Supplementary Material (ESI) for Dalton Transactions

$Pb_nI_{4n+2}^{(2n+2)-}$ Ribbons (n= 3, 5) as Dimensional Reduction of 2D Perovskite Layer in Cystamine Cations Based Hybrids also Incorporating Iodine Molecules or Reversible Guest Water Molecules

Nicolas Louvain,[a] Wenhua Bi,[a] Nicolas Mercier,*[a] Jean-Yves Buzaré,[b] Christophe Legein[c], Gwenaël Corbel[c]

Supporting information

1- Tables of atomic coordinates, bond lengths, atomic displacement parameters and hydrogen bonds for 1, 2, 3, 4

A- $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_4Pb_3I_{14},I_2$ (1)

Table 1A_a. Crystal data and structure refinement for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_4Pb_3I_{14},I_2$

Empirical formula	C16 H56 I16 N8 Pb3 S8
Formula weight	3269.14
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 17.607(2) A alpha = 90 deg.
	b = 8.8354(10) A beta = 102.810(10) deg.
	c = 22.375(3) A gamma = 90 deg.
Volume	3394.0(7) A^3
Z, Calculated density	2, 3.199 Mg/m^3
Absorption coefficient	14.968 mm^-1
F(000)	2860
Crystal size	0.4 x 0.3 x 0.2 mm
Theta range for data collection	2.67 to 25.02 deg.
Limiting indices	-20<=h<=20, -10<=k<=9, -26<=l<=24
Reflections collected / unique	26874 / 5836 [R(int) = 0.0687]
Completeness to theta = 25.02	97.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5836 / 0 / 237
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.0696
R indices (all data)	R1 = 0.0991, wR2 = 0.0795
Extinction coefficient	0.000026(12)
Largest diff. peak and hole	1.588 and -1.681 e.A^-3

Table 1A_b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_4Pb_3I_{14},I_2$ U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

C(8)	8469(7)	9681(16)	7578(6)	62(4)
C(6)	7403(7)	11072(15)	5439(6)	60(4)
C(4)	2637(11)	4387(18)	6617(7)	93(6)
C(5)	6924(7)	9711(13)	5379(6)	50(3)
S(2)	1886(3)	5981(5)	5598(2)	108(2)
C(7)	8438(7)	8847(13)	6996(6)	47(3)
N(4)	9258(5)	10232(12)	7867(5)	61(3)
N(3)	6279(7)	9815(14)	5665(6)	86(4)
N(2)	2509(6)	5558(16)	7009(6)	90(4)
C(2)	1120(9)	3761(18)	4640(7)	88(5)
S(4)	8760(2)	9926(4)	6415(2)	58(1)
S(3)	7926(2)	11591(4)	6194(2)	62(1)
I(7)	2552(1)	9862(1)	6418(1)	53(1)
I(4)	6266(1)	9419(1)	7321(1)	58(1)
I(3)	4477(1)	7650(1)	5771(1)	51(1)
I(5)	4387(1)	12346(1)	7931(1)	58(1)
I(1)	5277(1)	7443(1)	4027(1)	60(1)
I(6)	4250(1)	7339(1)	7830(1)	61(1)
I(2)	6727(1)	5507(1)	5807(1)	66(1)
Pb(1)	5000	5000	5000	34(1)
Pb(2)	4407(1)	9906(1)	6929(1)	32(1)
N(1A)	563(12)	5670(20)	3894(11)	70(5)
N(1B)	967(18)	5130(30)	3696(15)	70(5)
I(8)	4300(1)	4892(1)	9567(1)	80(1)
C(1A)	1222(14)	4630(30)	4092(13)	61(6)
C(1B)	890(20)	5190(40)	4317(18)	61(6)
S(1B)	1101(14)	4070(20)	5418(10)	70(6)
C(3)	2679(7)	4876(19)	6001(7)	83(5)
S(1A)	997(9)	4854(19)	5340(8)	86(4)

Table 1A_c. Bond lengths [A] and angles [deg] for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_4Pb_3I_{14},I_2$

C(8)-N(4)	1.478(15)
C(8)-C(7)	1.486(16)
C(6)-C(5)	1.458(15)
C(6)-S(3)	1.796(12)
C(4)-N(2)	1.407(18)
C(4)-C(3)	1.46(2)
C(5)-N(3)	1.425(15)
S(2)-C(3)	1.777(15)
S(2)-S(1A)	1.837(18)
S(2)-S(1B)	2.16(2)
C(7)-S(4)	1.802(12)
C(2)-C(1B)	1.46(4)
C(2)-C(1A)	1.49(3)
C(2)-S(1B)	1.77(3)
C(2)-S(1A)	1.89(2)
S(4)-S(3)	2.060(5)
I(7)-Pb(2)	3.2129(9)
I(4)-Pb(2)	3.2246(9)
I(3)-Pb(1)	3.1636(8)
I(3)-Pb(2)	3.2938(9)
I(5)-Pb(2)	3.1147(10)
I(1)-Pb(1)	3.1784(8)
I(1)-Pb(2)#1	3.3024(9)
I(6)-Pb(2)	3.0867(10)
I(2)-Pb(1)	3.2051(11)

Pb(1)-I(3)#2	3.1636(8)
Pb(1)-I(1)#2	3.1784(8)
Pb(1)-I(2)#2	3.2051(11)
Pb(2)-I(1)#1	3.3024(9)
N(1A)-C(1A)	1.47(4)
N(1B)-C(1B)	1.42(5)
I(8)-I(8)#3	2.782(2)
N(4)-C(8)-C(7)	113.3(11)
C(5)-C(6)-S(3)	117.5(9)
N(2)-C(4)-C(3)	114.8(14)
N(3)-C(5)-C(6)	114.1(11)
C(3)-S(2)-S(1A)	112.4(8)
C(3)-S(2)-S(1B)	93.7(8)
S(1A)-S(2)-S(1B)	18.8(7)
C(8)-C(7)-S(4)	114.4(9)
C(1B)-C(2)-C(1A)	38.7(14)
C(1B)-C(2)-S(1B)	106.9(18)
C(1A)-C(2)-S(1B)	139.5(16)
C(1B)-C(2)-S(1A)	84.3(17)
C(1A)-C(2)-S(1A)	118.2(14)
S(1B)-C(2)-S(1A)	22.6(7)
C(7)-S(4)-S(3)	103.3(4)
C(6)-S(3)-S(4)	103.5(5)
Pb(1)-I(3)-Pb(2)	160.58(3)
Pb(1)-I(1)-Pb(2)#1	177.30(3)
I(3)-Pb(1)-I(3)#2	180.0
I(3)-Pb(1)-I(1)	88.75(3)
I(3)#2-Pb(1)-I(1)	91.25(3)
I(3)-Pb(1)-I(1)#2	91.25(3)
I(3)#2-Pb(1)-I(1)#2	88.75(3)
I(1)-Pb(1)-I(1)#2	180.0
I(3)-Pb(1)-I(2)	86.80(2)
I(3)#2-Pb(1)-I(2)	93.20(2)
I(1)-Pb(1)-I(2)	91.15(3)
I(1)#2-Pb(1)-I(2)	88.85(3)
I(3)-Pb(1)-I(2)#2	93.20(2)
I(3)#2-Pb(1)-I(2)#2	86.80(2)
I(1)-Pb(1)-I(2)#2	88.85(3)
I(1)#2-Pb(1)-I(2)#2	91.15(3)
I(2)-Pb(1)-I(2)#2	180.0
I(6)-Pb(2)-I(5)	91.26(3)
I(6)-Pb(2)-I(7)	89.56(3)
I(5)-Pb(2)-I(7)	95.27(3)
I(6)-Pb(2)-I(4)	87.55(3)
I(5)-Pb(2)-I(4)	93.98(3)
I(7)-Pb(2)-I(4)	170.36(3)
I(6)-Pb(2)-I(3)	95.35(3)
I(5)-Pb(2)-I(3)	173.33(3)
I(7)-Pb(2)-I(3)	85.69(2)
I(4)-Pb(2)-I(3)	85.43(3)
I(6)-Pb(2)-I(1)#1	175.31(3)
I(5)-Pb(2)-I(1)#1	90.33(3)
I(7)-Pb(2)-I(1)#1	94.68(3)
I(4)-Pb(2)-I(1)#1	87.95(3)
I(3)-Pb(2)-I(1)#1	83.01(3)
N(1A)-C(1A)-C(2)	110(2)
N(1B)-C(1B)-C(2)	112(3)
C(2)-S(1B)-S(2)	98.8(10)
C(4)-C(3)-S(2)	116.3(11)
S(2)-S(1A)-C(2)	106.9(10)

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

Table 1A_d. Anisotropic displacement parameters (A^2 x 10^3) for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_4Pb_3I_{14},I_2$

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
C(8)	56(9)	84(11)	48(9)	-7(8)	15(7)	-10(8)
C(6)	56(8)	62(9)	50(9)	12(7)	-15(7)	-8(8)
C(4)	134(16)	75(11)	60(13)	-5(10)	1(11)	26(11)
C(5)	59(8)	45(8)	38(8)	-9(6)	-7(7)	-11(7)
S(2)	145(4)	62(3)	87(4)	12(2)	-42(3)	-6(3)
C(7)	46(7)	36(7)	54(9)	3(7)	2(7)	11(6)
N(4)	48(6)	76(8)	53(7)	13(6)	-4(5)	-6(6)
N(3)	65(8)	99(10)	97(11)	26(8)	24(8)	-20(7)
N(2)	57(8)	149(13)	63(9)	-6(9)	14(7)	5(8)
S(4)	42(2)	85(3)	46(2)	4(2)	10(2)	-5(2)
S(3)	70(2)	47(2)	56(2)	6(2)	-13(2)	-15(2)
I(7)	33(1)	67(1)	53(1)	-8(1)	0(1)	5(1)
I(4)	32(1)	67(1)	68(1)	-5(1)	-1(1)	1(1)
I(3)	55(1)	48(1)	48(1)	-23(1)	6(1)	12(1)
I(5)	53(1)	59(1)	60(1)	-30(1)	8(1)	3(1)
I(1)	85(1)	44(1)	49(1)	17(1)	13(1)	-16(1)
I(6)	63(1)	59(1)	62(1)	29(1)	15(1)	0(1)
I(2)	72(1)	68(1)	59(1)	2(1)	19(1)	2(1)
Pb(1)	50(1)	23(1)	28(1)	-1(1)	11(1)	0(1)
Pb(2)	34(1)	30(1)	31(1)	-2(1)	7(1)	0(1)
I(8)	92(1)	79(1)	67(1)	-24(1)	18(1)	-9(1)
S(1B)	58(11)	104(15)	52(9)	-9(10)	22(8)	-23(11)
C(3)	48(8)	137(15)	65(11)	-4(11)	11(8)	4(9)
S(1A)	42(4)	131(12)	82(7)	0(9)	7(4)	1(8)

