Structural Studies of Group 5B–Halide–Dithio-ligand Complexes. Part 4.† Crystal Structures of Bis(tetraethylammonium) Di-μ-iodo-bis[(*NN*-diethyldithiocarbamato)di-iodobismuthate(III)] and a Partially Brominated Analogue

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Crystallization of 1 : 1 stoicheiometric dimethylformamide solutions of $[Bi(S_2CNEt_2)I_2]$ and $[NEt_4]I$ yields a complex of stoicheiometry $[NEt_4][Bi(S_2CNEt_2)I_3]$. Single-crystal *X*-ray diffraction studies show it to be $[NEt_4]_2[I_2(Et_2NCS_2)BiI_2Bi(S_2CNEt_2)I_2]$, with a centrosymmetric anion containing iodine bridges. Use of $[NEt_4]Br$ instead, yields the isostructural monobromide; its structure has also been determined and the bromine found to occupy one of the non-bridging co-ordination positions about the bismuth atom. The unit cell is triclinic, with *a* *ca.* 13.0, *b* *ca.* 10.7, *c* *ca.* 9.6 Å, α *ca.* 68, β *ca.* 79, and γ *ca.* 75°.

THE preceding papers[1,2] have been directed towards elucidating the structures of some of the members of the series $[Bi(S_2CNEt_2)_{3-n}X_n]$, $n = 1$ or 2, X = Cl, Br, or I. We have found that evaporation of dimethylformamide solutions containing 1 : 1 stoicheiometric quantities of $[Bi(S_2CNEt_2)I_2]$ and $[NEt_4]I,Br$ yields crystalline materials with the stoicheiometry $[NEt_4][Bi(S_2CNEt_2)I_3]$, (1), and $[NEt_4][Bi(S_2CNEt_2)I_2Br]$, (2). We have therefore extended the structural studies of the above series to encompass these complexes also (Found: C, 18.1; H, 3.2; I, 43.4; N, 3.2; S, 7.5. Calc. for $C_{13}H_{30}BiI_3N_2S_2$: C, 18.0; H, 3.5; I, 43.9; N, 3.2; S, 7.4%).

CRYSTALLOGRAPHY

Crystal Data.—(1). $C_{13}H_{30}BiI_3N_2S_2$, $M = 868.0$, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 12.966(4)$, $b = 10.829(4)$, $c = 9.720(3)$ Å, $\alpha = 68.02(2)$, $\beta = 79.10(2)$, $\gamma = 75.15(2)°$, $U = 1\,216.6(6)$ Å^3, $D_m = 2.37(1)$, $Z = 2$, $D_c = 2.37$ g cm^{-3}, $F(000) = 792$, μ(Mo) = 103 cm^{-1}. Specimen size: 0.23 × 0.47 × 0.23 mm, $2\theta_{max.} = 55°$, $n = 5\,447$, $n_o = 4\,264$. Values of R, R', S are 0.040, 0.051, 1.8 respectively.

(2). $C_{13}H_{30}BiBrI_2N_2S_2$, $M = 821.0$, space group as above, $a = 12.962(6)$, $b = 10.644(5)$, $c = 9.571(3)$ Å, $\alpha = 67.59(3)$, $\beta = 78.34(3)$, $\gamma = 75.30(3)°$, $U = 1\,172.6(8)$ Å^3, $D_m = 2.35(1)$, $Z = 2$, $D_c = 2.33$ g cm^{-3}, $F(000) = 756$, μ(Mo) = 118 cm^{-1}. Specimen size: 0.09 × 0.28 × 0.18 mm, $2\theta_{max.} = 50°$, $n = 4\,162$, $n_o = 2\,772$. Values of R, R', S are 0.053, 0.066, 2.1 respectively.

Table 1 contains the non-hydrogen atom fractional cell co-ordinates; see Supplementary Publication No. SUP 22977 (31 pp.) ‡ for structure factor amplitudes, thermal parameters, hydrogen-atom parameters, and least-squares planes.

TABLE 1

Non-hydrogen atom fractional cell co-ordinates for (1) and (2)

