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THE CRYSTAL STRUCTURES OF
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AND TETRAMETHYLAMMONIUM TETRACHLORO-
NICKELATE(II).

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THE CRYSTAL STRUCTURES OF BIS(ETHYLENEDIAMINE)-
PALLADIUM(II) CHLORIDE AND TETRAMETHYL-
AMMONIUM TETRACHLORONICKELATE(II)

by

JOEL ROBERT WIESNER

A thesis submitted in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF WASHINGTON

1966

Approved by

(Chairmen of Supervisory Committee)

(Chemistry)

(Departmental Faculty Sponsoring Candidate)

Date

27 September 1966
UNIVERSITY OF WASHINGTON

Date: September 7, 1966

We have carefully read the dissertation entitled The Crystal Structures of Bis(ethylenediamine)palladium(II) Chloride and Tetramethylammonium Tetrachloronickelate(II) submitted by Joel Robert Wiesner in partial fulfillment of the requirements of the degree of Doctor of Philosophy and recommend its acceptance. In support of this recommendation we present the following joint statement of evaluation to be filed with the dissertation.

This dissertation reports the results of x-ray crystallographic investigation of the crystal structure of bis(ethylenediamine)palladium(II) chloride and of the isomorphous triad, tetramethylammonium tetrachlorocobaltate(II), tetrachloronickelate(II), and tetrachlorozincate(II).

Bis(ethylenediamine)palladium(II) chloride is the first ethylenediamine chelate of a metal ion of the second long period of the periodic system for which a structure determination has been carried out. The triclinic crystals contain discrete bis(ethylenediamine)palladium(II) ions and chloride ions, laced together by N-H···Cl hydrogen bonds.

The tetramethylammonium tetrachlorometallates exhibit some disorder in the orientation of the tetrahedral ions. The metal-halogen distances and distortion of the tetrahedra are discussed.

The work appears to have been carefully done and the discussion is well formulated. The dissertation makes a significant contribution to the field of coordination chemistry.

Dissertation Reading Committee:  

E. C. Lingafelter  

Lill Jensen  

M. Gregory
In presenting this thesis in partial fulfillment of the requirements for an advanced degree at the University of Washington I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature: Joel R. W. [Signature]

Date: 9/27/66
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Dr. Henry Montgomery spent much of his time initiating me to the experimental aspects of crystallography in the earlier stage of my career as a graduate student. I would like to thank him for this help. Thanks are also extended to my graduate student colleagues, Drs. Roger V. Chastain, Jr. and Robert L. Braun who contributed much to my advancement through valuable discussions.

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I would especially like to thank my wife, Helaine, for her continuing encouragement and faith in me.
To my wife,

HELAINE,

who, in a way, is responsible for this.
I. THE CRYSTAL STRUCTURE OF BIS(ETHYLENEDIAMINE) PALLADIUM(II) CHLORIDE

A. INTRODUCTION

For many years it was generally assumed that the ethylenediamine chelate ring existed in a planar conformation. Only in the past few years have a sufficient number of crystal structures of ethylenediamine chelates been determined to allow this assumption to be contradicted. All of these structures show the ethylenediamine residue to be in the gauche conformation. That is, one carbon atom is above the plane formed by the metal and the two nitrogen atoms and the other carbon atom is below this plane.

The conformational aspects of chelate rings have been reviewed by Gillard and Irving. It appears that conformational considerations will provide many areas of fruitful study in the future which could lead to insight into such properties as thermodynamic stability, kinetics of reactions, etc. Several crystal structures have been determined which were directed towards a study of the ethylenediamine chelate ring.

The only crystal structures of ethylenediamine metal complexes that have been determined are those containing first-row transition elements. It seemed of interest to determine the structure of an ethylenediamine complex with a second-row transition element and to
compare all of the known structures. Bis(ethylenediamine)palladium (II) chloride was chosen for this purpose.
B. DETERMINATION OF THE CRYSTAL STRUCTURE

Some previous work on the space group and cell dimensions has been carried out. Cox and Preston\textsuperscript{10} report that Pd(en)$_2$Cl$_2$ is isomorphous with Pt(en)$_2$Cl$_2$ and has almost identical cell dimensions. They report Pt(en)$_2$Cl$_2$ as crystallizing in space group \textit{P}\textbar{T} and having lattice parameters as follows:

\begin{align*}
a &= 8.37 \text{ Å} \\
b &= 4.95 \\
c &= 6.86
\end{align*}

\begin{align*}
\alpha &= 100^\circ46' \\
\beta &= 111^\circ40' \\
\gamma &= 81^\circ56'
\end{align*}

or, in the standardized form recommended by Donnay,\textsuperscript{12}

\begin{align*}
a &= 6.86 \text{ Å} \\
b &= 8.37 \\
c &= 4.95
\end{align*}

\begin{align*}
\alpha &= 98^\circ4' \\
\beta &= 100^\circ46' \\
\gamma &= 68^\circ20'
\end{align*}

Watt and Klett\textsuperscript{54} have also reported the space group and cell dimensions for Pt(en)$_2$Cl$_2$ which in the form recommended by Donnay\textsuperscript{12} are

\begin{align*}
a &= 6.881 \text{ Å} \\
b &= 8.339 \\
c &= 4.937
\end{align*}

\begin{align*}
\alpha &= 98^\circ0' \\
\beta &= 100^\circ4' \\
\gamma &= 108^\circ22'
\end{align*}

with space group \textit{P}\textbar{T} or \textit{P}1 (morphology suggests \textit{P}\textbar{T}), and $Z = 1$.

These two sets of cell dimensions agree in all respects except for the angle gamma. We have been unable to find the reason for this disagreement. However, as explained below, it appears that those given by Watt and Klett\textsuperscript{54} are correct.

For the present investigation, bis(ethylenediamine)palladium(II) chloride was prepared\textsuperscript{28} by the reaction of $K_2\text{PdCl}_4$ with excess
ethylene diamine. Evaporation of an aqueous solution at room temperature yielded colorless prismatic crystals which were used for the structure determination.

Oscillation and equi-inclination Weissenberg photographs taken with \( c \) as the rotation axis show the crystal to be triclinic. Thus, the space group is either \( \text{P}1 \) or \( \text{P}1 \). The latter was assumed to be the correct space group and was verified by the structure determination.

Accurate lattice parameters were determined at room temperature, using \( \text{CuK}_\alpha \) radiation (\( \lambda = 1.54178 \) A), from the best least squares fit to single-crystal measurements of thirty 2\( \theta \) values taken on a Picker diffractometer fitted with a General Electric Goniostat:

\[
\begin{align*}
a &= 6.8607(4) \text{ Å} \\
b &= 8.3610(8) \\
c &= 4.9940(3)
\end{align*}
\]

\[
\begin{align*}
\alpha &= 97.716(6)^\circ \\
\beta &= 100.683(5) \\
\gamma &= 108.571(6)
\end{align*}
\]

The errors indicated are the estimated standard deviations as obtained from the least squares refinement, and as such, measure the precision of the determination, but not necessarily the accuracy. These values are in good agreement with those given by Watt and Klett for \( \text{Pt(en)}_2\text{Cl}_2 \). Thus, it appears that \( \text{Pd(en)}_2\text{Cl}_2 \) and \( \text{Pt(en)}_2\text{Cl}_2 \) are isomorphous as reported by Cox and Preston, but that the correct cell parameters for \( \text{Pt(en)}_2\text{Cl}_2 \) are as given by Watt and Klett. It was assumed for purposes of this structure determination that there is one molecule per cell as reported by Cox and Preston. This assumption was subsequently confirmed by the successful structure determination.
The x-ray intensity data were recorded on multiple films (Ilford Industrial G X-ray Film) on a Nonius integrating Weissenberg camera with CuKα radiation. The photographs were integrated in one direction only (perpendicular to the rotation axis); the unidirectionally-integrated diffraction spots were then scanned normal to the direction of camera integration using a Moll-type densitometer feeding into a Leeds and Northrup amplifier and recorder with a logarithmic slide wire. The tracings thus obtained were planimetered and the area under each peak taken as the relative intensity. Only those spots appearing within the linear response range of the film were measured. One film pack (consisting of four films) was used for each level. The four films per level were scaled together by comparison of spots appearing on two adjacent films. All interfilm scaling ratios for a film pack were averaged together to obtain a single interfilm ratio for each film pack. Usually from twenty to forty ratios were used to obtain this average ratio. The average interfilm ratio increased from 2.69 for the zero level to 4.76 for the fourth level. A range of intensities of 1 to 1200 was obtained.

Of the 1190 unique reflections theoretically obtainable in the Cu sphere, 1022 were recorded, 52 of which were classified as unobserved reflections and assigned an intensity equal to the minimum observable intensity for the particular level on which the reflection should have appeared.
Data were collected for levels hk0 through hk4. Intensities from different levels were placed on a common scale by use of an h0l Weissenberg photograph taken in the same manner as described above. Some additional reflections on this photograph which were not obtained in the hk0 through hk4 data were included in the final data set. Lorentz and polarization factors were applied, but no correction was made for absorption or dispersion. The linear absorption coefficient for Cu radiation is 191 cm$^{-1}$ and the crystal size was 0.098 mm x 0.073 mm x 0.24 mm. It has been shown$^{49}$ for this compound that the failure to make absorption corrections causes no "statistically significant" change in the atomic positions of the final structure, although the temperature factors are affected markedly.

