# 1/3 magnetization plateau observed in the spin-1/2 trimer chain compound $Cu_3(P_2O_6OH)_2$

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We report magnetic properties of $Cu_3(P_2O_6OH)_2$. A spin-1/2 trimer chain with $J_1-J_2-J_2$ interactions exists, where $J_1$ and $J_2$ denote two antiferromagnetic (AF) exchange interactions. A 1/3 magnetization plateau was observed above 12 T in a magnetization curve at 1.6 K. The appearance of the plateau is consistent with the theorem of Oshikawa, Yamanaka, and Affleck [Phys. Rev. Lett. **78**, 1984 (1997)]. Experimental results of magnetic susceptibility and magnetization agree well with quantum Monte Carlo results for the trimer chain with $J_1=95$ and $J_2=28$ K. To our knowledge, $Cu_3(P_2O_6OH)_2$ is the first model compound of trimer chains with only AF interactions showing a magnetization plateau.

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## I. INTRODUCTION

Many phenomena are ruled by quantum mechanics. However, we are usually unconscious of quantization in many-body quantum systems, because discrete levels collapse into continuous bands due to large system size. Of course, we realize intriguing examples of appearance of quantization in macroscopic scale such as the quantum Hall effect in two-dimensional electron systems and quantization of flux in superconductors. A phenomenon of quantum spin chains is analogous to the quantum Hall effect—topological quantization of a physical quantity under a changing magnetic field. This phenomenon is called the magnetization plateau.

One important result on the magnetization plateau is the following theorem. Magnetization curves at 0 K in quantum spin chains might have plateaus at $m'$ that satisfies the formula of $n(S'-m')=$integer.[1] Here, $n$ is the period of the ground state; $S'$ and $m'$, respectively, represent the total spin and magnetization per unit cell. This theorem is a necessary, but not sufficient, condition for occurrence of magnetization plateaus. For example, according to the theorem, a 1/3 magnetization plateau is expected to appear in spin-3/2 antiferromagnetic (AF) uniform chains. No magnetization plateau, however, appears when single-ion anisotropy is small.[2,3] Therefore, it is necessary to investigate conditions of appearance of magnetization plateaus in each spin system. Studies of magnetization plateaus have been developed rapidly in this decade. Magnetization plateaus have been observed in several spin systems both theoretically[4–8] and experimentally.[9–17]

A trimer chain is the first spin system that has been confirmed theoretically to be able to have a magnetization plateau.[4] Inspired by experimental results on $3CuCl_2\cdot 2dx$ (dx=dioxane),[18] Hida studied a spin-1/2 ferromagnetic-ferromagnetic-antiferromagnetic Heisenberg trimer chain and found a 1/3 magnetization plateau. No magnetization plateau, however, was seen experimentally in $3CuCl_2\cdot 2dx$. Theoretically, no magnetization plateau appears when a ratio ($|J_F/J_{AF}|$) of magnitude of the ferromagnetic (F) interaction ($J_F$) to that of the antiferromagnetic (AF) one ($J_{AF}$) is greater than 15.4.[19] Because $|J_F/J_{AF}|$ in $3CuCl_2\cdot 2dx$ is estimated as a large value (about 4.5),[4] it was probably difficult to observe the magnetization plateau experimentally.

To our knowledge, only one model compound of a trimer chain shows a magnetization plateau. The compound is $Cu(3\text{-Chloropyridine})_2(N_3)_2$, which includes a F-AF-AF trimer chain.[20] Accordingly, experimental investigations are insufficient for understanding trimer chain magnetism. It is important to find more model compounds of trimer chains that have magnetization plateaus.[21]

Very recently, it was reported that a newly synthesized copper hydroxydiphosphate $Cu_3(P_2O_6OH)_2$ had a spin-1/2 trimer chain.[22] We measured magnetization of this compound and found a 1/3 magnetization plateau. This cuprate is the first model compound of trimer chains that has only AF interactions and that shows a magnetization plateau.

