- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Co^{2+}.

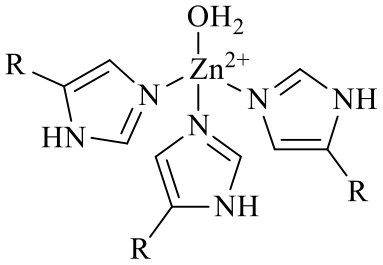
Marks
2

• Name the complex $[CoCl_2(en)_2]$. en = ethylenediamine = $NH_2CH_2CH_2NH_2$	**Marks 4**
Draw all possible isomers of this complex.	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 7

- The structure below represents the active site in carbonic anhydrase, which features a Zn^{2+} ion bonded to 3 histidine residues and a water molecule.



The pK_a of uncoordinated water is 15.7, but the pK_a of the water ligand in carbonic anhydrase is around 7. Suggest an explanation for this large change.

When studying zinc-containing metalloenzymes, chemists often replace Zn^{2+} with Co^{2+}. Using the box notation to represent atomic orbitals, work out how many unpaired electrons are present in the Zn^{2+} and Co^{2+} ions.

Suggest why it is useful to replace Zn^{2+} with Co^{2+} when studying the nature of the active site in carbonic anhydrase.

Suggest two differences in the chemistry of Zn^{2+} and Co^{2+} ions that may affect the reactivity of the cobalt-containing enzyme.

Marks 8

- Use the information already provided to complete the following table.
  (ox = oxalate = $C_2O_4^{2-}$)

Formula	$[CrCl_2(NH_3)_4]^n$	$[Fe(ox)_3]^n$	$[ZnCl_2(NH_3)_2]^n$
Oxidation state of transition metal ion		+III	
Number of *d*-electrons in the transition metal ion			10
Number of unpaired *d*-electrons in the transition metal ion			
Charge of complex (*i.e.* n)	1+		
Is the metal atom paramagnetic?			

The complex $[PtCl_2(NH_3)_2]$ has two isomers, while its zinc analogue (in the table) exists in only one form. Using diagrams where appropriate, explain why this is so.

Marks 6

- Complete the following table.

Formula	Geometry of complex	Ligand donor atom(s)
$[Zn(OH)_4]^{2-}$		
$[CoCl(NH_3)_5]SO_4$		
$K_4[Fe(CN)_6]$		
$[Ag(CN)_2]^-$		

Select any complex ion from the above table and state whether it is paramagnetic, diamagnetic or neither. Explain your reasoning.

• Which of the following complexes is/are chiral? Explain your reasoning. Use diagrams where necessary. acetylacetonate ion = $CH_3COCHCOCH_3^-$ ethylenediamine = $NH_2CH_2CH_2NH_2$	**Marks 3**
tris(acetylacetonato)chromium(III)	
trans-bis(ethylenediamine)difluoridochromium(III) chloride	
acetylacetonatobis(ethylenediamine)chromium(III) iodide	

Marks 7

- What is the solubility of $Cu(OH)_2$ in mol L^{-1}? K_{sp} ($Cu(OH)_2$) is 1.6×10^{-19} at 25 °C.

Answer:

The overall formation constant for $[Cu(NH_3)_4]^{2+}$ is 1.0×10^{13}. Write the equation for the reaction of Cu^{2+} ions with excess ammonia solution.

Calculate the value of the equilibrium constant for the following reaction.

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

Answer:

Would you expect $Cu(OH)_2(s)$ to dissolve in 1 M NH_3 solution? Briefly explain your answer.

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Cu^{2+}. **2**

- Provide a systematic name for the complex [NiBrCl(en)] and draw both of its possible structures. (en = $NH_2CH_2CH_2NH_2$ = ethylenediamine = ethane-1,2-diamine) **4**

Is either complex chiral? Explain your reasoning.