Table 1A_e. Hydrogen bonds for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_4Pb_3I_{14},I_2$ [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(01A)...I(1)#4	0.89	2.86	3.671(10)	151.5
N(4)-H(01C)...S(4)	0.89	2.73	3.183(11)	113.1
N(4)-H(01C)...I(6)#5	0.89	3.01	3.824(10)	153.3
N(3)-H(01H)...I(4)	0.89	2.90	3.726(13)	155.1
N(3)-H(01I)...I(3)	0.89	3.04	3.757(11)	139.0
N(2)-H(1L)...I(6)	0.89	2.80	3.570(12)	145.3
N(2)-H(1N)...I(7)#6	0.89	2.74	3.598(12)	163.4
N(2)-H(1M)...I(5)#6	0.89	2.94	3.722(11)	147.3
N(1A)-H(1C)...I(6)#7	0.89	2.94	3.42(2)	115.7
N(1A)-H(1A)...I(5)#7	0.89	2.99	3.75(2)	143.4
N(1B)-H(2A)...S(3)#1	0.89	2.67	3.47(3)	149.6
N(1B)-H(2C)...I(6)#7	0.89	3.07	3.91(3)	158.6

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

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#4 x+1/2,-y+3/2,z+1/2    #5 -x+3/2,y+1/2,-z+3/2
#6 -x+1/2,y-1/2,-z+3/2    #7 x-1/2,-y+3/2,z-1/2
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B- $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$ (2)

Table 1B_a.Crystal data and structure refinement for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$

Empirical formula	C24 H92 I22 N12 O4 Pb5 S12
Formula weight	4825.50
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 23.23250(10) A alpha = 90 deg.
	b = 8.77140(10) A beta = 100.9840(10) deg.
	c = 25.81180(10) A gamma = 90 deg.
Volume	5163.61(7) A^3
Z, Calculated density	2, 3.098 Mg/m^3
Absorption coefficient	14.975 mm^-1
F(000)	4224
Crystal size	0.27 x 0.11 x 0.04 mm
Theta range for data collection	2.82 to 30.03 deg.
Limiting indices	-32<=h<=32, -12<=k<=12, -36<=l<=36
Reflections collected / unique	83432 / 15029 [R(int) = 0.1123]
Completeness to theta = 30.03	99.5 %
Absorption correction	Gaussian
Max. and min. transmission	0.5534 and 0.0307
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15029 / 0 / 353
Goodness-of-fit on F^2	0.965
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.0737
R indices (all data)	R1 = 0.1715, wR2 = 0.0933
Extinction coefficient	0.000014(5)
Largest diff. peak and hole	1.825 and -2.135 e.A^-3

Table 1B_b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pb(1)	0	0	0	29(1)
Pb(3)	-3304(1)	-75(1)	-2721(1)	34(1)
Pb(2)	-1613(1)	5047(1)	-1450(1)	31(1)
I(10)	-4088(1)	141(1)	-1808(1)	66(1)
I(7)	-2451(1)	2694(1)	-2108(1)	56(1)
I(3)	-614(1)	2642(1)	-776(1)	41(1)
I(4)	-1045(1)	5634(1)	-2494(1)	51(1)
I(9)	-4053(1)	2358(1)	-3442(1)	51(1)
I(1)	-828(1)	-2452(1)	-672(1)	58(1)
I(5)	-2448(1)	7673(1)	-1883(1)	57(1)

I(8)	-2522(1)	-616(1)	-3562(1)	48(1)
I(2)	905(1)	-785(1)	-755(1)	46(1)
S(2)	358(1)	4585(3)	8359(1)	42(1)
S(5)	4548(1)	9544(3)	5673(1)	57(1)
S(1)	810(1)	6235(3)	8045(1)	48(1)
S(6)	4086(1)	11125(3)	5997(1)	54(1)
I(6)	-2288(1)	4424(1)	-510(1)	51(1)
C(2)	1093(4)	5302(11)	7524(3)	54(3)
N(1)	207(4)	4085(9)	7016(3)	67(3)
C(1)	675(6)	5164(12)	7022(4)	79(4)
I(11)	-4072(1)	-2693(1)	-3247(1)	50(1)
N(5)	3930(3)	10439(8)	4473(3)	59(2)
N(6)	4713(3)	11054(9)	7178(3)	59(2)
C(11)	3862(4)	10141(10)	6541(4)	58(3)
C(9)	3603(4)	9586(10)	4811(4)	52(3)
C(10)	3991(5)	8590(11)	5196(4)	72(3)
C(12)	4361(5)	9727(10)	6973(4)	58(3)
S(3)	3218(1)	4956(3)	4440(1)	68(1)
S(4)	2791(2)	3350(3)	4788(1)	85(1)
N(2)	821(3)	5163(7)	9573(3)	51(2)
C(3)	933(4)	3615(9)	8811(3)	37(2)
N(3)	2621(3)	4675(8)	3229(3)	56(2)
C(4)	1244(4)	4526(10)	9255(3)	42(2)
C(6)	2655(4)	6062(10)	4061(4)	61(3)
C(5)	2295(5)	5326(12)	3609(4)	73(3)
O(1)	-5117(4)	4872(8)	-4248(3)	100(3)
C(7)	2819(6)	4065(15)	5462(4)	105(5)
N(4)	2100(6)	5475(11)	5780(6)	180(7)
O(2)	4618(4)	2984(10)	4964(3)	129(3)
C(8A)	2208(11)	4860(30)	5394(8)	61(6)
C(8B)	2686(12)	5340(30)	5618(10)	80(8)

Table 1B_c. Bond lengths [A] and angles [deg] for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$

Pb(1)-I(1)#1	3.1725(6)
Pb(1)-I(1)	3.1725(6)
Pb(1)-I(2)#1	3.2028(6)
Pb(1)-I(2)	3.2028(6)
Pb(1)-I(3)#1	3.2132(5)
Pb(1)-I(3)	3.2132(5)
Pb(3)-I(11)	3.0618(7)
Pb(3)-I(8)	3.1225(7)
Pb(3)-I(9)	3.1316(7)
Pb(3)-I(10)	3.2449(7)
Pb(3)-I(5)#2	3.3006(7)
Pb(3)-I(7)	3.3379(7)
Pb(2)-I(5)	3.0813(7)
Pb(2)-I(7)	3.1102(7)
Pb(2)-I(6)	3.1769(7)
Pb(2)-I(4)	3.2585(7)
Pb(2)-I(1)#3	3.2820(7)
Pb(2)-I(3)	3.3657(6)
I(1)-Pb(2)#2	3.2821(7)
I(5)-Pb(3)#3	3.3006(7)
S(2)-C(3)	1.809(8)
S(2)-S(1)	2.044(3)
S(5)-C(10)	1.812(10)
S(5)-S(6)	2.029(3)

S(1)-C(2)	1.802(8)
S(6)-C(11)	1.807(9)
C(2)-C(1)	1.470(13)
N(1)-C(1)	1.440(11)
N(5)-C(9)	1.465(10)
N(6)-C(12)	1.462(10)
C(11)-C(12)	1.492(14)
C(9)-C(10)	1.490(12)
S(3)-C(6)	1.767(10)
S(3)-S(4)	2.028(4)
S(4)-C(7)	1.838(10)
N(2)-C(4)	1.503(9)
C(3)-C(4)	1.469(10)
N(3)-C(5)	1.465(10)
C(6)-C(5)	1.451(12)
C(7)-C(8B)	1.25(2)
C(7)-C(8A)	1.56(2)
N(4)-C(8A)	1.20(2)
N(4)-C(8B)	1.50(2)

I(1)#1-Pb(1)-I(1)	180.00(3)
I(1)#1-Pb(1)-I(2)#1	85.512(18)
I(1)-Pb(1)-I(2)#1	94.488(18)
I(1)#1-Pb(1)-I(2)	94.488(18)
I(1)-Pb(1)-I(2)	85.512(18)
I(2)#1-Pb(1)-I(2)	180.000(17)
I(1)#1-Pb(1)-I(3)#1	89.851(16)
I(1)-Pb(1)-I(3)#1	90.149(16)
I(2)#1-Pb(1)-I(3)#1	92.324(15)
I(2)-Pb(1)-I(3)#1	87.676(15)
I(1)#1-Pb(1)-I(3)	90.149(16)
I(1)-Pb(1)-I(3)	89.851(16)
I(2)#1-Pb(1)-I(3)	87.676(15)
I(2)-Pb(1)-I(3)	92.323(15)
I(3)#1-Pb(1)-I(3)	180.00(3)
I(11)-Pb(3)-I(8)	86.812(18)
I(11)-Pb(3)-I(9)	92.14(2)
I(8)-Pb(3)-I(9)	91.202(18)
I(11)-Pb(3)-I(10)	90.353(19)
I(8)-Pb(3)-I(10)	174.29(2)
I(9)-Pb(3)-I(10)	93.854(19)
I(11)-Pb(3)-I(5)#2	93.955(19)
I(8)-Pb(3)-I(5)#2	90.366(19)
I(9)-Pb(3)-I(5)#2	173.78(2)
I(10)-Pb(3)-I(5)#2	84.887(18)
I(11)-Pb(3)-I(7)	177.83(2)
I(8)-Pb(3)-I(7)	93.926(19)
I(9)-Pb(3)-I(7)	89.889(19)
I(10)-Pb(3)-I(7)	88.733(19)
I(5)#2-Pb(3)-I(7)	84.002(19)
I(5)-Pb(2)-I(7)	90.70(2)
I(5)-Pb(2)-I(6)	92.150(19)
I(7)-Pb(2)-I(6)	87.349(19)
I(5)-Pb(2)-I(4)	84.703(18)
I(7)-Pb(2)-I(4)	87.907(18)
I(6)-Pb(2)-I(4)	174.27(2)
I(5)-Pb(2)-I(1)#3	87.735(19)
I(7)-Pb(2)-I(1)#3	173.95(2)
I(6)-Pb(2)-I(1)#3	86.867(18)
I(4)-Pb(2)-I(1)#3	97.765(19)
I(5)-Pb(2)-I(3)	168.76(2)