Throughout this structure determination, structure factors were calculated using the scattering factors for neutral atoms as given in the International Tables for X-Ray Crystallography$^{23}$ for Pd, Cl, N, and C. Those for H were obtained from McWeeny.$^{33}$ Isotropic temperature factors were used in the form

$$\exp[-(B\sin^2\theta)/\lambda^2]$$

and anisotropic temperature factors in the form

$$\exp[-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} h_{i} a_{i}^{*} B_{ij}].$$

The discrepancy factor $R = \langle \Sigma |F_o| - |F_c| \rangle / \Sigma |F_o|$, where the summation is over the unique observed reflections only.
Assuming the space-group \( \text{P}1 \) with one molecule in the cell, the Pd atom may be placed at the origin. An initial structure factor calculation with Pd at 0, 0, 0 gave an \( R \) of 0.314. A three-dimensional Fourier synthesis phased on this structure factor calculation gave the coordinates of all atoms except the hydrogen atoms. Structure factors with these coordinates gave an \( R \) of 0.165. After three cycles of positional refinement by successive electron density calculations in which an overall isotropic temperature factor of \( B = 1.95 \, \text{Å}^2 \) was used, \( R \) was reduced to 0.119. Three cycles of full matrix least squares refinement of the positions and individual isotropic temperature factors of all atoms, except of course the position of the Pd atom, which is fixed by symmetry, resulted in an \( R \) of 0.088.

All least squares refinements were carried out using the program ORFLS\(^8\) as modified by J. M. Stewart for inclusion in the Crystal Structures Calculations System.\(^11\) The function minimized was \( \Sigma w (|F_o| - |F_c|)^2 \). A modified Hughes\(^21\) weighting scheme was used with \( \sqrt{w} = 0 \) for unobserved reflections satisfying \( |F_c| \leq F_o \); \( \sqrt{w} = 1 \) for unobserved reflections with \( |F_c| > F_o \) and for observed reflections with \( F_o \leq 32 \); and \( \sqrt{w} = 32/F_o \) for observed reflections with \( F_o > 32 \).

Hydrogen atoms were then introduced in their calculated positions (C-H distance assumed to be 1.05 Å, N-H distance assumed to be 0.95 Å) reducing \( R \) to 0.085. Each hydrogen atom was given an
isotropic temperature factor equal to that of the atom to which it was attached.

At this point it was decided to use a weighting scheme for the final least squares refinement which would be determined from an examination of the differences between observed and calculated structure factors as a function of the observed structure factor. The observed reflections were grouped in intervals of 2 units in $F_0^1$, the average $|F_0^1 - |F_C^1| \equiv |\Delta F|$ of each group was plotted against the average $F_0^1$ of that group. This graph is shown in Figure 1. The scatter of the points at high values of $F_0^1$ is caused by the small number of reflections in those groups (less than 10 per group in most cases). The sloping portion of the curve can be described by the equation $|\Delta F| = 0.0905 F_0^1 - 0.42$. The following assignment of weights were made: for unobserved reflections with $|F_C| \leq F_0^1$, $\sqrt{w} = 0$; for unobserved reflections with $|F_C| > F_0^1$, $\sqrt{w} = 1$; for observed reflections with $F_0^1 \leq 18$, $\sqrt{w} = 1$; for observed reflections with $F_0^1 > 18$, $\sqrt{w} = 1/|\Delta F|$, $|\Delta F|$ being determined from the above equation. Four cycles of full-matrix least-squares refinement varying atomic positions and anisotropic temperature factors of the non-hydrogen atoms and including the hydrogen atoms in their calculated positions, but not refining them, reduced $R$ to 0.062. After this, two cycles of least squares were run, varying only the individual level scale factors, which up to this point had been held constant at their experimentally
Figure 1. Variation of $|\Delta F|$ with $F_o$ used to determine least squares weighting.
determined values. This reduced $R$ to 0.060. Then two final cycles of least squares varying atom positions and anisotropic temperature factors of the non-hydrogen atoms gave an $R$ of 0.059. For the last least squares cycle the maximum ratio of shift to error was 0.33 and the average ratio of shift to error was 0.05. Final atomic coordinates, temperature factor parameters, and estimated standard deviations for the non-hydrogen atoms are given in Table 1.

After the final stage of least squares refinement a difference synthesis was calculated, using only the observed reflections with $(\sin \theta)/\lambda$ less than 0.48, for the purpose of locating the hydrogen positions. The $R$ value for the structure factors calculated excluding the hydrogen atoms was 0.067. In this difference synthesis there were thirteen peaks above $0.4 \text{ e}^-/\text{A}^3$. Eight of these (ranging in height from $0.61 \text{ e}^-/\text{A}^3$ to $1.09 \text{ e}^-/\text{A}^3$) were located very close to the calculated hydrogen positions, and the remaining five (ranging in height from $0.55 \text{ e}^-/\text{A}^3$ to $0.89 \text{ e}^-/\text{A}^3$) were too distant from any atom to be considered bonded to it and were, therefore, removed from further consideration. The smallest distance of any of these latter peaks to an atom was 1.53 A to N(1). Table 2 contains the hydrogen positions as obtained from this difference map along with their isotropic temperature parameters. The parameters for non-hydrogen atoms as given in Table 1 and the parameters for hydrogen atoms as given in Table 2 were used to calculate the final set of structure factors given in Table 3.
The $R$ index of 0.059 for this structure factor calculation is the same as that obtained when the calculated hydrogen positions are used.
Table 1. Final Parameters for Non-Hydrogen Atoms as Obtained from the Least Squares Refinement. Positions are multiplied by $10^4$, temperature parameters are multiplied by $10^2$. Estimated Standard Deviations are given in parentheses.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>$B_{11}$</th>
<th>$B_{22}$</th>
<th>$B_{33}$</th>
<th>$B_{12}$</th>
<th>$B_{13}$</th>
<th>$B_{23}$</th>
</tr>
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<tbody>
<tr>
<td>Pd</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>184(2)</td>
<td>182(2)</td>
<td>189(3)</td>
<td>84(2)</td>
<td>48(2)</td>
<td>18(2)</td>
</tr>
<tr>
<td>Cl</td>
<td>-3201(3)</td>
<td>2594(3)</td>
<td>4212(4)</td>
<td>320(8)</td>
<td>416(9)</td>
<td>209(7)</td>
<td>192(7)</td>
<td>82(7)</td>
<td>29(7)</td>
</tr>
<tr>
<td>N(1)</td>
<td>269(11)</td>
<td>-2336(8)</td>
<td>157(15)</td>
<td>328(28)</td>
<td>221(23)</td>
<td>237(30)</td>
<td>124(21)</td>
<td>146(23)</td>
<td>89(20)</td>
</tr>
<tr>
<td>N(2)</td>
<td>-2763(11)</td>
<td>-1060(9)</td>
<td>1146(16)</td>
<td>247(26)</td>
<td>260(26)</td>
<td>288(34)</td>
<td>74(21)</td>
<td>112(22)</td>
<td>31(22)</td>
</tr>
<tr>
<td>C(1)</td>
<td>-1770(15)</td>
<td>-3570(10)</td>
<td>288(22)</td>
<td>375(38)</td>
<td>204(29)</td>
<td>430(49)</td>
<td>70(27)</td>
<td>163(33)</td>
<td>105(28)</td>
</tr>
<tr>
<td>C(2)</td>
<td>-2697(15)</td>
<td>-2619(11)</td>
<td>2213(21)</td>
<td>341(36)</td>
<td>277(32)</td>
<td>368(46)</td>
<td>87(27)</td>
<td>179(31)</td>
<td>129(29)</td>
</tr>
</tbody>
</table>
Table 2. Final Parameters of the Hydrogen Atoms. Positions are multiplied by $10^4$. Temperature parameters are multiplied by $10^2$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a$^+$</th>
<th>y/b$^+$</th>
<th>z/c$^+$</th>
<th>B*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>883</td>
<td>-2595</td>
<td>-1058</td>
<td>272</td>
</tr>
<tr>
<td>H(2)</td>
<td>1417</td>
<td>-2000</td>
<td>1654</td>
<td>272</td>
</tr>
<tr>
<td>H(3)</td>
<td>-2806</td>
<td>-4022</td>
<td>-1667</td>
<td>342</td>
</tr>
<tr>
<td>H(4)</td>
<td>-1717</td>
<td>-4786</td>
<td>577</td>
<td>342</td>
</tr>
<tr>
<td>H(5)</td>
<td>-4150</td>
<td>-3476</td>
<td>2577</td>
<td>325</td>
</tr>
<tr>
<td>H(6)</td>
<td>-1533</td>
<td>-2131</td>
<td>4115</td>
<td>325</td>
</tr>
<tr>
<td>H(7)</td>
<td>-4000</td>
<td>-1500</td>
<td>-539</td>
<td>272</td>
</tr>
<tr>
<td>H(8)</td>
<td>-2733</td>
<td>-119</td>
<td>2692</td>
<td>272</td>
</tr>
</tbody>
</table>

$^+$ Determined from a final difference Fourier.

* Set equal to temperature factor of heavy atom at end of isotropic refinement.
Table 3. Observed and calculated structure factors for bis(ethylenediamine)palladium(II) chloride. Columns are k index, \(10 F_o\), and \(10 F_c\). Unobserved reflections are marked by \(*\).
C. DESCRIPTION AND DISCUSSION

The shortest Pd-Cl distance in the structure is 4.180 ± 0.002 Å. This is much longer than the shortest non-bonding Pd-Cl distance of 3.85 Å between chains in the crystal structure of PdCl₂. Therefore, it appears that there is no bonding between palladium and chlorine and it seems proper to describe the crystal structure of Pd(en)₂Cl₂ as consisting of discrete \([\text{Pd(en)}₂]^{2+}\) and Cl⁻ ions.

