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LETTER

Model for the Possible 'Endogenous' Bridge in Oxy-hemocyanin: a Di-μ-$(OR)_2$-bridged Dicopper(II) Complex (R = H, alkyl) with Low-energy Charge-transfer Absorption

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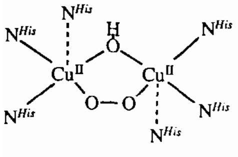
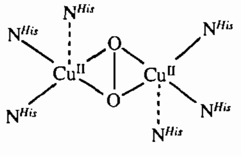
From recent investigations on both protein as well as model systems, two possible structures for the active site of oxy-hemocyanin (oxy-Hc, molluscan and arthropodal dioxygen carrier [1–3]) are currently being considered. One, proposed originally by Solomon and co-workers [1, 2, 4], suggests that two tetragonally coordinated Cu(II) ions are bridged by the exogenous peroxo ligand (derived from the addition of O_2 to deoxy-Hc) in addition to an 'endogenous' hydroxo ligand. The latter was suggested to be present to account for the strong spectroscopic analogy of oxy-Hc to oxidized dicopper(II) 'met' derivatives, where an OH^- bridging ligand could help account for (i) the strong magnetic coupling observed in these dicopper(II) forms, and (ii) an absorption observed at 420 nm in oxy-Hc [1, 2, 4]. More recently, a μ-η^2:η^2-peroxo structure without additional bridging group is also being considered, since our own group [5, 6] and that of Kitajima and co-workers [7] have observed such synthetically derived model compounds having UV–Vis spectroscopic properties similar to oxy-Hc, and Kitajima has now confirmed this structure via an X-ray crystallographic study [7].





In this report, we address the matter of the UV–Vis spectroscopy associated with hydroxo or alkoxo bridged dicopper(II) systems, as it relates to the observed 420 nm band in oxy-Hc. Here, we have synthesized and characterized two tetragonally coordinated dicopper(II) complexes, each having a low energy CT absorption band and possessing the Cu^{II}–(μ-OR')(μ-OR)–Cu^{II} core (R'O$^-$ is derived from the dinucleating ligand and R is Me or H for the exogenous group). We utilize pyridine-containing dinucleating ligands and in both cases the complexes were obtained after oxidation of related dicopper(I) compounds. We have been able to determine the structure of the methoxo bridged complex through an X-ray crystallographic analysis.

Following our own previously utilized procedures for spectroscopically characterizing Cu_2–O_2 complexes with ligands having variable alkane chains connecting two tridentate bis[2-(2-pyridyl)ethyl]amine (PY2) groups [5, 6], we synthesized the dicopper(I) complexes **1** and **2**, containing the dinucleating ligand N3OH [8] or N3OR (R = acryloyl)*. At −80 °C in CH_2Cl_2, reaction of O_2 with **1** produces a green hydroperoxo species $[Cu_2(N3O-)(OOH)](PF_6)_2$ (Manometry, Cu:O_2 = 2:1) [9, 10] which gives **3** upon warming the solution to room temperature, precipitating a green complex with Et_2O and then recrystallizing from MeOH/Et_2O**. The methoxo analogue was generated by reaction of **2** with O_2 at room temperature in methanol and X-ray quality crystals were obtained by precipitation (Et_2O) and recrystallization**. Reaction of the ligand ester **2** to give the alkoxide containing complex **4** involves a hydrolysis reaction; further work will be required to determine if this occurs by attack of a copper bound peroxo ligand or hydrolysis (by water or MeOH/OMe$^-$) after oxidation to Cu(II).

The complex $[Cu_2(N3O-)(OMe)](PF_6)_2 \cdot MeOH \cdot H_2O$ (**4**) crystallizes in the monoclinic space group $C2/m$ with $a = 16.856(6)$, $b = 14.382(6)$, $c = 18.923(6)$ Å, $\beta = 112.75(2)°$, $V = 4230.8$ Å^3 and $Z = 4$. A total of 1834 unique reflections have been refined to a current R value of 0.88 (Mo Kα, $\lambda = 0.71073$ Å). The structure of the dicationic portion is shown in Fig. 1. It contains a dicopper(II) unit with alkoxo (from N3O–) and methoxo doubly bridging

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*Synthesized from $Cu(CH_3CN)_4PF_6$ plus ligand; satisfactory microanalytical data have been obtained for these complexes. Complex 1: IR (Nujol) νOH, 3550(s); νCO, 2070(s) cm^{-1}. Complex 2: IR (Nujol) νCO, 1715(s) cm^{-1}.

