter wavelength: $[Co(NH_3)_6]^{3+}$ or $[CoF_6]^{3-}$?

Answers at the end of the chapter.

SECTION I

Limits of crystal field theory

I

Know what the model cannot do.

- It treats ligands as point charges, so it cannot explain why neutral CO is a stronger ligand than charged F^- or OH^-.
- It ignores covalent character in metal–ligand bonds; ligand field theory and MO theory correct this.
- **Jahn–Teller distortion:** octahedral complexes with unequal filling of eg — high-spin d^4 and d^9 (Cu^{2+}) — distort, usually by lengthening the two axial bonds. This is why Cu^{2+} complexes are rarely perfect octahedra.

SECTION J

Exam trap gallery

J

Where marks are lost in this chapter.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
In an octahedral field, dxy, dyz, dxz are raised.	They form the lower t_2g set; dz^2 and dx^2-y^2 (eg) are raised.
WHY eg orbitals point straight at the ligands.	
✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Tetrahedral complexes are low spin with strong-field ligands.	Tetrahedral complexes are almost always high spin.
WHY $\Delta t = 4/9\ \Delta o$ is usually smaller than P.	
✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
d^3 complexes can be high or low spin.	Only d^4–d^7 octahedral complexes have the choice.
WHY Three electrons fit singly in t_2g either way.	
✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
CFSE of high-spin d^5 is $-2.0\ \Delta o$.	High-spin d^5 is 0; low-spin d^5 is $-2.0\ \Delta o + 2P$.
WHY $3(-0.4) + 2(+0.6) = 0$.	
✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Tetrahedral CFSE uses -0.4 and +0.6.	Tetrahedral uses -0.6 (e) and +0.4 (t_2) with Δt.
WHY The pattern is inverted.	

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
F^- is a strong-field ligand because F is very electronegative.	F^- is weak field; CN^- and CO are strong.
WHY Use the spectrochemical series, not electronegativity.	

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$[Ni(CN)_4]^{2-}$ is tetrahedral and paramagnetic.	It is square planar and diamagnetic.
WHY Strong-field d^8 → square planar.	

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
A complex absorbing red light looks red.	It looks the complementary colour (green-blue).
WHY We see the light that is not absorbed.	

SECTION K

Practice MCQs

K

Levels: Easy, Moderate, Tough.

Q01 In an octahedral field the eg set consists of: [EASY]

(a) dxy, dyz
(b) dz^2, dx^2-y^2
(c) dxy, dxz, dyz
(d) dxz, dz^2

Q02 The strongest-field ligand among these is: [EASY]

(a) Cl^-
(b) H_2O
(c) NH_3
(d) CN^-

Q03 Δt in terms of Δo is: [EASY]

(a) (4/9) Δo
(b) (9/4) Δo
(c) (1/2) Δo
(d) 2 Δo

Q04 Which complex is colourless? [EASY]

(a) $[Ti(H_2O)_6]^{3+}$
(b) $[Cu(H_2O)_6]^{2+}$
(c) $[Zn(H_2O)_6]^{2+}$
(d) $[Ni(H_2O)_6]^{2+}$

Q05 Each electron in t_2g of an octahedral complex contributes: [EASY]

(a) +0.6 Δo
(b) -0.4 Δo
(c) -0.6 Δo
(d) +0.4 Δo

Q06 The number of unpaired electrons in $[Fe(CN)_6]^{3-}$ is: [MODERATE]

(a) 5
(b) 3
(c) 1
(d) 0

Q07 CFSE of high-spin d^4 octahedral is: [MODERATE]

(a) −1.6 Δo (b) −0.6 Δo
(c) −0.4 Δo (d) 0

Q08 $[CoF_6]^{3-}$ is: [MODERATE]

(a) diamagnetic, low spin (b) paramagnetic, high spin
(c) diamagnetic, high spin (d) paramagnetic, low spin

Q09 Which has the largest Δo? [MODERATE]

(a) $[Co(H_2O)_6]^{2+}$ (b) $[Co(H_2O)_6]^{3+}$
(c) $[Rh(H_2O)_6]^{3+}$ (d) $[Co(NH_3)_6]^{2+}$

Q10 The geometry of $[Ni(CN)_4]^{2-}$ is: [MODERATE]

(a) tetrahedral (b) square planar
(c) octahedral (d) trigonal bipyramidal

Q11 Spin-only μ of $[Fe(H_2O)_6]^{2+}$ is about: [MODERATE]

(a) 0 (b) 2.83 BM
(c) 4.90 BM (d) 5.92 BM

Q12 CFSE of tetrahedral d^2 (in Δt) is: [MODERATE]

