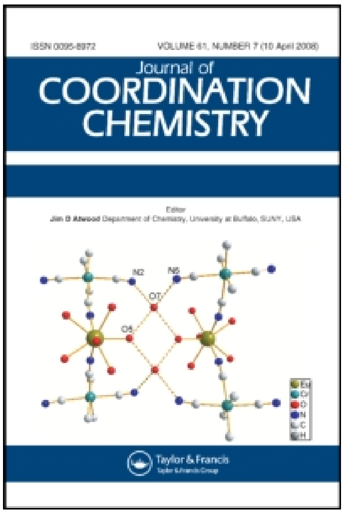

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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(p-NITROPHENACETURO)DIAQUOCOPPER(II)

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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(p-NITROPHENACETURO)DIAQUOCOPPER(II)

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The crystal and molecular structure of $[Cu(p{-}NO_2C_6H_5CH_2CONHCH_2CO_2)_2(H_2O)_2]$ has been determined by single-crystal, x-ray diffraction techniques. The compound is centrosymmetric crystallizing in a monoclinic unit cell ($P2_1/c$) with two molecules per unit cell. The cell dimensions are: a = 11.588(1)Å, b = 11.405(1)Å, c = 8.041(1)Å and β = 93.47 ± (1). The structure was solved by Patterson methods and refined to a value of R = 0.063. The coordination about the copper assumes an unexpected square planar geometry in which two phenaceturic moieties are each coordinated through the carboxylic oxygen (Cu–O = 1.933Å) and the two waters complete the coordination ($Cu{-}O_w$ = 1.959Å). The overall conformation of the phenaceturic acid is retained although there is a rotation of 180° about the peptide C–N bond.

INTRODUCTION

This study of the copper complex of p-nitrophenaceturic acid continues our series of structure analyses of α-amino acid and their copper complexes.[1,2,3,4] These acids form model systems analogous to the principal side chain of Penicillin G. Hence, metal complexes of these acids (with Cu^{+2}, for example) are studied to assess which of the multiple coordination sites are utilized and ultimately to lend some insights into the mechanism whereby penicillins are deactivated either through decomposition or polymerization. Cressman, for example,[5] postulated copper coordination at both the amide nitrogen and the β-lactam oxygen in the penicillin sidechain. Contrary to this, the only previous analogue, namely the copper hippurate,[2,3] has coordination only through the carboxylic oxygen. The coordination about the copper is of some interest. We have already observed the (4 + 1) square pyramidal coordination in the analogous hippurates[2,3] whereas square planar coordination has been occasionally observed in cases where the amidic protons have been removed[6] and also in bidentate acid complexes.[7]

EXPERIMENTAL

A cylindrical crystal of the copper complex, approximately 0.3 mm long, was mounted on a General Electric XRD-5 diffractometer with the (O1O) axis as the spindle axis. Using Cu-K_α radiation, extinctions of k odd for (OkO) and l odd for (hOl) were found which uniquely fixed the monoclinic space group as $P2_1/c$. Lattice constants were determined by a least-squares fit of 20 carefully measured two-theta values (1° take-off angle and 0.05° slit) at $2\theta > 68°$ where the Cu–$K\alpha_1$ and Cu–$K\alpha_2$ doublet is resolvable. The resultant lattice constants and their estimated standard deviations, together with other pertinent cell data are:

a = 11.558 ± .001 Å
b = 11.405 ± .001 Å   V = 1149.8 Å^3
c = 8.041 ± .001 Å   m.w. = 575.9
β = 93.47 ± .01°

The calculated density of 1.66 g/cc for two molecules per unit cell agrees with the experimental density of 1.65 g/cc measured by flotation techniques.

Three dimensional intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-counter, stationary-crystal method using balanced nickel and cobalt filters with copper $K\alpha$ radiation. A total of 2462 independent reflections were measured to a two-theta maximum of 120°(d = .889), with 1788 of these considered statistically significant by the criterion:

$$(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 400$$

where the sigmas were based solely on counting statistics for the 10 second counts. The intensities were corrected for $\alpha_1 - \alpha_2$ splitting as a function of two-theta and for absorption as a function of phi (linear $\mu = 18.9\ \mathrm{cm}^{-1}$ with a 12% maximum deviation in the phi scan at chi = 90°). Lorentz-polarization corrections were made and the intensities reduced to structure amplitudes in the usual manner.

