The Crystal Structure of Nickel Dialpha-amino Isobutyrate Tetrahydrate

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Recently the present author succeeded in constructing an electronic device[1] to compute the minimum-functions[1] proposed by Buerger[2]. The present paper will give a structure analysis of nickel(II) α-amino isobutyrate tetrahydrate, which seemed to present a suitable problem for applying this device.

A good deal of the structures of amino acids has been elucidated in the past several years, but not so much has been done for the amino acid salts. The differences in the configuration of acid groups between the free acid and salt might be one of the most interesting problems from the chemical point of view. This paper will present its findings by reviewing the X-ray analysis of nickel α-amino isobutyrate tetrahydrate.

Experimental

The crystals used in this investigation were prepared by adding an excess of freshly prepared nickel(II) hydroxide to a warm aqueous solution of α-amino isobutyric acid. The solution was then filtered and allowed to evaporate slowly. This procedure made it possible to obtain blue needle-like crystals, the direction of elongation being along the a-axis.

Crystallographic Data

Laue, oscillation and Weissenberg photographs taken with copper K_α radiation (λ= 1.542 Å) confirmed the unit cell dimensions of the crystal reported by Hirokawa et al.[3,4]:

$$a=9.92\pm0.02\ \text{Å} \qquad c=11.42\pm0.02\ \text{Å}$$
$$b=14.24\pm0.05\ \text{Å} \qquad \beta=107.5\pm0.5^\circ$$

The space group of the crystal was concluded to be $P2_1/a$ from the systematic absences of the following spectra: $(h\,k\,l)$ for all, $(0\,k\,0)$ for $k=2n+1$, and $(h\,0\,l)$ for $h=2n+1$.

The density of the crystal, measured by the floatation method, was found to be 1.48 g./cc., corresponding to four formula units, $4Ni(NH_2\cdot(CH_3)_2C\cdot COO)_2\cdot 4H_2O$, in the unit cell. There are two kinds of amino acid groups and four kinds of water molecules which are crystallographically non-equivalent.

Determination of the Structure

The intensities of the $(0\,k\,l)$, $(h\,0\,l)$ and $(h\,k\,0)$ reflections were estimated visually from Weissenberg photographs. The intensities of the reflections on different films were put on the same scale by comparing the intensities of the same reflections appearing on successive photographs.

No correction were made for absorption, because the crystals used were cut into suitable sizes and shapes, having dimensions less than 0.2 mm.×0.4 mm. in cross section.

After a correction for the Lorentz and polarization factors, the measured intensities were converted to an absolute scale by using Wilson's statistical method (Wilson, 1949)[5].

Using the F^2 values thus obtained, three sets of Patterson syntheses were computed along the a-, b- and c-axis. The minimum-function method (Buerger, 1951) was applied first to $P(v, w)$, using the image seeker described in a preceding paper[1]. The obtained minimum function (M_2) is given in Fig. 1. It gives a clue to the structure, giving approximate

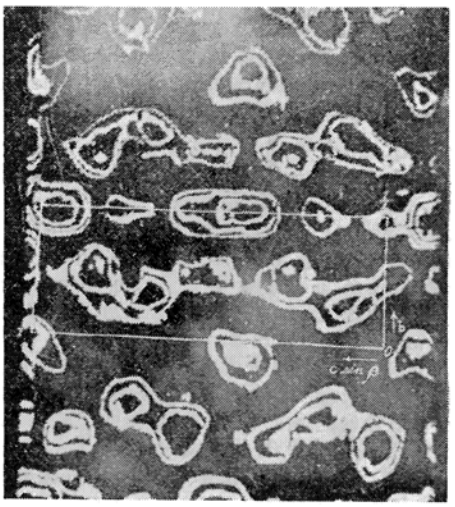

Fig. 1. M_2-Map from $P(v, w)$ obtained by the application of the newly designed image-seeker.

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1) T. Noguchi, to be published in Ōyōbutsuri, 1961.

2) M. J. Buerger, *Acta Cryst.*, **4**, 531 (1951).

3) S. Hirokawa, and S. Kuribayashi, *Annual Report of the Institute for Fibre Research, Osaka University*, **5**, 4 (1950).

4) S. Hirokawa, S. Kuribayashi and I. Nitta, This Bulletin, **25**, 192 (1952).

5) A. J. C. Wilson, *Nature*, **150**, 151 (1949).

