According to Ramachandran & Lakshminarayanan (1966), the γ atoms‡ in amino acids or peptides can occupy one of the three positions, (I), (II) and (III), as a result of the internal rotation of the C_α–C_β bond, where (I) is the *trans* position to the α-N atom, (II) is that to C′‡ and (III) is that to α-H. They found some systematic relations between the positions of the γ atoms and the properties of the relevant amino acids. In arginine the C_γ atoms occupy all three positions (Ramachandran, Mazumdar, Venkatesan & Lakshminarayanan, 1966). It may be of some significance to extend these considerations to ornithine and lysine. The C_γ atom of ornithine in the hydrochloride is on (I), while the C_γ atoms of the ornithine residues in ferrichrome-A occupy positions (II) and (III). Since lysine has a number of common characteristics with ornithine and arginine, it may be expected that all these amino acids in the crystals can take any of the three conformations according to the three positions of the C_γ atom. These conformations seem to depend on the intermolecular forces, especially on those due to hydrogen bonds. Although there are not enough examples, there seems to exist a simple relation between the molecular conformations and the other components in the crystals. In the hydrochlorides (ornithine.HCl and arginine.HCl), C_γ is on (I), and α-N is on the plane of the side chain; the deviation of the α-N atom from the plane of the carboxyl group is one of the biggest among the amino acids so far investigated. In the hydrate crystal (arginine.$2H_2O$) C_γ is on (III). In the crystals of hydrochloride hydrates (lysine.HCl.$2H_2O$ and arginine.HCl.(H_2O) C_γ is on II), and C′ is on the plane of the side chain.

The authors are indebted to Dr T. Takano and all the staff in this laboratory for their kind cooperation. They thank the Computing Center of the University of Tokyo and 'UNICON' for making the HITAC 5020 and IBM 7090 computers available to them.

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‡ C′, C_α, C_β and C_γ are respectively C(1), C(2), C(3) and C(4) in the other paragraphs.

Acta Cryst. (1967). **22**, 870

Crystal and Molecular Structure of *N*-Salicylideneglycinatoaquocopper(II) Hemihydrate

By T. Ueki, T. Ashida, Y. Sasada* and M. Kakudo

Institute for Protein Research, Osaka University, Osaka, Japan

(*Received* 19 *October* 1966)

Crystals of *N*-salicylideneglycinatoaquocopper(II) hemihydrate, $[Cu(C_9H_7NO_3.H_2O)].\frac{1}{2}H_2O$, are monoclinic, space group $C2/c$, with eight formula units in the unit cell with dimensions $a = 17{\cdot}16$, $b = 6{\cdot}84$, $c = 17{\cdot}57$ Å, $\beta = 111{\cdot}29°$. A three-dimensional analysis has been performed, using a complete set of diffractometer data. The final R index for 1881 'observed' reflections is 0·069. The molecule is not planar. Rather, it consists of two planes, one formed by salicylaldiminatocopper groups and the other formed by glycinatocopper groups. The coordination of copper ion is square pyramidal and the distances of copper environment are: Cu–O 1·953, 1·928, Cu–N 1·949, Cu–OH_2 2·016 and Cu–O″ (the bond to the carboxyl oxygen of the adjacent molecule) 2·334 Å.

The molecules are bound together by hydrogen bonds, the coordination bond of copper ion to oxygen atoms in neighboring molecules, and unusually close intermolecular contacts.

Introduction

Some evidence suggested that the chelation of the Schiff bases to metal ions may play an important role in the nonenzymatic transamination reaction of the Schiff bases prepared from vitamin B_6 and amino acids. These bases are of much interest as model compounds for the transaminase enzymes (Metzler & Snell, 1952; Metzler, Ikawa & Snell, 1954; Longenecker & Snell, 1957; Metzler, Longenecker & Snell, 1954). It was recently proved that the coordination of copper ion with the Schiff base derived from salicylaldehyde and glycine results in stabilization of the double bond,

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* Present address: Faculty of Science, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo, Japan.

$\begin{array}{l}\diagdown\\ \;\mathrm{Cu=N-},\\ \diagup\end{array}$ under conditions that would promote its rupture in the absence of the metal ion (Eichhorn & Marchand, 1956).

Recently, a molecular and crystal structure of Mn(II)–pyridoxylidenevaline chelate was established by the X-ray diffraction method (Willstadter, Hamor & Hoard, 1963). However, the structure concluded was different from that proposed by a spectroscopic investigation (Christensen, 1957).

A serial study of these model compounds by X-ray diffraction method was planned in this laboratory and a structure determination of *N*-salicylideneglycinato-aquocopper(II) hemihydrate,

$$\mathrm{Cu(C_9H_7NO_3.H_2O).\tfrac{1}{2}H_2O},$$

is dealt with in the present paper. The result obtained confirmed the structure proposed on the basis of spectroscopic and other techniques (Nakahara, 1959; Eichhorn & Marchand, 1956; Christensen, 1957).

Experimental

The crystals were prepared and kindly supplied by Professor A. Nakahara of this university. They are dark green prisms. A crystal with dimensions $0{\cdot}2\times0{\cdot}2\times0{\cdot}1$ mm was selected and mounted on a goniometer head with its *b* axis vertical. Oscillation and Weissenberg photographs were taken with Cu $K\alpha$ radiation to determine the approximate cell dimensions and systematic absences. The crystal was then set on a goniostat on a General Electric XRD-5 apparatus equipped with a krypton-filled proportional counter. Cell dimensions were redetermined by the goniostat, using Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å). Intensities were measured for each independent reflection with $\sin\theta/\lambda$ less than 0·639 ($2\theta\le54°$) by the stationary-crystal stationary-counter technique. The fixed time method was applied with 20 seconds counting time for each reflection.

