Perovskites

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Structural Diversity in Non-Layered Hybrid Perovskites of the $RMCl_3$ Family**

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Perovskites, of simplest generic formula ABX_3 (A, B = metal cations, X = anion; usually oxide), are probably the most-studied family of solid-state inorganic compounds.[1] Literally thousands of metal oxide perovskites are known and their physical properties encompass almost every known type of phenomenon, from ferroelectricity to superconductivity to colossal magnetorestive effects,[2] which correlate closely with their crystal structures. The atomic arrangement in perovskites may be visualized in two ways, the most familiar being a three-dimensional network of corner-sharing BX_6 octahedra enclosing nominal twelve-coordinate holes occupied by the A cations. Its highest possible aristotype[3] symmetry is cubic, although most real perovskites show lower symmetry. Alternately, a sphere-packing model regards the structure as consisting of cubic-close-packed (stacking sequence ABCABC…) layers of composition AX_3 encompassing octahedral holes, of which $^1/_4$ are occupied by the B cations such that no A···B contacts occur.[4] The second representation is helpful in emphasizing the relationship of the cubic perovskite structure to its hexagonal variants (prototype phase $BaNiO_3$),[5] which are constructed from hexagonal-close-packed (ABAB…) AX_3 layers, equating to face-sharing one-dimensional columns of BX_6 octahedra in the polyhedral description.

Layered hybrid perovskites, in which slabs of various thicknesses of vertex-sharing metal halide octahedra (i.e. the cubic perovskite topology) are separated by layers of organic cations are a well known family of phases.[6,7] Some of these possess important properties such as tunable metal–semiconductor transition in the $(C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Sn_nI_{3n+1}$ series.[8] Here, we describe the syntheses and single-crystal structures of what might be called a "missing link" between these two families: namely six new hybrid, non-layered, perovskite networks containing both inorganic (alkali metal and chloride ions) and organic constituents: $C_4H_{12}N_2{\cdot}KCl_3{\cdot}H_2O$ (**1**), $C_4H_{12}N_2{\cdot}RbCl_3{\cdot}H_2O$ (**2**), $C_4H_{12}N_2{\cdot}CsCl_3{\cdot}H_2O$ (**3**), $C_6H_{14}N_2{\cdot}KCl_3$ (**4**), $C_6H_{14}N_2{\cdot}RbCl_3$ (**5**), and $C_6H_{14}N_2{\cdot}CsCl_3$ (**6**) ($C_4H_{12}N_2^{2+}$ = piperazinium dication; $C_6H_{14}N_2^{2+}$ = 1,4-diazoniabicyclo[2.2.2]octane or "dabconium" dication), which display a striking range of ABO_3-like perovskite-like structures. Earlier, we described[9] $C_4H_{12}N_2{\cdot}NH_4Cl_3{\cdot}H_2O$ and $C_4H_{14}N_2{\cdot}NH_4Cl_3$, which contain non-metallic "molecular" perovskite-like networks of ammonium-centered octahedra.

The three phases **1**, **2**, and **3** containing piperazinium ($C_4H_{12}N_2^{2+}$) dications are isostructural and may be described together. Their structures (Figure 1) consist of a cubic-perovskite-like array of vertex-sharing MCl_6 (M = K, Rb, Cs) octahedra extending in three orthogonal directions. The resulting orthorhombic unit cell (space group *Pbcm*) may be regarded as an $(a \times 2b \times 2c)$ super-cell of a nominal cubic MCl_6 octahedral array with $a \approx 6.5$ Å (i.e. twice the approximate M−Cl bond length). In these orthorhombic phases, the metal ion lies on a crystallographic mirror plane, and of the three distinct chloride ions, one lies on a two-fold axis, one on a mirror plane and one on a general position, thus yielding the overall 1:3 M:Cl ratio. Mean M−Cl distances of 3.207 Å, 3.243 Å and 3.319 Å arise for the potassium, rubidium and cesium phases, respectively, in conformity with the trend in ionic radii of the metal ions: the corresponding M−Cl distances in KCl, RbCl and CsCl (rock salt polymorph) are 3.148 Å,[10] 3.285 Å[11] and 3.462 Å,[12] respectively.

