Structural Studies of Group 5B–Halide–Dithio-ligand Complexes. Part 5.† Crystal Structures of Pentanuclear $[Bi_5(S_2CNEt_2)_8X_7]$,‡ X = Cl, Br, or I, and the Pyridinium Salt of the Tetranuclear $[Bi_4(S_2CNEt_2)_4Br_{10}]^{2-}$ Anion §

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

Recrystallization of the complexes $[Bi(S_2CNEt_2)X_2]$, X = Cl, Br, or I, from dimethylformamide–n-butanol results in the formation of $[Bi_5(S_2CNEt_2)_8X_7]$·dmf (dmf = dimethylformamide). The three complexes are isomorphous and have been characterized structurally by single-crystal *X*-ray diffraction, showing the structure to be comprised of a $[BiX_6]^{3-}$ species acting as a central bridging unit by co-ordinating to four surrounding $[Bi(S_2CNEt_2)_2]^+$ species, with an additional halide bridge preserving electroneutrality. The overall unit has crystallographically imposed *2* symmetry; the unit cell is monoclinic, space group *C2/c*, with *a ca.* 19.5, *b ca.* 20.5, *c ca.* 21.5 Å, and β *ca.* 102.5°. Recrystallization of $[Bi(S_2NCEt_2)Br_2]$ from pyridine–n-butanol results in the formation of $[NC_5H_6]_2[Bi_4(S_2CNEt_2)_4Br_{10}]$ (solvated). The complex anion has a crystallographically imposed two-fold symmetry element.

In the course of attempting recrystallization of derivatives $[Bi(S_2CNEt_2)X_2]$,[1] X = Cl, Br, or I, a variety of solvent systems were investigated. It was found that slow mixing of a solution of the complexes in dimethylformamide (dmf) with n-butanol resulted in the deposition of a new series of complexes for X = Cl or Br. The analogous iodide complex results from slow evaporation of the dimethylformamide–butanol solution of $[Bi(S_2CNEt_2)I_2]$. In view of the somewhat unexpected and incomprehensible analytical figures obtained, the structure of the chloride was determined by single-crystal *X*-ray diffraction methods, subsequently followed by the bromide and iodide analogues. The results establish the stoicheiometry of the complexes to be $[Bi_5(S_2CNEt_2)_8X_7]$·dmf, (1, X = Cl; 2, X = Br; 3, X = I) [Found: C, 19.9; H, 3.5; Bi, 42.2; Cl, 10.3; N, 4·8; S, 21.1. Calc. for $C_{43}H_{87}Bi_5Cl_7N_9OS_{16}$, (1): C, 19.4; H, 3.3; Bi, 42.2; Cl, 10.0; N, 4.5; S, 20.7%. Found: C, 18.1; H, 3.1; Bi, 36.7; Br, 19.8; N, 4.2; S, 18.0. Calc. for $C_{43}H_{87}Bi_5Br_7N_9OS_{16}$, (2): C, 18.0; H, 3.1; Bi, 36.5; Br, 19.5; N, 4.4; S, 17.9%].

Attempted recrystallization of $[Bi(S_2CNEt_2)Br_2]$ from a pyridine–n-butanol mixture by slow evaporation yielded a small quantity of fine crystalline yellow material. The stoicheiometry of this compound also has been established crystallographically as $[NC_5H_6]_2[Bi_4(S_2CNEt_2)_4Br_{10}]\cdot 2C_4H_9OH$, (4).

CRYSTALLOGRAPHY

Crystal Data.—(1). $C_{40}H_{80}Bi_5Cl_7N_8S_{16}$·dmf, *M* = 2 479.2 + 73.1, Monoclinic, space group *C2/c* (C^6_{2h}, no. 15), *a* = 19.36(2), *b* = 20.362(8), *c* = 21.14(2) Å, β = 102.68(6)°, *U* = 8 128(9) Å^3, *Z* = 4, D_c = 2.03 (without solvent), 2.09 g cm^{-3} (with solvent), *F*(000) = 4 824, μ(Mo) = 110 cm^{-1}. Specimen size: 0.30 × 0.25 × 0.20 mm, $2\theta_{max.}$ = 40°, *n* = 3 814, n_o = 3 419. Values of *R*, *R′*, *S* are 0.076, 0.087, 1.91 respectively.

(2). $C_{43}H_{87}Bi_5Br_7N_9OS_{16}$, *M* = 2 863.5, symmetry as for (1), *a* = 19.443(8), *b* = 20.685(10), *c* = 21.366(7) Å, β = 102.45(4)°, *U* = 8 391(7) Å^3, D_m = 2.27(1), *Z* = 4, D_c = 2.27 g cm^{-3}, *F*(000) = 5 328, μ(Mo) = 138 cm^{-1}. Specimen size: 0.28 × 0.28 × 0.12 mm, $2\theta_{max.}$ = 50°, *n* = 5 266, n_o = 3 127. Values of *R*, *R′*, *S* are 0.043, 0.047, 1.43 respectively.

(3). $C_{43}H_{87}Bi_5I_7N_9OS_{16}$, *M* = 3 192.5, symmetry as for (1), *a* = 19.64(1), *b* = 21.15(1), *c* = 21.82(1) Å, β = 102.19(4)°, *U* = 8 860(10) Å^3, D_m = 2.37(1), *Z* = 4, D_c = 2.39 g cm^{-3}, *F*(000) = 5 832, μ(Mo) = 122 cm^{-1}. Specimen size: 0.19 × 0.08 × 0.08 mm, $2\theta_{max.}$ = 50°, *n* = 5 592, n_o = 2 405. Values of *R*, *R′*, *S* are 0.059, 0.058, 1.51 respectively.

(4). $[NC_5H_6]_2[Bi_4(S_2CNEt_2)_4Br_{10}]\cdot 2C_4H_9OH \equiv C_{38}H_{72}Bi_4Br_{10}N_6O_2S_8$, *M* = 2 536.5, Monoclinic, space group *C2/c* (C^6_{2h}, no. 15), *a* = 23.70(1), *b* = 13.81(1), *c* = 29.32(2) Å, β = 121.95(5)°, *U* = 8 142(12) Å^3, *Z* = 4, D_c = 2.07 g cm^{-3}, *F*(000) = 4 672, μ(Cu) = 229 cm^{-1}. Specimen size: 0.10 × 0.20 × 0.04 mm, $2\theta_{max.}$ = 100°, *n* = 3 892, n_o = 1 731. Values of *R*, *R′*, *S* are 0.12, 0.14, 5.7 respectively.

