tive ligands leaving the equilibrium symmetry undisturbed.

The evidence concerning the $M_6X_{12}^{n+}$ ions in solutions is more complicated.[1]   Again it is clear that the Ta polynucleus is subject to large deformations while the Nb polynucleus is not.   The sense of the deformations is such that it would be consistent with hexasolvated complex ions with two X^- and four H_2O solvated to the elongated $Ta_6X_{12}^{2+}$ ions and four X^- and two H_2O solvated to the flattened $Ta_6X_{12}^{4+}$ ions.   However, the spectroscopic evidence does not support this view.   Robin[10] and Kuebler found an identical split-

ting of the metal–metal bands for the $Ta_6Cl_{12}^{2+}$ ion when the anionic species was any one of Cl^-, OH^-, ClO_4^-, or CN^-.   If these various anions were solvating the $Ta_6-Cl_{12}^{2+}$ ion, the spectral splitting would be expected to be different in each case.

Acknowledgment.—The author wishes to thank M. B. Robin for suggesting this problem, for providing the $Ta_6Cl_{14} \cdot 7H_2O$ crystals, and for helpful and stimulating discussion.

(10) M. B. Robin, private communication.

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
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The Crystal Structure of Bis(triphenylmethylarsonium)tetrachloronickel(II), [(C₆H₅)₃CH₃As]₂[NiCl₄], of the Isomorphous Compounds of Mn, Fe, Co, and Zn, and of the Corresponding Bromides

BY PETER PAULING

The crystal structure of bis(triphenylmethylarsonium)tetrachloronickel(II), [(C₆H₅)₃CH₃As]₂[NiCl₄], has been determined from the three-dimensional sharpened Patterson function and phased observed Fourier syntheses and refined by least-squares methods.   Crystals of the compound are cubic, space group T^4-$P2_13$, $a_0 = 15.557 \pm 0.004$ A with four formula units per unit cell.   The crystals contain the tetrachloronickel ion, $[NiCl_4]^{2-}$, and two crystallographically distinct kinds of the triphenylmethylarsonium ion, $[(C_6H_5)_3CH_3As]^+$.   The arsenic and nickel atoms, one of the four chlorine atoms, and the carbon atoms of the methyl groups lie in special positions of the space group on threefold axes.   All the complex ions are tetrahedral, the three phenyl groups of each arsonium ion being crystallographically equivalent and three of the chlorine atoms of each tetrachloronickel ion being crystallographically equivalent.   The $[NiCl_4]^{2-}$ group is regularly tetrahedral to within experimental error, the Ni–Cl distances being 2.267 ± 0.008 and 2.271 ± 0.007 A and the Cl–Ni–Cl angles being $109°$ $19' \pm 14'$ and $109°$ $38' \pm 17'$.   Crystals of the corresponding compounds containing the complex ions $[MnCl_4]^{2-}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$, $[ZnCl_4]^{2-}$, $[MnBr_4]^{2-}$, $[CoBr]^{2-}$, $[NiBr_4]^{2-}$, and $[ZnBr_4]^{2-}$ have been shown by single-crystal and powder diffraction photographs to be isomorphous with the compound containing the $[NiCl_4]^{2-}$ ion.   Crystals of the corresponding compounds of $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ are isomorphous with each other; those of the chloride are orthorhombic, $a = 32.27 \pm 0.02$, $b = 25.24 \pm 0.02$, $c = 8.943 \pm 0.003$ A, space group Fdd2, eight formula units per unit cell.   Crystals of the tetraiodides of Mn, Fe, Co, Ni, and Zn are isomorphous with each other but have a different crystal structure from the chlorides and bromides.

Introduction

Of the several high-symmetry ligancy forms adopted by transition metal coordination compounds, the regularly tetrahedral form has been extensively discussed in recent years.   One of the major problems is why it does not occur more often in certain electronic configurations such as d^2 or d^8.   According to simple chemical bond[1] theory, paramagnetic tetrahedral nickel(II) should be stable.   Most of the compounds thought to contain tetrahedral nickel(II), such as bis(acetylacetonato)nickel(II), have turned out to be polymeric and have octahedral coordination.[2]

An explanation for the difficulty[3] in finding tetra-

hedrally coordinated nickel(II) compounds has been put forward by Orgel[4] by a consideration of the interaction of the electrostatic field of the ligands and the d electrons of the metal.   For this effect alone the tetrahedral configuration is destabilized relative to the octahedral configuration because of the splitting of the d electron shells by the cubic fields.   Furthermore, according to the theory of Jahn and Teller,[5] wherever there might exist degeneracy in the electronic states with a symmetric structure, there exists a more stable nondegenerate state with a less symmetric structure.   Therefore, since regularly tetrahedrally coordinated nickel(II) is degenerate in d_ϵ electronic states we expect the configuration to distort in some manner as to remove this degeneracy.

(1) L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931); L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 153, 168.
(2) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).
(3) M. A. Porai-Koshits, *Russ. J. Inorg. Chem.*, **1**, 332 (1959).

(4) L. E. Orgel, Report to the Xth Solvay Council, Brussels, 1956, pp 289–338.
(5) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A161**, 220 (1937).

Dunitz and Orgel[6] have shown that a distortion of the tetrahedron from 23 symmetry to $\bar{4}$ symmetry will do so. This is the pseudosymmetry shown by the series of compounds dihalobis(triphenylphosphine)nickel(II) with chlorine, bromine, and iodine prepared and analyzed by Venanzi.[7] The LCAO molecular orbital treatment is able to give the relative order of the energy of the molecular orbitals for each of the coordination types, but has not so far been able to predict the coordination expected for any particular compound. Arguments similar to those applicable to the d[8] nickel-(II) case are also applicable with somewhat different conclusions to d[5] Mn(II), d[6] Fe(II), d[7] Co(II), d[9] Cu-(II), and d[10] Zn(II).

A series of compounds of the form $[(C_6H_5)_3CH_3As]_2$-$[M^{II}X_4]$ where M^{II} is Mn, Fe, Co, Ni, Cu, or Zn and X is Cl, Br, or I has been prepared by Gill and Nyholm.[8] The physical properties of these compounds suggested that they are tetrahedral coordination complexes. They are 2:1 electrolytes in organic solvents, light in color, and spin free. A preliminary diffraction investigation showed the tetrachlorocobalt compound, which is expected to be stable as a tetrahedral complex, to be isostructural with the tetrachloronickel compound. The high magnetic moment of the tetrachloronickel compound (3.89 BM) is a large increase on the spin-only value of 2.83 BM and suggests that the complex ion is regularly tetrahedral. The excess magnetic moment over the spin-only value can be explained by a large orbital contribution[9] resulting from regularity.

An investigation of the crystal structure of the compound bis(triphenylmethylarsonium)tetrachloronickel-(II), a blue paramagnetic salt, has been undertaken in order to determine the stereochemistry of the tetrachloronickel ion and of the other complex ions of this series.

