Chain Compounds Formed by the Reaction of Copper(II) Carboxylate [$Cu_2(O_2CR)_4$] (R = $C(CH_3)_3$, CCl_3) and Bridging Ligand L (L = Pyrazine, 4,4'-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane)

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(Received April 17, 1995)

Reaction of copper(II) carboxylates, $Cu_2(O_2CR)_4$ (R = $C(CH_3)_3$ and CCl_3) with bridging ligands, L (L = pyrazine (pyz), 4,4'-bipyridine (4,4'-bpy), and 1,4-diazabicyclo[2.2.2]-octane (dabco)) gave compounds, $[Cu_2(O_2CC(CH_3)_3)_4L]_n$ (L = pyz (**1**), 4,4'-bpy (**2**), and dabco (**3**)), $[Cu_2(O_2CCCl_3)_4L_2]\cdot nH_2O$ (L = pyz; n = 1 (**4**), L = 4,4'-bpy; n = 1 (**5**), and L = dabco; n = 3 (**6**)), and $[Cu_4(OCH_3)_4(O_2CCCl_3)_4(CH_3OH)_2(pyz)]_n\cdot 2nCH_3OH$ (**7**). The X-ray structure analyses of **1** and **7** show chain structures where the carboxylate dimer units or the cubane tetranuclear units are linked by the pyrazine molecules.

One-dimensional chain compounds have been the focus of very active research because of their unique physicochemical properties.[1] In order to achieve synthesis of such chain compounds, we have introduced pyrazine (pyz), 4,4'-bipyridine (4,4'-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco) as bridging ligands for metal carboxylate dimers. Until now, we have reported Mo, Rh, and Ru systems which have metal-metal bonds.[2-4] As for Cu system, the examples of the linear chain compounds are still limited despite a vast number of the dimeric copper(II) carboxylates and their adducts, $[Cu_2(O_2CR)_4X_2]$.[5] For example, pyrazine and 1,4-diazabicyclo[2.2.2]octane adducts of copper(II) acetate represent linear-chain compounds in which copper(II) acetate units are linked by the bridging ligands.[6] In the course of our studies on Cu system, we have found an unexpected chain compound which cubane tetranuclear units are linked by pyrazine molecules. Herein we report the preparation and X-ray crystal structure of the novel chain compound together with other preliminary results for Cu system.

When copper(II) pivalate[7] was treated with equivalent amount of the bridging ligand, L, in tetrahydrofurane or acetonitrile, chain compounds of the dimeric copper(II) carboxylates were isolated like the case for copper(II) acetate.[6] Microanalysis figures of C, H, and N agree with the formulation $[Cu_2(O_2CC(CH_3)_3)_4L]$ (L = pyz (**1**), 4,4'-bpy (**2**), and dabco (**3**)). Their IR spectra show two stretching bands,[8] the difference in energy of which is characteristic of bridging carboxylate groups.[9] The diffuse reflectance spectra show two absorption bands in the visible and near UV region.[10] The near UV band is characteristic of carboxylate-bridge dinuclear structure.[5] The linear-chain structure was confirmed by the X-ray crystal analysis of **1**.[11] A perspective view of **1** is shown in Figure 1. The complex has the crystallographic inversion center at the center of the CuCu core. The Cu-Cu separation is 2.584(2) Å. The pyrazine molecules link the $Cu_2(O_2CC(CH_3)_3)_4$ units with a Cu-N distance of 2.195(8) Å. It is to be noted that the Cu-Cu-N angle is crystallographically 180° showing a good linearity of the chain structure. In spite of the chain structure, the magnetic susceptibility data (80—300 K) of **1** could be interpreted in terms of the Bleaney-Bowers equation ($g = 2.09$, $J = -183\ \mathrm{cm^{-1}}$, and $N\alpha = 60 \times 10^{-6}$ cgs emu).[12] This means that interdimer interaction through the pyrazine molecules is negligibly small in **1**.

