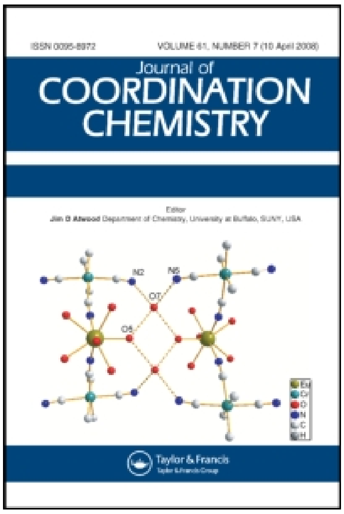

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SHORT COMMUNICATION

X-ray Structure Analysis of a Dicopper Complex of a New Binucleating Ligand Containing a para-Xylyl Connecting Group; Large Cu···Cu Separation in $[(CuCl_2C_{18}H_{20}N_3)_2]\cdot 2H_2O$

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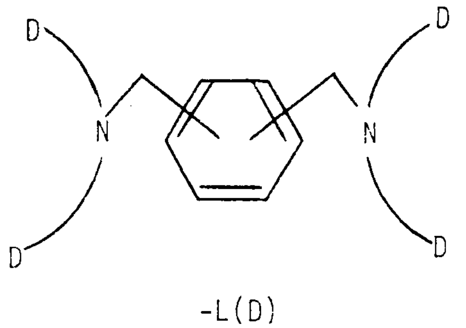
Bimetallic coordination complexes containing two copper ions in close proximity are currently under extensive study. These structural units are known to be important in biological reactions involving molecular oxygen[1] including oxygen transport,[2] oxygen activation in the copper monooxygenase tyrosinase[3] and the reduction of O_2 in the copper oxidases.[4] Examination of model systems is necessary to help elucidate the nature and mechanism of action of the copper containing active sites. In addition, model systems are of interest in studies of metal-metal interactions,[5] mixed valence compounds[6] and redox catalysts.[7]

As part of our own investigations into the chemistry of binuclear Cu(I) and Cu(II) complexes,[8] we have initiated studies utilizing the ligand system -L(D) (D = donor group), where two tridentate ligand donor groups are separated by an ortho-, meta-, or para-xylene bridge. A *p*-xylyl system containing phosphine donor atoms was first reported by Taqui Khan and Martell,[9] and this, and related *p*-xylyl ligands have been shown to be effective in the formation of binuclear complexes.[9,10] A binuclear cobalt complex containing *p*-L(NH_2),[11] and a bimetallic Cu(I) species with a *p*-xylyl group bridging two macrocyclic ligands[12] have recently been shown to bind O_2 reversibly. However, no x-ray structural studies have been reported on any of these systems. Here, we present the first x-ray structural characterization of a binuclear Cu(II) complex of a new *p*-xylyl ligand.



-L(D)

The ligand, *p*-L(py) where py = 2-pyridyl, was synthesized by the reaction of bis(2-(2-pyridyl)-ethyl)amine with α,α'-dibromo-*p*-xylene in methanol in the presence of K_2CO_3. Reaction of *p*-L(py) with two equivalents of $CuCl_2$ in methanol, followed by recrystallization of the resulting precipitate from DMF/CH_3CN gave green crystals consistent with the formula $[Cu_2Cl_4C_{36}H_{40}N_6]\cdot 2H_2O$. The complex crystallizes in the monoclinic space group $P2_1/C$ with $a = 8.752(4)$ Å, $b = 15.149(9)$ Å, $c = 14.468(5)$ Å, and $\beta = 98.52(3)°$. 1907 independent reflections with $F_{obs} \geqslant 2.58\sigma(F_{obs})$, Mo K$\alpha$ radiation, were used in the structure determination to yield a current value for the error index, R, of 0.049 with all nonhydrogen atoms having anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions in the final cycles of least-square refinement as fixed contributors.

The molecule exists as a discrete dimers with a crystallographically imposed center of symmetry relating the two halves of the dimeric unit which is located at the center of the benzene ring, Figure 1. There are two dimers per unit cell.

