The Crystal and Molecular Structure of Bis(L-prolinamidato)-nickel(II) Dihydrate

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The crystal structure of bis(L-prolinamidato)nickel(II) dihydrate has been determined by three dimensional X-ray analysis. The crystals are vermilion needles and belong to the space group $P2_1$. . The unit cell has dimensions $a=10.915$, $b=7.319$, $c=9.445$ Å, $\beta=112.6°$ and contains two structure units. The structure has been solved using Patterson synthesis, minimum function and Fourier synthesis and refined by diagonal and block-diagonal least-squares methods on 1115 independent reflections. The final R value was 0.054. The nickel atom exhibits square planar coordination. Two proline-amide molecules are approximately related to each other by a two fold axis and these two ligand molecules coordinate to the central nickel atom in *trans* form. The oxygen atom of water does not coordinate to the nickel atom.

It is well known that nickel(II) complexes have octahedral, tetrahedral or square planar coordination. From the spectroscopic studies of the complexes of glycine-, L-alanine-, L-leucine-, and L-proline-amides, Komorita *et al.*[1,2] proposed that the nickel atom exhibits a square planar coordination and two ligand molecules are coordinated to the central nickel atom with four nitrogen atoms in *trans* form. The present study was undertaken to establish the configuration about the nickel of bis(L-prolinamidato)nickel(II) complex in solid state.

Experimental

The vermilion needle crystals of bis(L-prolinamidato)nickel-(II) dihydrate were kindly supplied by Dr. T. Komorita. Preliminary Weissenberg and oscillation photographs established that the crystal was monoclinic with the b axis along the needle axis. The systematic extinction of $(0k0)$ for k odd restricted the space group to $P2_1$. The crystal data are listed in Table 1.

TABLE 1. CRYSTAL DATA

Ni (L-$C_5H_9N_2O)_2\cdot 2H_2O$		M. W.=321.02
Monoclinic		$P2_1$
$a=10.915$ Å	$b=7.319$ Å	$c=9.445$ Å
$\alpha=\gamma=90.0°$	$\beta=112.6°$	
$D_{cal}=1.51$ g/cm^3		
$D_{obs}=1.53$ g/cm^3		(by floatation)

A nickel filtered Cu-K_α radiation was used to collect intensity data for all the reflections in the range $0°<\theta<60°$ within the octants (hkl) and $(\bar{h}kl)$. All the intensities were measured on a Rigaku Denki computer-controlled four-circle diffractometer. A crystal of approximate dimensions $0.03\times0.15\times0.04$ mm^3 was used for the intensity measurement of 1115 reflections. The ω-2θ scan technique was employed with a scan speed 2°/min by ω, and the back grounds were measured for 10.0 sec at each start and end points of a scan range. A scan range of ω for each reflection was calculated by the formula $\Delta\omega=1.50°+0.15°\tan(\theta)$. Attenuators were automatically inserted when the maximum counting rate exceeded 8000 cps. The intensities were corrected only for Lorentz and polarization factors.

Measurement of the two reference reflections (500) and (060) was repeated for every thirty reflections. For 52 repetitions of the measurement, $|F_0(500)|=97.13\pm0.72$ and $|F_0(060)|=50.84\pm0.93$.

Structure Determination and Refinement

A trial structure derived from the three-dimensional

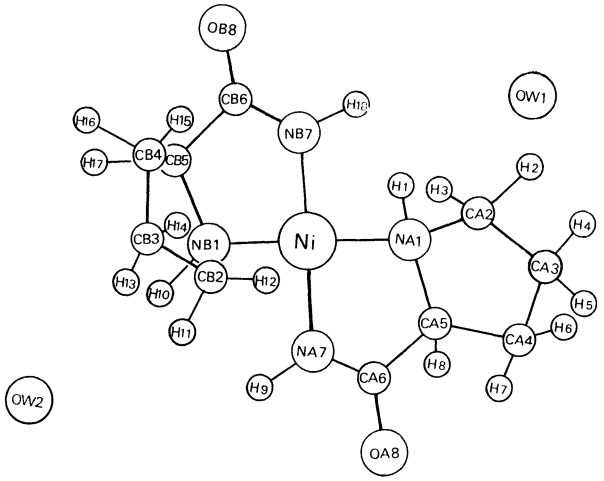

Fig. 1. Numbering of atoms in bis(L-prolinamidato)nickel(II) dihydrate.

