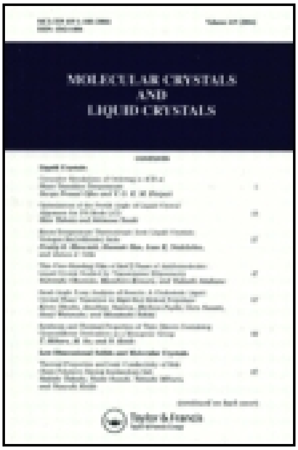

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Coordination Polymers of Copper(II) and Copper(I) Trifluoroacetates with Pyrazine

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Coordination Polymers of Copper(II) and Copper(I) Trifluoroacetates with Pyrazine

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New coordination polymers of copper(II) and copper(I), $[Cu(tfa)_2(pyz)_2]_n$ (Htfa = trifluoroacetic acid, pyz = pyrazine) (**1**), $[Cu_2(tfa)_2(CH_3O)_2\text{-}(pyz)_2]_n$ (**2**), and $[Cu_2(tfa)_2(pyz)_3]_n$ (**3**), have been synthesized and characterized structurally. The crystal structure of **2** consists of methoxo-bridged dinuclear copper(II) units which are connected by pyrazine molecules to form a two-dimensional network. The crystal structure of **3** shows a two-dimensional net-like structure, where each copper(I) atom has a distorted tetrahedral arrangement. The magnetic property of **2** is antiferromagnetic.

Keywords: coordination polymer; copper(II) complex; copper(I) complex; crystal structure; magnetic property

INTRODUCTION

Coordination polymers are currently attracting considerable attention for potential applications in catalysis, magnetic materials, and nonlinear optical materials[1]. We have been interested in chemistry of copper(II) carboxylates in order to examine the potential utility as "building blocks" in combination with linkage ligands for coordination polymer formation[2-4]. Recently, we reported that chain compounds can be obtained by using bridging ligands such as pyrazine, 4,4'-bipyridine, and 1,4-diazabicyclo[2.2.2]octane for copper(II) pivalate[2], copper(II) trichloroacetate[2], and copper(II) benzoate[4]. Among copper(II) carboxylates, copper(II) trifluoroacetate is unique in the structure and magnetic property[5]. In this study, copper(II) trifluoroacetate was treated with pyrazine because we expected the formation of interesting various extended structures. We report herein three new coordination polymers which are made from copper(II) trifluoroacetate and pyrazine.

EXPERIMENTAL

Synthesis

Copper(II) trifluoroacetate was prepared by nearly the same way as that of the literature[5].

$[Cu(tfa)_2(pyz)_2]_n$ (**1**)

An acetonitrile solution (10 cm^3) of pyrazine (96 mg) was slowly diffused into an acetonitrile solution (10 cm^3) of copper(II) trifluoroacetate (403 mg). The solution was allowed to stand at room temperature for three days. Pale blue crystals of **1** were formed. They were collected by filtration and washed with ditethyl ether: Yield, 188 mg. Found: C, 31.78; H, 1.60; N, 12.50%. Calcd for $C_{12}H_8CuF_6N_4O_4$: C, 32.05; H, 1.79; N, 12.46%. IR: $\nu_{as}(COO)$ 1700, 1678, $\nu_s(COO)$ 1426, $\nu(CF_3)$ 1100—1200, $\nu(pyz)$ 1132, 1063 cm^{-1}. Diffuse reflectance spectra: λ_{max} 244, 728 nm.

$[Cu_2(tfa)_2(CH_3O)_2(pyz)_2]_n$ (**2**)

A methanol solution (10 cm^3) of pyrazine (130 mg) was slowly diffused into a methanol solution (10 cm^3) of copper(II) trifluoroacetate (503 mg). The solution was allowed to stand at room temperature for one week to give green plates: Yield, 159 mg. Found: C, 29.24; H, 2.34; N, 9.64%. Calcd for $C_{14}H_{14}Cu_2F_6N_4O_6$: C, 29.23; H, 2.45; N, 9.74%. IR: $\nu_{as}(COO)$ 1683, $\nu_s(COO)$ 1426, $\nu(CF_3)$ 1100—1200, $\nu(pyz)$ 1121, 1072 cm^{-1}. Diffuse reflectance spectra: λ_{max} 258, 325, 675 nm.