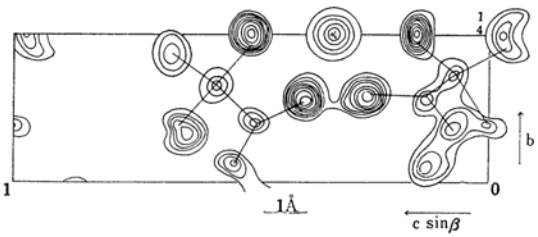

Fig. 2. Fourier projection $\rho(y,z)$. Contours for lighter atoms are drawn at equal intervals on an arbitrary scale.

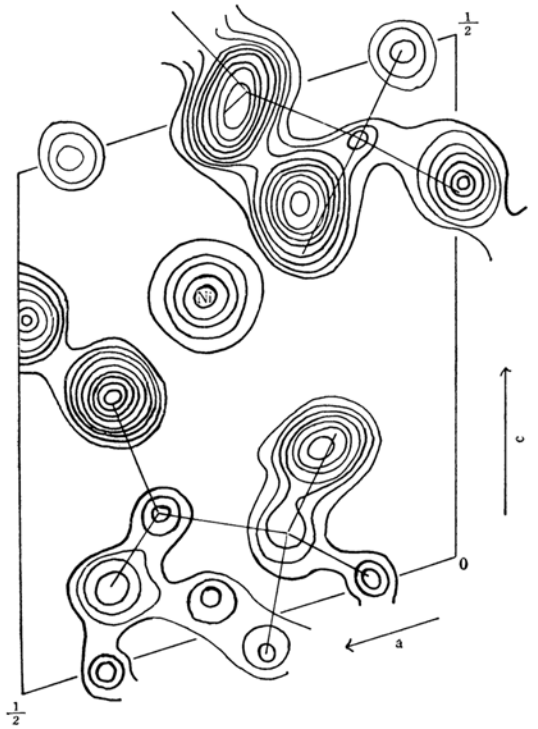

Fig. 3. Fourier projection $\rho(x,z)$. Contours for lighter atoms are drawn at equal intervals on an arbitrary scale.

values of the y- and z-coordinates not only for the nickel atom but also for several light atoms. The same procedures were applied to $P(u,v)$ and $P(u,w)$. Though the obtained maps were rather poor to resolve the location of each atom, a rough lay-out of the structure was obtained from the interpretation of these three minimum function maps.

Structure factors for $(0\,k\,l)$, $(h0l)$ and $(hk0)$ were calculated using the parameters found from the three sets of M_2-maps. These parameter-values were first refined by the Fourier syntheses. The locations of some atoms on the projected electron-density maps were obscured on account of overlappings. The coordinates of these atoms were obtained by successive refinement, using the trial-and-error method.

TABLE I. ATOMIC COORDINATES

		x	y	z
	Ni	0.285	0.250	0.326
A	O_2	0.395	0.152	0.252
	O_3 (H_2O)	0.387	0.363	0.263
B	O_4	0·175	0.140	0.392
	O_5 (H_2O)	0.177	0.350	0.383
A	O_6	0.397	0.092	0.075
B	O_7	0.233	0.032	0.532
	O_8 (H_2O)	0.017	0.077	0.630
	O_9 (H_2O)	0.170	0.475	0.135
A	N_{10}	0.133	0.238	0.152
B	N_{11}	0.439	0.237	0.498
A	C_{12}	0.338	0.149	0.132
A	C_{13}	0.192	0.182	0.071
A	C_{14}	0.218	0.229	0.963
A	C_{15}	0.095	0.100	0.005
B	C_{16}	0.263	0.105	0.490
B	C_{17}	0.392	0.165	0.572
B	C_{18}	0.496	0.091	0.652
B	C_{19}	0.328	0.218	0.667

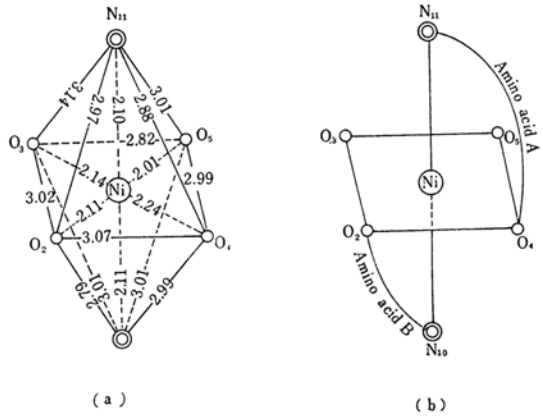

Fig. 4. (a) Interatomic distances around the nickel ion.
(b) The chelation of the amino acid molecules around the nickeous ion.

