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The Crystal and Molecular Structure of Tetraethylammonium Tetrachloronickelate(II)*

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The crystal structure of tetraethylammonium tetrachloronickelate(II) has been determined by full-matrix least-squares refinement of three-dimensional Mo $K\alpha$ intensity data. The space group is $P4_2/nmc$, with $Z=2$. Cell constants are $a=b=9{\cdot}05$, $c=15{\cdot}01$ Å. The corresponding cobalt salt is isomorphous, with $a=b=9{\cdot}00$, $c=14{\cdot}97$ Å. The tetraethylammonium groups were found to be disordered about intersecting mirror planes. Qualitatively, the distortions of the anion from tetrahedral symmetry are similar to those of the $CoCl_4^{2-}$ anion in Cs_3CoCl_5.

Introduction

Compounds containing the tetrahedral tetrahalonickelate(II) anion have been the subject of numerous recent investigations (Figgis, Lewis, Mabbs & Webb, 1966; Bose, Mitra & Rai, 1965; Ballhausen, 1964). Figgis & Lewis (1964) first proposed that the magnetic properties of the tetrahalonickelate(II) anions could be explained in terms of deviations from T_d symmetry. For this reason and as part of a study of the structural and magnetic properties of first row transition metal halide complexes (Stucky, D'Agostino & McPherson, 1966), the determination of the three-dimensional crystal structure of $[(C_2H_5)_4N]_2NiCl_4$ was undertaken.

Experimental

Crystals of $[(C_2H_5)_4N]_2NiCl_4$ and $[(C_2H_5)_4N]_2CoCl_4$ were obtained by first preparing solutions of reagent grade $(C_2H_5)_4NCl$ and anhydrous metal chloride in hot nitromethane, then slowly adding the metal chloride solution to an excess of $(C_2H_5)_4NCl$. On cooling and allowing the nitromethane to evaporate in a desiccator, large blue polyhedral crystals of both compounds were formed. The nickel crystals are aqua when seen in aggregates of small crystals, while those of cobalt are royal blue. $[(C_2H_5)_4N]_2NiCl_4$ crystals are deliquescent if the relative humidity is 60% or higher.

Analyses

Calc. for $C_{16}H_{40}N_2NiCl_4$: C 41·7, H 8·8, N 6·1, Ni 12·7, Cl 30·7%. M.W. 461·03. Found: C 42·2, H 8·7, N 5·3, Ni 12·4, Cl 29·3%.

Calc. for $C_{16}H_{40}N_2CoCl_4$: C 41·7, H 8·7, N 6·1, Co 12·8, Cl 30·7%. M.W. 461·25. Found: C 40·0, H 8·4, N 5·1, Co 13·6, Cl 30·0%.

A careful optical examination of crystals was made before the X-ray data were collected. No twinning or peculiar extinction effects were observed in polarized light and both compounds were found to be uniaxial positive. In agreement with the latter observation, the Laue symmetry for both crystals was determined from Weissenberg and precession photographs to be $P4/mmm$ (D_{4h}). For $[(C_2H_5)_4N]_2CoCl_4$, precession data (Mo $K\alpha$) gave

$$a=b=9{\cdot}00\pm0{\cdot}02\ \text{Å}$$
$$c=14{\cdot}97\pm0{\cdot}03\ \text{Å}$$
$$V=1213{\cdot}3\ \text{Å}^3\,.$$

The film to crystal distance was calibrated with a single-crystal zero layer photograph of sodium chloride. Lattice constants for $[(C_2H_5)_4N]_2NiCl_4$ were determined with Mo $K\alpha$ radiation and a Picker diffractometer to be

$$a=b=9{\cdot}05\pm0{\cdot}01\ \text{Å}$$
$$c=15{\cdot}01\pm0{\cdot}02\ \text{Å}$$
$$V=1230{\cdot}6\ \text{Å}^3\,.$$

The calculated and observed densities are 1·26 and 1·28 ± 0·03 g.cm^{-3} for $[(C_2H_5)_4N]_2CoCl_4$ and 1·26 and 1·25 ± 0·03 g.cm^{-3} for $[(C_2H_5)_4N]_2NiCl_4$. Densities were determined by the flotation method in a 10 ml pycnometer and a mixture of 2-bromopentane and *p*-bromotoluene at 24°C. The pycnometer was calibrated with distilled water at the same temperature.

Crystals of $[(C_2H_5)_4N]_2NiCl_4$ and $[(C_2H_5)_4]_2CoCl_4$ were mounted with [010] parallel to the camera rotation axis and the space group determined from zero through third-level Weissenberg and precession photographs. The systematic absences are $hk0$, $h+k\neq2n$; hhl, $l\neq2n$. The space group was uniquely determined to be $P4_2/nmc$ (D_{4h}^{15}) for both $[(C_2H_5)_4N]_2NiCl_4$ and $[(C_2H_5)_4N]_2CoCl_4$. No further studies were made of the cobalt complex and the following discussion refers entirely to $[(C_2H_5)_4N]_2NiCl_4$.

Determination of the structure

Two three-dimensional sets of X-ray data were collected for the solution of the structure. Weissenberg and precession film data were collected on a poly-

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hedral crystal (maximum diameter less than 0·15 mm) with Mo $K\alpha$ radiation. 542 reflections were measured by Weissenberg multiple-film techniques and visual comparison of intensities with a series of timed exposures of the 103 reflection. 191 of these were related by symmetry to members of the remaining 351 reflections and were averaged with these after Lorentz and polarization corrections were made for the crystal rotating about [010]. Of the 351 reflections, 98 were unobserved. The linear absorption coefficient for Mo $K\alpha$ was estimated to be 11·8 cm^{-1} and no absorption corrections were made.

The most probable positions for the atoms with 2 molecules in a cell are:

Ni atoms in set 2(*b*) with D_{2d} symmetry: $\pm(\frac{3}{4},\frac{1}{4},\frac{1}{4})$
Cl atoms in set 8(*g*) with C_s symmetry: $\pm(\frac{1}{4},x,z;\ \frac{1}{4},\frac{1}{2}-x,z;\ x,\frac{1}{4},\frac{1}{2}+z;\ \frac{1}{2}-x,\frac{1}{4},\frac{1}{2}+z)$
N atoms in set 4(*d*) with C_{2v} symmetry: $\pm(\frac{1}{4},\frac{1}{4},z;\ \frac{1}{4},\frac{1}{4},\frac{1}{2}+z)$

Methylene carbon atoms in set 8(*g*) and methyl carbon atoms in set 8(*g*).

The chlorine and carbon atoms cannot be on the C_2 axes required by set 8(*f*) if the nickel is assumed to be tetrahedrally coordinated, and similarly the highest crystallographic symmetry the carbon atoms can have is mirror (C_s) symmetry. The approximate nickel and chlorine positions were determined from the above considerations assuming T_d symmetry for the $NiCl_4^{2-}$ anions and a nickel–chlorine distance of 2·3 Å based on the cobalt–chlorine distances in $CoCl_4^{2-}$ (Figgis, Gerloch & Mason, 1964). The magnitude of the *c* axis did not permit the nitrogen atoms to be placed in the set 4(*c*). Structure factors were calculated and the nitrogen position was found to be ($\frac{1}{4},\frac{1}{4}$,0·09) from the resulting Fourier synthesis. Assignments found for the carbon atoms were ambiguous, and least-squares refinement of the film data was used to differentiate between two possible sets of positions for the carbon atoms (see below). Adjustments were made to the chlorine position and structure factors again calculated, this time including the nitrogen atom. A Patterson map was also calculated at this point and was found to be consistent with the above interpretation of the nickel, chlorine and nitrogen positions.

Ni^0, Cl^0, N^0 and C^0 scattering factors from Table 3.3.2*C* of *International Tables for X-ray Crystallography* (1962) were used in the least-squares refinement. The weighting scheme used was

$$\sigma(F) = \frac{|F|}{\sqrt{n}\sqrt{30}}\left[\frac{6I_{\min}}{I_{\text{obs}}}\right]^2 ;\ I_{\text{obs}} \le 6I_{\min}$$

$$\sigma(F) = \frac{F}{\sqrt{n}\sqrt{30}}\ \frac{I_{\text{obs}}}{6I_{\min}} ;\ I_{\text{obs}} > 6I_{\min} ,$$

where *n* is the number of times a given reflection was observed through its equivalent forms. Unobserved reflections were given raw intensities equal to $I_{\min}/3$.

