

## The Crystal and Molecular Structure of *bis*-( $\beta$ -aminobutyrate)-Copper (II) dihydrate, $\text{Cu}(\text{C}_4\text{H}_8\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$

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Crystals of *bis*-( $\beta$ -aminobutyrate)-copper (II) dihydrate,  $\text{Cu}(\text{C}_4\text{H}_8\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$ , are triclinic, the unit cell dimensions being:

$$a = 6.69 \pm 0.02, b = 5.06 \pm 0.02, c = 9.87 \pm 0.04 \text{ \AA}; \\ \alpha = 87^\circ 30' \pm 45', \beta = 104^\circ 55' \pm 50', \gamma = 105^\circ 45' \pm 50'.$$

The proposed space group is  $P\bar{1}$ ,  $Z = 1$ .

The molecular structure of the complex has been determined by X-ray diffraction methods from three, two-dimensional, electron-density projections and refined by least-squares analysis. Each Cu atom lies at the centre ( $\bar{1}$ ) of a distorted octahedron whose mid-plane is defined by the  $-\text{NH}_2$  group and one carboxyl oxygen of each of two acid residues (*trans*- configuration,  $\text{Cu}-\text{O} = 2.00 \pm 0.02$ ,  $\text{Cu}-\text{N} = 1.99 \pm 0.02 \text{ \AA}$ ) the Cu atom thus forming part of two six-membered ring systems. Each remaining apex of the octahedron is occupied by a water molecule,  $\text{Cu}-\text{H}_2\text{O} = 2.45 \pm 0.02 \text{ \AA}$ .

Interatomic distances within the molecule are normal (e.s.d.  $\text{C}-\text{C} = 0.03 \text{ \AA}$ ) and the molecules are held together in the  $a$  and  $b$  directions by hydrogen bonds. Normal van der Waal's forces operate in the  $c$  direction.

### Introduction

This paper describes part of an investigation of the structures of the copper (II) complexes formed by various  $\omega$ -amino acids. Thus, Tomita & Nitta have used X-ray diffraction techniques to determine the structures of the cupric complexes of glycine and of  $\beta$ -alanine (Tomita, 1960*a, b*; Tomita & Nitta, 1960). Here we present the results of an analysis of the crystal and molecular structure of *bis*-( $\beta$ -aminobutyrate)-copper (II) dihydrate,  $\text{Cu}(\text{C}_4\text{H}_8\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$ .

### Experimental

The complex is prepared by heating in a water bath for about two hours an aqueous solution of  $\beta$ -aminobutyric acid with an excess of freshly prepared cupric oxide. The resultant blue solution is filtered and the complex crystallizes from the filtrate as well formed deep-blue plates, roughly hexagonal in shape, elongated along  $a$ , and with (010) developed. The crystals lose water on exposure to the air and were enclosed in thin-walled Lindemann glass capillaries during the X-ray photography.

### Crystal data

The unit cell dimensions and space group were determined from  $30^\circ$  precession photographs taken with Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The crystals belong to the triclinic system with:

$$a = 6.69 \pm 0.02, b = 5.06 \pm 0.02, c = 9.87 \pm 0.04 \text{ \AA}; \\ \alpha = 87^\circ 30' \pm 45', \beta = 104^\circ 55' \pm 50', \gamma = 105^\circ 45' \pm 50'.$$

The observed density (by flotation) is  $1.60_7 \text{ g.cm.}^{-3}$ , and that calculated assuming one formula weight per unit cell is  $1.61_3 \text{ g.cm.}^{-3}$ . The space group was assumed to be  $P\bar{1}$  with the copper atom occupying a centre of symmetry.