STRUCTURE DETERMINATION

Analysis of the three-dimensional Patterson function confirmed that there were only two copper atoms in a given unit cell and hence occupied special positions within the cell. With the coppers at ½, 0, 0 and ½, ½, ½ a Fourier map was phased and used to find coordinates for the other non-hydrogen atoms. The structure was refined using block-diagonal least-squares with isotropic temperature factors and unit weights to a value of $R = 0.124$.[8] The temperature factors were then converted to the anisotropic form and further refinements led to a value of $R = 0.084$ for the non-hydrogen atoms.

A difference electron density map was calculated to find coordinates for the hydrogen atoms. Unfortunately, although regions of positive density were at the chemically expected locations for hydrogen atoms, these regions were sufficiently diffuse that the centers could not be easily located. Attempts to refine selected positions thus were not successful. Finally, the coordinates of the 9 hydrogen atoms (excluding those on the water molecule) were calculated based on expected geometry. These coordinates were included in subsequent refinements but were not allowed to vary. The final refinements using $1/\sigma^2$ weights were considered completed when all shifts in parameters were less than one-tenth of the respective estimated standard deviations. At the termination of refinement, a residual factor of $R = 0.06_3$ was attained.

RESULTS AND DISCUSSION

The final least-squares coordinates and anisotropic temperature factors for the non-hydrogen atoms with estimated standard deviations for each parameter are summarized in Table I. The calculated hydrogen atom coordinates are listed in Table II. Figure 1 shows a schematic drawing with atom labels, bond distances, and bond angles for a unique half of the molecule. The estimated standard deviations (ESDs) are less than 0.004 Å and 0.2° for the Cu–O distances and angles respectively, and 0.01 Å and 0.7° for those of the other non-hydrogen atoms.

The coordination about the copper is square planar with each copper bonded to four oxygen atoms. Two of the oxygens are the terminal carboxyl

TABLE I

Fractional coordinates and anisotropic thermal parameters
(Anisotropic thermal parameters × 10^4, estimated standard deviations in parentheses refer to last decimal place)

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.5400(4)	0.0000(0)	0.0000(0)	40(1)	29(1)	70(2)	−1(1)	−3(1)	−6(1)
O1	0.3724(3)	0.0948(3)	−0.0013(4)	40(3)	22(3)	41(6)	2(2)	1(3)	−6(3)
C2	0.3829(5)	0.1950(5)	0.0724(7)	41(4)	25(4)	33(8)	1(3)	6(5)	8(5)
O3	0.4681(3)	0.2356(3)	0.1304(5)	34(3)	33(3)	98(8)	−1(3)	−5(4)	−13(4)
C4	0.2764(5)	0.2576(5)	0.0859(7)	35(4)	25(4)	69(10)	4(3)	1(5)	3(5)
N5	0.2853(4)	0.3776(4)	0.1416(6)	44(4)	25(4)	47(7)	11(3)	7(4)	6(4)
C6	0.3189(5)	0.4614(5)	0.0393(7)	30(4)	21(4)	82(10)	9(3)	−5(5)	0(5)
O7	0.3368(4)	0.4405(4)	−0.1084(5)	69(4)	37(4)	48(6)	−8(3)	25(4)	−7(4)
C8	0.3272(5)	0.5835(5)	0.1111(7)	51(5)	22(4)	73(10)	5(4)	−21(5)	−15(5)
C9	0.2437(5)	0.6684(5)	0.0369(7)	33(4)	20(4)	67(9)	1(3)	1(5)	−10(5)
C10	0.2615(5)	0.7867(5)	0.0575(8)	37(5)	25(5)	131(13)	−5(4)	−13(6)	−8(6)
C11	0.1912(6)	0.8633(5)	−0.0042(9)	50(5)	19(5)	169(14)	0(4)	5(7)	−1(6)
C12	0.1033(5)	0.8297(5)	−0.0897(8)	47(5)	34(5)	108(11)	14(4)	15(6)	16(6)
C13	0.0777(5)	0.7126(6)	−0.1108(8)	42(5)	52(6)	110(12)	6(4)	−16(4)	0(7)
C14	0.1515(6)	0.6322(5)	−0.0463(9)	56(5)	20(5)	140(13)	4(4)	−35(7)	−8(6)
N15	0.0263(6)	0.9157(5)	−0.1730(8)	63(5)	67(6)	161(12)	31(4)	24(6)	14(7)
O16	−0.0578(5)	0.8823(6)	−0.2345(9)	58(5)	126(7)	317(17)	33(5)	−29(7)	75(9)
O17	0.0553(5)	1.0182(5)	−0.1730(8)	107(6)	59(5)	299(16)	32(4)	13(8)	64(7)
W	0.4724(3)	−0.0594(3)	0.2216(5)	47(3)	37(3)	55(6)	7(3)	6(4)	9(4)