Abnormal Features.—Specimens of complexes (2) and (3) were relatively small and did not diffract strongly. The data accordingly were rather weak, and refinement somewhat problematical because of high thermal motion on the ligand peripheries and solvent and some disorder in the latter. Thermal motion of some peripheral and solvent atoms was refined isotropically; while it was considered worthwhile to locate ligand hydrogen atoms in (2), this was possible only for some of the ligands (see Table 1).

The problem of collecting useful data for compound (4) was so acute that recourse was made to the use of nickel-filtered copper radiation. Only the atoms of the anion core could be successfully defined and refined with meaningful positional parameters (Table 2). The cation and solvent molecules, although observable in difference maps, would not refine smoothly in respect of all atoms and eventually they were constrained, the cation being refined as a rigid body. Atomic co-ordinates for these are deposited (see below).

Unit-cell diagrams are not given because of the size of the systems.

Tables of structure-factor amplitudes, thermal parameters, hydrogen-atom parameters, and least-squares

---

† Part 4 is ref. 8. Part 1 (ref. 7) contains general descriptive crystallographic and definitional material.

‡ μ-Halogeno-μ$_4$-hexahalogenobismuthato(III)-tetrakis[bis(diethyldithiocarbamato)bismuth(III)].

§ Di-μ-bromo-tetra-μ$_3$-bromo-tetrakis[bromo(diethyldithiocarbamato)bismuthate(III)].

TABLE 1

Non-hydrogen atom co-ordinates

Atom	(1)			(2)			(3)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
(*a*) Bi(1) and associated ligands									
Bi(1)	0.104 68(8)	0.072 82(7)	0.203 89(7)	0.107 30(4)	0.073 59(4)	0.202 72(4)	0.110 26(8)	0.075 31(8)	0.201 64(7)
X(1)	0.000 0(—)	−0.003 8(8)	0.250 0(—)	0.000 0(—)	−0.010 5(2)	0.250 0(—)	0.000 0(—)	−0.019 0(2)	0.250 0(—)
(*i*) Dithiocarbamate ligand ' a '									
S(1)	0.107 7(5)	0.124 4(5)	0.082 7(5)	0.108 3(3)	0.124 1(2)	0.081 3(2)	0.110 8(5)	0.124 0(5)	0.081 9(4)
S(2)	0.087 0(6)	−0.014 6(5)	0.111 9(5)	0.090 3(3)	−0.012 8(2)	0.112 0(3)	0.095 7(6)	−0.010 2(5)	0.112 8(5)
C(1)	0.102(2)	0.046(2)	0.056(2)	0.099 5(9)	0.046 4(9)	0.057 2(8)	0.102(2)	0.049(2)	0.058(2)
N	0.102(1)	0.028(1)	−0.006(1)	0.098 7(9)	0.028 3(7)	−0.003 4(8)	0.099(2)	0.029(1)	−0.003(1)
C(2)	0.090(2)	0.079(2)	−0.063(2)	0.094(1)	0.078(1)	−0.060(1)	0.092(2)	0.080(2)	−0.060(2)
C(3)	0.168(3)	0.090(3)	−0.056(3)	0.161(2)	0.092(1)	−0.060(1)	0.167(3)	0.094(2)	−0.063(2)
C(4)	0.096(2)	−0.039(2)	−0.024(2)	0.094(1)	−0.039(1)	−0.025(1)	0.102(2)	−0.039(2)	−0.024(2)
C(5)	0.169(3)	−0.068(3)	−0.022(2)	0.167(1)	−0.068(1)	−0.018(1)	0.174(2)	−0.067(2)	−0.013(2)
(*ii*) Dithiocarbamate ligand ' b'									
S(1)	0.244 3(5)	0.064 6(6)	0.206 5(5)	0.245 8(3)	0.068 9(3)	0.207 6(3)	0.248 0(5)	0.075 9(5)	0.209 8(5)
S(2)	0.174 1(6)	−0.019 4(6)	0.287 2(6)	0.177 4(3)	−0.015 4(3)	0.284 8(3)	0.182 9(6)	−0.010 6(6)	0.282 2(6)
C(1)	0.246(2)	0.005(2)	0.265(2)	0.251 4(11)	0.008 3(11)	0.262 9(11)	0.257(2)	0.022(2)	0.265(2)
N	0.314(2)	−0.021(2)	0.288(2)	0.314 6(9)	−0.015 5(13)	0.291 6(12)	0.321(2)	−0.020(2)	0.289(2)
C(2)	0.383(3)	−0.015(3)	0.260(2)	0.384(1)	−0.005(2)	0.265(1)	0.392(2)	−0.006(2)	0.258(2)
C(3)	0.404(4)	0.035(4)	0.307(4)	0.415(2)	0.036(2)	0.309(2)	0.417(3)	0.046(3)	0.307(2)
C(4)	0.317(—)	−0.052(—)	0.355(—)	0.320(2)	−0.090(1)	0.335(1)	0.324(3)	−0.080(3)	0.333(3)
C(5)	0.317(—)	−0.107(—)	0.342(—)	0.337(2)	−0.056(2)	0.388(2)	0.340(3)	−0.051(3)	0.388(2)
(*b*) Bi(2) and associated ligands									
Bi(2)	−0.001 99(8)	0.265 34(8)	0.052 44(7)	−0.000 83(4)	0.263 31(4)	0.050 96(4)	0.000 88(8)	0.261 49(8)	0.048 90(7)
(*i*) Dithiocarbamate ligand ' a '									
S(1)	0.120 3(6)	0.262 3(5)	0.004 9(5)	0.123 5(3)	0.260 3(3)	0.005 5(3)	0.125 0(5)	0.257 1(6)	0.005 3(5)
S(2)	0.015 1(6)	0.367 5(5)	−0.017 1(6)	0.016 7(3)	0.362 9(3)	−0.018 6(3)	0.019 6(6)	0.359 4(5)	−0.019 7(5)
C(1)	0.096(2)	0.333(2)	−0.030(2)	0.094 9(10)	0.331 8(9)	−0.030 1(9)	0.100(2)	0.328(2)	−0.031(2)
N	0.130(2)	0.363(1)	−0.068(1)	0.129 9(8)	0.361 6(7)	−0.067 4(8)	0.137(2)	0.355(1)	−0.066(1)
C(2)	0.195(2)	0.337(2)	−0.084(2)	0.198(1)	0.334(1)	−0.081(1)	0.205(2)	0.326(2)	−0.074(2)
C(3)	0.184(2)	0.293(2)	−0.140(2)	0.189(1)	0.287(1)	−0.134(1)	0.190(2)	0.286(2)	−0.128(2)
C(4)	0.101(3)	0.426(3)	−0.106(3)	0.106(1)	0.419(1)	−0.102(1)	0.110(2)	0.414(2)	−0.102(2)
C(5)	0.126(3)	0.491(3)	−0.071(2)	0.136(2)	0.480(1)	−0.069(1)	0.148(2)	0.473(2)	−0.067(2)
(*ii*) Dithiocarbamate ligand ' b '									
S(1)	−0.064 7(6)	0.199 7(6)	−0.050 8(6)	−0.061 6(3)	0.197 2(3)	−0.050 8(3)	−0.056 9(6)	0.195 7(5)	−0.050 8(5)
S(2)	−0.141 1(6)	0.299 9(6)	0.008 8(5)	−0.137 7(3)	0.295 5(3)	0.008 1(3)	−0.135 7(5)	0.288 9(6)	0.005 5(5)
C(1)	−0.140(2)	0.242(2)	−0.055(2)	−0.138 8(10)	0.243 2(10)	−0.053 8(9)	−0.133(2)	0.241(2)	−0.051(2)
N	−0.197(2)	0.238(2)	−0.101(2)	−0.191 6(8)	0.235 8(8)	−0.102 5(8)	−0.186(2)	0.231(1)	−0.102(1)
C(2)	−0.197(2)	0.190(2)	−0.157(2)	−0.190(1)	0.194(1)	−0.162(2)	−0.183(3)	0.188(2)	−0.156(2)
C(3)	−0.251(3)	0.143(3)	−0.151(3)	−0.242(2)	0.145(2)	−0.155(2)	−0.236(3)	0.137(3)	−0.147(3)
C(4)	−0.258(2)	0.284(2)	−0.110(2)	−0.250(1)	0.280(1)	−0.109(1)	−0.250(2)	0.279(2)	−0.111(2)
C(5)	−0.243(3)	0.349(2)	−0.144(2)	−0.240(1)	0.341(1)	−0.142(1)	−0.231(2)	0.334(2)	−0.137(2)
(*c*) Bi(3) and associated halogen atoms									
Bi(3)	0.000 00(—)	0.253 63(10)	0.250 00(—)	0.000 00(—)	0.256 24(5)	0.250 00(—)	0.000 00(—)	0.260 89(10)	0.250 00(—)
X(31)	0.050 3(5)	0.159 8(5)	0.339 1(5)	0.053 6(1)	0.158 3(1)	0.341 8(1)	0.058 6(1)	0.156 4(1)	0.344 8(1)
X(32)	0.122 1(6)	0.239 7(6)	0.210 9(5)	0.128 3(1)	0.242 4(1)	0.206 3(1)	0.135 8(1)	0.249 0(1)	0.202 4(1)
X(33)	0.037 5(7)	0.350 8(5)	0.341 0(5)	0.040 9(1)	0.356 4(1)	0.343 0(1)	0.047 1(2)	0.364 6(1)	0.347 0(1)
(*d*) Solvent									
C(1)	0.500(—)	0.265(4)	0.250(—)	0.500(—)	0.296(4)	0.250(—)	0.500(—)	0.264(3)	0.250(—)
C(2)	0.480(3)	0.222(3)	0.297(3)	0.492(2)	0.242(2)	0.285(2)	0.489(5)	0.194(3)	0.277(4)
C(3)	0.500(—)	0.157(7)	0.250(—)	0.482(2)	0.167(2)	0.280(2)			

