Copper(II) Acetate Complexes, $[CuL_m(OAc)_2]_n$ ($L = HNPPh_3$), Stable in the Solid State Either as a Dimer ($m = 1$, $n = 2$) or a Monomer ($m = 2$, $n = 1$)

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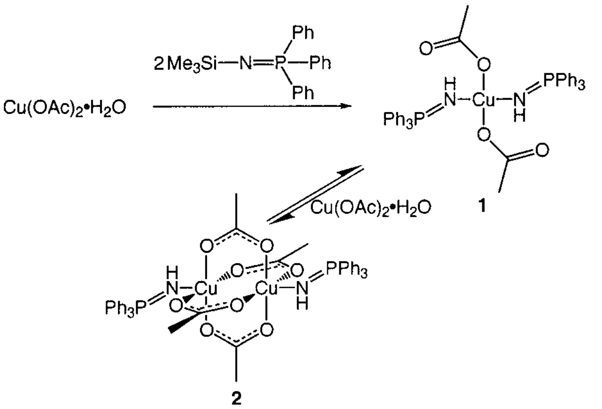
The familiar "paddlewheel" structure of copper(II) carboxylates has been known for many years.[1] There are far fewer examples of crystal structures of copper carboxylate monomers, most of which are stabilized by bulky alkyl or aryl groups on the carboxylate anion.[2] Although there have been reports of equilibria in solution between the copper acetate monomer and dimer,[3] to our knowledge, there are no examples of copper acetate complexes where the monomer and dimer have been structurally characterized in the solid state. Herein we report the first example of copper acetate complexes, $[CuL_m(OAc)_2]_n$, that have been structurally characterized as a monomer ($m = 2$, $n = 1$) and a dimer ($m = 1$, $n = 2$).

Our interest in these compounds arose from ongoing research on copper clusters that mimic the Cu_Z catalytic site in nitrous oxide reductase.[4] Our copper clusters contain copper cations bridged by phosphoraneiminato ligands. The phosphoraneiminate anion, NPR_3^-, has been used as a ligand with many transition metals,[5] as well as with main group elements.[6] The coordination mode of the NPR_3^- ligand is varied, ranging from μ_1 to μ_3, depending predominantly on the oxidation state of the metal. Complexes of divalent metal ions with phosphoraneiminato ligands have the general formula $[MX(NPR_3)]_4$ (X = halide; R = Me, Et, Ph), possess a heterocubane structure, and are well represented for most of the mid- to late-transition metals, with solid-state structures reported for Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}.[5] Interestingly, there are no examples of the heterocubane cluster where $M = Cu^{2+}$. A recent computational study of $[MX(NPR_3)]_4$ heterocubane clusters suggests that there have been no reported examples of $[CuX(NPR_3)]_4$ due to destabilization from Jahn−Teller distortions.[7] Very few copper complexes of any type with phosphoraneiminato ligands have been reported.[8]

Scheme 1



When a CH_2Cl_2 slurry of $Cu(OAc)_2{\cdot}H_2O$ is treated with a CH_2Cl_2 solution of $Me_3SiNPPh_3$, the Si−N bond is hydrolyzed to produce triphenylphosphinimine, Ph_3PNH, which coordinates to the copper ions via the imine nitrogen atom to produce deep blue $Cu(HNPPh_3)_2(OAc)_2$ (**1**, Scheme 1).[9] The solid-state structure of **1**, determined from a single-crystal X-ray diffraction study, reveals a square planar geometry around the copper(II) ion with the ligands in a trans conformation (Figure 1).[10] The copper atom lies on the inversion center, and the acetate anions are coordinated in a syn-monodentate fashion. The same arrangement of ligand atoms was observed in the closely related copper phosphinimine complex where R = Et, $Cu(HNPEt_3)_2(OAc)_2$,[9a] and the Cu−N and Cu−O bond distances in **1** are nearly identical to those reported for $Cu(HNPEt_3)_2(OAc)_2$.

