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Coordination Chemistry — CFSE & Crystal Field Notes

Splitting diagrams, the spectrochemical series, high-spin and low-spin filling, CFSE and magnetism tables, colour, and solved numerical examples.

WHAT YOU WILL BE ABLE TO DO

- Draw octahedral, tetrahedral and square planar splitting diagrams from memory
- Decide high spin or low spin from the metal, its charge and the ligand
- Calculate CFSE and the spin-only magnetic moment for any d^n ion
- Explain the colour of a complex and calculate Δ_o from its absorption

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SECTION A

Why the d orbitals split

A

Five d orbitals, one energy, until ligands arrive. Then the orbitals that point at the ligands are pushed up and the rest are pushed down.

IN ONE LINE

Ligands split the d orbitals by Δ; comparing Δ with the pairing energy P decides colour, magnetism and CFSE.

Crystal field theory treats each ligand as a point negative charge (or the negative end of a dipole). An electron in a d orbital that points **at** a ligand is repelled strongly and its energy rises. An electron in an orbital that points **between** the ligands is repelled less.

Orbitals	Where they point	In an octahedral field
d(x²−y²), d(z²)	Along the x, y, z axes	Raised: the **eg** set, +0.6 Δ_o
d(xy), d(yz), d(xz)	Between the axes	Lowered: the **t_2g** set, −0.4 Δ_o

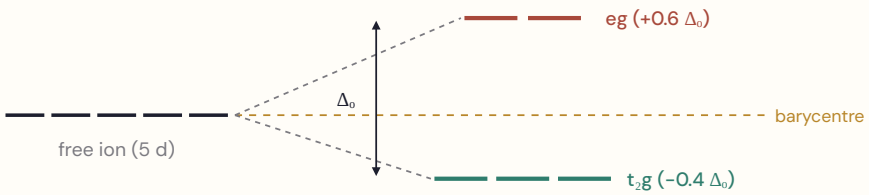
KEY IDEA

The average energy (barycentre) doesn't change: 2 × (+0.6) + 3 × (−0.4) = 0. Whatever the eg pair gains, the t_2g trio loses.

SECTION B

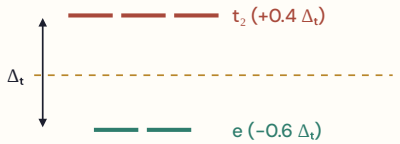
Three splitting diagrams

OCTAHEDRAL · SIX LIGANDS ON THE AXES



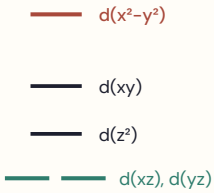
The two orbitals pointing at ligands rise; the three pointing between them fall.

TETRAHEDRAL · FOUR LIGANDS BETWEEN THE AXES



$\Delta_t \approx (4/9)\,\Delta_o$ · order reversed

SQUARE PLANAR · FOUR LIGANDS ON X AND Y



d^8 + strong field → top orbital empty

MEMORY HOOK

Octahedral: "two up, three down". Tetrahedral: flip it and shrink it to four-ninths.

SECTION C

What decides Δ

C

Factor	Effect on Δ	Example
Ligand	Set by its place in the spectrochemical series	CN^- gives a far larger Δ_o than F^-
Charge on metal	Higher charge pulls ligands closer → larger Δ	$[Co(H_2O)_6]^{3+}$ > $[Co(H_2O)_6]^{2+}$
Period of metal	4d and 5d metals → larger Δ than 3d	Most 4d/5d complexes are low spin
Geometry	Octahedral ≫ tetrahedral	$\Delta_t \approx (4/9)\,\Delta_o$

The spectrochemical series (NCERT order)

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

weak field (small Δ) ⟶ strong field (large Δ)

EXAM TRAP

Thiocyanate appears twice. Bonded through sulphur (SCN^-) it is a weak-field ligand; bonded through nitrogen (NCS^-) it is stronger than water.

