

Synthesis and Crystal Structure of New Salicylate-Bridged Coordination Polymer, $[\text{Cu}_2(\text{sal})_2(\text{pyz})(\text{MeOH})_2]_n$

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The title compound, $\{[\text{Cu}_2(\text{sal})_2(\text{pyz})] \cdot 2\text{MeOH}\}_n$ (H_2sal = salicylic acid, pyz = pyrazine) (**1**), has been synthesized, and structurally characterized. Each sal ligand connects the three copper centers to afford a novel 2-D network structure. The Cu^{II} -sal framework forms a rhombus type two-dimensional coordination framework. The pyz molecules, which fill the voids of the network, bind to the Cu site to afford zigzag chain.

Synthesis of a coordination polymer with the bridging ligand that has not been exploited for the network synthesis is of interest because such synthetic study could develop a designed construction of a novel self-assembled network.¹ In the field of coordination polymers, bridging ligands such as 4,4'-bipyridine or 1,4-dicarboxylate have been widely used for the synthesis of the coordination polymers.^{1,2} On the other hand, although salicylate (sal) molecule has been widely employed for the synthesis of mononuclear or multinuclear coordination compounds,³⁻⁶ the synthetic example of the coordination polymer is quite rare. To the best of our knowledge, one-dimensional structure of compound $[\text{Mo}_2(\text{sal})_4]$ is the only example.⁴ We have succeeded in the synthesis and structural characterization of a new coordination polymer, $\{[\text{Cu}_2(\text{sal})_2(\text{pyz})] \cdot 2\text{MeOH}\}_n$ (**1**), which shows the first two-dimensional coordination network constructed from metal ion and sal molecule.

Compound **1** was synthesized by diffusion of a methanol solution (2 mL) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.05 mol/L) and H_2sal (0.20 mol/L) into an aqueous solution of pyz (0.05 mol/1.2 mL). Green crystals suitable for an X-ray analysis were obtained after one week. Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{CuNO}_4$: C, 44.20; H, 3.71; N, 5.15%. Found: C, 44.40; H, 3.75; N, 5.37%. Complete deprotonation of sal was confirmed by the absence of strong absorption bands due to protonated hydroxy groups (ca. 1385 cm^{-1}) in the FT-IR spectrum.⁵

Single-crystal X-ray diffraction study clearly demonstrated the network structure of this compound.⁷ The coordination circumstance and the two-dimensional network structure are shown in Figures 1 and 2, respectively. The elongated octahedral geometry around Cu^{II} atom is completed by one nitrogen atom from pyrazine, one oxygen from methanol and four oxygen atoms from three sal molecules, in which the one phenolate oxygen atom, $\text{O}(1^*)$, and one methanol oxygen atom, $\text{O}(4)$, are in the axial position. The unique feature of this metal site is formation of the dimeric Cu_2O_2 core bridged by the two phenolate oxygen atoms. The Cu-Cu distance is about 3.32 \AA , indicative of no direct bonding.

Each sal ligand binds three copper atoms to afford a two-dimensional coordination network, which extends in the bc plane (Figure 2a). These layers stack along the a axis without

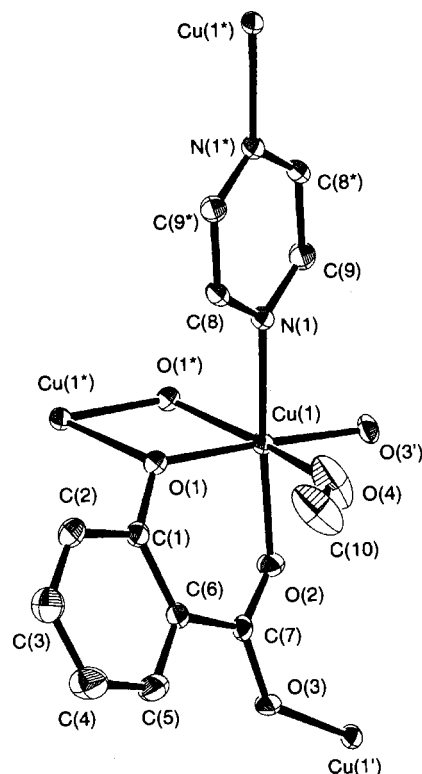


Figure 1. ORTEP drawing of **1** around the Cu center (ellipsoids at 30% probability): Symmetry codes, *: -x, -y, -z, †: -x, 1/2+y, 1/2-z. Selected bond distances [\AA] and angles [$^\circ$]: Cu(1)-O(1) 1.914(3), Cu(1)-O(1*) 2.437(3), Cu(1)-O(2) 1.941(3), Cu(1)-O(3') 1.959(3), Cu(1)-O(4) 2.631(5), Cu(1)-N(1) 2.049(3), O(1)-Cu(1)-O(1*) 81.4(1), O(1)-Cu(1)-O(2) 90.7(1), O(1)-Cu(1)-O(3') 174.3(1), O(1)-Cu(1)-O(4) 85.5(1), O(1)-Cu(1)-N(1) 91.0(1), O(1*)-Cu(1)-O(2) 97.9(1), O(1*)-Cu(1)-O(3') 94.7(1), O(1*)-Cu(1)-O(4) 165.8(1), O(1*)-Cu(1)-N(1) 86.9(1), O(2)-Cu(1)-O(3') 85.7(1), O(2)-Cu(1)-O(4) 87.8(2), O(2)-Cu(1)-N(1) 175.1(1), O(3')-Cu(1)-O(4) 98.8(1), O(3')-Cu(1)-N(1) 92.9(1), O(4)-Cu(1)-N(1) 87.8(2).

significant bindings. When the coordination framework of Cu^{II} -sal is considered, the framework has a rhombus type structure with angles of about 60° and 120° as shown in Figure 2b, in which the center of the Cu_2O_2 square is placed in the crossing point of the rhombus framework. This study reveals that the two-dimensional coordination framework of $[\text{Cu-sal}]_n$ is created without pyz linking.

