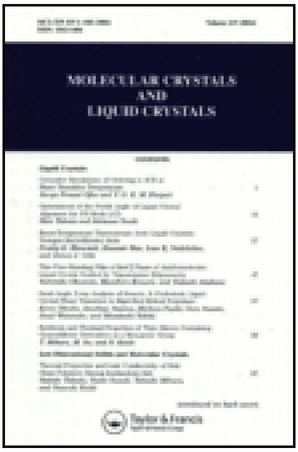

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# Coordination Polymers of Copper(II) Propionate with Linkage Ligands

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# Coordination Polymers of Copper(II) Propionate with Linkage Ligands

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New coordination polymers of copper(II) propionate, $[Cu_4(pro)_4(CH_3O)_4]$ (Hpro = propionic acid) (**1**), $[Cu_4(pro)_4(CH_3O)_4(pyz)]_n$ (pyz = pyrazine) (**2**), and $[Cu_2(pro)_2(CH_3O)_2(CH_3OH)_2(bpy)]_n \cdot 2nCH_3OH$ (bpy = 4,4'-bipyridine) (**3**), have been synthesized and characterized structurally. The crystal structures of **1** and **2** consist of methoxo- and propionato-bridged tetranuclear copper(II) units which are connected by propionato-oxygen atoms of adjacent units or pyrazine molecules to form a two-dimensional network. The crystal structure of **3** shows a one-dimensional chain structure. The magnetic properties of **1** and **2** are antiferromagnetic.

Keywords: coordination polymers; copper(II) complexes; crystal structures; magnetic property

## INTRODUCTION

Coordination polymers have been attracting much attention for potential applications in magnetic materials and catalysis[1]. A variety of coordination polymers have been prepared from linkage ligands such as pyrazine and 4,4'-bipyridine. We have been engaged in chemistry of copper(II) carboxylates in order to study the utility as "building blocks" in combination with linkage ligands for polymer formation[2-6]. Recently, we reported that coordination polymers can be obtained by using linkage ligands for copper(II) pivalate[2], copper(II) trichloroacetate[2], copper(II) benzoate[4], and copper(II) trifluoroacetate[5]. In this study, copper(II) propionate was treated with some linkage ligands because we expected the formation of interesting various extended structures. We report herein three new coordination polymers which are made from copper(II) propionate.

## EXPERIMENTAL

### Preparations

Copper(II) propionate was prepared by the same way as that of the literature[6].

### $[Cu_4(pro)_4(CH_3O)_4]$ (**1**)

Copper(II) propionate (129 mg) was dissolved in methanol (20 cm$^3$). The solution was allowed to stand at room temperature for one month. Blue plates of **1** were deposited. They were collected by filtration: Yield, 42.6 mg. Found: C, 28.75; H, 4.84%. Calcd for $C_{16}H_{32}Cu_4O_{12}$: C, 28.66; H, 4.81%. IR: $\nu_{as}$(COO) 1576, $\nu_s$(COO) 1430 cm$^{-1}$. Diffuse reflectance spectra: $\lambda_{max}$ 231, 720 nm.

### $[Cu_4(pro)_4(CH_3O)_4(pyz)]_n$ (**2**)

A methanol solution (3 cm$^3$) of pyrazine (48.0 mg) was slowly diffused into a methanol solution (3 cm$^3$) of copper(II) propionate (124 mg) by connecting 13.5 cm$^3$ of methanol in a H-shaped tube. The solution was allowed to stand at room temperature for one week to give blue plates: Yield, 21.5 mg. Found: C, 31.53; H, 4.68; N, 3.57%. Calcd for $C_{20}H_{36}Cu_4N_2O_{12}$: C, 32.00; H, 4.83; N, 3.73%. IR: $\nu_{as}$(COO) 1567, $\nu_s$(COO) 1430, $\nu$(pyz) 1132, 1036 cm$^{-1}$. Diffuse reflectance spectra: $\lambda_{max}$ 249, 670 nm.