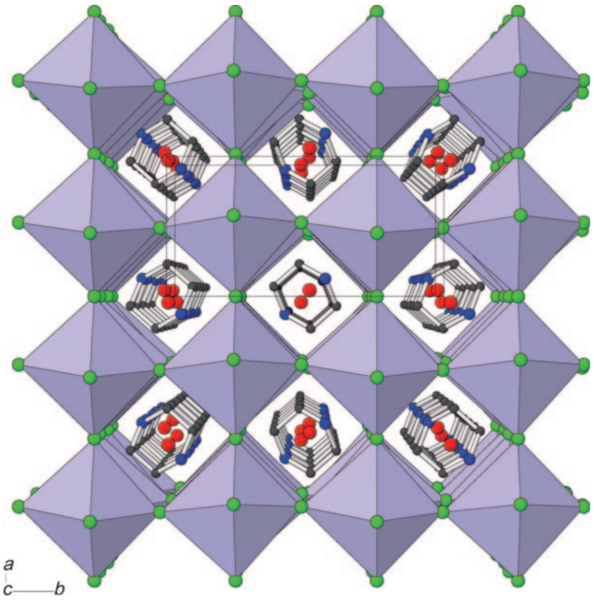

Figure 1. Polyhedral plot of **1**, viewed down the *c* axis, showing the corner-sharing network of KCl_6 octahedra incorporating the organic cation and water molecule (H atoms omitted for clarity). Color key: KCl_6 octahedra lilac, Cl green, C dark gray, N blue, O red.

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It is notable that the metal ions in these hybrid perovskites are significantly displaced from the geometric centers of their octahedra, by 0.190 Å, 0.240 Å, and 0.370 Å for the K, Rb, and Cs phases, respectively. In each case, the displacement is primarily towards a vertex, defined by Cl1. These displacements result in some substantial deviations from the nominal 90° and 180° Cl-M-Cl bond angles for the alkali metal chloride octahedra; for example, one Cl-Cs-Cl angle in **3** is 76.143(15)°. At the same time, the mean M-Cl-M bridging (inter-octahedral) bond angles [171.2° (K), 169.7° (Rb), 166.0° (Cs)] show a clear trend and indeed a good inverse linear correlation exists between the mean M–Cl distance and mean M-Cl-M bond angle. This has a close parallel to the size-mismatch effect in ABO_3 oxide perovskites in which the size of the A cation correlates with the deviation of the B-O-B angles from 180°.[13]

The structures of **1**, **2**, and **3** are completed by doubly protonated piperazinium ($C_4N_2H_{12}^{2+}$) dications and water molecules. Each piperazinium species occupies the central region of a cage formed of eight MCl_3 octahedra (the topologically equivalent site to the twelve-coordinate A cation in a cubic oxide perovskite), as shown in Figure 2. The complete organic dication, which adopts a typical chair conformation, is generated by inversion symmetry. The water molecule, which occupies a square site (four surrounding octahedra) in the (110) plane, completes the structure. Hydrogen bonding is clearly an important structural feature of these phases: the unique piperizinium NH_2^+ grouping participates in one NH···Cl bond and one NH···O (water) bond and the water molecule makes two OH···Cl bonds in the (110) plane. Throughout the crystal, this results in a "balanced" hydrogen bonding network, in which the three unique chloride ions act as acceptors for two hydrogen bonds each. Initial results suggest that bromide-containing analogues of these structures can also be prepared.

