Dinuclear Copper(II) Complexes of Free Radical Carboxylic Acids

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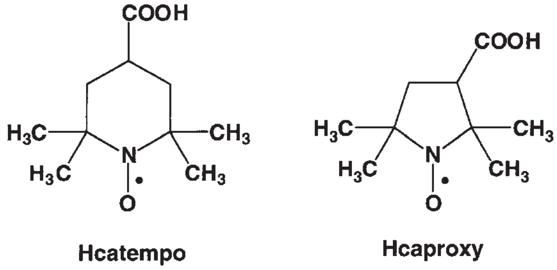
(Received February 28, 2002; CL-020194)

Copper(II) complexes of 4-carboxyl-2,2,6,6,-tetramethylpiperidinyloxy (Hcatempo) and 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (Hcaproxy), $[Cu_2(catempo)_4(H_2O)_2]$ (**1**) and $[Cu_2(caproxy)_4(H_2O)_2]$ (**2**), have been synthesized and characterized by X-ray crystallography, electronic spectroscopy and magnetic susceptibility measurement.

Metal complexes of nitronyl nitroxides have been subjected to intensive study for the past decades.[1] Some efforts to make nitroxide adducts have been done for systems of copper(II) carboxylates and nitronyl nitroxide radicals in order to develop high-spin molecules via coupling of these spins.[2] However, earlier attempts to produce such compounds were unsuccessful, because of the structural change from the well-known lantern-type dinuclear core, leading to strong antiferromagnetic interaction between the radical and copper(II) spins.[2] Recently, we and other groups successfully isolated adducts of copper(II) carboxylate and nitronyl nitroxides, in which the lantern-type core is maintained.[3,4] In these adducts, the organic radical occupies the axial position of the copper atom and the magnetic interaction between the radical and copper(II) spins is still antiferromagnetic. It might be possible that these spins interact ferromagnetically if the organic radicals occupy the substituent-group positions of the bridging carboxylate, and the copper(II) magnetic orbital and the radical orbitals are orthogonal using the carboxylate bridges. We have prepared new copper(II) carboxylate dimers bearing four radical spins by introducing organic radicals into the substituent groups of the carboxylate bridges. We report here the first example of copper(II) salts of the free radical carboxylic acids: 4-carboxy-2,2,6,6-tetramethylpiperidinyloxy (Hcatempo) and 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (Hcaproxy), $[Cu_2(catempo)_4(H_2O)_2]$ (**1**) and $[Cu_2(caproxy)_4(H_2O)_2]$ (**2**).



Scheme 1.

Reaction of Hcatempo with $Cu(NO_3)_2 \cdot 6H_2O$ in H_2O results in the formation of **1** as a light green powder. Recrystallization of **1** from CH_3CN gave green crystals.[5] Similarly, treatment of copper(II) nitrate with Hcaproxy led to a green solution and subsequent isolation of a copper salt **2** as light green powder.[6] Analytical data of these complexes are consistent with the formulation of carboxylato-bridged dinuclear species.[5,6] The *syn-syn* bridging configuration of the carboxylate groups can be deduced from Δ values $[\nu_{as}(COO) - \nu_s(COO)]$ of infrared spectra of **1** $[\nu_{as}(COO)\ 1634,\ \nu_s(COO)\ 1418\,cm^{-1}]$ and **2** $[\nu_{as}(COO)\ 1625,\ \nu_s(COO)\ 1423\,cm^{-1}]$.[7] Diffuse reflectance spectra of these complexes show a distinctive band at 350 (for **1**) or 371 (for **2**) nm, which is characteristic of copper(II) carboxylate dimer core,[8] and a broad band at around 520 nm (for **1** and **2**), which can be assigned to d-d transition bands. The dinuclear structure was confirmed by the X-ray crystal structure analysis of **1**.[9] A perspective view of the structure is shown in Figure 1. The complex has the crystallographic inversion center at the center of the Cu_2 core. The Cu–Cu′ distance (2.6138(8) Å) is comparable to those of copper(II) carboxylate dimers.[10] The coordination geometry of the copper atom is a square pyramid as normally found in copper(II) carboxylate dimers. The copper atom is displaced towards the water molecule from the basal O1–O2′–O3–O4′ plane by 0.19 Å. It is to be noted that the N–O bond lengths of four catempo ligands [1.279(7) and 1.292(7) Å] are similar and are nearly same to the corresponding bond length (1.283(9) Å) of tempo, which is consistent with the isolated free radical.[11] Although several metal salts of Hcatempo and Hcaproxy have been reported in the literature, to our knowledge, this is the first example of copper(II) complexes of the free radical carboxylic acids and the first example in which the radical