Atom	(1)			(2)		
(*a*) Anion	*x*	*y*	*z*	*x*	*y*	*z*
Bi	0.339 09(3)	0.130 23(3)	0.080 38(4)	0.338 50(5)	0.125 88(7)	0.080 46(7)
I(1)	0.533 82(5)	−0.097 50(7)	0.234 75(7)	0.530 49(12)	−0.092 74(17)	0.234 32(17)
I(2)	0.194 79(5)	−0.081 77(6)	0.229 48(8)	0.195 44(12)	−0.083 06(16)	0.232 07(18)
I(3)/Br	0.170 19(6)	0.333 93(7)	−0.099 13(8)	0.179 56(15)	0.322 17(18)	−0.092 86(20)
S(1)	0.422 9(2)	0.341 4(3)	0.079 7(3)	0.419 8(4)	0.344 0(5)	0.077 0(5)
S(2)	0.267 8(2)	0.205 5(2)	0.316 9(3)	0.265 8(4)	0.199 7(5)	0.322 8(5)
C(1)	0.343 7(7)	0.330 9(9)	0.244 4(9)	0.343 0(13)	0.326 1(16)	0.251 3(19)
N	0.339 5(6)	0.413 9(7)	0.315 1(8)	0.337 8(12)	0.410 6(14)	0.323 7(14)
C(2)	0.395 3(9)	0.530 5(10)	0.254 6(12)	0.391 2(18)	0.531 6(22)	0.253 7(26)
C(3)	0.504 3(11)	0.492 3(13)	0.306 2(14)	0.500 6(25)	0.488 1(28)	0.308 7(29)
C(4)	0.273 7(9)	0.403 3(10)	0.461 2(10)	0.274 8(16)	0.391 5(18)	0.472 4(20)
C(5)	0.160 8(10)	0.480 8(12)	0.445 3(12)	0.160 9(17)	0.468 8(23)	0.462 6(22)
(*b*) Cation						
N	0.832 6(6)	0.163 5(7)	0.234 8(8)	0.839 2(11)	0.174 6(13)	0.223 9(15)
C(1A)	0.843 6(8)	0.265 4(10)	0.302 9(11)	0.848 2(16)	0.274 3(18)	0.297 9(20)
C(2A)	0.957 9(10)	0.271 2(12)	0.310 8(13)	0.964 4(18)	0.278 1(22)	0.303 2(24)
C(1B)	0.879 0(8)	0.021 9(10)	0.334 1(11)	0.882 8(15)	0.025 3(19)	0.320 3(23)
C(2B)	0.870 8(10)	−0.091 5(10)	0.285 0(14)	0.874 6(16)	−0.086 6(18)	0.267 4(24)
C(1C)	0.714 4(8)	0.179 1(11)	0.225 5(11)	0.722 6(15)	0.192 4(20)	0.210 0(21)
C(2C)	0.646 6(8)	0.138 5(12)	0.373 7(14)	0.653 1(17)	0.151 0(26)	0.364 9(25)
C(1D)	0.892 6(8)	0.189 1(10)	0.082 2(10)	0.906 4(16)	0.202 0(20)	0.066 3(20)
C(2D)	0.860 4(9)	0.331 8(12)	−0.027 2(11)	0.871 0(18)	0.355 8(23)	−0.044 8(22)

DISCUSSION

Complex (1).—The structure determination confirms the stoicheiometry as $[NEt_4][Bi(S_2CNEt_2)I_3]$. The

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† Part 3 is ref. 2. Part 1 (ref. 1) contains general descriptive crystallographic and definitional detail.

