Synthesis, Structure, and Magnetic Properties of Dinuclear Copper(II) Complexes with Novel Triple Carboxylato-Bridging Linkages

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Novel triply carboxylato-bridged dinuclear copper(II) complexes, $[Cu_2(Ph_2CHCOO)_3(L)_2]BF_4$, where L is bpy or phen, have been prepared. X-Ray structural analyses have revealed that each complex consists of a dicopper(II) core with unusual bridging geometries (*syn-syn* and μ_2,η^1 carboxylato-modes) reflected the versatility of carboxylates as bridging ligands. Magnetic susceptibility measurements for the present complexes show a weak antiferromagnetic coupling.

Recently, we have described both the crystal structures and the magnetic properties for carboxylato-bridged dinuclear copper(II) complexes with 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) functioned as a bidentate chelating ligand.[1,2] Related works have more recently been reported by Christou et al.[3,4] Moreover, bioinorganic chemists direct their attention to the versatility of binding modes of carboxylates in metalloprotain active sites.[5] In this paper, as an extension of our studies, we report on the preparation, the structural characterization, and the magnetism of the novel dicopper(II) complexes, $[Cu_2(Ph_2CHCOO)_3(bpy)_2]BF_4{\cdot}CH_3CN$ (**1**·CH_3CN) and $[Cu_2(Ph_2CHCOO)_3(phen)_2]BF_4$ (**2**), possessing some interesting carboxylate bridging modes in each triply bridged dicopper(II) core. Further, we have began to systematize the formation process of a new series of carboxylato-bridged dicopper(II) and dimanganese(II) complexes with bpy or phen.[2,6]

The compounds were obtained as follows. Complex **1**·CH_3CN: A 45% aqueous solution of $Cu(BF_4)_2$ (2 mmol) was added to a solution of $Ph_2CHCOOH$ (2 mmol) and bpy (2 mmol) in 10 cm^3 of acetonitrile/methanol 1:1 mixture under stirring. To the resulting sky-blue solution *ca.* 1 cm^3 of triethylamine was added under stirring. The earlier precipitates were filtered off, and then the filtrate was allowed to stand for one day at room temperature. Deep-blue crystals were collected, washed with acetonitrile, and dried in air. The solvent molecules were lost upon drying of the crystals, so that the sample employed in magnetic susceptibility measurements was analyzed as **1**. Complex **2**: To a solution of $Ph_2CHCOOH$ (1 mmol) and phen·H_2O (1 mmol) in 10 cm^3 of methanol a 45% aqueous solution of $Cu(BF_4)_2$ (1 mmol) was added under stirring, and then the resulting solution was adjusted to pH 2.6 with triethylamine. The bluish-green solution was filtered and the filtrate was stored for three days at room temperature. Bluish-green crystals were collected, washed with cold methanol, and dried in air. Anal. Found (**1**) : C, 64.13; H, 4.36; N, 4.73; Cu, 11.09%. Calcd for $C_{62}H_{49}BCu_2F_4N_4O_6$: C, 64.20; H, 4.26; N, 4.83; Cu, 10.96%. Found (**2**) : C, 65.57; H, 4.13; N, 4.61; Cu, 10.70%. Calcd for $C_{66}H_{49}BCu_2F_4N_4O_6$: C, 65.62; H, 4.09; N, 4.64; Cu, 10.52%. In addition, we have found a novel copper(II) analogue of the hemerythrin active center, $[Cu_2(OH)(Ph_2CHCOO)_2(bpy)_2]BF_4$, can be isolated by addition of triethylamine to an acetonitrile solution of the doubly carboxylato-bridged dicopper(II) complex, $[Cu(Ph_2CHCOO)(bpy)(H_2O)]_2(BF_4)_2$, obtained by a modified method of the preparation for **1**. X-Ray

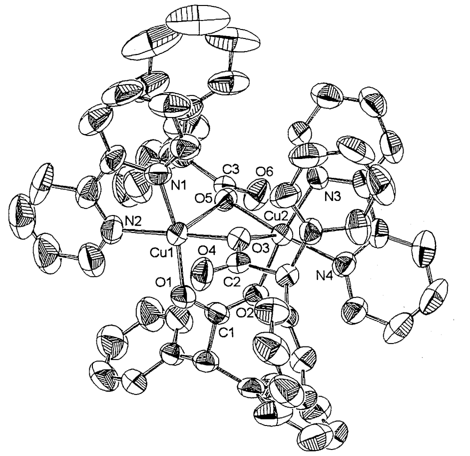

Figure 1. An ORTEP drawing for the complex cation **1**·CH_3CN. Selected bond distances(Å) and angles(°): Cu1–O1 1.937(5), Cu1–O3 1.959(4), Cu1–O5 2.316(5), Cu1–N1 1.968(6), Cu1–N2 1.996(6), Cu2–O2 1.959(5), Cu2–O3 2.269(5), Cu2–O5 1.957(4), Cu2–N3 1.984(6), Cu2–N4 1.987(6), Cu1...O4 2.846(5), Cu2...O6 2.908(5), Cu1...Cu2 3.146(2); O1–Cu1–N1 168.3(2), O3–Cu1–N2 174.4(2), O2–Cu2–N3 171.2(2), O5–Cu2–N4 170.4(2), Cu1–O3–Cu2 95.9(2), Cu1–O5–Cu2 94.5(2).

