28.2 COLOUR OF COMPLEXES

Learning outcomes

Candidates should be able to:

1. Define and use the terms degenerate and non-degenerate d orbitals

2. Describe the splitting of degenerate d orbitals into two non-degenerate sets of d orbitals of higher energy, and use of ΔE in:

   (a) octahedral complexes, two higher and three lower d orbitals

   (b) tetrahedral complexes, three higher and two lower d orbitals

3. Explain why transition elements form coloured compounds in terms of the frequency of light absorbed as an electron is promoted between two non-degenerate d orbitals

4. Describe, in qualitative terms, the effects of different ligands on ΔE, frequency of light absorbed, and hence the complementary colour that is observed

5. Use the complexes of copper(II) ions and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions as examples of ligand exchange affecting the colour observed

Introduction

Figure : Vanadium and its oxidation states: **a** a solution containing VO_2^+ ions, **b** a solution containing VO^{2+} ions, **c** a solution containing V^{3+} ions, **d** a solution containing V^{2+} ions.

Some substances have outer electron levels that are sufficiently close together for visible radiation to have enough energy to bring about electronic excitation. Under these circumstances, the substance appears coloured. The resulting colour seen is white light minus the colour being absorbed.

The colour we see is therefore the **complementary** colour to the colour being absorbed. To absorb in the visible region, the substance must have two energy levels that are very close together. Close energy levels come about in two ways, namely **charge transfer** and **d-to-d transitions**.

White light is made up of all the colours of the visible spectrum. When a solution containing a transition metal ion in a complex appears coloured, and part of the visible spectrum is absorbed by the solution.

The colour we see is called the complementary colour, made up of light with frequencies not absorbed. For example, copper(II) ions absorb light from the red end of the spectrum, so the complementary colour seen is a pale blue (called cyan). Here is a list of complementary pairs of colours:

red	cyan
yellow	blue
green	magenta

To explain why part of the spectrum is absorbed by transition metal ions, we must look in more detail at the d orbitals in the ions.

Degenerate and non-degenerate orbitals

The five d orbitals in an isolated transition metal atom or ion are described as **degenerate orbitals**, meaning they are all at the same energy level.

1. The 3d orbitals in an isolated Ag^+ ion are degenerate.
   Define degenerate d orbitals.

   ……

   …… [1]

In the presence of ligands, a transition metal ion is not isolated. The dative (or co-ordinate) bonding from the ligands causes the five d orbitals in the transition metal ion to split into two sets. The two sets of orbitals are described as **non-degenerate orbitals** as they are at slightly different energy levels.

2. In an isolated Cu^{2+} ion the d-orbitals are all degenerate. In a complex ion such as $[Cu(H_2O)_6]^{2+}$ the d-orbitals are non-degenerate.
   Define degenerate and non-degenerate in this context.

   degenerate .....

   non-degenerate ..... [1]

3. Define the term non-degenerate d-orbitals.

   .....

   ..... [1]

Splitting of degenerate orbitals

In a complex with six ligands, the ligands are arranged in an octahedral shape around the central metal ion. The lone pairs donated by the ligands into the transition metal ion repel electrons in the two $d_{x^2-y^2}$ and d_{z^2} orbitals more than those in the other three d orbitals. This happens because these two d orbitals line up with the dative (co-ordinate) bonds in the complex's octahedral shape. As the electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals are closer to the bonding electrons in the octahedral arrangement, the repulsion between electrons increases. Therefore, the d orbitals are split, with these two d orbitals at a slightly higher energy level than the d*yz*, d*xz* and d*xy* orbitals.

