

lide (1-). The term R_e is the electrostatic ligand-ligand repulsion. The term A_p is the attraction term caused by the interaction of the central cation charge with the induced dipole of the halide. The assumed polarizabilities were 2.98 and 4.24 Å³ for Cl and Br, respectively. The other variables are defined as follows; ρ is a softness parameter (discussed later), b is the single repulsion parameter and is variable, r^{+1} is the ionic radius of the Cu²⁺ ion in the axial direction, r^{+2} is the Cu²⁺ ionic radius in the equatorial direction, r^- is the halide radius, r_{12} is the axial-equatorial distance ($\sqrt{r_1^2 + r_2^2}$), r_{22} is the equatorial-equatorial distance ($\sqrt{3}r_2$), and r_{11} is the axial-axial distance ($2r_1$). The softness parameter, ρ , has been found to be approximately constant for all of the alkali halides.^{21,22} We have used an average value of those found previously, 0.339 Å. Ionic radii of the Huggins-Mayer form²² were chosen. These were 1.65 for Cl⁻, 1.90 for Br⁻, and 0.86 Å for Cu²⁺ (axial, r^{+1}). The value for r^{+2} was chosen as $r^{+1} + \Delta r$, where Δr is the difference in the axial and equatorial ionic radii. It is this number that we wish to determine. It will be seen that there are now only two variable parameters: b and Δr . We have the equilibrium requirement that $\partial U/\partial r_i = 0$. This gives a total of four observations, two each for CuCl₅³⁻ and CuBr₅³⁻. A nonlinear least-squares refinement can now be carried out, minimizing the function

$$R = \sum_i \left(\frac{\partial U}{\partial r_i} \right)^2$$

We have used for this refinement the full-matrix least-

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squares program ORGLS.²³ Derivatives were determined numerically, and iteration was performed until convergence. The resultant Δr is 0.12 (1) Å for $b = 0.026$. Therefore, in the absence of any ligand-ligand repulsion effects the axial bond lengths would be expected to be 0.12 Å shorter than the equatorial.

Discussion

The difference in axial and equatorial bond lengths in CuBr₅³⁻, 0.0691 (26) Å, as compared with CuCl₅³⁻, 0.0948 (23) Å, confirms the trend predicted earlier.¹ It can be expressed adequately on a quantitative basis by a simple force field calculation which explicitly includes the ligand-ligand repulsion and anisotropy in the effective ionic radius of the copper ion in a trigonal-bipyramidal environment. The geometry observed for CuBr₅³⁻ contradicts that predicted by Allen and El-Sharkawy²⁴ to explain the apparent anomaly that the ligand field splitting for CuBr₅³⁻ is greater than that for CuCl₅³⁻. The values of Δ_1 and Δ_2 , as defined by Allen and Hush,²⁵ are $\Delta_1 = 906$ and 945 cm⁻¹ and $\Delta_2 = 932$ and 986 cm⁻¹ for CuCl₅³⁻ and CuBr₅³⁻, respectively. This is probably best explained by the introduction of covalent terms in the ligand field calculations as explicitly considered by Smith.²⁶

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The Crystal and Molecular Structure of Bis(phenoxyacetato)triquocopper(II), a Monomeric, Pentacoordinate Cupric Carboxylate Adduct

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A single-crystal X-ray structural analysis has shown bis(phenoxyacetato)triquocopper(II) to be one of the very few known examples of a discrete and monomeric five-coordinate copper(II) complex in which a copper atom is bound to five monodentate ligands. This compound crystallizes in the triclinic space group $P\bar{1}$ with four formula units in a cell of dimensions $a = 6.40$ (1) Å, $b = 9.28$ (2) Å, $c = 32.01$ (6) Å, $\alpha = 100^\circ 7' (10')$, $\beta = 78^\circ 50' (10')$, and $\gamma = 90^\circ 12' (10')$. Observed and calculated densities are 1.55 (2) and 1.518 g/cm³, respectively. The structural determination was based upon 2185 visually estimated film data and a least-squares refinement which converged to a conventional R factor of 0.084. In the crystalline state, Cu(O₂CCH₂OC₆H₅)₂(H₂O)₃ exists as monomeric pentacoordinate molecules linked by hydrogen bonds into sheets perpendicular to the c axis. Essentially identical configurations are observed for the two crystallographically independent molecules. The copper atom is coordinated to two monodentate phenoxyacetate groups and three water molecules in a distorted square-pyramidal configuration, with Cu-O bonds ranging in length from 1.954 (16) to 2.280 (17) Å. Opposite the apical coordination site, the copper atom is involved in long contacts of *ca.* 2.96 Å to two uncoordinated carboxylate oxygen atoms.

Introduction

Magnetic susceptibility studies of a series of copper(II) carboxylate derivatives have been carried out by Hatfield, *et al.*,¹ in a study of the relationship between

the tendency toward adoption of the binuclear cupric acetate structure for a particular carboxylate and the magnitude of the dissociation constant of the parent acid.^{2,3} Among the compounds examined were hy-

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drates of the copper(II) salts of phenoxyacetic acid and its ortho chloro and para nitro derivatives. These compounds were, respectively, formulated as mono-, di-, and trihydrates and exhibited differing magnetic properties. Thus the product formulated as $\text{Cu}(\text{C}_6\text{H}_5\text{OCH}_2\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ gave bulk susceptibility values (77–300°K) characteristic of magnetically dilute copper compounds, while the two substituted phenoxyacetates both displayed magnetic moments indicative of copper-copper interaction (but differing from each other in the details of their temperature dependences). In no case did the magnetic data permit strong inferences regarding the detailed structures of the complexes to be drawn. Our interest in the structures and magnetic properties of cupric carboxylates and related systems^{4,5} led us to consider undertaking structural analyses of some of these compounds.