I(7)-Pb(2)-I(3)	99.484(18)
I(6)-Pb(2)-I(3)	83.664(17)
I(4)-Pb(2)-I(3)	100.289(17)
I(1)#3-Pb(2)-I(3)	81.643(18)
Pb(2)-I(7)-Pb(3)	174.44(3)
Pb(1)-I(3)-Pb(2)	162.67(2)
Pb(1)-I(1)-Pb(2)#2	174.81(3)
Pb(2)-I(5)-Pb(3)#3	160.82(2)
C(3)-S(2)-S(1)	102.5(3)
C(10)-S(5)-S(6)	103.3(4)
C(2)-S(1)-S(2)	105.2(3)
C(11)-S(6)-S(5)	104.3(3)
C(1)-C(2)-S(1)	115.0(8)
N(1)-C(1)-C(2)	115.7(8)
C(12)-C(11)-S(6)	113.5(7)
N(5)-C(9)-C(10)	112.4(8)
C(9)-C(10)-S(5)	116.4(7)
N(6)-C(12)-C(11)	112.2(8)
C(6)-S(3)-S(4)	104.7(4)
C(7)-S(4)-S(3)	104.5(4)
C(4)-C(3)-S(2)	116.1(6)
C(3)-C(4)-N(2)	110.7(7)
C(5)-C(6)-S(3)	117.0(7)
C(6)-C(5)-N(3)	114.7(9)
C(8B)-C(7)-C(8A)	50.2(14)
C(8B)-C(7)-S(4)	130.2(15)
C(8A)-C(7)-S(4)	100.4(11)
C(8A)-N(4)-C(8B)	52.5(13)
N(4)-C(8A)-C(7)	116.0(19)
C(7)-C(8B)-N(4)	117(2)

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

Table 1B_d. Anisotropic displacement parameters (A^2 x 10^3) for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$

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(1)	33(1)	24(1)	28(1)	-1(1)	1(1)	-1(1)
Pb(3)	32(1)	32(1)	36(1)	-1(1)	3(1)	0(1)
Pb(2)	31(1)	26(1)	32(1)	-2(1)	-2(1)	0(1)
I(10)	61(1)	80(1)	60(1)	13(1)	17(1)	13(1)
I(7)	65(1)	43(1)	54(1)	-12(1)	-3(1)	-23(1)
I(3)	46(1)	39(1)	38(1)	10(1)	8(1)	15(1)
I(4)	40(1)	69(1)	45(1)	-2(1)	10(1)	0(1)
I(9)	48(1)	47(1)	55(1)	11(1)	7(1)	12(1)
I(1)	71(1)	41(1)	53(1)	-7(1)	-14(1)	-24(1)
I(5)	63(1)	49(1)	54(1)	10(1)	1(1)	28(1)
I(8)	36(1)	63(1)	47(1)	0(1)	13(1)	1(1)
I(2)	51(1)	46(1)	45(1)	3(1)	20(1)	4(1)
S(2)	41(2)	56(2)	30(1)	4(1)	6(1)	-1(1)
S(5)	39(2)	76(2)	52(2)	-11(1)	-3(1)	13(2)
S(1)	64(2)	41(2)	37(1)	4(1)	8(1)	-5(1)
S(6)	53(2)	59(2)	46(2)	-4(1)	-3(1)	9(1)
I(6)	41(1)	67(1)	45(1)	-5(1)	13(1)	3(1)
C(2)	59(8)	70(7)	37(6)	-1(5)	23(5)	-22(6)

N(1)	78(7)	76(7)	42(5)	-12(5)	2(5)	-7(6)
C(1)	107(11)	79(9)	55(8)	5(6)	27(8)	-15(8)
I(11)	50(1)	48(1)	52(1)	-10(1)	7(1)	-21(1)
N(5)	65(6)	74(6)	39(5)	-15(4)	10(4)	-27(5)
N(6)	47(6)	77(7)	50(5)	5(5)	0(4)	0(5)
C(11)	49(7)	66(7)	60(7)	-14(6)	14(6)	-9(6)
C(9)	46(7)	50(7)	56(7)	-12(5)	-1(6)	-7(6)
C(10)	84(9)	55(7)	72(8)	-18(6)	2(7)	5(7)
C(12)	76(8)	55(7)	44(6)	5(5)	16(6)	-8(6)
S(3)	56(2)	94(2)	54(2)	-6(2)	9(2)	10(2)
S(4)	145(3)	54(2)	63(2)	1(2)	34(2)	24(2)
N(2)	61(6)	55(5)	38(5)	2(4)	9(4)	-1(4)
C(3)	31(6)	34(5)	49(6)	8(4)	18(5)	6(4)
N(3)	62(6)	64(6)	43(5)	5(4)	12(4)	7(5)
C(4)	41(6)	57(6)	30(5)	1(5)	9(5)	15(5)
C(6)	72(9)	38(6)	76(8)	0(6)	27(7)	0(6)
C(5)	62(9)	86(9)	70(8)	-20(7)	11(7)	14(7)
C(7)	152(15)	103(11)	70(9)	-6(8)	46(9)	4(10)
N(4)	232(18)	62(8)	287(19)	32(10)	154(15)	38(9)

Table 1B_e. Hydrogen bonds for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$ [A and deg]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1C)...I(4)#4	0.89	2.83	3.682(8)	160.0
N(1)-H(1D)...I(2)#5	0.89	2.86	3.752(8)	176.1
N(1)-H(1E)...S(2)	0.89	2.75	3.443(7)	135.1
N(1)-H(1E)...I(4)#6	0.89	2.90	3.648(8)	142.1
N(5)-H(5C)...O(2)#3	0.89	2.02	2.893(11)	165.4
N(5)-H(5D)...I(8)#7	0.89	2.91	3.650(8)	141.0
N(5)-H(5E)...I(9)#7	0.89	2.93	3.672(7)	142.4
N(6)-H(6C)...S(6)	0.89	2.68	3.118(7)	111.6
N(6)-H(6C)...I(9)#8	0.89	2.99	3.721(7)	140.1
N(6)-H(6D)...I(10)#8	0.89	2.65	3.532(7)	172.8
N(6)-H(6E)...I(11)#9	0.89	2.78	3.550(7)	145.0
N(2)-H(2C)...S(2)	0.89	2.64	3.155(7)	117.4
N(2)-H(2D)...I(2)#10	0.89	2.94	3.668(7)	140.4
N(2)-H(2E)...I(1)#11	0.89	2.81	3.699(7)	173.2
N(3)-H(3C)...I(7)#7	0.89	2.82	3.664(7)	158.5
N(3)-H(3D)...I(8)#1	0.89	3.17	3.680(7)	118.9
N(3)-H(3E)...S(3)	0.89	2.70	3.179(8)	115.3
N(3)-H(3E)...I(11)#1	0.89	3.03	3.784(7)	143.3
N(4)-H(4E2)...I(5)#4	0.89	2.89	3.733(13)	159.3
N(4)-H(4D2)...I(6)#5	0.89	2.84	3.576(10)	141.1
N(4)-H(4D2)...I(6)#5	0.89	2.84	3.576(10)	141.1
N(4)-H(4E2)...I(5)#4	0.89	2.89	3.733(13)	159.3

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z #2 x,y-1,z #3 x,y+1,z #4 -x,y-1/2,-z+1/2
#5 -x,y+1/2,-z+1/2 #6 x,y,z+1 #7 -x,-y+1,-z
#8 x+1,y+1,z+1 #9 -x,y+3/2,-z+1/2 #10 x,y+1,z+1
#11 -x,-y,-z+1

B'- $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$ (2) obtained from the 3 → 2 transformation.

Interestingly, the **2** → **3** transformation is a reversible single-crystal-to-single-crystal transformation. Thus, **3** is able to become **2** by catching the water in the air after a few hours at room temperature. A summary of the data collection conditions together with the main results of the crystallographic data of the crystal of 2, resulting from the **3** → **2** transformation, are given:

Empirical formula	C24 H84 I22 N12 O4 Pb5 S12
Formula weight	4817.50
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 1 21/c 1
Unit cell dimensions	a = 23.2430(2) A alpha = 90 deg. b = 8.7718(10) A beta = 100.93(2) deg. c = 25.776(5) A gamma = 90 deg.
Volume	5160.0(12) A^3
Z, Calculated density	2, 3.098 Mg/m^3
Absorption coefficient	14.975 mm^-1
F(000)	4224
Crystal size	0.27 x 0.11 x 0.04 mm
Theta range for data collection	1.98 to 30.02 deg.
Limiting indices	-32<=h<=32, -12<=k<=12, -36<=l<=36
Reflections collected / unique	86263 / 14554 [R(int) = 0.0768]
Completeness to theta = 30.02	96.4 %
Absorption correction	Gaussian
Max. and min. transmission	0.5562 and 0.2566
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14554 / 0 / 353
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.1198
R indices (all data)	R1 = 0.1273, wR2 = 0.1530
Extinction coefficient	0.000119(17)
Largest diff. peak and hole	2.052 and -1.671 e.A^-3

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

	x	y	z	U(eq)
Pb(1)	0	0	0	29(1)
Pb(3)	-3311(1)	-65(1)	-2716(1)	35(1)
Pb(2)	-1615(1)	5050(1)	-1449(1)	31(1)
I(10)	-4096(1)	150(1)	-1803(1)	66(1)
I(7)	-2452(1)	2694(1)	-2105(1)	56(1)
I(3)	-612(1)	2648(1)	-774(1)	41(1)
I(4)	-1045(1)	5640(1)	-2493(1)	51(1)
I(9)	-4053(1)	2372(1)	-3442(1)	52(1)
I(1)	-827(1)	-2449(1)	-673(1)	59(1)
I(5)	-2453(1)	7671(1)	-1881(1)	58(1)
I(8)	-2520(1)	-612(1)	-3556(1)	49(1)
I(2)	907(1)	-786(1)	-756(1)	45(1)

	S(2)	357(1)	4578(4)	8360(1)	42(1)
	S(5)	4547(2)	9561(5)	5666(2)	68(1)
	S(1)	812(1)	6243(3)	8043(1)	47(1)
	S(6)	4089(2)	11134(4)	5990(1)	58(1)
	I(6)	-2288(1)	4425(1)	-505(1)	51(1)
	C(2)	1088(6)	5343(16)	7513(5)	55(3)
	N(1)	227(5)	4085(14)	7011(4)	69(3)
	C(1)	703(8)	5198(17)	7001(5)	79(5)
	I(11)	-4076(1)	-2688(1)	-3248(1)	51(1)
	N(5)	3917(5)	10454(14)	4478(4)	68(3)
	N(6)	4705(5)	11050(13)	7176(4)	68(3)
	C(11)	3880(6)	10070(17)	6530(5)	65(4)
	C(9)	3597(6)	9544(15)	4816(5)	56(4)
	C(10)	3995(6)	8558(16)	5197(5)	67(4)
	C(12)	4361(7)	9687(15)	6968(6)	58(4)
	S(3)	3216(2)	4962(5)	4440(2)	66(1)
	S(4)	2795(2)	3348(4)	4789(2)	87(1)
	N(2)	811(5)	5164(10)	9569(4)	50(3)
	C(3)	935(5)	3608(12)	8809(4)	40(3)
	N(3)	2615(5)	4705(12)	3216(4)	59(3)
	C(4)	1244(5)	4483(14)	9248(5)	45(3)
	C(6)	2642(6)	6107(15)	4055(5)	58(4)
	C(5)	2284(7)	5342(18)	3601(6)	70(4)
Sof=1	O(1)	-5146(7)	4884(15)	-4290(6)	125(5)
	C(7)	2847(9)	4080(20)	5466(6)	96(6)
	N(4)	2108(9)	5496(18)	5831(11)	193(12)
Sof=1	O(2)	4630(7)	3052(19)	4976(6)	155(6)
	C(8A)	2267(16)	4820(40)	5403(13)	74(9)
	C(8B)	2705(14)	5370(40)	5670(13)	72(9)

