N. Mercier et al.

“Reduced Band Gap Hybrid Perovskites Resulting from Combined Hydrogen and Halogen Bonding at the Organic-Inorganic Interface**”,**

Supporting informations

1 - Tables of atomic coordinates, bond lengths, atomic displacement parameters, hydrogen bonds and checkCIF report for $(Cl(CH_2)_2NH_3)_2PbI_4$

Table 1a. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **$(Cl(CH_2)_2NH_3)_2PbI_4$**
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pb	2799(1)	5410(1)	2500	26(1)
I(1)	3004(1)	5340(1)	4038(1)	38(1)
I(2)	7753(1)	5452(1)	2500	41(1)
I(3)	2648(1)	2940(1)	2500	44(1)
Cl	6896(3)	1818(2)	4762(1)	48(1)
N	8005(9)	4089(5)	4225(4)	51(2)
C(2)	7938(14)	3165(7)	3805(5)	59(2)
C(1)	6229(17)	2426(6)	4018(5)	62(2)

Table 1b. Bond lengths [A] and angles [deg] for **$(Cl(CH_2)_2NH_3)_2PbI_4$**

Pb-I(3)	3.1722(6)
Pb-I(1)#1	3.2019(8)
Pb-I(1)	3.2019(8)
Pb-I(2)	3.2055(9)
Pb-I(3)#2	3.2616(6)
Pb-I(2)#3	3.2657(9)
I(2)-Pb#4	3.2657(9)
I(3)-Pb#5	3.2616(6)
Cl-C(1)	1.785(9)
N-C(2)	1.474(12)
C(2)-C(1)	1.523(12)
I(3)-Pb-I(1)#1	88.461(9)
I(3)-Pb-I(1)	88.461(9)
I(1)#1-Pb-I(1)	174.255(19)
I(3)-Pb-I(2)	92.736(19)
I(1)#1-Pb-I(2)	87.652(9)
I(1)-Pb-I(2)	87.652(9)
I(3)-Pb-I(3)#2	173.149(11)
I(1)#1-Pb-I(3)#2	91.817(9)
I(1)-Pb-I(3)#2	91.817(9)
I(2)-Pb-I(3)#2	94.115(19)
I(3)-Pb-I(2)#3	89.191(18)
I(1)#1-Pb-I(2)#3	92.403(9)

I(1)-Pb-I(2)#3	92.403(9)
I(2)-Pb-I(2)#3	178.07(3)
I(3)#2-Pb-I(2)#3	83.957(18)
Pb-I(2)-Pb#4	178.07(3)
Pb-I(3)-Pb#5	176.68(2)
N-C(2)-C(1)	110.5(7)
C(2)-C(1)-Cl	110.4(7)

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

Table 1c. Anisotropic displacement parameters (A^2 x 10^3) for **$(Cl(CH_2)_2NH_3)_2PbI_4$**
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
Pb	22(1)	24(1)	33(1)	0	0	1(1)
I(1)	35(1)	46(1)	32(1)	0(1)	0(1)	3(1)
I(2)	18(1)	51(1)	53(1)	0	0	-4(1)
I(3)	55(1)	19(1)	59(1)	0	0	1(1)
Cl	42(1)	50(1)	51(1)	14(1)	0(1)	-5(1)
N	41(4)	46(4)	65(5)	16(3)	-8(3)	-4(3)
C(2)	78(6)	50(5)	49(5)	11(4)	11(4)	0(4)
C(1)	78(6)	49(5)	60(5)	11(4)	-12(5)	-16(4)

Table 1d. Hydrogen bonds for **$(Cl(CH_2)_2NH_3)_2PbI_4$** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N-H(0A)...I(1)	0.89	2.75	3.633(6)	170.5
N-H(0B)...I(1)#4	0.89	2.76	3.632(6)	166.1
N-H(0C)...I(1)#7	0.89	3.02	3.745(8)	140.1
N-H(0C)...**Cl**	0.89	2.78	3.203(7)	110.8
N-H(0C)...**Cl#6**	0.89	2.92	3.484(7)	123.2

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

1e- CheckCIF: (Cl(CH2)2NH3)2PbI4

Bond precision: C-C = 0.0130 A Wavelength=0.71073
Cell: a=6.4703(13) b=12.8390(7) c=20.797(4)
alpha=90 beta=90 gamma=90

	Calculated	Reported
Volume	1727.7(5)	1727.7(5)
Space group	Pbnm	P b n m
Hall group	-P 2c 2ab	-P 2c 2ab
Moiety formula	I4 Pb, 2(C2 H7 Cl N)	C4 H14 CL2 I4 N2 PB1
Sum formula	C4 H14 Cl2 I4 N2 Pb	C4 H14 Cl2 I4 N2 Pb
Mr	875.87	875.86
Dx,g cm-3	3.367	3.367
Z	4	4
Mu (mm-1)	17.195	17.196
F000	1520.0	1520.0
F000'	1501.54	
h,k,lmax	9,18,29	8,18,29
Nref	2587	2561
Tmin,Tmax	0.011,0.300	0.043,0.308
Tmin'	0.011	

Correction method= 'GAUSSIAN'

Data completeness= Ratio = 0.99 Theta(max)= 30.03

R(reflections)= 0.0395(2027) wR2(reflections)= 0.0984(2561)

S = 1.073 Npar= 66

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT761_ALERT_1_A CIF Contains no X-H Bonds ..... ?
PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles ..... ?

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field. Absorption correction given as gaussian
RINTA01_ALERT_3_C The value of Rint is greater than 0.10 Rint given 0.101
PLAT020_ALERT_3_C The value of Rint is greater than 0.10 ..... 0.10
PLAT042_ALERT_1_C Calc. and Rep. MoietyFormula Strings Differ .... ?
PLAT128_ALERT_4_C Non-standard setting of Space group Pnma .... Pbnm
PLAT199_ALERT_1_C Check the Reported _cell_measurement_temperature 293 K
PLAT200_ALERT_1_C Check the Reported _diffrn_ambient_temperature . 293 K

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PLAT342_ALERT_3_C Low Bond Precision on C-C bonds (x 1000) Ang ...
13
PLAT480_ALERT_4_C Long H...A H-Bond Reported H0C    ..  CL      ..
2.92 Ang.
PLAT720_ALERT_4_C Number of Unusual/Non-Standard Label(s) ........
3
PLAT764_ALERT_4_C Overcomplete CIF Bond List Detected (Rep/Expd) .
1.22 Ratio
```

Alert level G

```
ABSTM02_ALERT_3_G  The ratio of expected to reported Tmax/Tmin(RR) is >
2.00
            Tmin and Tmax reported:      0.043     0.308
            Tmin and Tmax expected:      0.016     0.300
            RR =      2.689
            Please check that your absorption correction is appropriate.
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   2 ALERT level A = In general: serious problem
   0 ALERT level B = Potentially serious problem
  11 ALERT level C = Check and explain
   1 ALERT level G = General alerts; check
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2 - Tables of atomic coordinates, bond lengths, atomic displacement parameters, hydrogen bonds and checkCIF report for α1-$(Br(CH_2)_2NH_3)_2PbI_4$

Table 2a. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for α1-$\mathbf{(Br(CH_2)_2NH_3)_2PbI_4}$ U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pb	15000	-6615(1)	12500	34(1)
I(1)	17525(1)	-4156(1)	12501(1)	56(1)
I(2)	15610(1)	-6533(1)	13994(1)	70(1)
Br	18033(2)	-4548(2)	15220(1)	87(1)
N	20624(14)	-2135(14)	15768(6)	82(3)
C(2)	19830(20)	-3040(30)	16201(8)	119(8)
C(1A)	18430(30)	-3350(40)	16046(13)	79(9)
C(1B)	19540(40)	-4480(40)	16028(13)	93(11)

Table 2b. Bond lengths [A] and angles [deg] for α1-$\mathbf{(Br(CH_2)_2NH_3)_2PbI_4}$

Pb-I(2)	3.1689(9)
Pb-I(2)#1	3.1689(9)
Pb-I(1)	3.2187(8)

