Structure and magnetic properties of a novel copper halide framework $\{[^t\mathrm{BuNH}_3]_2[\mathrm{Cu}_3(\mu_3\text{-OH})(\mu_2\text{-H}_2\mathrm{O})\mathrm{Cl}_7]\}_n$ synthesized *via in situ* templation†

Tristram Chivers,*[a] Zhiyong Fu[a] and Laurence K. Thompson[b]

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The use of the tris(alkylamido)phosphate $OP[N(H)^tBu]_3$ as an *in situ* source of the templating agent $[^tBuNH_3]^+$ produces the copper halide chain $\{[^tBuNH_3]_2[Cu_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)Cl_7]\}_n$ (1) in a solvothermal process; the novel antiferromagnetically coupled trinuclear fragment $Cu_3(OH)(H_2O)Cl_7$ is the building block in the polymeric anion in 1.

Copper(II) halide framework materials have attracted much attention for their interesting magnetic properties and structural richness.[1] The most commonly employed technique to modulate the anionic network of inorganic materials, *e.g.*, aluminosilicates, aluminophosphates or copper halide systems, involves the direct addition of an organic cation as a templating reagent.[2] Recently, the use of P–N bond cleavage in $OP(NMe_2)_3$ to control the release of an organic amine has emerged as a new templating method for the synthesis of unprecedented zinc phosphate frameworks.[3] Since the formation of anionic networks is kinetically controlled and highly sensitive to reaction conditions, this indirect template effect is a potentially versatile approach for the production of novel inorganic frameworks. Studies of the indirect method may also contribute to an understanding of the mechanism of network formation.[4] Here, we report the first example of the application of this strategy to copper halide systems using a tris(alkylamido)-phosphate $OP[N(H)^tBu]_3$ as a source of the organic cation. The *in situ* formation of $[^tBuNH_3]^+$ during the solvothermal reaction directs the assembly of a copper halide chain $\{[^tBuNH_3]_2[Cu_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)Cl_7]\}_n$ (**1**) in which the repeating unit is a novel trinuclear cluster. By contrast, the direct addition of $[^tBuNH_3]^+$ ion to a $CuCl_2{\cdot}2H_2O$ solution produces the polymer $[^tBuNH_3][CuCl_3]\}_n$ (**2**), which contains a known anionic structural motif, *cf.* $[(CH_3)_2CHNH_3][CuCl_3]$.[5] The protonated complex $[P(OH)(NH^tBu)_3]_4[Cu_2Cl_6]{\cdot}C_7H_8$ (**3**) was characterized as a by-product in the synthesis of **1**.

The solvothermal reactions of $CuCl_2{\cdot}2H_2O$ with $OP[N(H)^tBu]_3$ in a molar ratio of 1 : 1 at 80 °C led to the formation of yellow crystals, which were identified by X-ray crystallography as $\{[^tBuNH_3]_2[Cu_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)Cl_7]\}_n$ (**1**).† The use of $[^tBuNH_3]Cl$ instead of $OP[N(H)^tBu]_3$ produced $[^tBuNH_3]$-$[CuCl_3]\}_n$ (**2**) in *ca.* 50% yield. The repeating unit in the polymer chain in **1** is a trinuclear cluster $[Cu_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)Cl_7]$, which lies across a mirror plane of symmetry (Fig. 1). This building block can be viewed as a *seco*-cube in which alternate corners are occupied by non-metal (two chlorines and two oxygens) and metal (three copper) atoms. Two kinds of copper centers exist in the structure. One (Cu1) exhibits distorted square pyramidal coordination with three chlorine and one oxygen donors in the equatorial plane, while the second oxygen atom occupies the axial position. The Cu–Cl distances, which lie in the range 2.2564(13)–2.2821(11)Å, and the Cu1–O1 bond length of 2.012(2)Å are similar to previously reported values for copper halide anions.[6,7] However, the Cu1–O2 bond distance of 2.327(3) Å is substantially longer and the bond angle ∠O1–Cu1–Cl1 is approximately linear (177.11(11)°), indicating that the geometry of this five coordination copper center is a typical folded 4 + 1.[1] The geometry of the other copper atom (Cu2) is approximately octahedral ($CuOCl_5$). Four chlorine atoms lie in a plane with bond lengths of Cu2–Cl2 = 2.5115 (12)Å, Cu2–Cl4 = 2.5161(12)Å; the coordination sphere is completed by one chlorine and one oxygen atom (Cu2–O1 = 1.944(4)Å, Cu2–Cl3 = 2.2462(15)Å). The CuO_2Cl_3 square pyramid and $CuOCl_5$ octahedron share a common edge (Cl_4, Cl_{4a} and O_1) to form a μ_3-O_1-centered Cu_3 configuration. This overall arrangement results in Cu–Cu contacts of 3.182Å and 3.311Å. Chloride bridges link these trinuclear clusters forming a one dimensional structural motif.