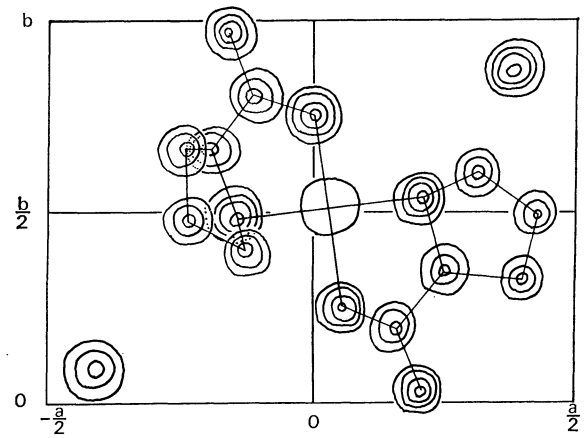

Fig. 2. The composite electron density map of bis(L-prolinamidato)nicel(II) dihydrate.

1) T. Komorita, J. Hidaka, and Y. Shimura, This Bulletin, **41**, 854 (1968).

2) T. Komorita, private communication.

Patterson synthesis, minimum function and Fourier synthesis was refined to $R=0.12$, ($R=\sum||F_o|-|F_c||/\sum|F_o|$), by using a diagonal least-squares program which minimizes the function $\sum(|F_o|-k|F_c|)^2$ with individual isotropic thermal parameters for all the non-hydrogen atoms. The atomic scattering factors were taken from International Tables for X-ray Crystallography (1962). Three cycles of block-diagonal least-squares refinement of the positional and the thermal parameters of all the non-hydrogen atoms with a program written by Dr. T.

TABLE 2. FINAL ATOMIC PARAMETERS

Atom	x	y	z	Atom	x	y	z
Ni	0.02838	0.50000	0.21031	OW1	0.37338	0.88067	0.07596
OW2	0.40278	0.58725	−0.11192	OA8	0.19271	0.02997	0.17173
OB8	−0.14625	0.97044	0.21276	NA1	0.20036	0.52841	0.19868
NA7	0.05503	0.24845	0.20255	NB1	−0.13714	0.47726	0.23624
NB7	0.00143	0.75010	0.21415	CA2	0.30052	0.60139	0.34425
CA3	0.42113	0.49388	0.37448	CA4	0.39207	0.32498	0.29409
CA5	0.25067	0.34078	0.17307	CA6	0.15923	0.19274	0.18222
CB2	−0.12229	0.40095	0.39062	CB3	−0.23866	0.47184	0.41912
CB4	−0.24645	0.67290	0.35965	CB5	−0.20616	0.65857	0.22192
CB6	−0.11038	0.80874	0.21661	H1	0.1891	0.6210	0.1082
H 2	0.3101	0.7525	0.3417	H3	0.2805	0.5184	0.4443
H 4	0.4925	0.5705	0.3515	H5	0.4815	0.4664	0.4891
H 6	0.4627	0.2733	0.2453	H7	0.4062	0.2043	0.3696
H 8	0.2643	0.3168	0.0770	H9	−0.0068	0.1608	0.2061
H10	−0.2135	0.3934	0.1481	H11	−0.1235	0.2677	0.3849
H12	−0.0261	0.4303	0.4830	H13	−0.3398	0.3999	0.3495
H14	−0.2222	0.4792	0.5235	H15	−0.3614	0.7343	0.3128
H16	−0.1907	0.7551	0.4528	H17	−0.3085	0.6738	0.1227
H18	0.0587	0.8482	0.2039				

