Unexpectable Hydrolytic Transformation of New Type Hybrid Bromobismuthates with Methylpyrazinium Dication

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Contents

Details for refinement of structures **1**, **4, 5, 6** *and* **10**

In **1**, one of the cations is disordered around two-fold (2) axis, its geometry is restricted (AFIX 66 + ISOR 0.01 commands), and part of disordered atoms is refined isotropically.

Compound **4** possesses space group Pc with angle β equal to 90.014(2)º which results in the pseudomerohedral and centrosymmetric twinning with domain ratio of 0.280(16): 0.237(16) : 0.263(16) : 0.221(16). Two of three cations are disordered with 1:1 ratio. Disordered cations are restricted geometrically (SAME command), all disordered atoms are refined isotropically.

To collect experimental data for **5**, the spliced crystals have been investigated. The main domain made up ~ 70% of the volume and the latter part contained more than 5 domains thus not allowing one to take absorbance into account correctly.

In **6**, one of nine Br atoms as well as one of two $[MePz]^+$ cations are disordered with occupancies of 0.63:0.37 and 0.39:0.37:0.24, respectively. O atoms of H_3O^+ and H_2O partially occupy five positions (0.60, 0.28, 0.26, 0.22 and 0.14). Disoredered $[MePz]^+$ cations are restricted geometrically (AFIX66 + FLAT + DFIX commands). Disordered Br atom was refined anisotropically, while disordered C, N and O atoms were refined isotropically.

In the crystal structure of **10**, eight of nine positions of X ligands in $[Bi_2X_9]^{3-}$ are statistical, and ratio of the corresponding occupancies, Br:I, varies from 0.30:0.70 to 0.82:0.18. These values were obtained *via* the isotropic refinement with U_{iso} = 0.03, and were set as constant in further calculations. The coordinates of Br and I atoms were refined independently, distances between the corresponding positions are in the 0.021-0.607 Å range. Cations are geometrically restricted (AFIX66 command).

Table S1. Crystal data and structure refinement for **1-6, 8, 10, 11**.

Identification code	**1**	**2**	**3**	**4**
Empirical formula	$C_{15}H_{24}Bi_2Br_{12}N_6$	$C_{12}H_{24}Bi_2Br_{10}N_4O_2$	$C_7H_{14}BiBr_5N_2O$	$C_{24}H_{44}Bi_2Br_{12}N_6O$
Formula weight	1665.28	1473.41	750.73	1809.53
Temperature, K	150(2)	120(2)	150(2)	120(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbcn	$P2_1/n$	$P2_1/c$	Pc
a, Å	13.3678(6)	11.1553(14)	9.1129(7)	11.0371(6)
b, Å	14.1378(6)	11.2184(14)	22.6442(16)	13.4220(7)
c, Å	19.1085(8)	13.2282(16)	8.2570(6)	15.1336(8)
β, °	90	109.653(3)	107.174(2)	90.014(2)
Volume, $Å^3$	3611.3(3)	1559.0(3)	1627.9(2)	2241.9(2)
Z	4	2	4	2
D (calc), Mg/m^3	3.063	3.139	3.063	2.681
μ, mm^{-1}	23.028	24.105	23.088	18.561
F(000)	2968	1312	1344	1648
Crystal size, mm	0.08 x 0.02 x 0.02	0.18 x 0.16 x 0.1	0.14 x 0.12 x 0.06	0.28 x 0.26 x 0.2
θ range, °	2.097, 30.561	2.073, 31.710	2.339, 30.061	2.284, 27.152
Index ranges	-19<=h<=19 -20<=k<=20 -27<=l<=26	-16<=h<=16 -15<=k<=16 -19<=l<=19	-12<=h<=12 -31<=k<=31 -11<=l<=11	-14<=h<=14 -17<=k<=17 -19<=l<=19
Reflections collected	48897	16066	24625	27279
Independent reflections, Rint	5522, 0.0750	5158, 0.0416	4765, 0.0632	9873, 0.0613
Completeness to θ = 25.242°	100.0 %	100.0 %	100.0 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max,. min. transmission	0.2657, 0.1296	0.0526, 0.0106	0.0504, 0.0135	0.0943, 0.0273
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5522 / 43 / 175	5158 / 0 / 138	4765 / 0 / 148	9873 / 302 / 290
Goodness-of-fit	0.994	0.998	0.954	0.993

R1, wR2 [I>2sigma(I)]	0.0329, 0.0750	0.0257, 0.0554	0.0403, 0.0965	0.0472, 0.1023
R1, wR2 (all data)	0.0636, 0.0854	0.0353, 0.0585	0.0611, 0.1057	0.0646, 0.1113
Largest diff. peak and hole, e.Å^{-3}	1.360, -1.373	1.807, -1.398	1.853, -1.199	3.555, -1.213

Identification code	**5**	**6**	**8**
Empirical formula	$C_8H_{15}BiBr_6N_4O_2$	$C_{20}H_{36}Bi_4Br_{18}N_8O_3$	$C_{20}H_{28}Bi_4Br_{16}N_8$
Formula weight	887.68	2710.87	2494.98
Temperature, K	120(2)	150(2)	150(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	C2/c	$P2_1/c$
a, Å	8.9423(6)	26.4520(10)	12.7987(3)
b, Å	9.2461(6)	9.7440(4)	10.7742(2)
c, Å	14.0873(8)	22.4625(8)	19.2670(4)
α, °	77.477(2)	90	90
β, °	86.384(2)	102.7780(10)	107.6870(10)
γ, °	65.451(2)	90	90
Volume, Å^3	1033.79(11)	5646.3(4)	2531.25(9)
Z	2	4	2
D (calc), Mg/m^3	2.852	3.189	3.273
μ, mm^{-1}	20.129	25.199	26.517
F(000)	800	4792	2192
Crystal size, mm	0.24 x 0.20 x 0.14	0.1 x 0.08 x 0.03	0.1 x 0.08 x 0.04
θ range, °	2.477, 28.305	2.157, 30.057	2.192, 31.545
Index ranges	-11<=h<=11	-37<=h<=37	-18<=h<=18
	-12<=k<=12	-13<=k<=13	-15<=k<=15
	-17<=l<=18	-31<=l<=31	-28<=l<=28
Reflections collected	13137	54121	58576
Independent reflections, Rint	5098, 0.0385	8278, 0.0759	8437, 0.0647
Completeness to θ = 25.242°	100.0 %	100.0 %	100.0 %
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical

	from equivalents	from equivalents	from equivalents
Max,. min. transmission	0.0299, 0.0060	0.0504, 0.0182	0.0526, 0.0165
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5098 / 0 / 194	8278 / 21 / 220	8437 / 0 / 219
Goodness-of-fit	1.039	1.040	0.975
R1, wR2 [I>2sigma(I)]	0.0418, 0.1115	0.0470, 0.0962	0.0352, 0.0811
R1, wR2 (all data)	0.0534, 0.1172	0.0960, 0.1132	0.0599, 0.0907
Largest diff. peak and hole, e.Å^{-3}	4.489, -1.068	1.658, -1.231	2.270, -1.085

Identification code	**10**	**11**
Empirical formula	$C_{15}H_{21}Bi_2Br_{5.16}I_{3.84}N_6$	$C_{15}H_{21}Bi_2I_9N_6$
Formula weight	1602.97	1845.44
Temperature, K	150(2)	150(2)
Wavelength, Å	0.71073	0.67522
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	$Pna2_1$
a, Å	15.0541(6)	28.8902(5)
b, Å	12.8474(5)	9.5425(2)
c, Å	34.9720(15)	13.4798(2)
β, °	90	90
Volume, Å^3	6763.8(5)	3716.17(12)
Z	8	4
D (calc), Mg/m^3	3.148	3.298
μ, mm^{-1}	20.011	14.693
F(000)	5625	3184
Crystal size, mm	0.24 x 0.2 x 0.1	0.03 x 0.01 x 0.01
θ range, °	2.694, 26.424	1.963, 32.680
Index ranges	-18<=h<=18 -16<=k<=16 -43<=l<=43	-44<=h<=44 -10<=k<=10 -21<=l<=21

Reflections collected	75467	34170
Independent reflections, Rint	6939, 0.0950	12387, 0.0634
Completeness to θ = 25.242°	99.9 %	97.1 %*
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max,. min. transmission	0.0195, 0.0015	1, 0.61732
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6939 / 90 / 325	12387 / 1 / 292
Goodness-of-fit	1.074	0.988
R1, wR2 [I>2sigma(I)]	0.0537, 0.1510	0.0379, 0.0856
R1, wR2 (all data)	0.0793, 0.1739	0.0467, 0.0901
Absolute structure parameter		-0.005(4)
Largest diff. peak and hole, e.$Å^{-3}$	2.511, -1.371	1.331, -2.338

* Completeness to θ = 23.899°

Table S2. Bi-Hal Bond lengths [Å] for **1-6, 8, 10, 11**.

1	
Bi(1)-Br(1)	2.8367(6)
Bi(1)-Br(2)	2.8682(6)
Bi(1)-Br(3)	2.9053(6)
Bi(2)-Br(5)	2.8334(6)
Bi(2)-Br(6)	2.8607(6)
Bi(2)-Br(4)	2.8624(6)
2	
Bi(1)-Br(1)	2.7328(5)
Bi(1)-Br(5)	2.7606(5)
Bi(1)-Br(2)	2.8144(5)
Bi(1)-Br(3)	2.8591(5)
Bi(1)-Br(4)	2.9952(5)
Bi(1)-Br(4) (-x+1, -y+1, -z)	3.0482(5)
3	
Bi(1)-Br(4)	2.7177(8)
Bi(1)-Br(1)	2.7608(8)
Bi(1)-Br(3)	2.8178(8)
Bi(1)-Br(2)	2.8731(8)
Bi(1)-Br(5)	3.0293(8)
Bi(1)-Br(5) (x, -y+1/2, z+1/2)	3.0576(8)
4	
Bi(1)-Br(5)	2.773(6)
Bi(1)-Br(3)	2.787(5)
Bi(1)-Br(6)	2.833(2)
Bi(1)-Br(4)	2.883(2)
Bi(1)-Br(2)	2.894(6)
Bi(1)-Br(1)	2.921(6)
Bi(2)-Br(11)	2.805(2)
Bi(2)-Br(7)	2.835(5)
Bi(2)-Br(8)	2.844(6)
Bi(2)-Br(10)	2.874(5)
Bi(2)-Br(9)	2.882(5)
Bi(2)-Br(12)	2.933(2)
5	
Bi(1)-Br(1)	2.8301(8)
Bi(1)-Br(2)	2.8551(8)

Bi(1)-Br(3)	2.8572(9)
Bi(2)-Br(5)	2.8429(9)
Bi(2)-Br(6)	2.8447(8)
Bi(2)-Br(4)	2.8509(9)

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Bi(1)-Br(5)	2.7110(10)
Bi(1)-Br(4)	2.7644(12)
Bi(1)-Br(6)	2.7711(10)
Bi(1)-Br(1)	2.9902(9)
Bi(1)-Br(2)	2.9907(11)
Bi(1)-Br(3)	3.0173(11)
Bi(2)-Br(92)	2.695(5)
Bi(2)-Br(7)	2.7377(10)
Bi(2)-Br(8)	2.7468(10)
Bi(2)-Br(9)	2.837(3)
Bi(2)-Br(3) (-x+1/2, -y+1/2, -z+1)	2.9974(11)
Bi(2)-Br(2)	3.0133(10)
Bi(2)-Br(1)	3.0239(10)

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Bi(1)-Br(4)	2.6816(7)
Bi(1)-Br(5)	2.7154(7)
Bi(1)-Br(3)	2.8703(7)
Bi(1)-Br(2)	2.8831(7)
Bi(1)-Br(1) (-x, -y+1, -z)	3.1171(7)
Bi(1)-Br(1)	3.1792(7)
Bi(2)-Br(6)	2.6837(7)
Bi(2)-Br(7)	2.7133(7)
Bi(2)-Br(8)	2.7171(7)
Bi(2)-Br(2)	3.1106(7)
Bi(2)-Br(3) (-x, -y+1, -z)	3.1535(7)
Bi(2)-Br(1)	3.1571(7)

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Bi(1)-Br(4)	2.839(12)
Bi(1)-I(4)	2.845(4)
Bi(1)-I(2)	2.852(7)
Bi(1)-Br(3)	2.85(3)
Bi(1)-Br(2)	2.895(9)
Bi(1)-I(3)	2.929(9)
Bi(1)-Br(1)	3.056(3)

Bi(1)-I(1)	3.06(2)
Bi(1)-Br(5)	3.17(2)
Bi(1)-I(5)	3.174(2)
Bi(1)-I(6)	3.2500(14)
Bi(2)-Br(7)	2.696(7)
Bi(2)-I(8)	2.712(14)
Bi(2)-Br(8)	2.748(5)
Bi(2)-Br(9)	2.796(15)
Bi(2)-I(7)	2.84(2)
Bi(2)-I(9)	2.96(4)
Bi(2)-Br(1)	2.984(4)
Bi(2)-I(1)	3.04(3)
Bi(2)-Br(5)	3.09(2)
Bi(2)-I(5)	3.164(2)
Bi(2)-I(6)	3.1798(12)

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Bi(1)-I(4)	2.9076(9)
Bi(1)-I(5)	2.9255(11)
Bi(1)-I(6)	2.9672(10)
Bi(1)-I(2)	3.1931(9)
Bi(1)-I(1)	3.3120(9)
Bi(1)-I(3)	3.3269(10)
Bi(2)-I(7)	2.9443(9)
Bi(2)-I(9)	2.9566(10)
Bi(2)-I(8)	2.9640(10)
Bi(2)-I(2)	3.2325(9)
Bi(2)-I(1)	3.2376(9)
Bi(2)-I(3)	3.2386(9)