Marks 6

- Complete the following table. (ox = oxalate = $C_2O_4^{2-}$)

Formula	$Na[FeCl_4]$	$[CrCN(NH_3)_5]Br_2$	$K_3[VO_2(ox)_2]\cdot 3H_2O$
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Species formed upon dissolving in water			

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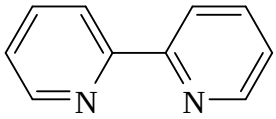
	Marks
• The following three complex ions can all exhibit isomerism. Name the type of isomerism involved in each case and draw the structures of the isomeric pairs. ox = oxalate = $C_2O_4^{2-}$	**9**
$[CrCl_2(NH_3)_4]^+$	
$[Fe(ox)_3]^{3-}$	
$[Co(NH_3)_3(OH_2)_3]^{3+}$	
• Give the systematic name of each of the following compounds. en = ethylenediamine = 1,2-diaminoethane = $NH_2CH_2CH_2NH_2$	**3**
$Cs_2[PtF_6]$	
$[Co(en)_2(NH_3)_2]Br_3$	

Marks 5

- Complete the following table. NCS^- = isothiocyanate ion

bipy = 2,2'-bipyridine = $(C_5H_4N)_2$ = 

Formula	$K_2[Zn(CN)_4]$	$[Co(bipy)(NH_3)_4]Cl_3$	$[Co(bipy)_2(NCS)_2]$
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Coordination geometry of the complex ion			
List all the ligand donor atoms			

- Titanium has three common oxidation states, +II, +III and +IV. Using the box notation to represent atomic orbitals, predict whether compounds of Ti^{2+}, Ti^{3+} and Ti^{4+} would be paramagnetic or diamagnetic. **2**

- Provide a systematic name for the complex *trans*-$[NiBr_2(en)_2]$ and draw its structure. Is this complex chiral? Explain your reasoning. **4**

  en = ethylenediamine = ethane-1,2-diamine

Page Total:

- Complete the following table. (EDTA = ethylenediaminetetraacetate)

Marks 5

Formula	$[Ni(NH_3)_6](NO_3)_2$	*trans*-$[PtCl_2(NH_3)_2]$	Na[Fe(EDTA)]
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Coordination geometry of the complex ion			
List all the ligand donor atoms			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Co^{2+}.

2

Marks 9

- Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

Formula	$K_2[CoCl_4]$	$Na_3[FeBr(CN)_5]$	$[Zn(en)_2(NO_3)_2]$
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Charge of the complex ion			
Geometry of the complex ion			
List all the ligand donor atoms			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Explain why compounds of *d*-block elements are frequently paramagnetic. Use examples in your answer. **2**

- Provide a systematic name for *cis*-$[Co(en)_2Cl_2]Cl$. Is this complex chiral? Explain your reasoning by drawing the structure of the complex.
  en = $NH_2CH_2CH_2NH_2$ = ethane-1,2-diamine = ethylenediamine **3**

- Derive expressions for the equilibrium constants for the complexation of Pb^{2+} (K_1) and of Ca^{2+} (K_2) by $EDTA^{4-}$.

3

Briefly explain why the chelating agent, EDTA, is administered as $[Ca(EDTA)]^{2-}$ to treat lead poisoning and determine which of K_1 or K_2 must be greater for the therapy to be effective.

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, explain why most Fe^{2+} and Fe^{3+} compounds are paramagnetic.

2

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 9

- Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

Formula	$(NH_4)_2[CoCl_4]$	$[Cr(NH_3)_5(H_2O)]Cl_3$	*cis*-$[PtCl_2(en)_2]$
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Charge of the complex ion			
Geometry of the complex ion			
List all the ligand donor atoms			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

3

- Calculate the equilibrium constant for the following reaction.

$$AgI(s) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq) + I^-(aq)$$

Data: K_{stab} of $[Ag(CN)_2]^-$ = 3×10^{20}; K_{sp} of AgI = 8.3×10^{-17}

Answer:

- Which of the cations, $[Fe(OH_2)_6]^{3+}$ and $[Fe(OH_2)_6]^{2+}$, has the larger pK_a? Briefly explain why.