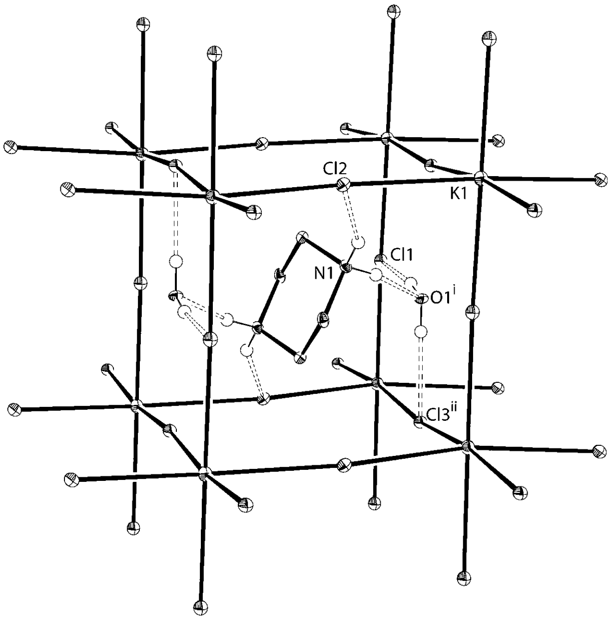

Figure 2. Fragment of **1** showing the environment of the piperazinium dication within a cage formed by eight KCl_6 octahedra, akin to the A cation site in oxide perovskites. Atoms are represented by 50% displacement ellipsoids, hydrogen bonds are indicated by double-dashed lines and C-bonded H atoms are omitted for clarity. Symmetry codes: i) $x-1, y, z$; ii) $2-x, -y, -z$.

Unlike the isostructural series of piperazinium-templated compounds, the $C_6H_{14}N_2{\cdot}KCl_3$, $C_6H_{14}N_2{\cdot}RbCl_3$, and $C_6H_{14}N_2{\cdot}CsCl_3$ series, containing 1,4-diazoniabicyclo[2.2.2]octane or "dabconium" dications, display a remarkable diversity of perovskite-type structures.

$C_6H_{14}N_2{\cdot}KCl_3$ (**4**) adopts a hexagonal-perovskite-like[5] arrangement (in this case the crystal symmetry is trigonal; space group $R\bar{3}c$) of parallel columns of face-sharing KCl_3 octahedra, interspersed by the organic species (Figure 3). Of the two distinct potassium ions, K1 (site symmetry $\bar{3}$), is constrained by symmetry to lie at the exact center of its octahedron. The other (site symmetry 3), is displaced towards an octahedral face by 0.065 Å. In tracking up the *c*-axis, the sequence ···K1···K2···K2··· occurs within each column. The bridging K-Cl-K angles [71.993(14) and 72.782(8)° for Cl1 and Cl2, respectively] are almost those expected for undistorted face-shared octahedra. The $C_6H_{14}N_2^{2+}$ organic cation replicates the behavior of the A cation in hexagonal oxide perovskites and lies between the columns; each metal halide stack is surrounded by six stacks of cations. The complete molecule is generated by two-fold symmetry and its N···N axis lies almost perpendicular to the axes of the KCl_3 columns and interacts with them by way of strong N1H1···Cl1 hydrogen bonds (Figure 4).

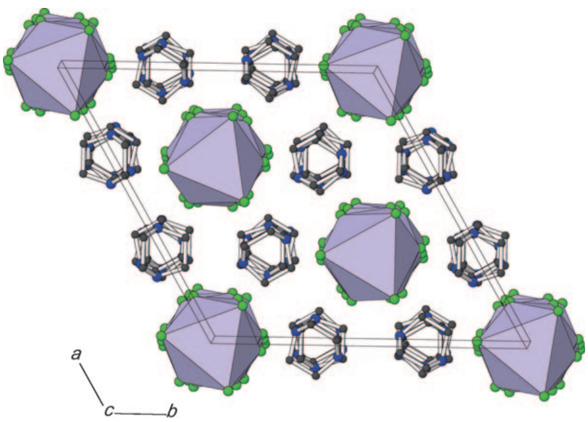

Figure 3. Polyhedral plot of **4**, viewed approximately down the *c* axis, showing the columns of face-sharing KCl_6 octahedra interspersed by the dabconium cations (H atoms omitted for clarity). Color key: KCl_6 octahedra lilac, Cl green, C dark gray, N blue.

