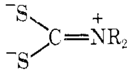
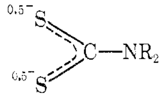
The bond distances and angles in the $(C_6H_5)_4As^+$ ion are all close to the normal, accepted values.[17] However, the angles of rotation of the four phenyl groups about their respective As–C(n1)–C(n4) axes are such that the $(C_6H_5)_4As^+$ ion does not approximate to any symmetrical conformation (such as D_{2d} or S_4). In some other cases such high symmetries have been found[23,24] although more or less drastic departures from symmetry seem to be common.[25,26] It is precisely this flexibility which makes $(C_6H_5)_4As^+$ such a useful cation for obtaining crystalline salts of large, irregularly shaped anions.


V


VI

---

(23) R. C. L. Mooney, *J. Am. Chem. Soc.*, **62**, 2995 (1940).
(24) B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).
(25) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **5**, 416 (1966).
(26) J. G. Bergman, Jr., and F. A. Cotton, *ibid.*, **5**, 1420 (1966).

CONTRIBUTION FROM THE PHYSICS AND CHEMISTRY DEPARTMENTS,
DUQUESNE UNIVERSITY, PITTSBURGH, PENNSYLVANIA 15219

The Crystal and Molecular Structure of Bis(pyridine-2-carboxamido)nickel(II) Dihydrate[1]

BY SHIH C. CHANG, DONG Y. PARK, AND NORMAN C. LI

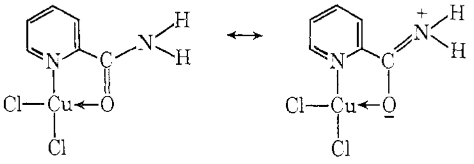
Received January 22, 1968

The crystal and molecular structure of bis(pyridine-2-carboxamido)nickel(II) dihydrate, $Ni(C_6H_5N_2O)_2 \cdot 2H_2O$, isolated from aqueous solution of pH 11.5, has been determined from three-dimensional X-ray data collected by the multiple-film Weissenberg method. The unit cell dimensions are: $a = 7.63 \pm 0.02$ Å, $b = 4.49 \pm 0.01$ Å, $c = 12.45 \pm 0.06$ Å, $\beta = 90.0 \pm 0.3°$. The crystal is a twinned composite with monoclinic components. The space group is $P2_1/c$, $Z = 2$, and the measured and calculated densities are 1.59 and 1.56 g cm^{-3}, respectively. The intensity data show essentially the orthorhombic mmm symmetry due to microscopic twinning. By using an incoherent twinning model, the structure was solved and refined by a least-squares method. Without the hydrogens, the final R factor is 10.7% for the 840 reflections. The pyridine ring nitrogen and the amide nitrogen are bonded to nickel with bond lengths of 1.92 and 1.87 (±0.01) Å, respectively. The four nitrogens of the two ligands bonded to nickel form a planar structure in *trans* configuration, and the water molecules are not coordinated to nickel. The molecules form infinite zigzag layers perpendicular to the b axis. The layers are held together by the hydrogen bonds of the waters of hydration and the van der Waals forces between the molecules. The twinning factor observed (m) is 0.56. It may be that a layer of the reversed structure stacks on one constituent structure component thus causing the twinning phenomenon.

Introduction

Crystal and molecular structures of amino acids, peptides, and acid amides have been investigated in detail by several authors because of their biological importance. Recently Conley and Martin[2] reported that picolinamide (pyridine-2-carboxamide), a derivative of an α-amino acid, forms different complexes with Cu^{2+} or Ni^{2+} in aqueous solution at different pH values and found that titration of solutions containing 2 mol of picolinamide per mol of Cu^{2+} or Ni^{2+} requires the addition of 2 equiv of base per mol of metal ion to reach pH 10. The original blue picolinamide–cupric and picolinamide–nickel ion solutions at the beginning of the titration change color to violet and to yellow-orange, respectively, during the course of the titration, and these color changes are typical of those found in peptides where amide hydrogens undergo cupric[3] or nickel[4] ion promoted ionizations. Conley and Martin[2] suggested that cupric or nickel ion promotes the ionization of two amide hydrogens forming at high pH a 2:1 ligand–metal complex with the ligands chelated through nitrogen atoms. Conley and Martin[2] also described the preparation of a neutral bis(pyridine-2-carboxamido)nickel(II) complex yielding red needles.

Nagano, *et al.*,[5] reported the isolation in the solid state of a 1:1 $CuCl_2$ complex of picolinamide and suggested that the structure of the complex is


I, picolinamide–cupric chloride

Their suggestion was based solely on the directions of shift of the infrared bands of the C=O and C—N stretching vibrations and the ring vibrations. Since, at the time this research was undertaken, the crystal and molecular structure of metal complexes of picolin-

(1) Research sponsored by the National Science Foundation, Grant No. GB-4065. Material to be presented by D. Y. Park to the Graduate School of Duquesne University as part of his Ph.D. thesis in the Chemistry Department.
(2) H. L. Conley, Jr., and R. B. Martin, *J. Phys. Chem.*, **69**, 2914 (1965).
(3) W. L. Koltun, R. H. Roth, and F. R. N. Gurd, *J. Biol. Chem.*, **238**, 124 (1963); W. L. Koltun, M. Fried, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **82**, 233 (1960).
(4) R. B. Martin, M. Chamberlin, and J. T. Edsall, *ibid.*, **82**, 495 (1960); R. B. Martin and J. T. Edsall, *ibid.*, **82**, 1107 (1960).
(5) K. Nagano, H. Kinoshita, and A. Hirakawa, *Chem. Pharm. Bull.* (Tokyo), **12**, 1198 (1964).

amide had not received previous investigation, this paper describes the result of an X-ray diffraction study with bis(pyridine-2-carboxamido)nickel(II) dihydrate.[6,7]

Experimental Section

Preparation.—The crystals (red orthorhombic needles) were prepared from aqueous solutions containing 0.3 *M* picolinamide, 0.1 *M* $NiSO_4$, and 0.1 *M* sodium carbonate (pH ~11.5). Conley and Martin[2] have suggested that the red needles should be a 2:1 picolinamide–nickel ion complex with amide hydrogens ionized on both ligands. *Anal.* Calcd for $Ni(C_6H_5N_2O)_2 \cdot 2H_2O$: Ni, 17.42; C, 42.77; H, 4.19. Found: Ni, 17.15; C, 42.09; H, 4.29. The solubility is less than 0.05 mg/100 g of water at 20°.

