Problem 9 Simple experiments with copper(II) chloride

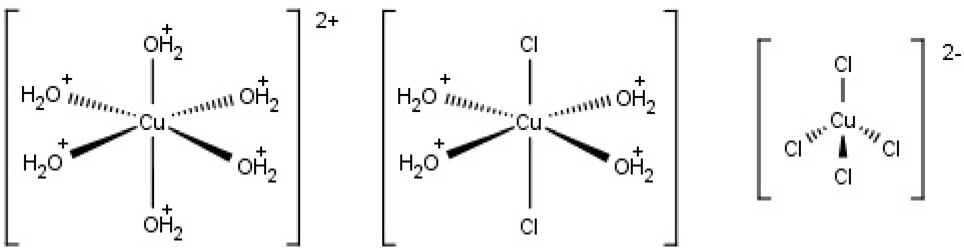
Copper(II) chloride forms brown crystals soluble in water.

1. *The color of the solutions depends on concentration. Explain this fact.*
2. *Draw the structure of at least three copper containing species that can be present in the solution.*
3. *To the aliquots of the copper chloride(II) solution in the test tubes (a) zinc powder and the solutions of (b) sodium iodide, (c) sodium nitrate, (d) sodium sulfide were added dropwise. What changes happen if they are? Provide equations. In what cases copper is completely or partly reduced?*
4. *Suggest a synthetic route to copper chloride(II) starting from copper(II) sulfate aqueous solution.*

Solution

1. Copper(II) gives coordination complexes with water molecules and chloride.
These coordination complexes have two different colors, light blue and green.
This depends on crystal-field splitting parameter: according to the spectrochemical series, H_2O produces a larger split on copper's d orbitals than Cl^- and for this reason $[Cu(H_2O)_6]^{2+}$ is light blue and $[CuCl_4]^{2-}$ is green (larger Δ_{oct} means higher energy and lower wavelength).
When we start to dissolve the salt, $[Cl^-]$ is extremely lower than $[H_2O]$ and the only complex in the solution is $[Cu(H_2O)_6]^{2+}$ that has a light blue color.
When the concentration of chloride increases enough, Cl^- replaces some water molecules and generates new types of complexes.
At the end, when $[Cl^-]$ is very high, Cu^{2+} is completely complexed by chloride and gives $[CuCl_4]^{2-}$ green.

2. Three copper containing species that can be present in the solution are:



The first one is the complex that copper makes with water.
The second one is a mixed complex between copper, water and some chloride.
The last one is the complex of copper and chloride.

3. a). When we add zinc powder, this reaction takes place: $Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+}$.
This happens because Zn has lower standard reduction potential than Cu.

b). NaI reacts with Cu^{2+} and Zn^{2+} and gives:

$2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI_2 \rightarrow 2\ CuI + I_2$ and

$Zn^{2+} + 2\ I^- \rightarrow ZnI_2$.

The I_2 formed in the first reaction can oxidate Cu^0 and Zn^0 because it has higher standard reduction potential (I_2/I^- = 0,54 V; Cu^{2+}/Cu^0 = 0,34 V; Zn^{2+}/Zn^0 = -0,76 V).
The favorite equation is $Zn^0 + I_2 \rightarrow Zn^{2+} + 2\ I^-$ because ΔG^0 is proportional to $-\Delta E^0$ but the copper formed by the equation at point a. is oxidated by I_2 and reacts with I^-.
At the equilibrium we'll find CuI crystals and ZnI_2 crystals. Here copper is reduced to copper(I).

c) . Adding $NaNO_3$ to the solution increases the ionic force.
$NaNO_3$ don't react with any species and nitrate don't give an insoluble salt that precipitates.

There isn't particular changes in the solution. Here, copper is completely reduced by zinc powder.

d. NaS contributes to reduce Cu^{2+}.
The couple ZnS/Zn^0 has a standard potential reduction of -1,44 V.
This means that takes place the $Zn^0 + S^{2-} + Cu^{2+} \rightarrow ZnS + Cu^0$ because $\Delta E^0 > 0$.
In this case, copper is completely and quickly reduced.

4. **First method**: Add $BaCl_2$ on the solution, $BaSO_4$ will precipitate and can be removed. Then we'll evaporate the solvent to obtain $CuCl_2$.

Second method: Add $NaHCO_3$ to the dissolved $CuSO_4$ to obtain a precipitate of $CuCO_3$. Dissolve this in HCl then evaporate the solution to obtain $CuCl_2$.

Solution proposed by
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