Synthesis of Macrocyclic Complexes of Nickel(II)

An example of a metal ion templated cyclization reaction

Objectives:  
- Synthesis of coordination complexes (C)  
- Use of metal ion as a template for a cyclization reaction (C)  
- Use $^1$H NMR and infrared spectra to characterize structural changes (T)  
- Determination of magnetic susceptibility by NMR method (T)

Time Required:  Two lab periods.

Introduction

A major portion of inorganic chemistry may be called coordination chemistry, that is the investigation of the properties, structure, and reactions of complexes formed by ligands coordinated to a transition metal center. Complexes with chelating ligands generally have increased stability relative to those of monodentate ligands, and even greater stability when the donor atoms are incorporated into a cyclic ligand that surrounds the metal ion, commonly referred to as a macrocyclic ligand. The fact that some macrocyclic ligands can be made only in poor yields, or not at all, in the absence of metal ions has lead to the concept of the "template effect", i.e., that the metal coordinates and properly arranges the ligand precursor fragments in its coordination sphere, thereby assisting the linking process that produces the macrocyclic ligand.

One of the earliest examples of a templated reaction involves the reaction of ethylenediamine (en), H$_2$NCH$_2$CH$_2$NH$_2$, with acetone in the presence of nickel(II) ion. The products of this reaction A and B are remarkable in their stability under conditions that would destroy many other nickel(II) compounds, i.e., strongly acidic, oxidizing and reducing conditions.

In this sequence of experiments you will prepare [Ni(en)$_3$](BF$_4$)$_2$ and complex A by allowing a solution of the complex in acetone to stand from one lab period to the next. The very high kinetic stability of this complex will be illustrated by the oxidation and reduction of A without dissociation of the ligand (decomposition) from the metal. The sequence of reactions to be completed is:

\[
\text{[Ni(OH$_2$)$_6$](BF$_4$)$_2$ + 3 en} \rightarrow \text{[Ni(en)$_3$](BF$_4$)$_2$}
\]

In an six-coordinate environment a d$^8$ ion such as nickel(II) should have a t$_{2g}$, e$_g$ configuration and according to Hund’s rule,

\[
\begin{align*}
\text{[Ni(OH$_2$)$_6$](BF$_4$)$_2$ + 3 en} \rightarrow & \quad \text{[Ni(en)$_3$](BF$_4$)$_2$} \\
\text{[Ni(en)$_3$](BF$_4$)$_2$} \rightarrow & \quad \text{[Ni(en)$_3$}(\text{acetone})_{2}\text{](BF$_4$)$_2$} \\
\text{[Ni(en)$_3$}(\text{acetone})_{2}\text{](BF$_4$)$_2$} \rightarrow & \quad \text{[Ni(en)$_3$}(\text{acetone})_{2}\text{](BF$_4$)$_2$}
\end{align*}
\]

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1. The early history of this and related chemistry is recorded in Curtis, N. F. Coord. Chem. Rev. 1968, 3, 3.
2. Actually both A and B are formed; however, the amount of B is small and its greater solubility allows for the isolation of pure A.
solution. Information on magnetic susceptibility and magnetic moment are given in the Appendix to this experiment.

**Procedure**

**Synthesis of [Ni(en)](BF$_4$)$_2$**. Dissolve a 30 mmol portion of [Ni(OH)$_2$]$_2$(BF$_4$)$_2$ in 40 mL of water and, with efficient stirring, add 100 mmol of ethylenediamine. After addition is complete, stir the solution for a few minutes and then gravity filter to remove any solid. Evaporate the solution until crystallization begins, then cool the solution in an ice-bath for 15 min to complete the crystallization. Separate the violet product by suction filtration, wash with 10 mL of ice-cold ethanol, then with 10 mL of ether and allow the material to air dry. Determine the quantity of dry product and obtain infrared (KBr pellet) and electronic (aqueous solution) spectra.

Add ca. 0.2 g of the violet complex to 1-2 mL of conc. HNO$_3$. Record your observation.

