

Communication

**Synthesis and Crystal Structure of the Dicopper(II) Complex
[Cu₂{Ph₂P(=O)(*o*-C₆H₄)CO₂}₂(THF)₂(H₂O)₂][BF₄]₂ by Oxidation of
[Cu{Ph₂P(*o*-C₆H₄)C(=O)H}₂(NCMe)][BF₄] with Aqueous H₂O₂**

Wen-Yann Yeh^{a*} (葉文彥), Gene-Hsiang Lee^b (李錦祥) and Shie-Ming Peng^b (彭旭明)

^aDepartment of Chemistry, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, R.O.C.

^bDepartment of Chemistry, National Taiwan University, Taipei 106, Taiwan, R.O.C.

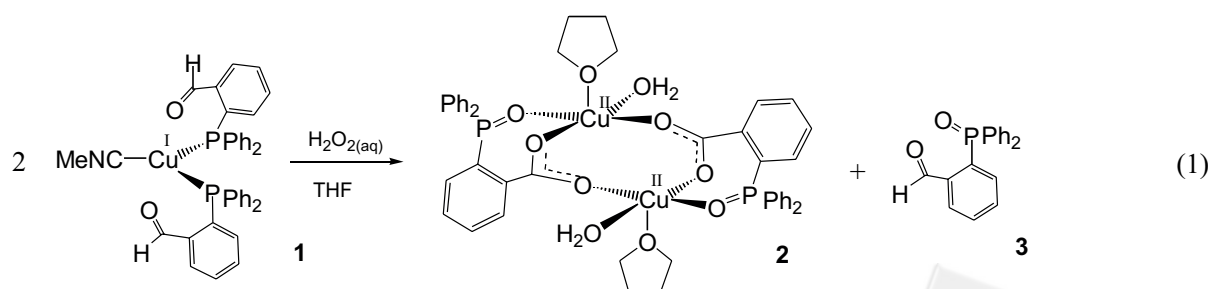
Treatment of [Cu(pcho)₂(NCMe)][BF₄] **1** (pcho = 2-(diphenylphosphino)benzaldehyde) with aqueous H₂O₂ in THF solvent affords [Cu₂(dpb)₂(THF)₂(H₂O)₂][BF₄]₂ **2** (dpb = 2-(diphenylphosphinoyl)benzoate) after crystallization from diethyl ether. This reaction involves oxidation of Cu(I) to Cu(II) ion, phosphine to phosphinoyl, and benzaldehyde to benzoate species. The crystal structure of **2** consists of two copper(II) atoms bridged by two carboxylate moieties of the dpb ligands. The coordination about each copper(II) atom is a distorted trigonal bipyramid.

Keywords: Cu(II) complex; 2-(Diphenylphosphinoyl)benzoate; 2-(Diphenylphosphino)benzaldehyde.

Copper-catalyzed substrate oxygenation is an important biochemical process.¹⁻³ It may possess mononuclear, dinuclear, or trinuclear copper-active sites.⁴ For instance, the mononuclear copper-active site was found in dopamine β-monooxygenase and quercetin 2,3-dioxygenase,⁵ and the dinuclear copper-active site was found in tyrosinases and catechol oxidases.^{6,7} Recently, the reactions of an oxidant (eg., O₂ or H₂O₂) with a mononuclear copper complex to lead to products comprising [Cu₂(μ-O)₂]ⁿ⁺ or isomeric [Cu₂(O₂)]ⁿ⁺ cores have attracted considerable attention aimed at understanding the mechanisms of oxidation catalysis in synthetic and biological systems.⁸⁻¹⁰ We have prepared the trigonal complex [Cu(pcho)₂(NCMe)][BF₄] **1**¹¹ (pcho = 2-(diphenylphosphino)benzaldehyde), where the copper(I) atom is bonded to an acetonitrile ligand and two phosphine groups of the pcho ligands. In this paper we wish

to report the reaction of **1** with H₂O₂ to give a dinuclear copper(II) complex concomitant with oxidation of the pcho ligands.

Typically, compound **1** (220 mg, 0.30 mmol) was dissolved in THF (15 mL) and an excess amount of aqueous H₂O₂ (30%; 1 mL, 7.9 mmol) was added. The solution was stirred at ambient temperature for 12 h to result in a solution color change from yellow to light blue. The solution was topped with 30 mL of diethyl ether to afford crystals of the dicopper(II) complex [Cu₂(dpb)₂(THF)₂(H₂O)₂][BF₄]₂ **2**¹² (dpb = 2-(diphenylphosphinoyl)benzoate) in 71% (120 mg, 0.107 mmol), while the known organic product 2-(diphenylphosphinoyl)benzaldehyde **3**¹³ (51 mg, 0.17 mmol) was isolated from the mother liquid as a white powder (eq. 1). There was no reaction by stirring the THF solution of **1** in air (20% O₂) for three days. The formation of **2**



apparently involves three oxidation steps, namely Cu(I) to Cu(II) ion, phosphine to phosphin oxide,¹⁴ and benzaldehyde to benzoate species. Since treating pcho molecules with aqueous H₂O₂ in THF afforded **3** exclusively, the copper centers must play an important role in the transformation of pcho to dpb ligands. It is plausible that a reactive bis(μ -oxo)dicopper intermediate is formed,¹⁵ followed by oxygen-transfer to the formyl group to generate a carboxylate species. However, the details remain unclear at this stage.

