Lab Manual

Advanced Inorganic Chemistry Laboratory

2002-2003

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Advanced Inorganic Chemistry Experiments

Synthesis of Hexaaminechromium(III) nitrate (1 week)

Introduction to Coordination Complexes (1.5 weeks)

Synthesis of $[Ti(urea)_6]I_3$: An Air Stable d^1 complex (1.5 weeks)

Synthesis, Electrochemistry and Luminescence of $[Ru(bpy)_3]^{2+}$ (2.5 weeks)

Synthesis and Characterization of Macrocyclic Nickel(II) Complexes (2 weeks)

Synthesis of Ferrocene and derivatives (2 weeks)

NMR Inverstigation of Molecular Fluxionality: Synthesis of Allylpalladium Complexes (1.5 weeks)

Bioinorganic Experiments (Myoglobin binding) and or cytochrome C electrochemistry (1 or 2 weeks)

Appendix 1 Magnetic Susceptibility

Appendix 2 The Literature of Inorganic Chemistry

The Synthesis and Characterization of Ni(II) Complexes

Introduction: The term coordination chemistry is generally applied to transition metal complexes. However, the term "coordination compound" can be extended to any Lewis Acid-Base complex and thus to the vast majority of compounds known in inorganic chemistry. As applied to the transition metals, coordination compounds are among the most extensively investigated areas in the field of inorganic chemistry; and in fact, the first inorganic chemist to win a Nobel Prize, Alfred Werner, won the prize for work on coordination compounds. These compounds exhibit extensive and interesting spectral and magnetic properties in addition to widely varying structures and stoichiometries. In this experiment you will prepare several nickel salts and determine the spectrochemical ordering of several ligands using visible spectroscopy. Magnetic measurements will be made which will aid in the determination of their structure.

Experimental[1]:

a. **The preparation of $[Ni(en)_3]Cl_2 \cdot 2H_2O$.** Dissolve 6.0g of $NiCl_2 \cdot 6H_2O$ in 3mL of H_2O. A little warming improves the rate of dissolution. Cool the solution in ice while adding 5.0g (5.6 mL) of ethylenediamine. Add the ethylenediamine slowly because the reaction is quite exothermic. Cool. Add 15 mL of cold ethanol to initiate crystallization. Keep cold for 10 min. The collect the product on a Büchner funnel and wash with two 5 mL portions of ethanol. Dry in air. Record the yield.

b. **The preparation of $[Ni(NH_3)_6]Cl_2$.** Dissolve 3.0g of $NiCl_2 \cdot 6H_2O$ in 5 mL of warm H_2O in a 125 mL Erlenmeyer flask and add 5.8mL of concentrated NH_4OH. Cool with an ice bath and observe the precipitation of large violet crystals. Add 15 mL of cold ethanol to complete the precipitation. Collect the crystals on a Büchner funnel and wash with two 5 mL portions of ethanol. Dry in air. Record the yield.

c. The preparation of $[Ni(en)_2]Cl_2 \cdot 2H_2O$. 1.25 g of $NiCl_2 \cdot 6H_2O$ and 3.02 g of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ are gently refluxed in a mixture of 22 mL of methanol and 1.0 mL of H_2O for five minutes. Keep the solution hot and gravity filter into a 400 mL beaker. Rinse the flask twice with 1.5 mL of hot methanol. In order to initiate crystallization cool the blue solution on ice seed crystals are obtained by the following method: Take 1 mL of the cold solution in a test tube and add 1 or 2 mL of acetone dropwise. Scratch or shake until crystals form. The separation of two layers indicated too much acetone was added. Stir the bulk chilled solution. Add 15 mL of acetone dropwise for about two minutes. Add another 10 mL of acetone and an occasional seed crystal. When the seed crystals no longer dissolve add all of the seed crystals. Continue to stir for about 10 min. after the last acetone addition. Collect the blue crystals using a sintered glass filter. Wash twice with 7-10 mL of acetone and allow to dry. Record the yield.

Note: All filtrate may go down the drain.
This crystallization is tricky. **Follow all directions closely**, measure amounts of reagents accurately.

Characterization:

Obtain the visible spectra of the hexaminenickel(II) chloride (about 0.1 M) (in 3M NH_4OH,), the bis- and tris-ethylenediaminenickel(II) chloride (in H_2O) and the nickel(II) chloride hexahydrate (in H_2O). From these data you should determine the energy of the three transitions and the spectrochemical ordering of the ligands NH_3, H_2O, and en. (See Wulfsberg *Inorganic Chemistry* for a discussion of how this is done and for a general reference on Crystal/Ligand Field Theory).

The magnetic susceptibilities of each compound will be measured using the Johnson and Matthey susceptibility balance (See **Appendix 1**). $[Ni(en)_2]Cl_2$ appears to be a 4- coordinate Ni(II) complex (tetrahedral or square planar?) although it could be octahedral wih the two chloride ions in

the coordination sphere. Show how the magnetic data might permit you to eliminate some of the structural possibilities. Is the structure uniquely defined by the magnetic moment in this case? Why or why not?

References:

[1]Figgis*, et al*., *Prog. Inorg. Chem*. (1964).

Evans, *J. Chem. Soc.,* 2003 (1959). [Evan's Method reference]

To include in report (besides for the obvious): Visible Spectra (save Data in Excel and paste the graphs into your Word document) with molar absorptivities and the energies of each transition (there may be more than on observed for some of the complexes, Why?). Magnetic Susceptibilities (include example calculations, values of the gram, molar and corrected molar susceptibilities, the magnetic moment and the calculated number of unpaired electrons). Proposed structures of the complexes including nickel(II) chloride hexahydrate as well as crystal field diagrams with electrons for each complex.

Synthesis of $[Ti(urea)_6]I_3$: An air stable d^1 Complex

Lower-valent complexes of early transition metals

In general, the only complexes of the early transition metals (Sc, Ti, V) that are stable to oxygen and water are those with the metals in the highest oxidation states. These transition metals have a high affinity for oxygen. For example, the most common and air-stable complexes of vanadium incorporate the vanadyl ion, VO^{2+}. The most common titanium material is titanium dioxide, which is used as a whitener in paints.

However, lower-valent complexes of these transition metals are interesting as well. Care must be taken to exclude oxygen and water in the synthesis of the complexes because the starting materials and products will react with oxygen and/or water to give unwanted oxidized products. The complex $[Ti(urea)_6]I_3$ is unique in that it is reasonably air stable if kept dry. [It is believed to be stabilized by hydrogen bonding between adjacent urea molecules. This stability is kinetic rather than thermodynamic (Why?)]

Synthesis of $[Ti(urea)_6]I_3$

Materials needed: $TiCl_3$ (air and moisture sensitive!)
solution of 25g urea in 25 mL H_2O
solution of 50g KI in 30 mL H_2O

Prepare the two solutions needed on the day of the synthesis. Warming of the mixtures to 40-50 degrees C may be necessary. ***Quickly*** weigh out 4.00g $TiCl_3$ into a tared vial, tightly cap the vial.

Perform the next step in a properly vented fume hood!

Add the $TiCl_3$ to the solution of urea in a beaker quickly and carefully with stirring. Anhydrous $TiCl_3$ fumes in moist air. The reaction of $TiCl_3$ with water is very exothermic, and the resulting warm mixture (about 45-50 degrees C) should be filtered to remove any TiO_2 solid. Add the solution of KI with stirring. Cool the reaction mixture in an ice bath and collect the deep blue crystals of $[Ti(urea)_6]I_3$ by filtration. Dry the crystals by continuous suction and transfer them to a beaker. Store the beaker overnight in a dessicator filled with fresh dessicant, then transfer the crystals to a vial. The vial should be filled completely with tightly packed product and capped to exclude oxygen. There is a pronounced color change upon decomposition.

Characterization of$[Ti(urea)_6]I_3$

1. Determine the IR spectra of the reactants and product.
2. Determine the UV-Vis spectra of the product dissolved in KI solution and in a freshly prepared urea solution. Compare both spectra to that of $Ti(H_2O)_6^{3+}$ (available in most standard inorganic chemistry textbooks).

3. Determine the weight percent of titanium in the product. Heat a weighed amount of the product in a dry, weighed crucible to red heat **in the fume hood**. All components except titanium are decomposed to volatile products, and titanium is left behind as TiO_2. Decomposition proceeds with the evolution of a very unpleasant smoke. Weigh the residue.
4. Determine the magnetic moment of the complex using the Gouy balance.

Computational Chemistry

1. Build the structures $[Ti(water)_6]^{3+}$ and $[Ti(urea)_6]^{3+}$. Remember to designate the titanium atom as a cation with d^2sp^3 hybridization, +3 charge and a radius of 0.745 Å.
2. Minimize the structures.
3. Optimize the geometry of both molecules in ZINDO. Specify the state as doublet (one unpaired electron on the Ti^{3+}).
4. Do a configuration interaction calculation in ZINDO. Specify the state as doublet (one unpaired electron on the Ti^{3+}), and choose the SCF type as ROHF.
5. Create an electron density map of each molecule using the density gradient.

Report

1. Report the yield, percent yield and characterization of $[Ti(urea)_6]I_3$.
2. Report the obtained and theoretical percent titanium in the product. Using this information, determine the purity of the product.
3. Identify and assign pertinent bands in the IR spectra of urea and $[Ti(urea)_6]I_3$. They should be bands useful for distinguishing between urea bonded to Ti through N or O.
4. Using the results of the UV-Vis and IR spectra, determine the coordination sphere about the Ti ion and the ease with which the urea ligands are replaced. Is I^- coordinated to Ti^{3+}?
5. Report the magnetic moment of the complex. Compare your value with the spin-only value for a d^1 ion (2.73 B.M.) and the published value for $[Ti(urea)_6]I_3$. Is your result consistent with the assignment of the complex as a Ti^{3+} complex?
6. Analyze the computed spectra of the two molecules. How do they compare to the experimental results? Based on the modeling results of the urea complex, can you explain why there are two bands in the UV-Vis spectrum when only one is expected?
7. Look at the electron density maps of the two molecules. Based on these, can you explain why the urea complex is kinetically stable?

References

Pickering, Miles. Magnetic and spectral properties of an airstable d1 titanium complex. *J. Chem. Educ.* **1985** *62* 442.

Kassman, Allen J. Energy levels of d1 and d9 ions in chemically significant symmetry sites. *J. Chem. Educ.* **1974** *51* 605.

Wasson, John R.; Stoklosa, Henry J. Electronic spectra of low-symmetry d1 and d9 ion complexes. *J. Chem. Educ.* **1973** *50* 186.

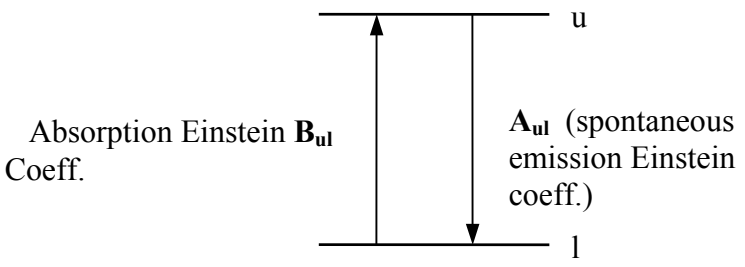
Synthesis, Electrochemistry and Luminescences of $[Ru(bpy)_3]^{2+}$

Purpose:

The purpose of this experiment is to synthesize tris-bipyridylruthenium(II) and to study the optical and electron-transfer properties of the Ru(II) complex.