### Intensity data

These were collected from  $30^\circ$  precession photographs taken, using Mo radiation, about the three crystal axes. Timed exposures were used to ensure that each independent reflexion was recorded within a measurable range of intensity, where possible more than once. Visual estimates of intensity were made using a specially prepared scale. The range of diffracted intensity was 1000 to 1. 192 reflexions were recorded and measured in ( $h0l$ ), 127 and 96 in ( $0kl$ ) and ( $hkl$ ) respectively. Two crystals were used in recording the diffraction pattern, each of approximate reflecting cross-section  $0.3 \times 0.1 \text{ mm}$ . The linear absorption coefficient of the complex for Mo  $K\alpha$  radiation is  $18.4 \text{ cm.}^{-1}$  and so errors due to absorption would be expected in the measured intensities. However, since the aim of the analysis was to determine the configuration of the complex rather than very accurate molecular dimensions, no allowance was made for this effect. Lorentz and polarization corrections were applied and the corrected intensities reduced to relative structure amplitudes.

### Structure determination

The presence of a copper atom at a centre of symmetry

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in the crystal makes it possible to apply the heavy atom method of phase determination with great effectiveness. A preliminary calculation of the expected contribution of the copper atom to the structure factors in all three zones showed that, in all but a very few instances, it was sufficiently large to unambiguously determine the sign of each reflexion. Accordingly, Fourier syntheses were calculated for each of the three principal zones using all reflexions of supposedly definite positive sign and from the resulting electron-density projections it was a simple

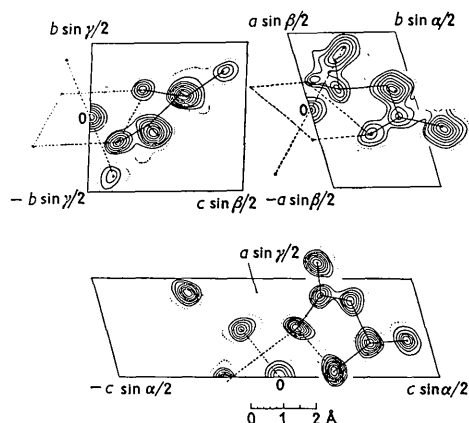


Fig. 1. Final electron-density projections. The contour levels are at equal but arbitrary intervals (approximately  $1 \text{ e. \AA}^{-2}$ ). The coordination octahedron is outlined by the broken lines, the acid residues being indicated by the solid lines.

matter to establish the position and arrangement of all of the atoms in the unit cell. A complete structure factor calculation based on these positions showed only about half a dozen reflexions to be of negative sign and a second round of Fourier syntheses gave the final electron-density projections shown in Fig. 1. Excluding unobserved reflexions the value of the index  $R$  was 0.26 at this stage.

### Refinement of the structure

A least-squares refinement of the averaged atomic parameters derived from the Fourier maps was carried out on an IBM 704 data processing machine using the crystallographic least-squares refinement program of Busing & Levy. All 400 or so equatorial reflexions were included in this refinement; to reduce absorption errors a choice of axial reflexions was made,  $h0l$  and  $00l$  being chosen from  $(h0l)$  and  $0k0$  from  $(hkl)$ . The weighting scheme proposed by Hughes (1941) was used and individual isotropic temperature factors were employed to modify the atomic scattering functions which were, for the light atoms, those given by McWeeny (1951), and, for copper, that given by Berghuis *et al.* (1955). No allowance was made for the presence of hydrogen atoms in the structure. After the fourth cycle of the refinement process the shifts in the atomic parameters were less than one tenth the standard deviations calculated by the program and the values of the parameters taken from this cycle were considered as final. They are listed in Table 1

Table 1. Atomic parameters with their calculated standard deviations

Atom	$x/a$	$y/b$	$z/c$	$\sigma(r)$ (Å)	$B$	$\sigma(B)$
Cu	0.0000	0.0000	0.0000	—	4.23	0.22
N	0.0252	0.1842	0.1803	0.018 <sub>1</sub>	5.86	0.50
O(1)	0.2427	-0.1636	0.0882	0.014 <sub>2</sub>	6.60	0.44
O(2)	0.5765	-0.1175	0.2156	0.014 <sub>2</sub>	6.97	0.47
O(3)	0.2365	0.4025	-0.0791	0.014 <sub>4</sub>	8.41	0.41
C(1)	0.4073	-0.0527	0.1910	0.023 <sub>3</sub>	4.78	0.63
C(2)	0.3940	0.1556	0.2882	0.022 <sub>9</sub>	5.52	0.68
C(3)	0.1735	0.1283	0.3046	0.022 <sub>5</sub>	5.49	0.65
C(4)	0.1797	0.3090	0.4221	0.023 <sub>3</sub>	7.55	0.62