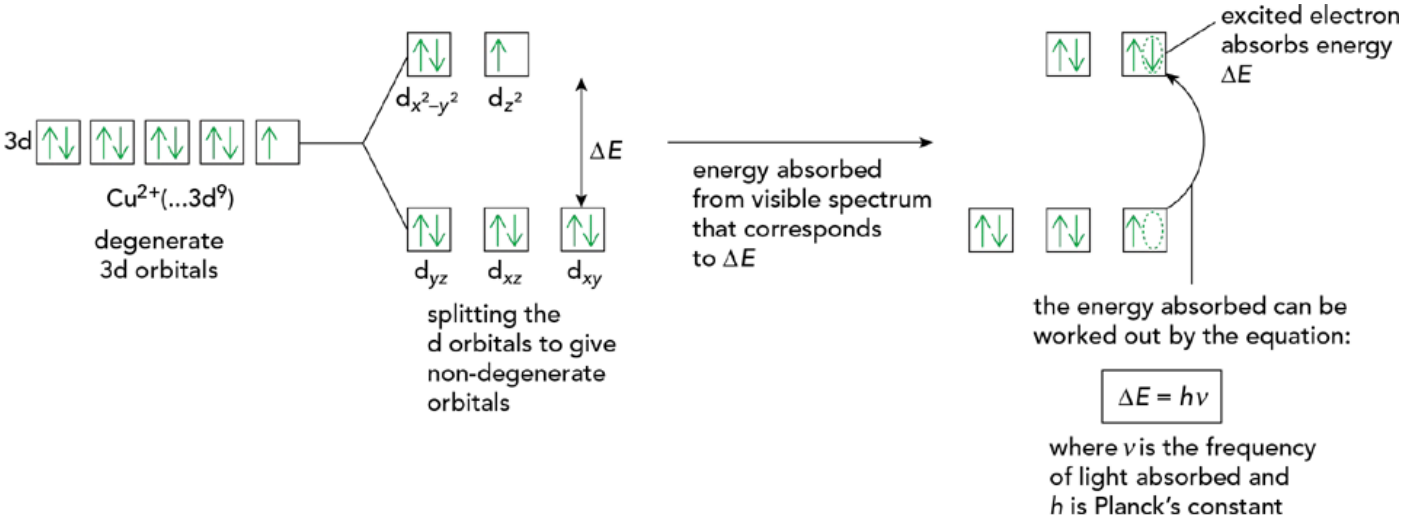


Fig: The splitting of the 3d orbitals in the octahedral $[Cu(H_2O)_6]^{2+}$ complex ion.

A Cu^{2+} ion has an electronic configuration of [Ar] $3d^9$. The above figure shows how the nine d electrons are distributed between the non-degenerate orbitals formed in a complex with ligands. The difference in energy between the non-degenerate d orbitals is labelled Δ*E*.

Δ*E* corresponds to part of the visible spectrum of light. So, when light shines on the solution containing the $[Cu(H_2O)_6]^{2+}$ complex, an electron absorbs this amount of energy. It uses this energy to jump into the higher of the two non-degenerate energy levels. In copper complexes, the rest of the visible spectrum that passes through the solution makes it appear blue in colour.

<u>In tetrahedral complexes</u>, such as $[CoCl_4]^{2-}$, the splitting of the d orbitals is different. The bonding pairs of electrons from four ligands line up with the d*yz*, d*xz* and d*xy* orbitals of the transition metal ion.

