Chapter 5

Inorganic Microscale Laboratory Techniques

5.A MICROSCALE DETERMINATION OF MAGNETIC SUSCEPTIBILITY

5.A.1 Introduction

Transition metals, by definition, have at least one oxidation state with an incomplete *d* or *f* subshell. Since electrons spin and generate a magnetic field, the magnetic properties of transition metals are of great interest in determining the oxidation state, electronic configuration, and so on. Most organic compounds and main group element compounds have all their electrons paired. Such molecules are diamagnetic and have very small magnetic moments. Many transition metal compounds, however, have one or more unpaired electrons, and are termed paramagnetic. The number of unpaired electrons on a given metal ion determines the magnetic moment, μ, affecting it both by virtue of their spin and their orbital motion. The spin part is the more important, and a close estimate of the magnetic moment can be obtained using the equation

$$\mu_s = g\sqrt{S(S+1)} \tag{5.1}$$

where g is the gyromagnetic ratio for an electron (≈ 2) and S is the total spin of the unpaired electrons (at $\frac{1}{2}$ each).

For one unpaired electron (as in Ti^{3+})

$$\mu_s = 2\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = 1.732 \tag{5.2}$$

The units of the magnetic moment are Bohr magnetons (BM). Actual magnetic moments are somewhat larger than the spin-only values obtained above, because of the orbital contribution.

Magnetic moments are not measured directly. Instead, the magnetic moment is calculated from the magnetic susceptibility, as described in Section 5.A.2. Experiments 24 and 25 directly utilize magnetic susceptibility measurements to help determine bonding within a complex. The technique could also be used to determine the electronic configuration of any of the transition metal complexes prepared or used in this book.

5.A.2 Measurement of Magnetic Susceptibility

There are a number of techniques that were used to determine the magnetic susceptibility of transition metal complexes. These include the Gouy method, the Faraday method, and the determination of magnetic susceptibility by nuclear magnetic resonance (NMR). Of these techniques, only the last two qualify as microtechniques, and can be carried out practically with 50 mg or less of sample. More recently, a new type of magnetic susceptibility balance, developed by D. F. Evans of Imperial College, London and Johnson Matthey/AESAR has appeared.[1] The balance is compact, lightweight, and self-contained. It does not require a separate magnet or power supply, and is therefore easily portable. The instrument has a digital readout that provides quick and accurate readings and whose sensitivity matches that of traditional methods. This balance can handle microscale quantities of solids as well as determine the magnetic susceptibility of liquids and solutions. As such, it is an ideal instrument for microscale inorganic work. The balance is shown in Figure 5.1.

In the Gouy method, a sample is suspended from a balance between the two poles of a magnet. The balance measures the apparent change in the mass of the sample, because it is repelled or attracted by the magnetic field. The attraction is due to the magnetic field generated by the unpaired electrons in a paramagnetic sample. Diamagnetic samples are repelled by the balance. The Evans balance has the same basic equipment configuration as in the Gouy method, but instead of measuring the force that the magnet exerts on the sample, it measures the equal and opposite force the sample exerts on a suspended permanent magnet. The Evans balance measures the change in current required to keep a set of suspended permanent magnets in balance after their magnetic fields interact with the sample. The magnets are on one end of a balance beam, and after interacting with the sample, change the position of the beam. This change is registered by a pair of photodiodes set on opposite sides of the balance beam's equilibrium position. The diodes send signals to an amplifier that in turn supplies current to a coil that will exactly cancel the interaction force. A digital voltmeter, connected across a precision resistor, in series with the coil, measures the current directly and this is displayed on the digital readout.

