Type Structure, Which Is Composed of Organic Diammonium, Triiodide and Hexaiodobismuthate, Varies According to different structures of incorporated Cations.

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Supporting information

1 - Tables of atomic coordinates, bond lengths, atomic displacement parameters, hydrogen bonds and checkCIF report for $(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6$

1a- checkCIF/PLATON report

Bond precision: C-C = 0.0200 A Wavelength=0.71073
Cell: a=11.954(2) b=12.521(2) c=11.888(2)
alpha=90 beta=95.680(10) gamma=90

	Calculated	Reported
Volume	1770.6(5)	1770.5(5)
Space group	C 2/m	C 1 2/m 1
Hall group	-C 2y	?
Moiety formula	4(C2 H7 N S), Bi I6, I3	C4 H10 BI1 I4 N2 S2
Sum formula	C8 H28 Bi I9 N4 S4	C8 H28 Bi I9 N4 S4
Mr	1659.70	1659.66
Dx,g cm-3	3.113	3.113
Z	2	2
Mu (mm-1)	13.067	13.068
F000	1456.0	1456.0
F000'	1441.23	
h,k,lmax	15,16,15	15,16,15
Nref	2140	2122
Tmin,Tmax	0.461,0.593	0.289,0.591
Tmin'	0.142	

Correction method= 'GAUSSIAN'
Data completeness= Ratio = 0.992 Theta(max)= 27.510
R(reflections)= 0.0409(1654) wR2(reflections)= 0.1085(2122)
S = 1.125 Npar= 67

Alert level A
PLAT432 ALERT 2 A Short Inter X...Y Contact S1 .. C2 .. 2.95 Ang.
PLAT432 ALERT 2 A Short Inter X...Y Contact S2 .. C2 .. 2.98 Ang.
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
PLAT201 ALERT 2 B Isotropic non-H Atoms in Main Residue(s) 2

1b- Table : Crystal data and structure refinement for **$(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6$**

Formula weight	1659.66
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 1 2/m 1
Unit cell dimensions	a = 11.954(2) A alpha = 90 deg.
	b = 12.521(2) A beta = 95.680(10) deg.
	c = 11.888(2) A gamma = 90 deg.
Volume	1770.5(5) A^3
Z, Calculated density	2, 3.113 Mg/m^3
Absorption coefficient	13.068 mm^-1
F(000)	1456
Crystal size	0.15 x 0.05 x 0.04 mm
Theta range for data collection	3.68 to 27.51 deg.
Limiting indices	-15<=h<=15, -16<=k<=16, -12<=l<=15
Reflections collected / unique	25214 / 2122 [R(int) = 0.0769]
Completeness to theta = 27.51	99.1 %
Absorption correction	Gaussian
Max. and min. transmission	0.5915 and 0.2889
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2122 / 0 / 67
Goodness-of-fit on F^2	1.125
Final R indices [I>2sigma(I)]	R1 = 0.0409, wR2 = 0.1018
R indices (all data)	R1 = 0.0598, wR2 = 0.1085
Largest diff. peak and hole	1.848 and -1.111 e.A^-3

1c- Table : Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **$(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6$**

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Bi	5000	5000	0	41(1)
I(5)	5000	7467(1)	0	55(1)
I(4)	2516(1)	5000	453(1)	59(1)
I(1)	0	5000	-5000	70(1)
I(3)	4258(1)	5000	-2552(1)	71(1)
I(2)	211(1)	5000	-2522(1)	81(1)
S(1)	2930(6)	3581(5)	-5072(5)	88(2)
C(1)	3323(13)	2664(13)	-6942(13)	116(5)
C(2)	2545(13)	3245(16)	-6375(13)	131(6)
N(1)	2695(7)	2203(8)	-8106(7)	78(2)
S(2)	1441(6)	2646(6)	-5818(6)	100(2)

1d - Table :. Bond lengths [A] and angles [deg] for **$(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6$**

Bi-I(4)	3.0701(9)
Bi-I(4)#1	3.0701(9)
Bi-I(3)	3.0749(10)
Bi-I(3)#1	3.0749(10)
Bi-I(5)#1	3.0885(8)
Bi-I(5)	3.0885(8)
I(1)-I(2)#2	2.9313(13)
I(1)-I(2)	2.9313(13)
S(1)-C(2)	1.627(16)
C(1)-C(2)	1.404(19)
C(1)-N(1)	1.615(16)
C(2)-S(2)	1.707(18)
I(4)-Bi-I(4)#1	180.0
I(4)-Bi-I(3)	89.04(3)
I(4)#1-Bi-I(3)	90.96(3)
I(4)-Bi-I(3)#1	90.96(3)
I(4)#1-Bi-I(3)#1	89.04(3)
I(3)-Bi-I(3)#1	180.0
I(4)-Bi-I(5)#1	90.0
I(4)#1-Bi-I(5)#1	90.0
I(3)-Bi-I(5)#1	90.0
I(3)#1-Bi-I(5)#1	90.0
I(4)-Bi-I(5)	90.0
I(4)#1-Bi-I(5)	90.0
I(3)-Bi-I(5)	90.0
I(3)#1-Bi-I(5)	90.0
I(5)#1-Bi-I(5)	180.0
I(2)#2-I(1)-I(2)	180.0
C(2)-C(1)-N(1)	108.8(12)
C(1)-C(2)-S(1)	116.9(13)
C(1)-C(2)-S(2)	122.2(15)
S(1)-C(2)-S(2)	84.3(8)

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

1e- Table : Anisotropic displacement parameters (A^2 x 10^3) for **$(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6$**

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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
Bi	39(1)	38(1)	48(1)	0	5(1)	0
I(5)	55(1)	33(1)	79(1)	0	12(1)	0
I(4)	37(1)	61(1)	80(1)	0	14(1)	0
I(1)	43(1)	60(1)	108(1)	0	8(1)	0
I(3)	78(1)	83(1)	52(1)	0	6(1)	0
I(2)	75(1)	71(1)	95(1)	0	3(1)	0
S(1)	127(5)	72(3)	64(3)	-7(3)	-1(3)	11(3)
N(1)	72(5)	82(6)	80(6)	-11(5)	12(4)	-10(4)
S(2)	103(5)	96(5)	102(5)	5(4)	15(4)	30(4)

1f- Table : Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1C	0.890	3.086	131.76	3.738	I5 [-x+1, -y+1, -z-1]
N1-H1C	0.890	3.145	126.91	3.747	I2 [-x+1/2, -y+1/2, -z-1]
N1-H1D	0.890	3.070	154.24	3.891	I4 [x, y, z-1]
N1-H1E	0.890	2.882	165.33	3.750	I3 [-x+1/2, -y+1/2, -z-1]

2 - Tables of atomic coordinates, bond lengths, atomic displacement parameters, hydrogen bonds and checkCIF report for $(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6,0.5H_2O$

2a- checkCIF/PLATON report

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Bond precision:      C-C = 0.0250 A              Wavelength=0.71073
Cell:    a=23.450(5)      b=12.724(3)      c=12.401(3)
         alpha=90         beta=108.45(3)   gamma=90
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	Calculated	Reported
Volume	3510.0(15)	3510.0(12)
Space group	C 2	C 2
Hall group	C 2y	?
Moiety formula	4(C4 H14 N2 S2), 2(Bi I6), 2(I3), O	C8 H28 BI1 I9 N4 S4 O0.5
Sum formula	C16 H56 Bi2 I18 N8 O S8	C8 H28 BI I9 N4 O0.50 S4
Mr	3335.41	1667.66
Dx,g cm-3	3.156	3.156
Z	2	4
Mu (mm-1)	13.185	13.185
F000	2928.0	2928.0
F000'	2898.46	
h,k,lmax	32,17,17	32,17,17
Nref	5339(10249)	9998
Tmin,Tmax	0.224,0.268	
Tmin'	0.078	

