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Article

$CdCu_3(OH)_6(NO_3)_2$: An $S = {}^1/_2$ Kagomé Antiferromagnet

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The cadmium copper hydroxide nitrate, $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$, is furnished from oxygenated suspensions of Cu_2O in aqueous $Cd(NO_3)_2$. The compound possesses the kagomé structural motif and shows no evidence of magnetic ordering to temperatures as low as 5 K, despite exhibiting a Curie−Weiss temperature of $\Theta = -114 \pm 27$ K, thus giving a spin frustration parameter, $f = 22.8$.

Introduction

A quantum spin liquid results from the annihilation of antiferromagnetic order by quantum fluctuations in dimensions greater than one. Such a spin liquid represents a fundamentally new state of matter[1,2] that has been postulated to be responsible for the formation of the Cooper pairs of a superconductor.[3] The theory of spin liquids has developed in the absence of an experimental framework[4] owing to a paucity of inorganic materials that are capable of achieving a spin liquid ground state. With the exception of one-dimensional spin chains, geometrical frustration and low spin numbers (such as $S = {}^1/_2$) are believed to be needed to defeat antiferromagnetic ordering and enable a quantum spin liquid to be manifested.[5,6] Accordingly, an antiferromagnetic kagomé lattice is an exceptionally promising candidate for the spin liquid because the corner-sharing triangular network enforces one of the most highly frustrated networks in two dimensions.[4,6−14] Indeed, a kagomé lattice possessing Cu^{2+} as the magnetic center[15] exhibits no magnetic ordering down to 50 mK[16−19] and no observable spin gap down to 0.1 meV[16] despite a Curie−Weiss temperature of −314 K. These observations have provided an imperative for the synthesis of kagomé lattices of high purity[20,21] and especially kagomé lattices with Cu^{2+} as the magnetic center.[15,22,23] For this reason, we were intrigued by the magnetic properties of the cadmium copper hydroxide nitrate, $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$. Whereas a crystal structure of the material shows it to be composed 2-D kagomé layers, a rational synthesis of a pure material does not exist. The only known reported synthesis of $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$ ($x = 0.5-3$) occurs over several years.[24] We now report a streamlined procedure for the synthesis of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$. Magnetic measurements reveal that $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ is appreciably spin frustrated. No magnetic ordering for $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ is observed to 5 K, despite the observation of a Curie−Weiss temperature of $\Theta = -114 \pm 27$ K.

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Experimental Section

General Procedures. Water was distilled and deionized with a Milli-Q filtering system. The reagents CuO (Strem Chemicals, 99.999+%), $Cu(NO_3)_2 \cdot 2.5H_2O$ (Aldrich, 99.99+%), NaOH (Mallinckrodt, 98+%), Cu_2O (Strem Chemicals, 99.9%); $Cd(NO_3)_2 \cdot 4H_2O$ (Strem Chemicals, 98%), and O_2 (Airgas) were obtained from commercial vendors and used without further purification. Elemental analysis was performed by H. Kolbe Mikroanalytisches Laboratorium.

Synthesis of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$. A 250 mL Schlenk flask was charged with 3.53 g (24.7 mmol) of Cu_2O, 15.45 g (50.1 mmol) of $Cd(NO_3)_2 \cdot 4H_2O$, and 12.5 mL of water. A rubber septum was used to seal the flask, and oxygen was introduced into the flask to saturate the cadmium nitrate solution and fill the headspace above the reaction slurry. The flask was quickly sealed with a greased glass stopper and Keck clip. Over the course of 2 months, the stirred suspension gradually changed color from red to purple. To ensure the presence of adequate oxygen for the oxidation during this time the headspace of the slurry was charged with oxygen on occasion. Over the next 5 months, the reaction slurry turned color from purple to pale green; the pale green solid was collected by vacuum filtration. The solid was rinsed with three 15 mL aliquots of water and left on the Büchner funnel to dry overnight under suction. The pale green product was collected (8.17 g). Elemental analysis by ICP and pXRD indicated the presence of unreacted Cu_2O along with the desired $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$ product (matching both PDF # 01-072-1433 for the $P\bar{1}$ structure and 01-070-1904 for the $P\bar{3}m1$ structure). The 8.17 g of pale green solid was placed in a 250 mL Schlenk flask, which was recharged with 15.45 g (50.09 mmol) of $Cd(NO_3)_2 \cdot 4H_2O$ and 12.5 mL of water. Oxygen was introduced to saturate the solution and fill the headspace above the slurry. Over the course of an additional 3 months, the solution turned pale green to pale blue. At the end of this time period, the pale blue powdered product was again vacuum filtered, rinsed with three 15 mL aliquots of H_2O, collected by filtration, and dried to yield 8.13 g (90% based on starting Cu) of pale blue solid. The total reaction time was 42 weeks (322 days). Anal. Calcd for $Cu_3CdH_8O_{13}N_2$ ($CdCu_3(OH)_6(NO_3)_2 \cdot H_2O$): Cu, 34.84; Cd, 20.55; H, 1.47; N, 5.12. Found: Cu, 34.71; Cd, 20.48; H, 1.45; N, 5.15.

