BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1509—1514 (1969)

The Molecular and Crystal Structure of Bis(2-hydroxyethyliminopyruvato)copper(II) Tetrahydrate

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(Received October 23, 1968)

A new copper(II) chelate of the Schiff base derived from pyruvic acid and ethanolamine has been prepared. The crystal structure of this complex, $[Cu(pyv{=}etham)_2]\cdot 4H_2O$, has been determined from three dimensional X-ray diffraction data. The dimensions of monoclinic cell are $a=6.50$Å, $b=19.75$Å, $c=7.26$Å, $\beta=113.0°$ and $Z=2$. The space group is $P2_1/n$. The structure has been refined by three dimensional difference syntheses to $R=0.126$. It has been disclosed that copper(II) links to the 2-hydroxyethyliminopyruvate anion through the terminal carboxylate group, and the nitrogen of the Schiff base linkage. Having a center of symmetry, the complex molecule is in the *trans*-configuration and has normal bond distances and angles. The coordination around copper(II) is square planar; the Cu–O and Cu–N distances are 1.92 and 2.00Å, respectively. Two additional oxygen atoms of the water molecules at 2.57Å complete a distorted octahedron around copper(II). The complex molecules are held together in the crystal by the O–H···O hydrogen bonds, forming a three dimensional network.

The reaction of copper(II) with the Schiff base derived from salicylaldehyde and ethanolamine results in the formation of the copper(II) Schiff base complex of either one-to-one type or one-to-two type, depending upon the condition employed there.[1] On the other hand, a similar reaction of copper(II) with the Schiff base derived from pyruvic acid and ethanolamine exclusively gives the copper(II) Schiff base complex of one-to-two type, regardless of the method of preparation. The molecular structure of these one-to-two type copper(II) Schiff base complexes is not always easy to predict, in view of the fact that there are three donating groups in those Schiff base ligands, though the donating tendency of alcoholic oxygen is estimated to be comparatively weak. It is also important to know the geometrical configuration of the two 2-hydroxyethyliminopyruvate ions around the copper(II). The main purpose of the present work was to elucidate these points and determine the detailed structure of the complex.

*1 Deceased on Aug. 1, 1968.

1) A. Nakahara, H. Matsumoto and H. Yamamoto, *Sci. Rep.*, College of General Education, Osaka Univ., **12**, 11 (1963).

Experimental

The preparation of bis(2-hydroxyethyliminopyruvato)-copper(II).

A mixture of copper(II), pyruvic acid and ethanolamine in 1 : 2 : 2 molar ratio was treated at about 60°C for two hours in aqueous ethanol (one-to-one by volume mixture).

A dark blue solution was gradually obtained, being accompanied by precipitation of pale blue microscopic crystals.

The precipitate was filtered by suction and recrystallized from an aqueous ethanol solution. The final pure product appears as thin pale blue needles elongated along the *c*-axis. The result of the elementary analysis nearly coincides with the calculated values for bis(2-hydroxyethyliminopyruvato)copper(II) tetrahydrate.

Found: C, 30.42; H, 5.98; N, 6.92%. Calcd: C, 30.34; H, 6.07; N, 7.08%.

Cell dimensions were calculated from measurements on rotation and Weissenberg photographs, calibrated with Cu wire ($a_0=3.6147$), using Cu$K\alpha$ radiation ($\lambda=1.5418$Å).

The results are:

$a=6.50\pm0.01$Å, $b=19.75\pm0.02$Å, $c=7.26\pm0.01$Å

$\beta=113.0\pm0.2°$.

The cell contains two formula units of ($[Cu(HOCH_2CH_2NCCH_3COO)_2]\cdot4H_2O$); density calculated: 1.53 g·cm^{-3}; density measured: 1.52 g·cm^{-3}. Systematic absence indicates the space group to be $P2_1/n$. Relative intensities were obtained from equi-inclination Weissenberg photographs taken with Cu$K\alpha$ radiation using multiple films. The crystal was a rod of dimensions $0.1\times0.05\times2.0$ mm. Data were collected for all levels from $hk0$ through $hk6$ and $h0l$.

The intensities were estimated visually by comparison with a calibrated scale and corrected for the usual Lorentz and polarization factors. No absorption correction was made.

The range of relative intensities was 1 to 30000.