$C_6H_{14}N_2{\cdot}RbCl_3$ (**5**) is a chiral perovskite (Figure 4), crystallizing in the enantiomorphous space group $P3_212$ (No. 153). Refinement of the Flack absolute structure parameter[14] for this material indicated that the crystal studied is enantiomerically pure. The crystal chirality must originate from a helical motif of the non-chiral structural units[15] and the bulk sample must consist of an equal number of crystals of both chiralities (i.e. space groups $P3_112$ and $P3_212$).

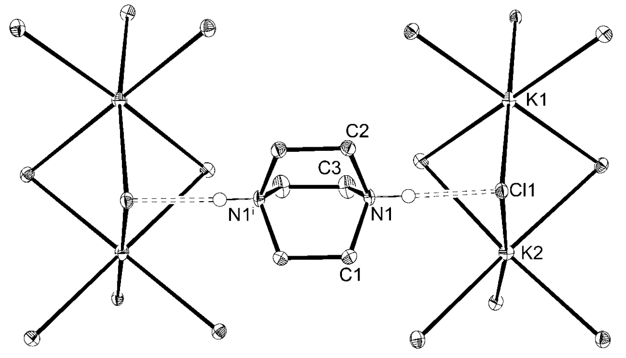

Figure 4. Detail of **4** showing the dabconium ion participating in NH···Cl hydrogen bonds to two adjacent octahedral columns. Atoms are represented by 50% displacement ellipsoids, hydrogen bonds are indicated by double-dashed lines, and C-bonded H atoms are omitted for clarity. Symmetry code: i) 1/3+*x*−*y*, 2/3−*y*, 1/6−*z*.

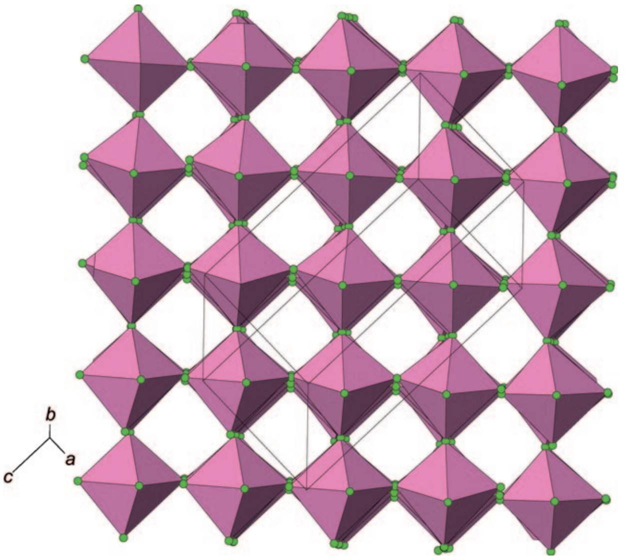

Figure 5. Polyhedral plot of **5** showing the cubic-perovskite-like network of $RbCl_3$ octahedra and its orientation with respect to the unit-cell outline. Color key: $RbCl_6$ octahedra crimson, Cl green.

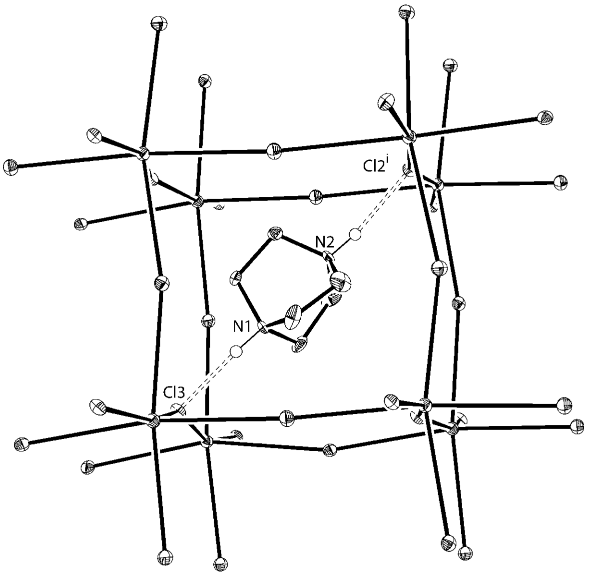

Figure 6. Fragment of **5** showing the environment of the dabconium dication within a cage formed by eight $RbCl_6$ octahedra, akin to the A cation site in oxide perovskites. Atoms are represented by 50% displacement ellipsoids, hydrogen bonds are indicated by double-dashed lines, and C-bonded H atoms are omitted for clarity. Symmetry code: i) −*x*+*y*, −*x*, 1/3+*z*.