### $[Cu_2(pro)_2(CH_3O)_2(CH_3OH)_2(bpy)]_n \cdot 2nCH_3OH$ (**3**)

A methanol solution (3 cm$^3$) of 4,4'-bipyridine (15.6 mg) was slowly diffused into a methanol solution (3 cm$^3$) of copper(II) propionate (42.6 mg) by connecting 13.5 cm$^3$ of methanol in a H-shaped tube. The solution was allowed to stand at room temperature for one week to give small amount of bluish green plates with green powder. The former crystals were collected. IR: $\nu_{as}$(COO) 1567, $\nu_s$(COO) 1417, $\nu$(bpy) 1075, 1022 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 JASCO MFT-2000 FT-IR Spectrometer in the 4000—600 cm$^{-1}$ region. Magnetic susceptibilities were measured over the 4.5—300 K temperature range on a Quantum Design MPMS-5S SQUID susceptometer.

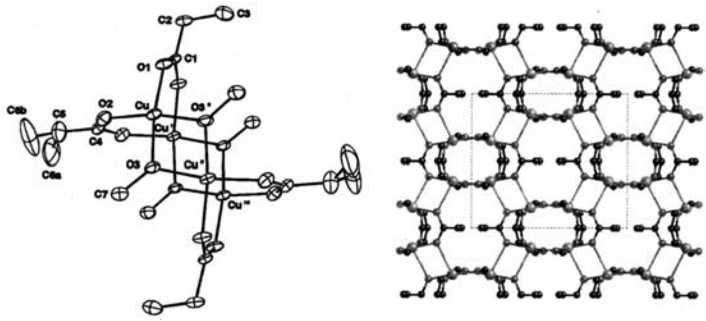
X-Ray Crystal Structure Analyses

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 **1**; $C_{16}H_{32}Cu_4O_{12}$, *F.W.* = 670.61, monoclinic, *C2/m*, $a$ = 11.437(3), $b$ = 9.835(2), $c$ = 10.976(3) Å, $\beta$ = 93.61(11)°, $V$ = 1232.1(4) Å$^3$, $Z$ = 2, $D_m$ = 1.80, $D_c$ = 1.81 gcm$^{-3}$, $\mu$(Mo Kα) = 34.71 cm$^{-1}$, crystal dimensions 0.31×0.32×0.11 mm, 1559 reflections measured ($2\theta_{max}$ = 56.0°), 1238 [$I \geq 3\sigma(I)$] used in the refinement, $R$ = 0.045, $R_w$ = 0.055. For **2**, $C_{20}H_{36}Cu_4N_2O_{12}$, *F.W.* = 750.70, triclinic, $P\bar{1}$, $a$ = 10.286(5), $b$ = 11.163(8), $c$ = 7.617(6) Å, $\alpha$ = 105.83(4), $\beta$ = 110.44(3), $\gamma$ = 63.56(7)°, $V$ = 726.6(9) Å$^3$, $Z$ = 1, $D_m$ = 1.72, $D_c$ = 1.72 gcm$^{-3}$, $\mu$(Mo Kα) = 29.54 cm$^{-1}$, crystal dimensions 0.35×0.31×0.21 mm, 2544 reflections measured ($2\theta_{max}$ = 50.0°), 2038 [$I \geq 3\sigma(I)$] used in the refinement, $R$ = 0.027, $R_w$ = 0.036. For **3**, $C_{20}H_{34}Cu_2N_2O_8$, *F.W.* = 557.59, triclinic, $P\bar{1}$, $a$ = 9.000(4), $b$ = 10.796(5), $c$ = 7.785(4) Å, $\alpha$ = 91.81(3), $\beta$ = 101.61(3), $\gamma$ = 102.28(3)°, $V$ = 721.7(6) Å$^3$, $Z$ = 1, $D_c$ = 1.28 gcm$^{-3}$, $\mu$(Mo Kα) = 15.14 cm$^{-1}$, crystal dimensions 0.20×0.15×0.10 mm, 2531 reflections measured ($2\theta_{max}$ = 50.0°), 2185 [$I \geq 3\sigma(I)$] used in the refinement, $R$ = 0.046, $R_w$ = 0.065.

