A Geometrically Asymmetric Dinuclear Copper(II) Complex Derived from A New Unsymmetric 'End-off' Compartmental Ligand

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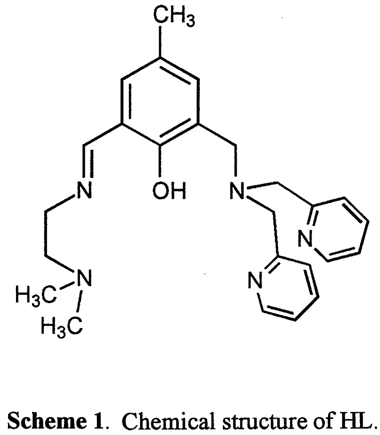
An unsymmetrical 'end-off' compartmental lignd, 2-[N,N-di(2-pyridylmethyl)aminomethyl]-6-{N-[2-(dimethylamino)-ethyl]iminomethyl}-4-methylphenol, forms a μ-phenoxo-μ-hydroxodicopper(II) core complex which has a geometric asymmetry being comprised of square-pyramidal Cu(II) and trigonal-bipyramidal Cu(II) ions.

Phenol-based 'end-off' dinucleating ligands, having two chelating arms attached to the 2 and 6 positions of the phenol ring, have often been used to provide dinuclear metal complexes bridged by the endogenous phenolic oxygen and one or two exogenous groups.[1-4] These complexes are of interest as structural or functional models for the active sites of some bimetallic biosites.[5] For example, such ligands having two bidentate chelating arms form μ-phenoxo-bis(μ-carboxylato)-dimanganese(II) core complexes that are good functional models of manganese catalase and disproportionate H_2O_2.[1] Analogous ligands having two tridentate chelating arms have been extensively used by Suzuki[2] to provide dinuclear iron complexes relevant to nonheme bimetallic biosites. Recently, it was recognized that most bimetallic biosites are unsymmetrical with respect to donor atom array, geometric disposition, coordination number, and/or metal ion.[5] It is considered that biological systems employ such unsymmetrical cores to achieve a specific function by the conjunction of distinct roles for the two metal ions. In this context it is important to design dinucleating ligands that can provide asymmetric dinuclear cores.[6]

Here we report an unsymmetrical compartmental 'end-off' ligand, 2-[N,N-di(2-pyridylmethyl)aminomethyl]-6-{N-[2-(dimethylamino)ethyl]iminomethyl}-4-methylphenol (HL, Scheme 1), that has a bidentate and a tridentate chelating arms attached to the 2 and 6 positions of the phenol ring. It forms a μ-phenoxo-μ-hydroxodicopper(II) core complex which has a geometric asymmetry being comprised of square-pyramidal Cu(II) and trigonal-pyramidal Cu(II) ions.



Scheme 1. Chemical structure of HL.

The precursor ligand, 3-[N,N-di(2-pyridylmethyl)amino-methyl]-5-methylsalicylaldehyde (HL'), was prepared by the reaction of 3-chloromethyl-5-methylsalicylaldehyde and di(2-pyridylmethyl)amine in tetrahydrofuran and characterized by ^{1}H-NMR spectroscopy.[7]

The unsymmetrical ligand HL was prepared in situ by refluxing a solution of HL' (70 mg, 0.2 mmol) and N,N-dimethylethylenediamine (20 mg, 0.2 mmol) in methanol (10 cm^3). The ligand solution was reacted with copper(II) acetate monohydrate (80 mg, 0.4 mmol) at reflux temperature, and addition of $NaClO_4$ to the reaction mixture resulted in the precipitation of $[Cu_2(L)(OH)](ClO_4)_2 \cdot CH_3COOH$ as green plates.[8]

An ORTEP drawing[9] of this complex is given in Figure 1. The pair of Cu ions are bridged by the endogenous phenolic oxygen O1 and the exogenous hydroxide oxygen O2; the Cu--Cu intermetallic separation is 2.938(1) Å. The Cu1 bound to the bidentate arm has a near square-pyramidal geometry with

