

# Structure and magnetic behaviour of mononuclear and dinuclear Cu(II)/Zn(II) monocarboxylate-pyridine derivatives studied by crystal engineering

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Metal organic frameworks such as copper(II) monocarboxylate (formate and benzoate) pyridine derivatives and zinc(II) monocarboxylate (*p*-phenyl benzoate and benzoate) pyridine derivatives have been prepared. The complexes were synthesized at room temperature using pyridine or *p*-phenyl pyridine to grow single crystals, which were subsequently analyzed using single-crystal X-ray analysis. These structures are formed by hydrogen bonding and self-assembly by the  $\pi$ -stacking of mononuclear units. The magnetic susceptibilities of the copper(II) complexes obeyed the Curie–Weiss law over the range of 2–300 K. The Weiss constants  $\theta$  indicated the existence of small antiferromagnetic interactions arising from the hydrogen bonding.

Key words: *mononuclear metal complex; single-crystal X-ray analysis; antiferromagnetic interaction*

## 1. Introduction

For many years metal organic frameworks were unknown and attempts were made to prepare them by using a variety of combinations of metal ions and organic ligands. In recent years, however, numerous significant advances in the design concepts of metal organic frameworks have been reported.

The transition metal carboxylates species are interesting due to their capabilities for gas storage, ion exchange, catalytic activity, etc. The syntheses and structures of transition metal carboxylates are also critically important for their properties and applications. Previously, we have reported that dinuclear copper(II) dicarboxylates [1], molybdenum(II) dicarboxylates [2], ruthenium(II) or (II, III) dicarboxylates [3], and rhodium(II) tetracarboxylate exhibit gas-occlusion properties and catalytic activity for the hydrogenation of ethylene and propene [4].

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Recently, we have conducted crystal engineering on mononuclear Cu(II), Ni(II), and Zn(II) carboxylates-pyridine systems in order to obtain porous materials with a large number of cavities [5]. In the present study, we chose three sample mononuclear units: copper(II) formate-*p*-phenyl pyridine (**a**), copper(II) benzoate-pyridine (**b**), zinc(II) *p*-phenyl benzoate-pyridine (**c**), and one sample dinuclear unit, zinc(II) benzoate-pyridine (**d**), and we investigated their crystal structures and magnetic behaviours.

## 2. Experimental procedure

**Materials and methods.** Copper(II) formate tetrahydrate, Zn(II) nitrate hexahydrate, and benzoic acid were purchased from Wako Chemical Company. All other organic ligands were purchased from Tokyo Kasei Chemical Company and used as received without further purification. Elemental microanalyses of the complexes were conducted on crystalline samples using a Perkin-Elmer PE 2400 series II CHNS/O analyser. Thermogravimetric analysis was performed using TG8101D and TAS300 with an aluminium pan in an ordinary atmosphere, at the scan rate of 1 °C/min. The temperature dependence of the magnetic susceptibilities of the copper(II) complexes was measured by a Quantum Design MPMS-5S SQUID magnetometer in the temperature range of 2–300 K, at 5000 Oe.

**Preparation of complexes.** The synthetic methods used for the ligand exchange procedure were similar to those reported previously, obtaining single-crystal samples of the complexes [5]. Forms of mononuclear and dinuclear Cu(II)/Zn(II) monocarboxylate-pyridine derivatives were synthesized as follows.

**Copper(II) formate-*p*-phenyl pyridine.** A DMSO solution ( $40.0 \times 10^{-3} \text{ dm}^3$ ) of *p*-phenyl pyridine (0.2751 g) was added to an aqueous solution ( $40.0 \times 10^{-3} \text{ dm}^3$ ) of copper(II) formate tetrahydrate (0.2000 g). The mixture was then allowed to stand for several days at room temperature, after which it yielded deep blue, plate-like single crystals that were formulated as  $\text{Cu}^{\text{II}}(\text{O}_2\text{C}-\text{H})_2(\text{C}_6\text{H}_5-\text{C}_5\text{H}_4\text{N})_2 \cdot (\text{H}_2\text{O})$  (**a**). Anal. calcd. for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_5\text{Cu}$ : C, 59.81; H, 4.60; N, 5.81%. Found: C, 59.48; H, 4.46; N, 5.73%.

