Volume 1 | Number 1 | Jan 2013 | Pages 1–100

CrystEngComm

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Journal Name

Communication

Preparation, Crystal Structure, and Magnetic Properties of Copper Hydroxy Salt with Diamond Chain Magnetic Network

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Copper hydroxy salt, α-[Cu$_3$(OH)$_2$(CH$_3$CO$_2$)$_2$(H$_2$O)$_4$](C$_6$H$_5$SO$_3$)$_2$, exhibited a distorted diamond chain magnetic network and paramagnetism with the dominance of the
10 antiferromagnetic interactions down to 2 K.

Copper hydroxy salts Cu(OH)$_{2-x}$A$_x$, where A is an inorganic anion, form beautiful crystals that are blue or green owing to the divalent copper ion.[1] Their crystal structures and colors are dependent on the size, shape, and charge number of A, in addition
15 to the compositional ratio of Cu, OH, and A. Copper hydroxy salts yield an $S = 1/2$ quantum spin system with geometrically frustrated magnetic networks such as two-dimensional triangular lattices,[2] kagomé lattices,[3] pyrochlore lattices,[4] and diamond chain lattices.[5] New quantum mechanical phenomena induced by
20 spin frustration effects are expected of these materials at low temperatures.[6]

Copper hydroxy salts with an organic anion as A can be prepared chemically by the intercalation methods.[7] Recently, we investigated the magnetic properties of copper hydroxy salts with
25 various organic anions, and found that they exhibited unique magnetic properties that strongly depended on the molecular length and alignment of the organic carboxylates.[8] In particularly, the derivative that contained a large organic anion, Cu$_2$(OH)$_3$(8-((p-(phenylazo)phenyl)oxy)octanoate), showed paramagnetism
30 down to 2 K after soaking it in methanol and weak ferromagnetism below 10.8 K after soaking in acetonitrile.[9] The origin of the magnetic modification was due to the change in the orientation of the organic moieties, induced by the organic solvent molecules. The material can be regarded as a prototype
35 for new magnetic sensors or switching devices. Thus, the combination of copper hydroxides and organic anions may yield new functional materials.

Crystal structure elucidations are necessary in order to discuss the magneto-structural correlations in these materials. Single
40 crystals of copper hydroxy salts with small inorganic anions are typically prepared by hydrothermal methods.[2] However, single crystals of the derivatives with organic anions are not obtained by hydrothermal methods because of decomposition to copper oxides etc. at high temperatures. The intercalation methods do not
45 give single crystals but powder samples. Recently, single crystals of copper hydroxy salts with organic carboxylate anions, namely, formate, acetate, and propionate, were successfully obtained by the hydrolysis of their carboxylate anions under mild conditions,

and their crystal structures were investigated.[10] The hydrolysis
90 method is useful for the preparation of the organic derivatives, and may lead to novel structures or functionalities. In this study, we prepared a new copper hydroxy salt with benzenesulfonate and acetate ions as organic anions, [Cu$_3$(OH)$_2$(CH$_3$CO$_2$)$_2$(H$_2$O)$_4$](C$_6$H$_5$SO$_3$)$_2$. This material had two
95 polymorphs, α and β. In this paper, we describe the crystal growth, structure, and magnetic properties of the α-phase (**1**).
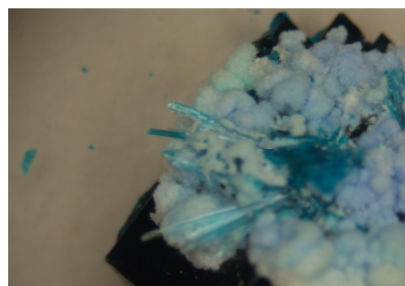

Fig. 1 Photograph of light blue crystals of **1** in the reaction mixture.

