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ARTICLE

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

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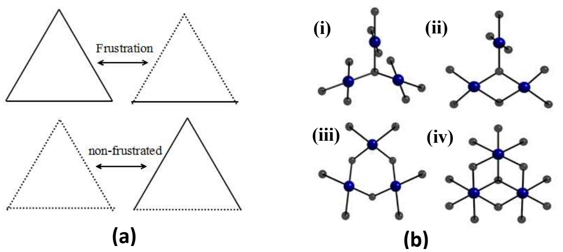
Two copper hydroxychlorides $A_3Cu_3(OH)Cl_8$ (A = Cs, Rb) were synthesized by a hydrothermal method, which crystallize in the space group $P2_1/c$. All copper atoms are coordinated with three Cl atoms and one OH group forming quite distorted squares of $CuCl_3(OH)$, which further share one edge and one corner to form an isolated triangle unit of $[Cu_3(OH)Cl_8]^{3-}$ with μ_2-Cl and μ_3-OH cores. Interestingly, two isostructural compounds possess an antiferromagnetic ordering at low-temperature and the dominant exchange coupling in the isolated triangle is found to be of ferromagnetic type, ruling out geometrical frustration effect. The origin of such ferromagnetic interaction is suggested to arise likely from the folding $[Cu(2)Cu(3)(OH)Cl_5]^{2-}$ dimers with a Cu(2)-Cl(5)-Cu(3) route.

Introduction

Transition-metal compounds containing trinuclear copper have received considerable interest not only as bioinorganic model complexes[1] and catalysts[2], but also for their interesting relationship between structure and exotic magnetism in magnetochemistry[3]. As shown in Scheme **1a**, it is known that geometrical frustration will arise in a triangle (tricopper) with completely antiferromagnetic couplings or one antiferromagnetic and two ferromagnetic couplings[4]. While completely ferromagnetic couplings or one ferromagnetic and two antiferromagnetic couplings present in a triangle, geometrical frustration does not happen. Current interest is mainly focused on searching for strongly frustrated tricopper compounds, but some tricopper complexes are also found to show non-frustrated with ferromagnetic couplings[5].

In general, most of the geometrically frustrated lattices are composed of equilateral or isosceles triangle units, including diamond chain, sawtooth chain, kagome, triangle, pyrochlore, and spinel lattices. For example, diamond chains in $Cu_3(CO_3)_2(OH)_2$[6] built by alternate edge and corner-sharing CuO_4 squares show a 1/3 magnetization plateau. $ZnCu_3(OH)_6Cl_2$[7] with kagome lattice constructed by corner-sharing CuO_4 squares presents a possible spin liquid state. $LiZn_2Mo_3O_8$ displays a possible valence-bond condensation due to discrete clusters of Mo_3O_{13} with a $S = 1/2$ magnetic moment in a standard triangle lattice[8]. For Cu-based frustrated magnets, triangle fragment built from CuO_6 octahedra or CuO_4 squares can be divided into four cases as shown in Scheme **1b**: (i) one corner in $BiCu_3(SeO_3)_2O_2Cl$[9], (ii) one edge and one corner in $Cu_3(CO_3)_2(OH)_2$ with diamond-like chain[6], (iii) three corners in $MCu_3(OH)_6Cl_2$ (M = Mg, Zn)[7,10], and (iv) three edges in $BCu_3(V_2O_8)(OH)_2$ (B = Ba, Sr)[11], $CdCu_3(OH)_6(NO_3)_2$[12] and $Cu_3(OH)_2(V_2O_7)(H_2O)_2$[13]. Moreover, it is noted that most of trinuclear copper units are easily constructed via OH[14], O[15], Cl[16], Br[17], or MeO[18] as a central bridging ligand. To the best of our knowledge, isolated triangular tricopper can only be found in two inorganic materials of $La_4Cu_3MoO_{12}$[19] and $SrCu(OH)_3Cl$[20] with the type of one corner and three corners, respectively. Although both compounds show large spin frustration, they have different magnetic behaviours, in which $La_4Cu_3MoO_{12}$



Scheme 1. (a) Frustrated and non-frustrated triangles with possible magnetic couplings and (b) triangle fragments built from octahedral CuO_6 or CuO_4 squares in geometrically frustrated magnets. The solid line and the doted line represent the antiferromagnetic and ferromagnetic couplings, respectively. Color code: blue, copper; gray, oxygen.

