New Variant of Highly Symmetric Layered Perovskite with Coordinated NO_3^- Ligand: Hydrothermal Synthesis, Structure, and Characterization of $Cs_2PbCl_2(NO_3)_2$

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A new highly symmetric layered lead chloride material, $Cs_2PbCl_2(NO_3)_2$ has been synthesized by a hydrothermal reaction method using $Pb(NO_3)_2$, CsCl, and water at 240 °C. The structure has been determined by single-crystal X-ray diffraction. $Cs_2PbCl_2(NO_3)_2$ has a novel two-dimensional layered structure containing PbO_4Cl_4 polyhedra and NO_3 trigonal planes. $Cs_2PbCl_2(NO_3)_2$ is a novel variant on the layered perovskite theme, of which the structure is closely related to the $n = 1$ layered perovskite families. Detailed structural analysis, Infrared and UV−vis diffuse reflectance spectra, thermogravimetric analysis, and ion-exchange reactions of $Cs_2PbCl_2(NO_3)_2$ are reported. Crystal data: $Cs_2PbCl_2(NO_3)_2$, tetragonal, space group $I4_1/amd$ (No. 141), $a = b = 5.6905(6)$ Å, $c = 32.946(5)$ Å, $V = 1066.9(2)$ Å^3, and $Z = 4$.

Introduction

Materials containing layered structures exhibit many interesting characteristics such as optical property, intercalation behavior, ion-exchanging property, superconductivity, and storage of radioactive cations.[1−8] Besides, the constituting elements of the framework arrays in the layers reveal the extremely rich crystal chemistry. Thus, the development of superior performing new layered materials strongly remains a challenge for synthetic chemists. One of the extremely important layered materials that have drawn strong attention is the layered perovskite families ($A_{n-1}B_nO_{3n+1}$, n: the size of the two-dimensional slabs). Since these families show a variety of interesting properties with their superb structures, preparing new variants of layered perovskite materials has been of great interest to the solid-state materials chemistry field.[9−12]

Until now, synthetic solid-state material chemists have been using a number of synthesis techniques to prepare functional layered materials. Among them, one of the most extensively studied and well-established synthetic methods are the hydrothermal reactions.[13−16] Whether the reaction condition is subcritical or supercritical, the approach is an effective method of increasing the solubility and the reactivity of sparingly soluble reagents by introducing the acid or base mineralizers.[17,18] Another important factor that significantly influence on the formation of the product is the selection of suitable structure-directing agents.[19] Organic or inorganic templates are routinely used in most hydrothermal reactions because of some observed correlation between the framework structures of the materials and the employed templates. However, the exact function of the structure-directing agents on the formation and crystallization of the extended structures is hardly understood yet. Recently, extensive in situ mechanistic studies under hydrothermal conditions have been performed to understand the nature of crystallizations

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of the high-dimensional framework materials.[20,21] We have used a hydrothermal reaction technique to synthesize a novel inorganically templated lead chloride nitrate layered material, of which the structure is closely related to the layered perovskites. Several lead halide based layered perovskite structures have been reported.[22-26] However, most of the reported materials contain organic "A" cations. In this paper, we report the first synthesis, structure, characterization, and reactivity of a pure inorganic variant of the lead halide layered perovskite with unprecedented apical NO_3^- ligands.

Experimental Section

Reagents. $Pb(NO_3)_2$ (99.5+%, WACO), CsCl (99+%, Alfa Aesar), $PbCl_2$ (99%, Hayashi), and $CsNO_3$ (99%, Aldrich) were used as received.

Synthesis. $Cs_2PbCl_2(NO_3)_2$ was synthesized by a hydrothermal reaction method. 0.994 g (3.00×10^{-3} mol) of $Pb(NO_3)_2$, 0.253 g (1.50×10^{-3} mol) of CsCl, and 5 mL of H_2O were combined and transferred to a Teflon-lined stainless steel autoclave. The autoclave was subsequently sealed and heated to 240 °C, held for 4 days, and cooled slowly down to room temperature at a rate of 6 °C h^{-1}. After cooling, the autoclave was opened, and the product was recovered by filtration and washed with water. A colorless crystalline product was recovered in 52% yield based on $Pb(NO_3)_2$. It should be noted that an alternative reaction pathway using a stoichiometric amount of $PbCl_2$ and $CsNO_3$ under the same reaction condition produced exactly the same product. The powder X-ray diffraction pattern on the synthesized phase is in good agreement with the calculated pattern from the single-crystal data (see the Supporting Information).

