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LETTER

Pyridine ligand donor substituent effects upon structure, redox properties and O_2 reactivity of xylyl dinuclear copper(I) complexes

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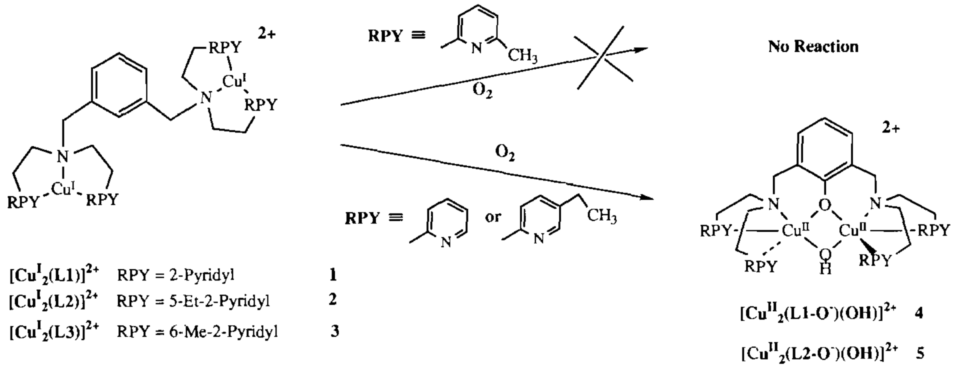
We have previously described a tyrosinase (*o*-phenol monooxygenase) functional model, in which a dicopper(I) complex containing a *m*-xylyl dinucleating ligand XYL (≡L1), $[Cu_2(L1)]^{2+}$ (**1**), reacts with molecular oxygen, resulting in the hydroxylation of the arene group to give $[Cu_2(L1\text{-}O^-)]^{2+}$ (**4**) (Scheme 1). Extensive investigations demonstrate that a peroxo intermediate $[Cu_2(L1)(O_2)]^{2+}$ initially forms, and this attacks the aromatic substrate by a process which is electrophilic (e.g. N.I.H. shift) by nature [1, 2]. Insights into the hydroxylation mechanism have in part come from studies of either 2- or 5-substituted XYL ligands and their complexes [1, 3, 4]. The nature of the ligand donor to copper(I) in these xylyl dinuclear complexes has been observed to be critical in determining whether hydroxylation occurs; the alternative reaction pathway is the irreversible oxidation of Cu(I) to hydroxo–Cu(II) complexes, i.e. without xylyl hydroxylation. Sorrell *et al.* [5] found that substitution of the pyridyl donors for pyrazolyl or imidazolyl ligands precluded the hydroxylation reaction. We also wished to examine possible steric and/or electronic consequences and O_2 reactivity when placing a substituent on the pyridyl donor ligand of the two bis[2-(2-pyridyl)ethyl]amine (PY2) tridentate chelate groups. Here, we describe the chemistry using dinucleating ligands having 5-ethyl (L2) and 6-methyl (L3) pyridine substitution.

Ligands L2 and L3 were prepared via the acetic acid catalyzed addition (in MeOH) of an excess of the appropriate 2-vinylpyridine with *m*-xylenediamine [6]. 5-Ethyl-2-methylpyridine was reacted with paraformaldehyde in EtOH affording 5-ethyl-2-hydroxyethylpyridine and dehydration (by distillation from KOH) of this or 6-methyl-2-hydroxyethylpyridine gave the appropriate 2-vinylpyridines. Dicopper(I) complexes $[Cu_2(L2)]^{2+}$ (**2**) and $[Cu_2(L3)]^{2+}$ (**3**) were synthesized by addition of two equivalents of $[Cu(CH_3CN)_4]PF_6$ in CH_2Cl_2 under argon, precipitation with diethyl ether, and recrystallization from CH_2Cl_2/Et_2O. *Anal.* Calc. for $[Cu_2(L2)](PF_6)_2\cdot 0.5CH_2Cl_2$ (**2**-$(PF_6)_2$), $C_{44.5}H_{57}ClCu_2F_{12}N_6P_2$: C, 47.40; H, 5.05; N, 7.45. Found: C, 47.73; H, 5.16; N, 7.37%. ^1H NMR (CD_3NO_2, δ): 1.24 (t, 12H), 2.64 (q, 8H), 3.13 (s, br, 16H), 3.66 (s, 4H), 5.44 (1H, CH_2Cl_2), 7.15 (m, 1H), 7.25 (d, 2H), 7.31 (d, 4H), 7.42 (s, 1H), 7.78 (d, 4H), 8.36 (s, 4H). Calc. for $[Cu_2(L3)](PF_6)_2$ (**3**-$(PF_6)_2$), $C_{40}H_{48}Cu_2F_{12}N_6P_2$: C, 46.65; H, 4.70; N, 8.16. Found: C, 47.25; H, 4.67; N, 8.22%. ^1H NMR (CD_2Cl_2, δ): 2.70 (s, 12H), 3.02–3.20 (d, br, 16H), 3.46 (s, 4H), 6.81–7.77 (m, 16H).



