# Structural Variations in (001)-Oriented Layered Lead Halide Perovskites, Templated by 1,2,4-Triazolium

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## Supplementary Information

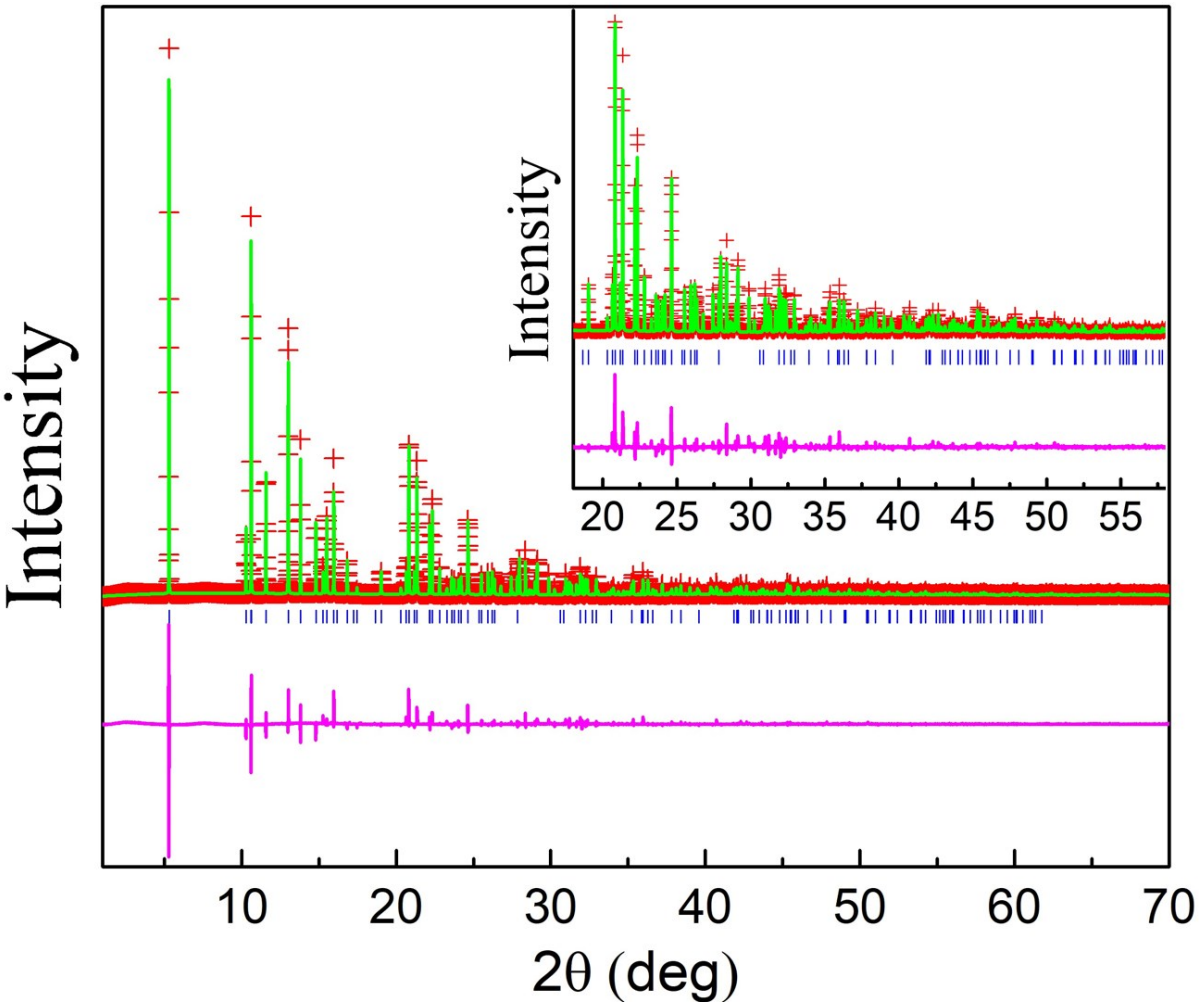


**Figure S1.** The Rietveld high resolution (synchrotron, 298 K) P-XRD and expanded (inset) data for $T_2PbCl_4$ ($\chi^2$ = 19.03, *wRp* = 0.145), the corresponding colours represent the experimental (red), the calculated (green) pattens and the difference between these two patterns (purple). This is included simply to demonstrate phase purity.