TABLE II
Calculated hydrogen coordinates
(Isotropic temperature factor fixed at 4.0 Å^2)

Atom[a]	X	Y	Z
H4	0.2339	0.2124	0.1654
H4′	0.2371	0.2569	-0.0272
H5	0.2662	0.3983	0.2577
H8	0.4004	0.6154	0.0914
H8′	0.3204	0.5785	0.2346
H10	0.3302	0.8138	0.1217
H11	0.2045	0.9559	0.0112
H13	0.0081	0.6863	-0.1708
H14	0.1364	0.5450	-0.0625

[a] Numbers refer to bonding atom

oxygens of two p-nitrophenaceturate ions and the other two are water molecules. The trans arrangement of the acids and the absence of planar distortion make the structure centrosymmetric about the copper atom. Electronic arguments supporting square planar coordination for copper invoke ligands which allow metal to ligand π-bonding to replace very weak interactions of the d_z^2 copper orbital with a ligand at the fifth and/or sixth position. Hence Cu–O distances in such square planar complexes are expected to be shorter than in octahedral complexes.[9–13] Our copper-water distance of 1.95$_0$ Å falls at the lower end end of the 1.95–1.99 Å range found in other copper II-water complexes.[14–16] Similarly, our copper-carboxyl oxygen distance of 1.93$_3$ Å also falls at the lower end of the 1.91–2.01 Å range found in copper–carboxylate oxygen complexes. However, the

