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# The Crystal and Molecular Structure of Bis(N-acetylglycinato)diaquocopper(II) Dihydrate

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*The crystal structure of bis(N-acetylglycinato) diaquocopper(II) dihydrate was determined by X-ray diffraction studies and was refined by least-squares methods to R = 3.7% for 1565 reflections measured. The compound is monoclinic, space group C2/c. The unit cell parameters are* a *= 21.145(6),* b *= 5.046(2),* c *= 18.248(5) Å, $\beta$ = 127.55(4)°, V = 1543.7 Å$^3$; $d_c$ = 1.582, $d_m$ = 1.57 g cm$^{-3}$, Z = 4.*

*The molecule is centrosymmetric with the copper atom being surrounded by two oxygen atoms of the water molecules and two oxygen atoms of the carboxylate groups in a square planar arrangement with Cu–O distances of 1.944(2) and 1.952(2) Å, respectively. Two much longer out-of-plane Cu–O bonds to the remaining oxygen atoms of the carboxyl groups (2.619(2) Å) complete a distorted square bipyramidal coordination of the metal atoms. The angle between this long Cu–O vector and the normal to the square plane is 36.4°. The remaining two water molecules are involved in hydrogen bonding with the bonded water molecules and the peptide oxygen of the ligand.*

## Introduction

N-acetylglycine is of special interest in the study of interactions of metal ions with amino acids as it is one of the simplest systems containing a peptide group. A part of our study involves the investigation of the interactions of metal ions with physiologically important ligands. Chemical shift data [1] on metal complexes of N-acetylglycine suggest that the ligand probably chelates through the peptide and the carboxylate groups to the metal. However, electronic spectra indicate that the ligand is unidentate through the carboxylate bonding to the metal [2, 3]. In this context, it was thought interesting to study the crystal structure of copper(II) N-acetylglycinate tetrahydrate. The study was expected to provide information about the binding nature of similar ligands to metal atoms and the structural aspects of copper(II).

## Experimental

Copper(II) N-acetylglycinate tetrahydrate, Cu($CH_3CONHCH_2COO)_2\cdot 4H_2O$ was prepared [3] by interacting a hot aqueous solution of N-acetylglycine with a slight excess of basic copper carbonate. The reaction mixture was kept on a water bath till the reaction was complete. The unreacted copper carbonate was filtered and the filtrate was kept aside for slow evaporation; blue needle-like crystals were separated out.

The cell dimensions were determined by preliminary Weissenberg and precession photographs, and were refined by least-squares from diffractometer coordinates of 15 high-order reflections.

The crystals are monoclinic with *a* = 21.145(6), *b* = 5.046(2), *c* = 18.248(5) Å, $\beta$ = 127.55(4)°, V = 1543.7 Å$^3$. The density measured by the flotation method, $d_m$ = 1.57(1) g cm$^{-3}$ is in agreement with the calculated value of $d_c$ = 1.58 g cm$^{-3}$ for Z = 4. The systematic absences noticed from the photographs (hkl, h + k = 2n + 1 and h0l, l = 2n + 1) suggested the possible space groups Cc or C2/c. From the statistical distribution of the normalized structure factors and from the successful completion of the structure analysis, the crystal was found to be centrosymmetric with the space group C2/c–$C_{2h}^6$ (No. 15).

X-ray intensity data for a 0.08 × 0.06 × 0.22 mm$^3$ single crystal (needle axis [10$\bar{1}$]) were collected at 22 °C on a Syntex P2$_1$ four-circle diffractometer, using graphite-monochromated MoK$\alpha$ radiation (K$\alpha_1$ 0.70926 Å, K$\alpha_2$ 0.71354 Å, $\omega$–$2\theta$ scan, scintillation counter, take-off angle 6°). The sampling interval (in $2\theta$) for each reflection was from 1.0° below the calculated MoK$\alpha_1$ maximum to 1.0° above the calculated MoK$\alpha_2$ maximum. The scan rate varied from 2°/min to 15°/min (in $2\theta$), depending on the intensity of the reflection. Background measurements with the total time for background counts being