TABLE 2

Anion co-ordinates in (4)

Atom	Section *n* = a			Section *n* = b		
	x	*y*	*z*	*x*	*y*	*z*
Bi(*n*)	0.001 1(2)	0.117 4(3)	0.175 2(2)	−0.099 6(2)	0.424 7(3)	0.177 2(2)
Br(*n*)	0.122 6(4)	0.062 6(6)	0.178 7(3)	−0.212 6(3)	0.485 1(6)	0.185 9(3)
Br(*n*1)	0.000 0(—)	−0.058 6(9)	0.250 0(—)	0.000 0(—)	0.600 0(8)	0.250 0(—)
Br(*n*2)	−0.123 7(3)	0.190 0(5)	0.183 1(3)	0.032 5(3)	0.354 2(5)	0.179 8(3)
S(*n*1)	−0.068 5(16)	−0.024 5(23)	0.103 2(11)	−0.125 8(14)	0.563 0(21)	0.102 9(11)
S(*n*2)	−0.056 9(16)	0.181 0(26)	0.071 9(10)	−0.178 6(13)	0.361 5(21)	0.076 2(11)
C(*n*1)	−0.091 0(—)	0.059 5(—)	0.050 2(—)	−0.176 4(—)	0.481 1(—)	0.052 4(—)
N(*n*)	−0.130 4(—)	0.035 7(—)	−0.001 3(—)	−0.210 4(—)	0.505 1(—)	0.000 6(—)
C(*n*2)	−0.157 7(—)	−0.063 3(—)	−0.017 8(—)	−0.207 2(—)	0.603 9(—)	−0.017 5(—)
C(*n*3)	−0.093 2(—)	−0.146 3(—)	−0.006 7(—)	−0.152 5(—)	0.663 4(—)	0.004 0(—)
C(*n*4)	−0.149 0(—)	0.106 9(—)	−0.044 8(—)	−0.253 2(—)	0.434 1(—)	−0.041 6(—)
C(*n*5)	−0.084 8(—)	0.097 6(—)	−0.046 7(—)	−0.194 9(—)	0.370 7(—)	−0.056 0(—)

planes for (1)—(4) are in Supplementary Publication No. SUP 22979 (69 pp.).*

DISCUSSION

Complexes (1), (2), *and* (3).—The structure determinations establish the three complexes to be isomorphous and their stoicheiometry to be $[Bi_5(S_2CNEt_2)_8X_7]\cdot$dmf, X = Cl, Br, or I, with a dimethylformamide solvent molecule per pentanuclear unit. The solvent molecule is ill defined and disordered about a crystallographic two-fold rotor with high thermal motion and may not be fully populated. Because of this and the high thermal motion generally at the molecular peripheries and the small crystal sizes, the precision of the three determinations is not high as a result of the limited extent and intensity of the data.

