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The Crystal Structure of *trans*-Diaquo-bis(pyridine-2-carboxamide)-nickel(II) Chloride, $[Ni(H_2O)_2(piaH)_2]Cl_2$[*1]

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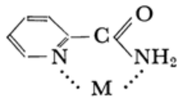
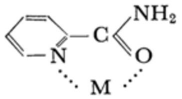
The crystal structure of *trans*-diaquo-bis(pyridine-2-carboxamide)nickel(II) chloride, $[Ni(H_2O)_2(piaH)_2]Cl_2$, was determined by X-ray diffraction and refined by three-dimensional least-squares method. The crystals are monoclinic with space group $P2_1/a$, $a=13.567$, $b=10.067$, $c=6.355$ Å and $\beta=113.73°$. There are two formula units in the unit cell. The structure is built up of centrosymmetric complex ions and chloride ions. Two ligand molecules are coordinated to the nickel atom in trans position with amide oxygen atoms and ring nitrogen atoms. (Ni–N, 2.02 Å, Ni–O, 2.05 Å). The ligand molecules are nearly planar and they are approximately in one plane with the nickel atom. Two water molecules are coordinated at a distance of 2.14 Å and complete the octahedral arrangement around the nickel atom.

Metal chelates of pyridine-2-carboxamide, picolinic acid amide, have scarcely been studied. Recently copper and nickel chelates were synthesized and their physical properties were studied.1) In the following, the ligand, pyridine-2-carboxamide, $C_5H_4NCONH_2$ is abbreviated as piaH. The nickel(II) chelates prepared were a. $Ni(pia)_2 \cdot 2H_2O$ and b. $Ni(piaH)_2Cl_2 \cdot 2H_2O$. Substance a is fine orange-red crystals and diamagnetic, while b is blue needles and paramagnetic with the magnetic moment 3.25 B. M. From the measurements of absorption spectra and magnetic moments, it has almost been established that the coordination around the nickel atom in substance a is square planar and that in b is octahedral. Pyridine-2-carboxamide may be coordinated as bidentate ligands in two ways, namely by means of two nitrogen atoms (I) or one nitrogen and one oxygen atom (II), since the rotation around the C–N bond is possible. To decide between these two possibilities and to establish the conformation of the chelate ring, the crystals were subjected to X-ray crystal analysis. In this paper the crystal structure of the substance b will be reported. That of the substance a will be described in the subsequent paper.2)


(I)


(II)

Experimental

The crystals, kindly supplied by Professor K. Yamasaki were blue, needle like and elongated along the *c*-axis.

The unit cell dimensions were determined from higher-order reflections of Weissenberg photographs ($CuK\alpha_1$, $\lambda=1.5405$ Å).

The systematic absences were: $0k0$ for k odd and $h0l$ for h odd. Hence the space group was unequivocally determined. The crystal data are listed in Table 1.

TABLE 1. CRYSTAL DATA

trans-Diaquo-bis(pyridine-2-carboxamide)nickel(II) chloride, $[Ni(H_2O)_2(C_5H_4NCONH_2)_2]Cl_2$
F.W. = 410

Monoclinic	$a=13.567 \pm 0.005$ Å
	$b=10.067 \pm 0.005$ Å
	$c=6.355 \pm 0.005$ Å
	$\beta=113.73 \pm 0.10°$
	$V=794.6$ Å^3
Space group	C_{2h}^5-$P2_1/a$
$Z=2$,	
$D_x=1.713$ g cm^{-3}	

Three dimensional Weissenberg data were recorded about the *b*- and *c*-axes up to the eighth and the fifth layer respectively, with $CuK\alpha$ radiation. The intensities were estimated visually and were corrected for Lorentz, polarization and spot shape effects. The data were placed on a single scale by use of 2094 reflections which were measured about the *b*- and *c*-axes. A total of 1600 independent reflections were collected.

The crystals used had a cross section of about 0.02 × 0.03 cm. The absorption correction was not made.

