# The Preparation and Analysis of a Coordination Compound of Cobalt(III)

Background

When the 26 year-old Swiss chemist Alfred Werner began his study of the compounds formed by cobalt(III) with aqueous ammonia and chloride ion at the end of the 19th century, very little was understood about the nature of the chemical bonds and molecular geometry of these substances. By 1913 he had been awarded a Nobel prize for his investigations and his theories became the basis for our modern understanding of coordination compounds.
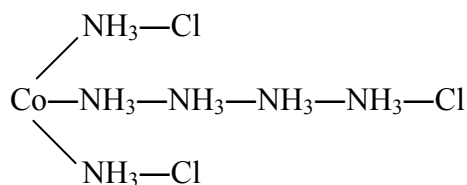
Simply preparing the compounds was an initial challenge. Chemists still face that challenge today whether they are preparing coordination compounds or new biochemicals for clinical trials. Although a large number of "recipes" have been developed for most of the classic coordination compounds, their preparation is often complicated and each step is not always easily explained. Only a few simple compounds of Co(III) exist. The hydrated cation is such a strong oxidizing agent that it reacts with water, liberating oxygen. However, if strongly binding ligands are present the +3 oxidation state is stabilized. For this reason the initial step in synthesizing these coordination compounds is to react aqueous Co(II) with concentrated aqueous ammonia.

With excess ammonia it is possible to form the hexammine complex ion of cobalt(II):

$$[Co(H_2O)_6]^{2+} + (excess)\ NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6\ H_2O$$
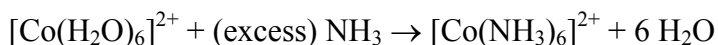
Hydrogen peroxide is then generally used to oxidize the Co(II) to Co(III). For reasons which we will not go into here, it is fairly easy to replace one of the ammonia ligands at this point and various complex ions can be produced by careful addition of different reagents. Chloride salts of these complex cations can then be isolated by taking advantage of their relatively low solubility. Chloride ion itself is a potential ligand, however, and therefore part of the mystery about the structure of the compounds which Werner set out to solve is how to determine what exactly is attached to what (and eventually, how to make sure things go where you want them to go).

One of the early structural theories for coordination compounds was proposed by Blomstrand and Jorgensen. Because they believed that metal ions could only form bonds until their valences were satisfied, they developed a "chain" structure for hexamminecobalt(III) chloride and related compounds in which cobalt made only three bonds and what we now call the ligands were connected in chains:

$$
\begin{array}{c}
\quad\quad NH_3\!\!-\!\!Cl \\
\quad\quad / \\
Co\!\!-\!\!NH_3\!\!-\!\!NH_3\!\!-\!\!NH_3\!\!-\!\!NH_3\!\!-\!\!Cl \\
\quad\quad \backslash \\
\quad\quad NH_3\!\!-\!\!Cl
\end{array}
$$

The fact that the chlorides were not directly connected to the cobalt ion was taken as justification for the immediate precipitation of all three with $AgNO_3$.

In other related structures, some chlorides *were* connected directly to the cobalt because experiment showed that only some of the chloride was directly precipitated from aqueous solution. This puzzling aspect of the compounds eventually became the downfall of the model when a compound was synthesized which contained three chlorides, *none* of which would precipitate with silver nitrate.

Werner himself used terms like "primary valence" and "secondary valence" to describe the combining potential for the central metal ion in complexes. For example, Werner examined a green compound of cobalt(III) containing ammonia and chloride to which had been assigned the formula $CoCl_3 \cdot 4\ NH_3$ [initially formulas for coordination compounds were written like hydrates]. The "primary valence" for the cobalt ion is +3, shown by the three chloride ions in the formula. Today we would call this the *oxidation state* of the cobalt. The "secondary valence" might appear to be 4 but Werner's analysis of the compound suggested otherwise.

Werner performed careful conductivity measurements on this and other related compounds in solution [by 1890 at least four different cobalt(III) compounds with ammonia and chloride had been made, all with different colors!]. He concluded that the total number of ions per mole of $CoCl_3 \cdot 4\ NH_3$ in solution was two moles. When a 1 M solution of the compound was treated with excess silver nitrate, only one mole of AgCl was obtained. This suggested to Werner that not all of the chloride ions were chemically equivalent in the compound.

