

responds to a rotation of the $-\text{CH}=\text{CH}-$ group around the coordination axis of 17° for both molecules.

Relatively low energies should be involved in such rotations since the formation of hydrogen bonds seems to be responsible for the stable occurrence of different conformational isomers. The crystal structure appears also largely determined by the hydrogen bonding between carboxylic groups. Two different patterns of hydrogen bonding are observed. For the sake of simplicity one of them is shown in a separate figure (Figure 2). Each "A" molecule is bonded to four others of the same type. Carbon atoms and oxygen atoms of neighboring CHCOOH groups correlated by the screw axis lie on a plane. All deviations from the least-squares plane ($0.0997Y + 0.5109Z = 1$) are less than 0.03 \AA . A complete packing model projected along the a axis is shown in Figure 3. Crystallographically independent

molecules of the B and C types are hydrogen bonded. The carbon and oxygen atoms of two CHCOOH groups connected by hydrogen bonds are also practically planar.

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(16) A. Damiani, F. De Santis, E. Giglio, and A. Ripamonti, *Ric. Sci., Rend., Sez. A*, **33**, 965 (1963).

(17) V. Albano, A. Domenicano, and A. Vaciago, *Gazz. Chim. Ital.*, **96**, 922 (1966).

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The Crystal Structure of μ -Chloro-bis(chlorotetra(benzimidazole)nickel(II)) Chloride-4-Acetone¹

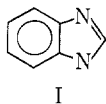
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The crystal structure of μ -chloro-bis(chlorotetra(benzimidazole)nickel(II)) chloride-4-acetone has been determined by single-crystal X-ray techniques. The crystals are monoclinic, space group $P2_1/c$ with cell dimensions $a = 12.551 (5)$, $b = 16.517 (7)$, $c = 17.794 (7) \text{ \AA}$, $\beta = 106.72 (5)^\circ$. The unit cell contains two cations of formula $\text{Ni}_2\text{Cl}_3(\text{C}_7\text{H}_6\text{N}_2)_8^+$, two chloride ions Cl^- , and eight molecules of acetone. The observed and calculated densities are 1.35 ± 0.01 and 1.354 g cm^{-3} , respectively. The intensities of 2492 reflections above background were collected by counter methods and the structure has been refined to a conventional R factor of 0.101. The cations are of the form $\text{Cl}-\text{Ni}(\text{C}_7\text{H}_6\text{N}_2)_4-\text{Cl}-\text{Ni}(\text{C}_7\text{H}_6\text{N}_2)_4-\text{Cl}^+$, with the bridging chlorine atom on a center of symmetry. The $\text{Cl}-\text{Ni}-\text{Cl}-\text{Ni}-\text{Cl}$ chain is closely linear ($\text{Cl}-\text{Ni}-\text{Cl} = 179.3 (1)^\circ$), and the two nickel-chlorine distances are appreciably different ($\text{Ni}-\text{Cl}(\text{terminal}) = 2.425 (4) \text{ \AA}$, $\text{Ni}-\text{Cl}(\text{bridging}) = 2.941 (2) \text{ \AA}$).

Introduction

During studies^{2,3} of the nickel(II) complexes with benzimidazole (I), three compounds, colored blue,



green, and olive green, of the general formula $\text{Ni}(\text{C}_7\text{H}_6\text{N}_2)_4\text{Cl}_2((\text{CH}_3)_2\text{CO})_2$ were prepared. These three compounds had differing magnetic properties, with magnetic moments of 3.15, 3.06, and 2.35 BM at room temperature and Weiss constants of -8 , -77 , and -400° , respectively. The green compound held to Curie-Weiss behavior over the range $200\text{--}300^\circ\text{K}$: in the range $100\text{--}200^\circ\text{K}$, deviation from the law is small but on reaching 100°K , the susceptibility values show a sudden drop and the initially crystalline solid is found

to be reduced to an amorphous powder without loss of acetone. In order to form a reference point for consideration of these compounds, the crystal structure of the green complex has been determined by three-dimensional X-ray analysis.

