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Bis(*N*-acetylglucinato)-1,10-phenanthrolinecopper(II)

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Abstract. C₂₀H₂₀CuN₄O₆, monoclinic, space group *C2/c*, *a* = 8.85 (1), *b* = 16.45 (1), *c* = 14.74 (3) Å, β = 102.3 (1)°, *U* = 2097 (2) Å³, FW 494.0, *Z* = 4, *D_m* = 1.53, *D_x* = 1.55 g cm⁻³, μ (Mo *K*α) = 10.78 cm⁻¹. Final residual *R* = 3.6%. Coordination is square planar, slightly distorted tetrahedrally, involving two N atoms from the phenanthroline ligand and two O atoms from the carboxyl group; the phenanthroline moiety is planar. Packing is mainly determined by N–H···O hydrogen bonds and by van der Waals contacts.

Introduction. Many simple amino acids have been complexed with a large number of transition metals ions on the assumption that the complexes formed act as models for the metal-binding sites of proteins (Freeman, 1967). Cu^{II} complexes of amino acids have been studied in considerable detail, and if there are no bulky donor side chains, the anion coordinates solely through the carboxylato groups, forming five-membered rings with the metal ion, as found for each naturally occurring L-α-amino acid (Freeman, 1967; Hughes, 1972; Chow & McAuliffe, 1975). In the framework of an investigation on the coordination properties of the amino acids containing an *N*-amino substituent, such as the acetyl group (Marcotrigiano & Pellacani, 1974), we have previously considered the crystal structure of bis(*N*-acetylglucinato)diaqua-

copper(II) dihydrate (Marcotrigiano, Pellacani, Battaglia & Bonamartini Corradi, 1976).

The title compound was obtained by mixing methanolic solutions of CuA₂·4H₂O (*A* = acetyl-glycine) (1 mM) and 1,10-phenanthroline (1 mM), adding ethyl ether, and cooling to 0°C. Recrystallization from methanol produces dark-blue prismatic crystals.

Table 1. Final fractional coordinates ($\times 10^4$) for non-hydrogen atoms and their standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Cu	0	0	2500
O(1)	1558 (2)	624 (1)	2980 (1)
O(2)	350 (2)	493 (1)	4137 (2)
O(3)	4340 (2)	-1526 (1)	5029 (2)
N(1)	1330 (2)	2344 (1)	3107 (1)
N(2)	2217 (2)	-763 (1)	4902 (1)
C(1)	2675 (3)	2311 (2)	3716 (2)
C(2)	3465 (3)	3021 (2)	4072 (2)
C(3)	2866 (3)	3770 (2)	3792 (2)
C(4)	1435 (3)	3815 (1)	3147 (2)
C(5)	723 (2)	3082 (1)	2828 (1)
C(6)	693 (3)	4559 (1)	2808 (2)
C(7)	1353 (3)	298 (1)	3729 (2)
C(8)	2535 (3)	-357 (2)	4091 (2)
C(9)	3192 (3)	-1355 (2)	5314 (2)
C(10)	2775 (4)	-1737 (2)	6154 (2)

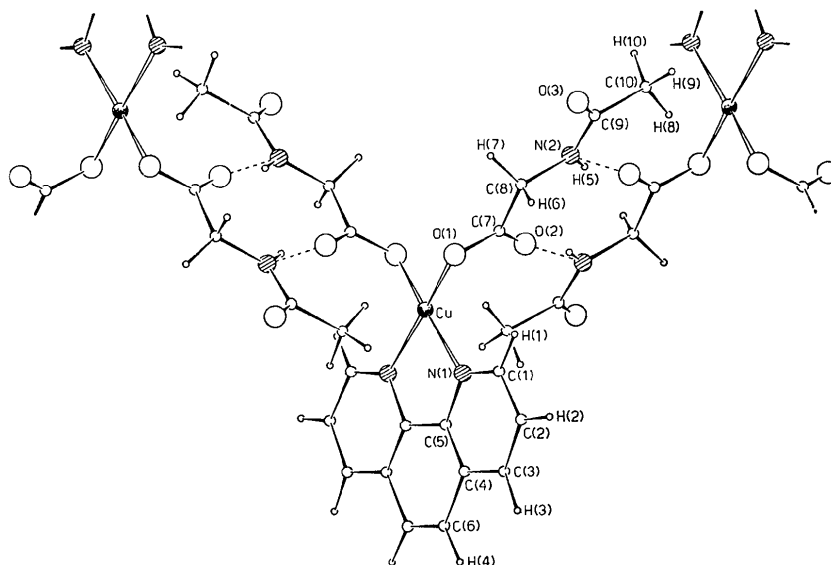


Fig. 1. Projection of the structure.