A total of 2093 independent reflections were measured exclusive of space group extinctions, among which 212 were recorded as zero. The observed intensities ranged from 5451 to 0·5 c.p.s. No correction was made for the absorption effect, although the linear absorption coefficient is estimated to be $\mu=22$ cm^{-1} for Mo $K\alpha$ radiation and $\mu R=0{\cdot}4$ or less. The extinction effect was not serious and the correction for it was neglected. Thus, these are the limiting factors in the accuracy of the intensity data. Calculations for the goniostat setting and usual Lorentz and polarization corrections were made on an NEAC-2101 computer with a program written by one of us (T. Ueki).

Unit cell and space group

Crystals of *N*-salicylideneglycinatoaquocopper(II) hemihydrate are monoclinic with

$$\begin{aligned} a&=17{\cdot}16\pm0{\cdot}03\ \text{Å}\\ b&=6{\cdot}84\pm0{\cdot}02\\ c&=17{\cdot}57\pm0{\cdot}01\\ \beta&=111{\cdot}29\pm0{\cdot}05°\\ V&=1920{\cdot}2\ \text{Å}^3\,. \end{aligned}$$

With eight formula units in a unit cell the density was calculated to be 1·85 g.cm^{-3}, which is to be compared with the value, 1·88 g.cm^{-3}, obtained by the flotation method. The systematic absences are:

$$hkl \text{ absent if } h+k\ne2n;$$
$$h0l \text{ absent if } l\ne2n\,.$$

Thus, the space group is either $C2/c$ or Cc. No pyroelectricity was observed and, further, a statistical $N(z)$ test applied to all the three-dimensional data indicated conclusively the existence of a center of symmetry in the crystal (Howell, Phillips & Rogers, 1950). Therefore, the analysis was started by assuming the centrosymmetric space group, $C2/c$. This assumption was later justified by the success of the structure determination.

Determination of the structure

From the space group assumed, all the atoms of one formula unit were expected to be at the general positions $8(f)$: $(000;\ \tfrac{1}{2},\tfrac{1}{2},0)\pm(x,y,z;\ -x,y,\tfrac{1}{2}-z)$, except for the non-coordinating water molecules, which should be at the fourfold positions $4(e)$: $(000;\ \tfrac{1}{2},\tfrac{1}{2},0)\pm(0,y,\tfrac{1}{4})$.

From a three-dimensional Patterson function the copper ion was easily located at $x=0{\cdot}12$, $y=0{\cdot}10$ and $z=0{\cdot}20$. An electron density function was calculated with the phases of the copper ion, and the Fourier maps showed all the atoms in the *N*-salicylideneglycinatoaquocopper(II). In addition, two independent peaks were also observed at the $4(e)$ position, which may correspond to the non-coordinating water molecule. The first peak located at $y=0{\cdot}42$ was tentatively identified as the water molecule since the second one was far lower than the first. Using these atomic positions found in the maps a structure factor calculation was carried out with the copper ion and fifteen non-hydrogen light atoms. At this stage the discrepancy index, $R=\Sigma\,\|F_o|-|F_c\|/\Sigma\,|F_o|$, was 0·35. The corresponding three-dimensional Fourier maps, however, revealed that the assignment of the first peak to a water molecule was incorrect and the non-coordinating water molecule, $W(2)$, is actually located at $y=0{\cdot}60$ corresponding to the second peak in the first Fourier maps. Another cycle of structure factor and electron density calculation confirmed the position of the water molecule $W(2)$ and gave the correct structure of the crystal.

The R index was 0·22 at this stage. Successive block-diagonal least-squares refinements resulted in $R=0{\cdot}093$ after three cycles, with isotropic temperature factors of the form $\exp[-B(\sin\theta/\lambda)^2]$ for all the non-hydrogen light atoms, and anisotropic temperature factors for copper ion of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. Further refinement by the block-diagonal least-squares method with all the intensity data gave $R=0·075$ after three cycles, in which all the atoms were treated as anisotropic.

For the oxygen atom of the water molecule *W*(2) on the twofold axis, the condition $\beta_{12}=\beta_{23}=0$ was put in the least-squares process. At this stage all of ten independent hydrogen atoms appeared in the difference Fourier maps. A final least-squares refinement, giving isotropic temperature factors to hydrogen atoms, gave the final values of atomic parameters for all the atoms. After three cycles the R index was 0·069. The final atomic parameters are listed in Table 1 and in Table 2 with their estimated standard deviations. The observed and calculated structure factors are listed in Table 3.

A block-diagonal least-squares program and Fourier summation program were written by us (T. Ashida and

Table 1. *Positional parameters of atoms and estimated standard deviations* (*e.s.d.'s in* Å)