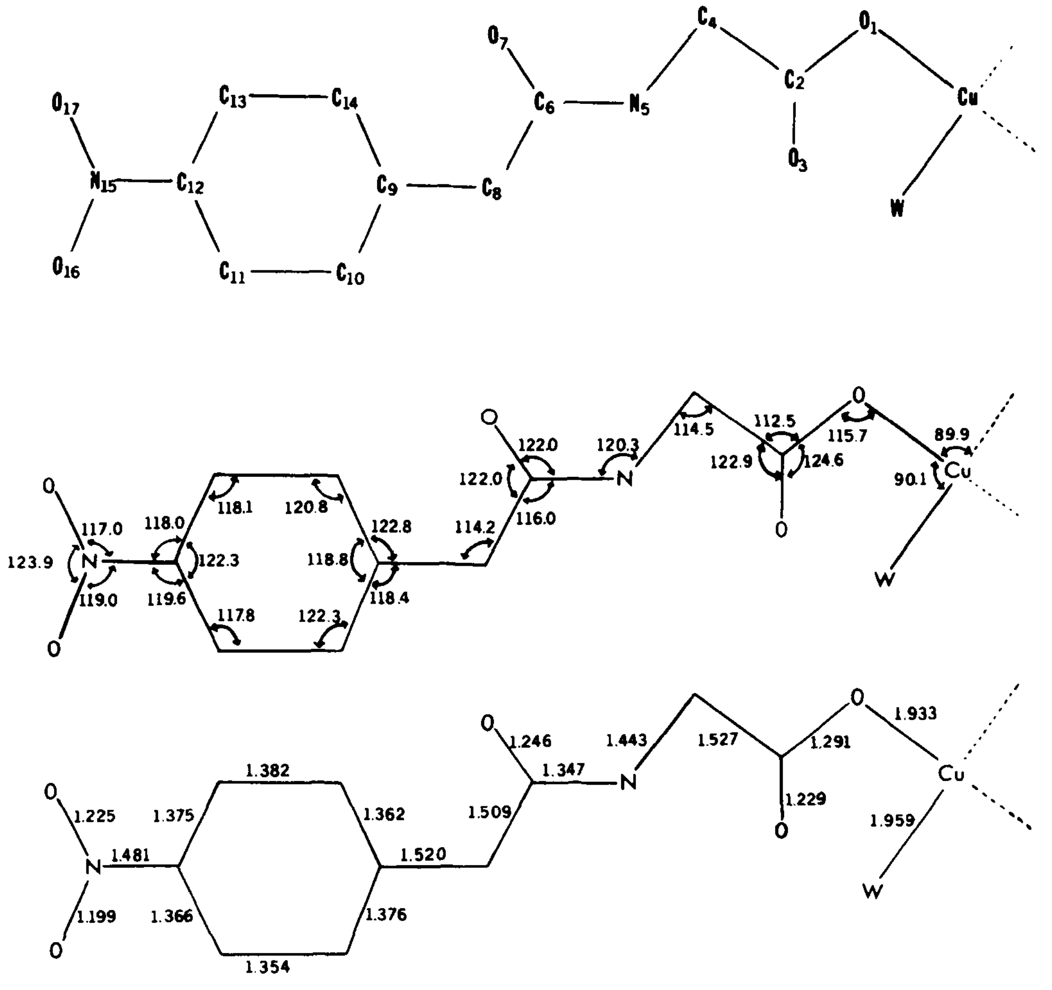

FIGURE 1 Schematic drawings of molecules showing bond distances and bond angles.

geometry of our system makes such π-bonding effects extremely unlikely. Instead, the possible fifth and sixth coordination sites of each copper are partially blocked by the other non-bonding carboxyl oxygens of each of the two acid molecules. Furthermore, these non-bonding oxygens are oriented so as to exclude the possibility of their sp^2 orbitals interacting with the $3d_z^2$ or $4p_z$ orbital of the copper. Apparently, the square planar coordination in this compound is entirely the result of steric effects even though the Cu–O distances are among the shorter ones found in such complexes.

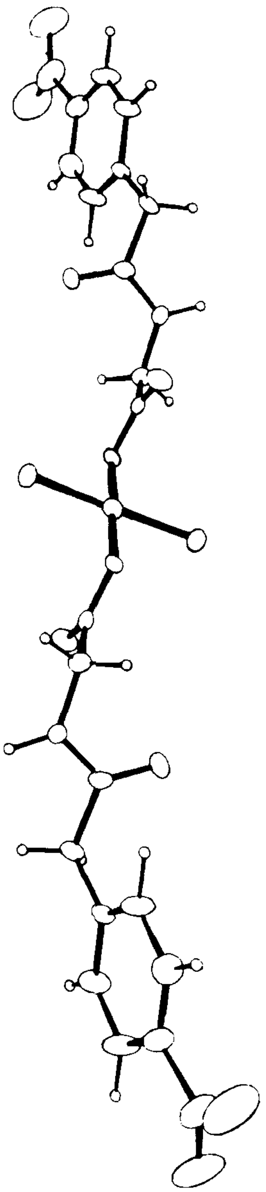

FIGURE 2 ORTEP view of the molecules.

The effects of the coordination to the copper on the p-nitrophenaceturic moiety are evident by comparing the molecular parameters in this study to those obtained in the x-ray study of the uncomplexed acid.[4] Within the carboxylate ion, the C_2-O_1 bond in the complexes is shortened to 1.29 Å (vs. 1.32 Å) while the C_2-O_3 bond is lengthened to 1.23 Å (vs. 1.20 Å) as would have been anticipated. The amide portion shows the usual C–N shortening to 1.347 Å and C=O lengthening to 1.246 Å as in the free acid and the phenyl parameters are comparable to those obtained in numerous past studies. Figure 2 is an ORTEP view of the molecule.

The conformation of the Cu-complex is similar to the free acid in the sense that the dihedral angles between the dominant planes in the structure are closely akin. Figure 3a illustrates these angles, namely ∠ I–II = 82° and ∠ II–III = 77° for the complex. In Figure 3b the corresponding angles for the free acid are 79° and 90°, respectively. However, the complex and the free acid conformations differ dramatically in

