Transition elements - 2021

1. Nov/2021/Paper_41/No.5

(a) $[MnCl_4]^{2-}$ is a complex ion.

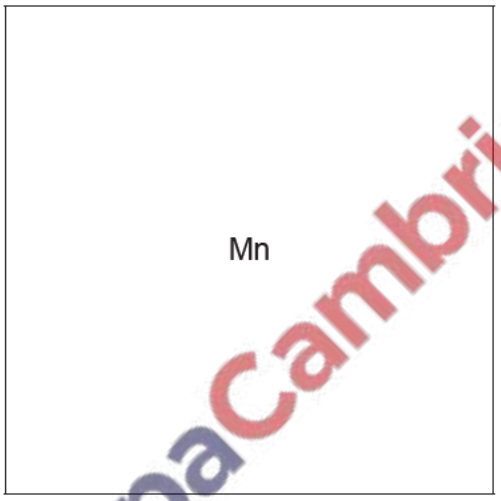
(i) Deduce the oxidation state of manganese in $[MnCl_4]^{2-}$.

oxidation state = ... [1]

(ii) The $[MnCl_4]^{2-}$ complex does **not** contain any 180° bond angles.

Draw a three-dimensional diagram to show the shape of the $[MnCl_4]^{2-}$ complex.

State one bond angle on your diagram.



[2]

(b) A solution of cobalt(II) sulfate contains the complex ion $[Co(H_2O)_6]^{2+}$.

A solution containing $[Co(H_2O)_6]^{2+}$ is reacted separately with an excess of each of NaOH(aq), NH_3(aq) and NaCl(aq).

Write an equation for each of these reactions. State **one** observation that can be made immediately after the reaction, include the colour and state of the cobalt-containing product.

(i) $[Co(H_2O)_6]^{2+}$ and an excess of NaOH(aq)

equation .....

observation .....

[2]

(ii) $[Co(H_2O)_6]^{2+}$ and an excess of $NH_3(aq)$

equation .....

observation .....

[2]

(iii) $[Co(H_2O)_6]^{2+}$ and an excess of $NaCl(aq)$

equation .....

observation .....

[2]

(iv) Name the type of reaction that occurs in **(b)(iii)**.

..... [1]

(c) Cobalt forms the complex ion $[Co(NH_3)_2(en)_2]^{2+}$. The abbreviation en is used for the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$. The complex ion shows both geometrical and optical isomerism.

(i) Define the term *bidentate ligand*.

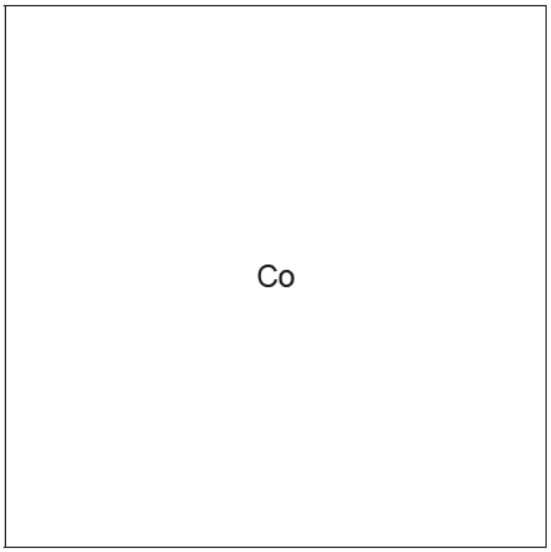
.....