The general expression for the mass magnetic susceptibility, X_g, for the Evans

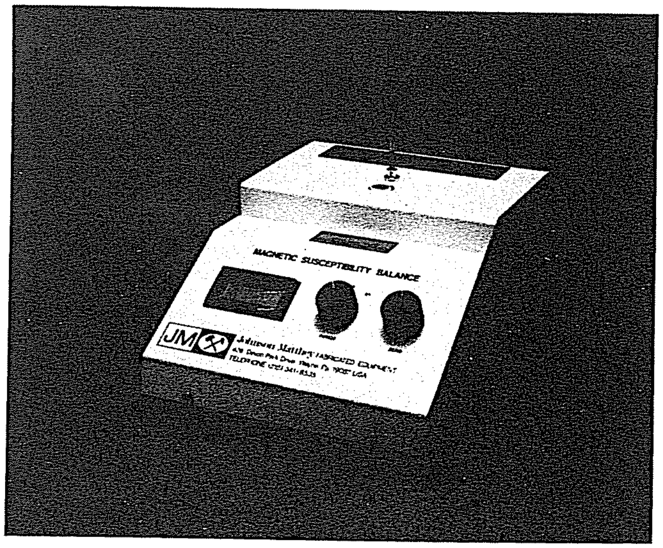

Figure 5.1. *The Evans balance. (Courtesy of Johnson Matthey, Catalytic Systems Division, Wayne, PA.)*

balance is

$$X_g = \frac{L}{m}\left\{C(R - R_0) + X'_v A\right\} \tag{5.3}$$

where L = sample length in centimeters
m = sample mass in grams
C = balance calibration constant (different for each balance; printed on the back of the instrument)
R = reading from the digital display when the sample (in the sample tube) is in place in the balance
R_0 = reading from the digital display when the empty sample tube is in place in the balance
X'_v = volume susceptibility of air (0.029×10^{-6} erg·G^{-2} cm^{-3})
A = cross-sectional area of the sample

The calibration standards usually employed in magnetic susceptibility measurements are $Hg[Co(SCN)_4]$ or $[Ni(en)_3]S_2O_3$, and have values of 1.644×10^{-5} and 1.104×10^{-5} erg·G^{-2} cm^{-3}, respectively. The volume susceptibility of air is usually ignored with solid samples, so that the mass magnetic susceptibility equation can be rewritten as follows:

$$X_g = CL(R - R_0)/(1 \times 10^9(m)) \tag{5.4}$$

where X_g is in centimeter-gram-second (cgs) units of erg·G^{-2} g^{-1}.

The magnetic susceptibility of liquids and solutions must include the volume susceptibility term, and, if the density of the liquid or the solution is known, the mass susceptibility of the solution, X_s, or of the solvent, X_0, may be calculated by

$$X_s \text{ or } X_0 = \frac{C(R - R_0)}{1 \times 10^9 A\, d_s} + \frac{X'_v}{d_s} \tag{5.5}$$

The terms C, A, R, R_0, and X'_v are as defined above and d_s is the density of the liquid or solution. The mass susceptibilities X_s and X_0 are in cgs units of erg·G^{-2} g^{-1}. The solution susceptibility, X_s, can be converted to the mass suceptibility, X_g, using the Weidmann additivity relationship

$$X_s = \frac{m_1}{m_1 + m_0} X_g + \frac{m_0}{m_1 + m_0} X_0 \tag{5.6}$$

where m_1 is the mass of the sample and m_0 is the mass of the solvent in grams.

The other method that can be used to determine the magnetic susceptibility of solutions is the NMR method developed by Evans.[2] The relationship between the mass susceptibility, X_g, and the change in frequency, $\Delta\nu$, of an indicator species in the solution is given by

$$X_g = \frac{3\Delta\nu}{2\,\pi\nu\, c} + X_0 + \frac{X_0(d_0 - d_s)}{c} \tag{5.7}$$

where the other terms given in the equation are defined as shown below:

ν = frequency of the nucleus under investigation in hertz (Hz)
c = concentration of the sample in grams per milliliter ($g{\cdot}mL^{-1}$)
X_0 = mass susceptibility of the solvent in cgs units
d_0 = density of the solvent in grams per milliliter
d_s = density of the solution in grams per milliliter

The third term is used to correct for the difference in density between the solvent and solution. This term usually makes only a small correction and is often ignored. Thus, the equation reduces to

$$X_g = \frac{3\,\Delta\nu}{2\,\pi\nu\,c} + X_0 \tag{5.8}$$

5.A.3 Calculation of Magnetic Moment from Magnetic Susceptibility

Once the mass susceptibility of the sample has been determined by one of the previous methods, the effective magnetic moment in Bohr magnetons (BM) can be calculated from the molar susceptibility (which has cgs units of $erg{\cdot}G^{-2}\,mol^{-1}$). However, this is after diamagnetic corrections for the inner-core electrons, ligands, atoms, or ions in the compound have also been made. The molar susceptibility, X_M, is calculated as shown below.