Experimental Section

Crystals of $[(C_6H_5)_3CH_3]_2[M^{II}X_4]$ were prepared by Dr. Naida Gill by the evaporation of an alcohol solution of stoichiometric quantities of $(C_6H_5)_3CH_3AsX$ and $M^{II}X_2$. The compounds of chlorine, bromine, and iodine have been prepared with the divalent metals manganese, iron, cobalt, nickel, copper, and zinc, except for the compounds containing $[FeBr_4]^{2-}$ and $[CuI_4]^{2-}$.[8]

The nine substances $[(C_6H_5)_3CH_3As]_2[M^{II}X_4]$, where X is chlorine or bromine and M^{II} is manganese, iron, cobalt, nickel, or zinc, except $[FeBr_4]^{2-}$, crystallize as dendrites. The similarity between these dendrites and conical fir trees is striking. The trunk is a long thick needle consisting of three crystals grown together with reentrant angles about a threefold axis parallel to the trunk axis. The developed faces parallel to the trunk are planes of the form {110} and cyclic permutations, each crystal of the three having as its major development one of these planes and being terminated at the edge by the other two. The trunk is terminated at the top by a point being the intersection of the three planes of the form {100} taken two at a time to form domes that terminate the three crystals. Attached to the trunk are three groups of branches at an angle of 120° from each other and at an angle of 109° 28′ from the trunk, with another threefold

axis parallel to the axis of each branch. The branches are developed similarly to the trunk consisting of three crystals. Sometimes the trunk and three branches grow together to form a regular tetrahedron. Single crystals are optically isotropic.

Powder diffraction photographs of the nine compounds taken on a 114.83-mm diameter Philips Debye–Scherrer camera with Cu Kα radiation are almost identical, showing that the several compounds are isomorphous.

Powder and single-crystal diffraction photographs show that the $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ compounds are isomorphous with each other but have a different structure from that of the nine other compounds. Weissenberg and precession photographs (Cu Kα) of the $[CuCl_4]^{2-}$ compound are of Laue group mmm and can be indexed in terms of an orthorhombic unit cell: $a = 32.27 \pm 0.02$, $b = 25.24 \pm 0.02$, $c = 8.943 \pm 0.003$ A. The systematic absences uniquely determine the space group as Fdd2. The unit cell volume of 7330 A[3] compared to 3765 A[3] for the cubic [NiCl₄][2-] compound indicates eight molecules per unit cell. This implies that the sixteen $[(C_6H_5)_2CH_3As]^+$ groups are crystallographically equivalent and lie in the general position of the space group and that the Cu atoms of the $[CuCl_4]^{2-}$ group lie in the unique special position 8a2 of the space group. The coordination polyhedron or polygon of the Cu atom therefore has symmetry 2. This restriction is not sufficient to indicate the nature of the coordination polyhedron as all the simple polyhedra including the tetrahedron have a twofold axis as a symmetry element.

Crystals of compounds of the form $[(C_6H_5)_2CH_3As]_2[M^{II}I_4]$ with M^{II} = Mn, Fe, Co, Ni, and Zn are isomorphous as shown by powder diffraction photographs. Crystals of the $[ZnI_4]^{2-}$ compound are flat, approximately hexagonal plates and appear to belong to class $\bar{3}$ or 32 with developed faces {0001} and one form of {hkil}. The poor diffraction data available indicate the crystals are twinned or trilled. The observed systematic absences are not consistent with trigonal space group theory. The measured trigonal unit cell is $a = 19.14$, $c = 20.19$ A.

Small pieces of single crystal of the compounds $[(C_6H_5)_3CH_3-As]_2[M^{II}Cl_4]$ were cut from the dome-end portion of sections of multiple crystals and were mounted with one twofold axis parallel to the rotation axis. The crystals were dipped several times in a 2% solution of Formvar 15/19E (polyvinylformal, Monsanto) in dry ethylene dichloride to protect them from atmospheric hydration.

Single-crystal zero-layer and first-layer Weissenberg photographs taken with unfiltered copper radiation about a twofold rotation axis and about a threefold rotation axis of the five chlorides are identical except for small lattice changes. The effect of anomalous dispersion was not observed though the series of metals includes the absorption edge for Cu Kα radiation.

The diffraction symmetry is T_h-m3. The only systematic absences are the planes (h00) with $h = 2n + 1$. Reflections in approximately the positions of (500) and (900) appear with weak intensity. The apparent reflection (500) was interpreted as arising from the strong reflection (400) with Fe Kα radiation due to contamination of the X-ray tube, and the apparent reflection (900) was interpreted as arising from (10.0.0) with Cu Kβ radiation. From these data and from the fact that it was difficult to fit the contents of the unit cell into the other space groups in the Laue group M3 (P23 and Pm3) the space group T^4-P2₁3 was assigned. This space group assignment was subsequently confirmed from the Patterson function by a consideration of the various possible Harker sections.

The cell parameter of the nickel compound is 15.557 ± 0.004 A as determined by measurement of (600) at $\pm 2\theta$ on the diffractometer (λ Cu Kα = 1.54178). The density of $[(C_6H_5)_3CH_3As]_2[NiCl_4]$ measured by pycnometer is 1.46 g/cm^{3}; that calculated for four formula units per unit cell is 1.49 g/cm^{3}.

Three-dimensional diffraction data to a limit of $2\theta = 90°$ with nickel-filtered Cu Kα radiation of a single crystal of $[(C_6H_5)_3CH_3As]_2[NiCl_4]$ of approximately cubic shape with edge 0.5 mm were collected with the four-circle proportional counter diffractometer built by U. W. Arndt in the Davy Faraday Research Labo-

(6) J. D. Dunitz and L. E. Orgel, *Advan. Inorg. Chem. Radiochem.*, **2**, 1 (1960).

(7) L. M. Venanzi, *Proc. Chem. Soc.*, 6 (1958).

(8) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959); N. S. Gill, *ibid.*, 3512 (1961).