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TABLE I. Coordinates of the Atoms (Other than Hydrogen) in the Unit Cell of Bis(N-acetylglycinato)diaquocopper(II) Dihydrate.[a]

| | x | y | z |
|---|---|---|---|
| Cu | 0.25 | 0.25 | 0.0 |
| O1 | 0.19269(9) | 0.53176(32) | 0.01051(11) |
| O2 | 0.23866(11) | 0.29164(34) | 0.13465(12) |
| O3 | 0.06160(11) | 0.27391(39) | 0.09606(13) |
| O4 | 0.15520(12) | 0.02831(41) | −0.06542(14) |
| O5 | 0.47030(13) | 0.34186(51) | 0.07503(18) |
| N | 0.15471(12) | 0.58690(43) | 0.17945(14) |
| C1 | 0.19973(13) | 0.47990(46) | 0.08443(15) |
| C2 | 0.15515(16) | 0.66680(51) | 0.10334(18) |
| C3 | 0.10558(15) | 0.39898(53) | 0.16877(17) |
| C4 | 0.10579(25) | 0.34885(91) | 0.25023(26) |

[a] Estimated standard deviations are given in all tables in parentheses in units of the last significant digits.

TABLE III. Experimental Coordinates and Temperature Factors of the Hydrogen Atoms.

| | x | y | z | B |
|---|---|---|---|---|
| H1 | 0.183(2) | 0.837(6) | 0.117(2) | 2.5(6) |
| H2 | 0.097(2) | 0.685(6) | 0.045(2) | 3.5(7) |
| H3 | 0.188(2) | 0.669(6) | 0.231(2) | 3.2(7) |
| H4 | 0.142(2) | 0.446(8) | 0.301(2) | 7.0(11) |
| H5 | 0.056(3) | 0.402(9) | 0.233(3) | 7.9(12) |
| H6 | 0.106(2) | 0.174(9) | 0.262(3) | 6.1(1) |
| H7 | 0.121(2) | 0.076(8) | −0.065(2) | 4.7(10) |
| H8 | 0.165(2) | −0.125(9) | −0.047(2) | 5.9(10) |
| H9 | 0.493(2) | 0.475(8) | 0.086(2) | 5.5(11) |
| H10 | 0.463(2) | 0.289(8) | 0.032(3) | 5.8(12) |

equal to the scan time were made at the beginning and end of each scan with the counter stationary. A standard reflection was measured for every 50 reflections.

A complete set of 1565 unique reflections was measured up to $(\sin \theta)/\lambda = 0.64$ Å$^{-1}$, 1343 of which were accepted as statistically above background on the basis that $I \geqslant 1.96\sigma(I)$. An absorption correction was not necessary ($\mu = 15.2$ cm$^{-1}$). Data reduction was done applying Lorentz and polarization corrections including a Wilson plot.

## Determination and Refinement of the Structure

The structure was solved by direct methods, using the MULTAN program system [4]. The program was allowed to select origin-defining reflections; the correct solution was readily apparent from the combined figure of merit. Most of the non-hydrogen atoms were located from the E-map, the remaining ones and (after isotropic refinement of the heavy atoms) all hydrogen atoms were found from subsequent difference Fourier maps. The atomic scattering factors for Cu, O, N, C and H were taken from the International Tables [5]. Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms and isotropic ones for the hydrogens converged to residuals of $R_1 = 0.031$ (including unobserved data: 0.037), $R_2 = 0.037$, where $R_1 = \Sigma \,||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$. The weighting scheme was based on counting statistics of the intensities. The shifts in the final cycle were below $0.02\sigma$, the final difference Fourier had no significant features.

The final positional and thermal parameters of the atoms are given in Tables I, II and III. A table of the calculated and observed structure factors is available from the Editor.

TABLE II. Coefficients of the Anisotropic Temperature Factors.[a]

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Cu | 1.95(2) | 1.55(2) | 1.91(2) | 0.30(1) | 1.39(1) | 0.22(1) |
| O1 | 2.53(7) | 1.97(7) | 2.27(7) | 0.45(6) | 1.81(6) | 0.33(6) |
| O2 | 2.80(8) | 2.66(8) | 2.48(7) | 0.83(6) | 1.61(6) | 0.69(6) |
| O3 | 3.27(8) | 3.63(9) | 2.97(8) | −1.28(7) | 1.88(7) | −0.92(7) |
| O4 | 2.41(8) | 2.09(8) | 3.33(9) | 0.13(7) | 1.98(7) | 0.05(7) |
| O5 | 2.67(9) | 3.47(10) | 3.91(11) | −0.41(8) | 2.14(8) | −0.56(8) |
| N | 2.44(9) | 2.77(9) | 1.97(9) | −0.56(8) | 1.52(7) | −0.66(7) |
| C1 | 1.58(9) | 1.71(9) | 2.19(10) | −0.16(7) | 1.13(8) | −0.06(8) |
| C2 | 2.60(11) | 2.13(9) | 2.45(10) | 0.16(8) | 1.80(9) | 0.05(8) |
| C3 | 2.38(10) | 2.85(11) | 2.21(10) | −0.06(9) | 1.49(9) | −0.11(9) |
| C4 | 4.58(18) | 5.52(19) | 3.30(15) | −1.31(16) | 2.88(14) | −0.13(14) |

