Topic Date

TRANSITION ELEMENTS

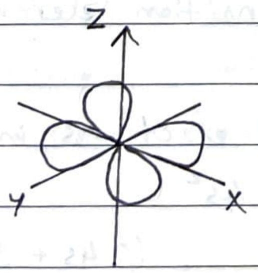
Transition elements : d-block elements which form one /more stable ions with ~~an~~ an incomplete d subshell.

- all metals
- found in d-block of periodic table (btwn Groups 2- 13)
- not all d-block elements are transition elements
  - ↳ Scandium
    - only forms 1 ion : Sc^{3+}.
    - Sc^{3+} ion has no e^- in 3d subshell ; has electronic configuration of [Ar].
  - ↳ Zinc
    - only forms 1 ion : Zn^{2+}
    - Zn^{2+} ion has complete 3d subshell ; has electronic configuration of $[Ar]3d^{10}$.

Shapes of 3d orbitals

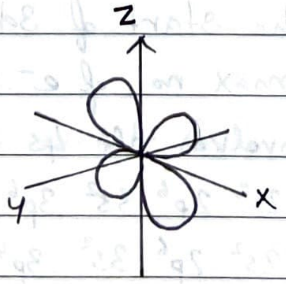
5 orbitals in d subshell :

- $3d_{yz}$
- $3d_{xz}$
- $3d_{xy}$
- $3d_{x^2-y^2}$
- $3d_{z^2}$



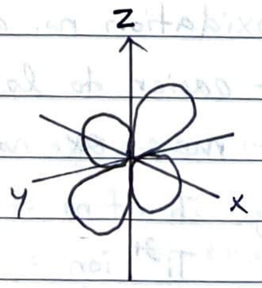
$\boxed{3d_{xy}}$

4 lobes point btwn x & y axes.



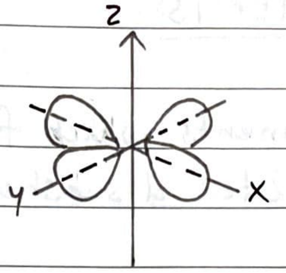
$\boxed{3d_{xz}}$

4 lobes point btwn x & z axes.



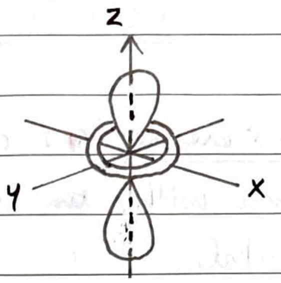
$\boxed{3d_{yz}}$

4 lobes point btwn y & z axes.



$3d_{x^2-y^2}$

4 lobes point along x and y axes.



$3d_{z^2}$

2 main lobes form dumbbell shape, and point along z axis, with ring around the centre.

Properties of transition elements

1) variable oxidation states
2) behave as catalysts
3) form complex ions
4) form coloured compounds

Ti	[Ar] $4s^2 3d^2$	+3, +4
V	[Ar] $4s^2 3d^3$	+2, +3, +4, +5
Cr	[Ar] $4s^1 3d^5$	+3, +6
Mn	[Ar] $4s^2 3d^5$	+2, +4, +6, +7
Fe	[Ar] $4s^2 3d^6$	+2, +3
Co	[Ar] $4s^2 3d^7$	+2, +3
Ni	[Ar] $4s^2 3d^8$	+2
Cu	[Ar] $4s^1 3d^{10}$	+1, +2

① Variable oxidation states

- variable oxidation states can

orbitals are similar in energy. ⇒ similar amount of energy needed to remove diff no. of e^-.

- when transition elements form ions, e^- in 4s lost first, then 3d.

→ oxidation no. at the start of 3d transition elements

- easier to lose max no. of e^-.
- max. ox. no. involves all 4s & 3d electrons in the atom.

eg. Ti atom = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$

Ti^{3+} ion = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$ (2 4s + 1 3d e^- lost)

Ti^{4+} ion = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ (2 4s + 2 3d e^- lost)

→ oxidation no. at the end of 3d transition elements

- more likely to adopt +2 oxidation state.

∵ Across d-block:

nuclear charge ↑ ⇒ nuclear attraction for 3d e^- ↑ ⇒ harder to remove 3d e^- ⇒ ~~higher oxidations~~ stability of higher oxidation states ↓

eg. Ni atom = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

Ni^{2+} ion = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$ (only 4s e^- lost)

② **Behave as catalysts**

- ability to form ions w/ >1 stable oxidation state.
- contain vacant d-orbitals.

→ Oxidation states

- can accept/lose e^- to go from one ox. state to another.
- ∴ catalyse redox reactions by acting as both O.A & R.A

eg. Fe can form Fe(II) & Fe(III) ions

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (acts as R.A)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (acts as O.A)

- transition elements w/ high ox. states = powerful O.A ∵ they readily accept e^-.

eg. $KMnO_4$ (ox. state of Mn = +7)

→ Vacant d orbitals

- when transition metals form ions they have vacant d orbitals energetically accessible (not too high in energy)
- ∴ dative bonds can be formed btwn transition element ion and ligands : each ligand provides pair of e^- to form bond, which is donated into vacant d-orbital.