Pb-I(1)#1	3.2187(8)
Pb-I(1)#2	3.2410(8)
Pb-I(1)#3	3.2410(8)
I(1)-Pb#4	3.2410(8)
Br-C(1B)	2.04(3)
Br-C(1A)	2.07(3)
N-C(2)	1.51(2)
C(2)-C(1A)	1.30(3)
C(2)-C(1B)	1.38(4)
I(2)-Pb-I(2)#1	177.30(4)
I(2)-Pb-I(1)	88.04(2)
I(2)#1-Pb-I(1)	90.07(2)
I(2)-Pb-I(1)#1	90.07(2)
I(2)#1-Pb-I(1)#1	88.04(2)
I(1)-Pb-I(1)#1	91.40(3)
I(2)-Pb-I(1)#2	91.86(2)
I(2)#1-Pb-I(1)#2	90.07(2)
I(1)-Pb-I(1)#2	178.49(3)
I(1)#1-Pb-I(1)#2	90.099(9)
I(2)-Pb-I(1)#3	90.07(2)
I(2)#1-Pb-I(1)#3	91.86(2)
I(1)-Pb-I(1)#3	90.099(9)
I(1)#1-Pb-I(1)#3	178.49(3)
I(1)#2-Pb-I(1)#3	88.40(3)
Pb-I(1)-Pb#4	178.49(3)
C(1B)-Br-C(1A)	41.1(14)
C(1A)-C(2)-C(1B)	65(2)
C(1A)-C(2)-N	120(2)
C(1B)-C(2)-N	117(2)
C(2)-C(1A)-Br	112(2)
C(2)-C(1B)-Br	110(2)

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

Table 2c. Anisotropic displacement parameters (A^2 x 10^3) for α1-**$(Br(CH_2)_2NH_3)_2PbI_4$**
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
Pb	31(1)	31(1)	41(1)	0	4(1)	0
I(1)	46(1)	47(1)	72(1)	6(1)	4(1)	-20(1)
I(2)	78(1)	78(1)	51(1)	-3(1)	3(1)	6(1)
Br	92(1)	98(1)	67(1)	-9(1)	1(1)	-43(1)
N	78(8)	80(8)	88(9)	-8(7)	11(7)	-11(7)
C(2)	130(16)	170(20)	55(9)	-20(11)	9(9)	-76(15)
C(1A)	63(16)	120(30)	55(14)	10(15)	19(12)	-43(18)
C(1B)	110(30)	100(30)	52(16)	11(16)	-11(16)	-30(20)

Table 2d. Hydrogen bonds for α1-**$(Br(CH_2)_2NH_3)_2PbI_4$** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N-H(0A)...I(2)#5	0.89	2.74	3.610(13)	165.0
N-H(0B)...I(2)#6	0.89	2.83	3.598(13)	146.1
N-H(0C)...I(2)#4	0.89	3.14	3.845(13)	138.0

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

2e - CheckCIF: α1-$(Br(CH_2)_2NH_3)_2PbI_4$

Bond precision: N- C = 0.0200 A Wavelength=0.71073
Cell: a=9.1263(10) b=9.1429(10) c=21.450(2)
alpha=90 beta=98.6500(10) gamma=90

	Calculated	Reported
Volume	1769.5(3)	1769.4(3)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	I4 Pb, 2(C2 H7 Br N)	C4 H14 BR2 I4 N2 PB1
Sum formula	C4 H14 Br2 I4 N2 Pb	C4 H14 Br2 I4 N2 Pb
Mr	964.77	964.78
Dx,g cm-3	3.622	3.622
Z	4	4
Mu (mm-1)	21.003	21.004
F000	1664.0	1664.0
F000'	1642.73	
h,k,lmax	11,11,27	11,11,27
Nref	2041	2010
Tmin,Tmax	0.015,0.350	0.044,0.359
Tmin'	0.009	

Correction method= 'GAUSSIAN'
Data completeness= Ratio = 0.98 Theta(max)= 27.52
R(reflections)= 0.0408(1673) wR2(reflections)= 0.1032(2010)
S = 1.053 Npar= 71

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT761_ALERT_1_A CIF Contains no X-H Bonds .....
?
PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles .....
?

Alert level B

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PLAT241_ALERT_2_B Check High      Ueq as Compared to Neighbors for
C2
```

Alert level C

```
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
            a literature citation. This should be contained in the
            _exptl_absorpt_process_details field.
            Absorption correction given as gaussian
PLAT042_ALERT_1_C Calc. and Rep. MoietyFormula Strings Differ ....
?
PLAT199_ALERT_1_C Check the Reported _cell_measurement_temperature
293 K
PLAT200_ALERT_1_C Check the Reported _diffrn_ambient_temperature .
293 K
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for
Pb
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for
C1A
PLAT301_ALERT_3_C Main Residue  Disorder .......................
5.00 Perc.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H0C    ..  I2      ..
3.14 Ang.
PLAT720_ALERT_4_C Number of Unusual/Non-Standard Label(s) ........
11
PLAT779_ALERT_2_C Suspect or Irrelevant (Bond) Angle in CIF ......
41.10 Deg.
              C1B  -BR   -C1A     1.555   1.555   1.555
PLAT804_ALERT_4_C ARU-Pack Problem in PLATON Analysis ............
!
PLAT804_ALERT_4_C ARU-Pack Problem in PLATON Analysis ............
!
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Alert level G

```
ABSTM02_ALERT_3_G  The ratio of expected to reported Tmax/Tmin(RR) is >
2.00
            Tmin and Tmax reported:      0.044     0.359
            Tmin and Tmax expected:      0.019     0.350
            RR =      2.285
            Please check that your absorption correction is appropriate.
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   2 ALERT level A = In general: serious problem
   1 ALERT level B = Potentially serious problem
  12 ALERT level C = Check and explain
   1 ALERT level G = General alerts; check
```

3 - Tables of atomic coordinates, bond lengths, atomic displacement parameters, hydrogen bonds and checkCIF report for α2-$(Br(CH_2)_2NH_3)_2PbI_4$

Table 3a. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for α2-$\mathbf{(Br(CH_2)_2NH_3)_2PbI_4}$ U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

Pb	7714(1)	9634(1)	2500	29(1)
I(2)	2675(1)	9566(1)	2500	44(1)
I(3)	7610(1)	12097(1)	2500	50(1)
I(1)	7862(1)	9700(1)	994(1)	48(1)
Br	2045(2)	13273(1)	4776(1)	52(1)
C(1)	1360(20)	12595(9)	3979(5)	81(4)
C(2)	2896(19)	11808(9)	3801(5)	69(3)
N	2861(13)	10910(7)	4212(5)	65(2)

Table 3b. Bond lengths [A] and angles [deg] for α2-**$(Br(CH_2)_2NH_3)_2PbI_4$**

Pb-I(3)	3.1798(8)
Pb-I(1)#1	3.1858(6)
Pb-I(1)	3.1858(6)
Pb-I(2)#2	3.2168(8)
Pb-I(2)	3.2679(8)
Pb-I(3)#3	3.2799(8)
I(2)-Pb#4	3.2168(8)
I(3)-Pb#5	3.2799(8)
Br-C(1)	1.949(11)
C(1)-C(2)	1.471(16)
C(2)-N	1.448(14)
I(3)-Pb-I(1)#1	88.494(13)
I(3)-Pb-I(1)	88.494(13)
I(1)#1-Pb-I(1)	175.37(2)
I(3)-Pb-I(2)#2	92.78(2)
I(1)#1-Pb-I(2)#2	88.320(12)
I(1)-Pb-I(2)#2	88.320(12)
I(3)-Pb-I(2)	90.30(2)
I(1)#1-Pb-I(2)	91.763(12)
I(1)-Pb-I(2)	91.763(12)
I(2)#2-Pb-I(2)	176.92(3)
I(3)-Pb-I(3)#3	175.104(12)
I(1)#1-Pb-I(3)#3	91.650(13)
I(1)-Pb-I(3)#3	91.650(13)
I(2)#2-Pb-I(3)#3	92.12(2)
I(2)-Pb-I(3)#3	84.80(2)
Pb#4-I(2)-Pb	176.92(3)
Pb-I(3)-Pb#5	177.55(3)
C(2)-C(1)-Br	112.1(9)
N-C(2)-C(1)	112.9(10)

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

Table 3c. Anisotropic displacement parameters (A^2 x 10^3) for α2-**$(Br(CH_2)_2NH_3)_2PbI_4$**

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
Pb	26(1)	29(1)	33(1)	0	0	-1(1)
I(2)	23(1)	56(1)	54(1)	0	0	2(1)
I(3)	63(1)	23(1)	65(1)	0	0	-2(1)
I(1)	46(1)	61(1)	38(1)	1(1)	0(1)	-4(1)
Br	56(1)	49(1)	52(1)	-8(1)	2(1)	3(1)
C(1)	126(11)	64(6)	53(7)	-3(6)	-5(7)	25(7)
C(2)	93(8)	68(7)	45(6)	-8(5)	8(6)	-1(6)
N	62(5)	57(5)	76(6)	-13(5)	-14(4)	8(4)