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† Electronic supplementary information (ESI) available: X-ray crystallographic files in CIF format, the crystal pictures (Fig. S1), important bond lengths and angles (Tables S1-6), simulated and experimental XRD patterns (Fig. S2). See DOI: 10.1039/x0xx00000x

shows a long-range antiferromagnetic ordering below 2.6 K,[19] while $SrCu(OH)_3Cl$ shows magnetic disorder down to 2 K, which can be viewed as a dimension reduction of $ZnCu_3(OH)_6Cl_2$ with kagome lattice[20]. Besides inorganic compounds, the frustrated triangular tricopper is also found in some coordination complexes[21]. It may be a challenge to prepare inorganic compounds with isolated triangle tricopper.

Recently we have investigated the A-Cu-OH-Cl (A = alkali metals) system and found two new copper hydroxychlorides $Cs_3Cu_3(OH)Cl_8$ (**1**) and $Rb_3Cu_3(OH)Cl_8$ (**2**). In these two compounds, Cu^{2+} ions coordinate with three Cl atoms and one OH group forming distorted squares $CuCl_3(OH)$ because of Jahn-Teller effect of Cu^{2+} ($3d^9$) ions. Adjacent $CuCl_3(OH)$ sharing one edge and one corner form isolated triangle units of $[Cu_3(OH)Cl_8]^{3-}$ with μ_3-OH and μ_2-Cl groups. Magnetic measurements and theoretical simulation confirm that a strong ferromagnetic coupling exists in the folded dimer and two compounds show an antiferromagnetic long-range ordering at ~2.5 K and ~3.9 K in **1** and **2**, respectively.

Experimental Section

Syntheses of samples

Single crystals of **1** and **2** were obtained via a hydrothermal reaction combined solution method. A mixture of 3 mmol $CuCl_2\cdot 2H_2O$(0.5102 g), 2 mmol ACl (CsCl: 0.3360 g; RbCl: 0.2400 g), 1 mmol A_2CO_3 (Cs_2CO_3:0.1620 g; Rb_2CO_3: 0.1500 g), 1.3 mmol H_3BO_3 (0.0800 g) and 1 mL H_2O were separately sealed in an autoclave equipped with a Teflon liner (28 mL). The autoclaves were put into a furnace which was then heated at 230 °C for 6 days under autogenous pressure, followed by cooling to room temperature at 3 K/h, acquiring the bright green solution. Then the brown sheet crystals were acquired by natural evaporation under room temperature in several days (Fig. S1, Supporting information). The crystals of **1** and **2** were quickly dissolved in distilled water and powdered samples for magnetic measurements were prepared by grinding single crystals. Element analysis (Figure S2) was carried out on several single crystals using the energy dispersive spectrometry (EDS), confirming that no other elements can be detected except for Cs or Rb, Cu, O and Cl. Further an average molar ratio of Cs(Rb)/Cu/Cl was found to be 2.95(4): 3.03(5) :8.12(1) and 2.95(3): 3.04(2) :8.07(5) agreeing with the results determined from single-crystal X-ray structural studies.

X-ray crystallographic studies

Small crystals of **1** and **2** were selected and mounted on glassy fibers for single crystal X-ray diffraction (XRD) measurements. Data collections were performed on Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by Multi-scan method[22]. The structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by *SHELX*-97[23]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were located at calculated positions and refined with isotropic thermal parameters. The final refined structural parameters were checked by the *PLATON* program[24]. Crystallographic data and structural refinements are summarized in Table 1. The final refined atomic positions and structural parameters of **1** and **2** are seen in the Supporting Information (Tables S1-6). CSD 429467 and 429468.