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1) K. Yamasaki and M. Sekizaki, This Bulletin, **38**, 2206 (1965); *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **78**, 1053 (1966).

2) Y. Nawata, H. Iwasaki and Y. Saito, This Bulletin, **40**, 515 (1967).

Structure Determination and Refinement

The structure was initially solved in the projections along the *b*- and *c*-axes. Since two formula units of Ni(piaH)$_2$Cl$_2$·2H$_2$O are contained in the unit cell, the nickel atom has to lie on a center of symmetry. Thus the complex ion is required to be centrosymmetric and the two ligand molecules must be coordinated to the nickel atom in *trans* positions with respect to each other. The chlorine position was easily found by the Patterson projections along the *b*- and *c*-axes.

First electron-density projections along the *b*- and *c*-axes, which were synthesized using phases determined by the nickel and chlorine atoms showed the heavy nickel and chlorine atoms quite clearly resolved, together with fairly distinct outlines of lighter atoms in the unit cell. Six peaks around the nickel seemed to be of ligand atoms. It was thus expected that the nickel atom has coordination number six and an octahedral environment. This is consistent with the magnetic property of the crystal. All the atoms in the structure were immediately located, since the approximate shape and size of the ligand molecules were known.[3] Two cycles of the structure-factor calculations and Fourier summations gave an approximate structure accurate enough to start three-dimensional refinement. The reliability factors $R=\sum||F_o|-|F_c||/\sum|F_o|$ were 0.18 and 0.22 for $h0l$'s and $hk0$'s respectively.

The atomic scattering factors used for the calculations in the two-dimensional analysis were those of Forsyth and Wells.[4]

At this stage of the refinement, however, it was not possible to distinguish between oxygen atoms and nitrogen atoms of the amide groups and the same atomic scattering factor as oxygen's was initially applied to those atoms in the two-dimensional analysis. Then the structure factors of all *hkl* reflections were calculated on the basis of the atomic coordinates deduced from the two-dimensional analysis. In this case all structure factors were calculated for both of the form I and II.

TABLE 2. ATOMIC PARAMETERS AND THEIR e. s. d.'s

Positional parameters are expressed as fractions of the lattice parameters.
Thermal parameters are in the form $\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.00000	0.00000	0.00000	0.00133	0.00142	0.00424	−0.00031	−0.00019	−0.00007
				9	14	39	8	14	17
Cl	−0.15471	0.36438	0.16436	0.00191	0.00309	0.00741	−0.00005	0.00057	0.00049
	12	15	25	9	14	41	9	15	18
O(H$_2$O)	−0.13824	0.04697	0.06808	0.00207	0.00355	0.01710	−0.00041	0.00237	−0.00125
	38	49	81	32	48	139	31	55	64
O(9)	−0.03316	0.15138	−0.23314	0.00232	0.00284	0.00379	−0.00047	−0.00074	0.00078
	34	43	71	27	42	120	27	46	55
N(1)	0.08017	0.14975	0.21167	0.00134	0.00156	0.00530	−0.00022	0.00030	−0.00090
	38	48	80	29	46	127	29	49	60
N(8)	0.00282	0.36361	−0.27505	0.00318	0.00328	0.01004	−0.00003	0.00101	0.00212
	47	59	98	36	57	163	37	63	77
C(2)	0.08028	0.26461	0.10471	0.00152	0.00264	0.00235	−0.00004	0.00056	0.00009
	46	58	96	33	53	154	33	59	70
C(3)	0.13675	0.37432	0.21859	0.00220	0.00299	0.00945	−0.00097	0.00148	−0.00184
	51	66	108	39	61	174	38	67	80
C(4)	0.19220	0.36414	0.45621	0.00319	0.00499	0.00948	−0.00169	0.00073	−0.00276
	57	74	121	45	70	201	45	78	93
C(5)	0.19047	0.24723	0.56812	0.00271	0.00575	0.00793	−0.00053	0.00065	−0.00089
	55	72	118	43	68	196	43	76	91
C(6)	0.13172	0.14226	0.44045	0.00253	0.00337	0.00440	−0.00006	0.00076	−0.00095
	50	63	106	38	60	168	38	65	79
C(7)	0.01200	0.25745	−0.14892	0.00085	0.00158	0.00708	−0.00029	0.00011	−0.00046
	45	57	95	33	52	152	33	58	69

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

4) J. B. Forsyth and M. Wells, *ibid.*, **12**, 412 (1959).