Initial investigations were concerned with Cu(II) derivatives of unsubstituted phenoxyacetic acid. Variations of the procedure specified by Hatfield, *et al.*,¹ yielded three distinct products—triclinic platelike crystals, monoclinic prismatic crystals, and a light green polycrystalline material. Chemical analyses of the two crystalline forms failed to yield unambiguous results (*vide infra*) and the triclinic form, being the most readily obtained, was chosen for initial structural study. While this work was in progress, a report of a structural analysis of the monoclinic form (a dihydrate) was published.⁶ That form was shown to be composed of monomeric, six-coordinate molecules in which each of the two phenoxyacetate ligands is coordinated to the copper atom in a chelating fashion through one phenoxy and one carboxy oxygen atom. We have now shown the triclinic form to be a trihydrate, with monodentate phenoxyacetate ligands in five-coordinate monomeric molecular units. A preliminary communication of these results has been published.⁷

Collection and Reduction of the Intensity Data

Bis(phenoxyacetato)triaquocopper(II) was prepared from cupric carbonate and phenoxyacetic acid in aqueous ethanol as described by Hatfield, *et al.*¹ Crystals began to appear on cooling the ethanol-water solution and numerous satisfactory crystals were obtained upon slow evaporation in an open beaker. Chemical analyses failed to establish unequivocally the stoichiometry of this material.⁸ Further evaporation of solutions from which crystals of the trihydrate had been removed sometimes gave crystals of the dihydrate.

Preliminary X-ray photographs of the trihydrate showed no evidence of monoclinic or higher symmetry and a Delaunay reduction verified the triclinic symmetry of the crystal lattice. Initial short-exposure precession and Weissenberg photographs displayed the apparent systematic absences $0k0$, $k \neq 2n$, and $h0l$, $l \neq 2n$; however, clear violations of the latter absence were evident on longer exposures.

Lattice constants at 23° were determined from zero-level precession photographs which were calibrated by superposition of a single-crystal zero-level NaCl ($a = 5.6409 \text{ \AA}$) exposure. Zirconium-filtered Mo $K\alpha$ radiation ($\lambda 0.71069 \text{ \AA}$) was used

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(8) Analytical results corresponded to more than one but less than three water molecules per copper atom. In retrospect, this was probably due to partial dehydration of the samples analyzed—though the crystals were stable in the open air they showed evidence of deterioration when stored in a desiccator. The weight loss of a freshly prepared crystalline sample of the triclinic form heated at 110° to constant weight agreed closely with that calculated on the basis of loss of three molecules of water per copper atom.

throughout the structure analysis. The direct lattice constants with standard deviations in parentheses estimated from the reproducibility of the measurements and from past experience with this calibration technique are $a = 6.40 (1)$, $b = 9.28 (2)$, $c = 32.01 (6) \text{ \AA}$, $\alpha = 100^\circ 7' (10')$, $\beta = 78^\circ 50' (10')$, and $\gamma = 90^\circ 12' (10')$. The three shortest noncoplanar lattice translations define a cell with $a = 6.40$, $b = 9.28$, $c = 31.13 \text{ \AA}$, $\alpha = 93^\circ 48'$, $\beta = 89^\circ 34'$, and $\gamma = 90^\circ 12'$. The transformation matrix to the reduced cell is

$$\begin{bmatrix} 100 \\ 010 \\ 1\bar{1}\bar{1} \end{bmatrix}$$

All results are reported in terms of the nonreduced cell.

The density of the compound was determined to be $1.55 (2) \text{ g/cm}^3$ by floatation in a $\text{CHCl}_3\text{-CH}_3\text{I}$ mixture. The calculated density for 4 formula units per cell is 1.518 g/cm^3 . Of the two possible triclinic space groups, $P\bar{1}$ was initially assumed; the structure was solved and refined successfully in this centrosymmetric space group.

Multiple-film equiinclination Weissenberg intensity data were collected from a diamond-shaped tabular crystal rotated about the b axis, which was approximately coincident with the long face diagonal. The $0.54 \times 0.50 \times 0.14 \text{ mm}$ crystal was fastened with shellac to the tip of a fine glass fiber. Data were taken for layers 0–8. A standard timed intensity scale was prepared from the crystal used in data collection. A full 360° of data (two sets of films per layer) were collected and only the reflections falling on the top half of each film were estimated. A total of 2185 independent nonzero intensity data were obtained in this manner. Spot-extension corrections were applied as well as Lorentz, polarization, and absorption corrections. The calculated transmission factors ranged from 0.66 to 0.85 for a linear absorption coefficient $\mu = 12.85 \text{ cm}^{-1}$.

Solution and Refinement of the Structure

Trial coordinates for the two independent copper atoms were

TABLE I
Atomic Positional and Thermal Parameters for
 $\text{Cu}(\text{O}_2\text{CCH}_2\text{OC}_6\text{H}_5)_2(\text{H}_2\text{O})_3^a$

