PROSPERITY ACADEMY

A2 CHEMISTRY 9701

Crash Course

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TRANSITION METALS

COMPLETE NOTES

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Transition Metals:- A transition element is a d-block element that forms one or more stable ions with incomplete d-orbitals.

Give shorthand configurations of :-

a) Ti: $[Ar]\ 4s^2\ 3d^2$
b) V: $[Ar]\ 4s^2\ 3d^3$
c) Cr: $[Ar]\ 4s^1\ 3d^5$
d) Fe $[Ar]\ 4s^2\ 3d^6$
e) Cu: $[Ar]\ 4s^1\ 3d^{10}$

Elements Scandium (Sc) and Zinc (Zn) are not transition metals:-

Sc forms Sc^{3+} which has completely unfilled d-orbitals.
Zn forms Zn^{2+} which has completely filled d-orbitals.

Sc: $[Ar]\ 4s^2\ 3d^1 \longrightarrow Sc^{3+}: [Ar]$
Zn: $[Ar]\ 4s^2\ 3d^{10} \longrightarrow Zn^{2+}: [Ar]\ 3d^{10}$

Electronic Configuration of ions:- 4s orbital loses electrons before 3d.

V^{2+}: $[Ar]\ 3d^3$
Cr^{2+}: $[Ar]\ 3d^4$
Fe^{3+}: $[Ar]\ 3d^5$
Cu^+: $[Ar]\ 3d^{10}$

Variable Oxidation states:- Due to small difference in energy between 4s and 3d orbitals, transition metals have variable oxidation states.

Successive ionization energies of Mg:- 736, 1450, (huge gap) 7740, 10500
Successive ionization energies of Fe:- 762, 1560, (small gap) 2960, 5400

More energy is released in forming the +3 ionic bond than +2 so it is favourable for iron to form Fe^{3+}.

- +2 oxidation state is stable for all transition metals in first row

Catalysis:- Discussed in reaction Kinetics.

Redox Reactions:-

- Fe^{2+} ions are good reducing agents and form Fe^{3+}
  pale green ⟶ red-brown
- $Cr_2O_7^{2-}$ ions are good oxidising agents and form Cr^{3+}
  orange ⟶ green
- MnO_4^- ions are good oxidising agents and form Mn^{2+}
  purple ⟶ colourless

Ligands and Complexes:-

Ligand:- A species having 1 or more lone pairs which it uses to datively bond to a central metal atom/ion

Complex:- A molecule or ion formed by a central metal ion/atom by datively bonding to one or more ligands around it.

- Transition metals can absorb lone pairs to empty d orbitals

Coordination number:- Number of coordinate bonds in a complex.

Shapes of complex ions:- Can be either linear, octahedral, tetrahedral or square planar

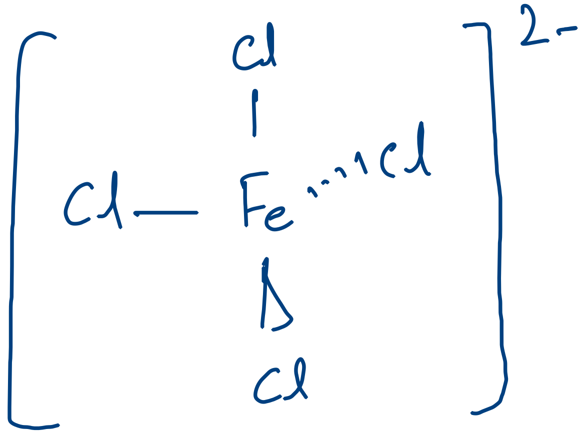
Linear:- e.g. $[Ag(NH_3)_2]^+$

$$[H_3N \longrightarrow Ag \longleftarrow NH_3]^+$$

Coordination number:- 2

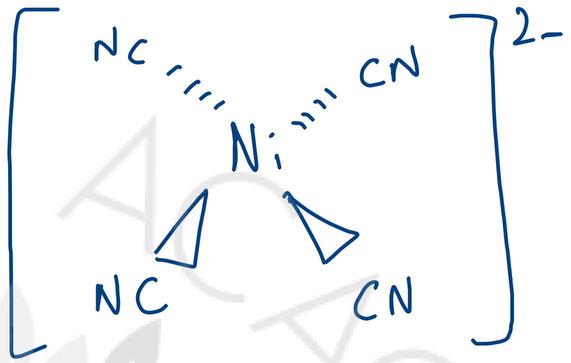
Oxidation no. of Ag:- +1

Tetrahedral:- e.g. $[FeCl_4]^{2-}$



Coordination number:- 4
Oxidation no. of Fe :- +2

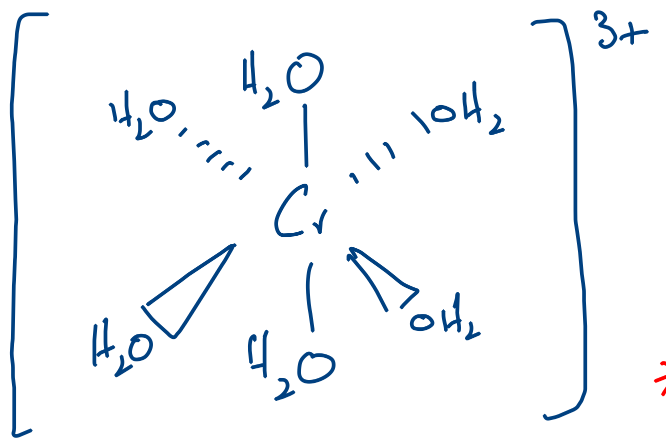
Square planar:- e.g. $[Ni(CN)_4]^{2-}$



Coordination number:- 4
Oxidation no. of Ni :- +2

* Note:- Pt and Ni form square planars usually
  - rest form tetrahedral usually

Octahedral:- e.g. $[Cr(H_2O)_6]^{3+}$



Coordination number:- 6
Oxidation no. of Cr :- +3

* Note: All common transition metals form $[M(H_2O)_6]^{x+}$ octahedral complexes

- All above examples had monodentate ligands → ligands that form only 1 dative bond.
- There are 2 bidentate ligands in course → ligands that form 2 dative bonds
  - 1,2-diaminoethane (en) (learn structure)

    $:NH_2 - CH_2 - CH_2 - \ddot{N}H_2$

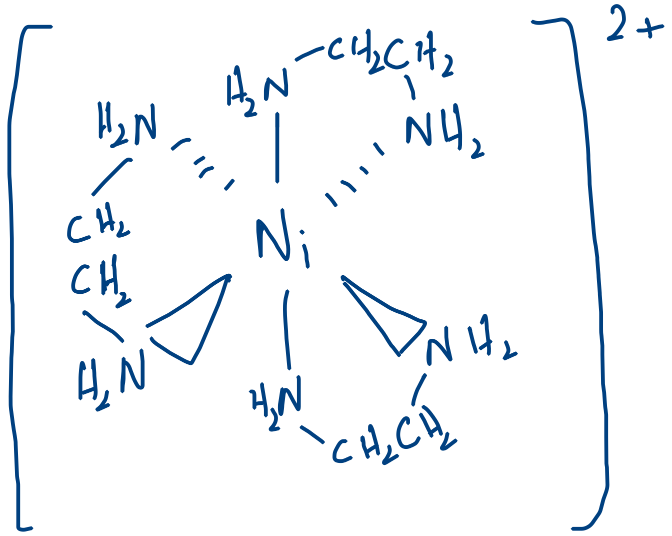
    charge = 0
  - ethanedioate ion (ox) (learn structure)

    $:\overset{\ominus}{O} - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - \overset{\ominus}{O}:$

    charge = -2

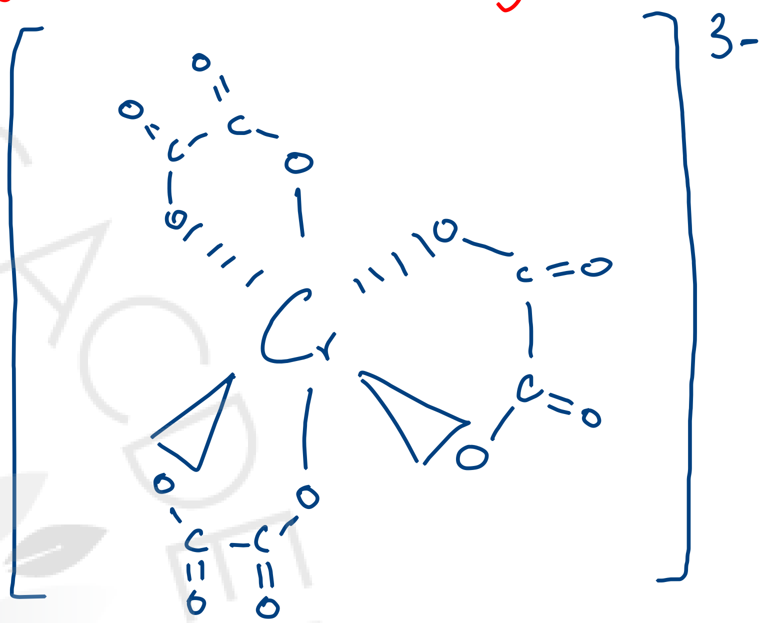
Octahedral bidentate :- e.g. $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$

