THE CRYSTAL STRUCTURE OF NICKEL ETHYLENEDIBIGUANIDE CHLORIDE MONOHYDRATE

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(Abstract)

The crystal structure of nickel ethylenedibiguanide has been determined from three-dimensional, x-ray diffractometer data (3087 reflections). The compound, $Ni(C_6H_{16}N_{10})Cl_2 \cdot H_2O$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$. The unit cell contains four molecules and has dimensions:
$a=6.911\pm0.001$, $b=11.678\pm0.001$, $c=18.055\pm0.002$ Å, $\beta=101.39\pm0.01^\circ$

An initial structure was obtained from the nickel-nickel, nickel-chlorine, and chlorine-chlorine vectors on a three-dimensional Patterson map. The trial structure was refined by the method of least squares until a reliability factor of R=4.85% and a goodness-of-fit of 1.11 was obtained. Hydrogen positions and isotropic temperature factors as well as positions and anisotropic temperature factors of the heavy atoms were allowed to refine in the final stages.

The organic ligand molecule complexes in a square planar array about the central nickel atom. The entire molecule is planar, except for the two ethylene carbons, and has point group symmetry C_2. The chemically equivalent bonds differ in length by the order of magnitude of the standard deviations of the positions of the bonding atoms. All bond distances have been correlated with both molecular orbital and valence bond descriptions of the molecule, with very satisfactory results.

The hydrogen atoms on the nitrogens all participate in hydrogen bonding to the chlorines and to the oxygen of the water

molecule. Likewise, the hydrogens on the oxygen are hydrogen-bonded to chlorines. It appears that, because of hydrogen bonding to chlorines, the animo hydrogens are distorted from sp^2 planarity with the nitrogen, so that the nitrogen is almost tetrahedral. Nevertheless, the carbon-nitrogen bond distance clearly reflects double-bond character.

Introduction

Interest in the structure of nickel ethylenedibiguanide (henceforth abbreviated Ni EDG) centers primarily upon three structural aspects: the nature of the chelation of the organic ligand with the nickel, the valence-bond and molecular-orbital descriptions of the bonding within the molecule, and the packing and hydrogen bonding that occur in the crystal. The first aspect is important in understanding the nature of nickel-nitrogen square planar metal-to-ligand bonding. The second is important because of the alternating carbon-nitrogen bonding as exemplified in the EDG organic chelate. (The study of carbon-nitrogen bonds is fundamental to the understanding of peptide linkages, for example.) The third aspect is interesting because of the stacking phenomenon observed in this crystal. Furthermore, the effect of the ionic forces, hydrogen bonds, and van der Waals forces between molecules and between the nickel chelate cation and its associated hydrogen bond acceptors (chlorides and waters) can be correlated with structural details, such as distortions in the EDG chelate and packing considerations.

Cotton and Wilkinson[1] review the properties of a silver analog of Ni EDG. The chelation in Ag EDG is reportedly thought to be tetradentate about the silver, but apparently the true nature of the EDG chelate itself is not known. This paper will clarify the nature of both these structural aspects, insofar as the nickel compound is concerned.

Experimental

Ni EDG chloride monohydrate crystallizes in orange monoclinic needles (the needle axis was designated the a-axis), which do not melt below 350° C. At about 150° C., the crystals begin to shatter and turn opaque as the water of hydration is driven out. At 260° C., the crystals start to darken and at 330° C. begin to turn dark brown. At 350° C., decomposition is evidenced by the blackness of the crystals, but they remain solid, nevertheless, indicating a high degree of ionic bonding in the crystal. The crystals (obtained from Dr. B.D. Sharma*) remained stable to the atmosphere and exposure to x-rays over the period of investigation (four years). Apparently dehydration occurs to a very small degree at room temperature since only a few crystals in the original sample were observed to have become opaque (characteristic of dehydration). One such crystal was compared in a flotation density measurement with a clear, intact crystal, and was found to have a lower density, as expected.

From a crystal mounted for rotation about the needle (a)

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axis, oscillation, rotation, and equi-inclination Weissenberg photographs were taken of the 0, 1, and 2 layers. Reflections 0k0 with k odd and h0l with l odd were absent, indicating that the crystal belongs to the centrosymmetric space group, $P2_1/c$.

Unit cell dimensions (see Table 1.) were obtained from precision Weissenberg photographs of two crystals: one mounted for rotation about the a-axis and one about the b-axis. (Copper radiation was used; wavelengths are given in Table 1.) Bragg angles were measured for 30 0kl and 39 h0l reflections and entered into a unit cell least squares calculation of the unit cell parameters. There were two h0l films and one 0kl film which were correlated pairwise, in order to obtain two complete sets of unit cell dimensions. All of the results were then weighted, according to to the relative standard deviations of each parameter, giving preference to single-film calculations and to the better of the two h0l films. Least squares calculations including absorption and eccentricity corrections were also done, but the corrections were found to be insignificant.

The density was calculated assuming four $Ni(C_6H_{16}N_{10})Cl_2 \cdot H_2O$ (MW=375.9) per unit cell (see Table 1.). The density was also measured by the method of flotation in a mixture of chloroform and dibromoethane. The observed and calculated densities differed by less than one part per hundred (or about two hydrogens per unit cell).

Visual data was collected from a crystal mounted along the needle axis. The diameter of the crystal for an irregular hex-

agonal cross-section, 0.06 mm., was roughly one-third of the length of the crystal, so that for the purposes of preliminary structural determination, no absorption correction was needed. Reflections of the type 0kl through 2kl were collected on multiple-film equi-inclination Weissenberg photographs (using copper radiation). The intensities of 266 zero layer reflections were visually estimated using a graduated intensity strip. Lorentz and polarization corrections were applied, and the intensities from the different films were placed on the same scale by a weighted least-squares method. An 0kl Patterson projection was prepared, and vectors that were thought to be Ni-Ni, Ni-Cl, and Cl-Cl vectors were observed. The y and z coordinates of the nickel and chlorines were used to phase a structure factor calculation for an a-axis Fourier projection. The result did show new peaks, but they could not be correlated with any chemical model. (In retrospect, the projection failed to give any conclusive results because of inversion in the packing of molecules on top on one another along the a-direction, rather than because of poor or insufficient data.)

Another crystal, to be used for collecting automatic diffractometer data, was mounted so as to rotate about the a-axis. The crystal was nearly cubical, with sides of approximately 0.1mm., which was small enough so that absorption errors were minimized (the linear absorption coefficient was calculated to be 54.8 $cm.^{-1}$, so that μR for a sphere of radius 0.05 mm. was found to be less than 0.3; consequently, the absorption correction factor could be expected to vary about 2% over all values of 2θ).

From this crystal, the intensities of 3246 reflections were measured on the General Electric automatic diffractometer, using nickel-filtered copper radiation. In the initial data processing, Wilson statistics were done to determine an overall temperature factor and an overall scaling factor, which was then applied to the counter data. The dispersion correction for nickel was also included in the data preparation. Reflections for which the background count was larger than the scan count were given zero weight.

Determination and Refinement of the Structure.

The coordinates of the nickel and chlorines were determined from the Ni-Ni, Ni-Cl, and Cl-Cl vectors of a three-dimensional Patterson map. Enough of the phases of the observed structure factors were determined from the F_{calc}'s so that the lighter carbon, nitrogen, and oxygen atoms could be resolved in a three-dimensional Fourier electron density map. In the projection calculated from the visual data, it was impossible to decide whether the chelation of the organic with the nickel was tetradentate onto one nickel or bidentate onto two nickels (the organic part then being stretched out into a linear array). From the three-dimensional diffractometer data it was possible to determine that the chelation was tetradentate, with the ligand organic molecule wrapped around a single nickel atom. From the trial structure thus obtained, a structure factor calculation was carried out, resulting in a reliability factor of R=49.55%.

Refinement of the trial structure was begun with two least

squares cycles (minimizing $\Sigma w(k^2|F_{obs}|^2 - |F_{calc}|^2)^2$) in which the coordinates of the 20 heavier atoms in the asymmetric unit were allowed to shift. The isotropic temperature factors were fixed at 2.5 $\AA^2$ and not allowed to vary. The resulting R index was 18.53%. Reflections for which systematic space group extinctions occur were edited from the data, after which two more least squares cycles were performed, in which anisotropic temperature factors for nickel and chlorine were introduced and allowed to refine (the isotropic temperature factors for the other atoms were still fixed); also, the atomic coordinates were allowed to refine. The R index dropped to 11.06%. Bond distances and angles and a least squares plane of the molecule were calculated. Planes in which the hydrogens on the amino nitrogens and ethylene carbons might be expected were calculated for difference Fourier maps; unfortunately, the resulting peaks were doughnut-shaped, so that the orientations of the hydrogens could not be determined. Therefore, hydrogen atom coordinates for NH, NH_2, and CH_2 groups were calculated from the expected geometries, assuming coplanarity of all NH and NH_2 groups with the rest of the molecule, and tetrahedral CH_2 groups. The hydrogen parameters were not allowed to vary in the next two least squares cycles; anisotropic temperature factors were introduced for the other atoms and allowed to vary along with their coordinates. The resulting R value was 6.09%. ΔF's were derived from structure factors calculated without the hydrogen coordinates (R=7.04%), using the signs of the final F_{calc}'s for the F_{obs}'s in order to prepare difference maps. This time, the hydrogens were clearly resolved.

For the final stages of refinement, the water hydrogen positions were calculated by determining the positions of the two nearest chlorines to the oxygen and assuming hydrogen bonding to them. In the final stages, all parameters including atomic coordinates, heavy atom (Ni, Cl, O, N, C) anisotropic temperature factors, hydrogen isotropic temperature factors, the scale factor for F_{obs}, and the secondary extinction factor were allowed to refine until their full shifts were no larger than one-fifth of their standard deviations, until the actual goodness of fit approached 1.0, and until the reliability factor R approached minimum; then the refinement would have to be considered complete. Four cycles of least squares were performed with one matrix containing all coordinates and isotropic temperature factors and another containing anisotropic temperature factors, the scale factor, and the secondary extinction factor. R dropped to 4.86%. The shifts of the parameters of some of the atoms (one of the CH_2 groups and all of the NH_2 groups) were still large compared to their standard deviations. In the final two least squares cycles, these parameters were all put into one matrix. A second matrix contained all other heavy atom coordinates and associated hydrogen parameters, except for the water molecule. The anisotropic temperature factors for the second matrix, plus the water molecule parameters, plus the scale factor and secondary extinction coefficient were all put into a third matrix. By dividing the parameters up in this manner, it was hoped that the interactions of the shifts of the parameters would be maximized so that the refinement would be

hastened. The final R value reached a minimum at 4.85%. The actual goodness-of-fit reached a minimum (approaching 1.0) at 1.1111. And finally most of the parameter shifts settled down to less than one fifth of their standard deviations, the largest shift being 0.23 times its standard deviation (the x coordinate of a water hydrogen). Refinement was considered complete. 3087 reflections were included in the final structure factor calculation, of which 2879 contributed to the least squares sums (and to the R index). Tables 2, 3, 4, and 5 give the final atomic parameters and their deviations. Table 14 lists the observed and calculated structure factors. The final electron density map is shown in Fig. 1. as the section in the final least squares plane of the molecule; the final difference map for the same section is shown in Fig. 2.

