Supporting Information

Synthesis, Structure and Magnetic Properties of Hydroxychlorides $A_3Cu_3(OH)Cl_8$ (A = Cs, Rb) with Isolated Tricopper

Wenbin Guo,[†] Yingying Tang,[†, #] Suyun Zhang,[†] Hongping Xiang,[†] Ming Yang,[†] Zhangzhen He[*,†, ‡]

[†]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

[‡]Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China

[#]University of the Chinese Academy of Sciences, Beijing, 100039, P. R. China

* E-mail: hcz1988@hotmail.com; hezz@fjirsm.ac.cn

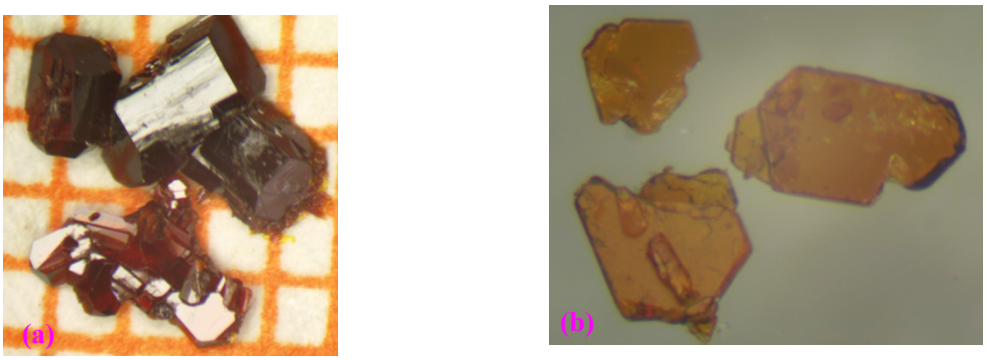
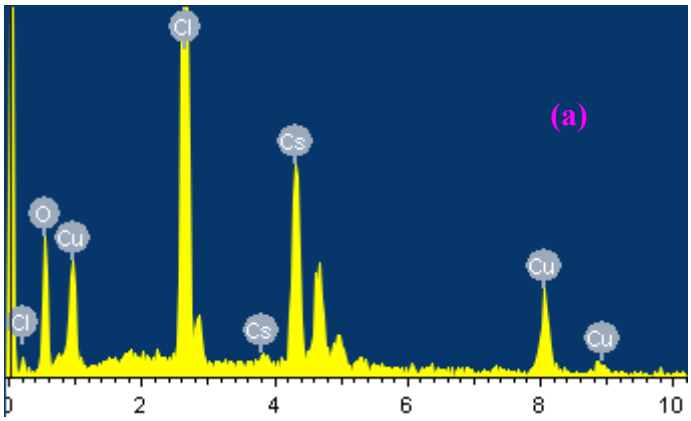


Figure S1. The grown crystals of (a) $Cs_3Cu_3(OH)Cl_8$ and (b) $Rb_3Cu_3(OH)Cl_8$.



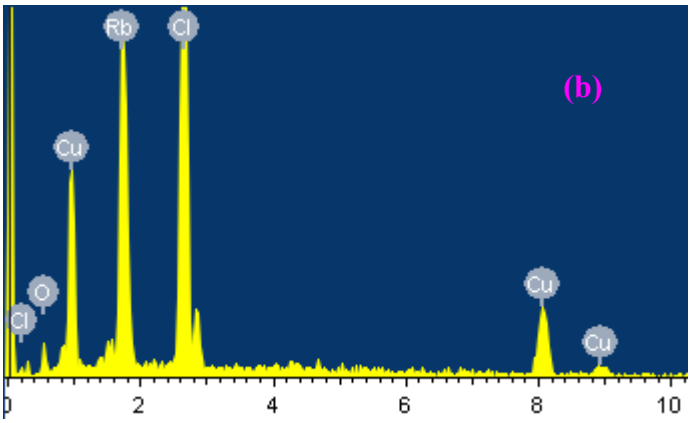


Figure S2. Energy-dispersive X-ray spectroscopy of (a) $Cs_3Cu_3(OH)Cl_8$ and (b) $Rb_3Cu_3(OH)Cl_8$.

Figure S3. The coordinated environments of Cu and Cs atoms.

