PREPARATION AND ANALYSIS OF CHIRAL TRIS(1,10-PHENANTHROLINE)COBALT(III)[1]

Inorganic Chemistry (CHE-258)   Spring 2004   Gustavus Adolphus College

Introduction

Metal ions, being Lewis acids, tend to bond to chemical species that are electron-rich relative to each particular metal ion. The bonding in these metal complexes (also known as coordination compounds) covers a continuum from predominantly ionic to predominantly covalent, and is dependent on the nature of both the metal and the molecule or ion which is bound to the metal (such a bound species is called a ligand). Examples of complexes that are bound predominantly by ionic forces (ion-dipole interaction) are aqueous alkali metal ions (where the water molecules of solvation act as ligands), and crown ether complexes of alkali metal ions. Compounds such as ferrocene, $Fe(C_5H_5)_2$, and bis(benzene)chromium(I) cation, $(C_6H_6)_2Cr^+$, where the metal is bound to the hydrocarbon through the hydrocarbon's π system, exhibit predominately covalent bonding. The bonding in coordination complexes such as $Cu(NH_3)_4^{2+}$ and $Fe(CN)_6^{2-}$ falls between these two extremes.

Many ligands can be grouped according to the number of individual electron pairs that they are able to donate for coordination to a particular metal. Unidentate (literally 'one-toothed') ligands donate one electron pair; bidentate ligands [also known as chelating ligands, from the Greek word chele (claw)] donate two electron pairs, tridentate ligands three, and so forth. Polydentate ligands generally form complexes which are more stable than those of the analogous unidentate ligands. This stabilization arises because the entropy of complexation is less unfavorable for the polydentate ligands, which are pre-arranged into structures that can easily attain the proper geometry for complexation. For example, the tris(ethylenediamine) complex[2] of Co(II) is much more stable than the hexaammine complex[3], even though they are similar in that both have six sp^3 nitrogen atoms bound to cobalt.

Stability of Coordination Complexes

The enhanced stability of chelate complexes which is discussed in the preceding section arises from the thermodynamics of the complexation reaction. A second type of stability arises from the rate at which the ligands can exchange for other ligands. A complex that is stable toward ligand interchange (i.e. exchange occurs very slowly or not at all) is called an inert complex; if ligand exchange occurs rapidly, the complex is termed labile. An inert complex is not necessarily stable in a thermodynamic sense; inertness arises simply from a high activation energy (lack of a suitable low-energy path) for substitution. Cobalt(II) complexes are labile, whereas cobalt(III) complexes are inert. During the course of this experiment, you will take advantage of both of these characteristics.

Chirality in Octahedral Systems

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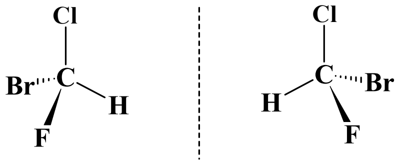
[1] Adapted from Hunt, Harold R., Jr. *J. Chem. Educ.* 1977, *54*, 710.

[2] ethylenediamine is a common non-IUPAC name for 1,2-ethanediamine, $H_2N\text{-}CH_2CH_2\text{-}NH_2$

[3] $Co(NH_3)_6^{2+}$

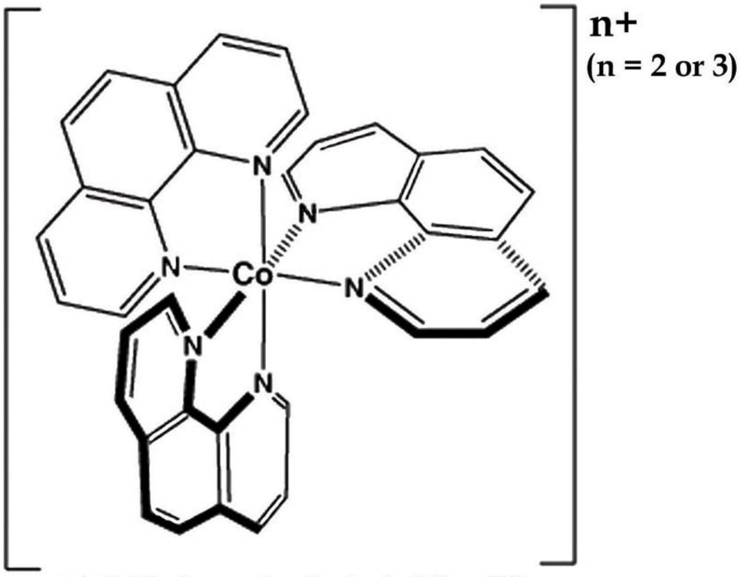
An object has the potential for existence in either of two chiral (right- or left-handed) forms when it lacks planes of symmetry. The most well-known manifestation of this phenomenon on a molecular level arises in the case of tetrahedral carbon. Substitution of the four bonding positions of a tetrahedral carbon atom with four different substituents removes all of the planes of symmetry of the tetrahedron, as illustrated below.