(9) M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).
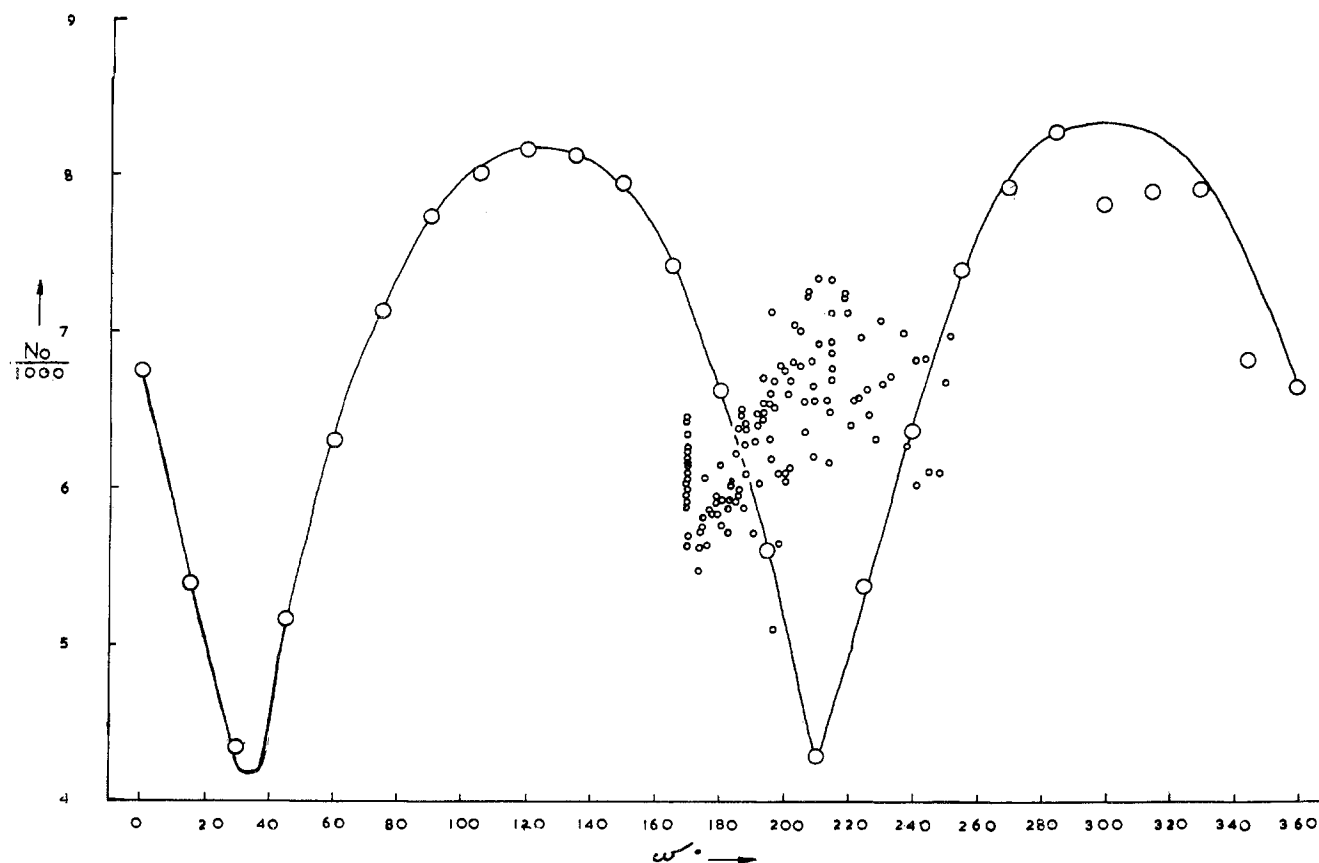
Figure 1.—A plot of the measured intensity of (002) as a function of ϕ showing the effect mostly of absorption and of all measured intensities of the standardizing reflection (006) as a function of ϕ showing the effect of absorption and variation with time of the counting system.

ratory of the Royal Institution of Great Britain. The instrument had the geometry described by Furnas and Harker[10] and used a semiautomatic stepped ω scan. The maximum diffraction angle of the instrument was limited to 90° by mechanical interference. The three diffractometer angles were determined using the analog computer of Arndt and Phillips,[11] and the instrument was set by hand. The angular coordinates of the intensity maximum for each measured reflection were determined experimentally by observing the counting rate. The measurement was made by counting the background 1° in ω[12] to one side of the reflection maximum for 10,000 monitor counts, stepping ω through twenty steps of 0.1° each, counting at each stationary point for 1000 monitor counts, and counting the background at the end of the scan for 10,000 monitor counts. A total of 890 measurements were taken over a period of 10 days, 117 reflections being too small to be observed. Of these 890, 180 were standardizing counts of the plane (006). The total count for each reflection was corrected for background by subtracting the two background counts and for Lorentz and polarization factors by means of a chart showing the combined correction as a function of 2θ. The linear absorption coefficient of the substance is about 56 cm^{-1}, and the data were empirically corrected for absorption and variation in counter sensitivity by applying a correction based on the measurement of the plane (006) as a function of the angular parameter ϕ[12] and time. The plane (006) is in the reflecting position with $\chi = 90°$ and is independent of ϕ, and variations in its measured intensity give a measurement of the absorption of the crystal as a function of ϕ.

The three-dimensional data were measured in lines of constant ϕ parallel to the crystal twofold axis c, and at the time of taking the data along any such line, the plane (006) was measured with

the value of ϕ of the line. These measurements and those of (002) as a function of ϕ are shown in Figure 1. The data along any line were multiplied by the ratio of a standard value of (006) to the value of (006) measured with the line.

The average over-all temperature factor and the absolute scale of the data were determined roughly by use of the statistical method of Wilson.[13] The data were scaled and sharpened by the function $0.71e^{(4.33 \sin^2 \theta/\lambda^2)}$ by plotting as a function of $(h^2 + k^2 + l^2)$ and calculating $(h^2 + k^2 + l^2)$ by inspection for each plane. A threefold multiplication of the unique data was generated by hand through the cyclic permutation of the indices, and the sharpened three-dimensional Patterson function was calculated on a Ferranti Pegasus computer with an mmm Fourier program especially written by Dr. D. W. Green.

Analysis and Refinement

The space group assignment was confirmed by the observation that the Harker peaks for the heavy atoms appear in the plane $P(x, y, 1/2)$. From the space group and the contents of the unit cell, the two arsenic atoms, the nickel atom, and one chlorine atom must lie in the special position of $P2_13$ on one of the four nonintersecting threefold axes. The location of these atoms was determined primarily by a study of the plane in the Patterson function $P(x, 1/2 - x, z)$ being the locus of all points from one threefold axis of the space group to another nonintersecting threefold axis. The image of each set of atoms along a threefold axis reflected through each atom along another axis should appear in a symmetric fashion in two directions in this section of the

(10) T. C. Furnas and D. Harker, *Rev. Sci. Istr.*, **26**, 449 (1955).

(11) U. W. Arndt and D. C. Phillips, *Acta Cryst.*, **10**, 508 (1957).

(12) U. W. Arndt and D. C. Phillips, *ibid.*, **11**, 509 (1958).

(13) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

three-dimensional Patterson function. Absolute co-ordinates for the atoms were obtained by the interpretation of the Harker peaks which appear in each image axis.

The coordinates of the chlorine atom in the twelve-fold general position were determined by the interpretation of the peaks in the three-dimensional Patterson function corresponding to the vectors from the two arsenic and one nickel atoms to this general chlorine atom. This was done by plotting, as projections on a major section, spherical shells in the Patterson function at a distance 2.25 A from the peaks interpreted as vectors from the two arsenic and the nickel atoms to the nickel atom on the same threefold axis and a twofold screw-related threefold axis. A set of three coordinates for the chlorine atom in the general position was determined from these six images. No attempt was made to find the positions of the lighter atoms from the Patterson function.