There are surprisingly few structures reported in the literature of the tetraethylammonium group and in all of these the carbon positions are poorly defined. The two orientations which seem to be preferred by the tetraethylammonium ion are a 'swastika' configuration, and a *trans* arrangement in which the ethyl carbon atoms lie on mirror planes. Some recent structures by Forrester, Zalkin & Templeton (1964) show that the tetra-n-butylammonium cation approaches the latter configuration. The tetraethyl groups were refined in both the swastika (disordered) and the *trans* (ordered) configurations. The best fit was obtained with a disordered swastika model in which the methylene carbon atoms were rotated approximately 45° from the two mirror planes which intersected at the nitrogen position, and the chlorine atoms were slightly off ($x=0{\cdot}22$) the mirror plane at $x=0{\cdot}25$. For observed data, isotropic least-squares refinement gave

$$R_1 = \frac{\Sigma\,||F_o|-|F_c||}{\Sigma\,|F_o|} = 0{\cdot}149\,.$$

The results of the above analysis were unsatisfactory primarily because large isotropic thermal parameters found for two of the carbon atoms prevented their refinement. Secondly, a difference Fourier synthesis of the isotropic model suggested significant anisotropic displacement of the Cl and the C atoms about their refined positions. This latter problem could have been solved by collecting a second set of film data about another crystallographic axis; however, since at the time a Picker diffractometer became available it was decided to collect three-dimensional diffractometer data. The following discussion pertains to these data.

The crystal used for diffractometer data was grown from a new preparation of $[(C_2H_5)_4N]_2NiCl_4$ and was ground to an approximate sphere in a dry box. After mounting the crystal in a capillary, a closer examination showed that the crystal could be approximated by an ellipsoid with axial diameters of 0·34, 0·44 and 0·34 mm. Absorption corrections were made for all reflections using this boundary surface and led to transmission factors ranging from 0·68 to 0·74. The crystal was examined optically, as well as with Weissenberg and precession photographs, and showed no evidence of twinning. The optical and crystallographic properties given above were confirmed with this second crystal.

The diffracted beams were filtered through 3·0 mil zirconium foil. The pulse height analyzer was centered on the Mo $K\alpha$ peak to allow approximately 90% transmission. Linearity of response was checked and the linear counting range was not exceeded during the data collection. The intensities were collected by the θ–2θ scan technique, with a take-off angle of 0·6° and a scan rate of 1 °min⁻¹. This take-off angle gave a peak intensity for a typical reflection of about 90% of the maximum value as a function of take-off angle. The 2θ scan range used was from 0·75° below to 0·91° above the Mo $K\alpha$ 2θ value. Stationary-crystal, stationary-counter background counts of 40 seconds were taken at the beginning and end of each scan. Standard reflections were measured during the data collection and indicated no decomposition. Two symmetry related sets of intensity data, all positive *hkl*, were collected for the tetragonal crystal to a 2θ value of 50°. The intensities fell off rapidly with θ and a limited amount of useful data could be collected beyond this point. A total of 1126 reflections were measured, of which 488 were unobserved. Later examination showed that 53 of the 1126 reflections or about 5% had been improperly measured and these were subsequently discarded and their symmetry equivalents retained. No averaging was done and all data were carried through the least-squares refinement. Out of the total of 1073 observed and unobserved reflections used in the least-squares refinement, 614 were unique. Of these 614 reflections, 258 were unobserved.

A Patterson map was calculated; however, a thorough study of the map gave the same parameters as were obtained previously with the film data. Isotropic refinement of these coordinates were carried out in the sub-space group $P\bar{4}2_1c$ (nondisordered) as well as in $P4_2/nmc$. The refinement for observed data only stopped at $R_1 = 21{\cdot}3\%$ for the former and $R_1 = 12{\cdot}9\%$ (*cf.* 14·9% film data) for the latter. Some interatomic distances calculated at this point are given in Table 1. Subsequent anisotropic refinement of the $P4_2/nmc$ model gave a structure which differed grossly from the film data model only in the chlorine coordinate of $x = 0{\cdot}25$ (ordered $NiCl_4^{2-}$ group). The final discrepancy indices were

$R_1 = 0{\cdot}067$ observed data

$R_2 = (\Sigma W(F_o - F_c)^2/\Sigma WF_o^2)^{\frac{1}{2}} = 0{\cdot}074$, unobserved and observed data .

The effects of anomalous dispersion of Ni and Cl were included in F_c; the values of f' and f'' were taken from Table 3.3.2*C* of *International Tables for X-ray Crystallography*. Unobserved reflections $[I_{\text{obs}} < 3\sigma(I)]$ were given zero weight if $F_{\text{obs}} > F_{\text{calc}}$. The remaining reflections, unobserved and observed, were weighted from counting statistics. Final observed and calculated structure factors are listed in Table 5 with unobserved reflections indicated by an asterisk. A final difference Fourier synthesis showed no peaks above background.

Table 1. *Interatomic distances at the end of isotropic refinement*

$R_1 = 12{\cdot}9\%$, observed data only

Ni —Cl	2·276 Å
N—C(1)	1·44
N—C(2)	1·45
C(1)-C(3)	1·56
C(2)-C(4)	1·54

Discussion

The disorder in the structure is clearly indicated in Fig. 1. The root-mean-square displacements have been included in Table 3 in order to indicate more explicitly the extent of the anisotropic displacement of the atoms. Inter- and intra-molecular distances are given in Table 4. In addition, a three-dimensional packing model of the structure was constructed and showed no unusual packing or 'holes' in the structure. Figs. 2 and 3 indicate the orientation of the thermal ellipsoids of the atoms with respect to the corresponding molecules. Both C(3) and C(4) of the $(C_2H_5)N^+$ cation were initially included as statistical atoms. In the final stages of the refinement, C(3) oscillated about $x = 0{\cdot}25$. The x coordinate of C(3) was subsequently fixed at $x = 0{\cdot}25$ and C(3) was refined as an 'ordered' atom. As expected, the main displacements in the $NiCl_4^{2-}$ are across the

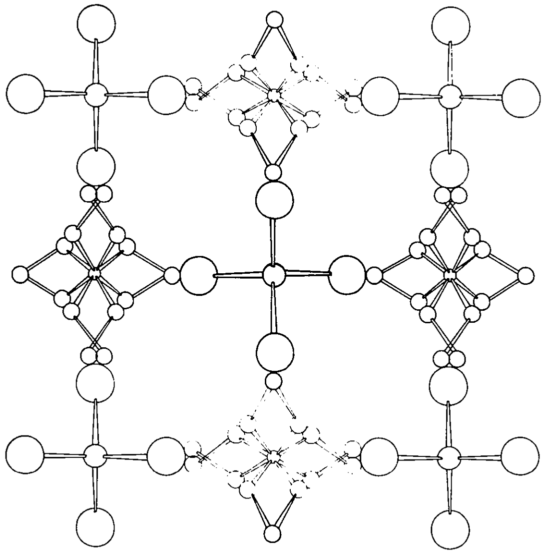

Fig. 1. View along [001] in the crystal. The section shown is approximately $\frac{3}{4}$ of a unit-cell dimension in *c* and one full unit-cell dimension in *a* and *b*. $NiCl_4{}^{2-}$ ions at the corners are at $z = \frac{1}{4}$, $NiCl_4{}^{2-}$ at the center is at $z = \frac{3}{4}$. The nitrogen atoms of the $(C_2H_5)_4N^+$ ions at the bottom and top are at $z = 0{\cdot}087$, while those at the sides are at $z = 0{\cdot}413$.

