Structural Studies of Group 5B–Halide–Dithio-ligand Complexes. Part 1.† Crystal Structures of Bis(*NN*-diethyldithiocarbamato)-iodo- and -bromo-bismuth(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 structures of the two compounds [Bi(S_2CNEt_2)$_2$I], (1), and [Bi(S_2CNEt_2)$_2$Br], (2), have been determined by single-crystal *X*-ray diffraction methods at 295(1) K and refined by least-squares procedures to conventional residuals of 0.044 and 0.040 respectively for 1 859 and 3 055 ' observed ' reflections. Crystals of (1) are monoclinic, space group $P2_1/c$, with a = 12.054(2), b = 18.444(3), c = 8.815(2) Å, β = 108.09(1)°, and Z = 4. The structure is a linear polymer with bridging iodine atoms *cis* in the co-ordination sphere of the six-co-ordinate bismuth [Bi–I, 3.257(2), 3.354(1) Å; Bi–S, 2.646(4)—2.860(5) Å]. Crystals of (2) are triclinic, space group $P\bar{1}$, with a = 14.388(7), b = 14.033(5), c = 10.297(2) Å, α = 99.56(2), β = 104.70(3), γ = 108.10(3)°, and Z = 4. The structure comprises a tetranuclear centrosymmetric unit with the bismuth atoms bridged by two- and three-co-ordinate bromine atoms.

THE chemistry of the 1 : 1 dithio-chelates of the main-group elements is less widely explored than that of the transition metals;[1,2] this is particularly so of the heavy-metal complexes, and also in regard to their structural characterization. For the dithiocarbamate complexes of the trivalent Group 5 metals, with which we shall be particularly concerned, compounds of the type [M(S_2CNR_2)$_{3-n}$X$_n$] have been synthesized and characterized for n = 0, 1, or 2 for X = Cl, Br, I, or organic radical, and M = As, Sb, or Bi. Examination of the crystal structures of [M(S_2CNR_2)$_3$] (M = As, ref. 3; M = Sb or Bi, ref. 4) shows that with the small metals there is a tendency for the metal to be unsymmetrically chelated by the three ligands, the metal point symmetry being a good approximation to C_3, and presumably so because of the presence of a stereochemically active lone pair. As the metal size increases and the capacity of achieving higher co-ordination number increases, a tendency toward centrosymmetric sulphur-bridged dimer formation is noticed, the metal in [{Bi(S_2CNEt_2)$_3$}$_2$] being pseudo-eight-co-ordinate and the lone pair less sterically active. For compounds of the type [M(S_2CNR_2)$_{3-n}$X$_n$] as above ,the structural data are sparse. The compounds [As(S_2CNEt_2)$_2$Ph] (ref. 5) and [As(S_2CNEt_2)$_2$Br] (ref. 6) have pseudo-square-pyramidal co-ordination geometries, [As(S_2CNEt_2)Br$_2$] [7] is a loosely bound centrosymmetric dimer in the solid state, while the [Sb(S_2CNEt_2)$_2$]$^+$ species has been described as a pseudo-trigonal bipyramid with an equatorial lone pair.[8]

In the above context we considered it to be of interest to examine the chemistry and structures of the mixed-ligand halide–dithiocarbamate structures more closely. We chose bismuth as the special object of the study because, on the one hand, so little is known of its co-ordination chemistry and on the other, it is potentially the most interesting of the Group 5 elements by virtue of its tendency to high co-ordination number, sterically ambivalent lone pairs, and the number of thio–halide complexes already established to be oligonuclear. Throughout the present study we have restricted ourselves to the use of the *NN*-diethyldithiocarbamate ligand, $S_2CNEt_2^-$. In the present paper we commence with the complexes [Bi(S_2CNEt_2)$_2$X] (1; X = I, 2; X = Br). The complexes [Bi(S_2CNEt_2)$_2$X], X = Cl, Br, or I, were prepared as described previously.[9,10] The bromo- and iodo-complexes were obtained as small yellow plates and needles respectively by the slow interdiffusion of a solution of the complex in dimethylformamide with n-butanol. Despite several attempts using a variety of solvent systems we were unable to obtain the chloro-complex in any crystalline form substantial enough for single-crystal *X*-ray work.

CRYSTALLOGRAPHY

The following comments are general in nature and apply to all papers in the present series. All specimens were examined photographically before mounting on the diffractometer in order to establish approximate cell dimensions and space group. Densities were determined by neutral buoyancy. Precise cell dimensions and data for structure determination purposes were obtained using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers equipped with monochromatic Mo-K_α radiation ($\lambda = 0.710\ 6_9$ Å) in a laboratory held at 295(1) K. Unique data sets were measured within a preset $2\theta_{\text{max.}}$ limit yielding n independent reflections; of these n_o with $I > 3\sigma(I)$ were considered ' observed ' and used in the structure solutions and refinements after absorption correction. Structures were solved either by standard direct methods or vector procedures. For the smaller structures refinement was by full-matrix least squares; for the larger (basically) 9 × 9 block-diagonal least squares, variations being made in some cases in order to enable refinement of the parameters of the heavy metal and its immediate environment as a single block, and, in those cases where hydrogen-atom parameter refinement was feasible, these were included in the block of the parent non-hydrogen atom. Reflection weights in the refinement were $[\sigma^2(F_o) + 0.000\,3(F_o)^2]^{-1}$. For the non-hydrogen atoms, anisotropic thermal parameters were refined except where otherwise stated {form: $\exp[-2\pi^2(U_{11}h^2a^{*2} \ldots + 2U_{23}klb^*c^*)]$}. In those cases where hydrogen-atom positions

