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Synthesis and Structure of a Novel Dicopper(I) Complex of a New Binucleating Ligand

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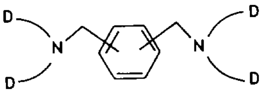
Bimetallic coordination complexes containing two copper ions in close proximity are currently under extensive study. These structural units are thought to be important in biological reactions involving molecular oxygen [1], including oxygen transport [2] as well as oxygen activation in the mono-oxygenases tyrosinase [3] and dopamine beta hydroxylase [4]. Examination of model systems is necessary to help elucidate the nature and mechanism of action in these copper containing active sites. In addition, such binuclear copper complexes are of interest in studies of metal–metal interactions [5], mixed valence compounds [6] and a redox catalysts [7].

We are particularly interested in the synthesis, characterization and reaction chemistry of binuclear Cu(I) compounds containing nitrogen and sulfur donor ligands. Cu(I) is known to interact with O_2 in the biological systems [8] and in spite of the fact that Cu(I) is an intimate part of the Cu(I)–Cu(II) redox couple, its coordination chemistry is rather undeveloped.

As part of extensive investigations into the chemistry of binuclear copper complexes [9, 10], we are utilizing a new series of binucleating ligands, –XYL(D), D = nitrogen or sulfur donor group, where two tridentate ligand donor groups are separated by an *ortho-*, *meta-*, or *para*-xylene bridge. Cobalt [11] and copper [12] complexes of related *para*-xylyl systems react reversibly with O_2 and we have published the crystal structure of the binuclear copper complex Cu_2Cl_4[*p*-XYL(py)]·$2H_2O$ [10]. Recently we reported the first example of a *meta*-xylyl copper complex, showing that when a Cu(I) derivative of *m*-XYL(py) reacts with O_2, hydroxylation of the xylyl ligand occurs, giving a phenolate bridged binuclear Cu(II) complex [13].



-XYL(D)

–XYL(py)
py = 2-pyridyl
–XYL(SEt)
SEt = -ethylthio

In order to study the chemistry of possible Cu(I) species involved in this important reaction, we have reacted Cu(I) with *p*-XYL(SEt), containing thioether donor groups which should help stabilize the reduced state of copper [14]. Here, we report the syntheses and X-ray crystal structure determination of [Cu_2(*p*-