(a) −0.8 Δt (b) −1.2 Δt
(c) −0.6 Δt (d) −0.4 Δt

Q13 Which shows Jahn–Teller distortion? [TOUGH]

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Cu(H_2O)_6]^{2+}$
(c) $[Fe(CN)_6]^{4-}$ (d) $[Zn(NH_3)_6]^{2+}$

Q14 $[Ni(H_2O)_6]^{2+}$ is green; $[Ni(en)_3]^{2+}$ is violet. This means en: [TOUGH]

(a) is a weaker field ligand (b) gives a larger Δo
(c) gives no d–d transition (d) makes the complex tetrahedral

Q15 CFSE of low-spin d^6 octahedral (counting extra pairs only) is: [TOUGH]

(a) −2.4 Δo + 2P (b) −0.4 Δo
(c) −2.4 Δo + 3P (d) −1.8 Δo + P

Answer key with explanations

Q01 **(b)** dz^2, dx^2-y^2 — They point at the ligands.

Q02 **(d)** CN^- — Near the end of the series.

Q03 **(a)** **(4/9) Δo** — Fewer ligands, none pointing at orbitals.

Q04 **(c)** $[Zn(H_2O)_6]^{2+}$ — Zn^{2+} is d^{10}.

Q05 **(b)** **−0.4 Δo** — Lower set.

Q06 **(c)** **1** — Low-spin d^5: t_2g^5.

Q07 **(b)** **−0.6 Δo** — $t_2g^3\ eg^1$: −1.2 + 0.6.

Q08 **(b) paramagnetic, high spin** — F^- weak field; d^6 high spin, 4 unpaired.

Q09 **(c) $[Rh(H_2O)_6]^{3+}$** — Higher charge and 4d metal.

Q10 **(b) square planar** — Strong-field d^8.

Q11 **(c) 4.90 BM** — High-spin d^6: 4 unpaired.

Q12 **(b) -1.2 Δt** — e^2: 2 × (−0.6).

Q13 **(b) $[Cu(H_2O)_6]^{2+}$** — d^9: unequal eg filling.

Q14 **(b) gives a larger Δo** — Absorbs shorter wavelength.

Q15 **(a) -2.4 Δo + 2P** — t_2g^6; two more pairs than high spin.

Check-yourself answers

C1 Four (Co^{3+} d^6, F^- weak field → t_2g^4 eg^2).

C2 -1.2 Δo (t_2g^6 eg^2: -2.4 + 1.2).

C3 Sc^{3+} is d^0 — no d electron, so no d–d transition.

C4 $[Co(NH_3)_6]^{3+}$ — NH_3 is stronger field, so Δo is larger and the absorbed light has a shorter wavelength.

QUICK REVISION

One-page revision

Read this page the night before the exam.

Octahedral

- t_2g (dxy, dyz, dxz): −0.4 Δo
- eg (dz^2, dx^2-y^2): +0.6 Δo
- Choice only for d^4–d^7
- Δo > P → low spin

Series

- $I^- < Br^- < Cl^- < F^- < OH^- < H_2O$
- $< NH_3 <$ en $< CN^- <$ CO
- Higher charge → larger Δ
- 4d, 5d → almost always low spin

CFSE

- (−0.4x + 0.6y) Δo + extra pairs × P
- HS d^5 = 0; LS d^5 = −2.0 Δo + 2P
- LS d^6 = −2.4 Δo + 2P
- d^8 = −1.2 Δo; d^{10} = 0

Tetrahedral and sq. planar

- e (lower), t_2 (upper); −0.6, +0.4
- Δt = 4/9 Δo → high spin
- Sq. planar: d^8 + strong field
- $[Ni(CN)_4]^{2-}$ diamagnetic; $[NiCl_4]^{2-}$ 2 unpaired

Magnetism

- μ = √[n(n+2)] BM
- $[Fe(CN)_6]^{4-}$ 0; $[Fe(H_2O)_6]^{2+}$ 4
- $[CoF_6]^{3-}$ 4; $[Co(NH_3)_6]^{3+}$ 0
- $[Fe(CN)_6]^{3-}$ 1; $[Fe(H_2O)_6]^{3+}$ 5

Colour and limits

- Δo = hc/λ; seen = complementary
- d^0, d^{10} colourless
- $[Ti(H_2O)_6]^{3+}$: 498 nm, 240 kJ mol^{-1}
- Jahn–Teller: HS d^4, d^9 (Cu^{2+})

END OF NOTES · RAMGOVINDYADAV.COM