X-Ray Diffraction.—The crystals used for the present investigation were of the size 0.15 × 0.2 × 0.2 mm. Cu Kα radiation was chosen, and the diffracted beams were filtered through 1.0-mil Ni foil (λ 1.5418 Å). The linear absorption coefficient (μ) of the compound for Cu Kα radiation is 21.2 cm^{-1}. No corrections were made for absorption, since the maximum estimated error to structure factors is ±3%. The Lorentz and polarization corrections were made and the intensity data were reduced to a common scale by a program written by Shiono,[8] using the least-squares method of Hamilton, Rollett, and Sparks.[9] The unit cell parameters at 22°, as determined from the equatorial Weissenberg photographs along the *a* and *b* axes, are $a = 7.63 \pm 0.02$ Å, $b = 4.49 \pm 0.01$ Å, $c = 20.45, \pm 0.06$ Å, $\beta = 90.0 \pm 0.3°$. The diffraction patterns of sodium chloride powder were superimposed on the same films for calibration. The systematic absences that were observed on Weissenberg photographs are *l* odd for $\{h0l\}$ and *k* odd for $\{0k0\}$, which correspond to the $P2_1/c$ space group, with $\beta = 90°$. For two formula units in the cell the calculated density is 1.56 g cm^{-3}; the observed density is 1.59 (±0.02) g cm^{-3} determined by flotation. Nickel is at the inversion center, as it is required by the crystallographic symmetry conditions. Six crystals were examined before choosing two for data collection. They all showed approximately the mmm Laue symmetry. The intensity data for the reciprocal lattice layers—$k = 0$, 1, and 2, and $h = 0$, 1, 2, and 3—were recorded on multiple films using the equiinclination Weissenberg technique and estimated visually against a standard scale.

Although an orthorhombic space group was at first suspected, because $\beta = 90.0°$ and the intensities showed essentially the orthorhombic mmm Laue symmetry, there was however no orthorhombic space group which would give the observed systematic absences on Weissenberg photographs. Two ways of handling the data were used at the first stage of the investigation. The structure factors $F(hkl)_o$ and $F(hk\bar{l})_o$ were averaged to yield a set of orthorhombic data. However, on the basis of an assumption that these crystals are a twinned composite of the monoclinic components which are only pseudo-orthorhombic, we read the intensities of the reflections for *hkl* and $hk\bar{l}$ independently as is usually done in monoclinic data collection. The total number of independent observations counted in this way is 840.

Structure Determination

Without a definite idea about whether the crystal under investigation is disordered orthorhombic or monoclinic, our policy was to carry out calculations using both and to judge the correctness of the results of these refinements.

If we regard the systematic absences of *k* odd for $\{0k0\}$ as accidental, then an orthorhombic space group $Pmc2_1$ or Pmcm could be adopted. Since the molecule of bis(pyridine-2-carboxamido)nickel(II) is centrosymmetric and the molecules should distribute evenly in the crystal, the space group Pmcm is to be preferred. In order to fulfill the symmetry requirements, the molecules have to be disordered. The atomic positions were easily located after assigning Ni to the special position at the origin. After cycles of refinements, the *R* factor was reduced to 0.18, with positive temperature parameters for all of the atoms. The *R* factor could be reduced to 0.165. However, some of the temperature parameters became negative and the bond lengths became absurd. The idea was abandoned as incorrect.

By adopting the monoclinic space group $P2_1/c$ as dictated by the systematic absences and using the data as they were read from the photographs, the atomic positions were again located after assigning Ni to the special position at the origin. The *R* factor stayed at about 0.19 and would not improve.

The incoherent twinning model was then adopted. Like Wei, *et al.*,[10] we set

$$|F(hkl)_o|^2 = m|F(hkl)_{o'}|^2 + (1 - m)|F(hk\bar{l})_{o'}|^2$$

$$|F(hkl)_c|^2 = m|F(hkl)_{c'}|^2 + (1 - m)|F(hk\bar{l})_{c'}|^2$$

where *m* is the fraction of one monoclinic twinning component lattice, and $|F(hkl)_{o'}|$ and $|F(hk\bar{l})_{o'}|$ are defined as

$$|F(hkl)_{o'}| = \left[|F(hkl)_o|^2 \frac{|F(hkl)_{c'}|^2}{|F(hkl)_c|^2}\right]^{1/2}$$

$$|F(hk\bar{l})_{o'}| = \left[|F(hk\bar{l})_{o'}|^2 \frac{|F(hk\bar{l})_{c'}|^2}{|F(hk\bar{l})_c|^2}\right]^{1/2}$$

Note that $|F(hk\bar{l})_{o'}|$ is defined differently from that of Wei, *et al.*[10] Our refinement was made to minimize the usual expression

$$\sum w[|F(hkl)_{o'}| - s|F(hkl)_{c'}|]^2$$

where the summation includes both positive and negative *l*, and *s* is the adjusted scale factor.

When the method was used, the *R* factor, defined as $R = \Sigma[|F_{o'}| - |F_{c'}|]/\Sigma|F_{o'}|$, dropped quickly. With the anisotropic temperature factors and the twinning factor *m* refined,[11,12] the final *R* factor became 0.107. Hydrogen atoms were not included. The final weighted *R* factor is 0.128, with the weighted *R* factor defined as

$$\text{weighted } R = [\sum w(F_{o'} - sF_{c'})^2/\sum wF_{o'}{}^2]^{1/2}$$

Hughes' weighting scheme was used.[11] To justify the weighting scheme, we can rearrange the function minimized as shown below.

---

(6) After the completion of the structure analysis, we noticed a paper by Nawata, *et al.*,[7] on the crystal structure of this compound. Differences are noted and are discussed later in this paper.

(7) Y. Nawata, H. Iwasaki, and Y. Saito, *Bull. Chem. Soc. Japan*, **40**, 515 (1967).

(8) R. Shiono, unpublished work, 1965.

(9) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, **18**, 129 (1965).

(10) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967).

(11) The original least-squares program was written by Busing, *et al.*[12] The program we used was first modified by Dr. R. Shiono and used at the University of Pittsburgh; it was then modified for the CDC G-20 computer at Duquesne University.