The structures were solved by the direct method and refined by the full-matrix least-squares method using MolEN program package[7].

## RESULTS AND DISCUSSION

The present complexes show characteristic absorption bands of the



(a) (b)

Figure 1 (a) Coordination environments around the copper atoms of **1** with 35% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu-Cu' 2.950(1), Cu-Cu" 2.984(1), Cu-Cu"' 4.196(1), Cu-O1 1.968(3), Cu-O2 1.932(4), Cu-O3 1.933(3), Cu-O3" 1.908(4), Cu-O1* 2.607(3); Cu-O3-Cu" 102.0(2), O1-Cu-O2 93.6(2), O1-Cu-O3 171.1(2), O2-Cu-O3 93.8(2). (b) Crystal packing of **1**.

antisymmetric and symmetric stretching vibrations of carboxylate group. The Δ values [$\nu_{as}$(COO) - $\nu_s$(COO)] are 146, 137, and 150 cm$^{-1}$ for complexes **1**, **2**, and **3**, respectively, which are similar to those of the bridging carboxylato complexes or between those of the monodentate and didentate carboxylates.

The crystal structure of **1** is shown in Figure 1. The complex adopts a centrosymmetric open-cubane-like arrangement of four copper(II) and four methoxo ions with a mirror plane containing C1, C2, C3, C4, and C5 atoms as required from the crystallographic symmetry. The two copper atoms (Cu and Cu') are bridged by two propionato ions in a *syn-syn* configuration. In the crystal, these tetranuclear units are connected by carboxylato-oxygen atoms of adjacent tetranuclear units to form a two-dimensional network (Figure 1 (b)).

The magnetic moment of **1** is 3.22 B.M./tetramer at 300 K, which

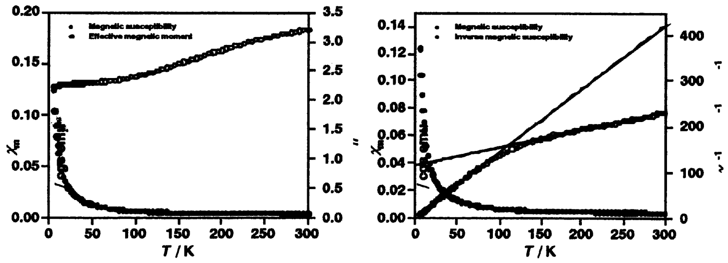
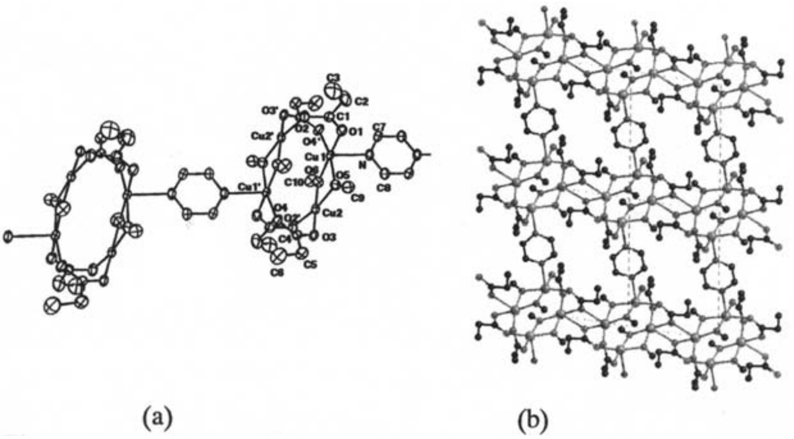


Figure 2 Magnetic susceptibility and magnetic moment of **1**.