It was his good fortune to have four related compounds to compare (two of which will be synthesized in this experiment). As he examined his data for the entire set he concluded that the "secondary valence" (what we now call the *coordination number*) had to be six in every case. In other words, six groups (molecules or anions) were always attached to the cobalt ion by bonds which were <u>not</u> ionic. In modern notation the green compound should thus be written $[Co(NH_3)_4Cl_2]Cl$. Werner guessed that the geometry of the ligands around the cobalt ion would have to be octahedral and his subsequent work on isomerism in these types of compounds confirmed that suspicion.

(*one* possible isomer)   OR   OR
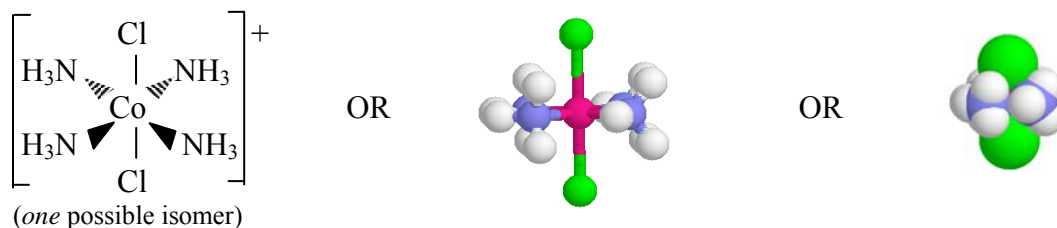
The *coordination complex* (or complex ion) is in the square brackets and the enclosed groups or *ligands* are attached by *coordinate covalent bonds*. The single chloride ion outside the coordination sphere accounts for the single mole of AgCl produced per mole of compound in aqueous solution. It also suggests that the complex ion itself remains intact in solution (i.e., the ligand chlorides are not released simply by dissolving in water) and supports the observation that there is little, if any, free ammonia present in a solution of the compound.

Werner had no ready explanation for the distinct colors of his compounds. Today the colors can be explained by noting that the ligand complement in each ion is different. Ammonia exerts a significantly stronger electrostatic field than does chloride ion and more or less of one in the coordination sphere of the Co^{3+} ion should alter the splitting of the *d*-orbitals which contributes to the color of the complex ion.

The placement of the electrons in the split *d*-orbitals [high or low spin---or in the terminology of the Valence Bond model, *outer* or *inner*] can also be examined today in light of what is known about the magnetic properties of coordination complexes. Faraday first classified substances as *diamagnetic* and *paramagnetic* in the mid-1800's. Diamagnetism is possible in substances with paired electrons in completed levels. It actually arises only in the presence of an external magnetic field and results in a very small repulsion of the applied field.

In contrast, paramagnetism is due to <u>un</u>paired electrons that generate small, permanent magnetic moments in a molecule or ion. These magnetic moments align with an external field, drawing the substance further into it. The paramagnetic effects are many times larger than diamagnetic effects and are diminished only slightly by them [most paramagnetic substances also contain paired electrons in lower completed levels]. Paramagnetism can be detected on reasonably large samples of material with a very strong magnet. In the classic Gouy balance, a sample of solid or solution is suspended from a balance arm and placed between the poles of a very strong magnet. The difference in mass with and without the external magnetic field can be used to determine the *magnetic susceptibility* of the sample and, through a series of calculations and comparisons with standards, the number of unpaired electrons.

Advances in magnetic materials have made it possible to replicate these types of measurements with an ordinary analytical balance and small neodymium magnets. For these measurements the crushed solid sample is placed in an NMR tube and clamped into position above the pan of the balance:
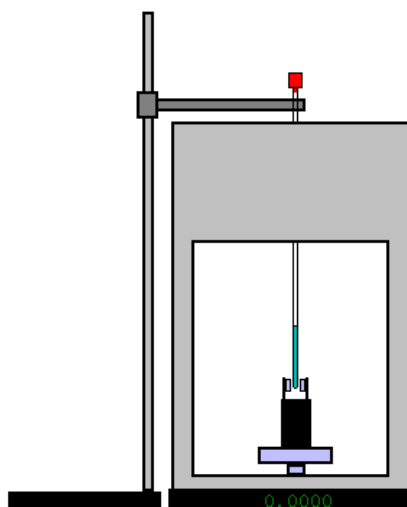
The apparatus resting on the balance pan consists of an ordinary plastic 35 mm film capsule which holds a U-shaped strip of iron and two powerful neodymium disc magnets with a small gap between them. [there is a zinc strip attached to the iron strip at the bottom of the capsule to help inhibit corrosion of the iron]. When the sample tube is clamped in the gap between the magnets the entire apparatus will be weakly attracted to the sample if it is paramagnetic. This will result in an apparent mass <u>decrease</u> for the apparatus on the balance pan. Diamagnetic samples show either a small increase in mass or essentially no change (remember, the diamagnetic effect is much smaller).