Discussion of the Structure

Molecular Dimensions and Geometry

The bond distances and angles are illustrated in Fig. 3 and summarized in Tables 6 and 10. The standard deviations of bond lengths (calculated from the positional standard deviations) are given in Table 7. A two-fold rotation axis, in a line from the nickel atom to the center of the bond between the ethylene carbons, is observed in the Ni EDG cation, strongly suggesting C_2 point group symmetry. This can be tested by comparing bond distances between equivalent atoms and bond angles between equivalent bonds across the line of this two-fold axis. For the heavy atoms shown in Fig. 3., the equivalent bond distances differ from

each other by one or two calculated standard deviations, at most . The equivalent bond angles, perhaps the most sensitive test of C_2 symmetry, differ by one-half of a degree, at most.

The bond distances to hydrogen atoms and their associated bond angles do not reflect the C_2 symmetry as well as the heavier atoms do, primarily because of distortions caused by hydrogen bonding to the acceptors shown in Fig. 3. The stereoscopic drawing (Fig. 4.) shows quite dramatically the effect of the hydrogen bond acceptors on the animo hydrogens as well as the obvious C_2 symmetry of the ethylene hydrogens. One can also see that the molecule is planar except for the ethylene carbons, which are in the staggered configuration so as to minimize the steric hindrance of their associated hydrogens. Comparing the amino groups related by the two-fold axis, one can see that the tilts of the two hydrogens on N(2) and N(4) relative to the plane of the molecule are parallel--likewise for N(4) and N(7). That is, both H(2) and H(14) are "up" relative to H(3) and H(15), and both H(6) and H(12) are "up" relative to H(5) and H(11), as is required for C_2 symmetry.

In the bonding treatment, the symmetry of the pi-bonding system of the Ni EDG cation (namely, all the heavier atoms except the two tetrahedral ethylene carbons) was taken to be D_{2h}, because of the hypothetical existence of a mirror plane in the plane of the molecule, and two perpendicular to the plane of the molecule (and to each other) along the line of the C_2 two-fold axis and along the line formed by N(3), Ni, and N(8). (See Fig. 5 for illustration

of the pi-system.) However, the bond distances I-IV (see Table 6) do not demonstrate D_{2h} symmetry nearly as well as C_2 symmetry. For example, the maximum discrepancy in the group of type I bonds is four times the calculated standard deviation of the N-C bond. A similar result is obtained for type II and III bonds. For the Ni-ligand N bond. however, the difference ($7\frac{1}{2}$ standard deviations) between the two different pairs of C_2-related bonds indicates that actually two distinct kinds of ligand-metal bonds occur in the molecule. Nevertheless, these discrepancies are small enough to allow a D_{2h} approximation for the valence-bond and molecular orbital calculations of the bonding. (It must be borne in mind that this can be only a very rough first approximation.) As can be seen from the shortness of the bonds, the three types of N-C bonds are I > II > III (1.29 Å. < 1.35 Å. < 1.37 Å.)in order of double bond character.

A quantitative description of the planarity of the molecule is given in Table 11. (In order to compare the deviations from planarity in this table with the stereoscopic drawing of Fig. 4, one must interpret a positive deviation as being away from the observer, i.e., down into the page; a negative deviation is above the page.) A least squares plane calculation was carried out giving pi-system atoms weights inversely proportional to the standard deviations of their x-coordinates relative to nickel. This weighting scheme was chosen because the normal to the plane is approximately parallel to the a-axis. Clearly, the Ni EDG cation is planar, except for the ethylene portion and the amino

hydrogens. An edge-on view is given in the molecular packing drawing, Fig. 9, which demonstrates more dramatically the degree of planarity.

Temperature Parameters

The magnitudes (B's) and orientations (direction cosines) of the principal axes of the thermal ellipsoids of the 20 heavier atoms were calculated; and from the B's, thermal displacements (U's) in Å. were calculated according to the formula $U = (B/8\pi^2)^{\frac{1}{2}}$. These values are tabulated in Table 13. Fig. 4 gives a three-dimensional, stereoscopic depiction of the thermal motion. The principal motion is along the a-axis, indicating a lattice or packing "vibration" along the direction of stacking of the planar molecules. A secondary motion can be described as a libration, or twisting, of the molecule about the nickel atom, along the direction of bonds in the three rings. Thus, the secondary motion is emphasized in the stereoscopic view, since the motion normal to the plane of the molecule is viewed head-on. The libration can also be seen in the electron density map of Fig. 1.

Description of the Bonding in the Ni EDG^{+2} Cation

The bonding in the Ni EDG^{+2} cation has been investigated through two approaches: the valence bond theory and the molecular orbital theory. The input structure for both approaches is shown in Fig. 6. In this state, the organic chelate (in its most probable valence-bond form) has combined with a Ni^{+2} by forming dative bonds to the nickel, utilizing the electron pairs of the ligand nitrogens. Thus, the nitrogens become positively charged and the nickel charged -2. In other words, the nickel starts out in a d^8 ground configuration and then forms a square-planar,

tetradentate dsp^2 complex, with room in its orbitals for two more electrons in pi-bonding to the ligands. (The pi-bonding system has been described in Fig. 5.) Since the molecule is planar and the pi-system has D_{2h} symmetry, the molecular-orbital Hückel calculation is simplified considerably.

The assumptions used in the Hückel calculation are listed in Table 12. The coulomb integrals of nickel and nitrogen relative to carbon are dependent on the electronegativities relative to carbon; that is, the more electronegative an atom is, the more negative its coulomb integral becomes (and usually its resonance integral to another atom). Since the electronegativities of the three atoms are in the order N>C>Ni, the coulomb integrals are in the order A(N)<A(C)=A<A(Ni). (In interpreting the assumptions of Table 12, one must remember that the coulomb and resonance integrals of carbon are negative qualities.) Since the ligand nitrogen, in forming a dative sigma-bond to the nickel, becomes more positively charged, the coulomb integral of ligand N is even more negative than that of the terminal and ring nitrogens. To the ring carbon, the ligand N appears to be more electronegative than the other neighboring nitrogens; consequently, the ligand N-C resonance integral is more negative than for the other N-C bonds. These other resonance integrals were determined empirically from the observed bond distances. Due to the electroneutrality principle, the nickel will not readily accept more electrons from the terminal and ring nitrogens, which have free electron pairs for donation as mobile pi-electrons. Therefore, only a small amount of pi-bonding is allowed, which is reflected by the small resonance integral

between ligand N's and nickel.

The results of a Hückel calculation are given in Table 12. In order to convert calculated pi-bond orders to bond distances, a graph of N-C bond distance versus pi-bond order was made by drawing a straight line through the single-bond value of 1.47 Å (PBO=0), the partial double-bond value of 1.31 Å (PBO=2/3), and the theoretical double-bond value of 1.24 Å (PBO=1). The partial double-bond value is the bond distance of symmetric triazine (C-N analog of benzene)[3]. The double-bond value was calculated according to the formula given by Pauling[4]:

$$D(A\text{-}B) = r_A + r_B - 0.09|x_A - x_B| \text{ Å.},$$

where x = Pauling's electronegativity, r_C is given as 0.667 Å and r_N as 0.62 Å. The electronegativity correction was not applied in the case of the nickel (r_{Ni} =1.15 Å) and ligand nitrogen bond, because it is doubtful that the correction is valid for bonds between transition metals and the first row elements. Pauling has given a formula[5] for calculating the increase in length (relative to the single bond length) of a bond whose total bond order n is less than one (primarily for metal-ligand bonds):

$$D(n<1) = D(1) - 0.60 \log n.$$

This can also be applied to a bond whose total bond order is greater than one. The result for the Ni-ligand N bond (n=PBO + 1, n=1.176) is 1.85 Å, a reduction of 0.04 Å from the single bond value of 1.89 Å.

The molecular orbital theory explains the bonding quite well; the predicted bond lengths match the D_{2h} average bond lengths within 0.01 Å. The theory perhaps overestimates the amount of pi-bonding

to the nickel, in effect necessitating the reduction of B(Ni-lig.N). A bigger fault lies in the theory's prediction of a significant positive charge on the ring carbon, which ought to be neutral. The first step in correcting the model would be to remove the D_{2h} symmetry of the pi-system. The non-planarity of the ethylene carbons destroys this hypothetical symmetry anyway, by forcing a more tetrahedral nature on the bridged ligand nitrogens. One can see (Fig. 3) that the bond distances from these nitrogens to carbons and to nickel reflect less double-bond character than the D_{2h}-related distances for the other ligand nitrogens, which have non-restrictive, planar hydrogen atoms bonded to them. Although the puckering of the ethylene-bridged ring reduces the strain caused by the steric hinderance of the tetrahedral ethylene hydrogens, the reduction of the single C-C bond length from a predicted 1.54 Å to the observed 1.51 Å demonstrates that there is probably still residual strain in the bridge. The molecular orbital results are summarized in Fig. 7.

The valence bond approach, although its quantitative bond length results are not as good as the molecular orbital approach (see Table 12.), is, in other ways, a better theory and is arrived at much more easily. The valence bond number and bond length correlation for N-C bonds is similar to the molecular orbital case, except that the partial double bond is given a bond number of 1.5, and a smooth curve is drawn through the three points. This curve can be obtained from the pi bond order straight-line relationship in a more reproducible manner by fitting the three known points by a quadratic approximation, which yields the following relation-

ship between the valence bond theory (valence bond number = n') and the molecular orbital theory (pi bond order = p):

$$n' = \tfrac{1}{4}\,(9 - (25 - 24p)^{\frac{1}{2}}).$$

It was assumed that no pi bonding to nickel occurs, thereby confining the resonance to the biguanide portions of the cation and still maintaining D_{2h} symmetry in the pi-system. The three contributing canonical structures are shown in Fig. 6. The input structure was considered to be five times more important than either of the other two forms shown, although the second form is actually four times as probable as the third, because the second form can be written three other equivalent ways (for the bonds equivalent by D_{2h} symmetry). Consequently, the percent contributions of the three structures are 50%, 40%, and 10%, respectively. The results of this straightforward treatment are given in Table 12. The less closely fit bond distances are compensated by the more reasonable charge distributions. For example, the carbon is neutral, as would be expected; but another interesting correlation is to be noticed. X-ray crystallographic methods determine the centers of electron clouds surrounding the nuclei of atoms; if an easily polarized hydrogen is bonded to an electronegative atom, a significant fraction of the electron density about the hydrogen will be drawn toward that atom, and the bond will appear to be shortened in an x-ray experiment. Interestingly enough, the average observed N-H bond distances for the three kinds of nitrogens exhibit this tendency relative to the valence bond calculated charges--the more positive a nitrogen is, the closer its

hydrogen appears to be. The results of the valence bond treatment are shown pictorially in Fig. 8.