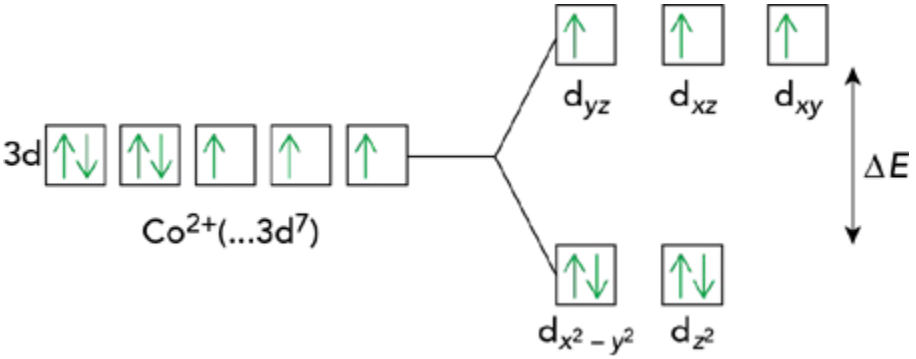
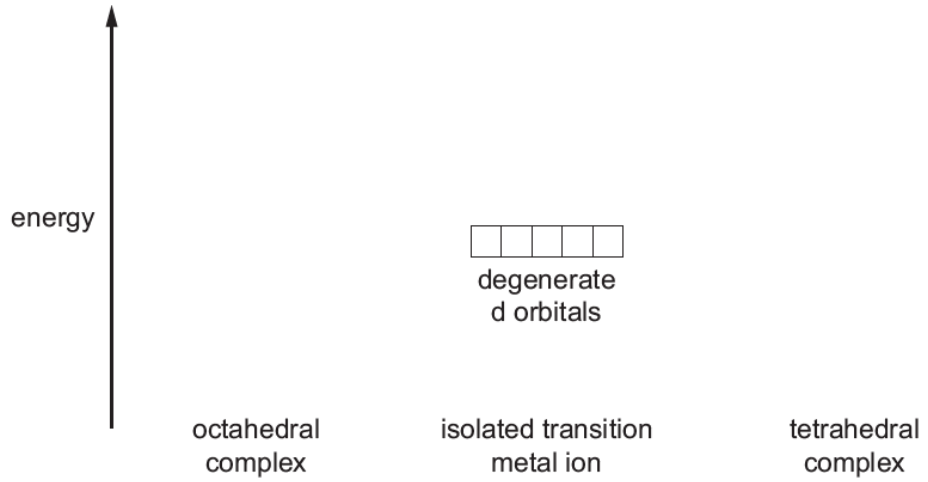


Fig: The splitting of the 3d orbitals in the tetrahedral $[CoCl_4]^{2-}$ complex ion.

Unlike the octahedral arrangement, the d_{x2-y2} and d_{z2} orbitals in a tetrahedral complex lie between the metal–ligand bonds. So, there is less repulsion between electrons in d_{x2-y2} and d_{z2} orbitals and the lone pairs of bonding electrons donated by the ligands. Therefore, when the d orbitals split in this case, the d_{x2-y2} and d_{z2} are at a lower, more stable energy level than the d*yz*, d*xz* and d*xy* orbitals.

The exact energy difference (Δ*E*) between the non-degenerate d orbitals in a transition metal ion is affected by many factors. One of these factors is the identity of the ligands that surround the transition metal ion. As you have seen, a solution containing $[Cu(H_2O)_6]^{2+}$ is a light blue, whereas a solution containing $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is a very deep shade of blue. The colour change arises because the presence of the ammonia ligands causes the d orbitals to split by a different amount of energy. This means that the size of Δ*E* changes, and this results in a slightly different amount of energy being absorbed by electrons jumping up to the higher orbitals. Therefore, a different colour is absorbed from visible light, so a different colour is seen.

4. The transition elements are able to form stable complexes with a wide range of molecules and ions.
The d orbitals in an isolated transition metal ion are degenerate. In complexes, the d orbitals occupy two energy levels.
Complete the diagram to show the arrangement of d orbital energy levels in octahedral and in tetrahedral complexes. [1]



5. The complex ion $[CoCl_4]^{2-}$ has tetrahedral geometry.
The 3d orbitals in an isolated Co^{2+} ion are degenerate.
Complete Fig. 2.2 to show the relative energies of the 3d orbitals in an isolated Co^{2+} ion and in Co^{2+} in a tetrahedral complex.

