

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 magnetoresistive 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. Alternatively, 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 $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{SnI}_{3n+1}$ 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: $\text{C}_4\text{H}_{12}\text{N}_2\cdot\text{KCl}_3\cdot\text{H}_2\text{O}$ (**1**), $\text{C}_4\text{H}_{12}\text{N}_2\cdot\text{RbCl}_3\cdot\text{H}_2\text{O}$ (**2**), $\text{C}_4\text{H}_{12}\text{N}_2\cdot\text{CsCl}_3\cdot\text{H}_2\text{O}$ (**3**), $\text{C}_6\text{H}_{14}\text{N}_2\cdot\text{KCl}_3$ (**4**), $\text{C}_6\text{H}_{14}\text{N}_2\cdot\text{RbCl}_3$ (**5**), and $\text{C}_6\text{H}_{14}\text{N}_2\cdot\text{CsCl}_3$ (**6**) ($\text{C}_4\text{H}_{12}\text{N}_2^{2+}$ = piperazinium dication; $\text{C}_6\text{H}_{14}\text{N}_2^{2+}$ = 1,4-diazoniabicyclo[2.2.2]octane or “dabco-nium” dication), which display a striking range of ABO_3 -like

perovskite-like structures. Earlier, we described^[9] $\text{C}_4\text{H}_{12}\text{N}_2\cdot\text{NH}_4\text{Cl}_3\cdot\text{H}_2\text{O}$ and $\text{C}_4\text{H}_{14}\text{N}_2\cdot\text{NH}_4\text{Cl}_3$, which contain non-metallic “molecular” perovskite-like networks of ammonium-centered octahedra.

The three phases **1**, **2**, and **3** containing piperazinium ($\text{C}_4\text{H}_{12}\text{N}_2^{2+}$) 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,

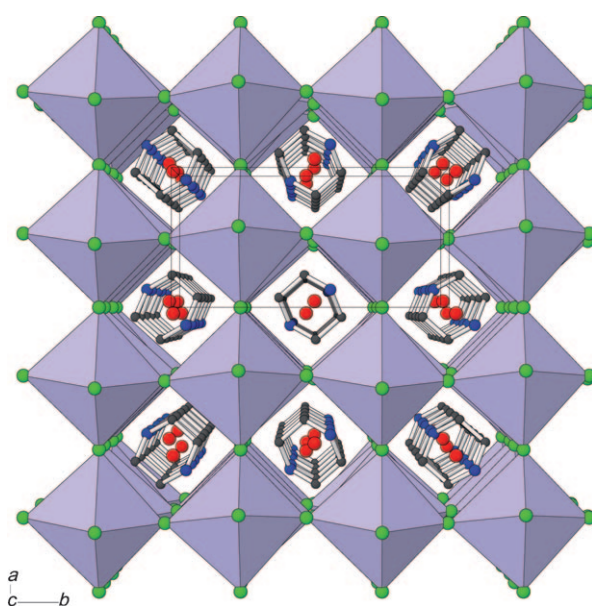


Figure 1. Polyhedral plot of **1**, viewed down the *c* axis, showing the corner-sharing network of KCl_6 octahedra incorporating the organic cation and water molecule (H atoms omitted for clarity). Color key: KCl_6 octahedra lilac, Cl green, C dark gray, N blue, O red.

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 1:3M: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.

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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 ABO₃ 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 (C₄N₂H₁₂²⁺) dication and water molecules. Each piperazinium species occupies the central region of a cage formed of eight MCl₃ octahedra (the topologically equivalent site to the twelve-coordinate A cation in a cubic oxide perovskite), as shown in Figure 2.

