Synthesis and Characterization of a Novel Dicopper(I) Complex of a Thiaether Containing *meta*-Xylyl Binucleating Ligand

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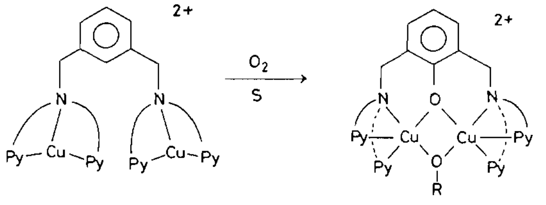
We are currently investigating the chemistry of new bimetallic copper(I) and copper(II) complexes with a number of binucleating ligand systems. Such studies are relevant to the development of redox and oxygenation catalysis with copper. Biological binuclear centers are thought to occur in the oxygen carrier hemocyanin [1, 2], the monooxygenase tyrosinase [1, 3] and the other 'type 3' copper centers found in the multicopper blue oxidases. All of these copper proteins are important in biological reactions involving dioxygen. It is well established that it is the reduced state of copper which interacts with dioxygen in these systems [4], and so studies of the coordination chemistry and reactivity of new cuprous compounds are of interest.

We recently reported a novel reaction of a new binucleating ligand, XYL-D (D = a nitrogen or sulfur donor group), where a dinuclear three-coordinate complex, $Cu(I)_2XYLpy_2^{+2}$, *1* (py2 = bis(2-(2-pyridyl)-ethyl)amine) [5], reacts with O_2, resulting in oxygenation of the xylyl ligand and concomitant formation of a phenoxy-bridged binuclear Cu(II) complex [5, 6]. This reactivity closely resembles the action of the copper monooxygenases such as tyrosinase and dopamine beta-monooxygenase [6b]. The hydroxylation reaction does not occur when the pyl analog (pyl = bis(2-pyridylmethyl)amine) is utilized, nor if related para-substituted xylyl ligands are employed.



1

R = Me, S = MeOH
R = H , S = CH_2Cl_2

To better understand the coordination requirements involved in Cu(I)–O_2 activation, it is important to characterize Cu(I) derivatives of *meta*–XYL-D ligands in order to probe their coordination tendencies, metal–metal separations and interactions, and reactivity patterns. Thioether ligands are known to stabilize Cu(I) relative to their Cu(II) analogs [7], and in this communication we report the results of a X-ray structural study of the cuprous derivative of *meta*-XYL-SEt (SEt = ethylthioether).

The ligand m-XYL-SET was synthesized by reaction of bis(2-ethylthio)ethylamine with 2,2'-dibromo-m-xylene in ethyl acetate in the presence of diisopropylethylamine. Reaction with two equivalents of $Cu(CH_3CN)_4PF_6$ [8] in dichloromethane under argon results in dissolution of the cuprous starting material. Precipitation to give colorless crystals of the product *2* was effected by slow diffusion of diethylether into the dichloromethane solution under argon.*

$$2Cu(CH_3CN)_4PF_6 + \text{m-XYL-SEt} \longrightarrow Cu_2(\text{m-XYL-SEt})(CH_3CN)_2(PF_6)_2$$

2

$Cu_2C_{28}H_{54}N_4S_4(PF_6)_2$, *2*, crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.153(3)$, $b = 20.459(5)$, $c = 14.181(3)$ Å, $\beta = 97.87(2)°$, $V = 4355$ Å^3 and $Z = 4$. A total of 1923 symmetry independent reflections with $F_{obs} \geq \sigma 4\ F_{obs}$ were refined to yield the current residuals of R = 0.0910 and Rw = 0.0816 (Mo Kα, $\bar{\lambda} = 0.71069$ Å).

In contrast to the structure of the analogous complex derived from *para*-XYL-SEt which was previously reported [9], the structure of 2 (Fig. 1) is a discrete binuclear complex. Each cuprous ion is in an analogous chemical environment exhibiting tetracoordination with ligation to two thioether sulfur atoms and an amino nitrogen atom from the NS_2 tridentate moiety as well as a fourth coordinated acetonitrile molecule. As has been found for other structures of *meta*- or *para*-XYL ligand complexes which do not possess potentially bridging ligands [5, 10], the cuprous ion moieties are well separated in *2*, Cu...Cu = 9.949(5) Å.