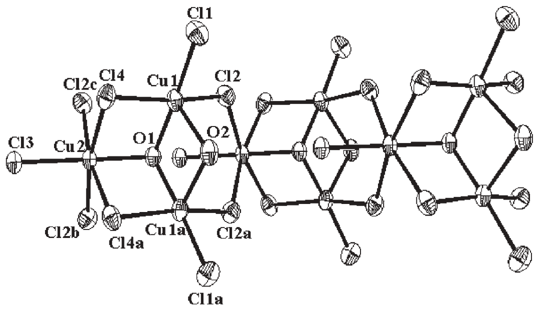

Fig. 1 X-Ray crystal structure of $[Cu_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)Cl_7]\}_n$ (**1**), 70% thermal ellipsoids are shown. Hydrogen atoms have been omitted.

Ligand–lattice interactions and crystal packing effects are important factors in determining the configuration of anionic frameworks.[1] In **1** the two rows of $[^tBuNH_3]^+$ ions occupy the interspace between two chains whereas the distribution of $[^tBuNH_3]^+$ ions in **2** consists of a single wave-like chain (Fig. 2). Because the density of $[^tBuNH_3]^+$ ions in **1** is higher than that in **2**, more organic cations have interactions with halide ions, which can reduce the ligand–ligand repulsion effects. Consequently, a more complex structural unit with copper centres in higher coordination

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† Electronic supplementary information (ESI) available: details of the syntheses and crystal data of **1**, **2** and **3**, and an ORTEP drawing of **3**. See http://www.rsc.org/suppdata/cc/b5/b501040c/

*chivers@ucalgary.ca

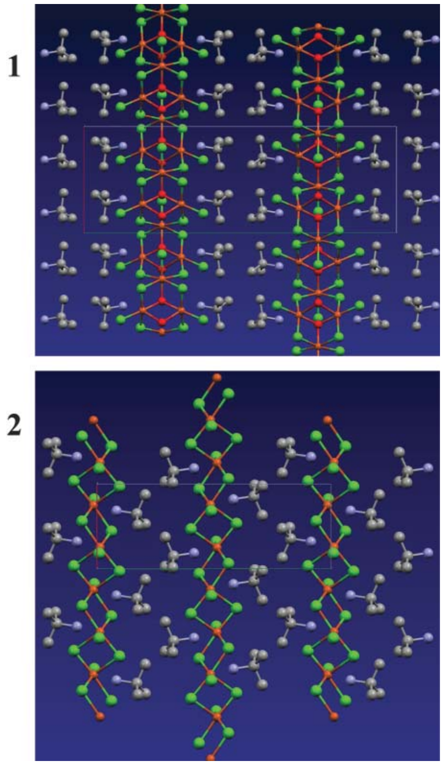
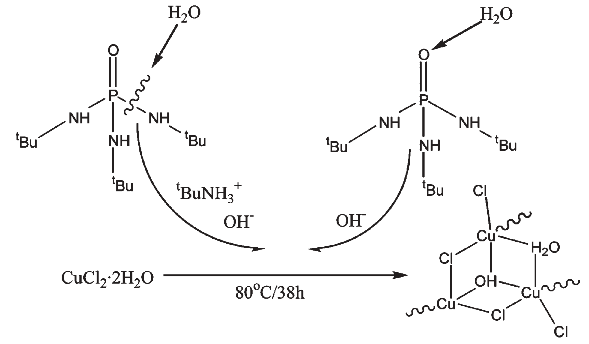


Fig. 2 Packing diagrams of the unit cells of **1** and **2** viewed along the [001] direction.

sites may be formed. The node of the chain in **1** is a trimeric cluster, whereas in **2** it is a single metal centre. The formulation of **1** as $\{[{}^{t}BuNH_3]_2[Cu_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)Cl_7]\}_n$ with a triply bridging OH^- ion and three Cu(II) centres is supported by bond valence sum analyses.[8] The calculated charge for Cu1 is 2.013 and that for Cu2 is 1.984.