Table S3. Hydrogen bonds for **1-6**, **8**, **10**, **11** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
		1		
N(2)-H(2B)...Br(1)#1	0.88	2.81	3.445(6)	130
N(2)-H(2B)...Br(2)#2	0.88	2.65	3.349(5)	138
N(4)-H(4B)...Br(3)#3	0.88	2.57	3.329(7)	146
C(2)-H(2A)...Br(3)#4	0.95	2.85	3.680(6)	147
C(3)-H(3A)...Br(2)	0.95	2.74	3.625(6)	155
C(7)-H(7A)...Br(1)#5	0.95	2.54	3.464(9)	165
C(8)-H(8A)...Br(3)#6	0.95	2.69	3.419(7)	134
#1 x, -y, z-1/2; #2 -x+1, -y, -z+1; #3 -x+1, -y+1, -z+1; #4 -x+3/2, -y+1/2, z-1/2; #5 x-1/2, -y+1/2, -z+1; #6 x, -y+1, z-1/2				
		2		
O(1)-H(1)...Br(3)#1	0.97	2.35	3.316(3)	172
O(1)-H(2)...Br(1)	1.00	2.49	3.454(3)	163
N(2)-H(2A)...O(1)#2	0.88	1.82	2.671(4)	163
C(1)-H(1A)...Br(5)	0.95	2.71	3.551(4)	148
C(3)-H(3A)...Br(4)#3	0.95	2.83	3.723(4)	158
C(4)-H(4A)...Br(2)#4	0.95	2.89	3.716(4)	146
#1 -x+ 3/2, y+1/2, -z+1/2; #2 x-1/2, -y+1/2, z-1/2; #3 x, y-1, z; #4 x+1/2, -y+1/2, z+1/2				
		3		
O(1)-H(1)...Br(3)#1	0.84	2.57	3.404(7)	177
O(1)-H(2)...Br(4)#2	0.86	2.70	3.558(9)	178
N(2)-H(2A)...O(1)	0.88	1.81	2.690(10)	176
C(3)-H(3A)...Br(2)#3	0.95	2.92	3.810(9)	156
C(4)-H(4A)...Br(1)#3	0.95	2.89	3.574(8)	130
#1 -x, -y, -z+1; #2 x-1, y, z; #3 -x+1, -y, -z+1				
		4		
O(1)-H(1)...Br(4)#1	0.97	2.25	3.21(2)	178
O(1)-H(2)...Br(9)	0.90	2.35	3.25(2)	180
N(2)-H(3)...O(1)	0.88	1.63	2.50(2)	170
N(4)-H(4)...Br(10)#2	0.88	2.91	3.74(2)	157
N(42)-H(5)...Br(9)#3	0.88	2.78	3.62(3)	160
N(6)-H(6)...Br(9)#4	0.88	2.84	3.69(3)	162
N(62)-H(7)...Br(12)	0.88	2.42	3.10(4)	135
C(12)-H(12A)...Br(9)#3	0.95	2.37	3.26(2)	156

C(122)-H(12B)...Br(10)#2	0.95	2.49	3.35(3)	150
C(20)-H(20A)...Br(8)	0.95	2.72	3.35(5)	124
C(20)-H(20A)...Br(12)	0.95	2.41	3.13(4)	132
N(62)-H(7)...Br(8)	0.88	2.88	3.42(4)	121
C(202)-H(20B)...Br(9)#4	0.95	2.80	3.69(2)	157

#1 x, -y+1 ,z+1/2; #2 x+1, -y+1, z-1/2; #3 x+1, y-1, z; #4 x+1, y, z

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O(1)-H(1)...N(1)#1	1.00	1.71	2.646(9)	154
O(1)-H(2)...N(3)#2	0.84	1.80	2.636(10)	177
O(1)-H(3)...O(2)	0.76	1.78	2.532(9)	171
O(2)-H(4)...Br(5)#3	0.97	2.40	3.329(6)	161
O(2)-H(5)...Br(3)#4	0.91	2.52	3.267(6)	140
N(2)-H(6)...Br(3)#5	0.88	2.62	3.399(8)	148
N(4)-H(7)...Br(6)	0.88	2.52	3.261(8)	143
C(2)-H(2A)...O(2)#6	0.95	2.54	3.279(11)	135
C(3)-H(3A)...Br(2)	0.95	2.87	3.589(10)	134
C(4)-H(4A)...Br(6)	0.95	2.99	3.718(10)	135
C(5)-H(5A)...Br(2)#4	0.95	2.97	3.646(10)	129
C(6)-H(6A)...Br(1)#4	0.95	2.97	3.598(10)	124
C(8)-H(8A)...Br(6)#3	0.95	2.88	3.723(10)	149

#1 x-1, y+1, z; #2 x-1, y, z; #3 x, y+1, z; #4 x+1, y, z; #5 -x, -y, -z+1; #6 -x+1, -y, -z+1

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C(1)-H(1A)...Br(2)#1	0.95	2.82	3.568(12)	136
N(2)-H(2B)...O(1)	0.88	1.86	2.712(16)	163
N(2)-H(2B)...O(5)	0.88	1.80	2.53(4)	139
C(3)-H(3A)...Br(1)#2	0.95	2.94	3.651(10)	133
C(4)-H(4A)...Br(5)	0.95	2.93	3.531(10)	122
C(6)-H(6A)...Br(8)#2	0.95	2.75	3.56(3)	144
C(7)-H(7A)...Br(7)#2	0.95	2.84	3.79(2)	180
C(9)-H(9A)...Br(6)#3	0.95	2.81	3.67(3)	152
C(10)-H(10C)...Br(8)#4	0.98	2.92	3.56(5)	124
C(10)-H(10C)...O(5)#5	0.98	2.01	2.61(5)	118
C(62)-H(62A)...Br(8)#2	0.95	2.93	3.544(17)	123
C(72)-H(72A)...O(1)#6	0.95	2.50	3.41(2)	161
C(82)-H(82A)...Br(6)#3	0.95	2.52	3.335(15)	144
C(73)-H(73A)...Br(4)#3	0.95	2.74	3.563(14)	145
C(73)-H(73A)...N(43)#7	0.95	2.38	2.94(3)	117
C(83)-H(83A)...Br(4)#8	0.95	2.93	3.677(13)	136
C(83)-H(83A)...Br(7)#2	0.95	2.95	3.734(14)	141

C(93)-H(93A)...Br(8)#2	0.95	2.83	3.733(13)	159

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

8

C(1)-H(1A)...N(2)#1	0.95	2.39	3.335(9)	174
C(4)-H(4A)...Br(7)#2	0.95	2.82	3.637(7)	144
C(5)-H(5B)...Br(3)#1	0.98	2.99	3.868(9)	149
C(5)-H(5C)...N(4)	0.98	2.54	3.514(11)	172
C(6)-H(6A)...Br(2)#3	0.95	2.83	3.694(8)	152
C(7)-H(7A)...Br(7)#3	0.95	2.98	3.747(8)	138
C(8)-H(8A)...Br(1)#4	0.95	2.95	3.582(7)	125
C(9)-H(9A)...Br(1)#4	0.95	3.04	3.623(7)	121
C(9)-H(9A)...Br(8)	0.95	3.08	3.644(7)	120
C(10)-H(10A)...Br(2)#3	0.98	2.85	3.788(7)	160

#1 -x+1, y-1/2, -z+1/2; #2 -x, y+1/2, -z+1/2; #3 -x, -y, -z; #4 -x, y-1/2, -z+1/2

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C(2)-H(2A)...Br(2)#1	0.95	3.07	3.580(12)	116
C(3)-H(3A)...Br(7)	0.95	2.98	3.683(12)	132
C(3)-H(3A)...I(7)	0.95	2.93	3.62(3)	130
C(3)-H(3A)...I(9)	0.95	3.23	4.01(4)	140
C(4)-H(4A)...Br(9)#2	0.95	2.98	3.840(16)	152
C(4)-H(4A)...I(9)#2	0.95	2.88	3.71(4)	147
C(5)-H(5A)...Br(9)#2	0.98	3.00	3.93(3)	157
C(5)-H(5A)...I(9)#2	0.98	2.91	3.80(5)	152
C(5)-H(5B)...I(6)#3	0.98	3.30	4.081(17)	138
C(6)-H(6A)...Br(7)	0.95	3.07	3.676(12)	123
C(6)-H(6A)...I(7)	0.95	2.64	3.25(2)	122
C(7)-H(7A)...Br(8)#3	0.95	2.78	3.729(8)	174
C(7)-H(7A)...I(8)#3	0.95	2.68	3.621(17)	173
C(8)-H(8A)...Br(4)#4	0.95	2.93	3.680(14)	13
C(8)-H(8A)...N(6)#5	0.95	2.66	3.17(5)	114
C(9)-H(9A)...I(5)#4	0.95	3.31	3.834(9)	117
C(9)-H(9A)...I(6)#4	0.95	3.21	4.101(7)	156
C(10)-H(10A)...I(6)#4	0.98	3.16	4.11(3)	166
C(10)-H(10B)...I(8)#6	0.98	2.89	3.58(3)	128
C(10)-H(10B)...I(9)#4	0.98	3.15	3.67(4)	115
C(10)-H(10C)...I(7)	0.98	2.95	3.70(3)	134
C(10)-H(10C)...I(9)	0.98	3.00	3.74(4)	133
C(11)-H(11A)...Br(1)#7	0.95	2.68	3.622(8)	172

C(12)-H(12A)...Br(5)#7	0.95	3.05	3.88(2)	146
C(14)-H(14A)...I(2)	0.95	3.25	4.130(10)	155
C(14)-H(14A)...I(3)#8	0.95	3.23	3.790(13)	120
C(15)-H(15A)...I(2)	0.98	3.19	4.14(2)	163
C(15)-H(15C)...N(4)#9	0.98	2.48	3.45(5)	170

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

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C(1)-H(1A)...I(6)#1	0.95	3.00	3.923(15)	164
C(2)-H(2A)...N(6)	0.95	2.47	3.378(19)	161
C(3)-H(3A)...I(2)#2	0.95	3.27	3.941(14)	130
C(3)-H(3A)...I(3)#2	0.95	3.18	3.951(14)	139
C(4)-H(4A)...I(6)#3	0.95	3.04	3.950(16)	161
C(5)-H(5A)...I(4)#3	0.98	3.20	3.91(2)	131
C(5)-H(5B)...I(3)#3	0.98	3.30	4.09(2)	139
C(7)-H(7A)...I(7)#2	0.95	3.27	3.897(15)	125
C(7)-H(7A)...I(9)#4	0.95	3.08	3.599(14)	116
C(9)-H(9A)...I(3)#5	0.95	3.30	4.041(14)	136
C(9)-H(9A)...N(2)#4	0.95	2.58	3.266(18)	130
C(10)-H(10A)...I(8)#5	0.98	3.32	3.859(16)	117
C(10)-H(10B)...I(8)#4	0.98	3.31	3.978(15)	127
C(10)-H(10C)...I(9)#2	0.98	3.02	3.965(14)	163
C(11)-H(11A)...I(1)#6	0.95	2.98	3.884(17)	159
C(13)-H(13A)...I(1)#1	0.95	3.20	3.857(15)	128
C(14)-H(14A)...I(1)#1	0.95	3.19	3.842(16)	128
C(14)-H(14A)...I(3)#1	0.95	3.18	3.922(15)	136
C(15)-H(15A)...I(8)#1	0.98	3.10	4.048(14)	164
C(15)-H(15B)...I(2)#6	0.98	3.12	3.866(14)	134
C(15)-H(15C)...I(1)#6	0.98	3.27	4.056(15)	138

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, z+1/2; #2 -x+1, -y+1, z-1/2; #3 x+1/2, -y+3/2, z; #4 x, y+1, z; #5 -x+1, -y+2, z-1/2; #6 -x+1, -y, z+1/2

Table S4. Results of EDX analysis for **1** (heavy atoms).

Spectrum	Bi (at%)	Br (at%)	I (at%)	Br/Bi
Spectrum 1	13.83	85.92	0.25	6.21
Spectrum 2	13.70	86.09	0.21	6.28
Spectrum 3	13.25	86.82	-0.06	6.55
Spectrum 4 (overview)	14.42	85.79	-0.21	5.95

Table S5. Results of EDX analysis for **2** heavy atoms).

Spectrum	Bi (at%)	Br (at%)	I (at%)	Br/Bi
Spectrum 1	16.04	83.86	0.10	5.23
Spectrum 2	16.70	83.19	0.11	4.98
Spectrum 3	14.84	84.44	0.72	5.69
Spectrum 4 (overview)	16.59	83.45	-0.04	5.03

Table S6. Results of EDX analysis for **3** (heavy atoms).

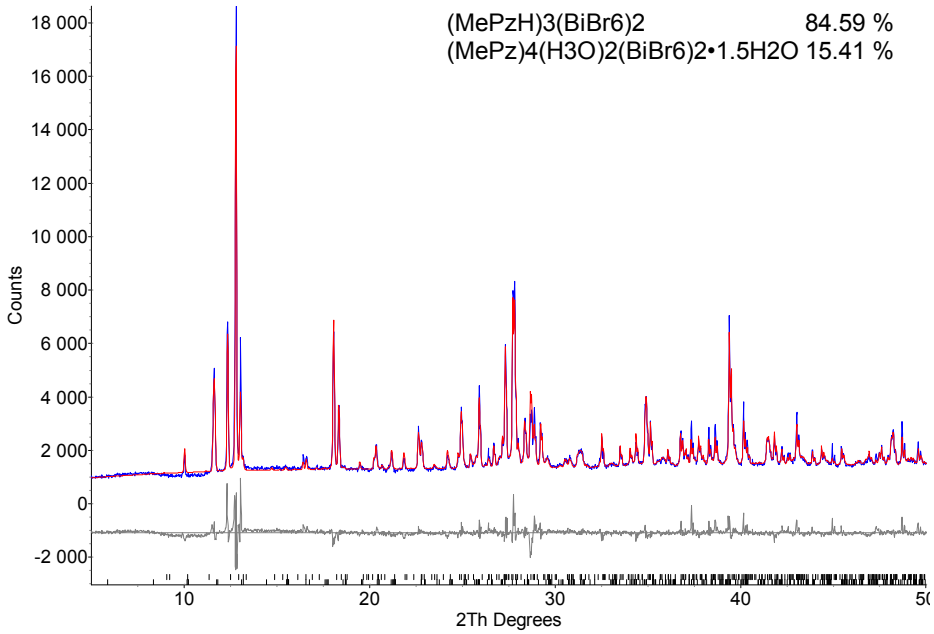
Spectrum	Bi (at%)	Br (at%)	I (at%)	Br/Bi
Spectrum 1	16.21	83.87	-0.09	5.17
Spectrum 2	16.43	83.57	0.00	5.09
Spectrum 3	16.79	83.03	0.18	4.95
Spectrum 4 (overview)	16.76	83.32	-0.08	4.97

Table S7. Results of EDX analysis for **4** (heavy atoms).