155 The preparation of **1** was carried out as follows: 1 g of sodium benzenesulfonate and 1 g of copper acetate monohydrate were dissolved in 20 mL of water. The aqueous solution was heated at 50 °C until all liquid evaporated. It took one or two days until completion of the evaporation. Figure 1 shows a photograph of
160 the residue after drying. In the mixture of dark greenish crystals, a colorless powder, and a light blue powder among others, light blue crystals of **1** and polymorph β were found. The blue crystals were separated from the mixture under microscope. The largest crystal of **1** was 10 x 2 x 0.5 mm^3. It was difficult to pick all the
165 blue crystals from the mixture. In particularly, small crystals could not isolate from it. There have been cases when we could not obtain the crystals from a batch at all. The yield of **1** was 30 mg at a maximum (Anal. Calcd. for C$_{16}$H$_{26}$O$_{16}$S$_2$Cu$_3$: C, 26.36; H, 3.59; S, 8.80 Found C, 26.00; H, 3.50; S, 8.45.). The crystals
170 of **1** were stable under air, but gradually powdered in water or methanol. Meanwhile, very small amount of the β phase was obtained and prevented investigations regarding its magnetic properties.

The structure of **1** was determined by X-ray crystallographic
95 analysis. Figure 2 shows the crystal structure of **1**. It crystallized in triclinic space group P–1 with a crystallographically
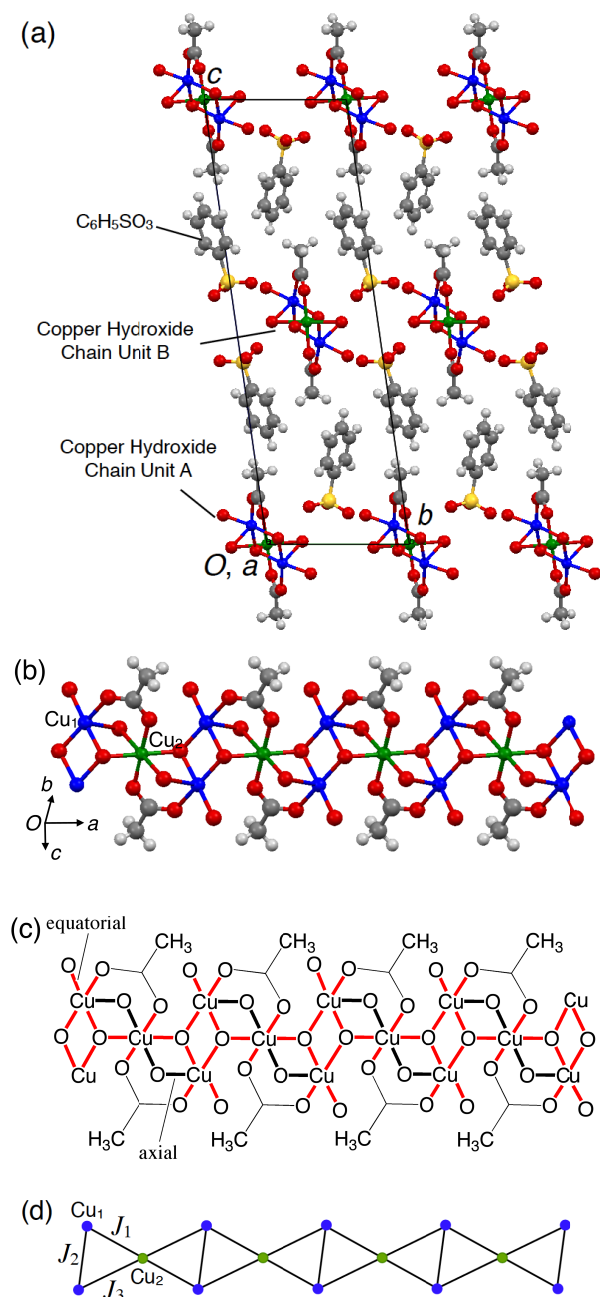
Fig. 2 Crystal Structure of **1**. (a) View along the *a* axis. (b) Atomic alignment of the copper hydroxide chain unit A. (c) Schematic presentation of the copper hydroxide chain units A and B. The black bold lines and red lines indicate the axial and equatorial Cu–O bonds, respectively. (d) Schematic presentation of the magnetic network in **1**.

