

## The magnetic-structural relationship of $[\text{CuX}_6]^{4-}$ [X = Cl or Br] perovskites containing *n*-carboxyalkylammonium cations of various chain lengths

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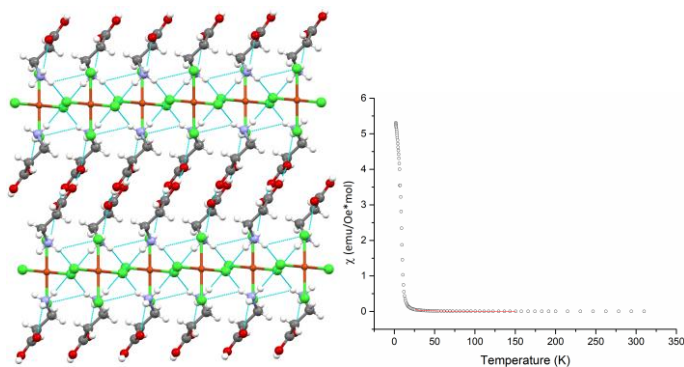
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Three-dimensional (3D) hybrid perovskites of  $\text{Pb}^{2+}$  halides have recently gained significant interest due to their use as sensitizers in perovskite solar cells [1]. However, the toxicity of  $\text{Pb}^{2+}$  has required researchers to look for an alternative to  $\text{Pb}^{2+}$  containing perovskites. Organic-inorganic (O-I) hybrid  $\text{Cu}^{2+}$  perovskites containing methylammonium cations and  $\text{Cl}^-$  or  $\text{Br}^-$  halide anion have been studied, as an alternative to  $\text{Pb}^{2+}$  halide perovskites for solar cell applications [2]. Hybrid perovskites of  $\text{Cu}^{2+}$  halides typically form two-dimensional (2D) layered perovskite structures, even with smaller cations like methylammonium, resulting in band gaps too large for solar cell applications [3]. Despite their large band-gap and low power conversion efficiency, recent studies have shown an improvement in performance of perhalocuprate(II) perovskites, creating opportunity for further research [3]. The 2D hybrid perovskites of  $\text{Cu}^{2+}$  are of interest as they are low-dimensional magnetic systems and can be used as models for high temperature superconductors [4]. The  $\text{Cu}^{2+}$  ion is a  $S = \frac{1}{2}$  ion, with quenched orbital angular momentum, simplifying the system magnetically, and is typically described by the  $S = \frac{1}{2}$  Heisenberg Hamiltonian.

The crystal structures, magnetic properties and magneto-structural correlations of eleven novel *bis*-(*n*-carboxyalkylammonium) tetrahalidocuprate(II) compounds, of the formula  $^{+}(\text{NH}_3(\text{CH}_2)_n\text{COOH})_2[\text{CuX}_4]^{2-}$  are presented, with  $n = 2, 3, 4, 5$  and  $10$  and  $X = \text{Cl}$  or  $\text{Br}$ . Thermotropic phase transitions were exhibited by two chlorido members of the series, namely *bis*-(3-carboxylpropylammonium) tetrachloridocuprate(II),  $^{+}(\text{NH}_3(\text{CH}_2)_3\text{COOH})_2[\text{CuCl}_4]^{2-}$ , and *bis*-(5-carboxylpentylammonium) tetrachloridocuprate(II),  $^{+}(\text{NH}_3(\text{CH}_2)_5\text{COOH})_2[\text{CuCl}_4]^{2-}$ . Dominant ferromagnetic (FM) interactions are displayed at high temperatures, while the systems shifted to an antiferromagnetic (AFM) state below the ordering temperature,  $T_c$ , as shown in Fig. 1. Hysteresis effects, zero field-cooled (ZFC)/field-cooled (FC) cool plots indicated the presence of coercive fields and remembrance effects in some of the compounds. The two-dimensional chlorido structures exhibited an in-plane  $J$  value of 14.332 K to 15.109 K and the bromido containing structures displayed an in-plane  $J$  value of 18.56 K to 23.65 K.



**Figure 1.** The layered assembly of the  $\text{Cu}^{2+}$  structures discussed and corresponding  $\chi$  vs  $T$  plot.

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