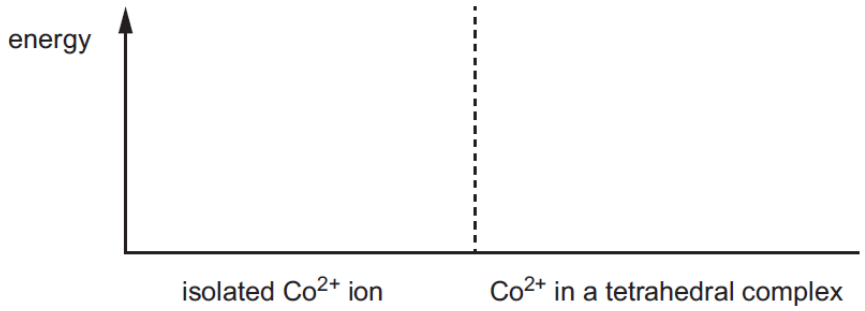
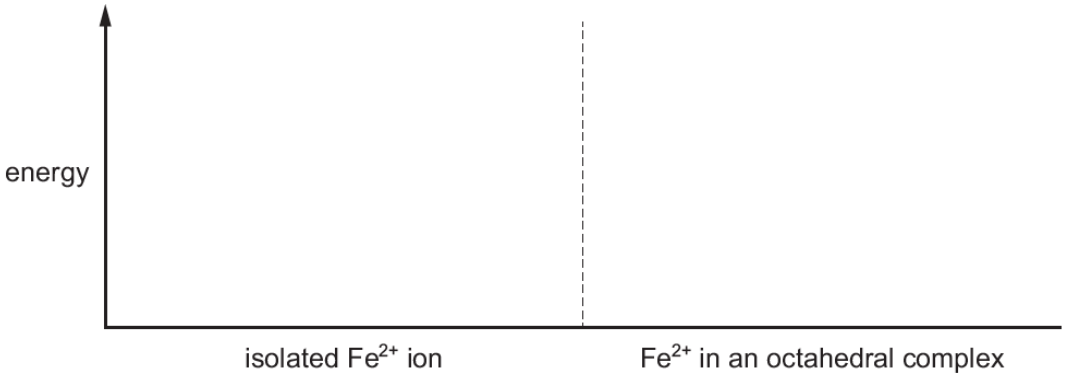


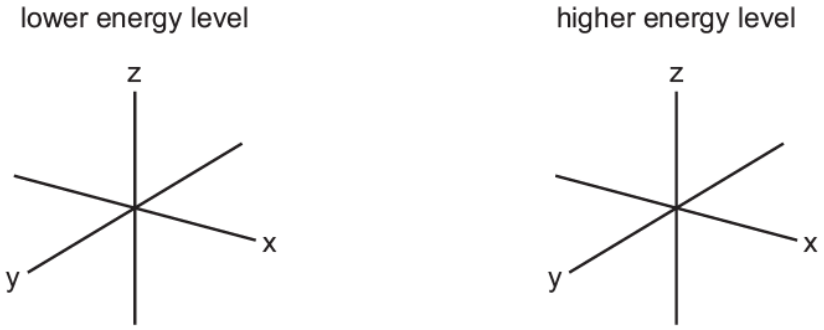
Fig. 2.2

6. The 3d orbitals in an isolated Fe^{2+} ion are degenerate.
Complete the diagram to show the splitting of the 3d orbital energy levels in an isolated Fe^{2+} ion and when Fe^{2+} forms an octahedral complex. [2]



7. Sketch the shape of **two** d orbitals:
- one d orbital from the lower energy level in an octahedral complex
- one d orbital from the higher energy level in an octahedral complex.

Use the axes below. [2]



8. Fe^{2+} and Fe^{3+} ions are able to form a variety of complexes with different species.
(i) Table 3.1 gives some details of different complexes of Fe^{2+} and of Fe^{3+}.
Complete Table 3.1.
Table 3.1

complex	ion	ligand	coordination number	formula and charge of complex
E	Fe^{2+}	NH_3	6	
F				$[FeCl_4]^{2-}$
G		en		$[Fe(en)_3]^{3+}$

(ii) Complete Fig. 3.1 to show the splitting of the d-orbitals in a tetrahedral complex. [1]

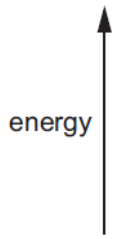


Fig. 3.1

9. L is an uncharged tridentate ligand. L donates three lone pairs to a metal atom or ion.
Cobalt forms an octahedral complex ion, E, with L. Complex ion E has a 2+ charge.
(i) Give the formula of E.