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† This paper contains general descriptive, crystallographic, and definitional detail pertinent to all subsequent papers in the series.

could not be refined but could confidently be estimated at trigonal or tetrahedral sites, they were included as invariants. Hydrogen-atom thermal parameters throughout were restricted to isotropic estimates based on $U_H = \langle U_{ii}$ (parent non-hydrogen atom)$\rangle \times 1.5$ (methyl), $\times 1.25$ (non-methyl). The function minimized in the refinement was $\Sigma w \Delta |F|^2$ and conventional residuals R,R' are quoted on F. Least-squares planes where quoted are given in the form $pX + qY + rZ = s$ and referred to the orthogonal right-handed Å frame (X, Y, Z). Atom deviations and σ (defining atoms) are in Å. X lies parallel to a, Z in the ac plane. Computation was carried out using a local variant of the X-RAY '76 program system [11] implemented on CYBER 73 and Perkin-Elmer 8/32 computers by S. R. Hall. Neutral-atom scattering factors were employed throughout, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[12-14] Results quoted in each case comprise non-hydrogen atom co-ordinates (see Tables 1 and 2) (except where those for the hydrogen atoms are also of special significance) and non-hydrogen atom geometries (similarly); where unit-cell and molecular diagrams display thermal ellipsoids these are at the 20% probability level for the non-hydrogen atoms.

TABLE 1

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

	Ligand ' a '			Ligand ' b '		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Bi	0.217 88(6)	0.291 17(3)	0.270 44(7)			
I	0.397 08(11)	0.309 05(6)	0.062 15(14)			
Dithiocarbamate ligand						
S(1)	−0.026 1(4)	0.258 7(2)	0.174 5(6)	0.148 8(4)	0.355 4(2)	0.501 0(5)
S(2)	0.084 8(4)	0.375 9(3)	0.044 4(6)	0.353 2(4)	0.403 7(2)	0.410 3(5)
C(1)	−0.043 3(15)	0.332 8(9)	0.051 9(18)	0.268 3(13)	0.410 3(7)	0.533 6(17)
N	−0.145 2(12)	0.358 5(8)	−0.036 8(16)	0.293 8(11)	0.458 8(7)	0.651 3(15)
C(2)	−0.257 7(20)	0.323 2(13)	−0.018 8(28)	0.220 8(16)	0.468 3(9)	0.759 2(18)
C(3)	−0.296 5(23)	0.263 3(17)	−0.130 5(33)	0.136 3(18)	0.527 8(12)	0.702 9(24)
C(4)	−0.154 1(17)	0.424 3(10)	−0.136 5(25)	0.400 7(16)	0.507 2(8)	0.689 7(19)
C(5)	−0.173 8(29)	0.411 8(13)	−0.307 4(24)	0.503 3(17)	0.468 0(10)	0.792 3(20)

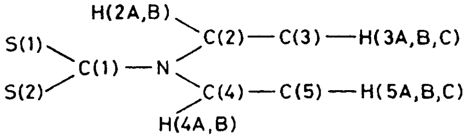
TABLE 2

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

	Ligands ' a' and ' c '			Ligands ' b' and 'd '		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Bi	0.245 11(6)	−0.116 61(5)	0.180 15(6)	0.177 15(5)	0.170 49(4)	0.080 11(6)
Br	0.080 5(1)	−0.080 5(1)	−0.029 0(2)	0.343 3(2)	0.121 2(1)	0.286 0(2)
(*a*) Dithiocarbamate ligands ' a,' ' b '						
S(1)	0.361 7(4)	−0.135 9(3)	0.413 7(4)	0.152 9(4)	−0.321 0(3)	0.070 0(5)
S(2)	0.149 9(4)	−0.140 7(4)	0.375 9(5)	0.356 6(4)	−0.210 0(4)	0.044 3(5)
C(1)	0.262(1)	−0.138(1)	0.480(1)	0.256(1)	−0.324(1)	0.015(1)
N	0.277(1)	−0.142(1)	0.613(1)	0.255(1)	−0.414(1)	−0.049(1)
C(2)	0.371(1)	−0.144(1)	0.703(1)	0.169(1)	−0.514(1)	−0.077(2)
C(3)	0.446(1)	−0.037(2)	0.791(2)	0.087(1)	−0.539(1)	−0.210(2)
C(4)	0.195(1)	−0.143(1)	0.676(2)	0.336(2) *	−0.418(2) *	−0.135(2) *
C(5)	0.123(2)	−0.253(1)	0.663(2)	0.402(2) *	−0.448(2) *	−0.049(3) *
(*b*) Dithiocarbamate ligands ' c,' ' d '						
S(1)	0.299 6(4)	0.149 0(3)	−0.075 8(4)	0.105 7(3)	0.324 7(3)	0.176 9(4)
S(2)	0.110 6(4)	0.195 0(4)	−0.171 2(4)	0.321 2(3)	0.360 6(3)	0.190 4(4)
C(1)	0.212(1)	0.170(1)	−0.207(1)	0.232(1)	0.405(1)	0.234(1)
N	0.220(1)	0.167(1)	−0.333(1)	0.262(1)	0.505(1)	0.309(1)
C(2)	0.308(1)	0.143(1)	−0.364(2)	0.186(1)	0.545(1)	0.345(2)
C(3)	0.401(2)	0.240(2)	−0.329(2)	0.155(2)	0.509(1)	0.467(2)
C(4)	0.158(2) *	0.205(2) *	−0.447(2) *	0.370(1)	0.578(1)	0.358(2)
C(5)	0.088(2) *	0.117(2) *	−0.542(3) *	0.424(2)	0.595(2)	0.509(2)

* Thermal parameters were refined isotropically; associated hydrogen atoms were not located.

