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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

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Approved by E. C. Lingafelter
(Chairmen of Supervisory Committee)

Department Chemistry
(Departmental Faculty Sponsoring Candidate)

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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

L. H. Jensen

W. W. Gregory

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Date 9/28/66

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I would also like to thank the National Science Foundation for financial support of this work and the University of Washington Computer Center for a grant of computer time.

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.[17] 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.[17] 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.[3, 4, 27, 32]

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[10] report that $Pd(en)_2Cl_2$ is isomorphous with $Pt(en)_2Cl_2$ and has almost identical cell dimensions. They report $Pt(en)_2Cl_2$ as crystallizing in space group $P\bar{1}$ and having lattice parameters as follows:

$a = 8.37$ A $\quad \alpha = 100°46'$
$b = 4.95 \quad \beta = 111°40'$
$c = 6.86 \quad \gamma = 81°56'$,

or, in the standardized form recommended by Donnay,[12]

$a = 6.86$ A $\quad \alpha = 98°\ 4'$
$b = 8.37 \quad \beta = 100°46'$
$c = 4.95 \quad \gamma = 68°20'$

Watt and Klett[54] have also reported the space group and cell dimensions for $Pt(en)_2Cl_2$, which in the form recommended by Donnay[12] are

$a = 6.881$ A $\quad \alpha = 98°\ 0'$
$b = 8.339 \quad \beta = 100°\ 4'$
$c = 4.937 \quad \gamma = 108°22'$

with space group $P\bar{1}$ or $P1$ (morphology suggests $P\bar{1}$), 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[54] are correct.

For the present investigation, bis(ethylenediamine)palladium(II) chloride was prepared[28] by the reaction of K_2PdCl_4 with excess ethylenediamine. 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 <u>c</u> as the rotation axis show the crystal to be triclinic. Thus, the space group is either P1 or $P\bar{1}$. 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 CuKα radiation (λ = 1.54178 A), from the best least squares fit to single-crystal measurements of thirty 2θ values taken on a Picker diffractometer fitted with a General Electric Goniostat:

a = 6.8607(4) A
b = 8.3610(8)
c = 4.9940(3)

α = 97.716(6)°
β = 100.683(5)
γ = 108.571(6)

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[54] for $Pt(en)_2Cl_2$. Thus, it appears that $Pd(en)_2Cl_2$ and $Pt(en)_2Cl_2$ are isomorphous as reported by Cox and Preston,[10] but that the correct cell parameters for $Pt(en)_2Cl_2$ are as given by Watt and Klett.[54] It was assumed for purposes of this structure determination that there is one molecule per cell as reported by Cox and Preston.[10] 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 $h0\ell$ 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

$$\exp[-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j a_i^* a_j^* B_{ij}].$$

The discrepancy factor $R = (\Sigma\,||F_o| - |F_c||)/\Sigma|F_o|$, where the summation is over the unique observed reflections only.

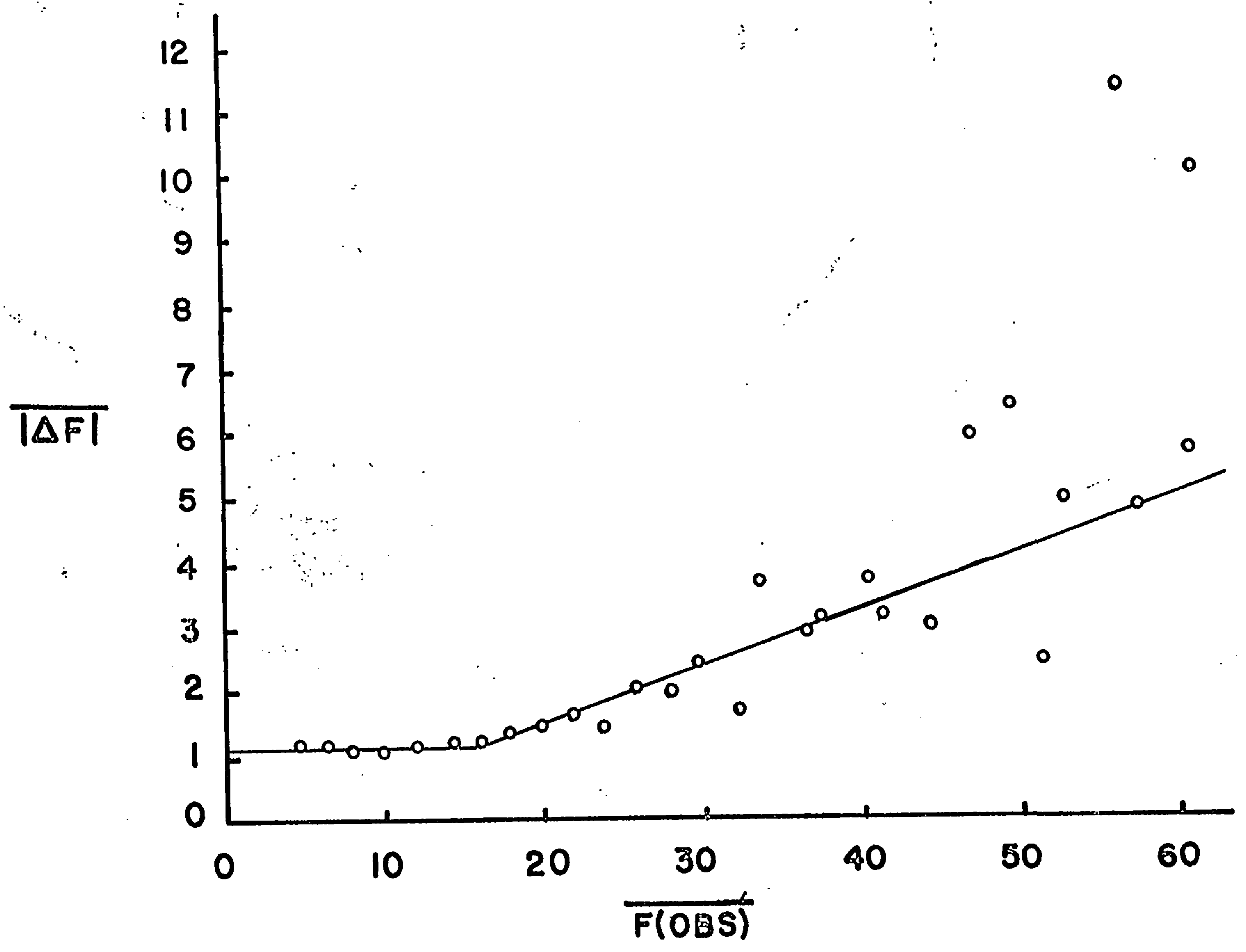
Assuming the space-group $P\overline{1}$ with one molecule in the cell, the Pd atom may be placed at the origin. An initial structure factor calculation with Pd at 0, 0, 0 gave an R of 0.314. A three-dimensional Fourier synthesis phased on this structure factor calculation gave the coordinates of all 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 $B = 1.95\ A^2$ 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 A, N-H distance assumed to be 0.95 A) 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_o, the average $||F_o| - |F_c|| \equiv \overline{|\Delta F|}$ of each group was plotted against the average F_o of that group. This graph is shown in Figure 1. The scatter of the points at high values of F_o 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 $\overline{|\Delta F|} = 0.0905\ F_o - 0.42$. The following assignment of weights were made: for unobserved reflections with $|F_c| \leq F_o$, $\sqrt{w} = 0$; for unobserved reflections with $|F_c| > F_o$, $\sqrt{w} = 1$; for observed reflections with $F_o \leq 18$, $\sqrt{w} = 1$; for observed reflections with $F_o > 18$, $\sqrt{w} = 1/\overline{|\Delta F|}$, $\overline{|\Delta F|}$ 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 $\overline{|\Delta F|}$ with $\overline{F_o}$ used to determine least squares weighting.



$\overline{|\Delta F|}$
12
11
10
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
$\overline{F(OBS)}$

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 e^-/A^3. Eight of these (ranging in height from 0.61 e^-/A^3 to 1.09 e^-/A^3) were located very close to the calculated hydrogen positions, and the remaining five (ranging in height from 0.55 e^-/A^3 to 0.89 e^-/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.

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

Table 2. Final Parameters of the Hydrogen Atoms. Positions are multiplied by 10^4. Temperature parameters are multiplied by 10^2.

