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

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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 of a monohydrate of copper(I) phenoxyacetate having the stoichiometry 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. reported the crystal structure of the mononuclear 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 Haffield et al. The unit-cell parameters are in agreement with those reported by Haffield et al. 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.

The crystal structure of bis(phenoxyacetato)triaquocopper(II) was determined by single-crystal X-ray diffraction. The crystal structure 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.

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 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(6)°; the former angle arises from a bending of O(4) 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.

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.

* 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(11) carboxylate* and nitrate* complexes and probably play a role in stabilizing this configuration.

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