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The Crystal Structure of Bis(pyridine-2-carboxamido)nickel(II) Dihydrate*

Yoshiharu NAWATA,*2 Hitoshi IWASAKI*3 and Yoshihiko SAITO

The Institute for Solid State Physics, The University of Tokyo, Azabu, Tokyo

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The orange-red, diamagnetic crystals of $[Ni(pia)_2]\cdot 2H_2O$ (piaH: pyridine-2-carboxamide) have been subjected to X-ray crystallographic analysis. They are orthorhombic, space group $Pm2_1b\text{-}C_{2v}^2$, with two formula units in a cell of dimensions: $a=7.61$, $b=20.19$ and $c=4.46$ Å. The crystals consist of planar molecules in which Ni(II) exhibits a square planar coordination and the two ligands are coordinated to the central nickel atom with four nitrogen atoms in *trans*-configuration. The molecules are tilted about 40° with respect to the plane (001), and are piled up above one another along the c-axis to form columns. These columns are linked with each other by intermolecular hydrogen bonds of N–H⋯O type, thus forming layers parallel to the plane (010). The layers are piled up along the b-axis by way of two water molecules which are hydrogen-bonded to the oxygen atoms of the amide groups. There exist stacking faults along this direction.

Two nickel chelates of pyridine-2-carboxamide, abbreviated hereafter as piaH, were synthesized by Yamasaki *et al.*1) One is orange-red diamagnetic crystals of the composition, $Ni(pia)_2\cdot 2H_2O$, and the other blue crystals are paramagnetic with magnetic moment 3.25 B. M., having the chemical formula $[Ni(H_2O)_2(piaH)_2]Cl_2$. From the spectroscopic data and the magnetic properties the red one was considered to have a square-planar environment around the central nickel atom, while the blue one was supposed to be an octahedral complex. This latter fact was indeed verified by X-ray crystal structure analysis and the details of the structure of the complex ion has been revealed.2) In connection with this investigation the crystals of $Ni(pia)_2\cdot 2H_2O$ were taken up in order to establish the configuration of the complex.

Experimental

Crystals of bis(pyridine-2-carboxamido)nickel(II) dihydrate were kindly supplied from Professor K. Yamasaki. They are orange-red thin plates and exhibit marked dichroism under a polarizing microscope. From the Laue symmetry and the systematic absences ($hk0$ with $k=2n+1$), the possible space group was found to be one of $Pm2_1b\text{-}C_{2v}^2$, $P2mb\text{-}C_{2v}^4$ and $Pmmb\text{-}D_{2h}^5$.

Lattice constants were determined from the equatorial Weissenberg photographs around the a- and c-axes taken with $CuK\alpha$ radiation ($\lambda=1.5418$ Å): $a=7.61\pm$

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*2 Present address: Research Laboratories, Chugai Pharmaceutical Co., Ltd., Takadaminami-cho, Toshima-ku, Tokyo.

*3 Present address: The Institute of Physical and Chemical Research, Yamato-machi, Saitama.

1) K. Yamasaki and M. Sekizaki, This Bulletin, **38**, 2206 (1966); *Nippon Kagaku Zasshi (J. Chem. Soc. Japan Pure Chem. Sect.)*, **87**, 1053 (1966).

2) A. Masuko, T. Nomura and Y. Saito, This Bulletin, **40**, 511 (1967).

0.01, $b=20.19\pm0.01$, $c=4.46\pm0.02$ Å. The diffraction patterns of copper wire ($a=3.6073$ Å)³⁾ were superimposed on the same films for calibration. Rough estimates of the density of the crystals showed that a unit cell contained two formula units of $Ni(pia)_2 \cdot 2H_2O$ (calculated density: 1.64 gcm^{-3}). The specimens, $0.03\times0.10\times0.6$ mm and $0.04\times0.12\times0.12$ mm, were used for the collection of the intensity data around the *c*- and *a*-axes respectively. Reflection data about the *a*- and *c*-axes up to the sixth and the third layer respectively were recorded on the equi-inclination Weissenberg films using multiple-film technique with Cu$K\alpha$ radiation. Independent 620 (of possible 820) reflections were observed. Intensities were estimated with a calibrated intensity standard. Usual Lorentz, polarization and spot shape corrections were applied. However, no absorption correction was made, since the linear absorption coefficient of this crystal for Cu$K\alpha$ was only 24 cm^{-1} and the specimens were small enough to neglect this correction. The observed structure amplitudes were placed on the same scale by least-squares method.

Determination of the Crystal Structure

The general positions of the space group $Pm2_1b$, $P2mb$ and $Pmmb$ are four-, four- and eitht-fold respectively. Since there exist only two nickel atoms in the unit cell, they must be located on some kind of special positions.