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



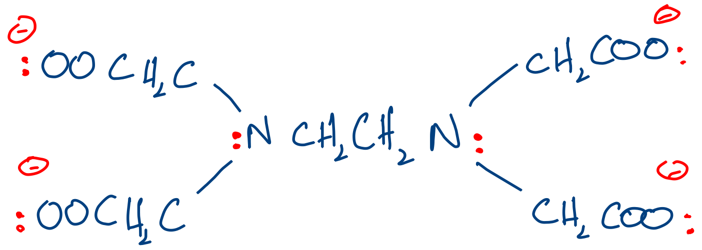
Coordination number = 6
Oxidation number of Ni = +2

e.g $[Cr(C_2O_4)_3]^{3-}$ or $[Cr(ox)_3]^{3-}$



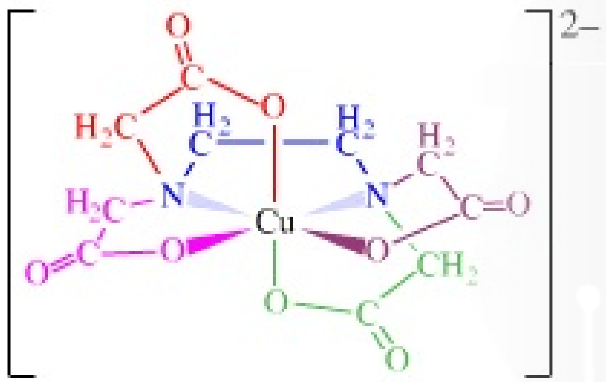
Coordination number :- 6
oxidation no. of Cr :- +3

- There is 1 polydentate ligand in course → ligands that form more than 2 dative bonds.
- $EDTA^{4-}$ (donot learn structure)



charge = -4

Octahedral polydentate :- e.g. $[Cu(EDTA)]^{2-}$ (Will not be asked to draw)

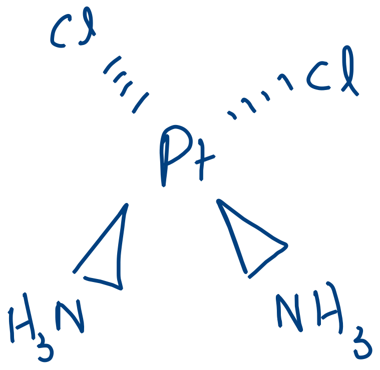


Coordination number :- 6
Oxidation no. of Cu :- +2

Stereoisomerism in complexes:-

1) Geometric / cis-trans isomerism is only possible in square planar and octahedral complexes

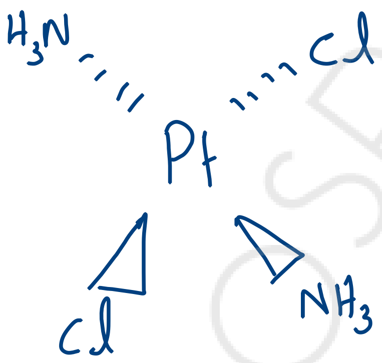
e.g. $Pt(NH_3)_2Cl_2$



cis-platin
polar

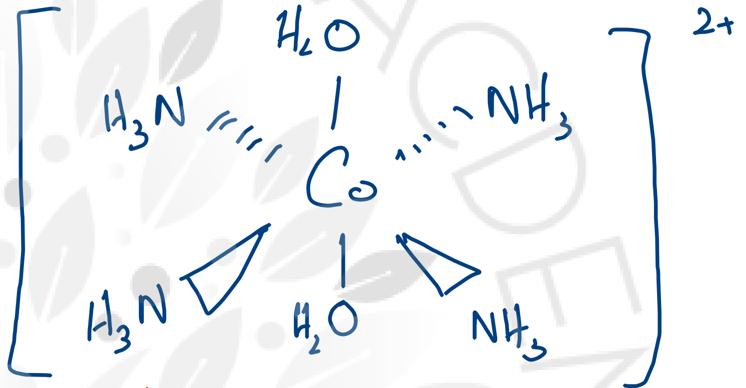
used as anti cancer drug as it binds to sections of DNA in cancer cells preventing cell division

or



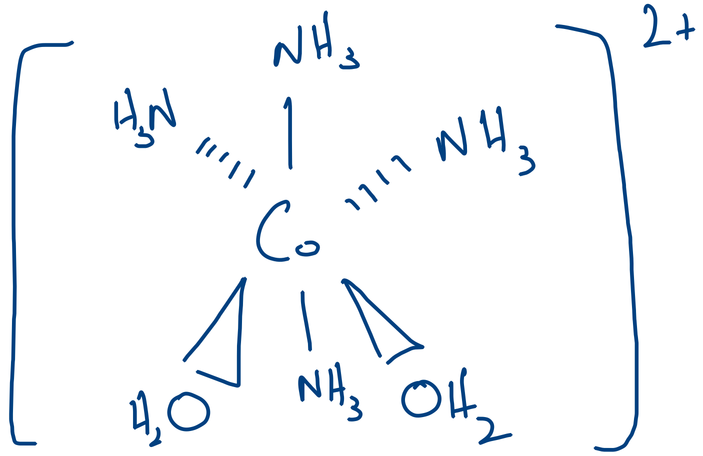
trans-platin
non polar

e.g. $[Co(NH_3)_4(H_2O)_2]^{2+}$



trans
non polar

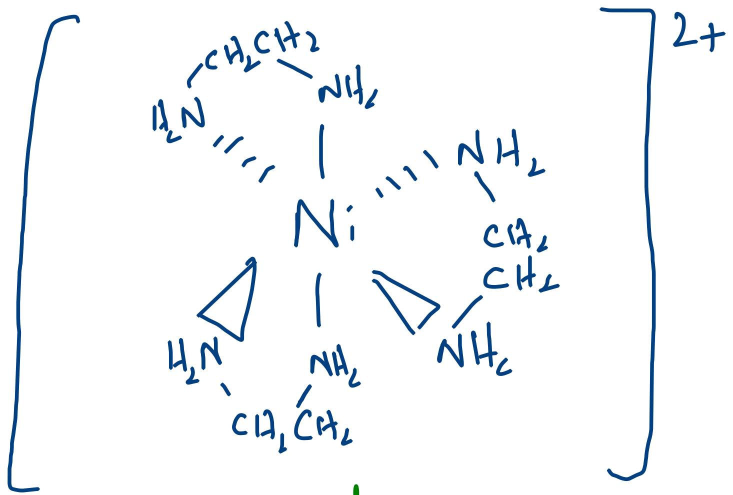
or



cis
polar

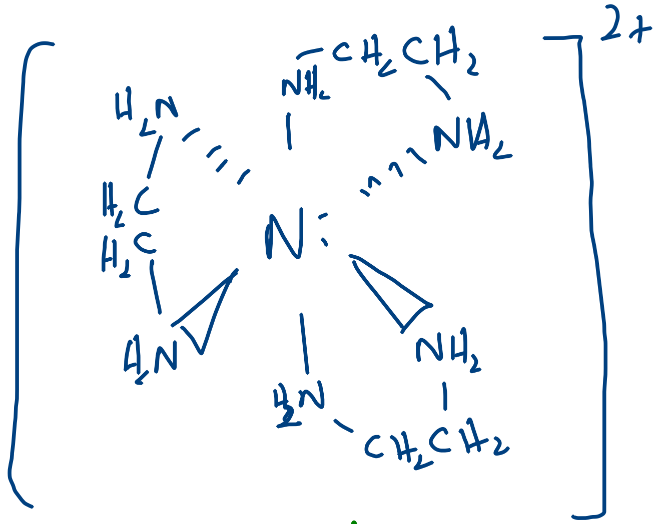
2) Optical isomerism is exhibited by octahedral complexes having bidentate ligands