Table 3d. Hydrogen bonds for α2-**$(Br(CH_2)_2NH_3)_2PbI_4$** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N-H(0A)...Br	0.89	2.90	3.317(8)	110.6
N-H(0A)...Br#6	0.89	2.98	3.612(8)	129.2
N-H(0A)...I(1)#7	0.89	3.17	3.878(10)	138.2
N-H(0B)...I(1)#1	0.89	2.80	3.624(8)	155.5
N-H(0C)...I(1)#8	0.89	2.74	3.623(8)	175.3

Symmetry transformations used to generate equivalent atoms:
#1 x,y,-z+1/2 #2 x+1,y,z #3 -x+3/2,y-1/2,z
#4 x-1,y,z #5 -x+3/2,y+1/2,z #6 x+1/2,-y+5/2,-z+1
#7 -x+1,-y+2,z+1/2 #8 x-1,y,-z+1/2

3e - CheckCIF: α2-$(Br(CH_2)_2NH_3)_2PbI_4$

Bond precision: C-C = 0.0170 A Wavelength=0.71073
Cell: a=6.4824(3) b=12.9046(8) c=21.1409(16)
alpha=90 beta=90 gamma=90

	Calculated	Reported
Volume	1768.50(19)	1768.49(19)
Space group	Pbnm	P b n m
Hall group	-P 2c 2ab	-P 2c 2ab
Moiety formula	I4 Pb, 2(C2 H7 Br N)	C4 H14 BR2 I4 N2 PB1
Sum formula	C4 H14 Br2 I4 N2 Pb	C4 H14 Br2 I4 N2 Pb
Mr	964.77	964.78
Dx,g cm-3	3.624	3.624
Z	4	4
Mu (mm-1)	21.015	21.015
F000	1664.0	1664.0
F000'	1642.73	
h,k,lmax	9,18,29	9,18,29
Nref	2639	2597
Tmin,Tmax	0.141,0.122	
Tmin'	0.141	

Correction method= Not given

```
Data completeness= Ratio = 0.98          Theta(max)= 29.99
R(reflections)= 0.0396(     wR2(reflections)= 0.0894(
1927)                       2597)
S = 1.069        Npar= 66
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level A

```
PLAT093_ALERT_1_A No su's on H-atoms, but refinement reported as .
mixed
PLAT761_ALERT_1_A CIF Contains no X-H Bonds ......................
?
PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles ..........
?
```

Alert level C

