Structural and Spectroscopic Aspects of a Strained Dicopper Complex with a Tripodal Binucleating Ligand

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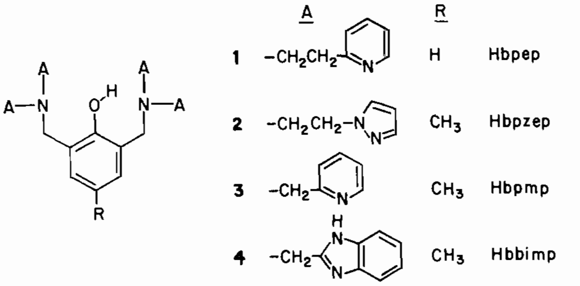
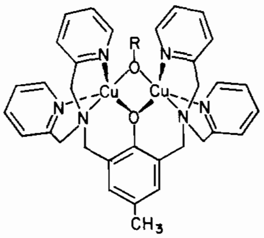
Binucleating ligands which present tripodal coordination sites to two copper ions have yielded interesting models of dicopper protein active sites [1–6]. Representative ligands of this type are 2,6-bis(bis(2′-pyridylethyl)aminomethyl)phenol, Hbpep (**1**) studied extensively by Karlin [1] and 2,6-bis(bis(1′-pyrazolylethyl)aminomethyl)-4-methylphenol, Hbpzep (**2**) prepared and studied by Sorrell [2]. Each tripodal coordination site provided by these ligands forms three six-membered chelate rings (6-6-6) with a metal ion. Ligand **1** produces square-pyramidal dicopper(II) complexes [1] in which the phenolate oxygen and an additional exogenous ligand provide double bridging in the basal planes of the Cu(II) coordination spheres. This type of structure is observed for the exogenous bridging ligands hydroxide, methoxide, and 1,1-azide [1]. The hydroxy-bridged dicopper(II) complex of **2** is unique in that one Cu(II) ion is square-pyramidal while the other is distorted toward trigonal bipyramidal geometry [2].



During the course of our studies on transition metal complexes with binucleating ligands we have prepared and characterized several examples of dicopper(II) complexes with 2,6-bis(bis(2′-pyridylmethyl)aminomethyl)-4-methylphenol, Hbpmp (**3**). This ligand, also reported by Suzuki [3] and Nishida [4], differs from **1** and **2** in that it provides two 5-5-6 tripodal coordination sites. The presence of 5-5-6 chelate ring size arrangements for both tripodal coordination sites suggests that bpmp$^-$ will have difficulty in accommodating square-pyramidal geometries about the two copper ions together with a monoatom exogenous bridge. On the basis of stoichiometry, spectral and conductance data, Suzuki [3] concluded that the complexes $[Cu_2(bpmp)X_2]^+$, where $X^- = Cl^-$ or N_3^-, have an 'open' structure in which two square-pyramidal copper(II) ions are bridged only by the phenolate donor. In contrast, the derivatives $[Cu_2(bpmp)Y]^{2+}$, where Y^- = acetate or imidazolate, were proposed to be doubly bridged by phenolate and the exogenous ligand. Suzuki [3] suggested that the constraining nature of bpmp$^-$ renders the formation of monoatom exogenous bridges difficult. The proposed 'open' structure for the chloride complex and the 1,3-bridged structure of the acetate derivative were confirmed by Nishida [4]. An 'open' structure was also observed [5] for a dicopper(II) complex of the related ligand **4** which also provides two 5-5-6 tripodal coordination sites to the metal ions. In this structure, coordination of a water molecule to each Cu(II) ion completes a square-pyramidal coordination geometry.

We report here the isolation and spectral characterization of two additional dicopper(II) complexes of **3**, $[Cu_2(bpmp)(OH)](ClO_4)_2$ (**5a**) and $[Cu_2(bpmp)(OCH_3)](ClO_4)_2\cdot 0.5CH_3OH$ (**5b**) and the X-ray structure of the methoxy-bridged complex **5b**. The unique, strained structure of **5b** illustrates that monoatom exogenous bridging is possible with binuclear copper(II) complexes of **3** and also provides a basis for interpreting the electronic spectral behavior of both the methoxy- and hydroxy-bridged complexes.



5a R=H
5b R=CH_3

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*$[Cu_2(bpmp)(OMe)](ClO_4)_2\cdot 0.5CH_3OH$, $Cu_2Cl_2O_{10.5}N_6C_{34.5}H_{38}$ (formula weight = 902.71 g/mol), crystallized in space group $P\bar{1}$, with a = 13.571(4), b = 12.316(3), c = 14.072(3) Å, α = 91.43(2), β = 103.59(2), γ = 122.80(2), V = 1888(1) Å^3, Z = 2, D(obs.) = 1.59, and D(calc.) = 1.588 g/cm^3. 5158 reflections were collected for $2\theta = 2–50°$ on a Syntex $P2_1$ diffractometer using Mo Kα monochromated radiation (λ = 0.71073 Å), obtaining 3084 observed ($I > 3\sigma$) reflections. The UCLA Crystallographic Package was used for solution and refinement of the structure, yielding R = 0.062, R_w = 0.073, and goodness of fit = 2.12, with one poorly behaved perchlorate ion causing several weak residual peaks. See 'Supplementary Material' for further structural information.