The mass change can be used to determine the number of unpaired electrons in the *d*-orbitals in the following way. First, the change (Δm) is divided by the number of moles (n) of compound in the sample (to equalize for different sample sizes):

$$|\Delta m/n| = \text{mass change per mole of compound}$$

The adjusted mass difference is related to the total magnetic moment, μ, by the expression:

$$\mu^2 = k\,|\Delta m/n|$$

where k is a proportionality constant for the apparatus used. The total magnetic moment for various compounds can be found in the literature and if a few measurements are made, k can be determined graphically.

The total magnetic moment, μ, is actually composed of the spin-only magnetic moment, μ_s, and another factor due to spin-orbital coupling, μ_m. This second value is near zero for many first-row transition metal compounds. The spin-only moment, μ_s, is related to the number of unpaired spins, n, in the following way:

$$\mu_s = \sqrt{n(n+2)}$$

Since an experimentally determined μ will always be greater than or equal to μ_s [$\mu = \mu_s + \mu_m$] and it is apparent from a compound formula whether there is an odd or even number of d-electrons present, this simple method allows the determination of the number of unpaired electrons in a central metal ion with a few measurements.

The preparation of one of Werner's compounds presents a significant challenge. Determining the formula of the compound goes several steps beyond. Without such information, however, the possible structures for the four compounds would have remained mysteries. A complete analysis of such a compound might take several directions. For this experiment you will concentrate on the following:

1) the moles of ammonia present in a sample
2) the total moles of chloride ion present a sample
3) the moles of cobalt present in a sample
4) the charge on the complex cation

Taken together this information allows construction of a formula which distinguishes between chloride ligands (if any) and ionic bonded chloride anions, and yields the coordination number of the complex cation.

With the exception of the fourth determination, none of the analyses involve unusual or unique techniques. Although the ammonia ligands are tightly held, they *can* be removed by heating with a strong base such as aqueous NaOH [the displacement of ammonia from a compound by addition of strong base is a classic qualitative test for the presence of ammonia or ammonium ion]. If the mixture is boiled the ammonia will distill off and can be collected in dilute acid. An ordinary acid/base titration can then be used to determine the amount of ammonia liberated from the sample.

During the boiling process described above the coordination compound is destroyed and any other non-volatile ligands go into solution. The Co(III) forms insoluble Co_2O_3 which can be separated by centrifugation. The oxide is soluble in HCl and if excess iodide ion is present it will be oxidized to triiodide ion [while the cobalt(III) is reduced to cobalt(II)] which can be titrated with standardized thiosulfate, using a starch indicator. This allows determination of the amount of cobalt in the sample and thus an approximate molar mass (since there can only be one atom of cobalt in the formula). It also makes possible the final comparison of moles of each component in the sample in order to arrive at a formula for the compound.

The alkaline supernatant solution from the centrifugation contains the complete chloride complement of the coordination compound, i.e., <u>all</u> chloride, regardless of whether it was a ligand or simply the anion in the salt. When the solution is acidified and excess silver nitrate is added, the AgCl precipitate can be collected by centrifugation, washed and dried. With the moles of chloride in the sample determined there is finally sufficient information to determine the formula of the substance.

Determining the distribution of chloride in the compound could be accomplished by dissolving a sample and treating with excess silver nitrate as above. Only the chloride <u>outside</u> the coordination sphere would precipitate immediately. Conductivity measurements could also be made on the solution and, after comparison with some standard solutions, the number of ions present could be determined. A third method (and the one used in this experiment) would be to determine the charge on the complex cation by *ion exchange*.

Ion exchange is a fairly simple process in which a synthetic polymer with a strong affinity for either cations or anions is used to quantitatively determine the concentration of an ion. Home water softeners work on the principle of *cation exchange*. A synthetic resin polymer in the device is "charged" with excess sodium ions. This means all the available sites which strongly attract cations are occupied by sodium ions. As domestic water passes through the resin more highly charged calcium and magnesium ions displace the sodium and are trapped on the resin. The result is "soft" water. Each divalent ion displaces two univalent sodium ions.