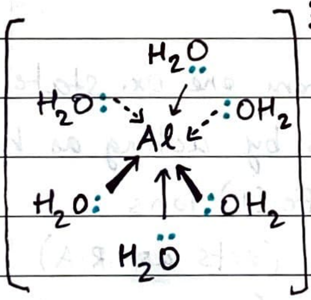
③ complex ions

complex: molecule/ion formed by central metal atom/ion surrounded by one/more ligands.

- complex can ~~be~~ have overall +ve/-ve charge OR be neutral.
  $\overset{2}{\text{complex}}$ ion
- transition elements can easily form complex ions ∵ energetically accessible vacant d orbitals.
- transition element in centre accepts pairs of e^- from ligands into empty d orbitals - dative bonds.
  (central metal ion)

*ligand : a species w/ a lone pair of e^- that can be donated to metal ion. (to form dative bond)

eg.



$[Al(H_2O)_6]^{3+}$ (aq)

Transition metal complexes

Eg.

central metal ions	ligands
Cu(II)	H_2O
Co(II)	NH_3
	OH^-
	Cl^-

Co(II) & Cu(II) complexes with H_2O & NH_3

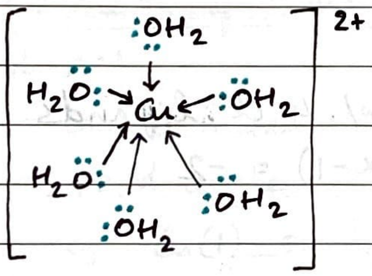
→ H_2O & NH_3 = neutral ligands
→ small ligands
→ H_2O donates lone pair from O atom; NH_3 from N atom.

→ up to 6 H_2O/NH_3 ligands can fit around central metal ion ⇒ 6 dative covalent bonds

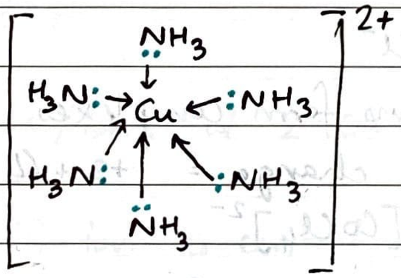
→ 6 dative bonds :
  - → octahedral shape
  - → coordination no. = 6 (no. of dative bonds formed btwn central metal ion & ligands)

→ overall charge of complex = charge on central metal ion (+2) + charge on each ligand (0)

$$= +2 + 6\times 0 = 2+$$



$[Cu(H_2O)_6]^{2+}$



$[Cu(NH_3)_6]^{2+}$

(Same for Co)
- octahedral
- overall charge = 2+

Co(II) & Cu(II) complexes with OH^- & Cl^-

→ OH^- & Cl^- = -ve charged ligands

→ each donates lone pair of e^-

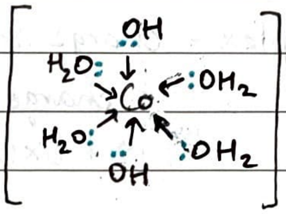
→ OH^- = small ligand
  - → up to 6 OH^- can fit around central metal ion.
  - → 6 dative covalent bonds.
  - → octahedral shape.
  - → Cordination no. = 6.

→ Cl^- = large ligand
  - → up to 4 Cl^- can fit around central metal ion.
  - → 4 dative covalent bonds.
  - → tetrahedral shape.
  - → cordination no. = 4.

→ Co(II) & OH^-

- Co(II) ions form complexes w/ $2OH^-$ ligands (remaining 4 ligands = H_2O)
- overall charge = $+2 + (4 \times 0) + (-2) = 0$

$[Co(H_2O)_4(OH)_2]$

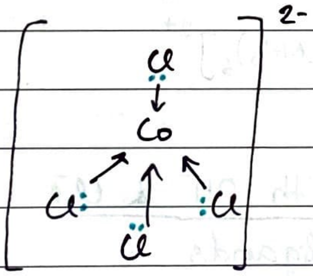


- octahedral
- overall charge = 0 (same for Cu)

→ Co(II) & Cl^-

- Co(II) ions form complexes w/ 4 Cl^- ligands
- overall charge = $+2 + (4 \times -1) = -2$

$[CoCl_4]^{2-}$



- tetrahedral
- overall charge = -2 (same for Cu)

Ligands

species w/ one or more lone pairs of e^-.

① **Monodentate ligands**

form 1 dative bond to central metal ion.

eg. H_2O, NH_3, Cl^-, CN^-, OH^-, SCN^-

② **Bidentate ligands**

each form 2 dative bonds to central metal ion.

