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A SPECTROPHOTOMETRIC INVESTIGATION OF NICKEL(II)
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DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Stephen Frank Pavkovic, B.S., M.S.

****

The Ohio State University
1964

Approved by

[Signature]
Adviser
Department of Chemistry
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VITA

October 9, 1932 .............................................. Born - Highland Park, Michigan

1955 ......................................................... B.S.; Wayne State University

1961 ......................................................... M.S.; Wayne State University

1955-1957 ..................................................... United States Army

1957-1959 ..................................................... Instructor, Department of Chemistry
                                               Henry Ford Community College
                                               Dearborn, Michigan

1959-1961 ..................................................... Instructor, Department of Chemistry
                                               Hillsdale College, Hillsdale, Mich.

1961-1963 ..................................................... Teaching Assistant, Department of
                                               Chemistry, The Ohio State University
                                               Columbus, Ohio

1963-1964 ..................................................... Research Fellow

FIELDS OF STUDY

Major Field: Inorganic Chemistry

Studies in Coordination Chemistry. Professor Devon W. Meek.
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>ii</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTIAL</td>
<td>14</td>
</tr>
<tr>
<td>A. Materials</td>
<td></td>
</tr>
<tr>
<td>1. Solvents</td>
<td>14</td>
</tr>
<tr>
<td>2. Nickel(II) compounds</td>
<td>15</td>
</tr>
<tr>
<td>3. Ligands</td>
<td>15</td>
</tr>
<tr>
<td>B. Preparation of Ni(ClO₄)₂ Complexes</td>
<td>15</td>
</tr>
<tr>
<td>1. Tris(ligand) complexes</td>
<td>15</td>
</tr>
<tr>
<td>2. Bis(ligand) complexes</td>
<td>20</td>
</tr>
<tr>
<td>3. Perchlorato(ligand) complexes</td>
<td>23</td>
</tr>
<tr>
<td>4. Diaquobis(ligand) complexes</td>
<td>25</td>
</tr>
<tr>
<td>5. Tetrakis(N-isopropylene)nickel(II) perchlorate</td>
<td>26</td>
</tr>
<tr>
<td>6. Other preparations</td>
<td>27</td>
</tr>
<tr>
<td>C. Preparation of NiCl₂ Complexes</td>
<td>28</td>
</tr>
<tr>
<td>1. Mono(ligand) complexes</td>
<td>28</td>
</tr>
<tr>
<td>2. Bis(ligand) complexes</td>
<td>32</td>
</tr>
<tr>
<td>D. Conductivity Measurements</td>
<td>37</td>
</tr>
<tr>
<td>E. Magnetic Measurements</td>
<td>37</td>
</tr>
<tr>
<td>F. Spectral Measurements</td>
<td>37</td>
</tr>
<tr>
<td>1. Infrared absorption spectra</td>
<td>37</td>
</tr>
<tr>
<td>2. Electronic absorption spectra</td>
<td>38</td>
</tr>
</tbody>
</table>
## CONTENTS (Contd.)

### III. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Spectra of Octahedral Ni(II) Complexes</td>
<td>40</td>
</tr>
<tr>
<td>Theory</td>
<td>40</td>
</tr>
<tr>
<td>B. Nickel(II) Perchlorate Complexes</td>
<td>54</td>
</tr>
<tr>
<td>1. Tris(ligand) complexes</td>
<td>54</td>
</tr>
<tr>
<td>2. Bis(ligand) complexes</td>
<td>67</td>
</tr>
<tr>
<td>3. Perchlorato(ligand) complexes</td>
<td>74</td>
</tr>
<tr>
<td>4. Diaquobis(ligand) complexes</td>
<td>95</td>
</tr>
<tr>
<td>5. Tetrakis(N-isopropyl)nickel(II) perchlorate</td>
<td>106</td>
</tr>
<tr>
<td>C. Nickel(II) Chloride Complexes</td>
<td>112</td>
</tr>
<tr>
<td>1. Mono(ligand) complexes</td>
<td>113</td>
</tr>
<tr>
<td>2. Bis(ligand) complexes</td>
<td>125</td>
</tr>
<tr>
<td>D. Comments on N,N-diethylen and N,N-dimethylen nickel(II) complexes</td>
<td></td>
</tr>
<tr>
<td>prepared by Goodgame and Venanzi</td>
<td>149</td>
</tr>
<tr>
<td>E. Summary</td>
<td>152</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>159</td>
</tr>
</tbody>
</table>
### TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. pK\textsubscript{b} Values for Methyl and Ethyl Substituted Amines</td>
<td>2</td>
</tr>
<tr>
<td>2. Ligands Used in the Investigation, and their Abbreviations</td>
<td>8</td>
</tr>
<tr>
<td>3. Boiling Points of Ligands Used</td>
<td>16</td>
</tr>
<tr>
<td>4. Physical and Spectral Properties of the Solid Complexes (<a href="%5Ctext%7BClO%7D_4">\text{Ni(ligand)}_3</a>_2)</td>
<td>55</td>
</tr>
<tr>
<td>5. Absorption Spectra of (<a href="%5Ctext%7BClO%7D_4">\text{Ni(ligand)}_3</a>_2) in Solution Using the Respective Ligands as Solvents</td>
<td>59</td>
</tr>
<tr>
<td>6. Absorption Spectra of (<a href="%5Ctext%7BClO%7D_4">\text{Ni(ligand)}_3</a>_2) in Aqueous Solution</td>
<td>60</td>
</tr>
<tr>
<td>7. Color, Corrected Magnetic Susceptibility, and Calculated Magnetic Moment—and Reflectance Spectra of (<a href="%5Ctext%7BClO%7D_4">\text{Ni(ligand)}_2</a>_2) Complexes</td>
<td>68</td>
</tr>
<tr>
<td>8. Physical and Electronic Absorption Spectral Properties of the Ni(II) Perchlorato Complexes</td>
<td>76</td>
</tr>
<tr>
<td>9. Infrared Spectra of the Perchlorate and Amine Bands for the Ni(II) Perchlorato Complexes</td>
<td>77</td>
</tr>
<tr>
<td>10. Changes in the Physical Properties on Heating (<a href="%5Ctext%7BClO%7D_4">\text{Ni(N-methylene)}_2(H_2O)_2</a>_2)</td>
<td>79</td>
</tr>
<tr>
<td>11. Donor Species Present in the First Coordination Sphere for the Perchlorato Complexes</td>
<td>94</td>
</tr>
<tr>
<td>12. Magnetic Moment and Reflectance Spectra of (<a href="%5Ctext%7BClO%7D_4">\text{Ni(ligand)}_2(H_2O)_2</a>_2) Complexes</td>
<td>96</td>
</tr>
<tr>
<td>13. Amine and Aquo Infrared Absorptions of (<a href="%5Ctext%7BClO%7D_4">\text{Ni(ligand)}_2(H_2O)_2</a>_2)</td>
<td>99</td>
</tr>
</tbody>
</table>
TABLES (Contd.)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(<a href="%5Ctext%7BClO%7D_4">\text{Ni(N-isopropyl)}_4</a>_2)</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>Absorption Spectra Band Maxima in (\text{cm}^{-1}) for</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>(\text{Ni(ligand)Cl}_2) Complexes</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>Gram and Corrected Molar Magnetic Susceptibilities and Magnetic Moments for</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>(\text{Ni(ligand)Cl}_2) Complexes</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>Gram and Corrected Molar Magnetic Susceptibilities and Magnetic Moments for</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>(\text{Ni(ligand)}_2\text{Cl}_2) Complexes</td>
<td></td>
</tr>
<tr>
<td>18.</td>
<td>Absorption Spectra Band Maxima in (\text{cm}^{-1}) for Type A</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>(\text{Ni(ligand)}_2\text{Cl}_2) Complexes</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td>Absorption Spectra Band Maxima in (\text{cm}^{-1}) for Type B</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>(\text{Ni(ligand)}_2\text{Cl}_2) Complexes</td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>Absorption Spectra Band Maxima in (\text{cm}^{-1}) for Type C</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>(\text{Ni(ligand)}_2\text{Cl}_2) Complexes</td>
<td></td>
</tr>
<tr>
<td>21.</td>
<td>Structures of Nickel Halide Complexes with Diamine Ligands</td>
<td>151</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1.</td>
<td>The effect of electronic repulsion and spin-orbit coupling on the atomic and octahedral terms for Nickel(II) ion</td>
<td>43</td>
</tr>
<tr>
<td>2.</td>
<td>Orgel energy diagram for a $d^8$ system in an octahedral field</td>
<td>45</td>
</tr>
<tr>
<td>3.</td>
<td>Tanabe-Sugano energy diagram for a $d^8$ system in an octahedral field</td>
<td>50</td>
</tr>
<tr>
<td>4.</td>
<td>$d^8$ Octahedral energy diagram including spin-orbit coupling</td>
<td>52</td>
</tr>
<tr>
<td>5.</td>
<td>Reflectance spectrum of $<a href="%5Ctext%7BClO%7D_4">\text{Ni}(\text{N-ethylen})_3</a>_2$</td>
<td>58</td>
</tr>
<tr>
<td>6.</td>
<td>$Dq$ vs. N-alkyl substituent on the ligand in $<a href="%5Ctext%7BClO%7D_4">\text{Ni}(\text{ligand})_3</a>_2$</td>
<td>61</td>
</tr>
<tr>
<td>7.</td>
<td>Reflectance spectrum of $<a href="%5Ctext%7BClO%7D_4">\text{Ni}(\text{N,N'-diethylen})_2</a>_2$</td>
<td>70</td>
</tr>
<tr>
<td>8.</td>
<td>Maki energy diagram for 4-coordinate $d^8$ system in $D_{4h}$ symmetry</td>
<td>72</td>
</tr>
<tr>
<td>9.</td>
<td>Vibrations of the ClO$_4^-$ Group as a function of symmetry</td>
<td>81</td>
</tr>
<tr>
<td>10.</td>
<td>Perchlorate regions in the infrared spectrum of A - $<a href="%5Ctext%7BClO%7D_4">\text{Ni}(\text{N-methylen})_2(\text{H}_2\text{O})_2</a>_2$ and B - $[\text{Ni}(\text{N-methylen})_2(\text{ClO}_4)_2]$</td>
<td>82</td>
</tr>
<tr>
<td>11.</td>
<td>Perchlorate regions in the infrared spectrum of $[\text{Ni}(\text{N,N'-dimethylen})_2(\text{ClO}_4)_2]$</td>
<td>84</td>
</tr>
<tr>
<td>12.</td>
<td>Perchlorate regions in the infrared spectrum of $[\text{Ni}(\text{N,N,N'-trimethylen})_2(\text{ClO}_4)_2]$</td>
<td>85</td>
</tr>
<tr>
<td>13.</td>
<td>Electronic absorption spectra of: $[\text{Ni}(\text{N,N',N'-trimethylen})_2(\text{ClO}_4)_2]$; $[\text{Ni}(\text{N-methylen})_2(\text{ClO}_4)_2]$; $<a href="%5Ctext%7BClO%7D_4">\text{Ni}(\text{N-methylen})_2(\text{H}_2\text{O})_2</a>_2$</td>
<td>88</td>
</tr>
<tr>
<td>14.</td>
<td>Maki energy diagram for 6-coordinate $d^8$ system in $D_{4h}$ symmetry</td>
<td>89</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>15.</td>
<td>Structure proposed for $[\text{Ni}(N,N,N',\text{trimethylen})_2 \ (\text{ClO}_4)_2]$</td>
<td>91</td>
</tr>
<tr>
<td>16.</td>
<td>Reflectance spectrum of $[\text{Ni}(\text{ethylen})_2(\text{H}_2\text{O})_2 \ (\text{ClO}_4)_2$</td>
<td>97</td>
</tr>
<tr>
<td>17.</td>
<td>Infrared spectrum of $[\text{Ni}(\text{ethylen})_2(\text{H}_2\text{O})_2 \ (\text{ClO}_4)_2$ from 4000 to 1300 cm$^{-1}$ (Nujol mull)</td>
<td>100</td>
</tr>
<tr>
<td>18.</td>
<td>Possible structure for the hydrolysis product of $[\text{Ni}(N-\text{isopropyl})_2(\text{ClO}_4)_2$</td>
<td>102</td>
</tr>
<tr>
<td>19.</td>
<td>Reflectance spectra of $[\text{Ni}(N-\text{isopropyl})_4]$ \ $(\text{ClO}_4)_2$</td>
<td>109</td>
</tr>
<tr>
<td>20.</td>
<td>Structure proposed for $[\text{Ni}(N-\text{isopropyl})_4]$ \ $(\text{ClO}_4)_2$</td>
<td>110</td>
</tr>
<tr>
<td>21.</td>
<td>Furlani energy diagram for a $d^8$ system in octahedral and $C_{2v}$ symmetries</td>
<td>119</td>
</tr>
<tr>
<td>22.</td>
<td>Reflectance spectra of: $\text{Ni}(\text{en})\text{Cl}_2$ and $\text{Ni}(N,N'-\text{diethylen})\text{Cl}_2$</td>
<td>121</td>
</tr>
<tr>
<td>23.</td>
<td>Absorption spectra of: $\text{Ni}(N,N,N',\text{trimethylen})\text{Cl}_2$ and $\text{Ni}(N,N,N',N'-\text{tetramethylen})\text{Cl}_2$ in CH$_2$Cl$_2$</td>
<td>123</td>
</tr>
<tr>
<td>24.</td>
<td>Crystal structure of Nipy$_2$Cl$_2$</td>
<td>126</td>
</tr>
<tr>
<td>25.</td>
<td>Possible crystal structure of 1:1 series compounds</td>
<td>127</td>
</tr>
<tr>
<td>26.</td>
<td>Reflectance spectra of: $\text{Ni}(\text{en})_2\text{Cl}_2$ and $\text{Ni}(N,N-\text{dimethylen})_2\text{Cl}_2$</td>
<td>133</td>
</tr>
<tr>
<td>27.</td>
<td>Infrared spectrum of $\text{Ni}(\text{en})_2\text{Cl}_2$ from 4000 to 1300 cm$^{-1}$ (Nujol mull)</td>
<td>135</td>
</tr>
<tr>
<td>28.</td>
<td>Absorption spectra of: $\text{Ni}(N-\text{methyl-N'-ethylen})_2\text{Cl}_2$ and $\text{Ni}(N,N'-\text{diethylen})_2\text{Cl}_2$</td>
<td>140</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>29.</td>
<td>Reflectance spectra of: Ni(N-methyl-N'-ethylen)$_2$Cl$_2$ and Ni(N,N'-diethylen)$_2$Cl$_2$</td>
<td>141</td>
</tr>
<tr>
<td>30.</td>
<td>Reflectance spectra of: Ni(N,N,N'-trimethylen)$_2$Cl$_2$ and Ni(N,N-diethylen)$_2$Cl$_2$</td>
<td>143</td>
</tr>
<tr>
<td>31.</td>
<td>Reflectance spectra of Nipy$_2$Cl$_2$</td>
<td>145</td>
</tr>
<tr>
<td>32.</td>
<td>Absorption spectrum of Ni(N,N,N'-trimethylen)$_2$Cl$_2$ in CH$_2$Cl$_2$ solution</td>
<td>148</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

A very large area of chemical study is devoted to acid-base properties and reactions. This endeavor has steadily increased its scope, just as the definitions of acids and bases have expanded from the Bronsted to Lewis concepts. The present work is concerned with the coordination properties of bases, and, in particular, basic nitrogen compounds; i.e., secondary and tertiary amines.

In the Lewis sense, a base has electron pairs available for use in forming bonds with those substances which can accept such electron pairs; i.e., acids. The acid can be a proton with empty s-orbitals, a transition metal ion with empty d-orbitals, or a metal with filled nd-orbitals but with empty (n+1)s and (n+1)p orbitals. It is generally accepted that the same fundamental bonding process is involved for all Lewis acids upon reaction with a base; i.e., a sigma bond is formed as acid-base orbitals overlap. However, in many instances a given series of bases may behave quite differently toward various Lewis acids.

As the hydrogen atoms on ammonia are progressively replaced with alkyl groups, the increasing inductive effects should render the nitrogen lone pair of electrons more polar (1), and thus more available for donation to a Lewis acid. Therefore, if the inductive factor were a major contributor, the substituted amines would be better electron pair donors than ammonia. Then the order of donor ability
would be $R_3N > R_2NH > RNH_2 > NH_3$. This will be referred to as the inductive order.

In fact, the inductive order is not observed for reaction of a series of alkyl amines with either the proton (2) or transition metal ions (3). To illustrate the observed basicity order in aqueous solutions, the values for methyl and ethyl substituted amines are listed in Table 1.

**TABLE 1**

*pK_b* Values for Methyl and Ethyl Substituted Amines

<table>
<thead>
<tr>
<th>R =</th>
<th>Methyl</th>
<th>Ethyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_3NH$</td>
<td>3.37</td>
<td>3.27</td>
</tr>
<tr>
<td>$R_2NH$</td>
<td>3.22</td>
<td>2.89</td>
</tr>
<tr>
<td>$R_3N$</td>
<td>4.20</td>
<td>3.36</td>
</tr>
</tbody>
</table>

For both methyl and ethyl amine series, the order of basicity is $2^o > 1^o > 3^o > NH_3$. This will be referred to as the aqueous order of basicity.

It is obvious that the effect of increasing substitution on the amine would hinder lone electron pair availability. This would lead to a steric order that may affect the donor ability exactly in the opposite manner to the inductive order, i.e., $NH_3 > RNH_2 > R_2NH > R_3N$. Such an order has been proposed for transition metal ions, since they form progressively weaker complexes with primary, secondary, and tertiary amines (4). Thus to understand the behavior of amine donors,
one needs to investigate systematically the factors which most influence coordination stability both toward protons and transition metal ions.

Investigations of Lewis acid-base phenomena relative to the proton have been fruitful as well as plentiful. Less liberal attention has been applied to transition metal ions, and therein lies the subject of this work. Previous work in this area has been spotted and non-definitive; similar experiments have often led to conflicting interpretations.

An early attempt to examine the basicity order of simple amines utilized boron derivatives as the Lewis acid. Systematic variations in the amine and acid substituents resulted in formation of adducts with a wide range of stabilities. Brown et al. (5) measured the dissociation constants of adducts in the gas phase, and the order of amine stability was found to be identical to the aqueous order. It was assumed that the same factors were operative as in the aqueous system, and subsequent studies (6-8) proposed a beta and a F strain to be the major factors. In essence, the aqueous order resulted from the competition of steric and inductive forces which were so balanced that secondary amines displayed optimum basicity followed by primary, etc.

Verhoek and Bruehlman (9) determined the first and second association constants for the reaction between primary and secondary amines with silver ion in aqueous solution. A plot of the first association constants for the complexes against the pK value of the amines resulted in two straight lines; one for the primary amines, and one for the
secondary amines. Thus, the amine-silver ion interaction in aqueous solution, is dependent upon the type of amine (primary or secondary), as also is true for the proton. Similarly, a kinetic study using stopped-flow techniques (10) has been reported for several substituted pyridine complexes with nickel ion. It has been found that the stronger the pyridine base, the slower its complex dissociates (11).

Methyl-substituted anilines are known to catalyze the ionization of nitramide in nonaqueous solvents. The order of catalytic efficiency was found (12) to be $3^0 > 2^0 > 1^0$; i.e., it follows the predicted inductive order. However, the pKb value for these bases determined in aqueous solutions is in just the reverse order. This suggested that solvation is an important factor in determining amine basicities; the more hydrogen atoms on the amine, the greater the interaction with hydroxylic solvents. Trotman-Dickenson (12) proposes that this solvation interaction rivals the inductive effect and causes the observed order of basicity. In the absence of hydroxylic solvents, the inductive order prevails.

Hall (13) correlated pKa to $-\sum\sigma^+$ for non-aromatic amines and concluded that solvation effects could account for basicity orders and their anomalies, whereas steric effects were much less successful in this regard. Several other investigators also have observed the inductive order in absence of interacting solvents. For example, ion-pair formation between n-butyl amines and 2,4-dinitrophenol takes place in chlorobenzene. The formation constants (14) are in the order $3^0 > 2^0 > 1^0$, although the aqueous pKb values for these amines are $2^0 > 1^0 > 3^0$. Identical results also were found when the other
halobenzenes were used as solvents (15). In addition, measurement of a charge transfer band associated with amine-iodine adducts indicates that the energy of the transition decreases with increasing substitution on the amine (16). This is a manifestation of the inductive order, for band wave length reflects the adduct stability. If the third row in the periodic table is examined, it is observed that the phosphines display a basicity order dependent primarily on inductive factors (17). This is to be expected as a result of the larger valence shell of phosphorus compared with nitrogen; consequently, the basicity is influenced less by steric factors. These various studies indicate the validity of a basicity order founded on inductive effects when other effects, such as solvation, are not operative.

To upset this appealing correlation of basicity with inductive factors, other investigators have found evidence for different apparent orders of basicity. Thus, formation constants of some monoalkyl-substituted diamines with copper(II) and nickel(II) (18) decrease with increasing ligand complexity, i.e., $1^0 > 2^0 > 3^0$. This supports a basicity order strongly dependent on steric factors. The same conclusion was drawn from a study of the stability constants for disubstituted diamines with nickel, copper, and zinc ions in aqueous solutions (19). Similarly, determination of the stoichiometry for the ethylamines reacting with calcium, cobalt(II), and zinc, indicate that increasing alkyl substitution leads to a decreasing coordination tendency (20). In addition, it has been postulated that the less substituted amines may hydrogen-bond to the metal ion in a complex (21).
This would lead to a stabilizing situation that is not possible with a tertiary amine.

A variety of basicity orders resulted from a kinetic study of amine-acid reactions in several nonaqueous solvents (22). Although no specific trend was observed, it appeared that solvation played an important part. Addition of hydroxylic solvents to the nonaqueous systems invariably affected the primary amines more than secondary. Pearson and Williams (23) examined the efficiency of the alkylamines to catalyze the ionization of nitroethane. An order was observed for the ethylamines which did not agree with that found for the methyl derivatives, and again solvation was believed to be the principal cause. Pearson, Boston, and Basolo (24) found that the rate of aquation of the trans-[Co(AA)\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{+} complexes increased with increasing length of the alkyl substituent on the N-alkylethylenediamines except for the methyl derivative. The slower rate of hydrolysis for this one example was attributed to the inductive effect which more than compensated for the steric requirement of the methyl group.

Bjerrum has tabulated the data of several investigators in such a manner as to emphasize the rather good correlation between the hydrogen ion affinity of particular ligands and their tendency toward complex formation with metal ions (25). Such a correlation would lead to the prediction that increasing alkyl substitution on nitrogen would produce better ligands than ammonia. However, others have concluded that primary aliphatic amines coordinate less readily than ammonia; secondary amines coordinate less readily than do the primary; and tertiary amines are almost devoid of ability to coordinate to metal ions (3).
It should be clear at this point that various investigators have concluded that several orders of amine basicity exist. Then, the objective of any study in this area should not aim at finding the absolute basicity order; the multitude of factors which compose basicity preclude any single correct order. Rather, quantitative information is sorely needed for each of the various basicity orders encountered above, in order to determine the most pertinent factors for each case. In an effort to examine some of these factors, the present study was undertaken.

As a result of the relatively recent clarification by ligand field methods of transition metal ion spectra (26), it is feasible to initiate a spectrophotometric study of the coordination interaction of amines with transition metal ions. The ligand field parameter Dq is taken as a measure of amine coordinating ability, and as such can be utilized to determine the donor order for a series of amines. This is of prime importance in correlating the factors which affect coordinating ability in the solid complexes.

Simple primary monoamines form weak complexes with transition metal ions which are readily decomposed in water (4). Since a mono-dentate ligand produces a weaker ligand field than when the same ligand atom is incorporated into a chelate, the N-substituted ethylenediamines were chosen for this study. The enhanced stability of the complexes which result from chelating amines allows for easier manipulation. It was proposed to substitute the N-hydrogens on ethylenediamine with simple alkyl groups such as methyl, ethyl, n-propyl, and isopropyl. From a systematic variation of the N-substituents, both inductive and
steric factors could be changed regularly. Thus the ligands used are all N-alkyl substituted derivatives of ethylenediamine; they are listed in Table 2, along with their abbreviations.

**TABLE 2**  
Ligands Used in the Investigation and Their Abbreviations

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylenediamine</td>
<td>en</td>
</tr>
<tr>
<td>N-methylethylenediamine</td>
<td>N-methylen</td>
</tr>
<tr>
<td>N-ethylethylenediamine</td>
<td>N-ethylen</td>
</tr>
<tr>
<td>N-propylethylenediamine</td>
<td>N-propylen</td>
</tr>
<tr>
<td>N-isopropylethylenediamine</td>
<td>N-isopropylen</td>
</tr>
<tr>
<td>N,N-dimethylethylenediamine</td>
<td>N,N-dimethylen</td>
</tr>
<tr>
<td>N,N'-dimethylethylenediamine</td>
<td>N,N'-dimethylen</td>
</tr>
<tr>
<td>N,N-diethylethylenediamine</td>
<td>N,N-diethylen</td>
</tr>
<tr>
<td>N,N'-diethylethylenediamine</td>
<td>N,N'-diethylen</td>
</tr>
<tr>
<td>N-methyl-N'-ethylethylenediamine</td>
<td>N-methyl-N'-ethylen</td>
</tr>
<tr>
<td>N,N,N'-trimethylethylenediamine</td>
<td>N,N,N'-trimethylen</td>
</tr>
<tr>
<td>N,N,N',N'-tremamethylethylenediamine</td>
<td>N,N,N',N'-tetramethylen</td>
</tr>
</tbody>
</table>

Nickel(II) was the transition metal ion selected as the Lewis acid for the following reasons. Nickel(II) has a large crystal field stabilization energy in an octahedral field, and chelated octahedral
complexes are possible with the ligand system used. Spectra of octahedral nickel complexes are very well known and adequately explained (27). Whereas it might be possible that tetragonal six-coordinate or four-coordinate square-planar species may form as well, such geometries for nickel(II) complexes have spectra distinctively different from the octahedral cases (28). Thus, the spectra would greatly assist the correct structural assignment. The ground state both in octahedral and tetragonal nickel(II) complexes is orbitally non-degenerate with a triplet spin state. Excited states of the triplet multiplicity will be perturbed only to a small extent by spin-orbit coupling (29). At room temperature, the effect of spin-orbit coupling broadens the absorption bands, but no sign of band splitting is to be expected. Thus, band energies can be measured adequately and unambiguous assignments are possible.

