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# The Hydrogen-Bonded Framework of the First Anti-Zeotype: $[\{(H_2NEt_2)_2\}_2(CuCl_4)][AlCl_4]$**

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Zeolites are the archetypal class of porous framework materials whose host–guest interactions have been tailored to a variety of industrial processes such as catalysis and gas separation.[1] Zeolites are constructed from silicate and aluminate building blocks in which the tetrahedral cations are covalently linked by two-coordinate anions (oxygen) into a plethora of micro- and mesoporous frameworks.[2–4] In these systems the size and shape of the pore structure is controlled during synthesis by molecular or cationic templating species. By use of charge-matching techniques, numerous oxide-based framework materials analogous to zeolites have been reported, including frameworks rich in transition metals such as the recently reported cobalt phosphates.[5] We recently demonstrated an extension of such charge-matching techniques to include substitution of framework anions, as well as cations, in the preparation of halozeotypes $[Cu_nZn_{m-n}Cl_{2m}]^{n-}$, which are direct analogues of aluminosilicates.[6] The preparation of other non-oxide zeotype materials has recently been reviewed.[4] Here we describe the first example of an "inverse" charge-matching strategy, by which an anti-zeotype framework structure is constructed from the linkage of tetrahedral anions by two-coordinate cations.

The synthesis of open-framework materials based on principles of structural anti-types, in which the positions of the framework anions and cations are reversed (such as in fluorite, $CaF_2$, and anti-fluorite structures, $Li_2O$) has to our knowledge never been reported. Unlike classic zeotype frameworks, in which an anionic or neutral framework is templated by extra-framework cations or molecules, our anti-zeotype constructions, in which tetrahedral anions are linked by two-coordinate cations, can be utilized to prepare cationic frameworks templated by noncoordinating extra-framework anions. Such anion templating is expected to yield both novel open-framework structures and unique properties.[7]

Previously, several metal-organic cationic frameworks have been prepared in which neutral, bidentate ligands link cationic metal centers into covalent networks.[4, 8, 9] However, in these metal-organic frameworks, the cationic metal centers are coordinatively saturated by the two-coordinate linker ligands such that the internal surface of the framework cavity which surrounds the anionic template consists of the neutral ligands. By contrast, in our anti-zeotype constructions, the internal surface of the open-framework voids will be composed of two-coordinate cationic linking units. This cationic surface of the framework void may be exploitable to increase anion-binding affinities.

Because of the utility of hydrogen bonding for the construction of supramolecular assemblies, dialkylammonium cations were examined as potential two-coordinate cations to link $[MCl_4]^{n-}$ tetrahedral anions. In spite of the importance of hydrogen bonding between cations and anions for supramolecular assembly and molecular recognition in biological systems, to date only a small number of organic and metal-organic supramolecular hydrogen-bonded frameworks have been constructed using exclusively ionic components,[7, 10–12] compared with the number of hydrogen-bonded assemblies prepared using neutral molecules as donors and acceptors.[13–16] Nevertheless the strength of interionic hydrogen bonds of around 40–190 $kJ\,mol^{-1}$[10] make such ionic constructions attractive for the preparation of more robust framework structures. In this present work, we exploit the hydrogen-bonding ability of dialkylammonium cations to link $[CuCl_4]^{3-}$ tetrahedral anions into the novel anti-zeotype framework $[\{(H_2NEt_2)_2\}_2(CuCl_4)]^+$, in which $[AlCl_4]^-$ anions fill the framework void. This cationic partial structure is shown in Figure 1. Such hydrogen-bonded frameworks are not expected to provide the rigid structures found for covalent zeolite-type frameworks; however, Yaghi et. al. have recently demonstrated microporosity in a framework constructed from hydrogen-bonded metal-organic complexes.[15]