## II. EXPECTED SPIN SYSTEM IN $Cu_3(P_2O_6OH)_2$

The space group of $Cu_3(P_2O_6OH)_2$ is $P\bar{1}$ (No. 2); its lattice constants are $a=4.78191(6)$, $b=7.03699(8)$, $c=8.35740(8)$ Å, $\alpha=66.6790(6)$, $\beta=76.9930(7)$, $\gamma=72.0642(6)°$, and $Z=1$ (1 formula per unit cell).[22] Only the $Cu^{2+}$ ions have spin 1/2. Positions of Cu and O connecting to Cu are shown schematically in Fig. 1. Two crystallographic Cu sites [Cu(1) and Cu(2)] exist along with two kinds of short Cu-Cu bonds. Distances of Cu-Cu in the first-shortest and second-shortest bonds, which are indicated, re-

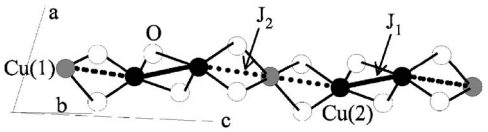


FIG. 1. Schematic drawing of positions of Cu and O connecting to Cu in $Cu_3(P_2O_6OH)_2$. Grey, black, and white circles indicate Cu(1), Cu(2), and O sites, respectively. Thick solid and dotted bars represent the first-shortest and second-shortest Cu-Cu bonds, respectively. Thin solid bars represent Cu-O bonds. The spin-1/2 trimer ($J_1-J_2-J_2$) chain exists. Its Hamiltonian is expressed as $\mathcal{H}=\Sigma_i J_1 S_i S_{i+1}+J_2 S_{i+1} S_{i+2}+J_2 S_{i+2} S_{i+3}$.

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TABLE I. Cu-O-Cu angles, whose values are in the vicinity of 98°, and signs and values ($J$) of exchange interactions in cuprates. We chose Cu-Cu bonds whose two Cu-O-Cu angles are identical or similar.

| Cu-O-Cu angle (°) | $J$ (K) | Compound | Cu-Cu distance (Å) | Ref. | |
|---|---|---|---|---|---|
| | | | | Struct. | Magn. |
| | Ferromagnetic (F) | | | | |
| 94.0 | −100 | $Li_2CuO_2$ | 2.86 | 23 | 24 |
| | Antiferromagnetic (AF) | | | | |
| 97.0 | 209 | $Na_4CuMo_3O_{12}$ | 3.40 | 25 | 26 |
| 97.1 | 24 | $Cu_3(CO_3)_2(OH)_2$ | 3.02 | 27 | 16 |
| 97.7 | 209 | $Na_4CuMo_3O_{12}$ | 3.46 | 25 | 26 |
| 97.8 | 85 | $SrCu_2(BO_3)_2$ | 2.90 | 28 | 11 and 29 |
| 98.4 | 150–160 | $CuGeO_3$ | 2.94 | 30 | 31–33 |
| 99.2 | 160 | $Cu_2CdB_2O_6$ | 2.98 | 34 | 17 |
| 100.5 | Not determined | $\alpha$-$Cu_2P_2O_7$ | 3.05 | 35 | 36 |
| 101.8 | Not determined | $\alpha$-$Cu_2P_2O_7$ | 3.32 | 35 | 36 |
| 102.4 | 279 | $Cu_2Fe_2Ge_4O_{13}$ | 3.02 | 37 | 38 |
| 100.8 | 95 | $Cu_3(P_2O_6OH)_2$ | 3.06 | 22 | This work |
| 98.0, 98.5 | 28 | $Cu_3(P_2O_6OH)_2$ | 3.28 | 22 | This work |

spectively, by solid and dotted bars, are 3.06 and 3.28 Å. The first-shortest Cu-Cu bond has two identical Cu-O-Cu paths whose angle is 100.8°. The second-shortest Cu-Cu bond has two Cu-O-Cu paths, but they differ slightly from each other. Angles in the two paths are 98.0 and 98.5°. From the Cu-Cu distances and Cu-O-Cu angles, exchange interactions are expected to exist in the first-shortest and second-shortest Cu-Cu bonds. The respective values of their interactions are defined as $J_1$ and $J_2$. In contrast, Cu-Cu distances in the other bonds are greater than 4.27 Å. Therefore, exchange interactions in these bonds are expected to be smaller than $J_1$ and $J_2$. Consequently, $Cu_3(P_2O_6OH)_2$ is probably a compound including the spin-1/2 trimer ($J_1-J_2-J_2$) chain.