Atom	$B_{11}\times10^4$	$B_{22}\times10^4$	$B_{33}\times10^4$	$B_{12}\times10^4$	$B_{13}\times10^4$	$B_{23}\times10^4$
Ni	72 (1)	91 (2)	121 (2)	1 (4)	84 (2)	21 (6)
OW1	169 (9)	146 (14)	214 (14)	24 (22)	187 (19)	− 75 (27)
OW2	127 (9)	302 (25)	408 (21)	−91 (24)	214 (23)	−254 (37)
OA8	113 (7)	101 (14)	229 (12)	42 (18)	173 (16)	− 10 (24)
OB8	105 (7)	27 (12)	266 (13)	− 3 (16)	163 (16)	− 4 (22)
NA1	81 (7)	85 (16)	140 (11)	25 (20)	95 (15)	37 (27)
NA7	76 (9)	165 (17)	174 (15)	− 2 (20)	131 (20)	11 (27)
NB1	64 (7)	134 (17)	122 (11)	−13 (22)	74 (14)	6 (28)
NB7	95 (9)	63 (14)	189 (14)	−23 (17)	133 (19)	10 (23)
CA2	90 (11)	188 (25)	270 (23)	−50 (29)	116 (26)	−227 (44)
CA3	135 (13)	583 (48)	431 (35)	241 (55)	−114 (36)	−650 (88)
CA4	84 (11)	173 (27)	376 (29)	20 (31)	27 (30)	−216 (50)
CA5	80 (10)	121 (21)	142 (16)	−72 (25)	113 (22)	−106 (31)
CA6	93 (11)	91 (17)	134 (16)	−13 (23)	102 (22)	2 (29)
CB2	127 (13)	152 (20)	167 (18)	91 (28)	175 (25)	139 (33)
CB3	133 (10)	100 (23)	176 (18)	47 (28)	180 (23)	47 (37)
CB4	122 (13)	137 (21)	183 (20)	−26 (27)	188 (27)	− 14 (34)
CB5	63 (9)	89 (18)	137 (15)	58 (22)	66 (20)	34 (28)
CB6	82 (10)	41 (14)	150 (16)	−17 (21)	76 (21)	27 (27)

Atom	B	e. s. d.	Atom	B	e. s. d.
H 1	6	3	H 2	2	2
H 3	3	2	H 4	7	3
H 5	5	3	H 6	4	3
H 7	6	3	H 8	1	2
H 9	1	2	H10	5	3
H11	4	2	H12	1	2
H13	2	2	H14	5	3
H15	2	2	H16	2	2
H17	4	3	H18	6	3

Temperature Factor $=\exp(-(B_{11}\times h^2+B_{22}\times k^2+B_{33}\times l^2+B_{12}\times hk+B_{13}\times hl+B_{23}\times kl))$
or $=\exp(-B(\sin\theta/\lambda)^2)$

Table 4. Intramolecular distances with their e. s. d.'s

Bond	Length	e. s. d.	Bond	Length	e. s. d.
Ni–NA1	1.929 Å	0.009 Å	Ni–NB1	1.918 Å	0.010 Å
Ni–NA7	1.872	0.008	Ni–NB7	1.855	0.008
NA1–CA2	1.509	0.015	NB1–CB2	1.532	0.014
NA1–CA5	1.493	0.013	NB1–CB5	1.459	0.013
CA2–CA3	1.455	0.025	CB2–CB3	1.493	0.015
CA3–CA4	1.416	0.026	CB3–CB4	1.540	0.015
CA4–CA5	1.535	0.018	CB4–CB5	1.534	0.014
CA5–CA6	1.494	0.013	CB5–CB6	1.535	0.013
CA6–NA7	1.313	0.012	CB6–NB7	1.323	0.013
CA6–OA8	1.267	0.012	CB6–OB8	1.245	0.012
NA1–H1	1.06	0.12	NB1–H10	1.11	0.12
CA2–H2	1.11	0.09	CB2–H11	0.98	0.09
CA2–H3	1.06	0.09	CB2–H12	1.10	0.08
CA3–H4	1.05	0.17	CB3–H13	1.17	0.09
CA3–H5	1.05	0.10	CB3–H14	0.93	0.13
CA4–H6	1.11	0.10	CB4–H15	1.24	0.09
CA4–H7	1.11	0.10	CB4–H16	1.05	0.08
CA5–H8	0.99	0.08	CB5–H17	1.16	0.11
NA7–H9	0.94	0.07	NB7–H18	0.98	0.10