Background:

Principles of Photochemistry



Spontaneous Emission Einstein Coefficient.

$$A_{ul} = \frac{8\pi h \nu_{ul}^3}{c^3} B_{ul} = \frac{64\pi^4 \nu_{ul}^3}{3hc^3} \mu_{ul}^2$$

The rate constant for absorption is proportional to the square of the transition moment.

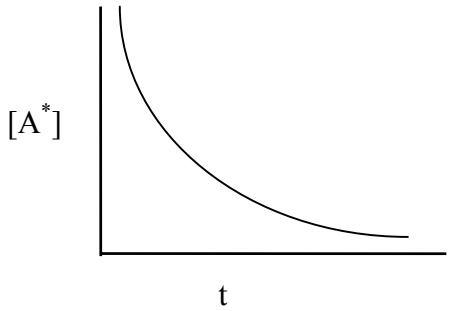
The rate constant for emission is based on the rate of absorption.
(the easier it is to go up, the easier it is to come down.)

Since the rate of population of particular states is what is important in this discussion ***Kinetics*** is utilized (the rate of decay of the excited state is measured).

$$v = \frac{-d[A^*]}{dt} = k[A^*] = A_{ul}[A^*]$$

$$\frac{d[A^*]}{[A^*]} = -A_{ul}\,dt \Rightarrow \ln\frac{[A^*]}{[A^*]_o} = -A_{ul}t$$

$$[A^*] = [A^*]_o e^{-A_{ul}t}$$



τ_o ——> Lifetime of the excited state. Time it takes to go from [A*] / e. or cut concentration of [A*] by 1/ e.

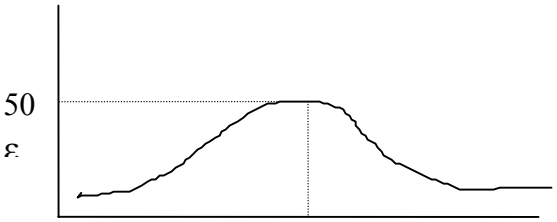
$$\frac{[A^*]_o}{e} = [A^*]_o e^{-A_{ul}\tau_o} \rightarrow \frac{1}{e} = e^{-A_{ul}\tau_o}$$

$$\ln(1/e) = -A_{ul}\tau_o \rightarrow -1 = -A_{ul}\tau_o$$

$$\tau_o = \frac{1}{A_{ul}}$$

τ_o, Intrinsic Lifetime (if only possible excited state deactivation is by fluorescence).

EXAMPLE: $Cr(urea)_3^{3+}$



$$\int \varepsilon d\tilde{\nu} = 9x10^4\, m^{-1}cm^{-2}s^{-1}$$

$$f = 4.33x10^{-9}\int \varepsilon d\tilde{\nu} = 3.9x10^{-4}$$

the magnitude of the oscillator strenght, *f* indicates that this transition is very weak, i.e. a forbidden transition.

$$A_{ul} = \frac{8\pi h \nu_{ul}^3}{c^3} B_{ul}$$

$$B_{ul} = \frac{2303c^2}{hN_a \nu_o} \int \varepsilon d\tilde{\nu}$$

$$A_{ul} = \frac{\tilde{\nu}^2 \int \varepsilon d\tilde{\nu}}{3.47x10^8} = 6.9x10^4\, s^{-1}$$

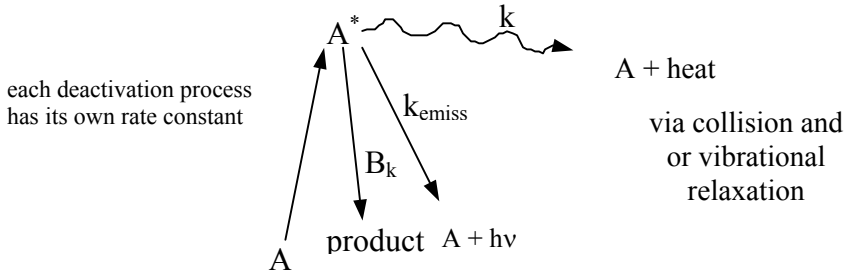
$$\tau_o = \frac{1}{6.9x10^4\, s^{-1}} = 1.45x10^{-5}\ \text{sec} \Rightarrow 14.5\mu\text{sec}$$

The experimental value of the lifetime is 2 μsec. Indicating other methods of deactivation of the excited state besides emission via fluorescence.

$\tau_o \approx \frac{10^{-4}}{\varepsilon_{max}}$ Approximate intrinsic lifetime.

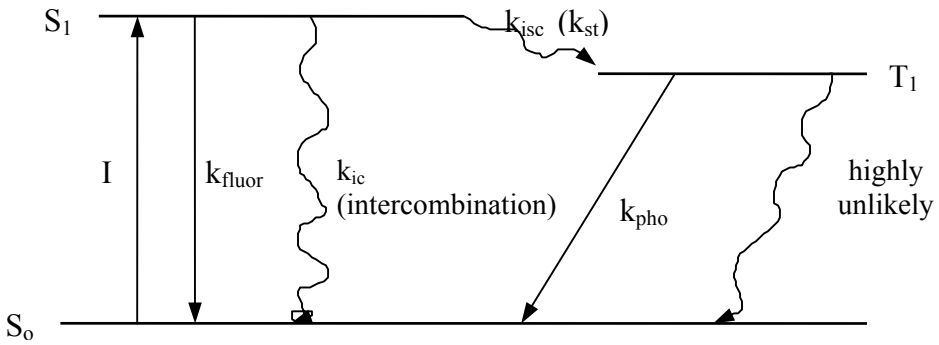
Large molar absorptivity yields shorter lifetimes
$\pi \rightarrow \pi^*$ 20,000 for molar absor. therefore the lifetimes are very short.

What is occurring to make the actual lifetime of $Cr(urea)_3^{3+}$ equal to 2 μsec.



$$\tau_o = \frac{1}{k[A_{ul}]} \Rightarrow \frac{1}{k_f} \Rightarrow \frac{1}{\sum_i k_i}$$

Kasha's Rule: All emission takes place from the lowest excited state.



If the triplet state is populated, then phosphorescence will occur.

Kinetics of Excited State Deactivation

Assume S_1 does not change concentration in time (Steady State).
(Rate of Production = Rate of Loss)
Assume first order.

$$I = k_f [S_1] + k_{ic} [S_1] + k_{isc} [S_1]$$

I, the intensity (# of photons / second)

Quantum Yield, ϕ can be defined for any process one is interested in.

$$\phi = \frac{rate\_of\_process}{rate\_of\_absorption\_of\_photons}$$

or

$$\phi = \frac{moles\_of\_process}{moles\_of\_photons}$$

A mole of photons is called an einstein.

$$\phi_f = \frac{k_f[S_1]}{I} = \frac{k_f[S_1]}{(k_f + k_{ic} + k_{isc})[S_1]} = \frac{k_f}{\sum k}$$

$$\phi_f = \frac{\tau_f}{\tau_o}$$ ← actual lifetime

$$\phi_f = \frac{1}{\sum k}\left(\frac{1}{\tau_o}\right) \Rightarrow \tau = \frac{1}{\sum_i k_i}$$

real lifetime

Quenching of Fluorescence

(A simple quenching process is as follows)

$$D \xrightarrow{h\nu} D^*$$

$$D^* \rightarrow D + h\nu' \quad k_e$$

$$D^* \rightarrow D + heat \quad k_2$$

bimolecular step $D^* + Q \rightarrow Q^* + D \quad k_q$

$$I = k_e [D^*] + k_2 [D^*] + k_q [Q] [D^*]$$

$$\phi_e = \frac{k_e [D^*]}{(k_e + k_2 + k_q [Q])[D^*]} \Rightarrow \frac{k_e}{k_e + k_2 + k_q [Q]}$$

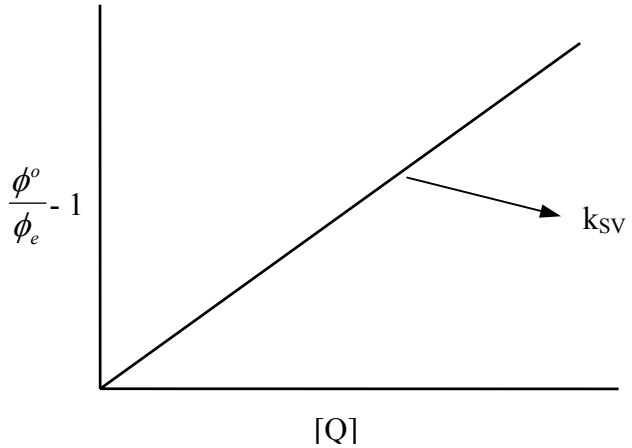
$$\phi^o = \frac{k_e}{k_e + k_2}$$

without quencher

Stern-Volmer Method:

$$\frac{\phi^o}{\phi_e} = \frac{(k_e + k_2) + k_q [Q]}{(k_e + k_2)} = 1 + \frac{k_q [Q]}{(k_e + k_2)}$$

$$k_{SV} = \frac{k_q}{(k_e + k_2)} \Rightarrow \frac{\phi^o}{\phi_e} - 1 = k_{SV} [Q]$$



$$k_{SV} = \frac{k_q}{k_e + k_2} \Rightarrow k_q \frac{1}{k_e + k_2} = k_q \tau$$

Lifetime without quencher.

bimolecular quenching rate constant

Quenching Mechanisms:

Quenching, as described in above is not the only means of energy transfer. In many systems, there is another ay excitation energy may be drained from D^*: electron transfer.

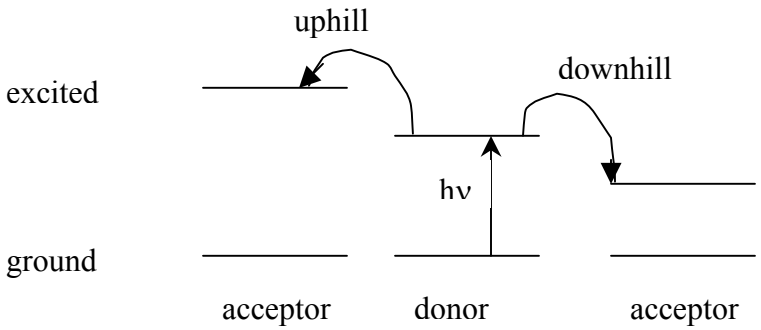
$$D^* + Q \xrightarrow{k_q} D + Q^* \qquad \text{energy transfer}$$

$$D^* + Q \xrightarrow{k_q} D^+ + Q^- \qquad \text{electron transfer (photoreduction of Q)}$$

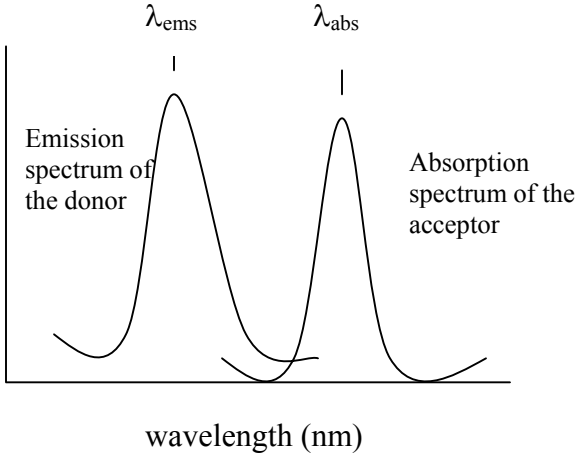
$$D^* + Q \xrightarrow{k_q} D^- + Q^+ \qquad \text{electron transfer (photooxidation of Q)}$$

Both reactions have D^* and Q as reactants, but the products are quite different. The Stern-Volmer equation doe not differentiate between the two schemes. Therefore, determining k_q does not give any insight into the mechanism of quenching. For a given system, k_q may reflect a combination of energy and electron transfer processes. There as some criteria, however, that govern the relative efficiencies of energy transfer and electron transfer. When applied to simple systems, these criteria help determine the predominant mechanism of quenching.