```
PLAT042_ALERT_1_C Calc. and Rep. MoietyFormula Strings Differ ....
?
PLAT128_ALERT_4_C Non-standard setting of Space group Pnma    ....    Pbnm
PLAT199_ALERT_1_C Check the Reported _cell_measurement_temperature
293 K
PLAT200_ALERT_1_C Check the Reported _diffrn_ambient_temperature .
293 K
PLAT241_ALERT_2_C Check High      Ueq as Compared to Neighbors for
C1
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for
Pb
PLAT342_ALERT_3_C Low Bond Precision on C-C bonds (x 1000) Ang ...
17
PLAT480_ALERT_4_C Long H...A H-Bond Reported H0A    ..  BR      ..
2.98 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H0A    ..  I1      ..
3.17 Ang.
PLAT720_ALERT_4_C Number of Unusual/Non-Standard Label(s) ........
3
PLAT764_ALERT_4_C Overcomplete CIF Bond List Detected (Rep/Expd) .
1.22 Ratio
```

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   3 ALERT level A = In general: serious problem
   0 ALERT level B = Potentially serious problem
  11 ALERT level C = Check and explain
   0 ALERT level G = General alerts; check

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing
data
   2 ALERT type 2 Indicator that the structure model may be wrong or
deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
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4 - Tables of atomic coordinates, bond lengths, atomic displacement parameters, hydrogen bonds and checkCIF report for $(I(CH_2)_2NH_3)_2PbI_4$

Table 3a. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **$(I(CH_2)_2NH_3)_2PbI_4$**
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pb	5000	-5000	-5000	31(1)
I(1)	3106(1)	-1995(1)	-4481(1)	45(1)
I(2)	5248(1)	-5917(1)	-2566(1)	52(1)
I(3)	6027(1)	-2581(1)	-60(1)	58(1)
N	6146(8)	201(6)	-2911(5)	58(2)
C(1)	6634(9)	-1753(8)	-1542(6)	61(2)
C(2)	5771(9)	-368(8)	-1877(6)	56(2)

Table 3b. Bond lengths [A] and angles [deg] for **$(I(CH_2)_2NH_3)_2PbI_4$**

Pb-I(2)#1	3.1775(6)
Pb-I(2)	3.1775(6)
Pb-I(1)#1	3.2225(5)
Pb-I(1)	3.2225(5)
