NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY
APPLICATION TO CYCLOHEXANE AND CYCLOHEXENE

By

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Dissertation

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DEGREE OF Bachelor of Science in Chemistry

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ABSTRACT

Several pyridine-levir acid adducts were synthesized for study by
14° npr, using dpc techniques. A brief introduction to npr is given,
with an explanation of the "subetner model" for analyzing data obtained
via npr for certain nitro-reconstituting bases. The pyridine adduct of
the tetrachloride was successfully synthesized and analyzed in terms of
the Subetner model. The base-paired base of 1-methyl-ctetone hemi-
hydroydride hemihydrate was also synthesized and its npr a obtained.
ACKNOWLEDGMENTS

My thanks go to Professor T. L. Brown for the opportunity to work on this project, and to all the group members for their help during the past year. Special thanks are due Les Butler and Pete Novicijevic for running the nmr spectra.
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NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY
APPLICATION TO PYRIDINE-LITHIUM ACID COMPLEXES

1. INTRODUCTION

A. General Introduction

Much of chemistry is the study of bonding between atoms, and much of
that bonding is covalent bonding, electron sharing between those atoms.
Therefore there is a great deal of interest in physical and chemical methods
which give some information about the distribution of electrons in molecules
and allow some statements to be made about bonding. Of these methods, var-
ious types of spectroscopy provide the best information and, in fact, "the
development of modern inorganic chemistry is based on the ever-increasing
use of spectroscopic methods, "[1]

There are many types of spectroscopy and the number is growing. All,
however, involve the interaction of electromagnetic radiation with matter.
In rotational, vibrational, and electronic spectroscopy, it is the electric
field component of radiation which interacts with the molecules; in nuclear
magnetic resonance and electron paramagnetic resonance spectroscopy it is
the magnetic component.[2] The method to be discussed in this paper, nuclear
quadrupole resonance spectroscopy, is the double resonance level crossing
technique, involves both.

Nuclear quadrupole resonance spectroscopy (nqr) involves the interaction
of a nucleus which has a non-spherical charge distribution with an external
electric field. This external electric field arises from the electrons about
the nucleus, and information gained from the nqr experiment can indicate the
distribution of these electrons and provide insight into the bonding of the atom containing these nuclei. The double resonance level crossing technique (drlc) is used to detect the low frequency nmr spectra of species such as $^{14}$N, $^2$H, and $^{17}$O using the nuclear magnetic resonance of a second system of nuclei, usually $^1$H, in the detection of resonance. It is a sensitive technique, and in the case of $^{14}$N species it is especially useful in looking at the distribution of the electrons from the lone pair on nitrogen in bases such as pyridine when they form adducts with Lewis acids. A model developed by Brown and Subenacker $^{7,8}$ allows a quantitative calculation of the number of electrons remaining in the orbital after coordination to acids using parameters obtained from nmr experiments. Such quantitative estimates of electron compositions in series of similar compounds allow correlations to be seen between the electron distributions and other chemical behavior, such as periodic trends in electronegativity and acid strength.

Subenacker gathered data on pyridine coordinated to Lewis acid centers, including protons, halogens, metal centers, and non-metal acids. The object of this research was to prepare further pyridine-Lewis acid adducts, obtain the nmr parameters, analyze these in terms of the model, and to correlate resulting electron distributions with related compounds. Several compounds were chosen which would provide interesting additions to the "reference library" of nmr data on pyridine adducts; however, they proved also to be challenging syntheses and the bulk of the research time went into simply preparing the compounds. In this thesis I will discuss the drlc nmr experiment, the Subenacker model for interpreting the nmr parameters, and some of the results gotten from pyridine adducts. I also describe the compounds studied in this project, why they are of interest, how they were prepared, and what results were obtained.
Nuclear Quadrupole Resonance

Nuclear quadrupole resonance spectroscopy measures the amount of energy needed to change the orientation of a quadrupolar nucleus in an external electric field. A quadrupolar nucleus is one with a nuclear spin, $I$, greater than or equal to one. Such a nucleus has an ellipsoidal distribution of electric charge in the nucleus, as shown in Figure 1. It is said to have a quadrupole moment $Q$, where $e$ is the unit of electrostatic charge and $Q$ is a measure of the deviation of the charge distribution from spherical symmetry. $Q$ may be either positive or negative and indicates the direction of the charge accumulation relative to the principal axis.\(^7\)

When the nucleus is surrounded by an inhomogeneous electric field, such as that arising from a non-spherical distribution of electrons about the nucleus, it can assume various possible orientations with respect to the field. These orientations are of different energies. They are quantized, with $2I + 1$ orientations, given by $n$, the nuclear magnetic quantum number (ranging from $-I$ to $+I$). Nuclear quadrupole resonance spectroscopy measures the energy difference between the orientations by detecting which frequencies of electromagnetic radiation are absorbed, indicating a transition between energy levels. These frequencies are generally in the range of 1 to 700 kHz, i.e., the radiofrequency region.\(^7\)

A description of the quantum mechanics of the nor experiment may be found in references such as Brage. The quadrupole Hamiltonian may be written as:

$$H_Q = 4\pi \frac{Q}{\hbar(2I-1)} \left[ \frac{3}{2} (I_z^2 - I^2) - \frac{1}{2} \left( I_+^2 + I_-^2 \right) \right]$$

The product $\frac{Q}{\hbar}$ is the quadrupole coupling constant, $Q = q_{22}$, and $\frac{Q}{\hbar} = \frac{Q}{\hbar z}$ is the asymmetry parameter. The $q_{ij}$ are the field gradient
Figure 1. Representations of quadrupolar nuclei
parameters and constitute the electronic portion of the Hamiltonian. They are defined as $\frac{\partial V}{\partial E}$, $V$ being the electronic potential energy function generated by the external charge distribution. The axis system is set up so that the $q_{ij}$ matrix is diagonalized, and labeled such that $|q_{yy}| > |q_{ii}| > |q_{ij}|$. There is an additional condition that arises from Fermi’s equations, that $q_{ii} + q_{yy} + q_{xy} = 0$. The parameters can be expressed in the two variables $e^2\eta/n$ and $\eta$. Also, $0 < \eta < 1$.