---

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

The pentanuclear species lies about a crystallographic two-fold axis, and contains three independent bismuth atoms all of which have different co-ordination environments (Figure 1). The central bismuth atom of the oligomer lies on the two-fold axis and is surrounded by an array of halide ions exclusively. The bismuth–halogen distances for this bismuth, Bi(3), differ only trivially, although there are very pronounced deviations from octahedral geometry in the $[\mathrm{BiX_6}]^{3-}$ array. The mean Bi(3)–Cl distance is 2.71 Å, and appears to be a 'standard' octahedral $\mathrm{Bi^{III}}$–Cl distance, being comparable, *e.g.* with the unperturbed 'equatorial' Bi–Cl distance observed in $[\mathrm{BiCl_5(py)}]^{2-}$ (py = pyridine) (ref. 2, 2.70 Å), or the $[\mathrm{BiCl_6}]^{3-}$ species itself [2.66(1) Å].[3] All of the chlorine atoms have other interactions with neighbouring bismuth atoms; these are very variable in nature [Cl(31) has two contacts at 3.43(1), Cl(32) one at 3.42(1), and Cl(33) one at 3.04(1) Å] and, in view of this, show surprisingly little variation in their Bi(3)–Cl bond lengths. The mean Bi(3)–Br, I distances, 2.8_6, 3.0_7 Å respectively, are similar to those observed in $[\mathrm{NMe_2H_2}]_3[\mathrm{BiBr_6}]$,[4] 2.84 Å, and $[\mathrm{Rb_5I(I_3)}][\mathrm{BiI_6}]\cdot\mathrm{2H_2O}$,[5] 3.07 Å.

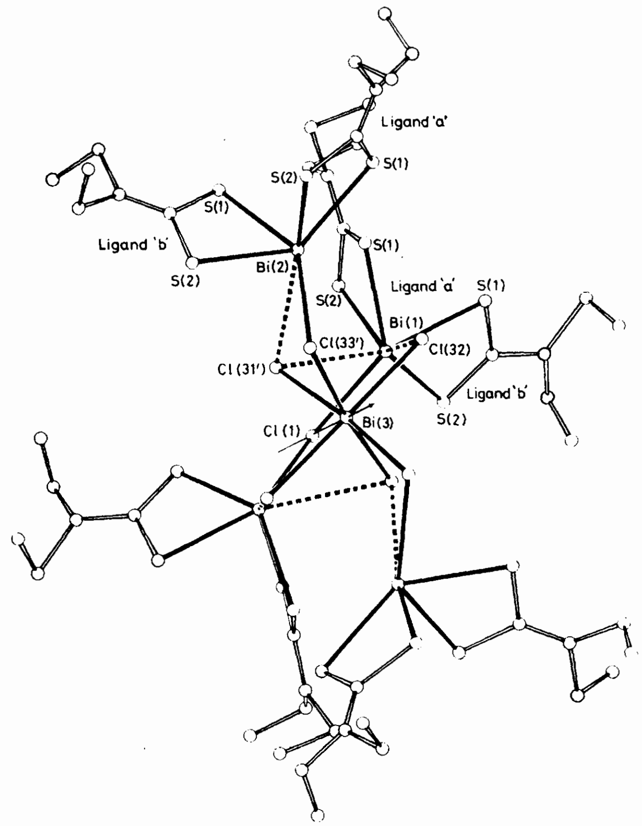

FIGURE 1 The pentanuclear $[\mathrm{Bi_5(S_2CNEt_2)_8Cl_7}]$ unit of (1)

The peripheral bismuth atoms have different environments (Table 3). Each has a pair of dithiocarbamate ligands co-ordinated (to a first approximation) quasi-symmetrically. The Bi(2) atom has two other longer halide contacts, *e.g.* to Cl (31, 3) [3.42(1), 3.04 (1) Å], in the chloride complex, bridging it to Bi(3), so that its co-ordination environment may be regarded as that of [Bi(bidentate)$_2$(bidentate′)]. Atom Bi(1) has two long halide contacts, *e.g.* to Cl (31, 2) [3.43(1), 3.42(1) Å], in the chloride complex also bridging it to Bi(3); there is a much stronger bond [to Cl(1) in the chloride complex, at 2.89(1) Å] bridging it to its two-fold rotation image, with the halide labelled (1) lying on the two-fold axis. The complex overall may thus be regarded as $[\mathrm{Bi(S_2CNEt_2)_2}]_4$-$[\mathrm{BiX_6}]$, with the additional latter halide ion X(1) making up the electroneutrality of the system. In formulating the complex in this manner, comparison is invited with the antimony derivative $[\mathrm{Sb(S_2CNBu^n{}_2)_2}]_2[\mathrm{Cd_2I_6}]$ [6] which has a rather more definitively ionic formulation; in the present compound Bi(2) is the atom likely to most nearly resemble the antimony species, and we use the geometry of the Bi(2) atom in the iodide complex (3) for comparison. The comparative geometries are given in Figure 2. The similarity is striking; the overall (non-crystallographic) point symmetry of the $[\mathrm{Sb(S_2CNBu^n{}_2)_2}]^+$ species is approximately *2*, the chief disparity lying in the difference of 0.05 Å between the two long Sb–S distances. The geometry found for Bi(2) in (3) has not quite as exact a correspondence to *2* symmetry, but nevertheless comparable to the antimony geometry, the geometry for Bi(1) being rather further removed. In both Bi(2) and Bi(1) an angular discrepancy is found. In the antimony derivative the $[\mathrm{Cd_2I_6}]^{2-}$ groups link