Pb-I(1)#2	3.2243(5)
Pb-I(1)#3	3.2243(5)
I(1)-Pb#4	3.2243(5)
I(3)-C(1)	2.151(7)
N-C(2)	1.483(9)
C(1)-C(2)	1.461(10)
I(2)#1-Pb-I(2)	180.0
I(2)#1-Pb-I(1)#1	88.658(13)
I(2)-Pb-I(1)#1	91.342(13)
I(2)#1-Pb-I(1)	91.342(13)
I(2)-Pb-I(1)	88.658(13)
I(1)#1-Pb-I(1)	180.0
I(2)#1-Pb-I(1)#2	89.452(15)
I(2)-Pb-I(1)#2	90.548(15)
I(1)#1-Pb-I(1)#2	87.668(9)
I(1)-Pb-I(1)#2	92.332(9)
I(2)#1-Pb-I(1)#3	90.548(15)
I(2)-Pb-I(1)#3	89.452(15)
I(1)#1-Pb-I(1)#3	92.332(9)
I(1)-Pb-I(1)#3	87.668(9)
I(1)#2-Pb-I(1)#3	180.0
Pb-I(1)-Pb#4	147.379(15)
C(2)-C(1)-I(3)	110.9(5)
C(1)-C(2)-N	111.7(6)

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

Table 3c. Anisotropic displacement parameters (A^2 x 10^3) for **$(I(CH_2)_2NH_3)_2PbI_4$**
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
Pb	30(1)	29(1)	34(1)	2(1)	8(1)	-1(1)
I(1)	37(1)	40(1)	58(1)	2(1)	9(1)	15(1)
I(2)	72(1)	49(1)	35(1)	6(1)	10(1)	9(1)
I(3)	58(1)	71(1)	47(1)	9(1)	13(1)	2(1)
N	79(5)	45(3)	52(4)	3(3)	16(4)	-2(3)
C(1)	60(5)	62(5)	65(5)	13(4)	27(4)	5(4)
C(2)	60(5)	61(4)	52(5)	1(4)	23(4)	2(4)

Table 3d. Hydrogen bonds for **$(I(CH_2)_2NH_3)_2PbI_4$** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N-H(00A)...I(1)	0.89	2.85	3.654(6)	150.4
N-H(00B)...I(2)#3	0.89	2.75	3.614(7)	164.9
N-H(00C)...I(2)#5	0.89	2.69	3.526(6)	157.1

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

4e- CheckCIF: (I(CH2)2NH3)2PBI4

Bond precision: C-C = 0.0100 A Wavelength=0.71073
Cell: a=8.7534(10) b=8.7470(10) c=12.720(2)
alpha=90 beta=97.630(10) gamma=90

	Calculated	Reported
Volume	965.3(2)	965.3(2)
Space group	P 21/a	P 1 21/a 1
Hall group	-P 2yab	-P 2yab
Moiety formula	I4 Pb, 2(C2 H7 I N)	C4 H14 I6 N2 PB1
Sum formula	C4 H14 I6 N2 Pb	C4 H14 I6 N2 Pb
Mr	1058.77	1058.76
Dx,g cm-3	3.643	3.643
Z	2	2
Mu (mm-1)	18.310	18.310
F000	904.0	904.0
F000'	892.44	
h,k,lmax	12,12,17	12,12,17
Nref	2829	2814
Tmin,Tmax	0.067,0.577	0.098,0.515
Tmin'	0.067	

Correction method= 'GAUSSIAN'
Data completeness= Ratio Theta(max)= 30.03

= 0.99