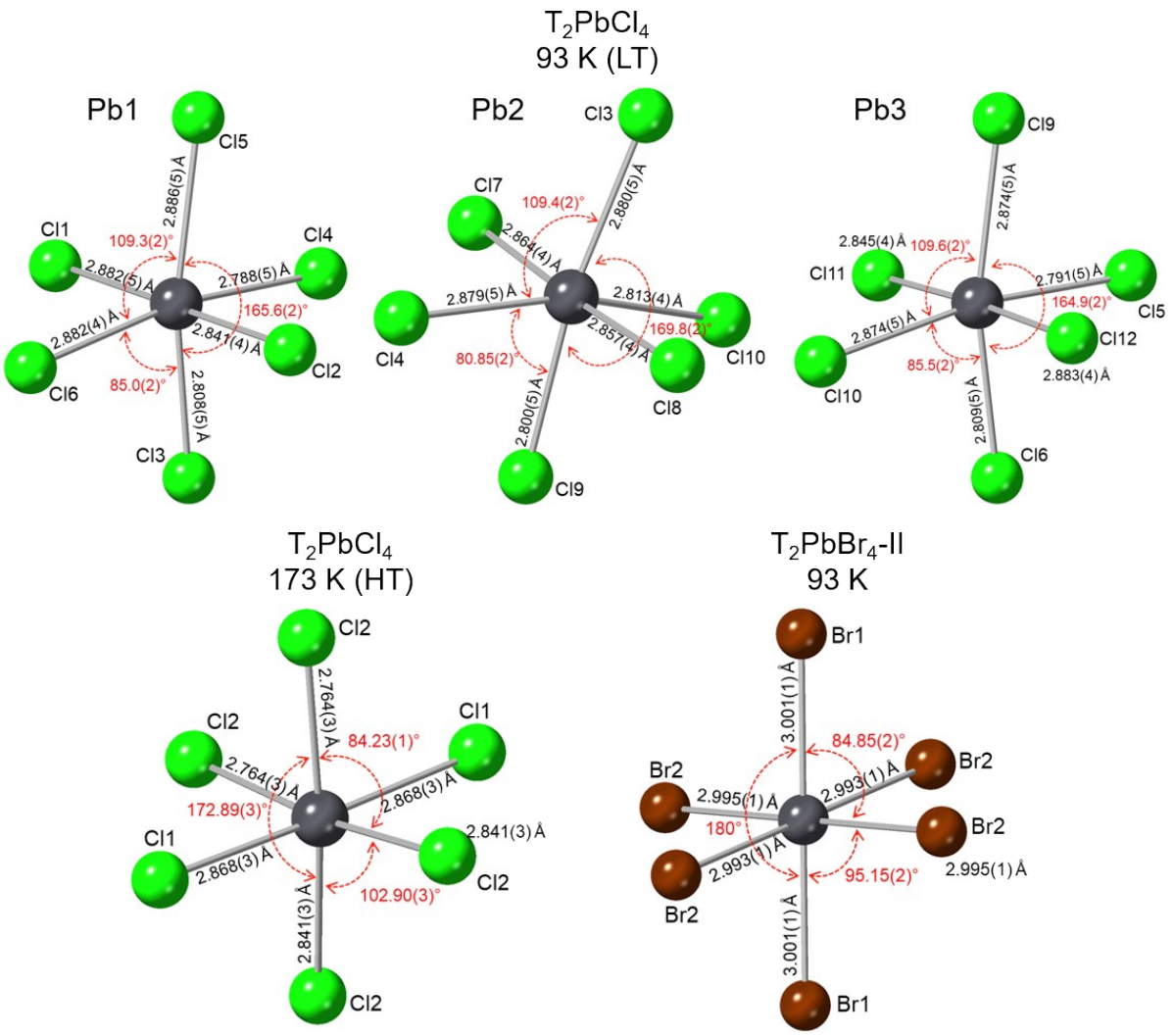


**Figure S2.** Ball and stick representations of the octahedra present in $T_2PbCl_4$ (93 K and 173 K) and $T_2PbBr_4$-II at 173 K highlighting the distortion in both bond lengths and bond angles.

