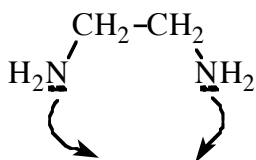


Experiment 8

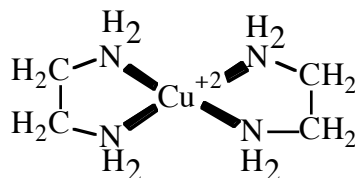
Chelatometric Analysis of the Complex for Cobalt Using EDTA

Discussion

In the formation of many coordination complexes a ligand may occupy more than one coordination position if it contains more than one electron pair donor site. For example, if ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ - abbreviated "en") is used in place of ammonia, the complex with the cupric ion is



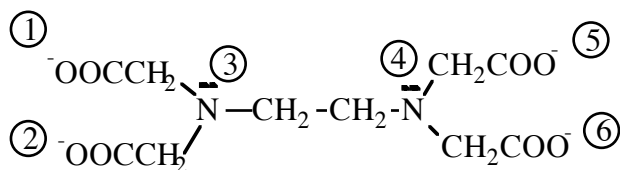
Ethylenediamine



Copper Complex

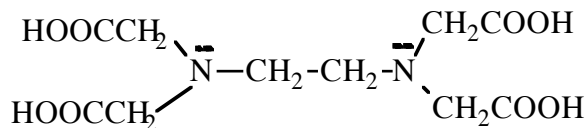
and such complexes are much more stable than those formed with ligands containing but one donor site. Ligands containing 1, 2, 3, ... donor sites are termed mono-, bi-, tridentate, etc., and complexes containing polydentate ligands are **chelates**, the ligands being termed **chelating agents**.

In this experiment we shall use a hexadentate ligand - the ethylenediaminetetraacetate (EDTA) ligand.



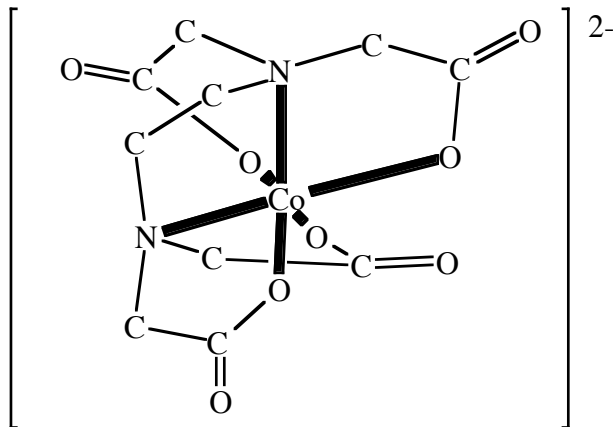
The six donor sites, indicated in the formula, and their positions in the ligand are such that this chelating agent can form stable complex ions with almost all metal ions by occupying all six octahedral sites.

It is important to note that the EDTA ion is a base so that at low pH (high hydrogen ion concentration) it would exist as the acid



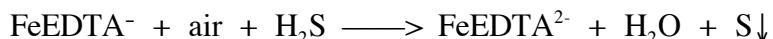
which would be unable to form very stable complexes. For this reason we will carry out the present experiment in an alkaline solution.

Thus with cobalt(II) cation we have



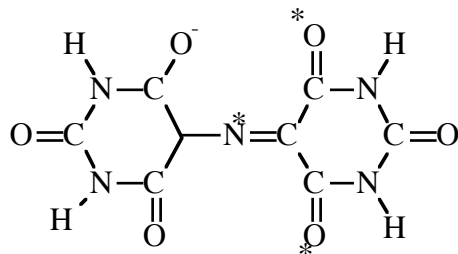
EDTA is widely used in interesting chemical reactions. When administered to a person suffering from lead (Pb^{2+}) poisoning, the EDTA forms a stable complex with the lead ions and the EDTA-Pb complex is excreted as waste.

Chelates such as EDTA can also modify the reactivity of metal ions to speed up oxidation-reduction reactions. Hydrogen sulfide (H_2S - "rotten egg gas") is an extremely poisonous environmental contaminant resulting from the combustion of fossil fuels. The following reaction in an industrial chimney precipitates elemental sulfur.



Principle of Chelatometric Analysis

An organic dye, purpuric acid, whose color depends on the pH of the solution and which forms a weakly bonded colored complex with cobalt ions, will be the end-point indicator for titration. Purpuric acid, represented by the abbreviated symbol, H_5D , readily loses one proton to give the ion called the murexide anion, H_4D^- which in ammoniacal or alkaline solution is deep violet:



Murexide ion (H_4D^-).