R(reflections)= 0.0339(1954) wR2(reflections)= 0.0720(2814)

S = 0.961 Npar= 63

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT761_ALERT_1_A CIF Contains no X-H Bonds ..... ?

PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles ..... ?

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as gaussian

PLAT042_ALERT_1_C Calc. and Rep. MoietyFormula Strings Differ .... ?

PLAT128_ALERT_4_C Non-standard setting of Space group P21/c P21/a

PLAT199_ALERT_1_C Check the Reported _cell_measurement_temperature 293 K

PLAT200_ALERT_1_C Check the Reported _diffrn_ambient_temperature . 293 K

PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Pb

PLAT342_ALERT_3_C Low Bond Precision on C-C bonds (x 1000) Ang ... 10

PLAT720_ALERT_4_C Number of Unusual/Non-Standard Label(s) 7

PLAT764_ALERT_4_C Overcomplete CIF Bond List Detected (Rep/Expd) . 1.11 Ratio

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Alert level G

ABSTM02_ALERT_3_G The ratio of expected to reported Tmax/Tmin(RR) is > 1.50

Tmin and Tmax reported: 0.098 0.515
Tmin and Tmax expected: 0.068 0.577
RR = 1.629
Please check that your absorption correction is appropriate.

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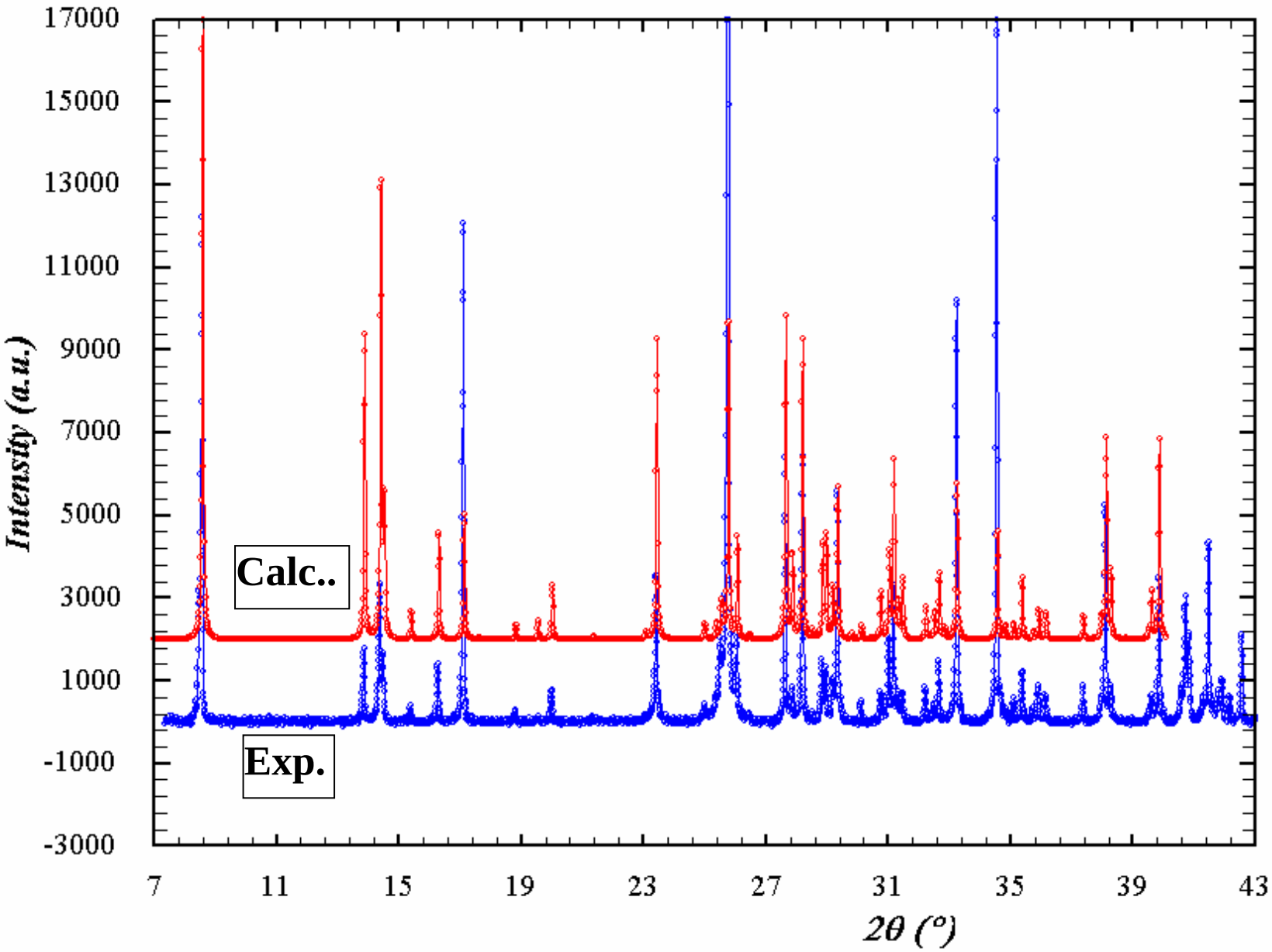
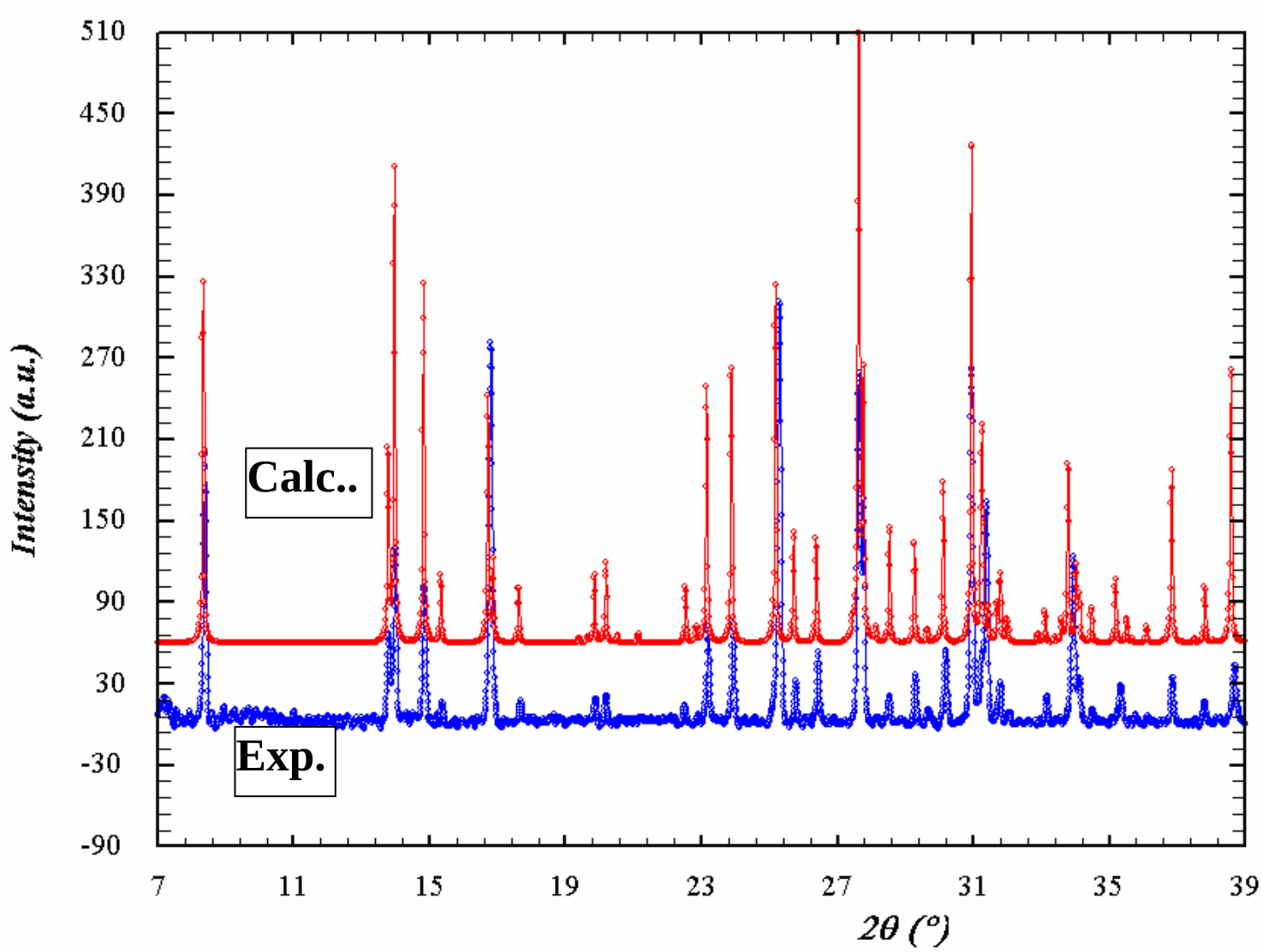
2 **ALERT level A** = In general: serious problem
0 **ALERT level B** = Potentially serious problem
9 **ALERT level C** = Check and explain
1 **ALERT level G** = General alerts; che

5 Calculated and Experimental X-ray patterns of $(X(CH_2)_2NH_3)_2PbI_4$

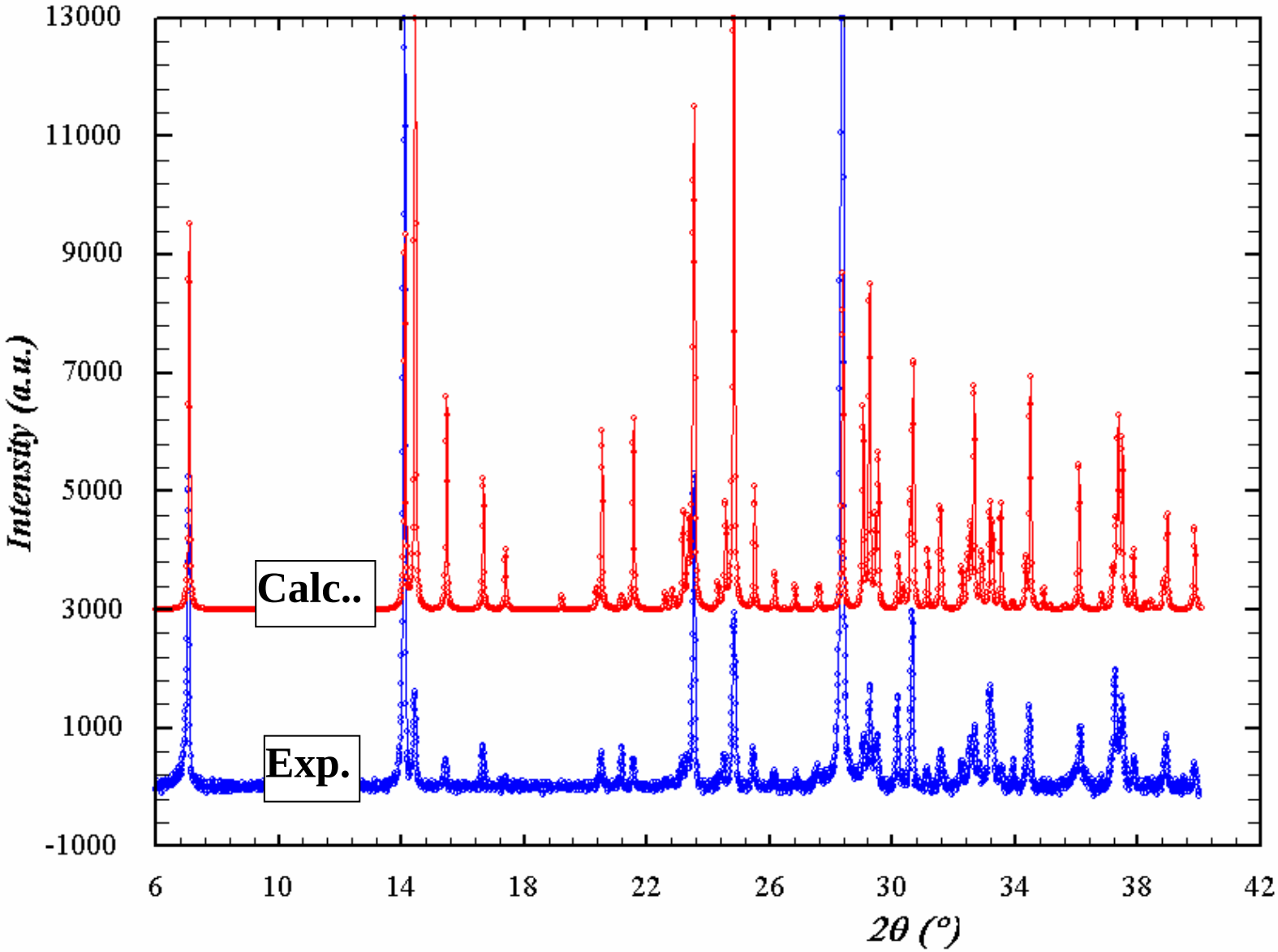
5a- **Calc. and Exp. X-ray powder patterns of (Cl-(CH2)2NH3)2PbI4**



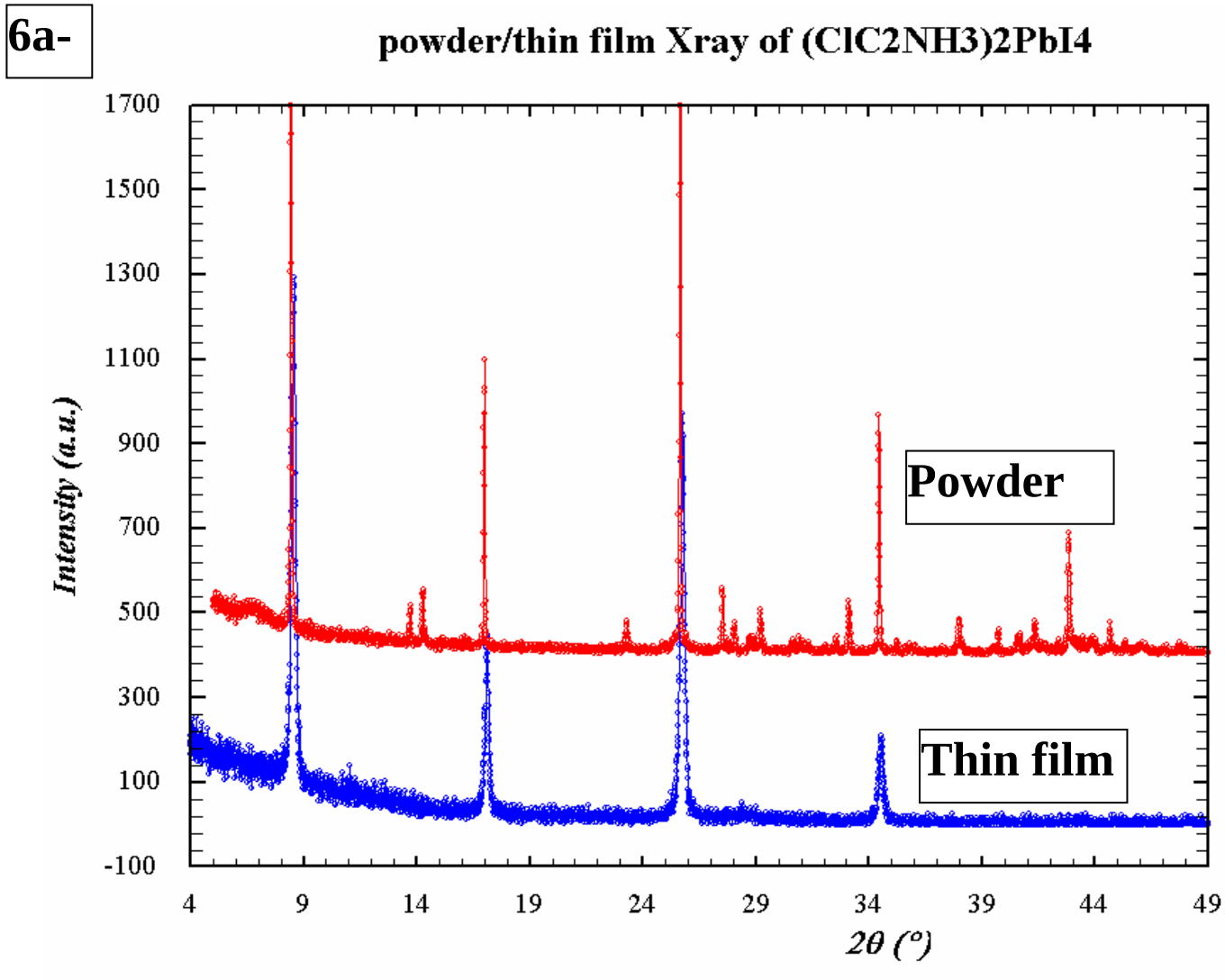
5b- **Calculated and experimental powder X-ray patternsof α1-$(Br(CH_2)_2NH_3)_2PbI_4$ (compound 2a)**



5c- Calc. and Exp. powder X-ray patterns of (I(CH2)2NH3)2PbI4

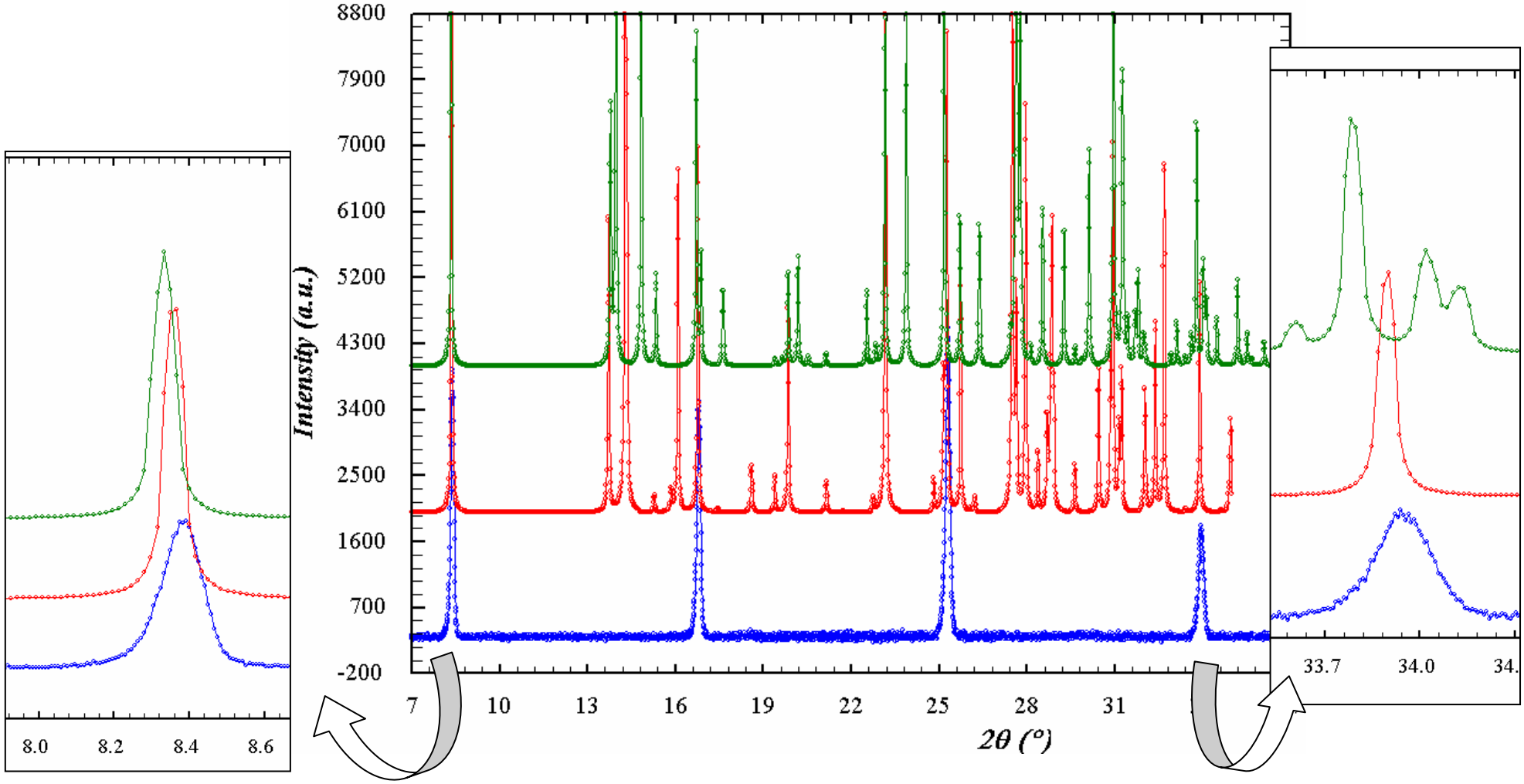


6–Thin film X-ray patterns of **$(X(CH_2)_2NH_3)_2PbI_4$**