‡ For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

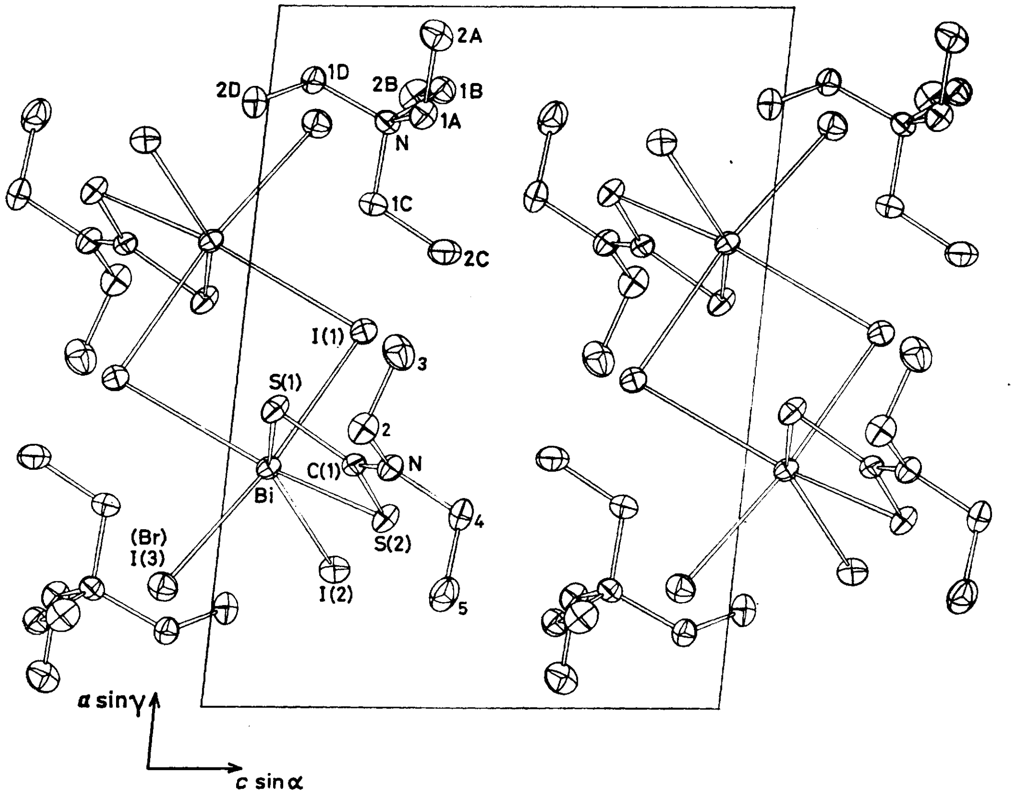

FIGURE 1 Unit-cell contents of (1) projected down *b*; the position of the bromine substituent in (2) is also indicated

anionic component of the structure, however, is found to be a centrosymmetric dimer with a pair of bismuth atoms bridged by an iodine atom and its centrosymmetric inverse, so that the structure is better described as $[NEt_4]_2[I_2(Et_2NCS_2)BiI_2Bi(S_2CNEt_2)I_2]$ with one-half of the latter formula unit comprising the asymmetric unit of the structure (Figure 1). The bismuth–bismuth separation is 4.755(2) Å, and the angle subtended at the iodine atom 94.38(3)°. The cation is well ordered and its geometry (Table 2) conventional, as is that of the dithiocarbamate ligand (Table 3).

TABLE 2

Cation geometry in (1) and (2)
The two values in each entry are for (1), (2) respectively

(*a*) Distances/Å	
N–C(1A)	1.53(2), 1.52(3)
N–C(1B)	1.51(1), 1.53(2)
N–C(1C)	1.52(1), 1.50(2)
N–C(1D)	1.50(1), 1.54(2)
C(1A)–C(2A)	1.52(2), 1.53(3)
C(1B)–C(2B)	1.51(2), 1.49(3)
C(1C)–C(2C)	1.51(1), 1.54(3)
C(1D)–C(2D)	1.52(1), 1.58(3)
(*b*) Angles/°	
C(1A)–N–C(1B)	108.5(8), 110.6(14)
C(1A)–N–C(1C)	107.8(7), 107.7(14)
C(1A)–N–C(1D)	111.0(7), 111.4(14)
C(1B)–N–C(1C)	110.9(7), 110.2(14)
C(1B)–N–C(1D)	108.8(7), 106.4(12)
C(1C)–N–C(1D)	109.9(7), 110.6(14)
N–C(1A)–C(2A)	115.2(9), 113.1(16)
N–C(1B)–C(2B)	115.1(9), 117.4(17)
N–C(1C)–C(2C)	115.4(9), 113.2(16)
N–C(1D)–C(2D)	114.8(8), 111.7(15)

TABLE 3

Dithiocarbamate non-hydrogen geometry in (1) and (2). The two values in each entry are for (1), (2) respectively

(*a*) Distances/Å	
C(1)–S(1)	1.712(8), 1.729(17)
C(1)–S(2)	1.736(10), 1.728(19)
S(1) · · · S(2)	2.957(4), 2.958(4)
C(1)–N	1.31(1), 1.31(3)
N–C(2)	1.49(1), 1.48(3)
N–C(4)	1.49(1), 1.46(2)
C(2)–C(3)	1.50(2), 1.51(4)
C(4)–C(5)	1.49(2), 1.50(3)
(*b*) Angles/°	
Bi–S(1)–C(1)	86.2(4), 85.9(7)
Bi–S(2)–C(1)	89.6(3), 89.8(7)
S(1)–C(1)–S(2)	118.1(6), 118.0(12)
S(1)–C(1)–N	121.8(7), 121.5(13)
S(2)–C(1)–N	120.1(6), 120.3(12)
C(1)–N–C(2)	123.3(8), 121.0(15)
C(1)–N–C(4)	122.5(8), 120.6(16)
C(2)–N–C(4)	114.2(9), 118.3(18)
N–C(2)–C(3)	111.7(8), 107.5(17)
N–C(4)–C(5)	113.2(8), 113.0(14)

Within the anion, the bismuth environment is found to be six-co-ordinate, each bismuth atom essentially having a pair of *cis* bidentate ligands attached and bridged by one of them from its inversion image (Table 4). As in the previous six-co-ordinate bismuth environment examined in this series, we find that one face of a