The Patterson projections $P(uv)$ and $P(vw)$ were then computed. From these projections approximate positions of the nickel atoms were found to be: 0 0 0 and 0 $^1/_2$ $^1/_2$. Moreover, the general features of the distribution of the Patterson peaks suggested that the crystal consists of planar molecules with a square planar environment around the nickel atom and they are inclined about 40° with respect to the plane (001). Since the approximate shape and size of the ligand molecule are known, two scale models, each corresponding to the *cis*- and *trans*-configuration were set up. According to the symmetry of the possible space groups, trials were made to pack these molecular models so oriented as the Patterson maps suggest. These trials at once showed that the proper symmetry of the special positions of any of the possible space groups cannot be achieved by any regular static arrangement of the molecules. In fact, on the Weissenberg photographs fairly distinct diffuse scatterings were observed, indicating the existence of a stacking fault along the *b*-axis. Accordingly, disordered structures were considered.*⁴ Positions of the ligand atoms deduced from these trial structures were then tested by calculating the structure factors *hk*0 and 0*kl* and comparing them with the observed values. After various trials it was found that a disordered structure in which the molecules with *trans*-configuration are arranged according to the space group $Pm2_1b$ was most promising. The atomic parameters obtained from this trial structure were first refined in projection by Fourier method. Positions of oxygen atoms of water of crystallization were found on the Fourier maps. The atomic parameters were refined by the diagonal least-squares refinement program with isotropic temperature factors and the *R*-factor for *hk*0 and 0*kl* was reduced to 0.14. Three-dimensional refinements were started from *R*-factor 0.27 with the block diagonal least-squares refinement program*⁵ using isotropic temperature factors, and after two cycles, the *R*-factor dropped to 0.165. At this stage, the agreements between the observed and the calculated structure amplitudes were fairly good, except a few lower order reflections which exhibited extinction effect, so the structure was supposed to be essentially correct. However, small ripples could not be removed from the difference Fourier map, and also a few absurd bond lengths were found. Anisotropic temperature factors were then introduced to the block diagonal matrix, first only for the nickel atom and then for all the atoms. By these refinements, however, the situation could not be improved any more. So far the *y*-coordinates of nitrogen atoms in the amide groups and the *x*-coordinates of nitrogen in the pyridine rings were fixed at zero during the refinements. The strong parameter interaction,⁴⁾ caused by the disordered structure appeared to make the refinement extremely difficult.

Finally attempts were made to adjust the absurd bond lengths and angles with reference to those found in crystals of pyridine-2-carboxamide,⁵⁾ and to refine the adjusted parameters again by the block diagonal approximations of least-squares matrix. Anisotropic temperature factors were applied to the nickel atom, while for other atoms isotropic temperature factors were used. The *R*-factor was reduced to 0.160. Because of the existence of stacking disorder, we thought it was advisable not to proceed with further refinement. In Table 1 are listed the final calculated structure factors together with the observed structure amplitudes. The final positional and thermal parameters are listed in Table 2, together with their standard deviations. The average standard deviations of bond lengths and angles calculated on the basis of these parameters are 0.05 Å for the bond

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3) R. W. G. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, Inc., New York (1960), table page 17.

[*4] The Weissenberg photographs indicated no evidence for twinning.

4) S. Geller, *Acta Cryst.*, **14**, 1026 (1961).

[*5] The program used for this calculation was originally written by Dr. Y. Okaya and revised by Dr. T. Ashida.