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $Cs_3Cu_3(OH)Cl_8$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	x	y	z	U(eq)
Cs(1)	3104(1)	4039(1)	4274(1)	28(1)
Cs(2)	5647(1)	3844(1)	1989(1)	25(1)
Cs(3)	681(1)	895(1)	1842(1)	29(1)
Cu(1)	2211(1)	3873(1)	869(1)	17(1)
Cu(2)	2706(1)	6624(1)	65(1)	17(1)
Cu(3)	1297(1)	6584(1)	1365(1)	17(1)
Cl(1)	3457(1)	5445(1)	2152(1)	20(1)
Cl(2)	781(1)	4510(1)	1862(1)	19(1)
Cl(3)	3172(1)	2069(1)	1786(1)	26(1)
Cl(4)	1543(1)	7357(1)	-2103(1)	24(1)
Cl(5)	1892(1)	8466(1)	627(1)	20(1)
Cl(6)	864(1)	2557(1)	-417(1)	22(1)
Cl(7)	4219(1)	7795(1)	310(1)	26(1)
Cl(8)	3207(1)	4588(1)	-471(1)	23(1)
O	1482(2)	5606(2)	190(2)	14(1)

Table S2. Bond lengths [A] and angles [deg] for $Cs_3Cu_3(OH)Cl_8$.

Cu(1)-O	1.980(2)	Cu(2)-O	1.991(2)
Cu(3)-O	1.975(2)	Cu(1)-Cl(3)	2.2332(11)
Cu(1)-Cl(6)	2.3142(11)	Cu(1)-Cl(1)	2.4038(11)
Cu(1)-Cl(8)	2.7789(11)	Cu(1)-Cl(2)	2.8510(11)
Cu(2)-Cl(7)	2.2327(11)	Cu(2)-Cl(8)	2.3143(11)
Cu(2)-Cl(5)	2.3934(11)	Cu(2)-Cl(4)	2.8084(13)
Cu(2)-Cl(1)	2.8458(13)	Cu(3)-Cl(4)#1	2.2366(11)
Cu(3)-Cl(2)	2.3314(11)	Cu(3)-Cl(5)	2.3902(11)
Cu(3)-Cl(6)#2	2.7697(13)	Cu(3)-Cl(1)	2.8646(12)
Cu(3)-O-Cu(1)	103.67(11)	Cu(3)-O-Cu(2)	102.75(11)
Cu(1)-O-Cu(2)	101.69(11)	Cu(1)-Cl(1)-Cu(2)	71.25(3)
Cu(1)-Cl(1)-Cu(3)	71.73(3)	Cu(2)-Cl(1)-Cu(3)	65.72(2)
Cu(1)-Cl(6)-Cu(3)#2	121.38(4)	Cu(3)#3-Cl(4)-Cu(2)	155.28(5)
Cu(3)-Cl(2)-Cu(1)	72.96(3)	Cu(3)-Cl(5)-Cu(2)	80.73(4)
Cu(2)-Cl(8)-Cu(1)	73.75(3)	Cl(3)-Cu(1)-Cl(6)	94.25(4)
Cl(3)-Cu(1)-Cl(1)	91.72(4)	Cl(6)-Cu(1)-Cl(1)	173.50(4)
Cl(3)-Cu(1)-Cl(8)	104.11(4)	Cl(6)-Cu(1)-Cl(8)	94.38(4)
Cl(1)-Cu(1)-Cl(8)	86.65(4)	Cl(3)-Cu(1)-Cl(2)	104.51(4)
Cl(6)-Cu(1)-Cl(2)	90.89(4)	Cl(1)-Cu(1)-Cl(2)	85.11(4)
Cl(8)-Cu(1)-Cl(2)	150.40(3)	Cl(7)-Cu(2)-Cl(8)	96.80(4)
Cl(7)-Cu(2)-Cl(5)	94.51(4)	Cl(8)-Cu(2)-Cl(5)	168.55(4)
Cl(7)-Cu(2)-Cl(4)	95.51(4)	Cl(8)-Cu(2)-Cl(4)	89.41(4)
Cl(5)-Cu(2)-Cl(4)	91.29(4)	Cl(7)-Cu(2)-Cl(1)	98.02(4)
Cl(8)-Cu(2)-Cl(1)	86.81(4)	Cl(5)-Cu(2)-Cl(1)	89.85(4)
Cl(4)-Cu(2)-Cl(1)	166.29(3)	Cl(7)-Cu(2)-Cu(1)	135.47(3)
Cl(8)-Cu(2)-Cu(1)	60.06(3)	Cl(5)-Cu(2)-Cu(1)	110.03(3)
Cl(4)-Cu(2)-Cu(1)	119.52(3)	Cl(1)-Cu(2)-Cu(1)	47.68(2)
Cl(4)#1-Cu(3)-Cl(2)	94.10(4)	Cl(4)#1-Cu(3)-Cl(5)	95.66(4)
Cl(2)-Cu(3)-Cl(5)	169.65(4)	Cl(4)#1-Cu(3)-Cl(6)#2	90.76(4)
Cl(2)-Cu(3)-Cl(6)#2	91.00(4)	Cl(5)-Cu(3)-Cl(6)#2	92.34(4)
Cl(4)#1-Cu(3)-Cl(1)	95.65(4)	Cl(2)-Cu(3)-Cl(1)	86.12(4)
Cl(5)-Cu(3)-Cl(1)	89.47(3)	Cl(6)#2-Cu(3)-Cl(1)	173.14(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z+1/2 #2 -x,-y+1,-z #3 x,-y+3/2,z-1/2