Let us now consider signs of $J_1$ and $J_2$. Signs of exchange interactions are determined mainly by Cu-O-Cu angles in Cu-O-Cu paths with short Cu-O bonds (typically less than 2.5 Å). It is natural to consider that the $J_1$ interaction is AF because of the 100.8° angle. The sign of $J_2$, on the other hand, cannot be judged immediately. For that reason, we selected Cu-Cu bonds whose Cu-O-Cu angles are close to 98 in other cuprates, and investigated signs of exchange interactions in those bonds (Table I). The two Cu-O-Cu angles of the $J_2$ interaction are close to each other. Therefore, we chose Cu-Cu bonds whose two Cu-O-Cu angles are identical or similar. We could not, however, find Cu-Cu bonds whose two Cu-O-Cu angles are not identical. All exchange interactions in Table I are AF when Cu-O-Cu angles are greater than 97°. As a result, we can infer that the $J_2$ interaction in $Cu_3(P_2O_6OH)_2$ is AF. The first-shortest bond has a larger value of the Cu-O-Cu angles than the second-shortest bond. Therefore, $J_1$ is probably larger than $J_2$. As shown later, magnetism of $Cu_3(P_2O_6OH)_2$ is explainable quantitatively using the trimer chain with $J_1=95$ and $J_2=28$ K.

## III. METHODS OF EXPERIMENTS AND CALCULATION

We synthesized crystalline powder of $Cu_3(P_2O_6OH)_2$ from a mixture of 0.5 g of CuO and 20 mL of $H_3PO_4$. The mixture was stirred continuously and heated until CuO was dissolved perfectly. Then the mixture was kept in a furnace in air at 463 K for 48 h. The $Cu_3(P_2O_6OH)_2$ appeared as light blue powder. We used x-ray diffraction measurement to confirm the formation of $Cu_3(P_2O_6OH)_2$ and the absence of other materials. We measured magnetizations up to 5 T using a superconducting quantum interference device (SQUID) magnetometer produced by Quantum Design. High-field magnetizations up to 30 T were measured using an extraction-type magnetometer in a hybrid magnet at the High Magnetic Field Center, NIMS, Tsukuba, Japan. Specific heat was measured using a relaxation technique with Physical Property Measurement System (PPMS; Quantum Design).

We calculated the susceptibility and magnetization of trimer chains by quantum Monte Carlo (QMC) techniques using the loop algorithm[39] and using the directed-loop algorithm in the path-integral formulation,[40] respectively. The numbers of Cu sites in the QMC simulations are described in figure captions. We have performed more than one million updates. Finite-size effects and statistical errors are negligible in the scale of figures represented in this paper.

## IV. RESULTS AND DISCUSSION

The solid curves in Fig. 2(a) and its inset show the temperature $T$ dependence of magnetic susceptibility $\chi(T)$ of $Cu_3(P_2O_6OH)_2$ measured in the magnetic field of $H=0.1$ T. On cooling, the susceptibility increases following the Curie-Weiss law from 300 K, shows weak temperature dependence around 40 K, increases rapidly below about 20 K, and has a maximum around $T_{max}=3$ K. Our result on the susceptibility agrees with that above 5 K reported by Baies *et al.*[22,41] The curves in Fig. 3 and its inset represent the temperature dependence of specific heat $C(T)$ of $Cu_3(P_2O_6OH)_2$ in the absence of a magnetic field. No magnetic long-range order appears above 2 K. Thus, the maximum of $\chi(T)$ around 3 K