The coordination geometry for each crystallographically independent cuprous ion is distorted tetrahedral as indicated by the dihedral angle of N1Cu1N2/S1Cu1S2 = 89°. Distortions come about because of the chelating nature of the NS_2 tridentate ligand. In a variety of structures of both mono- and binuclear Cu(I) complexes containing this NS_2 tridentate [9, 11], the Cu–N, Cu–S distances and

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**Analysis*: Calcd for $Cu_2C_{28}H_{54}N_4S_4(PF_6)_2$: C, 33.91; H, 5.45; N, 5.65. Found C, 34.13; H, 5.17; N, 5.03.

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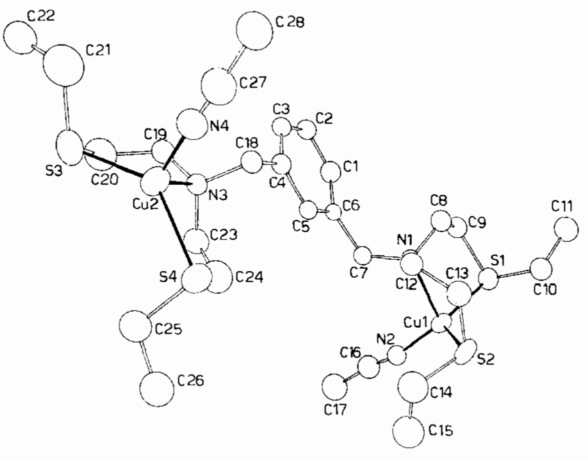

Fig. 1. ORTEP diagram of the $Cu_2(C_{28}H_{54}N_4S_4)$ cation, *2*, showing the atom labelling scheme. Selected bond lengths (Å) and angles (deg) are Cu... Cu, 9.949(5), Cu1–S1, 2.286(6); Cu1–S2, 2.273(7); Cu1–N1, 2.211(12); Cu1–N2, 1.878(15); Cu2–S3, 2.287(7); Cu2–S4, 2.239(10); Cu2–N3, 2.206(13); Cu2–N4, 1.859(17); S1–Cu1–S2, 120.0(2); S1–Cu1–N1, 89.0(4); S1–Cu1–N2, 116.1(5); S2–Cu1–N1, 91.1(4); S2–Cu1–N2, 119.2(5); N1–Cu1–N2, 112.0(6); S3–Cu2–S4, 104.1(3); S3–Cu2–N3, 90.0(4); S3–Cu2–N4, 114.9(6); S4–Cu2–N3, 89.2(4); S4–Cu2–N4, 134.8(6); N3–Cu2–N4, 111.9(6).

the N–Cu–S, S–Cu–S angles are seen to be essentially invariant. The present structure is consistent with these observations, where the S–Cu–S angles are close to 120° and the N1–Cu–S (or N3–Cu–S) angles are *ca.* 90° (See Figure Caption). The Cu(I)–SSR′ and Cu(I)–Namine bond lengths are in the range found for these bonds in related cuprous complexes [9, 11].

The coordinated acetonitrile molecules are essentially linear, having Cu–N bond distances (1.88 and 1.86 Å) which are short by comparison with other CH_3CN containing Cu(I) complexes [12]. Two ν_{CN} bands in the infra-red at 2280 and 2310 cm^{-1} are observed comparing closely with the tetracoordinate cationic complex $Cu(CH_3CN)_4^+$ [13].