Scheme 1.

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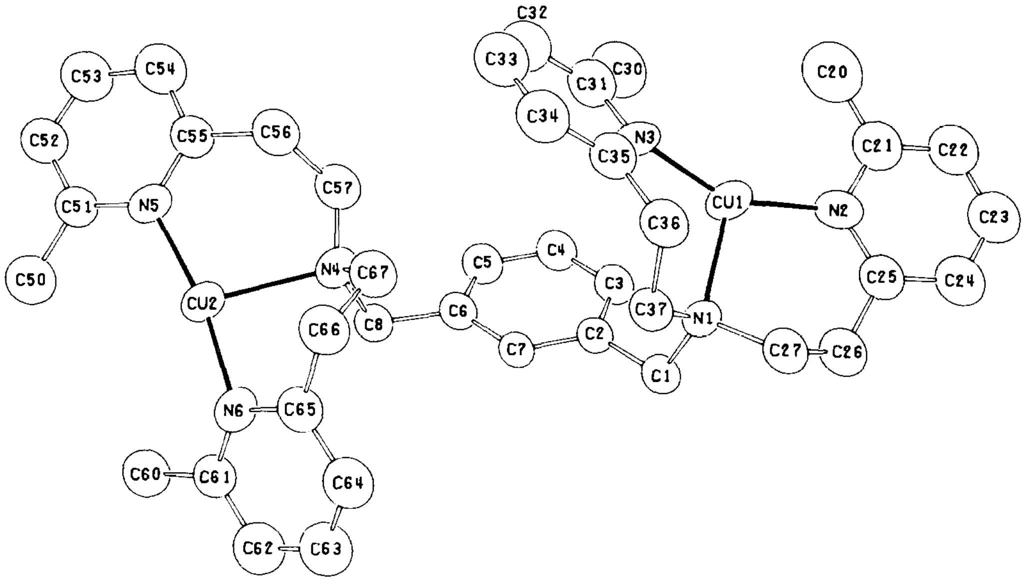

Fig. 1. ORTEP diagram of the dication part of $[Cu_2(L3)](PF_6)_2$ (3-$(PF_6)_2$) showing the atom labeling scheme. Selected bond lengths (A°) and angles (°) are: Cu···Cu, 8.904; Cu1–N1, 2.160(7); Cu1–N2, 1.953(8); Cu1–N3, 1.973(8); Cu2–N4, 2.294(7); Cu2–N5, 1.942(7); Cu2–N6, 1.961(7); N1–Cu1–N2, 103.7(3); N1–Cu1–N3, 99.3(3); N2–Cu1–N3, 152.5(3); N4–Cu2–N5, 101.9(3); N4–Cu2–N6, 89.1(3); N5–Cu2–N6, 169.0(3).

X-ray quality crystals of $[Cu_2(L3)](PF_6)_2$ (**3**-$(PF_6)_2$) could be obtained. The structure* of the dication (Fig. 1) is similar to that found for $[Cu_2(L1)]^{2+}$ (**1**) [2], with each copper found in a tricoordinate environment and the Cu atoms extended away from each other such that Cu···Cu = 8.904 Å; bond distances and angles around Cu1 are analogous to that for **1**. However, some distortions occur for Cu2, such that its coordination geometry is very T-shaped, with the N_{py}–Cu2–N_{py} angle of 169.0° as compared to values ranging from 151–153° around Cu1 in this structure or values found in **1**. Accompanying this variation around Cu2, the Cu2–N4 (amine) bond distance is lengthened by more than 0.1 Å, compared with values for Cu1 or those in complex **1**, Overall, the presence of 6-methyl groups in **3** does not appear to grossly affect the Cu(I) coordination and structure, however, the Cu ions do appear to be less accessible to a fourth ligand, because of a 'pocket' that appears to be formed.