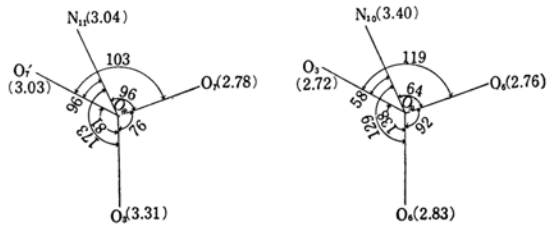

Fig. 5. The interatomic distances and angles around two water molecules, which bind the structure.

Fourier projections $\rho(y,z)$ and $\rho(x,z)$ are shown in Figs. 2 and 3. The atomic coordinates are tabulated in Table I, where A and B denote two different amino-radicals in the crystal respectively.

TABLE II. COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c
0 0 1	78.5	−94.8	0 4 0	8.7	0.4	0 8 0	80.3	83.0	0 12 4	11.5	−16.3
0 0 2	22.0	23.4	0 4 1	2.9	− 7.1	0 8 1	24.1	−25.0	0 12 5	7.6	− 8.4
0 0 3	83.1	82.0	0 4 2	6.5	−11.0	0 8 2	21.5	−27.8	0 12 6	10.9	13.3
0 0 4	54.1	−51.8	0 4 3	7.6	− 6.8	0 8 3	22.1	19.8	0 12 7	4.1	− 8.5
0 0 5	57.9	−52.0	0 4 4	5.9	−11.8	0 8 4	5.0	1.9	0 12 8	7.6	− 8.6
0 0 6	47.6	45.2	0 4 5	53.9	−62.4	0 8 5	22.1	−24.9	0 12 9	8.8	7.1
0 0 7	21.2	−21.4	0 4 6	81.2	88.2	0 8 6	42.9	35.2	0 12 10	< 2.4	− 2.1
0 0 8	11.7	22.9	0 4 7	< 2.9	0.5	0 8 7	< 4.1	6.3			
0 0 9	< 2.9	0.7	0 4 8	34.4	−41.0	0 8 8	< 4.1	3.7	0 13 1	14.1	−14.9
0 0 10	8.8	−14.8	0 4 9	28.2	29.1	0 8 9	< 4.1	5·5	0 13 2	< 4.1	− 6.4
0 0 11	20.2	−16.7	0 4 10	5.0	− 8.3	0 8 10	< 2.9	0.3	0 13 3	< 4.1	− 3.3
0 0 12	20.5	17.4	0 4 11	19.4	−25.1	0 8 11	16.2	−16.0	0 13 4	20.9	−26.0
0 0 13	< 2.9	3.1	0 4 12	13.2	5.0	0 8 12	10.6	9.5	0 13 5	10.3	15.8
			0 4 13	< 2.9	− 1.7				0 13 6	4.1	5.2
0 1 1	127.1	−162.2				0 9 1	74.1	−86.9	0 13 7	20.6	−19.7
0 1 2	2.9	− 0.8	0 5 1	9.7	19.2	0 9 2	47.9	53.2	0 13 8	10.6	9.3
0 1 3	7.6	5.3	0 5 2	18.5	−22.3	0 9 3	4.1	9.3	0 13 9	5.0	5.7
0 1 4	47.0	−48.6	0 5 3	9.7	15.0	0 9 4	23.5	−19.7			
0 1 5	38.8	26.4	0 5 4	31.7	−26.6	0 9 5	48.8	55.8	0 14 0	12.3	−13.3
0 1 6	16.8	17.9	0 5 5	44.7	54.6	0 9 6	< 4.1	2.4	0 14 1	4.1	0.9
0 1 7	5.0	5.7	0 5 6	30.3	35.6	0 9 7	< 4.1	6.7	0 14 2	< 4.1	− 9.9
0 1 8	6.5	− 0.3	0 5 7	49.4	−51.7	0 9 8	< 4.1	− 4.4	0 14 3	5.9	0.7
0 1 9	< 2.9	1.4	0 5 8	17.1	14.4	0 9 9	< 4.1	− 8.7	0 14 4	5.0	− 4.8
0 1 10	5.9	− 0.2	0 5 9	21.7	29.0	0 9 10	10.6	−14.4	0 14 5	15.3	18.1
0 1 11	10.3	8.3	0 5 10	30.6	−31.9	0 9 11	5.9	5.6	0 14 6	20.3	−20.2