SECTION D

High spin or low spin

For d^1–d^3 and d^8–d^{10} in an octahedral field there is only one way to fill the orbitals. For **d^4 to d^7** the fourth electron has a choice:

Δ_o < P · WEAK FIELD

Electrons go up into eg before pairing → **high spin**, more unpaired electrons.

Δ_o > P · STRONG FIELD

Electrons pair in t_{2g} first → **low spin**, fewer unpaired electrons.

EXAM TRAP

Tetrahedral complexes are high spin: Δ_t is almost always smaller than P. Don't pair electrons in a tetrahedral question unless it tells you to.

SECTION E

CFSE table, d^1 to d^{10}

$$CFSE = (-0.4\,x + 0.6\,y)\,\Delta_o + m\,P$$

x = electrons in t_{2g} · y = electrons in eg · m = extra pairs forced by the field (many books omit P)

d^n	High spin	CFSE	Unpaired	Low spin	CFSE	Unpaired
d^1	t_{2g}^1	$-0.4\,\Delta_o$	1	same as high spin		
d^2	t_{2g}^2	$-0.8\,\Delta_o$	2	same		
d^3	t_{2g}^3	$-1.2\,\Delta_o$	3	same		

d^n	High spin	CFSE	Unpaired	Low spin	CFSE	Unpaired
d^4	$t_2g^3\ eg^1$	−0.6 Δ_o	4	t_2g^4	−1.6 Δ_o + P	2
d^5	$t_2g^3\ eg^2$	0	5	t_2g^5	−2.0 Δ_o + 2P	1
d^6	$t_2g^4\ eg^2$	−0.4 Δ_o	4	t_2g^6	−2.4 Δ_o + 2P	0
d^7	$t_2g^5\ eg^2$	−0.8 Δ_o	3	$t_2g^6\ eg^1$	−1.8 Δ_o + P	1
d^8	$t_2g^6\ eg^2$	−1.2 Δ_o	2	same		
d^9	$t_2g^6\ eg^3$	−0.6 Δ_o	1	same		
d^{10}	$t_2g^6\ eg^4$	0	0	same		

MEMORY HOOK

Two zeros: high-spin d^5 and d^{10}. The t_2g gain is cancelled exactly by the eg loss.

SECTION F

Magnetism and colour

F

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

n = number of unpaired electrons (spin-only formula)

n	0	1	2	3	4	5
μ (BM)	0	1.73	2.83	3.87	4.90	5.92

Measure μ, read off n, and you know whether the complex is high spin or low spin.

Why complexes are coloured

An electron in the lower set absorbs a photon of energy Δ and jumps to the upper set (a **d–d transition**). The complex shows the **complementary** colour of the light absorbed.

- **d^0 and d^{10}** ions (Sc^{3+}, Ti^{4+}, Zn^{2+}, Cu^{+}) have no d–d transition and are usually colourless.
- **No ligand, no splitting:** anhydrous $CuSO_4$ is white; with water, $[Cu(H_2O)_4]^{2+}$ forms and is blue.
- **Change the ligand, change the colour:** a stronger-field ligand absorbs higher-energy (shorter-wavelength) light.
- **High-spin d^5** (e.g. $[Mn(H_2O)_6]^{2+}$) is only very pale pink: every d–d transition would need a spin flip, so all are weak.

SECTION G

Solved numericals

SOLVED EXAMPLE 01 — SAME METAL, TWO LIGANDS

Compare $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$: configuration, unpaired electrons, μ and CFSE.

1. Fe^{3+} is d^5.
2. F^- is weak-field → high spin, $t_2g^3\ eg^2$, 5 unpaired, μ = 5.92 BM, CFSE = 0.
3. CN^- is strong-field → low spin, t_2g^5, 1 unpaired, μ = 1.73 BM, CFSE = −2.0 Δ_o + 2P.

ANSWER $[FeF_6]^{3-}$ strongly paramagnetic; $[Fe(CN)_6]^{3-}$ weakly paramagnetic.

SOLVED EXAMPLE 02 — CHARGE MATTERS

Why is $[Co(NH_3)_6]^{3+}$ diamagnetic while $[CoF_6]^{3-}$ has μ ≈ 4.90 BM?

