Preparation of DichloroBis-(ethylenediamine)cobalt(III) chloride and Characterization with Single Crystal X-ray Diffraction

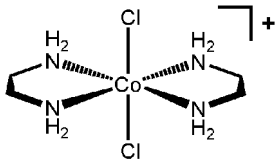
Introduction

As synthetic chemists prepare new compounds, they face two challenges in characterizing their compounds. They must establish the composition and structure of their compounds. Composition, the molecular formula, can be determined through elemental analysis (EA) or high-resolution mass spectrometry (MS). Definitively yielding a single experimentally determined molecular formula requires small deviations from the proposed formula (e.g. 0.05% error in EA measurements or <5 ppm error in observed molecular mass in MS).

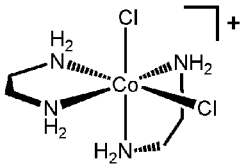
Despite finding the desired molecular formula, many isomeric possibilities remain, thus establishing the structural connectivity is also required. Organic chemistry strongly relies on nuclear magnetic resonance (NMR) for ^{1}H-^{1}H coupling and through correlation spectroscopy for ^{1}H-^{13}C coupling for connectivity. Inorganic complexes can be studied with NMR but many times, the ^{1}H or ^{13}C spectra give no information about the coordination geometry around the metal center. As a result, single crystal x-ray diffraction crystallography is employed to "take a picture" of the complex. The data yield the atom positions and based on van der Waals radii connectivity is proposed.

We will use x-ray crystallography to determine the structure of a cobalt complex from the three possible isomers. Reaction of cobalt(II) chloride with ethylenediamine (en) followed by oxidation with H_2O_2 to a Co^{III} complex with three possible structures, eq 1.[1]

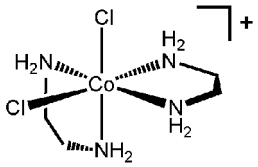
$$CoCl_2{\cdot}6H_2O + 2\ en + xs\ H_2O_2 + xs\ HCl \rightarrow [Co(en)_2Cl_2]Cl{\cdot}HCl \qquad (1)$$



trans-$[Co(en)_2Cl_2]^+$



cis-$[Co(en)_2Cl_2]^+$



cis-$[Co(en)_2Cl_2]^+$

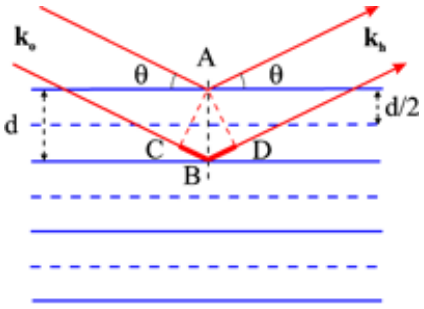
Ethylenediamine is a bidentate ligand yielding three geometric isomers for $[Co(en)_2Cl_2]^+$. The *trans* isomer has a 180° angle between the chlorides which are situated on either side of the octahedral coordination sphere of Co^{III}. With a 90° angle between the chlorides, the complex is defined as being the *cis* isomer. There are two different ways in which we can put two Cl atoms

cis to one another, and these are enantiomers. We will use single crystal x-ray crystallography to identify the stereochemistry of the product of our reaction.

Single Crystal X-ray Crystallography

X-ray diffraction is a powerful characterization technique for powders and single crystals. We will focus on single crystal diffraction where x-rays diffract after interacting with the atoms in a crystal lattice. X-rays are used because their wavelengths (Mo Kα radiation λ = 0.7107Å) are smaller than the interatomic distances (1.2 -3.0 Å) being interrogated. Also it is important to have a crystalline material where the atoms are regularly ordered in the material. Larger atoms diffract better than smaller ones and hydrogen atoms are essentially considered to not diffract at all. As a result, structure determination, data quality, and ease of data collection are all enhanced when at least one "heavy atom" (greater than carbon) is present.

Interatomic distances are determined through the constructive interference of diffracted x-rays. Consider the picture at right where incident x-rays at k_o interact with the planes of atoms in a crystal. The pathlength of the two rays is different. The lower ray travels an additional distance CB + BD. This distance is critical to the constructive interference of the x-rays. If the x-rays leave the crystal in phase, it means that the lower ray has traveled a longer distance that is some integer times the wavelength of light. If the rays leave the crystal out of phase, then the distance is not an integer times wavelength and no reflection is observed. As a result, the problem becomes trigonometric where the wavelength and the incident angle are known and d is found. Braggs Law represents this trigonometric relationship (eq 1),



IUCr Online Dictionary of Crystallogarphy.

