$(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2(CH_3NH_3)Pb_2I_7$: a predicted non-centrosymmetrical structure built up from carboxylic acid supramolecular synthons and bilayer perovskite sheets

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Supplementary data

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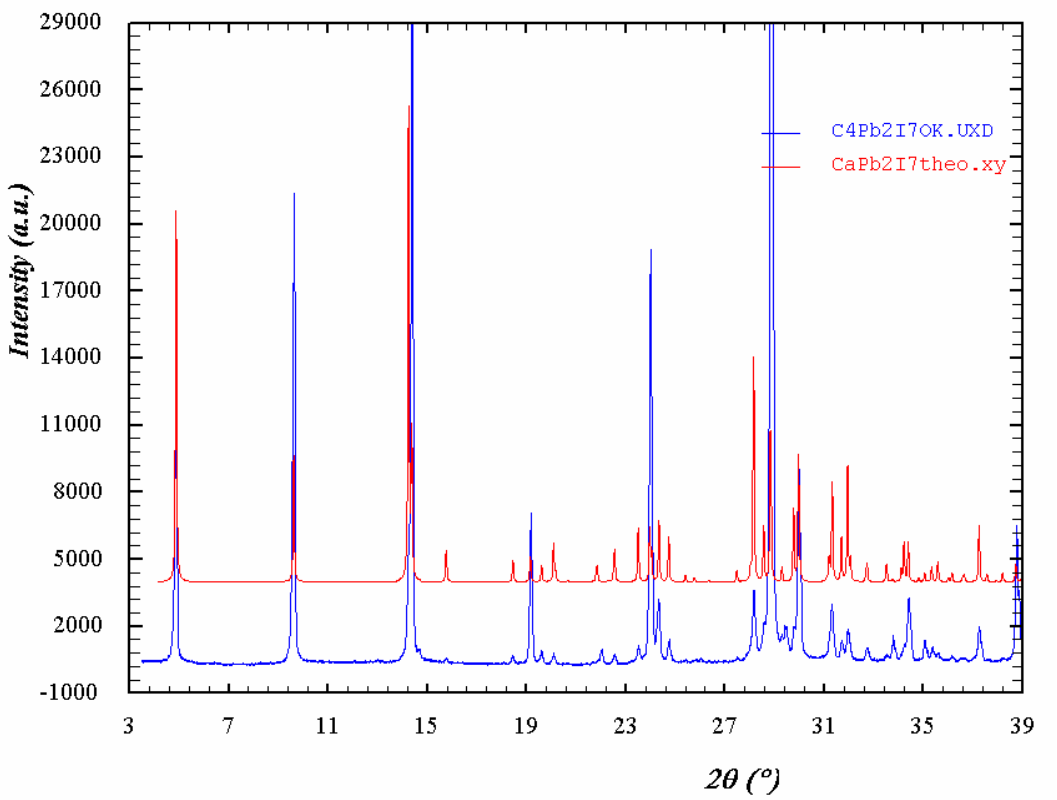
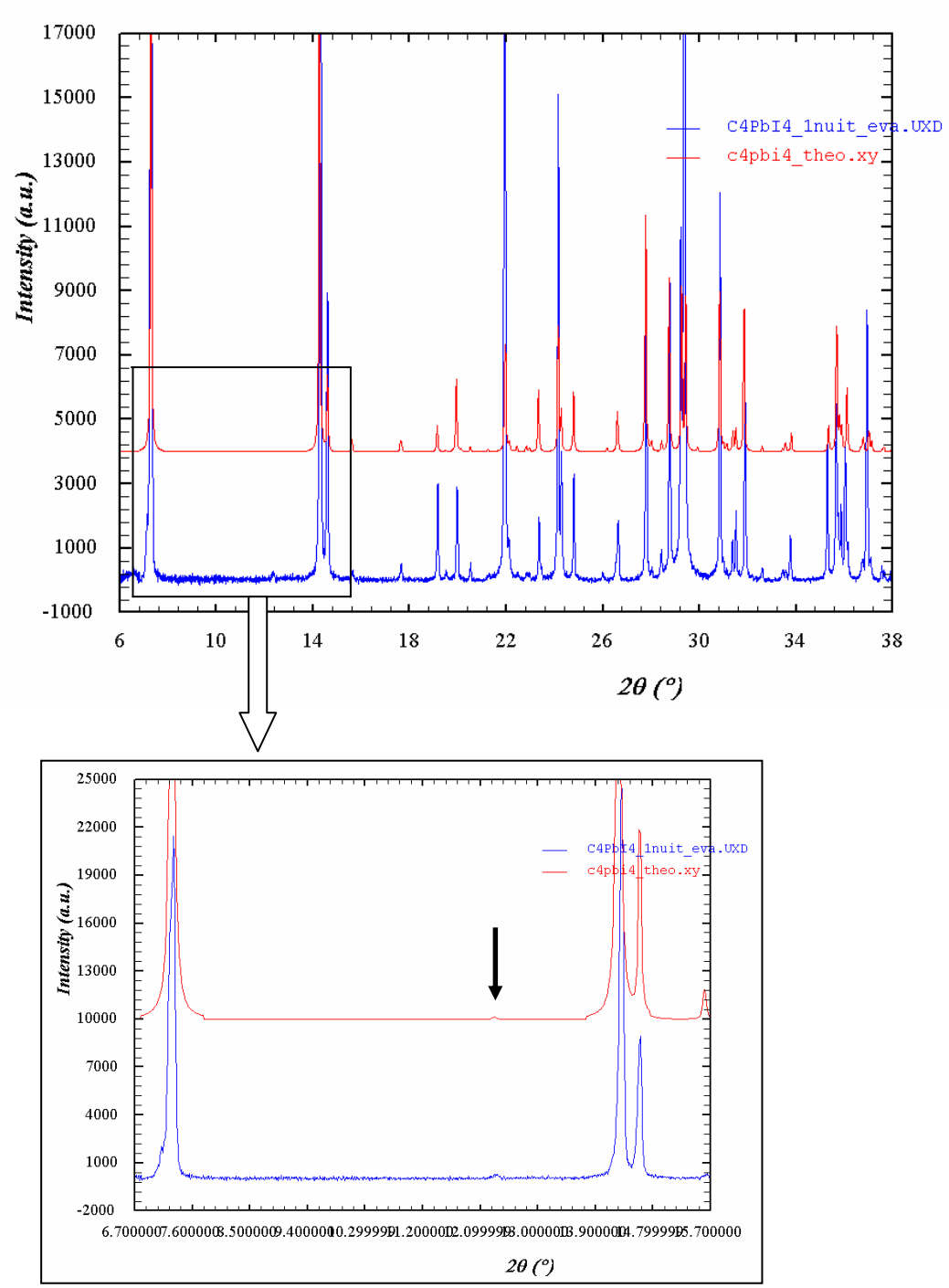
1) Experimental powder X-Ray pattern of a red sample of $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2(CH_3NH_3)Pb_2I_7$ (compound **1**), C4Pb2I7OK.uxd, and calculated powder X-ray pattern from single crystal data (orthorhombic cell, a = 9.1196(5)Å, b = 37.326(1)Å, c = 8.8987(4)Å)