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

TABLE 1. OBSERVED AND CALCULATED STRUCTURE FACTORS

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
$k, l=0$		0	5	18.7	17.8	2	7.8	12.4	4	28.4	27.9	4	21.6	21.7	7	2.7	6.1
1*	56.6	77.5	6	10.5	14.2	3	3.2	7.3	5	20.8	21.7	5	17.6	15.8	$k, l=18$		1
2	51.6	63.3	7	10.9	13.2	$k, l=0$		1	6	15.8	16.6	6	6.4	9.1	2	3.9	1.4
3	7.5	3.5	8	7.8	8.9	1	14.6	3.0	7	13.0	15.4	7	5.5	7.2	3	7.8	4.3
4	46.7	52.2	$k, l=12$		0	2	6.4	6.3	8	10.6	10.4	8	4.0	7.9	4	5.7	3.8
5	18.7	22.5	0	52.7	51.6	3	4.1	4.6	9	4.9	6.9	$k, l=12$		1	6	4.6	1.5
6	23.9	26.8	1	38.8	43.2	4	7.5	6.8	$k, l=6$		1	0	10.2	6.6	$k, l=19$		1
7	18.5	22.7	2	24.5	27.6	6	8.7	2.8	0	21.4	21.4	1	6.8	4.4	0	13.2	11.0
8	9.4	9.0	3	18.7	23.8	7	6.6	2.0	1	16.7	13.8	2	14.8	11.9	1	9.4	9.5
9	6.9	9.6	4	22.7	22.6	8	6.5	1.9	2	9.2	5.2	3	20.4	15.3	2	13.7	16.2
$k, l=2$		0	5	17.0	17.9	$k, l=1$		1	3	10.4	5.4	4	15.3	11.1	3	15.2	14.8
0*	59.2	83.0	6	11.3	15.2	0	34.0	36.3	4	9.9	9.5	6	3.9	2.2	4	12.9	13.5
1	47.2	52.6	7	9.2	10.8	1	6.5	2.5	5	5.6	3.8	7	4.7	1.8	5	7.1	9.3
2	8.1	8.7	8	5.1	8.0	2	32.5	31.8	6	5.7	2.4	$k, l=13$		1	6	2.9	6.7
3	37.2	48.4	$k, l=14$		0	3	41.8	45.4	7	6.9	2.6	0	21.4	21.4	$k, l=20$		1
4	38.0	41.8	0	43.0	44.5	4	38.9	45.0	$k, l=7$		1	1	18.3	16.6	2	6.5	1.5
5	23.5	23.0	1	10.3	8.9	5	16.1	15.5	0	11.0	9.0	2	21.8	22.9	3	6.9	4.1
6	17.3	20.9	2	24.2	27.9	6	9.2	9.7	1	50.7	51.1	3	22.3	21.6	5	3.5	1.2
7	15.9	18.6	3	17.1	17.6	7	8.5	12.4	2	14.3	15.7	4	22.1	18.2	$k, l=21$		1
8	9.8	13.1	4	25.6	27.3	8	7.7	9.8	3	41.8	42.1	5	11.5	10.7	0	3.7	4.5
9	6.8	7.0	5	14.4	14.1	9	4.7	7.0	4	25.1	25.0	6	6.4	9.9	1	10.4	12.1
$k, l=4$		0	6	10.2	12.6	$k, l=2$		1	5	23.1	22.5	8	2.1	6.7	2	10.4	12.0
1	14.0	4.6	7	7.5	9.9	0	43.8	49.3	6	7.6	13.7	$k, l=14$		1	3	12.5	13.7
2	32.4	33.8	8	2.5	5.9	1	27.8	18.9	7	10.4	12.0	0	6.7	4.8	4	7.3	8.0
3	46.6	53.9	$k, l=16$		0	2	17.3	12.8	8	10.0	11.6	1	5.7	2.3	$k, l=22$		1
4	44.7	45.7	0	10.1	12.4	3	10.5	7.1	$k, l=8$		1	2	4.8	4.4	1	3.3	2.4
5	18.0	18.7	1	16.7	18.6	4	12.8	9.7	0	47.9	48.6	3	13.6	4.5	2	5.5	2.8
6	10.1	7.8	2	15.5	20.1	5	6.2	2.2	1	12.3	9.2	4	11.9	3.2	3	5.4	1.5
8	8.3	10.3	3	32.5	32.3	6	10.3	8.7	2	18.4	15.2	5	5.0	3.5	5	2.1	1.0
9	3.3	6.7	4	19.9	20.9	7	11.2	7.8	3	18.1	13.9	6	6.3	2.3	$k, l=23$		1
$k, l=6$		0	5	12.1	10.5	$k, l=3$		1	6	7.6	4.7	7	6.8	0.9	0	10.3	11.0
0	20.4	16.3	6	5.0	9.0	0	89.1	92.4	8	6.8	3.0	$k, l=15$		1	1	7.4	9.3
1	55.1	61.6	7	3.1	7.8	1	71.2	76.2	$k, l=9$		1	0	33.3	32.3	2	5.9	9.1
2	7.2	8.3	$k, l=18$		0	2	7.4	5.2	0	50.2	48.2	1	20.8	19.5	3	4.9	4.8
3	33.7	34.8	0	15.6	15.8	3	27.5	26.0	1	24.2	26.9	2	15.2	18.2	4	1.8	5.3
4	22.0	22.5	1	15.0	17.3	4	28.0	26.3	2	30.0	34.5	3	12.3	11.1	$k, l=24$		1
5	19.5	21.0	2	9.5	13.4	5	20.5	22.1	3	22.0	23.5	4	12.9	11.6	1	6.1	1.5
6	8.8	3.2	3	16.8	15.3	6	14.0	14.6	4	32.0	29.4	5	8.9	9.0	2	5.6	3.9
8	7.5	9.5	4	8.4	8.2	7	11.3	11.7	5	19.8	18.5	6	6.5	10.4	3	2.5	3.2
9	3.1	5.8	5	7.1	5.8	8	9.2	10.6	6	7.2	9.5	7	5.7	9.2	$k, l=25$		1
$k, l=8$		0	6	5.4	7.0	9	3.7	6.6	7	5.8	8.4	$k, l=16$		1	0	5.3	8.0
1	37.8	40.7	$k, l=20$		0	$k, l=4$		1	8	6.7	8.0	0	12.5	11.5	1	5.1	8.0
2	13.7	6.7	0	14.4	12.7	0	84.3	85.4	$k, l=10$		1	2	15.6	11.6	$k, l=0$		2
3	10.7	10.9	1	12.8	14.0	1	32.1	27.1	0	21.3	16.0	3	7.3	5.4	0	29.5	29.4
4	9.0	9.8	3	7.9	1.7	2	21.1	19.1	1	7.5	8.0	4	9.2	8.4	1	19.6	23.3
5	21.0	20.4	4	7.0	1.9	3	11.5	8.2	2	12.2	6.7	6	3.3	2.0	2	7.3	3.1
6	8.8	3.2	5	5.2	7.1	4	13.8	11.7	4	11.7	7.7	$k, l=17$		1	3	5.6	5.3
8	8.8	11.5	$k, l=22$		0	6	10.5	8.0	6	8.8	5.5	0	20.2	18.8	4	17.3	16.0
$k, l=10$		0	0	6.4	5.5	7	8.8	5.5	7	5.7	3.8	1	21.8	20.7	5	16.7	18.1
0	45.6	43.6	1	10.0	11.4	$k, l=5$		1	$k, l=11$		1	2	7.2	7.0	6	6.5	7.7
1	19.3	20.3	2	4.9	8.4	0	83.4	83.2	0	24.8	22.6	3	11.8	10.9	7	4.7	7.5
2	32.3	35.6	3	7.4	7.4	1	34.8	33.9	1	23.2	23.8	4	9.1	9.3	8	8.7	8.5
3	14.0	12.8	$k, l=24$		0	2	22.4	24.4	2	15.6	17.2	5	10.1	11.1	$k, l=1$		1
4	22.7	22.5	0	4.0	4.6	3	12.7	11.1	3	21.8	22.6	6	6.8	9.5	0	25.3	27.5