[a] The anisotropic temperature factors are expressed in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

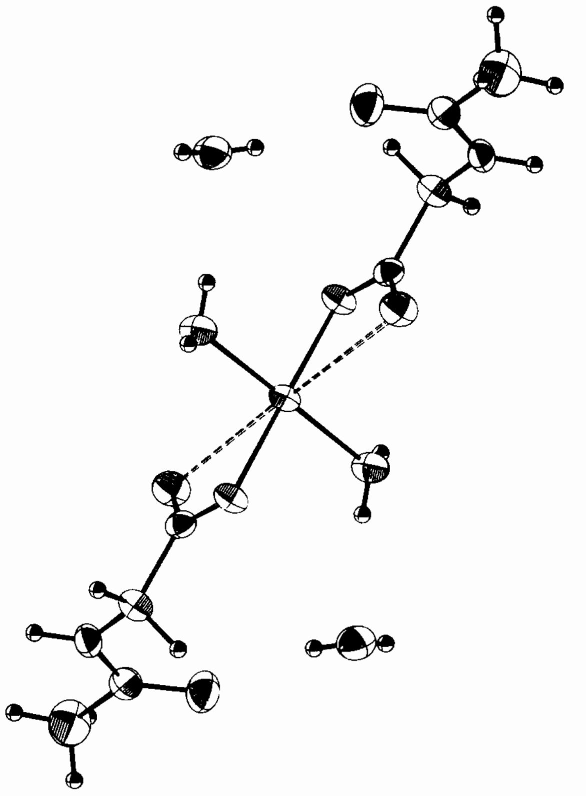

Figure 1. ORTEP plot of bis(N-acetylglycinato)diaquocopper(II) dihydrate. The thermal ellipsoids are drawn to 50% probability.

## Results and Discussion

The crystal structure consists of centrosymmetric bis(N-acetylglycinato)diaquocopper(II), $[Cu(OOCCH_2NHCOCH_3)_2(H_2O)_2]$, units which are linked by two other water molecules per complex unit through hydrogen bonds. The geometrical arrangement of the atoms in the molecule can be visualized through Figure 1. A representation of the unit cell which also gives an indication of the atom numbering and the hydrogen bridge system is shown in Figure 2.

The copper atom in the molecule is strongly bonded to the oxygen atoms of the two water molecules and to an oxygen atom of each carboxyl group. The four oxygen atoms, O1–O4–O1′–O4′ make a square plane with the central copper atom. The Jahn–Teller distorted coordination around copper is completed by the remaining oxygen atoms of the carboxyl groups in the out-of-plane axial position. These oxygen atoms are only weakly bonded to the metal atom with a distance of 2.619 Å (Table IV). The O1–O2–O1′–O2′ plane is inclined at an angle of 59.6° to the O1–O4–O1′–O4′ plane. The O2–O4–O2′–O4′ plane makes 33.8 and 45.9° angles with the planes O1–O4–O1′–O4′ and O1–O2–O1′–$O_2$, respectively.

Copper(II) assumes a variety of structural arrangements, namely, square, distorted tetrahedral, trigonal bipyramidal, distorted tetragonal pyramidal, tetra-