Both the molecular orbital and the valence bond treatment give quite satisfactory explanations of the bonding, as first approximations. Both have limitations due to input assumptions, but the discrepancies of both theories can be traced directly to errors in these assumptions, thus paving the way to better approximations.

Hydrogen Bonding and Molecular Packing in the Crystal

The melting point data of the crystal demonstrate that a great deal of ionic bond and hydrogen bond packing energy is involved in the crystal structure, just as the high temperature of decomposition indicates that the Ni EDG^{+2} complex itself is very stable. Figs. 3 and 4 show the locations of chloride ions and water molecules about the Ni EDG cation. These positions maximize both ionic contact with positively charged nitrogens and hydrogen bonding of NH's and NH_2's to chlorides. Meanwhile, the hydrogen bond acceptors have positioned themselves so as to stay as far apart as possible. Thus, they do not all lie in the plane of the molecule, causing the amino hydrogens to be distorted from sp^2 planarity. For example, one can see in Fig. 4 that the hydrogens on the amino nitrogen N(2) are pointed down toward acceptors below the plane of the molecule, as are the hydrogens of N(7). N(9) and N(4) each have one hydrogen pointing toward an acceptor in the plane and one pointing out of the plane. Moreover, H(6) and H(1) are pointing "up" and "down", respectively, because of steric hindrance with the ethylene hydrogens. In effect, the plane of

the amino hydrogens is tilted so that H(6) points between H(7) and H(8) (the "up" CH_2 hydrogen pair) and H(11) points between H(9) and H(10) (the "down" pair). (This effect, incidently, confirms the basic C_2 symmetry of the molecule.) The ring and two ligand nitrogens that have single hydrogens are hydrogen-bonded to two chlorides and a water, which are in the plane of the molecule (see Fig.1). These three acceptors are in the plane of the molecule because they are bonded to the molecule by two hydrogen bonds each. In spite of the numbering scheme that was adopted early in the structure determination procedures, the two planar chlorides, Cl(1)' and Cl(2)''', clearly "belong" to the molecule more than the ones initially chosen.

The hydrogen bond distances from donor to acceptor are given in Table 8. Clearly, all available hydrogens participate in hydrogen bonding. The shorter distances are for N to O hydrogen bonds, principally because of the larger electronegativity difference. As can be seen quite convincingly in Fig. 4, the water hydrogens are pointed toward chlorides almost on line, just as predicted before the least squares refinement.

The packing of cations and anions in the crystal is principally in layers parallel to the planes of the cations. A view of the packing is presented in Fig. 9. Packing distances between the parent molecule and the ones above and below it related by inversion centers are given in Table 9. This inversion is necessary to minimize the contact of the ethylene hydrogens. In addition, the cation has a dipole moment along its C_2 axis;

the dipole-dipole interaction tends to make the molecules stack with dipoles opposed. The nickels are slightly staggered so that they rest with their negative charges on top of the positively charged ligand nitrogens. Other van der Waals repulsions are minimized if the molecules are stacked in a parallel fashion, which requires a center of symmetry between layers.

The layers lie at roughly one-fourth and three-fourth along the a-axis, but the layer at $-\frac{1}{4}$,(-x, -y, -z), is slightly closer to the layer at $\frac{1}{4}$,(x, y, z), than the one at $\frac{3}{4}$,(1 - x, -y, -z). The molecules stacked in the a-direction are linked by hydrogen-bond bridges between the cation and its associated water molecule, to the chloride acceptor, which is hydrogen-bonded to the cation above the first. (See Fig. 9) There are two such bridges between x, y, z and -x, -y, -z. There are similiar H_2O-Cl^- bridges between x, y, z and 1 - x, -y, -z. Chloride ions are direct hydrogen-bond bridges in the lateral direction along the bc diagonals. The number of ionic interactions such as these makes this a very stable, high melting-point crystal.

The distortions caused by the ionic and hydrogen bonding are relatively minor so that one could expect roughly the same structure for other anions or for other metal analogs of the cation. The distinguishing structural distortion by hydrogen bonding is the non-planarity of the $\rangle C{=}NH_2$ system, so that the nitrogen appears to be tetrahedral (i.e., pyramidal NH_2) in spite of the double-bond character of the C-N bond.

TABLE 1.

SPACE GROUP $P2_1/C$ MONOCLINIC
UNIT CELL PARAMETERS AND THEIR STANDARD DEVIATIONS

A = 6.911(.001) A.
B = 11.678(.001) A.
C = 18.055(.002) A.
β = 101.39(.01) DEG.
λ(CU Kα) = 1.5418 A.
λ(CU Kα_1) = 1.5405 A.

DENSITY (CALC) = 1.748 GRAMS/CM^3 FOR 4 MOLECULES/UNIT CELL
DENSITY (OBS) = 1.735 GRAMS/CM^3

TABLE 2.

FINAL ATOMIC COORDINATES AND THEIR CALCULATED STANDARD DEVIATIONS (ALL VALUES MULTIPLIED BY 10^4)

NO.	ATOM	X	Y	Z
1	NI	2573(.6)	391(.3)	88(.2)
2	CL(1)	2472(1)	-3615(.5)	-2755(.3)
3	CL(2)	3339(1)	-290(.5)	-3463(.3)
4	N(1)	2895(3)	788(2)	1102(1)
5	C(1)	3377(3)	1751(2)	1428(1)
6	N(2)	3601(4)	1937(2)	2182(1)
7	N(3)	3635(3)	2708(2)	1020(1)
8	C(2)	3318(3)	2798(2)	244(1)
9	N(4)	3483(4)	3875(2)	0(1)
10	N(5)	2968(3)	1907(1)	-186(1)
11	C(3)	2588(5)	2112(2)	-1007(1)
12	C(4)	2695(4)	994(2)	-1417(1)
13	N(6)	2259(3)	40(1)	-941(1)
14	C(5)	1909(3)	-948(2)	-1265(1)
15	N(7)	1752(4)	-1137(2)	-2007(1)
16	N(8)	1637(3)	-1921(2)	-863(1)
17	C(6)	1813(3)	-2008(2)	-97(1)
18	N(9)	1523(4)	-3075(2)	146(1)
19	N(10)	2173(3)	-1124(2)	335(1)
20	O	1242(5)	-4492(2)	-1257(1)
21	H(1)	2805(32)	294(18)	1411(12)
22	H(2)	3679(47)	1379(25)	2442(17)
23	H(3)	4441(37)	2509(23)	2369(14)
24	H(4)	3699(37)	3299(20)	1233(14)
25	H(5)	3534(41)	4384(22)	318(15)
26	H(6)	3075(40)	4049(22)	-474(15)
27	H(7)	3523(36)	2651(22)	-1156(13)
28	H(8)	1290(36)	2464(21)	-1187(13)
29	H(9)	1787(35)	1005(20)	-1884(13)
30	H(10)	4055(39)	878(21)	-1543(14)
31	H(11)	2190(39)	-652(22)	-2271(14)
32	H(12)	1680(39)	-1835(22)	-2152(14)
33	H(13)	1426(35)	-2564(21)	-1101(13)
34	H(14)	1527(38)	-3610(21)	-165(14)
35	H(15)	1967(43)	-3265(24)	610(15)
36	H(16)	2168(34)	-1290(18)	756(13)
37	H(17)	1591(54)	-4424(32)	-1595(20)
38	H(18)	68(51)	-4689(30)	-1397(19)

TABLE 3.

POSITIONAL STANDARD DEVIATIONS

KIND OF ATOM	ST. DEV. (A.)
NI	0.0003
CL	0.0006
C	0.002
N	0.002
O	0.003
H ON N	0.03
H ON O	0.04

TABLE 4.

FINAL ANISOTROPIC TEMPERATURE FACTORS AND THEIR CALCULATED STANDARD DEVIATIONS (ALL VALUES MULTIPLIED BY 10^4), $T=EXP-(B11 \cdot H^2+B22 \cdot K^2+B33 \cdot L^2+ +B12 \cdot HK+B13 \cdot HL+B23 \cdot KL)$

NO.	ATOM	B11	B22	B33	B12	B13	B23
1	NI	135(.9)	30(.3)	13.2(.1)	0(.9)	16(.5)	-1(.3)
I	CL(1)	219(2)	50(.5)	25.4(.2)	-7(2)	23(1)	-22(.5)
3	CL(2)	377(2)	46(.5)	18.5(.2)	-47(2)	20(1)	11(.5)
4	N(1)	192(5)	37(1)	14.9(.5)	-3(4)	24(3)	6(1)
5	C(1)	137(6)	43(2)	15.1(.6)	10(5)	18(3)	-3(2)
6	N(2)	270(7)	57(2)	14.5(.6)	-28(6)	20(3)	-7(2)
7	N(3)	207(6)	34(1)	16.6(.6)	-13(4)	19(3)	-9(1)
8	C(2)	146(6)	34(2)	19.0(.7)	-3(5)	26(3)	1(2)
9	N(4)	299(7)	34(1)	19.9(.7)	-31(5)	37(4)	-4(2)
10	N(5)	160(5)	37(1)	13.7(.5)	4(4)	14(3)	0(1)
11	C(3)	256(8)	43(2)	17.1(.7)	-17(6)	28(4)	6(2)
12	C(4)	190(7)	46(2)	15.7(.7)	-0(6)	33(4)	2(2)
13	N(6)	147(5)	35(1)	15.5(.6)	3(4)	20(3)	-2(1)
14	C(5)	140(6)	42(2)	18.5(.7)	17(5)	20(3)	-7(2)
15	N(7)	307(8)	48(2)	17.9(.7)	1(6)	43(4)	-15(2)
16	N(8)	193(5)	32(1)	20.4(.6)	-1(4)	22(3)	-8(1)
17	C(6)	130(6)	37(2)	22.3(.7)	13(5)	21(3)	1(2)
18	N(9)	266(7)	35(2)	28.7(.8)	1(5)	25(4)	7(2)
19	N(10)	180(5)	38(1)	16.7(.6)	-6(4)	20(3)	4(1)
20	O	373(9)	122(3)	27.0(.8)	-84(8)	54(4)	-24(2)

TABLE 5.

FINAL ISOTROPIC TEMPERATURE FACTORS AND THEIR CALCULATED STANDARD DEVIATIONS, $T=EXP-(B \cdot ((SIN\ \theta)/\lambda)^2)$

NO.	ATOM	B
21	H(1)	2.8(.5)
22	H(2)	6.0(.9)
23	H(3)	4.1(.7)
24	H(4)	4.5(.6)
25	H(5)	4.4(.7)
26	H(6)	4.6(.7)
27	H(7)	4.6(.6)
28	H(8)	4.0(.6)
29	H(9)	3.3(.6)
30	H(10)	4.5(.7)
31	H(11)	3.9(.7)
32	H(12)	4.2(.7)
33	H(13)	3.9(.6)
34	H(14)	5.1(.7)
35	H(15)	5.2(.8)
36	H(16)	3.7(.6)
37	H(17)	6.8(1.2)
38	H(18)	7.1(1.1)

TABLE 6.