Table 2. Interatomic distances and angles within the crystal with their estimated standard deviations

(See also Figs. 3, 4 and 5)

Distance	$d$	$\sigma(d)$	Angle	$\sigma$	
Cu—O(1)	2.00 <sub>4</sub> Å	0.014 Å	O(3)—Cu—N	93° 32'	12'
Cu—N	1.99 <sub>2</sub>	0.018	O(1)—Cu—N	91° 53'	12'
Cu—O(3)	2.45 <sub>3</sub>	0.014	O(1)—Cu—O(3)	92° 58'	19'
O(1)—C(1)	1.30 <sub>3</sub>	0.027	O(1)—C(1)—O(2)	122° 42'	2° 10'
O(2)—C(1)	1.22 <sub>4</sub>	0.027	O(1)—C(1)—C(2)	120° 55'	2° 37'
C(1)—C(2)	1.49 <sub>1</sub>	0.033	O(2)—C(1)—C(2)	116° 57'	2° 28'
C(2)—C(3)	1.49 <sub>4</sub>	0.033	C(1)—C(2)—C(3)	113° 1'	1° 51'
C(3)—C(4)	1.49 <sub>1</sub>	0.033	C(2)—C(3)—C(4)	111° 8'	1° 46'
C(3)—N	1.43 <sub>6</sub>	0.030	C(4)—C(3)—N	108° 42'	2° 21'
O(3) ··· O(1)III	2.78 <sub>8</sub>	0.020	C(2)—C(3)—N	113° 35'	2° 38'
O(3) ··· O(2)II	2.73 <sub>2</sub>	0.020	I = $\bar{x}, \bar{y}, \bar{z}$		
O(3) ··· NIII	3.05 <sub>7</sub>	0.023	II = $x + 1, y, z$		
N ··· O(2)V	3.07 <sub>9</sub>	0.023	III = $\bar{x}, \bar{y} + 1, \bar{z}$		
N ··· O(1)I	2.77 <sub>9</sub>	0.023	IV = $x, y + 1, z$		
N ··· O(1)	2.87 <sub>2</sub>	0.023	V = $x - 1, y, z$		
O(3) ··· O(1)	3.24 <sub>7</sub>	0.020			

Table 3. *Table of observed and calculated structure factors for the non-zero reflexions*