**Copper(II) benzoate-pyridine.** A pyridine solution ( $30.0 \times 10^{-3} \text{ dm}^3$ ) of benzoic acid (0.0905 g) was added to an aqueous solution ( $10.0 \times 10^{-3} \text{ dm}^3$ ) of copper(II) nitrate trihydrate (0.1500 g). The mixture was then allowed to stand for several days at room temperature, after which it yielded deep blue, plate-like single crystals that were formulated as  $\text{Cu}^{\text{II}}(\text{O}_2\text{C}-\text{C}_6\text{H}_5)_2(\text{C}_5\text{H}_5\text{N})_2 \cdot (\text{H}_2\text{O})$  (**b**). Anal. calcd. for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_5\text{Cu}$ : C, 59.81; H, 4.60; N, 5.81%. Found: C, 60.73; H, 5.12; N, 5.23%.

**Zinc(II) *p*-phenyl benzoate-pyridine.** An aqueous solution ( $10.0 \times 10^{-3} \text{ dm}^3$ ) of zinc(II) nitrate hexahydrate (0.0300 mg) was added to a pyridine solution ( $10.0 \times 10^{-3} \text{ dm}^3$ ) of *p*-phenyl benzoic acid (0.0400 mg). The mixture was then allowed to stand for

several days at room temperature, after which it yielded colourless, plate-like single crystals that were formulated as  $\text{Zn}^{\text{II}}(\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5)_2(\text{C}_5\text{H}_5\text{N})_2$  (**c**). Anal. calcd. for  $\text{C}_{36}\text{H}_{28}\text{N}_2\text{O}_4\text{Zn}$ : C, 69.96; H, 4.57; N, 4.53%. Found: C, 67.85; H, 4.77; N, 4.31%.

**Zinc(II) benzoate-pyridine.** An aqueous solution ( $10.0 \times 10^{-3} \text{ dm}^3$ ) of zinc(II) nitrate hexahydrate (0.5000 mg) was added to a pyridine solution ( $10.0 \times 10^{-3} \text{ dm}^3$ ) of benzoic acid (0.4100 mg). The mixture was then allowed to stand for several days at room temperature, after which it yielded colourless, plate-like single crystals that were formulated as  $\text{Zn}_2^{\text{II}}(\text{O}_2\text{C}-\text{C}_6\text{H}_5)_4(\text{C}_5\text{H}_5\text{N})_2$  (**d**). Anal. calcd. for  $\text{C}_{38}\text{H}_{30}\text{N}_2\text{O}_8\text{Zn}_2$ : C, 59.01; H, 3.91; N, 3.62%. Found: C, 58.76; H, 3.42; N, 4.51%.

**X-ray crystal structure determinations.** The crystal structures of **a**, **b**, and **d** were determined by X-ray diffraction using a Rigaku R-Axis RAPID diffractometer with graphite-monochromated  $\text{MoK}_\alpha$  radiation. The crystal structure of **c** was determined by X-ray diffraction using a Rigaku CCD Mercury diffractometer with graphite-monochromated  $\text{MoK}_\alpha$  radiation. The structures of all complexes were solved by a direct method using the program SIR-92 and were refined by full-matrix least-squares iterations. The non-hydrogen atoms (Cu, Zn, C, O, and N) were refined anisotropically. All the H atoms were idealized by using riding models, which were located in a difference Fourier map and then refined isotropically. No disorder was observed in any of the structures.

### 3. Results and discussion

#### 3.1. X-ray single-crystal analysis

The use of pyridine as a solvent is satisfactory for crystallization. Introducing the concept of crystallization using pyridine and pyridine derivatives is very useful for understanding metal-organic structures. In this work, we have succeeded in the synthesis of mononuclear and dinuclear Cu(II)/Zn(II) monocarboxylate-pyridine derivatives. Crystallographic data and other pertinent information are summarized in Table 1.