According to Förster, efficient energy transfer depends on a number of factors. Some of these are geometrical in nature; for example, the efficiency of energy transfer increases with decreasing distance between the donor and the acceptor. For a given distance, energy transfer will depend strongly on the relative energies of the excited states of the donor and acceptor. Efficient energy transfer is expected to occur if the excited state of the donor is higher in energy that the excited state of the acceptor, on which the excitation energy will reside ultimately.



In thermodynamic terms, this means that energy transfer is most effective when it is downhill energetically. This makes good chemical sense! In spectroscopic terms, this means that **the emission spectrum of the donor molecule must be blue-shifted (shorter wavelengths) relative to the absorption spectrum of the acceptor molecule.**



Electron transfer also is more efficient when it is thermodynamically downhill. However, the energetic requirement is not met by an explicit ordering of excited states, but rather by an ordering of the reduction potentials of donor and acceptor. Namely, for electron transfer to be effective at the thermodynamic standard state (1 bar gases, 1M solutions), the following must hold

$$\Delta G^o = -nF\Delta E^o$$

where n is the number of transferred electrons, F is Faraday's constant, and ΔE^o is the standard change in reduction potentials.

The considerations above provide a basis for the design of an experiment on the photochemistry of $[Ru(bpy)_3]^{2+}$. Using a fluorimeter, we obtain intensity data for the complex as a function of concentration of a quencher, such as aquated Fe^{3+}, $[Fe(H_2O)_6]^{3+}$. By obtaining the emission spectrum of the complex and the absorption spectrum of the quencher, the relevance of energy transfer processes in the quenching mechanism may be evaluated. Likewise, the importance of electron transfer may be estimated by considering the reduction potentials of donor and acceptor.

Photochemistry of $[Ru(bpy)_3]^{2+}$:

$[Ru(bpy)_3]^{2+}$ is highly luminescent. The emission, a "mixture" of fluorescence and phosphorescence, may be quenched by transfer of excitation energy or by electron transfer to several inorganic and organic species in solution.

Energy transfer: $^*[Ru(bpy)_3]^{2+} + Q \rightarrow [Ru(bpy)_3]^{2+} + {}^*Q$

Electron transfer: $^*[Ru(bpy)_3]^{2+} + Q \rightarrow [Ru(bpy)_3]^{3+} + Q^-$

Light-induced electron transfer reactions mediated by $[Ru(bpy)_3]^{2+}$ and related compounds are currently being considered as the basis for solar energy conversion technologies. The free energy released by the electron transfer may be used to generate H_2 and O_2 from H_2O.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+}$$

$$^*Ru(bpy)_3^{2+} + Q \xrightarrow{k_q} Ru(bpy)_3^{3+} + Q^-$$

$$2Ru(bpy)_3^{3+} + H_2O \rightarrow 2Ru(bpy)_3^{2+} + \frac{1}{2}O_2 + 2H^+$$

$$Q^- + H^+ \rightarrow Q + \frac{1}{2}H_2$$

Subsequently, the H_2 and O_2 may be used as fuels in a device known as a *full cell*. In a full cell, H_2 is "burned" to yield H_2O and free energy. The released free energy may be used in the form of useful electrical work, for example.

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O + \text{free energy}$$

Because the reaction is catalytic in $[Ru(bpy)_3]^{2+}$ and Q, and also regenerates H_2O, the chemical source of fuel, this technology is potentially clean. It is also independent of fossil fuels, since solar energy is the only source of free energy in the entire process.

Experimental:Synthesis of $[Ru(bpy)_3](BF_4)_2$

Place 1 mmol (ca. 275 mg) of $RuCl_3$ in a 50 mL Erlenmeyer flask with 10 mL 1,5-pentanediol, 1 mL of H_2O and a stir bar. Heat and stir until the metal salt dissolves, then add 3.5 mmol of 2,2'-bipyridine ($C_{10}H_8N_2$) and 0.5-1.0 mmol ascorbic acid and heat to boiling for 15 min. Allow the reaction mixture to cool, dilute it to about 40 mL with H_2O, and adjust the pH of this solution to about 8 using dilute sodium hydroxide. If necessary, filter the solution to clarify it, then precipitate the product by adding an excess (~5g) of $NaBF_4$. The orange solid recovered is $[Ru(bpy)_3](BF_4)_2$. This should be divided roughly into halves. One half can be recrystallized from water (with ethanol added if necessary), while the other half may converted into its hexafluorphosphate salt by metathesis with KPF_6 in water. The hexafluorphosphate salt will be used for the electrochemistry and electrogenerated chemiluminescence experiments.

1. **Preparation of Solutions. (10^{-3} =mM and 10^{-6} = μM)**
   a. In a volumetric flask, make a stock solution $[Ru(bpy)_3](BF_4)_2$. 25-50 mL of a solution which is about 25 μM in complex, use 0.5 M HCl as the solvent. Use the Beer-Lambert Law to determine the exact concentration of complex in the flask. ($A=\varepsilon cl$, where ε (at 452 nm) = 14, 600 $M^{-1}cm^{-1}$ and l= 1.00 cm. Dilute or concentrate the solution if it is far from 25 μM in concentration. By the way obtain the visible spectrum of this solution for later use (between 350- and 800 nm)

   b. Make a stock solution of $[Fe(H_2O)_6]^{3+}$ from $FeCl_3$ and 0.5 M HCl (aprox. 0.01 M).

c. From the stock solutions and additional 0.5 M HCl, make at least six solutions (4-5mL each), each having the same concentration of complex (about 8 μM) and a known concentration of quencher (a range of 0 to 3 mM is appropriate). **The concentration of complex in the "quenched" solutions should not be less than 4.5 μM.**

d. Prepare 100 mL of a solution containing 1.0 mM $[Ru(bpy)_3](PF_6)_2$ and 0.1 M tetrabutylammonium hexafluorophosphate using acetonitrile (*must be very dry!*) as the solvent.

e. Transfer 0.12 mmol of $[Ru(bpy)_3](BF_4)_2$ into a 100 mL volumetric flask with 25 mL of 0.2 M KH_2PO_4 buffer solution. Add 0.95 mL of tri-*n*-propylamine ($C_9H_{21}N$) to the flask. Dilute to the mark with acetonitrile. Mix thoroughly.

2. Absorption Spectra

Obtain the absorption spectrum (between 300-700 nm) of the quencher solution, $[Fe(H_2O)_6]^{3+}$. Dilute some of the $FeCl_3$ stock in 0.5 M HCl. If the solution is too concentrated (A>>1), dilute with 0.5 M HCl and try again. The spectral information will be useful in an evaluation of the quenching mechanism.

3. Emission Measurements

Immediately prior to the emission measurement, transfer enough solution to a 1 cm fluorescence cell, purge the solution in the cell for 30-40 sec. And cap immediately. The excitation wavelength should be set to the 452 nm absorption band of $[Ru(bpy)_3]^{2+}$. The emission spectrum should be collected between 400-700 nm. With the instrument set, obtain data for all six purged solutions (solutions c).

4. Redox Potentials of $[Ru(bpy)_3]^{2+}$ by Cyclic Voltammetry

Using ***solution d*** obtain the cyclic voltammograms showing the electrochemical processes of $[Ru(bpy)_3]^{2+}$. Not the type of reference and working electrodes used.

5. Electrogenerated Chemiluminescence (EGCL or ECL)

Place 80 mL of ***solution e*** into a 100 mL beaker, add a magnetic stir bar and cover with Parafilm. Place the platinum electrodes through the Parafilm, wraping a strip of Parafilm around each electrode so they do not fall through the covering. Attach alligator clips to the electrodes in the solution and connect the wires to the positive and negative terminals on the dc power supply (set to 3 volts). The luminescence will appear at the electrode surface which is connected to the positive terminal (the coiled electrode). Place the beaker on a stir plate. Stir the solution so that the reagents are constantly flowing past the electrode surfaces. Dim the lights and flip the power switch. Read about this phenomenon in the paper attached to this lab experiment.

Data Analysis

Using the Stern-Volmer equation and your data, calculate the K_{sv} for the $[Ru(bpy)_3]^{2+}/Fe^{3+}$ system. From this and the accepted value of $\tau = 600$ ns, calculate k_q for the reaction.

Next, determine the mechanism of the reaction. Recall that one cannot distinguish between energy and electron transfer processes by simply looking at the k_q value. Some of the questions that need to be answered in order to propose a mechanism are:

a. Is the emission spectrum of $[Ru(bpy)_3]^{2+}$ blue or red shifted relative to the absorption spectrum of $[Fe(H_2O)_6]^{3+}$?
b. Is transfer of an electron from the excited state of the Ru complex to $[Fe(H_2O)_6]^{3+}$energetically feasible at least in the standard state?

To answer this last question, we need to know the redox potential of $[Fe(H_2O)_6]^{3+}$ and the redox potential of the *excited* state of $[Ru(bpy)_3]^{2+}$, E^*. The former quantity can be obtained from any handbook or textbook as the reduction

potential of Fe^{3+} ion. The latter quantity has been determined by Lin *et al.* to be – 0.84 volts.

From a consideration of these energetic constraints, you will be able to propose a mechanism for the quenching reaction. For example, if the absorption of $[Fe(H_2O)_6]^{3+}$ shows no feactures in or immediately beyond the 600-650 nm region, where the $[Ru(bpy)_3]^{2+}$ complex emits, then energy transfer may be ruled out as a predominant source of quenching. On the other hand, if the free energy change for the redox reaction involving oxidation of the of the excited state of the Ru(II) complex by $[Fe(H_2O)_6]^{3+}$ is very large and positive, then electron transfer is not expected to be very efficient.

From the cyclic voltammogram determine the $E_{1/2}$ values for the Ru(III)/(Ru(II) and the $[Ru(bpy)_3]^{2+/+}$ processes.

Determine the free energy change for the above redox reaction. Then calculate the percentage of the reductive free energy that is carried off by the photon in the case where the photon is produced.

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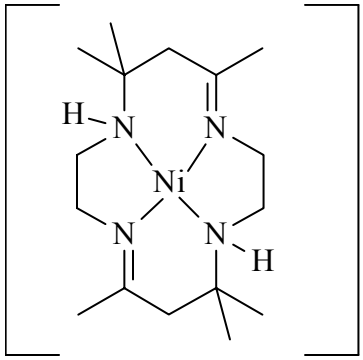
Synthesis and Characterization of a Macrocyclic Nickel Complex

A well-known nickel (II) macrocyclic complex is prepared and characterized as an example of a template condensation.

