The Structures of Bis(1H$^+$,5H$^+$-S-methylisothiocarbonohydrazidium) Di-μ-chloro-octachlorodibismuthate(III) Tetrahydrate and Tris(1H$^+$-S-methylisothiocarbonohydrazidium) Esachlorobismuthate(III)

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The structures of bis(1H$^+$,5H$^+$-S-methylisothiocarbonohydrazidium) di-μ-chlorooctachlorodibismuthate(III) tetrahydrate: $(C_2H_{10}N_4S)_2(Bi_2Cl_{10})\cdot 4H_2O$ (compound [I]) and of tris(1H$^+$-S-methylisothiocarbonohydrazidium) esachlorobismuthate(III): $(C_2H_9N_4S)_3(BiCl_{5.67}I_{0.33})$ (compound [II]) were determined from single crystal X-ray diffractometer data. Both compounds crystallize as triclinic ($P\bar{1}$); crystals [I] with Z = 1 formula unit in a cell of constants: $a = 10.621(3)$, $b = 9.989(5)$, $c = 7.439(3)$ Å, $\alpha = 88.31(2)$, $\beta = 84.51(2)$, $\gamma = 68.88(2)^\circ$, final $R = 0.0427$ for 2229 unique reflections with $I \geqslant 2\sigma(I)$; crystals [II] with Z = 2 and cell dimensions: $a = 14.109(4)$, $b = 12.209(9)$, $c = 8.206(7)$ Å, $\alpha = 103.54(3)$, $\beta = 104.95(2)$, $\gamma = 81.96(2)^\circ$, final $R = 0.0411$ for 3637 unique reflections ($I \geqslant 2\sigma(I)$). The structure of [I] is built up of diprotonated organic cations, water molecules and dinuclear centrosymmetric $[Bi_2Cl_{10}]^{4-}$ anions held together by N–H···Cl, N–H···O, O–H···Cl hydrogen bonds and Van der Waals interactions. The $[Bi_2Cl_{10}]^{4-}$ complex consists of two edge-sharing octahedra in which three pairs of bonds of similar length are observed ($Bi-Cl_{av}$ = 2.602(5), 2.712(4), 2.855(5) Å). The structure of [II] consists of monoprotonated cations and $[BiCl_{5.67}I_{0.33}]^{3-}$ anions held together by a tridimensional network of hydrogen bonds. Each bismuth atom is octahedrally surrounded by six chlorine atoms, one of which is statistically substituted by a iodine atom.

Introduction

Whereas several studies have been made in the solid state on complexes between bismuth(III) and bromide or iodide, only few complexes of bismuth(III) chlorides with organic cations have been investigated. The crystal structures of bis(1H$^+$,5H$^+$-S-methylisothiocarbonohydrazidium) di-μ-chloro-octachlorodibismuthate(III) tetrahydrate and of tris(1H$^+$-S-methylisothiocarbonohydrazidium) esachlorobismuthate(III) have been determined as part of research on compounds formed between non-transition metal chlorides and thiocarbonohydrazide and its derivative: S-methylisothiocarbonohydrazide.

Experimental

Two kinds of crystals were isolated by slow evaporation of a hydrochloric solution of bismuth chloride and 1H$^+$-S-methylisothiocarbonohydrazidium iodide, and only the structural analyses revealed the different stoichiometries owing to the scarcity and to the non-homogeneity of the product.

The relevant data concerning the crystal structure analyses are summarized in Table I. All the reflections were collected with the θ–2θ scan technique and were corrected for Lorentz and polarization effects. Corrections for absorption and extinction were applied using the method of Walker and Stuart [1]. Both structures were solved and refined by full-matrix least-squares using the SHELX-76 program [2] with initially isotropic and then anisotropic thermal parameters for all non-hydrogen atoms (except Cl2 and I of compound [II] which are statistically interchangeable in two positions with site occupancy factors of 0.67 and 0.33 respectively, as found from the refinement). In fact the refinement with only Cl atoms in the bismuthate complex gave a very doubtful residue of 4.4 eÅ^{-3} at 0.4 Å from Cl2 and a too low thermal parameter for this last atom; after several attempts the two atoms, Cl2 and I, were distinguished and all the structure was refined. The final ΔF syntheses were not valuable in locating all the H atoms. In the refinements the best results were obtained using unit weights as expected from the analyses of the variation of $|\Delta F|$ with respect to $|F_o|$. The atomic scattering factors and the anomalous scattering coefficients are from International Tables for X-ray Crystallography [3]. Final coordinates and thermal parameters are given in Table II. A list of the observed and calculated

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TABLE I. Experimental Data for the Crystallographic Analyses.