Table 1. Crystal data and structure refinements for **1** and **2**.

formula	**1**	**2**
fw	889.98	747.66
T, K	room temp	room temp
λ, Å	0.71073	0.71073
space group	$P\ 2_1/c$	$P\ 2_1/c$
a, Å	13.450(4)	13.118(3)
b, Å	9.757(3)	9.580(8)
c, Å	13.706(7)	13.377(3)
α, deg	90	90
β, deg	114.824(5)	113.795(1)
γ, deg	90	90
V, Å^3	1632.5(8)	1538.3(6)
Z	4	4
D_{calcd}, g cm^{-3}	3.617	3.224
μ, mm^{-1}	11.746	14.898
GOF on F^2	1.031	0.898
R1,wR2 [$I > 2\sigma(I)$]^a	0.0239, 0.0513	0.0461, 0.1036
R1,wR2 (all data)	0.0272, 0.0524	0.0723, 0.1129

^{a}R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $\{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Magnetic Measurements

Magnetic measurements were performed using a commercial Quantum Design Physical Property Measurement System (PPMS). Powdered samples of **1** and **2** (20.21 mg for **1** and 11.88 mg for **2**) were placed in a gel capsule sample holder which were suspended in a plastic drinking straw. Magnetic susceptibilities were measured at 0.1 T (2 - 300 K), and magnetization were measured at 2 K in applied field from 0 to 8 T. For **1**, heat capacity was also measured at 2-10 K with applied fields of 0 and 5 T. Diamagnetic corrections were estimated by using Pascal constants and background correction by experimental measurement on sample holders[25].

Results and Discussions

Structural Description

Single crystal X-ray diffraction analysis indicates that **1** and **2** crystallize in monoclinic space group $P2_1/c$. As they are isostructural, here we will take **1** as an example to describe their structures in detail.

Its asymmetric unit contains three Cs, three Cu, seven Cl, and one O, in which all atoms locate at the general Wyckoff positions of 4e. O atoms are only coordinated with three Cu atoms with the average Cu-O bond length of 1.982(2) Å. The bond valence sum (BVs) calculations indicates O atoms in **1** are

0.947, confirming O should be OH^- group for charge balancing the formula. As shown in Fig. S3, each Cu atom is coordinated by one O and three Cl atoms forming quite distorted $CuCl_3(OH)$ because of great Jahn-Teller effect of Cu^{2+} ($3d^9$) ions, where the normal Cu-Cl bond lengths vary from 2.232(7) Å to 2.403(8) Å. The bond valence sum (BVs) calculations indicates Cu(1), Cu(2), and Cu(3) in **1** are 1.541, 1.531, 1.539, respectively. The similar distorted square of $CuCl(OH)_3$ has been reported in Cu(OH)Cl[26]. Cs(1) and Cs(3) are seven-coordinated while Cs(2) is eight-coordinated with Cs-Cl bond lengths ranging from 3.423(7) Å to 3.656(1) Å (Fig. S2).

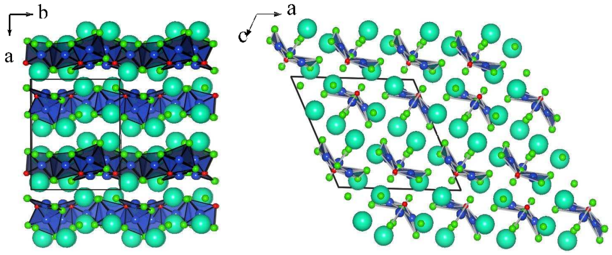


Fig. 1. The 3D structure of $Cs_3Cu_3(OH)Cl_8$ viewing along *c* (left) and *b* (right) direction.

The 3D framework of **1** is constructed by isolated trimers of $[Cu_3(OH)Cl_8]^{3-}$, in which the trimers are separated by Cs cations(Fig. 1). On the *a-b* plane(Fig. 1a), $Cs_3Cu_3(OH)Cl_8$ shows a layered structure, where the shortest distance between layers is 7.005(8) Å. In fact, such layer is built by isolated trimer units $[Cu_3(OH)Cl_8]^{3-}$, in which Cs(3) cations are located between trimers. The distance of the nearest trimers is 4.438(8) Å. To further examine the linkages in tricopper, we note that Cu(2) and Cu(3) ions share OH and Cl(5) forming a folding dimer with dihedral of 141.8°, while $Cu(1)Cl_3OH$ cuts the folding dimer via corner-sharing O atom (Fig. 2). The angle of Cu(2)-Cl(5)-Cu(3) is 80.735(3)° while ones of Cu-O-Cu are 102.749(1)°, 103.662(9)°, and 101.688(9)°. It is noted that three Cu sites form a slightly distorted triangle with μ_3-OH, which is neither an equilateral triangular nor isosceles triangle with the Cu···Cu distance of 3.078 (7) Å, 3.098(2) Å and 3.109(2) Å, respectively(Fig. 2b).