(12) W. R. Busing, D. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

TABLE I

THE OBSERVED STRUCTURE FACTORS OF THE TWINNED CRYSTAL AS REDUCED FROM THE INTENSITY DATA

L	10Fo
k=0 h=0	
-2	714
6	240
-6	241
10	487
-10	485
12	605
-12	611
14	477
-14	472
16	101
-16	98
18	167
-18	169
20	153
-20	153
22	74
-22	73
24	35
-24	24
k=0 h=1	
0	707
2	683
-2	503
4	237
-4	240
6	595
-6	633
8	410
-8	394
10	212
-10	237
12	449
-12	467
14	119
-14	83
16	197
-16	179
18	188
-18	154
20	152
-20	134
22	114
-22	84
24	42
-24	33
k=0 h=2	
0	658
2	133
-2	153
4	360
-4	506
6	83
-6	120
8	135
-8	135
10	374
-10	317
12	275
-12	253
14	275
-14	302
16	151
-16	181
18	77
-18	104
20	45
-20	45
22	49
-22	64
24	95
-24	88
k=0 h=3	
0	48
2	434
-2	389
4	523
-4	598
6	323
-6	385
8	123
-8	196
10	198
-10	252
12	189
-12	200
14	194
-14	221
16	374
-16	405
18	176
-18	177
20	84
-20	81
22	74
-22	94
24	33
-24	50
k=0 h=4	
0	514
2	377
-2	530
4	420
-4	629
6	319
-6	251
8	96
-8	99
10	215
-10	266
12	228
-12	298
14	263
-14	458
16	203
-16	365
18	99
-18	90
20	40
-20	56
22	40
-22	51
k=0 h=5	
0	200
2	353
-2	277
4	213
-4	208
6	204
-6	268
8	219
-8	247
10	185
-10	269
12	188
-12	188
14	146
-14	146
16	90
-16	106
18	65
-18	58
20	42
-20	60
22	33
-22	38
k=0 h=6	
0	314
2	203
-2	218
4	151
-4	230
6	56
-6	56
8	93
-8	93
10	124
-10	109
12	117
-12	135
14	104
-14	123
16	40
-16	74
-18	93
-20	58
k=0 h=7	
0	244
2	254
-2	197
4	74
-4	66
6	46
-6	56
8	46
-8	92
10	112
-10	226
12	92
-12	164
14	70
-14	91
16	39
-16	72
18	30
-18	73
k=0 h=8	
0	111
2	119
-2	157
4	95
-4	147
6	83
-6	109
8	108
-8	116
10	89
-10	109
12	70
-12	95
14	44
-14	90
k=0 h=9	
0	90
2	79
-2	111
4	65
-4	79
6	48
-6	43
8	32
-8	49
k=1 h=0	
1	301
2	435
3	740
-3	756
4	712
-4	815
5	722
-5	796
6	179
-6	218
7	83
-7	118
8	487
-8	590
9	537
-9	704
10	202
-10	276
11	247
-11	333
12	75
-12	97
13	240
15	351
16	100
17	209
19	121
23	104
25	61
k=1 h=1	
0	267
1	95
-1	77
2	298
-2	263
3	674
-3	822
4	356
-4	355
5	400
-5	367
6	154
-6	117
7	485
-7	507
8	107
-8	130
9	263
-9	251
10	76
-10	70
11	231
-11	231
12	68
-12	77
13	163
-13	153
14	71
-14	44
15	214
-15	237
17	247
19	112
21	112
23	75
25	59
k=1 h=2	
0	93
1	328
-1	392
2	127
-2	162
3	98
-3	77
4	211
-4	187
5	231
-5	214
6	116
-6	124
7	130
-7	121
8	189
-8	181
9	336
-9	309
10	107
-10	97
11	176
-11	133
12	139
-12	149
13	219
-13	213
-14	52
15	139
-15	130
16	150
-16	126
19	133
21	101
22	65
23	71
24	61
25	45
k=1 h=3	
0	45
1	506
-1	496
2	98
-2	117
3	259
-3	226
4	101
-4	114
5	160
-5	178
6	97
-6	105
7	384
-7	407
8	169
-8	174
9	212
-9	204
10	53
-10	47
11	188
-11	215
12	175
-12	203
13	207
-13	186
14	103
-14	109
15	111
-15	100
16	70
-16	55
17	149
-17	121
18	76
-18	77
19	164
20	61
21	150
24	29
k=1 h=4	
0	117
1	532
-1	440
2	134
-2	101
3	222
-3	240
4	109
-4	180
5	255
-5	261
6	77
-6	110
7	243
-7	256
9	292
-9	325
10	167
-10	156
11	215
-11	236
12	138
-12	196
13	183
-13	243
-14	55
15	113
-15	95
16	84
-16	112
17	76
-17	93
18	52
-18	74
19	127
-19	161
21	90
23	28
k=1 h=5	
1	142
-1	187
2	83
-2	98
3	237
-3	201
5	225
-5	172
6	89
-6	88
7	220
-7	231
9	204
-9	154
11	174
-11	174
13	106
-13	94
-14	55
15	93
-15	76
17	101
-17	86
19	74
k=1 h=6	
0	131
1	75
-1	109
2	131
-2	93
3	118
-3	185
4	77
-4	119
5	176
-5	133
7	84
-7	96
8	113
-8	78
9	55
-9	55
10	96
-10	55
11	55
-11	55
-12	54
13	53
-13	75
15	85
-15	93
17	73
-17	73
k=1 h=7	
1	78
-1	112
2	78
-2	121
3	112
-3	112
4	78
-4	78
5	153
-5	134
6	110
-6	77
7	94
-7	109
8	53
-8	93
9	52
-9	91
10	51
-10	51
11	50
-11	70
13	64
-13	78
15	77
-15	85
17	41
k=1 h=8	
1	87
-1	87
3	95
-3	95
5	106
-5	118
7	101
-7	113
9	74
-9	61
11	54
-11	54
13	44
-13	54
k=1 h=9	
1	76
-1	54
3	74
-3	37
-5	61
k=2 h=0	
0	278
1	249
2	103
-2	110
3	110
-3	124
4	387
-4	446
5	91
-5	144
6	552
-6	661
7	247
-7	365
8	526
-8	596
9	54
-9	71
10	288
-10	328
11	133
-11	138
12	71
-12	93
13	101
-13	127
14	172
-14	274
15	37
16	52
17	26
18	117
19	44
20	143
22	68
24	38
k=2 h=1	
0	165
1	131
-1	112
2	407
-2	381
3	172
-3	173
4	181
-4	189
5	229
-5	245
6	241
-6	245
7	183
-7	205
8	326
-8	367
9	184
-9	196
10	176
-10	186
11	76
-11	70
12	207
-12	192
-13	24
14	137
-14	144
15	86
-15	81
16	139
-16	117
17	54
18	83
20	91
22	70
24	30
k=2 h=2	
0	15
1	176
-1	179
2	59
-2	56
3	44
-3	48
4	287
-4	306
5	117
-5	90
6	235
-6	233
7	43
-7	43
8	218
-8	220
9	142
-9	124
10	202
-10	213
11	48
-11	66
12	81
-12	99
13	104
-13	93
14	68
-14	90
16	95
-16	75
17	52
-17	38
18	120
-18	150
20	105
21	37
22	54
k=2 h=3	
0	25
1	28
-1	37
2	264
-2	297
3	107
-3	118
4	261
-4	233
5	83
-5	67
6	209
-6	197
7	50
-7	74
8	267
-8	252
9	58
-9	58
10	214
-10	220
11	87
-11	113
12	156
-12	163
13	95
-13	75
14	76
-14	99
15	85
-15	120
16	97
-16	138
17	51
-17	44
18	59
-18	65
19	41
-19	41
20	61
22	69
k=2 h=4	
0	161
1	43
-1	78
2	188
-2	166
3	73
-3	49
4	332
-4	275
5	46
-5	82
6	287
-6	290
7	68
-7	116
8	225
-8	338
9	62
-9	111
10	197
-10	212
11	52
-11	69
12	88
-12	75
13	70
-13	60
14	91
-14	95
16	79
-16	71
17	48
-17	35
18	76
-18	101
22	44
k=2 h=5	
0	154
1	105
-1	61
2	152
-2	185
3	69
-3	78
4	164
-4	134
5	36
-5	50
6	163
-6	221
7	37
-7	26
8	155
-8	91
9	38
10	92
-10	75
11	59
-11	95
12	105
-12	69
13	26
-13	37
14	93
-14	83
15	24
-15	35
16	64
-16	72
18	48
-18	62
20	45
k=2 h=6	
0	52
1	26
-1	52
2	101
-2	69
3	52
-3	84
4	109
-4	70
5	65
-5	84
6	139
-6	140
7	52
-7	75
8	98
-8	123
9	37
-9	37
10	58
-10	68
-11	36
12	42
-12	60
13	46
-13	46
14	39
-14	31
-15	36
16	38
18	27
k=2 h=7	
0	51
1	37
2	44
-2	63
3	36
-3	44
4	79
-4	104
6	83
-6	126
7	35
-7	35
8	92
-8	83
9	92
-9	51
10	73
-10	70
-11	21
12	35
-12	52
-13	32
14	38
k=2 h=8	
0	77
-1	30
2	74
-2	83
-3	30
4	70
-4	81
5	36
-5	21
6	69
-6	66
8	48
-8	63
9	24
10	50
-10	67
k=3 h=0	
1	240
2	61
3	129
4	51
5	258
7	155
8	87
9	228
10	81
11	266
12	92
13	83
k=3 h=1	
0	42
1	305
-1	289
2	60
-2	60
3	169
-3	121
4	75
5	76
-5	76
6	64
-6	90
7	112
-7	79
k=3 h=2	
1	168
-1	200
-3	123
4	111
-4	157
5	176
-5	231
7	100
-7	100
9	104
-9	85
-10	86
k=3 h=3	
1	156
-1	163
2	75
-2	43
3	153
-3	134
4	98
-4	63
5	219
-5	181
6	64
-6	78
7	178
-7	189
8	104
-8	92
9	93
-9	81
10	66
-10	82
11	187
-11	105
13	168
-13	121
15	161
-15	75
17	95