C- $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},2H_2O$ (3)

Table 1C_a. Crystal data and structure refinement for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},2H_2O$

Empirical formula	C24 H88 I22 N12 O2 Pb5 S12
Formula weight	4789.58
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P21/c
Unit cell dimensions	a = 23.25610(10) A alpha = 90 deg.
	b = 8.77790(10) A beta = 100.3660(10) deg.
	c = 25.57040(10) A gamma = 90 deg.
Volume	5134.74(7) A^3
Z, Calculated density	2, 3.102 Mg/m^3
Absorption coefficient	15.057 mm^-1
F(000)	4212
Crystal size	0.27 x 0.11 x 0.04 mm
Theta range for data collection	2.83 to 30.04 deg.
Limiting indices	-32<=h<=32, -12<=k<=12, -35<=l<=35
Reflections collected / unique	101625 / 14785 [R(int) = 0.0888]
Completeness to theta = 30.04	98.3 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14785 / 0 / 326
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0558, wR2 = 0.0855
R indices (all data)	R1 = 0.1535, wR2 = 0.1049
Extinction coefficient	0.000017(5)
Largest diff. peak and hole	1.491 and -1.269 e.A^-3

Table 1C_b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},2H_2O$
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pb(1)	10000	0	10000	35(1)
Pb(2)	8369(1)	5059(1)	8563(1)	38(1)
Pb(3)	6650(1)	-28(1)	7312(1)	45(1)
I(1)	10911(1)	-755(1)	9239(1)	54(1)
I(2)	9379(1)	2642(1)	9224(1)	52(1)
I(3)	9170(1)	7544(1)	9333(1)	68(1)
I(4)	8944(1)	5641(1)	7522(1)	65(1)
I(5)	7509(1)	7630(1)	8134(1)	73(1)
I(6)	7702(1)	4406(1)	9522(1)	65(1)
I(7)	7546(1)	2675(1)	7915(1)	71(1)
I(8)	7486(1)	-592(1)	6478(1)	64(1)
I(9)	5950(1)	2431(1)	6573(1)	66(1)
I(10)	5860(1)	224(1)	8214(1)	80(1)

I(11)	5898(1)	-2631(1)	6758(1)	66(1)
N(1)	212(5)	4117(14)	7007(4)	102(4)
C(1)	637(9)	5197(19)	6993(5)	126(7)
C(2)	1061(6)	5357(14)	7489(4)	72(4)
S(1)	800(1)	6268(3)	8033(1)	60(1)
S(2)	356(1)	4614(3)	8354(1)	53(1)
C(3)	926(5)	3626(12)	8803(4)	53(3)
C(4)	1236(5)	4544(12)	9245(4)	58(3)
N(2)	828(4)	5190(10)	9568(3)	67(3)
N(3)	7356(4)	5352(11)	6798(3)	76(3)
C(5)	7693(6)	4715(18)	6424(6)	96(5)
C(6)	7363(6)	3978(15)	5969(5)	82(4)
S(3)	6794(2)	5002(5)	5587(1)	88(1)
S(4A)	7057(5)	6539(9)	5195(3)	74(1)
S(4B)	7332(5)	6725(9)	5257(3)	74(1)
C(7)	7153(7)	5920(19)	4552(6)	111(5)
C(8B)	7325(12)	4630(30)	4370(11)	82(6)
C(8A)	7767(13)	5330(30)	4648(11)	82(6)
N(4)	7900(7)	4595(18)	4229(6)	159(6)
N(5)	6138(5)	5484(12)	10587(4)	84(3)
C(9)	6395(6)	4594(16)	10220(5)	82(4)
C(10)	5965(7)	3740(15)	9848(6)	103(5)
S(5)	5436(2)	4806(7)	9407(2)	123(2)
S(6)	5900(2)	6248(5)	9049(1)	90(1)
C(11)	6082(7)	5110(17)	8492(6)	105(5)
C(12)	5629(8)	4610(20)	8017(7)	134(6)
N(6)	5321(6)	5939(17)	7863(6)	144(5)
O(1A)	5343(12)	8510(30)	10017(11)	204(10)
O(1B)	5010(20)	9810(50)	10404(16)	204(10)

Table 1C_c Bond lengths [A] and angles [°] for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},2H_2O$

Pb(1)-I(3)#1	3.1774(7)
Pb(1)-I(3)#2	3.1774(7)
Pb(1)-I(1)#3	3.1932(7)
Pb(1)-I(1)	3.1932(7)
Pb(1)-I(2)#3	3.2204(6)
Pb(1)-I(2)	3.2204(6)
Pb(2)-I(5)	3.0829(8)
Pb(2)-I(7)	3.1054(8)
Pb(2)-I(6)	3.1813(8)
Pb(2)-I(4)	3.2255(8)
Pb(2)-I(3)	3.2842(8)
Pb(2)-I(2)	3.3825(7)
Pb(3)-I(11)	3.0660(8)
Pb(3)-I(9)	3.1253(8)
Pb(3)-I(8)	3.1723(8)
Pb(3)-I(10)	3.2041(9)
Pb(3)-I(5)#2	3.3367(8)
Pb(3)-I(7)	3.3458(8)
I(3)-Pb(1)#4	3.1774(7)
I(5)-Pb(3)#4	3.3367(8)
N(1)-C(1)	1.376(16)
C(1)-C(2)	1.466(18)
C(2)-S(1)	1.804(11)
S(1)-S(2)	2.037(4)

S(2)-C(3)	1.811(10)
C(3)-C(4)	1.468(13)
C(4)-N(2)	1.480(13)
N(3)-C(5)	1.453(15)
C(5)-C(6)	1.428(16)
C(6)-S(3)	1.745(13)
S(3)-S(4A)	1.850(10)
S(3)-S(4B)	2.224(10)
S(4A)-C(7)	1.783(16)
S(4B)-C(7)	1.910(17)
C(7)-C(8B)	1.32(3)
C(7)-C(8A)	1.50(3)
C(8B)-N(4)	1.45(3)
C(8A)-N(4)	1.33(3)
N(5)-C(9)	1.433(14)
C(9)-C(10)	1.458(17)
C(10)-S(5)	1.780(16)
S(5)-S(6)	1.989(6)
S(6)-C(11)	1.850(15)
C(11)-C(12)	1.52(2)
C(12)-N(6)	1.389(19)
I(3)#1-Pb(1)-I(3)#2	180.000(1)
I(3)#1-Pb(1)-I(1)#3	86.41(2)
I(3)#2-Pb(1)-I(1)#3	93.59(2)
I(3)#1-Pb(1)-I(1)	93.59(2)
I(3)#2-Pb(1)-I(1)	86.41(2)
I(1)#3-Pb(1)-I(1)	180.000(1)
I(3)#1-Pb(1)-I(2)#3	89.75(2)
I(3)#2-Pb(1)-I(2)#3	90.25(2)
I(1)#3-Pb(1)-I(2)#3	92.724(18)
I(1)-Pb(1)-I(2)#3	87.276(18)
I(3)#1-Pb(1)-I(2)	90.25(2)
I(3)#2-Pb(1)-I(2)	89.75(2)
I(1)#3-Pb(1)-I(2)	87.276(18)
I(1)-Pb(1)-I(2)	92.724(18)
I(2)#3-Pb(1)-I(2)	180.000(1)
I(5)-Pb(2)-I(7)	90.33(3)
I(5)-Pb(2)-I(6)	91.77(2)
I(7)-Pb(2)-I(6)	87.18(2)
I(5)-Pb(2)-I(4)	85.95(2)
I(7)-Pb(2)-I(4)	88.50(2)
I(6)-Pb(2)-I(4)	175.10(2)
I(5)-Pb(2)-I(3)	89.33(2)
I(7)-Pb(2)-I(3)	174.87(3)
I(6)-Pb(2)-I(3)	87.72(2)
I(4)-Pb(2)-I(3)	96.59(2)
I(5)-Pb(2)-I(2)	169.81(2)
I(7)-Pb(2)-I(2)	98.59(2)
I(6)-Pb(2)-I(2)	83.82(2)
I(4)-Pb(2)-I(2)	99.11(2)
I(3)-Pb(2)-I(2)	81.34(2)
I(11)-Pb(3)-I(9)	92.50(2)
I(11)-Pb(3)-I(8)	86.58(2)
I(9)-Pb(3)-I(8)	90.98(2)
I(11)-Pb(3)-I(10)	91.77(3)
I(9)-Pb(3)-I(10)	94.81(2)
I(8)-Pb(3)-I(10)	174.05(3)
I(11)-Pb(3)-I(5)#2	93.40(2)
I(9)-Pb(3)-I(5)#2	173.83(3)
I(8)-Pb(3)-I(5)#2	87.58(2)

I(10)-Pb(3)-I(5)#2	86.81(2)
I(11)-Pb(3)-I(7)	176.33(3)
I(9)-Pb(3)-I(7)	90.14(2)
I(8)-Pb(3)-I(7)	90.84(2)
I(10)-Pb(3)-I(7)	90.54(3)
I(5)#2-Pb(3)-I(7)	83.88(2)
Pb(1)-I(2)-Pb(2)	162.51(3)
Pb(1)#4-I(3)-Pb(2)	175.35(3)
Pb(2)-I(5)-Pb(3)#4	162.13(3)
Pb(2)-I(7)-Pb(3)	175.33(3)
N(1)-C(1)-C(2)	114.7(12)
C(1)-C(2)-S(1)	116.3(11)
C(2)-S(1)-S(2)	105.1(4)
C(3)-S(2)-S(1)	103.3(4)
C(4)-C(3)-S(2)	115.3(8)
C(3)-C(4)-N(2)	111.4(9)
C(6)-C(5)-N(3)	115.9(12)
C(5)-C(6)-S(3)	117.7(10)
C(6)-S(3)-S(4A)	112.9(6)
C(6)-S(3)-S(4B)	98.1(5)
S(4A)-S(3)-S(4B)	15.1(3)
C(7)-S(4A)-S(3)	112.7(7)
C(7)-S(4B)-S(3)	93.7(7)
C(8B)-C(7)-C(8A)	54.5(16)
C(8B)-C(7)-S(4A)	133.3(17)
C(8A)-C(7)-S(4A)	103.2(14)
C(8B)-C(7)-S(4B)	128.7(17)
C(8A)-C(7)-S(4B)	86.2(14)
S(4A)-C(7)-S(4B)	19.9(4)
C(7)-C(8B)-N(4)	117(2)
N(4)-C(8A)-C(7)	113(2)
C(8A)-N(4)-C(8B)	55.4(16)
N(5)-C(9)-C(10)	112.9(12)
C(9)-C(10)-S(5)	117.3(10)
C(10)-S(5)-S(6)	104.8(5)
C(11)-S(6)-S(5)	103.2(5)
C(12)-C(11)-S(6)	123.4(13)
N(6)-C(12)-C(11)	103.3(15)