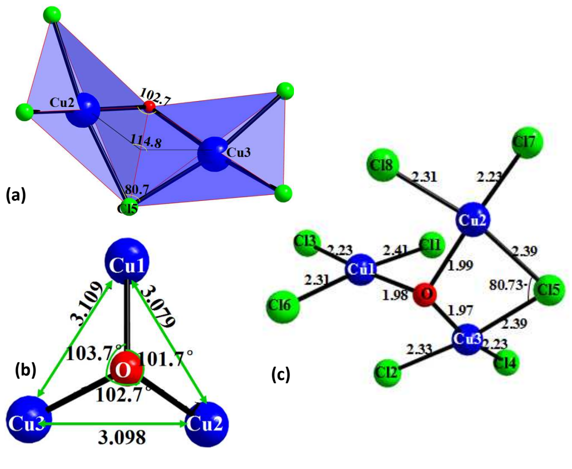


Fig. 2. (a) The folding dimer of $[Cu_2(OH)Cl_5]^{2-}$ with a dihedral of 141.8°, (b)the triangle geometry containing μ_3-OH group and (c) the tricopper unit of $[Cu_3(OH)Cl_8]^{3-}$.

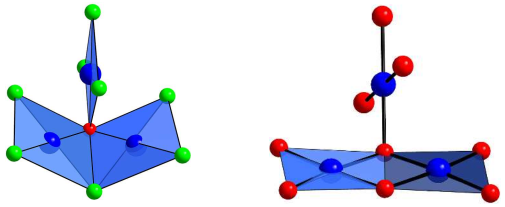
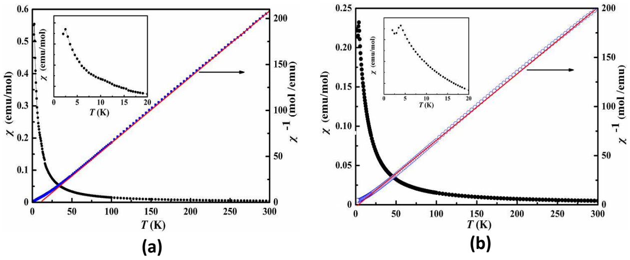


Fig. 3. The triangle fragment in the title compounds (left) and $Cu_3(CO_3)_2(OH)_2$ (right). The dimer in $Cu_3(CO_3)_2(OH)_2$ is almost at a plane while in title compounds it is folded.

It is interesting to compare the triangle units in the titled compounds and $Cu_3(CO_3)_2(OH)_2$[6], which all belong to the type of (b) with one edge and a corner. As shown in Fig. 3, the dimer in triangle fragment of $Cu_3(CO_3)_2(OH)_2$ is almost located at a plane while in title compounds the dimer are folded. The angles of Cu-O-Cu in μ_3-OH of $Cu_3(CO_3)_2(OH)_2$ are larger than that in the titled compounds, suggesting that the different bond lengths and angles resulted from longer bond length of Cu-Cl may greatly influence the magnetic couplings and ground states.