$$\sum w\left[\left|F(hkl)_{\mathrm{o}}\right| \frac{\left|F(hkl)_{\mathrm{c}'}\right|}{\left|F(hkl)_{\mathrm{c}}\right|} - s\left|F(hkl)_{\mathrm{c}'}\right| \left|\frac{F(hkl)_{\mathrm{c}'}}{F(hkl)_{\mathrm{c}}}\right|\right]^2 =$$

$$\sum_{l\geqslant 0}\left\{w(hkl)\,[\left|F(hkl)_{\mathrm{o}}\right| - s\left|F(hkl)_{\mathrm{c}}\right|]^2 \left[\frac{\left|F(hkl)_{\mathrm{c}'}\right|}{\left|F(hkl)_{\mathrm{c}}\right|}\right]^2 + w(hk\bar{l})\,[\left|F(hk\bar{l})_{\mathrm{o}}\right| - s\left|F(hk\bar{l})_{\mathrm{c}}\right|]^2 \left[\frac{\left|F(hk\bar{l})_{\mathrm{c}'}\right|}{\left|F(hk\bar{l})_{\mathrm{c}}\right|}\right]^2\right\}$$

This form is the usual one except that each term contains a quotient

$$[\left|F(hkl)_{\mathrm{c}'}\right|/\left|F(hkl)_{\mathrm{c}}\right|]^2 \text{ or } [\left|F(hk\bar{l})_{\mathrm{c}'}\right|/\left|F(hk\bar{l})_{\mathrm{c}}\right|]^2$$

which may have any value between 0 and $1/m$. However, when the two quotients are added, the sum is close to a constant of 2, if the twinning parameter m is approximately 0.5. This shows that for each pair of observations, namely, $|F(hkl)_{\mathrm{o}}|$ and $|F(hk\bar{l})_{\mathrm{o}}|$, a certain weight factor is applied, for $|F(hkl)_{\mathrm{o}}|$ and $|F(hkl)_{\mathrm{c}}|$ are approximately equal to $|F(hk\bar{l})_{\mathrm{o}}|$ and $|F(hk\bar{l})_{\mathrm{c}}|$, respectively, and $w(hkl)$ is approximately equal to $w(hk\bar{l})$. Our refinement is therefore valid in conjunction with the Hughes weighting scheme. The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography."[13] The value of m was 0.563, which is as expected since the symmetry of the twinned composite is orthorhombic except for minor differences. The value is an average of the two crystals used for data collection, and its estimated maximum possible error is ±0.003.

Experimental values of $F(hkl)_{\mathrm{o}}$ as obtained from reduction of the intensity data are shown in Table I.[14]

The final difference Fourier map does indicate a few possible locations for hydrogens of the water molecules. Since not all of the hydrogens appeared, we did not continue the refinements to include the hydrogens.

TABLE II

(a) Fractional Atomic Coordinates with Their Standard Deviations

Atom	x	y	z
Ni(1)	0.0000[a]	0.0000	0.0000
O(1)	−0.4622 (6)	−0.2008 (20)	0.0798 (3)
O(2)	0.4602 (10)	−0.0543 (20)	0.2113 (4)
N(1)	0.0022 (9)	−0.2766 (22)	0.0718 (3)
N(2)	−0.2429 (10)	−0.0281 (25)	0.0095 (4)
C(1)	0.1417 (11)	−0.4092 (29)	0.1007 (5)
C(2)	0.1191 (12)	−0.6110 (27)	0.1519 (4)
C(3)	−0.0519 (13)	−0.6643 (27)	0.1764 (4)
C(4)	−0.1935 (13)	−0.5334 (30)	0.1490 (5)
C(5)	−0.1639 (11)	−0.3492 (26)	0.0956 (4)
C(6)	−0.3057 (13)	−0.1760 (30)	0.0604 (5)