∵ each ligand contains 2 atoms w/ lone pairs of e^-

eg. $H_2NCH_2CH_2NH_2$, $C_2O_4^{2-}$

↓ written as 'en' ↓ written as 'ox'

③ **Polydentate ligands**

each form >2 dative bonds to central metal ion

∴ each ligand contains >2 atoms w/ lone pairs of e^-

eg. $EDTA^{4-}$ = hexadentate ligand

Geometry of complexes

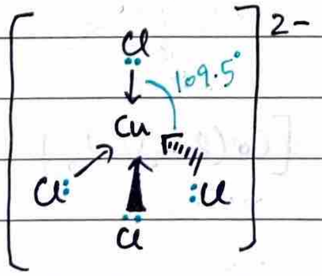
① **linear**

- central metal atoms / ions w/ 2 coordinate bonds.
- bond angle = 180°
- eg. Cu(I) or Ag(I) ion as central metal ion + $2NH_3$ ligands

$$[H_3N\!:\rightarrow \underbrace{Cu}_{180°} \leftarrow :NH_3]^+ \qquad [H_3N\!:\rightarrow Ag \leftarrow :NH_3]^+$$

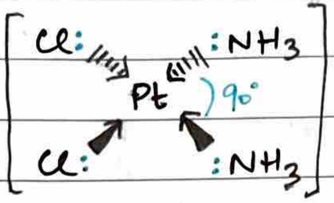
② **tetrahedral**

- 4 coordinate bonds
- bond angle = 109.5°
- eg. complexes w/ 4 Cl^- ions ligands

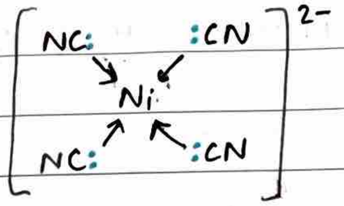


③ **Square planar**

- 4 coordinate bonds
- bond angle = 90°
- eg. complexes w/ ~~cyanide~~ CN^- ligands



cisplatin



$[Ni(CN)_4]^{2-}$

④ octahedral

- 6 coordinate bonds
- bond angle = 90°

→ 6 coordinate bonds w/ 6 small monodentate ligands

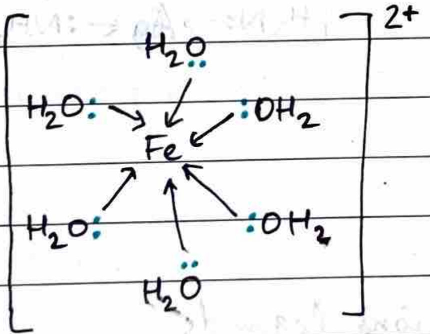
eg. H_2O, NH_3, OH^-, SCN^-

→ 6 coordinate bonds w/ 3 bidentate ligands

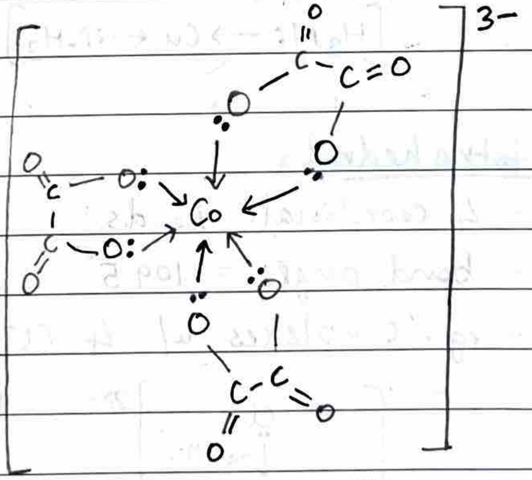
eg. $C_2O_4^{2-}$, $H_2NCH_2CH_2NH_2$

→ 6 coordinate bonds w/ 1 hexadentate ligand

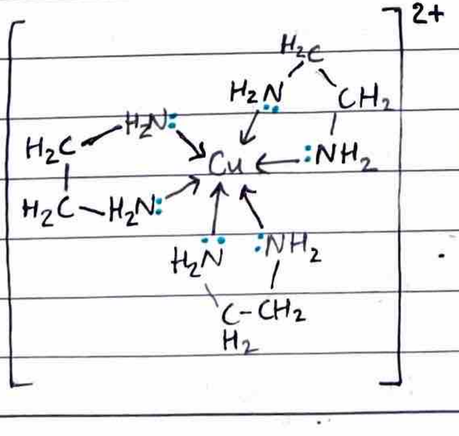
eg. $EDTA^{4-}$



$[Fe(H_2O)_6]^{2+}$



$[Co(C_2O_4)_3]^{3-}$



$[Cu(en)_3]^{2+}$

Geometry	no. of coordinate bonds	bond angle	ligand (s) involved
linear	2	180°	NH_3
tetrahedral	4	109.5°	Cl^-
square planar	4	90°	CN^-
octahedral	6	90°	H_2O, NH_3, OH^-, SCN^-, $C_2O_4^{2-}$, H_2N[illegible]$H_2CH_2NH_2$

NOTE: no. of dative (coordinate) bonds = coordination no.
NOT no. of ligands.

Ligand exchange (ligand substitution)

- when 1 ligand in a complex is replaced by another.
- forms a new complex that is more stable than the original.
- ligands in original complex are partially or entirely substituted
- if ligands of same size, no change in coordination no. / geometry of complex (vice versa).