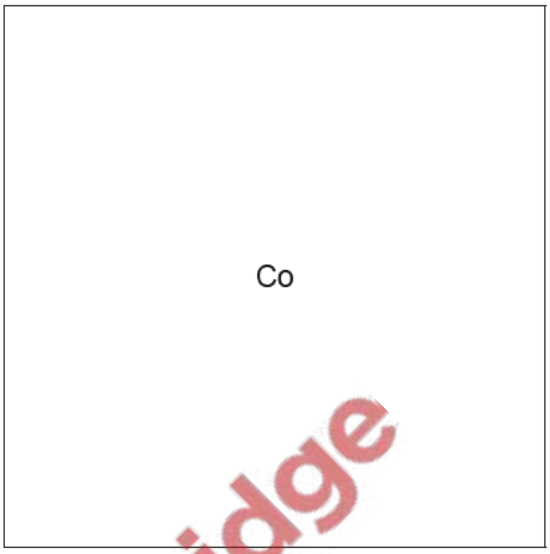
..... [2]

(ii) Draw three-dimensional diagrams for the two **optical** isomers of $[Co(NH_3)_2(en)_2]^{2+}$.

Each en ligand can be represented using 

.





[2]

[Total: 14]

2. Nov/2021/Paper_42/No.5

Transition elements form complexes.

(a) Molybdenum, Mo, forms an octahedral complex consisting of one Mo atom surrounded by carbon monoxide, CO, molecules. CO is a monodentate ligand. Iron forms an octahedral complex consisting of one Fe^{3+} and a number of cyanide, CN^-, ions. CN^- is a monodentate ligand.

(i) Define the term *monodentate ligand*.

.....

..... [1]

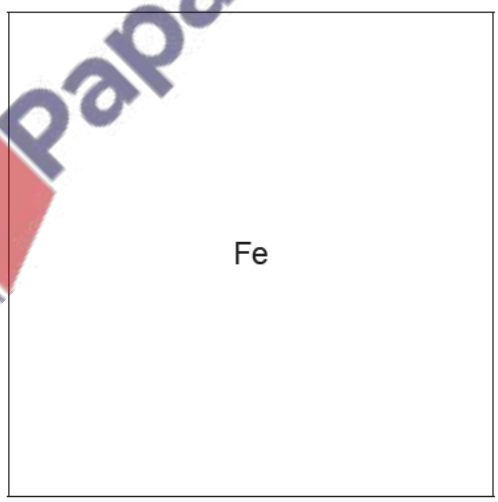
(ii) Complete the table by stating the formulae and charges of the complexes described.

	formula	charge
molybdenum complex		
iron(III) complex		

[2]

(iii) Draw a three-dimensional diagram to show the shape of this iron(III) complex.

Label one 180° bond angle on your diagram.



[1]

(b) An excess of aqueous ammonia is added to dilute copper(II) sulfate solution. A dark blue complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, is formed.

(i) Write an ionic equation for this reaction.

..... [1]

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

.....

.....

.....

.....

.....

..... [4]

(c) 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.

.....

..... [1]

[Total: 15]

3. Nov/2021/Paper_42/No.6

An excess of aqueous ammonia is added to a solution containing the complex ion $[Co(H_2O)_6]^{2+}$.

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

(a) Complete the sentence to describe the colour change that will be seen during this reaction.

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

(b) Write an expression for the stability constant, K_{stab}, of $[Co(NH_3)_6]^{2+}$.

K_{stab} =

[1]

(c) The numerical value of K_{stab} of $[Co(NH_3)_6]^{2+}$ is 7.7×10^4.

What deduction about the properties of $[Co(NH_3)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ can be made from this K_{stab} value?

..... [1]

(d) Oxygen can oxidise $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ under standard conditions in alkaline solutions.

$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad E^\ominus = +0.10\,V$$

(i) Use this information and the *Data Booklet* to calculate the $E^\ominus_{cell}$ value for this oxidation of $[Co(NH_3)_6]^{2+}$.

.....

.....

$E^\ominus_{cell}$ = ... V

[1]

(ii) Write an ionic equation for this oxidation of $[Co(NH_3)_6]^{2+}$.

..... [1]

(iii) Predict, by selecting suitable data from the *Data Booklet*, whether oxygen can oxidise $Co^{2+}(aq)$ in **acidic** solution, in the absence of ammonia. Explain your answer.

