Supporting Information for

A Structurally Perfect $S = 1/2$ Kagomé Antiferromagnet

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Experimental Section	S2
Magnetic Characterization of $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$	S6
X-ray structural data for 1 , $\text{Zn}_{0.33}$ -paratacamite	S10
X-ray structural data for 1 , $\text{Zn}_{0.42}$ -paratacamite	S19
X-ray structural data for 2 , $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$	S28

Experimental Section

Preparation of Compounds. Water was distilled and deionized with a Milli-Q filtering system. All other reagents were obtained from commercial vendors and used without further purification. Hydrothermal reactions were carried out under autogenous pressure in 23 mL and 125 mL Teflon-lined pressure vessels purchased from Parr Instruments; large-scale preparations of compounds were carried out in a custom-built 800 mL vessel. Fisher Isotemp programmable ovens with forced air circulation were used to obtain the desired temperature profiles for the hydrothermal reactions.

“ $\text{Cu}_4(\text{OH})_{6.73}\text{Cl}_{1.27}$ ”, claringbullite. A 125 mL liner was charged with 2.21 g of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (10.0 mmol), 0.36 g of NaCl (6.2 mmol), 50 mL of water, and 1.0 mL of 48 % tetrafluoroboric acid (7.7 mmol), capped and placed into a steel hydrothermal bomb. The bomb was heated to 180 °C at a rate of 1 °C/min, maintained for 48 h, and cooled to room temperature at a rate of 0.1 °C/min. Blue hexagonal prismatic crystals were isolated from the liner by filtration, washed with deionized water, and dried in air to afford 1.82 g (88 %) of product. Powder X-ray diffraction (XRD) analysis of the product was consistent with that obtained for the naturally occurring mineral claringbullite (PDF 01-086-0899).

$\text{CuCu}_3(\text{OH})_6\text{Cl}_2$, clinoatacamite. A 23 mL Teflon liner was charged with 0.662 g of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (2.99 mmol), 0.426 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2.50 mmol), and 10 mL of water. The liner was capped and placed into a steel hydrothermal bomb under ambient room atmosphere. The tightened bomb was heated at a rate of 1 °C/min to 210 °C, which was maintained for 48 h. The oven was then cooled to 40 °C at a rate of 0.1 °C/min. The resulting powder was washed with deionized water and dried in air to afford 0.717 g (84 %) of product. A small amount of a dark colored phase (CuO by XRD) was also present in the sample but isolated to large flakes. The flakes were separated from the bulk powder with a #60 sieve (250 μm pore size) after weighing the entire sample. The remaining green powder gave an XRD pattern consistent with

clinoatacamite (PDF 50-1559). Anal. Calcd. for $\text{H}_6\text{Cu}_4\text{O}_6\text{Cl}_2$: H, 1.42; Cu, 59.51; Cl, 16.60 Found: H, 1.41; Cu, 59.55; Cl, 16.54.

$\text{Zn}_{0.50}\text{Cu}_{3.50}(\text{OH})_6\text{Cl}_2$, $\text{Zn}_{0.50}$ -paratacamite (1). This sample was prepared in a manner similar to clinoatacamite, syn., except that the liner was charged with 0.663 g of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (3.00 mmol), 0.204 g anhydrous ZnCl_2 (1.50 mmol), 0.170 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.00 mmol), and 10 mL of water. Yield: 0.684 g (80 %). The sieved powder gave an XRD pattern consistent with the Zn-paratacamite substructure (PDF 01-087-0679). Anal. Calcd. for $\text{H}_6\text{Cu}_{3.50}\text{Cl}_2\text{O}_6\text{Zn}_{0.50}$: H, 1.41; Cu, 51.96; Cl, 16.57; Zn, 7.64. Found: H, 1.41; Cu, 52.02; Cl, 16.45; Zn, 7.63.

$\text{Zn}_{0.66}\text{Cu}_{3.34}(\text{OH})_6\text{Cl}_2$, $\text{Zn}_{0.66}$ -paratacamite (1). This sample was prepared in a manner similar to clinoatacamite, syn., except that the liner was charged with 0.662 g of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (2.99 mmol), 0.271 g anhydrous ZnCl_2 (1.99 mmol), 0.085 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.50 mmol), and 10 mL of water. Yield: 0.762 g (89 %). The sieved powder gave an XRD pattern consistent with the Zn-paratacamite substructure (PDF 01-087-0679). Anal. Calcd. for $\text{H}_6\text{Cu}_{3.34}\text{Cl}_2\text{O}_6\text{Zn}_{0.66}$: H, 1.41; Cu, 49.55; Cl, 16.55; Zn, 10.07. Found: H, 1.38; Cu, 49.53; Cl, 16.46; Zn, 10.18.

$\text{Zn}_{0.80}\text{Cu}_{0.20}\{\text{Cu}_3(\text{OH})_6\text{Cl}_2$, $\text{Zn}_{0.80}$ -paratacamite (1). An 800 mL liner was charged with 1.00 g of claringbullite, syn. (2.4 mmol), 25.13 g of ZnCl_2 (0.18 mol) 400 mL of water, and 0.6 mL of concentrated HCl (6.0 mmol). The liner was capped and placed in a steel hydrothermal bomb under ambient room atmosphere. The tightened vessel was heated at a rate of 1 °C/min to 240 °C, which was maintained for 24 h. The oven was cooled to room temperature at a rate of 0.1 °C/min. Green triangular plate crystals and a green powder were isolated from the base of the liner by filtration, washed with deionized water and dried in air to afford 1.03 g (80 %) of product. Both the crystals and powder gave XRD patterns consistent with the Zn-paratacamite substructure (PDF 01-087-0679). The powder was separated from the crystals by sieving prior to chemical analysis. Anal. Calcd. for $\text{H}_6\text{Cu}_{3.20}\text{Cl}_2\text{O}_6\text{Zn}_{0.80}$: H, 1.41; Cu, 47.44; Cl, 16.54; F, 0.00; Zn, 12.20. Found: H, 1.25; Cu, 47.19; Cl, 16.61; F, 0.08; Zn, 11.98.

ZnCu₃(OH)₆Cl₂ (2). A 23 mL liner was charged with 0.66 g of Cu₂(OH)₂CO₃ (2.98 mmol), 0.31 g of ZnCl₂ (2.27 mmol), and 10 mL of water, capped and placed into a steel hydrothermal bomb under ambient room atmosphere. The tightened bomb was heated at a rate of 1 °C/min to 210 °C, which was maintained for 24 h. The oven was cooled to room temperature at a rate of 0.1 °C/min. A light blue powder was isolated from base of the liner by filtration, washed with deionized water, and dried in air to afford 0.80 g (94 %) of product. The powder gave an XRD pattern consistent with the Zn-paratacamite substructure (PDF 01-087-0679); no CuO was detected by XRD. Anal. Calcd. for H₆Cu₃Cl₂O₆Zn: H, 1.41; Cu, 44.44; Cl, 16.53; Zn, 15.24. Found: H, 1.42; Cu, 44.38; Cl, 16.46; Zn, 15.18.

X-ray Structure Determinations. Structures were determined for Zn_xCu_{4-x}(OH)₆Cl₂ (*x* = 0.33, 0.42, 1.00). The crystals were selected from the reaction that produced the bulk sample of Zn_{0.8}Cu_{3.2}(OH)₆Cl₂. Single crystals were coated with Paratone-N oil, attached to fibers, transferred to the diffractometer, and cooled in a dinitrogen stream. Initial lattice parameters were obtained from a least-squares analysis of at least 9 carefully centered reflections; these parameters were later refined against all data. None of the crystals showed significant decay during data collection. Data were integrated and corrected for Lorentz and polarization effects with SAINT+ 6.22 and were corrected for absorption effects with SADABS 2.03.