Solutions of *2* are oxygen sensitive, and a green color develops in dichloromethane. The nature of this product is under investigation to determine if hydroxylation occurs as described above for the pyridine ligand system. Complex *2* is very poorly behaved electrochemically as determined by cyclic voltammetry.* Multiple peaks, including those due to adsorption are observed. Upon addition of 1-methylimidazole (MeIm) or 2-picoline, the redox behavior is improved. Addition of 1.5 equivalents of MeIm per Cu(I) ion gives a quasireversible wave with $E_{1/2}$ = +0.18 Volts *vs.* NHE suggesting coordination by MeIm in place of acetonitrile. This would give binuclear cuprous ion centers with N_2S_2 coordination environments which are expected to be redox active by analogy to other compounds [15].

Further investigations of Cu(I) and Cu(II) derivatives of -XYLSEt including their redox behavior and dioxygen chemistry in the presence of oxidizable substrates are in progress.

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*Dimethylformamide solvent; 0.11 *M* tetra-n-butyl ammonium hexafluorophosphate supporting electrolyte; glassy carbon electrode. Potentials are *versus* NHE where ferrocene is used as calibrant [14].

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References

1 E. I. Solomon, in T. G. Spiro, (Ed.) 'Metal Ions in Biology', Vol. 3; Wiley–Interscience, New York, 1981, pp. 41–108.
2 (a) R. J. P. Williams, in J. V. Bannister, (Ed.) 'Structure and Function of Hemocyanin'; Springer Verlag, Heidelberg, 1977. (b) R. Lontie, R. Witters and H. Sigel (Ed.), in 'Metal Ions in Biological Systems', Vol. 13; Marcel Dekker, New York, 1981, pp. 229–258.
3 (a) W. H. Vanneste and A. Zuberbuhler, in O. Hayishi, Ed., 'Molecular Mechanisms of Oxygen Activation'; Academic Press, New York, 1974, pp. 371–404. (b) K. Lerch, in H. Sigel, Ed., 'Metal Ions in Biological Systems', Vol. 13; Marcel Dekker, New York, 1981, pp. 143–186.
4 A. D. Zuberbuhler, in H. Sigel, Ed., 'Metal Ions in Biological Systems', Vol. 5; Marcel Dekker, New York, 1976, pp. 325–367.
5 K. D. Karlin, Y. Gultneh, J. P. Hutchinson and J. J. Zubieta, *Am. Chem. Soc.*, in press.
6 (a) K. D. Karlin, P. L. Dahlstrom, S. N. Cozzette, P. M. Scensny and J. Zubieta, *J. Chem. Soc. Chem. Commun.*, 881 (1981). (b) K. D. Karlin, J. C. Hayes, R. W. Cruse, J. P. Hutchinson, J. R. Hyde and J. Zubieta, submitted.
7 E. R. Dockal, T. E. Jones, W. F. Sokol, R. J. Engerer, D. B. Rorabacher and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, *98*, 4322 (1976).
8 G. J. Kubas, *Inorg. Synth.*, *19*, 90 (1979).
9 K. D. Karlin, J. R. Hyde and J. Zubieta, *J. Inorg. Chim. Acta*, *66*, L23 (1982).
10 K. D. Karlin, P. L. Dahlstrom, L. T. DiPierro, R. A. Simon and J. J. Zubieta, *J. Coord. Chem.*, *11*, 61 (1981).
11 (a) K. D. Karlin, P. L. Dahlstrom, M. L. Stanford and J. Zubieta, *J. Chem. Soc. Chem. Commun.*, 465 (1979). (b) K. D. Karlin, P. L. Dahlstrom, J. R. Hyde and J. Zubieta, *J. Chem. Soc. Chem. Commun.*, 906 (1980). (c) K. D. Karlin, J. C. Hayes, P. L. Dahlstrom and J. Zubieta, to be submitted.
12 B. N. Storhoff and H. C. Lewis, Jr., *Coord. Chem. Rev.*, *23*, 1 (1977).
13 (a) B. J. Hathaway, D. G. Holah and J. D. Postlethwaite, *J. Chem. Soc.*, 3215 (1961). (b) T. Ogura, *Trans. Met. Chem.*, *1*, 179 (1976).
14 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, *19*, 2854 (1980).
15 K. D. Karlin and S. E. Sherman, *Inorg. Chim. Acta*, *65*, L39 (1982).