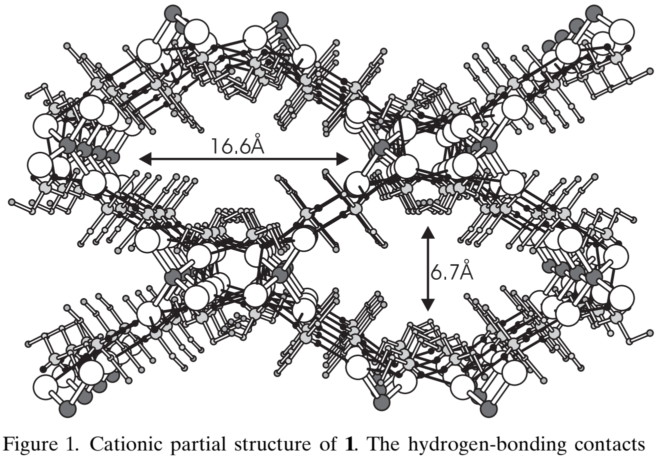

Figure 1. Cationic partial structure of **1**. The hydrogen-bonding contacts are indicated by solid lines. Cl: large open spheres, Cu: large black spheres, N: large gray spheres, C: small gray spheres, H: small black spheres.

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Slow cooling of a melt (250 °C) of CuCl, $AlCl_3$, and $H_2NEt_2Cl$ yielded $[(H_2NEt_2)_4(CuCl_4)][AlCl_4]$ (**1**) as a single-phase, microcrystalline product, as confirmed by Guinier X-ray powder diffraction and elemental analysis. Single crystals suitable for X-ray diffraction studies were obtained from the reaction of CuCl, $AlCl_3$, and wet $HNEt_2$.[17] In the crystal structure, the $[AlCl_4]^-$ tetrahedra exhibit ideal tetrahedral geometry with Al–Cl bond lengths of 2.1322(8) Å, and four Cl-Al-Cl angles of 109.36(4)° and two of 109.69(4)°. The $[CuCl_4]^{3-}$ tetrahedra, however, exhibit a slight tetragonal elongation with a Cu–Cl bond length of 2.3761(7) Å, and two Cl-Cu-Cl angles of 104.82(2)° and four of 119.23(3)°. Interestingly the only short N–H ··· Cl contacts, indicative of hydrogen bonding, are to the $[CuCl_4]^{3-}$ tetrahedra with Cl ··· H distances of 2.43–2.61 Å (Cl–N 3.2–3.3 Å). The shortest contacts of the ammonium cations to the aluminum-bound chloride atoms are by the alkyl groups with distances of 3.9 Å between the aluminum-bound chloride and the methyl carbon atoms (Cl–N 4.5 Å). This is consistent with previous reports which indicate that the $[AlCl_4]^-$ ion is a poor hydrogen-bond acceptor due to the highly Lewis acidic $Al^{III}$ center.[18] These same properties make $[AlCl_4]^-$ a noncoordinating anion that is well suited as a framework template.[19]

In the crystal structure of **1,** the dialkylammonium cations demonstrate a pairwise linkage between $[CuCl_4]^{3-}$ tetrahedra (Figure 2). Atom H(2) is hydrogen bonded to a single chloride ion at a distance of 2.43 Å, whereas H(1) is hydrogen bonded to the edge of a neighboring $[CuCl_4]^{3-}$ tetrahedron with Cl–H distances of 2.54 and 2.61 Å. Nevertheless, each pair of inversion-related diethylammonium cations exclusively connects two tetrahedral anions. Four such pairwise linkages to nearest neighbor tetrahedra result in the $[\{(H_2NEt_2)_2\}_{4/2}(CuCl_4)]^+$ tetrahedral building blocks shown in Figure 2. These tetrahedral units are then assembled into a three-dimensional diamondoid network. For ease of visualization, each linking pair of ammonium cations is replaced by a sphere on the inversion center that relates them, and the $[CuCl_4]^{3-}$ anion is represented by a sphere at the tetrahedral center in Figure 3, so that the "$A_2T$" ($A = [(H_2NEt_2)_2]^{2+}$, $T = [CuCl_4]^{3-}$) anti-zeotype connectivity is readily apparent. A similar $A_2T$ framework is observed for the structure of $Cu_2O$; however, in this case two such frameworks interpenetrate.[20]

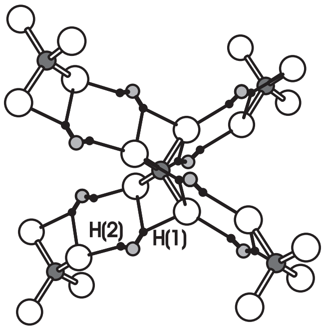

Figure 2. Representation of the $[\{(H_2NEt_2)_2\}_{4/2}(CuCl_4)]^+$ tetrahedral building blocks to highlight the hydrogen bonded connectivity. The ethyl groups have been removed for clarity.

