# Structural Studies of Group 5B–Halide–Dithio-ligand Complexes. Part 3.† Crystal Structure of Polymeric (*NN*-Diethyldithiocarbamato)di-iodobismuth(III)

By **Colin L. Raston, Graham L. Rowbottom, and Allan H. White,** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

The crystal structure of the title compound, $[Bi(S_2CNEt_2)I_2]$, has been determined by single-crystal *X*-ray diffraction methods at 295(1) K and refined by least-squares procedures to a conventional residual of 0.045 for 1 537 'observed' reflections. Crystals are monoclinic, space group $P2_1/c$, with $a$ = 10.673(3), $b$ = 15.001(3), $c$ = 8.149(2) Å, β = 90.86(2)°, and $Z$ = 4. The structure comprises an infinite linear polymeric array, successive bismuth atoms being bridged by a pair of iodine atoms and a ligand sulphur atom.

In reporting previous work, we have described the crystal structures and molecular geometries of $[Bi(S_2CNEt_2)_3]$ [1] and $[Bi(S_2CNEt_2)_2X]$ ($X$ = Br or I).[2] We now turn to examine structurally the next member of the series $[Bi(S_2CNEt_2)_nX_{3-n}]$, namely $[Bi(S_2CNEt_2)X_2]$. The compounds $[Bi(S_2CNEt_2)X_2]$ ($X$ = Cl, Br, or I) were prepared as described previously.[3] However, only the iodide derivative could be sufficiently well crystallized to permit structural work; this was achieved by interdiffusion of a solution of the complex in dimethylformamide with n-butanol; use of the same conditions for $X$ = Cl or Br resulted in complexes of the type $[Bi_5(S_2CNEt_2)_8X_7]$.[4]

## CRYSTALLOGRAPHY

*Crystal Data.*—$C_5H_{10}BiI_2NS_2$, $M$ = 611.0, Monoclinic, space group $P2_1/c$ ($C_{2h}^5$, no. 14), $a$ = 10.673(3), $b$ = 15.001(3), $c$ = 8.149(2) Å, β = 90.86(2)°, $U$ = 1 304.7(6) Å³, $Z$ = 4, $D_c$ = 3.11 g cm⁻³, $F(000)$ = 1 072, $\mu(Mo)$ = 179 cm⁻¹. Specimen size: 0.07 × 0.10 × 0.22 mm, $2\theta_{max.}$ = 50°, $n$ = 2 309, $n_o$ = 1 537. Values of $R$, $R'$,$S$ are 0.045, 0.052, 1.69 respectively.

Table 1 contains the non-hydrogen atom fractional cell co-ordinates; see Supplementary Publication No. SUP 22976 (9 pp.) ‡ for structure-factor amplitudes, thermal parameters, and hydrogen-atom parameters.

TABLE 1

Non-hydrogen atom fractional cell co-ordinates

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Bi | 0.220 18(7) | 0.206 49(5) | 0.771 48(8) |
| I(1) | 0.428 51(12) | 0.206 81(9) | 0.061 04(15) |
| I(2) | 0.032 84(13) | 0.152 47(9) | 1.029 23(16) |
| Dithiocarbamate ligand | | | |
| S(1) | 0.134 0(5) | 0.113 7(3) | 0.510 9(6) |
| S(2) | 0.322 2(5) | 0.048 6(3) | 0.755 1(6) |
| C(1) | 0.238 2(16) | 0.030 3(11) | 0. 574 0(19) |
| N | 0.250 6(14) | −0.043 7(9) | 0.489 1(16) |
| C(2) | 0.190(2) | −0.057(1) | 0.331(2) |
| C(3) | 0.284(2) | −0.043(2) | 0.190(2) |
| C(4) | 0.332(2) | −0.117(1) | 0.552(3) |
| C(5) | 0.261(3) | −0.183(1) | 0.654(3) |

*Abnormal Features.*—Because of twinning problems 53 reflections were deleted from the data set in the final refinement.

