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Crystal and Molecular Structure of Tetra-μ-N-acetylglycinatodiaquodicopper(II)

M. R. UDUPA* and B. KREBS

Anorganisch-chemisches Institut der Universität Münster, Gievenbecker Weg 9, D-4400 Münster, F.R.G.

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The crystal structure of binuclear copper(II) N-acetylglycinate monohydrate, $[Cu(OOCCH_2NHCOCH_3)_2(H_2O)]_2$ *was determined by three-dimensional X-ray diffraction studies. The compound crystallizes in the monoclinic system with the space group* $P2_1/c$. *The cell parameters are* a = *7.288(2),* b = *8.892(2),* c = *19.473(3)* Å, β = *103.04(3)°, V = 1229.5* $Å^3$, *Z = 4,* d_c = *1.695 and* d_m = *1.69 g* cm^{-3}.

Full-matrix least-squares refinement using 2059 independent reflections has reached the R value of 0.041.

The two copper atoms in the molecule are held together in a dimeric unit by the four carboxylate groups, and each copper atom is further bonded to a water molecule, resulting in a square pyramidal geometry. The mean Cu–O(carboxylate), Cu–O(water) and Cu–Cu distances are 1.971(3), 2.108(3) and 2.666(1) Å, *respectively. Hydrogen bonding is observed between the peptide-NH and the carboxylate groups, and the peptide-CO groups and the water molecules.*

Introduction

N-acetylglycine, as a simple amino acid containing a peptide group, offers a system in which the effect of various structural features of protein-like donor molecules on the interaction with metal ions can be investigated. The ligand complexes [1, 2] with copper(II) resulting in the compositions copper(II) N-acetylglycinate tetrahydrate and copper(II) N-acetylglycinate monohydrate. The magnetic properties of the complexes showed [1–3] that the tetrahydrate exhibits the normal magnetic momentum whereas the monohydrate shows the subnormal value of 1.4 B.M. In an earlier report, we have communicated [4] the crystal structure of the tetrahydrate, and now the crystal structure of the monohydrate is presented in this paper.

Experimental

Copper(II) N-acetylglycinate monohydrate could be easily prepared [2] by either treating copper(II) N-acetylglycinate tetrahydrate in alcohol or heating it at 100 °C. But owing to the formation of very small crystals in the process which were found to be unsuitable for diffraction studies, the following method was employed for the formation of satisfactory crystals: A saturated alcoholic solution of copper(II) N-acetylglycinate tetrahydrate was taken in a long loosely stoppered glass tube and was kept at laboratory temperature undisturbed for several days. Crystals of satisfactory dimensions were deposited at the top inner walls of the glass tube.

The cell dimensions of the crystal 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 = 7.288(2), b = 8.892(2), c = 19.473(3) Å, β = 103.04(3)°, V = 1229.5 $Å^3$. The density measured by the flotation method, d_m = 1.69(1) g cm^{-3}, is in agreement with the calculated value of d_c = 1.695 g cm^{-3} for four formula units, Z = 4. The systematic absences noticed from the photographs (0k0, k = 2n + 1 and h0l, h = 2n + 1) indicated the space group $P2_1/c$ (C_{2h}^5, No. 14).

X-ray intensity data were measured at 22 °C for a 0.08 × 0.20 × 0.16 mm^3 single crystal on a Syntex $P2_1$ four-circle diffractometer (MoK_α radiation, λ = 0.71069 Å, ω–2θ scan, scintillation counter, graphite monochromator, scan range 2° in 2θ, scan rate from 2°/min to 30°/min in 2θ, depending on intensity, reference reflection every 50 reflections). A complete set of 2706 unique observations were measured in the range up to $(\sin\theta)/\lambda = 0.64$ $Å^{-1}$, 2059 of which were accepted as being statistically above background on the basis that $1 \geqslant 1.96\ \sigma(I)$; zero weight was assigned to the rest. The data were reduced to structure factors by Lorentz and polarization corrections, including a Wilson plot. No absorption correction was made (μ = 21.9 cm^{-1}).

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*Permanent address: Department of Chemistry, Indian Institute of Technology, Madras-600 036, India.