Thermogravimetric analysis (TGA) of the product shows loss of 1.64% by mass (or $\sim$0.5H_2O per formula unit) to 226 °C, followed by a loss of an additional 10.08% ($\sim$3H_2O) and 20.07% by mass at 240 and 500 °C, respectively. The residue is 69.09% of the original mass, and pXRD shows it to contain CuO (PDF # 01-080-0076, also known as tenorite) and CdO (PDF # 03-065-2908, also known as monteponite, 01-073-2245).

Synthesis of $Cu_2(OH)_3NO_3$. The procedure of Tanaka and Terada[25] was modified by placing 4.67 g of $Cu(NO_3)_2 \cdot 2.5\,H_2O$ (20.1 mmol) in 200 mL of water. To a separate 100 mL solution of water was added 1.14 g (28.5 mmol) of NaOH. The two solutions were mixed with stirring to afford a blue-green precipitate. The reaction mixture was allowed to sit for 1 day prior to vacuum filtration and drying. The product, rouaite, was obtained in 75% yield (1.80 g). The identity of the product was determined by pXRD (PDF # 04-010-3058 for rouaite).

Physical Methods. Powder X-ray diffraction patterns were measured using a Rigaku RU300 rotating anode X-ray diffractometer with Cu Kα radiation (λ = 1.5405 Å), which was wavelength-selected with a single-crystal graphite monochromator. Samples were spread onto a glass slide fixed with double-sided Scotch tape. Samples were rotated through $2\theta/\theta$ space and intensity was recorded as a function of 2θ from 10 to 60°. Patterns were indexed with MDI Jade software version 8.0 and referenced using the JCPDS powder diffraction database.

Direct current (DC) magnetic susceptibility data were collected on (ground-up) crystalline samples contained in gelatin capsules using Quantum Design MPMS-5S and MPMS-XL SQUID magnetometers at temperatures ranging from 1.8 to 350 K and field strengths varying from −50 to 50 kOe. The data were corrected for diamagnetic contributions of the sample holder by measurement of an empty capsule, and of the sample itself by use of Pascal's constants.

Infrared spectra of samples in KBr pellets were recorded on a Nicolet Magna-IR 860 spectrometer equipped with a KBr beam splitter and a DTGS detector. Raman spectra were recorded using a Kaiser Hololab 5000R Raman Spectrometer and Microprobe using an excitation wavelength of 785 nm, large fibers, 10× objective, 8 min exposure, 1 accumulation, and 3 mW laser power. Diffuse reflectance UV−vis spectra were recorded using a Varian Cary 5E with a Harrick Praying Mantis Accessory. An aluminum mirror was used as the 100% reflectance standard. FTIR, Raman, and diffuse reflectance UV−vis spectra are presented in the Supporting Information. Thermogravimetric analysis measurements were performed using a Seiko Dual TG/DTA 320 Thermogravimetric/Differential Thermal Analyzer (SC). Samples were referenced and measured in aluminum pans, with N_2 as a purge gas flowing at 150 cc/min. Data were recorded at 0.2 s increments from 20 to 500 °C at a 5 °C/min heating rate.