e.g $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Ni(en)_3]^{2+}$



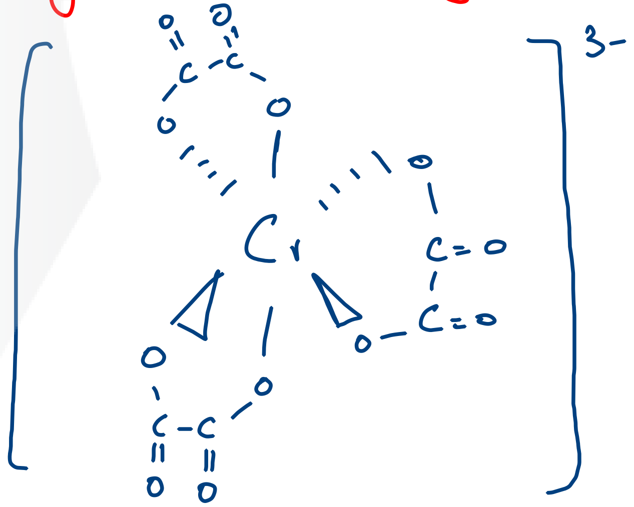
non polar

or



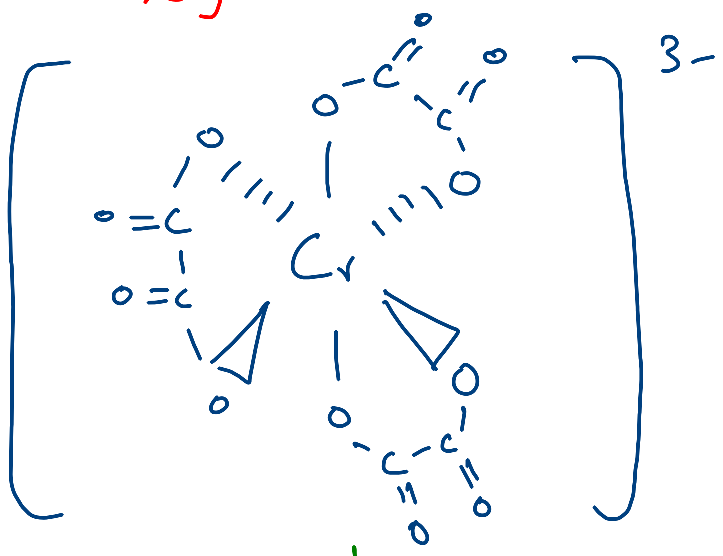
non polar

e.g. $[Cr(C_2O_4)_3]^{3-}$ or $[Cr(ox)_3]^{3-}$



non polar

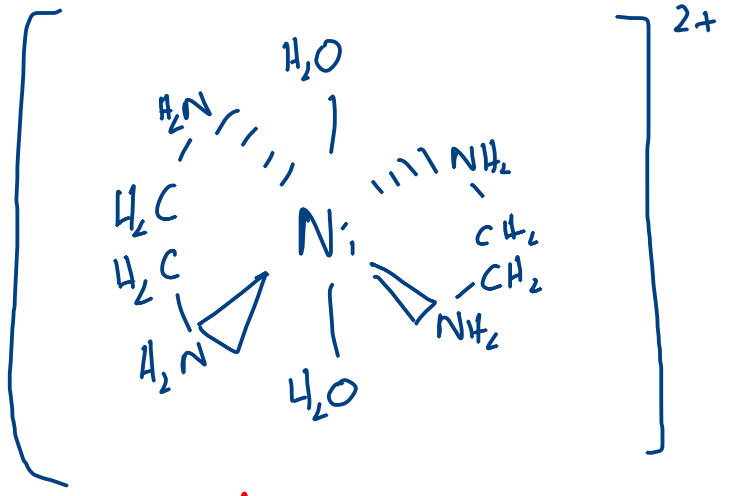
or



non polar

3) Octahedral complexes with 2 bidentate and 2 monodentate ligands show optical as well as geometric isomerism

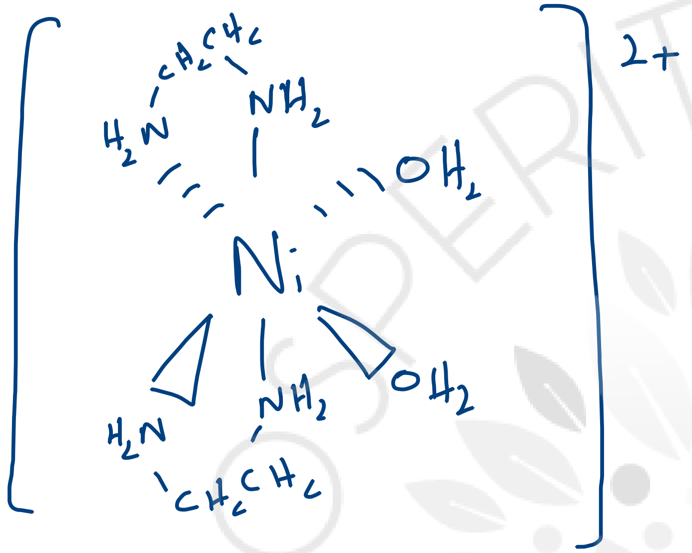
e.g. $[Ni(en)_2(H_2O)_2]^{2+}$



trans

non polar

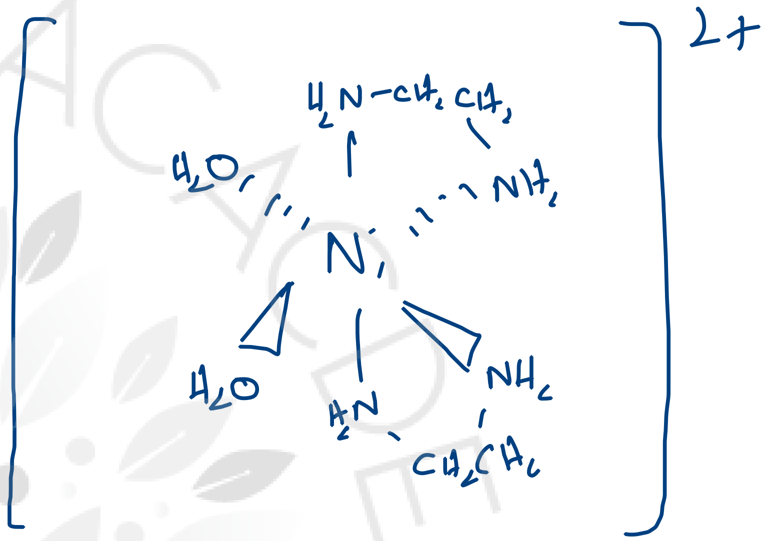
or



cis

polar

or



cis

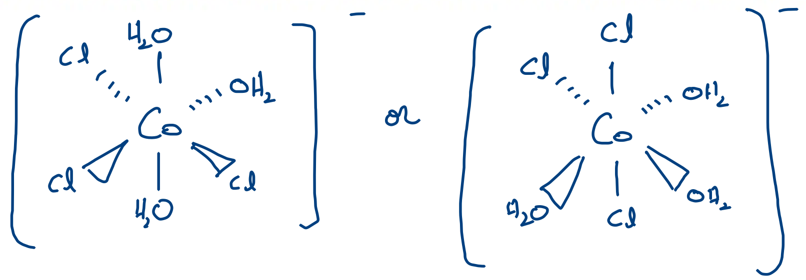
polar

(c) Cobalt(II) forms a six co-ordinate complex containing three water molecules and three chloride ions.

(i) Write the formula of this complex showing the overall charge, if appropriate.

$[Co(H_2O)_3(Cl)_3]^-$ [1]

(ii) Explain, with the aid of diagrams, how many isomers of the complex in **(i)** exist.



[2]

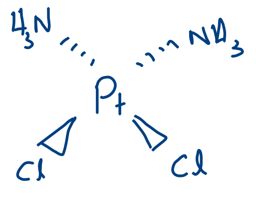
(d) Platinum(II) forms a four co-ordinate complex containing two ammonia molecules and two chloride ions.

(i) Write the formula of this complex showing the overall charge, if appropriate.

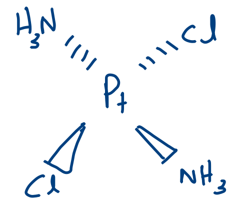
$Pt(NH_3)_2(Cl)_2$ [1]

(ii) This complex exists as two isomers.

Draw the structure of these isomers and give their names.



cis-platin



trans-platin

[3]

(iii) One of the isomers in **(ii)** is an important anticancer drug.

State which isomer this is and explain why this isomer is effective.

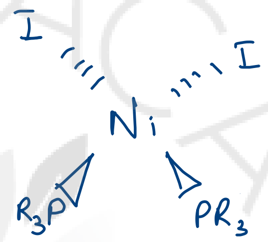
isomer cis-platin

reason It can bind with DNA in cancer cells and stop them from replicating.

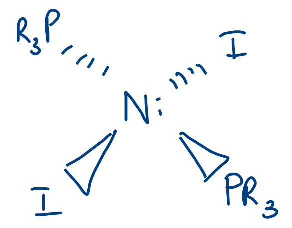
[2]

(b) There are two isomers with the formula $Ni(R_3P)_2I_2$, but only one structure with the formula $Co(R_3P)_2I_2$. (R = alkyl, R_3P is a monodentate ligand)

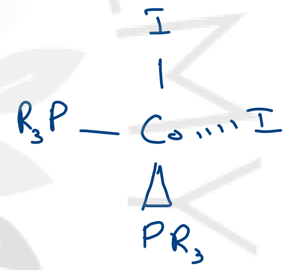
Draw diagrams showing the structure of $Co(R_3P)_2I_2$ and the two isomers of $Ni(R_3P)_2I_2$.