Table 5. Intramolecular bond angles with their e. s. d.'s

Angle	degree	e. s. d.	Angle	degree	e. s. d.
NA1–Ni–NA7	85.8°	0.4°	NB1–Ni–NB7	84.8°	0.4°
NA1–Ni–NB7	94.0	0.4	NB1–Ni–NA7	95.5	0.4
Ni–NA1–CA5	110.6	0.6	Ni–NB1–CB5	113.8	0.7
Ni–NA1–CA2	111.4	0.7	Ni–NB1–CB2	113.0	0.7
Ni–NA1–H1	107.5	8.0	Ni–NB1–H10	115.6	5.9
CA2–NA1–CA5	107.9	0.8	CB2–NB1–CB5	107.0	0.8
H1–NA1–CA2	109.4	7.8	H10–NB1–CB2	102.7	5.9
NA1–CA2–CA3	104.7	1.2	NB1–CB2–CB3	103.9	0.8
NA1–CA2–H2	113.3	4.9	NB1–CB2–H11	108.5	5.4
NA1–CA2–H3	115.1	5.1	NB1–CB2–H12	112.8	4.7
H2–CA2–H3	103.9	7.0	H11–CB2–H12	105.0	7.1
H2–CA2–CA3	115.9	5.9	H11–CB2–CB3	113.1	5.4
H3–CA2–CA3	104.0	5.2	H12–CB2–CB3	113.7	4.7
CA2–CA3–CA4	111.6	1.6	CB2–CB3–CB4	102.2	0.9
CA2–CA3–H4	111.3	8.1	CB2–CB3–H13	113.1	4.6
CA2–CA3–H5	117.1	5.8	CB2–CB3–H14	112.9	7.7
H4–CA3–H5	92.3	9.8	H13–CB3–H14	116.5	9.1
H4–CA3–CA4	112.7	7.9	H13–CB3–CB4	109.0	4.6
CA3–CA4–CA5	106.8	1.3	CB3–CB4–CB5	104.1	0.8
CA3–CA4–H6	117.7	5.6	CB3–CB4–H15	112.6	4.3
CA3–CA4–H7	113.7	7.7	CB3–CB4–H16	109.2	4.7
H6–CA4–H7	92.8	9.8	H15–CB4–H16	104.2	6.4
H6–CA4–CA5	112.4	5.5	H15–CB4–CB5	108.7	4.3
H7–CA4–CA5	112.4	7.6	H16–CB4–CB5	118.3	4.9
CA4–CA5–NA1	105.5	0.9	CB4–CB5–NB1	107.0	0.8
CA4–CA5–CA6	113.6	0.9	CB4–CB5–CB6	113.3	0.8
CA4–CA5–H8	102.5	4.8	CB4–CB5–H17	99.6	5.5
H8–CA5–NA1	118.8	4.7	H17–CB5–NB1	117.0	5.5
H8–CA5–CA6	105.8	4.7	H17–CB5–CB6	111.6	5.5
CA5–CA6–OA8	118.3	0.8	CB5–CB6–OB8	119.4	0.8
CA5–CA6–NA7	115.1	0.8	CB5–CB6–NB7	114.3	0.8
OA8–CA6–NA7	126.6	0.9	OB8–CB6–NB7	126.3	0.9
CA6–NA7–Ni	117.4	0.7	CB6–NB7–Ni	118.1	0.7
CA6–NA7–H9	120.0	4.9	CB6–NB7–H18	114.7	7.3
H9–NA7–Ni	122.5	4.9	H18–NB7–Ni	126.9	7.3
NA1–CA5–CA6	109.9	1.0	NB1–CB5–CB6	108.4	0.8