BOND DISTANCES (A.) WITHIN THE MOLECULE

FROM ATOM	TO ATOM	DISTANCE (A.)	AVERAGE (A.)	DESCRIPTION
N(1)	C(1)	1.283		
N(10)	C(6)	1.289		
N(5)	C(2)	1.292		
N(6)	C(5)	1.295		
			1.290	(I) LIG. N - C
N(2)	C(1)	1.356		
N(9)	C(6)	1.349		
N(4)	C(2)	1.345		
N(7)	C(5)	1.341		
			1.348	(II) TERM. N - C
N(3)	C(1)	1.369		
N(8)	C(6)	1.368		
N(3)	C(2)	1.379		
N(8)	C(5)	1.381		
			1.374	(III) RING N - C
NI	N(1)	1.858		
NI	N(10)	1.858		
NI	N(5)	1.872		
NI	N(6)	1.873		
			1.865	(IV) NI - LIG. N
C(3)	N(5)	1.473		
C(4)	N(6)	1.474		
C(3)	C(4)	1.510		

(CONTINUED)

(TABLE 6. CONTINUED)

FROM ATOM	TO ATOM	DISTANCE (A.)	AVERAGE (A.)	DESCRIPTION
H(1)	N(1)	0.81		
H(16)	N(10)	0.78		
			0.80	H - LIG. N
H(2)	N(2)	0.80		
H(3)	N(2)	0.90		
H(15)	N(9)	0.86		
H(14)	N(9)	0.84		
H(6)	N(4)	0.87		
H(5)	N(4)	0.82		
H(11)	N(7)	0.83		
H(12)	N(7)	0.85		
			0.85	H - TERM. N
H(4)	N(3)	0.79		
H(13)	N(8)	0.86		
			0.83	H - RING N
H(7)	C(3)	0.98		
H(8)	C(3)	0.98		
H(10)	C(4)	1.02		
H(9)	C(4)	0.95		
			0.98	
H(17)	O	0.70		
H(18)	O	0.83		
			0.77	

TABLE 7.

STANDARD DEVIATIONS OF BOND DISTANCES

KIND OF BOND	ST. DEV. (A.)
NI - N	0.002
N - C	0.003
C - C	0.003
N - H	0.03
O - H	0.04

TABLE 8.

HYDROGEN BOND DISTANCES (A.) (ATOMS IN FIRST COLUMN BELONG TO REFERENCE MOLECULE AT X,Y,Z)

FROM ATOM	TO ATOM	IN MOLECULE AT	DISTANCE (A.)
N(7)	CL(1)	X,Y,Z	3.272
O	CL(1)	X,Y,Z	3.161
N(7)	CL(2)	X,Y,Z	3.199
N(8)	O	X,Y,Z	3.086
N(9)	O	X,Y,Z	3.000
N(1)	CL(1)	X, -1/2-Y, 1/2+Z	3.321
N(10)	CL(1)	X, -1/2-Y, 1/2+Z	3.427
N(9)	CL(2)	X, -1/2-Y, 1/2+Z	3.206
N(2)	CL(1)	1-X, -Y, -Z	3.341
N(2)	CL(2)	1-X, -Y, -Z	3.405
N(3)	CL(2)	X, 1/2-Y, 1/2+Z	3.175
N(4)	CL(2)	X, 1/2-Y, 1/2+Z	3.247
O	CL(2)	-X, -1/2+Y, -1/2-Z	3.242
N(4)	O	X, 1+Y, Z	3.131

TABLE 9.

PACKING DISTANCES LESS THAN 3.5 A. (ATOMS IN FIRST COLUMN BELONG TO REFERENCE MOLECULE AT X,Y,Z)

FROM ATOM	TO ATOM	IN MOLECULE AT	DISTANCE (A.)
NI	N(10)	-X, -Y, -Z	3.330
N(1)	C(5)	-X, -Y, -Z	3.396
N(1)	N(8)	-X, -Y, -Z	3.348
C(1)	N(8)	-X, -Y, -Z	3.420
C(2)	N(9)	-X, -Y, -Z	3.295
N(5)	C(6)	-X, -Y, -Z	3.443
N(5)	N(9)	-X, -Y, -Z	3.404
C(1)	C(5)	1-X, -Y, -Z	3.458
C(1)	N(7)	1-X, -Y, -Z	3.399
N(2)	N(7)	1-X, -Y, -Z	3.418
N(3)	N(8)	1-X, -Y, -Z	3.459

TABLE 10.

BOND ANGLES (DEG.) WITHIN THE MOLECULE

ATOM	ATOM	ATOM	ANGLE (DEG.)
N(1)	NI	N(5)	91.6
N(10)	NI	N(6)	92.1
N(1)	NI	N(10)	89.7
N(5)	NI	N(6)	86.5
NI	N(1)	C(1)	129.9
NI	N(10)	C(6)	129.6
C(2)	N(5)	NI	128.5
C(5)	N(6)	NI	128.2
N(1)	C(1)	N(2)	124.7
N(10)	C(6)	N(9)	124.5
N(4)	C(2)	N(5)	125.1
N(7)	C(5)	N(6)	124.7
N(1)	C(1)	N(3)	121.1
N(10)	C(6)	N(8)	121.3
N(3)	C(2)	N(5)	121.5
N(8)	C(5)	N(6)	121.9
N(2)	C(1)	N(3)	114.1
N(9)	C(6)	N(8)	114.1
N(3)	C(2)	N(4)	113.4
N(8)	C(5)	N(7)	113.4
C(1)	N(3)	C(2)	126.7
C(6)	N(8)	C(5)	126.8
NI	N(5)	C(3)	114.4
NI	N(6)	C(4)	114.5
C(2)	N(5)	C(3)	116.6
C(5)	N(6)	C(4)	116.9
N(5)	C(3)	C(4)	109.6
N(6)	C(4)	C(3)	109.4

(CONTINUED)

(TABLE 10. CONTINUED)

ATOM	ATOM	ATOM	ANGLE (DEG.)
NI	N(1)	H(1)	119.3
H(1)	N(1)	C(1)	110.7
NI	N(10)	H(16)	119.8
H(16)	N(10)	C(6)	110.5
H(2)	N(2)	C(1)	116.1
H(2)	N(2)	H(3)	114.8
H(3)	N(2)	C(1)	115.5
H(15)	N(9)	C(6)	120.4
H(15)	N(9)	H(14)	114.3
H(14)	N(9)	C(6)	116.7
H(6)	N(4)	C(2)	120.5
H(5)	N(4)	H(6)	118.5
H(5)	N(4)	C(2)	116.3
H(11)	N(7)	C(5)	119.3
H(12)	N(7)	H(11)	118.7
H(12)	N(7)	C(5)	116.8
H(4)	N(3)	C(1)	116.9
H(4)	N(3)	C(2)	114.4
H(13)	N(8)	C(6)	114.2
H(13)	N(8)	C(5)	118.7
H(7)	C(3)	N(5)	112.7
H(7)	C(3)	H(8)	104.5
H(7)	C(3)	C(4)	108.8
H(8)	C(3)	N(5)	111.8
H(8)	C(3)	C(4)	109.3
H(10)	C(4)	N(6)	109.4
H(10)	C(4)	H(9)	106.3
H(10)	C(4)	C(3)	111.2
H(9)	C(4)	N(6)	110.7
H(9)	C(4)	C(3)	109.7
H(17)	O	H(18)	104.4

TABLE 11.

LEAST SQUARES PLANE OF MOLECULE

DIRECTION COSINES RELATIVE TO A, B, AND C*

C1 = 0.9788
C2 = -0.1741
C3 = -0.0883

ORIGIN TO PLANE DISTANCE = 1.658 A.

DEVIATION FROM PLANARITY
(THE WEIGHT FOR AN ATOM IS INVERSELY PROPORTIONAL TO THE STANDARD DEVIATION OF ITS X COORDINATE, RELATIVE TO THAT OF NICKEL)

ATOM	DEVIATION (A.)	WEIGHT	
NI	-0.011	1.00	
N(1)	-0.035	0.17	
N(10)	-0.012	0.20	
N(5)	-0.008	0.20	
N(6)	0.012	0.20	
C(1)	0.043	0.17	
C(6)	-0.008	0.17	
C(2)	-0.021	0.17	
C(5)	0.028	0.17	
N(2)	0.036	0.14	
N(9)	-0.026	0.14	
N(4)	-0.090	0.14	
N(7)	0.079	0.14	
N(3)	0.088	0.17	
N(8)	-0.022	0.17	
C(3)	-0.176	0.00	(TETRAHEDRAL CARBONS NOT INCLUDED IN
C(4)	0.189	0.00	PLANAR PI SYSTEM)
H(1)	-0.046	0.00	(ALL HYDROGENS GIVEN ZERO WEIGHT)
H(16)	-0.049	0.00	
H(2)	0.161	0.00	
H(3)	0.459	0.00	
H(15)	0.239	0.00	
H(14)	0.136	0.00	
H(6)	-0.326	0.00	
H(5)	-0.209	0.00	
H(11)	0.318	0.00	
H(12)	0.195	0.00	
H(4)	-0.023	0.00	
H(13)	0.004	0.00	
H(7)	0.371	0.00	
H(8)	-1.097	0.00	
H(10)	1.153	0.00	
H(9)	-0.353	0.00	

TABLE 12.

VALENCE BOND (VB) AND MOLECULAR ORBITAL (MO) TREATMENTS OF BONDING IN NICKEL ETHYLENEDIBIGUANIDE DIPOSITIVE CATION

SUMMARY OF ASSUMPTIONS IN HUCKEL CALCULATION (MOLECULAR ORBITAL THEORY)

A(J) = COULOMB INTEGRAL ON ATOM J
B(IJ) = RESONANCE INTEGRAL BETWEEN ATOMS I AND J
B(IJ) = 0 FOR ATOMS I,J NOT DIRECTLY BONDED
S(IJ) = OVERLAP INTEGRAL BETWEEN ATOMS I AND J
S(JJ) = 1, S(IJ) = 0 IF I DIFFERENT FROM J
LET A = A(CARBON) AND B = B(CARBON-CARBON)

A(NI) = A - 0.7B (X = PAULING'S ELECTRONEGATIVITY, X(NI) - X(C) = -0.7)
A(C) = A
A(TERM. N) = A(RING N) = A + 0.5B (X(N) - X(C) = +0.5)
A(LIG. N) = A + B

B(LIG. N-C) = 2.2B
B(TERM. N-C) = 1.3B
B(RING N-C) = B
B(NI-LIG. N) = 0.25B

(1.) PREDICTED BOND LENGTHS (R) FROM VALENCE BOND NUMBERS (VBN) AND MOLECULAR ORBITAL (HUCKEL CALCULATION) MOBILE PI BOND ORDERS (PBO)

KIND OF BOND	AVER. R(OBS)	VBN	R(VB)	PBO	R(MO)
I. LIG. N - C	1.29 A.	1.5	1.31 A.	0.745	1.30 A.
II. TERM. N - C	1.35	1.3	1.36	0.526	1.35
III. RING N - C	1.37	1.2	1.39	0.374	1.38
IV. NI - LIG. N	1.87	1.0	1.89	0.176	1.85
SINGLE BOND N - C	1.47	1.0	1.47	0.000	1.47
SINGLE BOND C - C	1.51	1.0	1.54	0.000	1.54

(2.) PREDICTED CHARGES (Q) ON ATOMS

KIND OF ATOM	Q(VB)	Q(MO)	AVER. OBSERVED N-H DISTANCE
LIG. N	+0.5	+0.51	0.80 A.
RING N	+0.4	+0.25	0.83
TERM. N	+0.3	+0.25	0.85
C	0.0	+0.15	--
NI	-2.0	-2.10	--

TABLE 13.