Compound **2** forms light blue crystals, indicating the presence of d⁹ Cu(II) atoms. Thus, the ³¹P NMR shows no signal for the phosphin oxide group, likely due to the paramagnetic effects,¹⁶ and the ¹H NMR spectrum shows several broad signals in the range δ 8.7–1.9 ppm. The X-band EPR spectrum measured on a powder sample at 77 K shows $g_{\parallel} = 2.56$ and $g_{\perp} = 2.18$. The IR spectrum of **2** in a KBr pellet shows broad and intense bands at 1600 and 1368 cm⁻¹, corresponding to the $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ vibration of the bridging carboxylate group within a dinuclear species.¹⁷

The structure of **2**¹⁸ consists of discrete cations [Cu₂(dpb)₂(THF)₂(H₂O)₂]²⁺ and tetrafluoroborate counter anions. The ORTEP drawing for the cation is depicted in Fig. 1, and the selected bond distances and bond angles are collected in Table 1. There is a crystallographic center of symmetry imposed on the complex. Each dpb ligand is triden-

Table 1. Selected bond distances (Å) and bond angles (°) for compound **2**

Bond distance			
Cu–O1	1.956(1)	Cu–O2	1.939(1)
Cu–O3	1.925(1)	Cu–O4	1.959(2)
Cu–O5	2.250(2)	C1–C2	1.499(3)
C1–O1	1.256(2)	C1–O2A	1.263(2)
P1–O3	1.519(2)		
Bond angle			
O1–Cu–O2	91.97(6)	O1–Cu–O3	88.80(6)
O1–Cu–O4	172.72(6)	O1–Cu–O5	94.28(6)
O2–Cu–O3	154.71(7)	O2–Cu–O4	87.87(6)
O2–Cu–O5	105.18(6)	O3–Cu–O4	88.24(6)
O3–Cu–O5	99.96(6)	O4–Cu–O5	92.78(7)
O1–C1–C2	120.1(2)	O1–C1–O2A	123.7(2)
C1–O1–Cu	127.7(1)	C1A–O2–Cu	124.4(1)
C7–P1–O3	112.27(9)	P1–O3–Cu	122.89(8)

tate, with the carboxylic group bridging two copper centers and the phosphin oxide group σ -coordinated to one copper atom. The two copper atoms are separated by 4.46 Å. The coordination about the Cu(II) ion can be described as a distorted trigonal bipyramid (Fig. 2), where the equatorial sites are linked to a THF (O5), a phosphin oxide (O3), and a benzoate (O2) ligands, and the axial sites are linked to a water (O4) and another benzoate (O1) ligand. The Cu–O (1–4) distances are comparable, ranging from 1.925(1) Å through 1.959(2) Å, while the Cu–O5 distance to the THF