1292 reflections fell within this range, whereas 385 others were too weak to be observed.

Determination of Structure

The presence of two formula units in a unit cell of the space group $P2_1/n$ requires the copper atoms to occupy one of the sets of twofold positions. Without loss of generality they can be placed at 000 and ½ ½ ½.

Attempts were made to deduce the positions of the lighter atoms from a three dimensional Patterson function and Fourier synthesis of electron density, $\rho(x,y)$, of which all the phases were assumed to be positive. It was possible to locate all the atoms except one water oxygen atom.

The first three dimensional structure factor calculation on the basis of the deduced atomic positions led to an R index of 0.24. All the atomic positions were fixed by three dimensional F_o synthesis. In this calculation all those F_os were excluded for which $F_c<\frac{1}{2}F_o$. The structure was then refined by a three dimensional difference synthesis. Finally R index was reduced to 0.126. All calculations were carried out on a FACOM231 computer.

Table 1. Final coordinates, standard deviation and temperature factors

Atom	x/a	y/b	z/c	B
Cu	0.0000	0.0000	0.0000	3.5
O(1)	−0.1885(14)	−0.0190(6)	0.1425(15)	3.0
O(2)	−0.2850(17)	0.0270(7)	0.3760(18)	3.6
O(3)	−0.0120(40)	0.2285(7)	0.0590(34)	4.6
O(4)	0.3380(22)	−0.0570(7)	0.2715(18)	3.6
O(5)	0.0805(31)	0.3195(8)	0.3615(28)	5.0
N	0.0855(17)	0.0830(4)	0.1715(15)	2.4
C(1)	−0.1785(31)	0.0275(6)	0.2720(22)	2.6
C(2)	−0.0140(22)	0.0850(7)	0.2930(18)	2.4
C(3)	0.0220(43)	0.1360(9)	0.4520(23)	3.9
C(4)	0.2490(26)	0.1320(9)	0.1705(25)	3.1
C(5)	0.1365(48)	0.1865(11)	0.0110(40)	4.0

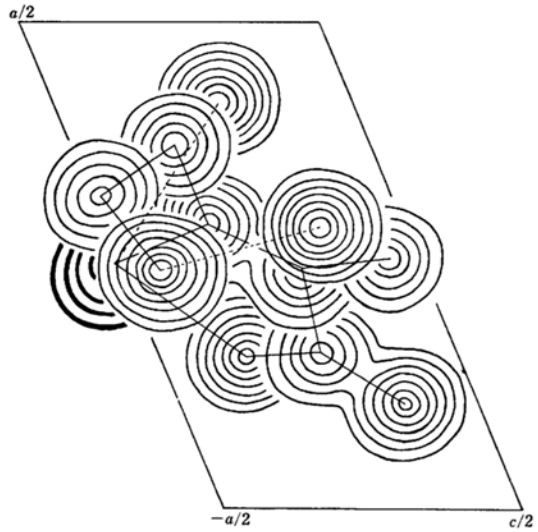

Fig. 1. Composite Fourier diagram of section parallel to (010).
Contours at intervals 1.0 e. Å^{-3}, the lowest being at 2.0 e.Å^{-3}. (Contours above 10 e. Å^{-3} are drawn at intervals of 6.0 e. Å^{-3} with thick lines).

The final atomic positions, and isotropic temperature factors and their estimated standard deviations are given in Table 1.

Table 2 gives the comparison of observed and calculated structure factors. The superimposed sections of the final electron density distribution are shown in Fig. 1.

Description and Discussion of the Structure

The structure projected upon a plane normal to the b-axis is shown in Fig. 2, and the environment of each copper atom is illustrated in Fig. 3. The interatomic distances and the bond angles calculated on the basis of the atomic parameters in Table 1 are given in Table 3.