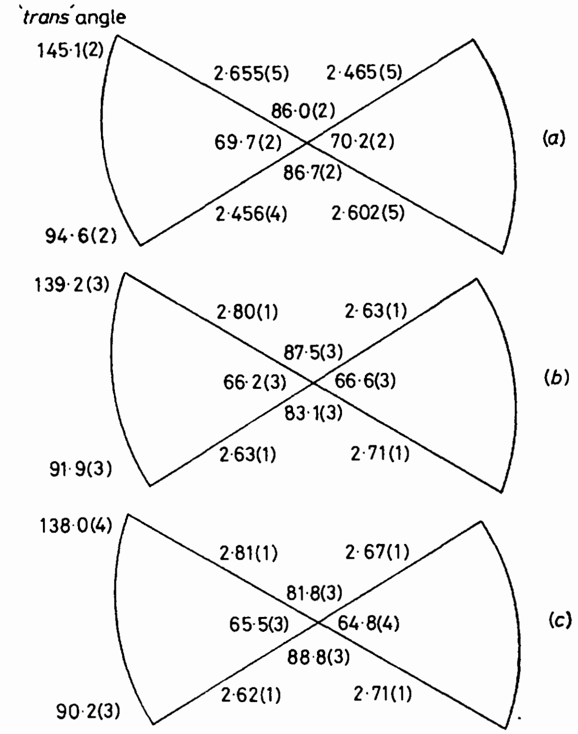

FIGURE 2 Co-ordination geometries of (*a*) Sb in $[\mathrm{Sb(S_2CNBu^n{}_2)_2}]_2$-$[\mathrm{Cd_2I_6}]$ (ref. 4); (*b*) Bi(2) of compound (3); (*c*) Bi(1) of compound (3)

TABLE 3

The bismuth environments in (1), (2), and (3): $r_{\mathrm{Bi-X}}$ is in Å; the other entries in the matrices are the angles (°) subtended at the bismuth by the relevant atoms at the head of each row and column. Primed atoms are generated by the two-fold symmetry operation (x, y, $\frac{1}{2} - z$)

(*a*) Bi(1)

(*i*) Compound (1)

	$r_{\mathrm{Bi-X}}$	Cl(32)	S(1a1)	S(1a2)	S(1b1)	S(1b2)	Cl(31′)
Cl(1)	2.89(1)	126.3(3)	132.2(2)	84.0(3)	137.1(3)	72.1(3)	74.4(3)
Cl(32)	3.42(1)		69.0(3)	135.1(3)	88.4(3)	129.0(3)	64.5(3)
S(1a1)	2.78(1)			66.2(3)	79.6(3)	138.6(3)	75.8(3)
S(1a2)	2.60(1)				86.5(3)	88.7(3)	101.0(3)
S(1b1)	2.70(1)					66.0(3)	148.4(3)
S(1b2)	2.72(1)						143.9(3)
Cl(31′)	3.43(1)						
[Cl(31)	3.71(1)]						

(*ii*) Compound (2)

	$r_{\mathrm{Bi-X}}$	Br(32)	S(1a1)	S(1a2)	S(1b1)	S(1b2)	Br(31′)
Br(1)	3.050(2)	130.06(6)	131.4(1)	82.5(1)	136.2(1)	71.4(1)	75.09(7)
Br(32)	3.515(3)		68.0(1)	133.9(1)	85.6(1)	128.6(1)	66.73(5)
S(1a1)	2.800(5)			65.9(2)	80.9(2)	138.8(2)	75.4(1)
S(1a2)	2.604(5)				88.2(2)	88.9(2)	100.2(1)
S(1b1)	2.673(5)					65.6(2)	148.7(1)
S(1b2)	2.700(6)						143.8(1)
Br(31′)	3.533(3)						
[Br(31)	3.785(3)]						

(*iii*) Compound (3)

	$r_{\mathrm{Bi-X}}$	I(32)	S(1a1)	S(1a2)	S(1b1)	S(1b2)	I(31′)
I(1)	3.278(3)	134.37(8)	130.9(2)	80.9(3)	135.2(3)	71.1(3)	75.76(8)
I(32)	3.706(4)		67.3(2)	132.8(2)	82.0(3)	127.4(2)	69.68(7)
S(1a1)	2.81(1)			65.5(3)	81.8(3)	138.0(4)	75.7(2)
S(1a2)	2.62(1)				90.2(3)	88.8(3)	99.6(2)
S(1b1)	2.67(1)					64.8(4)	148.9(3)
S(1b2)	2.71(1)						144.1(3)
I(31′)	3.680(3)						
[I(31)	3.882(3)]						

(*b*) Bi(2)

(*i*) Compound (1)

	$r_{\mathrm{Bi-X}}$	S(2a2)	S(2b1)	S(2b2)	Cl(31′)	Cl(33′)
S(2a1)	2.77(1)	65.7(3)	87.9(3)	137.6(3)	127.7(3)	129.2(3)
S(2a2)	2.61(1)		91.7(4)	80.9(3)	165.0(3)	92.2(3)
S(2b1)	2.62(1)			67.0(3)	95.3(3)	140.4(4)
S(2b2)	2.74(1)				89.7(3)	74.8(3)
Cl(31′)	3.42(1)					73.9(3)
Cl(33′)	3.04(1)					

(*ii*) Compound (2)

	$r_{\mathrm{Bi-X}}$	S(2a2)	S(2b1)	S(2b2)	Br(31′)	Br(33′)
S(2a1)	2.793(6)	65.8(2)	88.2(2)	138.6(2)	128.1(1)	128.4(1)
S(2a2)	2.606(6)		91.7(2)	81.5(2)	164.9(1)	90.6(2)
S(2b1)	2.624(6)			67.2(2)	94.4(1)	140.0(1)
S(2b2)	2.704(6)				88.2(1)	73.7(1)
Br(31′)	3.469(3)					75.91(7)
Br(33′)	3.194(3)					

(*iii*) Compound (3)

	$r_{\mathrm{Bi-X}}$	S(2a2)	S(2b1)	S(2b2)	I(31′)	I(33′)
S(2a1)	2.80(1)	66.2(3)	87.5(3)	139.2(3)	128.8(2)	128.9(2)
S(2a2)	2.63(1)		91.9(3)	83.1(3)	164.2(3)	88.1(3)
S(2b1)	2.63(1)			66.6(3)	93.7(3)	139.1(3)
S(2b2)	2.71(1)				85.7(2)	72.8(2)
I(31′)	3.582(3)					78.0(1)
I(33′)	3.421(4)					

