Complex Ions with Acid and Base

A Level P P P Further A P P P

Complex ions can undergo a variety of reactions. Either the coordinated ligands themselves can react *e.g.* by protonation or deprotonation, or they can be replaced by a new ligand in a substitution reaction.

Part A $[Cu(H_2O)_6]^{2+}$ with aqueous ammonia

What is the formula of the initial precipitate formed when $[Cu(H_2O)_6]^{2+}$ reacts with aqueous ammonia solution?

Give the formula of the complex in the format $[Cu\cdots]^{n\pm}$

Part B $[Cu(H_2O)_6]^{2+}$ with excess aqueous ammonia

When this precipitate is allowed to react with *excess* aqueous ammonia, it dissolves to give a dark blue solution. What is the formula of this new product?

Give the formula of the complex in the format $[Cu\cdots]^{n\pm}$

Part C $[Fe(H_2O)_6]^{2+}$ with aqueous ammonia

What is the formula of the precipitate formed when $[Fe(H_2O)_6]^{2+}$ reacts with aqueous ammonia solution?

Give the formula of the complex in the format $[Fe\cdots]^{n\pm}$

Part D $[Fe(H_2O)_6]^{3+}$ with aqueous ammonia

What is the formula of the precipitate formed when $[Fe(H_2O)_6]^{3+}$ reacts with aqueous ammonia solution?

Give the formula of the complex in the format $[Fe\cdots]^{n\pm}$

Part E $[Cu(H_2O)_6]^{2+}$ with concentrated hydrochloric acid

What is the formula of the yellow complex formed when $[Cu(H_2O)_6]^{2+}$ reacts with concentrated hydrochloric acid?

Give the formula of the complex in the format $[Cu\cdots]^{n\pm}$

Transition Metal Oxidation States

A Level

Part A Possible oxidation states

The table shows the possible oxidation states of five d-block elements in the Periodic Table. (The elements are represented by letters which are not their symbols.)

Element	Oxidation States						
P	-	-	3	-	-	-	-
Q	-	2	3	4	-	-	-
R	1	2	3	4	5	-	-
S	-	-	3	4	5	6	-
T	-	2	-	4	5	6	7

Which of the following ions is likely to exist?

- RO_4^{2-}
- TO_2^{2+}
- PO_2^{+}
- QO_3^{-}
- SO_4^{-}

Part B Compounds of titanium

Titanium has the electronic structure $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$.

Which of the following compounds is **unlikely** to exist?

- $TiCl_3$
- TiO_2
- TiO
- K_3TiF_6
- K_2TiO_4

Part A adapted with permission from UCLES, A-Level Chemistry, June 1992, Paper 4, Question 14;
Part B adapted with permission from UCLES, A-Level Chemistry, November 1992, Paper 4, Question 20.

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Complex Ions Oxidation States

A Level

Give the oxidation number of the transition metal in the following complexes:

Part A $[CuCl_4]^{3-}$

Part B $[FeF_5(H_2O)]^{2-}$

Part C $[Co(NH_2CH_2CH_2NH_2)_2F_2]^{+}$

Adapted with permission from UCLES, A-Level Chemistry, November 1995, Paper 2, Question 1.

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Cobalt Electrochemistry

A Level

Replacement of water molecules by other ligands generally changes the redox potentials of transition metal ions. Use the following information to answer this question.

	$E^{\ominus}/V$
$[Co(H_2O)_6]^{3+}(aq) + e^- \longrightarrow [Co(H_2O)_6]^{2+}(aq)$	$+1.81$
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O(l)$	$+1.23$
$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$	$+0.00$
$[Co(CN)_6]^{3-}(aq) + e^- \longrightarrow [Co(CN)_6]^{4-}(aq)$	-0.83

Part A Cobalt(III) sulfate in water

What products are likely to be formed when cobalt(III) sulfate is dissolved in water? Give an equation for the reaction.