A few crystals of a by-product **3** from the synthesis of **1** were isolated and characterized by IR spectroscopy and single crystal X-ray diffraction.† The IR data indicate that the $PO(NH^tBu)_3$ molecule acts as a proton acceptor. A well-defined band at 3504 cm^{-1} is attributed to an OH vibration. The X-ray analysis identified **3** as $[P(OH)(NH^tBu)_3]_4[Cu_2Cl_6]\cdot C_7H_8$ composed of four $[P(OH)(NH^tBu)_3]^+$ cations encircling the tetraanion $[Cu_2Cl_6]^{4-}$. The P–O bond distance of the protonated tris(amido)phosphate (P1–O1 = 1.494(6)Å, P2–O2 = 1.498(7)Å) is a little longer than that of the neutral precursor $PO(NH^tBu)_3$ (P–O = 1.474(3)Å), and is shorter than that of the monoanion $[PO(N^tBu)(NH^tBu)_2]^-$ (P–O = 1.517(2)Å) in the trimeric lithium salt.[9]

In **1** two oxygens from water of crystallization in $CuCl_2\cdot 2H_2O$ bridge the copper centers forming a Cu_2O_2 unit , while in **2** they are no water molecules in the framework. Although water may be a successful competitor for ligand sites, it is surprising that it seldom coordinates to copper centers as a bridging ligand even in hydrothermal reactions.[10] The different behaviour may be related to the pH value. A pH regulator, *e.g.* NaOH, can enable a water molecule to occupy a position in the copper coordination sphere as a bridging ligand in **1** in preference to a chloride ligand, for example, in $[Cu_7(OH)_6Cl_2(pn)_6(H_2O)_2][C(CN)_3]_4Cl_2$.[7] In the indirect method, $OP[N(H)^tBu]_3$ not only generates the templating ion $[{}^{t}BuNH_3]^+$ but also accepts a proton in the solvothermal process thus enabling water to occupy a position as a bridging ligand. The generation of OH^- ions is an important factor in the formation of the $[Cu_3(OH)(H_2O)Cl_7]^{2-}$ cluster. As indicated in Scheme 1, there are two possible ways to produce the OH^- ions in this process. One alternative involves P–N bond cleavage, generating the OH^- and $[{}^{t}BuNH_3]^+$ ions simultaneously. The other implicates protonation of $PO(NH^tBu)_3$ during the solvothermal reaction.



Scheme 1

The variable temperature magnetic properties of **1** are shown in Fig. 3 as plots of χ_{mol} and μ_{mol} as a function of temperature. A slight shoulder is visible in the χ_{mol}–T profile at ~50 K indicative of antiferromagnetic exchange, but the low temperature moment of 0.91 μ_B at 2 K is much lower than would be expected for a triangular copper(II) system involving just intra-trinuclear exchange coupling (the ground state for an isolated triangle of Cu(II) centers would be $S = 1/2$). Antisymmetric exchange has been invoked in rare cases to explain lower than expected moments at low temperatures for symmetric μ_3-OH[11] and μ_3-OMe[12] triazole and pyrazole (respectively) bridged triangular $Cu(II)_3$ complexes, where moments dropped to around 1.4 μ_B, and there is no indication of any significant intermolecular exchange. In the current system the triangular subunits are not isolated, and are part of a chain structure, and so interpretation of the global exchange situation requires a close inspection of the intramolecular and intermolecular connections, and in particular the magnetic ground states of each copper ion.

The overall chain structure in **1** involves the triangular subunits, which are linked through two Cu(1)–Cl(2)–Cu(2) connections. The Cu(1) centers have square pyramidal geometries

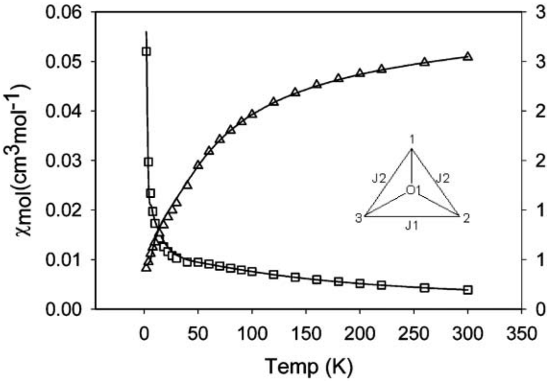


Fig. 3 Plot of magnetic susceptibility χ_m *vs.* T (□) and magnetic moment μ_m *vs.* T (△) for **1**.