The trial coordinates of the heavy atoms determined from the three-dimensional sharpened Patterson function were used to phase an observed Fourier synthesis using a program specially written for the space group $P2_13$. The program calculates the noncentrosymmetric structure factors, generates the planes related to the unique planes by a threefold axis of symmetry, and sorts the resultant list either of calculated, phased observed or difference structure factors for one octant into an order convenient for the subsequent Fourier synthesis. This and subsequent calculations were done on the University of London Ferranti Mercury computer. The three-dimensional observed synthesis was calculated using the Fourier program of Mills.[14] All the carbon atoms appear well in this synthesis except that one methyl group (C(7)) attached to an arsenic atom did not show up strongly and a ghost peak appeared along the threefold axis on the other side of the arsenic atom. Coordinates for all other carbon atoms were determined from this synthesis and the coordinates for the heavy atoms were slightly adjusted. These coordinates were used to calculate structure factors and a difference synthesis from which the position of the methyl group (C(7)) was determined and all atomic coordinates were slightly refined.

The structure was refined with isotropic thermal parameters using a program written for the space group. The program calculates a 4 × 4 block matrix for positional and isotropic thermal parameters for each atom in general position, a 2 × 2 block matrix for the one positional parameter and the isotropic thermal parameter for each atom in a special position along the threefold axis, and a 2 × 2 block matrix for the scale factor and an over-all thermal parameter. The shifts were determined in the usual way, the thermal parameter shifts being determined by the relationship $B + B_t - B_{ii}$, where B is the shift determined from the 4 × 4 or 2 × 2 atomic matrix, B_{ii} is the suggested shift in the

over-all temperature factor as determined using the diagonal term of the inverse 2 × 2 over-all thermal factor and scale factor matrix, and B_t is the over-all B shift using the complete 2 × 2 matrix.[15] The structure was refined by 16 rounds of least-squares refinement of this form with use of equal weight for all observed planes. The scattering factors used in this refinement were for Ni(0),[16] Cl(0),[17] As(0),[17] and C(0).[18] The scattering factor of nickel(0) was corrected for the real part of the effect of anomalous dispersion (-3.1).[19] The hydrogen atom positions were not determined in the analysis and were not used in the refinement. Full shifts were used and parameters were not restricted by interatomic distance or thermal constraints. The final shifts are less than 0.05 of the estimated standard deviation of the parameter for the heavy atoms and less than 0.08 for the carbon atoms. The final coordinates are listed in Table I along with estimated standard deviations determined from the least-squares matrices using the relationship

$$\sigma_i{}^2 = \frac{A_{ii}\Sigma w\Delta^2}{n - s}$$

where A_{ii} is the diagonal term of the inverse least-squares matrix for the appropriate parameter, $\Sigma w\Delta^2$ is the sum of the squares of the residuals of the individual structure factors (scaled $F_o - F_c)^2$, $w = 1$, n is the number of observations (500), and s is the number of parameters (65). Observed and calculated structure factors for the parameters listed in Table I are given in Table II. Unobserved reflections were not used in the refinement but are included in Table II indicated by negative F_o. The residual $R = \Sigma|\Delta F|/\Sigma F_o$ for the 500 observed planes is 0.074 with the refined atomic coordinates and isotropic thermal parameters of Table I.

Figure 2 shows $\overline{w\Delta^2} = \sum_n w\Delta^2/n$ as a function of sin θ/λ and F_o. The appropriate weighting scheme for a least-squares refinement should result in $\overline{w\Delta^2}$ vs. any variable being constant for the refined structure, and these curves indicate that other than unit weight for all planes would have been more appropriate. While data available to higher diffraction angle would be valuable, the ratio of available observations to parameters and the statistical standard deviations indicate that this analysis is not invalidated by the 90° 2θ limit of the observations.

A drawing showing sections of the observed electron density function through each atom is shown in Figure 3. The drawing shows all of the atoms (except H) of the complex ions lying along the threefold axis passing through the origin, and while overlap of some phenyl rings is severe, crystallographically equivalent groups appear clearly. Interatomic distances and interatomic angles are listed in Figure 4. The varia-

(14) O. S. Mills and J. S. Rollett in "Computing Methods and the Phase Problem in X-ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., report of the conference at Glasgow, 1960, Pergamon Press, Oxford, 1961, pp 107–124.

(15) D. W. J. Cruickshank, *ibid.*, p 43; R. A. Sparks, *ibid.*, p 174.
(16) R. E. Watson and A. J. Freeman, *Acta Cryst.*, **14**, 27 (1961).
(17) A. J. Freeman and R. E. Watson, personal communication, 1961.
(18) J. A. Hoerni and J. A. Ibers, *Acta Cryst.*, **7**, 744 (1954).
(19) International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, 1962, p 214.

Table I

Refined Coordinates and Isotropic Thermal Parameters (A) and Estimated Standard Deviations of Atoms in the Crystal Structure of $[(C_6H_5)_3CH_3As]_2[NiCl_4]$

				x/a^a	y/a^a	z/a^a	B	$\sigma(B)$
Ni	4	a	3	0.0597 (3)	0.0597 (3)	0.0597 (3)	3.49	0.15
Cl(1)	12	b	1	0.1815 (4)	0.0938 (4)	−0.0127 (4)	3.98	0.14
Cl(2)	4	a	3	−0.0246 (4)	−0.0246 (4)	−0.0246 (4)	4.26	0.26
As(1)	4	a	3	0.7824 (2)	0.7824 (2)	0.7824 (2)	3.86	0.10
C(1)				0.750 (1)	0.900 (1)	0.770 (2)	3.44	0.55
C(2)				0.806 (2)	0.962 (2)	0.793 (2)	4.17	0.59
C(3)	12	b	1	0.783 (2)	1.050 (2)	0.790 (2)	4.15	0.59
C(4)				0.700 (2)	1.074 (2)	0.761 (2)	5.01	0.66
C(5)				0.647 (2)	1.010 (2)	0.738 (2)	5.92	0.71
C(6)				0.666 (2)	0.920 (2)	0.740 (2)	4.40	0.61
C(7)	4	a	3	0.710 (1)	0.710 (1)	0.710 (1)	3.10	0.87
As(2)	4	a	3	0.5092 (2)	0.5092 (2)	0.5092 (2)	3.94	0.10
C(8)				0.393 (1)	0.555 (1)	0.505 (1)	3.25	0.53
C(9)				0.329 (1)	0.499 (2)	0.483 (2)	3.73	0.54
C(10)	12	b	1	0.245 (2)	0.530 (2)	0.478 (2)	5.58	0.71
C(11)				0.229 (2)	0.621 (2)	0.494 (2)	7.16	0.83
C(12)				0.300 (2)	0.673 (2)	0.515 (2)	5.42	0.68
C(13)				0.382 (2)	0.643 (2)	0.522 (2)	3.95	0.57
C(14)	4	a	3	0.582 (2)	0.582 (2)	0.582 (2)	5.31	1.17

