12-1-1977

Electronic structures of two different azido complexes of the 5,7,7,12,14,14-hexamethyl-I,4,8,11-TE TRAA zacyclote trade canenichel(II) ion

Raymond Ngai
ATLANTA UNIVERSITY

Follow this and additional works at: http://digitalcommons.auctr.edu/dissertations

Recommended Citation
http://digitalcommons.auctr.edu/dissertations/3816

This Thesis is brought to you for free and open access by DigitalCommons@Robert W. Woodruff Library, Atlanta University Center. It has been accepted for inclusion in ETD Collection for AUC Robert W. Woodruff Library by an authorized editor of DigitalCommons@Robert W. Woodruff Library, Atlanta University Center. For more information, please contact cwiseman@auctr.edu.
ABSTRACT

CHEMISTRY

NGAI, RAYMOND
B.Sc., CHU HAI COLLEGE,
HONG KONG, 1972

ELECTRONIC STRUCTURES OF TWO DIFFERENT AZIDO COMPLEXES
OF THE 5,7,7,12,14,14-HEXAMETHYL-1,4,8,11-
TETRAAZACYCLOTETRADECANENICKEL(II) ION

Advisor: Professor James L. Reed
Thesis dated December 1977

The electronic structures of the complex dimer, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II)-μ-diazo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) ion, \([\text{Ni(tet-b)N}_3]^2+\), and the diazido complex, diazido-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II), \([\text{Ni(tet-a)(N}_3)_2]\), have been studied. Spectroscopic and crystal field data of the two azido complexes are presented. Energies of the d-d transition and charge transfer bands were also determined. An attempt to show the generation of nitrene intermediate by the photolysis of \([\text{Ni(tet-b)N}_3]^2+\) ion was unsuccessful.
ELECTRONIC STRUCTURES OF TWO DIFFERENT AZIDO COMPLEXES
OF THE 5,7,7,12,14,14-HEXAMETHYL-1,4,8,11-
TETRAAZACYCLOTETRADECANENICKEL(II) ION

A THESIS
SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

BY
RAYMOND NGAI

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA
MAY 1977

\[ R = \sqrt{p} = 51 \]
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>LITERATURE REVIEW</td>
<td>3</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>18</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>31</td>
</tr>
<tr>
<td>CONCLUSION</td>
<td>49</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>50</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENT

I am deeply indebted to my advisor, Dr. James L. Reed, who has been very patient and helpful and under whose direction I have found what constitutes a good chemist. Any of my future success in chemistry should be accredited to him. I also want to express my most sincere respect to Dr. Thomas W. Cole for his kind regard. I am also grateful to the Atlanta University Chemistry Department and other sources from which I have received financial support during the course of my study. The staff and students also merit my appreciation for their friendly discussion of chemical and nonchemical problems.

Finally, I am very grateful to my family, especially my mother for her unlimited patience, love and encouragement during my residence.
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>31</td>
</tr>
<tr>
<td>2.</td>
<td>34</td>
</tr>
<tr>
<td>3.</td>
<td>34</td>
</tr>
<tr>
<td>4.</td>
<td>36</td>
</tr>
<tr>
<td>5.</td>
<td>36</td>
</tr>
<tr>
<td>6.</td>
<td>39</td>
</tr>
<tr>
<td>7.</td>
<td>39</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>The weak field approach procedure</td>
<td>8</td>
</tr>
<tr>
<td>2.</td>
<td>The strong field approach procedure</td>
<td>8</td>
</tr>
<tr>
<td>3.</td>
<td>Schematic diagram of the preparation of the two forms of the cyclic tetraaminenickel(II)</td>
<td>17</td>
</tr>
<tr>
<td>4.</td>
<td>A double compartment nmr tube</td>
<td>24</td>
</tr>
<tr>
<td>5.</td>
<td>The spectrum of $[\text{Ni(tet-a)}(\text{N}_3)\text{$_2$}]$</td>
<td>25</td>
</tr>
<tr>
<td>6.</td>
<td>The spectrum of $<a href="%5Ctext%7BBF%7D_4">(\text{Ni(tet-b)}\text{N}_3)\text{$_2$}</a>\text{$_2$}$</td>
<td>26</td>
</tr>
<tr>
<td>7.</td>
<td>The diagram for the triplet states of a $d^8$ configuration</td>
<td>27</td>
</tr>
<tr>
<td>8.</td>
<td>A proposed scheme for the trapping of nitrene intermediates</td>
<td>29</td>
</tr>
<tr>
<td>9.</td>
<td>Gross structure of $[\text{Ni(tet-a)}(\text{N}_3)\text{$_2$}]$</td>
<td>41</td>
</tr>
<tr>
<td>10.</td>
<td>Gross structure of $<a href="%5Ctext%7BBF%7D_4">(\text{Ni(tet-b)}\text{N}_3)\text{$_2$}</a>\text{$_2$}$</td>
<td>43</td>
</tr>
<tr>
<td>11.</td>
<td>Complex $\text{trans}[\text{MA}_4\text{E}_2]$</td>
<td>43</td>
</tr>
<tr>
<td>12.</td>
<td>Complex $\text{cis}[\text{MA}_4\text{E}_2]$</td>
<td>43</td>
</tr>
</tbody>
</table>
INTRODUCTION

In the past decade, photochemical studies on coordinated azides gave rise to a new research problem, based on whether photolysis will yield nitrene intermediates, azide radicals or both. The formation of a nitrene intermediate and azide radical from the irradiation of hydrazoic acid and azide ion are shown in equations (1) and (2), respectively.\textsuperscript{1,2}

\[
\begin{align*}
\text{HN}_3 & \xrightarrow{h\nu} \text{NH} + \text{N}_2 \quad (1) \\
\text{N}_3^- & \xrightarrow{h\nu} \text{e}^- (aq) + \text{N}_3 \quad (2)
\end{align*}
\]

Although the formation of nitrene intermediates is common in photolysis of organic azides, it is common for coordinated azides to yield azide radical intermediates upon irradiation.\textsuperscript{3,4} Basolo et al.\textsuperscript{5-7} have found that to date, only the azido-ammine complexes of rhodium(III) and iridium(III) yield nitrene intermediates.

Presently, two different azide complexes of the 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) ion have been prepared.\textsuperscript{8} However, studies on the formation of a coordinated nitrene intermediate by photolysis are still in the process of being completed. Rhodium, iridium, and nickel all belong to the same group. As a consequence, the success of trapping the nitrene intermediate from the azido-ammine complexes of rhodium and iridium has given some impetus
to the investigation of the formation of nitrene intermediates in the case of the azido complexes of these cyclic tetraamines of nickel(II). The determination of the gross structures of the azido complexes is essential for further study because the azido complexes may be either a monomer or a dimer. They may be tetrahedral, square planar or octahedral.

Photochemical activation is selective in nature. Firstly, molecules of a solute can be excited by selective radiation without any direct excitation of the surrounding solvent molecules. Secondly, each of the various electronically excited states of the compound under investigation may be obtained in principle by using suitable, nearly-monochromatic radiations. In order to know which particular excited state is reached with the radiations used, the electronic spectrum of the compound must be known and its absorption bands must be assigned.

Ligand field theory, which has proved to be of great value in discussions of the properties of transition metal complexes, is utilized in this thesis to interpret the electronic spectra of the two different azido complexes of nickel(II).

The main purpose of employing the ligand field theory in this research is to investigate the structure and the energy states of the two different azido complexes of nickel(II).
Spectroscopy

In general, several bands with very different extinction coefficients are found in the ultraviolet and visible spectra of most coordination compounds. The assignment of the various bands to transitions which lead to specific excited states is a very difficult problem. For convenience, scientists often use a preponderant molecular orbital to describe each state and then make a classification of the electronic transitions according to the location of the molecular orbitals involved. In general, three types of electronic transitions may be distinguished.

1. Transitions between molecular orbitals mainly localized on the central metal. Molecular orbitals of these types are derived from the metal d orbitals. These transitions are usually called d-d transitions or ligand field transitions.