Ashida gave a value of R of 0.09. To take into account the anomalous scattering by nickel atom, $\Delta f'(-3.1)$ and $\Delta f''(0.6)$ were included in the calculations of the refinement. An (F_o-F_c) synthesis revealed all the hydrogen atoms in the complex. After several cycles of the refinement of the positional parameters, of the anisotropic thermal parameters for the non-hydrogen atoms and of the isotropic thermal parameters for hydrogen atoms, the R value decreased to 0.054. The final parameters of all atoms, and $|F_o|$ and $|F_c|$ are listed in Tables 2 and 3,[3] respectively. The standard deviations in positional parameters were: for Ni, 0.0015 Å, for O, N, and C, 0.012 Å and for H, 0.12 Å. The final composite electron density map is given in Fig. 2.

Molecular and Crystal Structure

The nickel atom exhibits four fold coordination, and lies on the plane formed by the four ligand atoms: two imino-nitrogen atoms and two amide-nitrogen atoms which exhibit sp^3 and sp^2 configuration, respectively (Fig. 3). The environment around the nickel atom indicates the coordination dsp^2 configuration. Two proline-amide molecules of the same complex are approximately related to each other by a two fold axis, so that the two ligand molecules coordinate to the central nickel atom in *trans* form. Two of the four bond distances between nickel and nitrogen atoms, Ni–NA1 and Ni–NB1, are significantly shorter than the other two, Ni–NA7 and Ni–NB7. These four bonds

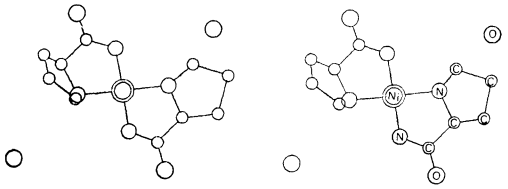

Fig. 3. The structure of bis(L-prolinamidato)nickel(II) complex shown by a stereo pair, illustrating the configuration.

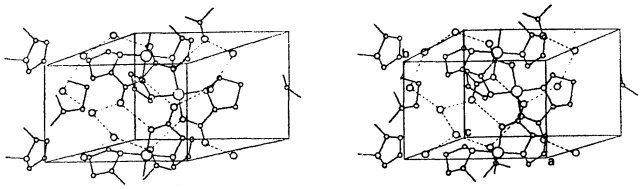

Fig. 4. The crystal structure of bis(L-prolinamidato)nickel(II) dihydrate shown by a stereo pair. Hydrogen bonds are indicated by broken lines.

Table 6. Equations of the least-squares planes through atoms

Equation	Atom	Deviation
$-0.0869X+0.0130Y+1.7701=Z$	NA1	−0.039Å
	NA7	0.039
	NB1	−0.040
	NB7	0.040
	*Ni	0.023
	*CA2	−1.346
	*CA3	−1.723
	*CA4	−1.038
	*CA5	0.110
	*CA6	0.105
	*CB2	−1.354
	*CB3	−1.475
	*CB4	−0.951
	*CB5	0.163
	*CB6	0.131
	*OA8	0.146
	*OB8	0.212
$0.9720X+0.7291Y-2.3724=Z$	NA1	0.089
	CA2	−0.121
	CA3	0.092
	CA4	−0.051
	CA5	−0.009
$-0.9129X-0.6485Y+2.411=Z$	NB1	0.156
	CB2	−0.259
	CB3	0.189
	CB4	−0.181
	CB5	0.093

Where $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$
* Atoms not included in the least-squares calculations.