## DISCUSSION

The structure determination confirms the ascribed stoicheiometry as $[Bi(S_2CNEt_2)I_2]$, the formula unit being identical with the asymmetric unit (Figure 1). The structure comprises an infinite polymeric array, the backbone of which is successive bismuth atoms generated by the two-fold screw axis and spaced at 4.279(2) Å. The bridging between the bismuth atoms is more complex than in $[\{Bi(S_2CNEt_2)_2I\}_\infty]$ [2] and comprises both the iodine and one of the dithiocarbamate sulphur atoms, so that effectively the bridge is triple; the bridging sulphur link is long, however. In $[Bi(S_2CNEt_2)_2I]$, a single iodine bridge is found with the two Bi–I bonds reasonably symmetrically disposed [3.257(2), 3.354(1) Å] and Bi–I–Bi 89.68(4)°. In the present case, the co-ordination about I(1) is similarly reasonably symmetrical although the iodine atoms are more tightly bound [Bi–I 3.218(2), 3.113(2) Å] (Table 2); in spite of this Bi–I–Bi is reduced to 85.02(4)°; and Bi · · · Bi reduced from 4.662(1) to 4.279(2) Å, suggesting that the angular decrease accompanying the Bi–I decrease may be assisted by some Bi · · · Bi bonding interaction. More plausible, however, is the explanation that the angular compression is assisted by the additional, albeit less powerful, bridging effect of I(2) and S(1). The co-ordination about I(2) is less symmetrical [Bi–I 3.032(2), 3.501(2) Å], and Bi–I–Bi is still small [81.49(4)°]. The bonding to the dithiocarbamate group is similarly tight and unsymmetrical [Bi–S(1,2), 2.690(5), 2.611(5) Å]; the longer of the two bonds within the chelate is to that sulphur atom which interacts with the environment of the next bismuth atom in the chain at a distance of 3.462(5) Å. Table 3 lists the significant interspecies non-bonding contacts.

As in $[Bi(S_2CNEt_2)_2X]$, $X$ = Br or I, we find the three most tightly bound atoms [S(1,2), I(2) in this case] occupying a fairly compact triangular face of the co-ordination polyhedron [I(2)–Bi–S(1,2), S(1)–Bi–S(2), 100.8(1), 94.2(1), 68.2(2) °] and lying opposed to a sparsely co-ordinated region of the co-ordinated poly-

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† Part 2 is the preceding paper. Part 1 (ref. 2) contains general crystallographic and definitional detail.