$Ni(R_3P)_2I_2$



$Ni(R_3P)_2I_2$



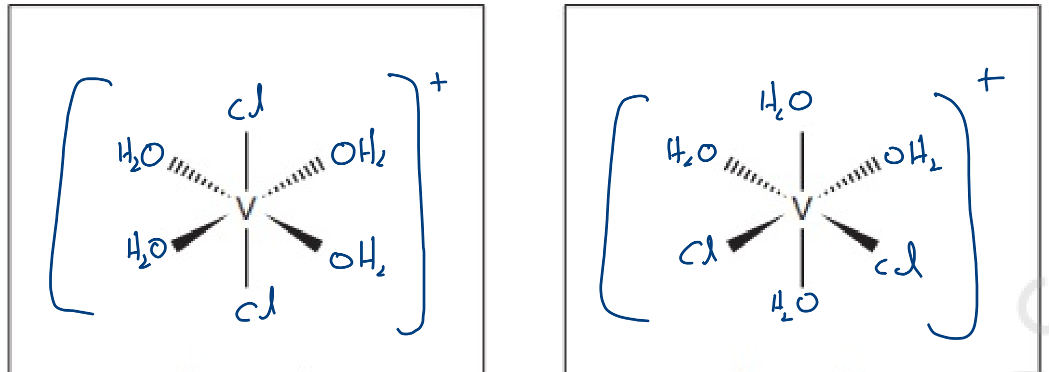
$Co(R_3P)_2I_2$

[3]

(d) (i) In the presence of chloride ions, $[V(H_2O)_6]^{3+}$ reacts to form a mixture of isomeric octahedral complexes.

$$[V(H_2O)_6]^{3+} + 2Cl^- \rightleftharpoons [V(H_2O)_4Cl_2]^+ + 2H_2O$$

Complete the three-dimensional diagrams to show the **two** isomers of $[V(H_2O)_4Cl_2]^+$.



isomer 1 isomer 2

[2]

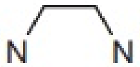
(ii) State the type of isomerism shown by isomer 1 and isomer 2 in **(i)**.

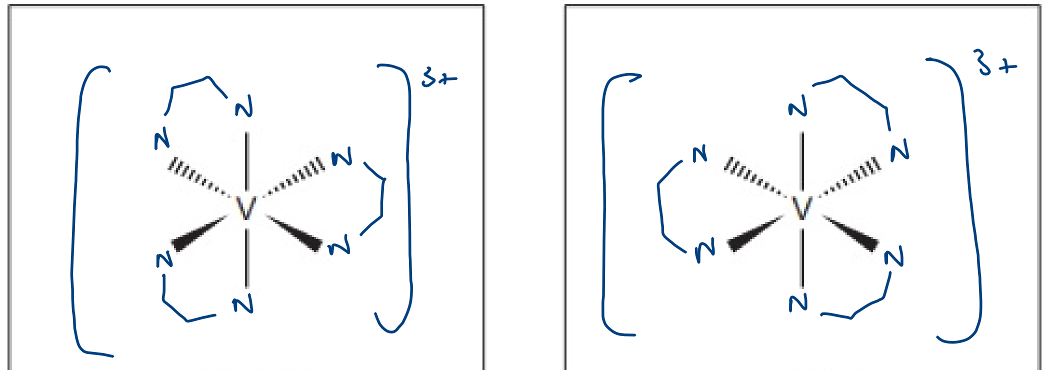
geometric [1]

(e) (i) The complex $[V(H_2O)_6]^{3+}$ also reacts with ethane-1,2-diamine (*en*), $H_2NCH_2CH_2NH_2$, to form a mixture of isomeric octahedral complexes.

$$[V(H_2O)_6]^{3+} + 3en \rightleftharpoons [V(en)_3]^{3+} + 6H_2O$$

Complete the three-dimensional diagrams to show the **two** isomers of $[V(en)_3]^{3+}$.

You may use  to represent *en*.



isomer 1 isomer 2

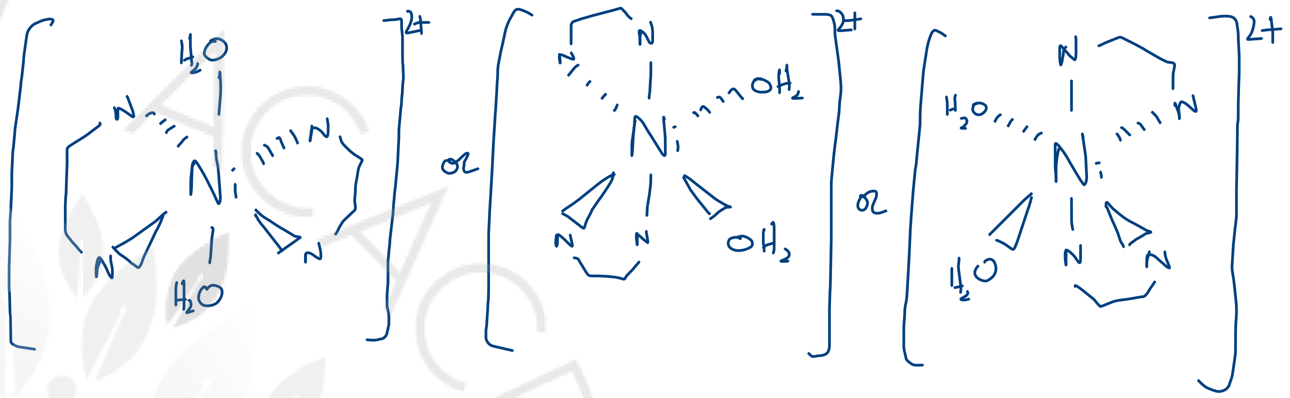
[2]

(ii) State the type of isomerism shown by isomer 1 and isomer 2 in **(i)**.

optical [1]

(iii) Adding a limited amount of *en* to $[Ni(H_2O)_6]^{2+}$ forms the complex $[Ni(H_2O)_2(en)_2]^{2+}$.

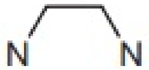
Suggest the number of possible stereoisomers of $[Ni(H_2O)_2(en)_2]^{2+}$. Explain your answer. You are advised to include three-dimensional diagrams in your answer.

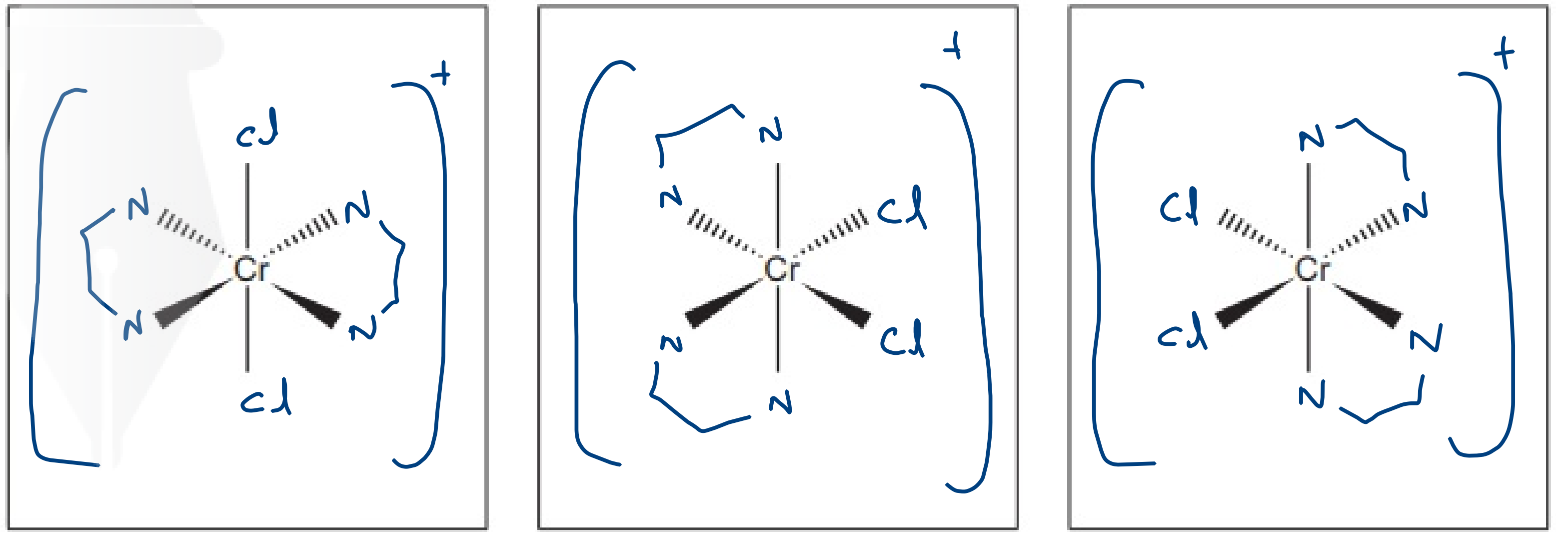


There will be 3 isomers. 2 cis-trans isomers as the H_2O molecules can be opposite to each other or be on same side and the cis isomer will have 1 more optical isomer due to a different arrangement creating a non superimposable isomer [2]

(ii) There are three isomeric complex ions with the formula $[Cr(en)_2Cl_2]^+$.