2. Transitions between molecular orbitals mainly localized on the ligands and molecular orbitals mainly localized on the central metal. They are known as charge transfer (CT) or electron transfer transitions. Depending on whether the excited electron is originally located on the ligands or on the central metal, ligand-to-metal (LM) or metal-to-ligand (ML) charge transfer transitions can occur respectively. Generally speaking, the simple crystal field
and ligand field theories cannot be used to discuss the charge transfer bands; a molecular orbital approach is required. Because of the difficulties in making quantitative molecular orbitals calculations, the interpretation of the charge transfer bands is not attempted as often as the interpretation of the ligand field bands. The assignment of absorption bands to charge transfer transitions is based on the assumption that the central atom and the ligands are separated systems which only interact weakly with each other. As such, the ground state can be described by a preponderant electronic configuration consisting of localized molecular orbitals and thus a well-defined oxidation state of the central metal can be determined. Furthermore, charge transfer transitions can be defined as those adding or removing one electron from the partly filled shell of the metal and hence changing its oxidation state by -1 or +1. Ligand to metal charge transfer (LMCT) bands usually occur in the UV and the visible spectral region.

3. Transitions between molecular orbitals mainly localized on the ligands. Transitions of this type are called internal ligand or intra-ligand transitions. These transitions only involve "ligand" orbitals which are almost unaffected by coordination to the metal. Despite the fact that many coordination compounds should exhibit internal ligand bands, there are only a few cases where such bands have
been recognized. This is partly due to experimental difficulties since the internal ligand bands lie in the ultra-violet (UV) spectral region. Thus, they are often covered by the very intense charge transfer bands.

**Ligand Field Theory**

The ligand field theory is actually a modified crystal field theory. The latter treats the metal-ligand bonding as a purely electrostatic attraction, and all metal electrons are in pure metal orbitals; that is, the neighboring ions do not overlap with the central ion under consideration. However, in reality, appreciable overlapping with the surrounding ligands may be present. The general theory which deals with such situations is called the ligand field theory. The ligands can be ions or molecular dipoles.

The basic idea of the crystal theory was first proposed by Bacquerel in 1929. In the same year, Bethe developed it into a theory. He used an NaCl lattice to explain the theory. He supposed that the ions are hard spheres and the interactions between them are due only to the electrostatic potential set up by their charges. The total potential at any point near the central ion is the summation of the individual potentials from the surrounding ions. The relation is shown in (3).

\[
V_{(x,y,z)} = \sum_{i=1}^{n} V_{(i,x,y,z)} \quad (3)
\]
It was not until 1932 that the theory was first applied to chemistry by another famous scientist, Van Vleck, who set up a crystalline field model to explain the paramagnetism of the first transition series. Many excellent methods of working on the crystal field theory were set up by Van Vleck and his colleagues during this period. The work of Penney and Schlapp and Gorter had explained many of the magnetic properties of the salts of the transition metals. By that time, its most important features were obvious.

Actually, the theory can be approached semiempirically with its parameters to be determined experimentally, or it may also be interpreted (with less success) purely theoretically. In this case, its parameters are calculated using atomic functions of the central atom.

Theory of Electronic Spectra

The energy states of equivalent electrons moving in a central and crystal field can be found by the Schroedinger equation (4).

\[ H = E \Psi \]  

(4)

The total Hamiltonian for the electrons of the metal ion is given by:

\[ H = \sum_{i} \left( \frac{\mathbf{p}_{i}^{2}}{2m} - \frac{Z_{e}^{2}}{r_{i}} + \xi \left( r_{i} \right) \mathbf{L}_{i} \mathbf{S}_{i} \right) + \sum_{i<j} \frac{\mathbf{e}^{2}}{r_{ij}} + V_{C.F.} \]  

(5)

where \( Z \) is the effective nuclear charge, \( \xi \) is the coupling constant, \( n \) is the number of electrons, \( r_{i} \) is the distance of the \( i \)th electron from the nucleus, and \( r_{ij} \) is the distance
between the $i$th and $j$th electrons. The first term sums the kinetic energy over all the electrons, the second sums the attraction of all the electrons by the nucleus, the third term concerns the magnetic coupling between the spin and orbital magnetic momenta. The fourth term sums the mutual repulsion between each pair of electrons. An approximate rather than exact solution may be obtained from the Schroedinger equation. Either the weak field or strong field approach can be utilized to solve the equation. Fig. 1 and 2 show the two different approaches. By comparing the expectation values of the last three terms of (5), it is possible to distinguish three cases.

1. $\xi (r)(\ell \cdot s) < V_{C.F.} < \frac{e^2}{r_{ij}}$ Russell-Saunders coupling weak field case

2. $\xi (r)(\ell \cdot s) < \frac{e^2}{r_{ij}} < V_{C.F.}$ strong field case

3. $\frac{e^2}{r_{ij}} < V_{C.F.} < \xi (r) (\ell \cdot s)$ spin-orbit coupling

The Hamiltonian shown in equation (5) is, in general, not exactly soluble. Therefore, attempts to find approximate solutions using perturbation theory will be made.

The Hamiltonian of the unperturbed system is:

$$H_0 = \Sigma \frac{-\hbar^2}{2m} \frac{2}{V_i} \frac{Z_e}{r_i}$$

(6)

thus, the solution becomes

$$H_0 \psi_0 = E_0 \psi_0$$

(7)
Atomic Configuration \( (e^2/r_{ij}) \) Atomic states \( S,P,D,F \), etc. \( (V_{C.F.}) \) states of the complex

Fig. 1. The weak field approach procedure.

Atomic Configuration \( (V_{C.F.}) \) Complex Configuration \( (e^2/r_{ij}) \) states of the complex

Fig. 2. The strong field approach procedure.

If only the last two terms in equation (5) are considered, then the perturbation operator becomes:

\[
H_1 = \sum_{i<j} \frac{e^2}{r_{ij}} + V_{C.F.} = H_{e1} + H_{C.F.}
\]

(8)

Thus,

\[
H = H_0 + H_1
\]

(9)

The weak-field case

In the first step the influence of the electron interaction partially or completely removes the degeneracy of the unperturbed system. The second step studies how the electron-ligand interaction affects those terms which appear as a result of the splitting induced by the electron interaction.

The strong-field case

The strong-field case is the opposite of the weak-field case. In this situation, the electron interaction is assumed to be weak as compared to the ligand field interaction. Then, the consequences of the electron interaction are considered in the second step.
The success of using a crystal field model to identify the spectral relationships in monoacidopentaamine and diacidotetraamine complexes of cobalt(III) by Wentworth and Piper\textsuperscript{14} aroused considerable interest in the assignment of spectra of metal complexes and the interpretations of the ligand field parameters $D_s$ and $D_t$ or $\delta_\sigma$ and $\delta_\pi$.\textsuperscript{14}

In most cases, if the metal ion under consideration is octahedrally coordinated, a simple crystal field parameter, $D_q$, is sufficient to give fair approximation. In a regular octahedral environment, the five $d$ orbitals split into two groups. One group comprises the three orbitals $d_{xy}$, $d_{xz}$, and $d_{yz}$ known as the $t_{2g}$ orbitals and the other the orbitals $d_{x^2-y^2}$ and $d_{z^2}$ also known as $e_g$. $D_q$ is defined so that the separation between the two groups of $d$ orbitals is $10 D_q$. Actually, $D_q$ can be determined experimentally or theoretically.

However, if in a system the crystal fields have components with axial symmetry, then $D_s$ and $D_t$ are also required. The tetragonal radial parameters $D_s$ and $D_t$ may be considered as a tetragonal perturbation on the octahedral field.

Since the main interest of this research is in the transition energies, the first three terms of equation (5) need not be evaluated, as these are assumed to be constant. Evaluation of the secular determinant whose elements are given by

$$H_{pq} = \langle \psi_p / H' / \psi_q \rangle$$

(10)
where $\Psi_p$ and $\Psi_q$ are determinantal wave functions and

$$H' = \sum_{i<j}^n \frac{e^2}{r_{ij}} + \sum_i^n V_{C.F.}(r_i) \quad (11)$$

gives a solution of the secular determinant of the form

$$E = XB + X'C + X''Dq + X'''Ds + X''''Dt \quad (12)$$

where $B$ and $C$ are the Racah parameters and the $Dq$, $Ds$, and $Dt$ are the crystal field parameters. The $X$'s are coefficients and they are obtained from the solution of the secular determinant.