The anions associated with the nickel(II) salt were chloride and perchlorate. Chloride ion was utilized because of its ability to act as a ligand. It would be more difficult to prepare Ni(AA)₃⁺⁺ complexes with nickel chloride than with nickel perchlorate. However, Ni(AA)₂⁺⁺ and Ni(AA)⁺⁺ complexes with ethylenediamine derivatives could be prepared more directly with nickel chloride, since advantage would be taken of chloride ion coordinating ability in these latter two cases.

The coordination compound Ni(en)₃Cl₂ certainly ranks among the most extensive and accurately studied of chelated complexes. Preparation of this complex was first noted by Werner (30) and in view of the vast interest associated about the compound, it is surprising that
other stoichiometric ratios between Ni(II) and ethylenediamine were not investigated as thoroughly, or that preparations using substituted ethylenediamines have not been more extensive. Werner also isolated Ni(en)$_2$Cl$_2$, and at a later date Dalietos (31) prepared Ni(en)Cl$_2$. Thus it is possible that three types of chelated complexes may be prepared with nickel chloride, i.e., complexes which contain one, two, and three ethylenediamine molecules, respectively. Formation of tris complexes will be dependent on the donor properties of chloride ion. Although Cl$^-$ occupies a position below ethylenediamine in the spectrochemical series, (see p. 40) amine substitution may affect the coordination stability of the amine and favor bonding by the chloride ion.

The Ni(AA)$_2$Cl$_2$ complexes have attracted more attention in the past than those of the Ni(AA)Cl$_2$ type, and the preparation of Ni(en)$_2$Cl$_2$ is listed in Inorganic Synthesis (32). The complex Ni(en)$_2$Cl$_2$ exists as a dimeric species of the form [Ni$_2$(en)$_2$Cl$_2$]Cl$_2$ (33). The two coordinated chloride ions are in cis-positions of the octahedral configuration, and form a bridge between two nickel ions. The two remaining chloride ions are outside the coordination sphere. A similar compound, Ni(en)$_2$(NO$_2$)$_2$Cl, does not occur in a dimeric arrangement. The structure of the latter compound is believed to be octahedral with the anions occupying trans-positions (34). However, another related complex, Ni(en)$_2$(NO$_2$)$_2$ClO$_4$, is shown by X-ray analysis to have a chain structure in which two nickel ions are bridged by a nitrito oxygen atom (35). Furthermore, the complex Ni(en)$_2$(NCS)$_2$, has a trans-octahedral structure (36). Apparently, the Ni(en)$_2$ system occurs in a variety of structures.
Some reactions of Ni(en)$_2$X$_2$ complexes have been examined. The thermal dissociation of ammine and ethylenediamine complexes of Ni(II) has been studied by thermal gravimetric analytical techniques (37,38). The diamines appear to be lost in a step-wise fashion with increasing temperature. In another inquiry, substitution reactions involving the anions of Ni(en)$_2$AB were investigated (39). Complexes were isolated with mixed anionic groups in which A = NO$_2^−$ or NCS$^−$, and B = Cl$^−$, Br$^−$, and I$^−$. The formation of Ni(AA)$_2$Cl$_2$ complexes with the ligands N,N-dimethylethlen (40) and N,N-diethylethlen (41) is reported by Goodgame and Venanzi. By varying the anion, they were able to isolate complexes of different spectral and structural types. Examples of pseudo octahedral, tetragonal, and square-planar Ni(II) structures are contained in their work. It will be of interest to compare their results with the present study in which only the ligand has been altered.

It is conceivable that cases could arise when complex formation would be impossible because of ligand steric requirements. In such a case, chloride ion would be available to occupy a coordination site and offer another possibility for complex formation. Perchlorate ions are expected to serve in just the opposite capacity. The poor coordinating ability of perchlorate ion would favor the maximum number of coordinated amine molecules in the Ni(II) complex ion. However, a few complexes containing coordinated perchlorate ions have been reported.

Harris et al. (42) postulated on the basis of conductance measurements that [Ni(phen)$_2$(ClO$_4$)$_2$] and [Cu(dipy)$_2$ClO$_4$]PF$_6$ were formed. Very recently, McWhinnie (43) and Quagliano et al. (44) reported the
isolation and infrared characterization of the compounds [Cu(en)₂(ClO₄)₂] and [Ni(3,5-lutidine)₂(ClO₄)₂]. The 3-bromo; 3,5-dimethyl-; and 4-isopropyl-pyridine ligands have been reported to form complexes of the type [Ni(x-Py)₄(ClO₄)₂] also (45). In each of the last three cases above, the infrared data indicate that the perchlorate ion is coordinated as a monodentate ligand. A bidentate perchlorate group has been postulated in anhydrous Cu(ClO₄)₂ (46) and (CH₃)₃SnClO₄ (47). More recently, the first anionic complexes, containing only the perchlorate ion as a ligand, have been prepared (48).

Typical examples of N-alkyl-substituted ethylenediamine complexes of Ni(ClO₄)₂ also have been reported. Some complexes of interest were prepared by Glaser and Pfeiffer (49). They isolated [Ni(en)₃](ClO₄)₂ and [Ni(N-ethylen)₃](ClO₄)₂, and they also prepared complexes of the type [Ni(AA)₂(H₂O)₂](ClO₄)₂ with the ethylenediamine and N,N'-diethylen ligands. They list evidence for the formation of a bis complex when N,N-diethylen and nickel(II) thiocyanate are reacted. Keller and Edwards (50) isolated the complex [Ni(N-methylen)₃]Br₂ and some tris N-hydroxyalkylethylene diamine complexes of Ni(II) from ethanol, but no further work was undertaken to evaluate their stabilities compared to the ethylenediamine complex. Both N-methylen and N-ethylen were reported by Basolo and Murmann (51), to form tris(ligand) Ni(II) complexes in solution, although no compounds were isolated. Goodgame and Venanzi (40,41) also have reacted N,N-diethylen and N,N-dimethyl en with Ni(ClO₄)₂, but they isolated no tris diamine complexes.

In the present study, the nickel salts are reacted with the
ligands (Table 2) in nonaqueous systems to minimize complications with the water molecule acting as a ligand. It has been demonstrated that the instability of secondary and tertiary amine complexes in aqueous solutions cannot be used as a quantitative measure of metal-amine interactions because many other energy terms are operative (52).

In order to resolve the conflicting situation regarding the relative Lewis basicities of primary, secondary, and tertiary amines compared to their transition metal complex stabilities, this investigation was undertaken. The complexes which are possible from the twelve ligands used in this study, coupled with the two types of anions, and compounded by the various geometries that nickel complexes are known to display, imply that the proposed thesis investigation will provide greatly needed data and have significance beyond just the area of amine coordinating stability.
II. EXPERIMENTAL

A. Materials
1. Solvents

The absolute methanol (Mallinckrodt A. R.) and ethanol (commercial bulk solvent) used in this study were purified in the following manner. In a two liter flask, one liter of the alcohol was contained over 5 grams of clean magnesium metal and one gram of iodine for 12 hours. The mixture was refluxed for 12 hours, followed by fractionation through a heated column packed with helices; the boiling points were: methanol (64.5°) and ethanol (78.5°). Practical grade 2,2-dimethoxypropane (DMP) was obtained from Matheson Coleman and Bell, and was purified by refluxing over barium oxide for 6 hours followed by fractionation (79.4°). Dimethylformamide (Mallinckrodt), anhydrous diethylether (Mallinckrodt), dichloromethane (Mallinckrodt A. R.), and 70-72% perchloric acid (G. F. Smith Chemicals Company) were used as obtained from the manufacturers without further purification. When required, doubly distilled ion-free water was used. Practical grade nitromethane was purified by washing ten times with a 5% bicarbonate solution followed by drying 24 hours over anhydrous calcium chloride. The solution was then decanted and fractionated. The fraction boiling at 101.0°C was used for conductivity measurements.
2. **Nickel(II) compounds**

Nickel(II) perchlorate 6-hydrate was obtained from G. F. Smith Chemicals Company, and used without further treatment. Anhydrous yellow nickel(II) chloride was prepared from nickel(II) chloride 6-hydrate (J. T. Baker Chemical Company A. R.) by heating the latter to 110° for 3 days.

3. **Ligands**

Ethylenediamine and pyridine were obtained from Distillation Products Industries. All the other ligands used in this study were obtained from Ames Laboratories, Incorporated, with the exception of N-isopropylene. This ligand was prepared by the method of Coleman and Callen (53), whereby N-isopropylamine is added to ethylenimine in the presence of AlCl₃, and a yield of 75% was realized. The unsymmetrically substituted ethylenediamines were purified by distillation from clean sodium metal, but symmetrically substituted ethylenediamines required the use of anhydrous barium oxide instead. The observed boiling points of the ligands are listed in Table 3, and reported literature values are included for comparison.

B. **Preparation of Ni(ClO₄)₂ Complexes**

1. **Tris(ligand) complexes**

   **Tris(ethylenediamine)nickel(II) perchlorate**.—To 23.3 g. (0.075 mole) of Ni(en)₃Cl₂, 85 ml. of water were added and the resulting solution filtered. A solution of 25 g. (0.19 mole) anhydrous NaClO₄ in 12 ml. water was prepared, filtered, and slowly added to the purple solution containing the complex while stirring
### TABLE 3
Boiling Points of Ligands Used

<table>
<thead>
<tr>
<th>Ligand</th>
<th>b.p. °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylenediamine</td>
<td>118</td>
<td>117.2</td>
</tr>
<tr>
<td>N-methylen</td>
<td>116</td>
<td>114-115</td>
</tr>
<tr>
<td>N-ethylen</td>
<td>128</td>
<td>125-126</td>
</tr>
<tr>
<td>N-propylen</td>
<td>152</td>
<td>152-153</td>
</tr>
<tr>
<td>N-isopropylen</td>
<td>136</td>
<td>137-138</td>
</tr>
<tr>
<td>N,N-dimethylen</td>
<td>105</td>
<td>101-104</td>
</tr>
<tr>
<td>N,N'-dimethylen</td>
<td>120</td>
<td>118-119</td>
</tr>
<tr>
<td>N,N,N'-trimethylen</td>
<td>115</td>
<td>115-117</td>
</tr>
<tr>
<td>N,N,N',N'-tetramethylen</td>
<td>122</td>
<td>120</td>
</tr>
<tr>
<td>N-methyl-N'-ethylen</td>
<td>137</td>
<td>135</td>
</tr>
<tr>
<td>N,N-diethylen</td>
<td>146</td>
<td>142-144</td>
</tr>
<tr>
<td>N,N'-diethylen</td>
<td>152</td>
<td>148-150</td>
</tr>
</tbody>
</table>
at room temperature. A purple precipitate appeared immediately, and was isolated by filtration. The solid was washed with water-ethanol, ethanol-ether, and ether solutions in that order, and was then air dried; yield 8.4 grams. The filtrate also was purple.

**Anal. Calcd. for [Ni(NH₂CH₂CH₂NH₂)₃](ClO₄)₂:**

C, 16.46; H, 5.52; N, 19.19.

**Found:** C, 16.20; H, 5.47; N, 19.04.

**Tris(N-methylen)nickel(II) perchlorate.**---One hundredth mole (3.66 g.) of nickel(II) perchlorate hexahydrate was dehydrated (59) with a 10% excess (6.1 ml.) of 2,2-dimethoxypropane (DMP) while stirring. The dehydration is endothermic, and when the resulting solution had warmed to room temperature, the reaction was considered to be complete; this usually required 20-30 minutes. The solution was diluted with 5 ml. ethanol and filtered into a pressure equalizing addition funnel, care being taken to avoid exposure to the atmosphere. Three ml. of the ligand and 25 ml. ethanol were mixed and filtered into a 300 ml. 3-neck round bottom flask. The metal ion solution was added dropwise to the ligand solution, while stirring at room temperature. A purple solid separated, and was isolated by filtration on a fritted glass filter, washed three times with ethanol, and dried in a moisture-free air stream; yield 4.6 g. The filtrate was light purple.

**Anal. Calcd. for [Ni(CH₃NHCH₂CH₂NH₂)₃](ClO₄)₂:**

C, 22.52; H, 6.30; N, 17.51.

**Found:** C, 22.62; H, 6.21; N, 17.79.

All glassware used had standard-taper ground glass joints, and was rinsed three times with anhydrous alcohol before use. Many of the
following preparations employed the same technique as above, and therefore only an abbreviated preparation will be reported for these.

**Tris(N-ethylen)nickel(II) perchlorate.**—A solution of one hundredth mole nickel ion, 6.2 ml. DMP, and 10 ml. ethanol was added to a solution of 5 ml. ligand in 12 ml. ethanol at 0°C. Warming the solution followed by several cycles of stirring, scratching the flask sides with a glass rod, and recooling resulted in a purple solid. The solid was washed three times with ether and dried; yield 4.4 g. The filtrate was yellow. The solid was redisolved in 100 ml. methanol, and one ml. of ligand added to the boiling solution. Upon cooling to 0°C and slow addition of ether, a purple solid separated which was isolated, washed with ether, and air dried; yield 2.5 g. The filtrate was clear.

**Anal. Calcd. for [Ni(CH$_3$CH$_2$NHCH$_2$CH$_2$NH$_2$)$_3$(ClO$_4$)$_2$]:**

C, 27.61; H, 6.95; N, 16.10.

**Found:** C, 27.78; H, 6.75; N, 15.98.

**Tris(N-propylen)nickel(II) perchlorate.**—A solution of one hundredth mole nickel ion, 7.4 ml. DMP, and 7 ml. ethanol was added to a solution of 6 ml. ligand in 20 ml. ethanol at 0°C. The resulting purple solution was stirred 16 hours and contained a purple solid. The filtrate was yellow, and indicated the presence of the bis complex. Therefore, an additional 4 ml. of ligand in 10 ml. ethanol was added and the solution stirred for 6 hours. The purple solid was isolated, washed three times with a 1:1 ethanol-ether mixture, and both air and vacuum dried; yield 5.11 g. The filtrate was clear.
Anal. Calcd. for \([\text{Ni(CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2}]\)(\text{ClO}_4)_2:

\[\begin{array}{ccc}
C & 31.94; & H, 7.50; & N, 14.90.
\end{array}\]

Found:  C, 31.77; H, 7.36; N, 14.89.

**Tris(N,N'-dimethylen)nickel(II) perchlorate.**—A solution of one hundredth mole nickel ion, 6 ml. DMP, and 10 ml. methanol was added to a solution of 5 ml. ligand in 20 ml. methanol at 0°C. A blue solution formed and the slow addition of 25 ml. ether (until the point of cloudiness) resulted in a mixture of purple and orange crystals. An additional three ml. of ligand were added and only a purple solid separated. The solid was isolated, washed with ether, and air and vacuum dried; yield 4.61 g. The filtrate was clear.

Anal. Calcd. for \([\text{Ni(CH}_3\text{NHCH}_2\text{CH}_2\text{NHCH}_3}]\)(\text{ClO}_4)_2:

\[\begin{array}{ccc}
C & 27.61; & H, 6.95; & N, 16.10.
\end{array}\]

Found:  C, 27.30; H, 6.82; N, 15.84.

**Tris(N,N-dimethylen)nickel(II) perchlorate.**—A solution of one hundredth mole nickel ion, 7 ml. DMP, and 5 ml. ethanol was added to a solution of 6 ml. ligand, 17 ml. ethanol, and 20 ml. ether. A blue solution resulted and further addition of 30 ml. ether and stirring produced a blue solid. The solid was isolated, washed with ether, and air dried; yield 3.52 g. The filtrate was blue.

Anal. Calcd. for \([\text{Ni(CH}_3\text{2NCH}_2\text{CH}_2\text{NH}_2}]\)(\text{ClO}_4)_2:

\[\begin{array}{ccc}
C & 27.61; & H, 6.95; & N, 16.10.
\end{array}\]

Found:  C, 27.72; H, 7.01; N, 16.29.

**Tris(N-methyl-N'-ethylen)nickel(II) perchlorate.**—A solution of one hundredth mole of nickel ion and 6 ml. DMP was added to 8 ml. ligand at 0°C. A blue solution resulted, and the slow addition of
10 ml. ether resulted in a blue solid. The reflectance spectrum of the isolated solid indicated that the material contained both the bis and tris complexes; thus the compound was refluxed in a mixture of 4 ml. of the ligand and 25 ml. of anhydrous ether for 4 hours. Subsequently, the reflectance spectrum of the isolated complex showed no trace of the bis complex.

**Anal. Calcd.** for \([\text{Ni}(C_2H_3NHCH}_2\text{CH}_2\text{NHCH}_3)_3](\text{ClO}_4)_2\):

- C, 31.94; H, 7.50; N, 14.90.
- Found: C, 31.98; H, 7.57; N, 14.72.

2. **Bis(ligand) complexes**

**Bis(N-ethylen)nickel(II) perchlorate.**—A solution of 2 ml. ligand in 10 ml. ethanol was filtered into a dropping funnel and slowly added dropwise to a solution of one hundredth mole nickel ion, 6 ml. DMP, and 20 ml. ethanol at room temperature. A pale green solution resulted and slow addition of 50 ml. ether produced a coral solid. The solid was isolated, washed with ether, and air dried; yield 2.36 g. The filtrate was light blue.

**Anal. Calcd.** for \([\text{Ni}(\text{N-ethylen})_2](\text{ClO}_4)_2\):

- C, 22.14; H, 5.58; N, 12.91.
- Found: C, 21.94; H, 5.58; N, 13.05.

**Bis(N-propylen)nickel(II) perchlorate.**—A solution of 2.2 ml. ligand in 10 ml. ether was added to a solution of one hundredth mole of nickel ion, 6 ml. DMP, and 10 ml. ethanol. A blue-green solution resulted, and slow addition of 50 ml. ether produced a coral solid. The solid was isolated, washed with ether, and air and vacuum dried; yield 2.63 g. The filtrate was green.
Anal. Calcd. for \([\text{Ni}(\text{N-propylen})_2]\text{(ClO}_4\text{)}_2\):

\[
\begin{align*}
\text{C,} & \quad 26.00; \text{H,} \quad 6.11; \text{N,} \quad 12.13. \\
\text{Found: C,} & \quad 25.84; \text{H,} \quad 6.13; \text{N,} \quad 12.16.
\end{align*}
\]

Bis(N-isopropyl)nickel(II) perchlorate—A portion (1.83 g.) of the purple complex \([\text{Ni}(\text{N-isopropyl})_4]\text{(ClO}_4\text{)}_2\) (see p. 26) was placed in a clean 4 oz. bottle fitted with a #5 one-hole rubber stopper, and attached to a vacuum pump. The bottle and contents were heated to 100° by an oil bath while under vacuum for 6 hours. The solid became yellow and subsequent determination of magnetic moment showed a decrease from 3.10 to 1.06 B.M. The sample was further heated to 130° for 6 hours and its magnetic moment was now 0.63 B.M.; yield 1.08 g.

Anal. Calcd. for \([\text{Ni}(\text{N-isopropyl})_2]\text{(ClO}_4\text{)}_2\):

\[
\begin{align*}
\text{C,} & \quad 26.00; \text{H,} \quad 6.11; \text{N,} \quad 12.13. \\
\text{Found: C,} & \quad 26.29; \text{H,} \quad 6.13; \text{N,} \quad 12.16.
\end{align*}
\]

Bis(N,N'-dimethylen)nickel(II) perchlorate—I am indebted to Miss Shirley Ehrhardt for the preparation of bis(N,N'-dimethylen) nickel(II) perchlorate. Directions for this preparation are in her Masters thesis, The Ohio State University, 1963.

Anal. Calcd. for \([\text{Ni}(\text{N,N'}-\text{dimethylen})_2]\text{(ClO}_4\text{)}_2\):

\[
\begin{align*}
\text{C,} & \quad 22.10; \text{H,} \quad 5.54; \text{N,} \quad 12.91. \\
\text{Found: C,} & \quad 21.92; \text{H,} \quad 5.46; \text{N,} \quad 12.84.
\end{align*}
\]

Bis(N,N-dimethylen)nickel(II) perchlorate—Two ml. of ligand were added to a solution of one hundredth mole nickel ion, 6.2 ml. DMP, and 50 ml. ethanol. A green solution resulted, and upon
stirring for 30 minutes a yellow solid formed. The solid was isolated, washed with 1:1 ethanol-ether mixture, and air and vacuum dried; yield 2.41 g. The filtrate was green.

**Anal. Calcd. for** \([\text{Ni}((\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2](\text{ClO}_4)_2]\):

- **C**, 22.14; **H**, 5.78; **N**, 12.91.
- **Found:** **C**, 22.40; **H**, 5.55; **N**, 12.58.

**Bis(N-methyl-N'-ethylen)nickel(II) perchlorate.**—A solution of 2.4 ml. ligand in 10 ml. ethanol was added to a solution of one hundredth mole nickel ion, 6.4 ml. DMP, and 10 ml. ethanol. A green solution resulted and slow addition of ether produced an orange solid. The infrared spectrum of the isolated solid showed the presence of solvent bands at 3450 and 1650 cm\(^{-1}\). The solid was heated in vacuo to successive temperatures of 100, 120, and 130\(^\circ\)C for 24 hour periods before the solvent band disappeared from the infrared spectrum.

**Anal. Calcd. for** \([\text{Ni}(\text{N-methyl-N'-ethylen})_2](\text{ClO}_4)_2]\):

- **Found:** **C**, 26.15; **H**, 6.18; **N**, 11.94.

**Bis(N,N'-diethylen)nickel(II) perchlorate.**—A portion (1.50 g.) of the purple complex \([\text{Ni}(\text{N,N'-diethylen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2]\) (see p. 26) was heated in vacuo to 120 \(^\circ\)C for 24 hours, in a manner analogous to the preparation of \([\text{Ni}(\text{N-isopropyl})_2](\text{ClO}_4)_2\); yield 1.1 g. of a yellow solid.

**Anal. Calcd. for** \([\text{Ni}(\text{N,N'-diethylen})_2](\text{ClO}_4)_2]\):

- **C**, 29.41; **H**, 6.58; **N**, 11.43.
- **Found:** **C**, 29.15; **H**, 5.96; **N**, 11.46.
Bis(N,N-diethyliden)nickel(II) perchlorate.--A solution of 2.4 ml. ligand in 10 ml. ethanol was added to a solution of one hundredth mole nickel ion, 6 ml. DMP, and 10 ml. ethanol at room temperature. A yellow solid was produced, isolated, washed with ether, and air and vacuum dried; yield 4.0 g. The filtrate was pale green. This compound has been characterized previously (41), and therefore only the nitrogen content was determined.

**Anal. Calcd. for** [Ni((CH₂CH₂)₂NCH₂CH₂NH₂)₂](ClO₄)₂: N, 11.43.

**Found:** N, 11.52.

3. **Perchlorate(ligand) complexes**

The complexes prepared in this study which contain coordinated perchlorate ions were formed by heating the respective solid non-coordinated perchlorate derivatives to elevated temperatures in vacuo. Transition metal amine perchlorate complexes are hazardous and some have been reported to explode under rather mild temperature and shock conditions. Although an explosion has never occurred in this study, it must be emphasized that the compounds and this procedure are potentially very dangerous. The compounds were heated only after extensive safety precautions had been taken. The reaction vessel was shielded on all sides and never disturbed while hot. Less than one gram of each of the compounds was used for each preparative attempt. The temperature was increased very slowly, and frequent inspections were made to determine the appearance of the compound.

Diperchloratobis(N-methylene)nickel(II).--A yellow compound was formed when less than one gram of the complex [Ni(N-methylene)₂(H₂O)₂](ClO₄)₂ (see p.25) was heated under vacuum at 50°C for 18 hours.
Subsequent heating under vacuum to 100°C for 20 hours produced an orchid product. Presence of coordinated perchlorate ion was confirmed by the infrared spectra.

**Anal. Calcd. for [Ni(N-methylene)$_2$(ClO$_4$)$_2$]:**

\[
\begin{array}{ccc}
C & 17.76; & H, 4.97; \ N, 13.81.
\end{array}
\]

*Found: C, 17.66; H, 4.97; N, 13.71.*

**Diperclo ratobis(N,N'-dimethyl en)nickel(II).**—Approximately one gram of an analyzed sample of the yellow, square-planar [Ni(N,N'-dimethylene)$_2$(ClO$_4$)$_2$] (see p. 21) was heated under vacuum to 120-125°C for 60 hours. The infrared spectrum of the resulting violet compound demonstrates that the perchlorate ion is coordinated.