..... [1]

(ii) Identify the oxidation state of cobalt in E.

..... [1]

(iii) The d-orbitals of the cobalt atom or ion present in E are split in energy.
State the number of d-orbitals that are at a higher energy level and the number of d-orbitals that are at a lower energy level.
number of d-orbitals at a higher energy level ……

number of d-orbitals at a lower energy level …….. [1]

10. Explain why chromium complexes are coloured. (9701 s 21 qp23) [4]

{MS:
M1: (complexes have two sets of) d orbital(s) of different energy / d-d splitting occurs
OR d orbital(s) / d (sub)-shell splits
OR (inferred from a movement of an electron) from a lower d to higher d orbital
M2: electron(s) promoted / excited
OR electron(s) moves to higher (d–)orbital
OR electron(s) jumps up (to d–orbital) / jumps to higher (d–orbital)
M3: wavelength / frequency / light / photon / hν absorbed
OR radiation / energy from visible (region) absorbed
M4: colour seen is complementary (to colour absorbed)
OR wavelength / frequency / colour / light not absorbed is transmitted / reflected / seen}

11. Explain why compounds of transition elements are usually coloured. (9071 w 16 qp 42) [3]

{MS: d orbitals split into lower and upper orbitals [1]
light /photon absorbed [1]
electron(s) promoted / excited / jumps up to (higher) (d–) orbital or
electron(s) moves / jumps (from lower (d–)) to higher (d–) orbital[1]}

12. Potassium iron(III) ethanedioate, $K_3[Fe(C_2O_4)_3]$, dissolves in water to form a green solution.
Explain why transition elements form coloured compounds.

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..... [3]

13. Explain why iron complexes are coloured.

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..... [3]

14. Explain the origin of colour in copper(II) complexes.

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..... [4]

15. Explain why $BaCrO_4(s)$ is coloured.

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..... [3]

16. The TiO^{2+} ion forms when TiO_2 reacts with an excess of sulfuric acid.
TiO^{2+} can be reduced by zinc metal in acidic conditions to form a purple solution containing $Ti^{3+}(aq)$.
$TiO^{2+}(aq)$ is a colourless ion.
Suggest why.

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..... [2]

17. Suggest why a solution of Cu^{2+} is coloured but solid CuI is white.

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..... [2]

18. The Ni^{2+} ion forms many different complexes. A solution containing the $[Ni(H_2O)_6]^{2+}$ complex ion is green. When an excess of 1,2-diaminoethane, *en*, $H_2NCH_2CH_2NH_2$, is added, the colour of the solution changes to blue. This is due to the formation of the $[Ni(en)_3]^{2+}$ complex ion.
Explain why the two solutions are coloured, and why the colours are different. [4]

{MS:

- **d orbital(s)** of different energy **/ d-d** splitting occurs [1]
- **electron**(s) promoted / excited [1]
- wavelength of visible light absorbed

AND complementary colour seen [1]

- different energy gap / different ΔE

OR different frequency/wavelength of light is absorbed [1]*}*

19. Iron forms complex ions with the monodentate ligand, CN^-.
(i) Complex ion A contains one Fe^{3+} ion and six CN^- ligands.
Complex ion B contains one Fe^{2+} ion and six CN^- ligands.
State the formulae of these two complex ions. Include the overall charge of each complex ion.

complex ion A .....

complex ion B ..... [1]

(ii) Explain why a solution containing complex ion A and a solution containing complex ion B are different colours.

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..... [2]

20. $[Cr(H_2O)_6]^{2+}$ and $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ are both complexes of chromium(II) and have different colours.
Explain why the colours of these complexes are different.

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..... [2]

21. A solution of $Cr^{3+}(aq)$ and a solution of $Fe^{3+}(aq)$ have different colours.
Explain why the two complexes have different colours.