Experimental Section

Crystals of the green compound, immersed in acetone, were provided by Dr. M. J. Weeks. Preliminary photographs by the Weissenberg technique showed a monoclinic lattice. The cell dimensions were measured at room temperature ($\sim 23^\circ$) with a General Electric quarter-circle goniostat ($\lambda 0.70926 \text{ \AA}$ for $\text{Mo K}\alpha_1$). They are $a = 12.551 (6)$, $b = 16.517 (7)$, $c = 17.794 (7) \text{ \AA}$, $\beta = 106.72 (5)^\circ$. The errors in the last digits (in parentheses) are subjective estimates of the standard deviations. The observed density (by flotation in a mixture of benzene and ethylene bromide) is $1.35 \pm 0.01 \text{ g cm}^{-3}$. The calculated density for two formula units of $[\text{Ni}_2\text{Cl}_3(\text{C}_7\text{H}_6\text{N}_2)_8]\text{Cl} \cdot 4(\text{CH}_3)_2\text{CO}$ in the unit cell is 1.354 g cm^{-3} . The Weissenberg photographs show that reflections are absent for $h0l$ if $l = 2n + 1$ and for $0k0$ if $k = 2n + 1$. These rules are characteristic of space group $P2_1/c$ and this choice is confirmed by the structure determination.

The diffraction data were obtained from a crystal of approximate dimensions $0.4 \times 0.3 \times 0.3 \text{ mm}$ mounted with b parallel

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) M. J. Weeks, Ph.D. Thesis, University of London, 1966.

(3) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc. A*, 1125 (1967).

TABLE I
 FINAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10$) FOR $\text{Ni}(\text{C}_7\text{H}_6\text{N}_2)_3\text{Cl}_2\cdot 2(\text{CH}_3)_2\text{CO}^a$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Ni	453 (1)	1252 (1)	1227 (1)	39 (1)	42 (1)	40 (1)	0 (1)	15 (1)	1 (1)
Cl(1)	808 (3)	2292 (2)	2230 (2)	51 (2)	46 (2)	45 (2)	-4 (2)	17 (2)	-2 (2)
Cl(2)	0	0	0	67 (4)	73 (4)	59 (3)	-10 (3)	17 (3)	12 (3)
Cl(3)	5000	5000	5000	49 (3)	106 (5)	83 (4)	27 (3)	37 (3)	47 (4)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
N(1a)	2092 (8)	876 (6)	1441 (6)	44 (3)	N(1b)	-1254 (9)	1521 (7)	825 (6)	45 (3)
C(2a)	2517 (11)	755 (8)	831 (8)	46 (3)	C(2b)	-1975 (13)	915 (9)	721 (8)	55 (4)
N(3a)	3640 (10)	611 (7)	1095 (7)	58 (3)	N(3b)	-3040 (10)	1242 (8)	510 (7)	68 (3)
C(4a)	3957 (13)	631 (9)	1885 (9)	56 (4)	C(4b)	-2962 (15)	2069 (11)	457 (9)	75 (4)
C(5a)	5027 (15)	534 (10)	2485 (11)	83 (5)	C(5b)	-3791 (15)	2699 (12)	298 (10)	88 (5)
C(6a)	5011 (17)	621 (12)	3281 (12)	111 (6)	C(6b)	-3340 (16)	3457 (12)	310 (11)	101 (6)
C(7a)	4064 (17)	792 (11)	3481 (11)	99 (6)	C(7b)	-2166 (15)	3660 (11)	509 (9)	83 (5)
C(8a)	3000 (14)	905 (10)	2934 (10)	75 (5)	C(8b)	-1397 (12)	3023 (10)	689 (8)	59 (4)
C(9a)	2995 (12)	803 (9)	2146 (9)	55 (4)	C(9b)	-1817 (12)	2247 (9)	680 (8)	46 (3)
N(1c)	141 (8)	377 (6)	1967 (6)	38 (2)	N(1d)	739 (8)	1995 (6)	375 (6)	38 (2)
C(2c)	491 (11)	-387 (8)	1987 (8)	43 (3)	C(2d)	36 (11)	2027 (9)	-360 (8)	53 (4)
N(3c)	210 (9)	-838 (7)	2544 (7)	55 (3)	N(3d)	389 (10)	2617 (8)	-775 (7)	67 (3)
C(4c)	-375 (11)	-334 (9)	2909 (8)	44 (3)	C(4d)	1293 (13)	3011 (10)	-316 (9)	59 (4)
C(5c)	-839 (12)	-491 (9)	3523 (8)	59 (4)	C(5d)	1911 (14)	3683 (11)	-444 (9)	76 (4)
C(6c)	-1384 (13)	172 (10)	3755 (9)	71 (4)	C(6d)	2805 (13)	3869 (10)	172 (10)	72 (4)
C(7c)	-1473 (12)	934 (9)	3372 (9)	63 (4)	C(7d)	3145 (12)	3471 (10)	887 (9)	71 (4)
C(8c)	-1012 (11)	1089 (8)	2717 (8)	49 (3)	C(8d)	2466 (12)	2823 (9)	1040 (8)	52 (4)
C(9c)	-427 (10)	420 (8)	2545 (8)	43 (3)	C(9d)	1558 (11)	2613 (8)	430 (8)	46 (3)
O(1e)	2217 (12)	3967 (9)	3995 (8)	136 (5)	O(1f)	-1881 (11)	2997 (7)	3004 (7)	93 (5)
C(1e)	3225 (17)	4058 (12)	3058 (12)	120 (7)	C(1f)	-2888 (19)	3070 (14)	2913 (13)	101 (6)
C(2e)	3468 (18)	2945 (14)	4041 (12)	132 (7)	C(2f)x	-3664 (29)	2444 (22)	2410 (21)	87 (10)
C(3e)	2986 (19)	3645 (15)	3676 (14)	125 (7)	C(2f)y	-3549 (46)	3282 (35)	2152 (35)	186 (19)
					C(3f)x	-3457 (51)	3166 (39)	3560 (37)	171 (24)
					C(3f)y	-3292 (45)	3655 (34)	3391 (33)	144 (19)

