

- 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 CCl_4 ?

In 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 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 2NH_3 ligands:



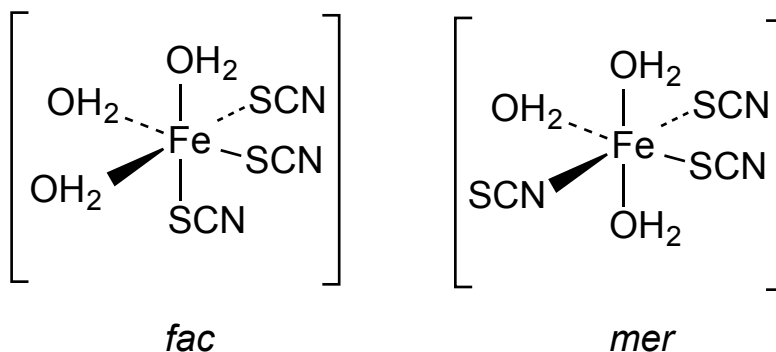
The reaction involves breaking 2 Ni-N bonds and making 2 Ni-N bonds, so the enthalpy change is small. There are 2 reactant molecules and 3 product molecules so the entropy has increased.

Marks
2

- 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, 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.

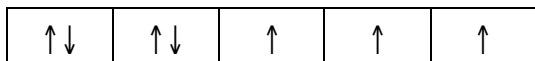
$\text{Fe}^{3+}(\text{aq})$ contains octahedral $[\text{Fe}(\text{OH}_2)_6]^{3+}$ ions and addition of 3 SCN^- will lead to $[\text{Fe}(\text{OH}_2)_3(\text{SCN})_3]$. There are 2 possible stereoisomers (i.e. ignoring possible linkage isomers):



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

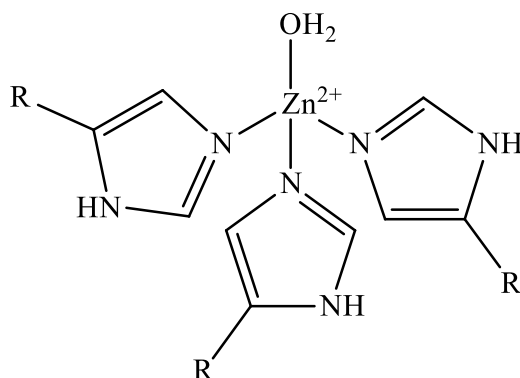
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Cobalt is in group 9 so Co^{2+} has $(9 - 2) = 7$ valence electrons: its configuration is $3d^7$. These electrons occupy the five $3d$ orbitals according to Hund's rule to minimise electron – electron repulsion.



It has 3 unpaired electrons and so it is paramagnetic.

- The structure below represents the active site in carbonic anhydrase, which features a Zn^{2+} ion bonded to three 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 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 such as this, chemists often replace Zn^{2+} with Co^{2+} because of their different magnetic properties. Predict which of these species, if either, is attracted by a magnetic field. Explain your reasoning.

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

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

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$

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.

Marks
4

- The nickel(II) ion exists as the $[\text{Ni}(\text{OH}_2)_6]^{2+}$ complex ion in aqueous solution. Define the term complex.

A complex is a species that consists of a central metal ion which acts as a Lewis acid surrounded by a number of ligands that act as Lewis bases. The charge on the complex may be positive, negative or neutral depending on the charge on the cation and the number and charge of all the ligands.

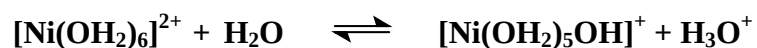
What is the name of this complex ion?

hexaaquanickel(II) ion

Why is such a solution acidic?

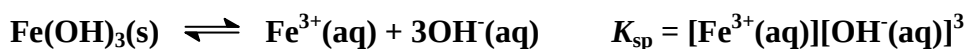
H_2O donates a lone pair to form a coordinate bond to Ni^{2+} . The pull of the cation on these electrons weakens the O–H bonds as the oxygen has to pull electron density from these bonds.

Write a balanced equation for the corresponding reaction.



- The K_{sp} of $\text{Fe}(\text{OH})_3$ is $2.0 \times 10^{-39} \text{ M}^4$. What is the solubility of $\text{Fe}(\text{OH})_3$ in g L^{-1} ?

The solubility equilibrium and constant for the dissolution of $\text{Fe}(\text{OH})_3$ are:



If S moles of $\text{Fe}(\text{OH})_3$ dissolve, S mol of $\text{Fe}^{3+}(\text{aq})$ and $3S$ mol of $\text{OH}^{-}(\text{aq})$ are formed. Thus,

$$K_{sp} = (S) \times (3S)^3 = 27S^4 = 2.0 \times 10^{-39}$$

$$S = 9.3 \times 10^{-11} \text{ M}$$

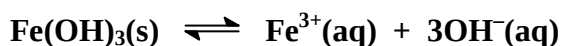
The formula mass of $\text{Fe}(\text{OH})_3$ is $(55.85 (\text{Fe}) + 3 \times (16.00 (\text{O}) + 1.008 (\text{H}))) \text{ g mol}^{-1} = 106.874 \text{ g mol}^{-1}$. Thus, as $9.3 \times 10^{-11} \text{ mol}$ dissolves in 1.0 L , the mass which dissolves in 1.0 L is:

$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{formula mass} \\ &= (9.3 \times 10^{-11} \text{ mol}) \times 106.874 \text{ g mol}^{-1} = 9.9 \times 10^{-9} \text{ g} \end{aligned}$$

Answer: $9.9 \times 10^{-9} \text{ g L}^{-1}$

What effect does lowering the pH have on the solubility of $\text{Fe}(\text{OH})_3$? Explain your answer.

The equilibrium for the reaction:



lies to the left. Addition of H^{+} removes the OH^{-} and hence, from Le Chatelier's principle more $\text{Fe}(\text{OH})_3(\text{s})$ will dissolve.

Hence, lowering the pH will increase the solubility.