Dissolve ca. 0.2 g of the violet complex in 1-2 mL of water and add 50 mg of NaBH$_4$ and briefly heat the solution. Record your observation.

**Synthesis of Complex A.** Dissolve [Ni(en)$_3$](BF$_4$)$_2$ in acetone (1 g complex per 2.5 mL acetone; use all but 1-2 g of your ethylenediamine complex) in an appropriate sized Erylenmeyer flask. Stopper the flask tightly with a rubber stopper and allow the solution to stand in the dark until the following week.

To the dark orange solution that results, slowly add anhydrous ethanol while stirring the solution until a slight cloudiness persists (this will take ca. 10 mL per gram of complex). At this point scratch the bottom/wall of the flask with a glass stirring rod until crystallization begins. Slowly add another 5-10 mL of ethanol per gram of complex and then place the flask in an ice-bath for 30 min to complete crystallization. Collect the yellow crystals by suction filtration and wash them with 5 mL portions of absolute ethanol and allow it to air dry. Determine the quantity of dry product and obtain infrared (KBr pellet) and electronic (acetone) spectra.

**Oxidation of complex A to complex C.** Place approximately 200 mg (accurately weighed) of A contained in a large test tube, add 1 mL of concentrated HNO$_3$. Bring the mixture to a boil by carefully heating the tube in the flame of a Bunsen burner. Observe the evolution of NO, fumes and the formation of a dark orange solution. Cool the tube briefly, then add a solution of about 200 mg of NH$_4$PF$_6$ in 1 mL of water. Swirl to mix and cool the tube in an ice bath for 15 min. Collect the light yellow crystals by suction filtration and wash them with 5 mL portions of ice-water, ice-cold ethanol and ether. Allow the product to air dry. Determine the quantity of dry product and obtain infrared (KBr pellet) and electronic (acetone) spectra.

**Reduction of complex A to complex D.** Suspend about 200 mg (accurately weighed) of A in 5 mL of water in a small beaker and heat the mixture to about 80 °C. Add about 100 mg of NaBH$_4$ in small portions (keep the borohydride salt in a closed container except when transferring portions) over a period of 15-20 min with frequent stirring. After all of the reducing agent has been added, continue to heat the reaction mixture for 20-30 min until gas evolution has ceased and the solution has clarified. Filter off any insoluble material by suction filtration and adjust the pH of the solution to 2-3 with dilute HCl. Add a solution of about 200 mg of NH$_4$PF$_6$ in 1 mL of water to the filtrate (still contained in the suction flask) and mix well. Reduce the volume of the solution by about 1/3 by pulling air over it with the aspirator (through the fritted funnel). Cool the flask in an ice bath for 10-15 min, then suction filter the orange product and wash with a small amount of cold ethanol followed by a few milliliters of ether. Allow the product to air dry. Determine the quantity of dry product and obtain infrared (KBr pellet) and $^1$H NMR (d$_6$-acetone) spectra.

**Analysis for nickel content of Complex A.** This is a micro analysis and should be done in duplicate. To maximize working efficiency, weigh out both samples, digest each, and then perform the titrations in sequence.

Weigh 8-12 mg of complex into the digestion/titration flask provided. Add 2 drops of conc. H$_2$SO$_4$ and 5 drops of conc. HNO$_3$ to the tube. **Safety: Remember that concentrated mineral acids are extremely corrosive. If any contacts the skin it should be washed off immediately with copious quantities of water.** In the hood, swirl the flask in the flame of a Bunsen burner, taking care to point the open end away from you, until white fumes begin to appear and continue until fumes largely dissipate. Let the flask cool somewhat and add 2 drops of conc. perchloric acid and two drops of conc. nitric acid, rotate the flask to wash all solids to the bottom and in the flame until all of the liquid has disappeared. Sulfuric and perchloric acids are high boiling so that this will take a few minutes. There should be a small amount of lightly colored solid remaining in the tube. If the solid is dark brown or black, then the digestion process should be repeated. Set the tube aside to cool.