Substitution in copper (II) complexes

$Cu^{2+}(aq) = [Cu(H_2O)_6]^{2+}(aq)$ — blue solution

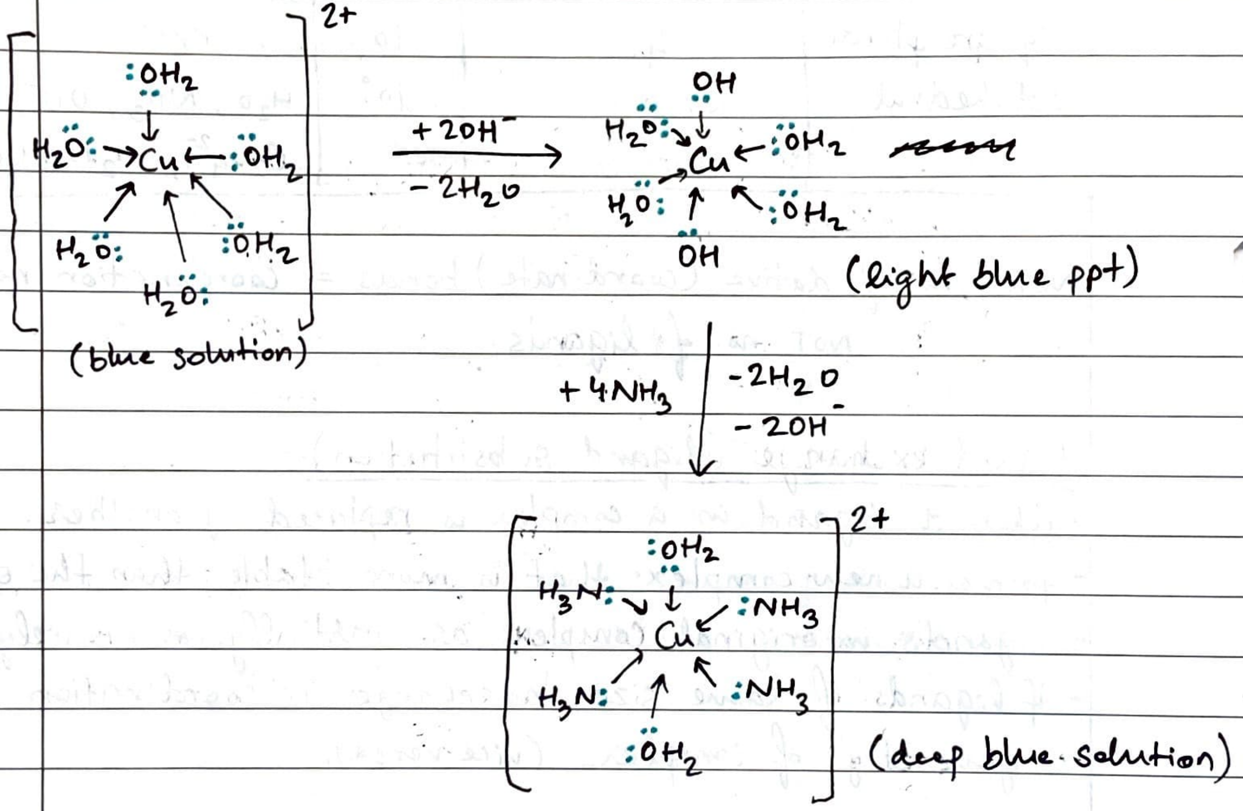
(i) $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow [Cu(H_2O)_4(OH)_2](s) + 2H_2O(l)$
(blue solution) (pale blue ppt)

- dropwise addition of $NaOH(aq)$
- partial ligand substitution of $2H_2O$ ligands by $2OH^-$.

(ii) $[Cu(H_2O)_4(OH_2)](s) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l) + 2OH^-(aq$
(pale blue ppt) (deep blue solution)

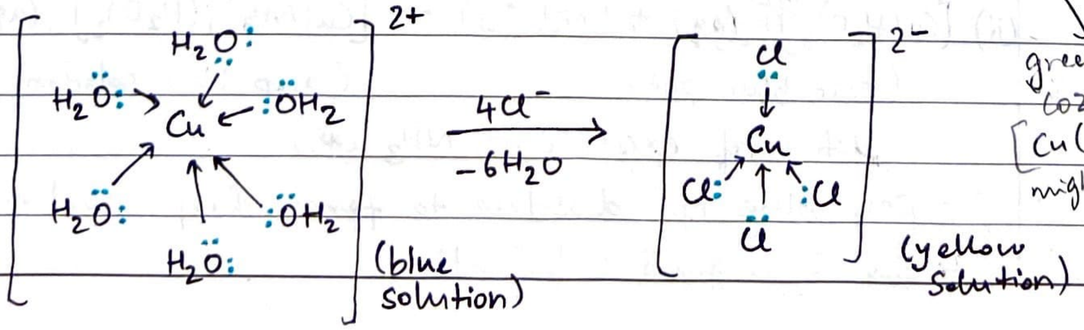
- addition of excess conc. $NH_3(aq)$
- pale blue ppt dissolves to form deep solution.
- partial ligand substitution

NOTE: if conc. NH_3 (aq) added dropwise to $[Cu(H_2O)_6]^{2+}$ (aq), light blue ppt forms, which then dissolves in excess NH_3 (aq) to form deep blue solution.