Table S3. Anisotropic displacement parameters (A^2 x 10^3) for $Cs_3Cu_3(OH)Cl_8$. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

atom	U11	U22	U33	U23	U13	U12
Cs(1)	23(1)	32(1)	32(1)	4(1)	13(1)	-4(1)
Cs(2)	14(1)	32(1)	30(1)	1(1)	11(1)	1(1)
Cs(3)	25(1)	26(1)	44(1)	7(1)	23(1)	3(1)
Cu(1)	11(1)	15(1)	24(1)	1(1)	6(1)	0(1)
Cu(2)	11(1)	17(1)	29(1)	-2(1)	13(1)	-2(1)
Cu(3)	16(1)	17(1)	22(1)	-3(1)	12(1)	-2(1)
Cl(1)	11(1)	24(1)	24(1)	-1(1)	6(1)	-1(1)
Cl(2)	14(1)	20(1)	27(1)	1(1)	12(1)	-1(1)
Cl(3)	20(1)	20(1)	34(1)	6(1)	7(1)	4(1)
Cl(4)	23(1)	28(1)	21(1)	7(1)	10(1)	2(1)
Cl(5)	17(1)	18(1)	30(1)	-1(1)	14(1)	0(1)
Cl(6)	13(1)	21(1)	29(1)	-4(1)	7(1)	-1(1)
Cl(7)	13(1)	30(1)	40(1)	-4(1)	15(1)	-7(1)
Cl(8)	22(1)	21(1)	32(1)	0(1)	19(1)	3(1)
O	9(1)	14(1)	22(1)	0(1)	10(1)	-1(1)

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $Rb_3Cu_3(OH)Cl_8$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	x	y	z	U(eq)
Rb(1)	4347(1)	3814(1)	2961(1)	34(1)
Rb(2)	6881(1)	1009(1)	5750(1)	37(1)
Rb(3)	699(1)	5963(1)	1839(1)	44(1)
Cu(1)	1302(1)	1630(1)	1368(1)	24(1)
Cu(2)	2744(1)	1676(1)	14(1)	24(1)
Cu(3)	2282(1)	-1134(1)	886(1)	24(1)
Cl(1)	3329(2)	-419(2)	-461(2)	33(1)
Cl(2)	804(2)	-463(2)	1935(2)	27(1)
Cl(3)	-912(2)	2492(2)	399(2)	30(1)
Cl(4)	3523(2)	468(2)	2193(2)	28(1)
Cl(5)	1899(2)	3555(2)	611(2)	30(1)
Cl(6)	3257(2)	-2979(2)	1810(2)	36(1)
Cl(7)	1489(2)	2221(2)	-2106(2)	33(1)
Cl(8)	4245(2)	2947(2)	207(2)	36(1)
O	1512(4)	612(5)	172(4)	23(1)

Table S5. Bond lengths [A] and angles [deg] for $Rb_3Cu_3(OH)Cl_8$.