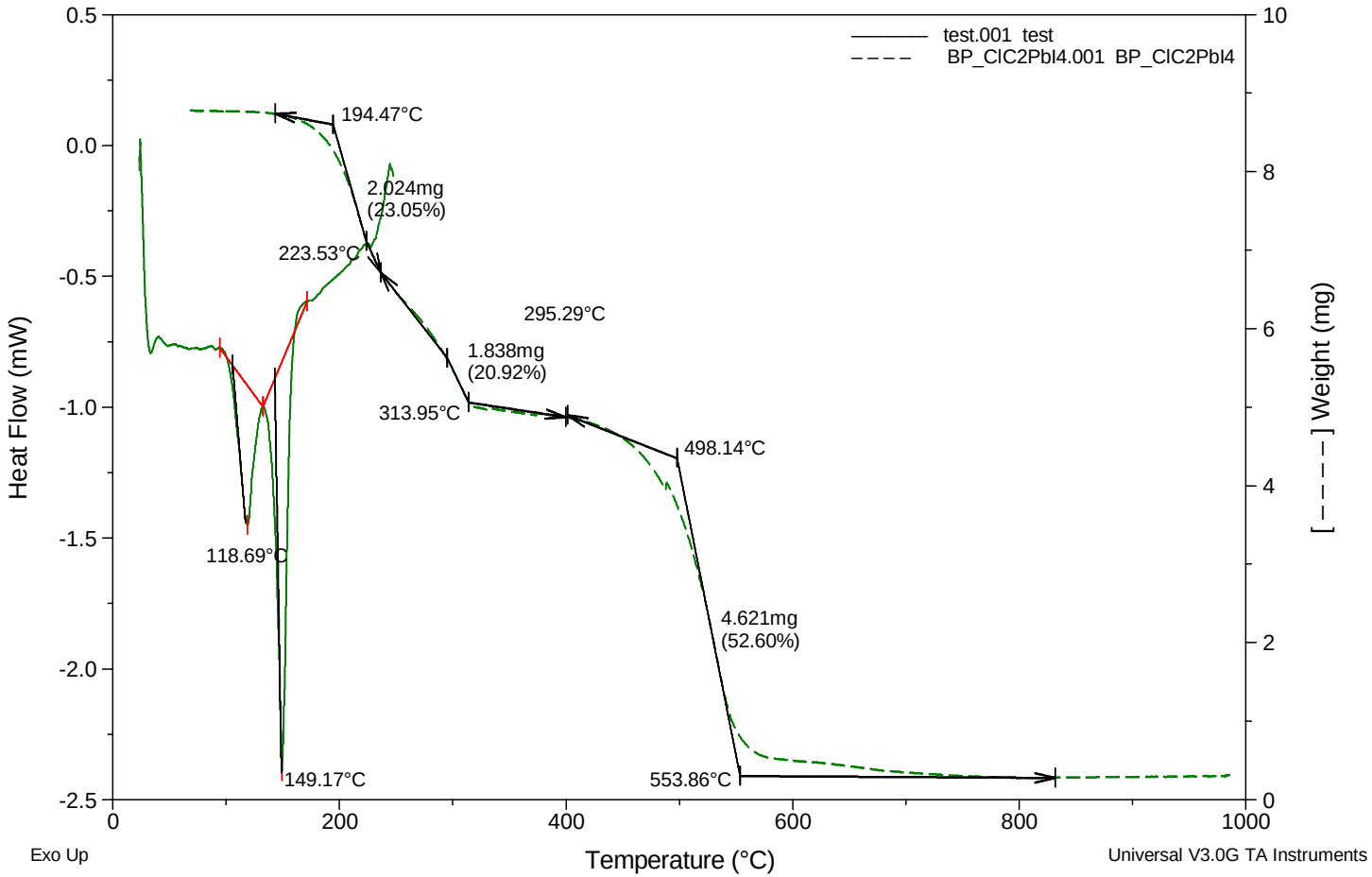
6b-

Powder X-ray pattern of a thin film prepared from a sample containing polymorphs 2a and 2b, together with theoretical XRPD of 2a and 2b. Zooms of regions around the (002) and the (008) lines show that the crystallized thin film would correspond to the 2b phase only (α2-($Br(CH_2)_2NH_3)_2PbI_4$)).

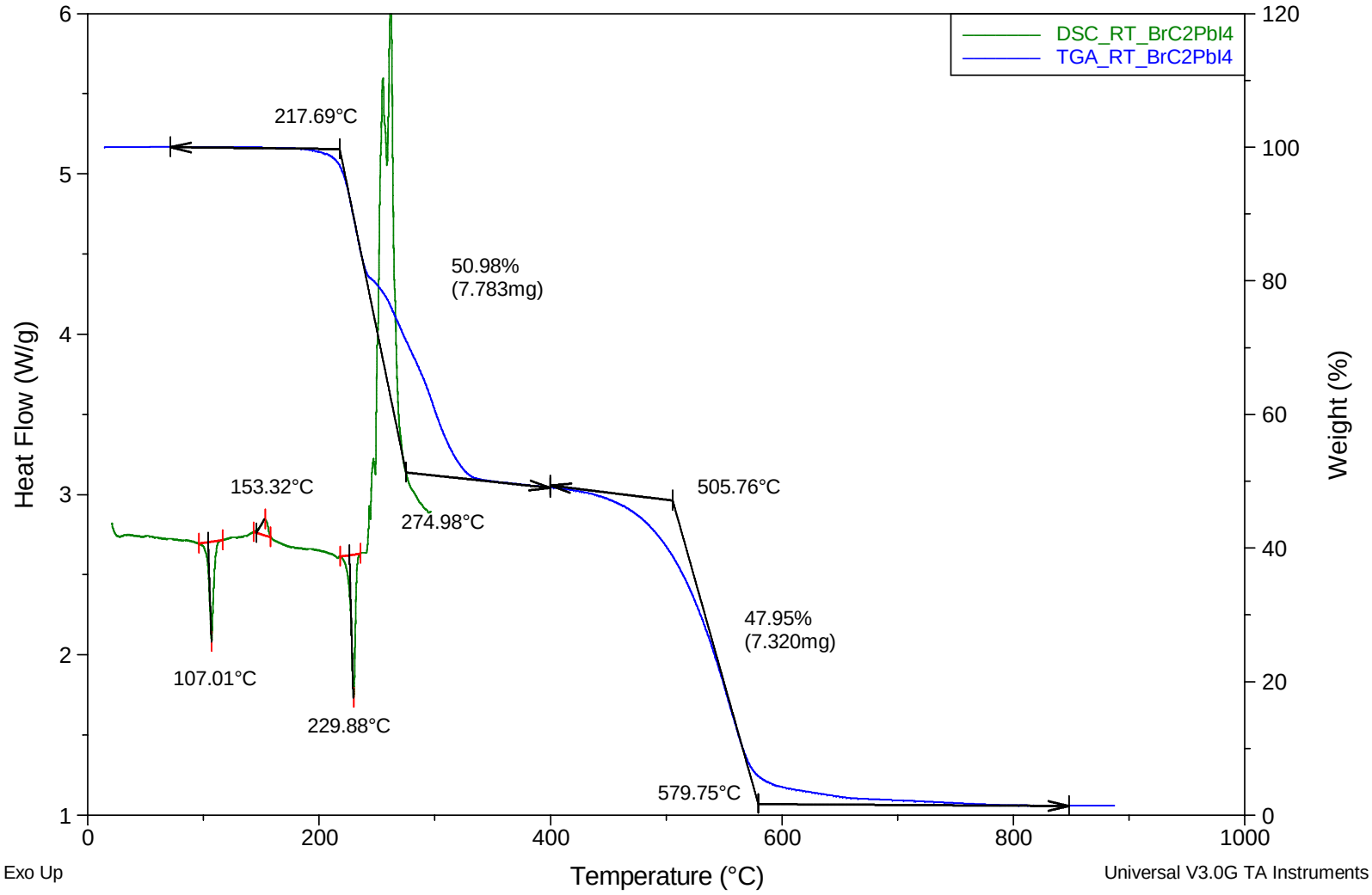


7 – DSC and TG analysis

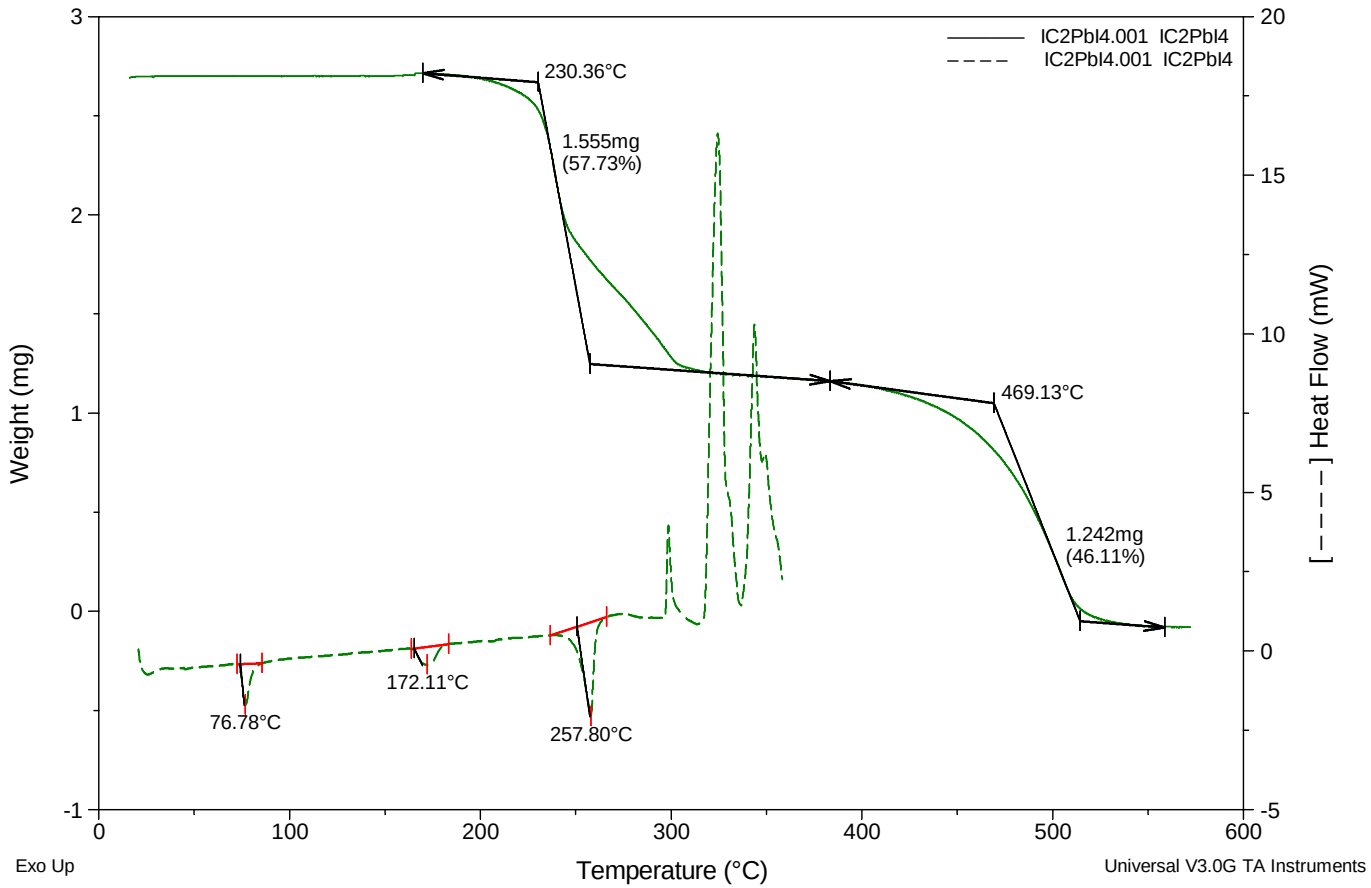
7a – $(Cl(CH_2)_2NH_3)_2PbI_4$ (compound **1**)



7b – α1- + α2-$(Br(CH_2)_2NH_3)_2PbI_4$ (compounds **2a** and **2b**)



7c – $(I(CH_2)_2NH_3)_2PbI_4$ (compound **3**)



8 – CPMAS ^{1}H-^{13}C solid state NMR experiments

Cross polarization (CP) combined with magic angle spinning (MAS) solid state ^{1}H-^{13}C NMR experiments were carried out at room temperature on a Bruker Avance 300 wide bore spectrometer at 75.47 Mhz. 2.5 mm CPMAS probe was used at spinning frequency equal to 10 kHz. ^{13}C Chemical shift are expressed in ppm using TMS as external reference. The ^{1}H radiofrequency (rf) was set in order to obtain $\tau_{\pi/2}$ = 4 µs. 16 k transients were accumulated. The recycle delay was 1 s. The reconstructions of the spectra were performed with DMFIT software (Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J-O.; Bujoli, B.; Gan, Z.; Hoatson, G. *Magn. Reson. Chem.* **2002**, *40*, 70-76).

CPMAS ^{1}H-^{13}C solid state NMR experiments were carried out on $(Br(CH_2)_2NH_3)Br$ salt firstly in order to estimate the isotropic chemical shift values of the C(Br) and $C(NH_3)$ atoms for $Br(CH_2)_2NH_3^+$ cation. Figure A displays its spectrum showing two resonances at 30.5 and 45.6 ppm assigned to C(Br) and $C(NH_3)$ respectively (Table A).

Figure B shows the CPMAS solid state ^{1}H-^{13}C NMR spectrum of $(Br(CH_2)_2NH_3)_2PbI_4$ showing two resonances at 38.9 and 45.4 ppm assigned to C(Br) and $C(NH_3)$ respectively (Table B).