In the structure of **5**, two rubidium ions (both with site symmetry 2), three chloride ions (general positions), and one dabonium cation (all atoms on general positions) make up the asymmetric unit. The topology of the corner-sharing $RbCl_3$ octahedra is that of the ABO_3 cubic perovskite (Figure 5), although its chiral nature is unprecedented.[15] Interestingly, the $Rb1L_6$ octahedron shows a substantial displacement of the Rb^+ cation towards an octahedral edge, whereas the Rb^+ ion is almost at the center of the $Rb2L_6$ moiety. The dabconium cation occupies the A cation site and interacts with the $RbCl_3$ network by way of NH···Cl hydrogen bonds (Figure 6). When the complete structure is considered, it is found that Cl2 and Cl3 accept two NH···Cl bonds each: it is notable that the corresponding two Rb-Cl-Rb bond angles [165.24(3) and 161.35(3)°] are substantially smaller than the Rb-Cl-Rb bond angle [172.08(3)°] for the chloride ion (Cl1) that does not accept a hydrogen bond.

$C_6H_{14}N_2{\cdot}CsCl_3$ (**6**) crystallizes with an exceptionally large monoclinic unit cell [$V = 9542.7(3)$ Å^3, $Z = 32$] containing no fewer than five distinct cesium ions (three on general positions, one with site symmetry 2 and one with site symmetry $\bar{1}$) and twelve chloride ions (all sited on general positions). Again, each cesium coordination polyhedron is a $CsCl_6$ octahedron and the topology of the cesium chloride framework is that of the vertex-sharing cubic perovskite structure. The four distinct dabconium ions each form two NH···Cl hydrogen bonds, such that eight of the twelve chloride ions accept one of these interactions. These eight hydrogen bonds cover a notably narrow range of H···Cl distances (from 2.09 to 2.17 Å) and NH···Cl angles (from 158 to 172°), which perhaps indicates that optimizing the hydrogen bond arrangement is a key factor in the formation of this large super-cell. However, the correlation between the Cs-Cl-Cs bond angle and whether the Cl atom accepts a hydrogen bond (mean = 159.7° for the acceptors; 162.0° for the non-acceptors) is much weaker than in the case of **5**.

These six new phases, prepared in single-crystal form by simple solution chemistry, represent a "missing link" between three-dimensional inorganic metal oxide perovskites and layered composite metal halide/organic cation perovskites. The alkali metal centered octahedra in these compounds display similar displacements of the metal ions (towards a vertex in **1**–**3**, towards an edge in **5**, and towards a face in **4**) from the octahedral centers as do transition metal ions in oxide perovskites.[16] Trends in the inter-octahedral M-Cl-M bond angles may be observed that parallel the trends seen in oxide perovskites in terms of the size of the species occupying the A site, but in the present family the presence of guest–host

NH···Cl hydrogen bonds also affect the inter-octahedral bond angles. These compounds display a remarkable variety of crystal symmetries and live up to the reputation of oxide perovskites in this respect, and they may be susceptible to an octahedral-tilt analysis.[13] Other atomic substitutions appear to be plausible in this novel family (e.g. bromide for chloride, alkaline earth metal ions + univalent organic cations for alkali metal cations + divalent organic cations) and further synthetic studies are now being made in these areas.

Experimental Section

Compounds **1**–**6** were prepared from stoichiometric 1:2:1 mixtures of aqueous solutions of the metal chloride, hydrochloric acid and the organic species. The resulting colorless solutions (pH ≈ 1–2) were left in Petri dishes at 20 °C for several days, during which time faceted colorless blocks of all the products grew. They were harvested by vacuum filtration and rinsed with acetone. They all appear to be indefinitely stable when stored in air.