a Numbers in parentheses are standard deviations in least significant digits.
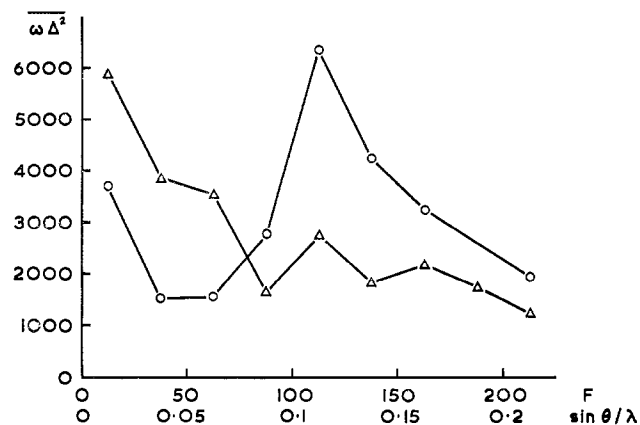
Figure 2.—$\overline{w\Delta^2}$, $w = 1$, as a function of $\sin \theta/\lambda$ (triangles) and F (circles) for the refined structure.
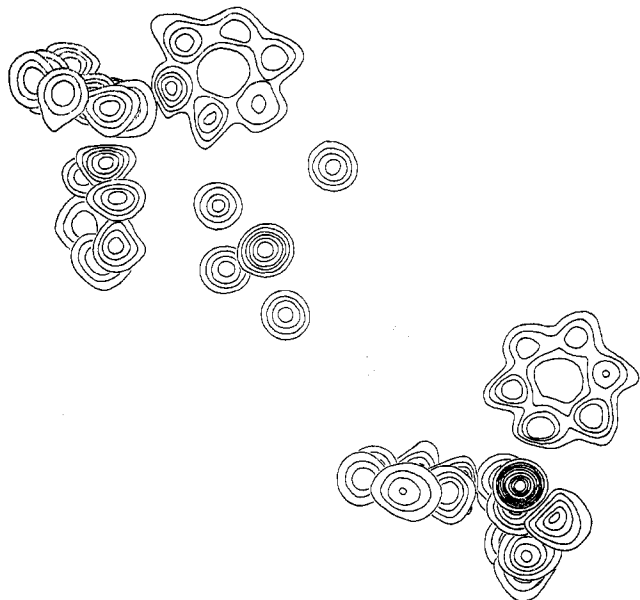
Figure 3.—Composite sections perpendicular (001) through the atomic centers of the observed Fourier synthesis of the compound $[(C_6H_5)_3CH_3As]_2[NiCl_4]$. Contours are at 0 and 4.0 e/A³ for heavy atoms and 2.0 e/A³ for carbon atoms.
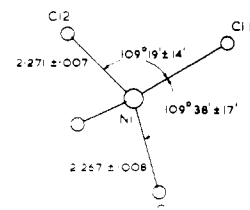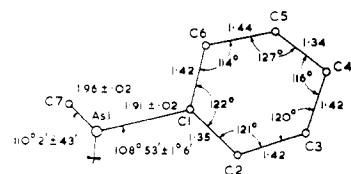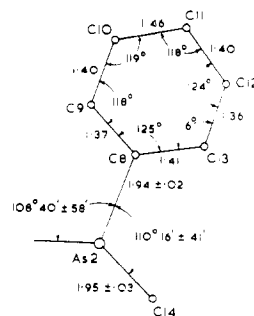
Figure 4.—Interatomic distances and angles with statistical estimated standard deviations (no allowance for esd of cell parameter) of $[(C_6H_5)_3CH_3As]_2[NiCl_4]$; esd of C–C distances is 0.04 A.

tions in refined C–C distances show that this analysis is not of much value for determining the structure of the phenyl ring, but the standard deviations of the metal-halogen distances and angles are usefully low.

Discussion

The $[NiCl_4]^{2-}$ group is regularly tetrahedral to within experimental error, the observed difference in Ni–Cl distance of 0.004 A being about one-half of the estimated standard deviations for these distances and

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE COMPOUND [(C₆H₅)₃CH₃As]₂[NiCl₄] [a]

