New Trinuclear Copper Complexes Using Cage-Type Ligands: Model for Multicopper Oxidases

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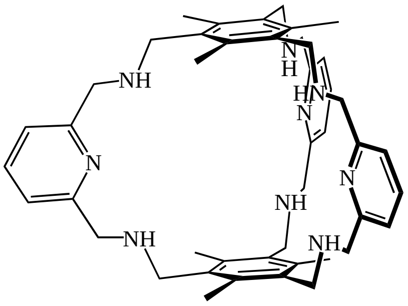
Multicopper oxidases, such as ascorbate oxidase, laccase, ceruloplasmin proceed a four-electron reduction of O_2 to H_2O at their trinuclear copper centers. The model compounds for the multicopper centers of these enzymes have been synthesized for the purpose of elucidating their reaction mechanisms. The X-ray crystal structure analyses of ascorbate oxidase revealed that three Cu···Cu distances of triangular copper atoms are almost the same in the range 3.7-4.5 Å. The three coordination planes around these copper ions cross each other. We synthesized C_3 symmetric cage-type ligand L and prepared the trinuclear copper core structures inside the cage as biomimetic models for multicopper sites of these enzymes. By the use of a cage-type ligand, the trinuclear center will be stabilized further.



In this report, we describe the preparation and characterization of trinuclear copper(I) and copper(II) complexes with L, $[\mathrm{Cu^{I}_3LCl_3}]$ (**1**) and $[\mathrm{Cu^{II}_3L}(\mu_3\text{-}\mathrm{CO_3})](\mathrm{ClO_4})_4$ (**2**). X-ray analysis for **1** clearly showed that the two copper(I) ions have trigonal planar environments and the other one has a tetrahedral environment with two nitrogen atoms of L and one or two chloride atoms. That for **2** also showed that the square planar coordination around copper(II) ions were almost equivalent and the equatorial positions were occupied with three nitrogen atoms of L and an oxygen atom of μ_3-type bridging carbonate. These coordination planes of copper atoms in **1** and **2** were crossed, the averaged distances between the two copper atoms being in the range 2.72-5.78 and 4.90-4.93 Å for **1** and **2**, respectively. Therefore, the cage-type ligand L is considered to promote the formation of tricopper cores with almost the same steric requirements as multicopper sites of enzymes. Electrochemical studies indicated that the tricopper(I) core of **1** was oxidized stepwise in the way of one-electron oxidation $\mathrm{Cu_3(I)/Cu(II)Cu_2(I)}$ at $E_{1/2} = -597$ mV (v.s. $\mathrm{Fc/Fc^+}$), followed by two-electron oxidation of the other. The reaction of tricopper(I) complex **1** and dioxygen will also be described.