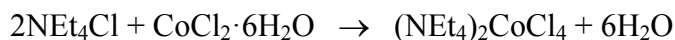


## Chem 151L, Spring 2012

### Expt. 2a. Synthesis of Bis(tetraethylammonium)tetrachlorocobaltate(II)

The tetrahedral tetrachlorocobalt(II) salts are a perfect contrast to the octahedral complexes of cobalt(III). Their preparation utilizes large counter-cations to crystallize the complex from a weakly coordinating solvent.<sup>1</sup> The synthesis of tetrachlorocobaltate(II) salts again begins with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ :



Dissolve 2.6 g  $\text{NEt}_4\text{Cl} \cdot \text{H}_2\text{O}$  in 30 mL absolute ethanol. Slowly add a solution of 1.78 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in 35 mL absolute ethanol. The desired compound crystallizes at this stage as a blue precipitate. Heat the solution to  $\sim 50^\circ\text{C}$ , adding more ethanol if necessary to obtain a clear solution. Slowly cool to crystallize the compound as deep blue crystals. Collect the crystals with a sintered glass filter (a Buchner funnel is alright but use two pieces of filter paper). Analyze the product by IR and UV-Vis (prepare 8 mg in 25 mL spectroscopy, calculate the extinction coefficient of the complex and the percent yield).

#### Questions:

- 1) Determine the spectrochemical series for the ligands used in this experiment. How does this compare with crystal field theory?
- 2) Why is ethanol used instead of water as the solvent?
- 3) Is your product paramagnetic? If so, how many spins are there? What is the calculated magnetic moment?
- 4) How would your UV-Vis spectrum change if  $\text{Br}^-$  were instead the halide ligand?

### Expt. 2b. Determination of the Charge on Hexamminecobalt(III) Chloride

Werner used conductivity and quantitative chemical analysis to determine the coordination of cobalt salts. We will use an ion exchange resin to determine the charge of the hexamminecobalt(III) cation prepared in the previous lab. As the metal complex binds to the resin, an equivalent amount of  $\text{H}^+$  is released according to the charge of the metal complex. Titration with sodium hydroxide allows for determination of the equivalents of proton(s) displaced and in turn the charge of the complex.

Prepare a 15 cm (it will later expand) chromatography column of the resin in a 50 cc burette with a sintered-glass disc (or use glass wool) at the bottom of the burette. The ion exchange resin is in the  $\text{H}^+$  form and soaked in 2 M HCl. Pour the slurry of resin into the tube containing  $\sim 15$  cm of water (helps in packing the resin bed). Take care so

that no air bubbles are trapped. Rinse the column with distilled water until the effluent is just alkaline to methyl orange or litmus paper. The resin is now ready for use.

Dissolve an accurately weighed amount (~ 50 mg) of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  in 2 mL deionized water and load on top of the resin. Allow a constant flow of 3 to 4 mL per minute and begin collecting the effluent. Never allow the level of water to drop below the upper surface of the resin in the column. Continue collecting the effluent until it is neutral to litmus paper.

Titrate the effluent with 0.05 M NaOH solution.  $[\text{Co}(\text{NH}_3)_6]^{3+}$  theoretically displaces 3 equivalents of  $\text{H}^+$  from the resin. Calculate the charge on the cation using the acidity of the effluent (determined by titration) and the weight of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ .

### Questions:

- 1) Why did you use litmus, phenolphthalein and methyl orange indicators?
- 2) What other indicators would have been suitable?

### References

- 1) Gill, N. S.; Taylor, F. B. *Inorg. Syntheses*, **1967**, 9, 136-142 (in library reference section, but a scanned copy is provided on the 151L website).