^a Standard deviations estimated by least squares for the least significant digit are given in parentheses. Designation of atoms follows. Atoms in the four benzimidazole and two acetone groups are written as X(*ng*): X refers to the atom type—carbon, oxygen or nitrogen; *n* refers to the position of an atom in the group; and *g* identifies the group—a, b, c, or d for the four benzimidazole groups and e or f for the two acetone molecules. The half-atoms in the acetone molecule f are identified by an additional symbol x or y.

to the instrument axis. The crystal was stuck to the inside of a glass capillary. Diffraction intensities were measured with a General Electric XRD-5 apparatus equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. The diffracted beam was limited by an aperture 0.1 cm in diameter and 3.3 cm from the crystal and by a slit 0.3 cm wide and 15.3 cm from the crystal. A molybdenum tube was used at 50 kV and 20 mA with a zirconium filter at the receiving slit. The stationary crystal, stationary counter method was used to measure 3284 reflections ($2\theta \leq 40^\circ$) with a 4° takeoff angle. The counting time was 10 sec. The intensities of a few equivalent reflections were checked, but no systematic measurement of such reflections was undertaken. Individual backgrounds were measured for those reflections whose counts were seriously affected by streaking of other orders. For other reflections, backgrounds were taken from plots of background as functions of 2θ for various values of ϕ and χ . Of the 3284 reflections, 792 gave counts less than or equivalent to the estimated backgrounds and were given zero weight in the subsequent refinement. Several standard reflections were measured repeatedly during the course of the experiment, but no significant change in intensity was detected. No corrections were made for extinction. The linear absorption coefficient for Mo K α radiation is estimated as 7.41 cm^{-1} and the maximum variation in transmission coefficient as 15%. The glass capillary probably contributes to the relatively high background counting rate, but we have no evidence that it aggravates the variation in transmission factors. No corrections for absorption were made.

Calculations were made using the IBM 7044 and CDC 6600 computers. We used our own unpublished programs for Fourier series and interatomic distances and angles and our own modified version of the Gantzel-Sparks-Trueblood full-matrix least-squares program, which minimizes $\sum w|\Delta F|^2/\sum w|F_o|^2$. The atomic scattering factors were chosen as follows: Ni²⁺ from