1. Co^{3+} is d^6.
2. With F^- (weak field): $t_2g^4\ eg^2$, 4 unpaired → 4.90 BM.
3. The +3 charge makes Δ_o large enough that NH_3 forces pairing: t_2g^6, 0 unpaired.

ANSWER Low spin t_2g^6 for NH_3 (CFSE −2.4 Δ_o + 2P); high spin for F^- (CFSE −0.4 Δ_o).

SOLVED EXAMPLE 03 — Δ FROM COLOUR

$[Ti(H_2O)_6]^{3+}$ absorbs most strongly at about 498 nm. Calculate Δ_o in kJ mol^{-1}.

1. Ti^{3+} is d^1: one $t_{2g} \rightarrow e_g$ jump, so photon energy = Δ_o.
2. $E = hc/\lambda = (6.626 \times 10^{-34} \times 2.998 \times 10^{8}) / (498 \times 10^{-9}) = 3.99 \times 10^{-19}$ J per ion.
3. $\times 6.022 \times 10^{23} = 2.40 \times 10^{5}$ J mol^{-1}.

ANSWER $\Delta_o \approx 240$ kJ mol^{-1} (≈ 20,100 cm^{-1}). It absorbs blue-green, so it looks violet.

SOLVED EXAMPLE 04 — GEOMETRY FROM MAGNETISM

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

1. Ni^{2+} is d^8; both have four ligands.
2. Cl^- (weak) → tetrahedral, $e^4\, t_2^4$, 2 unpaired.
3. CN^- (strong) → square planar; all 8 electrons paired below $d(x^2-y^2)$.

ANSWER Tetrahedral (paramagnetic) vs square planar (diamagnetic).

SOLVED EXAMPLE 05 — TETRAHEDRAL CFSE

Find the CFSE and μ of $[CoCl_4]^{2-}$.

1. Co^{2+} is d^7; four Cl^- → tetrahedral, high spin.
2. Fill e first: $e^4\, t_2^3$ → 3 unpaired.
3. CFSE = $(-0.6 \times 4 + 0.4 \times 3)\, \Delta_t = -1.2\, \Delta_t$.

ANSWER CFSE = $-1.2\, \Delta_t$; $\mu = \sqrt{15} = 3.87$ BM.

SECTION H

Traps and check yourself

H

#	The trap	The fix
1	Using octahedral numbers for a tetrahedral complex	e below t_2; −0.6/+0.4 Δ_t; $\Delta_t \approx (4/9)\,\Delta_o$
2	Worrying about field strength for d^3 or d^8 octahedral	Only d^4–d^7 octahedral have a high/low-spin choice
3	Pairing electrons in a tetrahedral complex	Tetrahedral is high spin
4	Giving the absorbed colour as the colour seen	The complex shows the complementary colour
5	Wrong oxidation state, so wrong d^n	Charge on complex − ligand charges; then group number − oxidation state
6	Including P when options show only Δ_o multiples	Match the form of the options

Where CFT falls short

It treats ligands as point charges and ignores covalency, so it can't explain why neutral NH_3 and CO split more strongly than F^-, or why OH^- is weaker than H_2O. Ligand field and MO theory fix this.

CHECK YOURSELF

1. CFSE (in Δ_o) of a high-spin d^7 octahedral ion?
2. Larger Δ_o: $[Fe(H_2O)_6]^{2+}$ or $[Fe(H_2O)_6]^{3+}$?
3. $[MnCl_4]^{2-}$ has $\mu \approx 5.9$ BM. Unpaired electrons and geometry?
4. Why is $[Zn(H_2O)_6]^{2+}$ colourless?
5. μ of $[Cr(H_2O)_6]^{3+}$?

Answers: (1) $t_2g^5\ eg^2$: −0.8 Δ_o. (2) Fe^{3+}, higher charge. (3) Five; tetrahedral high-spin d^5. (4) d^{10}, no d–d transition. (5) d^3, 3 unpaired: 3.87 BM.

END OF NOTES · RAMGOVINDYADAV.COM