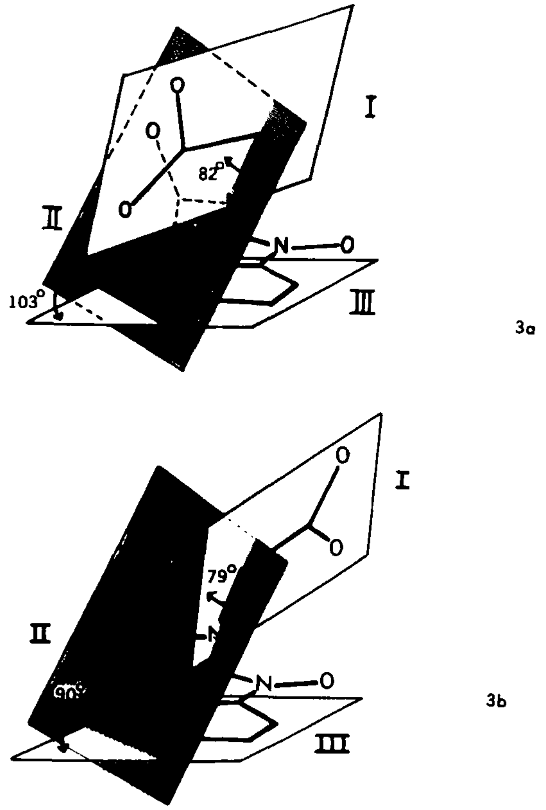

FIGURE 3 (a) Arrangement of planes in complex. (b) Arrangement of planes in free acid.

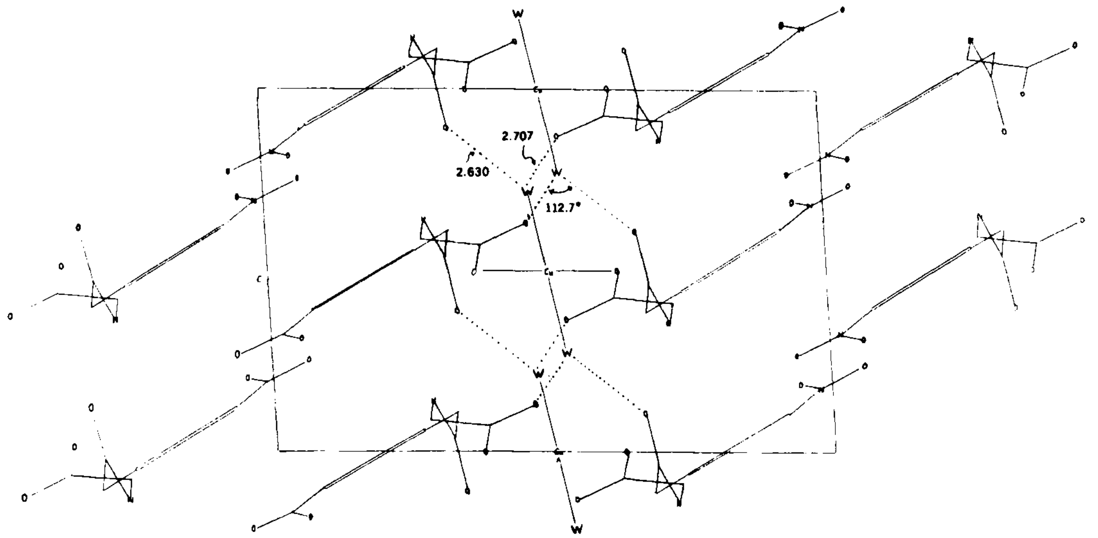

FIGURE 4 Contents of unit cell projected down b-axis. Hydrogen-bonding shown.

the sense that one is rotated 180° (about the N_5-C_4 bond) with respect to the other.

Cressman[5] had postulated that copper complexes to the penicillin side chain would be bidentate through the β-lactam oxygen and the amide nitrogen forming a relatively stable five-membered ring. The results with the phenaceturic acid do not substantiate these assumptions since this complex is not a bidentate and since there is, in fact, a rotation of the back side of the molecule during the complexation.

Looking down the *b*-axis, as shown in Figure 4, one can see layers formed by the *p*-nitrophenyl groups. This crystal packing is caused by the intermolecular hydrogen bonding indicated in the diagram. A water molecule, W_1 on one copper, is hydrogen-bonded to two oxygens on a second molecule. One bond is to the carbonyl oxygen, O_7, in the amide group of the molecule and the second is to the carbonyl oxygen, O_3, of the carboxyl group. The $W-O_3$ and $W-O_7$ distances are 2.707 Å and 2.630 Å, respectively, forming an O_3-W-O_7 angle of 112.7°. This bonding continues forming infinite chains parallel to the *c*-axis.

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