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Cu	0·12172	0·09512	0·20439	0·00094	0·00108	0·00094
O(1)	0·0068	0·1730	0·1500	0·0055	0·0062	0·0054
O(2)	0·2287	0·9576	0·2457	0·0054	0·0066	0·0057
O(3)	0·3421	0·8799	0·2162	0·0058	0·0068	0·0061
W(1)*	0·0943	0·9736	0·2962	0·0059	0·0065	0·0058
W(2)*	0·0000	0·5964	0·2500	—	0·0106	—
N	0·1530	0·1430	0·1099	0·0066	0·0072	0·0068
C(1)	0·2743	0·9673	0·2018	0·0078	0·0083	0·0077
C(2)	0·2400	0·0987	0·1262	0·0088	0·0088	0·0093
C(3)	0·1025	0·1887	0·0382	0·0082	0·0084	0·0080
C(4)	0·0141	0·2352	0·0168	0·0078	0·0084	0·0075
C(5)	0·4704	0·2073	0·4346	0·0089	0·0091	0·0082
C(6)	0·3863	0·1570	0·4081	0·0094	0·0093	0·0085
C(7)	0·3446	0·1582	0·4620	0·0094	0·0092	0·0089
C(8)	0·1133	0·2840	0·4563	0·0082	0·0097	0·0085
C(9)	0·0282	0·2287	0·4280	0·0081	0·0082	0·0080
H(1)	0·048	0·060	0·319	0·12	0·12	0·12
H(2)	0·089	0·857	0·299	0·12	0·13	0·12
H(3)	0·047	0·499	0·251	0·10	0·11	0·11
H(4)	0·285	0·204	0·140	0·11	0·11	0·11
H(5)	0·246	0·012	0·077	0·10	0·11	0·10
H(6)	0·130	0·211	−0·007	0·10	0·10	0·10
H(7)	−0·001	0·296	−0·103	0·10	0·10	0·10
H(8)	−0·133	0·384	−0·139	0·11	0·12	0·11
H(9)	−0·205	0·417	−0·045	0·09	0·09	0·09
H(10)	−0·141	0·263	0·078	0·11	0·11	0·11

* *W*(1) represents the oxygen atom of the coordinated water molecule, and *W*(2) that of the free water molecule.

Table 2. *Thermal parameters*

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0·00157	0·01825	0·00156	0·00107	0·00121	0·00061
O(1)	0·0019	0·0195	0·0016	0·0018	0·0010	0·0020
O(2)	0·0018	0·0224	0·0020	0·0009	0·0016	0·0008
O(3)	0·0019	0·0228	0·0024	0·0040	0·0014	0·0021
W(1)	0·0025	0·0202	0·0021	0·0009	0·0024	0·0031
W(2)	0·0043	0·0187	0·0057	—	0·0055	—
N	0·0018	0·0169	0·0021	0·0013	0·0017	0·0008
C(1)	0·0019	0·0144	0·0017	−0·0004	0·0012	0·0004
C(2)	0·0024	0·0140	0·0030	0·0013	0·0019	0·0006
C(3)	0·0022	0·0145	0·0019	0·0010	0·0014	0·0038
C(4)	0·0019	0·0155	0·0016	0·0002	0·0009	−0·0006
C(5)	0·0028	0·0172	0·0017	−0·0012	0·0011	−0·0025
C(6)	0·0031	0·0164	0·0018	0·0018	0·0003	0·0003
C(7)	0·0030	0·0151	0·0022	−0·0008	0·0001	0·0008
C(8)	0·0017	0·0214	0·0021	0·0016	0·0003	0·0020
C(9)	0·0021	0·0127	0·0020	0·0011	0·0010	0·0011
H(1)	2·8					
H(2)	3·3					
H(3)	2·1					
H(4)	2·0					
H(5)	1·2					
H(6)	1·1					
H(7)	1·0					
H(8)	2·1					
H(9)	0·3					
H(10)	1·9					

Thermal parameters for hydrogen atoms are isotropic B values in Å^2.

Table 3. *Observed and calculated structure factors* (*each multiplied by* 5)