Results

The initial crystals of $CdCu_3(OH)_6(NO_3)_2 \cdot H_2O$ were observed after 15 years as the product of oxidation by atmospheric oxygen of a copper metal sheet in a saturated solution of aqueous cadmium nitrate. One strategy employed by Oswald to reproduce this product in a shorter time frame used CuO as the Cu^{2+} source. The kinetics of the reaction were not reported, but it presumably took place over several years.[24] We revisited the chemistry to examine its reaction times of formation. After 588 days, reactions of CuO (50.0 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (50.0 mmol) in aqueous solution indicated significant amounts of unreacted CuO together with the desired product, of $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$, as determined by pXRD. We suspect that the product forms according to the reaction,

$$3CuO + Cd(NO_3)_2 + 4H_2O \rightarrow CdCu_3(OH)_6(NO_3)_2 \cdot H_2O \quad (1)$$

Attempts to hydrothermally (T = 180−240 °C) accelerate this reaction were unsuccessful. The use of $Cu(OH)_2$ and aqueous $Cd(NO_3)_2$ as precursors both with and without added HNO_3 resulted in product mixtures of CuO and $Cu_2(OH)_3NO_3$, rouaite (PDF # 04-010-3058),[26,27] a monoclinic dimorph of the orthorhombic mineral gerhardtite.[28−31] Aqueous suspensions of CuO and $Cd(NO_3)$, with and without added HNO_3, resulted in no apparent reaction after several days. Other copper starting materials, such as malachite, ($Cu_2(OH)_2CO_3$), and $Cd(NO_3)_2$ in the presence and

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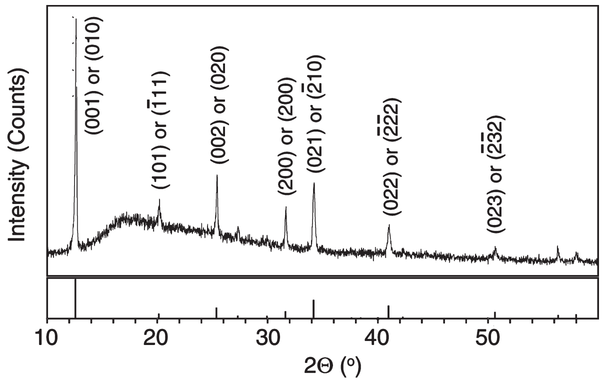

Figure 1. pXRD of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ as synthesized, matching patterns 01-072-1433 ($P\bar{3}m1$ structure) and 01-070-1904 ($P\bar{1}$ structure) in Jade 8. Miller indices are labeled for both space groups.

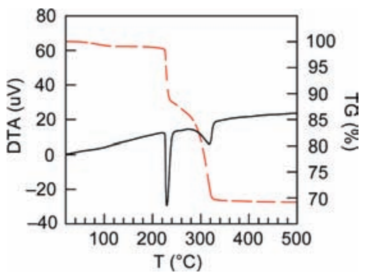

Figure 2. Thermogravimetric (red dashed line) and differential thermal analysis (black solid line) for a powder sample of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$.

absence of HNO_3 yielded product mixtures of CuO and rouaite. At the lowest temperatures (130 °C) and pHs studied, these reactions yielded exclusively rouaite after 3−4 d. Attempts to precipitate $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$ from a basic aqueous solution of $Cu(NO_3)_2$and $Cd(NO_3)_2$ at room temperature and reaction of Cu metal with aqueous solutions of $Cd(NO_3)_2$ with added HNO_3 at room temperature yielded rouaite. We examined the possibility that rouaite may be formed as a precursor to the eventual production of $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$. However, no reaction of rouaite was observed with different cadmium sources ($Cd(NO_3)_2$, $Cd(OH)_2$) both with and without added HNO_3, under all hydrothermal conditions attempted. From this multitude of experiments, we concluded that the $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$ compound is likely to be a metastable phase and unstable at hydrothermal temperatures.

An intriguing observation suggested to us that the copper synthon should be introduced by a redox reaction. A microscopic blue powder overlaid a red corrosion film of Cu_2O on a sheet of Cu metal submerged in a saturated solution of aqueous $Cd(NO_3)_2$ after 452 days. Having made this observation, we employed Cu_2O as a synthon. $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ is produced by the gradual oxidation of Cu_2O over 42 weeks under an O_2 atmosphere in 4 M aqueous solution of $Cd(NO_3)_2$ (pXRD, Figure 1). The thermogravimetric trace of the powder sample shown in Figure 2 is accounted for by the loss of ~$0.5H_2O$ over the range of 47−226 °C followed by the decomposition of six hydroxyls to $3H_2O$ by 240 °C. Volatile oxides of nitrogen are subsequently lost, eventually leaving non-volatile oxides, which match the pXRD of CuO (tenorite, PDF # 01-080-0076) and CdO (PDF # 03-065-2908, monteponite, 01-073-2245).

