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Synthesis and Structure of a CO-containing Phenoxo-bridged Dicopper(I) Complex

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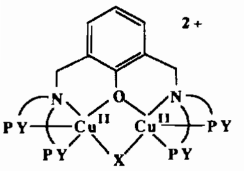
In the last few years, we and others have extensively utilized phenol-containing dinucleating ligands for copper, in attempts to model the dicopper binding sites known to occur in proteins such as hemocyanin [1] (O_2 transport in arthropods and molluscs) and tyrosinase [1, 2] (ubiquitous monooxygenase, monophenol → *o*-diphenol). This class of ligands were first developed by Robson [3] and they have generally found to be very useful in modeling ligand-bridged met (*i.e.* oxidized dicopper(II)) protein derivatives, and reduced dicopper(I) forms [4–6]. In particular, we have examined dicopper complexes of XYL–OH (PY = 2-pyridyl), which form a variety of X-bridged (e.g. $X^- = OR^-$, N_3^-, Cl^-, Br^-, $RCOO^-$) complexes $[Cu^{II}_2(XYL\text{–}O^-)(X)]^{2+}$ (1) [7, 8], and a phenoxo-bridged dicopper(I) compound, $[Cu^I_2(XYL\text{–}O^-)]^+$ (2), which binds O_2 reversibly [9].



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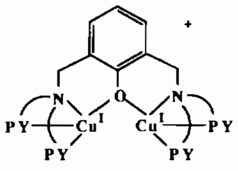
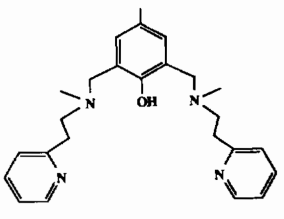
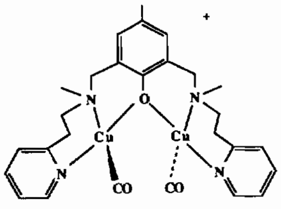


2

The XYL–OH ligand contains the tridentate ligand, PY2 (PY2 = bis([2-(2-pyridyl)ethyl]amine), and the resulting dicopper(II) complexes possess pentacoordinate Cu(II) moieties. As an attempt to systematically develop the chemistry of these types of ligands, we thought to modify XYL–OH by reducing the number of potential ligand donors to copper, possibly forming dicopper(I) compounds which were tri-coordinate, whereupon oxygenation might give stable planar tetra-coordinate dicopper(II) species. To these ends, we synthesized the new dinucleating ligand L–OH, and here we report the synthesis and structure of a bis-carbonyl adduct, $[Cu^I_2(L\text{–}O^-)(CO)_2]^+$ (3).



L–OH



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The ligand L–OH was synthesized by reaction of HCl with 1,3-bis(hydroxymethyl)-*p*-cresol, reaction of the chloromethyl product with 2-(2-methylaminoethyl)pyridine and triethylamine, followed by chromatography on alumina (1/1, acetone/ethyl acetate). The deprotonated ligand (L–OH plus NaH in diethyl ether) was then added to a suspension of two equivalents of $[Cu(CH_3CN)_4]PF_6$ in CO saturated dichloromethane. Carbon monoxide saturated Et_2O was layered onto the solution obtained after stirring for one hour, and colorless crystals deposited after several days. They were isolated by filtering and drying under a stream of CO[§].

Complex 3–PF_6 crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.545$ (3), $b = 14.317$ (3), $c = 18.772$ (4) Å, $\alpha = 84.90$ (2)°, $\beta = 79.82$ (2)°, $\gamma = 86.55$ (2)°, $V = 3301.9$ Å^3, and $Z = 4$. A total of 4588 unique reflections have been refined to an *R* value of 0.0590 (Mo Kα, $\lambda = 0.71073$ Å). The structure of a cationic dicopper(I) complex is shown in Fig. 1 and selected bond lengths and angles are given in the caption. There are two molecules in each asymmetric unit, each consisting of a phenoxo-bridged dicopper(I) moiety. Each Cu(I) ion is found in a distorted tetrahedral environment with ligation from the tertiary amino (N1, N3) and pyridyl (N2, N4) nitrogen atoms, the carbonyl carbon atom (C10, C11) and the bridging phenoxo (O1) donor. The Cu···Cu separation is 3.587 Å, comparable to the distance observed in 2 [9].

While we had hoped to investigate the dicopper(I)/O_2 chemistry with the ligand L–OH, we find in fact that in the absence of CO (as in 3), disproportionation occurs, even at low temperatures, and metallic copper is deposited. Thus stabilization of a copper(I) derivative of L–OH seems only possible by using carbon monoxide. We note that Sorrell and coworkers [10] have synthesized a ligand very similar to 3, and characterized its bis-(CO) dicopper(I) complex as well as diamagnetic phenoxo and 1,3-azido dicopper(II) species. The only difference in the two

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[§] *Anal* for $[Cu_2(L\text{–}O^-)(CO)_2](PF_6)$ (3). Calc. for $C_{26}H_{29}Cu_2F_6N_4O_3P$: C, 41.08; H, 4.04; N, 6.86. Found: C, 41.85; H, 4.21; N, 7.03%. IR (Nujol): $\nu_{CO} = 2080$ and 2068 (sh) cm^{-1}.

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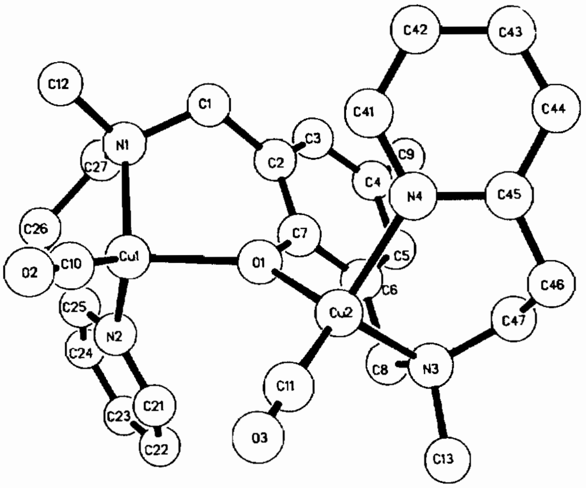

Fig. 1. ORTEP diagram of the cationic portion of complex **3**–PF_6, showing the atom labeling scheme. Selected bond lengths (Å) and angles (°) are as follows: Cu1···Cu2 3.587; Cu3···Cu4, 3.561, Cu1–O1, 2.026 (5); Cu1–N1, 2.110 (7); Cu1–N2, 2.037 (7); Cu1–C10, 1.749 (11); C10–O2, 1.118 (14), Cu2–O1, 2.016 (6); Cu2–N3, 2.106 (7); C2–N4, 2.038 (7); Cu2–C11, 1.764 (11); C11–O3, 1.111 (15); O1–Cu1–N1, 95.3 (2); O1–Cu1–N2, 97.3 (2); O1–Cu1–C10, 114.2 (4); N1–Cu1–N2, 97.4 (3); N1–Cu1–C10, 120.2 (4); N2–Cu1–C10, 126.2 (4); Cu1–O1–Cu2, 125.1 (3).

systems is that Sorrell uses a pyrazole instead of a pyridyl donor. No evidence for the formation of a dioxygen adduct with copper was observed in the case of reaction of O_2 with the pyrazole-containing dicopper(I) compound. However, we suggest that further modifications in this type of ligating system could lead to interesting new $Cu(I)_n/O_2$ chemistry.

Acknowledgement

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