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Convenient Crystal Growth, Structural Determination, and Magnetic Studies of Layered Copper Hydroxides Containing Aromatic Sulfonates

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Wataru Fujita[a]

Single crystals of layered copper hydroxides, **1**–**4**, with aromatic sulfonate ions, *p*-toluenesulfonate, *p*-ethylbenzensulfonate, 1-naphthalenesulfonate, and 1,5-naphthalenedisulfonate, respectively, were conveniently prepared by the hydrolysis of copper acetate aqueous solutions containing the organic sulfonates. X-ray structure analyses revealed that these compounds had alternating stacks of copper hydroxide layers and aggregated layers of the organic ions. The atomic alignment of their copper hydroxide layers was similar to the inorganic layer of hydrotalcite, $[Mg_6Al_2(OH)_{16}]•CO_3•16H_2O$. However, their copper hydroxide layers were not isostructural among **1**–**4**. In the copper hydroxide layers, not only hydroxide ions but also water molecules, acetate ions, or the organic sulfonate ions were coordinated to the copper ions. The copper ions exhibited elongated octahedral geometry in **1** and **2**, and elongated octahedral or square pyramidal geometry in **3** and **4**. The organic ions formed a bilayer arrangement for **1** and **2**, and a monolayer arrangement in **3** and **4**. Magnetic measurements revealed primarily antiferromagnetic interactions between neighbouring copper ions. Magnetic behaviours of these materials resembled antiferromagnetic ordering behaviour at low temperatures. The maximum values of χ_p were observed at 3.8 K, 3.5 K, 3.2 K, and 9.1 K for **1**–**4**, respectively. The exchange coupling constants were estimated from an $S = 1/2$ Heisenberg model with a two-dimensional triangular lattice magnetic network, where J/k_B = 42.2 K, 36.8 K, 80.1 K, and 84.9 K for **1**–**4**, respectively. The magnetic differences in these materials are due to the structural differences in their copper hydroxide layers. Thus, it was demonstrated that hydrolysis methods are suitable for the preparation of single crystals of various copper hydroxide derivatives with organic anions.

1. Introduction

Layered metal hydroxides containing an exchangeable inorganic anion can form intercalation compounds with appropriate organic anions to produce functional materials, allowing their application in fields such as photochemistry, magnetism, highly efficient chemical reaction fields, drug delivery, and as adsorbents for pollutants.[1,2] Copper hydroxy salts ($Cu(OH)_{2-x}A_x•mH_2O$, where A is an inorganic ion) are of particular interest in the field of magnetism. A divalent copper ion has a spin quantum number of 1/2. Thus, some copper hydroxyl salts exhibit geometrically frustrated magnetic networks[3–6] such as two-dimensional triangular lattices, kagomé lattices, pyrochlore lattices, and diamond chain lattices via superexchange couplings[7] between the copper ions through hydroxide ions or inorganic ions (A). Novel magnetic networks and new quantum mechanical phenomena induced by spin frustration effects may be observed in these materials at low temperaturees.[8]

Botallackite[3] $[Cu_2(OH)_3A]$ (A = Cl) has a layer-type structure similar to hydrotalcite $[Mg_6Al_2(OH)_{16}]•CO_3•16H_2O$,[9] and it forms intercalation compounds with various alkanecarboxylate ions by the exchange of anions A.[10] Their magnetic properties of such intercalation compounds strongly depend on the molecular length and orientation of the alkanecarboxylate employed,[11–14] presumably because of the structurally sensitive Cu–O–Cu bridge superexchange paths.[15] It has also been reported that the layered copper hydroxides with long alkanecarboxylate ions show both weak ferromagnetism and spin-glass like behaviour originating from spin frustration.[16]

In order to understand the functionality of these organic-inorganic hybrid materials, it is necessary to carry out detailed structural investigations by means of single-crystal X-ray analyses. Single crystals of layered metal hydroxides containing inorganic guest ions can be prepared by the hydrothermal method.[17] However, single crystals of layered metal hydroxides with organic ions decompose at high temperature conditions and hence are rarely obtained by hydrothermal methods.[18] Typically, layered metal hydroxides containing organic anions are prepared by ion-exchange method at around room

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[a] *Department of Information and Basic Science, Graduate School of Natural Science, Nagoya City University, 1 Yamanohata, Mizuho-cho, Mizuho-ku Nagoya 467-8501, Japan.*

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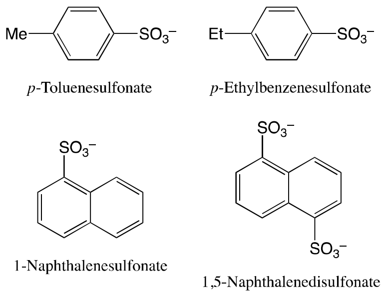
temperature. However, since these materials are obtained as powders, it is very difficult to determine their crystal structure.

Recently, Svarcova et al. have succeeded in the single-crystal structure analysis of the layered copper hydroxide with acetate ion, $[Cu_2(OH)_3CH_3CO_2]•H_2O$, obtained by the hydrolysis of the carboxylate ion.[19] In our previous studies, single crystals of layered copper hydroxides with formate, or propionate ions were obtained and their crystal structures were determined, using the related carboxylate ions as hydrolysis reagents.[20,21] However, copper hydroxides incorporating aromatic or bulky carboxylates were not obtained because copper salts of their organic carboxylates were precipitated immediately. Then, we attempted preparation of copper hydroxides with organic sulfonate ions because of copper salts of aromatic sulfonates are more soluble than the corresponding carboxylate salts. In our most recent research, we succeeded crystal growth and structure determination of copper hydroxides with benzenesulfonate using a mixed aqueous solution of acetate ion benzenesulfonate.[22] Commonly, the crystal structures of copper hydroxyl salts are dependent on the ratio of Cu, OH, A, and H_2O, and shape and charge number of the anion A. Organic sulfonate ions have more diverse molecular structures than inorganic ions and may adopt more various molecular orientations via van der Waals interactions. Copper hydroxides containing organic ions may form novel magnetic networks and exhibit useful magnetic properties.

In this study, the crystal growth by hydrolysis and structural analyses of layered copper hydroxides containing the aromatic sulfonate ions, *p*-toluenesulfonate, *p*-ethylbenzenesulfonate, 1-naphthalenesulphonate, and 1,5-naphthalenedisulfonate (Scheme 1), are demonstrated. Single crystals of these materials were easily obtained by heating an aqueous solution containing copper acetate and the organic sulfonate ion under atmospheric conditions. The resulting crystals have a layered structure composed mainly of copper hydroxides with S = 1/2 two-dimensional triangular lattice magnetic layers and aggregated organic ion layers. Furthermore, they exhibit different magnetic properties that originate from their crystal structures.



