Experiment 6

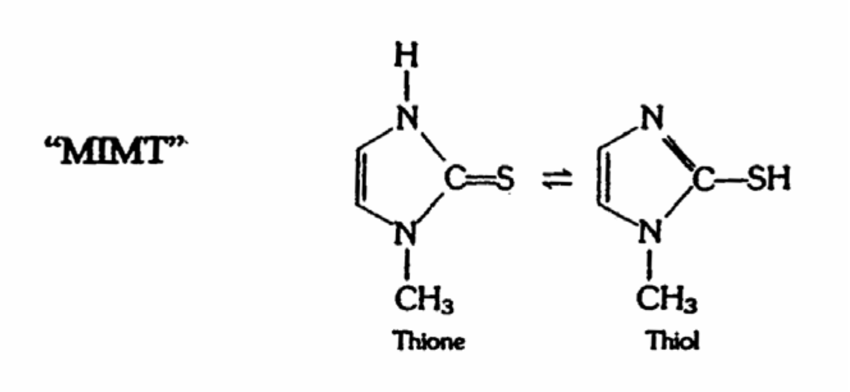
Thione-Thiol Tautomerism in Co(II) complexes

***** This lab has been adapted from “Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience,” 1991, John Wiley and Sons, New York, NY, pg 207.

Introduction

This experiment demonstrates how spectroscopic and magnetic data for many transition metal complexes can be used to determine the coordination geometry of a set of ligands about the transition metal ion. You will prepare cobalt(II) complexes using the monodentate organic ligand, 2-mercapto-1-methylimidazole (MIMT) and characterize them with UV/VIS and IR spectroscopy. Two complexes will be formed. Complex **A** has the formula $[Co(MIMT)_4(NO_3)_2]$, while complex **B** has the formula $Co(MIMT)_2(NO_3)_2$.

The structure of the MIMT ligand is depicted below. MIMT is one example of a ligand that can bond to a transition metal in more than one manner. Such ligands are said to be *ambidentate*. This behavior arises from the fact that MIMT can exist in two tautomeric forms, namely the -thione and -thiol forms. The behavior of MIMT is very similar to that of the keto-enol tautomerism which you learned about in organic chemistry.



In the thione form, MIMT coordinates to a metal through the sulfur atoms, while in the thiol form it coordinates through the imidazole ring nitrogen atom. In the two complexes prepared here, MIMT adopts the thione form. The coordination sphere in **A** is CoS_4 while that in **B** is CoS_2O_2, with the oxygens coming from the two coordinated nitrate ions.

MIMT by itself exists in the thione form. Since the C=S bond of the parent MIMT ligand has an IR stretching frequency at 745 cm^{-1}, the spectrum for the complexes can be monitored in this region to see what happens to this bond on coordination of the sulfur to the cobalt atom. This frequency should increase if the electron density in the bond is being enhanced, and will decrease if the electron density in the bond is reduced. The UV/VIS spectra of **A** and **B** should also differ, reflecting the difference in the *d*-orbital splitting capability of the four sulfurs in **A** versus the two sulfurs and two oxygens in **B**.

Procedure:

CAUTION: The MIMT ligand is a toxic compound. Exercise care when weighing out your samples. Wear gloves to prevent it coming into contact with your hands.

Preparation of Complex A – [$Co(MIMT)_4(NO_3)_2$]

In a small Erlenmeyer flask, prepare the solvent to be used for these reactions by mixing 8 ml of absolute (100%) ethanol with 0.45 ml of triethylorthoformate. We will refer to this solvent as TF-ETOH.

In a 25ml round-bottomed flask equipped with a magnetic stirring bar, dissolve 228 mg (2.0 mmol) of MIMT in 2.5 ml of your TF-ETOH solvent. You may need to warm this solution to get the MIMT ligand to fully dissolve. Use a Pasteur pipette to add a separately prepared solution of 73 mg hydrated cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, in 2 ml TF-ETOH.

Fill a drying tube with $CaCl_2$ at the appropriate lab station, working over the plastic tub to contain $CaCl_2$ spills. Attach a water condenser capped with your $CaCl_2$ drying tube to the round-bottomed flask, and clamp the apparatus in a sand bath set atop a magnetic stirring hot plate. Heat the resulting mixture at reflux with stirring for about 30 min. Then use a Pasteur pipette to transfer the hot liquid to a small Erlenmeyer flask (10ml) containing a boiling stone.

Reduce the volume by about 10% by heating on a sand bath IN THE HOOD, and then allow the solution to cool to room temperature. Further cooling in an ice bath should induce crystallization. Collect the resulting emerald green crystals by filtration using a Hirsch funnel and wash them with a 1ml portion of cold absolute ethanol. If this does not work, further reduce the sample volume, and try again. Using dried product, estimate your yield and measure the melting point of the product (the literature value is between 150 and 200°C). If you complete this reaction but fail to produce a solid sample of **A**, it is still possible to obtain an UV/VIS spectrum of the solution. Estimate your yield and measure the melting point of the product.

Preparation of Complex B – ($Co(MIMT)_2(NO_3)_2$)

In a small Erlenmeyer flask, prepare the solvent to be used for these reactions by mixing 8 ml of ethyl acetate with 0.45 ml of triethylorthoformate. We will refer to this solvent as TF-EA.

In a 25ml round-bottomed flask equipped with a magnetic stirring bar, dissolve 114 mg (1.0 mmol) of MIMT in 1.5 ml of your TF-EA solvent. You may need to warm this solution to get the MIMT ligand to fully dissolve. Use a Pasteur pipette to add a separately prepared solution of 146 mg hydrated cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, in 5 ml TF-EA.

