Activation of O_2 by a Binuclear Copper(I) Compound. Hydroxylation of a new Xylyl-binucleating Ligand to produce a Phenoxy-bridged Binuclear Copper(II) Complex; *X*-Ray Crystal Structure of $[Cu_2\{OC_6H_3[CH_2N(CH_2CH_2py)_2]_2\text{-}2,6\}(OMe)]$ (py = 2-pyridyl)

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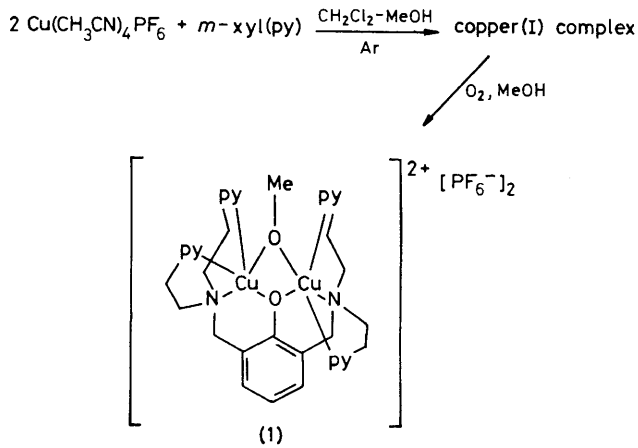
Summary Reaction of O_2 with a binuclear Cu^I species derived from a new *meta*-xylyl-binucleating ligand, *NNN'N'*-tetrakis[2-(2-pyridyl)ethyl]-α,α'-diamino-*m*-xylene [*m*-xyl(py)], has resulted in hydroxylation of the ligand to produce the binuclear Cu^{II} complex (**1**); the *X*-ray crystal structure of the dication of (**1**) shows two pentaco-ordinate Cu^{II} ions bridged by the phenoxy-group of the ligand and a methoxy-group.

WE are investigating the chemistry of new bimetallic copper(I) (especially reactions with O_2) and copper(II) complexes of a number of binucleating ligand systems[1,2] which may be important in biological reactions involving molecular oxygen,[3] such as oxygen transport[4] and oxygen activation in the copper mono-oxygenases tyrosinase[5] and dopamine β-hydroxylase.[6] Of particular interest are copper complexes which contain the new binucleating ligands

xyl(d)

xyl(d) (d = a nitrogen or sulphur donor-group; xyl = *NNN'N'*-tetra-alkyl-α,α'-diaminoxylene), in which two tridentate ligand-donor groups are separated by an *ortho*-, *meta*-, or *para*-xylene bridge (*para*-xylyl ligands were first reported by Taqui-Khan and Martell[7]). Cobalt[8] and copper[9,10] complexes of related *para*-xylyl systems react reversibly with O_2 and we have reported the crystal structure of a binuclear copper complex which contains *p*-xyl(py) ligands (py = 2-pyridyl).[2] In this communication, we report the first copper complex of a *meta*-xylyl ligand and that a binuclear copper(I) complex of *m*-xyl(py) reacted with O_2 to hydroxylate the xylyl ligand and concomitantly form the phenoxy-bridged binuclear Cu^{II} complex (**1**).



(1)

The ligand *m*-xyl(py) was synthesized by reaction of bis[2-(2-pyridyl)ethyl]amine with α,α'-dibromo-*m*-xylene in ethyl acetate in the presence of di-isopropylethylamine. Reaction with $Cu(MeCN)_4PF_6$ (2 equiv.) in $MeOH\text{–}CH_2Cl_2$ under argon gave a pale yellow-brown solution of a binuclear copper(I) complex.† This solution was extremely air-sensitive and, when exposed to an atmosphere of oxygen, a green solution developed rapidly. Reaction with O_2 overnight followed by precipitation of a green crystalline solid with diethyl ether afforded the phenoxy- and methoxy-bridged complex (**1**) in 73% yield.‡ Crystals of compound

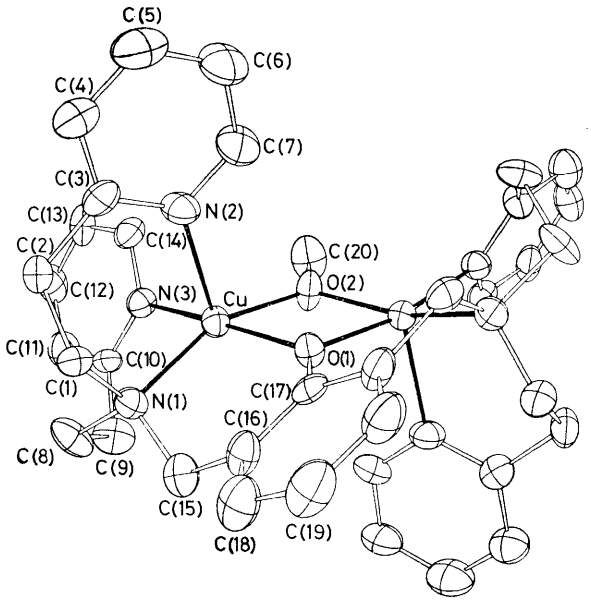


FIGURE. A perspective view of the $[Cu_2C_{37}H_{42}N_6O_2]^{2+}$ unit. Relevant bond lengths (Å) and angles (°) are: Cu···Cu **3·121(3)**, Cu–N(1) 2·095(8), Cu–N(2) 2·218(8), Cu–N(3) 2·005(7), Cu–O(1) 1·964(5), and Cu–O(2) 1·946(5); N(2)–Cu–N(1) 92·2(3), N(2)–Cu–N(3) 94·9(3), N(2)–Cu–O(1) 94·0(2), N(2)–Cu–O(2) 103·3(2), N(1)–Cu–N(3) 93·0(3), N(1)–Cu–O(1) 92·7(3), N(1)–Cu–O(2) 157·0(3), N(3)–Cu–O(2) 97·3(3), N(3)–Cu–O(1) 168·8(3), and O(1)–Cu–O(2) 74·1(3).