$$X_M = X_g{\cdot}(\text{molecular weight in } g{\cdot}mol^{-1}) \tag{5.9}$$

Table 5.1 Diamagnetic Corrections for Ions and Molecules[a]

Cations	Correction	Anions[b]	Correction	Molecules[b]	Correction
Li^+	1	F^-	9	H_2O	13
Na^+	7	Cl^-	23	NH_3	16
K^+	15	Br^-	34	en	47
Rb^+	22	I^-	50	py	49
Cs^+	33	$CH_3CO_2^-$	29	PPh_3	167
NH_4^+	13	$C_6H_5CO_2^-$	71		
Mg^{2+}	4	CN^-	13		
Ca^{2+}	9	CNO^-	23		
Sr^{2+}	16	CNS^-	34		
Ba^{2+}	26	ClO_4^-	32		
Cu^+	15	CO_3^{2-}	28		
Ag^+	27	$C_2O_4^{2-}$	28		
Zn^{2+}	13	HCO_2^-	17		
Cd^{2+}	20	NO_3^-	19		
Hg^{2+}	36	O^{2-}	6		
Tl^+	36	OH^-	11		
Pb^{2+}	32	S^{2-}	28		
First-row transition metals[c]	13	SO_4^{2-}	38		
		$S_2O_3^{2-}$	46		
		acac$^-$	55		

[a] All values are $10^6\,X_M$ cgs, that is, $Li^+ = 1 \times 10^{-6}\,erg{\cdot}G^{-2}\,mol.^{-1}$

[b] acac = acetylacetonate; en = ethylenediamine; PPh_3 = tgriphenylphosphine; and py = pyridine.

[c] Inner-core electrons.

The molar susceptibility includes diamagnetic contributions from the other atoms in the molecule or compound, making the apparent molar susceptibility smaller than it really is. Thus, these contributions must be added to the value of X_M, so that the molar susceptibility of the paramagnetic atom, X_A, can be determined. There are a number of tables of diamagnetic corrections in the literature.[3,4] Table 5.1 lists some of these values. If a ligand or other group in the molecule does not appear in this table, the diamagnetic correction can be obtained by summing the values for each atom or type of atom in the group.

In order to use these corrections and to find the molar susceptibility of the paramagnetic atom, the following equation is used.

$$X_A = X_M + \text{sum of all diamagnetic corrections} \tag{5.10}$$

The relationship between X_A and μ_{eff} can be used to calculate the effective magnetic moment in Bohr magnetons.

$$\mu_{eff} = \left[\frac{3kTX_A}{N\beta^2}\right]^{1/2} \tag{5.11}$$

where k is Boltzmann's constant, N is Avogadro's number, and β is the Bohr magneton. This reduces to

$$\mu_{eff} = 2.828(X_A T)^{1/2} \tag{5.12}$$

The value of μ_{eff} can then be compared to the calculated value from the "spin-only" formula that assumes the ligand field "quenches" the orbital angular momentum.

$$\mu_s = g\sqrt{S(S+1)} \tag{5.13}$$

Values of μ_s for various numbers, n, of unpaired electrons are given next.

n	μ_s (BM)	n	μ_s (BM)
1	1.73	5	5.92
2	2.83	6	6.93
3	3.87	7	7.94
4	4.90		

The value of μ_{eff} may vary slightly from one compound to another. Table 5.2 has a list of transition metal ions with the typical range of μ_{eff} values for each. The effective magnetic moment for lanthanides and actinides cannot be calculated from the spin-only equation, since the orbital motion contribution cannot be ignored.