Scheme 1 Molecular structure of the organic sulfonate ions.

2. Experimental

Chemicals

All chemicals using in this study were purchased from Tokyo Kasei Co. Ltd. or Wako Chemicals Co. Ltd. and used without further purification.

Preparation of $[Cu_2(OH)_3(p\text{-}CH_3C_6H_4SO_3)]$, 1. An aqueous solution (100 mL) containing 1 g of copper acetate monohydrate and 1 g of sodium *p*-toluenesulfonate was kept at 55 ˚C for several hours. A light blue powder formed and was removed by filtration. The filtrate was then heated at 60 ˚C for two days while light blue plate-like crystals formed. Yield: 80 mg. Anal. Calcd. for $C_7H_{10}O_6Cu_2S$: C, 24.07%; H, 2.89%, Found: C, 24.09%; H, 2.78%.

Preparation of $[Cu_2(OH)_3(p\text{-}CH_3CH_2C_6H_4SO_3)]$, 2. An aqueous solution (100 mL) containing 1 g of copper acetate monohydrate and 1 g of sodium *p*-ethylbenzenesulfonate was kept at 55 ˚C for several hours. A light blue powder formed and was removed by filtration. The filtrate was than heated at 60 ˚C for two days while light blue plate-like crystals formed. Yield: 83 mg. Anal. Calcd. for $C_8H_{12}Cu_2O_6S$: C, 26.45%; H, 3.33%, Found: C, 26.46%; H, 3.32%.

Preparation of $[Cu_4(OH)_6(CH_3CO_2)(H_2O)]•(1\text{-}C_{10}H_7SO_3)•2H_2O$, 3. An aqueous solution (100 mL) containing 1 g of copper acetate monohydrate and 1 g of 1-naphthalenesulfonate was kept at 50 ˚C for several days while light blue plate-like crystals formed. Yield: 120 mg. Anal. Calcd. for $C_{12}H_{22}O_{14}Cu_4S$: C, 21.30%; H, 3.28%, Found: C, 21.40%; H, 3.10%.

Preparation of $[Cu_5(OH)_8(H_2O)_2]•(1,5\text{-}C_{10}H_6(SO_3)_2)•4H_2O$, 4. An aqueous solution (30 mL) containing 0.5 g of copper acetate monohydrate and 0.5 g of 1,5-naphthalenedisulfonate was kept at 55 ˚C for 1 hour. Light blue microcrystals were formed and removed by filtration. The filtrate was heated at 55 ˚C for 2 days while light blue plate-like crystals were formed. Yield: 72 mg. Anal. Calcd. for $C_{10}H_{26}O_{20}Cu_5S_2$: C, 14.16%; H, 3.09%, Found: C, 14.18%; H, 2.96%.

Single Crystal X-ray Analyses. X-ray diffraction data were collected on a Rigaku Mercury CCD diffractometer at 200 K, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. All structures were solved using a direct method with the SHELXS program and refined by successive differential Fourier syntheses and a full-matrix least-squares procedure using the SHELXL program.[23,24] Anisotropic thermal factors were applied to all non-hydrogen atoms. The crystal parameters of **1** and some botallackite-type derivatives are summarised in Table 1. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre: Deposition numbers CCDC-1061271, 1061270, 1061269, and 1061268 for **1**–**4**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Magnetic Measurements. Magnetic measurements were carried out for microcrystalline samples on a SQUID magnetometer (Quantum Design MPMS 7 or XL-7). The dc magnetic measurements were carried out under 500 Oe in the temperature range 2–300 K. The field dependence of the magnetization was measured at 2 K. The experimental raw data were corrected for diamagnetism, and the molar paramagnetic susceptibilities were obtained.

3. Results and Discussion

3.1 Preparation

Novel layered copper hydroxides, **1**–**4**, with the aromatic sulfonate ions, *p*-toulenesulfonate, *p*-ethylbenzenesulfonate, 1-naphthalenesulfonate, or 1,5-naphthalenedisulfonate, respectively, were prepared by the hydrolysis of acetate ions in an aqueous solution containing copper acetate and sodium salts of the aromatic sulfonate ions. Scheme 2 shows the formation reaction of the layered copper hydroxides. The hydroxide ions, formed by hydrolysis, react with copper ions so that copper hydroxides containing the aromatic sulfonate ions are gradually precipitated. Since the acetic acid formed in the reaction is gradually evaporated from the reaction system, crystal growth is promoted.

$$CH_3CO_2^- + H_2O \rightleftharpoons OH^- + CH_3CO_2H \uparrow$$

$$Cu^{2+} + (2-x)\,OH^- + x/n\,A^{n-} + m\,H_2O \rightleftharpoons Cu(OH)_{2-x}A_{x/n}\cdot mH_2O \downarrow$$

Scheme 2 Formation of the layered copper hydroxides.

In a typical procedure, 1 g of sodium organic sulfonate and 1 g of copper acetate monohydrate were dissolved in 100 mL of water, and the aqueous solution was heated to 60 ˚C. After several hours, a small amount of light bluish green precipitate formed, and was removed by filtration. The filtrate was reheated to 60 ˚C and, after several days, small plate-like single crystals of **1**–**4**, corresponding to the ions, *p*-toulenesulfonate, *p*-ethylbenzenesulfonate, 1-naphthalenesulphonate, and 1,5-naphthalenedisulfonate, respectively, were formed on the bottom of the glass bottle. The yields of the single crystals were mainly dependent on the evaporation rate of water in the solutions. In some cases, needle-like crystals of other phases were formed upon prolonged heating for more than one week near room temperature.

