Supporting Information

$RbPb_8O_4Cl_9$: First Alkali Metal Lead Oxyhalide with Distorted $[PbO_3Cl_3]$ and $[PbOCl_5]$ Mixed-Anion Groups

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Table S1 Atomic coordinates and equivalent isotropic displacement parameters of $RbPb_8O_4Cl_9$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	S.O.F.	*x*	*y*	*z*	U(eq)	BVS[a]
Pb(1)	1	1073(1)	6921(1)	6512(1)	19(1)	2.12
Pb(2)	1	123(1)	6660(1)	1703(1)	22(1)	2.20
Rb(1)	0.819	2500	2500	3327(8)	22(1)	1.09
Rb(2)	0.181	2500	2500	2230(30)	5(5)	1.29
Cl(1)	1	-1282(2)	5688(3)	3996(4)	32(1)	1.03
Cl(2)	1	1273(3)	4649(2)	1195(4)	30(1)	0.91
Cl(3)	1	2500	7500	0	32(2)	0.95
O(1)	1	1387(7)	7021(7)	3699(9)	16(2)	2.42

[a] The bond valence sum is calculated by bond-valence theory ($S_i = \exp[(R_o - R_i/B]$, where R_o is an empirical constant, R_i is the length of bond I (in angstroms), and B= 0.37).

Table S2 Symmetry, selected bond lengths and angles of $RbPb_8O_4Cl_9$.

Pb(1)-O(1)#1	2.325(8)	O(1)-Pb(2)-Cl(2)	86.4(2)	Cl(1)#4-Rb(1)-Cl(2)#8	105.42(8)
Pb(1)-O(1)#3	2.373(8)	O(1)-Pb(2)-Cl(3)	69.6(2)	Cl(1)#3-Rb(1)-Cl(2)#9	69.20(8)
Pb(1)-O(1)	2.274(7)	Cl(1)#7-Rb(1)-Cl(1)#6	66.40(11)	Cl(2)#8-Rb(1)-Cl(2)#9	120.3(2)
Pb(2)-Cl(1)	2.740(3)	Cl(1)#3-Rb(1)-Cl(1)#6	66.40(11)	Cl(2)#8-Rb(1)-Cl(2)	75.66(9)
Pb(2)-Cl(2)	2.800(3)	Cl(1)#3-Rb(1)-Cl(1)#4	66.40(11)	Cl(2)-Rb(1)-Cl(2)#9	75.66(9)
Pb(2)-Cl(3)	3.3046(5)	Cl(1)#3-Rb(1)-Cl(1)#7	101.5(2)	Cl(2)#9-Rb(1)-Cl(2)#10	75.66(9)
Pb(2)-O(1)	2.234(8)	Cl(1)#4-Rb(1)-Cl(1)#6	101.5(2)	Cl(2)-Rb(1)-Cl(2)#10	120.3(2)
Rb(1)-Cl(1)#3	3.370(5)	Cl(1)#4-Rb(1)-Cl(1)#7	66.40(11)	Cl(2)#8-Rb(1)-Cl(2)#10	75.66(9)
Rb(1)-Cl(1)#6	3.370(5)	Cl(1)#3-Rb(1)-Cl(2)#8	169.99(18)	Pb(2)-Cl(1)-Rb(1)#4	114.44(12)
Rb(1)-Cl(1)#4	3.370(5)	Cl(1)#3-Rb(1)-Cl(2)	105.43(8)	Pb(2)-Cl(2)-Rb(1)	141.86(15)
Rb(1)-Cl(1)#7	3.370(5)	Cl(1)#7-Rb(1)-Cl(2)#8	69.20(8)	Pb(2)-Cl(2)-Rb(2)	156.1(4)
Rb(1)-Cl(2)#8	3.410(5)	Cl(1)#3-Rb(1)-Cl(2)#10	111.33(8)	Pb(1)-O(1)-Pb(1)#1	99.4(3)
Rb(1)-Cl(2)#9	3.410(5)	Cl(1)#7-Rb(1)-Cl(2)#10	105.42(8)	Pb(1)-O(1)-Pb(1)#3	100.9(3)
Rb(1)-Cl(2)#10	3.410(5)	Cl(1)#4-Rb(1)-Cl(2)	69.20(8)	Pb(2)-O(1)-Pb(1)#1	108.5(3)