Table 2. Final fractional coordinates ($\times 10^3$) for hydrogen atoms and their standard deviations in parentheses

	x	y	z
H(1)	316 (3)	176 (1)	394 (2)
H(2)	449 (3)	298 (2)	455 (2)
H(3)	349 (3)	432 (2)	399 (2)
H(4)	124 (3)	508 (1)	306 (2)
H(5)	131 (3)	-62 (1)	514 (2)
H(6)	363 (3)	-9 (2)	429 (2)
H(7)	252 (3)	-78 (2)	358 (2)
H(8)	227 (3)	-135 (2)	651 (2)
H(9)	371 (3)	-194 (2)	657 (2)
H(10)	207 (3)	-220 (2)	596 (2)

A crystal ($0.29 \times 0.42 \times 0.75$ mm) was mounted on a Siemens AED single-crystal computer-controlled diffractometer (Mo $K\alpha$ radiation) and 2861 reflections with $6^\circ < 2\theta < 58^\circ$ were collected; 2238 of them with $I > 2\sigma(I)$ were used in the structure analysis. During the data collection a standard reflection was measured every 20 reflections and its intensity was found to be constant.

Intensities were corrected for Lorentz and polarization factors. Data were put on an absolute scale first by Wilson's (1942) method, then by comparing observed and calculated values. No correction for absorption was made.

The Cu atom was located from a three-dimensional Patterson map and the successive Fourier synthesis gave all the coordinates of the non-hydrogen atoms. Refinement was carried out by block-diagonal isotropic and anisotropic least squares down to a

conventional R index of 4.5%, minimizing the function $\sum w|\Delta F|^2$ with unit weights. The coordinates of the H atoms, located from a final ΔF synthesis were then refined isotropically, improving the final R value to 3.6%.

The final positional parameters with their estimated standard deviations are given in Tables 1 and 2.* The atomic scattering factors used were those of Cromer & Mann (1968) for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the H atoms.

All the calculations were performed on the CDC 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna.

Discussion. As shown in Fig. 1, the *N*-acetylglycinate ion coordinates through the carboxyl group, the peptide group being not involved in coordination as found in bis(*N*-acetylglycinato)diaquacopper(II) dihydrate (Marcotrigiano *et al.*, 1976). The Cu atom, which lies on the twofold axis, is surrounded by four ligand atoms in a square-planar arrangement with a slight tetrahedral distortion [O(1) and N(1) are 0.14 and 0.15 Å, respectively, out of the mean coordination plane]. The dimensions of the molecule are shown in Table 3. Distances and angles in the carboxylic and peptide groups are in a good agreement with

* Structure factor tables are available from the authors on request and have also been deposited, along with the anisotropic thermal parameters, with the British Library Lending Division as Supplementary Publication No. SUP 32854 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Bond distances (Å) and angles (°) in the structure with *e.s.d.*'s in parentheses

