

Title	STRUCTURAL STUDIES OF Cu(II) CHELATES OF SOME SCHIFF BASES WHICH RELATE TO THE NON-ENZYMATIC TRANSAMINATION REACTIONS
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STRUCTURAL STUDIES OF Cu(II) CHELATES OF SOME SCHIFF  
BASES WHICH RELATE TO THE NON-ENZYMATIC TRANSAMINATION  
REACTIONS.

by Tatzuo Ueki.

## Introduction

In the broad field of the structural chemistry of coordination compounds, many works have been done by means of techniques such as spectroscopy, magnetic susceptibility and X-ray diffraction. Among these techniques the X-ray diffraction may be one of the strongest approach to the field.

Recently, Lingefelter and his collaborators<sup>1,2,3</sup> in the University of Washington reported many structural work on metal chelates of salicylaldehydes ligands to clarify the molecular dimensions of the ligand molecules and the coordination bonds. On the other hand, Freeman and his colleagues<sup>4,5,6,7,8</sup> in the University of Sidney worked out the structures of the metal complexes of glycine-oligopeptides to find out the role of metal ions in the living organisms. Both of the groups presented very interesting coordination configurations around the metal ions with respect to the numbers of ligand atoms and their specific coordination geometry by X-ray diffraction method. Especially in the latter complexes, penta-coordination configuration around the copper(II) ion was commonly found, which is now apparent to pervade the Periodic Table<sup>9</sup>.

In the decade of nineteen-fifties, Metzler and Snell<sup>10,11,12,13</sup> had made an intensive work on the metal chelates of Schiff bases derived from amino acids and vitamin B<sub>6</sub> and had opened the field which connects the chemistry of the coordination compounds and biochemistry; some evidences suggested that the chelation of the Schiff bases to metal ions may play an

important role in the non-enzymatic transamination reaction of the Schiff bases prepared from vitamin B<sub>6</sub> and amino acids. These bases are of much interest as model compounds for the transaminase enzymes. It was also proved that the coordination of copper(II) ion with Schiff base derived from salicylaldehyde and glycine results in stabilization of the double bond, >C=N-, under conditions that would promote its rupture in the absence of the metal ion<sup>14</sup>. Recently, Nakahara and his collaborators<sup>15</sup> reported a clear-cut non-enzymatic transamination reaction, in which the migration of the double bond was taken place; they proved that the complex isolated in the crystalline state from the copper(II)-glyoxalate-alaninate system was in fact pyruvideneglycinatoaquocopper(II) instead of glyoxylidenealaninatoaquocopper(II). Also they came to a conclusion that no transamination reaction was observed in case of copper(II)-pyruvate-β-alaninate and copper(II)-glyoxalate-β-alaninate system.

The molecular structure analyses of these complexes may be an interesting approach to make the reaction mechanism of transamination reactions clear since these complexes are expected to be the catalytic intermediates in the reactions. Hence the structure analyses of these were planned to obtain a considerable precision in the accuracy of molecular dimensions by means of X-ray diffraction method. With an aim to find the coordination configuration of copper(II) ion, the different types of complexes with respect to the ligand molecules were selected.

In this thesis the crystal structures of three complex crystals are described and these are:

- I. N-salicylidene-glycinato-aquocopper(II) hemihydrate  
 $[\text{Cu}(\text{C}_9\text{H}_7\text{NO}_3 \cdot \text{H}_2\text{O})] \cdot \frac{1}{2}\text{H}_2\text{O}$  (abbreviated as SGCH hereafter),
- II. N-salicylidene-glycinato-aquocopper(II) tetrahydrate  
 $[\text{Cu}(\text{C}_9\text{H}_7\text{NO}_3 \cdot \text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$  (abbreviated as SGCT hereafter),
- III. Pyruvidene- $\beta$ -alaninato-aquocopper(II) dihydrate  
 $[\text{Cu}(\text{C}_6\text{H}_7\text{NO}_4 \cdot \text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  (abbreviated as PACD hereafter).

All of these complexes are the type of 'three-coordinated' complexes, and I and II contain planar five- and six-membered chelate rings, while III has a non-planar six- and a planar five-membered rings. In crystals I and II the substantial part of the molecule are the same, though the crystal structure may be completely different from each other. The complexes I and II are closely related to the transamination reactions, with the  $\text{>C=N-}$  double bond migration expected, and the third complex does not show the migration.

The molecules of these complexes are shown in Figs. 1, 3 and 5 with the molecular dimensions obtained in the present analyses.

## Experimental

Crystals of SGCH, SGCT and PACD were prepared<sup>16,17</sup> and kindly supplied by Professor A. Nakahara of the Osaka University. The appearance and the color of them are:

<u>SGCH</u>	dark green prisms,
<u>SGCT</u>	bright green needles(unstable at the room temperature),
<u>PACD</u>	deep blue prisms.

The crystals used throughout the experiments have the dimensions 0.20x0.20x0.10mm in SGCH, 0.12x0.07x0.22mm in SGCT and 0.11x0.15x0.19mm in PACD crystal, respectively. The b axes were mounted along the spindle axis of the goniometer head for all the crystals, although the needle axis of SGCT crystal is parallel to the c axis. Oscillation and Weissenberg photographs were taken with Cu K $\alpha$  radiation(nickel filtered) to determine the approximate cell dimensions and space groups for each of them. The crystals were then set on a goniostat on a General Electric XRD-5 apparatus equipped with a krypton-filled proportional counter. The cell dimensions were redetermined on the goniostat, using Mo K $\alpha$  radiation( $\lambda=0.71069\text{\AA}$ ) monochromatized by zirconium foil.

Intensities of the reflections were measured for each independent reflection within the sphere of radii  $r(=2\sin\theta/\lambda)$  by the stationary-crystal stationary-counter technique. The fixed time method was applied for each reflection and the background corrections were made by using a background curve ob-

tained in advance to the data collection. In case of SGOT the experiment was carried out below 15°C because of its instability at the higher temperature. The numbers of reflections exclusive of space group extinctions and the numbers of reflections recorded as zero are listed below:

	<u>SGCH</u>	<u>SGCT</u>	<u>PACD</u>
radii of the sphere $\underline{r}(=2\sin\theta/\lambda)$	1.278	0.962	1.190
$2\theta(\text{max.})$ corresponding to $\underline{r}$	54.0	40.0	50.0
fixed time(seconds)	20	10	20
total no. of reflections	2,093	1,245	1,759
no. of reflections recorded as zero	212	164	148
the largest counts	10,902	10,365	7,978

No correction was made for the absorption effect, though it is not negligible. The extinction effect was not observed noticeably at the final stage of the refinement and the correction for it was ignored. Thus, these two effects are the limiting factors in the accuracy of the intensity data.

Calculation for the goniostat setting angles and usual Lorentz and polarization corrections were made on an NEAC-2101 computer at the Institute for Protein Research, Osaka University, with a program written by the author.

### Crystal Data

The crystallographic data of the crystals, SGCH, SGCT and PACD, are listed below.

	<u>SGCH</u>	<u>SGCT</u>	<u>PACD</u>
crystal system	monoclinic	monoclinic	monoclinic
a(Å)	17.16 ± 0.03	10.721±0.010	6.860±0.005
b(Å)	6.84 ± 0.02	17.769±0.006	11.398±0.003
c(Å)	17.57 ± 0.01	13.895±0.006	13.358±0.003
β(°)	111.29± 0.05	94.71±0.05	106.93±0.05
U(Å <sup>3</sup> )	1,920	2,638	999
Z	8	8	4
dm(g.cm <sup>-3</sup> )	1.88	-	1.821
dx(g.cm <sup>-3</sup> )	1.85	1.744	1.823
μ(cm <sup>-1</sup> )(for Mo Kα)	22	18	23
space group	C2/c	C2/c	P2 <sub>1</sub> /c

The space groups possible for SGCH and SGCT crystals are Cc and C2/c. The test for the alternative choice of the space groups was carried out for the SGCH crystal; no pyroelectricity was observed and further, a statistical N(z) test<sup>18</sup>, applied to all the three-dimensional data, indicated conclusively the existence of a center of symmetry in the crystal. Therefore, the structure analysis of SGCH was started by assuming the centrosymmetric space group, C2/c, and this assumption was later justified by the success of the structure determination. For SGCT crystal the space group was also



assumed as C2/c and confirmed by the successful structure analysis. The space group for PACD was uniquely determined as P2<sub>1</sub>/c from the systematic absences.

### Determination of the Structure

From a three-dimensional Patterson function, calculated after the corrections for Lorentz and polarization factors, the positions of the copper(II) ion were easily determined. For SGCH and PACD the successive Fourier calculation with phases based on the heavy atom, copper(II) ion, revealed all the non-hydrogen light atoms. For SGCT the minimum function superposed on copper(II) ion clearly showed the non-hydrogen light atoms, though there were seven possible positions for the crystallization water molecules.

Further refinement of the crystal structure were carried out by the block-diagonal least-squares method as follows;

	<u>SGCH</u>	<u>SGCT</u>	<u>PACD</u>
isotropic thermal parameters	0.093	0.071	0.110
anisotropic thermal parameters	0.075	0.061	0.079
including hydrogen atoms	0.069	0.050	0.071

The above-mentioned numbers are the discrepancy index R, which is expressed by  $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$ . The isotropic refinement is the one with isotropic thermal parameters applied for the atoms of the form  $\exp(-B \sin^2 \theta / \lambda^2)$ , and in anisotropic refinement the parameters are of the form  $\exp(-\beta_{11}h^2 + \beta_{22}k^2 +$

$\beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl$ ). The positions of hydrogen atoms were found in the difference Fourier maps with the coefficients (Fo-Fc) after the anisotropic refinement. In the least-squares calculations a unit weight was assigned for each reflection, and the minimized function is  $\Sigma(\Delta F)^2$ .

The final atomic parameters are listed in Tables 1 and 2 for SGCH, in Tables 3 and 4 for SGCT and in Tables 5 and 6 for PACD. The observed and calculated structure factors are listed in Tables 7, 8 and 9 for SGCH, SGCT and PACD, respectively. The atomic scattering factors for copper(II) ion and for neutral C, N, O, H atoms were taken from the International Tables for X-Ray Crystallography<sup>19</sup>. A correction for the anomalous dispersion effect<sup>20</sup> of copper(II) ion,  $\Delta f' = 0.3$ , was included in the structure factors calculations.

The calculations of the structure analyses were made by the programs as follows; the least-squares calculation, Fourier summation, distances, angles and best planes calculation were made by the program written by Dr. T. Ashida of the Institute for Protein Research, Osaka University, on HITAC-5020 computer at the Tokyo University. The calculation of the Patterson function was carried out partly on NEAC-2206 computer of the Osaka University by the program written by Dr. T. Takano of the Institute for Protein Research, and also on HITAC-5020 computer by the program written by Mr. N. Yasuoka of the Faculty of Engineering, Osaka University as well as the program of minimum function for HITAC-5020 computer.

## Description of the Structure

### I. Molecular Structure.

- a. N-salicylidene-glycinato-aquocopper(II) hemihydrate(SGCH) and tetrahydrate(SGCT).

The bond lengths and angles in the molecules of SGCH and SGCT are shown in Figs. 1, 2 and 3, 4, respectively. They are also listed in Tables 10 and 11 with their standard deviations. The least-squares planes (best planes) of these molecules are listed in Table 16 with the normal distances from the planes.

Both of the complexes lie approximately on the planes described by the equations P(1) in Table 16. The plane for SGCH is roughly perpendicular to the b axis ( $61^\circ$ ) and that of SGCT nearly perpendicular to the c axis ( $18^\circ$ ). The largest deviations of atoms from these planes are O(2) in SGCH by  $0.326\text{\AA}$  and W(1) atom in SGCT by  $0.253\text{\AA}$ . In SGCH several atoms have the normal distances from the plane P(1) by more than  $0.2\text{\AA}$  as can be seen in Table 16, and this fact shows that the plane of SGCT has the better planarity than that of SGCH. Since the complexes are not on complete planes they can be better described by two planar groups, one being salicylidinatocopper group which forms the plane P(4), and the other the glycinatocopper group which forms the plane P(3) in Table 16, although several atoms still deviate from the planes by significant amounts. Of these planes the better fit is ob-

served for the plane of glycinatocopper group in SGCT than in SGCH since the nitrogen atom deviates from the plane by only a half of the amount observed in the former than the latter. This difference may be explained by the rotation around the C(1)-C(2) bond and hence the rotation around this bond from the carboxyl plane is less in the former than that of the latter. The planes of salicylaldiminatocopper groups in both SGCH and in SGCT are fairly good planes and could not be detected any significant differences between these two. The deviations of the nitrogen atoms from these planes P(4) are  $0.07\text{\AA}$  in SGCH and  $0.06\text{\AA}$  in SGCT, respectively. These values can be compared with the similar values observed in bis-(5-chlorosalicylaloximato)copper(II)( $0.10\text{\AA}$ )<sup>3</sup>, bis(salicylaloximato)copper(II)( $0.04\text{\AA}$ )<sup>2</sup> and in complexes with the same kind of ligand molecules. This deviation from the plane may be due to the distortion caused in the formation of the six-membered rings between copper(II) ion and salicylaldimino ligands. The dihedral angles between these two planes, P(3) and P(4), is  $16.5^\circ$  in SGCH and  $9.5^\circ$  in SGCT. These angles also indicate the better planarity of the complexes as a whole in SGCT than in SGCH.

The bond distances in the benzene rings both in SGCH and SGCT are significantly fluctuated as can be seen in Table 10. The fluctuation of them are  $0.02\text{\AA}$  from the mean,  $1.403\text{\AA}$ , in SGCH and  $0.05\text{\AA}$  from the mean,  $1.400\text{\AA}$ , in SGCT. The contribution of the quinone type resonance structure seems rather small in these complexes while it is appreciable in

salicylic acid<sup>21</sup>. The amount of the fluctuation is too big to be accounted for by the values calculated by a simple molecular orbital approximation given by Lingafelter and Braun<sup>1</sup>, as follows;

	<u>SGCH</u>	<u>SGCT</u>	L.B.	MO	mean( <u>SGCH-SGCT</u> )
C(4)-C(3)	1.457	1.450	1.430	1.42	1.453
C(4)-C(5)	1.420	1.389	1.423	1.40	1.405
C(4)-C(9)	1.409	1.409	1.415	1.42	1.409
C(6)-C(5)	1.389	1.394	1.367	1.38	1.392
C(6)-C(7)	1.379	1.391	1.384	1.39	1.385
C(8)-C(7)	1.409	1.367	1.388	1.38	1.388
C(8)-C(9)	1.412	1.447	1.415	1.40	1.429
C(9)-O(3)	1.337	1.350	1.312	1.31	1.343

where L.B. are the values from the experiments by Lingafelter and Braun<sup>1</sup> as mentioned below.