Atom	x	y	z	$B, \text{ \AA}^2$
Molecule A				
Cu	0.15039 (33)	0.25332 (22)	0.00212 (8)	...
O(1)	-0.2040 (23)	0.2587 (15)	0.0034 (4)	2.29 (27)
O(2)	0.1171 (19)	0.4310 (12)	0.0505 (4)	2.39 (23)
O(3)	0.2448 (20)	0.0806 (13)	-0.0460 (5)	2.82 (25)
O(4)	0.1745 (21)	0.3778 (13)	-0.0420 (5)	2.66 (25)
O(5)	0.1104 (23)	0.1326 (15)	0.0483 (5)	3.24 (32)
O(6)	0.5265 (22)	0.3762 (14)	-0.0473 (5)	3.16 (26)
O(7)	0.4545 (21)	0.1200 (14)	0.0450 (15)	2.99 (26)
O(8)	0.5967 (22)	0.5321 (14)	-0.1123 (5)	3.31 (27)
O(9)	0.0205 (20)	-0.0287 (13)	0.1079 (4)	2.88 (25)
C(1)	0.2676 (27)	0.0883 (17)	0.0594 (8)	1.85 (30)
C(2)	0.3715 (27)	0.4074 (17)	-0.0602 (6)	1.77 (30)
C(3)	0.2435 (29)	-0.0120 (18)	0.0929 (8)	2.34 (33)
C(4)	0.3764 (30)	0.4861 (19)	-0.0989 (7)	2.58 (35)
Molecule B				
Cu	0.14965 (36)	0.25012 (22)	0.50208 (9)	...
O(1)	-0.2002 (26)	0.2471 (16)	0.4965 (5)	2.72 (31)
O(2)	0.2443 (19)	0.3650 (12)	0.4541 (4)	2.47 (23)
O(3)	0.1206 (19)	0.1285 (12)	0.5494 (4)	2.53 (23)
O(4)	0.1758 (21)	0.0702 (13)	0.4587 (5)	2.89 (25)
O(5)	0.1060 (23)	0.4269 (15)	0.5464 (5)	3.54 (30)
O(6)	0.5308 (20)	0.0670 (13)	0.4525 (4)	2.78 (25)
O(7)	0.4506 (21)	0.4318 (13)	0.5450 (5)	2.86 (25)
O(8)	0.5868 (20)	-0.1635 (13)	0.3875 (4)	2.64 (24)
O(9)	0.0214 (21)	0.6568 (13)	0.6103 (5)	3.00 (26)
C(1)	0.2635 (27)	0.4797 (17)	0.5593 (6)	1.85 (30)
C(2)	0.3691 (29)	0.0163 (18)	0.4416 (6)	2.18 (32)
C(3)	0.2460 (30)	0.6190 (19)	0.5958 (7)	2.68 (35)
C(4)	0.3721 (30)	-0.1146 (19)	0.4034 (7)	2.77 (35)

Anisotropic Thermal Parameters ($\times 10^5$)^b

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu ^A	700 (52)	418 (43)	55 (3)	-116 (32)	-29 (8)	71 (5)
Cu ^B	1310 (60)	335 (41)	61 (3)	25 (36)	-62 (9)	-10 (5)

^a Numbers in parentheses in tables and in the text are standard deviations in the least significant figures. ^b Superscripts A and B are used to designate molecule A and molecule B, respectively. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE II
GROUP POSITIONAL PARAMETERS OF THE PHENYL RINGS^a

Group	x_0	y_0	z_0	ϕ	θ	ρ
Molecule A						
Ring 1 ^b	-0.1316 (16)	-0.1779 (10)	0.1757 (3)	-114.7 (5)	-171.8 (5)	44.4 (6)
Ring 2	0.7171 (14)	0.6895 (9)	-0.1770 (3)	-90.7 (5)	-155.2 (4)	-132.9 (5)
Molecule B						
Ring 1	-0.1062 (15)	0.9007 (9)	0.6733 (3)	-72.7 (5)	-170.1 (5)	138.0 (5)
Ring 2	0.6847 (15)	-0.4095 (9)	0.3226 (3)	-84.8 (5)	-163.6 (5)	-45.5 (5)

^a x_0 , y_0 , and z_0 are the fractional coordinates of the origin of the orthogonal group coordinate system (a_1' , a_2' , a_3') with respect to the crystal axes. These coordinates correspond to the centers of gravity of the individual groups. An orthogonal system of crystal axes (A_1 , A_2 , A_3) is defined in terms of the crystal axes by: A_2 parallel to b ; A_1 parallel to $b \times c$; A_3 parallel to $A_1 \times A_2$. The angles ϕ , θ , and ρ are the successive counterclockwise rotations (in degrees) about A_3 , A_1 , and A_2 required to bring the orthogonal coordinate system A into alignment with the internal system a' of a group. ^b In each molecule, ring 1 is the phenyl ring bonded to O(9) and ring 2 is bonded to O(8).

TABLE III
POSITIONAL AND THERMAL PARAMETERS OF GROUP ATOMS^a

Atom	x	y	z	$B, \text{\AA}^2$
Molecule A				
C(1-1)	-0.0454 (22)	-0.1071 (15)	0.1416 (4)	2.77 (36)
C(1-2)	0.0842 (16)	-0.1966 (16)	0.1572 (5)	3.62 (42)
C(1-3)	-0.0020 (24)	-0.2673 (15)	0.1912 (5)	4.46 (48)
C(1-4)	-0.2178 (26)	-0.2486 (18)	0.2097 (5)	5.17 (55)
C(1-5)	-0.3474 (17)	-0.1592 (18)	0.1941 (5)	5.77 (61)
C(1-6)	-0.2613 (20)	-0.0884 (14)	0.1601 (5)	3.80 (43)
C(2-1)	0.6473 (21)	0.6071 (14)	-0.1448 (4)	1.79 (29)
C(2-2)	0.8566 (18)	0.6529 (12)	-0.1518 (4)	2.92 (37)
C(2-3)	0.9264 (15)	0.7351 (16)	-0.1840 (5)	3.39 (40)
C(2-4)	0.7869 (23)	0.7718 (16)	-0.2091 (4)	3.53 (42)
C(2-5)	0.5776 (20)	0.7260 (14)	-0.2021 (4)	4.01 (45)
C(2-6)	0.5078 (15)	0.6438 (15)	-0.1699 (4)	3.34 (40)
Molecule B				
C(1-1)	-0.0329 (23)	0.7801 (15)	0.6413 (4)	2.49 (33)
C(1-2)	0.1111 (15)	0.8784 (16)	0.6567 (5)	3.84 (42)
C(1-3)	0.0378 (21)	0.9990 (14)	0.6887 (5)	4.78 (53)
C(1-4)	-0.1795 (23)	1.0212 (16)	0.7053 (4)	4.30 (47)
C(1-5)	-0.3235 (16)	0.9228 (16)	0.6900 (5)	4.59 (49)
C(1-6)	-0.2502 (21)	0.8023 (14)	0.6579 (5)	3.86 (44)
C(2-1)	0.6260 (24)	-0.2880 (15)	0.3551 (4)	2.22 (30)
C(2-2)	0.8388 (21)	-0.3349 (13)	0.3424 (5)	4.54 (53)
C(2-3)	0.8975 (16)	-0.4564 (17)	0.3098 (5)	4.48 (51)
C(2-4)	0.7434 (24)	-0.5310 (16)	0.2900 (4)	3.64 (35)
C(2-5)	0.5306 (22)	-0.4841 (14)	0.3028 (5)	4.57 (52)
C(2-6)	0.4720 (16)	-0.3626 (17)	0.3353 (5)	4.89 (54)

^a The estimated standard deviations of the group atoms are derived from the esd's of the group parameters tabulated in Table II and are meant for use in estimating standard deviations of distances and angles other than those within a group.

