Synthesis of Hexaammine Cobalt(III) Chloride

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**Introduction**

The purpose of this experiment was to synthesize a 6-coordinate cobalt(III) compound from $CoCl_2 \cdot 6H_2O$. This is made difficult by the fact that Co^{2+} ion is more stable than Co^{3+} for simple salts. There are only a few salts of cobalt(III), such as CoF_3, that are known. However, cobalt(III) can be made stable when in octahedrally coordinated compounds..

Originally, it was questioned whether the chlorine atoms in hexaammine cobalt(III) chloride were coordinated or ionic. It has since been determined that the chlorine atoms are indeed ionic. There are many ways to ascertain this, the most successful of which is to complex the cobalt iodometrically and titrate the liberated iodine with sodium thiosulfate solution.

A difficulty in this experiment is the oxidation of cobalt(II) to cobalt(III). This could be accomplished through the addition of hydrogen peroxide, but this method is not suitable for this experiment. A more suitable method is the air oxidation of cobalt with carbon as a catalyst. An additional benefit of carbon as a catalyst is its ability to shift the equilibrium in favor of the desired product.

Theory

As was indicated in the introduction, cobalt(II) is oxidized to cobalt(III) via the following reaction:

$$CoCl_2 \cdot 6H_2O + 5NH_3 + NH_4Cl \rightleftharpoons [Co(NH_3)_6]Cl_3 + 6H_2O + H^+ \qquad (1)$$
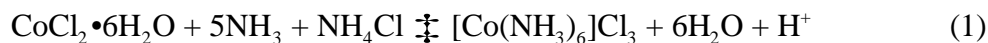
in the presence of air and carbon. The UV-Visible spectrum may then be used to judge the quality of the product.

Experimental

A vacuum filtration apparatus was assembled and connected. 6.0065 g of $CoCl_2 \cdot 6H_2O$ was massed and placed into a 150 mL beaker. Then, 4.0164 g of NH_4Cl was massed and added to the 150 mL beaker. To this beaker was added 5 mL nanopure water, and the solution was stirred until most of the crystals dissolved. This solution was a dark red-purple color. Next, 13.0 mL of concentrated ammonia was added to the beaker. This caused the color to change from dark purple to a brighter red. After time, it appeared that there were two layers: one dark purple and another the brighter red color. The contents of the 150 mL beaker were then transferred to a 125 mL sidearm flask and 0.13 g activated carbon was added. A water aspirator was hooked to the 125 mL sidearm and air was passed through the solution in order to oxidize the cobalt. The air was allowed to pass through the solution for 2 1/2 hours, but the cobalt did not appear to be oxidized at that point. Thus, the contents of the sidearm flask were stored for 7 days. After storage, the solution appeared purple in color. This solution was filtered on a Buchner funnel. This filtrate was then added to 40 mL water to which 0.5 mL concentrated HCl had been added. To insure that the solution was acidic, 4 more drops of con. HCl were added. The solution was then heated to 60°C and filtered to remove the decolorizing carbon. To the warm, filtered solution was added 10 mL con. HCl. This was allowed to cool to room temperature. After the HCl was added, orange crystals began to form in the bottom of the beaker to which the solution was transferred. Once this solution had cooled to room temperature, the beaker was placed into an ice bath and allowed to cool to 0°C. Upon cooling, more orange crystals formed. These crystals were filtered on a Buchner funnel and washed with 60% and 95% solutions of ethanol. The orange crystals were then dried

until completely free of water. The contents were saved and the UV-Visible spectrum was taken of a dilute solution of the product.

Results and Discussion

The UV-Visible spectrum of hexaammine cobalt(III) chloride is shown below:
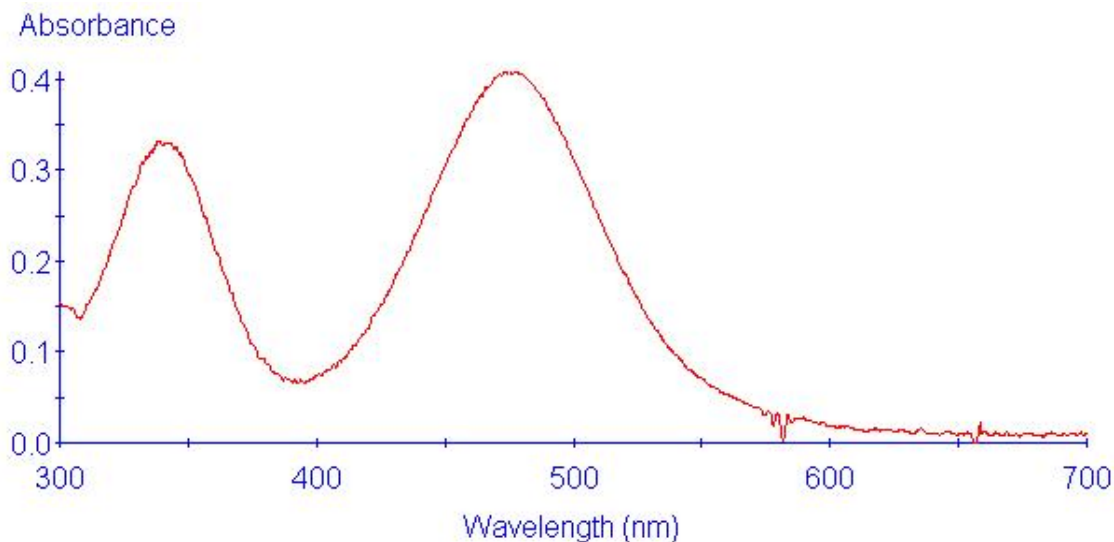
The absorption peak from approximately 400 nm to 600 nm means that the compound absorbs light in the violet-blue-green range. The sum of the non-absorbed, or reflected, wavelengths gives the product is orange color. The two peaks on the spectrum are d-d transitions for the d^6 cobalt complex. Judging by the Tanabe-Sugano diagram for d^6 complexes, the ground state ^5D would be split into a $^5T_{2g}$ and a ^5E_g. The stronger of the two peaks is most likely the transition between these two states. The weaker peak may be a spin-forbidden transition, which can not be accurately predicted. The hexaammine complex is most likely weak field, with four unpaired electrons. Since the ligand NH_3 is of intermediate field strength, this assumption is based on a calculation of *Dq/B* of 1.8 for the complex, which is in the weak field region of the Tanabe-Sugano diagram.

A table of products and reactants is shown below:

Formula	MW	Mass, Vol Used	Moles	Density
$CoCl_2 \bullet 6H_2O$	237.71	6.0065 g	0.02527	
NH_3	17.031	10.02 g, 13.0 mL	0.5873	0.7710 g mL^{-1}
NH_4Cl	52.484	4.0164 g	0.07653	
$[Co(NH_3)_6]Cl_3$	267.48	5.340 g (actual)	0.02000	
		6.760 g (theoretical)	0.02527	

A 79.1% yield of hexaammine cobalt(III) chloride was obtained. This was very reasonable considering the literature stated to expect approximately an 85% yield. If this experiment was to be performed again, a different method of oxidation may be chosen, due to the large amount of time required for air oxidation to be effective.

Reference

G. Pass, H. Sutcliffe (1974), *Practical Inorganic Chemistry,* Chapman and Hall, Ltd: New York. 80-81.

J. Tanaka, S.L. Suib (1999), *Experimental Methods in Inorganic Chemistry,* Prentice Hall: Upper Saddle River, NJ. 272-74.