Even by considering the standard deviations of these bonds the difference in C(8)-C(9) in SGCT from the value of MO calculation is too big, and rather the consistency between average of SGCH-SGCT and L.B., which are the averages of nine salicylaldiminato ligands of complexes from the list given by Lingafelter and Braun<sup>1</sup>, are excellent. Lingafelter and Braun also indicated that the three bonds(C(5)-C(6), C(6)-C(7), C(7)-C(8)) which are comparatively farther from the metal have the average length less than 1.39Å, while the four bonds(C(3)-C(4), C(4)-C(5), C(4)-C(9), C(8)-C(9)) which are nearer to the metal all have an average lengths greater than 1.41Å. These

values were taken from the nine complexes as stated, and they proved that this difference was significant by means of a simple MO calculation quoted above. These two kinds of the averages are listed below;

complex	nearer four	farther three
<u>SGCH</u>	1.424Å	1.384Å
<u>SGCT</u>	1.425	1.392
values by MO calculation	1.41	1.38

From the list the differences between the nearer four and the farther three in both SGCH and SGCT are considered significant. This effect is also observed in manganese(II) chelate of pyridoxylidenevaline<sup>22</sup>. The angles in benzene rings have the averages of 120.0° both in SGCH and SGCT. The planarity of these rings, as expressed by the equations P(5) in Table 16, are excellent within the standard deviations.

The bond distance of C(9)-O(3) is 1.337Å and 1.350Å for SGCH and SGCT respectively in the present analyses, and this elongated bonds, comparing with the value, 1.312Å, given by Lingafelter and Braun, may be reasonable if the coordination bonds, Cu-O(3), are taken into account, where the coordination bonds are significantly shorter in the present analyses than those by Lingafelter and Braun.

The glycine residues of these complexes have the normal bond distances and angles as in usual amino acids, though the shifts of the nitrogen atoms from the carboxyl planes are

0.35Å in SGCH and 0.12Å in SGCT. These amounts of shifts from the planes are compared with the values, 0.44Å, 0.58Å, 0.31Å in  $\alpha$ -,  $\beta$ - and  $\gamma$ -glycine<sup>23,24,25</sup>. This value usually has more variety in other amino acids. The small amount, 0.12Å, in SGCT corresponds to the better planarity of P(3), and relates to the rotation around the bond C(1)-C(2) from the carboxyl plane as stated previously.

The coordination of copper(II) ion is not the usual distorted octahedron observed in the copper(II) complexes with the salicylaldiminato ligands, but is a square pyramid in the present analyses, which is now the growing class of the configuration of five-coordinated copper(II) ion. The distances of copper(II) environment are Cu-W(1) 2.016, 1.965Å, Cu-O(1) 1.953, 1.959Å, Cu-N 1.949, 1.913Å and Cu-O(3)(phenolic) 1.928, 1.936Å for SGCH and SGCT, respectively. These distances are shown in Figs. 7 and 8. The Cu-O(carboxyl) distances are the quite commonly found values and coincide with the distances in metal peptide complexes. The average value from the metal peptide complexes is 1.963Å. The Cu-O(phenolic) bonds have a shorter distances than the average, 1.902Å, given by Lingafelter and Braun, and this may have something to do with the longer C(9)-O(3) bonds. This was the case both in SGCH and SGCT. The Cu-N bond distance of SGCT is significantly shorter than that in SGCH. However, these two values have the property similar to the metal peptide complexes rather than metal salicylaldimine complexes since our values are closer

to the distances of metal peptide complexes with five-membered rings, the average value being  $1.963\text{\AA}$ .

The angles,  $O(1)-Cu-N$  and  $O(3)-Cu-N$ , for SGCH and SGCT are  $83.9^\circ$ ,  $83.4^\circ$  and  $93.4^\circ$ ,  $94.6^\circ$ . The former angles are the same as those in metal peptide complexes with five-membered rings and the latter coincide with those in metal salicylaldimine complexes with six-membered rings.

The major difference between SGCH and SGCT in its coordination configuration is the fifth coordination ligand atoms, and this difference is also the major factor in the difference of their crystal structures of SGCH and SGCT. In SGCH the copper(II) ion is also weakly coordinated by the  $O(2^{11})$  atom of the adjacent complex related by the two-fold screw axis. The weakly coordinated atom  $O(2^{11})$  lies at the apex of the square pyramid of which corners of the approximately square base are occupied by the strongly coordinated ligand atoms. The bond distance of  $Cu-O(2^{11})$  is  $2.334\text{\AA}$  and is significantly shorter distance than the van der Waals contacts. In SGCT the fifth coordination atom  $W(2)$  also lies at the apex of the square pyramid at a distance,  $2.352\text{\AA}$ , from the copper(II) ion. These coordination configurations are shown in Figs. 7 and 8.

b. Pyruvidene- $\beta$ -alaninatoaquocopper(II) dihydrate(PACD).

Bond lengths and angles in the complex of PACD are shown in Figs. 5 and 6, and also listed in Table 12 with their



standard deviations.

The complex almost lies on the plane described by the equation P(1) in Table 17 which is nearly perpendicular to the c axis. However, the  $\beta$ -alaninate atoms deviate from the P(1), as expected: O(1), C(2) and C(3) atoms are out of the plane by  $-0.20$ ,  $0.61$  and  $-0.22\text{\AA}$ , respectively. The pyruvate atoms are planar, expressed by the equation P(4), and the largest deviation from it is  $0.012\text{\AA}$  of C(4) atom. The copper(II) ion is off from it by  $0.067\text{\AA}$ . Six atoms around the  $>C=N$ - double bond are also coplanar and C(6) atom deviates from the plane, P(5), by only  $0.020\text{\AA}$ , though the strain in the complex formation, if exists, might be detected in some of these atoms. Hence no twist around the double bond occurs.

The carboxyl group of  $\beta$ -alaninate group is expressed by the plane P(3). The dihedral angle between P(3) and the one containing C(1), C(2) and C(3) atoms is  $52.4^\circ$  and this value is different from those found in  $\beta$ -alanine( $9.3^\circ$ )<sup>26</sup> and nickel  $\beta$ -alanine dihydrate( $30.3^\circ$ )<sup>27</sup>, while the angle between the plane passing through C(1), C(2), C(3), and the one containing C(2), C(3) and N atoms is  $68.5^\circ$  ( $83.8^\circ$  in  $\beta$ -alanine,  $73.7^\circ$  in nickel  $\beta$ -alanine dihydrate and  $70^\circ$  in copper  $\beta$ -alanine hexahydrate<sup>28</sup>). From the dihedral angles the conformation of the  $\beta$ -alaninate group in the present work is different from those quoted above with respect to the rotation around C(1)-C(2) bond and the deviation is mainly observed in C(3). This atom deviates from the plane, P(3), by  $1.12\text{\AA}$ .

In the two carboxyl groups of  $\beta$ -alaninate and pyruvate groups the C-O (coordinated) bond distances are 1.282 and 1.278 Å, and the 'free' C-O bonds have 1.231 and 1.234 Å. These values are in good agreement with the values, 1.277 Å, which corresponds to the C-O<sub>H</sub> or C-O---Me distances, and 1.232 Å for 'free' C-O distance, averaged in the amino acid hydrohalides and metal complexes of amino acids. The angles  $\angle$ OCO in carboxyl groups, 121.5°, 124.9°, are consistent with the values found in amino acids, and the C-C bond distances in this complex are all reasonable.

The carbon-nitrogen double bond, N-C(4), has a bond distance of 1.247 Å and this value is considered abnormally short, even for the pure double bond distance (the sum of the double bond radii<sup>30</sup> of carbon and nitrogen atoms is 1.29 Å). This distance corresponds to the shortest in the bond distances table of metal salicylaldehyde complexes given by Lingafelter and Braun. This short distance can be compared with the values in SGCH and SGCT, including the single bond, C(3)-N, in relation to the transamination reactions. This will be discussed in the last section of this thesis.

The copper(II) ion forms a square pyramidal configuration coordinated by two carboxyl oxygen atoms, O(1), O(4), the nitrogen atom and two water molecules, of which one is strongly coordinated and the other weakly. The coordination configuration is shown in Fig. 9, and bond lengths and angles

of these bonds are listed in Table 12. The Cu-O(carboxyl) distances are 1.906 and 1.963Å, and the longer one which is involved in five-membered ring formation is consistent with the mean value, 1.963Å, found in the complexes of square pyramidal configuration with five-membered rings(quoted in the section of molecular structures of SGCH and SGCT). On the other hand, the shorter distance is significantly shorter than this average. This may be the character of the less stable six-membered ring. There are few reports<sup>28,29</sup> of this type of six-membered ring, and they are inadequate to discuss small amount of differences. At this point one can find a list of copper(II) chelates<sup>1</sup> of salicylaldehyde ligands as quoted in the previous section. They gave four chelates in the list from which one can obtain that the Cu-O distance in six-membered rings have the mean value of 1.902Å, although the chelate rings form nearly planar configuration and the oxygen atoms are the phenolic. Hence it is not fully acceptable to compare the distances with the different type of chelate rings, but the agreement is very good.

As regards the Cu-N bond the present analysis gave 1.963Å which lies between two means, 1.932Å from the complexes of square pyramidal configuration and 1.970Å given by Lingafelter and Braun. The former is from the five-membered and the latter is from the six-membered chelate rings. The Cu-N bond in the present work has the nature closer to the six-membered chelate ring.

The strongly coordinated water molecule lies in the

square of the coordination plane and the Cu-W(1) distance, 1.946Å, is significantly shorter than the value, 2.016Å, in SGCH. The fifth coordination bond formed by the weakly bound water molecule, W(3), which lies at the apex of the square pyramid. The distance, 2.413Å, is a reasonable value, considering the other complexes of square pyramidal configuration in which the values range from 2.30Å in copper(II) monoglycylglycine trihydrate<sup>33</sup> at the shortest to 2.48Å in (β-alanyl-1-histidinato)copper(II) dihydrate<sup>8</sup>. The distance of this fifth coordination bond is usually shorter than those in the complexes of octahedral configuration.

The angles, O-Cu-N, are 82.2° and 96.6° for the five- and six-membered ring, respectively. These values agree with the mean values, 83.3° and 93.8° taken from the complexes of square pyramid.

From the above-mentioned discussion gives rise to a conclusion that the copper(II) chelates to the organic ligand molecules of square pyramidal configuration can be described by a fairly uniform configuration model, with four short and one long coordination bond.

## II. Crystal Structure

### a. N-salicylidene-glycinato-aquocopper(II) hemihydrate (SGCH).

A strong interaction between molecules exists in the crystal; the fifth coordination bond to copper(II) ion is formed between the adjacent complexes so that the complexes are connected by this bond in an endless chain along the b axis. In this chain the next complex is related by the two-fold screw axis. There are several very short intermolecular atomic contacts as can be seen in Table 13. Of these the shortest carbon-carbon contact is C(4)-C(4<sup>1</sup>), 3.276Å, and four other short contacts are observed between the molecules related by the center of symmetry. Therefore, the complex molecules construct a thick plate of complexes along the (10 $\bar{1}$ ) plane. All of the abnormally short contacts are included in this plate structure, and this plate is connected to the next by a fairly strong hydrogen bond between W(1) and O(3<sup>iii</sup>) atoms with the distance of 2.64Å. There is also a weak hydrogen bond between these plates via the crystallization water molecule. This hydrogen bond is 2.95Å long.

Thus, by the coordination bond, short intermolecular atomic contacts and two hydrogen bonds are the major factors to construct the rigid structure. The packing of the complex molecules in the crystal is shown in the Fig. 10, looking down along the b axis, and is shown in Fig. 11, along the a axis.

b. N-salicylidene-glycinato-aquocopper(II) tetrahydrate (SGCT).

In spite of the similarity of the molecular structure to that of SGCH, the crystal structure of SGCT is completely different from that of SGCH. A part of the packing of the complex molecules and the hydrogen bonding system is shown in Fig. 12. The major cause of the difference of the crystal structure is the difference of the fifth coordination bonds in SGCH and SGCT. In SGCT the fifth coordination bond is formed by one of the water molecules, and no coordination bonds are involved in constructing the crystal structure.

The planar complex molecules lie nearly perpendicular to the c axis and four molecules are piled up along the c axis. Between these there are several intermolecular short contacts as listed in Table 14. Since two water molecules are coordinated to copper(II) ion the residual water molecules are located between the molecules as the crystallization water. Of the ten possibilities of hydrogen bonds eight hydrogen bonds are observed with the distances from 2.74Å to 3.13Å. Via the crystallization water molecules the complex molecules are joined together, though the packing is not as rigid as that in SGCH, and hence corresponds to the comparatively large thermal vibrational parameters obtained in the final stage of the structure determination.

c. Pyruvidene- $\beta$ -alaninatoaquocopper(II) dihydrate(PACD).

The crystal structure along the two crystallographic axes are shown in Figs. 12 and 13. The complex plane is nearly perpendicular to the c axis and four complex molecules are piled up along the c axis as in SGCT crystal, although the area of overlap between molecules are not to such an extent as the case of SGCT. Between these complex molecules there are some short intermolecular, atomic contacts, for instance, C(5)-C(4<sup>i</sup>) is 3.43Å as listed in Table 15.

More important than this is the hydrogen bonds between the complex molecules. The two hydrogen bonds, W(3)-O(3<sup>ii</sup>) and O(2)-W(3<sup>ii</sup>), have the distances of 2.85Å and 2.73Å, and these two connect directly the complex molecules which are related by the two-fold screw axis along the b axis.

Therefore, the complex molecules are constructing a chain along the b axis by hydrogen bonds, and some van der Waals contacts, as listed above, hold them along the c axis. The crystallization water molecule is located in the room between the complex molecules and is connected to them by a hydrogen bond.