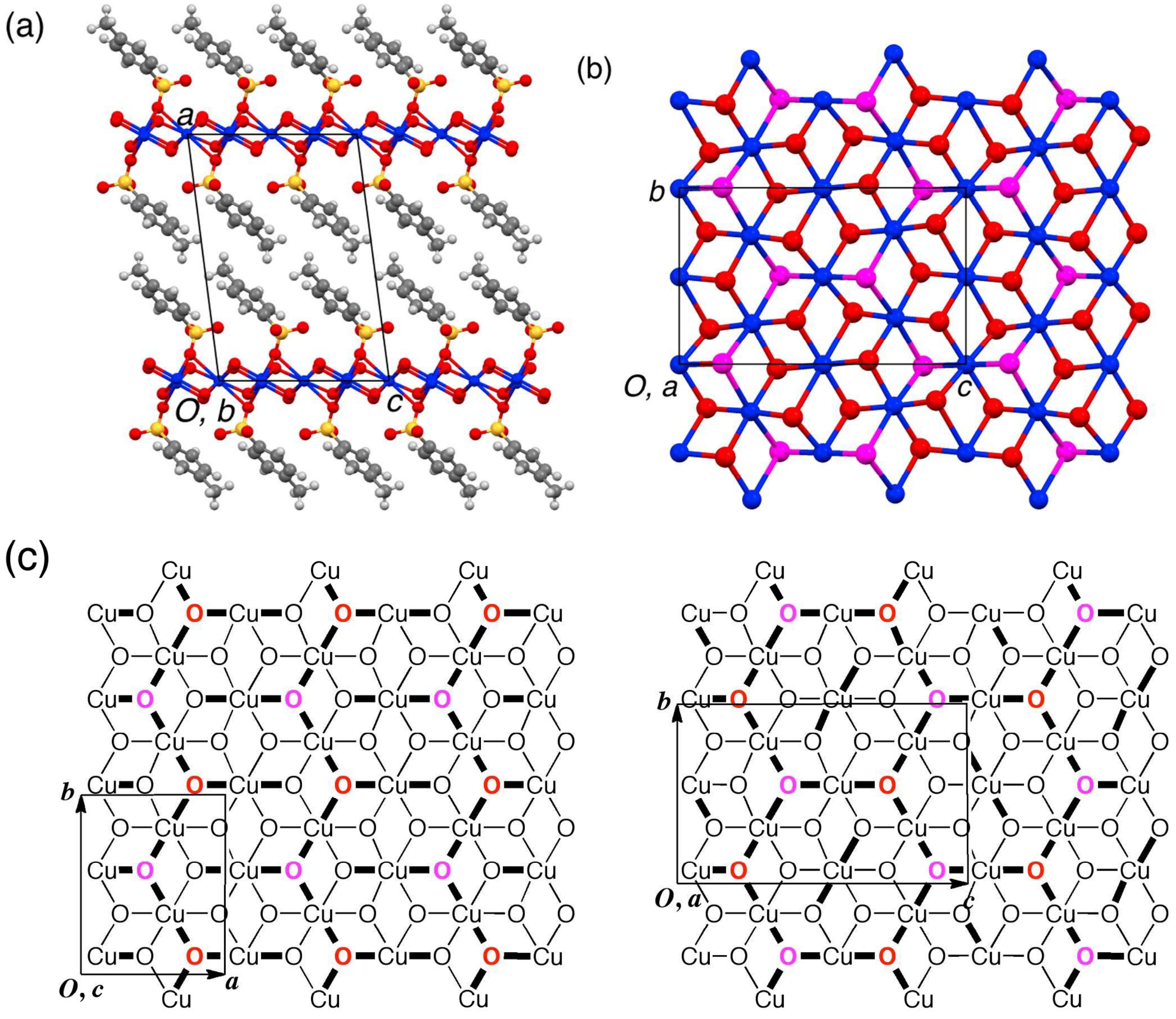
In this method, crystal growth of layered copper hydroxides including organic sulfonate ions is performed under lower temperature conditions as compared to those in the hydrothermal method, and hence decomposition of the products is prevented.

3.2 Crystal Structure

The structures and compositions of the resulting crystals for the layered copper hydroxides **1**–**4** were determined by X-ray crystallographic analyses and element analyses. The chemical formulae and crystallographic data of **1**–**4** are summarized in Table 1. Compounds **1**–**4** have copper hydroxide layers similar to botallackite, which has the formula $[Cu_2(OH)_3A]$(A = Cl) and its related materials Br^-, I^-, NO_2^-, NO_3^-, HCO_2^-, and

Table 1. Crystallographic data for **1** – **4**.

	1	□**2**	**3**	**4**
Formula	$[Cu_2(OH)_3(p\text{-}CH_3C_6H_4SO_3)]$	$[Cu_2(OH)_3(p\text{-}CH_3CH_2C_6H_4SO_3)]$	$[Cu_4(OH)_6(CH_3CO_2)(H_2O)]\bullet(1\text{-}C_{10}H_7SO_3)\bullet 2H_2O$	$[Cu_5(OH)_8(H_2O)_2]\bullet(1,5\text{-}C_{10}H_6(SO_3)_2)\bullet 4H_2O$
Crystal dimension	0.20 × 0.20 × 0.02	0.20 × 0.20 × 0.02	0.70 × 0.50 × 0.02	0.30 × 0.20 × 0.05
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P–1	P–1
a / Å	15.493(4)	16.769(12)	8.1058(6)	5.4530(5)
b / Å	6.4490(14)	6.450(4)	8.5966(7)	8.0998(8)
c / Å	10.597(3)	10.595(7)	15.1429(12)	14.4067(17)
α / ˚	90.0000	90.0000	90.034(4)	95.208(10)
β / ˚	97.476(7)	95.894(7)	95.059(5)	98.408(9)
γ / ˚	90.0000	90.0000	99.868(5)	107.430(7)
V / Å^3	1049.8(5)	1139.9(13)	1035.40(15)	594.44(11)
Z	4	4	2	1
R_1	0.0358	0.0544	0.0486	0.0369
wR_2	0.0853	0.1239	0.1368	0.1024
Temperature	200	200	200	200



[$Cu_2(OH)_3(HCO_2)$], Botallackite-Type

[$Cu_2(OH)_3(CH_3C_6H_4SO_3)$], **1**

Fig. 1 Crystal structure of **1**. The hydrogen atoms of hydroxide ions are omitted. Spheres correspond to Cu (blue), O (red), C (dark grey), S (yellow), and H (light grey). (a) Stacking of the copper hydroxide layers and the organic anion layers. (b) Projection of the atomic arrangement of the copper hydroxide layer along the *a* axis. (c) Schematic representation of the copper hydroxide layer and the Cu–O–Cu bridges of **1** and a botallackite-type material [$Cu_2(OH)_3HCO_2$] showing the Cu–O bonds and the direction of the dz^2 orbitals of Cu(II) ions in the copper hydroxide layer. Coloured O's correspond to the oxygen atoms of p-toluene sulfonate or formate anions. The bold lines are the axial bonds. The red and magenta symbols correspond to the oxygen atoms of the aromatic ions that are located to the front and back of the copper hydroxide layer, respectively.