After the tube has cooled, add about 1 mL of 0.1 M HCl and heat briefly to dissolve all solids. Add 1 mL of pH 10 buffer and about 1 mL of distilled water to the sample along with a very small amount of powdered Murexide indicator and swirl to dissolve. The solution should be a light yellow color after the indicator is added. Titrate with standard 0.010 M EDTA solution until the endpoint is reached. Remember to reset the electronic burette prior to beginning the titration so that the volume read is the actual titer. The end point occurs when the pale yellow color just disappears to give a persistent violet color. Calculate the percent nickel in the sample.

**Determination of the magnetic susceptibility and magnetic moment of [Ni(en)](BF$_4$)$_2$.** The determination of magnetic susceptibility by the Evans’ method requires the simultaneous determination of two spectra, one of a reference solution and one for the sample solution. In each case the solvent resonance and that of any added reference material is generally all that is observed because the resonances for the sample are usually both highly broadened and frequently shifted to unusual chemical shifts. Accurately prepare 5 mL of a 0.10 to 0.15 M solution of the complex in D$_2$O (use an analytical balance and volumetric flask). Just before filling the volumetric to the mark, add 5
drops of t-butyl alcohol, which will serve as the reference for measurement of $\Delta f$. Place enough of this solution in the nmr tube so that the depth is about 2 inches after the insert, which contains t-butyl alcohol in D$_2$O, is placed in the outer tube. Record the spectrum, which should consist of just two peaks. Accurately determine the position of both peaks; their separation is $\Delta f$ in the expression for calculating susceptibility. Calculate the magnetic susceptibility and magnetic moment for the compound.$^4$

$^4$See the appendix for a discussion of magnetic susceptibility, methods for its determination, and for calculation of the magnetic moment.
Appendix: Magnetic Susceptibility and Magnetic Moment

Some useful references:


Introduction

The magnetic moment for a transition metal compound can generally be directly related to the number of unpaired electrons for the metal ion. This is particularly true for first row transition metals where the experimentally determined magnetic moment is usually very similar to the spin-only value, i.e., µso = 2[S(S+1)]1/2.

The experimental magnetic moment is determined from the magnetic susceptibility, which is related to the magnetization of the sample in the magnetic field. When a substance is placed in a magnetic field of magnitude H the magnetic induction (flux density) B is given by:

\[ B = \mu_0 (H + I) \text{ (SI)} \]

where I is the intensity of magnetization due to the substance itself. If the substance is diamagnetic then I is negative, if paramagnetic then it is a positive quantity.

There is a very significant problem with units in the area of magnetism and consultation of multiple sources usually leads to confusion. The unit of magnetic field in the cgs system is the Oersted, Oe. In the SI system magnetic field is expressed as A m\(^{-1}\); 1 Oe = 79.6 Oersted, Oe. In the SI system magnetic field is expressed as A m\(^{-1}\).

Magnetic susceptibility has no units in the cgs system but has units of kg M s\(^{-2}\) A\(^{-2}\) in the SI system.

The magnetic permeability of a substance is given by:

\[ \mu = B/H = 1 + 4\pi I/H \text{ (cgs)} \]
\[ \mu = B/H = \mu_0 (1 + I/H) \text{ (SI)} \]

Magnetic permeability has no units in the cgs system but has units of kg M s\(^{-2}\) A\(^{-2}\) in the SI system.

The ratio I/H or \(\kappa\), which is dimensionless in either the cgs or SI system, is a proportionality constant that is specific to the substance under consideration. It is termed the magnetic susceptibility per unit volume or the volume susceptibility. Of greater use to the chemist are the mass (\(\chi\)) and molar (\(\chi_m\)) susceptibilities, which are obtained as follows (\(\rho\) is the density of the sample):

\[ \chi = \kappa/\rho \text{ (cgs, cm}^3\text{ g}^{-1}; \text{SI, m}^3\text{ kg}^{-1}) \]
\[ \chi_m = \chi \times MW \text{ (cgs, cm}^3\text{ mol}^{-1}; \text{SI, m}^3\text{ mol}^{-1}) \]