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Correction method= Not given
Data completeness= 1.87(0.98)  Theta(max)= 30.010
R(reflections)= 0.0485( 6394)     wR2(reflections)= 0.1198( 9998)
S = 1.073            Npar= 246
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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.
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Alert level A

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PLAT093 ALERT 1 A No su's on H-atoms, but refinement reported as .      mixed
PLAT213 ALERT 2 A Atom N3      has ADP max/min Ratio .....              5.90 prola
PLAT306 ALERT 2 A Isolated Oxygen Atom (H-atoms Missing ?) .....          O
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 ..........        ?
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Alert level B

ABSTM02 ALERT 3 B The ratio of Tmax/Tmin expected RT(exp) is > 1.20
Absorption corrections should be applied.
Tmin and Tmax expected: 0.219 0.268
RT(exp) = 1.223
PLAT111 ALERT 2 B ADDSYM Detects (Pseudo) Centre of Symmetry ..... 89 PerFi
PLAT342 ALERT 3 B Low Bond Precision on C-C bonds (x 1000) Ang ... 25

2b- Table : Crystal data and structure refinement for **$(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6,0.5H_2O$**

Empirical formula	C8 H29 Bi I9 N4 O0.50 S4
Formula weight	1668.66
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2
Unit cell dimensions	a = 23.450(5) A alpha = 90 deg.
	b = 12.724(3) A beta = 108.45(3) deg.
	c = 12.401(3) A gamma = 90 deg.
Volume	3510.0(12) A^3
Z, Calculated density	4, 3.156 Mg/m^3
Absorption coefficient	13.185 mm^-1
F(000)	2928
Crystal size	0.3 x 0.2 x 0.1 mm
Theta range for data collection	3.18 to 30.01 deg.
Limiting indices	-32<=h<=32, -17<=k<=17, -17<=l<=14
Reflections collected / unique	35506 / 9998 [R(int) = 0.0668]
Completeness to theta = 30.01	99.3 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9998 / 1 / 246
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.1047
R indices (all data)	R1 = 0.0999, wR2 = 0.1198
Absolute structure parameter	0.279(8)
Largest diff. peak and hole	2.947 and -1.663 e.A^-3

2c- Table : Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **$(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6,0.5H_2O$**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Bi	7416(1)	1810(1)	2349(1)	29(1)
I(7)	5000	1912(1)	5000	34(1)
I(6)	7467(1)	4243(1)	2331(1)	38(1)
I(4)	8754(1)	1756(1)	2558(1)	42(1)
I(5)	7463(1)	-603(1)	2417(1)	42(1)
I(1)	7767(1)	1866(1)	5002(1)	44(1)
I(9)	10000	1912(1)	0	38(1)
I(2)	7151(1)	1806(1)	-218(1)	41(1)
I(8)	6262(1)	1930(1)	6422(1)	47(1)

I(10)	8710(1)	1887(1)	-1211(1)	48(1)
I(3)	6062(1)	1697(1)	2065(1)	52(1)
S(2)	9880(2)	3251(3)	-3000(4)	49(1)
S(3)	10240(2)	210(3)	2600(4)	46(1)
S(1)	10416(2)	4509(4)	-3022(5)	52(1)
S(4)	9675(2)	-952(4)	2728(4)	49(1)
C(8)	9118(8)	-879(13)	385(13)	41(4)
N(4)	8540(7)	-449(12)	576(13)	50(4)
C(7)	9455(7)	-1565(12)	1354(14)	41(4)
C(3)	9158(7)	3812(11)	-3311(16)	47(4)
C(4)	8939(7)	4292(14)	-4500(13)	44(4)
C(5)	11155(8)	-926(16)	4168(15)	56(5)
N(2)	8332(5)	4790(10)	-4693(11)	53(3)
N(3)	11129(5)	-246(12)	5129(10)	58(4)
N(1)	11461(6)	4085(12)	-690(13)	57(5)
C(1)	10888(8)	4417(15)	-642(16)	55(5)
C(2)	10548(8)	5085(13)	-1719(16)	50(5)
C(6)	10990(6)	-387(12)	3092(15)	44(4)
O	10000	922(12)	5000	62(4)

2d- Table :. Bond lengths [A] and angles [deg] for
$(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6,0.5H_2O$

Bi-I(2)	3.0449(11)
Bi-I(4)	3.0668(11)
Bi-I(5)	3.0726(13)
Bi-I(3)	3.0844(11)
Bi-I(6)	3.0989(13)
Bi-I(1)	3.1295(12)
I(7)-I(8)#1	2.9269(13)
I(7)-I(8)	2.9269(13)
I(9)-I(10)	2.9200(12)
I(9)-I(10)#2	2.9200(12)
S(2)-C(3)	1.764(15)
S(2)-S(1)	2.040(6)
S(3)-C(6)	1.834(14)
S(3)-S(4)	2.025(6)
S(1)-C(2)	1.710(18)
S(4)-C(7)	1.794(16)
C(8)-C(7)	1.49(2)
C(8)-N(4)	1.55(2)
C(3)-C(4)	1.53(2)
C(4)-N(2)	1.506(18)
C(5)-C(6)	1.44(2)
C(5)-N(3)	1.49(2)
N(1)-C(1)	1.43(2)
C(1)-C(2)	1.57(2)
I(2)-Bi-I(4)	87.32(4)
I(2)-Bi-I(5)	91.19(4)
I(4)-Bi-I(5)	87.04(4)
I(2)-Bi-I(3)	91.03(4)
I(4)-Bi-I(3)	175.73(4)
I(5)-Bi-I(3)	89.05(3)
I(2)-Bi-I(6)	89.39(4)
I(4)-Bi-I(6)	88.96(3)
I(5)-Bi-I(6)	175.93(2)
I(3)-Bi-I(6)	94.97(3)
I(2)-Bi-I(1)	176.49(3)

I(4)-Bi-I(1)	89.41(4)
I(5)-Bi-I(1)	89.93(4)
I(3)-Bi-I(1)	92.32(4)
I(6)-Bi-I(1)	89.26(4)
I(8)#1-I(7)-I(8)	179.09(8)
I(10)-I(9)-I(10)#2	178.78(9)
C(3)-S(2)-S(1)	103.5(5)
C(6)-S(3)-S(4)	104.7(5)
C(2)-S(1)-S(2)	104.5(6)
C(7)-S(4)-S(3)	104.0(6)
C(7)-C(8)-N(4)	110.5(13)
C(8)-C(7)-S(4)	115.5(11)
C(4)-C(3)-S(2)	112.3(12)
N(2)-C(4)-C(3)	109.6(13)
C(6)-C(5)-N(3)	113.4(15)
N(1)-C(1)-C(2)	110.9(16)
C(1)-C(2)-S(1)	117.6(12)
C(5)-C(6)-S(3)	117.0(12)

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

2e- Table : Anisotropic displacement parameters (A^2 x 10^3) for **$(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6,0.5H_2O$**