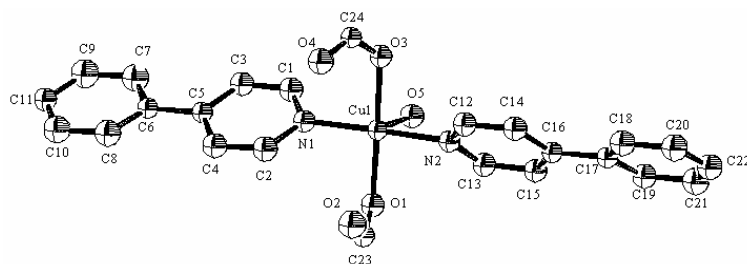
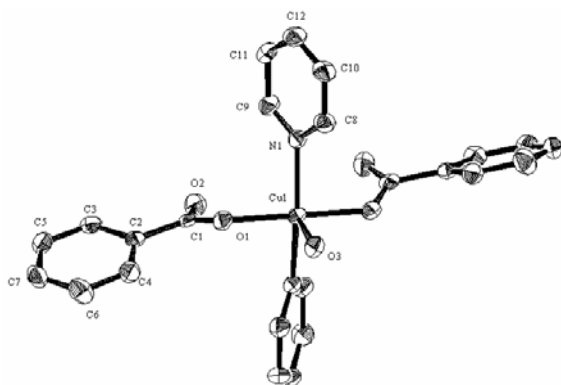
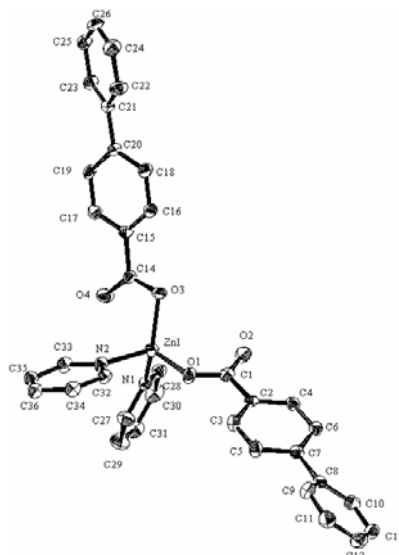


Fig. 1. ORTEP view of **a**, showing the numbering scheme (50% probability).  
The hydrogen atoms have been omitted for clarity

Table 1. Crystallographic data and structure refinement parameters for complexes **a–d**

Parameter	Compound			
	<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>
Chemical formula	C <sub>24</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Cu	C <sub>12</sub> H <sub>10</sub> NO <sub>2.5</sub> Cu <sub>0.5</sub>	C <sub>36</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> Zn	C <sub>19</sub> H <sub>15</sub> NO <sub>4</sub> Zn
Formula mass, Da	459.82	239.99	618.01	386.71
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
<i>a</i> , Å	5.757	15.651(3)	9.5397(5)	9.663(4)
<i>b</i> , Å	15.165	45.697(7)	10.5192(5)	10.450(3)
<i>c</i> , Å	24.151	5.973(1)	29.201(2)	17.363(6)
$\alpha$ , deg	90	90	90	90
$\beta$ , deg	90	90	96.4334(7)	98.67(2)
$\gamma$ , deg	90	90	90	90
<i>V</i> , Å <sup>3</sup>	2108.63	4272.1(1)	2911.9(3)	1733.4(1)
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	1.45	1.492	1.410	1.482
<i>T</i> , K	123	143	143	143
<i>R</i> <sup>a</sup>	0.074	0.072	0.040	0.034
<i>Rw</i>	0.213 <sup>b</sup>	0.083 <sup>b</sup>	0.054 <sup>b</sup>	0.040 <sup>c</sup>
<i>Z</i>	4	16	4	4
$\mu$ , cm <sup>−1</sup>	10.73	10.618	8.877	14.397

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}. \quad ^c R_w = [\Sigma (w(F_o^2 - F_c^2))^2 / \Sigma (F_o^2)^2]^{1/2}.$$

Fig. 2. ORTEP view of **b**, showing the numbering scheme (50% probability). The hydrogen atoms have been omitted for clarityFig. 3. ORTEP view of **c**, showing the numbering scheme (50% probability). The hydrogen atoms have been omitted for clarity

In Figures 1–4, we present ORTEP drawings of the unit containing Cu and Zn atoms and all attached atoms for each structure. The atomic numbering scheme for the

species is defined in each figure. In the process of crystallization, the intermolecular interaction between the aromatic rings of the ligands (carboxylate or pyridine), the so-called  $\pi$ - $\pi$  stack, might act as a driving force for the self-assembly of the mononuclear or dinuclear units by suspending no guest molecules.