On the other hand, bis-L adducts of the dimeric copper(II) carboxylates were isolated when copper(II) trichloroacetate[13] was used as the metal source. Addition of a methanol solution of copper(II) trichloroacetate to a methanol solution of L both in 1:1 and 1:2 molar ratios resulted in the formation of microcrystalline precipitate of $[Cu_2(O_2CCCl_3)_4L_2]\cdot nH_2O$ (L = pyz; n = 1 (**4**), L = 4,4'-bpy; n = 1 (**5**), and L = dabco; n = 3 (**6**)).[14] The IR and diffuse reflectance spectra are consistent with the carboxylate-

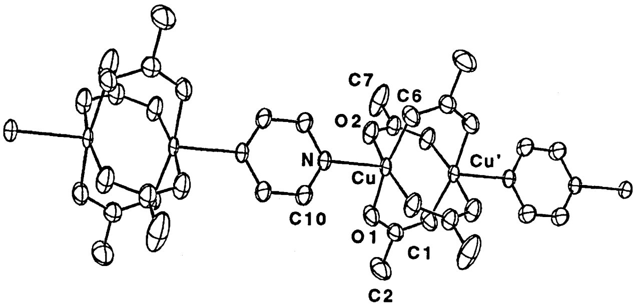

Figure 1. Perspective view of the portion of the chain of **1** (CH_3 groups of the pivalate ions are omitted for clarity). Selected interatomic distances (l/Å): Cu-Cu' 2.584(2), Cu-O1 1.963(7), Cu-O2 1.966(4), Cu-N 2.195(8). Prime refers to the equivalent position (-x, -y, -z).

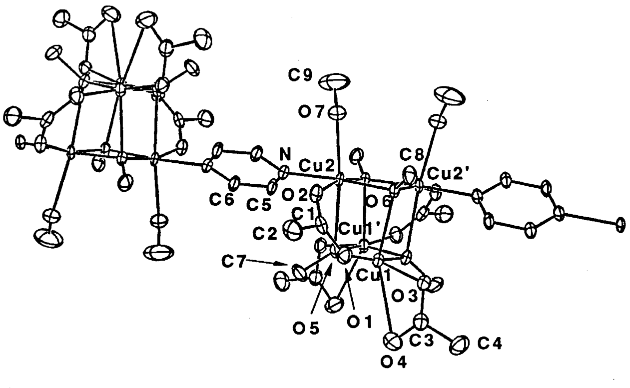

Figure 2. Perspective view of the portion of the chain of **7** (Cl atoms of the trichloroacetate ions are omitted for clarity). Selected interatomic distances (l/Å) and angles (ϕ/°): Cu1-Cu1' 2.946(2), Cu2-Cu2' 2.980(1), Cu1-Cu2 3.064(1), Cu1-Cu2' 3.373(1), Cu1-O1 1.981(6), Cu1-O3 1.948(6), Cu1-O4 2.757(8), Cu1-O5 1.935(6), Cu1-O5' 1.943(6), Cu1-O6 2.402(6), Cu2-O2 1.979(6), Cu2-O5 2.526(6), Cu2-O6 1.970(5), Cu2-O6' 1.947(6), Cu2-O7 2.325(7), Cu2-N 2.043(6); Cu1-O5-Cu1' 98.9(2), Cu1-O5-Cu2 85.7(2), Cu1'-O5-Cu2 97.2(2), Cu1-O6-Cu2 88.4(2), Cu1-O6-Cu2' 101.2(2), Cu2-O6-Cu2' 99.1(3). Primes refer to the equivalent positions (3/2 - x, y, 1/2 - z).

