comme dans la méthode des ravins (Gelfand, Vul, Glinzburg & Fedorov, 1966), par la somme du résidu et d'un terme de contrainte qui prend une valeur nulle si les contraintes sont toutes vérifiées, et positives dans le cas contraire.

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Crystal and Molecular Structure of Pyruvidene-β-alaninatoaquocopper(II) Dihydrate

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Pyruvidene-β-alaninatoaquocopper(II) dihydrate crystallizes in monoclinic form with cell dimensions $a=6{\cdot}860$, $b=11{\cdot}398$, $c=13{\cdot}358$ Å, $\beta=106{\cdot}93°$. The space group is $P2_1/c$ with four formula units in a unit cell. The crystal structure was established by using three-dimensional diffractometer data. The final R index for 1611 'observed' reflexions is 0·071. The coordination configuration of copper(II) ion is a square pyramid with a water molecule weakly bound at its apex. The distances around the copper(II) ion are: Cu–O 1·906 and 1·963 Å, Cu–N 1·963 Å, Cu–$W(1)$ 1·946 Å, and Cu–$W(3)$ (weakly bound) 2·413 Å. The complex as a whole shows a considerable deviation from planarity (the $W(3)$ oxygen atom was eliminated in the calculation of the best plane). The approximate plane of the complex is nearly perpendicular to the c axis. Each complex is joined together by hydrogen bonds to construct a three-dimensional network.

Introduction

Some metal chelates of Schiff bases derived from amino acids and vitamin B_6 (or analogues) had been supposed to be catalytic intermediates of the non-enzymatic transamination reactions in solution (Longenecker & Snell, 1956). In relation to the mechanism of the reactions, one of these chelates, *N*-salicylideneglycinatoaquocopper(II) hemihydrate, was studied by the X-ray diffraction method in this laboratory (Ueki, Ashida, Sasada & Kakudo, 1967). Recently, Nakahara and his collaborators reported two cases of non-enzymatic reactions, one being a transamination reaction which takes place in Cu(II) glyoxylate α-alaninate and the other a reaction in the solution of Cu(II) pyruvate β-alaninate. Since no transamination reaction was found in the latter case, it is of interest to find out the bond distances around the nitrogen atom in this case and to compare these with the values found in *N*-salicylideneglycinatoaquocopper(II) hemihydrate.

In recent years the crystal structures of a number of complexes of copper(II) ion with organic ligands were reported, and some of them were found to show interesting features with respect to the coordination configuration of copper(II) ion (Muetterties & Schunn, 1966). Thus, it seems to be necessary to obtain more information in relation to the multiformity of the configuration. The configurations having so far been found are tetrahedral, square planar, square pyramidal, trigonal bipyramidal and octahedral.

Experimental

Deep blue prismatic crystals were supplied by Professor A. Nakahara of this university. A crystal with dimensions $0{\cdot}11\times0{\cdot}15\times0{\cdot}19$ mm was mounted on a goniometer head with its b axis vertical. Oscillation and Weissenberg photographs were taken to determine the approximate cell dimensions and the space group. The accurate cell dimensions were determined on a General Electric XRD-5 diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å). The crystal data are: $[Cu(C_6H_7NO_4).(H_2O)].2H_2O$, monoclinic with $a=6{\cdot}860\pm0{\cdot}005$, $b=11{\cdot}398\pm0{\cdot}003$, $c=13{\cdot}358\pm0{\cdot}003$ Å, $\beta=106{\cdot}93\pm0{\cdot}05°$, $Z=4$, $D_m=1{\cdot}821$ g.cm^{-3}, $D_x=1{\cdot}823$ g.cm^{-3}, $\mu=22{\cdot}7$ cm^{-1} (for Mo $K\alpha$). Space group $P2_1/c$ (uniquely determined).

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Intensities were measured for each independent reflexion within the sphere of radius $2\sin\theta/\lambda = 1{\cdot}19$ ($2\theta \leq 50°$) on the diffractometer. The stationary-crystal stationary-counter technique was used, with a counting time of 20 seconds for each reflexion. A total of 1759 independent reflexions were collected, of which 148 were too weak to be measured. No absorption corrections were made. The extinction effect was found to be negligible at the final stage of the refinement.

Determination of the structure

From a three-dimensional Patterson function the copper(II) ion was easily located. Successive structure factor and Fourier calculations revealed all the non-hydrogen atoms. A block-diagonal least-squares refinement resulted in $R = 0{\cdot}11$ after three cycles with isotropic temperature factors of the form $\exp(-B\sin^2\theta/\lambda^2)$ for all the atoms. Further refinements by the least-squares method, by assigning unit weights for non-zero reflexions and zero weight for reflexions with zero intensities, gave $R = 0{\cdot}079$ after three cycles. In this refinement all the atoms were treated as anisotropic of the form

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right].$$

At this stage all the hydrogen atoms could be found in the difference Fourier maps. A final least-squares refinement assuming hydrogen atoms as isotropic gave the final atomic parameters for all the atoms. After two cycles the R index was 0·071. The final atomic parameters are listed in Tables 1 and 2 with their standard deviations. The observed and calculated structure factors are listed in Table 3.

The minimized function used in the block-diagonal least-squares calculations was $\Sigma(\Delta F)^2$. The atomic scattering factors for copper(II) ion and neutral C, N, O, H atoms were taken from *International Tables for X-ray Crystallography* (1962). The real part of the anomalous dispersion effect for Cu(II) ion, $\Delta f' = 0{\cdot}3$, was included in the least-squares calculations (Dauben & Templeton, 1955).

Description of the structure and discussion

Bond lengths and angles in the complex are shown in Figs. 1 and 2, and also are listed in Table 4 with their standard deviations. The best plane through the complex [excluding $W(3)$] is described by equation $P(1)$ in Table 5. Some atoms of the β-alaninate residue deviate significantly from the plane $P(1)$. The atoms of pyruvidene residue are planar and lie on the plane $P(5)$. The largest deviation from the plane is 0·012 Å for the C(4) atom. Six atoms around the >C=N– double bond are also coplanar.

The carboxyl group of the β-alaninate residue lies in the plane $P(3)$. The dihedral angle between $P(3)$ and the plane containing C(1), C(2), C(3) atoms is 52·4°. This value is different from those found in β-alanine (9·3°) (Jose & Pant, 1965) and nickel β-alanine dihydrate (30·3°) (Jose, Pant & Biswas, 1964). The angle between the plane passing through C(1), C(2), C(3) and the plane containing C(2), C(3), N atoms is 68·5° [83·8° in β-alanine, 73·7° in nickel β-

Table 1. *Atomic positional parameters and their standard deviations (e.s.d.'s in* Å)

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Cu	−0·21146	0·16314	0·09610	0·00094	0·00094	0·00109
$W(1)$	−0·4958	0·1804	0·0149	0·0061	0·0057	0·0069
$W(2)$	0·4186	0·1081	0·4312	0·0066	0·0068	0·0072
$W(3)$	−0·2475	0·1596	0·2705	0·0061	0·0061	0·0079
O(1)	−0·1960	0·3299	0·1051	0·0057	0·0055	0·0067
O(2)	−0·0445	0·5013	0·1332	0·0064	0·0060	0·0075
O(3)	−0·0131	−0·1631	0·1108	0·0063	0·0055	0·0067
O(4)	−0·2193	−0·0079	0·0777	0·0055	0·0057	0·0064
N	0·0824	0·1337	0·1511	0·0061	0·0065	0·0065
C(1)	−0·0380	0·3950	0·1184	0·0087	0·0081	0·0091
C(2)	0·1605	0·3390	0·1150	0·0089	0·0081	0·0102
C(3)	0·2247	0·2325	0·1891	0·0078	0·0082	0·0099
C(4)	0·1334	0·0285	0·1533	0·0074	0·0078	0·0077
C(5)	−0·0445	−0·0565	0·1115	0·0079	0·0076	0·0080
C(6)	0·3424	−0·0243	0·1946	0·0081	0·0086	0·0094
H(1)	−0·593	0·114	0·002	0·12	0·12	0·12
H(2)	−0·555	0·243	0·000	0·11	0·12	0·12
H(3)	0·527	0·101	0·391	0·11	0·11	0·11
H(4)	0·312	0·085	0·383	0·11	0·11	0·11
H(5)	−0·184	0·224	0·276	0·13	0·13	0·13
H(6)	−0·182	0·106	0·291	0·12	0·12	0·12
H(7)	0·170	0·310	0·038	0·10	0·10	0·10
H(8)	0·280	0·404	0·131	0·13	0·13	0·13
H(9)	0·216	0·252	0·277	0·09	0·09	0·09
H(10)	0·393	0·225	0·165	0·12	0·12	0·12
H(11)	0·326	−0·065	0·264	0·10	0·10	0·10
H(12)	0·384	−0·083	0·110	0·11	0·11	0·11
H(13)	0·445	0·029	0·202	0·12	0·12	0·12

alanine dihydrate and 70° in copper β-alanine hexahydrate (Tomita, 1961)]. From these dihedral angles it is concluded that the conformation of the β-alaninato residue found in the present work is different from those cases quoted above, with respect to the rotation around the C(1)–C(2) bond.

