

## The Crystal Structure of Bis(imidazole)copper(II) Diacetate

BY H. Å. HENRIKSSON

Department of Medical Biochemistry, University of Göteborg, Fack, S-400 33 Göteborg 33, Sweden

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The crystal structure of bis(imidazole)copper(II) diacetate has been determined from 486 independent reflexions. The reflexions were recorded on equi-inclination Weissenberg photographs with graphite-monochromatized Cu  $K\alpha$  radiation and were estimated on an Optronic international system P-1000 photoscanner. The orthorhombic *Pccn* unit cell has the dimensions  $a = 11.660$  (3),  $b = 12.284$  (4),  $c = 9.375$  (3) Å, and contains four asymmetric units. The structure has been solved by the heavy-atom method and refined by least squares ( $R = 0.059$ ). Two imidazole and two acetate molecules are coordinated to the Cu atom *via* their pyridine N and carboxylate O atoms [Cu–N = 2.004 (8), Cu–O = 1.921 (9) Å], and they form discrete complexes with the Cu atom. These centrosymmetric ligand atoms form an almost square plane, and are *trans* with respect to each other. The second O atoms of the two carboxylate groups interact weakly with the Cu atom, one above and one below the square plane, forming a distorted octahedron [Cu–O = 2.799 (8) Å].

### Introduction

As part of a general study on Cu–protein interaction (Österberg, 1974), the Cu ion complex bis(imidazole)copper(II) diacetate has been investigated. The particular ligands present in this structure are intended as models for those Cu binding sites in Cu proteins that contain both carboxylate and imidazole side chains. The crystal structure of bis(imidazole)copper(II) diacetate, combined with an earlier reported structure, copper(I)–imidazole–perchlorate, may serve as a model system for the change in the coordination within a protein when Cu<sup>II</sup> is reversibly reduced to Cu<sup>I</sup> (Henriksson, Sjöberg & Österberg, 1976).

### Experimental

The crystals used were prepared from a solution of copper(II) acetate and imidazole in *n*-butanol. After a few days at room temperature, dark violet crystals in the form of thin plates appeared. Elementary analysis of the violet crystals yielded: Found: Cu 19.97, C 38.0, N 17.5, H 4.5%. Calculated: Cu 19.96, C 37.7,

N 17.6, H 4.4%. The crystal and experimental data are given in Table 1.

The space group was determined to be *Pccn*, from systematic extinctions (*International Tables for X-ray Crystallography*, 1952). The density was measured by flotation in a mixture of methyl iodide, carbon tetrachloride and *o*-xylene. The unit-cell dimensions were obtained from a powder photograph taken on a Guinier camera at 21°C, with Pb(NO<sub>3</sub>)<sub>2</sub> as an internal standard, and the  $\sin^2 \theta$  values were refined with the program *POWDER* (Lindqvist & Wengelin, 1967). The parameters  $\lambda(\text{Cu } K\alpha_1)$  (1.54051 Å) and  $a[\text{Pb}(\text{NO}_3)_2]$  (7.8566 Å) were those listed in *International Tables for X-ray Crystallography* (1962).

Equi-inclination, multiple-film Weissenberg data for nine layers were recorded by using graphite-monochromatized Cu  $K\alpha$  radiation and rotating the crystal about the *a* axis. A crystal 0.3 × 0.13 × 0.2 mm was used and 486 independent reflexions were recorded. The intensities were estimated by an Optronic international system P-1000 photoscanner, and were then corrected for Lorentz and polarization factors.

### Structure determination and refinement

Fourfold special positions, 0,0,0;  $\frac{1}{2}, \frac{1}{2}, 0$ ;  $0, \frac{1}{2}, \frac{1}{2}$ ;  $\frac{1}{2}, 0, \frac{1}{2}$ , for the Cu atoms were indicated on a Patterson map. With the phases calculated from the Cu atom, a three-dimensional Fourier synthesis revealed the remaining non-hydrogen atoms. The positions of the non-hydrogen atoms were refined by block-diagonal least-squares calculations with constant isotropic temperature factors. Structure factors calculated after three cycles of full-matrix least squares yielded an *R* index of 0.100;  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ . Anisotropic

Table 1. *Crystal data*

C <sub>10</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub> Cu	Systematic absences
FW 317.17	$h0l: l = 2n + 1$
$a = 11.660$ (3) Å	$hk0: h + k = 2n + 1$
$b = 12.284$ (4)	$0kl: l = 2n + 1$
$c = 9.375$ (3)	Space group: <i>Pccn</i>
$V = 1341$ Å <sup>3</sup>	$Z = 4$
$D_c = 1.57$ g cm <sup>-3</sup>	$\mu(\text{Cu } K\alpha) = 24.8$ cm <sup>-1</sup>
$D_m = 1.55$	$F(000) = 596$
$\lambda(\text{Cu } K\alpha) = 1.5418$ Å	

temperature factors further reduced  $R$  to 0.086. At this stage, a difference Fourier synthesis indicated the locations of the H atoms. When the refinement was continued, including H atoms with constant isotropic temperature factors, the  $R$  value dropped to 0.069. Also included in this refinement was the correction for the absorption of the crystal.