(*c*) Bi(3)

(*i*) Compound (1)

	$r_{\mathrm{Bi-X}}$	Cl(32)	Cl(33)	Cl(31′)	Cl(32′)	Cl(33′)
Cl(31)	2.71(1)	86.2(3)	91.2(3)	90.3(3)	85.3(3)	174.4(4)
Cl(32)	2.68(1)		100.2(4)	85.3(3)	167.9(4)	88.6(4)
Cl(33)	2.74(1)			174.4(4)	88.6(4)	87.7(3)
Cl(31′)	2.71(1)				86.2(3)	91.2(3)
Cl(32′)	2.68(1)					100.2(4)
Cl(33′)	2.74(1)					

TABLE 3 (*continued*)

(*ii*) Compound (2)

	r_{Bi-X}	Br(32)	Br(33)	Br(31′)	Br(32′)	Br(33′)
Br(31)	2.855(2)	86.45(7)	91.75(7)	89.65(7)	85.41(7)	174.8(2)
Br(32)	2.860(3)		99.65(7)	85.41(6)	168.52(7)	88.68(8)
Br(33)	2.862(3)			174.8(1)	88.68(7)	87.30(7)
Br(31′)	2.855(2)				86.45(7)	91.75(7)
Br(32′)	2.860(3)					99.65(7)
Br(33′)	2.862(3)					

(*iii*) Compound (3)

	r_{Bi-X}	I(32)	I(33)	I(31′)	I(32′)	I(33′)
I(31)	3.079(3)	86.59(8)	91.96(9)	88.28(10)	86.67(8)	175.5(2)
I(32)	3.070(3)		97.81(9)	86.67(8)	170.6(2)	88.96(8)
I(33)	3.053(3)			175.5(2)	88.96(9)	88.2(1)
I(31′)	3.079(3)				86.59(8)	91.96(9)
I(32′)	3.070(3)					97.81(9)
I(33′)	3.053(3)					

the antimony atoms into a polymeric chain by bridging. In the bismuth derivatives (1), (2), and (3), the central $[BiX_6]^{3-}$ group acts as a chelate to each of the two $[Bi(S_2CNEt_2)_2]^+$ species.

It is of interest also to examine the manner in which this $[Bi(S_2CNEt_2)_2]^+$ geometry varies with the nature of the halide ligand. Comparative geometries are given in Table 4. Here we see that the disparities in bond length and angles commented on above vary only marginally with changes in halide groups for both Bi(1) and Bi(2).

TABLE 4

Comparative BiS_4 geometries in (1), (2), and (3)

	(1)	(2)	(3)
(*a*) Bi(1)			
(*i*) Distances/Å			
Bi–S(1a1)	2.78(1)	2.800(5)	2.81(1)
Bi–S(1a2)	2.60(1)	2.604(5)	2.62(1)
Bi–S(1b1)	2.70(1)	2.673(5)	2.67(1)
Bi–S(1b2)	2.72(1)	2.700(6)	2.71(1)
(*ii*) Angle/°			
S(1a1)–Bi–S(1a2)	66.2(3)	65.9(2)	65.5(3)
S(1b1)–Bi–S(1b2)	66.0(3)	65.6(2)	64.8(4)
S(1a1)–Bi–S(1b1)	79.6(3)	80.9(2)	81.8(3)
S(1a2)–Bi–S(1b2)	88.7(3)	88.9(2)	88.8(3)
S(1a1)–Bi–S(1b2)	138.6(3)	138.8(2)	138.0(4)
S(1b1)–Bi–S(1a2)	86.5(3)	88.2(2)	90.2(3)
(*b*) Bi(2)			
(*i*) Distances/Å			
Bi–S(2a1)	2.77(1)	2.793(6)	2.80(1)
Bi–S(2a2)	2.61(1)	2.606(6)	2.63(1)
Bi–S(2b1)	2.62(1)	2.624(6)	2.63(1)
Bi–S(2b2)	2.74(1)	2.704(6)	2.71(1)
(*ii*) Angles/°			
S(2a1)–Bi–S(2a2)	65.7(3)	65.8(2)	66.2(3)
S(2b1)–Bi–S(2b2)	67.0(3)	67.2(2)	66.6(3)
S(2a1)–Bi–S(2b1)	87.9(3)	88.2(2)	87.5(3)
S(2a2)–Bi–S(2b2)	80.9(3)	81.5(2)	83.1(3)
S(2a1)–Bi–S(2b2)	137.6(3)	138.6(2)	139.2(3)
S(2b1)–Bi–S(2a2)	91.7(4)	91.7(2)	91.9(3)

In examining the compounds $[Bi(S_2CNEt_2)_2I]$ and $[Bi(S_2CNEt_2)_2Br]$,[7] we observed that in the bromide derivative the tendency towards the above *2* symmetry within the $Bi(S_2CNEt_2)_2$ unit was pronounced. In the iodide, however, the geometry was more unequivocally the usual trigonal-pyramidal geometry with the three shortest bonds occupying a compact triangular face of the co-ordination polyhedron; the same tendency is still evident in the present series of complexes (Figure 2, Table 4) as well as in $[Bi(S_2CNEt_2)_2I]$ and $[Bi(S_2CNEt_2)_2Br]$, in spite of the tendency to *2* symmetry, and, presumably in all cases, is the origin of the one longer Bi–S bond. It is further of interest that in the present three complexes there is a close interligand sulphur–sulphur distance S(1a1) · · · S(2a1) between the different $Bi(S_2CNEt_2)_2$ groups at a distance substantially less than the van der Waals sum, namely 3.29(1), (1); 3.295(8), (2); 3.31(2) Å, (3); in the case of both bismuth atoms, it is the longest of the four Bi–S distances that is involved. No such close contacts are found to the corresponding sulphur atom in the other complexes studied with similar geometries and similar unusually long Bi–S distances, and it is unlikely that the lengthening in the present compounds can be ascribed to this interaction or incipient bond formation.