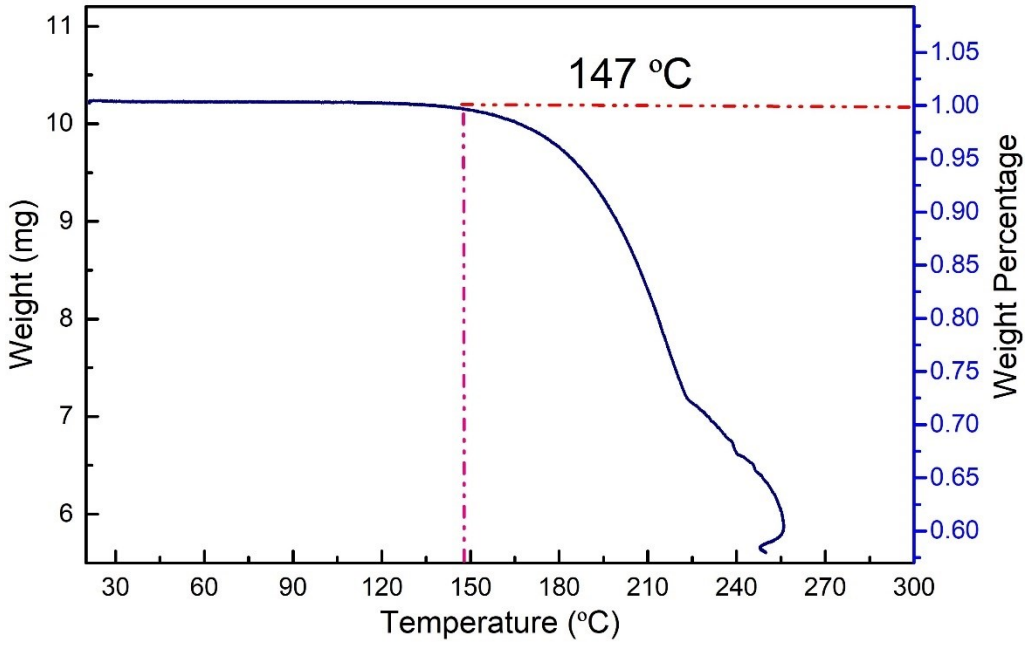


**Figure S3.** Thermal Gravimetric Analysis (TGA) for $T_2PbCl_4$ in air, demonstrating sample stability up to ~ 150 ºC.

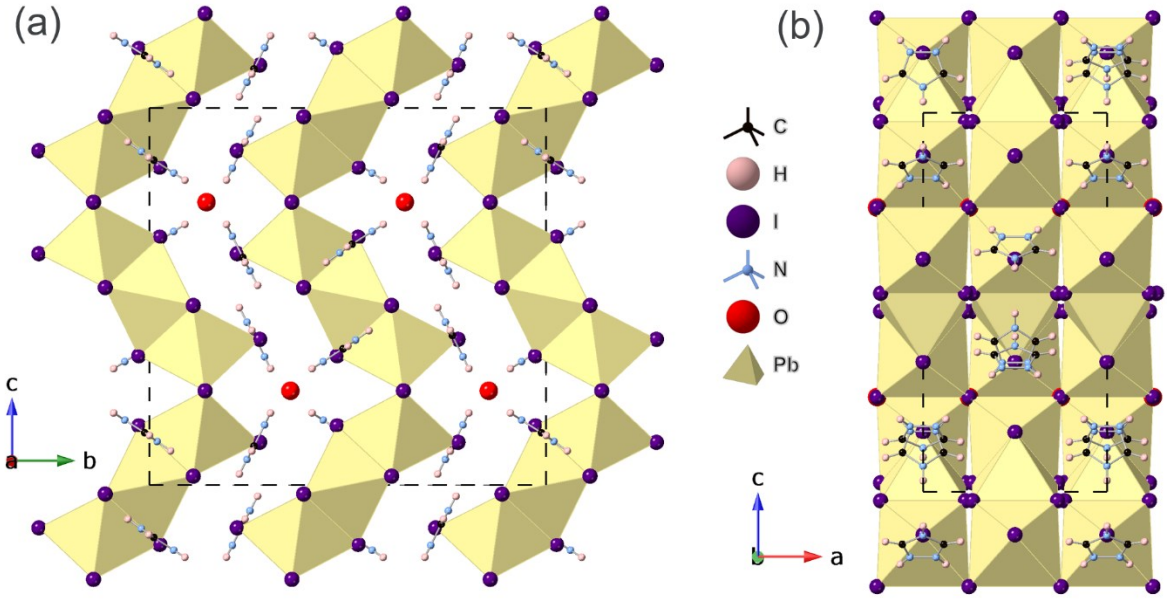


**Figure S4.** Crystal structure of $T_4Pb_3I_{10}\square 2H_2O$, view along (a) *a*-axis and (b) *b*-axis.

**Table S1.** Single crystal and structure refinement data for $T_2PbCl_4$ and $T_4Pb_3I_{10}\cdot 2H_2O$.

| Temperature | 298 K | 125 K | 93 K |
|---|---|---|---|
| **Formula** | $C_4H_8N_6PbCl_4$ | $C_4H_8N_6PbCl_4$ | $C_8H_{16}N_{12}Pb_3I_{10}\cdot 2H_2O$ |
| **Formula weight** | 489.15 | 489.15 | 2206.93 |
| **Colour/Habit** | Colorless/Platelet | Colorless/Platelet | Yellow/Prism |
| **Crystal size ($mm^3$)** | 0.24 × 0.13 × 0.06 | 0.15 × 0.10 × 0.01 | 0.02 × 0.01 × 0.01 |
| **Crystal system** | Orthorhombic | Orthorhombic | Orthorhombic |