* These reflections were excluded from the calculation of the R-factor, because they are unreliable due to extinction effect.

TABLE 1 (continued)

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*h*	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*h*	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*h*	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*h*	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*h*	$\lvert F_o\rvert$	$\lvert F_c\rvert$
1	15.2	12.8	8	8.4	9.0	5	11.5	11.0	5	4.8	1.9	0	10.9	10.3	0	17.5	17.3
2	17.1	13.1	*k*, *l*=7		2	6	5.4	7.6	*k*, *l*=20		2	1	9.7	11.0	1	7.7	11.0
3	5.5	4.9	0	26.9	30.4	7	6.5	6.3	0	18.1	17.7	2	15.7	16.4	2	7.2	5.0
4	8.0	7.5	1	21.4	19.0	*k*, *l*=13		2	1	12.6	12.9	3	7.5	10.0	*k*, *l*=13		3
5	9.1	4.8	2	7.6	6.5	0	12.7	10.4	2	13.4	13.4	4	11.8	11.4	0	12.3	10.8
6	5.8	4.0	3	8.6	8.4	2	10.8	6.3	3	8.9	9.2	5	7.1	4.3	1	18.1	17.7
7	5.8	2.8	4	10.2	6.5	3	12.4	10.2	4	10.4	10.0	*k*, *l*=5		3	2	12.5	13.0
8	3.8	2.8	5	4.7	3.7	4	10.4	5.0	5	5.4	8.3	0	28.8	29.9	3	13.6	14.3
k, *l*=2		2	6	6.3	3.9	5	4.7	2.5	*k*, *l*=21		2	1	9.6	12.2	4	9.8	10.5
0	14.1	16.2	7	5.4	3.8	6	6.6	3.4	0	5.9	3.6	2	21.3	22.0	5	7.6	10.3
1	39.2	42.7	8	3.5	2.2	7	5.4	2.4	1	4.1	3.0	3	17.3	19.7	6	3.5	7.0
2	5.9	9.1	*k*, *l*=8		2	*k*, *l*=14		2	2	7.0	3.1	4	20.1	21.7	*k*, *l*=14		3
3	30.2	28.5	0	49.1	54.0	0	19.1	16.6	3	3.8	1.8	5	9.8	9.4	1	6.8	4.7
4	22.4	19.5	1	34.2	33.2	1	16.2	16.8	4	4.4	1.8	*k*, *l*=6		3	2	6.8	4.3
5	18.3	18.1	2	23.4	26.7	2	11.1	13.0	*k*, *l*=22		2	0	6.3	11.0	*k*, *l*=15		3
6	8.7	8.5	3	27.9	28.3	3	10.1	9.5	0	8.0	9.3	1	9.9	8.1	0	7.3	6.4
7	7.8	7.8	4	33.4	28.2	4	13.2	10.5	1	7.1	8.9	3	7.0	7.9	1	10.2	11.7
8	10.4	9.3	5	18.8	16.3	5	12.2	11.0	2	7.6	8.3	4	5.7	7.7	2	13.4	13.3
k, *l*=3		2	6	15.3	14.2	6	5.8	5.8	3	7.1	9.0	*k*, *l*=7		3	3	10.4	11.8
0	15.7	12.2	7	2.5	11.4	7	2.9	4.0	*k*, *l*=23		2	0	21.6	24.4	4	9.3	10.5
1	17.8	18.3	8	7.0	7.2	*k*, *l*=15		2	1	2.4	2.6	1	12.7	12.2	5	7.1	9.7
2	6.3	7.5	*k*, *l*=9		2	0	8.1	8.1	*k*, *l*=24		2	2	13.7	14.1	*k*, *l*=16		3
3	12.9	11.5	0	7.8	10.1	1	6.9	4.6	0	4.3	6.6	3	18.7	17.1	0	6.7	6.2
4	8.0	8.3	1	20.3	18.0	2	10.4	3.5	1	3.3	6.2	4	13.5	15.1	1	6.0	6.0