## Discussions

### I. The Coordination Configuration of Copper(II) Ion.

The copper(II) chelates of N-alkylsalicylaldimine usually show the six-coordinated octahedral configuration with small number of exceptions such as tetragonal and tetrahedral<sup>31,32</sup> configuration. In its octahedron four short coordination bonds with distances, 1.9-2.0Å, make the square base and two ligand atoms locate on its each side at the distance of 2.6-3.0Å. On the other hand, the metal chelates of peptides construct mostly the square pyramidal configuration with four short and one long bond (the distance of the latter is 2.3-2.5Å).

From the ligand molecule, therefore, the structure of PACD is easily considered to have the latter type of the coordination configuration. However, the coordination configuration of the SGCH and SGCT molecules could have the either of the structures since their ligand molecule has the character in between these two cases. As a result both of SGCH and SGCT complex molecules have the coordination configuration similar to that of the latter type. However, the bond distances and angles give more complicated conclusion; the dimensions of the six-membered rings have the nature of the former complexes, copper(II)-N-alkylsalicylaldimine, and those of the five-membered rings have, in contrast to the six-membered rings, the property of the latter type of the



complexes. Hence, in this sense, both SGCH and SGCT complex molecules have the coordination configuration of the middle of these two cases.

One of the nature of the square pyramid configuration is the appreciable amount of shift of the copper(II) ion toward the apical ligand atoms, and this is the commonly found structures in metal chelates with peptides. The best planes of the square bases in SGCH and SGCT are described by the equations P(2) in Table 16, and that in PACD is given by the equation P(2) in Table 17.

In SGCH the copper(II) ion is shifted toward the apical O(2<sup>11</sup>) atom by 0.227Å, in SGCT toward the apical W(2) atom by 0.135Å, and in PACD toward W(3) atom by 0.125Å, each from the plane P(2) as described. These values are in good agreement with the values found in some metal peptides complexes: 0.17Å in (glycyl-1-histidinato)copper(II) sesquihydrate<sup>7</sup>, 0.13Å in (β-alanyl-1-histidinato)copper(II) dihydrate<sup>8</sup>, 0.13Å in glycyglycyglycino copper(II) chloride sesquihydrate<sup>4</sup> and 0.115Å in sodium glycyglycyglycino cuprate monohydrate<sup>5</sup>. From these, the shift is the common feature of the five-coordinated copper(II) ion complexes to peptides in the crystalline state. More general information about the other metal ions may be obtained elsewhere<sup>9</sup>. The another feature of the configuration is found by the careful investigation of the structure; from the least-squares plane of the square bases

the normal distances from them imply the tendency that the ligand atoms are located so as to take a 'very flattened' tetrahedral configuration. Of course, this tendency was observed more or less in many five-coordinated complexes with square pyramidal configuration. As can be seen in Tables 16 and 17, this effect is not negligible in SGCT and PACD molecules where two ligand atoms are above the planes and the other two are below it by more than  $0.05\text{\AA}$ , in the tetrahedral manner. The more apparent example, as pointed out by Freeman et al., is the crystal of ( $\beta$ -alanyl-l-histidinato) copper(II) dihydrate<sup>8</sup> in which the amount is  $0.23\text{\AA}$ .

In the broad sense the square bases can be described as planar, but these amounts are very significant and can not be ignored.

## II. The Relation of the Complexes to the Transamination Reactions.

The double bond character of the bonds around the nitrogen atoms in these complexes is of much interest in relation to the non-enzymatic transamination reactions. The bond lengths around the nitrogen atoms in these three complexes are listed below:

complex	$\text{>C=N-}$	$\text{>O-N-}$
<u>SGCH</u>	1.282 $\text{\AA}$	1.446 $\text{\AA}$
<u>SGCT</u>	1.302	1.461

mean( <u>SGCH</u> - <u>SGCT</u> )	1.292	1.453
<u>PACD</u>	1.247	1.480

The sum of the double bond radii<sup>30</sup> for C=N is 1.29Å and that for the single bond radii for C-N is 1.49Å. In SGCH and SGCT the values are similar so that the average of these two are taken to compare with the values in PACD and the calculated values from the bond radii.

In SGCH and SGCT the C=N double bonds have the normal double bond lengths, while the C-N have the lengths shorter than the normal single bond distance by about 0.04Å. On the other hand, in PACD the C=N has a very short distance than the usual double bond length by 0.04Å and the C-N bond has the normal single bond distance. From these, first of all, there must be electrons flowing into the site of nitrogen atoms in these complexes so that the distances around the nitrogen atoms are somewhat shorter than the normal distances, whether they are the single bonds or the double. This might be due to the hyperconjugation of CH<sub>2</sub> or CH<sub>3</sub> groups, or might have something to do with the coordination bonds to the copper(II) ions. In the latter case the structure of non-coordinated ligand molecules must have the normal dimensions, while in the former case they must have the similar abnormal dimensions as stated above even before the coordination to the metal ion.

These two cases of the bond lengths around the nitrogen atoms are in the opposite situation and these results suggest

that the double bonds in SGOH and SGOT are partially migrated toward the single bonds and hence the single bond show a slightly shorter distance in each case, even if the double bond lengths seem normal. Thus, the transamination reaction could be observed in these complex system as reported by Snell et al.<sup>13</sup> On the other hand, the double bond in PACD does not show the partial migration and also the single bond length is normal, these fact indicating that the electrons are localized around the double bond. Hence no transamination reaction was observed<sup>15</sup>.

From the reaction in the solution the coordination to the metal ion is the essential factor in accelerating the reaction, so the migration of the double bond toward single must have a substantial correlation to the Cu-N coordination bonds in these complexes and the dimensions of non-coordinated ligand molecules have to be found for the further discussions.

The crystal structure of manganese(II) chelate of pyridoxylidenevaline was established by Willstadter et al.<sup>22</sup> which is also related to the catalytic intermediate in the reaction of non-enzymatic transamination. In its structure the bonds in question have the distances,  $\text{>C=N- } 1.27\text{\AA}$  and  $\text{>C-N- } 1.45\text{\AA}$ . This situation is very similar to the present results.

### III. The Crystal Structures of SGCH and SGCT.

Since the crystals of SGCH was prepared above 30°C and SGCT crystals were obtained below 10°C, the behaviour of the SGCT crystals at the temperature between them is another interest. After the structure analysis of SGCT we found a high isotropic thermal parameter for W(5) oxygen atom,  $7.5\text{\AA}^2$ , when the experiment was carried out between 10°C to 15°C. This rather high temperature factor, considering the other four water oxygen atoms with the normal temperature factors, implies a large thermal vibration or the existence of the disorderness on this site in the crystal.

The crystal used in the experiment was kept from 15°C to 25°C in the air. After six months the crystal showed a powder pattern which coincided neither SGCH nor SGCT crystals.

Kishita et al.<sup>16</sup> had prepared a complex in this temperature range and found the complex to be the mixture of SGCH and SGCT. However, the present analysis of the powder pattern did not coincide either to the mixture of them. The quantitative analysis of elements about the nontransparent crystals which were kept in the air as stated above resulted that the crystals obtained are N-salicylidene-glycinatocopper (II) hemihydrate, which must have a completely different molecular structure and, of course, the crystal structure from both SGCH and SGCT.

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Table 1. Positional parameters of atoms and their standard deviations (s.d.'s in Å) in the molecule of N-salicylideneglycinatoaquocopper(II) hemihydrate.

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Cu	0.12172	0.09512	0.20439	0.00094	0.00108	0.00094
O(1)	0.2287	0.9576	0.2457	0.0054	0.0066	0.0057
O(2)	0.3421	0.8799	0.2162	0.0058	0.0068	0.0061
O(3)	0.0068	0.1730	0.1500	0.0055	0.0062	0.0054
W(1)	0.0943	0.9736	0.2962	0.0059	0.0065	0.0058
W(2)*	0.0000	0.5964	0.2500	0.0000	0.0106	0.0000
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

\* The standard deviations,  $\sigma(x)$  and  $\sigma(z)$  of W(2) can not be estimated since W(2) lies on a two-fold axis so that x and z parameters have restrictions.

Table 2. Thermal parameters in the molecule of N-salicylidene-glycinatoaquocopper(II) hemihydrate.

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	0.00157	0.01825	0.00156	0.00107	0.00121	0.00061
O(1)	0.0018	0.0224	0.0020	0.0009	0.0016	0.0008
O(2)	0.0019	0.0228	0.0024	0.0040	0.0014	0.0021
O(3)	0.0019	0.0195	0.0016	0.0018	0.0010	0.0020
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	0.0171	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					

\*  $\beta_{12}$  and  $\beta_{23}$  for W(2) are zero since this atom is restricted on the two-fold axis.

Thermal parameters for hydrogen atoms are isotropic B values in  $\text{\AA}^2$

Table 3. Positional parameters of atoms and their standard deviations (s.d.'s in Å) in the molecule of N-salicylidene-glycinatoaquocopper(II) tetrahydrate.

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Cu	0.12566	0.14374	0.09551	0.0011	0.0011	0.0011
O(1)	0.3028	0.1636	0.0806	0.0057	0.0061	0.0059
O(2)	0.4933	0.1116	0.1007	0.0060	0.0067	0.0074
O(3)	-0.0487	0.1172	0.1031	0.0057	0.0059	0.0056
W(1)	0.0749	0.2405	0.0361	0.0061	0.0062	0.0060
W(2)	0.1471	0.2020	0.2479	0.0061	0.0063	0.0059
W(3)	0.4018	0.2341	0.3115	0.0065	0.0069	0.0067
W(4)	0.2965	0.3127	0.4566	0.0063	0.0067	0.0063
W(5)	0.0550	0.3410	0.3606	0.0079	0.0088	0.0097
N	0.1830	0.0441	0.1264	0.0068	0.0072	0.0065
C(1)	0.3782	0.1088	0.1028	0.0085	0.0097	0.0091
C(2)	0.3193	0.0375	0.1367	0.0088	0.0095	0.0096
C(3)	0.1167	-0.0167	0.1327	0.0087	0.0092	0.0087
C(4)	-0.0191	-0.0185	0.1261	0.0088	0.0083	0.0081
C(5)	-0.0771	-0.0878	0.1344	0.0097	0.0094	0.0090
C(6)	-0.2065	-0.0953	0.1325	0.0102	0.0099	0.0100
C(7)	-0.2790	-0.0306	0.1201	0.0098	0.0097	0.0087
C(8)	-0.2275	0.0388	0.1078	0.0091	0.0091	0.0087
C(9)	-0.0929	0.0468	0.1122	0.0085	0.0085	0.0078
H(1)	0.355	0.036	0.213	0.08	0.08	0.08
H(2)	0.347	-0.013	0.116	0.10	0.10	0.10
H(3)	0.171	-0.061	0.146	0.12	0.12	0.12
H(4)	-0.023	-0.136	0.146	0.12	0.13	0.12
H(5)	-0.245	-0.143	0.137	0.08	0.09	0.08
H(6)	-0.390	-0.030	0.112	0.08	0.08	0.08
H(7)	-0.273	0.096	0.098	0.09	0.09	0.09
H(8)	0.230	0.212	0.251	0.08	0.08	0.08
H(9)	0.099	0.166	0.289	0.13	0.13	0.13
H(10)	0.042	0.276	0.068	0.12	0.12	0.12
H(11)	0.118	0.275	-0.016	0.09	0.09	0.09
H(12)	0.382	0.263	0.358	0.13	0.14	0.13
H(13)	0.383	0.200	0.288	0.12	0.13	0.12
H(14)	0.375	0.337	0.495	0.13	0.13	0.13
H(15)	0.244	0.364	0.466	0.14	0.14	0.13
H(16)	0.124	0.332	0.409	0.12	0.12	0.12
H(17)	0.073	0.280	0.323	0.12	0.12	0.12

Table 4. Thermal parameters in the molecule of N-salicylidene-glycinatoaquocopper(II) tetrahydrate.

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	0.0061	0.0026	0.0044	0.0002	0.0015	0.0007
O(1)	0.0064	0.0030	0.0051	0.0012	0.0011	0.0003
O(2)	0.0058	0.0034	0.0097	0.0017	0.0034	0.0000
O(3)	0.0068	0.0029	0.0041	0.0008	0.0015	0.0012
W(1)	0.0090	0.0029	0.0049	0.0009	0.0021	0.0017
W(2)	0.0087	0.0034	0.0044	-0.0025	0.0018	-0.0001
W(3)	0.0090	0.0039	0.0066	-0.0012	0.0014	-0.0031
W(4)	0.0086	0.0037	0.0055	0.0002	-0.0012	-0.0018
W(5)	0.0114	0.0057	0.0137	-0.0002	0.0024	0.0055
N	0.0062	0.0029	0.0029	0.0008	0.0002	0.0015
C(1)	0.0052	0.0034	0.0049	-0.0004	0.0013	-0.0015
C(2)	0.0058	0.0030	0.0057	0.0000	-0.0004	0.0016
C(3)	0.0067	0.0029	0.0040	0.0000	0.0023	0.0000
C(4)	0.0083	0.0019	0.0027	0.0011	0.0006	0.0005
C(5)	0.0098	0.0028	0.0039	-0.0013	0.0005	-0.0019
C(6)	0.0107	0.0028	0.0059	-0.0046	0.0008	-0.0008
C(7)	0.0103	0.0033	0.0030	-0.0011	0.0007	-0.0001
C(8)	0.0081	0.0026	0.0039	0.0005	0.0019	0.0008
C(9)	0.0072	0.0026	0.0023	-0.0024	0.0013	0.0000
H(1)	1.0					
H(2)	3.9					
H(3)	7.4					
H(4)	6.9					
H(5)	1.7					
H(6)	1.4					
H(7)	2.6					
H(8)	0.4					
H(9)	8.1					
H(10)	5.5					
H(11)	2.7					
H(12)	8.6					
H(13)	7.0					
H(14)	8.1					
H(15)	9.5					
H(16)	7.0					
H(17)	9.0					

Thermal parameters for hydrogen atoms are isotropic B values in  $\text{\AA}^2$ .

Table 5. Positional parameters of atoms and their standard deviations (s.d.'s in Å) in the molecule of pyruvate-β-alaninatoaquocopper(II) dihydrate.