Thomas and Umeda⁴ and Cl⁻ and neutral O, C, and N from International Tables.⁵ Corrections for the real and imaginary parts of the anomalous dispersion were made for nickel and chlorine using the values given in "International Tables."⁶ The temperature factor was defined as $\exp(-B\lambda^{-2} \sin^2 \theta)$ when isotropic or as

$$\exp(-0.25 \sum_i \sum_j h_i h_j b_i b_j B_{ij}) \quad (i, j = 1, 2, 3)$$

where b_i is the *i*th reciprocal cell dimension. The 2492 nonzero reflections were assigned equal weights initially. Later in the refinement, weights were assigned on the basis of standard deviations of structure factors derived from an estimate of the accuracy of the net intensity *I* (in counts)

$$\sigma^2(I) = 4000 + 10I + (0.03I)^2$$

Typical backgrounds ranged from 400 to 2000 counts, with higher values where streaking was involved. The strongest reflection, 100, was observed as 430,000 counts. This estimate assumes and the final results tend to confirm that counting statistics is not the limiting factor in the accuracy.

Determination of the Structure

The Ni-Ni vectors were identified in a three-dimensional Patterson function. A three-dimensional electron density map calculated with signs based on the Ni structure showed the chlorine atoms and some of the benzimidazole group atoms. After several alternations of least-squares refinements and Fourier summations,

(4) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(5) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, p 210.

(6) See ref 5, p 215.

the positions of 46 of the 48 independent atoms (excluding hydrogen) had been obtained, but the positions of the two methyl groups of one acetone molecule remained in doubt. The oxygen and central carbon atoms of this acetone molecule had nearly equal y coordinates. In a difference Fourier map, based on parameters from 46 atoms, the two methyl groups appear as peaks spreading over 1 Å in the y direction. The maximum heights for the two spread peaks were 1.4 and 1.3 $e/\text{Å}^3$. It proved impossible to refine these positions as individual atoms and it was decided to consider each methyl group as made up of two half-atoms at either end of the 1-Å spread peak. These half-atoms were refined successfully with isotropic temperature factors. The maximum peak in these areas after a subsequent difference Fourier map was 0.5 $e/\text{Å}^3$. The nickel and chlorine atoms were refined anisotropically and the light atoms isotropically. This anisotropic refinement is justified by the fact that the three independent heavy atoms in the cation remain nearly isotropic while the chloride ion is anisotropic in a manner which is related in a plausible way to the geometry of hydrogen bonding as discussed below. With equal weights and before the imaginary dispersion correction was introduced, the conventional R ($=\Sigma|\Delta F|/\Sigma|F_o|$) was reduced to 0.095 for 2492 reflections but with large discrepancies for many of the numerous very weak reflections. With the final weighting scheme and full correction for anomalous dispersion, R increased to 0.101 for 2492 reflections and 0.150 for the complete set of 3284 reflections, but the weighted R' ($=\Sigma w|\Delta F|^2/\Sigma w|F_o|^2$)^{1/2} was 0.081, and the distribution of discrepancies was much more consistent with the assigned weights. The standard deviation of an observation of unit weight was 1.58. The final difference Fourier map showed a maximum peak of 0.5 $e/\text{Å}^3$ or about 15% of the average height of a carbon atom. Introduction of the imaginary dispersion correction had a very trivial effect on both the atomic coordinates and the thermal parameters, but the change in the weighting scheme led to some variation in the parameters. The maximum shift in a position of an atom in one of the benzimidazole groups was 0.05 Å; the average shift was 0.02 Å and only one of the bond distances changed by more than 1 σ . The values quoted in the following tables are taken from the weighted refinement where, in the final cycle, the shifts of all parameters, except those of the disordered methyl groups, were less than 0.15 of their standard deviations.

The final values of the parameters are listed in Table I. Table II lists the rms amplitudes of vibration. Table III lists the bond distances and angles in the structure. Table IV shows the final observed and calculated structure factors.