If the same cation exchange resin is charged with <u>hydrogen ions</u> instead of sodium ions, displacement of the hydrogen ions by more highly charged ions (like the complex ion in this experiment) allows a simple acid/base titration to yield information regarding the charge on the complex ion. Since a molar mass has already been established by determining the compound formula, the moles of complex ion added to the resin is known. The moles of hydrogen ion displaced is found by titration and a simple ratio gives the charge of the complex ion. Once the charge of the ion is known, a complete structure for the compound can be determined.

The Experiment

There are six parts to this experiment:

- preparation of a cobalt(III) coordination compound
- analysis for Co^{3+}, NH_3 and Cl
- ion exchange determination of the complex ion charge
- magnetic susceptibility determinations
- lability comparison with hexamminecobalt(II) chloride
- visible absorbance spectrum comparison

The following non-locker materials will be provided:

- activated charcoal
- cobalt(II) chloride hexahydrate
- ammonium chloride
- concentrated aqueous ammonia [fume hood]
- 30% hydrogen peroxide [instructor dispensed]
- 6% hydrogen peroxide
- 6 M HCl
- concentrated HCl [fume hood]
- ethanol
- 1.0 M HCl
- two 10 mL volumetric pipets w/bulb
- 3 M NaOH
- bromcresol green indicator
- glass tubing and stopper for delivery tube
- small glass funnel
- 6 M HNO_3
- 6 M HCl
- 0.30 M NaOH
- centrifuge w/tubes
- pH paper
- potassium iodide
- starch indicator
- 0.050 M sodium thiosulfate solution
- 4 M $AgNO_3$
- 100 mL volumetric flask
- Dowex 50W-X2 cation exchange resin, 100-200 mesh
- jumbo beral pipets, cotton
- 0.005 M NaOH
- phenolphthalein
- buret
- solid $[Co(NH_3)_6]Cl_2$

The Chemicals

Cobalt(II) chloride is generally obtained as the hexahydrate, in pink to red slightly deliquescent crystals. The structure is reported to be $[Co(H_2O)_4]Cl_2·2 H_2O$. All waters are lost on heating to 140^oC. Aqueous solutions are pink to red, becoming blue on heating. The compound has been used in "invisible" inks, humidity indicators, for painting on glass and porcelain and in the manufacture of vitamin B_{12}.

Ammonium chloride (sal ammoniac) consists of colorless crystals with a saline taste and a tendency to cake. The compound sublimes when heated. It is very soluble in water and strongly endothermic as it dissolves. It has been used in ordinary dry cell batteries, to clean soldering irons, in safety explosives, and for snow treatment (slows melting) on ski slopes.

Ammonia is a gas at room temperature. Laboratory solutions of aqueous ammonia have sometimes been erroneously called "ammonium hydroxide" although there is little evidence for the existence of that compound. Aqueous solutions of ammonia are basic.

Ammonia gas can be manufactured from industrial gases associated with the processing of "coke", a spongy form of carbon obtained from processing coal and essential in steel-making. In the Haber-Bosch process nitrogen and hydrogen from these industrial gas mixtures are combined at high temperature and pressure in the presence of a catalyst to form ammonia. The gas and its aqueous solutions are colorless with a very pungent odor (lower limit of human perception: 0.04 g/m^3). Mixtures of ammonia gas and air can explode when ignited under favorable conditions. At room temperature ammonia is soluble to the extent of 31% in water, only 16% in methanol. It is used in the manufacture of nitric acid, explosives, fertilizers and in refrigeration. In anhydrous liquid form it is a good solvent for many elements and compounds, notably the alkali metals which yield blue solutions when dissolved in liquid ammonia.

Inhalation of the concentrated vapor causes swelling in the respiratory tract, spasms and asphyxia.

Hydrogen peroxide can be made from barium peroxide and dilute phosphoric acid. In the 30% concentration it is a clear, colorless liquid which contains 30% by weight of H_2O_2. It is an extremely strong oxidizing agent and will attack skin and eyes. Drying of spilled solution on clothing may cause fire. Trace contamination of the solution can cause rapid evolution of oxygen gas and heat.