Symmetry code: (i) $\bar{x}, y, \frac{1}{2} - z$.			
Cu—O(1)	1.928 (3)	N(1)—C(1)	1.330 (4)
Cu—O(2)	2.819 (6)	C(1)—C(2)	1.404 (5)
Cu—N(1)	2.007 (3)	C(2)—C(3)	1.370 (5)
C(7)—O(1)	1.275 (4)	C(3)—C(4)	1.414 (5)
C(7)—O(2)	1.217 (4)	C(4)—C(5)	1.395 (3)
C(7)—C(8)	1.518 (4)	C(4)—C(6)	1.428 (3)
C(8)—N(2)	1.449 (4)	C(5)—C(5')	1.430 (3)
N(2)—C(9)	1.332 (4)	C(5)—N(1)	1.356 (3)
C(9)—O(3)	1.221 (4)	C(6)—C(6')	1.362 (5)
C(9)—C(10)	1.517 (5)		
(C—H) mean	1.02	N—H	0.97
N(1)—Cu—O(1)	92.6 (1)	N(2)—C(9)—O(3)	122.1 (3)
N(1)—Cu—N(1')	82.1 (1)	N(2)—C(9)—C(10)	115.7 (2)
O(1)—Cu—O(2)	51.4 (1)	O(3)—C(9)—C(10)	122.3 (3)
O(1)—Cu—O(1')	93.9 (1)	N(1)—C(1)—C(2)	121.4 (3)
O(1)—Cu—O(2')	83.3 (1)	C(1)—C(2)—C(3)	120.4 (3)
O(1)—Cu—N(1')	169.7 (1)	C(2)—C(3)—C(4)	118.9 (3)
O(2)—Cu—N(1)	94.7 (1)	C(3)—C(4)—C(5)	117.2 (2)
O(2)—Cu—O(2')	114.2 (1)	C(3)—C(4)—C(6)	124.0 (2)
O(2)—Cu—N(1')	137.6 (1)	C(4)—C(5)—N(1)	123.4 (2)
Cu—O(1)—C(7)	112.5 (2)	C(4)—C(5)—C(5')	120.2 (2)
O(1)—C(7)—O(2)	124.8 (2)	C(4)—C(5)—N(1)	123.4 (2)
O(1)—C(7)—C(8)	112.9 (2)	C(4)—C(6)—C(6')	121.0 (2)
O(2)—C(7)—C(8)	122.3 (3)	C(5)—N(1)—C(1)	118.8 (2)
C(7)—C(8)—N(2)	112.1 (2)	N(1)—C(5)—C(5')	116.4 (2)
C(8)—N(2)—C(9)	118.7 (2)		

those quoted by Freeman (1966) for cupric-peptide complexes, the typical ranges being: H₂C—CO(peptide) 1.51–1.57, C=O(peptide) 1.23–1.28, OC—N<(peptide) 1.29–1.32, H₂C—N<(peptide) 1.43–1.48, H₂C—CO(carboxyl) 1.49–1.53, C=O(carboxyl) 1.21–1.25, C—O(carboxyl) 1.24–1.33 Å; C—C=O(peptide) 117–112, C—CO—N 113–117, OC—N—C 117–126, C—C=O(carboxyl) 116–126, O=C—O 117–129, C—CO—O 113–121°.

The torsion angle C(8)—N(2)—C(9)—O(3) in the present compound is exactly 0.0°, while it is 4.5° in bis(*N*-acetylglycinato)diaqua-Cu^{II} dihydrate and 5.8° in *N*-acetyl-L-glutamine (Narasimhamurthy, Venkatesan & Winkler, 1974).

The phenanthroline molecule coordinates to Cu forming a five-membered chelate ring with an angle at Cu (82.1°) in good agreement with those found in other Cu^{II}-phenanthroline complexes [81.6 and 80.8° in bis(1,10-phenanthroline)thiourea-copper(II) perchlorate monohydrate (Belicchi Ferrari, Gasparri Fava & Montenero, 1975); 79.7° in dichloro-aqua(2,9-dimethyl-1,10-phenanthroline)copper(II) (Preston &

Kennard, 1969); 81.6, 77.2° in tris(1,10-phenanthroline)copper(II) perchlorate (Anderson, 1973)], its value being determined only by the metal—N distance since the N...N bite distance (2.636 Å) has no flexibility. The Cu atom lies in the chelate-ring plane, and in the plane of the phenanthroline molecule. The phenanthroline ligand shows no distortion from planarity; its bond distances and angles correlate quite well with Pauling's (1967) π -bond orders as found, for example, in tris(1,10-phenanthroline)nickel(II) penta-carboxylmanganate(–I) (Frenz & Ibers, 1972).

The main packing interaction is the hydrogen bond O(2)...H(7)—N(2ⁱ) of length 2.957 (5) Å, \angle O(2)...H(7)—N(2ⁱ) = 167 (2)°, which joins together two centrosymmetrically related acetylglycinate ligands. The other contacts correspond to normal van der Waals interactions ($i \equiv 1 - x, y, 1 - z$).

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