Single-Crystal X-ray Diffraction. The structure of Cs_2PbCl_2-$(NO_3)_2$ was determined by standard crystallographic methods. A colorless plate crystal ($0.02 \times 0.02 \times 0.03$ mm^3) was used for single-crystal X-ray diffraction. The data were collected using a Bruker SMART APEX CCD X-ray diffractometer in the Korea Basic Science Institute at room temperature using graphite monochromated Mo Kα radiation. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in omega, and an exposure time of 5 s per frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was < 1%. The data were integrated using the Bruker SAINT program,[27] with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. Ψ-scans were used for the absorption correction on the hemisphere of data. The data were solved and refined using SHELXS-97 and SHELXL-97, respectively.[28,29] All of the atoms were refined with anisotropic displacement parameters and converged for $I > 2(I)$. All calculations were performed using

Table 1. Crystallographic Data for $Cs_2PbCl_2(NO_3)_2$ and $CsPb_2Cl_5$

formula	$Cl_2Cs_2N_2O_6Pb$	Cl_5CsPb_2
fw	667.93	724.54
space group	$I4_1/amd$ (No. 141)	$I4/mcm$ (No. 140)
$a = b$ (Å)	5.6905(6)	8.1070(11)
c (Å)	32.946(5)	14.698(3)
V (Å^3)	1066.9(2)	966.0(3)
Z	4	4
T (°C)	298.0(2)	223.0(2)
λ (Å)	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	4.158	4.982
μ (mm^{-1})	23.04	39.822
$R(F)^a$	0.0306	0.0247
$R_w(F_o^2)^b$	0.0873	0.0458

$^a R(F) = \sum ||F_o| - |F_c||/\sum |F_o|.$ $^b R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}.$

the WinGX-98 crystallographic software package.[30] The final Fourier difference map revealed minimum and maximum peaks of −2.044 and 3.046 e Å^{-3}. Crystallographic data for Cs_2PbCl_2-$(NO_3)_2$ are given in Table 1.

Powder X-ray Diffraction. Powder XRD patterns were collected on a SCINTAG XDS2000 diffractometer using Cu Kα radiation at room temperature with 35 kV and 30 mA. Samples were mounted on glass sample holders and scanned in the 2θ range 5−70° with a step size of 0.02° and a step time of 1 s.

Infrared and UV−vis Diffuse Reflectance Spectra. Infrared spectrum was recorded on a Varian 1000 FT-IR spectrometer in the 400−4000 cm^{-1} range, with the sample intimately pressed between two KBr pellets. UV−visible diffuse reflectance data for the reported compound were collected on a Varian Cary 500 scan UV−vis-NIR spectrophotometer over the spectral range 200−1500 nm at room temperature. Poly(tetrafluoroethylene) was used as a reference material. Reflectance spectra were converted to the absorbance using the Kubelka−Munk function.[31,32]

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed on a Setaram LABSYS TG-DTA/DSC Thermogravimetric Analyzer. The polycrystalline Cs_2PbCl_2-$(NO_3)_2$ sample was contained within a platinum crucible and heated at a rate of 10 °C min^{-1} from room temperature to 1000 °C under flowing argon.

Ion-Exchange Experiments. Ion-exchange reactions were performed by stirring about 100 mg of $Cs_2PbCl_2(NO_3)_2$ sample in 2 mL of 1 M aqueous solution of the following metal salts: $NaNO_3$, KNO_3, NaCl, and KCl. The reactions were performed at room temperature for 24 h. The reaction products were recovered by filtration, washed with excess H_2O, and dried in air for 1 d.

Scanning Electron Microscope/Energy Dispersive Analysis by X-ray (SEM/EDAX). SEM/EDAX analyses have been performed using a Hitachi S-3400N/Horiba Energy EX-250 instruments. EDAX for $Cs_2PbCl_2(NO_3)_2$ reveals a Cs/Pb/Cl ratio of 2:1:2.