2) Experimental powder X-Ray pattern of a orange sample of $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2PbI_4$ (compound **2**, C4PbI4_1nuit_eva.uxd), and calculated powder X-ray pattern (c4pbi4_theo.xy) from single crystal data (orthorhombic cell, a = 8.904(1)Å, b = 9.266(1)Å, c = 24.261(3)Å).



3) Crystallographic data for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2(CH_3NH_3)Pb_2I_7$ (compound **1**) : 4 tables

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2(CH_3NH_3)Pb_2I_7$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	12914(6)	7577(2)	10449(6)	38(1)
O(2)	13185(7)	7704(2)	8058(5)	39(1)
C(1)	12607(10)	7495(3)	9158(7)	32(2)
C(3)	11105(8)	6981(3)	9983(7)	34(2)
C(2)	11721(8)	7188(2)	8667(9)	33(2)
C(4)	10075(12)	6682(2)	9466(8)	38(2)
N(1)	9253(9)	6522(2)	10788(9)	53(2)
C(5)	14620(30)	10000	10000	129(11)
N(2)	15850(20)	10108(6)	9220(30)	83(6)
Pb	9962(1)	9131(1)	10033(1)	27(1)
I(4)	12878(1)	9139(1)	12050(1)	52(1)
I(1)	9960(2)	10000	10000	63(1)
I(2)	7025(1)	9148(1)	7956(1)	44(1)
I(3)	10242(1)	8306(1)	9812(1)	38(1)

Table 2. Bond lengths [A] and angles [deg] for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2(CH_3NH_3)Pb_2I_7$.