.....

..... [2]

4. March/2021/Paper_42/No.1

(a) The most common oxidation states of cobalt are +2 and +3.

Complete the electronic configurations of the following free ions.

- Co^{2+} [Ar] .....
- Co^{3+} [Ar] .....

[1]

(b) Co^{2+} and Co^{3+} both form complexes with $edta^{4-}$.

half-equation	$E^{\ominus}$/V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.82
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$[Co(edta)]^- + e^- \rightleftharpoons [Co(edta)]^{2-}$	+0.38
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28

Use the data in the table to predict what happens, if anything, when separate aqueous solutions of Co^{3+} and $[Co(edta)]^-$ are left to stand in the air.

aqueous solution of Co^{3+}

.....

.....

aqueous solution of $[Co(edta)]^-$

.....

.....

[3]

(c) 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.

.....

.....

.....

..... [2]

(d) Explain why the thermal stability of the Group 2 nitrates increases down the group.

.....

.....

.....

..... [2]

[Total: 8]

5. March/2021/Paper_42/No.4

The transition elements are able to form stable complexes with a wide range of molecules and ions.

(a) State the meaning of *transition element*.

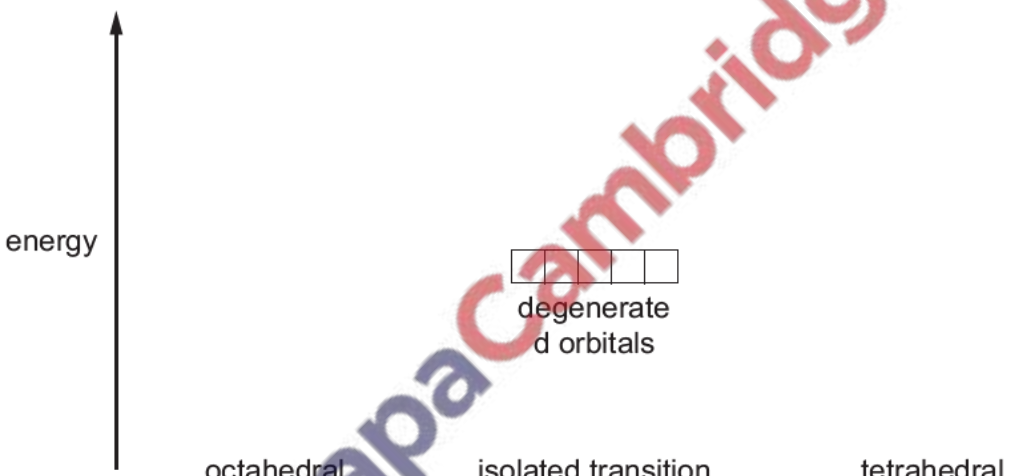
.....

.....

..... [1]

(b) The d orbitals in an isolated transition metal ion are degenerate. In complexes, the d orbitals occupy two energy levels.

(i) Complete the diagram to show the arrangement of d orbital energy levels in octahedral and in tetrahedral complexes.



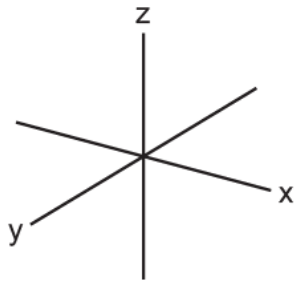
[1]

(ii) Sketch the shape of **two** d orbitals:

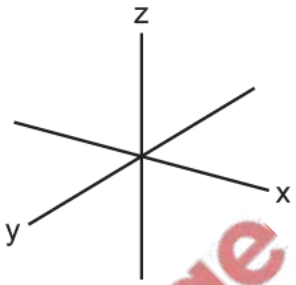
- one d orbital from the lower energy level in an octahedral complex
- one d orbital from the higher energy level in an octahedral complex.