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

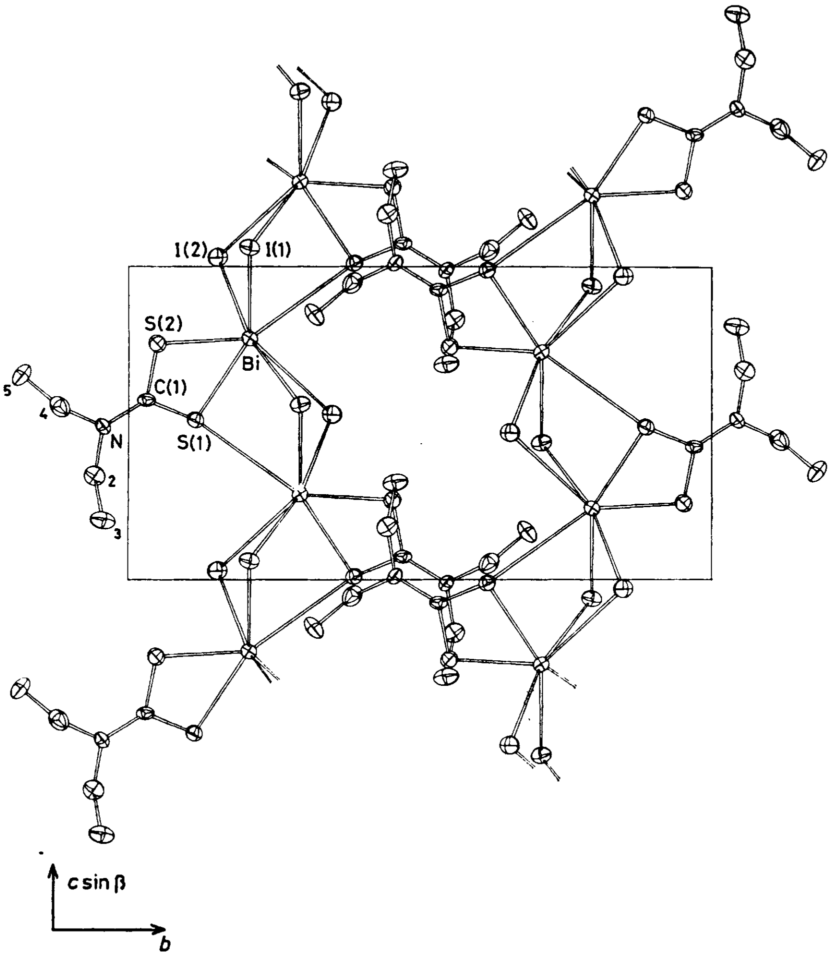

FIGURE 1 Unit-cell contents projected down *a*

TABLE 2

The bismuth environment, $r_{Bi-X}$ is in Å; the other entries in the matrix are the angles (°) subtended by the relevant atoms at the bismuth

| Atom | $r_{Bi-X}$ | I(2) | S(1) | S(2) | $S(1^I)$ | $I(1^{II})$ | $I(2^{II})$ |
|---|---|---|---|---|---|---|---|
| I(1) | 3.218(2) | 87.02(5) | 143.5(1) | 75.8(1) | 76.84(9) | 84.95(5) | 142.68(4) |
| I(2) | 3.032(2) | | 100.8(1) | 94.2(1) | 68.5(1) | 167.75(7) | 100.09(4) |
| S(1) | 2.690(5) | | | 68.2(2) | 139.2(1) | 91.1(1) | 71.4(1) |
| S(2) | 2.611(5) | | | | 148.2(1) | 92.8(1) | 139.0(1) |
| $S(1^I)$ | 3.462(5) | | | | | 100.55(8) | 72.08(8) |
| $I(1^{II})$ | 3.113(2) | | | | | | 81.00(4) |
| $I(2^{II})$ | 3.501(2) | | | | | | |

Symmetry transformations are: I $x, \frac{1}{2} - y, \frac{1}{2} + z$; II $x, \frac{1}{2} - y, z - \frac{1}{2}$.

hedron. Nevertheless, it is somewhat uncertain in the present case that the presence of a sterically active lone pair can be presumed, opposed to the tightly populated region of the co-ordination sphere. Consideration of the metal environment from the point of view of the opposed I(2) $\cdots$ I(1) ($x, \frac{1}{2} - y, z - \frac{1}{2}$) axis [I–Bi–I 167.75(7)°] shows the presence of a belt of five atoms about the bismuth atom, namely S[1,2,1 ($x, \frac{1}{2} - y, \frac{1}{2} + z$)], I(1), I(2) ($x, \frac{1}{2} - y, z - \frac{1}{2}$). The sum of the angles subtended at the bismuth is 364.1°; the deviation of the atoms from a least-squares plane through them is −0.12, −0.11, −0.37, 0.26, 0.33 Å ($\sigma$ 0.29 Å), with the bismuth deviation being −0.08 Å. The co-ordination geometry is thus pseudo-pentagonal bipyramidal (Figure 2), with the position of the lone pair doubtful; probably, if it has