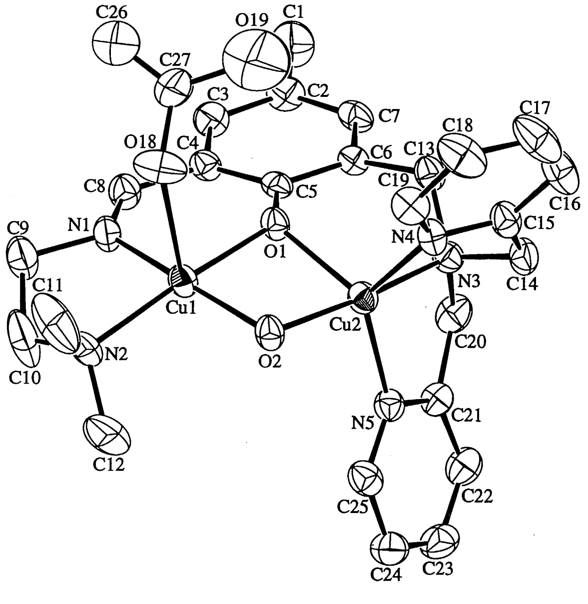
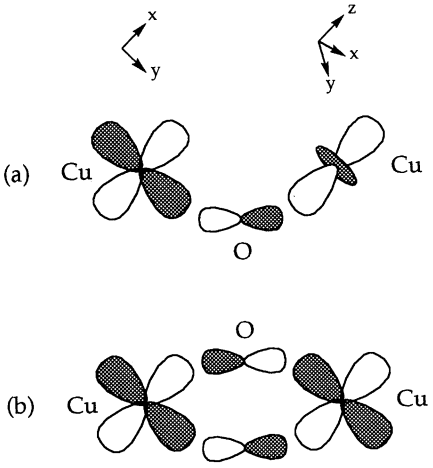


Figure 1. An ORTEP view of $[Cu_2(L)(OH)](ClO_4)_2 \cdot CH_3COOH$. Selected bond distances and angles: Cu1-O1 1.942(3), Cu1-O2 1.939(4), Cu1-N1 1.932(5), Cu1-N2 2.037(4), Cu1-O18 2.495 (5), Cu2-O1 2.060(4), Cu2-O2 1.908(3), Cu2-N3 2.014(4), Cu2-N4 2.058(5), Cu2-N5 2.029(5) Å; O1-Cu1-O2 82.9(1), O1-Cu1-N1 91.3(2), O1-Cu1-N2 173.2(2), O2-Cu1-N1 171.2(2), O2-Cu1-N2 98.8(2), N1-Cu1-N2 86.2(2), O1-Cu2-O2 80.6(1), O1-Cu2-N3 91.6(2), O1-Cu2-N4 111.2(2), O1-Cu2-N5 119.4(2), O2-Cu2-N3 171.4(2), O2-Cu2-N4 103.7(2), O2-Cu2-N5 98.2 (2), N3-Cu2-N4 82.4(2), N3-Cu2-N5 82.4(2), N4-Cu2-N5 127.3(2), Cu1-O1-Cu2 94.4(2), Cu1-O2-Cu2 99.6(2)°.

N1 and N2 of the arm and the two bridging oxygens on the equatorial base and acetic acid oxygen O18 at the apex. The in-plane Cu1-O1, Cu1-O2 and Cu1-N1 bond distances are similar (1.932(5) - 1.942(3) Å) but the Cu1-N2 bond is slightly longer (2.037(4) Å) owing to a strain in the chelate ring. The axial Cu-O18 bond is much elongated (2.495(5) Å) due to the Jahn-Teller effect.

The Cu2 bound to the tridentate arm has a five-coordinate geometry. The coordination geometry at the metal can be described as trigonal-bipyramid (discrimination parameter τ[10]: 0.74) with the hydroxo oxygen O2 and the articular nitrogen N3 at the axial sites and the phenolic oxygen O1 and two pyridine nitrogens N4 and N5 on the trigonal base. The O2-Cu2-N3 angle is 171.4° and the sum of the O1-Cu2-N4, N4-Cu2-N5 and O1-Cu2-N5 angles is 357.9°. The axial Cu2-O2 and Cu2-N3 bond distances (1.908(3) and 2.014(4) Å, respectively) are short compared with the equatorial Cu2-O1, Cu2-N4 and Cu2-N5 bond distances (2.060(4), 2.058(5) and 2.029(5) Å, respectively). This suggests that the unpaired electron of Cu2 resides in the d_{z^2} orbital.