Methane is a highly symmetrical molecule: it has six planes of symmetry and four threefold roation axes. These can be visualized by consideration of the symmetry of a tetrahedron (shown to the right of CH_4).



Bromochlorofluoromethane has no symmetry elements; reflection therough a mirror plane generates an isomer which is non-superimposable on the original.

Octahedral objects such as hexacoordinate metal ion complexes can be configured so as to have no planes of symmetry. One way in which this can be done is to substitute neighboring coordination sites of the octahedron with chelating ligands, as shown below for $Co(phen)_3^{n+}$. This type of substitution pattern results in a propeller-shaped complex; such complexes, like propellers, can have either a right- or left-handed twist orientation. Reflection of one enantiomer of the complex through a mirror plane results in a non-superimposable, enantiomeric isomer, as shown in the schematic diagrams below. The relationship is somewhat more difficult to visualize than that of the analogous tetrahedral case; construction of molecular models is advised for clarification of this point.



tris(1,10-phenanthroline)cobalt(I or III)

As is the case with chiral molecules based on tetrahedral atoms, the enantiomers of chiral transition metal complexes differ, within an achiral medium such as water, only in the direction in which they cause rotation of plane-polarized light. Introduction of a chiral reagent, however, can cause a significant difference in the behavior of each enantiomer. In this experiment, a racemic mixture (1:1 mixture of enantiomers) of $Co(phen)_3^{2+}$ will be prepared. One enantiomer of $Co(phen)_3^{2+}$ will then be separated from the racemic mixture by interaction with a chiral resolving agent, antimony potassium tartrate. The antimony tartrate ion forms a salt of low solubility with (+)-$Co(phen)_3^{2+}$. As the (+) enantiomer precipitates, the (-) enantiomer converts partially to (+) in order to re-establish equilibrium; this process is rapid since $Co(phen)_3^{2+}$ is labile. At the end of these two coupled processes, all of the originally racemic $Co(phen)_3^{2+}$ will have precipitated as the (+) salt with the antimony tartrate ion.

The (+) complex can be characterized by its optical rotation. This measurement must be done in solution; however, re-dissolution of the labile Co(II) complex would lead to rapid racemization. Racemization can be avoided by first oxidizing the solid (+)-$Co(phen)_3^{2+}$ antimony tartrate salt to the analogous Co(III) complex, which is highly inert. In this experiment, oxidation of Co(II) to Co(III) is done with elemental chlorine, generated from bismuthate (or permanganate) and chloride in acidic solution; the resulting inert (+)-$Co(phen)_3^{3+}$ salt has good solubility in water, thus allowing its optical rotation to be determined. This sequence is illustrated on the flow chart that accompanies this handout.

