

- Transition metals are often found in coordination complexes such as  $[\text{NiCl}_4]^{2-}$ . What is a complex?

**A complex contains a metal cation surrounded by ligands which bond to the cation using one or more lone pairs. The complex can be positive, negative or neutral depending on the charges on the metal and ligands.**

How does the bonding in the complex  $[\text{NiCl}_4]^{2-}$  differ from the bonding in  $\text{CCl}_4$ ?

**In  $\text{CCl}_4$ , the C-Cl bonds are polar covalent; each involves the sharing of 1 electron from C and 1 electron from Cl to make a 2 electron bond.**

**In  $[\text{NiCl}_4]^{2-}$ , the Ni-Cl bonds also involve 2 electrons. However, both originate on the Cl ion which donates a lone pair to the  $\text{Ni}^{2+}$  ion to make the bond. This type of bond is sometimes called a 'dative' or 'coordinate' bond.**

What is a chelate complex?

**Some ligands have more than one atom with a lone pair and can bond to a metal ion more than once. An example of this type of ligand is ethylenediamine (en) which has the formula  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ . As there is a lone pair on each of the N atoms, it can bond twice to a metal ion.**

**Complexes containing ligands which do this are called chelate complexes.**

Why is a chelate complex generally more stable than a comparable complex without chelate ligands?

**When a chelate ligand bonds to a metal ion, it releases other ligands: if the chelate can bond twice to a metal ion, it will release two ligands and if the chelate can bond three times to a metal ion, it will release three ligands.**

**If the bond strengths are similar, the enthalpy change is small. However, the release of ligands increases the entropy of the system and this favours the formation of the chelate complex.**

**For example, en can bond twice to a metal ion so in the reaction below, it can replace  $2\text{NH}_3$  ligands:**

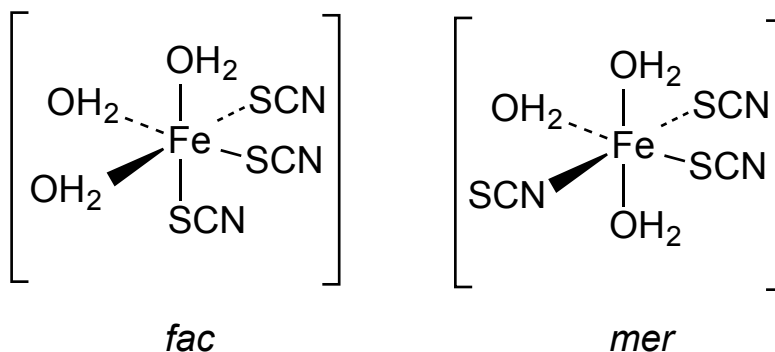


**The reaction involves breaking 2 Ni-N bonds and making 2 Ni-N bonds, so the enthalpy change is small. There are 2 reactant molecules and 3 product molecules so the entropy has increased.**

- An aqueous solution of iron(III) nitrate is pale yellow/brown. Upon addition of three mole equivalents of potassium thiocyanate (KSCN) a bright red colour develops. Draw the metal complex responsible for the red colour, including any stereoisomers.

**Thiocyanate,  $\text{SCN}^-$ , has a lone pair on both the S and N ends and so can form Fe-SCN and Fe-NCS complexes, which are linkage isomers.**

**$\text{Fe}^{3+}(\text{aq})$  contains octahedral  $[\text{Fe}(\text{OH}_2)_6]^{3+}$  ions and addition of 3  $\text{SCN}^-$  will lead to  $[\text{Fe}(\text{OH}_2)_3(\text{SCN})_3]$ . There are 2 possible stereoisomers (i.e. ignoring possible linkage isomers):**



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

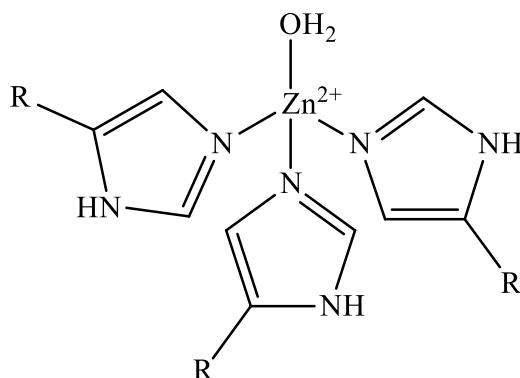
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**Cobalt is in group 9 so  $\text{Co}^{2+}$  has  $(9 - 2) = 7$  valence electrons: its configuration is  $3d^7$ . These electrons occupy the five  $3d$  orbitals according to Hund's rule to minimise electron – electron repulsion.**



**It has 3 unpaired electrons and so it is paramagnetic.**

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



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

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

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

When studying zinc-containing metalloenzymes such as this, chemists often replace  $\text{Zn}^{2+}$  with  $\text{Co}^{2+}$  because of their different magnetic properties. Predict which of these species, if either, is attracted by a magnetic field. Explain your reasoning.

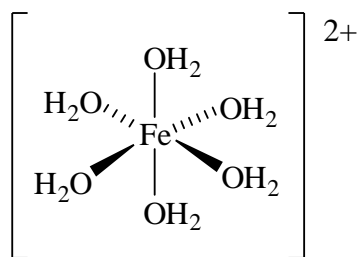
$\text{Zn}^{2+}, 3d^{10}$

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

↑↓	↑↓	↑↓	↑↓	↑↓
↑↓	↑↓	↑	↑	↑

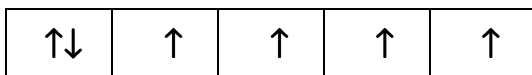
**$\text{Zn}^{2+}$  has 0 unpaired  $d$  electrons,  $\text{Co}^{2+}$  has 3 unpaired  $d$  electrons.  $\text{Co}^{2+}$  is therefore paramagnetic and will be attracted by a magnetic field.**

- Dissolution of iron(II) chloride in water leads to formation of  $\text{Fe}^{2+}(\text{aq})$  and  $\text{Cl}^{-}(\text{aq})$  ions. Draw a picture of the complex ion present, clearly showing the stereochemistry and which atoms are bonded to the Fe(II) ion.