90% hydrogen peroxide is used as a rocket fuel while 3% solutions are sold over the counter as a disinfectant. 6% solutions are used in hair bleaching preparations. Hydrogen peroxide is also used in the plastics industry, for bleaching and dyeing, artificially aging wines and liquors, and in pharmaceutical preparations.

Potassium iodide is a white solid, slightly deliquescent, and prone to oxidation in air. It is used in the manufacture of photographic emulsions, and in table salt and some drinking water to help prevent iodine deficiency disease.

Sodium thiosulfate (photographer's "hypo") is most commonly obtained as a pentahydrate in colorless, odorless crystals or granules. It melts at 48^oC and has a tendency to form supersaturated solutions. The compound dissolves silver halides and many other salts of silver. It is used as a fixer in photography, for extraction of silver from ores, as a mordant in dyeing and printing textiles and in the manufacture of leather. The compound has relatively low toxicity. Large doses orally cause purging.

Hydrochloric acid is also known as muriatic acid. It is the same liquid acid that is often used in controlling the pH of swimming pool water. It is sometimes colored yellow by iron impurities, traces of chlorine and organic matter. Reagent grade HCl contains about 38% hydrogen chloride gas, close to the limit of its solubility at room temperature.

Hydrochloric acid in concentrated form (12 M) has the sharp, choking odor of hydrogen chloride. It is used in the production of other chlorides and in refining some ores (tin and tantalum), cleaning metal products, removing scale from boilers and heat-exchange equipment, and as an important laboratory reagent (often in diluted form).

Concentrated solutions cause severe burns; permanent visual damage may occur. Inhalation causes coughing, choking; inflammation and ulceration of the respiratory tract may occur. Ingestion can be fatal.

Ethanol or ethyl alcohol is a clear, colorless liquid with a pleasant odor and a burning taste. It absorbs water readily from the air and is miscible with water and many organic liquids. Most ethanol is used in alcoholic beverages in dilute form. It is also used in the laboratory as a common solvent, in pharmaceuticals, and as a common topical antiseptic. Nearly all ethanol sold as "alcohol" (not for drinking) has been *denatured* (including the ethanol in the lab). Denaturing in this context means adding some substance which does not markedly interfere with the behavior or properties of ethanol except to render it unfit for drinking. Most denaturants are toxic.

Bromcresol green (3,3',5,5'-tetrabromo-*m*-cresolsulfonphthalein) is used as an indicator, pH 3.8 being yellow and pH 5.4 being blue-green. The indicator solution is generally prepared by dissolving the solid material in dilute NaOH.

bromcresol green
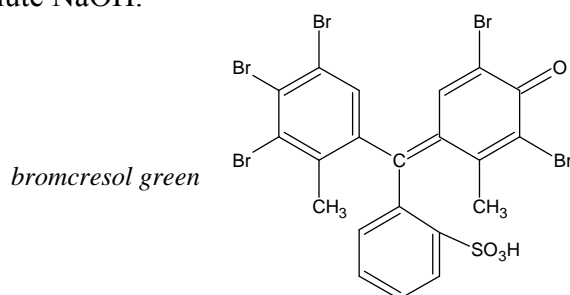
Sodium hydroxide is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO_2. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

Phenolphthalein is a white powder, a complex hydrocarbon derivative that was formerly used in laxatives such as Ex-Lax™. It also functions very well as an acid/base indicator for most titrations except those involving ammonia. It is very sensitive to CO_2 (which can dissolve in water to a small extent) and for very accurate determinations all water for solutions must be boiled to expel CO_2. For titrations it is used in a 1% ethanol solution. It is practically insoluble in water.

phenolphthalein
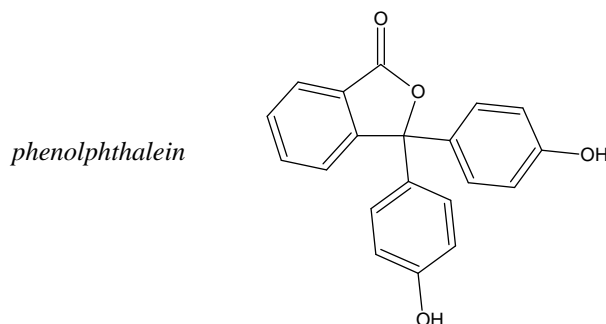
Nitric acid has been called "aqua fortis" (strong water). It is generally produced by the oxidation of ammonia followed by reaction of the gaseous products with water. When pure it is a colorless liquid that fumes in air with a characteristic choking odor. "Concentrated" nitric acid is a water solution containing 70% HNO_3. Even dilute solutions will stain woolen fabrics and animal tissue yellow. It is a very strong oxidizing agent, reacting violently with most organic matter.

