

Exercise walk-through

28.4

Stereoisomerism in transition element complexes

A-Level Chemistry

Four key properties

variable oxidation state

– 3d & 4s close in energy

complex ions

– vacant d orbitals accept lone pairs

catalyst

– more than one stable state, vacant d orbitals

coloured

compounds – electrons jump split d orbitals

A **transition element**

forms ions with **incomplete d orbitals** (so Sc and Zn don't count).



Ruby

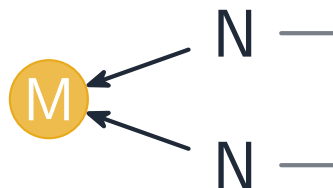
Ligands and denticity

A **ligand** donates a **lone pair** in a **dative bond** :

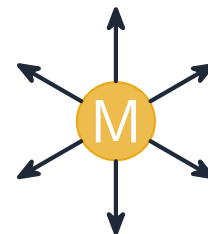
- **monodentate** – 1 bond (H_2O , NH_3)
- **bidentate** – 2 bonds (en)
- **polydentate** – many (EDTA: 6)



monodentate: 1 bond
(H_2O , NH_3 , Cl^-)



bidentate: 2 bonds
("en")



polydentate: many
(EDTA uses 6)

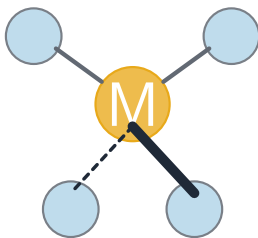
Complex shapes

The **coordination number** (dative bonds to the metal) sets the shape:

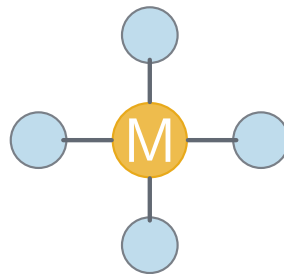
- 6 → **octahedral**
- 4 → tetrahedral or square planar
- 2 → linear



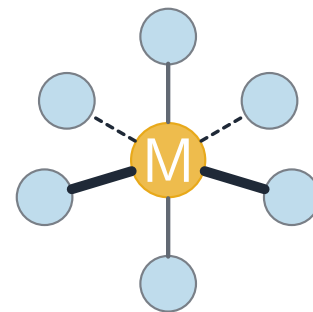
linear
CN 2



tetrahedral
CN 4



square planar
CN 4



octahedral
CN 6

The 3d orbitals, and the bond that makes a complex

the orbitals

the $3d_{xy}$ orbital has **four lobes pointing between** the axes; the $3d_{x^2-y^2}$ has four lobes pointing **along** them

why that matters

ligands approach along the axes, so those two sets are pushed up by **different amounts**

non-degenerate

the five 3d orbitals, equal in the free ion, split into two energy levels in a complex

a dative covalent bond

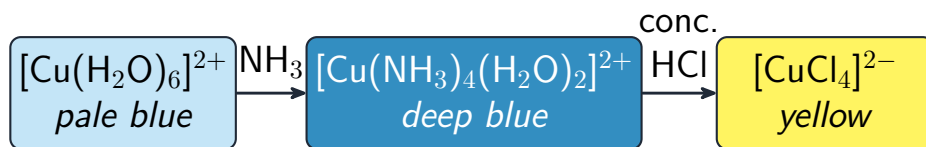
the ligand supplies **both** electrons to the bond with the metal ion

the colour

an electron absorbs light to jump the split, and the **complementary** colour is what we see

Change the ligand and you change the size of the split, so you change the colour. That is why ligand exchange is visible.

Ligand exchange



In **ligand exchange** one ligand replaces another, often with a colour change. Copper(II): pale blue (water) $\rightarrow$ deep blue (NH_3) $\rightarrow$ yellow ($[\text{CuCl}_4]^{2-}$).

Exercises 2.1·2.2

2.1 Name the type of stereoisomerism shown by $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. [1]

2.2 State what makes a complex show optical isomerism. [1]

Exercises 2.1·2.2

2.1 Name the type of stereoisomerism shown by $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. [1]

2.1

- geometrical (cis/trans) isomerism
-

2.2 State what makes a complex show optical isomerism. [1]

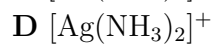
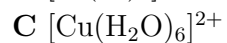
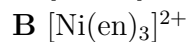
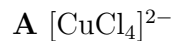
2.2

- it has two non-superimposable mirror images (e.g. an octahedral complex with bidentate ligands)

Exercises 3.1·3.2

3.1 Optical isomerism is shown by:

[1]

☐

3.2 The *trans* isomer of a square planar complex is often:

[1]

☐

A polar

B non-polar (dipoles cancel)

C optically active

D coloured only

Exercises 3.1·3.2

3.1 Optical isomerism is shown by:

[1]

☐

A $[\text{CuCl}_4]^{2-}$

B $[\text{Ni}(\text{en})_3]^{2+}$

C $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

D $[\text{Ag}(\text{NH}_3)_2]^+$

3.1 B

- $[\text{Ni}(\text{en})_3]^{2+}$ (octahedral with three bidentate ligands) shows optical isomerism

3.2 The *trans* isomer of a square planar complex is often:

[1]

☐

A polar

B non-polar (dipoles cancel)

C optically active

D coloured only

3.2 B

- In the *trans* form the dipoles cancel, so it is non-polar

Exercise 3.3

3.3 (a) Draw the cis and trans isomers of the square planar complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. [2]

(b) Explain why $[\text{Ni}(\text{en})_3]^{2+}$ shows optical isomerism. [2]

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3.3

(a)

- cis – the two NH_3 (and two Cl) adjacent; trans – the two NH_3 (and two Cl) opposite

(b)

- it is octahedral with three bidentate (en) ligands, giving two non-superimposable mirror images (enantiomers)

Exercise 3.4

3.4 State, with a reason, which of the cis or trans form of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is polar. [2]

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3.4

- the cis form is polar; its two Pt–Cl dipoles are on the same side and do not cancel, while in the trans form they are opposite and cancel

Exercise 3.5 (a)

3.5 The complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is square planar; $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is octahedral; $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]$ is octahedral with three bidentate ligands.

(a) Draw the two geometrical isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and label each cis or trans. [3]

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(a)

- Square planar with Pt at the centre; **cis** has the two Cl on adjacent corners, **trans** has them opposite

Exercise 3.5 (b)

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(b) Explain which of the two is polar, and why the other is not.

[2]

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(b)

- The **cis** isomer is polar: its two Pt–Cl bond dipoles point to the same side and add, whereas in the trans isomer they point in exactly opposite directions and cancel, so the molecule has no overall dipole

Exercise 3.5 (c)

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(c) State how many geometrical isomers $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has, and describe how they differ. [2]

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(c)

- Two: in the *cis* form the two chloride ligands occupy adjacent (90°) positions, in the *trans* form they are opposite (180°)

Exercise 3.5 (d)

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(d) Explain what makes $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$ **optically** active, and describe how the two forms could be told apart.

[4]

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(d)

- The three bidentate ligands wrap round the metal in a propeller arrangement, so the complex has no plane of symmetry; it is therefore **chiral** and exists as two non-superimposable mirror images (optical isomers / enantiomers). They rotate the plane of plane-polarised light by equal amounts in **opposite** directions, which a polarimeter detects; in every other physical and chemical property they are identical