(b) Atomic Anisotropic Thermal Parameters[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	$10^2\,\beta_{23}$
Ni(1)	1.62 (4)	6.52 (23)	0.19 (1)	0.00 (7)	0.12 (1)	0.03 (3)
O(1)	0.56 (9)	11.33 (75)	0.23 (2)	−0.47 (21)	0.20 (3)	0.51 (10)
O(2)	2.46 (16)	6.51 (70)	0.30 (2)	0.09 (27)	0.10 (4)	−0.09 (10)
N(1)	1.50 (14)	6.01 (77)	0.12 (2)	−0.16 (26)	0.20 (4)	−0.16 (10)
N(2)	1.42 (14)	9.87 (89)	0.16 (2)	−0.44 (30)	0.22 (4)	0.30 (11)
C(1)	0.93 (13)	7.79 (101)	0.22 (2)	−0.08 (31)	0.05 (4)	−0.33 (13)
C(2)	1.59 (16)	5.32 (85)	0.19 (2)	0.10 (31)	0.12 (5)	−0.03 (11)
C(3)	1.97 (19)	4.16 (83)	0.18 (2)	−0.16 (33)	0.01 (5)	0.04 (11)
C(4)	1.82 (17)	6.87 (101)	0.19 (2)	0.19 (37)	0.07 (5)	0.16 (13)
C(5)	1.38 (15)	3.48 (77)	0.17 (2)	0.23 (29)	0.07 (4)	0.24 (11)
C(6)	1.84 (19)	7.00 (92)	0.18 (2)	−0.81 (36)	0.01 (5)	0.30 (13)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.
[b] The anisotropic temperature factor is expressed in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

---

(13) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

(14) In Table I many $F(hk\bar{l})_{\mathrm{o}}$ were not listed for high l indices, because they were not recorded on the photographs, and not because they are of zero intensity. Values of F_{o}', and F_{c}' as defined in this section, are given in the Ph.D. thesis of D. Y. Park.

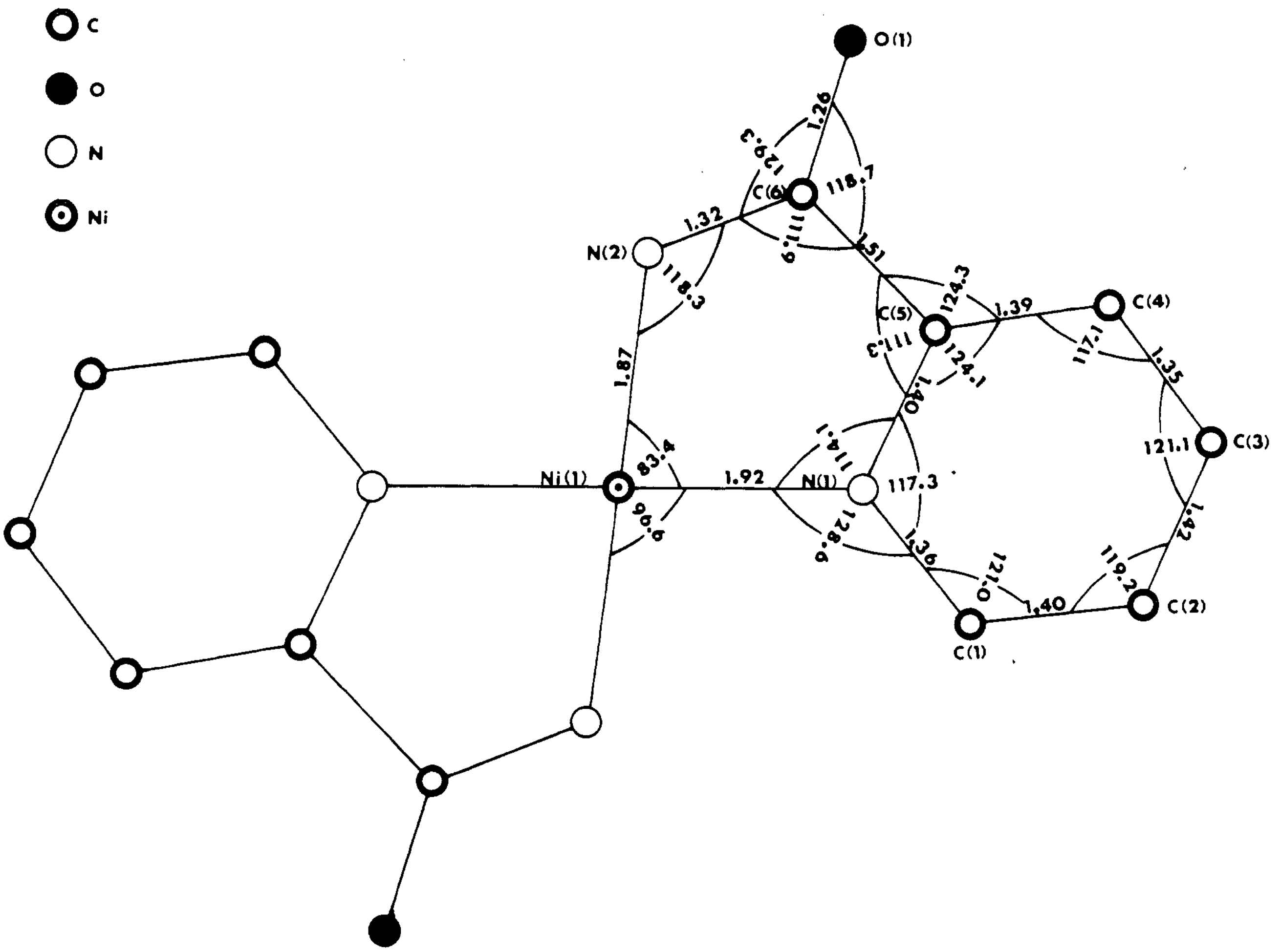


Figure 1.—Intramolecular bond lengths and angles in bis(pyridine-2-carboxamido)nickel(II) dihydrate.

TABLE III

BOND DISTANCES (Å) AND ANGLES (DEG)

Bonds	Bond distances in Bis(pyridine-2-carboxamido)nickel(II) dihydrate	Picolinamide[15] Theoret	Picolinamide[15] Exptl
Ni(1)–N(1)	1.92 (1)		
Ni(1)–N(2)	1.87 (1)		
N(1)–C(1)	1.36 (2)	1.370	1.349
N(1)–C(5)	1.40 (2)		1.335
N(2)–C(6)	1.32 (2)		1.330
C(1)–C(2)	1.40 (2)	1.380	1.374
C(2)–C(3)	1.42 (2)	1.395	1.367
C(3)–C(4)	1.35 (2)		1.404
C(4)–C(5)	1.39 (2)		1.372
C(5)–C(6)	1.51 (2)		1.515
O(1)–C(6)	1.26 (2)		1.241

Bond angles in bis(pyridine-2-carboxamido)nickel(II) dihydrate			
N(1)–Ni(1)–N(2)	83.4 (8)	C(2)–C(3)–C(4)	121.1 (8)
Ni(1)–N(1)–C(1)	128.6 (8)	C(3)–C(4)–C(5)	117.1 (8)
Ni(1)–N(1)–C(5)	114.1 (8)	C(4)–C(5)–N(1)	124.1 (8)
N(1)–C(5)–C(6)	111.3 (8)	C(1)–N(1)–C(5)	117.3 (8)
Ni(1)–N(2)–C(6)	118.3 (8)	C(4)–C(5)–C(6)	124.3 (8)
N(1)–C(1)–C(2)	121.0 (8)	C(5)–C(6)–O(1)	118.7 (8)
C(1)–C(2)–C(3)	119.2 (8)	N(2)–C(6)–O(1)	129.3 (8)