An alternative description based upon the intensity of magnetization, I, is given by:

\[ I = m/A \]

where m is the induced pole strength and A is the total area, i.e., the magnetic polarization of the substance in question. This is readily converted to another form by multiplying by distance/distance (\(I/l\)) which gives:

\[ I = mI/V \]

but since \(m \ell = \mu\) then

\[ I = \mu/V \]

When a magnetic dipole of strength \(m\) and length \(\ell\) is placed in a magnetic field (such that the dipole is not already aligned with the external field vector) it experiences a turning effect that tends to align it with the external field. The tendency to turn is given by force x distance or \(mH \times \ell\) or \(\mu I\). The fundamental unit of magnetic moment, \(\mu_0\) or the Bohr magneton is

\[ \mu_0 = \frac{eh}{4\pi mc} = 9.274 \times 10^{-21} \text{ erg Oe}^{-1} \text{ (cgs)} \]
\[ \mu_0 = \frac{eh}{4\pi m} = 9.274 \times 10^{-24} \text{ A m}^2 \text{ (SI)} \]

In a normal (magnetically dilute) paramagnet the effective moment results from both rotation of the electron and from its movement about the nucleus. If both of these contribute fully then the moment is related to the spin and orbital quantum numbers (S and L by the expression:

\[ \mu_{\text{eff}} = [4S(S+1) + L(L+1)]^{1/2} \]

In fact, for most transition metal ions most of the orbital contribution, but not all (see below), is "quenched" and the value of \(\mu_{\text{eff}}\) is fairly close to that predicted by consideration of only the electron spin. This is often termed \(\mu_s\) for spin only moment. It is given by

\[ \mu_s = 2[S(S+1)]^{1/2} \]

The expression \(\mu_s = [n(n+2)]^{1/2}\) is also sometimes given where \(n\) is the number of unpaired electrons. Experimental values are typically up to 0.5 higher then the spin only value for many complexes but they may be considerably higher for complexes that have three-fold degenerate ground states (T states). This is a result of incomplete "quenching" of the orbital contribution to the moment. Note that the above expressions do not involve temperature so that the magnetic moment, unlike the magnetic susceptibility (see below), is independent of temperature.

The relationship of the magnetic moment, in this case \(\mu_{\text{eff}}\) to the magnetic susceptibility was derived by Van Vleck from considerations of the change in energy of a sample when placed in a magnetic field. The change in energy is related to the
alignment of magnetic dipoles in the sample with the applied external field. Such alignment is opposed by the tendency of randomization of these dipoles by thermal energy so that it becomes a problem in statistical mechanics to derive the appropriate expression. The relationship between $\chi_M$ and $\mu_{eff}$ is:

$$\chi_M = N\mu_0^2\mu_{eff}^2/3kT \text{ (cgs)}$$

$$\chi_M = N\mu_0^2\mu_{eff}^2/3kT \text{ (SI)}$$

Note that these expressions indicate that the susceptibility should vary linearly with $1/T$. This was determined experimentally by Curie and expressed as $\chi = C/T$ (the Curie law) where $C$, the Curie constant, is a characteristic of a particular paramagnetic substance.

Rearranging the Van Vleck equation and introducing the values of the constants gives the following equations, which are used to compute magnetic moments from experimentally determined susceptibilities.

$$\mu_{eff} = [3k/N\mu_0^2]^{1/2}[\chi_M T]^{1/2} = 2.83[\chi_M T]^{1/2} \text{ (cgs)}$$

$$\mu_{eff} = [3k/N\mu_0^2]^{1/2}[\chi_M T]^{1/2} = 798[\chi_M T]^{1/2} \text{ (SI)}$$

In both cases the unit of the magnetic moment is stated to have units of Bohr magnetons. There is some confusion on this point since the value is really dimensionless. However, it does represent the magnetic moment in multiples of $\mu_B$.