Material deposited in each case as a Supplementary Publication comprises tables of structure-factor amplitudes, thermal parameters, the less important hydrogen-atom positional and thermal parameters and geometries, and least-squares planes [in this case No. SUP 22973 (28 pp.)*]. Final difference maps were computed for all structures and showed no abnormal features unless specifically mentioned. The numbering scheme (shown below) is common to all dithiocarbamate ligands defined in this series; S(1) always lies



adjacent (*cis*) to C(2). Where it is necessary to distinguish between more than one ligand, these are labelled a, b, *etc.*

Crystal Data.—(1). $C_{10}H_{20}BiIN_2S_4$, $M = 632.3$, Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 12.054(2)$, $b = 18.444(3)$, $c = 8.815(2)$ Å, $\beta = 108.09(1)°$, $U = 1\,863.0(5)$

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

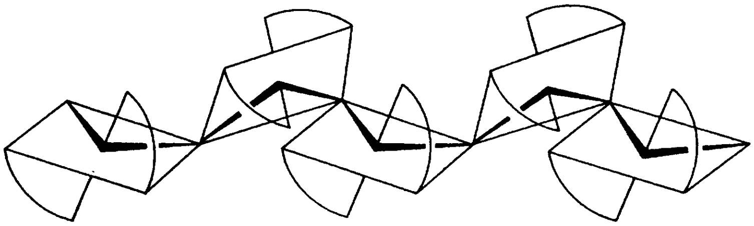
Å^3, $D_m = 2.28(1)$, $Z = 4$, $D_c = 2.25$ g cm^{-3}, $F(000) = 1\ 176$, μ(Mo) = 111 cm^{-1}. Specimen size: 0.026 × 0.075 × 0.290 mm, $2\theta_{max.} = 50°$, $n = 3\ 305$, $n_o = 1\ 859$. Values of R, R', S are 0.044, 0.045, 1.20 respectively.

(2). $C_{10}H_{20}BiBrN_2S_4$, $M = 585.4$, Triclinic, space group $P\bar{1}$(C_i^1, no. 2), $a = 14.388(7)$, $b = 14.033(5)$, $c = 10.297(2)$ Å, $\alpha = 99.56(2)$, $\beta = 104.70(3)$, $\gamma = 108.10(3)°$, $U = 1\ 842(1)$ Å^3, $D_m = 2.06(1)$, $Z = 4$, $D_c = 2.11$ g cm^{-3}, $F(000) = 1\ 104$, μ(Mo) = 115 cm^{-1}. Specimen size: 0.15 × 0.03 × 0.20 mm, $2\theta_{max.} = 45°$, $n = 4\ 823$, $n_o = 3\ 055$. Values of R, R', S are 0.040, 0.043, 1.44 respectively.

Abnormal Features.—Thermal motion on two of the ligand ethyl substituents in (2) was very high and valid anisotropic refinement was not possible; the carbon atoms concerned were refined with isotropic thermal parameters (Table 2) and unlocated hydrogen atoms. In (1), also, the high thermal motion of one of the ligand substituents precluded location of the associated hydrogen atoms and these were omitted.

DISCUSSION

Compound (1).—The structure determination confirms the ascribed stoicheiometry as [Bi(S_2CNEt_2)$_2$I], one formula unit of which comprises the asymmetric unit. The structure comprises an infinite one-dimensional polymeric array, the backbone of which is successive bismuth and iodine atoms. The spacings Bi–I are approximately regular, being 3.257(2), 3.354(1) Å alternatively (Table 3); the angles subtended at the bismuth and iodine atoms respectively in the chain are 96.09(4) and 89.68(4)°. The polymer backbone is aligned along c; the generating symmetry operation of the polymer is the associated two-fold screw axis. Successive bismuth spacings are 4.662(1) Å and successive iodine spacings 4.917(2) Å. Figures 1(a) and (b) show projections of the structure along c and a respectively; it will be evident from these that there are no close significant interchain interactions. This is borne out by the high thermal motion apparent on the polymer hydrocarbon peripheries; the only contacts with I ··· H < 3.5 Å; S ··· H < 3.0 Å are I ··· H(5B) (x, y, $z - 1$), 3.4$_2$ Å. It is of interest to compare the present structure with that of the [Sb(S_2CNEt_2)$_2$I] polymer found in the adducts of $CHCl_3$ and 0.5 I_2.[15] The angles subtended at the antimony atom in the latter are 120—127°, while those at the iodine are even more variable being 100 and 135°; this disparity is presumed to be due to differing interactions with the lattice molecules in both of the antimony adducts. In the bismuth complex no interactions are found at all at the bridging iodine atom. A schematic drawing of the polymer chain relevant to both bismuth and antimony derivatives is shown below.



