

Complex Ion Reactions

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We are now going to look at the reactions (and colours) of complex ions. There are two main reactions: **ligand substitution (exchange)** and **deprotonation (precipitation)**.

Ligand Substitution

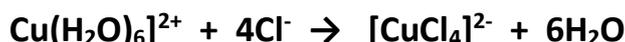
In a ligand exchange reaction, you simply swap one or more ligands in a complex ion for something else. You can get complete or partial substitution.

Complete substitution:

Monodentate ligands



All we have done is swap **all** the waters for **all** the ammonias. Both are neutral ligands so the overall charge doesn't change.

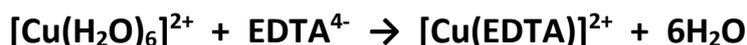


In this example we are adding chloro ligands to an octahedral complex. Cl^- is provided by HCl usually.

We mentioned in the previous part of the tutorial that you can only fit four chloro atoms around a metal due to their greater size. This means that there is a **change in shape** to tetrahedral.

- ✓ This is still complete substitution, as all the waters have been removed, even although we have only added four chloro atoms.
- ✓ Also note the change in charge on the complex.

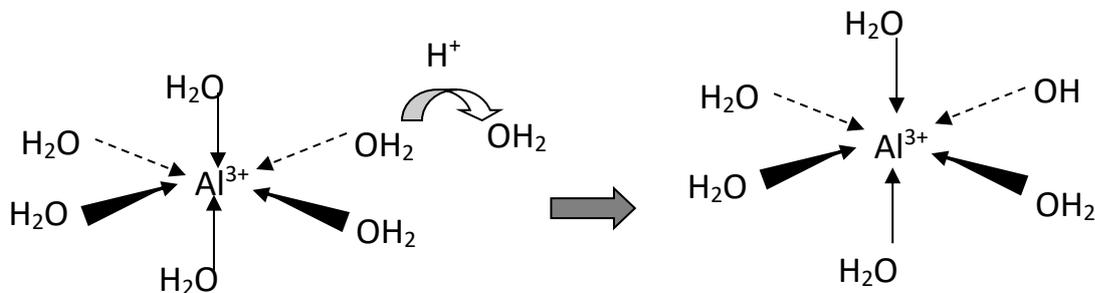
Multi or bidentate ligands



The above example is very common. We only need **one** EDTA molecule to **replace all 6 H_2O molecules**.

Entropy

An important point... in the above reaction there is an **increase in entropy (system)** and the resulting EDTA complex is therefore very stable. This usually occurs when you swap monodentate ligands for bidentate or multidentate.



- There is a slight difference in the acidity of the solution formed between a 2+ and a 3+ complex → the **3+** complex produces a **more acidic** solution. This is due to the higher charge, meaning that the O-H bond in the ligand is **more polarised** i.e. stronger δ^+ and δ^- , therefore it is easier to lose an H^+ .

Complex ion reactions and colours

Ok...I'll be honest with you. This is the *vital* part of the transition metal complex coming up, if there is one part to be an **absolute boss** at...then this is it!

If you can understand what is going on here, write out equations or each reaction and know the colours then you've cracked it.

The 4 ions looked at are **Fe²⁺**, **Fe³⁺**, **Cu²⁺** and **Al³⁺**

- we will look at this table in depth below. Remember the two main reactions: **deprotonation** and **ligand substitution/exchange**. There is **no redox** going on in the table below:

Complex	Few drops NaOH or NH ₃	excess NaOH	excess NH ₃	Na ₂ CO ₃
[Fe(H ₂ O) ₆] ²⁺ pale green	Dirty green ppt Fe(H ₂ O) ₄ (OH) ₂	No reaction	No reaction	Green ppt FeCO ₃
[Al(H ₂ O) ₆] ³⁺ colourless	White ppt Al(H ₂ O) ₃ (OH) ₃	Colourless soln [Al(OH) ₆] ³⁻	No reaction	White ppt Al(H ₂ O) ₃ (OH) ₃
[Fe(H ₂ O) ₆] ³⁺ yellow	brown ppt Fe(H ₂ O) ₃ (OH) ₃	No reaction	No reaction	Brown ppt Fe(H ₂ O) ₃ (OH) ₃
[Cu(H ₂ O) ₆] ²⁺ blue	pale blue ppt Cu(H ₂ O) ₄ (OH) ₂	No reaction	Deep blue soln [Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺	Green/blue ppt CuCO ₃

- ✓ watch out for the $[\text{Al}(\text{OH})_6]^{3-}$ complex. I've seen it written as $[\text{Al}(\text{OH})_4]^-$. You can use either.
- ✓ the precipitates can be written as, for example, $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3$ or $\text{Cr}(\text{OH})_3$
- ✓ watch out for $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ by air oxidation. It is usually the precipitate they refer to and a green \rightarrow red/brown colour change.
- ✓ note that a small amount of NaOH and NH_3 do the same thing but when added in excess they react very differently.

We will now look at each column in this table in more detail.

Reaction 1: precipitate formation (a few drops of base)

- ✓ the starting point for all these reactions is the metal ion with 6 water ligands around it.