TABLE 3

Interspecies non-bonding contacts:
$H \cdots I < 3.5$ Å, $H \cdots S < 3.3$ Å, $I \cdots S < 4.0$ Å

| Contact | Distance/Å |
|---|---|
| $H(3A) \cdots I(1^I)$ | 3.3(—) |
| $H(4A) \cdots I(1^{II})$ | 3.1(—) |
| $H(5B) \cdots I(2^{III})$ | 3.3(—) |
| $I(2) \cdots S(1^{IV})$ | 3.674(5) |
| $H(5C) \cdots I(1^V)$ | 3.4(—) |

Transformations of the asymmetric unit: I ($x, y, z - 1$); II ($1 - x, y - \frac{1}{2}, \frac{3}{2} - z$); III ($\bar{x}, y - \frac{1}{2}, \frac{3}{2} - z$); IV ($x, \frac{1}{2} - y, z + \frac{1}{2}$); V ($1 - x, \bar{y}, 2 - z$).

credibility, it is directed in the equatorial plane toward S(1) ($x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$), the central atom and the furthest from the bismuth of the I(1), S(1) ($x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$), I(2) ($x$, $\frac{1}{2} - y$, $z - \frac{1}{2}$) triad.

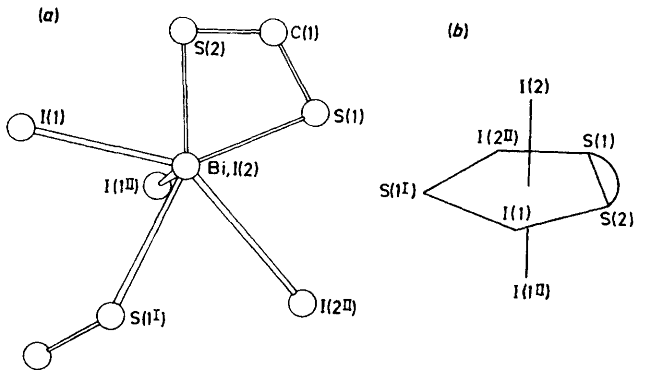

FIGURE 2 (*a*) Projection of the bismuth environment down the Bi–I(2) bond; (*b*) schematic representation of the corresponding idealized co-ordination environment

For the $S_2CNEt_2$ ligand, a least-squares plane defined by $S_2CNC_2$ has atom deviations S(1,2) C(1,2,4) N(1), −0.06, 0.06, 0.01, 0.07, −0.07, −0.01 Å (δBi 0.15 Å) (σ 0.06 Å) indicative of substantial torsion about the central C–N bond. The terminal methyl groups are disposed on either side of the ligand plane. The geometry lies very close to that of the free ion (Table 4).[2]

TABLE 4

Dithiocarbamate ligand non-hydrogen geometry. Primes denote the transformation ($x$, $\frac{1}{2} - y$, $z - \frac{1}{2}$)

(*a*) Distances/Å

| | | | |
|---|---|---|---|
| S(1)–C(1) | 1.75(2) | N–C(2) | 1.44(2) |
| S(2)–C(1) | 1.74(2) | N–C(4) | 1.49(3) |
| S(1) · · · S(2) | 1.972(7) | C(2)–C(3) | 1.55(3) |
| C(1)–N | 1.31(2) | C(4)–C(5) | 1.49(3) |

(*b*) Angles/°

| | | | |
|---|---|---|---|
| Bi–S(1)–Bi′ | 87.2(1) | S(2)–C(1)–N | 122(1) |
| Bi–S(1)–C(1) | 86.0(5) | C(1)–N–C(2) | 123(1) |
| Bi′–S(1)–C(1) | 123.4(6) | C(1)–N–C(4) | 120(1) |
| Bi–S(2)–C(1) | 88.7(6) | C(2)–N–C(4) | 117(1) |
| S(1)–C(1)–S(2) | 117.1(10) | N–C(2)–C(3) | 111(2) |
| S(1)–C(1)–N | 121(1) | N–C(4)–C(5) | 112(2) |

[0/1047 *Received, 7th July*, 1980]

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