Spectrum	Bi (at%)	Br (at%)	I (at%)	Br/Bi
Spectrum 1	14.55	85.49	-0.04	5.88
Spectrum 2	14.60	85.33	0.07	5.84
Spectrum 3	14.44	85.48	0.08	5.92
Spectrum 4 (overview)	15.06	84.91	0.03	5.64

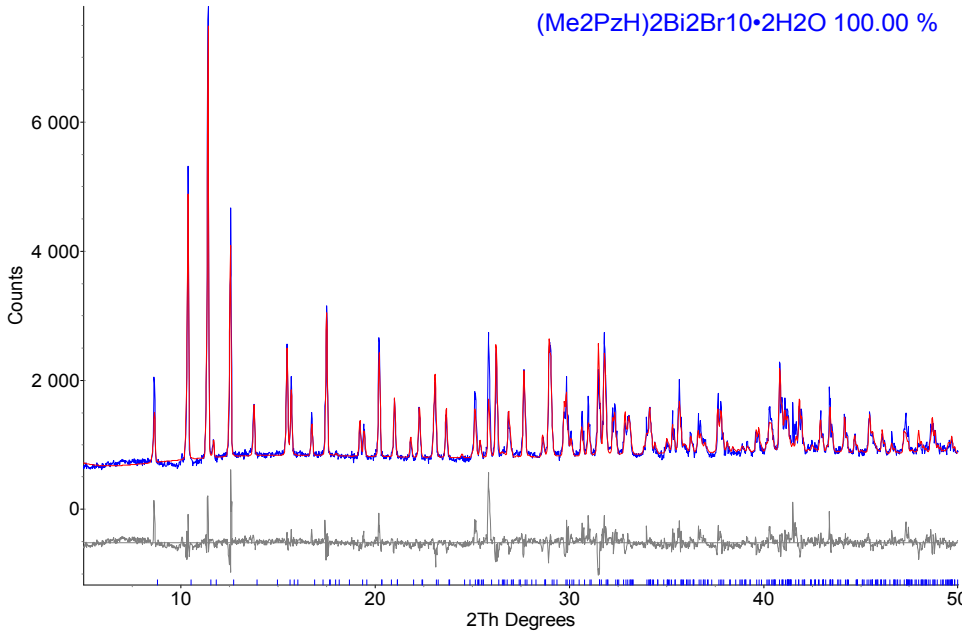
Table S8. Results of EDX analysis for **5** (heavy atoms).

Spectrum	Bi (at%)	Br (at%)	I (at%)	Br/Bi
Spectrum 1	15.45	84.53	0.03	5.47
Spectrum 2	14.97	85.06	-0.02	5.68
Spectrum 3	14.36	85.56	0.09	5.96
Spectrum 4 (overview)	14.93	85.43	-0.36	5.72



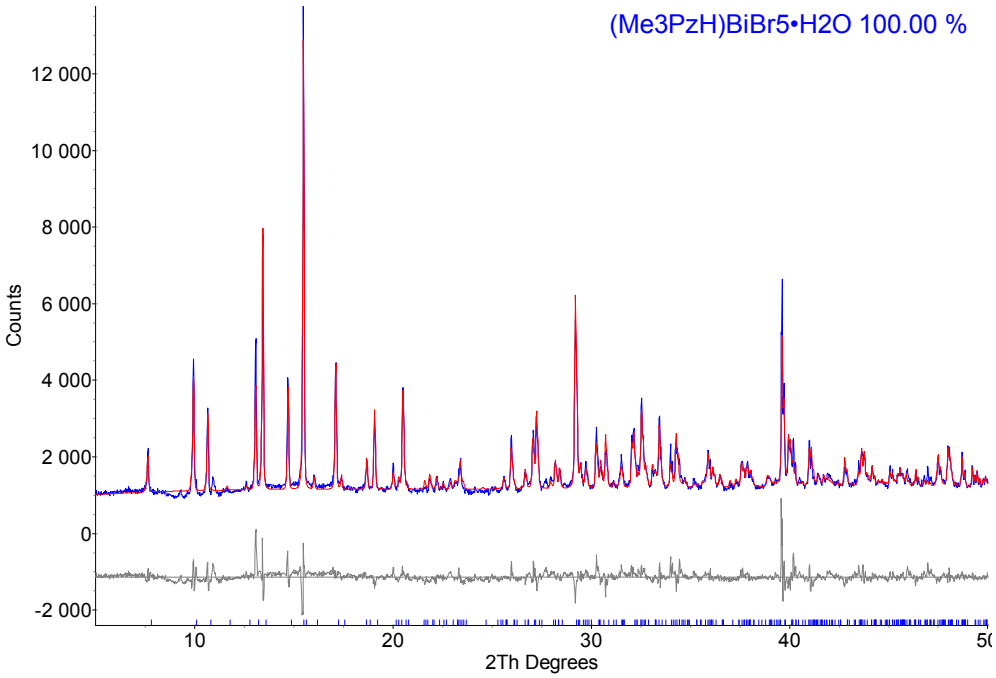
Details of the Rietveld refinement. Structural parameters as follows: product **1** (84.59%) / product **7** (15.41%)): space group for **1** Pbcn, a = 13.40991(35)Å , b = 14.14476(41)Å, c = 19.17870(48)Å, space group for **7** $I4_1/a:2$, a = 21.1674(27)Å, b = 21.1674(27)Å, c = 21.3866(58)Å, R_{exp}: 2.43%, R_{wp}: 6.80%, R_p: 4.81%, GOF: 2.80.

a



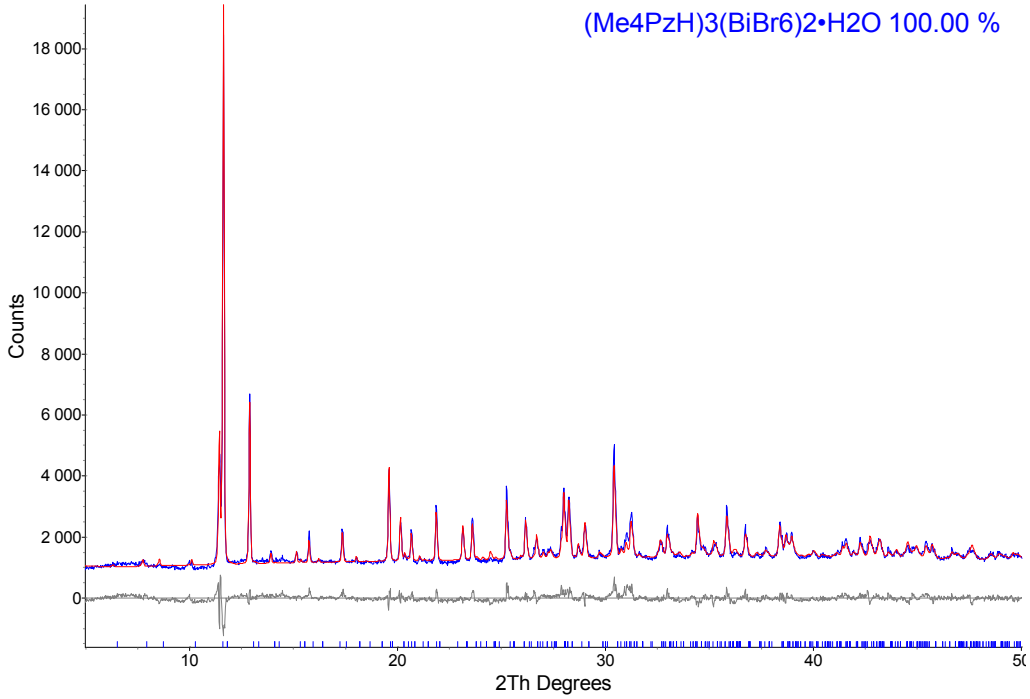
Details of the Rietveld refinement: space group $P2_1/n$, a = 11.22959(45)Å, b = 11.18195(58)Å, c = 13.60574(61)Å, β = 110.9181(35), R_{exp}: 3.12%, R_{wp}: 7.86%, R_p: 5.72%, GOF: 2.52.

b



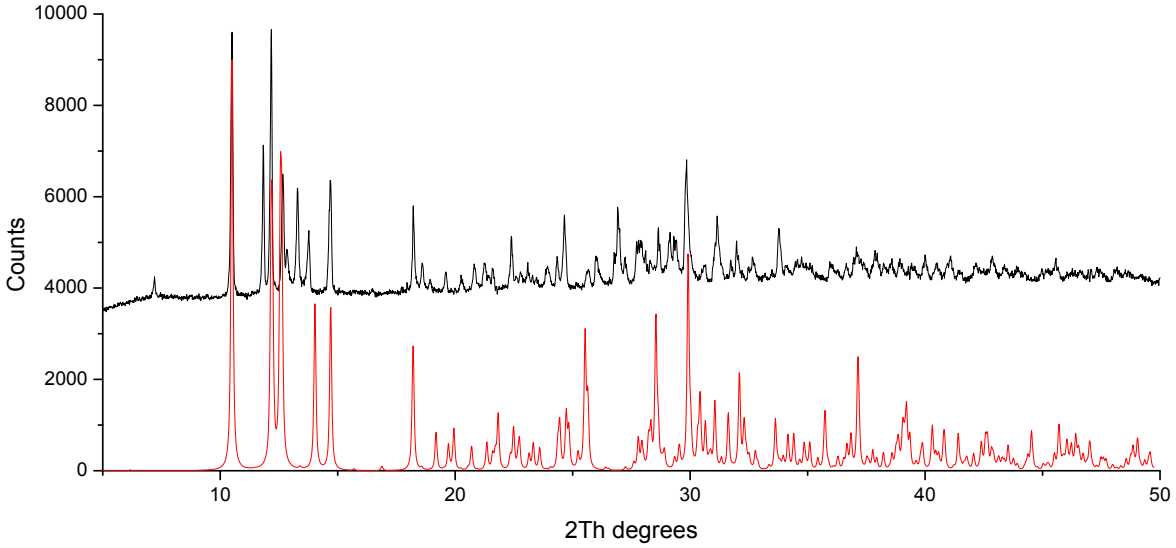
Details of the Rietveld refinement: space group $P2_1/c$, a = 9.15484(38)Å, b = 22.64292(48)Å, c = 8.31679(31)Å, β = 107.0854(38), R_{exp}: 2.61%, R_{wp}: 7.33%, R_p: 5.46%, GOF: 2.81.

c



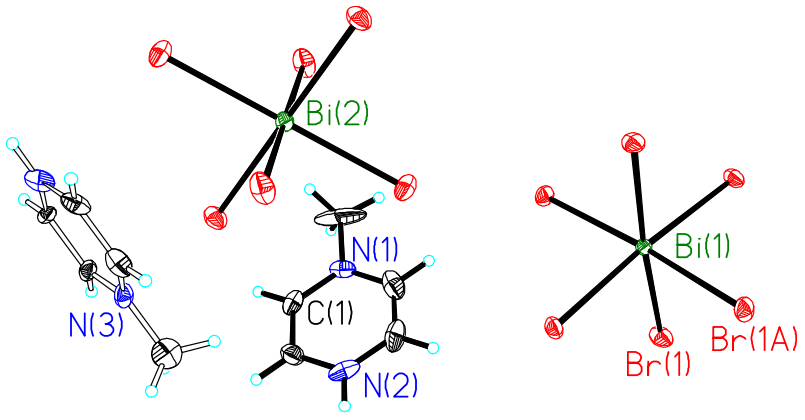
Details of the Rietveld refinement: space group Pc, a = 11.11359(56)Å, b = 13.52591(47)Å, c = 21293(79) Å, β = 90.000(42), R_{exp}: 2.58%, R_{wp}: 6.18%, R_p: 4.82%, GOF: 2.39.15.

d

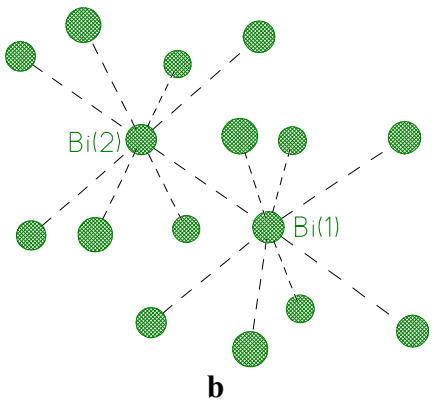


e

Fig. S1. X-ray Rietveld refinement profiles for **1**+**7** (a), **2** (b), **3** (c) and **4** (d) performed for room temperature powder XRD data. Red and blue lines correspond to the calculated profile and experimental pattern respectively. The bottom trace shows the difference curve. The vertical bars are the calculated positions of the Bragg peaks. The XRD data of **5** (e). Red and black lines correspond to the calculated profile and experimental pattern respectively.