Results and Discussion

Structure. $Cs_2PbCl_2(NO_3)_2$ crystallizes in a highly symmetric tetragonal space group $I4_1/amd$ (No. 141). The structure is composed of PbO_4Cl_4 polyhedra and NO_3 trigonal planes that are connected through oxygen atoms (see Figure 1). The Pb^{2+} cations are connected to four oxygen and four chlorine atoms. The Pb−O and Pb−Cl bond distances are 2.789(7) and 2.8607(5) Å, respectively. The O−Pb−O and Cl−Pb−Cl bond angles range

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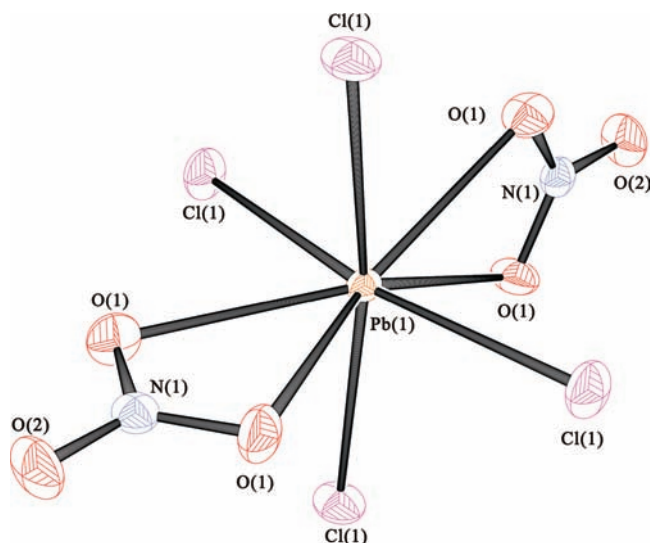(32) Tauc, J.; Kubelka *Mater. Res. Bull.* **1970**, *5*, 721.

Figure 1. ORTEP (50% probability ellipsoids) drawing of Cs_2PbCl_2-$(NO_3)_2$. Note the two *trans* NO_3 ligands are perpendicularly aligned each other.
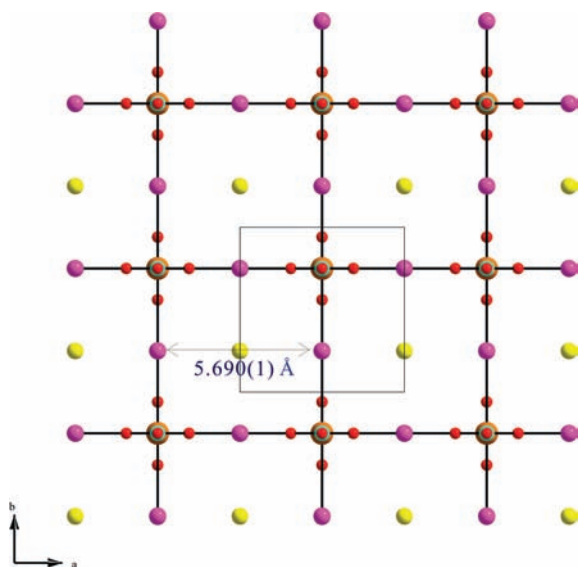

Figure 2. Ball-and-stick representation for one layer of $Cs_2PbCl_2(NO_3)_2$ in the *ab*-plane (yellow, Cs; orange, Pb; purple, Cl; cyan, N; red, O). Eight-membered square rings are observed in the layer.

45.74(19)−148.10(1)° and 90.616(17)−168.09(16)°, respectively. The two nitrate bidentate ligands with a trigonal planar geometry are coordinated to the Pb^{2+} center through oxygen atoms. Interestingly, the two *trans* NO_3 ligands coordinated to the lead are perpendicularly aligned each other (see Figure 1). The N−O bond lengths that were used for the coordination to the Pb^{2+} are relatively longer (1.263(10) Å) than those of uncoordinated N−O bond (1.224(17) Å). The eight-coordinate distorted PbO_4Cl_4 polyhedra are sharing their corners through chlorine atoms along the [100] and [010] directions and are forming a two-dimensional layered structure in the *ab*-plane (see Figure 2). Eight-membered square rings are observed in the layer. The dimensions of the square rings are approximately 5.690(1) Å × 5.690(1) Å. The cesium cations reside in the interlayer space. The unique Cs^+ cation is in 12-fold coordination

environments with eight Cs−O contacts ranging from 3.165(5) to 3.704(8) Å and four Cs−Cl contacts ranging 3.543(3)−3.925(3) Å. In connectivity terms, Cs_2PbCl_2-$(NO_3)_2$ can be formulated as consisting of $\{[PbO_{4/2}$-$Cl_{4/2}]^{4-} \; 2[NO_{2/2}O_{1/1}]^+\}^{2-}$ anionic layers, with charge balance maintained by the two Cs^+ cations. Bond valence calculations[33,34] resulted in values 2.28, 1.00, and 4.91 for Pb^{2+}, Cs^+, and N^{5+}, respectively.