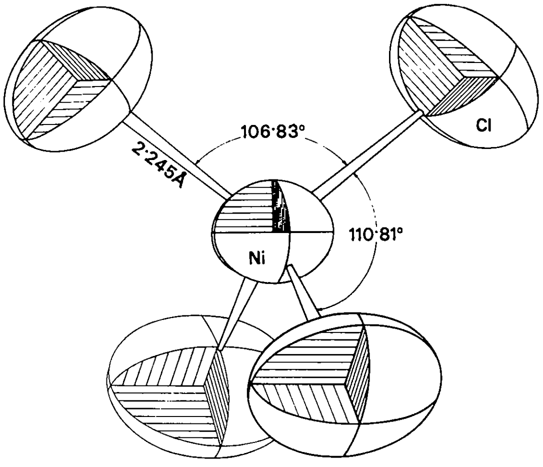

Fig. 2. Root-mean-square displacement and dimensions of $NiCl_4{}^{2-}$ ion in $[(C_2H_5)_4N]_2NiCl_4$.

Table 2. *Positional and thermal parameters for* $[(C_2H_5)_4N]_2NiCl_4$

Atom	x	y	z	B_{11}*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N	0·2500	0·2500	0·0874 (4)†	0·0165 (11)	0·0140 (10)	0·0049 (3)	0·0000	0·0000	0·0000
Cl	−0·0508 (3)	0·2500	0·3392 (1)	0·0220 (3)	0·0446 (5)	0·0032 (1)	0·0000	−0·0047 (1)	0·0000
C(1)	0·1772 (15)	0·1598 (19)	0·1499 (12)	0·0420 (40)	0·0769 (53)	0·0334 (18)	−0·0015 (31)	−0·0037 (20)	0·0447 (29)
C(2)	0·1432 (17)	0·3120 (20)	0·0346 (13)	0·0707 (50)	0·0542 (68)	0·0334 (20)	0·0216 (37)	−0·0374 (29)	−0·0040 (26)
C(3)	0·2500	0·0362 (12)	0·1933 (9)	0·0892 (55)	0·0485 (28)	0·0241 (11)	0·0000	0·0000	0·0203 (15)
C(4)	0·0258 (11)	0·2278 (47)	−0·0133 (8)	0·0279 (17)	0·0430 (61)	0·0125 (7)	−0·0017 (33)	−0·0087 (9)	−0·0116 (26)
Ni	−0·2500	0·2500	0·2500	0·0165 (3)	0·0165 (3)	0·00436 (7)	0·0000	0·0000	0·0000

* The form of the anisotropic ellipsoid is $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$.

† Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

mirror planes on which the chlorine atoms are located (r.m.s.d. = 0·430 Å). The other relatively large component normal to the Ni–Cl bond (r.m.s.d. = 0·353 Å), which is suggestive of a $\nu(E)$ vibrational mode in a tetrahedral molecule, may imply that the disorder is not a simple rotation about the $\bar{4}$ axis passing through the nickel atom. The bond parameters (Fig. 2) can be compared with the values 2·289(6) Å, 107·6°(1·6) and 110·4°(0·8) obtained from the isotropic film data refinement.

Table 3. *Root-mean-square amplitudes of vibrations* (Å) *along the principal axes, R*

See Figs. 2 and 3.

Atom	$R=1$	$R=2$	$R=3$
N	0·237 (8)	0·241 (9)	0·262 (9)
Cl	0·246 (2)	0·353 (3)	0·430 (3)
C(1)	0·199 (16)	0·410 (20)	0·812 (23)
C(2)	0·243 (18)	0·475 (29)	0·784 (24)
C(3)	0·306 (11)	0·608 (15)	0·619 (14)
C(4)	0·201 (20)	0·379 (19)	0·500 (31)
Ni	0·223 (2)	0·262 (5)	0·262 (7)

The optical and magnetic properties of the $NiCl_4^{2-}$ ion are of some interest and have been studied by Ballhausen (1964) in both $[(C_6H_5)_3CH_3As]_2NiCl_4$ and $[(C_2H_5)_4N]_2NiCl_4$. Ballhausen (1964) reports that $[(C_6H_5)_3CH_3As]_2NiCl_4$ crystals are not dichroic, while crystals of $[(C_2H_5)_4N]NiCl_4$ are weakly dichroic. A second difference found in the two compounds is the absorption spectra in the region 12000–16000 cm^{-1} at 77°K. The triphenylmethyl salt gives no absorption maxima in this region, while the tetraethyl complex exhibits a sharp absorption at 11670 cm^{-1} and two maxima of medium intensity at 12270 and 12580 cm^{-1}.

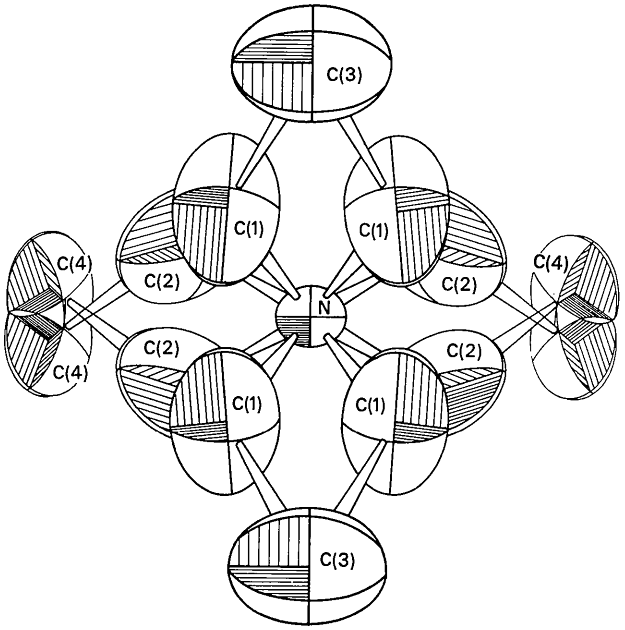

Fig. 3. Root-mean-square displacement of $(C_2H_5)_4N^+$ ion in $[(C_2H_5)_4N]_2NiCl_4$.

Table 4. *Selected distances and angles*

Errors in the lattice parameters are included in the estimated standard deviations.

Bonded distances	
N—C(1)	1·41 (1) Å
N—C(2)	1·37 (1)
C(1)-C(3)	1·45 (1)
C(2)-C(4)	1·49 (3)
Ni —Cl	2·245 (3)

Near-neighbor distances within an ion*	
Cl—Cl	3·697 (4)
Cl—Cl	3·606 (6)
C(1)-C(1)	2·10 (3)
C(1)-C(2)	2·23 (2)
C(1)-C(3)	2·90 (2)
C(1)-C(4)	2·87 (2)
C(2)-C(2)	2·24 (3)
C(2)-C(3)	2·91 (2)
C(2)-C(4)	3·10 (2)
C(3)-C(3)	3·87 (2)
C(3)-C(4)	4·09 (2)
C(4)-C(4)	4·08 (2)
C(3)-N	2·50 (1)
C(4)-N	2·54 (1)

Near-neighbor distances between ions*	
C(1)-Cl	3·60 (2) Å
C(2)-Cl	3·77 (2)
C(3)-Cl	3·99 (1)
C(4)-Cl	3·92 (3)
C(3)-C(3)	4·04 (1)
C(3)-C(4)	4·39 (2)
C(4)-C(4)	4·17 (9)

Bond angles	
Cl—Ni —Cl	106·83 (14)°
Cl—Ni —Cl	110·81 (7)
C(1)-N—C(1)	96·38 (1·63)
C(1)-N—C(2)	107·04 (93)
N—C(1)-C(3)	122·25 (1·11)
N—C(2)-C(4)	124·84 (2·00)

* With the exception of Cl-Cl, for which both non-bonded distances are given, the shortest distance of the type specified is given.