Complete the three-dimensional diagrams of the isomers in the boxes.

You may use  to represent *en*.



[3]

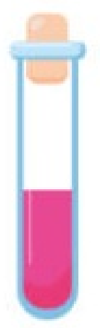
Ligand exchange reactions:- The ligands in complexes can be substituted completely or partially by other ligands

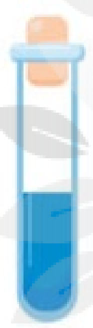
- Oxidation number of metal does not change
- learn every thing!

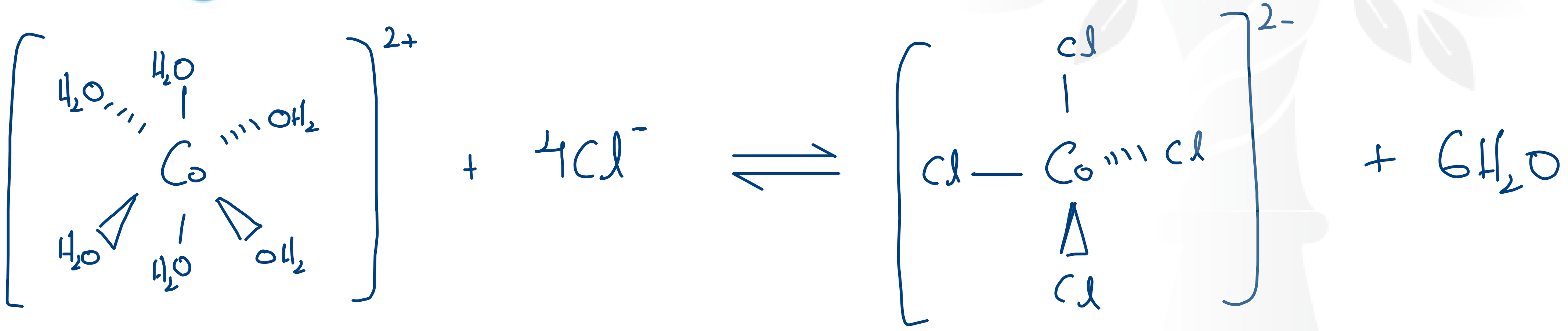
1) Aqueous Cobalt (II) ions reacting with excess conc. HCl :-

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

pink → blue





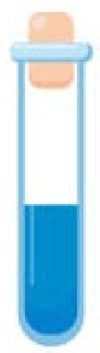


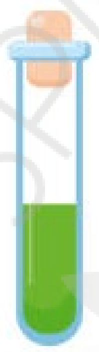
- To obtain partial substitution use dilute HCl in limited amount
- To favour the reverse reaction add water

2) Aqueous copper(II) ions reacting with excess conc. HCl:-

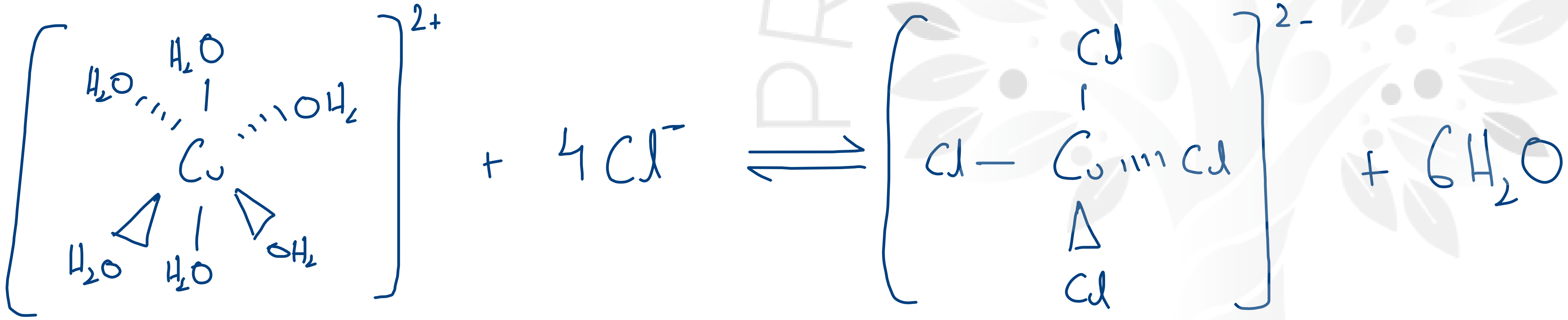
$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)} + 6H_2O$$

blue ⟶ yellow





looks green due to both complexes (blue + yellow = green)

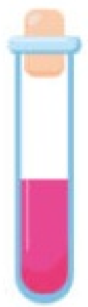


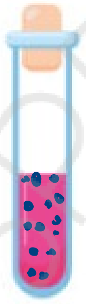
- To obtain partial substitution use dilute HCl in limited amount
- To favour the reverse reaction add water

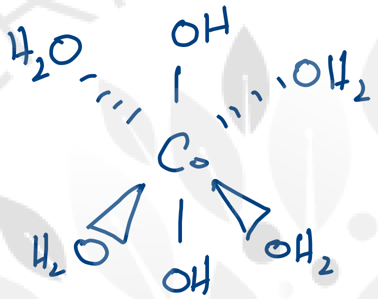
3) Aqueous cobalt (II) ions reacting with $NaOH_{(aq)}$:-

$$[Co(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons Co(H_2O)_4(OH)_{2(s)} + 2H_2O_{(l)}$$

pink ⟶ blue ppt





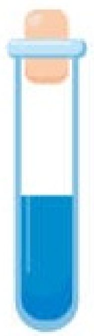


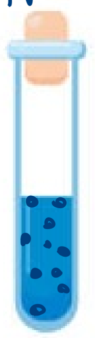
- blue ppt does not dissolve in excess NaOH
- The solution turns pink again upon standing (reverse reaction happens)
- This is NOT Ligand exchange. It is Acid - base reaction.

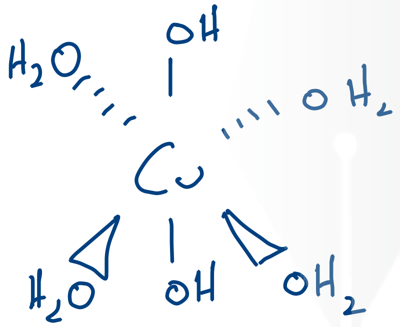
4) Aqueous Copper(II) ions reacting with $NaOH_{(aq)}$:-

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons Cu(H_2O)_4(OH)_{2(s)} + 2H_2O_{(l)}$$

blue ⟶ blue ppt





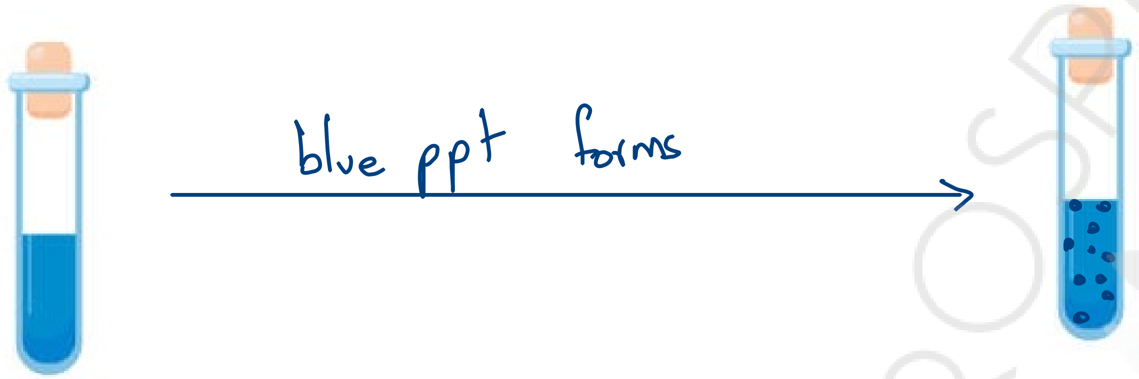


- blue ppt does not dissolve in excess NaOH
- This is NOT Ligand exchange. It is acid - base reaction.