Magnetic Properties

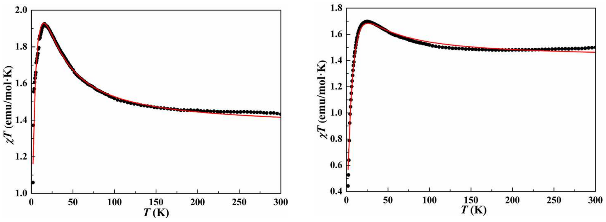
Fig. 4 shows temperature dependence of the magnetic susceptibility measured at 0.1 T. The magnetic susceptibility increases with decreasing temperature, while a sharp peak is observed at ~2.5 K for **1** (~3.9 K for **2**), indicating the onset of antiferromagnetic ordering. A typical Curie-Weiss behavior is observed above 50 K, giving the Curie constant C = 1.41(6) emu K/mol and Weiss temperature θ = 5.00(3) K for **1** (C = 1.46(8) emu K/mol and θ = 3.08(8) K for **2**). The effective magnetic moments of Cu^{2+} ions are calculated to be 1.94(2) μ_B and 1.97(8) μ_B for **1** and **2**, respectively, which are slightly larger than the theoretical value of 1.732 μ_B for Cu^{2+} ions ($S = 1/2$, $g = 2$) obtained by $\mu_{eff}^2 = g^2S(S+1)$[27], indicating orbital moment contribution of Cu^{2+} ions in such distorted squares. Moreover, as seen in Fig. 5, the value of χT increases and reaches at a maximum, and then decreases rapidly with decreasing temperature. This behavior is quite similar to that reported in some complexes with FM trimers[5].



(a)

(b)

Fig. 4. Temperature dependence of magnetic susceptibilities and reciprocal susceptibilities of (a) **1** and (b) **2**. The inset show an enlarged view of magnetic susceptibility at low-temperature.



(a) (b)

Fig. 5. The χ*T* versus temperature (*T*) of (a) **1** and (b) **2**. The red solid lines are the fittings using the Equation (3).

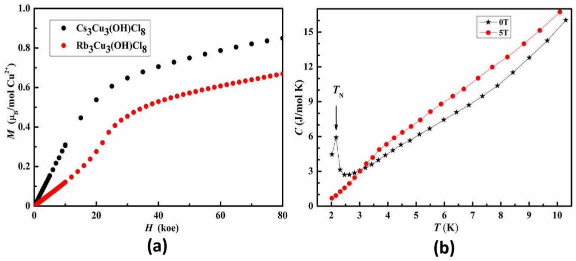
Fig. 6a shows the magnetization as a function of applied field at 2 K for **1** and **2**. A linear increase is observed for **1** at low field of H < 2T, agreeing with the antiferromagnetic ground state, while a slope change is observed at H = 2T, indicating a field-induced magnetic transition. Similarly, a linear increase is observed for **2** at H < 2T, while a jump of magnetization is observed at H = ~2T. The magnetization shifts to saturate at high field range, showing the appearance of a metamagnetic transition. In order to further identify the magnetic transition at low temperature, heat capacity data for **1** were measured. As shown in Fig. 6b, only a λ-type anomaly was observed at ~2.3 K with zero filed, suggesting that the peak in magnetic susceptibility means the appearance of a long-range antiferromagnetic ordering. Moreover, the λ-type peak can be suppressed in the applied field of 5 T, showing the weak intertrimer couplings. It is obvious that spin frustration is absent in this tricopper system, according to an empirical formula of $f = |\vartheta_{CW}|/T_C$, where ϑ_{CW} is the Weiss temperature and T_C is an ordering temperature[4a]. The *f* values of **1** and **2** are assumed to be 2.01 and 0.79, respectively, ruling out the geometrical frustration, because a measure of $f > 10$ suggests the presence of geometrical frustration[4a].

To understand the nature of magnetic behaviors of the titled compounds, we try to use a spin model for fitting of their magnetic data. It is well-known that the Hamiltonian for a

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3) \qquad (1)$$

$$\chi_{trimer} = \frac{Ng^2\beta^2}{4kT} \times \frac{(5e^{3J/kT}+1)}{(e^{3J/kT}+1)} \qquad (2)$$

$$\chi_M = \frac{\chi_{trimer}}{1-(2zj'/Ng^2\beta^2)\chi_{trimer}} \qquad (3)$$



(a) (b)

Fig. 6. (a) Magnetization plot for $A_3Cu_3(OH)Cl_8$ at 2 K and (b) heat capacity under zero field for **1**. The solid line are guided for the eye.

trimer spin-lattice can be expressed as the equation (1) according to the isotropic Heisenberg-Dirac-Van Vleck theory. Thus the magnetic susceptibility (χ_M) can further be expressed as the equation (2) by considering a similar interaction between magnetic ions in such triangle lattice (Fig. 2b, $J_1 = J_2 = J_3 = J$)[5, 20]. When the intertrimer interaction (*J'*) is also taken into account, the equation (2) is usually written as the equation (3), where *N, g, β,* and *k* are Avogadro's number, Lande factor, Bohr magneton, and Boltzmann's constant, respectively.