In the two carboxyl groups of the complex the C–O [O atom bonding to Cu(II)] bond distances are 1·282

Table 2. *The thermal parameters and their standard deviations* (*in* 10^{-4})

	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
Cu	110	2	38	1	59	1	−1	2	21	2	−5	1
W(1)	152	14	47	5	78	5	−10	13	−49	13	−6	8
W(2)	199	16	78	6	78	5	−24	16	2	15	−28	9
W(3)	145	14	51	5	110	6	2	13	−54	15	−8	9
O(1)	141	13	41	4	79	5	−22	14	17	13	−8	8
O(2)	191	16	45	5	95	6	−12	14	18	15	−7	8
O(3)	207	16	36	4	73	5	13	13	−49	14	7	7
O(4)	124	13	50	5	70	4	−8	14	−1	12	−8	7
N	105	14	53	5	40	4	−15	18	18	12	−6	8
C(1)	181	21	42	6	58	6	−17	19	27	18	−5	10
C(2)	179	21	39	6	83	7	−28	17	102	20	0	11
C(3)	90	17	46	6	79	7	−39	17	−3	17	2	11
C(4)	116	17	53	6	38	5	12	17	43	14	−8	9
C(5)	142	18	42	6	42	5	−7	17	30	15	6	9
C(6)	120	18	56	7	63	6	22	18	−5	17	10	11
H(1)	5·4*											
H(2)	4·1											
H(3)	3·3											
H(4)	4·0											
H(5)	6·7											
H(6)	3·6											
H(7)	1·4											
H(8)	5·7											
H(9)	0·5											
H(10)	5·3											
H(11)	1·6											
H(12)	3·2											
H(13)	5·1											

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

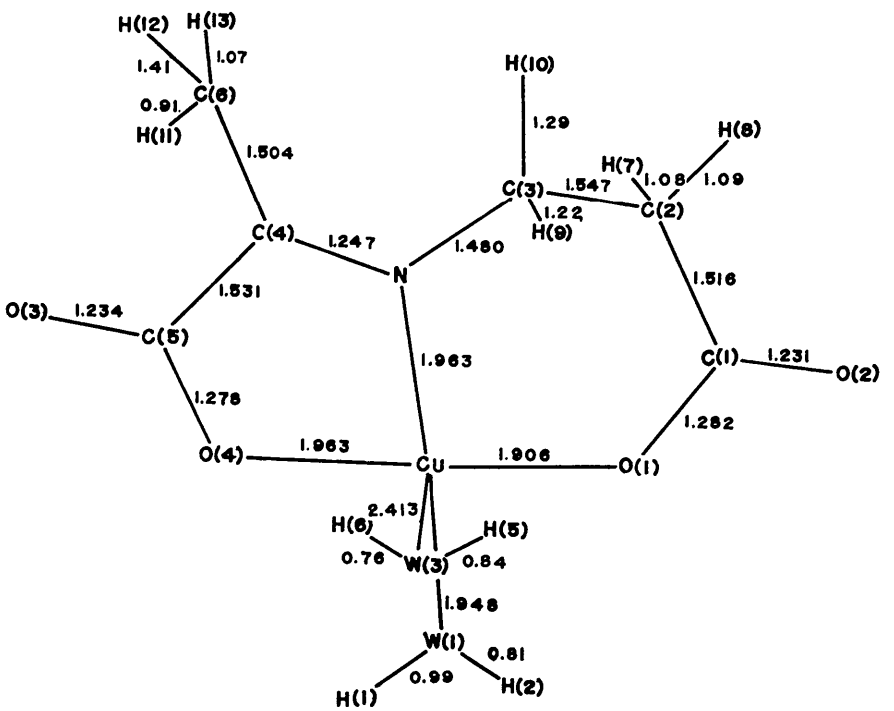

Fig. 1. The bond distances in the molecule.

and 1·278 Å. The 'free' C–O [O atom not bonding to Cu(II)] bond distances are 1·231 and 1·234 Å. These values are in good agreement with the values, 1·277 Å for the average C–O (O atom bonding to metals) and 1·232 Å for the average 'free' C–O (O atom not bonding to metals) bonds in the metal complexes of amino acids. They are comparable to the values, 1·29 Å for C–O_H and 1·23 Å for the C=O bonds, in carboxylic acids (Nardelli, Fava & Giraldi, 1962). The angles < OCO in the carboxyl groups, 121·5°, 124·9°, are con-