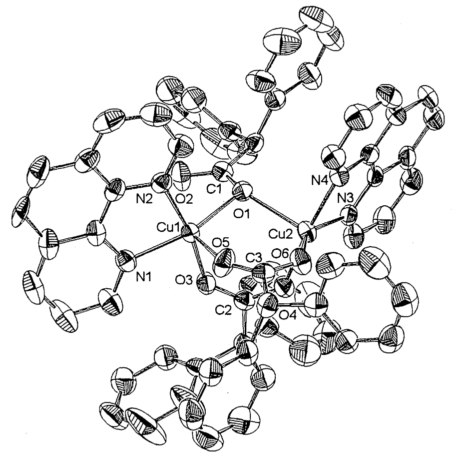

Figure 2. An ORTEP drawing for the complex cation **2**. Selected bond distances(Å) and angles(°): Cu1–O1 2.030(4), Cu1–O3 1.961(4), Cu1–O5 2.136(4), Cu1–N1 2.017(4), Cu1–N2 2.009(5), Cu2–O1 2.232(4), Cu2–O4 1.939(4), Cu2–O6 1.936(4), Cu2–N3 2.043(4), Cu2–N4 2.005(5), Cu1...O2 2.550(4), Cu1...Cu2 3.357(2); O1–Cu1–N1 158.9(2), O3–Cu1–N2 168.9(2), O4–Cu2–N4 171.1(2), O1–Cu2–O6 110.0(2), O1–Cu2–N3 102.0(2), O6–Cu2–N3 147.7(2), Cu1–O1–C1 101.7(3), Cu2–O1–C1 139.1(3), Cu1–O1–Cu2 103.8(2).

structural analysis for the complex is in progress.[7] The remarkable feature as a bridging ligand of diphenylacetate anion affording various linkages in these complexes is greatly interesting, though it is not clear whether this ability of diphenylacetate anion is attributable to strength of its Lewis basicity or another factors such as some steric factors.

The crystal structures of **1**·CH_3CN and **2** are shown in Figures 1 and 2, respectively.[8,9] The complex **1**·CH_3CN consists of a dicopper(II) core with three 2,2-diphenylacetate bridges and two bidentate ligands of bpy. One of the bridging carboxylates is in the familiar bidentate *syn-syn* mode and the others have the unique μ_2,η^1 bridging mode. The coordination around each copper(II) ion is essentially a square pyramidal geometry with the basal plane comprised of two nitrogen atoms of bpy and two oxygen atoms of carboxylates. Each axial site is occupied by a monoatomic bridging carboxylate oxygen atom (O5 for Cu1 and O3 for Cu2). The Cu–O distances at the axial sites were considerably longer by 0.31–0.38 Å than those in the basal plane. The Cu1–O3–Cu2 and Cu1–O5–Cu2 angles are 95.9(2)° and 94.5(2)°, respectively. Thus this monoatomic bridging mode has formed a rare carboxylato-linkage resulting an asymmetric bridging structure.[10] Further, the Cu1...O4 and Cu2...O6 separations are 2.846(5) and 2.908(5) Å, respectively. In the monoatomic bridging carboxylates, each C–O distances concerning the dangling oxygen atom appears somewhat longer by 0.074 and 0.080 Å than the other C–O distances, indicating the presence of some double bond character in the C2–O4 and C3–O6 bonds. These results suggest that the sixth coordination from the dangling oxygen atoms toward each copper(II) ion is very weak.

The complex cation of **2** consists of a triply bridged core contains two copper(II) ions linked by three 2,2-diphenylacetate ligands. These carboxylates have formed two bidentate *syn-syn* bridging mode and one μ_2,η^1 bridging mode.[3] The environment of Cu1 is a pseudo-square pyramidal geometry with O5 at apical position. The deviation of Cu1 from the O1, O3, N1, N2 least-squares plane toward O5 is 0.25 Å. In contrast, the coordination around Cu2 is a fairly distorted trigonal-bipyramidal geometry with O1, O6 and N3 in the equatorial plane and O4 and N4 at apices. The Cu1...O2 distance is 2.550(4) Å and the twisted carboxylate ligand is tilted toward Cu1, as can be seen from that the Cu1–O1–C1 angle(101.7(3)°) being significantly smaller than the Cu2–O1–C1 angle(139.1(3)°). These results indicate an obvious coordination of dangling carboxylate oxygen O2 to the sixth vacant sites of Cu1. Such a weak bonding interaction may elongate the Cu2–O1 bond length (2.232(4) Å) and cause a distortion from the trigonal-bipyramidal configuration toward the square pyramidal geometry around Cu2.