This complex is paramagnetic. Using the box notation to represent atomic orbitals, account for this property.

**Fe is in group 8: it has 8 valence electrons.  $\text{Fe}^{2+}$  has lost 2 so has  $(8 - 6) = 2$  electrons:  $d^6$ . These are arranged in the 5 available  $d$  orbitals to maximize the number of unpaired electrons and so minimize the electron – electron repulsion, as shown below.**



**Paramagnetism occurs whenever there are unpaired electrons.**

Solutions containing the  $\text{Fe}^{2+}(\text{aq})$  ion are acidic. Account for this property and write the chemical equation for the reaction that leads to this acidity.

**$\text{Fe}^{2+}$  has a reasonably high charge density and this polarises the Fe–OH<sub>2</sub> bonds. This in turn weakens the O–H bonds and leads to H<sup>+</sup> being released.**

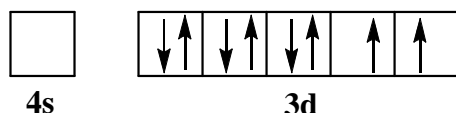


- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of  $\text{Ni}^{2+}$ .

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The Ni atom has the electron configuration  $[\text{Ar}] 4s^2 3d^8$  and the  $\text{Ni}^{2+}$  ion has the configuration  $[\text{Ar}] 3d^8$  as the two electrons are removed from the 4s orbitals.

The electrons in the d-orbitals are arranged to minimize the repulsion between them. This results in two of the electrons being unpaired.



The presence of unpaired electrons leads to paramagnetism.

- Complete the following table.

6

Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of <i>d</i> -electrons in the complex ion	Species formed upon dissolving in water
$\text{K}_3[\text{Mn}(\text{CN})_6]$	<b>III</b>	<b>6</b>	<b>4</b>	$\text{K}^+(\text{aq})$ $[\text{Mn}(\text{CN})_6]^{3-}(\text{aq})$
$[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)](\text{NO}_3)_2$	<b>II</b>	<b>6</b>	<b>6</b>	$[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}(\text{aq})$ $\text{NO}_3^-(\text{aq})$
$[\text{Cr}(\text{en})_3]\text{Cl}_3$	<b>III</b>	<b>6</b>	<b>3</b>	$[\text{Cr}(\text{en})_3]^{3+}(\text{aq})$ $\text{Cl}^-(\text{aq})$

en = ethylenediamine =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

- Complete the following table.

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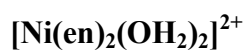
Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of <i>d</i> -electrons in transition metal	Species formed upon dissolving in water
$\text{Na}_2[\text{Ni}(\text{CN})_4]$	<b>II</b>	<b>4</b>	<b>8</b>	<b><math>\text{Na}^+(\text{aq})</math>, <math>[\text{Ni}(\text{CN})_4]^{2-}(\text{aq})</math></b>
$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	<b>III</b>	<b>6</b>	<b>3</b>	<b><math>[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{aq})</math>, <math>\text{Cl}^-(\text{aq})</math></b>
$[\text{Cu}(\text{en})_3]\text{Br}_2$	<b>II</b>	<b>6</b>	<b>9</b>	<b><math>[\text{Cu}(\text{en})_3]^{2+}(\text{aq})</math>, <math>\text{Br}^-(\text{aq})</math></b>

en = ethylenediamine =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

- Consider the compound with formula  $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ .  
(en = ethylenediamine =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ).

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Write the formula of the complex ion.



Write the symbols of the ligand donor atoms.

**N ( × 4 ) and O ( × 2 )**What is the *d* electron configuration of the metal ion in this complex? **$\text{Ni}^{2+}: 3d^8$**



**Marks**  
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- Explain in terms of their electronic configurations and trends in ionisation energies across a period why the alkali metals (Group 1) are powerful *reducing* agents.

**Ionisation energies increase across a period in the periodic table because the increasing nuclear charge holds the electrons more tightly. Hence, in any period, the Group 1 element is the one that most easily loses its electron (from the *s* subshell).**

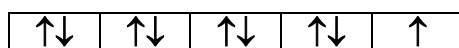
**This electron is then available to reduce another species.**

**2**

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

**$\text{Cu}^{2+}$  has the electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$  (or  $[\text{Ar}] 3d^9$ ).**

**Hence as it has an odd number of electrons, the  $\text{Cu}^{2+}$  ion has an unpaired electron and must therefore be paramagnetic. The nine electrons occupy the  $3d$  orbitals with the arrangement:**



**6**

- Complete the following table.

Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of <i>d</i> -electrons in metal in complex ion	Species formed upon dissolving in water
$\text{K}_2[\text{Ni}(\text{CN})_4]$	<b>II</b>	<b>4</b>	<b>8</b>	$\text{K}^+(\text{aq}), [\text{Ni}(\text{CN})_4]^{2-}(\text{aq})$
$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	<b>III</b>	<b>6</b>	<b>3</b>	$[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{aq}), \text{Cl}^-(\text{aq})$
$[\text{Co}(\text{en})_3]\text{Br}_3$	<b>III</b>	<b>6</b>	<b>6</b>	$[\text{Co}(\text{en})_3]^{3+}(\text{aq}), \text{Br}^-(\text{aq})$

en = ethylenediamine =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$