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

Table 1C_d Anisotropic displacement parameters (A^2 x 10^3) for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},2H_2O$

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(1)	40(1)	29(1)	35(1)	-3(1)	1(1)	-1(1)
Pb(2)	40(1)	33(1)	39(1)	-3(1)	-3(1)	0(1)
Pb(3)	41(1)	40(1)	51(1)	-1(1)	4(1)	-1(1)
I(1)	58(1)	55(1)	54(1)	3(1)	23(1)	5(1)
I(2)	59(1)	49(1)	49(1)	14(1)	11(1)	19(1)
I(3)	84(1)	48(1)	63(1)	-10(1)	-13(1)	-28(1)
I(4)	53(1)	85(1)	56(1)	-2(1)	11(1)	1(1)

I(5)	92(1)	62(1)	59(1)	7(1)	-1(1)	40(1)
I(6)	57(1)	83(1)	58(1)	-7(1)	17(1)	3(1)
I(7)	83(1)	54(1)	68(1)	-15(1)	-5(1)	-30(1)
I(8)	48(1)	84(1)	62(1)	-3(1)	15(1)	1(1)
I(9)	65(1)	57(1)	75(1)	14(1)	7(1)	14(1)
I(10)	72(1)	104(1)	67(1)	6(1)	24(1)	17(1)
I(11)	64(1)	58(1)	76(1)	-12(1)	10(1)	-23(1)
N(1)	124(12)	115(10)	60(7)	-18(7)	1(7)	15(9)
C(1)	210(20)	117(14)	54(9)	-19(9)	35(11)	-88(14)
C(2)	89(10)	74(9)	65(8)	-4(6)	45(7)	-32(7)
S(1)	81(2)	50(2)	49(2)	4(1)	12(2)	-6(2)
S(2)	52(2)	65(2)	40(1)	7(1)	8(1)	-1(1)
C(3)	51(7)	58(7)	51(6)	1(5)	16(5)	1(6)
C(4)	70(8)	60(7)	45(6)	2(5)	11(6)	6(6)
N(2)	101(8)	65(6)	37(5)	6(4)	21(5)	-3(6)
N(3)	91(8)	87(8)	51(6)	5(5)	13(6)	23(6)
C(5)	74(10)	118(13)	88(10)	-33(9)	-7(8)	25(9)
C(6)	96(11)	79(10)	75(9)	6(8)	25(8)	5(8)
S(3)	69(2)	129(3)	65(2)	-5(2)	7(2)	12(2)
N(5)	82(8)	101(9)	66(7)	-2(6)	5(6)	3(7)
C(9)	72(10)	103(11)	68(8)	7(8)	7(7)	27(9)
C(10)	154(16)	67(9)	91(11)	4(8)	25(11)	-27(10)
S(5)	54(2)	229(6)	79(2)	46(3)	-6(2)	-30(3)
S(6)	94(3)	104(3)	67(2)	6(2)	2(2)	-12(2)

Table 1C_e. Hydrogen bonds for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},2H_2O$ [A and deg.].

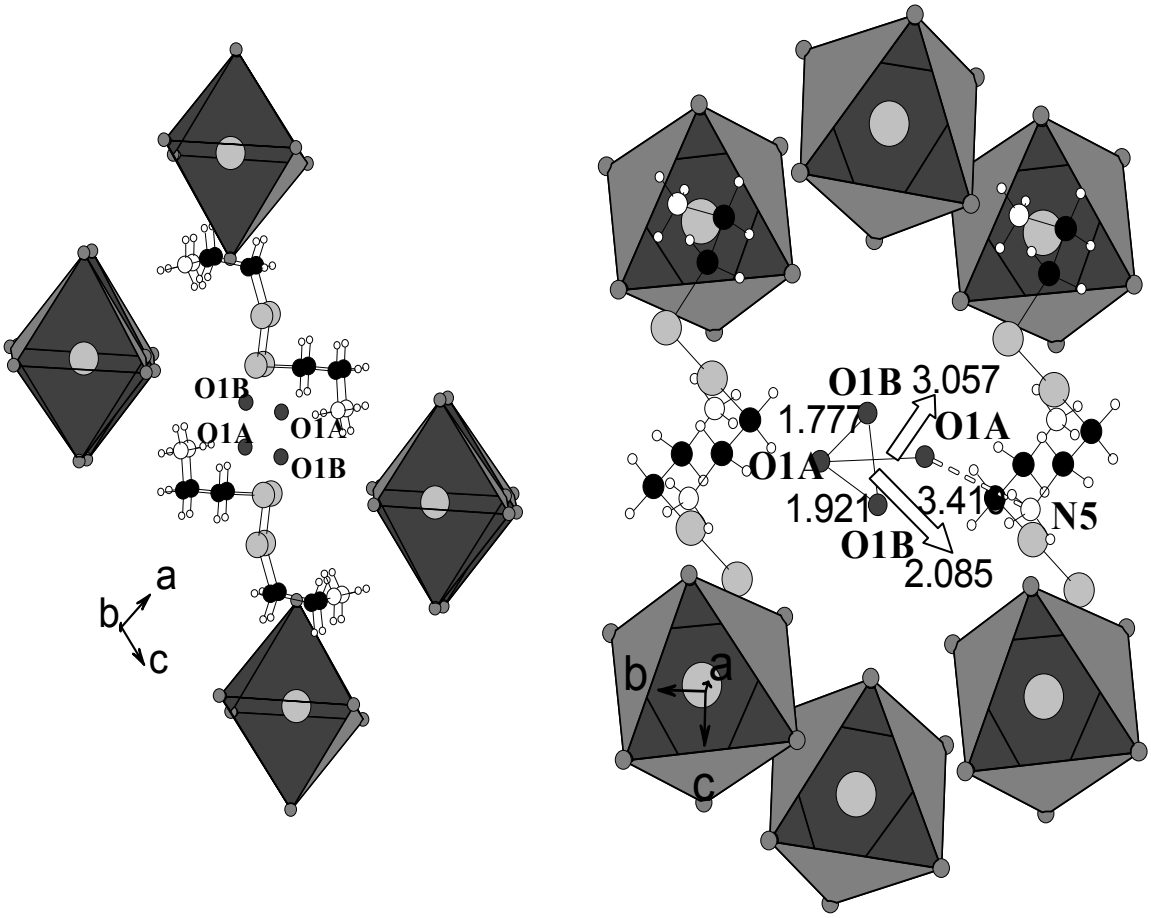
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...I(4)#5	0.89	2.83	3.710(12)	171.5
N(1)-H(1B)...I(1)#6	0.89	2.89	3.740(11)	159.7
N(1)-H(1C)...S(2)	0.89	2.89	3.427(10)	120.8
N(1)-H(1C)...I(4)#7	0.89	2.85	3.690(12)	159.0
N(2)-H(2A)...I(1)#8	0.89	3.02	3.670(9)	131.4
N(2)-H(2B)...I(6)#9	0.89	3.07	3.789(10)	138.7
N(2)-H(2B)...I(2)#9	0.89	3.09	3.731(8)	130.6
N(2)-H(2C)...I(3)#9	0.89	3.13	3.695(8)	123.5
N(3)-H(3C)...S(3)	0.89	2.71	3.152(10)	112.1
N(3)-H(3C)...I(11)#4	0.89	3.06	3.810(10)	142.6
N(3)-H(3E)...I(7)	0.89	2.90	3.663(9)	144.6
N(4)-H(4E2)...I(6)#10	0.89	2.94	3.638(16)	136.4
N(4)-H(4D2)...I(5)#11	0.89	2.82	3.698(16)	169.3
N(4)-H(4D2)...I(5)#11	0.89	2.82	3.698(16)	169.3
N(4)-H(4E2)...I(6)#10	0.89	2.94	3.638(16)	136.4
N(5)-H(5C)...S(5)	0.89	2.77	3.219(11)	112.3
N(5)-H(5D)...I(8)#12	0.89	2.89	3.528(10)	130.4
N(5)-H(5E)...I(9)#12	0.89	2.81	3.674(10)	164.1
N(6)-H(6C)...S(6)	0.89	2.49	3.100(15)	126.1
N(6)-H(6C)...I(9)#6	0.89	3.18	3.749(14)	124.1
N(6)-H(6D)...I(10)#6	0.89	2.74	3.579(14)	156.9
N(6)-H(6E)...I(11)#4	0.89	2.73	3.569(14)	156.6

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+2 #2 x,y-1,z #3 -x+2,-y,-z+2
#4 x,y+1,z #5 -x+1,y-1/2,-z+3/2 #6 -x+1,y+1/2,-z+3/2
#7 x-1,y,z #8 x-1,y+1,z #9 -x+1,-y+1,-z+2

#10 x,-y+1/2,z-1/2 #11 x,-y+3/2,z-1/2 #12 x,-y+1/2,z+1/2

Figure 1C: Water molecules in **3**

Two water molecules O1A and O1B have been located. Their occupation rate x(O1A) and x(O1B) have been refined in such a way that x(O1A)+ x(O1B)= 1, the isotropic thermal motion of O1A and O1B being constrained to be equal. Finally, x(O1A)= 0.61, x(O1B)= 0.39, Ueq(O1A, O1B)= 0.200.



