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Synthesis of a Novel μ-Oxo Binuclear Copper(II) Complex Ligated by Hydrotris(3,5-dimethyl-1-pyrazolyl)borate

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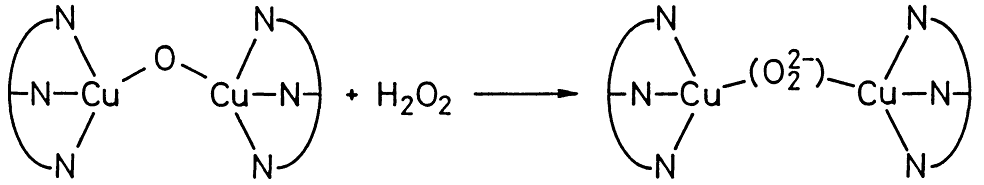
A novel μ-oxo binuclear copper(II) complex, $[CuHB(3,5-Me_2-Pz)_3]_2O$ in which the each of coppers coordinates to three nitrogens, was prepared by the reaction of a copper(I) triphenylphosphine complex with iodosylbenzene.

Recently, we have reported the synthesis of μ-peroxo binuclear copper(II) complex which serves as a synthetic model of oxyhemocyanin from μ-oxo binuclear copper(II) complex (1) as follows.1)



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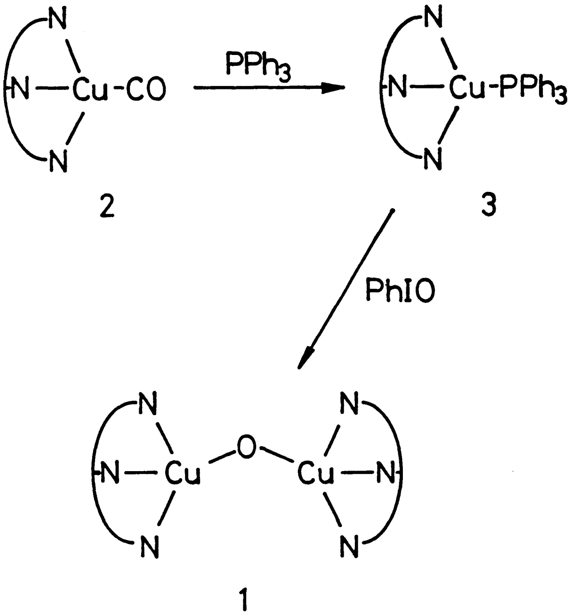
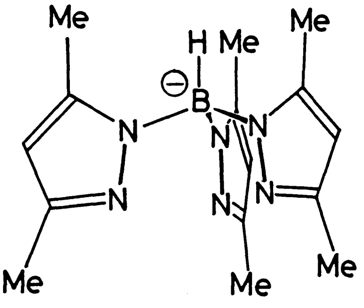
In this communication, the synthesis and properties of 1 are described. Although there have been considerable efforts for preparing μ-oxo binuclear copper(II) complexes,2) to our knowledge, there is only one isolated example reported so far.3)

$Cu(CO)HB(3,5-Me_2Pz)_3$ (2) prepared by the literature method,4) readily reacts with 1 equiv. PPh_3 in benzene at room temperature, to give $Cu(PPh_3)HB(3,5-Me_2Pz)_3$5) (3) in an quantitative yield. When 3 was stirred with 1.5 equiv. iodosylbenzene in CH_2Cl_2, the colorless solution gradually turned greenish and resulted in a dark green solution after 6 h. Filtration and reduction of the solvent followed by cooling at -20 °C affords greenish blue crystalline solids 1 (40% yield). Although all our efforts to get a single crystal suitable for X-ray diffraction have been unsuccessful so far, the satisfactory elemental analysis[6)] and the spectroscopic properties as well as the oxygen transfer reactions described below established that 1 is a μ-oxo binuclear copper(II) complex.





HB(3,5-Me$_2$Pz)$_3$

The visible spectrum of 1 in $CHCl_3$ indicates two characteristic absorption bands at 335 (ε 2560 mol^{-1} dm^3 cm^{-1}) and 660 nm (105) which are tentatively ascribed to the O→Cu charge transfer band and d-d transition of the copper(II) ion, respectively. The magnetic susceptibility of 1 in $CDCl_3$ determined by Evans method[8)] at 25 °C, was ca. 1.3 B.M./2Cu. This implies that 1 has the polynuclear structure in which the coppers are bridged with a certain ligand; the most reasonable candidate is oxo, causing the strong antiferromagnetism. Accordingly, 1 does not show any EPR signal but gives the characteristic NMR spectrum; ^{1}H-NMR ($CDCl_3$, 25 °C) δ ppm 12.60 (br, 1H, pz), 2.45 (br, 3H, Me), 1.86 (s, 3H, Me). The down field shifted peak at 12.60 ppm, whose chemical shift strongly depends on the temperature measured, is especially characteristic for 1 since all of copper(I) complexes having HB(3,5-Me$_2$pz)$_3$ give the pyrazol ring proton around at 5.7 ppm[4,9)] besides none of mononuclear copper(II) complexes are detectable by NMR. Finally, the field desorption MS spectra of 1 and the sample obtained from 3 and PhI^{18}O, gave the corresponding molecular cation peaks with the isotopic distribution expected for 1 as μ-oxo binuclear