O(1)-C(1)	1.221(8)	I(3)-Pb-I(4)#2	96.250(17)
O(2)-C(1)	1.359(10)	I(4)-Pb-I(4)#2	92.175(19)
C(1)-C(2)	1.469(12)	I(3)-Pb-I(1)	173.73(3)
C(3)-C(2)	1.512(10)	I(4)-Pb-I(1)	89.79(3)
C(3)-C(4)	1.529(12)	I(4)#2-Pb-I(1)	89.87(2)
C(4)-N(1)	1.517(11)	I(3)-Pb-I(2)	92.974(18)
C(5)-N(2)	1.38(3)	I(4)-Pb-I(2)	178.230(19)
C(5)-N(2)#1	1.38(3)	I(4)#2-Pb-I(2)	88.38(3)
N(2)-N(2)#1	1.60(4)	I(1)-Pb-I(2)	88.53(3)
Pb-I(3)	3.0946(8)	I(3)-Pb-I(2)#3	85.450(17)
Pb-I(4)	3.2089(11)	I(4)-Pb-I(2)#3	88.74(3)
Pb-I(4)#2	3.2174(10)	I(4)#2-Pb-I(2)#3	178.09(2)
Pb-I(1)	3.2440(6)	I(1)-Pb-I(2)#3	88.45(2)
Pb-I(2)	3.2544(10)	I(2)-Pb-I(2)#3	90.655(19)
Pb-I(2)#3	3.2583(9)	Pb-I(4)-Pb#4	160.22(3)
I(4)-Pb#4	3.2174(10)	Pb#1-I(1)-Pb	179.94(6)
I(1)-Pb#1	3.2440(6)	Pb-I(2)-Pb#5	159.75(3)
I(2)-Pb#5	3.2584(9)		

O(1)-C(1)-O(2)	116.5(9)
O(1)-C(1)-C(2)	126.9(8)
O(2)-C(1)-C(2)	116.5(6)
C(2)-C(3)-C(4)	111.6(6)
C(1)-C(2)-C(3)	111.9(7)
N(1)-C(4)-C(3)	110.8(6)
N(2)-C(5)-N(2)#1	71(2)
C(5)-N(2)-N(2)#1	54.5(12)
I(3)-Pb-I(4)	88.637(18)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+2,-z+2 #2 x-1/2,y,-z+5/2
#3 x+1/2,y,-z+3/2 #4 x+1/2,y,-z+5/2
#5 x-1/2,y,-z+3/2

Table 3. Anisotropic displacement parameters (A^2 x 10^3) for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2(CH_3NH_3)Pb_2I_7$.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	45(3)	48(4)	22(3)	0(3)	-5(2)	-8(3)
O(2)	48(3)	48(4)	22(3)	4(3)	-1(3)	-17(3)
C(1)	46(5)	30(4)	19(3)	0(4)	7(4)	6(4)
C(3)	25(4)	55(6)	23(4)	7(4)	3(4)	-1(4)
C(2)	33(4)	38(5)	29(4)	2(4)	7(3)	-2(4)
C(4)	61(6)	36(5)	18(3)	2(3)	0(4)	-15(5)
N(1)	46(5)	60(6)	53(5)	19(4)	6(4)	-5(4)
C(5)	91(19)	140(20)	160(20)	90(20)	0	0
N(2)	76(14)	89(15)	85(16)	4(13)	7(11)	-33(12)
Pb	27(1)	28(1)	26(1)	-1(1)	0(1)	1(1)
I(4)	43(1)	69(1)	42(1)	-12(1)	-22(1)	9(1)
I(1)	82(1)	25(1)	80(1)	2(1)	0	0
I(2)	37(1)	58(1)	37(1)	-5(1)	-17(1)	3(1)
I(3)	42(1)	28(1)	45(1)	1(1)	-3(1)	-1(1)

Table 4. Hydrogen bonds for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2(CH_3NH_3)Pb_2I_7$. [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...I(2)#6	0.89	2.89	3.73(1)	157
N(1)-H(1B)...I(4)#7	0.89	3.01	3.75(1)	140
N(1)-H(1B)...I(3)#7	0.89	3.23	3.75(1)	119
N(1)-H(1C)...O(2)#7	0.89	2.38	3.21(1)	156

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+2,-z+2 #2 x-1/2,y,-z+5/2 #3 x+1/2,y,-z+3/2
#4 x+1/2,y,-z+5/2 #5 x-1/2,y,-z+3/2 #6 x+1/2,-y+3/2,-z+2
#7 x-1/2,-y+3/2,-z+2