Space group assignments were based on systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the SHELXTL 6.10 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in the difference-Fourier map, restrained to maintain an O-H bond distance of 0.83(1) Å, and refined with isotropic thermal parameters. For all three structures reported herein, original refinements were carried out in which the Zn (interlayer) site was fully occupied by a Zn atom. Those refinements were compared with an alternative refinement strategy in which the site was occupied by a Cu/Zn mixture (adding up to full occupancy, the ratio was allowed to refine as

a free variable). The Hamilton R-factor test (ref. 11 in manuscript) indicated that there was a statistically significant preference for Cu/Zn mixture for two of the crystals ($x = 0.33$ and $x = 0.42$) but not the third. For the former structures, the Cu and Zn thermal parameters were constrained to be equal to each other.

Magnetic Measurements. DC magnetic susceptibility data were collected on (ground-up) powdered samples contained in gelatin capsules using Quantum Design MPMS-5S and MPMS-XL SQUID magnetometers at temperatures ranging from 2 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.

Other Physical Measurements. 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. Powder X-ray diffraction patterns were measured using a Rigaku RU300 rotating anode X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$), 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 5 to 60° . Patterns were indexed with MDI Jade software version 7.0 and references using the JCPDS powder diffraction database.

Figure S1. Temperature dependence of χ_M for $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ as measured under zero-field cooled conditions at 100 Oe. The lines are guides to the eye. Top: Zn occupancy on the interlayer site ranges from 0 to 100 %. Bottom: Expansion of the upper plot showing the presence of the ferromagnetic transition in $\text{Zn}_{0.66}\text{Cu}_{3.33}(\text{OH})_6\text{Cl}_2$ and its absence in samples in which all interlayer Cu(II) ions have been substituted with Zn(II).

Figure S2. Temperature dependence of χ_M for $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, (**2**), as measured under zero-field and field cooled conditions ($H_c = H_m = 100$ Oe). The lines are guides to the eye. There is almost no difference between zero-field and field cooled susceptibility, which supports the absence of spin-glass behavior.

Figure S3. Temperature dependence of χ_M^{-1} for $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ plotted from 5 to 355 K.

Figure S4. Temperature dependence of χ_M^{-1} for $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$. Values for Θ_{CW} were determined by fitting data in the temperature range $150 \leq T \leq 350$ K, except for $x = 0.8$, which was fit from 200 to 300 K. Data are labeled as in Figure S3, red lines indicate best fits obtained.

Figure S5. A portion of the crystal structure of $\text{Zn}_{0.33}\text{Cu}_{3.67}(\text{OH})_6\text{Cl}_2$. 50% ellipsoids are shown. Atoms labeled with letters correspond to symmetry equivalent atoms as found in Tables S3 and S4. Hydrogen atoms are not labeled.

Table S1. Crystal data and structure refinement for $\text{Zn}_{0.33}\text{Cu}_{3.67}(\text{OH})_6\text{Cl}_2$.

Identification code	mps3atest	
Empirical formula	$\text{H}_6\text{Cl}_2\text{Cu}_{3.67}\text{O}_6\text{Zn}_{0.33}$	
Formula weight	427.72	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral (obverse)	
Space group	$R\bar{3}m$	
Unit cell dimensions	$a = 6.8293(6)$ Å	$\alpha = 90^\circ$
	$b = 6.8293(6)$ Å	$\beta = 90^\circ$
	$c = 14.024(2)$ Å	$\gamma = 120^\circ$
Volume, Z	$566.46(12)$ Å ³	3
Density (calculated)	3.761 g/cm ³	
Absorption coefficient	11.917 mm ⁻¹	
F(000)	613	
Crystal size	$0.07 \times 0.05 \times 0.02$ mm	
θ range for data collection	3.74 to 24.70°	
Limiting indices	$-7 \leq h \leq 8$	
	$-7 \leq k \leq 7$	
	$-16 \leq l \leq 16$	
Reflections collected	1161	
Independent reflections	138 ($R_{\text{int}} = 0.0404$)	
Completeness to $\theta = 24.70^\circ$	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	138 / 1 / 20	
Goodness-of-fit on F^2	1.213	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0202$	$wR_2 = 0.0531$
R indices (all data)	$R_1 = 0.0202$	$wR_2 = 0.0531$
Largest diff. peak and hole	0.394 eÅ ⁻³	-0.776 eÅ ⁻³

Table S2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $\text{Zn}_{0.33}\text{Cu}_{3.67}(\text{OH})_6\text{Cl}_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zn(1)	0	0	0	7(1)
Cu(2)	0	0	0	7(1)
Cu(1)	3333	1667	1667	8(1)
O(1)	1267(3)	2535(6)	1054(2)	13(1)
Cl(1)	0	0	3057(1)	10(1)

Symmetry transformations used to generate equivalent atoms: ^a $-x, -y, -z$; ^b $x - y, x, -z$; ^c $-x + y, -x, z$; ^d $-y, x - y, z$; ^e $y, -x + y, -z$; ^f $x - 2/3, y - 1/3, z - 1/3$; ^g $-x + y + 1/3, -x + 2/3, z - 1/3$; ^h $-y + 1/3, x - y - 1/3, z - 1$; ⁱ $-x + 2/3, -y + 1/3, -z + 1/3$; ^j $x - y + 2/3, x + 1/3, -z + 1/3$; ^k $x + 2/3, y + 1/3, z + 1/3$.

Table S3. Bond lengths [Å] for Zn_{0.33}Cu_{3.67}(OH)₆Cl₂.

Zn(1)-O(1) ^a	2.105(3)	Cu(2)-O(1) ^d	2.105(3)
Zn(1)-O(1)	2.105(3)	Cu(2)-O(1) ^e	2.105(3)
Zn(1)-O(1) ^b	2.105(3)	Cu(2)-Cu(1)	3.0578(3)
Zn(1)-O(1) ^c	2.105(3)	Cu(2)-Cu(1) ^d	3.0578(3)
Zn(1)-O(1) ^d	2.105(3)	Cu(2)-Cu(1) ^c	3.0578(3)
Zn(1)-O(1) ^e	2.105(3)	Cu(2)-Cu(1) ^f	3.0578(3)
Zn(1)-Cu(1)	3.0578(3)	Cu(2)-Cu(1) ^g	3.0578(3)
Zn(1)-Cu(1) ^d	3.0578(3)	Cu(2)-Cu(1) ^h	3.0578(3)
Zn(1)-Cu(1) ^c	3.0578(3)	Cu(1)-O(1) ⁱ	1.9794(16)
Zn(1)-Cu(1) ^f	3.0578(3)	Cu(1)-O(1) ^c	1.9794(16)
Zn(1)-Cu(1) ^g	3.0578(3)	Cu(1)-O(1)	1.9794(16)
Zn(1)-Cu(1) ^h	3.0578(3)	Cu(1)-O(1) ^j	1.9795(16)
Cu(2)-O(1) ^a	2.105(3)	Cu(1)-Zn(1) ^k	3.0578(3)
Cu(2)-O(1)	2.105(3)	Cu(1)-Cu(2) ^k	3.0578(3)
Cu(2)-O(1) ^b	2.105(3)	O(1)-Cu(1) ^d	1.9794(16)
Cu(2)-O(1) ^c	2.105(3)		

Symmetry transformations used to generate equivalent atoms: ^a -x, -y, -z; ^b x - y, x, -z; ^c -x + y, -x, z; ^d -y, x - y, z; ^e y, -x + y, -z; ^f x - 2/3, y - 1/3, z - 1/3; ^g -x + y + 1/3, -x + 2/3, z - 1/3; ^h -y + 1/3, x - y - 1/3, z - 1; ⁱ -x + 2/3, -y + 1/3, -z + 1/3; ^j x - y + 2/3, x + 1/3, -z + 1/3; ^k x + 2/3, y + 1/3, z + 1/3.

Table S4. Bond angles [°] for Zn_{0.33}Cu_{3.67}(OH)₆Cl₂.