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

[+] 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 *.

```
      0,K,0
 1  348   456
 2  117   475
 3  434   389
 4  414   467
 5  200   201
 6   99    76
 7  185   170
 8  247   238
 9  127   124
      1,K,0
 0  380   446
 1  377   406
 2  302   327
 3   70    87
 4  274   337
 5  346   370
 6  189   199
 7  140   110
 8  171   128
 9  144   125
      2,K,0
 0   79    72
 1  200   207
 2  437   469
 3  281   308
 4  205   198
 5  236   229
 6  231   204
 7  135   133
 8   77    73
      3,K,0
 0  492   539
 1  389   408
 2  150   138
 3  201   223
 4  299   318
 5  156   146
 6   74    52
 7  123   112
      4,K,0
 0  302   316
 1  409   402
 2  164   147
 3   97    81
 4  176   173
 5  150   152
 6  103   102
      5,K,0
 0  140   125
 1  139   118
 2  202   197
 3  173   173
 4   87    80
 5  115   108
      6,K,0
 0  208   225
 1  142   131
 2  102   108
 3  143   147
 4  135   120
      7,K,0
 0  160   161
 1  176   187
 2  120   103
      8,K,0
 0   77    68
     -1,K,0
 1  364   377
 2  403   418
 3  504   600
 4  302   336
 5  190   193
 6  284   258
 7  179   165
 8  121   113
 9  136   161
10  126   105
     -2,K,0
 1  533   508

 2  384   360
 3  172   158
 4  307   333
 5  453   472
 6  266   296
 7  148   177
 8  150   130
 9  198   195
10  112   101
     -3,K,0
 1  306   296
 2   51*   79
 3  313   265
 4  456   483
 5  186   195
 6   78    74
 7  273   276
 8  227   262
 9  147   126
10   79    88
     -4,K,0
 1  142   141
 2  338   329
 3  440   417
 4  277   248
 5  145   120
 6  161   158
 7  272   245
 8  171   170
 9   88    96
10  148   137
     -5,K,0
 1  283   259
 2  324   323
 3  140   177
 4  184   177
 5  339   328
 6  215   220
 7   78*   66
 8  141   141
 9  166   169
10   92    99
     -6,K,0
 1  159   154
 2  104*   68
 3  176   179
 4  273   267
 5  192   189
 6  108   114
 7  157   156
 8  189   206
 9  120   118
     -7,K,0
 1   99*   73
 2  121   117
 3  220   231
 4  141   141
 5  100*   38
 6  156   144
 7  191   203
 8  116   118
     -8,K,0
 1  123   139
 2  153   154
 3   94   100
 4   92   100
 5  122   137
 6  134   124
 7   75    74
      0,K,1
-10   96    97
 -9  140   163
 -8  167   167
 -7  123   119
 -6  306   328
 -5  296   307
 -4  117   126
 -3  246   230
 -2  423   478
  0  402   516
  1  369   431
  2  447   513
  3  342   351
  4  [illegible]
  5  [illegible]
  6  [illegible]
  7  121   107

  8  126   115
  9  162   140
      1,K,1
-10   68*   52
 -9  151   163
 -8  249   241
 -7  121   125
 -6   46*   50
 -5  254   250
 -4  613   590
 -3  414   378
 -2   49*   49
  0  716   884
  1  144   143
  2   82    75
  3  311   333
  4  304   315
  5  166   155
  6  122   113
  7  182   186
  8  170   176
      2,K,1
-10  101    97
 -9  104   115
 -8  144   136
 -7  246   248
 -6  212   220
 -5  175   177
 -4  504   449
 -3  289   315
 -2  243   210
 -1  177   161
  0  320   319
  1  379   409
  2  200   213
  3  106   104
  4  260   275
  5  287   286
  6  119   124
  7  111    97
      3,K,1
-10  133   137
 -9  166   175
 -8  114   124
 -7  183   182
 -6  305   297
 -5  326   300
 -4  172   162
 -3  194   180
 -2  405   384
 -1  289   272
  0  117    94
  1  307   315
  2  309   370
  3  182   183
  4  153   138
  5  169   177
  6  160   146
      4,K,1
-10   71    83
 -9  138   139
 -8  255   233
 -7  172   171
 -6  104*   52
 -5  264   237
 -4  304   349
 -3  178   165
 -2  154   137
 -1  370   314
  0  377   367
  1  272   220
  2  107   110
  3  203   189
  4  189   179
  5   79*   75
      5,K,1
-10   71    90
 -9   73*   65
 -8  168   173
 -7  209   203
 -6  123   115
 -5  105   110
 -4  253   260
 -3  361   341
 -2  191   181
 -1   97   100
  0  267   233
  1  237   226
  2   91*   69
  3   88    85
  4  147   138

      6,K,1
 -9  139   135
 -8   82    93
 -7  101   107
 -6  276   272
 -5  210   203
 -4   92   101
 -3  182   173
 -2  136   175
 -1  143   179
  0   91*   77
  1  171   173
  2  170   147
  3  131   105
      7,K,1
 -8  159   155
 -7  107   108
 -6  104    97
 -5  151   151
 -4  176   169
 -3  106    93
 -2   81*   78
 -1  157   150
  0  147   138
  1   81    88
      8,K,1
 -4  148   138
 -3  171   156
     -1,K,1
 -9   83    87
 -8  105   128
 -7  189   190
 -6  238   232
 -5  255   262
 -4  247   240
 -3  377   398
 -2  367   355
 -1   82    56
  0  324   314
  1  606   688
  2  286   299
  3  209   212
  4  361   387
  5  383   396
  6  197   196
  7   95*   66
  8  151   144
  9  162   173
     -2,K,1
 -9   79    89
 -8  162   148
 -7   90   107
 -6  107*   90
 -5  296   280
 -4  417   439
 -3  169   182
 -2  165   175
  0  307   386
  1  162   165
  2  115    93
  3  413   447
  4  471   519
  5  161   159
  6  158   158
  7  281   285
  8  189   195
  9  115   101
     -3,K,1
 -8  102    91
 -7   93    90
 -6  115   117
 -5  197   200
 -4  202   204
 -3   97   103
 -2  292   293
 -1  376   351
  0  358   309
  1  265   244
  2  404   381
  3  314   319
  4  232   214
  5  147   162
  6  127   170
  7  237   242
  8  143   146
  9  136   136
 10  148   145

     -4,K,1
 -7  108   174
 -6  177   164
 -5   96    86
 -4  114   126
 -3  233   244
 -2  170   185
 -1  118   124
  0  237   274
  1  431   437
  2  369   355
  3  124   127
  4  240   286
  5  384   385
  6  127   122
  7   97*   55
  8  187   147
  9  182   183
 10   99    96
     -5,K,1
 -6   87    94
 -5  144   147
 -4  182   184
 -3  195   194
 -2   76    87
 -1  218   204
  0  248   300
  1  117   171
  2  117   108
  3  324   311
  4  344   339
  5  195   195
  6  122   122
  7  185   193
  8  195   209
  9   97    85
     -6,K,1
 -4  113   101
 -3   92*   82
 -2  178   172
 -1  247   245
  0  158   169
  1  107*   64
  2  186   188
  3  289   281
  4  121   170
  5   90    92
  6  233   236
  7  199   213
  8  113   117
  9  100   102
     -7,K,1
 -3   99   101
 -2  176   131
 -1   81    88
  0  130   139
  1  213   225
  2  155   156
  3  101    93
  4  190   190
  5  177   189
  6  119   123
  7   71    74
  8  148   134
     -8,K,1
  0  108   125
  1  122   121
  2   67    77
  3  139   137
  4  201   204
  5  110   112
  6   67*   51
  7  110   121
      0,K,2
-10   79    80
 -9   88   101
 -8  191   179
 -7  274   210
 -6  169   207
 -5  162   159
 -4  255   256
 -3  381   403
 -2  147   144
 -1   21    45
  0  521   533
  1  516   540
  2  194   201
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  3  143   149
  4  101   105
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  3  249   263
  4  188   203
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  7  162   149
      3,K,2
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  3  110   127
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  1   97    89
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  4  347   351
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  5  233   235
  6  202   226
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  5   99   101
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 -6  158   153
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 -6  [illegible]
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 -2   32    69
 -1  129   128
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  5  211   213
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  4  213   213
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  4  174   148
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 -5   78    80
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  8  183   207
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  2  [illegible]
  3  [illegible]
  4  [illegible]   179

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  0   59*   55
  1  136   140
  2  213   210
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  4   99    90
  5  153   136
  6  166   166
  7   71    81
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  1  109   115
  2   68    63
  3   84    83
  4  176   177
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 -7  142   135
 -6  161   155
 -5  141   144
 -4  161   166
 -3  281   270
 -2  208   200
 -1   61    59
  0  160   170
  1  237   267
  2  142   159
  3   98   103
  4  169   160
  5  189   193
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 -8  135   126
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 -6  161   166
 -5  223   232
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 -2  205   200
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  1  101   113
  2  217   238
  3  209   197
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  5   96    89
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 -7  131   124
 -6   60    61
 -5  105   105
 -4  251   244
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 -2   78    68
 -1  194   190
  0  257   267
  1  140   142
  2   89    72
  3  103   112
  4  133   134
      3,K,4
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 -6  125   126
 -5   67    61
 -4  176   169
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 -2  150   149
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  2  [illegible]
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 -6  119   120

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 -3   78    70
 -2  143   153
 -1  141   144
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  1   76    91
  2  170   131
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 -5   46   110
 -4  133   144
 -3   74    86
 -2   56    62
 -1  111   114
  0  114   135
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 -8  131   135
 -7  129   125
 -6   62*   24
 -5  147   135
 -4  267   297
 -3  194   226
 -2   70    91
  0  218   346
  1  177   209
  2   51*    4
  3  149   149
  4  174   197
  5  134   125
  6   70    68
     -2,K,4
 -8   88    86
 -7   77    70
 -6  105   103
 -5  191   189
 -4  138   138
 -3   54    59
 -2  217   272
 -1  307   319
  0  169   168
  1  166   151
  2  242   244
  3  197   213
  4  104   107
  5   90    88
  6  145   147
  7  125   128
     -3,K,4
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 -6  142   141
 -5  123   172
 -4  121   126
 -3  160   154
 -2  170   173
 -1  146   132
  0  154   152
  1  264   273
  2  297   258
  3  102   104
  4  170   155
  5  246   227
  6  113   124
  7   60    52
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 -5   99   101
 -4  224   227
 -3  192   181
 -2   58*   72
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  0  316   298
  1  180   140
  2   57*   28
  3  188   168
  4  294   285
  5  172   166
  6   50    51
  7  138   126
     -5,K,4
 -5  121   113
 -4   97   100
 -3   95    94
 -2  136   138
 -1  213   218
  0  203   187
  1   81    70
  2  155   137

  3  247   210
  4  117   104
  5   90    79
  6  164   148
  7  156   147
     -6,K,4
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 -2  157   156
 -1   89    94
  0  107    44
  1  203   197
  2  205   190
  3  110    98
  4   96    87
  5  158   161
  6  141   132
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  1  119   117
  2   50    46
  3  132   133
  4  264   211
  5  131   110
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      1,K,5
  0  170   169
      2,K,5
  0   74    70
      3,K,5
  0  144   128
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  0   83    85
     -2,K,5
  0  163   159
     -3,K,5
  0  262   234
     -4,K,5
  0  107   103
     -5,K,5
  0  125   134
     -6,K,5
  0  171   176
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  0   51    47
     -1,K,6
  0  143   154
     -2,K,6
  0  140   152
     -3,K,6
  0   59    51
     -4,K,6
  0  119   136
```

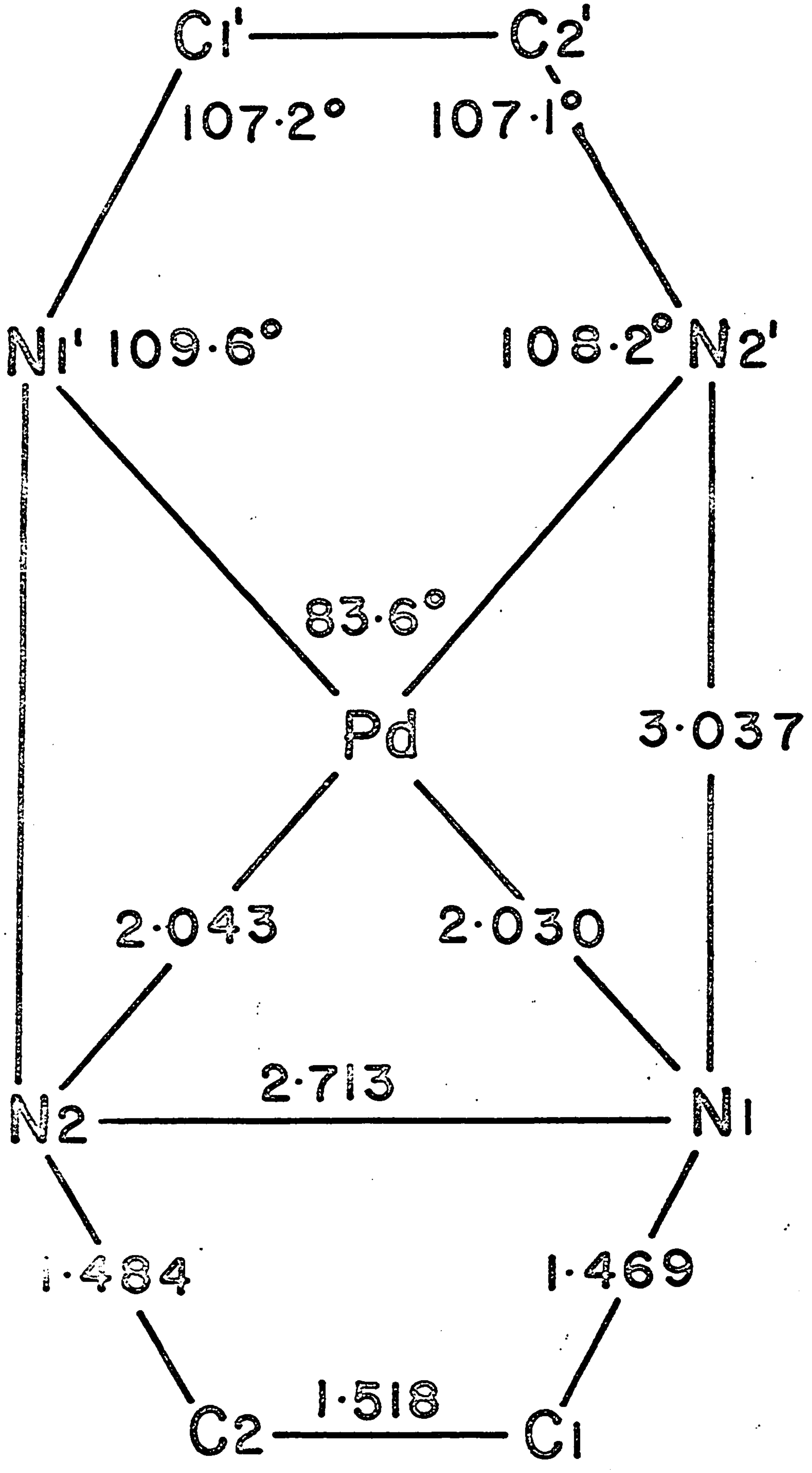
C. DESCRIPTION AND DISCUSSION

The shortest Pd-Cl distance in the structure is 4.180 ± 0.002 A. This is much longer than the shortest non-bonding Pd-Cl distance of 3.85 A between chains in the crystal structure of $PdCl_2$.[55] Therefore, it appears that there is no bonding between palladium and chlorine and it seems proper to describe the crystal structure of $Pd(en)_2Cl_2$ as consisting of discrete $[Pd(en)_2]^{2+}$ and Cl^- ions.

An orthogonal projection of the $[Pd(en)_2]^{2+}$ ion onto a plane parallel to the coordination plane is shown in Figure 2. The molecular symmetry required by the space group is $\bar{1}$. 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 A above the N(1)-Pd-N(2) plane while atom C(2) is 0.39 A 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 Bailar[9] 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 $[Pd(en)_2]^{2+}$ ion onto the Pd-N(1)-N(2) plane.


C1'
C2'
107·2°
107·1°
N1'
109·6°
108·2°
N2'
83·6°
Pd
3·037
2·043
2·030
2·713
N2
N1
1·484
1·469
1·518
C2
C1

$Pd(en)_2Cl_2$, it must exist in the kk' form, which has been found for all reported structures of bis(ethylenediamine) complexes.[17]

The interatomic distances and angles are given in Table 4. The standard deviations given were calculated using the program ORFFE[7] as modified for inclusion in the Crystal Structures Calculations System[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[30] found the O-C and C-C bond distances and the O-C-C 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.