5	10.6	7.3	2	15.1	12.7	3	12.9	7.5	*k*, *l*=0		3	5	6.9	5.2	3	4.5	3.7
6	7.8	5.4	3	9.4	7.3	4	5.0	2.9	1	7.0	12.5	*k*, *l*=8		3	5	4.8	2.9
7	6.6	4.0	4	12.4	7.5	5	4.9	2.6	2	3.2	7.4	0	14.3	14.0	*k*, *l*=17		3
8	3.9	2.6	5	6.1	6.3	6	5.0	1.9	3	9.1	7.7	1	3.5	4.9	0	10.5	10.5
k, *l*=4		2	6	4.7	4.5	7	2.5	1.4	5	7.6	5.9	3	12.5	13.5	1	11.1	12.5
0	39.3	45.8	7	6.2	2.9	*k*, *l*=16		2	6	4.8	3.9	4	8.5	8.8	2	11.3	12.6
1	22.4	21.5	8	4.3	2.5	0	9.2	5.6	*k*, *l*=1		3	6	6.9	3.7	3	8.5	9.3
2	32.6	34.0	*k*, *l*=10		2	1	14.7	13.1	0	24.9	29.0	*k*, *l*=9		3	4	7.9	8.9
3	29.0	28.3	0	28.3	29.2	2	11.4	12.1	1	31.7	37.7	0	24.7	25.1	5	5.7	8.2
4	35.8	30.8	1	17.7	17.8	3	13.5	11.7	2	19.6	20.4	1	9.4	10.7	*k*, *l*=18		3
5	17.5	15.5	2	22.9	22.3	4	10.7	8.7	3	16.7	19.1	2	8.9	8.9	2	8.0	4.7
6	12.5	11.2	3	25.6	22.5	5	10.0	8.9	4	16.2	16.2	3	9.3	10.4	3	6.1	2.6
7	11.7	11.9	4	23.7	20.0	6	4.8	5.9	5	16.2	17.4	4	12.6	12.3	*k*, *l*=19		3
8	8.8	9.0	5	10.0	11.1	7	1.3	4.9	6	10.7	10.3	5	9.4	7.8	0	7.8	9.4
k, *l*=5		2	6	7.3	10.4	*k*, *l*=17		2	7	6.1	9.2	6	9.6	9.2	1	6.4	6.1
0	11.8	12.8	7	9.1	10.6	2	9.1	4.4	8	6.1	9.0	7	4.9	8.4	2	7.4	8.2
1	27.0	24.9	8	6.2	6.9	3	7.3	4.4	*k*, *l*=2		3	*k*, *l*=10		3	3	5.9	3.8
2	9.8	8.3	*k*, *l*=11		2	4	7.1	3.1	0	7.9	9.5	0	13.0	15.0	*k*, *l*=21		3
3	5.5	6.2	0	16.0	12.3	5	3.9	2.3	1	8.1	10.2	1	9.5	7.2	0	5.0	7.5
4	8.3	7.8	1	10.1	7.5	6	3.6	1.9	2	4.9	6.2	2	11.2	8.5	1	5.2	6.0
5	7.1	6.5	2	9.0	7.0	*k*, *l*=18		2	3	7.6	8.1	3	5.8	5.2	*k*, *l*=0		4
6	8.0	2.7	3	10.3	7.9	0	11.9	13.2	4	7.5	6.9	4	4.8	6.3	0	13.2	11.2
8	4.9	2.3	4	10.3	8.3	1	9.4	10.9	*k*, *l*=3		3	6	8.4	3.4	1	8.1	10.4
k, *l*=6		2	5	10.6	5.7	2	15.7	15.5	0	17.4	16.9	*k*, *l*=11		3	2	13.9	15.9
0	55.1	59.9	6	5.7	2.8	3	9.7	9.5	1	17.9	19.1	0	26.8	24.5	3	13.9	19.1
1	25.4	26.2	7	4.7	1.9	4	11.1	9.8	2	9.7	11.8	1	24.7	23.7	4	18.5	18.4
2	24.8	26.0	*k*, *l*=12		2	5	7.6	7.9	3	14.2	16.8	2	9.0	12.3	5	13.3	11.0
3	23.2	23.3	0	9.0	9.4	6	3.2	6.7	4	17.4	18.2	3	13.7	15.0	*k*, *l*=1		4
4	33.8	30.2	1	23.0	23.7	*k*, *l*=19		2	5	16.8	15.5	4	11.5	12.2	1	7.9	6.9
5	22.1	17.2	2	9.5	5.5	0	7.7	5.7	6	8.2	9.2	5	11.0	11.3	3	8.3	9.4
6	17.3	14.9	3	20.2	16.4	1	4.6	3.3	8	4.1	7.6	6	6.6	9.1	*k*, *l*=2		4
7	13.7	12.7	4	11.9	9.3	3	5.3	2.3	*k*, *l*=4		3	*k*, *l*=12		3	0	14.1	18.3