O(1) ^a -Zn(1)-O(1)	180.00(14)	O(1) ^b -Cu(2)-Cu(1)	140.01(4)
O(1) ^a -Zn(1)-O(1) ^b	76.17(13)	O(1) ^c -Cu(2)-Cu(1)	39.99(4)
O(1)-Zn(1)-O(1) ^b	103.83(13)	O(1) ^e -Cu(2)-Cu(1)	94.44(9)
O(1) ^a -Zn(1)-O(1) ^c	103.83(13)	O(1) ^d -Cu(2)-Cu(1)	85.56(9)
O(1)-Zn(1)-O(1) ^c	76.17(13)	O(1) ^a -Cu(2)-Cu(1) ^d	140.01(4)
O(1) ^b -Zn(1)-O(1) ^c	180.0(2)	O(1)-Cu(2)-Cu(1) ^d	39.99(4)
O(1) ^a -Zn(1)-O(1) ^e	76.17(13)	O(1) ^b -Cu(2)-Cu(1) ^d	94.44(9)
O(1)-Zn(1)-O(1) ^e	103.83(13)	O(1) ^c -Cu(2)-Cu(1) ^d	85.56(9)
O(1) ^b -Zn(1)-O(1) ^e	76.17(13)	O(1) ^e -Cu(2)-Cu(1) ^d	140.01(4)
O(1) ^c -Zn(1)-O(1) ^e	103.83(13)	O(1) ^d -Cu(2)-Cu(1) ^d	39.99(4)
O(1) ^a -Zn(1)-O(1) ^d	103.83(13)	Cu(1)-Cu(2)-Cu(1) ^d	67.884(9)
O(1)-Zn(1)-O(1) ^d	76.17(13)	O(1) ^a -Cu(2)-Cu(1) ^c	94.44(9)
O(1) ^b -Zn(1)-O(1) ^d	103.83(13)	O(1)-Cu(2)-Cu(1) ^c	85.56(9)
O(1) ^c -Zn(1)-O(1) ^d	76.17(13)	O(1) ^b -Cu(2)-Cu(1) ^c	140.01(4)
O(1) ^d -Zn(1)-O(1) ^d	180.0(3)	O(1) ^c -Cu(2)-Cu(1) ^c	39.99(4)
O(1) ^a -Zn(1)-Cu(1)	140.01(4)	O(1) ^e -Cu(2)-Cu(1) ^c	140.01(4)
O(1)-Zn(1)-Cu(1)	39.99(4)	O(1) ^d -Cu(2)-Cu(1) ^c	39.99(4)
O(1) ^b -Zn(1)-Cu(1)	140.01(4)	Cu(1)-Cu(2)-Cu(1) ^c	67.884(9)
O(1) ^c -Zn(1)-Cu(1)	39.99(4)	Cu(1) ^d -Cu(2)-Cu(1) ^c	67.884(9)
O(1) ^e -Zn(1)-Cu(1)	94.44(9)	O(1) ^a -Cu(2)-Cu(1) ^f	39.99(4)
O(1) ^d -Zn(1)-Cu(1)	85.56(9)	O(1)-Cu(2)-Cu(1) ^f	140.01(4)
O(1) ^a -Zn(1)-Cu(1) ^d	140.01(4)	O(1) ^b -Cu(2)-Cu(1) ^f	39.99(4)
O(1)-Zn(1)-Cu(1) ^d	39.99(4)	O(1) ^c -Cu(2)-Cu(1) ^f	140.01(4)
O(1) ^b -Zn(1)-Cu(1) ^d	94.44(9)	O(1) ^e -Cu(2)-Cu(1) ^f	85.56(9)
O(1) ^c -Zn(1)-Cu(1) ^d	85.56(9)	O(1) ^d -Cu(2)-Cu(1) ^f	94.44(9)
O(1) ^e -Zn(1)-Cu(1) ^d	140.01(4)	Cu(1)-Cu(2)-Cu(1) ^f	180.0
O(1) ^d -Zn(1)-Cu(1) ^d	39.99(4)	Cu(1) ^d -Cu(2)-Cu(1) ^f	112.117(9)
Cu(1)-Zn(1)-Cu(1) ^d	67.884(9)	Cu(1) ^c -Cu(2)-Cu(1) ^f	112.117(9)
O(1) ^a -Zn(1)-Cu(1) ^c	94.44(9)	O(1) ^a -Cu(2)-Cu(1) ^g	85.56(9)
O(1)-Zn(1)-Cu(1) ^c	85.56(9)	O(1)-Cu(2)-Cu(1) ^g	94.44(9)
O(1) ^b -Zn(1)-Cu(1) ^c	140.01(4)	O(1) ^b -Cu(2)-Cu(1) ^g	39.99(4)
O(1) ^c -Zn(1)-Cu(1) ^c	39.99(4)	O(1) ^c -Cu(2)-Cu(1) ^g	140.01(4)
O(1) ^e -Zn(1)-Cu(1) ^c	140.01(4)	O(1) ^e -Cu(2)-Cu(1) ^g	39.99(4)
O(1) ^d -Zn(1)-Cu(1) ^c	39.99(4)	O(1) ^e -Cu(2)-Cu(1) ^g	140.01(4)

Cu(1)-Zn(1)-Cu(1) ^c	67.884(9)	Cu(1)-Cu(2)-Cu(1) ^g	112.117(9)
Cu(1) ^d -Zn(1)-Cu(1) ^c	67.884(9)	Cu(1) ^d -Cu(2)-Cu(1) ^g	112.117(9)
O(1) ^a -Zn(1)-Cu(1) ^f	39.99(4)	Cu(1) ^c -Cu(2)-Cu(1) ^g	180.0
O(1)-Zn(1)-Cu(1) ^f	140.01(4)	Cu(1) ^f -Cu(2)-Cu(1) ^g	67.883(9)
O(1) ^b -Zn(1)-Cu(1) ^f	39.99(4)	O(1) ^a -Cu(2)-Cu(1) ^h	39.99(4)
O(1) ^c -Zn(1)-Cu(1) ^f	140.01(4)	O(1)-Cu(2)-Cu(1) ^h	140.01(4)
O(1) ^e -Zn(1)-Cu(1) ^f	85.56(9)	O(1) ^b -Cu(2)-Cu(1) ^h	85.56(9)
O(1) ^d -Zn(1)-Cu(1) ^f	94.44(9)	O(1) ^c -Cu(2)-Cu(1) ^h	94.44(9)
Cu(1)-Zn(1)-Cu(1) ^f	180.0	O(1) ^e -Cu(2)-Cu(1) ^h	39.99(4)
Cu(1) ^d -Zn(1)-Cu(1) ^f	112.117(9)	O(1) ^d -Cu(2)-Cu(1) ^h	140.01(4)
Cu(1) ^c -Zn(1)-Cu(1) ^f	112.117(9)	Cu(1)-Cu(2)-Cu(1) ^h	112.116(9)
O(1) ^a -Zn(1)-Cu(1) ^g	85.56(9)	Cu(1) ^d -Cu(2)-Cu(1) ^h	180.0
O(1)-Zn(1)-Cu(1) ^g	94.44(9)	Cu(1) ^c -Cu(2)-Cu(1) ^h	112.116(9)
O(1) ^b -Zn(1)-Cu(1) ^g	39.99(4)	Cu(1) ^f -Cu(2)-Cu(1) ^h	67.883(9)
O(1) ^c -Zn(1)-Cu(1) ^g	140.01(4)	Cu(1) ^g -Cu(2)-Cu(1) ^h	67.883(9)
O(1) ^e -Zn(1)-Cu(1) ^g	39.99(4)	O(1) ⁱ -Cu(1)-O(1) ^c	98.0(2)
O(1) ^d -Zn(1)-Cu(1) ^g	140.01(4)	O(1) ⁱ -Cu(1)-O(1)	180.0
Cu(1)-Zn(1)-Cu(1) ^g	112.117(9)	O(1) ^c -Cu(1)-O(1)	82.0(2)
Cu(1) ^d -Zn(1)-Cu(1) ^g	112.117(9)	O(1) ⁱ -Cu(1)-O(1) ^j	82.0(2)
Cu(1) ^c -Zn(1)-Cu(1) ^g	180.0	O(1) ^c -Cu(1)-O(1) ^j	180.0
Cu(1) ^f -Zn(1)-Cu(1) ^g	67.883(9)	O(1)-Cu(1)-O(1) ^j	98.0(2)
O(1) ^a -Zn(1)-Cu(1) ^h	39.99(4)	O(1) ⁱ -Cu(1)-Cu(2)	136.89(10)
O(1)-Zn(1)-Cu(1) ^h	140.01(4)	O(1) ^c -Cu(1)-Cu(2)	43.11(10)
O(1) ^b -Zn(1)-Cu(1) ^h	85.56(9)	O(1)-Cu(1)-Cu(2)	43.11(10)
O(1) ^c -Zn(1)-Cu(1) ^h	94.44(9)	O(1) ^j -Cu(1)-Cu(2)	136.89(10)
O(1) ^e -Zn(1)-Cu(1) ^h	39.99(4)	O(1) ⁱ -Cu(1)-Zn(1)	136.89(10)
O(1) ^d -Zn(1)-Cu(1) ^h	140.01(4)	O(1) ^c -Cu(1)-Zn(1)	43.11(10)
Cu(1)-Zn(1)-Cu(1) ^h	112.116(9)	O(1)-Cu(1)-Zn(1)	43.11(10)
Cu(1) ^d -Zn(1)-Cu(1) ^h	180.0	O(1) ^j -Cu(1)-Zn(1)	136.89(10)
Cu(1) ^c -Zn(1)-Cu(1) ^h	112.116(9)	Cu(2)-Cu(1)-Zn(1)	0.0
Cu(1) ^f -Zn(1)-Cu(1) ^h	67.883(9)	O(1) ⁱ -Cu(1)-Zn(1) ^k	43.11(10)
Cu(1) ^g -Zn(1)-Cu(1) ^h	67.883(9)	O(1) ^c -Cu(1)-Zn(1) ^k	136.89(10)
O(1) ^a -Cu(2)-O(1)	180.00(14)	O(1)-Cu(1)-Zn(1) ^k	136.89(10)
O(1) ^a -Cu(2)-O(1) ^b	76.17(13)	O(1) ^j -Cu(1)-Zn(1) ^k	43.11(10)
O(1)-Cu(2)-O(1) ^b	103.83(13)	Cu(2)-Cu(1)-Zn(1) ^k	180.0