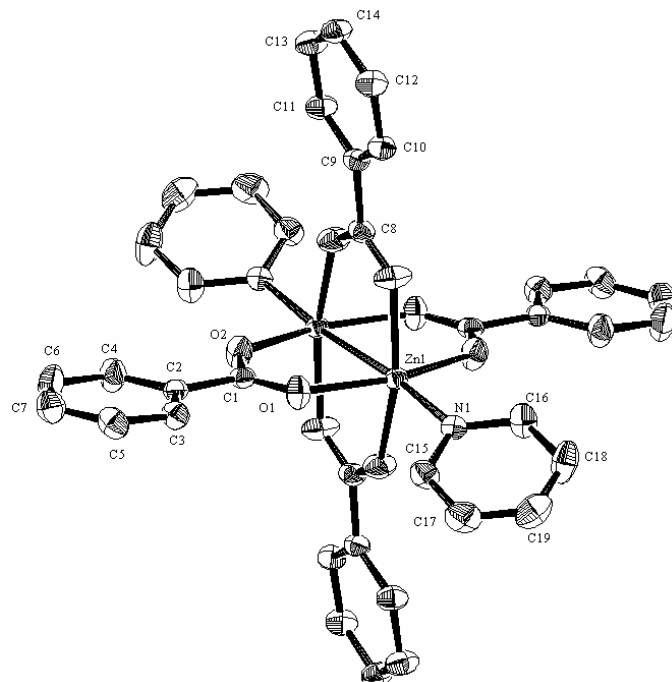


Fig. 4. ORTEP view of **d**, showing the numbering scheme (50% probability)

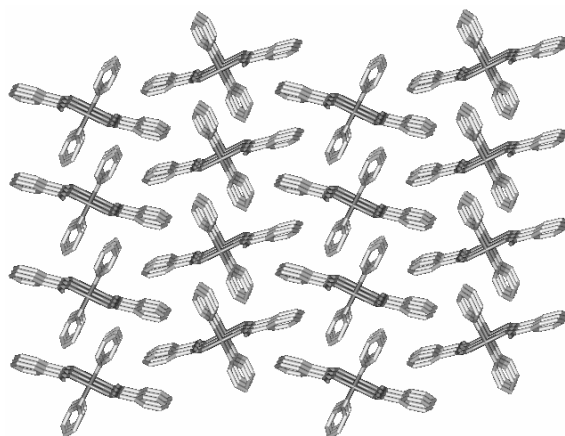


Fig. 5. Structural features of **b** using the Rigaku/MS program package. The chain complex consisting of hydrogen bonding between Cu(II) ions effectively bridged between the carboxyl substituents and coordinated water molecules, forming a one-dimensional chain. For clarity, the hydrogen atoms have been omitted

Mononuclear copper(II) monocarboxylates have a regular one-dimensional structure with hydrogen bonding, clearly characterized by X-ray crystallography. Hydrogen bonding occurs between one mononuclear unit and adjacent mononuclear units through the O atoms of the carboxylate groups and coordinated water molecules, increasing the structural dimensionality. Figure 5 shows the packing diagram of **b**. These structures are one-dimensional ones, very similar to those of mononuclear copper(II) terephthalate-pyridine derivatives [5].

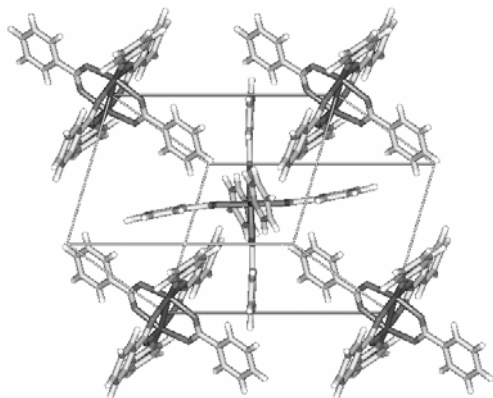


Fig. 6. Packing diagram view of **d**, using the Rigaku/MSC program package. For clarity, the hydrogen atoms have been omitted

In contrast to the copper(II) complexes, the crystal structures of **c** and **d** contain no coordinated water molecules and, thus, no water hydrogen bonding. These structures are simply constructed by the intermolecular interactions between one mononuclear or dinuclear unit and the surrounding mononuclear or dinuclear units, as shown in Fig. 6. In preparation of **d**, the dinuclear Zn(II) complex (but not the mononuclear Zn(II) complex) was nevertheless synthesized by a similar procedure. This result is attributable to a slight difference of pH value in the reaction solvent when using a different organic ligand.

### 3.2. Stability of complexes

TG-DTA analysis shows that the coordinated solvent is eliminated from the network as temperature rises. When the coordinated solvents are released, the colour of **a** and **b** changes from deep blue to pale blue [5]. Similarly, the colour of **c** and **d** changes from colourless to white. These networks are stable during the initial weight loss of the coordinated solvent, whereas they are not stable during the loss of coordinated molecules (pyridine and/or water) from these frameworks [5].