L	FO	FC
H,K=	0	0
2	199	-183
4	164	161
6	77	-65
8	105	-105
10	114	113
12	150	-151
14	76	64
16	35	-20
18	53	-45
20	58	62
H,K=	2	0
0	71	65
2	52	-47
4	27	17
6	36	-41
8	20	18
10	54	-53
12	30	-30
14	83	91
16	58	-57
18	46	48
20	17	-14
-2	257	278
-4	35	-25
-6	121	114
-8	129	-126
-10	17	16
-12	94	94
-14	17	-13
-16	36	40
-18	55	-56
-20	11	11
H,K=	4	0
0	153	-155
2	102	100
4	55	-51
6	51	-45
8	151	146
10	166	-158
12	150	151
14	27	-24
16	31	27
18	16	13
-2	73	68
-4	128	-126
-6	8	7
-8	183	179
-10	216	-215
-12	175	183
-14	24	-26
-16	78	78
-18	0	2
-20	43	-44
-22	17	20
H,K=	6	0
0	49	27
2	162	166
4	147	-150
6	124	121
8	81	-81
10	15	-11
12	69	67
14	35	-37
16	37	41
-2	47	-48
-4	110	110
-6	124	-128
-8	190	188
-10	52	-57
-12	38	-26
-14	91	89
-16	103	-106
-18	106	104
-20	36	-39
-22	8	6
H,K=	8	0
0	300	315
2	129	-133
4	40	37
6	19	18
8	79	-76
10	61	61
12	86	-82
14	40	43
16	14	-10
-2	89	-95
-4	63	69
-6	8	1
-8	29	-9
-10	89	89
-12	69	-70
-14	33	35
-16	19	-12
-18	54	-52
-20	76	75
-22	29	-33
H,K=	10	0
0	65	44
2	96	-98
4	131	132
6	53	-55
8	43	43
10	26	-25
12	17	-18
14	34	30
-2	82	80
-4	105	-107
-6	171	175
-8	145	-144
-10	60	56
-12	8	7
-14	39	-30
-16	65	65
-18	81	-82
-20	69	67
-22	8	1
H,K=	12	0
0	71	-60
2	42	40
4	14	-4
6	26	-25
8	75	74
10	55	-55
12	31	27
-2	63	67
-4	98	-85
-6	55	55
-8	104	105
-10	98	-92
-12	71	70
-14	46	-45
-16	38	36
-18	13	2
-20	25	-27
-22	34	38
H,K=	14	0
0	44	-30
2	26	21
4	107	-106
6	98	92
8	45	-44
10	14	-10
-2	49	-52
-4	121	124
-6	114	-119
-8	184	187
-10	26	-32
-12	19	17
-14	53	53
-16	99	-98
-18	78	78
-20	30	-33
H,K=	16	0
0	37	26
2	40	-38
4	10	-6
6	29	31
8	34	-36
-2	62	-62
-4	21	23
-6	25	24
-8	15	12
-10	46	45
-12	39	-42
-14	52	53
-16	24	-19
-18	18	-17
-20	39	42
H,K=	18	0
0	47	47
2	64	-62
4	87	75
-2	0	4
-4	57	-57
-6	72	72
-8	60	-60
-10	35	37
-12	28	-21
-14	37	-37
-16	60	59
-18	48	-53
H,K=	20	0
0	40	-38
-2	57	55
-4	52	-50
-6	18	24
-8	38	31
-10	34	-43
-12	44	45
-14	40	-42
H,K=	1	1
0	149	144
1	137	-125
2	248	-239
3	93	86
4	151	143
5	29	-32
6	25	-26
7	87	-77
8	32	29
9	46	-39
10	30	32
11	70	-67
12	87	-83
13	9	67
14	85	84
15	65	-62
16	41	-40
17	20	16
18	11	4
19	0	-1
20	14	12
-1	138	131
-2	7	8
-3	97	90
-4	135	-129
-5	42	-37
-6	167	162
-7	72	73
-8	169	-170
-9	55	-53
-10	153	150
-11	54	54
-12	67	-65
-13	18	-4
-14	12	-4
-15	6	-2
-16	18	33
-17	14	16
-18	45	-47
-19	29	-29
-20	49	51
-21	30	31
H,K=	3	1
0	93	-80
1	120	114
2	119	116
3	26	-25
4	8	-0
5	84	-82
6	40	-40
7	14	18
8	38	37
9	113	-109
10	72	-71
11	61	59
12	24	22
13	20	-19
14	17	15
15	37	-35
16	40	-40
17	19	18
18	39	37
19	14	-20
-1	66	-61
-2	98	81
-3	151	146
-4	88	-84
-5	204	-202
-6	112	111
-7	63	60
-8	4	-1
-9	32	32
-10	54	-51
-11	75	-72
-12	56	56
-13	92	92
-14	33	-34
-15	11	-7
-16	11	7
-17	53	49
-18	22	-20
-19	19	-17
-20	8	-8
-21	14	-10
H,K=	5	1
0	146	-148
1	46	43
2	174	173
3	97	-95
4	170	-168
5	80	78
6	51	55
7	21	-19
8	24	22
9	15	-12
10	82	-82
11	57	58
12	93	95
13	42	-42
14	64	-63
15	13	9
16	29	31
17	11	-11
18	8	-9
-1	41	-36
-2	102	100
-3	17	14
-4	17	-16
-5	105	-99
-6	137	-134
-7	128	-124
-8	219	216
-9	41	43
-10	150	-150
-11	16	-16
-12	97	101
-13	31	32
-14	12	-16
-15	74	76
-16	32	-31
-17	10	2
-18	52	56
-19	46	41
-20	65	-65
-21	20	-18
-22	28	39
H,K=	7	1
0	71	26
1	59	-61
2	35	30
3	16	-16
4	84	-81
5	74	75
6	114	118
7	85	-90
8	76	-69
9	29	28
10	75	73
11	47	-44
12	30	-25
13	7	5
14	13	-12
15	19	15
16	20	21
17	19	-17
-1	145	148
-2	69	-74
-3	79	-84
-4	8	9
-5	57	64
-6	27	-30
-7	96	-35
-8	38	-36
-9	18	-13
-10	61	60
-11	21	24
-12	72	-72
-13	55	-56
-14	101	99
-15	57	97
-16	54	-54
-17	24	-26
-18	18	18
-19	7	7
-20	15	16
-21	8	9
-22	18	-22
H,K=	9	1
0	140	140
1	36	-42
2	168	-168
3	54	47
4	139	142
5	41	-44
6	38	-39
7	95	-91
8	26	21
9	43	-40
10	10	3
11	42	-38
12	49	-54
13	42	43
14	44	49
15	16	-15
-1	52	54
-2	38	-42
-3	63	57
-4	28	-28
-5	34	-35
-6	89	90
-7	80	81
-8	124	-126
-9	57	-54
-10	90	92
-11	43	39
-12	61	-57
-13	24	-24
-14	9	3
-15	6	4
-16	41	38
-17	25	24
-18	58	-62
-19	42	-48
-20	50	54
-21	20	18
-22	31	-32
H,K=	11	1
0	37	-38
1	29	31
2	24	20
3	6	5
4	34	36
5	94	-90
6	45	-46
7	0	8
8	10	3
9	64	-62
10	18	-18
11	31	35
12	11	-7
13	0	-3
-1	29	-30
-2	61	65
-3	73	78
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-19	11	-15
H,K=	12	4
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1	57	61
2	35	-34
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4	18	9
5	0	-7
6	26	27
7	33	35
8	37	-33
9	21	-22
10	28	29
-1	35	-35
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H,K=	14	4
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3	32	-33
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-9	17	-19
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H,K=	18	4
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13	7	-6
14	46	-41
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5	33	-38
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7	35	38
8	80	-80
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10	27	25
11	16	-13
12	15	-15
13	7	-3
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8	67	63
9	7	-3
10	43	-40
11	18	15
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7	13	-9
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9	0	-12
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12	26	25
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4	34	30
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H,K=	9	6
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9	11	-14
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5	0	-4
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8	8	-6
9	29	28
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H,K=	7	7
0	13	-8
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2	22	-24
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4	11	-9
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H,K=	9	7
0	19	-17
1	37	30
2	0	6
3	20	-22
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H,K=	11	7
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-5	20	-22
H,K=	0	8
0	8	3
1	52	40
2	8	-3
3	26	-30
4	0	-0
5	14	10
6	0	-2
7	11	9
8	0	2
H,K=	2	8
0	0	-2
1	11	-2
2	0	4
3	11	-9
4	0	10
5	49	42
6	8	6
7	17	-14
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-7	29	-24
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H,K=	4	8
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3	38	32
4	14	9
5	19	15
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-2	0	8
-3	20	-29
-4	0	-0
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-6	0	3
-7	18	15
-8	0	-1
-9	25	-24
H,K=	6	8
0	0	9
1	22	-18
2	0	5
3	28	24
-1	8	10
-2	0	-1
-3	0	17
-4	0	8
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-6	0	-2
-7	29	27
-8	14	7
H,K=	8	8
0	0	0
-1	36	-32
-2	0	0
-3	14	20
-4	0	3
-5	0	2
-6	0	-0