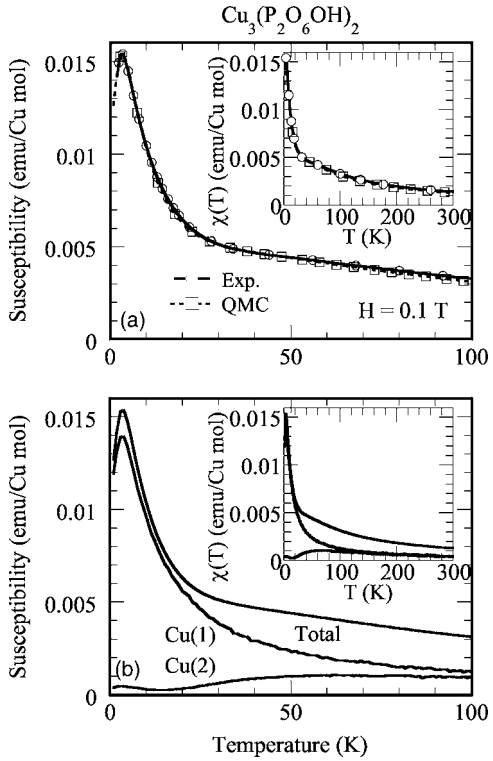


FIG. 2. (a) Magnetic susceptibility $\chi(T)$ of $Cu_3(P_2O_6OH)_2$ measured in 0.1 T (solid curve) and the QMC results of $\chi(T)$ for the spin-1/2 trimer chains with $J_1=95$ and $J_2=28$ K (dashed curve). The inset shows the same results up to 300 K. In the QMC simulation, the number of Cu sites is 600. Because the solid and dashed curves overlap with each other, the dashed curve cannot be seen clearly. The circles and squares represent some points of the experimental and QMC results, respectively. We draw these symbols in order to indicate that two curves exist. (b) The QMC results of $\chi(T)$ for the total, Cu(1), and Cu(2) spins. The inset shows the same results up to 300 K. We use the value of $\chi(T)$ per 1, 1/3, and 1/3 Cu mol for the total spin, Cu(1) spin, and Cu(2) spin, respectively. We calculated $M(H)$ of the Cu(1) and Cu(2) spins in $H=0.67$ T and defined $\chi(T)$ as $M(H)/H$. The number of Cu sites is 360 in the QMC simulation.

indicates development of AF short-range correlation. The specific heat increases with decreasing $T$ at low $T$. This result suggests development of AF short-range correlation or existence of magnetic long-range order below 2 K. Even if the increase of $C(T)$ is caused by AF short-range correlation, it is not necessary that $C(T)$ has a maximum around 3 K. For example, temperature of a maximum of $C(T)$ is lower than that of $\chi(T)$ in spin-1/2 AF uniform chains.

The solid curve in Fig. 4(a) indicates the magnetic-field $H$ dependence of magnetization $M(H)$ of $Cu_3(P_2O_6OH)_2$ at 1.6 K. The magnetization is expressed as a spin value $S=M(H)/g\mu_B N_A$ where $g$, $\mu_B$, and $N_A$ are the powder-averaged gyromagnetic ratio of $Cu^{2+}$, Bohr magneton, and Avogadro's constant, respectively. We determined $g=2.12$ in an electron spin resonance (ESR) measurement at room temperature. The most prominent feature is a 1/3 magnetization plateau above 12 T. The 1/3 magnetization plateau is consistent with the theorem of Ref. 1.

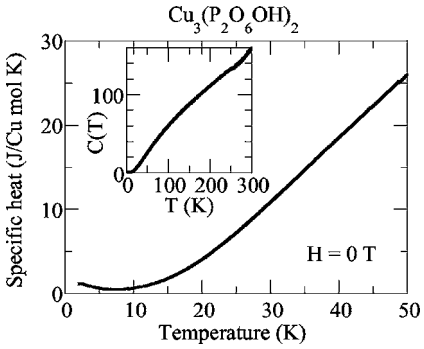


FIG. 3. Specific heat $C(T)$ of $Cu_3(P_2O_6OH)_2$ in the absence of the magnetic field. The inset shows $C(T)$ up to 300 K.

In order to investigate whether magnetism of $Cu_3(P_2O_6OH)_2$ can be explained by a trimer chain, we compared the experimental results with QMC results of $\chi(T)$ and $M(H)$. Because the experimental $\chi(T)$ has the characteristic structure, the susceptibility maximum around 3 K, we compared first the experimental $\chi(T)$ with calculated $\chi(T)$. We calculated susceptibilities for several values of $j\equiv J_2/J_1$. In each calculated $\chi(T)$, a value of $J_1$ was determined in order that the calculated $\chi(T)$ was close to the experimental $\chi(T)$ at low $T$. Among calculated susceptibilities, we chose calculated $\chi(T)$ that could reproduce the experimental $\chi(T)$ best. The dashed curves in Fig. 2(a) and its inset show the best