Cu(1)-O	1.985(5)	Cu(2)-O	1.993(5)
Cu(3)-O	1.987(5)	Cu(1)-Cl(7)#1	2.244(2)
Cu(1)-Cl(2)	2.329(2)	Cu(1)-Cl(5)	2.383(2)
Cu(1)-Cl(3)	2.786(2)	Cu(1)-Cl(4)	2.889(2)
Cu(2)-Cl(8)	2.239(2)	Cu(2)-Cl(1)	2.327(2)
Cu(2)-Cl(5)	2.412(2)	Cu(2)-Cl(7)	2.694(2)
Cu(2)-Cl(4)	2.911(2)	Cu(3)-Cl(6)	2.239(2)
Cu(3)-Cl(3)#2	2.320(2)	Cu(3)-Cl(4)	2.401(2)
Cu(3)-Cl(1)	2.757(2)	Cu(3)-Cl(2)	2.887(2)
Cu(1)-Cu(2)	3.1014(13)	Cu(1)-Cu(3)	3.1219(13)
Cu(2)-Cu(3)	3.0899(13)	Cu(1)-O-Cu(3)	103.6(2)
Cu(1)-O-Cu(2)	102.5(2)	Cu(3)-O-Cu(2)	101.9(2)
Cl(7)#1-Cu(1)-Cl(2)	93.88(8)	Cl(7)#1-Cu(1)-Cl(5)	94.19(8)
Cl(2)-Cu(1)-Cl(5)	171.21(7)	Cl(7)#1-Cu(1)-Cl(3)	89.32(7)
Cl(2)-Cu(1)-Cl(3)	91.70(7)	Cl(5)-Cu(1)-Cl(3)	91.87(7)
Cl(7)#1-Cu(1)-Cl(4)	96.80(7)	Cl(2)-Cu(1)-Cl(4)	85.19(7)
Cl(5)-Cu(1)-Cl(4)	90.40(7)	Cl(3)-Cu(1)-Cl(4)	173.30(6)
Cl(8)-Cu(2)-Cl(1)	97.41(8)	Cl(8)-Cu(2)-Cl(5)	93.21(8)
Cl(1)-Cu(2)-Cl(5)	168.57(8)	Cl(8)-Cu(2)-Cl(7)	98.69(8)
Cl(1)-Cu(2)-Cl(7)	90.46(8)	Cl(5)-Cu(2)-Cl(7)	92.10(7)
Cl(8)-Cu(2)-Cl(4)	99.43(8)	Cl(1)-Cu(2)-Cl(4)	84.80(7)
Cl(5)-Cu(2)-Cl(4)	89.32(7)	Cl(7)-Cu(2)-Cl(4)	161.71(7)
Cl(6)-Cu(3)-Cl(3)#2	93.75(8)	Cl(6)-Cu(3)-Cl(4)	91.94(8)
Cl(3)#2-Cu(3)-Cl(4)	173.11(8)	Cl(6)-Cu(3)-Cl(1)	103.46(8)
Cl(3)#2-Cu(3)-Cl(1)	95.51(8)	Cl(4)-Cu(3)-Cl(1)	86.93(7)
Cl(6)-Cu(3)-Cl(2)	104.69(8)	Cl(3)#2-Cu(3)-Cl(2)	90.82(7)
Cl(4)-Cu(3)-Cl(2)	83.97(7)	Cl(1)-Cu(3)-Cl(2)	150.64(7)
Cu(3)-Cl(4)-Cu(1)	71.65(6)	Cu(3)-Cl(4)-Cu(2)	70.39(6)
Cu(1)-Cl(4)-Cu(2)	64.65(5)	Cu(2)-Cl(1)-Cu(3)	74.31(6)
Cu(1)-Cl(2)-Cu(3)	72.65(5)	Cu(1)-Cl(5)-Cu(2)	80.59(7)
Cu(1)#3-Cl(7)-Cu(2)	148.07(10)	Cu(3)#2-Cl(3)-Cu(1)	121.89(8)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z+1/2 #2 -x,-y+1,-z #3 x,-y+3/2,z-1/2

Table S6. Anisotropic displacement parameters (A^2 x 10^3) for $Rb_3Cu_3(OH)Cl_8$. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

atom	U11	U22	U33	U23	U13	U12
Rb(1)	31(1)	37(1)	40(1)	-1(1)	19(1)	-1(1)
Rb(2)	35(1)	39(1)	40(1)	6(1)	17(1)	-4(1)
Rb(3)	51(1)	35(1)	62(1)	10(1)	39(1)	4(1)
Cu(1)	31(1)	21(1)	25(1)	-3(1)	18(1)	-3(1)
Cu(2)	24(1)	22(1)	32(1)	-1(1)	18(1)	-2(1)
Cu(3)	27(1)	19(1)	27(1)	1(1)	12(1)	0(1)
Cl(1)	41(1)	26(1)	44(1)	4(1)	30(1)	7(1)
Cl(2)	29(1)	26(1)	33(1)	4(1)	19(1)	-1(1)
Cl(3)	26(1)	27(1)	34(1)	-5(1)	9(1)	0(1)
Cl(4)	26(1)	29(1)	29(1)	-2(1)	11(1)	-2(1)
Cl(5)	37(1)	21(1)	39(1)	-1(1)	23(1)	0(1)
Cl(6)	37(1)	25(1)	41(1)	10(1)	10(1)	3(1)
Cl(7)	37(1)	36(1)	26(1)	8(1)	13(1)	-2(1)
Cl(8)	28(1)	33(1)	52(1)	0(1)	21(1)	-7(1)
O	29(3)	23(3)	24(3)	4(2)	17(2)	4(2)