Pd-N(1)	2.030(6) A	∠ N(1)-Pd-N(2)	83.6(3)°
Pd-N(2)	2.043(7)	∠ Pd-N(1)-C(1)	109.6(5)
N(1)-C(1)	1.469(11)	∠ Pd-N(2)-C(2)	108.2(5)
N(2)-C(2)	1.484(11)	∠ N(1)-C(1)-C(2)	107.2(7)
C(1)-C(2)	1.518(13)	∠ N(2)-C(2)-C(1)	107.1(7)
N(1)-N(2)	2.713(10)		
N(1)-N(2)'	3.037(10)		

N(2)' is related to N(2) by inversion through the center of symmetry.

Table 5. Comparison of Bond Lengths and Angles

		Two-Dimensional Structure Determinations						
Compound	Ref.	N-N (within a chelate ring)	M-N	N-C	C-C	∠N-M-N	∠M-N-C	∠N-C-C
$[Cr(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$	42	2.87 A	2.11 A 2.13	1.44 A 1.48	1.57 A	85°	106° 108	117° 107°
$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$	38	2.81	1.98 2.00	1.48 1.47	1.55	90	104 106	110 108
$[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$	43	2.77	2.00 2.01	1.52 1.51	1.55	87	109 108	108 110
$[Co(en)_2Cl_2]NO_3$	44	2.71	1.99 2.00	1.46 1.46	1.59	86	112 107	105 110
$[Co(en)_3]Cl_3 \cdot NaCl \cdot 6H_2O$	41	2.76	1.98 2.00	1.48 1.47	1.54	82 87	110 109	109 110
$[Co(en)_3]Cl_3 \cdot 3H_2O$	40	2.84	2.00 2.00	1.47 1.47	1.54	90	105 105	113 113
$[Co(en)_3]Br_3 \cdot H_2O$	39	2.76 2.77	2.03 1.98 2.00	1.44 1.50 1.49	1.54 1.54	86 88	105 109 109	111 102 114
$Ni(en)_2(NCS)_2$	3	2.77	2.09 2.11	1.46 1.50	1.50	82	107 110	112 106

Table 5. Continued

Compound	Ref.	N-N (within a chelate ring)	M-N	N-C	C-C	∠N-M-N	∠M-N-C	∠N-C-C
			Two-Dimensional Structure Determinations					
$[Hg(SCN)_4][Cu(en)_2]$	48	2.45 A	2.08 A	1.41 A	1.53 A	71°	117°	106°
		2.78	2.13	1.45	1.55	85	119	95
		2.76	1.94	1.36	1.50	85	94	107
			2.17	1.36			95	91
			2.00	1.43			96	107
			2.09	1.43			100	92
$Cu(en)_2Cl_2$	18	2.77	2.02	1.53	1.53	85	108	109
			2.07	1.49			110	111
$[Cu(en)_2Cl(H_2O)]Cl\cdot H_2O$	32	2.80	1.98	1.51	1.52	89	106	113
		2.80	1.99	1.47	1.50	89	107	108
			1.99	1.50			107	114
			1.98	1.50			107	108
$[Cu(en)_2Br(H_2O)]Br\cdot H_2O$	32	2.79	1.98	1.50	1.51	90	106	113
		2.78	1.97	1.47	1.54	89	111	109
			1.98	1.50			106	106
			1.98	1.49			106	119
			Three-Dimensional Structure Determinations					
$[Co(en)_2Cl_2]_2S_6O_6\cdot H_2O$	13	2.67	1.98(3)	1.46(5)	1.57(6)	88(1)	111(2)	108(3)
		2.70	1.95(3)	1.57(5)	1.54(6)	86(1)	108(2)	112(3)
			1.98(3)	1.49(5)			109(2)	106(3)
			1.93(3)	1.49(5)			114(2)	102(3)

Table 5. Continued

Compound	Ref.	N-N (within a chelate ring)	M-N	N-C	C-C	$\angle$N-M-N	$\angle$M-N-C	$\angle$N-C-C
		Three Dimensional Structure Determinations						
$[Ni(en)_2][AgBr_2]_2$	25	2.663(20) A	1.939(14) A	1.473(22) A	1.451(33) A	86.7(6)$^\circ$	107(1)$^\circ$	108(1)$^\circ$
$Ni(en)_3(NO_3)_2$	51	2.790(25)	2.120(13)	1.500(25)	1.498(28)	82(1)	110(1)	111(2)
$K[Ni(en)_3][SeCN]_3$	25	2.791	2.138(13) 2.124(12)	1.466(18) 1.488(18)	1.557(21)	82	109 108	108 107
$Cu(en)_2(NO_3)_2$	27	2.772	2.044(13) 2.012(13)	1.487(25) 1.476(25)	1.545(27)	86	109 109	110 111
$Cu(en)_2(SCN)_2$	4	2.70(3)	1.99(1) 2.01(1)	1.46(3) 1.49(3)	1.56(4)	85	111 109	109 105
$Pd(en)_2Cl_2$	This work	2.713(10)	2.030(6) 2.043(7)	1.469(11) 1.484(11)	1.518(13)	83.6(3)	108.2(5) 109.6(5)	107.2(7) 107.1(7)
Average		2.76	2.01	1.48	1.535	86	108	109
Range		0.21	0.24	0.15	0.12	8	7	15

(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 A); the average deviation from the mean is 0.04 A in both cases. It is also interesting to note that the average N-N distance (2.76 A) is close to the average O-O distance (2.78 A). 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 A and 2.043 ± 0.007 A are in good agreement with the Pd-N distances of 2.031 ± 0.002 A in bis(N-isopropyl-3-ethylsalicylaldiminato)palladium(II),[2] 2.022 ± 0.007 A in bis(2, 2'-dipyridyliminato)palladium(II),[15] 2.032 ± 0.003 A in the tetragonal form of bis(N-isopropyl-3-methylsalicylaldiminato)-palladium(II),[24] and 2.019 ± 0.008 A in the monoclinic form of the latter compound.[24]

The chloride ions are surrounded by four hydrogen atoms at distances of 2.44 A, 2.43 A, 2.40 A, and 2.24 A, 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 A + 1.2 A = 3.0 A) 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 A to 3.41 A. 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.

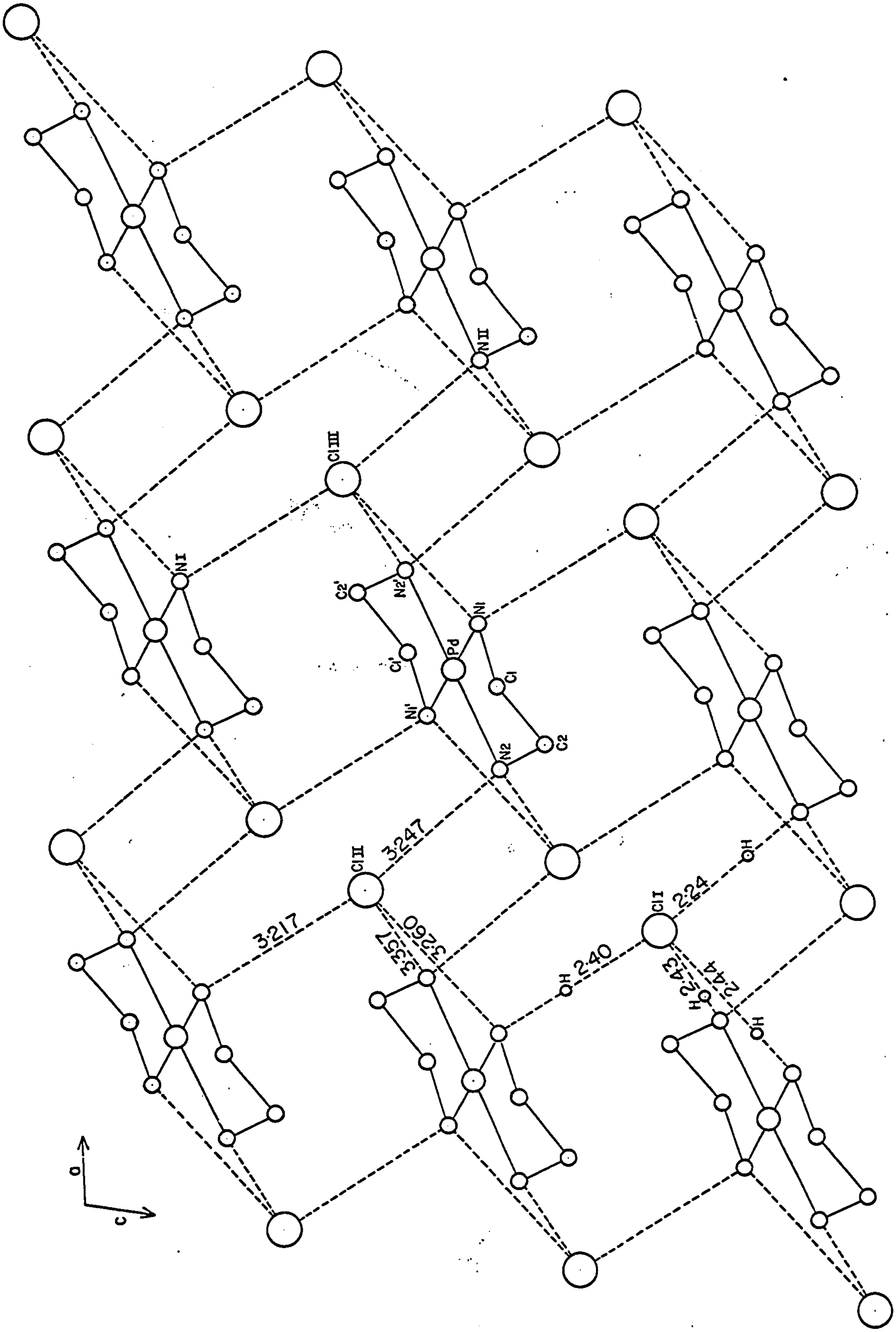

Cl III
N II
N I
C2'
N2'
Pd
N1
C1'
C1
N1'
N2
C2
Cl II
3·247
3·217
3·260
3·357
Cl I
2·24
H
2·40
H
2·43
H
2·44
H
a
c

Table 6. Pertinent Data Involved in the Hydrogen Bonding Scheme. The lettering refers to the atoms surrounding Cl(III) in Figure 3.

atoms defining line	distance of hydrogen from the line
Distances of the Hydrogen Atoms from the Line Joining the Chloride Ion and the Nitrogen Atoms.	
N(1) - Cl(III)	0.16 A
N(2)' - Cl(III)	0.36
N(I) - Cl(III)	0.35
N(II) - Cl(III)	0.03
Angles Involved in the Hydrogen Bonding Geometry	
∠ N(1) - Cl(III) - N(2)'	54.6°
∠ N(1) - Cl(III) - N(I)	100.9
∠ N(2)' - Cl(III) - N(I)	87.6
∠ N(I) - Cl(III) - N(II)	153.4
∠ N(2)' - Cl(III) - N(II)	76.1
∠ N(1) - Cl(III) - N(II)	86.8

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 $[Pd(en)_2]^{2+}$ and 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 A and 3.933 A between carbon atoms on adjacent molecules and 3.867 A between a carbon atom and a nitrogen atom on adjacent molecules. Taking the van der Waals radius of a methylene group as 2.0 A[46] 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 $Cl-NH_2$ distance of 3.23 A in the crystal structure of $(CH_3)_2NH_2CuCl_3$.[56] 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.[34] 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.[52] A crystal structure determination[50] 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).[5]

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[53] reported that x-ray diffraction data showed the compound to be definitely tetrahedral; however, it was not until 1963 that a full report[16] 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(benzyldiphenylphosphine)dibromonickel(II) has appeared.[26] The cell contains three molecules; two are tetrahedral, one is planar. Two recently determined structures of N-substituted-salicylaldimine nickel(II) chelates[2, 14] 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[29] 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[19] showed quite conclusively that the tetrahedral $[NiCl_4]^{2-}$ 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[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[8] as modified for inclusion in the Crystal Structures Calculations System, X-Ray 63.[11]

1. Tetramethylammonium Tetrachlorozincate(II)

The crystal structure of tetramethylammonium tetrachlorozincate had previously been determined from three dimensional film data by Morosin and Lingafelter.[36] They had refined the structure to a final reliability index $(\Sigma||F_o - F_c||/\Sigma|F_o|)$ 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 $B=15.5\ A^2$ for some of the carbon atoms and $B=8.5\ A^2$ 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 ($\lambda = 0.71068$ A). The results are (with the estimated standard deviations as obtained from the least squares refinement in parentheses):

$$a = 12.276(2)\ A$$
$$b = 8.998(2)$$
$$c = 15.541(2)$$

These are in agreement with the values given by Morosin and Lingafelter:[36]

a = 12.268(7) A
b = 8.964(7)
c = 15.515(12)

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 ϕ axis of the diffractometer. Intensity data were collected with MoKα radiation on a Picker diffractometer fitted with a General Electric single-crystal orienter by the ω-2θ 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: $\sigma_I = (S + B1 + B2)^{\frac{1}{2}}$. Reflections were examined in shells of 2θ to a maximum of 47° at which point the intensities were falling off so rapidly that it was deemed not worthwhile to collect data at any higher 2θ 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[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 ($Pn2_1a$). The essential difference between these two space groups is that, with four molecules in the cell, Pnma requires the $[NiCl_4]^{2-}$ and $N(CH_3)_4^+$ tetrahedra to lie on mirror planes parallel to (010) and at $\underline{y} = \frac{1}{4}$, while, in $Pn2_1a$ 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 $Pn2_1a$.