The CPMAS solid state ^{1}H-^{13}C NMR spectrum of $(I(CH_2)_2NH_3)_2PbI_4$ (Figure C) exhibits two peaks at 4 and 45 ppm assigned to C(I) and $C(NH_3)$ respectively. Each peak is reconstructed with three contributions (Table C) with slightly different isotropic chemical shift values indicating carbon atom environments slightly different in this salt.

CPMAS ^{1}H-^{13}C solid-state NMR experiments unambiguously confirm the presence of $I\text{-}(CH2)_2\text{-}NH_3$ entities in $(I(CH_2)_2NH_3)_2PbI_4$.

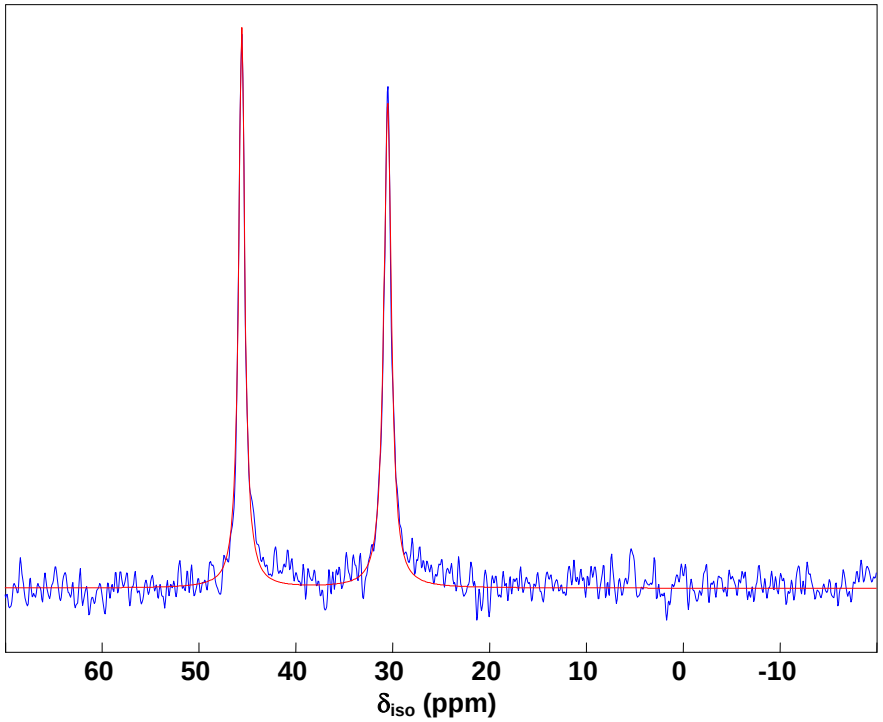


Figure A. Experimental (in blue) and reconstructed (in red) CPMAS solid state ^{1}H-^{13}C NMR spectrum of $(Br(CH_2)_2NH_3)Br$.

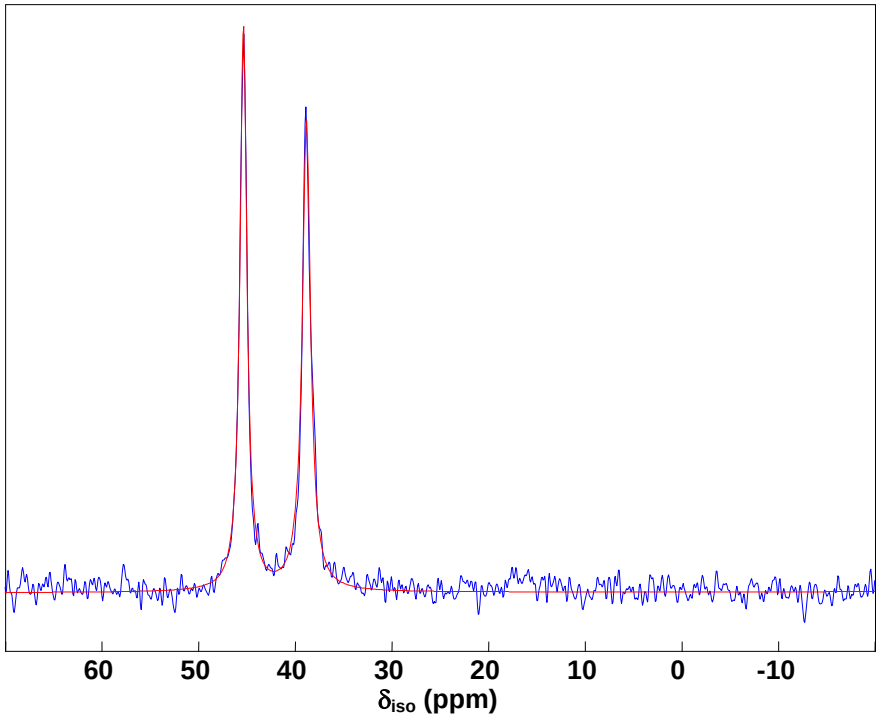


Figure B. Experimental (in blue) and reconstructed (in red) CPMAS solid state ^{1}H-^{13}C NMR spectrum of $(Br(CH_2)_2NH_3)_2PbI_4$.

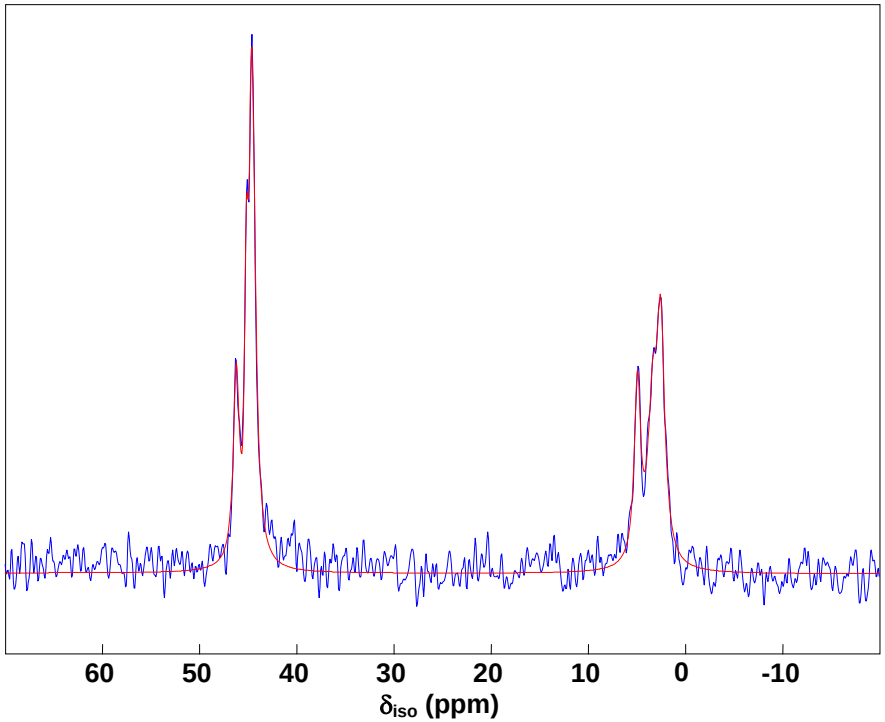


Figure C. Experimental (in blue) and reconstructed (in red) CPMAS solid state ^{1}H-^{13}C NMR spectrum of $(I(CH_2)_2NH_3)_2PbI_4$.

Table A. Isotropic Chemical Shifts, δ_{iso} (ppm), Line Widths (ppm) and Relative Intensities (%) As Deduced from Spectrum Reconstruction of $(Br(CH_2)_2NH_3)Br$ and Line Assignments.

δ_{iso} (ppm)	Line width (ppm)	Relative intensity	Line Assignments
30.5	0.90	50.8	C(Br)
45.6	0.76	49.2	$C(NH_3)$

Table B. Isotropic Chemical Shifts, δ_{iso} (ppm), Line Widths (ppm) and Relative Intensities (%) As Deduced from Spectrum Reconstruction of $(Br(CH_2)_2NH_3)_2PbI_4$ and Line Assignments.

δ_{iso} (ppm)	Line width (ppm)	Relative intensity	Line Assignments
38.9	1.03	50.0	C(Br)
45.4	0.85	50.0	$C(NH_3)$

Table C. Isotropic Chemical Shifts, δ_{iso} (ppm), Line Widths (ppm) and Relative Intensities (%) As Deduced from Spectrum Reconstruction of $(I(CH_2)_2NH_3)_2PbI_4$ and Line Assignments.

δ_{iso} (ppm)	Line width (ppm)	Relative intensity	Line Assignments
2.6	1.01	21.2	C(I)
3.4	1.04	13.1	
4.9	0.79	12.8	
44.6	0.80	37.3	$C(NH_3)$
45.2	0.37	4.1	
46.2	0.71	11.6	