

Supramolecular assembly of ligand-directed triangular $\{\text{Cu}^{\text{II}}_3\text{Cl}\}$ clusters with spin frustration and spin-chain behaviour†

Georg Seeber,^a Paul Kögerler,^b Benson M. Kariuki^c and Leroy Cronin^{*a}

^a Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ.

E-mail: L.Cronin@chem.gla.ac.uk

^b Ames Laboratory and Department of Physics & Astronomy, Iowa State University, Ames, IA 50011, USA

^c School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT

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Triangular $\{\text{Cu}^{\text{II}}_3\text{Cl}\}$ clusters, containing a chloro ligand in an unprecedented trigonal planar coordination mode, are assembled in a 3-D array by the combination of coordinative and hydrogen-bonded interactions, which result in magnetically isolated 1-D chains exhibiting a combination of spin frustration and spin-chain behaviour.

Polynuclear coordination clusters represent an extraordinarily expanding and diverse subset of molecules with potential for the pursuit of interesting and technologically applicable properties.¹ Traditionally, cluster synthesis has been achieved using both rational² and serendipitous³ approaches, but common to both approaches is the use of bridging and chelating ligands to encourage the aggregation of the metal centres.^{1–3} An interesting route to the construction of a more diverse set of clusters may be achieved by ligands that can both be involved in coordinative and hydrogen bonded interactions simultaneously; thereby providing a route for the external hydrogen bonding of anions to influence the structure of the cluster formed.⁴ For this to be feasible, a rigid ligand with well defined metal binding sites and hydrogen bond donor/acceptor sites must be utilised.⁴

In this context we report the novel $\{\text{Cu}^{\text{II}}_3\text{Cl}\}$ triangular cluster compounds **1** and **2** ($[\text{Cl}(\text{CuCl}_2\text{tachH})_3]\text{X}_2$, tach = *cis,trans*-1,3,5-triamino-cyclohexane, X = Cl in **1** and X = Br in **2**),^{†5} that are formed by simultaneous coordinative and hydrogen bonded interactions facilitated by the utilisation of the *trans*-tach ligand, see Fig. 1. As a result of the combination of these interactions, the triangular clusters are arranged into magnetically isolated infinite chains, within a 3-D network, that is formed by hydrogen bonded interactions between triangular $\{\text{Cu}^{\text{II}}_3\text{Cl}\}$ cluster units, see Fig. 2.⁶ These materials exhibit a combination of spin frustration and spin-chain behaviour.⁷ Furthermore, the trimeric cluster entities represent the first examples of a coordination complex to support a μ_3 -chloro ligand in a trigonal planar coordination mode.⁸

The trimeric clusters are composed of three $[\text{CuCl}_2\text{tachH}]^+$ units with each of the copper(II) ions chelated by two *cis*-positioned N

sites of tach (average Cu–N distance = 2.008 Å). The remaining two basal sites of the tetragonal-pyramidal Cu coordination environment are occupied by two terminal chloro ligands (average Cu–Cl distance = 2.325 Å). The fifth, apical site, is completed by a trigonal planar μ_3 -chloro ligand, a previously unknown coordination mode for chloro ligands,⁸ linking the three $[\text{CuCl}_2\text{tachH}]^+$ units (average μ_3 -Cl–Cu distance = 2.576 Å). Each cluster is anchored within an extended 3-D array of 36 hydrogen bonded interactions, see Fig. 2. Within the crystallographic *ab* plane, the 2-D network consists of intra- and intermolecular hydrogen bonded interactions. The intramolecular interactions consist of H-bonds between terminal chloro ligands and coordinating amino groups (green dotted lines, average $-\text{NH}_2\cdots\text{Cl}(\text{Cu})$ distance = 3.385 Å) facilitating the unusual trigonal planar coordination mode of the central μ_3 -chloro ligand. Additionally, intermolecular H-bonds are found between protonated *trans*-amino groups and either two non-coordinated chloride (**1**), or two bromide (**2**) counter-ions (blue dotted lines, average $-\text{NH}_3^+\cdots\text{X}$ distance = 3.176 Å when X = Cl and 3.313 Å when X = Br), which are themselves located on crystallographic 3-fold axes. Furthermore, each cluster is involved in bifurcated intermolecular hydrogen bonded interactions between protonated *trans*-amino groups and terminal chloro ligands (pink dotted lines, average $-\text{NH}_3^+\cdots\text{Cl}(\text{Cu})$ distance = 3.219 Å). In addition to the extensive hydrogen bonded network within each layer, the coordinating amino groups and terminal chloro ligands interconnect the $\{(\mu_3\text{-Cl})\text{Cu}^{\text{II}}_3\}$ triangles of neighbouring layers with an average $\text{Cu}-\text{NH}_2\cdots\text{Cl}-\text{Cu}$ distance of 3.299 Å to form 1-D chains along the *c* axis (red dotted lines).