Once the effective magnetic moment is determined, it is a simple matter to find the number of unpaired electrons, and from that, the electron configuration of the metal. This can then lead to an understanding of the geometry and bonding in the molecule. For example, $Fe_2(CO)_9$ is known to have three terminal carbonyl groups on each iron and three bridging carbonyl groups between the two iron atoms.[3] The magnetic susceptibility of the complex shows it to be diamagnetic (no unpaired electrons). Therefore, there must be a metal–metal bond joining the two iron atoms with the two electrons paired. This is confirmed by a short Fe—Fe distance in the X-ray structure.

Table 5.2 Oxidation States and Magnetic Moments for Octahedral Complexes

Metal Ion	Configuration	Number of Unpaired Electrons	Magnetic Moment (BM)
Ti^{3+}	d^1	1	1.7–1.8
Ti^{4+}	d^0	0	0
V^{3+}	d^2	2	2.7–2.9
V^{4+}	d^1	1	1.7–1.8
V^{5+}	d^0	0	0
Cr^{2+}	d^4	4 (High spin)	4.8–5.0
		2 (Low spin)	3.0–3.3
Cr^{3+}	d^3	3	3.7–3.9
Mn^{2+}	d^5	5 (High spin)	5.7–6.0
		1 (Low spin)	2.0
Mn^{3+}	d^4	4 (High spin)	4.8–5.0
		2 (Low spin)	3.0–3.3
Mn^{4+}	d^3	3	3.7–3.9
Fe^{2+}	d^6	4 (High spin)	5.9–5.6
		0 (Low spin)	0
Fe^{3+}	d^5	5 (High spin)	5.7–6.0
		1 (Low spin)	2.2–2.5
Co^{2+}	d^7	3 (High spin)	4.3–5.2
		1 (Low spin)	2.0–2.7
Co^{3+}	d^6	0 (Low spin)	0
Cu^{+}	d^{10}	0	0
Cu^{2+}	d^9	1	1.8–2.1

5.A.4 Operation of the Evans–Johnson Matthey Balance for Solids

1. Turn the RANGE knob on the balance to × 1 and allow the balance to warm up for 30 min.
2. Adjust the ZERO knob until the display reads 000. The zero should be readjusted if the range is changed.

> **NOTE:** ***The zero knob on the balance has a range of 10 turns. It is best to operate the balance in the middle of this range. This can be accomplished by turning the knob 5 turns from one end and then, ignoring the bubble level, adjusting the back legs of the balance until the digital display reads about zero. Once this is done at the beginning of the laboratory period, all further adjustments can be made with the knob on the front of the instrument.***

3. Place an empty tube of known weight into the tube guide and take the reading R_0.

> **NOTE:** ***The instrument can drift over short periods of time and should be rezeroed before each measurement.***

On the × 1 setting the digital display should fluctuate by no more than ± 1. However, when you record R or R_0 take a "visual average" of this fluctuation and use this as your reading.

4. Carefully fill the opening at the top of the sample tube with the solid and tap the bottom of the tube gently on a hard surface to pack the sample. Obtain the mass, in grams. You must have at least 1.5 cm of solid to obtain a stable reading of R.
5. Rezero, place the packed sample tube into the tube guide on the top of the balance, and take the reading R. A negative reading indicates a diamagnetic sample.

> **NOTE:** ***A critical part of the technique is correctly packing the well-powdered sample of the solid in the sample tube. To be sure you have the true value of R after the first reading, repeatedly tap the bottom of the tube firmly but gently on a hard surface (preferably not the table the balance is on) for about 30–60 s, then take another reading of R. Continue this until you have three values that agree within ± 1. Also during the tapping process ensure that the solid forms an even surface in the tube and is not sloped to one side.***

6. If the reading is off-scale, change the RANGE knob to × 10, rezero, and multiply the reading by 10.
7. Calculate the mass susceptibility using the equation

$$X_g = \frac{CL(R - R_0)}{1 \times 10^9 \text{ m}}$$

> **NOTE:** ***Along with a recording of R, R_0, L, and m you should also determine the temperature to 0.1 °C with a thermometer placed or suspended near the balance.***

8. The sample may be removed by gently tapping the tube upside down on a piece of weighing paper. Do not tap too hard since the glass lip can be easily broken during this procedure. After the tube is empty it can then be rinsed with the appropriate solvent using a microliter syringe or disposable pipette with a fine tip. The solvent is shaken out and the process repeated until the tube is clean. Place the tube upside down in a small breaker to dry.