(iii) $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$
(blue solution) (yellow solution)

- addition of conc HCl (aq)
- complete ligand substitution
- coordination no: 6 → 4 ∵ Cl^- > H_2O ligands
- geometry: octahedral → tetrahedral
- reversible reaction ∴ adding water to solution causes ligand substitution again, blue solution returns.



green solution coz some $[Cu(H_2O)_6]^{2+}$ (aq) might still be present

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Substitution in cobalt (II) complexes

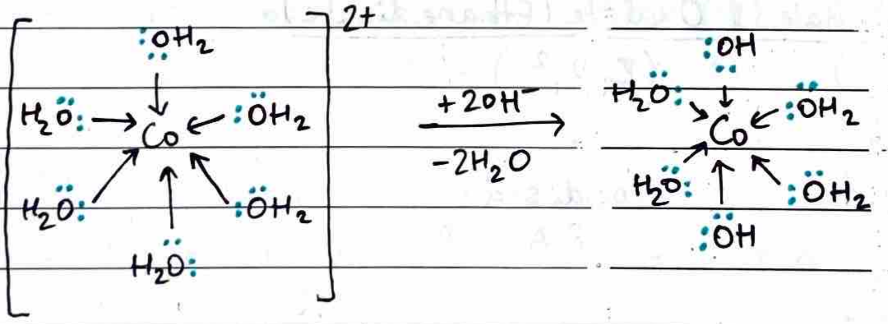
$Co^{2+}(aq) = [Co(H_2O_{\cancel{8}})_6]^{2+}(aq)$ — pink solution

(i) $[Co(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow [Co(H_2O)_4(OH)_2](s) + 2H_2O(l)$
(pink solution) (blue ppt)

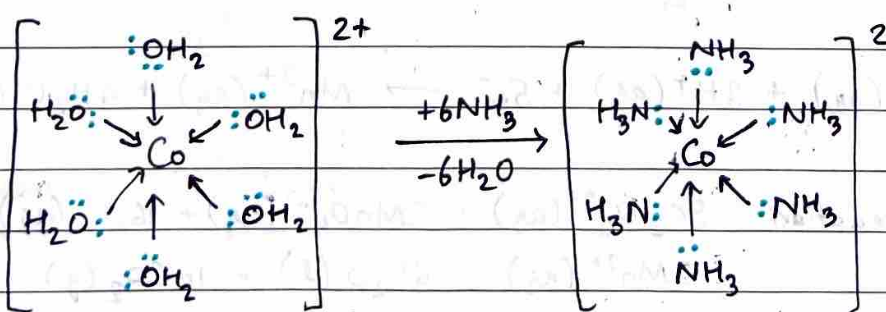
- dropwise addition of NaOH (aq)
- <u>partial</u> ligand substitution of $2H_2O$ ligands by $2OH^-$.
- if alkali added in excess, blue ppt turns red when warmed

(ii) $[Co(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \longrightarrow [Co(NH_3)_6]^{2+}(aq) + 6H_2O(l)$
(pink solution) (brown solution)

- addition of excess conc. $NH_3(aq)$; no ppt since $NH_3(aq)$ added in excess & not dropwise.
- <u>complete</u> ligand substitution of H_2O ligands by NH_3
- NH_3 ligands make Co^{2+} ion so unstable that it is readily oxidized in air to Co^{3+}. $[Co(NH_3)_6]^{3+}$



(pink solution) (blue ppt)

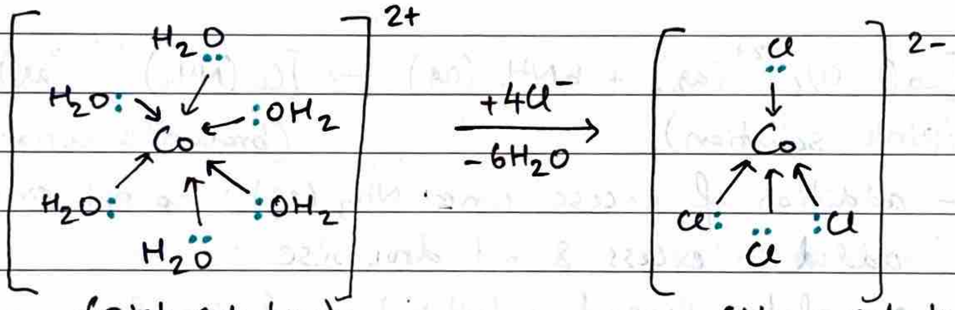


(pink solution) (brown solution)

(iii) $[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \longrightarrow [CoCl_4]^{2-}(aq) + 6H_2O(l)$

(pink solution) (blue solution)

- addition of conc HCl (aq)
- <u>complete</u> ligand substitution
- coordination no: 6 → 4
- geometry: octahedral → tetrahedral
- reversible reaction ∴ adding water to solution causes Cl^- ligands to be displaced by H_2O, pink solution returns.