Rb(1)-Cl(2)	3.410(5)	Cl(1)#6-Rb(1)-Cl(2)#10	69.20(8)	Pb(2)-O(1)-Pb(1)	125.4(4)
Cl(2)-Rb(2)	3.071(7)	Cl(1)#7-Rb(1)-Cl(2)	111.33(8)	Pb(2)-O(1)-Pb(1)#3	116.3(3)
O(1)-Pb(1)-O(1)#1	78.6(3)	Cl(1)#4-Rb(1)-Cl(2)#9	111.33(8)	Cl(2)#8-Rb(2)-Cl(2)#9	148.8(8)
O(1)#1-Pb(1)-O(1)#3	76.2(3)	Cl(1)#6-Rb(1)-Cl(2)#8	111.33(8)	Cl(2)#9-Rb(2)-Cl(2)#10	85.8(2)
O(1)-Pb(1)-O(1)#3	77.6(3)	Cl(1)#7-Rb(1)-Cl(2)#9	169.99(18)	Cl(2)-Rb(2)-Cl(2)#8	85.8(2)
Cl(1)-Pb(2)-Cl(2)	91.90(11)	Cl(1)#6-Rb(1)-Cl(2)#9	105.42(8)	Cl(2)#8-Rb(2)-Cl(2)#10	85.8(2)
Cl(1)-Pb(2)-Cl(3)	158.39(8)	Cl(1)#4-Rb(1)-Cl(2)#10	169.99(18)	Cl(2)-Rb(2)-Cl(2)#9	85.8(2)
Cl(2)-Pb(2)-Cl(3)	77.26(8)	Cl(1)#6-Rb(1)-Cl(2)	169.99(18)	Cl(2)-Rb(2)-Cl(2)#10	148.8(8)
O(1)-Pb(2)-Cl(1)	91.3(2)				

[#1]y-1/2,-x+1,-z+1; [#2]-x+1/2,-y+3/2,z; [#3]-y+1,x+1/2,-z+1; [#4]-x,-y+1,-z+1; [#5]-x,-y+1,-z; [#6]x+1/2,y-1/2,-z+1; [#7]y-1/2,-x,-z+1; [#8]-y+1/2,x,z; [#9]y,-x+1/2,z; [#10]-x+1/2,-y+1/2,z;

Table S3 Anisotropic displacement parameters of $RbPb_8O_4Cl_9$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	18(1)	18(1)	20(1)	0(1)	5(1)	-1(1)
Pb(2)	22(1)	23(1)	22(1)	0(1)	-7(1)	-2(1)
Rb(1)	19(1)	19(1)	27(3)	0	0	0
Rb(2)	3(4)	3(4)	11(13)	0	0	0
Cl(1)	30(2)	26(2)	41(2)	-6(1)	9(1)	-6(1)
Cl(2)	28(2)	29(2)	34(1)	-9(1)	-6(1)	0(1)
Cl(3)	37(2)	37(2)	23(3)	0	0	0
O(1)	16(4)	20(5)	12(4)	-4(3)	3(3)	-3(3)

Table S4 The band gaps of the title compound and the simple lead oxyhalides.

Compounds	Band gap
$RbPb_8O_4Cl_9$	**3.66 eV**
$Pb_{17}O_8Cl_{18}$	3.44 eV [1]
$Pb_3O_2Cl_2$	Unknown [2]
$Pb_{18}O_8Cl_{15}I_5$	2.82 eV [3]
$Pb_{13}O_6Cl_4Br_{10}$	3.05 eV [4]
$Pb_{13}O_6Cl_7Br_7$	3.13 eV [4]
$Pb_{13}O_6Cl_9Br_5$	3.23 eV [4]