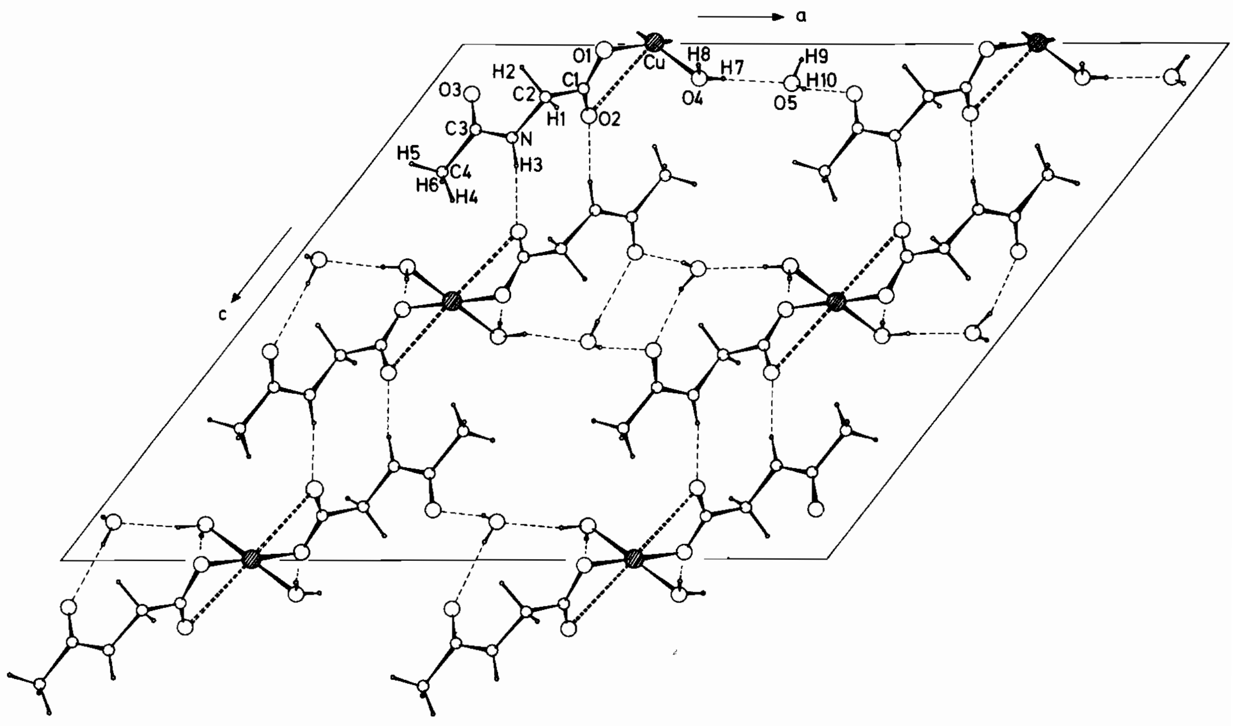

Figure 2. Unit cell as viewed down the *b* axis with atom numbering and hydrogen bridge system.

TABLE IV. Interatomic Distances and Bond Angles.

| Distances (Å) | | Angles (°) | |
|---|---|---|---|
| Cu Coordination[a] | | | |
| Cu–O1(O1′) | 1.952(2) | O1–Cu–O2 | 55.4(1) |
| Cu–O2(O2′) | 2.619(2) | O1–Cu–O4 | 90.6(1) |
| Cu–O4(O4′) | 1.944(2) | O2–Cu–O4 | 91.6(1) |
| | | O1–Cu–O2′ | 124.6(1) |
| | | O1–Cu–O4′ | 89.4(1) |
| | | O2–Cu–O4′ | 88.4(1) |
| N-acetylglycinate Ion | | | |
| C1–C2 | 1.515(4) | Cu–O1–C1 | 105.8(2) |
| C1–O1 | 1.290(3) | Cu–O2–C1 | 76.4(2) |
| C1–O2 | 1.225(3) | O1–C1–O2 | 122.4(2) |
| C2–N | 1.452(4) | C2–C1–O1 | 114.9(2) |
| C3–C4 | 1.505(6) | C2–C1–O2 | 122.7(3) |
| C3–N | 1.330(4) | C1–C2–N | 114.4(3) |
| C3–O3 | 1.233(4) | C2–N–C3 | 121.2(3) |
| | | O3–C3–N | 122.2(3) |
| | | C4–C3–N | 116.3(3) |
| | | C4–C3–O3 | 121.6(3) |
| C2–H1 | 0.99(3) | C1–C2–H1 | 104(2) |
| C2–H2 | 1.02(4) | C1–C2–H2 | 110(2) |
| N–H3 | 0.87(3) | N–C2–H1 | 111(2) |
| C4–H4 | 0.91(4) | N–C2–H2 | 108(2) |
| C4–H5 | 0.93(6) | C2–N–H3 | 116(2) |
| C4–H6 | 0.91(4) | C3–N–H3 | 123(2) |
| | | C3–C4–H4 | 115(3) |
| | | C3–C4–H5 | 107(3) |
| | | C3–C4–H6 | 113(3) |
| | | H1–C2–H2 | 110(3) |
| | | H4–C4–H5 | 105(4) |
| | | H4–C4–H6 | 114(4) |
| | | H5–C4–H6 | 102(4) |
| Water Molecules | | | |
| O4–H7 | 0.82(4) | Cu–O4–H7 | 116(3) |
| O4–H8 | 0.76(5) | Cu–O4–H8 | 113(3) |
| O5–H9 | 0.78(4) | H7–O4–H8 | 108(4) |
| O5–H10 | 0.75(4) | H9–O5–H10 | 105(5) |