		[I]	[II]
Compound		$(C_2H_{10}N_4S)_2(Bi_2Cl_{10})\cdot 4H_2O$	$(C_2H_9N_4S)_3(BiCl_{5.67}I_{0.33})$
F.W.		1088.927	815.417
Space group		$P\bar{1}$	$P\bar{1}$
a/Å		10.621(3)	14.109(4)
b/Å		9.989(5)	12.209(9)
c/Å		7.439(3)	8.206(7)
α/°		88.31(2)	103.54(3)
β/°		84.51(2)	104.95(2)
γ/°		68.88(2)	81.96(2)
V/Å^3		732.8(5)	1323(2)
Z		1	2
D_c/Mg m^{-3}		2.467	2.047
reflections for lattice parameters	number	22	24
	θ-range/°	8–14	8–14
crystal data and intensity data	radiation	Mo-K$\bar{\alpha}$ (Nb-filtered)	Mo-K$\bar{\alpha}$ (Nb-filtered)
	wavelength/Å	0.71069	0.71069
F(000)		508	783.8
temperature/°C		22	22
crystal size/mm^3		0.03 × 0.26 × 0.30	0.05 × 0.30 × 0.46
diffractometer		Siemens AED	Siemens AED
μ/mm^{-1}		13.041	7.851
absorption correction (min-max)		0.7743–1.6095	0.7612–1.6685
extinction correction (min-max)		0.9558–1.0201	0.8782–1.0261
range θ/°		3–26	3–25
h-range		−12/13	−16/16
k-range		−12/12	−14/14
l-range		0/9	0/9
standard reflection		1 4 3	$\bar{7}$ 3 2
intensity variation		none	none
no. of measured reflections		2868	4600
conditions for observed reflections		$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$
no. of unique reflections		2229	3637
method for solving structure		Patterson	Patterson
anisotropic least-squares on F		full-matrix	full-matrix
maximum least-squares shift to error ratio		0.33	1.23
min-max height in final ΔF/e Å^{-3}		−0.621/0.599	−1.449/0.979
no. of refined parameters		136	253
R		0.0427	0.0411
R_w $[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma wF_o^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$)		0.0527	0.0479

structure factors and of the most relevant contacts and probable hydrogen bonds (less than 3.40 Å) have been deposited with the Editor.

The calculations were carried out on the CYBER 76 computer of the 'Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell' Italia Nord-Orientale (CINECA, Casalecchio, Bologna)' with the financial support of the University of Parma, and the GOULD-SEL 32/77 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma)'. In addition to the quoted program, PARST [4], ASSORB [5], PLUTO [6] and ORTEP [7] programs were used.

Results and Discussion

The structure of bis(1H$^+$,5H$^+$-S-methylisothiocarbonohydrazidium) di-μ-chloro-octachlorodibismu-