Methods for Resolving Overlapping Electronic Absorption Bands

An excellent method of resolving the overlapping electronic absorption bands was introduced by Fox et al.\textsuperscript{15} It is called the simple digital method. The method provides information of individual component peak positions, extinction coefficients and band widths. The greatest benefit is its easy applicability to computer methods. A general description of the method is given below.

A series of equations are set up by assuming that the wavelength spectrum, $\phi(\nu)$, has a single Gaussian peak centered at $\nu = \Lambda$, with extinction coefficient, $\varepsilon$, and width, $w$. The width is related to the standard deviations, $s$, defined in equation (13) by

$$w = 2s (2 \ln 2)^{\frac{1}{2}} \quad (13)$$

where
\[ \phi(\nu) = e^{-\frac{1}{2}(\nu-A)^2} \quad (14) \]

\[ \Psi(\nu) = d (-\ln \phi)/d\nu \quad (15) \]

\[ \Psi(\nu) = \frac{\nu-A}{s^2} \quad (16) \]

If there is only one single peak in the wavenumber spectrum, the quantity, \( \Psi(\nu) \), is linear in \( \nu \) with slope \( s^{-2} > 0 \) and \( \Psi(0) = A \). This is also true when one peak dominates all the others.

First, the spectral data are put into the transformation equation (15). The method proceeds as follows: the transformed data, the positive slopes and straight portions are given. Each of these straight portions indicates a region where one peak dominates all the other peaks. The value of \( s \) and \( A \) are estimated from equation (16), and used to obtain \( \varepsilon \) as

\[ \varepsilon = \phi(\nu) e^{\frac{1}{2} (\nu-A)^2/s^2} \quad (17) \]

The next step is to subtract the peak from the original spectrum and then repeat the process for the next peak and continue the same process until all the peaks are removed. For a more detailed description, refer to the original paper. In this work, computer programs are applied to the process of deconvolution.
Azide and Metal Azide Photochemistry

Generally speaking, the photochemistry of azide and organic azido compounds has been found to proceed via nitrene intermediates. Some typical reactions will be discussed in the following section. However, with the exception of azido complexes of rhodium and iridium, photolysis of azido complexes of most transition metals results in the formation of azide radical intermediates. Examples of the formation of azide radicals from the irradiation of some particular metal-azide complexes are shown in equations (18) and (19).

$$\text{Pt(dien)} N_3^{1+} \xrightarrow{hv} \text{Pt(dien)}^{3+} + N_3^- \quad (18)$$

(dien = diethylenetriamine)

$$\text{Cr(NH}_3)_5 N_3^{2+} \xrightarrow{hv} \text{Cr(NH}_3)_5^{2+} + N_3^- \quad (19)$$

Examples of the formation of nitrene intermediates from the irradiation of the azidopentaammines of iridium and rhodium are shown in equation (20) and (21).

$$\text{Ir(NH}_3)_5 N_3^{2+} \xrightarrow{hv} \text{Ir(NH}_3)_5 NH^{3+} + N_2 \quad (20)$$

$$\text{Rh(NH}_3)_5 N_3^{2+} \xrightarrow{hv} \text{Rh(NH}_3)_5 NH^{3+} + N_2 \quad (21)$$

Nitrenes

The simplest nitrene, NH, sometimes called imidogen, is an electron deficient, neutral species. Nitrene and its derivatives are extremely reactive intermediates. An excellent book about nitrenes was written by Lwowski. In this
thesis, no attempt has been made to describe the different
types of nitrene derivatives.

Some typical reactions of nitrenes are shown as (22) and
(23) below.

\[ \text{NH} + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{OH} \quad (22) \]

\[ \text{NH} + \text{HCl} \rightarrow \text{NH}_2\text{Cl} \quad (23) \]

Glen\textsuperscript{17} found that the nitrene molecule will react with
water to form hydroxylamine or with hydrogen chloride to
form chloroamine as shown in equations (22) and (23), respec-
tively. It has also been found that the nitrene intermediate
will undergo a free radical reaction in the presence of ethy-
lene to form \((\text{CH}_3\text{CH} = \text{NH})_n\) and \(\text{CH}_2 = \text{NCH}_3\).\textsuperscript{18} However, in the
condensed phase, aziridine is the only product.\textsuperscript{19}

\[ \text{NH} + \text{C}_2\text{H}_4 \rightarrow \text{HN} \triangleleft \quad (24) \]

An additional example is given by Jacox et al.\textsuperscript{19} In
the photolysis of azidoformate, nitrenoformate is generated
(25).

\[ \text{H} - \text{C} - \text{N}_3 \xrightarrow{\text{hv}} \text{H} - \text{C} - \text{N} + \text{N}_2 \quad (25) \]

In the presence of cyclohexene, the nitrene adds to
the double bond forming an aziridine derivative (26).

\[ \text{H} - \text{C} - \text{N} + \text{C}_6\text{H}_{12} \rightarrow \text{H} - \text{C} - \text{N} \triangleleft (26) \]
Magnetic Susceptibility by NMR

This thesis also offers a study of the magnetic susceptibility of \([\text{Ni(tet-b)}N_3]_2(\text{BF}_4)_2\) and \([\text{Ni(tet-a)}(N_3)_2]\) by nuclear magnetic resonance. This technique is based on that proposed by Evans.\(^{20}\)

The frequency at which proton resonance occurs depends on the magnetic environment of the proton and changes in this environment produce corresponding changes in the resonance frequency. If the environmental change is caused by the presence of a paramagnetic solute, it should be possible to relate the susceptibility of this solute to the change \((\Delta f)\) in the resonance frequency of a proton of the solvent. This is the basis of the Evans method in which the resonance frequency of a standard substance in a solution is compared to that of the same substance in an otherwise pure solvent.

The solvent is placed in a capillary tube. The solution under investigation is placed coaxially inside a normal NMR tube. The tubes are spun as is usual during NMR measurements. Under these circumstances, it can be shown that the gram magnetic susceptibility, \(\chi\), of the paramagnetic solute is

\[
\chi = \frac{3\Delta f}{2\pi fm} + \chi_0 + \frac{\chi_0 (d_o-d_s)}{m}
\]

(27)

where \(f\) is the frequency of the proton resonance in cycles per second, \(\chi_0\) is the mass susceptibility of the solvent, \(d_o\) is the density of the solvent, \(d_s\) is the density of the
solution and \( m \) is the mass of the substance contained in 1 ml of solution. For highly paramagnetic substances and with dilute solutions, the last two terms in equation (27) are cancelled without serious error.

The Synthesis of the Two Forms of the Azide Complexes of the 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Ion

The first and foremost synthetic macrocyclic ligand containing four nitrogen donors was prepared by Curtis by the reaction between ethylenediamine and acetone in the presence of nickel(II) salts.\(^{21}\) The structure of the complex is shown as (I) in the following equation (28).

\[ \text{Reduction} \]

Many such substances are now known. They form a new class of coordination compounds. Compound (I) in equation (28) is reduced to give two cyclic tetraaminenickel(II) complexes, (IIa) and (IIb). The difference between complexes (IIa) and (IIb) is the chirality of the two asymmetric carbon atoms. The two compounds can be readily separated by their
difference in solubilities. For detailed information refer to the original papers of Curtis.\textsuperscript{21} In addition, the azido complex of (IIa) which is neutral is soluble in chloroform. For this reason, (IIa) and (IIb) may be separated as their azido complexes. Figure 3 shows how $[\text{Ni(tet-a)}(\text{N}_3)_2]$ and $[\text{Ni(tet-b)}\text{N}_3]^2+$ can be prepared by a modification of the Curtis method, and how they are converted to the azido complexes by the method of Reed.\textsuperscript{8}

**Statement of the Problem**

The discussion presented in the previous section has come to this conclusion. Firstly, photochemical studies on azido complexes are few. Although azide and organic azides yield nitrene intermediates upon irradiation with ultraviolet radiation, most coordinated azides yield azide radical intermediates upon irradiation. Secondly, the success of trapping the nitrene intermediate from the azidoammine complexes of rhodium and iridium consequently inspires the study on $[\text{Ni(tet-a)}(\text{N}_3)_2]$ and $[\text{(Ni(tet-b)}\text{N}_3)_2]^2+$ ion.