One very interesting structural feature of Cs_2PbCl_2-$(NO_3)_2$ is that the structure is closely related to that of layered perovskites $(A_{n-1}B_nO_{3n+1})$. In general, layered perovskites are composed of infinite two-dimensional layers of the ABO_3 type structure that are separated by some motif. Depending on the motif that separates the layers and their offsetting manners, a few major families of layered perovskites have been classified, which include Ruddlesden−Popper (RP) compounds, Aurivillius phases, Dion-Jacobson (DJ) phases, and layered brownmillerites.[35−39] Figure 3(a) shows a representative structure of $n = 1$ Ruddlesden−Popper phase, Sr_2RuO_4.[40] As seen in Figure 3(a), the corner-sharing RuO_6 octahedra form infinite two-dimensional slabs and the slabs are separated by Sr cations. And also, the layers are offset by a (1/2, 1/2) translation along the [100] and [010] directions. Whereas, $Cs_2PbCl_2(NO_3)_2$ reveals slabs consisting of corner-shared PbO_4Cl_4 polyhedra through chlorine atoms and the layers are taken apart by Cs^+ cations (see Figure 3(b)). Although the B site is 8-coordinate, the $Cs_2PbCl_2(NO_3)_2$ still shares a similar structural motif with the $n = 1$ layered perovskites. And also, the PbO_4Cl_4 polyhedra contain NO_3^- apical ligands, which have never been observed in any perovskite families (see Figure 3(b)). Upon examining the structure more closely, one can find that the coordinated NO_3^- ligands play a very important role on the offset of the layers in $Cs_2PbCl_2(NO_3)_2$. As can be seen in Figure 3(b), the slabs 2 and 3 are offset by a 1/2 translation along [010] direction. No offset is observed from the slabs 1 and 2 or the slabs 3 and 4 along the [010] direction. However, there are offsets by a 1/2 translation along the [100] direction between the slabs 1 and 2 or the slabs 3 and 4. All these offsets seem to be attributable to the perpendicularly coordinated planar NO_3^- ligands to prevent unfavorable direct contacts of the layers. Thus, the framework structure of $Cs_2PbCl_2(NO_3)_2$ can be built up by fitting slab 1 and slab 2 (or slab 3 and slab 4) with the NO_3^- "studs" along the *a*-direction, and then further interlocking of those fitted double slabs along the *b*-direction.

Spectroscopic Studies. The infrared spectrum of $Cs_2PbCl_2(NO_3)_2$ has been recorded. The N−O vibrations were observed at 1433 (m, sh), 1384 (s), 1304 (s), 1039 (m), 833 (m, sh), 824 (m), 820 (m), and 712 (m) cm^{-1}. The assignments are consistent with those previously reported.[41]