Atom	x	y	z	σ(x)	σ(y)	σ(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	0.1551	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

Table 6. Thermal parameters in the molecule of pyruvidene- $\beta$ -alaninatoaquocopper(II) dihydrate.

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	0.0110	0.0038	0.0059	-0.0001	0.0021	-0.0005
W(1)	0.0152	0.0047	0.0078	-0.0010	-0.0049	-0.0006
W(2)	0.0199	0.0078	0.0078	-0.0024	0.0002	-0.0028
W(3)	0.0145	0.0051	0.0110	0.0002	-0.0054	-0.0008
O(1)	0.0141	0.0041	0.0079	-0.0022	0.0017	-0.0008
O(2)	0.0191	0.0045	0.0095	-0.0012	0.0018	-0.0007
O(3)	0.0207	0.0036	0.0073	0.0013	-0.0049	0.0007
O(4)	0.0124	0.0050	0.0070	-0.0008	-0.0001	-0.0008
N	0.0105	0.0053	0.0040	-0.0015	0.0018	-0.0006
C(1)	0.0181	0.0042	0.0058	-0.0017	0.0027	-0.0005
C(2)	0.0179	0.0039	0.0083	-0.0028	0.0102	0.0000
C(3)	0.0090	0.0046	0.0079	-0.0039	-0.0003	0.0002
C(4)	0.0116	0.0053	0.0038	0.0012	0.0043	-0.0008
C(5)	0.0142	0.0042	0.0042	-0.0007	0.0030	0.0006
C(6)	0.0120	0.0056	0.0063	0.0022	-0.0005	0.0010
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  $\text{\AA}^2$ .















Table 10. Bond lengths in the molecules of SGCH and SGCT and their standard deviations.

Bond	<u>SGCT</u>	<u>SGCH</u>	Bonds to hydrogen atoms in <u>SGCH</u> .
Cu - W(1)	1.965(06)	2.016(06)	W(1)-H(1),H(2) 0.81, 1.17
- O(1)	1.959(06)	1.953(06)	W(2)-H(3) 1.04
- N	1.913(07)	1.949(07)	C(2)-H(4),H(5) 1.03, 1.08
- O(3)	1.936(06)	1.928(06)	C(3)-H(6) 1.07
C(1) - O(1)	1.287(11)	1.284(10)	C(5)-H(7) 0.96
- O(2)	1.238(12)	1.249(10)	C(6)-H(8) 0.82
- C(2)	1.509(14)	1.533(12)	C(7)-H(9) 0.96
N - C(2)	1.461(12)	1.446(11)	C(8)-H(10) 0.90
- C(3)	1.302(12)	1.282(11)	
C(4) - C(3)	1.450(13)	1.457(11)	in <u>SGCT</u>
- C(5)	1.389(13)	1.420(12)	W(1)-H(10),H(11) 0.88, 1.1
- C(9)	1.409(12)	1.409(11)	W(2)-H(8),H(9) 0.91, 1.0
C(6) - C(5)	1.394(14)	1.389(13)	W(3)-H(12),H(13) 0.86, 0.7
- C(7)	1.391(14)	1.379(13)	W(4)-H(14),H(15) 1.09, 1.1
C(8) - C(7)	1.367(13)	1.409(12)	W(5)-H(16),H(17) 1.01, 1.2
- C(9)	1.447(13)	1.412(11)	C(2)-H(1),H(2) 1.11, 1.0
C(9) - O(3)	1.350(10)	1.337(10)	C(3)-H(3) 1.01
			C(5)-H(4) 1.06
			C(6)-H(5) 0.98
			C(7)-H(6) 1.20
			C(8)-H(7) 1.15

The standard deviations for the bonds are listed in parentheses.

Table 11. Bond angles in SGOH and SGCT.

Angle	<u>SGCT</u>	<u>SGCH</u>	Angles with hydrogen atoms. <u>SGCT</u>
W(1)- Cu -O(1)	92.0	88.0	C(2) with H(1), H(2) 102, 121, 99, 111, 112
W(1)- Cu -O(3)	89.8	91.0	C(3) with H(3) 111, 124
O(1)- Cu - N	83.9	83.4	C(5) with H(4) 120, 118
O(3)- Cu - N	93.4	94.6	C(6) with H(5) 121, 121
W(1)- Cu - N	168.0	165.3	C(7) with H(6) 125, 113
O(1)- Cu -O(3)	174.8	166.3	C(8) with H(7) 131, 109
Cu -O(1)-C(1)	115.7	116.5	H(10)-W(1)-H(11) 99
O(1)-C(1)-O(2)	124.8	125.3	H(8)-W(2)-H(9) 127
O(2)-C(1)-C(2)	119.1	119.5	H(12)-W(3)-H(13) 139
O(1)-C(1)-C(2)	116.1	115.2	H(14)-W(4)-H(15) 89
C(1)-C(2)- N	110.0	109.8	H(16)-W(5)-H(17) 86
C(2)- N - Cu	113.4	112.3	
C(3)- N - Cu	128.1	125.5	
C(2)- N -O(3)	118.3	121.8	
N -C(3)-C(4)	124.3	125.1	
C(3)-C(4)-O(5)	117.7	116.1	
C(3)-C(4)-O(9)	122.9	124.3	
C(5)-C(4)-O(9)	119.4	119.6	
C(4)-C(5)-C(6)	122.4	120.7	<u>SGCH</u>
C(5)-C(6)-C(7)	117.9	120.2	C(2) with H(4), H(5) 112, 123, 117, 89, 107
C(6)-C(7)-C(8)	122.3	120.0	C(3) with H(6) 116, 118
C(7)-C(8)-C(9)	119.7	121.1	C(5) with H(7) 120, 120
C(8)-C(9)-O(3)	116.4	117.4	C(6) with H(8) 114, 125
C(4)-C(9)-O(3)	125.4	124.3	C(7) with H(9) 113, 124
C(8)-C(9)-C(4)	118.2	118.4	C(8) with H(10) 117, 122
C(9)-O(3)- Cu	125.4	125.8	H(1)-W(1)-H(2) 112

Table 12. Bond lengths and angles in PAOD with their standard deviations for lengths.

Bond		Angle	
Cu -W(1)	1.946(06)	O(4)- Cu -W(1)	92.5
-O(1)	1.906(06)	W(1)- Cu -O(1)	87.9
- N	1.963(06)	O(1)- Cu - N	96.6
-O(4)	1.963(06)	O(4)- Cu - N	82.2
O(1)-O(1)	1.282(10)	W(1)- Cu - N	168.3
-O(2)	1.231(10)	O(1)- Cu -O(4)	175.7
-O(2)	1.516(12)	Cu -O(1)-C(1)	127.9
O(3)-C(2)	1.547(12)	Cu - N -C(3)	120.1
- N	1.480(10)	Cu - N -C(4)	115.1
C(4)- N	1.247(10)	Cu -O(4)-C(5)	113.3
-C(6)	1.504(12)	O(1)-C(1)-O(2)	121.5
O(5)-C(4)	1.531(12)	O(1)-C(1)-C(2)	118.9
-O(3)	1.234(10)	O(2)-C(1)-C(2)	119.6
-O(4)	1.278(10)	C(1)-C(2)-C(3)	113.7
W(1)-H(1)	0.99	C(2)-C(3)- N	110.0
-H(2)	0.81	C(3)- N -C(4)	124.8
W(2)-H(3)	1.03	N -C(4)-C(6)	128.6
-H(4)	0.86	N -C(4)-C(5)	114.3
W(3)-H(5)	0.84	C(5)-C(4)-C(6)	117.0
-H(6)	0.76	C(4)-C(5)-O(3)	120.3
O(2)-H(7)	1.09	C(4)-C(5)-O(4)	114.8
-H(8)	1.08	O(3)-C(5)-O(4)	124.9
O(3)-H(9)	1.22	around C(2) with H(7), H(8)	
-H(10)	1.29	117, 110, 106, 111, 98	
O(6)-H(11)	1.07	around O(3) with H(9), H(10)	
-H(12)	1.41	114, 121, 115, 105, 91	
H( -H(13)	0.91	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

The standard deviations for the bonds are listed in parentheses.

Table 13. Hydrogen bonds and some closest contacts of atoms in neighboring molecules, in SGOH.

Hydrogen bonds

W(2) - O(2 <sup>11</sup> )	2.952 <sup>o</sup> Å
W(1) - O(3 <sup>111</sup> )	2.637

Close contacts of atoms less than 3.5<sup>o</sup>Å

O(1)-O(6 <sup>1</sup> )	3.398 <sup>o</sup> Å	O(1)-O(2 <sup>11</sup> )	3.295 <sup>o</sup> Å
N - O(6 <sup>1</sup> )	3.382	O(3)-O(2 <sup>11</sup> )	3.134
O(1)-O(6 <sup>1</sup> )	3.458	N - O(1 <sup>11</sup> )	3.382
O(2)-O(7 <sup>1</sup> )	3.456	N - O(2 <sup>11</sup> )	3.432
O(3)-O(4 <sup>1</sup> )	3.456	O(1)-O(1 <sup>11</sup> )	3.481
O(3)-O(9 <sup>1</sup> )	3.424	O(2)-O(1 <sup>11</sup> )	3.240
O(4)-O(4 <sup>1</sup> )	3.276	W(1)-W(1 <sup>111</sup> )	3.048
Cu - O(1 <sup>11</sup> )	3.444	W(1)-O(8 <sup>111</sup> )	3.444
Cu - O(2 <sup>11</sup> )	2.344*	W(1)-O(9 <sup>111</sup> )	3.406
Cu - O(1 <sup>11</sup> )	3.200	O(3)-W(2 <sup>111</sup> )	3.410
W(1)-O(2 <sup>11</sup> )	3.021	W(2)-W(1 <sup>1v</sup> )	2.996
O(1)-O(1 <sup>11</sup> )	3.488	O(8)-O(2 <sup>v</sup> )	3.448

Code for superscripts

1	-x, -y, -z
11	$\frac{1}{2}$ -x, $\frac{1}{2}$ +y, $\frac{1}{2}$ -z
111	-x, y, $\frac{1}{2}$ -z
1v	x, 1+y, z
v	$-\frac{1}{2}$ +x, $\frac{1}{2}$ +y, z

\* This contact is taken as the fifth coordination bond to copper(II) ion in the crystal.



Table 14. Hydrogen bonds and some close intermolecular atomic contacts in neighboring molecules, in SGCT.

Hydrogen bonds

W(2) - W(3)	2.86 <sup>o</sup> Å	(within the original set)
W(2) - W(5)	3.13	(within the original set)
W(3) - W(4)	2.77	(within the original set)
W(4) - W(5)	2.86	(within the original set)
W(1) - W(5 <sup>11</sup> )	2.74	
W(2) - O(3 <sup>11</sup> )	2.85	
W(1) - O(1 <sup>111</sup> )	2.76	
W(4) - O(3 <sup>v</sup> )	2.79	

Close contacts of atoms less than 3.5<sup>o</sup>Å

Cu - C(5 <sup>1</sup> )	3.35 <sup>o</sup> Å	C(5) - C(5 <sup>11</sup> )	3.49 <sup>o</sup> Å
Cu - C(6 <sup>1</sup> )	3.46	O(2) - W(1 <sup>111</sup> )	3.29
O(3) - C(9 <sup>1</sup> )	3.43	W(1) - C(1 <sup>111</sup> )	3.36
O(7) - C(1 <sup>1</sup> )	3.48	W(4) - C(3 <sup>1v</sup> )	3.43
O(1) - C(6 <sup>1</sup> )	3.29	W(4) - C(8 <sup>v</sup> )	3.40
O(4) - C(4 <sup>11</sup> )	3.44	W(4) - C(9 <sup>v</sup> )	3.45
W(5) - W(5 <sup>11</sup> )	3.20	W(4) - W(1 <sup>v</sup> )	3.24
W(2) - C(9 <sup>11</sup> )	3.45	O(2) - C(8 <sup>v1</sup> )	3.26

Code for superscripts

i	-x, -y, -z
ii	-x, y, $\frac{1}{2}$ -z
iii	$\frac{1}{2}$ -x, $\frac{1}{2}$ -y, -z
iv	$\frac{1}{2}$ -x, $\frac{1}{2}$ +y, $\frac{1}{2}$ -z
v	$\frac{1}{2}$ +x, $\frac{1}{2}$ -y, $\frac{1}{2}$ +z
vi	1+x, y, z

Table 15. Hydrogen bonds and some close intermolecular atomic contacts in the neighboring molecules, in PACD.

Hydrogen bonds

O(2) - W(2 <sup>11</sup> )	2.74 <sup>o</sup> Å
W(3) - O(3 <sup>11</sup> )	2.85
O(2) - W(3 <sup>11</sup> )	2.73

Close contacts of atoms less than 3.5Å

O(3) - N <sup>1</sup>	3.41 <sup>o</sup> Å	O(1) - W(2 <sup>11</sup> )	3.49 <sup>o</sup> Å
O(4) - O(4 <sup>1</sup> )	3.31	O(2) - N <sup>11</sup>	3.33
O(5) - O(4 <sup>1</sup> )	3.43	O(2) - O(5 <sup>11</sup> )	3.35
O(5) - O(5 <sup>1</sup> )	3.46	O(6) - W(3 <sup>111</sup> )	3.42
O(1) - W(2 <sup>11</sup> )	3.49	O(3) - W(1 <sup>111</sup> )	3.47
O(2) - O(4 <sup>11</sup> )	3.10	W(2) - O(2 <sup>1v</sup> )	3.47

Code for superscripts

1	-x, -y, -z
11	-x, $\frac{1}{2}+y$ , $\frac{1}{2}-z$
111	1+x, y, z
1v	x, $\frac{1}{2}-y$ , $\frac{1}{2}+z$

Table 16. Equations of least-squares planes and normal distances from the planes in SGCH and SGCT.