Table 3. *The observed and calculated structure factors (on absolute scale)*

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L= 0 0			9	6	-4	8	17	-17	3	17	-14	8	2	-2	4	10	-11	5	10	-16	11	0	0	7	42	41
2	20	-19	10	8	-8	9	10	-11	4	9	-1	9	5	5	5	24	23	6	8	1	H,L= 2-10			8	0	1
4	70	-70	11	22	-22	10	8	7	5	9	2	10	13	-15	6	0	2	7	33	-35	0	38	-36	9	0	2
6	147	152	H,L= 0 9			11	14	12	H,L= 1 14			11	0	1	7	12	11	8	5	-6	1	34	32	10	0	-3
8	19	-5	1	8	6	12	0	3	0	9	5	H,L= 1 -9			8	35	33	9	11	12	2	11	10	11	33	-33
10	33	-31	2	23	21	13	18	20	1	10	-9	1	14	15	9	11	-12	10	8	1	3	3	1	H,L= 3	9	
12	50	50	3	24	-25	H,L= 1	4		2	0	-3	2	15	15	10	11	-10	11	11	-11	4	14	14	1	13	12
H,L= 0 1			4	21	-21	0	13	12	3	3	-4	3	19	-19	11	8	8	12	8	3	5	26	-26	2	42	42
1	13	44	5	2	4	1	43	-41	H,L= 1 -1			4	6	-6	12	3	-4	13	16	-18	6	17	-18	3	13	15
2	51	-51	6	10	-9	2	13	-11	1	10	10	5	18	17	H,L= 2 4			H,L= 2 -2			7	8	7	4	45	-45
3	56	-57	7	4	1	3	6	6	2	41	37	6	7	-6	0	48	45	0	10	-11	8	5	-3	5	2	1
4	52	50	8	3	3	4	2	2	3	62	58	7	16	17	1	36	35	1	72	-71	9	0	2	6	0	-2
5	64	66	9	21	-20	5	52	51	4	47	-48	8	14	13	2	94	-93	2	33	-27	10	6	6	7	20	19
6	22	17	10	13	-12	6	8	8	5	41	-40	9	26	-27	3	30	27	3	22	17	H,L= 2-11			8	23	22
7	33	33	H,L= 0 10			7	10	-11	6	17	-14	10	0	2	4	19	-21	4	12	-10	1	24	-23	9	4	7
8	24	-20	0	48	49	8	4	4	7	26	-24	11	4	2	5	29	-28	5	84	85	2	4	-2	10	23	-23
9	50	-50	1	5	-4	9	10	10	8	42	41	H,L= 1-10			6	68	68	6	55	-54	3	29	26	11	0	0
10	11	4	2	25	-25	10	7	-8	9	27	25	0	21	20	7	20	20	7	48	-48	4	10	-10	H,L= 3	6	
11	6	1	3	7	-5	11	23	23	10	18	-17	1	25	25	8	26	-25	8	10	9	5	16	-13	0	48	48
12	10	10	4	19	-17	12	5	7	11	19	-20	2	10	-10	9	11	11	9	0	1	6	3	1	1	17	18
13	15	15	5	0	-1	H,L= 1 5			12	7	-7	3	8	6	10	24	-21	10	5	6	7	19	-18	2	20	-20
H,L= 0 2			6	30	31	1	0	3	13	7	-10	4	19	-18	11	10	-12	11	37	40	8	7	4	3	6	-3
0	40	36	7	8	7	2	52	-52	H,L= 1 -2			5	28	-28	12	24	22	12	25	-23	9	20	20	4	31	-31
1	112	-119	8	15	-16	3	31	27	0	120	-119	6	15	15	H,L= 2 8			13	8	-9	H,L= 2-12			5	8	-9
2	18	-18	9	0	3	4	62	60	1	69	61	7	15	17	1	73	72	H,L= 2 -3			0	44	-42	6	40	38
3	17	17	10	16	-15	5	10	10	2	37	35	8	9	-8	2	11	-11	1	13	-11	1	18	-16	7	0	0
4	35	-35	H,L= 0 11			6	11	12	3	9	9	9	6	6	3	45	-43	2	27	-24	2	7	-2	8	0	-2
5	85	90	1	25	24	7	11	11	4	57	54	10	6	-6	4	9	10	3	53	46	3	2	-1	9	5	-3
6	32	31	2	13	12	8	28	-29	5	39	-37	H,L= 1-11			5	19	19	4	46	43	4	12	11	10	18	-18
7	40	-42	3	23	-23	9	18	19	6	70	-70	1	6	-2	6	8	-7	5	25	23	5	12	11	H,L= 3	7	
8	18	-17	4	11	11	10	28	29	7	9	-5	2	7	13	7	49	42	6	12	11	6	21	-19	1	10	10
9	12	-10	5	17	17	11	8	8	8	16	17	3	4	11	8	11	-11	7	11	-12	7	8	-8	2	28	-28
10	6	3	6	8	-1	12	15	16	9	9	8	4	5	-17	9	6	-7	8	30	-28	8	4	3	3	40	-39
11	31	31	7	15	13	H,L= 1 6			10	7	6	5	4	5	10	0	1	9	26	25	H,L= 2-13			4	0	0
12	15	13	8	0	0	0	72	-73	11	8	-6	6	4	-6	11	15	16	10	37	35	1	9	-8	5	12	10
13	18	-18	9	12	-13	1	57	-55	12	28	-29	7	0	-1	H,L= 2 6			11	3	4	2	19	-19	6	15	13
H,L= 0 3			H,L= 0 12			2	40	41	13	10	10	8	3	14	0	47	47	12	10	11	3	7	4	7	17	17
1	22	-19	0	15	12	3	0	2	H,L= 1 -3			9	0	7	1	74	-73	13	6	-7	4	13	11	8	0	-4
2	24	-23	1	24	-23	4	13	13	1	55	-54	H,L= 1-12			2	13	-12	H,L= 2 -4			5	9	-7	9	16	-16
3	6	-4	2	6	-5	5	12	15	2	44	-44	0	30	-28	3	16	-18	0	-13	13	6	4	5	H,L= 3	8	
4	22	22	3	6	5	6	46	-48	3	82	77	1	10	8	4	11	-10	1	76	-72	7	5	-5	0	18	17
5	8	7	4	6	-5	7	33	-33	4	8	-7	2	10	9	5	54	53	2	32	-30	H,L= 2-14			1	31	-32
6	16	17	5	23	22	8	22	26	5	51	-50	3	8	-7	6	57	55	3	18	-14	0	9	7	2	2	-3
7	10	-2	6	13	12	9	6	-8	6	4	5	4	20	18	7	52	-50	4	12	-9	1	9	-10	3	0	3
8	25	-22	7	8	-7	10	16	17	7	32	-31	5	18	-14	8	4	-4	5	80	77	2	5	0	4	0	0
9	8	6	8	0	-1	11	23	27	8	6	-6	6	17	-16	9	12	-12	6	15	17	3	5	-2	5	24	24
10	14	12	H,L= 0 13			12	18	-22	9	50	51	7	7	7	10	14	-11	7	37	-37	4	4	-1	6	15	14
11	17	19	1	7	3	H,L= 1 7			10	12	10	8	9	7	11	24	23	8	18	-16	5	13	13	7	25	-24
12	0	0	2	15	-14	1	50	-50	11	0	0	H,L= 1-13			H,L= 2 7			9	0	1	6	4	4	8	0	0
13	4	-2	3	4	0	2	36	-37	12	3	-5	1	7	-5	1	8	7	10	0	0	H,L= 2-15			9	7	-8
H,L= 0 4			4	17	16	3	50	50	13	16	-16	2	4	-1	2	63	-62	11	31	29	1	3	5	H,L= 3	9	
0	157	-168	5	3	1	4	2	-3	H,L= 1 -4			3	17	16	3	2	-1	12	8	8	2	3	-3	1	6	7
1	36	-36	6	0	1	5	25	-27	0	261	-294	4	0	-2	4	36	36	H,L= 2 -5			3	8	-7	2	22	-21
2	20	-18	7	6	5	6	0	3	1	31	-28	5	8	-8	5	3	6	1	6	6	4	9	8	3	0	-1
3	13	15	H,L= 0 14			7	25	-25	2	9	1	6	5	5	6	8	6	2	19	-18	H,L= 3 0			4	11	11
4	41	42	0	11	-9	8	12	-14	3	29	20	7	6	-4	7	0	-1	3	49	-48	0	74	-71	5	5	5
5	59	59	1	13	-13	9	19	20	4	31	29	H,L= 1-14			8	38	-37	4	43	44	1	90	-89	6	0	1