0 1 12	22.3	19.3	0 5 11	14.1	13.5	0 9 12	5.9	3.2	0 14 7	5.0	2.0
0 1 13	12.9	−12.0	0 5 12	< 2.9	4.8				0 14 8	12.9	12.9
			0 5 13	7.1	− 3.8	0 10 0	64.7	−63.5			
0 2 0	109.4	−132.7				0 10 1	30.9	31.7	0 15 1	8.2	7.7
0 2 1	27.1	28.6	0 6 0	67.3	−64.8	0 10 2	28.8	34.3	0 15 2	10.9	−16.8
0 2 2	47.9	54.5	0 6 1	14.1	12.8	0 10 3	25.9	−13.9	0 15 3	< 2.9	− 0.6
0 2 3	76.5	−80.4	0 6 2	< 4.1	− 6.1	0 10 4	13.5	13.5	0 15 4	15.0	16.6
0 2 4	< 4.1	− 6.0	0 6 3	53.8	−64.7	0 10 5	6.5	7.3	0 15 5	9.7	−10.6
0 2 5	29.1	−29.7	0 6 4	13.5	7.5	0 10 6	7.6	− 7.4	0 15 6	2.9	0.7
0 2 6	48.8	−42.8	0 6 5	38.5	42.4	0 10 7	6.5	− 9.9	0 15 7	20.3	19.3
0 2 7	6.5	7.4	0 6 6	63.2	−76.5	0 10 8	< 2.9	− 2.1			
0 2 8	27.0	28.7	0 6 7	24.7	32.3	0 10 9	8.2	− 1.9	0 16 0	< 3.2	− 8.7
0 2 9	15.9	−10.8	0 6 8	18.2	19.9	0 10 10	< 2.9	5.0	0 16 1	< 2.9	− 3.0
0 2 10	< 4.1	2.0	0 6 9	18.5	−17.2	0 10 11	10.6	12.3	0 16 2	11.5	−10.7
0 2 11	23.2	23.1	0 6 10	< 2.9	− 1.8				0 16 3	13.5	8.5
0 2 12	21.5	−19.4	0 6 11	9.4	8.2	0 11 1	37.7	33.5	0 16 4	2.9	− 1.0
0 2 13	< 2.9	− 4.6	0 6 12	12.3	−14.4	0 11 2	25.3	−24.9	0 16 5	8.2	− 5.8
			0 6 13	< 2.4	1.3	0 11 3	7.1	−10.0	0 16 6	13.5	5.5
0 3 1	43.5	46.6				0 11 4	19.7	20.8			
0 3 2	77.6	−92.0	0 7 1	37.9	34.1	0 11 5	15.3	−13.2	0 17 1	16.2	−12.6
0 3 3	12.0	−13.9	0 7 2	41.5	−42.8	0 11 6	4.1	− 6.3	0 17 2	9.7	8.4
0 3 4	19.4	19.8	0 7 3	< 4.1	1.9	0 11 7	10.3	14.2	0 17 3	< 2.4	0.4
0 3 5	66.1	−73.9	0 7 4	18.2	13.6	0 11 8	10.6	−10.1	0 17 4	7.6	− 8.1
0 3 6	10.3	−13.3	0 7 5	17.3	− 3.6	0 11 9	< 2.9	− 0.7			
0 3 7	46.7	44.1	0 7 6	21.5	−24.2	0 11 10	7.6	6.5	0 18 0	16.4	−15.8
0 3 8	23.8	−29.3	0 7 7	38.5	37.2	0 11 11	4.1	− 4.7	0 18 1	4.1	4.4
0 3 9	4.1	− 2.9	0 7 8	13.5	−16.1						
0 3 10	16.8	12.9	0 7 9	7.6	−10.9	0 1 20	40.6	41.0	2 0 $\bar{1}$	3.8	2.7
0 3 11	10.9	−10.3	0 7 10	11.5	8.1	0 1 21	10.3	− 7.7	2 0 $\bar{2}$	16.7	−26.1
0 3 12	2.9	− 3.7	0 7 11	6.5	− 4.4	0 1 22	13.8	− 6.9	2 0 $\bar{3}$	57.9	64.1
0 3 13	5.9	3.8	0 7 12	9.7	− 6.8	0 1 23	20.6	25.3	2 0 $\bar{4}$	44.5	−45.6

TABLE II. (Continued)