D- $(NH_3(CH_2)_2SS(CH_2)_2NH_3)PbBr_4$ (4)

Table 1D_A Crystal data and structure refinement for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)PbBr_4$

Empirical formula	C4 H14 Br4 N2 Pb S2
Formula weight	681.12
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 11.4941(5) A alpha = 90 deg. b = 11.6541(5) A beta = 91.45 deg. c = 23.092(1) A gamma = 90 deg.
Volume	3092.2(3) A^3
Z, Calculated density	8, 2.926 Mg/m^3
Absorption coefficient	21.488 mm^-1
F(000)	2448
Crystal size	0.181 x 0.14 x 0.04 mm
Theta range for data collection	2.49 to 30.02 deg.
Limiting indices	-16<=h<=16, -16<=k<=16, -26<=l<=32
Reflections collected / unique	23307 / 4503 [R(int) = 0.0794]
Completeness to theta = 30.02	99.4 %
Absorption correction	Sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4503 / 0 / 122
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.0708
R indices (all data)	R1 = 0.0860, wR2 = 0.0792
Extinction coefficient	0.00028(2)
Largest diff. peak and hole	1.653 and -1.798 e.A^-3

Table 1D_b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)PbBr_4$ U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pb	2431(1)	942(1)	2538(1)	25(1)
Br(4)	2535(1)	888(1)	1269(1)	40(1)
Br(1)	5000	1488(1)	2500	35(1)
Br(2)	2493(1)	701(1)	3876(1)	39(1)
Br(3)	0	153(1)	2500	41(1)
Br(5)	3162(1)	-1518(1)	2540(1)	37(1)
S(2)	5228(2)	1479(2)	4949(1)	46(1)
S(1)	5867(2)	3101(2)	4927(1)	52(1)
N(1)	5887(5)	3335(5)	3577(3)	39(2)
C(4)	4439(8)	1815(7)	6062(4)	48(2)
C(1)	4747(6)	3359(7)	3854(4)	40(2)
C(2)	4830(8)	3826(7)	4452(4)	51(2)

C(3)	4049(7)	1608(7)	5447(4)	46(2)
N(2)	4979(6)	751(6)	6323(3)	46(2)

Table 1D_c Bond lengths [A] and angles [deg] for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)PbBr_4$

Pb-Br(4)	2.9363(8)
Pb-Br(3)	2.9405(4)
Pb-Br(5)	2.9877(7)
Pb-Br(1)	3.0244(3)
Pb-Br(5)#1	3.0417(7)
Pb-Br(2)	3.1010(9)
Br(1)-Pb#2	3.0244(3)
Br(3)-Pb#3	2.9405(4)
Br(5)-Pb#4	3.0417(7)
S(2)-C(3)	1.806(8)
S(2)-S(1)	2.029(3)
S(1)-C(2)	1.809(9)
N(1)-C(1)	1.472(9)
C(4)-C(3)	1.497(11)
C(4)-N(2)	1.507(10)
C(1)-C(2)	1.485(11)
Br(4)-Pb-Br(3)	91.493(16)
Br(4)-Pb-Br(5)	87.81(2)
Br(3)-Pb-Br(5)	88.11(3)
Br(4)-Pb-Br(1)	84.897(16)
Br(3)-Pb-Br(1)	173.04(3)
Br(5)-Pb-Br(1)	85.81(2)
Br(4)-Pb-Br(5)#1	88.68(2)
Br(3)-Pb-Br(5)#1	95.24(3)
Br(5)-Pb-Br(5)#1	175.209(10)
Br(1)-Pb-Br(5)#1	90.63(3)
Br(4)-Pb-Br(2)	172.60(2)
Br(3)-Pb-Br(2)	89.964(15)
Br(5)-Pb-Br(2)	84.99(2)
Br(1)-Pb-Br(2)	92.875(15)
Br(5)#1-Pb-Br(2)	98.41(2)
Pb-Br(1)-Pb#2	155.71(4)
Pb-Br(3)-Pb#3	143.55(4)
Pb-Br(5)-Pb#4	150.60(3)
C(3)-S(2)-S(1)	102.4(3)
C(2)-S(1)-S(2)	102.5(3)
C(3)-C(4)-N(2)	110.9(7)
N(1)-C(1)-C(2)	112.0(6)
C(1)-C(2)-S(1)	114.8(6)
C(4)-C(3)-S(2)	114.0(6)

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

Table 1D_d. Anisotropic displacement parameters (A^2 x 10^3) for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)PbBr_4$

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	23(1)	22(1)	29(1)	1(1)	0(1)	0(1)
Br(4)	44(1)	43(1)	31(1)	0(1)	-4(1)	-7(1)
Br(1)	23(1)	37(1)	44(1)	0	-6(1)	0
Br(2)	41(1)	36(1)	39(1)	-5(1)	-1(1)	1(1)
Br(3)	20(1)	50(1)	51(1)	0	-2(1)	0
Br(5)	45(1)	21(1)	44(1)	-1(1)	7(1)	-1(1)
S(2)	63(1)	41(1)	34(1)	4(1)	10(1)	8(1)
S(1)	58(1)	63(2)	34(1)	-4(1)	-2(1)	-15(1)
N(1)	46(4)	35(4)	36(4)	-1(3)	3(3)	1(3)
C(4)	62(6)	42(5)	41(5)	2(4)	15(5)	13(4)
C(1)	30(4)	46(5)	46(5)	14(4)	-2(4)	0(4)
C(2)	65(5)	42(5)	46(5)	13(4)	21(5)	16(4)
C(3)	51(5)	49(5)	38(5)	13(4)	0(4)	8(4)
N(2)	49(4)	52(5)	36(4)	5(3)	-1(3)	5(3)

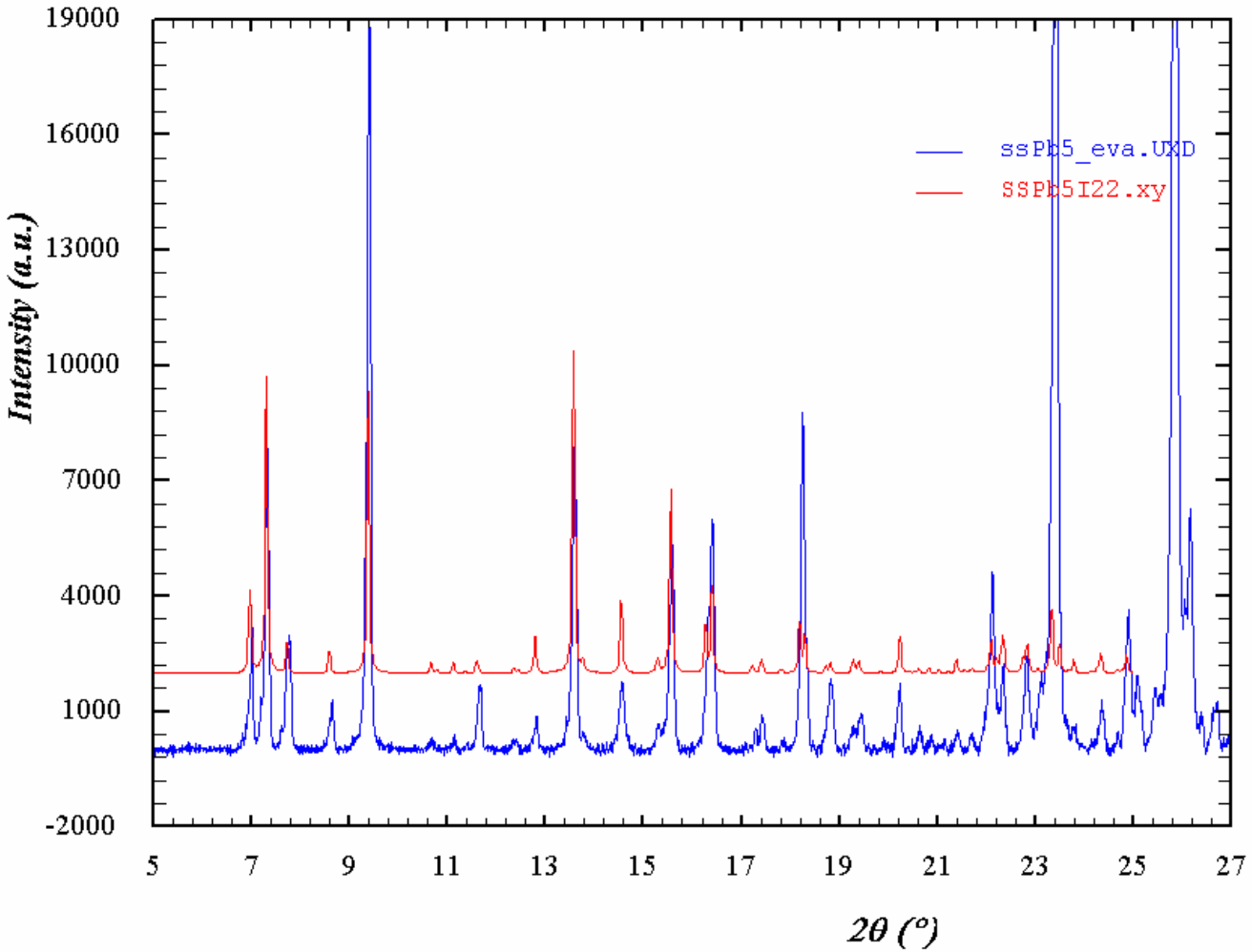
Table 1D_e. Hydrogen bonds for $(NH_3(CH_2)_2SS(CH_2)_2NH_3)PbBr_4$ [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...Br(2)#5	0.89	2.49	3.381(6)	175.2
N(1)-H(1B)...Br(1)	0.89	2.76	3.424(6)	132.6
N(1)-H(1B)...Br(3)#5	0.89	2.85	3.403(6)	121.4
N(1)-H(1C)...Br(4)#2	0.89	2.54	3.394(6)	160.5
N(2)-H(2C)...Br(4)#6	0.89	2.54	3.397(7)	162.6
N(2)-H(2D)...Br(5)#7	0.89	2.64	3.460(7)	154.6
N(2)-H(2E)...Br(2)#7	0.89	2.65	3.404(6)	143.5