Part B $Co(CN)_6{}^{4-}$ with oxygen

If an aqueous solution of cobalt(II) chloride is mixed with an excess of aqueous potassium cyanide, the ion $[Co(CN)_6]^{4-}(aq)$ is formed. This mixture absorbs oxygen from the air. Write an equation for this reaction with oxygen.

Part C No oxygen

Suggest another reaction which might take place in the cyanide mixture from Part B if air were excluded.

Adapted with permission from OCSEB A-Level Chemistry, June 1994, Paper 3/4, Question 8.

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Iron Chemistry

A Level C C C Further A C C C

Part A Red ink

Letters written on paper using aqueous ammonium thiocyanate are invisible until turned blood red by brushing the paper with aqueous iron(III) chloride. If the ammonium thiocyanate is first made alkaline, the letters are orange and less clear.

Which of the following substances, when formed on the paper in these reactions, best explains these observations?

	with aqueous ammonium thiocyanate	with alkaline aqueous ammonium thiocyanate
A	$Fe-NH_3$ complex	$Fe(OH)_3$
B	$Fe-CNS$ complex	$Fe-NH_3$ complex
C	$Fe-CNS$ complex	$Fe(OH)_3$
D	$Fe-CNS$ complex	$Fe-OH^-$ complex

- **A**
- **B**
- **C**
- **D**

Part B hexa-aquo iron(III) hydrolysis

The hexa-aquo iron(III) ion hydrolyses as shown below.

$$[\mathrm{Fe(H_2O)_6}]^{3+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons [\mathrm{Fe(H_2O)_5OH}]^{2+}\,(\mathrm{aq}) + \mathrm{H_3O^+}\,(\mathrm{aq})$$

Which of the following statements are correct?

1. This hydrolysis is favoured by low pH values.
2. The iron undergoes a change in oxidation state.
3. The corresponding iron(II) ion $[\mathrm{Fe(H_2O)_6}]^{2+}$ is less likely to undergo hydrolysis.

- **3** only is correct
- **1**, **2** and **3** are correct
- **2** and **3** only are correct
- **1** and **2** only are correct
- **1** only is correct

Part C Electronic configuration

Iron has a proton (atomic) number of 26.

What is the electronic configuration of the iron cation which can form the complex ion $[\mathrm{Fe(CN)_6}]^{4-}$?
($[\mathrm{Ar}] = 1\mathrm{s}^2\ 2\mathrm{s}^2\ 2\mathrm{p}^6\ 3\mathrm{s}^2\ 3\mathrm{p}^6$)

- $[\mathrm{Ar}]\ 3\mathrm{d}^6\ 4\mathrm{s}^2$
- $[\mathrm{Ar}]\ 3\mathrm{d}^6\ 4\mathrm{s}^0$
- $[\mathrm{Ar}]\ 3\mathrm{d}^4\ 4\mathrm{s}^2$
- $[\mathrm{Ar}]\ 3\mathrm{d}^3\ 4\mathrm{s}^2$
- $[\mathrm{Ar}]\ 3\mathrm{d}^8\ 4\mathrm{s}^0$

Part A adapted with permission from UCLES, A-Level Chemistry, June 1994, Paper 4, Question 19;
Part B adapted with permission from UCLES, A-Level Chemistry, June 1991, Paper 1, Question 37.

Mn Oxidation States

A Level

When a solution of potassium manganate(VII) in aqueous potassium hydroxide is partially evaporated, a dark green solution is obtained from which a dark green solid **X** can be isolated. **X** contains potassium, manganese and oxygen only. On treatment with dilute acid, a sample of **X** reacted to give $0.714\,\mathrm{g}$ of manganese(IV) oxide and a purple solution that was just decolourised by the addition of $40.0\,\mathrm{cm^3}$ of $0.500\,\mathrm{mol\ dm^{-3}}$ iron(II) sulfate.

Part A Purple solution

Suggest the identity of the purple solution.

Part B X oxidation number

Calculate the oxidation number of manganese in **X**.

Part C X formula

Hence deduce the formula of **X**.