O(1) ^a -Cu(2)-O(1) ^c	103.83(13)	Zn(1)-Cu(1)-Zn(1) ^k	180.0
O(1)-Cu(2)-O(1) ^c	76.17(13)	O(1) ⁱ -Cu(1)-Cu(2) ^k	43.11(10)
O(1) ^b -Cu(2)-O(1) ^c	180.0(2)	O(1) ^c -Cu(1)-Cu(2) ^k	136.89(10)
O(1) ^a -Cu(2)-O(1) ^e	76.17(13)	O(1)-Cu(1)-Cu(2) ^k	136.89(10)
O(1)-Cu(2)-O(1) ^e	103.83(13)	O(1) ^j -Cu(1)-Cu(2) ^k	43.11(10)
O(1) ^b -Cu(2)-O(1) ^e	76.17(13)	Cu(2)-Cu(1)-Cu(2) ^k	180.0
O(1) ^c -Cu(2)-O(1) ^e	103.83(13)	Zn(1)-Cu(1)-Cu(2) ^k	180.0
O(1) ^a -Cu(2)-O(1) ^d	103.83(13)	Zn(1) ^k -Cu(1)-Cu(2) ^k	0.0
O(1)-Cu(2)-O(1) ^d	76.17(13)	Cu(1) ^d -O(1)-Cu(1)	119.20(15)
O(1) ^b -Cu(2)-O(1) ^d	103.83(13)	Cu(1) ^d -O(1)-Zn(1)	96.90(11)
O(1) ^c -Cu(2)-O(1) ^d	76.17(13)	Cu(1)-O(1)-Zn(1)	96.90(11)
O(1) ^e -Cu(2)-O(1) ^d	180.0(3)	Cu(1) ^d -O(1)-Cu(2)	96.90(11)
O(1) ^a -Cu(2)-Cu(1)	140.01(4)	Cu(1)-O(1)-Cu(2)	96.90(11)
O(1)-Cu(2)-Cu(1)	39.99(4)	Zn(1)-O(1)-Cu(2)	0.0

Symmetry transformations used to generate equivalent atoms: ^a -x, -y, -z; ^b x - y, x, -z;
^c -x + y, -x, z; ^d -y, x - y, z; ^e y, -x + y, -z; ^f x - 2/3, y - 1/3, z - 1/3; ^g -x + y + 1/3, -x +
2/3, z - 1/3; ^h -y + 1/3, x - y - 1/3, z - 1; ⁱ -x + 2/3, -y + 1/3, -z + 1/3; ^j x - y + 2/3, x +
1/3, -z + 1/3; ^k x + 2/3, y + 1/3, z + 1/3.

Table S5. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $\text{Zn}_{0.33}\text{Cu}_{3.67}(\text{OH})_6\text{Cl}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	7(1)	7(1)	8(1)	0	0	4(1)
Cu(2)	7(1)	7(1)	8(1)	0	0	4(1)
Cu(1)	7(1)	8(1)	10(1)	0(1)	-1(1)	4(1)
O(1)	11(1)	9(2)	19(2)	6(1)	3(1)	5(1)
Cl(1)	11(1)	11(1)	10(1)	0	0	5(1)

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Zn}_{0.33}\text{Cu}_{3.67}(\text{OH})_6\text{Cl}_2$.

	x	y	z	U(eq)
H(1)	1920(20)	3840(40)	840(40)	40(20)

Figure S6. A portion of the crystal structure of $\text{Zn}_{0.42}\text{Cu}_{3.58}(\text{OH})_6\text{Cl}_2$. 50% ellipsoids are shown. Atoms labeled with letters correspond to symmetry equivalent atoms as found in tables S9 and S10. Hydrogen atoms are not labeled.

Table S7. Crystal data and structure refinement for $\text{Zn}_{0.42}\text{Cu}_{3.58}(\text{OH})_6\text{Cl}_2$.

Identification code	c04041a	
Empirical formula	$\text{H}_6\text{Cl}_2\text{Cu}_{3.58}\text{O}_6\text{Zn}_{0.42}$	
Formula weight	427.87	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral (obverse)	
Space group	$R\bar{3}m$	
Unit cell dimensions	$a = 6.8233(9)$ Å	$\alpha = 90^\circ$
	$b = 6.8233(9)$ Å	$\beta = 90^\circ$
	$c = 14.030(3)$ Å	$\gamma = 120^\circ$
Volume, Z	$565.67(17)$ Å ³ ,	3
Density (calculated)	3.768 g/cm ³	
Absorption coefficient	11.964 mm ⁻¹	
F(000)	613	
Crystal size	$0.07 \times 0.06 \times 0.01$ mm	
θ range for data collection	3.74 to 24.72°	
Limiting indices	$-8 \leq h \leq 8$	
	$-8 \leq k \leq 7$	
	$-15 \leq l \leq 16$	
Reflections collected	1087	
Independent reflections	138 ($R_{\text{int}} = 0.0350$)	
Completeness to $\theta = 24.72^\circ$	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	138 / 1 / 20	
Goodness-of-fit on F^2	1.319	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0218$	$wR_2 = 0.0476$
R indices (all data)	$R_1 = 0.0218$	$wR_2 = 0.0476$
Largest diff. peak and hole	0.513 eÅ ⁻³	-0.832 eÅ ⁻³

Table S8. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $\text{Zn}_{0.42}\text{Cu}_{3.58}(\text{OH})_6\text{Cl}_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zn(1)	0	0	0	8(1)
Cu(2)	0	0	0	8(1)
Cu(1)	3333	1667	1667	9(1)
O(1)	1269(2)	2538(5)	1053(2)	14(1)
Cl(1)	0	0	3054(1)	11(1)

Table S9. Bond lengths [$\text{\AA}$] for $\text{Zn}_{0.42}\text{Cu}_{3.58}(\text{OH})_6\text{Cl}_2$.