An orthogonal projection of the \([\text{Pd(en)}₂]^{2+}\) ion onto a plane parallel to the coordination plane is shown in Figure 2. The molecular symmetry required by the space group is \(\overline{1}\). Accordingly, the ligand nitrogen atoms are arranged about the palladium atom in a planar configuration. The carbon atoms of the ethylenediamine are in the "gauche" conformation as has been found in all structures of ethylenediamine complexes so far reported.¹⁷ The atom C(1) lies 0.33 Å above the N(1)-Pd-N(2) plane while atom C(2) is 0.39 Å below this plane. These distances are not considered to be significantly different. The N(1)-Pd-N(2) plane makes an angle of 28.3° with the C(1)-Pd-C(2) plane.

It has been pointed out by Corey and Bailar⁹ that a consequence of the fact that the ethylenediamine ring occurs in the "gauche" conformation is that it can exist in two enantiomeric forms, designated \(k\) and \(k'\) by them. Because of the required centrosymmetry of
Figure 2. Orthogonal projection of the \([\text{Pd(en)}_2]^{2+}\) ion onto the Pd-N(1)-N(2) plane.
Pd(en)$_2$Cl$_2'$ it must exist in the $kk'$ form, which has been found for all reported structures of bis(ethylenediamine) complexes.\textsuperscript{17}

The interatomic distances and angles are given in Table 4. The standard deviations given were calculated using the program ORFFE\textsuperscript{7} as modified for inclusion in the Crystal Structures Calculations System\textsuperscript{11} and therefore include the effects of correlation. Table 5 contains interatomic distances and angles of interest in all of the reported structures of ethylenediamine chelates known to the author.

In a recent study of metal chelates of acetylacetone, Lingafelter and Braun\textsuperscript{30} found the O-C and C-C bond distances and the O-C-O and C-C-C bond angles to be rather constant in the several compounds they surveyed. However, the M-O and O-O (bite) distances and the O-M-O and M-O-C angles varied significantly. It would seem reasonable to look for similar effects among the ethylenediamine chelates. It is known that two-dimensional structure determinations are often rather unreliable. Unfortunately, there are very few three-dimensional structure determinations of ethylenediamine chelates and quite a number of two-dimensional structure determinations. This precludes a detailed study like Lingafelter and Braun's, but, it is possible to speculate on a few trends; see Table 5. The averages and ranges given in this table do not include the values for [Hg(SCN)$_4$][Cu(en)$_2$] since this structure is very inaccurate.
Table 4. Interatomic Distances and Angles. Standard deviations in the least significant digits are shown in parentheses.

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N(2)' is related to N(2) by inversion through the center of symmetry.
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(1) The N-C and C-C bond distances and the N-M-N and M-N-C angles appear to be constant to within reasonable estimated errors. For the angles, this is in contrast with the acetylacetone structures where the O-M-O angle varies significantly over a range of 22.82° and the M-O-C angles varies over a range of 12.25°. (2) The N-C-C angle varies considerably, even among the three-dimensional structures, in contrast to the corresponding angle in the acetylacetone structures. This may be due to the fact that the N-C-C-N portion of the chelate ring can rotate around the N-N line and thus affect this angle; or it may be entirely due to experimental error.

(3) The variation of the M-N distance is to be expected, not only as a function of the metal atom, but also as a function of the configuration polyhedra (e.g., compare the planar [Ni(en)$_2$]AgBr$_2$ with the octahedral K[Ni(en)$_3$][SeCN]$_3$). This effect has been observed by many authors. (4) The N-N distances vary over about the same range as the O-O distances in the acetylacetone complexes (0.248 Å); the average deviation from the mean is 0.04 Å in both cases. It is also interesting to note that the average N-N distance (2.76 Å) is close to the average O-O distance (2.78 Å). Many more crystal structures will have to be accurately determined before any definitive statement concerning the cause of this variation can be made. In particular, if an isomorphous series of complexes could be found in which only the metal atom differs, then any variation due to crystal packing forces
could be eliminated and all differences could then be ascribed to the metal atom only.

The Pd-N distances of 2.030 ± 0.006 Å and 2.043 ± 0.007 Å are in good agreement with the Pd-N distances of 2.031 ± 0.002 Å in bis(N-isopropyl-3-ethylsalicylaldiminato)palladium(II), 2 2.022 ± 0.007 Å in bis(2,2'-dipyridyliminato)palladium(II), 15 2.032 ± 0.003 Å in the tetragonal form of bis(N-isopropyl-3-methylsalicylaldiminato)-palladium(II), 24 and 2.019 ± 0.008 Å in the monoclinic form of the latter compound. 24

The chloride ions are surrounded by four hydrogen atoms at distances of 2.44 Å, 2.43 Å, 2.40 Å, and 2.24 Å, as shown for Cl(I) in Figure 3. (Note that the hydrogen-atom parameters are not very accurate and are used only to establish a hydrogen-bonding scheme; they were determined from only one difference synthesis and were not refined.) These H...Cl distances are all significantly smaller than the sum of the van der Waals radii of chlorine and hydrogen (1.8 Å + 1.2 Å = 3.0 Å) as given by Pauling. 46 The distances from the chloride ion to the nitrogen atoms to which these hydrogen atoms are attached are shown around Cl(II) in Figure 3. Pimentel and McClellan 47 list N...Cl hydrogen-bonded distances ranging from 2.91 Å to 3.41 Å. These distances in the present structure fall quite nicely within this range. Table 6 gives the distances of the hydrogen atoms from the lines joining the chloride ion and the nitrogen atoms.
Figure 3. Orthogonal projection of structure onto (010). The hydrogen atoms around Cl(I) are depicted schematically only.
Table 6. Pertinent Data Involved in the Hydrogen Bonding Scheme. 
The lettering refers to the atoms surrounding Cl(III) in Figure 3.

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<th>atoms defining line</th>
<th>distance of hydrogen from the line</th>
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<td>N(2)' - Cl(III)</td>
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<td>N(II) - Cl(III)</td>
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</table>

Distances of the Hydrogen Atoms from the Line Joining the Chloride Ion and the Nitrogen Atoms.

Angles Involved in the Hydrogen Bonding Geometry

\[
\begin{align*}
\angle N(1) - Cl(III) - N(2)' & = 54.6^\circ \\
\angle N(1) - Cl(III) - N(I) & = 100.9 \\
\angle N(2)' - Cl(III) - N(I) & = 87.6 \\
\angle N(I) - Cl(III) - N(II) & = 153.4 \\
\angle N(2)' - Cl(III) - N(II) & = 76.1 \\
\angle N(1) - Cl(III) - N(II) & = 86.8
\end{align*}
\]
The positions of the hydrogen atoms thus suggest hydrogen bonding between the chloride ions and the nitrogen atoms. Some pertinent angles concerning the geometry of the nitrogen atoms surrounding the chloride ion are also given in Table 6.

The \( [\text{Pd(en)}_2]^{2+} \) and \( \text{Cl}^- \) ions are bound together in sheets parallel to (010) by a network of these hydrogen bonds. These sheets have only van der Waals forces binding them together in the crystal. The closest approach distances between the sheets are 3.949 Å and 3.933 Å between carbon atoms on adjacent molecules and 3.867 Å between a carbon atom and a nitrogen atom on adjacent molecules. Taking the van der Waals radius of a methylene group as 2.0 Å\(^4\) the carbon-carbon approach distances seem quite reasonable. The orthogonal projection of one of these sheets onto (010) is shown in Figure 3. This layered structure gives rise to the cleavage plane parallel to (010) which has been observed.

In connection with the hydrogen bonds it may be of interest to note that Willett has reported a short \( \text{Cl}-\text{NH}_2 \) distance of 3.23 Å in the crystal structure of \( (\text{CH}_3)_2\text{NH}_2\text{CuCl}_3 \).\(^5\)\(^6\) He has not determined hydrogen positions and does not attribute this short distance to hydrogen bonding. However, if hydrogen bonding were taking place this would explain an unusual feature of the structure. Because of the layered structure of this compound there should be a cleavage plane perpendicular to the \( c \) axis, but this is not observed experimentally.
However, the short Cl-NH$_2$ distance is in such a direction that, if hydrogen bonding were present, these layers would be bound together, thus explaining the absence of the cleavage plane.
II. THE CRYSTAL STRUCTURE OF TETRAMETHYLAMMONIUM TETRACHLORONICKELATE(II)

A. INTRODUCTION

For many years the question of tetrahedral coordination of nickel(II) was vigorously debated. Only within the past ten years has sufficient evidence been accumulated to show that tetrahedral complexes of nickel(II) do exist. If a compound had a stoichiometry which suggested four-coordination and if it were paramagnetic, it was usually assumed to be tetrahedral. However, it has become clear that this criterion must be used with extreme caution. For example, even though the green compound bis(salicylaldehydato)nickel(II) was known to be a dihydrate, it was assumed to be tetrahedral on the basis of its paramagnetism. A crystal structure determination showed it to be six-coordinated and octahedral. Also, compounds that are expected to be tetrahedral on this basis can sometimes actually be polymerized six-coordinated species; e.g., bis(acetylacetonato)nickel(II).

For this reason it is very desirable to have x-ray crystal structure determinations of these compounds. However, very few of these have been reported.

The first x-ray structure determination of a tetrahedral nickel(II) complex was that of dichlorobis(triphenylphosphine)nickel(II). In 1958 Venanzi reported that x-ray diffraction data showed the
compound to be definitely tetrahedral; however, it was not until 1963 that a full report of these data appeared. This determination was only accurate enough to establish the tetrahedral nature of the compound and did not provide accurate lengths and angles. A preliminary report of the crystal structure of the green form of bis(benzylidiphenylphosphine)dibromonickel(II) has appeared. The cell contains three molecules; two are tetrahedral, one is planar. Two recently determined structures of N-substituted-salicylaldimine nickel(II) chelates have a tetrahedral configuration about the nickel.