TABLE II. Fractional Atomic Coordinates ($\times 10^5$ for Bi and $\times 10^4$ for the Other Non-Hydrogen Atoms) and Anisotropic Thermal Parameters of Isotropic Thermal Parameters ($\times 10^4$ Å^2) with e.s.d.'s. in Parentheses for Compounds [I] and [II]. Anisotropic Thermal Parameters are in the Form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Compound [I]									
Bi	17386(6)	4769(6)	−8465(8)	264(2)	247(2)	273(3)	9(2)	−3(2)	−98(2)
Cl1	3382(4)	1085(4)	1073(5)	356(18)	391(18)	384(20)	14(15)	−71(15)	−160(15)
Cl2	3106(4)	−2379(4)	−467(5)	382(18)	293(16)	430(21)	5(15)	−63(16)	−106(14)
Cl3	120(4)	465(4)	2462(5)	409(19)	465(21)	368(20)	−55(16)	2(16)	−208(16)
Cl4	238(4)	3266(4)	−1413(5)	404(19)	233(16)	461(22)	17(15)	104(17)	−53(14)
Cl5	3110(4)	434(4)	−3957(5)	413(19)	382(18)	336(19)	−34(15)	49(15)	−186(15)
S1	4503(4)	3493(4)	4023(5)	399(20)	417(19)	317(19)	−21(16)	35(16)	−36(16)
O1	2476(12)	−2193(11)	4121(15)	571(69)	329(55)	408(62)	35(47)	−38(52)	−40(50)
O2	725(12)	3272(13)	4008(18)	487(69)	481(67)	712(86)	−75(60)	−197(63)	−62(55)
N1	3787(12)	3507(12)	7580(17)	326(61)	286(58)	449(73)	59(53)	−79(53)	−140(48)
N2	4885(12)	2118(12)	7438(17)	355(65)	246(58)	427(72)	89(52)	−69(54)	−16(49)
N3	2401(11)	5306(12)	5996(15)	251(55)	300(58)	265(58)	39(46)	20(45)	53(45)
N4	1595(12)	5753(13)	7690(16)	358(64)	363(63)	355(67)	−63(52)	57(52)	−150(52)
C1	3551(13)	4127(13)	6065(18)	264(67)	229(63)	310(76)	3(58)	24(58)	−57(51)
C2	3415(17)	4490(18)	2340(22)	504(96)	469(91)	366(87)	−52(71)	−2(73)	29(76)
Compound [II]									
Bi	75513(3)	20724(4)	−16520(6)	317(2)	303(2)	335(2)	65(1)	67(1)	−15(1)
Cl1	7785(2)	949(3)	−4766(4)	616(18)	534(18)	334(15)	31(13)	129(13)	−49(14)
Cl2	7155(4)	4173(5)	−2560(8)	468(15)					
I	6944(3)	4140(3)	−2942(5)	524(14)					
Cl3	8054(2)	−8(3)	−693(4)	622(18)	447(16)	510(18)	187(14)	145(14)	−4(14)
Cl4	7426(2)	3148(3)	1577(4)	660(19)	523(19)	450(17)	42(14)	204(14)	−80(15)
Cl5	9507(2)	2400(2)	−835(4)	362(14)	478(16)	575(18)	82(14)	66(13)	−64(12)
Cl6	5647(2)	1691(3)	−2328(5)	324(14)	546(19)	863(24)	123(17)	77(15)	−47(13)
S1	10656(2)	3631(3)	4080(4)	600(18)	434(16)	440(17)	100(13)	115(14)	−124(14)
S2	4392(3)	3138(3)	3331(6)	715(24)	604(23)	1165(35)	120(23)	476(24)	−98(19)
S3	6726(3)	7239(3)	2133(6)	735(23)	449(19)	1011(29)	116(18)	522(22)	−7(16)
N1	9438(7)	2397(8)	4598(12)	541(59)	418(54)	475(58)	61(45)	198(47)	−32(45)
N2	9053(8)	3473(8)	5390(14)	730(73)	392(56)	634(70)	31(50)	307(58)	−18(51)
N3	10509(7)	1395(8)	3047(12)	453(53)	346(50)	524(59)	100(44)	61(45)	−26(41)
N4	10009(8)	416(8)	2879(14)	607(63)	341(52)	682(70)	87(49)	204(54)	−63(46)
N5	4551(8)	973(10)	3038(14)	554(65)	669(74)	586(68)	67(57)	106(53)	−122(55)
N6	3755(8)	1229(10)	3866(16)	627(72)	631(73)	811(84)	89(63)	326(64)	−60(57)
N7	5701(8)	1583(10)	2081(14)	534(65)	811(83)	528(66)	117(59)	179(53)	−6(58)
N8	6050(9)	437(11)	1604(17)	564(71)	813(89)	893(92)	31(72)	274(65)	49(63)
N9	8495(7)	7414(7)	1855(12)	600(60)	337(50)	444(55)	100(42)	108(46)	−92(44)
N10	8199(8)	8571(8)	2292(14)	699(70)	351(54)	685(72)	102(50)	244(57)	21(48)
N11	8101(7)	5588(7)	1417(13)	494(56)	313(49)	587(62)	−15(44)	119(47)	38(42)
N12	9057(8)	5249(9)	1088(16)	518(63)	441(60)	970(91)	39(59)	299(62)	39(49)
C1	10173(8)	2367(9)	3869(13)	389(58)	457(65)	309(57)	113(49)	−10(45)	−59(49)
C2	11634(10)	3181(12)	2949(19)	566(80)	711(92)	781(99)	181(77)	321(73)	−14(68)
C3	4942(9)	1791(11)	2766(16)	568(76)	534(75)	442(70)	73(58)	93(58)	−114(60)
C4	5184(15)	3988(15)	2797(32)	1209(157)	736(118)	2063(237)	404(135)	917(163)	−162(109)
C5	7873(8)	6686(10)	1774(14)	457(64)	510(70)	386(62)	124(53)	110(50)	−7(53)
C6	6189(12)	5989(11)	2100(24)	858(106)	453(78)	1363(149)	241(86)	614(105)	−130(72)