As shown in Fig. 5, the best fit using the equation (3) gives $g = 2.27$, $J = 9.911$ K, $zJ' = -0.377$ K ($R = 7.45\times10^{-4}$) for **1** and $g = 2.24$, $J = 9.355$ K, $zJ' = -1.256$ K ($R = 7.45\times10^{-4}$) for **2**, respectively, where the agreement factor is defined by $R = \Sigma(\chi_m T_{cal} - \chi_m T_{exp})^2/\Sigma(\chi_m T_{exp})^2$. The obtained parameters suggest a strong intratrimer ferromagnetic interaction and a weak intertrimer antiferomagnetic coupling in the systems. The results are in good agreement with magnetic behaviors of a positive Weiss temperature and a low Neel temperature. A quite similar magnetic behaviors can also be observed in $3CuCl_2$·dioxane[28].

As shown in Scheme 1a, the spin-frustration does not happen in a triangle, when one or three ferromagnetic couplings present. For the titled compounds, if only ferromagnetic couplings exist in trimers, the magnetization at 2 K should saturate at high field, which is quite conflict with magnetization data at 8T (0.81 μ_B and 0.66 μ_B for **1** and **2**). Hence, we suggest one ferromagnetic and two antiferromagnetic couplings in the tricopper units of the titled compounds. From angle of Cu-Cl-Cu (80.735(3)°) and Cu-O-Cu (102.749(1)°, 103.662(9)°, and 101.688(9)°) in $[Cu_3(OH)Cl_8]^{3-}$, we deduce that the interaction of Cu(2)-Cu(3) in the folded $Cu_2Cl_5(OH)$ dimer is of ferromagnetic, while those of corner-sharing Cu(1)-Cu(3) and Cu(1)-Cu(2) are of antiferromagnetic. Moreover, the angle of Cu(2)-Cl(5)-Cu(3) in folded dimer $Cu_2(OH)Cl_5$ is 80.735(3)° which is quite smaller than the critical angle of ~93° changed from ferromagnetic to antiferromagnetic coupling in choloride-bridged salts[28]. Therefore, it is reasonable to suggest that the strong ferromagnetic coupling in $[Cu_3(OH)Cl_8]^{3-}$ trimers may arise likely from the Cu(2)-Cl(5)-Cu(3) routes, leading to non-frustration in trinuclear copper units on the basis of a triange lattice with one ferromagnetic and two antiferromagnetic couplings.

Conclusions

Two new copper hydroxychlorides $A_3Cu_3(OH)Cl_8$ (A = Cs, Rb) have been synthesized by a hydrothermal method. These compounds are isostructural which crystallize in the monoclinic system with a space group $P2_1/c$. All of Cu^{2+} ions are coordinated by three Cl atoms and one OH group forming a distorted $CuCl_3(OH)$ square and three distorted squares further connect to each other via corner- and edge-sharing, forming an isolated triangular building unit of $[Cu_3(OH)Cl_8]^{3-}$. Magnetic measurements confirmed that both of compounds exhibit antiferromagnetic ordering at low-temperature, ruling out geometrical frustration effect. Antiferromagnetic ordering is suggested to arise from a weak antiferromagnetic interaction between trimers, whlie non-frustration effect in trinuclear coppe units may be due to a dominative ferromagnetic coupling originated from the Cu(2)-Cl(5)-Cu(3) route in the folded dimers.

Acknowledgements

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

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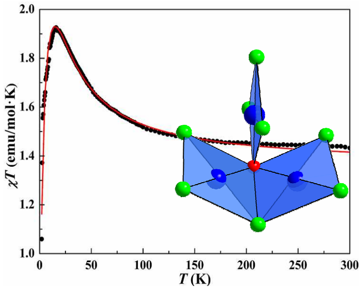
Graphic content



$A_3Cu_3(OH)Cl_8$ (A = Cs, Rb) feature an isolated triangular building unit of $[Cu_3(OH)Cl_8]^{3-}$, displaying ferromagnetic coupling via the Cu(2)-Cl(5)-Cu(3) route.