The dithiocarbamate ligand geometries (Table 5) are normal, with, however, the qualification that in ligand 1a the terminal methyl groups lie on the same side of the ligand plane. Among the bridging halide atoms, we find in all cases that the angle subtended at the atom diminishes as we pass from the chloride to the bromide to the iodide complex (Table 6).

Complex (4).—The structure of (4) is regrettably imprecise; the unit-cell contents comprise poorly defined pyridinium cations and n-butanol solvent molecules together with complex bismuth–halide–dithiocarbamate anions and only the latter will be discussed here. The anion is shown to be $[Bi_4(S_2CNEt_2)_4Br_{10}]^{2-}$. Each anion is located on a crystallographic *2* axis so that only one half is crystallographically independent; the half anion, one solvent, and one cation comprise the asymmetric unit of the structure (Figure 3). Although the crystallographically imposed symmetry is *2*, the molecule contains non-crystallographic quasi-exact pseudo-symmetry, being a good approximation to *222* (Figure 3), the environment of each of the two independent bromine atoms showing no non-trivial differences. There are three independent bromine atoms associated with each bismuth atom; one is terminal and does not bridge to any neighbouring bismuth atoms

TABLE 5

The dithiocarbamate geometries in (1), (2), and (3). Entries under each ligand are for compounds (1), (2), and (3) respectively

Ligand	1a	1b	2a	2b
(*a*) Distances/Å				
S(1)–C(1)	1.68(3), 1.68(2), 1.66(4)	1.72(4), 1.71(2), 1.64(4)	1.64(4), 1.70(2), 1.72(4)	1.68(4), 1.77(2), 1.76(4)
S(2)–C(1)	1.77(3), 1.73(2), 1.75(4)	1.64(4), 1.68(2), 1.73(4)	1.79(4), 1.72(2), 1.78(4)	1.79(4), 1.71(2), 1.61(4)
S(1) · · · S(2)	2.94(1), 2.943(7), 2.95(1)	2.95(2), 2.911(9), 2.89(1)	2.92(2), 2.936(8), 2.96(2)	2.96(2), 2.950(9), 2.93(2)
C(1)–N	1.36(4), 1.35(2), 1.38(5)	1.40(6), 1.34(3), 1.53(6)	1.30(5), 1.31(3), 1.29(5)	1.30(4), 1.30(2), 1.37(4)
N–C(2)	1.58(5), 1.57(3), 1.63(5)	1.57(8), 1.59(4), 1.75(7)	1.47(5), 1.52(3), 1.53(5)	1.55(6). 1.55(4), 1.49(6)
N–C(4)	1.41(5), 1.45(3), 1.52(6)	1.54(4), 1.79(4), 1.59(8)	1.57(6), 1.42(3), 1.49(5)	1.49(5), 1.45(3), 1.59(5)
C(2)–C(3)	1.51(8), 1.35(4), 1.50(7)	1.41(9), 1.31(5), 1.38(7)	1.45(6), 1.47(4), 1.42(6)	1.44(8), 1.46(4), 1.55(8)
C(4)–C(5)	1.52(7), 1.51(3), 1.50(6)	1.13(–), 1.31(5), 1.33(8)	1.52(8), 1.50(4), 1.57(6)	1.55(6), 1.47(4), 1.39(6)
(*b*) Angles/°				
Bi–S(1)–C(1)	86(1), 84.7(6), 85(1)	85(1), 88.1(8), 90(2)	88(2), 84.9(7), 87(1)	91(1), 88.7(6), 86(1)
Bi–S(2)–C(1)	90(1), 90.2(6), 90(1)	86(1), 87.9(8), 87(1)	90(1), 90.8(7), 91(1)	85(1), 87.4(7), 86(1)
S(1)–C(1)–S(2)	117(2), 119(1), 119(2)	122(2), 118(1), 118(2)	117(2), 118(1), 116(2)	117(2), 116(1), 121(2)
S(1)–C(1)–N	125(3), 123(1), 125(3)	113(3), 120(2), 127(4)	123(3), 121(2), 122(3)	126(3), 119(2), 115(3)
S(2)–C(1)–N	119(2), 118(1), 116(3)	125(3), 121(2), 112(3)	120(3), 120(1), 122(3)	117(3), 125(2), 125(3)
C(1)–N–C(2)	122(3), 123(2), 121(3)	130(4), 123(2), 110(3)	124(3), 122(2), 120(3)	119(3), 125(2), 125(3)
C(1)–N–C(4)	121(3), 124(2), 126(3)	108(4), 120(2), 126(4)	122(4), 124(2), 120(3)	125(3), 118(2), 117(3)
C(2)–N–C(4)	115(3), 113(2), 113(3)	121(3), 110(2), 123(4)	114(3), 114(2), 120(3)	116(3), 115(2), 117(3)
N–C(2)–C(3)	93(3), 104(2), 104(3)	87(5), 97(3), 94(4)	116(3), 115(2), 107(3)	103(4), 100(2), 100(4)
N–C(4)–C(5)	111(3), 112(2), 115(3)	100(–), 88(2), 99(5)	115(4), 115(2), 110(3)	112(3), 114(2), 109(3)

[Br(a,b)]. Another bridges to the crystallographically related bismuth atom [Br(a,b1)] and has an angle of 84.4(3), 84.3(3)° subtended at it by them (Table 7). The other is triply bridging to the two nearest bismuth atoms. Each bismuth atom thus has a co-ordination sphere dominated by the three short contacts, two to the dithiocarbamate ligand and one to the terminal bromine (Bi–S, 2 × 2.71 Å; Bi–Br, 2.93 Å) occupying a compact co-ordination face, the angles between these ligands being Br(*n*)–Bi–S(na,b) S(*n*a)–Bi–S(*n*b) *ca.* 92, 77, 68° (Table 8). The four other contacts to each bismuth are all much longer, being derived from the bridging bromine atoms.