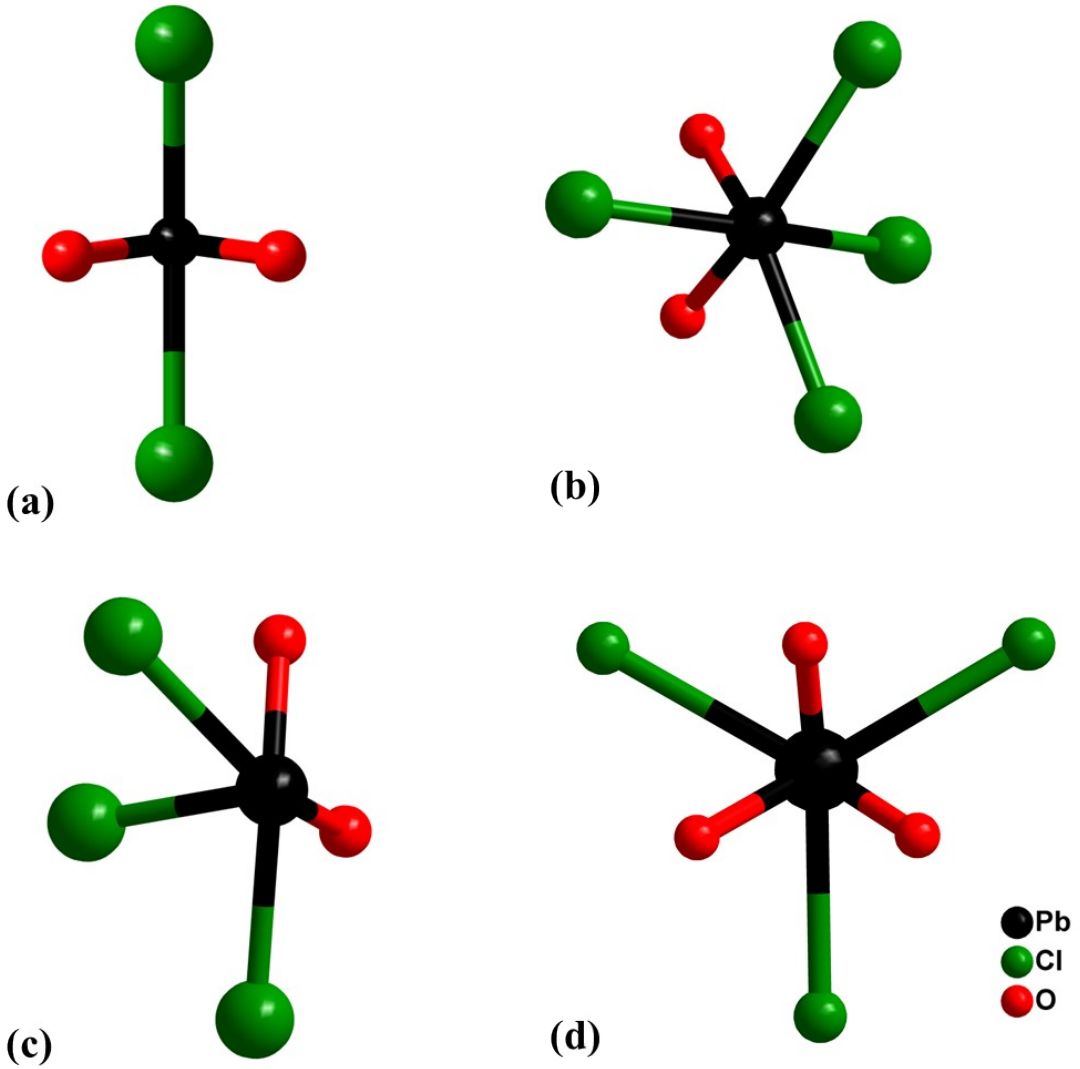

Figure S1 The structure of $[PbO_2Cl_4]$ (a) and $[PbO_2Cl_2]$ (b) in $Pb_3O_2Cl_2$; (c) The structure of $[PbO_2Cl_3]$ in $Pb_{17}O_8Cl_{18}$; (d) The structure of $[PbO_3Cl_3]$ in $Ba_{27}Pb_8O_8Cl_{54}$.