(pink solution) (blue solution)

Redox systems

① **Permanganate & Oxalate (Ethanedioate)**

(MnO_4^-) ↓ reduced O.A

$(C_2O_4^{2-})$ ↓ oxidised R.A

$\underset{+3}{C_2}O_4^{2-}(aq) \longrightarrow 2\underset{+4}{C}O_2(g) + 2e^-$; oxidation

$\underset{+7}{Mn}O_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow \underset{+2}{Mn^{2+}}(aq) + 4H_2O(l)$; reduction

overall reaction: $5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow$
$2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

- this is an autocatalysis reaction: Mn^{2+} acts as autocatalyst.
  - ↳ transition metal ions acts as autocatalysts ∴ they can change oxidation state during reaction.
- titration used to find conc. of $C_2O_4^{2-}$ (toxic)
- endpoint: all $C_2O_4^{2-}$ have reacted, MnO_4^- slightly in excess; first permanent pink colour appears.

② Ferrous & permanganate

(Fe^{2+})	(MnO_4^-)
↓	↓
oxidised	reduced
R.A	O.A

$$\underset{+2}{Fe^{2+}}(aq) \longrightarrow \underset{+3}{Fe^{3+}}(aq) + e^- \text{ ; oxidation}$$

$$\underset{+7}{MnO_4^-}(aq) + 8H^+(aq) + 5e^- \longrightarrow \underset{+2}{Mn^{2+}}(aq) + 4H_2O(l) \text{ ; reduction}$$

overall reaction: $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

- titration used to find conc. of Fe^{2+}
- endpoint: all Fe^{2+} have reacted, MnO_4^- slightly in excess; first permanent pink colour.

③ Cupric & iodide

(Cu^{2+})	(I^-)
↓	↓
reduced	oxidised
O.A	R.A

$$\underset{-1}{2I^-}(aq) \longrightarrow \underset{0}{I_2}(aq) + 2e^- \text{ ; oxidation}$$

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$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$; reduction
$+2$ $\quad$ $+1$

overall reaction : $2I^-(aq) + 2Cu^{2+}(aq) \rightarrow 2Cu^+(aq) + I_2(aq)$

- when excess I^- reacted w/ Cu^{2+} :

reaction 1: $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow \underset{(ppt)}{2CuI(s)} + I_2(aq)$

- titration used to find conc. of Cu^{2+}, by finding amount of I_2 liberated :
  - i) known conc. of sodium thiosulfate solution added to mixture formed in reaction 1 from burette.

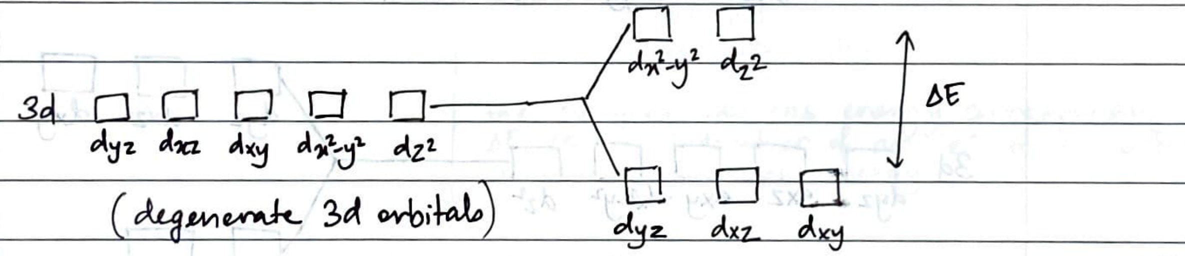
reaction 2 : $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

  - as I_2 used up brownish colour of solution gets lighter.
  - ii) drops of starch indicator added
    - turns blue-black with remaining $I_2(aq)$
  - iii) titrate further until blue-black colour disappears ⇒ all I_2 reacted

To find conc. of Cu^{2+} :
- mol of I_2 = $\frac{1}{2}$ mol of $S_2O_3^{2-}$ (reaction 2)
- mol of Cu^{2+} = 2 mol of I_2 = mol of $S_2O_3^{2-}$
- mol of Cu^{2+} ÷ volume = conc.