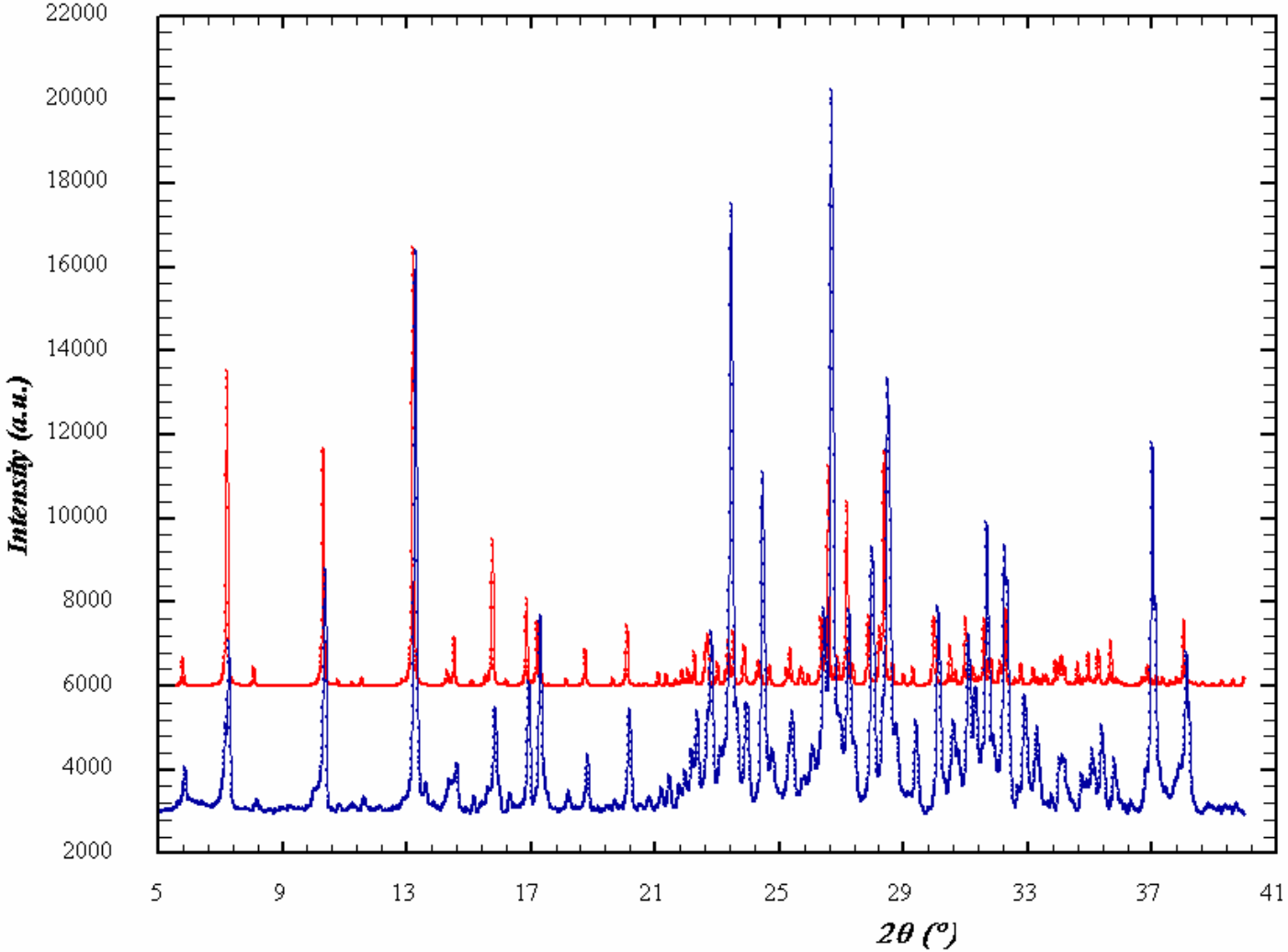
Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2 #2 -x+1,y,-z+1/2 #3 -x,y,-z+1/2
#4 -x+1/2,y-1/2,-z+1/2 #5 x+1/2,y+1/2,z #6 x,-y,z+1/2

3- Powder X-ray patterns

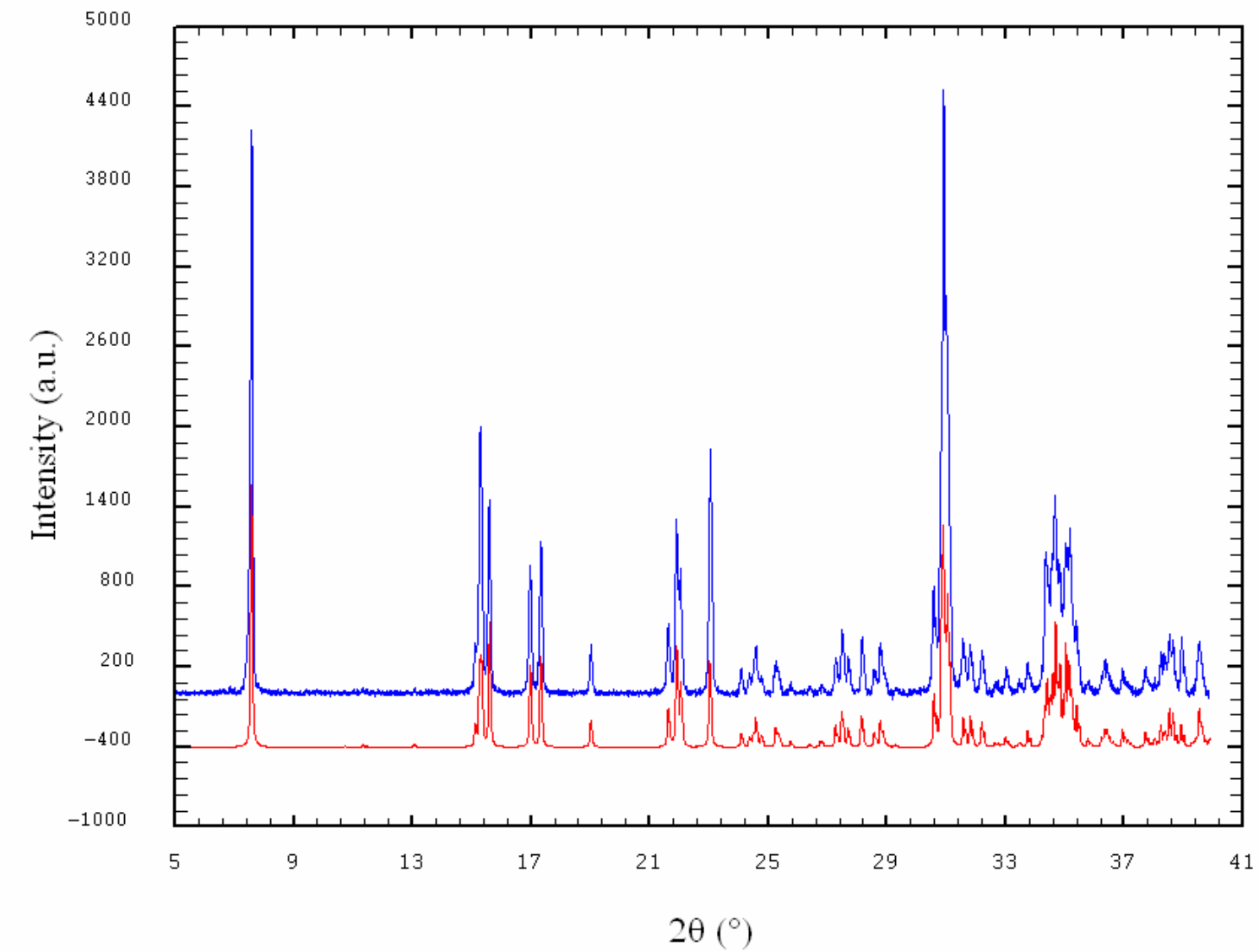
A- Powder X-Ray pattern of a crystallized powder of $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$ (2) (blue line), together with the theoretical one calculated from the crystal X-ray data (red line)



B- Powder X-Ray pattern of crushed selected crystals of $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_4Pb_3I_{14},I_2$ (1) (blue line) together with the theoretical one calculated from the crystal X-ray data (red line)



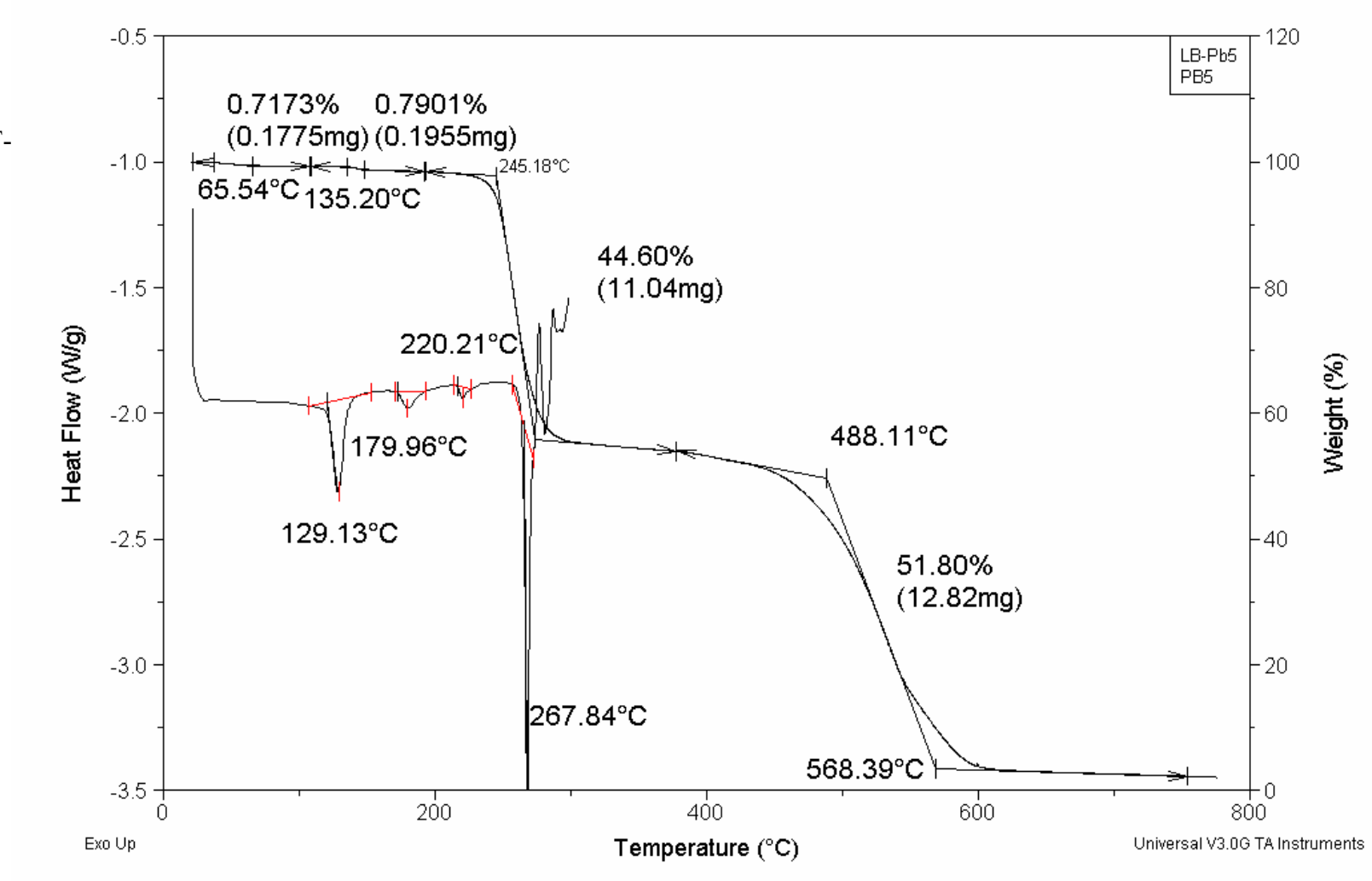
C- Powder X-Ray pattern of crystals of $(NH_3(CH_2)_2SS(CH_2)_2NH_3)PbBr_4$ (4) (blue line) together with the theoretical one calculated from the crystal X-ray data (red line)