**Determination of Magnetic Susceptibility**

The magnetic susceptibility of a substance has traditionally been determined by measuring the change in the behavior of a sample when placed in a magnetic field. There are a number of ways of detecting this change. The classical (Gouy) method involves the determination of the change in mass of a sample that is suspended such that there is a field gradient over the length of the sample. The usual method is to pack powdered sample in a small diameter glass tube and to suspend it from a balance so that the lower end of the tube is between the pole faces of a magnetic. Relatively large samples are required (0.1 to 1 g) with the exact amount determined by the diameter of the tube used. With this arrangement, the variation of force experienced by the sample per volume element $dF/dV = H_xdH_x/dz$ where $dH_x/dz$ represents the variation of the horizontal field gradient over the length of the sample. Integration over the range of field gradients gives $F_x = \frac{1}{2}Ax(H_2 - H_0^2)$ where $A$ is the cross section of the sample, $H$ is the field strength at the bottom of the sample and $H_0$ is the field strength at the top which is approximately zero. The susceptibility of the sample must be allowed for so that $F_x$ for the sample is at the top which is approximately zero. The susceptibility of the sample in a small diameter glass tube and to suspend it from a balance so that the lower end of the tube is between the pole faces of a magnetic. Relatively large samples are required (0.1 to 1 g) with the exact amount determined by the diameter of the tube used. With this arrangement, the variation of force experienced by the sample per volume element $dF/dV = H_xdH_x/dz$ where $dH_x/dz$ represents the variation of the horizontal field gradient over the length of the sample. Integration over the range of field gradients gives $F_x = \frac{1}{2}Ax(H_2 - H_0^2) + \delta$ where $\delta$ is the correction term for the tube. Upon substituting $\chi_\rho$ for $\kappa$ and $\Delta w$ and for $F$ followed by rearrangement this gives:

$$\Delta w = \frac{1}{N}(H_2 - H_0^2)\mu_B$$

If the same experimental parameters (length of sample, field strength, etc.) are used for every measurement then:

$$\chi = C[(\Delta w - \delta)/m]$$

In the usual case the constant $C$ is determined by using a substance of known susceptibility to determine $\Delta w$ for a given sample and set of experimental parameters. Once this is done the derived constant is then used for the determination of the susceptibility of unknown materials.

The Gouy method can be used to determine the susceptibilities of paramagnetic materials in solution, but the accuracy of such measurements is usually low.

In a related technique, known as the Faraday method, a much smaller sample (5-50 mg) is suspended in a magnetic field between pole pieces designed to provide a constant value of $H_0dH_x/dz = C$ for the entire sample. In this case $F_x = \kappa VC$. From the relationships, $F = \Delta w$, $\rho mV$ and $\kappa = \chi_\rho$ one obtains:

$$\chi = \beta \Delta w/m$$

he actual application $\Delta w$ for the sample must be corrected for the accompanying change in mass of the container holding the sample (often called a boat) so that the expression becomes

$$\chi = \beta (\Delta w - \Delta w_0)m$$

where $\beta$ is a constant (equal to $l/C$) that is determined using a substance of known susceptibility.

Unlike the Gouy method where the accuracy (and precision) of the measurement depends upon the homogeneity of the sample in the tube, the Faraday method depends only on the uniformity of the magnetic field in the region of the sample. The Faraday method cannot be used to determine the susceptibility of paramagnetic species in solution.

There is another practical method of determining magnetic susceptibilities that is applicable only to measurements on solutions. This method involves the use of NMR spectroscopy to measure the difference in chemical of a reference line in the presence and absence of the paramagnetic substance. This measurement relies upon the fact that the field, or frequency, position of a line (resonance) depends upon the bulk susceptibility of the medium in which the molecule is located. For a molecule that does not interact directly with the paramagnetic center, the shift $\Delta H/H$ produced by the presence of a paramagnetic metal species is given by $2\pi\Delta \chi /3$ (permanent or conventional electromagnet) or $-4\pi\Delta \chi /3$ (superconducting solenoid magnet) where $\Delta \chi$ is the change in volume susceptibility between the solutions with and without the paramagnetic species. The signs to the above shifts indicate that the direction of the shift is upfield of the reference peak in the former case and downfield of the reference peak in the latter case. The shift is twice as great for a solenoid magnet as for the permanent or conventional electromagnet. Converted to frequency (Hz) and utilizing earlier relationships the expression becomes

$$\chi = 3\Delta f/2\pi fm + \chi_\rho + \chi_\rho(d_\rho - d)/m \text{ (non-solenoid)}$$

$$\chi = -3\Delta f/4\pi fm + \chi_\rho + \chi_\rho(d_\rho - d)/m \text{ (solenoid)}$$