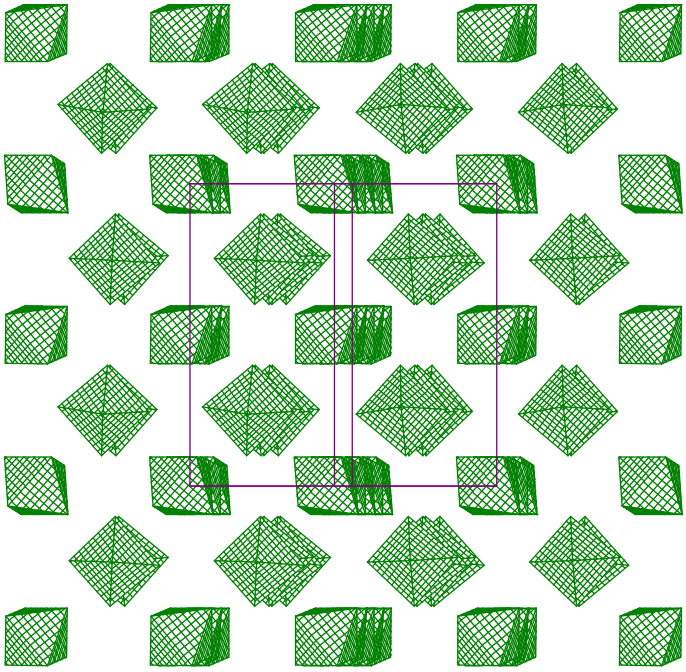


a

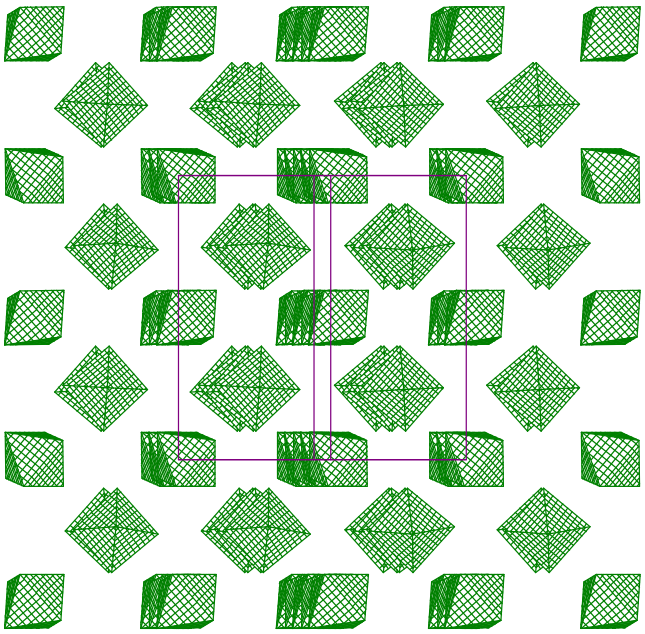


b

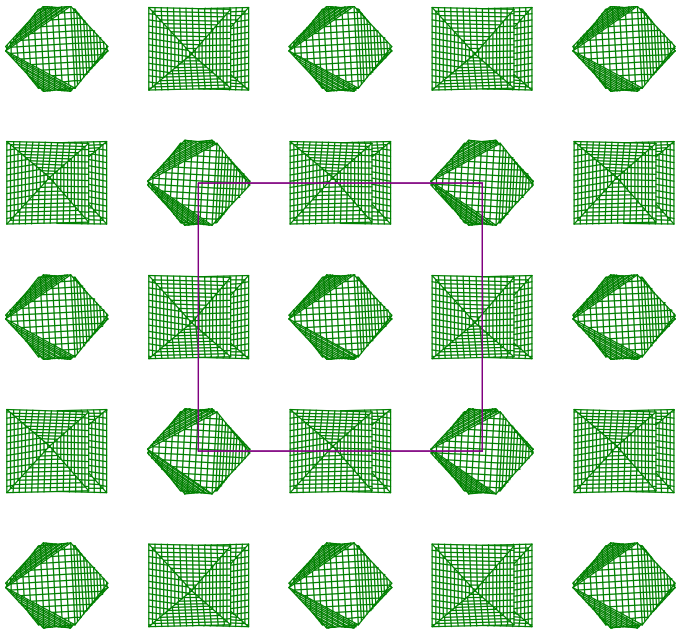
Fig. S2. An asymmetric unit in the structure of compound **1** with thermal ellipsoids shown at 50% probability (a) and mutual position of $[BiBr_6]^{3-}$ (b).



a



b



c

Fig. S3. The projection of the structure of **1** along [110] (**a**), [1-10] (**b**) and [001] (**c**) directions. Only $[BiBr_6]^{3-}$ are shown.

a

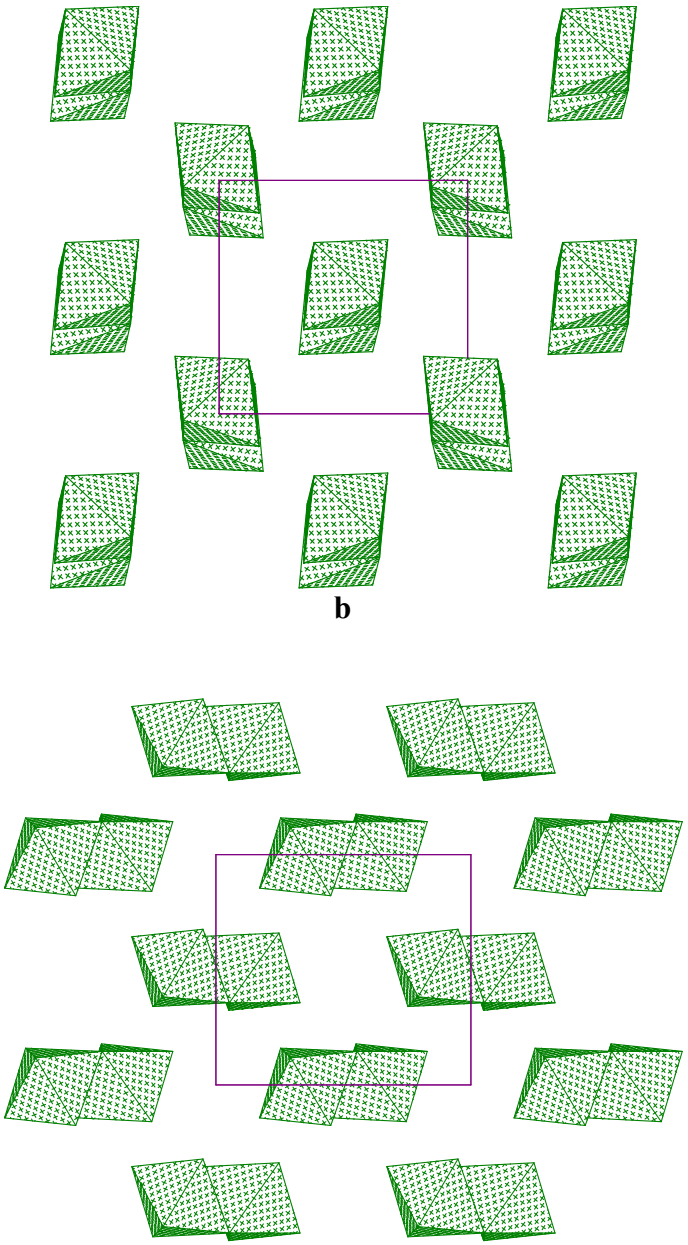


Fig. S4. 2D-layers in the crystal structure of **2** with some of H atoms omitted for clarity (a) and the projection of the structure of **2** along [100] (b) and [001] (c) directions (only $[Bi_2Br_{10}]^{4-}$ are shown).

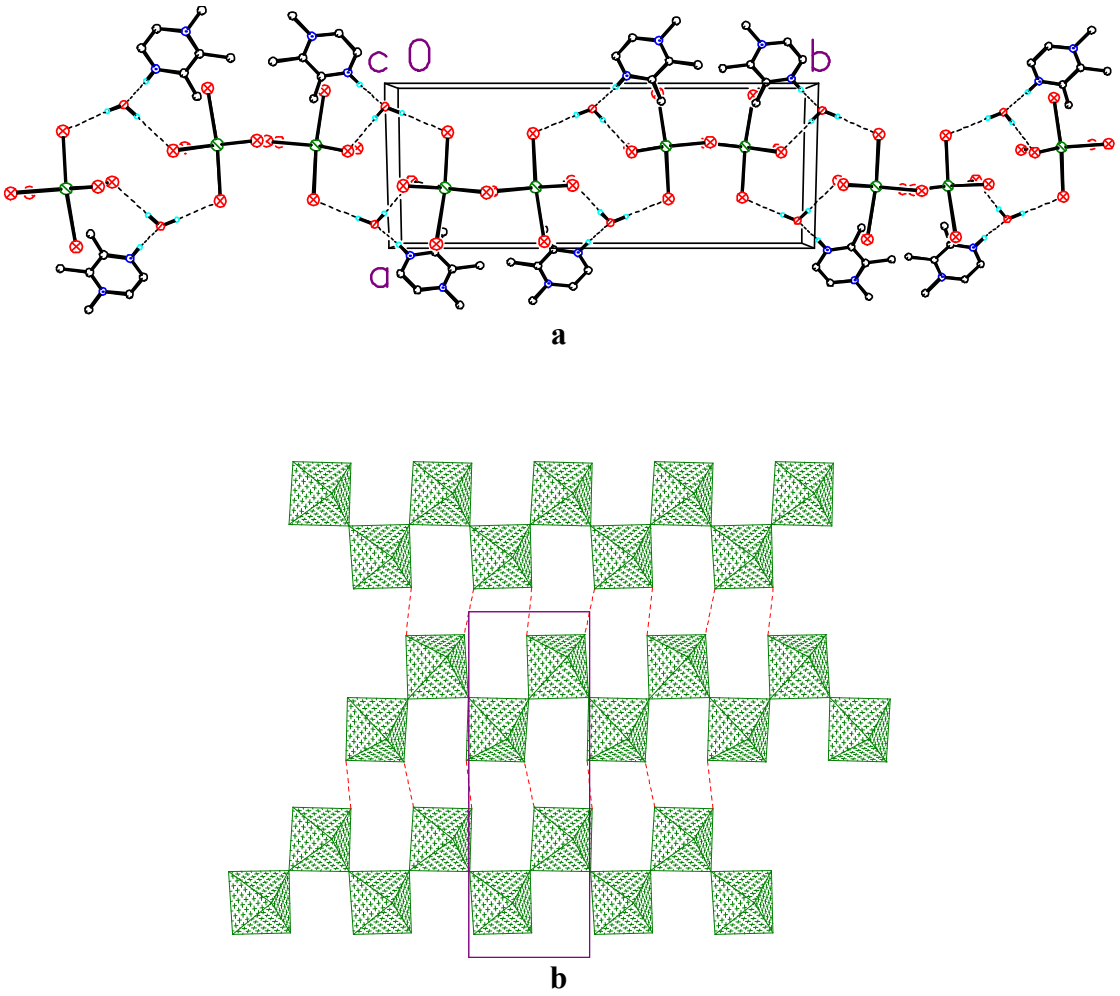
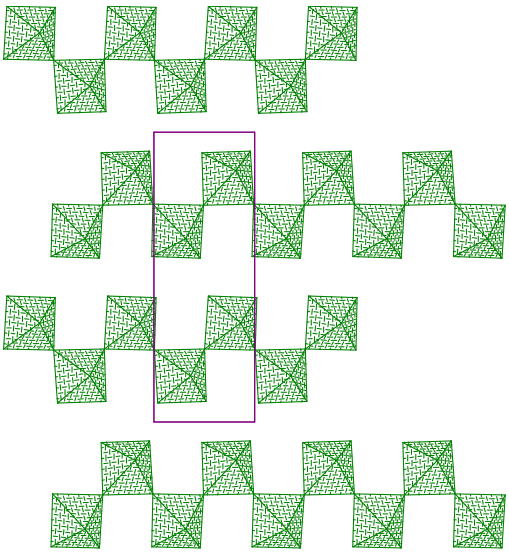
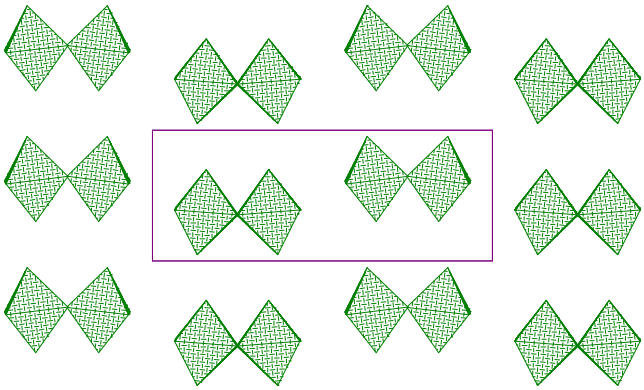


Fig. S5. The projection of supramolecular 2D-layer is the structure of **3** along the *a* axis.

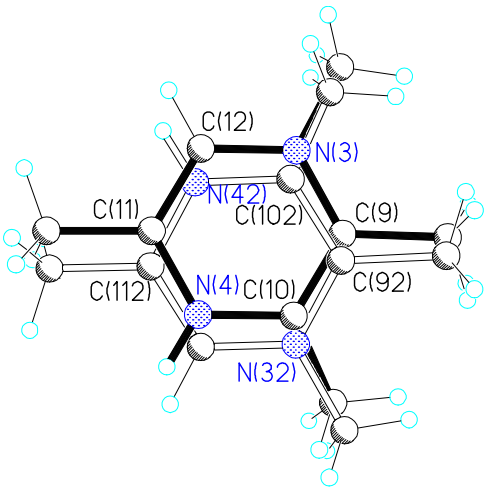


a

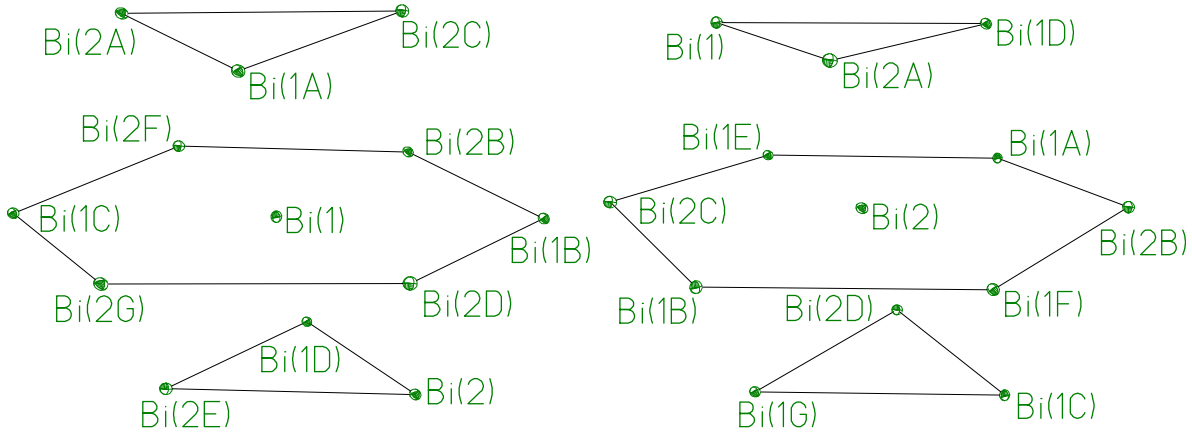


b

Fig. S6. The projection of the structure of **3** along [100] (a) and [001] (b) directions with only $[BiBr_5]_n^{2n-}$ polymeric chain shown.