(a) (b)

Figure 3 (a) Molecular structure of **2** with 35% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu1-Cu2 2.987(1), Cu1-Cu2' 2.977(1), Cu1-O1 1.968(2), Cu1-O4' 1.954(3), Cu1-O5 1.923(2), Cu1-O6 1.931(3), Cu1-N 2.303(4), Cu2-O2' 1.968(2), Cu2-O3 1.941(2), Cu2-O5 1.914(2), Cu2-O6 1.922(3), Cu2-O2" 2.558(3); Cu1-O5-Cu2 102.2(1), Cu1-O6-Cu2 101.7(1). (b) Crystal packing of **2**.

is considerably smaller than the spin-only value for four uncoupled 1/2 spins. Temperature dependence of the magnetic data obey the Curie-Weiss law with $\theta$ = -292.6 and –2.32 K for the temperature ranges 125—300 and 4.5—100 K, respectively, as shown in Figure 2. This means that antiferromagnetic interaction occurs through the methoxo- and propionato-bridges.

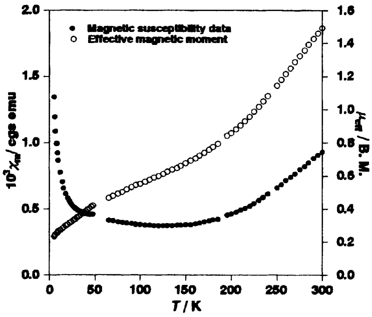


Figure 4 Temperature dependences of magnetic susceptibility and magnetic moment of **2**.

The crystal structure of **2** shows that each copper atom takes a distorted square pyramidal coordination involving two propionato-oxygen, two methoxo-oxygen, and one pyrazine-nitrogen atoms, being bridged by two propionato ions in a *syn-syn*

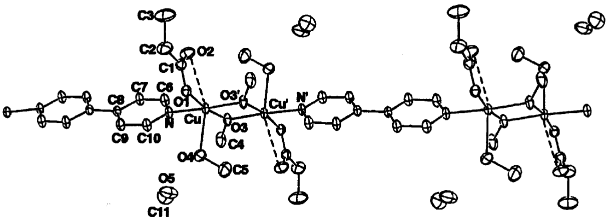


FIGURE 5 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu-Cu' 2.991(1), Cu-O1 1.958(3), Cu1-O2 2.785(4), Cu-O3 1.930(3), Cu-O3' 1.939(4), Cu-O4 2.406(5), Cu-N 2.021(4); Cu-O3-Cu' 101.3(2).

configuration. The open-cubane-like tetranuclear units are further connected by carboxylato-oxygen atoms of adjacent tetranuclear units, which leads to infinite chains having a ribbon-like pattern along *c* axis. The chains are held together by pyrazine molecules to form a two-dimensional sheet (Figure 3). The magnetic moment of this complex is 1.50 B.M. at 300 K. Temperature dependence of magnetic data shows that the magnetic property is antiferromagnetic (Figure 4).

The crystal structure of **3** shows a chain structure where methoxo-bridged dinuclear copper(II) units are connected by 4,4'bipyridine molecules (Figure 5). Coordination mode of propionato ions is between the monodentate and didentate fashions.

References

[1.]For example, see D. J. Chesnut, D. Hagrman, P. J. Zapf, R. P. Hammond, R. LaDuca, R. C. Haushalter, and J. Zubieta, *Coord. Chem. Rev.*, **190-192**, 737 (1999).

[2.]M. Mikuriya, R. Nukada, H. Morishita, and M. Handa, *Chem. Lett.*, 617 (1995).

[3.]M. Mikuriya, H. Azuma, R. Nukada, and M. Handa, *Chem. Lett.*, 57 (1999).

[4.]R. Nukada, W. Mori, S. Takamizawa, M. Mikuriya, M. Handa, and H. Naono, *Chem. Lett.*, 367 (1999).

[5.]M. Mikuriya, H. Azuma, and M. Handa, *Mol. Cryst. Liq. Cryst.*, **342**, 205 (2000).

[6.]M. Mikuriya, H. Azuma, R. Nukada, Y. Sayama, K. Tanaka, J.-W. Lim, and M. Handa, *Bull. Chem. Soc. Jpn.*, **73**, 2493 (2000).

[7.]C. K. Fair, *MolEN Structure Determination System*, Delft Instruments, Delft (1990).