### 3.3. Magnetic properties

The magnetic susceptibilities of mononuclear copper(II) carboxylate-pyridine derivatives with linear chains of hydrogen bonds obey the Curie-Weiss law; the obtained Weiss

constants indicate ferromagnetic or antiferromagnetic interactions. We have clarified the paramagnetic properties of the mononuclear copper(II) monocarboxylate-pyridine derivatives by magnetic measurements. The complexes **a** and **b** exhibit small antiferromagnetic interactions ( $\theta = -0.74$  K for **a** and  $\theta = -0.44$  K for **b**), albeit much weaker. The temperature dependence of the magnetic susceptibility for **b** is shown in Fig. 7. In addition, the magnetic properties for similar systems, mononuclear copper(II) dicarboxylate-pyridines, have been reported – small antiferromagnetic interactions and ferromagnetic interactions through hydrogen-bonded pathways in  $[\text{Cu}(\text{II})(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})]\cdot\text{py}\cdot\text{H}_2\text{O}$  ( $\theta = -1.4$  K) [5],  $[\text{Cu}(\text{II})(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(p\text{-C}_6\text{H}_5\text{-C}_5\text{H}_4\text{N})_2(\text{H}_2\text{O})]\cdot 2\text{MeOH}$  ( $\theta = 5.5$  K) [5], and  $[\text{Cu}(\text{II})(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-Br})(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})]$  ( $\theta = 9.0$  K) [6]. In these complexes, in which one copper(II) ion is linked by hydrogen bonding between two bridging carboxylate groups and one coordinated water molecule, two pathways are provided for super exchange interaction between the copper(II) ions.

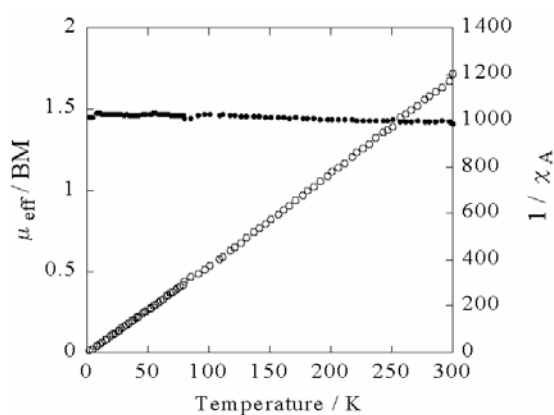


Fig. 7. Temperature dependence of the effective magnetic moment (●) and magnetic susceptibility (○) of **b**

These results suggest that ferromagnetic and antiferromagnetic interactions play an important role in determining bridge geometries and super-exchange interactions between copper(II) ions through Cu–O–C–O–H–O–Cu pathways [5]. In contrast, the magnetic behaviour of mononuclear copper(II) tetracarboxylate-pyridine (CuTCPPpy), in which no hydrogen bonding exists, is scarcely affected by the magnetic interaction between copper(II) ions [7].

#### 4. Conclusions

We have synthesized three samples of mononuclear metal(II) monocarboxylate-pyridine derivatives: copper(II) formate-*p*-phenyl pyridine (**a**), copper(II) benzoate-pyridine (**b**), zinc(II) *p*-phenyl benzoate-pyridine (**c**), and one sample dinuclear zinc(II) monocarboxylate, zinc(II) benzoate-pyridine (**d**). The crystal structures and

magnetic behaviour of these samples were investigated. Copper(II) complexes, which are self-assembled by hydrogen bonding and the  $\pi$ -stacking of mononuclear units, form one-dimensional structures. The use of pyridine as a solvent simplified obtaining single crystals for mononuclear and dinuclear metal(II) carboxylates. Furthermore, we believe that it is possible to control the synthesis of mononuclear and dinuclear units for metal(II) carboxylates using different pH reaction solvents.

We have demonstrated the paramagnetic properties of **a** and **b**, as elucidated by magnetic measurements (SQUID), whereas **c** and **d** were found to be diamagnetic. The magnetic susceptibilities of **a** and **b** obeyed the Curie–Weiss law over the range of 2–300 K ( $\theta = -0.74$  K for **a**, and  $\theta = -0.44$  K for **b**). The Weiss constants  $\theta$  indicated the existence of small antiferromagnetic interactions arising from the hydrogen bonding.

Compared to important industrial adsorbents, the system discovered in the present work is the simplest and most advantageous adsorbent for studies in pure and applied chemistry, because mononuclear copper(II) carboxylates-pyridine derivatives can be converted into special absorbents and exhibit large amounts of gas-occlusion properties with axial ligand exchange. That is the subject of further studies [8].

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