Finding the eigenvalues for the Hamiltonian yields the energy levels of the system. For $I=1$, as is the case with $^1S_0$, it may be solved directly for all values of $\eta$ to give:

$$
\begin{align*}
\epsilon_{+1} &= n^2 e^2 \eta/(1 + \eta) \\
\epsilon_{-1} &= n^2 e^2 \eta/(1 - \eta) \\
\epsilon_0 &= -n^2 e^2 \eta
\end{align*}
$$

These give transition frequencies of:

$$
\begin{align*}
\nu_+ &= \frac{1}{2} \left[ e^2 \eta/n \left( 1 + \eta/\xi \right) \right] \\
\nu_- &= \frac{1}{2} \left[ e^2 \eta/n \left( 1 - \eta/\xi \right) \right] \\
\nu_0 &= \frac{1}{2} \left[ e^2 \eta/n \right]
\end{align*}
$$

These can be seen in the energy level diagram in Figure 2. This diagram also shows that $\nu_+ = \nu_- + \nu_0$. Solving for the quadrupole coupling constant and asymmetry parameter yields:

$$
\begin{align*}
e^2 \eta/n &= \frac{1}{3} (\nu_+ + \nu_-) \\
\eta &= \frac{3}{\nu_0/(\nu_+ + \nu_-)}
\end{align*}
$$

From experimentally determined transition frequencies, then, the quadrupole coupling constant and the asymmetry parameter can be computed. These in turn are related to the $q_{ij}$ and hence to the electron distribution around the nucleus.
Figure 2. Energy level diagram for an ion nucleus
and the Double Resonance Level Crossing Techniques

Nitrogen is an important element in many organic, inorganic, and biological systems. Compounds containing nitrogen often form adducts with Lewis acid centers using the lone pair left on the nitrogen when it is sp$^3$ hybridized. For example, the reaction of ammonia with boron trifluoride:

\[
\text{H}_3\text{N} \cdot \text{H} + \text{BF}_3 \rightarrow \text{H}_3\text{N} : \text{BF}_2
\]

In biological systems, nitrogen is found in the amino acids and nucleotides, and plays an important role in hydrogen bonding. Nitrogen shows up in a number of important ligands in transition metal chemistry as well. Not much has been learned about the bonding of nitrogen's lone pair through nmr, however, because of experimental difficulties in detecting the $^{14}$N nmr transitions.

The nmr resonances of $^{14}$N are typically in the 0.2 to 6 MHz range. This energy level difference is very small compared to 18 even at liquid nitrogen temperatures ($\Delta \omega / \hbar = 3 \times 10^{-12}$), so all energy levels are nearly equally populated and direct detection is very difficult. Double resonance techniques have been developed which use the nuclear magnetic resonance (nmr) of a second spin system (the I system) to indirectly indicate nmr absorptions in the first system (the J system).

In the double nmr experiment, a change in the magnitude of the free induction decay (FID) curve following a 90° pulse to the J spin system is used to indicate resonant absorption in the J spin system. This is done by having spin "information" be exchanged between the two systems at some point, called the "level crossing" point. Level crossing is achieved by moving the sample from a region of high applied magnetic field to a region of low magnetic
field, as Figure 3 shows, there will be points in this process at which
interaction between the nuclear spin levels will be the same for the L spin
and each pair of nitrogen spin levels. At these points there can be mutual
side ripples and information is passed from one system to the other. If there
is a change in the spin population of the L system due to absorption of a
magnetic frequency, this will be reflected in the N of the L system. 5

In the axial experiment, the sample must have both the quadrupolar nuclei
to be studied and a second spin system which has an easily measured nmr signal.
This system is usually protons. The experiment begins with the sample in
a region of high applied field, where the I and 3 spin systems are allowed
to equilibrate. The sample is then quickly lifted to a region of low field.
The magnetic field strength changes during this process, going through field
strengths where level crossing is possible. For reasons explained elsewhere,
the I spin temperature will be lower than the 3 spin temperature, and there
is a transfer of energy from the 3 system to the I system at level crossing.
As the time required for level crossing is on the order of microseconds,
while the entire transit time is about 1-2 seconds, there is enough time spent
at the level-crossing points for nearly complete energy transfer between the
spin systems. In the low field region a radio-frequency field is applied to
the sample, in the range for absorption by the 3 system. If the frequency
is at or near a transition frequency, there will be resonant absorption and
the spin population of the 3 system will change. The sample is then returned
to the high field region, again undergoing level crossing as the magnetic
field changes. Again there is a transfer of information about spin populations
between the 3 and the I spin systems. If there was an absorption of energy
by the 3 system, this is reflected by a higher I spin temperature. In the
Figure 5. Points of applied field where level crossing occurs.
When field region, the I system is given a 90° pulse and the 32P examined. The switched spin temperature, occurring when the S system absorbs energy, is detected as a decrease in the 32P. The S channel frequency source is incremented by a fixed amount for the next cycle. A plot of the amplitudes of the 32P versus the S channel irradiation frequency reveals points of resonance.

The development of double resonance techniques such as this one has allowed nmr data to be gathered on a number of nitrogen-containing compounds. Almstedt has studied the nmr spectra of nitrogen in some amino acids, in some tetrahedral model compounds, and in some purines, pyrimidines, and nucleosides.6 Green and co-workers have reported the 14N nmr spectra for pyridine complexes of In(III) and Gd(III), and for (pyClO4).Br(py)ClO4, H(pyr)ClO4, and 1-picoline-N-oxide.6 Subenacker prepared and analyzed a number of additional pyridine alcohols with Lewis acids.1 Roberts worked on the nmr spectra of the nitrogens in a series of 1,2-dipiperidinoethane complexes in a project similar to this one.1 Still, the number of compounds analyzed by 14N nmr is relatively small, especially for metal complexes coordinated directly through nitrogens.