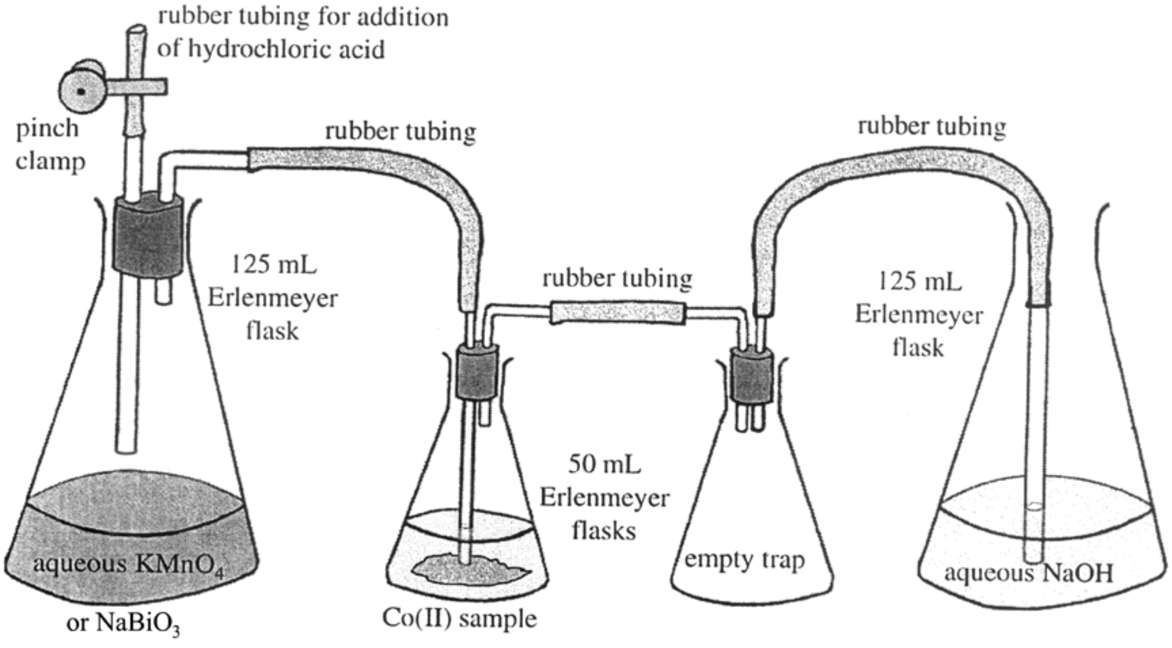
The observed rotation, α_{obs}, is read directly from the polarimeter. The specific rotation, $[\alpha]$, is calculated by use of the relation $[\alpha]$ = (corrected α_{obs}, deg.)/[(conc., g/cc)(path length, decimeters)]; thus, the concentration of (+)-$Co(phen)_3^{3+}$ in the sample must be determined. This is done in this case by the addition of sodium tetraphenylborate, which quantitatively precipitates (+)-$Co(phen)_3^{3+}$ as (+)-$Co(phen)_3^{3+}(BPh_4^-)_3$. The original concentration of (+)-$Co(phen)_3^{3+}$ can be calculated from the mass of the tetraphenylborate salt.

After precipitation and removal of (+)-$Co(phen)_3^{3+}(BPh_4^-)_3$, the residual optical activity of the supernatant must be measured, and subtracted from α_{obs} to give the corrected α_{obs}. This small residual activity comes from the chiral resolving agent, the antimony tartrate ion, which remains in solution.

Experimental Procedure

Add 0.200 g of 1,10-phenanthroline•H_2O to a 50 mL Erlenmeyer flask. Using an automatic buret (your instructor will show you how to use the automatic buret), add 30.0 mL of 0.0111 M $CoCl_2$ solution. Heat the solution with continuous swirling in a hot water bath until the phenanthroline is completely dissolved. Quickly add 0.33 g of antimony potassium tartrate to the hot solution, swirl to dissolve the solid, and let the solution cool slowly (about 20 minutes) to room temperature to precipitate the greenish-yellow Co(II) complex. To ensure complete precipitation cool the flask in an ice water bath for an additional 15 minutes.

While waiting for the Co(II) complex to precipitate, assemble the chlorine generator as shown in the figure. This should be done in a hood in order to minimize the exposure of the laboratory occupants to gaseous chlorine. Place approximately seven grams of sodium bismuthate (or approximately three grams of potassium permanganate) and 15 mL of water in the generator. Place approximately 60 mL of 1 M NaOH in the trap to absorb excess chlorine when the generator is in operation. **DO NOT** begin the generation of chlorine at this point.



Apparatus for generation of chlorine and oxidation of Co(II) to Co(III)

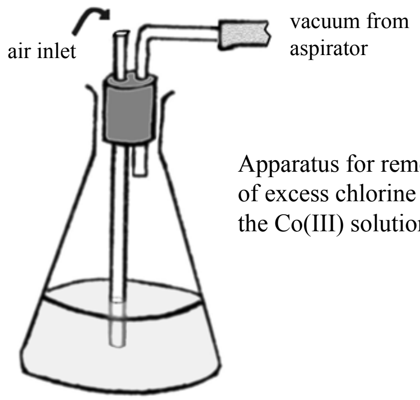
When the precipitation of the Co(II) complex is finished, the supernatant liquid should be almost colorless. **BEFORE THE REACTION WITH CHLORINE:** carefully decant and discard the supernatant, removing as much of the liquid as possible without loss of any of the solid. Then add 15 mL of distilled water to the sample flask, and connect it to the chlorine generator.