The bismuth environment is six-co-ordinate, being essentially a *cis* array consisting of a pair of iodide atoms and a pair of dithio-chelate ligands. If we consider the geometry of the array as pseudo-octahedral, we find a considerable distortion imposed, as much in the angular geometry as in the necessarily variable bond lengths. One of the octahedral faces, that subtended by I, I′ (*i.e.* x, $\frac{1}{2} - y$, $\frac{1}{2} + z$), and S(a1) is considerably splayed, the associated angles, I–Bi–I′, I–Bi–S(a1), and I′–Bi–S(a1), being 96.09(4), 131.0(1), and 118.0(1)° respectively, and it is of interest that the associated bonds are the three longest in the co-ordination sphere. By contrast, the face supporting the three shortest bonds (all Bi–S; one of the dithio-chelate ligands is quite unsymmetrical) is relatively closely contracted: S(a1)–Bi–S(b1), S(a1)–Bi–S(b2), and S(b1)–Bi–S(b2) being 92.9(1), 91.7(1), and 66.5(1)°, suggesting, overall, a considerable tendency towards the conventional trigonal-pyramidal array of the trivalent Group 5 complexes, with a stereochemically active lone pair directed away from the closely co-ordinated face, *i.e.* through the face I, I′, S(a2). Alternatively, if the lone pair is regarded as comprising a co-ordination site in itself, the capped octahedron with the lone pair in the capping site is a very reasonable description (Figure 2).

TABLE 3

The bismuth environment in (1): r_{Bi-X} is in Å; the other entries in the matrix are the angles (°) subtended at the metal by the relevant atoms concerned. I′ is generated from I by the symmetry operation (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$)

Atom	r_{Bi-X}	S(a1)	S(a2)	S(b1)	S(b2)	I′
I	3.257(2)	131.0(1)	82.5(1)	142.6(1)	76.5(1)	96.09(4)
S(a1)	2.860(5)		64.7(1)	77.6(1)	135.9(1)	118.0(1)
S(a2)	2.646(4)			92.9(1)	91.7(1)	177.0(2)
S(b1)	2.698(5)				66.5(1)	86.59(9)
S(b2)	2.691(4)					85.38(9)
I′	3.354(1)					

Compound (2).—The structure determination confirms the ascribed stoicheiometry [Bi(S_2CNEt_2)$_2$Br]; the

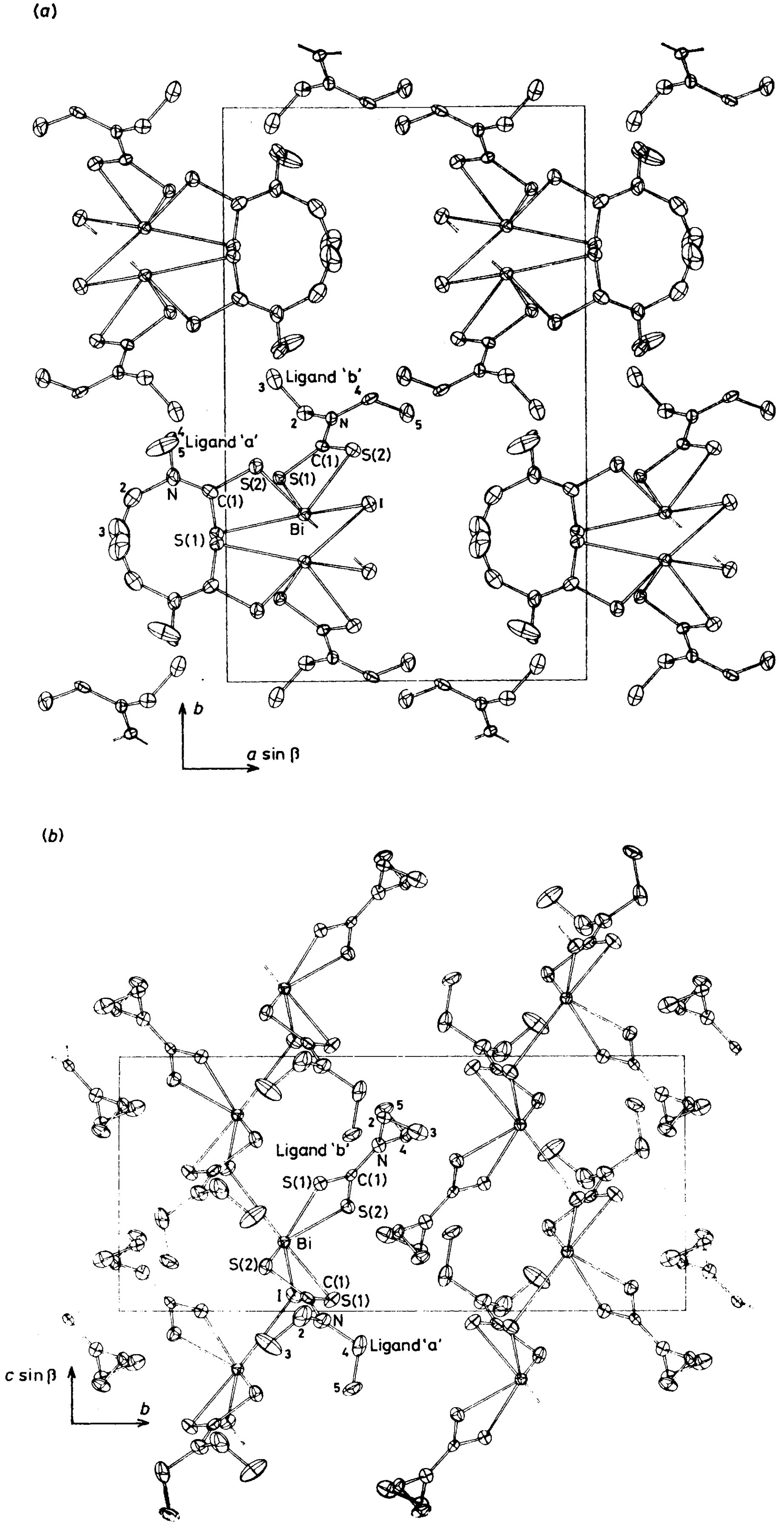


FIGURE 1 Unit-cell contents of (1) projected down *c* (*a*), and *a* (*b*)