TABLE I. Coordinates of the Atoms in the Unit Cell.[a]

	x	y	z
Cu	0.34672(6)	0.07445(5)	−0.03306(2)
O1	0.1415(3)	0.2174(3)	−0.0935(1)
O2	0.2193(3)	−0.1222(3)	−0.0520(1)
O3	0.4805(3)	−0.2459(3)	0.0013(1)
O4	0.2711(3)	0.0757(3)	0.0578(1)
O5	0.5346(3)	−0.0433(3)	0.1124(1)
O6	0.2052(4)	−0.3393(3)	0.1005(1)
O7	0.1964(4)	0.1211(4)	0.2925(1)
N1	0.2699(4)	−0.4919(4)	0.0177(2)
N2	0.1335(4)	0.0803(4)	0.1762(1)
C1	0.3069(5)	−0.2383(4)	−0.0287(2)
C2	0.1969(6)	−0.3852(5)	−0.0374(2)
C3	0.2752(5)	−0.4574(4)	0.0848(2)
C4	0.3729(8)	−0.5655(6)	0.1395(2)
C5	0.3771(5)	0.0172(4)	0.1103(2)
C6	0.3169(6)	0.0132(5)	0.1795(2)
C7	0.0877(5)	0.1274(5)	0.2350(2)
C8	−0.1106(7)	0.1907(6)	0.2261(3)
H1	0.056(6)	0.167(5)	−0.111(3)
H2	0.177(6)	0.256(5)	−0.133(3)
H3	0.208(5)	−0.420(4)	−0.083(2)
H4	0.075(5)	−0.357(4)	−0.042(2)
H5	0.323(5)	−0.561(4)	0.011(2)
H6	0.372(5)	−0.654(4)	0.122(2)
H7	0.494(6)	−0.522(4)	0.155(2)
H8	0.306(5)	−0.585(5)	0.169(2)
H9	0.409(5)	0.065(4)	0.215(2)
H10	0.324(5)	−0.086(4)	0.196(2)
H11	0.045(6)	0.090(5)	0.132(3)
H12	−0.196(5)	0.174(4)	0.179(2)
H13	−0.096(6)	0.288(5)	0.223(2)
H14	−0.138(5)	0.196(4)	0.273(2)

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

Structure Determination and Refinement

Using the MULTAN programme system, the structure could be solved from direct methods [5]. Besides the origin-defining reflections, three starting reflections and two reflections phased by Σ_1 relations were used as starting set. The correct solution was readily apparent from the figures of merit. Most of the non-hydrogen atoms were located from the E-map, the others and (after isotropic refinement of the heavy atoms) the hydrogen atoms were found from subsequent ΔF maps. Full matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms and fixed isotropic ones (4.0 Å^2) for the hydrogens resulted in residuals of $R_1 \doteq 0.041$, $R_2 = 0.036$ for the 2059 observed data, where $R_1 \doteq \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. The atomic scattering factors for Cu, O, N, C and H were taken from the International Tables [6]. The weighting scheme was based on counting statistics. The final positional and thermal parameters of the atoms are given in Tables I and II. A Table of the calculated and observed structure factors is available from the Editor.

Results and Discussion

The crystal structure consists of centrosymmetric dimeric units in which two copper atoms are held together through carboxylate bridges. Each copper atom is bonded further to a water molecule. The configuration of the binuclear complex with all the non-hydrogen atoms is shown in Fig. 1. The interatomic bond distances and bond angles are listed in Table III.

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

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1.30(2)	1.67(2)	1.65(2)	0.08(2)	0.50(1)	−0.03(2)
O1	2.02(11)	4.53(16)	2.91(12)	0.68(11)	0.64(9)	1.32(12)
O2	1.77(10)	1.97(12)	2.73(11)	−0.09(9)	0.23(9)	−0.08(9)
O3	1.47(10)	2.27(12)	2.94(11)	−0.21(9)	0.34(9)	−0.18(10)
O4	2.03(10)	3.16(12)	2.12(10)	0.08(11)	0.87(8)	−0.13(11)
O5	2.16(11)	3.24(15)	2.38(11)	0.34(10)	1.00(9)	−0.02(10)
O6	2.94(13)	3.65(16)	4.35(14)	0.85(12)	1.46(11)	−0.42(12)
O7	3.28(13)	7.77(23)	2.10(11)	1.56(14)	0.25(10)	−1.29(13)
N1	2.52(15)	1.82(15)	2.94(15)	−0.17(12)	0.76(12)	−0.26(13)
N2	2.06(12)	3.95(16)	1.92(11)	0.10(15)	0.84(10)	−0.41(14)
C1	1.88(16)	2.27(17)	1.51(14)	−0.20(13)	0.70(12)	−0.14(13)
C2	2.24(16)	2.40(20)	3.18(18)	−0.48(14)	0.36(15)	−0.15(15)
C3	1.70(15)	2.13(19)	3.55(19)	−0.44(13)	0.99(14)	−0.10(14)
C4	4.63(24)	3.45(24)	3.59(22)	−0.32(24)	0.96(18)	0.15(22)
C5	2.59(17)	1.87(15)	1.95(15)	−0.72(14)	0.95(14)	−0.43(13)