Degenerate & non-degenerate d Orbitals

- isolate transition element (not bonded to anth else) atom / ion has 5 d orbitals.
- these d orbitals are at same energy level (equal in energy) = degenerate orbitals.
- when ligands are attached, transition element ion no longer isolated.
- dative bonding from ligands causes the 5 d-orbitals to split into 2 sets : not equal in energy ∴ non-degenerate orbitals.
- diff in energy btwn the 2 sets = ΔE.



splitting in octahedral complex

(2 sets of non-degenerate orbitals)

Splitting of 3d orbitals in octahedral complexes

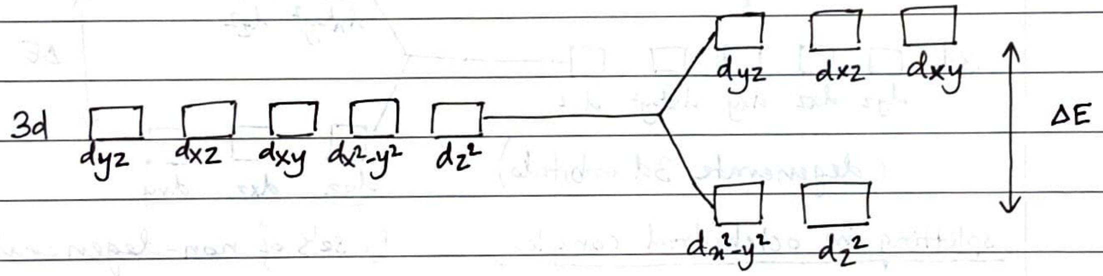
- in octahedral complex, 6 ligands arranged around central metal ion.
- lone pairs of the ligands repel e^- in x^2-y^2 and z^2 orbitals of metal ion more than e^- in yz, xz, xy orbitals.
- ∵ $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals line up with the dative bonds in the complex's octahedral shape.
- ∵ ligands are attached / approach central metal ion along x, y, z axes, and the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals have lobes along these axes.
- e^- in these 2 orbitals are closer to bonding e^- ∴ more repulsion.

⇒ when d orbitals split, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are at slightly higher energy level than the other 3. (fig. above)

Splitting of 3d orbitals in tetrahedral complexes

- in tetrahedral complex, 4 ligands arranged around central metal ion.
- lone pairs of the ligands repel e^- in yz, xz, xy orbitals more than e^- in x^2-y^2 & z^2 orbitals.
- ∵ bonding pair of e^- from the 4 ligands line up with 3dyz, 3dxz, 3dxy orbitals of central metal ion.
- $3dx^2-y^2$, $3dz^2$ orbitals lie btwn the metal-ligand bonds.

⇒ when d-orbitals split, $3d_{x^2-y^2}$ & $3d_{z^2}$ are at a lower and more stable energy level thank the other 3.



Coloured Complexes

- a coloured transition element complex solution absorbs part of the EM spectrum, in the visible light region.
- observed colour = complementary colour made up of light frequencies that are NOT absorbed.
  - eg. Cu^{2+} absorbs red ; observed colour = pale blue (complementary)

Electron promotion

- When light shines on transition element complex solution, an e^- will absorb exact amount of energy ΔE (energy diff btwn 2 sets of non-degenerate orbitals).

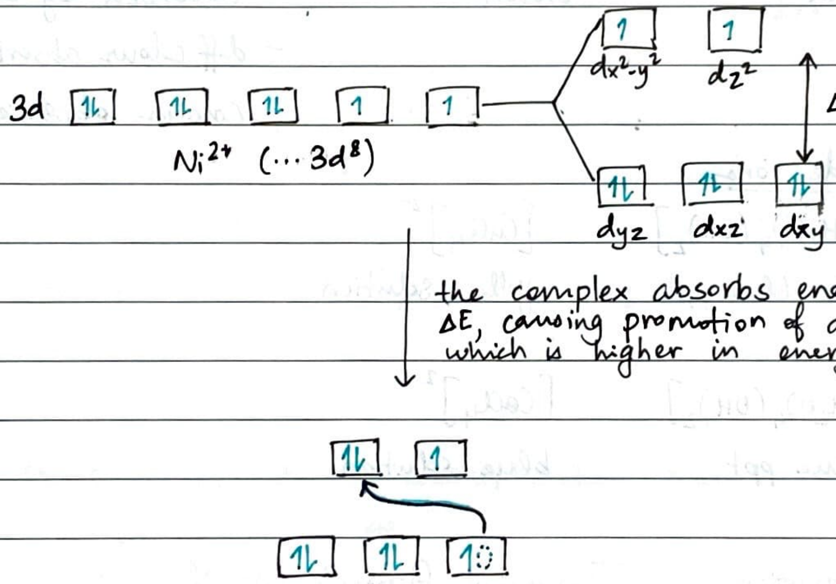
$\boxed{\Delta E = h \times v}$

h = Planck's constant (6.626×10^{-34} m^2 kg s^{-1})

v = frequency (Hz)

- the e^- uses this energy from light to jump into a higher, non-degenerate energy level → electron promotion.
- the other frequencies of light not absorbed combine to make the complementary colour.

electron promotion of Ni(II) complex when light shines on solution:



the complex absorbs energy corresponding to ΔE, causing promotion of an e^- to an orbital which is higher in energy.

Effects of ligands on complementary colour

- the exact energy diff (ΔE) btwn. non-degenerate orbitals is affected by the diff ligands that surround transition element ion.
- diff ligands split the d orbital by diff amount of energy.
- this depends on repulsion experienced by the d-orbitals from these ligands.
- ∴ size of ΔE and corresponding frequency of light absorbed by the e^- will be slightly diff.
- ∴ diff colour of light is absorbed by complex solution & diff complementary colour is absorbed.
  - ↳ complexes w/ same transition element ion but diff ligands can have diff colours.