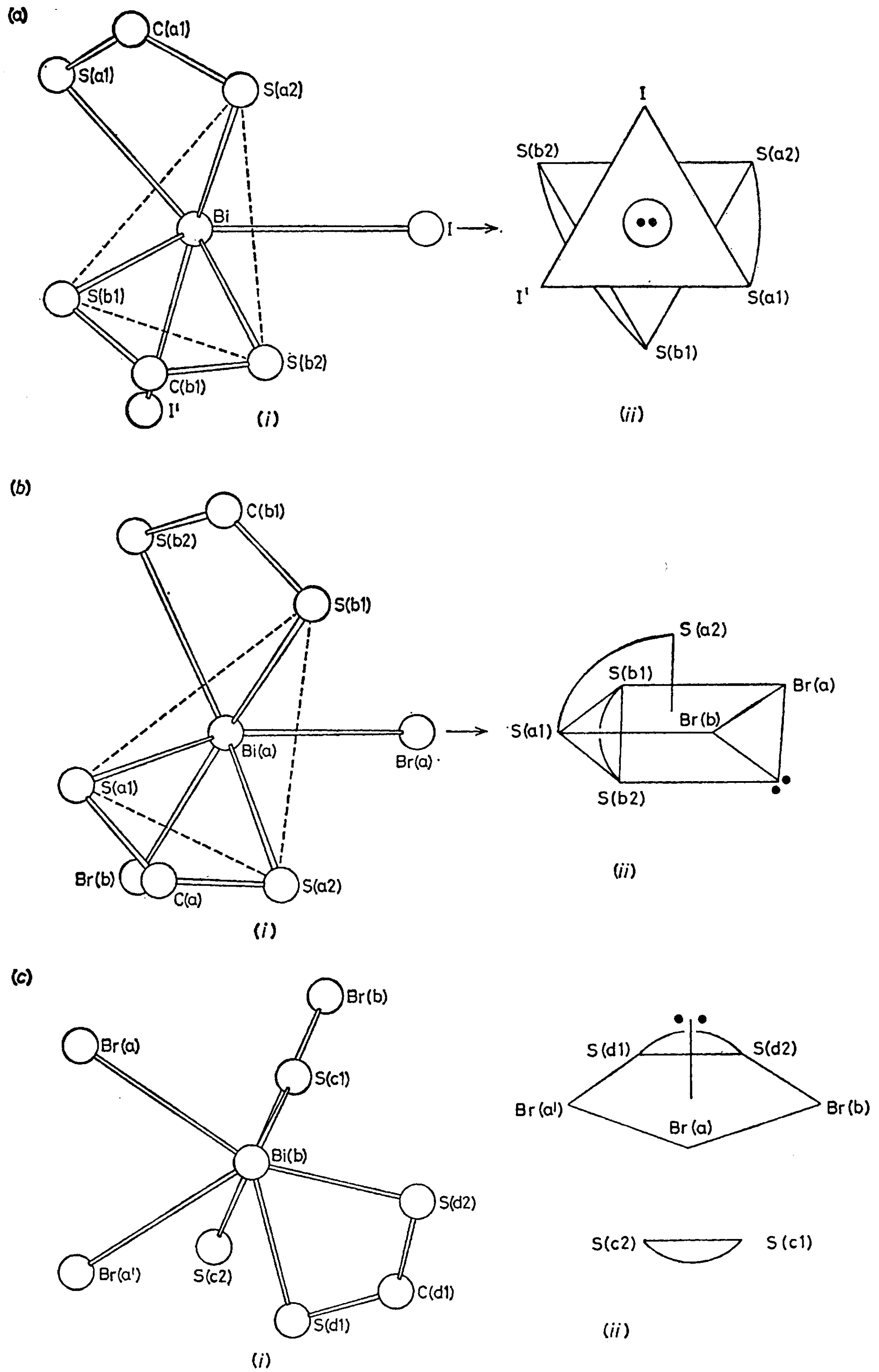


FIGURE 2 (*a*) (*i*) The bismuth environment in (1) projected down the line through the centre of the closely co-ordinated face and the bismuth atom, (*ii*) idealized capped octahedral co-ordination environment in (1); (*b*) (*i*) and (*ii*) the same for Bi(a) in structure (2); (*c*) (*i*) projection of the Bi(b) environment in (2) down a vector through the bismuth atom and the midpoint of the S(c1) · · · S(c2) line, (*ii*) idealized co-ordination geometry corresponding to (*i*)