Magnetic susceptibility measurements for the complexes **1** and **2** were carried out in the temperature range of 80–300 K. The temperature dependence of the magnetic susceptibilities (χ_A) and the effective magnetic moments (μ_{eff}) per Cu(II) ion are shown in Figure 3. The μ_{eff} values for **1** and **2** slightly decrease 1.91 B.M. and 1.89 B.M. at the room temperature to 1.87 B.M. and 1.88 B.M. at 81.2 K, respectively. A nonlinear least-squares fitting procedure of the magnetic data to the Bleaney-Bowers equation[11] gave the following spin exchange coupling parameters : (**1**), $-2J = 13\ cm^{-1}$ and $g = 2.23$; (**2**), $-2J = 8\ cm^{-1}$ and $g = 2.21$. These results revealed that a weak antiferromagnetic interaction is operative in the present complexes. The antiferromagnetic interaction in **1** can be operative primarily via the *syn-syn* carboxylato bridge directed toward the $d_{x^2-y^2}$ magnetic orbitals with unpaired spin density on the two copper(II) ions. In complex **2**, the weaker antiferromagnetic interaction may be due to the spin coupling through the in-plane carboxylato bridge (Cu1–O3–C2–O4–Cu2) along the magnetic orbitals of $d_{x^2-y^2}$ (Cu1) and d_{z^2} (Cu2).[12] These results contrast finely with the observed ferromagnetic interaction for $[Cu_2(OH)(HCOO)_2(bpy)_2]BF_4$ ($-2J = -99\ cm^{-1}$),[2] in which the d_{z^2} magnetic orbital directs toward the out-of-plane hydroxo bridge. In addition, the magnetic behavior of **2** is similar to that of the analogous acetate complex, $[Cu_2(CH_3COO)_3(bpy)_2]ClO_4$,[3] in the 80–300 K temperature range, though this acetate complex was observed to be ferromagnetic below 60 K.

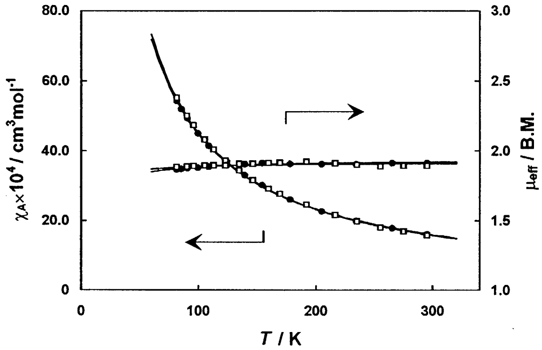

Figure 3. Magnetic susceptibilities χ_A and effective magnetic moments μ_{eff} for **1** (●) and **2** (□). The solid curves were obtained as described in the text.

References and Notes

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7 $[Cu_2(OH)(Ph_2CHCOO)_2(bpy)_2]BF_4$: The current *R* value is 0.071 for 6145 unique reflections.; $[Cu(Ph_2CHCOO)(bpy)(H_2O)]_2(BF_4)_2$: Single crystals suitable for the X-ray analysis have not been obtained yet.

8 Crystal data for **1**·CH_3CN: $C_{64}H_{52}BCu_2F_4N_5O_6$, Mw = 1201.04, monoclinic, $P2_1/c$, $a = 14.803(5)$, $b = 13.151(6)$, $c = 29.898(7)$ Å, $\beta = 98.96(3)°$, $V = 5750(3)$ Å^3, $Z = 4$, $D_x = 1.387$ g cm^{-3}, $D_m = 1.39$ g cm^{-3}, $R = 0.058$ and $R_w = 0.068$ for 10631 unique reflections.

9 Crystal data for **2**: $C_{66}H_{49}BCu_2F_4N_4O_6$, Mw = 1208.03, triclinic, $P\bar{1}$, $a = 13.683(8)$, $b = 18.163(2)$, $c = 13.204(3)$ Å, $\alpha = 105.86(1)$, $\beta = 110.28(3)$, $\gamma = 100.18(3)°$, $V = 2823(2)$ Å^3, $Z = 2$, $D_x = 1.421$ g cm^{-3}, $D_m = 1.43$ g cm^{-3}, $R = 0.049$ and $R_w = 0.055$ for 12958 unique reflections.

10 Rardin et al. have reported only the crystal structure of the complex with this bridging linkage as unpublished results in ref. 5.

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