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Structural Polymorphs of Copper(II) 4-Fluorophenoxyacetate

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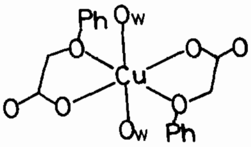
The first complex of copper(II) with 4-fluorophenoxyacetic acid (LH) has been described [1] and represents the only known example of a copper phenoxyacetate having both coordinated and adducted carboxylate species. In this complex, $[Cu(L)_2(H_2O)_2]\cdot 2LH\cdot 2H_2O$ (1), the centrosymmetric copper(II) species has bidentate phenoxyacetate ligands coordinating through both carboxylate and ether oxygens.



Although this mode of complexation is relatively common among the copper(II) phenoxyacetates [2], the presence of strongly hydrogen bonded acid species has no precedence among the metal(II) phenoxyalkanoates outside the manganese(II) 2,4,5-trichlorophenoxyacetate polytypes. With these, both conventional types [3] and adducted complexes [4] are found. The nature of the complex formed between manganese(II) and 2,4,5-trichlorophenoxyacetate (2,4,5-T) was found to be dependent upon both the relative concentrations of free ligand and the presence of water in the crystallizing mixture. The early formed product was $[Mn(2,4,5\text{-}T)(H_2O)_5]^+(2,4,5\text{-}T)^-$ [3], while the final product was the adduct $[Mn(2,4,5\text{-}T)_2(H_2O)_4]\cdot 2(2,4,5\text{-}TH)$ [4]. A third polymorph, crystallized from 95% ethanol, was a polymeric form $[Mn_2(2,4,5\text{-}T)_4(H_2O)_4]_n$ [5].

With the copper(II) 4-fluorophenoxyacetate system, two products were also obtained. The structure of the product (2), formed in the early stages of the fractional crystallization, is reported here and compared with that of the adduct 1. Complex 2 is disordered and has the stoichiometry $[Cu_{1.5}(L)_3(H_2O)_{5.5}]$.

Experimental

The copper(II) 4-fluorophenoxyacetate complexes were prepared by the reaction of a hot 50% aqueous ethanolic solution of 4-fluorophenoxyacetic acid with excess copper(II) carbonate. Complex 2 was obtained as large, pale blue prismatic plates on allowing the filtered digest to partially evaporate at room temperature.

Crystal Data

$C_{24}H_{29}Cu_{1.5}F_3O_{14.5}$, $M_r = 701.8$, monoclinic, space group $P2_1/c$, $a = 21.624(7)$, $b = 7.293(3)$, $c = 18.872(7)$ Å, $\beta = 105.43(3)°$, $V = 2869(2)$ Å^3, $D_c = 1.624$, $D_m = 1.63$ g cm^{-3}, $Z = 4$, $F(000) = 719$, μ(Mo Kα) = 6.30 cm^{-1}, $T = 293$ K.

Collection of X-ray Data and Structure Solution

Data were collected from one crystal (0.49 × 0.24 × 0.13 mm), mounted on a Nicolet R3m four-circle diffractometer, using graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). Of 3642 unique reflections collected up to $2\theta = 55°$, 2759 with $I > 2.5\sigma(I)$ were considered observed and used in structure refinement. No corrections were made for absorption. The structure was solved by the Patterson method and refined by blocked-matrix least-squares using SHELX-76 [6] to a residual of 0.14. No hydrogens were included. Considerable disorder was in evidence in parts of the structure, including the water molecules, so these were given partial occupancy and refined isotropically. The second copper was also found from least-squares to have half occupancy but was refined anisotropically.

Bond distances and angles about the coordination spheres are listed in Table 1.

Discussion

Although the overall refinement of the structure of 2 did not reach a satisfactory convergence due to the disorder in several parts of the molecule, the coordination spheres about the two copper centres are sufficiently well defined to provide a meaningful comparison with polymorph 1 [1]. The overall structure of 2 is shown in Fig. 1, and is based upon two independent and different copper centres. The first, Cu(1), has tetragonally distorted octahedral six-coordination, involving three water molecules [including $O_w(4)$ and $O_w(5)$ which are disordered over two half-sites], and three oxygens from two separate 4-fluorophenoxyacetate ligands. Ligand B is bonded through an unidentate carboxylate oxygen [Cu–O, 1.95(1) Å, while ligand A is a bidentate chelate via both carboxylate and ether oxygens [Cu–O, 1.96(1),

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TABLE 1. Bond distances (Å) and angles (degrees) about the coordination spheres for Cu(1) and Cu(2). The disordered sites for $O_w(4)$ and $O_w(5)$ are included