**Anal. Calcd. for [Ni(N,N'-dimethylene)$_2$(ClO$_4$)$_2$]:**

\[
\begin{array}{ccc}
C & 22.14; & H, 5.58; \ N, 12.91.
\end{array}
\]

*Found: C, 21.93; H, 5.69; N, 12.78.*

**Diperclo rato b is(N,N,N'-trim ethylen)nickel(II).**—Mixing the dehydrated solution of Ni(II) perchlorate with an ethanol solution of N,N,N'-trimethylene produced a mixture of coral colored [Ni(amine)$_2$] (ClO$_4$)$_2$ and blue [Ni(amine)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ crystals. However, on heating one gram of this mixture under vacuum to 110°C for 48 hours a homogeneous green compound, which has no water peaks in the infrared spectrum, was formed.

**Anal. Calcd. for [Ni(N,N,N'-trimethylene)$_2$(ClO$_4$)$_2$]:**

\[
\begin{array}{ccc}
C & 25.98; & H, 6.11; \ N, 12.13.
\end{array}
\]

*Found: C, 25.59; H, 6.20; N, 11.83.*
4. Diaquobis(ligand) complexes

Dianaqobis(N-methylen)nickel(II) perchlorate.—The intermediate tris-amine complex [Ni(N-methylen)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2} was prepared as previously (see p. 17). A violet colored solution of 20 ml. methanol, 4 ml. water, and 4.11 g. (8.5 x 10\textsuperscript{-3} mole) of [Ni(N-methylen)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2} was prepared. A 30% aqueous solution containing 1.70 x 10\textsuperscript{-2} mole of perchloric acid was added slowly to the above solution. The blue hydrolyzed solution was evaporated to a syrup and then further evaporated at 100\textdegree C for two hours. Eight ml. of ethanol were added to the yellow cooled syrup and blue crystals formed. The crystals were collected upon a filter, washed with a mixture of 1:1 ethanol-ether, and dried in a dry air stream; yield 2.06 g. Distinct and intense infrared absorption peaks at 3550, 3480, and 1632 cm\textsuperscript{-1} indicated the presence of coordinated water molecules and the analytical data correspond to [Ni(N-methylen)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}.

**Anal. Calcd. for [Ni(N-methylen)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}:**

C, 16.30; H, 5.47; N, 12.66.

**Found:** C, 16.56; H, 5.23; N, 12.97.

Dianaqobis(N-ethylen)nickel(II) perchlorate.—A portion (1.50 g.) of the complex [Ni(N-ethylen)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} was placed in a 50 ml. micro flask fitted with a six inch water jacket condenser. Twenty-five ml. of ether then was added and the slurry was refluxed. One-half ml. of water was added and a blue layer appeared. The ether layer was decanted, and the remaining blue syrup produced blue crystals upon exposure to air for 2 days. Care was taken to prevent the entrance of dust and dirt into the flask. The infrared spectrum of the solid
showed sharp and well defined bands at 3610, 3540, and 1631 cm$^{-1}$, which confirm the presence of water in the complex.

**Anal. Calcd. for [Ni(N-ethylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$:**

C, 20.61; H, 6.03; N, 11.94.

**Found:** C, 21.40; H, 6.15; N, 12.22.

**Diaquobis(N,N'-dimethylene)nickel(II) perchlorate.**—This complex was prepared from [Ni(N,N'-dimethylene)$_2$(ClO$_4$)$_2$] in essentially the same manner as that given for [Ni(N-ethylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$. However, in this case the water was added in a dropwise manner to the ether slurry while shaking the flask instead of refluxing.

**Anal. Calcd. for [Ni(N,N'-dimethylene)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$:**

C, 20.61; H, 6.03; N, 11.94.

**Found:** C, 20.98; H, 5.99; N, 12.08.

**Diaquobis(N,N'-diethylen)nickel(II) perchlorate.**—A solution of one hundredth mole nickel ion, 6 ml. DMP, and 10 ml. ethanol was added to a solution of 6.1 ml. ligand in 30 ml. ethanol. A blue solution resulted and a purple solid was produced. The isolated solid was washed with a 1:1 ethanol-ether mixture and air dried; yield 3.97 g. The filtrate was pale green.

**Anal. Calcd. for [Ni(N,N'-diethylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$:**

C, 27.42; H, 6.88; N, 10.66.

**Found:** C, 27.44; H, 7.07; N, 11.49.

5. **Tetrakis(N-isopropylcnylen)nickel(II) perchlorate**

A solution of one hundredth mole nickel ion, 6 ml. DMP, and 5 ml. ethanol was added to a solution of 12 ml. ligand in 10 ml. ethanol at
0°C. As the two solutions react, a momentary brown color is noticed, then a blue solution resulted and a purple solid was formed. The isolated solid was washed with ether and air and vacuum dried; yield 5.30 g. The filtrate was clear, but yielded a yellow solid when an excess of ether was added.

**Anal.** Calcd. for [Ni(N-isopropyl)en](4)[ClO4]2:

C, 36.05; H, 8.47; N, 16.82.

Found: C, 36.89; H, 8.18; N, 16.59.

6. Other preparations

**Using the ligand Ni,N,N',N'-tetramethyl.**—A solution of one hundredth mole nickel ion, 6 ml. DMP, and 10 ml. ethanol was added to a solution of 10 ml. ligand in 10 ml. ethanol. A gray solution formed and a gray solid mass was present. After stirring for 2 hours the solution became green and well defined green needles separated. The isolated solid was washed with ether, and air and vacuum dried; yield 1.83 g. The filtrate was red-brown.

**Anal.** Found: C, 27.17; H, 6.55; N, 10.56.

The filtrate from the above preparation was exposed to air overnight and well defined maroon crystals formed along with a small amount of white solid. The white solid was soluble in ethanol, whereas the maroon crystals were not. The maroon crystals were washed with ethanol and then ether. They were air and vacuum dried; yield 1.55 g. The filtrate was clear.

**Anal.** Found: C, 27.69 and 28.28; H, 7.05 and 7.02;

N, 8.58 and 8.47; Cl, 10.79; Ni, 14.80.
Three ml. of the ligand were added to a solution of one hundredth mole of nickel ion in 14 ml. DMP. A blue-green solution resulted and a bright red solid rapidly formed. The isolated solid was washed with ether and air and vacuum dried; yield 2.66 g. The filtrate was red-brown. These three substances containing the \( N,N',N'\)-tetramethylen ligand were not completely characterized, and are, therefore, omitted from the discussion section.

**Anal.** Found: C, 28.41; H, 6.76; N, 8.46.

Using the ligand \( 1,3-N,N',N'\)-tetramethyldiaminebutane.—Preparation of complexes also was attempted using the ligand \( 1,3-N,N',N'\)-tetramethyldiaminebutane. Several preliminary reactions gave little indication for complex formation; indeed, a green solid precipitated upon reaction, and from its infrared spectrum the solid was assumed to be nickel hydroxide; however, the liquor above the hydroxide was yellow, but a solid could not be isolated. Thus a more thorough synthetic effort was not undertaken with this N-substituted amine.

C. **Preparation of NiCl\(_2\) Complexes**

1. **Mono(ligand) complexes**

\( \text{Mono(ethylenediamine)nickel(II) chloride.} \) Two hundredths mole (2.56 g.) of anhydrous nickel(II) chloride was added to 50 ml. methanol and stirred for 12 hours. The flask contents were protected from atmospheric moisture by a Drierite drying tube. The green solution was filtered and 1.25 ml. ligand were added dropwise at room temperature. A dark green solution resulted and the slow addition of 40 ml. ether caused formation of a light green solid. The isolated solid was washed with ether and air and vacuum dried; yield 2.61 g. The filtrate was blue.
**Mono(N-methylen)nickel(II) chloride.**—Two hundredths mole of nickel(II) chloride was added to 75 ml. methanol, stirred 12 hours, and then filtered. To this solution 1.1 ml. of ligand were added and the slow addition of 250 ml. ether caused a light green solid to separate. The isolated solid was washed with ether and air and vacuum dried; yield 2.63 g. The filtrate was yellow.

**Anal. Calcd. for Ni(en)Cl₂:**  
C, 17.68; H, 4.95; N, 13.75  
**Found:** C, 17.90; H, 4.88; N, 13.78.

**Mono(N-ethylen)nickel(II) chloride.**—Two hundredths mole of NiCl₂ was added to 50 ml. methanol, stirred overnight, and filtered. To this solution 2.2 ml. ligand were added and a dark green solution resulted. The solvent was evaporated with a dry air stream and a light green solid precipitated. The isolated solid (2.56 g.) was dissolved in 43 ml. methanol and the solution was boiled. Three drops of ligand were added to the hot solution which was then filtered. The slow addition of 20 ml. ether caused precipitation. The isolated solid was washed with 1:1 methanol-ether mixture and air dried; yield 1.25 g. The filtrate was green.

**Anal. Calcd. for Ni(N-ethylen)Cl₂:**  
C, 22.06; H, 5.55; N, 12.86  
**Found:** C, 21.89; H, 5.44; N, 12.70.

**Mono(N-propylen)nickel(II) chloride.**—Two hundredths mole of NiCl₂ was added to 50 ml. methanol, stirred overnight, and filtered. To this solution 4 ml. ligand were added and after stirring for 3 hours, a light blue solid was formed which was separated by filtration (0.97 g.).
Fifty ml. of ether were added slowly to the green filtrate, and a light green solid was isolated, washed with ether, and air dried; yield; 1.48 g. The filtrate was green.

**Anal. Calcd. for Ni(N-propylen)Cl$_2$:**

- C, 25.91; H, 6.09; N, 12.09.
- Found: C, 24.55; H, 5.94; N, 12.39.

**Mono(N,N'-dimethylen)nickel(II) chloride.**—This compound was prepared by Miss Ehrhardt, and details appear in her Masters Thesis, The Ohio State University, 1963.

**Anal. Calcd. for Ni(N,N'-dimethylen)Cl$_2$:**

- C, 22.06; H, 5.55; N, 12.86.
- Found: C, 22.30; H, 5.65; N, 12.91.

**Mono(N,N-dimethylen)nickel(II) chloride.**—Two hundredths mole NiCl$_2$ was added to 75 ml. methanol, stirred overnight, and filtered. To this solution 1.6 ml. ligand were added, and the slow addition of 125 ml. ether resulted in a green precipitate. The isolated solid was washed with ether and air and vacuum dried; yield 2.80 g. The filtrate was yellow.

**Anal. Calcd. for Ni(N,N-dimethylen)Cl$_2$:**

- C, 22.06; H, 5.55; N, 12.86.
- Found: C, 22.20; H, 5.61; N, 12.99.

**Mono(N-methyl-N'-ethylen)nickel(II) chloride.**—Two hundredths NiCl$_2$ was added to 100 ml. methanol, stirred overnight, and filtered. To this solution 3.6 ml. ligand were added, and the slow addition of 500 ml. ether resulted in a green precipitate. The isolated solid was washed with ether and air dried; yield 1.43 g. The filtrate was blue-green.
**Mono(N,N'-diethylen)nickel(II) chloride.**—Two hundredths mole of NiCl<sub>2</sub> was added to 50 ml. methanol, stirred overnight, and filtered. To this solution 3.1 ml. ligand were added and a green precipitate formed. The isolated solid was washed with ether and air dried; yield 1.74 g. The filtrate was green.

**Mono(N,N,N'-trimethylen)nickel(II) chloride.**—Two hundredths mole of NiCl<sub>2</sub> was added to 75 ml. methanol, stirred overnight, and filtered. To this solution 4.5 ml. ligand were added, and the slow addition of 200 ml. ether caused a green solid to form. The isolated solid was washed with ether, and air and vacuum dried; yield 3.53 g. The filtrate was green.

**Mono(N,N,N',N'-tetramethylen)nickel(II) chloride.**—Two hundredths mole of NiCl<sub>2</sub> was added to 100 ml. methanol, stirred overnight, and filtered twice. To this solution 13 ml. ligand were added and a green precipitate gradually formed. The isolated solid was washed with ether, and air and vacuum dried; yield 2.73 g. The filtrate was green.
Anal. Calcd. for Ni(N,N,N',N'-tetramethylen)Cl₂:

C, 29.32; H, 6.56; N, 11.40.

Found: C, 30.18; H, 6.96; N, 11.38.

2. Bis(ligand) complexes

Bis(ethylenediamine)nickel(II) chloride.—Two hundredths mole of NiCl₂ was added to 50 ml. methanol, stirred overnight, and filtered. To this solution 2.1 ml. ligand were added and after stirring for 3 hours a blue solid formed. The isolated solid was washed with a 1:1 methanol-ether mixture and air dried; yield 2.69 g. The filtrate was blue.

Anal. Calcd. for Ni(en)₂Cl₂: C, 19.23; H, 6.46; N, 22.43.

Found: C, 19.02; H, 6.40; N, 22.39.

Bis(N-methylen)nickel(II) chloride.—Two hundredths mole of NiCl₂ was added to 75 ml. methanol, stirred overnight, and filtered. To this solution 2.5 ml. of ligand were added and the slow addition of 75 ml. ether resulted in the separation of a blue solid. The isolated solid was recrystallized from 50 ml. methanol and 10 ml. ethanol. The complex was separated by filtration, washed with a 1:1 ethanol-ether mixture, and air and vacuum dried; yield 2.48 g. The filtrate was blue.

Anal. Calcd. for Ni(N-methylen)₂Cl₂:

C, 25.93; H, 7.25; N, 20.16.

Found: C, 26.09; H, 7.40; N, 19.96.

Bis(N-ethylen)nickel(II) chloride.—Two hundredths mole of NiCl₂ were added to 100 ml. ethanol, stirred for 48 hours, and filtered.
To this solution 4.5 ml. ligand were added and a green solution formed. The further addition of 4 ml. ligand caused separation of a blue solid. The isolated solid was washed with a 1:1 ethanol-ether mixture and air dried; yield 3.1 g. The filtrate was green.

**Anal. Calcd. for Ni(N-ethylen)$_2$Cl$_2$:**

\[
\begin{align*}
\text{C} & : 31.41; \\
\text{H} & : 7.91; \\
\text{N} & : 18.31.
\end{align*}
\]

**Found:** C, 31.18; H, 7.86; N, 18.10.

**Bis(N-propylen)nickel(II) chloride.**—Two hundredths mole of NiCl$_2$ was added to 50 ml. methanol, stirred overnight, and filtered. To this solution 4 ml. ligand were added and after stirring for 3 hours a blue solid formed. The isolated solid was washed with a 1:1 methanol-ether mixture and air dried; yield 0.97 g. The filtrate was green.

**Anal. Calcd. for Ni(N-propylen)$_2$Cl$_2$:**

\[
\begin{align*}
\text{C} & : 35.96; \\
\text{H} & : 8.45; \\
\text{N} & : 16.78.
\end{align*}
\]

**Found:** C, 35.69; H, 8.43; N, 16.51.

**Bis(N-isopropylen)nickel(II) chloride.**—Two hundredths mole of NiCl$_2$ was added to 100 ml. ethanol, stirred 4 days, and filtered. To this solution 6 ml. ligand were added and after stirring one hour a blue precipitate formed. The isolated solid was recrystallized from a solution of 80 ml. methanol and 10 ml. ligand, separated by filtration, washed with a 1:1 ethanol-ether solution, and air dried; yield 1.16 g. The filtrate was green.

**Anal. Calcd. for Ni(N-isopropylen)$_2$Cl$_2$:**

\[
\begin{align*}
\text{C} & : 35.94; \\
\text{H} & : 8.45; \\
\text{N} & : 16.78.
\end{align*}
\]

**Found:** C, 36.04; H, 8.54; N, 16.57.
**Bis(N,N'-dimethylen)nickel(II) chloride.**—This compound was prepared by Miss Ehrhardt, and directions appear in her Masters thesis, The Ohio State University, 1963.

**Anal. Calcd. for Ni(N,N'-dimethylen)$_2$Cl$_2$:**

\[
\begin{align*}
    C & : 31.41; \\
    H & : 7.91; \\
    N & : 18.31.
\end{align*}
\]

**Found:**

\[
\begin{align*}
    C & : 31.35; \\
    H & : 7.81; \\
    N & : 18.13.
\end{align*}
\]

**Bis(N,N-dimethylen)nickel(II) chloride.**—Two hundredths mole of NiCl$_2$ was added to 100 ml. ethanol, stirred overnight, and filtered twice. To this solution 10 ml. ligand were added and after stirring for 2 hours a blue solid was formed. The isolated solid was washed with a 1:1 ethanol-ether mixture and air and vacuum dried; yield 3.60 g. The filtrate was green.

**Anal. Calcd. for Ni(N,N-dimethylen)$_2$Cl$_2$:**

\[
\begin{align*}
    C & : 31.41; \\
    H & : 7.91; \\
    N & : 18.31.
\end{align*}
\]

**Found:**

\[
\begin{align*}
    C & : 31.39; \\
    H & : 7.97; \\
    N & : 17.21.
\end{align*}
\]

**Bis(N,N,N'-trimethylen)nickel(II) chloride.**—Two hundredths mole of NiCl$_2$ was added to 100 ml. ethanol, stirred for 24 hours, and filtered twice. To this solution 10 ml. ligand were added and a green solid gradually separated. The isolated solid was washed with ether; and air and vacuum dried; yield 2.85 g. The filtrate was green.

**Anal. Calcd. for Ni(N,N,N'-trimethylen)$_2$Cl$_2$:**

\[
\begin{align*}
    C & : 35.96; \\
    H & : 8.45; \\
    N & : 16.78.
\end{align*}
\]

**Found:**

\[
\begin{align*}
    C & : 36.22; \\
    H & : 8.68; \\
    N & : 16.65.
\end{align*}
\]

**Bis(N-methyl-N'-ethylen)nickel(II) chloride.**—Two hundredths mole of NiCl$_2$ was added to 100 ml. ethanol, stirred for 20 hours, and filtered twice. To this solution 6.3 ml. ligand were added and a dark
blue solution resulted. The slow addition of 400 ml. ether caused 
separation of a blue solid which was isolated by filtration, washed 
with ether, and air dried; yield 4.53 g. The filtrate was green.

Anal. Calcd. for Ni(N-methyl-N'-ethylen)_2Cl_2:

C, 35.96; H, 8.45; N, 16.78.

Found:  C, 35.67; H, 8.46; N, 16.53.

**Bis(N,N'-diethylen)nickel(II) chloride.**—Two hundredths mole of 
NiCl_2 was added to 100 ml. ethanol, stirred for 20 hours, and fil-
tered twice. To this solution 7 ml. ligand were added and a blue solid 
gradually formed. The isolated solid was washed with ether and air 
dried; yield 2.51 g. The filtrate was blue.

Anal. Calcd. for Ni(N,N'-diethylen)_2Cl_2:

C, 39.81; H, 8.91; N, 15.48.

Found:  C, 41.37; H, 9.20; N, 14.53.

**Bis(N,N-diethylen)nickel(II) chloride.**—Two hundredths mole of 
NiCl_2 was added to 100 ml. ethanol, stirred 20 hours, and filtered 
twice. To this solution 6 ml. of ligand were added and a green solid 
gradually formed. The isolated solid was washed with ether and air 
dried; yield 5.09 g. The complex was recrystallized from an ethanol-
methanol mixture. The filtrate was green.

Anal. Calcd. for Ni(N,N-diethylen)_2Cl_2:

C, 39.81; H, 8.91; N, 15.48.

Found:  C, 39.56; H, 8.80; N, 15.23.

**Bis(pyridine)nickel(II) chloride.**—Two hundredths mole of NiCl_2 
was added to 100 ml. ethanol, stirred for 24 hours, and filtered. 
To this solution 2.8 ml. ligand were added and a green solution re-
sulted. A light green solid gradually formed while the solution was
stirred. The isolated solid was washed with ether and air dried; yield 4.6 g. The filtrate was green.

**Anal. Calcd. for Ni(py)$_2$Cl$_2$: N, 9.75. Found: N, 9.39.**

D. **Conductivity Measurements**

Molar conductance measurements were carried out using an Industrial Instruments Model RC-16B conductivity bridge. The measurements were obtained in approximately $10^{-3}$ molar solutions of nitromethane and used a cell with a constant of 1.47. The temperature was held at 24.6° with a constant temperature bath.

E. **Magnetic Measurements**

Magnetic moments were determined by the Gouy method at room temperature using Hg[Co(NCS)$_4$] as the standard. The field strength was approximately 7,000 gauss and the measurements were made using a Consolidated Engineering Corporation magnet and power supply. A Sauter Monopan Balance was used to determine the change in weight of the powdered sample in the magnetic field. The molar susceptibility in each case was corrected for the diamagnetism of the ligands (60). The susceptibility of [Ni(N-methylen)$_2$(ClO$_4$)$_2$] was determined by the Faraday technique.

F. **Spectral Measurements**

1. **Infrared absorption spectra**

Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer and a Beckman IR-9 high resolution spectrophotometer. The samples were prepared as Nujol mulls between crystalline KBr discs and as solutions in dichloromethane. The
polystyrene spectrum was used for calibration. Samples used in the spectral measurements for those complexes containing coordinated perchlorate ion were manipulated and prepared in a nitrogen filled dry box, and, thus, they were never in contact with moist air.

2. **Electronic absorption spectra**

**Reflectance spectra.**—Spectra of finely ground solid samples were obtained with a Beckman DU spectrophotometer equipped with a standard Beckman reflectance attachment using U.S.P. MgCO₃ as a blank (61). The use of plastic cover plates permitted examination over the range from 1100 to 300 mμ. Readings were taken at 10 mμ intervals except in the regions of absorption maxima where readings were taken every 5 mμ.

Reflectance spectra also were determined on the Cary Model 14 recording spectrophotometer. The basic procedure using Nujol mulls was reported recently by Lee, Griswold, and Kleinberg (62). Personal experience has shown this to be a very reliable and quick method. Two 4.25 cm filter paper discs were saturated with Nujol, and the excess removed by compressing the discs between tissue. A mull was prepared and placed on one disc with a curved micro spatula. Since the paper discs were set on the ends of the usual Cary Model 14 solution cell carriages, an area on the disc no larger than the carriage optical opening need to be covered with the Nujol mull. The discs were held in place with a large ball-joint clamp. Operation during measurement of the spectrum was in the normal manner. The position of the spectrum on the chart paper, and the slit width could be controlled by addition or removal of Nujol from the reference disc. Spectra obtained in this manner were identical to the Beckman DU measurements for all cases.
examined with the exception of the diaquobis(ligand) complexes (see p. 104).

**Solution spectra**—Solution spectra of the complexes were obtained with a Cary Model 14 recording spectrophotometer using sets of matched one, five, and ten cm quartz cells. The tris(ligand) solutions were prepared by dehydrating a weighed amount of nickel(II) perchlorate hexahydrate in a volumetric flask using 2,2-dimethoxypropane (DMP), and then adding the particular ligand to the volumetric mark to form the complex and act as solvent. In the cases of the symmetrical-dialkylethlenediamines small amounts of dimethylformamide were required to maintain solution. The ligand solution spectra were examined over the wave length range from 1300 to 330 m\(\mu\). A sharp dip in the absorption band at 1050 m\(\mu\) was observed in the ligand spectra, and was found to be caused by the presence of acetone and methyl alcohol in the sample cell which originated from the DMP used for dehydration of the nickel salt. Since the positions and intensities of the absorption bands of the complexes showed no changes due to the presence or absence of DMP or any of its reaction products, it was employed regularly as the dehydrating agent.

Aqueous and dichloromethane solutions were prepared by dissolving weighed amounts of analyzed complexes in the respective solvent. It was possible to examine the \(\text{CH}_2\text{Cl}_2\) solutions from 1700 to 300 m\(\mu\).
III. RESULTS AND DISCUSSION

A. Spectra of Octahedral Ni(II) Complexes-Theory

Spectra of transition metal complexes have their origin in electronic transitions within the central ion d-orbitals. Two parameters which can be determined from the spectrum of complex ion are Dq and beta, the nephelauxetic parameter. These behave quite regularly as functions of the central ion and ligand.

Crystal field perturbations affect the angular part of the metal ion wave function to a first magnitude \((63)\). This gives rise to the parameter Dq, which is a measure of ligand ability to split metal d-orbitals in a crystal field. Dq is determined from the spectra, and for octahedral nickel ion, the energy of the first spin-allowed band is 10 Dq. Various ligands impose different crystal field effects, and therefore different values of Dq. The arrangement of ligands in terms of their Dq magnitude in complexes is called a spectro-chemical series. For the more common ligands the spectro-chemical series is:

\[
I^- < Br^- < SCN^- < Cl^- < NO_3^- < F^- < \text{urea} < \text{OH}^- < \text{ONO}^- < \text{HCOO}^- < \]
\[
Ox^-2 < H_2O < \text{NCS}^- < \text{glycine} < \text{EDTA} < \text{py} < \text{NH}_3 < \text{en} < \text{den} < \text{tren} < \text{dipy} < \text{phen} < \text{NO}_2^- < \text{CN}^- .
\]

There exists a second parameter which affects the radial part of the wave function \((65)\). This is associated with the nephelauxetic parameter \(\beta\). Electron-electron repulsion gives rise to spectroscopic
terms, and these replace spdf electronic configurations as a valid description of the metal ion energy state. The energy separations between terms in the complex are always less than that found for the free gaseous metal ion. This can be simply interpreted as a decrease in metal electron-electron repulsion in the complex. The magnitude of the decrease has been correlated with the polarizability of the ligand; the more polarizable ligand will delocalize its electrons in the complex, allowing metal d-electrons to "mix-in" and move from the nucleus. Ligands arranged in order of their ability to expand metal d-electron clouds form a nephelauxetic series. For the common ligands this is:

$$F^- < H_2O < \text{urea} < NH_3 < OX^- < \text{en} < \text{NCS} < Cl^- < CN^- < Br^-.$$  

Thus the measure of Dq will indicate the relative coordinating ability of the ligands, while beta (nephelauxetic parameter), is related to the amount of metal-ligand orbital mixing; i.e., ligand covalency. Both of these parameters will be used to examine the coordinating ability of the amines. In order to more completely interpret the information contained in Dq and β values, some of the theory related to the spectra of nickel(II) complexes will be surveyed.