The complex 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienatonickel (II) iodide (see below) is prepared in two distinct steps.



I_2

$Ni[4,11\text{-}dieneN_4]I_2$

Firstly, the macrocyclic ligand is prepared by the Schiff's Base condensation of one mole of ethylenediamine monohydroiodide with two moles of acetone after the manner of Curtis and Hay (1). This experiment can be carried out easily in a three-hour lab period. The second step involves the reaction of the macrocyclic ligand dihydroiodide with nickel (II) acetate forming the nickel iodide complex. This complex is well known and well characterized in the literature (2).

Macrocyclic metal complexes have been studied extensively (3,4) because of their similarity to the macrocyclic metal complexes found in biological systems. The metal complexes of the porphin and corrin macrocycles provide a variety of compounds with manifold biological functions; this has stimulated the design of synthetic macrocycles with other functional capabilities.

The mechanism of the formation of the ligand appears to be quite complex; however, in reality it essentially involves only three steps shown in Figure #1.

Firstly, the base-catalyzed self-condensation of the acetone forms mesityl oxide. Secondly, a Michael addition of the amine to this α,β-unsaturated ketone produces a substituted amino-ketone (5). Any further reaction with the second amino group on the ethylenediamine is blocked by the acid (H^+).

The third step is a proton (H-bond network)-templated Schiff's Base condensation of the amine with the keto group of the other molecule, forming the cyclized product.

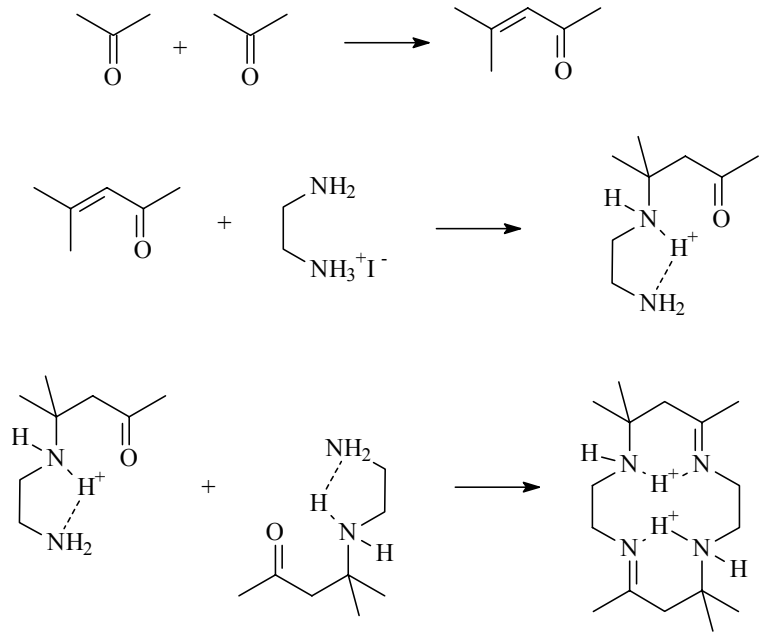


Figure 1

The order of the three steps has not been confirmed experimentally, but it is apparent that this mechanism or one similar to this forms the product as shown. The reaction takes place equally as well beginning with mesityl oxide (a) which would indicate that the first step is indeed likely the one shown here (1).

The formation of the nickel (II) complex with this protonated ligand depends upon the fact that the acetate ion is the conjugate base of a weak acid and thus deprotonates the macrocyclic ligand allowing the metal complex to form. The remaining iodide in the solution acts as the counter ion, so that the final product formed is the [Ni([14]-7,11-diene N_4])I_2.

The complex will be characterized by conductivity and infrared, uv-visible, and mass spectroscopies and the results compared to those in the literature.

Transition metal complexes usually show three types of electronic bands: d-d (crystal-field) transitions (300 - 1,500 nm) with $10^{-2} < \varepsilon < 10^{3}$ M^{-1} cm^{-1}; charge-transfer transitions (200 - 500 nm) with $10^{3} < \varepsilon < 10^{5}$ and transitions localized on the ligands. The last are n—>π* or π—>π*, with $10^{3} < \varepsilon < 10^{5}$ and usually occur in the ultraviolet region (unless the ligand itself is colored, of course). These are affected by coordination, the usual consequence being that the wavelengths shift slightly and the ε's are altered somewhat.

Experimental Procedure:

Preparation of 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca4,11-diene dihydrogen iodide ([14] 4,11-diene N_4 2HI)

The ligand, 4,11-Diene $N_4 \cdot 2HI$, is prepared using a method similar to that reported by Curtis and Hay (1). A 0.2 mol sample of ethylenediamine (13.2 mL) is put into 10 mL EtOH and cooled in an ice bath. A 0.20 mol (36.2 mL of 47%) sample of colorless hydroiodic acid is slowly added to the cool ethylenediamine solution being careful not to let the solution boil over, as this strong acid-strong base reaction is quite exothermic. Note that the diamine:HI ratio is 1:1; enH_2^{2+} is unproductive in the subsequent steps ! After the HI is added, 30 mL of acetone is added (0.4 mol) and the solution is allowed to stand for several hours (overnight). The white crystalline product is filtered off (Büchner funnel) and dried crudely by pulling air through it for 20 min. while it is on the filter paper. The yield is typically about 20%. Your lab instructor may ask you to reserve a portion of this for recrystallization, determination of the melting-point, infrared and mass spectra.

Preparation of 5,7,7,l2,l4,14-hexamethyl-1,48,11-tetraazacyclotetradeca4,11-dienatonickel(II)iodide, Ni([14]4,1, diene-N_4)I_2

During the 20-min drying period, a 50 mL round bottom flask with a reflux condenser and a magnetic stir bar is set up in a heating mantel and on a stir plate. (A less complex set-up using a beaker on a hot plate or steam bath and a glass rod as a stirrer also works well.). The crude ligand is weighed, and an equimolar amount of $Ni(OAc)_2 \cdot 4H_2O$

is dissolved in 40 mL MeOH. The ligand is then added to this, and the solution is refluxed for about 1 hr. After the heating period is over, the solution is filtered, and the volume reduced on a steam bath or at rotary evaporator until crystals begin to form. Then either: (1) stopper the flask and cool for an hour or more in an ice-bath, or (2) allow the solution to stand until the next lab period.

The yellow crystalline product is filtered off from the solution (Büchner funnel) and recrystallized from aqueous ethanol. (If the filtration is difficult, filter just a little at a time or fish the crystals out of solution and air dry them). The recrystallization should be done fairly rapidly using a rotary evaporator to reduce the volume of EtOH if necessary. The recrystallized product is then dried and stored in a desiccator until the physical measurements are to be made.

Conductivity. The molar conductivity is measured using the calibrated cell supplied. For this purpose, make up a 10^{-3}M acetonitrile solution (10 – 25 mL) of precisely known actual concentration of the nickel complex. Compare the measured value for this with a pair of "standard" electrolytes (*e.g.*, tetrabutylammonium iodide and methyldabconium iodide) in the same solvent.

Infrared Spectra.

Obtain the IR spectra of the ligand-precursor and of the nickel macrocycle, pressed as KBr pellets.

A characteristic feature of the ligand-precursor spectrum is the quaternary amine bands that caused the sloping baseline in the 2000 2800 cm^{-1} region. This is typical of all quaternary amines and should be totally absent in the spectrum of the nickel complex. Another characteristic band to look for in both spectra is the imine stretch at 1665 cm^{-1}. It is important to note that there are no bands in the 1700-1800 cm^{-1} region which would indicate the presence of the acetate ion. If a band should appear in this region, recrystallization of the complex is necessary.

KBr pellet IR spectra show strong bands centered around 3500 cm^{-1} which are due to moisture that is picked up during the grinding of the compound with KBr. The band that should be present (in the dry compound) at 3180 cm^{-1} due to N-H stretch is consequently shifted because of the resulting hydrogen bonding (1) and is not observed. This phenomenon is well known and cannot be prevented easily in the lab.

UV-Visible Spectrum

As ever, the initial goal is to obtain absorption bands which are within a sensibly readable range on the spectrophotometer (say $0.3 < A < 2.0$). This suggests that for solutions in a 1.0 cm cell, the concentration should be of the order of 10^{-2} M for testing suitability in the d-d band region, and about 10^{-4} M for the CT/π–π* region. The absorption spectrum of the nickel complex should be run in a solvent which is transparent throughout the region of interest: 220 – 600 nm, a criterion which is met by CH_3CN, the solvent also used for the conductance measurements. Submit the absorption spectra, together with the associated values of λ and ε. Is the d-d transition near 450 nm characteristic of high- or low-spin nickel(II) ? How does this result relate to the conductivity measurements ?

Mass spectra:

What mode of mass spectrometry was used for the ligand-precursor ? What does it suggest for the composition ? What mode of mass spectrometry was used for the mass spectrum of the complex, and what were the major ions obtained ? Note these on the MS charts you submit.

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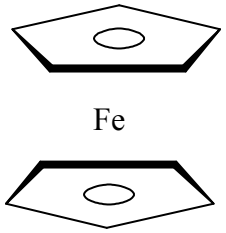
The Synthesis and Characterization of Ferrocene and its Derivitives

Modern organometallic chemistry of the transition metals began with the synthesis of bis(cyclopentadienyl)iron(II), ferrocene, $(C_5H_5)_2Fe$, in 1951 by Kealy and Pauson while attempting to synthesis fulvalene.[1] Sir. Geoffrey Wilkinson latter correctly assigned the structure of ferrocene as a sandwich-π complex. Since that time, cyclopentadienyl complexes of a wide variety of metals, including all of the transition elements, have been prepared.



Preparation of Ferrocene[2]: 60 g of KOH (pellets) are quickly ground with a mortar and pestle until the largest particles are less than 0.5 mm in diameter. Because it is very difficult to pulverize a large quantity of potassium hydroxide at one time, the pulverization should be carried out in batches of 15 g or less. It is important to minimize the exposure of the KOH powder to the atmosphere; therefore, it is stored in a tightly capped tared bottle.

