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Synthesis, Structure, and Magnetic Properties of a Novel Copper(II) Analogue of the Hemerythrin Active Center

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A novel binuclear copper(II) complex with a μ-hydroxo-bis(μ-carboxylato)dicopper core has been prepared. The crystal structure of the complex consists of dimeric $[Cu_2(OH)(HCOO)_2(bpy)_2]^+$ cations. The magnetic susceptibility data of the complex revealed that a ferromagnetic spin interaction exists in this complex.

Binuclear metal units consisting of μ-oxo(or hydroxo)-bis(μ-carboxylato)-bridges are a potential common structural feature of the active sites of hemerythrin, and purple acid phosphatase. Many transition metal complexes containing such frameworks, $[M_2(\mu\text{-O or }\mu\text{-OH})(\mu\text{-RCOO})_2]^{n+}$, have recently been prepared as the model complexes for those metalloproteins.[1] However, to the best of our knowledge no copper(II) complexes with such a core are known. In our recent papers, we have described both the magnetic properties and the crystal structures of bis(μ-carboxylato)-bridged binuclear copper(II) complexes, $[Cu(RCOO)(phen)(H_2O)]_2(NO_3)_2\cdot 4H_2O$.[2] As a part of continuing projects in this study, we have found that a novel μ-hydroxo-bis(μ-formato)-bridged binuclear copper(II) complex, $[Cu_2(OH)(HCOO)_2(bpy)_2]BF_4$ (where bpy=2,2'-bipyridine) is isolated by adjusting the pH of a reaction mixture in the preparation of bis(μ-carboxylato)-bridged copper(II) complexes.

The complex was obtained as follows. Formic acid (5 mmol) and bpy (5 mmol) were dissolved in 10 cm^3 of methanol, and the resulting solution was adjusted to pH 6.40 with triethylamine. To this solution 10 mmol of 45% aqueous $Cu(BF_4)_2$ was added under stirring, and then the pH was adjusted to 6.60 with triethylamine. Earlier precipitates were filtered off, and the filtrate was allowed to stand overnight at room temperature. Blue-green crystals were collected by filtration, washed with cold water, and dried in air. Anal. Found: C, 41.71; H, 3.03; N, 8.86; Cu, 20.26%. Calcd for $C_{22}H_{19}BCu_2F_4N_4O_5$: C, 41.72; H, 3.02; N, 8.85; Cu, 20.07%.

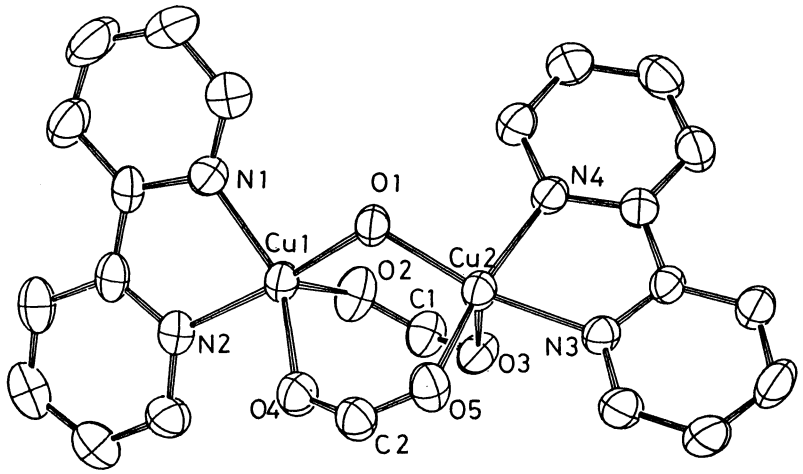

Fig. 1. ORTEP drawing for the complex cation with thermal ellipsoids scaled at the 50% probability level. Hydrogen atoms and BF_4^- have been omitted for clarity. Selected bond lengths (1/Å) and angles (ϕ/°): Cu1...Cu2 3.171(1), Cu1-O1 1.927(4), Cu1-O2 2.140(5), Cu1-O4 2.029(5), Cu1-N1 2.027(5), Cu1-N2 2.004(5), Cu2-O1 1.928(4), Cu2-O3 2.190(5), Cu2-O5 1.968(5), Cu2-N3 2.012(5), Cu2-N4 2.012(5); Cu1-O1-Cu2 110.7(2), O1-Cu1-N2 172.8(2), O4-Cu1-N1 147.2(2), Cu1-O4-C2 131.4(4), Cu1-O2-C1 124.5(4), O1-Cu2-N3 162.8(2), O5-Cu2-N4 168.2(2), Cu2-O3-C1 123.9(4), Cu2-O5-C2 125.8(4).