thate(III) tetrahydrate (compound [I]) consists of dinuclear $[Bi_2Cl_{10}]^{4-}$ complexes (Fig. 1), diprotonated organic cations, and water molecules while in tris(1H$^+$-S-methylisothiocarbonohydrazidium) esachlorobismuthate(III) (compound [II]) mononuclear $[BiCl_{5.67}I_{0.33}]^{3-}$ complexes (Fig. 1), and monoprotonated organic cations are present. The packing of cations and anions in both compounds is depicted in Figs. 2 and 3 respectively, where the atom numbering scheme used in the tables is defined. Bond distances and angles are listed in Table III.

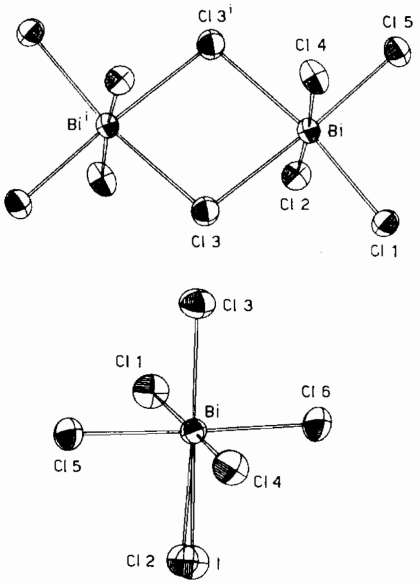


Fig. 1. Perspective views of the di- and mononuclear halobismuthate(III) complexes. Thermal ellipsoids are drawn at the 50% probability level.

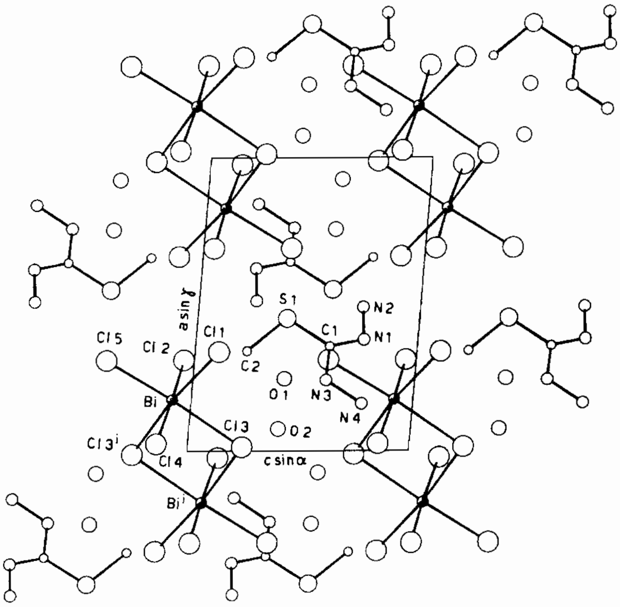


Fig. 2. Projection of the compound [I] structure viewed along *b*.