Discussion of the Structure

The unit cell contains two cations with the general formula $\text{Ni}_2\text{Cl}_3(\text{C}_7\text{H}_6\text{N}_2)_8^+$, two chloride ions Cl^- , and eight acetone molecules. The acetone molecules occupy general positions, while the free chloride ion

TABLE II

RMS AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Ni	0.210 (3)	0.229 (3)	0.233 (3)
Cl(1)	0.233 (5)	0.236 (5)	0.260 (5)
Cl(2)	0.248 (5)	0.282 (6)	0.335 (7)
Cl(3)	0.207 (5)	0.243 (5)	0.431 (9)

TABLE III

BOND DISTANCES AND ANGLES^a

Atoms	Dist, Å			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
Ni-N(1)	2.076 (10)	2.102 (11)	2.067 (10)	2.061 (10)
N(1)-C(2)	1.35 (2)	1.33 (2)	1.33 (2)	1.35 (2)
N(1)-C(9)	1.43 (2)	1.38 (2)	1.41 (2)	1.43 (2)
C(2)-N(3)	1.37 (2)	1.39 (2)	1.36 (2)	1.37 (2)
N(3)-C(4)	1.35 (2)	1.37 (2)	1.39 (2)	1.36 (2)
C(4)-C(9)	1.44 (2)	1.41 (2)	1.40 (2)	1.43 (2)
C(4)-C(5)	1.46 (2)	1.44 (3)	1.40 (2)	1.41 (2)
C(5)-C(6)	1.43 (3)	1.37 (3)	1.41 (2)	1.36 (3)
C(6)-C(7)	1.37 (3)	1.45 (3)	1.42 (2)	1.39 (2)
C(7)-C(8)	1.42 (3)	1.40 (2)	1.46 (2)	1.44 (2)
C(8)-C(9)	1.41 (2)	1.38 (2)	1.41 (2)	1.37 (2)

Atoms	Dist, Å	Atoms	Dist, Å
Ni-Cl(1)	2.425 (4)	C(1f)-C(3f)	1.53, 1.47
Ni-Cl(2)	2.941 (2)	O(1e)-C(1e)	1.36 (3)
O(1f)-C(1f)	1.23 (3)	C(1e)-C(2e)	1.40 (3)
C(1f)-C(2f)	1.52, 1.41	C(1e)-C(3e)	1.38 (3)

Atoms	Angle, deg			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
Cl(1)-Ni-N(1)	96.6 (3)	93.1 (3)	93.2 (3)	94.9 (3)
Cl(2)-Ni-N(1)	84.4 (3)	86.3 (3)	87.1 (3)	84.9 (3)
Ni-N(1)-C(2)	119.7 (8)	118.4 (9)	123.9 (8)	122.1 (8)
Ni-N(1)-C(9)	132.7 (8)	131.7 (9)	131.0 (8)	130.4 (8)
C(2)-N(1)-C(9)	107 (1)	110 (1)	105 (1)	107 (1)
N(1)-C(2)-N(3)	111 (1)	108 (1)	113 (1)	109 (1)
C(2)-N(3)-C(4)	109 (1)	109 (1)	107 (1)	111 (1)
N(3)-C(4)-C(5)	134 (1)	132 (2)	130 (1)	133 (1)
N(3)-C(4)-C(9)	109 (1)	106 (1)	106 (1)	106 (1)
C(5)-C(4)-C(9)	118 (1)	122 (2)	123 (1)	121 (1)
C(4)-C(5)-C(6)	116 (2)	113 (2)	115 (1)	114 (1)
C(5)-C(6)-C(7)	123 (2)	127 (2)	123 (1)	127 (2)
C(6)-C(7)-C(8)	124 (2)	118 (2)	123 (1)	119 (1)
C(7)-C(8)-C(9)	114 (1)	117 (1)	113 (1)	116 (1)
C(8)-C(9)-N(1)	129 (1)	129 (1)	127 (1)	130 (1)
C(8)-C(9)-C(4)	125 (1)	124 (1)	124 (1)	122 (1)
C(4)-C(9)-N(1)	105 (1)	107 (1)	109 (1)	107 (1)

Atoms	Angle, deg	Atoms	Angle, deg
Cl(1)-Ni-Cl(2)	179.3 (1)	O(1e)-C(1e)-C(3e)	118 (2)
N(1a)-Ni-N(1b)	170.1 (4)	N(1c)-Ni-N(1d)	172.0 (4)
N(1a)-Ni-N(1c)	91.9 (4)	N(1b)-Ni-N(1c)	90.2 (4)
N(1a)-Ni-N(1d)	86.6 (4)	N(1b)-Ni-N(1d)	90.0 (4)
O(1e)-C(1e)-C(2e)	114 (2)	C(2e)-C(1e)-C(3e)	128 (2)

^a Standard deviations for the least significant digit are given in parentheses.