PRINCIPAL AXES OF THERMAL ELLIPSOIDS

U(J) = ROOT MEAN SQUARE DISPLACEMENT (A.) ALONG AXIS J,
DIRECTION COSINES ARE RELATIVE TO A, B, C AXES OF CRYSTAL

ATOM	AXIS J	U(J) (A.)	COS A(J)	COS B(J)	COS C(J)
NI	1	0.178	-0.998	-0.007	0.129
	2	0.146	-0.040	-0.750	0.655
	3	0.144	-0.056	0.661	0.744
CL(1)	1	0.229	-0.920	-0.245	0.482
	2	0.221	0.393	-0.561	0.637
	3	0.160	-0.006	0.790	0.602
CL(2)	1	0.303	-0.984	0.178	0.204
	2	0.188	0.136	0.714	0.646
	3	0.155	-0.115	-0.677	0.735
N(1)	1	0.212	-0.992	0.050	0.084
	2	0.167	-0.022	0.828	0.554
	3	0.146	-0.123	-0.559	0.828
C(1)	1	0.183	-0.824	-0.566	0.194
	2	0.170	0.546	-0.776	0.202
	3	0.153	-0.155	0.278	0.960
N(2)	1	0.254	-0.978	0.200	0.138
	2	0.198	-0.207	-0.960	0.228
	3	0.149	-0.016	0.198	0.964
N(3)	1	0.221	-0.997	0.074	0.163
	2	0.172	-0.072	-0.585	0.806
	3	0.142	0.040	0.808	0.569
C(2)	1	0.185	0.895	-0.032	0.259
	2	0.171	-0.437	0.127	0.959
	3	0.152	-0.085	-0.991	0.115
N(4)	1	0.265	-0.981	0.132	0.057
	2	0.176	-0.159	-0.152	0.988
	3	0.150	0.107	0.980	0.145
N(5)	1	0.195	-0.998	-0.057	0.207
	2	0.159	-0.056	0.998	0.050
	3	0.148	0.013	-0.039	0.977
C(3)	1	0.246	-0.988	0.124	0.110
	2	0.178	0.048	0.801	0.575
	3	0.156	-0.144	-0.586	0.810
C(4)	1	0.210	0.964	0.003	0.069
	2	0.179	-0.036	0.992	0.126
	3	0.153	-0.262	-0.126	0.990

(CONTINUED)

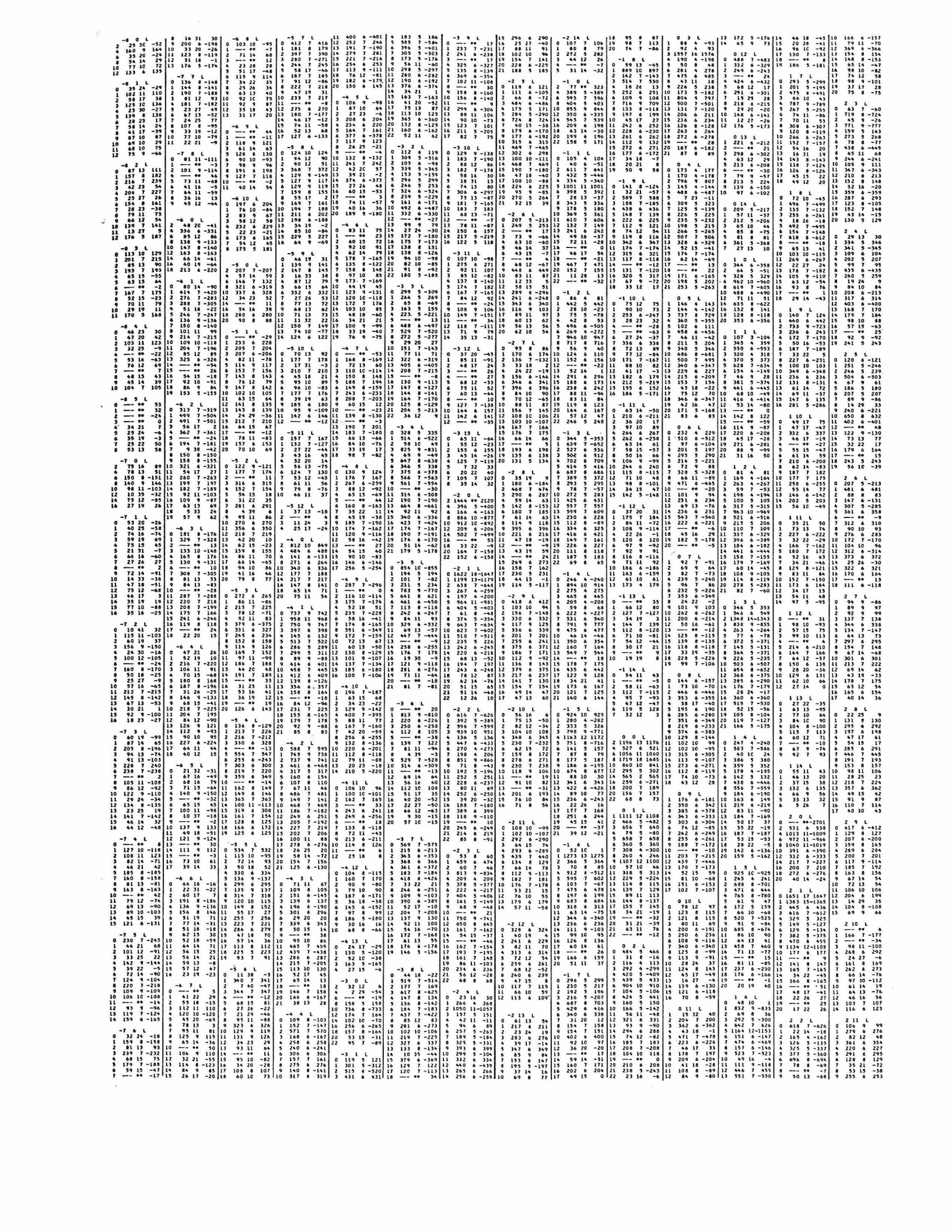
(TABLE 13. CONTINUED)

ATOM	AXIS J	U(J) (A.)	COS A(J)	COS B(J)	COS C(J)
N(6)	1	0.185	-0.990	-0.061	0.073
	2	0.159	-0.062	-0.609	0.788
	3	0.152	-0.124	0.791	0.612
C(5)	1	0.190	-0.713	-0.618	0.466
	2	0.176	0.594	-0.279	0.623
	3	0.155	-0.374	0.735	0.628
N(7)	1	0.267	-0.986	-0.011	0.029
	2	0.197	-0.087	-0.825	0.565
	3	0.147	-0.146	0.566	0.824
N(8)	1	0.213	-1.000	-0.028	0.186
	2	0.184	-0.001	-0.349	0.919
	3	0.144	-0.031	0.937	0.348
C(6)	1	0.188	-0.103	0.021	0.995
	2	0.177	-0.905	-0.417	0.095
	3	0.156	-0.413	0.909	0.021
N(9)	1	0.251	-0.995	0.024	0.289
	2	0.215	0.097	0.161	0.944
	3	0.153	-0.009	-0.987	0.162
N(10)	1	0.206	-0.995	0.090	0.156
	2	0.168	0.027	0.651	0.738
	3	0.155	-0.095	-0.754	0.657
O	1	0.321	0.677	-0.696	0.101
	2	0.266	-0.730	-0.677	0.237
	3	0.197	-0.096	0.239	0.966

TABLE 14.

OBSERVED AND CALCULATED STRUCTURE FACTORS

(THE FOUR COLUMNS WITHIN EACH GROUP CONTAIN THE VALUES OF L, 10·F(OBS), 10·σ(F(OBS)), AND 10·F(CALC). REFLECTIONS INDICATED BY ASTERISKS (**) WERE GIVEN ZERO WEIGHT IN LEAST SQUARES CALCULATIONS.)



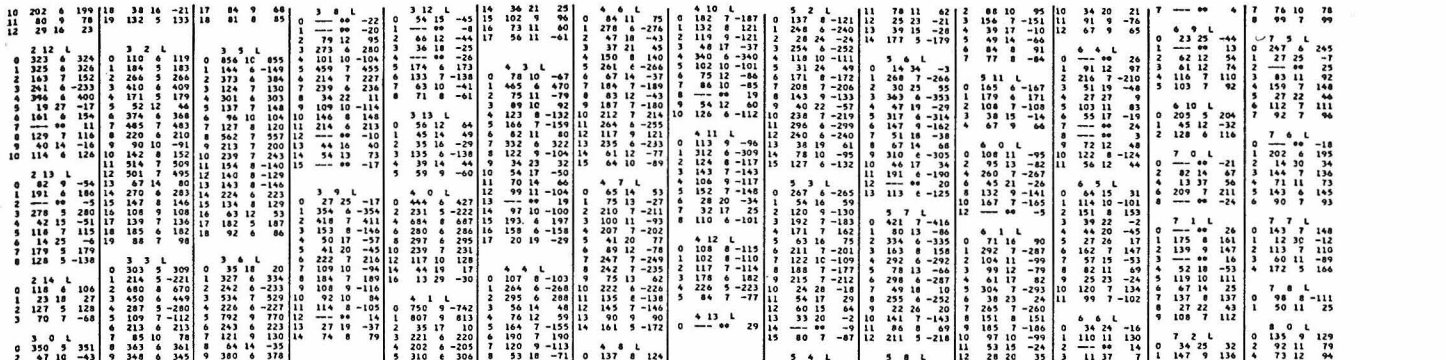


Figure 1

Final electron density map in the least squares plane of the molecule. Contours are drawn at 2, 4, 6,...,e. $Å^{-3}$.