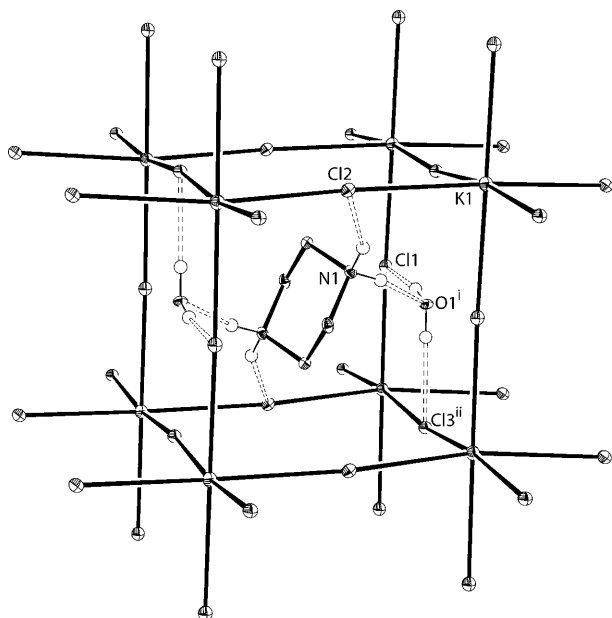


Figure 2. Fragment of **1** showing the environment of the piperazinium dication within a cage formed by eight KCl₃ octahedra, akin to the A cation site in oxide perovskites. Atoms are represented by 50% displacement ellipsoids, hydrogen bonds are indicated by double-dashed lines and C-bonded H atoms are omitted for clarity. Symmetry codes: i) $x-1, y, z$; ii) $2-x, -y, -z$.

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 piperazinium NH₂⁺ 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.

Unlike the isostructural series of piperazinium-templated compounds, the C₆H₁₄N₂·KCl₃, C₆H₁₄N₂·RbCl₃, and C₆H₁₄N₂·CsCl₃ series, containing 1,4-diazoniabicyclo-[2.2.2]octane or “dabconium” dication, display a remarkable diversity of perovskite-type structures.

C₆H₁₄N₂·KCl₃ (**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 KCl₃ octahedra, interspersed by the organic species (Figure 3). Of the two distinct potassium ions, K1 (site symmetry $\bar{3}$), is

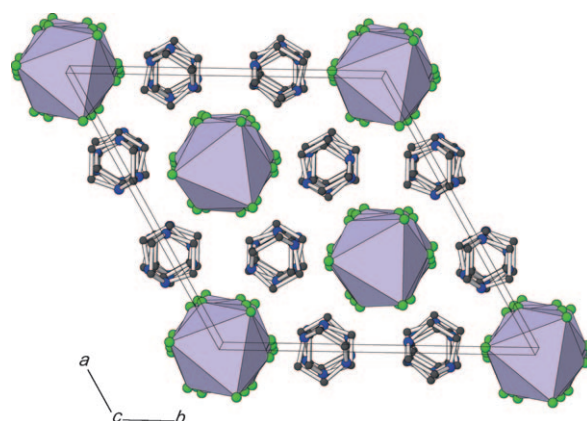


Figure 3. Polyhedral plot of **4**, viewed approximately down the c axis, showing the columns of face-sharing KCl₃ octahedra interspersed by the dabconium cations (H atoms omitted for clarity). Color key: KCl₃ octahedra lilac, Cl green, C dark gray, N blue.

constrained by symmetry to lie at the exact center of its octahedron. The other (site symmetry $\bar{3}$), 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 C₆H₁₄N₂²⁺ 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 KCl₃ columns and interacts with them by way of strong N1H1⋯Cl1 hydrogen bonds (Figure 4).

C₆H₁₄N₂·RbCl₃ (**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 $P3_212$).

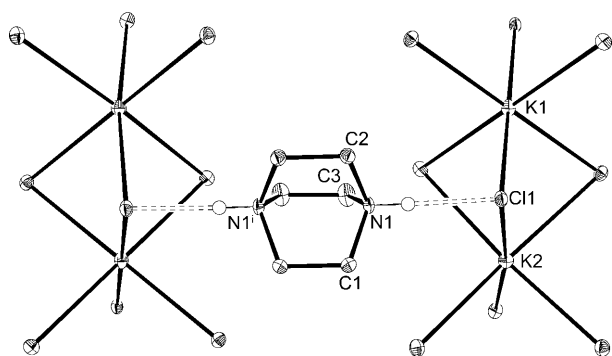


Figure 4. Detail of **4** showing the dabconium ion participating in $\text{NH}\cdots\text{Cl}$ hydrogen bonds to two adjacent octahedral columns. Atoms are represented by 50% displacement ellipsoids, hydrogen bonds are indicated by double-dashed lines, and C-bonded H atoms are omitted for clarity. Symmetry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