The Cu−N−P bond angle of 138.01(11)° for **1** is slightly more obtuse than the analogous angle of 133.3° reported for $Cu(HNPEt_3)_2(OAc)_2$, presumably due to increased steric interactions between the phenyl rings and the acetate ligands. Indeed, the acetate methyl group is in a position that minimizes interaction with the nearby atoms, lying between the two proximal phenyl rings of the phosphinimine ligand. The N1−H1···O2A angle and the short H1···O2A distance (see Figure 1 caption) indicate that hydrogen bonding occurs, perhaps giving rise to the stabilization

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[10] Crystal data for **1**: $C_{40}H_{38}CuN_2O_4P_2$, MW = 736.20, blue, block-shaped crystal (0.54 × 0.52 × 0.48 mm), triclinic, space group *P*-1 with $a = 8.7983(10)$, $b = 9.4952(10)$, $c = 12.5588(13)$ Å, $\alpha = 109.609(7)$, $\beta = 103.008(8)$, $\gamma = 99.475(8)$, $V = 929.42(17)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.315$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), 198(2) K. Data were collected using a Siemens P4 single-crystal diffractometer, and the structure was solved via direct methods. Full-matrix least-squares refinement on F^2 using SHELXTL V5.1 converged with final $R1 = 0.0350$ and $wR2 = 0.0930$ for 3273 independent reflections, with $I > 2\sigma(I)$ and 229 parameters.

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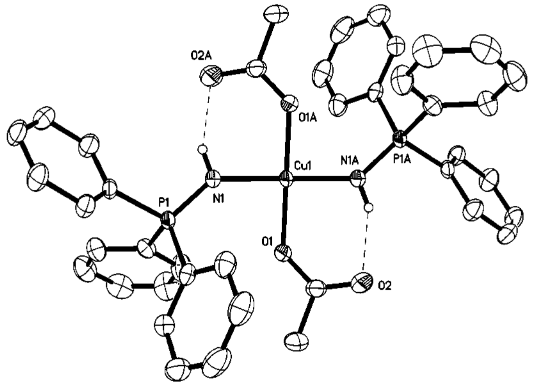

Figure 1. Representation of the X-ray crystal structure of **1** as 50% thermal ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cu1−N1, 1.9309(15); Cu1−O1, 1.9621(13); P1−N1, 1.5811(15); N1−O2A, 2.7651(15); N1−H1, 0.81(2); O2A···H1, 2.01(2); N1−Cu1−N1A, 180.00(11); O1A−Cu1−O1, 180.00(9); N1−Cu1−O1A, 91.23(6); N1−Cu1−O1, 88.77(6); P1−N1−Cu1, 138.01(11) N1−H1···O2A, 154(2).

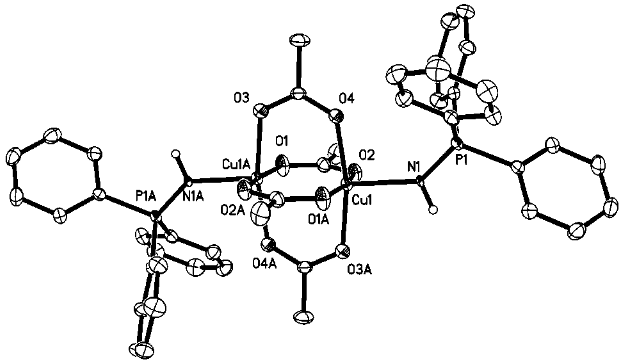

Figure 2. Representation of the X-ray crystal structure of **2** as 50% thermal ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cu1−Cu1A, 2.664(3); Cu1−N1, 2.128(3); Cu1−O1A, 1.966(3); Cu1−O2, 1.966(3); Cu1−O3A, 1.963(3); Cu1−O4, 1.968(3); P1−N1, 1.511(3); O3A−Cu1−O1A, 87.98(13); O1A−Cu1−O4, 90.15(13); O2−Cu1−O4, 89.98(12); O3A−Cu1−O2, 89.09(12); O1A−Cu1−O2, 167.26(8); O3A−Cu1−O4, 167.26(8); O3A−Cu1−N1, 98.69(14); O1A−Cu1−N1, 94.97(12); O2−Cu1−N1, 97.73(12); O4−Cu1−N1, 94.02(13); P1−N1−Cu1, 138.05(13).

of the monomeric form of **1**.[11] Further proof of hydrogen bonding is evident in the FTIR spectrum of **1**, which displays a broadened N−H stretch centered at approximately 3400 cm^{-1} (Figure S1). This type of hydrogen bonding in copper(II) carboxylate monomers has been observed in the related complex $Cu(HNPEt_3)_2(OAc)_2$,[9a] and in a complex coordinated by a sterically bulky carboxylate and methanol.[2a]