$CH_3CO_2^-$ as ions A.[3,19–21,25]

3.2.1 Crystal structure of 1 and 2. The copper hydroxyl salts containing *p*-toluenesulfonate and *p*-ethylbenzenesulfonate, **1** and **2**, crystalized in a monoclinic $P2_1/c$ space group with the formulae [$Cu_2(OH)_3(p\text{-}CH_3C_6H_4SO_3)$] and [$Cu_2(OH)_3(p\text{-}CH_3CH_2C_6H_4SO_3)$], respectively. One copper atom, two of half copper atoms, three hydroxide groups and one corresponding organic anion, were crystallographically asymmetric. Compounds **1** and **2** have the same features in their crystal structures (Figure S1); however, **2** has a larger interlayer distance than **1**, which is related to the molecular length of the organic ion. Figure 1 shows the crystal structure of **1**. The structural features and composition of **1** resemble those of the botallackite-type materials. The copper hydroxide units in **1** form a sheet in the *bc* plane and stack along the *a* axis, as shown in Fig. 1(a), and the copper hydroxide layers are magnetically isolated by the *p*-toluenesulfonate ion layers. *p*-Toluenesulfonate ions tilt toward the copper hydroxide layer and are aggregated as a bilayer. There are short interatomic O•••O distances between the oxygen atoms of the sulfonate groups and the hydroxide groups of the copper hydroxide layer in this material, due to formation of hydrogen bonds.[26]

Figure 1(b) shows the projection of the copper hydroxide layer in **1** along the *a* axis. The organic ions are omitted, except for the coordinated oxygen atoms. The copper hydroxide layer consists of edge-sharing CuO_6 octahedra, where the oxygen atoms are from the sulfonates or hydroxide ions. In Fig. 1(b), the red and magenta spheres represent the oxygen atoms of hydroxide and the organic sulfonate ions, respectively. As a result of Jahn-Teller distortion,[26] there exist two types of Cu–O bonds in the CuO_6 octahedra. The lengths of the axial Cu–$O_{sulfonate}$ and Cu–$O_{hydroxide}$ bonds are 2.438(3)–2.461(2) Å and 2.385(2) Å, respectively, and those of the equatorial Cu–$O_{hydroxide}$ bonds are in the range 1.942(2)–2.036(2) Å (Figure S2). These bond lengths are characteristic of the divalent copper ion. Hence, the copper ions in this material have a spin quantum number of $S = 1/2$. The copper ions are bridged by two oxygen atoms to form an $S = 1/2$ two-dimensional triangular lattice magnetic network. The Cu–O–Cu bridges are chemically non-equivalent on each edge of the triangle. The bridging angles are in the range 77.46(7)–108.85(10)° (Figure S2). The values of the bond lengths and bridging angles in the copper hydroxide layer of **2** are very close to those of **1** (Figure S3).

Figure 1(c) shows schematic representations of the copper hydroxide layers in **1** and the botallackite-type material $[Cu_2(OH)_3(HCO_2)]$,[20] and emphasizes the axial Cu–O bonds and the oxygen atoms of the aromatic ions coordinated to the copper ions for **1**, and of formate ions for the the botallackite material. The axial and equatorial Cu–O bonds in the elongated CuO_6 octahedron are represented by the bold and narrow black lines, respectively. The oxygen atoms of the organic ions coordinated to copper ions are represented by the bold red and magenta atomic symbols, which indicate the oxygen atoms that are located to the front and back of the copper hydroxide layer, respectively. All organic ions are coordinated to copper ions via the axial positions. The orientation pattern of the CuO_6 octahedra in **1** is different from that in the botallackite-type copper hydroxides, as are the positions of the oxygen atoms of the organic ions coordinated to the copper ions.

3.2.2 Crystal structure of 3. Figure 2 shows the crystal structure of the copper hydroxide compound with 1-naphthalenesulfonate (**3**), which belongs to the triclinic *P*–1 space group with a formula unit of $[Cu_4(OH)_6(CH_3CO_2)(H_2O)]\bullet(1\text{-}C_{10}H_7SO_3)\bullet 2H_2O$, which is crystallographically asymmetric. The formula is different from those of **1** and the botallackite derivatives. Compound **3** exhibits a layered structure, similar to **1**, as shown in Fig. 2(a). Compound **3** contains two kinds of organic ions: acetate and 1-naphthalenesulfonate. The organic sulfonate ions do not coordinate to copper ions, but are positioned between the copper hydroxide layers together with water molecules, and compensate the positive charge of the copper hydroxide layers. The organic sulfonate ions form an interdigitated monolayer with a head-to-tail molecular alignment, in contrast to the bilayer aggregates in the organic ion layer of **1**.

In the copper hydroxide layers, acetate ions and water molecules, in addition to hydroxide ions, coordinate to copper ions. The Cu–O bond lengths are in the range 1.934(4)–2.606(3) Å (Figure S4). The oxygen atoms marked by arrows in Fig. 2(a) form long axial Cu–O bonds , i.e., lengths of 2.560(4) Å and 2.606(3) Å for Cu4–O10 and Cu5–O10. These bonds are longer than the axial Cu–$O_{hydroxide}$ bonds in **1** (2.385(2) Å). The oxygen atoms by the arrows belong to water molecules. The coordinated water molecules and hydroxide ions are distinguishable, because the axial Cu–O_{water} bond lengths are longer than the Cu–$O_{hydroxide}$ bond lengths.[26] There are many short interatomic O•••O distances (2.683(3)–2.897(6) Å) due to the