Nitric acid is used in the manufacture of fertilizers, dye intermediates and explosives.

Starch (soluble starch, *amylodextrin*) is a white, odorless, tasteless powder which is soluble in water when heated. It is frequently used in the lab as an indicator for iodometric analysis since it forms an intense blue-to-black complex with I_2 but not with I^-.

Silver nitrate forms colorless, transparent crystals. It is stable and not darkened by light in pure air but darkens in the presence of organic matter and H_2S. It decomposes at low red heat into metallic silver. It is used in photography and the manufacture of mirrors, silver plating, indelible inks, hair dyes, etching ivory and as an important reagent in analytical chemistry.

It has been used as a topical antiseptic in a 0.1 to 10% solution. However, it is caustic and irritating to skin. Silver nitrate stains skin and clothing. These stains will wear off skin in a few days to a week but clothing is generally ruined. Swallowing silver nitrate can cause severe gastroenteritis that may end fatally. **CAUTION: IN THE CONCENTRATION USED IN THIS EXPERIMENT (4 M) SILVER NITRATE IS PARTICULARLY CAUSTIC. GLOVES ARE RECOMMENDED.**

Technique Discussion

You will be assigned one of the following two preparations. Most of the initial work must be done in the fume hood due to the use of concentrated solutions of ammonia and hydrochloric acid. Observe *all* of the instructions carefully. Seemingly minor deviations from the procedures can result in drastically reduced yields.

_____

Compound A

1. dissolve 1.0 g of NH_4Cl in 9 mL conc. NH_3 in a 125 mL Erlenmeyer flask
2. add 2.0 g of finely ground $CoCl_2 \cdot 6 \, H_2O$ in portions, agitating continuously (yellow-pink ppt.)
3. add 2 mL of 30% H_2O_2 at a rate of about 2 drp/sec, mixing well after each addition
4. heat the mixture carefully on a hotplate, swirling
5. when vigorous effervescence has ceased, cautiously add 6 mL conc. HCl while swirling
   [a purple ppt. should form, leaving a pale green-blue solution above]
6. heat at 70^oC (water bath) for 15 minutes
7. cool to room temperature and suction filter; wash with three 1.5 mL portions of <u>ice</u> water
8. wash with three 1.5 mL portions of chilled 6 M HCl (10^oC or below); suction dry
9. dry in oven at 100^oC for 1 hr.

Compound B

1. add 2.0 g of NH_4Cl to 5 mL of water in a 100 mL beaker and carefully bring solution to a boil
2. add 3.0 g finely ground $CoCl_2 \cdot 6 \, H_2O$
3. add to 0.15 g of activated charcoal (break up chunks) in a clean 100 mL beaker
4. rinse original beaker with 8 mL conc. NH_3 and add washing to beaker with charcoal
5. cool solution to 10^oC or below
6. add 8 mL of 6% H_2O_2 at a rate of about 2 drp/sec, stirring
7. heat the mixture at 60^oC (water bath) for 30 min, stirring often (<u>pinkish tint should disappear</u>)
   [if crystals have not formed at this point, ask for assistance]
8. cool in an ice bath for about 10 minutes and suction filter; use filtrate to rinse remaining solid into filter
9. drain on filter bed for 5 minutes
10. transfer solid to a 100 mL beaker containing a <u>boiling</u> mixture of 25 mL water + 1 mL conc. HCl
11. filter out charcoal, recovering hot solution in <u>clean</u> filter flask
12. transfer filtrate to clean 100 mL beaker, add 3 mL conc. HCl and cool in ice bath
13. suction filter; wash with two 3 mL portions of <u>ice-cold</u> ethanol
14 dry in oven at 110^oC for 30 minutes

You will need approximately 0.3 g of material for the analysis which follows. If your yield is less than this, notify the instructor.

The remaining parts of the experiment may be completed in any order except that the actual chemical analysis of the compound for cobalt, ammonia and chloride ion must be done in the sequence given to minimize both the time spent removing unwanted material and the amount of sample required. Magnetic susceptibility measurements and visible absorbance spectra may be run at any time the instruments are available [samples will be supplied for these parts so you will not need to use your own].