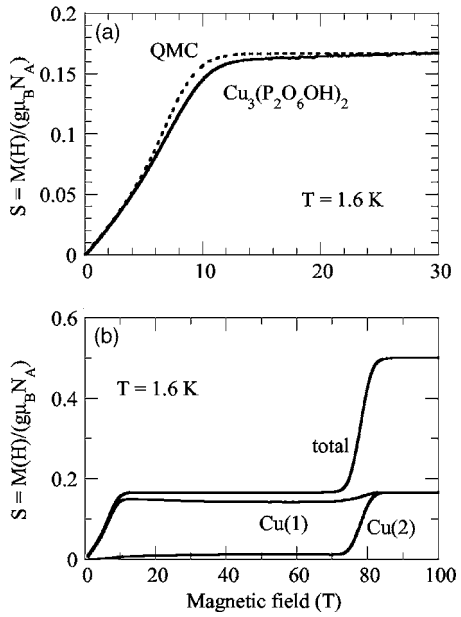


FIG. 4. (a) Magnetization [$M(H)$ emu/Cu mol] of $Cu_3(P_2O_6OH)_2$ (solid curve) and QMC results of $M(H)$ for the spin-1/2 trimer chain with $J_1=95$ and $J_2=28$ K (dashed curve) at 1.6 K. Magnetizations are expressed as a spin value $S=M(H)/g\mu_B N_A$ where $g$, $\mu_B$, and $N_A$ represent, respectively, the $g$ value of $Cu^{2+}$ (2.12), the Bohr magneton, and Avogadro's constant. (b) The QMC results of $M(H)$ for total, Cu(1), and Cu(2) spins of the same model at 1.6 K. We use the value of $M(H)$ per 1, 1/3, and 1/3 Cu mol for the total, Cu(1), and Cu(2) spins, respectively. In both (a) and (b), the number of Cu sites is 360 in the QMC simulation.

curve that has $j=0.29$ and $J_1=95$ K ($J_2=28$ K).[42] The dashed curve in Fig. 4(a) indicates QMC results of $M(H)$ for the same model and is consistent with the experimental magnetization except for slight discrepancy around 10 T. Consequently, the spin-1/2 trimer chain with $J_1=95$ and $J_2=28$ K can explain magnetic properties of $Cu_3(P_2O_6OH)_2$.[43] Calculated susceptibilities with $j=0.28$ and $J_1=101.5$ K or $j=0.30$ and $J_1=90$ K differ a little from the experimental one. Thus, we estimated errors of $J_1$ and $J_2$ as about 7% (101.5/95–1.07).

Figure 2(b) shows the QMC results of $\chi(T)$ for the total, Cu(1), and Cu(2) spins. The susceptibility of the Cu(2) spins increases with decreasing $T$ from 300 K, shows a maximum at 62 K, and decreases to small values at low $T$. Because the $J_1$ interaction is dominant in $Cu_3(P_2O_6OH)_2$, two Cu(2) spins connected by the $J_1$ interaction form a state that resembles a spin-singlet pair. Therefore, $\chi(T)$ of the Cu(2) spins is similar to $\chi(T)$ of an isolated AF dimer. When the exchange interaction is 95 K, $\chi(T)$ of an isolated AF dimer has a maximum at 59 K, which is close to $T_{max}=62$ K in $\chi(T)$ of the Cu(2) spins. In contrast to $\chi(T)$ of an isolated AF dimer, $\chi(T)$ of the Cu(2) spins is not negligible at low $T$ because the Cu(1) spins affect the Cu(2) spins through the finite $J_2$ interaction. The susceptibility of the Cu(1) spins increases with decreasing $T$ from 300 K and shows a maximum at 3 K like low-dimensional antiferromagnets. An effective interaction exists between two Cu(1) spins through the AF dimer formed by the Cu(2) spins and the system consisting of the Cu(1) spins behaves as an effective AF chain. The value of the effective interaction is estimated roughly as $J_{eff}-J_2^2/J_1=8$ K.[38] The value of $T_{max}$ is 5 K in an AF uniform chain with exchange interaction of 8 K. It is close to $T_{max}=3$ K in $\chi(T)$ of the Cu(1) spins as seen in Fig. 2(b).

