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Synthesis and X-ray Crystal Structure of a Trinuclear Copper(I) Cluster

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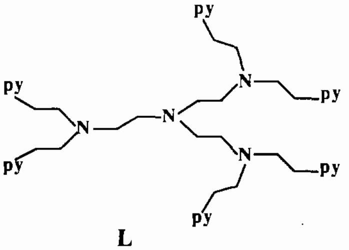
In connection with biomimetic studies of copper-mediated reversible dioxygen binding or activation (i.e. monooxygenation), we have been studying the interactions of O_2 with mono- and dinuclear copper(I) complexes [1]. Most recently, we are also turning our attention to systems involving tri- or tetranuclear copper clusters. A trinuclear copper cluster may be of importance in a number of the multicopper blue oxidases, such as ascorbate oxidase and laccase [2–5]. These multicopper blue oxidases catalyze the four-electron reduction of dioxygen to water with concomitant one-electron oxidation of a variety of substrates, such as polyphenols, aromatic polyamines, and ascorbate [6–9]. These enzymes have been described as containing different types of Cu environments, designated as Type 1, Type 2 and Type 3 centers, based on their spectroscopic properties [10]. Using azide ion to probe the active site chemistry and spectroscopy of laccase, Solomon and coworkers have demonstrated that a single N_3^- binds to a trinuclear Cu(II) site, bridging one of the magnetically coupled Cu(II) Type 3 ions and the paramagnetic Type 2 center [2, 4, 5]. Following suggestions that a laccase-like trinuclear active site occurs in ascorbate oxidase (AO) [3, 11], an important and recent X-ray structural determination on oxidized AO from zucchinni by Messerschmidt and coworkers [11] unambiguously demonstrated the existence of this trinuclear center.

The functional unit has four copper ions bound in mononuclear and trinuclear moieties, as shown. The isolated Type 1 'blue' copper is bound to two histidines, a cysteine and a methionine ligand. The trinuclear cluster has a biologically unprecedented structure with the three copper ions arranged in a near isosceles triangle, as shown.

We are using a biomimetic approach in an attempt to understand the function of the trinuclear copper cluster in the molecular mechanism of the four-electron reduction of dioxygen to water in multicopper oxidases. In this connection, we have begun by exploring the chemistry of the trinucleating ligand L. In this report, we describe the synthesis and the crystal structure of a trinuclear copper(I) cluster, $[Cu_3L(PPh_3)_2](PF_6)_3 \cdot 2CH_3CN$.



L

py = 2-pyridyl

The ligand L was synthesized straightforwardly by the acid-catalyzed reaction of an excess of 2-vinylpyridine with tris(2-aminoethyl)amine (tren) in CH_3OH, followed by chromatography on alumina (9/1, ethyl acetate/methanol). A tricopper(I) complex, $[Cu_3L(PPh_3)_2](PF_6)_3 \cdot 2CH_3CN$, was synthesized by reaction of $[Cu(CH_3CN)_4](PF_6)$ with the ligand L under Ar in CH_2Cl_2 containing PPh_3 (to help stabilize Cu(I)), followed by precipitation using diethyl ether, and recrystallization in acetonitrile/isopropanol. The recrystallization process produced pale yellow X-ray quality crystals. Satisfactory elemental analyses have been obtained: IR (Nujol), 845 (PF_6^-, s, br) cm^{-1}.

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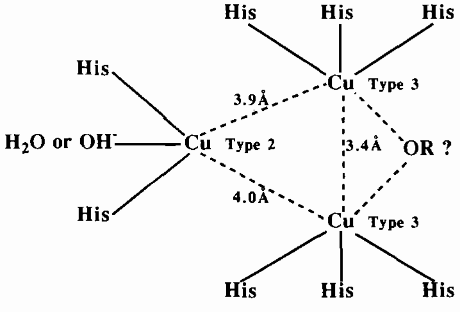
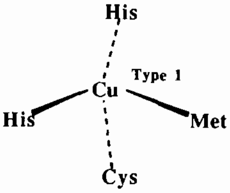