3. The Subenacker Model

Many of the Lewis acid-nitrogen-containing compounds which have been analyzed by 14N nmr were prepared and examined by Subenacker in the course of his work for a doctorate. The data he gathered were used to formulate and test a model which allows the computation of the amount of electron density remaining in the lone pair orbital of nitrogen in bases such as pyridine after coordination to Lewis acids.

The Subenacker model is an extension of one developed by Townes and Dailey for analysis of 14N nmr data.5 Models are necessary for the analysis of nmr
Data in terms of molecular orbitals since only two independent variables are measured experimentally and three quantities, \( q_{ux} \), \( q_{uy} \), and \( q_{uz} \), are wanted. Several simplifying assumptions are made. Since the electric field varies as \( 1/r^2 \) and the electric field gradient is the first derivative of this, the field gradient varies as \( 1/r^3 \) and the effects of the field gradient on the quadrupolar nucleus fall off very rapidly with distance. Therefore only the orbitals centered on the quadrupolar nucleus itself need to be considered, to a good approximation. Furthermore, since spherical distributions make no contribution to the electric field gradient, s shells and filled shells contribute nothing. Orbitals higher in energy than the valence orbitals have small contributions in the filled molecular orbitals and lie further out as well and can be neglected. For nitrogen-14 then, this leaves only the valence p orbitals (denoted \( \pi_n \)).

In nitrogen, the contribution of each p orbital to the field gradient is evaluated separately. In terms of the axis system of the molecule,

\[
q_{ux} = \left( \frac{1}{2} \left( P_{ux} + P_{uy} \right) \right) q_{oo}
\]

\[
q_{uy} = \left( \frac{1}{2} \left( P_{ux} - P_{uy} \right) \right) q_{oo}
\]

\[
q_{uz} = \left( \frac{1}{2} \left( P_{ux} + P_{uy} \right) \right) q_{oo}
\]

where \( q_{oo} \) is the quadrupole coupling constant produced by a single electron in a nitrogen atom 2p orbital.

In pyridine, the main bond of interest here, the nitrogen is hybridized, assuming sp^2 hybridization, with a C-N bond angle of 120° as shown in Figure 5. The nitrogen orbitals are assigned occupancies of \( \pi \) for the \( p_y \), \( \delta \) for the orbitals directed towards carbon, and \( \sigma \) for the donor orbital. These are expressed as:

\[
\delta = \frac{3}{2} p_y
\]
Figure 5. Coordinate system and orbital designations for purine.
\[ a = \left( \frac{2}{v_0^2} \right) a_b + \left( \frac{2}{v_0^2} \right) b_b + \left( 1 - \frac{v_0^2}{v_0^2 + 2} \right) b_b + \left( 1 - \frac{v_0^2}{v_0^2 + 2} \right) a_b. \]

Upon this gives:

\[ a_{00} = \left( \frac{1}{v_0^2} \left( \frac{2}{v_0^2} \right) \right) a + \left( \frac{1}{v_0^2} \left( \frac{2}{v_0^2} \right) \right) b + \left( 1 - \frac{v_0^2}{v_0^2 + 2} \right) a + \left( 1 - \frac{v_0^2}{v_0^2 + 2} \right) b. \]

This treatment works for pyridine, and for any dia- or trivalent nitrogen having \( \sigma_{00} \) point group symmetry. Subsequently developed methods to obtain \( \Delta \) and \( \gamma \) from experimental data. From molecular orbital calculations and measurements on small molecules approximating atomic nitrogen, \( e^2 \sigma_{00} / h \) is assigned a value of 3.0 eV (detailed reasons for this choice are found in reference 7). Using experimental data, plus this value for \( \sigma_{00} \), and the bond angle \( \alpha \), one can compute values for the electric field gradient due to the \( \pi \) orbital electrons. 5

Experimental data for free pyridine allowed the calculation of the parameters \( \Delta = 0.136 \) and \( \Delta = 0.20 \). For coordinated pyridine, a flow of electrons into the \( \pi \) and \( \pi^* \) sigma bonds due to the inductive effect is expected as electron density is withdrawn from the donor orbital, and hence \( \Delta \) and \( \gamma \) are approximated as linear functions of \( \sigma \):

\[ \Delta = \Delta_0 + \Delta(2 - \sigma) \]
\[ \gamma = \gamma_0 + \gamma(2 - \sigma) \]

When subjected to the restrictions explained by Schumacher in his thesis, and varied to best fit the experimental data, values of \( \Delta = 0.466 \) and \( \gamma = 0.1217 \) were obtained. Varying \( \Delta \) and \( \sigma_{00} \) as functions of \( \sigma \) brought no further improvement of the fit. 5

Evaluation of \( \sigma \), the donor orbital occupation, from experimentally
determined parameters \( e^2 n/\hbar \) and \( \gamma \). To do this, the minimum deviation \( \delta = \sqrt{\delta_x^2 + \delta_y^2 + \delta_z^2} \) is computed, where \( \delta_x \), \( \delta_y \), and \( \delta_z \) are the vertical distances, for a constant value of \( \delta \), between the experimentally determined field gradient parameters and the calculated lines for \( \gamma_x \), \( \gamma_y \), and \( \gamma_z \), as shown in Figure 1. The procedure is repeated to give the minimum \( \delta \) for each compound, and the value of \( \delta \) at this point is the estimated donor orbital population. The experimentally determined field gradient parameters are calculated from the parameters \( e^2 n/\hbar \) and \( \gamma \). There are twelve possible correspondences between the calculation axis system of the field gradient parameters and the molecular axis system; the correspondence that minimizes \( \delta \) is the one chosen.\(^5\) Due to the large number of basically simple but iterative calculations, a computer program is used to find the best \( \delta \) for the experimental parameters, an approximate value of \( \delta \) can be obtained from a graph such as the one in Figure 1, and the curves are drawn using data from a large number of compounds.