asymmetric unit of $[Cu_6(OH)_4(CH_3CO_2)_4(H_2O)_8](C_6H_5SO_3)_4$. The hydrogen atoms of the hydroxide ions and water molecules could not be found. This salt included two kinds of organic anions, namely benzenesulfonate and acetate anions. This suggested that copper hydroxy salts with anions that cannot be hydrolyzed could be prepared by using mixed solutions of appropriate carboxylate anions and the anions. Derivatives with layered structures were

not formed under the reaction conditions, although layered derivatives were often obtained by the hydrolysis method in the previous studies.[2,10] Figure 2a shows the view of the crystal structure of **1** from the *a* axis. Copper ions, acetate ions, hydroxyl ions, and water molecules formed a copper hydroxide chain unit toward the *a* axis. Each copper hydroxide chain unit was surrounded and isolated by large benzenesulfonate ions. Two chain units were crystallographically independent, namely A and B in Fig. 2a. Figure 2b shows the atomic alignment of the copper hydroxide chain unit A. Copper ions existed in square pyramidal (Cu_1; blue) or octahedron (Cu_2; green) sites. The octahedral unit and a dimer of the square pyramidal unit aligned alternatively. The chain unit B was almost the same structure as the chain unit A. Figure 2c shows a schematic presentation of the copper hydroxide chain unit. The bold black and red lines correspond to the axial and equatorial Cu–O bonds, respectively. When a Cu(II) ion exits in elongated octahedron or square pyramidal environments, its unpaired electron occupies the $dx^2–y^2$ orbital, corresponding to the red lines in Fig. 2c. It can be recognized that a magnetic network was formed in the copper hydroxide chain unit. The copper ions were bridged via hydroxyl ions, acetate ions, and/or water molecules. There are three kinds of bridging fashions, namely, a mono-oxo, a di-oxo, and, di-oxo and syn-syn carboxylate bridges. In this case, super-exchange interactions via oxygen atoms or carboxylate groups may occur between the copper ions. There were three kinds of the magnetic exchange paths because they are non-equivalent crystallographically. Figure 2d shows a schematic view of the magnetic network in **1**. The divalent copper ions are positioned on the vertices of the diamond mark. The diamond marks have the vertices in common and are aligned regularly in one direction. Such a lattice is called a diamond chain lattice.[5,11] In this magnetic lattice system, the magnetic ground state at low temperatures and magnetic behaviors under high magnetic fields are actively discussed. Salt **1** may be regarded as a model substance of an $S = 1/2$ distorted diamond chain magnetic network with magnetic coupling constants J_1, J_2, and J_3,[12] corresponding to the di-oxo and syn-syn carboxylate bridges, the di-oxo bridges, and, the mono-oxo bridge in Fig. 2c, respectively. Magnetic coupling constants of the chain unit B may be the same as those of the chain unit A because there are little structural defferences between them. The β phase observed in this study had similar structure with the diamond chain network of **1**.

Magneto-structural correlations in hydroxo-bridged copper dimer complexes have been extensively studied. A linear correlation between the singlet-triplet gap $\Delta E/k_B$ and the Cu–O–Cu angle $\theta(°)$ has been experimentally proposed by Crawford et al:[13]

$$\Delta E/k_B = 11100 - 113.4\theta(°) \quad (1)$$

where the singlet-triplet gap ΔE is the difference between the energies of the singlet state E_1 and the triplet state E_3 in the dimer. The exchange path with the coupling constant J_2, as shown in Fig. 2d, is quite similar in the structure with the dimer complexes studied by Crawford et al. The averaged Cu–O–Cu bridge angle in the exchange path J_2 in the chain units A and B was estimated

(a)