Hydrogen-bonding distances	
O(1)···HO(2)[a]	2.83 (2)
O(2)H···O′(2)	2.81 (2)
O(2)···HO″(2)	2.81 (2)
N(2)H···O′(1)[b]	3.07 (2)

Hydrogen-bonding angles in bis(pyridine-2-carboxamido)nickel(II) dihydrate	
O(1)···HO(2)H···O′(2)	107.8 (6)
O′(2)···HO(2)···HO″(2)	105.9 (6)
O(1)···HO(2)···HO′(2)	132.4 (6)

[a] O(2), O′(2), and O″(2) are adjacent water oxygens and are related by the twofold screw axis. [b] O′(1) refers to O(1) of the adjacent centrosymmetrically related picolinamide molecule.

Description of the Structure

Table II lists the final atomic coordinates and thermal parameters. Figure 1 shows the molecular structure of bis(pyridine-2-carboxamido)nickel(II) with the bond lengths and angles indicated. Table III shows the intramolecular and intermolecular bond lengths and angles for bis(pyridine-2-carboxamido)-nickel(II) dihydrate. Included for comparison are literature values for picolinamide itself.[15] Results on root-mean-square displacements and the directions of the principal axes of the thermovibrational el-

---

[15] T. Takano, Y. Sasada, and M. Kakudo, *Acta Cryst.*, **21**, 514 (1966).

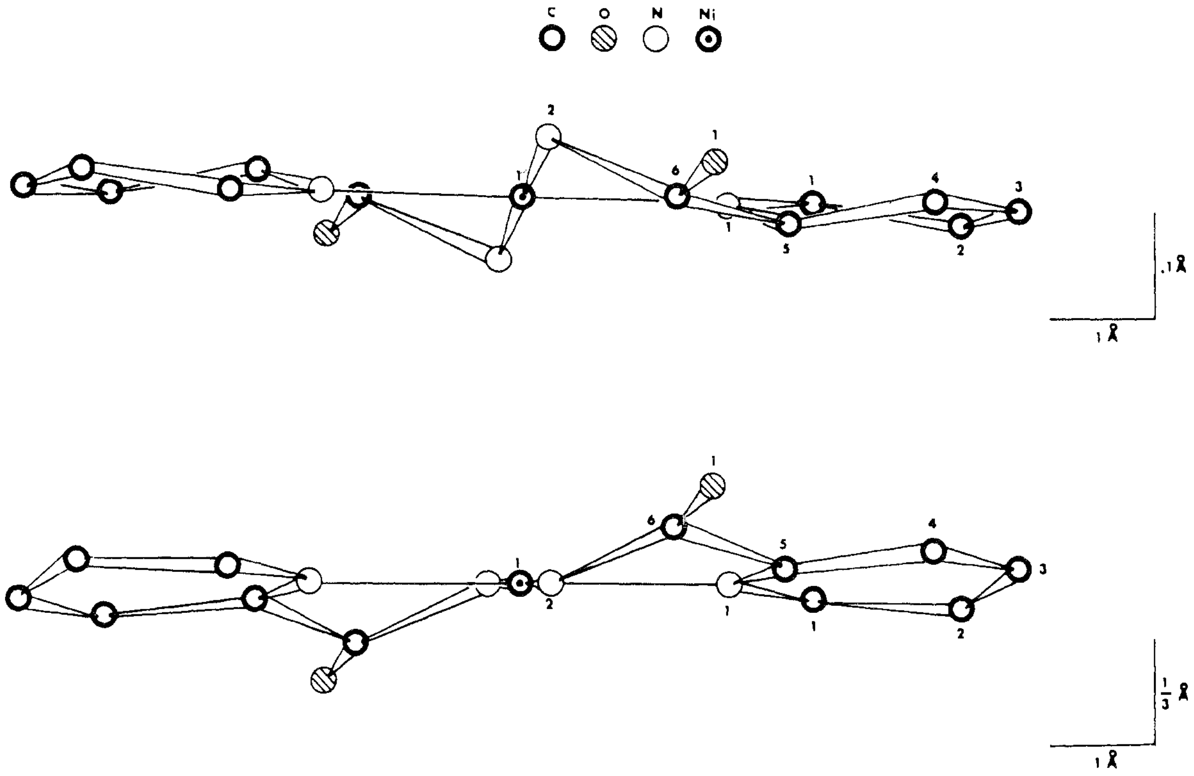


Figure 2.—Deviations of the atoms of bis(pyridine-2-carboxamido)nickel(II) dihydrate from a planar structure: (a) the horizontal plane perpendicular to the page is the least-squares plane of the pyridine ring; (b) the horizontal plane is the Ni-coordination plane.