TABLE 6

Halogen angular geometry (°) in (1), (2), and (3). Primed atoms are related by the two-fold symmetry operation ($x, y, \frac{1}{2} - z$)

	(1) (X = Cl)	(2) (X = Br)	(3) (X = I)
Bi(1)–X(1)–Bi(1′)	114.7(5)	110.5(1)	105.1(1)
Bi(3)–X(31)–Bi(1′)	91.1(3)	89.77(6)	87.84(7)
Bi(3)–X(31)–Bi(2′)	85.0(3)	83.89(7)	82.14(8)
Bi(1′)–X(31)–Bi(2′)	98.6(3)	96.74(6)	93.99(8)
Bi(3)–X(32)–Bi(1)	91.9(3)	90.06(6)	87.51(8)
Bi(3)–X(33)–Bi(2)	92.2(3)	89.01(7)	85.24(9)

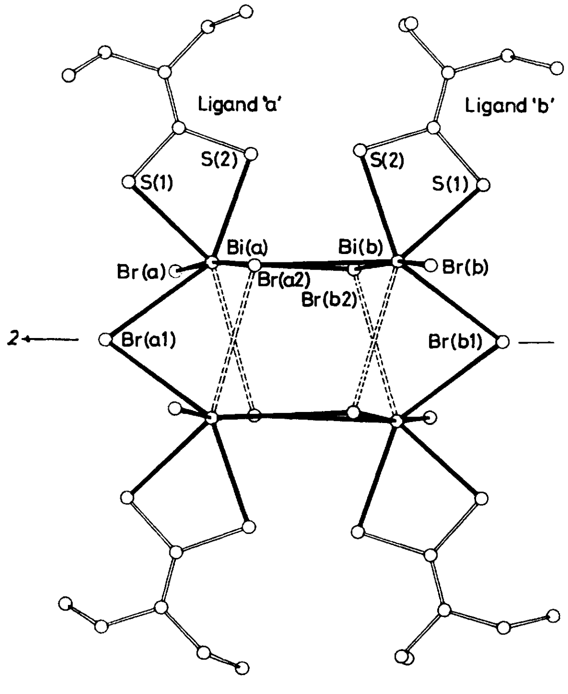

FIGURE 3 The anion of compound (4)

TABLE 7

Bromine angular geometry in (4). The two values in each entry correspond to sections *n* = a and b respectively. Primed atoms are generated by ($\bar{x}, y, \frac{1}{2} - z$); italicised atoms lie in the alternate section *n* = a, b

Atoms	Angle/°
Bi–Br(*n*1)–Bi′	84.4(3), 84.3(3)
Bi–Br(*n*2)–Bi′	78.1(2), 77.3(2)
Bi–Br(*n*2)–*Bi*	96.3(3), 95.8(2)
Bi′–Br(*n*2)–*Bi*	105.4(2), 104.7(2)

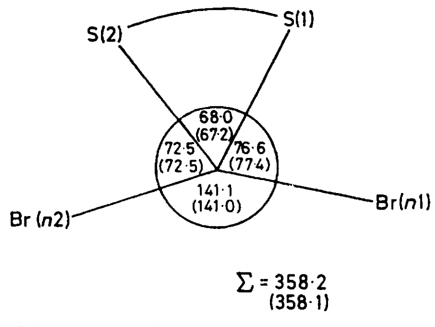

FIGURE 4 Disposition of angles in the median co-ordination plane of Bi(a) and Bi(b) (values in parentheses) for compound (4)

An alternative description of the co-ordination spheres

TABLE 8

The bismuth environments in (4) (see heading to Table 3)

(*a*) Bi(a)

	$r_{\mathrm{Bi-X}}$	S(a2)	Br(a)	Br(a1)	Br(a2)	Br(b2)	Br(a2′)
S(a1)	2.71(3)	68.0(10)	91.3(9)	76.6(8)	94.4(9)	140.4(7)	148.9(7)
S(a2)	2.73(3)		91.7(9)	143.5(7)	92.1(9)	72.5(7)	142.0(7)
Br(a)	2.93(1)			98.1(2)	174.0(2)	93.3(3)	81.9(2)
Br(a1)	3.28(1)				81.5(2)	141.1(2)	74.5(2)
Br(a2)	3.24(1)					83.5(2)	92.3(2)
Br(b2)	3.34(1)						70.5(2)
Br(a2′)	3.73(1)						

(*b*) Bi(b)

	$r_{\mathrm{Bi-X}}$	S(b2)	Br(b)	Br(b1)	Br(b2)	Br(a2)	Br(b2′)
S(b1)	2.71(3)	67.2(9)	92.2(8)	77.4(6)	92.2(8)	139.4(6)	149.8(6)
S(b2)	2.68(3)		93.0(8)	143.6(7)	91.7(7)	72.5(7)	142.1(7)
Br(b)	2.94(1)			96.3(2)	174.6(2)	94.8(3)	81.0(2)
Br(b1)	3.26(1)				81.5(2)	141.0(2)	74.3(2)
Br(b2)	3.24(1)					84.0(2)	93.6(2)
Br(a2)	3.31(1)						70.7(2)
Br(b2′)	3.74(1)						

may be given in terms of an axis Br(*n*1)–Bi–Br(*n*2) [angle 174.0(2) (a), 174.6(2)° (b)]; the remainder of the ligating atoms are then approximately coplanar (Figure 4). A similar disposition is observed about the bismuth atom in the $[I_2(Et_2NCS_2)BiI_2Bi(S_2CNEt_2)I_2]^{2-}$ anion;[8] the angle opposite the bidentate ligand in that case is much smaller, however (110.3_2°). The increased splaying in the present case may arise from the presence of a stereochemically active lone pair of electrons and/or the additional long Bi ··· Br contact approximately bisecting this angle (Figure 3), Bi(*n*) ··· Br(*n*2′), 3.73(1) (a), 3.74(1) Å (b).

[0/1049 *Received*, *7th July*, 1980]

REFERENCES

[1] Part 3, C. L. Raston, G. L. Rowbottom, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1366.

[2] Part 8, C. L. Raston, G. L. Rowbottom, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1389.

[3] L. P. Battaglia, A. B. Corradi, M. Nardelli, and M. E. V. Tani, *J. Chem. Soc., Dalton Trans.*, 1978, 583.

[4] W. G. McPherson and E. A. Meyers, *J. Phys. Chem.*, 1968, **72**, 3117.

[5] F. Lazarini, *Acta Crystallogr.*, 1977, **B33**, 1957.

[6] P. J. H. A. M. van de Leemput, J. A. Cras, and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, 1977, **96**, 288.

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

[8] Part 4, C. L. Raston, G. L. Rowbottom, and A. H. White, preceding paper.