TABLE IV
INTRAMOLECULAR DISTANCES (\AA)

Atoms	Molecule A	Molecule B	Atoms	Molecule A	Molecule B
Cu-O(1)	2.261 (15)	2.280 (17)	Cu...O(6)	2.956 (15)	2.990 (15)
Cu-O(2)	2.036 (13)	2.018 (13)	Cu...O(7)	2.975 (15)	2.938 (15)
Cu-O(3)	2.022 (14)	2.023 (13)	O(1)...O(2)	3.065 (19)	3.184 (21)
Cu-O(4)	1.959 (14)	1.961 (14)	O(1)...O(3)	3.292 (21)	3.211 (21)
Cu-O(5)	1.984 (15)	1.954 (16)	O(1)...O(4)	2.895 (21)	2.855 (21)
O(5)-C(1)	1.225 (21)	1.231 (21)	O(1)...O(5)	3.035 (21)	3.072 (23)
O(7)-C(1)	1.250 (21)	1.249 (20)	O(2)...O(4)	2.866 (20)	2.795 (17)
C(1)-C(3)	1.525 (25)	1.570 (25)	O(2)...O(5)	2.759 (18)	2.871 (21)
C(3)-O(9)	1.432 (22)	1.447 (22)	O(3)...O(4)	2.773 (18)	2.811 (20)
O(9)-C(1-1)	1.403 (20)	1.372 (18)	O(3)...O(5)	2.927 (22)	2.790 (18)
O(4)-C(2)	1.331 (20)	1.313 (21)	O(5)...O(9)	2.606 (20)	2.660 (21)
O(6)-C(2)	1.200 (20)	1.221 (21)	O(6)...O(8)	2.648 (20)	2.680 (19)
C(2)-C(4)	1.541 (26)	1.562 (26)	O(6)...O(7)	4.066 (24)	4.049 (20)
C(4)-O(8)	1.450 (22)	1.416 (22)			
O(8)-C(2-1)	1.398 (20)	1.398 (17)			

obtained from a three-dimensional Patterson function. Full-matrix least-squares refinement of thirteen scale factors and copper positional and individual isotropic thermal parameters led to discrepancy factors $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.341$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.421$ for a random half of the $h0l-h6l$ data. Five oxygen atoms surrounding each copper atom were readily found from a difference Fourier map phased on the copper atom contributions to F_o . These twelve atoms were arranged in two nearly identical sets of six separated by

half a lattice translation along c . Hence the coordinates of the remaining nonhydrogen atoms were determined from superimposed images appearing on difference maps calculated on the basis of only the l -even terms.

In the refinement of the full structure, the phenyl rings were treated as rigid groups⁹ with C-C = 1.392 \AA and C-C-C = 120°. Because of limitations imposed by the storage capacity of our computer, the two molecules comprising one asymmetric unit were refined individually in alternate least-squares cycles. The seventeen scale factors were varied in every cycle of refinement. Refinement with individual isotropic thermal parameters assigned to all atoms (including group atoms) converted to $R_1 = 0.093$ and $R_2 = 0.114$, based upon all 2185 observed intensity data. A difference map calculated at this stage revealed no residual positive electron density greater than 0.8 $e/\text{\AA}^3$, compared with peak heights of 1.3-2.9 $e/\text{\AA}^3$ found for carbon and oxygen atoms in the previous difference map. No convincing evidence for the effects of hydrogen atoms was found on this map. Further refinement with anisotropic thermal parameters assigned to the copper atoms converged to the final discrepancy factors $R_1 = 0.084$ and $R_2 = 0.103$. In the final cycles of refinement, weights were assigned to the observed structure amplitudes as $w = 1/\sigma^2(F_o)$ where $\sigma(F_o) = 1$ for $I \leq 30I_{\min}$ and $\sigma(F_o) = [I^{3/2}/(30I_{\min})^{3/2}]^{1/2}$ for $I > 30I_{\min}$. Here I is the uncorrected intensity and I_{\min} is the minimum observed value of the raw intensity for the entire data set. The final weighting scheme eliminated any dependence of the mean value of $w(\Delta F)^2$ calculated for subsets of the data on F_o , uncorrected intensity, or the Bragg angle. The quantity minimized throughout the refinement was $\sum w(\Delta F)^2$ and the final standard deviation of an observation of unit weight was 1.07. Calculation of structure factors for unobserved data showed that only 12 of the 4187 accessible zero

data had F_o greater than twice the minimum observed F for their reciprocal lattice level.

The final positional and thermal parameters of the nongroup atoms are given in Table I; group parameters for the four phenyl rings are listed in Table II. In these tables and henceforth in the text, the two crystallographically nonequivalent molecules

(9) R. J. Doedens in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 198-200.

are designated as molecules A and B. Because the refinement was carried out in blocks, the standard deviations tabulated in these two tables include only the effects of correlations between parameters within a block (the parameters of one molecule plus the scale factors constituted a block). The fact that no variations beyond those expected are observed in presumably chemically equivalent bond lengths and angles suggests that the neglect of interblock correlations did not lead to serious underestimates of standard deviations. The positional and thermal parameters of the group carbon atoms are given in Table III. Tables IV and V contain intra- and intermolecular distances, respectively,