bridge structures of these compounds.[8,10] Blue crystalls of **4** were obtained by diffusing together methanol solutions of $Cu_2(O_2CCCl_3)_4$ and pyz in a 1:2 ratio for several days. Interestingly, the blue crystalline form of **4** undergoes a complete change into the dark-green crystalline form (**7**) when left in contact with the methanolic mother-liquor over the period of a few months. The IR spectrum of this compound shows two kinds of ν_{as}(COO) and ν_s(COO) bands which correspond to the bridging and bidentate trichloroacetate groups.[8] The diffuse reflectance spectrum of **7** does not show the near-UV band characteristic of the dimeric carboxylate structure,[10] being different from that of **4**. The structure revealed by X-ray crystallography shows that an unprecedented chain molecule, $[Cu_4(OCH_3)_4(O_2CCCl_3)_4(CH_3OH)_2(pyz)]_n\cdot 2nCH_3OH$,[14] is formed by alternated arrangement of the tetranuclear cubane unit and the pyrazine molecule which has a crystallographic inversion center (Figure 2).[11] Each tetranuclear cubane has a crystallographic 2-fold axis and is formed by four copper atom and four triply bridging methoxo-oxygen atoms with four short Cu-Cu distances of 2.946(2)–3.064(1) Å and two long ones of 3.373(1) Å. Two of the four trichloroacetate groups are bidentate in an unsymmetrical way (Cu1-O3 1.948(6) Å, Cu1-O4 2.757(8) Å); the others bridge the two copper atoms in a syn-syn configuration (Cu1-O1 1.981(6) Å, Cu2-O2 1.979(6) Å). The sixth coordination site of the Cu2 atom is occupied by the methanol oxygen O7. Similar cubane-type structures have been found in some alkoxo-bridged copper(II) complexes.[15] The Cu_4O_4 cores are usually classified into two groups according to the arrangement of long and short Cu-O bonds. The present Cu_4O_4 core belongs to type C complexes which obey the Curie-Weiss law with negative Weiss constants, θ.[15] The magnetic moment of **7** decreases from 2.06 B.M./Cu at 299 K to 1.41 B.M./Cu at 80 K. The susceptibility data (80—300 K) follow the Curie-Weiss law with θ = -205 K, indicating that there is a significant antiferromagnetic interaction between the copper ions.

The different product of **7** from the cases for the pivalate and acetate seems to come from the electron-withdrawing nature of the chlorine atoms on the carboxylate groups, which enhances the metal acidity. In ordet to elucidate the origin of the formation of the novel chain structure, further extensive studies are necessary. Such efforts are now under way.

References and Notes

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8 IR (Nujol mull, ν/cm^{-1}) **1**: ν_{as}(COO) 1610, ν_s(COO) 1420; **2**: ν_{as}(COO) 1616, ν_s(COO) 1422; **3**: ν_{as}(COO) 1616, ν_s(COO) 1420; **4**: ν_{as}(COO) 1662, ν_s(COO) 1352; **5**: ν_{as}(COO) 1664, ν_s(COO) 1336; **6**: ν_{as}(COO) 1652, ν_s(COO) 1336; **7**: ν_{as}(COO) 1676, 1646, ν_s(COO) 1338, 1326.

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10 Diffuse reflectance spectra: λ_{max}/nm **1**: 394, 667; **2**: 388, 702; **3**: 374sh, 706; **4**: 379, 719; **5**: 340sh, 756; **6**: 350, 820; **7**: 735.

11 Crystal data for **1**: $C_{24}H_{40}N_2O_8Cu_2$, M = 611.68, monoclinic, space group $C2/m$, a = 16.505(1), b = 9.761(1), c = 12.557(1) Å, β = 129.63(1)°, V = 1558.2(2) Å^3, Z = 2, D_c = 1.31 gcm^{-3}, D_m = 1.31 gcm^{-3}, μ(Mo-Kα) = 14.1 cm^{-1}, F(000) = 640, T = 298 K, R = 0.062, R_w = 0.086. A total of 1224 reflections were measured in the range $2 \le 2\theta \le 47°$; 1023 with $I \ge 3\sigma(I)$ were assumed observed. For **7**: $C_{20}H_{32}N_2O_{16}Cl_{12}Cu_4$, M = 1236.1, monoclinic, space group $P2/n$, a = 14.876(7), b = 10.432(2), c = 14.998(4) Å, β = 102.55(1)°, V = 2272(1) Å^3, Z = 2, D_c = 1.81 gcm^{-3}, D_m = 1.81 gcm^{-3}, μ(Mo-Kα) = 26.2 cm^{-1}, F(000) = 1228, T = 298 K, R = 0.060, R_w = 0.071. A total of 3627 reflections were measured in the range $2 \le 2\theta \le 48°$; 2706 with $I \ge 3\sigma(I)$ were assumed observed. For the determination of both structures, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by the direct methods and refined by the full-matrix least-squares methods using the MolEN program package.

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