A magnetic stirring bar, 120 mL of 1,2-dimethoxyetane, and 50 g of powdered KOH are placed in a three-necked flask. One side neck is stoppered and the other in connected to the T-tube bubbler and the nitrogen cylinder (see figure 1). While the mixture is slowly stirred and the flask is being flushed with a stream of nitrogen, 10.0 mL

of cyclopentadiene* is added. The main neck is then fitted with the dropping funnel with its stopcock open. Flush the flask with nitrogen for 10 min, and close the stopcock. A solution of 13.0 g of $FeCl_2 \cdot 4H_2O$ in 50 mL of dimethylsulfoxide is placed in the dropping funnel. The mixture is stirred vigorously. After 10 min., the nitrogen flow is lowered to a slow purge, and drop-by-drop addition of the iron(II) chloride solution is begun. The rate of addition is adjusted so that the entire solution is added in 45 min. Then the dropping funnel stopcock is closed and vigorous stirring is continued for a further 30 min. Finally, the nitrogen flow is stopped, and the mixture is added to a

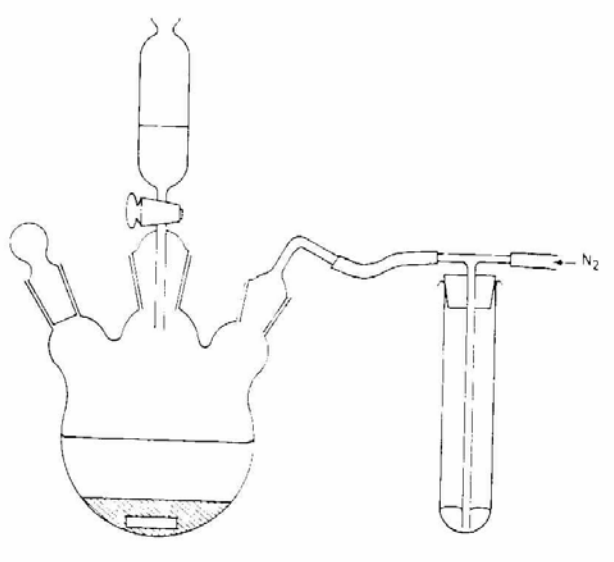


Figure 1. Apparatus for the preparation of ferrocene

mixture of 6M HCl and about 200 g of crushed ice. Some of the resulting slurry may be used to rinse the reaction flask. The slurry is stirred for about 15 min., and the precipitate is collected on a sintered-glass funnel and washed with four 25 mL portions of water. The moist solid is spread on a large watch glass and dried in air overnight. The yield should be about 11.5 g of ferrocene. This product should be quite satisfactory as an intermediate for subsequent syntheses. Half of the ferrocene is to be purified purified by

sublimation, for physical measurements. The material to be sublimed is placed in the inverted cover of a Petri dish so that none of the material is within 2 mm of the side wall of the cover. The Petri dish itself (the smaller of the pair) is inverted and placed in the cover, and the apparatus is then placed on a hot plate, shown in figure 2. The hot plate is gradually warmed up until the top surface of the apparatus is almost too hot to touch (setting 2 on the hot plate). The ferrocene will sublime onto the upper part of the dish.

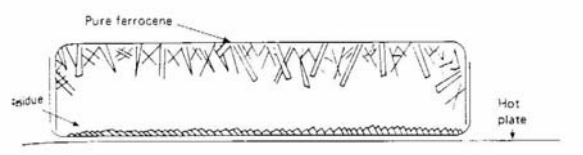


Figure 2. Sublimation of ferrocene

Characterization:

Include percent yield, melting point, and molar absorptivities (for UV-visible spectra)

1. Obtain the infrared spectrum as a KBr pellet, assign significant peaks.
2. Obtain the NMR spectrum and interprete.
3. Obtain the UV-visible spectrum in ethanol or hexane (~10^{-2} M) between 260-700 nm) and compare with the literature spectrum.[3]
4. Obtain the cyclic voltammogram in acetonitrile (scan from 0.0 to 1.0 V *vs*. Ag/AgCl) , The supporting electrolyte (tetrabutylammonium hexafluorophosphate) concentration should be about 0.01M. The ferrocene concentration in the solution should be approximately 3.2 x10^{-3} M.

Preparation of ferrocene derivatives: Since the initial preparation of ferrocene in 1951, numerous investigators have examined the reactions of this compound to determine wheather the cyclopentadienyl rings are similar to benzene in their chemical reactivity. In fact, many substitution reactions on the cyclopentadienyl rings do occur, and ferrocene

usually undergoes these reactions more readily than does benzene. These observations have been interpreted in indicate that the cyclopentadienyl rings in ferrocene are "more aromatic" than benzene. Regardless of how one defined aromaticity, it is at ferrocene readily undergoes electrophilic subsitution. One such reaction is the Friedel-Crafts acylation, which occurs 3x 10^6 times faster than with benzene.

$$Cp_2Fe + CH_3COCl \longrightarrow (Cp)(CpCOCH_3)Fe + (CpCOCH_3)_2Fe$$

Whether the mono- or diacetyl product is obtained is determined by the amounts of the reactants and the conditions of the reaction.

There are lots of other reactions, besides for acetylation, which are observed with ferrocene, such as sulfonation, and metallation by butyllithium.[4,5]

Note: Which ever ferrocene derivative is synthesized, it must be characterized by IR, UV-visible, melting point, and NMR, according to the methods discussed above for ferrocene.

References:

*The cyclopentadiene is prepared by the thermal cracking of dicyclopentadiene. Dicyclopentadiene is slowly distilled through a fractionating column, collecting only the material which refluxes below 44°C (cyclopentadiene boils at 42.5°C, and dicyclopentadiene at 170°C). We will need at least 50 mL of cyclopentadiene. The freshly distilled cyclopentadiene should be placed in a stoppered round-bottom flask, wrapped in aluminium foil.

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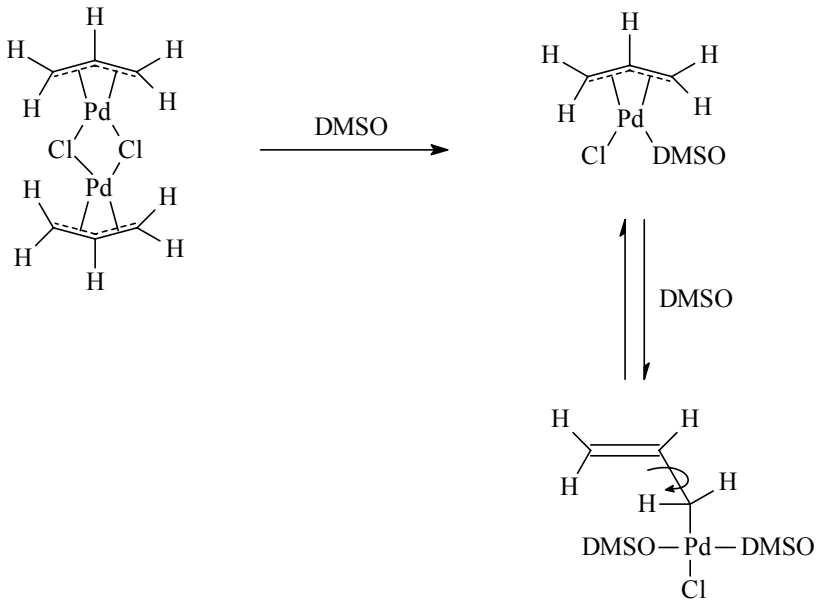
NMR Inverstigation of Molecular Fluxionality: Synthesis of Allylpalladium Complexes†

Introduction Palladium(II) forms a large variety of square planar organometallic complexes with various olefinic organic groups. In the case of the reaction of PdCl2 with allyl bromide, the allylpalladium-chloro complexes shown below may be synthesized.

Complexes between a metal salt and an olefin have been know since 1827. In the palladium complexes, the olefin donates electron density from its filled π orbital to an empty palladium π symmetry orbital. The palladium, in turn donates electron density from a filled σ orbital to the empty olefin π* orbital. This results in a lowering of the C-C bond order and a consequent lowering of the olefin IR absorption frequency.

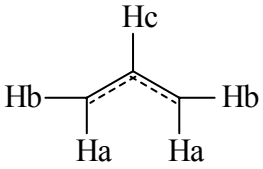
There is some difficulty in assigning the number of electrons donated by the allyl group. Viewing the allyl group as a neutral ligand (most convenient in this case), it would function a 1 (*monohapto*)- or 3 (*trihapto*)-electron donor, depending on whether it were σ or π bound. If π bound, the allyl group bidentate (occupies two coordination sites), while if σ bound, it is monodentate. Alternatively, the allyl group can be treated as an anion, where it functions as a 2- or 4- electron donor.

In noncoordinating solvents, the complex is found in the π form, where it is a 16-electron species[1] ,the most stable electronic arrangement for square planar geometry. (The simplest electron cound in this case is Pd^{2+} = 8 electrons, allyl anion = 4, 2 x chloride ion = 4, total = 16 electrons.) In a strongly complexing solvent, the dimer is cleaved, forming the monomeric species [Pd(η^3-C_3H_5)Cl(DMSO)], also a 16-electron system. (Pd^{2+} = 8 electrons, allyl anion = 4, 2 x chloride ion = 4, total = 16 electrons.) Additional, reversible, interaction with the relatively basic DMSO solvent allows conversion from the π allylic to the σ bonded form, [Pd(η^1-C_3H_5)Cl($DMSO)_2$]. This reaction is shown below.



Allylpalladium chloride dimer and DMSO cleavage.

When the allyl group is π bound, the complex is stereochemically rigid. There are three types of nonequivalent hydrogen atoms, shown below. Hydrogen *c* is clearly unique, being part of the only CH group. The *b* hydrogen atoms are *syn* to hydrogen *c*, and the *a* hydrogen atoms are *anti* to hydrogen *c*. The ^{1}H NMR spectrum would therefore show three signals. When the allyl group is σ bound, there is free rotation about the C-C single bond, thus rendering the *a* and *b* hydrogen atoms equivalent. The ^{1}H NMR spectrum would therefore show only two signals. Molecules showing this kind of motion are said to be fluxional.



Nonequivalent protons in the allyl group.

Experimental Section[1] Add 100 mg (0.56 mmol) of finely divided $PdCl_2$ to a 25 mL round bottom flask equipped with a magnetic stir bar. Add 3 mL of glacial acetic acid (graduated cylinder) and 3 mL of water. Attach a water condenser and place the apparatus in a bath on a magnetic stirring hot plate. Heat the mixture, with stirring, to 100 ^{o}C for 15 min. [**NOTE:** At the end of this time, if all of the solid has not dissolved,

filter the mixture by suction filtration, retaining the liquid.] Using an automatic delivery pipet, add 500 μL (3.69 mmol) of allyl bromide to the reaction solution through the top of the condenser. Heat the solution to 60 ^{o}C, with stirring, for 1 hr. [**NOTE:** Do not heat the solution over 60 oC or decomposition will occur!]. Cool the pale yellow mixture to room temperature. Add 3 mL of methylene chloride, swirl, and transfer the supernatant liquid into a clean 25 mL round-bottom flask using a Pasteur pipet. Repeat this extraction procedure two additional time if any solid remains. Combine the liquid extraction and dry them for 10 min. over anhydrous $MgSO_4$.

Transfer the liquid from the drying agent using a Pasteur filter pipet (see instructor) to a 25 mL round bottom flask, and rotary evaporate the solution to dryness. The resulting orange-yellow powder is the allylpalladium dimmer, di-μ-chloro(η3-allyl)dipalladium(II). Dry the product in a petri dish and determine the percentage yield. If desired, the product may be recrystallized from a minimum amount of hot methanol.

Characterization of the Product

Infrared Spectrum Obtain the IR spectrum of the product as a KBr pellet and compare the spectrum to that of allyl bromide.

NMR Spectra Dissolve one half of the product (~20 mg) in a minimum amount of $CDCl_3$ and obtain the ^{1}H NMR spectrum. Dissolve the other half of the product in a minimum amount of DMSO-d^{6} and obtain the room temperature ^{1}H NMR spectrum. Obtain the DMSO-d^{6} spectrum at 0, 40, and 60 ^{o}C in addition to that at room temperature.[2]

Questions 1. Account for the multiplicities in the ^{1}H NMR spectra of both products.