Use the axes below.

lower energy level



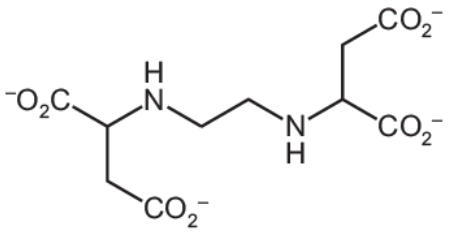
higher energy level



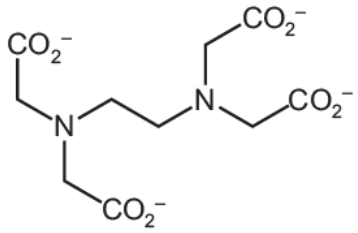
[2]

(c) $Edds^{4-}$ and $edta^{4-}$ are polydentate ligands that form octahedral complexes with $Fe^{3+}(aq)$.

$edds^{4-}$



$edta^{4-}$



The formulae of the complexes are $[Fe(edds)]^-$ and $[Fe(edta)]^-$ respectively.

(i) On the diagram of $edds^{4-}$, circle each atom that forms a bond to the Fe^{3+} ion in $[Fe(edds)]^-$. [1]

(ii) $[Fe(edds)]^-$ is red and $[Fe(edta)]^-$ is yellow.

Explain why the two complexes have different colours.

.....

.....

.....

.....

..... [2]

(iii) When $edds^{4-}(aq)$ is added to $Fe^{3+}(aq)$, the following reaction occurs.

$$[Fe(H_2O)_6]^{3+}(aq) + edds^{4-}(aq) \rightleftharpoons [Fe(edds)]^-(aq) + 6H_2O(l)$$

State the type of reaction that occurs.

..... [1]

(iv) Write an expression for the stability constant, K_{stab}, of $[Fe(edds)]^-(aq)$.

K_{stab} =

[1]

(v) The table shows the values for the stability constants, K_{stab}, of both complexes.

complex	K_{stab} / $mol^{-1}\,dm^3$
$[Fe(edds)]^-$	3.98×10^{20}
$[Fe(edta)]^-$	1.26×10^{25}

Predict which of the $[Fe(edds)]^-$ and $[Fe(edta)]^-$ complexes is more stable.

Explain your answer with reference to the K_{stab} value for each complex.

.....

.....

..... [1]

(vi) When an excess of $edta^{4-}(aq)$ is added to $[Fe(edds)]^-(aq)$, the following equilibrium is established.

$$[Fe(edds)]^-(aq) + edta^{4-}(aq) \rightleftharpoons [Fe(edta)]^-(aq) + edds^{4-}(aq)$$

Calculate the equilibrium constant, K_c, for this equilibrium, using the K_{stab} values given in the table in **(c)(v)**.

K_c = ... [1]

[Total: 11]

6. June/2021/Paper_41/No.2

(a) Explain why chromium complexes are coloured.

.....

.....

.....

.....

..... [4]

(b) Four different compounds can be obtained when anhydrous chromium(III) chloride reacts with water under various conditions. When samples of each compound are reacted separately with aqueous silver nitrate, different amounts of silver chloride are precipitated. The precipitation leaves the complex ions **P**, **Q**, **R** and **S** in solution.

formula of compound	moles of AgC*l* precipitated per mole of complex ion	complex ion	property of complex ion
$CrCl_3(H_2O)_6$	3	**P**	non-polar
$CrCl_3(H_2O)_5$	2	**Q**	polar
$CrCl_3(H_2O)_4$	1	**R**	polar
$CrCl_3(H_2O)_4$	1	**S**	non-polar

(i) Draw three-dimensional diagrams for the structures of complex ions **P**, **Q**, **R** and **S**. Include the charges for each complex ion.