In the structure of **5**, two rubidium ions (both with site symmetry 2), three chloride ions (general positions), and one dabconium 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),

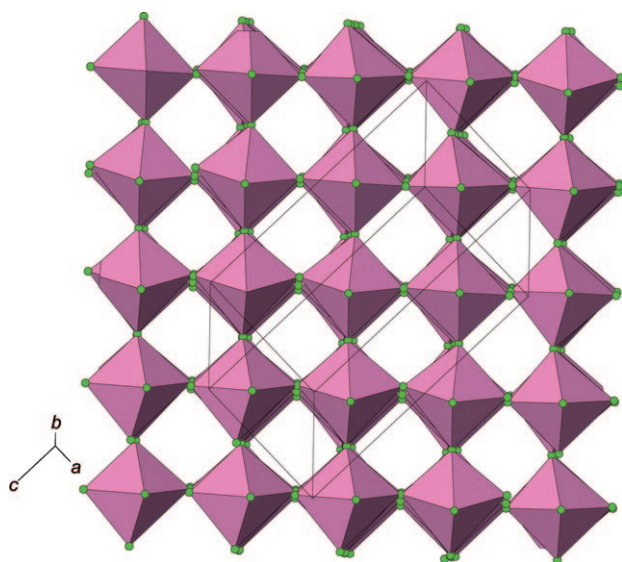


Figure 5. Polyhedral plot of **5** showing the cubic-perovskite-like network of RbCl_3 octahedra and its orientation with respect to the unit-cell outline. Color key: RbCl_6 octahedra crimson, Cl green.

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 $\text{NH}\cdots\text{Cl}$ hydrogen bonds (Figure 6). When the complete structure is considered, it is found that Cl2 and Cl3 accept two $\text{NH}\cdots\text{Cl}$ bonds each: it is notable that the corresponding two $\text{Rb}-\text{Cl}-\text{Rb}$ bond angles $[165.24(3)$ and $161.35(3)^\circ]$ are substantially smaller than the $\text{Rb}-\text{Cl}-\text{Rb}$ bond

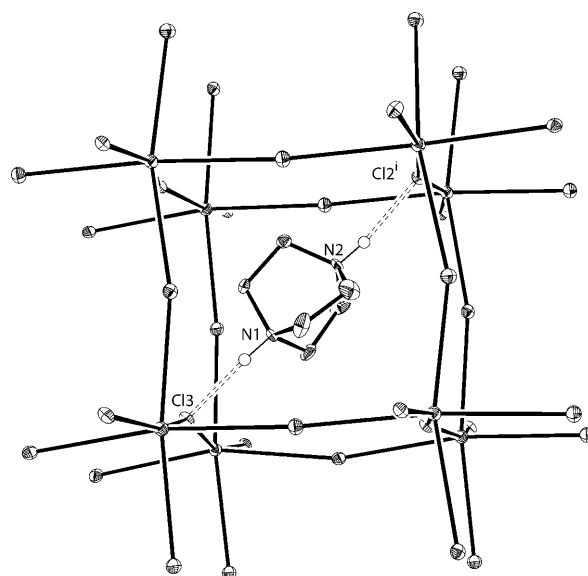


Figure 6. Fragment of **5** showing the environment of the dabconium cation within a cage formed by eight RbCl_3 octahedra, akin to the A cation site in oxide perovskites. Atoms are represented by 50% displacement ellipsoids, hydrogen bonds are indicated by double-dashed lines, and C-bonded H atoms are omitted for clarity. Symmetry code: i) $-x + y, -x, 1/3 + z$.

angle $[172.08(3)^\circ]$ for the chloride ion (Cl1) that does not accept a hydrogen bond.