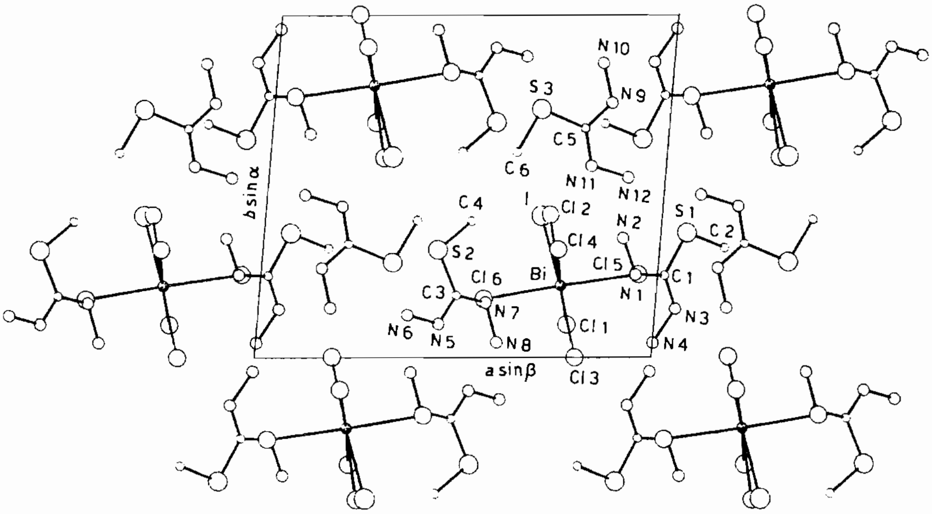


Fig. 3. Projection of the compound [II] structure viewed along *c*.

Chlorobismuthate(III) Complexes

In compound [I] the Bi atoms are surrounded by six Cl^- ions in a distorted octahedral arrangement. Two chlorine atoms bridge nearly symmetrically the two metals related by a crystallographic centre of inversion, so the two coordination octahedra share an edge. Bond angles at bismuth range from 83.4(1) to 96.2(1)°, showing significant departures from the ideal octahedral values. A better view of the metal environments can be achieved by considering the deviations of the non-bridging atoms from the plane defined by the Bi, Cl3, Bi^i, $Cl3^i$ atoms, coplanar for symmetry: 1) Cl1 results −0.244(4) Å out of this plane while Cl5 is coplanar; the displacements of Cl2 and Cl4 from the same plane are −2.697(4) and 2.707(4) Å respectively, 2) the deviation of the Bi–Cl2 vector from the perpendicular to the above mentioned plane is larger than that of Bi–Cl4 (6.6(1) and 2.0(1)° respectively).

In compound [II] the metal atom coordination is again distorted octahedral with a range of 85.5(1)–94.5(2)° for bond angles. The Cl1, Cl4, Cl5, Cl6 atoms are coplanar, being the deviations from the weighted least-squares plane through them of +0.004(4), +0.004(4), −0.002(3), −0.004(4) Å respectively). The displacement of the Bi atom from

TABLE III. Bond Distances (Å) and Angles (°) with e.s.d.'s in Parentheses.