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
2 0 $\bar{5}$	11.1	−11.7	6 0 $\bar{3}$	2.7	1.8	10 0 $\bar{8}$	< 1.9	− 1.8	2 14 0	18.0	19.8
2 0 $\bar{6}$	27.4	−22.5	6 0 $\bar{4}$	93.9	−100.7	10 0 $\bar{9}$	5.5	2.6	2 15 0	< 5.0	0.6
2 0 $\bar{7}$	7.9	−10.9	6 0 $\bar{5}$	80.7	69.5	10 0 $\bar{10}$	9.0	− 5.9	2 16 0	9.1	− 6.1
2 0 $\bar{8}$	50.1	51.8	6 0 $\bar{6}$	14.3	13.8	10 0 $\bar{11}$	< 1.1	2.3	2 17 0	< 5.0	− 1.1
2 0 $\bar{9}$	22.0	−20.3	6 0 $\bar{7}$	51.4	−56.8	10 0 $\bar{12}$	10.8	16.5			
2 0 $\bar{10}$	4.8	2.6	6 0 $\bar{8}$	25.0	30.3				3 1 0	33.3	32.9
2 0 $\bar{11}$	28.1	35.1	6 0 $\bar{9}$	< 1.9	− 6.2	10 0 0	20.0	21.2	3 2 0	17.8	−26.4
2 0 $\bar{12}$	11.2	− 7.1	6 0 $\bar{10}$	36.4	−34.4	10 0 1	16.1	24.6	3 3 0	< 5.0	9.3
2 0 $\bar{13}$	14.2	−13.8	6 0 $\bar{11}$	4.8	− 5.2	10 0 2	25.9	−23.8	3 4 0	9.4	4.2
2 0 $\bar{14}$	16.9	19.8	6 0 $\bar{12}$	5.7	−11.5	10 0 3	21.5	25.9	3 5 0	< 5.0	4.4
			6 0 $\bar{13}$	2.3	− 4.0	10 0 4	9.7	9.7	3 6 0	12.0	11.3
2 0 0	123.6	−129.6	6 0 $\bar{14}$	2.3	1.7	10 0 5	2.3	− 0.9	3 7 0	11.0	9.8
2 0 1	33.7	46.5							3 8 0	24.0	14.7
2 0 2	4.3	7.0	6 0 0	1.9	4.9	12 0 $\bar{1}$	1.9	1.2	3 9 0	12.0	−15.1
2 0 3	86.6	−101.8	6 0 1	21.8	17.6	12 0 $\bar{2}$	< 1.7	− 1.3	3 10 0	14.6	20.0
2 0 4	72.5	74.7	6 0 2	41.6	−47.6	12 0 $\bar{3}$	< 1.7	3.7	3 11 0	< 5.0	3.9
2 0 5	61.0	76.2	6 0 3	10.8	19.2	12 0 $\bar{4}$	< 1.7	− 6.1	3 12 0	11.3	6.6
2 0 6	51.6	−45.2	6 0 4	38.4	−47.6	12 0 $\bar{5}$	2.3	4.0	3 13 0	5.0	8.1
2 0 7	8.9	3.9	6 0 5	5.3	− 8.0	12 0 $\bar{6}$	3.6	− 3.9	3 14 0	14.7	−14.4
2 0 8	< 1.9	2.8	6 0 6	9.7	− 6.3	12 0 $\bar{7}$	5.0	10.3	3 15 0	< 5.0	0.6
2 0 9	7.0	− 7.4	6 0 7	27.9	29.1	12 0 $\bar{8}$	7.9	9.4	3 16 0	< 5.0	1.8
2 0 10	3.4	− 1.2	6 0 8	4.1	1.5	12 0 $\bar{9}$	8.1	− 4.7			
2 0 11	13.4	13.5	6 0 9	5.6	− 2.2				4 1 0	10.0	17.8
2 0 12	2.7	1.3	6 0 10	8.3	8.4	12 0 0	1.2	0.7	4 2 0	5.0	5.8
2 0 13	1.1	1.3							4 3 0	36.0	42.1
			8 0 $\bar{1}$	36.8	41.0	1 1 0	14.7	−23.3	4 4 0	64.0	64.0
4 0 $\bar{1}$	87.9	−104.7	8 0 $\bar{2}$	31.0	−25.2	1 2 0	77.5	−110.6	4 5 0	45.3	−47.7
4 0 $\bar{2}$	7.8	13.7	8 0 $\bar{3}$	8.9	− 9.4	1 3 0	20.0	21.1	4 6 0	64.0	−56.8