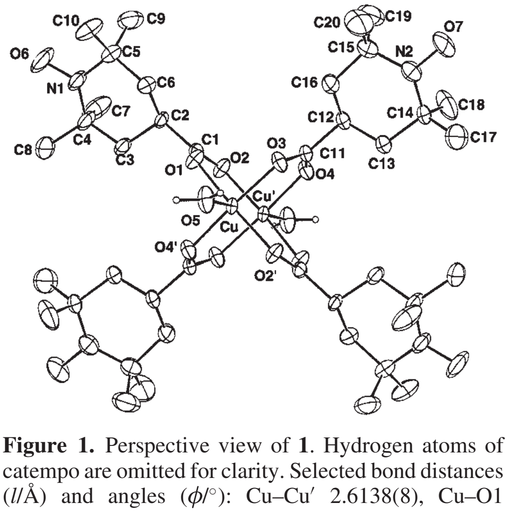


Figure 1. Perspective view of **1**. Hydrogen atoms of catempo are omitted for clarity. Selected bond distances (l/Å) and angles (ϕ/°): Cu–Cu′ 2.6138(8), Cu–O1 1.967(4), Cu–O2′ 1.960(4), Cu–O3 1.976(4), Cu–O4′ 1.973(4), Cu–O5 2.138(4), O1C1 1.255(6), O2–C1 1.258(6), O3–C11 1.264(7), O4–C11 1.233(6), O6–N1 1.279(7), O7–N2 1.292(7); O1–Cu–O2′ 169.0(2), O1–Cu–O3 88.6(2), O1–Cu–O4′ 89.6(2), O1–Cu–O5 95.4(2), O2′–Cu–O3 89.2(2) O2′–Cu–O4′ 90.6(2), O2′–Cu–O5 95.5(2), O3–Cu–O4′ 168.8(2), O3–Cu–O5 94.7(2), O4′–Cu–O5 96.5(2).

molecule is incorporated as a bridging ligand for the two metal atoms. In the crystal, the nitroxide oxygen atoms are hydrogen-bonded to the neighboring water molecules coordinated to the copper atoms of the carboxylate dimers [O5· · ·O6 (1/2–*x*, 1/2–*y*, 5/2–*z*), 2.738(7), O5· · ·O7 (1/2–*x*, 1/2–*y*, 3/2–*z*) 2.755(6) Å] to form a three-dimensional network (Figure 2).

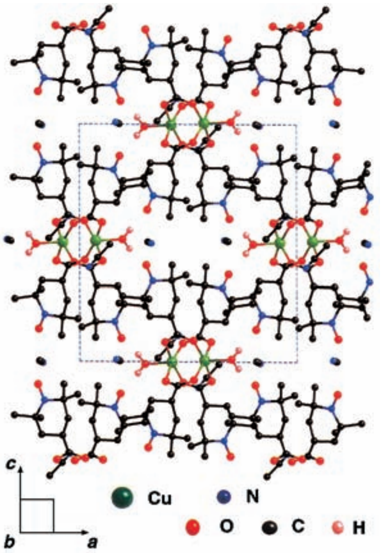


Figure 2. Crystal packing of **1**. Hydrogen atoms of catempo are omitted for clarity.