5) Aqueous copper (II) ions reacting with $NH_{3(aq)}$:-

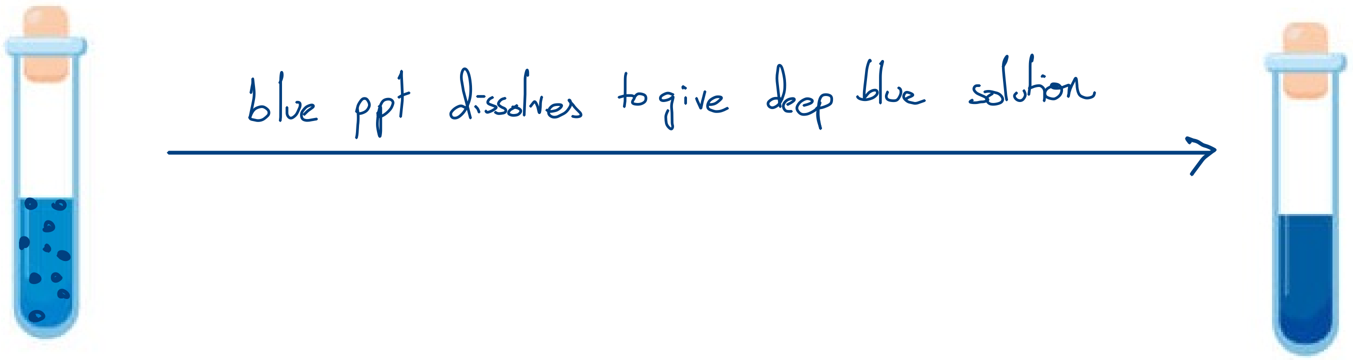
1) First an acid-base reaction takes place :-

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons Cu(H_2O)_4(OH)_{2(s)} + 2NH_4^+{}_{(aq)}$$



2) Upon addition of excess ammonia, precipitate dissolves (Ligand exchange)

$$Cu(H_2O)_4(OH)_{2(s)} + 2NH_4^+{}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)} + 4H_2O_{(l)}$$



Net equation:-

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)} + 4H_2O_{(l)}$$

- To reverse add dil. HCl → will neutralise NH_4^+

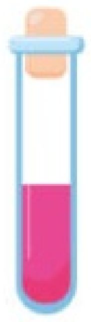
→ not concentrated otherwise it will do ligand exchange itself

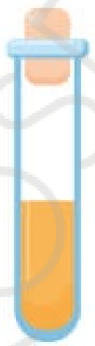
6) Aqueous cobalt(II) ions reacting with $NH_{3(aq)}$:-

- All water ligands are replaced by ammonia.

$$[Co(H_2O)_6]^{2+}_{(aq)} + 6NH_{3(aq)} \rightleftharpoons [Co(NH_3)_6]^{2+}_{(aq)} + 6H_2O_{(l)}$$

pink ⟶ straw coloured





Stability Constant :- The equilibrium constant for the formation of a complex ion in a solvent from its constituent ions or molecules.

- Water is omitted as it is in large excess so can be considered constant

Q. Give K_{stab} for :-

1) Reaction of aqueous copper(II) ions with excess ammonia

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

$$K_{stab} = \frac{[[Cu(NH_3)(H_2O)_2]^{2+}]_{eqm}}{[[Cu(H_2O)_6]^{2+}]_{eqm}[NH_3]^4_{eqm}} = \frac{\cancel{mol\ dm^{-3}}}{\cancel{mol\ dm^{-3}}\ (mol\ dm^{-3})^4}$$

$$= dm^{12}\ mol^{-4}$$

2) Reaction between aqueous copper(II) ions and conc. excess HCl

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

$$K_{stab} = \frac{[[CuCl_4]^{2-}]_{eqm}}{[Cl^-]^4_{eqm}[[Cu(H_2O)_6]^{2+}]_{eqm}} = dm^{12}\ mol^{-4}$$

(c) Hexaaquairon(III) ions are pale violet. They form a colourless complex with fluoride ions, F^-, equilibrium **1**, and a deep-red complex with thiocyanate ions, SCN^-, equilibrium **2**.

$[Fe(H_2O)_6]^{3+}$ (violet) + F^- ⇌ $[Fe(H_2O)_5F]^{2+}$ (colourless) + H_2O equilibrium **1** K_{stab} = 2.0 × 10⁵ mol⁻¹ dm³

$[Fe(H_2O)_6]^{3+}$ (violet) + SCN^- ⇌ $[Fe(H_2O)_5SCN]^{2+}$ (deep-red) + H_2O equilibrium **2** K_{stab} = 1.0 × 10³ mol⁻¹ dm³

Usually given in comparison to aqueous ion (>1 so means more stable in comparison to aqueous ion)

(i) Predict and explain the **sequence** of colour changes you would observe in each of the following experiments.

- A few drops of KSCN(aq) are added to 5 cm³ of Fe^{3+}(aq), followed by a few drops of KF(aq).

deep red and then colourless as $K_{stab}(Fe(H_2O)_5F)^{2+} > K_{stab}(Fe(H_2O)_5SCN)^{2+} > K_{stab}(Fe(H_2O)_6)^{3+}$

- A few drops of KF(aq) are added to 5 cm³ of Fe^{3+}(aq), followed by a few drops of KSCN(aq).

colourless and then stays colourless (same reason as above)

[4]

(ii) What *type of reaction* is occurring during the experiments in **(i)**?

ligand exchange [1]

[Total: 9]

1 Copper is a transition element and has atomic number 29.

(a) Complete the electronic configuration for the copper atom and the copper ion in the +2 oxidation state.

- copper atom [Ar] $4s^1 3d^{10}$
- copper ion in the +2 oxidation state [Ar] $3d^9$

[2]

(b) The following equilibrium exists between two complex ions of copper in the +2 oxidation state.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

(i) Name the *type of reaction* occurring here.

Ligand exchange [1]

(ii) State the colours of these two complex ions.

$[Cu(H_2O)_6]^{2+}$ green $[CuCl_4]^{2-}$ blue [1]

(iii) State the shape of the $[CuCl_4]^{2-}$ ion.

tetrahedral [1]

(iv) Write the expression for the stability constant, K_{stab}, for this equilibrium.

$$K_{stab} = \frac{[[CuCl_4]^{2-}]_{eqm}}{[[Cu(H_2O)_6]^{2+}]_{eqm}[Cl^-]^4_{eqm}}$$ [1]

(c) Copper also forms the complex ions $[Cu(NH_3)_2(H_2O)_4]^{2+}$ and $[Cu(en)(H_2O)_4]^{2+}$ where *en* is the bidentate ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O$ equilibrium 1

$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(en)(H_2O)_4]^{2+} + 2H_2O$ equilibrium 2

(i) What is meant by the term *bidentate ligand*?

A species containing 2 lone pairs both of which it uses to form 2 dative bonds to a central metal atom/ion [2]

(ii) The table lists the values of stability constants for these two complexes.

	stability constant, K_{stab}
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	7.94 × 10⁷
$[Cu(en)(H_2O)_4]^{2+}$	3.98 × 10¹⁰

What do these K_{stab} values tell us about the relative positions of equilibria 1 and 2?

both equilibrium positions lie towards right hand side and equilibrium 2 favours right hand side more than equilibrium 1 [1]

(b) Copper forms complexes with NH_3 and *en* according to equilibria 1 and 2.

equilibrium 1 $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

equilibrium 2 $Cu^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq)$

(i) Write the expressions for the stability constants, K_{stab1} and K_{stab2}, for equilibria 1 and 2. Include units in your answers.

$K_{stab1} = \dfrac{[[Cu(NH_3)_4]^{2+}]_{eqm}}{[Cu^{2+}]_{eqm}\,[NH_3]^4_{eqm}}$ $\dfrac{mol\,dm^{-3}}{mol\,dm^{-3} \times (mol\,dm^{-3})^4}$

units = $dm^{12}\,mol^{-4}$

$K_{stab2} = \dfrac{[[Cu(en)_2]^{2+}]_{eqm}}{[Cu^{2+}]_{eqm}\,[en]^2_{eqm}}$ $\dfrac{mol\,dm^{-3}}{mol\,dm^{-3} \times (mol\,dm^{-3})^2}$

units = $dm^{6}\,mol^{-2}$ [3]

$$K_{eq3} = \frac{dm^6\,mol^{-2}}{dm^{12}\,mol^{-4}}$$

$$= dm^{6-12} \times mol^{-2+4}$$

$$= dm^{-6} \times mol^{+2}$$

$[Cu(NH_3)_4]^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq) + 4NH_3(aq)$

−92 −100

$Cu^{2+}(aq) + 2en + 4NH_3$

$+92 - 100 = -8$

(ii) An equilibrium is set up when both *en* and NH_3 ligands are added to a solution containing $Cu^{2+}(aq)$ as shown in equilibrium 3.

equilibrium 3 $[Cu(NH_3)_4]^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq) + 4NH_3(aq)$

Write an expression for the equilibrium constant, K_{eq3}, in terms of K_{stab1} and K_{stab2}.