4 0 $\bar{3}$	16.2	7.7	8 0 $\bar{4}$	39.2	49.6	1 4 0	14.4	24.6	4 7 0	49.3	45.0
4 0 $\bar{4}$	15.0	14.6	8 0 $\bar{5}$	9.7	− 4.9	1 5 0	21.3	−20.6	4 8 0	< 5.0	− 0.3
4 0 $\bar{5}$	31.7	−29.5	8 0 $\bar{6}$	13.8	−14.0	1 6 0	4.5	−13.2	4 9 0	< 5.0	8.8
4 0 $\bar{6}$	39.2	36.0	8 0 $\bar{7}$	24.7	27.0	1 7 0	8.7	−10.5	4 10 0	< 5.0	2.6
4 0 $\bar{7}$	16.4	16.2	8 0 $\bar{8}$	9.4	−10.6	1 8 0	14.3	25.4	4 11 0	11.3	10.9
4 0 $\bar{8}$	43.1	−40.7	8 0 $\bar{9}$	< 1.9	5.1	1 9 0	< 5.0	2.9	4 12 0	9.3	8.3
4 0 $\bar{9}$	13.2	10.1	8 0 $\bar{10}$	< 1.7	− 7.6	1 10 0	< 5.0	− 6.4	4 13 0	10.4	− 6.5
4 0 $\bar{10}$	40.1	37.6	8 0 $\bar{11}$	< 1.4	4.8	1 11 0	< 5.0	− 4.0	4 14 0	18.0	−15.4
4 0 $\bar{11}$	9.7	− 8.9	8 0 $\bar{12}$	6.3	− 9.8	1 12 0	6.4	4.1	4 15 0	17.0	11.7
4 0 $\bar{12}$	< 1.2	− 1.7	8 0 $\bar{13}$	14.9	12.6	1 13 0	5.0	− 8.8	4 16 0	8.7	9.0
4 0 $\bar{13}$	6.6	4.5				1 14 0	< 5.0	−13.2			
4 0 $\bar{14}$	11.2	−12.0	8 0 0	< 1.9	1.8	1 15 0	7.0	11.6	5 1 0	8.0	11.2
			8 0 1	34.8	−37.7	1 16 0	< 5.0	9.8	5 2 0	< 5.0	−13.6
4 0 0	10.0	−10.8	8 0 2	11.7	10.0	1 17 0	< 5.0	5.6	5 3 0	13.0	−11.2
4 0 1	52.2	−46.9	8 0 3	< 1.9	− 5.0				5 4 0	23.9	−30.5
4 0 2	39.2	32.9	8 0 4	9.1	− 9.0	2 1 0	40.6	62.9	5 5 0	5.3	7.5
4 0 3	52.5	57.9	8 0 5	4.8	3.5	2 2 0	74.3	82.7	5 6 0	< 5.3	−11.1
4 0 4	21.2	−21.2	8 0 6	< 1.7	0.4	2 3 0	24.7	−23.6	5 7 0	< 5.3	− 8.2
4 0 5	3.4	−11.4	8 0 7	6.1	− 7.1	2 4 0	80.7	−82.3	5 8 0	< 5.0	− 3.0
4 0 6	58.9	59.9	8 0 8	< 1.1	6.1	2 5 0	8.6	−13.1	5 9 0	< 5.0	−16.8
4 0 7	55.7	−65.9				2 6 0	6.2	− 5.1	5 10 0	< 5.0	− 8.6
4 0 8	2.7	− 2.1	10 0 $\bar{1}$	21.0	−22.3	2 7 0	24.7	−31.3	5 11 0	< 5.0	4.6
4 0 9	12.2	11.9	10 0 $\bar{2}$	9.6	14.6	2 8 0	62.6	−54.3	5 12 0	< 5.0	− 8.8
4 0 10	13.5	−15.6	10 0 $\bar{3}$	21.3	21.7	2 9 0	10.6	7.1	5 13 0	< 5.0	6.0
4 0 11	< 1.1	− 3.0	10 0 $\bar{4}$	19.7	−19.5	2 10 0	36.0	39.6	5 14 0	< 5.0	− 4.5
			10 0 $\bar{5}$	3.0	6.5	2 11 0	22.0	−22.5	5 15 0	< 5.0	− 1.3
6 0 $\bar{1}$	11.3	−17.3	10 0 $\bar{6}$	7.0	−13.8	2 12 0	10.3	− 2.0			
6 0 $\bar{2}$	22.3	15.3	10 0 $\bar{7}$	13.0	−11.7	2 13 0	< 5.0	1.6	6 1 0	11.0	12.1

