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Crystal and Molecular Structure of *Trans*-Diacetatobis(Collidine)Copper(II): A Novel Square-Planar Monomer

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Only a few monomeric copper(II) carboxylate adducts have been reported, and all have been with haloacetate salts [1]. In complexes for which structural data are available [2], the copper is six-coordinated with the haloacetate groups acting as bidentate ligands and the addends in *trans* positions. Formation of monomeric rather than the more common dimeric complexes has been attributed [1] to the relative instability of the binuclear structure as a result of increased Cu–Cu repulsion in salts of the strong haloacetic acids. The only known structure for an acetate (or any other alkonoate) complex with this stoichiometry has been that with ammonia [3]. We have recently [4] reported the preparation and characterization of similar monomeric complexes of copper(II) acetate with pyridine and γ-picoline, and suggested that the instability of α- and β-picoline analogs is caused by greater steric hinderance in complexes of these ligands. We now report the preparation and structure determination of a copper(II) acetate bis-adduct with the highly sterically hindered ligand collidine. Results of this study further demonstrate the role of steric requirement of the addend in affecting the structural properties of copper carboxylate adducts. The increased steric crowding around copper due to the α-methyl groups of collidine prevents formation of the expected six-coordinate complex. Although the new compound has the stoichiometry and general characteristics of previously reported monomeric bis-adducts, it exhibits different coordination and geometry and represents the first example of a four-coordinate, square-planar complex among these adducts.

Reaction of the neat ligand with anhydrous copper(II) acetate yields a purple precipitate which can be recrystallized from acetonitrile/collidine solution. A crystal was mounted inside a thin glass capillary containing a small amount of collidine for the X-ray data collection. *Crystal data*: $Cu(CH_3CO_2)_2(C_8H_{11}N)_2$, M = 423.99; monoclinic, space group $P2_1/c$; a = 7.819(4) Å, b = 16.319(7) Å, c = 8.304(2) Å; β = 101.89(2); V = 1036.9 $Å^3$, Z = 2, D_c = 1.36 g/cm^3, D_m = 1.39(5) g/cm^3. Diffraction intensities were collected in ω–2θ scan mode using graphite monochromated Mo-Kα radiation on an Enraf-Nonius CAD-4F automatic diffractometer. A total of 3020 reflections were measured, and refinement using 1032 reflections $\{I > 3\sigma(I)\}$ resulted in a weighted and unweighted R factors of 0.042 and 0.052, respectively.

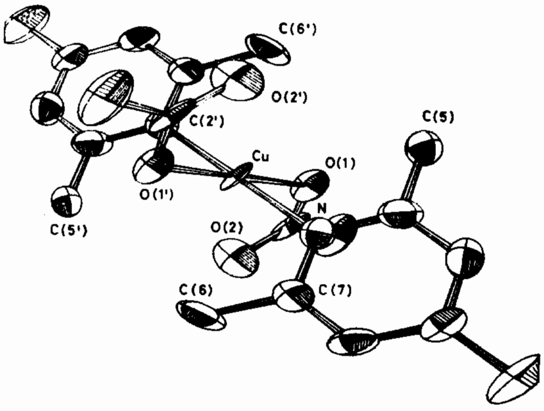

Fig. 1. The structure of $Cu(OAc)_2(Col)_2$. Bond lengths (A): Cu–N, 2.034(4); Cu–O(1), 1.952(3); C(1)–O(1), 1.257(6); C(1)–O(2), 1.209(6). Nonbonded distances (A): Cu–O(2), 2.772(4); Cu–C(5), 3.10; O(2)–C(5), 3.196(5). Bond angles (°): O(1)–Cu–O(1'), 180.0(3); O(1)–Cu–N, 90.3(1); O(1)–Cu–N', 89.67(1); Cu–N–C(7), 120.5(1); O(1)–C(1)–O(2), 124.4(4); O(1)–C(1)–C(2), 116.4(4); O(2)–C(1)–C(2), 119.2(4); Cu–O(1)–C(1), 111.2.

The structure of the complex is shown in Fig. 1, which includes some bond distances and angles. The complex is centrosymmetric with C_{2h} molecular symmetry. Copper is coordinated to two collidines, with a Cu–N bond distance of 1.034 Å, and one oxygen of each of the two acetate groups, with a Cu–O bond distance of 1.952 Å. The collidine ring shows the expected planarity and is twisted 69.7° out of the N–Cu–O plane. This conformation is apparently favored in order to avoid steric interaction with the non-coordinated oxygen of the acetate group. The distance between each pair of opposing α-methyl groups, C(5)–C(6') and C(6)–C(5'), is 4.87 Å and as a result steric repulsion between the group is negligible. A similar *cis*-configuration of the methyl groups has been observed in the structures of α-picoline bis-adducts of some copper(II) salts [2, 5, 6]. The acetate groups are normal to the N–Cu–O plane and the dihedral angle between the acetate and collidine planes is 73°. A result of this conformation

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is that the collidine α-methyl groups block further copper bonding to the second oxygen of each acetate group. This is reflected in the presence of two different acetate C–O bond lengths (8σ). The distance of the second acetate oxygen from copper is 2.772 Å, which is comparable to the sum of their van der Waal's radii of 2.80 Å. It is much longer than the Cu–O(1) bond distance of 1.952 Å in this complex and longer than any Cu–O bond distance reported for six-coordinate copper(II) carboxylate complexes. One exception, however, is a comparable distance of 2.707 Å reported for $Cu(ClCH_2CO_2)_2(\alpha\text{-pic})_2$ for which the oxygen atom was considered weakly bonded to copper and the stereochemistry of the complex was described as 'an extremely tetragonally distorted octahedron' [2a]. In the closely related dichloracetate complex [2b], a Cu–O distance of 2.711 Å was considered not bonding since the oxygen is sterically blocked by the methyl groups of the picoline rings and the complex was described as five-coordinate.

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