Ligand exchange in copper (II) & cobalt (II) complexes

1) Ammonia

$[Cu(H_2O)_6]^{2+}$ light blue

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue

$[Co(H_2O)_6]^{2+}$ pink

$[Co(NH_3)_6]^{2+}$ brown

- colour change ∵ NH_3 ligands cause d orbitals to split by diff amount of energy (ΔE).
- Size of ΔE and freq. of e^- absorbed by e^- is diff.
- diff colour absorbed, diff comp. colour observed.

2) Chloride ions

$[Cu(H_2O)_4(OH)_2]$ pale blue ppt

$[CuCl_4]^{2-}$ yellow solution

$[Co(H_2O)_4(OH)_2]$ blue ppt

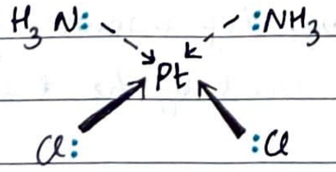
$[CoCl_4]^{2-}$ blue solution

Stereoisomerism in Transition Element Complexes

Geometrical (cis-trans) isomerism

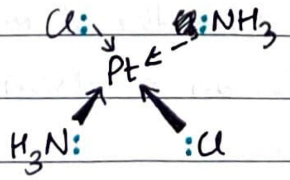
- exhibited by square planar and octahedral complexes with 2 pairs of different ligands.

Square planar



cisplatin

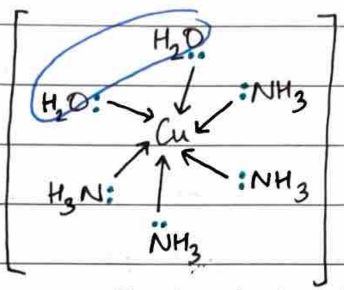
2 adjacent Cl^- ligands



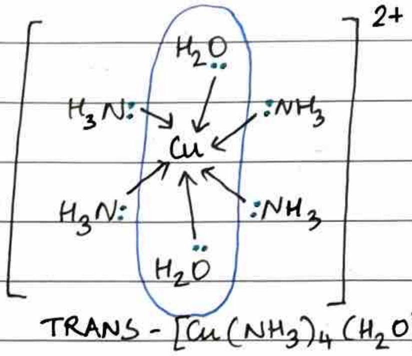
transplatin

2 Cl^- ligands opposite each other

octahedral



CIS - $[Cu(NH_3)_4(H_2O)_2]^{2+}$



TRANS - $[Cu(NH_3)_4(H_2O)_2]^{2+}$

- octahedral complexes exhibit geometrical isomerism when they have 2 ligands attached that are diff from the rest.
- cis isomer: the 2 diff ligands are next to each other.
  trans isomer: the 2 diff ligands are opp each other.

Optical isomerism

- exhibited by octahedral complexes with bidentate ligands
  (chk pg. 8 – eg. 2 & 3 in octahedral show optical isomerism)

Polarity of Complexes

square planar

- cisplatin: → $2Cl^-$ atoms on same side
  → these atoms have stronger pull on e^- in dative bond and will carry partial -ve charge.
  → imbalance of charge causes complex to become polar.
- transplatin: → $2Cl^-$ atoms opp. each other
  → pull on e^- in the dative bonds is balanced.
  → balanced charge ∴ complex is non-polar.

cis-isomer → polar   trans-isomer → non-polar octahedral

- trans-isomer → non-polar ; cis-isomer → polar
- cis-$[Co(NH_3)_4(H_2O)_2]^{2+}$, O atoms in H_2O ligands are more electronegative than N atoms in NH_3.
- this causes the side containing H_2O ligands to be partially -ve.
- charge imbalance causes complex to become polar.
- in trans-isomer charge is evenly distributed due to symmetrical arrangement ∴ non-polar.

Stability Constant (K_{stab})

- when transition metal ions are in aqueous solution, they automatically become hydrated; H_2O molecules surround the ion and act as ligands by forming dative bonds w/ central metal ion.
- when there are other potential ligands present in solution, there's a competing equilibrium in ligand exchange and the most stable complex will be formed.
- stability constant = equilibrium constant for the formation of the complex ion in a solvent from its constituent ions / molecules.

eg. $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

$$\boxed{K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2]^{2+}}{[Cu(H_2O)_6]^{2+}\ [NH_3]^4}}$$

* conc. of H_2O is not included in expression as water is in excess.

↳ any H_2O produced in reaction is negligible compared to water already present.

K_{stab} ↑ ⇒ stability of complex ↑

→ Ligand exchange in a complex occurs to form a more stable complex w/ larger K_{stab}.

eg. $[CoCl_4]^{2-} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 4Cl^-$

↳ K_{stab} of NH_3 ligand > K_{stab} of Cl^- ligand

∴ ammonia complex more stable; eq. position shifts RHS