Zn(1)-O(1) ^a	2.105(3)	Cu(2)-Cu(1)	3.0573(5)
Zn(1)-O(1)	2.105(3)	Cu(2)-Cu(1) ^d	3.0573(5)
Zn(1)-O(1) ^b	2.105(3)	Cu(2)-Cu(1) ^c	3.0573(5)
Zn(1)-O(1) ^c	2.105(3)	Cu(2)-Cu(1) ^f	3.0574(5)
Zn(1)-O(1) ^d	2.105(3)	Cu(2)-Cu(1) ^g	3.0573(5)
Zn(1)-O(1) ^e	2.105(3)	Cu(2)-Cu(1) ^h	3.0574(5)
Zn(1)-Cu(1)	3.0573(5)	Cu(1)-O(1)	1.9793(13)
Zn(1)-Cu(1) ^d	3.0573(5)	Cu(1)-O(1) ⁱ	1.9792(13)
Zn(1)-Cu(1) ^c	3.0573(5)	Cu(1)-O(1) ^c	1.9793(13)
Zn(1)-Cu(1) ^f	3.0574(5)	Cu(1)-O(1) ^j	1.9793(13)
Zn(1)-Cu(1) ^g	3.0573(5)	Cu(1)-Cl(1) ⁱ	2.7692(10)
Zn(1)-Cu(1) ^h	3.0574(5)	Cu(1)-Cl(1)	2.7692(10)
Cu(2)-O(1) ^a	2.105(3)	Cu(1)-Zn(1) ^k	3.0573(5)
Cu(2)-O(1)	2.105(3)	Cu(1)-Cu(2) ^k	3.0573(5)
Cu(2)-O(1) ^b	2.105(3)	O(1)-Cu(1) ^d	1.9793(13)
Cu(2)-O(1) ^c	2.105(3)	Cl(1)-Cu(1) ^c	2.7692(10)
Cu(2)-O(1) ^d	2.105(3)	Cl(1)-Cu(1) ^d	2.7692(10)
Cu(2)-O(1) ^e	2.105(3)		

Symmetry transformations used to generate equivalent atoms: ^a $-x, -y, -z$; ^b $x - y, x, -z$; ^c $-x + y, -x, z$; ^d $-y, x - y, z$; ^e $y, -x + y, -z$; ^f $x - 2/3, y - 1/3, z - 1/3$; ^g $-x + y + 1/3, -x + 2/3, z - 1/3$; ^h $-y + 1/3, x - y - 1/3, z - 1/3$; ⁱ $-x + 2/3, -y + 1/3, -z + 1/3$; ^j $x - y + 2/3, x + 1/3, -z + 1/3$; ^k $x + 2/3, y + 1/3, z + 1/3$.

Table S10. Bond angles [°] for Zn_{0.42}Cu_{3.58}(OH)₆Cl₂.

O(1) ^a -Zn(1)-O(1)	180.00(11)	Cu(1)-Cu(2)-Cu(1) ^d	67.828(12)
O(1) ^a -Zn(1)-O(1) ^b	76.21(11)	O(1) ^a -Cu(2)-Cu(1) ^c	94.44(7)
O(1)-Zn(1)-O(1) ^b	103.79(11)	O(1)-Cu(2)-Cu(1) ^c	85.56(7)
O(1) ^a -Zn(1)-O(1) ^c	103.79(11)	O(1) ^b -Cu(2)-Cu(1) ^c	140.01(3)
O(1)-Zn(1)-O(1) ^c	76.21(11)	O(1) ^c -Cu(2)-Cu(1) ^c	39.99(3)
O(1) ^b -Zn(1)-O(1) ^c	180.00(12)	O(1) ^d -Cu(2)-Cu(1) ^c	39.99(3)
O(1) ^a -Zn(1)-O(1) ^d	103.79(11)	O(1) ^e -Cu(2)-Cu(1) ^c	140.01(3)
O(1)-Zn(1)-O(1) ^d	76.21(11)	Cu(1)-Cu(2)-Cu(1) ^c	67.828(12)
O(1) ^b -Zn(1)-O(1) ^d	103.79(11)	Cu(1) ^d -Cu(2)-Cu(1) ^c	67.828(12)
O(1) ^c -Zn(1)-O(1) ^d	76.21(11)	O(1) ^a -Cu(2)-Cu(1) ^f	39.99(3)
O(1) ^a -Zn(1)-O(1) ^e	76.21(11)	O(1)-Cu(2)-Cu(1) ^f	140.01(3)
O(1)-Zn(1)-O(1) ^e	103.79(11)	O(1) ^b -Cu(2)-Cu(1) ^f	39.99(3)
O(1) ^b -Zn(1)-O(1) ^e	76.21(11)	O(1) ^c -Cu(2)-Cu(1) ^f	140.01(3)
O(1) ^c -Zn(1)-O(1) ^e	103.79(11)	O(1) ^d -Cu(2)-Cu(1) ^f	94.44(7)
O(1) ^d -Zn(1)-O(1) ^e	180.00(13)	O(1) ^e -Cu(2)-Cu(1) ^f	85.56(7)
O(1) ^a -Zn(1)-Cu(1)	140.01(3)	Cu(1)-Cu(2)-Cu(1) ^f	180.0
O(1)-Zn(1)-Cu(1)	39.99(3)	Cu(1) ^d -Cu(2)-Cu(1) ^f	112.173(12)
O(1) ^b -Zn(1)-Cu(1)	140.01(3)	Cu(1) ^c -Cu(2)-Cu(1) ^f	112.173(12)
O(1) ^c -Zn(1)-Cu(1)	39.99(3)	O(1) ^a -Cu(2)-Cu(1) ^g	85.56(7)
O(1) ^d -Zn(1)-Cu(1)	85.56(7)	O(1)-Cu(2)-Cu(1) ^g	94.44(7)
O(1) ^e -Zn(1)-Cu(1)	94.44(7)	O(1) ^b -Cu(2)-Cu(1) ^g	39.99(3)
O(1) ^a -Zn(1)-Cu(1) ^d	140.01(3)	O(1) ^c -Cu(2)-Cu(1) ^g	140.01(3)
O(1)-Zn(1)-Cu(1) ^d	39.99(3)	O(1) ^d -Cu(2)-Cu(1) ^g	140.01(3)
O(1) ^b -Zn(1)-Cu(1) ^d	94.44(7)	O(1) ^e -Cu(2)-Cu(1) ^g	39.99(3)
O(1) ^c -Zn(1)-Cu(1) ^d	85.56(7)	Cu(1)-Cu(2)-Cu(1) ^g	112.173(13)
O(1) ^d -Zn(1)-Cu(1) ^d	39.99(3)	Cu(1) ^d -Cu(2)-Cu(1) ^g	112.173(13)
O(1) ^e -Zn(1)-Cu(1) ^d	140.01(3)	Cu(1) ^c -Cu(2)-Cu(1) ^g	180.0
Cu(1)-Zn(1)-Cu(1) ^d	67.828(12)	Cu(1) ^f -Cu(2)-Cu(1) ^g	67.827(13)
O(1) ^a -Zn(1)-Cu(1) ^c	94.44(7)	O(1) ^a -Cu(2)-Cu(1) ^h	39.99(3)
O(1)-Zn(1)-Cu(1) ^c	85.56(7)	O(1)-Cu(2)-Cu(1) ^h	140.01(3)
O(1) ^b -Zn(1)-Cu(1) ^c	140.01(3)	O(1) ^b -Cu(2)-Cu(1) ^h	85.56(7)
O(1) ^c -Zn(1)-Cu(1) ^c	39.99(3)	O(1) ^c -Cu(2)-Cu(1) ^h	94.44(7)
O(1) ^d -Zn(1)-Cu(1) ^c	39.99(3)	O(1) ^d -Cu(2)-Cu(1) ^h	140.01(3)
O(1) ^e -Zn(1)-Cu(1) ^c	140.01(3)	O(1) ^e -Cu(2)-Cu(1) ^h	39.99(3)