TABLE II. (Continued)

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
6 2 0	< 5.0	6.3	7 4 0	8.0	13.6	8 7 0	24.0	17.0	9 11 0	12.0	−12.5
6 3 0	64.0	−61.6	7 5 0	< 5.0	− 8.5	8 8 0	< 5.0	− 4.3			
6 4 0	< 6.0	− 8.1	7 6 0	< 5.0	1.4	8 9 0	19.3	−17.0	10 1 0	20.0	12.1
6 5 0	55.4	54.4	7 7 0	11.3	− 3.2	8 10 0	< 5.3	6.8	10 2 0	< 5.0	− 7.5
6 6 0	15.3	19.2	7 8 0	< 5.0	7.3	8 11 0	23.3	17.9	10 3 0	< 5.0	1.8
6 7 0	45.3	−45.7	7 9 0	< 5.0	1.3	8 12 0	< 5.0	2.4	10 4 0	< 5.0	− 6.7
6 8 0	11.3	− 9.8	7 10 0	< 5.0	0.2	8 13 0	15.5	− 9.7	10 5 0	< 5.0	− 8.8
6 9 0	8.0	15.9	7 11 0	< 5.0	− 1.9				10 6 0	< 5.0	− 6.9
6 10 0	< 5.0	− 5.3	7 12 0	12.7	11.6	9 1 0	< 5.0	6.3	10 7 0	< 5.0	− 4.4
6 11 0	11.3	−10.5	7 13 0	< 5.0	3.8	9 2 0	< 5.0	1.7	10 8 0	< 5.0	1.4
6 12 0	8.8	− 3.5	7 14 0	8.7	10.3	9 3 0	< 5.0	5.5	10 9 0	11.3	9.9
6 13 0	16.0	15.4				9 4 0	< 5.0	− 8.7			
6 14 0	14.7	13.9	8 1 0	39.3	−33.1	9 5 0	< 5.0	13.0	11 1 0	< 5.0	− 5.2
6 15 0	16.7	−15.9	8 2 0	11.0	17.3	9 6 0	< 5.0	− 2.6	11 2 0	< 5.0	− 3.8
			8 3 0	14.0	6.8	9 7 0	< 5.0	− 1.9	11 3 0	< 5.0	− 0.9
7 1 0	12.0	− 7.8	8 4 0	11.3	−15.0	9 8 0	< 5.0	− 0.6	11 4 0	< 5.0	− 2.7
7 2 0	12.3	10.1	8 5 0	< 5.0	− 8.3	9 9 0	< 5.0	5.3	11 5 0	< 5.0	− 5.7
7 3 0	< 5.0	− 3.2	8 6 0	9.3	− 9.5	9 10 0	< 5.0	− 1.6			

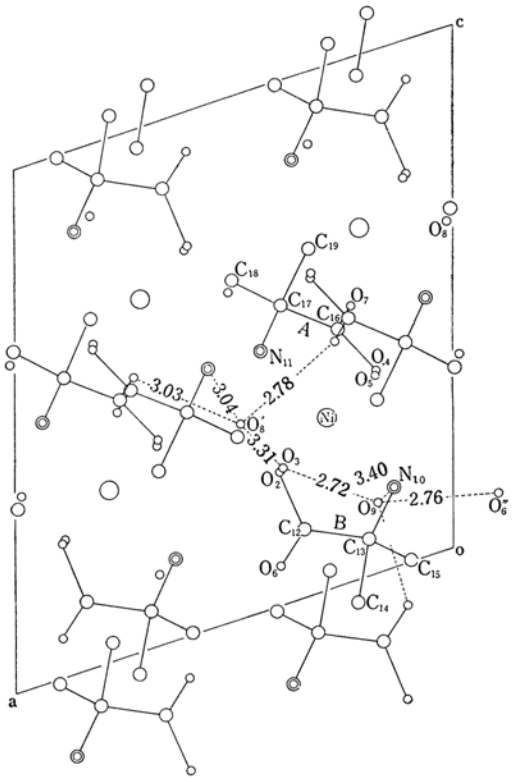

Fig. 6. The structure of nickel dialpha-amino isobutyrate tetrahydrate viewed along the b-axis.

○ Ni ◦ O ◎ N ○ C

Comparison of F_o are tabulated in Table II, where the F_c-values include the overall temperature factor ($-3.15 \sin^2\theta/\lambda^2$).