K_{eq3} = Kstab2 / Kstab1 [1]

(iii) The numerical values for these stability constants are shown.

$K_{stab1} = 1.2 \times 10^{13}$ $K_{stab2} = 5.3 \times 10^{19}$

Calculate the value of K_{eq3} stating its units.

K_{eq3} = 4.4×10^6 unit = $mol^2\,dm^{-6}$ [2]

(c) ΔS° values for equilibria 1 and 2 differ greatly, as can be seen in the table. All values are at a temperature of 298 K.

equilibrium	ΔH° / kJ mol^{-1}	ΔS° / J K^{-1} mol^{-1}	ΔG° / kJ mol^{-1}
1	–92	–60	–74
2	–100	+40	-112

(i) Explain why ΔS°_{eq2} is so different from ΔS°_{eq1}.

In equation 2, fewer moles reacted to produce 1 mol of product while in equation 1, more moles reacted. [1]

(ii) Calculate ΔG°_{eq2} at 298 K.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= (-100) - 298(40 \times 10^{-3}) = -111.92$

ΔG°_{eq2} = -112 kJ mol^{-1} [2]

(iii) What conclusion can be made about the relative feasibility of equilibria 1 and 2?

Explain your answer.

equilibria 2 is more feasible in forward direction than equilibrium 1 [1]

(iv) Using data from the table, suggest a value of ΔH° for equilibrium 3.

-8 [1]

(v) State the *type of reaction* that is occurring in equilibrium 2.

Ligand exchange [1]

(c) The table shows numerical values of the stability constants for the following equilibrium where M can be one of the metal ions listed and L one of the ligands which replaces **one** H_2O molecule.

$$[M(H_2O)_6]^{n+}(aq) + L^-(aq) \rightleftharpoons [M(H_2O)_5L]^{(n-1)+}(aq) + H_2O(l)$$

metal ion, M	ligand, L	stability constant, K_{stab}
Fe^{3+}	F^-	1.0×10^6
Fe^{3+}	Cl^-	2.5×10^1
Fe^{3+}	SCN^-	9.0×10^2
Hg^{2+}	Cl^-	5.0×10^6

→ in comparison to aq ion

(i) What is meant by the term *stability constant*, K_{stab}?

equilibrium constant for the formation of a complex ion in a solvent from its constituent ions / atoms [1]

(ii) Use the data in the table to predict the formula of the complex formed in the greatest amount when

- a solution containing equal concentrations of both F^- and SCN^- ions is added to Fe^{3+}(aq),

  $[Fe(H_2O)_5F]^{+2}$

- a solution containing equal concentrations of both Fe^{3+} and Hg^{2+} ions is added to Cl^-(aq).

  $[Hg(H_2O)Cl]^{+}$

[1]

(b) Six different compounds or complexes, **H**, **J**, **K**, **L**, **M** and **N**, are formed when an excess of aqueous NH_3, aqueous NaOH and concentrated aqueous HC*l* are separately added to separate solutions containing Cu^{2+}(aq) or Co^{2+}(aq).

solution	reagent		
	an excess of NH_3(aq)	an excess of NaOH(aq)	an excess of concentrated HC*l*(aq)
Cu^{2+}(aq)	**H**	**J**	**K**
Co^{2+}(aq)	**L**	**M**	**N**

(i) State the colours of the following compounds or complexes.

H blue

K yellow

M blue

[2]

(ii) Write the formulae of the following compounds or complexes.

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

N $[CoCl_4]^{2-}$

[2]

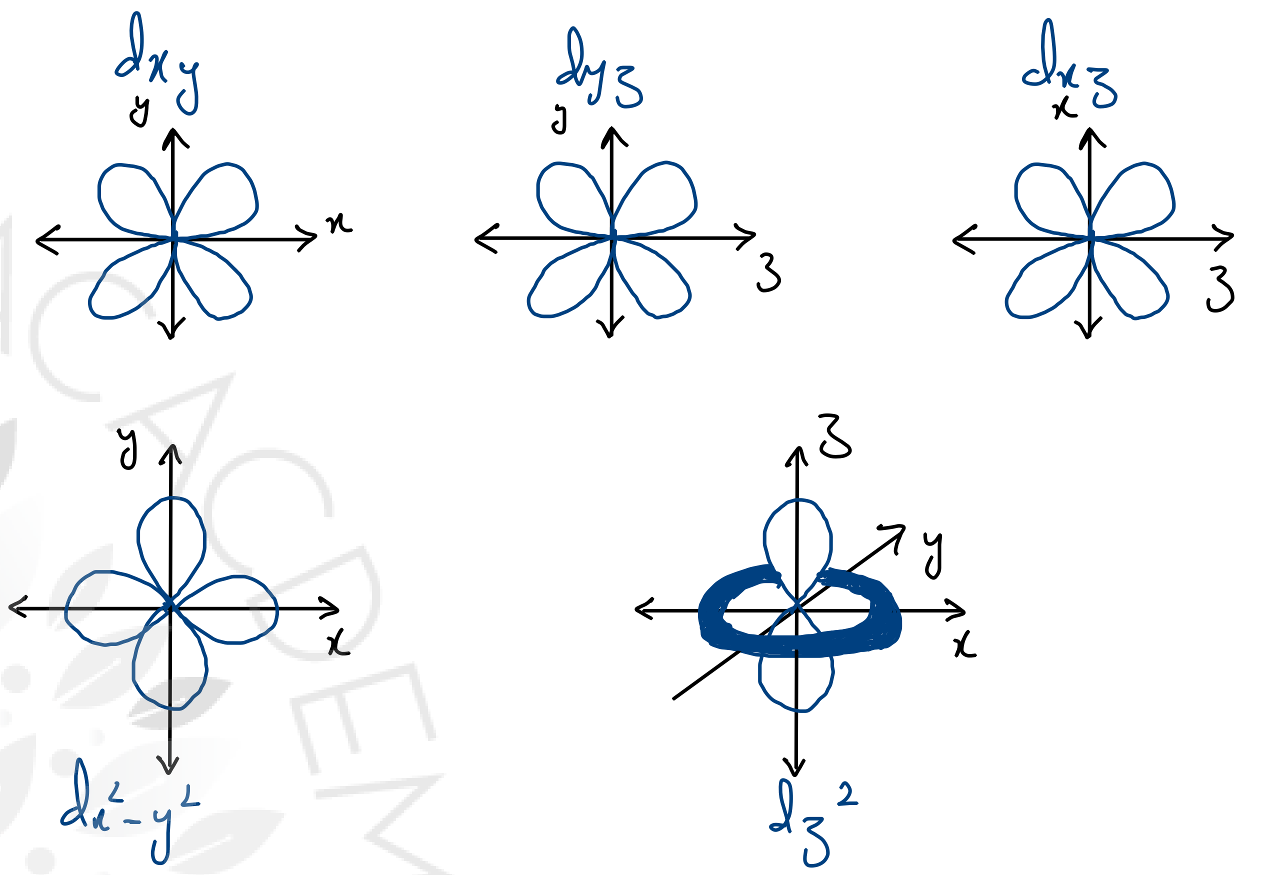
(iii) State the appearance of compound **J**.

blue precipitate [1]

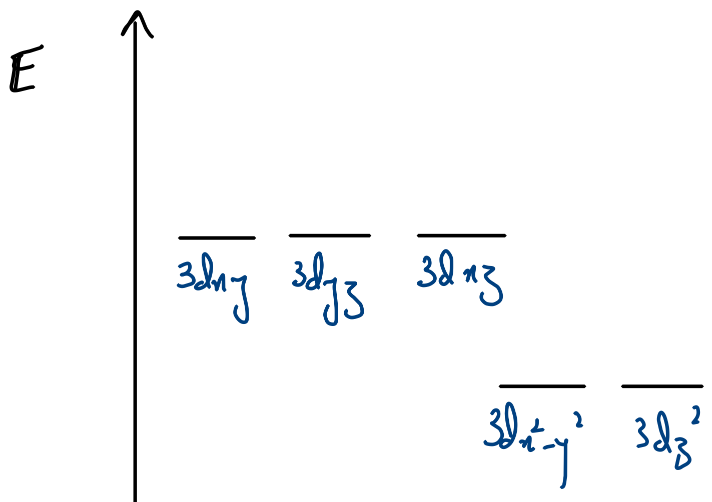
[Total: 7]

Origin of Colour in complexes:-

- 3d has 5 orbitals of equal energy
- 3 of them have electron density pointing between the axes:-

