Experiment 20

Metal Complexes of Dimethyl Sulfoxide

Part A: Preparation of CuCl₂·2DMSO
Part B: Preparation of PdCl₂·2DMSO
Part C: Preparation of RuCl₂·4DMSO

INTRODUCTION

The infrared (IR) spectrum is a valuable tool for determining the nature of bonding in a particular compound. As an example of the use of IR spectroscopy in determining the nature of bonding in a compound, compare the IR spectra of acetone, CH₃COCH₃, and acetyl chloride, CH₃COCl, shown in Figure 8.1. Both compounds have a C=O double bond and would be expected to have a major IR absorbance at about 1700 cm⁻¹. For acetyl chloride, however, the carbon atom would bear a partial positive charge because of electron donation to the electronegative chlorine, and would be a poorer electron source. The second resonance form (below) is therefore relatively unimportant for acetyl chloride, but would be more important for acetone.

\[ \text{O} \quad \text{\ldots} \quad \text{O} \quad \text{\ldots} \]
\[ \text{R-C}-\text{Cl} \quad \text{R-C}-\text{Cl} \]

Thus, the CO bond order is higher in the case of acetyl chloride than it is in the case of acetone, and the IR absorbance comes at higher frequency (~1800 cm⁻¹).

In this experiment, IR spectroscopy is used to investigate a series of DMSO complexes (DMSO, CH₃SOCH₃). Dimethyl sulfoxide is structurally similar to acetone, with a sulfur replacing the carbonyl carbon. The normal absorption of the S=O bond occurs at 1050 cm⁻¹. This is lower than the C=O frequency, since the SO bond has a larger reduced mass than the CO bond resulting in the frequency shift.

Metals can bond to DMSO either through its oxygen or its sulfur. If the bonding is to the sulfur, the metal donates electrons from its π orbitals (the t₂g) into an empty π orbital on the DMSO ligand, thereby increasing the S-O bond order. Thus, if the metal is bonded to the DMSO at the sulfur, the frequency of the S=O absorption increases. If the bonding is to the oxygen of the DMSO, the metal forms a bond with one of the lone pairs on the oxygen, and thereby withdraws electron density from the oxygen. This favors the second resonance form in Eq. 20.1, since the oxygen will "seek" to gain electrons to compensate for the electrons donated to the metal. The net effect is that the S=O bond order declines and the S=O absorption appears at lower frequency.

Three different metal complexes of DMSO are synthesized. The metals used are copper (as anhydrous CuCl₂), palladium (as PdCl₂), and ruthenium (as RuCl₃). In each case, the metal forms an adduct with DMSO.

\[ \text{CuCl}_2 + 2(\text{CH}_3)\text{S}=\text{O} \rightarrow \text{CuCl}_2\cdot2(\text{CH}_3)\text{S}=\text{O} \]
\[ \text{PdCl}_2 + 2(\text{CH}_3)\text{S}=\text{O} \rightarrow \text{PdCl}_2\cdot2(\text{CH}_3)\text{S}=\text{O} \]
\[ \text{RuCl}_3 + 4(\text{CH}_3)\text{S}=\text{O} \rightarrow \text{RuCl}_2\cdot4(\text{CH}_3)\text{S}=\text{O} \]
Figure 8.1. Infrared spectra of (a) acetone and (b) acetyl chloride. (Courtesy of Aldrich Chemical Co., Milwaukee, WI.)
The ruthenium reaction is somewhat unusual, as it is also a redox reaction. The ruthenium is reduced from Ru(III) to Ru(II) and some of the excess DMSO in solution is oxidized to sulfone.

**Prior Reading and Techniques**

Section 2.F: Reflux and Distillation  
Section 5.D.3: Isolation of Crystalline Products (Suction Filtration)  
Section 6.C: Infrared Spectroscopy

**Related Experiments**

Copper Chemistry: Experiments 24, 47, and 49  
Palladium Chemistry: Experiments 39, 41, and 46  
Ruthenium Chemistry: Experiment 44

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**EXPERIMENTAL SECTION**

**Safety Recommendations**

- **Copper(II) chloride** (CAS No. 7447-39-4): This compound is harmful if swallowed or inhaled. IPR-MUS LD50: 7400 μg/kg.

- **Palladium(II) chloride** (CAS No. 7647-10-1): This compound may be fatal if swallowed, inhaled, or absorbed through the skin. It may be carcinogenic. ORL-RAT LD50: 2704 mg/kg.

- **Ruthenium(III) chloride trihydrate** (CAS No. 14898-67-0): This compound is harmful if swallowed, inhaled, or absorbed through the skin. IPR-RAT LD50: 360 mg/kg.

- **Dimethyl sulfoxide** (CAS No. 67-68-5): This compound is harmful if swallowed, inhaled, or absorbed through the skin. ORL-RAT LD 50: 14,500 mg/kg.

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**CHEMICAL DATA**

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<th>Compound</th>
<th>FW</th>
<th>Amount</th>
<th>mmol</th>
<th>bp (°C)</th>
<th>mp (°C)</th>
<th>Density</th>
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<td>PdCl₂</td>
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<td>RuCl₃·3H₂O</td>
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<td>Various</td>
<td>Various</td>
<td>189</td>
<td>18.4</td>
<td>1.101</td>
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</tbody>
</table>

**NOTE:** It is convenient in this experiment to do Parts 20.A–C simultaneously.

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**Part A:** Preparation of CuCl₂·2DMSO

**Required Equipment**

Magnetic stirring hot plate, 10-ml. Erlenmeyer flask, calibrated Pasteur pipet, automatic delivery pipet, magnetic stirring bar, Hirsch funnel, clay tile or filter paper.