For a free gaseous ion, the effect of coulombic repulsion gives rise to the spectroscopic terms (66). In the case of nickel ion (67), the d⁸ configuration is described by terms 3F, 1D, 3P, 1G, and 1S. Inclusion of spin-orbit coupling (68) partially removes the degeneracy of these terms and they become 3F → 3F₄, 3F₃, 3F₂; 1D₂; 3P → 3P₂, 3P₁, 3P₀; 1G₄; 1S.

For first row transition metal complexes, crystal field effects are of greater magnitude than spin-orbit coupling (69), therefore, field effects are determined first. In an octahedral field (70), the
terms are split as $3^F - 3^A_{2g}, 3^T_{2g}, 3^T_{1g}; 1^D - 1^E_g, 1^T_{2g}; 3^P - 3^T_{1g}$; and of the $G$ and $S$ terms, it is sufficient to note that a $1^A_{1g}$ state arises from the $G$ term. These states do not vary in the same fashion with field strength; thus the energies of the $3^A_{2g}$ and $3^T_{2g}$ states are a linear function of $Dq$, whereas the two $3^T_{1g}$ states interact and curve away from each other. If spin-orbit coupling is now considered, the states are further split in the following manner (27), $3^A_{2g} - \gamma_5$; $3^T_{2g} - \gamma_2, \gamma_3, \gamma_4, \gamma_5; 3^T_{1g} - \gamma_1, \gamma_3, \gamma_4, \gamma_5; 1^E_g - \gamma_3$. The effect of all these factors on the free gaseous nickel ion and nickel ion in an octahedral field are diagramatically shown in Figure 1.

Our main interest lies in the variation of term state energy as a function of octahedral crystal field strength, or $Dq$. Matrices for the $d^8$ weak field case have been reported by Orgel (26). They are for the indicated states:

$$\begin{array}{c|cc|c}
T_{1g} & 6 & 4 & F \\
 & 4 & 0 & P \\
T_{2g} & -2 & F \\
A_{2g} & -12 & F \\
\end{array}$$

The one dimensional matrices representing the $3^A_{2g}$ and $3^T_{2g}$ terms express the linearity of these states as a function of $Dq$. Their slopes are $-12$ and $-2$ $Dq$ respectively, and their difference is $10$ $Dq$. Thus the energy of the first spin-allowed transition is $10$ $Dq$. The two dimensional matrix for the $T_{1g}$ states signify that a quadratic equation is required to describe their variation with $Dq$. Its solution is straight forward (71,72), and the two roots represent energies of the $3^T_{1g}(F)$ and
Figure 1 The effect of electronic repulsion and spin-orbit coupling on the atomic and octahedral terms for Nickel (II) ion.
\[ \begin{align*}
3_{T_{1g}}(p) & \text{ above zero energy of the } F \text{ state.} \\
[1] (6Dq - E)(E_{3p} - E) - 16(Dq)^2 & = 0 \\
\text{or; } \\
E & = \frac{6Dq + E_{3p}}{2} \pm \frac{1}{2} \sqrt{(6Dq + E_{3p})^2 - 4[(6Dq)(E_{3p}) - 16(Dq)^2]} \\
\text{where } E_{3p} \text{ is the energy of the } 3p \text{ level relative to the zero energy of } 3F. \text{ A graphic representation of the state energies for the weak field case as a function of } Dq \text{ is called an Orgel diagram. This is shown in Figure 2. The arrows signify the expected transitions, three spin allowed, and one spin forbidden.}
\end{align*}
Figure 2: Orgel energy diagram for a $d^8$ system in an octahedral field.
\[
\frac{16Dq^2 + 6DqZ - Z^2}{6Dq - Z} = \frac{(6Dq - Z)(2Dq + Z)}{(6Dq - Z)}
\]

[4] \( E_{3p} = \frac{(Z + 2Dq)(Z - 8Dq)}{(Z - 6Dq)} \)

The energy difference of the \(^3F - ^3P\) terms in the complex, \(E_{3p}\), could now be substituted into equation [1], and the energy of \(v_3\) calculated. As a calculation check, the remaining root must equal \(v_4\) observed, since this was the value originally used to determine \(E_{3p}\). The calculation of \(v_3\) is simplified by the following considerations.

Equation [5]

[5] \( E = \frac{6Dq + E_{3p}}{2} \pm \frac{1}{2} \sqrt{\left(6Dq + E_{3p}\right)^2 - 4\left[(6Dq)(E_{3p}) - 16(Dq)^2\right]} \)

may be symbolically represented as;

[6] \( E = \frac{6Dq + E_{3p}}{2} + x \)

The energies of \(v_4\) and \(v_3\) are related to [6] by the following;

\( v_4 \text{ obs} = \frac{6Dq + E_{3p}}{2} + x + 12Dq \)

or

[7] \( x = v_4 \text{ obs} - \frac{6Dq + E_{3p}}{2} + 12Dq \)

and;

[8] \( v_3 \text{ calc} = \frac{6Dq + E_{3p}}{2} - x + 12Dq \)
upon substituting [7] into [8];

\[ v_3 \text{ calc} = \frac{6Dq + E_3^{p}}{2} - \left\{ \nu_4 \text{ obs} - \left[ \frac{6Dq + E_3^{p}}{2} + 12Dq \right] \right\} + 12Dq \]

and upon expanding;

\[ v_3 \text{ calc} = \frac{6Dq + E_3^{p}}{2} - \nu_4 \text{ obs} + \frac{6Dq + E_3^{p}}{2} + 12Dq + 12Dq \]

\[ = 2 \left( \frac{6Dq + E_3^{p}}{2} \right) + 2(12Dq) - \nu_4 \text{ obs} \]

\[ = 6Dq + E_3^{p} + 24Dq - \nu_4 \text{ obs} \]

then;

[9] \[ v_3 \text{ calc} = E_3^{p} + 30Dq - \nu_4 \text{ obs}. \]

It is believed that use of equations

[2] \[ Z = \nu_4 - 12Dq, \]

and

[4] \[ E_3^{p} = \frac{(Z + 2Dq)(Z - 8Dq)}{(Z - 6Dq)} , \]

reduce the labor involved in using [1]. In addition, solving [9] for \( E_3^{p} \) results in the definition of \( 15B(65) \), the term used in determining the nepphaleuxetic parameter \( \beta \).

So that,

[10] \[ E_3^{p} = \nu_4 \text{ obs} + v_3 \text{ calc} - 3\nu_1 = 15B \]
As an example of the operation of these equations, the reflectance spectrum of $[$Ni(N-ethylen)$_3$]($ClO_4$)$_2$ will be used and the energy of $v_3$ calculated. The spin allowed bands are observed at $v_1 = 10,780\text{ cm}^{-1}$, $v_2 = 17,760 \text{ cm}^{-1}$, and $28,170 \text{ cm}^{-1}$. $Dq$ is therefore $1078 \text{ cm}^{-1}$, and multiples of $Dq$ useful for equations [2], [4], and [9] are:

- $2Dq = 2156$
- $6Dq = 6468$
- $8Dq = 8624$
- $12Dq = 12,936$
- $30Dq = 32,340 \text{ cm}^{-1}$

**Eq. [2]**

$$Z = 28,170 - 12,936 = 15,234 \text{ cm}^{-1}$$

**Eq. [4]**

$$= \frac{(15,234 + 2156)(15,234 - 8624)\text{ cm}^{-1}}{(15,234 - 6468)}$$

$$= \frac{(17,390)(6610)}{8766} = 13,113 \text{ cm}^{-1}$$

**Eq. [9]**

$$v_3^{\text{calc}} = 13,113 + 32,340 - 28,170$$

$$= 17,283 \text{ cm}^{-1}$$

$$\Delta v_3 = v_3^{\text{obs}} - v_3^{\text{calc}} = 477 \text{ cm}^{-1}$$

The good agreement between calculated and observed $v_3$, indicate the complexes are octahedral. The nephelauxetic parameter $\beta$ is:

**Eq. [11]**

$$\beta = \frac{15B}{15,840} = \frac{E_{3P}}{15,840} = 0.828$$

Thus in this complex the $^3P$ level is 0.828 above the zero of the state compared to [11] the free gaseous ion.

The variation of $d^8$ energy levels for the strong field case has been examined (75). The energies are expressed in terms of $Dq$ and the Racah parameters (76) $A$, $B$, and $C$. The parameter $A$ is related to the attraction between the valence electrons and the central field of
the nucleus in which they move. For a series of terms arising from
the same configuration, A is constant and therefore may be ignored.
The parameters B and C are related to the repulsion between differ­
ent electrons in the valence shell and to the exchange interaction.
C only appears when the ground and excited states have different
multiplicities. Thus β and Dq are sufficient to describe the energies
of all triplet states in a d\(^8\) system. For free gaseous nickel ion,
\[
B = \frac{\text{15,840}}{15} = 1057 \text{ cm}^{-1}.
\]
The equations which describe the state energies in the strong field
are (77);
\[
1 = 10Dq \\
3 = 15Dq + 7.5B - 6B [1 + \mu]^{1/2} \\
4 = 15Dq + 7.5B + 6B [1 + \mu]^{1/2}
\]
where \(\mu = \frac{(10Dq - 9B^2)}{12B}\)

Usually, the procedure involves selection of a value for B which gives
the best fit to the spectrum.

A strong field energy diagram using Dq, B, and C, may be called
a Tanabe-Sugano diagram, and is illustrated for Ni(II) in Figure 3.
At low values of Dq, the Orgel and Tanabe-Sugano diagrams are very
similar. The close agreement between observed \(\gamma_3\) energies and those
calculated with the weak field equations did not warrant use of the
strong field approximations for the tris complexes in the present
study.

The complete theory for the spectra of strong field octahedral
Figure 3 Tanabe-Sugano energy diagram for a $d^8$ system in an octahedral field.

$\gamma = 4.709$

$B = 1030 \text{ cm}^{-1}$
nickel(II) complexes, including spin-orbit coupling, has been derived by Liehr and Ballhausen (27). For all practical purposes, it is concluded that none of the excited states will be observed to split at room temperature. Inclusion of spin-orbit coupling in the complex removes degeneracy of the terms arising from the octahedral field. The splitting due to spin-orbit coupling is determined by the direct product of spin and orbital irreducible representations \( \otimes \), and the divided levels are represented using double group symbols \( \Gamma_n \). The energy diagram including spin-orbit coupling is illustrated in Figure 4.

These various schemes for determining energy levels allow examination of the spectra to degrees of completeness as may be required by the investigator. It is now in order to consider some aspects of the characteristics of d-d absorption bands.

Orgel diagrams are derived most readily using group theoretical methods. The weak field splitting of free ion spectroscopic terms produces states labeled according to their transformation properties. An infinitely strong octahedral field results in direct electron transfer from the \( t_{2g} \) to \( eg \) d-orbitals. The strong field states and their transformation properties are determined by the direct product of the \( t_{2g}^n \) and \( eg^m \) occupancy numbers. The energy diagram results from correlation of like representations found in the strong and weak field cases. States which arise from the same strong field \( t_{2g}^n \) \( eg^m \) configurations may then be scrambled after correlation with the weak field states, and transitions can occur between them. When these transitions take place, the Franck-Condon principle can apply rigorously since no reorganization will be required between ground and
Figure 4. d^8 octahedral energy diagram including spin-orbit coupling.
excited states. Such transitions are characterized by narrow band widths, and in the Orgel diagram states of like strong-field origin are indicated by identical slopes. On the other hand, transitions between all other states require some reorganization prior to absorption in order to preserve the Franck-Condon principle. This can occur as the result of thermal energy inducing vibrations in the complex, and transitions then take place between vibrationally distorted states. Absorption bands which originate in this manner are broad, and their character changes with temperature.

In atomic spectra, selection rules govern the feasibility of energy transfer between two states. Spectra of transition metal complexes are required to violate the rule $\Delta l = 1$. Normally transitions do not occur between states with the same value, or within a state of particular $l$ value. However, d-d transitions in complexes do take place, but at the expense of band intensity. Such transitions are termed Laporte forbidden. Their intensities are $10^3 - 10^4$ less than Laporte allowed bands, and thus for octahedral nickel complexes molar extinction coefficients are in the range 10-100. Bands of weaker intensity also are observed in spectra of transition metal complexes. These are described as doubly forbidden transitions which not only violate $\Delta l = 1$ but $\Delta S = 0$ as well; they are termed spin-forbidden transitions. Thus the intensities dealt with here are very low and the bands have oscillator strengths of the order $10^{-5} - 10^{-6}$. 
B. Nickel(II) Perchlorate Complexes

1. Tris(ligand) complexes

The preparation and characterization of the tris complexes is of prime importance for examining amine coordinating ability. These complexes are expected to have an octahedral structure, and as previously mentioned the spectra of such Ni(II) complexes are well understood. Thus spectral information will be the basis for correlating donor ability.

Results.—The magnetic moments, conductance values in nitromethane, and reflectance spectra are listed in Table 4 for the solid compounds. The magnetic data demonstrate that the nickel ions in these compounds have two unpaired electrons and that the moment has an orbital contribution of typical magnitude. Conductivity measurements indicate that all of these compounds are bi-univalent electrolytes in nitromethane; this agrees with the proposed formulation of the compounds; i.e., $[\text{Ni(ligands)}_3\text{ClO}_4]_2$. The spectra are characteristic of $d^8$ octahedral systems and are interpreted accordingly. The elemental analyses, coupled with the magnetic susceptibility, conductivity, and spectral data, substantiate that all of the compounds are pseudo octahedral complexes of the N-substituted ethylenediamines.

The band maxima of the absorption spectra of Tables 4, 5, and 6 are listed in order of increasing energy. The energies represent the electronic transitions from the $^3A_g$ ground state to the successively higher excited states $^3T_{2g}$, $^1E_g$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$.

For all complexes both reflectance spectra and solution spectra were obtained in order to detect any gross changes in electronic or
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<th>Ligand</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>Molar conductance $10^{-3}\text{M}$ in CH$_3$NO$_2$ cm$^2$/A mole</th>
<th>$\lambda_{\text{max}}$ $^a$ (cm$^{-1}$)</th>
<th>Dq $^b$ (cm$^{-1}$)</th>
<th>$\nu_3/\nu_1$</th>
<th>Racah $\beta$ (cm$^{-1}$)</th>
<th>$\nu_3$ calc</th>
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<td>Dq <em>b</em></td>
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*a* The values represent the energy for the transitions:
$1^1, 3A_2^g \rightarrow 3T_2^g$; $2^1, 3A_2^g \rightarrow 1E_g$; $3^1, 3A_2^g \rightarrow 3T_1^g(F)$; and $4^1, 3A_2^g \rightarrow 3T_1^g$, respectively.

*b* The error limits of Dq are $\pm 7$ cm$^{-1}$. 
geometrical structures which might occur on dissolution. No signifi­
cant differences were observed between the spectra of the solid and

The reflectance spectrum of

[Ni(N-ethylen)_{3}](ClO_{4})_{2} is illustrated in Figure 5 as a typical example
for the tris complexes. A small amount of dimethylformamide must be
added to the solutions of the N,N'-dialkylethylenediamine complexes to
maintain solution, and, as a result, the lowest energy band of these
two complexes is split into two peaks which are separated by approxi­
mately 350 cm^{-1}. The splitting of ν₁ suggests that the complexes
distort from octahedral geometry in the DMF solutions. Therefore, the
spectral data for these complexes are not included in Table 5.

The spectra of aqueous solutions of the complexes of N,N'-
dimethylen, N,N-dimethylen, and N-methyl-N'-ethylen showed signs of
extensive hydrolysis. A flocculent precipitate formed in the cells
within ten minutes, and the band maxima moved toward lower energy.
Since the reaction with water limits the significance of the spectral
data for the above complexes, these three were not included in Table 6.

Discussion.—The N-monoalkyl substituted ethylenediamines become
slightly more basic with increasing length of the alkyl chain (18).
However, the spectra of the nickel complexes of these same ligands
show a systematic decrease in Dq values as the alkyl group becomes
more complex. This effect is illustrated in Figure 6. The same trend
is demonstrated in the Dq values of the N,N'-dialkylethylenediamines
(Table 4).

While it is true that the ethyl group is more electron releasing
Figure 5 Reflectance spectrum of $[\text{Ni(N-ethyl-enyl)}_3\text{ClO}_4]_2$.
### TABLE 5
Absorption Spectra of $[\text{Ni(ligand)}_3](\text{ClO}_4)_2$ in Solution Using the Respective Ligands as Solvents

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\varepsilon_{v_3}/\varepsilon_{v_3}^{*a}$</th>
<th>$\varepsilon_{\text{max}}^{*b}$</th>
<th>$\lambda_{\text{max}}^{*c}$ (cm$^{-1}$)</th>
<th>Dq $^{*d}$ (cm$^{-1}$)</th>
<th>$\nu_3 \delta^*$</th>
<th>Racah $\beta$ (cm$^{-1}$)</th>
<th>$\nu_3$ calc. - $\nu_3$ obs. (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>en</td>
<td>1.42</td>
<td>7.0</td>
<td>11,360</td>
<td>1136</td>
<td>1.62</td>
<td>0.823</td>
<td>18,053</td>
</tr>
<tr>
<td>N-methylen</td>
<td>1.59</td>
<td>7.9</td>
<td>10,940</td>
<td>1094</td>
<td>1.64</td>
<td>0.832</td>
<td>17,515</td>
</tr>
<tr>
<td>N-ethylen</td>
<td>1.60</td>
<td>8.3</td>
<td>10,760</td>
<td>1076</td>
<td>1.66</td>
<td>0.837</td>
<td>17,282</td>
</tr>
<tr>
<td>N-propylen</td>
<td>1.72</td>
<td>8.5</td>
<td>10,660</td>
<td>1066</td>
<td>1.67</td>
<td>0.843</td>
<td>17,164</td>
</tr>
<tr>
<td>N,N-dimethylen</td>
<td>1.85</td>
<td>8.0</td>
<td>10,000</td>
<td>1000</td>
<td>1.69</td>
<td>0.848</td>
<td>16,255</td>
</tr>
</tbody>
</table>

$a$ Octahedral complexes of Ni(II) with other bidentate ligands give typical ratios of 1.4 to 1.8 [C. K. Jørgensen, Acta Chem. Scand., 10, 887 (1956).] $b$ $\varepsilon$ is given in mole$^{-1}$ cm$^{-1}$ from the equation log $I/I_0 = 6$ Cl. $c$ The energy of the respective peaks is reported as in Table 1. $d$ The error limits of Dq are $\pm 5$ cm$^{-1}$. 
TABLE 6
Absorption Spectra of [Ni(ligand)](ClO₄)₂ in Aqueous Solution

<table>
<thead>
<tr>
<th>Ligand</th>
<th>ε₁/ε₃</th>
<th>ε max</th>
<th>λ max (cm⁻¹)</th>
<th>ν 3/ν₁</th>
<th>Racah β</th>
</tr>
</thead>
<tbody>
<tr>
<td>en</td>
<td>1.29</td>
<td>7.08</td>
<td>11,230</td>
<td>1.63</td>
<td>0.834</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12,600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.40</td>
<td></td>
<td>18,320</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.25</td>
<td></td>
<td>28,990</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-methylen</td>
<td>1.50</td>
<td>7.80</td>
<td>10,870</td>
<td>1.64</td>
<td>0.835</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12,350</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.42</td>
<td></td>
<td>17,860</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td></td>
<td>28,410</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-ethylen</td>
<td>1.82</td>
<td>7.16</td>
<td>10,730</td>
<td>1.62</td>
<td>0.822</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12,790</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.94</td>
<td></td>
<td>17,390</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.81</td>
<td></td>
<td>28,010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-propylen</td>
<td>1.73</td>
<td>7.4</td>
<td>10,570</td>
<td>1.64</td>
<td>0.836</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12,850</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td></td>
<td>17,320</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.70</td>
<td></td>
<td>27,930</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6: Dq vs N-alkyl substituent on the ligand in \([\text{Ni}(\text{Ligand})_3](\text{ClO}_4)_2\)
than the methyl group (1), this effect is often offset by its larger steric requirements. Thus, in the case of simple amines, trimethylamine (Me$_3$N) is a stronger base toward trimethylborane (BMe$_3$) than ethyldimethylamine (Me$_2$NEt) (79) or triethylamine (Et$_3$N) (2); here steric requirements outweigh inductive effects. Since both N,N'-dimethylen and N-methyl-N'-ethylen are stronger bases than ethylenediamine, the smaller Dq values for these two ligands indicate that the steric effect is of greater magnitude than the increased basicity of the substituted ethylenediamine ligands, and of more importance in determining the degree of interaction with the Ni(II) ion. Also, it is interesting that it was not possible to prepare the tris(N,N'-diethylethylenediamine) complex. Instead, the compound which was isolated repeatedly corresponded to [Ni(N,N'-diethylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (see p. 26), even when the dimethoxypropane dehydration procedure was followed. Previous attempts to prepare the tris complex of N,N'-diethylen also were unsuccessful (80,51). The Dq values, which reflect the net result of steric and inductive factors, produce the following spectrochemical series: en > N-methylen > N-ethylen > N-propylen > N,N'-dimethylen > N-methyl-N'-ethylen > N,N-dimethylen.

The spin-forbidden transition, ($^{3}$A$_{2g}$ - $^{1}$E$_{g}$) in the spectra of these compounds always appears as a shoulder on the high energy side of v$_1$, as one would predict for the intermediate range (Dq = 1000-1130 cm$^{-1}$) of field strengths exhibited by these ligands (81).

The ratio of v$_3$/v$_1$ gradually increases as Dq decreases; this is related to the interaction between the $^{3}$T$_{1g}$(F) and $^{3}$T$_{1g}$(P) term states. Reference to an Orgel diagram for an octahedral d$^8$ ion (see p. 45).
shows that if no interaction occurred between these two term states \( \text{T}_1^g(F) \),
the energy of the \( \text{T}_1^g(F) \) would be linear with respect to Dq and the
\( \nu_3/\nu_1 \) ratio would be \( 1.80 \). However, as the Dq value increases, the
degree of interaction also increases and the \( \text{T}_1^g(F) \) is depressed
below the calculated value and, thus, the ratio of \( \nu_3/\nu_1 \) is less than
1.80. All of the compounds reported here have \( \nu_3/\nu_1 \) ratios below
1.80, but approach this theoretical limit with decreasing field strengths
of the ligands.

The ratio of the energy of the \( 3\text{P}^0 \rightarrow 3\text{F}^0 \) term splitting in the com-
plex compared with the free ion value gives the Racah parameter, \( \beta \).
One can correlate qualitatively the extent to which the metal d-elec-
trons are delocalized on the ligand orbitals with this ratio. The \( \beta \) values of the complexes (Table 4) produce the following nephelauxetic
series: \( \text{N,N'\,-dimethylen} > \text{en} > \text{N\,-ethylen} > \text{N\,-methylen} > \text{N-methyl-N'\,-}
ethylen} > \text{N\,-propylen} > \text{N,N\,-dimethylen} \). The nephelauxetic effect seems
to be less sensitive to steric interaction than the Dq values.

One can explain the nephelauxetic series as being dependent
primarily on inductive and polarization factors. The greatest nephel-
auxetic effect is produced by \( \text{N,N\,-dimethylen} \) because the tris complex
of this ligand presents six, easily distortable, secondary amino groups
around the Ni(II) ion. The enhanced polarization and inductive factors
of the secondary nitrogen atoms more than offset the steric interaction
with respect to delocalization of the metal d-electrons on the ligand
atoms. The reverse behavior is exemplified by \( \text{N,N\,-dimethylen} \). Al-
though the tertiary nitrogen atom in this ligand potentially would
have larger distortability and inductive effects, it is apparent that
steric considerations override whatever contribution these tertiary nitrogens may offer and cause this ligand to occupy the last position in the nephelauxetic series. The remaining ligands seem to follow a logical order, with the possible exception that N-ethylen might have been expected to occupy a relative position between N-methylen and N-propylen. It is conceivable that N-ethylen might exert a greater nephelauxetic effect than N-methylen or N-propylen due to a combination of more favorable inductive and steric requirements of the ethyl group (5). However, the small variation in the value of $\beta$ for the three ligands approaches the experimental error and limits the importance that should be attached to the relative position of N-ethylen as determined by these data.

The relative energy differences between the observed and calculated $\nu_3$ are small, and it is probable that any distortions from an octahedral structure must be small as well. For all the complexes the calculated energy value is less than that actually observed. This may indicate that there is slightly less interaction between the two $^3T_{1g}$ terms than would be expected for a purely octahedral case, and may arise from a trigonal distortion present in these compounds. This is particularly important in the N,N-dimethylen complex, where the difference between the values of the observed and calculated $\nu_3$ is almost twice that for the other ligands. Whatever distortion may be present, however, is apparently weak in nature for none of the spectral bands showed any asymmetry as would be expected for either a trigonal or a tetragonal distortion.

The position of the first spin-allowed band for each of the
ligand solutions is almost identical with the corresponding band in the reflectance spectra (Figure 6). Thus the same spectrochemical series results from the spectra of the ligand solutions as for the solid state. This indicates that the ligand field conditions are essentially equivalent in the two environments.