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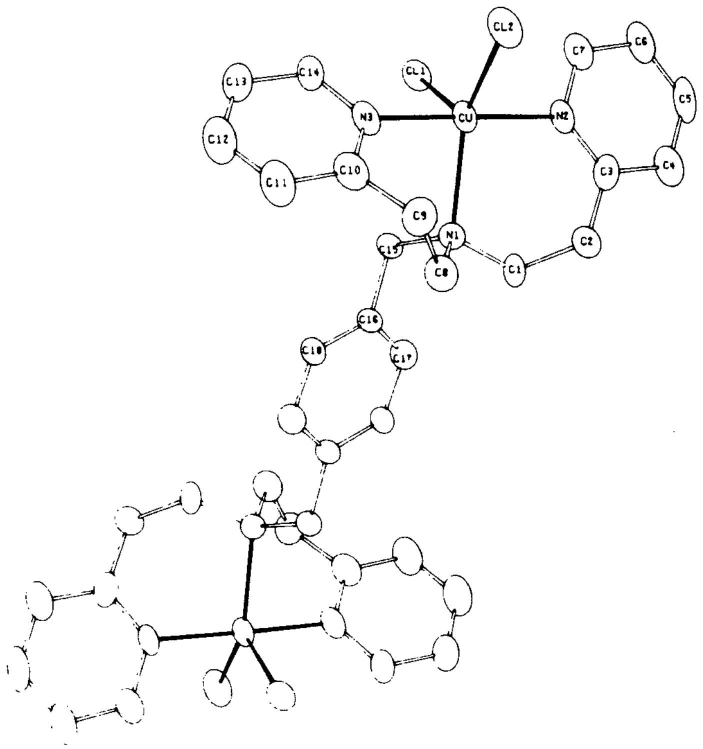

FIGURE 1 ORTEP representation of $[(CuCl_2C_{18}H_{20}N_3)_2]$ showing the atom labeling scheme. Relevant bond lengths (Å) and angles (deg) are: Cu-Cl(1), 2.446(2); Cu-Cl(2), 2.342(2); Cu-N(1), 2.214(5); Cu-N(2), 2.012(6); Cu-N(3), 2.004(6); Cu. . . Cu, 11.71; Cl(1)-Cu-Cl(2), 118.9(1); Cl(1)-Cu-N(1), 102.9(1); Cl(2)-Cu-N(1), 138.0(1); N(1)-Cu-N(2), 93.9(2); N(1)-Cu-N(3), 85.7(2); N(2)-Cu-N(3), 178.1(2).

The copper atom exhibits distorted trigonal bipyramidal coordination geometry. The two pyridyl nitrogens occupy the axial positions while the equatorial plane is shared by the amine nitrogen and the two chlorides. The copper atom is not significantly displaced from the equatorial plane as is expected since both axial positions are occupied by similar donor groups. The copper-nitrogen distances are similar to those reported previously.[13] The copper-N(amine) distance, 2.214 Å, is greater than the copper-N(pyridyl) distances, 2.012 Å and 2.004 Å, which are identical within a two sigma criterion. The copper-chloride distances, 2.446 Å and 2.342 Å, differ significantly, consistent with the lack of crystallographic symmetry about the copper atom. Some relevant bond lengths and angles are included in Figure 1.

It has been demonstrated or suggested that coordinating groups in these *p*-xylyl ligands may adopt configurations which enhance metal-metal interactions and/or cooperative activation of small molecules such as O_2.[11,12] The observation of large copper-copper separations for this complex suggests that *inter*molecular interactions could occur or that these binuclear copper systems are conformationally mobile allowing for *intra*molecular cooperative interactions.

Figure 1 shows that the tridendate donor units extend away from each other from the para positions in the benzene ring, with the result that the two copper coordination polyhedra are well separated, the copper-copper distance being 11.71 Å. Preliminary electrochemical and electron spin resonance studies are consistent with the maintenance of large metal-metal distances in solution. Cyclic voltammetric measurements of *p*-L(py)Cu_2Cl_4 reveal the presence of reversible one electron reductions for each copper atom at 0.40 V *vs*. SCE (DMF solvent, 0.1 M TBAP supporting electrolyte, Pt electrode). The epr spectrum (77°K, DMF–$CHCl_3$) shows no evidence for any copper-copper interactions and gives a rhombic spectrum with $g_1 = 2.23, A_1 = 123 \times 10^{-4}$ $cm^{-1}, g_2 = 2.06, g_3 = 2.00$, consistent with magnetically dilute copper ions in a distorted five-coordinate environment.[14] Extensive studies of Cu(I) and Cu(II) complexes of *p*-L(py) and related ligands are in progress.

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