Here, the trimeric cluster entities are stacked in a hexagonal fashion parallel to the crystallographic *c* axis (Fig. 3), such that the μ_3 -chloro centres are aligned above each other (inter-layer Cl–Cl separation: 6.314 Å (**1**) and 6.326 Å (**2**) compared to intra-layer Cl–Cl separations of 12.680 Å (**1**) and 12.696 Å (**2**)), while the $\{(\mu_3\text{-Cl})\text{Cu}^{\text{II}}_3\}$ triangles are rotated by 60° to each other.

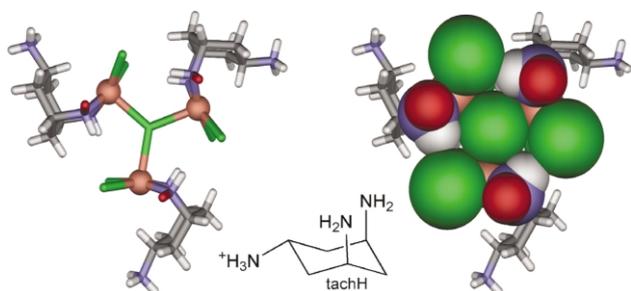


Fig. 1 Representations of the triangular clusters present in **1** and **2** (left: stick representation, the Cu ions are shown as spheres; right: CPK overlay of the primary coordination sphere). The non-coordinated hydrogen bonded halide counter-ions are omitted. (Cl: green, N: blue, C: grey, Cu: pink). The H positions are shown in white except those that are involved in the formation of the Heisenberg chains, shown in red.

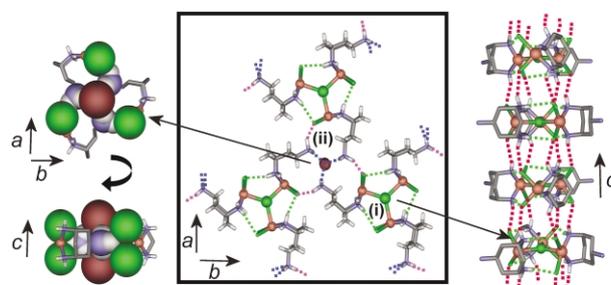


Fig. 2 The central view shows the 2-D network with the hydrogen bonded halide counter-ions in the centre linking three $\{\text{Cu}^{\text{II}}_3\text{Cl}\}$ triangular cluster units (i) via the different classes of hydrogen bonded interactions (coloured dotted lines). The left views show the primary coordination sphere around the hydrogen bonded halides (ii) (halides and nitrogen atoms shown as CPK); the top view is shown projected onto the *ab* plane and the bottom view is perpendicular to the *c* axis. The right view shows a representation of the 1-D chains formed between the $\{\text{Cu}^{\text{II}}_3\text{Cl}\}$ cluster units that run parallel to the *c* axis. H: white, Cl: green, N: blue, C: grey, Cu: pink, Cl/Br sites in **1** and **2**, respectively: brown.

† Electronic supplementary information (ESI) available: full synthetic and analytical details. See <http://www.rsc.org/suppdata/cc/b4/b402487g/>

This results in infinite linear stacks that are composed of alternating $\{\text{Cu}^{\text{II}}_3\}$ triangles along the crystallographic c axis, see Fig. 3. The observed temperature dependencies of the magnetic susceptibility of **1** and **2** are virtually identical and show antiferromagnetic coupling of the $S = \frac{1}{2}$ Cu^{II} centres. A model for these data cannot be solely based on the isolated, equilateral $\{\text{Cu}^{\text{II}}_3\}$ [$S = \frac{1}{2}$] $_3$ triangles—the most simple frustrated spin systems—but requires to take antiferromagnetic inter-triangle coupling into account that involves the six $\text{Cu}-\text{Cl}\cdots\text{H}-\text{N}-\text{Cu}$ super-exchange pathways between two $\{\text{Cu}^{\text{II}}_3\}$ triangles of neighbouring hexagonal layers.

The in-plane inter-triangle exchange is insignificant due to much longer exchange pathways (the closest $\text{Cu}\cdots\text{Cu}$ distance is 8.363 Å). At high temperatures, the magnetism of the system is dominated by the stronger antiferromagnetic intra-triangular coupling, thus resembling the properties of a $\{\text{Cu}^{\text{II}}_3\}$ triangle. At lower temperatures, the triangles effectively assume the net spin of their $S = \frac{1}{2}$ ground state, and the weaker antiferromagnetic inter-triangle exchange couples these net spins to an equidistant Heisenberg chain.⁷ As extensive numerical simulations are required to exactly describe a one-dimensional system such as **1** and **2**, we here only give estimates for the effective intra- and inter-triangle exchange interactions by fitting the susceptibility data for higher temperatures ($T > 10$ K) to the isotropic Heisenberg model for a $\{\text{Cu}^{\text{II}}_3\}$ triangle and for lower temperatures ($T < 6$ K) to the Bonner–Fisher model of a uniformly spaced linear Heisenberg chain (Fig. 4).⁹ This approach gives $J_{\text{intra}}/k = -9.2$ K for the intra-triangle and $J_{\text{inter}}/k = -2.7$ K for the total effective inter-triangle coupling and an isotropic g value of 2.095. This is supported by EPR X-band measurements of a powder sample of **2** at room temperature which shows a broad, symmetric line ($\Delta H_{\text{pp}} = 264$ G) corresponding to g_{iso} of 2.105.