TABLE 1. (continued)

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
1	13.9	15.5	3	9.5	7.9	0	8.7	10.2	3	10.6	11.5	5	5.1	6.9	1	6.0	7.0
2	14.8	14.8	4	5.3	7.3	1	10.0	10.2	4	8.2	9.7	$k, l=13$		4	$k, l=16$		4
3	14.0	14.6	5	8.1	7.5	3	11.7	10.4	5	6.2	5.8	1	4.9	5.8	0	6.9	11.7
4	14.5	13.6	$k, l=5$		4	4	9.4	9.4	$k, l=11$		4	3	6.3	5.4	1	7.7	10.2
5	10.0	9.1	5	5.2	4.6	5	8.0	7.0	1	7.4	7.4	$k, l=14$		4	$k, l=18$		4
$k, l=3$		4	$k, l=6$		4	$k, l=9$		4	$k, l=12$		4	0	10.4	13.4	1	3.2	5.9
1	11.6	13.3	0	10.0	13.4	0	7.8	8.6	0	7.9	9.8	1	9.7	11.4			
$k, l=4$		4	1	10.1	11.8	$k, l=10$		4	1	9.5	9.2	2	11.7	9.6			
0	15.9	21.5	3	8.0	6.6	0	7.7	9.6	2	9.8	10.7	3	6.9	7.6			
1	12.9	17.5	4	7.3	7.6	1	9.7	9.3	3	10.1	10.7	4	7.9	7.5			
2	11.3	9.4	$k, l=8$		4	2	9.4	10.9	4	10.1	9.8	$k, l=15$		4			

TABLE 2. FINAL ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	$\sigma(x)\times 10^3$	y	$\sigma(y)\times 10^3$	z	$\sigma(z)\times 10^3$	B(Å^2)	$\sigma(B)$
Ni	0.000*	(0)	0.000	(2)	0.019	(1)	※	
O(1)	0.463	(6)	0.077	(2)	0.211	(8)	4.5	(0.9)
O(2)	0.458	(6)	0.211	(2)	0.081	(9)	5.5	(1.1)
O(3)	−0.460	(6)	−0.077	(2)	−0.182	(9)	5.6	(1.1)
O(4)	−0.456	(5)	−0.211	(2)	−0.048	(8)	4.5	(0.9)
N(1)	0.253	(6)	0.015*	(—)	0.040	(14)	5.7	(1.3)
N(2)	0.012*	(—)	0.073	(2)	0.289	(8)	3.1	(0.6)
N(3)	−0.012*	(—)	−0.072	(2)	−0.270	(9)	3.8	(0.7)
N(4)	−0.252	(6)	−0.015*	(—)	−0.019	(14)	5.1	(1.1)
C(1)	0.172	(8)	0.095	(3)	0.399	(15)	4.6	(1.2)
C(2)	0.196	(8)	0.148	(3)	0.580	(13)	4.2	(1.2)
C(3)	0.045	(5)	0.177	(2)	0.687	(10)	3.0	(1.0)
C(4)	−0.112	(7)	0.154	(3)	0.615	(13)	3.4	(1.0)
C(5)	−0.134	(7)	0.105	(3)	0.396	(14)	3.8	(1.1)
C(6)	0.304	(7)	0.064	(3)	0.195	(14)	3.9	(1.2)
C(7)	−0.172	(7)	−0.095	(3)	−0.370	(12)	3.3	(0.9)
C(8)	−0.199	(7)	−0.147	(3)	−0.549	(13)	3.8	(1.1)
C(9)	−0.041	(7)	−0.177	(3)	−0.661	(13)	4.7	(1.4)
C(10)	0.121	(9)	−0.155	(3)	−0.575	(15)	5.2	(1.4)
C(11)	0.133	(8)	−0.104	(3)	−0.368	(14)	4.1	(1.1)
C(12)	−0.302	(7)	−0.063	(3)	−0.179	(13)	4.0	(1.2)