To get the precipitate we add a base: either **NH_3** or **NaOH** (they are both acting as bases).

when a small amount of base is added to a complex ion, a **precipitate** (a solid) forms

To form the precipitate the complex must **lose the charge** and become **neutral**. When the complex is neutral, it no longer stays in solution and a precipitate forms. This is **deprotonation**.

Example



Alternatively if we add NH_3 as the base:



- ✓ We get the **same** precipitate. The only difference is the **NH_4^+** formed instead of H_2O .
- ✓ To go from 2+ to neutral we are removing 2 x H^+ . And similarly, to go from 3+ to neutral we are removing 3 x H^+ . So the products formed are either $(\text{OH})_2$ or $(\text{OH})_3$. Very easy.

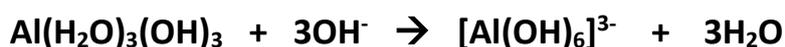
Reaction 2: redissolving the precipitate

We will still use NaOH and NH₃ but now there is a **difference** in how they react:

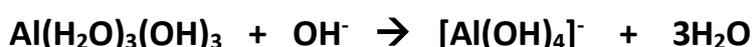
adding excess NaOH is further **deprotonation**. Adding excess NH₃ results in **ligand substitution**

Adding excess NaOH

The good news is, only the Al precipitate reacts, so there is not much to remember.



or



- ✓ Al(H₂O)₃(OH)₃ is said to be **amphoteric** i.e. reacts with acid or base. The other precipitates in the above table **do not** redissolve with NaOH.
- ✓ to go from the precipitate back to the original complex can be done by adding acid. **All** the precipitates do this reaction e.g.



Adding excess NH₃

When adding ammonia to a precipitate, only the Cu precipitate redissolves. This just a **ligand substitution** reaction:



Reaction 3: addition of carbonate

Two different **precipitates** are possible when adding carbonate to the complex ions.

If the complex has a **2+ charge** → **carbonate**

If the complex has a **3+ charge** → original **hydroxide precipitate**

Carbonate precipitate



- ✓ the precipitate forms and it appears that the water ligands have been substituted.

Hydroxide precipitate



- ✓ this can be classed as an **acid-base reaction**.

Different products?

The difference in products between the 2+ and 3+ complexes above is due to the **charge**. The higher 3+ charge ensures that the complexes are **acidic** enough to **react with bases** (as shown above), whereas the 2+ complexes are not acidic enough to do similarly.

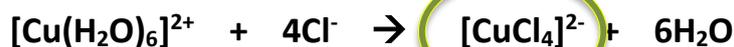
The difference in acidity is because the higher charge on the metal ion polarises the H₂O molecules enabling an H⁺ ion to be lost. Think of **charge density** (charge/size):

High charge and small size = higher polarising effect

Addition of HCl

The point of adding HCl is to provide Cl⁻ ions/ligands. You only need to know about Cu with Cl⁻ ligands.

Cu



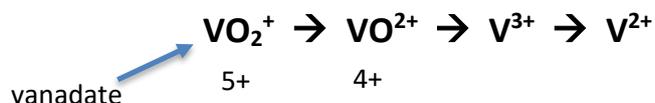
Yellow/green complex

- ✓ note the change from octahedral to tetrahedral. This would also apply to other ions such as Co²⁺ or Fe³⁺ (but different colours that you don't need to know).

Random points from the specification

There are a few points mentioned in the specification that seem a bit on their own so I'll address them here.

1. They mention that *zinc can reduce various vanadium species* (under acidic conditions):



- ✓ Zinc is a good reducing agent as are other metals so Zn gets oxidised to Zn^{2+} . I suppose you could write out half-equations if you really wanted to.
- ✓ I wouldn't bother with colours here. They are not mentioned in the specification.

Other than the above I am not sure what they want you to do with this knowledge!

2. They mention that the *redox potential of a transition metal changing from a higher to lower oxidation state is influenced by pH and the ligand*.

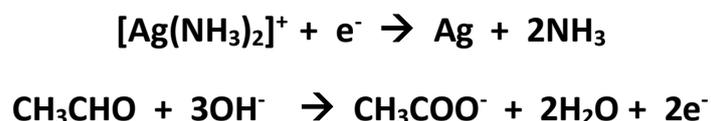
This feels like a statement more than anything else. You can view the phrase "redox potential" as the "likeliness" i.e. how likely it is that the transition metal will change oxidation state is related to the pH of the solution and the ligand in the complex.

3. Tollen's Reagent

We mentioned earlier that Ag^+ complexes are linear and that Tollen's reagent was a good example of this. You can write out half-equations to show what is going on.

They call it the "silver mirror" test, which just means that silver is formed i.e. $\text{Ag}^+ \rightarrow \text{Ag}$ (reduction). And you are reacting it with an aldehyde, which gets oxidised \rightarrow **carboxylic acid salt**.

- ✓ It is done under alkaline conditions which makes the aldehyde half-equation a bit difficult. You probably won't need it but here it is:



- ✓ If you want some more on balancing alkaline half-equations I have included this in the OCR A tutorials as they have been asked this quite a few times. [Click here](#) if you want to read more on this.

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