A ligand solution of the unsymmetrical N,N-diethylen complex exhibited a $\lambda_{\text{max}}$ at 10,3000 cm$^{-1}$. Since the steric requirement for the tris(N,N-diethylen) complex would be greater than for the tris-(N,N-dimethylen) compound, one would expect the Dq value to be less than 1000 cm$^{-1}$. The 1030 cm$^{-1}$ value suggests that $[\text{Ni(N,N-diethylen)}]^{2+}$ is not present in the solution. A possible species is $[\text{Ni(N,N-diethylen)}]^{2+}$; such a complex would have four-primary amino groups coordinated to the Ni(II) and would be expected to exhibit the higher Dq value of 1030 cm$^{-1}$. However, the analogous tetrakis complex of N-isopropylethylenediamine (see p. 106) has been characterized and its spectrum differs significantly from that of the Ni(II) complex which is present in the solution of N,N-diethylen. Attempts to isolate any compound, other than the square-planar $[\text{Ni(N,N-diethylen)}]_{2}([\text{ClO}_4]_2$, from the N,N-diethylen solutions were unsuccessful.

The ratio of the molar extinction coefficients ($\varepsilon_{\text{max}}$) for the second and third spin-allowed bands has been used as evidence for the presence of octahedral nickel(II) ion (8j). For the above series, this ratio and the values of the extinction coefficients determined from ligand solutions are within the range expected for chelated octahedral compounds. There is a gradual increase in the $\varepsilon_{\text{max}}$ values of the complexes as the size of the N-alkyl substituent on the ligand
increases. The $\varepsilon_{\text{max}}$ values reflect small distortions from Oh site symmetry since the electronic transitions become more probable as the distortion progresses from an octahedral to a trigonal structure.

The value of the Racah parameter, $B$, determined from the ligand solution spectra, produce the following nephelauxetic series:

$\text{en} > \text{N-methylen} > \text{N-ethylen} > \text{N-propylen} > \text{N,N-dimethylen}$. The definition of this series is more distinct than that determined from the reflectance spectra. Also, the position of $\text{N-ethylen}$ is clearly between $\text{N-methylen}$ and $\text{N-propylen}$ in this series, whereas its position was not so definitive from the spectra of the solids.

The difference between the observed and calculated value of $\nu_3$ in the ligand solution spectra increases with increasing size of the N-alkyl group. This effect is larger in the solution spectra than in the spectra of the solids and may be related to the compressed crystal-line field of the solid complexes compared to the solution environment (??). Sterically hindered systems should relax more in solution than would be possible in the crystal and produce a larger difference, in agreement with the data.

The spectrochemical series, the ratios of $\nu_3/\nu_1$, the nephelauxetic series, and the colors of the complex are identical in both the solid state and in ligand solution. These factors, coupled with the solution $\varepsilon_{\text{max}}$ values, show that the same octahedral complex must be present in both the solid state and in the ligand solutions. These results are in contrast to those obtained from aqueous solutions of the complexes.

The absorption bands of all the compounds shift to lower energy values in aqueous solutions. More extensive hydrolysis occurred when
[Ni(N,N'-dimethylen)₃](ClO₄)₂, [Ni(N-methyl-N'-ethylen)₃](ClO₄)₂, and [Ni(N,N-dimethylen)₃](ClO₄)₂ were dissolved in water.

Changes in the values of the ν₂/ν₁ ratio, 6ν₄/6ν₃, β, and the energies of the bands in water compared to the spectra in ligand solution and in the solid are most dramatic for the [Ni(N-ethylen)₃](ClO₄)₂ complex. For example, the Racah parameter, β, derived from aqueous solution spectra produce a nephelauxetic series where N-ethylen displays the largest nephelauxetic effect, and the remaining ligands are essentially equivalent. These data, coupled with the Dq value, indicate that the inductive character of N-ethylen is more pronounced in water than the other ligands, or that species other than the tris complex are present in the aqueous solution. An obvious possibility is the trans-[Ni(N-ethylen)₂(H₂O)₂]⁺², and indeed, the spectrum of an authentic sample of this compound does not differ significantly from that observed by dissolving [Ni(N-ethylen)₃](ClO₄)₂ in water (see p. 104).

2. **Bis(ligand) complexes**

A synthetic effort to prepare and characterize bis(ligand) complexes was undertaken to identify any relations which might exist between the complex spectra and ligand donor ability. Such a possibility has never been investigated systematically for the bis complexes.

**Results.**—The color, corrected magnetic molar susceptibility, calculated effective magnetic moment, and reflectance spectra are listed in Table 7 for the isolated bis complexes. The magnetic data demonstrate that the nickel ions in these compounds are diamagnetic;
### TABLE 7

Color, Corrected Magnetic Susceptibility, and Calculated Magnetic Moment—and Reflectance Spectra for [Ni(ligand)$_2$](ClO$_4$)$_2$ Complexes

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Color</th>
<th>$x_m \times 10^6$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-ethylen</td>
<td>Coral</td>
<td>291.2</td>
<td>840</td>
<td>472</td>
<td>21,200</td>
</tr>
<tr>
<td>N-propylen</td>
<td>Salmon</td>
<td>241.1</td>
<td>764</td>
<td>473</td>
<td>21,100</td>
</tr>
<tr>
<td>N-isopropyl en</td>
<td>Coral</td>
<td>162.2</td>
<td>626</td>
<td>467</td>
<td>21,400</td>
</tr>
<tr>
<td>N,N'-dimethyl en</td>
<td>Yellow</td>
<td>276.5</td>
<td>818</td>
<td>467</td>
<td>21,400</td>
</tr>
<tr>
<td>N,N'-dimethyl en</td>
<td>Yellow</td>
<td>316.0</td>
<td>875</td>
<td>465</td>
<td>21,500</td>
</tr>
<tr>
<td>N-methyl-N'-ethylen</td>
<td>Salmon</td>
<td>393.7</td>
<td>976</td>
<td>475</td>
<td>21,100</td>
</tr>
<tr>
<td>N,N'-diethyl en</td>
<td>Yellow</td>
<td>240.1</td>
<td>764</td>
<td>465</td>
<td>21,500</td>
</tr>
<tr>
<td>N,N'-diethylen</td>
<td>Yellow</td>
<td>706.0</td>
<td>1.31</td>
<td>467</td>
<td>21,400</td>
</tr>
</tbody>
</table>
therefore the ground state is assigned to a singlet term. The reflectance spectrum of \([\text{Ni}(\text{N},\text{N}'-\text{diethylen})_2](\text{ClO}_4)_2\) is shown in Figure 7, as a typical example for this series. The spectra are characteristic of d^8 four-coordinate, square-planar systems and are interpreted accordingly. The elemental analyses, coupled with the magnetic susceptibility and spectral data, substantiate that all of the compounds are bis(ligand) four-coordinate, square-planar complexes of nickel(II) perchlorate.

Discussion.--The single band observed from reflectance spectra has almost identical energies for the entire group of bis(ligand) complexes (Table 7). The band is assigned as \(1\,A_g \rightarrow 1\,A_{2g}\) in \(D_{4h}\) symmetry, or \(1\,A_g \rightarrow 1\,B_{2g}\) in \(D_{2h}\). The energy level diagrams and the spectra for d^8 square-planar complexes have been explained by Maki (84), and in \(D_{4h}\) geometry, four-coordinate complexes usually have a singlet ground state. This may be considered to arise from the \(1\,E_g\) state of the octahedral field which splits into an \(1\,A_{1g}\) and \(1\,B_{1g}\) levels in \(D_{4h}\) symmetry. It is the \(1\,A_{1g}\) term which becomes the ground state. A single spin-allowed transition is normally observed from ground state to the \(1\,A_{2g}(3)\) level; other singlet-singlet transitions occur at much higher energies. Maki has presented theoretical arguments which indicate that four-coordinate, square-planar Ni(II) complexes may exist with a triplet ground state as well. Thus her energy diagrams include ground states of both triplet and singlet term systems.

The approximate site symmetry of nickel ion in bis(N-alkylethylene-diamine) complexes is \(D_{4h}\), but if the whole structure is taken into account, the symmetry is much lower. Thus, it may be argued that the
bis complexes in the present study would have $D_{2h}^2$ symmetry rather than $D_{4h}^4$. But, the final effect remains unchanged and only one spin allowed transition is observed. However, in the $D_{2h}^2$ case the symmetry symbols become $^1A_g$ and $^1B_g$ for ground and excited states respectively. A Maki energy diagram for a four-coordinate $D_{4h}^4$ geometry is illustrated in Figure 8.

Recently, Goodgame and Venanzi published two papers on the bis complexes of N,N-diethylen (41) and N,N-diethylen (40) with nickel perchlorate and a large number of other nickel salts. Their data agree very well with those presented here, and allow extensions of the ideas developed in this thesis.

Very weak absorptions were observed in some spectra on the low energy side of the main band. These may be attributed to spin-forbidden transitions among the three triplet levels which lie between the first two singlet energy states.

The mean transition energy is 21,300 ± 200 cm$^{-1}$ and in view of such a narrow range of energies, the variation in visible color of the complexes is somewhat surprising. Color differences may be related to crystal size, but there also is evidence from reflectance spectra that a charge transfer band in the UV trials into the visible range. The presence of a low energy charge transfer band may account for the color variation, which becomes progressively more red as the number of N-methyl groups increases in the ligand.

Spectra obtained with a Beckman DU spectrophotometer are believed accurate to ±50 cm$^{-1}$ in the 465 μm range, so the wave number spread approximates experimental error, and little significance can be attached to the band maxima of the individual complexes. Thus the
Figure 8 Maki energy diagram for 4-coordinate $d^8$ system in $D_{4h}$ symmetry.
square-planar bis complexes display spectra which are quite insensitive to the N-alkyl substituent on the ligand.

The preparation of bis(ligand) complexes by heating respective six-coordinate trans-disolvated derivatives has been reported before (85), and these transformations have been examined by Maki as well (86). Bis complexes were not isolated by such methods for the ethylene-diamine and N-methylen ligands. The ligands invariably formed tris complexes even at a molar stoichiometry less than 2:1 compared with the metal ion. In addition, neither bis nor tris complexes could be obtained with the N,N,N'-trimethylen or N,N,N',N'-tetramethylen ligands, and obviously in these two cases the steric requirements are too great. Apparently the size of the small nickel ion also is important, for a bis(ligand) complex has been prepared with N,N,N',N'-tetramethylen and palladium (87). Nevertheless, the steric requirements for the ligands greatly influence the geometry of the isolated reaction products in the present investigation.

Measurement of magnetic susceptibility for the complexes indicate some magnetic activity. The singlet ground state requires the pairing of all electrons in nickel ion so that this residual magnetism is required to originate in some manner other than the first order effect. It is possible for a magnetic field to distort the electron distribution in the complex, and thus change the ground state to a small extent by mixing in a higher energy level (60). This slight change in the ground state gives rise to temperature independent magnetism (TIP) which is of the magnitude of $10^{-4}$ c.g.s.u. The molar susceptibilities listed in Table 7 and corrected for the presence of diamagnetic
materials, are of this order of magnitude. It also is possible that a very small amount of paramagnetic impurity could be partially responsible for the higher moments.

The magnetic moment due to TIP for \( [\text{Ni}(N,N\text{-diethyl})_2](\text{ClO}_4)_2 \) is considerably larger than the other series members. Ligand size may promote complex distortion and lead to a greater TIP effect in this example, but the possibility of a packing error during sample preparation must be considered as well. It is assumed that both of these factors were in operation, and that they weighted the calculated moment. It also is true that the larger moment may reflect the presence of some paramagnetic material, such as \( [\text{Ni}(N,N\text{-diethyl})_3](\text{ClO}_4)_2 \) or \( [\text{Ni}(N,N\text{-diethyl})_2(H_2O)_2](\text{ClO}_4)_2 \), but preparative procedures and the infrared spectrum discount this possibility. Preparations that used a ten-fold ligand excess still resulted in isolation of the bis species, and the infrared spectrum is completely devoid of absorptions due to water or solvent molecules. Therefore, the presence of paramagnetic nickel(II) from tris or diquobis complexes is doubted. The possibility of metal-metal bonding (88) to the trans-positions also is not believed feasible in terms of the size of the ligand substituent and the fact that no other series member displays such an inclination.

3. Perchlorato(ligand) complexes

Bis(ligand) complexes obviously do not utilize all available nickel ion coordination sites; the trans-positions above and below the plane of the four nitrogen donor atoms are vacant in such four-coordinate complexes. Synthetic attempts to fill these vacant positions have been reported (89) for other square-planar Ni(II) complexes,
and in the present investigation have resulted in six-coordinate derivatives which are of two types: 1) those containing coordinated perchlorate ions and 2) those containing coordinated water molecules. The complexes with coordinated perchlorate ions will be considered first.

**Results.**—The bis and/or diaquobis(ligand) complexes of nickel perchlorate with the N-methylen, N,N'-dimethylen, and N,N,N'-trimethylen ligands were heated under vacuum to temperatures of 100-130°C. In each case, six-coordinate species were formed which contain co-ordinated perchlorate ions. The magnetic moments, electronic absorption data, and the perchlorate and amine infrared peaks of the complexes are given in Tables 8 and 9. Similar information is included for the complex [Ni(N-methylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ for comparison. Contours in the reflectance spectra for the products are all very similar, but absorption energies shift to lower values as the ligand becomes more highly substituted. This spectral shift is particularly large in the case of the N,N,N'-trimethylen complex.

The [Ni(AA)$_2$](ClO$_4$)$_2$ complexes containing the ligands N-ethylen, N-propylen, N-isopropylen, N,N-dimethylen, N-methyl-N'-ethylen, N,N-diethyl, and N,N'-diethyl were subjected to similar conditions which led to perchlorato complexes in the three cases noted above. At elevated temperatures the color of each compound was violet or orchid, but this reverted to the original color upon cooling. Infrared spectra for these compounds remained unchanged after cooling to room temperature.

**Discussion.**—When [Ni(N-methylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ is heated in a
### TABLE 8

**Physical and Electronic Absorption Spectral Properties of the Ni(II) Perchlorate Complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>$\mu_{\text{eff.}}$ (B.M.)</th>
<th>Electronic spectra $\lambda_{\text{max}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni}(N\text{-methylene})_2,(\text{H}_2\text{O})_2]\text{(ClO}_4\text{)}_2$</td>
<td>Blue</td>
<td>3.25</td>
<td>12,700, 13,700, 17,900, 28,300</td>
</tr>
<tr>
<td>$[\text{Ni}(N\text{-methylene})_2,(\text{ClO}_4\text{)}_2]$</td>
<td>Orchid</td>
<td>3.27</td>
<td>12,900, 14,000, 18,200, 28,300</td>
</tr>
<tr>
<td>$[\text{Ni}(N,N'\text{-dimethylene})_2,(\text{ClO}_4\text{)}_2]$</td>
<td>Violet</td>
<td>3.31</td>
<td>12,700, 13,800, 18,200, 27,900</td>
</tr>
<tr>
<td>$[\text{Ni}(N,N,N'\text{-triemethylene})_2,(\text{ClO}_4\text{)}_2]$</td>
<td>Green</td>
<td>3.35</td>
<td>11,800, 11,600(4.7), 13,100, 12,900, 16,000, 16,000(6.7), 26,500, 26,500(30.3)</td>
</tr>
</tbody>
</table>

$^a$ Reflectance spectra of solid complexes. $^b$ Dichloromethane solution spectrum, molar extinction coefficients in parentheses.
## TABLE 9

Infrared Spectra of the Perchlorate and Amine Bands for the Ni(II) Perchlorato Complexes<sup>a,b</sup>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amine frequencies</th>
<th>Perchlorate frequencies and assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="ClO%3Csub%3E4%3C/sub%3E">Ni(N-methylen)&lt;sub&gt;2&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;2&lt;/sub&gt;</a>&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3360 s&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1110-1090 vi, br</td>
</tr>
<tr>
<td></td>
<td>3300 s.</td>
<td>930 w, m</td>
</tr>
<tr>
<td></td>
<td>1595 m.</td>
<td>626 m, m</td>
</tr>
<tr>
<td>[Ni(N-methylen)&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>3380 s.</td>
<td>2060 vw, br</td>
</tr>
<tr>
<td></td>
<td>3320 s.</td>
<td>1960 vw, br</td>
</tr>
<tr>
<td></td>
<td>1595 m.</td>
<td>1130 vi, s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1025 vi, s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>933 i, s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>630 i, m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>616 i, s</td>
</tr>
<tr>
<td>[Ni(N,N'-dimethylen)&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>3330 s.</td>
<td>2060 vw, br</td>
</tr>
<tr>
<td></td>
<td>3300 s.</td>
<td>1970 vw, br</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1122 vi, s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1040 vi, s</td>
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<tr>
<td></td>
<td></td>
<td>940 i, s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>632 i, m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>616 i, m</td>
</tr>
<tr>
<td>Compound</td>
<td>Amine frequencies</td>
<td>Perchlorate frequencies and assignments</td>
</tr>
<tr>
<td>----------</td>
<td>------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>[Ni(N,N,N′-trimethylen)2(ClO4)2]</td>
<td>3310 s. 2090 vw, br</td>
<td>Combination of $\nu_8$ and $\nu_2$ in C2v</td>
</tr>
<tr>
<td></td>
<td>3290 s. 2050 vw, br</td>
<td>Combination of $\nu_6$ and $\nu_2$ in C2v</td>
</tr>
<tr>
<td></td>
<td>1960 vw, br</td>
<td>Combination of $\nu_1$ and $\nu_2$ in C2v</td>
</tr>
<tr>
<td></td>
<td>1170 vi, s</td>
<td>$\nu_8$, asymm stretch ClO4</td>
</tr>
<tr>
<td></td>
<td>1125 vi, s</td>
<td>$\nu_6$, asymm stretch ClO4</td>
</tr>
<tr>
<td></td>
<td>1038 vi, s</td>
<td>$\nu_1$, symm stretch ClO4</td>
</tr>
<tr>
<td></td>
<td>928 i, s</td>
<td>$\nu_2$, symm stretch ClO4 $\dagger$</td>
</tr>
<tr>
<td></td>
<td>635 i, s</td>
<td>$\nu_3$, symm bend ClO4</td>
</tr>
<tr>
<td></td>
<td>623 i, s</td>
<td>$\gamma_7$, and $\nu_9$, rocking ClO4</td>
</tr>
<tr>
<td></td>
<td>617 i, s</td>
<td></td>
</tr>
</tbody>
</table>

* The spectra were determined as Nujol mulls between KBr discs.  
† Frequencies are listed in wave numbers.  
‡ The first symbol listed refers to the intensity of absorption: vi, very intense; i, intense;  
m, medium; w, weak; vw, very weak. The second symbol refers to the width of the peak: br, broad;  
m; medium; s, sharp.  
$\dagger$ Denotes vibrations which involve the oxygen atom(s) bonded to the Ni(II) ion.
vacuum, marked changes occur in the infrared spectrum and magnetic moment as the temperature is increased (Table 10).

**TABLE 10**

Changes in the Physical Properties on Heating $[\text{Ni(N-methylen)}_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>Temp. ($^\circ$C)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(N-methylen)}_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$</td>
<td>blue</td>
<td>3.25</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>yellow</td>
<td>1.22</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>yellow</td>
<td>1.15</td>
<td>100</td>
</tr>
<tr>
<td>$[\text{Ni(N-methylen)}_2(\text{ClO}_4)_2]$</td>
<td>orchid</td>
<td>3.27</td>
<td>115</td>
</tr>
</tbody>
</table>

$^a$ Temperature to which the original compound was heated at each step.

The reflectance spectra of both the starting compound $[\text{Ni(N-methylen)}_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ and the compound obtained after heating to $115^\circ$C, $[\text{Ni(N-methylen)}_2(\text{ClO}_4)_2]$, are almost identical (Table 8), but the intermediate yellow species contains an additional intense absorption band at 20,800 cm$^{-1}$, characteristic of square-planar Ni(II) complexes.

The decrease of the magnetic moment from 3.25 B. M. to 1.15 B. M. also indicates the presence of a diamagnetic square-planar intermediate. When the temperature is then raised to $115^\circ$C, the magnetic moment rises to 3.27 B. M., indicating that the water molecules have been removed during the heating process, and perchlorate ions subsequently become coordinated. This transformation is substantiated by the disappearance of three infrared bands at 3550, 3480, and 1632 cm$^{-1}$ which were due to coordinated water molecules, and the subsequent splitting of the perchlorate absorptions in the infrared spectrum.
The infrared bands attributable to perchlorate ions are assigned in accordance with the works of Hathaway and Underhill (46, 90). They have shown that as the perchlorate ion becomes involved in covalent bonding, its symmetry is lowered from Td to $C_{3v}$ to $C_{2v}$ depending on whether one or two of its oxygen atoms are used in bonding. The vibrations of the ClO$_4^-$ group as a function of symmetry are illustrated in Figure 9. In the infrared spectrum of the [Ni(N-methylen)$_2$(H$_2$O)$_2$] (ClO$_4^-$)$_2$ complex, which contains tetrahedral uncoordinated perchlorate ions, no absorption is observed for the symmetric bending mode ($v_2$) at 460 cm$^{-1}$, although this is found for several other nickel(II) perchlorate compounds prepared in the present study. The weak absorption at 2025 cm$^{-1}$ is a combination band of $v_1$ (930 cm$^{-1}$) and $v_3$ (1100 cm$^{-1}$) frequencies, and the band at 625 cm$^{-1}$ is assigned as $v_4$.

When the tetrahedral perchlorate ion becomes coordinated as a monodentate ligand, the symmetry of the ion is reduced to $C_{3v}$. Corresponding changes in the infrared involve splitting of $v_3$ (1100 cm$^{-1}$) into $v_1$, and $v_4$, and $v_4$ (625 cm$^{-1}$) is split into $v_3$ and $v_5$. The former $v_1$ (930 cm$^{-1}$) becomes $v_2$ in $C_{3v}$ symmetry and the intensity of this band increases, since it is infrared active when the symmetry is lowered from Td. Such infrared changes are observed for the complexes [Ni(AA)$_2$(ClO$_4^-$)$_2$] with the N-methylen and N,N'-dimethylen ligands. As a result, these compounds contain monodentate coordinated perchlorate ions. It is assumed that four nitrogen atoms are bonded in a plane about the nickel ion, and that the oxygen atoms are assumed to occupy trans-positions. Portions of the infrared spectra of [Ni(N-methylen)$_2$(H$_2$O)$_2$](ClO$_4^-$)$_2$ and [Ni(N-methylen)$_2$(ClO$_4^-$)$_2$] are shown in Figure 10;
**Vibrations of the ClO₄ Group as a Function of Symmetry**

<table>
<thead>
<tr>
<th>State of ClO₄</th>
<th>Symmetry</th>
<th>Symmetry</th>
<th>(v_2)</th>
<th>(v_6)</th>
<th>(v_4)</th>
<th>(v_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₄⁻</td>
<td>(C_{3v})</td>
<td>(A_1(I,R))</td>
<td>E(I,R)</td>
<td>A(I,R)</td>
<td>E(I,R)</td>
<td>A(I,R)</td>
</tr>
<tr>
<td>ClO₂⁺</td>
<td>(T_d)</td>
<td>A(R)</td>
<td>E(R)</td>
<td>T₂₁(I,R)</td>
<td>T₂₂(I,R)</td>
<td></td>
</tr>
<tr>
<td>ClO₂⁻</td>
<td>(C_{2v})</td>
<td>A₁(I,R)</td>
<td>A₁(R)</td>
<td>A₂(R)</td>
<td>B₁(R)</td>
<td>B₂₁(I,R)</td>
</tr>
</tbody>
</table>

\(A\) and \(B\), non-degenerate. \(E\), doubly degenerate. \(T\), triply degenerate. \(I\), infrared active. \(R\), Raman active. \(s\), symmetric. \(a\), antisymmetric. \(O\) refers to oxygen co-ordinated to metal.

**Figure 9**
Figure 10 Perchlorate regions in the infrared spectrum of
A - [Ni(N-methylene),H₂O](ClO₄)₂ and
B - [Ni(N-methylene),ClO₄]₂
the same portion is illustrated in Figure 11 for the $[\text{Ni}(N,N'\text{-dimethyl-en})_2(\text{ClO}_4)_2]$ complex.

The perchlorate asymmetric stretching frequency ($v_3$) is split approximately 100 cm\(^{-1}\) and the asymmetric bending mode ($v_4$) is split about 15 cm\(^{-1}\) on coordination. For both bands, the splitting is unsymmetrical from the position of the original absorption. One of the components occurs one-third of the total splitting to higher energy, from the original band position. The vibrational modes which split when perchlorate ion acts as a monodentate ligand are triply (T) degenerate, and in $C_3v$ symmetry they transform into a singly (A) and doubly (E) degenerate pair. In order for the center of symmetry of the energy to be maintained, the doubly degenerate E states should be shifted just one-half as far as the non-degenerate A states. Therefore, the higher energy band of each pair is assigned as the E state and the lower energy component as the A state (Table 9).

When the perchlorate ion is coordinated as a bidentate ligand, its symmetry is reduced to $C_2v$, and all vibrational states become non-degenerate. Thus, complexes which contain bidentate perchlorato groups are expected to show three bands near 625 cm\(^{-1}\) and three more near 1100 cm\(^{-1}\), in addition to the 930 cm\(^{-1}\) band. The complex $[\text{Ni}(N,N,N'\text{-trimethyl-en})_2(\text{ClO}_4)_2]$ displays just this type of spectrum (Figure 12), with three well defined perchlorate bands present in each of the $v_3$ and $v_4$ regions. The assignment is aided by the fact that the three bands at 1170, 1125, and 1038 cm\(^{-1}\) form combination bands with the 928 cm\(^{-1}\) band and reproduce the same splitting pattern at 2090, 2050, and 1960 cm\(^{-1}\). Thus, the infrared evidence demonstrates
Figure II Perchlorate regions in the Infrared spectrum of
\[ \text{[Ni(N,N'-dimethylene)\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2}] \]
Figure 12 Perchlorate regions in the Infrared spectrum of $[\text{Ni}(\text{N},\text{N},\text{N}', \text{trimethylen})_2(\text{ClO}_4)_2]$
that the perchlorate ions behave as bidentate ligands in this case. This compound is believed to be one of the best characterized examples of such bidentate coordination.