implying $d_{x^2-y^2}$ magnetic ground states, with a basal bridging connection though a μ_3-hydroxide O(1), and an apical bridging connection through water O(2). The Cu(1)–O(1)–Cu(1)′ angle of 110.74° would predictably lead to substantial antiferromagnetic exchange through this bridge, while the orthogonal connectivity through O(2) would not lead to significant exchange in comparison. The geometry at Cu(2) is unusual in that it is tetragonally compressed indicating a d_{z^2} magnetic ground state. The long Cu(2)–Cl(4) and Cu(2)–Cl(2) bonds (2.516 Å and 2.512 Å respectively) define the basal component, while the axial bonds (Cu(2)–O(1) 1.944 Å, Cu(2)–Cl(3) 2.246 Å) are much shorter. Within each triangular subunit Cu(2) is connected to the Cu(1) centers by O(1) and two Cl(4) bridges. These do not constitute orthogonal connections, because the d_{z^2} orbital has electron density spread over all three axes. The Cu(2)–O(1)–Cu(1) angles are 107.11°, and so a different antiferromagnetic exchange component would of necessity result, leading to an exchange model based on an isosceles triangle with two J values (Fig. 3; $J1$ and $J2$). The appropriate exchange Hamiltonian is given in eqn. (1). Normal spin vector coupling leads to a series of total spin (S') quantum numbers, and their associated energies, which can be substituted into the Van Vleck equation (eqn. (2)) to calculate the molar susceptibility as a function of temperature.

$$H_{\mathrm{ex}} = -2J1(S_2\cdot S_3) - 2J2[(S_1\cdot S_2 + (S_1\cdot S_3)] \qquad (1)$$

$$\chi_{\mathrm{M}} = \frac{N\beta^2 g^2}{3k(T-\theta)} \frac{\Sigma S'(S'+1)(2S'+1)\,e^{-E(S')/kT}}{\Sigma(2S'+1)\,e^{-E(S')/kT}} + \mathrm{TIP} \qquad (2)$$

The low residual moment at 2 K (0.91 μ_B) indicates that further antiferromagnetic exchange must be occurring, and logically this must be between the trinuclear subunits in the chain. The triangular subunits are linked through two Cl(2) bridges, and in fact could be considered as a triangular array of copper centers as well forming what is effectively a linear fusion of triangles. The connections between Cu(2) and Cu(1) *via* these bridges again are non-orthogonal, clearly representing the other antiferromagnetic component. In order to model this complex system we have adopted a simplified approach in which the trinuclear exchange equation derived from eqn. (2) is adapted with a molecular field correction term θ, where $\theta = z \times J3 \times \chi_{\mathrm{mol}}$, and $J3$ represents the exchange between pairs of trinuclear subunits. The fitted line in Fig. 3 was obtained by using a non-linear regression of the experimental data to eqns. (1) and (2) for g = 2.23, $J1 = -84.0$ cm^{-1}, $J2 = -15.0$ cm^{-1}, $J3 = -11$ cm^{-1} (z = 2), TIP = 200 × 10^{-6} cm^3 mol^{-1}, ρ = 0.003 (10^2R = 0.52; $R = [\Sigma(\chi_{\mathrm{obs}} - \chi_{\mathrm{calc}})^2/\Sigma\chi_{\mathrm{obs}}^{\,2}]^{1/2}$) (TIP = temperature independent paramagnetism, ρ = fraction of paramagnetic impurity).

The dominant exchange term ($J1$) is assigned reasonably to the Cu(1)–O(1)–Cu(1)′ non-orthogonal bridge (110.74°), involving direct superexchange between $d_{x^2-y^2}$ magnetic orbitals. $J2$ involves a combination of $d_{x^2-y^2}$ and d_{z^2} orbitals on Cu(1) and Cu(2) *via* O(1) and Cl(4), with smaller oxygen bridge angles and two chlorine bridges, and obviously a more diffuse overlap situation. The much weaker exchange in this case is therefore quite reasonable. The smaller exchange for $J3$ is by the same token sensible, since two somewhat similar chlorine bridges are involved. Given these reasonable assignments it is not necessary to consider antisymmetric exchange contributions within the triangular subunits.

In summary, the tris(alkylamido) phosphate OP[N(H)^{t}Bu]$_3$, serves both as a proton acceptor and as an indirect source of the [^{t}BuNH$_3$]$^+$ cation in the generation of a novel polymeric copper halide framework with a trinuclear cluster as the repeating unit. The identification of the [P(OH)(NH^{t}Bu)$_3$]$^+$ cation indicates that protonation plays an important role in the formation of the title compound. An understanding of the reaction mechanism of the *in situ* templation process will help in the rational design and synthesis of additional novel inorganic materials that are inaccessible by the direct approach.‡

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Tristram Chivers,*[a] Zhiyong Fu[a] and Laurence K. Thompson[b]
[a]Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4. E-mail: chivers@ucalgary.ca;
Fax: (+1 403) 289-9488; Tel: (+1 403) 220-5741
[b]Department of Chemistry, Memorial University, St John's, Newfoundland, Canada A1B 3X7

Notes and references

‡ Summary of crystal data for **1**, **2** and **3** are available as ESI. CCDC reference numbers 261137, 261138 and 261139. See http://www.rsc.org/suppdata/cc/b5/b501040c/ for crystallographic data in .cif format.

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