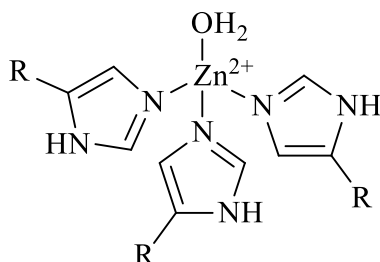


- The structure below represents the active site in carbonic anhydrase, which features a Zn^{2+} ion bonded to 3 histidine residues and a water molecule.



The $\text{p}K_{\text{a}}$ of uncoordinated water is 15.7, but the $\text{p}K_{\text{a}}$ of the water ligand in carbonic anhydrase is around 7. Suggest an explanation for this large change.

The high charge on the Zn^{2+} ion draws electron density out of the O–H bonds in the water molecule. This weakens the O–H so the H^+ is more likely to leave.

The water in carbonic anhydrase is therefore more acidic, as shown by the large decrease in $\text{p}K_{\text{a}}$.

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.

Zn^{2+} , $3d^{10}$

Co^{2+} , $3d^7$

↑↓	↑↓	↑↓	↑↓	↑↓
↑↓	↑↓	↑	↑	↑

Zn^{2+} has 0 unpaired d electrons, Co^{2+} has 3 unpaired d electrons. Co^{2+} is therefore paramagnetic and will be attracted by a magnetic field.

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

The ions have similar radii so the properties of natural carbonic anhydrase and the version with cobalt replacing zinc should have similar biological properties. The unpaired electrons on Co^{2+} however mean that it is paramagnetic and the magnetism can be used to study the active site.

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

Zinc only forms +2 ions but cobalt forms +2 and +3. The cobalt-containing enzyme may be susceptible to oxidation.

Zn^{2+} tends to form 4-coordinate tetrahedral complexes but Co^{2+} is slightly larger and often forms 6-coordinate octahedral complexes. The metal ion may change its coordination by bonding extra ligands.

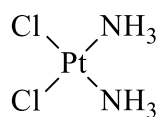
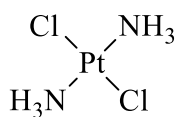
Marks
8

- 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	+III	+II
Number of <i>d</i> -electrons in the transition metal ion	3	5	10
Number of unpaired <i>d</i> -electrons in the transition metal ion	3	5	0
Charge of complex (<i>i.e.</i> <i>n</i>)	1+	3-	0
Is the metal atom paramagnetic?	Yes	Yes	No

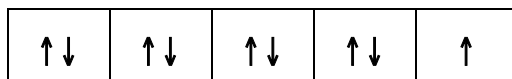
The complex $[PtCl_2(NH_3)_2]$ has two isomers, while its zinc analogue (in the table) exists in only one form. Using diagrams where appropriate, explain why this is so.

The Pt compound has square planar geometry and hence 2 isomers, where the Cl groups are either opposite each other (*trans*) or next to each other (*cis*). The Zn compound has tetrahedral geometry and hence only one structure exists

*cis*-isomer*trans*-isomer

2

- 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+} .

 Cu^{2+} is d^9 

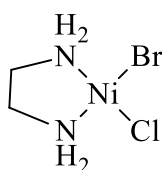
is paramagnetic

4

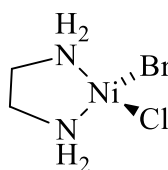
- Provide a systematic name for the complex $[\text{NiBrCl}(\text{en})]$ and draw both of its possible structures. (en = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ = ethylenediamine = ethane-1,2-diamine)

Both of the following names are acceptable:

- bromidochlorido(ethylenediamine)nickel(II)**
- bromidochlorido(ethane-1,2-diamine)nickel(II)**



square planar



tetrahedral

Is either complex chiral? Explain your reasoning.

No. Both structures are superimposable on (*i.e.* identical to) their mirror images.

• Complete the following table. (ox = oxalate = $C_2O_4^{2-}$)				Marks 6
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	+III	+III	+V	
Coordination number of transition metal ion	4	6	6	
Number of <i>d</i> -electrons in the transition metal ion	5	3	0	
Species formed upon dissolving in water	$Na^+(aq)$, $[FeCl_4]^-(aq)$	$[CrCN(NH_3)_5]^{2+}(aq)$, $Br^-(aq)$	$K^+(aq)$, $[VO_2(ox)_2]^{3-}(aq)$	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

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



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

K_1 must be greater than K_2 for the therapy to be effective.

$[\text{Ca}^{2+}]$ is much greater than $[\text{Pb}^{2+}]$ in the body, so need $K_1 > K_2$ to form the Pb complex. If EDTA is not administered as the Ca complex, it will strip Ca^{2+} from the body.