2. Write a mechanism showing the fluxionality of the monomer in DMSO. Be sure to show how the A and B protons can interconvert.

3. Why does the DMSO-d^{6} spectrum change with temperature?
4. From the literature give two other cases of organometallic molecular fluxionality not involving palladium.

References

† This experiment was adapted from: Szafran, Z.; Pike, R. A.; Singh, M. M., Microscale Inorganic Chemistry, John Wiley & Sons, Inc.:New York 1991 pg. 298.

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Bioinorganic Experiments

A. Binding of a Small Molecule to a Metalloprotein: Determination of the Equilibrium Binding Constant.

Purpose:

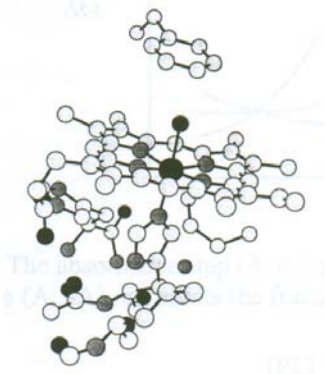
In this experiment we shall determine the equilibrium constant for the binding of thiocyanate and azide to horse heart myoglobin.

Background:

Proteins are capable of binding various small molecules by a variety of interactions. It is often the case that a given protein (e.g. human serum albumin) is cabalbe of binding several small molecules, with different affinities at different binding sites on the macromolecule. This binding is often reflective of the protein's native function. For example, myoglobin, a hem protein of mammalian physiology, reversibly binds dioxygen when in its iron(II) form:

$$Mb + O_2 \rightleftharpoons MbO_2$$

as the essential step of its function of intramuscular oxygen storage. Various heme proteins in their iron(III) ("ferric", $3d^5$-Fe(III) oxidation state) can no longer bind O_2, but will bind other, anionic molecules. This iron(III) form, aquametmyoglobin, thus binds one anion per molecule and (as in the case of the bound O_2) the anionic ligand is coordinated to the heme iron. This binding of the iron(III) hemes is one reason why azide and cyanide are so toxic. The picture below shows part of the myoglobin active-site architecture, with the macrocyclic heme iron coordinated below by a histidine imidazole nitrogen: the sixth coordination site is occupied by an H_2O, of which just the O-atom is shown.



Furthermore, this structure indicates why the binding interaction occurs with 1:1 stoichiometry. This simple binding also serves as a simple model for more complex protein/solute multiple binding phenomena.

The equilibrium for 1:1 stoichiometry is written as:

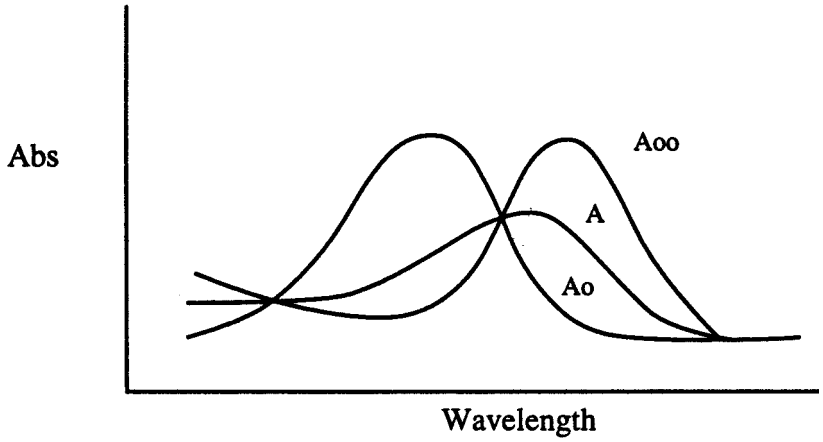
$$P + L \rightleftharpoons PL \qquad (1)$$

$$K = \frac{[PL]}{[P][L]} \qquad (2)$$

where, *P* is the protein, *L* is the ligand, and *PL* is the protein-ligand complex, the quantities bracketed above being their standing concentrations at equilibrium.

Such equilibria may be studied spectrohotometrically if some of the components absorb at convenient wavelengths, so that the concentrations of the species of interest may be obtained from optical absorbance measurements. This is indeed the case for myoglobins, hemoglobins and other heme proteins: the aromatic iron porphyrin (heme) prosthetic group has strong absorption bands in the visible region. There are normally in the 500-600 nm interval (α- and β-bands, ε =5,000-20,000 $M^{-1}cm^{-1}$) and at 380-435 nm (γ- or Soret band, ε= 80,000-200,000 $M^{-1}cm^{-1}$).

Consider the following hypothetical absorbance plot. A_∞ is the optical absorbance for the totally bound protein, in the presence of a saturating high concentration of ligand. *A* is the observed protein absorbance at any lesser, non-saturating concentration of ligand, and A_o is the absorbance of the protein in absence of any added ligand.



The absorbance step ($A-A_o$) reflects the fraction of the protein which is ligated, while ($A_\infty - A$) represents the fraction which is "free".

$$[PL] \propto (A-A_o) \qquad (3)$$

$$[P] \propto (A_\infty - A) \qquad (4)$$

$$\frac{[PL]}{[P]} = \frac{(A - A_o)}{(A_\infty - A)} \qquad (5)$$

So (2) and (5) give

$$K = \frac{(A - A_o)}{A_\infty - A)} \cdot \frac{1}{[L]} \qquad (6)$$

The total concentration of the ligand added, C_L, is partitioned by the reaction into bound and free ligand:

$$C_L = [L] + [PL]$$

$$[L] = C_L - [PL]$$

so that

If we have a small concentration of protein, and if the binding is not extremely strong, then we need a fairly high concentration of L to effect binding, and we have the situation that [PL] << [L]. Then it becomes true that [L] is approximately equal to C_L, which is the L measured into the system experimentally.

Therefore:
$$K = \frac{(A - A_o)}{A_\infty - A)} \cdot \frac{1}{[C_L]} \qquad (7)$$

If we then plot $(A-A_o)/ (A_\infty - A)$ vs. C_L the slope will be K.

The Mb(III) solutiuon will have been prepared for you prior to the lab period, by oxidizing a solution of horse heart Mb overnight with $[Fe(CN)_6]^{3-}$.

Procedure:

1. Chromatograph the oxidized solution to separate the myoglobin from the oxidizing agent. Using 0.1 M pH 7 phosphate buffer. On a Sephadex-G25 or BioGel-P4/P6 mini-column.
2. Prepare the spectrophotometer and obtain a spectrum (between 300-500 nm) to determine the concentration of the myoglobin solution. [Use the 0.1 M buffer as the blank]
3. The concentration of the myoglobin will be adjusted to ensure that the

concentration of ligand is at least 10x that of the protein. (The molar extintion coefficient of aquametmyoglobin is 188,000 $M^{-1}cm^{-1}$). The stock anion ligand solution is about 0.045 M (45 mM).

4. Add 3.0 mL of myoglobin to the UV cell. Run its spectrum *vs*. buffer blank. It's important to have precise and accurate absorption spectra. The myoglobin concentration should be about 3-5 μM.
5. 0.02 mL aliquots of ligand will be added and the spectrum run until at least seven spectra are obtained. The fourth spectrum should correspond to about 200 μM ligand. The arithmetic of these equilibria is such, that the more protein is ligated, the slower the rate of spectrum changing with respect to added ligand.
6. A_∞ will be obtained by finally adding several mg of the solid ligand to the solution.

Treatment of Data:

1. Select a wavelength at which you will collect absorbance data.
2. Adjust the absorbance readings for the dilution of the myoglobin solution caused by the additon of the ligand solution, so as to normalize them toward the nondiluted A-value.
3. Treat the data in the fashion described in the background section.
4. What is your value of K? Report the value also as $\log_{10}K$. How does it compare to the literature value?
5. If [L] is not considerably greater than [p], the data is not amenable to treatment in the above way. Why not?

Equilibrium and kinetic constants for the reaction of ferric horse myoglobin with anionic ligands, temperature = 21–23 °C. (From Blanck et al. 1961.)

Ligand	*p*H	*pK'*	*k'* (M^{-1} sec^{-1})	*k** (sec^{-1})
CN^-	7.0	4.75	1.7×10^2	3.0×10^{-3}
	8.2	5.33	4.0×10^2	1.9×10^{-3}
	9.1	5.36	3.1×10^2	1.4×10^{-3}
N_3^-	6.1	4.38	1.5×10^4	6.3×10^{-1}
	7.05	4.16	7.0×10^3	4.9×10^{-1}
	7.95	4.07	3.4×10^3	2.9×10^{-1}
	9.05	3.82	1.5×10^3	2.3×10^{-1}
OCN^-	7.1	2.38	4.1×10^2	1.7
	8.1	2.21	8.1×10^1	5.0×10^{-1}
	9.1	2.10	2.2×10^1	1.8×10^{-1}
SCN^-	6.2	2.40	8.1×10^3	3.2×10^{-1}
	7.1	2.35	5.9×10^3	2.7×10^1
	8.25	2.19	3.6×10^3	2.4×10^1
NO_2^-	7.0	1.87	4.7×10^2	6.4
	8.15	1.70	1.2×10^2	2.4
	9.15	1.57	4.2×10^1	1.1
F^-	6.05	1.85	2.0×10^1	2.9×10^{-1}
	7.00	1.80	3.6	5.7×10^{-2}
	7.95	1.75	5.3×10^{-1}	9.3×10^{-3}
	9.00	1.68	4.9×10^{-2}	1.3×10^{-3}
$HCOO^-$	6.05	1.28	6.8×10^2	3.5×10^1
	7.00	1.00	2.1×10^2	2.2×10^1
	8.05	0.96	7.3×10^1	8.1
	8.95	0.67	2.3×10^1	4.9
Imidazole	6.2	1.35	1.0×10^2	4.7
	7.1	1.80	2.8×10^2	4.5
	8.15	2.13	6.8×10^2	5.1
	9.1	1.98	5.4×10^2	5.7

* Calculated from the equilibrium constant and the combination velocity constant.

Above table from: Anonini, Eraldo and Brunori, Maurizio *Hemoglobin and Myoglobin in their Reactions with Ligands*. Amsterdam, North Holland Publishing Co., **1971**, p. 230.

B. Electrochemistry of Cytochrome *c*.

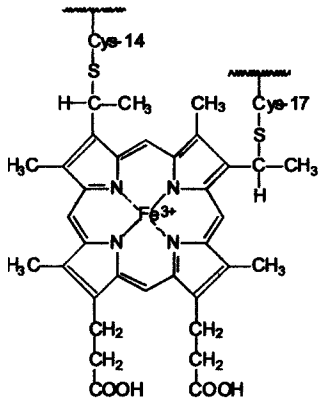
Purpose:

Your will use absorption spectrophotometry to measure the reduction potential of another heme-containing protein, cytochrome *c*.

Introduction:

Heme protein are very versitle. They act as carriers of oxygen in mammals (hemoglobin and myoglobin), studied in part A., carriers of electrons in photosynthesis and reperation (*e.g.*, cytochromes *b*, *c*, and *f*), and as catalyst for a variety of biochemical reactions involving O_2 (*e.g.*, cytochrome P450, catalase, cytochrome *c* oxidase).