The analysis of the solid requires 0.25 g of material. This solid should be placed in a tube that will fit in the centrifuge. The tube should be clamped at an angle on the ring stand and fitted with a long bent glass delivery tube w/stopper. Cut and bend the tube according to the sample available in the lab. The delivery tube should terminate in a short piece of rubber tubing attached to the stem of a small glass funnel.
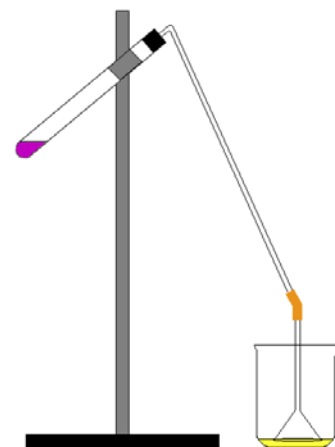
10 mL of 1.0 M HCl [record exact concentration] is pipetted into a 100 mL beaker and a few drops of bromcresol green indicator added. The mouth of the funnel from the delivery tube should be placed into the acid so that there is just a seal all around the funnel with the acid. Add 3 mL of 3 M NaOH to the sample in the centrifuge tube, stopper with the delivery tube and begin heating the sample *carefully*, bringing it to a gradual boil. Continue to boil the sample at a moderate rate until the solid residue is black, there seems to be no further local color change in the HCl (indicating that all of the ammonia has been removed from the compound), and the solution volume is reduced to almost 0 mL ("muddy" residue barely bubbles when heated). Do not heat the sample or any portion of it to dryness as chloride ions present can reduce Co^{3+} under these conditions.

Too rapid a rate of boiling may result in some ammonia escaping and/or cause sample to be ejected from the test tube.

The delivery tube and funnel should be rinsed into the HCl sample with a small amount of distilled water. The acid sample is then titrated with 0.30 M NaOH [record exact concentration] to a bromcresol green endpoint. This completes the ammonia analysis. Because some escape of ammonia is inevitable, this value is likely to be somewhat low.

The residue in the centrifuge tube contains cobalt(III) oxide and dissolved chloride ion in basic solution. Fill the test tube about ⅓ with distilled water and use a rubber policeman to loosen the black residue. Centrifuge the mixture and decant the liquid into a 100 mL volumetric flask. Repeat the washing step two more times, each time decanting the liquid into the volumetric flask. Acidify the solution with 6 M HNO_3 and dilute carefully to the etched line. Mix the flask contents thoroughly.

Mass a clean, dry centrifuge tube on the analytical balance. Pipet 10 mL of the diluted, acidified chloride solution into the test tube and add 10 drops of 4 M $AgNO_3$ [**caution!!!**]. Mix thoroughly. Allow the precipitate to settle and test for completeness of precipitation by adding an additional 5 drops to the clear solution above the precipitate. If no further sign of precipitation is observed, mix thoroughly and centrifuge. If additional precipitate forms, mix well, allow to settle and repeat the test until no further precipitate forms. Decant and discard the liquid from the centrifuged sample [**caution: contains excess AgNO₃**]. Wash the precipitate with several small portions of distilled water, mixing and centrifuging. Discard the washes. Dry the sample in the oven for 1 hr at 110°C and mass.

The black residue is Co_2O_3. Combine about 0.5 g KI and 10 mL of 6 M HCl. Add to the solid which should dissolve on mixing, forming aqueous Co^{3+} and triiodide ion. Quantitatively transfer the sample to a suitable titration vessel, using additional 6 M HCl if some solid residue remains. Prepare a buret with 0.050 M $Na_2S_2O_3$. Titrate as soon as possible. When the triiodide color is noticeably faded but not gone, add starch indicator and continue the titration to the usual starch endpoint [the final solution is clear but *pink* due to the presence of Co^{2+}].

The chemical analysis is now complete.