Several infrared bands are present in the 950 - 1200 cm\(^{-1}\) region of all three perchlorato complexes in addition to the absorptions which have been assigned to the ClO\(_4\) group. In order to definitively assign these bands to the respective ethylenediamine ligands, the corresponding NiCl\(_2\) complexes were prepared (see p. 32). Except for the perchlorate absorptions, the infrared spectra of the NiCl\(_2\) and the Ni(ClO\(_4\))\(_2\) complexes are identical; thus, the additional bands are ethylenediamine absorptions.

Magnetic moments (Table 8) indicate a triplet ground state for nickel ion in the perchlorato complexes, and this is consistent with their visible spectra as well. These data suggest that the complexes exhibit a six-coordinate pseudo octahedral structure. The simplest structural approach would be to consider only those atoms directly coordinated to nickel ion; four nitrogen atoms in a plane and two oxygen atoms in trans-positions for the [Ni(N-methylen)\(_2\)(ClO\(_4\))\(_2\)] and [Ni(N,N'-dimethylen)\(_2\)(ClO\(_4\))\(_2\)] complexes, and the reverse numbers and positions of atoms are postulated for the [Ni(N,N,N'-trimethylen)\(_2\)(ClO\(_4\))\(_2\)] example. The site symmetry of either combination is approximately D\(_{4h}\). Oxygen atom is a poorer donor than nitrogen, and its coordination leads to a tetragonal field about nickel ion in all three perchlorato complexes. The in-plane component of this field would be much less for the N,N,N'-trimethylen complex since it contains more coordinated oxygen atoms. Octahedral and tetragonal field forces are
so related that the excited energy states for the octahedral nickel ion will become split in a tetragonal field. Spectra of six-coordinate $D_{4h}$ complexes would then consist of more than three bands, which arise from term splitting. The complete reflectance spectra for the perchlorato complex of N-methylen, and solution spectra for the $N,N,N'$-trimethylen example, are illustrated in Figure 13.

Visible spectra of dipерchloratobis(N-methylen) and ($N,N'$-dimethylen) complexes, and the diaquobis(N-methylen) complex are quite similar. Reflectance data indicate the presence of a low energy transition with a maximum beyond 1100 μm, and two adjacent absorptions at 775 and 715 μm. For respective tris(ligand) octahedral complexes, the first spin-allowed band maximum is near 930 μm, a wave length intermediate between those observed for the perchlorato and diaquo complexes. Thus, the visible spectra for the perchlorato complexes display band splitting when compared with octahedral spectra and known tetragonal nickel(II) complexes exhibit similar splittings as well. The electronic transitions are assigned according to the six-coordinate $D_{4h}$ energy diagram given by Maki (84), and are illustrated in Figure 14. In terms of increasing energy the triplet-triplet transitions are from the $3B_{2g}$ ground state to the successively higher excited states $3E_g$ (too low in energy to be observed), ($3A_{2g}, 3B_{1g}$), $3E_g$, and ($3A_{2g}, 3E_g$).

Both solution and reflectance spectra of the $[Ni(N,N,N'^-trimethylen)_2(ClO_4)_2]$ complex are nearly identical and show the split bands typical of tetragonal complexes. However, transition energies are shifted to lower values compared with the monodentate perchlorato complexes, and this is due to the replacement of two nitrogen by two
Figure 13 Electronic absorption spectra of 

- \([\text{Ni(N,N',N'-trimethylen)}_2\text{(ClO}_4)_2]\) 
- \([\text{Ni(N-methylen)}_2\text{(H}_2\text{O)}_2\text{(ClO}_4)_2]\) 

Wavelength, m\(\mu\)
Figure 14 Maki energy diagram for 6-coordinate $d^8$ system in $D_{4h}$ symmetry.
oxygen atoms in the coordination sphere, which causes a subsequent decrease in total field strength. The spin-forbidden transition in this example now occurs at higher energy than its nearest spin-allowed transition. However, this is possible since Maki (28) has shown that as the in-plane field strength decreases, the $^1A_g$ level crosses the $^3A_{2g}, ^3B_{1g}$ levels and the triplet-triplet transitions occur at lower energies than the $^3B_{2g} - ^1A_g$ transition.

For the structure of $[\text{Ni}(N,N,N',\text{trimethylen})_2(\text{ClO}_4)_2]$ to be consistent with the spectral data and analytical composition and yet contain bidentate perchlorato groups, one end of each ligand must be uncoordinated, i.e.; the ligands must act as monodentate donors. Clearly, the dimethylamine group will be the end which is displaced, leaving the ligand coordinated only via its secondary nitrogen atom. Then the nickel ion will be bonded to four oxygen atoms in a plane and two nitrogen atoms in a tetragonal field (Figure 15). Both the reflectance and the solution spectra of the complex (Table 8) show a weak "average field" (91,92), consistent with this structural assignment.

There also is information of a more general nature compatible with the structure proposed for $[\text{Ni}(N,N,N',\text{trimethylen})_2(\text{ClO}_4)_2]$. Color differences between the monodentate (blue-violet) and bidentate (green) perchlorato complexes are reproduced in compounds of NiCl$_2$ with the present ligand system where it was found that two nitrogen and four weaker donor atoms result in green compounds, whereas opposite composition produces blue-violet colors. This has been noted in other nickel complexes with ligands of similar donor strength as well (93). Furthermore, solubility in dichloromethane must be greatly assisted by
Figure 15 Structure proposed for 
\([\text{Ni}(\text{N}, \text{N}, \text{N}'-\text{trimethylene})_2(\text{ClO}_4)_2]\)
the uncoordinated ligand ends in the \([\text{Ni}(N,N',N'-\text{trimethylen})_2(\text{ClO}_4)_2]\) complex. In this manner more organic character is presented to solvent molecules, and also the chelated perchlorate ions would expose fewer polar oxygen atoms. Both factors are inoperative for the monodentate perchlorato complexes, and they are insoluble in \(\text{CH}_2\text{Cl}_2\).

One can rationalize why the perchlorate group becomes coordinated during the heat treatment of certain \(N\)-alkylethylenediamine \(\text{Ni}(\text{II})\) complexes. If the perchlorate ions are packed in the crystals approximately in \textit{trans}-positions to the planar four-coordinate nickel ion, but at too great a distance for bond formation, it may be possible for the thermal vibrations to cause packing rearrangements to occur and "trap" the perchlorate ion in an environment such that the metal-anion distance is reduced to the bond distance necessary for coordination.

The preparation of the \([\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\) complex was attempted since ethylenediamine itself has the smallest volume (or steric) requirement of all the amine ligands used in this study. The reflectance spectra of the resulting product indicated that both four- and six-coordinate species were present. The mixture gave no change in the perchlorate regions of the infrared spectrum when heated to 130°C for five days. In this case, either the "steric border" around the planar nickel ion is not sufficient to "trap" the perchlorate ions, or the four primary amino groups create such a strong in-plane field that no ligand can be coordinated in the axial positions.

Isolation of stable perchlorato complexes with only the specific \(N\)-methylethylenediamines noted implies that the structural requirements of perchlorato complexes must be very critical. For example, the
[Ni(N,N-dimethylen)$_2$(ClO$_4$)$_2$] compound did not form a perchlorato complex. The compound was heated until it decomposed (130°C) but its diamagnetic character and infrared spectrum remained unchanged to the decomposition point. Neither could a stable [Ni(N,N-dimethylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ complex be prepared. However, the bis complex of the isomeric N,N'-dimethylen ligand readily forms both the diperoxidato and the diaquo complexes.

The synthesis of perchlorato complexes by this heating procedure has been successful only when two or more of the coordinated amine groups were monomethyl-substituted (Table II). The size of the alkyl ligand substituent then must be the deciding factor, for bis(ethylene-diamine), (N-ethylen), and (N,N-dimethylen) complexes do not react in this manner to form perchlorato complexes, and the disubstituted end of the N,N,N'-trimethylen ligand becomes uncoordinated during perchlorate ion complexation. This all lends support to the idea that perchlorate ion is trapped into coordination by occupying a tailored site. In addition, the storage properties of [Ni(AA)$_2$(ClO$_4$)$_2$] complexes relative to [Ni(AA)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, indicate that coordinated water is gradually released from the diaquobis(ligand) complexes whereas no change occurs in the perchlorato complexes over a six month period. Apparently, the smaller water molecule is able to leave the coordination site more readily than the "trapped" perchlorato group.

Then it may be predicted that a square-planar nickel complex with four-coordinated nitrogen atoms, three of which are methyl-substituted and the remaining nitrogen a primary amino group, should convert to a perchlorato species upon heating. Furthermore, any of several ethylene-diamine derivatives with a monomethylamine and another substituent
TABLE II
Donor Species Present in the First Coordination Sphere of the Perchlorato Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Primary amino groups</th>
<th>Methyl substituted amino groups</th>
<th>Coordinated oxygen atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(N-methylen)$_2$(ClO$_4$)$_2$]</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>[Ni(N,N'-dimethylen)$_2$(ClO$_4$)$_2$]</td>
<td>4</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>[Ni(N,N,N'-trimethylen)$_2$(ClO$_4$)$_2$]</td>
<td>2</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
sterically greater than the dimethyl group on the remaining amine, would be expected to form bidentate perchlorato complexes analogous with \([\text{Ni}(\text{N},\text{N},\text{N}'-\text{trimethylene})_2(\text{ClO}_4)_2]\).

4. Diaquobis(ligand) complexes

Results.—All the diaquobis(ligand) complexes are blue solids, and their magnetic moments and reflectance spectra are listed in Table 12. Magnetic data demonstrate that the nickel ions in these compounds have two unpaired electrons, and that the moment has an orbital contribution of typical magnitude. The reflectance spectra are characteristic of \(d^8\) six-coordinate tetragonal species and are interpreted as described in the section for complexes containing coordinated perchlorate ions. Transition assignments again are based on the Maki six-coordinate \(D_{4h}\) energy diagram (Figure 14), and in terms of increasing energy these are \(3B_{2g} \rightarrow (3A_{2g} + 3B_{2g})(12,700 \text{ cm}^{-1})\), \(1A_{1g} (13,700 \text{ cm}^{-1})\), \(3E_g (17,900 \text{ cm}^{-1})\), and \(3A_{2g} (28,300 \text{ cm}^{-1})\).

A band at approximately 33,000 \(\text{cm}^{-1}\) is expected for the transition \(3B_{2g} \rightarrow 3E_g(P)\), but could not be obtained by reflectance techniques.

A difference was observed for reflectance spectra measured with the Beckman DU and Cary Model 14 spectrophotometers at low wave numbers. In the DU spectrum, a split band appeared with minimum at 950 \(\mu\mu\), while the Cary Model 14 spectrum did not display such a split even when maximum precautions were taken to prevent sample dehydration. The reflectance spectrum of \([\text{Ni}(\text{N-ethylen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\) (measured on the Beckman DU) is illustrated in Figure 16 as a typical example for this group of complexes. Use of the Beckman DU spectrophotometer was particularly advantageous for determining the reflection spectra.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>$\lambda_{\text{max}}$</th>
<th>cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methylen</td>
<td>3.25</td>
<td>790</td>
<td>12,700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>730</td>
<td>13,700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>559</td>
<td>17,900</td>
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<td>28,300</td>
</tr>
<tr>
<td>N-ethylen</td>
<td>3.29</td>
<td>790</td>
<td>12,700</td>
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<td>735</td>
<td>13,600</td>
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<td>555</td>
<td>18,000</td>
</tr>
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<td></td>
<td></td>
<td>353</td>
<td>28,300</td>
</tr>
<tr>
<td>N,N'-dimethylen</td>
<td>3.20</td>
<td>860</td>
<td>11,600</td>
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<td></td>
<td>565</td>
<td>17,800</td>
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<td>356</td>
<td>28,100</td>
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<tr>
<td>N,N'-diethylen</td>
<td>3.25</td>
<td>810</td>
<td>12,300</td>
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<td></td>
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<td>750</td>
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<td>563</td>
<td>17,800</td>
</tr>
<tr>
<td></td>
<td></td>
<td>356</td>
<td>28,100</td>
</tr>
</tbody>
</table>
Figure 16: Reflectance spectrum of [Ni(N-ethylen)₂(H₂O)₂(CIO₄)₂].

Absorbance (arbitrary scale)
of diaquobis(ligand) complexes, for samples measured on the Cary Model 14 were partially transformed to respective bis(ligand) complexes during the measurement. Obviously, heat from the Cary Model 14 infrared source dehydrated the samples. The Beckman DU employs a tungsten source for the near infrared (up to 1100 μm) which has little if any heat radiation at the sample site, and samples were measured here without any detectable changes.

Infrared spectra of the complexes contain absorptions characteristic of coordinated water molecules. The frequencies assigned to water and amine infrared activity are listed in Table 13, and the infrared spectrum of \([\text{Ni}(\text{N-ethylen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\) is illustrated in Figure 17. Elemental analyses, coupled with the magnetic susceptibility and spectral data substantiate that all of the compounds are six-coordinate trans-diaquobis(ligand) species.

Discussion.—Preparation of diaquobis(ligand) compounds was attempted with all isolated \([\text{Ni}(\text{AA})_2](\text{ClO}_4)_2\) complexes using the method of hydrolyzing ether slurries (see p. 26). The \([\text{Ni}(\text{AA})_2](\text{ClO}_4)_2\) complexes containing the N-propylen, N,N-dimethylen, and N-methyl-N'-ethylen ligands formed blue aqueous layers in this manner, but upon drying either a crystalline product was not obtained or traces of the original yellow four-coordinate compound were present. Infrared spectra of these non-crystalline products displayed absorptions in the 3300-3600 cm\(^{-1}\) range, but they were poorly defined compared to those illustrated in Figure 17. The differences in crystalline form and infrared spectra are believed the result of incomplete or weak coordination by water in the above three examples. On the other hand,
<table>
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<th>Ligand</th>
<th>Water frequencies cm⁻¹</th>
<th>Amine frequencies cm⁻¹</th>
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<tr>
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<td>3370 3290 1595</td>
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<td>3610 3530 1631</td>
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<td>N,N'-dimethylen</td>
<td>3550 3460 1652</td>
<td>3310</td>
</tr>
<tr>
<td>N,N'-diethylen</td>
<td>3470 3420 1655</td>
<td>3310 3290</td>
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</table>
Figure 17 Infrared spectrum of $[\text{Ni(N-ethylen)$_2$(H$_2$O)$_2$}]$\text{(ClO$_4$)$_2$}$ from 4000 to 1300 cm$^{-1}$ (Nujol mull)
bis(N,N-diethylen) did not change in any manner, and the infrared spectra before and after the attempted reaction were identical.

Hydrolysis of the bis(N-isopropyl) complex resulted in formation of well-defined red crystals. The infrared spectrum of the product was distinguished by a very sharp band at 3660 cm\(^{-1}\) of medium intensity, a complex intense amine stretching group at 3330-3220 cm\(^{-1}\), and a split band at 1595 and 1584 cm\(^{-1}\) of medium intensity. It is possible to postulate a structure consistent with this infrared information. If the high energy band is assumed to be due to hydroxyl ion, then there would be only one stretching frequency as observed at 3660 cm\(^{-1}\), and no deformation mode would be possible at approximately 1600 cm\(^{-1}\). It is conceivable that the split band could arise from two amine deformation modes differing in energy by 10 cm\(^{-1}\) (see p. 136).

One structure which is consistent with such an infrared spectrum is illustrated in Figure 18. The postulated square-planar complex contains coordinated hydroxyl ion and the two primary amine groups have different environments in terms of their neighboring atoms. The cis-primary amine groups could account for the complexity of the stretching bands as well as the divided deformation mode.

The isolated diaquobis(ligand) complexes exhibit characteristic infrared spectra with respect to absorption of coordinated water; each shows two stretching bands at 3700-3400 cm\(^{-1}\) and one deformation band at approximately 1650 cm\(^{-1}\). The regularity in the infrared absorptions due to coordinated water suggests an equivalent environment for the two water molecules in the complex ion, and it is believed they occupy trans-positions.
Figure 18 Possible structure for the hydrolysis product of \([\text{Ni(N-isopropylen)_2(CIO}_4)_2]\)
Electronic absorption spectra are remarkably uniform for the diaquobis(ligand) complexes. In all cases three band groups are obtained; two distinctly separate bands plus a less intense apparently double band at lower wave numbers. The energies of any one absorption band varied by only 200 cm\(^{-1}\) among the entire series. The band maxima from the spectra of all \([\text{Ni}(\text{AA})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\) complexes are almost identical to that found for the \([\text{Ni}(\text{AA})_2(\text{ClO}_4)_2]\) complexes with the N-methylen and N,N'-dimethylen ligands. This agreement in spectral energy and contour strongly supports an equivalent structure about nickel ion for both types of complexes. In the first coordination sphere they would contain four planar nitrogen atoms and two trans-oxygen atoms about nickel ion. Thus, the transition energies appear to be insensitive to substituent changes on the four in-plane nitrogen atoms (which vary from two methyl to four ethyl groups in the isolated compounds), and are not greatly affected by the source of the trans-oxygen atoms (water molecules or perchlorate ions). Rather, the uniform absorption energies show that the specific types of donor atoms in the first coordination sphere are the principal factor which determines the spectral character, rather than the steric requirements of the ligand. Since all six donor atoms are alike in these complexes, their spectra are identical, and the identical spectra demonstrate an equivalent structure about nickel ion. This is a manifestation of Bjerrum's rule (94) which acknowledges the unimportant role played by atoms outside the first coordination sphere. Thus six-coordinate tetragonal structures are much less sensitive than the tris or bis complexes to changes on the N-alkyl substituents of the ligands.
Jørgensen (92) has tabulated spectral data which is consistent with this view. He lists the spectral energies of several complexes containing four nitrogen and two oxygen atoms coordinated to nickel ion, and the listed energies are very similar to the spectra of the 4-N + 2-O complexes isolated in the present study. In addition, the spectra of several 2-N + 4-O type complexes are also included in Jørgensen's report, and their energies are in accord with that observed for the \([\text{Ni(N}_4\text{N}_2\text{N'}-\text{trimethylen})_2(\text{ClO}_4)_2]\) complex. This is additional evidence in agreement with the postulated structures of the diaquo-bis(ligand) and dipерchlorato bис(ligand) complexes as reported in this thesis.

The variation in reflectance spectra obtained on the Beckman DU and Cary Model 14 spectrophotometers made an assessment of tetragonal distortion difficult; band splitting was magnified in the Beckman DU case. To resolve this point, it was proposed that aqueous solution spectra be measured, the thought being that diaquo-bis(ligand) complexes would go into solution without materially changing structure. In actual fact, solution spectra band maxima were found to be different from reflectance spectral data; in general contour the solution spectra resemble an octahedral Ni(II) spectrum. To compound matters, the solution spectrum of \([\text{Ni(N-ethylen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\) was found to be identical with the spectrum of an aqueous solution of \([\text{Ni(N-ethylen})_2]\)(\text{ClO}_4)_2. Thus it would seem plausible that neither of the formulated species is actually present in solution. The matter is not resolved but is probably connected with the state of the complex, i.e., solid or solution. It is suggested that a relaxation effect in solution may allow
expansion of the four in-plane nitrogen atoms to such a point that a pseudo octahedral field is presented to nickel ion, even though the two trans-oxygen donor atoms are poorer coordinating species than nitrogen (see p. 139). However, in the crystal, the four planar nitrogen atoms are fixed, and approach of the heterogeneous trans-components cannot be coupled with expansion of the in-plane donors, and this results in a tetragonal field. The spectrum reported for \([\text{Ni(en)}_2(H_2O)_2]^{+2}\) by Jørgensen (92) was measured in aqueous solution and none of the bands are split.

Comparison of diaquobis(ligand) complexes with the dipерchlorato-bis(ligand) compounds illustrates several factors. As mentioned above, the electronic absorption energies are almost identical for all the complexes, with the exception of \([\text{Ni(N}_2\text{N}_2\text{N}'-\text{trimethylene})_2(\text{ClO}_4)_2]\), and this supports infrared evidence for the presence of bidentate perchlorato groups and a 2-N + 4-O donor atom system in this single case. The unique properties of this one example remove it from further comparison with the remaining compounds. Band splitting, or the extent of tetragonal distortion, is more pronounced for the perchlorato compounds than for the diaquobis(ligand) series. An anion can disperse the charge on a central atom, whereas a neutral ligand cannot, and the enhanced splitting for the dipерchloratobis(ligand) complexes is believed due to electrostatic interaction of a magnitude which primarily effects the lower energy terms. Thus, the low wave number transitions are split without materially affecting higher energy terms.

An indication of relative stability of the two series is demonstrated by their storage properties. Perchlorato complexes were stable
for indefinite periods in a desiccator, and showed no signs of change
during infrared reflectance measurements with a Cary Model 14 spectrophotometer. Conversely, the diaquobis(ligand) complexes convert to
their four-coordinate bis(ligand) derivatives upon storage in a desiccator, and the conversion time in the solid state is directly related
to ligand substituent; methyl (1 week), ethyl (2 weeks), and diethyl
(6 months). These considerations point out the important role of
steric control. A water molecule smaller than perchlorate ion can
leave the coordination site easier. However, this action may be
retarded if large N-alkyl substituents are present, as in the case of
the N,N'-diethylen ligand. On the other hand, perchlorate ion does
not even coordinate unless specific in-plane steric conditions (two or
four N-methylamino groups) are available, and the resulting six-coordi-
nate product must fit together very well. The stability due to this
ideal site accommodation can be assisted by extensive hydrogen-bonding
between the free oxygen atoms of the coordinated perchlorate ion and
hydrogen atoms on the amines. Neither of these stabilizing features
is possible with coordinated water molecules, and thus the diaquobis-
(ligand) complexes are less stable upon storage.

5. \textit{Tetrakis(N-isopropylene)nickel(II) perchlorate}

The tris complex of the N-isopropylene ligand could not be prepared.
However, repeated attempts using large excesses of ligand resulted in
isolation of a violet complex. This product did not fit into any
classifications previously considered and will be reviewed here. Evi-
dence is presented which demonstrates that the product is

\[ [\text{Ni(N-isopropylene)}_4]\text{(ClO}_4\text{)}_2. \]
Results.—The magnetic moment, conductivity data, and reflectance spectrum are listed in Table 14. The magnetic data indicate that the complex is paramagnetic, and nickel ion has a triplet ground state. The conductivity measurement demonstrates the complex is a bi-univalent electrolyte in nitromethane, and this agrees with the proposed formulation, i.e., $[\text{Ni(N-isopropyl)}_4](\text{ClO}_4)_2$. The reflectance spectrum is a hybrid of octahedral and tetragonal contours, and although the lowest energy transition is not split, it is much too broad to be considered an octahedral type spectrum. The spectrum is illustrated in Figure 19. The second band is noticeably asymmetric, and thus distinct from the octahedral case as well. Band maxima are therefore best assigned using tetragonal six-coordinate $D_{4h}$ energy diagrams, i.e., $3_{B_2g}^g - 3_{E_g}^g + 3_{A_2g}^g$ (11,200 cm$^{-1}$ center), $1_{A_1g}$ (12,700 cm$^{-1}$), $(3_{E_g}^g + 3_{B_2g}^g)$ (17,700 cm$^{-1}$), and $(3_{A_2g}^g + 3_{E_g}^g)$ (27,900 cm$^{-1}$).

Elemental analysis, when coupled with the above experimental information, substantiate a tetrakis formula for the tetragonal complex.

Discussion.—The momentary appearance of a brown color during preparation, and isolation of the yellow square-planar bis compound from the final filtrate, suggest that the tetrakis complex is closely related to its four-coordinate bis derivative. If $[\text{Ni(N-isopropyl)}_2]^2$ is first formed during preparation, the two remaining ligand molecules required for the tetrakis complex cannot coordinate in a bidentate fashion; rather only one end of each ligand can be bound to the nickel ion. Steric requirements would demand the coordination of the smaller primary amine end, and the resulting structure is illustrated in Figure 20. In this structure, four primary amines are planar about
TABLE 14

Magnetic Moment, Conductivity Data, and Reflectance Spectrum of $[\text{Ni(N-isopropyl)}_4](\text{ClO}_4)_2$

<table>
<thead>
<tr>
<th>$X_g = 5.388 \times 10^{-6}$</th>
<th>c.g.s.u.</th>
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</thead>
<tbody>
<tr>
<td>$X_m = 3.981 \times 10^{-6}$</td>
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</tr>
<tr>
<td>$\mu = 3.10$ B.M.</td>
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</table>

molar conductivity = 1845 cm$^2$/ohm-moles

reflectance spectrum

<table>
<thead>
<tr>
<th>$m\mu$</th>
<th>cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>893</td>
<td>11,200</td>
</tr>
<tr>
<td>788</td>
<td>12,700</td>
</tr>
<tr>
<td>565</td>
<td>17,700</td>
</tr>
<tr>
<td>358</td>
<td>27,900</td>
</tr>
</tbody>
</table>
Figure 19 Reflectance spectra of $\text{[Ni(N-isopropylen)\textsubscript{4}]}(\text{ClO}_4\textsubscript{2})$.
Figure 20 Structure proposed for \([\text{Ni}(N\text{-isopropyleny})_4](\text{ClO}_4)_2\)
nickel ion, and both above and below this plane is a N-isopropyl substituted amine. Although there are six nitrogen donor atoms in the first coordination sphere, the size of the N-isopropyl substituent does not allow as close an approach in the trans-positions, and this gives rise to a slight tetragonal field. In the reflectance spectrum the slight tetragonal distortion is manifested as a broadening of the first transition and asymmetry of the second band. The structure is similar to that proposed for $\text{[Ni(N}_3\text{N}_2\text{N}^\prime\text{-trimethylen})_2(\text{ClO}_4)_2]$; both complexes contain two chelated ligands in a plane and two monodentate ethylenediamine derivatives in trans-positions. In both cases the uncoordinated ends of the trans-ligands are substituted with large alkyl groups, i.e., isopropyl and dimethyl groups. The spectral energies for the N-isopropylen complex (6-N) have higher values than the perchlorato complex (2-N + 4-0) because of the stronger "average field" about nickel ion in this example.

