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New Molecular Perovskites: Cubic $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ and 2-H Hexagonal $C_6N_2H_{14}{\cdot}NH_4Cl_3$

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Perovskites, of generic formula ABX_3 (A, B = metal cations, X = anion; usually oxide), are one of the most-studied families of solid-state inorganic compounds.[1] The perovskite structure may be pictured in two ways: as a three-dimensional network of corner-sharing BX_6 octahedra enclosing nominal 12-coordinate holes occupied by the A cations, or in terms of cubic-close-packed layers of composition AX_3 encompassing octahedral holes, of which $^1/_4$ are occupied by the B cations.[2] The second representation is helpful in showing the relationship of the cubic[3] perovskite structure to its 2-H hexagonal variant (prototype phase $BaNiO_3$),[4] which is constructed from a hexagonal-close-packed stacking sequence of AX_3 layers,[2] equating to face-sharing columns of BX_6 octahedra.

In this communication, we describe the room-temperature syntheses[5] and characterization of two novel nonmetallic, molecular, perovskites based on ammonium-chloride octahedral networks which are held together largely by hydrogen bonding. The connectivity of the $(NH_4)Cl_6$ octahedral building blocks in $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ and $C_6N_2H_{14}{\cdot}NH_4Cl_3$ replicates the packing of the BX_6 moieties in the cubic and 2-H hexagonal perovskite structures, respectively.

The structure[6] of piperazinium ammonium chloride hydrate, $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ (Figure 1), consists of a cubic-perovskite-like array of vertex-sharing $(NH_4)Cl_6$ octahedra extending in three orthogonal directions. The orthorhombic cell seen here is an $a \times 2b \times 2c$ supercell as compared to that of a nominal $Pm\bar{3}m$-symmetry $(NH_4)Cl_6$ octahedral array (which would necessitate disorder for the ammonium H atoms). The inclusion of water in this structure is a novel feature, and $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ could be regarded as a "perovskite hydrate." The six N···Cl contact distances range from 3.216 to 3.355 Å (average = 3.272 Å), as compared to 3.266 Å in sodium-chloride type β-NH_4Cl.[7] The inter-octahedral N···Cl···N bond angles (average = 166.6°) in $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ are all less than 180°, as are the corresponding B−O−B angles in oxide perovskites containing tilted octahedra.[3]

The $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ crystal structure is completed by doubly protonated piperazinium ($C_4N_2H_{12}^{2+}$) cations, each of which occupies the central region of a cage formed of eight octahedra, and water molecules which occupy a square site (four surrounding octahedra) in the (001) plane. The piperazinium cations adopt a typical chair conformation, and their geometrical parameters are unexceptional. Hydrogen bonding is clearly a key feature determining this structure. The NH_4^+ cation makes N−H···Cl bonds to four of its six chloride neighbors [d_{av}(H···Cl) = 2.38 Å; θ_{av}(N−H···Cl) = 171°]. The one unique piperizinium NH_2^+ grouping participates in one N−H···Cl bond [d(H···Cl) = 2.39 Å; θ(N−H···Cl) = 151°] and one N−H···O(water) bond. The water molecule makes two O−H···Cl bonds [d_{av}(H···Cl) = 2.16 Å; θ_{av}(N−H···Cl) = 172°] in the (001) plane. This results in the three unique chloride ions acting as acceptors for two H bonds each. A novel variant on metal perovskites is the fact that the charge of the divalent piperazinium, or A cation, is larger than that of the octahedral B cation (NH_4^+), whereas in well-characterized ABO_3 phases, the charge of the A cation is equal to, or less than, the charge of the B cation.[1]

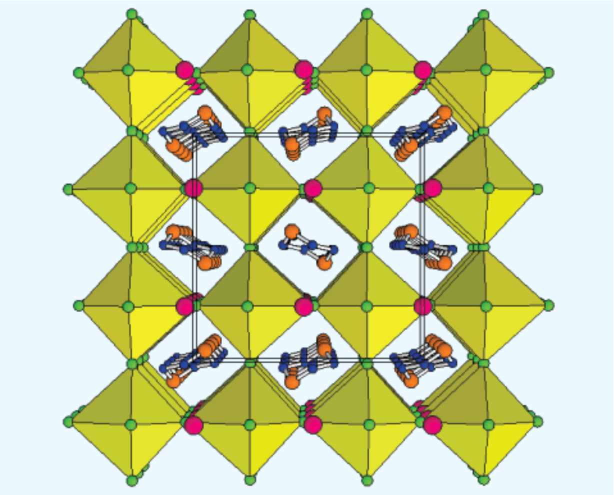

Figure 1. View down [100] of $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ showing the perovskite-like octahedral network encapsulating the piperizinium and water molecule guest species. H atoms omitted for clarity. Color key: $(NH_4)Cl_6$ octahedra, yellow; Cl atoms, green; piperazinium N atoms, orange; C atoms, blue; O atoms, rose pink.