After one cycle of full-matrix least-squares[*3] refinement with isotropic thermal parameters, R values reduced to 0.125 and 0.116 for the form I and II, respectively. At this stage, it was found by the calculation of the bond distances and angles that the amide oxygen atom was bonded to the nickel atom. The distance between the carbon atom and the atom which was coordinated to nickel was found to be 1.24 Å and the other atom attached to the carbon was 1.31 Å apart. These correspond to C=O double bond and C–N single bond found in the related molecules, respectively. One cycle of full-matrix least-squares refinement with anisotropic thermal parameters was carried out for the form II, only. The greatest change in the coordinates was about a half of the e. s. d. The R was 0.100 for all the observed reflections.[*4] The atomic scattering factors used for the calculations were taken from International Tables for X-ray Crystallography (1962). The calculations of the structure factors and electron densities were carried out on the PC-2 computer at this Institute and on the CDC 3600 computer at C. Ito Electronic Computing Service Co., Ltd.

The atomic parameters are listed in Table 2. The bond distances and angles are shown in Table 3, together with their standard deviations.

A composite electron-density diagram made from the sections of the three-dimensional Fourier synthesis is shown in Fig. 1.

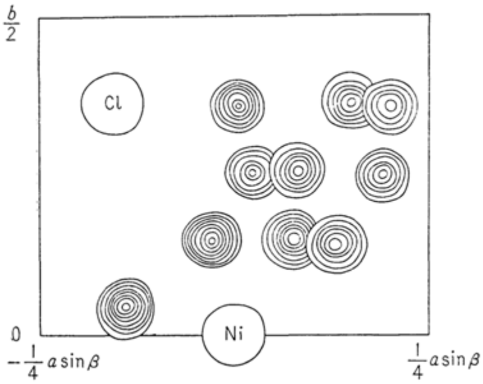


Fig. 1. Composite three dimensional Fourier diagram. Contours are drawn at intervals of 1 e.Å^{-3} with the lowest contour at 1 e.Å^{-3}; those for the nickel and the chlorine atom are not drawn.

Description of the Structure and Discussion

The atomic arrangement in the crystal is shown in projection along the c-axis in Fig. 2. The structure is essentially ionic and built up of the positively charged $[Ni(H_2O)_2(C_5H_4NCONH_2)_2]^{2+}$ ions and Cl^- ions. It is therefore proposed that the chemical formula should be written as: $[Ni(H_2O)_2(C_5H_4NCONH_2)_2]Cl_2$. The complex ion is centrosymmetric because of the requirement of the space group. The nickel atom has an octahedral

TABLE 3. INTERATOMIC DISTANCES AND ANGLES
Standard deviations are given in parentheses