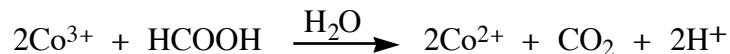
The murexide anion forms a complex with cobalt(II) ions, bonding to the metal by means of the central nitrogen and the two carbonyl groups (indicated by asterisks). At a pH of six or less, the CoH_4D^+ complex is orange, whereas in alkaline solution the metal-murexide complex is yellow. Moreover, the cobalt-murexide complex is less stable than the cobalt-EDTA complex described above. This is essential for the success of the titration.

For the chelatometric analysis, we measure out a known volume of the acidic cobalt solution to be analyzed, dilute this with water, and adjust the pH to about six with aqueous ammonia. Adding murexide indicator forms the orange CoH_4D^+ , and adding additional aqueous ammonia serves for the final adjustment of the pH as indicated by a change to yellow by the metal-murexide complex (probably CoH_2D^- now). Titrating the solution with standard EDTA first complexes the free cobalt ions and then finally complexes the cobalt which was up-to-now complexed by the murexide. The end point is visible by the sharp appearance of a violet color due to the breakdown of the yellow cobalt-murexide complex to the free violet murexide ions.

Procedure

Weigh out accurately about 0.35 g of the dried cobalt complex, place in a 250-mL beaker and add 20 mL of 0.1 M nitric acid. Heat gently to about 70 °C with careful swirling over a low flame (tripod and gauze) to dissolve the salt. Use a thermometer, and rinse the thermometer into the beaker after you observe complete solution. In the hood, add 5 mL of 6M NaOH to the solution of the cobalt salt and heat with careful swirling for 10 minutes just below 100°C. This procedure effects the decomposition of the cobalt complex to cobalt oxide (Co_2O_3) which precipitates out as a black solid. Note the evolution of ammonia as the decomposition proceeds.

Add 8 mL of 6 M nitric acid and then slowly add 8 mL of 90% formic acid. Heat at about 90°C with good stirring for about 25 minutes, during which period carbon dioxide will evolve as a result of the reaction:



Keep the solution from boiling to limit the loss of water. When all CO_2 has evolved, allow the solution to cool and carefully transfer the solution to a 100 mL volumetric flask; rinse the beaker into the flask, make up to volume and mix thoroughly.

Using a pipet, place 10 mL (measured accurately) of this solution in a clean, 250-mL Erlenmeyer flask and add approximately 30 mL of distilled water. Add one drop of methyl red indicator and then carefully add 1 M aqueous ammonia solution (with good swirling) until solution becomes yellow. Add one murexide tablet and swirl to dissolve. Record the **initial** reading and add about 3 mL of the standard EDTA from buret to prevent the precipitation of cobalt hydroxide. Add 5-10 mL more of 1 M aqueous ammonia and quickly titrate the solution with the standard EDTA solution until the color changes sharply from orange-pink to violet. This change will take place somewhat gradually, progressing from orange to pinkish-orange to orange-pink, and then one drop will bring a fairly abrupt change to violet. You can first perform an additional rough titration to get a feel for the amount needed and the colors to expect. Record the buret readings to the nearest 0.01 mL. Repeat on four more 10-mL samples to get consistent results. After standing a few minutes, already titrated solutions might lighten in color or even turn back to orange. This is normal, no cause for concern, and should be ignored. Note the concentration of the standard EDTA solution in your notebook.

Experiment 8 Worksheet – Chelatometric Analysis

Name _____

Date of Experiment: ___/___/___

Report: ___/___/___

Experimental Results from Volumetric Analysis

Average Weight % Co _____ ± _____

Please attach a sheet that shows your complete results and calculations.

Probable identity of compound
as inferred from Volumetric Analysis _____

What is the theoretical % Co in your proposed complex? _____

Calculate the percent yield of your cobalt complex based on your proposed formula. One mole of starting material ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ used in experiment 6), should yield (theoretically) one mole of your complex. From the data in Experiment 6 calculate the **theoretical yield** in moles of your complex. From your postulated formula (based on your results for experiments 7 and 8, calculate this **theoretical** yield of your complex in **grams**. Using your actual yield of complex in grams (from Experiment 6), calculate the percent yield from:

$$\text{Percent Yield} = \frac{\text{Actual Yield (g)}}{\text{Theoretical Yield (g)}} \times 100\%$$

Calculation of % Yield for Expt. 6:

Weight of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ used in Expt. 6 _____ g

Theoretical Yield of your complex _____ g

Actual Yield of your complex _____ g

Percent Yield of your complex _____ %

Any comments on your yield?