P

Cr

Q

Cr

R

Cr

S

Cr

[4]

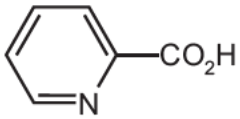
(ii) Suggest why complex ion **S** is non-polar.

.....

..... [1]

(c) The structure of picolinic acid is shown.

picolinic acid



The conjugate base of picolinic acid is a bidentate ligand, **Z**.

(i) Define the term *bidentate ligand*.

.....

..... [2]

(ii) Draw the structure of **Z**.

[1]

(iii) **Z** reacts with aqueous chromium(III) ions, $[Cr(H_2O)_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex.

State the coordination number and the geometry of the chromium(III) centre in the complex.

coordination number ..... geometry ..... [1]

(d) $(NH_4)_2Cr_2O_7$ decomposes readily on heating to form Cr_2O_3, steam and an inert colourless gas.

(i) Deduce the oxidation numbers of chromium in $(NH_4)_2Cr_2O_7$ and in Cr_2O_3.

$(NH_4)_2Cr_2O_7$ ..... Cr_2O_3 ..... [1]

(ii) Construct an equation for the thermal decomposition of $(NH_4)_2Cr_2O_7$.

..... [1]

[Total: 15]

7. June/2021/Paper_42/No.1

(a) An aqueous solution of chromium(III) contains the green $[Cr(H_2O)_6]^{3+}$ complex ion.

(i) Complete the electronic configuration of an isolated, gaseous Cr^{3+} ion.

$1s^2$ ..... [1]

(ii) Define the term *complex ion*.

.....

..... [1]

(b) $[Cr(H_2O)_6]^{3+}(aq)$ shows some similar chemical properties to $[Co(H_2O)_6]^{2+}(aq)$.

Samples of $[Cr(H_2O)_6]^{3+}$ are reacted separately with either NaOH(aq), $H_2O_2(aq)$, or excess $NH_3(aq)$.

Use this information and the *Data Booklet* to suggest the formula of the chromium species formed. State the type of reaction taking place in each case.

reagent added to $[Cr(H_2O)_6]^{3+}(aq)$	formula of chromium species formed	type of reaction
NaOH(aq)		
$H_2O_2(aq)$		
an excess of $NH_3(aq)$		

[5]

(c) $[Cr(H_2O)_6]^{2+}$ 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.

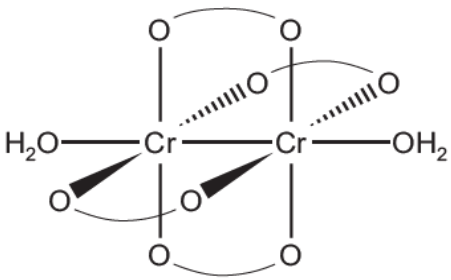
.....

.....

.....

..... [2]

(d) The structure of $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ is shown. Ethanoate ions act as ligands in this complex. The ethanoate ligand, $CH_3CO_2^-$, is shown as O⌒O.



(i) Water and ethanoate ions behave as different types of ligand in this complex.

Suggest an explanation for this statement.

.....

..... [1]

(ii) Deduce the coordination number of Cr and the geometry around each Cr atom in this structure.

coordination number .....

geometry around Cr atom .....

[1]

(iii) State the type of bond between the two atoms in the Cr–Cr bond.

..... [1]

(e) The $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ complex reacts with aqueous acid to form $Cr^{2+}(aq)$ ions.

$Cr^{2+}(aq)$ ions react with $O_2(aq)$ under acidic conditions. $Cr^{3+}(aq)$ ions are formed.

Use the *Data Booklet* to answer the following questions.

(i) Construct an ionic equation for the reaction of $Cr^{2+}(aq)$ with $O_2(aq)$ under acidic conditions.

..... [2]

(ii) Calculate $E^{\ominus}_{cell}$ for the reaction in **(e)(i)**.

$E^{\ominus}_{cell}$ = ... V [1]

[Total: 15]