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 ΔF 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 ΔF synthesis was calculated phased on the zinc and chlorine parameters. All nitrogen and carbon positions were found and were refined through a series of ΔF 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 fave 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 $B = 17.5\ A^2$. 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, $B = 4.0\ A^2$ for the zinc atom, $8.1\ A^2$ for the chlorine atoms, $5.0\ A^2$ for the nitrogen atoms, and $10.0\ A^2$ 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.[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;[1] for neutral chlorine, neutral nitrogen, and neutral carbon, those given in the International Tables for X-Ray Crystallography.[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.[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 ΔF 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 $Pn2_1a$, but must be 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 strucures. 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 ℓ index, $10\ F_o$, and $10\ F_c$. Unobserved reflections are marked with *.

0,0,L [illegible]

0,1,L [illegible]

0,2,L [illegible]

0,3,L [illegible]

0,4,L [illegible]

0,5,L [illegible]

0,6,L [illegible]

0,7,L [illegible]

0,8,L [illegible]

0,9,L [illegible]

1,0,L [illegible]

1,1,L [illegible]

1,2,L [illegible]

1,3,L [illegible]

1,4,L [illegible]

1,5,L [illegible]

1,6,L [illegible]

1,7,L [illegible]

1,8,L [illegible]

1,9,L [illegible]

2,0,L [illegible]

2,1,L [illegible]

2,2,L [illegible]

2,3,L [illegible]

2,4,L [illegible]

2,5,L [illegible]

2,6,L [illegible]

2,7,L [illegible]

2,8,L [illegible]

2,9,L [illegible]

3,0,L [illegible]

3,1,L [illegible]

3,2,L [illegible]

3,3,L [illegible]

3,4,L [illegible]

3,5,L [illegible]

3,6,L [illegible]

3,7,L [illegible]

3,8,L [illegible]

3,9,L [illegible]

4,0,L [illegible]

4,1,L [illegible]

4,2,L [illegible]

4,3,L [illegible]

4,4,L [illegible]

4,5,L [illegible]

4,6,L [illegible]

4,7,L [illegible]

4,8,L [illegible]

4,9,L [illegible]

5,0,L [illegible]

5,1,L [illegible]

5,2,L [illegible]

5,3,L [illegible]

5,4,L [illegible]

5,5,L [illegible]

5,6,L [illegible]

5,7,L [illegible]

5,8,L [illegible]

5,9,L [illegible]

6,0,L [illegible]

6,1,L [illegible]

6,2,L [illegible]

6,3,L [illegible]

6,4,L [illegible]

6,5,L [illegible]

6,6,L [illegible]

6,7,L [illegible]

6,8,L [illegible]

7,0,L [illegible]

7,1,L [illegible]

7,2,L [illegible]

7,3,L [illegible]

7,4,L [illegible]

7,5,L [illegible]

7,6,L [illegible]

7,7,L [illegible]

7,8,L [illegible]

8,0,L [illegible]

8,1,L [illegible]

8,2,L [illegible]

[illegible]

11,0,L [illegible]

11,1,L [illegible]

11,2,L [illegible]

11,3,L [illegible]

11,4,L [illegible]

11,5,L [illegible]

12,0,L [illegible]

12,1,L [illegible]

12,2,L [illegible]

12,3,L [illegible]

12,4,L [illegible]

13,0,L [illegible]

13,1,L [illegible]

13,2,L [illegible]

Table 8. Observed and calculated structure factors for tetramethylammonium tetrachlorozincate(II), film data. Columns are ℓ index, 10 F_o, and 10 F_c. Unobserved reflections are marked with *.

C,0,L

2	522	484
4	1809	-1944
6	304	-296
8	232	-173
10	308	287
12	480	410
14	244	-250
16	232	-272
18	47•	-33

0,1,L

1	756	-785
3	1705	-1690
5	364	244
7	1212	1218
9	980	858
11	55•	-31
13	476	-395
15	234	-259
17	53•	21

0,2,L

0	2190	-2095
2	1357	-1291
4	249	272
6	1485	1466
8	46•	97
10	681	-633
12	117	-164
14	236	226
16	195	184
18	44•	57

0,3,L

1	81	-83
3	1227	1220
5	411	413
7	1323	-1198
9	732	-693
11	115	173
13	220	250
15	234	195
17	48•	-6

0,4,L

0	1732	1787
2	585	524
4	778	-693
6	777	-695
8	53•	-54
10	371	305
12	211	233
14	59•	-126

0,5,L

1	869	-781
3	1074	-879
5	327	221
7	535	420
9	465	394
11	61•	49
13	221	-260
15	52•	-141

0,6,L

0	1044	-937
2	166	-220
4	509	416
6	483	410
8	60•	86
10	361	-271
12	117	-175
14	51•	111

0,7,L

1	58•	52
3	487	435
5	389	236
7	484	-415
9	330	-277
11	97	115
13	48•	109

0,8,L

0	385	309
2	61•	183
4	122	-193
6	301	-314
8	58•	33

0,9,L

1	205	-165
3	345	-262
5	57•	11

0,10,L

0	282	-263
2	51•	-24

1,0,L

1	12•	-14
2	1098	1376
3	498	367
4	432	-371
5	624	462
6	869	-738
7	237	217
8	591	-521
9	43•	-68
10	548	-479
11	256	-193
12	169	170
13	55•	0
14	353	372
15	56•	-6
16	53•	73

1,1,L

1	1198	1240
2	521	-245
3	93	-81
4	817	809
5	586	-529
6	206	157
7	538	-525
8	297	-262
9	44•	-50
10	66	102
11	253	258
13	55•	-19
14	56•	4
15	223	-240

1,2,L

1	406	410
2	179	136
3	724	-702
4	822	-815
5	413	-294
7	39•	-8
8	1063	1047
9	45•	-63
10	201	181
11	181	177
12	261	-253
13	56•	48
14	195	-209
15	55•	-19

1,3,L

1	674	-612
2	696	-625
3	514	-551
4	164	-157
5	799	794
6	88	80
7	558	562
8	45•	-5
9	264	-289
10	51•	-24
11	120	-171
12	55•	25
13	56•	49

1,4,L

1	81	-106
2	867	798
3	122	131
4	165	122
5	151	156
6	469	-415
7	46•	81
8	373	-360
9	51•	-26
10	246	-211
11	124	-121
12	56•	94
13	56•	-1
14	123	221

1,5,L

1	797	723
2	43•	-29
3	417	-382
4	268	228
5	297	-268
6	49•	35
7	51•	-98
8	91	-121
9	54•	-69
10	55•	46
11	218	203

1,6,L

1	67	63
2	339	-339
3	50•	-48
4	227	-136
5	52•	-66
6	53•	-61
7	54•	-15
8	278	272
9	56•	-0
10	125	178

1,7,L

1	92	-140
2	54•	-66
3	133	-170
4	54•	-45
5	294	258
6	56•	13
7	226	246
8	56•	10
9	158	-147

1,8,L

1	56•	-55
2	56•	78
3	56•	72
4	137	211
5	56•	-14
6	55•	-71
7	54•	-1
8	141	-188

1,9,L

1	144	143
2	54•	-16
3	54•	-63
4	53•	31
5	147	-112

1,10,L

1	47•	-8
2	123	-120

2,0,L

0	1434	-1433
1	179	-162
2	702	-604
3	934	-941
4	650	616
5	848	-807
6	369	360
7	414	423
8	224	198
9	42•	9
10	204	-146
11	229	-208
12	178	-187
13	53•	-45
14	54•	109

2,1,L

0	477	-280
1	1171	1021
2	161	-108
3	461	437
4	465	434
5	421	-385
6	251	195
7	550	-540
8	112	-100
9	561	-555
10	322	-337
11	49•	-50
12	207	-161
13	375	349
14	54•	-78

2,2,L

0	275	180
1	911	919
2	966	1011
3	676	668
4	116	-121
5	32•	4
6	888	-1005
7	38•	56
8	41•	-5
9	44•	71
10	352	362
11	50•	-33
12	52•	20
13	54•	99

2,3,L

0	362	414
1	29•	-87
2	150	-78
3	353	-433
4	336	-386
5	269	-241
6	38•	12
7	616	686
8	44•	-39
9	415	462
10	227	176
11	89	-92
12	151	181
13	210	-229
14	53•	28

2,4,L

0	756	-877
1	167	-175
2	320	-344
3	285	-298
4	530	510
5	294	-278
6	323	340
7	45•	95
8	117	-2
9	50•	102
10	52•	-136

2,5,L

0	192	181
1	626	626
2	209	-225
3	323	392
4	44•	40
5	228	-230
6	335	380
7	120	-156
8	88	-67
9	241	-249
10	219	-217
11	93	-72
12	53•	-1

2,6,L

0	300	339
1	116	105
2	189	192
3	204	227
4	170	-169
5	50•	78
6	262	-291
7	105	-144
8	93	-62
9	93	-11
10	216	186
11	53•	38

2,7,L

0	307	254
1	126	-64
2	52•	4
3	217	-209
4	206	-206
5	151	-137
6	54•	-6
7	217	214
8	54•	31
9	206	196

3,0,L

1	1680	-1485
2	934	-926
3	751	747
4	418	342
5	227	-231
6	264	265
7	349	-338
8	255	237
9	457	403
10	287	249
11	58•	18
12	219	-175
13	62•	50
14	276	-279
15	62•	118

3,1,L

1	860	-786
2	130	125
3	27•	17
4	329	-274
5	365	407
6	373	-373
7	156	170
8	351	-306
9	102	-131
10	110	-72
11	292	-266
12	61•	-34
13	62•	-35

3,2,L

1	224	239
2	146	-133
3	779	708
4	350	363
5	66	-61
6	73	-101
7	304	-255
8	516	-553
9	53•	32
10	57•	-89
11	60•	-3
12	255	199
13	167	-167
14	218	183
15	61•	-46

3,3,L

1	384	326
2	406	397
3	245	230
4	258	-272
5	405	-390
6	253	220
7	279	-269
8	390	423
9	193	167
10	59•	-90
11	237	205
12	62•	10

3,4,L

1	349	-383
2	307	-284
3	44•	76
4	186	-206
5	48•	39
6	191	149
7	54•	-53
8	271	301
9	59•	94

3,5,L

1	416	-440
2	264	289
3	204	232
4	182	-167
5	210	218
6	178	-159
7	154	101
8	60•	14
9	62•	-10
10	62•	-61
11	210	-197

3,6,L

1	167	187
2	233	209
3	57•	-123
4	184	185
5	60•	30
6	61•	-77
7	62•	-10
8	218	-240

3,7,L

1	106	127
2	137	125
3	62•	66
4	108	-152
5	166	-211

4,0,L

0	735	851
1	795	-963
2	114	78
3	175	-145
4	674	-645
5	764	694
6	514	-535
7	167	176
8	227	-230
9	54•	74
10	332	294
11	224	184
12	260	250
13	66•	-109
14	66•	-83

4,1,L

0	995	-1012
1	361	-294
2	483	-428
3	796	-779
4	197	152
5	276	-275
6	149	-106
7	585	560
8	224	203
9	372	348
10	84	115
11	108	-87
12	64•	81
13	257	-243

4,2,L

0	629	-644
1	296	-314
2	249	-242
3	71	-99
4	529	505
5	203	228
6	611	636
7	475	-475
8	107	126
9	229	-202
10	333	-327
11	63•	59
12	208	-189
13	66•	24

4,3,L

0	204	-216
1	406	354
2	571	579
3	731	728
4	222	246
5	125	116
6	326	-371
7	448	-492
8	58•	-29
9	248	-224
10	62•	43
11	64•	60
12	187	-164

4,4,L

0	685	767
1	249	-282
2	47•	84
3	49•	-52
4	408	-454
5	237	234
6	241	-278
7	100	98
8	61•	-100
9	62•	6
10	217	208
11	66•	95
12	231	187

4,5,L

0	434	-442
1	214	-203
2	54•	-16
3	387	-386
4	204	166
5	102	-100
6	191	-153
7	243	245
8	63•	89
9	238	199

