Supporting Information for:

New Variant of Highly Symmetric Layered Perovskite with Coordinated NO₃⁻ Ligand: Hydrothermal Synthesis, Structure, and Characterization of Cs₂PbCl₂(NO₃)₂

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S1. Experimental and calculated powder X-ray diffraction patterns for Cs₂PbCl₂(NO₃)₂

S2. UV-Vis diffuse reflectance spectrum of Cs₂PbCl₂(NO₃)₂

S3. Thermogravimetric analysis diagram for Cs₂PbCl₂(NO₃)₂

S4. Powder X-ray diffraction pattern of the product from the reaction between

 $Cs_2PbCl_2(NO_3)_2$ and NaCl (or KCl) at room temperature in H_2O .

S5. Atomic coordinates and equivalent isotropic displacement parameters for Cs₂PbCl₂(NO₃)₂

S6. Atomic coordinates and equivalent isotropic displacement parameters for CsPb₂Cl₅

S7. Selected bond distances (Å) for Cs₂PbCl₂(NO₃)₂ and CsPb₂Cl₅

S8. Ball-and-stick representation for CsPb₂Cl₅ in the *bc*-plane (yellow, Cs; orange, Pb; purple, Cl).

S9. Ball-and-stick representation for one layer of CsPb₂Cl₅ in the *ab*-plane (orange, Pb; purple, Cl).





S2. UV-Vis diffuse reflectance spectrum of Cs₂PbCl₂(NO₃)₂



The UV-vis diffuse reflectance data were collected on a Varian Cary 500 scan UV-vis-NIR spectrophotometer over the spectral range 300-1500 nm at room temperature. Polytetrafluoroethylene) was used as a reference material. Absorption (K/S) data were calculated from the following Kubelka-Munk function:

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

where *R* representing the reflectance, *K* the absorption, and *S* the scattering. In a *K/S vs. E* (eV) plot, extrapolating the linear part of the rising curve to zero provides the onset of absorption at 3.5 eV for $Cs_2PbCl_2(NO_3)_2$.

S3. TGA diagram for Cs₂PbCl₂(NO₃)₂



Thermogravimetric analysis (TGA) was performed on a Setaram LABSYS TG-DTA/DSC Thermogravimetric Analyzer. The sample was placed in a platinum crucible and heated at a rate of 10 °C min⁻¹ from room temperature to 1,000 °C under flowing argon. Figure S3 shows the TGA curve where the material is thermally decomposed through two steps exhibited at about 440 °C and 710 °C and finally mixtures of CsCl and some unknown materials remain.

S4. Powder X-ray diffraction pattern of the product from the reaction between $Cs_2PbCl_2(NO_3)_2$ and NaCl (or KCl) at room temperature in H_2O .



Note the strong preferred orientation along the (002l) attributable to the plate crystal morphology.

Atom	x	у	Ζ.	$U_{\rm eq}{}^a$ / Å ²
Pb(1)	0.5	0.25	0.125	0.0149(4)
Cs(1)	0	-0.25	0.05192(4)	0.0328(4)
Cl(1)	0.5	-0.25	0.11599(12)	0.0300(9)
N(1)	-0.5	-0.25	-0.0273(4)	0.020(3)
O (1)	-0.3095(14)	-0.25	-0.0470(2)	0.0290(17)
O(2)	-0.5	-0.25	0.0098(3)	0.034(3)

S5. Atomic coordinates and equivalent isotropic displacement parameters for Cs₂PbCl₂(NO₃)₂

 $\overline{}^{a}$ U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

S6. Atomic coordinates and equivalent isotropic displacement parameters for CsPb₂Cl₅

Atom	x	V	Ζ.	U_{eq}^{a} / Å ²
Pb(1)	0.16838(7)	0.33162(7)	0	0.0153(3)
Cs(1)	0	0	0.25	0.0171(4)
Cl(1)	0.3451(3)	0.1549(3)	0.1256(2)	0.0178(7)
Cl(2)	0	0	0	0.0133(12)

^{*a*} U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

S7. Selected bond distances (A	Å) for	$Cs_2PbCl_2(NO_3)_2$	and CsPb ₂ Cl ₅
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$Cs_2PbCl_2(NO_3)_2$			
$Pb(1)-O(1) \times 4$	2.789(7)	$Pb(1)-Cl(1) \times 4$	2.8607(5)
$N(1)-O(1) \times 2$	1.263(10)	N(1)–O(2)	1.224(17)
$Cs(1)-O(1) \times 4$	3.350(4)	$Cs(1)-O(1) \times 2$	3.704(8)
$Cs(1)-O(2) \times 2$	3.165(5)	$Cs(1)-Cl(1) \times 2$	3.543(3)
$Cs(1)-Cl(1) \times 2$	3.925(3)		
$CsPb_2Cl_5$			
$Pb(1)-Cl(1) \times 2$	2.741(4)	$Pb(1)-Cl(2) \times 2$	3.0151(5)
$Cs(1)$ – $Cl(1) \times 8$	3.570(2)	$Cs(1)$ – $Cl(2) \times 2$	3.6745(7)

S8. Ball-and-stick representation for CsPb₂Cl₅ in the *bc*-plane (yellow, Cs; orange, Pb; purple, Cl).



 $CsPb_2Cl_5$ crystallizes in a tetragonal space group *I4/mcm* (No. 140). The structure is composed of $PbCl_4$ polyhedra that are connected through chlorine atoms to form two-dimensional layers. Cs^+ cations reside in the inter-layer space and retain the charge balance.

S9. Ball-and-stick representation for one layer of $CsPb_2Cl_5$ in the *ab*-plane (orange, Pb; purple, Cl).



Asymmetric $PbCl_4$ see-saw moieties form eight-membered rings (8-MRs) in the layer. In the 8-MRs, two lone pairs in the Pb^{2+} cation point inward and the other two outward. The Cs^+ cations are not coplanar with the $PbCl_4$ ring, attributable to the lone pairs. Thus, the Cs^+ cations sit above and below the rings.