† Isolation and characterization of this complex is in progress. A binuclear Cu^I complex of *p*-xyl(SEt) is polymeric in the solid state and contains two copper ions per ligand and bridging thioether group (K. D. Karlin, J. R. Hyde, and J. Zubieta, to be submitted).

‡ When the reaction was run in the absence of MeOH, the product was the analogous phenoxy- and hydroxy-bridged complex which has been confirmed by *X*-ray analysis (K. D. Karlin, J. R. Hyde, and J. Zubieta, to be submitted).

(**1**) suitable for *X*-ray analysis were obtained from MeOH–diethyl ether.

Crystal data: $[Cu_2C_{37}H_{42}N_6O_2](PF_6)_2 \cdot MeOH$, $M = 1052$, monoclinic, space group $C2/c$, $a = 13{\cdot}481(2)$, $b = 14{\cdot}530(2)$, $c = 22{\cdot}393(3)$ Å, $\beta = 99{\cdot}81(1)°$, $V = 4322$ Å^3, $Z = 4$. A total of 1903 symmetry-independent reflections with $I_{obs} \geqslant 3\sigma(I_{obs})$(Mo-$K_\alpha$, $\bar{\lambda} = 0{\cdot}71073$ Å) contributed to the solution, which has been refined to a current R of 0·069.§

The structure of the dication of (**1**) is shown in the Figure. The Cu_2O_2 bridging unit is rigorously planar with a crystallographic 2-fold axis which passes through C(17) and C(19) of the benzene ring, the phenoxy-oxygen O(1), the methoxy-oxygen O(2), and the methoxy-carbon C(20). The ligand arrangement around each copper atom is *ca.* square pyramidal, with an axial pyridyl nitrogen atom N(2) and a basal N_2O_2 donor set which includes the tertiary amine N(1) and pyridyl N(3) atoms.

Incorporation of oxygen into an organic substrate (in this case, the xylyl ligand) is important in terms of metal-catalysed oxygenation[11] and of its similarity to the action of copper mono-oxygenases; few synthetic examples exist.[12] The phenoxy-bridged copper complexes formed are also of interest, since such compounds are being extensively investigated[13] in relationship to hemocyanin and the 'type III' copper–protein centres.[10,13] Compound (**1**) represents a new class of such complexes due to the co-ordination environment provided for the Cu^{II} ions.

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] K. D. Karlin, D. M. Feller, L. T. DiPierro, and R. A. Simon, Abstracts of 180th National Meeting of the American Chemical Society, August, 1980, Las Vegas, Nevada, INOR 105.
[2] K. D. Karlin, P. L. Dahlstrom, L. T. DiPierro, R. A. Simon, and J. Zubieta, *J. Coord. Chem.*, 1981, **11**, 61.
[3] H. S. Mason in 'Iron and Copper Proteins,' eds. K. T. Yasunobu, H. F. Mower, and O. Hayaishi, Plenum Press, New York, 1976, p. 464.
[4] R. Lontie and L. Vanquickenborne in 'Metal Ions in Biological Systems,' Vol. **3**, ed. H. Sigel, Marcel-Dekker, New York, 1974, pp. 183—200.
[5] W. H. Vanneste and A. Zuberbühler in 'Molecular Mechanisms of Oxygen Activation,' ed. O. Hayaishi, Academic Press, New York, 1974, p. 371.
[6] N. J. Blackburn, H. S. Mason, and P. F. Knowles, *Biochem. Biophys. Res. Commun.*, 1980, **95**, 1275.
[7] M. M. Taqui-Khan and A. E. Martell, *Inorg. Chem.*, 1975, **14**, 676.
[8] C. Y. Ng, A. E. Martell, and R. J. Motekaitis, *J. Coord. Chem.*, 1979, **9**, 255.
[9] J. E. Bulkowski, P. L. Burk, M. F. Ludmann, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1977, 498.
[10] P. L. Burk, J. A. Osborn, M.-T. Youinou, Y. Angus, R. Louis, and R. Weiss, *J. Am. Chem. Soc.*, 1981, **103**, 1273.
[11] J. E. Lyons in 'Aspects of Homogeneous Catalysis,' Vol. **3**, ed. R. Ugo, D. Reidel, Boston, 1977, p. 3.
[12] C. A. Sprecher and A. D. Zuberbühler, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 189; F. L. Urbach, V. Knopp, and A. D. Zuberbühler, *Helv. Chim. Acta*, 1978, **61**, 1097; H. Gampp and A. D. Zuberbühler, *Chimia*, 1978, **32**, 54; R. R. Gagne, R. S. Gall, G. C. Lisensky, R. E. Marsh, and L. M. Speltz, *Inorg. Chem.*, 1979, **18**, 771.
[13] J. J. Grzybowski and F. L. Urbach, *Inorg. Chem.*, 1980, **19**, 2604, and references therein.