4,6,L

0	307	-361
1	61•	92
2	61•	-88
3	62•	-26
4	197	189
5	63•	-37
6	224	218

4,7,L

0	113	-109
1	64•	31
2	64•	98
3	197	224
4	115	84
5	177	121
6	133	-116
7	187	-198
8	66•	-10

4,8,L

0	266	192

5,0,L

1	373	462
2	984	996
3	324	-284
4	883	920
5	147	146
6	224	-222
7	41•	37
8	593	-641
9	282	-305
10	205	-179
11	195	-174
12	302	300
13	57•	-35
14	224	212

5,1,L

1	794	870
2	118	94
3	239	-252
4	399	400
5	900	-909
6	202	154
7	484	-464
8	45•	27
9	399	373
10	200	180
11	443	440
12	57•	-7

5,2,L

1	27•	51
2	989	-1072
3	560	-574
4	690	-694
5	206	174
6	274	259
7	306	262
8	527	489
9	87	-86
10	198	182
11	228	183
12	247	-237
13	57•	123
14	221	-217

5,3,L

1	625	-732
2	345	-320
3	237	224
4	39•	43
5	741	749
6	62	-104
7	357	357
8	205	-190
9	284	-279
10	55•	-8
11	347	-355

5,4,L

1	209	184
2	765	805
3	43•	-40
4	491	457
5	47•	-36
6	183	-190
7	51•	79
8	397	-374
9	55•	-75
10	178	-163
11	170	-140
12	202	192

5,5,L

1	461	434
2	331	-300
3	49•	-43
4	347	352
5	549	-510
6	53•	64
7	267	-306
8	208	-162
9	252	226
10	57•	135
11	201	256

5,6,L

1	53•	13
2	418	-378
3	54•	-73
4	349	-365
5	55•	-68
6	56•	124
7	57•	59
8	285	305

5,7,L

1	309	-311
2	57•	-127
3	79	93
4	57•	51
5	296	307
6	57•	46

5,8,L

1	57•	-32
2	269	266

5,9,L

1	198	161

6,0,L

0	451	-537
1	185	259
2	341	-332
3	220	-229
4	482	495
5	543	-560
6	843	842
7	181	176
8	103	-107
9	49•	76
10	459	-458
11	54•	-102
12	231	-255
13	55•	10

6,1,L

0	191	201
1	472	501
2	25•	4
3	841	912
4	205	213
5	289	300
6	260	238
7	251	-252
8	104	-77
9	316	-323
10	139	-174
11	54•	119
12	55•	-60
13	216	233

6,2,L

0	743	819
1	505	509
2	146	155
3	297	301
4	612	-629
5	135	-94
6	557	-525
7	176	126
8	49•	84
9	51•	19
10	289	286
11	78	-84
12	224	274

6,3,L

0	257	240
1	561	-582
2	73	-117
3	596	-671
4	295	-271
5	44•	-61
6	64	14
7	83	100
8	51•	-11
9	292	277
10	124	96

6,4,L

0	356	-383
1	43•	-59
2	198	-201
3	153	-147
4	310	299
5	151	-146
6	507	489
7	51•	49
8	53•	-13
9	55•	37
10	302	-264

6,5,L

0	204	182
1	238	209
2	49•	-107
3	402	415
4	51•	-27
5	181	176
6	235	218
7	212	-198
8	55•	-49
9	238	-243

6,6,L

0	199	176
1	53•	35
2	201	179
3	54•	108
4	123	-162
5	55•	32
6	316	-349
7	56•	-53

6,7,L

0	224	192
1	224	-195
2	[illegible]	-47
3	250	-248
4	55•	-119

6,8,L

0	226	-218

reflections with $F_o \geq 24$, and $\sqrt{w} = 0$ for unobserved reflections for which $|F_c| \leq F_o$. The data consisted of 479 observed reflections and 182 unobserved reflections. This is contrary to the number given by Morosin and Lingafelter,[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[36] reported that tetramethylammonium tetrachlorocobaltate(II) was isomorphous with it and had the following cell dimensions:

a = 12.24(3) A
b = 8.92(2)
c = 15.39(3)

Crystals were prepared as described by Morosin and Lingafelter[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) A
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[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 a as the rotation axis and integrated equi-inclination Weissenberg intensity data were taken in the same manner as described for bis(ethylenediamine)palladium(II) chloride. The radiation used was $\text{FeK}\alpha$ ($\lambda = 1.93728$ 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[36] parameters for $[N(CH_3)_4]_2ZnCl_4$ 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.[23] 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.[20] 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[35] 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° 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 $[N(CH_3)_4]Cl$ and 0.1 mole of $NiCl_2.6H_2O$ 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 ℓ index, $10F_o$, and $10F_c$. Unobserved reflections are marked with *.

0,0,L
[illegible]

0,1,L
[illegible]

0,2,L
[illegible]

0,3,L
[illegible]

0,4,L
[illegible]

0,5,L
[illegible]

0,6,L
[illegible]

0,7,L
[illegible]

0,8,L
[illegible]

0,9,L
[illegible]

1,0,L
[illegible]

1,1,L
[illegible]

1,2,L
[illegible]

1,3,L
[illegible]

1,4,L
[illegible]

1,5,L
[illegible]

1,6,L
[illegible]

1,7,L
[illegible]

1,8,L
[illegible]

1,9,L
[illegible]

2,0,L
[illegible]

2,1,L
[illegible]

2,2,L
[illegible]

2,3,L
[illegible]

2,4,L
[illegible]

2,5,L
[illegible]

2,6,L
[illegible]

2,7,L
[illegible]

2,8,L
[illegible]

2,9,L
[illegible]

3,0,L
[illegible]

3,1,L
[illegible]

3,2,L
[illegible]

3,3,L
[illegible]

3,4,L
[illegible]

3,5,L
[illegible]

3,6,L
[illegible]

3,7,L
[illegible]

3,8,L
[illegible]

4,0,L
[illegible]

4,1,L
[illegible]

4,2,L
[illegible]

4,3,L
[illegible]

4,4,L
[illegible]

4,5,L
[illegible]

4,6,L
[illegible]

4,7,L
[illegible]

4,8,L
[illegible]

5,0,L
[illegible]

5,1,L
[illegible]

5,2,L
[illegible]

5,3,L
[illegible]

5,4,L
[illegible]

5,5,L
[illegible]

5,6,L
[illegible]

5,7,L
[illegible]

5,8,L
[illegible]

6,0,L
[illegible]

6,1,L
[illegible]

6,2,L
[illegible]

6,3,L
[illegible]

6,4,L
[illegible]

6,5,L
[illegible]

6,6,L
[illegible]

6,7,L
[illegible]

6,8,L
[illegible]

7,1,L
[illegible]

7,2,L
[illegible]

7,3,L
[illegible]

7,4,L
[illegible]

7,5,L
[illegible]

7,6,L
[illegible]

7,7,L
[illegible]

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 deliquescient 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 deliquescient 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 2θ values for 15 reflections. The data were taken, using CuKα radiation, as described for bis(ethylenediamine)palladium(II) chloride. The results are:

a = 12.2639(4) A
b = 8.9819(8)
c = 15.4861(10)

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 $0k\ell$ through $9k\ell$. The data were collected with Cu$k\alpha$ ($\lambda = 1.54178$ 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 Cu$k\alpha$ 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 $Pn2_1a$. 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 isomorph; 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 $B = 28\ A^2$ 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.[23] 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.[23] 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 Housty and Clastre[20] 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[21] 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 $|F_c| \leq F_o$. 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, $10 F_o$, and $10 F_c$. Unobserved reflections are marked by *. Reflections removed because of possible secondary extinction effects are marked by E.

0,0,L
[illegible]

0,1,L
[illegible]

0,2,L
[illegible]

0,3,L
[illegible]

0,4,L
[illegible]

0,5,L
[illegible]

0,6,L
[illegible]

0,7,L
[illegible]

0,8,L
[illegible]

0,9,L
[illegible]

0,10,L
[illegible]

1,0,L
[illegible]

1,1,L
[illegible]

1,2,L
[illegible]

1,3,L
[illegible]

1,4,L
[illegible]

1,5,L
[illegible]

1,6,L
[illegible]

1,7,L
[illegible]

1,8,L
[illegible]

1,9,L
[illegible]

2,0,L
[illegible]

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[illegible]

2,9,L
[illegible]

3,0,L
[illegible]

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[illegible]

3,3,L
[illegible]

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3,9,L
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4,0,L
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5,9,L
[illegible]

6,0,L
[illegible]

6,1,L
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6,2,L
[illegible]

6,3,L
[illegible]

6,4,L
[illegible]

6,5,L
[illegible]

6,6,L
[illegible]

6,7,L
[illegible]

7,0,L
[illegible]

7,1,L
[illegible]

7,2,L
[illegible]

7,3,L
[illegible]

7,4,L
[illegible]

7,5,L
[illegible]

7,6,L
[illegible]

7,7,L
[illegible]

8,0,L
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9,0,L
[illegible]

9,1,L
[illegible]

9,2,L
[illegible]

9,3,L
[illegible]

9,4,L
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9,5,L
[illegible]

9,6,L
[illegible]

9,7,L
[illegible]

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 $\underline{z}$ coordinate of the zinc atom and the $\underline{y}$ 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 $[N(CH_3)_4]_2MCl_4$.

Space group: Pnma, Z = 4

Cell Dimensions	Co	Ni	diffractometer Zn	film Zn
a	12.276(1)	12.2639(4)	12.276(2)	--
b	9.001(1)	8.9819(8)	8.998(2)	--
c	15.539(2)	15.4861(10)	15.541(2)	--
Method of data collection	film	film	diffractometer	film
Radiation	FeKα	CuKα	MoKα	CuKα & MoKα
Number of observed reflections	487	603	850	479
Number of unobserved reflections	315	436	433	182
Final R index	0.111	0.075	0.056	0.094
Weighting scheme	Hughes	Hughes	unit	Hughes

Table 12. Positional Parameters for $[N(CH_3)_4]_2MCl_4$

				diffractometer	film
Atom		Co	Ni	Zn	Zn
M	x/a	.2447(3)	.2429(2)	.2459(1)	.2459(4)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.4070(2)	.4070(1)	.4068(1)	.4073(2)
Cl(1)	x/a	.0631(7)	.0620(3)	.0631(3)	.0626(9)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.4055(6)	.4020(3)	.4062(3)	.4068(6)
Cl(2)	x/a	.3035(5)	.3018(3)	.3061(2)	.3057(7)
	y/b	.0432(6)	.0440(3)	.0456(3)	.0460(7)
	z/c	.3386(4)	.3401(2)	.3388(2)	.3387(4)
Cl(3)	x/a	.3145(8)	.3122(4)	.3142(4)	.3128(9)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.5420(5)	.5404(2)	.5414(2)	.5413(5)
N(1)	x/a	.1515(24)	.1463(10)	.1508(8)	.1537(30)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.0960(14)	.0958(6)	.0954(7)	.0979(13)
N(2)	x/a	.4936(19)	.4940(9)	.4914(8)	.4941(23)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.8269(15)	.8260(6)	.8256(6)	.8241(13)
C(1)	x/a	.2614(36)	.2678(12)	.2689(12)	.2737(47)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.0992(24)	.1006(12)	.1012(13)	.0968(27)
C(2)	x/a	.1118(28)	.1063(17)	.1098(17)	.1134(47)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.0043(26)	.0053(11)	.0084(11)	.0030(28)
C(3)	x/a	.1103(34)	.1046(16)	.1046(13)	.1042(38)
	y/b	.3737(39)	.3805(20)	.3708(18)	.3909(49)
	z/c	.1430(25)	.1407(13)	.1421(12)	.1368(31)
C(4)	x/a	.4370(38)	.4418(20)	.4436(20)	.4404(46)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.7378(27)	.7397(11)	.7377(11)	.7391(27)
C(5)	x/a	.4117(36)	.4119(20)	.4111(20)	.4072(57)
	y/b	.25(*)	.25(*)	.25(*)	.25(*)
	z/c	.8943(30)	.8964(15)	.8880(15)	.8847(41)
C(6)	x/a	.5404(38)	.5500(18)	.5530(16)	.5548(49)
	y/b	.3906(44)	.3873(18)	.3756(18)	.3788(50)
	z/c	.8434(21)	.8417(10)	.8415(10)	.8394(28)