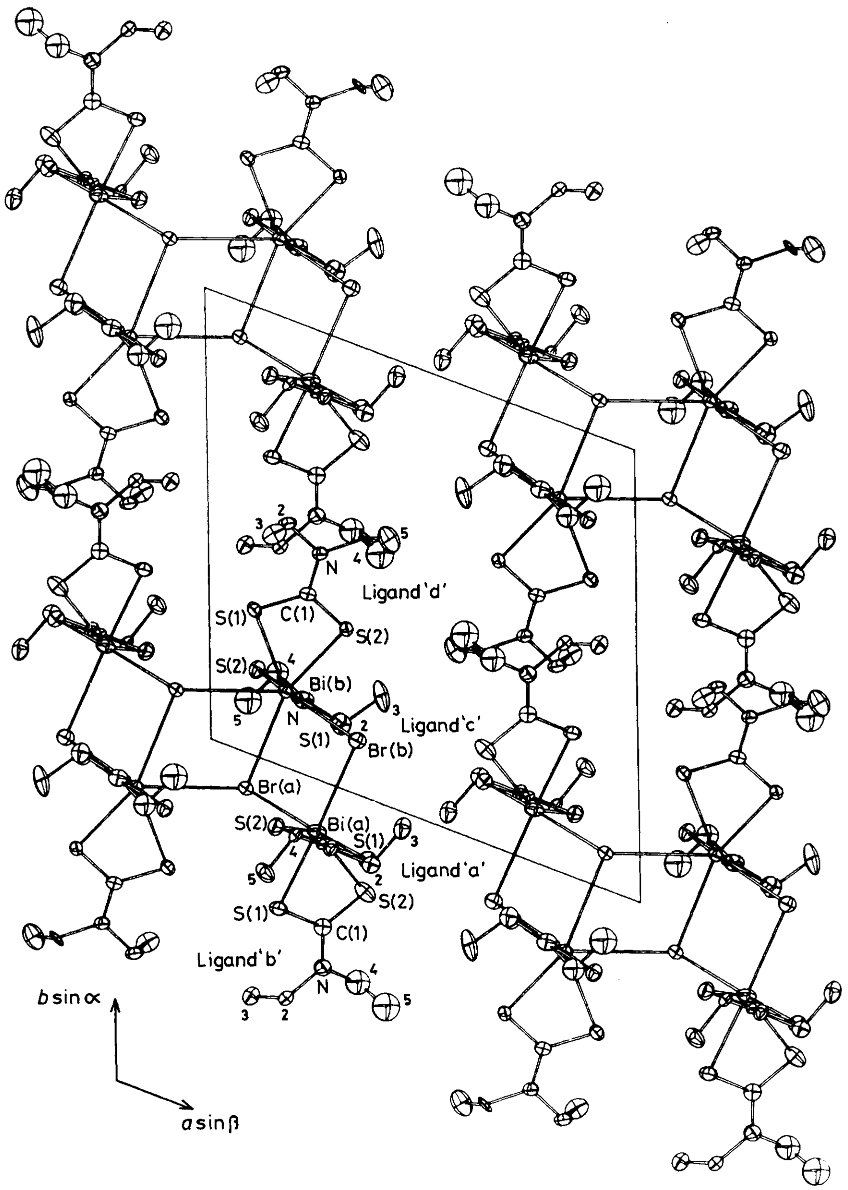


FIGURE 3 Unit-cell contents of (2) projected down *c*

asymmetric unit comprises two formula units which lie close to a crystallographic inversion centre, so that the basic unit of the structure is the tetramer $[\{Bi(S_2CNEt_2)_2Br\}_4]$ (Figure 3). The closest Bi ··· Bi distance within the tetramer is Bi(a) ··· Bi(b), 4.644(2) Å. The two independent bismuth-atom environments differ substantially as do those of the two independent bromine atoms, which bridge the bismuth atoms. One of the bromine atoms, Br(b), is two-co-ordinate [Br(b) ··· Bi(a,b), 3.066(2), 3.104(2) Å, Bi(a)–Br(b)–Bi(b) being 97.64(5)°]. The other is three-co-ordinate {Br(a) ··· Bi[a, b, b $(\bar{x}, \bar{y}, \bar{z})$]} being 3.004(2), 3.232(2), and 3.390(3) Å; the angles Bi(b)–Br(a)–Bi(b) $(\bar{x}, \bar{y}, \bar{z})$ are 96.19(5), 127.38(8), and 110.33(7)° (total: 333.8_7°) so that the bromine co-ordination is appreciably pyramidal. The bismuth atoms are each closely co-ordinated by a pair of halogen atoms *cis* in the co-ordination environment with a pair of unsymmetrical chelating dithiocarbamate ligands. The environment of Bi(a) (Table 4) is again highly irregular and the nature of the distortion from pseudo-octahedral symmetry resembles that observed in (1): the face of the co-ordination polyhedron supported by the three longest bonds, Bi–Br(a, b), and Bi–S(b2), is appreciably splayed, the relevant angles, Br(a)–Bi–Br(b), Br(a)–Bi–S(b2), and Br(b)–Bi–S(b2), being 85.27(5), 110.5(1), and 114.7(1)°. The angles subtended by the three 'opposed' short bonds, S(a1)–Bi–S(a2), S(a1)–Bi–S(b1), and S(a2)–Bi–S(b1), are 66.4(2), 93.3(1), and 87.5(2)° and again the possibility of a stereochemically active lone pair presents itself. While the above discussion is conducted in terms of the pseudo-trigonal-pyramidal co-ordination disposition suggested by (1), in both bismuth atoms in

TABLE 4

The bismuth environments in (2). A prime denotes the symmetry operation ($\bar{x}, \bar{y}, \bar{z}$)

(a) Bismuth ' a '

Atom	$r_{\text{Bi-X}}$/Å	Br(b)	S(a1)	S(a2)	S(b1)	S(b2)
Br(a)	3.004(2)	85.27(5)	163.6(1)	97.9(1)	90.8(1)	110.5(1)
Br(b)	3.066(2)		91.0(1)	94.8(1)	175.7(2)	114.7(1)
S(a1)	2.669(5)			66.4(2)	93.3(1)	85.6(2)
S(a2)	2.719(6)				87.5(2)	139.9(2)
S(b1)	2.657(4)					65.1(2)
S(b2)	2.843(7)					

(b) Bismuth ' b '