To begin generation of chlorine, insert a medicine dropper filled with concentrated hydrochloric acid into the rubber addition tube, and open the pinch clamp temporarily while squeezing the bulb of the medicine dropper. Swirl the generator flask to mix the reactants; this will initiate the generation of chlorine.

Swirl the sample flask occasionally during the oxidation, and continue the addition of chlorine until the solid has all dissolved and a clear yellow solution is obtained. About seven droppers full of hydrochloric acid should be required. Additional increments of concentrated hydrochloric acid can be added as needed. If you hear popping noises in the chlorine generator, or if the flow of chlorine becomes too vigorous, do not add further hydrochloric acid until the effect has subsided.

After completion of the reaction, remove the sample flask from the generator, connect it to an aspirator as shown in the figure on the next page, and draw a gentle stream of air through the solution for about two or three minutes to remove excess chlorine.

USE CARE: ***If you hook up the flask in reverse, the aspirator will suck all of your sample down the drain.***



Apparatus for removal of excess chlorine from the Co(III) solution

PERFORM THE OPERATIONS DESCRIBED IN THE NEXT PARAGRAPH IN THE HOOD.

Before measuring the optical activity of the Co(III) solution, discard the reaction mixture in the chlorine generation flask by pouring the contents of the flask into the container that will be provided in the hood. After you have disposed of the contents of the chlorine generation flask, rinse out any residue with water, or, if necessary, hydrochloric acid (if sodium bismuthate was used) or nitric acid (if potassium permanganate was used)..

Measurement of the Optical Activity of (+)-$Co(phen)_3^{3+}$

Five measurements each of α_{obs} and $\alpha_{residual}$ should be made, and the results averaged for your final calculation. Your instructor will show you how to fill the polarimeter cells and operate the polarimeter.

Precipitation of $Co(phen)_3(BPh_4)_3$

After you have measured the optical activity of the solution, pour the Co(III) solution into a clean 50 mL flask, add 0.5 g of $NaBPh_4$, and swirl the solution. A precipitate will form quickly, leaving the antimony *d*-tartrate resolving agent in solution. Cool the mixture in ice for about 15 minutes to ensure complete precipitation, then collect the product by gravity filtration on a previously weighed, fluted filter paper. If necessary, use one or more small portions of the filtrate to wash the last traces of product out of the sample flask onto the filter. Return all of the filtrate to the polarimeter cell (add a small amount of distilled water, if necessary, to fill the cell before closing) and measure its rotation five times.

Wash the product and filter paper using a few small squirts of water from a wash bottle. Let the filter drain well, and then wash the filter and product with three 5-mL portions of ethanol, letting each portion drain completely before adding the next. When the last portion of ethanol has drained completely, carefully open up the filter and place it on a paper towel or piece of filter paper to air-dry to constant weight.

If you have (+)-$Co(phen)_3^{3+}$ solution in excess of that needed for the measurement of the optical rotation, it should be treated with sodium tetraphenylborate and the mass of the precipitated complex determined; this number should be added to the mass determined in the preceding step so as to allow calculation of the percent yield of (+)-$Co(phen)_3^{3+}(BPh_4^-)_3$.

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Report - Preparation of a Chiral Cobalt(III) Complex

Calculate the corrected α_{obs} of the Co(III) complex, the concentration of the Co(III) solution, and the specific rotation [α]. Show all of your calculations clearly.

Report the weight of product and calculate the percent yield.

Inorganic Chemistry (CHE-258) Co(phen)$_3^{n+}$ - Prelab Questions Spring 2004

1. Write balanced half-reactions and a balanced overall equation for the oxidation-reduction reaction that is used to generate chlorine in this experiment.

2. How many planes of symmetry are present in each of the shapes or objects listed below?

sphere cube trigonal bipyramid

octahedron baseball (with seams)

3. Draw all of the possible isomers of $Cr(NH_3)_3Cl_3$ (for the purposes of this problem, assume that all are octahedral, covalently bound complexes).

Which, if any, are capable of existing as enantiomeric pairs?