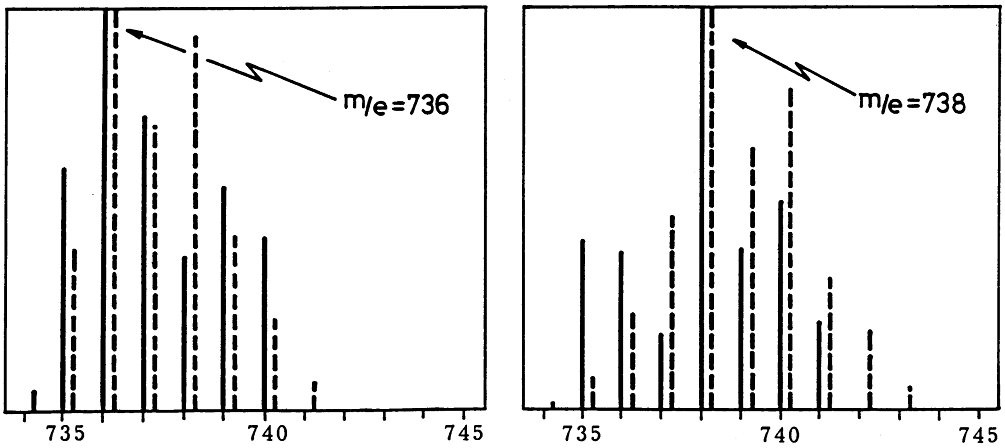
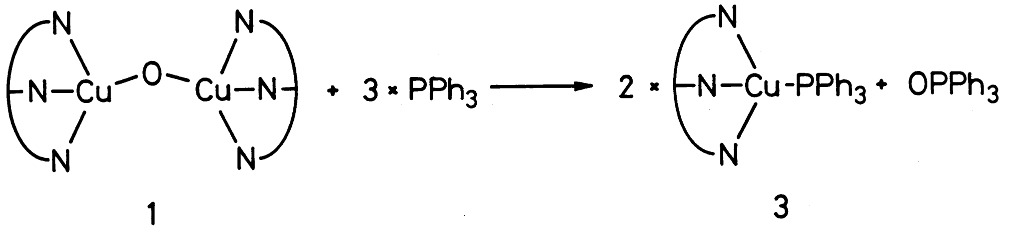


Fig. 1. FD-MS spectra of $[CuHB(3,5\text{-}Me_2Pz)_3]_2{}^{16}O$ (left) and $[CuHB(3,5\text{-}Me_2Pz)_3]_2{}^{18}O$ (prepared from (2) and $PhI^{18}O$; isotopic purity, 80%) (right): obsd (———), calcd as 80% ^{18}O incorporation (----).

complex as shown in Fig. 1.

The existence of μ-oxo in 1 was confirmed by the reaction of 1 with PPh_3. When the solution of 1 was treated with 5 equiv. PPh_3 at room temperature under argon, the solution turned to colorless. The ^1H and ^{31}P-NMR spectra of the resulted solution firmly establish the quantitative formation of 3 and PPh_3O.



When 1 was simply stirred in CH_2Cl_2 in the presence of the excess amount of dimethyl sulfide or cyclohexene, no oxidized product was generated. However, under UV irradiation in a quartz reactor, the readily reaction proceeding was noted; dimethylsulfoxide in 15% yield (based on 1) and 2-cyclohexene-1-ol in 10% yield was produced, respectively. Although the detailed mechanism is the future subject of our research, this notable photo-induced oxidation may involve an active copper-oxygen radical intermediate generateted by homolytic cleavage of copper-oxygen bond in 1.

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5) IR (KBr-disc) ν_{BH} 2504 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ ppm 7.65 (m, 5H, Ph), 5.62 (s, 1H, pz), 2.38 (s, 3H, Me), 1.68 (s, 3H, Me); Anal Found: C, 63.72; H, 6.43; N, 13.26%. Calcd for $C_{33}H_{37}N_6BPCu$: C, 63.62; H, 5.99; N, 13.49%.

6) IR (KBr-disc) ν_{BH} 2506 cm^{-1}; Anal Found: C, 48.41; H, 6.52; N, 23.21%. Calcd for $C_{30}H_{44}N_{12}B_2OCu_2$: C, 48.86; H, 6.01; N, 22.79%. Both 1 and 1 prepared from PhI^{18}O did not show an acurate absorption band assignable to asymmetric Cu-O-Cu stretching vibration. This may be due to the masking by the strong bands of the ligand in the region, 600—900 cm^{-1}. However, it can be the essential property of 1, since the previously known μ-oxo binuclear copper (II) complex does not give the accurate band$^{3)}$ either and several other μ-oxo complexes are also known to exhibit the very low intensity band.$^{7)}$

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