Photochemical activation is selective in nature. It has been suggested by Basolo et al.\textsuperscript{7} in the rhodium species that a low energy excited state of the azido group was responsible for nitrene formation and that a charge transfer, ligand to metal state, of the azido complex was responsible for the photoreduction. Hence, it is necessary to identify the energy states of $[\text{Ni(tet-a)}(\text{N}_3)_2]$ and $[\text{(Ni(tet-b)}\text{N}_3)_2]^2+$ ion.
Fig. 3. Schematic Diagram: Steps 1, 2, 3 show the preparation of the two forms of the cyclic tetra-aminenickel(II) by a modification of the Curtis\textsuperscript{26} method while steps 4 through 8 show the preparation of their azido complexes by the method of Reed\textsuperscript{8}
EXPERIMENTAL

Materials

All reagents were reagent grade and used without additional purification unless otherwise specified.

Physical Measurements

Visible, ultraviolet and near infrared absorption spectra were obtained on a Cary 17 recording spectrophotometer. Infrared spectra were obtained on a Beckman IR4240 and Bausch and Lomb 250 recording spectrometers. Reported proton magnetic resonance spectra were determined by using a Varian A-60 nmr spectrometer.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Perchlorate, [H₂(1,7CT)](ClO₄)₂.—The complex was prepared by a modification of the published method⁸ as shown in Fig. 3. One hundred grams of 70% perchloric acid (HClO₄) and 60 g of ethylenediamine (H₂NCH₂CH₂NH₂) were used. Drop-wise, ethylenediamine was introduced to a large beaker of perchloric acid. An ice bath was used to cool the solution for the exothermic reaction. A white material appeared first, then disappeared. The solution was cooled to room temperature. An excess of acetone was added to the solution which was stirred constantly. Usually, twice the required quantity of acetone was added. The solution was cooled to room temperature again, filtered, and the precipitate was washed and then
dried in vacuum. The yield was 128 g (80%).

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) Perchlorate, [Ni(1,7CT)](ClO₄)₂.—This complex was prepared by a modification of the published method. Eight grams of nickel acetate (NiO₄C₂·6H₂O) was dissolved in 20 ml of warm N,N-dimethylformamide (DMF). To the solution was added 7.2 g of [H₂(1,7CT)](ClO₄)₂ and the solution was stirred until all of the [H₂(1,7CT)](ClO₄)₂ was dissolved. The solution was filtered. Forty ml of water was added to the filtrate, then 2 g of sodium perchlorate dihydrate (NaClO₄·2H₂O) was added. The solution was chilled to 0° and filtered. The precipitate was washed in vacuum with ethanol and then with ether. It was then dried by evaporation. The yield was 5.76 g (80%).

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-nickel(II) Perchlorate [Ni(tet)](ClO₄)₂.—The complex was prepared by a modification of the published method. Eight grams of [Ni(1,7CT)](ClO₄)₂ were dissolved in 75 ml of water at 90° with constant stirring. About 1 g of sodium borohydride (NaBH₄) was added slowly to the solution. The solution was kept at 90° for half an hr and then boiled for 1 hr. The solution was made acidic with concentrated hydrochloric acid. It was boiled for 15 min or until the solution became clear. It was filtered while hot. The volume was reduced to 30 ml by boiling. While the solution was still hot, 1.2 g of
sodium perchlorate were added. The solution was cooled in an ice bath and then was filtered. The precipitate was washed with ethanol and then with ether. The yield was 2.8 g (70%).

**Azido Complexes of the 5,7,7,12,14,14-hexamethy-1,4,8,11-tetraazacyclotetradecanenickel(II) Perchlorate, [Ni(tet-a) (N₃)₂] and [(Ni(tet-b)N₃)₂](ClO₄)₂.**—Three grams of sodium azide (NaN₃) and 10 g [Ni(tet)](ClO₄)₂ were mixed. Then 50 ml methanol and 50 ml of methanol saturated with sodium azide were added. The solution was heated with stirring (but not boiled) for 30 min. It was then cooled and filtered. The precipitate was washed with ether and dried. Chloroform was used to extract the [Ni(tet-a)(N₃)₂] for 12 hr in an Soxlet extractor. The violet filtrate contained the [(Ni(tet-a)(N₃)₂](ClO₄)₂. The overall yield for the azido complex was 6 g, 60%, and the yield for the [(Ni(tet-b)N₃)₂](ClO₄)₂ was 2.4 g, 40% of the azido complexes.

**[Ni(tet-b)](ClO₄)₂.**—About 4.5 g of [(Ni(tet-b)N₃)₂](ClO₄)₂ was dissolved in 20 ml of boiling water. To the solution was added 6 ml of 12 M hydrochloric acid. The volume was reduced to 10 ml and 6 ml of 70% perchloric acid was added to the solution and chilled. The yield was 3.2 g (70%).

**[Ni(tet-b)](BF₄)₂.**—About 0.5 g [Ni(tet-b)](ClO₄)₂ was dissolved in 10 ml of water. The solution was mixed with 20 ml of Dowex 1 x 4 (50 - 100 mesh) anion resin in the chloride
form for 20 min. It was then filtered. The volume was reduced to 5 ml and then this solution was passed slowly over a column of the same resin. The column was washed thoroughly. The eluent and washings were reduced to 5 ml. The procedure was repeated several times. Then 5 ml of hydrofluroboric acid was filtered into this solution. The solution was then chilled and filtered. The precipitate was washed with 2:1 ethanol-ether solution and then with ether alone. The yield of \([\text{Ni}(\text{tet-b})]\text{Cl}_2\) was 0.25 g, 50%, and the yield of \([\text{Ni}(\text{tet-b})](\text{BF}_4)_2\) was 0.2 g (40%).

5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II)-u-diazido-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Tetrafluoroborate, \([(\text{Ni}(\text{tet-b})\text{N}_3)_2](\text{BF}_4)_2\).—Approximately 0.1 g of \([\text{Ni}(\text{tet-b})]\) (\text{BF}_4)_2 and 0.01 g of ammonium azide (NH$_4$N$_3$) were dissolved in 5 ml of anhydrous ethanol. The solution was boiled rapidly. Then, to the solution was added 5 ml of a saturated solution of ammonium azide in anhydrous ethanol. The solution was boiled for 2 min and then cooled and filtered. The yield was 0.046 g (46%).

Ammonium Azide, NH$_4$N$_3$.—Approximately 1.6 g of ammonium nitrate, NH$_4$NO$_3$, and 1.3 g NaN$_3$ were ground to fine powder separately and then mixed together. The powder was placed in a sublimer and sublimed at least two times at 200°. The spectrum of the product was identical to the standard IR spectrum of ammonium
azide.22

Ion Exchange Resins.—Dowex (50 - 100 mesh) anion exchange resin was obtained in the chloride form. The resin was slurried in water and poured into a column. The column was washed at least 10 times the columns volume with 8 M hydrochloric acid. The column was backwashed with water until the eluents were neutral. To eliminate backwashing in subsequent experiments, the resin was removed from the column and washed on a sintered glass fit until the washings were neutral.

Bio-Rad AG 50 w-X4 (200 - 400 mesh) cation exchange resin was obtained in the hydrogen form. The procedure was the same as that of anion exchange resin.

Deconvolution.—In this work, computer programs prepared by J. L. Reed of this department were employed. First, the experimental data for these compounds, including the initial wavelength of the absorption spectrum, the increment of the wavelength for the absorption spectrum at which the absorptions were recorded, the concentration of the sample, and the pathlength of the cell used for the absorption spectrum were put into the computer. By running the program, the extinction coefficients, band maxima and band widths of the absorption spectrum were obtained. The second step was to vary the values of the band maxima, band widths and extinction coefficients and feed these values into the computer
until the extinction coefficient of each point of the band was very close to the actual band but without negative absorption; that is, the calculated values were less than the experimental values. The peaks were then subtracted sequentially until they were all removed. Thus, the whole spectrum was resolved and all the overlapping peaks were plotted (Fig. 4 and 5).