Simple crystal field theory predicts that the ground electronic state of a tetrahedral nickel(II) complex is degenerate, and therefore subject to Jahn-Teller distortion. It was felt by most chemists for many years that tetrahedral nickel(II) complexes should show some distortion on this basis. Work by Liehr and Ballhausen indicates, however, that spin-orbit forces will remove the degeneracy and leave a ground state which is not subject to Jahn-Teller distortion. In order to test this theory a crystal structure of a nickel(II) ion surrounded tetrahedrally by four identical ligands would have to be determined. Furthermore, to be certain that crystal packing forces did not cause an observed distortion, crystal structures of isomorphous compounds which are not subject to a Jahn-Teller-caused distortion should be available for comparison.
Work by Gruen and McBeth\textsuperscript{19} showed quite conclusively that the tetrahedral $[\text{NiCl}_4]^{2-}$ ion exists in melts of nickel chloride dissolved in fused pyridinium chloride, lithium chloride, cesium chloride, and cesium tetrachlorozincate. Furthermore, the crystal structure of tetramethylammonium tetrachlorozincate(II) has been solved by Morosin and Lingafelter\textsuperscript{36} and was being further refined. The crystal structure of the isomorphous cobalt(II) analog was also being determined in this laboratory. Since Gruen and McBeth's work indicated a possibility of being able to prepare the compound, it therefore seemed desirable to attempt the determination of the crystal structure of tetramethylammonium tetrachloronickelate(II). The nickel(II) ion would be surrounded by four identical ligands, eliminating any distortion due to asymmetric ligand fields, and if it were isomorphous with the cobalt and zinc analogs these compounds would provide valuable comparisons.
B. DETERMINATION OF THE CRYSTAL STRUCTURES OF TETRAMETHYLAMMONIUM TETRACHLOROCOBALTATE(II), NICKELATE(II), AND ZINCATE(II)

Much of the work presented on the following pages was performed in collaboration with other investigators. The crystal structure of the cobalt isomorph was determined by Dr. Colin H. L. Kennard and that of the zinc isomorph was redetermined by Dr. Ramesh C. Srivastava. Only the final cycles of refinement on these compounds were carried out by the author in order to achieve a uniformity in weighting schemes, scattering factors, etc. throughout this series.

The results of these studies are presented here, along with the crystal structure determination of the nickel isomorph (which was performed by the author), because each crystal structure is dependent on the others for proper interpretation. This will be made clear in the discussion of these structures.

All least squares refinements referred to in this section were performed using the program ORFLS as modified for inclusion in the Crystal Structures Calculations System, X-Ray 63.

1. Tetramethylammonium Tetrachlorozincate(II)

The crystal structure of tetramethylammonium tetrachlorozincate had previously been determined from three dimensional film data by Morosin and Lingafelter. They had refined the structure to
a final reliability index \( \frac{\sum |F_o - F_c|}{\sum |F_o|} \) of 0.155 by a series of difference syntheses.

An attempt was made to refine the structure further, using the least squares method, but the temperature factors of the carbon and chlorine atoms became quite large, reaching values of \( B = 15.5 \text{ Å}^2 \) for some of the carbon atoms and \( B = 8.5 \text{ Å}^2 \) in the case of the chlorine atoms.

This behavior is typical of refinement attempts in which some systematic errors have been encountered in the collection of the data. It was therefore decided that it would be worthwhile to collect another set of data as accurately as possible on a single-crystal x-ray diffractometer which had recently become available.

Crystals of the compound were prepared according to the method described by Morosin and Lingafelter. \(^{36}\) Preliminary Weissenberg and oscillation photographs confirmed the possible space groups to be \( Pnma \) or \( Pn2_1a \) as reported by Morosin and Lingafelter. \(^{36}\) Accurate cell parameters were determined as described for bis(ethylenediamine)palladium(II) chloride from 2θ measurements of 14 reflections using MoK\(\alpha\) radiation (\(\lambda = 0.71068 \text{ Å}\)). The results are (with the estimated standard deviations as obtained from the least squares refinement in parentheses):

\[
\begin{align*}
a &= 12.276(2) \text{ Å} \\
b &= 8.998(2) \\
c &= 15.541(2)
\end{align*}
\]
These are in agreement with the values given by Morosin and Lingafelter:

\[
\begin{align*}
a &= 12.268(7) \text{ Å} \\
b &= 8.964(7) \\
c &= 15.515(12)
\end{align*}
\]

The crystal chosen for data collection was a prism approximately 0.31 mm x 0.26 mm x 0.28 mm in size. It was mounted with the \(c\) axis parallel to the \(\phi\) axis of the diffractometer. Intensity data were collected with MoK\(\alpha\) radiation on a Picker diffractometer fitted with a General Electric single-crystal orien ter by the \(\omega-2\theta\) scan method (moving crystal-moving counter). A background count at the beginning of the scan (B1) was taken with the crystal and counter stationary for one half the total scan time. Then, the scan was made (S) and another background count (B2) was taken at the end of the scan. The intensity of each reflection was calculated as: 

\[I = S - B1 - B2,\]

and the standard deviation of this intensity was calculated as:

\[\sigma_I = \frac{1}{(S + B1 + B2)^2}.\]

Reflections were examined in shells of 2\(\theta\) to a maximum of 47\(^\circ\) at which point the intensities were falling off so rapidly that it was deemed not worthwhile to collect data at any higher 2\(\theta\) values. Of the 1283 reflections examined, 433 had \(I < 2.7\sigma_I\) and were coded as unobserved reflections. The factor of 2.7\(\sigma_I\) was chosen so that all of the reflections coded as observed would have intensities significantly different from the background at greater than the 99% confidence level. Lorentz and polarization factors were
applied and the intensities were converted to relative structure factors. No absorption or dispersion corrections were made.

Hereafter, the data taken by Morosin and Lingafelter\textsuperscript{36} will be referred to as the film data and the data just described will be referred to as the diffractometer data.

Since problems with temperature factors were encountered in the attempted least squares refinement with the film data in the centric space group (Pnma), it was considered a distinct possibility that the correct space group might be the acentric one (Pn2\textsubscript{1}a). The essential difference between these two space groups is that, with four molecules in the cell, Pnma requires the [NiCl\textsubscript{4}]\textsuperscript{2-} and N(CH\textsubscript{3})\textsubscript{4}\textsuperscript{+} tetrahedra to lie on mirror planes parallel to (010) and at $\nu=\frac{1}{4}$, while, in Pn2\textsubscript{1}a these mirror planes are no longer present and the restriction that the tetrahedra lie on them is, of course, removed.

If calculations were made assuming the absence of the mirror planes, and they actually were present, the structure should still exhibit this symmetry. Therefore, initial calculations were made with the diffractometer data assuming space group Pn2\textsubscript{1}a.

The zinc and four chlorine positions were determined from a three-dimensional Patterson synthesis. The $R$ index for a structure factor calculation with these positions was 0.27. Three cycles of full matrix least squares refinement of positions and isotropic temperature factors reduced $R$ to 0.219. The $R$ calculated with Morosin
and Lingafelter's final parameters for the zinc and chlorine atoms was 0.229. The function minimized in the least squares refinement was \( \Sigma w(F_o - F_c)^2 \). Unit weights were used throughout, except that unobserved reflections with \( |F_c| \leq F_o \) were given a weight of zero. Through a series of \( \Delta F \) syntheses and subsequent least squares refinement of the atoms that had been found, a set of parameters for all of the atoms was determined. At this point \( R = 0.137 \). Three cycles of least squares refinement of positions and isotropic temperature factors of all the atoms reduced \( R \) to 0.122. However, the temperature factors of some of the carbon atoms had unusually high values and the tetramethylammonium tetrahedra were quite distorted.

A fresh attempt was therefore made to determine the positions of the nitrogen and carbon atoms. A \( \Delta F \) synthesis was calculated phased on the zinc and chlorine parameters. All nitrogen and carbon positions were found and were refined through a series of \( \Delta F \) syntheses, reducing \( R \) to 0.127. After three cycles of least squares refinement of positions and isotropic temperature factors of all atoms, \( R \) was 0.115. But, again, some of the temperature factors of the carbon atoms were high and the tetramethylammonium tetrahedra were distorted.

Nonetheless, it was decided to continue the refinement with four cycles of least squares, refining positions and anisotropic temperature factors of only the nitrogen and carbon atoms. The resulting
R was 0.107. Two further cycles of refinement of the positions and anisotropic temperature factors of the zinc and chlorine atoms gave an R of 0.090. The temperature factors were still unusually high and the tetrahedra quite distorted. It was noted, also, that the positions of the atoms were essentially the same as those given by Morosin and Lingafelter. 36

Since it appeared that a successful refinement was not being obtained in the acentric space group it was decided that a fresh attempt would be made with calculations being carried out in space group Pnma. Furthermore, since the trial structure was the same as that reported by Morosin and Lingafelter, 36 their parameters would be used as a starting point. A structure factor calculation with these parameters gave an initial R of 0.158. Three cycles of least squares refinement of an overall scale factor, positional parameters and isotropic temperature factors resulted in a decrease of R to 0.133. Again, the temperature factors of some of the atoms were unusually high, reaching a maximum value in the case of one of the carbon atoms of $B = 17.5 \text{ A}^2$. Nevertheless, two more cycles of least squares refinement were carried out. The resulting R was 0.128. The temperature factors were still high and the tetrahedra quite distorted. In these refinements some of the correlation coefficients between the scale factor and the various temperature factors were fairly high, ranging from 0.72 to 0.09. Using, as starting parameters, the
positions as obtained from the third cycle of least squares refinement, and arbitrarily setting the temperature factors to "reasonable" fixed values, namely, $B = 4.0 \, \text{A}^2$ for the zinc atom, $8.1 \, \text{A}^2$ for the chlorine atoms, $5.0 \, \text{A}^2$ for the nitrogen atoms, and $10.0 \, \text{A}^2$ for the carbon atoms, three cycles of refinement were carried out varying only the positions and scale factors but not the temperature factors. The initial $R$ for this calculation was 0.147 and the three cycles of refinement reduced it to only 0.140. Three more cycles varying positions and isotropic temperature factors, but not the scale factor, reduced $R$ to 0.127.