<i>h k l</i>	$ F_o $	$F_c$	<i>h k l</i>	$ F_o $	$F_c$	<i>h k l</i>	$ F_o $	$F_c$	<i>h k l</i>	$ F_o $	$F_c$
02 00 00	125	130	+01 05 00	131	140	-07 00 03	79	79	+02 00 08	149	148
03 00 00	153	152	-01 05 00	100	114	+08 00 03	41	57	-02 00 08	125	112
04 00 00	241	230	+02 05 00	29	49	-08 00 03	74	60	+03 00 08	57	56
05 00 00	353	350	-02 05 00	132	128				-03 00 08	197	230
06 00 00	34	42	+03 05 00	123	140	00 00 04	221	195	+04 00 08	112	98
07 00 00	112	116	+04 05 00	48	56	+01 00 04	75	74	+05 00 08	33	21
08 00 00	69	68	-04 05 00	188	197	-01 00 04	102	105	-06 00 08	80	108
00 00 01	300	256	-05 05 00	119	101	+02 00 04	409	374	-07 00 08	34	57
			-06 05 00	46	44	-02 00 04	312	301	-08 00 08	43	71
00 01 00	562	571	-07 05 00	33	40	+03 00 04	161	169			
+01 01 00	99	-86	-08 05 00	34	37	-03 00 04	248	267	00 00 09	134	121
-01 01 00	345	311				+04 00 04	107	103	+01 00 09	173	143
+02 01 00	371	338	00 06 00	86	97	+05 00 04	139	136	+02 00 09	81	82
-02 01 00	444	451	+01 06 00	80	97	+06 00 04	107	75	-02 00 09	76	84
+03 01 00	110	102	-01 06 00	63	61	-06 00 04	56	65			
-03 01 00	404	408	-02 06 00	90	90	+07 00 04	101	83	+03 00 09	57	65
+04 01 00	157	169	-03 06 00	50	42	-07 00 04	79	91	+04 00 09	41	41
+05 01 00	230	213	-04 06 00	126	122	-08 00 04	33	52	-04 00 09	98	130
-05 01 00	235	225	-05 06 00	114	91				+05 00 09	41	41
+06 01 00	47	39	-06 06 00	73	63	00 00 05	185	188	-05 00 09	80	96
-06 01 00	129	121				+01 00 05	192	192	-07 00 09	53	67
+07 01 00	90	75	-02 07 00	48	45	-01 00 05	153	144			
-07 01 00	192	171	-03 07 00	34	41	+02 00 05	356	357	00 00 10	214	190
-08 01 00	114	96	-04 07 00	59	63	-02 00 05	473	484	+01 00 10	99	66
						+03 00 05	217	220	-01 00 10	80	79
00 02 00	129	129	+01 00 01	39	43	-04 00 05	71	79	-02 00 10	126	158
+01 02 00	202	188	-01 00 01	452	455	+04 00 05	99	109	+03 00 10	109	96
-01 02 00	21	-2	+02 00 01	100	97	+05 00 05	151	134	+04 00 10	63	51
+02 02 00	279	271	-02 00 01	220	239	-05 00 05	107	129	-05 00 10	82	90
-02 02 00	148	154	+03 00 01	242	236	+06 00 05	89	80	-07 00 10	70	89
-03 02 00	433	492	-03 00 01	348	348	-06 00 05	112	122			
+04 02 00	115	116	+04 00 01	343	320	+07 00 05	102	78	00 00 11	141	114
-04 02 00	109	109	-04 00 01	366	326	-07 00 05	103	121	+01 00 11	81	63
+05 02 00	120	129	+05 00 01	153	189	-08 00 05	33	20	-01 00 11	116	99
-05 02 00	84	69	-05 00 01	150	139				+02 00 11	78	75
+06 02 00	48	60	-06 00 01	96	95	00 00 06	89	95	-02 00 11	58	69
-06 02 00	91	71	+07 00 01	79	71	+01 00 06	302	293	+03 00 11	105	72
-07 02 00	135	137	-07 00 01	79	88	-01 00 06	109	128	-04 00 11	72	114
-08 02 00	124	103	+08 00 01	30	46	+02 00 06	280	266	-05 00 11	80	83
			-08 00 01	123	127	-02 00 06	359	424			
00 03 00	40	-3				+03 00 06	216	190	00 00 12	79	77
+01 03 00	117	97	00 00 02	52	9	-03 00 06	235	217	+01 00 12	96	75
-01 03 00	261	261	+01 00 02	472	534	+04 00 06	144	159	-01 00 12	140	125
+02 03 00	122	135	-01 00 02	294	299	-05 00 06	80	80	+02 00 12	78	48
-02 03 00	181	150	+02 00 02	30	24	-05 00 06	147	127	-03 00 12	79	78
+03 03 00	128	122	-02 00 02	115	-117	+06 00 06	104	88	-04 00 12	79	100
-03 03 00	114	88	+03 00 02	129	129	-06 00 06	138	165	-05 00 12	75	82
+04 03 00	116	108	-03 00 02	144	148	+07 00 06	58	56	-06 00 12	82	75
-04 03 00	59	65	+04 00 02	171	179	-07 00 06	112	121			
+05 03 00	47	44	-04 00 02	460	445	-08 00 06	33	43	00 00 13	64	54
-05 03 00	125	106	-05 00 02	106	121				+01 00 13	41	41
+06 03 00	61	76	+06 00 02	112	105	00 00 07	69	69	-01 00 13	74	73
-06 03 00	133	120	-06 00 02	136	142	+01 00 07	150	162	-04 00 13	68	61
-07 03 00	56	56	+07 00 02	34	48	-01 00 07	253	253	-05 00 13	51	57
			+08 00 02	61	60	+02 00 07	151	150			
+01 04 00	129	160	-08 00 02	72	80	-02 00 07	193	193			
-01 04 00	177	174				+03 00 07	56	52	00 +01 01	234	221
+02 04 00	107	107	00 00 03	112	116	-03 00 07	201	227	00 -01 01	361	370
-02 04 00	256	238	+01 00 03	199	228	+04 00 07	80	62	00 +02 01	262	249
+03 04 00	140	164	-01 00 03	319	307	-04 00 07	77	63	00 -02 01	323	297
-03 04 00	88	91	+02 00 03	58	38	+05 00 07	78	69	00 +03 01	222	229
+04 04 00	64	77	-02 00 03	98	92	-05 00 07	78	100	00 -03 01	48	-26
-04 04 00	124	103	+03 00 03	134	122	+06 00 07	110	74	00 +04 01	127	153
+05 04 00	33	42	-03 00 03	93	71	-06 00 07	162	195	00 -04 01	53	36
-05 04 00	47	40	+04 00 03	127	134	-07 00 07	43	87	00 +05 01	219	190
+06 04 00	31	69	-04 00 03	38	78	-08 00 07	49	84	00 -05 01	112	106
-06 04 00	113	95	-05 00 03	129	124				00 +06 01	74	76
-07 04 00	67	68	+06 00 03	148	136	00 00 08	40	-38	00 -06 01	53	53
			-06 00 03	111	129	+01 00 08	98	75			
00 05 00	93	110	+07 00 02	41	42	-01 00 08	161	162	00 +01 02	275	233