TABLE V
INTERMOLECULAR DISTANCES (Å) LESS THAN 3.2 Å

Atoms	Transformation ^a	Distance
Molecule A		
O(2)···O(4)	-x, 1 - y, -z	2.664 (18)
O(2)···O(6)	-x, 1 - y, -z	2.891 (18)
O(2)···O(8)	1 - x, 1 - y, -z	2.923 (20)
O(3)···O(5)	-x, -y, -z	3.012 (20)
O(3)···O(7)	1 - x, -y, -z	2.690 (19)
O(3)···O(9)	-x, -y, -z	2.829 (20)
O(6)···O(1)	1 + x, y, z	2.917 (20)
O(7)···O(1)	1 + x, y, z	2.768 (20)
Molecule B		
O(2)···O(5)	-x, 1 - y, 1 - z	2.968 (19)
O(2)···O(7)	1 - x, 1 - y, 1 - z	2.710 (18)
O(2)···O(9)	-x, 1 - y, 1 - z	2.896 (20)
O(3)···O(4)	-x, -y, 1 - z	2.658 (18)
O(3)···O(6)	1 - x, -y, 1 - z	2.866 (18)
O(3)···O(8)	1 - x, -y, 1 - z	2.986 (19)
O(6)···O(1)	1 + x, y, z	2.799 (22)
O(7)···O(1)	1 + x, y, z	2.844 (21)

^a In each case, the transformation applies to the second atom of the pair listed.

and bond angles are listed in Table VI. A table of observed and calculated structure factors is available.¹⁰

TABLE VI
BOND ANGLES (DEG)

Atoms	Molecule A	Molecule B
O(1)-Cu-O(2)	90.8 (5)	95.4 (5)
O(1)-Cu-O(3)	100.3 (5)	96.3 (5)
O(1)-Cu-O(4)	86.3 (5)	84.3 (6)
O(1)-Cu-O(5)	91.0 (6)	92.7 (6)
O(2)-Cu-O(3)	168.8 (5)	168.0 (5)
O(2)-Cu-O(4)	91.7 (5)	89.2 (6)
O(2)-Cu-O(5)	86.7 (6)	92.6 (6)
O(3)-Cu-O(4)	88.3 (6)	89.8 (5)
O(3)-Cu-O(5)	93.9 (6)	89.1 (6)
O(4)-Cu-O(5)	176.8 (6)	176.6 (6)
Cu-O(4)-C(2)	116.3 (11)	117.2 (12)
Cu-O(5)-C(1)	119.0 (13)	117.7 (13)
C(4)-O(8)-C(2-1)	118.8 (15)	117.6 (14)
C(3)-O(9)-C(1-1)	119.3 (15)	117.2 (14)
O(5)-C(1)-O(7)	124.2 (18)	124.8 (18)
O(5)-C(1)-C(3)	120.4 (16)	122.0 (16)
O(7)-C(1)-C(3)	115.4 (15)	113.3 (15)
O(4)-C(2)-O(6)	123.0 (17)	124.3 (17)
O(4)-C(2)-C(4)	112.6 (15)	112.5 (16)
O(6)-C(2)-C(4)	124.4 (16)	123.1 (16)
C(1)-C(3)-O(9)	107.9 (14)	106.7 (14)
C(2)-C(4)-O(8)	105.8 (15)	107.7 (15)
O(9)-C(1-1)-C(1-2)	125.9 (12)	125.0 (13)
O(9)-C(1-1)-C(1-4)	174.1 (11)	174.9 (11)
O(9)-C(1-1)-C(1-6)	114.1 (14)	115.0 (13)
O(8)-C(2-1)-C(2-2)	114.9 (13)	114.9 (13)
O(8)-C(2-1)-C(2-4)	174.8 (11)	174.8 (11)
O(8)-C(2-1)-C(2-6)	125.1 (12)	125.1 (13)

(10) This table will appear in the microfilm edition of this journal. Single copies may be purchased from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

In all structure factor calculations the scattering factors tabulated in ref 11 were used for Cu, O, and C, and the anomalous scattering factors $\Delta f'$ and $\Delta f''$ of Cromer¹² were employed in the correction of the F_o values for anomalous scattering by the Cu atoms. Computer programs utilized in this structural analysis included the film data processing program DF3, the Weissenberg absorption correction program WABS (derived from Burnham's GNABS), a modified version of Zalkin's FORDAP Fourier summation program, the least-squares program UCIGLS (a highly modified version of the Busing-Martin-Levy program ORFLS), and the Busing-Martin-Levy function and error program ORFFE. Initial phenyl ring orientation parameters were obtained from a modified version of RBANG by S. F. Watkins. The program PLANET by D. L. Smith was employed in a modified form for calculations of least-squares planes and figures were prepared with the aid of Dellaca and Robinson's program DANFIG. The local program RSCAN was used for evaluation of partial $w(\Delta F)^2$ values as an aid in establishing a proper weighting scheme.

Description and Discussion of the Structure

Bis(phenoxyacetato)triacuocopper(II) exists in the crystalline state as monomeric molecular units linked into two-dimensional sheets by a network of hydrogen bonds. With the exception of a minor angular difference (*vide infra*) the two crystallographically independent molecules are identical within experimental error. No symmetry is imposed on the molecules by the triclinic space group, though their departure from C_s -m molecular symmetry is not great. The molecular configuration and selected bond distances (averaged over the two independent molecules¹³) are depicted in Figure 1. The relationship between molecules A and B is roughly that of a *c*-glide plane perpendicular to *b*. This approximate relationship holds fairly well for the central portion of the molecule and less well for atoms toward the periphery. The atom numbering is such that identically numbered atoms of the two molecules are related by this pseudosymmetry operation with the exception that O(2) and O(3) are interchanged.

The first coordination sphere of the copper atom consists of five oxygen atoms—three of them from coordinated water molecules and two from monodentate phenoxyacetate groups coordinated through a carboxyl oxygen atom. Although five-coordination is common for divalent copper,¹⁴⁻¹⁶ this is one of the very few examples of a *discrete* five-coordinate Cu(II) species in which all five ligands are monodentate. Other structurally characterized examples of such species include the pentahalocuprate(II) anions,¹⁷⁻¹⁹ the aquotetraamminecopper(II) cation in $[\text{Cu}(\text{NH}_3)_4\text{H}_2\text{O}^{2+}](\text{SO}_4^{2-})$,²⁰ and bis(phenoxyacetato)aquobis(pyridine)copper(II).²¹

The configuration about the cupric ions may be described as distorted square pyramidal with O(1) occu-

(11) C. H. MacGillivray, G. D. Rieck, and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, U. K., 1962, p 201.