***Anal.* for $[Cu_2(N3O-)(OH)](PF_6)_2 \cdot MeOH$ (3). Calc. for $C_{32}H_{42}Cu_2F_{12}N_6O_3P_2$: C, 39.38; H, 4.31; N, 8.61. Found: C, 39.07; H, 4.10; N, 8.48%. μ (r.t.) = 1.65 BM/Cu. $[Cu_2(N3O-)(OMe)](PF_6)_2 \cdot MeOH \cdot H_2O$ (4). Calc. for $C_{33}H_{46}Cu_2F_{12}N_6O_4P_2$: C, 39.37; H, 4.48; N, 8.34. Found: C, 39.08; H, 4.15; N, 8.17%.

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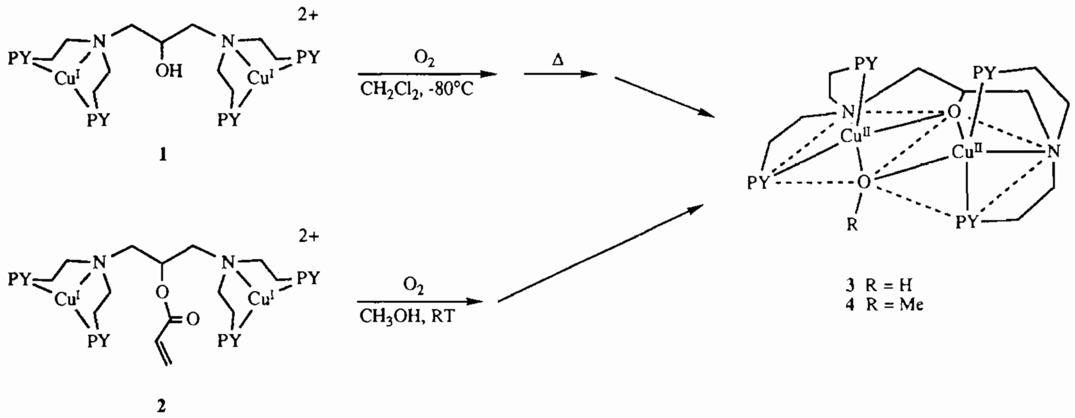

ligands. There is a crystallographic mirror plane passing through C2,O1,O2,C3 relating the two halves of the molecule, with Cu...Cu = 2.995(2) Å. Each copper is found in a distorted square-based pyramidal coordination environment with equatorial ligation from the amine nitrogen atom N1, pyridyl N3, as well as O1 and O2 OR$^-$ ligands. The Cu1 atom lies 0.223 Å above the basal plane towards the axial pyridine N2 donor which is bonded to the Cu(II) atom at a distance almost 0.25 Å further than the equatorial pyridine donor N3. The two Cu(II) basal planes (N1,N3,O1,O2 and N1a,N3a,O1,O2) make an angle of 32.3° with respect to one another.

In addition to d–d transitions in the 600–700 nm region (CH$_2$Cl$_2$ solvent: **3**; 686 nm, $\epsilon = 390\ \mathrm{M^{-1}\ cm^{-1}}$; **4**; 648 nm, $\epsilon = 260\ \mathrm{M^{-1}\ cm^{-1}}$), the complexes exhibit absorptions at 418 nm ($\epsilon = 820\ \mathrm{M^{-1}\ cm^{-1}}$) for $[\mathrm{Cu_2(N3O{-})(OH)}]^{2+}$ (**3**) (Fig. 2) and at 375 nm ($\epsilon = 740\ \mathrm{M^{-1}\ cm^{-1}}$) for $[\mathrm{Cu_2(N3O{-})(OMe)}]^{2+}$ (**4**). These are most reasonably assigned to exogenous OR$^-$-to-Cu(II) LMCT transitions. In particular, the 418 nm absorption in **3** is at a rather low energy compared to LMCT absorptions found in other Cu(II)–OR containing complexes [11–14]. Also, a number of other research groups have used dinucleating ligands derived from 2-hydroxy-1,3-diaminopropane