| **Space group** | *Cmcm* | $P2_12_12_1$ | *Cmce* |
| ***a* (Å)** | 8.3092(5) | 8.321(5) | 9.6028(12) |
| ***b* (Å)** | 7.5086(5) | 21.465(12) | 20.805(2) |
| ***c* (Å)** | 21.5925(17) | 22.084(10) | 19.776(3) |
| ***V* (Å$^3$)** | 1347.17(16) | 3944(4) | 3951.0(9) |
| ***Z*** | 4 | 12 | 4 |
| **$\rho_{calc}$ (g/cm$^3$)** | 2.412 | 2.471 | 3.710 |
| **$\mu$ (mm$^{-1}$)** | 13.296 | 13.623 | 20.593 |
| **F(000)** | 896 | 2688 | 3776 |
| **Reflns collected** | 5443 | 49442 | 20834 |
| **Independent reflns** | 653 | 6913 | 1847 |
| **F(000)** | [R(int) = 0.0491] | [R(int) = 0.0895] | [R(int) = 0.0443] |
| **Goodness of Fit** | 1.230 | 0.868 | 1.180 |
| **Final *R* indices ($I > 2\sigma(I)$)** | $R_1$ = 0.0240<br>$wR_2$ = 0.0566 | $R_1$ = 0.0339<br>$wR_2$ = 0.0692 | $R_1$ = 0.0151<br>$wR_2$ = 0.0336 |
| **Largest diff. peak/hole (e Å$^{-3}$)** | 1.124/-1.265 | 1.255/-3.435 | 0.799/-1.554 |