The magnetic moment at room temperature is 1.56 μ_B (per Cu) and decreases with decreasing temperature to 0.78 μ_B at liquid nitrogen temperature. The magnetic behavior observed is typical of dinuclear ($S_1=1/2$)-($S_2=1/2$) case exhibiting antiferromagnetic spin-exchange interaction and the magnetic simulations by means of the Bleaney-Bowers equation[11] gave an exchange integral of J = -85 cm^{-1} (based of $H = -2JS_1S_2$). Based on the X-ray crystallographic result discussed above, the superexchange pathway for this complex is depicted by the antibonding molecular orbital formed by the local $d_{x^2-y^2}$ orbital of Cu1, a filled p orbital of the hydroxy bridge and the local d_{z^2} orbital of Cu2 (Scheme 2(**a**)). This mechanism is less effective, in accord with the relatively weak antiferromagnetic interaction observed (J = -85 cm^{-1}), than the spin-exchange mechanism (**b**) for the dinuclear case having two planar or axially distorted Cu(II) ions bridged by two oxygenic groups in the coplane.



Scheme 2. Spin-exchange (**a**) between local $d_{x^2-y^2}$ orbital and local d_{z^2} orbital through a filled p orbital of hydroxo bridge and (**b**) between two local $d_{x^2-y^2}$ orbitals in coplanar arrangement through two p orbitals of oxygenic bridges.

The absorption spectrum of the complex in N,N-dimethylformamide (DMF) shows a superposed band of d-d transitions of the two Cu(II) ions around 653 nm (ε =220 M^{-1}cm^{-1}). In the cyclic voltammogram (glassy carbon electrode, in DMF) two quasi-reversible couples are observed at -0.49 and -0.98 V (vs. Ag/Ag$^+$). The former couple appearing at a considerably high potential is attributed to the reduction of the Cu(II) center in the trigonal-bipyramidal environment.

From the above discussion, HL is a well-designed ligand of end-off type that provides a dinuclear core with geometric asymmetry and so must be of relevance to the modelling of unsymmetrical bimetallic biosites.

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7 NMR data: τ11.72 (s, 1H; phenol proton), 10.43 (s, 1H; CHO), 8.58, 7.65, 7.44 and 7.21 (m, 8H; pyridine protons), 7.40, 7.37 and 7.21 (s, 4H; benzene protons), 3.89 (s, 4H; N-CH$_2$-py), 3.80 (s, 2H; benzyl protons), 2.27 ppm (s, 3H; CH$_3$).

8 Found: C, 39.28; H, 4.46; N, 8.77; Cu, 15.76 %. Calcd for $C_{27}H_{35}N_5O_{12}Cu_2Cl_2$: C, 39.57; H, 4.30; N, 8.55; Cu, 15.51 %.

9 Crystal data for $[Cu_2(L)(OH)](ClO_4)_2\cdot CH_3COOH$: F.W.=819.6 prisms, monoclinic, space group P21/c (#14) with a = 12.257(2), b = 17.087(2), c = 17.077(2) Å, β=102.57°, V = 3491(8) Å^3, Z = 4, D_c =1.559 g cm^{-3}, *F(000)* = 3584.0, μ(MoKα) =14.36 cm^{-1}. Cell parameters were defined by 25 reflections with $28.9 < 2\theta < 30.0°$. 6392 unique reflections were measured with $2\theta_{max}$ = 50°. Measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069) and a 12 kW rotation anode generator. The structure was solved, expanded and refined using the teXsan crystallographic software package from Molecular Structure Corporation. Non-hydrogen atoms were aniso-tropically refined. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement based on 3034 observed reflections ($I \geq 3\sigma(I)$) converged with R = 0.037 and R_w = 0.038.

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