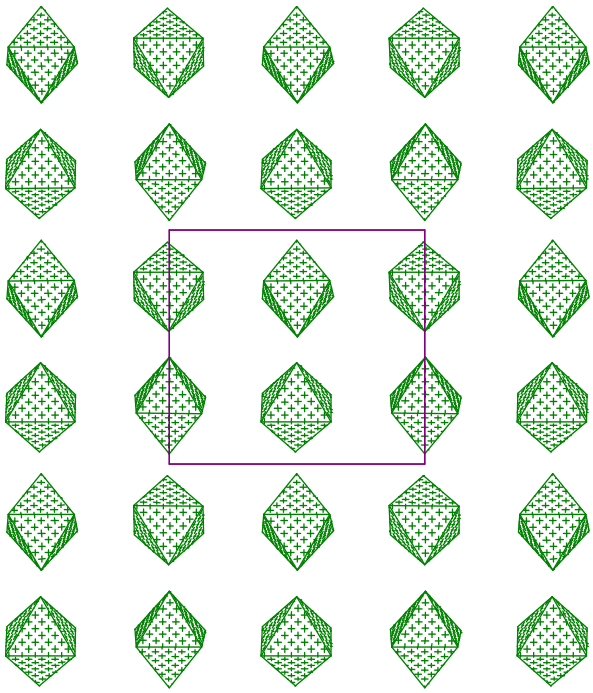


a

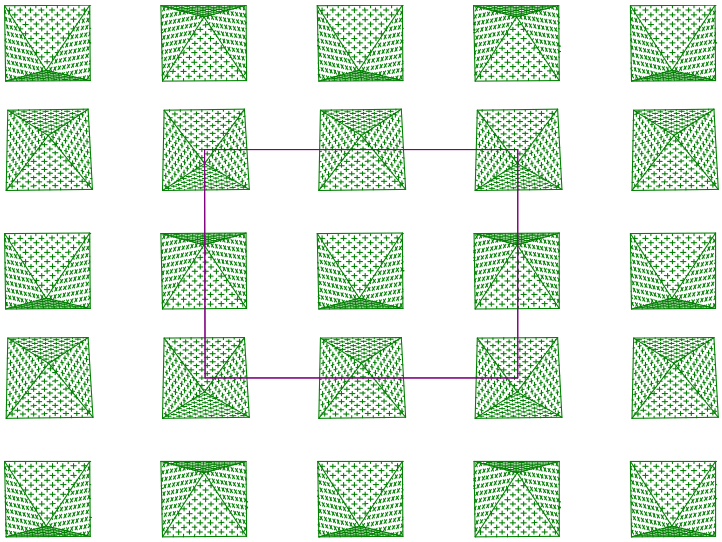


b

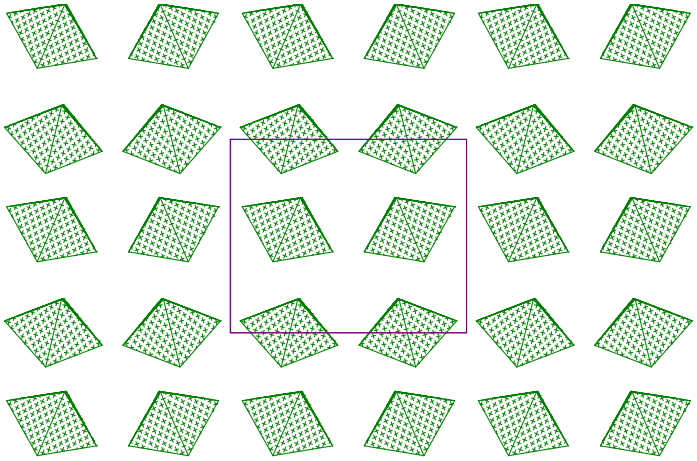
Fig. S7. The disordering of the cations (a) and mutual positions of $[BiBr_6]^{3-}$ anions (b) in the structure of **4**.



a



b



c

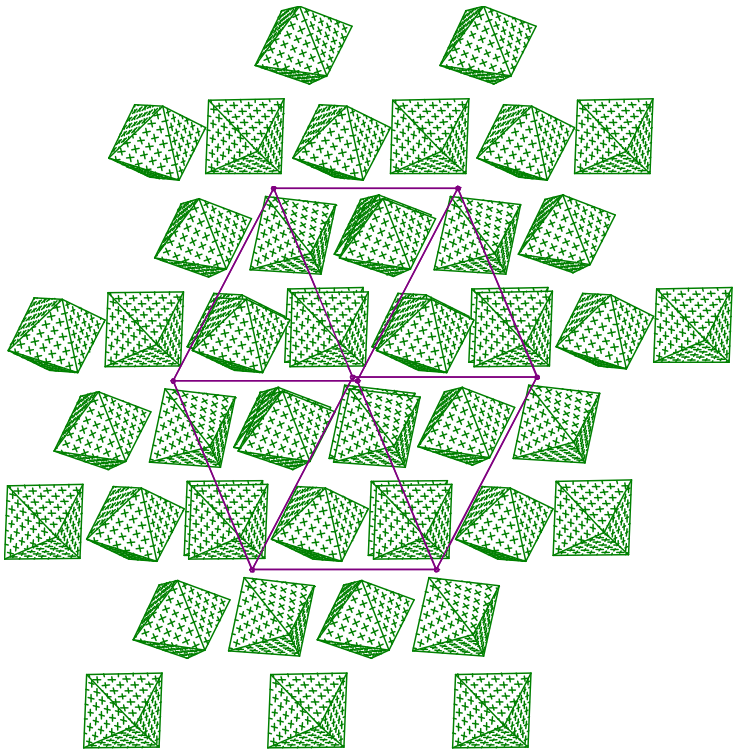


Fig. S8. The projection of the structure of **4** along [100] (a), [010] (b), [001] (c), ~ [111] (d) directions with only $[BiBr_6]^{3-}$ anions shown.

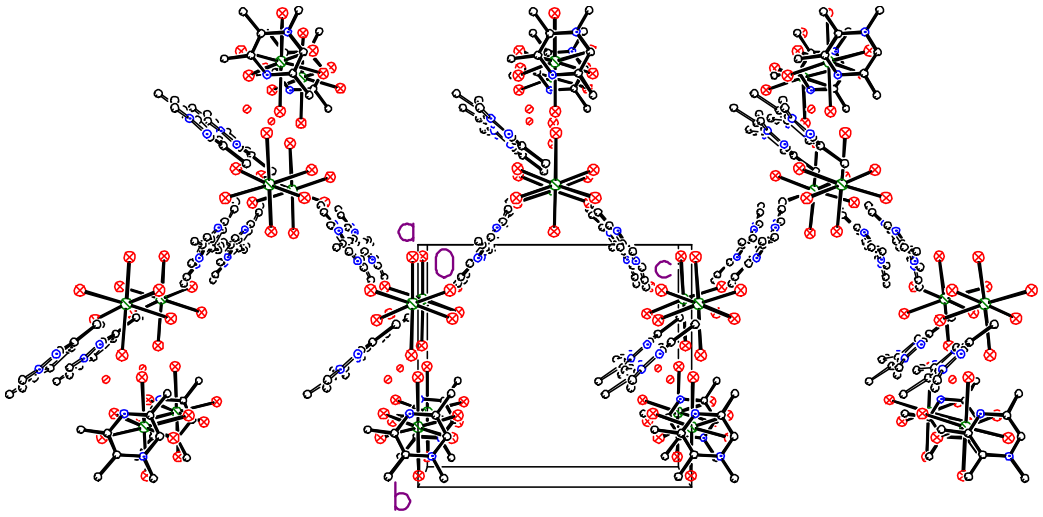


Fig. S9. The projection of the structure of **4** along [100] direction.

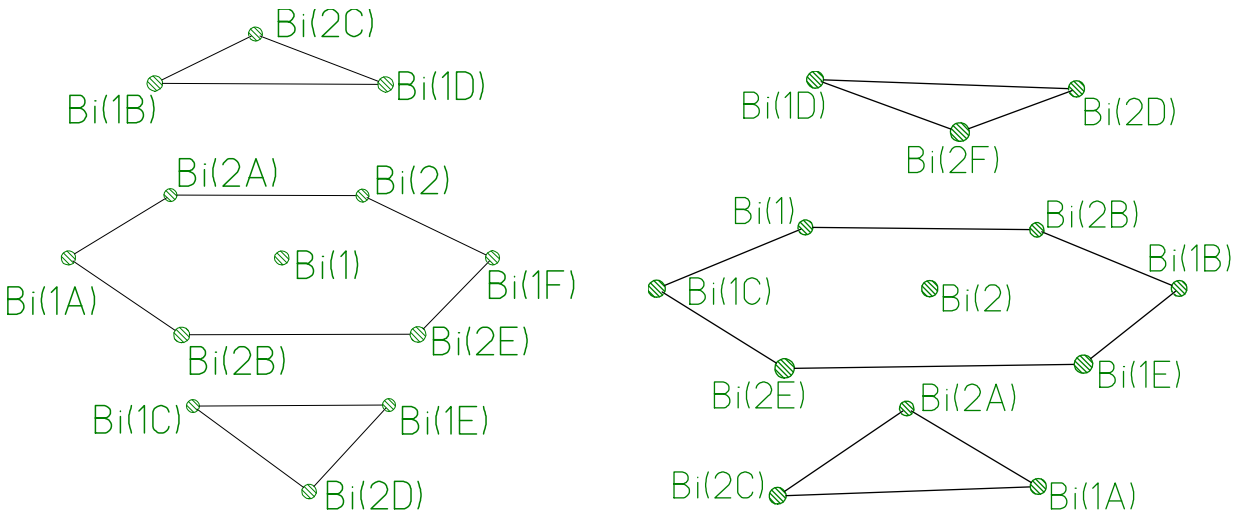
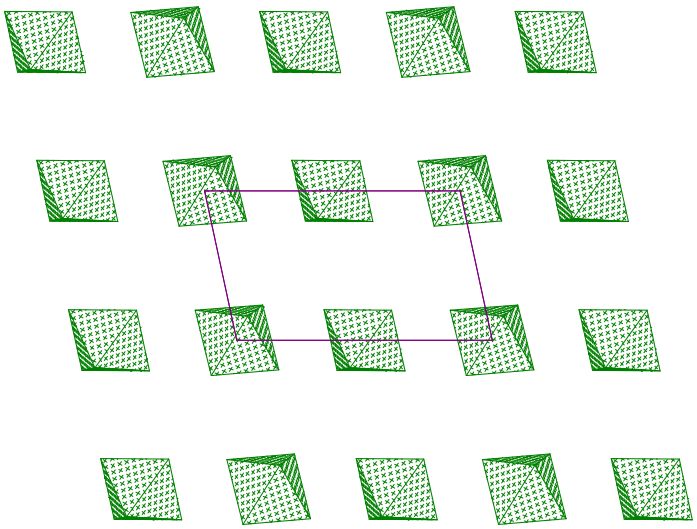


Fig. S10. The mutual positions of $[BiBr_6]^{3-}$ anions in the structure of **5**.



a

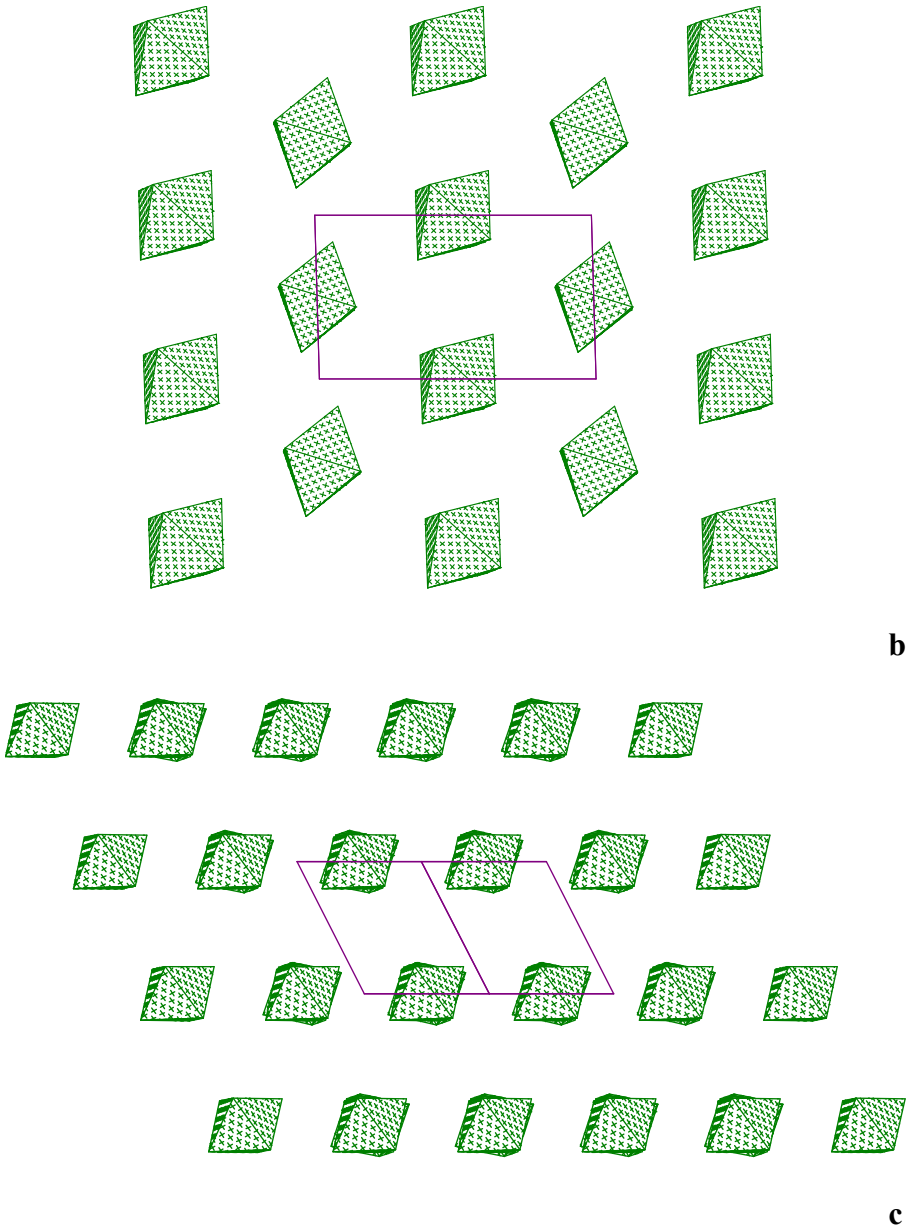


Fig. S11. The projection of the structure of **5** along [100] (a), [010] (b) and [10-1] (c) directions with only $[BiBr_6]^{3-}$ anions shown.