Y. Sasada) for the HITAC-5020 computer. In the former, $\Sigma w(k|F_o|-|F_c|)^2$ was minimized with unit weight assigned to all the reflections in this analysis. Distances, angles and least-squares planes were calculated with the program written by one of us (T. Ashida) for the HITAC-5020 computer. Atomic scattering factors for copper ion and for neutral C, N, O, H atoms were taken from *International Tables for X-ray Crystallography* (1962). A correction for the anomalous dispersion of copper ion, $\Delta f' = 0{\cdot}3$, was included in the structure factor calculations (Dauben & Templeton, 1955).

Description of the structure and discussion

Bond lengths and angles in the molecule of *N*-salicylideneglycinatoaquocopper(II) are shown in Figs. 1 and 2 and also listed in Table 4 with their standard deviations.

The molecule is not completely coplanar and several atoms in the molecule deviate from the plane by more than 0·3 Å. The molecule can be described approximately by two planar groups, one being the salicylaldiminatocopper group which forms the plane *P*(4) in

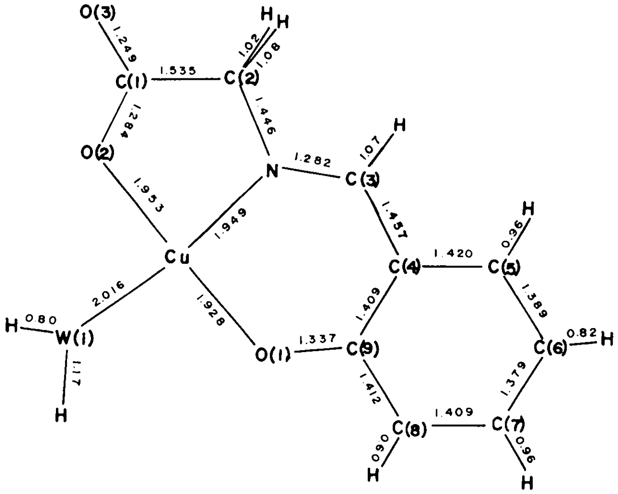

Fig. 1. Bond lengths in the *N*-salicylideneglycinatoaquocopper(II) molecule.

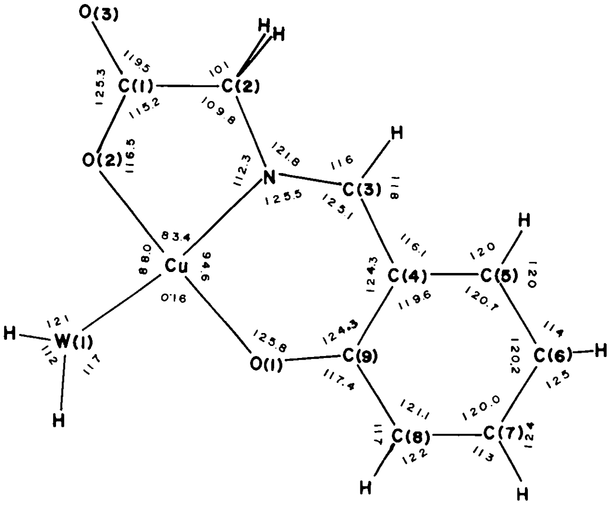

Fig. 2. Bond angles in the *N*-salicylideneglycinatoaquocopper(II) molecule.