Cl(3) occupies special position b. The cation is drawn in Figure 1. The central chlorine atom Cl(2) occupies a center of symmetry, special position a. In the cation, the angle subtended at the nickel by the terminal and bridging chlorine atoms Cl(1) and Cl(2) is 179.3 (1)°; thus the five "heavy" atoms are nearly collinear. The nickel to chlorine distances are appreciably different (Ni-Cl(1) = 2.425 (4) Å and Ni-Cl(2) = 2.941 (2) Å). The Ni-Cl(1) distance is similar to that observed in octahedral Ni(II)-Cl bonds. For example, in NiCl_2 ,

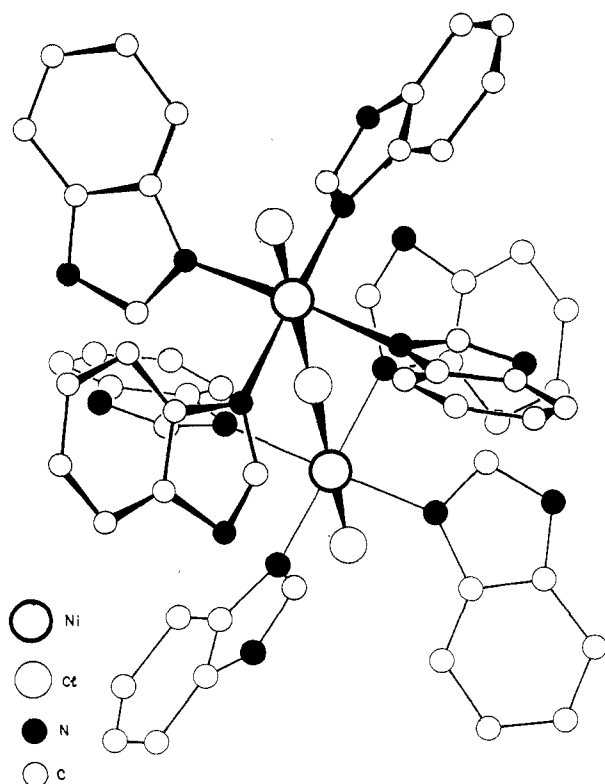


Figure 1.—A general view of the $\text{Ni}_2\text{Cl}_3(\text{C}_7\text{H}_6\text{N}_2)_8^+$ cation.

where each nickel occupies an octahedral site, the Ni-Cl distances are 2.426 Å,⁷ while in $\text{Ni}(\text{py})_4\text{Cl}_2$, Ni-Cl distances of 2.387 Å are found.⁸ These distances are greater than the value of 2.27 Å found in the tetrahedral NiCl_4^{2-} ion,⁹ as is to be expected.

Figure 2 shows the arrangement of the four independent benzimidazole groups around one nickel atom. The figure is a projection of *half* the cation down the Cl(2)-Ni vector, with the chlorine atoms Cl(1) and Cl(2) omitted for clarity. The cation comes close to fourfold (4/m) symmetry. The average N(1)-Ni-N(1) angle, for adjacent nitrogen atoms, is 89.7°. The four Ni-N(1) bonds are bent toward the bridging rather than the terminal chlorine, the average N(1)-Ni-Cl(1) angle being 94.2°. Thus the least-squares plane of the four nitrogen atoms N(1a), N(1b), N(1c), and N(1d) intersects the Cl(1)-Ni-Cl(2) line on the bridging chlorine side, 0.16 Å from the nickel atom; the maximum deviation of a nitrogen atom N(1g) from the plane of the four nitrogen atoms is 0.015 Å.

Results of the least-squares plane calculations for the four benzimidazole groups are shown in Table V. No atom deviates from the respective plane by more than 0.05 Å. The benzimidazole groups are therefore approximately planar and they are tilted such that the benzene rings are closer to the terminal chlorine Cl(1) than the bridging chlorine Cl(2). The four planes intersect the plane of the four nitrogen atoms N(1a), N(1b), N(1c), and N(1d) at an average angle of 46.5°