Compound [I] ($i = \bar{x}, \bar{y}, \bar{z}$)							
Bi–Cl1	2.597(5)	Cl1–Bi–Cl2	91.1(1)	Cl2–Bi–Cl4	175.1(1)	Cl3–Bi–Cl3^i	85.0(1)
Bi–Cl2	2.715(4)	Cl1–Bi–Cl3	87.4(1)	Cl2–Bi–Cl5	90.2(1)	Cl4–Bi–Cl5	89.0(1)
Bi–Cl3	2.866(4)	Cl1–Bi–Cl4	93.8(1)	Cl2–Bi–Cl3^i	83.4(1)	Cl4–Bi–Cl3^i	91.7(1)
Bi–Cl4	2.709(4)	Cl1–Bi–Cl5	96.2(1)	Cl3–Bi–Cl4	91.1(1)	Cl5–Bi–Cl3^i	91.4(1)
Bi–Cl5	2.606(4)	Cl1–Bi–Cl3^i	170.7(1)	Cl3–Bi–Cl5	176.5(1)	Bi–Cl3–Bi^i	95.0(1)
Bi–Cl3^i	2.844(5)	Cl2–Bi–Cl3	89.4(1)				
S1–C1	1.74(1)	C1–N3	1.36(1)	C1–S1–C2	103.9(8)	N1–C1–N3	117.8(1.2)
S1–C2	1.81(2)	N1–N2	1.45(1)	S1–C1–N1	125.0(1.1)	N2–N1–C1	113.1(1.1)
C1–N1	1.27(2)	N3–N4	1.44(2)	S1–C1–N3	117.0(1.0)	N4–N3–C1	115.6(1.1)
Compound [II]							
Bi–Cl1	2.681(4)	Cl1–Bi–Cl2	94.5(2)	Cl2–Bi–Cl3	176.9(2)	I–Bi–Cl6	88.7(1)
Bi–Cl2	2.779(7)	Cl1–Bi–I	90.5(1)	Cl2–Bi–Cl4	87.6(2)	Cl3–Bi–Cl4	92.3(1)
Bi–Cl3	2.778(4)	Cl1–Bi–Cl3	85.5(1)	Cl2–Bi–Cl5	88.2(2)	Cl3–Bi–Cl5	88.7(1)
Bi–Cl4	2.706(4)	Cl1–Bi–Cl4	176.5(1)	Cl2–Bi–Cl6	94.2(2)	Cl3–Bi–Cl6	88.8(1)
Bi–Cl5	2.730(3)	Cl1–Bi–Cl5	87.2(1)	I–Bi–Cl3	175.1(1)	Cl4–Bi–Cl5	90.0(1)
Bi–Cl6	2.684(3)	Cl1–Bi–Cl6	94.1(1)	I–Bi–Cl4	91.9(1)	Cl4–Bi–Cl6	88.6(1)
Bi–I	2.899(4)	Cl2–Bi–I	7.1(2)	I–Bi–Cl5	93.9(1)	Cl5–Bi–Cl6	177.1(1)
S1–C1	1.73(1)	C3–N7	1.30(2)	C1–S1–C2	101.7(6)	N5–C3–N7	120.4(1.3)
S1–C2	1.81(2)	N5–N6	1.42(2)	S1–C1–N1	117.3(9)	N6–N5–C3	119.2(1.2)
C1–N1	1.32(2)	N7–N8	1.42(2)	S1–C1–N3	123.4(9)	N8–N7–C3	117.4(1.2)
C1–N3	1.31(1)	S3–C5	1.73(1)	N1–C1–N3	119.3(1.1)	C5–S3–C6	101.5(7)
N1–N2	1.42(1)	S3–C6	1.79(2)	N2–N1–C1	117.8(1.0)	S3–C5–N9	116.9(9)
N3–N4	1.43(2)	C5–N9	1.31(2)	N4–N3–C1	118.0(1.0)	S3–C5–N11	121.3(9)
S2–C3	1.73(1)	C5–N11	1.32(1)	C3–S2–C4	101.3(9)	N9–C5–N11	121.8(1.1)
S2–C4	1.82(3)	N9–N10	1.40(1)	S2–C3–N5	116.4(1.0)	N10–N9–C5	117.9(1.0)
C3–N5	1.29(2)	N11–N12	1.43(2)	S2–C3–N7	123.2(1.1)	N12–N11–C5	115.4(1.0)

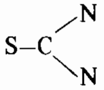
this equatorial plane is +0.057(2) Å towards the iodine atom, and results smaller than that observed in *catena*-di-μ-chloro-iodo(1H$^+$-S-methylisothiocarbonohydrazidium-N)cadmium(II) [8]: 0.324(2) Å. I, Cl2, and Cl3 are far from the equatorial plane by +2.953(4), +2.827(6), and −2.716(4) Å respectively.