During the final refinement the calculated structure factors were corrected for the anomalous dispersion of Cu,  $\Delta f' = -2.15$  and  $\Delta f'' = 0.75$  (Cromer, 1965), and this yielded a final  $R$  value of 0.059. An additional difference Fourier synthesis was calculated: the peaks were all within  $0 - |0.5| \text{ e}\text{\AA}^{-3}$ . The final atomic parameters are listed in Tables 2 and 3.\*

The scattering factors used for C, N, O and Cu<sup>+</sup> were those of Doyle & Turner (1968), and those for H were from Stewart, Davidson & Simpson (1965). In the final cycles of refinement, weights were used according to Cruickshank's (1965) formula:  $w = (30.0 + F_o + 0.001F_o^2 + 0.0F_o^3)^{-1}$ . The calculations were performed on an IBM 360/65 computer, using the program library of the Department of Inorganic Chemistry, University of Göteborg: *LALS*, least-squares full-

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32374 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) for non-hydrogen atoms

	x	y	z
Cu	0	0	0
O(1)	1562 (7)	-228 (5)	579 (9)
O(2)	1976 (7)	979 (6)	-1110 (9)
N(1)	-97 (9)	1298 (5)	1291 (8)
N(2)	385 (11)	2575 (7)	2735 (10)
C(1)	-996 (13)	1928 (10)	1515 (15)
C(2)	-729 (14)	2720 (9)	2408 (13)
C(3)	714 (12)	1728 (10)	2037 (12)
C(4)	2262 (17)	378 (12)	-152 (15)
C(5)	3457 (24)	269 (18)	265 (27)

Table 3. Positional parameters ( $\times 10^4$ ) for hydrogen atoms

$$B = 3.0 \text{ \AA}^2 \text{ for each atom.}$$

Bonded to	x	y	z	
H(1)	C(5)	3477	-421	435
H(2)	C(5)	3933	545	170
H(3)	C(5)	3185	-240	-666
H(4)	N(2)	758	3056	3283
H(5)	C(3)	1420	1516	2063
H(6)	C(1)	-1702	1821	1134
H(7)	C(2)	-1012	3185	2865

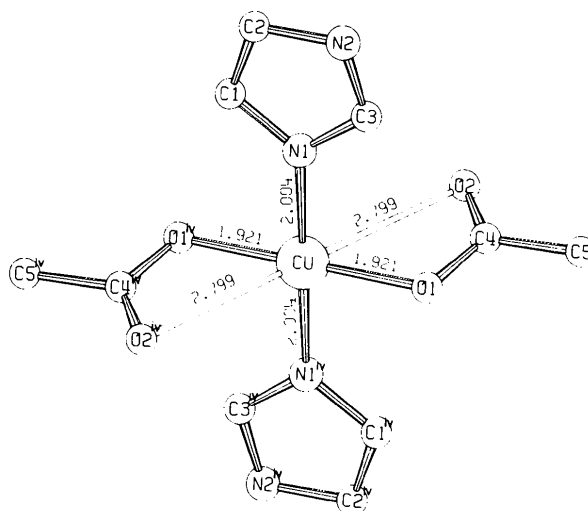


Fig. 1. Copper coordination with bond distances (Å).

matrix refinement, originally written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, University of California, Los Angeles; *DRF*, Fourier summations; and *DISTAN*, angles and distances and their deviations, originally written by A. Zalkin, University of California, Berkeley. The drawings were produced by *ORTEP*, written by Johnson (1965).

### Description of the structure

The atomic arrangement in the unit cell of bis(imidazole)copper(II) diacetate is shown in Fig. 1. Interatomic distances and angles, with standard deviations, are given in Table 4.