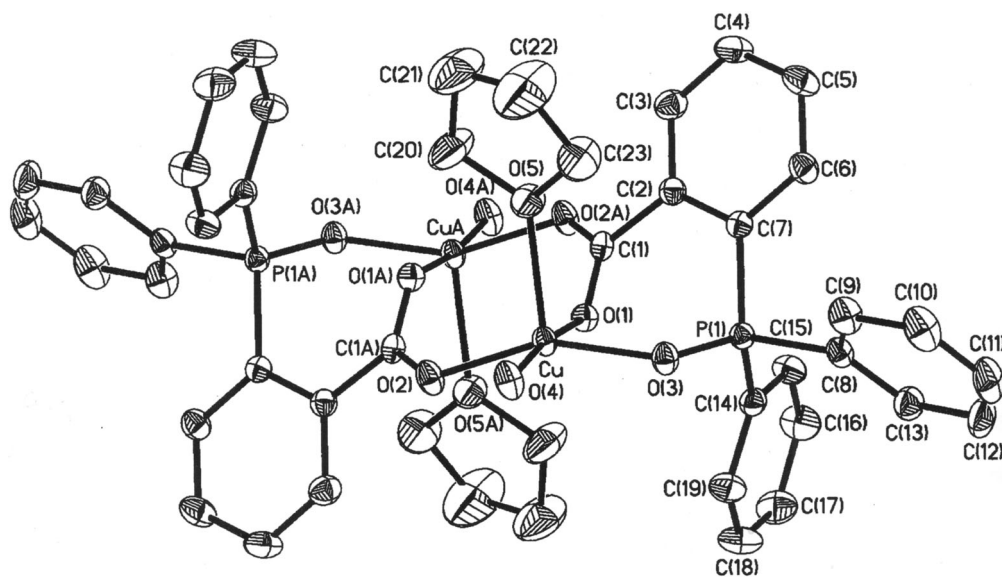


Fig. 1. Molecular structure of **2**. The BF₄⁻ anions and hydrogen atoms have been artificially omitted for clarity.



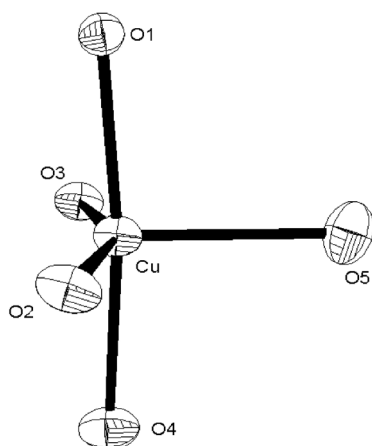


Fig. 2. The distorted trigonal bipyramidal coordination about the copper atom of **2**.

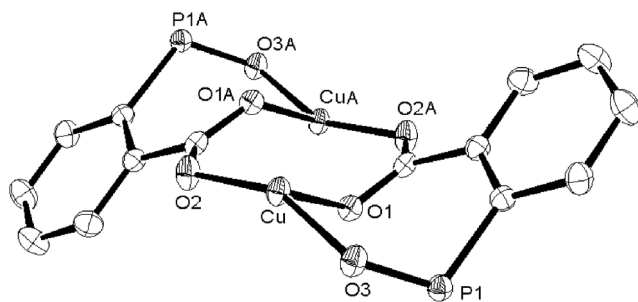


Fig. 3. Framework of **2** showing a fused pentacycle.

ligand is substantially longer, being 2.250(2) Å. The axial O1–Cu–O4 angle is 172.72(6)°. The three equatorial O–Cu–O angles sum to 359.9°, consistent with the small displacement of the copper atom from the plane (0.04 Å). However, the large, constrained O2–Cu–O3 bond angle (154.71(7)°) causes compression of the O2–Cu–O5 angle (105.18(6)°) and the O3–Cu–O5 angle (99.9(6)°) away from the idealized 120°, which should increase steric repulsions to the THF ligand. Therefore, lengthening of the Cu–O5 bond can be rationalized in terms of steric effects to relax ligand interactions. Overall, the framework of **2** can be viewed as a fused pentacycle (Fig. 3), which is unique in dicopper(II) systems.

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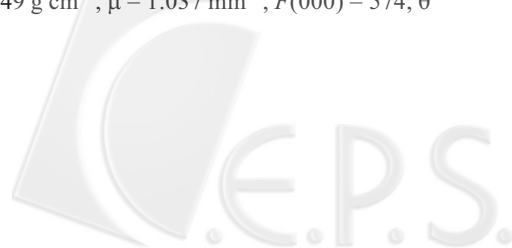
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- Characterization of **2**: MS FAB m/z : 855 $[(\text{Cu}_2(\text{dpb})_2(\text{BF}_4)]^+$. IR (KBr pellete): 3450, 3065, 1600, 1386, 1010 cm^{-1} . ^1H NMR (CD_3CN): δ 8.7 (br), 7.8 (br), 7.2 (br), 5.8 (br, Ph), 3.7 (br), 1.9 (br, THF) ppm. Anal. for $\text{C}_{46}\text{H}_{48}\text{B}_2\text{Cu}_2\text{F}_8\text{O}_{10}\text{P}_2$: Found C, 49.72; H, 4.23; Calcd. C, 49.18; H, 4.31%.
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- Crystal data of **2**: $M_f = 1123.48$, triclinic, space group $P\bar{1}$, $a = 10.10736$ Å, $b = 11.2948(7)$ Å, $c = 12.3737(8)$ Å, $\alpha = 67.534(1)^\circ$, $\beta = 68.348(1)^\circ$, $\gamma = 75.725(1)^\circ$, $V = 1204.1(1)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.549$ g cm^{-3} , $\mu = 1.037$ mm⁻¹, $F(000) = 574$, θ



range 1.87–27.50°, 316 variables refined with 5497 independent reflections to final *R* indices ($I > 2\sigma(I)$) of $R_1 = 0.0371$ and $wR_2 = 0.0905$, and $GOF = 1.046$. The crystallo-

graphic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 279033.