(12) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(13) Unless explicitly stated otherwise, individual bond distances quoted in the text are averages of two equivalent values observed in the two independent molecules and the standard deviation quoted is the larger of the two individual σ values.

(14) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

(15) J. A. Ibers, *Annu. Rev. Phys. Chem.*, **16**, 380 (1965).

(16) W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, **6**, 47 (1969).

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(18) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).

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(20) F. Mazzi, *Acta Crystallogr.*, **8**, 137 (1955).

(21) C. K. Prout, personal communication.

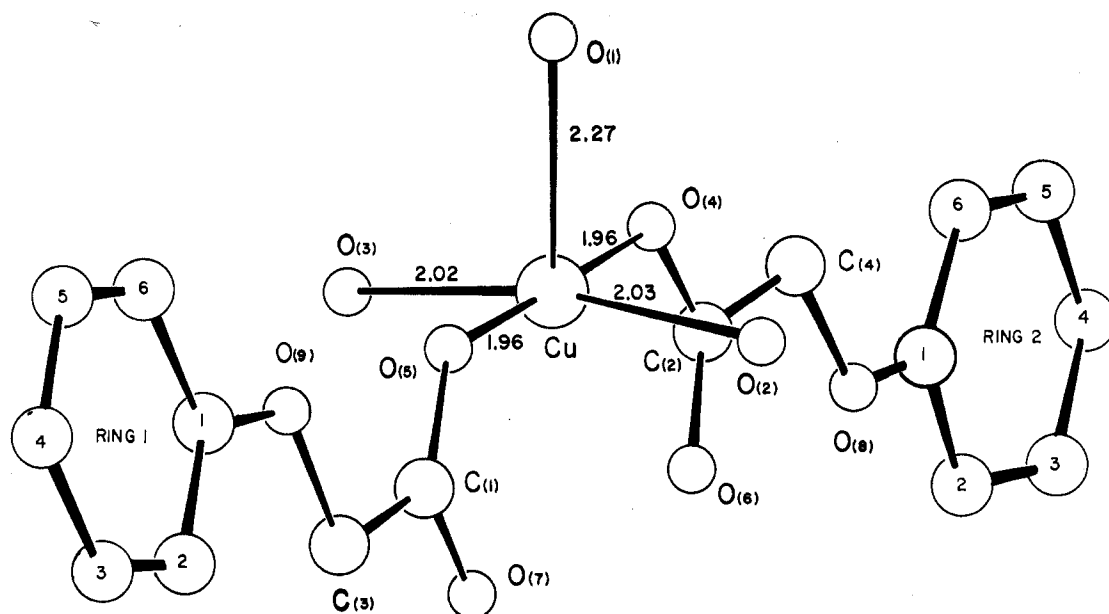


Figure 1.—A perspective view of the $\text{Cu}(\text{O}_2\text{CCH}_2\text{OC}_6\text{H}_5)_2(\text{H}_2\text{O})_3$ molecule. The atom numbering scheme is such that C(2-1) denotes carbon atom 1 of ring 2, etc.

pying the apical position at a distance of 2.269 (16) Å and Cu-basal O distances ranging from 1.958 (16) to 2.026 (13) Å. Opposite the apical coordination site, the copper atom is involved in contacts of 2.972 (15) and 2.958 (15) Å to O(6) and O(7), the two uncoordinated carboxy oxygen atoms. $\text{Cu}\cdots\text{O}$ contacts of this sort are not uncommon in five-coordinate copper(II) complexes of potentially bidentate ligands such as RCO_2^- ,²²⁻²⁵ NO_3^- ,²⁶⁻²⁹ or ONO^- .³⁰ The $\text{Cu}\cdots\text{O}$ distances associated with such contacts range in length from 2.5 to 3.0 Å; those observed in the present case are at the upper end of this range. The oxygen atoms involved in these long $\text{Cu}\cdots\text{O}$ contacts are generally displaced by 35–50° from a position directly opposite the apical coordination site of a distorted square pyramid. For the phenoxyacetate trihydrate this displacement, as measured by the departure of the $\text{O}(1)\text{—Cu}\cdots\text{O}$ angles from linearity, averages 43.3 (4)°. Though the magnitude of any metal-oxygen interaction associated with a contact of this sort must be small in comparison to ordinary bond energies, the $\text{Cu}\cdots\text{O}(6)$ and $\text{Cu}\cdots\text{O}(7)$ contacts probably do play a role in stabilizing the five-coordinate configuration of the phenoxyacetate, either by simply blocking the sixth octahedral coordination site or through a weak interaction with the metal ion. Both of these explanations have been advanced for related species;^{22,31} the polarized single-crystal electronic spectra of $\text{CaCu}(\text{CH}_3\text{COO})_4\cdot 6\text{H}_2\text{O}$ (which contains four $\text{Cu}\cdots\text{O}$ contacts of length 2.79 Å)³² have

been interpreted as favoring a weak "semicoordination" type of interaction.³¹ It has been noted that filled oxygen sp^2 orbitals are properly situated to interact with the copper d_{z^2} orbital and that weak π -bonding interactions are also in principle possible in this type of configuration.³¹ It will be of some interest to determine what effect (if any) the long $\text{Cu}\cdots\text{O}$ interactions in cupric phenoxyacetate trihydrate have on its electronic absorption spectrum in the crystalline state.