Table 4. *Bond lengths and angles in the molecule with their estimated standard deviations*

Bond	r	$\sigma(r)$
Cu—*W*(1)	2·016 Å	0·006 Å
-O(1)	1·928	0·006
-O(2)	1·953	0·006
-N	1·949	0·007
C(1)—O(2)	1·284	0·010
-O(3)	1·249	0·010
-C(2)	1·533	0·012
N—C(2)	1·446	0·011
-C(3)	1·282	0·011
C(4)—C(3)	1·457	0·011
-C(5)	1·420	0·012
-C(9)	1·409	0·011
C(6)—C(5)	1·389	0·013
-C(7)	1·379	0·013
C(8)—C(7)	1·409	0·012
-C(9)	1·412	0·011
C(9)—O(1)	1·337	0·010
W(1)-H(1)	0·81	0·15
-H(2)	1·17	0·15
W(2)-H(3)	1·04	0·15
C(2)—H(4)	1·03	0·15
-H(5)	1·08	0·15
C(3)—H(6)	1·07	0·15
C(5)—H(7)	0·96	0·15
C(6)—H(8)	0·82	0·15
C(7)—H(9)	0·96	0·15
C(8)—H(10)	0·90	0·15

Angle	
W(1)-Cu—O(2)	88·0°
O(2) -Cu—N	83·4
N—Cu—O(1)	94·6
O(1) -Cu—*W*(1)	91·0
Cu—O(2)-C(1)	116·5
O(2) -C(1)-C(2)	115·2
O(2) -C(1)-O(3)	125·3
O(3) -C(1)-C(2)	119·5
C(1) -C(2)-N	109·8
C(2)—N—Cu	112·3
C(2)—N—C(3)	121·8
C(3)—N—Cu	125·5
C(4)—C(3)-N	125·1
C(3)—C(4)-C(5)	116·1
C(3)—C(4)-C(9)	124·3
C(5)—C(4)-C(9)	119·6
C(4)—C(5)-C(6)	120·7
C(5)—C(6)-C(7)	120·2
C(6)—C(7)-C(8)	120·0
C(7)—C(8)-C(9)	121·1
C(8)—C(9)-C(4)	118·4
C(8)—C(9)-O(1)	117·4
C(4)—C(9)-O(1)	124·3
C(9)—O(1)-Cu	125·8

The e.s.d. for angles is about 0·7°.

Table 6, and the other the glycinatocopper group which forms the plane *P*(5) in Table 6, although C(2) and N atoms deviate significantly from the plane *P*(5). These two planes make an angle of 16·5° with each other. The planarity and the deviation of the nitrogen atom from the plane *P*(4) by 0·07 Å are quite similar to those in bis-(5-chlorosalicylaldoximato)copper(II) (Orioli, Lingafelter & Brown, 1964), in which the nitrogen atom deviates by 0·10 Å from the plane. The distances and angles in benzene ring do not significantly fluctuate and the average bond distance and angle are 1·403 Å and 120·0°, respectively. Contribution of the quinone type resonance structure seems to be rather small in the salicylaldiminato ligand in this crystal, while it is appreciable in salicylic acid (Sundaralingam & Jensen, 1965) and in bis-(5-chlorosalicylaldoximato)-copper(II).

Table 5. *Hydrogen bonds and closest contacts of atoms in neighboring molecules*

Hydrogen bonds

W(2)-O(3″)	2·952 Å
W(1)-O(1‴)	2·637

Close contacts of atoms less than 3·5 Å

O(2) -C(6′)	3·398 Å	O(2) -O(3″)	3·295 Å
N——C(6′)	3·382	O(1) -O(3″)	3·134
C(1)—C(6′)	3·458	N——O(2″)	3·382
C(2)—C(7′)	3·456	N——O(3″)	3·432
C(3)—C(4′)	3·456	C(1)—O(2″)	3·481
C(3)—C(9′)	3·424	C(2)—O(2″)	3·240
C(4)—C(4′)	3·276	*W*(1)-*W*(1‴)	3·048
Cu—O(2″)	3·444	*W*(1)-C(8‴)	3·444
Cu—O(3″)	2·344	*W*(1)-C(9‴)	3·406
Cu—C(1″)	3·200	O(1) -*W*(2‴)	3·410
W(1)-O(3″)	3·021	*W*(2)-*W*(1$^{\mathrm{iv}}$)	2·996
O(2) -O(2″)	3·488	C(8)—O(3$^{\mathrm{v}}$)	3·448

Code for superscripts

′	$-x, -y, -z$
″	$\frac{1}{2}-x, \frac{1}{2}+y. \frac{1}{2}-z$
‴	$-x, y, \frac{1}{2}-z$
iv	$x, 1+y, z$
v	$-\frac{1}{2}+x, \frac{1}{2}+y, z$

The distortion of the bond angles is mainly observed in the salicylaldiminato ligand, as in bis-(5-chlorosalicylaldoximato)copper(II) and other Schiff base complexes. In these compounds, the values of the angles corresponding to N–C(3)–C(4), C(3)–C(4)–C(9), and C(4)–C(9)–O(1) in the present compound are similar, while these values are larger than those found in salicylic acid. The strain is released as a result of the shift of the nitrogen atom out of the salicylaldiminato plane.

The glycinato residue has the normal molecular dimensions observed in the usual amino acids. The nitrogen atom deviates from the carboxyl plane by 0·35 Å, which is comparable with the values 0·44, 0·58, 0·31 Å, found in α-, β-, and γ-glycine (Marsh, 1958; Iitaka, 1960; Iikata, 1961) and these deviations are quite common in other amino acids.