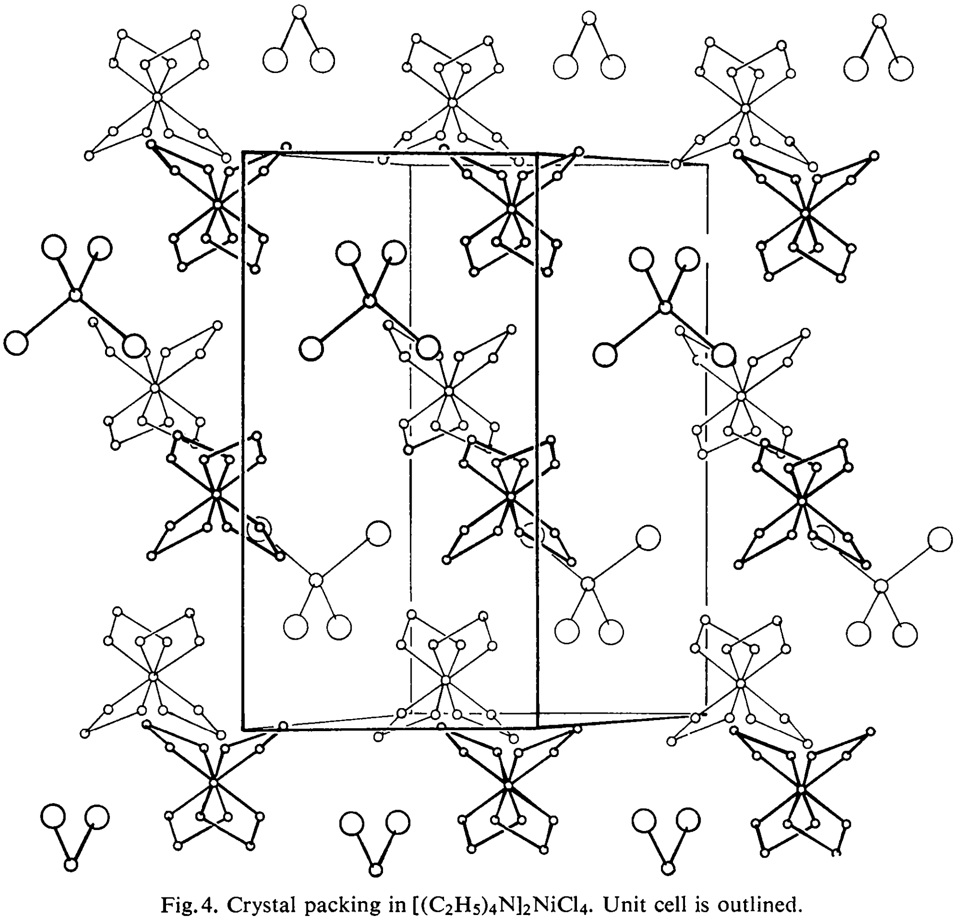

Fig. 4. Crystal packing in $[(C_2H_5)_4N]_2NiCl_4$. Unit cell is outlined.

Table 5. *Observed and calculated structure factors for* $[(C_2H_5)_4N]_2NiCl_4$

Unobserved reflections are indicated by an asterisk.