Two imidazole and two acetate molecules are coordinated to each Cu atom, the two imidazole molecules *via* pyridine N atoms, N(1), and the two acetate ions *via* carboxylate O atoms, O(1). Each Cu atom is centrosymmetrically surrounded by these four ligands. The coordination around the Cu atom is planar for the four closest, centrosymmetric ligand atoms, which nearly form a square (Fig. 1). These two O and N atoms are *trans* with respect to each other. The distances Cu-O(1), 1.921 (9), and Cu-N(1), 2.004 (8) Å, are in close agreement with those determined previously for similar Cu<sup>II</sup> structures (Freeman, 1967; Lundberg, 1972). Both the second carboxylate O atoms, O(2), interact weakly with the Cu atom at 2.799 Å, and as a result the Cu is six-coordinated; the ligand atoms form a distorted octahedron. The distortion is clearly indicated by the angle O(1)-Cu-O(2), 52.21 (28)°, and thus the Cu-O bonds are bent in the direction of their neighbouring O atom, O(1) (Fig. 1).

The following three planes formed by the centrosymmetric ligand atoms all pass through the central

Table 4. Bond distances (Å) and angles (°)

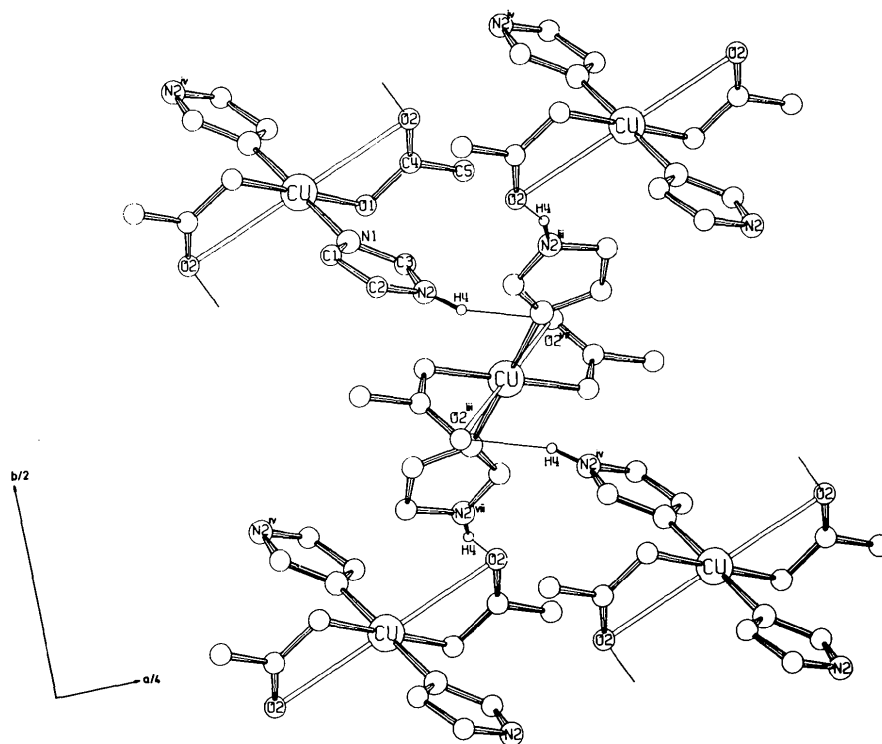
Symmetry code			
None $x, y, z$			
(i)	$\frac{1}{2} - x, \frac{1}{2} - y, z$	(iv)	$-x, -y, -z$
(ii)	$\frac{1}{2} + x, -y, \frac{1}{2} - z$	(v)	$\frac{1}{2} + x, \frac{1}{2} + y, -z$
(iii)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$	(vi)	$\frac{1}{2} - x, y, \frac{1}{2} + z$
		(vii)	$x, \frac{1}{2} - y, \frac{1}{2} + z$
(a) In the coordination polyhedron			
Cu—O(1)	1.921 (9)	O(1)—Cu—N(1)	89.97 (35)
Cu—O(2)	2.799 (8)	O(1)—Cu—O(2)	52.21 (28)
Cu—N(1)	2.004 (8)	O(2)—Cu—N(1)	85.94 (32)
(b) In the imidazole group			
N(1)—C(1)	1.319 (17)	C(1)—N(1)—C(3)	104.87 (93)
N(1)—C(3)	1.290 (15)	N(1)—C(3)—N(2)	112.78 (100)
N(2)—C(2)	1.347 (17)	C(3)—N(2)—C(2)	106.20 (78)
N(2)—C(3)	1.288 (12)	N(2)—C(2)—C(1)	105.92 (116)
C(1)—C(2)	1.321 (18)	C(2)—C(1)—N(1)	110.22 (135)
(c) In the acetate group			
O(1)—C(4)	1.300 (19)	O(2)—C(4)—O(1)	124.59 (170)
O(2)—C(4)	1.209 (17)	O(1)—C(4)—C(5)	114.06 (147)
C(4)—C(5)	1.454 (34)	O(2)—C(4)—C(5)	121.35 (169)
(d) Involving hydrogen atoms			
N(2)—H(4)	0.895	C(5)—H(1)	0.862
C(1)—H(6)	0.906	C(5)—H(2)	0.656
C(3)—H(5)	0.864	C(5)—H(3)	1.119
C(2)—H(7)	0.785		