The coordination of copper ion is not the usual distorted octahedral configuration found in bis(salicylaldoximato)copper(II) (Jarski & Lingafelter, 1964), bis-(5-chlorosalicylaldoximato)copper(II) and other copper complexes of such Schiff bases, but is a tetragonal pyramidal coordination like those found in di-μ-hydroxobis[dimethylaminecopper(II)] sulfate monohydrate (Iitaka, Simizu & Kwan, 1966), sodium glycylglycylglycinocuprate monohydrate (Freeman, Schoone & Sime, 1965) and other copper(II)-glycine–peptide complexes. The copper ion forms bonds to O(2), N, O(1) and a water molecule *W*(1). The copper ion is also weakly bonded to the O(3″) atom of the adjacent molecule. The weakly bound atom O(3″) lies at the apex of the pyramid of which corners of the approximately square base are occupied by the strongly bound ligand atoms, O(2), N, *W*(1), and O(1). The copper ion lies close to the center of the square, but is displaced in the direction of the O(3″) atom by 0·227 Å. This deviation from the plane of the square is comparable to the value, 0·115 Å, in sodium glycylglycylglycino cuprate(II) monohydrate. The vector Cu–O(3″) makes an angle of 80·5° to the plane of the square. This distortion of the copper ion environment, especially the shift of the copper ion toward O(3″), is significant and

Table 6. *Equations of least-squares planes and the deviations from the planes*

	Atoms included in calculation	Distances from the plane (Å)					
Square of ligand atoms with central copper atom							
P(1)	O(1) O(2) N *W*(1)	O(1)	O(2)	N	*W*(1)	Cu	
	$0{\cdot}1769x+0{\cdot}8712y+0{\cdot}4581z=2{\cdot}0112$	−0·005	−0·005	+0·005	+0·005	+0·227	
P(2)	O(1) O(2) N *W*(1) Cu	O(1)	O(2)	N	*W*(1)	Cu	
	$0{\cdot}1792x+0{\cdot}8671y+0{\cdot}4648z=2{\cdot}0822$	−0·066	−0·042	−0·054	−0·034	+0·177	
Benzene ring							
P(3)	C(4) C(5) C(6) C(7) C(8) C(9)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
	$0{\cdot}1827x+0{\cdot}9511y+0{\cdot}2489z=1{\cdot}6172$	+0·006	+0·003	−0·010	+0·008	+0·002	−0·009
Salicylaldiminatocopper group							
P(4)	Cu C(9) C(8) C(7) C(6) C(5)	Cu	O(1)	C(9)	C(8)	C(7)	C(6)
	C(4) C(3) N O(1)	−0·034	−0·021	−0·003	+0·029	+0·029	−0·019
	$0{\cdot}1627x+0{\cdot}9525y+0{\cdot}2575z=1{\cdot}6428$	C(5)	C(4)	C(3)	N		
		−0·027	−0·018	−0·006	−0·065		
Glycinatocopper group							
P(5)	Cu O(2) O(3) C(1) C(2) N	Cu	O(2)	O(3)	C(1)	C(2)	N
	$0{\cdot}2802x+0{\cdot}8267y+0{\cdot}4880z=2{\cdot}3668$	+0·024	+0·016	−0·060	−0·019	−0·027	+0·142

where x, y, z are referred to orthogonal axes, **a**, **b**, and **c***.

seems quite important in relation to the nature of the coordination of copper ion.

The bond distances Cu–O(1), Cu–N, are 1·928 and 1·949 Å, respectively, and the angle O(1)–Cu–N is 94·6°. These values correspond to those found in bis-(5-chlorosalicylaldoximato)copper(II) and in bis(salicylaldoximato)copper(II). The Cu–O(2) bond distance, 1·953 Å, is longer than the values in the Schiff base complexes quoted above and rather closer to the values in metal peptides complexes. The angle O(2)–Cu–N, 83·4°, is in good agreement with the values found in metal–peptide complexes. The Cu–*W*(1) bond distance is also closer to the values found in metal–peptide complexes. The weakly bound O(3) atom is at 2·334 Å from the copper ion, and this value is comparable to the values in glycylglycylglycinocopper(II) chloride sesquihydrate (Freeman, Robinson & Schoone, 1964), di-μ-hydroxobis(dimethylaminecopper(II)) sulfate monohydrate and copper(II) monoglycylglycine trihydrate (Strandberg, Lindqvist & Rosenstein, 1961).

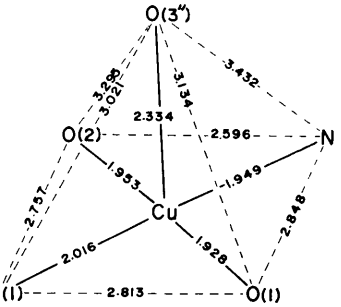

Fig. 3. Five ligand atoms around the copper(II) ion with bond distances.

The square pyramidal environment of five ligand atoms around the copper ion is shown in Fig. 3 with the bond distances.

The molecular structure is consistent with that postulated by Christensen, Nakahara and other workers. They proposed that the $>C=N-$ double bond is stabilized by the coordination of metal ion: it has the normal bond double distance as in other Schiff base complexes with metal ion. Concerning this point, however, a further study will be necessary on the configuration around the nitrogen atom and the molecular dimensions of metal chelates of Schiff bases and their ligands.

The molecules are bonded together in the crystal by the intermolecular hydrogen bond of *W*(1)–O(1‴),