Again, the temperature factors were high, having almost the same values as after the first five cycles of refinement in this series. The tetrahedra were also distorted. At this point it was decided to take the bold step of attempting an anisotropic refinement. Using the same starting parameters as the previous three cycles of refinement, two cycles were carried out varying positions and anisotropic temperature factors of all the atoms. This reduced $R$ to 0.063. Two further cycles reduced $R$ to 0.062. At this point the refinement was essentially complete, the average ratio of the change in any parameter to its estimated standard deviation being 0.06 and the maximum ratio being 0.52. Two further cycles refining positions and the scale factor gave an $R$ of 0.061.
Upon examining the data it became obvious that some errors had been made in collecting nine reflections, since the discrepancies between observed and calculated structure factors were unusually large for these reflections. Furthermore, comparison with the film data also indicated errors for these reflections. Upon correction of these errors, $R$ dropped to 0.058. The data were also examined for secondary extinction effects by the method used by Housty and Clastre.\textsuperscript{20} This involves plotting $\ln(F_o/|F_c|)$ against $I_c$, where $I_c = LpF_c^2$ ($L$ and $p$ are the Lorentz and polarization corrections). This plot showed no trend for $\ln(F_o/|F_c|)$ to become more and more negative as $I_c$ increases and therefore no correction was made.

At this point it was necessary to change scattering factors in order to obtain uniformity throughout the series of isomorphous compounds. The scattering factors used, up to this point were: for neutral zinc, those given by Berghuis, et al;\textsuperscript{1} for neutral chlorine, neutral nitrogen, and neutral carbon, those given in the International Tables for X-Ray Crystallography.\textsuperscript{23} The scattering factor for zinc was changed to that for the dipositive ion, and for chlorine to that for the negative ion, both as given in the International Tables.\textsuperscript{23} The other scattering factors were not changed. A structure factor calculation with the new set of scattering factors resulted in an $R$ of 0.067. Two cycles of least squares refinement varying positions and anisotropic temperature factors of all atoms gave a final $R$ of 0.056.
For the final cycle the average ratio of the change in any parameter to its estimated standard deviation was 0.05 and the maximum ratio was 0.22.

Although the crystal structure will be discussed in a later section it will be of interest to mention here, that the temperature factors were still unusually high and the tetrahedra were still distorted; however, it was felt that with an $R$ of such a low value, a satisfactory fit to the data had been obtained.

A successful refinement of the structure was thus obtained only when the large temperature factors and the "unreasonableness" of the structure were ignored and the least squares method was allowed to proceed in a normal manner.

As an independent check on the least squares refinement, a difference synthesis was calculated phased on the final parameters, but, with a carbon atom removed. A series of these were calculated removing a different carbon atom each time. These $\Delta F$ maps showed, in the vicinity of the removed carbon atom, an electron density that appeared to match the final least squares parameters quite closely.

However, the possibility still remained that the correct space group might be the acentric $Pn2_1a$; therefore, an attempt was made to refine the structure in this space group. The shifts indicated by this refinement caused all of the nitrogen and carbon atoms, except one, to have temperature factors which were non-positive definite.
This means that the temperature factor matrix described a thermal ellipsoid which had one or more axes that were negative. Since this is completely unreasonable, physically, it was concluded that the correct space group could not be \( \text{Pn}2_1\alpha \), but must be \( \text{Pnma} \).

The final observed and calculated structure factors are given in Table 7. The crystal structure is discussed in Section II C.

After this refinement using the diffractometer data it was felt that it would be of interest to refine the structure using the film data for this compound in a similar manner and to compare the two structures. The final parameters as obtained from the refinement with the diffractometer data were used as a starting point for two cycles of least squares refinement on all positional and anisotropic temperature factor parameters. The initial \( R \) obtained was 0.092; after the two cycles of refinement this had increased slightly to 0.094. In the second cycle the average ratio of the change in any parameter to its estimated standard deviation was 0.18 and the maximum ratio was 0.78; thus, the refinement was complete even though the \( R \) index had increased. During the first cycle there were several of these ratios greater than 1.0, the maximum being 3.50. Thus, the refinement had considerably shifted many of the parameters. The final set of observed and calculated structure factors is given in Table 8. For this refinement a modified Hughes weighting scheme \(^{21}\) was used in which \( \sqrt{w} = 1.0 \) for all reflections with \( F_o < 24 \), \( \sqrt{w} = 24/F_o \) for all
Table 7. Observed and calculated structure factors for tetramethylammonium tetrachlorozincate(II), diffractometer data. Columns are $\ell$ index, $10 F_0^*$, and $10 F_C$. Unobserved reflections are marked with *.
Table 8. Observed and calculated structure factors for tetramethylammonium tetrachlorozincate(II), film data. Columns are $l$ index, $10 F_0$, and $10 F_C$. Unobserved reflections are marked with *.
reflections with $F_o > 24$, and $\sqrt{w} = 0$ for unobserved reflections for which $|F_c| < F_o$. The data consisted of 479 observed reflections and 182 unobserved reflections. This is contrary to the number given by Morosin and Lingafelter,\(^\text{36}\) but it appears that their number of 540 observed reflections is in error.

2. Tetramethylammonium Tetrachlorocobaltate(II)

Along with their report of the crystal structure of tetramethylammonium tetrachlorozincate(II), Morosin and Lingafelter\(^\text{36}\) reported that tetramethylammonium tetrachlorocobaltate(II) was isomorphous with it and had the following cell dimensions:

$$
a = 12.24(3) \text{ Å} \\
b = 8.92(2) \\
c = 15.39(3)
$$

Crystals were prepared as described by Morosin and Lingafelter\(^\text{36}\) and preliminary oscillation and Weissenberg photographs were taken which confirmed this. Accurate cell parameters were determined as described for bis(ethylenediamine)palladium(II) chloride using MoKα radiation. Fourteen values for 2θ were measured and the results of the least squares refinement are:

$$
a = 12.276(1) \text{ Å} \\
b = 9.001(1) \\
c = 15.539(2)
$$

Although the two sets of cell parameters are "close," they do not agree by the standard statistical tests. This can be explained by
the following. The parameters given by Morosin and Lingafelter\textsuperscript{36} were taken from precession and Weissenberg photographs which were not standardized by superimposing a standard crystal pattern on the same films. Therefore, there is probably considerable systematic error in their measurements which was not taken into account.

The crystal chosen for intensity measurements was a rod-like prism approximately 0.20 mm x 0.12 mm x 0.6 mm in size. It was mounted with \( \text{a} \) as the rotation axis and integrated equi-inclination Weissenberg intensity data were taken in the same manner as described for \( \text{bis(ethylenediamine)palladium(II) chloride} \). The radiation used was FeK\( \alpha \) (\( \lambda = 1.93728 \text{ A} \)) and data were collected for 0k\( \ell \) through 7k\( \ell \). In all, 802 reflections were examined, 487 were coded as observed and 315 were coded as unobserved reflections. The unobserved reflections were given an intensity equal to the minimum observable intensity for that particular level. No cross level photographs were taken. Lorentz and polarization factors were applied and the intensities were converted to relative structure factors.

Attempts to refine the structure using Morosin and Lingafelter's\textsuperscript{36} parameters for \([\text{N(CH}_3)_4]_2\text{ZnCl}_4\) as a trial structure resulted in problems similar to those encountered in the refinement of the zinc isomorph. Only isotropic least squares refinements were attempted and always resulted in large temperature factors and distorted tetrahedra. Work on the structure was temporarily abandoned
pending the outcome of the determination of the structure of the zinc isomorph with the presumably more accurate diffractometer data.

The final parameters for the zinc isomorph were used as a trial structure for the refinement of the cobalt isomorph. The scattering factors used were those for dipositive cobalt ion, negative chloride ion, and neutral carbon and nitrogen atoms given in the International Tables. The weighting scheme used in the least squares refinements was a modified Hughes scheme in which $\sqrt{w} = 1$ for all reflections with $F_o < 40$; $\sqrt{w} = 40/F_o$ when $F_o \geq 40$; $\sqrt{w} = 0$ for those unobserved reflections with $|F_c| \leq F_o$.

Since no data had been taken to experimentally scale the individual levels together, initial individual level scale factors were determined by comparison between the observed structure factors and the structure factors calculated with the trial structure. The initial $R$ for this calculation was 0.131. Holding the scale factors constant, but refining positions and anisotropic temperature factors for two cycles of least squares, reduced $R$ to 0.113. Then, two cycles varying only the scale factors gave an $R$ of 0.112. Finally, two more cycles, again holding the scale factors constant and varying positions and anisotropic temperature factors, resulted in the final $R$ of 0.111. For the final cycle the average ratio of the change in a parameter to its estimated standard deviation was 0.03 and the maximum ratio was 0.26. The data were examined for secondary extinction
effects by the method of Housty and Clastre. Although there were some large differences between observed and calculated structure factors, these did not show a systematic trend in the plot and therefore no corrections were made.

The final list of observed and calculated structure factors is given in Table 9. The structure is discussed in Section II C.

3. Tetramethylammonium Tetrachloronickelate(II)

In his Ph. D dissertation, Morosin mentions that he tried to prepare tetramethylammonium tetrachloronickelate(II), but was unable to do so. It is now clear why his attempts failed.

