The Crystal and Molecular Structure of Bis(phenoxyacetato)triaquocopper(II), a Monomeric, Five-co-ordinate Hydrated Cupric Carboxylate

By CAROL VALLEY GOEBEL and ROBERT J. DOEDENS*

(*Department of Chemistry, University of California, Irvine, California* 92664)

Summary Bis(phenoxyacetato)triaquocopper(II) has been found to have a monomeric structure with five-co-ordinate cupric ions and monodentate carboxylate groups.

OUR interest in the hydrated cupric phenoxyacetates stems from the report[1] of a monohydrate of copper(II) phenoxyacetate having the stoicheiometry of dimeric cupric carboxylate complexes but displaying magnetically dilute behaviour. We have found that minor variations of the published preparative procedure yield products of two distinct crystalline forms—monoclinic prisms and triclinic plates. The triclinic crystals were most readily obtained and we elected to carry out a full structural analysis of that form. While this work was in progress, Prout *et al.*[2] reported the crystal structure of the monoclinic modification which was shown to be bis(phenoxyacetato)diaquocopper(II). The dihydrate consists of mononuclear molecules in which the copper atom is co-ordinated by two water molecules and two bidentate phenoxyacetate groups in a tetragonally distorted octahedral configuration. Each carboxylate group is bound through one carboxy-oxygen atom and the phenoxy-oxygen atom, with the third oxygen atom participating only in intermolecular hydrogen bonds. We have found the triclinic form to be a trihydrate, with five-co-ordinate copper atoms and monodentate phenoxyacetate ligands.

Greenish-blue diamond-shaped plates of triclinic bis(phenoxyacetato)triaquocopper(II) were prepared by the method of Hatfield *et al.*[1] The unit-cell parameters are $a = 6{\cdot}40(2)$, $b = 9{\cdot}28(2)$, $c = 32{\cdot}01(6)$ Å, $\alpha = 100°\ 7'\ (10')$, $\beta = 78°\ 50'\ (10')$, $\gamma = 90°\ 12'\ (10')$, and $Z = 4$. The space group is $P\bar{1}$. Observed and calculated densities are 1·55 and 1·52 g cm^{-3}, respectively. Multiple-film equi-inclination Weissenberg data for reciprocal lattice levels $h0l$—$h8l$ were estimated visually and corrected for Lorentz and polarization effects, spot shape, and absorption. All nonhydrogen atoms were located by Patterson and Fourier methods, complicated somewhat by a pseudosymmetry problem. Full-matrix least-squares refinement of atomic positional and thermal parameters, with phenyl rings treated as rigid groups, led to a final conventional R-factor of 8·4% for 2185 independent, non-zero data. In the final cycles the copper atoms were given anisotropic thermal parameters.

The crystal structure of bis(phenoxyacetato)triaquocopper(II) is composed of monomeric molecular units (see Figure) in which the copper atom is co-ordinated to three water molecules and two monodentate phenoxyacetate ligands.† Only a few small differences exist between the two crystallographically independent molecules. All distances and angles quoted are averages over the two molecules of values which are equivalent within experimental error. The five co-ordinate configuration about the copper atom is best described as distorted square-pyramidal. The copper–oxygen bond distances, given in the Figure, are consistent with this description. The angles in the basal plane are O(4)–Cu–O(5) = 176·8(6)° and O(2)–Cu–O(3) = 168·4(5)°; the former angle arises from a bending of O(4) and O(5) *toward* O(1). These parameters are most simply regarded as arising from distortion of a tetragonally elongated octahedron which lacks one apical ligand. In the direction of the sixth octahedral co-ordination site, the copper atom is involved in two short intramolecular contacts—Cu–O(6) = 2·97(2) Å and Cu–O(7) = 2·96(2) Å.

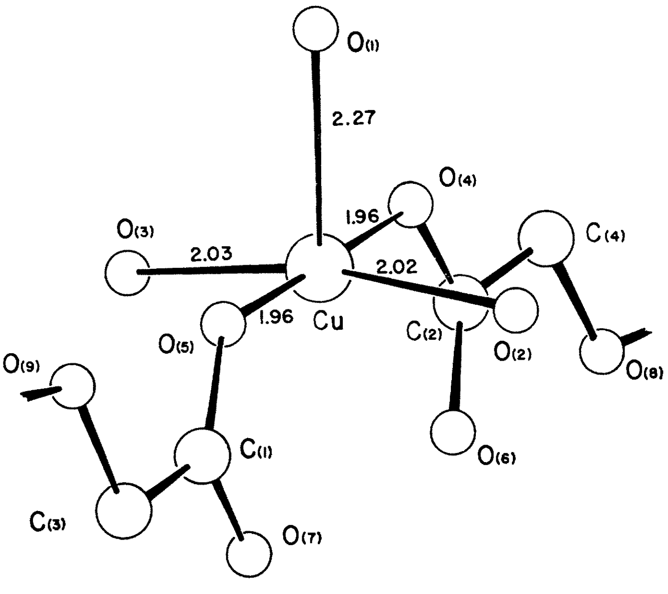

FIGURE. *The molecular configuration of bis(phenoxyacetato)-triaquocopper*(II), *with phenyl rings omitted for clarity. The mean standard deviation of the* Cu–O *bonds is* 0·015 Å.

The two phenoxyacetate ligands differ in stereochemistry about the C–C bond and also display one apparently significant difference in bond lengths—the C(1)–O(5) and C(2)–O(4) distances are 1·23(2) and 1·32(2) Å, respectively. This difference of five standard deviations is found in each of the two independent molecules. Other bond distances within the ligands have their expected values.

Although five-co-ordinate copper(II) is common, instances of co-ordination by five monodentate ligands are rare. The monodentate co-ordination of the phenoxyacetate ligand may be contrasted with the chelation found by Prout *et al.*[2] in five other copper(II) complexes of hydroxy-, alkoxy-, and

---

† The X-ray data alone provide no objective basis upon which to rule out an isomeric formulation in which one or both of the phenoxyacetate groups are protonated and one or two OH$^-$groups replace water molecules. However, we consider such a formulation unlikely in view of the fact that these crystals were obtained from solutions of pH as low as 4—5 and also because the weight loss upon dehydration corresponded closely to three water molecules per copper atom.

aryloxy-carboxylates. The Cu–O(6) and Cu–O(7) contacts are of a type frequently found in five-co-ordinate copper(II) carboxylate[3] and nitrate[4] complexes and probably play a role in stabilizing this configuration.

Support of this work by the U.S. National Science Foundation is gratefully acknowledged.

(*Received, May 4th,* 1970; *Com.* 666.)

---

[1] W. E. Hatfield, H. M. McGuire, J. S. Paschal, and R. Whyman, *J. Chem. Soc.* (*A*), 1966, 1194.

[2] C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1968, 2791.

[3] H. C. Freeman, G. Robinson, and J. C. Schoone, *Acta Cryst.*, 1964, **17**, 719; C. M. Gramaccioli and R. E. Marsh, *ibid.*, 1966, **21**, 594; J. F. Blount, K. A. Fraser, H. C. Freeman, J. T. Szymanski, and C.-H. Wang, *ibid.*, 1967, **22**, 396.

[4] B. Duffin and S. C. Wallwork, *Acta Cryst.*, 1966, **20**, 210; B. Duffin, *ibid.*, 1968, **B24**, 396; S. Scavnicar and B. Matkovic, *ibid.*, 1969, **B25**, 2046.