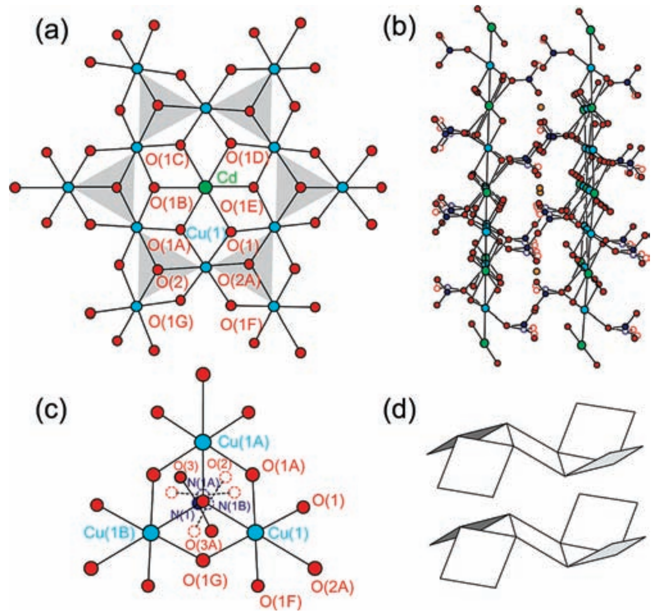

Figure 3. Crystal structure of the $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$ produced from Cu_2O: (a) The kagomé layer of $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$. H atoms and NO_2 (from $O-NO_2^-$ groups) have been omitted. (b) View of the structure down the (100) axis in $P\bar{3}m1$: d_{001} 7.012 Å. H-bonding occurs between the nitrate groups and the protons of $O(H_2O)$, the crystallographically located water molecule, to hold the layers together. (c) The basic magnetostructural unit of the kagomé is the triangle. 120° disorder of the nitrate group is shown. Selected bond angles: Cu(1)−O(2)−Cu(1A), 84.5°; Cu(1)−O(2)−N(1), 133.4°; Cu(1)−O(2)−N(1A)/N(1B), 119.7°. Cu atoms are in teal, N in blue, Cd in green, O in red, with the exception of OW, in orange. (d) Stacking of adjacent layers in $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$ where the $Cu(OH)_4$ planes are represented by squares.

The pXRD of powder $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ as prepared (Figure 1) is consistent with the single crystal X-ray structure of the monohydrate originally reported by Oswald (Figure 3).[24] No CuO is observed in the pXRD. $CdCu_3(OH)_6(NO_3)_2 \cdot xH_2O$ crystallizes in $P\bar{1}$ with $P\bar{3}m1$ superstructure if disorder in the nitrate groups is taken into account. The structure comprises Jahn−Teller distorted octahedra of $Cu(OH)_4(NO_3)_2$, which share edges to make up a kagomé lattice of corner-sharing $Cu_3(\mu-OH)_3$ triangles (Figure 3a). The three Cu^{2+} ions of each triangle share apical nitrate oxygen atoms, and the nitrate groups of adjacent triangles alternate above and below the kagomé plane. The pendant nitrate groups (with the exception of the apical oxygen atom) are statistically disordered over three positions at 120° to one another (Figure 3c). The Cd^{2+} ion is coplanar with the Cu^{2+} ions of a given sheet and resides in the hexagonal channel of the kagomé lattice. Cd^{2+} is in an angle-distorted octahedral environment with 6 equidistant OH^- groups and O−Cd−O angles of 76.3 and 103.7°. As shown in Figure 3b, hydrogen bonding of adjacent kagomé planes occurs between nitrate groups and interlayer water molecules; the interlayer water, therefore, plays a crucial role in holding the structure together. The layers stack in AA fashion (Figure 3d), and in this structure, the $Cu(OH)_4(NO_3)_2$ octahedra are at a tilt angle of 42.3° from the kagomé plane. The distance between the kagomé planes is 7.012 Å.