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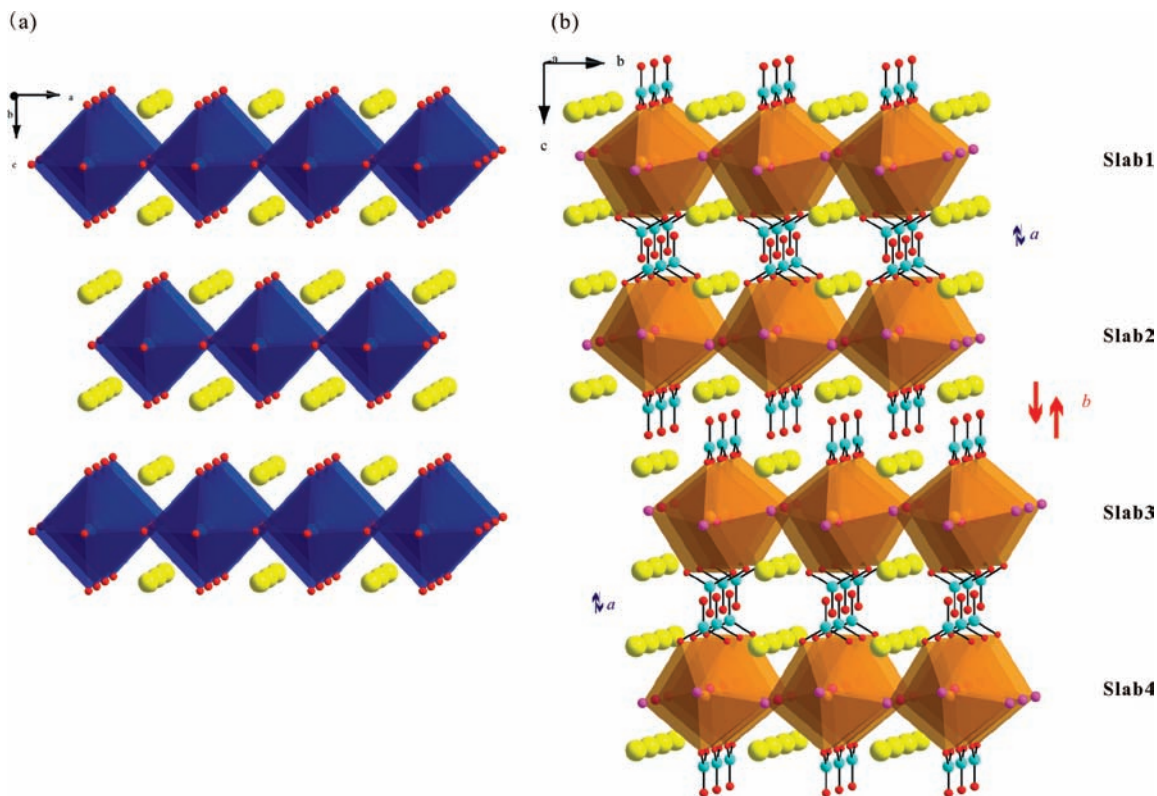(41) James, D. W.; Kimber, G. M. *Aust. J. Chem.* **1970**, *23*, 829.

Figure 3. (a) Polyhedral representation of the *n* = 1 Ruddlesden–Popper layered perovskite, Sr_2RuO_4. The structure is composed of infinite layers of corner-sharing RuO_6 octahedra. The interlayer sites are fully occupied by Sr^{2+} cations (yellow, Sr; blue, Ru; red, O). (b) Polyhedral representation of $Cs_2PbCl_2(NO_3)_2$ in the *bc*-plane to show how the slabs are offset attributable to the coordinated NO_3^- ligands (yellow, Cs; orange, Pb; purple, Cl; cyan, N; red, O). The 2D-layers of corner-sharing PbO_4Cl_4 polyhedra with apical NO_3^- ligands are separated by Cs^+ cations.

The UV–vis diffuse reflectance spectrum shows its transparency with a band gap of 3.5 eV. Absorption (*K*/*S*) data were calculated from the Kubelka–Munk function:[31,32]

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$

with *R* representing the reflectance, *K* the absorption, and *S* the scattering. In a *K*/*S* versus *E* (eV) plot, extrapolating the linear part of the rising curve to zero provides the onset of absorption at 3.5 eV. The overall band gap for the material may be attributable to the degree of the distortions arising from PbO_4Cl_4 polyhedra. The UV–vis diffuse reflectance spectrum for $Cs_2PbCl_2(NO_3)_2$ is deposited in the Supporting Information.

Thermogravimetric Analysis. The thermal behavior of $Cs_2PbCl_2(NO_3)_2$ was investigated using thermogravimetric analysis. $Cs_2PbCl_2(NO_3)_2$ is thermally stable up to approximately 440 °C. However, above the temperature, the product decomposed to a mixture of CsCl and unknown materials. The TGA data have been deposited in the Supporting Information.