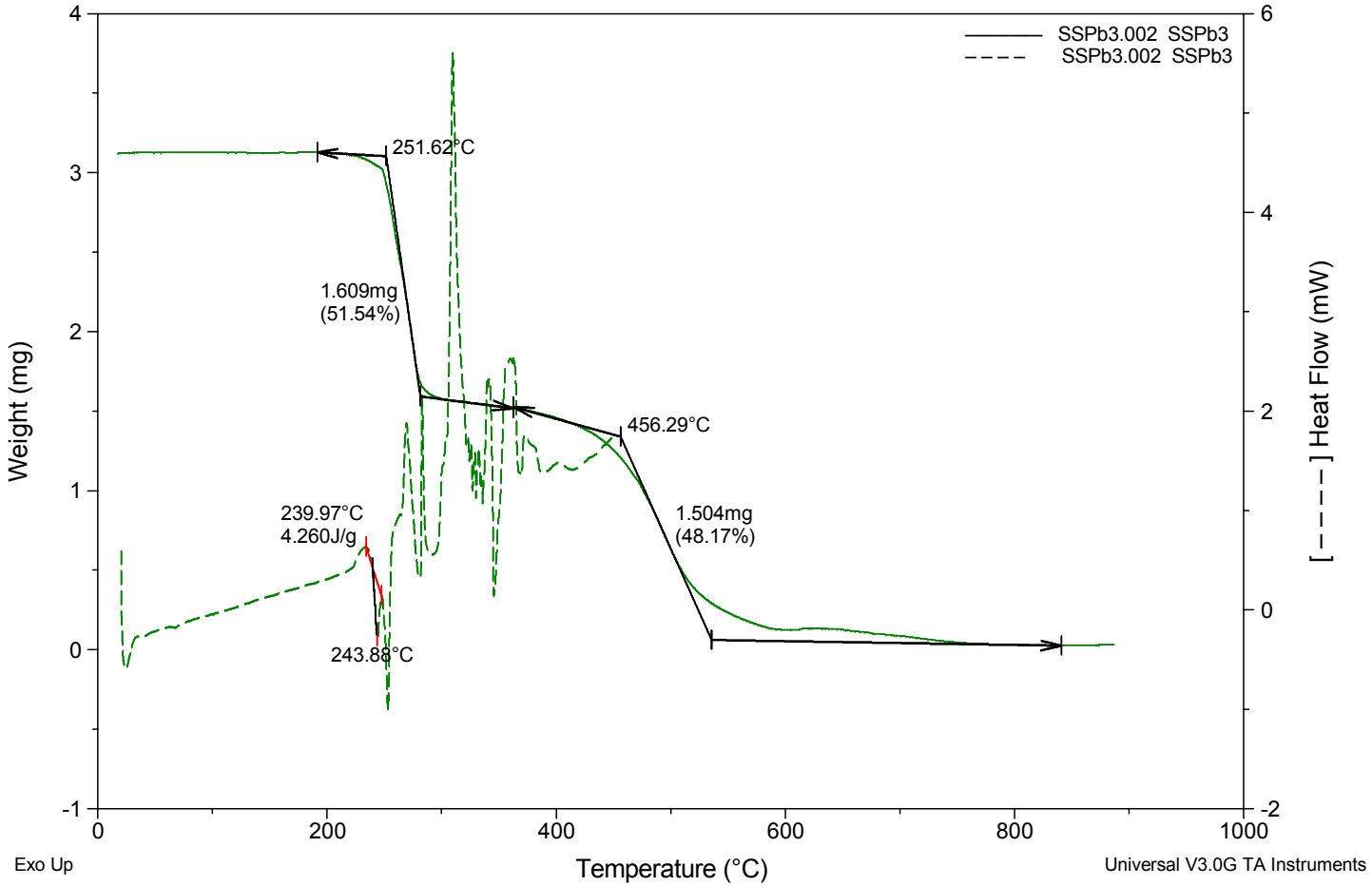
4- Thermal analysis

A)- DSC and ATG analysis of $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_6Pb_5I_{22},4H_2O$ (2)

DSC and ATG experiments in the RT-300°C and RT-800°C ranges respectively



B- DSC and ATG analysis of $(NH_3(CH_2)_2SS(CH_2)_2NH_3)_4Pb_3I_{14},I_2$



5- Solid state NMR

Figure 5A displays the CPMAS solid state ^{1}H-^{15}N NMR spectrum of **2**. This spectrum is tentatively reconstructed with five contributions (Table 5A) with isotropic chemical shift values ranging between -338 and -327 ppm. Despite the poor signal to noise ratio, the line relative intensities are compatible with six nitrogen sites with the same multiplicities, assigning the most intense line to two nitrogen sites.

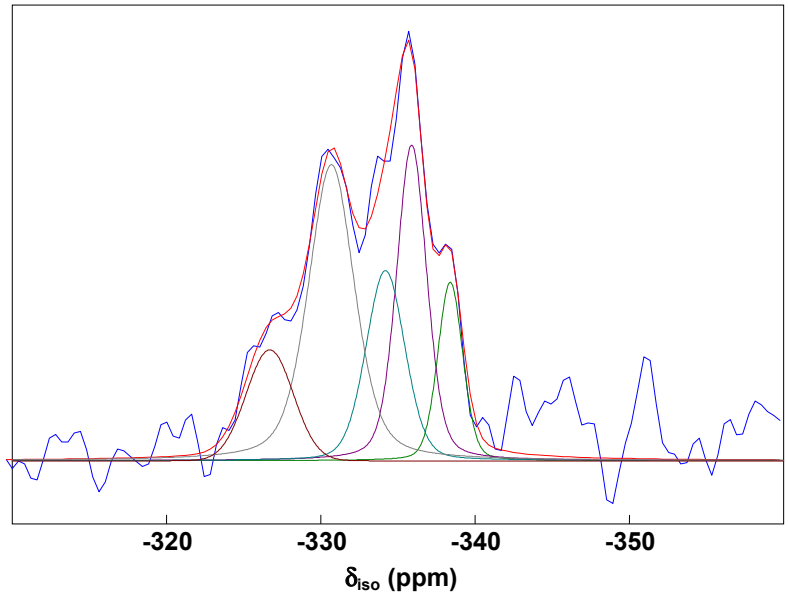


Figure 5A. Experimental (in blue) CPMAS solid state ^{1}H-^{15}N NMR spectrum of (**2**). The reconstructed spectrum (in red) corresponds to the summation of the five contributions.

δ_{iso}	Line width	Relative intensity (%)
-338.4	1.9	11
-335.9	2.3	24
-334.2	2.97	18
-330.7	3.51	35
-326.7	3.59	12

Table 5A. Isotropic chemical shifts, δ_{iso} (ppm), line widths (ppm) and relative intensities (%) as deduced from spectrum reconstruction of (**2**).

6- Complex Impedance Spectroscopy

After grinding crystals of **2**, the compaction into pellets was achieved by using a die placed in a uniaxial hydraulic press (5 mm diameter and 3-5 mm thickness, 500 MPa load). Thin platinum films electrodes were deposited by magnetron sputtering on both flat faces of the pellet. Two probes electrical conductivity measurements were carried out using a Schlumberger Solartron 1260 frequency response analyser connected to a Schlumberger Solartron 1296 dielectric interface over the frequency range 10 MHz to 0.05 Hz (ac voltage of 0.5V, 40 points/decade). Complex impedance spectra were recorded under dry nitrogen flow every 10K from 300 to 360K (temperature equilibration for 35min). Z-view 2.8d software was used to fit the whole impedance diagrams. The electronic conductivity was measured by the Wagner polarization method on a Schlumberger Solartron 1287/1260 electrochemical response analyser, in which platinum films were used as ion-blocking electrodes. Impedance diagrams plotted in the Nyquist complex plane present two semicircles and a spike at low frequencies characteristic of the electrode polarization. The high and lower frequency semicircles were least squares fitted with a series combination of (R//C) and (R//CPE) elements respectively. Based on the value of capacitance 10^{-12}F, the former arc was assigned to the bulk response while the later (10^{-10}F) is associated to the grain boundaries contribution.

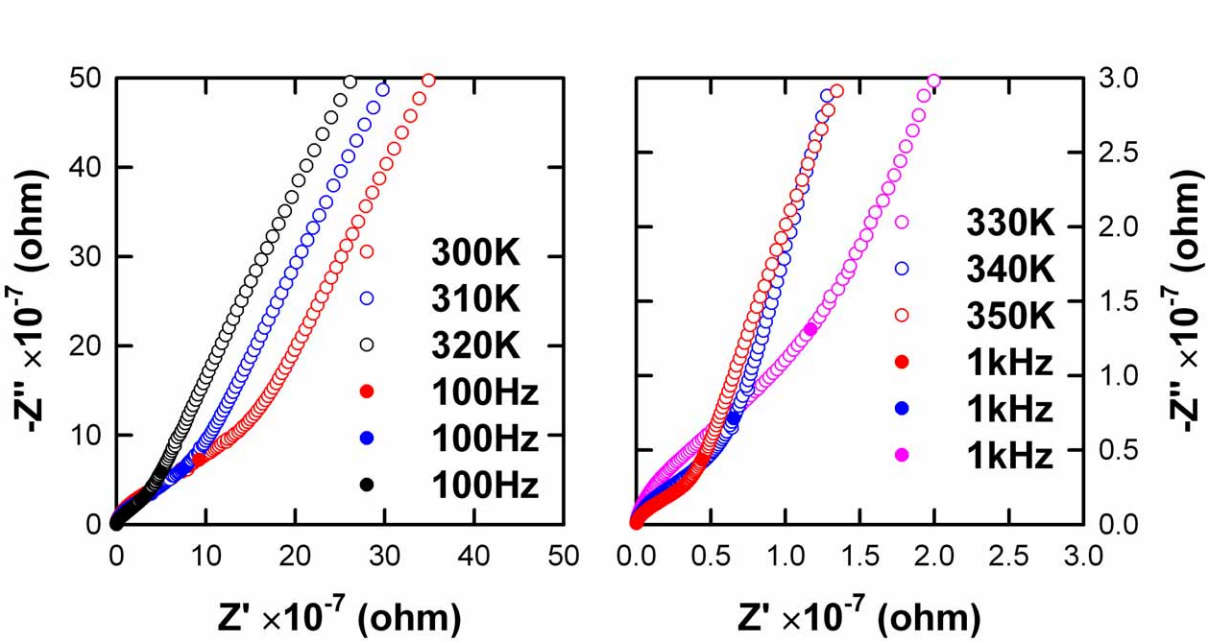


Figure 6A : Nyquist repesentation of impedance spectra at different temperatures.