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
Bi	26(1)	28(1)	31(1)	0(1)	6(1)	-2(1)
I(7)	45(1)	26(1)	29(1)	0	8(1)	0
I(6)	42(1)	27(1)	40(1)	0(1)	6(1)	1(1)
I(4)	26(1)	43(1)	54(1)	3(1)	8(1)	-2(1)
I(5)	44(1)	25(1)	52(1)	-1(1)	9(1)	-2(1)
I(1)	50(1)	51(1)	31(1)	-5(1)	12(1)	-10(1)
I(9)	57(1)	26(1)	33(1)	0	18(1)	0
I(2)	45(1)	49(1)	26(1)	-1(1)	7(1)	-2(1)
I(8)	40(1)	50(1)	44(1)	4(1)	4(1)	-1(1)
I(10)	51(1)	43(1)	48(1)	-1(1)	13(1)	5(1)
I(3)	31(1)	44(1)	81(1)	2(1)	21(1)	0(1)
S(2)	44(2)	37(2)	56(3)	7(2)	3(2)	0(2)
S(3)	58(3)	37(2)	34(2)	8(2)	2(2)	-1(2)
S(1)	48(3)	49(2)	57(3)	21(2)	13(2)	-2(2)
S(4)	40(2)	56(3)	45(3)	20(2)	3(2)	-4(2)
C(8)	59(11)	44(9)	22(7)	-7(6)	16(7)	-14(8)
N(4)	54(11)	61(9)	37(9)	-3(7)	19(8)	-16(8)
C(7)	28(8)	41(8)	53(11)	-13(7)	11(7)	-10(6)
C(3)	31(8)	30(8)	81(13)	14(8)	21(8)	7(6)
C(4)	26(7)	66(11)	25(8)	10(7)	-14(7)	2(7)
C(5)	48(10)	67(12)	53(11)	3(9)	17(9)	15(9)
N(2)	31(6)	65(9)	51(8)	9(7)	-2(6)	9(6)
N(3)	22(6)	104(12)	31(7)	30(7)	-16(6)	5(6)
N(1)	38(9)	65(10)	51(10)	-1(8)	-11(7)	14(8)
C(1)	44(11)	73(13)	53(12)	-21(9)	25(9)	-21(9)
C(2)	54(11)	40(9)	66(13)	-2(8)	34(10)	0(7)
C(6)	23(8)	42(8)	60(11)	10(7)	4(7)	7(6)
O	58(10)	75(11)	52(10)	0	15(8)	0

2f- Table : - Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N4-H4A	0.890	2.820	157.42	3.658	I4
N4-H4B	0.890	2.999	153.58	3.817	I2 [-x+3/2, y-1/2, -z]
N4-H4C	0.890	3.034	128.17	3.652	I6 [-x+3/2, y-1/2, -z]
N2-H2A	0.890	3.150	147.08	3.927	I1 [x, y, z-1]
N2-H2B	0.890	3.025	142.55	3.770	I8 [-x+3/2, y+1/2, -z]
N2-H2C	0.890	3.127	154.40	3.949	I3 [-x+3/2, y+1/2, -z]
N3-H3C	0.890	2.903	164.89	3.770	I1 [-x+2, y, -z+1]
N3-H3D	0.890	3.076	133.30	3.743	I5 [-x+2, y, -z+1]
N3-H3E	0.890	2.157	156.94	2.997	O
N1-H1A	0.890	2.685	116.93	3.189	S1
N1-H1A	0.890	3.088	127.30	3.696	I4 [-x+2, y, -z]
N1-H1B	0.890	2.977	147.80	3.760	I10 [-x+2, y, -z]
N1-H1C	0.890	2.965	154.57	3.788	I2 [x+1/2, y+1/2, z]

3 - Tables of atomic coordinates, bond lengths, atomic displacement parameters, hydrogen bonds and checkCIF report for $(H_3N(CH_2)_4NH_3)_2(I_3)_{0.5}(I(H_2O)_2)_{0.5}BiI_6$

3a- checkCIF/PLATON

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Bond precision: C-C = 0.0133 A          Wavelength=0.71073
Cell: a=8.5276(17)   b=10.405(2)   c=17.504(4)
      alpha=77.92(3) beta=87.39(3) gamma=85.29(3)
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	Calculated	Reported
Volume	1513.0(6)	1513.0(5)
Space group	P -1	P -1
Hall group	-P 1	?
Moiety formula	C4 H13.97 N2, C4 H14 N2, Bi I6, 0.5(I3), 0.5(I), O	?
Sum formula	C8 H27.97 Bi I8 N4 O	C8 H28 BI I8 N4 O
Mr	1420.49	1420.10
Dx,g cm-3	3.118	3.118
Z	2	2
Mu (mm-1)	13.993	13.994
F000	1237.9	1238.0
F000'	1223.13	

h,k,lmax	12,14,24	11,14,24
Nref	8849	8798
Tmin,Tmax	0.271,0.497	0.168,0.350
Tmin'	0.127	

Correction method= 'MULTI-SCAN'

Data completeness= Ratio = 0.994 Theta(max)= 30.030

R(reflections)= 0.0434(5330) wR2(reflections)= 0.0943(8798)

S = 1.026 Npar= 209

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

PLAT305 ALERT 2 A Isolated Hydrogen Atom (Outside Bond Range ??)
>H1A3

PLAT306 ALERT 2 A Isolated Oxygen Atom (H-atoms Missing ?) .....
O

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

PLAT201 ALERT 2 B Isotropic non-H Atoms in Main Residue(s) .....
1

PLAT241 ALERT 2 B Check High Ueq as Compared to Neighbors for
C8

3b- Table : Crystal data and structure refinement for
$(H_3N(CH_2)_4NH_3)_2(I_3)_{0.5}(I(H_2O)_2)_{0.5}BiI_6$

Empirical formula	C8 H28 Bi I8 N4 O
Formula weight	1420.52
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic , P-1
Unit cell dimensions	a = 8.5276(17) A alpha = 77.92(3) deg. b = 10.405(2) A beta = 87.39(3) deg. c = 17.504(4) A gamma = 85.29(3) deg.
Volume	1513.0(5) A^3
Z, Calculated density	2, 3.118 Mg/m^3
Absorption coefficient	13.994 mm^-1
F(000)	1238
Crystal size	0.70 x 0.30 x 0.20 mm
Theta range for data collection	3.05 to 30.03 deg.
Limiting indices	-11<=h<=11, -14<=k<=14, -24<=l<=24
Reflections collected / unique	52561 / 8798 [R(int) = 0.0549]
Completeness to theta = 30.03	99.5 %
Absorption correction	None
Max. and min. transmission	0.1662 and 0.0365
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8798 / 0 / 209
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.0825

R indices (all data)	R1 = 0.0935, wR2 = 0.0943
Largest diff. peak and hole	1.742 and -1.637 e.A^-3

3c- Table : Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(H_3N(CH_2)_4NH_3)_2(I_3)_{0.5}(I(H_2O)_2)_{0.5}BiI_6$
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Bi	4656(1)	4893(1)	2504(1)	40(1)
I(1)	2195(1)	5390(1)	1287(1)	64(1)
I(2)	2152(1)	4885(1)	3871(1)	60(1)
I(3)	7228(1)	4337(1)	3798(1)	53(1)
I(4)	7217(1)	4991(1)	1254(1)	60(1)
I(5)	4776(1)	7888(1)	2372(1)	60(1)
I(6)	4544(1)	1904(1)	2569(1)	56(1)
I(7)	0	0	0	76(1)
I(8)	490(1)	2459(1)	485(1)	87(1)
I(9)	0	0	5000	98(1)
O	8635(8)	7385(6)	4242(4)	84(2)
N(1A)	393(15)	2253(14)	3165(9)	75(4)
N(1B)	190(40)	2700(30)	2650(20)	90(11)
N(2)	-764(13)	-2938(9)	2462(8)	144(5)
N(3)	5167(9)	7268(6)	4514(4)	65(2)
N(4)	4882(10)	2801(6)	396(4)	73(2)
C(1)	-663(10)	1550(8)	2751(6)	64(2)
C(2)	104(11)	273(8)	2619(6)	71(3)
C(3)	-933(12)	-569(9)	2384(7)	89(3)
C(4)	-95(17)	-1831(10)	2227(9)	125(5)
C(5)	5235(12)	9276(8)	5036(6)	73(3)
C(6)	4620(13)	8673(8)	4449(6)	86(3)
C(7)	4665(11)	640(8)	63(6)	71(3)
C(8)	5555(13)	1538(10)	305(8)	106(4)