In this thesis, Kubaschek gives careful consideration to a number of other factors relating to and affecting the electron density from the donor orbital, but the basic idea important here is that a quantitative value of \( \delta \), the donor orbital population, can be computed from the parameters, and it is consistent to \( \approx 0.01 \) electron over a range of compounds, and to \( \approx 0.001 \) electron for closely related compounds.\(^5\)

II. Pyridine—Lewis Acid Adducts: Some Results

Kubaschek prepared and studied a large number of pyridine adducts, including pyridinium salts, pyridine complexes with metal centers in the (0), (I), and (II) oxidation states, dihalogen adducts, and pyridine—boron
Figure 6. Fitting of experimental field gradient parameters to calculated lines.
Figure 7. Quadrupole coupling constant and asymmetry parameter as a function of ion pair orbital occupancy. From [source].
tribalide adducts. Results and discussion are found in the thesis, of course, but one series illustrates especially nicely the type of information gained from the use of the model and what it shows about the chemistry of the Lewis acids involved.

The series is one of pyridine-dihalogen compounds and it shows the variation in donor orbital population consistent with the changing electronegativity of the bonded halogens. The geometry of the compounds is shown in Figure 3 and the calculated $\sigma$ values are listed in Table 1. As expected, the smallest amount of electron density is found for pyridine-1-Cl, as Cl is the most electronegative of the halogen atoms and draws over the most electron density from the donor orbital. The value of $\sigma$ gradually increases as less electronegative halogen atoms are used, ending up with the largest value of $\sigma$ for pyridine-1-Br.

F. Compounds Chosen for this Project

Hubenaker worked only with metals in the (0), (I), or (II) oxidation states. The intent of this project was to prepare some pyridine-metal halide adducts with metals in the (III) and (IV) states, to extend the "reference library" of our data of pyridine compounds and see how well results from applying the Hubenaker model to these compounds correlated with their known chemistries.

The first compound selected for synthesis was the pyridine adduct of lanthanum chloride, LaCl. The lanthanides are interesting because they are expected to have little metal-ligand orbital interaction, and this should be reflected in values close to two. Further, there is a decrease in radii in the Ln(III) ions going across the series, bringing about an
Figure 1. Geometry of pyridine-dihalogen adducts

Table 1. Donor orbital occupancies for pyridine-dihalogen adducts

<table>
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<th>Compound</th>
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<td>pyridine-Cl-Cl</td>
<td>1.226</td>
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<tr>
<td>pyridine-Br-Cl</td>
<td>1.550</td>
</tr>
<tr>
<td>pyridine-I-Cl</td>
<td>1.645</td>
</tr>
<tr>
<td>pyridine-I-Br</td>
<td>1.659</td>
</tr>
<tr>
<td>pyridine-I-I</td>
<td>1.744</td>
</tr>
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</table>

Figure 2. 1-thyl-cytosine
increase in the acidity of the metal centers. This should be reflected in a decrease in $F$ along across the series for similar adducts. Originally several of the lanthanide halide-pyridine adducts were to be prepared and analyzed to check these hypotheses, but experimental difficulties intervened.

Another compound selected for synthesis was the tin tetrachloride-pyridine complex, interesting because it is a de metal center and should be quite acidic, yielding a small $F$.

One compound which did not contain pyridine was also selected for synthesis and for analysis: 1-methyl-cytosine. This compound, shown in Figure 9, is of considerable interest for several reasons. In the solid state 1-methyl-cytosine hemihydrate has an unusual form, hydrogen-bonded dimer, which stacks. These stacking, hydrogen-bonded base pairs are proposed as the repeating units of the synthetic polynucleotide, hemiprotonated polycytidylic acid. In addition, the protonated cytosine-neutral cytosine pair resembles the guanine-cytosine base pairs in nucleic acids and may serve as a model compound for that biologically important pair. The structure of the dimer of 1-methyl-cytosine (the hemihydrate hemihydrate) as determined by Kistemscher et al. 2 is shown in Figure 10; compare it to the guanine-cytosine pair in Figure 11.

There is some debate as to whether the hydrogen bond between the two N(3) atoms is symmetric or asymmetric. Kistemscher states that it is asymmetric on the basis of the difference in the $C(2)-N(3)-O(4)$ bond angles seen in the crystal structure. If the bond is asymmetric, the dimer would be made of one protonated and one neutral cytosine molecule, with the proton definitely assigned to one of the cytosines. Other crystal structures indicate that the $C(2)-N(3)-O(4)$ bond angles in cytosine derivatives average 120°, while that of cytosines protonated at N(3) average 126°. In the 1-methyl-cytosine dimer, there is one $C(2)-N(3)-O(4)$ angle of 120.4° and one of 124.4°, indicating an
Figure 15. Crystal structure of (1-methylcytosine)$_2$·$\text{HCl}$·$\text{H}_2\text{O}$.
Figure 11. Structure of guanine-cytosine base pair
asymmetric hydrogen bond. Although a very complicated spectrum is expected because of the number of nonequivalent nitroso groups, an analysis of this compound should also give some information about this hydrogen bond. Ordinary 1-methyl-urea is not suitable for an nmr study, however, because the freely-rotating methyl group sets up a fluctuating magnetic field which causes rapid relaxation of the spin system. Replacing the methyl group with a deuterated methyl group slows the rotation sufficiently to make nmr spectra possible. It was the synthesis of the deuterated compound that was done for this project.
II. NORMALIZING

- Handling Techniques

Both the liquidus platinum- and the two chloroform-stabilized platinum are water sensitive and must be protected from atmospheric moisture during preparation and manipulation. Very careful precautions were carried out in a dry box or an glove box, but the bulk of the reactions were done in the open, using Schlenk techniques.

In using Schlenk techniques, an envelope of an inert gas, usually nitrogen or argon, is maintained over the reaction mixture to be protected. The most useful piece of equipment for the Schlenk flask, a round-bottomed flask with a side arm equipped with a stopcock, through which the inert gas can be admitted. With a strong flow of gas coming in the side arm, the neck of the flask can be opened and reagents added, equipment set up, etc. The reaction mixture is protected from atmospheric moisture by the envelope of inert gas flowing over it. Some Schlenk-type pieces of equipment and handling techniques are shown in Figure 10.

Reaction mixtures can be refluxed by attaching a nitrogen inlet to the top of the condenser, running a line from the inlet to a bubbler then to a nitrogen source. A very slight positive pressure is kept on the system, so a bubble escapes from the bubbler every few seconds. The system being tested is not closed, so there is no explosion hazard, yet no atmosphere.