※ b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
0.0095	0.0016	0.0189	0.000	0.000	0.0019
(0.0006)	(0.0001)	(0.0021)	(—)	(—)	(0.0019)

All the atoms except Ni are distributed on the positions listed above with a weight of 1/2. The parameters which have asterisk were fixed during the least-squares refinements, because they exhibited strong parameter interaction. Anisotropic temperature factors are expressed in the form:

$$\exp\left(-b_{11}\times h^2-b_{22}\times k^2-b_{33}\times l^2-b_{12}\times hk-b_{13}\times hl-b_{23}\times kl\right)$$

lengths involving Ni(II), 0.07 Å for others and 4° for bond angles.

Description of the Structure and Discussion

Figure 1 shows a composite three-dimensional Fourier diagram on which two alternative orientations of the molecules are indicated by full and dotted lines respectively. The crystal structures projected on the (001) and (100) planes are shown in Figs. 2 and 3, respectively. In Fig. 4 all the atoms in a complex molecule are projected on its best plane and the interatomic distances and bond angles are indicated. These were averaged assuming a center of symmetry at the nickel atom. The structure is built up of planar complex molecules in which Ni(II) exhibits a square planar coordination and two ligand molecules are coordinated to the central metal atom with ring nitrogen atoms and amide nitrogen atoms*[6] in *trans*-configuration. The nickel atom lies approximately in the position to be expected for covalent linkages of the dsp^2 square coplanar configuration, the N-Ni-N angle being 78°. Distortion to accommodate the nickel atom occurs by the bending (inplane) of the amide group with respect to the pyridine ring around the carbon atom C(1), the angle N(2)-C(1)-C(6) being 105°. The Ni-N distances of 1.93 and 1.95 Å are slightly shorter than those found in the blue octahedral complex, $[Ni(H_2O)_2(piaH)_2]Cl_2$ (Ni-N, 2.02 Å; Ni-O, 2.05 Å). This observation supports the ligand field theory which predicts that the stronger field produced by the ligands closer to the nickel will cause the d_γ-electrons to pair in the d_{z^2}-orbitals, so producing a diamagnetic complex which has no close neighbors in the z-direction. The molecule is very nearly planar, deviations of the atoms from the best plane being listed in Table 3. Although it is difficult to attain high accuracy in bond lengths and angles in such a disordered

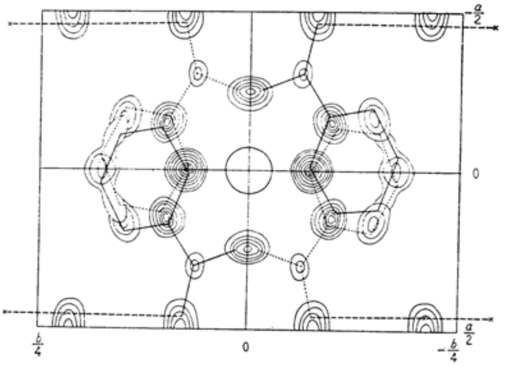

Fig. 1. Composite three dimensional Fourier diagram.
Contours are drawn at intervals of 1 e.Å^{-3} except for nickel atom, the lowest contour being 3 e.Å^{-3}.

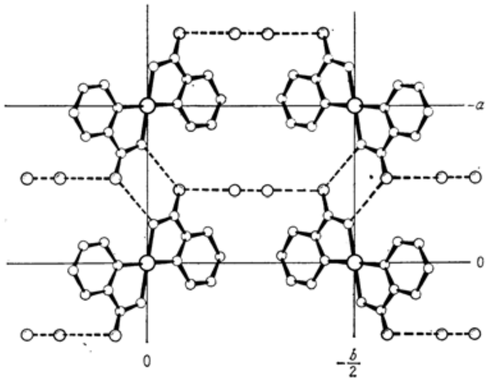

Fig. 2. Atomic arrangement projected along the *c*-axis.

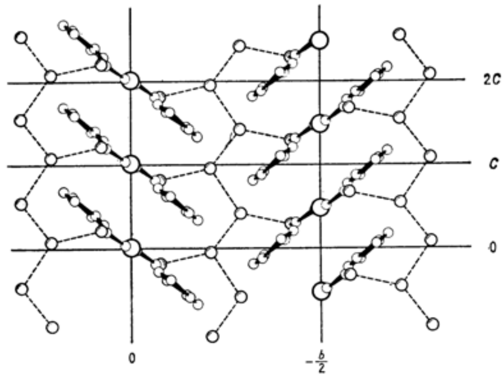

Fig. 3. Atomic arrangement projected along the *a*-axis.