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 $[N(CH_3)_4]_2MCl_4$

				diffractometer	film
		Co	Ni	Zn	Zn
M	B(11)	4.83(29)	8.42(12)	3.82(5)	4.41(47)
	B(22)	4.31(14)	6.10(8)	4.53(5)	5.23(14)
	B(33)	3.95(14)	5.26(7)	3.67(5)	4.37(13)
	B(12)	*	*	*	*
	B(13)	0.03(17)	-0.03(8)	0.08(6)	0.14(14)
	B(23)	*	*	*	*
Cl(1)	B(11)	4.21(62)	7.97(24)	3.78(15)	3.45(128)
	B(22)	7.45(43)	11.49(26)	9.31(24)	7.83(48)
	B(33)	7.09(42)	12.33(26)	9.58(24)	9.71(56)
	B(12)	*	*	*	*
	B(13)	0.43(39)	0.60(19)	0.33(18)	0.55(47)
	B(23)	*	*	*	*
Cl(2)	B(11)	7.17(41)	12.35(18)	8.02(15)	7.78(57)
	B(22)	6.11(26)	8.39(14)	6.80(14)	6.56(29)
	B(33)	8.82(33)	12.39(18)	10.75(19)	10.02(38)
	B(12)	1.44(25)	1.81(13)	1.86(13)	1.94(30)
	B(13)	0.55(28)	0.94(15)	0.65(15)	0.74(31)
	B(23)	-1.81(32)	-3.33(16)	-3.14(15)	-2.50(29)
Cl(3)	B(11)	8.28(73)	13.54(29)	8.65(26)	7.64(85)
	B(22)	14.07(75)	17.88(38)	16.70(41)	15.95(86)
	B(33)	4.27(35)	5.42(16)	4.24(17)	4.50(34)
	B(12)	*	*	*	*
	B(13)	-1.77(38)	-1.70(17)	-1.86(18)	-1.88(40)
	B(23)	*	*	*	*
N(1)	B(11)	5.25(192)	11.58(88)	4.34(46)	6.73(344)
	B(22)	3.30(89)	6.05(47)	5.04(49)	1.45(67)
	B(33)	4.96(103)	6.38(49)	6.12(54)	6.19(115)
	B(12)	*	*	*	*
	B(13)	-1.47(127)	0.19(51)	0.37(47)	-0.42(130)
	B(23)	*	*	*	*
N(2)	B(11)	4.03(154)	11.20(72)	4.65(49)	4.80(215)
	B(22)	3.57(93)	6.42(48)	4.99(49)	5.70(113)
	B(33)	5.97(125)	5.33(44)	4.31(46)	4.22(94)
	B(12)	*	*	*	*
	B(13)	-0.64(106)	-1.74(48)	-0.95(40)	-2.01(105)
	B(23)	*	*	*	*

Table 13. Continued

				diffractometer	film
		Co	Ni	Zn	Zn
C(1)	B(11)	3.23(323)	5.22(99)	3.79(74)	2.37(464)
	B(22)	23.40(506)	26.52(227)	21.55(205)	10.66(283)
	B(33)	8.56(221)	15.23(137)	12.03(128)	13.58(309)
	B(12)	*	*	*	*
	B(13)	-0.79(200)	-0.64(83)	-0.12(83)	-1.41(248)
	B(23)	*	*	*	*
C(2)	B(11)	2.29(255)	15.65(142)	11.63(148)	10.06(410)
	B(22)	31.63(656)	27.00(238)	23.67(239)	31.90(745)
	B(33)	8.70(230)	7.22(76)	6.64(96)	6.66(178)
	B(12)	*	*	*	*
	B(13)	-2.42(176)	-3.95(88)	-3.89(96)	-4.92(210)
	B(23)	*	*	*	*
C(3)	B(11)	16.90(305)	19.59(126)	14.68(120)	12.52(343)
	B(22)	11.94(220)	18.61(127)	15.66(124)	17.10(311)
	B(33)	19.20(320)	27.17(177)	22.37(160)	25.15(407)
	B(12)	5.66(205)	9.65(102)	5.46(101)	0.36(249)
	B(13)	-0.82(237)	-2.70(121)	-2.04(113)	2.87(289)
	B(23)	-7.31(246)	-12.27(135)	-11.26(121)	-13.14(320)
C(4)	B(11)	13.19(368)	25.93(207)	21.02(202)	17.34(452)
	B(22)	13.41(318)	11.61(110)	10.90(120)	11.83(290)
	B(33)	9.08(261)	11.16(110)	7.80(104)	10.32(264)
	B(12)	*	*	*	*
	B(13)	-4.40(237)	-10.21(123)	-9.31(121)	-10.29(284)
	B(23)	*	*	*	*
C(5)	B(11)	6.57(322)	14.92(184)	11.36(165)	13.01(571)
	B(22)	25.29(570)	39.20(490)	35.05(379)	44.24(1242)
	B(33)	10.71(312)	14.67(164)	10.52(151)	11.36(364)
	B(12)	*	*	*	*
	B(13)	3.55(241)	4.30(141)	1.42(132)	0.65(387)
	B(23)	*	*	*	*
C(6)	B(11)	26.36(451)	37.78(242)	29.45(201)	32.12(719)
	B(22)	14.92(271)	16.61(114)	16.79(127)	19.41(338)
	B(33)	10.98(215)	16.18(108)	15.16(119)	18.14(311)
	B(12)	-10.35(291)	-16.98(146)	-17.49(140)	-21.56(442)
	B(13)	-5.82(250)	-10.87(132)	-9.42(131)	-14.23(406)
	B(23)	1.24(233)	7.61(98)	7.47(105)	9.47(285)

* Required by symmetry to be equal to zero.

The temperature factor is defined by: $\exp\left[-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B(ij)\,h(i)\,h(j)\,a(i)^{*}\,a(j)^{*}\right]$

Estimated standard deviations in the last significant figures are given in parentheses.

Table 14. Bond Lengths and Angles for $[N(CH_3)_4]_2MCl_4$

Distance	Co	Ni	diffractometer Zn	film Zn
M - Cl(1)	2.229(9) A	2.220(4) A	2.244(4) A	2.250(12) A
M - Cl(2)	2.261(6)	2.240(3)	2.246(3)	2.246(7)
M - Cl(3)	2.266(9)	2.234(4)	2.253(4)	2.238(9)
N(1) - C(1)	1.35(5)	1.49(2)	1.45(2)	1.47(7)
N(1) - C(2)	1.51(5)	1.49(2)	1.44(2)	1.56(5)
N(1) - C(3)	1.43(4)	1.46(2)	1.42(2)	1.53(5)
N(2) - C(4)	1.55(5)	1.48(2)	1.49(2)	1.48(5)
N(2) - C(5)	1.45(5)	1.49(3)	1.38(3)	1.42(7)
N(2) - C(6)	1.41(4)	1.43(2)	1.38(2)	1.40(5)
Angle				
Cl(1) - M - Cl(2)	108.3(2)°	107.8(1)°	109.1(1)°	109.0(3)°
Cl(1) - M - Cl(2)'				
Cl(1) - M - Cl(3)	112.8(4)	114.4(2)	112.1(2)	111.8(4)
Cl(3) - M - Cl(2)	108.3(2)	107.8(1)	108.4(1)	108.8(3)
Cl(3) - M - Cl(2)'				
Cl(2) - M - Cl(2)'	110.8(4)	111.4(2)	109.9(2)	109.6(4)
C(1) - N(1) - C(2)	111(3)	112(1)	114(1)	108(3)
C(1) - N(1) - C(3)	110(2)	109(1)	111(1)	114(2)
C(1) - N(1) - C(3)'				
C(2) - N(1) - C(3)	112(2)	110(1)	110(1)	104(2)
C(2) - N(1) - C(3)'				
C(3) - N(1) - C(3)'	103(4)	107(2)	99(2)	112(4)
C(4) - N(2) - C(5)	110(3)	112(1)	111(1)	105(4)
C(4) - N(2) - C(6)	110(2)	111(1)	112(1)	113(2)
C(4) - N(2) - C(6)'				
C(5) - N(2) - C(6)	99(2)	102(1)	105(1)	107(3)
C(5) - N(2) - C(6)'				
C(6) - N(2) - C(6)'	127(4)	119(2)	110(2)	112(5)

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.

Table 15. RMS Component of Thermal Displacements Along Principal Axes for $[N(CH_3)_4]_2$ MCl_4 in Angstroms.

				diffractometer	film
Atom	Axis	Co	Ni	Zn	Zn
M	1	0.224(4)	0.258(2)	0.215(2)	0.232(6)
	2	0.234(4)*	0.278(2)*	0.221(2)	0.240(8)
	3	0.247(8)	0.327(2)	0.240(1)*	0.257(4)*
Cl(1)	1	0.229(17)	0.316(5)	0.218(4)	0.208(39)
	2	0.301(9)	0.382(4)*	0.343(5)*	0.315(10)*
	3	0.307(9)*	0.397(4)	0.349(4)	0.352(10)
Cl(2)	1	0.235(7)	0.273(3)	0.228(3)	0.228(8)
	2	0.318(8)	0.406(3)	0.337(3)	0.336(10)
	3	0.351(7)	0.425(3)	0.398(4)	0.379(7)
Cl(3)	1	0.214(10)	0.254(4)	0.212(5)	0.214(10)
	2	0.337(14)	0.419(5)	0.344(5)	0.329(16)
	3	0.422(11)*	0.476(5)*	0.460(6)*	0.450(12)*
N(1)	1	0.20(3)*	0.28(1)*	0.23(1)	0.14(3)*
	2	0.21(4)	0.28(1)	0.25(1)*	0.27(3)
	3	0.29(4)	0.38(1)	0.28(1)	0.30(6)
N(2)	1	0.21(3)*	0.25(1)	0.21(1)	0.18(4)
	2	0.22(4)	0.29(1)*	0.25(1)*	0.27(3)*
	3	0.28(3)	0.38(1)	0.26(1)	0.29(4)
C(1)	1	0.20(10)	0.26(2)	0.22(2)	0.17(17)
	2	0.33(4)	0.44(2)	0.39(2)	0.37(5)*
	3	0.54(6)*	0.58(2)*	0.52(2)*	0.42(5)
C(2)	1	0.14(11)	0.27(2)	0.24(2)	0.20(6)
	2	0.35(5)	0.47(2)	0.42(2)	0.41(6)
	3	0.63(7)*	0.58(3)*	0.55(3)*	0.64(7)*
C(3)	1	0.27(4)	0.28(1)	0.28(2)	0.29(4)
	2	0.46(4)	0.50(2)	0.43(2)	0.41(5)
	3	0.57(4)	0.70(2)	0.64(2)	0.67(5)
C(4)	1	0.28(5)	0.27(2)	0.19(2)	0.19(5)
	2	0.41(5)*	0.38(2)*	0.37(2)*	0.39(5)*
	3	0.45(5)	0.63(2)	0.57(3)	0.56(6)

Table 15. Continued

Atom	Axis	Co	Ni	diffractometer Zn	film Zn
C(5)	1	0.24(7)	0.36(2)	0.35(3)	0.38(6)
	2	0.40(6)	0.49(3)	0.40(3)	0.41(9)
	3	0.57(6)*	0.70(4)*	0.67(4)*	0.75(11)*
C(6)	1	0.30(4)	0.29(1)	0.24(2)	0.20(5)
	2	0.37(4)	0.38(1)	0.37(2)	0.37(4)
	3	0.65(5)	0.81(2)	0.77(2)	0.84(8)

*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

Atom	ellipsoid axis	cell edge	Co	Ni	diffractometer Zn	film Zn
M	1	a	92(11)	89(1)	113(13)	131(54)
		b	*	*	*	*
		c	2(11)	1(1)	23(13)	41(54)
	2	a	+	+	157(13)	139(54)
		b			*	*
		c			113(13)	131(54)
	3	a	2(11)	1(1)	+	+
		b	*	*		
		c	88(11)	91(1)		
Cl(1)	1	a	8(7)	8(2)	3(2)	5(4)
		b	*	*	*	*
		c	98(7)	98(2)	93(2)	95(4)
	2	a	82(7)	+	+	+
		b	*			
		c	8(7)			
	3	a	+	82(2)	87(2)	85(4)
		b		*	*	*
		c		8(2)	3(2)	5(4)
Cl(2)	1	a	119(4)	107(1)	116(1)	119(4)
		b	38(3)	34(1)	38(1)	39(3)
		c	68(3)	62(1)	65(1)	67(2)
	2	a	151(4)	162(2)	153(1)	150(4)
		b	113(6)	104(4)	110(2)	113(5)
		c	106(9)	101(6)	107(2)	108(7)
	3	a	94(8)	93(7)	95(2)	95(7)
		b	118(5)	120(2)	120(1)	119(4)
		c	28(6)	30(3)	30(2)	30(5)
Cl(3)	1	a	69(4)	79(1)	70(2)	65(5)
		b	*	*	*	*
		c	21(4)	11(1)	20(2)	25(5)
	2	a	159(4)	169(1)	160(2)	155(5)
		b	*	*	*	*
		c	69(4)	79(1)	70(2)	65(5)
	3	a	+	+	+	+
		b				
		c				