3d- Table :. Bond lengths [A] and angles [deg] for $(H_3N(CH_2)_4NH_3)_2(I_3)_{0.5}(I(H_2O)_2)_{0.5}BiI_6$

Bi-I(1)	2.9957(11)
Bi-I(4)	3.0120(11)
Bi-I(5)	3.0859(8)
Bi-I(6)	3.0982(8)
Bi-I(2)	3.1337(11)
Bi-I(3)	3.1590(11)
I(7)-I(8)#1	2.9257(10)
I(7)-I(8)	2.9257(10)
N(1A)-C(1)	1.504(15)
N(1B)-C(1)	1.43(3)
N(2)-C(4)	1.308(12)
N(3)-C(6)	1.480(10)
N(4)-C(8)	1.427(11)
C(1)-C(2)	1.489(11)
C(2)-C(3)	1.426(13)

C(3)-C(4)	1.512(13)
C(5)-C(6)	1.449(12)
C(5)-C(5)#2	1.508(16)
C(7)-C(8)	1.393(12)
C(7)-C(7)#3	1.461(15)
I(1)-Bi-I(4)	90.54(2)
I(1)-Bi-I(5)	90.30(3)
I(4)-Bi-I(5)	89.12(4)
I(1)-Bi-I(6)	88.27(3)
I(4)-Bi-I(6)	89.31(4)
I(5)-Bi-I(6)	177.867(18)
I(1)-Bi-I(2)	92.87(2)
I(4)-Bi-I(2)	175.866(17)
I(5)-Bi-I(2)	88.52(4)
I(6)-Bi-I(2)	93.13(3)
I(1)-Bi-I(3)	179.248(19)
I(4)-Bi-I(3)	89.93(2)
I(5)-Bi-I(3)	90.30(3)
I(6)-Bi-I(3)	91.15(3)
I(2)-Bi-I(3)	86.68(2)
I(8)#1-I(7)-I(8)	180.00(3)
N(1B)-C(1)-C(2)	121.5(14)
N(1B)-C(1)-N(1A)	37.0(11)
C(2)-C(1)-N(1A)	111.8(9)
C(3)-C(2)-C(1)	114.6(8)

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

3e- Table : Anisotropic displacement parameters (A^2 x 10^3) for **$(H_3N(CH_2)_4NH_3)_2(I_3)_{0.5}(I(H_2O)_2)_{0.5}BiI_6$**

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
Bi	33(1)	43(1)	45(1)	-13(1)	-1(1)	-5(1)
I(1)	53(1)	77(1)	68(1)	-32(1)	-24(1)	10(1)
I(2)	44(1)	80(1)	56(1)	-14(1)	9(1)	-5(1)
I(3)	42(1)	62(1)	59(1)	-21(1)	-12(1)	3(1)
I(4)	47(1)	75(1)	57(1)	-13(1)	13(1)	-4(1)
I(5)	68(1)	38(1)	76(1)	-12(1)	-9(1)	-6(1)
I(6)	54(1)	38(1)	76(1)	-12(1)	1(1)	-5(1)
I(7)	59(1)	99(1)	67(1)	-18(1)	-2(1)	9(1)
I(8)	92(1)	83(1)	86(1)	-23(1)	1(1)	5(1)
I(9)	94(1)	96(1)	106(1)	-22(1)	-12(1)	-18(1)
N(1A)	46(7)	69(9)	122(13)	-47(9)	1(8)	-10(7)
N(1B)	90(20)	70(20)	120(30)	-40(20)	-30(20)	41(16)
N(2)	111(9)	69(6)	245(15)	-29(8)	48(9)	-5(6)
N(3)	80(5)	50(4)	70(5)	-25(4)	-2(4)	-6(4)
N(4)	100(6)	50(4)	76(5)	-27(4)	-10(4)	-2(4)
C(1)	57(6)	53(5)	83(6)	-16(5)	4(5)	0(4)
C(2)	69(7)	62(5)	80(7)	-19(5)	-2(5)	11(5)
C(3)	77(7)	57(5)	145(10)	-49(6)	29(7)	-17(5)
C(4)	148(12)	66(7)	173(13)	-59(8)	79(10)	-37(7)
C(5)	76(7)	60(5)	88(7)	-32(5)	1(5)	3(5)
C(6)	100(8)	54(5)	110(8)	-33(6)	-32(7)	18(5)

C(7)	75(6)	54(5)	91(7)	-29(5)	-15(5)	0(4)
C(8)	75(8)	80(7)	179(13)	-65(8)	-38(8)	13(6)

3f- Table :Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.890	3.117	120.69	3.653	I6
N1-H1B	0.890	2.778	153.77	3.598	I3 [x-1, y, z]
N1-H1C	0.890				
N2-H2A	0.890	2.480	140.95	3.220	O [x-1, y-1, z]
N2-H2B	0.890	3.059	147.11	3.837	I2 [x, y-1, z]
N2-H2C	0.890	3.057	150.76	3.858	I4 [x-1, y-1, z]
N3-H3A	0.890	2.115	166.16	2.986	O
N3-H3B	0.890	3.005	135.69	3.695	I5
N3-H3C	0.890	2.832	162.44	3.691	I3 [-x+1, -y+1, -z+1]
N4-H4A	0.890	2.862	162.79	3.721	I4 [-x+1, -y+1, -z]
N4-H4B	0.890	2.856	165.20	3.724	I4
N4-H4C	0.890	3.139	131.28	3.785	I8

4 - Tables of atomic coordinates, bond lengths, atomic displacement parameters, hydrogen bonds and checkCIF report for

$(HO_2C(C_6H_{10})CH_2NH_3)_4(I_3)_2BiI_6,H_3O$ (4)

4a- checkCIF/PLATON

Bond precision: C-C = 0.0124 A Wavelength=0.71073
Cell: a=11.792(2) b=12.737(2) c=21.908(3)
alpha=90 beta=94.29(1) gamma=90

	Calculated	Reported
Volume	3281.3(9)	3281.2(9)
Space group	C 2/m	C 1 2/m 1
Hall group	-C 2y	?
Moiety formula	4(C8 H15 N O2), Bi I6, 2(I3), O	C32 H60 BI1 I12 N4 O8
Sum formula	C32 H60 Bi I12 N4 O9	C32 H67 BI I12 N4 O9
Mr	2376.62	2383.68
Dx,g cm-3	2.405	2.413
Z	2	2
Mu (mm-1)	8.371	8.371
F000	2142.0	2156.0
F000'	2123.64	
h,k,lmax	15,16,28	15,16,28
Nref	3945	3915
Tmin,Tmax	0.381,0.557	0.321,0.529
Tmin'	0.084	

Correction method= 'MULTI-SCAN'
Data completeness= Ratio = 0.992 Theta(max)= 27.500
R(reflections)= 0.0385(3032) wR2(reflections)= 0.0892(3915)
S = 1.095 Npar= 146

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

PLAT241 ALERT 2 B Check High Ueq as Compared to Neighbors for C3
PLAT242 ALERT 2 B Check Low Ueq as Compared to Neighbors for C2
PLAT242 ALERT 2 B Check Low Ueq as Compared to Neighbors for I5
PLAT250 ALERT 2 B Large U3/U1 Ratio for Average U(i,j) Tensor 4.23
PLAT430 ALERT 2 B Short Inter D...A Contact O1 .. O2 2.66 Ang.
PLAT430 ALERT 2 B Short Inter D...A Contact O2 .. O3 2.77 Ang.