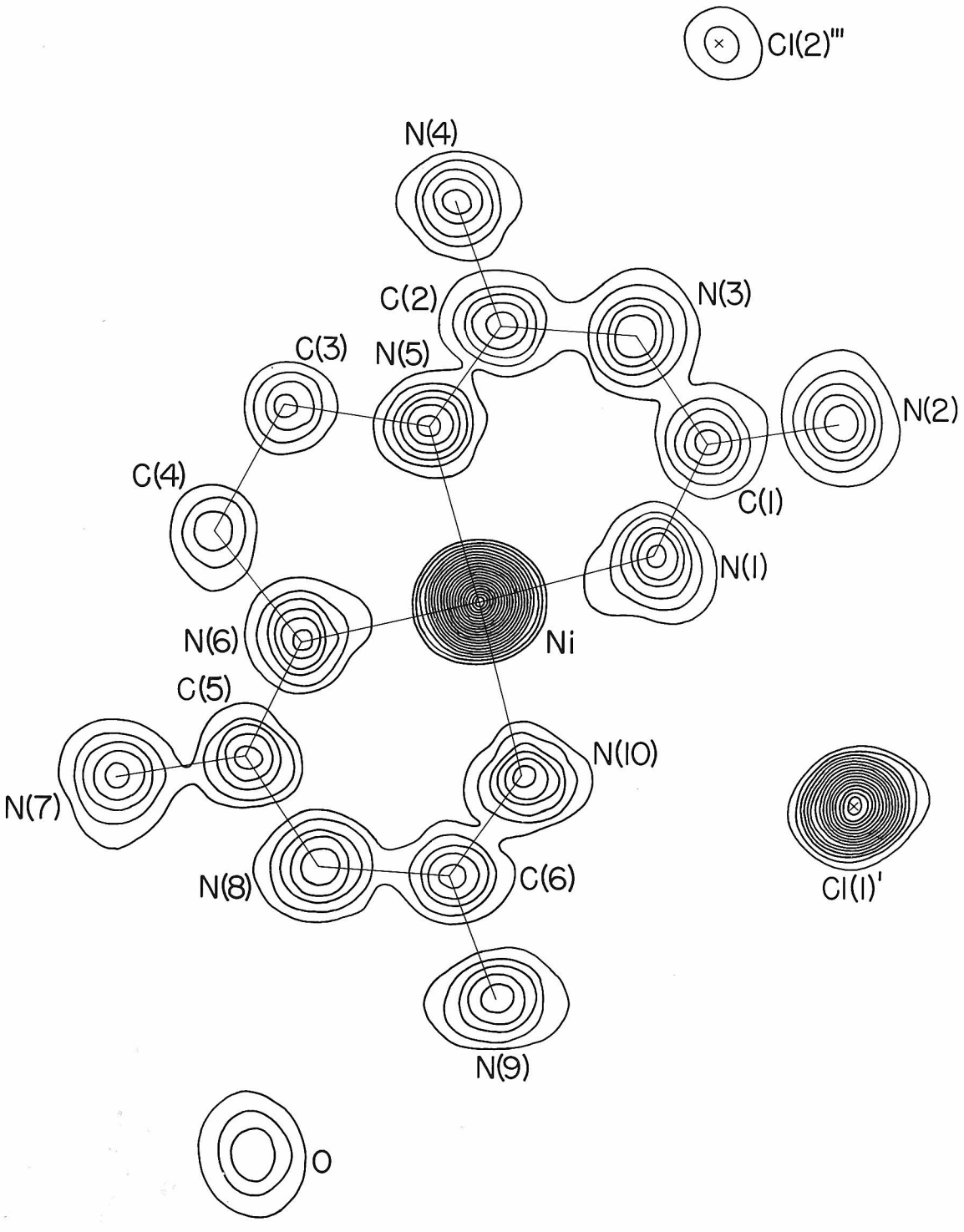

Cl(2)'''
N(4)
C(2)
N(3)
C(3)
N(5)
N(2)
C(4)
C(1)
N(1)
N(6)
Ni
C(5)
N(10)
N(7)
N(8)
C(6)
Cl(1)'
N(9)
O

Figure 2

Final difference map in the least squares plane of the molecule. Contours are drawn at 0.2 and 0.4 e. $Å^{-3}$.

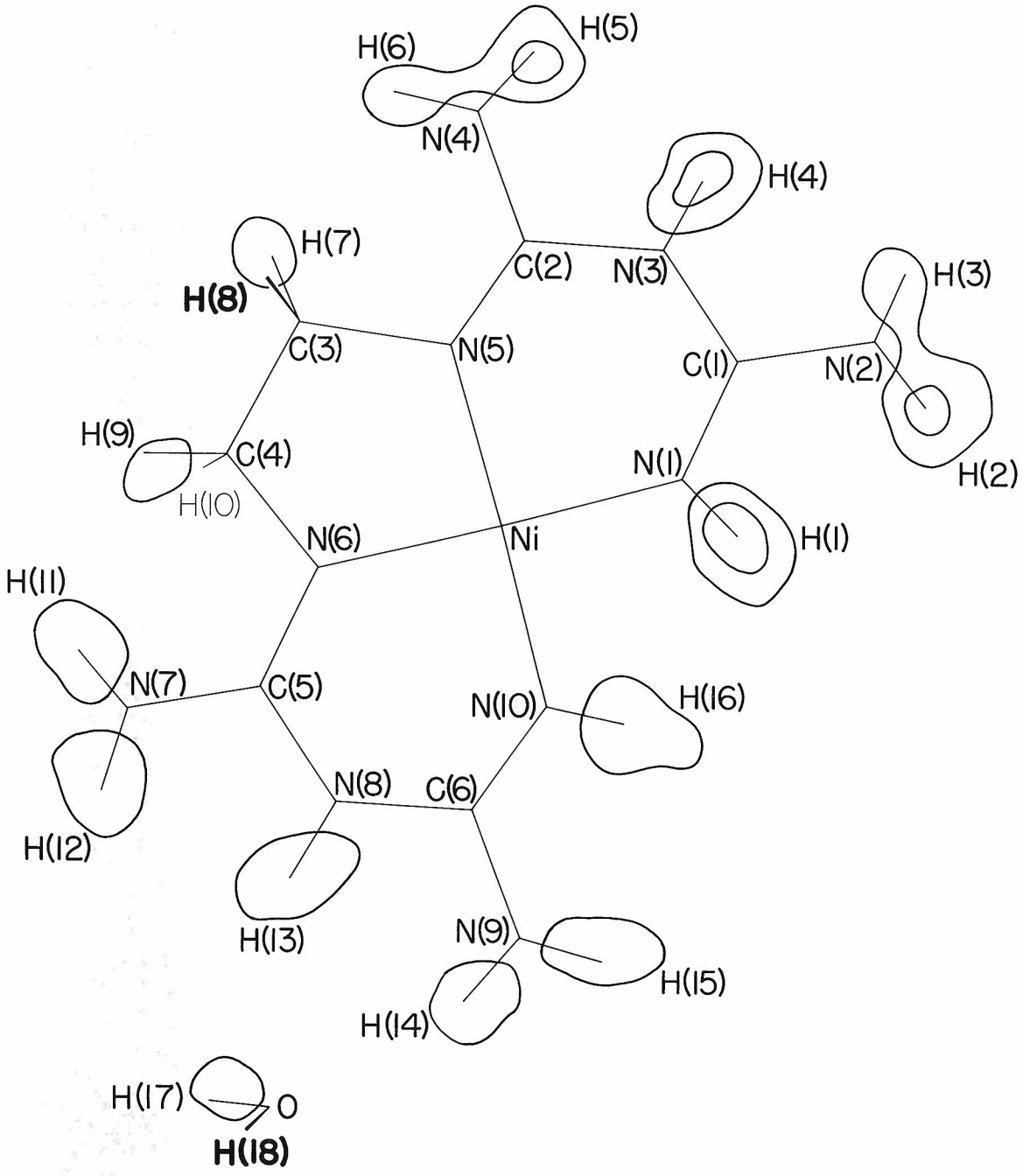

H(6)
H(5)
N(4)
H(4)
H(7)
C(2)
N(3)
H(3)
H(8)
C(3)
N(5)
C(1)
N(2)
H(9)
C(4)
N(1)
H(2)
H(10)
N(6)
Ni
H(1)
H(11)
N(7)
C(5)
N(10)
H(16)
N(8)
C(6)
H(12)
H(13)
N(9)
H(15)
H(14)
H(17)
O
H(18)

Figure 3

Bond angles (deg.) and bond distances (Å.). (Dashed lines indicate hydrogen bonds.)

Added hydrogen bond acceptors		In molecule at
O' = O(1)	in Fig.4.	x, 1 + y, z
Cl(1)' = Cl(11)		x, $-\frac{1}{2}$ - y, $\frac{1}{2}$ + z
Cl(2)' = Cl(12)		x, $-\frac{1}{2}$ - y, $\frac{1}{2}$ + z
Cl(1)'' = Cl(21)		1 - x, - y, -z
Cl(2)'' = Cl(22)		1 - x, - y, -z
Cl(2)''' = Cl(32)		x, $\frac{1}{2}$ - y, $\frac{1}{2}$ + z
$Cl(2)^{IV}$ = Cl(42)		-x, $-\frac{1}{2}$ + y, $-\frac{1}{2}$ - z