The distortions of the coordination geometry about the copper atoms (neglecting the long $\text{Cu}\cdots\text{O}$ contacts) from the "ideal" square-pyramidal configuration are substantial. Thus the four basal oxygen atoms are not coplanar (deviations of these atoms from their least-squares plane average 0.12 Å) and the $\text{O}(2)\text{—Cu—O}(3)$ and $\text{O}(4)\text{—Cu—O}(5)$ angles are 168.4 (5) and 176.8 (6)°, respectively. The latter angle arises from a bending of O(4) and O(5) toward the apical atom O(1). This unusual distortion does not appear to stem from crowding of the carboxylate oxygen atoms as the $\text{O}(6)\text{—O}(7)$ distance is 4.06 (2) Å, appreciably larger than the sum of two oxygen van der Waals radii (2.80 Å). In both molecules, the apical oxygen atom is asymmetrically disposed with respect to O(4) and O(5), with average angles $\text{O}(1)\text{—Cu—O}(4) = 85.4$ (6)° and $\text{O}(1)\text{—Cu—O}(5) = 91.8$ (6)°. One apparently significant difference exists between the two crystallographically independent molecules. This difference involves the angles $\text{O}(1)\text{—Cu—O}(2)$ and $\text{O}(1)\text{—Cu—O}(3)$, which are identical within experimental error in molecule B (95.4 (5) and 96.3 (5)°) but differ by *ca.* 19 standard deviations (90.5 (5) and 100.3 (5)°) in molecule A.

The coordinated phenoxyacetate ligands display several structural features of interest. Their monodentate coordination is in contrast to the chelation found by Prout, *et al.*, in cupric phenoxyacetate dihydrate and four related copper(II) carboxylates.⁶ Monodentate coordination of carboxylate groups is often associated with a special situation such as the long $\text{Cu}\cdots\text{O}$ contact in the present case or the intraligand $\text{O—H}\cdots\text{O}$ hy-

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(30) F. S. Stephens, *J. Chem. Soc. A*, 2081 (1969).

(31) D. E. Billing, B. J. Hathaway, and P. Nicholls, *ibid.*, A, 1877 (1970).

(32) D. A. Langs and C. R. Hare, *Chem. Commun.*, 890 (1967).

drogen bond in cupric salicylate tetrahydrate.³³ The two phenoxyacetate ligands differ in stereochemistry about the C-C bond such that the metal-bonded oxygen atom and the ether oxygen atom are trans in one group and cis in the other. These two types of carboxylate also display one apparently significant difference in bond distances—the O(5)-C(1) and O(4)-C(2) distances differ by 0.11 Å (five standard deviations) in molecule A and 0.08 Å (4σ) in molecule B. The fact that a comparable difference is observed in each molecule suggests that this disparity is real. Of course no *a priori* reason that the two ligands must be identical exists, since they have different configurations and presumably different hydrogen-bonding schemes (*vide infra*). The good agreement between independent measurements of chemically equivalent distances (*e.g.*, corresponding bond lengths in the two molecules differ by less than 2σ in all cases) implies that the least-squares standard deviations are not underestimated. Among carboxylate groups in which only one oxygen atom is metal coordinated, ample precedent exists for both equal^{6,24,25,33} and unequal^{12,23,34,35} carbon-oxygen bond distances.

Other bond lengths within the phenoxyacetate groups have normal values; average distances include C=O = 1.229 (22) Å, C-C = 1.550 (17) Å, C(3 or 4)-O = 1.436 (12) Å, and C(phenyl)-O = 1.392 (12) Å. The numbers in parentheses after these mean values are root-mean-square deviations of the four individual distances from the means. In all cases, the rms deviations are comparable to or less than the least-squares standard deviations of an individual distance. The O(5)···O(9) and O(6)···O(8) distances of 2.633 (21) and 2.664 (20) Å are slightly smaller than twice the oxygen van der Waals radius; the pattern of angles about C(1) and C(2) suggests some response to strain associated with this short contact. Likewise, the angles about C(1-1) and C(2-1) suggest a response to the short C(3)···C(1-2) and C(4)···C(2-6) contacts. As can be seen from Table VII, the O₂CC grouping in each ligand is coplanar, but the ligand as a whole deviates from planarity owing primarily to twisting about the O-C(phenyl) bond.

The packing of bis(phenoxyacetato)triacuocopper(II) molecules in the crystal is illustrated in Figure 2, a projection of the structure onto the *bc* plane. Crystallographically equivalent molecules are linked into sheets by a network of hydrogen bonds and sheets of molecules A and B are alternately stacked approximately perpendicular to the *c* axis. No opportunities exist for hydrogen bonding between molecules in different sheets. Within a sheet, the phenoxyacetate ligands lie in parallel planes (though they deviate, as described above, from strict planarity); the ligand planes of adjacent sheets are approximately perpendicular. The overall nature of the crystal packing is remarkably similar to that found for the dihydrate by Prout, *et al.*⁶

In Table V, all intermolecular contacts less than 3.2 Å are tabulated. These short O···O contacts each involve one oxygen atom of a water molecule and one oxy-

TABLE VII
Least-Squares Planes for the Phenoxyacetate Ligands^a

1. Plane Containing O(4), O(6), C(2), and C(4) of Molecule A -0.0403X - 0.7881Y - 0.6142Z = -2.1853			
Distances to Plane, Å			
O(4)	-0.0006	C(2)	0.0019
O(6)	-0.0008	C(4)	-0.0005
O(8)	-0.1309		
2. Plane containing O(5), O(7), C(1), and C(3) of Molecule A -0.0645X - 0.6791Y - 0.7313Z = -1.8075			
Distances to Plane, Å			
O(5)	-0.0002	C(1)	0.0006
O(7)	-0.0002	C(3)	-0.0002
O(9)	-0.0913		
3. Plane containing O(4), O(6), C(2), and C(4) of Molecule B -0.0574X + 0.7555Y - 0.6527Z = -10.9314			
Distances to Plane, Å			
O(4)	0.0068	C(2)	-0.0204
O(6)	0.0080	C(4)	0.0056
O(8)	-0.0215		
4. Plane containing O(5), O(7), C(2), and C(4) of Molecule B -0.0314X + 0.7227Y - 0.6904Z = 14.4394			
Distances to Plane, Å			
O(5)	0.0023	C(2)	-0.0059
O(7)	0.0021	C(4)	0.0016
O(9)	-0.0720		
Angles between Perpendiculars to These Planes, Deg			
Planes	Angle	Planes	Angle
1-2	9.3	2-3	91.8
1-3	101.1	2-4	89.1
1-4	98.3	3-4	3.2