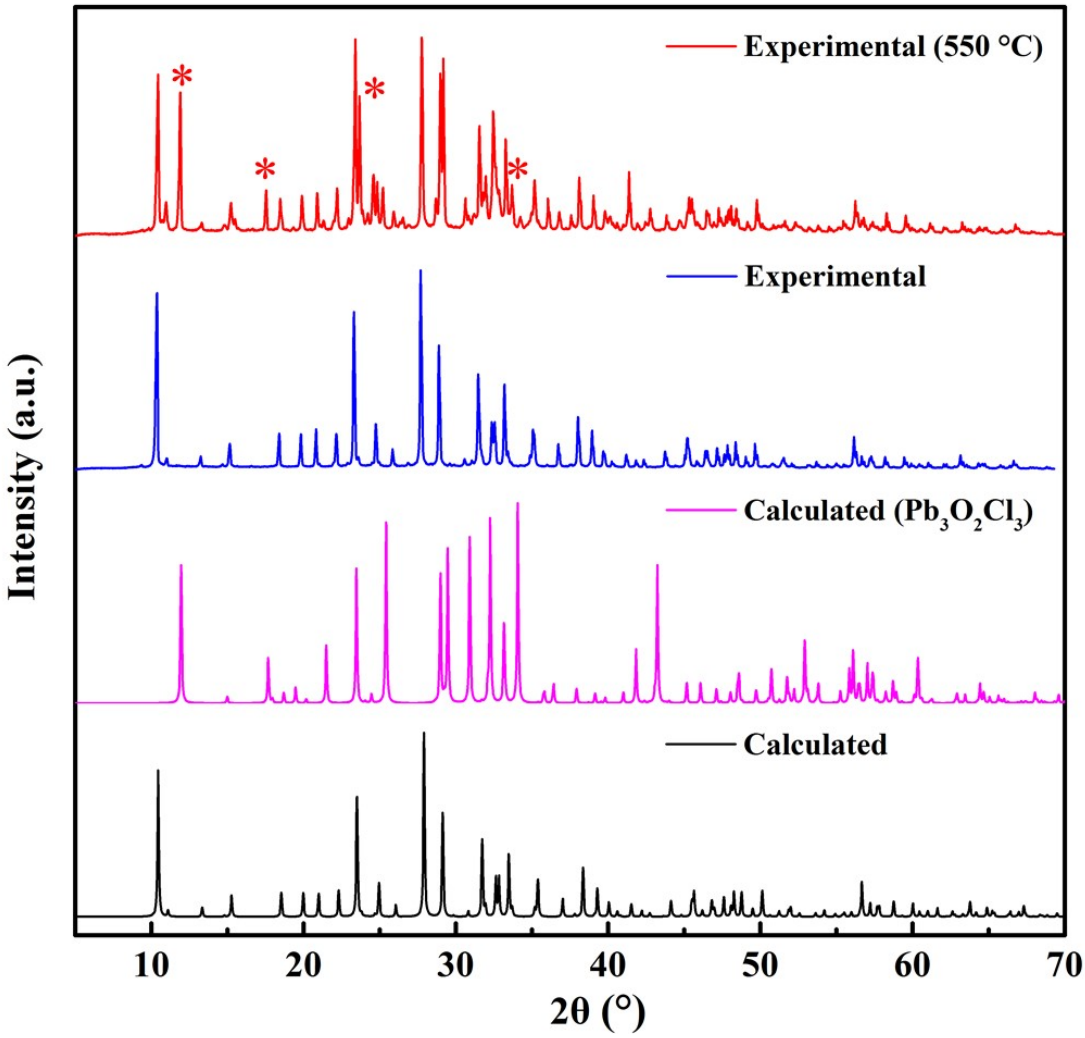

Figure S2 XRD patterns. The black and pink curves show the calculated XRD patterns of $RbPb_8O_4Cl_9$ and $Pb_3O_2Cl_2$, respectively. The thermal decomposition products should be $Pb_3O_2Cl_2$, RbCl (↑) and $PbCl_2$ (↑). The blue and red curves show the experimental XRD patterns of $RbPb_8O_4Cl_9$ before and after heating at 550 °C respectively.

Notes and references

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