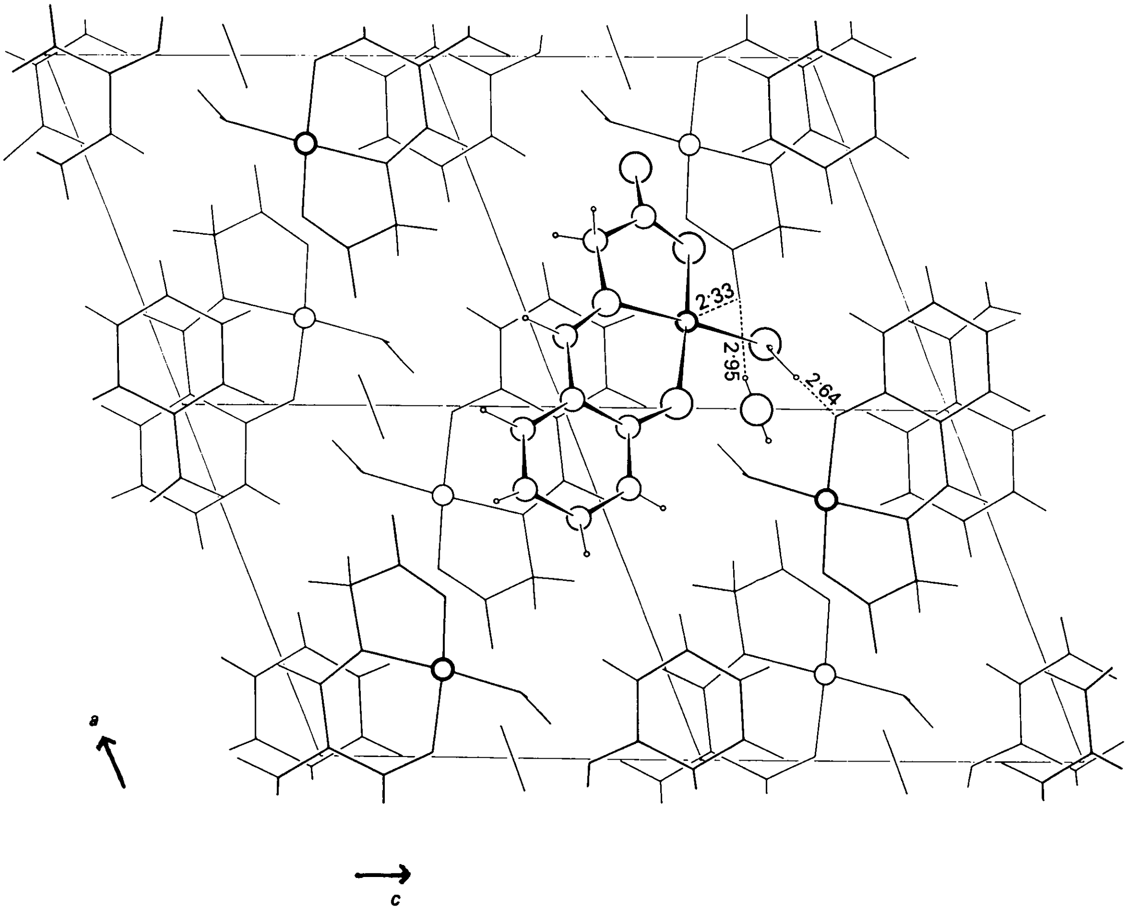

Fig. 4. Crystal structure of *N*-salicylideneglycinatoaquocopper(II) hemihydrate projected along the *b* axis.

2·637 Å, and by the fifth weak coordination bond of the O(3″) atom to the copper ion. Also there is a weak hydrogen bond *W*(2)–O(3″), 2·952 Å, holding the free water molecule *W*(2) in the crystal. The close intermolecular contacts are listed in Table 5. Many of them make fairly rigid contacts among molecules. Of these some are unusually short; for instance, C(4)–C(4′) is 3·276 Å. Probably corresponding to such rigid intermolecular contacts, smaller values were found for the thermal parameters.

The authors wish to express their appreciation to Professor A. Nakahara for his kindness in supplying the crystals and for useful discussions about some biologically important aspects of the non-enzymatic transamination reaction. They are also indebted to Dr T. Takano and all the staff in this laboratory for their kind cooperation. They thank the Computing Center of the Tokyo University and 'UNICON' for making computers HITAC-5020 and IBM-7090 available to them.

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The Crystal Structure of Monothiourea-cadmium Sulphate Dihydrate

BY L. CAVALCA, P. DOMIANO, G. FAVA GASPARRI AND P. BOLDRINI
Istituto di Chimica Fisica, Università degli Studi, Parma, Italy

(*Received* 1 *August* 1966)

The crystal structure of $Cd[SC(NH_2)_2]SO_4.2H_2O$ has been determined by a three-dimensional X-ray analysis and refined by differential methods using anisotropic thermal parameters; final $R = 12{\cdot}9\%$. Eight formula units are contained in the orthorhombic (*Pbca*) unit cell: $a = 13{\cdot}46_1$, $b = 7{\cdot}78_3$, $c = 15{\cdot}9_7$ Å. Coordination around each cadmium atom is octahedral as it coordinates to two sulphur atoms from two thiourea molecules [Cd–S 2·638(4) and 2·647(4) Å], two oxygen atoms from two sulphate groups [Cd–O 2·27(2) and 2·29(2) Å] and two oxygen atoms from two water molecules [Cd–O 2·31(1) and 2·27(2) Å]. The coordination polyhedra are linked in chains by sulphur and sulphato bridges, with the sulphur atom of thiourea and two oxygen atoms of each sulphate group bonded to two adjacent metal atoms.

Introduction

Cadmium sulphate forms with thiourea (*tu*) three complex compounds, $Cd\,tu\,SO_4.2H_2O$, $Cd\,tu_3SO_4$ and $Cd\,tu_4SO_4$, which can be obtained from aqueous solutions of the components by varying their molar ratios (Nardelli & Chierici, 1958). An X-ray analysis of the crystal structure of the first compound was undertaken to study the binding of the thiourea molecule and the sulphato group in it. Indeed, not only is the chemical composition alone insufficient to explain the behaviour of the ligands, but also it could lead to the erroneous conclusion that there is tetrahedral coordination around the cadmium atom.