Table 3 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$F_c$
00 -01 02	338	-376			00 -05 03	110	125			00 -02 08	206	125			00 -01 09	101	125		
00 +02 02	281	277			00 +06 03	87	76			00 +03 08	94	87			00 -01 09	119	122		
00 -02 02	136	140			00 -06 03	51	61			00 -03 08	129	165			00 +02 09	111	109		
00 +03 02	389	427								00 +04 08	114	122			00 -02 09	086	103		
00 -03 02	195	170			00 +01 05	332	345			00 +05 08	112	74			00 +03 09	54	49		
00 +04 02	175	188			00 -01 05	165	182								00 +04 09	51	48		
00 -04 02	155	182			00 +02 05	266	247			00 +01 07	33	31			00 -01 10	99	132		
00 +05 02	78	89			00 -02 05	134	142			00 -01 07	239	228			00 -01 10	139	152		
00 -05 02	149	144			00 +03 05	292	256			00 +02 07	35	25			00 +02 10	99	111		
00 +06 02	41	40			00 -03 05	180	177			00 -02 07	175	158							
00 -06 02	74	74			00 +04 05	127	107			00 +03 07	130	127							
					00 -04 05	208	211			00 -03 07	112	134			00 +01 11	58	84		
00 +01 03	277	261			00 +05 05	54	33			00 +04 07	135	168			00 -01 11	63	86		
00 -01 03	59	30			00 -05 05	68	73			00 +05 07	86	89							
00 +02 03	218	226			00 +06 05	58	38												
00 -02 03	186	167								00 +01 08	36	-50							
00 +03 03	177	190			00 -01 06	144	165			00 -01 08	238	215							
00 -03 03	132	130			00 +02 06	264	267			00 +02 08	53	63							
00 -04 03	264	297			00 -02 06	115	83												

together with their calculated standard deviations. Table 2 gives the values of various interatomic distances and angles within the crystal, also with their calculated standard deviations. Table 3 lists the values of  $|F_o|$  and  $F_c$  for the measured non-zero reflexions. The value of  $R$  for the reflexions listed is 0.11.