The new complex, bis(2-hydroxyethyliminopyruvato)copper(II) is in trans-configuration. The 2-hydroxyethyliminopyruvate group is coordinated to copper(II), as a bidentate chelate, through the terminal carboxylate oxygen and the nitrogen of the Schiff base linkage, while the alcohol group is free from coordination. This is quite reasonable since the donating tendency of the alcohol oxygen has been estimated to be comparatively weak. The coordination around copper is approximately square planar. The distances from the copper(II) to the four donor atoms are 2.00 Å for Cu–N and 1.92 Å for Cu–O. The fifth and the sixth coordination positions are occupied by oxygen atoms of water molecules, being 2.57 Å distant from the copper(II) atom; hence the copper(II) has a tetragonally distorted octahedral environment, as has very often been observed in copper(II) com-

TABLE 2. CALCULATED AND OBSERVED STRUCTURE FACTORS

Columns are k, F_o, F_c. Unobserved Marked by *

TABLE 2. (Continued)

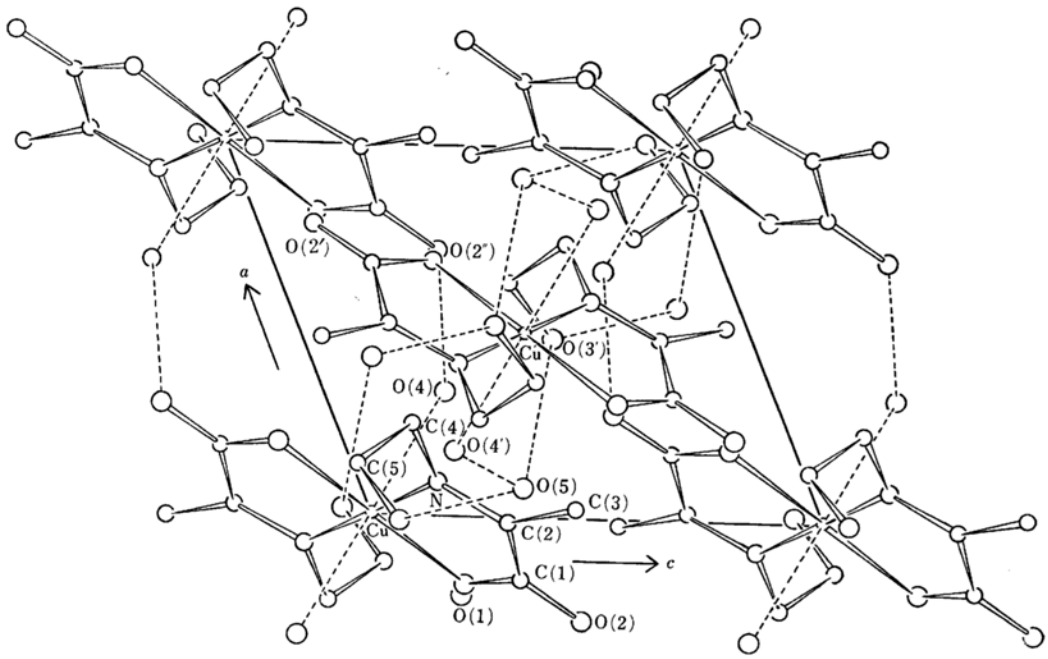

Fig. 2. Projection of the structure along the *b*-axis. Hydrogen bonds and the two long Cu···O interactions are indicated by dotted lines.

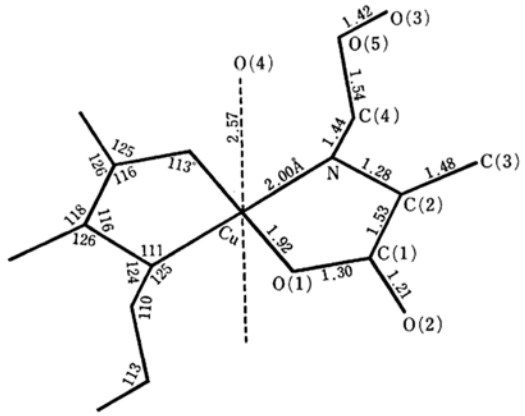

Fig. 3. The environment of the copper atom, showing bond distances and bond angles.

plexes. The N–Cu–O angle in the chelate ring is 84.6°; and the weaker Cu–OH_2 bond is inclined at an angle of 85° with respect to the plane of the copper and four ligand atoms.