The DC susceptibility plot of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$, shown in Figure 4 (top), exhibits an ordering transition at 5 K. The temperature dependence of χT

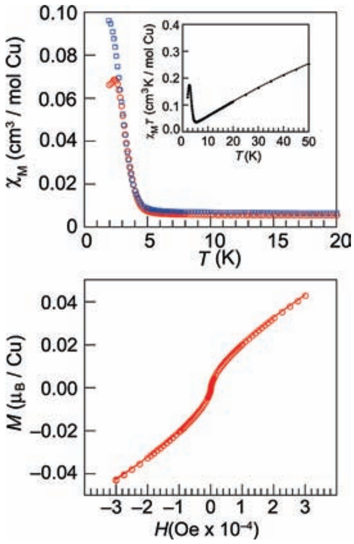

Figure 4. (a) ZFC (red open circles) and FC (blue open squares) susceptibility of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$, measured with 100 Oe field. For FC, H_C = 100 Oe; χT vs T (♦) is shown as an inset. (b) Magnetization (red open circles) versus field of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ shows no measurable hysteresis at 1.8 K.

(Figure 4, top, inset) is complicated. A decrease in χT from 300 to 5 K is indicative of a dominant antiferromagnetic interaction followed by an abrupt increase of χT between 5 and 2.9 K and a decrease in χT below 2.9 K. Magnetization versus field traces show no measurable hysteresis at 1.8 K (Figure 4, bottom), consistent with antiferromagnetic interactions dominating below 2.9 K. Curie−Weiss analysis of a linear χ^{-1} versus T plot over the temperature range of 50−300 K yielded a Curie−Weiss constant of $\Theta = -114 \pm 27$ K, revealing strong antiferromagnetic mean nearest-neighbor exchange. Alternating current (AC) susceptibility data shows no frequency-dependent temperature shift in its maximum, precluding spin-glass behavior to the low-temperature limit of the SQUID. We do observe, however, a frequency dependence of the magnitude of the susceptibility.

Discussion

The most common method of preparing kagomé lattices is by precipitation of the constituent ions. The drawback of this synthetic approach is that metastable phases are difficult to access for many kagomé lattices, which are unstable to the precipitation of simpler oxides. The kagomé lattice of $CdCu_3(OH)_6(NO_3)_2$ appears to be particularly unstable. To overcome the limitations of synthesis by precipitation, we have developed methods to slowly introduce the constituent magnetic ion of the kagomé lattice in a redox step.[32,33] In this way, the magnetic ion can be slowly introduced into the solution, and the rapid precipitation of more stable phases may be avoided. This appears to be the situation for $CdCu_3(OH)_6(NO_3)_2$. The oxidation of Cu_2O presumably proceeds according to

$$6Cu_2O + 12H_2O + 3O_2 \rightarrow 12Cu^{2+} + 24OH^- \qquad (2)$$

As Cu^{2+} forms in solution, the kagomé lattice may be furnished by

$$12Cu^{2+} + 28H_2O + 4Cd^{2+} + 8NO_3^- \rightarrow 4CdCu_3(OH)_6(NO_3)_2 \cdot H_2O + 24H^+ \qquad (3)$$

to give an overall reaction,

$$6Cu_2O + 16H_2O + 3O_2 + 4Cd^{2+} + 8NO_3^- \rightarrow 4CdCu_3(OH)_6(NO_3)_2 \cdot H_2O \qquad (4)$$

$CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ has a regular geometry of equilateral triangles shown in Figure 3a. The triangular subunit of the kagomé lattice, shown in Figure 3c, is not distorted. The Cu^{2+} ions reside of the vertices of an equilateral triangle with edges defined by d(Cu−Cu) = 3.261 Å. The confinement of an $S = {}^1/_2$ spin on the corners of these triangles gives rise to strong geometric frustration. The strong antiferromagnetic coupling, which is prerequisite for such strong spin frustration, arises from nearest-neighbor coupling via the σ-symmetry pathway defined by the Cu($d_{x^2-y^2}$)—O_H-(sp^3)— Cu($d_{x^2-y^2}$) orbital overlap. The Cu−O_H—Cu bond angle of 106.4° falls within the expected range for antiferromagnetic coupling; magnetostructural analysis of Cu(II) centers bridged by oxygen predicts that antiferromagnetic superexchange will prevail for μ-hydroxo-bridged Cu(II) centers with bridge angles larger than 97.54°.[34,35] Mean-field theory analysis,[35] assuming a nearest neighbor number per Cu(II) center is z = 4, yields a superexchange coupling constant of $J = -79 \pm 19$ cm^{-1} for $\Theta = -114 \pm 27$ K.