$[Cu_2(tfa)_2(pyz)_3]_n$ (**3**)

When a methanol solution of **2** was allowed to stand for two weeks, color of the solution changed to green from pale blue. Further standing this solution for two months caused the crystallization of **3** as reddish purple plates. IR: $\nu_{as}(COO)$ 1669, $\nu_s(COO)$ 1426, $\nu(CF_3)$ 1100—200, $\nu(pyz)$ 1132, 1053 cm^{-1}.

Measurements

Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JANSSEN Micro FTIR Spectrometer MFT-2000 in the 4000—600 cm^{-1}. Magnetic susceptibilities were measured over the 4.5—300 K temperature range on a Quantum Design MPMS-5S SQUID susceptometer.

X-Ray Crystal Structure Analyses

Each crystal was sealed in a glass capillary together with mother liquor and mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation at 25±1°C. Unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20<2\theta<30°$. Crystallographic data for **2**; $C_{14}H_{14}Cu_2F_6N_4O_6$, *F.W.* = 575.37, triclinic, $P\bar{1}$, a = 8.021(4), b = 8.085(5), c = 9.193(7) Å, α = 84.48(5), β = 75.23(5), γ = 60.43(7)°, V = 501.1(7) $Å^3$, Z = 1, D_m = 1.89, D_c = 1.91 gcm^{-3}, μ(Mo Kα) = 22.21 cm^{-1}, crystal dimensions 0.42×0.20×0.10 mm, 1770 reflections measured ($2\theta_{max}$ = 50.0°), 1379 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.040, R_w = 0.046. For **3**, $C_{16}H_{12}Cu_2F_6N_6O_4$, *F.W.* = 593.39, monoclinic, $P2_1/n$, a = 7.083(2), b = 16.898(2), c = 8.770(2) Å, β = 90.06(1)°, V = 1049.6(4) $Å^3$, Z = 2, D_m = 1.89, D_c = 1.88 gcm^{-3}, μ(Mo Kα) = 21.19 cm^{-1}, crystal dimensions 0.65×0.45×0.31 mm, 1928 reflections measured ($2\theta_{max}$ = 50.0°), 1359 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.044, R_w = 0.052.

The structures were solved by the direct method and refined by the full-matrix least-squares method using MolEN program package[6].

RESULTS AND DISCUSSION

Compound **1** was prepared from the reaction of copper(II) trifluoroacetate with a slightly insufficient amount of pyrazine in acetonitrile. Complexes **2** and **3** were obtained from the similar reaction in methanol. The compositions and structures of these complexes were established by elemental analysis and infrared spectral data. The antisymmetric and symmetric stretching vibrations of trifluoroacetate ligands show characteristic absorption bands at 1678, 1683, and 1669 and 1426, 1426, and 1426 cm^{-1} for complexes **1**, **2**, and **3**, respectively. The Δ values [ν_{as}(COO) - ν_s(COO)] are 252, 257, and 243 cm^{-1} for complexes **1**, **2**, and **3**, respectively, which are similar to those of the monodentate carboxylato complexes.

The crystal structure of **2** is shown in FIGURE 1. Each copper atom is coordinated to monodentate trifluoroacetato-oxygen atom, two pyrazine-nitrogen atoms which occupy *cis* positions each other, and two bridging methoxo-oxygen atoms. In the crystal, these dinuclear units are connected by pyrazine molecules to form a two-dimensional network (FIGURE 2).

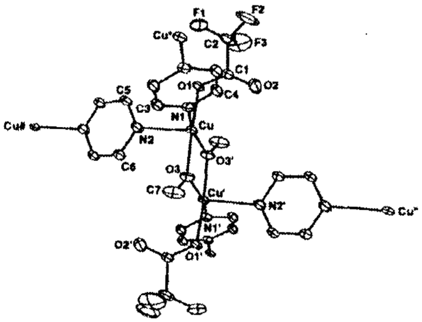

FIGURE 1 Coordination environments around the copper atoms of **2** with 35% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu-Cu' 3.007(1), Cu-O1 1.956(3), Cu-O3 1.923(3), Cu-O3' 1.932(4), Cu-N1 2.039(4), Cu-N2 2.331(5); Cu-O3-Cu' 102.5(2), O1-Cu-O3 173.9(2), O1-Cu-O3' 96.6(1), O1-Cu-N1 88.7(1), O1-Cu-N2 87.9(1), O3-Cu-O3' 77.5(1), O3-Cu-N1 96.4(1), O3-Cu-N2 94.1(2), O3'-Cu-N1 161.8(2), O3'-Cu-N2 93.9(2), N1-Cu-N2 103.7(2).