(continued on facing page)

TABLE II. *(continued)*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C6	2.81(18)	3.67(21)	2.31(17)	0.61(17)	1.27(15)	0.11(16)
C7	2.49(17)	3.48(20)	2.25(16)	0.14(15)	0.96(14)	0.50(14)
C8	3.44(23)	6.38(31)	2.60(19)	1.80(24)	0.79(17)	0.85(22)

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

TABLE III. Bond Distances and Bond Angles.[a]

Distances (A)		Angles (°)	
Cu Coordination			
Cu–Cu′	2.666(1)	Cu′–Cu–O1	168.8(1)
Cu–O1	2.108(3)	Cu′–Cu–O2	87.6(1)
Cu–O2	1.975(3)	Cu′–Cu–O3′	80.1(1)
Cu–O3′	1.986(3)	Cu′–Cu–O4	86.7(1)
Cu–O4	1.969(2)	Cu′–Cu–O5′	80.8(1)
Cu–O5′	1.954(2)	O1–Cu–O2	100.7(1)
		O1–Cu–O3′	91.8(1)
		O1–Cu–O4	101.0(1)
		O1–Cu–O5′	91.7(1)
		O2–Cu–O3′	167.6(1)
		O2–Cu–O4	87.6(1)
		O2–Cu–O5′	90.0(1)
		O3′–Cu–O4	90.1(1)
		O3′–Cu–O5′	89.6(1)
		O4–Cu–O5′	167.3(1)
N-Acetylglycinate			
C1–C2	1.522(6)	Cu–O2–C1	119.0(2)
C1–O2	1.245(4)	Cu′–O3–C1	126.7(2)
C1–O3	1.270(4)	C2–C1–O2	117.2(3)
C2–N1	1.441(5)	C2–C1–O3	116.8(3)
C3–C4	1.491(6)	O2–C1–O3	126.0(3)
C3–N1	1.334(5)	C1–C2–N1	112.7(3)
C3–O6	1.235(5)	C2–N1–C3	120.0(3)
C5–C6	1.508(5)	C4–C3–N1	117.0(4)
C5–O4	1.248(4)	C4–C3–O6	121.9(4)
C5–O5	1.260(5)	N1–C3–O6	121.1(4)
C6–N2	1.452(5)	Cu–O4–C5	119.1(2)
C7–C8	1.524(7)	Cu′–O5–C5	126.7(2)
C7–N2	1.331(5)	C6–C5–O4	119.4(3)
C7–O7	1.218(5)	C6–C5–O5	114.1(3)
		O4–C5–O5	126.6(3)
		C5–C6–N2	113.7(3)
		C6–N2–C7	119.9(3)
		C8–C7–N2	115.7(4)
		C8–C7–O7	121.7(4)
		N2–C7–O7	122.6(4)

[a] The primed atoms are related to the unprimed ones by the centre of inversion within the molecule.

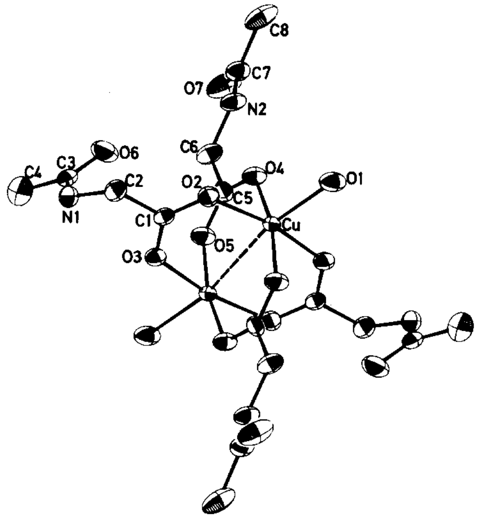

Fig. 1. Tetra-μ-N-acetylglycinatodiaquodicopper(II): ORTEP plot of the molecule with atom numbering (ellipsoids are drawn to 50% probability).

The copper atoms are coordinated by carboxylate oxygen atoms, O2, O3′, O4 and O5′ at distances, 1.975, 1.986, 1.969 and 1.954 Å respectively. The four ligand atoms constitute almost a planar arrangement with the central copper atom. The fifth oxygen atom of water (Cu–O1 = 2.108 Å) completes the square pyramidal coordination polyhedran around copper. The copper–copper distance across the dimeric unit is 2.666 Å.