Atom	$r_{\text{Bi-X}}$/Å	Br(b)	S(c1)	S(c2)	S(d1)	S(d2)	Br(a′)
Br(a)	3.232(2)	80.89(6)	82.5(1)	93.4(1)	135.2(1)	158.2(1)	69.66(5)
Br(b)	3.104(2)		79.3(1)	146.2(1)	120.0(1)	80.5(1)	126.54(6)
S(c1)	2.716(6)			66.9(2)	136.9(1)	83.1(1)	135.79(8)
S(c2)	2.641(5)				87.4(2)	95.9(1)	80.8(1)
S(d1)	2.814(5)					65.0(1)	66.26(9)
S(d2)	2.658(4)						131.3(1)
Br(a′)	3.390(3)						

(2), there is also a clear tendency towards adopting the disposition with *2* symmetry found in *e.g.* the $[Sb(S_2CNEt_2)_2]^+$ cation in $[Sb(S_2CNEt_2)_2]_2[Cd_2I_6]$.[8] This is the more readily appreciated by consideration of the $Bi(S_2CNEt_2)_2$ systems in isolation as in Figure 4. Detailed consideration of the angular geometry about the metal in this case suggests that rather than approximating to the seven-co-ordinate capped octahedral stereochemistry, the metal environment is better described in terms of the capped trigonal prismatic array shown in Figure 2(*b*).

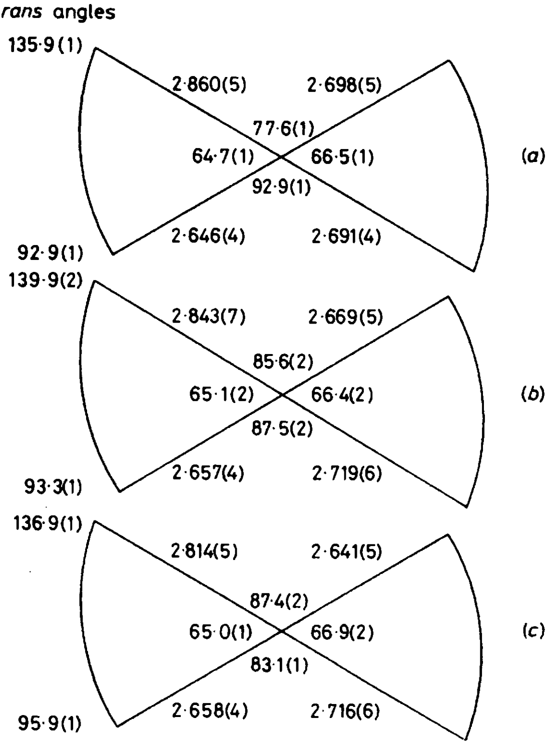


FIGURE 4 The geometry of the $Bi(S_2CNEt_2)_2$ units about the bismuth atoms of (*a*), compound (1); (*b*), compound (2) [Bi(a)]; (*c*), compound (3) [Bi(b)]

The co-ordination stereochemistry about bismuth ' b ' in (2) is even more complex and in fact quite novel; consideration of Figure 2(*c*) shows the stereochemical array of ligands to be 2 : 5, comprising a pair of sulphur atoms drawn from one of the dithiocarbamate ligands [S(c1, 2)] with, above it, a belt of five further ligands comprising the other dithiocarbamate ligand [S(d1, 2)] and three bromines [Br(a, b, a′)]. Above the five ligands and opposed to S(c1, 2) is a considerable vacancy suggesting the presence of a sterically active lone pair; if this also is counted as a co-ordination site, the stereochemistry is pseudo-eight-co-ordinate 5 : 2 : 1. Deviations of the defining atoms S(d1, 2), Br(a, b, a′) from a least-squares ' plane ' calculated through them are 0.26, —0.73, —0.63, 0.79, and 0.31 Å respectively (σ 0.65 Å), the bismuth deviation being —0.65 Å. The interligand angle sum for the plane is 362.3°.

In summary, the findings of this initial paper examining structure and stereochemistry in the bismuth(III)–halide–dithiocarbamate system foreshadows the features generally observed throughout the series: complexes of variable and irregular stereochemistries, the implied presence of lone pairs on the metal atom of variable stereochemistry, and copious potential for the formation of polymeric and oligomeric systems by way of bridging halide, and, later, dithiocarbamate groups. Before examining further bismuth systems in detail, in the next paper we turn to consider the antimony system analogous to the above, namely $[Sb(S_2CNEt_2)_2I]$, for comparison.

The NN-*Diethyldithiocarbamate Ligands of* (1) *and* (2).—In the free-ligand ion, as found in the sodium salt $Na[S_2CNEt_2]\cdot3H_2O$,[16] the (presumably) unperturbed ligand geometry has a pair of equivalent C–S bonds *ca.* 1.72 Å in length, an S_2C–N bond with a pronounced double-bond component, *ca.* 1.34 Å, and a pair of C–N distances, *ca.* 1.47 Å, the whole S_2CNC_2 system being very nearly planar. The length S · · · S is *ca.* 2.98 Å (*i.e.* 2 × 1.72 sin 60°). Among the angles, the S_2CN geometry is not significantly distorted from trigonal geometry, but the CNC_2 geometry is, the (ethyl $C)_2N$ angle being reduced substantially below the trigonal value, being *ca.* 114°. Symmetrically chelated *NN*-diethyldithiocarbamate ligands are found in a wide

TABLE 5

The dithiocarbamate ligand geometries in (1) and (2)