Table 7. Intermolecular atomic contacts

From atom	to atom	Distance	From atom	to atom	Distance
OW1	OW2 a	2.880 Å	OW1	OA8 c	2.696 Å
OW1	NB1 d	3.162	OW1	OW2 g	2.782
OW2	OW1 a	2.880	OW2	OB8 e	2.726
OW2	OW1 f	2.782	OA8	OW1 b	2.696
OA8	NB7 b	3.060	OB8	NA7 c	3.024
OB8	OW2 d	2.726	NA7	OB8 b	3.024
NB1	OW1 e	3.162	NB7	OA8 c	3.060

Key for the position of molecule

a (x	y	z)	b (x	$-1.0+y$	z)
c (x	$1.0+y$	z)	d ($-x$	$0.5+y$	$-z$)
e ($-x$	$-0.5+y$	$-z$)	f (1.0$-x$	$-0.5+y$	$-z$)
g (1.0$-x$	$0.5+y$	$-z$)			

3) Table 3 which shows the calculated and observed structure factors has been submitted to, and is kept as Document No. 7203 by, the office of the Bulletin of the Chemical Society of Japan, 1-5 Kanda-Surugadai, Chiyoda-ku, Tokyo. A copy may be secured by citing the Document number and by remitting, in advance, ¥400 for photo prints. Pay by check or money order payable to: Chemical Society of Japan.

are shorter than those of $(Ni(H_2O)_2$(pyridine-2-carboxamide)$_2Cl_2$, (Ni–N, 2.02 Å),[4] in which the nickel atom exhibits octahedral coordination. Nawata *et al.*[5] reported the same observation in Ni(pyridine-2-carboxamidato)$_2$ dihydrate in which the nickel atom exhibited square planar coordination. The observations are consistent with theory. The bond angles around the nickel atom deviate from that of dsp^2 configuration by about five degrees. The distortion is not great from the viewpoint of molecular orbital theory.

Table 6 gives the equations of the least-squares planes and the distances of individual atoms from the planes. The two γ-carbon atoms of pyrrolidine ring, CA(3) and CB(3), are not displaced from the respective rings as much as those formed in acetyl-L-proline-*N*-methylamide[6] and other proline derivatives in which the nitrogen atom of pyrrolidine ring exhibits sp^2 configuration. Kim and Jeffey[7] compared the geometries of pyrrolidine rings with each other in which nitrogen atoms have sp^3 configuration. Both the two pyrrolidine rings in this crystal take the same puckered form as that in hydroxy-L-proline.[8]

4) A. Masuko, T. Nomura, and Y. Saito, This Bulletin, **40**, 511 (1967).
5) Y. Nawata, H. Iwasaki, and Y. Saito, This Bulletin, **40**, 515 (1967).
6) T. Matsuzaki and Y. Iitaka, *Acta Crystallogr.*, **B27**, 507 (1971).
7) H. S. Kim and G. A. Jeffey, *ibid.*, **B27**, 1123 (1971).
8) J. Donohue and K. N. Trueblood, *ibid.*, **5**, 414, 419 (1952).

Table 8. Intermolecular angles

Angle	degree
CA6 (a)...OA8 (a)...NB7 (b)	112.9°
OA8 (a)...NB7 (b)...Ni (b)	122.5
OA8 (a)...NB7 (b)...CB6 (b)	118.3
CA6 (a)...NA7 (a)...OB8 (b)	119.0
Ni (a)...NA7 (a)...OB8 (b)	122.4
NA7 (a)...OB8 (b)...CB6 (b)	114.7
OB8 (e)...OW2(a)...OW1(f)	127.5
OB8 (e)...OW2(a)...OW1(a)	96.1
OW1(a)...OW2(a)...OW1(f)	129.1
OW2(a)...OW1(a)...OW2(g)	100.4
OW2(a)...OW1(a)...OA8 (c)	141.0
OA3 (c)...OW1(a)...OW2(g)	117.4

The subscripts indicate the same operations as in Table 5.

The molecular packing in the crystal is shown in Fig. 4. Tables 7 and 8 give all the hydrogen bonding schemes with distances and angles. The two amide groups of neighbouring complexes are bound to each other through the two NH···O hydrogen bonds. The hydrogen bonds between non-equivalent water molecules, and those between water and imino carbonyl group of the complex construct the framework of this crystal structure. There are no intermolecular contact between nickel atom and oxygen atom of water.

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