In [I] three pairs of bonds of similar length are observed as in ferricenium tetrachlorobismuthate [9], in 2-picolinium tetrabromobismuthate, and 2-picolinium tetraiodobismuthate [10] where the ions $[BiCl_4]_n^{n-}$, $[BiBr_4]_n^{n-}$ and $[BiI_4]_n^{n-}$ consist however of infinite 'skew' octahedral chains, and in bispiperidinium pentabromobismuthate [11] where the $[BiBr_5]_n^{2n-}$ ions shape a chain of octahedra sharing cis vertices. In this pattern of bond lengths the shortest bond distances are always opposite the longest ones. The 'short' non-bridging Bi–Cl bond distances observed in the present instance, 2.597(5) and 2.606(4) Å, are greater than those falling in the range 2.47–2.52 Å suggested for a reasonable 'single' Bi–Cl bond, such as in $BiCl_3$(g) [12]: 2.48(2) Å; in solid $BiCl_3$ [13]: 2.468(4), 2.513(7), 2.518(7) Å, and in $(C_5H_5)_2FeBiCl_4$ [9]: 2.500(3), 2.522(3) Å. It is however clear that the strong tendency to Cl bridging in Bi–Cl compounds precludes the designation of any specific value as a single-bond distance as both $BiCl_3$(g) and $BiCl_3$(s) are not monomeric. The values of the bridging Bi–Cl bond distances (2.844(5), 2.866(4) Å) are closer than in $(C_5H_5)_2FeBiCl_4$: 2.749(3), 3.101(4) and 2.702(3), 2.949(3) Å, and in $(C_5H_5NH)_6Bi_4Cl_{18}$ [14]: 2.850(2), 2.941(3) Å. In this last tetranuclear complex, where a third Cl atom bridges another metal atom, the bond length pattern is different in that two kinds of bond distances are observed, and the values of the shortest set of three (2.567(3), 2.585(2), 2.611(2) Å) are similar with those determined here. The Bi···Bi distance 4.208(2) Å is significantly smaller than those observed in $(C_5H_5NH)_6Bi_4Cl_{18}$ (4.350(2) Å) and in $(C_5H_5)_2FeBiCl_4$ (4.327(2) Å).

In salt [II] the Bi–Cl bond distances in the range 2.681(4)–2.779(7) Å are longer than those observed in other monomeric octahedral $[BiCl_6]^{3-}$ complexes (2.66(1) Å [15] and 2.66(2) Å [16]), where all the metal–halogen bond lengths are equal for symmetry, and this lengthening is probably due to the interactions between the halogen atoms and the cations. The Bi–I bond distance (2.899(4) Å) agrees very well with those observed in $[BiI_4]_n^{n-}$ (2.87(1), 2.90(2) Å).

S-Methyl-Isothiocarbonohydrazidium Cations

The π bond is more delocalized in the monoprotonated cations of compound [II] than in the biprotonated ones of compound [I] as it arises from the values of bond distances and by the planarity of the



moieties (maximum deviations: 0.01(1) for each C atom in [II] and 0.04(1) Å in [I]). A similar delocalization is observed in S-methylisothiocarbonohydrazidium iodide [17]. The methyl carbon atom of the biprotonated cation is 0.50(2) Å out of the weighted least-squares plane through all the other atoms of the organic molecule, while in the monoprotonated cations the deviations are much smaller (0.01(1), 0.10(2), 0.19(2) Å). In each cation the two S–C–N angles are significantly different: in the biprotonated cation the larger value is observed for the angle involving the nitrogen trans with respect to the methyl C atom, while the opposite situation is found in the monoprotonated organic molecule.

Packing

In compound [I] the cations and the water molecules exchange with one another and with the Cl atoms of the dinuclear $[Bi_2Cl_{10}]^{4-}$ groups, centred about the cell vertices, hydrogen bonds so forming chains running along *a*. In such a way, by considering only the contacts or probable hydrogen bonds less than 3.40 Å, each anion is surrounded by ten diprotonated cations and by eight water molecules.

The packing in compound [II] is determined by a tridimensional network of N–H···Cl hydrogen bonds so that each anion is surrounded by nine monoprotonated cations.

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