Fill a drying tube with $CaCl_2$ at the appropriate lab station, working over the plastic tub to contain $CaCl_2$ spills. Attach a water condenser capped with your $CaCl_2$ drying tube to the round-bottomed flask, and clamp the apparatus in a sand bath set atop a magnetic stirring hot plate. Heat the resulting mixture at reflux with stirring for about 30 min. Then use a Pasteur pipette to transfer the hot liquid to a small Erlenmeyer flask (10ml) containing a boiling stone.

Reduce the volume by about 10% by heating on a sand bath IN THE HOOD, and then allow the solution to cool to room temperature. Further cooling in an ice bath should induce crystallization. Collect the resulting dark blue crystals by filtration using a Hirsch funnel and wash them with a 1ml portion of cold absolute ethanol. Dry the product, calculate your yield, and measure the melting point of the product (should be between 150 and 200°C).

Characterization of Your Product:

Collect UV-VIS spectra of ***freshly*** prepared solutions of **A** and **B**, as these complexes degrade within a few minutes. Either dilute the respective mother liquor into ethanol (just before you filter off the crystals), or else prepare acetonitrile (CH_3CN) solutions. These spectra should differ considerably. Compare the positions of the strongest absorption maxima in the visible region and comment on the relative values for the two complexes and the reasons for these differences.

Obtain the IR spectrum of the solid product by preparing a KBr pellet, following the method suggested by your TA's. Compare this with the spectrum for the free MIMT ligand and comment on the variations (if any) of the C=S stretching frequency.

Questions:

1. Draw geometrically accurate Lewis dot structures of the thione and thiol forms of the MIMT ligand. Indicate which electron pairs may be participating in the bond with Co, and give the expected angle between the Co-N or Co-S bond and the plane of the MIMT ring.

2. What is the charge on the MIMT ligand? What is the charge on the Co in $Co(MIMT)_2(NO_3)_2$ and in $Co(MIMT)_4(NO_3)_2$?

3. While $Co(MIMT)_2(NO_3)_2$ is obviously tetrahedral, it not immediately obvious if $Co(MIMT)_4(NO_3)_2$ will adopt a tetrahedral or octahedral coordination environment, as the NO_3^- ions can either be coordinated directly to the Co atoms, or merely serving as counter-ions in solution. Based on your UV-VIS data and your knowledge of the relative sizes of the crystal field gaps Δ_O and Δ_T, explain which coordination environment for $Co(MIMT)_4(NO_3)_2$ you are observing in this lab. You may wish to refer to your calculations for question 8.

4. Draw the *d*-orbital splitting diagram for a Co(II) ion in these two complexes as discussed in class, and label the lines (levels) corresponding to the d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, and d_{3z^2-1} orbitals.

5. How many unpaired electrons does $Co(MIMT)_2(NO_3)_2$ have? How many unpaired electrons does $Co(MIMT)_4(NO_3)_2$ have? Draw crystal field energy level diagrams (based on your conclusions from question 3) to illustrate your answers.

6. What is the expected Co^{2+} magnetic moment (in μ_B) for tetrahedral, octahedral (high-spin), and octahedral (low-spin) geometries? What is the expected Co^{2+} magnetic moment (in μ_B) for tetrahedral, octahedral (high-spin), and octahedral (low-spin) geometries?

The magnetic moment (μ_{eff}) for ions (in units of μ_B) is given by the formula:

$$\mu_{eff} = \sqrt{2S(2S+2)}$$

where S is the total spin for the complex (Remember each unpaired electron contributes a value of S=1/2, so a compound with three unpaired electrons will have S=3/2).

7. Is it likely that the choice of coordinating ligands (O vs. S) will affect the magnetic moment of tetrahedral Co^{2+} or Co^{3+}? How about for octahedral Co^{2+} or Co^{3+}? Use crystal field diagrams to justify your answer.

8. Based on your UV-VIS data, estimate the size of the gaps Δ_O and Δ_T for the coordination environments in the table below, completing ALL 18 of the boxes. You can assume that the gap energy for the 50/50 O/S compounds is the average of the pure sulfur and oxygen compounds, and that the ideal relation between Δ_O and Δ_T discussed in class holds. Remember that $E = hc\lambda = hc\tilde{v}$ where $\tilde{v}$ is in units of wavenumbers (not to be confused with frequency units of Hz). Make sure that your units are correctly converted. ***Show sample calculations*** (using dimensional analysis where appropriate). Give the color of light that each compound will absorb most strongly. Label any "colors" outside of the visible range as "UV" or "IR".

1st coord sphere	Δ_O and Δ_T, E in cm^{-1}	λ in nm	color
CoS_4 (tetrahedral)			
CoS_2O_2 (tetrahedral)			
CoO_4 (tetrahedral)			
CoS_6 (octahedral)			
CoS_3O_3 (octahedral)			
CoO_6 (octahedral)			

(Bonus question) Using the CRC Windows computers, open the two .mry structures with the Mercury molecular viewing package (located at "C:\wingx\Mercury 1.3\mercury.exe"). What are the formulas of these two compounds (MIMTCP and MTMICO)? How do the ligands differ from those that you used? What are the charges on the Co atoms in these two compounds? Describe the coordination environment of the Co atoms in each molecule, using measured distances and angles to support your conclusions. Also describe the manner in which the MIMT-like ligands bind to the central Co (as thiols or thiones? with N or with S?).