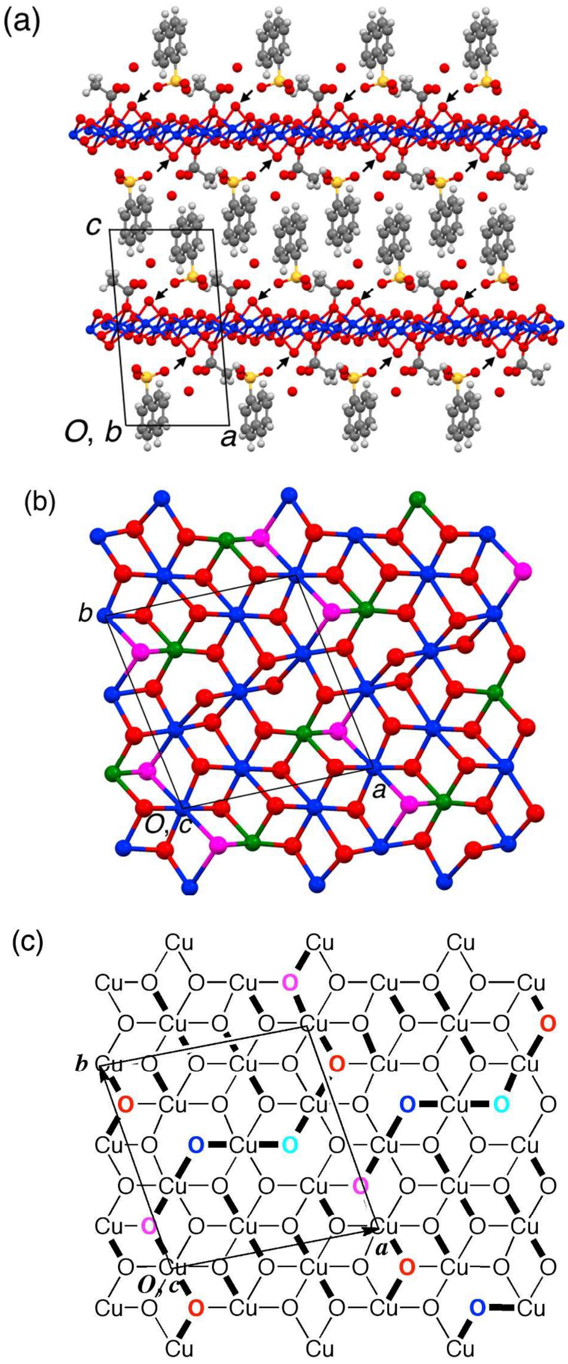


Fig. 2 Crystal structure of **3**. The hydrogen atoms of hydroxide ions and water molecules are omitted. Spheres correspond to Cu (blue, green), O (red), C (dark grey), S (yellow), and H (light grey). (a) Stacking of the copper hydroxide layers and the organic anion layers. (b) Projection of the atomic arrangement of the copper hydroxide layer along the *c* axis. (c) Schematic representation of the copper hydroxide layer and the Cu–O–Cu bridges of **3**, showing the Cu–O bonds and the direction of the dz^2 orbitals of Cu(II) ions in the copper hydroxide layer. Coloured O's correspond to the oxygen atoms of p-toluene sulfonate or formate anions. The bold lines are the axial bonds. The red and magenta highlights correspond to the oxygen atoms of acetate ions which are located on the front and back of the copper hydroxide layer, respectively. The blue and light blue highlights correspond to the oxygen atoms of water molecules that are located on the front and back of the copper hydroxide layer, respectively.

formation of hydrogen bonds,[27] such as those between the organic ions and the water molecules in the interlayer and so on (Figure S5).

Figure 2(b) shows a projection of the copper hydroxide layer in **3** along the *c* axis. The inoganic layer consists of edge-sharing CuO_6 octahedra (Cu_1: blue spheres) and CuO_5 square pyramids (Cu_2: green spheres), where the oxygen atoms are from hydroxide ions, water molecules, or acetate ions. The copper ions are bridged by one or two oxygen atoms and also form an S = 1/2 two-dimensional triangular magnetic lattice network due to superexchange interaction via bridging oxygen atoms, as in the case of **1**. The Cu–O–Cu bridging angles are in the range 72.81(6)–111.60(19)° (Figure S4). Figure 2(c) shows a schematic presentation of the copper hydroxide layer in **3**. The coordination positions of acetate anions or water molecules, and the orientation pattern of the octahedral or the square pyramids differ from those of **1**, **2**, and the botallackite-type compounds.

3.2.3 Crystal structure of 4. Figure 3 shows the crystal structure of the copper hydroxides containing the organic sulfonate ion, 1,5-naphthalenedisulfonate (**4**), which belongs to the triclinic *P*–1 space group, with the unit formula $[Cu_5(OH)_8(H_2O)_2]$•(1,5-$C_{10}H_6(SO_3)_2$)•$4H_2O$, and is crystallographically asymmetric. Compound **4** also has a layered structure, as shown in Fig. 3(a). The aromatic ions form a monolayer with water molecules between the copper hydroxide layers. The copper hydroxide layer consists of copper ions, hydroxide ions, and water molecules. The Cu–O coordination bond lengths are in the range 1.927(2)–2.624(2) Å, and the Cu–O–Cu bridging angles are in the range 75.01(5)–107.99(11)° (Figure S6). The water molecules coordinated to the copper ions are marked by arrows, as estimated from the characteristic Cu–O bond lengths of 2.578(2) and 2.624(2) Å for Cu1–O8 and Cu2–O8 discussed above. In addition, there are many hydrogen bonds in **4**. The organic sulfonate ions located close to the water molecules coordinating to the copper ions via short interatomic O•••O interactions of 2.842(2) and 2.891(3) Å for O3•••O8 and O1•••O8. The water molecules in the interlayers form a one-dimensional zigzag alignment via hydrogen bonds of short interatomic O•••O distances, 2.873(3) and 2.981(3) Å for O9•••O10, along the *a* axis (Figure 7).

Figure 3(b) shows the projection of the copper hydroxide layer in **4** along the *c* axis. In the copper hydroxide layer, copper ions are bridged by one or two oxygen atoms, and an S = 1/2 two-dimensional triangular lattice magnetic network is also formed, similarly to those seen in the other layered copper hydroxides. The copper hydroxide layer consists of edge-sharing CuO_6 octahedra (Cu_1; blue) and CuO_5 square pyramids (Cu_2; green), where the oxygen atoms are from hydroxide ions or water molecules. Compound **4** also has a distorted triangular lattice, and it differs from **3** in the orientations along the axial directions and ratio of the octahedra and pyramids. Figure 3(c) shows a schematic representation of the copper hydroxide layer in **4**. The water molecules, expressed by blue and light blue atomic symbols, bind the two copper ions via their axial positions. The local structure of **4** is different from those of the other layered copper hydroxides.