For the construction, the addition of the pyz molecule could be necessary since the reaction of Cu^{II} ion with sal affords no extended network but a monomeric compound.⁵ Crystal structure analysis indicates that the pyz molecule fills the voids of the two-dimensional $[\text{Cu-sal}]_n$ network, and direct-

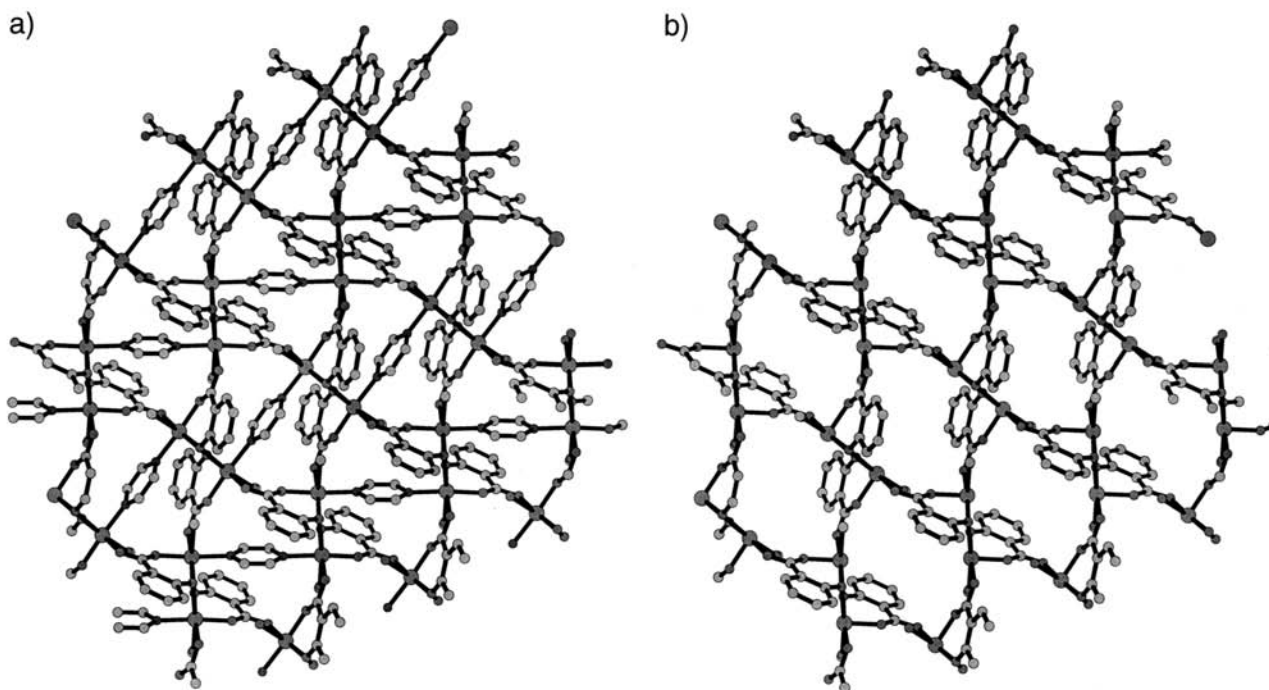


Figure 2. Two-dimensional structure of **1** (a) and the rhombus framework of $[\text{Cu}^{\text{II}}\text{-sal}]_n$ (b).

ly binds to the two copper atoms to yield a $[(\text{Cu}_2\text{O}_2)\text{-pyz}]_n$ zigzag chain. In other words, formation of the infinite coordination chain supports the creation of new extended coordination network from the organic molecules which have not afforded the infinite coordination network. This synthetic approach could develop the creation of novel coordination networks.

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References and Notes

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- 7 General crystallographic information: Intensity data were collected on the Rigaku Mercury CCD system using graphite monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$). The structure was solved by the direct method using SIR92 and refined by the full-matrix least-squares method using a teXsan program package. All calculations were performed on the workstation Indigo O2. Crystal data for $[\text{Cu}_2(\text{sal})_2(\text{pyz})(\text{MeOH})_2]_n$: $\text{C}_{10}\text{H}_{10}\text{CuNO}_4$, F.W.=271.74, monoclinic, space group $P2_1/c$, $a = 11.244(4)$, $b = 7.4944(6)$, $c = 12.4931(8) \text{ \AA}$, $\beta = 89.091(1)^\circ$, $V = 1052.7(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.715 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 20.71 \text{ cm}^{-1}$, $F(000) = 552$, $T = 293 \text{ K}$, crystal size $0.3 \times 0.2 \times 0.05 \text{ mm}$, 6016 reflections measured ($2\theta_{\text{max}} = 55.5^\circ$), 1179 [$I > 2.00\sigma(I)$] used in the refinement, $R = 0.037$, $R_w = 0.047$ and GOF = 2.64 for 145 parameters.