4b- Table : Crystal data and structure refinement for
$(HO_2C(C_6H_{10})CH_2NH_3)_4(I_3)_2BiI_6,H_3O$

Empirical formula	C32 H67 Bi I12 N4 O9
Formula weight	2383.68
Temperature	293(2) K

Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 1 2/m 1
Unit cell dimensions	a = 11.792(2) A alpha = 90 deg.
	b = 12.737(2) A beta = 94.290(10) deg.
	c = 21.908(3) A gamma = 90 deg.
Volume	3281.2(9) A^3
Z, Calculated density	2, 2.413 Mg/m^3
Absorption coefficient	8.371 mm^-1
F(000)	2156
Crystal size	0.3 x 0.1 x 0.07 mm
Theta range for data collection	3.52 to 27.50 deg.
Limiting indices	-15<=h<=15, -13<=k<=16, -28<=l<=28
Reflections collected / unique	24342 / 3915 [R(int) = 0.0355]
Completeness to theta = 27.50	99.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3915 / 0 / 146
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.0833
R indices (all data)	R1 = 0.0593, wR2 = 0.0892
Extinction coefficient	0.00020(3)
Largest diff. peak and hole	1.526 and -1.200 e.A^-3

4c- 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)
Bi	0	0	0	37(1)
I(3)	620(1)	0	1384(1)	53(1)
I(1)	0	2426(1)	0	56(1)
I(2)	2560(1)	0	-165(1)	53(1)
I(4)	4943(1)	0	1482(1)	78(1)
I(5)	4857(1)	0	2826(1)	73(1)
O(3)	1089(14)	0	4106(7)	68(4)
C(7)	1945(8)	2309(10)	2399(4)	102(4)
C(3)	3577(10)	3469(9)	2570(4)	110(4)
N	2706(7)	2089(7)	1078(3)	92(3)
C(4)	3584(9)	3272(9)	3247(4)	98(3)
C(6)	1954(9)	2087(9)	3068(3)	95(3)
C(1)	3059(8)	2924(7)	1519(3)	74(2)
C(8)	2484(9)	2717(9)	4124(4)	89(3)
C(2)	3027(7)	2653(6)	2184(3)	60(2)
C(5)	2446(8)	2952(8)	3437(4)	85(3)
O(1)	3082(8)	3351(8)	4475(3)	146(4)
O(2)	1948(8)	2000(6)	4331(3)	122(3)
I(6)	4797(2)	0	4138(1)	147(1)

4d- Table Bond lengths [A] and angles [deg] for sad.

Bi-I(3)	3.0647(7)
Bi-I(3)#1	3.0647(7)
Bi-I(2)#1	3.0674(8)
Bi-I(2)	3.0674(8)
Bi-I(1)#1	3.0894(8)
Bi-I(1)	3.0894(8)
I(4)-I(5)	2.9531(12)
I(5)-I(6)	2.8810(14)
C(7)-C(2)	1.459(11)
C(7)-C(6)	1.491(11)
C(3)-C(2)	1.462(11)
C(3)-C(4)	1.503(11)
N-C(1)	1.475(10)
C(4)-C(5)	1.491(12)
C(6)-C(5)	1.460(12)
C(1)-C(2)	1.501(9)
C(8)-O(2)	1.218(11)
C(8)-O(1)	1.288(11)
C(8)-C(5)	1.531(12)

I(3)-Bi-I(3)#1	180.000(5)
I(3)-Bi-I(2)#1	92.712(19)
I(3)#1-Bi-I(2)#1	87.288(19)
I(3)-Bi-I(2)	87.288(19)
I(3)#1-Bi-I(2)	92.712(19)
I(2)#1-Bi-I(2)	180.00(2)
I(3)-Bi-I(1)#1	90.0
I(3)#1-Bi-I(1)#1	90.0
I(2)#1-Bi-I(1)#1	90.0
I(2)-Bi-I(1)#1	90.0
I(3)-Bi-I(1)	90.0
I(3)#1-Bi-I(1)	90.0
I(2)#1-Bi-I(1)	90.0
I(2)-Bi-I(1)	90.0
I(1)#1-Bi-I(1)	180.0
I(6)-I(5)-I(4)	179.42(5)
C(2)-C(7)-C(6)	115.6(8)
C(2)-C(3)-C(4)	115.0(8)
C(5)-C(4)-C(3)	112.4(8)
C(5)-C(6)-C(7)	112.0(8)
N-C(1)-C(2)	116.3(7)
O(2)-C(8)-O(1)	121.5(8)
O(2)-C(8)-C(5)	122.4(8)
O(1)-C(8)-C(5)	116.1(9)
C(7)-C(2)-C(3)	112.7(7)
C(7)-C(2)-C(1)	117.9(7)
C(3)-C(2)-C(1)	110.9(7)
C(6)-C(5)-C(4)	112.4(8)
C(6)-C(5)-C(8)	112.2(8)
C(4)-C(5)-C(8)	111.5(8)

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

4e- Table Anisotropic displacement parameters (A^2 x 10^3) for sad.
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
Bi	39(1)	43(1)	31(1)	0	5(1)	0
I(3)	57(1)	70(1)	32(1)	0	7(1)	0
I(1)	74(1)	37(1)	60(1)	0	21(1)	0
I(2)	37(1)	82(1)	41(1)	0	8(1)	0
I(4)	80(1)	101(1)	53(1)	0	8(1)	0
I(5)	93(1)	62(1)	65(1)	0	7(1)	0
O(3)	96(11)	39(7)	65(9)	0	-10(8)	0
C(7)	96(7)	162(10)	50(5)	-20(6)	18(4)	-63(7)
C(3)	155(10)	130(9)	49(5)	-9(5)	30(5)	-82(8)
N	104(6)	131(7)	42(4)	-3(4)	10(4)	-48(5)
C(4)	109(7)	140(9)	46(5)	-14(5)	12(5)	-61(7)
C(6)	117(7)	132(8)	38(4)	-13(5)	22(4)	-63(7)
C(1)	113(7)	71(5)	38(4)	7(4)	8(4)	-17(5)
C(8)	106(7)	116(8)	47(5)	-23(5)	23(5)	-38(6)
C(2)	71(5)	71(5)	39(4)	5(3)	7(3)	-4(4)
C(5)	113(7)	95(7)	50(5)	-9(4)	24(5)	-11(6)
O(1)	213(9)	173(8)	54(4)	-30(5)	31(5)	-116(7)
O(2)	183(8)	136(6)	51(4)	-21(4)	39(4)	-80(6)
I(6)	236(2)	152(1)	56(1)	0	18(1)	0