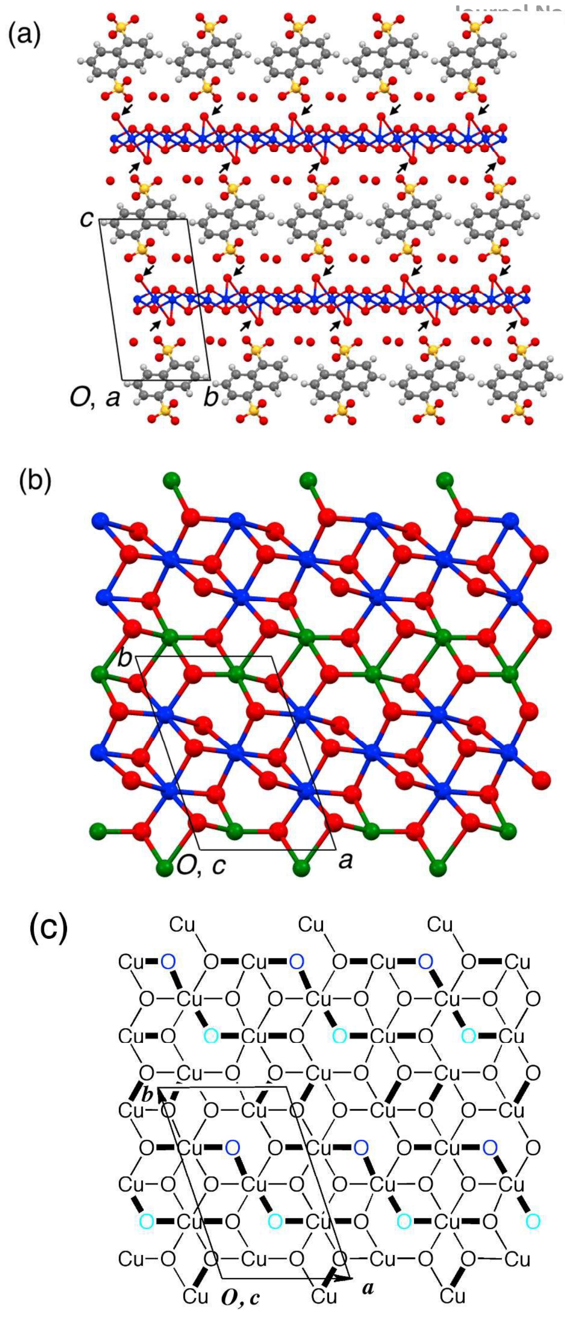


Fig. 3 Crystal structure of **4**. The hydrogen atoms of hydroxide ions and water molecules are omitted. Spheres correspond to Cu (blue, green), O (red), C (dark grey), S (yellow), and H (light grey). (a) Stacking of the copper hydroxide layers and the organic anion layers. (b) Projection of the arrangement of the copper hydroxide layer along the *c* axis. (c) Schematic representation of the copper hydroxide layer and the Cu–O–Cu bridges of **4** showing the Cu–O bonds and the direction of the dz^2 orbitals of Cu(II) ions in the copper hydroxide layer. Coloured O's correspond to the oxygen atoms of p-toluene sulfonate or formate anions. The bold lines are the axial bonds. The blue and light blue symbols correspond to the oxygen atoms of water molecules that are located to the front and back of the copper hydroxide layer, respectively.

3.2.4. Consideration of the crystal structures. Compounds **1**–**4** are composed of alternating stacks of a copper hydroxide layer comprising a two-dimensional triangular lattice alignment of copper ions bridged by oxygen atoms of hydroxide, acetate, the organic sulfonate ions and/or water molecules, and an aggregating layer of the aromatic ions. However, the local structures of the copper hydroxide layers and the molecular orientations of the aromatic ions are slightly different in each material, as revealed by the structural analyses. The copper hydroxide layers in previously reported layered copper hydroxides, typically botallackite materials, are composed of edge-sharing Cu–O octahedra. The copper hydroxide layers in **1** and **2** are also composed of edge-sharing Cu–O octahedra. However, **3** and **4** contain octahedra and square pyramids. Also, the orientation and the ratio of the octahedra and the square pyramids in the copper hydroxide layers are different in **1** (or **2**), **3**, and **4**. These structural differences in these materials are discussed in this section.

In **1** and **2**, the organic sulfonate ions directly coordinate to the copper ions in the copper hydroxide layers via oxygen atoms. However, the coordination positions of the organic sulfonate ions in **1** and **2** are different from those in the botallackite-type materials, as shown in Fig. 1(c). Figure 4 shows the molecular arrangements of acetate and *p*-toluenesulfonate ions in the botallackite-type material $[Cu_2(OH)_3(CH_3CO_2)]•H_2O$[19] and **1**, respectively. The atoms of the copper hydroxide layer are omitted. Figure 4(a) shows the molecular arrangement of acetate ions in $[Cu_2(OH)_3(CH_3CO_2)]•H_2O$ along the *c* axis. The magenta spheres represent the oxygen atoms of the acetate ions coordinated to the copper atoms. The grey acetate ions are coordinated to the neighbouring copper hydroxide layer. The acetate ions form an interdigitated molecular arrangement. This molecular arrangement becomes possible because the molecular size of the acetate ion is smaller than the distance between the coordination positions. In **1**, *p*-toluenesulfonate ions do not form an interdigitated arrangement, but instead form a bilayer arrangement, as shown in Fig. 1(b), because a *p*-toluenesulfonate ion is sterically bulkier than an acetate ion. Figure 4(b) shows the molecular arrangement of *p*-toluenesulfonate ions coordinated to the copper hydroxide layer in **1** along the *a* axis. The positions of the magenta spheres, that is, the coordination sites in **1** are different from those in the botallackite material because of differences in the molecular shape and molecular packing in the organic assemble layers. As shown in Fig. 1(c), these organic ions coordinate to the axial position of the copper ions. Therefore, in these materials, the molecular shape and molecular arrangement of the organic ions affect their coordination sites, that is, the orientation of the elongated octahedra in the copper hydroxide layer.

In **3** and **4**, the organic sulfonate ions do not coordinate to the copper ions, as shown in Figs. 2 and 3. The large size of the organic sulfonate ions with a naphthalene ring prevents to coordinate them to the copper ions due to their steric hindrance. Instead, water molecules and acetate ions in **3**, and water molecules in **4**, bind to the coordination sites. The water molecule coordinates to two copper ions, while the hydroxide or acetate ions coordinate to three copper ions. This is the reason why there exist square pyramids adjacent to the water molecules coordinated to the copper ions in **3** and **4**.