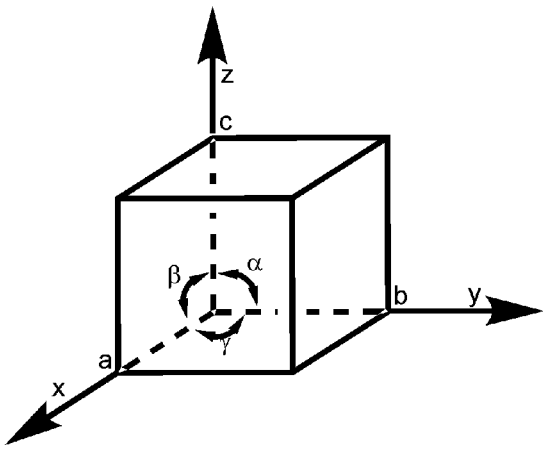
$$n\lambda = d \sin\theta \qquad (1)$$

where n is an integer of wavelengths, λ is the wavelength of monochromatic x-rays, d is the interatomic distance between planes of atoms. It can be seen that there may be multiple combinations of θ and n that yield observable reflections, which is useful in data collection.

Single crystal x-ray diffraction involves generating monochromatic x-rays, irradiating the sample at a specific angle, and observing the diffraction angle. The single crystal is mounted on a rotating goiniometer which rotates and revolves the crystal on multiple axes so that a

hemisphere of incident angles can be collected. Many times, the crystal is held at 173 K in a stream of liquid N_2 boil off to minimize atomic motions in the solid. Angle of reflection data is often collected with a CCD area detector on which a plane of reflection data is observed. The important data are the angle and intensity of the reflected x-rays. Data collection can take anywhere from 8 to 72 h depending on the type of detector.

After the collection of the reflections at many incident angles, the reflections are indexed and low intensity reflections may be removed from the data set. Remember the reflections tell us about the spacing between planes of atoms and the computer converts the angle, intensity, and spacing of reflections into a unit cell, crystal system, space group, and electron density map for the asymmetric unit. Unit cells constitute the smallest repeating unit in a crystal and may contain more than one molecule. The occupancy of the unit cell is indicated by Z, (e.g. Z = 2 for two molecules in the unit cell. Unit cells can come in a variety of crystal systems; the most common of which are *orthorhombic* (α, β, γ = 90°), *monoclinic* ((α = 90°, β, $\gamma \neq 90°$), and *triclinic* (α, β, $\gamma \neq 90°$). The lengths of a, b, and c can vary and are rarely the same. Determining a crystal's space group, requires the unit cell geometry and the symmetry operations (mirror planes, rotation axes, inversion centers, etc) at work inside the unit cell to go from one asymmetric unit (one molecule) to another inside the cell. For example, the space group P$\bar{1}$ (read: pea-one-bar) has an inversion center at the center.



Data analysis continues with determination of the crystal lattice packing and molecular structure. The packing of the molecules can be useful to identify H-bonding, π-π stacking interactions, voids, or solvent molecules in the solid state structure. Molecular structure is determined with either direct or Patterson methods in which an electron density map is used to model the structure of the molecule. The computer indicates the number of electrons at a diffraction location (e.g. 6…for carbon) and the chemist assigns that electron density as carbon. Since you have a good understanding of the substance under study such an assignment makes sense. As the molecular model is built up by assigning electron density, bonding relationships between adjacent atoms reveal themselves. Heavy atoms and organic moieties are placed, and a

theoretical diffraction pattern for the model is compared to the observed pattern and refined. Sometimes contraints and restraints have to be used to make aromatic rings flat or make the bond distances the same. Gradually, the difference between the theoretical pattern and the observed pattern decreases (R^1, wR^1, GOOF in reported structures), and the program places the hydrogen atoms in the molecule as appropriate. The final molecular structure is visualized with an Oak Ridge Thermal Ellipsoid Plot (ORTEP) at the 50 % probability level.

There are several good online tutorials on X-ray crystallography. I recommend:

1) http://www.matter.org.uk/diffraction/ (specifically Introduction to diffraction and X-ray diffraction.)

2) http://www.bmsc.washington.edu/people/merritt/bc530/bragg/ (Bragg's Law diffraction)

Recrystallization techniques

Recrystallization is a common technique for purifying organic and inorganic compounds. The basic premise is to dissolve the desired product and any impurities in as small amount of solvent as possible. It is best if the solubility of the impurities and the product are significantly different in the solvent. After a saturated solution has been prepared, the solubility of the solute in solution is reduced with three common techniques: *lowering the temperature, addition of a solvent with a lower solubility, or evaporation of the solvent*. By reducing the solubility of the solute in solution, precipitation of solid will occur. Ideally, the impurities will stay in solution and the desired product will precipitate out of solution.

For crystallography purposes, it is important that the solute come out of solution slowly so that molecules can organize into a regular pattern. Crystals and powders have very different properties. Remember it is the regular pattern of unit cells that will be most important to x-ray diffraction, so the same techniques for crystallization are used here but the goal is to change solute solubility slowly. However, in these efforts it is important that the solution be free of solids which could provide a nucleation site for very small crystals. As a result, solutions are often filtered before changes to solubility are made. Because organic solvents are often used, temperature changes to below 0 °C can often be made (for example Et_2O mp = -116 °C, hexanes mp = -95 °C). Since many compounds are soluble in polar solvents, solution polarity can be modified by adding a non-polar solvent by liquid-liquid diffusion (layering) or vapor-liquid diffusion. In each case, the non-polar solvent diffuses into the solution to reduce solubility and

enable crystal formation. Another common technique is to carefully control the evaporation of solvent from the solution decreasing solvent volume.