**Table S2.** Selected bond lengths (Å) and bond angles (°) for $T_2PbCl_4$ at 173 K and 298 K.

| Temperature | 173 K | 298 K |
|---|---|---|
| Pb(1)-Cl(2)#1 | 2.764(3) | 2.776(2) |
| Pb(1)-Cl(2) | 2.764(3) | 2.776(3) |
| Pb(1)-Cl(2)#2 | 2.841(3) | 2.834(3) |
| Pb(1)-Cl(2)#3 | 2.841(3) | 2.834(2) |
| Pb(1)-Cl(1) | 2.868(3) | 2.866(2) |
| Pb(1)-Cl(1)#4 | 2.868(3) | 2.866(2) |
| Cl(2)#1-Pb(1)-Cl(2) | 88.7(3) | 88.8(2) |
| Cl(2)#1-Pb(1)-Cl(2)#2 | 84.228(10) | 84.277(8) |
| Cl(2)-Pb(1)-Cl(2)#3 | 84.227(10) | 84.277(8) |
| Cl(2)#2-Pb(1)-Cl(2)#3 | 102.9(3) | 102.6(2) |
| Cl(2)#1-Pb(1)-Cl(1) | 89.43(5) | 89.45(4) |
| Cl(2)-Pb(1)-Cl(1) | 89.43(5) | 89.45(4) |
| Cl(2)#2-Pb(1)-Cl(1) | 90.50(4) | 90.49(3) |
| Cl(2)#3-Pb(1)-Cl(1) | 90.50(4) | 90.49(3) |
| Cl(2)#1-Pb(1)-Cl(1)#4 | 89.43(5) | 89.45(4) |
| Cl(2)-Pb(1)-Cl(1)#4 | 89.43(5) | 89.45(4) |
| Cl(2)#2-Pb(1)-Cl(1)#4 | 90.50(4) | 90.48(3) |
| Cl(2)#3-Pb(1)-Cl(1)#4 | 90.50(4) | 90.48(3) |
| Pb(1)-Cl(2)-Pb(1)#6 | 172.9(3) | 173.1(2) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2  #2 x-1/2,y-1/2,z  #3 -x+3/2,y-1/2,-z+3/2

#4 x,y,-z+3/2  #5 -x,y,z  #6 x+1/2,y+1/2,z

**Table S3.** Selected bond lengths (Å) and bond angles (°) for $T_2PbCl_4$ at 93 K and 125 K.

| Temperature | 93 K | 125 K |
|---|---|---|
| Pb(1)-Cl(4) | 2.788(5) | 2.790(5) |
| Pb(1)-Cl(3) | 2.808(5) | 2.815(5) |
| Pb(1)-Cl(2) | 2.841(4) | 2.846(5) |
| Pb(1)-Cl(1) | 2.882(4) | 2.879(5) |
| Pb(1)-Cl(6) | 2.882(5) | 2.883(5) |
| Pb(1)-Cl(5)#1 | 2.886(5) | 2.885(6) |
| Pb(2)-Cl(9) | 2.800(5) | 2.802(6) |
| Pb(2)-Cl(10) | 2.813(4) | 2.812(6) |
| Pb(2)-Cl(8) | 2.857(4) | 2.860(5) |
| Pb(2)-Cl(7) | 2.864(4) | 2.876(5) |
| Pb(2)-Cl(4) | 2.879(5) | 2.877(5) |
| Pb(2)-Cl(3)#1 | 2.880(5) | 2.878(5) |
| Pb(3)-Cl(5) | 2.791(5) | 2.794(6) |