[a] The primed atoms are related to the unprimed ones by a centre of inversion at the Cu site.

gonally distorted octahedral or square bipyramidal. The carboxylate ligands can interact with metal atoms in several structural types [6], notably as unidentate, unsymmetrical bidentate and bridging. A unique type of carboxylate bonding was recently reported [7] for copper hippurate, in which a single carboxyl oxygen binds to two copper atoms. Among typical copper(II) carboxylates whose structures are known [8] the Cu–O bond distances are in the range 1.89 to 2.02 Å. In the present complex, the bond distance of 1.95 Å (Cu–O1), as seen from Table IV, is of normal value. Likewise, Cu–O(water) bond distance of 1.952 Å (Cu–O1), as seen from Table IV, known to be between 1.92 and 2.04 Å [8]. The value of 1.944 Å observed in the compound reported here is in good agreement with the literature values. However, it is interesting to note that the Cu–O1 (carboxyl) distance is not shorter than the Cu–O2-($H_2O$) distance.

The apical bond distances in many of the reported [8] square bipyramidal copper(II) carboxylates show a large range in values in the interval 2.35 to 2.60 Å. The bond distance of 2.62 Å observed in the present complex definitely suggests bonding of the carboxyl oxygen to copper, though the interaction is assumed to be very weak. This observation is supported by reported [9, 10] bond distances of 2.71 Å in copper(II) chloroacetates. The angle between the Cu–O2 vector and the normal to the O1–O4–O1′–O4′ plane is calculated to be 36.4°.

Except for the carboxyl group, the bond distances and bond angles of N-acetylglycinate are not significantly different from those of the free ligand [11, 12]. Thus, in N-acetylglycine, experimental bond distances of C1–C2, C2–N, N–C3, C3–O3 and C3–C4 are 1.514(6), 1.444(6), 1.331(6), 1.252(6) and 1.507(6) Å respectively [12]. The corresponding values in the present complex are 1.515(4), 1.452(4), 1.330(4), 1.233(4) and 1.505(6) Å. The atoms C2, O1 and O2 lie in a plane with C1 deviating from the plane by 0.01 Å. On the other hand C4, C3, O3, N and C2 constitute a plane within the experimental error, the maximum deviation being 0.05 Å for C4. The least-squares equations of the two planes are $-0.6107x - 0.5850y - 0.5336z + 3.8652 = 0$ and $-0.6663x + 0.6724y - 0.3223z + 5.6785 = 0$ where x, y and z are referred to the monoclinic axes and expressed in Å units. Similar observations were also made [12] for the free ligand. However, the angle between the normals to the planes is 79.3° in comparison with 5.2° of the dihedral angle for the free ligand. Thus, it is inferred that in the complex there is greater twist in the C1–C2 bond.

TABLE V. Hydrogen Bonding in the Bis(N-acetylglycinato)diaquocopper(II) Dihydrate Structure.

| Distances (Å) | | | | Angles (°) | |
|---|---|---|---|---|---|
| O1...H8 | 1.93(4) | O1...O4 | 2.736(3) | O1...H8–O4 | 173(5) |
| O2...H3 | 2.04(3) | O2...N | 2.794(4) | O2...H3–N | 167(3) |
| O3...H9 | 2.02(4) | O3...O5 | 2.779(4) | O3...H9–O5 | 166(4) |
| O3...H10 | 2.08(4) | O3...O5 | 2.824(3) | O3...H10–O5 | 168(5) |
| O5...H7 | 1.88(5) | O5...O4 | 2.633(4) | O5...H7–O4 | 172(4) |

In Table V the hydrogen bond distances and bond angles are given (see also Figure 2). The non-coordinating water molecule is strongly hydrogen bonded to the peptide oxygen (2.78, 2.82 Å) and to the bonded water molecule (2.63 Å). It is interesting to note that the peptide group is not involved in coordination to the metal atom. However, besides the oxygen, the nitrogen atom also takes part in the hydrogen bonding (N...O2, 2.79 Å).

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