Preparation of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride Hydrochloride[2]

Dissolve 1.00 g of cobalt(II) chloride hexahydrate (4.2 mmol) in 2.5 mL of distilled water in an evaporating dish. Swirl until dissolved. Add 4 mL of 10% ethylenediamine solution (mmol) to the cobalt chloride solution and stir the solution without splattering with a stir bar for 10 min. After 10 minutes, slowly add dropwise 1.6 mL of 10% H_2O_2 to the solution while the solution is stirring. Stir for an additional 15 min. Add 3 mL of concentrated HCl. Turn off the stir plate and remove the magnetic stir bar using the magnetic stir bar retriever.

In the meantime, fill a 600-mL beaker approximately half full with water and heat to near boiling. Place a wire gauze on top of the beaker and place your evaporating dish with reaction solution on top of the wire gauze and bring the water to boiling. Reduce the solution's volume until there is a thick layer of dark green crystals and very little liquid left. This will take between 30 and 45 min. While the solution is concentrating, set up an ice bath and place 10 mL of methanol in a test tube in the ice bath.

After concentrating the reaction solution, place the evaporating dish on the benchtop of the hood to cool. Additional crystals should form while as the solution cools. Isolate your crystals with a Büchner funnel and vacuum filtration. Wet the filter paper with a few drops of cold methanol and transfer your crystals from the evaporating dish to the Büchner funnel using a spatula. Rinse your evaporating dish with some cold methanol and use the remaining methanol to wash your crystals. Air dry your crystals and obtain a yield.

Characterization of $[Co(en)_2Cl_2]Cl$

Absorbance spectroscopy

Prepare a solution of dichlorobis(ethylenediamine)cobalt(III) chloride hydrochloride with 0.5 M HCl as the solvent and mix thoroughly.[3, 4] Once dissolved, dilute the solution with water until the absorbance of the compound is between 0 and 1. Collect the electronic spectrum from 300 to 1000 nm and transfer the data for the complex to Excel for plotting and incorporation into your laboratory report.

Preparation of single crystals for diffraction

If necessary, we will recrystallize the $[Co(en)_2Cl_2]Cl$[5, 6] from a hot HCl solution and allow the solution to slowly cool followed by vacuum or gravity filtration the solution. Quality crystal

formation thrives on slowly changing the solubility of the solute in the solvent through either evaporation or cooling. The old saying goes, "Crystals thrive on neglect" meaning they form best when undisturbed.

Single Crystal X-Ray Diffraction

We will travel to California State University, Channel Islands to mount one of the class's crystals for data collection. You will have the opportunity to cut and mount crystals with the stereomicroscope. We will set up the data collection which will take several days to complete. During the following week's lab period, we will discuss and solve the structure of the cobalt complex.

Hazards and Safety Concerns

This lab utilizes concentrate HCl and 10% H_2O_2 solutions which are powerful and will readily yield burns through prolonged contact with the skin. Wear gloves when working with these solutions and rinse your hands afterwards. For any contacted areas wash with copious amounts of water.

References

1. Werner, A., *Ber.* **1901,** 34, 1733-1738.
2. Bailar, J. C., Jr., *Inorg. Syntheses* **1946,** II, 222-225.
3. McCaffery, A. J.; Stephens, P. J.; Schatz, P. N., *Inorg. Chem.* **1967,** 6, (9), 1614-1625.
4. Smith, A. A.; Haines, R. A., *J. Amer. Chem. Soc.* **1969,** 91, (23), 6280-6284.
5. Nakahara, A.; Saito, Y.; Kuroya, H., *Bull. Chem. Soc. Jpn.* **1952,** 25, 331-336.
6. Sharma, R.; Sharma, R. P.; Kariuki, B. M., *J. Fluorine Chem.* **2008,** 129, (5), 325-331.

Pre-lab Questions

1. The crystals in this lab will be "grown" from the cooling of a saturated aqueous solution. Suggest another method for preparing crystals for x-ray analysis.

2. Establishing the *R* or *S* configuration at a chiral center in an organic compound is critical for organic chemists who do "natural product" synthesis. Describe why x-ray crystallography and not mass spectrometry would be the appropriate technique for determining it.

3. Propose two complexes that would have sets of isomers that would be indistinguishable with ^{1}H NMR but that x-ray crystallography could differentiate.

4. How are atomic vibrations minimized in single crystal diffraction? How do you recognize atomic motion in an ORTEP diagram?

5. How are bonds between atoms identified in a crystal structure?