Spin frustration within the perfect triangular lattice is evident from the difference between the observed transition temperature, T_C, and the expected ordering temperature, given by Θ_{CW}. Because frustration inhibits the tendency for spins to order, T_C will be suppressed relative to Θ_{CW}. Ramirez has provided a measure for spin frustration by defining $f = \Theta_{CW}/T_C$, with values of $f > 10$ signifying a strong effect.[36] As is evident from the value of f = 22.8, $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ exceeds this criterion for strong spin frustration. We note that rouaite, too, bears a layered structure composed of $Cu_3(OH)_3$ triangles but their arrangement is triangular rather than a kagomé motif, and the triangles are distorted.[37] As observed previously,[38−40] roauite shows Néel ordering behavior at 11 K, and the lattice is not spin frustrated; a Curie−Weiss analysis (Supporting Information, Figure S5) yields $\Theta = -12$ K to furnish $f = |\Theta|/T_c = 1.1$.

Terms contained in the interaction Hamiltonian beyond isotropic Heisenberg exchange engender magnetic ordering at non-zero temperatures arising from weak interplanar coupling, spin anisotropy, and/or anisotropic exchange or lattice disorder. The latter ordering mechanism may be

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particularly relevant to $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ because the nitrate groups are disordered over three positions at 120° relative to one another. We do note, however, that the effect of the displacement of the nitrate group is slight because the position of the apical oxygen is unchanged thus giving rise to the same Cu−O−Cu bridge angle regardless of the disorder. Order by disorder may also arise from protonation of the intralayer hydroxide bridge by the interlayer water molecule. The crystallographically located $O(H_2O)$ atom is within 3.283 Å of the bridging hydroxyl oxygen. Because O−H bond distances typically range from 0.8−1 Å, the O···H distance of ~2.2 Å here permits the possibility of proton transfer between the interlayer water donor and the bridging hydroxyl group proton acceptor. Note that the disordered magnetic behavior in hydronium jarosite results from proton transfer from the interlayer water and intralayer bridging hydroxyl group.[21,41] In the hydronium jarosite system, the O···O distance between the interlayer hydronium ion and bridging hydroxyl moiety is roughly 2.8 Å, which is 0.6 Å shorter than that in $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$.

Spin frustration confines the localized magnetic moments composing the kagomé lattice to a 2-D plane of the array. This 2-D constraint may be lifted via the antisymmetric exchange owing to the Dzyaloshinsky−Moriya (DM) interaction,[42] which prevails if there is no inversion center between magnetic ions. In the case of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$, the inversion center between Cu^{2+} ions is abolished by the corrugation of the in-plane layers (see Figure 3d). The DM interaction can cause the spins on each $Cu^{II}{}_3(\mu{-}OH)_3$ triangle to form an umbrella structure of ferromagnetically aligned spins within each kagomé plane. If this ferromagnetic intralayer interaction is manifest, antiferromagnetic coupling can arise if the ferromagnetic moments within a plane couple antiferromagnetically between layers, thus explaining the magnetic behavior below 2.9 K.

In summary, the $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ complex adds to the growing list of $S = {}^1/_2$ kagomé lattices. The layered compound is furnished from the oxidation of Cu^+ by oxygen in the presence of Cd^{2+} in aqueous solution. The placement of antiferromagnetically coupled Cu^{2+} spins on the kagomé lattice sites of $CdCu_3(OH)_6(NO_3)_2 \cdot 0.5H_2O$ leads to a high degree of spin frustration, forcing spins into the 2-D plane of the array. A DM interaction can force spins to cant away from the geometrically frustrated 2-D plane to result in long-range ordering.

Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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