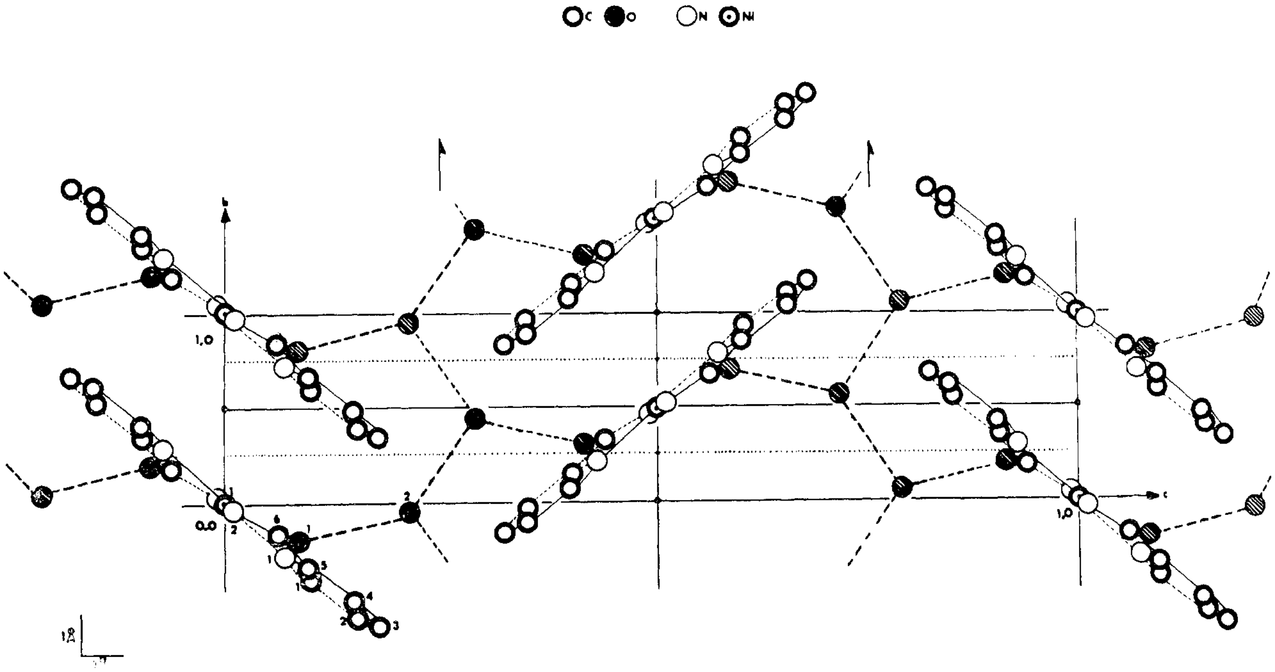


Figure 3.—The packing of bis(pyridine-2-carboxamido)nickel(II) dihydrate as shown projected down the *a* axis.

lipsoid show that O(1), N(2), C(1), and C(6) have the largest thermal vibrations and that these are nearly in a direction perpendicular to the plane of the molecule.

The closest van der Waals approach between two parallel molecules is about 3.5 Å. The dimensions of the pyridine ring in bis(pyridine-2-carboxamido)-nickel(II) dihydrate agree very well with those reported for picolinamide, nicotinamide, α-pyridoin, and nicotinic acid by Takano, *et al.*[15] The centrosymmetric molecule is essentially planar, although the nickel coordination plane and the pyridine ring are slightly distorted. The fact that the Ni–N(1) distance is slightly greater than the Ni–N(2) distance may be a result of steric hindrance offered by the pyridine ring; in any

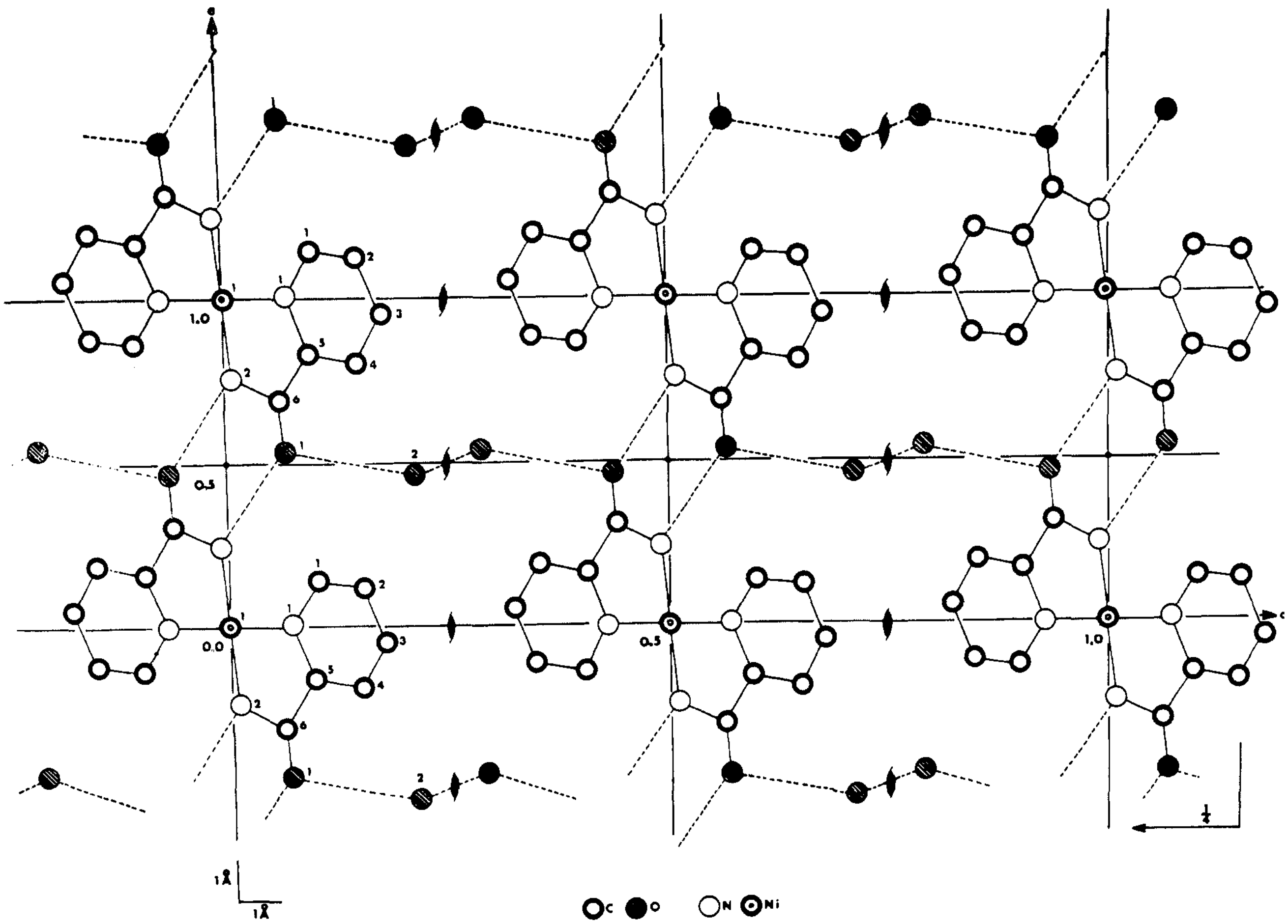


Figure 4.—The packing of bis(pyridine-2-carboxamido)nickel(II) dihydrate as shown projected down the *b* axis.

case, our data lead to the definite conclusion that the pyridine nitrogen and the amide nitrogen, rather than the carbonyl oxygen, are binding sites toward nickel. The least-squares plane passing through the pyridine ring is described by eq 1. The plane passing through the nickel and its coordinating nitrogens is described by eq 2. These results are also illustrated in Figure 2,

$$0.0784X + 0.7661Y + 0.6379Z = -0.0245 \quad \text{(pyridine)} \quad (1)$$

$$0.0158X + 0.7635Y + 0.6456Z = 0 \quad \text{(nickel coordination)} \quad (2)$$

where the XYZ coordinates are in the same directions as the crystal axes.

The molecules are held together by hydrogen bonds. Referring to Figure 3, we see that the waters of hydration form a zigzag chain about the twofold screw axis. The bond length $O(2)H\cdots O'(2)$ is 2.81 Å and the bond angle $O'(2)\cdots HO(2)\cdots HO''(2)$ is 106°. Each water molecule forms a hydrogen bond with another water molecule in the chain and a second hydrogen bond with the carbonyl oxygen. The bond length $O(1)\cdots HO(2)$ is 2.83 Å and the bond angle $O(1)\cdots HO(2)H\cdots O'(2)$ is 108°. There is also the weaker hydrogen bond $N(2)H\cdots O'(1)$ of 3.07 Å.