H	K	OBS	CAL
******L= 0*******			
2	0	103.9	106.8
4	0	100.1	91.2
6	0	35.9	35.1
8	0	7.4	8.9
10	0	10.3	9.7
1	1	12.4	9.1
3	1	11.5	10.0
5	1	40.8	40.5
7	1	6.3	6.0
9	1	6.8	5.4
0	2	104.3	106.8
4	2	29.3	28.7
6	2	17.6	18.8
8	2	2.6	5.7*
10	2	8.8	8.1
1	3	11.2	10.0
5	3	18.4	18.6
7	3	2.5	1.2*
9	3	6.0	3.6
0	4	101.5	91.2
2	4	29.5	28.7
4	4	43.8	42.4
6	4	25.4	22.3
1	5	40.3	40.5
3	5	19.1	18.6
5	5	14.9	19.0
7	5	3.0	4.7*
9	5	2.8	3.2*
0	6	36.7	35.1
2	6	17.9	18.8
4	6	24.6	22.3
6	6	12.2	13.2
8	6	2.8	5.4*
1	7	6.7	6.0
3	7	2.5	1.2*
5	7	2.6	4.7*
7	7	3.0	1.6*
0	8	9.0	8.9
2	8	2.5	5.7*
4	8	5.7	7.4
6	8	2.8	5.4*
1	9	2.6	5.4*
3	9	2.8	3.6*
5	9	2.8	3.2*
******L= 1*******			
2	0	24.8	26.3
3	0	25.7	25.4
4	0	7.5	5.5
5	0	58.6	59.9
7	0	8.9	9.0
8	0	2.7	4.4*
9	0	10.2	9.3
10	0	2.8	1.6*
0	1	119.6	105.6
2	1	46.9	41.1
3	1	32.2	30.8
4	1	41.3	42.1
6	1	27.7	24.6
7	1	6.0	6.5
8	1	5.2	5.5
9	1	2.7	.6*
10	1	7.2	6.9
0	2	24.4	26.3
1	2	46.8	41.1
3	2	4.9	5.6
4	2	2.1	4.6*
5	2	35.5	35.4
6	2	2.5	5.7*
7	2	2.4	4.2*
8	2	2.6	2.6*
9	2	7.2	7.3
10	2	2.8	1.6*
0	3	25.3	25.4
1	3	32.1	30.8
2	3	4.6	5.6
4	3	15.9	17.0
5	3	14.3	14.5
6	3	15.1	14.4
7	3	2.5	2.2*
8	3	2.6	3.9*
9	3	2.7	.8*
10	3	2.8	5.2*
0	4	6.4	5.5
1	4	40.5	42.1
3	4	16.1	17.0
5	4	29.0	28.3
6	4	2.5	2.1*
7	4	2.5	6.7*
8	4	2.6	1.8*
9	4	2.7	5.8*
0	5	57.4	59.9
1	5	9.0	10.9
2	5	34.7	35.4
3	5	13.8	14.5
4	5	26.8	28.3
6	5	15.7	15.4
7	5	3.6	2.9*
8	5	2.7	5.1*
9	5	2.7	.1*
0	6	3.6	2.9*
1	6	27.0	24.6
3	6	15.5	14.4
4	6	2.5	2.1*
5	6	16.5	15.4
7	6	2.8	5.3*
8	6	2.7	.9*
1	7	6.4	6.5
2	7	2.4	4.2*
3	7	2.5	2.2*
4	7	6.4	6.7
5	7	2.6	2.9*
6	7	2.7	5.3*
7	7	2.7	.0*
8	7	2.8	2.6*
0	8	2.5	4.4*
1	8	2.9	5.5*
2	8	2.5	2.6*
3	8	2.5	3.9*
4	8	2.6	1.8*
5	8	2.7	5.1*
6	8	2.7	.9*
7	8	2.8	2.6*
0	9	9.9	9.3
1	9	2.6	.6*
3	9	2.6	.8*
4	9	2.7	5.8*
5	9	2.7	.1*
******L= 2*******			
2	0	34.1	34.0
3	0	48.7	46.3
4	0	34.3	38.2
5	0	15.9	12.4
6	0	21.4	22.0
7	0	8.0	7.9
8	0	6.9	6.3
9	0	2.6	1.9*
10	0	6.2	5.4
0	1	38.7	37.8
1	1	91.1	82.2
2	1	60.1	67.5
3	1	33.9	34.8
5	1	39.1	38.5
6	1	2.4	.4*
7	1	10.6	10.9
8	1	7.7	8.9
9	1	9.2	9.6
10	1	2.7	1.3*
0	2	33.0	34.0
1	2	60.3	67.5
2	2	15.2	14.3
3	2	2.0	2.8*
4	2	23.7	24.0
5	2	30.1	29.5
6	2	15.8	15.8
7	2	2.5	.1*
8	2	6.3	4.9
9	2	2.7	3.1*
10	2	2.9	4.5*
0	3	47.7	46.3
1	3	33.9	34.8
2	3	1.9	2.8*
3	3	16.2	17.1
4	3	8.9	7.1
5	3	25.9	26.2
6	3	2.5	2.6*
7	3	8.5	8.8
8	3	2.6	5.5*
10	3	2.8	.9*
0	4	38.6	38.2
2	4	23.0	24.0
4	4	21.4	20.2
5	4	14.5	12.8
6	4	12.2	12.3
7	4	2.5	.6*
8	4	2.6	4.6*
9	4	2.7	1.7*
0	5	15.4	12.6
1	5	39.2	38.5
3	5	26.3	26.2
4	5	14.6	12.8
5	5	23.4	22.1
6	5	7.7	5.2
7	5	9.5	8.6
8	5	2.7	4.3*
9	5	2.7	5.4*
0	6	21.7	22.0
1	6	3.1	.4*
2	6	14.2	13.8
4	6	11.6	12.3
5	6	6.9	5.7
6	6	7.3	7.6
7	6	2.6	.2*
8	6	5.6	3.4
0	7	9.0	7.9
1	7	10.4	10.9
2	7	2.4	.1*
4	7	2.5	.6*
6	7	2.6	.2*
7	7	2.7	4.5*
8	7	2.8	1.3*
0	8	6.6	6.3
1	8	8.6	8.9
2	8	6.9	4.9
3	8	2.5	5.5*
4	8	5.9	4.6
5	8	2.6	4.3*
6	8	2.8	3.4*
7	8	2.7	1.3*
0	9	2.6	1.9*
1	9	8.9	9.6
2	9	2.6	3.1*
3	9	7.6	7.6
4	9	2.7	1.7*
5	9	2.7	5.4*
2	10	5.5	4.5
******L= 3*******			
1	0	39.8	37.2
2	0	133.1	129.3
3	0	37.1	35.5
4	0	8.5	10.4
5	0	20.5	22.3
6	0	4.9	3.9
7	0	12.8	13.4
8	0	7.2	6.8
9	0	7.9	7.2
10	0	2.7	2.7*
0	1	40.0	37.2
4	1	32.3	31.8
6	1	14.7	14.3
7	1	7.2	7.0
8	1	10.2	10.9
9	1	2.6	.1*
10	1	2.8	4.3*
0	2	133.9	129.3
1	2	42.6	46.0
3	2	37.7	37.7
4	2	31.6	31.6
5	2	21.0	21.2
6	2	7.7	7.6
7	2	12.2	12.4
8	2	2.7	2.8*
9	2	2.6	6.4*
10	2	2.7	2.7*
0	3	38.2	35.5
1	3	30.6	25.7
2	3	37.2	37.7
4	3	27.4	27.9
5	3	18.8	17.0
6	3	13.7	13.2
7	3	2.8	2.2*
8	3	8.4	9.2
9	3	2.8	.8*
10	3	2.8	3.8*
0	4	8.3	10.4
1	4	31.3	31.8
2	4	31.5	31.6
3	4	27.9	27.9
5	4	15.8	16.5
6	4	2.5	.8*
7	4	10.1	10.1
8	4	2.6	2.9*
9	4	2.9	4.9*
0	5	20.5	22.3
1	5	14.8	17.5
2	5	21.1	21.2
3	5	18.6	17.0
4	5	16.2	16.5
6	5	8.3	8.6
7	5	2.6	3.8*
8	5	2.7	5.9*
9	5	2.7	.1*
0	6	7.8	5.9
1	6	14.3	14.3
2	6	6.9	7.6
3	6	13.5	13.2
4	6	2.5	.8*
5	6	8.9	8.6
6	6	2.7	.0*
7	6	5.6	5.8
8	6	2.7	1.1*
0	7	12.6	13.4
1	7	8.2	7.0
2	7	12.8	12.4
4	7	10.2	10.1
5	7	2.1	3.8*
6	7	6.7	5.8
0	8	6.9	6.8
1	8	11.2	10.9
2	8	2.5	2.8*
3	8	8.8	9.2
4	8	2.6	2.9*
5	8	2.7	5.9*
6	8	2.7	1.1*
0	9	9.1	7.2
1	9	2.6	.1*
2	9	5.3	6.4
3	9	2.6	.8*
4	9	2.7	4.9*
5	9	2.7	.1*
******L= 4*******			
0	0	4.2	2.2
1	0	20.5	20.1
2	0	31.6	30.8
3	0	41.8	46.1
4	0	20.6	20.5
5	0	4.1	7.3
6	0	2.7	5.9*
7	0	14.3	15.3
9	0	2.7	.2*
10	0	2.7	1.5*
0	1	20.7	20.1
1	1	27.9	25.9
2	1	17.9	17.9
3	1	51.1	55.1
4	1	4.5	4.4
5	1	10.4	9.2
6	1	9.3	6.3
7	1	19.1	19.5
8	1	2.6	.7*
9	1	7.9	7.0
10	1	2.7	2.9*
0	2	31.0	30.8
2	2	49.4	45.7
3	2	13.4	15.2
4	2	28.5	26.5
5	2	13.8	14.1
6	2	9.5	9.3
7	2	8.1	10.1
8	2	11.3	11.1
9	2	2.8	.5*
10	2	2.8	1.8*
0	3	42.7	46.1
1	3	50.6	55.1
2	3	13.1	15.2
3	3	57.8	61.7
4	3	17.0	18.3
5	3	18.6	19.7
6	3	9.5	9.6
7	3	17.8	17.5
8	3	2.7	1.0*
9	3	6.8	6.3
10	3	2.8	2.5*
0	4	20.7	20.5
1	4	4.7	4.4
2	4	28.9	26.5
3	4	16.9	18.3
4	4	17.7	15.1
5	4	2.9	2.0*
7	4	6.6	7.2
8	4	7.8	7.6
9	4	2.7	.2*
0	5	4.0	7.3
1	5	9.7	9.2
2	5	13.7	14.1
3	5	18.5	19.7
4	5	2.3	2.0*
5	5	7.5	8.3
6	5	2.5	.5*
7	5	9.9	8.9
8	5	2.7	.5*
9	5	2.7	4.1*
1	6	8.6	6.3
2	6	10.1	9.3
3	6	8.8	9.6
4	6	5.9	6.5
5	6	2.5	.5*
6	6	2.7	4.0*
7	6	2.7	3.2*
8	6	2.8	4.1*
0	7	14.8	15.3
2	7	8.7	10.1
3	7	16.5	17.5
4	7	6.2	7.2
5	7	8.7	8.9
6	7	2.6	3.2*
7	7	2.7	5.8*
0	8	11.4	11.0
1	8	2.6	.7*
2	8	11.6	11.1
3	8	2.6	1.0*
4	8	7.6	7.6
5	8	2.7	.5*
6	8	2.8	4.1*
0	9	2.6	.2*
2	9	2.6	.5*
4	9	2.7	.2*
5	9	2.7	4.1*
******L= 5*******			
1	0	8.0	7.6
2	0	18.1	18.0
4	0	3.1	3.1*
5	0	2.7	.2*
6	0	2.4	.9*
7	0	11.8	14.2
8	0	2.7	2.3*
9	0	2.7	4.6*
10	0	2.1	.8*
0	1	6.7	7.6
2	1	50.5	51.9
3	1	6.5	7.7
4	1	17.2	14.9
5	1	2.2	2.7*
6	1	9.1	7.5
7	1	2.6	4.1*
8	1	15.0	14.5
9	1	2.7	2.6*
10	1	2.8	1.1*
0	2	18.0	18.0
1	2	51.0	51.9
3	2	60.3	63.9
4	2	8.9	8.4
5	2	16.0	17.6
6	2	2.4	1.9*
7	2	17.0	17.9
8	2	2.7	1.1*
9	2	2.7	5.7*
10	2	2.8	.8*
0	3	26.8	33.1
1	3	5.6	7.7
2	3	60.1	63.9
4	3	25.4	26.2
5	3	2.3	3.8*
6	3	11.9	12.2
7	3	2.6	2.7*
9	3	2.7	1.8*
0	4	2.0	3.1*
1	4	17.1	14.9
2	4	7.8	8.4
3	4	25.6	26.2
5	4	6.4	6.9
6	4	2.5	.1*
7	4	10.3	10.2
8	4	2.7	.9*
9	4	2.8	4.1*
0	5	2.7	.2*
1	5	5.4	2.7
2	5	15.3	17.6
3	5	4.4	3.8
4	5	6.1	6.9
6	5	2.5	5.4*
7	5	2.7	1.9*
8	5	2.8	6.0*
9	5	2.7	.7*
0	6	2.3	.9*
1	6	8.6	7.5
2	6	2.6	1.9*
3	6	11.5	12.2
4	6	2.5	.1*
5	6	2.5	5.4*
6	6	2.6	.0*
8	6	2.7	.3*
0	7	12.9	14.2
1	7	2.5	4.1*
2	7	17.6	17.9
4	7	10.3	10.2
5	7	2.6	1.9*
6	7	6.8	6.0
7	7	2.7	.0*
0	8	2.8	2.3*
1	8	15.0	14.5
2	8	2.6	1.1*
3	8	11.4	11.9
4	8	2.6	.9*
5	8	2.7	6.0*
6	8	2.8	.3*
0	9	2.8	4.6*
1	9	2.7	2.6*
2	9	5.9	5.7
3	9	2.8	1.8*
4	9	2.7	4.1*
******L= 6*******			
0	0	55.6	49.3
1	0	4.6	6.1
2	0	35.8	38.4
3	0	10.1	9.5
4	0	5.0	4.2
5	0	2.2	3.1*
6	0	21.1	18.2
7	0	2.5	.8*
8	0	12.3	13.7
10	0	2.8	2.3*
1	1	12.6	13.5
2	1	7.9	6.6
3	1	36.2	35.1
4	1	5.2	5.6
5	1	2.3	5.1*
6	1	2.4	3.0*
7	1	10.9	10.1
8	1	2.6	2.8*
9	1	2.8	2.8*
10	1	2.9	.1*
0	2	35.7	38.4
1	2	7.2	6.6
2	2	84.5	88.6
3	2	2.3	2.6*
4	2	38.3	32.9
5	2	5.2	3.8
7	2	2.6	.0*
8	2	12.6	14.1
9	2	2.7	.9*
0	3	10.0	9.5
1	3	36.6	35.1
2	3	2.2	2.6*
3	3	44.3	40.5
4	3	2.3	1.0*
5	3	7.3	6.2
6	3	2.8	4.0*
7	3	12.5	11.4
8	3	2.7	1.3*
9	3	2.8	3.1*
0	4	4.4	4.2
1	4	6.5	5.6
2	4	31.0	32.9
3	4	2.3	1.0*
4	4	10.6	12.8
5	4	2.8	4.6*
6	4	11.7	12.0
8	4	8.1	8.6
9	4	2.8	.1*
0	5	2.2	3.1*
2	5	4.3	3.8
3	5	7.2	6.2
4	5	2.4	4.6*
5	5	2.5	.7*
6	5	2.6	.4*
7	5	6.3	5.5
8	5	2.7	1.2*
0	6	21.6	18.2
1	6	2.4	3.0*
2	6	23.5	24.6
3	6	2.7	4.0*
4	6	10.9	12.0
5	6	2.5	.4*
6	6	7.8	7.7
7	6	2.6	.8*
0	7	2.5	.8*
1	7	10.1	10.1
2	7	2.5	.0*
3	7	13.0	11.4
4	7	2.6	.4*
5	7	5.1	5.5
6	7	2.7	.8*