Adjusting the stoichiometry of the reaction in Scheme 1 by using excess $Cu(OAc)_2 \cdot H_2O$ results in a mixture of **1** and a green crystalline product characterized as dimeric $[Cu(HNPPh_3)(OAc)_2]_2$ (**2**). Furthermore, monomer **1** can be converted to dimer **2**. When a CH_2Cl_2 solution of analytically pure **1** was treated with excess $Cu(OAc)_2 \cdot H_2O$, **2** was isolated as the sole product upon recrystallization. The identity of **2** was verified by X-ray crystallography to be a copper(II) dimer with the aforementioned familiar paddlewheel structure containing the four acetate bridging units, shown in Figure 2.[12] The coordination geometry around the copper atoms is square pyramidal, with the phosphinimine ligands occupying the apical positions and the oxygen atoms of the acetato bridging ligands making up the basal plane. The Cu···Cu distance of 2.664(3) Å is typical for binuclear copper(II) acetates that possess N-donating apical ligands, and the Cu−O and Cu−N bond lengths are all within expected ranges.[13] The copper(II) ions lie 0.217(1) Å above the basal planes created by the oxygen atoms of the bridging acetates. The Cu−N−P bond angle in **2** is identical to the Cu−N−P bond angle in **1** as a result of the similar disposition of the phenyl rings with respect to the acetate groups.

In contrast to **1**, there is no intramolecular hydrogen bonding in **2**, as evinced by the sharp N−H stretch at 3352 cm^{-1} in the FTIR spectrum (Figure S1). Moreover, the H1···O3A distance in **2** is over 2.9 Å and the N1−H1···O3A angle is 91°, precluding intramolecular hydrogen bonding. Inspection of the packing diagram for **2** (Figure S2) reveals the absence of any potential intermolecular hydrogen bonding contacts.

Although dimeric **2** is stable in the solid state, upon dissolution it dissociates into a monomeric species. When green **2** is dissolved in either CH_2Cl_2 or CH_3CN, the color quickly changes to blue, and the UV−visible spectrum of **2** in solution is identical to the spectrum of **1**. Furthermore, electrospray MS of CH_2Cl_2 solutions of **1** and **2** are nearly identical, with both spectra dominated by a parent ion at $m/z = 676.1$ ($[M - OAc]^+$). The ESI MS of **2** also contains a small fraction (<3% relative intensity) of higher molecular weight ions that are presumably multinuclear in nature. Finally, EPR spectra of frozen solutions of **1** and **2** both display axial signals typical for tetragonal copper complexes.[14]

In summary, the structures of copper acetate monomer **1** and dimer **2** have been determined. Hydrogen bonding plays a role in the stabilization of the monomer, while no hydrogen bonding is apparent in the dimer. Although both **1** and **2** are stable indefinitely in the solid state, only the monomer is present in solution.

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Supporting Information Available: Experimental details and spectroscopic characterization for **1** and **2**; FTIR of **1** and **2** (Figure S1); packing diagram of **2** (Figure S2) (PDF); X-ray structural information on **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Crystal data for **2**: $C_{44}H_{44}Cu_2N_2O_8P_2$, MW = 917.83, green, prism-shaped crystal (0.58 × 0.54 × 0.32 mm), triclinic, space group *P*-1 with $a = 8.866(9)$, $b = 9.685(10)$, $c = 13.041(13)$ Å, $\alpha = 90.06(9)$, $\beta = 104.59(11)$, $\gamma = 104.45(10)°$, $V = 1047.0(18)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.456$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), 173(2) K. Data were collected using a Siemens P4 single-crystal diffractometer, and the structure was solved via direct methods. Full-matrix least-squares refinement on F^2 using SHELXTL V5.1 converged with final $R1 = 0.0504$ and $wR2 = 0.1379$ for 4779 independent reflections, with $I > 2\sigma(I)$ and 264 parameters.

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[14] EPR of **1** (50:50 CH_2Cl_2/toluene, 9.420 GHz, 77 K) $g_\perp = 2.056$, $g_\parallel = 2.271$, $A_\parallel^{Cu} = 165$ G.