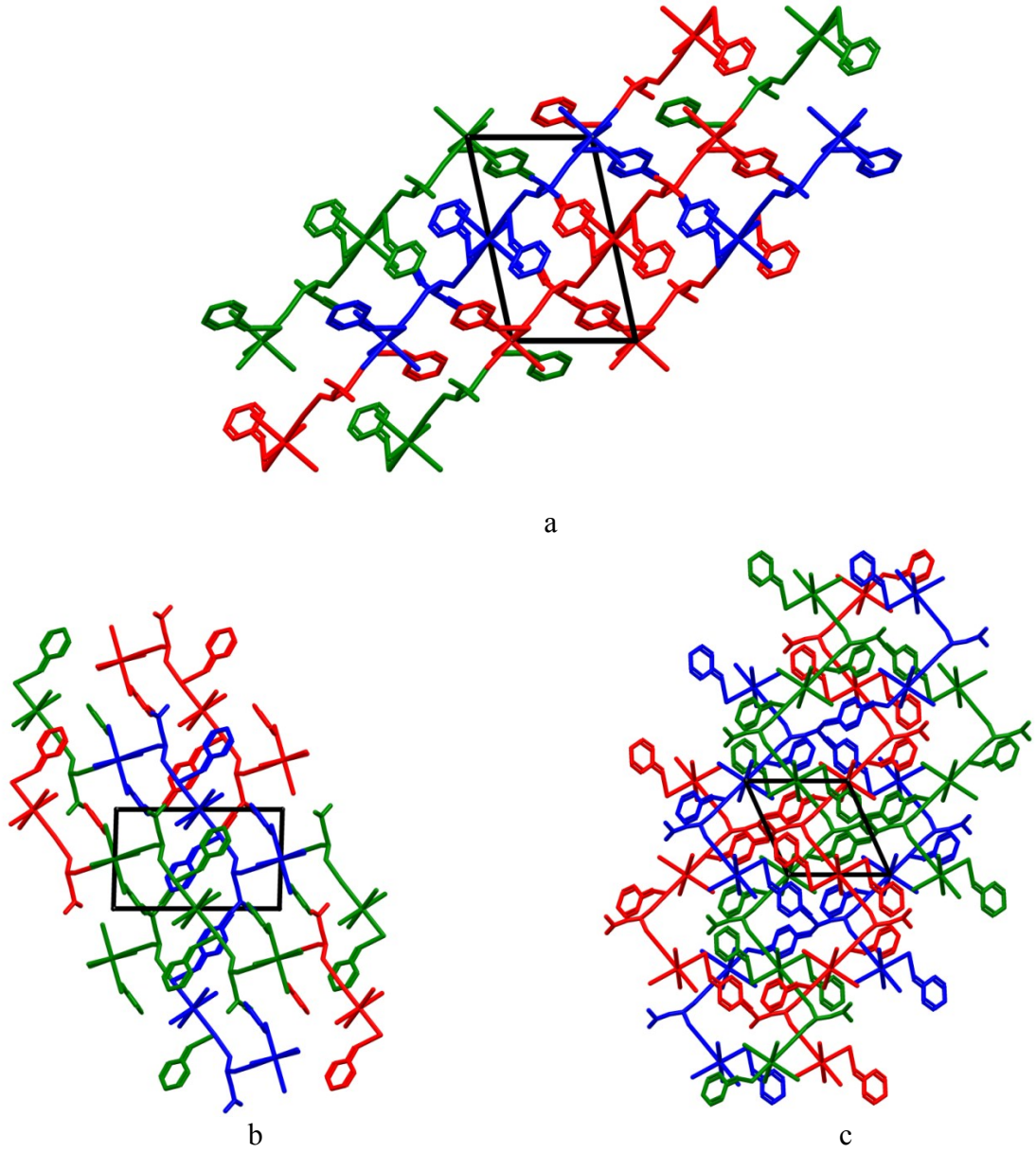
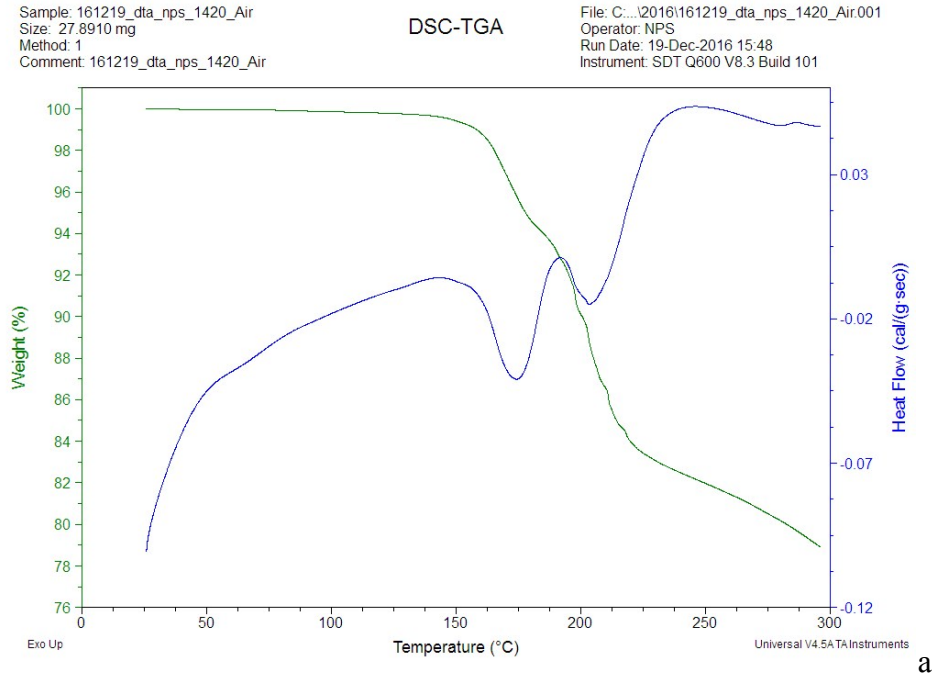
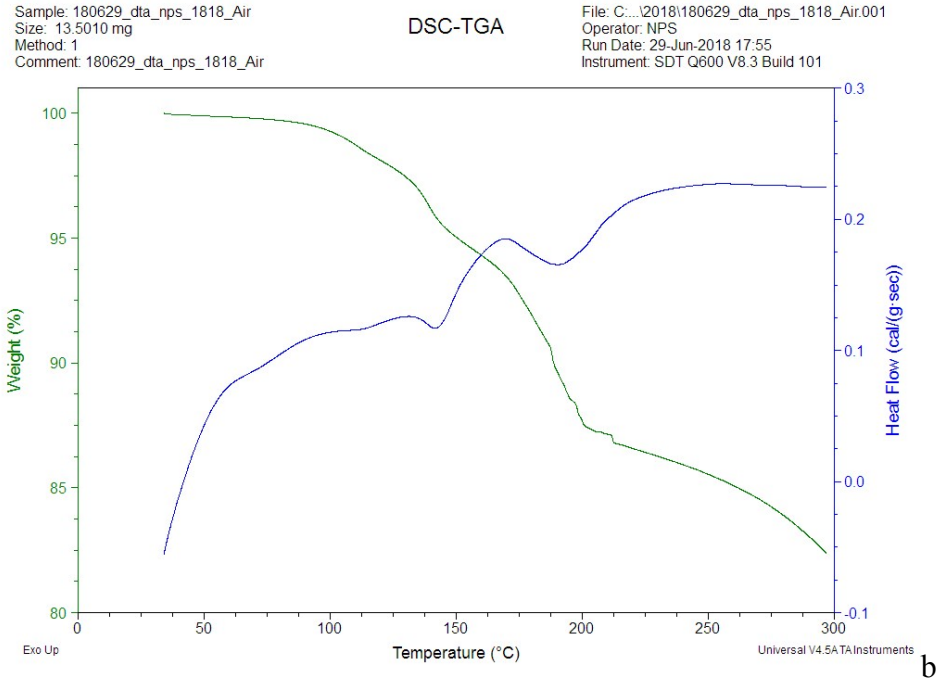


Fig. S12. The projection of the structure of **5** along [100] (a), [010] (b) and [001] (c) directions.



a



b

Fig. S13. TG (green) and DTA (blue) curves on heating compound **1** (a) and **1**+**7** mixture (b) under a flow of artificial air.

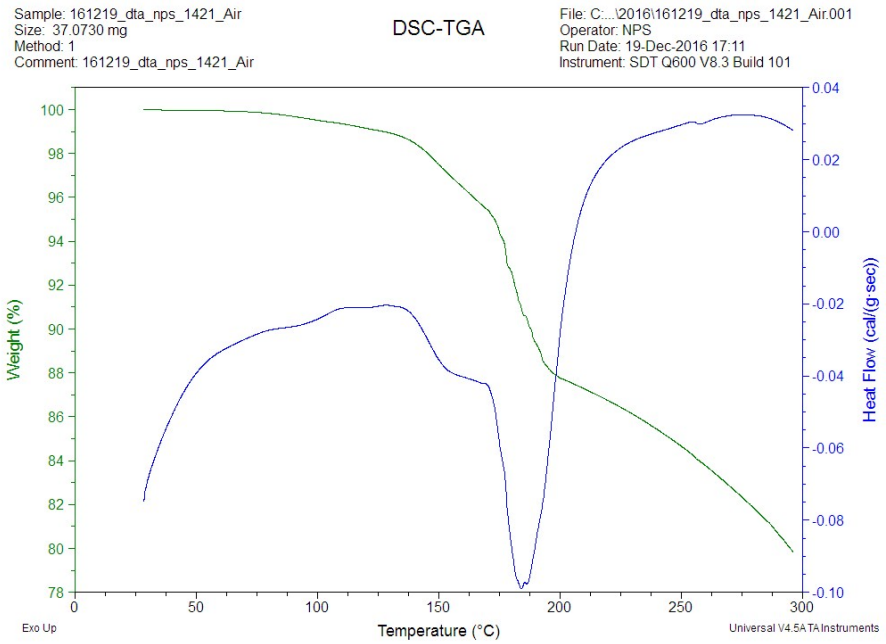


Fig. S14. TG (green) and DTA (blue) curves on heating compound **2** under a flow of artificial air.

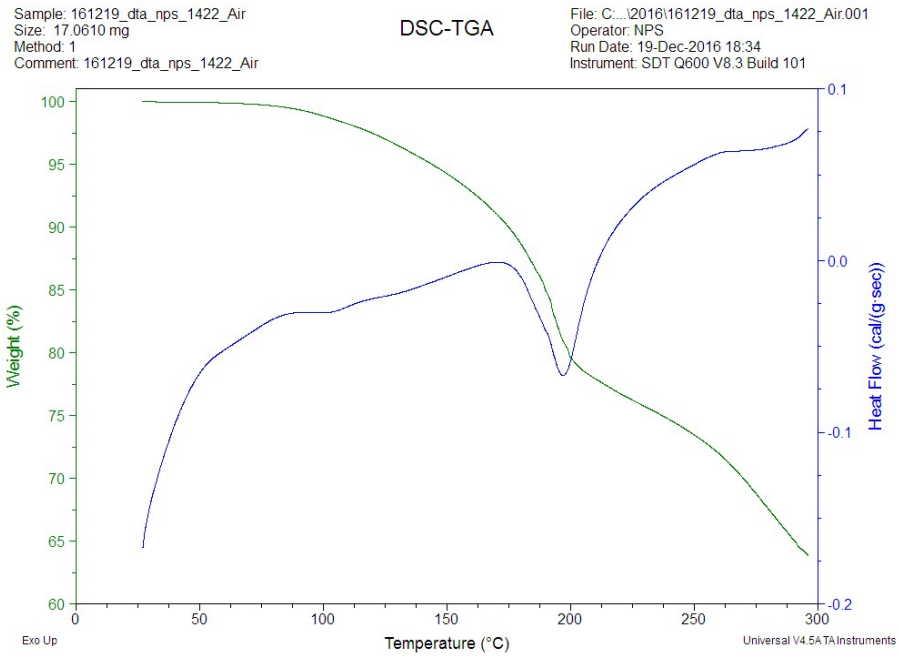


Fig. S15. TG (green) and DTA (blue) curves on heating compound **3** under a flow of artificial air.

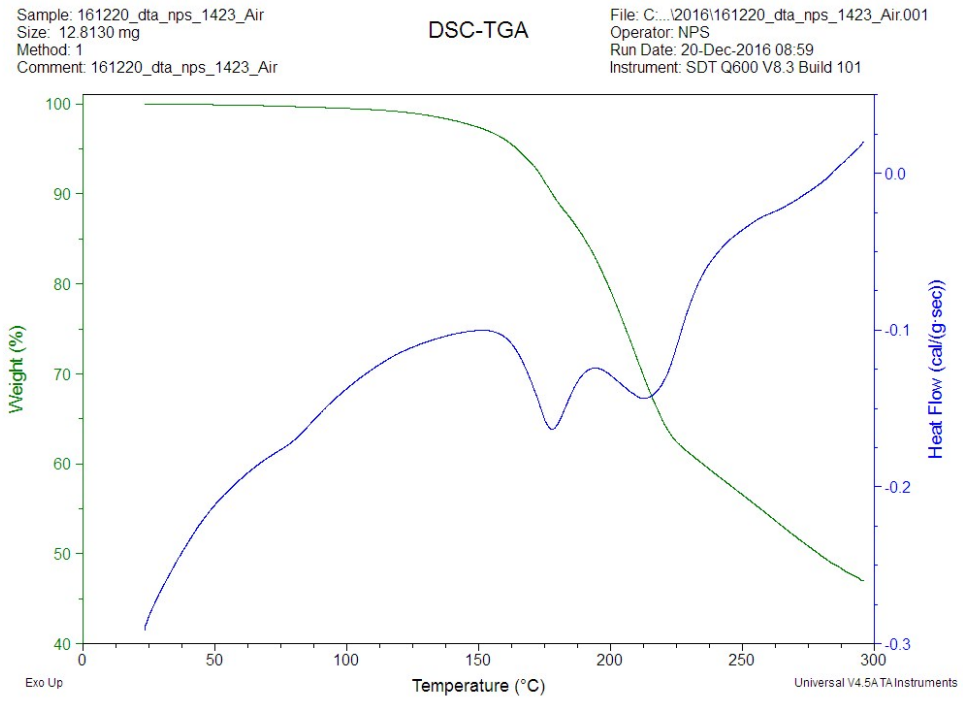


Fig. S16. TG (green) and DTA (blue) curves on heating compound **4** under a flow of artificial air.