3.3 Magnetic properties

Figure 5 shows the magnetic behaviour of **1**–**4**. The molar units of the paramagnetic susceptibility (χ_p) and the magnetization (M) correspond to one mole of Cu(II). Figure 5(a) shows the temperature dependence of χ_p for **1**–**4**. The χ_p value of **4** is much smaller than those of **1**–**3**, as shown in the inset of Fig. 5(a). The χ_p values of these materials increase with decreasing temperature, and reach maxima at 3.8 K, 3.5 K, 3.2 K, and 9.1 K for **1**–**4**, respectively. Their maximum values of χ_p are 0.0387 emu mol^{-1}, 0.0502 emu mol^{-1}, 0.01744 emu mol^{-1}, and 0.00539 emu mol^{-1}, respectively. The temperature dependence of χ_p in **1**–**3** is characteristic of antiferromagnetic ordering. However, the χ_p value of **4** at low temperatures remains almost constant from the maximum temperature below 10 K, compared with those of **1**–**3**. This trend resembles the magnetic behaviour of the single component organic conductor, κ-H_3(Cat-EDT-TTF)$_2$, which has an S = 1/2 triangular lattice and a quantum spin liquid state.[28]

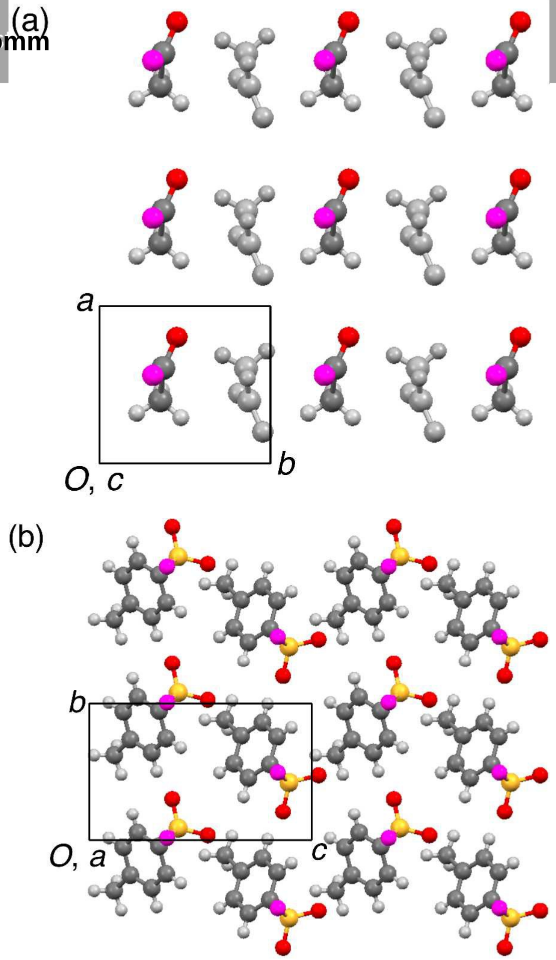


Fig. 4 Molecular alignment of the organic anions between the copper hydroxide layers. Spheres correspond to O (red, magenta), C (dark grey), S (yellow) and H (light grey). (a) Acetate ions in the botallackite-type material $[Cu_2(OH)_3(CH_3CO_2)]•H_2O$, where the gray acetate ions are coordinating to the neighboring copper hydroxide layer. (b) *p*-toluenesulfonate ions in **1**.

Some layered copper hydroxides with ions A show antiferromagnetic phase transitions at 7.2 K (A = Cl),[29] 9.2 K (A = Br),[30] 16.0 K (A = I),[30] 7 K (A = NO_3),[31] 5.4 K (A = HCO_2),[20] 2.6 K (A = CH_3CO_2),[11] and 3 K (A = $CH_3CH_2CO_2$).[21] The differences between the magnetic properties of the previously reported materials and **1**–**4** may indicate differences in the structures of their copper hydroxide layers, or in the intensity of the magnetic interlayer interactions. As shown in the inset of Fig. 5(a), the χ_p values of **3** and **4** exhibit shoulders around 40 K and 60 K, presumably as a result of short-range magnetic ordering. This behaviour is similar to the magnetic properties of the layered copper hydroxide (A = $CH_3CH_2CO_2$).[21]

Figure 5(b) shows the temperature dependence of the product of χ_p and T in **1**–**4**, where the χ_pT value decreases with decreasing temperature. This suggests that there are dominant antiferromagnetic interactions in the copper hydroxide layers of these materials. The Curie and Weiss constants[32] evaluated using the data for $T > 150$ K are 0.446 emu K mol^{-1} and –17.6 K for **1**, 0.439 emu K mol^{-1} and –

14.0 K for **2**, 0.443 emu K mol^{-1} and –31.7 K for **3**, and 0.447 emu K mol^{-1} and –38.6 K for **4**. Furthermore, the temperature dependences of χ_pT were fitted to the high-temperature series expansion of an $S = 1/2$ Heisenberg model with a two-dimensional triangular lattice model, employing the Padé approximants adopted by Tamura *et al.*[33] When the spin Hamiltonian in zero field adopted to describe the isotropic exchange interaction J between the neighbouring sites i and $i + 1$ is expressed by eq. 1,

$$H = J\sum_i S_i \bullet S_{i+1} \quad (J > 0) \qquad (1),$$

the theoretical χ_pT value can be further modified as follows,

$$\chi_pT = C\frac{1 + a_1x + \cdots + a_6x^6}{1 + b_1x + \cdots + b_7x^7} \qquad (2)$$

where C is the Curie constant, $x = J/(4k_BT)$, and J is defined as being positive (negative) for antiferromagnetic (ferromagnetic) interactions.

The values of the coefficients a_n and b_n are as follows: a_1 = 13.1382922, a_2 = 38.2639722, a_3 = 214.74454, a_4 = 260.983171, a_5 = 622.734802, a_6 = 186.114208, and b_1 = 19.1382922, b_2 = 38.2639722, b_3 = 597.98788, b_4 = 1902.06491, b_5 = 3943.84464, b_6 = 5164.9974, and b_7 = 3452.67229. On the basis of equation 2, the magnetic parameters J/k_B are 42.2 K, 36.8 K, 80.1 K, and 84.9 K for **1**–**4**, respectively, as estimated by curve fitting using T > 150 K, as shown in Fig. 4(b). Here, the J value obtained in this study may be regarded as an average value, because these magnetic networks are composed of distorted triangular lattices, and it is difficult to estimate individual magnetic exchange coupling constants by means of static magnetic measurements.