7	7	5.6	4.5
0	8	12.9	13.7
1	8	2.6	2.8*
2	8	13.0	14.1
3	8	2.6	1.3*
4	8	7.6	8.6
5	8	2.7	1.2*
6	8	5.3	5.1
0	9	2.7	.9*
1	9	2.6	2.8*
2	9	2.7	.9*
3	9	5.1	3.1
4	9	2.7	.1*
******L= 7*******			
1	0	14.8	13.3
2	0	20.8	20.0
3	0	29.5	28.3
5	0	2.5	.1*
6	0	2.5	2.6*
7	0	18.1	18.5
8	0	2.8	4.8*
9	0	2.7	2.9*
0	1	13.8	13.3
2	1	35.3	37.0
3	1	19.3	18.8
6	1	10.5	11.8
7	1	5.4	4.8
8	1	8.9	7.8
9	1	2.7	.3*
1	2	36.2	37.0
3	2	41.0	40.2
4	2	2.3	.2*
5	2	10.0	7.3
7	2	16.5	17.2
8	2	2.7	3.2*
9	2	2.7	3.0*
0	3	30.3	28.3
1	3	19.7	18.8
2	3	40.6	40.2
4	3	21.7	22.9
5	3	12.3	11.7
6	3	12.7	13.5
7	3	2.7	1.2*
8	3	8.8	7.7
9	3	2.8	.3*
0	4	2.5	12.1*
1	4	17.3	19.8
2	4	2.3	.2*
3	4	21.8	22.9
6	4	2.5	3.0*
7	4	10.5	10.6
8	4	2.8	2.7*
9	4	2.7	2.3*
1	5	9.3	11.6
2	5	9.4	7.3
3	5	12.4	11.7
4	5	5.9	5.3
6	5	6.5	5.5
7	5	2.7	1.3*
8	5	2.7	4.5*
0	6	2.5	2.6*
1	6	10.9	11.8
3	6	12.7	13.5
4	6	2.5	3.0*
5	6	2.6	5.5*
7	6	2.7	5.9*
0	7	18.3	18.5
1	7	5.5	4.8
2	7	15.8	17.2
3	7	2.6	1.2*
4	7	10.4	10.6
5	7	2.7	1.3*
6	7	5.9	5.9
0	8	2.7	4.8*
1	8	9.2	7.8
2	8	2.7	3.2*
3	8	9.0	7.7
4	8	2.6	2.7*
5	8	2.7	4.5*
0	9	2.8	2.9*
1	9	2.6	.3*
2	9	2.8	3.0*
3	9	2.7	.3*
4	9	2.7	2.3*
******L= 8*******			
0	0	18.3	19.1
1	0	25.2	25.5
2	0	25.5	26.3
3	0	36.5	35.6
4	0	11.1	11.1
5	0	10.5	7.6
6	0	9.2	11.8
7	0	12.2	10.6
8	0	7.1	6.2
9	0	2.7	1.7*
0	1	23.7	25.5
1	1	32.1	31.9
2	1	16.7	16.6
3	1	26.7	27.3
4	1	10.2	8.8
5	1	15.8	16.8
6	1	12.1	10.2
7	1	13.9	13.4
8	1	2.7	3.1*
9	1	2.8	2.7*
0	2	25.4	26.3
1	2	16.8	16.6
2	2	31.6	30.0
3	2	2.3	3.7*
4	2	16.0	14.7
6	2	13.4	12.1
7	2	2.6	4.1*
8	2	5.9	6.2
9	2	2.8	.6*
0	3	36.3	35.6
1	3	26.4	27.3
2	3	2.3	3.7*
3	3	20.5	21.9
4	3	10.3	13.0
6	3	7.1	8.1
7	3	10.5	10.5
8	3	2.7	1.2*
9	3	2.8	2.5*
0	4	11.3	11.1
3	4	10.3	13.0
4	4	10.0	9.3
5	4	2.5	.0*
7	4	2.7	3.5*
8	4	2.8	4.5*
0	5	10.8	7.6
1	5	16.8	16.8
2	5	8.0	6.7
3	5	12.6	13.5
4	5	7.5	.0*
5	5	9.6	9.1
6	5	2.6	.2*
7	5	2.8	6.9*
8	5	2.8	.9*
0	6	10.2	11.8
1	6	12.4	10.2
2	6	12.4	12.1
3	6	7.4	8.1
4	6	8.0	7.8
5	6	2.6	.2*
6	6	6.5	5.5
7	6	2.7	1.2*
0	7	11.8	10.6
1	7	13.5	13.4
2	7	2.6	4.1*
3	7	10.2	10.5
4	7	2.7	3.5*
5	7	2.7	6.9*
6	7	2.7	1.2*
0	8	7.2	6.2
1	8	2.7	3.1*
2	8	5.7	6.2
3	8	2.7	1.2*
4	8	2.8	4.5*
5	8	2.8	.9*
0	9	2.7	1.7*
1	9	2.7	2.7*
2	9	2.7	.6*
3	9	2.7	2.5*
******L= 9*******			
1	0	34.1	34.8
2	0	32.2	32.0
3	0	16.8	16.2
4	0	2.7	.6*
5	0	18.8	18.0
6	0	4.9	5.7
7	0	9.9	8.5
8	0	2.7	4.1*
9	0	3.1	2.9*
0	1	34.8	34.8
2	1	24.5	25.1
3	1	16.9	16.9
4	1	17.6	18.0
5	1	10.0	8.0
6	1	15.8	16.1
7	1	2.7	3.2*
8	1	2.7	3.9*
9	1	2.8	1.1*
0	2	32.2	32.0
1	2	24.8	25.1
4	2	13.5	14.2
5	2	15.3	16.3
6	2	2.6	1.0*
7	2	8.0	7.5
8	2	2.7	1.8*
9	2	2.8	2.9*
0	3	17.4	16.2
1	3	16.9	16.9
2	3	11.6	12.6
4	3	7.8	9.3
5	3	11.5	10.2
7	3	2.6	1.5*
8	3	2.7	3.5*
0	4	2.7	.6*
1	4	17.6	18.0
2	4	13.2	14.2
3	4	9.7	9.3
5	4	11.6	10.7
6	4	2.6	1.3*
8	4	2.7	.9*
0	5	18.0	18.0
1	5	8.5	8.0
2	5	15.0	16.3
3	5	11.0	10.2
5	5	2.6	.0*
6	5	8.8	9.4
7	5	2.8	3.2*
0	6	4.6	5.7
1	6	16.3	16.1
3	6	10.5	11.3
4	6	2.6	1.3*
5	6	8.9	9.4
7	6	2.8	4.0*
0	7	9.5	8.5
1	7	2.7	3.2*
2	7	7.7	7.5
3	7	2.6	1.5*
4	7	6.4	4.3
5	7	2.8	3.2*
6	7	2.8	4.0*
0	8	2.7	4.1*
1	8	2.7	3.9*
2	8	2.7	1.8*
3	8	2.7	3.5*
4	8	2.7	.9*
0	9	3.1	2.9*
1	9	2.7	1.1*
2	9	2.8	2.9*
******L=10*******			
0	0	39.6	38.5
2	0	18.6	19.6
3	0	2.4	5.6*
4	0	12.8	14.1
5	0	10.9	9.4
6	0	12.0	13.4
7	0	2.7	4.6*
8	0	2.8	1.6*
0	1	3.1	.4*
1	1	35.3	35.5
3	1	16.5	14.0
4	1	2.5	7.6*
5	1	27.1	25.5
6	1	2.6	3.3*
8	1	2.7	1.3*
0	2	19.2	19.6
1	2	13.5	12.3
2	2	5.4	6.0
3	2	2.4	2.7*
4	2	6.7	4.6
5	2	10.3	10.5
6	2	7.7	9.5
7	2	2.7	3.0*
8	2	2.6	.4*
0	3	2.4	5.6*
1	3	16.3	14.0
2	3	2.5	2.7*
3	3	5.0	6.3
4	3	3.1	1.8*
5	3	13.8	14.7
6	3	2.6	.8*
7	3	2.7	5.1*
8	3	2.8	.9*
0	4	13.3	14.1
1	4	2.6	2.6*
2	4	7.3	6.6
3	4	2.6	1.8*
4	4	9.0	7.9
5	4	2.6	4.7*
6	4	9.2	8.5
7	4	2.8	1.6*
0	5	11.0	9.4
1	5	25.7	25.5
2	5	10.2	10.5
3	5	14.0	14.7
4	5	2.6	4.7*
5	5	12.1	11.4
6	5	2.7	2.5*
7	5	2.8	4.8*
0	6	12.0	13.4
1	6	2.8	3.3*
3	6	2.6	.8*
4	6	9.6	8.5
5	6	2.7	2.5*
6	6	2.8	6.4*
0	7	2.6	4.6*
1	7	6.9	6.8
2	7	2.6	3.0*
3	7	2.7	5.1*
4	7	2.6	1.6*
5	7	2.8	4.8*
0	8	2.7	1.6*
1	8	2.6	1.3*
2	8	2.6	.4*
3	8	2.8	.9*
******L=11*******			
1	0	35.4	34.7
2	0	2.5	2.5*
3	0	20.0	19.2
4	0	3.1	3.1*
5	0	22.4	20.4
6	0	2.9	2.1*
7	0	8.1	4.3
8	0	2.7	.2*
2	1	10.8	10.1
3	1	2.5	1.2*
4	1	16.3	17.7
5	1	2.6	.5*
6	1	12.0	13.1
7	1	2.7	2.0*
8	1	2.8	2.3*
0	2	2.7	2.5*
1	2	10.7	10.1
3	2	2.6	2.1*
4	2	2.9	3.7*
5	2	10.9	10.7
6	2	2.6	.7*
7	2	2.7	2.1*
8	2	2.7	.7*
1	3	2.8	1.2*
2	3	2.4	2.1*
4	3	9.9	10.0
5	3	2.6	.7*
6	3	8.4	7.5
7	3	2.7	2.1*
0	4	3.1	3.1*
1	4	16.5	17.7
2	4	2.6	3.7*
3	4	10.3	10.0
5	4	11.4	11.8
6	4	2.7	.9*
7	4	2.8	4.6*
0	5	22.3	20.4
1	5	2.9	.5*
2	5	11.1	10.7
3	5	2.6	.7*
4	5	11.7	11.8
6	5	6.9	6.3
0	6	2.8	2.1*
1	6	12.5	13.1
2	6	2.6	.7*
3	6	8.0	7.5
4	6	2.7	.9*
5	6	6.5	6.3
1	7	2.7	2.0*
2	7	2.7	2.1*
3	7	2.7	2.1*
4	7	2.8	4.6*
0	8	2.7	.2*
1	8	2.7	2.3*
2	8	2.7	.7*
******L=12*******			
0	0	46.7	40.6
1	0	3.2	2.0*
2	0	22.1	19.7
3	0	7.6	8.2
4	0	23.9	24.0
6	0	10.3	9.9
7	0	2.8	.8*
0	1	2.4	2.0*
2	1	2.6	2.1*
3	1	5.5	5.5
5	1	12.5	13.2
7	1	2.8	2.2*
0	2	20.3	19.7
1	2	2.5	2.1*
2	2	5.5	5.2
3	2	2.5	4.8*
4	2	11.7	13.9
5	2	2.6	1.6*
6	2	7.5	6.7
7	2	2.7	1.1*
0	3	6.2	8.2
1	3	2.6	5.5*
3	3	2.8	.1*
4	3	2.6	1.5*
5	3	9.4	7.6
6	3	2.8	3.7*
7	3	2.7	.5*
0	4	24.0	24.0
1	4	2.6	1.7*
2	4	12.9	13.9
3	4	2.6	1.5*
4	4	16.1	14.4
5	4	2.7	2.5*
6	4	2.8	7.2*
0	5	2.9	1.2*
1	5	11.9	13.2
2	5	2.7	1.6*
3	5	8.8	7.6
4	5	2.7	2.5*
5	5	8.1	8.3
6	5	2.8	.7*
0	6	10.5	9.9
1	6	2.6	3.4*
2	6	5.6	6.7
3	6	2.7	3.7*
4	6	2.8	7.2*
5	6	2.7	.7*
0	7	2.8	.8*
1	7	2.7	2.2*
2	7	2.7	1.1*
3	7	2.7	.5*
******L=13*******			
1	0	16.8	18.1
2	0	9.1	8.7
3	0	10.7	11.6
4	0	2.8	4.0*
5	0	11.8	12.7
6	0	2.9	.9*
7	0	2.8	7.0*
2	1	11.5	10.4
3	1	5.8	6.4
4	1	11.6	12.1
5	1	2.7	4.0*
6	1	6.6	5.3
7	1	2.8	1.2*
1	2	10.8	10.4
3	2	7.2	7.0
4	2	2.7	1.2*
5	2	8.7	10.1
6	2	2.7	3.1*
7	2	2.8	2.0*
0	3	10.6	11.6
1	3	6.3	6.4
2	3	7.8	7.0
4	3	9.3	8.4
5	3	2.8	3.8*
6	3	5.6	4.1
0	4	3.0	4.0*
1	4	12.9	12.1
2	4	2.7	1.2*
3	4	9.7	8.4
5	4	7.9	8.1
6	4	2.7	1.8*
0	5	12.0	12.7
1	5	2.7	4.0*
2	5	10.1	10.1
3	5	2.8	3.8*
4	5	6.9	8.1
0	6	2.9	.9*
1	6	5.3	5.3
2	6	2.7	3.1*
4	6	2.8	1.8*
0	7	2.8	2.0*
1	7	3.0	1.2*
2	7	2.7	2.0*
******L=14*******			
0	0	8.5	11.2
2	0	9.2	9.8
3	0	2.7	5.7*
4	0	8.5	10.1
6	0	2.7	3.9*
0	1	3.2	1.7*
1	1	11.1	10.5
2	1	9.5	9.2
3	1	11.7	10.6
5	1	6.4	6.6
6	1	2.7	.4*
0	2	7.8	9.8
1	2	9.0	9.2
2	2	8.6	8.5
3	2	2.6	2.9*
4	2	8.2	8.5
5	2	6.5	6.7
6	2	2.8	3.3*
0	3	2.8	5.7*
1	3	11.1	10.6
2	3	2.7	2.9*
3	3	10.4	10.4
4	3	2.7	1.7*
5	3	7.5	6.5
1	4	3.0	1.4*
2	4	8.5	8.5
3	4	2.7	1.7*
4	4	8.2	7.3
5	4	2.8	2.1*
0	5	2.7	2.7*
1	5	7.5	6.6
2	5	5.4	6.2
3	5	6.5	6.5
4	5	2.8	2.1*
0	6	2.8	3.9*
1	6	2.9	.4*
2	6	2.8	3.3*
******L=15*******			
1	0	6.8	6.5
2	0	7.3	6.8
3	0	9.7	9.9
4	0	2.8	.5*
5	0	3.1	3.7*
2	1	9.0	8.7
3	1	2.7	3.2*
4	1	2.9	7.4*
5	1	2.7	2.3*
1	2	9.7	8.7
3	2	10.5	10.3
4	2	2.8	3.4*
5	2	2.9	3.8*
0	3	9.2	9.9
1	3	2.7	3.2*
2	3	10.6	10.3
4	3	7.4	8.1
5	3	2.8	3.0*
0	4	2.8	.5*
1	4	7.9	7.4
2	4	2.8	3.4*
3	4	8.9	8.1
0	5	3.0	3.7*
1	5	2.7	2.3*
2	5	2.8	3.8*
3	5	2.8	3.0*
******L=16*******			
0	0	3.6	.6*
1	0	2.7	2.3*
2	0	6.3	5.5
3	0	2.8	2.4*
4	0	2.9	3.3*
0	1	2.7	2.3*
1	1	8.1	7.4
2	1	2.7	.3*
3	1	8.5	9.7
4	1	2.8	2.2*
0	2	2.8	5.5*
1	2	2.7	.3*
2	2	9.7	8.8
3	2	2.8	.7*
4	2	7.4	5.4
0	3	2.7	7.4*
2	3	2.8	.7*
3	3	9.6	9.8
0	4	2.8	3.3*
1	4	2.7	7.2*
2	4	6.7	5.4
******L=17*******			
1	0	3.0	3.3*
2	0	2.8	.0*
3	0	6.2	5.4
0	1	2.9	3.3*
2	1	6.7	7.6
3	1	2.8	1.7*
0	2	2.8	.0*
1	2	7.1	7.6
0	3	6.3	5.4
1	3	2.8	1.2*