Torsional Angles, Deg

Bond	Angle		Bond	Angle	
	Molecule A	Molecule B		Molecule A	Molecule B
C(2)-C(4)	5.5 (12)	0.2 (16)	C(3)-O(9)	2.4 (18)	2.5 (15)
C(1)-C(3)	3.8 (21)	3.7 (26)	O(8)-C(2-1)	7.6 (12)	3.1 (15)
C(4)-O(8)	4.1 (7)	4.8 (14)	O(9)-C(1-1)	13.4 (21)	6.4 (25)

^a Unit weights were employed in the calculation of all planes. The equations of the planes are expressed with respect to coordinates (*X*, *Y*, *Z*) referred to an orthogonal system (*A*, *B*, *C*) oriented with respect to the crystallographic axes such that *A* is parallel to *a*, *B* is parallel to *c** × *a*, and *C* is parallel to *A* × *B*.

gen atom of a phenoxyacetate group; hence they all must be considered in a discussion of possible hydrogen-bonding schemes. The apical oxygen atom O(1) is involved in short contacts to the two ketonic oxygen atoms of an equivalent molecule removed by one translation along *a*. These contacts range in length from 2.768 (20) to 2.921 (20) Å and are probable hydrogen bonds. The remaining water oxygen atoms O(2) and O(3) each are associated with three short contacts—to a coordinated oxygen atom, an ether oxygen atom, and a ketonic oxygen atom. The details of the configurations about these two atoms differ, owing to the different configurations of the phenoxyacetate groups. Thus the shortest contacts of *ca.* 2.68 Å involve O(4), the coordinated oxygen atom of a trans phenoxyacetate ligand, and O(7), the ketonic oxygen atom of a cis phenoxyacetate group. Distinction between the various possible arrangements of hydrogen bonds involving O(2) and O(3) is not possible in the absence of knowledge of the hydrogen atom locations.

The trends in the isotropic thermal parameters are in accord with expectations, with the largest thermal motion associated with the carbon atoms of the phenyl rings and the smallest temperature factors found for

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(35) M. G. B. Drew, G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Amer. Chem. Soc.*, **91**, 7769 (1969).

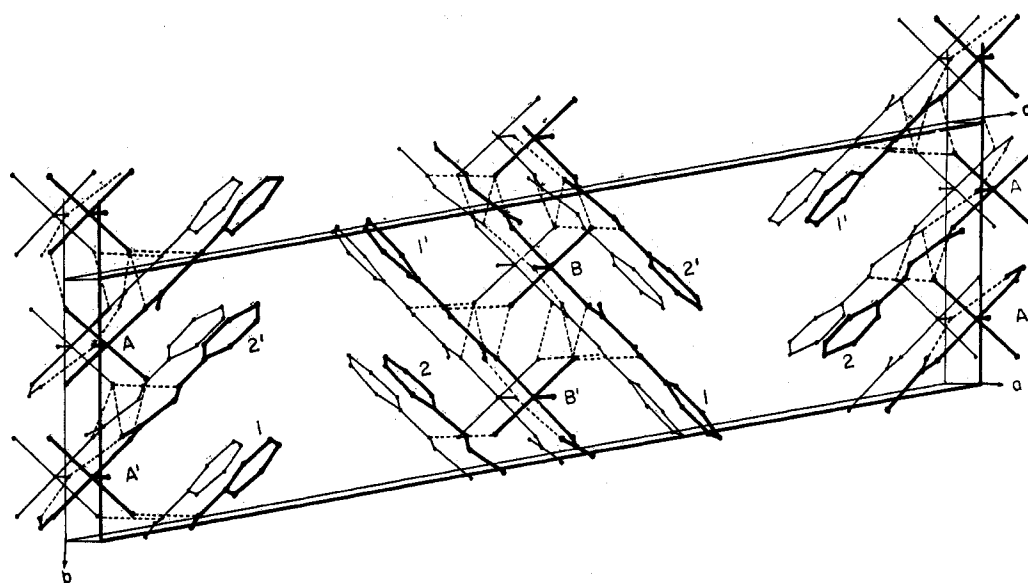


Figure 2.—A view of the packing of the $\text{Cu}(\text{O}_2\text{CCH}_2\text{OC}_6\text{H}_5)_2(\text{H}_2\text{O})_3$ molecules in the unit cell, projected onto the bc plane. Dotted lines represent the short intermolecular contacts tabulated in Table V. In order to include all such contacts, the contents of two cells along a have been included in the projection. The labels A and B designate the two independent molecules, the two phenyl rings per molecule are numbered 1 and 2 (*cf.* Figure 1), and molecules denoted by primed symbols are related to unprimed molecules by a center of symmetry.

C(1) and C(2). Root-mean-square amplitudes of vibration for the copper atoms are 0.104 (6), 0.128 (5), and 0.170 (4) Å for Cu^{A} and 0.115 (7), 0.161 (4), and 0.180 (4) Å for Cu^{B} . In each molecule, the direction of maximum thermal motion is perpendicular to the $\text{Cu}-\text{O}(1)$ vector and approximately perpendicular to the $\text{O}(4)-\text{O}(5)$ vector.

Crystallographic studies have now characterized the dihydrate⁶ and trihydrate of cupric phenoxyacetate as monomeric species differing in coordination geometry and in the mode of attachment of the phenoxyacetate ligand. In addition, the existence of a monomeric mono-

hydrate can be inferred from the magnetic studies of Hatfield, *et al.*¹ Further studies of the conditions for formation and possible interconversion of these species would be of interest, as would a detailed comparison of their spectral and magnetic properties. Some of these points are under investigation in other laboratories.^{36,37}

Acknowledgments.—Some of the early work on this and related systems was carried out by Mr. Thomas T. Gufrey. The support of this work by the National Science Foundation is gratefully acknowledged.

(36) W. E. Hatfield, personal communication.

(37) B. J. Hathaway, personal communication.