Dabconium ammonium chloride, $C_6N_2H_{14}{\cdot}NH_4Cl_3$ (Figure 2), contains[6] infinite columns of face-sharing $(NH_4)Cl_6$ octahedra, arranged in the same manner as the NiO_6 moieties in hexagonal 2-H $BaNiO_3$.[4] The large unit cell (Z = 18) of $C_6N_2H_{14}{\cdot}NH_4Cl_3$ contains five distinct NH_4 and Cl species and 1.5 distinct Dabconium cations. The $\sqrt{3}a \times \sqrt{3}a \times 3c$ supercell (which shows strong rhombohedral pseudo symmetry), as compared to that of $BaNiO_3$, can be related to the stacking pattern of the Dabconium cations along [001] and slight $(NH_4)Cl_6$ octahedral twists, which perhaps occur to optimize N−H···Cl hydrogen bonding. The ammonium nitrogen atoms occupy special positions with site symmetries 3 or $\bar{3}$, and their H atoms could not be located; they may be disordered over multiple sites. The chloride ion associated with the $\bar{3}$ symmetry N atom is unequally disordered over two adjacent [d(Cl···Cl) = 0.864 (9) Å] sites. The $C_6N_2H_{14}^{2+}$ Dabconium (doubly protonated 1,4-diazabicyclo[2.2.2]octane) cations possess typical geometrical parameters and occupy sites between the octahedral columns, akin to the barium cations in $BaNiO_3$. In the [001] projection (Figure 3), each octahedral column of $(NH_4)Cl_6$ groups is surrounded by six Dabconium stacks, and vice versa. Again, H bonding appears to be a key feature in stabilizing the crystal packing; ammonium N−H···Cl bonds are presumably present [d_{av}(N···Cl) = 3.255 Å],

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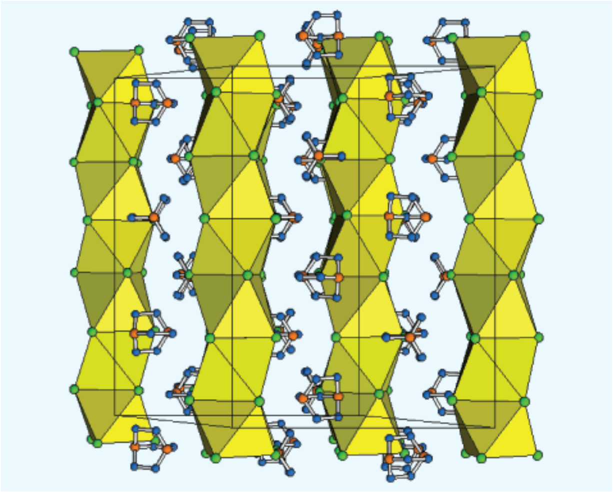

Figure 2. View down [210] of $C_6N_2H_{14}{\cdot}NH_4Cl_3$ showing the face-sharing $(NH_4)Cl_6$ octahedra propagating along [001], interspersed by stacks of Dabconium cations. The minor component of the disordered chloride ion and H atoms are omitted for clarity. Color key is as in Figure 1.

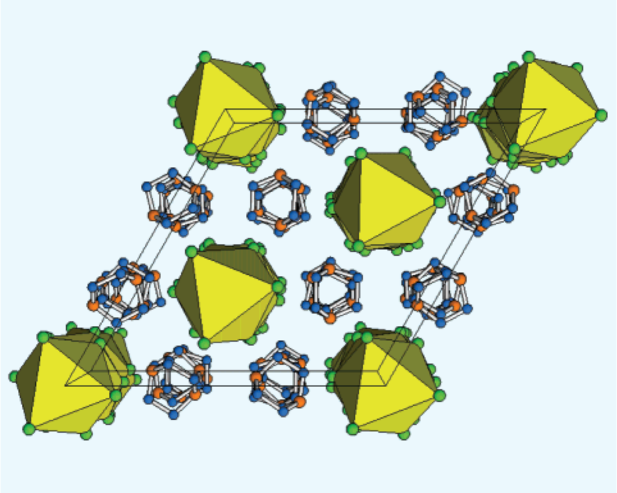

Figure 3. View down [001] of $C_6N_2H_{14}{\cdot}NH_4Cl_3$ showing the columns of face-sharing $(NH_4)Cl_6$ octahedra and stacks of Dabconium cations propagating out of the plane of the page. Color key is as in Figure 1.

and three strong, near-linear, Dabconium N−H···Cl links occur [$d_{av}(H\cdots Cl) = 2.11$ Å; $\theta_{av}(N{-}H\cdots Cl) = 175.9°$]. The average inter-octahedral N···Cl···N bond angle is 69.4° (Ni−O−Ni angle in $BaNiO_3 = 80.3°$). Once again, the A (Dabconium) cation is divalent, and the B (ammonium) cation is monovalent.