The zigzag infinite layers perpendicular to the *b* axis, as shown in Figure 4, may be regarded as the basic structural units of the crystal of bis(pyridine-2-carboxamido)nickel(II) dihydrate. The layers are held together by the hydrogen bonds of the waters of hydration and the van der Waals forces between the molecules. The needle axis is in the *b* direction and the crystal growth planes are the (100), (010), and (001) planes. Cleavage occurring in the crystal is always along the (100) plane corresponding to the breaking of the $N(2)H\cdots O'(1)$ and $O(1)\cdots HO(2)$ hydrogen bonds.

The nature of the twinning may be understood qualitatively as follows. The crystal seems to grow by stacking the hydrogen-bonded layers along the *b* axis. On approaching a layer, the first molecule to be deposited on the new layer has two alternatives, namely, either to continue the pattern of the original constituent of the twin or to start a reversed structure. The first choice should be preferred but the second is not excluded. This is because, as seen from Figure 3, the waters of hydration of the reversed structure should be shifted and the tilt of the molecules with respect to the *a* axis of the reversed structure should be reversed. However, the shift and the change in tilt are small. In all, we have examined six crystals and they all gave about the reflection pattern of the same symmetry. No diffused streaks were observed.

Within the accuracy of our experimental data, all of

TABLE IV

COMPARISON OF SEVERAL BOND DISTANCES (Å)

Compounds	C(5)–C(6)	C(6)–N(2)	Ni–N(1)	Ni–N(2)
Bis(pyridine-2-carboxamido)-nickel(II) dihydrate				
This research	1.51	1.32	1.92	1.87
Ref 7	1.47	1.27	1.93	1.95
Diaquobis(pyridine-2-carboxamide)nickel(II) chloride[a]	1.50	1.31	2.02	
Picolinamide[b]	1.51	1.33		
Amino acids, simple peptides, and related compounds[c]	1.53	1.32		

[a] A. Masuko, T. Nomura, and Y. Saito, *Bull. Chem. Soc. Japan*, **40,** 511 (1967). [b] See ref 15. [c] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1967, p 163.

the lattice points of a structure register the lattice points of the reversed structure. Twinning is most likely to occur according to Mallard's empirical theory.[16] The question as to whether β is exactly 90° is not answered here because of the limitation of our instrument.

[16] M. J. Buerger, "Crystal Structure Analysis," John Wiley & Sons, Inc., New York, N. Y., 1967, pp 53–76.

Comments on the Paper of Nawata, *et al.*

After the completion of the structure analysis of bis(pyridine-2-carboxamido)nickel(II) dihydrate, we noticed a paper by Nawata, *et al.*,[7] on crystal structure of the same compound, prepared according to the method of Yamasaki and Sekizaki,[17] with a final *R* factor of 0.160. By adopting a microscopic incoherent twinning model, we obtained a final *R* factor of 0.107. A comparison of several bond distances is given in Table IV. Our results indicate that coordination with nickel(II) does not affect the C(5)–C(6) and C(6)–N(2) bond distances.

Acknowledgments.—We thank Professor G. A. Jeffrey for permission to use his laboratory at the University of Pittsburgh for taking the X-ray intensity data and Dr. R. D. Rosenstein for help during data collection. Dr. W. R. Busing of Oak Ridge National Laboratory and Dr. R. Shiono of the University of Pittsburgh kindly provided us with versions of least-squares refinement programs. Mr. J. R. Hayes of Duquesne University helped in adapting programs to the computer system at Duquesne University.

[17] K. Yamasaki and M. Sekizaki, *Bull. Chem. Soc. Japan*, **38**, 2206 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND MATERIALS RESEARCH LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Structural and Spectroscopic Studies of Tetrachlorophosphonium Tetrachloroferrate(III), $[PCl_4][FeCl_4]$[1a]

BY T. J. KISTENMACHER[1b] AND G. D. STUCKY

Received May 10, 1968

The crystal and molecular structure of tetrachlorophosphonium tetrachloroferrate(III), $[PCl_4][FeCl_4]$, has been determined by three-dimensional X-ray data collected by counter methods. Full-matrix least-squares refinement on 1590 reflections gave a final *R* factor of 2.7% based on *F*. The crystal system is orthorhombic with the possible space groups D_{2h}^{11}-Pbcm or C_{2v}^{5}-Pbc2$_1$. The cell constants are $a = 6.231$, $b = 13.479$, $c = 14.078$ Å, with $Z = 4$. The calculated density of 2.08 g/cm^3 agrees well with the observed density of 2.09 ± 0.02 g/cm^3. The structure consists of isolated, nearly tetrahedral PCl_4^+ and $FeCl_4^-$ units. The effects on the bond distances due to thermal motion are considered. Results of infrared and optical spectral studies are also reported.

I. Introduction

The syntheses of many phosphorus pentahalide–metal trichloride complexes have been reported.[2] In most cases, the resulting complex has been postulated to be composed of the tetrachlorophosphonium cation and the tetrachlorometalate anion. The existence of the tetrachlorophosphonium cation has been crystallographically confirmed only in phosphorus pentachloride[3] itself. There are also few structural[4,5] and spectroscopic[6–10] data available on four-coordinate iron(III). In view of the above considerations and as part of an extended study of metal halide systems, the X-ray structure and spectral properties of $[PCl_4][FeCl_4]$ have been determined and are reported here.

II. Experimental Section

Crystals of $[PCl_4][FeCl_4]$ were prepared by the method of Groeneveld.[2] A typical preparation involved the mixing of a solution of anhydrous $FeCl_3$ in thionyl chloride (with a small

---

[1] (a) This work was supported in part by the Advanced Research Projects Agency under Contract SD-131; (b) Mobil Oil Corp. predoctoral fellow.

[2] W. L. Groeneveld, *Rec. Trav. Chim.*, **71**, 1152 (1952).

[3] D. Clark, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, 642 (1942).

[4] (a) B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957); (b) R. R. Richards and N. W. Gregory, *ibid.*, **69**, 239 (1965).

[5] M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Cryst.*, **23**, 581 (1967).

[6] H. L. Friedman, *J. Am. Chem. Soc.*, **84**, 167 (1962).

[7] C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962.

[8] A. P. Ginsberg, and M. B. Robin, *Inorg. Chem.*, **2**, 817 (1963).

[9] C. K. Jørgensen, "Structure and Bonding," Vol. I, Springer-Verlag, New York, N. Y., 1966, pp 3–31.

[10] S. Balt, *Rec. Trav. Chim.*, **86**, 1025 (1967).