Cu(1)-Zn(1)-Cu(1) ^c	67.828(12)	Cu(1)-Cu(2)-Cu(1) ^h	112.172(12)
Cu(1) ^d -Zn(1)-Cu(1) ^c	67.828(12)	Cu(1) ^d -Cu(2)-Cu(1) ^h	180.0
O(1) ^a -Zn(1)-Cu(1) ^f	39.99(3)	Cu(1) ^c -Cu(2)-Cu(1) ^h	112.172(12)
O(1)-Zn(1)-Cu(1) ^f	140.01(3)	Cu(1) ^f -Cu(2)-Cu(1) ^h	67.827(12)
O(1) ^b -Zn(1)-Cu(1) ^f	39.99(3)	Cu(1) ^g -Cu(2)-Cu(1) ^h	67.827(12)
O(1) ^c -Zn(1)-Cu(1) ^f	140.01(3)	O(1)-Cu(1)-O(1) ⁱ	180.0
O(1) ^d -Zn(1)-Cu(1) ^f	94.44(7)	O(1)-Cu(1)-O(1) ^c	82.02(16)
O(1) ^e -Zn(1)-Cu(1) ^f	85.56(7)	O(1) ⁱ -Cu(1)-O(1) ^c	97.98(16)
Cu(1)-Zn(1)-Cu(1) ^f	180.0	O(1)-Cu(1)-O(1) ^j	97.98(16)
Cu(1) ^d -Zn(1)-Cu(1) ^f	112.173(12)	O(1) ⁱ -Cu(1)-O(1) ^j	82.02(16)
Cu(1) ^c -Zn(1)-Cu(1) ^f	112.173(12)	O(1) ^c -Cu(1)-O(1) ^j	180.0
O(1) ^a -Zn(1)-Cu(1) ^g	85.56(7)	O(1)-Cu(1)-Cl(1) ⁱ	97.61(7)
O(1)-Zn(1)-Cu(1) ^g	94.44(7)	O(1) ⁱ -Cu(1)-Cl(1) ⁱ	82.39(7)
O(1) ^b -Zn(1)-Cu(1) ^g	39.99(3)	O(1) ^c -Cu(1)-Cl(1) ⁱ	97.61(7)
O(1) ^c -Zn(1)-Cu(1) ^g	140.01(3)	O(1) ^j -Cu(1)-Cl(1) ⁱ	82.39(7)
O(1) ^d -Zn(1)-Cu(1) ^g	140.01(3)	O(1)-Cu(1)-Cl(1)	82.39(7)
O(1) ^e -Zn(1)-Cu(1) ^g	39.99(3)	O(1) ⁱ -Cu(1)-Cl(1)	97.61(7)
Cu(1)-Zn(1)-Cu(1) ^g	112.173(13)	O(1) ^c -Cu(1)-Cl(1)	82.39(7)
Cu(1) ^d -Zn(1)-Cu(1) ^g	112.173(13)	O(1) ^j -Cu(1)-Cl(1)	97.61(7)
Cu(1) ^c -Zn(1)-Cu(1) ^g	180.0	Cl(1) ⁱ -Cu(1)-Cl(1)	180.0
Cu(1) ^f -Zn(1)-Cu(1) ^g	67.827(13)	O(1)-Cu(1)-Zn(1)	43.11(8)
O(1) ^a -Zn(1)-Cu(1) ^h	39.99(3)	O(1) ⁱ -Cu(1)-Zn(1)	136.89(8)
O(1)-Zn(1)-Cu(1) ^h	140.01(3)	O(1) ^c -Cu(1)-Zn(1)	43.11(8)
O(1) ^b -Zn(1)-Cu(1) ^h	85.56(7)	O(1) ^j -Cu(1)-Zn(1)	136.89(8)
O(1) ^c -Zn(1)-Cu(1) ^h	94.44(7)	Cl(1) ⁱ -Cu(1)-Zn(1)	85.45(2)
O(1) ^d -Zn(1)-Cu(1) ^h	140.01(3)	Cl(1)-Cu(1)-Zn(1)	94.55(2)
O(1) ^e -Zn(1)-Cu(1) ^h	39.99(3)	O(1)-Cu(1)-Cu(2)	43.11(8)
Cu(1)-Zn(1)-Cu(1) ^h	112.172(12)	O(1) ⁱ -Cu(1)-Cu(2)	136.89(8)
Cu(1) ^d -Zn(1)-Cu(1) ^h	180.0	O(1) ^c -Cu(1)-Cu(2)	43.11(8)
Cu(1) ^c -Zn(1)-Cu(1) ^h	112.172(12)	O(1) ^j -Cu(1)-Cu(2)	136.89(8)
Cu(1) ^f -Zn(1)-Cu(1) ^h	67.827(12)	Cl(1) ⁱ -Cu(1)-Cu(2)	85.45(2)
Cu(1) ^g -Zn(1)-Cu(1) ^h	67.827(12)	Cl(1)-Cu(1)-Cu(2)	94.55(2)
O(1) ^a -Cu(2)-O(1)	180.00(11)	Zn(1)-Cu(1)-Cu(2)	0.0
O(1) ^a -Cu(2)-O(1) ^b	76.21(11)	O(1)-Cu(1)-Zn(1) ^k	136.89(8)
O(1)-Cu(2)-O(1) ^b	103.79(11)	O(1) ⁱ -Cu(1)-Zn(1) ^k	43.11(8)

O(1) ^a -Cu(2)-O(1) ^c	103.79(11)	O(1) ^c -Cu(1)-Zn(1) ^k	136.89(8)
O(1)-Cu(2)-O(1) ^c	76.21(11)	O(1) ^j -Cu(1)-Zn(1) ^k	43.11(8)
O(1) ^b -Cu(2)-O(1) ^c	180.00(12)	Cl(1) ⁱ -Cu(1)-Zn(1) ^k	94.55(2)
O(1) ^a -Cu(2)-O(1) ^d	103.79(11)	Cl(1)-Cu(1)-Zn(1) ^k	85.45(2)
O(1)-Cu(2)-O(1) ^d	76.21(11)	Zn(1)-Cu(1)-Zn(1) ^k	180.0
O(1) ^b -Cu(2)-O(1) ^d	103.79(11)	Cu(2)-Cu(1)-Zn(1) ^k	180.0
O(1) ^c -Cu(2)-O(1) ^d	76.21(11)	O(1)-Cu(1)-Cu(2) ^k	136.89(8)
O(1) ^a -Cu(2)-O(1) ^e	76.21(11)	O(1) ⁱ -Cu(1)-Cu(2) ^k	43.11(8)
O(1)-Cu(2)-O(1) ^e	103.79(11)	O(1) ^c -Cu(1)-Cu(2) ^k	136.89(8)
O(1) ^b -Cu(2)-O(1) ^e	76.21(11)	O(1) ^j -Cu(1)-Cu(2) ^k	43.11(8)
O(1) ^c -Cu(2)-O(1) ^e	103.79(11)	Cl(1) ⁱ -Cu(1)-Cu(2) ^k	94.55(2)
O(1) ^d -Cu(2)-O(1) ^e	180.00(13)	Cl(1)-Cu(1)-Cu(2) ^k	85.45(2)
O(1) ^a -Cu(2)-Cu(1)	140.01(3)	Zn(1)-Cu(1)-Cu(2) ^k	180.0
O(1)-Cu(2)-Cu(1)	39.99(3)	Cu(2)-Cu(1)-Cu(2) ^k	180.0
O(1) ^b -Cu(2)-Cu(1)	140.01(3)	Zn(1) ^k -Cu(1)-Cu(2) ^k	0.0
O(1) ^c -Cu(2)-Cu(1)	39.99(3)	Cu(1)-O(1)-Cu(1) ^d	119.05(13)
O(1) ^d -Cu(2)-Cu(1)	85.56(7)	Cu(1)-O(1)-Cu(2)	96.90(9)
O(1) ^e -Cu(2)-Cu(1)	94.44(7)	Cu(1) ^d -O(1)-Cu(2)	96.90(9)
O(1) ^a -Cu(2)-Cu(1) ^d	140.01(3)	Cu(1)-O(1)-Zn(1)	96.90(9)
O(1)-Cu(2)-Cu(1) ^d	39.99(3)	Cu(1) ^d -O(1)-Zn(1)	96.90(9)
O(1) ^b -Cu(2)-Cu(1) ^d	94.44(7)	Cu(2)-O(1)-Zn(1)	0.0
O(1) ^c -Cu(2)-Cu(1) ^d	85.56(7)	Cu(1) ^c -Cl(1)-Cu(1) ^d	76.05(3)
O(1) ^d -Cu(2)-Cu(1) ^d	39.99(3)	Cu(1) ^c -Cl(1)-Cu(1)	76.05(3)
O(1) ^e -Cu(2)-Cu(1) ^d	140.01(3)	Cu(1) ^d -Cl(1)-Cu(1)	76.05(3)

