

Hydrothermal synthesis and structural characterization of $[\text{Cu}(\text{en})_2]_2\text{Cu}_7\text{Cl}_{11}$: a three-dimensional open-framework copper halide with occluded $[\text{Cu}(\text{en})_2]^{2+}$ cations

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A new type of three-dimensional open-framework copper chloride, prepared simply by the hydrothermal treatment of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ and en, is built up from unusual chloride bridged Cu_4 tetramers connected by $\text{CuCl}_{3/3}$ units and has voids in the framework that are filled with charge-compensating $[\text{Cu}(\text{en})_2]^{2+}$ cations.

While the utility of the aluminosilicate zeolites¹ derived from their shape selective absorptivities, reactive acid sites and substantial chemical and thermal stability remains unsurpassed, recent synthetic efforts have sought to expand the chemical reactivity and catalysis associated with open framework inorganic materials to a variety of new systems. Early efforts produced the large class of aluminophosphate materials.^{1d,2} In hopes of increasing the chances of observing new types of shape selective catalysis by incorporating d-block elements into these materials as stoichiometric framework constituents, organically templated solids such as molybdenum phosphates,³ vanadium phosphates,⁴ cobalt phosphates⁵ and vanadium oxides⁶ have recently been prepared. It appears that the organic templates used in the syntheses not only fulfill the requirement of leaving a molecular sized void in the framework upon post-synthesis removal, but are essential for the synthesis by providing a species that can allow the crystal to grow *via* charge neutralization at the crystal/solution interface by virtue of possessing a suitable shape and charge to volume ratio. Such incorporation of an organic molecule will necessarily induce a large degree of structural complexity into the system by virtue of the relatively large number of framework atoms required to totally encapsulate the large molecule. We report here an extension of this concept of templating a three-dimensional anionic framework with bulky cations to the copper halide system with the hydrothermal synthesis and structural characterization of $[\text{Cu}(\text{en})_2]_2\text{Cu}_7\text{Cl}_{11}$ **1** (en = ethylenediamine), a three-dimensional copper halide open-framework material with entrained $[\text{Cu}(\text{en})_2]^{2+}$ cations.

The halide $[\text{Cu}(\text{en})_2]_2\text{Cu}_7\text{Cl}_{11}$ **1** is prepared from the extremely simple reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, en and water in a mole ratio of 1 : 1.4 : 148 at 170 °C for 4 days, and is isolated as purple crystals.† The X-ray structural analysis of **1**‡ shows the material to be an open-framework solid with a topologically unique framework composed of copper and chlorine. The formulation of the framework as all diamagnetic Cu^+ with entrained $[\text{Cu}(\text{en})_2]^{2+}$ (d^9 $S = 1/2$) centers is supported by magnetic measurements which show the compound to be paramagnetic with μ_{eff} (300 K) = 2.43(1) μ_{B} and $\theta = -4.0(3)$ K.

The framework of **1** is constructed from the unusual Cu_4 tetrameric building blocks (Fig. 1) which contain copper tetrahedrally coordinated by chloride ligands. The tetramer is composed of a dimer of edge-sharing CuCl_4 tetrahedra, with the two Cl atoms which form the shared edge also coordinated to two copper atoms from a corner-sharing dimer of CuCl_4 tetrahedra, which results in these two Cl atoms connecting the

dimers in a μ_3 fashion. The tetramers are linked into a covalently bonded three-dimensional lattice by three coordinate Cu atoms (Fig. 2). The Cu atoms in these three-coordinate sites display slightly pyramidal trigonal coordination, with the Cu displaced 0.41 Å above the least-square plane of the three Cl atoms, and are crystallographically disordered into two sites on either side of this plane.

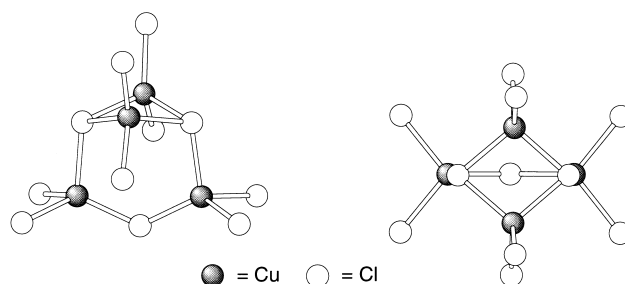


Fig. 1 Two views of the Cu_4 tetramer found in $[\text{Cu}(\text{en})_2]_2\text{Cu}_7\text{Cl}_{11}$ **1** which is composed of two-edge sharing CuCl_4 tetrahedra, the two bridging chloride ligands of which also form two vertices from a corner-sharing pair of CuCl_4 tetrahedra, thereby adapting a μ_3 coordination mode