Magnetic Susceptibility

An accurately weighed quantity of \([(\text{Ni}(\text{tet-b})\text{N}_3)_2](\text{BF}_4)_2\] was dissolved in 2 ml of methylene chloride (CH\(_2\text{Cl}_2\)). About 1 ml of the solvent was transferred to the inner capillary tube of a nmr tube and the sample solution to the outer nmr tube (Fig. 4). Spectra were run on an A-60 nmr spectrometer.

The method for \([\text{Ni}(\text{tet-a})(\text{N}_3)_2]\) was exactly the same as that of \([(\text{Ni}(\text{tet-b})\text{N}_3)_2](\text{BF}_4)_2\). The only difference was that chloroform was used as a solvent.

Application of Ligand Field Theory

The spectra of \([\text{Ni}(\text{tet-a})(\text{N}_3)_2]\) and \([(\text{Ni}(\text{tet-b})\text{N}_3)_2](\text{BF}_4)_2\) after deconvolution of the absorption bands from 1300 nm to 210 nm are shown in Figs. 5 and 6, respectively.

The first step is to assign the approximate band positions for the transitions between the energy levels derived from the \(3F\) terms in \(D_{4h}\) symmetry. The energies of the transitions derived from the \(3F\) terms in \(D_{4h}\) symmetry are provided by Busch et al.\(^{23}\) in equations 29 to 32, and their parentage is shown in Fig. 7.
Fig. 4. Double compartment nmr tube.
Fig. 5. The spectrum of [Ni(tet-a)(N₃)₂].
Fig. 6. The spectrum of \([\text{Ni(tet-b)N}_3]_2\text{BF}_4\)\(_2\).
Fig. 7. The diagram for the triplet states of a d$^8$ configuration. The subscript g is omitted for states in O$_h$ and D$_{4h}$ for clarity in presenting the diagram.
\[
\begin{align*}
\bar{v}_1 &= E(3E_g^a) - E(3B_{1g}) = 10 Dq - 8.75 Dt \quad (29) \\
\bar{v}_2 &= E(3B_{2g}) - E(3B_{1g}) = 10 Dq \quad (30) \\
\bar{v}_3 &= E(3A_{2g}) - E(3B_{1g}) = 18 Dq - 4Ds - 5Dt \quad (31) \\
\bar{v}_4 &= E(3E_g^b) - E(3B_{1g}) = 18 Dq - 2Ds - 6.25Dt \quad (32)
\end{align*}
\]

The energy state \(3E_g^a\) comes from the splitting of the \(3T_{2g}(F)\) in octahedral symmetry on going to \(D_{4h}\) symmetry.

The observed spectra are fitted to the above equation by varying the parameters \(Dq\), \(Ds\), and \(Dt\), until the best fit of experimental data is obtained. The in-plane ligand field splitting parameter is defined as \(Dq^{xy}\) and the axial ligand field splitting parameter is defined as \(Dq^z\).

According to Wentworth\(^{14}\), \(Dq\) depends only on the in-plane field of strength; thus, \(Dq\) equals \(Dq^{xy}\). Wentworth also defined the relationship between \(Dq^{xy}\) and \(Dq^z\) as in equation (33).

\[
Dt(D_{4h}) = \frac{4}{7} (Dq^{xy} - Dq^z) \quad (33)
\]

A computer program to minimize the least square error between the observed and calculated spectra was prepared by J. L. Reed of this department to obtain the best fit.

The Process of Trapping Nitrene Intermediates from the Photolysis of \([(Ni(tet-b)N_3)_2(BF_4)_2]\)

A proposed scheme for the trapping of nitrene intermediates is shown in Fig. 8. Excess cyclohexene was added
Fig. 8. A proposed scheme for the trapping of nitrene intermediates.
to a saturated solution of [(Ni(tet-b)N₃)₂](BF₄)₂ in CH₂Cl₂. The solution was then irradiated until [(Ni(tet-b)N₃)₂](BF₄)₂ was decomposed. The decomposition of [(Ni(tet-b)N₃)₂](BF₄)₂ was determined by the conversion of its blue color to a yellow color of [(Ni(tet-b)]²⁺ ion. Water was then added to the solution. The aqueous layer of the solution was separated and passed first through a column of cation resin and then a column of anion resin. It was expected that the chloride salt of cyclohexenimine could be obtained.
RESULTS AND DISCUSSION

Evidence for the Azide-bridged Dimer, \([\text{Ni(tet-b)N}_3\text{]}_2\)(BF\(_4\))\(_2\).

A comparison of the IR spectrum of \([\text{Ni(tet-b)N}_3\text{]}_2\)(BF\(_4\))\(_2\) and the azide-bridged complex \([\text{Ni(tren)}_2\text{(N}_3\text{)}_2\text{]}\text{(BPh}_4\text{)}_2\), (tren-2,2\'',2\'''-triaminotriethylamine), shows that \([\text{Ni(tet-b)N}_3\text{]}_2\)(BF\(_4\))\(_2\) may be an azide-bridged dimer. First, the \(v_a\)(N\(_3\)) bands of \([\text{Ni(tet-b)N}_3\text{]}_2\)(BF\(_4\))\(_2\) observed that 2087 cm\(^{-1}\) (very sharp = vs) and 2032 cm\(^{-1}\) (shoulder = sh) are consistent with that of \([\text{Ni}_2\text{(tren)}_2\text{(N}_3\text{)}_2\text{]}\text{(BPh}_4\text{)}_2\) at 2075 cm\(^{-1}\) (vs) and 2035 cm\(^{-1}\) (sh). In addition, Table 1 shows that the electronic structures of these two azide complexes are quite similar.

Table 1. Electronic Spectral Data for \([\text{Ni}_2\text{(tren)}_2\text{(N}_3\text{)}_2\text{]}\text{(BPh}_4\text{)}_2\) and \([\text{Ni(tet-b)N}_3\text{]}_2\)(BF\(_4\))\(_2\).

<table>
<thead>
<tr>
<th>([\text{Ni}_2\text{(tren)}_2\text{(N}_3\text{)}_2\text{]}\text{(BPh}_4\text{)}_2)</th>
<th>([\text{Ni(tet-b)N}_3\text{]}_2)(BF(_4))(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(nm)</td>
<td>extinction coefficient (M(^{-1})cm(^{-1}))</td>
</tr>
<tr>
<td>579</td>
<td>26.4</td>
</tr>
<tr>
<td>792</td>
<td>3.6</td>
</tr>
<tr>
<td>956</td>
<td>57.2</td>
</tr>
</tbody>
</table>
Magnetic Susceptibility

Of many techniques available to a coordination chemist, the measurement of magnetic moment has been one of the most consistently useful. It provides some fundamental information of the electronic structure, the bonding and stereochemistry of the complexes. In this research, only the Evans method\textsuperscript{20} of determining magnetic susceptibility was employed. According to Evans the last terms in equation (27) can be cancelled without serious error for highly paramagnetic substances. It turns out, then, that

\[
\chi = \frac{3\Delta f}{2\pi mf}
\]  

(34)

Furthermore, the gram susceptibility, \(\chi\), is related to the molar susceptibility, \(\chi_m\), by expression (35),

\[
\chi_m = \chi \cdot M
\]  

(35)

where \(M\) is the molecular weight of the substance. In addition, the molar magnetic susceptibility can be expressed by the Curie's law, as shown in (36),

\[
\chi_m = \frac{C}{T}
\]  

(36)

where \(T\) is the absolute temperature and \(C\) is the Curie constant. The magnetic moment, \(\mu\), a quantity of considerable interest to chemists, can be expressed either as

\[
\mu = 2.824 \sqrt{C}
\]  

(37)

with respect to the Curie constant, or as

\[
\mu = \sqrt{n(n + 2)}
\]  

(38)
with respect to the number of unpaired electrons, \( n \).