In addition to all these handling techniques, glassware can be easily flamed
Figure 12. Drum- type gasmeasur
by evacuating and filling with inert gas several times before sensitive reagents are added. Transfers of solutions and suspensions through plastic tubing can be done by utilizing the pressure difference between the two flasks.

Glassware can be dried of residual water and solvents by heating thoroughly with a heat gun while running a stream of inert gas through it.

3. Reagents, Analysis

Most of the chemicals were reagent grade and used as received. Several had to be dried, however. Pyridine was dried by refluxing with barium oxide for several hours, then fractionally distilling into a dry Schlenk flask, collecting the steady-boiling fraction, usually 110-115°C (literature boiling point 115-116°C 8). Acetone was dried over potassium carbonate and similarly distilled; the fraction collected boiled at 52-54°C (literature, 56.3°C 9). Anhydrous tin tetrachloride was distilled before use also, and the fraction boiling from 99-100°C was collected (literature, 114°C 10).

Elemental analyses were done at the University of Illinois Microanalytical Laboratory.

4. Synthesis of LaCl₃(pyridine)ₓ

Vonrads and Schilbach 12 give general instructions for the preparation of rare earth chloride adducts with pyridine. They dissolved or suspended the anhydrous chloride in acetone, added pyridine dropwise, and observed the formation of a viscous precipitate. This precipitate was filtered, washed with acetone, and dried over P₂O₅. Crystalline, hygroscopic products were reported; analysis for the lanthanum product yielded the formula LaCl₃·ₓ py.

Giffie 14 prepared a number of rare earth bromide adducts with pyridine
by simply refluxing the anhydrous bisulphide in neat pyridine, reducing the volume of the solutions, and obtaining crystalline precipitates. However, analytical data for the lanthanum bisulphide-pyridine adduct did not yield a clear formulation for the compound.

Synthesis of the pyridine adduct of lanthanum chloride was attempted several times. The first time, anhydrous LaCl₃ was refluxed with an excess of pyridine, neat, for six hours, with no apparent dissolving of the solid. The reaction mixture was allowed to sit at room temperature for one week. At the end of that time the supernatant fluid was ether colored and clear, as opposed to the original clear and colorless pyridine. A large amount of solid remained in the bottom of the flask. The ether fluid was filtered off and its volume reduced by evaporation at reduced pressure. A large mass of white solid then precipitated out. Some of this solid was removed to a weighing bottle in a small bell jar which also contained an open dish of concentrated sulfuric acid. Giffin, Katsiyama, and others suggest sulfuric acid as a “drying” agent to remove excess pyridine. The product dried for several days with the sulfuric acid, yielding a mass of white,acked solid, apparently not crystalline. Elemental analysis of the product suggested that the bispyridine adduct was formed; these data are found in Table 2. The percentages of elements added up to only 92%, however, and there may have been contamination by some water.

In an attempt to improve the analysis and to prepare crystalline products, the method of Kimm was tried. The LaCl₃ did not appear to dissolve at all in acetone, despite rapid stirring and heating. After a day of stirring with no visible results, pyridine was added in excess and the mixture stirred and heated for two days. The reaction mixture was then filtered and a white solid recovered. This was washed on to remove excess pyridine, then
dried over sulfuric acid. Elemental analysis of this solid, also seen in Table 2, shows the composition to be closer to the mono-pyridine adduct, but far from the correct values for SnCl₂·py. Calculations of the compound by refluxing the pyridine in heat pyridine was tried again. This time the reaction mixture was filtered hot, after it had refluxed for several days. White, crystalline solid precipitated out when the solution cooled. This was isolated, pressed on to dry, and finally dried over sulfuric acid. Elemental analysis shows similar results to the acetone preparation, but there is less water present (see Table 2).

B. Synthesis of SnCl₂·py

All references to the pyridine adduct of tin tetrachloride point to the method of Pfeiffer for its preparation. This method simply involves adding pyridine droplets to anhydrous tin tetrachloride. The adduct is formed, with much evolution of heat, as a white, finely divided powder. Lahmeyer and Smith add to this that the product is slowly attacked by atmospheric water, is insoluble in a wide variety of solvents, and is not susceptible to purification by vacuum sublimation.

Anhydrous tin tetrachloride is a liquid at room temperature, it was easily handled by distillation into the reaction flask. Freshly distilled pyridine was added dropwise to the tin tetrachloride. It reacted vigorously and thoroughly; pyridine was added until no further reaction was observed, a white, waxy-textured solid wet with pyridine was obtained; this was dried.
<table>
<thead>
<tr>
<th></th>
<th>Calculated for CaCl₂.1 py</th>
<th>Calculated for CaCl₂.2 py</th>
<th>First trial, in acetone</th>
<th>Second trial, in acetone</th>
<th>Third trial, in acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>46.91</td>
<td>20.27</td>
<td>34.91</td>
<td>16.71</td>
<td>16.69</td>
</tr>
<tr>
<td>H</td>
<td>1.59</td>
<td>0.56</td>
<td>2.56</td>
<td>1.37</td>
<td>2.24</td>
</tr>
<tr>
<td>Cl</td>
<td>40.17</td>
<td>4.84</td>
<td>6.17</td>
<td>3.61</td>
<td>5.23</td>
</tr>
<tr>
<td>N</td>
<td>43.42</td>
<td>54.43</td>
<td>44.86</td>
<td>46.99</td>
<td>46.99</td>
</tr>
<tr>
<td>Cl</td>
<td>57.79</td>
<td>94.36</td>
<td>92.43</td>
<td>90.52</td>
<td>90.43</td>
</tr>
<tr>
<td>Total</td>
<td>93.00</td>
<td>107.00</td>
<td>92.43</td>
<td>89.87</td>
<td>92.43</td>
</tr>
</tbody>
</table>
of excess pyridine by pumping on it. When a sealed-tube melting point determination was made, the product was seen to sublimate near 300°C, contrary to literature report. A vacuum sublimation was attempted, and the product sublimed, though slowly, at 300°C. An alternative route of procedure to remove excess pyridine by drying over sulfuric acid, which actually showed both methods to yield good results, corresponded to the conversion \( \text{InCl}_2 \cdot 2 \text{py} \), as seen in Table 6.