(a) Environment of Ni			
Ni–N(1)	2.022(5) Å	N(1)–Ni–O(9)	80.1(2)°
Ni–O(9)	2.045(4)	N(1)–Ni–O′(9)	99.2(2)
Ni–O	2.140(6)		
O–O(9)	3.000(8)	O(9)–N(1)–O′(9)	96.7(2)
O–O′(9)	2.921(6)	N(1)–O(9)–N′(1)	89.3(2)
O–N′(1)	2.917(7)		
N(1)–O(9)	2.618(6)	O–Ni–O(9)	91.5(2)
N(1)–O′(9)	3.112(7)	O–Ni–N(1)	88.9(2)
N(8)–C(3)	2.928(8)		
Ni–Cl	4.553	Ni–N(1)–C(2)	114.6(4)
Ni–Cl	4.578	Ni–O(9)–C(7)	113.7(4)
(b) Ligand molecule			
N(1)–C(2)	1.342(8) Å	C(2)–N(1)–C(6)	119.5(5)°
N(1)–C(6)	1.338(8)	N(1)–C(2)–C(3)	122.7(5)
C(2)–C(3)	1.373(8)	N(1)–C(6)–C(5)	121.6(6)
C(6)–C(5)	1.375(9)	C(2)–C(3)–C(4)	117.1(6)
C(3)–C(4)	1.394(9)	C(6)–C(5)–C(4)	118.5(6)
C(5)–C(4)	1.380(11)	C(3)–C(4)–C(5)	120.5(6)
C(2)–C(7)	1.503(7)	N(1)–C(2)–C(7)	112.1(5)
C(7)–N(8)	1.311(8)	C(3)–C(2)–C(7)	125.2(5)
C(7)–O(9)	1.240(7)	C(2)–C(7)–N(8)	118.8(5)
C(3)–N(8)	2.926(8)	C(2)–C(7)–O(9)	119.2(5)
		N(8)–C(7)–O(9)	121.9(5)
(c) Hydrogen bonds			
Cl···O	3.28 Å		
Cl···O (1/2−x, 1/2+y, −z)	3.18		
Cl···N (x, y, 1+z)	3.33		
Cl···N (x, 1+y, z)	3.33		
(d) Short contact between Cl^- and the complex ion, $[Ni[(H_2O)_2(piaH)_2]^{2+}$			
Cl···N(1)	3.75 Å		
Cl···C(2)	3.51		
Cl···C(3)	3.83		
Cl···C(7)	3.73		
Cl′···N(1) (1/2−x, 1/2+y, −z)	3.74		
Cl′···C(2) (1/2−x, 1/2+y, −z)	3.69		
Cl′···C(3) (1/2−x, 1/2+y, −z)	3.83		
Cl′···C(6) (1/2−x, 1/2+y, −z)	3.95		
Cl···C(4) (x, 1+y, z)	3.66		

When the coordinates are not indicated the atom is at $x\,y\,z$. The atom with a prime is located at $-x\ -y\ -z$.

[*3] CDC 3600 UNICS' ORFLS, originally programmed by W. R. Busing, K. O. Martin and H. A. Levy, modified by T. Sakurai and K. Okada.

[*4] A complete list of the observed and calculated structure factors has been submitted to and is kept as Document No. 6703 at the office of the Bulletin of the Chemical Society of Japan, 1-5, Kanda-Surugadai, Chiyoda-ku, Tokyo. A copy may be available on request.

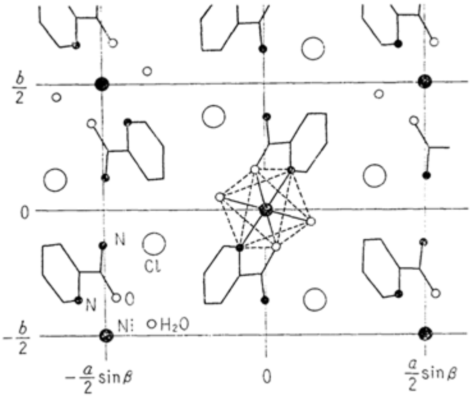


Fig. 2. Projection of the structure along the c-axis.

TABLE 4. BEST PLANE

	Chelate ring (A)		Pyridine ring (B)	
Ni	0.024 (Å)	*	0.133 (Å)	
N(1)	−0.033	*	0.018	*
C(2)	0.026	*	−0.013	*
C(3)	0.092		0.003	*
C(4)	0.044		0.002	*
C(5)	−0.047		0.003	*
C(6)	−0.109		−0.013	*
C(7)	0.006	*	−0.070	
N(8)	0.031		−0.132	
O(9)	−0.022	*	−0.046	