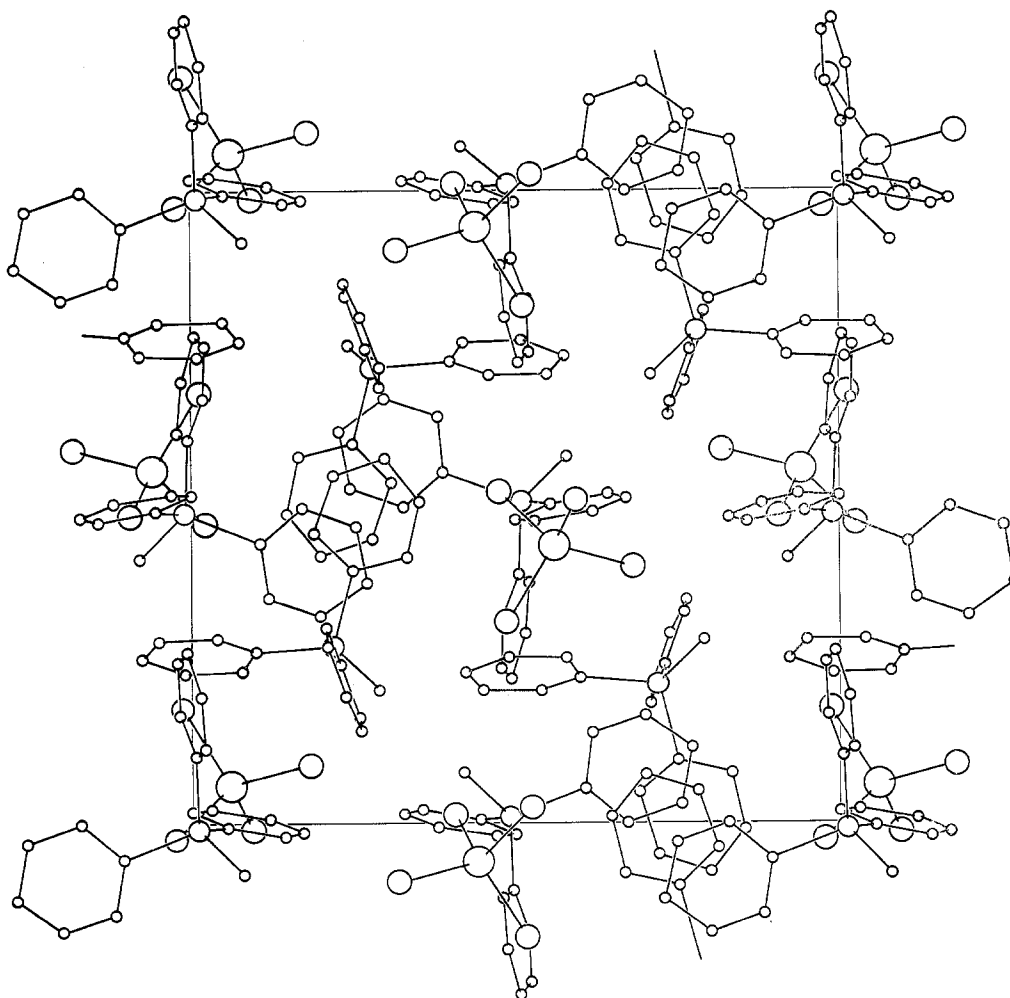| h	k	l	Fobs	Fcalc
2	0	0	1409	1564
4	0	0	3796	4272
6	0	0	887	791
8	0	0	505	572
10	0	0	1035	1137
12	0	0	292	299
14	0	0	439	489
1	1	0	129	160
2	1	0	1156	1306
3	1	0	2216	2309
4	1	0	1267	1192
5	1	0	729	663
6	1	0	1031	975
7	1	0	397	355
8	1	0	1096	1074
9	1	0	268	271
10	1	0	275	277
11	1	0	308	358
12	1	0	262	294
13	1	0	-224	116
14	1	0	169	168
1	2	0	735	757
2	2	0	2034	2209
3	2	0	1219	1215
4	2	0	1206	1073
5	2	0	556	468
6	2	0	1084	1089
7	2	0	710	627
8	2	0	108	64
9	2	0	720	675
10	2	0	89	88
11	2	0	338	331
12	2	0	763	721
14	2	0	260	276
1	3	0	767	815
2	3	0	258	319
3	3	0	1210	1183
4	3	0	1335	1267
5	3	0	537	575
6	3	0	112	162
7	3	0	154	134
8	3	0	1293	1280
9	3	0	-182	111
10	3	0	611	628
11	3	0	553	558
12	3	0	454	410
13	3	0	-228	50
1	4	0	70	103
2	4	0	1701	1702
3	4	0	1379	1420
4	4	0	1187	1208
5	4	0	469	477
6	4	0	442	370
7	4	0	1692	1787
8	4	0	528	539
9	4	0	412	377
10	4	0	714	709
11	4	0	765	751
12	4	0	-221	73
13	4	0	-228	20
1	5	0	619	718
2	5	0	665	662
3	5	0	805	844
4	5	0	237	211
5	5	0	180	125
6	5	0	1052	1086
7	5	0	773	721
8	5	0	285	274
9	5	0	294	304
10	5	0	275	240
11	5	0	226	299
12	5	0	177	263
13	5	0	342	315
1	6	0	868	856
2	6	0	1441	1407
3	6	0	847	789
4	6	0	752	714
5	6	0	1189	1224
6	6	0	1001	1068
7	6	0	420	407
8	6	0	1291	1264
9	6	0	853	827
10	6	0	437	455
11	6	0	-221	1
12	6	0	317	351
1	7	0	847	900
2	7	0	-151	152
3	7	0	856	811
4	7	0	467	471
5	7	0	218	205
6	7	0	139	79
7	7	0	469	405
8	7	0	186	152
9	7	0	-207	53
10	7	0	-217	99
11	7	0	708	702
12	7	0	199	210
1	8	0	488	432
2	8	0	577	619
3	8	0	184	181
4	8	0	144	131
5	8	0	-182	145
6	8	0	541	524
7	8	0	936	-979
8	8	0	758	796
9	8	0	289	354
10	8	0	412	398
11	8	0	651	635
1	9	0	444	386
2	9	0	273	301
3	9	0	653	672
4	9	0	323	362
5	9	0	448	436
6	9	0	-200	208
7	9	0	311	313
8	9	0	270	276
9	9	0	220	142
10	9	0	177	142
1	10	0	1339	1342
2	10	0	-193	79
3	10	0	249	204
4	10	0	695	651
5	10	0	822	747
6	10	0	758	794
7	10	0	-217	120
8	10	0	406	332
9	10	0	368	369
10	10	0	458	488
1	11	0	674	649
2	11	0	-203	200
3	11	0	268	269
4	11	0	442	453
5	11	0	-217	27
6	11	0	300	322
7	11	0	-224	158
8	11	0	-228	74
1	12	0	319	341
2	12	0	638	635
3	12	0	482	423
4	12	0	-221	85
5	12	0	313	323
6	12	0	444	461
1	13	0	-224	6
2	13	0	382	417
3	13	0	256	300
4	13	0	327	327
5	13	0	243	261
1	14	0	663	626
2	14	0	-228	144
1	1	1	1686	1724
2	1	1	604	656
3	1	1	1314	1320
4	1	1	1352	1286
5	1	1	587	649
6	1	1	615	536
7	1	1	1494	1474
8	1	1	1101	853
9	1	1	877	881
10	1	1	104	90
11	1	1	678	641
12	1	1	199	163
13	1	1	389	356
14	1	1	-228	120
2	2	1	596	640
3	2	1	927	970
4	2	1	891	883
5	2	1	796	622
6	2	1	61	107
7	2	1	1644	1613
8	2	1	917	894
9	2	1	596	586
10	2	1	623	591
11	2	1	332	299
12	2	1	469	460
13	2	1	258	310
14	2	1	376	324
2	3	1	805	732
3	3	1	720	717
4	3	1	968	899
5	3	1	1557	1492
6	3	1	591	521
7	3	1	839	781
8	3	1	577	597
9	3	1	695	685
10	3	1	501	472
11	3	1	591	562
12	3	1	344	326
13	3	1	585	607
2	4	1	558	547
3	4	1	881	812
4	4	1	845	807
5	4	1	1077	1151
6	4	1	826	821
7	4	1	919	907
8	4	1	406	428
9	4	1	368	375
10	4	1	701	711
11	4	1	397	400
12	4	1	355	326
13	4	1	-228	174
2	5	1	403	476
3	5	1	306	287
4	5	1	839	784
5	5	1	646	633
6	5	1	845	779
7	5	1	454	487
8	5	1	1029	1015
9	5	1	317	303
10	5	1	461	464
11	5	1	469	457
12	5	1	266	193
13	5	1	-228	147
2	6	1	668	615
3	6	1	368	377
4	6	1	771	608
5	6	1	630	695
6	6	1	741	729
7	6	1	490	530
8	6	1	936	859
9	6	1	524	558
10	6	1	150	126
11	6	1	-221	159
12	6	1	503	453
2	7	1	868	813
3	7	1	710	616
4	7	1	661	644
5	7	1	1046	1021
6	7	1	752	745
7	7	1	228	264
8	7	1	511	518
9	7	1	-207	33
10	7	1	503	519
11	7	1	247	300
12	7	1	376	378
2	8	1	562	502
3	8	1	530	557
4	8	1	744	735
5	8	1	234	203
6	8	1	678	679
7	8	1	287	357
8	8	1	304	316
9	8	1	494	541
10	8	1	194	155
11	8	1	-228	130
2	9	1	222	221
3	9	1	1134	1081
4	9	1	465	370
5	9	1	406	396
6	9	1	395	368
7	9	1	406	409
8	9	1	674	589
9	9	1	194	116
10	9	1	420	439
2	10	1	824	800
3	10	1	163	168
4	10	1	714	688
5	10	1	-207	129
6	10	1	475	444
7	10	1	285	271
8	10	1	192	178
9	10	1	283	335
10	10	1	365	378
2	11	1	357	377
3	11	1	414	559
4	11	1	406	418
5	11	1	511	488
6	11	1	560	553
7	11	1	-224	67
8	11	1	382	361