### Description of the structure

A representation of the structure of one molecule of the complex is shown in Fig. 2. Each copper atom is associated with two molecules of  $\beta$ -aminobutyric acid and two molecules of water. The coordination of atoms around the copper is octahedral. The mid-plane of the octahedron is defined by Cu, and O(1) and N of one acid residue. The remaining two apices of the octahedron are each occupied by a water molecule. All distances and angles within the coordination octahedron are normal, being comparable to those found in similar molecules (Orgel & Dunitz, 1957). The observed distortions in the octahedron are in accord with those expected on the basis of the theoretical considerations put forward by Orgel (1956) on the basis of the Jahn-Teller effect.

Other bond lengths and angles within the molecule are also normal, none of the observed bond lengths being significantly different from those commonly accepted (Sutton, 1958). The four carbon atoms of one acid residue deviate from the plane of equation

$$0.1307X - 0.7042Y + 0.6972Z - 1.7233 = 0$$

by amounts ranging from 0.06 to 0.07 Å ( $\sigma(r)C = 0.02_3$  Å). The torsion angle C(1)-C(2).C(3)-N is  $66^\circ 49'$ , establishing the *gauche*-configuration of the  $\beta$ -aminobutyric acid residue. This configuration is similar to that found for copper(II)-*bis*-( $\beta$ -alanine) hexahydrate (Tomita, 1960b).

The inter-molecular forces are of two kinds. In the  $c$  direction, as can be seen from Fig. 3, normal van der

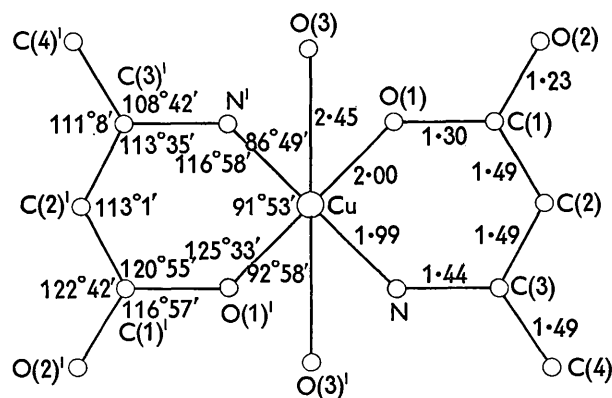


Fig. 2. Representation of one molecule of *bis*-( $\beta$ -aminobutyrate)-copper (II) dihydrate showing bond lengths and angles.

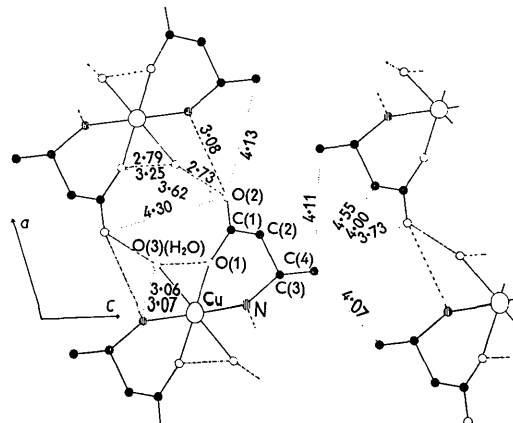


Fig. 3. Arrangement of molecules in the (010) projection showing *inter*-molecular approaches.

— Chemical bonds, - - - - - possible hydrogen bonds, . . . . . van der Waal's contacts.