The weak inter-triangle antiferromagnetic interactions are exclusively mediated by the hydrogen bonds¹⁰ between neighbouring

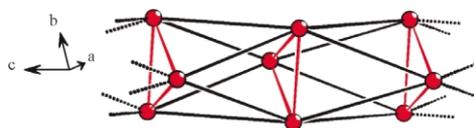


Fig. 3 The magnetic framework of **1** and **2** with halide-mediated intra-triangle exchanges (red bonds) and halide-amino-mediated inter-triangle exchanges (black bonds, intra/inter-triangle $\text{Cu}\cdots\text{Cu}$ distances: 4.46/6.82 Å).

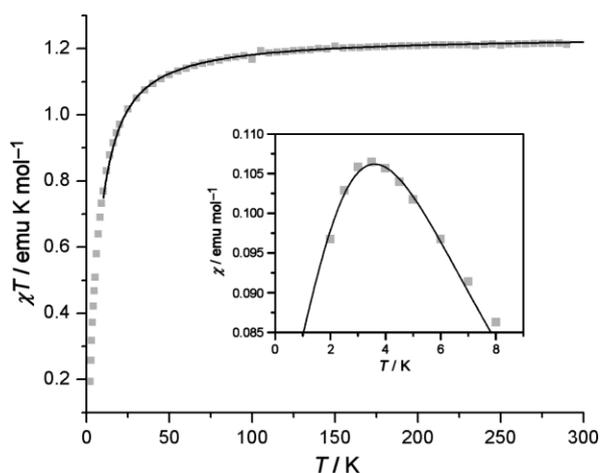


Fig. 4 Temperature dependence of χT at 0.1 Tesla for compound **2**. The solid line, superimposed over the experimentally derived values (grey squares), represents the fit of the high-temperature data (10–290 K) to the Heisenberg model for an equilateral $\{\text{Cu}^{\text{II}}_3\}$ triangle. The inset shows the observed low- T maximum around 3.5 K in the temperature dependence of the molar susceptibility with a best fit to the Bonner–Fisher model of an equidistant linear $S = \frac{1}{2}$ Heisenberg chain for the 2–7 K interval.

layers. However, for the intra-triangle interactions two exchange pathways exist: First, through intra-triangle H-bonds (which connect the coordinating amino groups and terminal chloro ligands and hence involve the magnetic $\text{Cu } d_{x^2-y^2}$ orbitals that span the basal plane of these ligands). Second, to a less significant degree, *via* the central μ_3 -chloro ligand (overlap between the $\text{Cu } d_{z^2}$ orbitals, which to a small degree may mix with the $d_{x^2-y^2}$ orbitals, and the Cl p orbitals).¹¹

In summary, the triangular $\{\text{Cu}^{\text{II}}_3\text{Cl}\}$ clusters **1** and **2** assemble into magnetically isolated chains, showing Heisenberg spin-chain behaviour at low T , facilitated by an unusual chloro coordination motif and extended 3-D hydrogen bonded network. The present study will be continued by additional theoretical and experimental studies to examine the nature of the exchange interactions, as well as further development of the use of both exogenous and coordinating anions to template and assemble new types of coordination clusters.

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Notes and references

† Crystallographic data: (**1**) $\text{C}_{18}\text{H}_{48}\text{N}_9\text{Cl}_7\text{Cu}_3$, $M = 900.32$ g mol⁻¹, trigonal, space group $P6_3/m$ (no. 176), $a = 12.6800(20)$, $b = 12.6800(20)$, $c = 12.6287(13)$ Å, $V = 1758.44(4)$ Å³, $Z = 2$, $\mu(\text{Mo}-\text{K}\alpha) = 2.508$ mm⁻¹, 14125 reflections measured, 1679 unique which were used in all calculations; structure solution and refinement as done using WINGX.¹² Final $R1 = 0.051$ and $wR2 = 0.133$ (all data). (**2**) $\text{C}_{18}\text{H}_{48}\text{N}_9\text{Br}_2\text{Cl}_7\text{Cu}_3$, $M = 989.24$ g mol⁻¹, trigonal, space group $P6_3/m$ (no. 176), $a = 12.6961(2)$, $b = 12.6961(2)$, $c = 12.66511(2)$ Å, $V = 1766.04(0)$ Å³, $Z = 2$, $\mu(\text{Cu}-\text{K}\alpha) = 9.841$ mm⁻¹, 6507 reflections measured, 1170 unique which were used in all calculations. Final $R1 = 0.056$ and $wR2 = 0.192$ (all data). CCDC 221962 and 219624. See <http://www.rsc.org/suppdata/cc/b4/b402487g/> for crystallographic data in .cif or other electronic format.

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