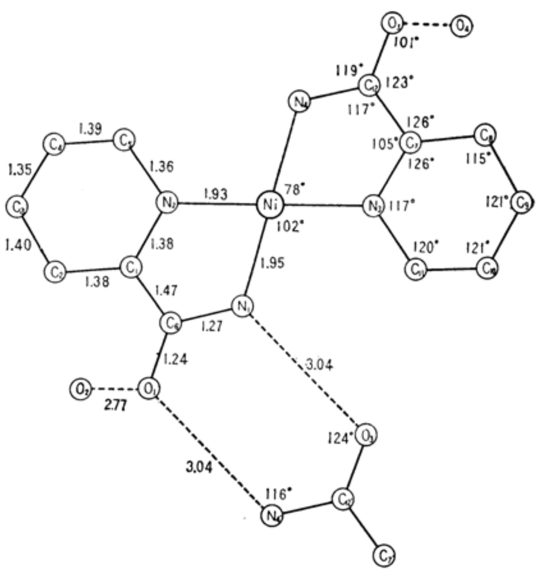

Fig. 4. Projection of molecules on its best plane with interatomic distances and bond angles.

TABLE 3. EQUATION FOR THE BEST PLANE AND THE DEVIATIONS OF THE ATOMS FROM IT

$$0.1348X - 3.779Y + 0.9867Z = 1$$

(X, Y and Z are the fractional coordinates refered to the crystal axes a, b and c.)

Ni	−0.02 Å	C(4)	−0.01 Å
O(1)	−0.12	C(5)	−0.13
O(3)	0.12	C(6)	−0.08
N(1)	0.01	C(7)	−0.15
N(2)	−0.00	C(8)	−0.10
N(3)	−0.03	C(9)	−0.01
N(4)	−0.03	C(10)	0.07
C(1)	0.16	C(11)	0.11
C(2)	0.09	C(12)	0.03
C(3)	0.00		

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*[6] This fact was indeed verified by infrared study of ^{15}N substituted complexes, M. Sekizaki and K. Yamasaki, Presented at the Symposium on Coordination Chemistry, Tokyo, December, 1966.

structure, it is certain that coordination does not affect the bond distances and angles of the ligand molecule very much.

The molecules are tilted at an angle of about 40° with respect to the plane (001) and are piled up above one another along the *c*-axis to form columns. The perpendicular distance between the layers are 3.40 Å, and two nickel atoms are situated at a distance of 4.46 Å. Successive complexes are stacked at such an inclination that each center of the aromatic ring of the complex lies approximately at one of the elongated octahedron about the nickel of an adjacent complex. In the orthorhombic crystal of bis(dimethylglyoximo)-nickel(II) the molecular planes are parallel to the plane (001) and piled up perfectly above one another in the *c*-axis direction. In this case the distance between the nickel atom is 3.245 Å⁶⁾ and the direct Ni···Ni interaction were observed.⁷⁾ Such an interaction may not exist in this crystal.

The molecular columns are linked with each other by intermolecular hydrogen bonds of N-H ···O type, thus forming layers parallel to the plane (010). The hydrogen bonding occurs between the oxygen and the nitrogen atoms of the adjacent molecules. This hydrogen bond distance of 3.04 Å may be compared with the value of 2.96 Å found in crystals of pyridine-2-carboxamide.⁵⁾

Between the molecular layers are located molecules of water of crystallization. The distances between the oxygen atoms of the water molecules, 2.63—2.90 Å, and those between the oxygen atom of the water and the amide oxygen atom, 2.77 Å, suggest the existence of hydrogen bonds. The molecular layers parallel to the plane (010) are thus held together by these hydrogen bonds, completing the whole structure. There exists a stacking fault between the layers, namely there are two alternative orientations of the molecules in the layer. These two possibilities can be stated as follows: if one molecular layer is given, the adjacent layer is generated by the operation of twofold screw axis parallel to the *b*-axis or of a glide plane *b*. The oxygen atoms of the water of crystallization are distributed on two sets of fourfold general positions with a weight of 1/2. In Figs. 2 and 3, only one of the two possible orientations of the molecules and the possible location of water molecules are illustrated, where the layers are related by twofold screw axis. The two alternative orientations occur with equal probability, thus the proper positional symmetry, *m*, of the special positions of nickel atoms are attained. A small correlation between the probabilities for each layer may cause weak diffuse scattering along the b^*-axis.

In the blue complex, $[Ni(H_2O)_2(piaH)_2]Cl_2$, the pyridine-2-carboxamide is coordinated to the nickel atom with amide oxygen atom and ring nitrogen atom, while in the present case they are coordinated with amide nitrogen atom and ring nitrogen atom. This ligand molecule thus exhibits, in different compounds, different modes of chelation, like biuret.⁸⁾ The present chelating agent adds another example of this class of compounds.

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The calculations were carried out on the FACOM-202 computer at this Institute and the HITAC-5020 computer at the Computer Center of this University.

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