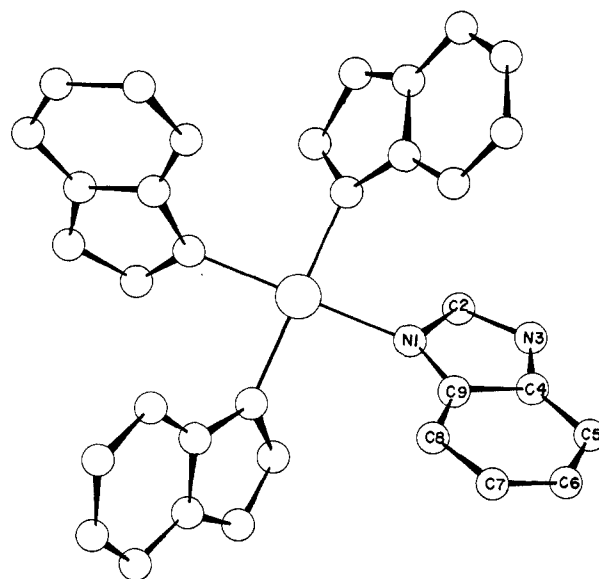


Figure 2.—The environment of a single nickel atom. The terminal and bridging chlorines are above and below the nickel atom in this projection.

(maximum deviation 3.1°). This arrangement of the four benzimidazole groups around the nickel atom has minimized the possible intramolecular contacts in the cation. The shortest distance across the center of symmetry between benzimidazole group atoms is 3.82 Å. For benzimidazole groups attached to the same nickel atom, the minimum intramolecular distance is 2.97 Å for C(2a)-N(1d).

The deviations between dimensions of similar type in four benzimidazole groups are little more than is to be expected from the standard deviations, and we failed to find any correlation between these deviations and the molecular environments.

The average bond distance C-C in the six-membered rings is 1.41 Å with a maximum deviation of 0.05 Å. The two internal angles at C(5) and C(8) are smaller than the remaining four angles in the six-membered ring. The dimensions of the four benzimidazole groups are more consistent with respect to the five-membered rings. This is not unexpected as the thermal motion is generally less for these five atoms than for the remaining four. The nickel atom subtends a lower angle at N(1) with C(2) than with C(9) (average value 121° as against 132°). This difference in angle increases the distance of the benzene rings from the Cl-Ni-Cl-Ni-Cl line. The Ni-N(1) distance (averaged at 2.076 Å) is similar to those found in a number of Ni(II) octahedral complexes, a list of which has been recently compiled.¹⁰

The *a* projection of the unit cell is shown in Figure 3. It is possible for the hydrogens attached to the N(3) atoms in the benzimidazole groups to participate in hydrogen bonding with the chlorine atoms. The configuration of the Cl(3) ion and N(3a) and N(3b), as shown in Figure 3, strongly suggests hydrogen bonding. Each Cl(3) ion, situated on a center of symmetry, is surrounded by four nitrogen atoms in an approximately

(7) A. Ferrari, A. Braibanti, and G. Bigliardi, *Acta Cryst.*, **16**, 846 (1963).

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TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS^a

Main data table containing observed and calculated structure factors with columns for observed (HkL) and calculated (HkL) values, and a column for the difference (HkL - HkL).

TABLE IV (Continued)

* Reflections marked with an asterisk were recorded as zero and given zero weight in the refinement.

TABLE V

RESULTS OF THE LEAST-SQUARES PLANE CALCULATIONS FOR THE BENZIMIDAZOLE GROUPS^a

Group	N(1)	C(2)	N(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
a	-0.01 (1)	0.01 (2)	0.01 (1)	-0.01 (2)	-0.00 (2)	0.00 (2)	0.00 (2)	0.01 (2)	-0.02 (2)
b	0.01 (1)	-0.01 (2)	-0.00 (2)	-0.03 (2)	0.03 (2)	0.01 (2)	-0.01 (2)	-0.01 (2)	0.02 (2)
c	0.03 (2)	-0.00 (2)	-0.02 (2)	-0.01 (2)	0.00 (2)	0.02 (2)	0.00 (2)	-0.04 (2)	0.02 (2)
d	-0.03 (1)	-0.01 (2)	0.05 (2)	0.01 (2)	-0.04 (2)	-0.02 (2)	0.05 (2)	0.00 (2)	-0.02 (2)

^a Distances from the plane given in ångströms. All atoms were given unit weight in the calculations.