(b)
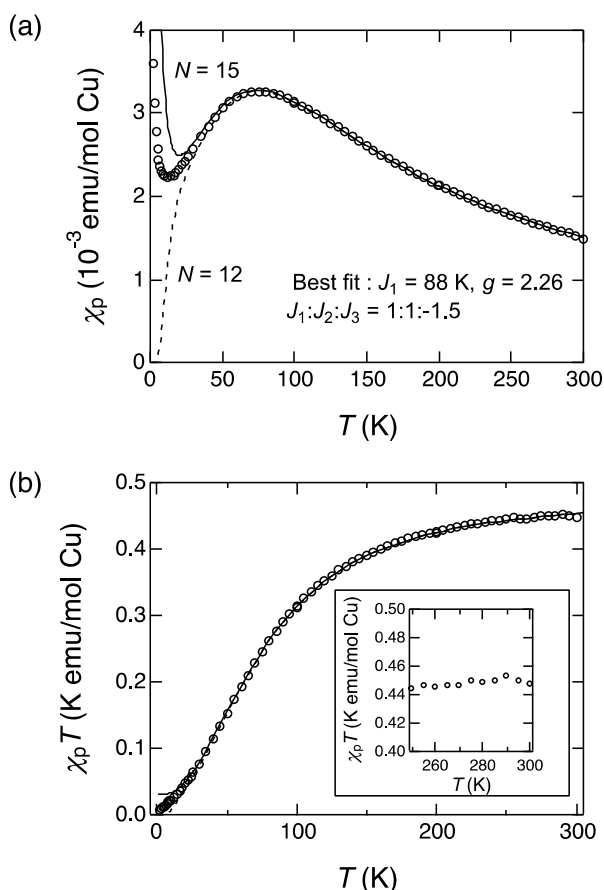
to be 98.60° from our X-ray studies. Using Eq. (1), the singlet-

Fig. 3 Magnetic properties of **1**. (a) Temperature dependence the paramagnetic susceptibility χ_p of **1** under an applied field of 500 Oe. The solid and broken lines are the theoretical best fits from the numerical exact diagonalization for 15 and 12 cluster analyses with periodic boundary condition, respectively. (b) $\chi_p T$ vs T plot. Inset shows the plots in the temperature range of 250 – 300 K. The solid line is the theoretical best fits from the numerical exact diagonalization for 15 cluster analysis with periodic boundary condition.

triplet gap $\Delta E/k_B$ of a copper dimer with the bridging angle was roughly estimated to be –81.2 K, namely antiferromagnetic. On the other hand, the magnetic coupling constants of the exchange paths J_1 or J_3 via a carboxylate group and hydroxyl and/or water molecules were also dependent on their structures.[14,15] However, the value of the exchange coupling constants could not be estimated from their structural data.

It has been reported that the following five materials have diamond chain magnetic networks: azurite $Cu_3(CO_3)_2(OH)_2$,[5] $[Cu_3(L^1)_2(OH)_2(H_2O)_4]$ (L^1 = adipate),[16] $[Cu_3(L^2)_2(OH)_2(H_2O)_2](X)_2 \cdot 2H_2O$ (L^2 = 1,3-bis(pyridine-4-carboxylato)propane; X = ClO_4 or NO_3),[17] $[Cu_3(L^3)_2(OH)_2(H_2O)_2] \cdot 4H_2O$ (L^3 = succinate),[18] and $[Cu_3(L^4)_2(OH)_2(H_2O)_2] \cdot 4H_2O$ (L^4 = thymine-1-acetate).[19] Azurite is different in its crystal structure from **1**. In azurite, copper ions existed in square pyramidal or square planar sites. The square planar unit and a dimer of the square pyramidal unit aligned

alternatively. There are no acetate ions as ligands in the intrachain. The interchain is bounded by carbonate ions via coordination bonds. Meanwhile, the later four compounds have a similar diamond chain networks with **1**. Their interchains are well separated by the large organic anions, as well as **1**. However, these materials were not regarded as diamond chain compounds by their authors, with the exception of azurite. The preparations of the aforementioned materials were different from the procedure used here. For examples, the use of gelling solutions,[16] preparation of complex organic molecules,[17,19] or pH control using ammonia,[18] are required in other preparation methods. The method used in this study was the simplest by comparison.