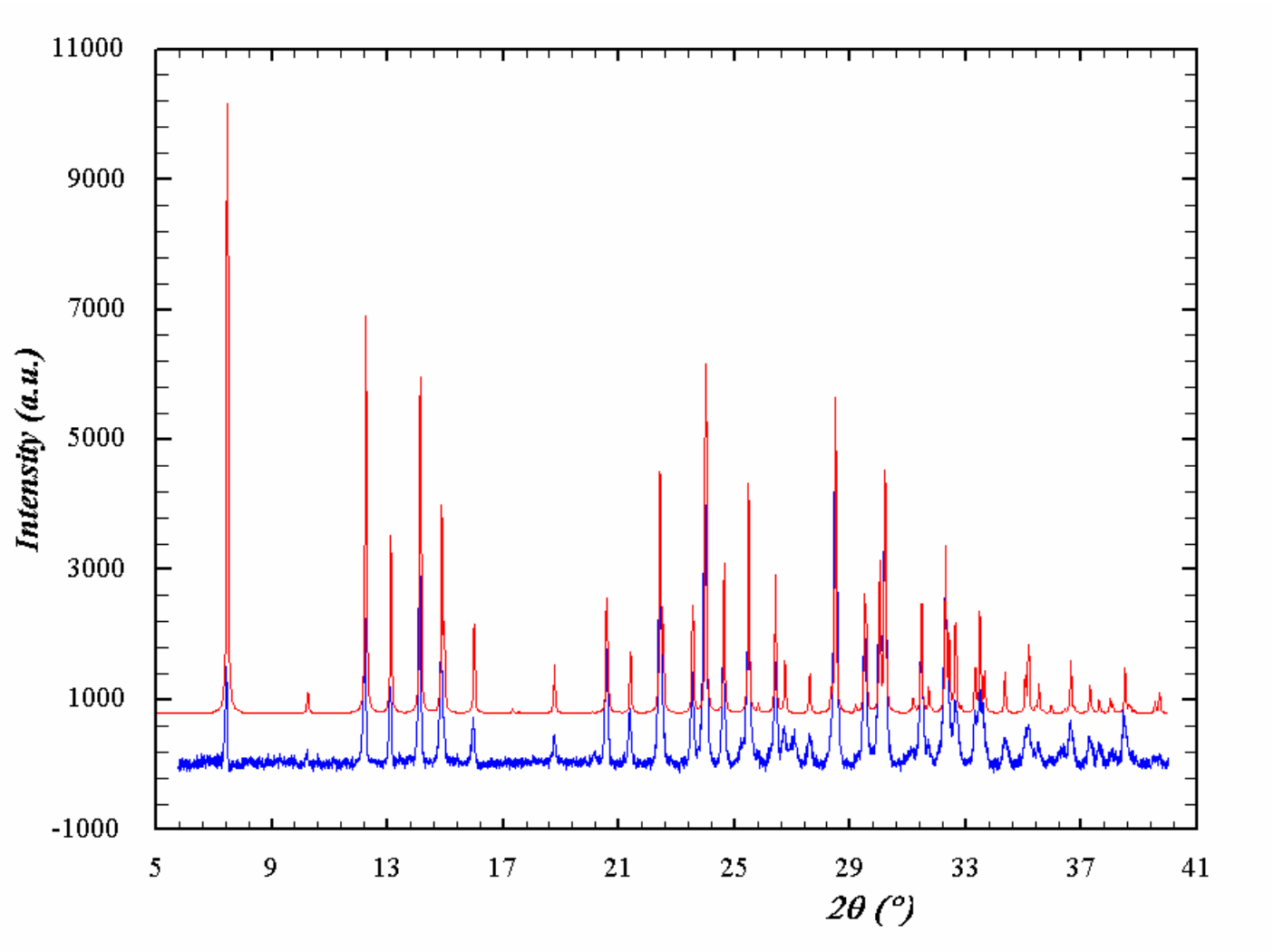
Table 4f- :Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg for $(HO_2C(C_6H_{10})CH_2NH_3)_4(I_3)_2BiI_6,H_30$

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N-H1A2_a	0.890	3.089	137.98	3.797	I3
N-H1A2_a	0.890	3.181	116.21	3.662	I1
N-H1B1_b	0.890	3.056	132.05	3.712	I1 [-x+1/2, -y+1/2, -z]
N-H1B2_b	0.890	2.967	139.51	3.690	I3
N-H1B3_b	0.890	2.719	165.35	3.587	I4

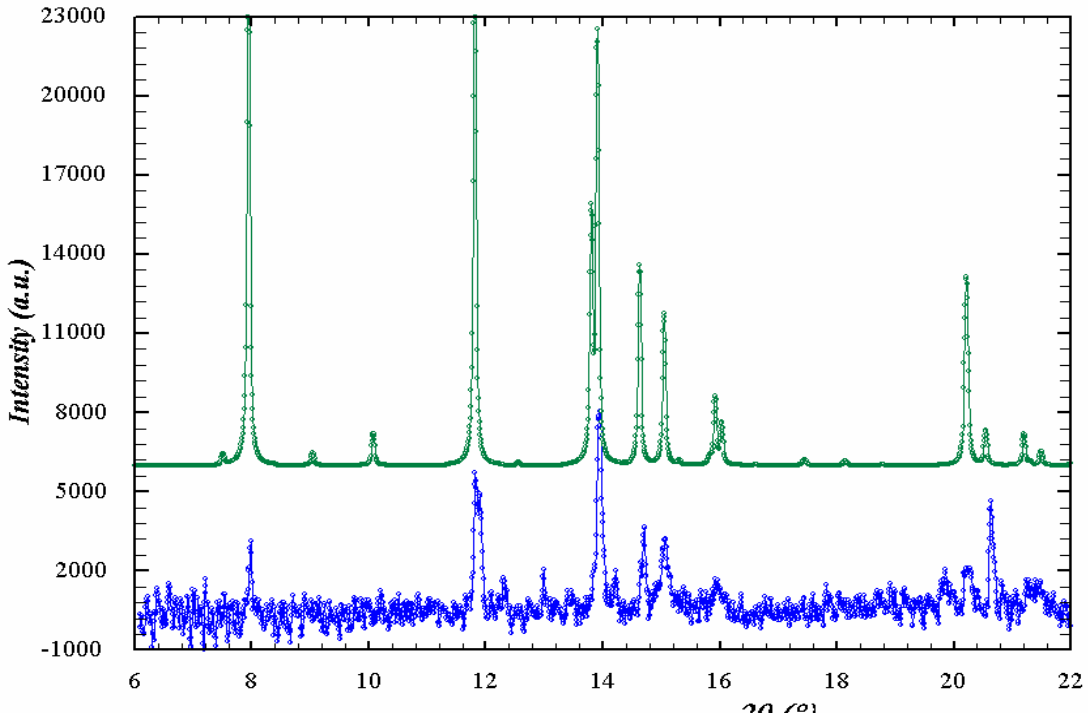
5- powder X-ray diffraction

5a- experimental (blue) and calculated (red) XRPD patterns of $(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6$ (1)



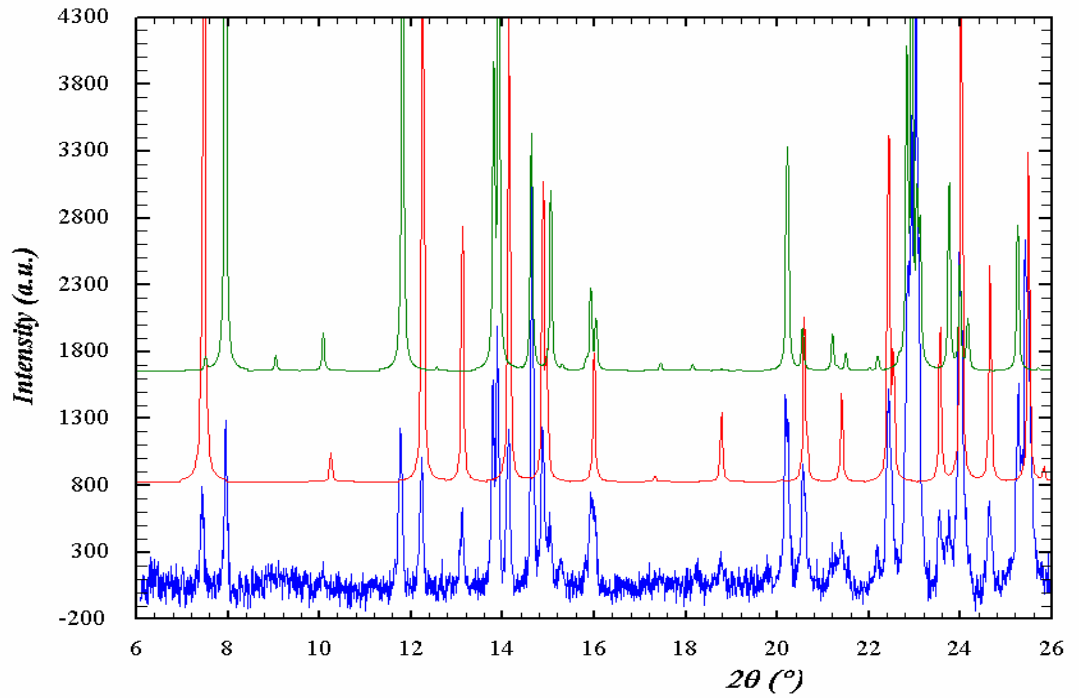
5b- experimental (blue) and calculated (green) XRPD patterns of $(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6,0.5H_2O$ (2)

Big crystals of (**2**) have been selected and slightly crushed (only) in order to avoid the transformation of (**2**) into (**1**) by loss of water molecules. That explains the poor quality of the diffractogram of (**2**).