| | | |
|---|---|---|
| Pb(3)-Cl(6) | 2.809(5) | 2.813(5) |
| Pb(3)-Cl(11) | 2.845(4) | 2.848(5) |
| Pb(3)-Cl(9)#2 | 2.874(5) | 2.876(6) |
| Pb(3)-Cl(10)#3 | 2.874(5) | 2.877(6) |
| Pb(3)-Cl(12) | 2.883(4) | 2.888(5) |
| Cl(4)-Pb(1)-Cl(3) | 84.57(15) | 85.15(17) |
| Cl(4)-Pb(1)-Cl(2) | 90.39(12) | 90.45(15) |
| Cl(3)-Pb(1)-Cl(2) | 88.59(13) | 88.63(16) |
| Cl(4)-Pb(1)-Cl(1) | 91.75(12) | 91.35(15) |
| Cl(3)-Pb(1)-Cl(1) | 89.15(12) | 88.98(15) |
| Cl(3)-Pb(1)-Cl(6) | 85.04(18) | 85.0(2) |
| Cl(2)-Pb(1)-Cl(6) | 88.65(13) | 88.59(15) |
| Cl(1)-Pb(1)-Cl(6) | 88.80(12) | 89.20(15) |
| Cl(4)-Pb(1)-Cl(5)#1 | 81.08(18) | 81.5(2) |
| Cl(2)-Pb(1)-Cl(5)#1 | 92.78(13) | 92.67(16) |
| Cl(1)-Pb(1)-Cl(5)#1 | 90.00(12) | 90.12(15) |
| Cl(6)-Pb(1)-Cl(5)#1 | 109.33(16) | 108.33(18) |
| Cl(9)-Pb(2)-Cl(10) | 84.36(15) | 85.05(18) |
| Cl(9)-Pb(2)-Cl(8) | 91.31(14) | 91.11(16) |
| Cl(10)-Pb(2)-Cl(8) | 90.18(14) | 90.13(17) |
| Cl(9)-Pb(2)-Cl(7) | 90.41(14) | 90.22(17) |
| Cl(10)-Pb(2)-Cl(7) | 86.92(14) | 87.16(16) |
| Cl(9)-Pb(2)-Cl(4) | 80.85(18) | 81.3(2) |
| Cl(8)-Pb(2)-Cl(4) | 92.27(12) | 92.28(15) |
| Cl(7)-Pb(2)-Cl(4) | 91.05(12) | 90.73(15) |
| Cl(10)-Pb(2)-Cl(3)#1 | 85.40(16) | 85.2(2) |
| Cl(8)-Pb(2)-Cl(3)#1 | 88.87(13) | 89.37(16) |
| Cl(7)-Pb(2)-Cl(3)#1 | 88.90(13) | 88.83(15) |
| Cl(4)-Pb(2)-Cl(3)#1 | 109.38(15) | 108.44(17) |
| Cl(5)-Pb(3)-Cl(6) | 84.51(16) | 85.05(18) |
| Cl(5)-Pb(3)-Cl(11) | 89.79(13) | 89.56(16) |
| Cl(6)-Pb(3)-Cl(11) | 87.77(12) | 87.75(15) |
| Cl(5)-Pb(3)-Cl(9)#2 | 80.42(17) | 81.0(2) |
| Cl(11)-Pb(3)-Cl(9)#2 | 92.27(13) | 92.13(16) |
| Cl(6)-Pb(3)-Cl(10)#3 | 85.48(17) | 85.6(2) |
| Cl(11)-Pb(3)-Cl(10)#3 | 88.58(14) | 89.04(16) |
| Cl(9)#2-Pb(3)-Cl(10)#3 | 109.59(15) | 108.33(18) |
| Cl(5)-Pb(3)-Cl(12) | 92.38(12) | 92.24(15) |
| Cl(6)-Pb(3)-Cl(12) | 90.44(12) | 90.47(16) |
| Cl(9)#2-Pb(3)-Cl(12) | 90.07(14) | 90.07(17) |
| Cl(10)#3-Pb(3)-Cl(12) | 88.94(14) | 88.87(16) |
| Pb(1)-Cl(3)-Pb(2)#4 | 145.95(19) | 147.6(2) |
| Pb(1)-Cl(4)-Pb(2) | 170.41(19) | 170.6(2) |
| Pb(3)-Cl(5)-Pb(1)#4 | 169.9(2) | 170.1(2) |
| Pb(3)-Cl(6)-Pb(1) | 145.3(2) | 147.0(2) |

| | | |
|---|---|---|
| Pb(2)-Cl(9)-Pb(3)#5 | 170.9(2) | 171.0(2) |
| Pb(2)-Cl(10)-Pb(3)#6 | 145.70(19) | 147.7(2) |

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+3/2,-y+1,z-1/2 #3 -x+1/2,-y+1,z-1/2