9	11	1	194	230
2	12	1	120	175
3	12	1	268	257
4	12	1	475	419
5	12	1	323	365
6	12	1	311	343
7	12	1	226	290
2	13	1	133	194
3	13	1	509	514
4	13	1	-228	228
5	13	1	321	303
2	14	1	342	354
2	2	2	1401	1504
3	2	2	1177	1273
4	2	2	1536	1620
5	2	2	708	683
6	2	2	401	319
7	2	2	598	637
8	2	2	186	164
9	2	2	270	268
10	2	2	534	517
11	2	2	114	151
12	2	2	258	303
13	2	2	-224	77
3	3	2	828	814
4	3	2	499	467
5	3	2	604	518
6	3	2	1014	878
7	3	2	701	675
8	3	2	384	431
9	3	2	480	469
10	3	2	192	157
11	3	2	184	209
12	3	2	108	99
13	3	2	-228	100
3	4	2	915	864
4	4	2	1272	1218
5	4	2	646	685
6	4	2	1215	1277
7	4	2	433	379
8	4	2	722	699
9	4	2	902	896
10	4	2	108	215
11	4	2	226	267
12	4	2	450	429
13	4	2	-228	214
3	5	2	642	647
4	5	2	845	827
5	5	2	294	274
6	5	2	357	292
7	5	2	773	742
8	5	2	395	396
9	5	2	437	414
10	5	2	260	322
11	5	2	463	430
12	5	2	315	397
13	5	2	247	291
3	6	2	811	803
4	6	2	1502	1516
5	6	2	422	449
6	6	2	611	568
7	6	2	1132	1147
8	6	2	803	861
9	6	2	142	288
10	6	2	492	486
11	6	2	560	512
12	6	2	139	190
3	7	2	932	893
4	7	2	461	394
5	7	2	630	637
6	7	2	289	243
7	7	2	344	300
8	7	2	376	396
9	7	2	399	421
10	7	2	201	218
11	7	2	163	222
12	7	2	188	175
3	8	2	-172	45
4	8	2	957	873
5	8	2	1172	1130
6	8	2	929	914
7	8	2	279	303
8	8	2	541	514
9	8	2	596	613
10	8	2	194	281
11	8	2	-228	212
3	9	2	594	576
4	9	2	754	692
9	9	2	215	242
10	9	2	247	215
3	10	2	1122	1075
4	10	2	357	373
5	10	2	334	341
6	10	2	858	850
7	10	2	826	781
8	10	2	184	221
9	10	2	-228	216
4	11	2	116	145
5	11	2	104	150
6	11	2	349	378
7	11	2	232	208
7	11	2	209	175
8	11	2	234	157
3	12	2	414	481
4	12	2	782	729
5	12	2	340	395
6	12	2	414	435
7	12	2	-228	164
3	13	2	-228	246
4	13	2	501	492
5	13	2	321	344
3	3	3	1153	1223
4	3	3	418	342
5	3	3	325	311
6	3	3	636	646
7	3	3	486	499
8	3	3	167	336
9	3	3	598	589
10	3	3	408	448
11	3	3	879	866
12	3	3	365	351
13	3	3	199	239
4	4	3	970	857
5	4	3	741	687
6	4	3	756	735
7	4	3	566	558
8	4	3	638	622
9	4	3	319	349
10	4	3	243	287
11	4	3	-217	106
12	4	3	851	824
13	4	3	-228	105
4	5	3	384	363
5	5	3	997	958
6	5	3	731	685
7	5	3	194	135
8	5	3	585	574
9	5	3	211	503
10	5	3	279	253
11	5	3	414	445
12	5	3	190	206
4	6	3	372	417
5	6	3	653	662
6	6	3	602	512
7	6	3	649	638
8	6	3	-196	67
9	6	3	351	385
10	6	3	429	421
11	6	3	237	251
12	6	3	420	379
4	7	3	955	979
5	7	3	-175	47
6	7	3	349	376
7	7	3	473	470
8	7	3	342	375
9	7	3	218	319
10	7	3	577	650
11	7	3	644	675
4	8	3	706	656
5	8	3	644	677
6	8	3	325	351
7	8	3	321	356
8	8	3	36	59
9	8	3	234	279
10	8	3	167	206
11	8	3	289	368
4	9	3	63	60
5	9	3	207	314
6	9	3	511	547
7	9	3	640	691
8	9	3	374	356
9	9	3	294	294
4	10	3	689	720
5	10	3	401	363
6	10	3	-214	88
7	10	3	209	219
8	10	3	-224	120
9	10	3	437	459
4	11	3	674	696
5	11	3	-221	71
6	11	3	-224	96
7	11	3	501	465
8	11	3	422	472
4	12	3	186	276
5	12	3	-228	231
6	12	3	152	182
4	13	3	-228	42
5	6	4	1035	999
6	6	4	714	715
7	6	4	211	261
8	6	4	801	783
9	6	4	553	541
10	6	4	163	219
11	6	4	-224	149
12	6	4	325	289
5	7	4	537	534
6	7	4	283	246
7	7	4	171	225
8	7	4	129	206
9	7	4	-217	110
10	7	4	270	336
11	7	4	391	370
5	8	4	393	340
6	8	4	701	714
7	8	4	661	699
8	8	4	562	620
9	8	4	368	353
10	8	4	484	485
5	9	4	194	224
6	9	4	313	353
7	9	4	285	310
9	9	4	118	134
5	10	4	691	640
6	10	4	486	499
7	10	4	-224	43
8	10	4	393	396
9	10	4	-228	260
5	11	4	-221	176
6	11	4	173	243
7	11	4	446	465
5	5	5	1160	1125
6	5	5	520	549
7	5	5	1229	1212
8	5	5	351	338
9	5	5	207	281
10	5	5	262	290
11	5	5	910	926
12	5	5	294	314
6	6	5	370	386
7	6	5	334	381
8	6	5	520	485
9	6	5	323	367
10	6	5	-221	28
11	6	5	414	466
6	7	5	323	350
7	7	5	76	122
8	7	5	522	573
9	7	5	541	529
10	7	5	-224	81
11	7	5	194	195
6	8	5	177	148
7	8	5	545	551
8	8	5	427	437
9	8	5	511	526
10	8	5	260	260
6	9	5	-214	11
7	9	5	725	721
8	9	5	429	373
9	9	5	226	275
8	10	5	-228	102
6	6	6	365	363
7	6	6	156	160
8	6	6	484	459
9	6	6	161	163
10	6	6	488	507
11	6	6	177	234
7	7	6	112	94
8	7	6	-217	78
9	7	6	230	207
10	7	6	454	452
7	8	6	211	262
8	8	6	370	349
9	8	6	287	290
7	9	6	499	474
8	9	6	-228	121
9	9	6	-228	125
7	10	6	306	354
8	10	6	213	229
7	7	7	1001	1021
8	7	7	247	194
9	7	7	173	135
10	7	7	-228	69
8	8	7	209	188
9	8	7	403	441
8	9	7	182	212
8	8	8	382	357