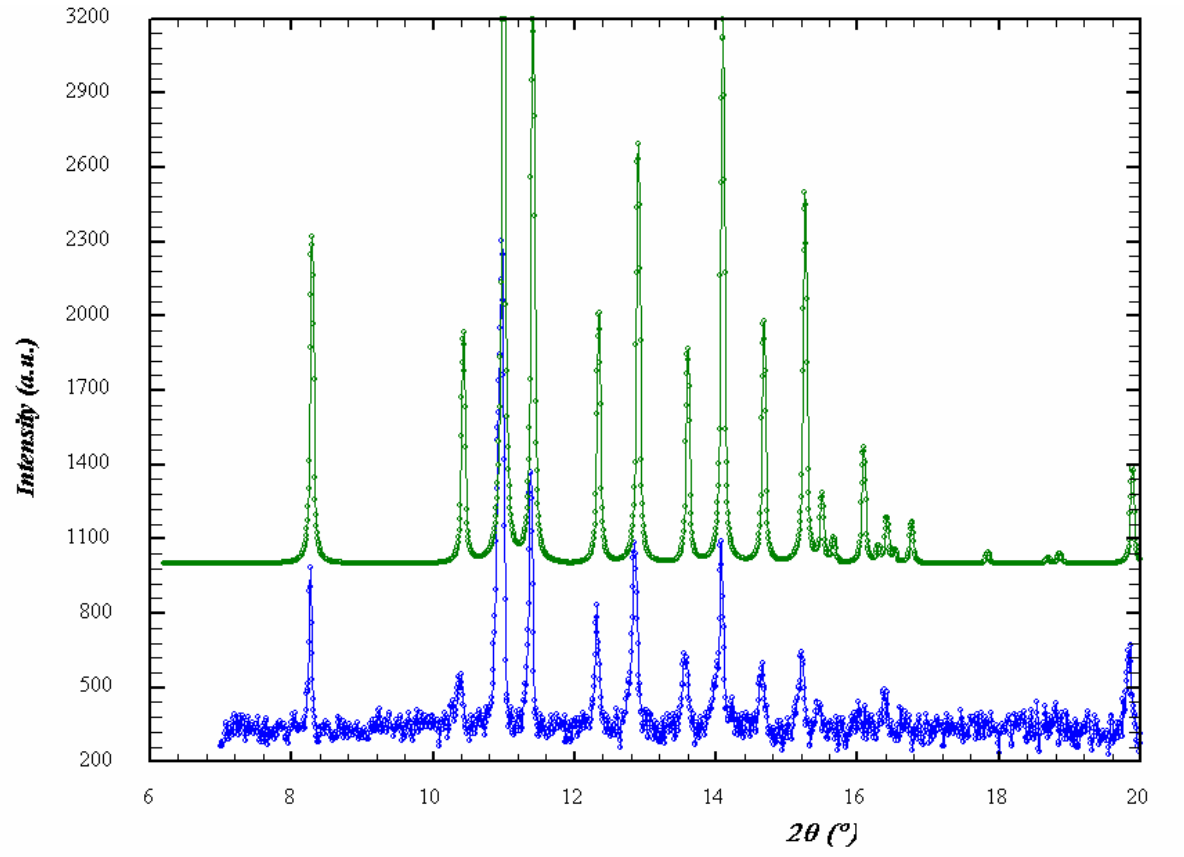


Transformation (2) to (1)

XRPD of the same sample of crystals of (**2**) energetically crushed, showing the presence of both phases (**1**) and (**2**), that demonstrates the transformation of (**2**) into (**1**). This transformation is a single-crystal to single-crystal one, as confirmed by a X-ray single crystal study (cell determination at RT (phase (**2**), and after a heating the crystal at 60°C during 20mn (phase (**1**).

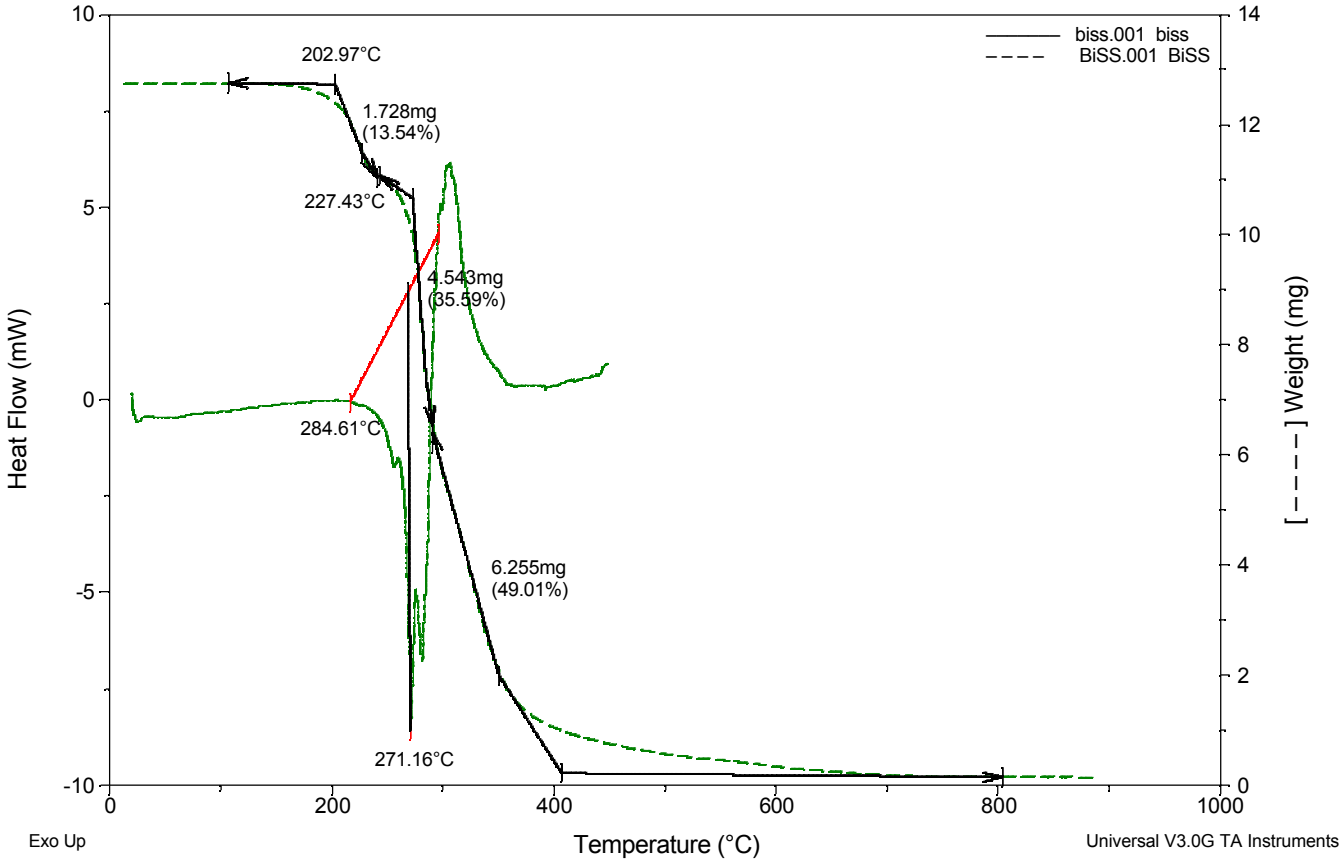


5c- experimental (blue) (crushed crystals previously selected) and calculated (green) XRPD patterns of $(HO_2C(C_6H_{10})CH_2NH_3)_4(I_3)_2BiI_6\ H_3O$ (**4**)