A number of copper(II) carboxylates [7] resemble the structure of classic dimeric copper(II) acetate monohydrate [8] whose structure has been recently reinvestigated independently by X-rays [9] and neutron diffraction studies [10]. In this class of compounds, where there exists a strong metal–metal bond, the Cu–Cu separations are in the range 2.616–2.645 Å. The Cu–Cu distance of 2.666 Å found in the present compound, though greater than 2.556 Å observed in metallic copper [11] and 2.544 Å in polymeric copper(I) acetate [12], is comparable with the several dimeric copper(II) carboxylates [7]. This suggests that there is a fairly strong interaction between the copper atoms in the complex. Further support for the strong Cu–Cu bond in the complex is achieved by considering the bridge lengths. In several dimeric copper(II) carboxylates the bridge length lies in the range 6.41 to 6.46 Å [7]. In the

TABLE IV. Hydrogen Bonding in the Structure.

A–H....B	Distances [A]			Bond Angle AHB [°]
	A–H	H...B	A...B	
O1–H2...O7	0.94(4)	1.84(4)	2.748(4)	162(1)
N1–H5...O3	0.76(4)	2.28(4)	3.030(4)	173(1)
N2–H11...O2	0.96(4)	2.20(4)	3.129(4)	162(1)

present compound the two bridge lengths, Cu–O2–C1–O3–Cu′ and Cu–O4–C5–O5–Cu′ are 6.476 and 6.431 Å respectively which are close to the values found in the literature.

Among the several copper(II) carboxylates [13] whose structures are known, the Cu–O bond distances are in the range 1.89 to 2.02 Å. In this complex, the average bond distance of 1.97 Å is of normal value suggesting strong Cu–O bonds. In copper(II) acetate hydrate, the Cu–O (water) bond distance is 2.16 Å [9, 10], which is comparable with the value of 2.11 Å observed in the present complex. However, it is interesting to note that in copper(II) N-acetylglycinate tetrahydrate the Cu–O (carboxylate) distance, 1.95 Å, is slightly longer than the Cu–O (water) distance, 1.94 Å, but in the present complex the reverse is true.

The bond distances and bond angles of the two N-acetylglycinate units are, although being not quite identical, not significantly different from those of the free ligand [14–15] except for the carboxylate group. Thus, in N-acetylglycine the experimental bond distances of C1–C2, C2–N, N–C3, C3–O3 and C3–C4 are 1.514, 1.444, 1.331, 1.252 and 1.507 Å respectively. The corresponding values in the two units in the present complex are 1.522, 1.441, 1.334, 1.235 and 1.491 and 1.508, 1.452, 1.331, 1.218 and 1.524 Å respectively. The atoms C1, C2, O2 and O3 constitute a plane with deviations from the plane being below 0.003 Å. On the other hand the atoms C2, N1, C3, O6 and C4 lie in a plane with deviations of –0.04, 0.05, 0.02, 0.01, –0.04 Å, respectively, from the plane. The least-squares equations of the two planes are $0.4394x - 0.1476y - 0.8861z - 1.8362 = 0$ [1] and $-0.8778x - 0.4705y - 0.0899z - 0.3156 = 0$ [2] where x, y and z are referred to the monoclinic axes and expressed in Å units. Similarly in the other N-acetylglycinate unit the atoms C5, C6, O4 and O5 constitute a plane with deviations being below 0.004 Å; C6, N2, C7, O7 and C8 lie in a plane with 0.02 Å maximum deviations of these atoms from the plane. The least-squares equations of the planes are $-0.4025x - 0.8814y - 0.2474z + 1.5593 = 0$ (3) and $0.3915x + 0.9084y - 0.1471z - 0.2159 = 0$ [4].

The angles between the normals to the planes [1] and [2], and [3] and [4] are 76.3° and 22.8°, respectively. The corresponding dihedral angle in the free ligand is 5.2° [15], which shows that in the complex the ligand molecules are twisted around the C1–C2 and C5–C6 bonds. The hydrogen bond distances and bond angles are given in Table IV. It is clear from the Table that the water molecule is strongly hydrogen bonded to a peptide oxygen atom (O1...O7), 2.75 Å). Further, the nitrogen atoms of the peptide group take part in hydrogen bonding with the oxygen atoms of the carboxyl group (N1...O3, 3.03; N2...O2, 3.13 Å).

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