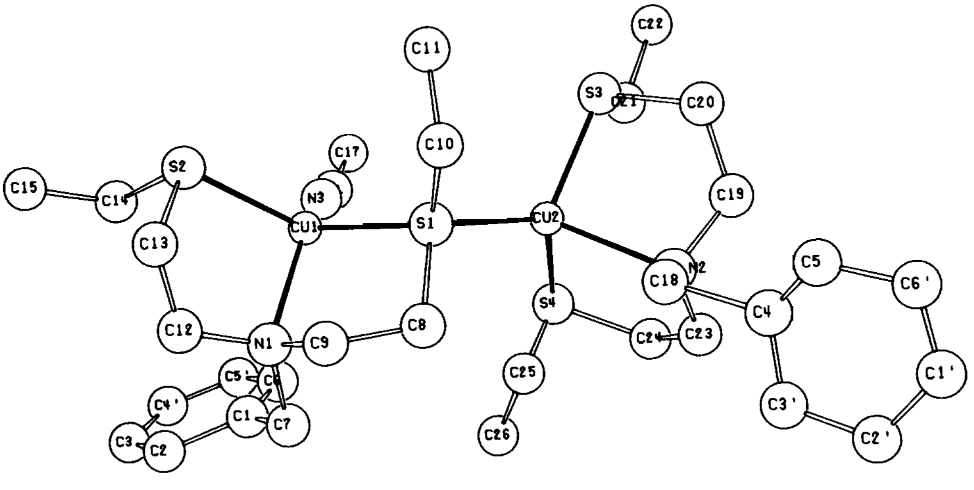


Fig. 1. A perspective view of the $(Cu_2C_{26}H_{47}N_3S_4)^{+2})$ unit, showing the atom labelling scheme. Relevant bond lengths (Å) and angles (deg) are: Cu1–S1, 2.312(5); Cu–S2, 2.276(6); Cu1–N1, 2 226(10); Cu1–N3, 1.853(16); Cu2–S1, 2.252(5); Cu2–S3, 2.269(5); Cu2–S4, 2.273(7); Cu2–N2, 2.182(12); N3–C16, 1.13(2); S1–Cu1–S2, 123.5(2); S1–Cu1–N1, 88.4(3), S1–Cu1–N3, 107.0(4), S2–Cu1–N1, 89.6(3); S2–Cu1–N3, 111.6(5); N1–Cu1–N3, 137.7(5); S1–Cu2–S3, 114.2(2), S1–Cu2–S4, 118.9(2); S1–Cu2–N2, 122.2(4); S3–Cu2–S4, 115.9(2); S3–Cu2–N2, 89.9(3); S4–Cu2–N2, 90.4(4); Cu1–N3–C16, 177.4(12).

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XYL(SEt))(CH$_3$CN)](PF$_6$)$_2$, which contains repeating dicopper(I) units in a novel coordination environment.

The ligand, *p*-XYL(SEt) was synthesized by reaction of bis(2-ethylthio)ethylamine with 2,2′-dibromo-*p*-xylene in ethyl acetate in the presence of diisopropylethylamine. Reaction with two equivalents of Cu(CH$_3$CN)$_4$PF$_6$ in dichloromethane under argon resulted in complete dissolution of starting materials. Precipitation with diethyl ether, and recrystallization from CH$_2$Cl$_2$–Et$_2$O gives colorless crystals.

$$2\mathrm{Cu(CH_3CN)_4PF_6} + p\text{-}\mathrm{XYL(SEt)} \rightarrow [\mathrm{Cu_2}(p\text{-}\mathrm{XYL,SEt})(\mathrm{CH_3CN})](\mathrm{PF_6})_2$$

1

Crystal data. Cu$_2$C$_{26}$H$_{47}$N$_3$S$_4$(PF$_6$)$_2$ crystallizes in the monoclinic space group P2$_1$/c with a = 12.005(2) Å, b = 14.376(2) Å, c = 22.753(4) Å, β = 103.54(1)°, V = 3817 Å^3 and Z = 4. A total of 1565 symmetry-independent reflections with $F_{obs} \geqslant 6\sigma F_{obs}$ (MoKα, $\bar{\lambda}$ = 0.71073 Å) contributed to the solution, which has been refined to the current residuals R = 0.0736, R$_w$ = 0.0572.

In the solid state, *1* is polymeric, with the structure of the basic repeating sequence as shown in Fig. 1. Two types of Cu(I) ions are found, both in similar but highly distorted tetrahedral environments. Cu(1) is coordinated by the tridentate NS$_2$ group, (N(1), S(1) and S(2)), and an acetonitrile molecule. One of these thioether sulfur atoms, S(1), acts as a bridging bidentate group and its coordination to Cu(2) provides the means for polymer formation. The NS$_2$ tridentate of the adjacent binucleating xylyl ligand provides the remaining ligands for Cu(2) giving it an overall NS$_3$ donor atom set.

Compound *1* represents one of the few structures known of a Cu(I) complex containing a binucleating ligand [15] thus demonstrating the utility of these xylyl ligands in studying the chemistry of dicopper(I) species. The strong preference for Cu(I) binding to thioether ligands results in polymer formation through a relatively rare bridging coordination [16], resulting in different coordination environments for the two copper ions. In view of the fundamental importance of studying the interactions of binuclear Cu(I) with O$_2$ and/or oxidizable substrates in relationship to the copper proteins, we are continuing to examine this and related complexes and their reaction chemistry.

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