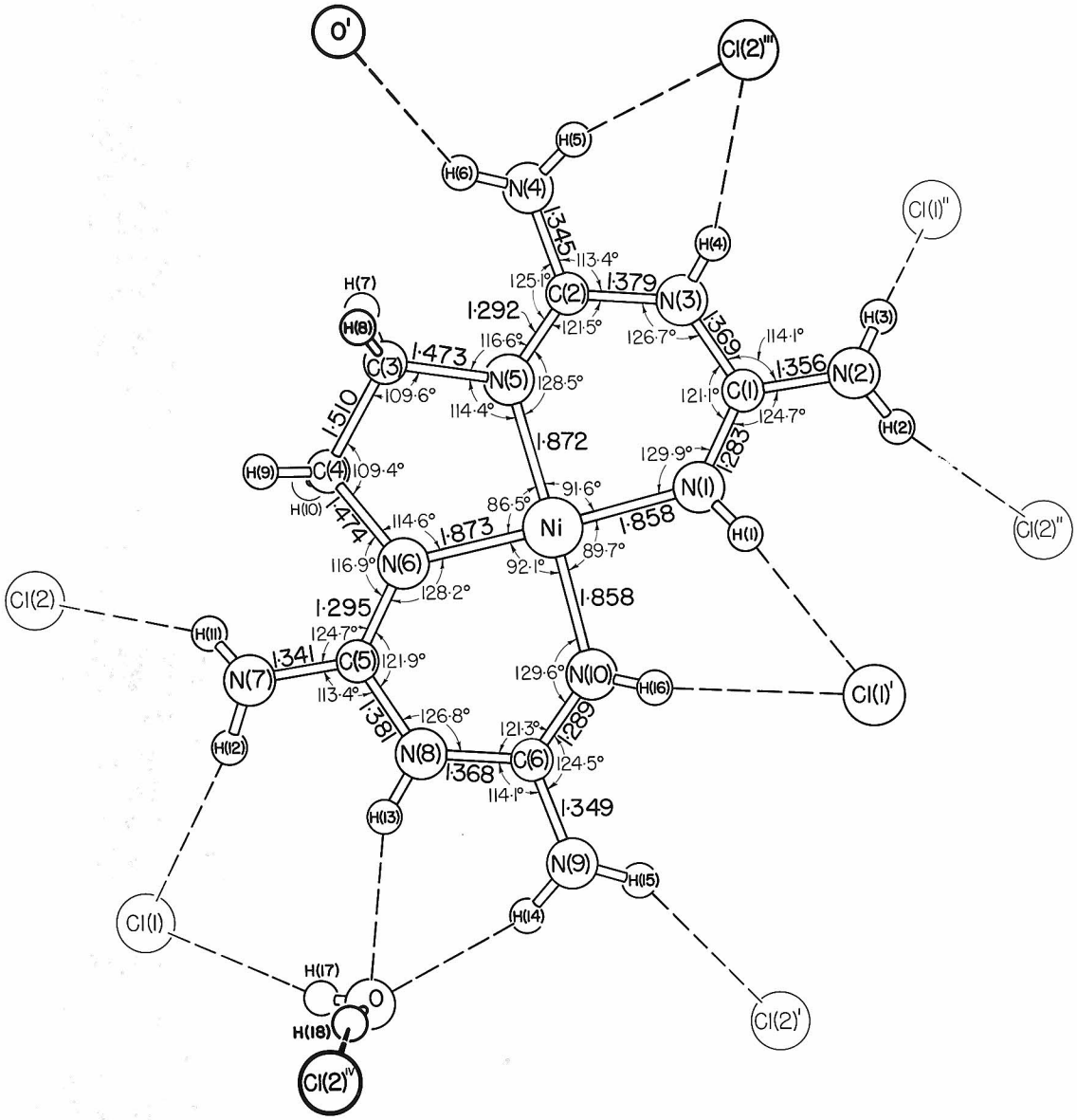

O'
Cl(2)'''
H(5)
H(6)
N(4)
1·345
113·4°
125·1°
C(2)
1·379
N(3)
H(4)
Cl(1)''
H(7)
H(8)
1·292
121·5°
126·7°
1·369
H(3)
114·1°
116·6°
C(3)
1·473
N(5)
128·5°
109·6°
1·356
N(2)
121·1°
C(1)
124·7°
1·510
114·4°
1·283
H(2)
1·872
129·9°
H(9)
C(4)
109·4°
91·6°
N(1)
86·5°
H(10)
1·474
114·6°
1·858
Cl(2)''
Ni
H(1)
1·873
89·7°
116·9°
N(6)
92·1°
Cl(2)
128·2°
1·858
1·295
124·7°
H(11)
1·341
C(5)
121·9°
129·6°
N(10)
H(16)
N(7)
113·4°
Cl(1)'
1·381
126·8°
121·3°
1·289
H(12)
N(8)
C(6)
124·5°
1·368
114·1°
H(13)
1·349
N(9)
H(15)
H(14)
Cl(1)
H(17)
O
H(18)
Cl(2)'
Cl(2)''

Figure 4

Stereoscopic view[4] of molecule along the a-axis; for the labelling of added hydrogen bond aceptors, see Fig. 3.

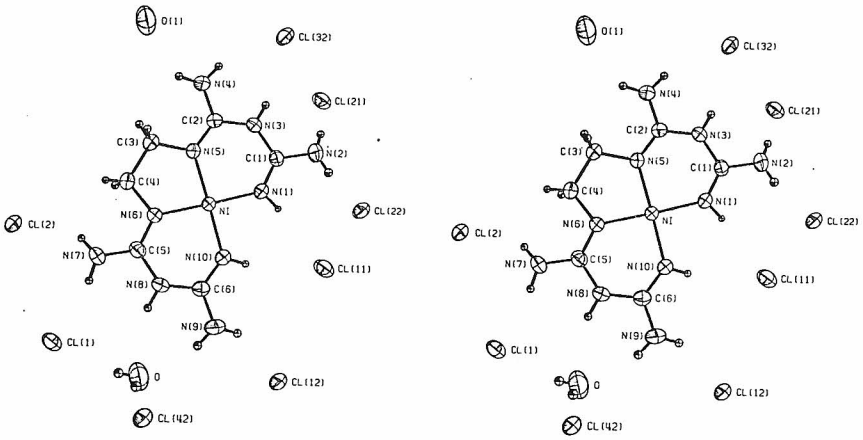
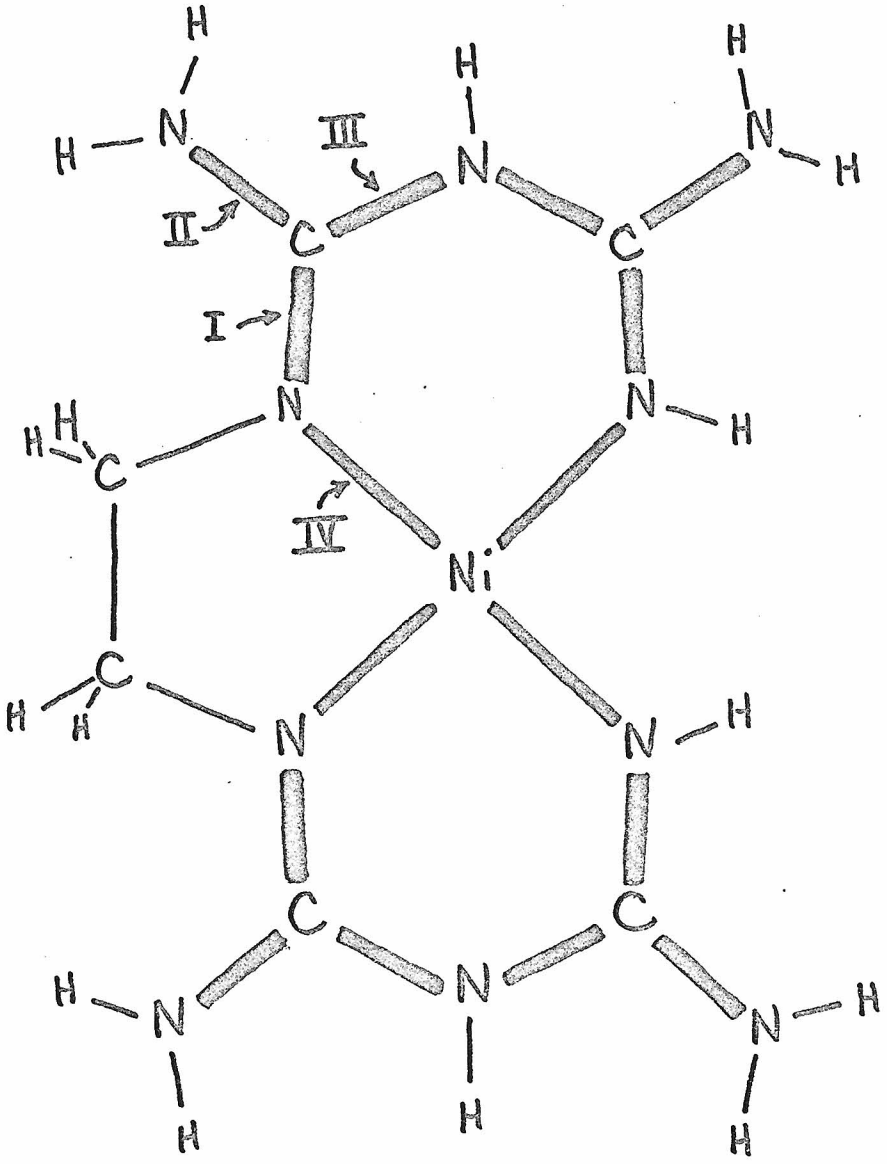

O(1)
CL(32)
N(4)
CL(21)
C(2)
N(3)
C(3)
N(5)
C(1)
N(2)
C(4)
N(1)
NI
N(6)
CL(2)
CL(22)
N(7)
C(5)
N(10)
CL(11)
N(8)
C(6)
N(9)
CL(1)
O
CL(12)
CL(42)

Figure 5

Sigma-bond and pi-bond systems.

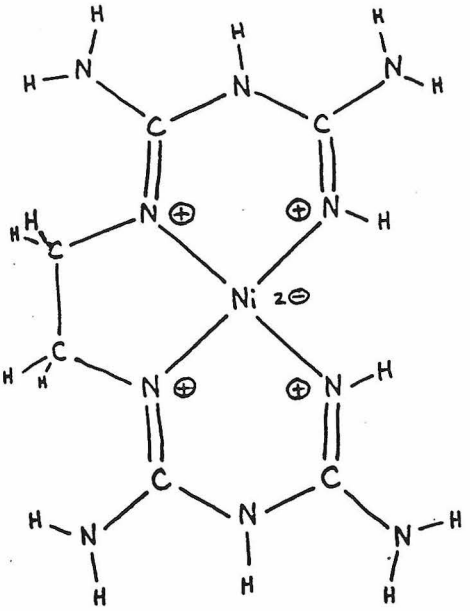


σ - system (C_2 point group)

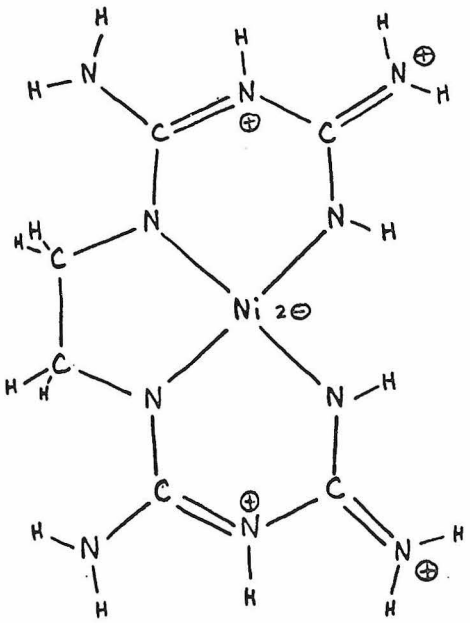
π - system (D_{2h})

Figure 6

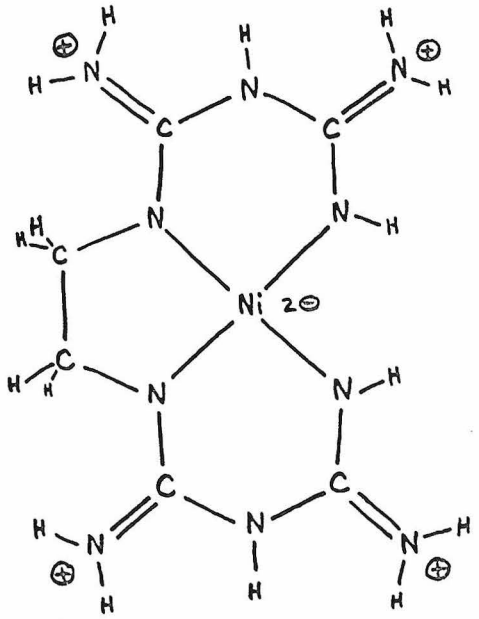
Canonical valence-bond structures of the Ni EDG^{+2} cation and percent contributions of each to the overall bonding scheme.