X-Ray structure analysis[3] revealed the structure of the complex consisting of dimeric $[Cu_2(OH)(HCOO)_2(bpy)_2]^+$ cations with five-coordinated copper ions linked by one hydroxo and two formato bridges (Fig. 1). The H atom position of the hydroxo group was located on a difference Fourier map and refined isotropically. The coordination geometries of the two copper atoms are significantly different. The geometry at Cu1 is better described as a distorted trigonal bipyramid (O1-Cu1-N2=172.8(2)°), with Cu1 lying 0.160 Å out of the equatorial plane. In contrast, the geometry at Cu2 is best described as distorted square pyramidal with O3 at the apex. The deviation of Cu2 from the N3, N4, O1, O5 least-squares plane is 0.215 Å. The Cu...Cu distance (3.171(1) Å) corresponds to the maximum value of those in bis(μ-carboxylato)-bridged copper(II) dimers (3.05-3.12 Å)[2,4] and in μ-hydroxo-μ-carboxylato-bridged copper(II) dimers (2.96-3.16 Å).[5] This elongation of the Cu...Cu distance is reflected on a significant increase of deformation in the bridging COO groups of the complex. The bond lengths of Cu1-O2, Cu1-O4, and Cu2-O3 are longer by 0.1-0.2 Å than the average Cu-O bond lengths (1.96-1.98 Å) in $[Cu(HCOO)(phen)(H_2O)]_2(NO_3)_2\cdot 4H_2O$[2] and the usual copper(II) formate dimers, $[Cu(HCOO)_2\cdot L]_2$.[6] The average Cu-O-C angles in the two bridging O-C-O moieties are 128.6(4)°

and 124.2(4)°, about 3-7° greater than those found in $[Cu(HCOO)_2 \cdot L]_2$. However, these angles are nearly equal to those observed for $[Cu(HCOO)(phen)(H_2O)]_2(NO_3) \cdot 4H_2O$. The Cu1-O1-Cu2 bridging angle is 110.7(2)° corresponding to the maximum value of those found in copper(II) dimers with the Cu-OH-Cu bridging system except those with only one hydroxo-bridge.

The magnetic data for the present complex is well represented by the Bleaney-Bowers equation,[7] $\chi_A = (Ng^2\beta^2/kT)[3 + \exp(-2J/kT)]^{-1} + N\alpha$. The value of $N\alpha$ was assumed to be 60×10^{-6} cm^3 mol^{-1}. The best-fit parameters of $-2J = -99$ cm^{-1} and $g = 2.17$ were obtained by a nonlinear least-squares fitting procedure. The effective magnetic moment per Cu, μ_{eff}, rises gradually from 1.95 B.M. at 293.3 K to 2.11 B.M. at 81.8 K (Fig. 2). This magnetic behavior is indicative of a strong ferromagnetic exchange interaction in the present complex, and quite different from that of $[Cu(HCOO)(phen)(H_2O)]_2(NO_3)_2 \cdot 4H_2O$ ($-2J = 125$ cm^{-1}).[2] The observed $-2J$ values for binuclear copper(II) complexes are composed of ferromagnetic and antiferromagnetic contributions, $-2J = J_{AF} - J_F$ (where J_{AF} and J_F represent the antiferromagnetic and ferromagnetic contributions, respectively).[8] In the trigonal-bipyramidal Cu1 site, the magnetic orbital is d_z2 with unpaired spin density primarily along the N2-Cu1-O1 axis. For square pyramidal Cu2, however, the magnetic orbital is $d_x2_{-y}2$ with lobes directed toward O1 and O5. The different geometries between two Cu ions in binuclear copper(II) complexes mean that the magnetic orbitals will be of different energies. Therefore, this σ-type pathway provided only a weak antiferromagnetic contribution; J_{AF} is very small and the net ferromagnetic coupling was observed. In addition, the smaller J_{AF} results from competition between two different magnetic exchange pathways, which may have opposite phases relative to each other, *i.e.* an orbital counter-complementary effect,[9] leading to the observed ferromagnetic interaction.

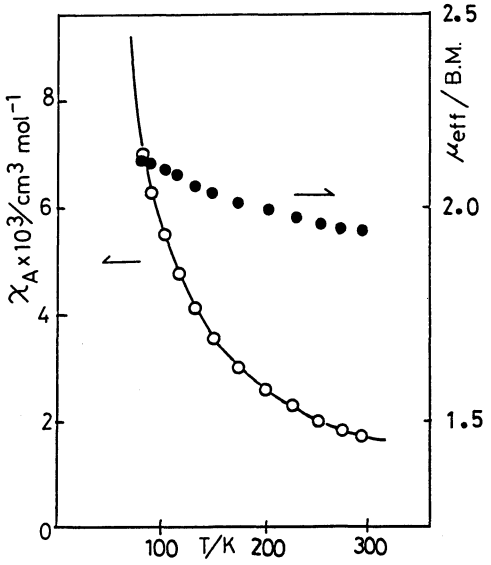

Fig. 2. Magnetic susceptibilities(○) and magnetic moments (●) for the complex. The solid curve was obtained as described in text.

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3) The crystal data: $C_{22}H_{19}BCu_2F_4N_4O_5$, MW=633.31, monoclinic, *C*2/*c*, *a*=33.260(8), *b*=10.614(14), *c*=13.776(10) Å, β=95.32(4)°, *V*=4843(7) Å^3, *Z*=8, μ(Cu *K*α)=27.95 cm^{-1}, D_m=1.73, D_x=1.737 g cm^{-3}, *R*=0.057, R_w=0.079. Intensity measurements were carried out for 2θ<120° on a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Cu *K*α radiation. Of the 3876 reflections measured, the unique 2881 reflections with I>3.00σ(I) were considered as observed. The structure is solved by direct methods using TEXRAY software package programs (TEXSAN). The non-hydrogen atoms were refined anisotropically.

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