5.A.5 Operation for Liquids and Solutions

The general procedure for making measurements on liquids and solutions is somewhat similar to that used on solid samples, however, there are some important differences. With this in mind please note the following:

1. For liquids and solutions the full expression for mass susceptibility, including the correction for the volume susceptibility of displaced air, must be used (Eq. 5.5). In this expression the cross-sectional area must be determined as well as the mass of the solute, mass of the solvent, and volume of solution (to calculate the density). It is therefore best to prepare the solution by

weighing an empty vial or volumetric flask, weighing the container after the solute has been added, and weighing it again after the solution is prepared. The volume of solution can be determined directly by using a small volumetric flask (1–10.00 mL), or by preparing the solution in a vial and measuring the volume of the solvent added with a microliter syringe. As long as the amount of solute is small there should be no detectable change in the volume of liquid when the solution is prepared. You can therefore use the volume of added solvent as the volume of solution.

2. Place at least 2.5 cm of solution into the sample tube using a microliter syringe. Tap out any air bubbles.
3. The mass susceptibility of the solvent, X_0, can be measured separately as described in Ref. 5.
4. The measurement of sample length, L, on liquid or solution samples, should be taken from the bottom of the meniscus to the bottom of the sample (not the bottom of the tube). The diameter of the thin bore and standard sample tubes are 2.00 and 3.23 mm, respectively. This can be used to calculate the value of A.

5.A.6 Determining Magnetic Susceptibility by NMR Spectroscopy

There have been many studies detailing the data collection and analysis of solution NMR measurements of magnetic susceptibility. The use of a sealed melting point capillary as the center tube of a 5-mm coaxial cell unit is perhaps the best method for measuring magnetic susceptibility by NMR.[6] Both compartments must contain the solvent, plus 1–2% of an indicator species. The best combinations of solvent and indicator are water and 1–2% *t*-butyl alcohol, chloroform and tetramethylsilane (TMS), or acetone and TMS. It is best to place the solution with the paramagnetic solute in the melting point capillary. The appropriate amount of solvent can then be adjusted in the outer tube to cause the capillary to stand up in the center of the outer tube. The NMR tube should be spun as quickly as possible (~50 rps or greater) to minimize spinning sidebands.

In order to lock to a ^{2}H resonance on an FT NMR spectrometer, D_2O, $CDCl_3$, and CD_3COCD_3 must replace the water, chloroform, and acetone in both the tubes of the coaxial cell. However, *t*-butyl alcohol and TMS can still be used as the indicator species. The sweep width on an FT NMR should be expanded, so that there will be little or no "foldover" of the spinning sidebands that can make determination of $\Delta\nu$ difficult. Since the indicator species in the capillary tube will have a weak signal, it can often be missed, particularly when there are numerous spinning sidebands. It is important to check all the peaks in the spectrum by calculating their distance from the main resonance of the indicator. Any pairs of peaks on either side and at equal distances from the main resonance are probably sidebands. If there is any doubt, the spin rate can also be changed to see if the peaks change frequency. If the frequency changes, the peak was a spinning sideband.

The temperature of the probe should be determined at each session by finding the $\Delta\nu$ between the methyl and hydroxyl protons of methanol or ethylene glycol. The chemical shift difference, $\Delta\nu$, is then compared to a calibration chart supplied with the spectrometer and the temperature of the probe is recorded. It was noted that the calibration charts supplied with some instruments are incorrect,[7] and even under the best conditions, cannot give an accuracy higher than ± 1 °C. A more complete overview of NMR temperature measurements may be found in Ref. 8.

Prepare a solution of the paramagnetic compound using the solvent–indicator mixture described in Section 5.A.5. Place a small quantity, ~2 cm in height, in a melting point capillary tube. Seal the tube with a microburner ~1 cm above the liquid level. Place the capillary in an NMR tube containing the solvent–indicator mixture, and adjust the liquid level in the tube to make the capillary tube "stand up." Cap the NMR tube and obtain the spectrum.