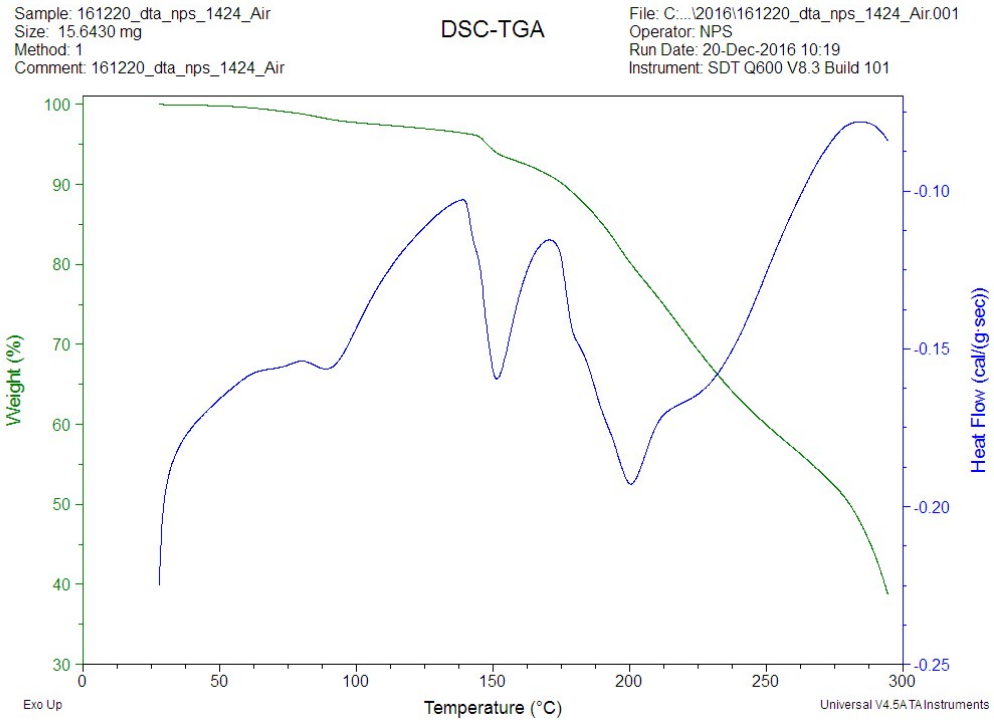
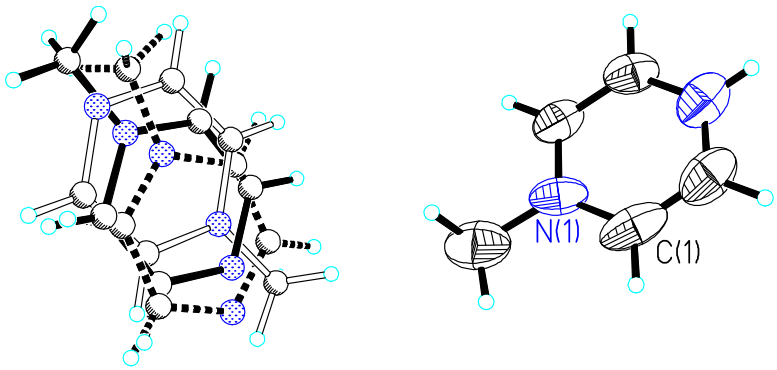


Fig. S17. TG (green) and DTA (blue) curves on heating compound **5** under a flow of artificial air.



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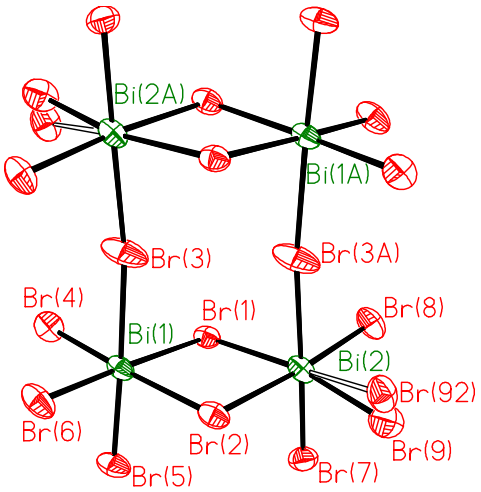

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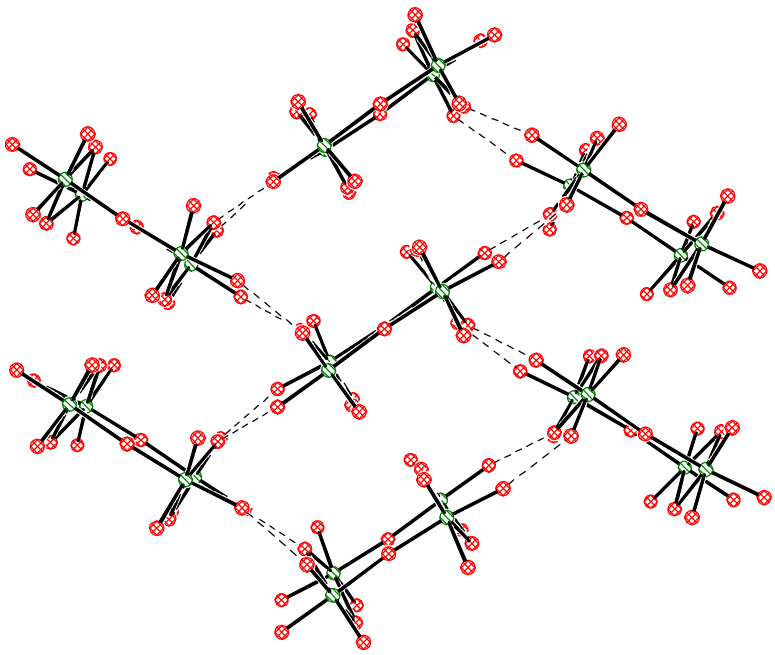


c

Fig. S18. The structure of the cations (a) and anion (b) in **6** (thermal ellipsoids are shown at 50% probability) and mutual positions of $[Bi_4Br_{18}]^{6-}$ anions (in the projection along the *a* axis) in **6**.

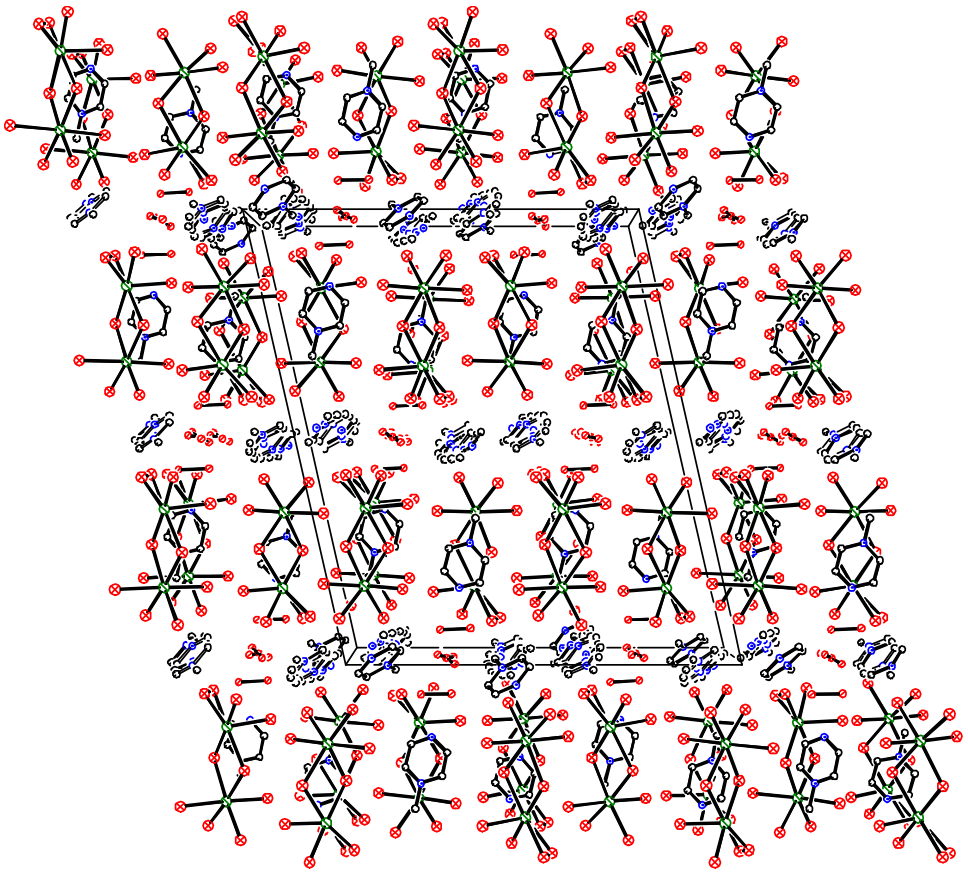


Fig. S19. Projection of the structure of **6** along the b axis.

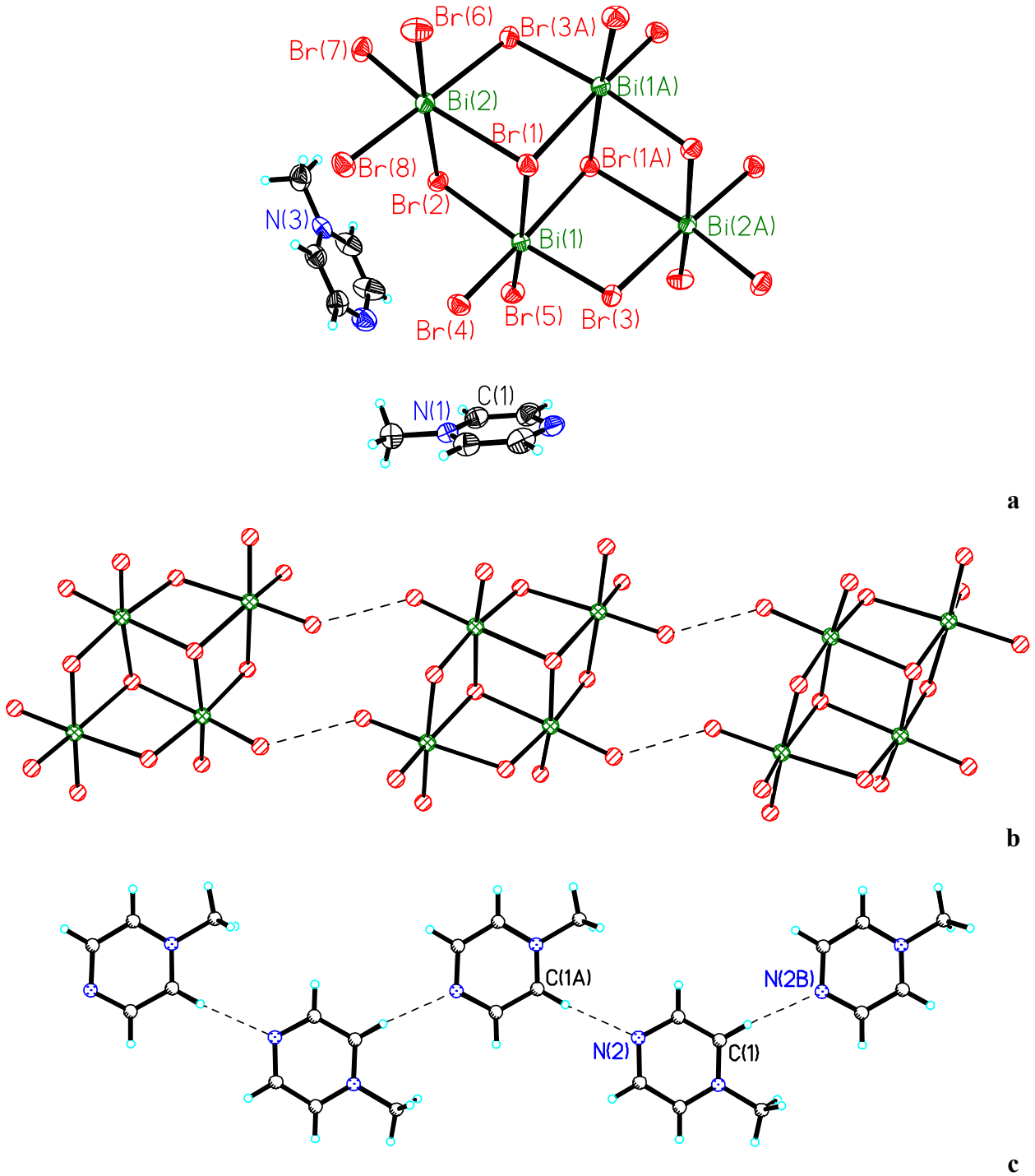
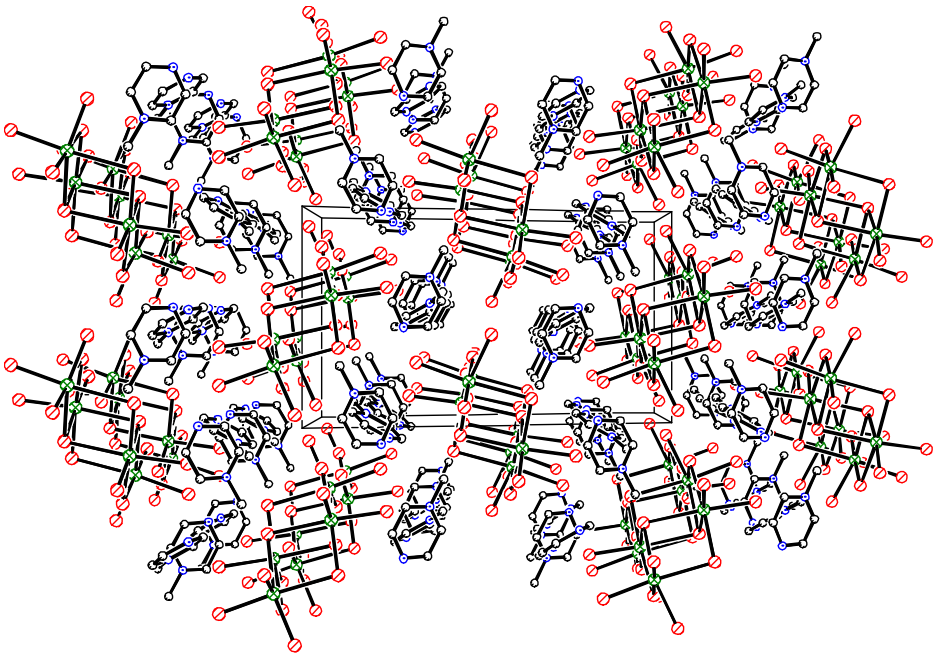


Fig. S20. The fragment of the structure of **8** (thermal ellipsoids are shown at 50% probability) (a), 1D-chains of $[Bi_4Br_{16}]^{4-}$ (b) and $[MePz]^{+}$ (c) in the structure of **8**.