5. Synthesis of 1-methyl-cytosine

The synthesis instructions for 1-methyl-cytosine were a modification by Miriam A. B. of a preparation by B. Y. M. and D. M. The synthesis went extremely smoothly as written; complications set in only when working with restricted amounts of 10%.

Originally the instructions from A. B. were used unchanged. About 1.11 g of cytosine, 20 ml hexamethyldisilazane and 1.5 ml chlorotrimethylsilane were refluxed together until the cytosine completely dissolved, about two to three hours, when this cooled, 35 ml methyl iodide was added, and the mixture was refluxed again for three to four hours. Then the solvents were removed by evaporation at reduced pressure, and 10 ml of 6 N acetic acid were added to cleave off the protecting silyl groups. The solution was evaporated down again to remove as much of the acetic acid as possible. The resulting solid, crude 1-methyl-cytosine hemihydrate-hydrate, was recrystallized from a minimum of hot water.

For the new study, however, the 1-D<sub>3</sub>-cytosine species was desired. This was achieved by using D<sub>3</sub>I in place of the ordinary methyl iodide. Because the deuterated reagent costs $175 for 10 ml, certain modifications to the
Table 1. Elemental analysis results for tin tetrachloride-pyridine adduct

<table>
<thead>
<tr>
<th></th>
<th>Calculated for SnCl₄ * 2 py</th>
<th>Sublimed product</th>
<th>Product dried over H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.59</td>
<td>3.70</td>
<td>3.67</td>
</tr>
<tr>
<td>H</td>
<td>2.41</td>
<td>2.47</td>
<td>2.36</td>
</tr>
<tr>
<td>N</td>
<td>6.89</td>
<td>6.77</td>
<td>6.27</td>
</tr>
<tr>
<td>S</td>
<td>5.87</td>
<td>5.71</td>
<td>4.25</td>
</tr>
</tbody>
</table>
The preparation, as described in the original article, uses something on the order of a 150-fold excess of methyl iodide. The instructions by Henzi require a 25-fold excess. If the preparation were to be used without change, the excess methyl iodide would have to be carefully recovered and the entire synthesis run repeatedly to get a useful amount of product for the methyl iodide used. This approach has the problems that the methyl iodide is extremely hard to recover, as it boils at only 42° C and is not all trapped out in a distillation; and that the product is quite soluble in water and is somewhat tedious to recover, making repeated synthesis runs less desirable. By trial-and-error it was discovered that the reaction could be successfully run with only a five-fold or so excess of methyl iodide, keeping the other proportions the same. Thus a useful amount of 1-methyl-cysteine could be made in a single synthesis run, and the problem of recovering the excess methyl iodide avoided.

This second approach was the one ultimately used here. Using 10 ml of CD$_3$I, 1.04 g of 1-CD$_3$-cysteine hydrochloride hydrohydrate were synthesized. Elemental analysis results are shown in Table 1.
Table 4. Elemental analysis results for \( \text{M}_{\text{H}} \text{O}_{\text{H}2} \text{O} \) in \( \text{CH}_{\text{H}2} \text{O} \text{H}_{\text{H}2} \text{O} \) hydrate

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>39.00</td>
<td>38.76</td>
</tr>
<tr>
<td>H</td>
<td>5.14</td>
<td>5.18</td>
</tr>
<tr>
<td>O</td>
<td>51.85</td>
<td>51.71</td>
</tr>
<tr>
<td>N</td>
<td>41.72</td>
<td>41.78</td>
</tr>
</tbody>
</table>
III. ANALYSIS AND RESULTS

A. Ball, tt

The elemental analysis data for each of the three preparations of the lanthanum chloride adduct were unsatisfactory. The first sample showed much more pyridine than the others; this is probably due to a very weakly coordinated second pyridine in the adduct or else just physically adsorbed pyridine, because this sample was not pumped on to remove much weakly held pyridine.

The second and third analyses turned out similar. The combination of low values for C, H, La, and Cl but high values for N, and the total adding up to only about 97%, suggests the presence of water in the compound. Lanthanum chloride is known to bind more strongly to oxygen-containing ligands than nitrogen-containing ones, and there is always residual water in the reagents, especially pyridine or acetone, so this is probably the reason for the poor results.

An infrared spectrum was run on the last sample prepared, the one from neat pyridine. The spectrum was taken on a Bujol unit, on BaF2 plates, on a Beckman IR-4 spectrophotometer. It was taken to check for C=N stretches due to water, and to see if the pyridine present was coordinated or not.

Several studies have been done which indicate the shifts in pyridine C=N stretching frequencies that occur upon the coordination of the pyridine nitrogen.19, 20 Lentwras, 20, 21, 22 list benzene characteristic of extremely weakly bound or physically adsorbed pyridine, weakly bound pyridine, and strongly bound pyridine, as seen from adsorption of pyridine on alumina.

Gill, 21, 22 give characteristic shifts of frequencies which occur
as pyridine is coordinated. These data are listed in Table 5. Relevant bands from the infrared spectra of allyl py are listed in Table 6.

The infrared spectra of allyl py were shown an absorption due to water, but it is not large. The spectrum also shows bands similar with the pyridine present in these most coordinated but not highly coordinated absorbed pyridine, a definite interaction between allyl py and pyridine exists in the solid.

The elemental analysis is confirmed because of the presence of a measurable amount of water, and because a small amount of uncoordinated pyridine.

In our spectra of this compound we were obtained due to lack of time.

1. allyl py

The elemental analysis data of the product, both the uncoordinated and the sulfur-sulfur-linked complexes, were satisfactory for the formulation allyl py.

An infrared scan was run on a Nujol mull of this compound as well, relevant bands are listed in Table 1. The strong band due to water was observed.

The band characteristic of coordinated pyridine was clear and strong, and no evidence is seen for uncoordinated pyridine.