6	69	-67	2	9	8	10	0	0	5	27	29	0	20	-19	9	3	4	5	19	20	2	60	58	7	0	4
7	46	-49	3	9	-4	11	7	-10	6	102	-103	1	8	-7	10	21	21	6	5	6	3	35	-34	8	9	-10
8	2	-1	4	6	7	H,L= 1 8			7	32	-32	2	10	9	H,L= 2 8			7	24	23	4	24	25	H,L= 3 10		
9	0	2	5	8	9	0	29	-31	8	0	3	3	3	-2	0	15	-16	8	33	-35	5	75	73	0	3	-1
10	22	20	H,L= 0 15			1	21	23	9	0	-2	4	9	8	1	45	-45	9	24	-25	6	93	-93	1	10	-9
11	26	25	2	14	-14	2	26	27	10	19	21	5	9	6	2	12	11	10	9	10	7	43	-42	2	18	20
12	24	-24	H,L= 1 0			3	9	10	11	16	17	6	12	-10	3	6	-8	11	14	15	8	19	19	3	0	0
13	13	-13	0	113	107	4	11	12	12	32	-32	H,L= 1-15			4	22	23	12	6	8	9	15	-12	4	10	11
H,L= 0 5			1	81	72	5	18	-17	13	10	-8	1	9	-5	5	38	39	H,L= 2 -6			10	18	17	5	10	12
1	18	-18	2	22	21	6	33	-34	H,L= 1 -5			2	4	0	6	19	-19	0	101	104	11	27	28	6	0	-3
2	38	-38	3	5	5	7	0	1	1	68	-71	3	4	4	7	23	-23	1	4	6	12	21	-21	7	7	-9
3	49	49	4	9	-8	8	11	12	2	89	-88	H,L= 2 0			8	7	7	2	33	-34	H,L= 3 1			H,L= 3 11		
4	21	22	5	102	-102	9	5	-6	3	34	36	0	71	-67	9	0	0	3	12	-10	1	88	-85	1	3	3
5	18	-18	6	52	47	10	11	12	4	59	59	1	30	29	10	13	13	4	36	-34	2	0	1	2	0	-1
6	14	8	7	67	67	11	6	-6	5	40	-39	2	97	95	H,L= 2 9			5	10	-9	3	46	46	3	14	18
7	32	-32	8	18	7	H,L= 1 9			6	18	20	3	4	-4	1	21	-21	6	70	69	4	22	22	4	4	7
8	8	-3	9	2	0	1	26	-26	7	23	-21	4	9	10	2	7	-8	7	30	28	5	33	-33	5	0	-4
9	48	48	10	18	-16	2	19	18	8	33	-33	5	48	-45	3	13	11	8	17	-15	6	10	9	H,L= 3 12		
10	20	18	11	43	-40	3	14	16	9	23	23	6	67	-66	4	18	18	9	0	-4	7	54	-54	0	21	-21
11	0	-1	12	15	13	4	23	-24	10	12	14	7	0	-1	5	3	-3	10	12	-12	8	9	-9	1	6	7
12	0	-1	13	20	20	5	6	-8	11	0	-2	8	10	-10	6	6	-5	11	14	-16	9	11	12	2	3	4
H,L= 0 6			H,L= 1 1			6	0	2	12	9	10	9	16	-15	7	21	-20	12	29	30	10	12	13	3	0	-1
0	80	-81	1	30	27	7	19	-19	H,L= 1 -6			10	32	32	8	0	-2	H,L= 2 -7			11	17	17	H,L= 3 -1		
1	44	42	2	83	77	8	18	19	0	32	32	11	15	-14	9	0	1	1	38	40	12	8	6	1	33	30
2	20	21	3	91	-86	9	0	1	1	84	-90	12	30	-28	H,L= 2 10			2	50	50	H,L= 3 2			?	81	-81
3	26	25	4	52	-49	10	9	-9	2	4	1	13	9	8	0	24	-24	3	53	-54	0	65	-84	3	16	-16
4	47	49	5	12	-8	H,L= 1 10			3	5	2	H,L= 2 1			1	4	2	4	21	-22	1	60	59	4	30	32
5	42	-40	6	21	-20	0	7	-6	4	5	-7	1	27	-26	2	14	14	5	19	18	2	27	27	5	11	-10
6	52	-53	7	39	37	1	38	39	5	71	71	2	48	46	3	3	3	6	7	-7	3	7	6	6	0	-1
7	9	13	8	24	23	2	6	-6	6	6	6	3	34	-29	4	10	8	7	20	20	4	29	29	7	20	20
8	16	15	9	52	-49	3	10	10	7	34	-34	4	84	-80	5	4	-6	8	10	19	5	42	-43	8	44	-46
9	13	11	10	37	-34	4	0	-2	8	8	11	5	6	-6	6	28	-26	9	28	-28	6	83	-82	9	0	-4
10	17	18	11	6	-1	5	28	-28	9	8	-7	6	2	-4	7	8	8	10	15	-17	7	53	53	10	17	18
11	8	-5	12	4	-5	6	15	-11	10	4	-4	7	28	-26	8	3	1	11	0	0	8	17	17	11	0	-1
12	28	-28	13	16	18	7	29	28	11	26	25	8	41	39	H,L= 2 11			H,L= 2 -8			9	13	13	12	6	7
H,L= 0 7			H,L= 1 -2			8	5	-6	12	0	1	9	21	-21	1	5	-5	0	77	72	10	20	19	H,L= 3 -2		
1	14	-10	0	65	62	9	5	6	H,L= 1 -7			10	35	-33	2	24	22	1	48	51	11	20	22	0	5	3
2	3	4	1	25	-24	H,L= 1 11			1	26	27	11	6	-4	3	20	18	2	11	9	12	25	21	1	108	-101
3	17	-16	2	0	-1	1	10	8	2	18	-10	12	17	-18	4	5	-6	3	9	-2	H,L= 3 3			2	17	-18
4	25	-24	3	55	-53	2	37	37	3	34	-35	13	4	-7	5	3	-2	4	8	6	1	45	-43	3	2	-2
5	28	-27	4	29	-30	3	14	-14	4	21	22	H,L= 2 2			6	7	-8	5	39	-41	2	67	65	4	19	-20
6	11	-9	5	16	14	4	21	-19	5	19	17	0	67	66	7	0	-5	6	25	25	3	42	39	5	54	49
7	17	-14	6	78	76	5	0	0	6	4	4	1	123	119	H,L= 2 12			7	38	33	4	24	-22	6	27	26
8	24	23	7	18	16	6	8	7	7	21	23	2	24	-22	0	9	7	8	0	1	5	19	-18	7	56	-53
9	0	2	8	18	-17	7	4	7	8	13	-12	3	13	12	1	6	4	9	6	6	6	16	-16	8	0	0
10	11	-10	9	9	-7	8	24	23	9	26	-29	4	6	4	2	0	0	10	4	-4	7	23	-21	9	10	-10
11	8	-10	10	18	-19	H,L= 1 12			10	9	8	5	69	-66	3	0	0	11	20	-20	8	29	28	10	17	-19
12	3	-3	11	16	-17	0	18	16	11	9	-11	6	23	21	4	4	-4	H,L= 2 -9			9	11	11	11	34	34
H,L= 0 8			12	34	34	1	13	14	12	0	-2	7	55	53	5	19	-18	1	30	30	10	18	-17	12	4	7
0	35	32	13	4	-4	2	12	-9	H,L= 1 -8			8	15	-17	H,L= 2 13			2	43	42	11	11	-12	H,L= 3 -3		
1	24	23	H,L= 1 13			3	8	2	0	107	108	9	15	11	1	3	3	3	6	3	H,L= 3 4			1	48	49
2	9	-10	1	44	37	4	14	-13	1	8	5	10	3	-2	2	10	9	4	37	-38	0	21	-20	2	18	-16
3	10	-10	2	58	56	5	10	-10	2	6	1	11	42	-40	3	8	-8	5	12	10	1	69	69	3	6	-4
4	20	-21	3	19	17	6	20	20	3	4	3	12	12	12	H,L= 2 -1			6	7	-6	2	8	8	4	34	30
5	36	-38	4	9	11	7	7	8	4	31	-31	H,L= 2 3			1	61	-56	7	7	4	3	4	4	5	7	5
6	21	21	5	38	38	H,L= 1 13			5	8	6	1	33	34	2	74	-70	8	23	25	4	16	-16	6	0	0
7	18	18	6	0	2	1	15	15	6	46	47	2	97	95	3	4	5	9	4	-2	5	64	-62	7	33	30
8	11	-12	7	31	33	2	0	-3	7	6	-6	3	37	-37	4	10	-11	6	9	-11	8	11	-10			