When one allows an aqueous solution of the appropriate stoichiometric amounts of tetramethylammonium chloride and nickel chloride to evaporate at room temperature, as Morosin did, one obtains a tan powder and not a blue solid (blue is the color reported for the tetrachloronickelate(II) ion\(^ {21}\)). However, when this tan solid is heated, either on a warm hot plate or in an oven at about 80\(^\circ\)C, the color changes to a deep blue. Since Morosin did not heat the compound he did not obtain the blue color.

Tetramethylammonium tetrachloronickelate(II) was prepared in this laboratory by M. Kellerman and B. J. Schein: 0.2 mole of \([\text{N(CH}_3]_4\text{Cl}\) and 0.1 mole of \(\text{NiCl}_2\cdot6\text{H}_2\text{O}\) were heated with mixing for several minutes on a steam bath to give a uniform tan paste, which
Table 9. Observed and calculated structure factors for tetramethylammonium tetrachlorocobaltate(II). Columns are \( \ell \) index, 10\( F_\alpha \), and 10\( F_\sigma \). Unobserved reflections are marked with *. c
after several hours in an oven at about 80°C had changed to a deep blue. Unlike the zinc and cobalt isomorphs, which can be safely handled in air, this blue compound is deliquescent and must be stored in a desiccator. The blue compound yields a light green aqueous solution from which the tan solid separates upon evaporation.

Suitable crystals were obtained by evaporation of a nitromethane solution in a vacuum desiccator containing Drierite. The deliquescent crystals were mounted in Lindemann glass capillaries in order to obtain the x-ray data.

Preliminary oscillation and Weissenberg photographs showed the compound to be isomorphous with the cobalt and zinc compounds. Accurate cell dimensions were determined from the least squares refinement of the differences between observed and calculated 20 values for 15 reflections. The data were taken, using CuKα radiation, as described for bis(ethylenediamine)palladium(II) chloride. The results are:

\[
\begin{align*}
a &= 12.2639(4) \text{ Å} \\
b &= 8.9819(8) \\
c &= 15.4861(10)
\end{align*}
\]

The density measured by the flotation technique was 1.35 gm/cm\(^3\) and that calculated on the basis of four molecules in the cell was 1.358 gm/cm\(^3\).

The crystal chosen for the collection of intensity data was an approximately cylindrical rod with rather poorly defined faces about
0.12 mm in diameter and 0.56 mm in length. It was mounted in a capillary with the rod axis (the $a$ axis) parallel to the rotation axis and equi-inclination Weissenberg photographs were taken for levels 0kl through 9kl. The data were collected with CuKα ($\lambda = 1.54178$ A) radiation exactly as described for bis(ethylenediamine)palladium(II) chloride. Individual level scale factors were determined using data for about 13 reflections per level collected on a Picker diffractometer with CuKα radiation in the same manner as described for the zinc isomorph. Of the 1039 reflections which were examined, 436 were coded as unobserved reflections and given an intensity equal to the minimum observable intensity for that particular level. Lorentz and polarization factors were applied and the intensities were converted to relative structure factors. No absorption corrections were made.

Since it was known that difficulties had been encountered in the refinement of the zinc and cobalt isomorphs, it was felt that this crystal structure should be determined completely independently from the others in order to eliminate any bias that might occur.

Initial calculations were made in space group $Pn\overline{2}1a$. The nickel and two of the chlorine atom positions were determined from a sharpened, origin removed, Patterson. An electron density map phased on these nickel and chlorine positions revealed the two other chlorine positions along with eight other peaks. A series of structure factor and Fourier calculations resulted in the determination of all of
the atomic positions. The R index at this stage was 0.255. Several attempts at isotropic least squares refinement were made at this time, but always with the same results as in the refinement of the zinc iso-
morph; the R index would be reduced to 0.18 - 0.20 and some of the temperature factors would become unusually large. A few ΔF Fourier maps were calculated to check that the atomic positions were not grossly in error. They indicated that no gross changes in the positions were necessary.

Because the R index could not be reduced lower than 0.18, the space group was changed to Pnma and further refinements were attempted. But, again, very similar behavior was observed. A series of isotropic least squares and ΔF refinements reduced R to 0.214, but the temperature factors were very high, reaching a maximum of $B = 28 \, \text{Å}^2$ in the case of one of the carbon atoms. Four cycles of anisotropic least squares refinements were carried out. This reduced the R index from 0.214 to 0.16. After the first cycle, five of the carbon atoms had temperature factors which were non-positive definite, however, the least squares program was allowed to proceed in spite of this. After the second cycle only three atoms had non-positive definite temperature factors, after the third cycle only one atom, and after the fourth cycle none of the atoms showed this behavior.

The structure was compared to the final zinc structure and was found to be equivalent to it.
Up to this point the scattering factors which were used were those for neutral nickel, chlorine, nitrogen and carbon atoms as given in the International Tables. The scattering factors for nickel and chlorine were changed to those of the dipositive nickel ion and uninegative chloride ion as given in the International Tables. Furthermore, the real part of the dispersion correction for the nickel ion with copper radiation was applied. The imaginary part of the dispersion correction, which amounts to 0.7, was ignored.

Three further cycles of anisotropic least squares refinement reduced $R$ to 0.13. Examination of the data by the method of Houstey and Clastre showed a secondary extinction effect. The nine reflections with the largest values of the calculated intensities were removed from any further consideration in the refinement. Removal of these reflections resulted in a decrease in the $R$ index to 0.127. One cycle of least squares refinement varying positions and anisotropic temperature factors reduced $R$ to 0.115. One cycle varying only the individual level scale factors, which up to this point had been held constant at their experimentally determined values (although an overall scale factor had been applied), reduced $R$ to 0.088. The changes in the scale factors on this cycle varied from 0.07% to 11.8%. Thus, it appears that some of the experimentally determined scale factors were in error. Following this, two final cycles of refinement were carried out varying the positional and temperature factor parameters.
only. The final $R$ index was 0.075. During the final cycle the average ratio of the change in a parameter to its estimated standard deviation was 0.26 and the maximum ratio was 1.16. The weighting scheme used for the least squares refinements was a modified Hughes scheme in which $\sqrt{w} = 1$ for those reflections with $F_o < 20$; $\sqrt{w} = F_o / 20$ for those reflections with $F_o \geq 20$; and $\sqrt{w} = 0$ for those unobserved reflections for which $|F_C| < F_o$. The final observed and calculated structure factors are given in Table 10.

The crystal structure is discussed in Section II C.
Table 10. Observed and calculated structure factors for tetramethylammonium tetrachloronickelate(II). Columns are \( l \) index, \( 10F^o \), and \( 10F^c \). Unobserved reflections are marked by *. Reflections removed because of possible secondary extinction effects are marked by E.
C. DISCUSSION

In order to facilitate comparison of the three isomorphous compounds, pertinent information on them is collected in Tables 11 through 17. Table 11 gives the cell dimensions and certain general information concerning the structure determinations. The final positional parameters are given in Table 12 and the thermal parameters are given in Table 13. Bond lengths and angles are given in Table 14.

Comparing the positional parameters of the zinc structures determined with the diffractometer and film data, we see that there are only two positions which differ by more than two estimated standard deviations, namely, the $z$ coordinate of the zinc atom and the $y$ coordinate of C(3), which differ by 2.3 and 3.9 standard deviations, respectively. The former cannot be considered significant. This leaves the latter as the only positional parameter which differs significantly between the two structures. Thus, there is very good agreement between the two structures. This can also be seen in the bond lengths and angles where the greatest difference between the two structures occurs in those quantities involving C(3). As expected, the estimated standard deviations are much smaller for the diffractometer data than for the film data.
Table 11. General Information on $\text{[N(CH}_3)_4\text{]}_2\text{MCl}_4\text{.}$

<table>
<thead>
<tr>
<th>Cell Dimensions</th>
<th>Co</th>
<th>Ni</th>
<th>diffractometer</th>
<th>film</th>
<th>Zn</th>
<th>film</th>
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<tbody>
<tr>
<td>a</td>
<td>12.276(1)</td>
<td>12.2639(4)</td>
<td>12.276(2)</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>9.001(1)</td>
<td>8.9819(8)</td>
<td>8.998(2)</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>15.539(2)</td>
<td>15.4861(10)</td>
<td>15.541(2)</td>
<td>--</td>
<td>--</td>
<td></td>
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</table>

<table>
<thead>
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<th>Method of data collection</th>
<th>film</th>
<th>film</th>
<th>diffractometer</th>
<th>film</th>
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</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>FeKα</td>
<td>CuKα</td>
<td>MoKα</td>
<td>CuKα &amp; MoKα</td>
</tr>
<tr>
<td>Number of observed reflections</td>
<td>487</td>
<td>603</td>
<td>850</td>
<td>479</td>
</tr>
<tr>
<td>Number of unobserved reflections</td>
<td>315</td>
<td>436</td>
<td>433</td>
<td>182</td>
</tr>
<tr>
<td>Final R index</td>
<td>0.111</td>
<td>0.075</td>
<td>0.056</td>
<td>0.094</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>Hughes</td>
<td>Hughes</td>
<td>unit</td>
<td>Hughes</td>
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Space group: Pnma, $Z = 4$
Table 12. Positional Parameters for $[\text{N(CH}_3)_4]^2\text{MCI}_4$

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<th>y/b</th>
<th>z/c</th>
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<th>Ni</th>
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Estimated standard deviations are given in parentheses

* Required by symmetry to be identically equal to 0.25, therefore e.s.d. is zero.
Table 13. Thermal Parameters for $[\text{N(CH}_3)_4]^2$MCl$_4$

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<th>film Zn</th>
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* Required by symmetry to be equal to zero.
The temperature factor is defined by: 
\[
\exp \left[ -\frac{1}{4} \sum_{i=1}^{3} \sum_{j=1}^{3} B(i) h(i) h(j) a(i) s(j) \right]
\]
Estimated standard deviations in the last significant figures are given in parentheses.
Table 14. Bond Lengths and Angles for $\left[N\left(CH_3\right)_4\right]_2MCl_4$

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<th>Ni</th>
<th>diffractometer</th>
<th>film</th>
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Primed atoms are related to unprimed by reflection in mirror plane at $y = 1/4$. The estimated standard deviations as obtained from the least squares refinement are given in parentheses.
The thermal parameters of the two structures also agree. This can be seen more clearly from Table 15, which gives the root mean square displacements along the principal axes of the thermal ellipsoids, and from Table 16, which gives the directions of these axes relative to the cell edges. The axes are listed in order of increasing size, axis 1 being the smallest and axis 3 being the largest. The thermal ellipsoids agree with respect to the lengths of the axes and orientation, except for N(1) and C(1); however, the ellipsoid of atom N(1) in the structure determined with the diffractometer data is spherical to within the estimated standard deviations, and therefore, any directions calculated for the axes have no physical significance. A similar relationship holds for axes 2 and 3 of atom C(1) in the structure determined with the film data. It is quite gratifying that the two independently determined structures agree so nicely.