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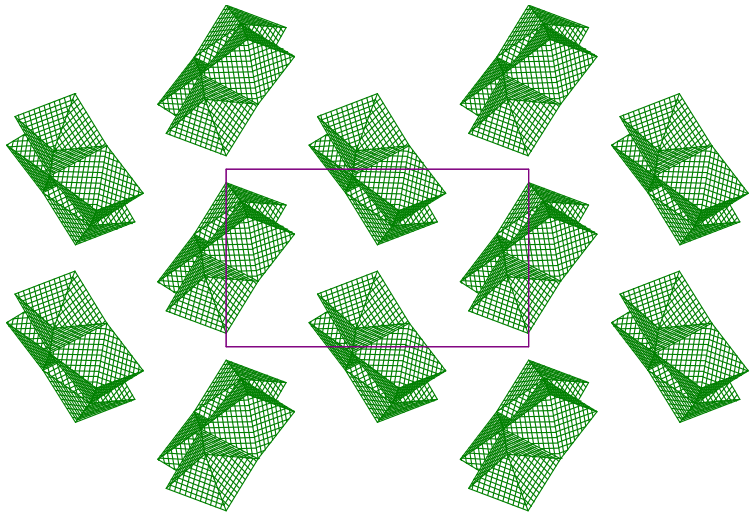
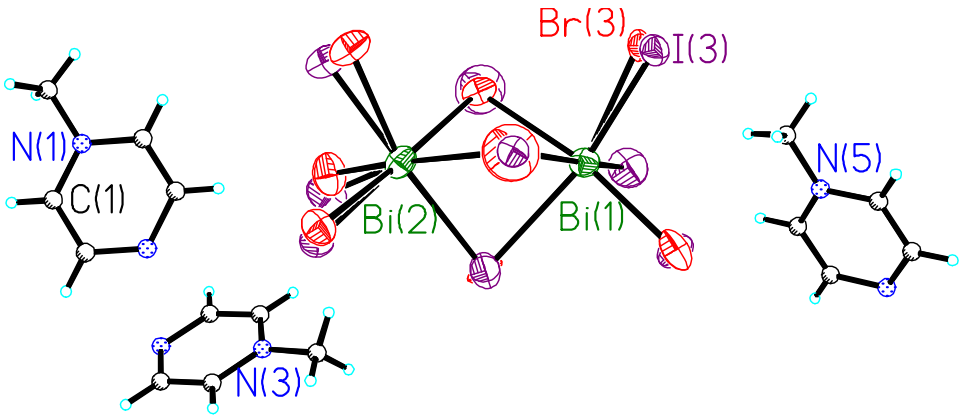
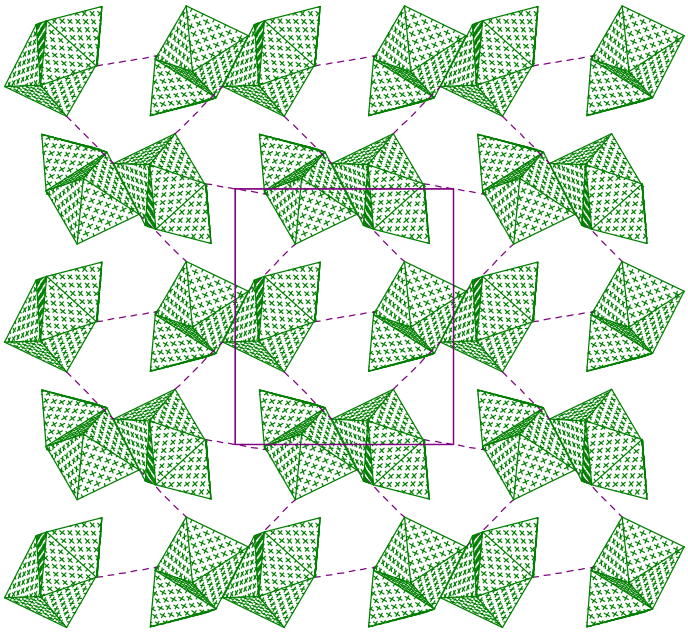


b

Fig. S21. The projection of the structure of **8** along the a axis (a) and that with only $[Bi_4Br_{16}]^{4-}$ shown (b).

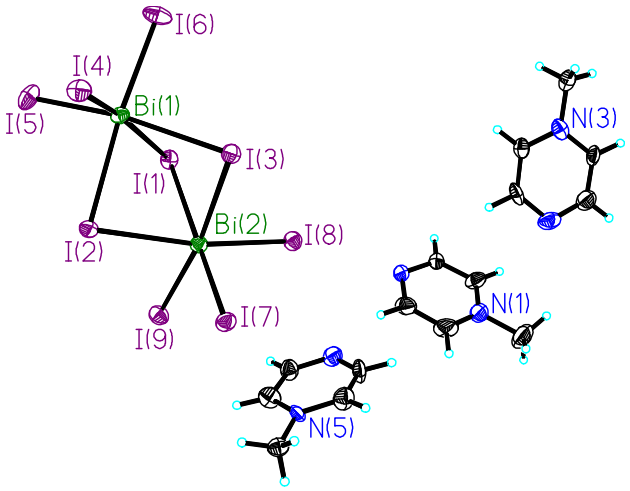


a

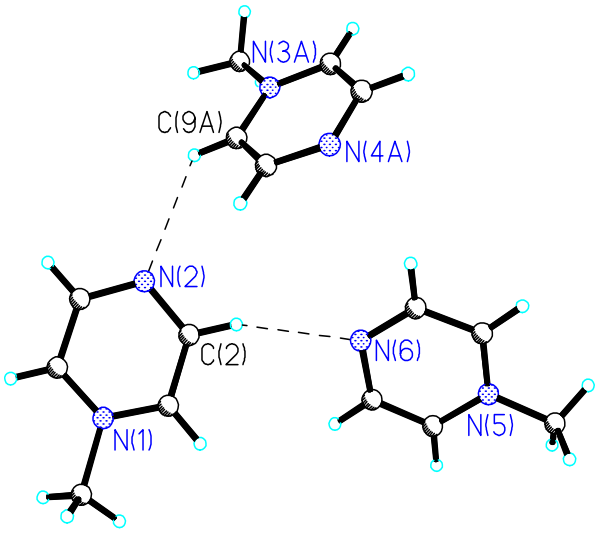


b

Fig. S22. An asymmetric unit of the structure of compound **10** (thermal ellipsoids are shown at 50% probability) (a) and mutual position of $[Bi_2Br_{5.16}I_{3.84}]^{3-}$ anions in the structure of **10** (b).

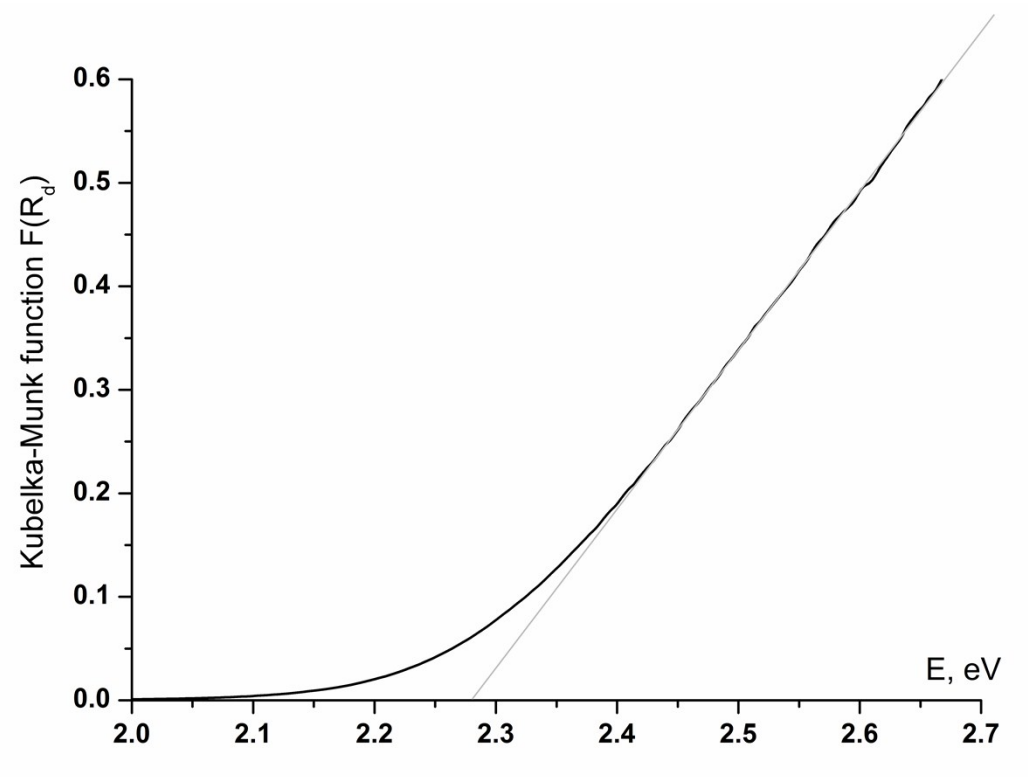


a

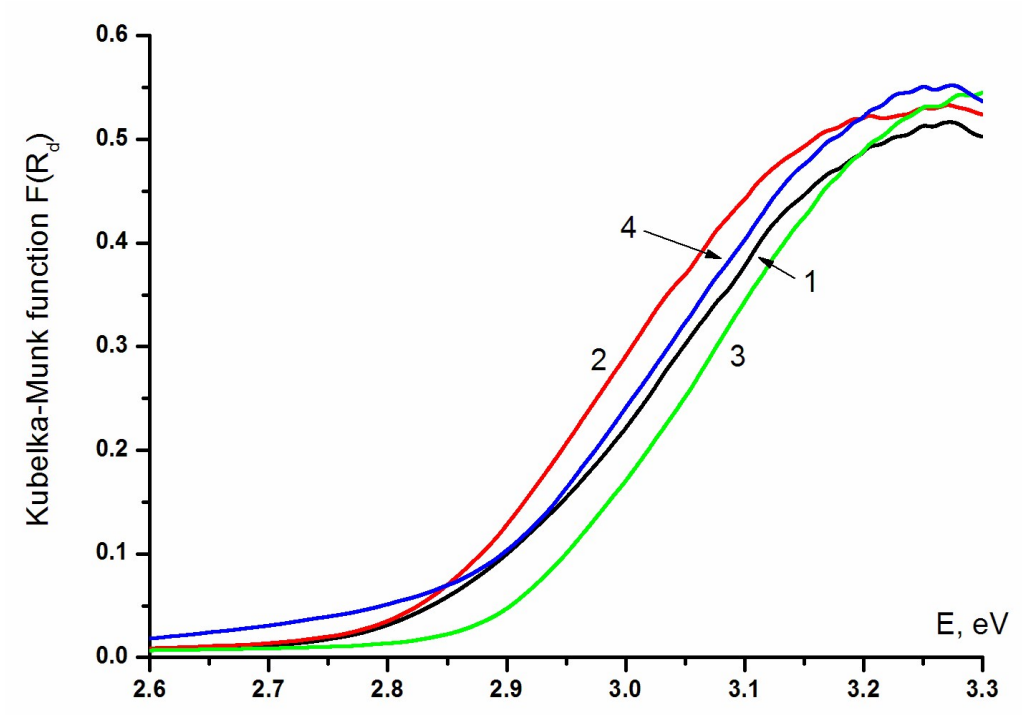


b

Fig. S23. An asymmetric unit of the structure of compound **11** (thermal ellipsoids are shown at 50% probability) (a) and mutual position of cations in the structure of **11** (b).



a



b

Fig. S24. The reflectance spectra of **5** (a) and the hydrolysis products of **1** (b1), **2** (b2), **3** (b3) and **4** (b4).

Resulting CONTCAR file (calculation using VASP program)

kotov44

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0.7242628388743029 0.9090023007116059 0.5635625658662775
0.3382108212489499 0.4562388325399525 0.2533652032816818
0.6637895072076745 0.5274106068088287 0.7488997155384354
0.1633462673380137 0.0267384284636023 0.7511250229054909
0.8475065853145693 0.9312663761277307 0.2467349107099039
0.6511066295750538 0.4294464766006740 0.2481424938802661
0.3560184098853583 0.5888634137028603 0.7533995899036938
0.8559052585384137 0.0897136922277824 0.7469936698521522
0.1608655655052402 0.9530085994860897 0.2519389484296823
0.3565193452322717 0.6359305218969666 0.2576523122736063
0.6231790344271388 0.3505714531170128 0.7466894719281854
0.1217824038071882 0.8501701070079406 0.7535887690454075
0.8340032777884474 0.1105273686900858 0.2443929799330675
0.6678199928233681 0.6084741056016369 0.2450589127300233
0.3173249575064432 0.4131973209344366 0.7556745022046201
0.8163215916809961 0.9142055404527767 0.7443709689115394
0.1457726531200620 0.1328905789523276 0.2560604630144780
0.5218787624133725 0.6996590721590792 0.2503149084280309
0.4502405660085316 0.3057917326153046 0.7529133573879037
0.9486660407154730 0.8061154754224518 0.7470957962047109
0.9817623196812093 0.1992475429621052 0.2495158744832935
0.5551820021540479 0.2988846028204364 0.2506732742900866
0.4346435017659047 0.3118404071794743 0.2917031800773842
0.4449041817211281 0.3155133691054957 0.1983470319762475
0.4677328900032336 0.7080824749854102 0.7514299663898072
0.5761769466664219 0.6788398184598208 0.8029793858922503
0.5852638392148393 0.6812208255404713 0.7095043399996186
0.9679152269176541 0.2082976781295898 0.7494514922432103
0.0857391006543082 0.1809014705337901 0.7907244530517161
0.0758048187213447 0.1791720128841803 0.6973054396183613
0.9414968306296885 0.7991386467993422 0.2515389544476179
0.0485336591619117 0.8139465230956588 0.1957470359413733

0.0647587285632696 0.8101842397713384 0.2886729006320863

FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)

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free energy   TOTEN =   -1262.85163409 eV

energy without entropy=   -1262.85163409 energy(sigma->0) =   -1262.85163409