An nmr spectrum was obtained for this compound, and it is shown in Figure 15. The relaxation times were satisfactory for the deca technique. The spectrum showed only a single peak, at 100 MHz. The presence of only a single band indicates that the two pyridines are in the center must be equivalent and that the symmetry parameters must be zero zero.

Equivalence of the two pyridines is possible for either a cis- or a trans-oriented octahedral complex. A crystal structure was found for this compound in the literature. No statement about the geometry can be made from the nmr data.

The nmr spectrum appears to show a single absorption. The peak is
Table 6. Relevant infrared bands of H₄⁺ L²⁺

<table>
<thead>
<tr>
<th>Band</th>
<th>Expected for weekly coordinated</th>
<th>Expected for uncoordinated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1630 cm⁻¹</td>
<td>1611-1615 cm⁻¹</td>
<td>1579 cm⁻¹</td>
</tr>
<tr>
<td>1600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1579</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1549-1533</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1480</td>
<td>1478-1480</td>
<td></td>
</tr>
<tr>
<td>1430</td>
<td>1420</td>
<td></td>
</tr>
<tr>
<td>990</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5. $^{14}$N nmr spectrum of SnCl$_4$$_2$W.
asymmetric, however, when closely examined, and may actually be the addition of two peaks. There are two possible interpretations of the data.

First, if there is only one peak, centered at 1300 KHz, it is the \( \nu_+ = \nu_- \) transition, and the nqr parameters can be calculated as:

\[
e^2\omega_0/h = 2/3 (\nu_+ + \nu_-) = 1940 \text{ KHz}
\]

\( \eta = 0 \)

When this combination of \( e^2\omega_0/h \) is located on the graph of donor orbital occupancy, \( \sigma \), as a function of \( e^2\omega_0/h \) and \( \eta \) (see Figure 7), it fits well with the other data points, and gives an estimate of \( \sigma = 1.64 \) electrons.

Second, what appears as one slightly asymmetric peak may actually be two peaks overlapping, as shown in Figure 14. If \( \eta \) is very small so that \( E_+ ^{+1} = E_+ ^{-1} \) are close in energy, then the \( \nu_+ \) and \( \nu_- \) transitions would be close in energy also, and \( \nu_0 \), the difference between \( \nu_+ \) and \( \nu_- \) would occur at a much lower frequency, out of the scanning range of the spectrum taken. If \( \nu_- \) is estimated to be buried under \( \nu_+ \) at 1300 KHz, then values for the nqr parameters can be estimated as:

\[
\nu_+ = 1300 \text{ KHz}, \quad \nu_- = 1340 \text{ KHz}, \quad \nu_0 = 40 \text{ KHz}
\]

\[
e^2\omega_0/h = 2/3 (\nu_+ + \nu_-) = 1915 \text{ KHz}
\]

\( \eta = 3 \nu_0 / (\nu_+ + \nu_-) = 0.044 \)

These parameters fit the graph of Figure 7 best for \( \sigma = 1.65 \).

Whether or not the asymmetry parameter is zero or just very small, the donor orbital occupancy is estimated to be around 1.64 electrons. When this is compared to values for some similar metal halide-pyridine complexes, a positive correlation is seen between the formal charge on the metal center and the amount of electron density drawn away from the donor orbital, as seen from the data in Table 6. The Sn(IV) fits very nicely in, having by far the least amount of electron density remaining in the donor orbital.
Figure 14. Possible overlapping of $\nu_+$ and $\nu_-$ to give asymmetric peak.
Table 3. Correlation of formal charge with donor orbital occupancy

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formal charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(pv)Cl</td>
<td>(I)</td>
</tr>
<tr>
<td>Ag(pv)₂Cl₁₀</td>
<td>(I)</td>
</tr>
<tr>
<td>Cd(pv)₂Cl₂</td>
<td>(II)</td>
</tr>
<tr>
<td>Sn(pv)₂Cl₂</td>
<td>(II)</td>
</tr>
<tr>
<td>Sn(pv)₂Cl₄</td>
<td>(IV)</td>
</tr>
</tbody>
</table>
6. 1-3D₃-cytosine Dimer

As hoped, the relaxation times on the deuterated sample were compatible with an nqr study of the 1-methyl-cytosine hemihydrate dimer. The nqr spectrum, shown in Figure 15, is very complicated, as there are four non-equivalent cytosines per unit cell, three nonequivalent nitrogens per cytosine, and each nitrogen theoretically produces three signals. The spectrum shown is a computer average of eight scans, an attempt to improve signal-to-noise ratio problems that make detection of the weaker peaks difficult. The peaks from this spectrum are listed in Table 9, but no assignments can be made at this time.

Table 9. ¹³C nqr peaks for 1-3D₃-cytosine dimer

<table>
<thead>
<tr>
<th>60 KHz</th>
<th>643</th>
<th>853</th>
<th>1045</th>
<th>1270</th>
<th>1390</th>
<th>1817</th>
<th>1927</th>
<th>2390</th>
<th>2422</th>
<th>2442</th>
<th>2590</th>
<th>2625</th>
</tr>
</thead>
</table>
Figure 15. Composite-averaged 1/3 octave spectrum of 1.035 g hotplate alone.
IV. CONCLUSIONS

Nitrogen-14 nmr, double resonance techniques, and the Rubenacker model form the background for this project. Several Lewis acid-pyridine adducts were synthesized for study by $^{14}$N nmr. The results from one, $\text{SnCl}_2 \cdot 2 \text{py}$, fit well with the Rubenacker model and with its known chemistry. The biochemically important base, 1-methyl-cytosine, was also synthesized and its nmr spectrum obtained. Although the compounds chosen did not provide as much an opportunity for study by nmr as had been wished, they did provide challenges in their syntheses, and many opportunities to learn more about chemistry and research.
REFERENCES


of capitalism are thrown into crisis. Increased productivity, in order to serve the economic health of society, must be exercised in the interests of the whole, and thus, in order to realize the full potentialities of society and restore economic stability and vitality, society must appropriate the means of production and the real economic possibilities of the productive forces, and consciously and purposively direct the economic and social wealth of society toward the interests of all individuals.