The measured molar magnetic susceptibility, \( \chi_M \), was corrected for the diamagnetic contribution by applying Pascal's method as shown in equation (39),

\[
\chi_M(\text{corr}) = \chi_M + \chi_{\text{diam}}
\]

(39)

where \( \chi_M(\text{corr}) \) is the corrected molar magnetic susceptibility and \( \chi_{\text{diam}} \) is the diamagnetic contribution. The diamagnetic contribution can be expressed as

\[
\chi_{\text{diam}} = \sum n_A \chi_A
\]

(40)

where \( n_A \) is the number of atoms of susceptibility \( \chi_A \) in the molecule. The diamagnetic contribution for \([\text{Ni(tet-a)}(\text{N}_3)_2]\) and \([\text{Ni(tet-b)}\text{N}_3)_2](\text{BF}_4)_2\) is \(-0.265 \times 10^{-3} \) cgs unit and \(-0.556 \times 10^{-3} \) cgs unit, respectively.

The results of the study of the magnetic susceptibility of \([\text{Ni(tet-a)}(\text{N}_3)_2]\) and \([\text{Ni(tet-b)}\text{N}_3)_2](\text{BF}_4)_2\) are listed in Tables 2 and 3, respectively.

From the above magnetic susceptibility data, it is obvious that both \([\text{Ni(tet-a)}(\text{N}_3)_2]\) and \([\text{Ni(tet-b)}\text{N}_3)_2](\text{BF}_4)_2\) are paramagnetic substances because only paramagnetic substances can provide splittings from their solvent peaks. The number of unpaired electrons obtained from the study of magnetic susceptibility supports a triplet ground state for \([\text{Ni(tet-a)}(\text{N}_3)_2]\). It turns out that these two compounds would have high spin configurations rather than low spin configurations. The number of unpaired electrons also agrees with our
Table 2. Magnetic Susceptibility Data for \([\text{Ni(tet-a)(N}_{3})_{2}]\) at 311°K.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Concentration (g/ml)</th>
<th>Splitting (Hz)</th>
<th>(\chi) (cgs unit)</th>
<th>(\chi_{M}) (cgs unit)</th>
<th>(\mu) (BM)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00380</td>
<td>3.70</td>
<td>7.75x10^{-6}</td>
<td>3.58x10^{-3}</td>
<td>2.98</td>
<td>2.14</td>
</tr>
<tr>
<td>2</td>
<td>0.00355</td>
<td>3.45</td>
<td>7.74x10^{-6}</td>
<td>3.58x10^{-3}</td>
<td>2.98</td>
<td>2.14</td>
</tr>
<tr>
<td>3</td>
<td>0.00384</td>
<td>3.70</td>
<td>7.67x10^{-6}</td>
<td>3.55x10^{-3}</td>
<td>2.97</td>
<td>2.13</td>
</tr>
<tr>
<td>4</td>
<td>0.00320</td>
<td>3.10</td>
<td>7.71x10^{-6}</td>
<td>3.56x10^{-3}</td>
<td>2.97</td>
<td>2.13</td>
</tr>
</tbody>
</table>

Table 3. Magnetic Susceptibility Data for \([[(\text{Ni(tet-b)N}_{3})_{2}]\text{(BF}_{4})_{2}]\) at 311°K.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Concentration (g/ml)</th>
<th>Splitting (Hz)</th>
<th>(\chi) (cgs unit)</th>
<th>(\chi_{M}) (cgs unit)</th>
<th>(\mu) (BM)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00140</td>
<td>1.82</td>
<td>1.034x10^{-5}</td>
<td>1.032x10^{-4}</td>
<td>4.78</td>
<td>4.16</td>
</tr>
<tr>
<td>2</td>
<td>0.00156</td>
<td>2.05</td>
<td>1.045x10^{-5}</td>
<td>1.043x10^{-4}</td>
<td>4.81</td>
<td>4.18</td>
</tr>
<tr>
<td>3</td>
<td>0.00384</td>
<td>1.85</td>
<td>1.015x10^{-5}</td>
<td>1.014x10^{-4}</td>
<td>4.73</td>
<td>4.11</td>
</tr>
<tr>
<td>4</td>
<td>0.00320</td>
<td>2.00</td>
<td>1.026x10^{-5}</td>
<td>1.025x10^{-4}</td>
<td>4.76</td>
<td>4.14</td>
</tr>
</tbody>
</table>
assumptions that [Ni(tet-a)(N3)2] is a d8 system with D4h symmetry; while [(Ni(tet-b)N3)2](BF4)2 is a d8 system but with C2v symmetry.

Deconvolution of Spectrum of [Ni(tet-a)(N3)2] and the [(Ni(tet-b)N3)2]^2+ Ion

In Fig. 4 and 5 are reported the electronic spectra from the near ultraviolet region to the near infrared region (250-1300 nm) of [Ni(tet-a)(N3)2] and the [(Ni(tet-b)N3)2]^2+ ion. By the process of deconvolution, spectral data of the azido complexes are obtained as shown in Tables 4 and 5, respectively.

Spin-allowed, Symmetry-forbidden Transitions

Because LaPorte's rule forbids d→d transitions for symmetric complexes, nearly, but not all, of the absorption bands corresponding to d→d transitions are weak. The intensity of d→d transition bands, thus, depends on whether they are a consequence of vibronic coupling or of the lack of an inversion center in the molecule. In general, the d→d transition band of most six coordinate transition metal complexes involving inorganic ligands have low values of molar extinction coefficients which seldom exceed 200. In our experiments, the molar extinction coefficients of [Ni(tet-a)(N3)2] and the [(Ni(tet-b)N3)2]^2+ ion at the visible and infrared regions are fairly small. The intensities of these observed absorption bands are consistent with
Table 4. Spectral Data of \([\text{Ni(tet-a)}(\text{N}_3)_2]\) After Deconvolution.

<table>
<thead>
<tr>
<th>Band maximum (nm)</th>
<th>Band maximum (kk)</th>
<th>Extinction coefficient (M(^{-1}\text{cm}^{-1}))</th>
<th>Band width (kk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1010</td>
<td>9.90</td>
<td>11.86</td>
<td>3.53</td>
</tr>
<tr>
<td>720</td>
<td>13.89</td>
<td>2.57</td>
<td>2.68</td>
</tr>
<tr>
<td>630</td>
<td>15.87</td>
<td>1.15</td>
<td>1.27</td>
</tr>
<tr>
<td>540</td>
<td>18.52</td>
<td>8.26</td>
<td>3.51</td>
</tr>
</tbody>
</table>

Table 5. Spectral Data of \([(\text{Ni(tet-b)}\text{N}_3)_2](\text{BF}_4)_2\) After Deconvolution.

<table>
<thead>
<tr>
<th>Band maximum (nm)</th>
<th>Band maximum (kk)</th>
<th>Extinction coefficient (M(^{-1}\text{cm}^{-1}))</th>
<th>Band width (kk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>790</td>
<td>12.66</td>
<td>8.90</td>
<td>1.41</td>
</tr>
<tr>
<td>1008</td>
<td>9.90</td>
<td>53.30</td>
<td>3.49</td>
</tr>
<tr>
<td>740</td>
<td>13.51</td>
<td>11.50</td>
<td>0.96</td>
</tr>
<tr>
<td>600</td>
<td>16.67</td>
<td>97.30</td>
<td>3.66</td>
</tr>
</tbody>
</table>
spin-allowed symmetry-forbidden transitions. These qualitative statements concerning the spectra of $d^8$ systems are valid for high spin complexes, that is, those where the ground state has the same multiplicity as the free ion. Studies on the complex, $^{25}$ [Ni(tet-a)Cl$_2$], are in agreement with the above discussion. The above evidence helps us to justify the application of equations (29-30).