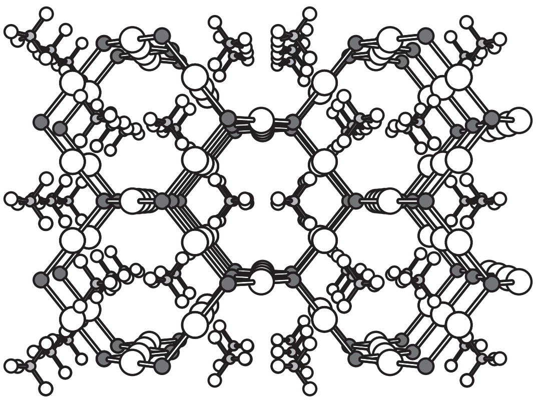

Figure 3. View of the diamondoid lattice of **1** in which the inversion-related pairs of $[H_2NEt_2]^+$ cations are represented as large open spheres and the $[CuCl_4]^{3-}$ anions are represented as dark spheres. The $[AlCl_4]^-$ anions template this hydrogen bonded network.

From this perspective it is clear that the cationic-framework partial structure of $[\{(H_2NEt_2)_2\}_2(CuCl_4)]^+$ adopts the cristobalite-related C9 structure,[21] where the T-A-T angle is required to be 180° because of the pairwise connectivity of the ammonium cations. By contrast, a collapsed C9 structure is observed for cristobalite with a T-O-T angle of approximately 137°. The resulting set of channels, which run through the framework along *a* and *b* exhibit C–C and Cu–Cu cross-channel contacts of 6.7 Å and 16.6 Å, respectively. In **1** the ethyl groups of the dialkylammonium cations, as well as the $[AlCl_4]^-$ anions, stuff and stabilize this expanded C9 structure type in the same fashion that $(tBu)_2O$ stabilizes the expanded cristobalite-type framework of $Cd(CN)_2$.[22] Numerous other stuffed cristobalite structures are common such as $NaAlO_2$[23] and $Na_2BeSiO_4$,[24] which also exhibit ionic conductivity through the channel structure.

## *Experimental Section*

All manipulations were performed under an atmosphere of dry nitrogen. $AlCl_3$ was purchased from Fluka and purified by literature procedures.[25] CuCl was prepared from Cu metal and $CuCl_2$ (Aldrich) according to literature methods.[26] $H_2NEt_2Cl$ was dried overnight at 100 °C under vacuum. CuCl (44 mg, 0.447 mmol), $AlCl_3$ (60 mg, 0.447 mmol), and $H_2NEt_2Cl$ (196 mg, 1.789 mmol) were mixed and added to a Pyrex ampoule, which was then evacuated and sealed. The reaction tube was heated to 250 °C for 12 h, and then cooled to room temperature at a rate of 10° $h^{-1}$. At room temperature a molten salt was produced which crystallized over a period of several days. Elemental analysis of the crystalline samples: calcd for $C_{16}H_{48}N_4AlCl_8Cu$: C 28.64, H 7.23, N 8.35; found: C 27.55, H 7.24, N 7.96.

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[17] Single crystal X-ray data of 1 ($C_{16}H_{48}AlCl_8CuN_4$) were collected at 298 K on an Enraf-Nonius CAD-4 diffractometer equipped with a $Mo_{K\alpha}$ source and a graphite monochrometer. The colorless crystals ($0.3 \times 0.3 \times 0.1$ mm) exhibited tetrahedral symmetry, space group $I4_1/a$ (no. 88), $a = 12.8059(4)$, $c = 20.434(2)$ Å, $V = 3351.0(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.33$ g cm$^{-1}$, $\mu(Mo_{K\alpha}) = 1.34$ cm$^{-1}$. A total of 3929 unique intensities with $2\theta < 54^\circ$ were collected with a $\theta-2\theta$ scan mode. Full-matrix least-squares calculations, based on $F$, of the 1284 observed unique reflections with $I_{net} > 1.0\sigma(I)$ and 117 variables were performed with the NRCVAX software package. All hydrogen atoms were located, and their positions refined. The structure was refined to a final model with $R = 0.039$ and $R_w = 0.046$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCD-101662. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

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