The magnetic coupling constants, $J_1 - J_3$, of **1** were investigated by magnetic measurements and theoretical analyses. Figure 3 shows the temperature dependence of the paramagnetic susceptibility χ_p for a powdered sample of **1** under an applied field of 500 Oe. The molar unit of the paramagnetic susceptibility χ_p was chosen as the quantity per one mole of Cu(II). The raw experimental data were corrected for diamagnetic susceptibility, as estimated from Pascal's constants.[20] As shown in Fig. 3a, the χ_p value exhibited a broad maximum around 75 K due to a short range magnetic order, and further increased below 12 K due to very small amount of impurities found in power X-ray diffraction patterns of the sample. The impurity is not intrinsic and did not prevent magnetic analyses in this study. No magnetic ordering was observed down to 2 K. Figure 3b shows the temperature dependence of the product of χ_p and T. The $\chi_p T$ value was nearly constant in the temperature range of $T > 250$ K, ca. 0.45 emu K mol^{-1} (see inset), corresponding to the theoretical value for the magnetic species with $g = 2.2$ and $S = 1/2$.[20] This can be regarded as Curie-like behavior[20] where $\theta \sim 0$. Below 250 K, the $\chi_p T$ value decreased monotonically with decreasing in temperature, indicating the dominance of the antiferromagnetic interactions between copper ions in the copper hydroxide chain unit at a lower temperature region. The diamond chain compounds reported by Bakalbassis et al.[16] or Amo-Ochoa et al.[19] were similar magnetic behaviors with **1**, while magnetic behaviors of azurite was different from **1**. Namely, two local maximums of the χ_p value at 5 K and 20 K appeared in the χ_p vs T plot of azurite.[5] These results reveal structural differences of **1** from azurite.

The magnetic properties of **1** were investigated using the numerical exact diagonalization up to 12- or 15-site clusters with periodic boundary condition for the $S = 1/2$ distorted diamond chain lattice model.[12,21] In the analysis, three assumptions were adopted; (i) the exchange path with the coupling constant J_2 was antiferromagnetic as determined by the above structural consideration, (ii) the sum, $J_2 + 2(J_1 + J_3)$, was zero because of $\theta \sim 0$ at the higher temperature region, and (iii) to simplify the model, $J_1 = J_2$, that is, $J_1 : J_2 : J_3 = 1 : 1 : –1.5$. The best fit of the theoretical curve for the $N = 15$ site clusters was for $g = 2.26$, $J_1/k_B = +88$ K, $J_2/k_B = +88$ K, and $J_3/k_B = –132$ K, as shown in Fig. 3a. Here, $J > 0$ means antiferromagnetic and $J < 0$ means ferromagnetic from the definition of the Hamiltonian.[12] In spite of $\theta \sim 0$ in the temperature range $T > 250$ K, this suggests that strong magnetic interactions may occur between copper ions in **1**. Further experimental and theoretical studies of this material are now in progress.

In conclusion, single crystals of the copper hydroxy salts with

large organic anions, $[Cu_3(OH)_2(CH_3CO_2)_2(H_2O)_4](C_6H_5SO_3)_2$ **1** were easily prepared by means of the hydrolysis method. Copper hydroxy salts have various magnetic networks and the Cu–O–Cu bridges in them are highly sensitive toward magnetic interactions. Copper hydroxy salts provide interesting magnetic systems to us. In the future, we will prepare other copper hydroxy salts with various shapes, sizes, and charges of the organic anions by means of the hydrolysis method. Diverse organic anions may lead to new materials and new functions.

Notes and references

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† Electronic Supplementary Information (ESI) available: detailed data for crystal structure analyses of **1** and the β phase, powder X ray diffraction pattern of **1**, magnetic data of **1**, Hamiltonian of the distorted diamond lattice. CCDC1015729 of **1**. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/b000000x/

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