Cytochrome *c* delivers electrons one at a time to cytochrome *c* oxidase, the enzyme responsible for the final step in respiration: the four-electron reduction of O_2 to H_2O. The redox-active part of cytochrome *c* is heme *c* (shown below), which is covalently linked to the protein via thioether bonds to cysteine residues. In the protein, the central iron atom is also ligated by one histidine nitrogen and one methionine sulfur. It is the iron atom that carries electrons, interconverting between the +3 and +2 oxidation states.



The heme *c* group.

Cytochrome *c* is brightly colored because the heme absorbs strongly in the visible range of the electromagnetic spectrum. Also, the reduced and oxidized forms of cytochrome *c* have different absorption spectra. Consequently, the reduction potentials of cytochrome *c* and indeed cytochromes in general are often determined via spectrophotometric methods.

We will use the so-called *equilibration method* for the determination of redox potentials. Consider the following reaction, where electrons are transferred between a cytochrome and a mediator compound D:

$$Cyt_{ox} + D_{red} \rightleftharpoons Cyt_{red} + D_{ox} \quad (1)$$

Application of the Nernst equation to this reaction yields:

$$\Delta E = \Delta E^o - \frac{RT}{F}\left(\frac{1}{n_{cyt}}\ln\frac{[cyt_{red}]}{[cyt_{ox}]} + \frac{1}{n_D}\ln\frac{[D_{ox}]}{[D_{red}]}\right) \quad (2)$$

where

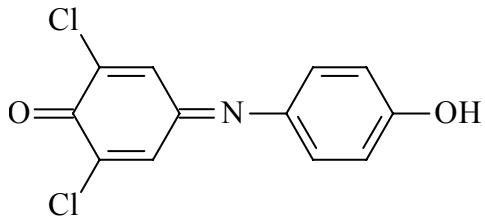
$$\Delta E^o = E^o_{cyt} - E^o_D \quad (3)$$

In this experiment, the standard electrode potentials will be given by using the biochemist's standard state, which is 1 atm and pH 7.

At equilibrium,

$$\Delta E^o = \frac{RT}{F}\left(\frac{1}{n_{cyt}}\ln\frac{[cyt_{red}]}{[cyt_{ox}]} + \frac{1}{n_D}\ln\frac{[D_{ox}]}{[D_{red}]}\right) \quad (4)$$

If we know the standard potential for species *D*, the standard reduction potential of cytochrome *c* may be measured from the equilibrium concentrations of cyt_{red}, cyt_{ox}, D_{red}, and D_{ox}. In order to use a spectrophotometer for these measurements, it is necessary that not only the cytochrome but also *D* have an absorption spectrum that depends on oxidation state. Ctyochrome *c* has a sharp absorption band at 550 nm in the reduced state. Upon oxidation, this band becomes weaker and broader. It is typical to determine the extent of reduction of cytochrome *c* by measuring the difference in absorbance at 550 nm and 570 nm. In this experiment, we will use the dye 2,6-dichloroindophenol (DCIP) as mediator. DCIP has a strong absorption band around 600 nm in the oxidized state and is transparent in this region in the reduced state.



DCIP (2,6-dichloroindophenol)

In a typical experiment, the first step consists of measuring the absorption spectrum of the system where both cyt *c* and DCIP are oxidized. The difference in absorbance between 550 nm and 570 nm is then denoted $A(cyt_{ox})$. The absorbacne at 600 nm is denoted $A(D_{ox})$. Then a reductant, such as sodium ascorbate, is titrated into the sample. After each addition of ascorbate, the absorbances A(cyt) and A(D) are measured as before. Finally, a small amount of a powerful reductant, such as sodium dithionite, is added to reduce the system fully. The absorbance $A(cyt_{red})$ and $A(D_{red})$ are measured as before.

The concentration ratios are given by:

$$\frac{[cyt_{ox}]}{[cyt_{red}]} = \frac{A(cyt_{red}) - A(cyt)}{A(cyt) - A(cyt_{ox})} \qquad (5)$$

$$\frac{[D_{ox}]}{[D_{red}]} = \frac{A(D) - A(D_{red})}{A(D_{ox}) - A(D)} \qquad (6)$$

Rearrangement of Equation (4) shows that a plot of $\ln\frac{[D_{ox}]}{[D_{red}]}$ vs. $\ln\frac{[cyt_{ox}]}{[cyt_{red}]}$ is a straight line with slope $\frac{n_D}{n_{cyt}}$ and an intercept of $\frac{n_c F}{RT}\Delta E^o$. Given that, in our case, $n_D = n_{cyt} = 1$, and the standard reduction potential of DCIP is 0.237 V at pH 6.5, the standard reduction potential of cytochrome *c* may be calculated easily.

Procedure:

Preparation of solutions: The class will require the followinf solutions. The workload will be distributed among the groups in the laboratory.

- 2.0 mg/ mL cytochrome c in deionized water (10 mL total)
- 1.0 mM potassium ferricyanide in deionized water (25 mL total)
- 50 mM citrate buffer , pH 6.5 (100 mL)
- 1.0 mM DCIP in deionized water (25 mL total)
- 10 mM ascorbic acid

The experiment: Please follow these procedures:

Put into a cuvette:

- 1 mL of the cytochrome c solution;
- 25 μL of the potassium ferricyanide solution (to oxidize any reduced cyrochrome c);
- 0.1 mL of the DCIP solution

- Mix well and measure the absorbance at 550, 570, and 600 nm. These readings correspond to fully oxidized cytochrome *c* and DCIP. Record the difference in absorbance between 550 and 570 nm, which we will call $A(cyt_{ox})$, and the absorbance at 600 nm, which we will call $A(D_{ox})$.
- Add 3 μL of the 10 mM ascorbate and mix. Allow one minute for the equilibration, then read the absorbace values A(cyt) and A(D) as before.
- Continue additions of ascorbate and absorbance readings until the absorbance at 600 nm is low and the readings are constant.
- Add a few crystals of sodium dithionite and take a final reading, corresponding to the fully reduced states $A(cyt_{red})$ and $A(D_{red})$.

Data Analysis:

From your absorbance readings and Equations (4)-(6), please determine the standard reduction potential of cytochrome c. Please take note of the electron stoichiometry of the reaction between cytochrome *c* and DCIP, so , $n_D = n_{cyt} = 1$. Therefore, the predicted value of the slope is 1; any significant deviations from this value result in lower accuracy in the final determination of the standard reduction potential of cytochrome *c*. Be sure to report values with the correct number of significant figures. Also, propagate the errors as needed. Compare your value of the standard reduction potential of cytochrome *c* with the literature value of +0.254 V at pH 7.0.

Reference:

The experiment is derived from:

Cammack, R. *Redox States and Potentials* In "Bioenergetics-A Practical Approach" (G. C. Brown, and C. E. Cooper, eds.) IRL Press, Oxford, **1995**, pp. 93-95.

Appendix 1

Magnetic Susceptibility

The magnetic properties of complexes in terms of unpaired electrons and their magnetic or spin properties are useful in determining structural features in transition metal compounds. Complexes that contain unpaired electrons are paramagnetic and are attracted into magnetic fields. Diamagnetic compounds are those with no unpaired electrons are repelled by a magnetic field. All compounds, including transition metal complexes, posses some diamagnetic component which results from paired electrons moving in such a way that they generate a magnetic field that opposes an applied field. A compound can still have a net paramagnetic character because of the large paramagnetic susceptibility of the unpaired electrons. The number of unpaired electrons can be determined by the magnitude of the interaction of the metal compound with a magnetic field. This is directly the case for 3d transition metals but not always for 4d or 5d transition metals, whose observed magnetic properties may arise not only from the spin properties of the electrons, but also from the orbital motion of the electrons.

The Johnson-Matthey magnetic susceptibility balance is very similar to the traditional Gouy balance but, instead of measuring the force which a magnet exerts on a sample, the opposite force that the sample exerts on a suspended permanent magnet is observed.

The mass susceptibility, χ_g , is calculated using:

$$\chi_g = \frac{C_{bal} l (R - R_o)}{10^9 m}$$

where: l = sample length (cm)

m= sample mass (g)

R= reading for tube plus sample

R_o = empty tube reading

C_{bal} = balance calibration constant

The molar susceptibility, χ_m, is then calculated by multiplying cg by the molecular mass of the substance. The molar susceptibility is positive if the substance is paramagnetic and negative if the substance is diamagnetic. The molar susceptibility measured is a sum of

the paramagnetic contribution from the unpaired electrons in the metal ion and the diamagnetic contributions from the ligands and the counter ions. This can be expressed by:

$$\chi_{total} = \chi_{para} + \chi_{dia.} \text{ (L+ ions)}$$

Therefore

$$\chi_{para} = \chi_{corr.} = \chi_{total} - \chi_{dia.}$$

Note: $\chi_{dia.}$ is negative

The diamagnetism factors for common ligands and ions as well as the Pascal constants used to calculate the diamagnetic corrections for complex ligands can be found at the end of the lab write up. Once the $\chi_{corr.}$ Is determined μ_{eff} can be calculated using:

$$\mu_{eff} = \sqrt{8\chi_{corr}T}$$

And it follows that in the absence of spin-orbit coupling the number of unpaired electrons can be determined by:

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

Pascal's Constants

TABLE I. *Molar susceptibilities* (χ_L) *of common ligands and ions*
All values $\times 10^{-6}$/mole

Cations		Anions	
Li^+	−1·0	F^-	−9·1
Na^+	−6·8	Cl^-	−23·4
K^+	−14·9	Br^-	−34·6
Rb^+	−22·5	I^-	−50·6
Cs^+	−35·0	CN^-	−13·0
NH_4^+	−13·3	CNS^-	−31·0
Mg^{2+}	−5·0	CO_3^{2-}	−28·0
Ca^{2+}	−10·4	ClO_4^-	−32·0
Zn^{2+}	−15·0	NO_2^-	−10·0
Hg^{2+}	−40·0	NO_3^-	−18·9
		OH^-	−12·0
		O^{2-}	−7·0
		$PtCl_6^{2-}$	−148
		SO_4^{2-}	−40·1
		SO_4H^-	−35·0

Common ligands

H_2O	water	−13	$C_2O_4^{2-}$	oxalate	−25
NH_3	ammonia	−18	$C_3H_2O_4^{2-}$	malonate	−45
N_2H_4	hydrazine	−20	$C_4H_7O_2^-$	acac	−52
CO	carbonyl	−10	$C_5H_5^-$	cyclopenta-dienyl	−65
CHO_2^-	formate	−17			
CH_4N_2O	urea	−34	C_5H_5N	py	−49
CH_4N_2S	thiourea	−42	$C_9H_6NO^-$	oxinate	−86
C_2H_4	ethylene	−15	$C_{10}H_8N_2$	bipy	−105
$C_2H_3O_2^-$	acetate	−30	$C_{12}H_8N_2$	phen	−128
$C_2H_4NO_2^-$	glycinate	−37	$C_{16}H_{14}N_2O_2^{2-}$	salen	−182
$C_2H_8N_2$	en	−46	$C_{10}H_{16}As_2$	diarsine	−194
			$C_{32}H_{16}N_4^{2-}$	phthalo-cyanine	−422

Evan's Method

Another useful method for measuring magnetic susceptibilities is the nmr, or Evan's method. The shifts of the proton resonance lines of inert reference molecules in solution caused by the presence of dissolved paramagnetic substances are given by the expression

$$\frac{\Delta H}{H} = \frac{2\pi}{3}\Delta\kappa$$

where $\Delta\kappa$ is the change in volume susceptibility. For aqueous solutions of paramagnetic substances, about 2 persent of *t*-butanol is added as a reference substance, and an aqueous *t*-butanol solution of the same concentration is used as an external reference in a capillary tube in the nmr tube. Two resonance lines are generally observed for the methyl protons of the *t*-butanol because of the differences in volume susceptibilities of the two solutions, with the line for the paramagnetic solution at the higher frequency. The gram susceptibility of the solute id given by the expression

$$\chi = \frac{3}{2\pi C}\cdot\frac{\Delta H}{H} + \chi_o + \frac{(d_o - d_s)\chi_o}{C}$$

where C is the solute concentration in grams per milliliter of solution, χ_o is the gram susceptibility of the solvent (-0.72×10^{-6} for dilute aqueous *t*-butanol solutions), d_o is the density of the solvent, and d_s the density of the solution. For highly paramagnetic substances, the last term can often be neglected.