Table 3 (*cont.*)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
9	10	9	9	6	6	9	27	28	8	33	35	1	16	14	5	31	-30	H=L= 9-12			8	12	-12	0	5	7
10	16	16	H=L= 3-12			H=L= 4	6		9	12	13	2	23	-23	6	8	-8	0	6	-1	9	21	21	1	32	34
11	5	7	0	12	-8	0	31	-29	10	13	-14	3	4	0	7	26	26	1	19	19	H=L= 6		-4	2	4	2
12	4	6	1	31	-33	1	26	24	11	7	-2	4	22	-23	8	3	2	2	3	0	0	37	-37	3	3	0
H=L= 3		-4	2	11	-11	2	25	-25	H=L= 4		-6	5	26	-28	9	0	1	3	4	3	1	23	-23	4	4	1
0	56	53	3	5	-2	3	5	-4	0	45	-45	6	42	41	10	0	-2	4	7	5	2	17	16	H=L= 7		3
1	4	2	4	11	-9	4	2	-2	1	33	33	7	11	12	H=L= 5		-3	5	10	-11	3	4	0	1	7	6
2	42	-38	5	26	24	5	28	-27	2	26	27	8	4	-5	1	7	-2	6	3	2	4	10	11	2	19	18
3	11	10	6	7	4	6	14	-14	3	5	-6	9	0	0	2	38	38	H=L= 9-13			5	30	30	H=L= 7		-1
4	11	-10	7	16	-15	7	21	22	4	25	25	10	8	-15	3	23	22	1	8	-7	6	24	-24	1	15	-16
5	15	14	8	6	-3	8	8	-5	5	10	-9	H=L= 5		1	4	23	-23	2	13	16	7	15	-18	2	16	-17
6	67	67	H=L= 3-13			9	0	0	6	43	-43	1	26	25	5	17	-17	3	6	7	8	4	6	3	26	28
7	7	7	1	6	-6	H=L= 4		7	7	29	30	2	7	-7	6	13	-12	4	5	-5	9	3	-1	4	15	16
8	11	-12	2	7	-11	1	4	-1	8	6	7	3	24	-22	7	10	4	5	3	0	H=L= 6		-5	5	6	-7
9	14	15	3	15	-14	2	15	16	9	4	4	4	3	3	8	16	15	H=L= 5-14			1	5	3	6	6	7
10	26	-27	4	12	14	3	25	-23	10	22	21	5	25	25	9	20	19	0	13	-12	2	16	-19	H=L= 7		-2
11	0	4	5	7	-1	4	19	-17	11	15	-15	6	7	-1	10	11	-10	1	6	3	3	0	-1	0	28	-28
12	29	29	6	3	0	5	5	4	H=L=	4	-7	7	22	22	H=L=	5	-4	2	9	7	4	24	25	1	28	-30
H=L=	3	-5	7	9	3	6	6	-7	1	34	-35	8	0	-1	0	80	-80	3	3	0	5	6	5	2	6	2
1	21	21	H=L= 3-14			7	4	5	2	7	-5	9	33	-34	1	16	16	H=L= 6		0	6	7	3	3	3	1
2	47	45	0	21	20	8	0	13	3	24	25	10	0	1	2	37	37	0	17	-5	7	8	1	4	8	7
3	7	-10	1	8	-4	H=L=	4	8	4	5	4	H=L=	5	2	3	4	2	1	34	34	8	13	-14	5	23	24
4	18	-18	2	9	-9	0	38	38	5	13	-12	0	62	63	4	36	35	2	6	0	9	11	-11	6	18	-18
5	9	7	3	4	-2	1	3	-1	6	6	5	1	31	-30	5	24	-23	3	10	8	H=L=	6	-6	H=L=	7	-3
6	2	3	4	10	-9	2	8	-8	7	24	-25	2	20	22	6	48	-47	4	6	6	0	44	44	1	5	-3
7	17	17	5	5	4	3	3	0	8	11	-10	3	4	3	7	16	17	5	36	-38	1	26	-26	2	27	-26
8	23	24	6	14	14	4	14	-13	9	3	5	4	11	-10	8	14	15	6	8	6	2	4	1	3	0	0
9	5	-7	H=L= 3-15			5	6	-7	10	0	-1	5	30	30	9	0	1	7	24	23	3	7	5	4	26	27
10	7	-8	1	10	10	6	28	31	11	6	-6	6	31	33	10	16	15	8	10	-10	4	5	-4	5	4	-1
11	8	7	2	8	6	7	0	0	H=L=	4	-8	7	21	-21	H=L=	5	-5	H=L= 6		1	5	21	22	6	4	4
12	6	-7	3	9	-8	8	15	-8	0	22	-21	8	0	1	1	35	-35	1	12	12	6	21	19	H=L= 7		-4
H=L=	3	-6	4	3	0	H=L=	4	9	1	26	-27	9	0	1	2	10	8	2	34	37	7	14	-14	0	18	22
0	6	2	H=L=	4	0	1	12	13	2	14	13	H=L=	5	3	3	43	44	3	14	-14	8	5	-4	1	19	-22
1	77	75	0	78	77	2	4	-3	3	10	-10	1	3	0	4	12	13	4	29	-31	H=L=	6	-7	2	10	-7
2	23	21	1	49	-49	3	16	-17	4	2	-1	2	12	-10	5	27	-26	5	6	5	1	11	9	3	8	-7
3	6	5	2	34	-35	4	0	3	5	12	10	3	10	11	6	10	-7	6	6	-6	2	4	-3	4	11	-11
4	13	11	3	7	-1	5	16	16	6	27	-26	4	17	17	7	32	-32	7	3	5	3	20	-19	5	21	23
5	59	-59	4	19	-17	6	0	-1	7	16	-14	5	0	1	8	4	-2	8	26	26	4	5	1	6	12	14
6	17	16	5	57	55	H=L=	4	10	8	4	2	6	8	7	9	23	23	H=L=	6	2	5	16	18	H=L=	7	-5
7	42	43	6	45	45	0	34	37	9	10	-11	7	0	1	10	4	0	0	62	64	6	5	3	1	15	16
8	5	2	7	42	-40	1	8	-8	10	9	-7	8	14	-14	H=L=	5	-6	1	15	16	7	9	4	2	5	7
9	0	2	8	12	-13	2	4	-2	H=L=	4	-9	9	4	-2	0	41	-39	2	15	-14	8	3	1	3	23	-24
10	6	4	9	0	-2	3	0	-1	1	5	4	H=L=	5	4	1	35	-36	3	4	-5	H=L=	6	-8	4	5	3
11	37	-38	10	9	-11	4	9	-10	2	29	-30	0	26	-25	2	13	11	4	22	-20	0	41	41	5	5	6
12	8	8	11	31	-30	H=L=	4	-1	3	5	-4	1	20	-19	3	4	1	5	12	11	1	7	5	6	8	-3
H=L=	3	-7	H=L=	4	1	1	57	56	4	15	15	2	8	6	4	21	21	6	43	43	2	71	-71	H=L=	7	-6
1	19	-18	1	5	-5	2	41	-40	5	5	-2	3	2	-2	5	38	37	7	0	2	3	8	-4	0	32	33
2	12	12	2	68	-69	3	63	-63	6	2	-3	4	5	5	6	33	-32	H=L=	6	3	4	22	-22	1	10	10
3	13	13	3	29	-27	4	3	0	7	0	0	5	25	27	7	16	-16	1	22	22	5	3	0	2	6	4
4	27	-28	4	51	50	5	34	35	8	20	-22	6	26	-28	8	4	4	2	7	5	6	23	25	3	0	3
5	14	-14	5	6	7	6	14	16	9	0	0	7	15	-16	9	0	0	3	34	-35	7	3	2	4	7	-4
6	6	-5	6	13	14	7	39	40	10	7	7	8	11	12	10	3	5	4	0	-2	8	11	-10	5	9	-10
7	12	-10	7	11	-13	8	8	-8	H=L=	4	-10	H=L=	5	5	H=L=	5	-7	5	13	13	H=L=	6	-9	6	22	22
8	17	17	8	32	-30	9	28	-29	0	10	8	1	17	-16	1	14	-13	6	7	-7	1	11	10	H=L=	7	-7
9	0	0	9	16	-15	10	6	6	1	30	-29	2	20	-21	2	30	-30	7	12	11	2	7	8	1	15	13
10	23	-25	10	24	23	11	12	13	2	16	-15	3	22	21	3	5	-1	H=L=	6	4	3	15	-16	2	16	18
11	5	-6	11	0	2	H=L=	4	-2	3	5	-2	4	14	13	4	26	26	0	31	31	4	14	-15	3	0	0
H=L=	3	-8	H=L=	4	2	0	77	73	4	7	-5	5	14	-13	5	12	-11	1	26	-28	5	9	7	4	13	-13
0	24	-23	0	26	-28	1	5	6	5	23	22	6	4	5	6	15	14	2	9	-8	6	4	0	5	8	9
1	21	22	1	35	-35	2	23	-23	6	7	6	7	10	-9	7	12	-13	3	4	-4	7	11	12	6	6	-4
2	24	25	2	27	30	3	4	1	7	21	-21	8	11	-11	8	16	-15	4	4	-4	H=L=	6	-10	H=L=	7	-8
3	9	8	3	9	10	4	36	-35	8	4	-5	H=L=	5	6	0	0	-2	5	18	17	0	9	7	0	4	2
4	11	10	4	37	36	5	9	-11	9	0	0	0	67	-67	10	14	14	6	15	15	1	23	23	1	15	15
5	30	-31	5	22	23	6	65	64	H=L=	4	-11	1	4	0	H=L=	5	-8	H=L=	6	5	2	6	-1	2	3	-2
6	39	-40	6	24	-22	7	15	-13	1	17	16	2	12	12	0	17	16	1	13	13	3	6	-1	3	3	0
7	7	8	7	18	-18	8	12	-13	2	7	-5	3	4	4	1	29	-29	2	16	-17	4	7	-5	4	0	3
8	14	15	8	3	0	9	6	-7	3	22	-22	4	23	22	2	9	-8	3	7	-6	5	25	-26	5	17	-17
9	3	-3	9	0	0	10	13	-13	4	9	10	5	0	-1	3	4	-1	4	25	25	6	14	10	H=L=	7	-9
10	9	10	10	13	15	11	0	1	5	7	7	6	38	-38	4	13	-17	5	12	11	7	14	14	1	8	-7
11	12	-12	11	10	16	H=L=	4	-3	6	3	3	7	3	5	5	27	27	H=L=	6	6	H=L=	6	-11	2	6	6
H=L=	3	-9	H=L=	4	3	1	49	47	7	11	12	H=L=	5	7	6	18	13	0	20	-19	1	4	1	3	8	7
1	7	-8	1	7	-5	2	24	23	8	5	-4	1	15	-16	7	21	-22	1	26	-27	2	15	15	4	14	-15
2	6	-3	2	10	11	3	23	-21	H=L=	4	-12	2	9	9	8	5	-6	2	4	5	3	10	8	5	6	-6
3	28	28	3	36	36	4	34	-32	0	15	13	3	24	24	9	3	-2	3	8	0	4	12	-11	H=L=	7	-10
4	10	-8	4	14	12	5	10	11	1	9	2	4	11	-11	H=L=	5	-9	H=L=	6	-1	5	5	0	0	27	-27
5	0	-5	5	16	-15	6	14	-15	2	11	-11	5	14	-14	1	24	23	1	13	-12	6	8	-8	1	6	6
6	5	-1	6	9	-8	7	34	36	3	4	0	6	0	3	2	33	-31	2	4	-3	H=L=	6	-12	2	4	0
7	12	-12	7	21	-21	8	19	20	4	7	-4	H=L=	5	8	3	19	-19	3	16	17	0	21	-19	3	3	-2
8	7	6	8	0	-2	9	7	-8	5	5	5	0	9	-11	4	9	8	4	11	-10	1	8	8	4	9	3
9	14	12	9	18	17	10	19	-19	6	25	24	1	29	30	5	8	6	5	9	-8	2	10	9	H=L=	7	-11
10	0	1	10	4	7	11	10	12	7	4	3	2	0	1	6	0	0	6	0	0	3	3	0	1	9	-9
H=L=	3	-10	H=L=	4	4	H=L=	4	-4	8	7	-7	3	5	3	7	19	19	7	12	-12	4	15	16	2	6	-5
0	35	-37	0	56	-54	0	28	29	H=L=	4	-13	4	3	1	8	11	-12	8	10	9	5	11	-8	3	11	11
1	18	-18	1	14	14	1	69	68	1	0	2	H=L=	5	9	9	9	-11	H=L=	6	-2	H=L=	6	-13	H=L=	8	-2
2	14	15	2	14	11	2	20	-16	2	11	10	1	0	0	H=L=	5	-10	0	58	-59	1	10	-9	0	7	8
3	3	2	3	6	-4	3	14	14	3	9	-11	H=L=	5	-1	0	33	35	1	13	12	2	5	4	1	17	-21
4	14	13	4	16	15	4	6	-3	4	7	-5	1	5	0	1	4	1	2	11	-12	3	8	9	H=L=	8	-3
5	19	21	5	0	-1	5	59	-57	5	0	2	2	13	14	2	14	-12	3	2	-1	H=L=	7	0	1	11	14
6	31	-33	6	28	-31	6	13	13	H=L=	3	-13	3	15	-14	3	11	10	4	14	11	0	44	-45	2	6	-4
7	22	-23	7	9	12	7	38	39	H=L=	4	-14	4	24	-24	4	15	-15	5	12	-9	1	9	5	H=L=	8	-4
8	6	6	8	0	1	8	2	-1	0	6	6	5	4	4	5	12	-13	6	37	-36	2	15	14	0	34	37
9	0	2	9	0	5	9	7	6	1	7	11	6	0	-2	6	24	26	7	3	3	3	3	1	1	9	10
10	6	7	10	6	8	10	0	-1	2	4	-3	7	19	10	7	9	-6	8	0	3	4	7	8	2	11	-11
H=L=	3	-11	H=L=	4	5	11	25	-27	3	3	0	8	11	11	8	5	-3	9	0	-3	5	3	0	H=L=	8	-5
1	14	-13	1	20	-18	H=L=	4	-5	4	4	-3	9	0	-1	H=L=	5	-11	H=L=	6	-3	6	29	-29	1	9	7
2	26	-25	2	27	24	1	41	-39	5	10	-11	10	10	-12	1	13	13	1	21	-21	H=L=	7	1	2	17	17
3	16	15	3	20	19	2	74	72	H=L=	4	-15	H=L=	5	-2	2	12	10	2	14	-14	1	18	-21	H=L=	8	-6
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5	6	-5	5	19	-19	4	32	-31	2	9	9	1	41	40	4	12	-10	4	9	9	3	19	21	1	24	27
6	5	2	6	0	-3	5	4	-1	3	4	2	2	12	-13	5	10	9	5	18	-18	4	22	-23	2	6	5
7	10	-9	7	17	-17	6	2	-3	H=L=	5	0	3	11	-13	6	7	-6	6	8	6	5	12	-11	H=L=	8	-7
8	15	-14	8	7	9	7	31	-31	0	70	72	4	13	-12	7	11	11	7	15	-15	H=L=	7	2	1	6	-4