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Experiment 24

Determination of Magnetic Moments in Metal–Metal Bonded Complexes

Part A: Synthesis of Rhodium(II) Acetate Ethanolate

Part B: Synthesis of Copper(II) Acetate Monohydrate

INTRODUCTION

The idea that metal atoms could individually bond to other metal atoms was one that arose comparatively late in the development of inorganic chemistry.[1] It was not until 1913 that a compound was discovered to have a metal–metal bond, and not until 1963 that compounds with metal–metal bonds were thought to be anything more than oddities.

The first compound with metal–metal bonds was found to have the formula $Ta_6Cl_{14}{\cdot}7H_2O$ by H. S. Harned. Earlier, the compound was thought to be $TaCl_2{\cdot}2H_2O$. Clearly, Harned's work indicated that there was some interaction between the tantalum atoms in this compound. The structure was shown some 40 years later to consist of an octahedron of mutually bonded tantalum atoms, with each edge of the octahedron being bridged by a chlorine. The formula would be best represented by $[Ta_6Cl_{12}]Cl_2$.

With the discovery of rhenium cluster compounds in 1963, the area of metal–metal bonding exploded with interest, with hundreds of such compounds currently known. Compounds are currently known containing not only M—M single bonds, but also double, triple, and even quadruple bonds. This experiment (and Experiment 25) allows us to synthesize and characterize a series of compounds containing metal–metal bonds.

Rhodium(II) and iridium(II) do not form simple complexes similar to those of the well-known cobalt species, $[Co(NH_3)_6]^{2+}$ or $[CoCl_4]^{2-}$. The most common complexes of Rh and Ir formed in the II oxidation state are bridged species that contain a metal–metal bond. The most familiar of these is tetrakis(acetato)-dirhodium(II), whose structure is shown in Figure 8.3.

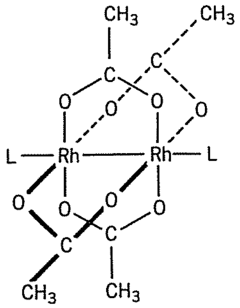

Figure 8.3. *Structure of rhodium(II) acetate alcoholate.*

In this complex, the unpaired electrons of rhodium(II) (d^7) are strongly coupled, and the complex is diamagnetic. (For a discussion of magnetic susceptibility, see Section 5.A.) The metal–metal bond is quite short, only 2.386 Å, leading to the conclusion that a rhodium–rhodium bond is present in this compound. Several other metals form similar acetates with metal–metal bonds.

This structure is similar to that exhibited by copper(II) acetate dihydrate, which *may* contain a copper–copper bond. In the copper complex, there is only a weak coupling of the unpaired electrons on the Cu(II) ions (d^9). Thus, while the ground state is diamagnetic, there is a low energy excited state that is paramagnetic. This excited state is appreciably populated at room temperature and the complex therefore appears to be paramagnetic. As the temperature increases, the magnetic moment increases as well. (The alternative explanation to this behavior, not involving Cu—Cu bonding, is described as an antiferromagnetic coupling of the unpaired spins.) Structural determination shows that the two copper atoms are separated by a distance of 2.64 Å. This compares to a 2.56-Å interatomic distance in metallic copper, making the assumption of a Cu—Cu bond more controversial.

The rhodium(II) acetate ethanolate is prepared via the direct reaction of rhodium(III) chloride hydrate and sodium acetate trihydrate in the presence of ethanol. It is the ethanol that is oxidized. The copper(II) acetate hydrate is synthesized via a less direct route, involving the intermediate formation of a tetraamine complex, conversion of the tetraamine complex to a precipitated hydroxide, and subsequent reaction with acetic acid.

$$CuSO_4{\cdot}5H_2O + 4NH_3\,(aq) \rightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

$$[Cu(NH_3)_4]^{2+} + NaOH \rightarrow Cu(OH)_2(s)$$

$$Cu(OH)_2 + CH_3CO_2H \rightarrow [Cu(CH_3CO_2)_2{\cdot}H_2O]_2$$

The solvent ligands, L (see Fig. 8.3), can be easily removed by heating in vacuum to yield the nonadducted complexes. In the case of the rhodium(II) complexes, if the ligand is an oxygen-bonded species (such as ethanol in the synthesis below), the complexes are blue-green in color. If the ligand is a π acid, such as triphenylphosphine, the complex is red.