Here $\Delta f$ is the frequency separation between the lines in the

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presence and absence of the paramagnetic species, \( f \) is the frequency of the spectrometer used for the measurement (both in Hz), \( m \) is the mass of substance contained in 1 mL of solution, \( \chi_s \) is the mass susceptibility of the solvent, and \( \delta_d \) and \( \delta_s \) are the densities of the pure solvent and solution, respectively. For highly paramagnetic species and dilute solutions the latter term can be neglected. In practice, a concentric tube assembly is used where the solution of paramagnetic substance and reference (which may be the solvent itself in some cases) is contained in one tube and the solvent and reference (if any) only is contained in the other. The spectra of the reference in both media are recorded simultaneously and \( \Delta f \) is the separation between the two resonances resulting from the reference material.

**Calculation of \( \chi_M \) and \( \mu_{\text{eff}} \) from the mass susceptibility**

It was earlier noted that diamagnetic substances are affected by a magnetic field, although in the opposite sense to paramagnetic substances. In the simplest case diamagnetism results in a repulsion by a magnetic field rather than an attraction. The effect is viewed as the result of a magnetic dipole being induced by the external field on orbital motions of paired electrons. The magnetization is of the opposite sense from that due to the spin of unpaired electrons and is temperature independent. Since all atoms except hydrogen have electron pairs, every substance will have a diamagnetism that is determined by the specific atoms (and even types of bonds) contained in it. Thus the apparent susceptibility of paramagnetic materials that is measured must be corrected for the diamagnetism of the constituent atoms. Such diamagnetic corrections have been tabulated (Table 1; these are sometimes called Pascal’s constants) and are used to correct the mass susceptibility according to:

\[
\chi_M^{\text{corr}} = \chi_M + \sum \chi_d
\]

where the summation is over all constituent atoms. Note that the \( \chi_d \)'s are tabulated as negative quantities but they should be used as positive values in the above expression. \( \chi_M \) is given by:

\[
\chi_M = \chi \times MW
\]

The above value of \( \chi_M^{\text{corr}} \) is used to compute \( \mu_{\text{eff}} \) using the expression

\[
\mu_{\text{eff}} = 2.83[\chi_M^{\text{corr}} T]^{1/2} \quad \text{(cgs)}
\]

\[
\mu_{\text{eff}} = 798[\chi_M^{\text{corr}} T]^{1/2} \quad \text{(SI)}
\]

and to determine the number of unpaired electrons per molecule of the sample by comparison of the experimentally derived value with those computed from \( \mu_{\text{so}} = 2[S(S+1)]^{1/2} \).
# Diamagnetic Corrections

(All values x 10^-6 mol^-1)

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<tr>
<th>Cations</th>
<th>Anions</th>
<th>Pascal’s Constants</th>
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<tr>
<td>Li⁺</td>
<td>1.0</td>
<td>F 9.1</td>
</tr>
<tr>
<td>Na⁺</td>
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<td>Br⁻ 34.6</td>
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<tr>
<td>Ni²⁺</td>
<td>12.8</td>
<td>OH⁻ 12.0</td>
</tr>
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</table>

Constitutive corrections and ligand corrections

| C=C | -5.5 | C-Cl | -3.1 | 2,2'-Bipyridine 105 |
| C=C-C=C | -10.6 | C-Br | -4.1 | Phenanthroline 128 |
| C≡C | -0.8 | C-I | -4.1 | Water 13 |
| N=N | -1.8 | | | |
| C=N-R | -8.2 | | | |
| C in phenyl | -0.24 | | | |


| Ag⁺ | 28 | BF₄⁻ | 37 | C₂H₅N 49 | CO 10 |
| Ba²⁺ | 24 | CH₃CO₂⁻ | 30 | C₆H₆ 55 | NH₃ 18 |