Symmetry transformations used to generate equivalent atoms: ^a -x, -y, -z ; ^b x - y, x, -z ; ^c -x + y, -x, z ; ^d -y, x - y, z ; ^e y, -x + y, -z ; ^f x - 2/3, y - 1/3, z - 1/3 ; ^g -x + y + 1/3, -x + 2/3, z - 1/3 ; ^h -y + 1/3, x - y - 1/3, z - 1/3 ; ⁱ -x + 2/3, -y + 1/3, -z + 1/3 ; ^j x - y + 2/3, x + 1/3, -z + 1/3 ; ^k x + 2/3, y + 1/3, z + 1/3.

Table S11. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $\text{Zn}_{0.42}\text{Cu}_{3.58}(\text{OH})_6\text{Cl}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(\text{ha}^*)^2\text{U}_{11} + \dots + 2\text{hka}^*\text{b}^*\text{U}_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	9(1)	9(1)	6(1)	0	0	4(1)
Cu(2)	9(1)	9(1)	6(1)	0	0	4(1)
Cu(1)	8(1)	9(1)	9(1)	0(1)	-1(1)	4(1)
O(1)	14(1)	11(1)	18(1)	7(1)	3(1)	5(1)
Cl(1)	13(1)	13(1)	9(1)	0	0	6(1)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Zn}_{0.42}\text{Cu}_{3.58}(\text{OH})_6\text{Cl}_2$.

	x	y	z	U(eq)
H(1)	1890(20)	3770(40)	830(30)	17(12)

Figure S7. A portion of the crystal structure of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. 50% ellipsoids are shown. Atoms labeled with letters correspond to symmetry equivalent atoms as found in tables S15 and S16. Hydrogen atoms are not labeled.

Table S13. Crystal data and structure refinement for ZnCu₃(OH)₆Cl₂.

Identification code	c05017a	
Empirical formula	H ₆ Cl ₂ Cu ₃ O ₆ Zn	
Formula weight	428.94	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral (obverse)	
Space group	<i>R</i> −3 <i>m</i>	
Unit cell dimensions	<i>a</i> = 6.8342(3) Å	$\alpha = 90^\circ$
	<i>b</i> = 6.8342(3) Å	$\beta = 90^\circ$
	<i>c</i> = 14.0320(12) Å	$\gamma = 120^\circ$
Volume, <i>Z</i>	567.58(6) Å ³	3
Density (calculated)	3.765 g/cm ³	
Absorption coefficient	12.133 mm ^{−1}	
<i>F</i> (000)	615	
Crystal size	0.05 × 0.04 × 0.04 mm	
θ range for data collection	3.74 to 24.69°	
Limiting indices	$-7 \leq h \leq 8$	
	$-7 \leq k \leq 8$	
	$-16 \leq l \leq 16$	
Reflections collected	1422	
Independent reflections	135 (<i>R</i> _{int} = 0.0333)	
Completeness to $\theta = 24.69^\circ$	97.8 %	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	135 / 1 / 19	
Goodness-of-fit on <i>F</i> ²	1.539	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0213	<i>wR</i> ₂ = 0.0642
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0213	<i>wR</i> ₂ = 0.0642
Largest diff. peak and hole	0.602 eÅ ^{−3}	−0.621 eÅ ^{−3}

Table S14. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zn(1)	0	0	0	7(1)
Cu(1)	3333	1667	1667	6(1)
O(1)	1265(4)	2529(8)	1050(3)	12(1)
Cl(1)	0	0	3052(2)	9(1)

Table S15. Bond lengths [Å] for ZnCu₃(OH)₆Cl₂.

Zn(1)-O(1) ^a	2.101(5)	Zn(1)-Cu(1) ^h	3.05971(16)
Zn(1)-O(1)	2.101(5)	Cu(1)-O(1) ⁱ	1.982(2)
Zn(1)-O(1) ^b	2.101(5)	Cu(1)-O(1)	1.982(2)
Zn(1)-O(1) ^c	2.101(5)	Cu(1)-O(1) ^c	1.982(2)
Zn(1)-O(1) ^d	2.101(5)	Cu(1)-O(1) ^j	1.982(2)
Zn(1)-O(1) ^e	2.101(5)	Cu(1)-Cl(1) ⁱ	2.7697(17)
Zn(1)-Cu(1)	3.05967(16)	Cu(1)-Cl(1)	2.7698(17)
Zn(1)-Cu(1) ^d	3.05967(16)	Cu(1)-Zn(1) ^k	3.05968(16)
Zn(1)-Cu(1) ^c	3.05967(16)	O(1)-Cu(1) ^d	1.982(2)
Zn(1)-Cu(1) ^f	3.05968(16)	Cl(1)-Cu(1) ^c	2.7698(17)
Zn(1)-Cu(1) ^g	3.05968(16)	Cl(1)-Cu(1) ^d	2.7698(17)

Symmetry transformations used to generate equivalent atoms: ^a -x, -y, -z ; ^b x - y, x, -z ; ^c -x + y, -x, z ; ^d -y, x - y, z ; ^e y, -x + y, -z ; ^f x - 2/3, y - 1/3, z - 1/3 ; ^g -x + y + 1/3, -x + 2/3, z - 1/3 ; ^h -y + 1/3, x - y - 1/3, z - 1/3 ; ⁱ -x + 2/3, -y + 1/3, -z + 1/3 ; ^j x - y + 2/3, x + 1/3, -z + 1/3 ; ^k x + 2/3, y + 1/3, z + 1/3.

Table S16. Bond angles [°] for ZnCu₃(OH)₆Cl₂.