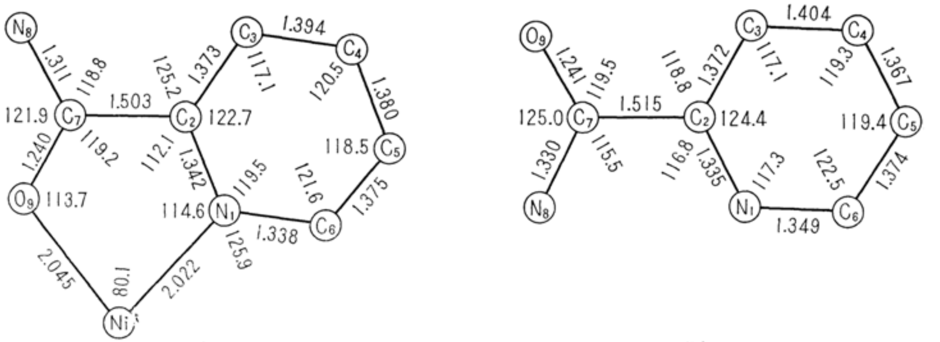
The equations of these planes (A) and (B) are:
(A) $2.7388X - Y - 2.3067Z = -0.93670$
(B) $2.2039X - Y - 1.7317Z = -4.2222$
where $X = x\sin\beta$, $Y = y$ and $Z = z + x\cos\beta$.
x, y and z are the fractional coordinates referred to the crystal axes.

* Only the atoms marked are included in the calculation of each plane.

environment. This fact combined with the observed magnetic moment indicates that the bond orbitals are sp^3d^2. Two ligand molecules are coordinated to the nickel atom with amide oxygen atoms and ring nitrogen atoms in trans positions. The Ni–N and Ni–O distances are 2.022 Å and 2.045 Å respectively, in agreement with those found in the related compounds. The ligand molecules are nearly planar and they are approximately in one plane with the nickel atom and on a line through the nickel atom and perpendicular to this plane are coordinated two water molecules at a distance of 2.14 Å.

Figure 3 shows the dimensions of the pyridine-2-carboxamide molecule found in the complex ion, together with those found in its crystalline state.³⁾ It can be easily seen from the figure that coordination does not seem to have any significant effect upon the linear and angular shape of the pyridine ring. The C–N and C–C distances in the ring are, on the average, 1.34 Å and 1.38 Å respectively. The distance C(7)–N(8) is shorter in the ligand than in the molecule in its crystalline state. Distortion to accommodate complex formation occurs by the inplane bending of the amide group with respect to the pyridine ring around the carbon atom C(2), the angle N(1)C(2)C(7) being 112°.

The displacements of the atoms from the best planes through the chelate ring and through the pyridine ring are listed in Table 4. In this table, those deviations which are not larger than 0.018 Å are not significant. In the case of the molecule in its crystalline state, pyridine ring and the atom C(7) are in a plane and the plane of the amide group makes an angle of 19° with the plane of the pyridine ring. While in the case of the nickel chelate, the amide group is rotated around the bond C(7)–C(2), in such a way that O(9) and N(1) are in the same side with respect to the long axis of the molecule. The five membered metal-chelate ring and the pyridine ring are almost planar, however, both rings are not exactly coplanar. The plane of the pyridine ring is twisted at an angle of about 4.0° around the axis through the midpoints of the bonds C(4)–C(5) and C(2)–N(1) with respect to the metal chelate ring in such a way that the distance between



(a) (b)

Fig. 3. Bond distances and angles of pyridine-2-carboxamide molecule. (a) in the nickel chelate (b) in its crystalline state.

C(3) and N(8) increases. This distortion may be in part due to the repulsion between the amino group and the hydrogen atom attached to C(3). The distance between the amide nitrogen and the ortho carbon atom is 2.93 Å, in agreement with those found in the related compounds.³⁾

A complex ion is surrounded by four chloride ions. The Ni–Cl distances are 4.55 and 4.58 Å. The distances between the chloride ions and the atoms of the ligand molecules are listed in Table 3. There are some possibilities of the formation of weak hydrogen-bonds between the chloride ions and the water oxygen atoms and between the chloride ions and the amide nitrogen atoms, these distances being 3.18 and 3.33 Å respectively.

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