The reliability index, neglecting unobserved reflections, is 16.8, 15.7 and 18.1% respectively for the $(0kl)$, $(h0l)$ and $(hk0)$ reflections.

Discussion of the Structure

The Amino Acid Radicals.—The interatomic distances and the bond angles for the two kinds of acid groups are given in Table III. Standard deviations were estimated to be ±0.05 Å for distances and ±5° for angles. For comparison, the reported values for the free acid (Hirokawa, 1952) are given in the last column of Table III.

In the structure of α-amino isobutyric acid (Hirokawa et al., 1952), the carboxyl group, C_α and N, is almost coplanar. The most characteristic feature of the structure of the nickel salt is that the nitrogen atoms are definitely out of the plane, the angles of twist around the C_α–C_o bonds being 17.8° and 24.1° respectively for groups A and B. It is interesting to note that the configurations and the dimensions of the two kinds of the amino acid groups are almost the same. The twist around the C_α–C_o bond may be caused by the coordination of amino groups around the nickel ion.

The nearest neighbors surrounding the nickel ion are two carboxylic oxygen atoms, two nitrogen atoms and two water molecules. They form a distorted octahedron, having the structural dimensions which are given in Table IV and Fig. 4 (a).

The two kinds of the amino acid groups form chelate rings with the nickel ion by the nitrogen atoms in the amino groups and by the carboxylic oxygen atoms, assuming a cis-configuration (Fig. 4 (b)).

TABLE III. MOLECULAR DIMENSIONS OF THE α-AMINO ACIDS

	Group A	Group B	Free molecule
(a) Interatomic distances, Å			
O_c-C_c	1.32	1.30	1.26
	1.29	1.22	1.20
C_c-C_α	1.48	1.58	1.52
C_α-N	1.47	1.48	1.49
C_α-C_β	1.50	1.57	1.53
	1.55	1.60	1.54
(b) Bond angles, °			
O_c-C_c-O_c	115	119	125
O_c-C_c-C_α	122	121	118
	119	119	118
C_c-C_α-N	113	112	109
C_c-C_α-C_β	114	105	114
	98	104	109
N-C_α-C_β	114	122	108
	118	109	105
C_β-C_α-C_β	100	104	112

TABLE IV. INTERATOMIC DISTANCES AROUND THE NICKEL ION, Å

Ni-O_2	2.11	N_{10}-O_5	3.01
Ni-O_3	2.14	N_{11}-O_2	2.97
Ni-O_4	2.24	N_{11}-O_3	3.14
Ni-O_5	2.01	N_{11}-O_4	2.88
Ni-N_{10}	2.11	N_{11}-O_5	3.01
Ni-N_{11}	2.10	O_2-O_3	3.02
N_{10}-O_2	2.79	O_2-O_4	3.07
N_{10}-O_3	3.03	O_3-O_5	2.82
N_{10}-O_4	2.99	O_4-O_5	2.99

Thus, two of the four water molecules are coordinated to the nickel ion, and the remaining two are found between these octahedra, playing the role of binding them. Each of the latter two water molecules has three carboxylic oxygen atoms and one nitrogen atom as its nearest neighbors. The interatomic distances and angles around these water molecules are shown in Fig. 5. It is rather difficult to say which of these contacts are hydrogen bonds, though the interatomic distances suggest they are O_7—$H_2O(O_8)$, O_3—$H_2O(O_9)$ and O'_6—$H_2O(O_9)$. These features may be compared to the hydrogen bonds in the structure of ice.

The structures viewed along the b-axis are shown in Fig. 6, where one can easily see the following structural features: the two amino acids and the two H_2O molecules are coordinated to the nickel ion, forming a complex. These groups are held together along the [101] and [100] directions by the other H_2O molecules, making short contacts between them.

Summary

The unit cell of nickel(II) dialpha-amino isobutyrate tetrahydrate has the follwing dimensions; a=9.92, b=14.24, c=11.42 Å, β=107.5°, and contains four chemical units. The space group is determined to be $P2_1/a$.

Buerger's minimum-function method was applied to the structure analysis, and the newly designed image-seeker was used. Two of the four water molecules are coordinated to the nickel ion, forming a distorted octahedron with the carboxylic oxygen and the amino nitrogen atoms. The other two water molecules play the role of binders for these octahedrons. The chelation of the amino acid molecules is of the cis-form. The structure of the skeleton of α-amino propionic acid in this complex is not planar, in contrast to that of its free acid.

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