Rhodium(II) acetate ethanolate, as well as other tetrakis(μ-carboxylato)-dirhodium(II) species, show some antitumor behavior by inhibiting DNA synthesis. The base adenine's nitrogen N7 hydrogen bonds to the carboxylate oxygen of the rhodium(II) species. The rhodium species then bridges between the DNA strands.[2]

Prior Reading and Techniques

Section 2.F: Reflux and Distillation

Section 5.A: Microscale Determination of Magnetic Susceptibility

Section 5.C.2: Purging with an Inert Gas

Section 5.D.3: Isolation of Crystalline Products (Suction Filtration)

Section 5.D.4: The Craig Tube Method

Section 6.C: Infrared Spectroscopy

Related Experiments

Copper Chemistry: Experiments 20, 47, and 49

Metal–Metal Bonding: Experiments 25 and 45

Rhodium Chemistry: Experiments 21, 34, and 42

EXPERIMENTAL SECTION

Part A: Synthesis of Rhodium(II) Acetate Ethanolate

Safety Recommendations

Rhodium(III) chloride hydrate (CAS No. 20765-98-4): This compound is harmful if swallowed, inhaled, or absorbed through the skin. ORL-RAT LD50:

1302 mg/kg. It is a possible mutagen, although this has not been definitively established.

Sodium acetate trihydrate (CAS No. 6131-90-4): This compound is not generally considered dangerous. The normal precautions should be observed. ORL-RAT LD50: 3530 mg/kg.

CHEMICAL DATA

Compound	FW	Amount	mmol	mp (°C)	Density
$RhCl_3 \cdot xH_2O$	263.26[a]	50 mg	0.19	100[b]	
$NaC_2H_3O_2 \cdot 3H_2O$	136.08	100 mg	0.73	58	1.45

[a] Based on calculations for the trihydrate.

[b] Decomposes.

Required Equipment

Magnetic stirring hot plate, 10-mL side arm round-bottom flask, magnetic stirring bar, Keck clip, automatic delivery pipet, source of nitrogen, sand bath, water condenser.

Time Required for Experiment: 2.5 h, plus overnight crystallization time

EXPERIMENTAL PROCEDURE[3]

Thoroughly flush a 10-mL side arm round-bottom flask equipped with a stirring bar with N_2 gas. Dissolve 50 mg (~0.19 mmol) of rhodium(III) chloride hydrate and 100 mg (0.73 mmol) of sodium acetate trihydrate in 1 mL of glacial acetic acid and 1 mL of absolute ethanol (automatic delivery pipet). Transfer this to the side arm flask using a Pasteur pipet and attach a water condenser with a Keck clip. Place the apparatus in a sand bath atop a magnetic stirring hot plate. Stir the mixture at room temperature, maintaining a positive pressure of nitrogen, until a red color develops.

Reflux the solution gently, under nitrogen, for 1 h. The red solution should become green, and a blue-green solid precipitates during this time.

Isolation of Product

Collect the blue-green solid product, $[Rh(OCOCH_3)_2]_2 \cdot 2C_2H_5OH$, by suction filtration using a Hirsch funnel.

Purification of Product

The rhodium(II) acetate ethanolate may be recrystallized by dissolving the product in the minimum amount of boiling methanol (~6 mL), and filtering if necessary. Concentrate the solution (**HOOD**) to a volume of approximately 4 mL using a gentle stream of nitrogen. Store the solution in a refrigerator overnight. Collect the first crop of crystals by suction filtration using a Hirsch funnel. Further concentration and cooling yields a second crop of crystals. The nonsolvated complex, $[Rh(OCOCH_3)_2]_2$, can be generated by heating at 45 °C in a vacuum for 20 h.

Characterization of Product

Acquire the IR spectrum of the product as a KBr pellet. Determine the magnetic moment of the product (see Section 5.A). Either the ethanolate or the nonsolvated complex may be used. Does it correspond to that of a diamagnetic complex?