The structures of **1**–**6** were determined from single-crystal X-ray diffraction data: in each case, intensity data were collected at 120 K using an Enraf–Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods with SHELXS-97 and the structural models optimized by least-squares refinement against $|F^2|$ data with SHELXL-97. The C-bound and N-bound H atoms were located geometrically and refined as riding atoms and O-bound H atoms were located in difference maps.

Full crystallographic details for **1**–**6** are available as electronic supplementary material (cif format), which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/uk/data request/cif, citing the deposition numbers noted below. $C_4H_{12}N_2 \cdot KCl_3 \cdot H_2O$ (**1**) (CCDC 776363): $M_r = 251.62$, orthorhombic, *Pbcm* (No. 57), $Z = 4$, $a = 6.4176(2)$ Å, $b = 12.7401(5)$ Å, $c = 12.7470(3)$ Å, $V = 1042.21(6)$ Å^3, $F(000) = 520$, $T = 120$ K, $\rho = 1.604$ g cm^{-3}, $\mu = 1.232$ mm^{-1}, $R(F) = 0.034$ (957 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.096$ (1066 reflections). $C_4H_{12}N_2 \cdot RbCl_3 \cdot H_2O$ (**2**) (CCDC 776364): $M_r = 297.99$, orthorhombic, *Pbcm* (No. 57), $Z = 4$, $a = 6.4927(1)$ Å, $b = 12.8109(3)$ Å, $c = 12.8837(3)$ Å, $V = 1072.31(4)$ Å^3, $F(000) = 592$, $T = 120$ K, $\rho = 1.846$ g cm^{-3}, $\mu = 5.320$ mm^{-1}, $R(F) = 0.019$ (1011 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.045$ (1099 reflections). $C_4H_{12}N_2 \cdot CsCl_3 \cdot H_2O$ (**3**) (CCDC 776365): $M_r = 345.43$, orthorhombic, *Pbcm* (No. 57), $Z = 4$, $a = 6.6402(2)$ Å, $b = 12.9026(5)$ Å, $c = 13.1485(4)$ Å, $V = 1126.51(7)$ Å^3, $F(000) = 664$, $T = 120$ K, $\rho = 2.037$ g cm^{-3}, $\mu = 3.956$ mm^{-1}, $R(F) = 0.019$ (1061 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.044$ (1152 reflections). $C_4H_{14}N_2 \cdot KCl_3$ (**4**) (CCDC 776366): $M_r = 259.64$, trigonal, $R\bar{3}c$ (No. 167), $Z = 18$, $a = 16.0494(2)$ Å, $c = 22.1570(2)$ Å, $V = 4942.64(12)$ Å^3, $F(000) = 2412$, $T = 120$ K, $\rho = 1.570$ g cm^{-3}, $\mu = 1.166$ mm^{-1}, twin domain ratio = 0.5596(9): 0.4404 (9), $R(F) = 0.026$ (1956 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.062$ (2109 reflections). $C_4H_{14}N_2 \cdot RbCl_3$ (**5**) (CCDC 776367): $M_r = 306.01$, trigonal, $P3_221$ (No. 154), $Z = 6$, $a = 9.3376(1)$ Å, $c = 22.3386(5)$ Å, $V = 1686.77(5)$ Å^3, $F(000) = 912$, $T = 120$ K, $\rho = 1.808$ g cm^{-3}, $\mu = 5.069$ mm^{-1}, Flack absolute structure parameter 0.009(9), $R(F) = 0.033$ (2103 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.068$ (2586 reflections). $C_4H_{14}N_2 \cdot CsCl_3$ (**6**) (CCDC 776368): $M_r = 353.45$, monoclinic, *C2/c* (No. 15), $Z = 32$, $a = 45.1511(6)$ Å, $b = 9.4912(2)$ Å, $c = 31.2121(4)$ Å, $\beta = 128.4835(9)°$, $V = 9542.7(3)$ Å^3, $F(000) = 5440$, $T = 120$ K, $\rho = 1.968$ g cm^{-3}, $\mu = 3.733$ mm^{-1}, $R(F) = 0.032$ (8803 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.069$ (10917 reflections).

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