Marks
2

- Consider the compound $[CrCl(OH_2)_4(NCS)]Cl{\cdot}2H_2O$.

3

What is the oxidation state of the transition metal ion?

What is the coordination number of the transition metal ion?

How many *d*-electrons in the transition metal ion?

List all the ligand donor atoms.

- Consider the complexes *cis*-$[PtCl_2(NH_3)_2]$ and *trans*-$[PtCl_2(NH_3)_2]$. Draw the structures of the two isomers, clearly illustrating the stereochemistry.

3

Briefly suggest why *cis*-$[PtCl_2(NH_3)_2]$ is an effective anti-cancer drug, but *trans*-$[PtCl_2(NH_3)_2]$ is not.

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of V^{3+}. **1**

Marks 3

- Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

Formula	$K_3[Fe(CN)_6]$	$[Cu(NH_3)_4(H_2O)_2](NO_3)_2$	*cis*-$[CrCl_2(en)_2]Cl$
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Species formed upon dissolving in water			

- What is a chelate ligand?

Marks
4

Draw all possible isomers of $[CoCl_2(en)_2]$. en = ethylenediamine = $NH_2CH_2CH_2NH_2$

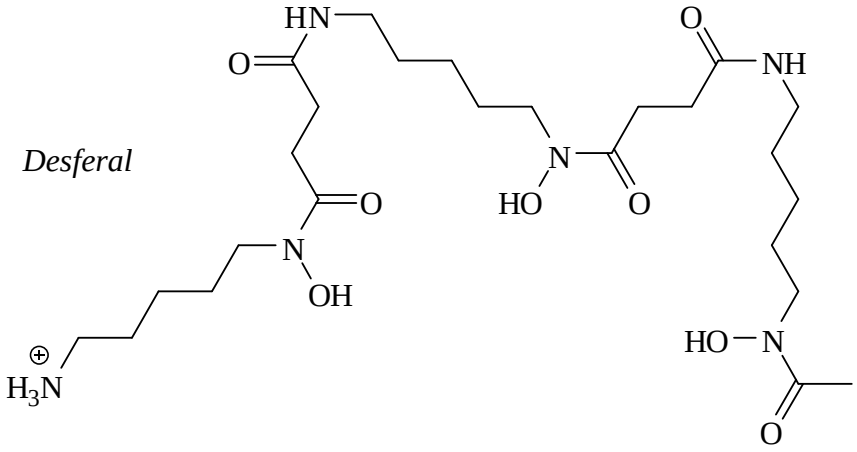
- Explain briefly why the $[Fe(H_2O)_6]^{3+}$ cation has a K_a of 6×10^{-3} M, whilst the $[Fe(H_2O)_6]^{2+}$ cation has a K_a of 4×10^{-9} M.

2

Marks 3

- Hemochromatosis or "iron overload" is a potentially fatal disorder in which excess iron is deposited in the bodily organs as insoluble hydrated iron(III) oxide. It can be treated by administration of desferioxamine B (*Desferal*), a natural substance isolated from fungi.

Desferal



Desferal is taken over 8-12 hour periods up to six times per week. A value of log K = 30.6 is associated with the following equilibrium:

$$Fe^{3+} + LH_3^{+} \rightleftharpoons FeL^{+} + 3H^{+} \qquad \text{where } LH_3^{+} = \textit{Desferal}$$

Briefly describe the chemical basis for the use of *Desferal* in iron overload therapy.

Marks
3

- Consider the compound with formula $[CoCl_2(NH_3)_4]Br \cdot 2H_2O$.

  Write the formula of the complex ion.

  Write the symbols of the ligand donor atoms.

  What is the *d* electron configuration of the metal ion in this complex?

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Cu^{2+}. **2**

- Complete the following table. **6**

Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of *d*-electrons in the transition metal	Species formed upon dissolving in water
$Na_2[CoCl_4]$				
$[Ni(NH_3)_5(H_2O)]SO_4$				
$[Cr(en)_3]Br_3$				

en = ethylenediamine = $NH_2CH_2CH_2NH_2$