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..... [2]

22. Aqueous solutions of complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5SCN]^{2+}$ are different colours.
Explain why these complexes are different colours.

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..... [2]

23. The two complex ions $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5NO]^{2-}$ are different colours.
Explain why the colours of the two complex ions are different.

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..... [2]

24. Explain the reason for the difference in colour of the two complexes $[Fe(H_2O)_6]3+$ and $[Fe(H_2O)5SCN]^{2+}$.

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..... [2]

25. An excess of sodium iodide is added to a solution of copper(II) sulfate. Iodine and a white precipitate of copper(I) iodide are formed.

(a) Write an equation for the reaction that occurs.

..... [1]

(b) (i) Explain why the copper(II) sulfate solution is coloured.

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..... [4]

(ii) Suggest why the precipitate of copper(I) iodide is white.

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..... [1]

26. An excess of concentrated hydrochloric acid is added to the dark blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. A new complex, **Z**, is formed. The colour of the solution changes.
(i) Write an equation for the formation of **Z** from the solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. Include the formula and charge of **Z**.

..... [2]

(ii) Name the type of reaction when **Z** forms from $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

..... [1]

(iii) State the geometry of **Z**.

..... [1]

(iv) State the colour of a solution of **Z**.

..... [1]

(v) Explain why the colour of a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is different from the colour of a solution of **Z**. You should refer to the energies of the orbitals involved in your answer.

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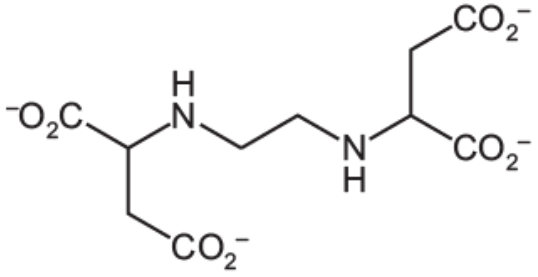
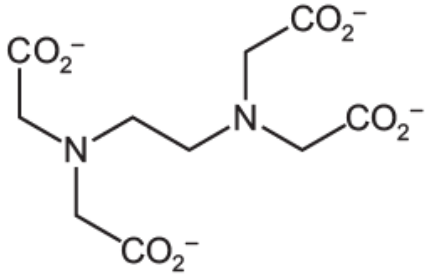
..... [1]

27. The formulae of the complexes are $[Fe(edds)]^-$ and $[Fe(edta)]^-$ respectively.
$Edds^{4-}$ and $edta^{4-}$ are polydentate ligands that form octahedral complexes with $Fe^{3+}(aq)$.

$edds^{4-}$



$edta^{4-}$



(i) $[Fe(edds)]^-$ is red and $[Fe(edta)]^-$ is yellow.
Explain why the two complexes have different colours.

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..... [2]

(iii) Explain why the solutions of the two complex ions in Table 5.1 are different colours.

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..... [1]

28. The solution of $[Cu(NH3)_4]^{2+}$ is heated gently in a fume cupboard so that NH3 is released. Some NH3 remains in solution and some forms NH3 gas. The colour of the solution changes; a precipitate of $Cu(OH)_2$ forms and is collected.
A sample of $Cu(OH)_2$ is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, Y.
A sample of $Cu(OH)_2$ is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, Z.
$[Cu(NH3)_4]^{2+}$, Y and Z are different colours.
Explain why complexes Y and Z are coloured and why their colours are different.