One explanation for these observed bands has been offered by Ballhausen (1964) on the basis of a vibronic model in T_d symmetry using the calculations of Liehr & Ballhausen (1959). This model assigns the bands at 12270 and 12580 cm^{-1} to a ${}^3\Gamma_1$ $(T_d)\rightarrow{}^1\Gamma_3$ (T_d) transition, and the band at 11670 cm^{-1} to a ${}^3\Gamma_1$ $(T_d)\rightarrow{}^1\Gamma_5$ (T_d) transition. This assignment disagrees with intensity considerations and does not explain why the bands do not occur in $[(C_6H_5)_3CH_3As]_2NiCl_4$.

An alternative explanation which is consistent with this structural analysis and that of Pauling (1965) for $[(C_6H_5)_3CH_3As]_2NiCl_4$ can be proposed on the basis of the difference in the site symmetries of the nickel atoms in the two compounds. In $[(C_6H_5)_3CH_3As]_2NiCl_4$, Cl–Ni–Cl angles are $109°19' \pm 14'$ and $109°38' \pm 17'$ with Ni–Cl bond lengths of $2{\cdot}271 \pm 0{\cdot}007$ and $2{\cdot}267 \pm 0{\cdot}008$ Å, so that within experimental error the $NiCl_4^{2-}$ possesses T_d symmetry. The D_{2d} site symmetry of the nickel atom in $[(C_2H_5)_4N]_2NiCl_4$ gives rise to a splitting of ${}^1\Gamma_3$ (T_d) and ${}^1\Gamma_5$ (T_d) $[{}^1\Gamma_3\,(T_d)\rightarrow{}^1\Gamma_1\,(D_{2d})+{}^1\Gamma_3\,(D_{2d});$ ${}^1\Gamma_5\,(T_d)\rightarrow{}^1\Gamma_4\,(D_{2d})+{}^1\Gamma_5\,(D_{2d})]$. Excited triplet levels of ${}^3\Gamma_4$ (D_{2d}) and ${}^3\Gamma_5$ (D_{2d}) symmetry are close enough in energy to the ${}^1\Gamma_4$ (D_{2d}) and ${}^1\Gamma_5$ (D_{2d}) levels (Ballhausen, 1964) to give them considerable triplet character. Within this approximation, the spin-forbidden character of the transitions may be relaxed sufficiently to allow the orbital selection rules to dominate. In the discussion which follows, the spin notation is retained to identify the states and should not be construed to indicate the spin character. Transitions from the ${}^3\Gamma_1$ (D_{2d}) ground state to the perturbed ${}^1\Gamma_4$ (D_{2d}) and ${}^1\Gamma_5$ (D_{2d}) states have the following selection rules in plane polarized light:

${}^3\Gamma_1\rightarrow{}^1\Gamma_4$ (allowed parallel to the S_4 axis)

${}^3\Gamma_1\rightarrow{}^1\Gamma_5$ (allowed perpendicular to the S_4 axis)

In the vibronic model given by Ballhausen (1964), the two bands observed at 12270 and 12580 cm^{-1} are associated with the transition to the ${}^1\Gamma_3$ (T_d) state. Assuming with Ballhausen (1964) that the totally symmetric vibronic mode gives rise to the intensity in this model, no difference in the intensities of the 12270 and 12580 cm^{-1} bands should arise as the orientation of the S_4 axis is changed with respect to plane polarized light. Low temperature single-crystal experiments are in progress to see if it is possible to assign the 12270 and 12580 cm^{-1} bands to the ${}^3\Gamma_1$ $(D_{2d})\rightarrow{}^1\Gamma_4$ (D_{2d}), ${}^1\Gamma_5$ (D_{2d}) transitions, leaving the remaining bands to be assigned to the electronically 'forbidden' transition, ${}^3\Gamma_1$ $(D_{2d})\rightarrow{}^1\Gamma_1$ (D_{2d}), ${}^1\Gamma_3$ (D_{2d}) components of ${}^1\Gamma_3$ (T_d). The weakly observable dichroism present in $[(C_2H_5)_4N]_2NiCl_4$ and absent in $[(C_6H_5)_3CH_3As]_2NiCl_4$ lends some credence to the lower-than-cubic site symmetry model.

Bulk magnetic susceptibility measurements [Figgis, Lewis, Mabbs & Webb (1966)], accurate from one to three per cent, do not distinguish between the anion in $[(C_6H_5)_3CH_3As]_2NiCl_4$ and $[(C_2H_5)_4N]_2NiCl_4$. This is significant in that there is a difference between the susceptibilities for the above compounds and that for Cs_3NiCl_5. If one makes the somewhat questionable assumption that Cs_3NiCl_5 is strictly isomorphous with Cs_3CoCl_5 (Cl–Co–Cl 106 and 111°), $[(C_2H_5)_4N]_2NiCl_4$ should behave magnetically more like Cs_3NiCl_5 than $[(C_6H_5)_3CH_3As]_2NiCl_4$ unless, perhaps, crystal field effects due to the smaller Cs^+ cation and additional Cl^- are important in Cs_3NiCl_5. From space group and cell constant data, we have found $[(C_2H_5)_4N]_2NiBr_4$ to be isostructural with $[(C_2H_5)_4N]NiCl_4$ and wish to point out that the bulk magnetic susceptibility moments for $[(C_3H_5)_4N]_2NiBr_4$ were recently incorrectly interpreted (Bose *et al.*, 1965) in terms of a cubic crystal system with a slight trigonal distortion of the $NiBr_4^{2-}$ anion.

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