Ion-Exchange Reactions. The layered structure of $Cs_2PbCl_2(NO_3)_2$ suggested the material may be able to undertake ion-exchange reactions where the Cs^+ cation is replaced by other cations. Approximately 100 mg of $Cs_2PbCl_2(NO_3)_2$ were stirred in 2 mL of 1 M solutions of $NaNO_3$, KNO_3, NaCl, and KCl for 1 day at room temperature. For the reactions with $NaNO_3$ or KNO_3, colorless needle crystals have been obtained. The powder XRD analyses on the recovered products revealed that

the crystals are Pb(OH)Cl.[42] The reactions with NaCl or KCl also showed another identical XRD patterns with high crystallinities (see the Supporting Information). The XRD pattern may be indexed on a tetragonal cell with $a = b \sim 8.12$ Å and $c \sim 14.73$ Å. EDAX analysis on the recovered polycrystalline material provided the Cs, Pb, and Cl with an approximate ratio of 1, 2, and 5, respectively, which gives a chemical formula of $CsPb_2Cl_5$. Thus, attempts have been made to prepare single-crystals of the reaction product to reveal the structure, and we were successful in growing them (see Table 1).[43] On the basis of the single-crystal X-ray diffraction analysis, the structure of $CsPb_2Cl_5$ is very similar to that of $CsSn_2Cl_5$.[44] Interestingly, upon adding the alkali metal chlorides to $Cs_2PbCl_2(NO_3)_2$ in water, $Cs_2PbCl_2(NO_3)_2$ converted to $CsPb_2Cl_5$ with the accompaning loss of nitrates. This transformation of the layer structure is shown schematically in Figure 4. As soon as the nitrates were removed from the layer of $Cs_2PbCl_2(NO_3)_2$, the coordination environment of Pb^{2+} has been changed to the more asymmetric $PbCl_4$ "see-saw" geometry. Full structural details along with the crystallographic information of $CsPb_2Cl_5$ are deposited in the Supporting Information.

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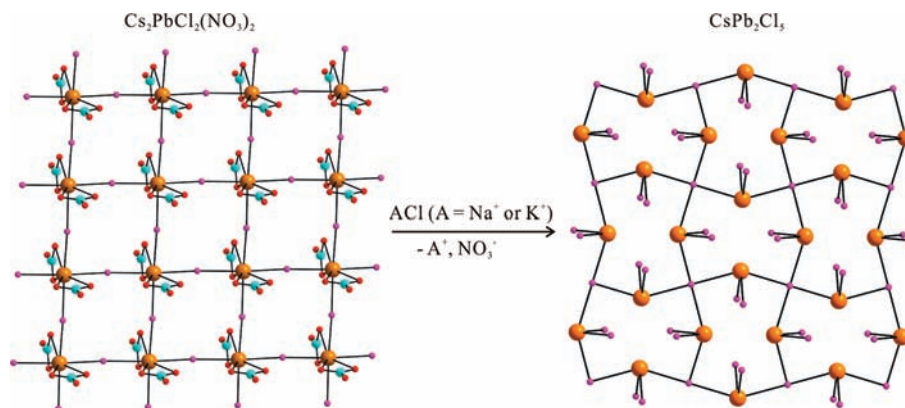
Figure 4. Ball-and-stick representations of $Cs_2PbCl_2(NO_3)_2$ and $CsPb_2Cl_5$. Note how the layer structure of $Cs_2PbCl_2(NO_3)_2$ converts to $CsPb_2Cl_5$ with the loss of nitrate anions.

Conclusions

We have successfully synthesized a new layered lead material, $Cs_2PbCl_2(NO_3)_2$, under mild hydrothermal reaction conditions. One very interesting structural feature of $Cs_2PbCl_2(NO_3)_2$ is that the material with apical NO_3^- ligands is a novel variant on the layered perovskite theme. Full spectroscopic characterizations, thermal analysis, and ion-exchange reactions have been performed on the new layered material. Additional experiments using different templates are ongoing and will be reported shortly.

Supporting Information Available: X-ray crystallographic files for $Cs_2PbCl_2(NO_3)_2$ and $CsPb_2Cl_5$ in CIF format; experimental and calculated powder X-ray diffraction patterns, thermogravimetric analysis diagram, UV−vis diffuse reflectance spectrum for $Cs_2PbCl_2(NO_3)_2$, XRD pattern of the product from the reaction with NaCl (or KCl), and full crystallographic data and structure of $CsPb_2Cl_5$. This material is available free of charge via the Internet at http://pubs.acs.org.