Cu(1)–O_w(1)	1.95(1)	Cu(2)–O_w(3)	1.85(1)
Cu(1)–O_w(2)	1.97(1)	Cu(2)–O_w(3)′	1.84(1)
Cu(1)–O_w(4)	2.46(3)	Cu(2)–O_w(8)	2.23(1)
Cu(1)–O_w(5)	2.39(3)	Cu(2)–O(10)A	2.05(1)
Cu(1)–O(7)A	2.48(1)	Cu(2)–O(11)C	2.38(1)
Cu(1)–O(11)A	1.96(1)		
Cu(1)–O(11)B	1.95(1)		
O_w(1)–Cu(1)–O_w(2)	171.6(5)	O_w(5)–Cu(1)–O(11)B	98.6(7)
O_w(1)–Cu(1)–O_w(4)	102.5(8)	O(7)A–Cu(1)–O(11)A	69.7(4)
O_w(1)–Cu(1)–O_w(5)	87.2(8)	O(7)A–Cu(1)–O(11)B	110.7(4)
O_w(1)–Cu(1)–O(7)A	87.6(5)	O(11)A–Cu(1)–O(11)B	179.6(4)
O_w(1)–Cu(1)–O(11)A	92.2(5)	O_w(3)–Cu(2)–O_w(3)′	165.8(8)
O_w(1)–Cu(1)–O(11)B	88.1(4)	O_w(3)′–Cu(2)–O_w(8)	94.0(9)
O_w(2)–Cu(1)–O_w(4)	84.5(8)	O_w(3)′–Cu(2)–O(10)A	89.6(8)
O_w(2)–Cu(1)–O_w(5)	100.4(8)	O_w(3)–Cu(2)–O(11)C	75.6(9)
O_w(2)–Cu(1)–O(7)A	87.2(5)	O_w(3)–Cu(2)–O_w(8)	89.1(9)
O_w(2)–Cu(1)–O(11)A	91.9(5)	O_w(3)–Cu(2)–O(10)A	104.0(9)
O_w(2)–Cu(1)–O(11)B	87.9(4)	O_w(3)–Cu(2)–O(11)C	90.3(9)
O_w(4)–Cu(1)–O_w(5)	18.3(9)	O_w(8)–Cu(2)–O(10)A	93.9(9)
O_w(4)–Cu(1)–O(7)A	158.2(7)	O_w(8)–Cu(2)–O(11)C	96.8(9)
O_w(4)–Cu(1)–O(11)A	90.5(7)	O(10)A–Cu(2)–O(11)C	162.3(8)
O_w(4)–Cu(1)–O(11)B	89.1(7)	C(1)A–O(7)A–Cu(1)	129(1)
O_w(5)–Cu(1)–O(7)A	150.0(7)	C(8)A–O(7)A–Cu(1)	110(1)
O_w(5)–Cu(1)–O(11)A	90.0(7)	C(9)A–O(11)A–Cu(1)	129(1)
		Cu(2)–O_w(3)–Cu(2)′	166(1)

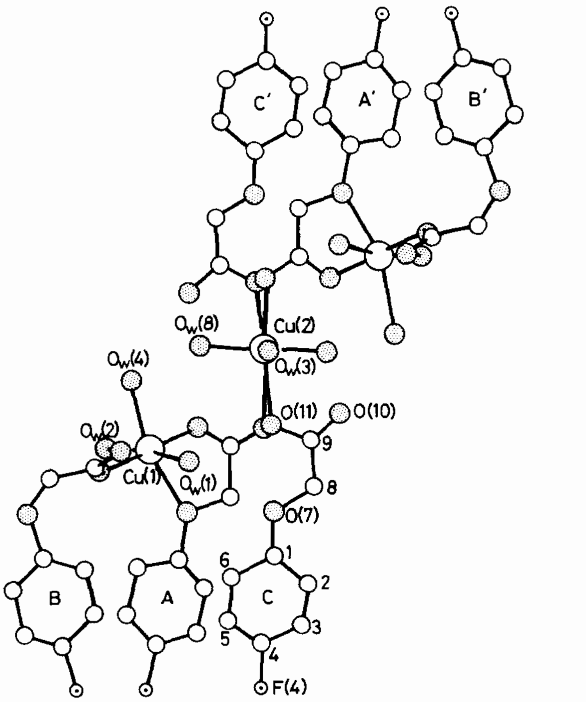
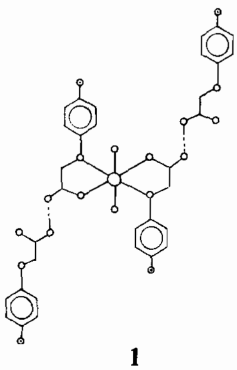


Fig. 1. The structure of 2 showing the atom numbering scheme.

2.48(1) respectively]. This group is analogous to those in the structure of **1**. However, the second carboxylate oxygen of ligand A does not form a hydrogen bond with the adducted acid molecule as in **1**. Instead, it is bonded to the second copper atom, Cu(2), [Cu–O, 2.05(1) Å]. In the site *trans* to this is the carboxylate oxygen of ligand C [Cu–O, 2.38(1) Å], while the square-pyramidal coordination is completed by water molecules, some with partial occupancy. Furthermore, this second copper has only half occupancy, as required for overall charge balance. Water molecule $O_w(3)$ forms an infinite bridging system with Cu(2), which extends down the



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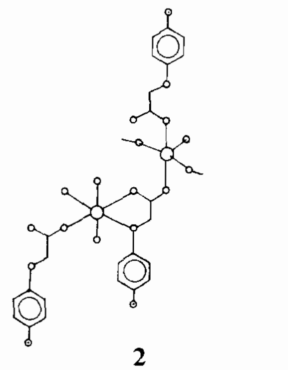

2

approximate *b* direction in the cell [Cu–O, 1.84, 1.85(1) Å; Cu–O–Cu, 166(1)°].

The structure of **2** may be compared with that for **1**, if it is considered as a disordered intermediate. In the presence of limited ligand concentration and excess water, **2** forms. With a larger ligand-to-metal ratio it acquires the structural stability found in **1**. This condition is usually found in the late stages of the crystallization process, when there is an excess of unreacted ligand [1, 4].

In most respects, this structural phenomenon is similar to that found for the copper phenoxyisobutyrate polymorphs [7]. With these, there is disorder in a $[Cu(H_2O)_4]^{2+}$ cation, which acquires stability via additional water ligands. However, the stable $[Cu_2L_6]^{2-}$ copper dimers in the structure remain unchanged.

Supplementary Material

Final atomic parameters, anisotropic thermal parameters, ligand interatomic bond distances and angles, and observed and calculated structure factors are available from the authors.

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