P(1) Plane of complex	0.3529x+0.9065y+0.2318z=1.8856	<u>SGCH</u>
	-0.0480x+0.2270y+0.9727z=1.6733	<u>SGCT</u>
P(2) Four about Cu(II)	0.1769x+0.8712y+0.4581z=2.0112	<u>SGCH</u>
	-0.0004x+0.3394y+0.9404z=1.9752	<u>SGCT</u>
P(3) Cu-glycinato	0.2802x+0.8267y+0.4880z=2.3668	<u>SGCH</u>
	0.0148x+0.2962y+0.9550z=1.9981	<u>SGCT</u>
P(4) Cu-salicylaldehyde	0.1627x+0.9525y+0.2575z=1.6428	<u>SGCH</u>
	-0.0502x+0.1479y+0.9877z=1.6993	<u>SGCT</u>
P(5) Benzene ring	0.1827x+0.9511y+0.2489z=1.6172	<u>SGCH</u>
	-0.0412x+0.1317y+0.9904z=1.6907	<u>SGCT</u>

Normal distances from the planes ( $\times 10^3 \text{\AA}$ )

Atom	P(1)		P(2)		P(3)		P(4)		P(5)	
	<u>SGCH</u>	<u>SGCT</u>	<u>SGCH</u>	<u>SGCT</u>	<u>SGCH</u>	<u>SGCT</u>	<u>SGCH</u>	<u>SGCT</u>	<u>SGCH</u>	<u>SGCT</u>
Cu	243	-134	<u>-227</u>	<u>-135</u>	24	<u>-40</u>	-34	77		
O(1)	101	79	-5	-60	16	24				
O(2)	362	115			-60	2				
O(3)	-155	-195	-5	-52		<u>51</u>	-21	-26		<u>1</u>
N	-254	-120	5	63	142	67	-65	-55		
O(1)	83	39			-19	8				
O(2)	-316	-162			-55	-55		<u>-105</u>		
O(3)	-77	6				<u>315</u>	-6	-17		<u>-45</u>
O(4)	-2	33					-18	6	6	-9
O(5)	124	170					-27	43	3	13
O(6)	183	159					-19	19	-10	-1
O(7)	91	29					29	-20	8	-14
O(8)	-25	-58					29	-6	2	16
O(9)	-64	-81					-3	-15	-9	-4
W(1)	205	253	5	54		243		<u>611</u>		

Those which are underlined were not included in the least-squares calculations. The coordinates (x,y,z) are referred to orthogonal axes, a, b, and c\*.

Table 17. Equations of least-squares planes and the normal distances from the planes in PAOD.

P(1) plane of complex	$0.3855x+0.0097y-0.9226z+1.6774=0$
P(2) four about Cu(II)	$0.4607x+0.0735y-0.8845z+1.6651=0$
P(3) Cu- $\beta$ -alaninato	$0.0447x+0.1601y-0.9861z+0.8014=0$
P(4) Cu-pyruvate	$0.4039x+0.0781y-0.9115z+1.6437=0$
P(5) $>C=N-$	$0.3925x+0.0897y-0.9153z+1.6565=0$

Normal distances( $\text{\AA}$ ) from the planes.

Atom	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	0.059		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) are referred to orthogonal axes, a, b, and c\*. A distance in parentheses indicates that the atom was not included in the least-squares calculation.

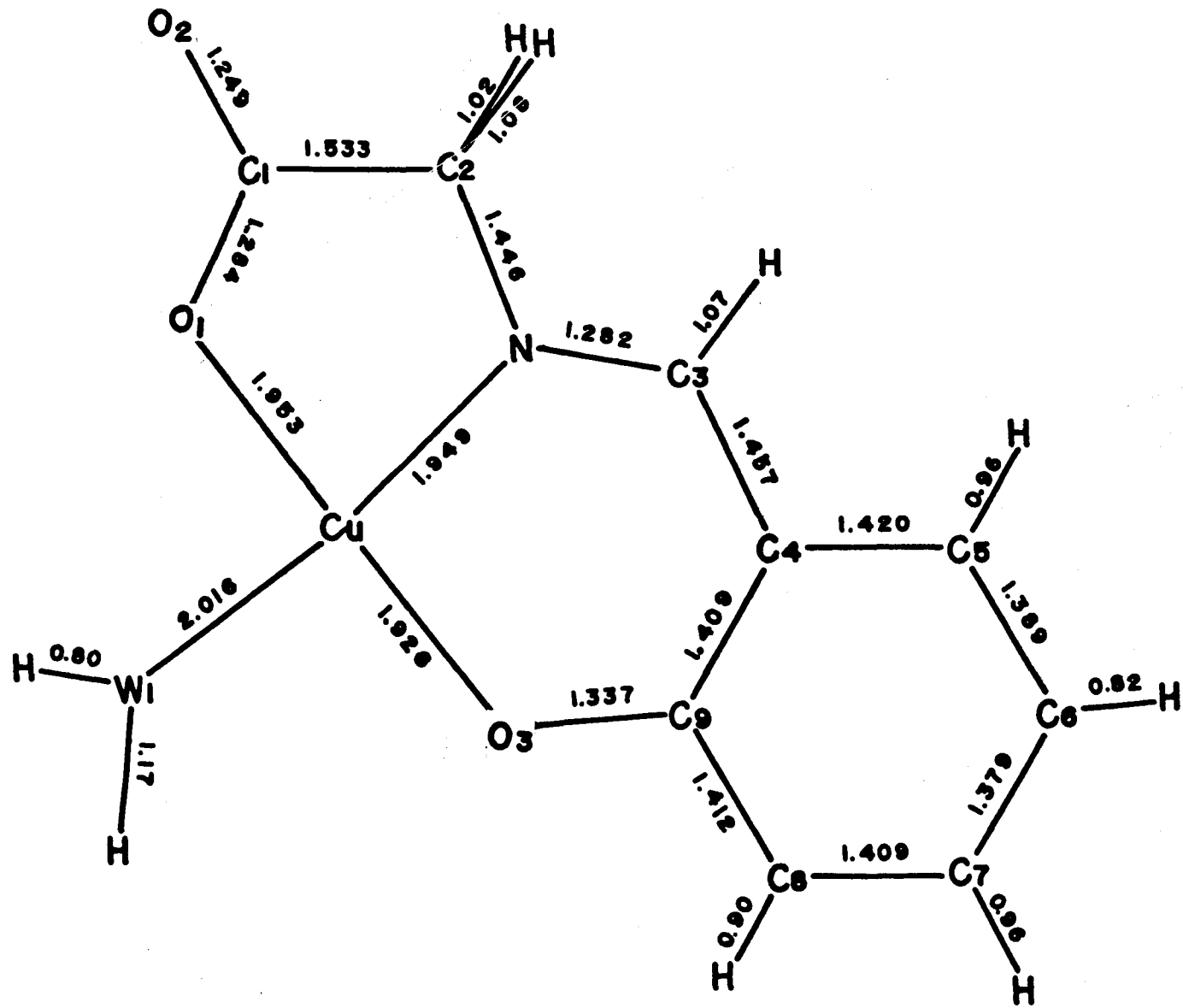


Fig. 1. Bond Lengths in the Molecule of SGCH.

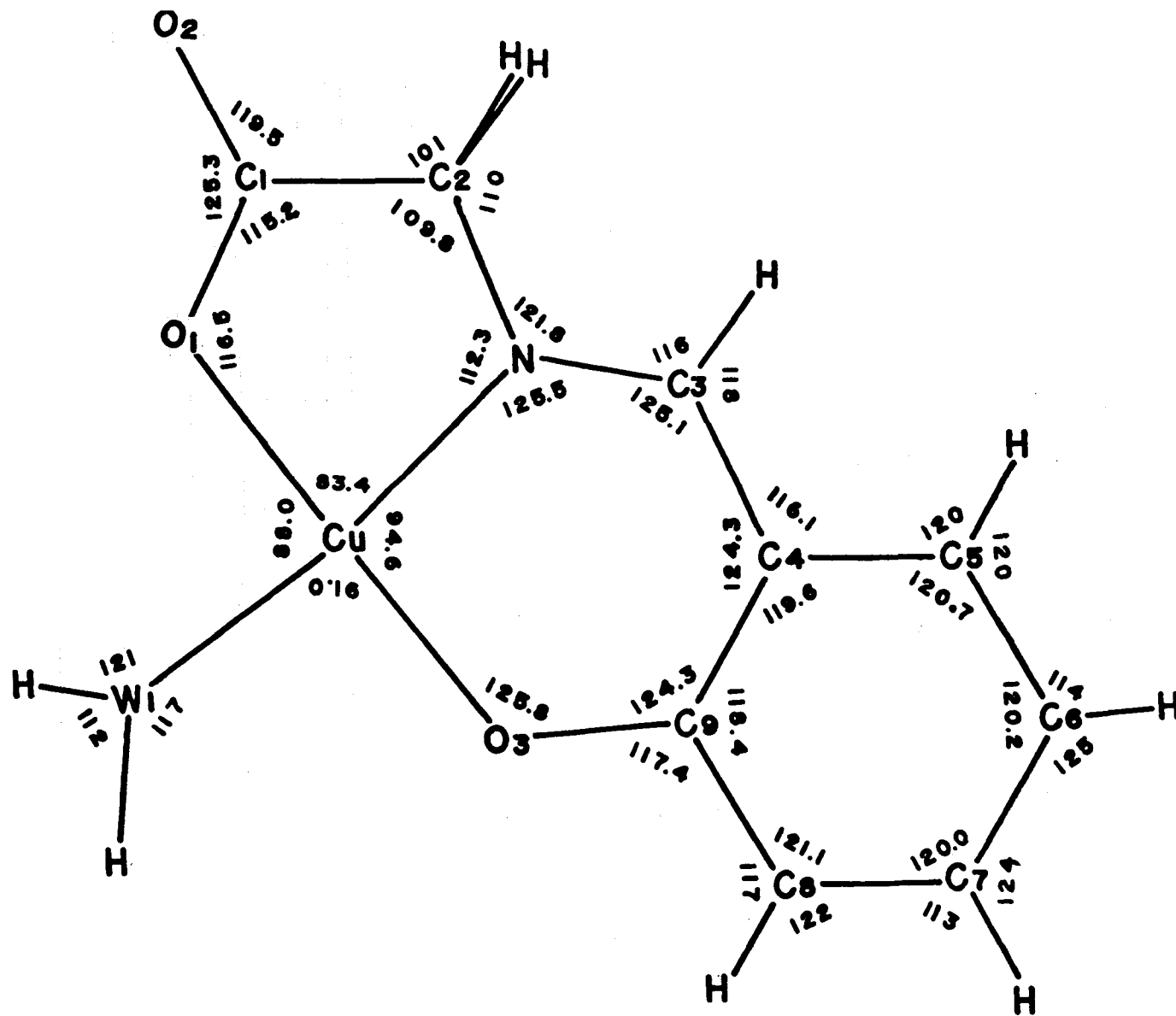


Fig. 2. Bond Angles in the Molecule of SGCH.

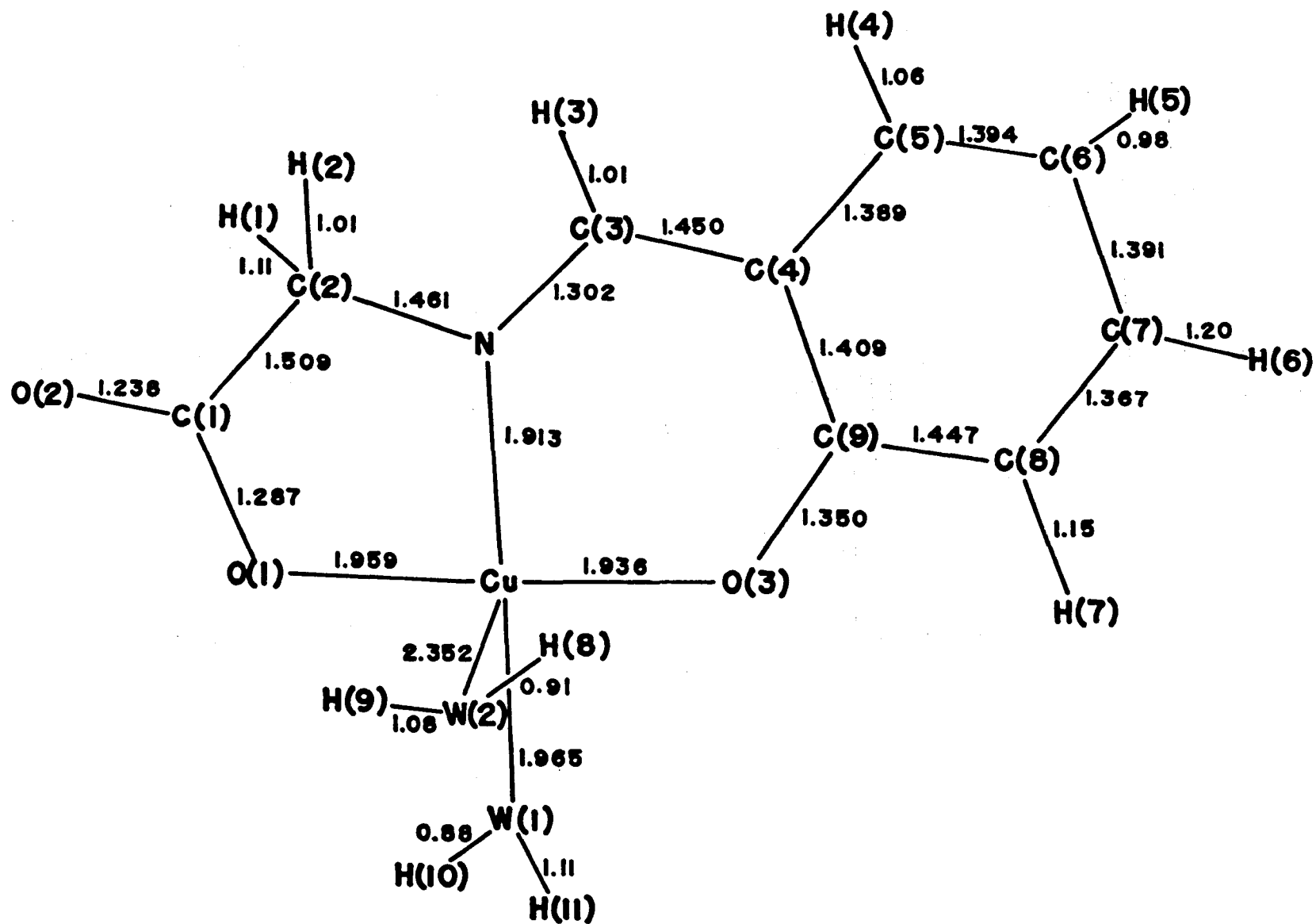


Fig. 3. Bond Lengths in the Molecule of SGCT.