sistent with the values found in amino acids and in carboxylic acids. The relevant C–C bond distances are also reasonable.

The ligand atoms around the copper(II) ion form a square pyramid consisting of two carboxyl oxygen atoms, O(1), O(4), the nitrogen atom and two oxygen atoms of water molecules, one being strongly bound and the other weakly (Fig. 5). The distances and angles between these atoms are listed in Table 4. The Cu–O distances are 1·906 and 1·963 Å. The longer distance, 1·963 Å, involved in the five-membered ring is consistent with the mean value, 1·96 Å, which is found in the complexes of square pyramidal configuration with five-membered rings. On the other hand, the former distance 1·906 Å is significantly shorter than this mean value. Lingafelter & Braun (1966) compiled the bond lengths in the chelates with salicylaldimine ligands. Four chelates in this list are complexes of Cu(II) ion. The mean value, 1·902 Å, of the Cu–O bond distances in these complexes is in agreement with the value found

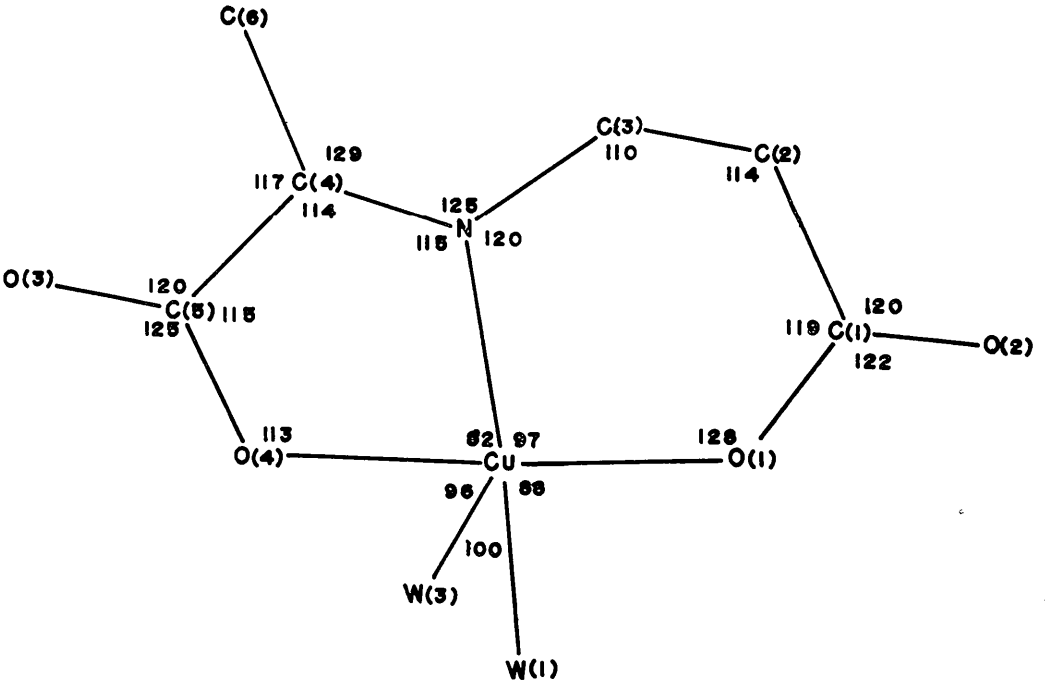

Fig. 2. The bond angles in the molecule.