$\text{C}_6\text{H}_{14}\text{N}_2\cdot\text{CsCl}_3$ (**6**) crystallizes with an exceptionally large monoclinic unit cell [$V = 9542.7(3) \text{ \AA}^3$, $Z = 32$] 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 $\text{NH}\cdots\text{Cl}$ 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 $\text{H}\cdots\text{Cl}$ distances (from 2.09 to 2.17 $\text{\AA}$) and $\text{NH}\cdots\text{Cl}$ angles (from 158 to 172 $^\circ$), 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 $\text{Cs}-\text{Cl}-\text{Cs}$ bond angle and whether the Cl atom accepts a hydrogen bond (mean = 159.7 $^\circ$ for the acceptors; 162.0 $^\circ$ 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 $\text{M}-\text{Cl}-\text{M}$ 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 $\approx$ 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 K α radiation (λ = 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. C₄H₁₂N₂·KCl₃·H₂O (**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) Å³, $F(000)$ = 520, T = 120 K, ρ = 1.604 g cm⁻³, μ = 1.232 mm⁻¹, $R(F)$ = 0.034 (957 reflections with $I > 2\sigma(I)$), $wR(F^2)$ = 0.096 (1066 reflections). C₄H₁₂N₂·RbCl₃·H₂O (**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) Å³, $F(000)$ = 592, T = 120 K, ρ = 1.846 g cm⁻³, μ = 5.320 mm⁻¹, $R(F)$ = 0.019 (1011 reflections with $I > 2\sigma(I)$), $wR(F^2)$ = 0.045 (1099 reflections). C₄H₁₂N₂·CsCl₃·H₂O (**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) Å³, $F(000)$ = 664, T = 120 K, ρ = 2.037 g cm⁻³, μ = 3.956 mm⁻¹, $R(F)$ = 0.019 (1061 reflections with $I > 2\sigma(I)$), $wR(F^2)$ = 0.044 (1152 reflections). C₄H₁₄N₂·KCl₃ (**4**)

(CCDC 776366): M_r = 259.64, trigonal, *R3c* (No. 167), Z = 18, a = 16.0494(2) Å, c = 22.1570(2) Å, V = 4942.64(12) Å³, $F(000)$ = 2412, T = 120 K, ρ = 1.570 g cm⁻³, μ = 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). C₄H₁₄N₂·RbCl₃ (**5**) (CCDC 776367): M_r = 306.01, trigonal, *P3₂21* (No. 154), Z = 6, a = 9.3376(1) Å, c = 22.3386(5) Å, V = 1686.77(5) Å³, $F(000)$ = 912, T = 120 K, ρ = 1.808 g cm⁻³, μ = 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). C₄H₁₄N₂·CsCl₃ (**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, β = 128.4835(9)°, V = 9542.7(3) Å³, $F(000)$ = 5440, T = 120 K, ρ = 1.968 g cm⁻³, μ = 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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- [1] R. H. Mitchell, *Perovskites Modern and Ancient*, Almaz Press, Thunder Bay, **2002**.
- [2] L. G. Tejuca, J. L. G. Fierro, *Properties and Applications of Perovskite-Type Oxides*, Marcel Dekker, New York, **1993**.
- [3] H. D. Megaw, *Crystal Structures: A Working Approach*, London, Saunders, **1973**, p. 216.
- [4] L. Katz, R. Ward, *Inorg. Chem.* **1964**, *3*, 205–211.
- [5] J. J. Lander, *Acta Crystallogr.* **1951**, *4*, 148–156.
- [6] A. Lemmerer, D. Billing, *CrystEngComm* **2010**, *12*, 1290–1301.
- [7] N. Mercier, N. Louvain, W. H. Bi, *CrystEngComm* **2009**, *11*, 720–734.
- [8] D. B. Mitzi, C. A. Feild, W. T. A. Harrison, A. M. Guloy, *Nature* **1994**, *369*, 467–469.
- [9] C. A. Bremner, M. Simpson, W. T. A. Harrison, *J. Am. Chem. Soc.* **2002**, *124*, 10960–10961.
- [10] A. Trzesowska, R. Kruszynski, *THEOCHEM* **2005**, *714*, 175–178.
- [11] P. Cortona, *Phys. Rev. B* **1992**, *46*, 2008–2014.
- [12] M. Blackman, I. H. Khan, *Proc. Phys. Soc. London* **1961**, *77*, 471–475.
- [13] P. M. Woodward, *Acta Crystallogr. Sect. B* **1997**, *53*, 32–43.
- [14] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876–881.
- [15] R. E. Morris, X. Bu, *Nat. Chem.* **2010**, *2*, 353–361.
- [16] P. Garcia-Fernandez, J. A. Arambarau, M. T. Barriuso, M. Moreno, *J. Phys. Chem. Lett.* **2010**, *1*, 647–651.