The X-ray powder patterns (Cu Kα radiation, $\lambda = 1.5418$ Å, $T = 25 \pm 2$ °C) of the title compounds gave sharp lines and were in good agreement with simulations based on the single-crystal structures, indicating phase purity and a high degree of crystallinity. TGA (ramp at 5 °C/min in air) for both $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ and $C_6N_2H_{14}{\cdot}NH_4Cl_3$ indicated 100% weight loss by 600 °C, confirming their nonmetallic nature. A distinct weight-loss step of 7.6% between 62 and 145 °C for $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ probably corresponds to water loss (calc. 7.8%).

Perhaps the closest relatives to the title compounds are the unusual $ASnY_3$ family of tin(II)-halide cubic perovskites[8] in which the A cation can be methylammonium ($CH_3NH_3^+$) as well as cesium, and Y = Br or I. However, no 2-H variants are known for the $ASnY_3$ family. Metal-halide octahedra are a feature of many layered composite perovskites,[9] in which slabs of vertex-sharing MX_6 groups incorporate a variety of organic cations into the A cation sites and interlayer regions of the structure. The interaction of metal-halide building blocks with organic cations has also been studied from a crystal engineering perspective,[10] and some of the resulting structures can be related to layered perovskites. A pioneering study in this area used electrochemical synthesis to prepare the remarkable family of phases exemplified by $(TTF^{\bullet+})_3(Cl^-)(Mo_6Cl_{14}^{2-})$ ($TTF^{\bullet+}$ = tetrathiafulvalene radical cation) which crystallize as molecular *anti*-(cubic)-perovskites.[11] In these phases, which possess novel magnetic properties,[12] a network of vertex-sharing $Y(TTF)_6$ (Y = Cl, Br, I) octahedra encapsulates anionic metal-halide clusters occupying the nominal perovskite A sites.

We are now seeking appropriate organic templating cations to promote the formation of noncentrosymmetric, or even chiral, perovskite-like octahedral networks akin to those described here. In this sense, the role of organic cations here parallels their use as templates in the formation of inorganic open frameworks.[13] Alternatively, altering the halide species could change the size of the "octahedral hole" occupied by NH_4^+, perhaps inducing a displacive distortion of the ammonium cation resulting in ferroelectric behavior.

Acknowledgment. Single-crystal data for $C_6N_2H_{14}{\cdot}NH_4Cl_3$ were collected by Dr. Peter Horton (EPSRC National X-ray Crystallography Service, University of Southampton). We thank Jim Marr for assistance with the TGA measurements.

Supporting Information Available: Crystallographic data for $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ and $C_6N_2H_{14}{\cdot}NH_4Cl_3$ in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) "Cubic" refers to the highest possible crystal symmetry (space group $Pm\bar{3}m$, No. 221) for the perovskite structure. Most so-called cubic perovskites show symmetry lowering and/or a supercell, but their octahedral topology is unchanged (see: Glazer, A. M. *Acta Crystallogr.* **1972**, *B28*, 3384). Cubic is used in a generic sense in this paper.

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(5) $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ was prepared from 1.942 g (10 mmol) of piperazine hexahydrate, 0.535 g (10 mmol) of NH_4Cl, and 2 mL (20 mmol) of 37% HCl, which were dissolved in 5 mL of water. The mixture was transferred to a Petri dish, and rod- and blocklike single crystals of $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$ grew over a few hours at 25 °C. They were recovered by vacuum filtration and rinsing with acetone. $C_6N_2H_{14}{\cdot}NH_4Cl_3$ was prepared from 0.535 g (10 mmol) of NH_4Cl, 1.121 g (10 mmol) of $C_6N_2H_{12}$, 2 mL (20 mmol) of 37% HCl, and 5 mL of water. Crystals of $C_6N_2H_{14}{\cdot}NH_4Cl_3$ grew in a Petri dish over 24 h and were recovered as above. Powders of both phases readily dissolve in cold water and can be subsequently recrystallized.

(6) Crystal data for $C_4N_2H_{12}{\cdot}NH_4Cl_3{\cdot}H_2O$: transparent block, 0.18 × 0.24 × 0.27 mm, $M_r = 230.56$, orthorhombic, *Pbcm* (No. 57), $a = 6.5279\,(13)$ Å, $b = 12.935\,(3)$ Å, $c = 12.849\,(3)$ Å, $V = 1085.0\,(4)$ Å^3, $Z = 4$, $R(F) = 0.031$, $wR(F^2) = 0.082$, $T = 20$ °C. $C_6N_2H_{14}{\cdot}NH_4Cl_3$, transparent plate, 0.10 × 0.25 × 0.30 mm, $M_r = 238.59$, trigonal, $P\bar{3}c1$ (No. 165), $a = 16.1616\,(2)$ Å, $c = 22.3496\,(4)$ Å, $V = 5055.5\,(2)$ Å^3, $Z = 18$, $R(F) = 0.068$, $wR(F^2) = 0.260$, $T = -153$ °C.

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