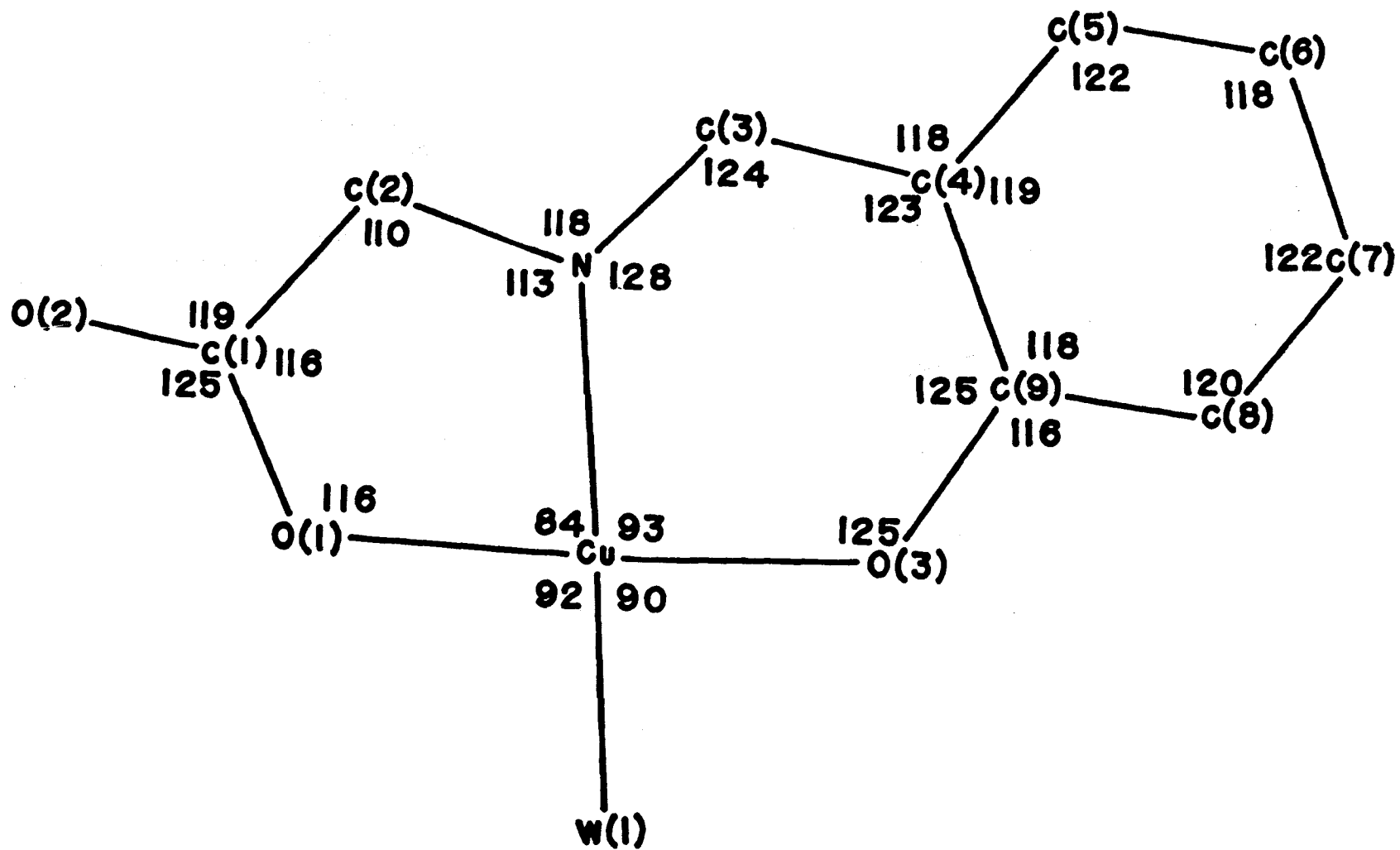


Fig. 4. Bond Angles in the Molecule of SGCT.



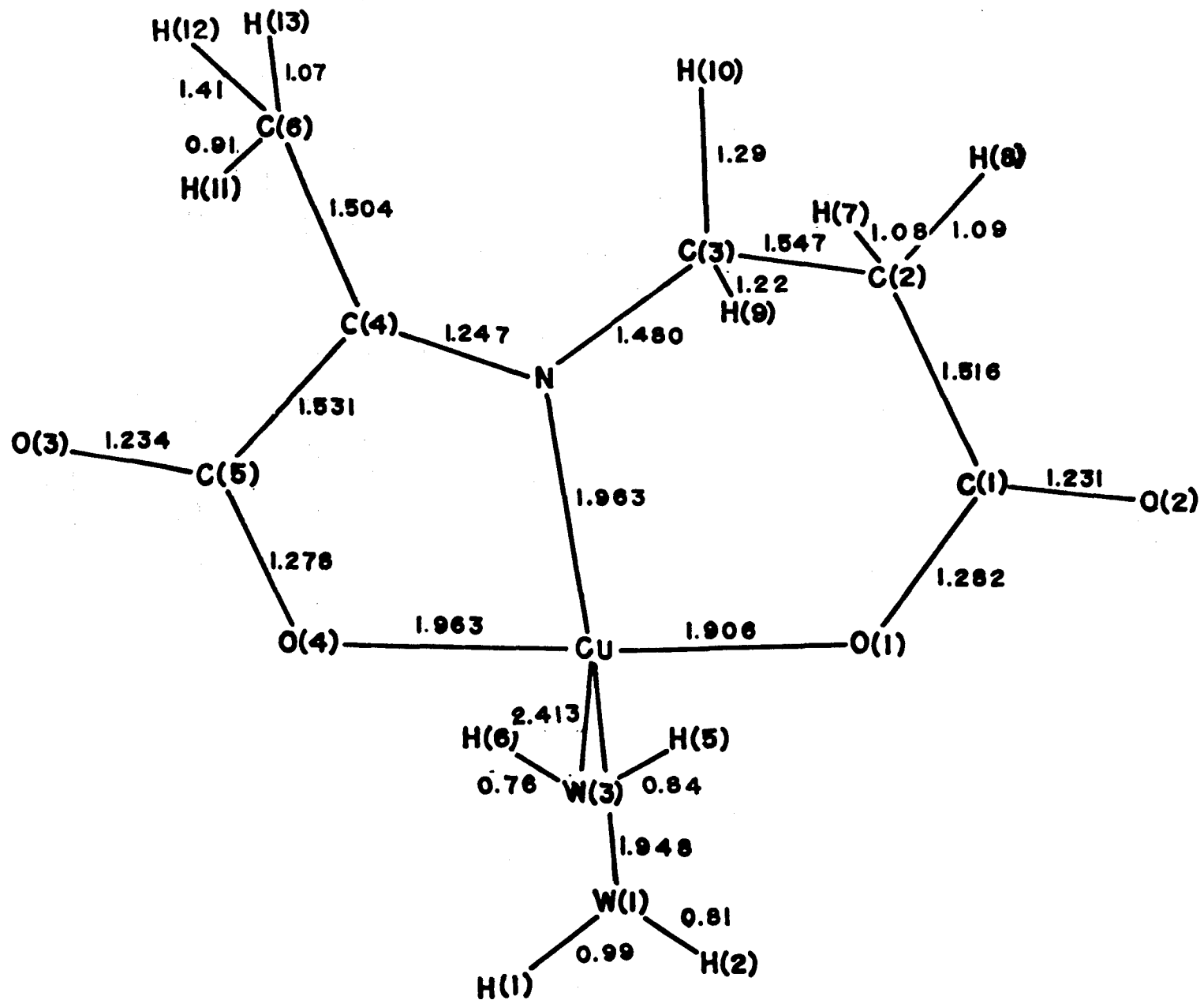


Fig. 5. Bond Lengths in the Molecule of PACD.

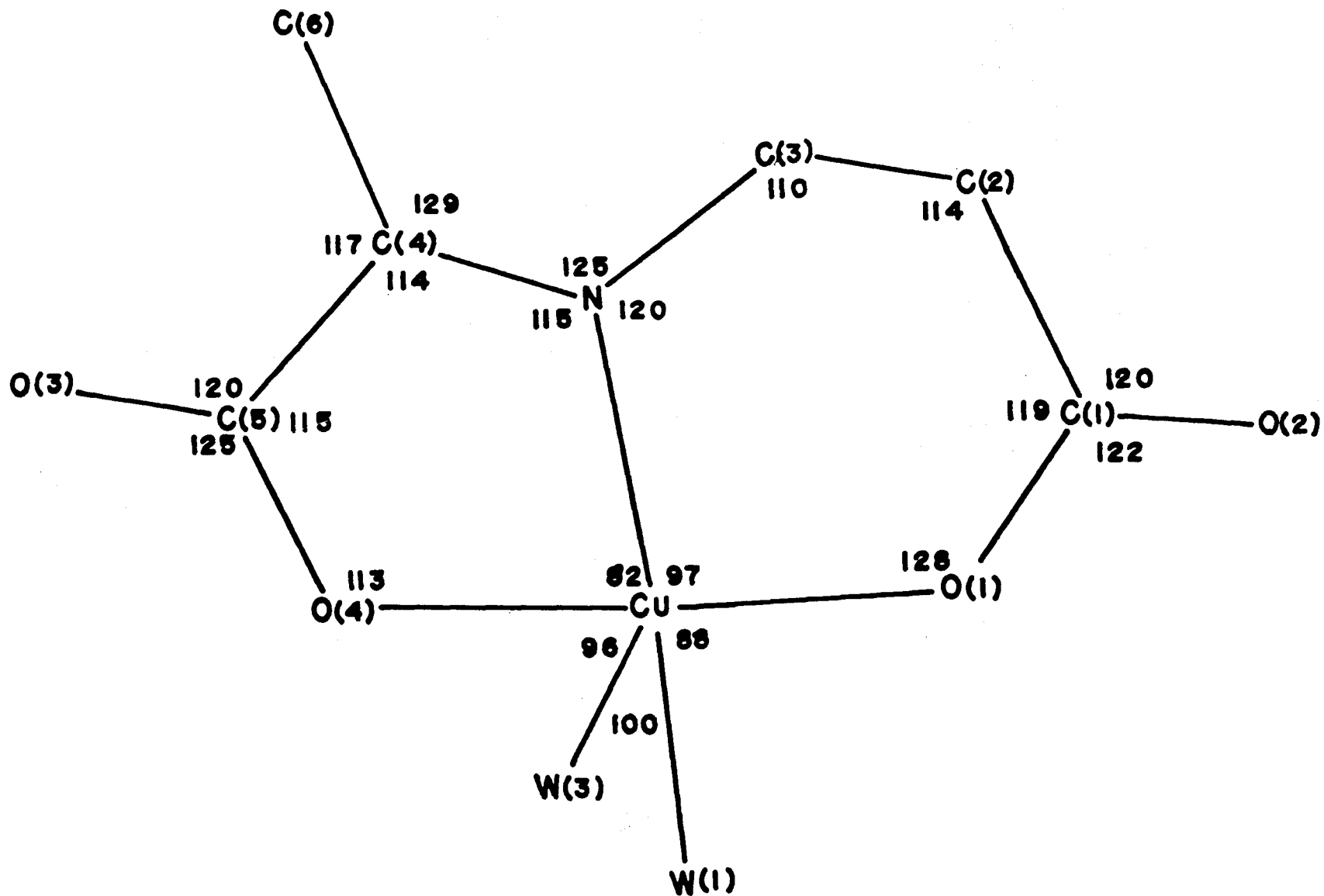


Fig. 6. Bond Angles in the Molecule of PACD.

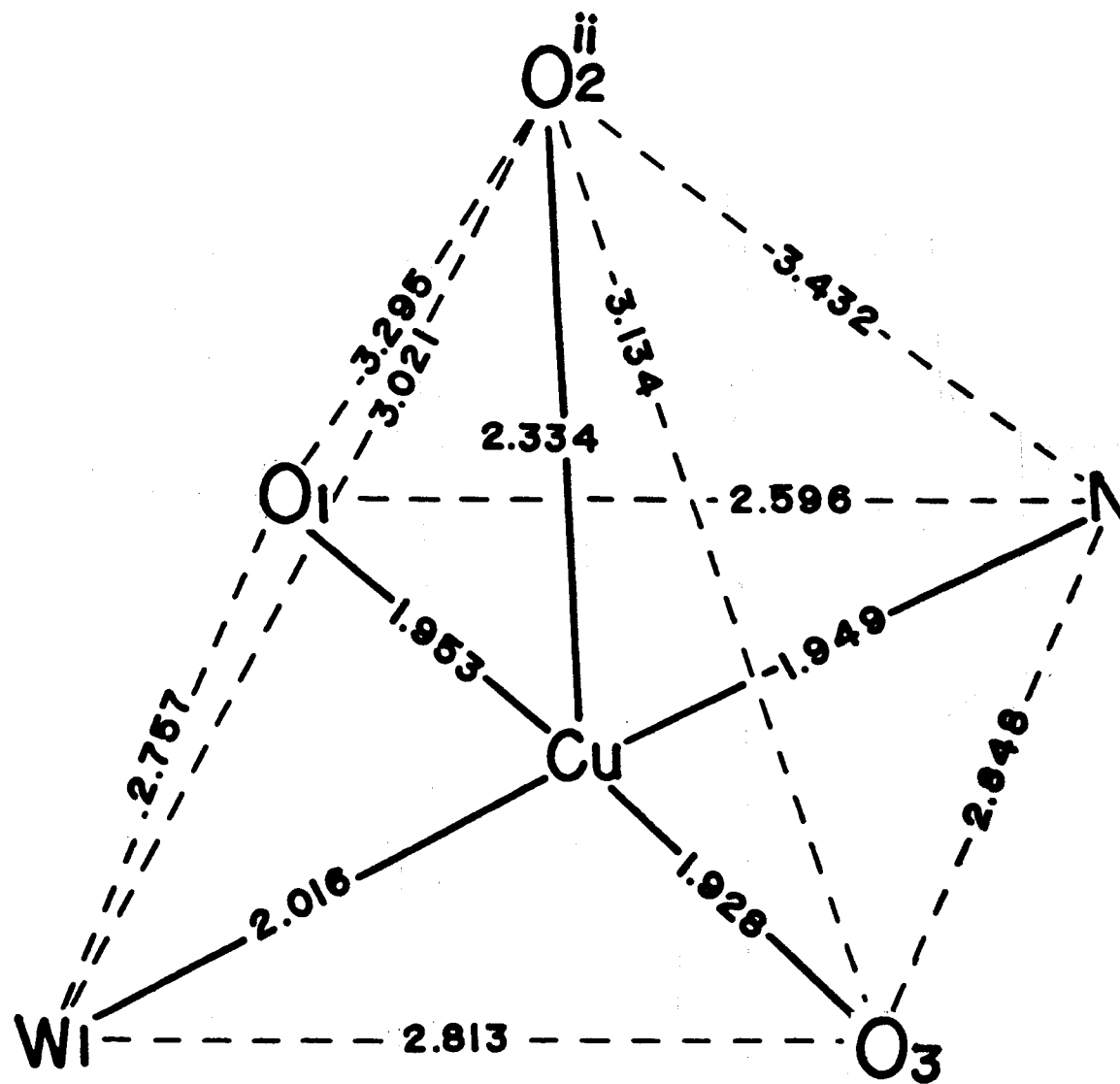


Fig. 7. The Environment of the Copper(II) Ion in SGCH.