square-planar configuration. The N-Cl(3) distances are 3.13 and 3.10 Å, which are within the range of hydrogen bonding of this type.¹¹ There is also a possibility of hydrogen bonding between the terminal chlorine Cl(1) of one cation and atoms N(3c) ($-x, 0.5 + y, 0.5 - z$) and N(3d) ($x, 0.5 - y, 0.5 + z$) on an adjacent cation. However, the N-Cl distances are longer (3.41 and 3.74 Å) and the geometrical arrangement is less favorable for hydrogen bonding than is the case for the Cl(3) ion with N(3a) and N(3b). Of the four "heavy" atoms refined anisotropically, only the Cl(3) ion shows

any appreciable anisotropy. The rms amplitudes of vibration of the Cl(3) ion are 0.207, 0.243, and 0.431; the direction cosines of the maximum amplitude of this ion with respect to the crystallographic axes are 0.182, 0.754, and 0.628. This direction is about 67° from the plane of the postulated hydrogen bonds, a fact which indicates that the hydrogen bonds are the principal constraint in the motion of the chlorine ion. The thermal parameters, bond distances, and evidence for disorder found for the acetone molecules show that for both acetone molecules the positions are not well defined. Therefore, we consider the description of the acetone molecules to have little or no physical signifi-

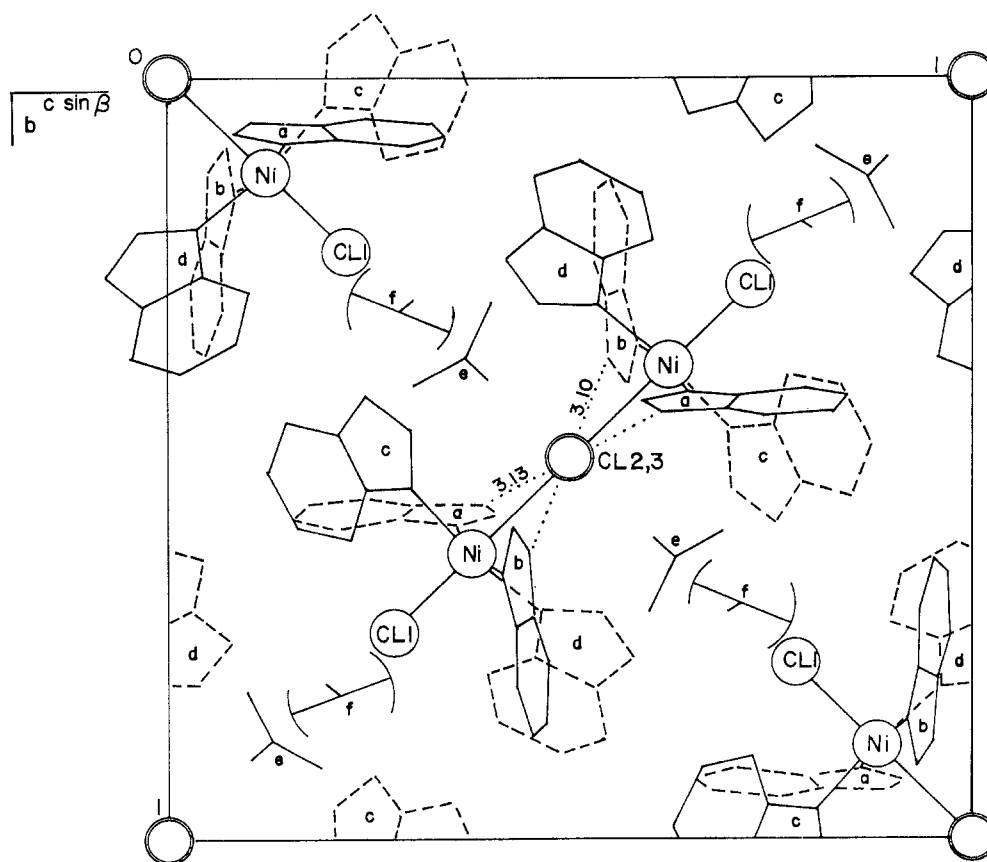


Figure 3.—The *a* projection of the unit cell.

cance. As can be seen from the packing diagram, the acetone molecules fill the gaps between the cations in an approximately symmetrical way.

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