The absence of a social unity based upon the complete socialization and appropriation of the preconditions of society's self-realization is also a condition of individualism. This social unity encompasses a comprehensive vision of the development of society and its individuals, and is predicated upon principles of freedom (individual self-realization), justice (the conditions of freedom), and equality (economic equality and social reciprocity). In the communal society, the social character of labor is presupposed. Labor-power is not socially defined as a commodity, and hence economic exchanges between private producers and individuals are eliminated, as well as the need for exchange-value. Each individual freely, consciously, and creatively participates in communal production, and shares equally in communal consumption. The abstract objective sociality of capitalism is replaced by universal subjective sociality—the true universal which not only preserves
individuality, but preconditions and accentuates individuality.

Individualism precludes individual self-realization. Self-realization, which requires the self-realization of society, is a human process of development and the positive assertion of individuality based upon the appropriation of the human essence, which is a dynamic, creative, and reciprocal mode of human social interaction. The potentialities of human subjectivity, and the infinite facets of individuality are not simply powers inherent to the individual. These are capabilities developed in and through the interaction of the individual with the social environment and other individuals. Thus, each depends upon each other and society for his or her self-realization. Self-realization could never occur in isolation, but is a process "identical" with social reciprocity and the mutual solicitude and creative expressiveness of society's members.

(Note: a social experience includes not only interpersonal interaction, but also individual involvement with creative products of other individuals.)

We see, therefore, that the structures and relations of capitalism which necessarily promote conditions of individualism and unreciprocity, preclude self-realization. Individualism alienates the individual from the human essence. And since individualism precludes the development of real individuality, conformity among individuals
characterized by almost exclusive self-interestedness and selfishness becomes a prevalent capitalistic phenomenon. Conformity is an empty and irrational social sameness which fails to preserve individuality, but negates it. The capitalist system which perpetuates individualism and unreciprocity prevents the development of the profound uniqueness of each individual personality and generates the mass exaltation of and identification with petty human interests, ideological symbols, and irrational abstractions. All these universals in capitalism negate individuality and reduce human subjectivity to barren common denominators. The pursuit of money, the greatest of all social abstractions in capitalism, becomes the impetuous passion of the alienated. Self-realization becomes reduced to material acquisition and selfish conquest; human love becomes reduced to sexual desire; and the possibility of the comprehensive social unity of individuals is negated by nationalism. Each penurious, alienated drive produced by capitalist society is pursued with an implacable zeal and reproduces individualism. Finally, individualism, by precluding the development of the individual personality, precludes creative expressiveness. Also, because human creative expression always is socially directed and entails a personalized statement intended for others, for true satisfaction in the act of creativity depends upon the recognition of others, and because the human
creative powers are cultivated in social interaction, the
preclusion of human creativity is the negation of individ-
uality (i.e. is individualism).

We have seen the emptiness of individual purpose
in capitalist society, a society which itself lacks purpose,
vision, and comprehensive self-unity. Once more, the
individual purposes prevalent in capitalism are directed
toward extrinsic objects, whose acquisition provides the
individual with only transient and relatively inconsequential
satisfaction. Individuals find themselves unable to organize
the experiences of their lives, the things they thought they
had learned, into a dynamic and comprehensive conception of
themselves, their future, their place in society, and the
possible contribution of their lives to the lives of others.
This loss of the individual sense of self-organization and
the individual capacity to creatively appropriate the
social experiences of an individual's life into a purposive
framework of individual social contribution and self-
realisation as an end in itself, at the same time, results
in the profound impairment of the human capacity of creative
expression. In capitalism, individuals cannot pursue self-
realisation as an end in itself, because self-realization
itself is precluded by society's self-alienation and the
social environment of individualism and unmutuality. Recip-
rocally, the inability to creatively appropriate social
experience and formulate individual social purpose results in the preoccupation with the self or individualism.

The absence of a universal vision and unity in society which preserves and accentuates individuality, and actively seeks the self-realization of social individuals, precludes the full actualization of the individual capacity, a capacity cultivated in reciprocal social interaction, to creatively appropriate the wealth of social experience that society, really and potentially, offers. Moreover, as Marx firmly emphasized, self-realization must be based upon the satisfaction of individual economic and material needs. As long as individuals are forced to compete to meet those needs, the capacity of true individual development cannot be actualized. Once more, for those whose economic needs are barely met at all, that is, the poor and the underprivileged, the possibility of individual development, of the fulfillment of that individual's real potential as a human individual, remains in the realm of absolute impossibility. This pandemic social tragedy is the real culmination of human degradation. Allowing individual lives to expire wastefully, without ever providing them with the single opportunity to contribute to society, and hence to make their lives meaningful ones, this is the greatest and gravest failure of any society. The possibility of society's self-realization is the absolute
and intrinsic standard of social judgment. All other relative standards, which employ external and numerical comparisons, already dehumanize and debase the human individual by rendering certain levels of degradation and exploitation acceptable or even commendable. Freedom, justice, and equality are not relative concepts, but absolute principles of a universal social unity. The truly free individual is the individual actively realizing the human social potential or essence. The truly free and just society is the society that actively promotes and provides the social conditions which allow every individual to develop his or her personality or individuality to its highest possible extent. Hence, social and individual freedom, social justice, and society’s self-realization, in the comprehensive and copious sense of all terms, are “identical” and inseparable concepts.

To conclude, we have analyzed the many facets of human alienation, including society’s self-alienation, and identified three dimensions of human alienation based upon a presupposed conception of the human essence and self-realization. However, we have seen, and this must be emphasized, that just as all aspects of human essence, including society’s self-realization, are internally related, so all dimensions of human alienation and society’s self-alienation are likewise internally related. At every step
of our analysis of alienation, we criticized and exposed the inadequacies of human existence always employing the standard of human essence, as the real possibility of an alternate mode of human existence, to guide and determine our examination. Alienation, in our conception, is the displacement of essence and existence, but it is a conception of palpable and amenable relevance to the real lives of individuals in capitalist society.
Notes


5. Ibid., p. 146 (Tucker's notes).

6. Ibid., p. 145.


10. Ibid., p. 254.