Cu atom by symmetry (Fig. 1 and Table 4): O(1)N(1)O(1<sup>iv</sup>)N(1<sup>iv</sup>) (plane *A*); O(1)O(2)O(1<sup>iv</sup>)O(2<sup>iv</sup>) (plane *B*); O(2)N(1)O(2<sup>iv</sup>)N(1<sup>iv</sup>) (plane *C*). The angle between the almost square plane (plane *A*) and plane *B*

Table 5. Least-squares planes

(a) Coefficients. The equations of the planes are expressed in the form  $AX + BY + CZ = D$  where  $X, Y,$  and  $Z$  are Cartesian coordinates obtained from fractional coordinates  $x, y,$  and  $z$  by the transformation:  $X = 11.66x, Y = 12.28y,$  and  $Z = 9.37z.$

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>		
Carboxylate plane						
[O(1)O(2)C(4)C(5)]	0.11425	-0.74152	-0.66113	0.05728		
Imidazole plane						
[N(1)N(2)C(1)C(3)C(2)]	0.26025	0.57899	-0.77268	-0.03581		
(b) Deviations from planes (Å). The figures in parentheses were not included in the calculation of the plane.						
Carboxylate plane						
O(1)	0.0010	0.0011	-0.0030	0.0008	(-0.0572)	
O(2)						
C(4)						
C(5)						
Cu						
Imidazole plane						
N(1)	-0.0058	0.0031	0.0077	0.0016	-0.0065	(0.0358)
N(2)						
C(1)						
C(3)						
C(2)						
Cu						

Fig. 2. Bis(imidazole)copper(II) diacetate viewed down the *c* axis showing the positions of the hydrogen bonds.

is  $84.8^\circ$ , and that between plane *B* and plane *C* is  $86.8^\circ$ . The carboxylate group forms a  $1.7^\circ$  angle with the plane of the carboxylate O atoms (plane *B*), and the imidazole ring forms a  $3.4^\circ$  angle with the plane of the coordinating atoms (plane *A*).

Bond lengths and angles for the ligand molecule are listed in Table 4. The C—C and C—N bond lengths and the corresponding angles agree with the mean values reported for other similar structures (Lundberg, 1972). The carboxylate group O(1), O(2), C(4) and C(5), and the imidazole group N(1), N(2), C(1), C(2) and C(3) are planar; their least-squares planes are given in Table 5.

The discrete bis(imidazole)copper(II) diacetate complexes are connected *via* hydrogen bonds from the pyrrole N atom N(2) in the imidazole ring to the O(2) carboxylate O atom of the neighbouring complex, forming a three-dimensional network (Fig. 2); N—H...O is  $2.787(8)$  Å and the angle N—H...O is  $158.35^\circ$ .

### Discussion

Bis(imidazole)copper(II) diacetate is shown to be essentially isostructural with bis(imidazole)cobalt(II) diacetate (Gadet, 1974); for instance, the shortest  $\text{Co}^{\text{II}}\text{—N}$  and  $\text{Co}^{\text{II}}\text{—O}$  distances are 1.97 and 2.01 Å (Gadet, 1974) and the corresponding  $\text{Cu}^{\text{II}}\text{—N}$  and  $\text{Cu}^{\text{II}}\text{—O}$  distances are 1.92 and 2.0 Å (Fig. 1). These data provide a structural basis for the fact that in a metalloprotein  $\text{Cu}^{\text{II}}$  can be replaced by a  $\text{Co}^{\text{II}}$  ion, this type of replacement having been done repeatedly for  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  metalloproteins [see, for instance, McMillin, Rosenberg & Gray (1974)].

There are many important differences between the present structure and other  $\text{Cu}^{\text{II}}$ —imidazole structures previously reported (*cf.* Freeman, 1967; Lundberg, 1972). The structure of bis(imidazole)copper(II) diacetate contains discrete complexes, but in the other  $\text{Cu}^{\text{II}}$ —imidazole structures polynuclear species or infinite

chains are formed *via* ligands that coordinate two neighbouring Cu atoms. This is one of the reasons why the present structure, rather than the other  $\text{Cu}^{\text{II}}$ —imidazole structures, might have more direct implications for the specific Cu binding sites in Cu proteins. Of further biological interest is the fact that the present structure and that of  $\text{Cu}^{\text{I}}$ —imidazole—perchlorate give some idea as to the mechanism for the reactions of those copper enzymes that involve transfer of both electrons and protons (Henriksson, Sjöberg & Österberg, 1976).

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