Part B: Synthesis of Copper(II) Acetate Monohydrate

Safety Recommendations

Copper(II) sulfate pentahydrate (CAS No. 20919-8): This compound is not normally considered dangerous, but the usual precautions should be taken. ORL-RAT LD50: 300 mg/kg, ORL-HMN LDLo: 1088 mg/kg.

Sodium hydroxide (CAS No. 1310-73-2): This compound is harmful if swallowed, inhaled, or absorbed through the skin. It is extremely caustic, especially on wet surfaces, forming a strongly alkaline solution. Solid sodium hydroxide is hygroscopic. IPR-MUS LD50: 40 mg/kg.

Acetic acid (CAS No. 10908-8): Acetic acid is harmful if swallowed, inhaled, or absorbed through the skin. Concentrated acetic acid is very corrosive and has an unpleasant smell. It has been found to have effects on male fertility and to have behavioral effects on newborns. ORL-RAT LD50: 3530 mg/kg.

CHEMICAL DATA

Compound	FW	Amount	mmol	bp (°C)	mp (°C)	Density
$CuSO_4 \cdot 5H_2O$	249.6	250 mg	1.0		110[a]	2.284
$NH_3(aq)$[b], 50%	35.05	Sufficient amount				0.900
NaOH	40.0	80 mg	2.0		318	2.130
CH_3CO_2H	60.1	Minimum amount		116	16	1.049

[a] Loses 4 equivalents of H_2O.

[b] Also known as NH_4OH.

Required Equipment

Magnetic stirring hot plate, 10-mL beaker, magnetic stirring bar, Pasteur pipet, Hirsch funnel, clay tile, or filter paper.

Time Required for Experiment: 1.5 h.

EXPERIMENTAL PROCEDURE[4]

In a 10-mL beaker equipped with a magnetic stirring bar, dissolve 160 mg (1.0 mmol) of copper(II) sulfate or 250 mg (1.0 mmol) of copper(II) sulfate pentahydrate in 5.0 mL of water. Stir the mixture, and warm it to 40–50 °C on a sand bath to aid the dissolution.

Using a Pasteur pipet, add 50% NH_3 (aq) to the warm, stirred, light blue solution, until the intense blue color of the copper ammonium complex is evident. During this addition, a precipitate of copper hydroxide may form initially, but it will dissolve on further addition of the NH_3 (aq) solution.

Add 80 mg (2.0 mmol) of sodium hydroxide flakes to the deep blue solution, and stir the mixture for 15–20 min at 55–65 °C. A light blue solid of copper(II) hydroxide precipitates during this time. Allow the mixture to cool to room temperature and collect the precipitate by vacuum filtration using a Hirsch funnel. Wash the blue solid with three 2-mL portions of warm water.

Transfer the solid $Cu(OH)_2$ to a 10-mL beaker, and dissolve it in the minimum amount of 10% acetic acid. Warming on the sand bath with stirring aids the dissolution process. Concentrate the solution nearly to dryness (**HOOD**) by warming it on a sand bath under a slow stream of nitrogen. Collect the beautiful deep blue crystals that form by filtration using a Hirsch funnel. Dry the product on a clay plate or on filter paper.

Characterization of Product

Acquire the IR spectrum of the product as a KBr pellet. Determine the magnetic moment of the product (see Section 5.A). Does it correspond to that of a diamagnetic or paramagnetic complex at room temperature? If paramagnetic, how many unpaired electrons seem to be present?

QUESTIONS

1. What physical indications, other than magnetic moment, might lead one to conclude that a metal–metal bond is present?
2. Even when the magnetic susceptibility seems to indicate that a metal–metal bond is present, the low magnetic susceptibility might be due to other reasons. Discuss this point.
3. One of the largest classes of metal–metal bonded compounds are the metal carbonyl clusters. Discuss the bonding in two such members of this class.
4. Metal clusters are under active investigation as "mimics" to bulk metals in catalysis. Perform a literature search and discuss several examples of metal clusters that were studied in this manner.

REFERENCES

1. A good introduction to this interesting area may be found in the following references.
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