Waal's forces operate, whilst in the  $a$  and  $b$  directions the structure is held together in addition by means of

hydrogen bonds. A word of explanation is necessary in connection with the hydrogen bonding. The nitrogen atom of one molecule makes two short contacts with atoms in neighbouring molecules:  $N \cdots O(2) (x-1, y, z) = 3.08 \text{ \AA}$ , and  $N \cdots O(3) (\bar{x}, \bar{y}+1, \bar{z}) = 3.06 \text{ \AA}$ . Fig. 4, however, shows that only  $N \cdots O(2)$  can be a feasible hydrogen bond involving a hydrogen atom of the amino group if the configuration of the bonds about the nitrogen atom is held to be tetrahedral, the distortion involved in forming  $N \cdots O(3)$  being prohibitive.

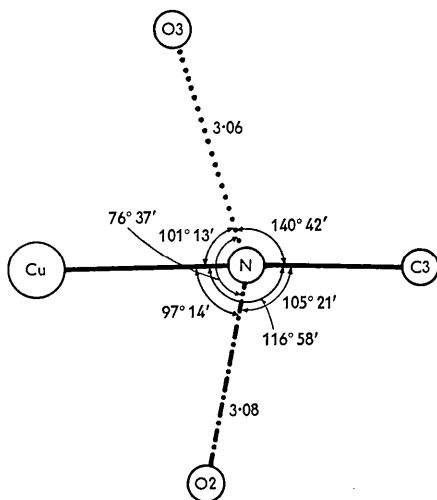


Fig. 4. Arrangement of atoms around the  $-\text{NH}_2$  group. Bond types as indicated in Fig. 3.

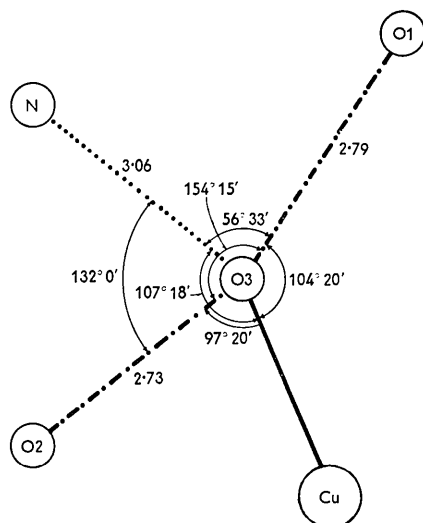


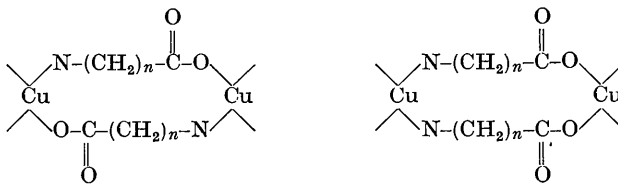
Fig. 5. Arrangement of atoms about the water molecule. Bond types as in Fig. 3.

The hydrogen bond system involving the water molecule is rather interesting. Here there are three short approaches of neighbouring molecules to the water molecule:  $O(3) \cdots N (\bar{x}, \bar{y}+1, \bar{z}) = 3.06 \text{ \AA}$  (the

same distance as discussed above),  $O(3) \cdots O(1) (x, y+1, z) = 2.79 \text{ \AA}$ , and  $O(3) \cdots O(2) (x+1, y, z) = 2.73 \text{ \AA}$ . Fig. 5 shows the arrangement of these various atoms relative to the bond  $\text{Cu}-\text{O}(3)$ . Assuming the distribution of orbitals about the oxygen atom of the water molecule to be tetrahedral, it is apparent that any one of these approaches might represent a hydrogen bond, but that it is impossible to form all three bonds, or indeed any two, simultaneously. A bond to the amino group involving donation of a hydrogen atom from the water molecule may be ruled out owing to the steric repulsion offered to such a hydrogen atom by the hydrogen of the amino group. We therefore assume that the water molecule is so arranged in the crystal that each of the bonds of type  $\text{O}-\text{H} \cdots \text{O}$  is formed with a probability  $\frac{1}{2}$ , or that it is free to rotate about the axis  $\text{Cu}-\text{O}$  and to achieve the same result on a time average basis. This latter alternative is perhaps the more likely when one notes that the value of the exponent  $B$  for the water molecule is 8.4, significantly higher than the corresponding values for the other oxygen atoms in the molecule, 6.6 and 7.0, and that the crystal also loses water readily on exposure to the air confirming that the water molecule is but loosely bound in the crystal.