50%
(input structure, non-degenerate)



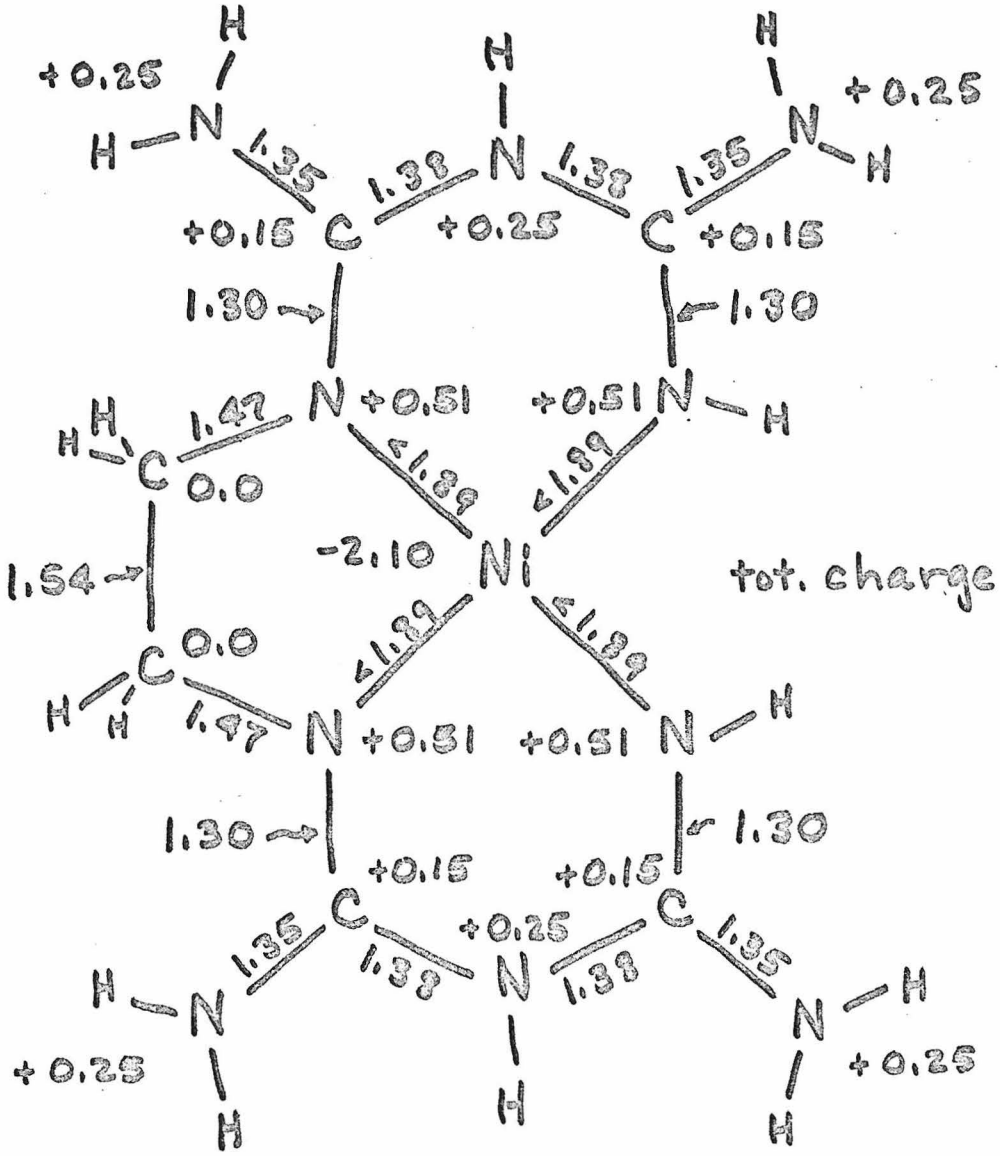
40%
(four-fold degenerate)



10%
(non-degenerate)

Figure 7

Molecular Orbital Results.



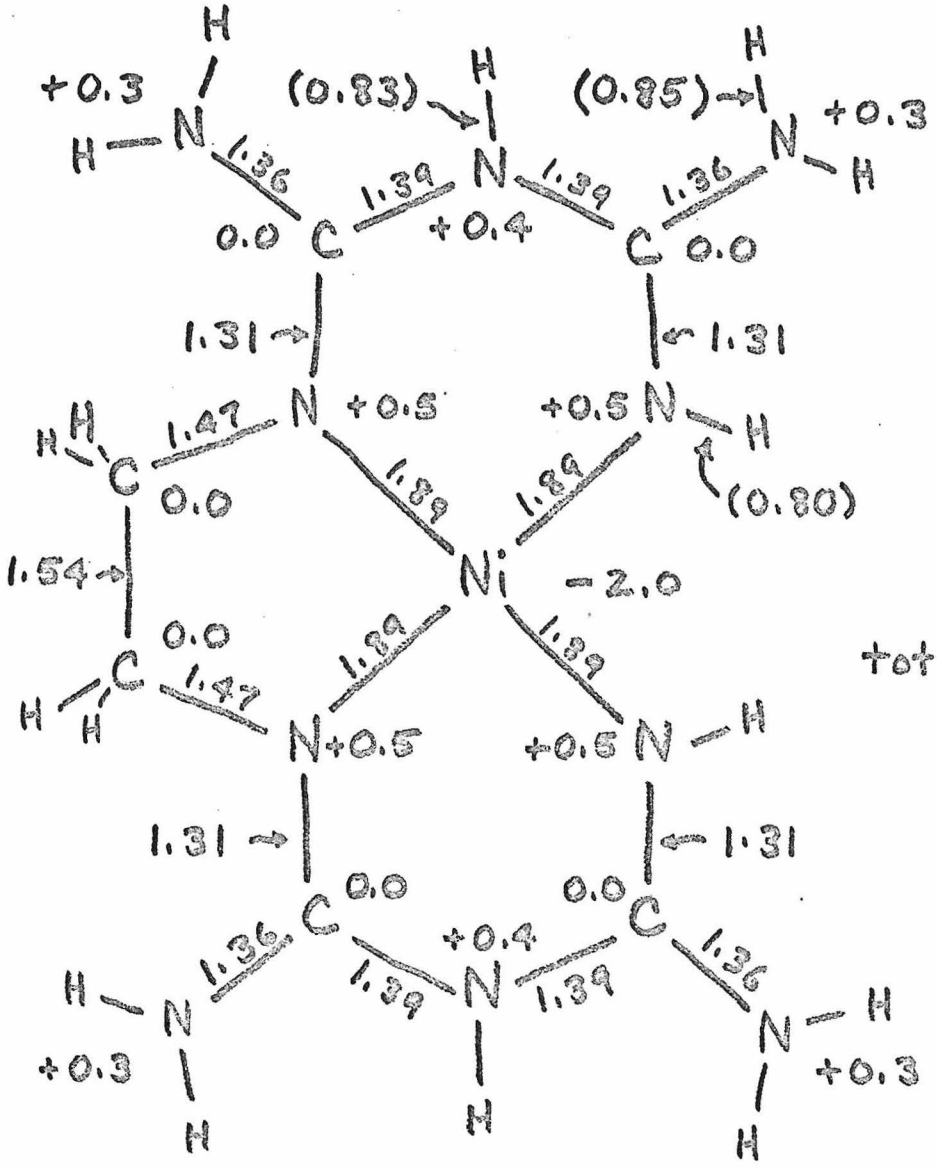
Molecular Orbital Hückel Calculation

Bond Lengths (Å)

Charges on Atoms

Figure 8

Valence Bond Results.



tot. charge = +2.0

Valence Bond Method

Bond Lengths (Å)

Charges on Atoms

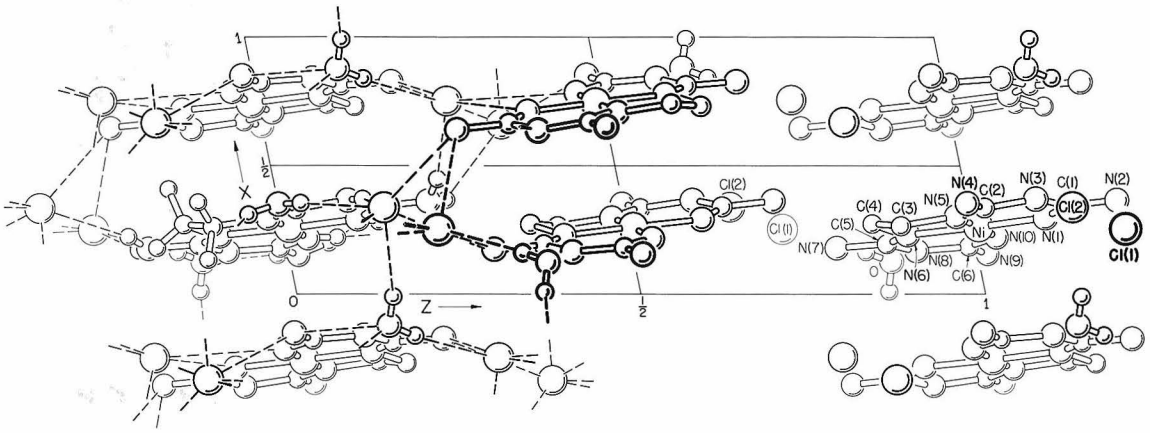
(Average N–H observed bond lengths in parentheses)

Figure 9

Molecular packing, viewed along b-axis. (Dashed lines indicate hydrogen bonds; hydrogens drawn in on parent molecule at xyz.)

Molecules shown in drawing are at :

1 - x, -y, -z	1 - x, $\frac{1}{2}$ + y, $\frac{1}{2}$ - z	1 - x, -y, 1 - z
x, y, z	x, $\frac{1}{2}$ - y, $\frac{1}{2}$ + z	x, y, 1 + z
-x, -y, -z		-x, -y, 1 - z


1
X
½
Cl(2)
Cl(1)
0
Z
½
N(4)
C(2)
N(3)
C(1)
N(2)
C(4)
C(3)
N(5)
Cl(2)
C(5)
Ni
N(10)
N(1)
N(7)
N(8)
N(9)
N(6)
C(6)
Cl(1)
1

Footnotes and Bibliography

All crystallographic data processing and calculations were carried out on the IBM 7094-7040 computer system at the Booth Computing Center, California Institute of Technology, utilizing the CRYRM Crystallographic Computing System developed by : Duchamp, D.J. (1964). A.C.A. Meeting, Bozeman, Montana, paper B-14, p. 29.

The Hückel Calculations were carried out utilizing the HK5 program developed by John D. Roberts, California Institute of Technology.

1. Cotton and Wilkinson (1967). Advanced Inorganic Chemistry, 2nd ed., New York: Interscience Publishers, p. 1047.

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3. Marsh, Bierstedt, and Eichhorn (1962). Acta. Cryst. 15, 310.

4. Pauling (1960). The Nature of the Chemical Bond, 3rd ed., Ithaca, New York: Cornell University Press. pp. 228-9.

5. Pauling, pp. 255-6.

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John D. Roberts, Hückel Calculation Program, HK5

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