These values may be compared with the corresponding values for other copper(II) complexes: Cu–O=1.95 Å, Cu-N(amino)=2.00 Å and N–Cu–O =85.2° in bis(glycinato)copper(II) monohydrate;[2] Cu–O=1.97—1.99 Å, Cu–N(amino)=2.00 Å and N–Cu–O=83.6° in copper(II) glutamate dihydrate;[3] Cu–O=1.88 Å and Cu–N(imino)= 1.99 Å in bis(*N*-phenylsalicylaldiminato)copper-(II).[4]

The bond distances in the chelate ring are: 1.30 Å for O(1)–C(1), 1.53 Å for C(1)–C(2) and 1.28 Å for O(2)–N, and are in good agreement with

Table 3. Interatomic distances and angles

I Distance			
Cu–N	2.00Å	C(1)–C(2)	1.53Å
Cu–O(1)	1.92	C(2)–C(3)	1.48
Cu–O(4)	2.57	C(4)–C(5)	1.54
O(1)–C(1)	1.30	C(3)···O(5)	2.72
O(2)–C(1)	1.21	O(3')···O(5)	2.65
O(3)–C(5)	1.42	O(4')···O(5)	2.75
N–C(2)	1.28	O(2'')···O(4)	2.81
N–C(4)	1.44		
II Angle			
N–Cu–O(1)	84.6°	N–C(4)–C(5)	110°
Cu–O(1)–C(1)	113	C(4)–C(5)–O(3)	113
O(1)–C(1)–C(2)	116	C(3)–C(2)–N	126
O(1)–C(1)–O(2)	125	C(2)–N–Cu	111
O(2)–C(1)–C(2)	120	C(2)–N–C(4)	124
C(1)–C(2)–N	116	Cu–N–C(4)	125
C(1)–C(2)–C(3)	118		
O(1)–Cu–O(4)	92		
N–Cu–O(4)	86		

2) H. C. Freeman, M. R. Snow, I. Nitta and K. Tomita, *Acta Cryst.* **19**, 1464 (1964).

3) C. M. Gramaccioli and R. E. Marsh, *Acta Cryst.* **21**, 594 (1966).

4) L. Wei, R. M. Stogsdill and E. C. Lingafelter, *Acta Cryst.* **17**, 1058 (1964).

those found in various complexes: C–O=1.28 Å and C–C=1.52 Å in bis(glcinato)copper(II) monohydrate and copper(II) glutamate dihydrate; C–O=1.31 Å and C–N(imino)=1.30 Å in bis(*N*-phenylsalicylaldiminato)copper(II) and disodium glycylglycylglycinatocuprate(II).[5]

In the carboxyl group, C(1)–O(1) bond has lengthened and C(1)–O(2) bond has shortened compared with the values found in glycine(both 1.25 Å). This fact indicates that these bonds have 20% and 80% double bond character, respectively.[6] O(2) atom of the carboxyl group, C(3) atom of the methyl group and C(4) atom of the ethanolamine group lie almost in the plane of the chelate ring, the deviation ranging from 0.04 Å to 0.09 Å. C(5) atom of the ethanolamine moiety is displaced from that plane and the angle between C(4)–C(5) bond and the plane is 62°.

The only contacts less than 3.5 Å between adjacent molecules are made by the free water oxygen O(5), the water oxygen O(4) weakly coordinated to the copper atom, the ethanolamine oxygen O(3) and the carboxyl oxygen O(2).

The distances are 2.67 Å—2.81 Å as shown in Fig. 2.

These short distances and the angles suggest hydrogen bonding between them. By these hydrogen bonds, the complexes are packed in layers parallel to the plane (101).

Stabilization within the layer is provided by hydrogenbonded bridges O(5)···O(3), O(5)···O(3') and O(5)···O(4').

Between adjacent layers there exists a hydrogen bond O(4)···O(2'') in the direction normal to the plane (100).

Part of the cost of this investigation has been defrayed by a Scientific Research Grant of the Ministry of Education, to which the authors' thanks are due.

Note added in proof: The crystal and molecular structures of the related complexes, pyruvidene-β-alaninatoaquocopper(II) dihydrate and *N*-salicylideneglycinatoaquocopper(II) hemihydrate, prepared by one of the authors (A. N.) have also been determined.[7,8]

5) H. C. Freeman and Max R. Taylor, *Acta Cryst.* **18**, 939 (1965).

6) T. Hahn, *Z. Kristallogr.*, **109**, 438 (1957).

7) T. Ueki, T. Ashida, Y. Sasada and M. Kakudo, *Acta Cryst.*, **B24**, 1361 (1968).

8) T. Ueki, T. Ashida, Y. Sasada and M. Kakudo, *ibid.*, **22**, 870 (1967).