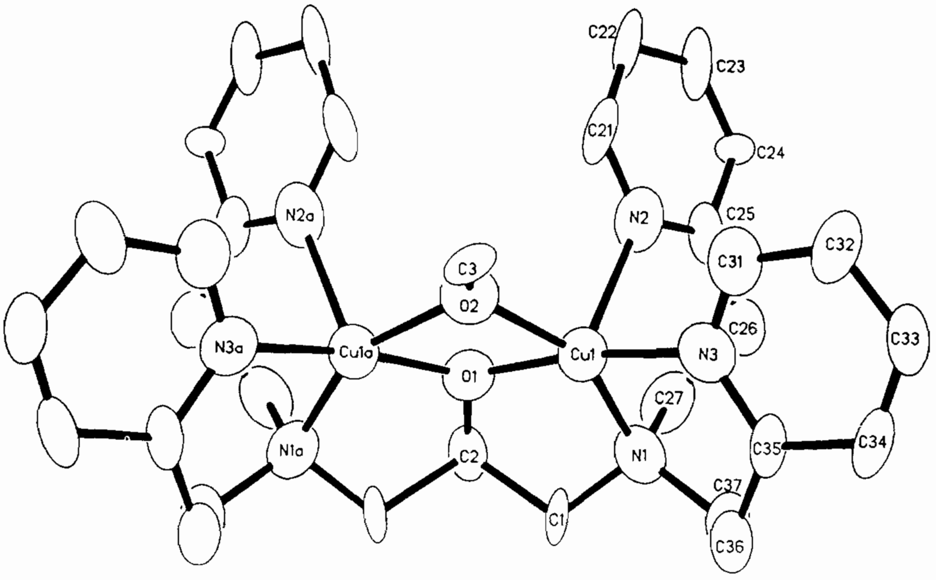

Fig. 1. ORTEP diagram of the dicationic portion of complex **4** showing the atom labeling scheme. Selected bond lengths (Å) and angles (°) are as follows: Cu1...Cu1a, 2.995(2); Cu1–N1, 2.060(22); Cu1–N2, 2.237(28); Cu1–N3, 1.998(25); Cu1–O1, 1.901(17); Cu1–O2, 1.958(19); N1–Cu1–N2, 96.2(9); N1–Cu1–N3, 97.2(12); N1–Cu1–O1, 81.8(14); N1–Cu1–O2, 153.5(13); N2–Cu1–O1, 98.4(12); N2–Cu1–O2, 101.9(7); N2–Cu1–N3, 91.3(7); N3–Cu1–O1, 170.3(14); N3–Cu1–O2, 101.5(8); O1–Cu1–O2, 76.6(8); Cu1–O2–C3, 128.3(12); Cu1–O1–C2, 119.3(14).

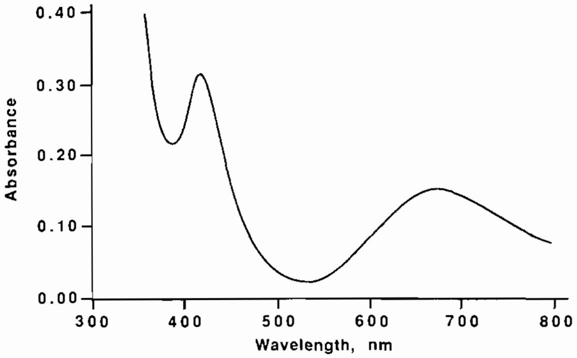

Fig. 2. Absorption spectrum for $[Cu_2(N3O-)(OH)]^{2+}$ (3).

and alkoxo bridged complexes have been prepared; however, OR^- derived CT bands appear to be lacking [15–17]. In particular, Reed and co-workers [18, 19] have previously described met-hemocyanin models with a ligand similar to N3O–, but with substituted benzimidazole groups (L-Et) instead of pyridine donors. Complexes of this type having exogenous bridging X groups, $[Cu_2(L\text{-}Et)(X)]^{2+}$ (X = N_3^-, OAc^-, NO_2^-, pyrazolate) also do not display any UV–Vis bands assignable to the alkoxo bridging group.

As it may pertain to the possible active site structure proposed for oxy-Hc, the results here demonstrate that the 420 nm absorption observed for the protein could indeed arise from the presence of a hydroxo bridged dicopper(II) species. Further studies (e.g. resonance Raman spectroscopy) will be necessary to confirm the LMCT assignment of these visible absorptions.

Acknowledgements

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