In lieu of the "in between" type of spectrum, it was of interest to obtain solution spectra of the complex as well. The compound was not soluble in its own ligand at concentrations useful for spectral measurement, and minimal amounts of dimethylformamide were required to affect solution. The resulting spectra were considerably different from reflectance determinations, because band splitting was now much more pronounced. Undoubtedly, the trans-monodentate ligands were displaced by the solvent and this increased the tetragonal distortion. Because of these differences in the solution spectrum, only results of reflectance measurements are considered valid.

During preparation, it appears that the bidentate coordinated
ligands are present in a plane first, and then the trans-positions are occupied. These trans-components are more vulnerable to displacement than the bidentate coordinated ligands, for as mentioned above (see p. 26) when the tetrakis complex is heated in vacuo trans-components are removed and the \([\text{Ni(AA)}_2\](\text{ClO}_4)_2\) compound results. The greater stability of the bidentate ligands is due to the "chelate" effect. This distinction between bidentate and trans-monodentate ligands is observed in conductivity measurements as well.

Conductivity measurements for the complex were determined in nitromethane. The color of the resulting solution was yellow compared to the violet solid, but the molar conductance based upon the tetrakis formula was exactly that expected for a 2:1 electrolyte. Obviously, the change occurring on solution did not alter any of the charged species in the complex. The only neutral components present are ligands, and the most direct alteration involving ligands would be removal of the two trans-molecules. This results in the square-planar four-coordinate complex, known to be yellow in the solid state, and accounts for the yellow nitromethane solution. The transformation on solution distinguishes two ligand types, those coordinated in a bidentate fashion, which are less susceptible to displacement, and the trans-monodentate type.

C. Nickel(II) Chloride Complexes

Complexes of nickel chloride with three chelated N-alkylethylene-diamine ligands do not differ in their spectra, magnetic moments, and molar conductivity values, from the respective tris(ligand) nickel
perchlorate complexes already discussed. For example, the infrared spectra of the two compounds \([\text{Ni(en)}_2]X_2 \quad (X = \text{Cl}^-, \text{ClO}_4^-)\) are found to be identical except for those frequencies due to anion absorptions. Because of this great similarity, the nickel chloride investigation was restricted to the \(\text{Ni(AA)}_n\text{Cl}_2 \quad (n = 1, 2)\) complexes. The mono(ligand) complexes of nickel chloride will be considered first; they are referred to as the \(1:1\) series.

1. Mono(ligand) complexes

**Results.**—All of the \(\text{Ni(AA)}\text{Cl}_2\) complexes are pale green in color and their infrared spectra demonstrate the absence of water or solvent molecules in the isolated solids. The dichloromethane solution and solid reflectance spectra of the complexes are listed in Table 15, and molar extinction coefficients are given in parentheses. Solution spectra in \(\text{CH}_2\text{Cl}_2\) were measured with only complexes containing the \(\text{N,N,N'}\)-trimethylen and \(\text{N,N,N',N'}\)-tetramethylen ligands, since none of the other series members were sufficiently soluble in solvents appropriate for spectral studies. In all of the spectra, there appear three bands separated by two others of much lower intensity. All the compounds are paramagnetic, and the gram and molar susceptibilities, and effective magnetic moments are listed in Table 16. A mono(ligand) complex could not be prepared with \(\text{N,N-diethyl} \), and products isolated upon reaction with the \(\text{N-isopropyl} \) ligand were of poor analytical quality.

**Discussion.**—Consideration of only the stoichiometry of the \(\text{Ni(AA)}\text{Cl}_2\) complexes implies a coordination number of four, i.e., two nitrogen atoms from the bidentate ligand and two chloride ions per
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Main</th>
<th>Shoulder</th>
<th>Main</th>
<th>Shoulder</th>
<th>Main</th>
<th>State</th>
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<td>15,000</td>
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nickel. Two common structures would be possible with a coordination number of four, they are the square-planar and tetrahedral arrangements. Square-planar complexes have already been discussed (see p.67) and for the present ligand system the square-planar Ni(II) complexes are diamagnetic and display one band in the region of the visible spectrum. Since the spectra of the 1:1 complexes are much more complicated than a typical square-planar spectrum, an alternative structure for these nickel chloride compounds must be considered.

There are only a few tetrahedral (95) complexes of nickel known, and the spectra of these examples differ from the 1:1 complexes prepared in this study. Tetrahedral nickel complexes are paramagnetic with effective moments generally in the 3.5 - 4.1 B.M. range (60), and while it is true that several of the 1:1 compounds display effective magnetic moments in this range, it is possible that errors arising from packing of the sample may be responsible for these larger values. The entire series of 1:1 complexes formed precipitates composed of very light plate-like aggregates, and recrystallization did not improve particle form or size. Thus filling the Guoy tube was more of a task for these complexes than any other type, and insufficient packing (relative to the Hg[Co(SCN)_4] standard) would increase their calculated magnetic moment values. The susceptibility measurements for these complexes would be determined best by the Faraday technique, which is independent of sample packing (96). Thus, the magnetic moments for some of the 1:1 complexes cannot be used to eliminate a tetrahedral structure, but only demonstrate paramagnetism of the order expected for two unpaired electrons in nickel ion. However, the differences
between spectra of the 1:1 NiCl₂ and tetrahedral complexes are adequate to discount the possibility of a tetrahedral arrangement. Thus, four-coordinate structures are incompatible with the spectral properties of the 1:1 complexes.

A six-coordinate structure is possible by the use of bridging chloride ions, since they have more than one donor electron pair available for coordination. For example, crystal x-ray studies of the Ni(py)₂Cl₂ complex have shown the structure to be pseudo octahedral (97); bridging chloride ions form a polymeric chain, and each nickel ion is coordinated to 4-Cl and 2-py. Such an arrangement is not uncommon, for nickel chloride also forms six-coordinate polymers with some substituted pyridines (98) as well as methyl cyanide (99) and substituted pyrazines (100), all of which employ bridging chloride ions. The reflectance spectrum of Ni(py)₂Cl₂ is reported (93,101) to display absorption maxima at 12,800; 14,000; 23,000; and 24,200 cm⁻¹, and is very similar in energy and contour to the 1:1 complexes. However, in Ni(py)₂Cl₂ the nitrogen atoms are trans-, while in the 1:1 series with chelating ligands, the nitrogen atoms could only be in the cis-positions. But more importantly, an analogous polymeric octahedral cis-complex, Ni(bipy)Cl₂ (62), has a spectrum similar to both the Ni(py)₂Cl₂ and the 1:1 series complexes, and an x-ray powder diffraction pattern similar to that of trans-[Co(py)₂Cl₂]⁺. Then by spectral analogy with the pyridine and bipyridine examples, the structure of the 1:1 series compounds is essentially octahedral with coordination of cis-nitrogen atoms and bridging chloride ions. In terms of group theory, the nickel ion site symmetry is effectively C₂v.
The spectra of six-coordinate nickel complexes with $C_{2\nu}$ geometry has been examined by Furlani (102). A $C_{2\nu}$ energy diagram can be derived from the octahedral case by examining the effect on term states as two cis-positions of the octahedral structure are progressively perturbed. Such an Oh-$C_{2\nu}$ energy diagram is illustrated in Figure 21. The transition energies measured from the diagram for a 50% $C_{2\nu}$ perturbation are 9,000; 13,400; 15,800; and 26,600 cm$^{-1}$. The fit with observed energies indicates that the 1:1 complexes are more rigorously $C_{2\nu}$ than the 50% limit of the Furlani diagram. In addition, further discrepancies can be attributed to the chelate effect. The observed absorption bands are then assigned to terms arising from a six-coordinate $C_{2\nu}$ symmetry about nickel ion, and in order of increasing energy the transitions from ground to excited states are: $3B_3 \rightarrow (3A_1 + 3B_2 + 3B_1)$, $1B_3(D)$, $(3B_1 + 3B_2 + 3B_3)$, $1B_1(G)$, $(3B_3 + 3B_1 + 3B_2)$. These energy levels are related to the more common transitions observed in octahedral case, and may be better assigned as $3A_{2g} \rightarrow 3T_{2g}$, $1E_g$, $3T_{1g}(F)$, $1T_{2g}$, $3T_{1g}(P)$. Weak, but very narrow bands were observed in all of the spectra at about 1550 m\(\mu\) (6400 cm$^{-1}$), and are believed to be overtones of the infrared amine stretching frequencies which occur at approximately 3200 cm$^{-1}$.

The variation in spectral energies for the entire series is quite small despite the full scope of ligands used. Such a narrow energy difference is reasonable though, for only the substituent on one third of the six donor atoms has been varied in the complexes. In addition, the presence of four monodentate Cl$^-$ fonors must greatly reduce crowding and allow the larger ligands to coordinate without difficulty.
Figure 21 Furlani energy diagram for a d^8 system in octahedral and C_{2v} symmetries.
The spectra of complexes which contain only primary and/or secondary amines display a particular trend; the spin-allowed band maxima are gradually shifted to lower energy values as the number and size of ligand substituents increase. In all cases, the contours of the spectra are nearly identical, and positions of the spin-forbidden bands remain unchanged. Even in the extremes of ligand substitution, i.e., ethylenediamine compared with N,N'-diethylen, the silhouette of the complex spectra is similar as shown in Figure 22. The spectral similarity reflects identical structures for this entire group of 1:1 complexes, and implies that the steric requirement of a secondary amine (compared with a primary) has little consequence on the gross structure, even though the amine substituent may be an ethyl group. These complexes are to be contrasted with the examples containing coordinated tertiary amines.

For mono(ligand) complexes which contain tertiary amines, it will be noted first that the ligand N,N-diethylen does not form a 1:1 complex. However, reaction with this ligand in the usual manner of preparation did result in a green paramagnetic product, but elemental analyses plus the magnetic moment and spectrum showed that the product was not a 1:1 complex. Obviously, the diethyl-substituted amine has steric requirements which either prevent its coordination, or interfere with the bridging chloride ions and obstruct polymerization. The latter prospect will be shown to be more consistent with the spectral information of isolated complexes which contain coordinated tertiary amines.

The 1:1 complexes with the ligands N,N-dimethylen,
Figure 22 Reflectance spectra of $\text{Ni(en)}\text{Cl}_2$ and $\text{Ni(N,N'-diethyl}en)\text{Cl}_2$. 
N,N,N'-trimethylen, and N,N,N',N'-tetramethylen contain coordinated tertiary amines, and their spectra show a progressively increasing asymmetry of the first absorption band, and the shoulder at 12,000 cm\(^{-1}\) becomes more pronounced compared to the other series members.

The solution spectra for the last two cases are illustrated in Figure 23. The N,N,N',N'-tetramethylen ligand contains two tertiary amines, and the spectrum of its 1:1 complex with NiCl\(_2\) is distinguished by an increased intensity of the 20,000 cm\(^{-1}\) band, and a blue shift in the highest measured absorption band relative to the other 1:1 series members. These two changes may arise from a splitting of the highest energy level. This is possible, since the splitting of the octahedral 3\(T_g(P)\) level with increasing \(C_{2v}\) perturbation is more pronounced in the Furlani diagram than for any other energy level.

These spectral changes reflect a structural change in the complex, which must be related to the coordination of tertiary amines for they are unique to this group of ligands.

It is impossible for the alkyl substituents on a chelated N,N-dialkylethlenediamine to contain themselves in the N-Ni-N plane; rather they must project above and below this plane. In so doing these substituents interfere with the potential coordination sites in the perpendicular trans-positions, and either perturb or prohibit the polymerization scheme. This is believed to be the rationale for spectral variations of the 1:1 N,N-diemthylene, N,N,N'-trimethylen, and N,N,N',N'-tetramethylen complexes compared to the other 1:1 series members, and also for the nonformation of a 1:1 complex for N,N-diethylen. This latter case will be considered further.

The N,N-diethylen ligand does form a square-planar \([\text{Ni(AA)}_2]\)(ClO\(_4\))\(_2\)
Figure 23: Absorption spectra of $\text{Ni} \{N,N',N''\text{-trimethylene}\} \text{Cl}_4$ and $\text{Ni} \{N,N,N',N''\text{-tetramethylene}\} \text{Cl}_4$ in $\text{CH}_2\text{Cl}_2$ solution.
complex, but attempts in the present study to fill the vacant trans-positions were futile. Apparently the ethyl groups block these sites or drastically restrict approaches to them. However, the existence of the bis(ligand) complex demonstrates that two ligands can coordinate in a plane about nickel ion, and therefore it is surprising that formation of a 1:1 NiCl$_2$ complex with only one ligand present is not achieved. But, in order for paramagnetic NiCl$_2$ 1:1 complexes of the N-alkylethlenediamines to exist, bridging chloride ions must be employed and the trans-positions effectively occupied by these bridging chloride ions. The ethyl groups in the N,N-diethylen ligand evidently interfere with neighboring molecules, from which the bridging chloride ions originate, to the degree that polymerization cannot occur. Then a four-coordinate structure could result with one bidentate ligand and two monodentate chloride ions coordinated to nickel. However, the tendency for nickel to form pseudo octahedral complexes is in fact maintained, and the green N,N-diethylen product is actually found to be Ni(N,N-diethylen)$_2$Cl$_2$. Evidence will be presented in the next section to show that the product is a six-coordinate polymeric complex with bridging chloride ions and monodentate coordinated ligands.

In a similar manner, a stable product that analyzed very well for the formula Ni(N-isopropylen)$_2$Cl$_2$ was isolated, whereas attempts to prepare a 1:1 complex with N-isopropylen were inconclusive. It also has been observed that Ni(py)$_2$I$_2$ is a bridged octahedral complex (103), but substitution on the pyridine ring leads to other structures with NiI$_2$. These two examples indicate that the pyridine substituents and isopropyl group interfere with the polymerization scheme, for the same
reasons as noted above with the N,N-diethylen complex. Thus forma-
tion of 1:1 complexes is not achieved in any of these three cases.

The site symmetry about nickel ion in the 1:1 complexes is $C_{2v}$, but the polymeric structure in the crystal must be quite different. The polymerization scheme for Ni(py)$_2$Cl$_2$ is known to be of the chain type as illustrated in Figure 24. However, in the 1:1 series, the ligands must coordinate to cis-positions, and such a chain polymer is impossible. A feasible alternative is the polymerization of dimeric units in a ladder fashion, as illustrated in Figure 25. The polymer model requires all chloride ions to be bridging, and therefore alike. This makes the geometry about nickel ion rigorously $C_{2v}$, and accounts for the lack of correlation of observed spectral energies with those determined from the Furlani diagram at only a 50% $C_{2v}$ perturbation.

This more involved polymeric model could be responsible for the poor packing quality of the complexes and their resulting high mag-
netic moment values. The reflectance and solution spectra of Ni(N,N,N′-trimethylen)Cl$_2$ and Ni(N,N,N′,N′-tetramethylen)Cl$_2$ are identical and indicate equivalent polymeric structures in both media. It is probable that solution without depolymerization can occur in these two cases through the interaction of solvent with ligand N-methyl substituents.

2. **Bis(ligand) complexes**

Reaction of NiCl$_2$ with the ligand system also resulted in a series of complexes with the general formula Ni(ligand)$_2$Cl$_2$. These will be referred to as the 1:2 complexes.
Figure 24 Crystal structure of Nipy$_2$Cl$_2$
Figure 25 Possible crystal structure of 1:1 series compounds
**Results.**—The infrared spectra of the Ni(AA)$_2$Cl$_2$ complexes demonstrate the absence of water or solvent molecules in the isolated solids. All the 1:2 complexes are paramagnetic, and their gram and molar susceptibilities, and effective magnetic moments are listed in Table 17. The magnetic moment values are well within the range expected for octahedral nickel ions. Reflectance and solution spectra for the 1:2 complexes are of three distinct types; these will be referred to as A, B, and C. The absorption band energies (in wave numbers) for the three spectral types are listed in Tables 18, 19, and 20, respectively. Solution spectra were measured in dichloromethane, and molar extinction coefficients are given in parentheses. The isolated complexes will be discussed in terms of their spectral classes. Compounds of spectral types A and B are blue, whereas type C compounds are green. Weak, but very narrow bands were observed in all of the spectra at about 1550 m$m$ (6400 cm$^{-1}$), and are believed to be overtones of the infrared amine stretching frequencies which occur at approximately 3200 cm$^{-1}$. It was not possible to prepare a 1:2 complex with the N,N,N',N'-tetramethylen ligand.

**Complexes of spectral type A.**—The complexes Ni(en)$_2$Cl$_2$ and Ni(N,N-dimethylen)$_2$Cl$_2$ have similar reflectance spectra as illustrated in Figure 26. Ni(en)$_2$Cl$_2$ is known to be a dimeric complex using bridging chloride ions, with a *cis*-dichloro octahedral arrangement about nickel ion (33,104). Other information on the compound is very sparse, and limited spectral data are available from only two determinations in aqueous solutions (105,106). Examples of *cis*-octahedral nickel complexes are unusual, and a more complete characterization of Ni(en)$_2$Cl$_2$ is required.
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Figure 26. Reflectance spectra of Nile yellow and N=N-N-dimethylpyrene.
The reflectance spectrum of this complex consists of three well-defined bands, and none is split. The arrangement of Cl\(^-\) and nitrogen atom donors about nickel can be described by \(C_2v\) geometry, and is comparable to the 1:1 complexes which contain cis-amine groups, but in this case the cis-components are bridging chloride ions. Spectral assignments may be based upon either \(C_2v\) or octahedral energy diagrams, and again the \(C_2v\)-Oh correlation diagram by Furlani (102) is particularly useful. In terms of increasing energy, the transition assignments are \(^3A_2g \rightarrow ^3T_2g, ^1E_g, ^3T_1g(P),\) and \(^3T_1g(P),\) or to the related states in \(C_2v\) characters. At a \(25\%\) \(C_2v\) perturbation, energy transitions taken from the Furlani diagram (Figure 21) have values of 10,200, 14,000, 17,100, and 27,200 cm\(^{-1}\); these values are based on an octahedral field of \(D_q = 1050\) cm\(^{-1}\). The fit of the energy level diagram with observed values (Table 18), is quite remarkable.

The coordinated amine groups may be present in one of two possible environments; either in the Cl-Ni-Cl plane, or perpendicular to it. The infrared spectrum of the complex consists of unique N-H stretching and deformation absorption bands, as illustrated in Figure 27. The higher frequency N-H stretching bands are more complex and cover a larger energy span (3360-3120 cm\(^{-1}\)) than any other complex measured in this investigation. Furthermore, the deformation band is split by 10 cm\(^{-1}\), in contrast to a single band for all other complexes measured, excepting the red hydrolysis derivative of \([\text{Ni}(N\text{-isopropylen})_2]\) \((\text{ClO}_4)_2\). These changes in the infrared are consistent with two distinct -NH\(_2\) environments, and are attributed to this condition. Baldwin (107) has reported a characteristic infrared band splitting
Figure 27 Infrared spectrum of Ni(en)$_2$Cl$_2$ from 4000 to 1300 cm$^{-1}$ (Nujol mull).
for \textit{cis}-[\textit{Co}(\textit{en})\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{+}, which occurs between 900-870 cm\textsuperscript{-1}, and in the \textit{trans}-complex appears as a single band. The infrared spectrum of Ni(\textit{en})\textsubscript{2}Cl\textsubscript{2} also contains a split band in this area, which in all other ethylenediamine complexes measured appears as a single band. This is additional evidence for a \textit{cis}-structure.

The reflectance spectrum of Ni(N,N-dimethylen)\textsubscript{2}Cl\textsubscript{2} has a silhouette similar to that of Ni(\textit{en})\textsubscript{2}Cl\textsubscript{2} (Figure 26), and similar structures are a possibility. If the tertiary amines of the ligand are either \textit{cis}- or \textit{trans}- to each other in a \textit{cis}-dichloro complex, local symmetry about nickel ion would be $C\textsubscript{2v}$. It is more likely that they would be in \textit{trans}-sites, so that the smaller primary amine groups could occupy adjacent positions. At a $C\textsubscript{2v}$ perturbation of approximately 35\%, transition energies taken from the Purlani diagram (Figure 21) occur at 9,600, 14,000, 16,600, and 26,300 cm\textsuperscript{-1}. The very close agreement of the diagram energies with observed spectral energies (Table 18) is taken as partial evidence for a \textit{cis}-structure. The observed transitions for Ni(N,N-dimethylen)\textsubscript{2}Cl\textsubscript{2} are assigned as for the Ni(\textit{en})\textsubscript{2}Cl\textsubscript{2} complex.

The infrared spectrum of the bis(N,N-dimethylen) complex also is comparable to that of Ni(\textit{en})\textsubscript{2}Cl\textsubscript{2}. The N-H stretching frequencies are distinctly different from those found in any other N,N-dimethylen complex measured, and the spectrum also contains a split band with peaks at 894 and 888 cm\textsuperscript{-1}, again similar to Ni(\textit{en})\textsubscript{2}Cl\textsubscript{2}.

The visible and infrared spectral similarities between the type A complexes, as well as spectral differences when compared with types B and C, confirm the structure of Ni(N,N-dimethylen)\textsubscript{2}Cl\textsubscript{2} as a \textit{cis}-dichloro octahedral complex.
The electronic spectral band maxima of the N,N-dimethylen complex are at lower energies than those for Ni(en)$_2$Cl$_2$ (Table 18). This is due to the poorer coordinating ability of tertiary relative to primary amines and indicates that steric factors are of greater importance for these complexes than inductive factors, as was also found for the tris complexes of Ni(ClO$_4$)$_2$ (see p. 63). Compared with the 1:1 series which have an equivalent C$_2v$ site symmetry about nickel ion, band energies are in the order Ni(en)$_2$Cl$_2$ > Ni(N,N-dimethylen)$_2$Cl$_2$ > 1:1 complexes. This is really just a manifestation of the change in the donor species present in the first coordination sphere, from four primary amines + two Cl$^-$, to two primary + two tertiary amines + two Cl$^-$, to two amines + four Cl$^-$. These changes are the source for the 25%, 35%, and 50% C$_2v$ perturbations necessary in order to fit the Furlani energy diagram to the observed spectra for these three complexes.

Complexes of spectral type B.—The complexes of this class are blue paramagnetic solids, and their spectra show signs of band splitting which is not apparent in the spectral types A and C. The contour of type B complexes is very similar to the reflectance spectrum of bis(o-phenylenediamine)nickel chloride, as reported by Maki (28); this complex has a strong in-plane field. Maki has interpreted this spectrum in terms of D$_{4h}$ six-coordinate tetragonal structure, and the transition energies she calculated have values of 8,600, 13,600, 15,000, 17,400, 27,900, and 32,500 cm$^{-1}$. These energies refer to the assignments $^3B_{2g} \rightarrow ^3E_g$, ($^3A_{2g} + ^3B_{2g}$), $^1A_{1g}$, $^3E_g$, $^3A_{2g}$, and $^3E_g$. The calculated values agree well with those observed (Table 19) for
type B complexes and indicate a tetragonal \textit{trans}-dichloro structure for this group.

The splitting observed in the type B and Ni(o-phenylenediamine)$_2$Cl$_2$ spectra is diagnostic for tetragonal nickel complexes. The basis for this has been described by Ballhausen and Jørgensen (108), and has been borne out experimentally. For example, the complex Ni(py)$_4$Cl$_2$ has transition energies of (9,500 and 11,000), 15,900 and 25,700 cm$^{-1}$; the first band is split (109). The structure of this complex is known to be \textit{trans}-dichloro from crystallographic x-ray studies (110). Recently, ethylthiourea has been shown to form cis- and \textit{trans}- isomers of formula Ni(etu)$_4$Cl$_2$, and the tetragonal \textit{trans}-complex was distinguished by its split absorption band (111).

Type B spectra may be further differentiated by their two highest energy absorption bands (Table 19). For complexes of the mono-alkyl substituted ligands (excepting N-isopropylen) these transitions occur at 27,450 ± 150 and 17,550 ± 50 cm$^{-1}$, whereas the di-substituted ligands (including N-isopropylen) have bands at lower energies; 26,550 ± 150 and 16,750 ± 250 cm$^{-1}$. The shift in band energies with ligand size is not gradual, as was true for the 1:1 NiCl$_2$ series, but rather an abrupt division is noted between ligands containing one compared with two alkyl substituents. This division seems to be quite independent of the specific alkyl substituent (except in the case for the isopropyl group), and is to be contrasted with the \textit{trans}-diaquobis and \textit{trans}-dipercioratobis Ni(ClO$_4$)$_2$ complexes (see p. 103) where it was found that all 4-N + 2-O complexes had identical spectral energies irrespective of the ligand substituents. Apparently the poorer donor
properties of Cl\textsuperscript{-} accent the changes in the ligands more than oxygen atom donors, which are closer to the amines in the spectrochemical series, and the trans-dichloro complexes show greater variation in their spectral energies.