#4 x+1,y,z #5 -x+3/2,-y+1,z+1/2 #6 -x+1/2,-y+1,z+1/2

**Table S4.** Selected bond lengths (Å) and bond angles (°) for $T_2PbBr_4$-II.

| **Temperature** | **173 K** |
|---|---|
| Pb(1)-Br(2) | 2.9926(6) |
| Pb(1)-Br(2)#1 | 2.9926(6) |
| Pb(1)-Br(2)#2 | 2.9951(6) |
| Pb(1)-Br(2)#3 | 2.9951(6) |
| Pb(1)-Br(1) | 3.0009(6) |
| Pb(1)-Br(1)#1 | 3.0009(6) |
| Br(2)-Pb(1)-Br(2)#2 | 89.920(6) |
| Br(2)#1-Pb(1)-Br(2)#2 | 90.080(6) |
| Br(2)-Pb(1)-Br(2)#3 | 90.080(6) |
| Br(2)#1-Pb(1)-Br(2)#3 | 89.920(6) |
| Br(2)-Pb(1)-Br(1) | 96.744(18) |
| Br(2)#1-Pb(1)-Br(1) | 83.257(18) |
| Br(2)#2-Pb(1)-Br(1) | 95.147(18) |
| Br(2)#3-Pb(1)-Br(1) | 84.853(18) |
| Br(2)-Pb(1)-Br(1)#1 | 83.256(19) |
| Br(2)#1-Pb(1)-Br(1)#1 | 96.743(19) |
| Br(2)#2-Pb(1)-Br(1)#1 | 84.853(18) |
| Br(2)#3-Pb(1)-Br(1)#1 | 95.147(18) |
| Pb(1)-Br(2)-Pb(1)#4 | 165.12(3) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x,-y+1/2,z-1/2 #3 -x+1,y+1/2,-z+3/2

#4 -x+1,y-1/2,-z+3/2

**Table S5.** Hydrogen bond lengths (Å) and angles (°) for $T_2PbCl_4$ at 173 K and 298 K.

| **$T_2PbCl_4$** | **D-H...A** | **d(D-H)** | **d(H...A)** | **d(D...A)** | **<(DHA)** |
|---|---|---|---|---|---|
| **173K** | N(1)-H(2)...Cl(1) | 0.91(2) | 2.27(4) | 3.147(7) | 163.0(9) |
| **298K** | N(1)-H(2)...Cl(1) | 0.90(2) | 2.27(3) | 3.156(6) | 168.0(10) |

**Table S6.** Hydrogen bond lengths (Å) and angles (°) for $T_2PbCl_4$ at 93 K.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1)...Cl(1) | 0.86 | 2.42 | 3.185(17) | 148.5 |
| N(3)-H(2)...Cl(1)#4 | 0.86 | 2.28 | 3.135(16) | 172.3 |
| N(4)-H(5)...Cl(2)#1 | 0.86 | 2.46 | 3.196(17) | 144.4 |
| N(4)-H(5)...Cl(6)#1 | 0.86 | 2.92 | 3.428(17) | 119.4 |
| N(6)-H(6)...Cl(2) | 0.86 | 2.28 | 3.130(16) | 170 |
| N(7)-H(9)...Cl(7)#4 | 0.86 | 2.41 | 3.171(18) | 148.3 |
| N(10)-H(13)...Cl(3) | 0.86 | 2.98 | 3.472(18) | 118.2 |
| N(10)-H(13)...Cl(8)#4 | 0.86 | 2.43 | 3.188(18) | 146.6 |
| N(12)-H(14)...Cl(8) | 0.86 | 2.28 | 3.137(17) | 171.6 |
| N(13)-H(17)...Cl(10)#2 | 0.86 | 2.99 | 3.472(18) | 117.6 |
| N(13)-H(17)...Cl(11)#4 | 0.86 | 2.43 | 3.191(18) | 147.7 |
| N(15)-H(18)...Cl(11) | 0.86 | 2.3 | 3.151(17) | 169.7 |
| N(16)-H(21)...Cl(12)#4 | 0.86 | 2.39 | 3.166(17) | 149.9 |
| N(18)-H(22)...Cl(12) | 0.86 | 2.28 | 3.135(17) | 173.6 |

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+3/2,-y+1,z-1/2 #3 -x+1/2,-y+1,z-1/2