Justification of cis and trans Structural Assignment

It has been suggested by Curtis$^{26}$ that the reflectance spectra of the diacido complexes of the type NiL$_4$X$_2$, for example, Ni(Py)$_4$Cl$_2$, Ni(Py)$_4$Br$_2$, (Py = pyridine), Ni(en)$_2$(NCS)$_2$ and [Ni(tet-a)Cl$_2$], are indicative of trans structures while those of the monoazido complexes, for example, Ni(en)$_2$Cl, (Ni(en)$_2$Br, the dichloro bridged structure [(en$_2$NiCl$_2$Ni(en)$_2$]Cl$_2$ and [Ni(tet-b)(en)](ClO$_4$)$_2$, are known to have cis structures. From the work of Curtis and his coworkers,$^{26}$ some essential points are obvious. Firstly, the $^{3}B_{2g}$ transition for the cis complexes appears at a shorter wavelength (approximately at 820 nm), as compared to that of trans complexes (approximately at 1000 nm) while the $^{3}B_{1g} \rightarrow ^{3}E_g$ transition for the trans complexes (approximately at 550 nm) shifts towards a shorter wavelength than the cis complexes (approximately at 600 nm). Secondly, it is also recognizable in Curtis' paper$^{26}$ that the spectrum of the cis-[Ni(en)$_2$NO$_3$]ClO$_4$ compound shows a greater intensity than does the trans-[Ni(en)$_2$](NO$_3$)$_2$. In our experiments, the
complex \([\text{Ni(tet-b)N}_3\text{)}_2\text{(BF}_4\text{)}_2\] must be cis and the \([\text{Ni(tet-a)(N}_3\text{)}_2\] is spectrally different. The spectral data presented in Tables 3 and 4 agree with Curtis' assignment; that is, the \(3B_{1g} \rightarrow 3E_g^a\) transition for \([\text{Ni(tet-b)N}_3\text{)}_2\text{(BF}_4\text{)}_2\] shifts to a shorter wavelength than \([\text{Ni(tet-a)(N}_3\text{)}_2\] and that the \(3B_{1g} \rightarrow 3E_g^b\) transition for \([\text{Ni(tet-a)(N}_3\text{)}_2\] shifts to a shorter wavelength than \([\text{Ni(tet-b)N}_3\text{)}_2\text{(BF}_4\text{)}_2\].

**Assignment of the Bands**

Before discussing the results, a discussion of how the assignments of the spectral bands were made is indispensable. Tables 6 and 7 show the calculated and observed band maxima of the two azido complexes, \([\text{Ni(tet-a)(N}_3\text{)}_2\] and \([\text{Ni(tet-b)N}_3\text{)}_2\text{)}^{2+}\) and their assigned transitions. Earlier, Wentworth and Piper had already provided a method of interpreting the spectral relationship in monoacidopentaamine and diacidotetraammine complexes of cobalt(II) by means of the crystal field model.\(^{14}\) Many of the later works on the interpretation on the electronic spectrum of other compounds,\(^{23,25}\) were simulated by Wentworth and his coworkers. Busch, in his paper on axial distortion and electronic structure in the macrocyclic complexes of diacido-s,s'-axyyl-2,3-pentanedionebis(mercaptoethylimine)-nickel(II),\(^{23}\) presented a possible adaptation of the Piper-Wentworth model for assigning the peaks of the spectra of pseudo-tetragonal complexes. In
Table 6. Experimental and Calculated Band Maximum Data and their Transitions of [Ni(tet-a)(N$_3$)$_2$].

<table>
<thead>
<tr>
<th>Band Maximum (kk)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental</strong></td>
<td><strong>Calculated</strong></td>
</tr>
<tr>
<td>9.90</td>
<td>9.91</td>
</tr>
<tr>
<td>13.89</td>
<td>13.97</td>
</tr>
<tr>
<td>15.87</td>
<td>15.87</td>
</tr>
<tr>
<td>18.52</td>
<td>18.68</td>
</tr>
</tbody>
</table>

Table 7. Experimental and Calculated Band Maximum Data and their Transition of [(Ni(tet-b)N$_3$)$_2$](BF$_4$)$_2$.

<table>
<thead>
<tr>
<th>Band Maximum (kk)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental</strong></td>
<td><strong>Calculated</strong></td>
</tr>
<tr>
<td>12.66</td>
<td>12.61</td>
</tr>
<tr>
<td>9.90</td>
<td>9.84</td>
</tr>
<tr>
<td>13.51</td>
<td>13.45</td>
</tr>
<tr>
<td>16.67</td>
<td>16.77</td>
</tr>
</tbody>
</table>
this paper, the transition between the energy levels derived from the $^3F$ term in $D_{4h}$ symmetry were developed. It was also mentioned that only the sum of the axial changes would determine the electronic structure when all of the internuclear distances were equal. Hence, it was also possible to treat the electronic properties of some nickel complexes as a $D_{4h}$ symmetry even though the true symmetry was a $C_{2v}$.

Shortly afterwards, Drago and his coworkers\textsuperscript{25} also emphasized the applicability of the Wentworth crystal field model to the interpretation of the electronic structure of tetragonal nickel(II) complexes.

The order and energies for the transition between the energy levels derived from the $^3F$ term in $D_{4h}$ symmetry are given as in equations (29-32).

From the energy level diagram in Fig. 7, $^3B_1$ is the ground state, $^3E$ is the lowest excited state and $^3B_2$ is the second lowest excited state.

$[\text{Ni(tet-a)(N}_3^\text{)}_2]$  

The case of $[\text{Ni(tet-a)(N}_3^\text{)}_2]$ is easier, because it is a monomer and its gross structure is shown as in Fig. 9. As mentioned by Busch,\textsuperscript{23} it was the transition $^3B_{1g} \rightarrow ^3E_{g}$ which measured the tetragonal character of the complexes because the transition, $^3B_{1g} \rightarrow ^3B_{2g}$ was independent of both $D_s$ and $D_t$. So, $^3B_{1g} \rightarrow ^3B_{2g}$ may be used to determine the in-plane ligand splitting parameter, $Dq^{xy}$. The band of
Fig. 9. Gross structure of [Ni(tet-a)(N₃)₂]. It has a D₄h micro symmetry.
[Ni(tet-a)(N₃)₂] at 13.89 kk is now assigned to the transition, \( {^3B_{1g}} \rightarrow {^3B_{2g}} \) and is denoted as \( v_2 \). In the case of [Ni(tet-a)Cl₂] this transition occurs at 14.26 kk. Secondly, the band at 9.90 kk, that is the lowest observed excited state, is assigned to be \( {^3B_{1g}} \rightarrow {^3E_g} \) transition and is denoted as \( v_1 \). Dt is then solved using equation (29). Afterwards, the \( {^3B_{1g}} \rightarrow {^3A_{2g}} \) transition, denoted as \( v_3 \), is assigned to a band and the value of Ds is obtained from equation (31). As such, \( v_4 \) can be solved by equation (33). If the value of \( v_4 \) is not close to our experimental value, the value of \( v_3 \) from equation (31) has to be assigned again until a close approximation of the calculated value to the observed value of \( v_4 \) is obtained. The parameters Dt and Ds of [(Ni(tet-a)N₃)₂] were obtained as 464 cm⁻¹ and 1785 cm⁻¹, respectively.

[(Ni(tet-b)N₃)₂]⁺⁺

[(Ni(tet-b)N₃)₂]⁺⁺ is a dimer and it has a C₂ᵥ symmetry. Its gross structure is shown in Fig. 10. But, as it has been suggested earlier by Busch et al.,²³ it is possible to treat a C₂ᵥ symmetry as a D₄h. In this case, the band at 9.90 kk is assigned to be the \( {^3B_{1g}} \rightarrow {^3B_{2g}} \) transition. Assigning the 10 Dq to be the lowest excited state came mainly from the work of Trevor et al.²⁷ In his paper, Trevor gave the relationships of the trans and cis form of complexes. The models of the two complexes are presented in Fig. 11 and 12.
Fig. 10. Gross structure of \([\text{Ni(tet-b)N}_3)_2]^{2+}\).

Fig. 11. Complex trans \([\text{MA}_4\text{E}_2]\).

Fig. 12. Complex cis \([\text{MA}_4\text{E}_2]\).
Trevor also presented equations for finding the Dq, Dt, and Ds of the cis and the trans complexes.