The magnetic properties of **1** and **2** are different from those of copper(II) carboxylate dimers.[10] The effective magnetic moment (4.00 and 3.78 B.M. per dinuclear molecule at 300 K for **1** and **2**, respectively) is a little lower than the spin-only value (4.24 B.M.) for non-interacting six 1/2 spins. The magnetic moment gradually decreases with lowering of temperature, and reaches a value of 3.02 and 2.45 B.M. for **1** and **2**, respectively, at 4.5 K (Figure 3). This features are rather similar to those of the adducts of copper(II) carboxylate and nitronylnitroxides.[3] However, the decreasing of the magnetic moments is quite small compared with those of these adducts, suggesting the cancellation of the antiferromagnetic interaction between the two copper ions due to relative increase of the paramagnetic component by the radical spins of the carboxylate bridges. In this case, intermolecular radical-radical interaction may be neglected, because the nitronyl nitroxide radicals are well separated in the crystal of **1**, where the closest intermolecular contact between the nitronyl nitroxide radicals is O6· · ·O7 (*x*, *y*, *z* + 1) [4.190(7) Å]. Therefore, the magnetic susceptibility data were analyzed by the equation based on a model consisting of a dinuclear copper(II) unit and four radicals, $\chi_M = (2Ng^2\beta^2/kT)[3 + \exp(-2J/kT)]^{-1} + C/(T-\theta) + 2N\alpha$.[3] The best fitting parameters ($J = -169$ and $-146\,\mathrm{cm}^{-1}$, $g = 2.2$ and 2.3, $\theta = -1.4$ and -2.2 K, $C = 1.51$ and $1.12\,\mathrm{cm^3Kmol^{-1}}$ for **1** and **2**, respectively) were obtained by fixing $N\alpha$ at $60 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$. The J values are comparable to those of copper(II) carboxylates.[10] Small negative θ values suggest that antiferromagnetic interaction between the nitroxide radicals and the copper atom become weak in the present complexes. These complexes can be useful as building blocks in producing new magnetic material. Further studies are now in progress.

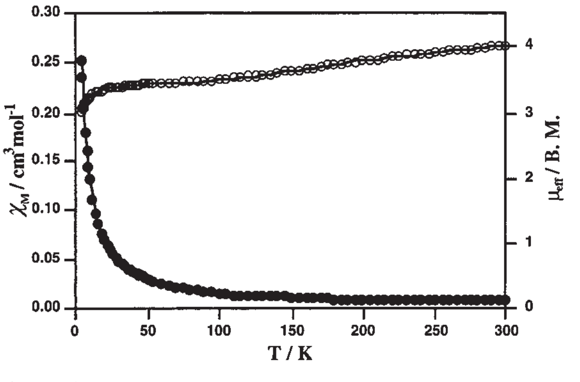


Figure 3. Temperature dependance of magnetic moment (○) and magnetic susceptibility (●) of **1**. The solid lines represent the fits using the parameters given in the text.

References and Notes

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5 Sodium hydroxide (101 mg, 2.24 mmol) was dissolved in distilled water (40 cm^3), then Hcatempo (300 mg, 1.50 mmol) was added with stirring. The solution was neutralized with nitric acid. Addition of copper(II) nitrate (182 mg, 0.753 mmol) and concentration gave light green precipitate. The precipitate was recrystallized from acetonitrile to give green columns of **1**. Yield 288 mg (68.3%). Found: C, 50.30; H, 7.51; N, 5.91%. Calcd for $C_{40}H_{72}Cu_2N_4O_{14}$ C, 50.04; H, 7.56; N, 5.84%. IR (KBr, cm^{-1}): ν_{as}(COO) 1634, ν_s(COO) 1418, ν(NO) 1362.

6 Compound **2** was prepared in the same way as that for **1**, except for using Hcaproxy instead of Hcatempo. Yield, 208 mg (61.6%). Found: C, 48.03; H, 6.72; N, 6.15%. Calcd for $C_{36}H_{64}Cu_2N_4O_{14}$ C, 47.85; H, 7.08; N, 6.20%. IR (KBr, cm^{-1}): ν_{as}(COO) 1625, ν_s(COO) 1423, ν(NO) 1366.

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9 Crystallographic data: for **1**·4CH$_3$CN; $C_{48}H_{84}Cu_2N_8O_{14}$, fw = 1124.33, monoclinic, space group $P2_1/n$, $a = 15.490(4)$, $b = 11.378(2)$, $c = 16.775(5)$ Å, $\beta = 90.84(1)°$, $V = 2956(1)$ Å^3, $Z = 2$, $D_m = 1.32$, $D_c = 1.26\,\mathrm{g\,cm^{-3}}$, μ(Mo Kα) = 7.82 cm^{-1}, crystal dimensions $0.35 \times 0.40 \times 0.65$ mm^3, 5777 reflections measured ($2\theta_{max} = 51°$), 3741 [$I \geq 3\sigma(I)$] used in the refinement, $R = 0.055$, $R_w = 0.066$. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by the direct method and refined by the full-matrix least-squares method using a MolEN program package.[3]

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