TABLE 4

Bismuth co-ordination environment in (1) and (2): $r_{\mathrm{Bi-X}}$ in Å; the remaining entries in the matrices are the angles (°) subtended by the relevant atoms at the bismuth. Primed atoms are generated by the inversion operation $(1 - x, \bar{y}, \bar{z})$

(*a*) Complex (1)

Atom	$r_{\mathrm{Bi-X}}$	I(2)	I(3)	S(1)	S(2)	I(1′)
I(1)	3.190(1)	88.01(4)	172.5(1)	93.36(6)	94.14(6)	85.62(4)
I(2)	3.091(1)		93.45(3)	150.92(6)	84.80(6)	110.32(4)
I(3)	2.965(1)			88.94(6)	93.30(5)	87.00(4)
S(1)	2.769(3)				66.12(8)	98.75(6)
S(2)	2.649(3)					164.85(6)
I(1′)	3.291(1)					

(*b*) Complex (2)

Atom	$r_{\mathrm{Bi-X}}$	I(2)	Br	S(1)	S(2)	I(1′)
I(1)	3.115(2)	89.81(6)	172.93(10)	92.37(10)	93.03(11)	85.18(5)
I(2)	3.006(2)		93.22(7)	150.12(12)	83.86(12)	111.31(7)
Br	2.813(2)			88.18(11)	93.65(11)	87.77(6)
S(1)	2.770(6)				66.27(15)	98.58(11)
S(2)	2.649(5)					164.69(12)
I(1′)	3.244(2)					

Angle Bi–I–Bi′ 94.38(3) for (1); 94.82(5)° for (2).

pseudo-octahedral co-ordination sphere is compactly occupied by the three most tightly bound ligand atoms, namely S(1,2), I(3), with S(1,2)–Bi–I(3), S(1)–Bi–S(2) being 88.94(6), 93.30(5), 66.12(8)° respectively (Figure 2). Opposed to these we find the three least tightly bound ligands occupying a less compact face [I(1), I(1′)$(1 - x, \bar{y}, \bar{z})$, I(2)] with I(1), I(1′)–Bi–I(2), I(1)–Bi–I(1′) being 88.01(4), 110.32(4), 85.62(4)°. In spite of these considerations, the presence or otherwise of a lone pair in this vicinity is *not* obvious. There is an obvious axis to the co-ordination sphere comprising I(1,3) [I–Bi–I, 172.5(1)°]. The remaining ligating atoms may be seen to occupy a plane approximately normal to this axis [I(2), S(1,2), I(1)$(1 - x, \bar{y}, \bar{z})$], the sum of the angles which they subtend at the bismuth atom being 360.0° and their deviations from a least-squares plane calculated through them being respectively 0.00, —0.01, 0.01, 0.00 Å, the bismuth deviation being —0.03 Å. Consideration of this angular geometry suggests that, in spite of the large angle observed between I(2) and I(1) $(1 - x, \bar{y}, \bar{z})$ (110.3°), and the long associated bonds, this cannot be regarded as unequivocal evidence for the presence of such a lone pair, since the small 'bite' of the dithiocarbamate ligand opposite automatically imposes such a distortion within the plane.

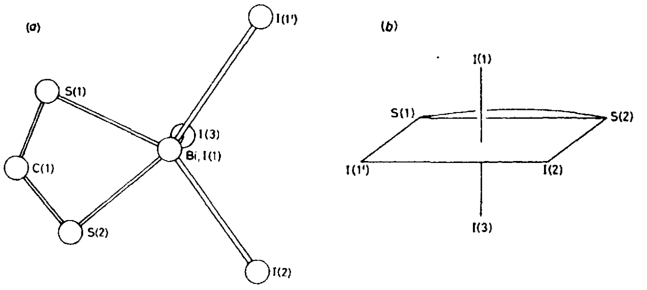

FIGURE 2 (*a*) The co-ordination environment of the bismuth atom in (1), seen in projection down the I(1)–Bi bond; (*b*) idealized stereochemistry of the bismuth environment

Complex (2).—This complex is found to be of stoicheiometry $[\mathrm{NEt_4}][\mathrm{Bi(S_2CNEt_2)I_2Br}]$; it is isostructural with (1), with Br replacing I(3), so that the complex is $[\mathrm{NEt_4}]_2[\mathrm{BrI(Et_2NCS_2)BiI_2Bi(S_2CNEt_2)BrI}]$. The bismuth–bismuth separation is 4.683(2) Å, and Bi–I–Bi is 9.482(5)°. Apart from the bromine geometry, itself, the effect of the bromide substitution is trivial and does not warrant further discussion.

[0/1048 *Received, 7th July*, 1980]

REFERENCES

[1] Part 1, C. L. Raston, G. L. Rowbottom, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1352.

[2] Part 3, C. L. Raston, G. L. Rowbottom, and A. H. White, preceding paper.