Turning now to a comparison of the three isomorphs, it can be seen from the data given in Tables 12, 13, 14, 15, and 16 that, in general, the structures are quite similar. A most exceptional feature exhibited by the structures is the unusually large values of the thermal parameters. It was, in fact, the persistance of these large values that caused the great difficulties in the refinement of the structures, and a satisfactory refinement was not obtained until it was decided to accept these large values.
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*Indicates axes which are required to be parallel to $b$ axis by symmetry.

Estimated standard deviations in the last significant figures are given in parentheses.
Table 16. Angle Between Thermal Ellipsoid Axes and Cell Edges for $[N(CH_{3})_{4}]_{2}MCl_{4}$ in Degrees

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*Required by symmetry to be perpendicular to b axis. +Required to be parallel to b axis.
Estimated standard deviations are given in parentheses.
It is highly unlikely that these temperature factors describe the true thermal motion of the atoms since they are much larger than any that are reported in other normal structures. The largest root mean square displacements reported for a normal structure are around 0.39 Å, the more usual values ranging up to about 0.32 Å, while the values in the present structures range to a maximum of 0.81 Å. The author feels that the large temperature factors indicate a disordering of the crystal structures. This point will now be discussed and a model for the disorder presented.

Normally, when difficulties such as these are encountered in a crystal structure determination, the cause may be found in a systematic error in the intensity data either as a result of mistakes in the collection of the data or lack of corrections for absorption. That this is not the case in the present structures is amply demonstrated. In order for the large values of the thermal parameters to have been caused by systematic errors, these errors would have been similar in all cases since (as will be shown later), all the structures show similar patterns in the thermal ellipsoids. It is difficult to see how this could have occurred, since the four different sets of data were collected by four different investigators from crystals which were of different sizes and shapes using a variety of experimental techniques.

Large temperature factors would arise from a disordered structure. For instance, if a disordered atom occupied two positions
close together, and the resulting electron density was fitted with a single atom, the position determined for this atom would lie somewhere in between the two true positions and the temperature parameters would be quite large, spreading out the electron density over the volume "occupied" by the two "half" atoms. The direction of largest motion, as indicated by the thermal parameters, would be the direction of "greatest" disorder.

The thermal ellipsoids (Table 16) of all the chlorine atoms show similar orientations, except for axes 2 and 3 of Cl(1). However, the ellipsoids for this atom are essentially isotropic in the plane defined by axes 2 and 3 in all of the isomorphs, and therefore, any orientation calculated for them has no physical significance.

The thermal ellipsoids for the carbon atoms of the nickel and zinc isomorphs are oriented similarly, without exception. The carbon thermal ellipsoids in the cobalt isomorph also agree with the other structures except for axes 1 and 2 of C(2) and axes 1 and 2 of C(6). Axes 1 and 2 of C(6) are of the same length; therefore, directions calculated for them have no physical significance. The orientations of the thermal ellipsoids for the metal atoms and the two nitrogen atoms do not generally agree in the three isomorphs. For the zinc and cobalt isomorphs, these are the atoms which are, to a large extent, isotropic. Again, this would give the directions of the axes no physical meaning.
Table 17 gives the orientation of the thermal ellipsoids of the chlorine and carbon atoms with respect to the bond between them and the central atom of their respective tetrahedra. For every atom except C(2) in the cobalt isomorph the axis with the smallest displacement is the one that is near to being parallel to the bond direction. The other two axes are then, of course, required to be approximately perpendicular to the bond direction. This indicates that the disorder is of the form of a rotation or oscillation of a tetrahedron about its central atom—an overall translation would cause some of the larger axes of the thermal ellipsoids to lie in directions other than perpendicular to the bonds. The thermal ellipsoids of the metal and nitrogen atoms are consistent with this description also, because the temperature parameters for these atoms are not excessively large and quite acceptable, indicating that they are not disordered.

The thermal parameters for the nickel isomorph are generally larger than for the other isomorphs. The cause for this is not apparent.

Thus, with the exception of only C(2) of the cobalt isomorph, all of the atoms which appear to be disordered in the structures have their thermal ellipsoids oriented in similar directions. It is interesting to note that the cobalt isomorph is the only one in which experimental cross level scaling was not available; this causes the $B_{11}$ values (those associated with the direction of the rotation axis) and the
Table 17. Angles Between Principal Axes of Thermal Ellipsoids and a Vector Defined by Two Atoms.

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The e.s.d.'s range from 1 to 10 degrees.
individual level scale factors to be completely degenerate\textsuperscript{31} and could, therefore, cause the temperature factors to be rather unrealistic. However, the initial scale factors were determined on the basis of a structure factor calculation using the final zinc parameters; thus, if the two structures are as isomorphous as they appear to be, these scale factors should be fairly accurate. Furthermore, if the $B_{11}$ values are incorrect, it is difficult to explain why only one atom does not agree, while the others agree quite well.

Analysis of the directions of the thermal ellipsoid axes of the chlorine atoms reveals the probable mode of disorder of the $[\text{MC}_{14}]^{2-}$ tetrahedra. There is a disorder caused by an oscillation of the tetrahedra in all directions about the central metal atom. Superimposed upon this is a disorder caused by an oscillation about the M-Cl(1) bond. An attempt to pictorially represent this is given in Figure 4 which is a schematic representation of the projections of the axes of the thermal ellipsoids onto a plane which is perpendicular to the M-Cl(1) bond. Since the M-Cl(1) bond is nearly parallel to the $a$ axis, the plane of projection is nearly parallel to the (100) plane. It can be seen from this figure that the longest thermal axes of Cl(2) and Cl(3) are arranged in relation to each other in such a manner as to be compatible with an oscillation about the M-Cl(1) bond. The data from the zinc diffractometer structure were used in this analysis,
Figure 4. Schematic representation of the projections of the thermal ellipsoid axes for the $[\text{MCl}_4]^2$-tetrahedra onto a plane perpendicular to the M-Cl(1) bond. The metal atom has been omitted for clarity since it would fall in the same place as Cl(2). The numbers in square parentheses are the $x$ coordinates of the atoms. Cl(1) and Cl(3) lie in the mirror plane.
but it can be seen that the same general pattern exists throughout the three isomorphs.

It is well known that determination of parameters for carbon and nitrogen atoms can not be accomplished with a great deal of accuracy in the presence of heavy atoms, as is the case in these structures. This is particularly true of the thermal parameters. For this reason, no analysis of the directions of the thermal ellipsoids for these atoms will be made.

Bearing in mind that because of the disorder of the structures, the positions determined for the atoms may not be very accurate, it is of interest to examine the metal-chlorine distances and the distortion of the $[\text{MCl}_4]^{2-}$ tetrahedra.

The ionic radii of the Co(II), Ni(II), and Zn(II) ions, as given by Pauling,\(^4\) are 0.74, 0.72, and 0.74 Å, respectively. On this basis it would be expected that the metal-chlorine distances should be about the same for the zinc and cobalt compounds, whereas, the nickel compound should show a smaller distance. It can be seen from Table 14 that while comparable zinc and cobalt distances are not equal, the nickel-chlorine distances are indeed smaller than comparable distances in the other compounds. The averages of the three independent metal-chlorine distances are 2.25, 2.23, and 2.25 Å for the cobalt, nickel, and zinc compounds, respectively. It is interesting to note that these average distances show exactly the same trend as Pauling's
ionic radii of the metal ions. The nickel-chlorine distance in dichlorobis(triphenylphosphine)nickel(II)\(^{16}\) is 2.27 Å, somewhat larger than in the present structure. While the disorder of the present structure will give bond lengths which are smaller than the actual values, it is also true that the structures of dichlorobis(triphenylphosphine)nickel(II) was determined from three rather inaccurate two-dimensional projections and, therefore, the errors are probably quite large. This would mean that the value of 2.27 Å for the nickel-chlorine bond length is probably not significantly different from the values obtained in the present investigation.