## Discussion

In forming complexes with  $\alpha$ -amino acids, the cupric ion is commonly found to participate in the formation of five-membered ring systems. In the case of  $\omega$ -amino acids, as the distance between the coordinating atoms in the acid residues increases, the ease with which complex formation occurs decreases, steric influences presumably inhibiting the formation of the larger rings. This analysis of the structure of copper (II) *bis*-( $\beta$ -aminobutyrate) dihydrate shows that, as in the case of copper (II) *bis*-( $\beta$ -alanine), the cupric ion may readily take part in the formation of a six-membered ring. We are at present examining the crystal structure of copper (II) *bis*-( $\gamma$ -aminobutyrate) dihydrate where a seven-membered ring system might be expected to occur. It is of some interest to discover whether the still larger rings, such as the eight-membered ring suggested by Nakahara *et al.* (1956) as occurring in copper (II) *bis*-( $\delta$ -aminovalerate), or the nine-membered ring proposed by Pfeiffer *et al.* (1952) for copper (II) *bis*-(hexamethylenediamine) perchlorate, do in fact occur, or whether the structure will be of the types shown below



Experiments designed to decide this question are planned.

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## A Mathematical Technique for the Precision Determination of Lattice Parameters\*

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A computer code has been developed for the precision determination of crystal lattice parameters, using the Hess method as a basis with the following modifications: (1) No approximations are made in the solution of the observation equation and (2) The method is extended to the hexagonal and orthorhombic crystal systems and to additional extrapolation functions. In the majority of the determinations, with randomly selected materials, the Hess approximation gave results comparable with the exact technique; however, because of certain restrictions the exact technique is recommended.

### Introduction

The precision determination of lattice parameters is a powerful technique for basic studies of the solid state. Examples include the precise measurement of bond distances, true densities, thermal expansions, compressibilities, and solid-solution effects.

Graphical extrapolation methods for the elimination of systematic errors in lattice-parameter measurements have been treated by many investigators. Their correct usage has been discussed by Kempter (1959), and the most useful extrapolation functions tabulated as a function of Bragg angle.

Analytical methods have been discussed by Cohen (1935, 1936*a*, 1936*b*) and Hess (1951). These methods are more readily applicable than extrapolation methods to non-cubic crystal systems, but the complexity of the calculations necessitates the use of a computing

machine. Of the two analytical methods, the Hess method is preferable since it assigns statistical weights to the observed points. This weighting is a necessity since the weighting function increases tremendously as the Bragg angle approaches  $90^\circ$ .

For the cubic system, using a Debye-Scherrer or symmetrical back-reflection focusing camera, Hess started his fitting procedure with the following general equation expressing the function  $F$ .

$$F = A_0\alpha + K_0\delta - \gamma, \quad (1)$$

where

$$\begin{aligned} A_0 &= 1/a_0^2; & a_0 &= \text{the lattice parameter;} \\ \alpha &= \frac{1}{2}\lambda^2 n^2 (h^2 + k^2 + l^2); & \lambda &= \text{wave length,} \\ & & n &= \text{an integer,} \\ & & hkl &= \text{Miller indices;} \end{aligned}$$

$K_0$  = the 'drift constant';

$$\delta = \Phi \sin \Phi, \text{ the error term, which assumes } \Delta\Phi \propto \Phi, \text{ where } \Phi = \pi - 2\theta;$$

$$\gamma = 1 + \cos \Phi = 2 \sin^2 \theta.$$

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