Table 16. Continued

	ellipsoid	cell			diffractometer	film
Atom	axis	edge	Co	Ni	Zn	Zn
N(1)	1	a	+	+	11(14)	+
		b			*	
		c			101(4)	
	2	a	132(24)	88(6)	+	119(107)
		b	*	*		*
		c	138(24)	178(6)		151(107)
	3	a	138(24)	2(6)	79(14)	29(107)
		b	*	*	*	*
		c	48(24)	88(6)	11(14)	119(107)
N(2)	1	a	+	75(4)	50(11)	49(18)
		b		*	*	*
		c		15(4)	40(11)	41(18)
	2	a	163(27)	+	+	+
		b	*			
		c	107(27)			
	3	a	107(27)	15(4)	140(11)	139(18)
		b	*	*	*	*
		c	17(27)	105(4)	50(11)	49(18)
C(1)	1	a	8(21)	4(5)	1(6)	7(12)
		b	*	*	*	*
		c	82(21)	86(5)	89(6)	83(12)
	2	a	82(21)	86(5)	89(6)	+
		b	*	*	*	
		c	172(21)	176(5)	179(6)	
	3	a	+	+	+	83(12)
		b				*
		c				173(12)
C(2)	1	a	18(13)	68(4)	61(6)	55(12)
		b	*	*	*	*
		c	71(13)	22(4)	29(6)	35(12)
	2	a	71(13)	158(4)	151(6)	145(12)
		b	*	*	*	*
		c	161(13)	68(4)	61(6)	55(12)
	3	a	+	+	+	+
		b				
		c				

Table 16. Continued

Atom	ellipsoid axis	cell edge	Co	Ni	diffractometer Zn	film Zn
C(3)	1	a	112(8)	120(3)	112(5)	109(19)
		b	35(6)	39(2)	38(2)	42(9)
		c	65(7)	67(2)	61(3)	54(6)
	2	a	145(14)	141(4)	152(5)	160(18)
		b	95(12)	101(3)	98(5)	109(16)
		c	125(16)	127(4)	116(4)	97(13)
	3	a	116(16)	113(3)	106(4)	85(8)
		b	124(6)	127(2)	127(2)	126(6)
		c	45(14)	46(3)	41(3)	36(5)
C(4)	1	a	57(15)	63(2)	63(3)	54(7)
		b	*	*	*	*
		c	33(15)	27(2)	27(3)	36(7)
	2	a	+	+	+	+
		b				
		c				
	3	a	33(15)	27(2)	27(3)	36(7)
		b	*	*	*	*
		c	123(15)	117(2)	117(3)	126(7)
C(5)	1	a	150(18)	134(9)	127(24)	109(106)
		b	*	*	*	*
		c	60(18)	44(9)	37(24)	19(106)
	2	a	120(18)	136(9)	143(24)	161(106)
		b	*	*	*	*
		c	150(18)	134(9)	127(24)	109(106)
	3	a	+	+	+	+
		b				
		c				
C(6)	1	a	59(7)	67(4)	57(3)	51(5)
		b	53(19)	28(2)	34(2)	40(7)
		c	52(22)	105(8)	96(6)	84(10)
	2	a	81(13)	115(4)	111(4)	105(8)
		b	50(19)	94(7)	83(6)	70(10)
		c	139(22)	154(5)	158(3)	155(6)
	3	a	32(6)	35(2)	40(2)	43(4)
		b	119(6)	118(1)	123(2)	123(3)
		c	104(6)	110(2)	111(2)	114(5)

*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 A, the more usual values ranging up to about 0.32 A, while the values in the present structures range to a maximum of 0.81 A. 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 over-all 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.

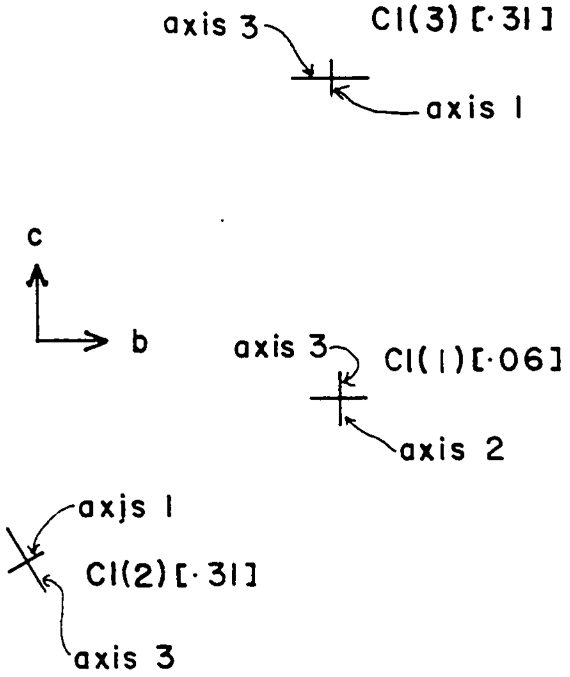
			angle between axis and vector			
					diffractometer	film
Atom	axis	defining vector	Co	Ni	Zn	Zn
Cl(1)	1	M - Cl(1)	171°	170°	177°	175°
	2		81	90	90	90
	3		90	100	93	95
Cl(2)	1	M - Cl(2)	169	179	173	169
	2		80	91	83	80
	3		93	90	91	92
Cl(3)	1	M - Cl(3)	2	11	2	4
	2		92	101	92	86
	3		90	90	90	90
C(1)	1	N(1) - C(1)	6	1	3	8
	2		84	89	93	90
	3		90	90	90	98
C(2)	1	N(1) - C(2)	127	178	172	163
	2		37	92	98	107
	3		90	90	90	90
C(3)	1	N(1) - C(3)	6	9	2	12
	2		94	99	89	87
	3		86	91	88	102
C(4)	1	N(2) - C(4)	174	179	176	171
	2		90	90	90	90
	3		84	89	86	81
C(5)	1	N(2) - C(5)	164	1	9	30
	2		106	91	81	60
	3		90	90	90	90
C(6)	1	N(2) - C(6)	31	26	16	7
	2		60	115	105	91
	3		97	94	95	97

The e.s.d.'s range from 1 to 10 degrees.

individual level scale factors to be completely degenerate[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 $[MCl_4]^{2-}$ 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 $[MCl_4]^{2-}$ 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 $\underline{x}$ coordinates of the atoms. Cl(1) and Cl(3) lie in the mirror plane.


axis 3
Cl(3) [·31]
axis 1
c
b
axis 3
Cl(1)[·06]
axis 2
axjs 1
Cl(2) [·31]
axis 3

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 os interest to examine the metal-chlorine distances and the distortion of the $[MCl_4]^{2-}$ tetrahedra.

The ionic radii of the Co(II), Ni(II), and Zn(II) ions, as given by Pauling,[46] are 0.74, 0.72, and 0.74 A, 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 A 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 A, 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, therfore, the errors are probably quite large. This would mean that the value of 2.27 A for the nickel-chlorine bond length is probably not significantly different from the values obtained in the present investigation.

The $[MCl_4]^{2-}$ 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 $\bar{4}$ 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 $[MCl_4]^{2-}$ 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 tetrachlorocuprate(II), which is approximately isomorphous with the present structures, contains a tetrahedral $[CuCl_4]^{2-}$ 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 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 N-substituted-salicylaldimine[2, 14] complexes as the only accurately determined crystal structures of tetrahedrally coordinated nickel.

The phase diagram of the $CsCl$-$NiCl_2$ system has been determined by Iberson, Gut, and Gruen[22] and they find that below 50 mole % $NiCl_2$ there is a solid to solid color change from yellow to blue at 417° C caused by the formation of the compound, Cs_3NiCl_5, which they have shown to be isomorphous to Cs_3CoCl_5 by powder methods.

Cs_3CoCl_5 is known to contain $[CoCl_4]^{2-}$ tetrahedra; therefore Cs_3NiCl_5 presumably contains $[NiCl_4]^{2-}$ 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 $[NiCl_4]^{2-}$ ion.

APPENDIX

THE CRYSTAL STRUCTURE OF TETRAETHYLENEPENTAMINENICKEL(II) THIOCYANATE, $Ni(C_8N_5H_{23})(SCN)_2$

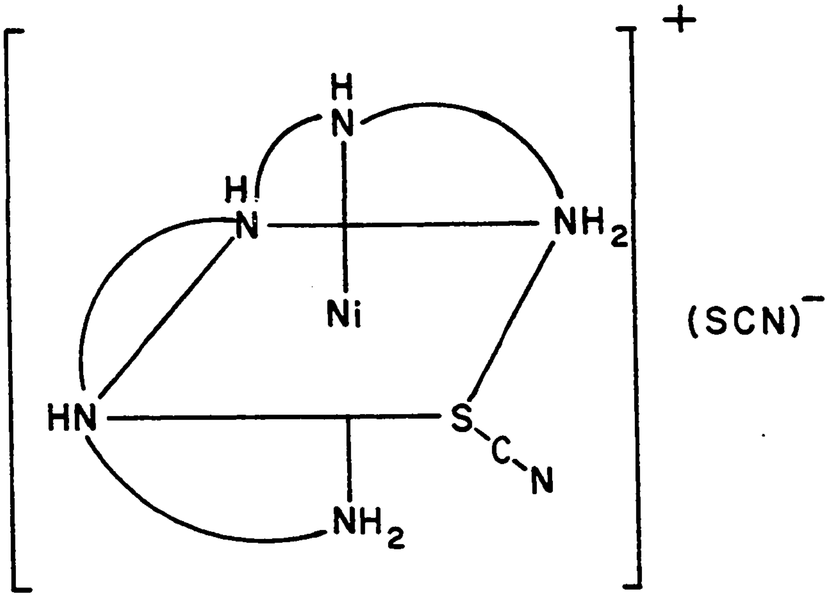
Crystals of tetraethylenepentaminenickel(II) thiocyanate were given to Professor E. C. Lingafelter by Professor P. Paoletti, University of Florence, Italy. A reasonable molecular structure for this compound would be as shown in Figure 5. It would also be possible for the tetraethylenepentamine to be tetradentate 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.

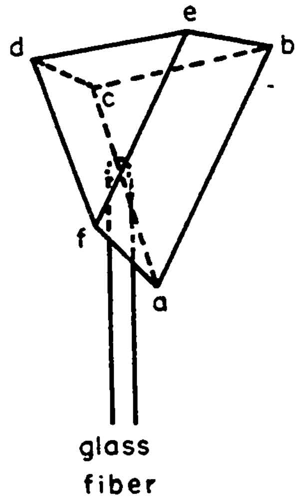
Preliminary rotation and Weissenberg photographs and investigation on x-ray diffractometer showed the Laue symmetry to be m3m. Systematic absences of $hk\ell$ for $h+k$, $k+\ell$, and $\ell+h = 2n+1$ showed the possible space groups to be F 432, F $\bar{4}$3m, or F m3m. The lattice parameter was determined, using MoKα (λ= 0.71069 A) radiation, from the least squares refinement of 2θ values for thirteen reflections measured on a single-crystal x-ray diffractometer. It is: $\underline{a}$ = 15.522(3) A.

The crystal chosen for intensity measurements was a truncated tetrahedron exhibiting {111} and (11$\bar{1}$). The [1$\bar{1}$0] 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.





abef = (111)
def = $(11\bar{1})$
abc = $(\bar{1}\bar{1}1)$
acdf = $(\bar{1}1\bar{1})$
bcde = $(1\bar{1}\bar{1})$

$(11\bar{1})$ and $(\overline{11}1)$ was approximately 0.176 mm. It was mounted along [100] and intensity measurements were taken by the ω-2θ scan method (moving crystal-moving counter) on a Picker diffractometer equipped with a General Electric single-crystal orienter. 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 2θ 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.[6] 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 $\mathrm{gm/cm^3}$. The density calculated on the basis of four molecules in the cell is 1.236 $\mathrm{gm/cm^3}$ and that calculated on the basis of five molecules in the cell is 1.545 $\mathrm{gm/cm^3}$. 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 $B = 6.194\ A^2$. 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.