Figure 5(c) depicts the field dependence of the magnetization of **1**–**4** at 2 K, where the magnetizations gradually increase with increasing magnetic field strength. In **1**–**3**, the magnetizations increase rapidly around 1 T and then increase gradually at higher magnetic field. Compound **4** exhibits an almost linear increase in magnetization, and no magnetic anomaly is observed below 7 T. Compounds **1**–**3** show spin-flop like behaviour, implying an antiferromagnetic-to-ferromagnetic phase transition. This behaviour resembles that of metamagnets. The magnetization values are 2,365, 2,288, and 957 erg Oe^{-1} mol^{-1} for **1**–**3** at 7 T, respectively. These values are smaller than the theoretical value 6,060 erg Oe^{-1} mol^{-1} for the ferromagnetic ordered state with 1 mole of S = 1/2 and g = 2.17 spin.[32] Thus, the magnetic behaviour of **1**–**3** cannot be explained as simple metamagnetism. In past studies, the botallackite-type layered copper hydroxides $[Cu_2(OH)_3(HCO_2)]$ and $[Cu_2(OH)_3(CH_3CO_2)]{\bullet}H_2O$ were reported to show metamagnetic-like behaviour with one half of the theoretical saturation magnetization value.[20,34] This magnetization behaviour may be related to the magnetization plateau that appears in spin-frustrated systems with two-dimensional triangular magnetic lattices.[8,35] In order to evaluate these magnetic behaviours, it is necessary to fully characterize these materials by heat capacity measurements, magnetization measurements under high magnetic field, neutron diffraction, and so on.

Although **1**–**4** have triangular lattice magnetic networks, they exhibit different magnetic behaviours because of differences in the crystal structures. In general, the sign and intensity of the superexchange interaction in an array such as $M^{n+}–O^{2-}–M^{n+}$ in metal oxide materials are dependent on the relative orientation of the magnetic orbitals.[7] The copper hydroxide material also has similar superexchange pathways. In **1**, **3**, and **4**, the equatorial planes of the octahedra or square pyramids are shown by narrow lines in Figs. 1–3(c), which indicate the direction of the $dx^2–y^2$ orbital, that is, the magnetic orbitals of the copper ion. These materials exhibit different

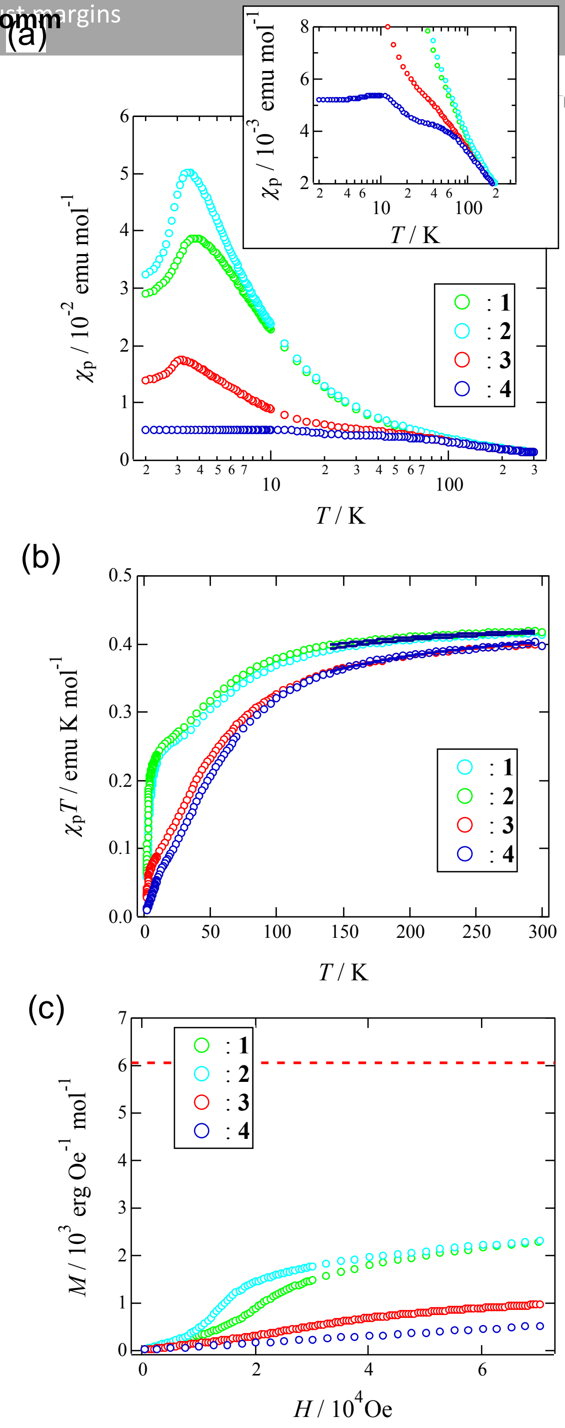


Fig. 5 Magnetic properties of **1–4**. (a) Temperature dependence of the paramagnetic susceptibility χ_p for non-oriented microcrystals under 500 Oe. (Inset) the magnified χ_p vs T plot of **4**. (b) The χ_pT vs T plot for non-oriented microcrystals. The solid curves indicate the theoretical best fits of Eq. (2). (c) Field dependence of the magnetization for non-oriented microcrystals of **1–4** at 2 K. The red broken line indicates the theoretical value of the saturation magnetization for S = 1/2 and g = 2.17.

orientation patterns in the magnetic orbitals between neighbouring copper ions. For this reason, **1**, **3**, and **4** exhibit different magnetic coupling constants.

4. Conclusion

Single crystals of novel layered copper hydroxides **1**–**4** with the organic sulfonate anions, *p*-toluenesulfonate, *p*-ethylbenzenesufonate, 1-naphthalenesulfonate, and 1,5-naphthalenedisulfonate, were successfully synthesized using a method based on the hydrolysis of acetate, and their structures were precisely determined by single-crystal X-ray structural analyses. They had a two-dimensional distorted triangular lattice magnetic network with $S = ½$, but their structures were different from that of the botallackite-type layered copper hydroxides. And they exhibit predominantly antiferromagnetic interactions with different magnetic coupling constants between neighbouring copper ions, and antiferromagnetic ordering behaviours at low temperatures. The magnetic differences in these materials originated from differences in the local structures of their copper hydroxide layers. Copper hydroxide derivatives with organic anions may give rise to novel phenomena involving quantum mechanical effects.

Many of the fine details of the structures of layered metal hydroxides with organic ions, such as bond lengths and bridging angles in the copper hydroxide layers, coordination environment of the metal cations, and arrangement of organic ions and water molecules between the copper hydroxide layers, are not fully understood. The hydrolysis method may provide a new way for the structural study of metal hydroxide materials.[36] Application of the hydrolysis method to the preparation of copper hydroxides with various organic ions and other metal hydroxide derivatives is currently in progress.

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Single crystals of layered copper hydroxides containing some organic sulfonate anions were obtained by hydrolysis of acetate. Crystal structure determination and magnetic measurements of them were carried out.