The temperature dependence of the total susceptibility can be understood as follows. At high $T$, the susceptibilities of both the Cu(1) and Cu(2) spins increase following the Curie-Weiss law. Below $T_{max}=62$ K, a decrease of $\chi(T)$ of the Cu(2) spins and an increase of $\chi(T)$ of the Cu(1) spins compensate and therefore the temperature dependence of the total susceptibility becomes weak around 40 K. Below 20 K, $\chi(T)$ of the Cu(2) spins is small and the total susceptibility is determined mainly by the Cu(1) spins. Consequently, the total susceptibility increases rapidly at low $T$ and has a maximum around 3 K.

Figure 4(b) shows QMC results of $M(H)$ for the total, Cu(1), and Cu(2) spins. As was mentioned above, because two Cu(2) spins that are connected by the $J_1$ interaction form a state that resembles a spin-singlet pair, the moment of the Cu(2) spins is small at low $H$. The moment of the Cu(1) spins, in contrary, is almost saturated in the plateau region because of the small value of $J_{eff}=8$ K. The AF uniform chain with exchange interaction of 8 K has a saturation field of 11 T for $g=2.12$, which is close to the starting field of the plateau. We have written that magnetism of $Cu_3(P_2O_6OH)_2$ can be explained qualitatively by a state of Cu(2) spins resembling a spin-singlet pair and weakly coupled Cu(1) spins with the effective interaction $J_{eff}$. We have confirmed, however, that the simple picture cannot explain quantitatively magnetism of $Cu_3(P_2O_6OH)_2$. We emphasize that the spin system is the spin-1/2 trimer chain with $J_1=95$ and $J_2=28$ K, and that the value of $J_2$ is not so small in comparison with that of $J_1$. Finally, we show a value of a gap in the plateau region. The total magnetization starts to increase again around 65 T, which means that the value of the gap is 92 K for $g=2.12$. That gap is determined mainly by the $J_1$ interaction. Therefore, the gap value is close to $J_1$ (95 K).

## V. CONCLUSION

We measured the temperature dependence of magnetic susceptibility and specific heat, and the magnetic-field dependence of magnetization of $Cu_3(P_2O_6OH)_2$. Two kinds of $Cu^{2+}$ sites exist and form a spin-1/2 trimer chain with $J_1$-$J_2$-$J_2$ interactions, where $J_1$ and $J_2$ indicate two kinds of antiferromagnetic exchange interactions. We found 1/3 magnetization plateau above 12 T in the magnetization at 1.6 K. The appearance of the plateau is consistent with the theorem of Ref. 1. Experimental magnetic susceptibility and magnetization can be reproduced well by quantum Monte Carlo results for the trimer chain with $J_1=95$ and $J_2=28$ K. To our knowledge, $Cu_3(P_2O_6OH)_2$ is the first model compound of the trimer chain that has only AF interactions and that shows a magnetization plateau.

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[41] Baies *et al.* fitted a sum of susceptibility of an AF uniform chain and susceptibility obeying the Curie law to the susceptibility of $Cu_3(P_2O_6OH)_2$, but agreed that the fit was poor. The susceptibility of $Cu_3(P_2O_6OH)_2$ cannot be explained solely by susceptibility of an AF uniform chain. For that reason, the authors speculated that impurities existed and caused Curie susceptibility. The susceptibility of our model, however, can reproduce quantitatively that of $Cu_3(P_2O_6OH)_2$. Thus, the assumption that an AF uniform chain exists is not correct. The authors also noted that two kinds of exchange interactions should be taken into account.
[42] We ignored a constant term of susceptibility attributable to Van Vleck paramagnetism and diamagnetism of closed ions because the constant term is much smaller than the spin susceptibility when we compared calculated susceptibility with that of $Cu_3(P_2O_6OH)_2$.
[43] We do not succeed in estimating the magnetic specific heat of $Cu_3(P_2O_6OH)_2$. There is no nonmagnetic isostructural compound [e.g., $Zn_3(P_2O_6OH)_2$]. In such a case, magnetic specific heat is extracted by subtraction of estimated phonon contribution. The phonon contribution is estimated by fitting some function to total specific heat at high temperatures on the assumption that only a phonon contribution exists at those temperatures. We calculated the specific heat of the spin-1/2 trimer chain with $J_1$=95 and $J_2$=28 K using the QMC technique. The calculated specific heat remains with non-negligible magnitude even at 200 K. Therefore, we could not assume a fitting function to estimate the phonon contribution and obtain magnetic specific heat of $Cu_3(P_2O_6OH)_2$.