#4 x+1,y,z #5 -x+3/2,-y+1,z+1/2 #6 -x+1/2,-y+1,z+1/2

**Table S7.** Hydrogen bond lengths (Å) and angles (°) for $T_2PbCl_4$ at 125 K.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1)...Cl(1) | 0.86 | 2.4 | 3.174(18) | 149.4 |
| N(3)-H(2)...Cl(1)#4 | 0.86 | 2.28 | 3.133(18) | 174.1 |
| N(4)-H(5)...Cl(2)#1 | 0.86 | 2.44 | 3.182(19) | 144.9 |
| N(4)-H(5)...Cl(6)#1 | 0.86 | 2.93 | 3.44(2) | 119.1 |
| N(6)-H(6)...Cl(2) | 0.86 | 2.29 | 3.137(17) | 170.5 |
| N(7)-H(9)...Cl(7)#4 | 0.86 | 2.43 | 3.194(18) | 148.8 |
| N(10)-H(13)...Cl(3) | 0.86 | 3.02 | 3.50(2) | 117.7 |
| N(10)-H(13)...Cl(8)#4 | 0.86 | 2.43 | 3.188(19) | 147.3 |
| N(12)-H(14)...Cl(8) | 0.86 | 2.28 | 3.133(18) | 172.7 |
| N(13)-H(17)...Cl(10)#2 | 0.86 | 3.04 | 3.53(2) | 117.7 |
| N(13)-H(17)...Cl(11)#4 | 0.86 | 2.43 | 3.194(19) | 148.4 |
| N(15)-H(18)...Cl(11) | 0.86 | 2.29 | 3.145(18) | 170.1 |
| N(16)-H(21)...Cl(12)#4 | 0.86 | 2.4 | 3.180(17) | 150.2 |
| N(18)-H(22)...Cl(12) | 0.86 | 2.28 | 3.140(17) | 173.4 |

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+3/2,-y+1,z-1/2 #3 -x+1/2,-y+1,z-1/2

#4 x+1,y,z  #5 -x+3/2,-y+1,z+1/2  #6 -x+1/2,-y+1,z+1/2

**Table S8.** Hydrogen bond lengths (Å) and angles (°) for $T_2PbBr_4$-II at 173 K.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1)...Br(1)#5 | 0.86 | 2.70 | 3.379(7) | 137.1 |
| N(1)-H(1)...Br(2)#6 | 0.86 | 3.01 | 3.654(6) | 133.3 |
| N(3)-H(2)...Br(1) | 0.86 | 2.52 | 3.316(6) | 154.2 |

Symmetry transformations used to generate equivalent atoms:

#5 x,y,z+1  #6 -x+1,-y+1,-z+2

**Distortion mode analysis**

The on-line crystallographic tool ISODISTORT provides a decomposition of a distorted crystal structure in terms of irreducible representation (*irrep*) analysis. In this case, ISODISTORT is used to compare the cif file for the refined crystal structure of $T_2PbCl_4$ at 93 K to that of an idealised 'parent' phase. For simplicity in comparing the '$BX_4$' layer structure of the present compound without needing to consider the organic moieties, the cif for the parent phase has been adjusted from the aristotype inorganic $n = 1$ RP phase $K_2NiF_4$ by removing K, renaming the Ni and F positions to Pb and Cl, respectively, and adjusting the unit cell parameters and *z*-coordinate of the Cl2 atom, to produce Pb-Cl bond lengths that are similar in dimensions to those expected. Since the ISODISTORT software uses normal mode analysis, none of these adjustments affect the key derived outputs, which are the symmetry-allowed distortion modes at the Brillouin zone boundary, and their magnitudes.

The primary modes evidenced act at the points *M* (***k*** = 1, 1, 1), *X* (***k*** = ½, ½, 0), Δ (***k*** = ⅙, ⅙, 0) and *Y* (***k*** = ⅙, ⅚, 0) of the parent *I*4/*mmm* Brillouin zone. The relevant *irrep*s are $M_5^-$, which describes the antiferrodistortive displacement of adjacent octahedral layers along the *b*-axis; $X_2^+$, the cooperative rotation of the $PbCl_6$ octahedra around the *b*-axis; and $\Delta_3$ and $Y_3$, which together define the sinusoidal 'rippling' of the $[PbCl_4]_\infty$ layers, leading to the tripled unit cell along *c*.

**Table S9:** Distortion mode amplitudes for the inorganic portion of the structure in $T_2PbCl_4$ at 93 K, obtained from the ISODISTORT software suite. The 'parent' phase is a simulated aristotype based on the Ruddlesden-Popper $K_2NiF_4$ structure. See attached file for full ISODISTORT output.

| **Mode** | **Amplitude (Å)** | ***k*-active** |
|---|---|---|
| $M_5^-$ | 1.89 | (1, 1, 1) |
| $X_2^+$ | 0.77 | (½, ½, 0) |
| $D_3$ | 0.55 | (⅙, ⅙, 0) |
| $Y_3$ | 0.18 | (⅙, ⅚, 0) |