4) Crystallographic data for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2PbI_4$ (compound **2**) : 4 tables

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2PbI_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4564(4)	-2989(4)	-2374(2)	37(1)
O(2)	6942(4)	-3255(5)	-2197(2)	41(1)
C(1)	5836(6)	-2714(5)	-2507(2)	29(1)
C(3)	4974(6)	-1133(6)	-3283(2)	35(1)
C(2)	6299(6)	-1782(6)	-2979(2)	37(1)
N	4218(6)	734(5)	-3948(2)	43(1)
C(4)	5493(6)	-105(6)	-3721(3)	38(1)
I(2)	2018(1)	2061(1)	-8(1)	42(1)
I(1)	5217(1)	-288(1)	-1291(1)	39(1)
Pb	5000	0	0	29(1)

Table 2. Bond lengths [Å] and angles [°] for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2PbI_4$.

O(1)-C(1)	1.206(6)	C(1)-C(2)-C(3)	112.8(4)
O(2)-C(1)	1.337(6)	N-C(4)-C(3)	111.1(5)
C(1)-C(2)	1.492(7)	Pb#1-I(2)-Pb	159.120(15)
C(3)-C(4)	1.500(8)	I(1)-Pb-I(1)#2	180.000(1)
C(3)-C(2)	1.516(7)	I(1)-Pb-I(2)#3	92.453(10)
N-C(4)	1.482(8)	I(1)#2-Pb-I(2)#3	87.547(10)
I(2)-Pb#1	3.2625(8)	I(1)-Pb-I(2)#4	87.547(10)
I(2)-Pb	3.2710(7)	I(1)#2-Pb-I(2)#4	92.453(10)
I(1)-Pb	3.1486(8)	I(2)#3-Pb-I(2)#4	180.000(7)
Pb-I(1)#2	3.1486(8)	I(1)-Pb-I(2)#2	84.638(10)
Pb-I(2)#3	3.2625(8)	I(1)#2-Pb-I(2)#2	95.362(10)
Pb-I(2)#4	3.2625(8)	I(2)#3-Pb-I(2)#2	92.31(2)
Pb-I(2)#2	3.2710(7)	I(2)#4-Pb-I(2)#2	87.69(2)
O(1)-C(1)-O(2)	117.5(5)	I(1)-Pb-I(2)	95.362(10)
O(1)-C(1)-C(2)	126.0(5)	I(1)#2-Pb-I(2)	84.638(10)
O(2)-C(1)-C(2)	116.5(5)	I(2)#3-Pb-I(2)	87.69(2)
C(4)-C(3)-C(2)	110.9(4)	I(2)#4-Pb-I(2)	92.31(2)
		I(2)#2-Pb-I(2)	180.000(8)

Symmetry transformations used to generate equivalent atoms:

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

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

Table 3. Anisotropic displacement parameters ($Å^2$x 10^3)for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2PbI_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	19(2)	48(2)	44(2)	6(2)	3(2)	0(2)
O(2)	19(2)	53(3)	52(3)	17(2)	-1(2)	1(2)
C(1)	21(2)	29(3)	38(3)	-3(2)	0(2)	0(2)
C(3)	31(3)	28(3)	46(3)	4(2)	0(2)	-3(2)
C(2)	27(3)	37(3)	47(3)	8(3)	2(2)	-1(2)
N	45(3)	35(3)	49(3)	7(2)	-4(2)	-3(2)
C(4)	30(3)	38(3)	45(3)	4(2)	3(3)	1(2)
I(2)	35(1)	34(1)	58(1)	-5(1)	-10(1)	12(1)
I(1)	43(1)	39(1)	37(1)	2(1)	-2(1)	-3(1)
Pb	26(1)	25(1)	35(1)	-2(1)	2(1)	-1(1)

Table 4. Hydrogen bonds for $(HO_2C\text{-}(CH_2)_3\text{-}NH_3)_2PbI_4$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N-H(5A)...I(2)#5	0.89	2.96	3.81(1)	160
N-H(5B)...I(2)#6	0.89	3.07	3.76(1)	135
N-H(5B)...I(1)#7	0.89	3.15	3.76(1)	128
N-H(5C)...O(2)#7	0.89	2.27	3.11(1)	156
O(2)-H(1)...O(1)#6	0.81(7)	1.80(7)	2.57(1)	159(7)

Symmetry transformations used to generate equivalent atoms:

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

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

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