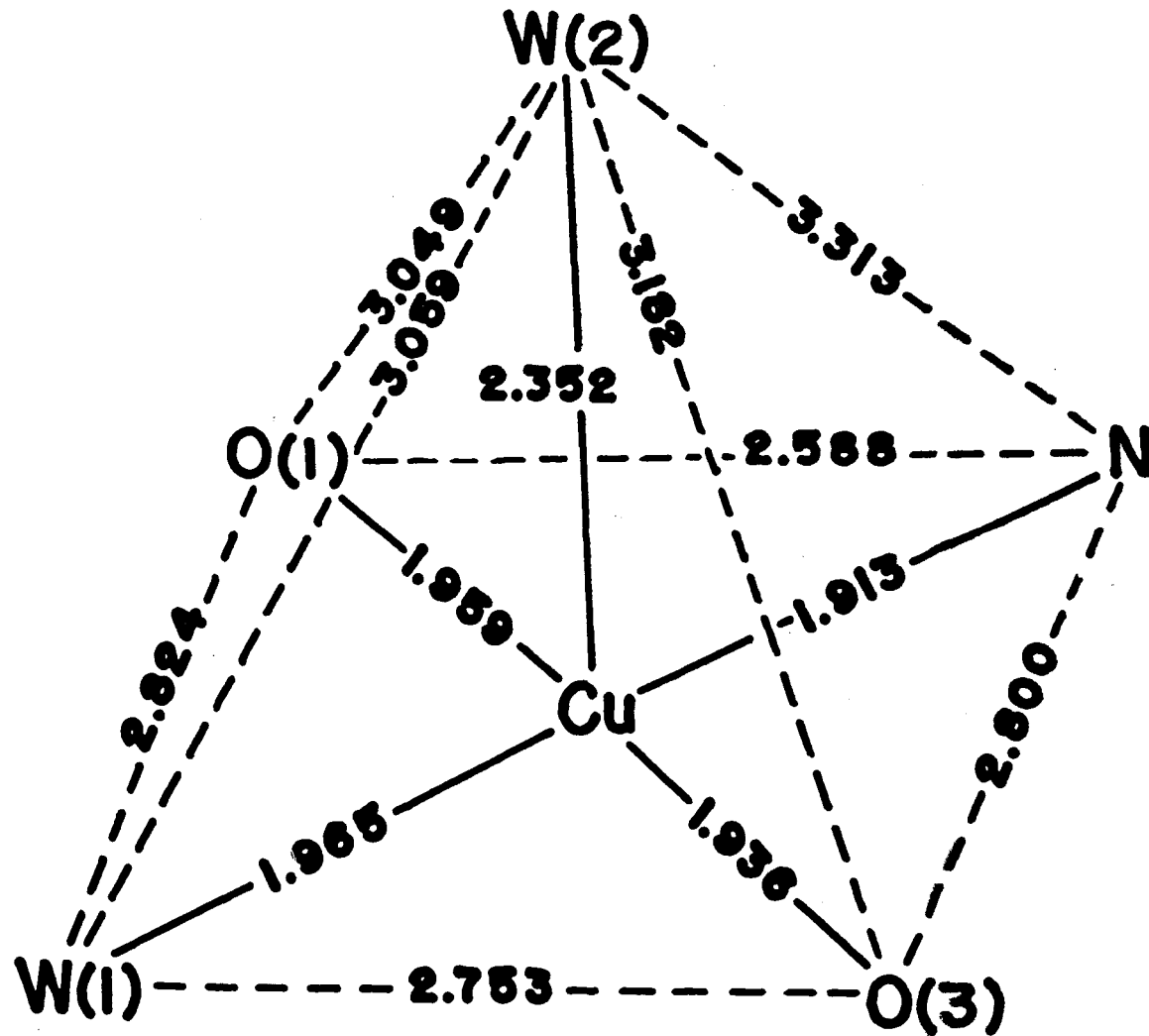


Fig. 8. Environment of the Copper(II) Ion in SGCF.

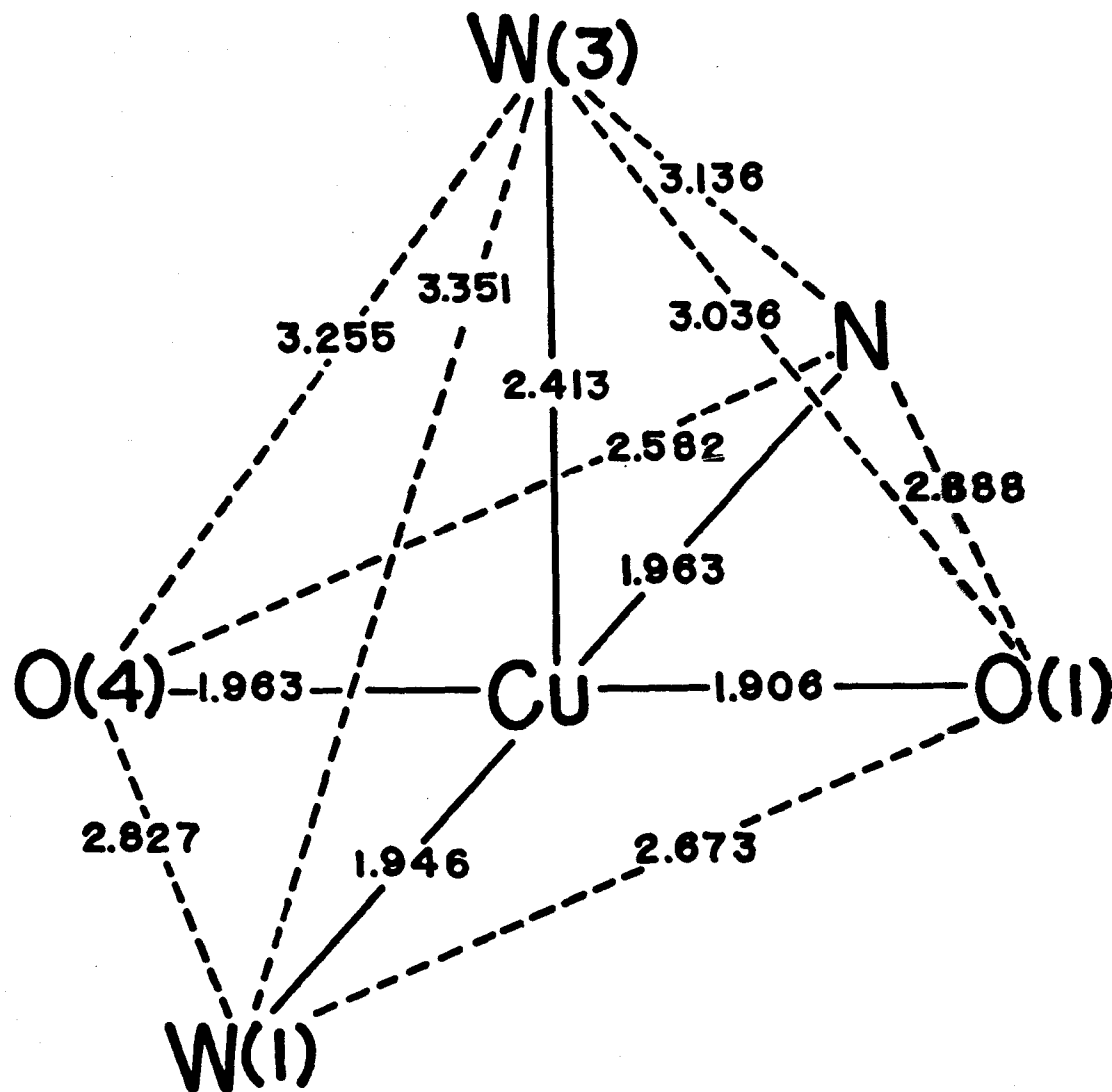


Fig. 9. Environment of the Copper(II) Ion in PACD.

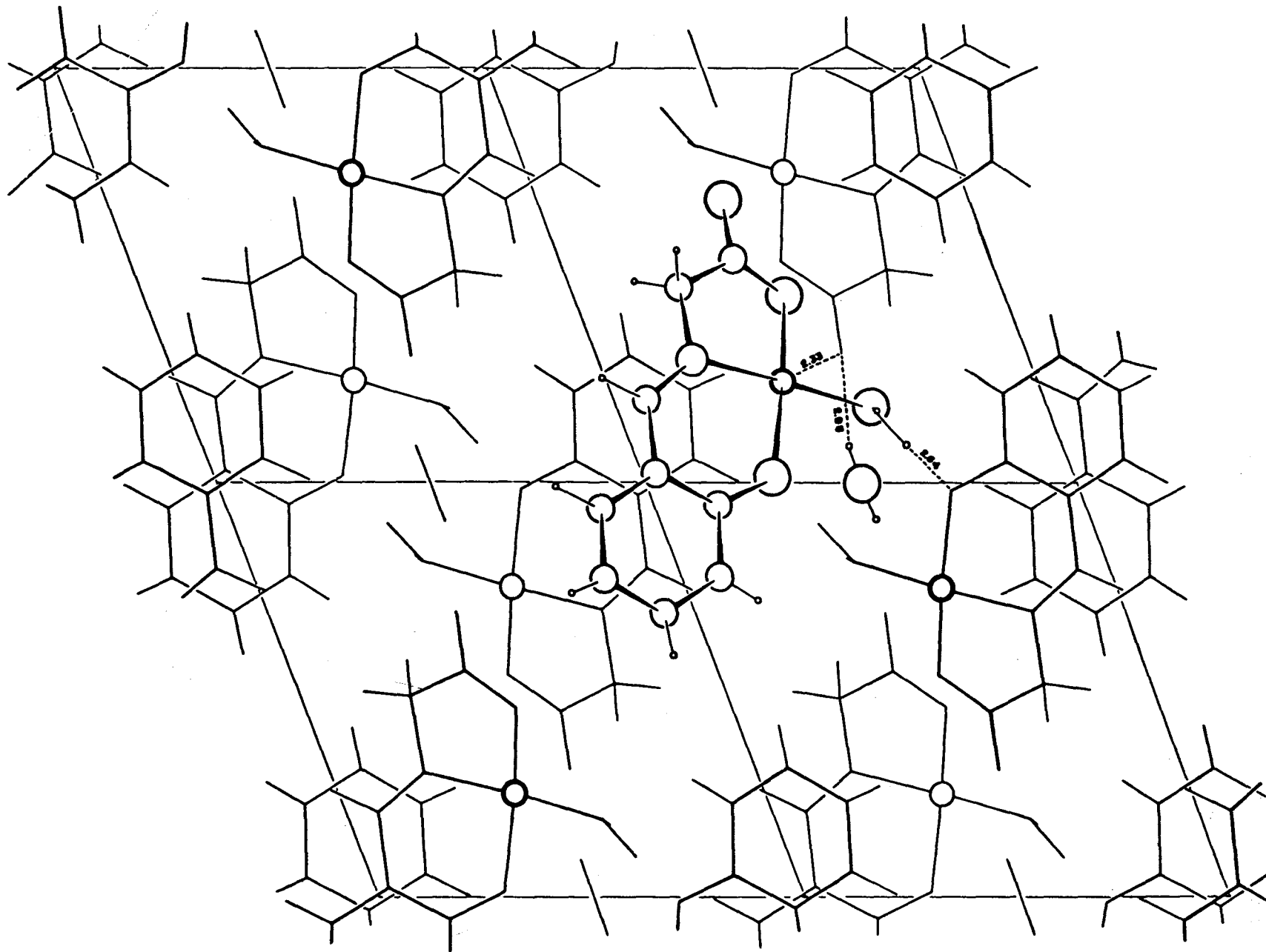


Fig. 10. The crystal structure of SGCH, looking down along the b axis.