Type 1 Cu - Type 3 Cu ≅ 12.2Å
Type 1 Cu - Type 2 Cu ≅ 14.8Å



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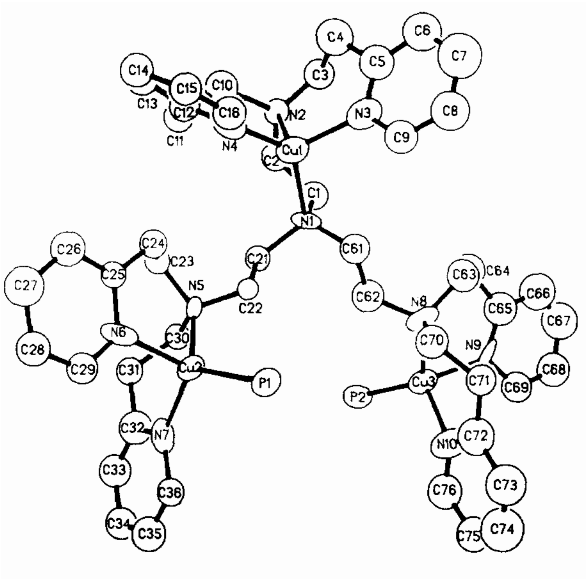

Fig. 1. ORTEP diagram of the cationic portion of complex $[Cu_3L(PPh_3)_2](PF_6)_3\cdot 2CH_3CN$, showing the atom labeling scheme. The phenyl groups of the PPh_3 ligands have been omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows: Cu1···Cu2, 6.056; Cu2···Cu3, 7.671; Cu1···Cu3, 7.433; Cu1–N1, 2.132(22); Cu1–N2, 2.134(21); Cu1–N3, 1.978(33); Cu1–N4, 1.988(30); Cu2–P1, 2.196(9); Cu2–N5, 2.158(19); Cu2–N6, 2.073(26); Cu2–N7, 2.068(25); Cu3–P2, 2.187(11); Cu3–N8, 2.191(25); Cu3–N9, 2.013(31); Cu3–N10, 2.017(25); N1–Cu1–N2, 87.7(9); N1–Cu1–N3, 110.6(12); N1–Cu1–N4, 131.8(11); N2–Cu1–N4, 99.2(11); N2–Cu1–N3, 100.1(10), N3–Cu1–N4, 114.9(12); P1–Cu2–N5, 121.0(7); P1–Cu2–N6, 116.1(6); P1–Cu2–N7, 117.7(7); N5–Cu2–N6, 93.5(8); N5–Cu2–N7, 100.0(8); N6–Cu2–N7, 104.6(10); P2–Cu3–N8, 121.5(8); P2–Cu3–N9, 118.7(7): P2–Cu3–N10, 118.4(9); N8–Cu3–N9, 95.1(11); N8–Cu3–N10, 97.3(9); N9–Cu3–N10, 100.9(12).

The complex $[Cu_3L(PPh_3)_2](PF_6)_3\cdot 2CH_3CN$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 23.493(7)$, $b = 15.555(6)$, $c = 27.592(10)$ Å; $\alpha = 90.00$, $\beta = 107.66(2)$, $\gamma = 90.00°$, $V = 9607.9$ Å^3 and $Z = 4$. A total of 11802 unique reflections have been refined to a current R value of 0.1049 (Mo Kα, $\lambda = 0.71073$ Å). The structure of a cationic tricopper(I) complex is shown in Fig. 1, and selected bond lengths and angles are given in the caption. There are four discrete molecules in the unit cell, each consisting of an unsymmetrical tricopper(I) moiety. Two of the copper(I) ions (Cu2 and Cu3) are found in a distorted tetrahedral environment with coordination to the tertiary amino (N5, N8) and pyridyl (N6, N7, N9, N10) nitrogen atoms, as well as the phosphorus atoms (P1, P2) of the triphenylphosphine ligand. However, one of the three copper(I) ions (Cu1) possesses a distorted trigonal pyramidal coordination with ligation to two pyridyl (N3, N4) and two amino (N1, N2) nitrogen atoms. The two pyridyl ligands and an amino nitrogen (N1) form the basal trigonal plane, with the amino nitrogen atom N2 in the apical position. A small displacement (0.19 Å) of the Cu1 atom from the basal trigonal plane reflects the distortion from trigonal pyramidal geometry, similar to that found in other tetra-coordinate trigonal pyramidal Cu(I) complexes [12, 13]. The unsymmetrical nature of the coordination in this cluster complex is also demonstrated by the interatomic Cu(I)···Cu(I) distances with Cu1···Cu2 = 6.056 Å, Cu2···Cu3 = 7.671 Å and Cu1···Cu3 = 7.433 Å.

This initial study demonstrates the feasibility of generating and characterizing unsymmetrical trinuclear copper clusters possessing aromatic nitrogen ligands. We are in the process of further developing the chemistry in order to examine relevant $Cu(II)_3$ structures and $Cu(I)_3/O_2$ reactivity with the ligand L and other new trinucleating ligands.

Supplementary Material

Tables of fractional atomic coordinates, thermal parameters, interatomic parameters, structure factor amplitudes and a full ORTEP diagram are available on request from the authors.

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