Appendix 2

The Literature of Inorganic Chemistry

The following list includes books, monographs and journals which you may find useful in Advanced Inorganic. Many of these sources will be especially useful in selecting an appropriate independent project for the last part of the course.

General Inorganic Chemistry Textbooks

A. Basic

a. *Inorganic Chemistry*, second edition, D. F. Shriver, P. W. Atkins, and C. H. Langford; W. H. Freeman and Co., New York, **1994**. 913 pp.
b. *Inorganic Chemistry*, J. R. Bowser; Brooks-Cole Publishing Co., Pacific Grove, CA, **1993**. 805 pp.
c. *Modern Inorganic Chemistry*, second edition,W. L. Jolly; McGraw-Hill Book Co., New York, **1991**. 655 pp.
d. *Introduction to Modern Inorganic Chemistry*, third edition, K. M. Mackay and R. A. Mackay; International Textbook Company, London, **1981**. 349 pp.
e. *An Introduction to Inorganic Chemistry*, K. F. Purcell and J. C. Kotz; Saunders College Publishing, Philadelphia, **1980**. 637 pp.
f. *The Principles of Inorganic Chemistry*, W. L. Jolly; McGraw-Hill, Inc., New York, **1976**. 376 pp.

B. Advanced

a. *Concepts and Models of Inorganic Chemistry*, third edition, B. E. Douglas, D. H. McDaniel and J. J. Alexander; John Wiley & Sons, Inc., New York, **1994**. 993 pp.
b. *Inorganic Chemistry: Principles of Structure and Reactivity*, fourth edition, J. E. Huheey, E. A. Kelter and R. L. Kelter; Harper Collins College Publisher, New York, **1993**. 1052 pp.
c. *Inorganic Chemistry, A Unified Approach*, second edition, W. W. Porterfield; Academic Press, Inc., New York, **1993**. 921 pp.
d. *Advanced Inorganic Chemistry*, fifth edition, F. A. Cotton and G. Wilkinson; Wiley-Interscience, New York, **1988**. 1455 pp.
e. *Chemistry of the Elements*, N. N. Greenwoo and A. Earnshaw; Pergamon Press, New York, **1984**. 1542 pp.
f. *Inorganic Chemistry, A Modern Introduction*, T. Moeller; John Wiley & Sons, New York, **1982**. 846 pp.
g. *Inorganic Chemistry*, A. G. Sharpe; Longman, London, **1981**. 682 pp.
h. *Inorganic Chemistry*, K. F. Purcell and J. C. Kotz; W. B. Saunders, Philadelphia, **1977**. 1116 pp.

C. Descriptive Inorganic Chemistry

a. *Principles of Descriptive Inorganic Chemistry*, G. Wulfsberg; University Science Books, Mill Valley, CA, 1991. 461 pp. This is an optional text for CHE 514.
b. *Simple Inorganic Substances*, R. T. Sanderson; R. E. Krieger Publishing Co., Malabar, FL, 1989. 500 pp.
c. *Chemistry of the Non-Metals*, R. Steudel, English edition by F. C. Nachod and J. J. Zuckerman; Walter de Gruyter, Berlin, 1977. 402 pp.

Inorganic Synthesis and Characterization

1. *Inorganic Experiments*, J. D. Woollins, editor; VCH Publishers, New York, NY, 1994. 286 pp.
2. *The Synthesis and Characterization of Inorganic Compounds*, W. L. Jolly; Prentice-Hall, Inc., Englewood Cliffs, NJ, 1970; reissued by Waveland Press, Prospect Heights, IL, 1991. 590 pp.
3. *Microscale Inorganic Chemistry, A Comprehensive Laboratory Experience*, Z. Szafran, R. M. Pike, and M. M. Singh; John Wiley & Sons, Inc., New York, 1991. 363 pp.
4. *Preparative Acetylenic Chemistry*, second edition, L. Brandsma; Elsevier Scientific Publishing Co., New York, 1988. 321 pp.
5. *Synthesis and Technique in Inorganic Chemistry*, second edition, R. J. Angelici; University Science Press, Mill Valley, CA, 1986. 237 pp.
6. *The Manipulation of Air-Sensitive Compounds*, second edition, D. F. Shriver and M. A. Drezdzon; John Wiley & Sons, Inc., New York, 1986. 326 pp.
7. *Synthesis of Acetylenes, Allenes and Cumulenes*: *A Laboratory Manual*, L. Brandsma and H. D. Verkruijsse; Elsevier Scientific Publishing Co., New York, 1981. 276 pp.
8. *Organic Syntheses Via Boranes*, H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland; John Wiley and Sons, Inc., New York, 1975. 283 pp.
9. *Synthetic Inorganic Chemistry*, W. L. Jolly; Prentice-Hall, Inc., Englewood Cliffs, NJ, 1960. 196 pp.
10. *Inorganic Preparations, A Laboratory Manual*, H. F. Walton; Prentice- Hall, Inc., New York, 1948. 183 pp.

Physical Inorganic techniques

1. *Physical Methods for Chemists*, second edition, R. S. Drago; Saunders, Philadelphia, 1992. 750 pp.
2. *Structural Methods in Inorganic Chemistry*, second edition, E. A. V. Ebsworth, D. W. H. Rankin, and S. Cradock; CRC Press: Boca Raton, FL, 1991. 510 pp.
3. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, third edition, K. Nakamoto; John Wiley and Sons, Inc., New York, 1978. 448 pp.
4. *Spectroscopic Methods in Organometallic Chemistry*, W. O. George, editor; Butterworth's, London, 1970. 224 pp.
5. *Physical Methods in Advanced Inorganic Chemistry*, H. A. O. Hill and P. Day; Interscience Publishers, New York, 1968. 627 pp.
6. *Physical Methods in Inorganic Chemistry*, R. S. Drago; Reinhold Publishing Corporation, New York, 1965. 430 pp.

Applied and Industrial

1. *Applied Inorganic Chemistry*, T. W. Swaddle; University of Calgary Press, Calgary, CA, 1990. 331 pp.
2. *Industrial Inorganic Chemistry*, W. Buchner, R. Schliebs, G. Winter, and K. H. Buchel; VCH Publishers, New York, 1989. 614 pp.

Monographs and Serials

A. General Inorganic Chemistry

1. *Comprehensive Inorganic Chemistry*, A. F. Trotman-Dickinson, editor; Pergamon Press, 1973. Five volumes. Coverage is by elements (or groups of elements) with additional chapters on topics such as organometallics.
2. *Inorganic Chemistry*, C. S. G. Phillips and R. J. P. Williams; Oxford University Press, New York, 1966. Two volumes. 685 + 683 pp.
3. *Handbuch der Preparativen Anorganische Chemie*, Bd. 3, G. Brauer; Enke, Stuttgart, 1981. The third edition of this useful book of preparations is available only in German. The UK Chemistry-Physics library has the first and second editions in English translation (second edition, Academic Press, Inc., New York, 1963-1965, two volumes. 1859 pp.).

B. Organometallics

1. *Metal Clusters*, M. Moskovits, editor; John Wiley and Sons, Inc., New York, 1986. 313 pp.
2. *Dictionary of Organometallic Compounds*, J. Buckingham, Executive editor; Chapman and Hall, London, 1984. Three volumes, plus many supplements.
3. *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone and E. W. Abel, editors; Pergamon Press, 1982. Nine volumes. This is the single most useful source of information on organometallic chemistry. An updated version will be available in late 1995
4. *Organometallic Chemistry*, H. Zeiss, editor; A.C.S. Monograph Series, No. **147**, Reinhold Publishing Corporation, New York, 1960. 549 pp.

C. Coordination compounds

1. *Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties and Applications of Coordination Compounds*, G. Wilkinson, R. D. Gillard, and J. A. McCleverty, editors; Pergamon Press, New York, 1987. Seven volumes. Vol. 1 is Theory and Background; Vol. 2 is Ligands; Vols. 3-5 are surveys by metal; Vol. 6 is applications; and Vol. 7 is indexes.
2. *Coordination Compounds*, S. F. A. Kettle; Appleton-Century-Crofts, New York, 1969. 220 pp.
3. *Classics in Coordination Chemistry, Part I: The Selected Papers of Alfred Werner*, G. B. Kauffman, editor; Dover Publications, Inc., New York, 1968. 190 pp.
4. *Elementary Coordination Chemistry*, M. M. Jones; Prentice-Hall, Inc., Englewood Cliffs, NJ, 1964. 473 pp.
5. *The Chemistry of the Coordination Compounds*, J. C. Bailar, Jr., editor; A.C.S. Monograph Series **131**, Reinhold Publishing Corporation, New York, 1956. 834 pp.

D. Synthesis and characterization

1. *Inorganic Syntheses*, 1939-1977; McGraw-Hill, Inc, New York (seventeen volumes); 1978-1995, John Wiley and Sons, Inc., New York (volumes 18 to 30). Nearly annual volumes of checked syntheses.
2. *Organometallic Syntheses*: Volume 1, Transition-Metal Compounds, R.B. King, 1965; Volume 2, Nontransition-Metal Compounds, J. J. Eisch, 1981; Academic Press, New York. Volume 3, 1986, Volume 4, 1988, R. B. King and J. J. Eisch, editors; Elsevier, New York. This has become a series like *Inorganic Syntheses*. Preparative details for many important starting materials.
3. *Preparative Inorganic Reactions*, W. L. Jolly, editor; John Wiley and Sons, Inc., New York, 1964-1971. Seven volumes.
4. *Experimental Inorganic Chemistry*, R. E. Dodd and P. L. Robinson; Elsevier Publishing Company. New York, 1954. 424 pp.

Selected Journals and Serials

A. Multidisciplinary Journals

1. Journal of the American Chemical Society
2. Journal of Chemical Education
3. Angewandte Chemie, International Edition in English
4. Chemische Berichte
5. Journal of the Chemical Society, Chemical Communications

B. Inorganic Chemistry

1. Inorganic Chemistry
2. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
3. Polyhedron
4. Journal of the Chemical Society, Dalton Transactions
5. Inorganica Chimica Acta

C. Organometallic chemistry

1. Organometallics
2. Journal of Organometallic Chemistry

D. Metals and complexes

1. Journal of Coordination Chemistry

E. Solid state chemistry

1. Journal of Solid State Chemistry
2. Chemistry of Materials