O(1) ^a -Zn(1)-O(1)	180.00(19)	O(1) ^e -Zn(1)-Cu(1) ^g	40.00(6)
O(1) ^a -Zn(1)-O(1) ^b	76.21(18)	Cu(1)-Zn(1)-Cu(1) ^g	112.108(4)
O(1)-Zn(1)-O(1) ^b	103.79(18)	Cu(1) ^d -Zn(1)-Cu(1) ^g	112.109(4)
O(1) ^a -Zn(1)-O(1) ^c	103.79(18)	Cu(1) ^c -Zn(1)-Cu(1) ^g	180.0
O(1)-Zn(1)-O(1) ^c	76.21(18)	Cu(1) ^f -Zn(1)-Cu(1) ^g	67.891(4)
O(1) ^b -Zn(1)-O(1) ^c	180.0(2)	O(1) ^a -Zn(1)-Cu(1) ^h	40.01(6)
O(1) ^a -Zn(1)-O(1) ^d	103.79(18)	O(1)-Zn(1)-Cu(1) ^h	139.99(6)
O(1)-Zn(1)-O(1) ^d	76.21(18)	O(1) ^b -Zn(1)-Cu(1) ^h	85.60(12)
O(1) ^b -Zn(1)-O(1) ^d	103.79(18)	O(1) ^c -Zn(1)-Cu(1) ^h	94.40(12)
O(1) ^c -Zn(1)-O(1) ^d	76.21(18)	O(1) ^d -Zn(1)-Cu(1) ^h	139.99(6)
O(1) ^a -Zn(1)-O(1) ^e	76.21(18)	O(1) ^e -Zn(1)-Cu(1) ^h	40.01(6)
O(1)-Zn(1)-O(1) ^e	103.79(18)	Cu(1)-Zn(1)-Cu(1) ^h	112.108(4)
O(1) ^b -Zn(1)-O(1) ^e	76.21(18)	Cu(1) ^d -Zn(1)-Cu(1) ^h	180.0
O(1) ^c -Zn(1)-O(1) ^e	103.79(18)	Cu(1) ^c -Zn(1)-Cu(1) ^h	112.108(4)
O(1) ^d -Zn(1)-O(1) ^e	180.0(2)	Cu(1) ^f -Zn(1)-Cu(1) ^h	67.891(4)
O(1) ^a -Zn(1)-Cu(1)	139.99(6)	Cu(1) ^g -Zn(1)-Cu(1) ^h	67.891(4)
O(1)-Zn(1)-Cu(1)	40.01(6)	O(1) ⁱ -Cu(1)-O(1)	180.0
O(1) ^b -Zn(1)-Cu(1)	139.99(6)	O(1) ⁱ -Cu(1)-O(1) ^c	98.3(3)
O(1) ^c -Zn(1)-Cu(1)	40.01(6)	O(1)-Cu(1)-O(1) ^c	81.7(3)
O(1) ^d -Zn(1)-Cu(1)	85.60(12)	O(1) ⁱ -Cu(1)-O(1) ^j	81.7(3)
O(1) ^e -Zn(1)-Cu(1)	94.40(12)	O(1)-Cu(1)-O(1) ^j	98.3(3)
O(1) ^a -Zn(1)-Cu(1) ^d	139.99(6)	O(1) ^c -Cu(1)-O(1) ^j	180.0
O(1)-Zn(1)-Cu(1) ^d	40.01(6)	O(1) ⁱ -Cu(1)-Cl(1) ⁱ	82.32(11)
O(1) ^b -Zn(1)-Cu(1) ^d	94.40(12)	O(1)-Cu(1)-Cl(1) ⁱ	97.69(11)
O(1) ^c -Zn(1)-Cu(1) ^d	85.60(12)	O(1) ^c -Cu(1)-Cl(1) ⁱ	97.69(11)
O(1) ^d -Zn(1)-Cu(1) ^d	40.01(6)	O(1) ^j -Cu(1)-Cl(1) ⁱ	82.32(11)
O(1) ^e -Zn(1)-Cu(1) ^d	139.99(6)	O(1) ⁱ -Cu(1)-Cl(1)	97.68(11)
Cu(1)-Zn(1)-Cu(1) ^d	67.892(4)	O(1)-Cu(1)-Cl(1)	82.31(11)
O(1) ^a -Zn(1)-Cu(1) ^c	94.40(12)	O(1) ^c -Cu(1)-Cl(1)	82.31(11)
O(1)-Zn(1)-Cu(1) ^c	85.60(12)	O(1) ^j -Cu(1)-Cl(1)	97.68(11)
O(1) ^b -Zn(1)-Cu(1) ^c	139.99(6)	Cl(1) ⁱ -Cu(1)-Cl(1)	180.0
O(1) ^c -Zn(1)-Cu(1) ^c	40.01(6)	O(1) ⁱ -Cu(1)-Zn(1)	137.05(13)
O(1) ^d -Zn(1)-Cu(1) ^c	40.01(6)	O(1)-Cu(1)-Zn(1)	42.95(13)
O(1) ^e -Zn(1)-Cu(1) ^c	139.99(6)	O(1) ^c -Cu(1)-Zn(1)	42.95(13)

Cu(1)-Zn(1)-Cu(1) ^c	67.892(4)	O(1) ^j -Cu(1)-Zn(1)	137.05(13)
Cu(1) ^d -Zn(1)-Cu(1) ^c	67.892(4)	Cl(1) ⁱ -Cu(1)-Zn(1)	85.57(4)
O(1) ^a -Zn(1)-Cu(1) ^f	40.00(6)	Cl(1)-Cu(1)-Zn(1)	94.43(4)
O(1)-Zn(1)-Cu(1) ^f	140.00(6)	O(1) ⁱ -Cu(1)-Zn(1) ^k	42.95(13)
O(1) ^b -Zn(1)-Cu(1) ^f	40.01(6)	O(1)-Cu(1)-Zn(1) ^k	137.05(13)
O(1) ^c -Zn(1)-Cu(1) ^f	139.99(6)	O(1) ^c -Cu(1)-Zn(1) ^k	137.05(13)
O(1) ^d -Zn(1)-Cu(1) ^f	94.40(12)	O(1) ^j -Cu(1)-Zn(1) ^k	42.95(13)
O(1) ^e -Zn(1)-Cu(1) ^f	85.60(12)	Cl(1) ⁱ -Cu(1)-Zn(1) ^k	94.43(4)
Cu(1)-Zn(1)-Cu(1) ^f	180.0	Cl(1)-Cu(1)-Zn(1) ^k	85.57(4)
Cu(1) ^d -Zn(1)-Cu(1) ^f	112.109(4)	Zn(1)-Cu(1)-Zn(1) ^k	180.0
Cu(1) ^c -Zn(1)-Cu(1) ^f	112.108(4)	Cu(1)-O(1)-Cu(1) ^d	119.1(2)
O(1) ^a -Zn(1)-Cu(1) ^g	85.60(12)	Cu(1)-O(1)-Zn(1)	97.04(15)
O(1)-Zn(1)-Cu(1) ^g	94.40(12)	Cu(1) ^d -O(1)-Zn(1)	97.04(15)
O(1) ^b -Zn(1)-Cu(1) ^g	40.01(6)	Cu(1) ^c -Cl(1)-Cu(1) ^d	76.17(5)
O(1) ^c -Zn(1)-Cu(1) ^g	139.99(6)	Cu(1) ^c -Cl(1)-Cu(1)	76.17(5)
O(1) ^d -Zn(1)-Cu(1) ^g	140.00(6)	Cu(1) ^d -Cl(1)-Cu(1)	76.17(5)

Symmetry transformations used to generate equivalent atoms: ^a -x, -y, -z ; ^b x - y, x, -z ; ^c -x + y, -x, z ; ^d -y, x - y, z ; ^e y, -x + y, -z ; ^f x - 2/3, y - 1/3, z - 1/3 ; ^g -x + y + 1/3, -x + 2/3, z - 1/3 ; ^h -y + 1/3, x - y - 1/3, z - 1/3 ; ⁱ -x + 2/3, -y + 1/3, -z + 1/3 ; ^j x - y + 2/3, x + 1/3, -z + 1/3 ; ^k x + 2/3, y + 1/3, z + 1/3.

Table S17. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	7(1)	7(1)	6(1)	0	0	4(1)
Cu(1)	5(1)	6(1)	7(1)	-1(1)	-1(1)	3(1)
O(1)	12(2)	10(3)	15(2)	6(2)	3(1)	5(1)
Cl(1)	9(1)	9(1)	8(1)	0	0	5(1)

Table S18. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$.

	x	y	z	U(eq)
H(1)	1920(30)	3840(60)	840(60)	40(30)