The \([\text{MCl}_4]^{2-}\) tetrahedra appear to be distorted in all three of the isomorphs. Simple crystal field theory predicts a Jahn-Teller distortion of tetrahedral Ni(II) complexes in the form of an elongation of the tetrahedron along the \(\overline{4}\) axis rather than a flattening of it.\(^{45}\) A tetrahedron distorted in this manner has four angles which are larger than the normal tetrahedral value and two angles which are smaller, while a flattened tetrahedron has four angles which are smaller and two which are larger. In all three isomorphs the \([\text{MCl}_4]^{2-}\) tetrahedra are flattened. For nickel(II) this is contrary to what simple crystal field theory predicts. It is true that the nickel isomorph has a distortion which is greater than the other two, but this is in the direction of greater flattening rather than in the direction of elongation. This would indicate (again, it should be borne in mind that this is
indeed only an indication, because of the disordering), that spin orbit
forces remove the degeneracy of the ground state leaving a complex
which is not susceptible to a Jahn-Teller distortion. Since the observed
distortions are similar, it would appear that they are caused by crystal
packing forces. The compound, tetramethylammonium tetrachloro-
cuprate(II), which is approximately isomorphous with the present
structures, contains a tetrahedral \([\text{CuCl}_4]^{2-}\) ion which is distorted
in an exactly similar manner, \(^{37}\) although to a greater extent. This is
quite compatible with crystal field theory which predicts a Jahn-Teller
distortion for \(\text{Cu(II)}\) complexes in the form of a flattened tetrahedron.

It is unfortunate that the structures are disordered since the
only other reported structure of a non-chelated tetrahedral complex
of nickel is that of dichlorobis(triphenylphosphine)nickel(II)\(^{16}\) which
was the first authenticated case of a tetrahedral nickel complex. As
mentioned earlier, it is only sufficiently accurate to establish the
tetrahedral nature of the nickel configuration. This leaves the \(\text{N-
substituted-salicylaldimine}^{2,14}\) complexes as the only accurately
determined crystal structures of tetrahedrally coordinated nickel.

The phase diagram of the \(\text{CsCl-NiCl}_2\) system has been deter-
mined by Iberson, Gut, and Gruen\(^{22}\) and they find that below 50 mole %
\(\text{NiCl}_2\) there is a solid to solid color change from yellow to blue at
417\(^\circ\) C caused by the formation of the compound, \(\text{Cs}_3\text{NiCl}_5\), which
they have shown to be isomorphous to \(\text{Cs}_3\text{CoCl}_5\) by powder methods.
$\text{Cs}_3\text{CoCl}_5$ is known to contain $[\text{CoCl}_4]^{2-}$ tetrahedra; therefore $\text{Cs}_3\text{NiCl}_5$ presumably contains $[\text{NiCl}_4]^{2-}$ tetrahedra. This author has prepared this compound in powder form and has found it to be stable at room temperature for long periods of time when stored in a desiccator. If single crystals of it can be prepared it would probably provide the necessary compound for an accurate structure determination of the tetrahedral $[\text{NiCl}_4]^{2-}$ ion.
APPENDIX

THE CRYSTAL STRUCTURE OF TETRAETHYLENEPENTAMINE-NICKEL(II) THIOCYANATE, $\text{Ni(C}_8\text{N}_5\text{H}_{23})_2(\text{SCN})_2$

Crystals of tetraethylenepentaminenickel(II) thiocyanate were given to Professor E. C. Lingafelter by Professor P. Paolletti, University of Florence, Italy. A reasonable molecular structure for this compound would be as shown in Figure 5. It would also be possible for the tetraethylenepentamine to be tetradoentate instead of pentadentate and for the other thiocyanate ion to fill out the octahedron. An x-ray structural investigation was undertaken to determine the correct molecular structure.

Preliminary rotation and Weissenberg photographs and investigation on x-ray diffractometer showed the Laue symmetry to be m3m. Systematic absences of $hkl$ for $h+k, k+l,$ and $l+h = 2n+1$ showed the possible space groups to be $F\bar{4}32, F\bar{4}3m,$ or $F\bar{m}3m.$ The lattice parameter was determined, using MoK$_\alpha$ ($\lambda = 0.71069$ Å) radiation, from the least squares refinement of 20 values for thirteen reflections measured on a single-crystal x-ray diffractometer. It is: $a = 15.522(3)$ Å.

The crystal chosen for intensity measurements was a truncated tetrahedron exhibiting {111} and {111}. The [110] edge was approximately 0.448 mm in length and the perpendicular distance between
Figure 5. Proposed molecular structure.

Figure 6. Crystal used for intensity measurements.
(111) and (111) was approximately 0.176 mm. It was mounted along [100] and intensity measurements were taken by the $\omega$-2$\theta$ scan method (moving crystal-moving counter) on a Picker diffractometer equipped with a General Electric single-crystal orien ter. A drawing of the crystal as it was mounted is shown in Figure 6. Zirconium-filtered molybdenum radiation was used to collect the data to a maximum 2$\theta$ of 55° (about the limit of copper radiation).

A total of 208 reflections were examined of these, there were 90 unique reflections and 59 pairs of symmetrically related reflections. Absorption corrections were applied using a program written by R. V. Chastain, Jr. which utilizes subroutines written by C. W. Burnham. The method is that given by Busing and Levy. The 59 pairs of related reflections were then averaged, giving a total of 149 unique reflections, of which 53 were coded as unobserved. Lorentz and polarization factors were applied and each intensity was converted to a relative structure factor.

The density of the crystals was measured by the flotation technique and resulted in a density of $1.42\,\text{gm/cm}^3$. The density calculated on the basis of four molecules in the cell is $1.236\,\text{gm/cm}^3$ and that calculated on the basis of five molecules in the cell is $1.545\,\text{gm/cm}^3$. Since the space group is face centered there must be at least four molecules in the cell, but, it is not possible to have five molecules in the cell since the next highest occupied position is an
eight-fold position in space groups \( F 432 \) and \( F m3m \) or a sixteen-fold position in \( F \bar{4}3m \). The high observed density could be caused by solvent being incorporated into the crystal. Therefore, calculations proceeded assuming four molecules in the cell. This would require the nickel atom to be placed at a special four-fold position. The origin is such a position and a Fourier synthesis was calculated phased on nickel at the origin using an isotropic temperature factor of \( B = 6.194 \text{ Å}^2 \). This value of \( B \) was estimated from the normal statistics of the normalized unitary structure factors using a program coded by J. R. Holden. This calculation was carried out in space group \( F 432 \). The same results would have been obtained in any of the other possible space groups, however, since the phases of all the structure factors would be positive because the only atom used in the calculation was at the origin. The \( R \) index for this calculation was 21%, a surprisingly low value considering that it reflects the contribution of only one atom to the structure factors.

The Fourier synthesis showed a few relatively small peaks in the electron density. Several structure factor calculations were carried out adding one or more of the atoms indicated by the Fourier synthesis, but, these always resulted in a greatly increased value of the \( R \) index, generally to about 40% or 50%. After these attempts, it was decided to try an interpretation of the Patterson function in order to obtain a trial structure. Consequently, a sharpened, origin removed
Patterson was calculated, but it was impossible to interpret this on the basis of the eight sulfur atoms in the cell.

At this point it was noticed that the relative structure factors monotonically decreased in value with increasing \((\sin \theta)/\lambda\). This is the behavior that would be expected if there were only one atom in the cell and it was at the origin. Each structure factor would have the value of the scattering factor for the atom at the proper \((\sin \theta)/\lambda\). Thus, a plot of relative structure factor versus \((\sin \theta)/\lambda\) should appear quite similar to a scattering factor curve. Such a plot for this particular compound is shown in Figure 7. The similarity between this and a scattering factor curve is unmistakable. Thus, it appears that the nickel atom is at the origin with the coordination polyhedron disordered about it. A grouping such as this would give the behavior described above.

In order to test the goodness of fit of this model, a structure factor calculation was carried out with one atom, whose scattering factor is the curve drawn in Figure 7, at the origin with a temperature factor of zero. A list of these calculated structure factors along with the observed structure factors is given in Table 18. The resulting \(R\) index was 15.1%.

This \(R\) index indicates that there probably is still some residual structure and that the compound is not completely disordered. Accordingly, a \(\Delta F\) synthesis was calculated phased on the previous
structure factor calculation. There were seven independent peaks apparent in this $\Delta F$ synthesis ranging in height from $2.8 \, \text{e}^-/\text{A}^3$ to $0.75 \, \text{e}^-/\text{A}^3$. They were all in positions which had been tried as atomic positions at an earlier stage in the determination of the structure. Their approximate positions and peak heights are given in Table 19. The peak at the origin is due to an incorrect value of the scattering factor at $(\sin \theta)/\lambda = 0$. This is caused by an erroneous extrapolation of the curve in Figure 7 to $(\sin \theta)/\lambda$ of zero.

This disordered model for the crystal structure explains the surprisingly low value of the R index obtained with only the nickel atom at the origin. A nickel atom, being rather large, would provide a fairly good approximation to a structure disordered in this manner, and would therefore be expected to give a low value for the R index.
Figure 7. Relative structure factor versus \((\sin \theta) / \lambda\).
Table 18. Observed and calculated structure factors for tetraethylenepentaminenickel(II) thiocyanate. The columns are k index, 10 F₀, and 10 F₁. Unobserved reflections are marked by *.
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REFERENCES


42. S. Ooi, Y. Komiyama, and H. Kuroya, ibid., 33, 354 (1960).
44. S. Ooi and H. Kuroya, ibid., 36, 1083 (1963).


VITA

Joel Robert Wiesner was born in Los Angeles, California on October 28, 1938 to Mr. and Mrs. Leonard Jack Wiesner. He received his early education in the public school system of the City of Los Angeles and was graduated from George Washington High School, Los Angeles in June 1956. He entered the University of California, Los Angeles in September of that year and received the Bachelor of Science degree in chemistry in January of 1961. He entered the graduate school of the University of Washington in September of 1961.

He is a member of the Society of Sigma Xi, Phi Lambda Upsilon, the American Crystallographic Association, and The Chemical Society (London).

He married Helaine Louise Gilner on June 14, 1959. They have two sons, Craig Howard, born January 7, 1962 and David Scott, born April 7, 1964.