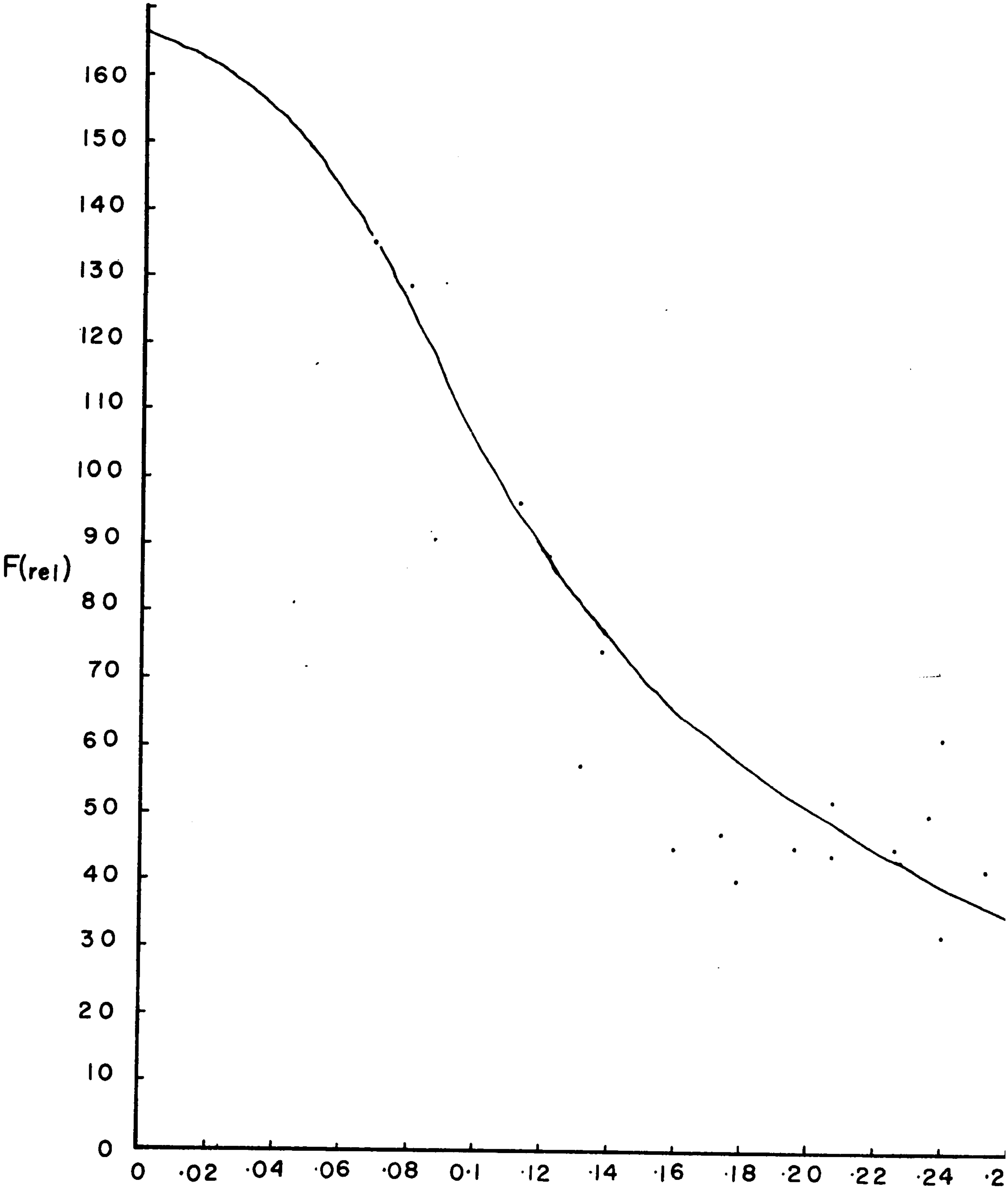
At this point it was noticed that the relative structure factors monotonically decreased in value with increasing $(\sin\theta)/\lambda$. This is the behavior that would be expected if there were only one atom in the cell and it was at the origin. Each structure factor would have the value of the scattering 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.

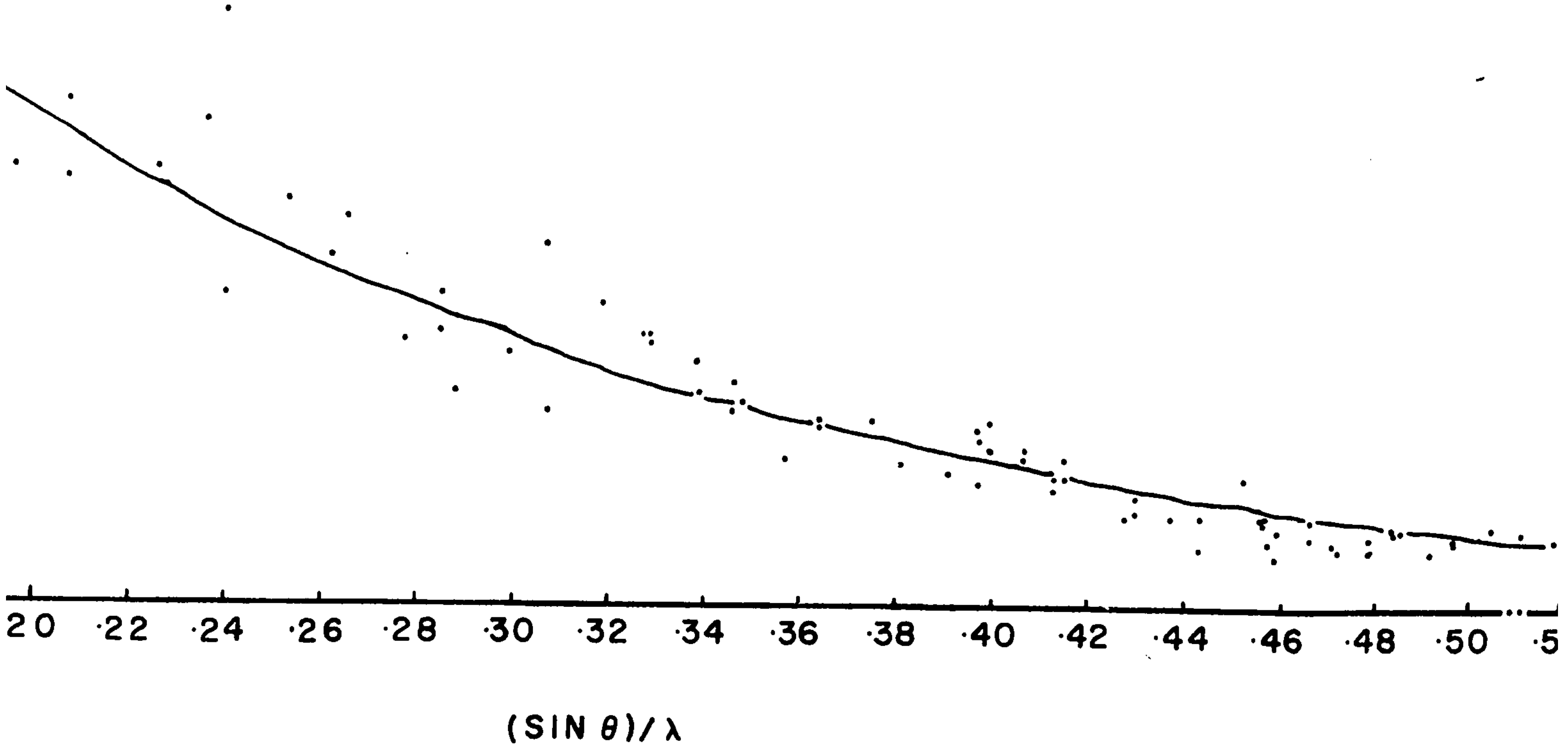
In order to test the goodness of fit of this model, a structure factor calculation was carried out with one atom, whose scattering factor is the curve drawn in Figure 7, at the origin with a temperature factor of zero. A list of these calculated structure factors along with the observed structure factors 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 ΔF synthesis was calculated phased on the previous structure factor calculation. There were seven independent peaks apparent in this ΔF synthesis ranging in height from 2.8 e^-/A^3 to 0.75 e^-/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 $(\sin\theta)/\lambda$.


F(rel)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
·02
·04
·06
·08
0·1
·12
·14
·16
·18
·20
·22
·24
·2


20
·22
·24
·26
·28
·30
·32
·34
·36
·38
·40
·42
·44
·46
·48
·50
·5
(SIN θ)/λ

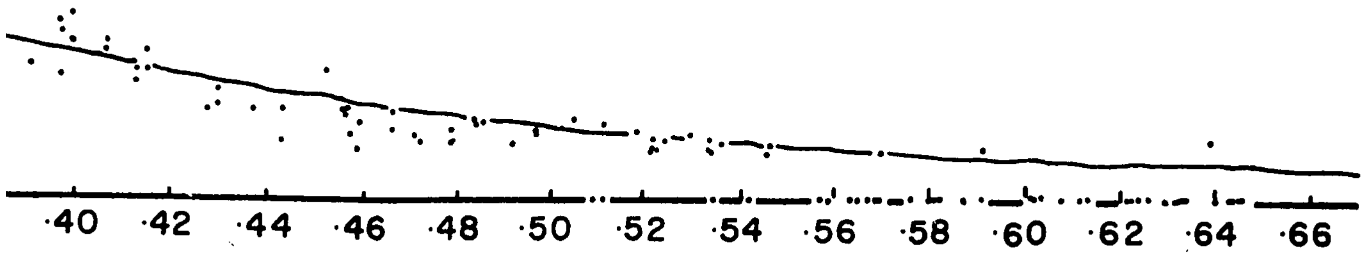

·40
·42
·44
·46
·48
·50
·52
·54
·56
·58
·60
·62
·64
·66

Table 18. Observed and calculated structure factors for tetraethylenepentaminenickel(II) thiocyanate. The columns are k index, 10 F_o, and 10 F_c. Unobserved reflections are marked by *.

0,K,0

2	5522	5025
4	1915	2648
6	2624	1584
8	1341	991
10	813	597
12	255	341
14	201*	201
16	249	136

0,K,2

2	4126	3810
4	1729	2115
6	1808	1464
8	1205	937
10	643	566
12	334	323
14	202*	194
16	213*	135

0,K,4

4	1945	1719
6	954	1181
8	670	789
10	467	488
12	337	275
14	202*	176

0,K,6

6	1083	886
8	690	597
10	404	379
12	209*	229
14	207*	151

0,K,8

8	565	421
10	194*	262
12	203*	182
14	213*	135

0,K,10

10	208*	194
12	216*	141

1,K,1

1	5780	5408
3	2439	3258
5	1909	1924
7	1379	1201
9	834	756
11	265	448
13	274	245
15	202*	158

1,K,3

3	2017	2184
5	2136	1616
7	876	1062
9	624	675
11	384	405
13	231	231
15	205*	148

1,K,5

5	1200	1201
7	876	848
9	524	544
11	325	327
13	200*	202
15	208*	138

1,K,7

7	789	605
9	381	405
11	215	245
13	204*	167

1,K,9

9	199*	265
11	206*	189
13	209*	138

1,K,11

11	216*	142

2,K,2

2	3176	3118
4	1920	2058
6	1709	1359
8	933	886
10	659	537
12	241	306
14	208	188

2,K,4

4	1375	1584
6	1132	1107
8	667	745
10	399	465
12	277	262
14	210*	171

2,K,6

6	894	836
8	678	566
10	269	360
12	229*	221
14	214*	147

2,K,8

8	325	399
10	309	251
12	209*	176

2,K,10

10	208*	188
12	218*	139

3,K,3

3	2226	1924
5	1539	1384
7	1209	951
9	543	605
11	281	364
13	242	216
15	213*	142

3,K,5

5	1597	1062
7	797	756
9	381	494
11	293	294
13	218*	189
15	216*	135

3,K,7

7	561	544
9	195	364
11	223	231
13	211*	158

3,K,9

9	210	245
11	208*	178
13	216*	135

3,K,11

11	218*	138

4,K,4

4	1172	1265
6	1153	937
8	587	630
10	232	399
12	281	236
14	213*	156

4,K,6

6	803	704
8	407	488
10	229*	306
12	235*	201
14	215*	139

4,K,8

8	294	341
10	234	229
12	220*	161

4,K,10

10	212*	171
12	219*	135

5,K,5

5	1008	848
7	729	605
9	278	405
11	225	245
13	223	167

5,K,7

7	398	448
9	292	294
11	207*	202
13	237*	142

5,K,9

9	211	216
11	212*	158

6,K,6

6	575	537
8	292	379
10	271	243
12	211*	171

6,K,8

8	327	262
10	218*	194
12	215*	141

6,K,10

10	215*	147

7,K,7

7	352	327
9	273	231
11	211*	167

7,K,9

9	210*	178
11	218*	138

8,K,8

8	209*	207
10	213*	156

9,K,9

9	218*	142

Table 19. Peaks in the ΔF Synthesis

x/a	y/b	z/c	height (e^-/A^3)
0.0	0.0	0.0	1.6
0.14	0.0	0.0	2.0
0.12	0.12	0.0	2.2
0.39	0.0	0.0	2.8
0.50	0.0	0.0	0.75
0.13	0.13	0.13	2.6
0.19	0.31	0.19	2.1

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