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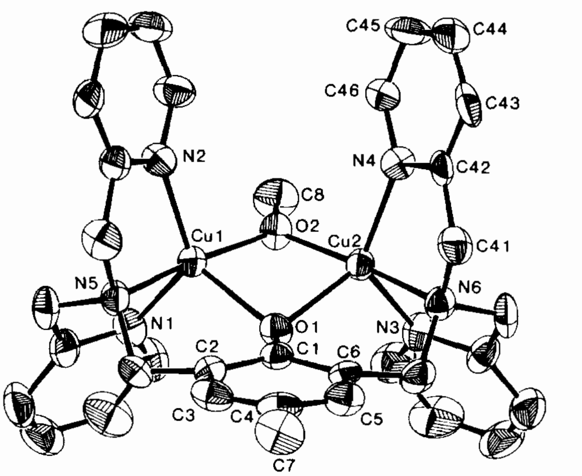

Fig. 1. ORTEP representation of the $[Cu_2(bpmp)(OCH_3)]^{2+}$ cation.

TABLE I. Selected Bond Lengths (Å) and Bond Angles (°) in $[Cu_2(bpmp)(OCH_3)](ClO_4)_2 \cdot 0.5CH_3OH$

Distances			
Cu(1)–Cu(2)	2.989(3)	Cu(2)–O(2)	1.896(7)
Cu(1)–O(2)	1.902(7)	Cu(2)–N(6)	2.024(9)
Cu(1)–N(5)	2.015(9)	Cu(2)–N(4)	2.050(9)
Cu(1)–N(2)	2.037(8)	Cu(2)–O(1)	2.068(7)
Cu(1)–O(1)	2.070(7)	Cu(2)–N(3)	2.087(9)
Cu(1)–N(1)	2.088(9)		
Angles			
Cu(1)–O(1)–Cu(2)	92.5(3)		
Cu(1)–O(2)–Cu(2)	103.8(3)		
O(2)–Cu(1)–N(5)	171.6(3)	O(2)–Cu(2)–N(6)	171.8(3)
O(1)–Cu(1)–N(1)	106.5(3)	O(1)–Cu(2)–N(3)	107.3(3)
O(1)–Cu(1)–N(2)	127.0(3)	O(1)–Cu(2)–N(4)	126.8(3)
N(1)–Cu(1)–N(2)	124.8(4)	N(3)–Cu(2)–N(4)	124.4(4)
C(12)–N(1)–Cu(1)	110.0(8)	C(32)–N(3)–Cu(2)	110.7(8)
C(16)–N(1)–Cu(1)	130.4(9)	C(36)–N(3)–Cu(2)	129.2(9)
C(22)–N(2)–Cu(1)	115.0(7)	C(42)–N(4)–Cu(2)	114.0(7)
C(26)–N(2)–Cu(1)	127.9(8)	C(46)–N(4)–Cu(2)	127.6(8)
C(10)–N(5)–Cu(1)	112.8(7)	C(30)–N(6)–Cu(2)	112.1(7)
C(11)–N(5)–Cu(1)	103.4(6)	C(31)–N(6)–Cu(2)	104.8(7)
C(21)–N(5)–Cu(1)	110.2(6)	C(41)–N(6)–Cu(2)	109.3(6)

The structure of **5b*** consists of a discrete dicationic complex ion (Fig. 1), two separated perchlorate anions, and a methanol molecule at the center of the cell. The two Cu(II) ions are in identical trigonal bipyramidal coordination environments with axial coordination provided by the tertiary aliphatic amines and the bridging methoxide. The anticipated 5-5-6 tripodal coordination about each copper is completed with the two pyridyl donors and the bridging phenolate occupying the equatorial positions. In order to adopt the doubly bridged binuclear structure, both Cu(II) ions lie 0.9 Å above the plane of the phenolate ring and the Cu_2O_2 core is bent with a dihedral angle of 27°. This arrangement contrasts with the strictly planar Cu_2O_2 core which has been observed with more flexible binucleating ligands [1, 2]. The doubly bridged coppers in **5b** are separated by only 2.99 Å. Furthermore, the stereochemistry about the bridging phenolate oxygen is close to pyramidal rather than the typically observed trigonal planar arrangement. A similar short Cu–Cu distance and a pyramidal bridging phenolate donor have recently been reported for the dicopper(II) complex of a related binucleating ligand produced by the reaction of two moles of 1-methylpiperazine with 2,6-bis(chloromethyl)-4-chlorophenol [6].