However, the reactions of dioxygen with $[Cu_2(L2)]^{2+}$ (**2**) and $[Cu_2(L3)]^{2+}$ (**3**) appear to be greatly affected by the pyridine alkyl substituent. $[Cu_2(L2)]^{2+}$ (**2**) readily reacts in either CH_2Cl_2 or dimethylformamide (DMF) to produce $[Cu_2(L2\text{-}O^-)(OH)]^{2+}$ (**5**) in high yield. This complex has chemical and physical properties closely matching those of the well-characterized phenoxo and hydroxo bridged compound **4** [2]. *Anal.* Calc. for $[Cu_2(L2\text{-}O^-)(OH)](PF_6)_2\cdot 0.5Et_2O$ (**5**-$(PF_6)_2$), $C_{46}H_{61}Cu_2F_{12}N_6O_{2.5}P_2$: C, 47.83; H, 5.28; N, 7.28. Found: C, 48.20; H, 5.20; N, 7.70%. IR (Nujol; cm^{-1}): 3600 (sharp, OH), 1600 (C=C, aromatic), 840 (br, PF_6). UV–Vis (CH_3CN; λ_{max} (nm) (ϵ, M^{-1} cm^{-1})): 213 (15 400), 256 (17 400), 377 (3200), 420 (weak sh.) 630 (190). $\mu_{eff} = 1.4 \pm 0.1$ BM/Cu (solid, 298 K). However, $[Cu_2(L3)]^{2+}$ (**3**) does not react with O_2 under any conditions. In fact, the solid material or solutions of **3** can be handled in air for long periods.

Cyclic voltammetric experiments for **1**–**3** were carried out in order to help understand the oxygenation behavior, since the ease of oxidation of Cu(I) by O_2 usually correlates with the Cu(II)/Cu(I) redox potential. As previously found for **1** [7], $[Cu_2(L2)]^{2+}$ (**2**) also exhibits a quasireversible electrochemical process in DMF with $E_{1/2} = +0.29$ V versus Ag/AgCl and $\Delta E_p = 320$ mV (0.1 M n-Bu_4NPF_6, where $E_{1/2} = +0.52$ V for Fc/Fc^+). This is the only redox process observed over the potential range +0.9 to −0.2 V, indicating that the two separate metal associated redox processes in the dinuclear complex occur at essentially the same potential. The half-wave potential compares well with that observed for $[Cu_2(L1)]^{2+}$ (**1**), where $E_{1/2} = +0.31$ versus Ag/AgCl; the slightly lower redox potential for **2** is consistent with the expected increased stabilization of Cu(II) relative to Cu(I) in a system possessing a more electron donating ligand (i.e. due to the Et substituent). A cyclic voltammogram of $[Cu_2(L3)]^{2+}$ (**3**) is not well behaved. Single oxidation and reduction processes both

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*Triclinic space group $P\bar{1}$ with $a = 11.095(4)$, $b = 12.704(4)$, $c = 16.118(6)$ Å, $\alpha = 90.07(3)$, $\beta = 101.22(3)$, $\gamma = 99.47(3)$°, $V = 2196.7(2)$ Å, $Z = 2$. A total of 3336 reflections was refined to $R = 0.071$ and $R_w = 0.074$ (Mo Kα, $\lambda = 0.71073$ Å).

occur and $E_{1/2}$ could be estimated to be $\sim +0.39$ V, however the peak to peak separation is ~ 600 mV. One can conclude that there is a severe kinetic barrier to facile electron transfer in **3**, and the 6-methylpyridyl substituent clearly affects the redox chemistry and O_2 reactivity with this dicopper(I) complex. As provided by the methyl substituents, a non-polar environment is well known to increase copper ion redox potentials [8] and Sorrell and Jameson [9] have specifically shown that to be the case in sterically hindered CuN_4 complexes of tripod ligands (with t-butyl groups).

From the study reported here, it is apparent that pyridyl donor substituents in the PY2 chelating tridentate ligand employed in these xylyl dinucleating ligands can greatly affect the chemistry. Due to the more positive redox potential for copper ion and steric effects (perhaps manifested in a dinuclear $Cu–O_2–Cu$ intermediate), the 6-methyl substituent in $[Cu_2(L3)]^{2+}$ (**3**) shuts down the O_2 reactivity of this tricoordinate Cu(I) complex.

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