Equations for trans $[\text{MA}_4\text{E}_2]$  

\[
\begin{align*}
Dq &= 1/6 \alpha^A_4 \\
Dt &= 2/21 (\alpha^A_4 - \alpha^E_4) \\
Ds &= 2/7 (\alpha^A_2 - \alpha^E_2)
\end{align*}
\]

Equations for cis $[\text{MA}_4\text{E}_2]$  

\[
\begin{align*}
Dq &= 1/12 (\alpha^A_4 + \alpha^E_6) \\
Dt &= 1/21 (\alpha^E_4 + \alpha^A_4) \\
Ds &= 1/7 (\alpha^E_2 + \alpha^A_2)
\end{align*}
\]

By comparing the parameters of Dq, Dt and Ds of the trans tetragonal complex with that of the cis complex, Trevor presented the relationship between these two forms. The relationship of the parameters are given in equations (47-49).

\[
\begin{align*}
Dq \,(\text{trans}) &= Dq \,(\text{cis}) - 7/4 \,Dt \,(\text{cis}) \\
Dt \,(\text{trans}) &= -2 \,Dt \,(\text{cis}) \\
Ds \,(\text{trans}) &= -2 \,Ds \,(\text{cis})
\end{align*}
\]

Although these relationships are only approximations, basically, they can be used to estimate the value of 10 Dq of the cis form. Since the value of Dq, Dt and Ds of the trans are known and they are positive values, therefore, the 10 Dq (trans) must be greater than the 10 Dq (cis). Consequently, the transition at 9.90 kk is assigned 10 Dq. After
solving 10 Dq, it is now possible to solve Dt by assigning v₁ as 12.66 kHz. Similarly, by assigning the value of v₃, the value of Ds is solved. Ds is then put into equation (32) and solved for v₄. The next step is to assign another value as v₃ and solve for Ds until a v₄ which is close to our experimental value is achieved. A computer program to minimize the least square error between the observed and calculated spectra was used to achieve the best values for Dq, Ds and Dt. In this case, the parameters Dt and Ds of [(Ni(tet-b)N₃)₂](BF₄)₂ were obtained as -317 cm⁻¹ and 1463 cm⁻¹, respectively.

Agreement of the Assignments with Dqₓᵧ and Dqᵺ

In addition, the in-plane ligand field splitting parameter Dqₓᵧ of [Ni(tet-a)Cl₂]²⁺ is 1,426 cm⁻¹ while [Ni(tet-a)(N₃)₂] is 1,397 cm⁻¹ and [(Ni(tet-b)N₃)₂](BF₄)₂ is 948 cm⁻¹. It turns out that the Dqₓᵧ of [Ni(tet-a)(N₃)₂] is very close to the [Ni(tet-a)Cl₂]. Consequently, [Ni(tet-a)(N₃)₂] is probably a trans and [Ni(tet-b)N₃]₂(BF₄)₂ must be a cis structure. The axial ligand field splitting parameter of Dqᵺ of Ni(PEX)(N₃)₂⁻²³ (PEX = s,s'-0-xylyl-2,3-pentanedionebismercaptoethylimine) is 918 cm⁻¹ and the Dqᵺ of Ni(PEX)Cl₂ is 794 cm⁻¹. According to Busch,²³ therefore, the observed spectrochemical series within the formulation of Ni(PEX)₂ is ClO₄⁻, I⁻ < Br⁻ < Cl⁻ < N₃⁻ < PEX < NCS. This series is typical for nickel(II). However, the Dqᵺ of
[Ni(tet-a)(N3)2] is 585 cm\(^{-1}\) and [(Ni(tet-b)N3)2]2(BF4)2 is 1539 cm\(^{-1}\). The Dq\(^Z\) of [Ni(tet-a)Cl2] is 420 cm\(^{-1}\). The value of Dq\(^Z\) of [Ni(tet-a)(N3)2] agrees with the position of N\(_3^-\) in the spectrochemical series. According to Trevor et al.,\(^2\) the Dq\(^Z\) of the cis form is equal to the Dq\(^XZ\) of the trans form. Consequently, the Dq of [(Ni(tet-b)N3)2](BF4)2 should be 1,397 cm. The value of Dq\(^Z\) of [(Ni(tet-b)N3)2](BF4)2 is thus close to the experimental value.

**Charge-transfer Bands**

The more intense absorptions in the near uv of both [Ni(tet-a)(N3)2] and [(Ni(tet-b)N3)2]2(BF4)2 should be the charge transfer bands. According to Jorgensen\(^2\)\(^8\)-\(^3\)\(^0\) the charge transfer transition energies may be directly related to the optical electronegativity of both the ligand and the transition metal. This relation can be expressed as in equation (50),

\[
\nu_{CT} = 30,000 \ x_{opt}(X) - x_{opt}(M) \quad (50)
\]

where \(\nu_{CT}\) is the charge transfer transition energy, \(x_{opt}(X)\) and \(x_{opt}(M)\) are the electronegativities of the donor and acceptor orbitals on the ligand and metal, respectively.

The transition energy, \(\nu_{CT}\) is corrected for inter-electronic repulsion variations by considering the spin pairing energy parameter, \(D\). The observed charge transfer transition energy becomes

\[
\nu_{CT}(observed) = \nu_{CT} + D \quad (51)
\]
In general, the spin pairing energy parameter, $D$, is approximately equal to $7B$. Schmidtke and Garthoff proposed the optical electronegativity of $N_3^-$ ion as 28. The optical electronegativity of Ni(II) is 2.0. Hence, $\nu_{CT}$ is equal to 24,000 cm$^{-1}$. As chloride is near azide in the nepheluaxetic series, therefore, it is possible to estimate the racah parameter, $B$, of $[\text{Ni(tet-a)}(N_3)_2]$ from $[\text{Ni(tet-a)}\text{Cl}_2]$. In the case of $[\text{Ni(tet-a)}\text{Cl}_2]$, $B$ is equal to 840 cm$^{-1}$. Therefore, it is predicted that the charge transfer band of $[\text{Ni(tet-a)}(N_3)_2]$ is near 30,000 cm$^{-1}$ (334 nm) using equation (51). It is found that $[\text{Ni(tet-a)}(N_3)_2]$ has a very intense peaks at 320 nm. This intense peak is consistent with spin-allowed and LaPorte-allowed transition. Therefore, it has a large extinction coefficient. Hence, it is obvious that the band which appears at 320 nm of $[(\text{Ni(tet-a)}(N_3)_2]$ is consistent with the charge transfer band. Similarly, the bands at 310 nm and 365 nm are also consistent with the charge transfer bands.

At this point, it is obvious that the assignments of the peaks are consistent with results presented in the literature and crystal field interpretation and it turns out that $[\text{Ni(tet-a)}(N_3)_2]$ is trans and $[(\text{Ni(tet-b)}N_3)_2](\text{BF}_4)_2$ is bridging. It has been observed in the papers on photolysis of $[\text{Rh(NH}_3)_5N_3]^{2+}$ and in $[\text{Ir(NH}_3)_5N_3]^{2+}$ by Basolo et al. that nitrenes were formed by irradiating both the
charge transfer and $d \rightarrow d$ bands and it was suggested that nitrene producing state was azide centered. Consequently, it is possible to perform experiments on the photolysis of the two azido complexes with confidence. In this thesis, only the photolysis of $[(\text{Ni(tet-b)N}_2)_2](\text{BF}_4)_2$ was performed. However, the experiments were unsuccessful in the process of trapping the nitrene intermediates in the photolysis of $[(\text{Ni(tet-b)N}_3)_2](\text{BF}_4)_2$. The failure could be partly due to the fact that only a small amount of $[(\text{Ni(tet-b)N}_3)_2](\text{BF}_4)_2$ was used in the photolysis; as a result, the nitrene intermediates were not detected. Nevertheless, it is certain that the irradiation of $[(\text{Ni(tet-b)N}_3)_2](\text{BF}_4)_2$ did cause decomposition of the compound.
CONCLUSION

The best achievement of this research is not only the presentation of additional evidence for the success of the Wentworth crystal field model but also the presentation of the spectroscopic and crystal field data of both [Ni(tet-a)(N₃)₂] and the [(Ni(tet-b)N₃)₂]²⁺ ion. The method of assigning the peaks to the energy status of these two azido complexes are reasonably stated. Special techniques, such as deconvolution and computer programs, were successfully applied here to increase the accuracy of the work. The attempt to obtain nitrene intermediates from the photolysis of [(Ni(tet-b)N₃)₂]²⁺ ion was unsuccessful due to the aforementioned factors. However, it is certain that [(Ni(tet-b)N₃)₂]²⁺ does decompose upon irradiation.
REFERENCES

8. J. L. Reed, Atlanta University, unpublished results, 1975.
17. H. Glen, Ber., 61, 702 (1928).