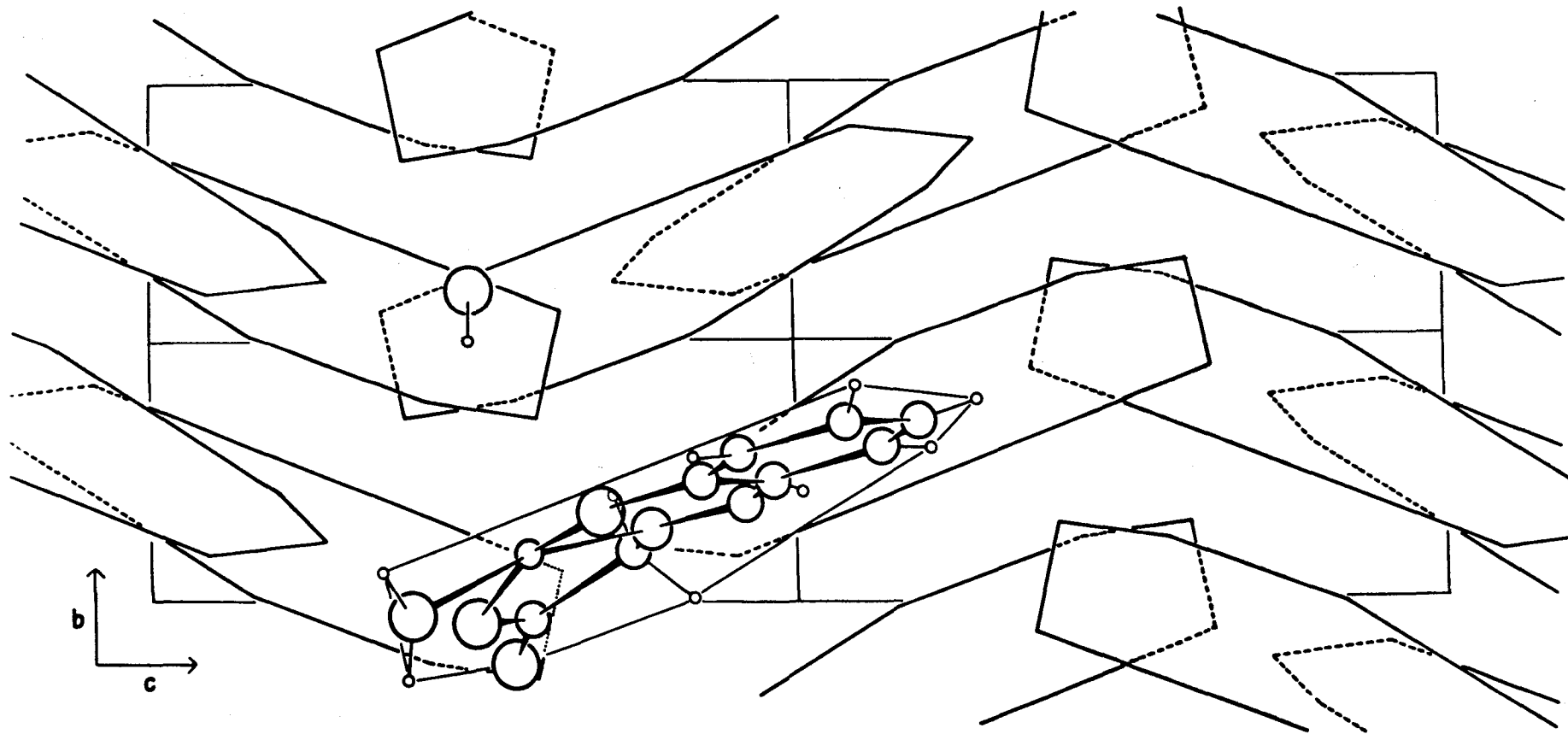


Fig. 11. A schematic Figure of the Crystal Structure of SGCE, looking down along the a axis.

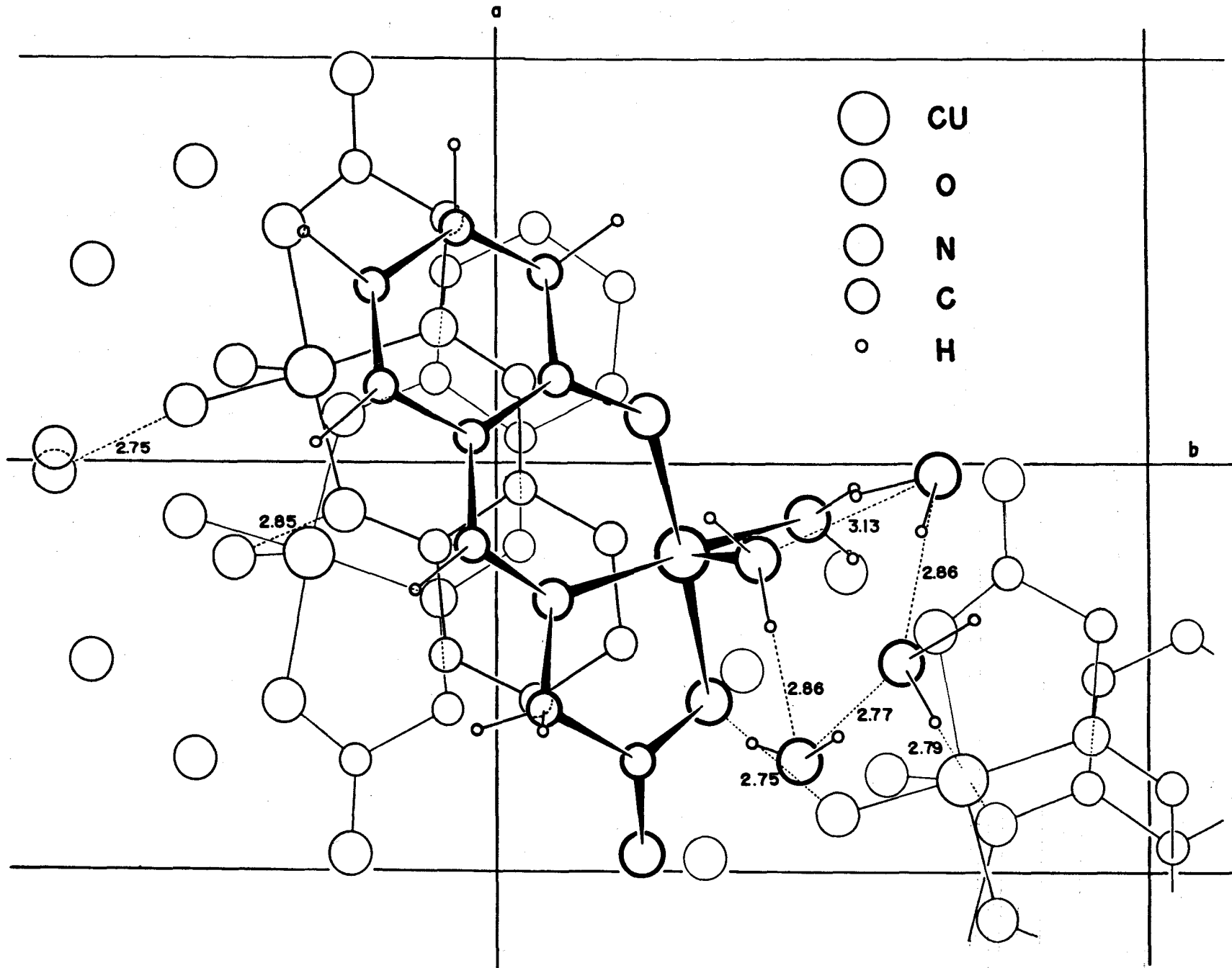


Fig. 12. A Part of the Crystal Structure of SGCT, looking along the c axis.



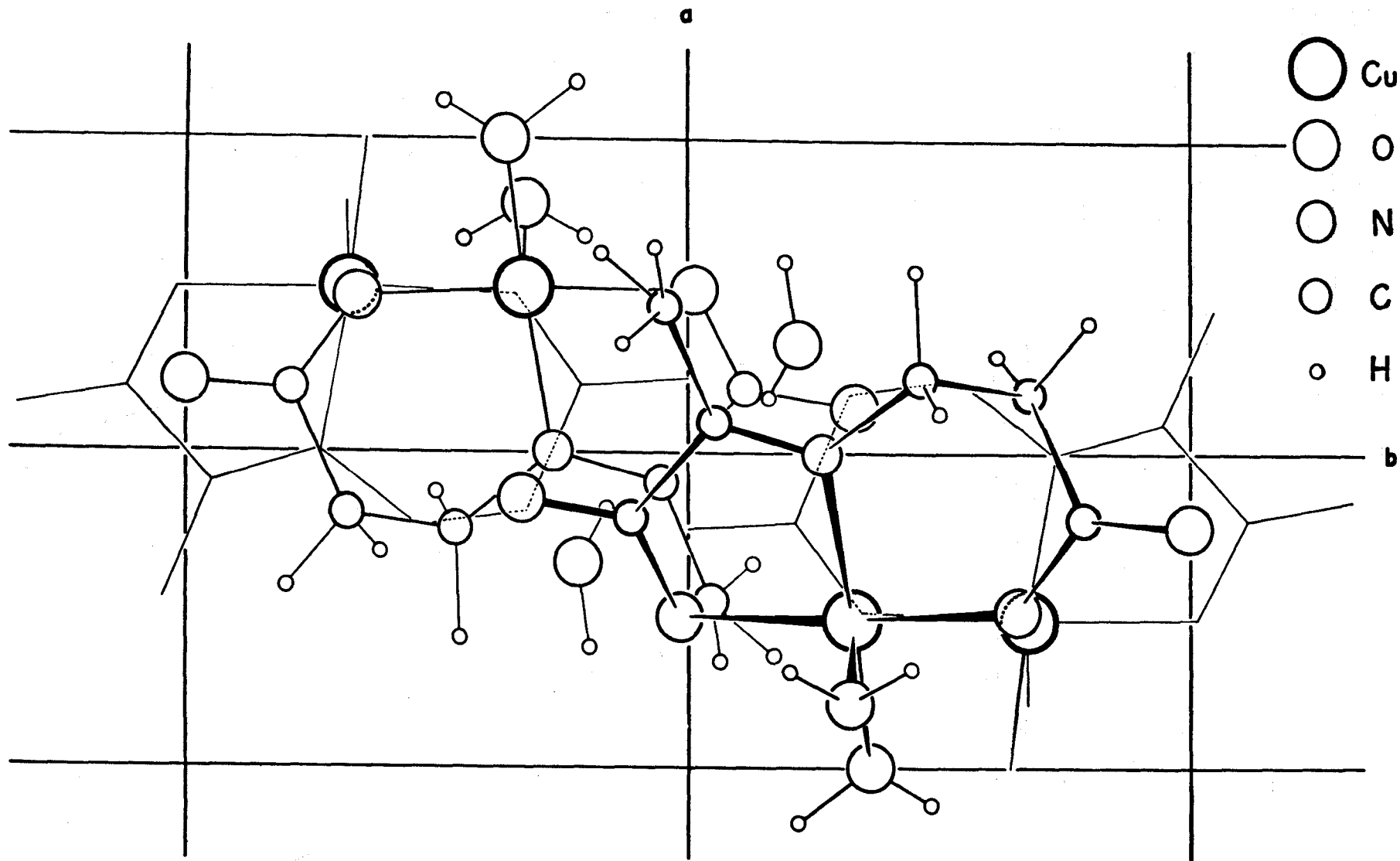


Fig. 13. The crystal Structure of PACD, looking along the c axis.

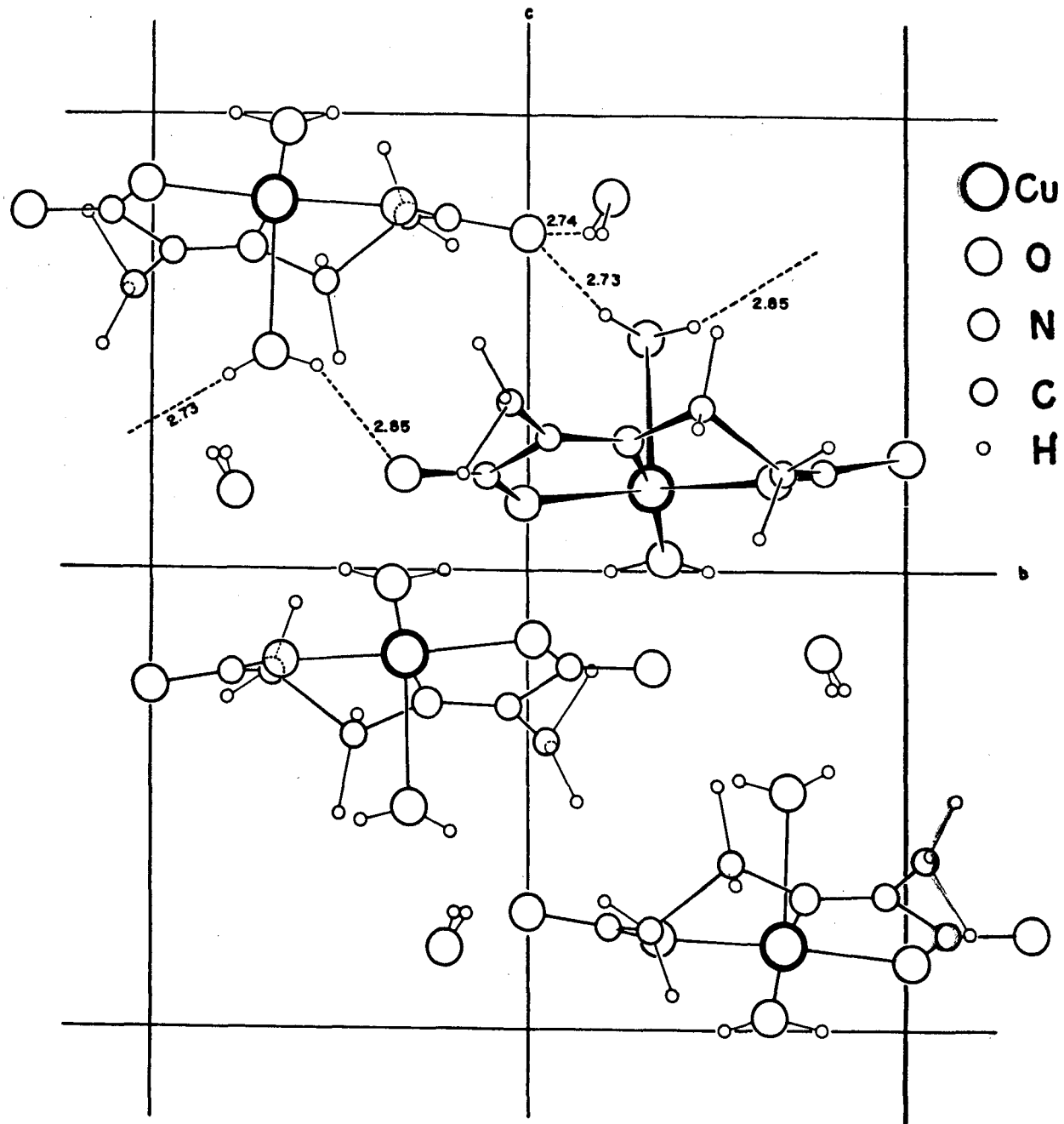


Fig. 14. The Crystal Structure of PACD, looking down along the a axis, with the Hydrogen Bonds.