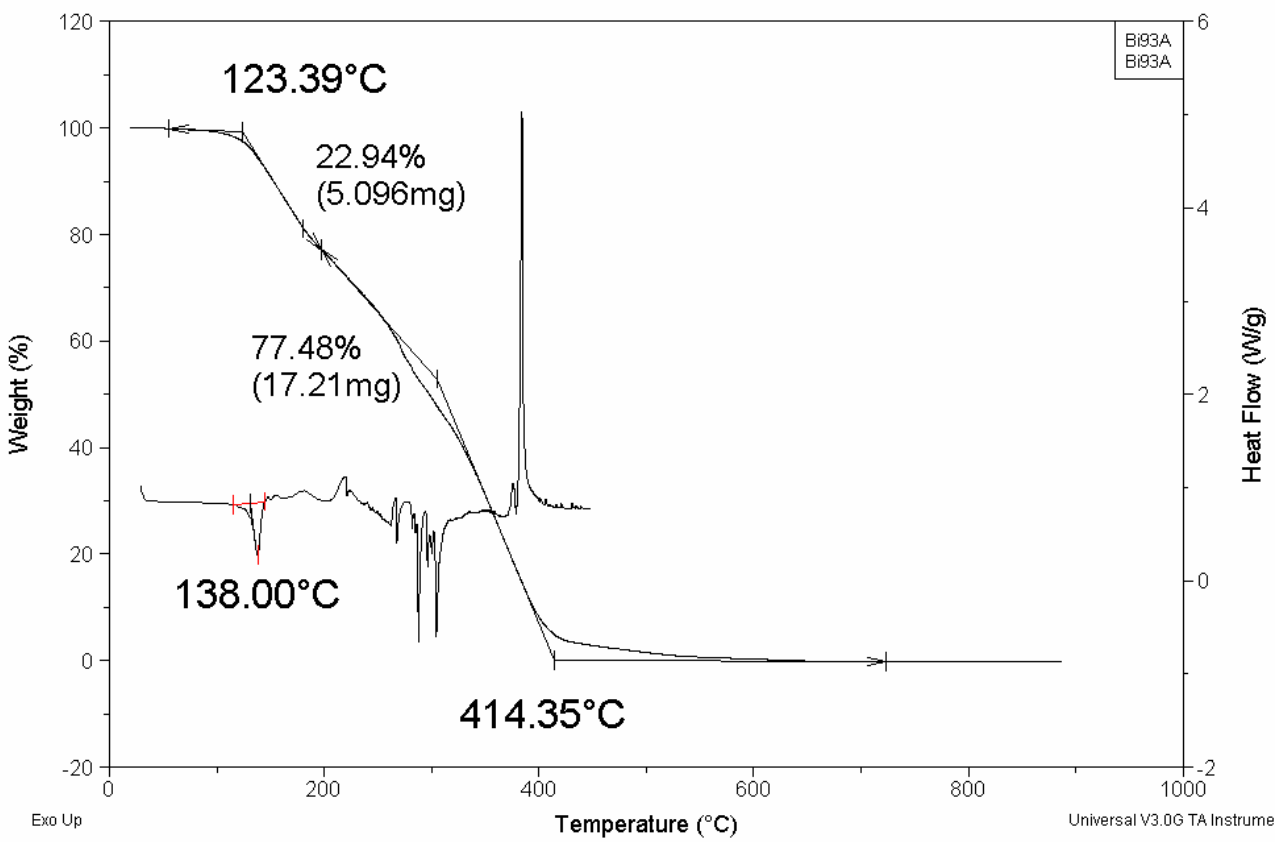


6- ATG-DSC analysis

6a- **(**$H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6$ **(1)**



6b- $(HO_2C(C_6H_{10})CH_2NH_3)_4(I_3)_2BiI_6\ H_3O$ (**4**)



7- SHG experiment of a polycrystalline sample of $(H_3N(CH_2)SS(CH_2)NH_3)_2I_3BiI_6,0.5H_2O$

The properties of the second harmonic generation were studied for a fundamental wavelength at 1064 nm from a Q-switch Nd:YAG laser (Model CONTINUUM Leopard D-10) with a pulse duration of 15 ps and a mean power of 1.62 mJ per pulse at the repetition frequency of 10 Hz. The power of the fundamental beam were changed with a half-wave plate and a Glan polarizer. The beam was focalised on the sample passing through a convergent lens with a focal length of 250 mm. The SH signal is collected using a second lens with a focal length of 150 mm. The second harmonic signal was detected by a tube photomultiplier (Hamamatsu R1828-01) than integrated by a box-car and processed by a computer. The nonlinear medium (sample) was turned by the step motor (Fig.1) controlled by a power station of acquisition with a resolution of 0.04° for the angle.

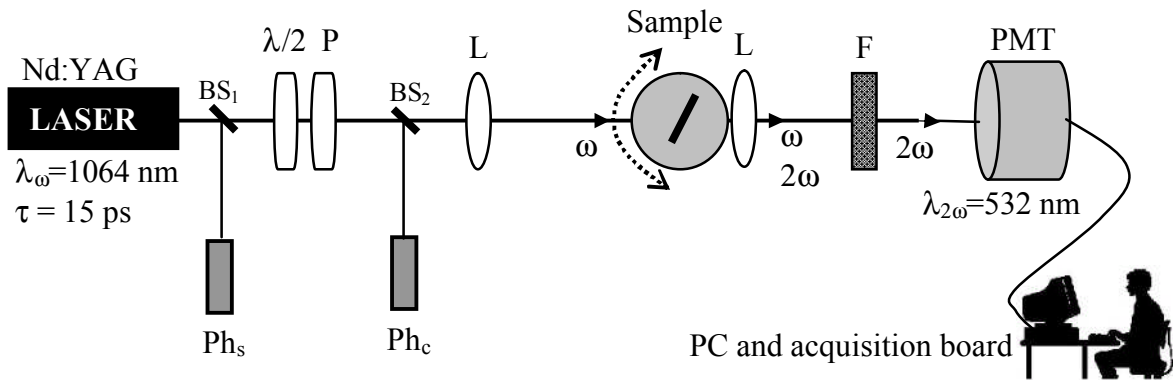


Fig.1. Experimental setup for the SHG: dichroic beam splitters ($BS_{1,2}$), half-wave plate ($\lambda/2$), Glan polarizer (P), convergent lens (L), filter at 532 nm (F), tube photomultiplier (PMT), and Ph_s photodiode of synchronization (Ph_s) and photodiode of control (Ph_c).

SHG efficiency was measured by powder Kurtz method. The ratio of the fundamental and harmonic intensities gives the conversion efficiency of the sample and it was calculated from the followed equation using the values of fundamental and second harmonic intensities from the oscilloscope traces.

$$\frac{c_{sample}^{<2>}}{c_{POM}^{<2>}} = \sqrt{\frac{I_{sample}^{SH}}{I_{POM}^{SH}}}$$

The measured SHG efficiency was compared with POM (3-methyl-4-nitropyridine-1-oxide) which is a reference material for the powders (12.0 pm/V, threshold damage 3.05 GW/cm² at 1064 nm).