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

Bond	r	$\sigma(r)$
Cu—W(1)	1·946 Å	0·006 Å
–O(1)	1·906	0·006
–N	1·963	0·006
–W(3)	2·413	0·008
–O(4)	1·963	0·006
C(1)–O(1)	1·282	0·010
–O(2)	1·231	0·010
–C(2)	1·516	0·012
C(3)–C(2)	1·547	0·012
–N	1·480	0·010
C(4)–N	1·247	0·010
–C(6)	1·504	0·012
C(5)–C(4)	1·531	0·012
–O(3)	1·234	0·010
–O(4)	1·278	0·010
W(1)–H(1)	0·99	0·12
–H(2)	0·81	0·12
W(2)–H(3)	1·03	0·11
–H(4)	0·86	0·11
W(3)–H(5)	0·84	0·13
–H(6)	0·76	0·12
C(2) –H(7)	1·09	0·10
–H(8)	1·08	0·13
C(3) –H(9)	1·22	0·09
–H(10)	1·29	0·12
C(6) –H(11)	1·07	0·10
–H(12)	1·41	0·11
–H(13)	0·91	0·12

Angle		
O(4) –Cu—W(1)	92·5°	0·3°
W(1)–Cu—O(1)	87·9	0·3
O(1) –Cu—N	96·6	0·3
W(1)–Cu—N	168·3	0·3
O(4)–Cu—N	82·2	0·3
O(1) –Cu—O(4)	175·7	0·3
Cu—O(1)–C(1)	127·9	0·6
Cu—N—C(3)	120·1	0·5
Cu—N—C(4)	115·1	0·6
Cu—O(4)–C(5)	113·3	0·5
O(1) –C(1)–O(2)	121·5	0·9
O(1) –C(1)–C(2)	118·9	0·8
O(2) –C(1)–C(2)	119·6	0·8
C(1) –C(2)–C(3)	113·7	0·8
C(2) –C(3)–N	110·0	0·8
C(3) –N—C(4)	124·8	0·7
N—C(4)–C(6)	128·6	0·8
N—C(4)–C(5)	114·3	0·7
C(5) –C(4)–C(6)	117·0	0·7
C(4) –C(5)–O(3)	120·3	0·7
C(4) –C(5)–O(4)	114·8	0·7
O(3) –C(5)–O(4)	124·9	0·8
Angles around C(2) with H(7), H(8) 117°, 110°, 106°, 111°, 98°		
Angles around C(3) with H(9), H(10) 114°, 121°, 115°, 105°, 91°		
Angles around C(6) with H(11), H(12), H(13) 99°, 107°, 113°, 125°, 118°, 94°		
H(1)–W(1)–H(2)	111°	
H(3)–W(2)–H(4)	100	
H(5)–W(3)–H(6)	116	

in the present work, although in the complexes of Lingafelter & Braun, the chelate rings are planar, six-membered rings and the oxygen atoms are phenolic. As regards the Cu–N bond, the present value, 1·963 Å, is closer to the ones given by Lingafelter & Braun (1966).

There is a strongly bound water molecule $W(1)$ lying in the square of the coordination plane. The Cu–$W(1)$ distance, 1·946 Å, is shorter than the value, 2·02 Å, in *N*-salicylideneglycinatoaquocopper(II) hemihydrate. The fifth coordination bond is formed by a weakly bound water molecule, $W(3)$, locating at the apex of the square pyramid. The distance, 2·413 Å, is reasonable for the complexes of the same type of configuration, since the corresponding distances in these complexes range from 2·30 Å to 2·48 Å. This value is usually smaller than those in the complexes of the octahedral configuration.

The angles O–Cu–N are 82·2° and 96·6° for the five-membered and the six-membered ring respectively. These values agree with the mean values, 83·3° and 93·8°, found in similar complexes of square pyramidal configuration.

The copper(II) ion is shifted by 0·125 Å from the least-squares plane $P(2)$ of the square ligand atoms towards the apical ligand $W(3)$. This amount coincides with the values in the complexes of the same configuration. The ligand atoms are not strictly coplanar in the square plane and they are located so as to take a very 'flattened' tetrahedron, as pointed out by Blount *et al.* (1967).

The carbon–nitrogen bonds in question show an interesting feature; the double bond, N–C(4), has a length of 1·247 Å and is abnormally short, even for the pure double bond distance (the sum of the double bond radii of carbon and nitrogen atoms is 1·29 Å).

Table 5. *Equations of least-squares planes and the normal distances from the plane*

$P(1)$	$0{\cdot}3855x+0{\cdot}0097y-0{\cdot}9226z+1{\cdot}6774=0{\cdot}0$
$P(2)$	$0{\cdot}4607x+0{\cdot}0734y-0{\cdot}8845z+1{\cdot}6650=0{\cdot}0$
$P(3)$	$0{\cdot}0447x+0{\cdot}1601y-0{\cdot}9860z+0{\cdot}8013=0{\cdot}0$
$P(4)$	$0{\cdot}3925x+0{\cdot}0897y-0{\cdot}9153z+1{\cdot}6565=0{\cdot}0$
$P(5)$	$0{\cdot}4039x+0{\cdot}0780y-0{\cdot}9114z+1{\cdot}6437=0{\cdot}0$

Normal distances (Å) from the planes.

	$P(1)$	$P(2)$	$P(3)$	$P(4)$	$P(5)$
Cu	−0·141	(−0·125)	(−0·193)	−0·017	(−0·067)
$W(1)$	0·188	0·054			
O(1)	−0·201	−0·054	0·001		
O(2)	−0·156		0·001		
O(3)	0·152			(−0·010)	−0·002
O(4)	0·064	−0·052		(0·031)	0·003
N	−0·098	0·058		0·017	−0·007
C(1)	0·048		−0·002		
C(2)	0·611		0·000	(0·915)	
C(3)	−0·215		(−1·121)	−0·001	(−0·026)
C(4)	−0·005			0·017	0·012
C(5)	0·072			0·005	−0·004
C(6)	−0·006			−0·020	−0·002

The coordinates (x,y,z) in Å are referred to the orthogonal axes, a, b, and c^*. Distances in parentheses concern the atoms which were not included in the least-squares calculation.

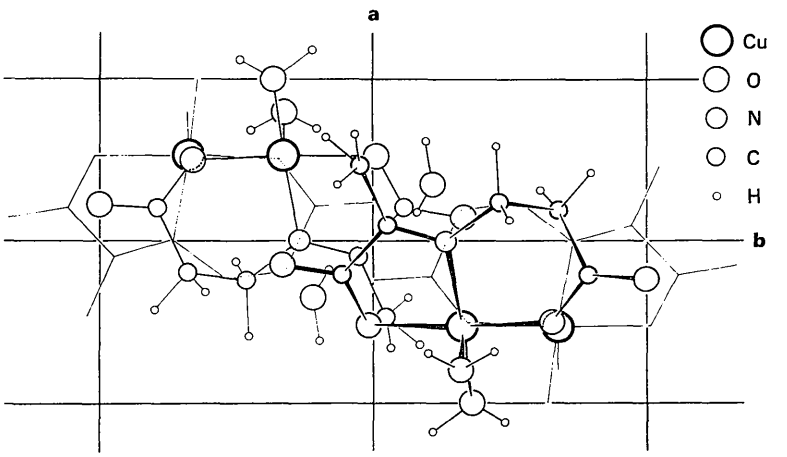

Fig. 3. The packing of the complex molecules in the crystal viewed down along the c axis.