A small additional sample is required for the complex cation charge determination. Dissolve approximately 0.01 g [analytical balance] of the compound in 20-30 mL of water. Measure out approximately 6 g of ion exchange resin into a small beaker and add 25 mL of 6 M HCl. Stir and allow to sit for a few minutes. Prepare a "column" for the resin by snipping off the curved top of a jumbo beral pipet. Place a small bed of cotton over the entry to the pipet stem, wetting it with water to help hold it in place, and suspend the pipet in a 1-hole stopper clamped on the ring stand. Add the resin mixture slowly, catching the liquid in a small beaker, until a resin bed fills about half of the pipet bulb (use all of the resin slurry).
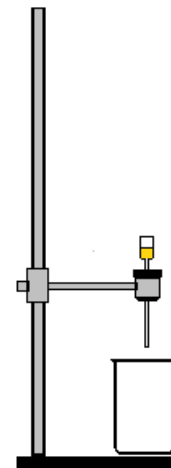
Rinse the resin bed with distilled water, each time filling the empty space in the pipet bulb and allowing the water to drain. After four rinsings check the pH of the wash as it emerges. When the pH is near 7 the column is ready. Place a clean beaker [suitable for titration] under the column and gradually add the solution of the cobalt compound. Follow with two rinses of distilled water. Titrate the collected HCl with 0.005 M NaOH [record exact concentration] to a phenolphthalein endpoint.

To compare the lability of your compound with $[Co(NH_3)_6]Cl_2$, take a small amount of both solids, dissolve each in distilled water and add a few drops of 1 M HCl. Note any changes.

The magnetic susceptibility comparisons require eight mass measurements. For each, the prepared sample tube must be *securely* clamped. If the tube is loose the mass change will be invalid. Each sample consists of a minimum 19 mm column of the pulverized compound. Tap each tube gently on the bench to settle the solid before measuring. The identities of the compounds and the sample masses are keyed by number to the list provided at the balances. **You need to record the values!**

Place the magnet assembly on the analytical balance. Rezero the balance. Position the ring stand and clamp so that the sample tube can be lowered through the top door of the balance compartment. The sample tube should be positioned so that the bottom is at the center of the magnet gap. Check for "zero mass" of the magnet assembly between measurements.

Solutions of both compound A and B (0.01 M) will be available near the spectrophotometers. Although these instruments were designed for measuring at a single wavelength, they can be used to produce a full-range visible spectrum by taking absorbance readings at fixed wavelength intervals. The only limitations are that the instrument must be rezeroed with a blank after each adjustment of the wavelength setting and the cuvettes used must be closely matched. Even with the best manual matching, it is possible to have some readings which are slightly negative. These should be recorded as "0.00" and will not affect the overall absorbance spectrum. Follow the procedure below to record BOTH spectra.

1. Start with wavelength control (knob on right side) at either 400 nm or 650 nm—wherever it was left by previous student.
2. Place blank (distilled water) in spectrophotometer and press the **100% T/0 A** button.
3. Place sample (either A or B—you need both!) in compartment and read absorbance. NOTE THAT THE SAMPLES AND BLANKS ARE IN MATCHED CUVETTES!!!! LOOK AT THE NUMBERS ON THE CUVETTES.
4. Change wavelength by 25 nm (up, if you start at 400, down if you start at 650) and zero the blank again.
5. Replace the sample and read the absorbance.
6. Continue in this way until you have data for the range from 400 nm to 650 nm.
7. Repeat with the other compound.

The Report

Your initial calculations should include:

1. The moles of ammonia in the sample

2. The moles of cobalt in the sample

3. The total moles of chloride in the sample

4. The empirical formula of the compound

5. The complex cation charge

6. The complete formula for the coordination compound

7. A graph of μ^2 [see table at right] vs. $|\Delta m/n|$ and the value of k

μ	unpaired e^-	compound
1.87	1	$CuSO_4 \cdot 5\ H_2O$
3.09	2	$NiSO_4 \cdot 6\ H_2O$
4.81	3	$CoCl_2 \cdot 6\ H_2O$
5.17	4	$FeSO_4 \cdot 7\ H_2O$
6.03	5	$MnSO_4 \cdot H_2O$

8. The magnetic moments for compounds A, B and $[Co(NH_3)_6]Cl_2$ and the number of unpaired electrons for each [ask a classmate who had the other compound what the formula was]

Remember, our magnetic susceptibility measurements are very simple and you may need to round your values intelligently to the only logical possibilities. Draw a splitting diagram and count out the electrons for each scenario <u>before</u> you draw a conclusion!

9. Absorption spectra plots for both compounds A and B

Your conclusion to this experiment should include an explanation of the different λ_{max} values for Compounds A and B [ask a classmate who had the other compound what the formula was] as well as a brief discussion of the numbers of unpaired electrons in the three cobalt compounds tested. Does this information correlate with the lability comparison of your compound and the cobalt(II) compound?