Part D Equation for X

Using the lowest possible integer coefficients, construct an equation for a possible reaction between aqueous potassium manganate(VII) and hydroxide ions that could have resulted in the formation of **X**.

Adapted with permission from UCLES A-Level Chemistry, June 1991, Paper 4, Question 2.

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Oxidising/Reducing Complex Ions

A Level

Part A Reducing complex ions

Which of the following ions is readily able to donate electrons?

- Fe^{2+}
- Cu^{2+}
- Mg^{2+}
- Zn^{2+}
- Al^{3+}

Part B Oxidising complex ions

Which of the following ions is readily able to accept electrons?

- Cu^{3+}
- Co^{3+}
- Zn^{2+}
- Mg^{2+}
- Cr^{3+}

Part A adapted with permission from UCLES, A-Level Chemistry, June 1993, Paper 4, Question 20;
Part B created for isaacphysics.org by R. Less

Nickel Salts

A Level

Aqueous solutions of nickel(II) salts are green due to the presence of the $[Ni(H_2O)_6]^{2+}(aq)$ ion. On adding aqueous ammonia to a solution of a nickel(II) salt, the colour changes to blue or purple as different complexes are formed through the displacement of H_2O ligands by NH_3.

One of the intermediate complexes has the formula $Ni[(H_2O)_x(NH_3)_y]Cl_2$.

A $1.00\,g$ sample of the complex produced $1.23\,g$ of silver chloride when treated with an excess of aqueous silver nitrate.

A $1.00\,g$ sample of the complex produced $0.29\,g$ of ammonia when boiled with an excess of aqueous sodium hydroxide.

Part A Moles of complex

How many moles of complex are present in a $1.00\,g$ sample?

Part B Moles of ammonia

How many moles of ammonia are present in the $1.00\,g$ sample?

Part C Formula

What is the formula of the complex?

Ions and Precipitates

A Level

C C C

Part A With excess ammonia

An aqueous solution containing a mixture of copper(II), iron(II) and lead(II) ions was treated with an excess of aqueous ammonia. What precipitate is left by this reaction?

- lead(II) hydroxide only
- iron(II) hydroxide only
- copper(II) hydroxide only
- iron(II) hydroxide and lead(II) hydroxide
- copper(II) hydroxide and iron(II) hydroxide

Part B With excess hydroxide

A crystalline salt **Z** was dissolved in water and then aqueous sodium hydroxide was added until present in excess. A white precipitate was formed, which turned brown on exposure to air.

Which one of the following could be **Z**?

- $Fe_2(SO_4)_3$
- $Al_2(SO_4)_3$
- $NiSO_4$
- $FeSO_4$
- $MnSO_4$

Part A adapted with permission from UCLES, A-Level Chemistry, 1989, Paper 3, Question 21;
Part B adapted with permission from UCLES, A-Level Chemistry, 1988, Paper 3, Question 21.

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Prussian Blue

A Level

C C C

Prussian blue is a deep blue insoluble pigment that is used as a dye for blueprint paper and ink. It can be made by mixing together aqueous solutions of $\mathrm{FeCl_3}$ and $\mathrm{K_4Fe(CN)_6}$. It consists entirely of iron ions in different oxidation states joined by an array of cyanide ($\mathrm{CN^-}$) ions.

Part A $\mathrm{FeCl_3}$ oxidation state

State the oxidation state of iron in $\mathrm{FeCl_3}$.

Part B $\mathrm{K_4Fe(CN)_6}$ oxidation state

State the oxidation state of iron in $\mathrm{K_4Fe(CN)_6}$.

Part C Formula

Assuming that the structure of Prussian blue consists only of iron ions and cyanide ions, suggest the simplest formula of this pigment. Start your formula with the metal as is conventional

Part D Shape of $\mathrm{K_4Fe(CN)_6}$

Describe the shape of the complex anion of $\mathrm{K_4Fe(CN)_6}$.

Adapted with permission from UCLES, A-Level Chemistry, November 1991, Paper 4, Question 1.