Several additional structural parameters indicate the strain inherent in the complex ion. The copper ions lie 0.15 Å out of the trigonal plane of the trigonal bipyramidal geometry toward the apical methoxide and the Cu–O(phenolate) bond distances are abnormally long (2.07 Å). The constraints provided by the 5-membered chelate rings produce a diminished orbital overlap between the Cu(II) and the equatorial pyridyl donors. Pyridyl rings 2 and 4 exhibit C_α–N–Cu angles of 115°, slightly decreased from the ideal angle of 120°. Pyridyl rings 1 and 3 have more distorted C_α–N–Cu angles of 110°, and the coppers lie 0.4 Å out of these pyridyl planes. This distortion produces the long Cu–N(1) and Cu–N(3) distances of 2.09 Å. Further selected bond distances and angles are given in Table I.

The electronic spectra of the hydroxy-bridged (**5a**) and the methoxy-bridged (**5b**) dicopper(II) complexes of **3** are identical in aqueous solution (pH 7) and consist of bands at 710 nm ($\epsilon = 250$), (d–d), 430 nm ($\epsilon = 270$sh), (phenolate to Cu(II) charge transfer), and a series of intense bands below 275 nm (N to Cu(II) charge transfer and $\pi \rightarrow \pi^*$ transitions). The low intensity of the phenolate–Cu(II) LMCT probably arises from poor overlap of the oxygen orbitals with the half-filled d orbital on the copper. We have not yet established the ground state for **5** but trigonal bipyramidal Cu(II) complexes typically exhibit a hole configuration of d_{z^2} [7]. With the phenolate oxygen occupying equatorial positions in both Cu(II) coordination spheres the overlap between the phenolate oxygen and the half-vacant copper d_{z^2} orbital is minimal and the intensity of the LMCT is expected to be weak.

Since the doubly bridged form of the binuclear complex appeared to be strained, we attempted to remove the exogenous hydroxide bridge by lowering the pH of a neutral aqueous solution of $[Cu_2(bpmp)(OH)](ClO_4)_2$. Large changes in the band assigned as the phenolate–Cu(II) LMCT were observed as the pH was lowered (Fig. 2). The weak shoulder at 430 nm became a distinct peak at 460 nm with an almost threefold increase in intensity. We attribute this spectral change to the protonation and cleavage of the hydroxide bridge and the relaxation of the complex ion to a less strained 'open' structure in

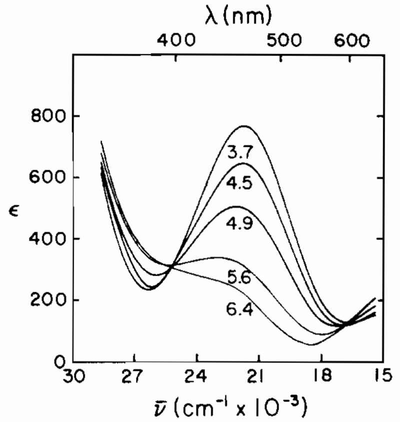

Fig. 2. Electronic spectrum of $[Cu_2(bpmp)(OH)](ClO_4)_2$ in H_2O (1.05 mM) in the region of the phenolate to Cu(II) charge transfer transition as a function of the pH values indicated. pH adjustments were made by the addition of 0.01 M or 0.1 M $HClO_4$ via a microsyringe.

which two tetragonal copper(II) ions are singly bridged by the phenolate donor. Improved overlap in the 'open' structure between the phenolate donor and the half-filled copper orbital (now presumably $d_{x^2-y^2}$) results in the dramatic increase in intensity for the phenolate to copper charge transfer band. The concomitant wavelength shift and intensity decrease in the d–d band (710 nm (ϵ = 250) at pH 6.4 to 690 nm (ϵ = 157) at pH 3.1) further suggests the conversion from trigonal bipyramidal to a tetragonal geometry about the coppers [7]. This interpretation of the spectral changes in terms of a conversion from a strained doubly bridged species into an 'open' structure is further supported by the lack of observed changes in the 240–275 nm region indicating no loss of N(pyridine) → Cu(II) charge transfer transitions which would occur if the terminal pyridine donors had been protonated.

Our studies show conclusively that examples of dicopper(II) complexes of $bpmp^-$ (3) can be achieved in which the two copper ions are bridged by the phenolate of the binucleating ligand and by a monoatomic exogenous bridging ion. The inherent strain revealed in the structure of the methoxy-bridged complex provides a basis for explaining the spectral properties of these complexes.

Supplementary Material

Tables of atom positional parameters and anisotropic thermal parameters for $[Cu_2(bpmp)(OCH_3)](ClO_4)_2 \cdot 0.5CH_3OH$ have been deposited with the Editor-in-Chief.

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