**Time Required for Experiment:** 0.5 h.
EXPERIMENTAL PROCEDURE

Place 150 mg (1.11 mmol) of copper(II) chloride in a 10-mL Erlenmeyer flask equipped with a magnetic stirring bar. Add 1 mL of absolute ethanol (calibrated Pasteur pipet) and stir until the copper(II) chloride dissolves. Slowly, add 250 μL of DMSO (automatic delivery pipet). The immediate exothermic reaction yields a light green precipitate. Stir the mixture for several minutes.

Isolation of Product
Collect the product by suction filtration using a Hirsch funnel. Wash the product crystals with two 500-μL portions of cold ethanol. Dry the material on a clay tile or on filter paper. Calculate a percentage yield and determine the melting point.

Part B: Preparation of PdCl$_2$$\cdot$2DMSO

Required Equipment
Magnetic stirring hot plate, 10-mL Erlenmeyer flask, 10-mL graduated cylinder, automatic delivery pipet, magnetic stirring bar, ice−water bath, Hirsch funnel, clay tile or filter paper.

Time Required for Experiment: 3 h.

EXPERIMENTAL PROCEDURE

Place 1.25 mL of DMSO (automatic delivery pipet—it may be necessary to add this in two portions) in a 10-mL Erlenmeyer flask equipped with a magnetic stirring bar. Slowly add, with stirring, finely powdered palladium(II) chloride (135 mg, 0.75 mmol). The solution turns dark brown, and after about 2.5 h of stirring, yields an orange crystalline product. Any unreacted PdCl$_2$ forms a dark, heavy, brown mass that will stay at the bottom of the flask.

Isolation of Product
Decant the orange suspension of product complex into a Hirsch funnel, taking care not to transfer the unreacted PdCl$_2$. Suction filter the product and wash it with two 500-μL portions of ether. Dry the material on a clay tile or on filter paper. Calculate the percentage yield and determine the decomposition point.

Part C: Preparation of RuCl$_2$$\cdot$4DMSO

Required Equipment
Magnetic stirring hot plate, magnetic stirring bar, 10-mL round-bottom flask, water condenser, Keck clip, sand bath, calibrated Pasteur pipet, Pasteur filter pipet, 10-mL beaker, ice bath.

Time Required for Experiment: 2 h.

EXPERIMENTAL PROCEDURE

Place 100 mg (0.383 mmol) of RuCl$_2$$\cdot$4H$_2$O in a 10-mL round-bottom flask equipped with a magnetic stirring bar. Attach a water condenser with a Keck clip. Place the apparatus in a sand bath, set atop a magnetic stirring hot plate. Add 1 mL of DMSO through the condenser using a calibrated Pasteur pipet.

Heat the mixture to reflux for 5 min. The red solution quickly turns orange-yellow. Cool the solution, and transfer it, using a Pasteur filter pipet, to a 10-mL beaker. Reduce the volume of solution to about 0.5 mL by passing a gentle stream of N$_2$ gas over the warmed liquid. (Yellow crystals may separate out at this point.)
Isolation of Product
Add 2 ml of dry acetone dropwise, to form two layers. Cool the mixture in an ice bath. On standing for 10–15 min, yellow crystals of product will form. Collect the product by suction filtration using a Hirsch funnel. Wash the product with one 500-μL portion of acetone, followed by the same portion of ether. Calculate the percentage yield and determine the melting point.

Characterization of Products
Acquire the IR spectrum of each product and determine the position of the S=O band. Assign all major bands. You will find it helpful to compare the spectrum to DMSO itself. Determine whether the DMSO is coordinated at the sulfur or oxygen in each case.

Deuterium Analogs
RuCl₂₄DMSO-d₆ may be prepared in a similar fashion to RuCl₂₄DMSO, using DMSO-d₆ as the solvent. What changes are observed in the IR spectrum? How can deuterium substitution be an aid to assignment of band frequencies?

QUESTIONS
1. Which element (sulfur or oxygen) would you expect platinum, mercury, iron, and zinc halides to coordinate with in DMSO?
2. Dimethyl sulfoxide is an aprotic dipolar solvent that readily dissolves many inorganic salts. Water is a protic dipolar solvent that dissolves inorganic salts. Compare the solubility characteristics of these two compounds in terms of the dissolution process.
3. Why would you expect some metals to complex at the sulfur and some at the oxygen? Look up hard–soft acid–base rules in the literature and determine which metals fall into each category.

REFERENCE

GENERAL REFERENCES

Experiment 21
Preparation of Trans-dichlorotetrapyridinerhodium(III) Chloride

INTRODUCTION
Rhodium(III) forms an extensive variety of complexes. Nearly all complexes of rhodium(III) are octahedral. Rhodium(III) is very stable and kinetically inert because of its extremely favorable d⁶ configuration, and is always low spin and diamagnetic.

The starting material in this synthesis, RhCl₃·nH₂O, is a hydrate of variable composition, n usually falling between 3 and 4. In order to calculate a proper percentage yield, it is necessary to have an accurate assay of the starting material. In this experiment, it will be assumed that the starting material is a trihydrate.

Complexes of RhCl₃ are readily formed by either the direct reaction of the trichloride hydrate with Lewis bases (pyridine, CO, phosphines, etc.) or by the