Solution spectra in dichloromethane were determined for the N-methyl-N'-ethylen and N,N'-diethylen complexes, and these are illustrated in Figure 28; the reflectance spectra are shown in Figure 29 for comparison. Correlation of the solution and reflectance spectral measurements for these complexes is fairly good, but all bands in solution are shifted to lower energies. This is believed to be associated with a relaxation effect which occurs upon solution, and also has been noted for the [Ni(AA)\textsubscript{2}(H\textsubscript{2}O)](ClO\textsubscript{4})\textsubscript{2} and [Ni(AA)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2} complexes in aqueous solution with the N-ethylen ligand (see pp. 67).

In reflectance spectra of type B complexes (Figure 29), there appears to be three shoulders between the larger bands at 17,000 and 8,400 cm\textsuperscript{-1}. However, in the solution spectra (Figure 28) there are only two bands present in this interval. The greater definition of solution spectra requires that more emphasis should be placed on their results, although the number of these weak bands may be dependent on the state of the complex, and therefore be a crystal effect in the solid state.

In the energy calculation by Maki, a transition from \textsuperscript{3}B\textsubscript{2g} to \textsuperscript{3}E\textsubscript{g}(P) is predicted to occur at 32,500 cm\textsuperscript{-1}. The high energy limit for reflectance spectra was 320 m\textmu, and it was impossible to measure this band using reflectance techniques. However, solution spectra were reliable at this wave number, and bands were observed at 32,300
Figure 28 Absorption spectra of $\text{Ni(N-methyl-N'-ethylene)}_2\text{Cl}_2$ and $\text{Ni(N,N'-diethylene)}_2\text{Cl}_2$ in CH$_2$Cl$_2$ solution.
Figure 29 Reflectance spectra of Ni(N-methyl-\(N\)-ethylen)_2Cl_2 and Ni(N,N-diethylen)_2Cl_2.
and 32,500 cm\(^{-1}\) for the N-methyl-N'-ethylen and N,N'-diethylen compounds respectively (Figure 28). This substantiates the six-coordinate tetragonal D\(_{4h}\) structure assigned for these complexes.

**Complexes of spectral type C.**—The complexes Ni(N,N,N'-trimethylen)\(_2\)Cl\(_2\) and Ni(N,N-diethylen)\(_2\)Cl\(_2\) have reflectance spectra of similar contours which are illustrated in Figure 30. The absorption bands are more asymmetric than type A but are not split as in type B spectra. Both complexes are green in color, and the ligands contain tertiary amine groups. This is the first reported preparation for the 1:2 complex of N,N,N'-trimethylen. The N,N-diethylen compound was prepared by Goodgame and Venanzi (41), but the structure has not been determined.

The color of these complexes suggests some peculiarity, since all other 1:2 NiCl\(_2\) complexes are blue. The only other green Ni(II) complexes isolated in this study were the 1:1 NiCl\(_2\) series and the complex [Ni(N,N,N'-trimethylen)\(_2\)ClO\(_4\)]\(_2\). In each of these cases, nickel ion is surrounded by two nitrogen atoms and four weaker donor atoms.

The reflectance spectra of type C compounds is very similar to that of Ni(N,N'-diphenylethylenediamine)\(_2\)Cl\(_2\) as reported by Maki (28). This complex has a weak in-plane field, and her calculated band energies based upon such a six-coordinate tetragonal model occur at 4,800, 8,000, 10,200, 11,400, 12,300, 14,500, 20,200, and 24,200 cm\(^{-1}\). These energies refer to the transitions, \(3B_{2g} \rightarrow 3E_g\), \(3B_{1g}\), \(3A_{2g}\), \(1B_{2g}\), \(3E_g\), \(1A_{1g}\), \(1E_g\), and \(3A_{2g}\). The calculated energy values agree very well with the trimethylen
Figure 30. Reflectance spectra of:- Ni(N,N'-trimethylene)Cl₂ -...
complex, and are fairly good for the N,N-diethylen case as well (Table 20). These similarities imply a $D_{4h}$ tetragonal structure with a weak in-plane field for the type C complexes.

If the ligands in the type C compounds are coordinated in a bidentate fashion, a cis-dichloro structure is improbable due to lack of any similarity to the known cis-dichloro complexes (Type A) and their spectra. Furthermore, a trans-dichloro structure is unlikely because the known trans-dichloro complexes (Type B) and their spectra are also quite different. On the other hand, the ligands may be coordinated in a monodentate fashion (it is assumed that the tertiary amine end would be free). Then a six-coordinate structure could arise through the use of bridging chloride ions. A weak in-plane field tetragonal structure would be possible with trans-coordinated monodentate ligands and bridging chloride ions, in a manner exactly analogous with the structure of Ni(py)$_2$Cl$_2$.

The reported (93,101) spectrum of Ni(py)$_2$Cl$_2$ does not include any measured absorption bands below 10,000 cm$^{-1}$. If the two Type C complexes were in fact analogous in structure to the Ni(py)$_2$Cl$_2$ complex, their spectra should be very similar. Both Ni(N,N,N'-trimethylen)$_2$Cl$_2$ and Ni(N,N-diethylen)$_2$Cl$_2$ display a band with maximum at approximately 8,300 cm$^{-1}$ and a shoulder at 10,200 cm$^{-1}$, and the remaining bands have energy values comparable with Ni(py)$_2$Cl$_2$. The bis(pyridine) complex was prepared and the reflectance spectrum measured from 300 to 1700 m$\mu$, using Nujol mulls. Absorption band maxima (Figure 31) for solid Ni(py)$_2$Cl$_2$ were observed at 8,200, 8,800 (sh), 12,200 (sh), 13,900, 23,000 (sh), and 24,300 cm$^{-1}$; the
Figure 3. Reflectance spectra of Nipy₂Cl₂
two low energy bands are reported here for the first time. The
lowest energy transition is essentially the same for all three com-
plexes (8,300 cm⁻¹), but the values of the highest energy band
maximum are of the order N,N-diethylen > N,N,N'-trimethylen > py.
This order is expected because of the donor strength and class of the
amine in the complex changes from 1 to 2 to 3°.

There is evidence which suggests another structural possibility
for the type C complexes. When the type C complexes are heated to
110°C, Ni(N,N,N'-trimethylen)₂Cl₂ is completely converted to
Ni(N,N,N'-trimethylen)Cl₂ in five hours, and the N,N-diethylen complex
decomposes forming a brown residue. The formation of Ni(N,N,N'-tri-
methylen)Cl₂ by heating the 1:2 complex is confirmed by electronic
and infrared spectra, and by the measured stoichiometric weight changes
as well. When the Ni(en)₂Cl₂ (type A) and Ni(N,N'-diethylen)₂Cl₂(type B)
complexes were heated to 110°C for four days, no weight or color
changes were observed. This demonstrates that one ligand in Ni(N,N,N'-
trimethylen)₂Cl₂ is less stable than the other, and is also less stable
than the ligands in the A and B types of 1:2 complexes. It may be
possible that the ligand lost upon heating is coordinated in a mono-
dentate fashion similar to the trans-monodentate ligands in
[Ni(N-isopropylen)₄](ClO₄)₂ (see p. 106). This implies a structure for
the type C complexes that contains both a mono- and bidentate ligand
donating three nitrogen atoms to Ni(II), which together with three
Cl⁻ completely fill the first coordination sphere. Since two N,N,N'-
trimethylen ligands apparently cannot coordinate with NiCl₂ in a
bidentate fashion, the possibility arises that one monodentate ligand
also may be present in \([\text{Ni}(N,N,N'\text{-trimethylen})_2(\text{ClO}_4)_2]\) as well. However, heating this perchlorato complex to 110°C for 24 hours did not result in any loss of ligand, and therefore the ligands are assumed to be bound in a similar manner in this compound. The 1:2 \(N,N\text{-diethylen}\) complex cannot form a 1:1 derivative because of the interference of the diethyl groups with the bridging halides necessary for a 1:1 complex (see p. 124) and therefore it is plausible that this substance should be decomposed by the heating process.

The solution spectrum in dichloromethane for the \(N,N,N'\text{-trimethylen}\) complex is illustrated in Figure 32. The reflectance and solution spectra are identical, except for the characteristic lower resolution of reflectance measurements.

Several cases have been postulated in this study when only one end of a substituted ethylenediamine ligand is coordinated leaving the other end free; examples are \([\text{Ni}(N,N,N'\text{-trimethylen})_2(\text{ClO}_4)_2]\), \([\text{Ni}(N\text{-isopropyleten})_4](\text{ClO}_4)_2\), \(\text{Ni}(N,N,N'\text{-trimethylen})_2\text{Cl}_2\), and \(\text{Ni}(N,N\text{-diethylen})_2\text{Cl}_2\). The tetrakis(isopropyleten) complex is blue and contains six nitrogen donor atoms whereas the other three examples are green, contain 2-\(N + 4\)-weaker donor atoms, and have a free uncoordinated tertiary amine. The isopropyl group is a large entity and in the formation of complexes it certainly causes steric difficulties, but it is not as consistently out of line in the sequence of complexes investigated as are the ligands with tertiary amines. It is apparent that ligands with tertiary amine groups assume structures which avoid occupancy of trans-sites by other donor atoms or else act as monodentate ligands because: 1) a stable \([\text{Ni}(\text{AA})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\) complex
Figure 32 Absorption spectrum of $\text{Ni}(N,N',N''$-trimethylene)$_2\text{Cl}_2$ in $\text{CH}_2\text{Cl}_2$ solution.
is not formed by the \( N,N\)-dimethylen, \( N,N,N'\)-trimethylen, or \( N,N\)diethylen ligands, 2) \( N,N,N'\)-trimethylen forms a coordinated per-
chlorate complex but only at the expense of chelation, 3) \( N,N\)-dimethylen forms a \textit{cis}-dichloro \( \text{Ni(AA)}_2\text{Cl}_2 \) complex with \( \text{NiCl}_2 \) rather than a \textit{trans}-structure, 4) the \( \text{NiCl}_2 \) 1:2 complexes of \( N,N,N'\)-trimethylen and \( N,N\)-diethylen only coordinate the lesser substituted diamine end.

Thus, the enhanced inductive effect of a tertiary amine relative to the other classes is of no consequence in stabilizing transition metal ion complexes. The \( N,N\)-dimethylen ligand is particularly interesting for it seems to be the limiting case of steric inhibition due to a tertiary amine. It forms both a \([\text{Ni(AA)}_3](\text{ClO}_4)_2\) and \textit{cis}- \( \text{Ni(AA)}_2\text{Cl}_2 \) complex, whereas these structures are not possible with the other ligands containing tertiary amines.

D. Comments on \( N,N\)-diethylen and \( N,N\)-
dimethylen Nickel(II) Complexes
Prepared by Goodgame and Venanzi

The complexes \( \text{Ni(}N,N\text{-dimethylen})_2\text{Cl}_2 \) and \( \text{Ni(}N,N\text{-diethylen})_2\text{Cl}_2 \) also have been examined by Goodgame and Venanzi (40,41). They report reflectance spectra band maxima with energies of 9,710, 12,500, 16,000, 22,200 (sh), and 26,100 cm\(^{-1}\) for the \( N,N\)-dimethylen complex and 13,200 (sh), 15,040, 23,500 (sh), and 25,500 cm\(^{-1}\) for the \( N,N\)-diethylen complex. For the latter complex, their measurements did not extend above 1000 m\(\mu\), and band maxima at 10,200 and 8,400 cm\(^{-1}\) which have been observed in the present study are reported here. The shoulder they report at 22,200 cm\(^{-1}\) for the \( N,N\)-dimethylen complex, was ob-
served in the present study with the Beckman DU spectrophotometer but
not by the Cary Model 14. However, all other band energies agree very well in the two investigations.

They used a variety of nickel salt anions and formed several complex types with these two ligands. Their results and conclusions for the chloride and bromide ion complexes are of interest in light of the present study.

With the N,N-diethylen ligand, NiBr₂ forms an orange diamagnetic complex with a one band visible spectrum (21,500 cm⁻¹). However, with N,N-dimethylen, a green paramagnetic product is isolated with spectral band maxima energies of 11,950, 15,050, 19,600 (sh), 20,850 (sh), and 24,800 cm⁻¹. The N,N-diethylen compound is undoubtedly a square-planar bis(ligand) complex with nickel ion in a singlet ground state. The green N,N-dimethylen complex has a spectrum almost identical to that of Ni(N,N,N'-trimethylen)₂Cl₂ (Table 20), and is assumed to have the same type of structure, which differs considerably from a square-planar complex as obtained with N,N-diethylen and NiBr₂.

It is instructive to arrange the structures of Ni(AA)₂X₂ (X = halide) complexes of ethylenediamine, N,N-dimethylen, and N,N-diethylen in tabular form. These are listed in Table 21. The Ni(en)₂X₂ (X = Cl⁻, Br⁻) complexes are known to have cis-dihalo octahedral structures, and the other ligands form structures which seem to be dependent on the ligand and anion steric requirements. The table shows a consistent diagonal relationship between the structure of the complex and the halide ion it contains, with Cl⁻ one step behind Br⁻, and Br⁻ one step behind I⁻ so to speak. It is expected that a N,N-dialkylen ligand with substituents larger than the ethyl group would form a four-coordinate square-planar complex with NiCl₂.
## TABLE 21

Structures of Nickel Halide Complexes with Diamine Ligands

<table>
<thead>
<tr>
<th>Halide</th>
<th>ethylenediamine</th>
<th>N\textsubscript{2}N-dimethylen</th>
<th>N\textsubscript{2}N-diethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>cis-dichloro Oh</td>
<td>cis-dichloro Oh</td>
<td>Oh with monodentate coordinated ligand</td>
</tr>
<tr>
<td>Bromide</td>
<td>cis-dibromo Oh</td>
<td>Oh with monodentate coordinated ligand</td>
<td>square-planar</td>
</tr>
<tr>
<td>Iodide</td>
<td></td>
<td>square-planar</td>
<td>square-planar</td>
</tr>
</tbody>
</table>
Thus, in light of the present study, the magnetic differences between NiCl$_2$ and NiBr$_2$ complexes of N,N-diethylen which were noted by Goodgame and Venanzi, simply result from a variation in the volume requirements of bromide and chloride ions relative to the ligand N,N-diethylen. This leads to complexes with different structures as indicated in Table 21. The differences in magnetic moment of these NiCl$_2$ and NiBr$_2$ complexes do not require any violation of Cl$^-$ and Br$^-$ Dq values determined from hexaquo complexes, in which the above volume relationships would be nonexistent. Similarly, the magnetic differences between the N,N-diethylen and N,N-dimethylen complexes of NiBr$_2$ which Goodgame and Venanzi also comment upon, do not require that the Et$_2$N- group coordinate stronger than the Me$_2$N- group as they indicate may be possible, but simply result from the variation in steric requirements of these two ligands relative to bromide ion, which again leads to complexes with different structures. Thus, the complexes with NiCl$_2$ as isolated in the present investigation allow the structures of Goodgame and Venanzi's NiBr$_2$ complexes to be postulated. The postulated structures in Table 21 are consistent with the experimental data.

E. Summary

The tris(ligand) complexes which were isolated in this investigation, are all paramagnetic solids. Their electronic absorption spectra agree well with those of known octahedral nickel compounds, and this is the structure assumed for the tris(ligand) complexes. The first d-d transition ($^3A_2g \rightarrow ^3T_2g$) of the complexes, in the solids and in their respective ligands as solvents, shifts
systematically to lower energy values as the alkyl group on the ethylenediamine ligand becomes more complex. The resulting spectro-chemical series is: \( \text{en} > \text{N-methylen} > \text{N-ethylen} > \text{N-propylen} > \text{N,N'-dimethylen} > \text{N-methyl-N'-ethylen} > \text{N,N-dimethylen} \). The order of Dq for the ligands is a direct consequence of the alkyl substituent size, whereas the nephelauxetic series is of a different order. Thus, coordination interaction of the amine is determined primarily by the steric requirements of the ligand rather than inductive factors. The positions of band maxima of ligand solution spectra are slightly shifted to lower energies when compared with the reflectance data, but the effect is slight and may be associated with relaxation of the first coordination sphere in ligand solution which is not possible for the crystalline solid. Spectra of the compounds dissolved in water differ considerably from the solid or liquid solution results, and imply that species other than tris complexes are probably present in aqueous solutions.

The bis(ligand) perchlorate complexes prepared in this study are all diamagnetic solids. Their visible spectra consist of only one absorption band with maximum of \( 21,300 \pm 200 \text{ cm}^{-1} \), and are typical of known diamagnetic square-planar nickel complexes. In some cases, very weak absorptions were observed on the low energy side of the main absorption band, and these are attributable to spin-forbidden transitions. The narrow range of energies for the visible absorption band afford little opportunity for correlation of ligand donor properties with spectra in the bis(ligand) complexes. However, the ease of preparing \([\text{Ni(AA)}_2](\text{ClO}_4)_2\) complexes seems to be related directly to the volume
requirements of the N-alkyl substituent, since such compounds were not isolated with ethylenediamine or N-methylen, whereas no other product was ever obtained for the N,N-diethylen ligand.

After the heat treatment of bis and/or diaquobis complexes of Ni(ClO$_4$)$_2$ with the ligands N-methylen, N,N'-dimethylen, and N,N,N'-trimethylen, both [Ni(N-methylen)$_2$(ClO$_4$)$_2$] and [Ni(N,N'-dimethylen)$_2$(ClO$_4$)$_2$] exhibit properties for two trans-monodentate perchlorate ions and two bidentate ligands (2-0 + 4-N), but for the [Ni(N,N,N'-trimethylen)$_2$(ClO$_4$)$_2$] example the coordinated species are more likely to be two bidentate perchlorate ions and two trans-monodentate ligands (4-0 + 2-N). The visible spectra of the [Ni(N-methylen)$_2$(ClO$_4$)$_2$] and [Ni(N,N'-dimethylen)$_2$(ClO$_4$)$_2$] complexes have very similar contours and positions of band maxima, whereas the spectrum of [Ni(N,N,N'-trimethylen)$_2$(ClO$_4$)$_2$] is shifted to lower energies and shows evidence of greater band splitting. These differences in spectral character are in keeping with the proposed structures.

Attempts to prepare other perchlorato species by heating bis-(ligand) complexes in vacuo were not successful. Since the isolated examples contain only methyl-substituted ligands, this implies that the presence of methyl substituents is a prerequisite for ClO$_4^-$ complexation, for neither [Ni(N-ethylen)$_2$(ClO$_4$)$_2$] nor [Ni(N,N'-diethylen)$_2$(ClO$_4$)$_2$] forms perchlorato complexes. In particular, only monomethyl-substituted amines appear suitable in this regard, for the [Ni(N,N'-dimethylen)$_2$(ClO$_4$)$_2$] complex (containing tertiary dimethylamines) does not react in this manner and also the monomethyl-substituted
end of the $N,N,N'$-trimethylen ligand is coordinated in the 
$[Ni(N,N,N'-\text{trimethylen})_2(ClO_4)_2]$ example. Thus, a specific steric
factor appears to be of primary importance here, and suggests that
the perchlorate ion is "trapped" in a tailored coordination site.

Complexes of the type $[Ni(AA)_2(H_2O)_2](ClO_4)_2$ were prepared by
the direct addition of water to the bis(ligand) complexes. The
presence of coordinated water molecules is confirmed by three very
distinct and intense infrared absorptions for the complexes corres-
ponding to HOH stretching and deformation modes. The visible spectra
of the diaquobis(ligand) complexes are similar both in contour and
position of band maxima to the perchlorato complexes with a 4-$N + 2-O$
donor atom system, and are assumed to have a tetragonal structure as
well. The equivalent structures and spectra for these two groups of
tetragonal complexes demonstrate that spectral character is quite
independent of influences outside of the first coordination sphere,
because the presence or absence of, and size or position of the $N$-alkyl
substituents on the ligand do not alter the spectra to a significant
degree. The lack of spectral similarity when compared with the data
for $[Ni(N,N,N'-\text{trimethylen})_2(ClO_4)_2]$ is additional evidence for the
unique coordination in this single example. Upon storage, some of
the diaquobis complexes gradually release coordinated water and the
$[Ni(AA)_2](ClO_4)_2$ compound is regenerated.

Two types of paramagnetic complexes were prepared with nickel
chloride and the ligands. They have the general formulas $Ni(AA)Cl_2$
(1:1 series), and $Ni(AA)_2Cl_2$ (1:2 series). The spin-allowed band
maxima for $Ni(AA)Cl_2$ complexes with ligands containing only primary
or secondary amino groups are gradually shifted to lower energy values as the number and size of ligand substituents increase. However, 1:1 complexes with ligands containing tertiary amines show an asymmetry in their lowest energy visible absorption band which is not displayed by the other series members. Furthermore, a 1:1 complex with the N,N-diethylen ligand is not formed, but rather a compound corresponding to Ni(AA)$_2$Cl$_2$ is isolated. These peculiarities arise from perturbations on the potential trans-coordination sites by the N,N-dialkylamine substituent which interfere or prohibit (in the case of N,N-diethylen) the utilization of bridging chloride ions necessary for a coordination number of six. A possible polymerization scheme in crystals of 1:1 complexes involves the coupling of dimeric units in a ladder fashion. In such an arrangement all chloride ions will be bridging, and this produces a geometry about nickel ion which is rigorously C$_{2v}$.

The 1:2 series of compounds may be divided into three classes (A, B, and C) which are based upon their spectral character. Type A complexes include the examples Ni(en)$_2$Cl$_2$ and Ni(N,N-dimethylen)$_2$Cl$_2$ which are blue solids. The Ni(N,N-dimethylen)$_2$Cl$_2$ complex has a reflectance spectrum similar to that of Ni(en)$_2$Cl$_2$, but positions of band maxima are shifted to lower energy values. A C$_{2v}$ perturbation of 35% defines transition energies on a Furlani Oh-C$_{2v}$ energy diagram which are in substantial agreement with those observed for the complex. The lower energies for band maxima and greater distortion from Oh symmetry in Ni(N,N-dimethylen)$_2$Cl$_2$ are the result of the poorer coordinating ability of tertiary compared with primary amines. The infrared spectrum of Ni(N,N-dimethylen)$_2$Cl$_2$ also is comparable with
that of Ni(en)$_2$Cl$_2$, both in the N-H stretching and deformation frequencies as well as containing the split band analogous with \textit{cis}-[Co(en)$_2$Cl$_2$]$^+$. This information substantiates a \textit{cis}-dichloro structure for Ni(N,N-dimethylen)$_2$Cl$_2$ with tertiary amines in trans-positions.

Type B complexes are blue solids. Their spectra show signs of band splitting, and are similar in contour and energy to known tetragonal complexes of Ni(II) with a strong in-plane field. Then the structure postulated for type B compounds is a trans-dichloro tetragonal arrangement. Compounds in this class may be further differentiated by positions of band maxima for their two highest energy visible absorption bands. For complexes with mono-alkyl substituted ligands these transitions occur at a constant higher energy value than for the di-alkyl substituted ligands. This is quite independent of substituent chain length, and therefore the number of substituents is more important in this case than their steric requirements. Maki has calculated a transition to occur at 32,500 cm$^{-1}$ for this type of complex, and for the two cases where solution spectra in CH$_2$Cl$_2$ are possible, bands are observed with maxima at 32,300 and 32,500 cm$^{-1}$. This substantiates the six-coordinate tetragonal structure assigned to these complexes.

Type C complexes include the green solids Ni(N,N,N'-trimethylen)$_2$Cl$_2$ and Ni(N,N-diethylen)$_2$Cl$_2$; both ligands contain tertiary amino groups. The only previous examples in the present study of compounds with such a visible color are the Ni(AA)Cl$_2$ (1:1 series) complexes and [Ni(N,N,N'-trimethylen)$_2$(ClO$_4$)$_2$] both of which contain two nitrogen
and four weaker donor atoms. The reflectance spectra of type C complexes are similar in energy and contour with tetragonal Ni(II) complexes having a weak in-plane field, but different from the spectra obtained for type A and B complexes. Because of these differences in spectra and the presence of tertiary amino groups, the ligands in type C complexes are postulated as being coordinated in a trans-mono-dentate fashion via only the less substituted amino group. In order to account for the paramagnetism and pseudo octahedral spectra, bridging chloride ions must be employed. The structure would be exactly analogous to that of Nipy$_2$Cl$_2$, which is known to be a chain polymer with trans-pyridine molecules. The electronic absorption spectrum of Nipy$_2$Cl$_2$ has been only partially reported, and additional bands have been observed in the present study. The complete spectrum has analogous counterparts in the type C complexes, and on the basis of spectral analogy their structures are assumed to be similar, i.e., a trans-amine tetragonal arrangement with planar bridging chloride ions. The lowest energy transition is identical in all three complexes, but the energy of the highest band maxima shifts to lower values in the order, N,N-diethylen, N,N,N'-trimethylen, and py. This order is directly related to the class of the amine coordinated in trans-positions, from 1 to 2 to 3°, and is consistent with the proposed structures. When the type C complexes are heated to 110°C, the N,N,N'-trimethylen example is converted to its 1:1 derivative losing one mole of ligand per mole of complex, and the N,N-diethylen complex is decomposed. This suggests that both mono- and bidentate ligands may be present in the type C complexes and infers another possible structure that would contain 3-N + 3-Cl⁻ donor atoms in the first coordination sphere.
BIBLIOGRAPHY


31. J. Dalietos, Praktika, 2, 754 (1931).


100. B. J. Hathaway and D. G. Holah, ibid., 1964, 2400.