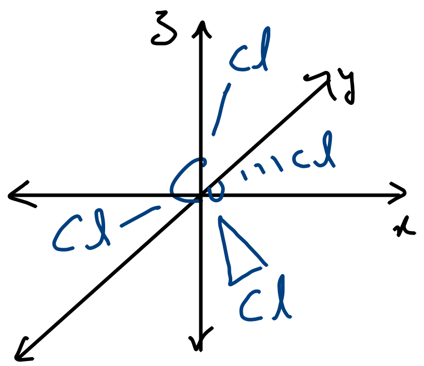


- 2 of them have electron density pointing along the axes:-

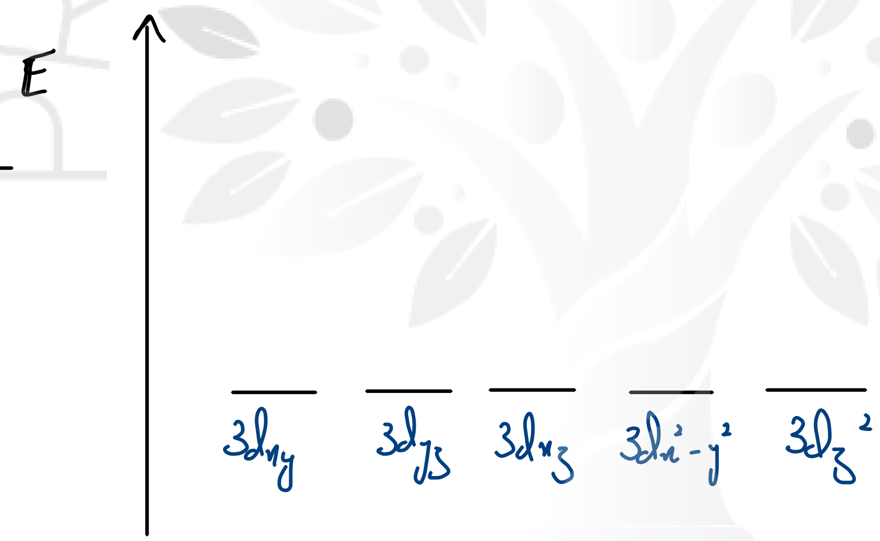


-orbitals split into 2 energy levels
- as the d orbitals are incomplete, when light falls onto electrons corresponding to the ΔE, the electrons get excited and jump upwards

Tetrahedral complex

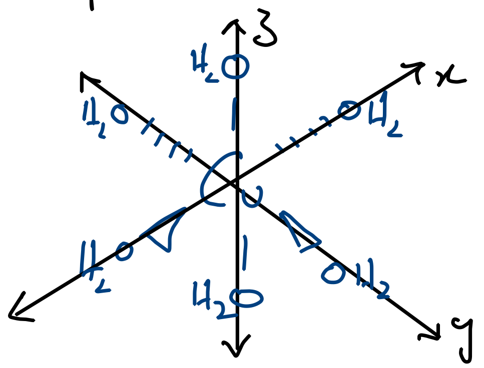


-ligands approach between axes
- $3d_{xy}$, $3d_{yz}$, and $3d_{xz}$ experience greater repulsion and therefore become higher energy

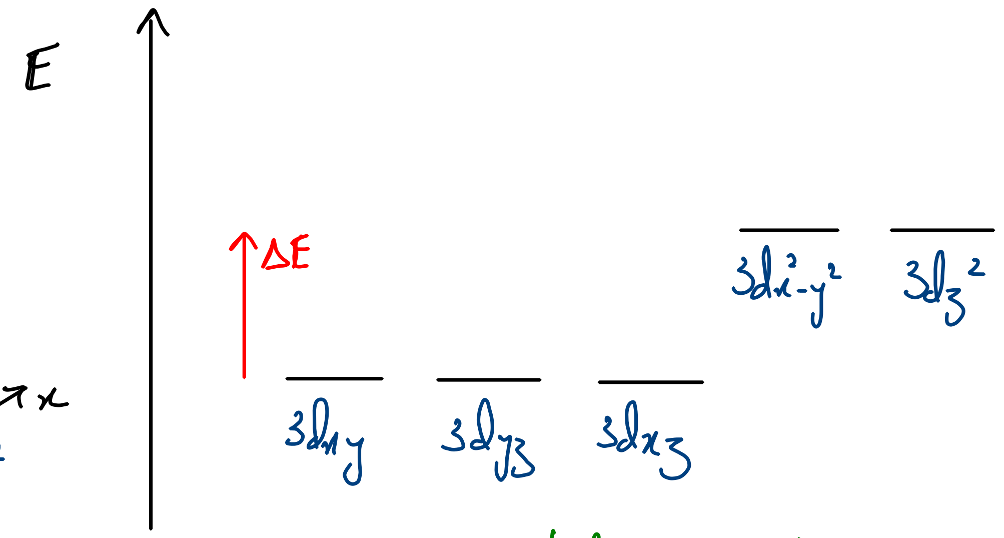


In ground state all are equal in energy

Octahedral Complex

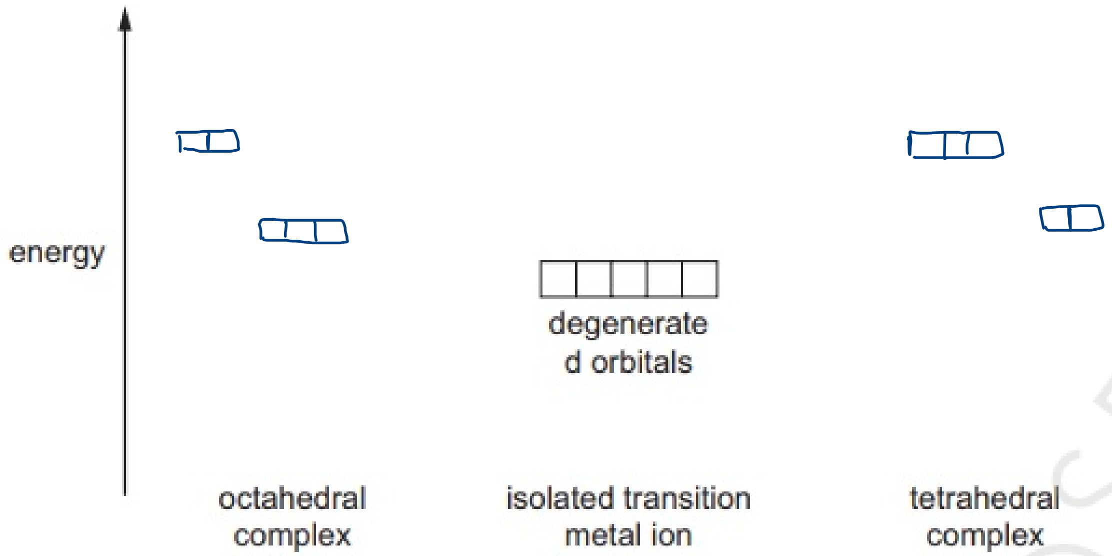


-ligands approach along axes
- $3d_{x^2-y^2}$ and $3d_{z^2}$ experience more repulsion and therefore become higher energy



-orbitals split into 2 energy levels
- as the d orbitals are incomplete, when light falls onto electrons corresponding to the ΔE, the electrons get excited and jump upwards

(b) (i) Complete the diagram to show how the presence of ligands around an isolated transition metal ion affects the **energy** of the d orbitals.



[1]

(ii) Explain why transition metal complexes are coloured.

In a complex, the d subshell splits into 2 levels. Electrons in the lower energy level absorb visible light of corresponding energy to jump to higher level. The colour observed is complementary to the colour absorbed [2]

(iii) $[Cu(H_2O)_6]^{2+}$ is pale blue but $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is deep purple-blue.

Suggest a reason for this.

The corresponding difference in energy between the levels are different. $[Cu(NH_3)_4(H_2O)_2]^{2+}$ absorbs strongly in red part of visible spectrum [1]

(iii) Octahedral complexes of Cu^{2+} with different ligands can have different colours.

Explain why.

The difference in energy (ΔE) between the 2 energy levels is different for different ligands. Therefore the observed colour is different as different complementary colours are being absorbed

[2]

(b) Copper(I) and silver(I) salts are colourless.

Suggest why.

Cu^+ and Ag^+ d orbitals are completly full. The electrons from the lower energy d orbitals cannot jump to higher energy incomplete d-orbitals

[2]

(c) When water is added to concentrated aqueous cobalt(II) chloride the colour of the solution changes from blue to pink. Explain this observation.

No equation is needed, but you should include reference to electron movement between orbitals in your answer.

A ligand exchange reaction takes place. The structure of the complex changes from tetrahedral to octahedral and therefore the splitting of the 5 d-orbitals in 2 energy levels becomes opposite ($3d_{x^2-y^2}$ and $3d_{z^2}$ become higher in energy to $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$). The difference in energy levels also changes in magnitude and so the colour of the light being absorbed and reflected changes

[3]