[a] Scale is 10× absolute for one formula unit.

the observed difference in the Cl–Ni–Cl angles of 19′ being about equal to the estimated standard deviation for these angles. This regularity is consistent with the observed high magnetic moment of the compound,[8] in which the degeneracy of the d electron levels gives rise to a high orbital contribution to the magnetic moment.[9] The distortion predicted by the theory of Jahn and Teller[5] does not appear and if present at all must be smaller than the observed experimental error of the structure.

The tetrahedral arrangement of ligands in the complex anion [NiCl₄]²⁻ is not stabilized in the compound

Figure 5.—A diagram of the structure of [(C₆H₅)₃CH₃As]₂[NiCl₄] projected on (001) showing the packing environment of the anion. In order of decreasing diameter, the circles represent nickel, chlorine, arsenic, and carbon atoms.

by crystal forces; that is, the forces exerted on the anion by the other components of the crystal or by these complex ions on each other do not force an otherwise unstable arrangement. Each complex group $[NiCl_4]^{2-}$ is effectively separated from other anions and shielded from the rest of the crystal by phenyl rings, which, like large flat leaves, surround the anion as shown in Figure 5. The phenyl rings are not closely constrained and do not constrain the anions. Evidence independent of this structure analysis that the complex anion is stable is that the magnetic moment of the substance in solution in nitromethane is the same as that of the solid.[20]

That the environment of the complex ion in this compound is so unrestrictive caused us to consider the possibility of a larger distortion than has been indicated that cannot easily be detected by X-ray analysis. Each anion has threefold symmetry derived from the crystal symmetry. It is consistent with the crystal symmetry that each anion have 23 symmetry and be regularly tetrahedral. It would be possible for each anion to be distorted along a twofold axis giving point symmetry $\bar{4}$ in a manner suggested by Dunitz and Orgel[6] and that the unique distortion axis resonate in time or

(20) N. S. Gill, personal communication.

be disordered in space among the four possible directions of the twofold axes of a regular tetrahedron and of the crystal. The effect of this distortion would not be observed in the positions of the ligands as determined by X-ray structure analysis; the coordination polyhedron would appear perfectly regular. The only observable effect of such resonating distortion or disorder would be interpreted as an increase in the anisotropic thermal vibration parameters.

The determination of thermal parameters by diffraction analysis is less precise than that of coordinate parameters. Nonetheless, an inspection of the difference synthesis calculated using the parameters of Table I in the region of the anion shown in Figure 6 shows that this form of distortion is not evident in this compound. The structure was refined using isotropic thermal parameters, and one would expect the anisotropy caused by normal thermal vibration alone to be largest in the direction perpendicular to the Ni–Cl bonds. This is the same direction as one would expect from the suggested distortion when mixed with the threefold symmetry of the crystal. The expected anisotropy is present but is not large, certainly small enough to indicate that this form of distortion is not present to any degree. It does indicate, however, that anisotropic
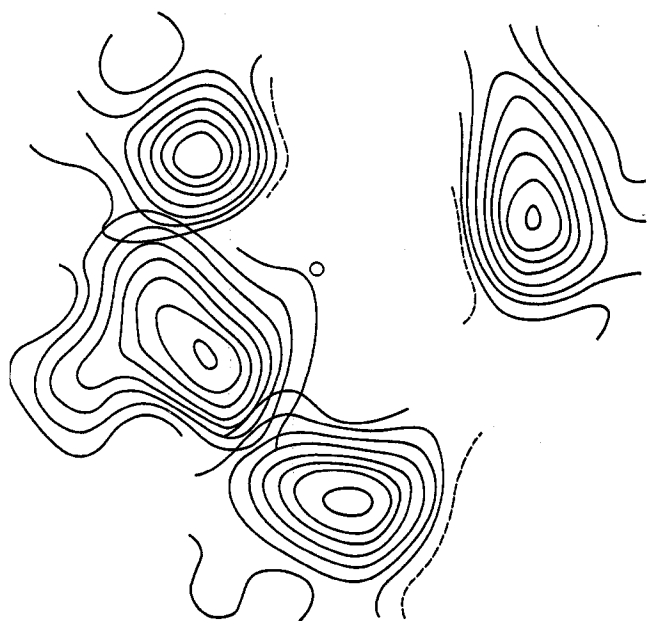
Figure 6.—Composite sections of the phased difference synthesis of the compound $[(C_6H_5)_3CH_3As]_2[NiCl_4]$ in the region of the anion $[NiCl_4]^{2-}$, excluding the nickel atom section, which is indicated by the small circle. Solid contour lines are at 0 and $+0.1$ e/A^3.

thermal parameters for the heavy atoms could be determined from the data.

The arsonium ions are regularly tetrahedral to within experimental error. The angle between the threefold axis and the axis of least inertia (all atoms given equal weight) of the (AsC_6) groups is $111°$ $12'$ for As(1)C(1)–C(6) and $110°$ $38'$ for As(2)C(8)–C(13). The related phenyl–arsenic–phenyl angles of the two groups are $107°$ $41'$ and $108°$ $17'$, respectively. The differences between these angles and regularity ($109°$ $28'$) are approximately 3σ, though the estimated standard deviations of the axes of minimum inertia have not been calculated accurately. The angle between the plane defined by the axis of minimum inertia of the (AsC_6) group (all atoms given equal weight) and the threefold axis and the plane of the ring (perpendicular to the axis of maximum inertia) or the pitch of the

phenyl groups is $20°$ $10'$ for As(1)C(1)–C(6) and $22°$ $50'$ for As(2)C(8)–C(13). The interatomic distances and angles of the arsenic atoms to their nearest neighbors and of the phenyl rings are given in Figure 4.

The cell parameters for the chlorides determined from Weissenberg photographs are listed in Table III. The individual photographs were not calibrated, but the camera was calibrated with pure aluminum wire. The relative changes in cell parameter are small but real as shown by film-to-film comparison.

TABLE III

CUBIC CELL PARAMETERS OF THE CHLORIDES
$[(C_6H_5)_3CH_3As]_2[M^{II}Cl_4]$ for M^{II} = Mn, Fe, Co, Ni, and
Zn, MEASURED FROM WEISSENBERG PHOTOGRAPHS (ESD 0.01 A)

Metal	a, A	Metal	a, A
Mn	15.63	Co	15.53
Fe	15.65	Ni	15.56
		Zn	15.55

The existence of this series of compounds with definite regularly tetrahedral coordination should allow a series of experiments involving the correlation of properties and structure. Among these are the studies of optical absorption spectra,[21] infrared spectra,[22] magnetic moment,[23] and heats of solution.[24]

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(23) B. N. Figgis, J. Lewis, F. Mabbs, and G. A. Webb, *Nature*, **203**, 1138 (1964).

(24) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, **3**, 5 (1964).