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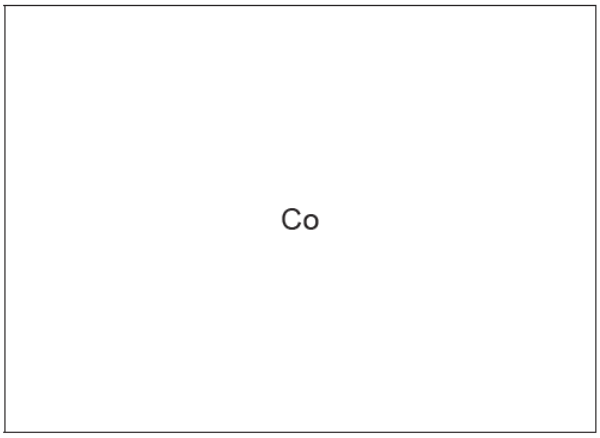
..... [5]

Ligand exchange

29. Cobalt(II) sulfate is added to water to form a pink solution containing complex ion P. An excess of concentrated hydrochloric acid is added to this solution to form a blue solution containing complex ion Q.
(i) Complete the diagram to show the three-dimensional structure of Q.
State the charge on this complex ion. [2]



charge .....

[2]

(ii) Name the type of reaction in which P forms Q.

..... [1]

(iii) Explain why solutions that contain transition element ions are often coloured.

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..... [4]

(iv) Explain why the colours of P and Q are different.

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..... [2]

30. Hexaaquanickel(II) ions are green. They form a green precipitate with hydroxide ions, OH^-, in equilibrium 1 and a blue complex with ammonia, NH_3, in equilibrium 2.

equilibrium 1 $[Ni(H_2O)_6]^{2+} + 2OH^- \rightleftharpoons Ni(OH)_2 + 6H_2O$

green ppt.

equilibrium 2 $[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$

blue

Use Le Chatelier's principle to suggest explanations for the following observations.

(i) Explain why when aqueous NH_3 is added dropwise to $[Ni(H_2O)_6]^{2+}$ a green precipitate is formed.

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..... [1]

(ii) Explain why when a large excess of aqueous NH_3 is added to $[Ni(H_2O)_6]^{2+}$, the green precipitate dissolves and a blue solution is formed.

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..... [1]

31. Hydrated cobalt(II) nitrate, $Co(NO_3)_2 \cdot 6H_2O$, is a red solid that behaves like hydrated magnesium nitrate, $Mg(NO_3)_2 \cdot 6H_2O$, when heated.
Describe in detail what you would expect to observe when crystals of $Co(NO_3)_2 \cdot 6H_2O$ are heated in a boiling tube, gently at first and then more strongly.

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……

…… [2]

(b) Co^{2+} ions form complex ion G.
Each G ion contains two Co^{2+} ions, both of which are octahedrally coordinated.
Each G ion contains one O_2 molecule, which donates one pair of electrons to each Co^{2+} ion, and one NH_2^- ion, which donates one pair of electrons to each Co^{2+} ion.
The remaining ligands are NH_3 molecules.
(i) Deduce the formula of complex ion G. Include its overall charge.

formula of G ..... [2]

(ii) The d-orbitals of the Co^{2+} ions present in complex ion G are split. State the number of d-orbitals that are at a higher energy level and the number of d-orbitals that are at a lower energy level in each Co^{2+} ion.

number of d-orbitals at a higher energy level: ……..

number of d-orbitals at a lower energy level: …….. [1]

(iii) Co^{2+} ions form a different complex ion, M.
Each M ion contains two Co^{2+} ions, both of which are octahedrally coordinated, but the ligands are different from the ligands in G.
Explain why G and M have different colours.

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..... [2]

32. **A** is a pale green salt containing Fe^{2+} ions. A sample of 2.62 g of **A** is dissolved in water and the solution is made up to exactly 100 cm^3 with water. 25.0 cm^3 samples of this solution are placed in conical flasks and titrated against 0.0100 mol dm^{-3} acidified potassium manganate(VII).

The equation for the only reaction that occurs is shown.

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

The average titre value is 35.0 cm^3 of 0.0100 mol dm^{-3} acidified potassium manganate(VII).

(i) Describe the colour change that is seen in the conical flask at the end-point of this titration.

The colour changes from ..... to …… . [1]

(ii) Calculate the percentage by mass of iron in **A**.

[*A*r: Fe, 55.8]

Percentage by mass of iron = ... % [2]

*****This is not a complete note. It is just to guide you. It is recommended to study the prescribed textbooks along with this material. *****