	(1)[a]	(2)[b]
(*a*) Distances/Å		
S(1)–C(1)	1.71(2), 1.71(2)	1.74(2), 1.73(2), 1.74(2), 1.70(1)
S(2)–C(1)	1.76(2), 1.71(2)	1.68(2), 1.71(2), 1.71(2), 1.71(2)
S(1) · · · S(2)	2.954(7), 2.955(7)	2.951(8), 2.962(8), 2.953(8), 2.945(7)
C(1)–N	1.32(2), 1.33(2)	1.34(2), 1.32(2), 1.33(2), 1.36(2)
N–C(2)	1.56(3), 1.49(3)	1.45(2), 1.47(2), 1.49(3), 1.46(3)
C(2)–C(3)	1.46(4), 1.47(3)	1.51(2), 1.46(2), 1.50(3), 1.54(3)
N–C(4)	1.48(2), 1.52(2)	1.49(2), 1.65(4), 1.56(3), 1.47(2)
C(4)–C(5)	1.47(3), 1.48(2)	1.53(2), 1.34(4), 1.35(3), 1.49(2)
(*b*) Angles/°		
Bi–S(1)–C(1)	86.1(6), 86.9(6)	87.2(5), 90.8(5), 85.9(7), 85.1(6)
Bi–S(2)–C(1)	92.3(5), 87.1(5)	86.6(6), 85.1(7), 88.9(5), 90.0(4)
S(1)–C(1)–N	124(1), 121(1)	117(1), 119(1), 122(2), 120(1)
S(2)–C(1)–N	119(1), 120(1)	123(1), 122(1), 120(1), 120(1)
S(1)–C(1)–S(2)	116.7(9), 119.3(8)	119.5(8), 118.9(10), 118.2(9), 119.3(8)
C(1)–N–C(2)	118(2), 122(1)	124(1), 123(2), 119(1), 121(1)
C(1)–N–C(4)	122(2), 123(1)	120(1), 120(1), 126(2), 122(2)
C(2)–N–C(4)	120(1), 115(1)	116(1), 115(1), 114(2), 117(1)
N–C(2)–C(3)	111(2), 111(1)	112(1), 114(2), 112(2), 113(2)
N–C(4)–C(5)	116(2), 110(1)	113(1), 101(2), 105(2), 114(2)

[a] Values are for ligands a and b respectively. [b] Values are for ligands a, b, c, and d respectively.

variety of transition-metal complexes and a survey of the general geometrical features suggests that in such complexes the above parameters are generally a good approximation, except that the angle S–C–S and associated S · · · S distances may be substantially reduced below 120°, depending on the size of the metal co-ordinated, and that the above C–N estimate may be too long by 0.01—0.02 Å and C–N–C may be a degree or two higher than above. In the sodium salt and in nearly all complexes, the terminal methyl groups lie disposed on either side of the ligand plane; in a rather few cases, they lie on the same side. Thus is defined the archetypal ligand for reference purposes in the present series of papers; in most cases, the heavy-atom component of the structure does not permit precise definition of the $CN(C_2)_2$ geometry or the associated hydrogen atoms, and we shall be primarily concerned with the sulphur atoms and their immediate environment, and the terminal methyl dispositions.

In (1), the terminal methyl disposition relative to the ligand plane is the usual one in ligand 'b' and the unusual one in ligand 'a'. There appear to be no intramolecular origin for this as the 'molecular unit' of the structure is quite uncrowded at its periphery, and apart from the polymerization, there appear to be no unusual packing forces. The remainder of the ligand 'b' dimensions are very similar to those of the free ion. However in ligand 'a' the asymmetry in the Bi–S distance is inversely reflected, as expected, in the C–S distances (Table 5), and also in the angular geometry about the carbon C(1) and the sulphur atoms. The bismuth atom lies 0.29 Å out of the S_2CNC_2 ligand 'a' plane (σ 0.03 Å) and 0.21 Å out of the corresponding ligand 'b' plane (σ 0.02 Å).

In (2), the terminal methyl dispositions are usual for ligands a—c; ligand 'd' is again abnormal in that the two terminal methyl groups lie on the same side of the ligand plane; in this case, the cause may be more clearly identified as being probably due to packing effects, as it is seen in Figure 3(*a*) that the periphery of ligand 'd' lies close to that of ligand 'b'. Deviations of the respective bismuth atoms from the planes of their associated ligands are (a—d), 0.02, 0.27, 0.22, and 0.06 Å. Ligands a and c lie almost normal to *b* and b and d almost normal to *c*.

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REFERENCES

[1] D. Coucouvanis, *Prog. Inorg. Chem.*, 1969, **11**, 233.
[2] D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 701.
[3] C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 2425.
[4] C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 791.
[5] R. Bally, *Acta Crystallogr.*, 1967, **23**, 295.
[6] R. Bally, *Compt. rend.*, 1970, **C271**, 1436.
[7] J. A. Cras, P. J. H. A. M. van de Leemput, J. Willemse, and W. P. Bosman, *Recl. Trav. Chim. Pays-Bas*, 1977, **96**, 78.
[8] P. J. H. A. M. van de Leemput, J. A. Cras, and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, 1977, **96**, 288.
[9] G. E. Manoussakis, C. A. Tsipis, and C. C. Hadjikostas, *Can. J. Chem.*, 1975, **53**, 1530.
[10] C. A. Tsipis and G. E. Manoussakis, *Inorg. Chim. Acta*, 1976, **18**, 35.
[11] 'The *X*-RAY System—Version of March, 1976,' ed. J. M. Stewart, Technical Report TR-446, Computer Science Center, University of Maryland, U.S.A.
[12] D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, **A24**, 321.
[13] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
[14] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[15] Part 2, G. McKie, C. L. Raston, G. L. Rowbottom, and A. H. White, following paper.
[16] M. Colapietro, A. Domenicano, and A. Vaciago, *Chem. Commun.*, 1968, 572.