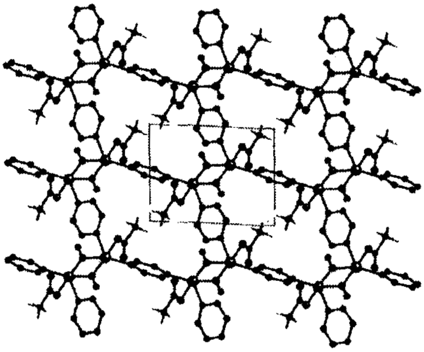

FIGURE 2 A view projected down the *a* axis, showing two-dimensional structure of **2**.

The magnetic moment of **2** is 0.97 B.M./dimer at 300 K, which is considerably smaller than the spin-only vale for uncoupled 1/2 spins (2.45 B.M./dimer). Temperature dependence of the magnetic data can be interpreted in terms of the Bleaney-Bowers equation [FIGURE 3, g = 2.2, J = -400 cm^{-1}, the mole fraction of paramagnetic impurity = 0.0154, and $N\alpha$ = 60×10^{-6} cgs emu]. This means that the strong antiferromagnetic interaction is mainly occurred within the methoxo-bridged dinuclear unit and inter-dimer interaction through the pyrazine molecules is negligibly small in **2** as the cases for copper(II) pivalate[2] and copper(II) benzoate[4].

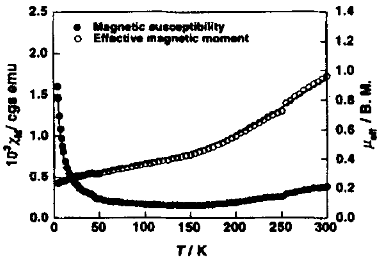

FIGURE 3 Temperature dependences of magnetic susceptibility and magnetic moment of **2**. The solid lines were calculated from the Bleaney-Bowers equation baseed on the Heisenberg model with parameters in the text.

The pale blue crystalline form of **2** changed into reddish purple crystals **3** when left in contact with the methanolic mother-liquor over the priod of two months. The structure revealed by X-ray crystallography

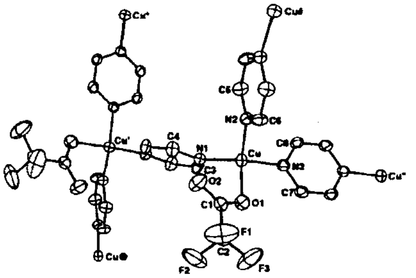

FIGURE 4 Coordination environments around the copper atoms of **3** with 35% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu-O1 2.100(4), Cu-N1 1.984(4), Cu-N2 2.057(4), Cu-N3 2.006(4); O1-Cu-N1 108.8(2), O1-Cu-N2 106.5(2), O1-Cu-N3 100.4(2), N1-Cu-N2 110.9(2), N1-Cu-N3 123.5(2), N2-Cu-N3 105.3(2).

shows that an unprecedented copper(I) species, $[Cu_2(tfa)_2(pyz)_3]_n$, formed (FIGURE 4). Each copper atom is coordinated to monodentate trifluoroacetate ion and three pyrazine molecules in a distorted tetrahedral fashion. All the pyrazine molecules connect the tetrahedral copper atoms forming a two-dimensional sheet structure, based on a rectangular arrangement of the copper atoms (FIGURE 5).

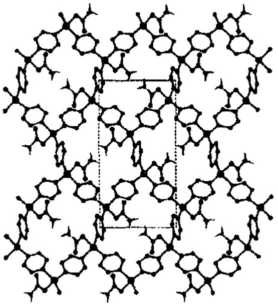

FIGURE 5 A view projected down the *a* axis, showing two-dimensional structure of **3**.

Acknowledgments

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