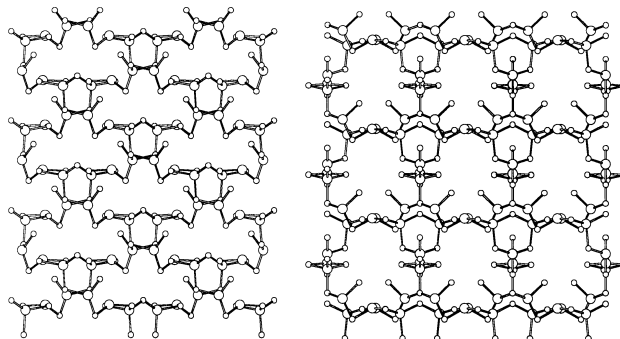


Fig. 2 Two views of the structure of $[\text{Cu}(\text{en})_2]_2\text{Cu}_7\text{Cl}_{11}$ **1** 45° apart and parallel to the *ab* plane showing the manner in which the Cu_4 tetramers are linked by the $\text{CuCl}_{3/3}$ groups; the $[\text{Cu}(\text{en})_2]^{2+}$ cations have been omitted for clarity

The three-dimensional copper halide framework can be conceptually envisioned as being built up in space group $P4_2nm$ from the aforementioned tetramers connected along the 4_2 screw axis *via* the trigonal $\text{CuCl}_{3/3}$ bridges into rectangular spirals. These spirals are in turn intertwined with another crystallographically identical spiral to give copper halide double helices as shown in Fig. 3. Unlike the recent example of chiral inorganic double helices found in the vanadium phosphate $[\text{NH}_2\text{Me}_2]\text{K}_4[\text{V}_{10}\text{O}_{10}(\text{H}_2\text{O})_2(\text{OH})_4(\text{PO}_4)_7] \cdot 4\text{H}_2\text{O}$ ⁷ mirror images of the double helix in the title compound must also exist in the crystal since $P4_2nm$ is not an enantiomorphic space group. In fact, each double helix is fused with and is surrounded by four identical double helices of the opposite handedness that

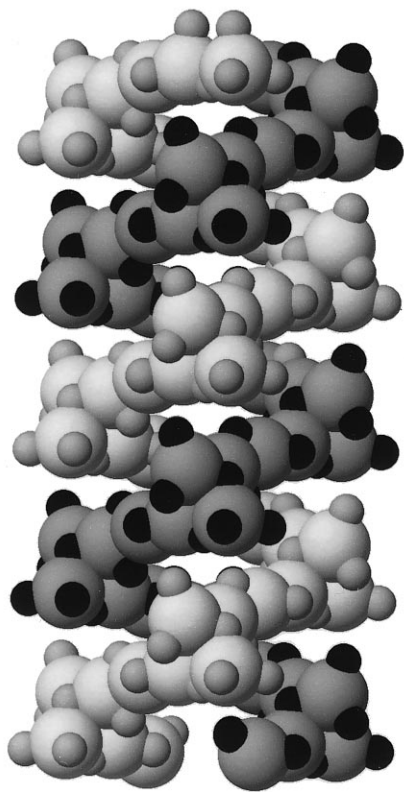


Fig. 3 The copper halide double helices in $[\text{Cu}(\text{en})_2]_2\text{Cu}_7\text{Cl}_{11}$ **1**

are related to one another by the mirror planes present on (110) and $(\bar{1}\bar{1}0)$.

This connectivity generates voids in the framework that are filled by charge-compensating $[\text{Cu}(\text{en})_2]^{2+}$ cations. The $[\text{Cu}(\text{en})_2]^{2+}$ cations interact with the framework not only via two long axial Cu–Cl interactions at 2.77 and 2.80 Å, but also with numerous interactions in the range 3.3–3.6 Å from the N atoms of the en to the Cl atoms of the framework which are presumably N–H...Cl hydrogen bonds. Bond angles for these N–H...Cl interactions range from 153.3 to 171.7°, further supporting the existence of hydrogen bonds.

The hydrothermally mediated, cation-directed crystallization of covalently bonded three-dimensional framework materials with large occluded cations has been extended to the halide system with the synthesis and structural characterization of $[\text{Cu}(\text{en})_2]_2\text{Cu}_7\text{Cl}_{11}$ **1**. It is clear that highly crystalline materials with covalently bonded three-dimensional frameworks as reported here would be very difficult to prepare at room temp. The increased solvating ability of water at higher temperatures is definitely necessary to provide the environment required for the assembly of covalent three-dimensional solids from simple precursor crystal growth. Since these reaction conditions or starting materials could hardly be simpler, this method should be applicable to the preparation of a very large number of new solids with potentially interesting or useful molecular sieving,

photochemical or catalytic properties. This method has yielded a variety of large copper halide clusters, one-dimensional polymers and layered solids with coordinated organic ligands, which will be reported shortly.

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Footnotes

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† *Experimental procedure*: ethylenediamine (0.20 ml, 0.0042 mol) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.51 g, 0.003 mol) in 8 ml water contained in a 23 ml polytetrafluoroethylene-lined Parr acid digestion vessel. The vessel was sealed and heated to 170 °C for four days under autogeneous pressure. After cooling, purple crystals were isolated and washed with water. Powder X-ray diffraction shows the product to be monophasic.

‡ *Crystal data for 1*: Tetragonal, space group $P4_2nm$, $a = 13.241(2)$, $c = 8.953(2)$ Å, $V = 1569.7(5)$ Å³, $Z = 8$, $M_w = 300.56$ g mol⁻¹, $D_c = 2.544$ g cm⁻³. The structure was solved by direct methods and refined using full-matrix least squares on F^2 with SHELXTL. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement was based on 1294 reflections with $I > 2.0\sigma(I)$ and converged with $R(R_w) = 0.0362(0.0843)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/490.

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