On the other hand, the single bond, C(3)–N, has the normal distance, 1·480 Å. This situation is in contrast with the case of *N*-salicylideneglycinatoaquocopper(II) hemihydrate. The transamination reactions are expected if the single bond, C(3)–N, has the double bond character. Therefore, the normal bond distance in the present case is in conformity with the fact that the transamination reaction has not so far been observed (Nakao, Sakurai & Nakahara, 1966).

The packing of the complexes is shown in Fig. 3. The hydrogen bonds between complexes and water molecules can be seen in Fig. 4. The complexes are connected by four hydrogen bonds, constructing a chain along the twofold screw axis. Between these chains there are two hydrogen bonds. As a result the complexes are joined together in a three-dimensional network.

The authors wish to express their appreciation to Professor A. Nakahara for his supplying the crystals and for discussions. They are also indebted to Dr T. Takano of this laboratory for his advice. They thank the Computing Center of the Tokyo University and

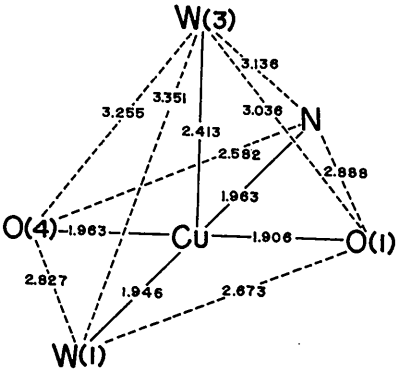

Fig. 5. The bond distances around the copper(II) ion.

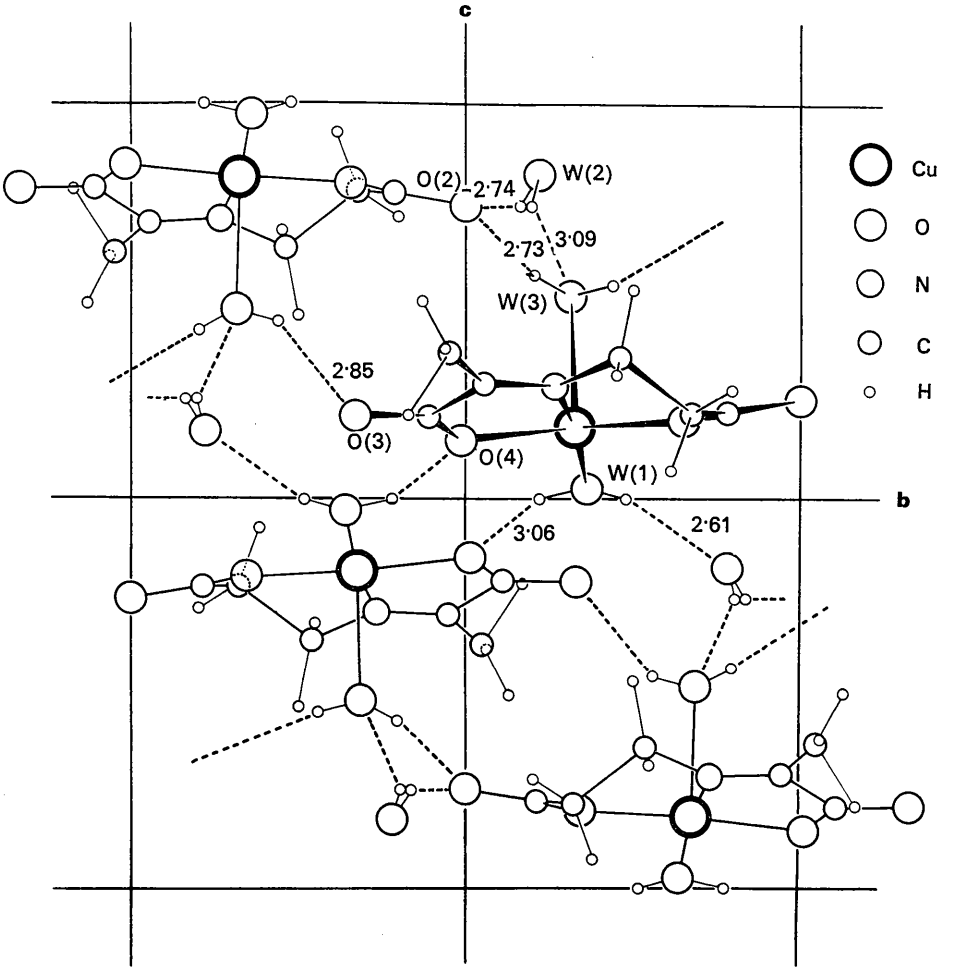

Fig. 4. The crystal structure looking along the *a* axis and the hydrogen bonding system between molecules.

'UNICON' for making computers HITAC-5020 and IBM-7090 available to them.

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The Crystal and Molecular Structure of the Complexes of 2,4,6-Trinitrophenetole with Caesium or Potassium Ethoxide (Meisenheimer Salts)

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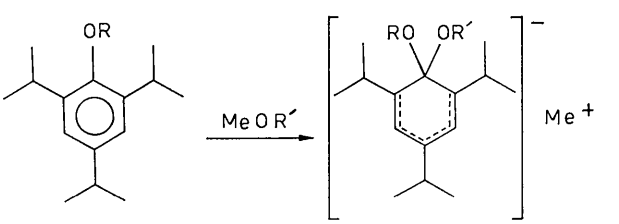
The crystal structures of two so-called Meisenheimer salts, the complexes of 2,4,6-trinitrophenetole with caesium or potassium ethoxide, have been determined and refined by three-dimensional least-squares methods. The caesium salt is monoclinic, space group $P2_1/c$, with $a=15{\cdot}564$, $b=10{\cdot}54$, $c=19{\cdot}919$ Å, $\beta=110{\cdot}31°$ and eight molecules per unit cell, whereas the potassium salt is triclinic, space group $P\bar{1}$, with $a=14{\cdot}744$, $b=10{\cdot}285$, $c=9{\cdot}992$ Å, $\alpha=105{\cdot}9°$, $\beta=104{\cdot}0°$, $\gamma=97{\cdot}2°$ and four molecules per unit cell. Although true isomorphism cannot be claimed, there is a definite geometrical analogy between the two structures. Intensity data were collected visually from Weissenberg photographs. The final R index is 0·102 for the caesium salt and 0·064 for the potassium salt. In the latter, the average standard deviations for bond lengths and angles are 0·008 Å and 0·6°; these data are given uncorrected for thermal motion.

In both compounds two equivalent alkoxyl groups are attached to the same carbon atom, which attains tetrahedral (sp^3) configuration; this is in agreement with theoretical predictions and spectroscopic or kinetic data. The six-membered ring derived from the parent aromatic compound is still virtually planar; deformation from a regular hexagon, which is required by the presence of one tetrahedral carbon atom, is evidenced in variations of the C–C bond lengths. For the potassium salt, a case of structural disorder is observed relative to one ethoxyl group; both theoretical and experimental evidence for this situation are given.

Introduction

In recent years, the structures of possible intermediates or activated complexes in aromatic substitution reactions have been the object of considerable interest (Bunnett, 1959; Ross, 1963; Simonetta & Carrà, 1964; Carrà, Raimondi & Simonetta, 1966). In a few examples of nucleophilic substitution reactions a stable intermediate has been isolated; the complexes of alkyl picrates with alkali alkoxides ('Meisenheimer salts'), which are relatively easy to obtain in good crystals, have been well known for a long time (Meisenheimer, 1902):



Among these compounds, the complexes of ethyl picrate (2,4,6-trinitrophenetole) with alkali ethoxides appeared to be the most suitable for crystallographic use, because of their stability and the absence of 'crys-